OL | Organic Letters

pubs.acs.org/OrgLett Letter

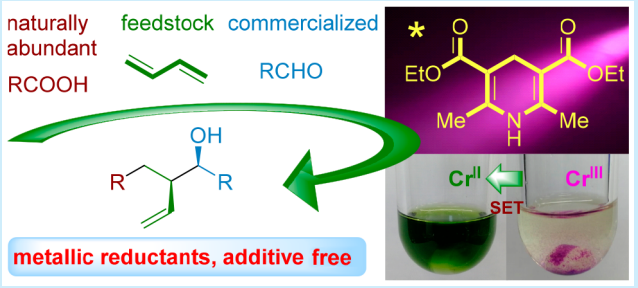
Activation of Chromium Catalysts by Photoexcited Hantzsch Ester for Decarboxylative Allylation of Aldehydes with Butadiene

Shuangjie Lin, Yuqing Chen, Huaipu Yan, Yonghong Liu, Yuchen Sun, Erjun Hao,* Caizhe Shi, Dandan Zhang, Nan Zhu, and Lei Shi*

Cite This: *Org. Lett.* 2021, 23, 8077–8081 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Metallaphotocatalysis often needs light-absorbing metal-polypyridyl complexes, semiconductors, or organic dyes, which can modify the oxidation state of metal catalysts. Here, we first report that photoexcitation of Hantzsch ester can directly activate chromium reagents through a single-electron transfer process. The synthetic application was demonstrated through a photoredox decarboxylative allylation of aldehydes with feedstock butadiene without exogenous photocatalysts, metallic reductants, or additives.



Downloaded via DALIAN UNIV OF TECHNOLOGY on November 4, 2021 at 06:49:03 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

In recent years, metallaphotocatalysis has become a powerful tool in organic synthesis and witnessed a rapidly growing number of newly discovered reaction modes under eco-friendly conditions.[1−5] The success of the metallaphotocatalysis depends on a light-absorbing photocatalyst, which can remove an electron from or donate an electron to an active metal and thus modulate its oxidation state. However, the high cost of photocatalysts, which are commonly precious metal-polypyridyl complexes or synthetically elaborated organic dyes, impedes their further application for large-scale industrial processes.

Hantzsch esters (HEs) are well understood as hydride (H^-) sources and sacrificial electron donors in their ground state (Figure 1a).[6,7] Recent studies found that these low-cost and easily available photoactive compounds can serve as strong single-electron photoreductants upon light irradiation for small molecule transformations.[8−10] Utilization of the photoreduction ability of excited HE* for metallaphotocatalysis is highly appealing but scarcely developed. Recently, Melchiorre reported a leading example in which photoexcited 4-alkyl-HEs* can act as an organic photoreductant to produce catalytically active Ni(0) bypassing exogenous photocatalysts.[11] Meanwhile, Molander showed another elegant example in which HE* can activate Ni(0) species in conjunction with decarboxylation of NHPI ester for $C(sp^3)-C(sp^2)$ bond formation.[12] Given that the redox potential of HE* was estimated to be −2.28 V versus SCE,[10] the reduction of Cr^{III} ($E_pCr^{III/II}$ = −0.51 V vs SCE in DMF)[13] by HE* should be thermodynamically feasible. Herein, we report that photoexcitation of HE can directly activate Cr catalysts (Figure 1b), avoiding stoichiometric metal reductants such as Zn and Mn that are usually used to reduce Cr^{III} to Cr^{II} in various reactions.[14−16] This novel activation model enabled a three-component decarboxylative allylation of aldehydes with feedstock butadiene and naturally abundant alkyl acids for the synthesis of value-added homoallylic alcohols.[17−20]

Butadiene is one of the most convenient industrial raw materials and frequently used for organic synthesis.[21,22] Recently, transition metal-catalyzed three-component allylation of carbonyls with butadiene has attracted a great deal of attention due to its overall synthetic efficiency and environ-

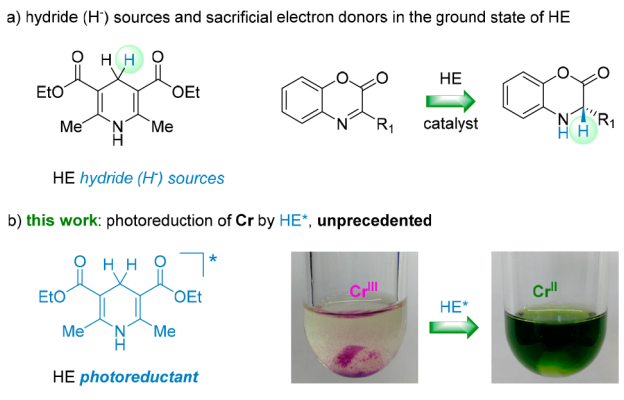


Figure 1. (a) Reduction of imines by HE in the ground state. (b) Concept for photoreduction of $CrCl_3$ by HE*.

Received: September 13, 2021
Published: October 4, 2021

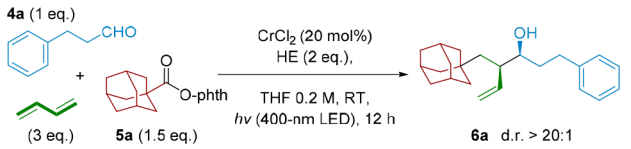
© 2021 American Chemical Society

https://doi.org/10.1021/acs.orglett.1c03098
Org. Lett. 2021, 23, 8077–8081

mental sustainability.[23−26] In particular, a radical-based Cr-catalyzed three-component allylation was first reported by Takai and further developed by Zhang and Glorius using fluoroalkyl iodides or 4-alkyl-HEs as radical precursors.[27−29] Carboxylic acids are highly attractive feedstocks in organic synthesis due to their excellent features, such as their low cost, abundance, easy operation, and large structural diversity. Photocatalytic radical decarboxylative functionalization through redox-active esters [*N*-hydroxyphthalimide (NHPI) esters] by forming an electron donor−acceptor complex has achieved great success.[30−33] Specifically, in this work, the multiple roles of HE are to reduce redox-active esters to deliver alkyl radicals, to activate Cr catalysts, and to break the Cr−alkoxy bond, thereby bypassing exogenous photocatalysts, metallic reductants, and additives.

The studies were started by examining butadiene, aliphatic aldehyde **4a**, and NHPI ester **5a** derived from 1-adamantanecarboxylic acid as radical precursors. After a systematic study of various reaction parameters, we successfully found the favorable conditions under which a mixture of **4a** (1 equiv), **5a** (1.5 equiv), HE (2 equiv), and $CrCl_2$ (20 mol %), in a butadiene solution of THF, irradiated with a 400 nm LED lamp for 12 h, afforded homoallylic alcohol **6a** in a satisfactory yield of 93% with exceptional regio- and diastereoselectivity [dr > 20:1 (Table 1, entry 1)]. A reasonable yield of 86% can

Table 1. Reaction Optimization for Aldehydes[a]



entry	variation from standard conditions	yield (%)
1	none	93
2	$CrCl_2$ (10 mol %), HE (3 equiv), **5a** (2 equiv), 24 h	86
3	$CrCl_3$ instead of $CrCl_2$	71
4	white LED instead 400 nm LED	<5
5	450 nm or 530 nm LED instead of 400 nm LED	<5
6	DIPEA (or TEA) instead of HE	0
7	DCE instead of THF	78
8	DMF/MeCN/toluene instead of THF	0

[a]Reaction conditions: **4a** (0.5 mmol, 1 equiv, 0.2 M THF), **5a** (0.75 mmol, 1.5 equiv). Yields were determined by ^{1}H NMR spectroscopy vs an internal standard. Diastereomeric ratios were determined by ^{1}H NMR spectroscopy.

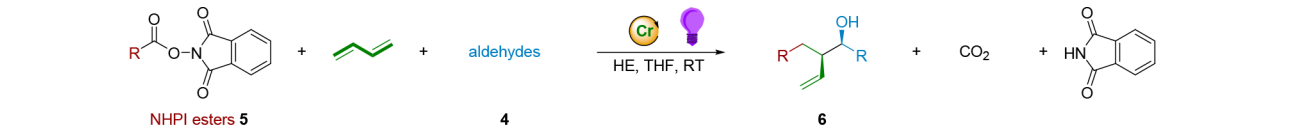
be obtained by using only 10 mol % $CrCl_2$ catalyst for a longer time (entry 2). When the bench stable $CrCl_3$ was used instead of $CrCl_2$, the reaction afforded the product in a slightly lower yield of 71% (entry 3). Importantly, the reaction is highly sensitive to the wavelength of light. For example, irradiation with a white LED, a 450 nm LED, or a 530 nm LED instead of a 400 nm LED resulted in very low yields of product (entries 4 and 5). Other organic electron donors such as *N*,*N*-diisopropylethylamine (DIPEA) or triethylamine (TEA), instead of HE, were tested and produced no product (entry 6). Different solvents, including dimethylformamide (DMF), acetonitrile (MeCN), and toluene, were evaluated, and they all afforded no product (entry 8). Notably, the allylation did not proceed without HE, chromium, or visible light. Condition-based sensitivity screening showed that the allylation is sensitive to H_2O and a high oxygen concentration (section S4 of the Supporting Information).[34] The preparation of **6a** was performed on a gram scale, and a pleasing yield of 83% was obtained, demonstrating the scalability of the reaction.

After optimizing the allylation reaction conditions, we further investigated the scope of the substrates. Remarkably, the reaction went well with various primary, secondary, and tertiary alkyl acids derived NHPI esters and abundant aliphatic/aromatic aldehydes, affording the homoallylic alcohols in generally good yields with excellent regio- and diastereoselectivity control (Scheme 1). Sterically hindered tertiary alkyl acids, such as bicyclo[2.2.2]octane acid **6i** and adamantane acid **6a**, worked efficiently and produced homoallylic alcohols in excellent yields. We were pleased to find that secondary cyclic alkyl acids, including strained three-, four-, five-, and six-membered rings participated in the allylation reaction affording good yields (**6n−6r**). Remarkably, under current conditions, the highly reactive primary radical generated from primary alkyl acids can add to butadiene and successfully produce alcohols in satisfactory yields. It was also found that the aryl substituent effect of aromatic aldehydes has no obvious effect on the reaction, including -OMe, -H, -F, -Cl, and -Br (**6d−6h**, respectively). The sterically hindered trimethylbenzaldehyde **6o** was successfully allylated. Heteroatoms, such as oxygen (**6t**), sulfur (**6v**), and protected amine (**6aa**) did not interfere with the catalytic cycle. In addition, this dual catalysis system was also compatible with various heteroarenes, including furan **6w** and thiophene **6v**, which are widely used as core structures in pharmaceutical synthesis. Three-membered ring **6n** and four-membered ring **6o** with ring tension were also successfully allylated. The fluorine atoms in **6u** remained intact under the current conditions. To illustrate the potential applicability of our strategy in late-stage functionalization, several drugs derivatives were used and the desired products **6ah−6ak** were obtained in good yields. In particular, the 1,3-disubstituted bicyclo[1.1.1]pentane (BCP)-derived NHPI ester can be introduced into the three-component allylation of **6ai** and **6aj**, and the remaining ester group can be further elaborated. This is quite useful as BCP motifs have been widely used in medicinal chemistry as pharmaceutical bioisosteres of benzene rings. Additionally, natural amino acids alanine and methionine were successfully used as radical sources to afford alcohols **6al** and **6am**, respectively, which are difficult to obtain from alkyl iodides. Additionally, the current photoreduction system is also suitable for asymmetric catalysis.[28,29] In the preliminary studies under non-optimized conditions, the reaction proceeded well and the desired product **6a**, **6b**, and **6w** were obtained in satisfactory yields and enantioselectivities (for details, see section S5b). Overall, the allylation reactions proceeded quite efficiently without the use of any exogenous photocatalysts or additives.

A reaction was conducted in the absence of Cr and aldehydes. In this case, dimerized product **9** and its isomers were obtained in 67% yield (Figure 2a; for details, see section S5c). This result indicated that the NHPI esters can be directly reduced by HE via the formation of an electron donor−acceptor (EDA) complex.[32] Additionally, excited HE* are reported to reduce ketone, resulting in ketyl radical. However, in this case, 2-phenylcyclopropane-1-carboxaldehyde **11** can be allylated successfully (Figure 2b) without the ring opening of cyclopropane. This suggested that excited HE* does not interact with carbonyls under the current conditions, and the ketyl radical intermediates are not likely involved in the reaction (Figure 2b). On the basis of these results and the

https://doi.org/10.1021/acs.orglett.1c03098
Org. Lett. 2021, 23, 8077−8081

Scheme 1. Scope of Alkyl Esters and Aldehydes for Allylation Reactions[a−c]



3° alkyl acids

1 — **6a** 93%, (d.r. > 20:1) 83%,1.34g; **6b** 84%, (d.r. > 20:1); **6c** 87%, (d.r. = 10:1); **6d** R = OMe 83%, (d.r. > 20:1); **6e** R = H 78%, (d.r. > 20:1); **6f** R = F 83%, (d.r. > 20:1); **6g** R = Cl 81%, (d.r. > 20:1); **6h** R = Br 88%, (d.r. > 20:1)

2 — **6i** 83% , (d.r. = 12:1); **6j** 69%, (d.r. > 15:1); **6k** 82%, (d.r. > 15:1); **6l** 74%, (d.r. > 20:1; **6m** 87% (d.r. > 20:1)

2° alkyl acids

3 — **6n** 72%, (d.r. > 20:1); **6o** 72%, (d.r. > 20:1); **6p** 81%, (d.r. = 10:1); **6q** 62%, (d.r. > 20:1); **6r** 68%, (d.r. > 15:1)

4 — **6s** 81%, (d.r. > 20:1); **6t** 71%, (d.r. > 20:1); **6u** 75%, (d.r. > 20:1); **6v** 78%, (d.r. > 15:1); **6w** 64%, (d.r. > 20:1)

1° alkyl acids

5 — **6x** 76%, (d.r. > 20:1); **6y** 67%, (d.r. > 20:1); **6z** 60%, (d.r. > 20:1); **6aa** 83%, (d.r. > 20:1)

6 — **6ab** 77% (d.r. > 20:1) 27% (3 eq. butadiene used); **6ac** 61%, (d.r. > 15:1); **6ad** R = H 72%, (d.r. = 9:1) **6ae** R = F 75%, (d.r. = 11:1) **6af** R = Br 74%, (d.r. = 11:1); [from methyl isoprene] **6ag** 35% (d.r. = 4:1) **6ag'** 23% (d.r. > 15:1)

complex molecules

7 — Oxaprozin **6ah** 81% (d.r. > 20:1); **6ai** 72% (d.r. = 11:1) Indomethacin

8 — **6aj** 73% (d.r. = 11:1) Probenecid; **6ak** 59% (d.r. > 20:1) Febuxostat

amino acids

from Alanine **6al** 67% (d.r. = 6:1)

from Methionine **6am** 63% (d.r. > 20:1)

[a]Reactions were performed on a 0.5 mmol scale with **4** (1 equiv, 0.1 M THF), **5** (2 equiv), $CrCl_2$ (20 mol %), HE (2 equiv), butadiene, and a 400 nm LED for 20 h (for details, see section S5a). [b]When the product and Hantzsch pyridine cannot be completely separated, yields were determined by ^{1}H NMR spectroscopy vs an internal standard. [c]Diastereomeric ratios were determined by ^{1}H NMR spectroscopy. [d]Butadiene (10 equiv) and HE (3 equiv) used for primary NHPI esters.

https://doi.org/10.1021/acs.orglett.1c03098
Org. Lett. 2021, 23, 8077−8081

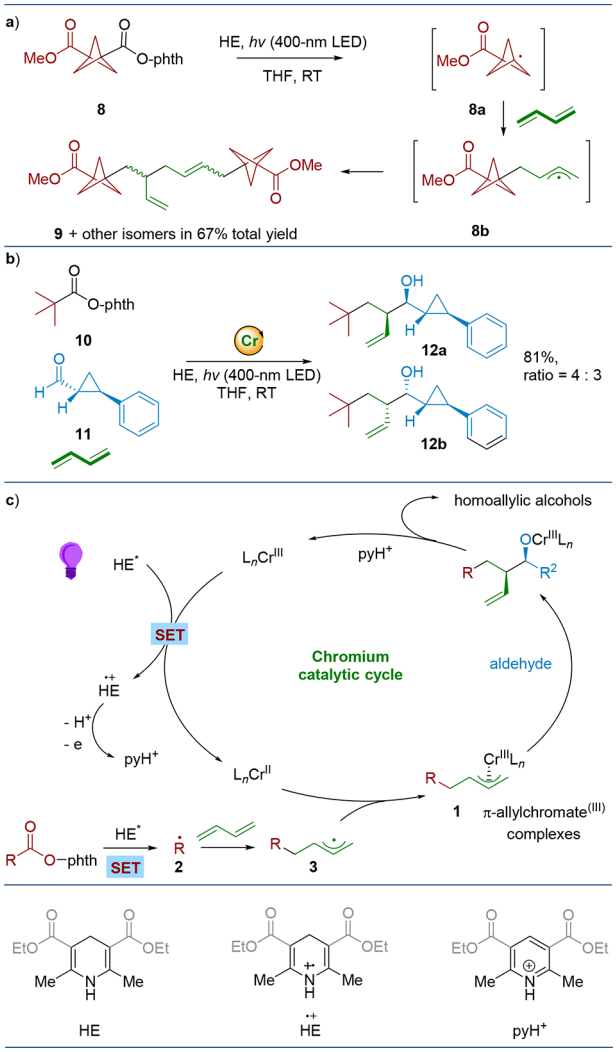


Figure 2. (a) Photoreduction of NHPI esters by excited HE* and the presence of an allyl radical **8b** and its dimerization. (b) Radical clock experiments. (c) Proposed catalytic mechanism.

previous reports,[27−29] the proposed catalytic cycle is as follows (Figure 2c). First, Cr^{III} is reduced to Cr^{II} by excited HE* via a SET process. The resulting $HE^{\bullet+}$ can further participate in electron transfer events and eventually produce pyH^+. Simultaneously, NHPI esters are reduced by another excited HE* via an EDA complex to produce alkyl radical **2**. Radical **2** rapidly adds to butadiene to produce allyl radical **3** (secondary and tertiary alkyl radicals can form reversible alkyl-Cr complexes). Then allyl radical **3** is trapped by Cr^{II} to produce nucleophilic **1**, which further couples with aldehydes. After hydrolysis of the O−Cr bond by pyH^+, the alcohols and free Cr^{III} species are released. The observed selectivity can be explained by the Zimmerman−Traxler transition state.[17]

In summary, this study first reported that photoexcitation of HE with 400 nm irradiation can directly reduce Cr^{III} to active Cr^{II} through a SET process, which is unprecedented in the literature. The synthetic application was demonstrated through a photoredox decarboxylative allylation of aldehydes with feedstock butadiene, without the need for exogenous photocatalysts, stoichiometric metal reductants, or additives. This eco-friendly and operationally easy method affords rapid access to various structurally diverse homoallylic alcohols.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c03098.

Detailed experimental procedures, absorption and emission spectra, HPLC spectra, characterization of new compounds, and copies of NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Erjun Hao − *School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China*; Email: hej@htu.edu.cn

Lei Shi − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China; School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China*; orcid.org/0000-0002-2644-1168; Email: shilei17@dlut.edu.cn

Authors

Shuangjie Lin − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Yuqing Chen − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Huaipu Yan − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Yonghong Liu − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Yuchen Sun − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Caizhe Shi − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Dandan Zhang − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China*

Nan Zhu − *Zhang Dayu School of Chemistry, Dalian University of Technology, Dalian 116024, China*; orcid.org/0000-0001-6029-6200

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c03098

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project is supported by the National Natural Science Foundation of China (2217010858), the Open Research Fund of the School of Chemistry and Chemical Engineering, Henan Normal University (2020YB03), the Key Scientific Research Projects of Higher Education Institutions in Henan Province (21A150002), and the University-Level College Student Innovation and Entrepreneurship Training Program Support Project (202010141010101010339). The authors thank WATT-CAS CHEM-TECH Co., Ltd., for kindly providing the photoreactor.

■ REFERENCES

(1) 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* (7), 52.

(2) Skubi, K. L.; Blum, T. R.; Yoon, T. P. Dual Catalysis Strategies in Photochemical Synthesis. *Chem. Rev.* **2016**, *116* (17), 10035−10074.

(3) Tellis, J. C.; Kelly, C. B.; Primer, D. N.; Jouffroy, M.; Patel, N. R.; Molander, G. A. Single-Electron Transmetalation via Photoredox/Nickel Dual Catalysis: Unlocking a New Paradigm for sp^3–sp^2 Cross-Coupling. *Acc. Chem. Res.* **2016**, *49* (7), 1429–1439.
(4) Ghosh, I.; Marzo, L.; Das, A.; Shaikh, R.; König, B. Visible Light Mediated Photoredox Catalytic Arylation Reactions. *Acc. Chem. Res.* **2016**, *49* (8), 1566–1577.
(5) Huang, H.; Koy, M.; Serrano, E.; Pflüger, P. M.; Schwarz, J. L.; Glorius, F. Catalytic radical generation of π-allylpalladium complexes. *Nat. Catal.* **2020**, *3* (4), 393–400.
(6) Chen, Q. A.; Chen, M. W.; Yu, C. B.; Shi, L.; Wang, D. S.; Yang, Y.; Zhou, Y. G. Biomimetic Asymmetric Hydrogenation: In Situ Regenerable Hantzsch Esters for Asymmetric Hydrogenation of Benzoxazinones. *J. Am. Chem. Soc.* **2011**, *133* (41), 16432–16435.
(7) Wang, P. Z.; Chen, J. R.; Xiao, W. J. Hantzsch esters: an emerging versatile class of reagents in photoredox catalyzed organic synthesis. *Org. Biomol. Chem.* **2019**, *17* (29), 6936–6951.
(8) Fukuzumi, S.; Hironaka, K.; Tanaka, T. Photoreduction of alkyl halides by an NADH model compound. An electron-transfer chain mechanism. *J. Am. Chem. Soc.* **1983**, *105* (14), 4722–4727.
(9) Emmanuel, M. A.; Greenberg, N. R.; Oblinsky, D. G.; Hyster, T. K. Accessing non-natural reactivity by irradiating nicotinamide-dependent enzymes with light. *Nature* **2016**, *540* (7633), 414–417.
(10) Jung, J.; Kim, J.; Park, G.; You, Y.; Cho, E. Selective Debromination and a-Hydroxylation of a-Bromo Ketones Using Hantzsch Esters as Photoreductants. *Adv. Synth. Catal.* **2016**, *358* (1), 74–80.
(11) Buzzetti, L.; Prieto, A.; Roy, S. R.; Melchiorre, P. Radical-Based C–C Bond-Forming Processes Enabled by the Photoexcitation of 4-Alkyl-1,4-dihydropyridines. *Angew. Chem.* **2017**, *129* (47), 15235–15239.
(12) Kammer, L.; Badir, S.; Hu, R.; Molander, G. Photoactive electron donor–acceptor complex platform for Ni-mediated C(sp3)–C(sp2) bond formation. *Chemical Science* **2021**, *12*, 5450–5457.
(13) (a) Bard, A. J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solutions*, 1st ed.; Marcel Dekker: New York, 1985. (b) Izutsu, K. *Electrochemistry in Nonaqueous Solutions*, 2nd ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2009.
(14) (a) Cong, X.; Zeng, X. Mechanistic Diversity of Low-Valent Chromium Catalysis: Cross-Coupling and Hydrofunctionalization. *Acc. Chem. Res.* **2021**, *54* (8), 2014–2026. (b) Zeng, X.; Cong, X. Chromium-catalyzed transformations with Grignard reagents – new opportunities for cross-coupling reactions. *Org. Chem. Front.* **2015**, *2*, 69–72.
(15) Li, J.; Ren, Q.; Cheng, X.; Karaghiosoff, K.; Knochel, P. Chromium(II)-Catalyzed Diastereoselective and Chemoselective Csp^2-Csp^3 Cross-Couplings Using Organomagnesium Reagents. *J. Am. Chem. Soc.* **2019**, *141* (45), 18127–18135.
(16) Tian, Q. S.; Zhang, G. Z. Recent Advances in the Asymmetric Nozaki–Hiyama–Kishi Reaction. *Synthesis* **2016**, *48* (23), 4038–4049.
(17) Schwarz, J. L.; Schäfers, F.; Tlahuext-Aca, A.; Lückemeier, L.; Glorius, F. Diastereoselective Allylation of Aldehydes by Dual Photoredox and Chromium Catalysis. *J. Am. Chem. Soc.* **2018**, *140* (40), 12705–12709.
(18) Tanabe, S.; Mitsunuma, H.; Kanai, M. Catalytic Allylation of Aldehydes Using Unactivated Alkenes. *J. Am. Chem. Soc.* **2020**, *142* (28), 12374–12381.
(19) Yus, M.; González-Gómez, J. C.; Foubelo, F. Diastereoselective Allylation of Carbonyl Compounds and Imines: Application to the Synthesis of Natural Products. *Chem. Rev.* **2013**, *113* (7), 5595–5698.
(20) Wang, P.; Shen, M.; Gong, L. Transition-Metal-Catalyzed Asymmetric Allylation of Carbonyl Compounds with Unsaturated Hydrocarbons. *Synthesis* **2018**, *50* (5), 956–967.
(21) (a) Wu, Z.; Zhang, W. Recent Advances in Metal-Catalyzed 1,2-Difunctionalization of Conjugated Dienes. *Youji Huaxue* **2017**, *37* (9), 2250.
(22) Wu, X.; Gong, L. Palladium (0)-Catalyzed Difunctionalization of 1,3-Dienes: From Racemic to Enantioselective. *Synthesis* **2019**, *51* (01), 122–134.
(23) Kimura, M.; Matsuo, S.; Shibata, K.; Tamaru, Y. Nickel (0)-Catalyzed Three-Component Connection Reaction of Dimethylzinc, 1,3-Dienes, and Carbonyl Compounds. *Angew. Chem., Int. Ed.* **1999**, *38* (22), 3386–3388.
(24) Boerth, J. A.; Maity, S.; Williams, S. K.; Mercado, B. Q.; Ellman, J. A. Selective and synergistic cobalt(iii)-catalysed three-component C–H bond addition to dienes and aldehydes. *Nature Catalysis* **2018**, *1* (9), 673–679.
(25) (a) Lin, S.; Chen, Y.; Li, F.; Shi, C.; Shi, L. Visible-light-driven spirocyclization of epoxides via dual titanocene and photoredox catalysis. *Chemical Science* **2020**, *11* (3), 839–844. (b) Li, F.; Chen, Y.; Lin, S.; Shi, C.; Li, X.; Sun, Y.; Guo, Z.; Shi, L. Visible-light-mediated Barbier allylation of aldehydes and ketones via dual titanium and photoredox catalysis. *Org. Chem. Front.* **2020**, *7* (21), 3434–3438. (c) Chen, Y.; Lin, S.; Li, F.; Zhang, X.; Lin, L.; Shi, L. $Cp_2Ti^{III}Cl$ Catalysis in a New Light. *ChemPhotoChem* **2020**, *4*, 659–663.
(26) Li, F.; Lin, S.; Chen, Y.; Shi, C.; Yan, H.; Li, C.; Wu, C.; Lin, L.; Duan, C.; Shi, L. Photocatalytic Generation of π-Allyltitanium Complexes via Radical Intermediates. *Angew. Chem., Int. Ed.* **2021**, *60* (3), 1561–1566.
(27) Takai, K.; Matsukawa, N.; Takahashi, A.; Fujii, T. Three-Component Coupling Reactions of Alkyl Iodides, 1,3-Dienes, and Carbonyl Compounds by Sequential Generation of Radical and Anionic Species with $CrCl_2$. *Angew. Chem., Int. Ed.* **1998**, *37*, 152–155.
(28) Xiong, Y.; Zhang, G. Enantioselective 1,2-Difunctionalization of 1,3-Butadiene by Sequential Alkylation and Carbonyl Allylation. *J. Am. Chem. Soc.* **2018**, *140* (8), 2735–2738.
(29) Schwarz, J. L.; Huang, H.; Paulisch, T. O.; Glorius, F. Dialkylation of 1,3-Dienes by Dual Photoredox and Chromium Catalysis. *ACS Catal.* **2020**, *10* (2), 1621–1627.
(30) Schwarz, J.; König, B. Decarboxylative reactions with and without light – a comparison. *Green Chem.* **2018**, *20* (2), 323–361.
(31) Mega, R. S.; Duong, V. K.; Noble, A.; Aggarwal, V. K. Decarboxylative Conjunctive Cross-coupling of Vinyl Boronic Esters using Metallaphotoredox Catalysis. *Angew. Chem., Int. Ed.* **2020**, *59* (11), 4375–4379.
(32) (a) Crisenza, G. E. M.; Mazzarella, D.; Melchiorre, P. Synthetic Methods Driven by the Photoactivity of Electron Donor–Acceptor Complexes. *J. Am. Chem. Soc.* **2020**, *142* (12), 5461–5476.
(33) Li, Y.; Zhang, J.; Li, D.; Chen, Y. Metal-Free $C(sp^3)$–H Allylation via Aryl Carboxyl Radicals Enabled by Donor–Acceptor Complex. *Org. Lett.* **2018**, *20* (11), 3296–3299.
(34) Pitzer, L.; Schäfers, F.; Glorius, F. Rapid Assessment of the Reaction-Condition-Based Sensitivity of Chemical Transformations. *Angew. Chem., Int. Ed.* **2019**, *58* (25), 8572–8576.

https://doi.org/10.1021/acs.orglett.1c03098
Org. Lett. 2021, 23, 8077–8081