

Base Metal Meets Photoredox Chemistry – Advances in Fully Catalytic Metal-Catalyzed Hydrogen Atom Transfer Reactions

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Abstract: Metal-catalyzed hydrogen atom transfer (MHAT) has become a valuable approach for the functionalization of alkenes and toward complex molecular structures. This review discusses recent advancements in the field, particularly the integration of metal catalysis with photoredox catalysis which obviates the need for sacrificial reagents. Key transformations, including heterocycle formation, olefin hydrofunctionalization, and semi-pinacol rearrangements are examined in detail, highlighting the potential of photo-MHAT for efficient and sustainable synthetic strategies.

Keywords: Heterocycles · Hydrofunctionalization · Photo-MHAT · Photoredox



Willi M. Amberg born in 1997 in Heidelberg, Germany, obtained his bachelor's degree from Heidelberg University in 2018 and his Master's degree from ETH Zurich in 2020. For his PhD studies he joined the group of Prof. Erick M. Carreira at ETH Zurich where he accomplished the first total synthesis of (+)-aberrarone. To broaden his scientific expertise, he investigated new catalytic systems in the context of photoredox catalysis.

His work resulted in the cyclopropanation of unactivated olefins, a photo- and cobalt-catalyzed synthesis of heterocycles, and a perovskite quantum dot catalyzed C–H bromination, amongst others. In 2024 Willi graduated from ETH Zurich and joined the group of Prof. John F. Hartwig as an SNSF postdoctoral fellow to specialize in organometallic chemistry.

1. Introduction

Catalysis plays a pivotal role across all branches of chemistry and is crucial toward a more sustainable future.^[1] The first documented catalyst, sulfuric acid, was used in 1552 for the conversion of alcohols to ethers.^[2] In particular over the past and current century, the field has evolved significantly to include diverse types of catalysts such as transition metal complexes,^[3] organocatalysts,^[4] photocatalysts,^[5] and enzymes.^[6] This broad selection provides modern synthetic chemists with an extensive toolkit. Even with these advancements, researchers are constantly exploring new methods and innovative catalytic systems to unlock new reactivity. In this regard, the integration of base metal and photoredox catalysis has opened up a new pathway for fully catalytic reactions.^[7] This review focuses on metal catalyzed hydrogen-atom transfer reactions (MHAT) which have traditionally relied on stoichiometric reductants and oxidants.

1.1 Metal Catalyzed Hydrogen Atom Transfer

A metal-catalyzed hydrogen atom transfer (MHAT) reaction is a powerful transformation which involves the transfer of a hydrogen atom from a donor molecule to an acceptor, typically mediated by a transition-metal catalyst.^[8] Classically, the use of Fe-, Mn-, and Co-complexes in combination with stoichiometric amounts of a hydride donor (*e.g.* hydrosilane, NaBH₄, *i*-PrOH) enable the Markovnikov selective functionalization of unactivated olefins with radical acceptors *via* a radical alkyl–Co(III) intermediate (Fig. 1).^[9]

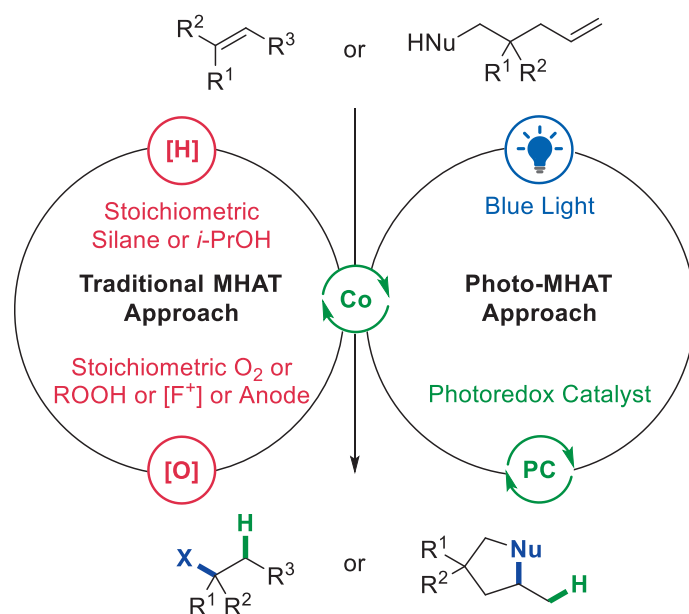
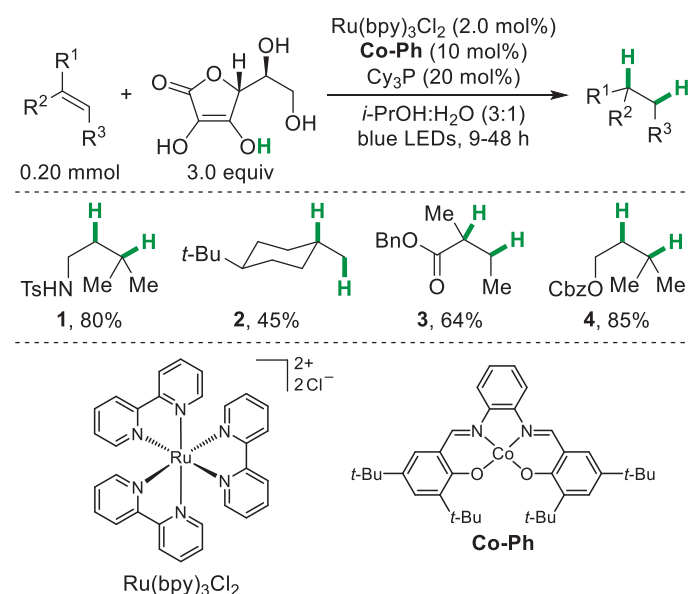


Fig. 1. Traditional MHAT approach with sacrificial reagents and photo-MHAT approach towards hydrofunctionalized and cycloisomerized olefins.

More recently, Shigehisa and coworkers demonstrated that the radical alkyl–Co(III) intermediate can be oxidized by superstoichiometric amounts of *N*-fluoropyridinium salts ($[F^+]$). The resulting electrophilic alkyl–Co(IV) species can subsequently be substituted by a nucleophile. The authors leveraged this reactivity to effect an intramolecular hydrofunctionalization of olefins with pendent amines, alcohols, acids, arenes, or thiols amongst others.^[10] Later, Zhu and coworkers explored substitutes for *N*-fluoropyridinium salts while preserving the same reactivity principle. In this regard they successfully employed molecular oxygen or anodic oxidation.^[11] Despite these efforts, stoichiometric silane reductants remained a requirement and a general procedure for MHAT which obviates the need for sacrificial reagents remained elusive and highly desirable.

2. Combining Cobalt with Photoredox Catalysis

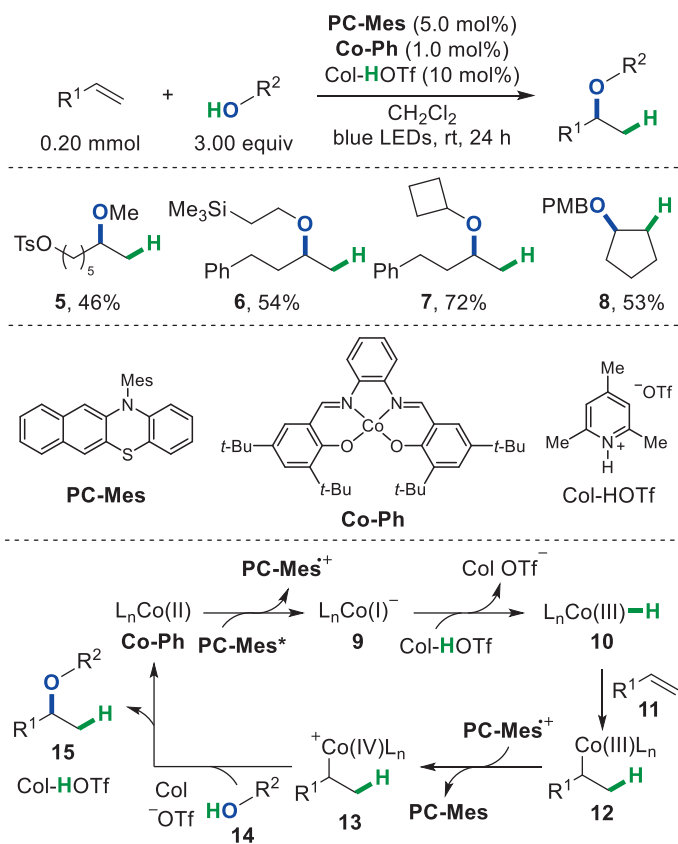
In 2021, Matsunaga and coworkers reported the hydrogenation of olefins which combined cobalt-catalyzed HAT with blue light photoredox catalysis. Notably, their approach did not require peroxide or silane (Scheme 1).^[12] Instead, the photocatalyst $Ru(bpy)_3Cl_2$ (2 mol%) was employed to reduce **Co-Ph** to $L_nCo(I)^-$. Subsequent protonation by ascorbic acid generated the $L_nCo(III)-H$ species which could undergo HAT. This concept of protonating a $L_nCo(I)^-$ species can be traced back to a 1965 report by Schrauzer and coworkers on cobalamin.^[13] They demonstrated that $L_nCo(III)-H$ could be generated by reduction of $L_nCo(III)-Cl$. Furthermore, they showed that protonation of $L_nCo(I)^-$ yields $L_nCo(III)-H$ which Schrauzer concluded is the conjugate acid of $L_nCo(I)^-$.



Scheme 1. Photo-MHAT hydrogenation of olefins.

In 2022, Ohmiya and Nagao applied the combination of photoredox catalysis and Co-catalyzed HAT to enable the hydroetherification and hydroesterification of olefins (Scheme 2). In their work, **Co-Ph** is first reduced by the excited state organophotocatalyst **PC-Mes*** to form the $L_nCo(I)^-$ species **9** which is then protonated by collidinium triflate to the familiar $L_nCo(III)-H$ species with concomitant formation of collidine. HAT to an olefin affords $L_nCo(III)-alkyl$ species **12** which is subsequently oxidized by **PC-Mes*** to $L_nCo(IV)-alkyl$ **13**, the latter exhibiting cationic character. The $L_nCo(IV)$ moiety in **13** is substituted by the pendent alcohol group, completing the catalytic cycle. Collidine assists the trapping of intermediate **13** by deprotonating alcohol **14** and regenerating collidinium triflate **Col-HOTf** in the process (Scheme 2). It is important to note that the photocatalyst plays a dual role as both the oxidant and reductant for the Co-catalyst. In concert

with catalytic amounts of **Col-HOTf**, this photo-MHAT does not require stoichiometric silanes and oxidants.



Scheme 2. Reaction overview of the photo-MHAT hydroetherification (top) and proposed mechanism (bottom).

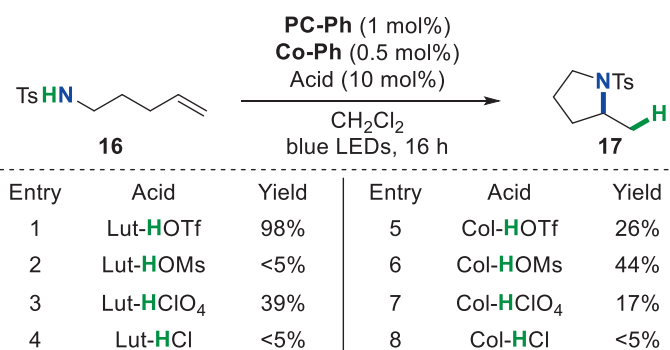
2.1 Fully Catalytic Cycloisomerization Reactions

At the onset of our studies, it was unclear whether a cobalt and photoredox catalyzed MHAT could be applied in cycloisomerization reactions for the synthesis of heterocycles in particular with nitrogen-based nucleophiles.^[14] Initial experiments with pent-4-en-1-amine, **PC-Ph**, **Co-Ph** and **Col-HOTf** were unsuccessful and no product was observed.

We suspected that the primary amine deprotonates **Col-HOTf**, disrupting the delicate acid-base interplay between **Col-HOTf** and $L_nCo(I)^-$. As a consequence, the basicity of the primary amine was reduced by *N*-tosylation.^[14] When tosyl amine **16** was resubjected to 5 mol% **PC-Ph**, 1 mol% **Co-Ph**, and 10 mol% **Col-HOTf** in CH_2Cl_2 , 64% of tosyl-protected pyrrolidine **17** was obtained.

Optimization studies further enabled us to decrease the catalyst loading of **PC-Ph** to 1 mol% and **Co-Ph** to 0.2–0.5 mol%. Investigation of various acid additives highlighted the sensitive interplay between the cobalt catalyst and the proton source. For instance, significant differences in product formation were observed when the lutidinium counterion was altered (Scheme 3, Lut-HOTf (98%) vs. Lut-HOMs (<5%)).^[14] Consequently, we recommend a thorough investigation of acids when employing photo-MHAT conditions on underexplored substrates or new transformations.

With optimized reaction conditions in hand, we synthesized several nitrogen containing heterocycles such as pyrrolidines, piperidines and tetrahydroisoquinolines in good to excellent yield (Scheme 4A). Guanidine derivatives were also competent nucleophiles under our photo-MHAT cycloisomerization conditions, affording *N*-protected imidazolidin-2-imines, tetrahydro-pyrimidin-2-imines and 1,3-diazepan-2-imines in 43–86% yield.^[15]



Scheme 3. Influence of the acid identity on the yield.

To further broaden the scope of the photo-cycloisomerization reaction, *N*-acyl sulfonamides, urea, and thiourea derivatives were explored (Scheme 4B).^[14,15] The corresponding heterocycles **24–27** were afforded in 76–98% yield. Carbamates were successfully cyclized to 2-oxazolidinones in 25–83% yield. When acyclic olefins with pendent alcohols or carboxylic acids were subjected to our photo-MHAT conditions, a variety of ring sizes including ep-

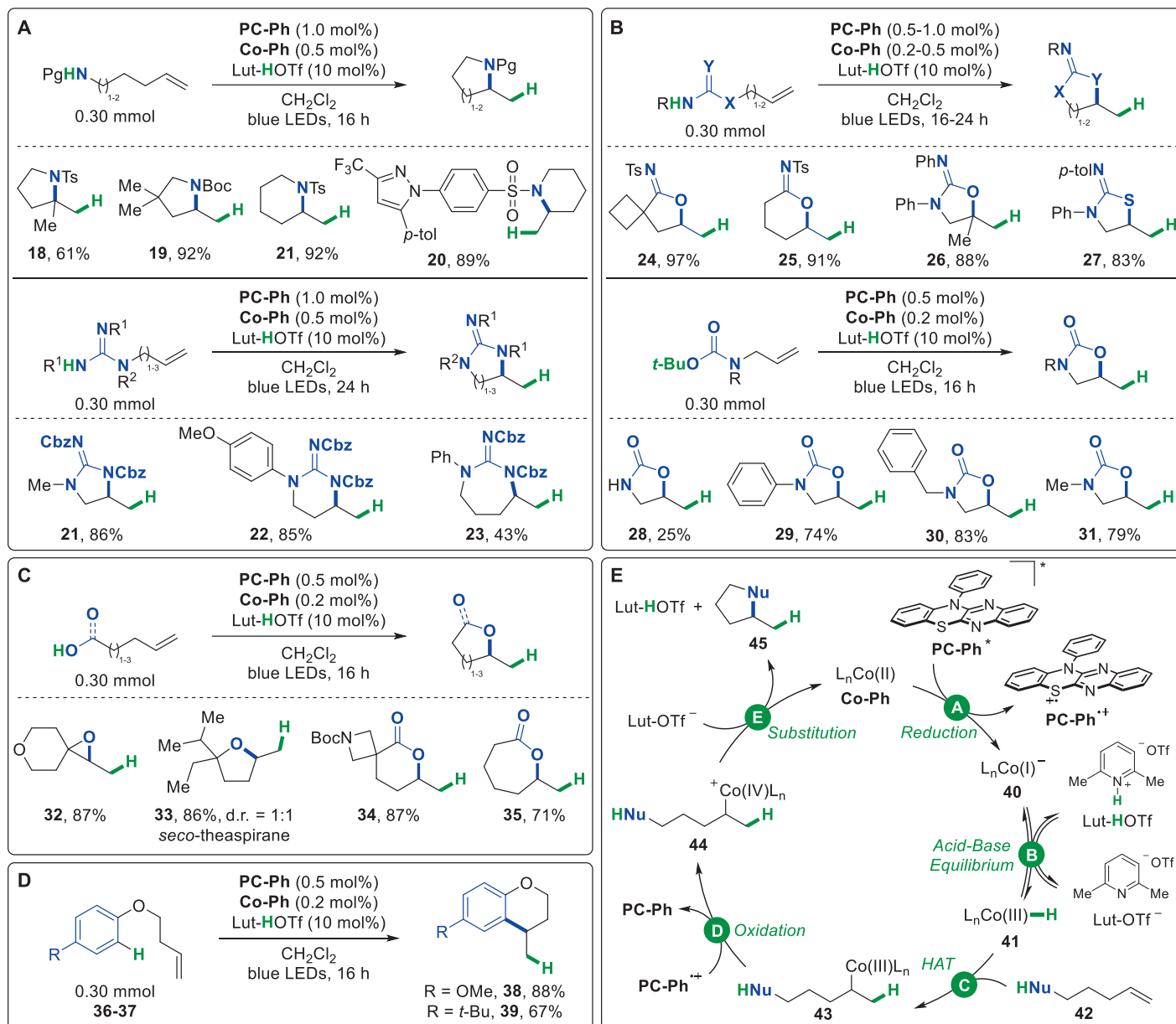
oxides, tetrahydrofuran and tetrahydropyran derivatives, γ -, δ -, and ϵ -lactones were obtained in good yield (Scheme 4C). Arenes also proved effective as nucleophiles, affording chromanes **38** and **39** in 88% and 67% yields, respectively (Scheme 4D).^[14]

Mechanistically, we propose that **Co-Ph** is reduced to $L_n\text{Co(I)}^-$ by **PC-Ph*** (Scheme 4E). Consistent with Schrauzer's report, this anionic complex subsequently undergoes reversible protonation by Lut-HOTf to afford the conjugate acid $L_n\text{Co(III)-H}$. The cobalt hydride species adds with excellent Markovnikov selectivity to the unactivated olefin and furnishes $L_n\text{Co(III)-alkyl}$ species **43**.

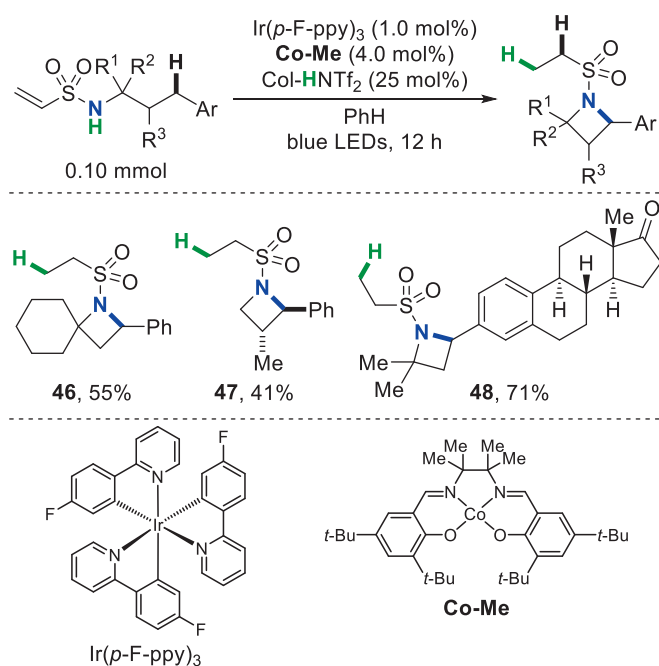
PC-Ph* subsequently oxidizes **43** to $L_n\text{Co(IV)-alkyl}$ **44**. The substitution event of the Co-complex by the pendent nucleophile is assisted by lutidine and leads to product formation, with regeneration of **Co-Ph**, and Lut-HOTf.^[14]

2.2 Further Applications of Photo-MHAT

In 2024, Ohmyia and Nagao reported a cycloisomerization reaction of vinyl sulfonamides to access azetidines (Scheme 5). This study further expanded the range of *N*-containing heterocycles accessible through a fully catalytic photo-MHAT reaction.^[16] Notably, for this transformation **Co-Me** performed best, while **Co-Ph** afforded substantially lower yields. Furthermore, the



Scheme 4. A-D: Synthesis of over 15 different heterocycles via photo-MHAT. E: Proposed mechanism.



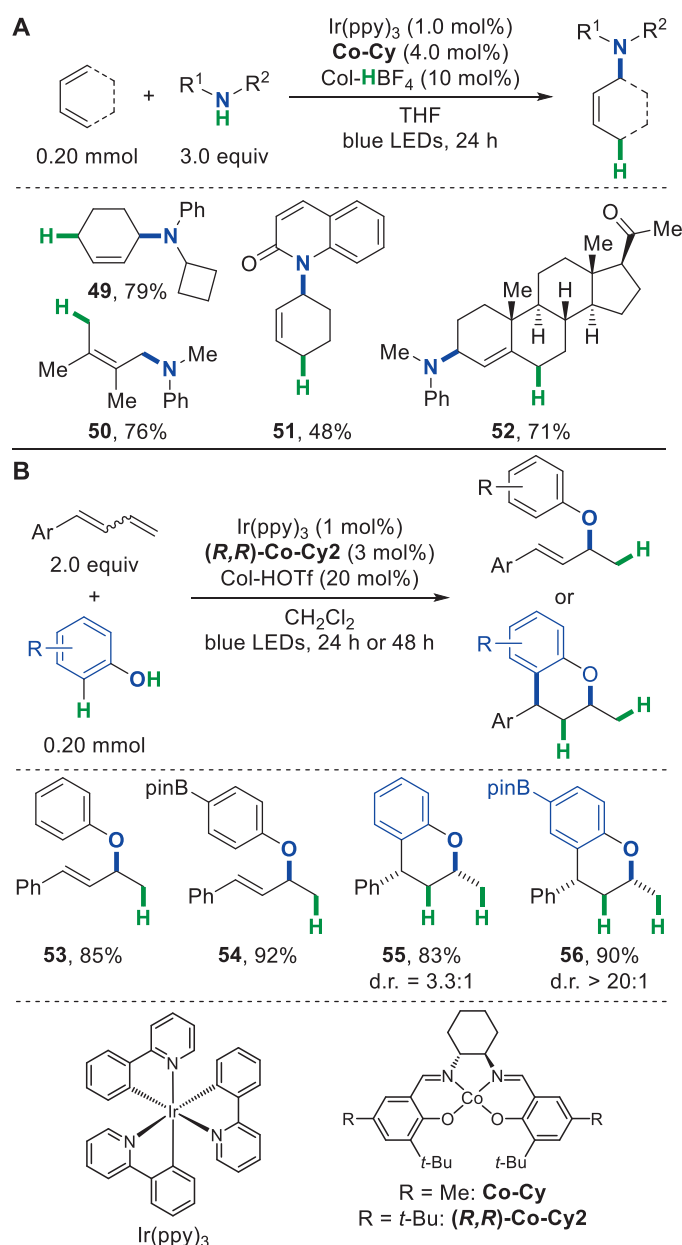
Scheme 5. Synthesis of azetidine via photo-MHAT.

acid Col-HNTf₂ performed best, while Col-HOTf and Col-HBF₄ afforded worse results.

Mechanistically, the authors propose that the photochemical reduction of **Co-Me** by Ir(*p*-F-ppy)₃* generates L_nCo(I), which is then protonated to form L_nCo(III)-H. HAT to the vinyl sulfone affords the more stabilized secondary radical. A 1,6-H-atom abstraction of the benzylic proton forms a benzylic radical which could be stabilized by Co(II), forming an L_nCo(III)-alkyl species. Oxidation by Ir(*p*-F-ppy)₃* to L_nCo(IV)-alkyl is followed by displacement of the cobalt moiety by the pendent nucleophile and affords the azetidine.^[16]

In an effort to expand the scope of the photo-MHAT reaction for the intermolecular hydroamination of olefins, Yu and coworkers successfully applied these conditions to the hydroamination of cyclic and acyclic 1,3-dienes.^[17] The reaction scope was primarily demonstrated on 1,3-cyclohexadienes with secondary unprotected aniline derivatives as the nucleophile (Scheme 6A). The hydroamination with aniline, piperidine, and *N*-methyl acetamide was unsuccessful. Optimization studies once again revealed that seemingly minute changes to the cobalt and acid catalyst can impact the reaction yield significantly. **Co-Ph** and **Co-Me** underperformed compared to **Co-Cy**. Amongst Col-HOTf (72%), Col-HBr (5%), and Col-HBF₄ (76%), the latter furnished the allyl amine under otherwise identical reaction conditions with the highest yield. When the organophotocatalyst **PC-Mes**, previously used by Ohmiya and Nagao for the hydroetherification and hydroesterification of olefins (*vide supra*), was employed, no reaction was observed.^[17]

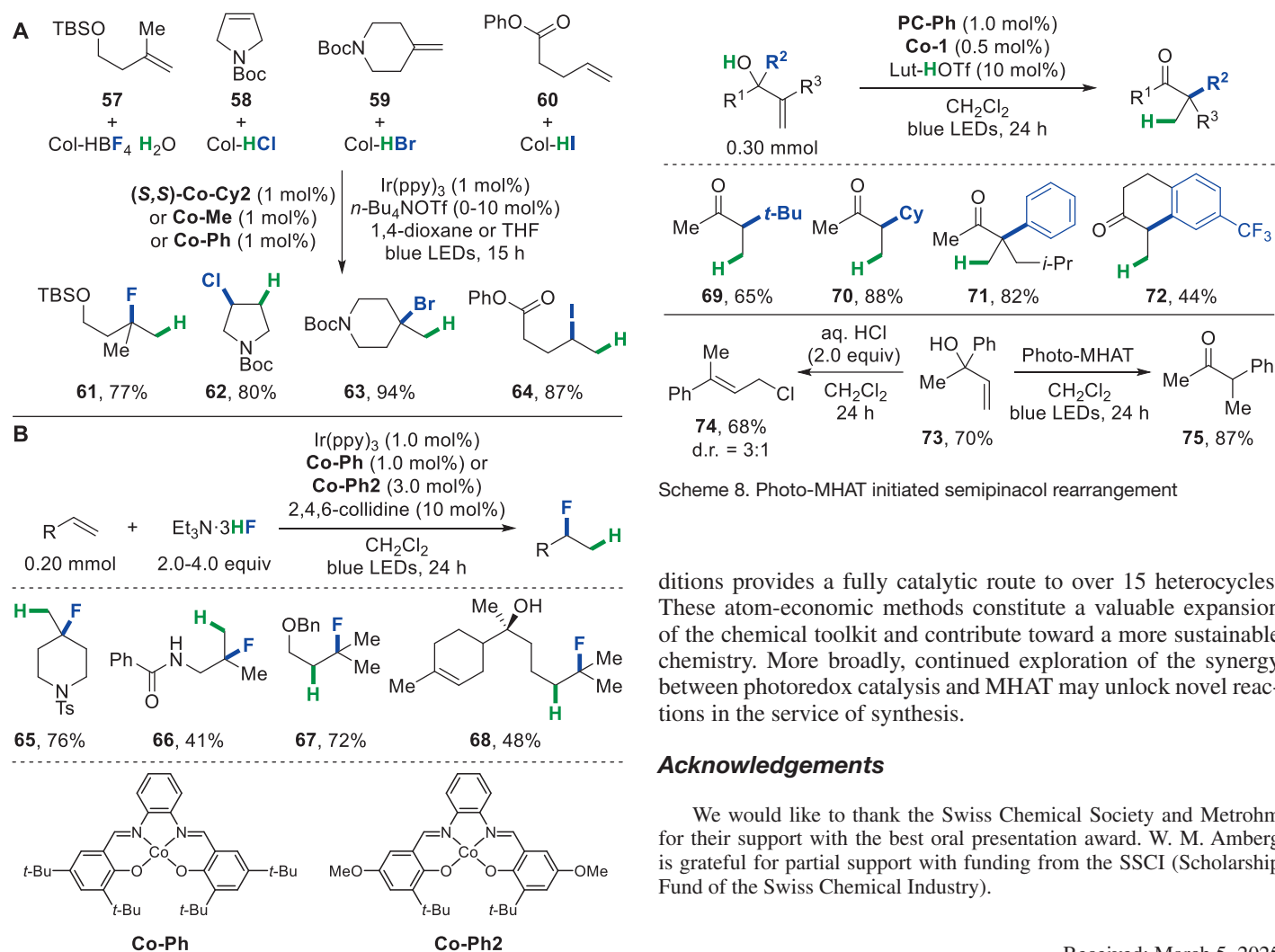
Following the work of Yu, Zhang and coworkers reported the hydroetherification of 1,3-dienes with phenols (Scheme 6B).^[18] The reaction scope was primarily demonstrated on 1-aryl-1,3-butadienes, and the authors found that regardless of whether the starting material was *E*-, *Z*-, or a mixture of diastereomers, the product always contained an *E*-olefin. To obtain the allylic aryl ethers **53** and **54** in good to excellent yield, the authors employed Ir(ppy)₃ (1 mol%), (**R,R**)-**Co-Cy2** (1 mol%) and Col-HOTf (20 mol%) in CH₂Cl₂ under blue light irradiation for 24 h.^[18] Intriguingly, when the reaction mixture was stirred for 48 hours instead of 24 hours, the allylic aryl ethers underwent a second photo-MHAT reaction, leading to the formation of substituted chromanes **55–56**.^[18]



Scheme 6. A: Hydroamination of 1,3-dienes with secondary anilines. B: Hydroetherification of 1,3-dienes with phenols and synthesis of substituted chromanes.

The hydrohalogenation of olefins was one of the first transformations investigated using MHAT.^[9b,9f,9g] In 2024, Ohmiya and Nagao revisited this reaction in the context of photo-MHAT. The authors successfully employed protonated collidine salts with the respective halogens as counterions (Col-HBF₄, Col-HCl, Col-HBr, and Col-HI) in combination with 1 mol% of a cobalt catalyst and 1 mol% of Ir(ppy)₃ to achieve the envisioned transformation (Scheme 7A).^[19]

At the same time, Lin and coworkers focused particularly on a photo-MHAT hydrofluorination of olefins. In contrast to Ohmiya and Nagao, Lin utilized Et₃N·3HF as the fluoride source instead of Col-HBF₄ (Scheme 7B).^[20] In concert with 10 mol% collidine, 1 mol% Ir(ppy)₃ and 1 mol% of a cobalt catalyst, the authors developed a hydrofluorination reaction which is compatible with *mono*-, *di*-, and *trisubstituted* olefins as well as both activated and unactivated alkenes. However, it is important to note that for each substrate class the reaction conditions need to be adjusted, particularly with respect to the choice of the cobalt catalyst.

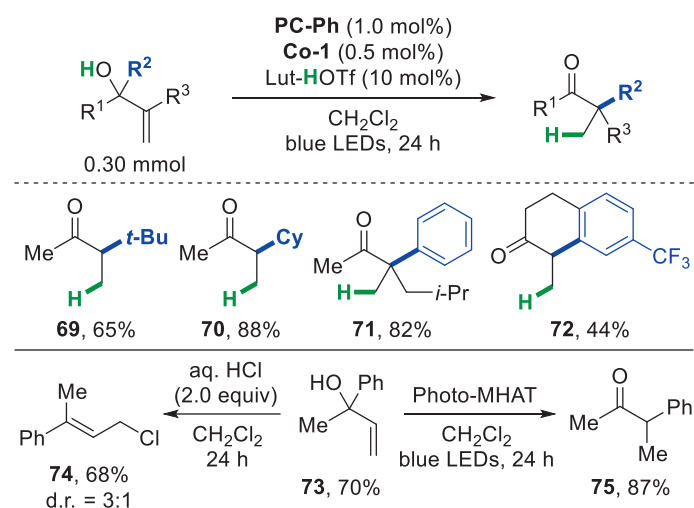


Scheme 7. A: Hydrohalogenation of alkenes with collidinium salts via photo-MHAT. B: Hydrofluorination of alkenes with $\text{Et}_3\text{N}\cdot\text{HF}$ via photo-MHAT.

The semipinacol rearrangement has found wide application in the synthesis of complex molecules, and discovering new pathways to initiate this rearrangement remains highly desirable.^[21] In this context we investigated a semipinacol rearrangement initiated by photo-MHAT (Scheme 8).^[22] Various allylic alcohols with different migratory groups were compatible with the reaction conditions (1 mol% **PC-Ph**, 0.5 mol% **Co-Ph**, 10 mol% Lut-HOTf), affording **69–72** in 44–88% yield. Intriguingly, the photo-MHAT reactivity is complementary to that observed with Brønsted acids. When **73** is treated with 2 M HCl, substitution of the alcohol moiety and formation of allyl chloride **74** is observed. In contrast, under photo-MHAT conditions, a semipinacol rearrangement occurs and ketone **75** is formed.

3. Conclusions

Metal-catalyzed hydrogen atom transfer reactions have emerged as a powerful tool in organic synthesis. Traditionally, these reactions prescribe stoichiometric reductants and oxidants. However, with the advent of photocatalysis, MHAT is experiencing exciting new developments. By employing a photoredox catalyst as both reductant and oxidant, the need for sacrificial reagents is eliminated. The efficiency of photo-MHAT has been demonstrated in reactions such as hydroetherification, hydroesterification, hydroamination, and hydrohalogenation of olefins as well as in semipinacol rearrangements. Additionally, cycloisomerization of olefins with pendent nucleophiles under photo-MHAT con-



Scheme 8. Photo-MHAT initiated semipinacol rearrangement

ditions provides a fully catalytic route to over 15 heterocycles. These atom-economic methods constitute a valuable expansion of the chemical toolkit and contribute toward a more sustainable chemistry. More broadly, continued exploration of the synergy between photoredox catalysis and MHAT may unlock novel reactions in the service of synthesis.

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- [1] a) J. Hagen, 'Industrial catalysis: a practical approach', John Wiley & Sons, **2015**; b) R. A. Sheldon, I. Arends, U. Hanefeld, 'Green chemistry and catalysis', John Wiley & Sons, **2007**.
- [2] J. Wisniak, *Educ. Quím.* **2010**, *21*, 60, [https://doi.org/10.1016/S0187-893X\(18\)30074-0](https://doi.org/10.1016/S0187-893X(18)30074-0).
- [3] a) J.-P. Corbet, G. Mignani, *Chem. Rev.* **2006**, *106*, 2651, <https://doi.org/10.1021/cr0505268>; b) I. F. Yu, J. W. Wilson, J. F. Hartwig, *Chem. Rev.* **2023**, *123*, 11619, <https://doi.org/10.1021/acs.chemrev.3c00207>; c) E. P. Beaumier, A. J. Pearce, X. Y. See, I. A. Tonks, *Nat. Rev. Chem.* **2019**, *3*, 15, <https://doi.org/10.1038/s41570-018-0059-x>; d) S. L. Rössler, D. A. Petrone, E. M. Carreira, *Acc. Chem. Res.* **2019**, *52*, 2657, <https://doi.org/10.1021/acs.accounts.9b00209>; e) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208, <https://doi.org/10.1039/B816696J>; f) T. W. Butcher, W. M. Amberg, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2022**, *61*, e202112251, <https://doi.org/10.1002/anie.202112251>; g) W. M. Amberg, E. M. Carreira, *J. Am. Chem. Soc.* **2022**, *144*, 15475, <https://doi.org/10.1021/jacs.2c07150>; h) N. Pierson, J. F. Hartwig, *Nat. Chem.* **2024**, *16*, 930, <https://doi.org/10.1038/s41557-024-01451-x>.
- [4] a) S. Mukherjee, J. W. Yang, S. Hoffmann, B. List, *Chem. Rev.* **2007**, *107*, 5471, <https://doi.org/10.1021/cr0684016>; b) A. G. Doyle, E. N. Jacobsen, *Chem. Rev.* **2007**, *107*, 5713, <https://doi.org/10.1021/cr068373r>; c) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606, <https://doi.org/10.1021/cr068372z>.
- [5] a) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322, <https://doi.org/10.1021/cr300503r>; b) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* **2016**, *116*, 10075, <https://doi.org/10.1021/acs.chemrev.6b00057>; c) W. M. Amberg, H. Lindner, Y. Sahin, E. Staudinger, V. Morad, S. Sabisch, L. G. Feld, Y. Li, D. N. Dirin, M. V. Kovalenko, E. M. Carreira, *J. Am. Chem. Soc.* **2025**, *147*, 8548, <https://doi.org/10.1021/jacs.4c17013>; d) W. M. Amberg, Doctoral Thesis, ETH Zurich, **2024**, <https://doi.org/10.3929/ethz-b-000714863>.
- [6] a) F. H. Arnold, *Angew. Chem. Int. Ed.* **2018**, *57*, 4143, <https://doi.org/10.1002/anie.201708408>; b) J. C. Reisenbauer, K. M.

- Sicinski, F. H. Arnold, *Curr. Opin. Chem. Biol.* **2024**, *83*, 102536, <https://doi.org/10.1016/j.cbpa.2024.102536>; c) O. Pàmies, J.-E. Bäckvall, *Chem. Rev.* **2003**, *103*, 3247, <https://doi.org/10.1021/cr020029g>; d) M. Hönl, P. Sondermann, N. J. Turner, E. M. Carreira, *Angew. Chem. Int. Ed.* **2017**, *56*, 8942, <https://doi.org/10.1002/anie.201612462>.
- [7] a) A. Y. Chan, I. B. Perry, N. B. Bissonnette, B. F. Buksh, G. A. Edwards, L. I. Frye, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley, N. L. Reed, H. A. Sakai, C. P. Seath, D. W. C. MacMillan, *Chem. Rev.* **2022**, *122*, 1485, <https://doi.org/10.1021/acs.chemrev.1c00383>; b) S. Jana, V. J. Mayerhofer, C. J. Teskey, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304882, <https://doi.org/10.1002/anie.202304882>.
- [8] a) A. Zombeck, D. E. Hamilton, R. S. Drago, *J. Am. Chem. Soc.* **1982**, *104*, 6782, <https://doi.org/10.1021/ja00388a051>; b) D. E. Hamilton, R. S. Drago, A. Zombeck, *J. Am. Chem. Soc.* **1987**, *109*, 374, <https://doi.org/10.1021/ja00388a051>; c) S. Inoki, K. Kato, T. Takai, S. Isayama, T. Yamada, T. Mukaiyama, *Chem. Lett.* **1989**, *18*, 515, <https://doi.org/10.1246/cl.1989.515>; d) S. Isayama, T. Mukaiyama, *Chem. Lett.* **1989**, *18*, 1071, <https://doi.org/10.1246/cl.1989.1071>.
- [9] a) S. W. M. Crossley, C. Obradors, R. M. Martinez, R. A. Shenvi, *Chem. Rev.* **2016**, *116*, 8912, <https://doi.org/10.1021/acs.chemrev.6b00334>; b) T. J. Barker, D. L. Boger, *J. Am. Chem. Soc.* **2012**, *134*, 13588, <https://doi.org/10.1021/ja3063716>; c) S. A. Green, J. L. M. Matos, A. Yagi, R. A. Shenvi, *J. Am. Chem. Soc.* **2016**, *138*, 12779, <https://doi.org/10.1021/jacs.6b08507>; d) J. Waser, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2005**, *127*, 8294, <https://doi.org/10.1021/ja052164r>; e) J. Waser, B. Gaspar, H. Nambu, E. M. Carreira, *J. Am. Chem. Soc.* **2006**, *128*, 11693, <https://doi.org/10.1021/ja062355+>; f) B. Gaspar, E. M. Carreira, *Angew. Chem. Int. Ed.* **2008**, *47*, 5758, <https://doi.org/10.1002/anie.200801760>; g) X. Ma, S. B. Herzon, *Chem. Sci.* **2015**, *6*, 6250, <https://doi.org/10.1039/C5SC02476E>.
- [10] a) H. Shigehisa, N. Koseki, N. Shimizu, M. Fujisawa, M. Niitsu, K. Hiroya, *J. Am. Chem. Soc.* **2014**, *136*, 13534, <https://doi.org/10.1021/ja507295u>; b) S. L. Shevick, C. V. Wilson, S. Kotesova, D. Kim, P. L. Holland, R. A. Shenvi, *Chem. Sci.* **2020**, *11*, 12401, <https://doi.org/10.1039/D0SC04112B>; c) H. Shigehisa, M. Hayashi, H. Ohkawa, T. Suzuki, H. Okayasu, M. Mukai, A. Yamazaki, R. Kawai, H. Kikuchi, Y. Satoh, A. Fukuyama, K. Hiroya, *J. Am. Chem. Soc.* **2016**, *138*, 10597, <https://doi.org/10.1021/jacs.6b05720>; d) H. Shigehisa, T. Ano, H. Honma, K. Ebisawa, K. Hiroya, *Org. Lett.* **2016**, *18*, 3622, <https://doi.org/10.1021/acs.orglett.6b01662>; e) S. Date, K. Hamasaki, K. Sunagawa, H. Koyama, C. Sebe, K. Hiroya, H. Shigehisa, *ACS Catal.* **2020**, *10*, 2039, <https://doi.org/10.1021/acscatal.9b05045>.
- [11] a) W.-T. Ye, R. Zhu, *Chem. Catal.* **2022**, *2*, 345, <https://doi.org/10.1016/j.checat.2021.12.003>; b) F. Yang, Y.-C. Nie, H.-Y. Liu, L. Zhang, F. Mo, R. Zhu, *ACS Catal.* **2022**, *12*, 2132, <https://doi.org/10.1021/acscatal.1c05557>; c) S. H. Park, G. Bae, A. Choi, S. Shin, K. Shin, C. H. Choi, H. Kim, *J. Am. Chem. Soc.* **2023**, *145*, 15360, <https://doi.org/10.1021/jacs.3c03172>.
- [12] Y. Kamei, Y. Seino, Y. Yamaguchi, T. Yoshino, S. Maeda, M. Kojima, S. Matsunaga, *Nat. Commun.* **2021**, *12*, 966, <https://doi.org/10.1038/s41467-020-20872-z>.
- [13] a) G. N. Schrauzer, R. J. Windgassen, J. Kohnle, *Chem. Ber.* **1965**, *98*, 3324, <https://doi.org/10.1002/cber.19650981032>; b) D. C. Lacy, G. M. Roberts, J. C. Peters, *J. Am. Chem. Soc.* **2015**, *137*, 4860, <https://doi.org/10.1021/jacs.5b01838>.
- [14] H. Lindner, W. M. Amberg, T. Martini, D. M. Fischer, E. Moore, E. M. Carreira, *Angew. Chem. Int. Ed.* **2024**, *63*, e202319515, <https://doi.org/10.1002/anie.202319515>.
- [15] H. Lindner, E. M. Carreira, *Org. Lett.* **2025**, *27*, 704, <https://doi.org/10.1021/acs.orglett.5c004695>.
- [16] M. Nakagawa, K. Nagao, H. Ohmiya, *ACS Catal.* **2024**, *14*, 8005, <https://doi.org/10.1021/acscatal.4c02004>.
- [17] P.-T. Li, Q. Mou, W. Yu, *Org. Lett.* **2025**, *27*, 1973, <https://doi.org/10.1021/acs.orglett.5c00281>.
- [18] Y. Wang, J. Miao, H. Dong, D. Zhang, B. Chen, M. Guan, G. Zhang, Q. Zhang, *Chem. Sci.* **2025**, <https://doi.org/10.1039/D5SC00438A>.
- [19] S. Shibutani, K. Nagao, H. Ohmiya, *J. Am. Chem. Soc.* **2024**, *146*, 4375, <https://doi.org/10.1021/jacs.3c10133>.
- [20] J. Liu, J. Rong, D. P. Wood, Y. Wang, S. H. Liang, S. Lin, *J. Am. Chem. Soc.* **2024**, *146*, 4380, <https://doi.org/10.1021/jacs.3c10989>.
- [21] Z.-L. Song, C.-A. Fan, Y.-Q. Tu, *Chem. Rev.* **2011**, *111*, 7523, <https://doi.org/10.1021/cr200055g>.
- [22] a) H. Lindner, E. M. Carreira, *Angew. Chem. Int. Ed.* **2024**, *63*, e202407827, <https://doi.org/10.1002/anie.202407827>; b) D. Lunic, N. Vystavkin, J. Qin, C. J. Teskey, *Angew. Chem. Int. Ed.* **2024**, *63*, e202409388, <https://doi.org/10.1002/anie.202409388>.

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