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Visible-light-induced reactions of methylenecyclopropanes (MCPs)

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Diverse, visible-light-induced transformations of methylenecyclopropanes (MCPs) have been reported in recent years, attracting significant attention from synthetic chemists. As readily accessible strained molecules, MCPs have sufficient reactivity to selectively generate different target products, through reactions with various radical species upon visible-light irradiation under regulated reaction conditions. These transformations can be classified into three subcategories of reaction pathway, forming ring-opened products, cyclopropane derivatives, and alkynes. These products include pharmaceutical intermediates and polycyclic/heterocyclic compounds that are challenging to obtain using traditional methods. This review summarizes the recent advancements in this field.

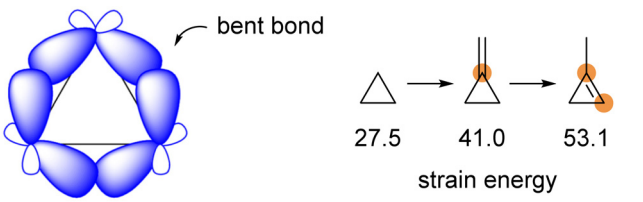
Introduction

Cyclopropane is strained because the "bent" carbon–carbon bonds overlap poorly (Scheme 1). The total ring strain in cyclopropane is 27.5 kcal mol^{-1}, in which about three-quarters of the strain is the bond angle strain. Introducing a nominally trigonal carbon center into a three-membered ring system increases its ring strain. The SE (strain energy) for methylenecyclopropane is 41.0 kcal mol^{-1}, while that for 1-methylcyclopropene is 53.1 kcal mol^{-1}.[1] Wiberg suggested that each additional sp^2 center in a three-membered ring increases the SE by 12–14 kcal mol^{-1} and recognized that part of the reason is due to the enlarged strain connected with the sp^2 carbon center. Afterwards, Borden concluded that the loss of a firm *tert*-C–H bond upon introducing the sp^2 carbon in methylenecyclopropane is the primary source of the additional strain energy.[1,2] As a class of highly strained but readily accessible and sufficiently reactive molecules, methylenecyclopropanes (MCPs) can undergo a range of ring-opening reactions in which the released strain provides a thermodynamic driving force.[3]

MCPs exhibit preeminent physical and chemical properties, which offer opportunities to participate in various attractive chemical transformations. These reactions can access cyclopropane-containing frameworks and other ring-opened compounds that are challenging to obtain conventionally.[4] These transformations usually occur smoothly under mild reaction conditions such as with heating,[5] Lewis/Brønsted acids,[6] transition metal catalysis,[7] radical-promoted processes,[8] and nucleophilic species-promoted ring-opening reactions,[9] giving tremendous potential in organic synthesis (Scheme 2).

In most radical reactions of MCPs and vinylcyclopropanes (VCPs), the dominant contributor to reactivity is the formation of **1**, the cyclopropylcarbinyl radical species (Scheme 3). The structure of **1**, deduced from its electronic spin resonance spectrum[10] and in agreement with calculations (STO-3G basis set),[11] is in the bisected conformation shown, and is predicted to be 1.4 kcal mol^{-1} more stable than its perpendicularly oriented counterpart. The opening of the cyclopropylcarbinyl radical to the butenyl radical **2** is among the fastest radical processes known, and has been widely designed as a radical clock to conduct mechanistic studies for probing radical processes.[12]

Precursors to cyclopropylcarbinyl radicals mainly cover VCPs and MCPs. Over the past three decades, many radical reactions of MCPs have been established, providing effective routes to access polycyclic and heterocyclic compounds, including bioactive drugs.[13a–am,8a] In the early 1990s, synthetic applications



Scheme 1 Three-membered rings with high strain (the SE is given in kcal mol^{-1}).

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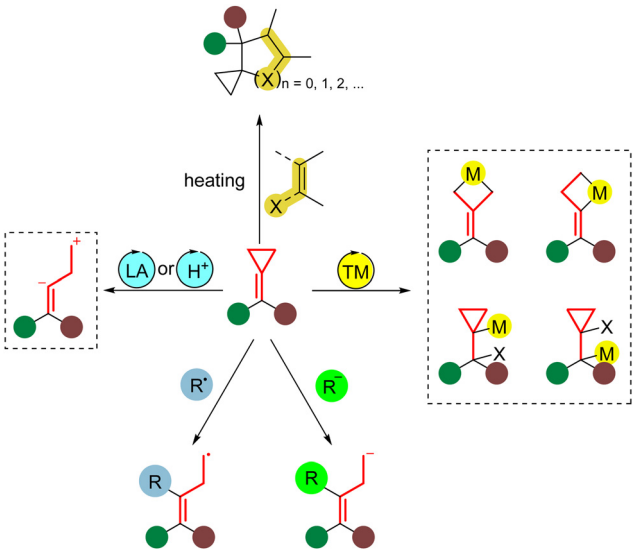
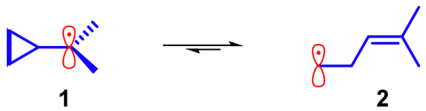
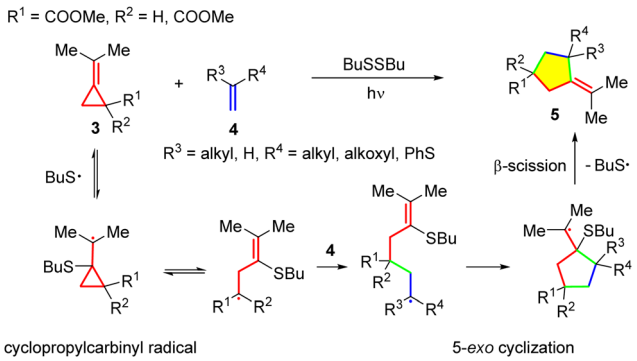


Scheme 2 Transformations of MCPs.



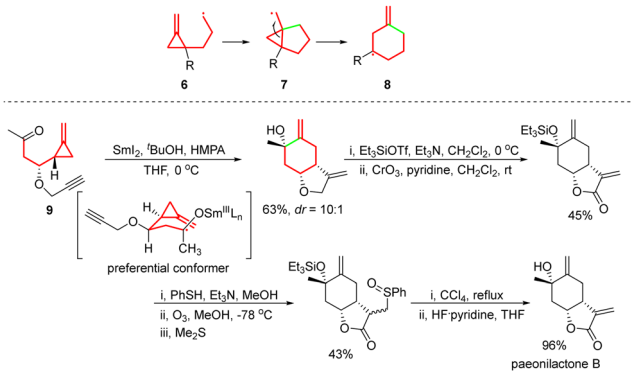
Scheme 3 Cyclopropylcarbinyl radical species.



Scheme 4 Thiyl-radical-catalyzed chain cyclization.

of radical reactions involving MCPs appeared. For example, in 1991, Priestley's group reported that readily available methylenecyclopropanes **3** efficiently undergo annulation with inactivated and electron-rich alkenes **4** to provide methylenecyclopentanes **5** *via* thiyl-radical-catalyzed chain cyclization (Scheme 4).[14]

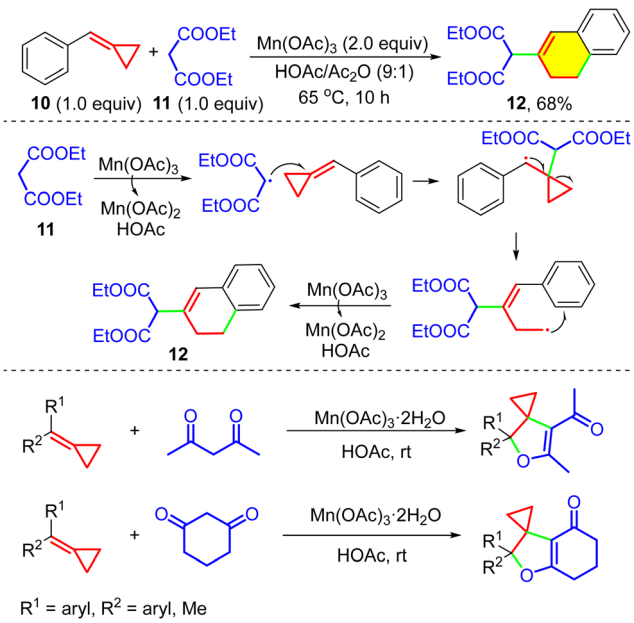
Afterwards, a brilliant and efficient method was established to access methylenecyclohexyl radicals from cyclopropylcarbinyl radicals. In this method, the (methylenecyclopropyl)propyl radical **6**, which is generated from the precursor, undergoes initial 5-*exo* cyclization, leading to the cyclopropylcarbinyl radical **7**, and then **7** undergoes ring-opening to afford the more stable methylenecyclohexyl radical **8**.[14,15] For instance, in 1998, the Kilburn group reported the SmI_2-mediated cascade



Scheme 5 Synthesis of paeonilactone B from MCPs.

reaction of methylenecyclopropyl ketone **9**, providing a short route to the natural product paeonilactone B (Scheme 5).[13e]

In 2004, Huang and co-workers reported the tandem radical cyclization reactions of MCPs for the first time (Scheme 6).[13n] In this protocol, MCP **10** reacted with $Mn(OAc)_3{\cdot}2H_2O$ and malonic acid diethyl ester **11** in HOAc/Ac_2O (9 : 1) *via* two SET processes, providing 2-(3,4-dihydronaphthalen-2-yl)malonic acid diethyl ester **12** in 68% yield. In 2005, our group also reported a radical-promoted cyclization reaction using $Mn(OAc)_3{\cdot}2H_2O$ (Scheme 6, bottom). In this protocol, MCPs were used as the substrates to react with 2,4-pentanedione or 1,3-cyclohexanedione, which was applied for α-carbonyl radical generation, producing 4,5-dihydrofuran derivatives in moderate to good yields.[13o] After that, tandem radical cyclization reactions of MCPs involving various radicals were abundantly developed, involving a variety of radicals, such as perfluoroalkyl radicals,[13q] phosphite radicals,[13p,13an] α-carbonyl radicals,[13r,13u] thiyl radicals,[13t] selenium radicals,[13s] trifluoromethyl radicals,[8a,16] and N-centered radicals.[13y]



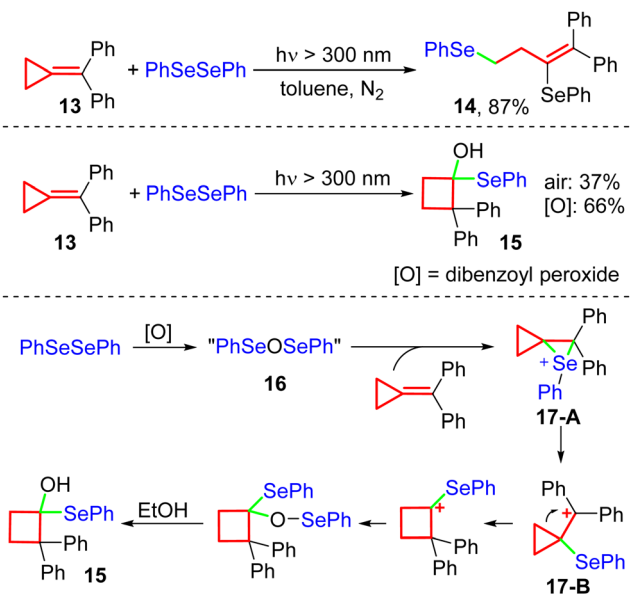
Scheme 6 Radical-promoted tandem cyclization reactions.

Although radicals are highly reactive species, manipulating radical reactions to undergo selective processes is highly significant. One of the most rapidly increasing areas of radical chemistry in organic synthesis is photoredox catalysis, and it has been a helpful tool for chemists to achieve unique chemical reactivity, especially with the breakthrough merger of organocatalysis and photocatalysis.[17] Based on the catalytic system employed, this field, in principle, can be classified into three subcategories: proceeding through a single electron transfer (SET) process, an energy transfer (EnT) process, or an atom transfer (AT) process.

In recent years, visible-light-induced organic reactions of MCPs have become well established, consisting of ring-opening reactions, cyclopropane-producing reactions, and ring-opening reactions *via* a non-classical radical clock. This feature article aims to introduce the recent developments in these reactions, from our group and other researchers.

Ring-opening reactions *via* cyclopropylcarbinyl radical intermediates

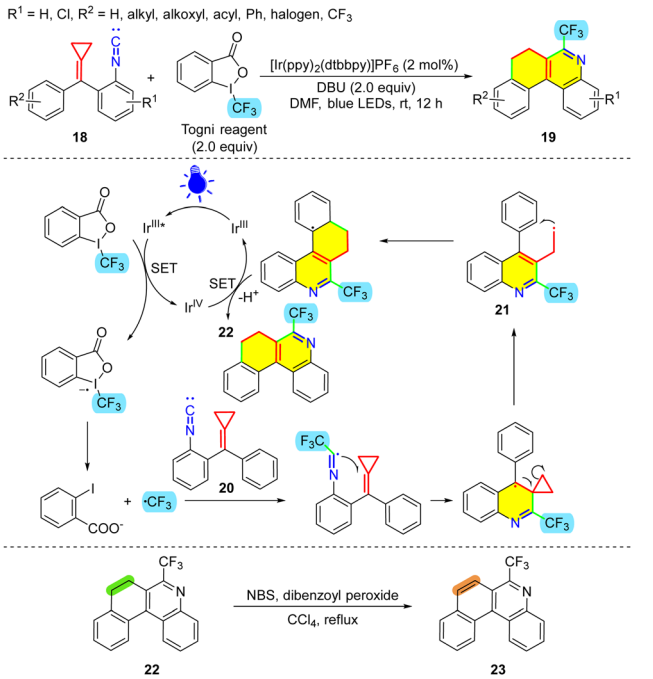
In 2006, the Huang's group reported the ring-opening process for MCPs under irradiation with a tungsten lamp (300 W) (Scheme 7).[13s] In this reaction, when MCP **13** and diphenyl diselenide were used as the substrates, with toluene as the solvent, the ring-opened product **14** was obtained under a nitrogen atmosphere. If N_2 protection was not applied and EtOH was used as the solvent, the cyclobutanol derivative **15** was generated in 37% yield, along with **14** in 25% yield. Subsequently, they found that adding dibenzoyl peroxide avoided the formation of **14**, and the yield of **15** was improved to 66%. This report demonstrated the following reaction process: diphenyl diselenide is first oxidized by oxygen or dibenzoyl peroxide to benzeneselenenic anhydride **16**. Then, cyclopropyl cationic intermediates **17-A** and **17-B** are generated upon the introduction of **13**. After rearrangement, S_N1 substitution, and alcoholysis, the final product **15** is generated. However, catalytic reactions of MCPs induced by visible-light irradiation were not established during the subsequent decade.



Scheme 7 Difunctionalization of MCPs with diphenyl diselenide.

Fluorinated compounds are essential in functional materials,[18] pharmaceuticals,[19] and agrochemicals.[20] Trifluoromethylation[21] and difluoroalkylation[22] are considered to be significant features in the preparation of fluorinated compounds because integrating these groups brings enhanced biological and pharmaceutical properties to the molecules, such as better metabolic stability, higher bioavailability, and greater lipophilicity.

Imidoyl radicals are vital synthetic intermediates that undergo intermolecular and intramolecular radical addition to olefins, alkynes, aromatics, *etc.*[23] They are often utilized to synthesize nitrogen-containing heterocycles such as indoles, pyrrolidines, and quinolines. One of the known methods to engender imidoyl radicals is the addition of radicals to isonitriles and isothiocyanates. In 2016, inspired by the previous work of Studer and co-workers,[24] our group disclosed the first protocol that applied photoredox catalysis for MCP transformation reactions (Scheme 8).[25] In this protocol, $[Ir(ppy)_2(dtbbpy)]PF_6$ is employed as the photocatalyst to enable the photocatalytic trifluoromethylation of isonitrile-tethered MCPs **18** with the Togni reagent. Two six-membered rings and three new C–C bonds were formed in a one-pot reaction, showing the high efficiency of the protocol. Moreover, these products can be easily transformed into 6-(trifluoromethyl)-benzo[*k*]phenanthridine derivatives. In the proposed mechanism, initially, the excited



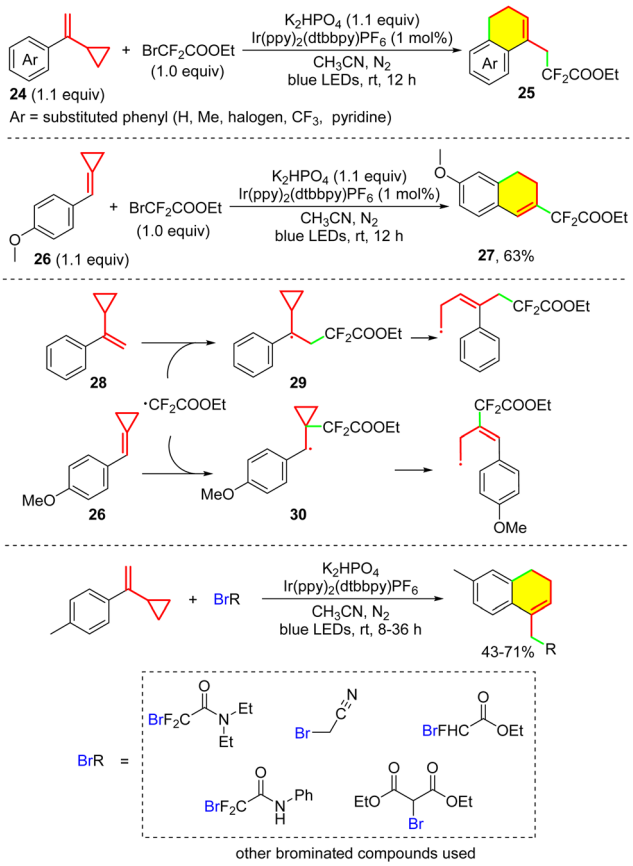
Scheme 8 Trifluoromethylation of isonitrile-tethered MCPs.

state ($E_{1/2}$ = −0.96 V *vs.* SCE) of the Ir catalyst reduces the Togni reagent ($E_{1/2}$ = −1.34 V *vs.* SCE)[26] to the trifluoromethyl radical through an SET process. It should be noted that the values of the redox potentials do not support a valid spontaneous SET process, although this is not impossible. Sharma *et al.* proposed an alternative mechanism in which the trifluoromethyl radical is generated *via* photo-induced fission without the intervention of the catalyst,[23b] which is conceivable because hypervalent iodine(III) reagents readily undergo photodecomposition upon exposure to weak UV light or visible-light to provide radicals.[27] Subsequently, in the reaction process, addition of the CF_3 radical to the isonitrile group in substrate **20** generates the imidoyl radical. Subsequent attack at the MCP and its ring-opening provide intermediate **21**, and **21** undergoes direct radical cyclization with its arene moiety to give the cyclohexadienyl radical. After SET oxidation and deprotonation, the final product **22** is afforded. To illustrate the synthetic utility of the products, in the presence of NBS and dibenzoyl peroxide, **22** can then be transformed to **23**, which contains a larger delocalized framework.

In the same year, Li and co-workers reported the catalytic difluoroalkylation/C–H cascade annulation reactions of cyclopropyl olefins, including VCPs **24** and MCP **26**, induced by visible-light irradiation for the synthesis of partially hydrogenated naphthalene and quinoline derivatives (**25**, **27**) with various difluorinated side chains (Scheme 9).[28] In this protocol, ethyl bromodifluoroacetate (or other brominated compounds as shown in Scheme 9) was used as the radical precursor to react with MCPs or VCPs, providing similar radical intermediates **29** and **30** after radical addition, as was described before. This protocol will provide access to other functionalized bicyclic compounds if further derivatization can be developed.

To realize the CF_2H functionalization of MCPs, Wu's group recently applied easily prepared $[Ph_3PCF_2H]^+Br^-$ (**32**)[29] for CF_2H radical generation, synthesizing CF_2H functionalized partially hydrogenated naphthalenes **33** from **31** (Scheme 10).[30] $[Ph_3PCF_2H]^+Br^-$ provides simple and practical access to CF_2H radicals for hydrodifluoromethylation,[31] compared with other CF_2H radical sources[32] such as HCF_2SO_2Cl, its derivatives and difuoromethylsulfinate salts which are prepared from gaseous HCF_2Cl through multiple steps.[32a] Interestingly, if MCP compounds are tethered with two phenyl rings (**13**) in this protocol, the difunctionalized product **34** will be obtained without ring-closing of the radical to the aryl moiety. In this report, Wu and co-workers also tested other halides **35** such as α-bromoketones and aryl sulfonyl chlorides **39** for MCPs (**31**, **37**), and found that various functionalized products (**36**, **38**, **40**) were obtained in moderate to excellent yields. Synthetic transformations, including epoxidation and cyclization, highlight the potential applications of this methodology in organic synthesis and the synthesis of pharmaceutical compounds (Scheme 10, bottom).

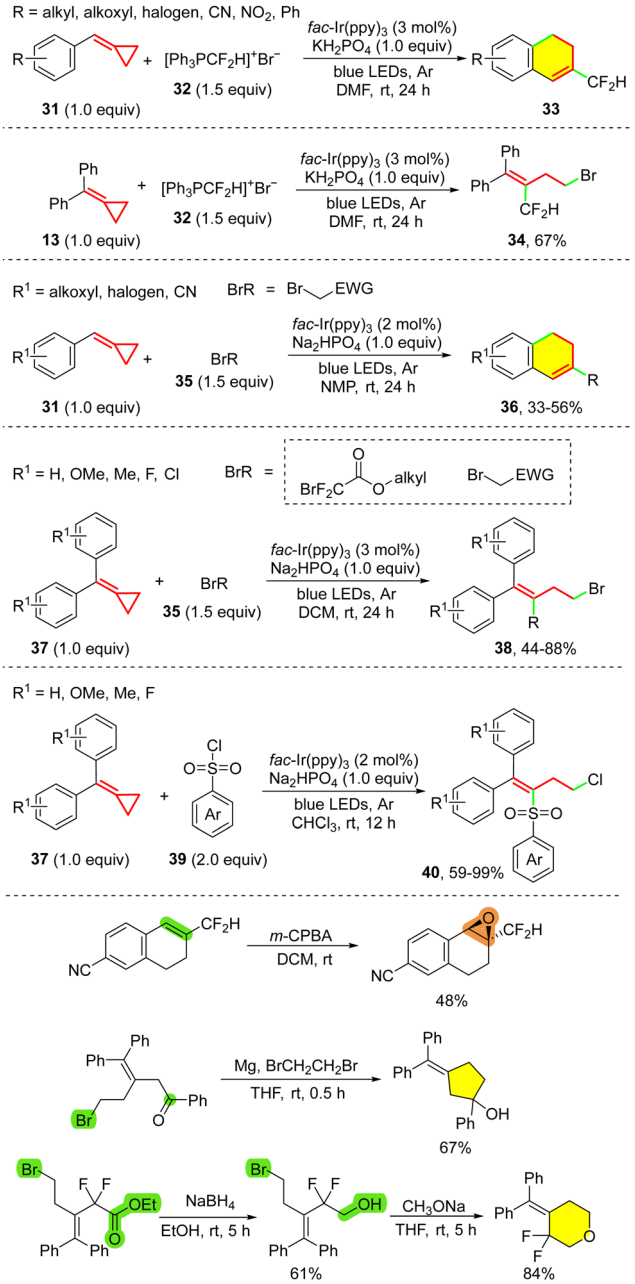
In recent years, *N*-functionalized pyridinium salts have been employed as versatile reagents for the redox-triggered release of various radical species for organic synthesis.[33] In 2017, Xu and co-workers used N-protected 1-aminopyridinium **42** to produce sulfamide radicals *via* reduction of the photoexcited catalyst *Ir(ppy)$_3$ (Scheme 11).[34] In this reaction, after addition of the



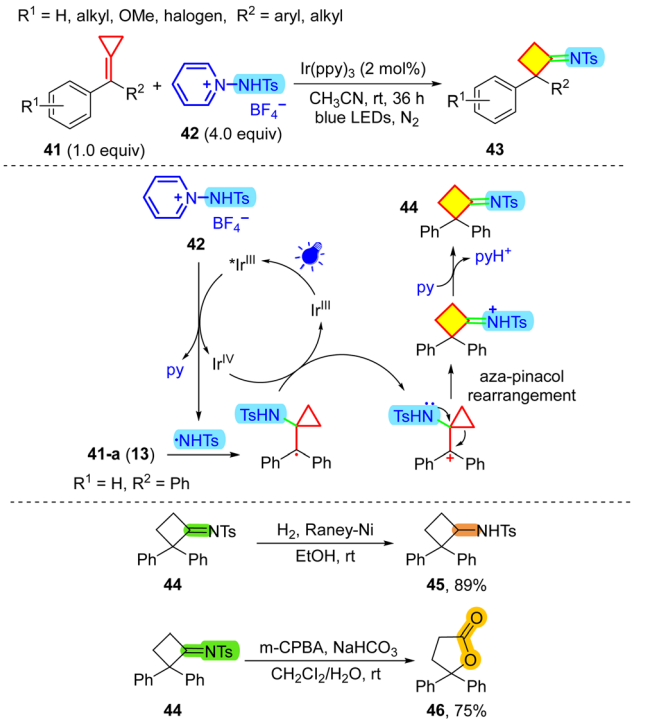
Scheme 9 Difluoroalkylation of MCPs and VCPs.

N-centered radical to MCP **13**, SET oxidation by Ir(IV) and aza-pinacol rearrangement, the strained cyclobutanimine derivative **44** was ultimately afforded. After reduction or oxidation, the formed motifs can easily be transformed into valuable groups (**45**, **46**) in natural products and bioactive molecules. In organic synthetic methodologies, pinacol and semi-pinacol rearrangement reactions are essential to construct all-carbon quaternary centers, although the aza-pinacol rearrangement has been less reported (Scheme 12).[35] Therefore, this novel visible-light-induced aza-pinacol rearrangement reaction provides a supplement to the ring-expansion reactions of MCPs with nitrogen compounds.[36]

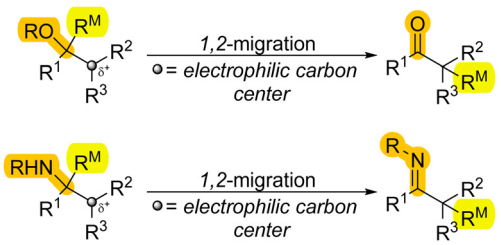
The sulfone moiety is also an essential motif in pharmaceuticals,[37] agrochemicals,[38] natural products,[39] and organic materials.[40] Among the synthetic routes to install the sulfonyl group, sulfonylation starting from stable and environmentally friendly sulfonyl sources is promising and attractive.[41] In 2019, Tang's group developed the visible-light-catalyzed sulfonylation of MCPs **47** with sulfonyl chlorides to synthesize 3-sulfonylated 1,2-dihydronaphthalene derivatives **48** (Scheme 13).[42] Compared with the work of Wu and co-workers as discussed above,[30] after sulfonyl radical-promoted ring-opening of the MCP, the carbon radical finally preferentially undergoes a ring-closing reaction instead of combining with a nucleophilic species after SET oxidation. It should be noted that the reactions were carried out at a higher temperature (100 °C); thus,



Scheme 10 CF_2H functionalization, bromination and chlorination of MCPs.



Scheme 11 Visible-light-induced aza-pinacol rearrangement reaction.

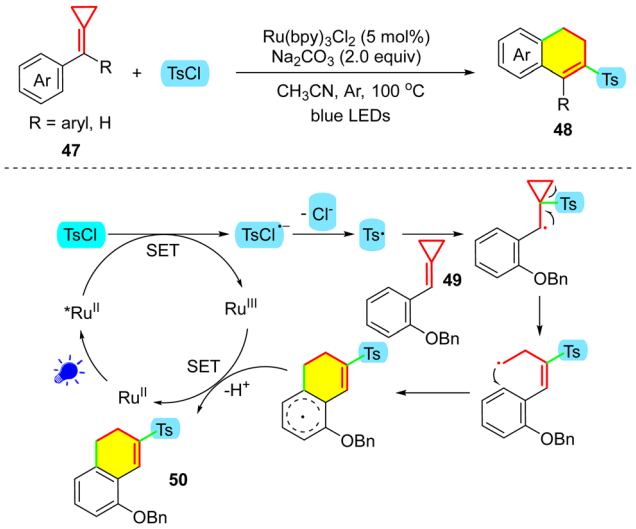


Scheme 12 Semi-pinacol rearrangement and aza-pinacol rearrangement.

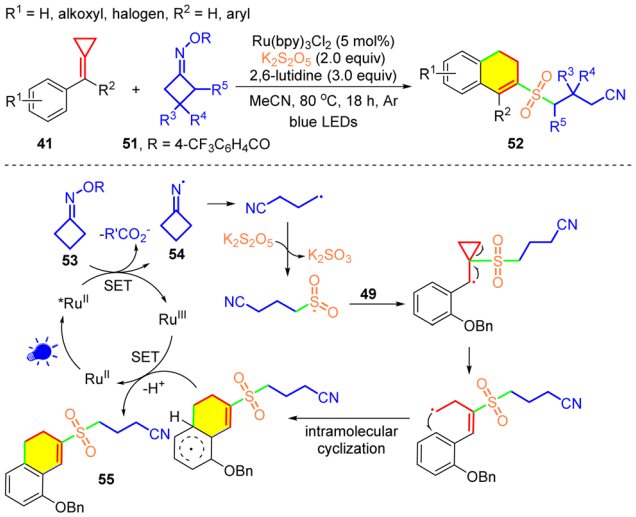
the ring-closing reaction can take place by overcoming the high energy barrier at high temperature.

Following this work, in 2020, Tang's group developed a new sulfonylation method for MCPs **41** using a cycloketone oxime **51** as the radical precursor (Scheme 14).[8d] The cycloketone oxime and its derivatives are both stable and easily prepared from cycloketones with hydroxylamine derivatives, and they are endowed with redox-active properties as they can not only accept an electron but also donate an electron in the SET mode.[43] Formation of the sulfonyl-radical-bearing alkylnitrile occurs *via* the SET reduction of **53**, β-scission of the iminyl radical intermediate **54**, and trapping of sulfur dioxide. Both the cyanoalkyl radical and the cyanoalkylsulfonyl radical were trapped using radical inhibitors. This protocol provides a facile and convenient route to access diverse 2-cyanoalkylsulfonated 3,4-dihydronaphthalenes **52**.

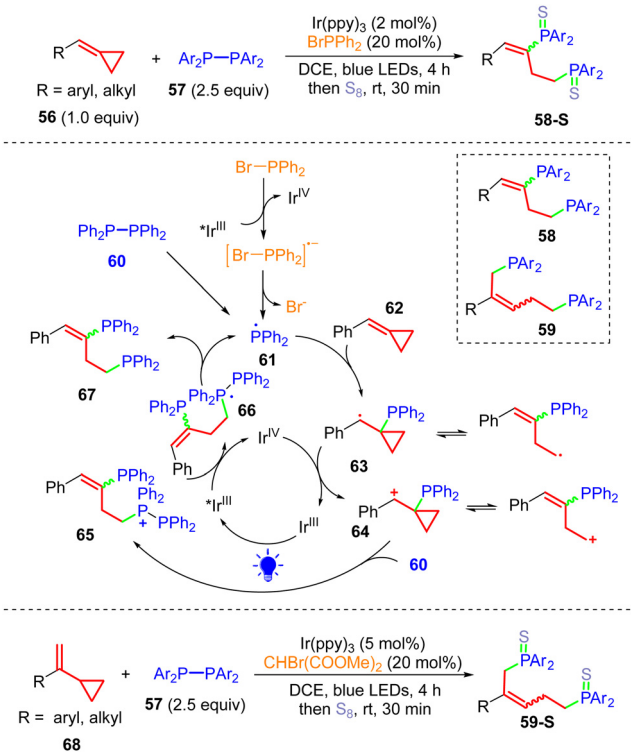
The radical-promoted ring-opening of MCPs can be extended to synthesize phosphine-containing compounds. Huang and co-workers proved that MCP is a suitable acceptor of P-centered radicals.[13p] In 2020, the group of Hirano and Miura developed the ring-opening diphosphination of MCPs **56** and VCPs **68** with tetraaryldiphosphines **57** to efficiently synthesize the corresponding 1,3-diphenylphosphinopropane- and 1,5-diphenylphosphinopentane-type bidentate ligands **58** and **59**, respectively (Scheme 15).[13an] The ligands **58** and **59** can be transformed to **58-S** and **59-S**, respectively, by reacting with S_8. The addition of $BrPPh_2$ can improve the product yield, and $BrPPh_2$ can be luminescence quenched by $Ir(ppy)_3$, indicating that the excited species Ir(III)* undergoes an SET process to reduce $BrPPh_2$. Since **58-S** can be obtained under additive-free conditions, the pathway in which **61** can be directly generated from **60** *via* an energy transfer (EnT) process might be competitive. After attack of the radical to afford



Scheme 13 Sulfonyl radical-promoted MCP ring-opening.



Scheme 14 Sulfonylation of MCPs with cycloketone oxime as the radical precursor.



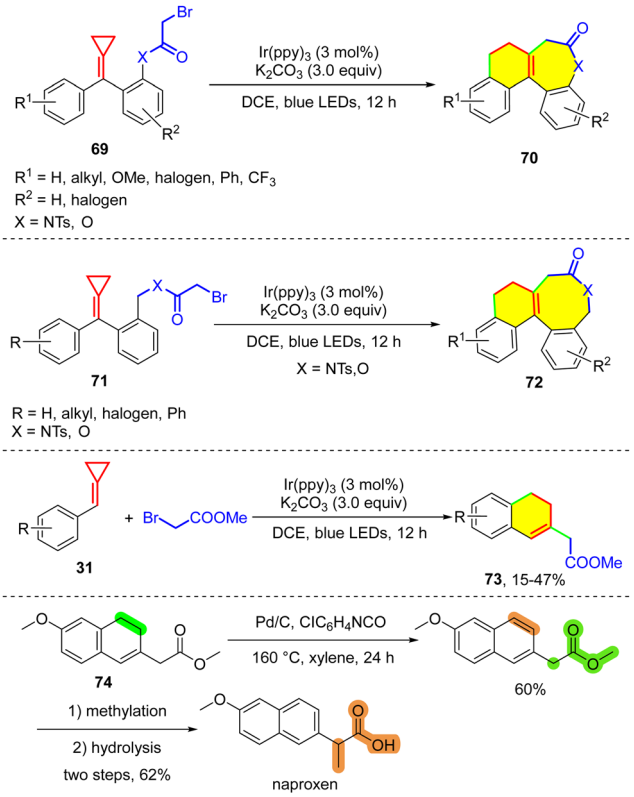
Scheme 15 Diarylphosphine-promoted difunctionalization of MCPs and VCPs.

63 and SET oxidation by Ir(IV), the formed cationic species **64** can be trapped by **60** to afford **65**, and the diarylphosphine radical **61** is regenerated after SET reduction of the phosphonium species **65**, providing **67**. This method can readily prepare electronically diverse substituted bidentate ligands.

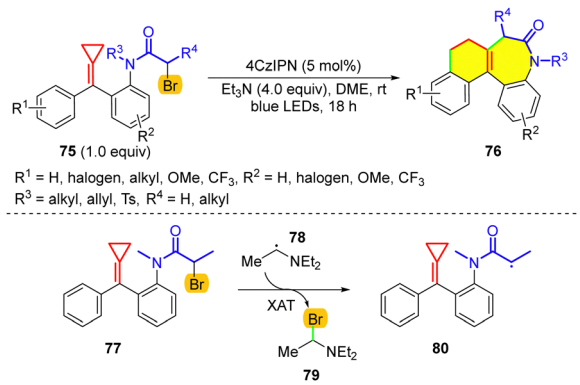
The generation of α-carbonyl radicals from the direct oxidization of an enolate usually needs stoichiometric oxidants,[44] in which the most frequently used reagent is $Mn(OAc)_3$. However, the debromination of α-carbonyl alkyl bromides[45] or radical conjugate addition to electron-deficient olefins[17e,46] can provide more atom-economic and environmentally friendly synthetic routes.

In 2019, our group developed a visible-light-induced photocatalytic cascade cyclization reaction of MCPs **69** and **71** to rapidly construct seven- and eight-membered ring-containing polycyclic lactams and lactones **70** and **72** (Scheme 16).[8c] In this reaction, substrate **69** or **71** produces an α-carbonyl radical through SET reduction, and subsequent cascade cyclization and SET oxidation enable the formation of polycyclic products. In addition, an intermolecular version of the reaction using MCP **31** and $BrCH_2COOEt$ as the reactants was also realized but with a lower productivity compared with $BrCF_2COOEt$,[28] of which the products **73** can be used as precursors of many valuable compounds. For example, naproxen (a non-steroidal anti-inflammatory drug) was synthesized from **74** through dehydrogenation, methylation and hydrolysis.

Halogen atom transfer (XAT)[47] is also an alternative means of realizing the debromination of α-carbonyl alkyl bromides. However, traditional reagents that enable XAT, which mainly contain organotin species, are usually toxic and hazardous. Therefore, ''Flight from the Tyranny of Tin'' has driven a quest for alternative reagents for the homolytic activation of C–halogen bonds.[48] For achieving XAT, silicon reagents have become competitive players.[49] Moreover, more efficient XAT processes under mild conditions have attracted the attention of researchers.[50] Inspired by the report of Leonori and co-workers, our group recently developed a metal-free version of the cascade cyclization that employs the α-aminoalkyl radical as the XAT species (Scheme 17).[51] In this reaction, initially, excited 4CzIPN undergoes SET oxidation with Et_3N to afford the α-aminoalkyl radical **78**, and subsequent XAT enables the generation of the α-carbonyl radical **80**. Then, similar cascade cyclization occurs, but the final oxidation can involve SET and XAT upon visible-light irradiation. This novel transformation of



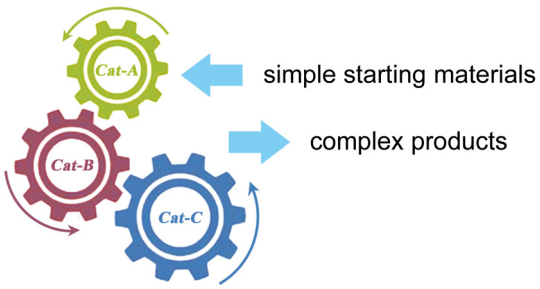
Scheme 16 α-Carbonyl-radical-promoted tandem cyclization of MCPs under visible-light irradiation.



Scheme 17 α-Carbonyl-radical-promoted tandem cyclization under metal-free conditions.

MCPs features a broad substrate scope and good functional group tolerance under mild conditions.

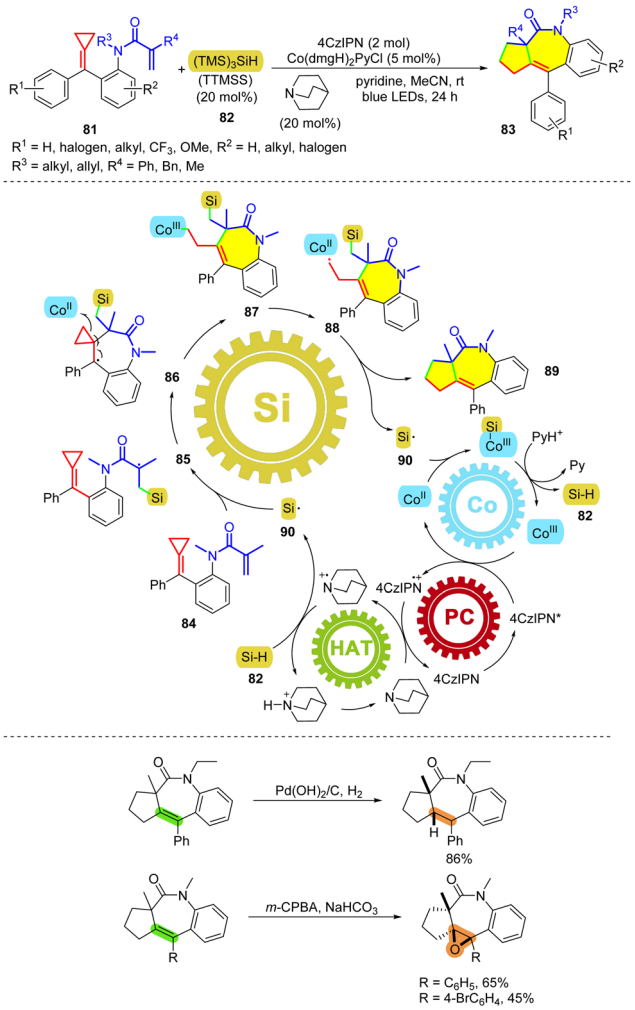
Radical addition to α,β-unsaturated compounds provides a convenient method to access α-carbonyl radicals, which have been used widely in visible-light-catalyzed reactions. In 2021, our group reported multiple-step catalysis to realize the tandem cyclization of MCPs tethered with acrylamide **81** (or vinyl sulfonamide) under visible-light irradiation (Scheme 19).[52] Multicatalysis has conspicuously contributed to the field of catalysis in synthetic chemistry, but the complicated details remain underinvestigated.[53] Clearly, governing several perfectly



Scheme 18 The concept of multicatalysis.

cooperative active catalysts in one pot without considerable entropic penalties is challenging when attempting to achieve mechanistic insight (Scheme 18). In our recent work, four catalysts – consisting of 4CzIPN, $Co(dmgH)_2PyCl$, silane **82** (TTMSS), and quinuclidine – are used to bring about cascade catalysis upon visible-light irradiation for the synthesis of polycyclic compounds **83**. We proposed a plausible mechanism through a series of mechanistic studies, including DFT calculations, radical trapping, and dark–light experiments. Under irradiation with blue light, the excited photosensitizer 4CzIPN* reduces $Co^{III}(dmgH)_2PyCl$ to afford Co^{II} species. Subsequently, the oxidized photosensitizer oxidizes quinuclidine to generate the quinuclidium cation. This is a reactive HAT species that abstracts the hydrogen atom of TTMSS to generate the corresponding silyl radical **90**. Addition of the silyl radical to a C–C double bond results in the α-carbonyl radical **85**, which then undergoes cyclization to give the silylated intermediate **86**, and intermediate **86** can be captured by Co^{II} to form intermediate **87**. The alkyl radical **88**, resulting from the photolysis of **87**, attacks the carbon atom connecting with the silyl unit, delivering the final product **89**, upon releasing the silyl radical. The silyl radical is then trapped by Co^{II} to afford the silyl–cobalt complex, the protonation of which regenerates Co^{III} and TTMSS (**82**) to complete the catalytic cycle. This protocol effectively synthesizes lactam- and sultam-containing polycyclic derivatives in moderate to good yields with a broad substrate scope and good functional group tolerance. In addition, this reaction can be achieved on a gram scale, and the corresponding products can be functionalized further to afford interesting compounds through hydrogenation or epoxidation.

The generation of cyclopropylcarbinyl radicals usually needs exogenous radicals to attack the MCP group, but research on other reaction pathways, *e.g.*, direct SET oxidation, has rarely been reported. In 2001, Beck proved the possibility of an MCP oxidation pathway *via* SET because MCP **13** is oxidized by ozone to afford cyclobutanone, peroxide, and ketone derivatives.[54] To extend the reactivity of MCPs, in 2021, our group reported the cascade cyclization of MCPs through the direct SET oxidation the MCPs **91** by merging photocatalysis and cobalt catalysis for the synthesis of 4-aryl-1,2-dihydronaphthalene derivatives **92** and **93** (Scheme 20).[55] In this report, two different oxidation pathways were proposed. In the formation of **96**, MCP **13** was initially oxidized by the excited photocatalyst to radical cation **94**, which was attacked by a nucleophilic fluorine anion

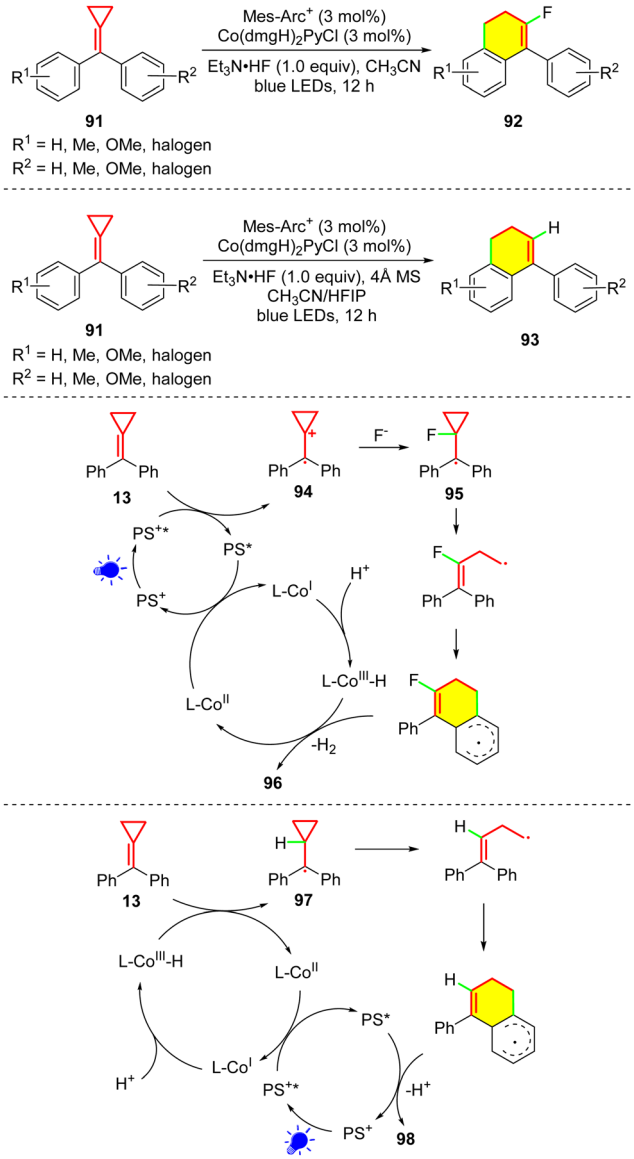


Scheme 19 Tandem cyclization of MCPs catalyzed by four species.

to generate the cyclopropylcarbinyl radical intermediate **95**. As for forming the hydrogen-atom-substituted product **98**, we suggested an MHAT process (or HAT from a metal hydride). The Co^{I} species was initially generated by the catalytic cycle, and it was then transformed into the Co^{III}–H species through combining a proton. Subsequently, an MHAT process occurred between Co^{III}–H and **13** to form the cyclopropylcarbinyl radical intermediate **97**, regenerating the Co^{II} species. This protocol demonstrates a robust synthetic strategy beyond photoredox catalysis to integrate single-electron oxidation and an MHAT process into MCP chemistry.

Visible-light-induced synthesis of cyclopropane derivatives from MCPs

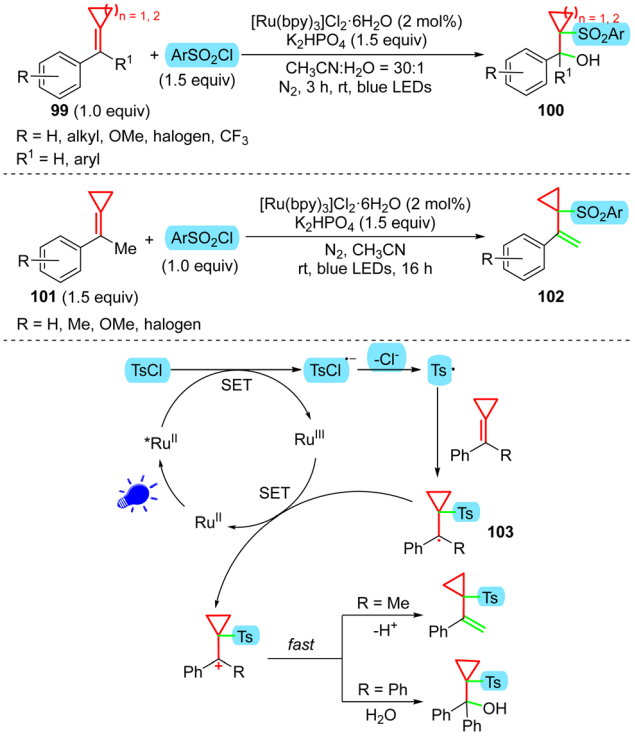
As described above, although MCPs **47** can react with TsCl under visible-light irradiation to provide cascade-cyclized[42] or difunctionalized[30] products, Wang's group found that if H_2O is present in the reaction system, the cyclopropane ring-preserved products **100** will be obtained from MCPs **99** (Scheme 21).[56] The X-ray diffraction analysis of **100** reveals that this different



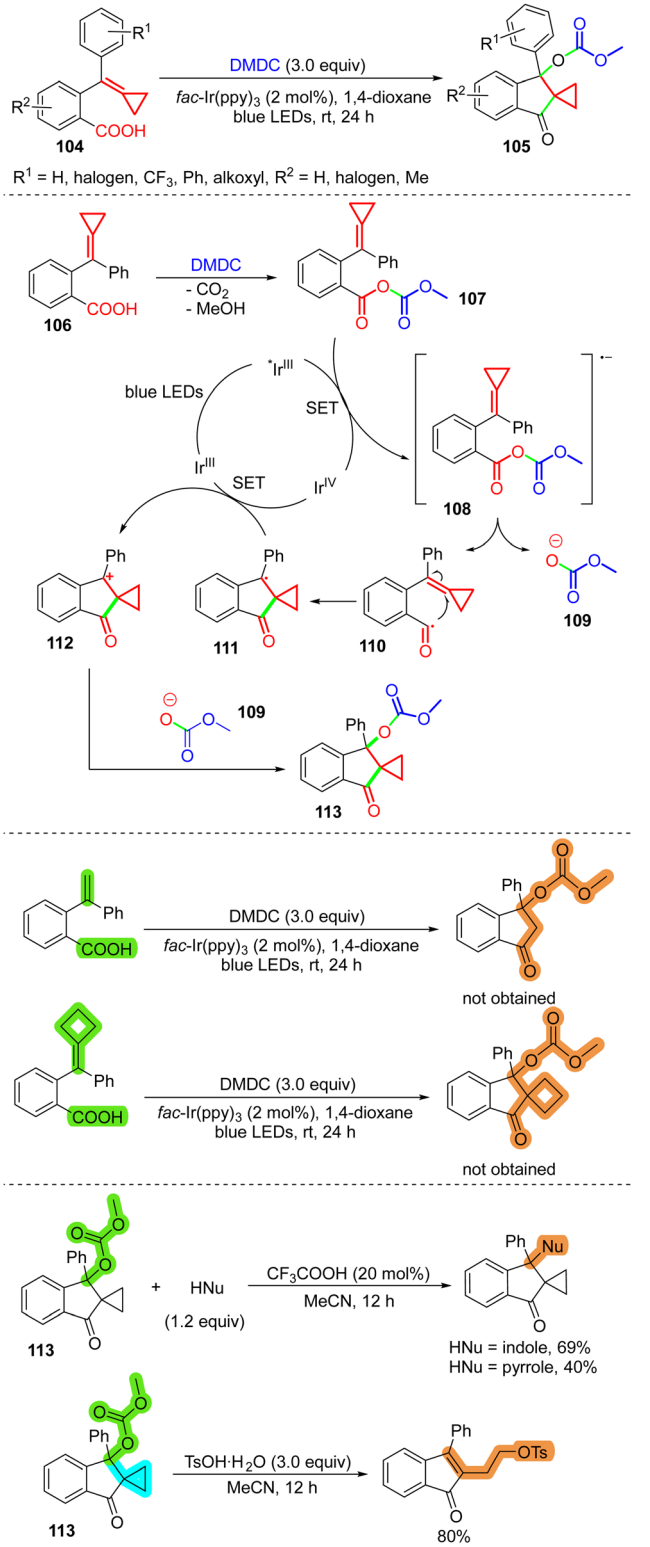
Scheme 20 Other pathways to generate cyclopropylcarbinyl radicals from MCPs.

reaction tendency is due to intramolecular hydrogen bonding between the hydroxyl and sulfonyl groups in **100**, which increases the stability. When MCPs **101**, derived from acetophenones, were used without additional water, an elimination process occurred, providing the cyclopropyl styrene products **102** in moderate to good yields. The driving force might cause results that are different from the previously reported sulfonylation reactions of MCPs,[8d,30,42] probably because the cyclopropylcarbinyl radical intermediate **103** is consumed rapidly through other pathways, such as S_N1 nucleophilic attack by H_2O or elimination *via* deprotonation, after SET oxidation (Scheme 21).

In 2021, our group developed a visible-light photoredox-catalyzed intramolecular difunctionalization of MCPs to access spiro[cyclopropane-1,2-indan]ones **105** from easily prepared MCPs **104** tethered with a carboxylic acid (Scheme 22).[8e]



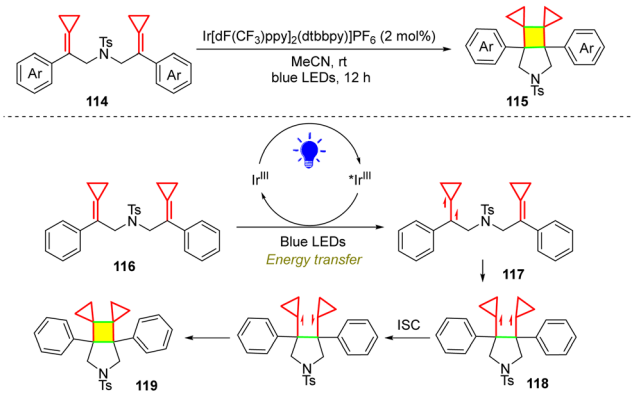
Scheme 21 Sulfonyl-radical-promoted cyclopropane ring-preserved reactions of MCPs.



Scheme 22 Visible-light-induced intramolecular difunctionalization of MCPs.

If **104**, DMDC (dimethyl dicarbonate), and $Ir(ppy)_3$ are employed under the irradiation of 5 W blue LEDs, with 1,4-dioxane as the solvent, the cyclopropyl-containing cyclized products **105** were obtained in high yields. It should be noted that a base is unnecessary for the cyclization reaction, which differs from the previously reported protocol that generates acyl radicals from carboxylic acid and DMDC.[57] In our reported reaction, **106** reacts with DMDC to generate **107**, which can be reduced by an excited Ir catalyst to **108**. Intermediate **108** is then transformed into two fragments, **109** and **110**. The cyclopropyl group can be preserved in this case, which is mainly attributed to the high stabilization of the cationic intermediate **112**. The cationic intermediate **112** is formed from the cyclization of **110** and the subsequent SET oxidation of **111**. The two aryl groups and the cyclopropyl moiety make the cation very stable, and next S_N1 attack by **109** provides **113** in excellent yield. If the cyclopropyl group adjacent to the cation is absent, control experiments indicated that the cyclization cannot proceed *via* the same pathway (Scheme 22, bottom). Besides DMDC, triphenylphosphine is an effective reagent for deoxygenation under visible-light irradiation,[58] by which a similar cyclization reaction can proceed smoothly. In addition, product **113** can undergo nucleophilic substitution with indole or pyrrole, affording the corresponding indolyl and pyrrolyl derivatives. Moreover, product **113** can be transformed into a ring-opened product, which features a 1-indanone structural motif in the presence of TsOH.

Visible-light-induced cycloaddition is also an important topic in organic synthesis. In 2021, our group reported a visible-light-induced intramolecular [2+2] cycloaddition of MCPs **114** for the construction of polysubstituted cyclic frameworks **115** (Scheme 23).[59] In this reaction, the triplet excited state **117** is produced through energy transfer (EnT) between

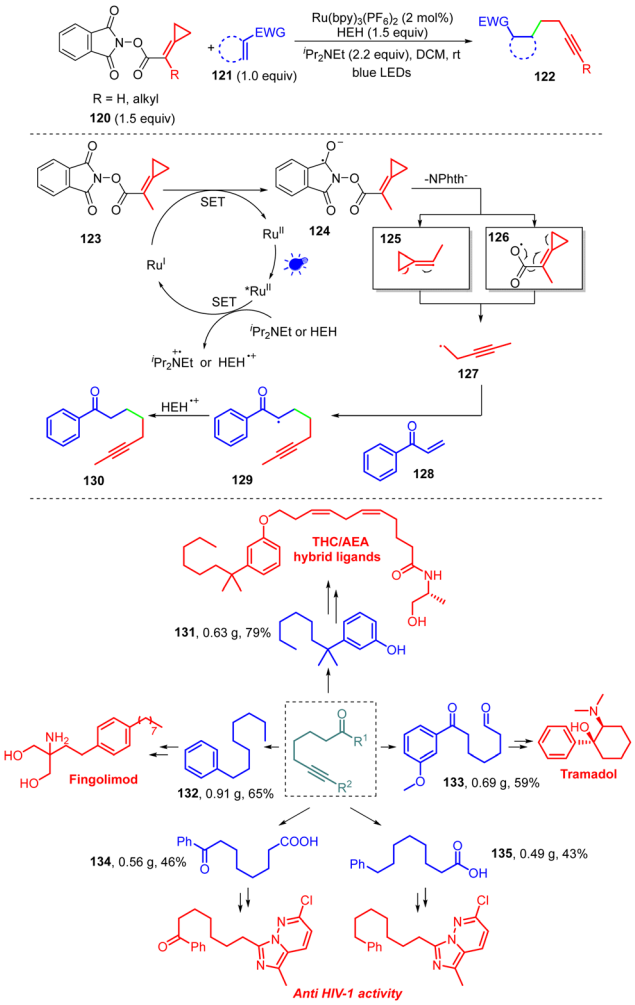


Scheme 23 Visible-light-induced intramolecular [2+2] cycloaddition of MCPs.

the excited state of *Ir(III) and **116**, in addition to subsequent intersystem crossing (ISC). Intermediate **117** undergoes intramolecular C–C bond formation with a closed-shell carbon–carbon double bond, yielding the 1,4-triplet biradical species **118**. The subsequent ISC then takes place to give a 1,4-singlet biradical species, through which subsequent C–C bond formation yields the desired [2+2] cycloaddition product **119**.

Ring-opening reaction *via* homopropargyl radical intermediates

Most MCP reactions involving radicals depend on the classical cyclopropylcarbinyl radical clock, and other potential reaction pathways deserve to be explored, *e.g.*, rearrangements such as β-scission of the ketiminyl radical.[60] In 2021, our group reported a non-classical ring-opening radical clock reaction of MCPs **120** tethered with NHPI ester, providing a direct method to prepare a variety of alkenyl derivatives **122** (Scheme 24).[61] NHPI esters have been used widely as alkyl radical precursors for photoredox or transition-metal-catalyzed coupling reactions.[62] In this protocol, readily available NHPI esters **120** and radical acceptors **121** are employed as substrates for the coupling reactions. We proposed a plausible catalytic cycle based on DFT calculations, Stern–Volmer quenching, and control experiments. The initial excitation of $Ru(bpy)_3(PF_6)_2$ produces excited-state $*Ru(bpy)_3(PF_6)_2$, which undergoes SET oxidation with $^iPr_2NEt$ or a Hantzsch ester to generate Ru(I) and a amine radical cation or Hantzsch ester radical cation. The *N*-(acyloxy) phthalimide **123** receives an electron from Ru(I), to transiently form the radical anion intermediate **124**. Next, entropically favored decarboxylation can proceed *via* two plausible pathways to generate the desired radical intermediate **127**, as shown in Scheme 24. In fact, the putative radical intermediate **125** or **126** will undergo a non-classical ring-opening radical clock rearrangement to afford the key intermediate **127**. The addition of this nucleophilic radical to the conjugate acceptor **128** generates the stabilized radical **129**, which then undergoes an SET or HAT process to form the functionalized alkyne **130** successfully. In addition, we used the products to synthesize the various synthetic



Scheme 24 Synthesizing alkenyl derivatives from MCPs under visible-light irradiation.

intermediates **131–135** on a gram scale, which could be further transformed into functional molecules that are useful in biochemistry and medicinal chemistry. Among these molecules, the drug fingolimod can be used for the treatment of multiple sclerosis (MS), the novel tetrahydrocannabinol/anandamide (THC/AEA) hybrid ligand can significantly improve its binding affinity to the CB1 receptor in biological research, and tramadol can be used as a painkiller by serving as a weak μ-opioid receptor agonist. Besides, products **134** and **135** can be further transformed into bioactive compounds that are exceptionally active against the reverse transcriptase of HIV.

Summary

In recent years, various visible-light-induced transformations of MCPs have been developed, the majority of which enable the rapid construction of polycyclic or heterocyclic frameworks in a simple operation. The target products can be obtained selectively *via* different terminal pathways by regulating the reaction conditions. These transformations are being exploited towards

green chemistry, such as in applying more efficient catalytic systems and metal-free conditions, and it is expected that further developments will be continuously reported in due course. Moreover, the products provided by these reactions can be further transformed into bioactive molecules used for the treatment of Multiple Sclerosis, relieving pain, inhibiting the reverse transcriptase of HIV, and so on; therefore, their synthetic applications deserve further exploration.

Author contributions

M. Shi and Y. Wei directed the perspective and revised the manuscript. H.-Z. Wei carried out the literature collection, organization, and wrote the manuscript. H.-Z. Wei drew the Schemes and checked over them.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, 1968, **90**, 3395–3397.
2 R. D. Bach and O. Dmitrenko, *J. Am. Chem. Soc.*, 2004, **126**, 4444–4452.
3 (*a*) A. Brandi, S. Cicchi, F. M. Cordero and A. Goti, *Chem. Rev.*, 2014, **114**, 7317–7420; (*b*) L. Yu, M. Liu, F. Chen and Q. Xu, *Org. Biomol. Chem.*, 2015, **13**, 8379–8392; (*c*) G. Fumagalli, S. Stanton and J. F. Bower, *Chem. Rev.*, 2017, **117**, 9404–9432; (*d*) H. Cao, F. Chen, C. Su and L. Yu, *Adv. Synth. Catal.*, 2019, **362**, 438–461; (*e*) J. Liu, R. Liu, Y. Wei and M. Shi, *Trends Chem.*, 2019, **1**, 779–793.
4 L. Z. Yu and M. Shi, *Chem. – Eur. J.*, 2019, **25**, 7591–7606.
5 (*a*) L.-Z. Yu, X.-B. Hu, Q. Xu and M. Shi, *Chem. Commun.*, 2016, **52**, 2701–2704; (*b*) H.-Z. Wei, Q.-Z. Li, Y. Wei and M. Shi, *Org. Biomol. Chem.*, 2020, **18**, 7396–7400; (*c*) H.-Z. Wei, L.-Z. Yu and M. Shi, *Org. Biomol. Chem.*, 2020, **18**, 135–139.
6 (*a*) B. Xu and M. Shi, *Org. Lett.*, 2003, **5**, 1415–1418; (*b*) L.-P. Liu and M. Shi, *J. Org. Chem.*, 2004, **69**, 2805–2808; (*c*) M. Shi, M. Jiang and L.-P. Liu, *Org. Biomol. Chem.*, 2007, **5**, 438–440; (*d*) L. Ackermann, S. Kozhushkov, D. Yufit and I. Marek, *Synlett*, 2011, 1515–1518.
7 (*a*) Y. Liu, S. Feng and X. Bao, *ChemCatChem*, 2018, **10**, 2817–2825; (*b*) Y. Liu, A. A. Ogunlana and X. Bao, *Dalton Trans.*, 2018, **47**, 5660–5669; (*c*) H. Z. Gui, Y. Wei and M. Shi, *Chem. – Asian J.*, 2020, **15**, 1225–1233; (*d*) D. Li, W. Zang, M. J. Bird, C. J. T. Hyland and M. Shi, *Chem. Rev.*, 2020, **121**, 8685–8755; (*e*) J. Yao, Z. Chen, L. Yu, L. Lv, D. Cao and C.-J. Li, *Chem. Sci.*, 2020, **11**, 10759–10763; (*f*) N. Kimura, S. Katta, Y. Kitazawa, T. Kochi and F. Kakiuchi, *J. Am. Chem. Soc.*, 2021, **143**, 4543–4549; (*g*) B. Niu, Y. Wei and M. Shi, *Org. Chem. Front.*, 2021, **8**, 3475–3501.
8 (*a*) Z.-Z. Zhu, K. Chen, L.-Z. Yu, X.-Y. Tang and M. Shi, *Org. Lett.*, 2015, **17**, 5994–5997; (*b*) X.-Y. Zhang, P.-H. Li and M. Shi, *Asian J. Org. Chem.*, 2018, **7**, 1924–1933; (*c*) M. Chen, Y. Wei and M. Shi, *Org. Chem. Front.*, 2020, **7**, 374–379; (*d*) Y. Liu, Q.-L. Wang, Z. Chen, H. Li, B.-Q. Xiong, P.-L. Zhang and K.-W. Tang, *Chem. Commun.*, 2020, **56**, 3011–3014; (*e*) H.-Z. Wei, Y. Wei and M. Shi, *Org. Chem. Front.*, 2021, **8**, 4527–4532.
9 H.-Z. Wei, Y. Wei and M. Shi, *Chem. Commun.*, 2021, **57**, 11201–11204.
10 (*a*) J. K. Kochi, P. J. Krusic and D. R. Eaton, *J. Am. Chem. Soc.*, 1969, **91**, 1877–1879; (*b*) K. S. Chen, D. J. Edge and J. K. Kochi, *J. Am. Chem. Soc.*, 1973, **95**, 7036–7043.
11 W. J. Hehre, *J. Am. Chem. Soc.*, 1973, **95**, 2643–2646.
12 (*a*) W. Zhang, F. Wang, S. D. McCann, D. Wang, P. Chen, S. S. Stahl and G. Liu, *Science*, 2016, **353**, 1014–1018; (*b*) L. Huang, A. M. Olivares and D. J. Weix, *Angew. Chem., Int. Ed.*, 2017, **56**, 11901–11905; (*c*) W. Zhao, R. P. Wurz, J. C. Peters and G. C. Fu, *J. Am. Chem. Soc.*, 2017, **139**, 12153–12156; (*d*) Q. Fu, Z.-Y. Bo, J.-H. Ye, T. Ju, H. Huang, L.-L. Liao and D.-G. Yu, *Nat. Commun.*, 2019, **10**, 3592; (*e*) J. H. Blackwell, R. Kumar and M. J. Gaunt, *J. Am. Chem. Soc.*, 2021, **143**, 1598–1609.
13 (*a*) C. Destabel, J. D. Kilburn and J. Knight, *Tetrahedron*, 1994, **50**, 11267–11288; (*b*) C. Destabel, J. D. Kilburn and J. Knight, *Tetrahedron*, 1994, **50**, 11289–11302; (*c*) M. Santagostino and J. D. Kilburn, *Tetrahedron Lett.*, 1994, **35**, 8863–8866; (*d*) M. Santagostino and J. D. Kilburn, *Tetrahedron Lett.*, 1995, **36**, 1365–1368; (*e*) R. J. Boffey, M. Santagostino, J. D. Kilburn, R. J. Boffey and W. G. Whittingham, *Chem. Commun.*, 1998, 1875–1876; (*f*) K. G. Pike, C. Destabel, M. Anson and J. D. Kilburn, *Tetrahedron Lett.*, 1998, **39**, 5877–5880; (*g*) R. J. Boffey, W. G. Whittingham and J. D. Kilburn, *Tetrahedron Lett.*, 1999, **40**, 5625–5628; (*h*) D. J. Penfold, K. Pike, A. Genge, M. Anson, J. Kitteringham and J. D. Kilburn, *Tetrahedron Lett.*, 2000, **41**, 10347–10351; (*i*) F. C. Watson and J. D. Kilburn, *Tetrahedron Lett.*, 2000, **41**, 10341–10345; (*j*) R. J. Boffey, W. G. Whittingham and J. D. Kilburn, *J. Chem. Soc., Perkin Trans. 1*, 2001, 487–496; (*k*) A. C. Saint-Dizier and J. D. Kilburn, *Tetrahedron Lett.*, 2002, **43**, 6201–6203; (*l*) L.-P. Liu and M. Shi, *Chem. Commun.*, 2004, 2878; (*m*) J. J. Underwood, G. J. Hollingworth, P. N. Horton, M. B. Hursthouse and J. D. Kilburn, *Tetrahedron Lett.*, 2004, **45**, 2223–2225; (*n*) H. Zhou, X. Huang and W. Chen, *J. Org. Chem.*, 2004, **69**, 5471–5472; (*o*) J.-W. Huang and M. Shi, *J. Org. Chem.*, 2005, **70**, 3859–3863; (*p*) X. Huang and L. Yu, *Synlett*, 2005, 2953–2957; (*q*) M. Shi and J.-W. Huang, *J. Fluorine Chem.*, 2005, **126**, 809–817; (*r*) X. Huang, W. Chen, H. Zhou and L. Ren, *Synthesis*, 2006, 609–614; (*s*) X. Huang and L. Yu, *Synlett*, 2006, 2136–2138; (*t*) X. Huang, L. Yu and M. Xie, *Synlett*, 2006, 0423–0426; (*u*) W.-J. Fu and X. Huang, *J. Organomet. Chem.*, 2007, **692**, 740–745; (*v*) L. Yu, B. Chen, X. Huang and L. L. Wu, *Chin. Chem. Lett.*, 2007, **18**, 121–123; (*w*) N. Hayashi, Y. Hirokawa, I. Shibata, M. Yasuda and A. Baba, *J. Am. Chem. Soc.*, 2008, **130**, 2912–2913; (*x*) J. Sheng, C. Fan, Y. Ding, X. Fan and J. Wu, *Chem. Commun.*, 2014, **50**, 4188; (*y*) K. Chen, Z.-Z. Zhu, J.-X. Liu, X.-Y. Tang, Y. Wei and M. Shi, *Chem. Commun.*, 2016, **52**, 350–353; (*z*) H. Xie and B. Xu, *Eur. J. Org. Chem.*, 2016, 2594–2598; (*aa*) M.-T. Chen, X.-Y. Tang and M. Shi, *Org. Chem. Front.*, 2017, **4**, 86–90; (*ab*) X. Fan, L.-Z. Yu, Y. Wei and M. Shi, *Org. Lett.*, 2017, **19**, 4476–4479; (*ac*) Y. Liu, Q.-L. Wang, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang and K.-W. Tang, *J. Org. Chem.*, 2017, **82**, 7394–7401; (*ad*) M. Chen, Y. Wei and M. Shi, *Org. Chem. Front.*, 2018, **5**, 2030–2034; (*ae*) Y. Liu, Q.-L. Wang, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang and K.-W. Tang, *J. Org. Chem.*, 2018, **83**, 4657–4664; (*af*) C. Liu, Y.-J. Yang, J.-Y. Dong, M.-D. Zhou, L. Li and H. Wang, *J. Org. Chem.*, 2019, **84**, 9937–9945; (*ag*) Y. Liu, Z. Chen, Q.-L. Wang, C.-S. Zhou, B.-Q. Xiong, C.-A. Yang and K.-W. Tang, *J. Org. Chem.*, 2019, **84**, 9984–9994; (*ah*) Y. Liu, Q.-L. Wang, Z. Chen, Q. Zhou, H. Li, W.-Y. Xu, B.-Q. Xiong and K.-W. Tang, *J. Org. Chem.*, 2019, **84**, 5413–5424; (*ai*) Y. Liu, Q.-L. Wang, Z. Chen, Q. Zhou, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang and K.-W. Tang, *Org. Biomol. Chem.*, 2019, **17**, 1365–1369; (*aj*) T. E. Anderson and K. A. Woerpel, *Org. Lett.*, 2020, **22**, 5690–5694; (*ak*) Y. Yuan, S. Zhang, Z. Sun, Y. Su, Q. Ma, Y. Yuan and X. Jia, *Org. Lett.*, 2020, **22**, 6294–6298; (*al*) Y. Su, S. Zhang, Y. Yuan, Q. Ma, Z. Sun, Y. Yuan and X. Jia, *Chem. Commun.*, 2021, **57**, 9878–9881; (*am*) Y. Nie, L. Cheng, L. Chen, Z. Li, Y. Leng and J. Wu, *Eur. J. Org. Chem.*, 2022, e202101406; (*an*) Y. Kato, N. Otomura, K. Hirano and M. Miura, *J. Org. Chem.*, 2020, **85**, 5981–5994.
14 D. A. Singleton, C. C. Huval, K. M. Church and E. S. Priestley, *Tetrahedron Lett.*, 1991, **32**, 5765–5768.
15 C. Destabel, J. D. Kilburn and J. Knight, *Tetrahedron Lett.*, 1993, **34**, 3151–3154.

16 L.-Z. Yu, Q. Xu, X.-Y. Tang and M. Shi, *ACS Catal.*, 2015, **6**, 526–531.
17 (*a*) J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, **40**, 102–113; (*b*) J. Xuan and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2012, **51**, 6828–6838; (*c*) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363; (*d*) N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166; (*e*) A. Y. Chan, I. B. Perry, N. B. Bissonnette, B. F. Buksh, G. A. Edwards, L. I. Frye, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley, N. L. Reed, H. A. Sakai, C. P. Seath and D. W. C. MacMillan, *Chem. Rev.*, 2021, **122**, 1485–1542.
18 (*a*) T. Okazoe, *Proc. Jpn. Acad., Ser. B*, 2009, **85**, 276–289; (*b*) J. Gardiner, *Aust. J. Chem.*, 2015, **68**, 13–22.
19 (*a*) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2013, **114**, 2432–2506; (*b*) J. Han, A. M. Remete, L. S. Dobson, L. Kiss, K. Izawa, H. Moriwaki, V. A. Soloshonok and D. O'Hagan, *J. Fluorine Chem.*, 2020, **239**, 109639; (*c*) M. Inoue, Y. Sumii and N. Shibata, *ACS Omega*, 2020, **5**, 10633–10640.
20 (*a*) T. Fujiwara and D. O'Hagan, *J. Fluorine Chem.*, 2014, **167**, 16–29; (*b*) Y. Ogawa, E. Tokunaga, O. Kobayashi, K. Hirai and N. Shibata, *iScience*, 2020, **23**, 101467.
21 (*a*) L. M. Yagupolskii, I. I. Maletina, N. V. Kondratenko and V. V. Orda, *Synthesis*, 1978, 835–837; (*b*) T. Umemoto, *Chem. Rev.*, 1996, **96**, 1757–1778; (*c*) R. P. Singh and J. N. M. Shreeve, *Tetrahedron*, 2000, **56**, 7613–7632; (*d*) G. K. S. Prakash and M. Mandal, *J. Fluorine Chem.*, 2001, **112**, 123–131; (*e*) P. Eisenberger, S. Gischig and A. Togni, *Chem. – Eur. J.*, 2006, **12**, 2579–2586; (*f*) I. Kieltsch, P. Eisenberger and A. Togni, *Angew. Chem., Int. Ed.*, 2007, **46**, 754–757; (*g*) T. Umemoto, K. Adachi and S. Ishihara, *J. Org. Chem.*, 2007, **72**, 6905–6917; (*h*) S. Noritake, N. Shibata, S. Nakamura, T. Toru and M. Shiro, *Eur. J. Org. Chem.*, 2008, 3465–3468; (*i*) Y. Nomura, E. Tokunaga and N. Shibata, *Angew. Chem., Int. Ed.*, 2010, **50**, 1885–1889; (*j*) C. Urban, F. Cadoret, J. C. Blazejewski and E. Magnier, *Eur. J. Org. Chem.*, 2011, 4862–4867; (*k*) H. Liu, Z. Gu and X. Jiang, *Adv. Synth. Catal.*, 2013, **355**, 617–626; (*l*) X. Liu, C. Xu, M. Wang and Q. Liu, *Chem. Rev.*, 2014, **115**, 683–730.
22 (*a*) Z. Feng, Q.-Q. Min, Y.-L. Xiao, B. Zhang and X. Zhang, *Angew. Chem., Int. Ed.*, 2014, **53**, 1669–1673; (*b*) J.-Y. Wang, Y.-M. Su, F. Yin, Y. Bao, X. Zhang, Y.-M. Xu and X.-S. Wang, *Chem. Commun.*, 2014, **50**, 4108–4111; (*c*) J.-Y. Wang, X. Zhang, Y. Bao, Y.-M. Xu, X.-F. Cheng and X.-S. Wang, *Org. Biomol. Chem.*, 2014, **12**, 5582–5585; (*d*) J.-W. Gu, Q.-Q. Min, L.-C. Yu and X. Zhang, *Angew. Chem., Int. Ed.*, 2016, **55**, 12270–12274; (*e*) G. Li, T. Wang, F. Fei, Y.-M. Su, Y. Li, Q. Lan and X.-S. Wang, *Angew. Chem., Int. Ed.*, 2016, **55**, 3491–3495; (*f*) Y. Wu, H.-R. Zhang, Y.-X. Cao, Q. Lan and X.-S. Wang, *Org. Lett.*, 2016, **18**, 5564–5567; (*g*) T. Xia, L. He, Y. A. Liu, J. F. Hartwig and X. Liao, *Org. Lett.*, 2017, **19**, 2610–2613; (*h*) D. Li, T. Mao, J. Huang and Q. Zhu, *J. Org. Chem.*, 2018, **83**, 10445–10452; (*i*) S. Tian, X. Song, D. Zhu and M. Wang, *Adv. Synth. Catal.*, 2018, **360**, 1414–1419; (*j*) Y. Chen, L. Li, Y. Ma and Z. Li, *J. Org. Chem.*, 2019, **84**, 5328–5338.
23 (*a*) J. Lei, J. Huang and Q. Zhu, *Org. Biomol. Chem.*, 2016, **14**, 2593–2602; (*b*) S. Sharma, A. P. Pandey and A. Sharma, *Adv. Synth. Catal.*, 2020, **362**, 5196–5218.
24 B. Zhang, C. Mück-Lichtenfeld, C. G. Daniliuc and A. Studer, *Angew. Chem., Int. Ed.*, 2013, **52**, 10792–10795.
25 Y.-C. Yuan, H.-L. Liu, X.-B. Hu, Y. Wei and M. Shi, *Chem. – Eur. J.*, 2016, **22**, 13059–13063.
26 S. P. Pitre, C. D. McTiernan, H. Ismaili and J. C. Scaiano, *ACS Catal.*, 2014, **4**, 2530–2535.
27 (*a*) H. Togo, M. Aoki and M. Yokoyama, *Tetrahedron Lett.*, 1991, **32**, 6559–6562; (*b*) H. Togo, M. Aoki and M. Yokoyama, *Tetrahedron*, 1993, **49**, 8241–8256; (*c*) A. De Mico, R. Margarita and G. Piancatelli, *Tetrahedron Lett.*, 1995, **36**, 3553–3556; (*d*) S. A. Moteki, A. Usui, S. Selvakumar, T. Zhang and K. Maruoka, *Angew. Chem., Int. Ed.*, 2014, **53**, 11060–11064; (*e*) H. Tan, H. Li, W. Ji and L. Wang, *Angew. Chem., Int. Ed.*, 2015, **54**, 8374–8377; (*f*) L. Wang and J. Liu, *Eur. J. Org. Chem.*, 2016, 1813–1824.
28 J. Li, J. Chen, W. Jiao, G. Wang, Y. Li, X. Cheng and G. Li, *J. Org. Chem.*, 2016, **81**, 9992–10001.
29 D. J. Burton and D. G. Naae, *J. Am. Chem. Soc.*, 1973, **95**, 8467–8468.
30 B. Zhu, Z. Wang, H. Xi, Z. Feng, B. Wang, W. Jiao, Z. Li, Z. Wang and J. Wu, *Org. Chem. Front.*, 2021, **8**, 6300–6308.
31 Q.-Y. Lin, X.-H. Xu, K. Zhang and F.-L. Qing, *Angew. Chem., Int. Ed.*, 2015, **55**, 1479–1483.
32 (*a*) Y. Fujiwara, J. A. Dixon, R. A. Rodriguez, R. D. Baxter, D. D. Dixon, M. R. Collins, D. G. Blackmond and P. S. Baran, *J. Am. Chem. Soc.*, 2012, **134**, 1494–1497; (*b*) Z. Li, Z. Cui and Z.-Q. Liu, *Org. Lett.*, 2013, **15**, 406–409; (*c*) X.-J. Tang, C. S. Thomoson and W. R. Dolbier, *Org. Lett.*, 2014, **16**, 4594–4597; (*d*) C. S. Thomoson, X.-J. Tang and W. R. Dolbier, *J. Org. Chem.*, 2014, **80**, 1264–1268; (*e*) Z. He, P. Tan, C. Ni and J. Hu, *Org. Lett.*, 2015, **17**, 1838–1841; (*f*) X.-J. Tang and W. R. Dolbier, *Angew. Chem., Int. Ed.*, 2015, **54**, 4246–4249; (*g*) Z. Zhang, X. Tang, C. S. Thomoson and W. R. Dolbier, *Org. Lett.*, 2015, **17**, 3528–3531.
33 (*a*) S. L. Rössler, B. J. Jelier, E. Magnier, G. Dagousset, E. M. Carreira and A. Togni, *Angew. Chem., Int. Ed.*, 2020, **59**, 9264–9280; (*b*) A. A. Volkov, *Chem. Heterocycl. Compd.*, 2020, **56**, 1149–1151; (*c*) Y. N. Li, F. Xiao, Y. Guo and Y. F. Zeng, *Eur. J. Org. Chem.*, 2021, 1215–1228; (*d*) D. A. Shabalin, *Org. Biomol. Chem.*, 2021, **19**, 8184–8204; (*e*) M. Hromadová and P. P. Lainé, *Curr. Opin. Electrochem.*, 2022, **34**, 100996; (*f*) C.-Y. Huang, J. Li and C.-J. Li, *Chem. Sci.*, 2022, **13**, 5465–5504; (*g*) Y. Wang, Y. Bao, M. Tang, Z. Ye, Z. Yuan and G. Zhu, *Chem. Commun.*, 2022, **58**, 3847–3864.
34 W.-D. Liu, G.-Q. Xu, X.-Q. Hu and P.-F. Xu, *Org. Lett.*, 2017, **19**, 6288–6291.
35 O. O. Sokolova and J. F. Bower, *Chem. Rev.*, 2020, **121**, 80–109.
36 (*a*) Y. Liang, L. Jiao, Y. Wang, Y. Chen, L. Ma, J. Xu, S. Zhang and Z.-X. Yu, *Org. Lett.*, 2006, **8**, 5877–5879; (*b*) W. Li and M. Shi, *Tetrahedron*, 2007, **63**, 11016–11020; (*c*) D. H. Zhang, Y. Wei and M. Shi, *Eur. J. Org. Chem.*, 2011, 4940–4944.
37 (*a*) M. Teall, P. Oakley, T. Harrison, D. Shaw, E. Kay, J. Elliott, U. Gerhard, J. L. Castro, M. Shearman, R. G. Ball and N. N. Tsou, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 2685–2688; (*b*) Y. Harrak, G. Casula, J. Basset, G. Rosell, S. Plescia, D. Raffa, M. G. Cusimano, R. Pouplana and M. D. Pujol, *J. Med. Chem.*, 2010, **53**, 6560–6571; (*c*) M. Feng, B. Tang, S. H. Liang and X. Jiang, *Curr. Top. Med. Chem.*, 2016, **16**, 1200–1216; (*d*) K. A. Scott and J. T. Njardarson, *Top. Curr. Chem.*, 2018, **376**, 5.
38 (*a*) K. Grossmann and T. Ehrhardt, *Pest Manage. Sci.*, 2007, **63**, 429–439; (*b*) Y. Noutoshi, M. Ikeda, T. Saito, H. Osada and K. Shirasu, *Front. Recent Dev. Plant Sci.*, 2012, **3**, 245; (*c*) W.-M. Xu, F.-F. Han, M. He, D.-Y. Hu, J. He, S. Yang and B.-A. Song, *J. Agric. Food Chem.*, 2012, **60**, 1036–1041; (*d*) P. Devendar and G.-F. Yang, *Top. Curr. Chem.*, 2017, **375**, 82.
39 (*a*) Y. Takaishi, Y. Murakami, M. Uda, T. Ohashi, N. Hamamura, M. Kidota and S. Kadota, *Phytochemistry*, 1997, **45**, 997–1001; (*b*) J. J. Petkowski, W. Bains and S. Seager, *J. Nat. Prod.*, 2018, **81**, 423–446; (*c*) N. Wang, P. Saidhareddy and X. Jiang, *Nat. Prod. Rep.*, 2020, **37**, 246–275.
40 (*a*) M.-a Kakimoto, S. J. Grunzinger and T. Hayakawa, *Polym. J.*, 2010, **42**, 697–705; (*b*) H. Sasabe, Y. Seino, M. Kimura and J. Kido, *Chem. Mater.*, 2012, **24**, 1404–1406; (*c*) G. Turkoglu, M. E. Cinar and T. Ozturk, *Top. Curr. Chem.*, 2017, **375**, 84.
41 (*a*) Y. Li and Y. Fan, *Synth. Commun.*, 2019, **49**, 3227–3264; (*b*) D. Q. Dong, Q. Q. Han, S. H. Yang, J. C. Song, N. Li, Z. L. Wang and X. M. Xu, *ChemistrySelect*, 2020, **5**, 13103–13134.
42 Y. Liu, Q.-L. Wang, Z. Chen, Q. Zhou, H. Li, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang and K.-W. Tang, *J. Org. Chem.*, 2019, **84**, 2829–2839.
43 (*a*) F. Xiao, Y. Guo and Y. F. Zeng, *Adv. Synth. Catal.*, 2020, **363**, 120–143; (*b*) I. B. Krylov, O. O. Segida, A. S. Budnikov and A. O. Terent'ev, *Adv. Synth. Catal.*, 2021, **363**, 2502–2528; (*c*) M. Latrache and N. Hoffmann, *Chem. Soc. Rev.*, 2021, **50**, 7418–7435; (*d*) R. I. Patel, S. Sharma and A. Sharma, *Org. Chem. Front.*, 2021, **8**, 3166–3200.
44 (*a*) M. A. Dombroski, S. A. Kates and B. B. Snider, *J. Am. Chem. Soc.*, 1990, **112**, 2759–2767; (*b*) G. G. Melikyan, *Synthesis*, 1993, 833–850; (*c*) J. Iqbal, B. Bhatia and N. K. Nayyar, *Chem. Rev.*, 1994, **94**, 519–564; (*d*) P. I. Dalko, *Tetrahedron*, 1995, **51**, 7579–7653; (*e*) G. G. Melikyan, *Organic Reactions*, John Wiley & Sons, Inc., 1996, pp. 427–675; (*f*) B. B. Snider, *Chem. Rev.*, 1996, **96**, 339–364; (*g*) T. Linker, *J. Prakt. Chem./Chem.-Ztg.*, 1997, **339**, 488–492; (*h*) V. Nair, J. Mathew and J. Prabhakaran, *Chem. Soc. Rev.*, 1997, **26**, 127–132; (*i*) G. A. Molander and C. R. Harris, *Tetrahedron*, 1998, **54**, 3321–3354; (*j*) T. Sommermann, *Synlett*, 1999, 834; (*k*) X.-Q. Pan, J.-P. Zou and W. Zhang, *Mol. Diversity*, 2009, **13**, 421–438; (*l*) M. Mondal and U. Bora, *RSC Adv.*, 2013, **3**, 18716.

45 (*a*) X.-H. Ouyang, R.-J. Song and J.-H. Li, *Chem. – Asian J.*, 2018, **13**, 2316–2332; (*b*) K. Matsuo, T. Kondo, E. Yamaguchi and A. Itoh, *Chem. Pharm. Bull.*, 2021, **69**, 796–801.
46 (*a*) A. L. Gant Kanegusuku and J. L. Roizen, *Angew. Chem., Int. Ed.*, 2021, **60**, 21116–21149; (*b*) S. Zhu, X. Zhao, H. Li and L. Chu, *Chem. Soc. Rev.*, 2021, **50**, 10836–10856; (*c*) D. M. Kitcatt, S. Nicolle and A.-L. Lee, *Chem. Soc. Rev.*, 2022, **51**, 1415–1453.
47 F. Juliá, T. Constantin and D. Leonori, *Chem. Rev.*, 2021, **122**, 2292–2352.
48 P. A. Baguley and J. C. Walton, *Angew. Chem., Int. Ed.*, 1998, **37**, 3072–3082.
49 (*a*) I. M. T. Davidson, *Q. Rev., Chem. Soc.*, 1971, **25**, 111; (*b*) C. Chatgilialoglu, *Chem. Rev.*, 1995, **95**, 1229–1251; (*c*) C. Chatgilialoglu, C. Ferreri, Y. Landais and V. I. Timokhin, *Chem. Rev.*, 2018, **118**, 6516–6572.
50 (*a*) T. Constantin, F. Juliá, N. S. Sheikh and D. Leonori, *Chem. Sci.*, 2020, **11**, 12822–12828; (*b*) T. Constantin, M. Zanini, A. Regni, N. S. Sheikh, F. Juliá and D. Leonori, *Science*, 2020, **367**, 1021–1026; (*c*) B. Górski, A.-L. Barthelemy, J. J. Douglas, F. Juliá and D. Leonori, *Nat. Catal.*, 2021, **4**, 623–630; (*d*) H. Zhao, A. J. McMillan, T. Constantin, R. C. Mykura, F. Juliá and D. Leonori, *J. Am. Chem. Soc.*, 2021, **143**, 14806–14813.
51 B. Mao, X.-Y. Zhang, Y. Wei and M. Shi, *Chem. Commun.*, 2022, **58**, 3653–3656.
52 X.-Y. Zhang, X.-Y. Wu, B. Zhang, Y. Wei and M. Shi, *ACS Catal.*, 2021, **11**, 4372–4380.
53 (*a*) L. M. Ambrosini and T. H. Lambert, *ChemCatChem*, 2010, **2**, 1373–1380; (*b*) S. P. Sancheti, Urvashi, M. P. Shah and N. T. Patil, *ACS Catal.*, 2020, **10**, 3462–3489.
54 R. F. Langler, R. K. Raheja, K. Schank and H. Beck, *Helv. Chim. Acta*, 2001, **84**, 1943–1951.
55 J. Liu, Y. Wei and M. Shi, *Org. Chem. Front.*, 2021, **8**, 94–100.
56 C. Liu, Y.-J. Yang, J.-Y. Dong, M.-D. Zhou, L. Li and H. Wang, *Org. Chem. Front.*, 2019, **6**, 3944–3949.
57 G. Bergonzini, C. Cassani and C.-J. Wallentin, *Angew. Chem., Int. Ed.*, 2015, **54**, 14066–14069.
58 (*a*) E. E. Stache, A. B. Ertel, T. Rovis and A. G. Doyle, *ACS Catal.*, 2018, **8**, 11134–11139; (*b*) M. Zhang, J. Xie and C. Zhu, *Nat. Commun.*, 2018, **9**, 3517; (*c*) M. Zhang, X.-A. Yuan, C. Zhu and J. Xie, *Angew. Chem., Int. Ed.*, 2018, **58**, 312–316; (*d*) J. I. Martinez Alvarado, A. B. Ertel, A. Stegner, E. E. Stache and A. G. Doyle, *Org. Lett.*, 2019, **21**, 9940–9944; (*e*) X.-Q. Hu, Y.-X. Hou, Z.-K. Liu and Y. Gao, *Org. Chem. Front.*, 2020, **7**, 2319–2324.
59 X. Gu, Y. Wei and M. Shi, *Org. Chem. Front.*, 2021, **8**, 6823–6829.
60 D. Griller and K. U. Ingold, *Acc. Chem. Res.*, 1980, **13**, 317–323.
61 X. Y. Zhang, C. Ning, B. Mao, Y. Wei and M. Shi, *Chem. Sci.*, 2021, **12**, 9088–9095.
62 S. Murarka, *Adv. Synth. Catal.*, 2018, **360**, 1735–1753.

