






Cite this: *Chem. Soc. Rev.*, 2023, 52, 8678

Received 31st August 2023

DOI: 10.1039/d3cs00366c

rsc.li/chem-soc-rev

Visible light-mediated halogenation of organic compounds

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The use of visible light and photoredox catalysis emerged as a powerful and sustainable tool for organic synthesis, showing high value for distinctly different ways of bond creation. Halogenated compounds are the cornerstone of contemporary organic synthesis: it is almost impossible to develop a route towards a pharmaceutical reagent, agrochemical, natural product, etc. without the involvement of halogen-containing intermediates. Moreover, the halogenated derivatives as final products became indispensable for drug discovery and materials science. The idea of this review is to understand and summarise the impact of visible light-promoted chemistry on halogenation and halofunctionalisation reactions.

1. Introduction

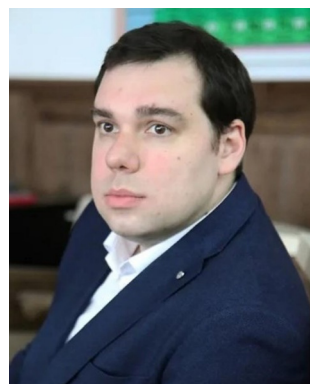
The introduction of a halogen atom into an organic molecule – a hydrocarbon, an aromatic compound, or a heterocycle – is a frequently employed process.^{1,2} The halogens are valuable as leaving group in i.a. substitution reactions and cross-couplings, and as property-defining groups in bioactive molecules or various materials.^{3–6} Halogenation is often the starting point in the synthesis of natural products, pharmaceuticals or

agrochemicals. Nowadays, it is hard to find a process not involving halogen-containing compounds. UV-light was historically employed for free radical halogenation, and the deep mechanistic understanding of those processes helps the contemporary research. Still, these methods lack selectivity and are usually unsuitable for late-stage functionalization.

Visible light photocatalysis has shown an immense growth since the success of pioneering works in 2008.^{7,8} This field emerged as a novel paradigm for bond creation in organic synthesis.^{9–12} Numerous reactions, novel in their concept and formidable in their applicability, have been developed since then. This review aims at assessing the impact of photoredox catalysis on halogenation and halofunctionalisation reactions, and it compares new opportunities with conventional approaches.

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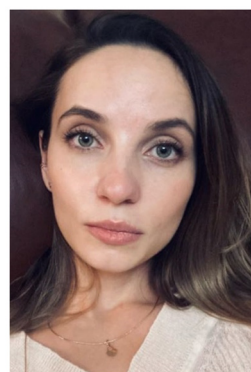
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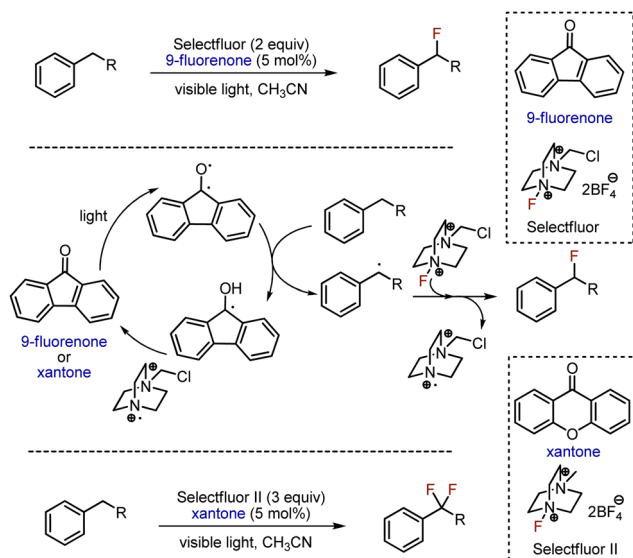


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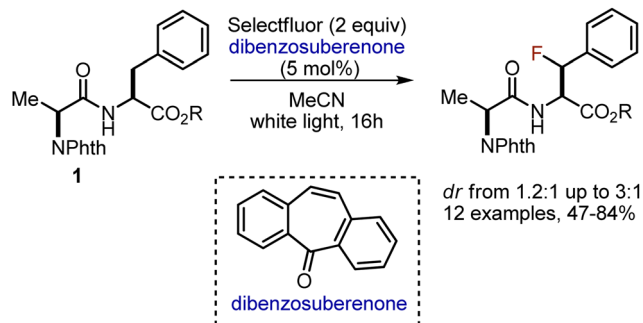


Scheme 1 Fluorination of benzylic C–H bonds.

2. Fluorination

2.1. Fluorination of C_{sp}³–H bonds

Direct fluorination of hydrocarbons using gaseous fluorine is unsafe and poses significant challenges, prompting only a limited number of laboratories around the world to be authorized to work with this reagent. Typically, safer alternatives such as Et₃N-*n*HF or Selectfluor, are used instead. Combined with the mild and sustainable energy source as visible light, these reagents were successfully employed for alkane fluorination. The first fluorination of an aliphatic C–H bond under visible light irradiation was achieved in 2013 (Scheme 1).¹³ The benzylic position was fluorinated with Selectfluor as fluorine source and fluorenone-9 as photocatalyst, under the irradiation with visible light. Interestingly, the reaction of ethylbenzene



Scheme 2 Fluorination of dipeptides.

was faster than of toluene (primary carbon) or cumene (tertiary carbon). Using Selectfluor II and xantone, two benzylic protons could be replaced by fluorines. Photoexcited aromatic ketone abstracted hydrogen atom from benzylic position, and the generated radical reacted with Selectfluor, giving fluorinated product. The photocatalyst was recycled by cation-radical from Selectfluor. Alternatively, benzylic fluorination was achieved in 2017 employing acridinium salt as photocatalyst.¹⁴

Later, the approach was adopted to functionalise benzylic positions of Phe- and Tyr-containing dipeptides **1**, employing dibenzosuberenone as photosensitizer (Scheme 2).¹⁵

The polar effect of the carbonyl group could be utilized to perform selective photoinduced β- or γ-fluorinations on rigid cyclic ketones.¹⁶ Ketone substrates **2** were irradiated with white LED in the presence of Selectfluor as fluorine source and benzil as photosensitizer in acetonitrile for 14 h (Scheme 3). The reaction has been prevalently employed for steroidal ketones, but other mono-, di-, and tricyclic ketones could be fluorinated as well. Continuous flow approach was later developed.¹⁷

Distal fluorination *via* 1,5-hydrogen atom transfer (HAT) approaches has been developed for various compound classes.¹⁸ In 2018 Leonori *et al.* reported a cascade of oxidation-ring



Leonid G. Voskressensky

focus on heterocyclic chemistry, domino reaction methodology, new MCR reactions as well as medicinal chemistry. Prof. Voskressensky has a vast experience in the field of heterocyclic chemistry.

Leonid G. Voskressensky received his PhD-degree in Organic Chemistry from the Peoples' Friendship University of Russia in 1999. In 2001 he joined the Prof. Cosimo Altomare (Universita Degli Studi di Bari, Italy) group as a Post-Doc Fellow (Medicinal Chemistry). In 2013 he became Full Professor of the Organic Chemistry department of the RUDN. Since 2013, he has been the Dean of the Science Faculty of the RUDN University. His scientific interests mainly

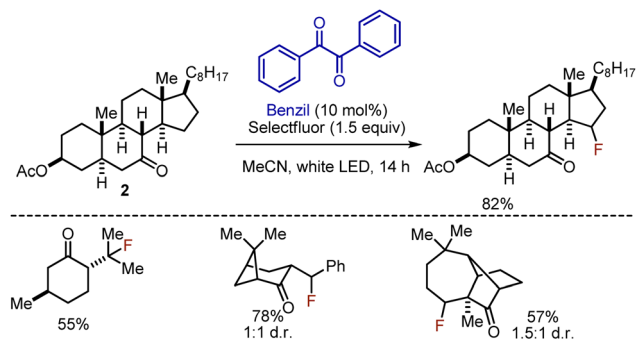


Erik V. Van der Eycken

activation, multicomponent reactions (MCRs), post-MCR modifications, and solid phase organic synthesis. Also Flow Chemistry and Photoredox Chemistry have been recently addressed. Until now 32 PhD-students performed their research under his guidance.

Erik V. Van der Eycken is Full Professor Organic Chemistry and head of the Division Molecular Design & Synthesis (>100 people), as well as head of the Laboratory for Organic & Microwave-Assisted Chemistry at the University of Leuven (KU Leuven), Belgium. He is also Visiting Professor at Peoples' Friendship University of Russia, Moscow (RUDN University). His research focuses on the application of microwave irradiation, transition metal catalysis, C–H

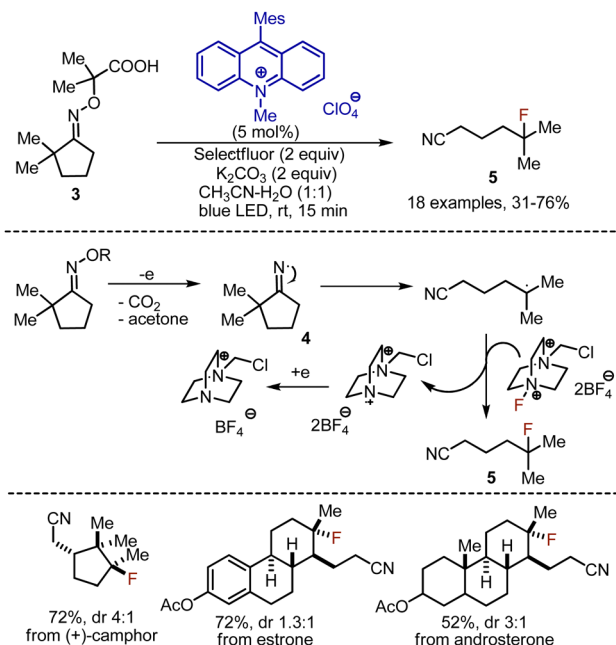




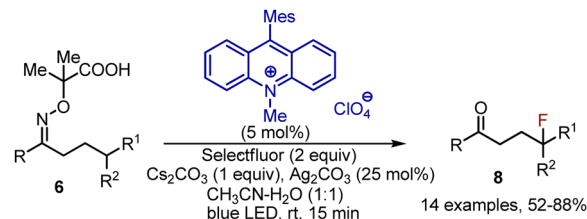
Scheme 3 Organophotoredox fluorination of ketones.

opening-fluorination reactions of oximes **3** under visible light-mediated conditions (Scheme 4).¹⁹ Acridinium salt was used as photocatalyst, which oxidised the carboxylic group into an oxime, leading to the release of CO₂ and acetone. The thus formed iminyl radical **4** underwent ring opening reaction to give a nitrile moiety and a C-centered radical. The latter abstracted fluorine from Selectfluor, forming the product **5**. The catalytic cycle was closed by single electron transfer (SET) reduction of a cation radical from Selectfluor with the reduced form of the acridinium catalyst. Short-lived radical chain propagation processes were found to be acting along with the photoredox pathway according to the quantum yield of the reaction measurements ($\Phi = 2.8$). Oximes derived from cyclobutanones reacted smoothly, whereas oximes derived from cyclopentanones, cyclohexanones, and cycloheptanones required an aromatic substituent in the α -position to stabilize the resulting radical. Interestingly, various natural products, like (+)-camphor, estrone, androsterone, *etc.* could be used.

Linear oxime derivatives **6** could be used as well, which were transformed into imines **7** instead of nitriles, and eventually



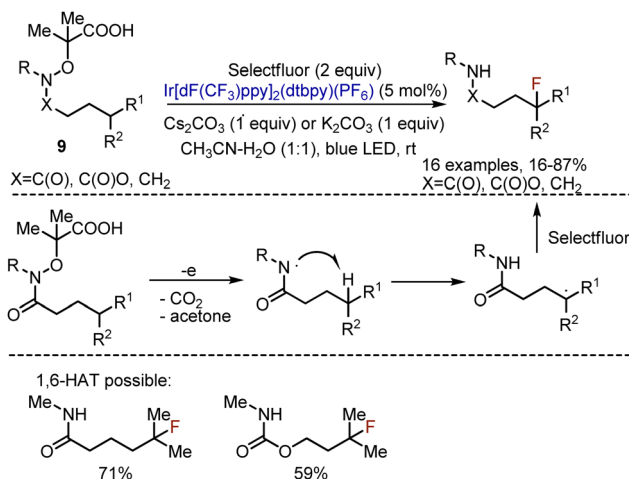
Scheme 4 Fluorination through iminyl radical formation.



Scheme 5 Fluorination-imine hydrolysis through iminyl radical formation.

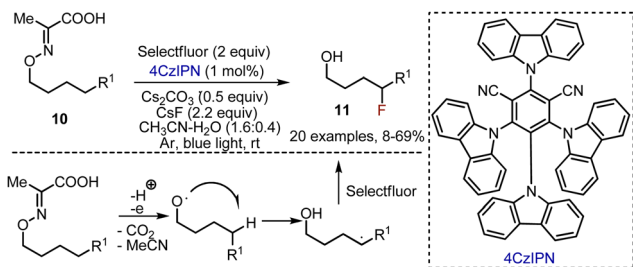
hydrolyzed into ketones **8** (Scheme 5). This process was compatible with the substrates, delivering tertiary carbon-radicals only due to the small difference in bond dissociation energies (BDE) of iminyl N–H and C–H bonds. If Selectfluor was replaced by NCS, chlorination took place, but hydrolysis of the imine did not occur.

To overcome the energetical limitation of iminyl radicals, the analogous fluorination of secondary carbon centers was performed with the help of amidyl radicals, formed from amides, carbamates or amines **9** (Scheme 6).²⁰ The process was operating through 1,5-HAT from C–H to the amidyl radical. The latter was formed analogously by the oxidation of the carboxylic group in the corresponding precursor *via* a photoredox cycle. In a standard procedure the substrate, Selectfluor, Ir-catalyst, and a base were irradiated with blue LED at rt in an CH₃CN–water mixture. As far as amidyl radicals were involved, secondary substrates were reactive ($R^1=H$). Protected amines participated in the reaction as well (**9**, X=CH₂, R = Boc or Ts). Despite 1,5-HAT was usually favoured, the 1,6-transposition



Scheme 6 Fluorination through amidyl radical formation.



Scheme 7 Visible light-mediated synthesis of δ -fluorinated alcohols.

could also be achieved for the substrates, bearing substituents at the corresponding positions (Scheme 6). Later, *N*-sulfonyl protected amines were fluorinated under the action of hypervalent iodine(III) reagent²¹ or with the use of a cheaper Ru(bpy)₃Cl₂ catalyst.²²

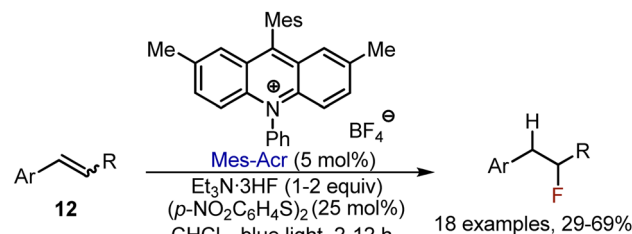
The approach with 1,5-radical translocation was interestingly used for the synthesis of δ -fluorinated alcohols by Yu *et al.*²³ Various oxime derivatives of pyruvic acid **10** were irradiated in the presence of Selectfluor and (4*s*,6*s*)-2,4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN) photocatalyst in an acetonitrile–water mixture at rt under argon atmosphere (Scheme 7). Caesium fluoride and carbonate were found to be a crucial mixture of bases to maintain the acceptable pH of the reaction mixture. To ease the isolation of the alcohols **11**, many of the products were *in situ* converted into the corresponding carbamates by the addition of 4-nitrophenyl isocyanate to the reaction mixture. The reaction was wide in scope, and worked smoothly to deliver fluorinated alcohols with aromatic, heterocyclic, cyclic, azide moieties, *etc.*

To involve non-activated alkanes in fluorination, shorter wavelength sources (375–400 nm) were used together with acetophenone,²⁴ tetra-*n*-butylammonium decatungstate (TBADT),²⁵ 1,2,4,5-tetracyanobenzene,²⁶ anthraquinone,²⁷ or uranyl compounds^{28–30} as photosensitisers.

2.2. Fluorination of unsaturated compounds

Photoredox-catalysed anti-Markovnikov hydrofluorination of alkenes **12** has been developed by Nicewicz in 2014.³¹ Styrenes were irradiated by blue light in the presence of Et₃N·3HF (1–2 equiv.), 4-nitrophenyl disulfide (25 mol%) in chloroform, employing 9-mesityl-2,7-dimethyl-10-phenylacridinium salt (Mes-Acr) as photocatalyst (Scheme 8). The reaction started with the oxidation of the alkene by the photo-excited catalyst, delivering a cation radical **13**, which could react with a fluoride anion. The recovery of the catalyst was achieved by reducing the phenylsulfide radical to its anion. The latter could get protonated and participate in a HAT process, quenching the alkyl radical. The reaction was limited to aryl and thienyl conjugated alkenes.

Various visible light-mediated fluorofunctionalizations are available for aryl alkenes. Alkylfluorination of styrenes was developed in 2018 by Li, Bao *et al.*³² The combination of photocatalyst Ru(bpy)₃Cl₂ and copper acetate was used to generate the alkyl radical from an acyl peroxide (Scheme 9). The

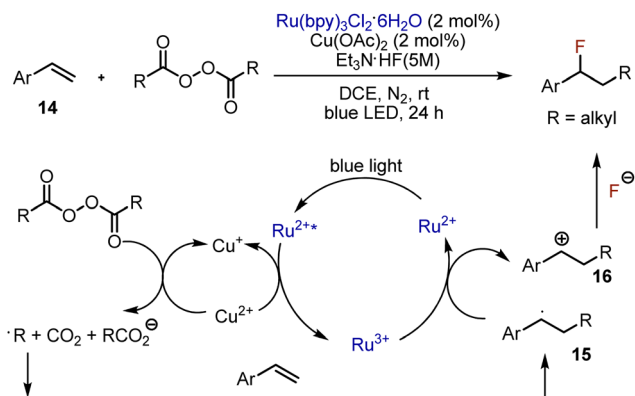


Scheme 8 Visible light-mediated hydrofluorination of alkenes.

alkyl radical reacted with styrene **14**, forming a benzyl radical **15** which was subsequently oxidized by Ru³⁺ to produce the corresponding carbocation **16**. The latter reacted with fluoride anion, delivering the final product. The proposed mechanism was supported by radical trapping and radical clock experiments. Moreover, when the reaction was performed in the presence of methanol, the respective ether was formed as a by-product, confirming the involvement of carbocationic species. The reaction worked smoothly with various styrenes bearing electron-donating or -withdrawing substituents. Disubstituted alkenes worked as well. Interestingly, thiazolyl-, and alkynyl-conjugated alkenes worked too. The scope of acyl peroxides was limited to aliphatic derivatives.

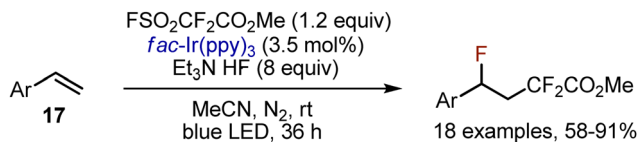
Fluorodifluoroacetylation of styrenes **17** was achieved by the action of Chen's reagent FSO₂CF₂CO₂Me in the presence of an Ir-complex (Scheme 10).³³

Synthesis of fluorinated α -amino acid derivatives was developed through a photoredox-catalysed alkylfluorination of dehydroaminoacids **18**.³⁴ When dehydroalanine and potassium alkyltrifluoroborate were subjected to irradiation with blue LED



Scheme 9 Alkylfluorination of styrenes.



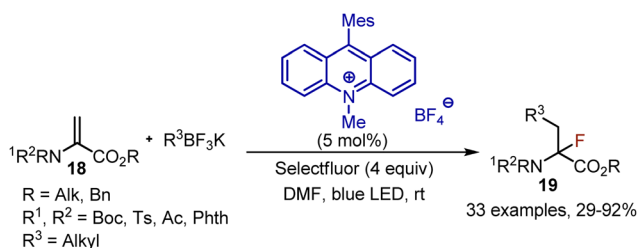


Scheme 10 Visible light-mediated fluorodifluoroacetylation of styrenes.

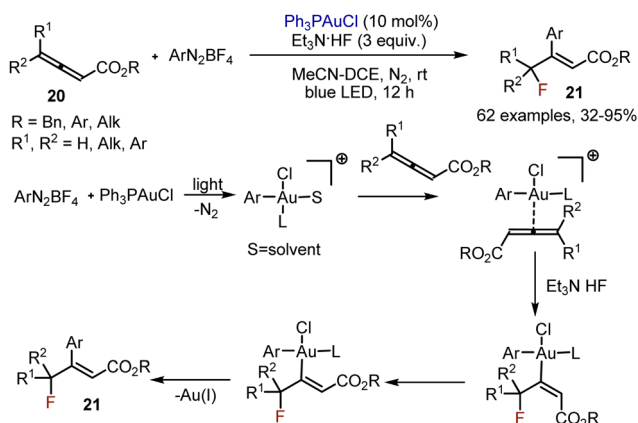
in the presence of acridinium salt as a photocatalyst, the desired α -fluoro- α -amino acid derivatives **19** were isolated with moderate to excellent yields (Scheme 11). Initially, the photoexcited acridinium salt oxidized trifluoroborate to generate an alkyl radical. The alkyl radical is added to the double bond of dehydroalanine, and the resulting radical can then abstract fluorine from Selectfluor to complete the transformation. The recyclization of the photocatalyst was achieved by the reaction of Acr-Mes with Selectfluor cation radical.

Visible light-mediated fluorination of non-activated alkenes has not yet been developed.

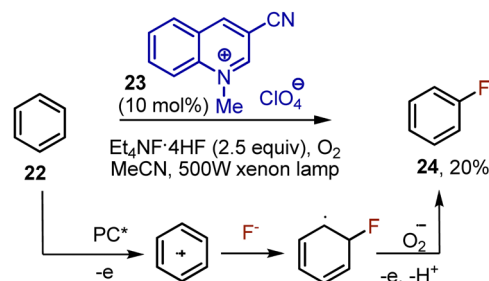
Fluorofunctionalisation of allenic esters **20** was achieved with the help of gold-complexes.³⁵ Aryldiazonium salts were used as aryl source, while $\text{Et}_3\text{N}\cdot 3\text{HF}$ was employed as fluorine source (Scheme 12). The following mechanism was proposed. The reaction started with the photomediated oxidative addition between the gold-complex and the aryldiazonium salt. The resultant gold-species coordinated with an allenic ester. This was followed by hydrogen bonding assisted nucleophilic addition of a fluoride anion. Isomerization of the double bond was



Scheme 11 Fluoroalkylation with alkyltrifluoroborates.



Scheme 12 Visible light-mediated fluoroarylation of allenics.

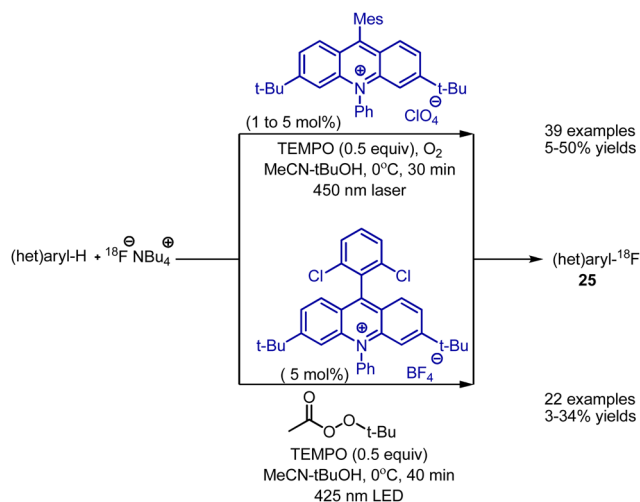


Scheme 13 Quinolinium-catalysed fluorination of benzene.

followed by reductive elimination, giving the desired product **21**, and regenerating the Au(I)-catalyst.

The direct visible light-mediated fluorination of aromatic $\text{Csp}^2\text{-H}$ bonds is still an underdeveloped area. In 2013, Fukuzumi reported the fluorination of benzene **22** catalyzed by quinolinium **23**.³⁶ Tetraethylammonium hydrofluoride was used as the source of fluoride, resulting in the formation of fluorobenzene **24** with a 20% yield. (Scheme 13). The irradiation with a powerful xenon lamp was needed. The photoexcited catalyst oxidized benzene, giving a cation radical, which reacted with a fluoride anion. Oxygen recycled the photocatalyst being transformed into an oxygen anion radical, which was further aromatizing the intermediate. The fluorination of halogenated benzenes was less effective, bromo- and chlorobenzene were *para*-fluorinated with only 6% and 7% yields, respectively.

Direct radiofluorination with nucleophilic fluoride was developed by Nicewicz *et al.* In the original report, $^{18}\text{FNBu}_4$, acridinium catalyst, TEMPO and laser irradiation was employed to generate radio-labelled fluorobenzenes **25** (Scheme 14).³⁷ The approach was also based on SET oxidation of an aromatic compound to the corresponding radical cation, further reacting with a fluoride anion. The process worked with electron-rich and electron-poor aromatic systems, heterocycles, and bioactive molecules. Moreover, the reaction was employed on positron

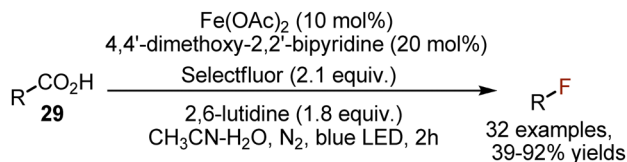


Scheme 14 Visible light-mediated radiofluorination of aromatic compounds.





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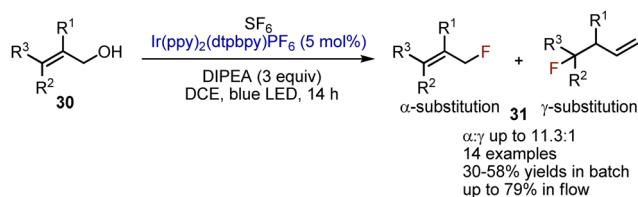


Scheme 18 Iron-catalysed decarboxylative fluorination.

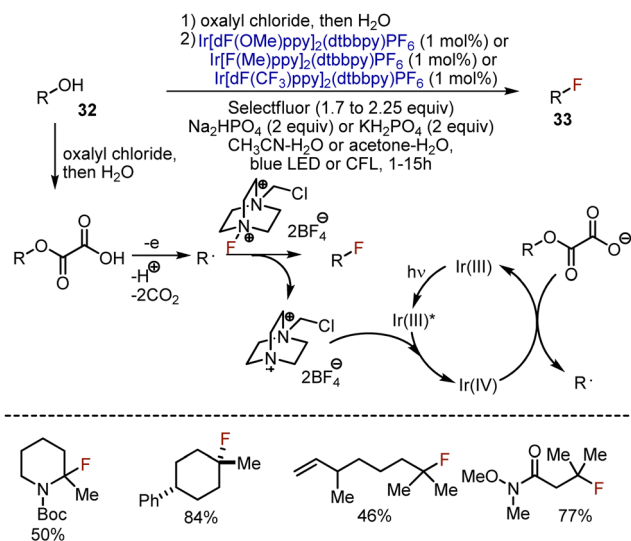
2.4. Deoxygenative fluorination

The use of safe and inexpensive, but inert SF_6 for deoxygenative fluorination has been reported by Jamison in 2016.⁴⁸ Allylic alcohols **30** could be transformed into allyl fluorides **31** with moderate yields when irradiated with blue LED-light in DCE in the presence of SF_6 , $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$ (5 mol%), and DIPEA (3 equiv.) (Scheme 19). Interestingly, when performed under continuous flow conditions, the yields were improved.

Replacement of the hydroxyl group in primary and secondary alcohols was established through $\text{S}_{\text{N}}2$ -type reactions, while tertiary alcohols were still challenging substrates. On the other hand, photoredox conditions employ free radical reactivity compatible with tertiary substrates. MacMillan *et al.* took advantage of this chemistry and developed a visible light-mediated deoxygenative fluorination for a broad scope of alcohols **32** (Scheme 20).⁴⁹ Initially, oxalic esters of alcohols were used in the reactions with an electrophilic fluorine source



Scheme 19 Deoxygenative fluorination of allylic alcohols.



Scheme 20 Deoxygenative fluorination through initial oxalyl chloride acylation.

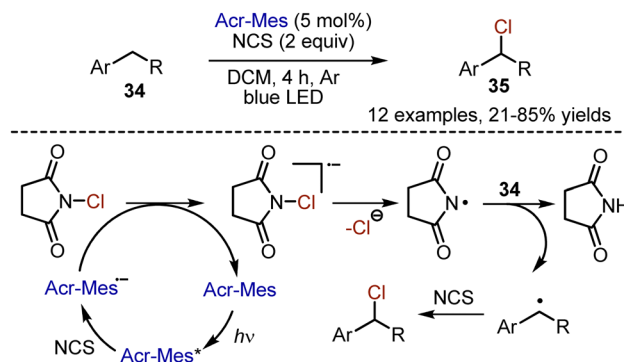
– Selectfluor – and various Ir photocatalysts. The addition of an inorganic base was crucial for the reaction to generate salts from oxalate derivatives. Importantly, the prefunctionalisation of an alcohol with oxalyl chloride could be performed in a one-pot fashion, and the isolation of the ester was not needed. The reaction started with the acylation of the alcohol with oxalyl chloride. The photoexcited $\text{Ir}(\text{III})^*$ reduced the Selectfluor cation radical, delivering $\text{Ir}(\text{IV})$ which was capable of oxidizing the carboxylate anion. The single electron oxidation of the carboxylate led to the extrusion of CO_2 (2 equiv.) and the formation of an alkyl radical, which abstracted the fluorine atom from Selectfluor to generate the final product **33**. The most valuable aspect of the transformation was the possibility to smoothly involve tertiary alcohols to give fluorinated derivatives with good to excellent yields.

3. Chlorination

3.1. Chlorination of $\text{C}_{\text{sp}^3}\text{-H}$ bonds

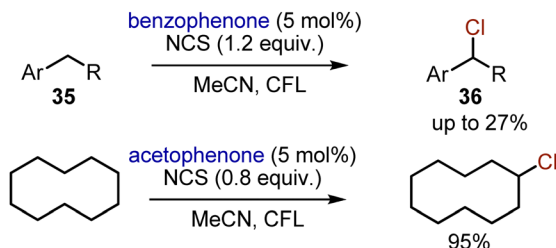
Selective chlorination with molecular chlorine is a challenging task due to the high reactivity of this halogen. Moreover, its toxicity and corrosive character complicate the transformations. A safer alternative for chlorination employs oxidation of chlorides, but the use of stoichiometric oxidants is needed. Visible light-mediated approaches suggest a more sustainable way for radical generation. In 2020, Wu *et al.* reported a visible light-mediated procedure for the chlorination of the benzylic position with NCS (Scheme 21).⁵⁰ Alkylbenzene **34** was irradiated with blue LED-light for 4 h in DCM solution, in the presence of acridinium salt as photocatalyst. The benzyl chlorides **35** were generated with 21–85% yields. It is proposed that the photoexcited acridinium salt oxidizes NCS and is transformed into a strongly reducing species, which gives an electron to NCS to generate the NCS anion radical. Subsequently this succinyl radical, abstracts a hydrogen atom from the alkyl benzene. This benzyl radical abstracts chlorine from NCS to give the final product.

When alkylbenzenes **35** were subjected to chlorination with NCS employing aromatic ketones as photocatalysts, the yields of the benzyl chlorides **36** were not exceeding 27%.⁵¹ Moreover, double chlorination could occur. Still, this approach could be very useful for visible light-mediated chlorination of



Scheme 21 Chlorination of alkylbenzenes with NCS.





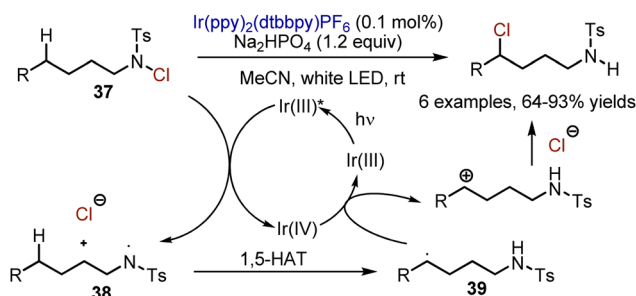
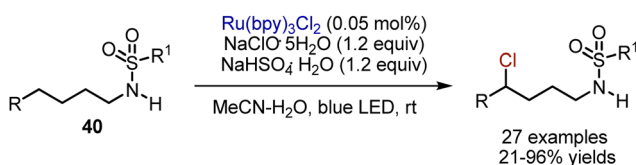
Scheme 22 Aromatic ketones sensitized chlorination of alkanes.

non-activated alkanes. For instance, cyclodecane could be mono-chlorinated in MeCN with 95% yield with NCS (0.8 equiv.) and acetophenone as a photocatalyst under irradiation with white CFL light (Scheme 22).

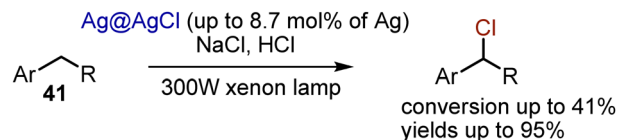
UV-light-mediated chlorination, followed by intramolecular chloride substitution with nitrogen is known as a Hofmann-Löffler-Freytag (HLF) reaction, operating through 1,5-hydrogen atom transfer from C_{sp^3} -H to an amidyl radical. In 2015, Yu and Qin developed an interrupted HLF reaction under visible light irradiation in the presence of $Ir(ppy)_2(dtbbpy)PF_6$ catalyst (Scheme 23).⁵² Photoexcited Ir(III) reduced *N*-chlorotosylamide 37 so it was transformed into an amidyl radical 38 and a chloride anion. The amidyl radical 38 could undergo intramolecular 1,5-HAT to deliver a carbon radical 39. This radical could be oxidized by Ir(IV) into a carbocation, which was quenched by a chloride.

Later, preliminary non-chlorinated sulfonamides 40 could be involved in an analogous transformation (Scheme 24).⁵³ The initial *N*-chlorination took place *in situ* in the presence of $NaClO \cdot 5H_2O$, while further amidyl radical generation-1,5-HAT and carbocation formation were promoted by $Ru(bpy)_3Cl_2$ photocatalyst under blue LED irradiation. Analogous transformation could also be performed with *t*-BuOCl as chlorine source, and $Mn_2(CO)_{10}$ as a photocatalyst.⁵⁴

N-Chlorosuccinimide and analogous reagents are abundant chlorine sources. Still, the use of various chlorides, like NaCl,

Scheme 23 Intramolecular 1,5-chlorination in *N*-chlorosulfonamides.

Scheme 24 Visible light-mediated chlorination of sulfonamides.

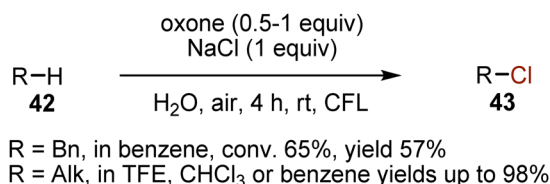


Scheme 25 Nano composite Ag catalyst for visible light-induced alkane chlorination.

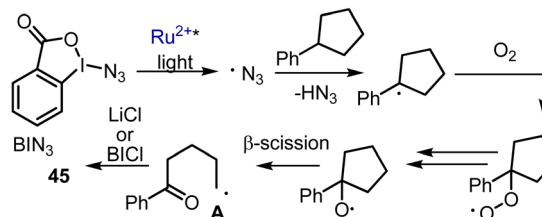
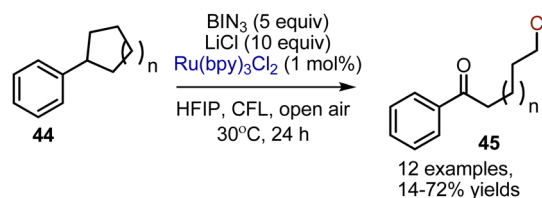
could be considered beneficial due non-toxic and low-cost qualities. Few methods for visible light-mediated chlorination with NaCl are known. For instance, alkylbenzenes 41 could be chlorinated by NaCl in the presence of a nano composite Ag@AgCl catalyst and irradiation with a xenon lamp, equipped with a UV cut-off filter (Scheme 25).⁵⁵ Although good selectivity with excellent chemical yields were achieved, the conversions were not high (up to 41%). Later, it was shown that the addition of a phase transfer catalyst like NBu_4Cl improved the performance of the nano composite catalyst.⁵⁶

Higher conversions were demonstrated for oxone-mediated chlorinations with NaCl (Scheme 26).⁵⁷ However, as electrophilic aromatic substitution could take place under these conditions, the solvent choice was crucial for the selectivity. This approach was successful for the chlorination of non-activated alkanes 42 as well. The role of oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was to oxidize chloride to generate chlorine Cl_2 . Without light, the yields of the products 43 were not higher than 4%, showing the need for the irradiation.

Ferrous chloride was also used as a source of chlorine in visible light-mediated chlorination of cyclohexane.⁵⁸



Scheme 26 NaCl-oxone mediated chlorination of alkanes.



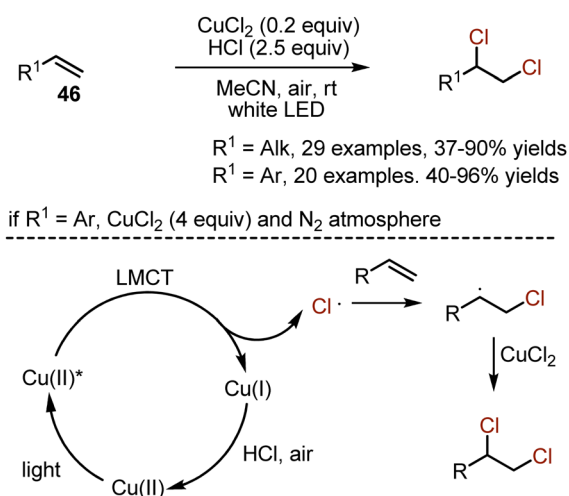
Scheme 27 Visible light-mediated deconstructive chlorination of aryl cycloalkanes.



Visible light-mediated deconstructive chlorination of aryl cycloalkanes **44** was developed recently, leading to the formation of chlorinated arylketones **45** (Scheme 27).⁵⁹ The reactions of aryl cycloalkane were performed in the presence of Zhdankin reagent BIN₃ – hyper valent benziodoxolone, – Ru(bpy)₃Cl₂ as a photocatalyst and LiCl as a chlorine source. Along with the desired chlorinated products, azidation usually took place. The following pathway for the transformation was suggested. Benzyl radical was generated by azido radical, which was produced from BIN₃ by SET reduction with photoexcited Ru²⁺*. Subsequent interaction with oxygen was followed by HAT and hydroperoxide homolysis to give an alkoxy radical. The latter underwent β-scission to deliver intermediate **A**, and the chlorination took place. It was suggested that the chlorine atom could have been finally abstracted from *in situ* formed BICl species. The formation of BICl was confirmed by mixing BIN₃ with LiCl. Alternatively, the oxidation of **A** by Ru³⁺ into a carbocation, followed by ionic reaction with LiCl could be proposed.

3.2. Chlorination of unsaturated compounds

Alkenes are reactive organic species, and the chlorination with molecular chlorine occurs without any additional conditions. However, toxicity, corrosiveness, and lack of selectivity of molecular chlorine are the challenges to overcome. Various methods have been developed, including the use of benign chloride salts with expensive oxidants, used in stoichiometric amounts. The recent employment of a visible light-induced ligand-to-metal charge transfer approach allowed to conquer the listed drawbacks (Scheme 28).⁶⁰ Aliphatic alkenes **46** could be dichlorinated by the action of a cheap CuCl₂ salt in the presence of HCl. The reaction was performed under irradiation with white LED and on air. The method was adapted for dichlorination of styrenes as well. Due to numerous side reactions, the transformations of styrenes were performed under N₂ atmosphere and with excess amounts of CuCl₂. The following mechanism was proposed. As a result of irradiation with light, copper(II) chloride underwent

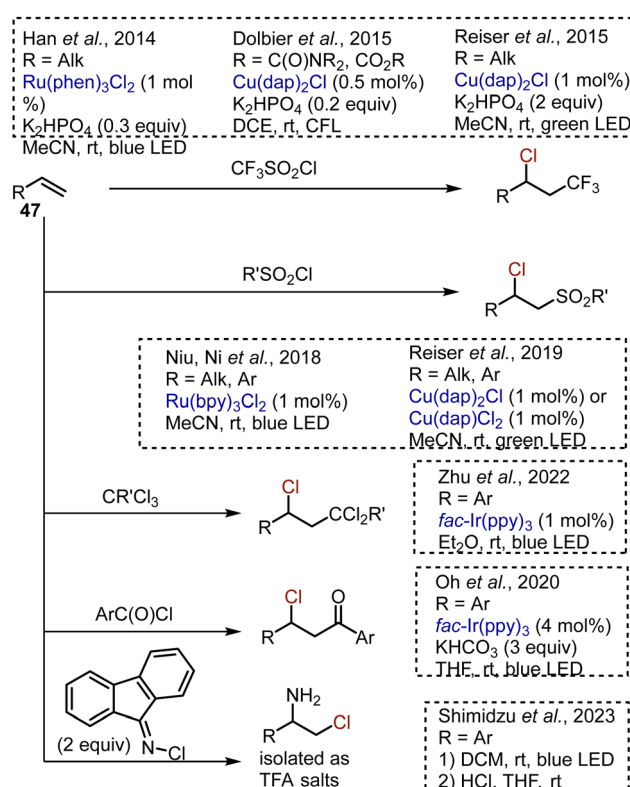


Scheme 28 Visible light-mediated copper-catalysed chlorination of alkenes.

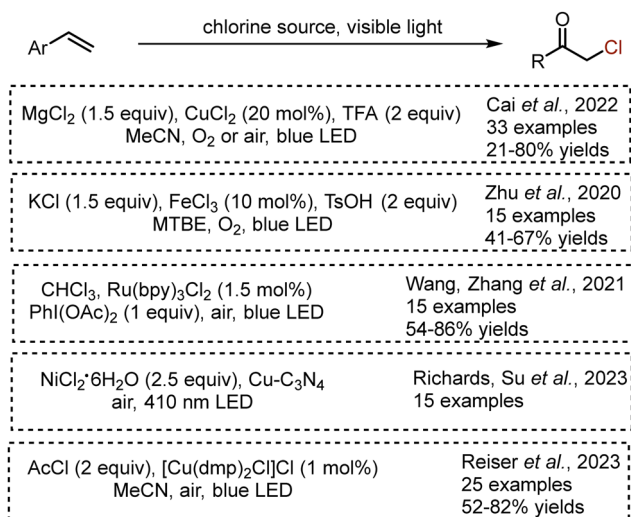
ligand-to-metal charge transfer, leading to the formation of CuCl and a chloride radical. The latter added to a double bond to form a carbon centered radical, which abstracted chlorine from CuCl₂. The HCl and air recycled Cu(I) to Cu(II) chloride.

Many visible light-mediated reactions of alkene **47** difunctionalisation were developed (Scheme 29). The chlorotrifluoromethylation of unactivated alkenes took place under the action of CF₃SO₂Cl in the presence of Ru(phen)₃Cl₂⁶¹ or Cu(dap)₂Cl⁶² photocatalysts. Unsaturated amides and esters, as well as other electron deficient alkenes, could be chlorotrifluoromethylated as well.⁶³ Recently, the eosin Y-catalysed chlorotrifluoromethylation of terminal alkenes was reported.⁶⁴ The use of other sulfonyl chlorides allowed the chlorosulfonylation processes without SO₂ extrusion.^{65,66} These reactions were compatible with both aryl and alkyl alkenes. Styrenes could be chloroacylated by benzoyl chlorides⁶⁷ or chlorodichloromethylated by chloroform,⁶⁸ using an Ir-catalyst. Chloroacylation of alkylidenecyclopropanes was reported as well.⁶⁹ Aminochlorination was achieved by irradiating alkenes with fluorenone-derived *N*-chlorimine, followed by a one-pot imine hydrolysis.⁷⁰

Moreover, several methods for alkene oxochlorination with various chlorine sources have been reported (Scheme 30). Oxochlorination of aryl alkenes was developed based on an LMCT approach – the combination of MgCl₂, CuCl₂, TFA and oxygen delivered α-chloroarylethanones with high yields through the formation of hydroperoxyl and chlorine atom radicals.⁷¹ The use of ferrous(III) chloride and KCl under blue LED irradiation delivered desired oxochlorination products with moderate yields.⁷²



Scheme 29 Visible light-mediated procedures for alkene difunctionalisation.

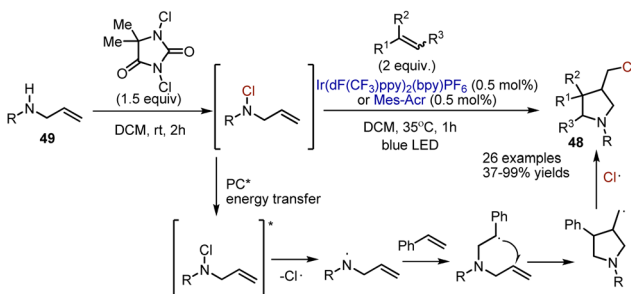


Scheme 30 Visible light-mediated procedures for alkene oxochlorination.

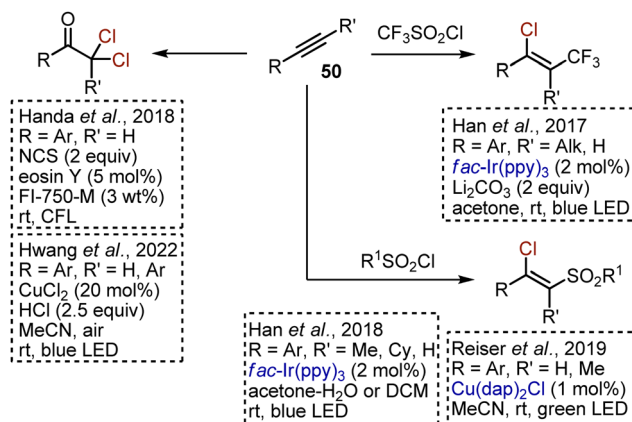
Another interesting source of chlorine – chloroform – was elegantly used in the combination with $\text{Ru}(\text{bpy})_3\text{Cl}_2$ photocatalyst and stoichiometric amounts of $\text{PhI}(\text{OAc})_2$.⁷³ Oxochlorination could be also achieved under heterogeneous photocatalysis by copper-modified graphitic carbon nitride ($\text{Cu}-\text{C}_3\text{N}_4$).⁷⁴ Recently, Reiser *et al.* succeeded in the use of acetyl chloride and Cu-complex for alkene oxochlorination.⁷⁵ Importantly, the latter method has been successfully employed for late stage functionalisation of bioactive molecules – estrone, fenofibrate, (–)-menthol, theophylline.

Free radical annulation of chlorinated pyrrolidine **48** was achieved by Crespin *et al.*⁷⁶ Initially, alkenyl-containing *N*-sulfonylamide **49** was transformed into an *N*-Cl derivative by the action of 1,3-dichloro-5,5-dimethylhydantoin in DCM at rt (Scheme 31). This derivative was used without purification, and the addition of alkene and photocatalyst led to a cascade cyclization. The authors suggest a pathway involving energy transfer from the photoexcited catalyst to *N*-Cl sulfonamide. The latter underwent homolytic cleavage into an amidyl radical and chlorine atom radical. Further, the amidyl radical added to the alkene double bond to produce a C-centered radical, which underwent an intramolecular cyclization. The reaction sequence was finalized by recombination with a chlorine radical.

Alkynes **50** present an appealing substrate class for the synthesis of various chlorinated derivatives through free radical



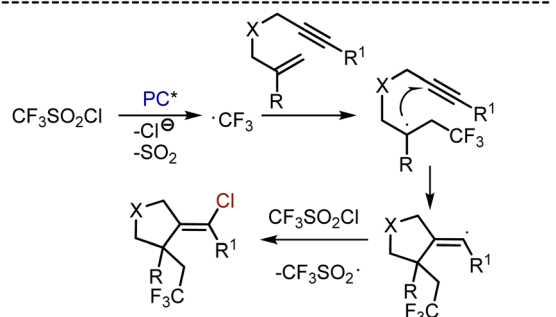
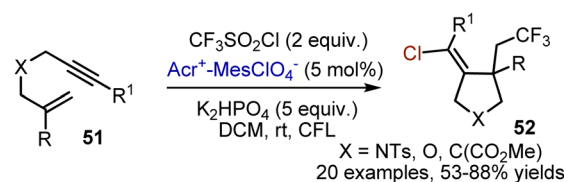
Scheme 31 Visible light-mediated synthesis of chlorinated pyrrolidines.



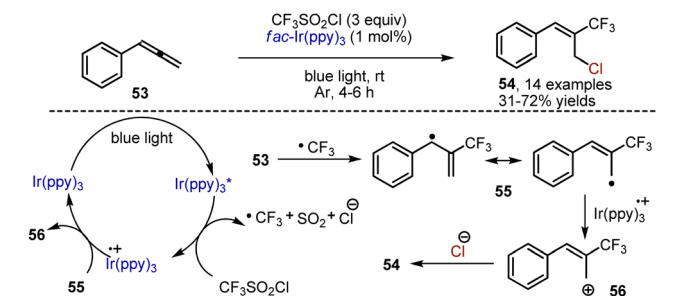
Scheme 32 Visible light-mediated chlorofunctionalisation of alkynes.

addition reactions under visible light irradiation (Scheme 32). Chlorotrifluoromethylation of aryl alkynes was reported by Han in 2017.⁷⁷ Trifluoromethylsulfonyl chloride was used as a source of CF_3 radicals and chlorine, while an Ir-catalyst was needed to perform the reaction. Other sulfonyl chlorides were found to undergo chlorosulfonylation reactions. Extrusion of SO_2 did not take place. These sulfonylative transformations were realized under Ir-catalysis,⁷⁸ and under Cu-catalysis.⁶⁶ Eosin Y-catalysed oxydichlorination of aryl alkynes with NCS was developed in 2018.⁷⁹ The reaction was facilitated by the use of proline-based surfactant FI-750-M. Later, an analogous transformation was developed under LMCT-conditions, using cheap CuCl_2 and HCl as chlorine sources.⁸⁰

Chlorotrifluoromethylative cyclization of enynes **51** was a useful approach towards chlorinated pyrrolidines **52** (Scheme 33).⁸¹ Trifluoromethylsulfonyl chloride was used as a well-established source of trifluoromethyl radicals. It underwent a single electron reduction by a photoexcited acridinium salt, followed by the decomposition into CF_3 radical, SO_2 , and chloride anion. It was proposed that addition of $\cdot\text{CF}_3$ to the double bond resulted in the formation of a C-centered radical, that readily cyclized



Scheme 33 Acridinium dye-catalysed cyclative chlorotrifluoromethylation.



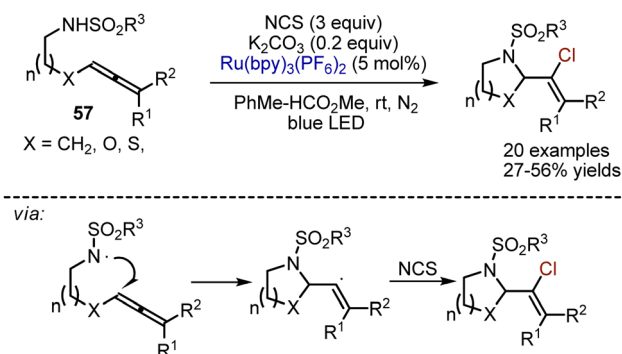
Scheme 34 Visible light-mediated chlorotrifluoromethylation of arylallenes.

onto the triple bond. The formed vinyl radical abstracted chlorine atom from $\text{CF}_3\text{SO}_2\text{Cl}$, propagating the chain process.

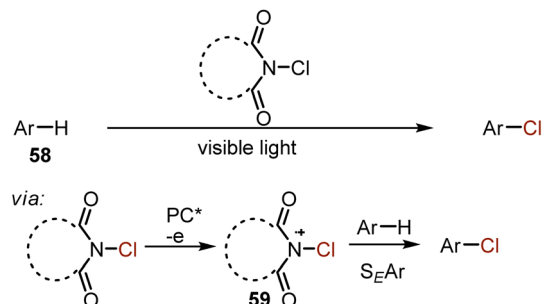
Visible light mediated transformations of allenes are yet underdeveloped. Chlorotrifluoromethylation of arylallenes **53** has been recently reported by Festa, Voskressensky *et al.*⁸² Valuable building blocks – trifluoromethylated allyl chlorides **54** – have been synthesized by treatment of arylallenes with trifluoromethylsulfonyl chloride, which is an inexpensive source of a trifluoromethyl radical. The reaction has been performed in the presence of $\text{Ir}(\text{ppy})_3$ catalyst in acetone under argon atmosphere (Scheme 34). The following mechanism is proposed. Initially, the photoexcited Ir-catalyst reduces $\text{CF}_3\text{SO}_2\text{Cl}$ to give an anion radical, decomposing into Cl^- , SO_2 and a CF_3 radical. The addition of the latter to an allene system delivers an allyl-type radical **55**, capable of undergoing oxidation to cation **56** with the Ir^{4+} -species. The interaction of the chloride anion with **56** furnishes the resulting trifluoromethylated allyl chloride. Importantly, these allyl chlorides were successfully employed for the preparation of a trifluoromethylated analog of the drug flunarizine.

Another visible-light induced method for allene transformation relies on an intramolecular cyclative aminochlorination.⁸³ Allenes **57**, containing a sulfonamide moiety, could participate in a $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ -catalysed reaction with NCS in a toluene-methylformate mixture under nitrogen atmosphere (Scheme 35). Potassium carbonate was used in catalytic amounts.

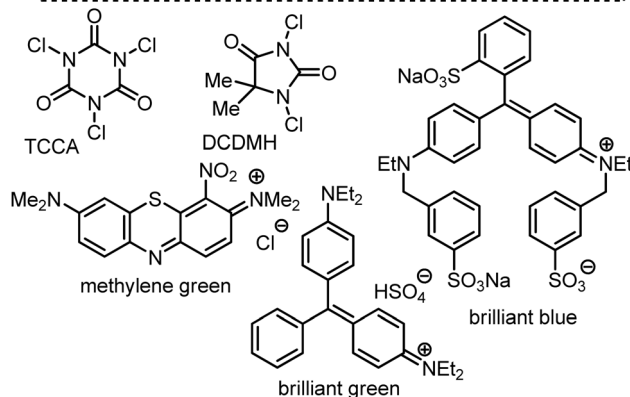
Some methods for chlorination of aromatic substrates **58** were developed under visible light irradiation (Scheme 36). Firstly, a series of works reported on visible light-mediated



Scheme 35 Photoredox-catalysed intramolecular aminochlorination of allenes.



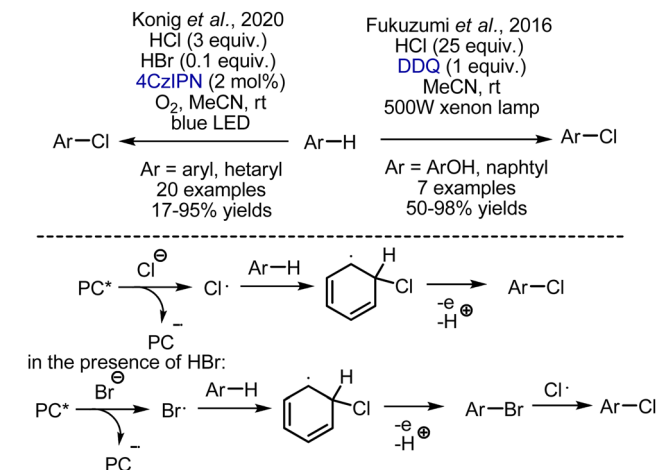
König *et al.*, 2016: NCS (1.2 equiv), $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (2 mol%), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (1.2 equiv), MeCN, H_2O , N_2 , rt, blue LED
Lamar *et al.*, 2019: NCS (1.1 equiv), methylene green (5 mol%), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.1 equiv), MeCN, rt, white LED
Li, Duan *et al.*, 2019: DCDMH (1.1 equiv), TBHP (3.5 equiv) DCM, rt, blue LED
Lamar *et al.*, 2019: TCCA (1.1 equiv), brilliant green (4 mol%), air, MeCN, rt, white LED
Lamar *et al.*, 2020: DCDMH (1.1 equiv), brilliant blue (4 mol%), air, MeCN, rt, white LED



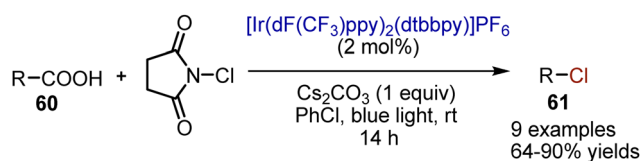
Scheme 36 Visible light-mediated chlorination of aromatic compounds.

processes, employing NCS or analogous reagents as chlorine sources. It is believed that the role of a photocatalyst in these transformations is usually to generate an active NCS cation radical **59**, which is more readily participating in aromatic electrophilic substitutions.^{84–88} The chlorination with NCS without light irradiation is a well-established process under the action of protic acids, Lewis acids, or transition metals. Visible-light mediated reactions benefit from the use of benign catalysts (like organic dyes) and mild conditions *i.e.* neutral medium and ambient temperature. Electron-rich and electron-neutral aromatic compounds, as well as π -excessive heterocycles are competent substrates.

The approaches that employ HCl as a source of chlorine are more intriguing. (Scheme 37). Fukuzumi *et al.* developed chlorination of phenols by a DDQ-HCl system under visible light irradiation.⁸⁹ Photoexcited DDQ was capable of chloride oxidation to generate a chlorine atom radical, which reacted with phenol. The reaction worked smoothly with phenols, while naphthalene was the only electron-neutral substrate. Another reaction, employing HCl as a chlorine source was developed by König *et al.*⁹⁰ The generation of chlorine atom radicals was performed by oxidation with photoexcited 4CzIPN organic



Scheme 37 Photochemical chlorination of aromatic compounds with HCl as chlorine source.



Scheme 38 Decarboxylative chlorination.

photocatalyst, while oxygen was regenerating the catalyst. It was shown that bromination with HBr was occurring faster, but bromo-derivatives were undergoing bromine substitution by chlorine.

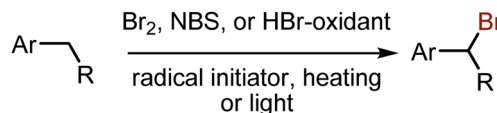
3.3. Decarboxylative chlorination

Aliphatic carboxylic acids **60** were smoothly halogenated with loss of the carboxylic group.⁹¹ The reaction was performed by irradiating an acid and *N*-chlorosuccinimide (NCS) in chlorobenzene in the presence of Cs₂CO₃ with blue light, employing [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ as photocatalyst (Scheme 38). Primary, secondary, and tertiary acids were reacting smoothly, delivering the desired products **61** with 64–90% yields. The protocol's utility has been effectively demonstrated through the synthesis of costly 1-bromoheptadecane using affordable stearic acid found in nature. The reaction is believed to initiate with the oxidation of cesium carboxylate by the photoexcited Ir-complex, resulting in the generation of an alkyl radical that seizes a chlorine atom from NCS. The catalytic cycle concludes by the reduction of the succinimidyl radical by Ir²⁺, thereby closing the cycle. Besides chlorination, the developed protocol also allows a decarboxylative bromination (diethyl bromomalonate instead of NCS), as well as iodination (NIS instead of NCS).

4. Bromination

4.1. Bromination of C_{sp}³–H bonds

Benzylic bromination with bromine is a well-established method (Scheme 39). Heating or light has been used for a long



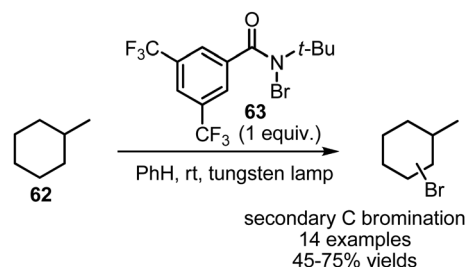
Scheme 39 Benzylic bromination.

time to initiate the bromine homolytic cleavage into bromine radicals.^{92–94} Being a toxic and corrosive reagent, molecular bromine is often replaced by NBS. Radical initiators,⁹⁵ heating, or visible light⁹⁶ are needed for NBS-mediated benzylic brominations. More recently brominations could be performed in water,⁹⁷ perfluoroalkane,⁹⁸ CH₃CN,⁹⁹ or without solvent.¹⁰⁰ More benign systems like HBr-oxidant or MBr-oxidant^{101–104} were also used with visible light irradiation. A photoredox process for benzylic bromination, employing Ir-complex as a photocatalyst and CBr₄ as a bromine source, has been developed as well.¹⁰⁵ Interestingly, oxybromination could be achieved for ethylarenes by subjecting them to aerobic visible light-mediated reactions with HBr in H₂O–EtOAc.^{106,107}

Several interesting processes for visible-light mediated bromination of non-activated alkanes **62** have been developed. Alexanian *et al.* have shown that bulky bromoamide **63** can present an advanced selectivity in visible light-mediated bromination of alkanes, favoring secondary C–H bonds over tertiary, which is very uncommon for free radical reactions (Scheme 40).¹⁰⁸

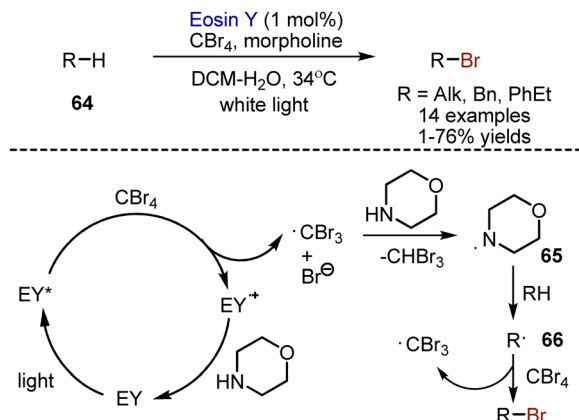
Non-activated alkanes, as well as alkylarenes **64** could be brominated with CBr₄ in the presence of eosin Y photocatalyst and morpholine (Scheme 41).¹⁰⁹ It was suggested that photo-excited eosin Y reduces CBr₄ to give an anion radical, which decomposes into a bromide anion and [•]CBr₃. Hydrogen atom transfer from morpholine to the tribromomethyl radical occurred, generating aminyl radical **65**, which could, in its turn, abstract hydrogen from alkane. The resulting carbon-centered radical **66** reacted with CBr₄ to produce the desired compound. The photocatalytic cycle could be closed by oxidation of morpholine. The process allowed bromination with moderate yields, but good selectivities.

Visible light has been found to enhance the bromination of non-activated alkanes **67** with potassium bromide (Scheme 42).¹¹⁰ A catalytic amount of NaNO₂ oxidizes the bromide anion into Br₂, which undergoes a free-radical reaction under white light irradiation. The reoxidation of NO to NO₂ occurs on ambient air. The visible light mediated bromination of alkanes has also been achieved with CBr₄ as a bromine source.¹¹¹

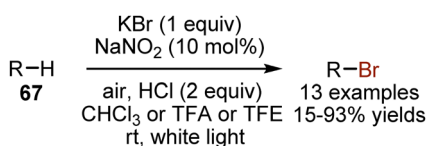


Scheme 40 Visible light-mediated bromination of secondary carbons.





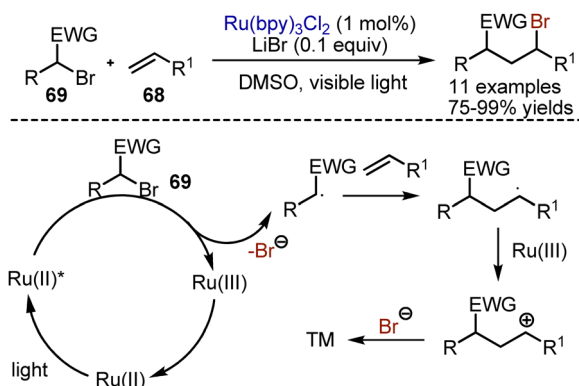
Scheme 41 Eosin Y-catalysed bromination with carbon tetrabromide.



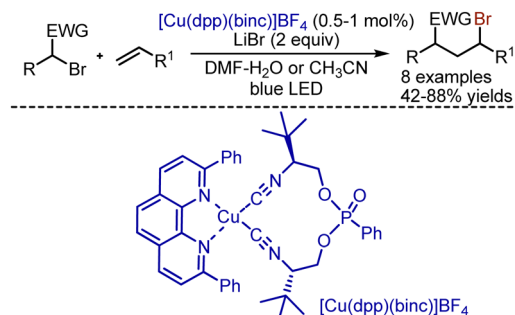
Scheme 42 Visible light-induced bromination with KBr.

4.2. Bromination of unsaturated compounds

Bromination of alkenes or alkynes with molecular bromine does not need visible light to proceed. On the contrary, atom transfer radical addition reactions of alkyl bromides are going smoothly under photoredox-catalytic conditions. In 2012, Stephenson reported a general haloalkylation of alkenes **68**, employing $\text{Ru}(\text{bpy})_3\text{Cl}_2$ as photocatalyst in DMSO with the addition of a catalytic amount of LiBr (Scheme 43).¹¹² The mechanism implied initial reduction of alkyl bromide **69** with the photoexcited catalyst, which led to the decomposition of the resultant anion radical into the bromide anion and a carbon-centred radical. The addition of the alkyl radical to a double bond formed another carbon-centred radical. The oxidation of the latter by $\text{Ru}(\text{III})$ closed the catalytic cycle and formed a cation, quenched by the bromide anion. This approach worked with



Scheme 43 Bromoalkylation of alkenes.



Scheme 44 Bromoalkylation of alkenes with Cu-complex.

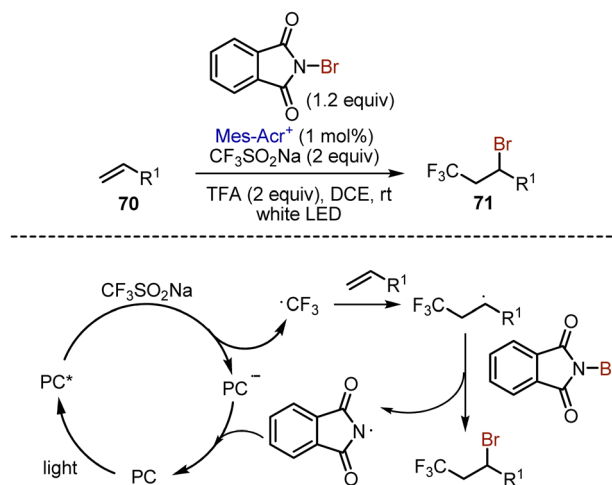
various alkyl bromides, containing electron-withdrawing groups, as well as with polyhalomethanes.

Analogous bromoalkylation was realized with the help of Cu-complexes by Reiser group (Scheme 44).¹¹³ It was found that various activated alkyl bromides reacted smoothly with alkenes under irradiation in the presence of $[\text{Cu}(\text{dpp})(\text{binc})]\text{BF}_4$ (dpp = 2,9-diphenyl-1,10-phenanthroline; binc = bis(2-isocyanophenyl) phenylphosphonate). Except for bromomalonates, benzyl bromides with nitro groups could be employed, but larger amounts of catalyst were needed, as well as excess amounts of alkenes.

Later, organophotoredox approach was developed for alkene **70** bromotrifluoromethylation (Scheme 45).¹¹⁴ The photoexcited acridinium salt oxidized Langlois' reagent to generate a trifluoromethyl radical, which added to the alkene double bond. The resulting radical abstracted a bromine atom from *N*-bromophthalimide, giving the target molecule **71**.

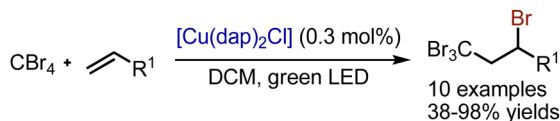
Copper-catalysed bromotribromomethylation with CBr_4 could be also realized (Scheme 46).¹¹⁵

When alkenes **72** were reacted with oxazolidine-containing alkyl bromides **73** under visible light irradiation, an interesting cleavage of the oxazolidine ring took place (Scheme 47).¹¹⁶ The reaction was performed with the $\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})(\text{PF}_6)$ photocatalyst in DMF. The initial steps were analogous to described above methods: SET-reduction of alkyl bromide,

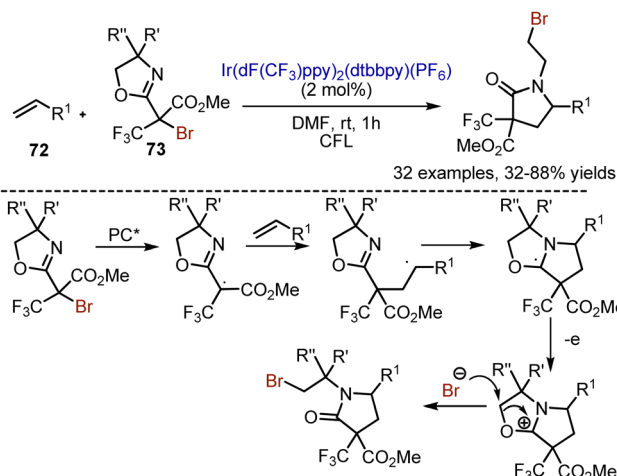


Scheme 45 Photoredox-catalysed bromotrifluoromethylation of alkenes.





Scheme 46 Photoredox-catalysed bromotrifluoromethylation of alkenes.

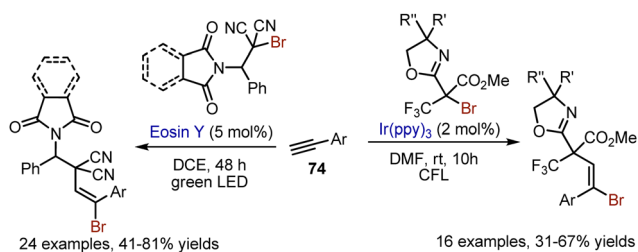


Scheme 47 Visible light-mediated synthesis of pyrrolidones through oxazolidine ring cleavage.

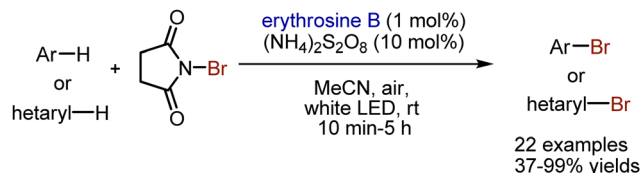
formation of alkyl radical, and addition to the double bond. The carbon-centered radical interacted with nitrogen of oxazolidine, and subsequent oxidation led to cation formation. The attack of the bromide anion cleaved the positively charged ring and finalized the sequence. Various aryl and alkyl alkenes, as well as enol ethers reacted smoothly under the reaction conditions.

This approach was amenable for alkyne **74** bromoalkylation too, but the oxazolidine ring was preserved (Scheme 48). Another bromoalkylation of alkynes was developed under eosin Y catalysis.¹¹⁷

Bromination of aromatic compounds under visible light-mediated conditions has been achieved by Lamar *et al.*¹¹⁸ Xanthene dye erythrosine B has been used as photocatalyst in the bromination of arenes with NBS (Scheme 49). Although ammonium peroxodisulfate was not found essential according to some control experiments, its presence facilitated the process. The conditions were compatible with bromination of



Scheme 48 Bromoalkylation of alkynes.

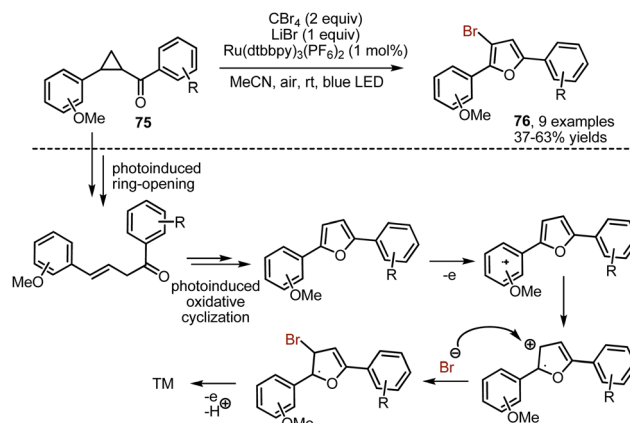


Scheme 49 Bromination of aromatic compounds.

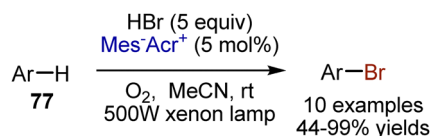
heteroarenes. In the suggested mechanism, the activation of NBS was achieved *via* SET oxidation by a photoexcited dye.

While investigating oxidative transformations of donor-acceptor cyclopropanes **75** into furans under visible light irradiation, Xia and-workers discovered that taking CBr₄ in an excess amounts led to the formation of brominated furans **76** (Scheme 50).¹¹⁹ The reaction was regioselectively producing 3-bromofurans. Carbon tetrabromide could be also exploited for the bromination of 8-aminoquinolines.¹²⁰

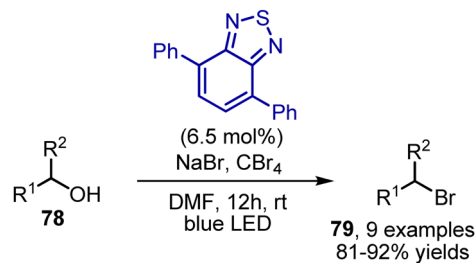
The more sustainable bromine source HBr, is usually employed for bromination under oxidative conditions, which can be performed with a photoredox catalyst. Fukuzumi reported an acridinium dye-catalysed bromination of electron-rich arenes **77** employing HBr and oxygen-saturated MeCN (Scheme 51).¹²¹ According to the mechanistic studies, the photoexcited acridinium salt oxidized the aromatic compound into a cation radical, which reacted with the bromide anion. Oxygen was recycling the photocatalyst. Later, a microporous organic polymer-catalysed bromination was reported. The polymer was based on 4,7-diphenylbenzo[*c*][1,2,5]thiadiazole photoactive units bridged with formaldehyde dimethyl acetal. An important advantage of the polymer catalyst is its high reusability potential.



Scheme 50 Visible light-mediated synthesis of 3-bromofurans from cyclopropanes.



Scheme 51 Acridinium dye-catalysed bromination of electron-rich arenes.



Scheme 52 Deoxygenative bromination.

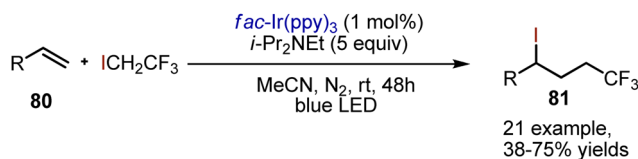
4.3. Deoxygenative bromination

Aliphatic alcohols **78** could be converted into bromides **79** when subjected to tetrabromomethane and NaBr in DMF under blue light irradiation in the presence of a benzothiadiazole catalyst (Scheme 52).¹²²

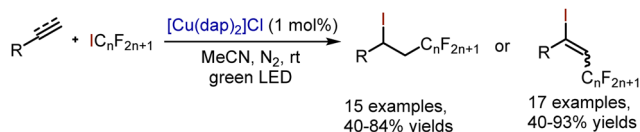
5. Iodination

5.1. Iodination of unsaturated compounds

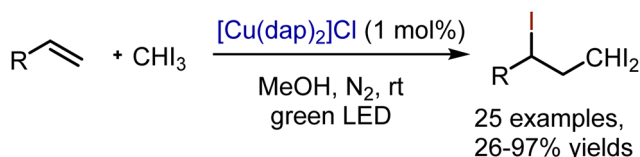
Atom transfer radical addition reactions to alkenes are applicable for iodofunctionalisations, as described earlier in other sections. Guo *et al.* have reported a photoredox-catalysed iodo-trifluoroethylation (Scheme 53).¹²³ Various terminal non-conjugated alkenes **80** have been evaluated, giving addition products **81** with moderate yields. Diisopropylethylamine has been used as a reductive quencher of photoexcited Ir(ppy)₃ to generate strongly reducing Ir(II). The latter interacted with 1,1,1-trifluoro-2-iodoethane, reducing it to an anion radical, which subsequently decomposed into an alkyl radical and iodide. Addition of the trifluoroethyl radical to an alkene was



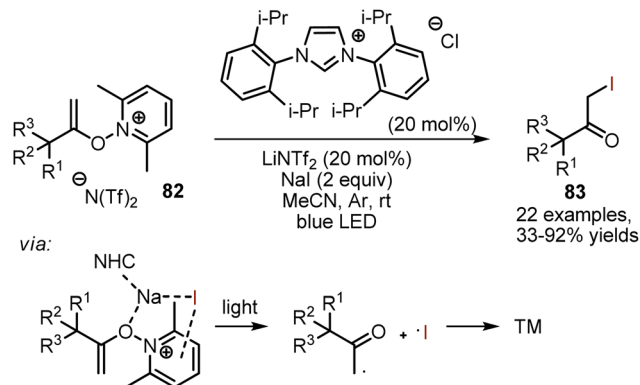
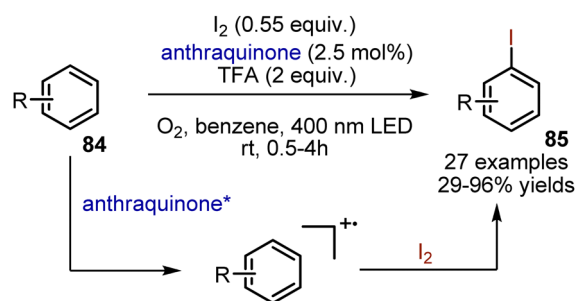
Scheme 53 Photoredox-catalysed alkene iodo-trifluoroethylation.



Scheme 54 Copper-catalysed alkene iodo-perfluoroalkylation.



Scheme 55 Copper-catalysed alkene iodo-perfluoroalkylation.

Scheme 56 Visible light-mediated NHC-catalysed iodination of *N*-alkenoxypyridinium salts.

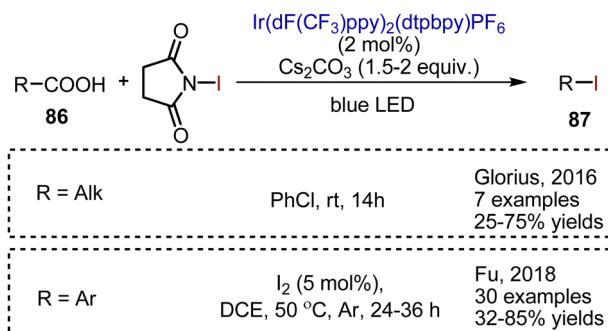
Scheme 57 Visible light-mediated iodination of aromatic compounds.

giving another carbon radical. The final iodination presumably took place by abstracting iodine from 1,1,1-trifluoro-2-iodoethane.

Iodoperfluoroalkylation of styrenes and aryl acetylenes has been accomplished through copper-catalysed ATRA reactions by Reiser *et al.* (Scheme 54).¹²⁴

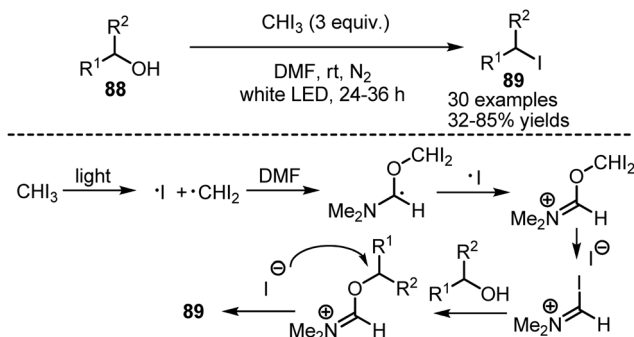
Analogously, addition of iodoform could occur under copper catalysis (Scheme 55).¹²⁵

Visible light-mediated iodination of *N*-alkenoxypyridinium salts **82** was giving α -iodo ketones **83** under *N*-heterocyclic carbene catalysis (Scheme 56).¹²⁶ According to the mechanistic studies, the pyridinium salt was forming a photoactive electron donor-acceptor (EDA) complex with sodium iodide. Excitation



Scheme 58 Decarboxylative iodination with NIS.





Scheme 59 Deoxygenative iodination with iodoform.

with light led to the formation of an alkyl radical, an iodine radical and 2,6-lutidine. It was suggested that the role of NHC was to facilitate the EDA-complex formation through electrostatic interaction with NaI. Base was needed to generate NHC from the imidazolium salt.

Iodination of aromatic compounds typically involves the use of terminal oxidants. Classical methods utilize a combination of I_2 with HNO_3 or $KMnO_4$. König *et al.* have described a visible light-mediated iodination method under mild conditions, utilizing oxygen as the terminal oxidant. (Scheme 57).¹²⁷ Electron-rich aromatic compounds **84** were irradiated in benzene under oxygen atmosphere in the presence of iodine, TFA and anthraquinone. The desired compounds **85** were obtained with 29–96% yields. Anisole was iodinated with high *para*-selectivity. No iodination of the benzylic position of alkylbenzenes was observed. Mechanistic studies suggested that the interaction of iodine with an arene radical cation takes place.

5.2. Decarboxylative iodination

Carboxylic acids **86** could be decarboxylatively iodinated employing an Ir-complex-catalyzed visible light-mediated reaction (Scheme 58). NIS has been used as iodine source, while cesium carbonate is needed to generate the cesium salt of the carboxylic acid. For the iodination of aliphatic carboxylic acids, the reaction was performed at rt in $PhCl$.¹²⁸ Aromatic acids are iodinationally decarboxylated on heating in DCE in the presence of a catalytic amount of molecular iodine.¹²⁹ The optimized conditions allowed the syntheses of alkyl and aryl iodides **87** with a broad substrate scope and moderate to very good yields.

5.3. Deoxygenative iodination

A photocatalyst-free protocol for the deoxygenative iodination of alcohols **88** has been developed by Zhao and Antonietti.¹³⁰ A solution of the alcohol and iodoform in anhydrous DMF was irradiated with white LED-light under nitrogen atmosphere, to deliver the corresponding iodides **89** with good to excellent yields (Scheme 59). It has been found that iodoform is capable of homolytic cleavage under visible light irradiation. The formed diiodomethyl radical interacted with DMF, forming a Vilsmeier type reagent, that iodinate the alcohol. The reaction worked smoothly with primary and secondary alcohols.

6. Conclusion

Visible light has become a useful tool for organic chemists. Numerous reactions for halogenation under visible light irradiation were recently developed. These reactions are usually performed under milder conditions, allowing to avoid high temperatures and non-selective UV-light. Benign halogenation reagents could be used with visible light, and some classical reactions were enhanced under these conditions. Major breakthroughs were developed in the field of difunctionalisation reactions, where other functionalities along with halogen were introduced under excellent control and with remarkable selectivity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The paper has been supported by the RUDN University Strategic Academic Leadership Program.

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