

Photocatalytic reactions of fluoroalkyl iodides with alkenes

G. I. Chernov,^a V. V. Levin,^b and A. D. Dilman^{b*}

^aResearch School of Chemistry and Applied Biomedical Sciences, Tomsk Polytechnic University,
30 prospekt Lenina, 634050 Tomsk, Russian Federation.

E-mail: gnc1@tpu.ru

^bN. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prospekt, 119991 Moscow, Russian Federation.

E-mail: dilman@ioc.ac.ru

Fluoroalkyl iodides are convenient sources of fluoroalkyl radicals under photocatalytic conditions. After the addition of a fluorine radical to a double bond, the resulting radical can react in several directions, including abstraction of an iodine atom from the starting iodide, abstraction of a hydrogen atom from a reducing agent, intramolecular interception by an aromatic system, and one-electron oxidation. These reactions make it possible to obtain a wide range of organofluorine compounds. The review summarizes data for the last five years.

Key words: organofluorine chemistry, fluoroalkyl iodides, alkenes, photocatalysis, radicals.

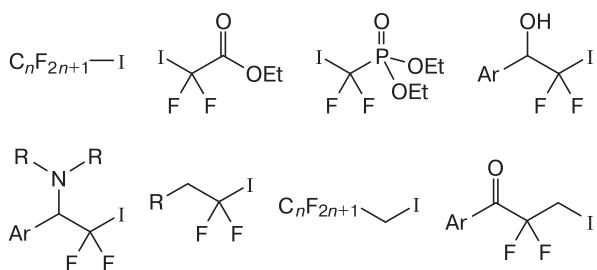
Introduction

Organofluorine compounds are widely used in medicinal chemistry^{2–6} and agrochemistry.⁷ The most accessible and convenient reagents for introducing a fluorinated group are fluorine-substituted alkyl halides. In the series of alkyl halides, alkyl iodides are the most reactive, which is due to their weakest carbon-halogen bond.⁸ They can produce alkyl radicals under reductive conditions, and these processes proceed rather easily because of the presence of fluorine atoms.^{9–12} It should be noted that fluorine atoms can affect the properties of free radicals themselves.^{13,14}

Photocatalysis is one of the most dynamically developing areas of organic chemistry as a method for carrying out free radical reactions.^{15–18} The use of redox-active systems, which are activated when exposed to visible light, opens up wide possibilities

for the generation of radicals. Photocatalytic activation of fluoroalkyl iodides is used quite often.^{10–12} This review considers reactions of fluoroalkyl iodides with unsaturated systems, *viz.*, alkenes, with an emphasis on the work of the last five years.

The most common representatives of fluoroalkyl iodides are perfluorinated alkyl iodides.¹⁹ However, there are many other types of reagents that differ both in methods of synthesis and in reactivity. In the vast majority of examples, iodides containing fluorine atoms at the α -carbon atom are used. Nevertheless, the effect of the fluorine atoms is also very significant in the case of β -fluorine-substituted substrates, making it possible to generate the corresponding radicals under redox conditions.

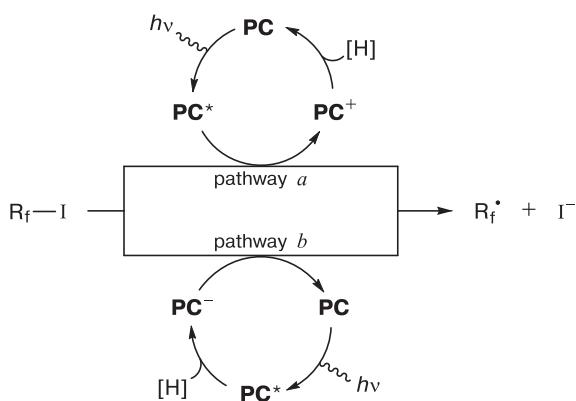


One-electron reduction with the formation of free radicals under the action of a photocatalyst (PC) proceeds by two mechanisms (Scheme 1). One

* Dilman Alexander Davidovich, born in 1976, Doctor of Chemical Sciences, Professor of the Russian Academy of Sciences, Deputy Director for Research at the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences (Moscow), an expert in the field of photocatalysis in organic and organofluorine chemistry, was elected a member correspondent of the Russian Academy of Sciences in 2022 (more detailed information is given in Ref. 1).

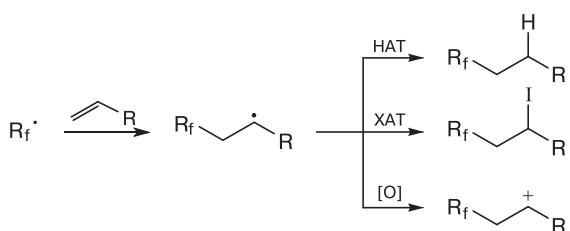
mechanism involves oxidative quenching of the excited state of PC by electron transfer from the excited catalyst to fluoroalkyl iodide (pathway *a* in Scheme 1). Photoexcited states of some catalysts cannot reduce fluoroalkyl iodides. In this case, an alternative path is possible, which includes the preliminary reduction of the photoexcited catalyst (reductive quenching) and the subsequent reduction of the alkyl iodide (pathway *b* in Scheme 1). In addition, reactions involving fluoroalkyl iodides can occur under irradiation without the addition of a catalyst, and examples of such reactions will also be given in this review.

Scheme 1



When a fluoroalkyl radical reacts with a double bond, a new radical is formed. It reacts further depending on specific conditions. Hydrogen atom transfer (HAT) is possible, and the source of the hydrogen atom can be either an additional reagent or a solvent (Scheme 2). The radical can abstract an iodine atom from the parent alkyl iodide, resulting in halogen atom transfer (XAT). It should be noted that the XAT processes are widely used in photocatalytic reactions.²⁰ Another pathway of standard

Scheme 2

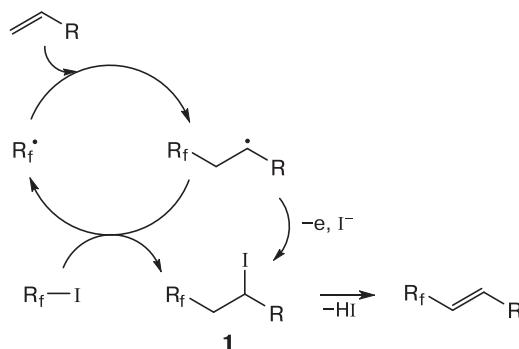


radical transformations consists in one-electron oxidation of the radical followed by reactions of the resulting carbocation (such as addition of a nucleophile or abstraction of a proton). In addition, intramolecular interception of the radical by an aromatic system with subsequent one-electron oxidation is possible.

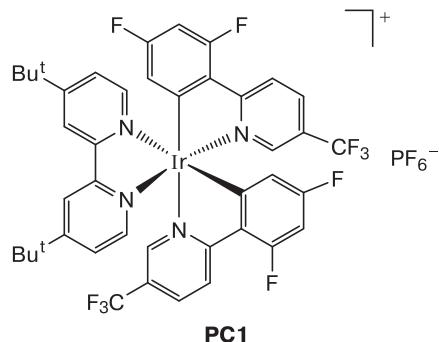
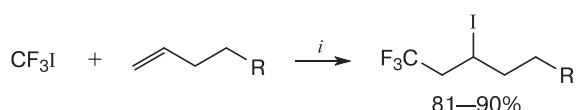
Atom-transfer radical addition reactions

Atom-transfer radical addition (ATRA) reactions represent the most atom-economical type of processes in which the product molecule contains two parent compounds.²¹ The mechanism of these reactions includes a chain process, in the course of which the organofluorine radical is regenerated at the step of iodine atom transfer (Scheme 3). Despite the fact that the formation of cationic intermediates does not occur during the chain radical process, the elimination of hydrogen iodide from primary product **1** under the action of a base can lead to the corresponding alkene. It is necessary to note that in the presence of redox active systems, the oxidation of the radical to carbocation and the subsequent addition of an iodide anion are possible, which leads to iodide **1**, the same transfer reaction product.

Scheme 3

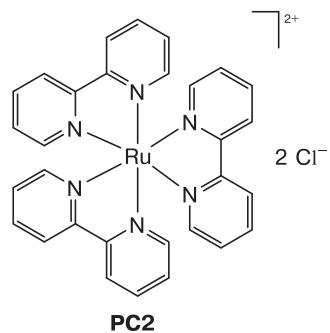


The first example of photocatalytic addition of trifluoromethyl iodide to alkenes was reported in 2011 (Scheme 4).²² The cationic iridium complex $[\text{Ir}(\text{dtbbpy})(\text{dF}(\text{CF}_3)\text{ppy})_2]\text{PF}_6$ (**PC1**) was used as a photocatalyst. Complex **PC1** has a very strong oxidation potential due to the presence of fluorine atoms and CF_3 groups in the pyridine ligand. Therefore, the mechanism involving the oxidation of the secondary alkyl radical seems to be the most realistic.

Scheme 4

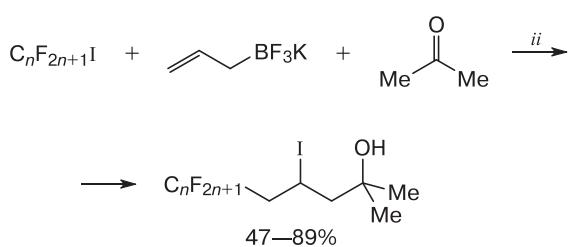
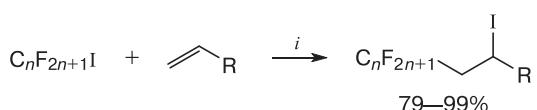
Reagents and conditions: *i.* 1% PC1, DMF, H₂O, blue light, ~20 °C, 48 h.

An attempt to apply the above conditions to the conversion of other perfluoroalkyl iodides such as C₈F₁₇I was unsuccessful. Later on, another photocatalytic system was proposed, in which the cationic ruthenium complex [Ru(bpy)₃]Cl₂ (PC2) was used as a photocatalyst.²³



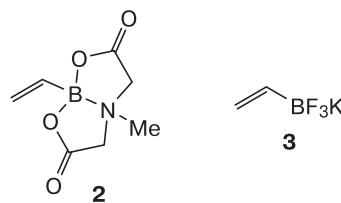
The stoichiometric addition of sodium ascorbate, which acts as an electron donor for the reductive quenching of the excited state, sharply increases the reaction rate (Scheme 5). Under optimized conditions, the addition of various perfluoroalkyl iodides to a wide range of terminal aliphatic alkenes was carried out.

Terminal alkynes also react to give the corresponding vinyl iodides in excellent yield as mixtures of geometric isomers. In the addition to alkynes, the radical chain mechanism is most probable since the oxidation of vinyl radical to carbocation is difficult. These conditions were successfully applied for addition of perfluoroalkyl iodides to MIDA boronate

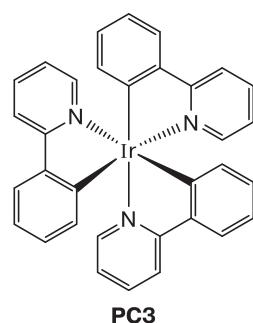
Scheme 5

Reagents and conditions: *i.* 1% PC2, sodium ascorbate, MeCN/MeOH, blue light, ~20 °C, 0.5–48 h. *ii.* 1% PC2, sodium ascorbate, acetone, blue light, ~20 °C, 24 h.

bearing a vinyl moiety (**2**)²⁴ and potassium vinyltrifluoroborate (**3**).²⁵



When potassium allyltrifluoroborate is used as an alkene component, and the reaction is carried out in acetone, alcohols are formed. This reaction consists of allylboration of the carbonyl group and following reaction of the terminal double bond with the perfluoroalkyl iodide. A method for the addition of 2,2,2-trifluoroethyl iodide (CF₃CH₂I) to aliphatic terminal alkenes using the neutral iridium complex *fac*-[Ir(ppy)₃] (PC3) was suggested.²⁶ It is found that an acceptable product yield can only be achieved if a significant excess of diisopropylethylamine is used. The latter compound plays a role of a reducing agent quenching the excited photocatalyst.



The above examples demonstrate the use of iridium and ruthenium complexes as the most common redox activators in photocatalytic processes. These complexes operate under the action of blue light (400–460 nm). However, it is possible to carry out the reaction under even milder conditions using green or red LED light sources.

An unusual system consisting of a platinum porphyrin complex (**PC4**) as a photocatalyst and oxalate anion as a reducing agent was used to carry out the addition of trifluoromethyl iodide to alkenes (Scheme 6).²⁷

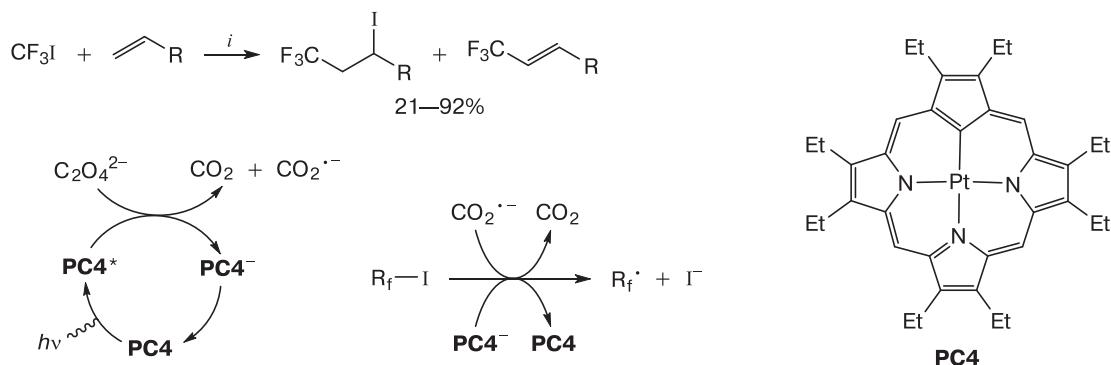
When a reaction mixture is irradiated with green light, a mixture of addition and addition–elimination products is formed from various terminal alkenes. Based on electrochemical data and results of photo-kinetic experiments, it was found that the excited state of the photocatalyst is reductively quenched by the oxalate anion, which results in the formation of a carbon dioxide radical anion, which acts as a reductive agent with respect to CF_3I similarly to the reduced catalyst. Therefore, two different processes of one-electron CF_3I reduction initiating subsequent chain reaction occur simultaneously.

The atom transfer reaction, which can be initiated by various photocatalytic systems, is shown in Scheme 7. It was suggested²⁸ to use the **PC5** sub-phthalocyanine photocatalyst for carrying out the reaction of addition of perfluoroalkyl iodides to alkenes and alkynes under the action of red light. Aliphatic terminal and internal alkenes of various structure and terminal alkynes can enter into this addition reaction. A mechanism proposed for this reaction includes a photocatalytic cycle with reductive quenching. Organic dyes can be used as photo-

catalysts. For instance, the addition of various perfluoroalkyl iodides to terminal alkenes and alkynes was performed by irradiation in the presence of the Eosin Y (**PC6**),²⁹ which is an organic photocatalyst. Quenching of the fluorescence of Eosin Y under the action of perfluoroalkyl iodide was observed in fluorometric experiments, indicating the occurrence of a photocatalytic cycle with oxidative quenching of the excited state. Sodium thiosulfate present in this system plays the role of a reducing agent that regenerates the neutral form of the photocatalyst. In the presence of the **PC7** photocatalyst synthesized on the basis of 1,4-phenylenediboronic acid, the addition of various perfluoroalkyl iodides to derivatives of boronic acids containing double bonds takes place under irradiation with blue light.³⁰

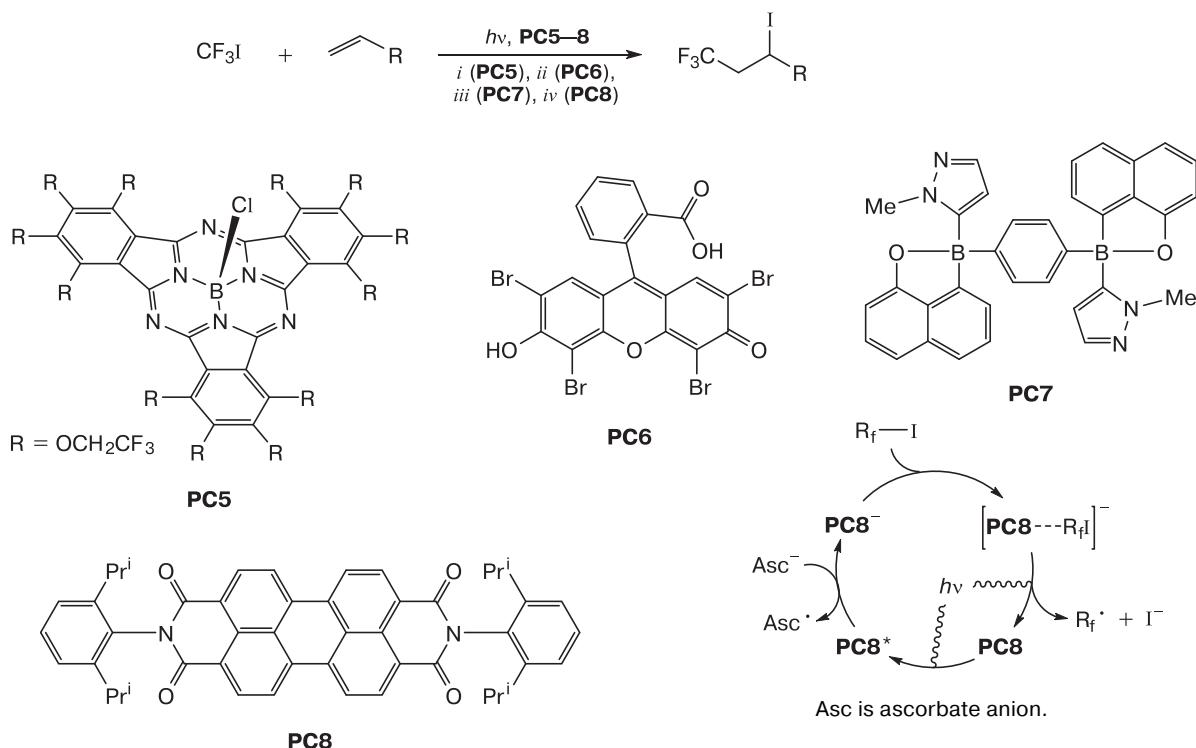
The **PC8** perylene derivative is an extremely effective photocatalyst of the atom-transfer addition processes with perfluoroalkyl iodides. The photocatalytic conversions performed using **PC8** required a record low photocatalyst loading.³¹ The reactions were carried out in the presence of sodium ascorbate under blue light irradiation. Structurally different aliphatic terminal alkenes were used as substrates. Note that the reactions do not occur in the absence of sodium ascorbate (NaAsc). Therefore, it can be assumed that this compound acts as a reductive quencher of the photocatalyst excited state. However, the reduced form of this photocatalyst is a reducing agent not sufficiently strong to directly reduce a perfluoroalkyl iodide. Instead, two-photon absorption can take place, producing a stronger reducing agent. At the same time, this is also unlikely due to the short lifetime of the excited state.

Scheme 6



Reagents and conditions: *i.* **PC4** (1%), $(\text{Bu}_4\text{N})_2\text{C}_2\text{O}_4$, MeCN, green light, $\sim 20^\circ\text{C}$, 48 h.

Scheme 7



Reagents and conditions: *i.* PC5 (1%), sodium ascorbate, AcONa, MeCN/MeOH, red light, ~20 °C, 1–6 h. *ii.* PC6 (1%), Na₂S₂O₃, MeCN, white light, ~20 °C, 1–6 h. *iii.* PC7 (1%), sodium ascorbate, DMSO, blue light, ~20 °C, 48 h. *iv.* PC8 (0.05%), sodium ascorbate, MeCN/MeOH, blue light, ~20 °C, 4 h.

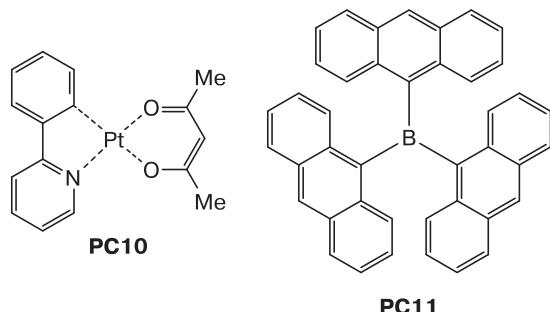
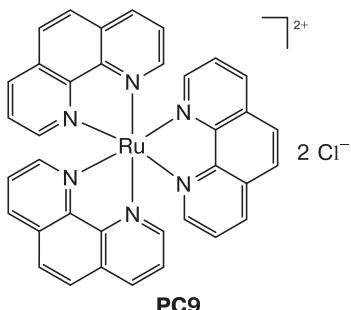
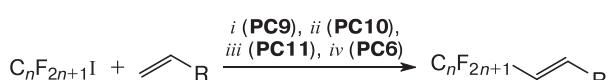
Another way of activation of perfluoroalkyl iodide is the formation of a donor-acceptor complex with a reduced form of the photocatalyst, which, upon repeated excitation, undergoes fragmentation with the formation of a perfluoroalkyl radical, which initiates a chain radical reaction. Using triethylamine as a reducing agent instead of sodium ascorbate, it is possible to achieve homogeneity of the reaction mixture and carry out the reaction in a flow reactor.³² It is noteworthy that by increasing the residence time of the reactants in the reactor, it is possible to achieve complete conversion even in the case of less active substrates such as cycloalkenes and alkynes.

To selectively obtain the addition–elimination products, the photocatalytic reaction has to be carried out in the presence of a strong base. In particular, trifluoromethylation of terminal aliphatic alkenes was performed using [Ru(phen)₃]Cl₂ (**PC9**) as a photocatalyst and DBU as a base (Scheme 8).³³

Photocatalytic reactions of fluoroalkylation of alkenes catalyzed by palladium and platinum complexes are also known. It was shown that the complex

[Pt(ppy)(acac)] (**PC10**) can be a photocatalyst of trifluoromethylation of terminal aliphatic alkenes.³⁴ A detailed study of the reation mechanism by photochemical methods revealed the occurrence of the oxidative quenching of the excited state of the platinum complex by trifluoromethyl iodide. A procedure for fluoroalkylation of styrene derivatives in the presence of a palladium complex and a base under blue light irradiation was also developed. Partially fluorinated alkyl iodides such as 2,2,2-trifluoroethyl iodide (CF₃CH₂I) and related compounds were used as reagents.³⁵

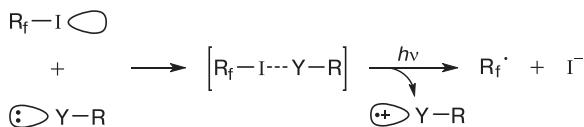
A photocatalyst of an unusual structure, tri(9-antryl)borane (**PC11**), was used for perfluoroalkylation of alkenes; it works when irradiated with light with a wavelength of 480 nm.³⁶ In the presence of this catalyst and a base, perfluoroalkylation of a wide range of terminal aliphatic alkenes is possible. In this reaction, DBU acts exclusively as a base and cannot act as a reducing agent because of the weak oxidizing activity of the excited state of the catalyst. Eosin Y (**PC6**) can also be used in the addition–elimination

Scheme 8

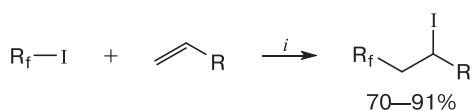
Reagents and conditions: *i.* PC9 (1%), DBU, MeCN, white light, ~20 °C, 2–10 h. *ii.* PC10 (1%), DBU, MeCN, blue light, ~20 °C, 5–10 h. *iii.* PC11 (0.5%), DBU, MeCN, $\lambda = 480$ nm, ~20 °C, 2–8 h. *iv.* PC6 (5%), Cs_2CO_3 , DMA, white light, ~20 °C, 48 h.

reaction with terminal aliphatic alkenes.³⁷ In this case, cesium carbonate was used as a base. The availability of Eosin Y allows it to be used in amounts of a few mole percent and above.

It is well known that the interaction of perfluoroalkyl iodides with various donor molecules results in the formation of donor-acceptor complexes containing a halogen bond connecting the region of the positive potential of the iodine atom with the donor atom carrying a lone electron pair.³⁸ Under the action of visible light, these complexes can dissociate to the donor molecule radical cation, iodide anion, and perfluoroalkyl radical (Scheme 9).³⁹

Scheme 9

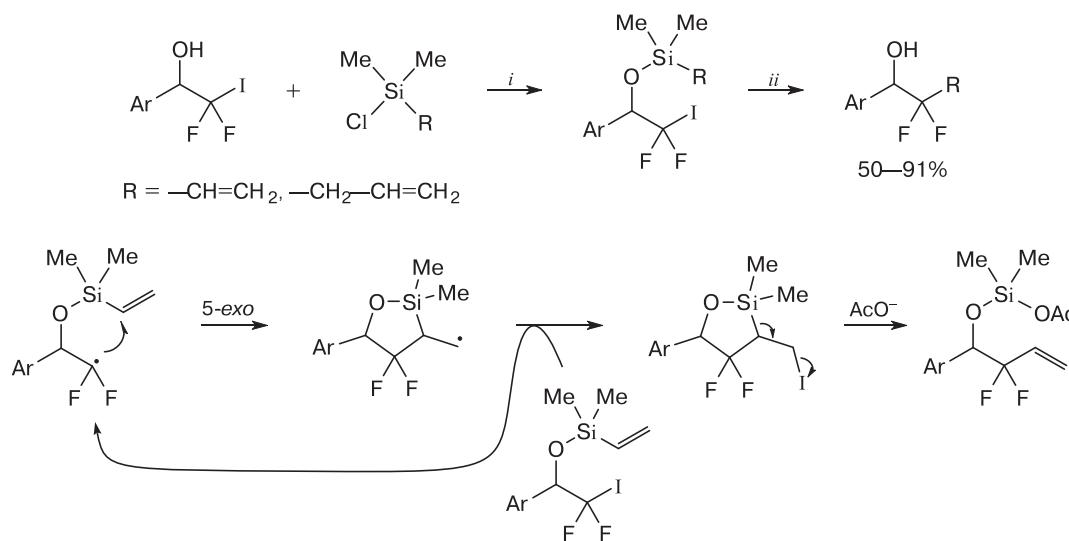
Aliphatic amines can be used as the Lewis bases. It is found that one of the most efficient activators of this type is *N,N,N',N'*-tetraethylmethylenediamine.⁴⁰ Addition reactions of perfluoroalkyl iodides to terminal aliphatic alkenes were carried out in its presence under white light irradiation (Scheme 10). A solvent can also play a role of a Lewis base. For example, the addition of perfluoroalkyl iodides to various terminal alkenes was carried out by blue light irradiation of the reaction mixture in acetone.⁴¹

Scheme 10

Reagents and conditions: *i.* $\text{Et}_2\text{N}(\text{CH}_2)_2\text{NEt}_2$ (3 equiv.), THF, white light, 30 °C, 36 h.

In addition-elimination reactions, besides a proton, the substrates may contain another leaving group, for example, a trimethylsilyl fragment. Methods were developed for replacing the iodine atom in the difluoriodomethyl moiety with the vinyl⁴² and allyl⁴³ group (Scheme 11). CF_2I -substituted alcohols, which can easily be prepared from aldehydes,^{44–46} were used as starting compounds. The alcohols were treated with a silylation reagent containing a vinyl or allyl group. The formed silyl ether was introduced into the photocatalytic reaction in the presence of an iridium photocatalyst, sodium acetate, and a substoichiometric amount (20%) of triphenylphosphine. Phosphine can perform several functions in this reaction: it can reductively quench the photocatalyst, remove residual oxygen from the reaction mixture, or facilitate the reduction of fluoroalkyl iodide by forming a donor-acceptor complex with it. As shown in Scheme 11, the radical formed during the C—I bond activation can undergo an intramolecular attack on the double bond, which corresponds to the 5-*exo*-cyclization in the case of vinyl fragment. The subsequent transfer of the radical chain leads to the formation of an intermediate compound with a C—I bond, in which the Si—C bond is broken during the nucleophilic attack of an acetate anion. In the case of the allyl group, the reaction proceeds according to a similar mechanism, including 7-*endo*-cyclization at the key step.

Scheme 11



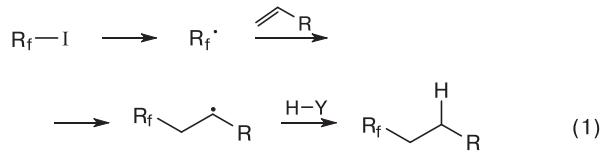
Reagents and conditions: *i.* NEt₃, MeCN, ~20 °C, 1–3 h. *ii.* PC3 (0.25%), Ph₃P (0.2 equiv.), AcONa (2 equiv.), $\lambda = 400$ nm, ~20 °C, 2 h.

Reductive addition reactions

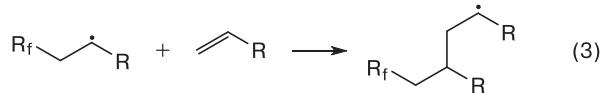
The reactions of reductive addition of perfluorinated groups to alkenes (hydroperfluoroalkylation reactions) are known for a long time.⁴⁷ The advent of photocatalysis opened up possibilities for carrying out such reactions under milder conditions. The key role in these reactions is played by a hydrogen atom donor, which intercepts a radical intermediate formed during the addition of a fluorinated radical to alkene (Scheme 12, reaction (1)). For the reaction to proceed successfully, it is necessary that the fluorinated radical reacts with the double bond faster than with the hydrogen atom donor to form a product of the fluoroalkyl iodide reduction (equation (2)). At the same time, the hydrogen donor should be active enough to prevent the addition of a new radical to the next alkene molecule (equation (3)).

A method was developed⁴⁸ for the reductive fluoroalkylation of acceptor alkenes based on the use of sodium cyanoborohydride (Scheme 13). The reaction occurs under blue light irradiation in the presence of stoichiometric amounts of pyridine as a base. The reaction mechanism involves the hydrogen atom transfer from cyanoborohydride anion⁴⁹ with the formation of the boron-centered radical, which abstracts an iodine atom from the starting alkyl iodide. This process occurs in the absence of a photocatalyst, therefore, the question of how the process is initiated is non-trivial. It can be assumed that the reaction of

Scheme 12



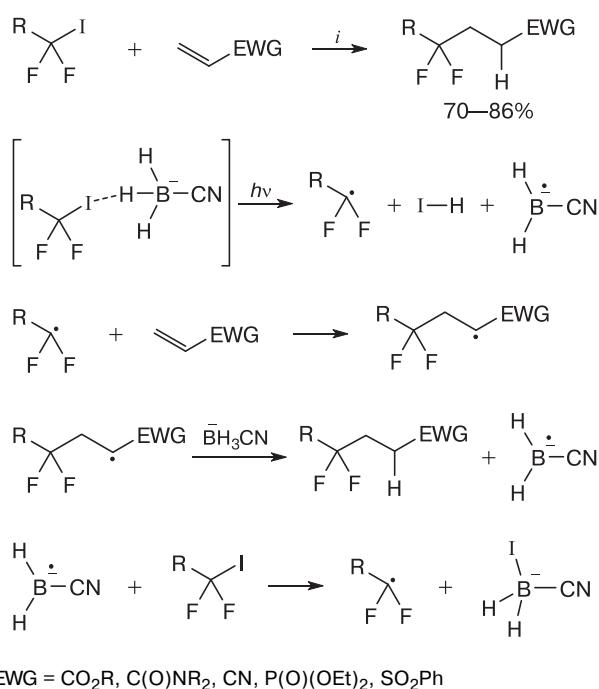
Side reactions:



fluoroalkyl iodide with the cyanoborohydride anion forms a complex, which decomposes under the action of light to form radicals.

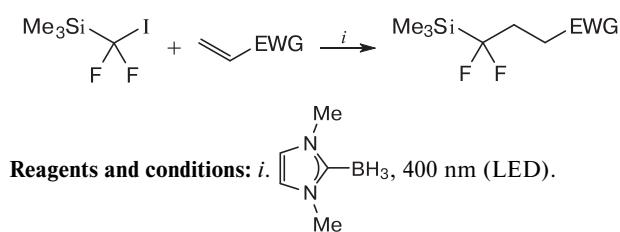
This method was applied to synthesize new fluorosilicon reagents by the addition of the silyldifluoromethyl group to electron deficient alkenes (Scheme 14).⁵⁰ The borane complex with *N*-heterocyclic carbene as a reductive agent proved to be more efficient in this reaction. The obtained difluoro-substituted silanes can further react due to their silicon–carbon bonds or their functional groups.

The reaction of reductive trifluoromethylation of styrenes with trifluoromethyl iodide was performed in the presence of the iridium catalyst PC3 and a stoichiometric amount of 4-hydroxythiophenol

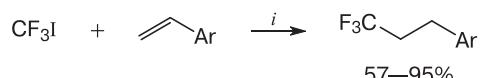
Scheme 13

$\text{EWG} = \text{CO}_2\text{R}, \text{C(O)NR}_2, \text{CN}, \text{P(O)(OEt)}_2, \text{SO}_2\text{Ph}$

Reagents and conditions: *i.* NaBH_3CN , Py, MeOH, blue light, $\sim 20^\circ\text{C}$, 20 h.

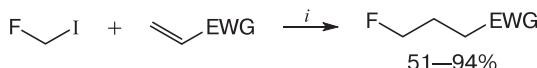
Scheme 14

(Scheme 15).⁵¹ In this reaction, thiophenol acts as a hydrogen atom donor. The replacement of thiophenol with cesium acetate and carrying out the reaction in *N,N*-dimethylformamide leads to the formation of unsaturated products: trifluoromethyl-substituted styrenes.

Scheme 15

Reagents and conditions: *i.* PC3 (0.05%), $\text{HS}-\text{C}_6\text{H}_4-\text{OH}$, DCE—EtOH (9 : 1), blue light, $\sim 20^\circ\text{C}$, 24 h.

Tris(trimethylsilyl)silane was used as a hydrogen source in the reaction of fluoromethyl group addition to electron deficient alkenes (Scheme 16).⁵² It should be especially noted that the reaction was carried out under blue light irradiation without addition of PC. It is assumed that tris(trimethylsilyl)silane participates in the fluoromethyl iodide activation.

Scheme 16

Reagents and conditions: *i.* $(\text{Me}_3\text{Si})_3\text{SiH}$, MeCN, blue light, $\sim 20^\circ\text{C}$, 16 h.

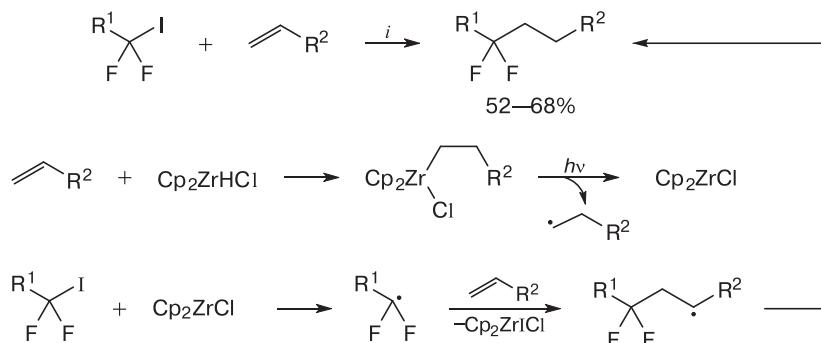
Recently, an unusual method with the use of the Schwartz reagent (zirconocene hydrochloride) was proposed for reductive fluoroalkylation of alkenes (Scheme 17).⁵³ Initially, the reaction of hydrozirconation of the double bond occurs to form an alkyl zirconium compound. Then, under the action of blue light, this Zr^{IV} complex undergoes homolytic cleavage of its zirconium–carbon bond, producing a Zr^{III} intermediate abstracting an iodine atom from alkyl iodide. Then, the fluorinated radical adds to alkene, and the formed secondary radical abstracts a hydrogen atom from solvent (dioxane).

Reactions of addition to alkynes, which are accompanied by an intramolecular addition to aromatic fragments

Radical intermediates formed in the course of the addition to double bonds can react with the aromatic system that is a part of the substrate, giving products of the cascade transformation. In addition, the step of reduction of the aromatic system may be accompanied by the breaking of the carbon–carbon bond.

A reaction of reductive addition of fluoroalkyl iodides to alkenes, which is accompanied by a 1,2-shift of aromatic fragment, was proposed (Scheme 18).⁵⁴ The reaction is carried out in trifluoroethanol (TFE) under blue light irradiation in the presence of PC3 and DBU and TMEDA bases. A wide range of substrates with aromatic fragments of various structures can be involved into this reaction. An unstable alkyl radical, which is formed during the reaction, reacts with the aromatic system, producing an intermediate containing a three-membered cycle. The opening of

Scheme 17



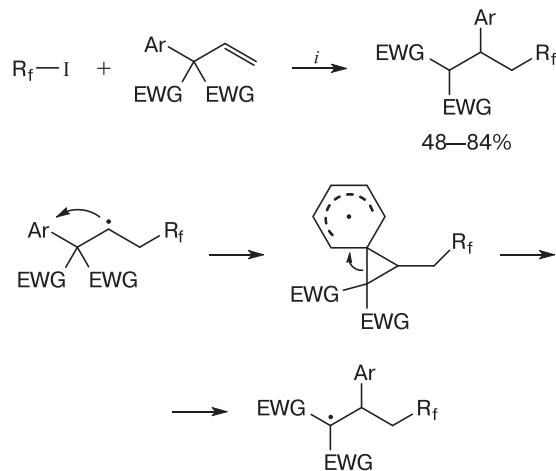
Reagents and conditions: *i.* Cp₂ZrHCl, dioxane/NMR, blue light, 40–45 °C, 12 h.

the cyclopropane fragment leads to the formation of a radical, in which the radical center is stabilized due to conjugation with two electron-withdrawing functional groups (EWG). The hydrogen atom transfer occurs from a molecule of DBU or the solvent, leading to the formation of the final product.

Oxindole derivatives were obtained by the reaction of perfluoroalkyl iodides with *N*-alkyl-*N*-(aryl-sulfonyl)methylacrylamide under conditions of the photoredox catalysis; the reaction was accompanied by elimination of sulfur dioxide (Scheme 19).⁵⁵ Only moderate yields were observed for the majority of studied substrates. Transformation of *N*-aryl-*N*-(arylsulfonyl)methylacrylamides (*R* = Ar) under similar conditions leads to an acyclic product with a low yield. The mechanism of the reaction involves generation of a perfluoroalkyl radical in the course of oxidative quenching of the excited state of the PC3 photocatalyst. The addition of the radical to the multiple bond of the substrate results in the formation of a radical intermediate, which sequentially undergoes cyclization with the aromatic system and then fragmentation with the release of sulfur dioxide and the formation of an amidyl radical. The further fate of the latter depends on the ability of the substituent at the nitrogen atom to stabilize the radical center. In the case of aliphatic substituents, the radical addition to the aromatic ring takes place, and the reaction ends with the oxidation of the dienyl radical under the action of Ir^{IV} and proton elimination. If the nitrogen atom bears an aromatic substituent stabilizing the radical intermediate, instead of cyclization, the hydrogen atom is abstracted from the solvent.

Oxindole derivatives were also obtained by the reaction of addition of fluoroalkyl iodides to *N*-aryl-

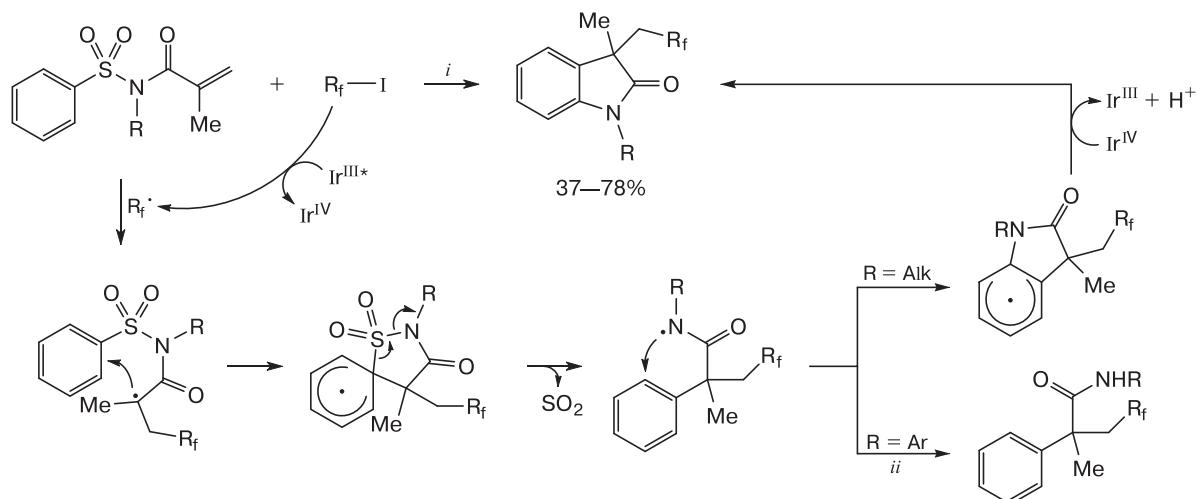
Scheme 18



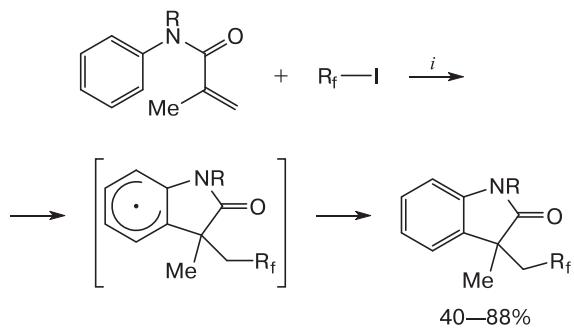
Reagents and conditions: *i.* PC3 (1%), DBU/TMEDA, TFE, blue light, ~20 °C, 12 h.

acrylamides.⁵⁶ This process can be carried out using the organic catalyst PC6 (Scheme 20). The reaction includes the intermediate formation of an analogous dienyl radical capable of aromatization under the action of the oxidized form of the photocatalyst.

Similar transformations accompanied by dearomatization of the benzene ring are also known. In particular, reactions of perfluoroalkyl iodides with *N*-benzylmethylacrylamides containing a methoxy group in the *para* position of the benzyl moiety lead to the formation of spiro-fused derivatives of cyclohexadienone under the photocatalytic conditions (Scheme 21).⁵⁷ The cyclization of the radical intermediate formed during the reaction proceeds in the *para* position to the methoxy group and results in the five-membered cycle formation. The subsequent

Scheme 19

Reagents and conditions: *i.* PC3 (2%), dioxane, K_3PO_4 , blue light, ~ 20 $^{\circ}C$, 24 h. *ii.* Dioxane.

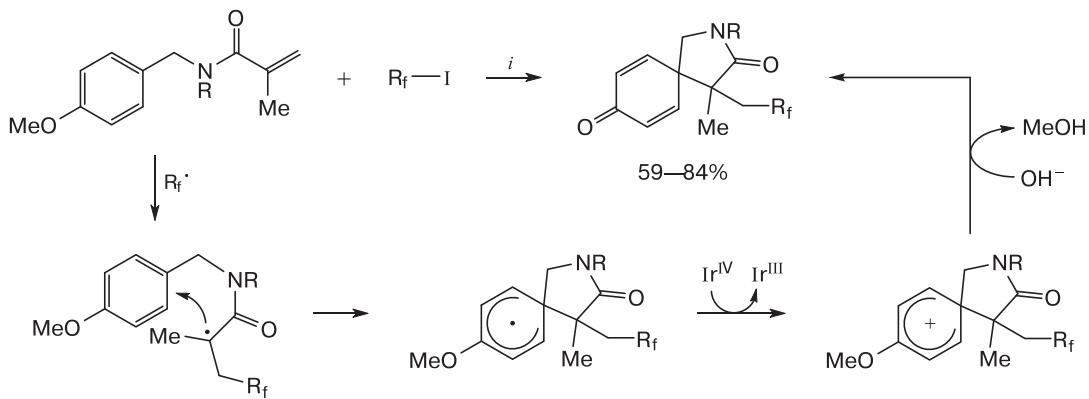
Scheme 20

Reagents and conditions: *i.* PC6 (5%), Cs_2CO_3 , DMA, white light, 65 $^{\circ}C$, 16 h.

one-electron oxidataion of the dienyl radical and nucleophilic demethylation lead to the formation of the cyclohexadienone system.

Conclusion

Fluoroalkyl iodides are very convenient precursors of fluorinated radicals in reactions occurring under the action of visible light. The cleavage of the C—I bond may occur both under the conditions of one-electron reduction by a photoexcited catalyst and under the action of light on donor-acceptor complexes, the formation of which is characteristic of

Scheme 21

Reagents and conditions: *i.* PC3 (2%), K_2CO_3 , DMF/ H_2O , blue light, ~ 20 $^{\circ}C$, 18 h.

fluoroalkyl iodides. In addition, fluoroalkyl iodides readily undergo iodine atom transfer in the reaction with alkyl radicals, which makes it possible to implement an atom economical reaction of addition to alkenes. These reactions make it possible to synthesize a wide range of products containing a perfluorinated or partly fluorinated group.

No human or animal subjects were used in this research.

The authors declare no competing interests.

References

1. Election of the Full Members (Academicians), Corresponding Members, and Foreign Members of the Russian Academy of Sciences, *Russ. Chem. Bull.*, 2022, **71**, 1559; DOI: 10.1007/s11172-022-3565-4.
2. M. Inoue, Y. Sumii, N. Shibata, *ACS Omega*, 2020, **5**, 10633–10640; DOI: 10.1021/acsomega.0c00830.
3. N. A. Meanwell, *J. Med. Chem.*, 2018, **61**, 5822–5880; DOI: 10.1021/acs.jmedchem.7b01788.
4. J. Han, A. M. Remete, L. S. Dobson, L. Kiss, K. Izawa, H. Moriwaki, V. A. Soloshonok, D. O'Hagan, *J. Fluorine Chem.*, 2020, **239**, 109639; DOI: 10.1016/j.jfluchem.2020.109639.
5. B. M. Johnson, Y.-Z. Shu, X. Zhuo, N. A. Meanwell, *J. Med. Chem.*, 2020, **63**, 6315–6386; DOI: 10.1021/acs.jmedchem.9b01877.
6. I. B. Chernikova, M. S. Yunusov, *Russ. Chem. Bull.*, 2022, **71**, 1; DOI: 10.1007/s11172-022-3370-0.
7. Y. Ogawa, E. Tokunaga, O. Kobayashi, K. Hirai, N. Shibata, *iScience*, 2020, **23**, 101467; DOI: 10.1016/j.isci.2020.101467.
8. M. Beller, F. Fischer, A. Locher, H. Neumann, C. Tae-schler, F. Ye, S. Zhang, *Chimia*, 2021, **75**, 923; DOI: 10.2533/chimia.2021.923.
9. X.-H. Liu, J. Leng, S.-J. Jia, J.-H. Hao, F. Zhang, H.-L. Qin, C.-P. Zhang, *J. Fluorine Chem.*, 2016, **189**, 59–67; DOI: 10.1016/j.jfluchem.2016.07.021.
10. G. Dagousset, A. Carboni, G. Masson, E. Magnier, in *Modern Synthesis Processes and Reactivity of Fluorinated Compounds*, Eds H. Grout, F. R. Leroux, A. Tressaud, Elsevier, 2017, pp. 389–426.
11. S. Barata-Vallejo, M. V. Cooke, A. Postigo, *ACS Catal.*, 2018, **8**, 7287–7307; DOI: 10.1021/acscatal.8b02066.
12. T. Chatterjee, N. Iqbal, Y. You, E. J. Cho, *Acc. Chem. Res.*, 2016, **49**, 2284–2294; DOI: 10.1021/acs.accounts.6b00248.
13. W. R. Dolbier, *Chem. Rev.*, 1996, **96**, 1557–1584; DOI: 10.1021/cr941142c.
14. E. V. Tretyakov, P. A. Fedyushin, *Russ. Chem. Bull.*, 2021, **70**, 2298; DOI: 10.1007/s11172-021-3346-5.
15. M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.*, 2016, **81**, 6898–6926; DOI: 10.1021/acs.joc.6b01449.
16. I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. Koenig, *Acc. Chem. Res.*, 2016, **49**, 1566–1577; DOI: 10.1021/acs.accounts.6b00229.
17. D. M. Schultz, T. P. Yoon, *Science*, 2014, **343**, 1239176; DOI: 10.1126/science.1239176.
18. J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem.*, 2012, **77**, 1617–1622; DOI: 10.1021/jo202538x.
19. N. O. Brace, *J. Fluorine Chem.*, 1999, **93**, 1–25; DOI: 10.1016/S0022-1139(98)00255-3.
20. F. Juliá, T. Constantin, D. Leonori, *Chem. Rev.*, 2022, **122**, 2292–2352; DOI: 10.1021/acs.chemrev.1c00558.
21. J. M. Munoz-Molina, T. R. Belderrain, P. J. Perez, *Eur. J. Inorg. Chem.*, 2011, **2011**, 3155–3164; DOI: 10.1002/ejic.201100379.
22. J. D. Nguyen, J. W. Tucker, M. D. Konieczynska, C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2011, **133**, 4160–4163; DOI: 10.1021/ja108560e.
23. C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner, C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2012, **134**, 8875–8884; DOI: 10.1021/ja300798k.
24. M. Kublicki, M. Dąbrowski, K. Durka, T. Kliś, J. Serwatowski, K. Woźniak, *Tetrahedron Lett.*, 2017, **58**, 2162–2165; DOI: 10.1016/j.tetlet.2017.04.075.
25. M. Kublicki, K. Durka, T. Kliś, *Tetrahedron Lett.*, 2018, **59**, 2700–2703; DOI: 10.1016/j.tetlet.2018.05.086.
26. M. Huang, L. Li, Z.-G. Zhao, Q.-Y. Chen, Y. Guo, *Synthesis*, 2015, **47**, 3891–3900; DOI: 10.1055/s-0035-1560260.
27. S. Kim, G. Park, E. J. Cho, Y. You, *J. Org. Chem.*, 2016, **81**, 7072–7079; DOI: 10.1021/acs.joc.6b00966.
28. K. Matsuzaki, T. Hiromura, E. Tokunaga, N. Shibata, *ChemistryOpen*, 2017, **6**, 226–230; DOI: 10.1002/open.201600172.
29. T. Yajima, M. Ikegami, *Eur. J. Org. Chem.*, 2017, **2017**, 2126–2129; DOI: 10.1002/ejoc.201700077.
30. M. Kublicki, B. Ogonowski, D. Wieczorkowski, K. Durka, T. Kliś, *Tetrahedron Lett.*, 2019, **60**, 1918–1923; DOI: 10.1016/j.tetlet.2019.06.032.
31. C. Rosso, G. Filippini, P. G. Cozzi, A. Gualandi, M. Prato, *ChemPhotoChem*, 2019, **3**, 193–197; DOI: 10.1002/cptc.201900018.
32. C. Rosso, J. D. Williams, G. Filippini, M. Prato, C. O. Kappe, *Org. Lett.*, 2019, **21**, 5341–5345; DOI: 10.1021/acs.orglett.9b01992.
33. N. Iqbal, S. Choi, E. Kim, E. J. Cho, *J. Org. Chem.*, 2012, **77**, 11383–11387; DOI: 10.1021/jo3022346.
34. W. J. Choi, S. Choi, K. Ohkubo, S. Fukuzumi, E. J. Cho, Y. You, *Chem. Sci.*, 2015, **6**, 1454–1464; DOI: 10.1039/C4SC02537G.
35. R. Adamik, T. Földesi, Z. Novák, *Org. Lett.*, 2020, **22**, 8091–8095; DOI: 10.1021/acs.orglett.0c03043.

36. J. Moon, Y. K. Moon, D. D. Park, S. Choi, Y. You, E. J. Cho, *J. Org. Chem.*, 2019, **84**, 12925–12932; DOI: 10.1021/acs.joc.9b01624.
37. D. P. Tiwari, S. Dabral, J. Wen, J. Wiesenthal, S. Terhorst, C. Bolm, *Org. Lett.*, 2017, **19**, 4295–4298; DOI: 10.1021/acs.orglett.7b01952.
38. G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.*, 2016, **116**, 2478–2601; DOI: 10.1021/acs.chemrev.5b00484.
39. C. G. S. Lima, T. de M. Lima, M. Duarte, I. D. Jurberg, M. W. Paixão, *ACS Catal.*, 2016, **6**, 1389–1407; DOI: 10.1021/acscatal.5b02386.
40. Y. Wang, J. Wang, G.-X. Li, G. He, G. Chen, *Org. Lett.*, 2017, **19**, 1442–1445; DOI: 10.1021/acs.orglett.7b00375.
41. T. Mao, M.-J. Ma, L. Zhao, D.-P. Xue, Y. Yu, J. Gu, C.-Y. He, *Chem. Commun.*, 2020, **56**, 1815–1818; DOI: 10.1039/c9cc09517a.
42. L. I. Panferova, M. I. Struchkova, A. D. Dilman, *Synthesis*, 2017, **49**, 4124–4132; DOI: 10.1055/s-0036-1590855.
43. L. I. Panferova, M. I. Struchkova, A. D. Dilman, *Eur. J. Org. Chem.*, 2018, 3834–3836; DOI: DOI:10.1002/ejoc.201800543.
44. M. D. Kosobokov, V. V. Levin, M. I. Struchkova, A. D. Dilman, *Org. Lett.*, 2014, **16**, 3784–3787; DOI: 10.1021/ol501674n.
45. V. V. Levin, V. O. Smirnov, M. I. Struchkova, A. D. Dilman, *J. Org. Chem.*, 2015, **80**, 9349–9353; DOI: 10.1021/acs.joc.5b01590.
46. L. I. Panferova, V. V. Levin, M. I. Struchkova, A. D. Dilman, *Chem. Commun.*, 2019, **55**, 1314–1317; DOI: 10.1039/c8cc09115c.
47. C.-M. Hu, Y.-L. Qiu, *Tetrahedron Lett.*, 1991, **32**, 4001–4002; DOI: 10.1016/0040-4039(91)80611-9.
48. V. I. Supranovich, V. V. Levin, M. I. Struchkova, J. Hu, A. D. Dilman, *Beilstein J. Org. Chem.*, 2018, **14**, 1637–1641; DOI: 10.3762/bjoc.14.139.
49. T. Kawamoto, I. Ryu, *Org. Biomol. Chem.*, 2014, **12**, 9733–9742; DOI: 10.1039/c4ob01784f.
50. V. I. Supranovich, V. V. Levin, M. I. Struchkova, A. A. Korlyukov, A. D. Dilman, *Org. Lett.*, 2017, **19**, 3215–3218; DOI: 10.1021/acs.orglett.7b01334.
51. N. J. W. Straathof, S. E. Cramer, V. Hessel, T. Noël, *Angew. Chem., Int. Ed.*, 2016, **55**, 15549–15553; DOI: 10.1002/anie.201608297.
52. S. M. Hell, C. F. Meyer, S. Ortalli, J. B. I. Sap, X. Chen, V. Gouverneur, *Chem. Sci.*, 2021, **12**, 12149–12155; DOI: 10.1039/D1SC03421A.
53. X. Ren, X. Gao, Q.-Q. Min, S. Zhang, X. Zhang, *Chem. Sci.*, 2022, **13**, 3454–3460; DOI: 10.1039/D1SC07061D.
54. Z. Li, M. Wang, Z. Shi, *Angew. Chem., Int. Ed.*, 2021, **60**, 186–190; DOI: 10.1002/anie.202010839.
55. S. Tang, L. Yuan, Y.-L. Deng, Z.-Z. Li, L.-N. Wang, G.-X. Huang, R.-L. Sheng, *Tetrahedron Lett.*, 2017, **58**, 329–332; DOI: 10.1016/j.tetlet.2016.12.027.
56. Z. Yang, A. Tang, *Synlett*, 2019, **30**, 1061–1066; DOI: 10.1055/s-0037-1611781.
57. S. Tang, L. Yuan, Z.-Z. Li, Z.-Y. Peng, Y.-L. Deng, L.-N. Wang, G.-X. Huang, R.-L. Sheng, *Tetrahedron Lett.*, 2017, **58**, 2127–2130; DOI: 10.1016/j.tetlet.2017.04.055.

Received July 15, 2022;
in revised form September 10, 2022;
accepted September 25, 2022