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Recent advances in $FeCl_3$-photocatalyzed organic reactions *via* hydrogen-atom transfer

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ABSTRACT

In recent years, $FeCl_3$-photocatalyzed direct C–H/Si–H bond functionalization reactions have attracted huge attention. In those transformations, chlorine radical ($Cl^{\bullet}$) could be generated from $FeCl_3$ *via* a ligand-to-metal charge transfer (LMCT)/homolysis process under light irradiation. The resulting chlorine radical subsequently acts as a hydrogen atom transfer (HAT) agent to abstract the hydrogen atom of aliphatic C–H, O–H, or Si–H bonds to give the corresponding C/Si/O-centered radicals for various organic transformations. In this review, we summarized the recent advances in the application of $FeCl_3$ as a HAT photocatalyst for the C/Si–H functionalization to construct C–C, C–N, C–Si, C–S, C–B, and C-P bonds.

1. Introduction

Hydrogen atom transfer (HAT) is identified as an efficient and atom economic strategy that simultaneously transfers a proton and an electron from one species to another in a single step [1–6]. Over the past century, impressive advances have been made in the inert C–H bond functionalization *via* the HAT process in organic synthesis and materials science [7,8]. In the past decade, photocatalytic organic chemistry has gained enormous attention [9–18]. In this context, the photocatalytic HAT strategy is an environmentally friendly and energy-efficient platform to achieve C–H/Si–H functionalization by generating corresponding radical intermediates for diverse organic transformations [7,19-20]. Until now, a vast variety of HAT photocatalysts have been reported, such as aryl ketones [21], decatungstate [22–25], uranyl cations [26–27], neutral eosin Y [28], and so on.

Halogen radicals ($Cl^{\bullet}$ or $Br^{\bullet}$) are efficient HAT agents that could abstract hydrogen atoms from various C–H/Si–H/O–H bonds to give the corresponding C/Si/O-centered radical and H–X (X = Cl, Br). Among them, the bond dissociation energy (BDE) of the H–Cl bond (103 kcal/mol) is higher than H–Br (88 kcal/mol) [29,30]. Therefore, chlorine radical is generally a more reactive and electrophilic radical for the activation of inert aliphatic C–H bonds [31]. Chloride anion (Cl^-) should be an ideal source for the generation of $Cl^{\bullet}$ *via* single electron oxidation because it is innocuous and abundant in diverse salt forms.

However, the single-electron oxidation of chloride anion into $Cl^{\bullet}$ is generally challenging due to the high redox potential ($E_{ox}(Cl^-/Cl^{\bullet}) = +2.03$ V *versus* SCE in MeCN) [32]. Significantly, in 1962 Kochi disclosed the generation of $Cl^{\bullet}$ and CuCl from the photolysis of $CuCl_2$ [33] *via* a successive ligand-to-metal charge transfer (LMCT) and Cu–Cl homolysis process. Typically, the photo-induced LMCT process involves an electronic transition from a filled orbital (n/π) of the ligand to an empty orbital (d) of the metal center, resulting in an excited LMCT state. The LMCT state undergoes a homolysis of the M–L to release an active radical $L^{\bullet}$, which could be a useful radical initiator in various reactions (Scheme 1). Since then, the application of photogenerated $Cl^{\bullet}$ has emerged as a powerful and promising tool to initiate various organic transformations [34–42].

On the other hand, the functionalization of C–H bonds is highly attractive because C–H bonds are the most abundant moieties in organic molecules. However, the ubiquitous C–H bonds, particularly C(sp^3)–H bonds are generally inert because of their relatively high BDEs [43,44]. Traditional methods of C–H activation rely on transition metal catalysts or stoichiometric amounts of oxidants, which usually require the pre-installation of suitable directing groups [45–47], or elevated reaction temperatures under harsh conditions [48,49]. Although elegant examples using traceless directing group strategy have been achieved [50–52], the direct functionalization of the C–H bond remains challenging in organic synthesis. Thus, the photogenerated $Cl^{\bullet}$-mediated HAT process brings

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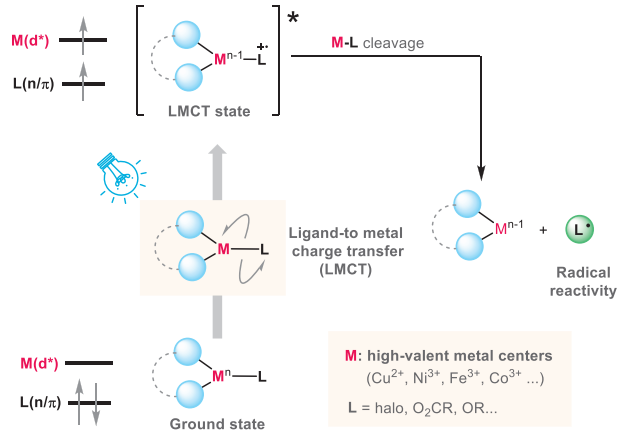


Scheme 1. Photo-inducted ligand-to-metal charge transfer (LMCT).

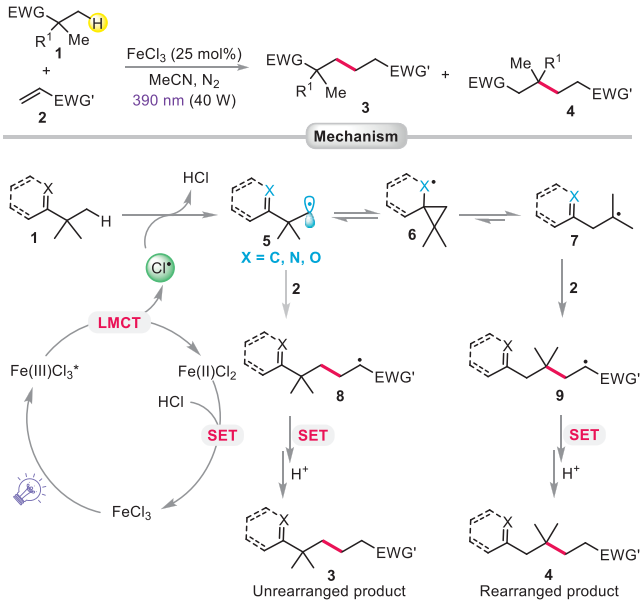
a useful and general method to achieve the functionalization of the C–H bond in organic synthesis.

Iron is one of the most abundant minerals in the Earth's crust. Importantly, it is also an essential metal element for human health [53]. Over the past decades, iron catalysis has captured huge attention in oxidative coupling reactions, reductive reactions, and hydrometallation reactions [54–56], *etc*. Up to now, several reviews related to iron-catalyzed organic synthesis have been reported [8,57-59], they cover a wide variety of iron catalysts and many types of organic reactions. However, $FeCl_3$ as an inexpensive, environmentally friendly, and safe catalyst [60,61], has been rapidly developed in the field of organic synthesis in recent years. Particularly, $FeCl_3$ has emerged as an effective photocatalyst for the synthesis of complex molecules and post-modification of bioactive molecules in recent years [62–68]. Therefore, we herein summarize the recent advances in $FeCl_3$-photocatalyzed organic reactions for the formation of C–C, C–N, C–Si, C–S, C–B, and C-P bonds, which involve photogenerated chlorine radical-initiated HAT. Notably, the elegant examples of $FeCl_3$-catalyzed photooxidation of polystyrene are not included [69,70].

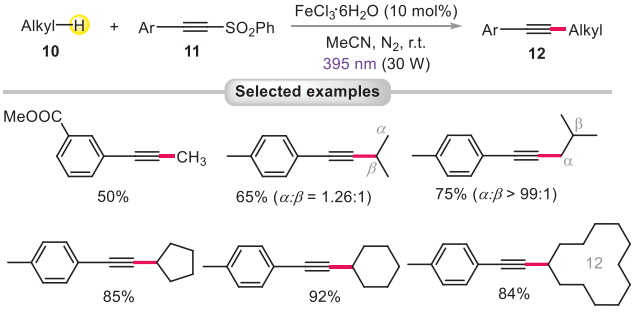
2. Formation of C–C bond

The Dowd–Beckwith rearrangement is a radical-mediated skeletal rearrangement involving a radical 1,2-rearrangement process. Rovis's group developed a $FeCl_3$-catalyzed C(sp^3)–H alkylation reaction *via* a Dowd-Beckwith ring expansion procedure under the irradiation of 390 nm LEDs in 2021 (Scheme 2) [71]. In this reaction, chlorine radical is generated from $FeCl_3$ *via* an LMCT/homolysis procedure under irradiation. Then, the Cl• abstracts a hydrogen atom of the C(sp^3)–H bond of substrate **1** to give an unstable 1° carbon-centered radical **5**. Then the addition of radical **5** to the olefin **2** produces the radical intermediate **8**, followed by a single electron transfer (SET) and protonation to afford the unrearranged product **3**. Alternatively, the unstable radical **5** could undergo an intramolecular skeletal rearrangement *via* cyclopropyl-containing radical intermediate **6** to generate a more stable radical intermediate **7**, which is converted into the corresponding rearranged products **4**.

In this work, a mixture of unrearranged and rearranged products was obtained in moderate yields. The ratios of products generally can be tuned by changing the concentration and temperature of the reaction. It turns out that the ratio of product 3/4 is increased at a low temperature and high concentration (r.t., 0.3 mol/L), while it is decreased at a high temperature and low concentration (60 °C, 0.1 mol/L). This protocol provides a simple method to accomplish the selective synthesis of the directly alkylated or the rearranged-alkylated products. However, the poor selectivity and the low yields in most cases limit the utilization of this method.

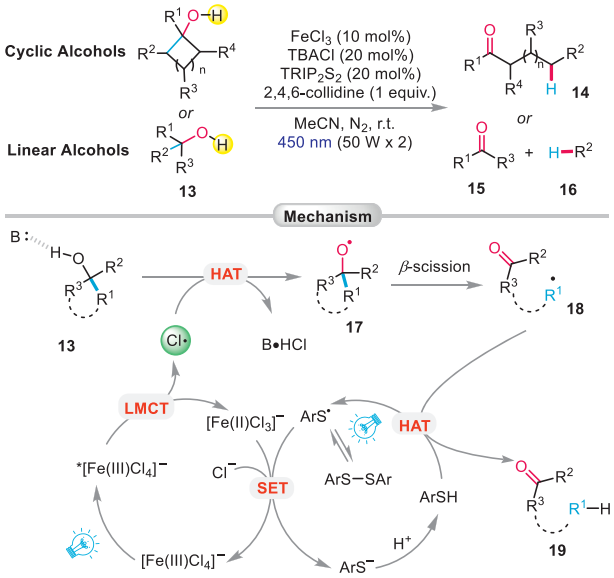


Scheme 2. $FeCl_3$-photocatalyzed C(sp^3)–H alkylation.

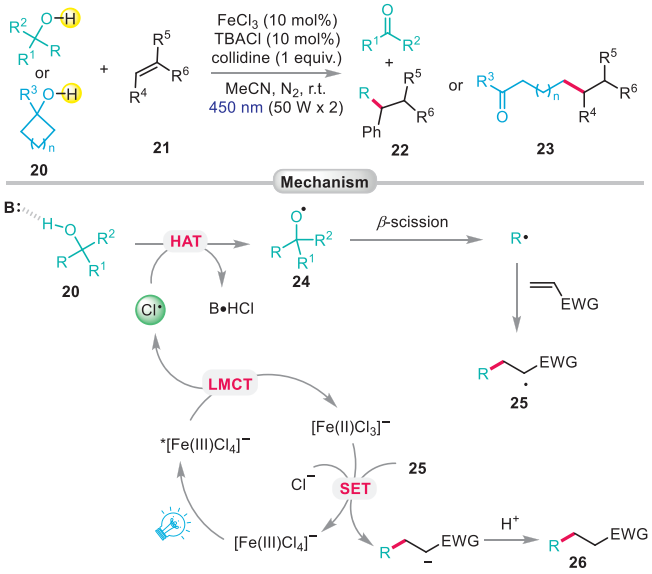


Scheme 3. $FeCl_3$-photocatalyzed alkynylation of light alkanes.

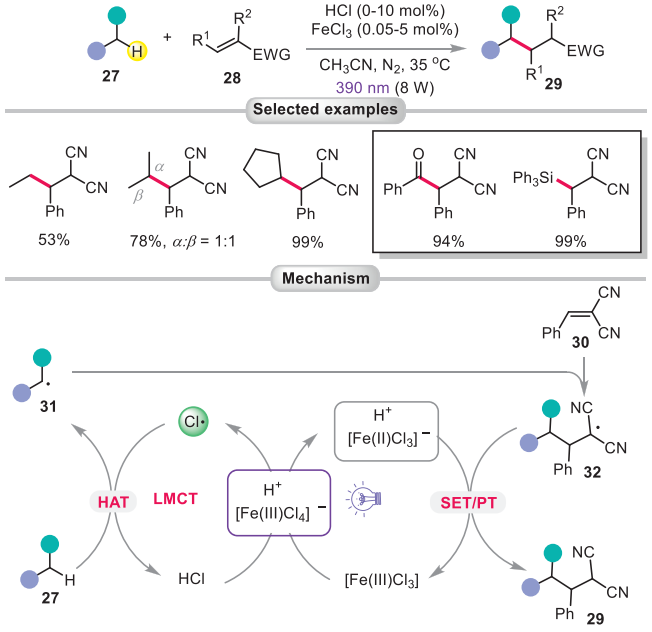
As a class of important building blocks and fundamental structural motifs, alkynes are widely used in the synthesis of pharmaceuticals and electronic materials [72]. On the other hand, the desulfonylative transformations of organic sulfones *via* C–SO_2 bond cleavage have been recognized as a versatile tool for the construction of new bonds [73–75]. In this context, in 2021 Jin and Duan's group developed an efficient and practical desulfonylative coupling of light alkanes **10** and alkynyl aryl sulfones **11** for the construction of valuable internal alkynes **12**, by using $FeCl_3·6H_2O$ (10 mol%) as a direct HAT photocatalyst under the irradiation of 395 nm light (Scheme 3) [76]. This oxidant-free protocol proceeds smoothly under mild conditions, especially for the light alkanes, including liquid alkenes and gaseous alkanes such as methane, ethane, and propane. Notably, when isobutane was employed as an alkylation reagent, the 1° and 3° C(sp^3)–H bond functionalization products (α/β) were observed with a ratio of 99/1. Additionally, a wide range of cycloalkanes such as cyclopentane, cyclohexane, cycloheptane, cyclooctane, and cyclododecane were also efficient alkylation reagents in this procedure to give the corresponding products in good to excellent yields. Similarly, the chlorine radical (Cl•) generated from $FeCl_3$ *via* an LMCT/homolysis procedure under irradiation is a critical initiator to abstract the hydrogen atom of the C(sp^3)–H bond of alkanes affording the corresponding alkyl radicals.



Scheme 4. $FeCl_3$-photocatalyzed C–C bond cleavage of cyclic alcohols.



Scheme 5. $FeCl_3$-photocatalyzed reaction of alcohols and electron-deficient alkenes.



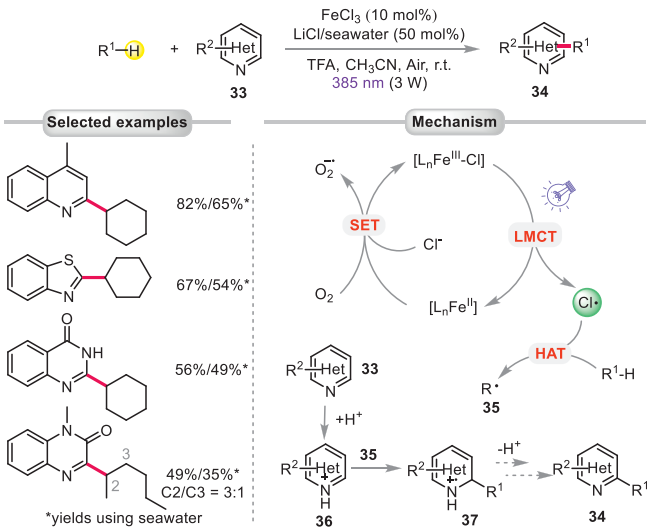
Scheme 6. $FeCl_3$/HCl-photocatalyzed functionalization of C(sp^3)–H bonds.

Selectively cleavage of C–C bond is a promising strategy to construct new compounds and complex molecules, which has received great attention in recent years [77–83]. However, selective cleavage of an inert C–C bond is always a tough task due to the large BDE [84]. Considering that alkoxy radicals can be transformed into C-centered radicals through an intramolecular HAT or the *β*-scission of the C–C bond [85–88], Hu's group in 2021 reported a visible-light-induced $FeCl_3$-catalyzed direct HAT strategy to generate alkoxy radicals from alcohols, leading to a C–C bond cleavage (Scheme 4) [89]. As can be seen in Scheme 4, under the irradiation of 430 nm blue light, $Cl^{\bullet}$ is generated from [$FeCl_4^-$] *via* an LMCT procedure. Then, $Cl^{\bullet}$ abstracts a hydrogen atom from the O–H bond of the cyclic/linear alcohol **13** with the assistance of a base, which gives the alkoxy radical **17**. Then, **17** undergoes an intramolecular *β*-scission to afford the carbon-centered radical **18**. Subsequently, the HAT process between radical **18** and *in situ* formed ArSH generates the corresponding ketone product **19**. As a result, a series of ketones and aldehydes were synthesized through this practical catalytic system.

This visible-light-induced reaction showed a wide range of substrate scope. For example, 1°, 2°, and 3° alcohols were all suitable for the transformation, and the yields of the ring-open products were up to 96%. Additionally, natural products and pharmaceutical molecules such as (-)-nopol, testosterone, and 7-methyltestosterone, showed good performance in this ring-open reaction, giving the corresponding products with moderate to good yields.

After that, the same group developed another $FeCl_3$-photocatalyzed C–C bond cleavage alkylation of alcohols with electron-deficient alkenes *via* the direct HAT and *β*-scission of various alcohols (Scheme 5) [90]. A series of control experiments indicated that a *β*-scission of the alkoxy radical progress is involved in this transformation. In the plausible mechanism, alkoxy radical **24** is generated from the corresponding alcohol by the HAT process of $Cl^{\bullet}$, which is generated from the photoexcited iron catalyst. Then, the alkoxy radical **24** undergoes a selective *β*-scission of the C–C bond to generate an alkyl radical. Subsequently, the addition of alkyl radical to electron-deficient olefins affords the radical intermediate **25**, which is finally transformed into the corresponding product **26** after a single electron reduction and protonation. Although these two above-mentioned $FeCl_3$-photocatalyzed reactions were realized under the irradiation of visible light (450 nm), a relatively high light intensity (50 W × 2) and a stoichiometric amount of base are required to facilitate the reaction due to the high BDE of the O–H bond (~105 kcal/mol) [29].

Direct transformed gaseous alkanes (such as methane, ethane, and propane) into high-value-added chemicals in mild conditions without the need for functionalized reagents is a meaningful issue [91]. In 2022, Wang and Gong's group reported a $FeCl_3$/HCl-photocatalyzed procedure to achieve the diverse functionalization of the C(sp^3)–H bonds under the irradiation of 390 nm LEDs (Scheme 6) [62], providing the alkylation, oxidation, chlorination, fluorination, amination, alkynylation, and sulfonylation products. Particularly, in the reaction of cyclohexane and 2-benzylidenemalononitrile, a turnover number (TON) of 9900 was observed. Light alkanes like ethane, propane, aldehyde and silane were successfully applied as substrates. In this catalytic system, the addition of HCl is found to be essential, which could promote $FeCl_3$



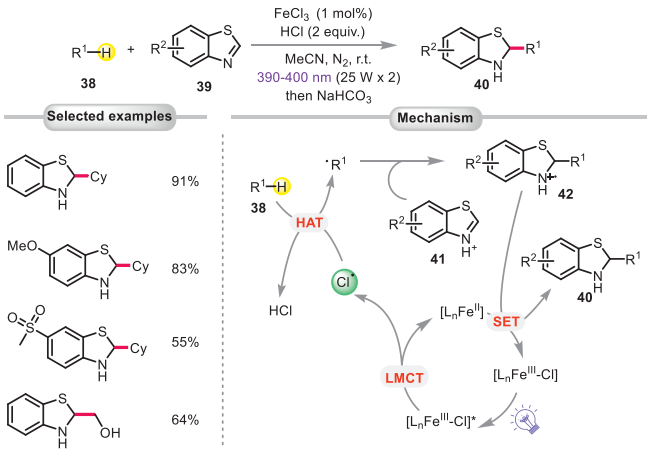
Scheme 7. $FeCl_3$-photocatalyzed alkylation of heteroarenes.

to generate more photoactive species [$FeCl_4^-$]. Under the irradiation of 390 nm LEDs, [$FeCl_4^-$] generates Cl• *via* an LMCT procedure. Then, Cl• abstracts a hydrogen atom from the C(sp^3)–H bond substrates **27** to give the carbon-centered radical **31**. Subsequently, **31** adds to olefin **30**, forming the radical adduct **32**. Finally, **32** undergoes a SET and protonation to afford the corresponding product **29**.

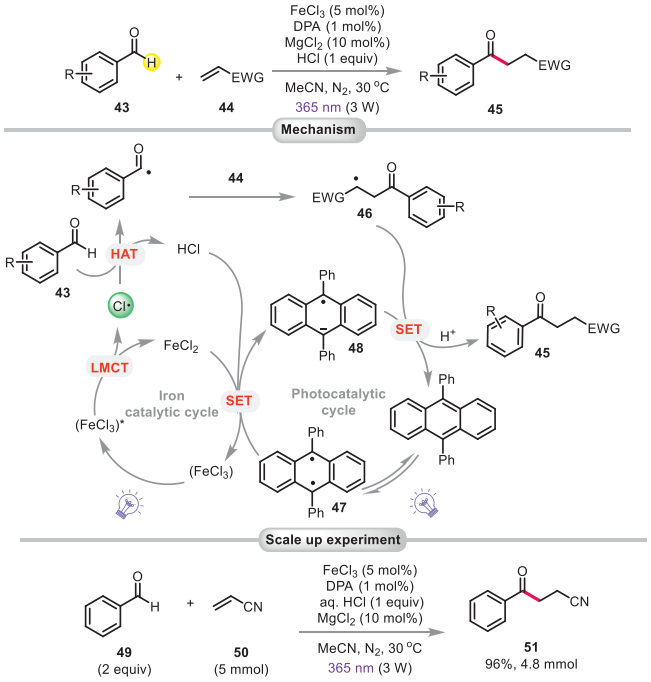
In the same year, Jin's group reported a similar $FeCl_3$-photocatalyzed protocol to achieve the transformation of gaseous alkanes *via* a Cl•-mediated HAT process [92]. In this neutral system, methane (5 MPa), ethane (0.1 MPa), propane (0.1 MPa), and *n*-butane (0.1 MPa) reacted with electron-deficient alkenes smoothly, affording the alkylation products with moderate to excellent yields.

N–Heteroarenes are an omnipresent component of many natural products, bioactive compounds, and pharmaceuticals. Particularly, benzothiazoles and quinolines have captured the interest of chemists worldwide [93–96]. Recently, Jian and Tong's group developed an elegant Minisci reaction to achieve the alkylation of *N*-heteroarene compounds by using $FeCl_3$ as a photocatalyst and LiCl as an additive (Scheme 7) [64]. This procedure is compatible with a variety of *N*-heteroarene substrates, such as quinolines, *p*-hydroxyquinazoline, quinazolinone, and benzothiazole, leading to the corresponding alkylation products in moderate to good yields. Interestingly, brine or seawater can replace LiCl to promote the reaction, which corresponds to the concept of sustainable and green chemistry. In the proposed mechanism, Cl• is generated from the $FeCl_3$ *via* an LMCT procedure under light irradiation. Then Cl• abstracts a hydrogen atom from the unactivated C(sp^3)–H bond of alkanes to give the alkyl radical **35**. Subsequently, **35** adds to the protonated heteroarene **36**, affording the intermediate **37**. Finally, **37** undergoes deprotonation and oxidation to give the product **34**. This photocatalytic reaction provides a convenient method for the installation of an alkyl group into *N*-heteroarene skeleton at room temperature. However, the excess amount of trifluoroacetic acid is necessary to assist the protonation procedure of *N*-heteroarenes.

Dearomatization is a constant challenge in both organic synthesis and pharmaceutical chemistry. Li's group developed a $FeCl_3$-photocatalyzed method to construct alkyl benzothiazolines through a dearomatizative addition of inert alkanes **38** and benzothiazoles **39** under mild conditions (Scheme 8) [97]. Under the irradiation of 390 nm LED, Cl• was generated from $FeCl_3$ *via* an intramolecular LMCT procedure, which directly abstracted a hydrogen atom from **38** to generate an alkyl radical (•R^1). Subsequently, the alkyl radical reacted with the protonated substrate **41** to produce intermediate **42**. Finally, a SET between **42** and the *in situ* generated Fe(II) species provided the target product **40** and completed the catalytic cycle. This method can be conveniently scaled up, and most of the alkylated products can be purified without chromatography.

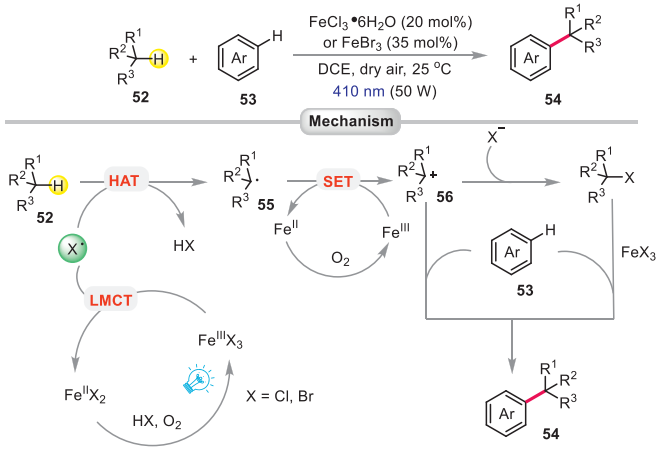


Scheme 8. $FeCl_3$-photocatalyzed dearomatizative alkylation of benzothiazoles.

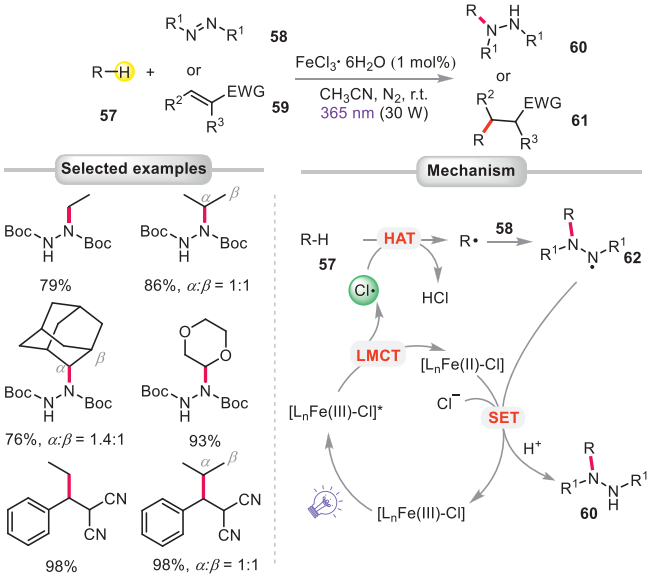


Scheme 9. $FeCl_3$-photocatalyzed alkylation of aldehydes.

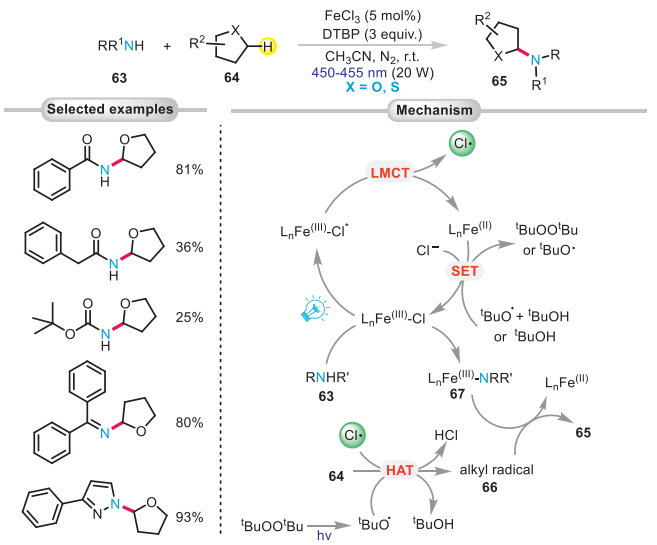
Inexpensive and easily available aldehydes could be applied as useful acylation reagents because the BDE of the C(O)–H bond is relatively weak (~86.9 kcal/mol of benzaldehyde). Recently, Reiser's group disclosed a Cl•-mediate acylation reaction by a $FeCl_3$/diphenylanthracene (DPA) dual photocatalytic system [98]. In this reaction, acyl radical was generated from aldehydes **43** in the presence of HCl (1 equiv.) and $MgCl_2$ (10 mol%) under the irradiation of 390 nm LEDs (Scheme 9). The *in situ* generated Cl• interacts with **43** giving the acyl radical. Then the addition of acyl radical to the electron-deficient olefin **44** produces the radical adduct **46**. Subsequently, the SET and protonation process between the radical **46** and the reduced DPA **48** generates the corresponding acylation product **45**. As a result, a broad range of aldehydes are compatible with this method, ranging from aromatic to aliphatic aldehydes to give the corresponding products in moderate to excellent yields.



Scheme 10. $FeCl_3$-photocatalyzed the cross-coupling of benzenes with aliphatic hydrocarbons.



Scheme 11. $FeCl_3$-photocatalyzed amination of alkanes.



Scheme 12. $FeCl_3$-photocatalyzed alkylation of amides and *N*-heterocycles.

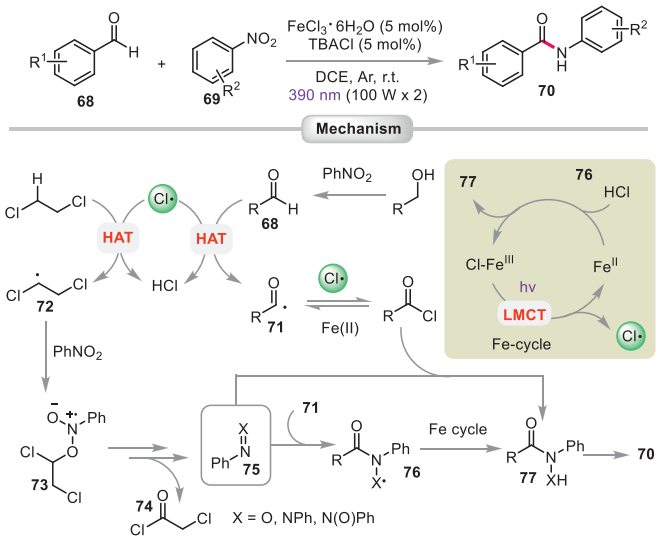
It must be mentioned that this procedure is practical and scalable as 96% yield was obtained when the reaction was conducted on a 5.0 mmol scale.

The construction of C(sp^2)-C(sp^3) bond from readily available starting materials benzenes and aliphatic hydrocarbons is generally a challenging task due to the intrinsic inertness of reactants. Recently, the coupling of benzenes with aliphatic hydrocarbons was realized by Gong's group with visible-light-induced iron salts ($FeCl_3$ or $FeBr_3$) catalytic system using air as a green oxidant (Scheme 10) [99]. This protocol provides an eco-friendly, cost-efficient approach to build C(sp^2)-C(sp^3) bond from a strong C(sp^2)-H bond and a robust C(sp^3)-H bond, affording a broad range of cross-coupling products with high yields and commendable chemo-, site-selectivity. It is worth mentioning besides the alkyl benzene derivates, the indole- and pyrrole-based heterocycles also showed good tolerance delivering alkylbenzene products in good regioselectivity and yields. Additionally, different C(sp^3)-H compounds such as adamantane, 1-methyl adamantine, cyclopentane, cyclohexane, cycloheptane, and 1,1-dimethyl cyclohexane, were successfully converted into the coupling product in moderate yields. In this protocol, the *in situ* generated Cl• initiates the C-centered radical **55** from the aliphatic hydrocarbon **52** *via* HAT. Subsequently, **55** was oxidized to carbocation **56** by Fe(III) species. Finally, the C(sp^2)-C(sp^3) cross-coupling of **56** and arene **53** was achieved through the electrophilic substitution process. Alternatively, the iron-catalyzed Friedel-Crafts-alkylation between arene and the *in situ*-produced alkyl halide pathway could not be ruled out.

3. Formation of C–N bonds

C–N bonds are omnipresent in biologically active compounds, natural products, and materials [100,101]. Over the past decades, numerous efforts have been devoted to the development of efficient methods for the construction of C–N bonds. The unsaturated N=N bond of the di-*tert*-butyl azodicarboxylate (DBAD) makes it a particularly useful alkyl radical acceptor for the synthesis of nitrogen-contained compounds. Jin and Duan's group developed a $FeCl_3 \cdot 6H_2O$-photocatalyzed protocol to furnish the direct amination of light alkanes, employing DBAD as the amination reagent (Scheme 11) [102]. This oxidant- and the acid-free procedure proceeds smoothly under the irradiation of 365 nm LEDs, giving the highest TON up to 8000. Similar to the above-mentioned systems, the *in situ* formed Cl• initiates a HAT process generating alkyl radical (R•) from the alkane substrate **57**, which is further accepted by the N=N bond of DBAD (**58**) affording the radical intermediate **62**. Subsequently, **62** undergoes a single electron reduction and protonation to give the corresponding products **60**. This photocatalytic reaction provides a convenient method for the synthesis of various nitrogen-contained compounds under mild conditions. It is worth mentioning that in the purification stage, column chromatography is unnecessary in most cases.

In 2022, Ni and coworkers reported a $FeCl_3$-photocatalyzed *N*-alkylation of amides and heterocycles under the irradiation of blue LEDs (450–455 nm) (Scheme 12) [103]. Notably, an excess amount of di–*tert*–butyl peroxide (DTBP) was required. A myriad of amides and NH-containing heterocycles were applicable in this reaction, affording the corresponding products in moderate to good yields. Moreover, the alkylation product could be transformed into amino alcohol *via* a ring-opening reaction demonstrating the applicability of this protocol. In this protocol, alkyl radical was possibly generated from two pathways: (a) under the irradiation of visible light, $L_nFe(III)\text{-}Cl^*$ underwent an LMCT procedure to generate a Cl•, which abstracted a hydrogen atom from **64** to produce the alkyl radical **66**; (b) the homolytic cleavage of DTBP under visible light gave *tert*–butoxy radical ($^tBuO^•$), which then reacted with

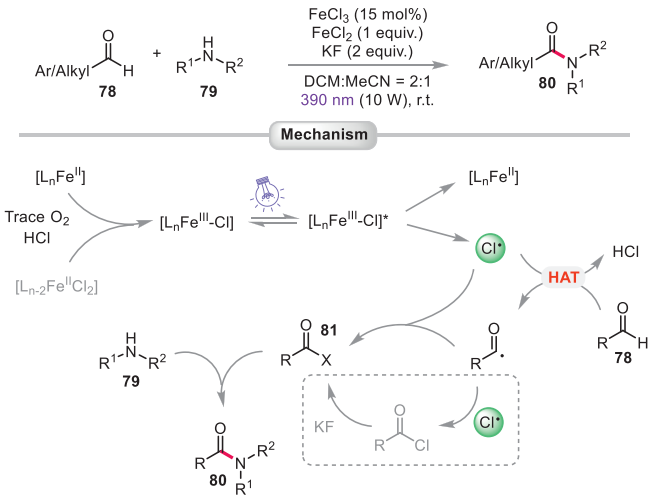


Scheme 13. $FeCl_3$-photocatalyzed amidation with nitroarenes.

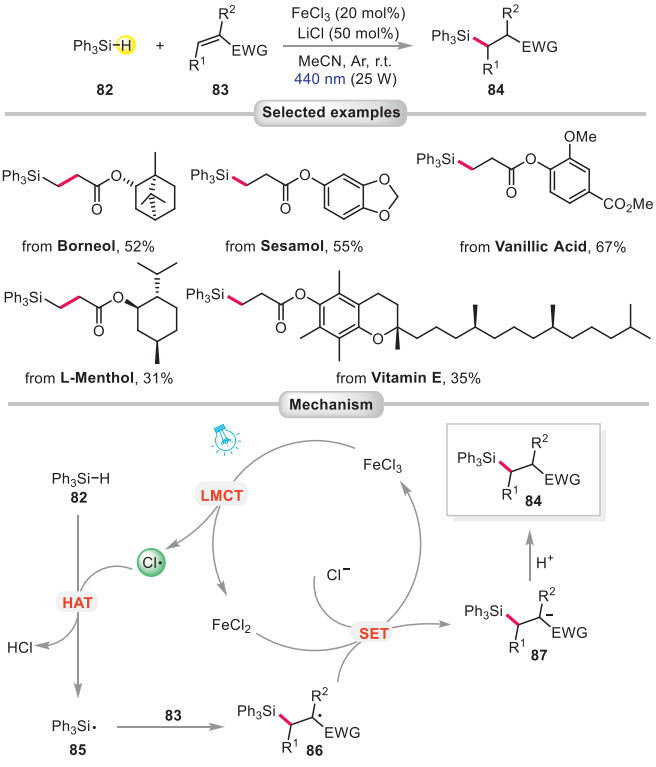
64 to generate the alkyl radical **66** *via* a HAT procedure. On the other hand, substrate **63** coordinates with $L_nFe(III)$-Cl to generate the iron complex **67**. Finally, the coupling of radical **66** and complex **67** generates product **65** along with the release of $L_nFe(II)$.

Amides are important functional groups in organic chemistry [104], which are ubiquitous in biological systems, natural products, organic materials, and pharmaceutical drugs. In 2022, Zeng's group reported a green method to synthesize amides from readily available aldehydes and nitroarenes using $FeCl_3$ as the photocatalyst (Scheme 13) [105]. In this oxidant- and reductant-free protocol, aromatic and aliphatic aldehydes were smoothly converted to the corresponding amides in moderate to excellent yields. Moreover, alcohols could also be utilized as starting materials to react with nitrobenzene, affording the corresponding amides in moderate yields. A solvent-assisted nitro-reduction mechanism was proposed as shown in Scheme 13. Firstly, the alkyl radical **72** was generated from solvent DCE and Cl• by a HAT process. On the other hand, the Cl• can also abstract the hydrogen atom from **68** to generate the acyl radical **71**, which reacts with **75** to produce **76** or couples with Cl• to generate acyl chloride. The following Fe-cycle with the **76** would regenerate the iron(III) and **77**. An alternative process might involve the direct reaction of the acyl chloride with **75** to produce **77**. Finally, the reduction of **77** produced the amide product **70**. This photocatalytic reaction provides a green method to construct amides from easily available material at room temperature. Notably, the excess amount of the reductant or oxidant is necessary for nitro-reduction in the previous reports [106–109]. However, the chlorine radical-mediated HAT process of 1,2-dichloroethane assists in the reduction of nitroarenes, avoiding to use of harsh reaction conditions.

Subsequently, Xia and Yang's group developed an iron-catalyzed direct dehydrogenative amination reaction of aldehydes and amines under visible light irradiation [110]. This protocol has a good functional group tolerance and broad substrate scope toward both aliphatic and aromatic components. Secondary *N*-methyl benzylamine derivatives, alkyl amines, and primary alkyl amines were suitable substrates. Additionally, commercially available pharmaceutical molecules, such as haloperidol and donepezil, were also amenable to this transformation. A nucleophilic addition of amines process was proposed as shown in Scheme 14. Acyl halide **81** as an intermediate was generated from aldehyde **78** *via* a photoinduced HAT. Then **81** reacted with the substrate amines **79** giving the corresponding amides **80**.



Scheme 14. $FeCl_3$-photocatalyzed dehydrogenative amination of aldehydes and amines.

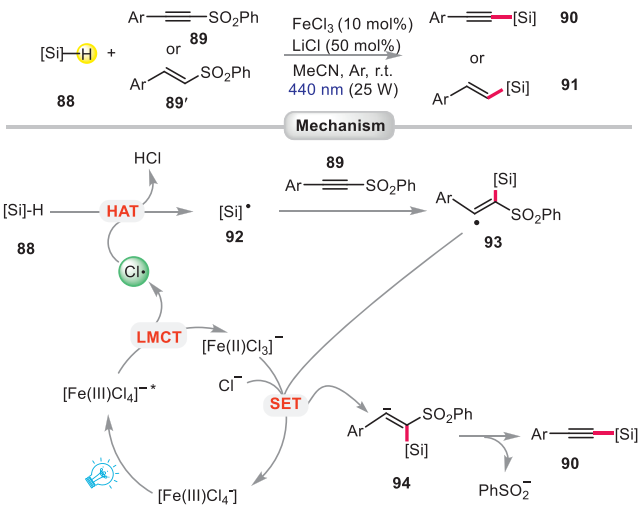


Scheme 15. $FeCl_3$-photocatalyzed hydrosilylation of electron-deficient alkenes.

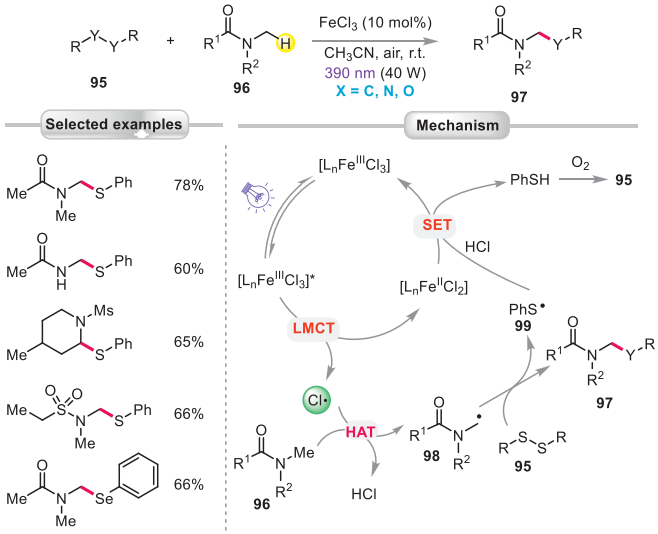
4. Formation of C–Si bonds

As a bioisostere of C–H, Si–H bond has a similar property, owing to both being group IV elements. Thus, organosilicon compounds were usually recognized as bio-isosteres of hydrocarbons. However, the difference in lipophilicity and electro-positivity between carbon and silicon makes silicone-containing compounds useful materials. In this context, the introduction of Si-containing functional groups into organic molecules has received huge attention in recent years [111].

In 2022, Wang's group developed a $FeCl_3$/LiCl photocatalytic system for the reaction of triphenyl silane **82** and electron-deficient olefins **83** under the irradiation of visible light (440–445 nm, 25 W) (Scheme 15) [112]. With this 100% atom-efficient



Scheme 16. $FeCl_3$-photocatalyzed alkynylation of hydrosilanes.



Scheme 17. $FeCl_3$-photocatalyzed thiolation of *N*-methyl amides.

protocol, the hydrosilylation products **84** were obtained in moderate to good yields. Notably, this sustainable procedure was successfully used for the late-stage functionalization of naturally occurring compounds, such as L-menthol, vanillic acid, vitamin E. Based on the control experiments, a plausible reaction pathway was proposed. With the irradiation of visible light, Cl• can be generated from $FeCl_3$ *via* an LMCT procedure, which abstracts a hydrogen atom from triphenyl silane **82** to give the silyl radical **85**. Then **85** adds to the olefin **83** to deliver the intermediate **86**, which undergoes a single electron reduction and protonation to give the product **84**.

The same $FeCl_3$/LiCl photocatalytic system was also applicable in the desulfonylation coupling of hydrosilanes **88** and alkynyl sulfones **89** (or vinyl sulfones **89′**) for the synthesis of alkynyl silanes or vinyl silanes (Scheme 16) [113]. This method has good functional group compatibility. All the sulfones containing the electron-withdrawing group (F-, Cl-, Br-, Ac-, CN-) or the electron-donating group (Me-, Et-, *t*Bu-, MeO-) work well in this procedure. When vinyl sulfones **89′** were applied as substrate, only *E*-vinylsilanes **91** were obtained, which might be a good tool for the regio- and stereoselective construction of vinylsilanes. Similarly, the desired silyl radical **92** is generated *via* HAT with the *in situ* generated Cl•. The radical **92** adds to sulfone **89** giving the radical intermediate **93**, which subsequently transformed into anion intermediate **94** *via* a SET procedure. Finally, the C–SO_2 bond cleavage of **94** affords the corresponding silylated product **90**.

5. Formation of C–S and C–B bonds

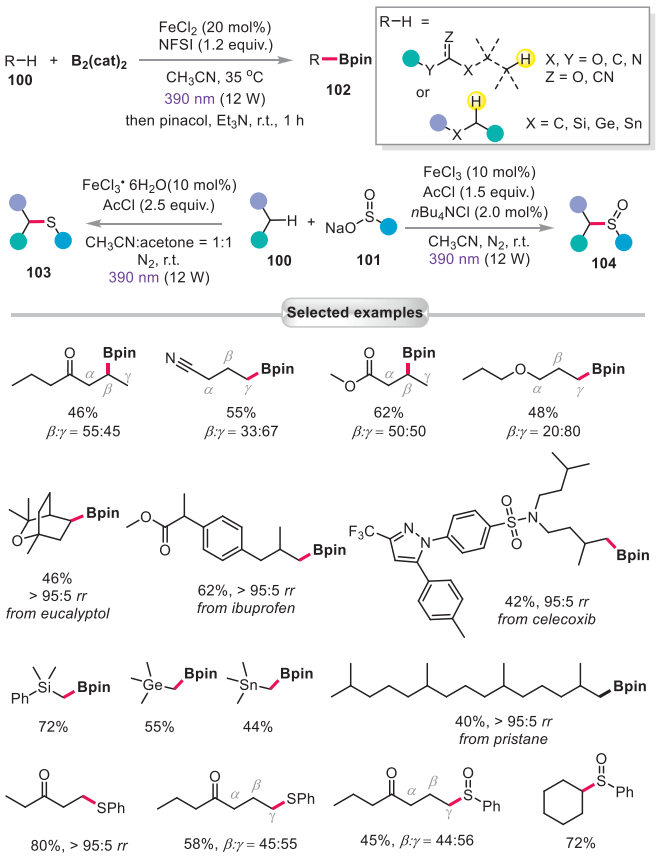
Sulfur-containing compounds are important chemicals in pharmaceuticals, agrochemicals, and functional materials [114]. Among the commercially available drugs approved by the FDA, over 20% of the molecules contain the sulfur element, which is the third largest heteroatom after oxygen and nitrogen. Particularly, amido-*N,S*-acetal is one of the most important moieties in natural products and antibacterials, such as penicillin, penicillin derivatives, and fusaperazine A. In 2022, Laulhéa and co-workers developed a $FeCl_3$-photocatalyzed protocol for the synthesis amido-*N,S*-acetal derivatives from diaryl disulfides/diselenides **95** and *N*-methyl amides **96** (Scheme 17) [115]. In this work, the absorbance of $FeCl_3$ in different solvents was studied by UV–vis spectrum. When CH_3CN was employed as the solvent, $FeCl_3$ showed the strongest absorbance in the visible region suggesting that acetonitrile could act as a ligand in this system. Under 390 nm LEDs irradiation, the acetonitrile-coordinated $FeCl_3$ generates Cl• *via* the LMCT procedure. Subsequently, Cl• selectively abstracts a hydrogen atom from the C–H bond of substrate **96** to deliver amidoalkyl radical **98**, which reacts with diaryl disulfides **95** to give the desired product **97** and radical **99**. Subsequently, **99** undergoes a SET process and oxidation to reproduce the substrate **95**.

Very recently, Guo and Xia's group reported an undirected iron-catalyzed C(sp^3)–H borylation, thiolation, and sulfinylation strategy that showed unconventional regioselectivity, compared with previous reports in which preference for activated and thermodynamically favored bonds. However, in this work, all reactions were preferentially at the distal methyl position (Scheme 18) [65]. The site selectivity is not only relevant to the HAT species but also largely affected by the nature of radical acceptors. For instance, in the C–H thiolation reaction the selectivity was controlled by the steric effect furnishing the distal methyl functionalized products. While the borylation reaction preferentially happened on the β-methylene rather than the terminal methyl group, giving borylation products of β-C(sp^3)-H and γ-C(sp^3)-H bond almost in 1:1 ratio proportion, which is probably due to an effect of boron–carbonyl oxygen interaction.

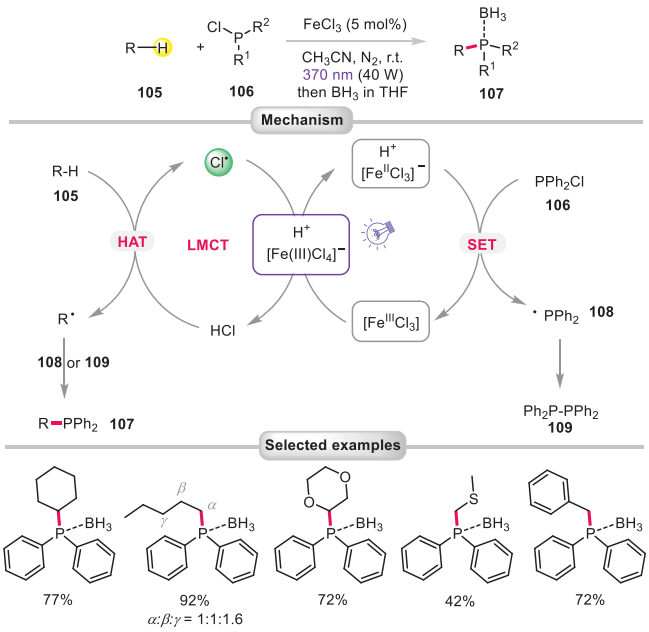
A broad range of ketones, nitriles, aliphatic esters, ethers, amides, and sulfonamides were all found to be efficiently transformed into the corresponding boronate esters in moderate to good yields. It is worth pointing out that this transformation preferentially occurred at β- or γ-position of the functionalized alkanes, and no borylation of α-C(sp^3)–H bond was observed. In addition, this strategy enabled C(sp^3)–H borylation of simply silanes, germane, and stannane, generating the corresponding borylation products in acceptable yields. Moreover, this iron photocatalyzed protocol can also be used for thiolation and sulfinylation as shown in Scheme 18. These reactions exhibit a remarkably broad scope (>150 examples), excellent substrate applicability, and functional group compatibility.

6. Formation of C-P bonds

Organophosphorus compounds play a vital role in organic synthesis, catalysis, materials chemistry, medicinal chemistry, and coordination chemistry. In this context, tertiary phosphines are a class of important compounds widely used as valuable reactants, organocatalysts, and ligands in organic chemistry. However, its synthesis usually requires harsh conditions, sensitive organometallic



Scheme 18. $FeCl_3$-photocatalyzed borylation, thiolation, and sulfinylation of C(sp^3)–H.



Scheme 19. $FeCl_3$-photocatalyzed phosphorylation of C(sp^3)–H.

reagents, and prefunctionalized substrates. Therefore, the development of new synthetic methods to create tertiary phosphine species is of great importance. In 2023, Hu's group developed a novel C(sp^3)–H phosphorylation protocol to construct a series of tertiary phosphines species from industrial phosphine(III) sources using $FeCl_3$ as a photocatalyst (Scheme 19) [116]. With the irradiation of 370 nm LEDs, Cl• can be generated from $FeCl_3$ *via* an LMCT procedure, then reacted with hydrocarbon **105** to give an alkyl radical *via* the HAT process. On the other hand, diphenylphosphinyl radical **108** was generated from phosphine(III) sources **106** and Fe(II)-species through a SET step with the generation of the Fe(III) catalyst for the next catalytic cycle. Subsequently, the corresponding product **107** was generated from alkyl radical and radical **108**. Moreover, the homo-coupling intermediate **109** should be a possible precursor for the final product.

This sustainable procedure provides a valuable solution toward tertiary phosphines(III) synthesis, avoiding the prefunctionalization of substrates and sensitive organometallic reagents in traditional approaches. Under mild photocatalytic conditions, a wide range of hydrocarbons were suitable for this transformation, including inert alkanes, cyclic ethers, dimethyl ether, and toluene derivatives. Additionally, this catalytic system can be applied for the polymerization of electron-deficient alkenes demonstrating the synthetic potential of this reaction in polymer material chemistry.

7. Conclusions

Photocatalytic HAT has been recognized as a concise and efficient tool to generate active radical intermediates for various organic reactions under mild conditions. From the viewpoint of green chemistry, the earth-abundant transition metal salt $FeCl_3$ is an inexpensive, nontoxic, and easily available green catalyst. Under light irradiation, $FeCl_3$ could produce the chlorine radical (Cl•) *via* an LMCT process, which is an initiator for the photocatalytic HAT processes. In this minireview, the recent advances in the photocatalytic organic transformations enabled by $FeCl_3$ were summarized. These catalytic systems are generally simple and practical by using a catalytic amount of $FeCl_3$ as a photocatalyst. The aid of halide compounds, such as LiCl, TBACl, and TBABr is also important to enhance the HAT process in some cases. Overall, the direct functionalization of C–H, O–H, and Si–H bonds could be achieved under mild conditions for the construction of C–C, C–N, C–Si, C–S, C–B and C–P bonds. It should be pointed out that in most of the above-mentioned examples, UV light with a wavelength of 365–395 nm is necessary to excite the $FeCl_3$ photocatalyst, which might limit the application of such a useful strategy. However, in some cases, the transformation could be conducted under irradiation of 440–455 nm blue light, probably due to the different additives and substrates. Therefore, it should be possible to realize $FeCl_3$-photocatalyzed reactions under the irradiation of visible light by using appropriate additives or solvent systems. This minireview should be helpful for the researchers interested in $FeCl_3$-promoted photocatalytic organic transformations. We believe the $FeCl_3$ photocatalysis strategy could be applied in more organic reactions even under the irradiation of visible light.

Declaration of competing interest

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

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