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Recent trends in perfluorinated sulfoximines

Développements récents de la chimie des sulfoximines perfluorées

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A B S T R A C T

The search for original perfluorinated moieties is a very modern and attractive challenge. Among the emergent groups, the *S*-perfluoroalkylated sulfoximines are very peculiar because of their structural diversity and promising properties. A literature survey shows that interest in these molecules is strongly increasing. This short review summarizes the recent works devoted to this topic.

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R É S U M É

La recherche de groupes fluorés originaux est un défi moderne de la chimie organique. Parmi ces entités fluorées, les sulfoximines *S*-perfluoroalkylées représentent une classe particulière de composés, en raison de leur structure, mais aussi de leurs propriétés intéressantes. L'intérêt pour ces molécules est en forte augmentation dans la littérature. Le but de cette mini-revue est de résumer les travaux récents dédiés à cette thématique.

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1. Introduction

Sulfoximines are very intriguing sulfur(VI) compounds and can be considered as monoaza analogues of sulfones [1a] (Fig. 1).

They nevertheless display much more diversity in terms of structure and reactivity than sulfones because of the multiple potential variations offered by the replacement of an oxygen by a nitrogen (Fig. 1). Two major differences may be highlighted. In the case of two different groups R_1 and R_2, this replacement brings the chirality to the sulfur center and also allows the introduction of a mostly unlimited number of substituents attached to the nitrogen. The variety of possible skeletons has then allowed the fine modulation of the electronic and configuration properties of these original structures, accounting for their use in various applications [1]. Numerous reactions using the chiral pool of the sulfoximines have been described in the field of asymmetric synthesis [2] and ligands for catalysis [3]. To a lesser extent, they also exhibit interesting properties for life science purposes [4] or as building blocks for the preparation of pseudopeptides [5]. Interestingly, a recent article

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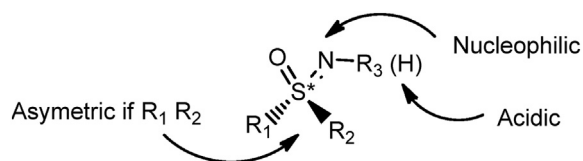*E-mail address:* emmanuel.magnier@uvsq.fr (E. Magnier).
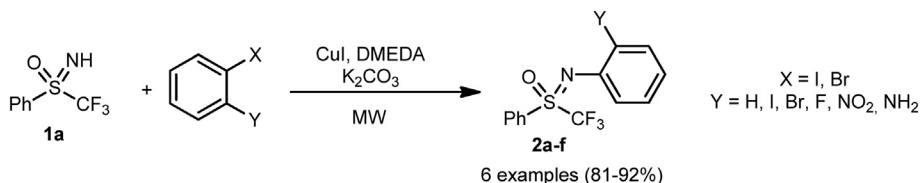
Fig. 1. General structure of sulfoximines.

has highlighted this particular heteroatomic group as a "neglected opportunity in life science" [6].

When one of the two groups (R_1 or R_2) bonded to the sulfur atom is a perfluoroalkyl chain, huge differences immediately appear whether it be for the synthesis or concerning the applications. Most of the synthetic routes reported for the preparation of nonfluorinated sulfoximines start from the corresponding thioethers or sulfoxides [7] and are not effective for the fluorinated series because of the tamed reactivity of the sulfur atom. Therefore, the synthesis of such compounds is a challenge for chemists. In 2009, a three-step methodology for the preparation of NH S-perfluoroalkylated sulfoximines was reported by our group paving the way for an extension of the structural diversity of these sulfur(VI) derivatives [8]. In the last decade, perfluoroalkylated sulfoximines were intensively studied because of their promising properties. They were described as highly electron-withdrawing substituents [9] or as building blocks for liquid crystals [10]. However, the most widespread applications involved their use as reagents for the transfer of the perfluoroalkyl group by electrophilic [11], nucleophilic [12], and very recently radical pathways [13]. In 2014, two reviews, independently written by Bolm et al. [14] and Shen and Hu et al. [15] have made a state in terms of syntheses, properties, and applications of fluorinated sulfoximines. This review will consequently focus on an overview of the new trends in this research area, since 2014. Accordingly, we will discuss the structural diversification of the skeleton of sulfoximines via N-functionalization or *ortho*-lithiation, their applications in catalytic and organocatalytic systems, their use as perfluoroalkylating reagents, and their potential as biologically active molecules.

2. Synthesis

2.1. N-Functionalization

We have previously demonstrated that the reactivity of the S-perfluoroalkylated sulfoximines depends on the group attached to the nitrogen atom [11f], highlighting thus the need for the development of efficient methods of N-functionalization of sulfoximines.

2.1.1. N-Functionalization of S-perfluoroalkylated sulfoximines

In 2011, our group described the copper-assisted N-arylation of perfluorinated sulfoximines [16]. However, this transformation required the reflux of toluene during several hours as reaction conditions. A slight improvement, using a microwave activation, enabled a significant reduction in the reaction time and an increase in the molecular diversity of the targeted N-arylated sulfoximines **2a−f** obtained in 81−92% yield (Scheme 1) [17].
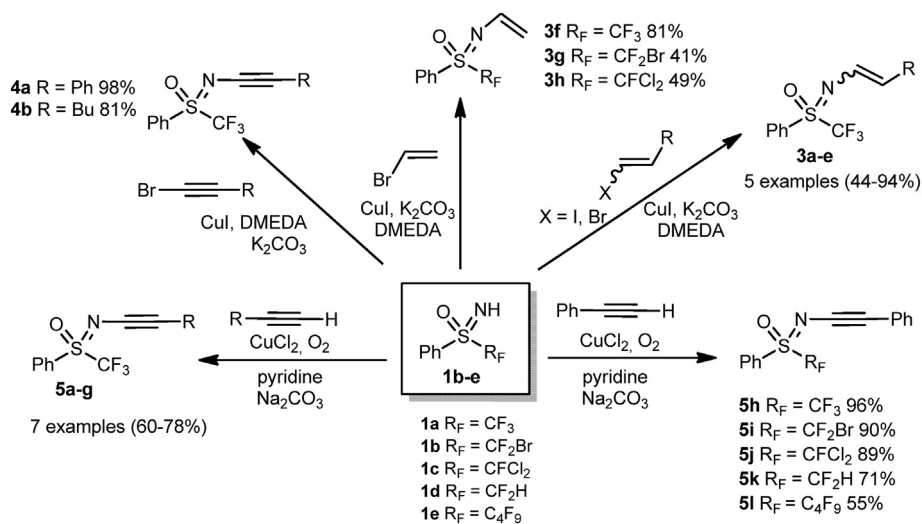
The copper-catalyzed preparation of N-alkenyl and N-alkynyl sulfoximines was consequently studied by our group [18]. A wide variety of N-alkenyl trifluoromethyl sulfoximines **3a−f** were synthesized in moderate to excellent yields (up to 94%) from the corresponding 1,2-disubstituted vinyl halides, with CuI as a catalyst, K_2CO_3 as a base, and DMEDA as a ligand (Scheme 2). This procedure was also extended to other perfluoroalkyl chains, in the presence of vinyl bromide, leading to the formation of **3g** and **3h** in moderate yield. The same reaction conditions, applied to bromophenylacetylene or 1-bromohexyne led to the formation of N-alkynyl sulfoximines **4a** and **4b** in 98% and 81% yield, respectively. The previous procedure did not succeed with phenylacetylene. Therefore, the reaction conditions were modified to perform the N-alkynylation of sulfoximines, using $CuCl_2$ as a catalyst, pyridine as a ligand, and Na_2CO_3 as a base, giving rise to products **5a−l** with good to excellent yields (55−96%).

We also demonstrated that the N-functionalization of sulfoximines could also occur via a nucleophilic pathway providing the use of smooth conditions (Scheme 3). The use of NaH and a catalytic amount of Bu_4NBr allowed the N-alkylation of the sulfoximine **1a** to give rise to compounds **6a** and **6b** with excellent yields. The nucleophilicity of the nitrogen atom of the sulfoximine was also underlined by the reaction between **1a** and phenylisocyanate to deliver sulfoximine thioureas **7a** and **7b**.

The presence of an iodine, bromine, or amino group in *ortho*-position in compounds **2** enabled a post-functionalization (Scheme 4). Bis-sulfoximines **8a** and **8b** were thereby synthesized with 76% and 81% yields, respectively, starting from dibromo- or diiodobenzene and the N-arylated sulfoximine **2a**. A two-step reductive amination delivered the molecule **10** in 97% yield, whereas the treatment of compound **2c** with isothiocyanate allowed the preparation of sulfoximine thioureas **9a** and **9b** in good yields.
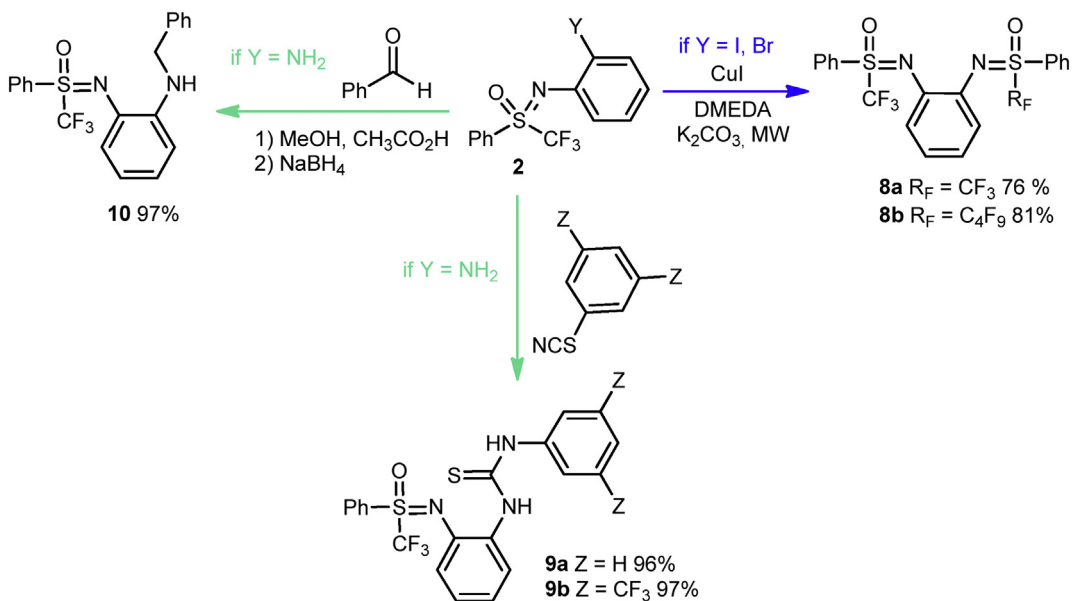
2.1.2. N-fluoroalkylation of sulfoximines

In 2015, Bolm et al. [19] reported that nonfluorinated sulfoximines can be successfully N-trifluoromethylated using a silver catalysis (Scheme 5). Twenty N-CF_3 sulfoximines **12** were synthesized by treatment of the
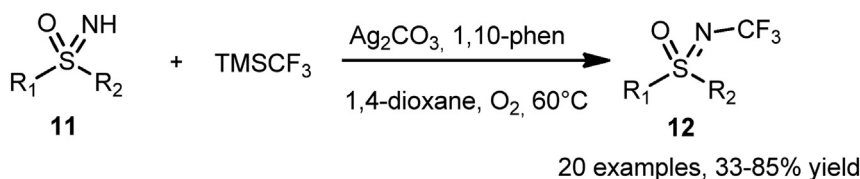

6 examples (81-92%)

Scheme 1. Copper-catalyzed N-arylation of sulfoximines.

Scheme 2. Copper-catalyzed N-alkenylation and alkynylation of sulfoximines.
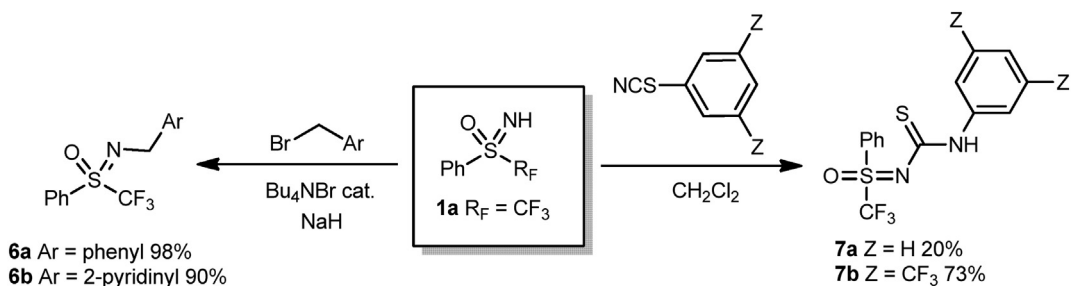
Scheme 3. N-functionalization of sulfoximines via a nucleophilic pathway.

Scheme 4. Postfunctionalization of N-substituted sulfoximines.

Scheme 5. Silver-mediated N-trifluoromethylation of sulfoximines.

corresponding *N*H-sulfoximines **11** with Ag_2CO_3 as the catalyst, 1,10-phenanthroline as the ligand, and $TMSCF_3$ as a fluorine source, with yields ranging from 33% to 85%.

Because of radical scavengers inhibiting the reaction, Bolm et al. proposed a radical pathway for this transformation (Scheme 6).

The same group also achieved the N-trifluoromethylthiolation starting from *N*-bromosulfoximines **13a**–**l** [20]. Treated by $AgSCF_3$ in acetonitrile, the latter gave rise to a new class of *N*-SCF_3 sulfoximines **14a**–**l** in good to excellent yields (51–98%) (Scheme 7).

The specific behavior of the sulfoximine **1a** was emphasized in this work. A one-pot cascade was set up to ensure the preparation of the *N*-SCF_3 sulfoximine **14n** with moderate yield (Scheme 8).

2.2. Perfluorinated sulfoximines as *ortho*-directing metalation group

Another challenge was the late functionalization of the aromatic ring directly bonded to the sulfur atom. In 2016, our group disclosed the first use of *N*H *S*-trifluoromethyl sulfoximines as an *ortho*-directing group [21]. The sulfoximine **1a** was treated with *n*-BuLi to form an *ortho*-lithiated intermediate, which was quenched with various electrophiles to deliver the functionalized sulfoximines **15a**–**m** with moderate to very good yields (Scheme 9). This reaction demonstrated a broad substrate scope as it enabled the introduction of halogens (**15a**–**c**), alcohol function (**15m**), azido group (**15h**), and allyl group (**15e**). Sulfur derivatives
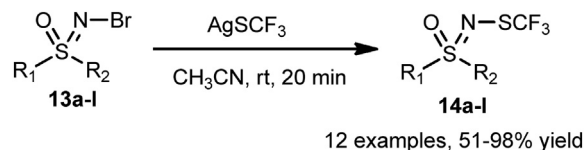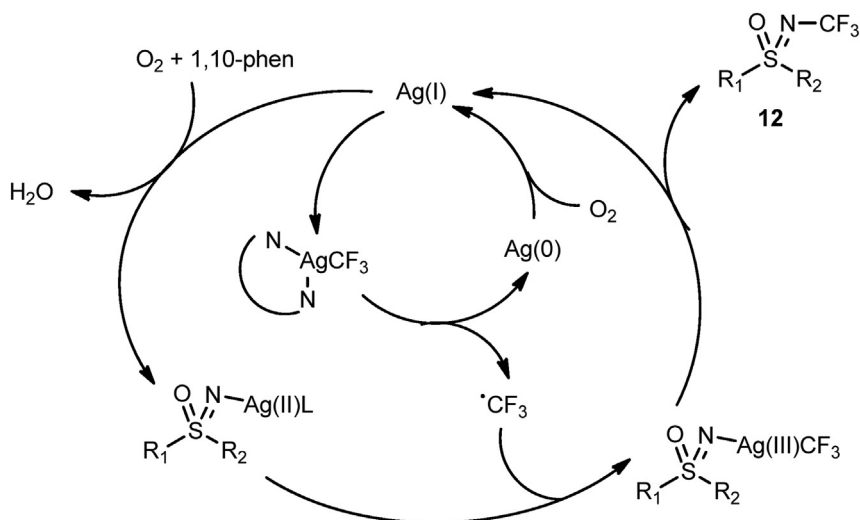

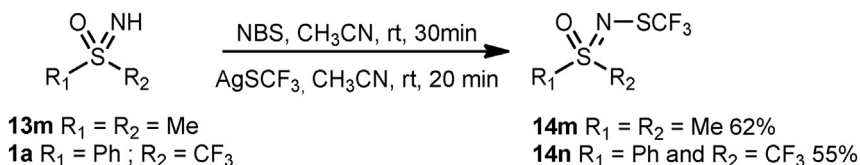**Scheme 7.** N-Trifluoromethylthiolation of nonfluorinated sulfoximines.

were also successfully synthesized (**15i**–**k**), as well as stannylated (**15f**), borylated (**15l**), and silylated (**15g**) molecules. Most of the isolated compounds possess reactive functions paving the way to further functionalization of the aromatic part by cross-coupling reaction. It is noteworthy that no N-functionalization was observed.

Nevertheless, thanks to the proper choice of an electrophile, this N-functionalization occurred and cyclic sulfoximines **16a**–**d** isolated (Scheme 10).

The deprotonated sulfoximine **1a** reacted with phenylisocyanate to give **16a** in 77% as sole diastereoisomer, the structure of which was confirmed by an X-ray analysis. When hexafluorobenzene was used as an electrophile, an additional treatment by K_2CO_3 was necessary to complete the full cyclization and give compound **16b** in 56% yield. Finally, the use of DMF as an electrophile delivered two different cyclic derivatives, depending on the final treatment of the reaction. Thus, final addition of water produced the sulfoximine **16c**, whereas a quench by a saturated solution of NH_4Cl led to the compound **16d**.

Scheme 6. Mechanism of the N-trifluoromethylation of sulfoximines.

Scheme 8. One-pot N-trifluoromethylthiolation of **1a** and **13m**.

2.3. Isolation of enantiomerically pure fluorinated sulfoximine

As mentioned in Section 1, the sulfoximine entity becomes chiral when R_1 is different from R_2 (Fig. 1). Nonfluorinated enantiomerically pure sulfoximines were extensively used in asymmetric synthesis as ligand, as pool chiral, or as chiral leaving group [1a,22]. Unfortunately, all the methods described for the preparation of the enantiopure sulfoximines failed to be adapted to the *S*-perfluoroalkyl series. To date, and to the best of our knowledge, no direct preparation of optically active *S*-perfluoroalkyl sulfoximines has been described. However, we succeeded in the separation of the two enantiomers of sulfilimine **18** [23] by supercritical fluid chromatography [24] (Scheme 11). They proved to be stable and no epimerization was detected even after several weeks at room temperature. The relative configuration has been secured, thanks to an X-ray analysis.

Further oxidation of each enantiomer of the sulfilimines **19a** and **19b** with KMnO$_4$ proceeded with retention of the relative configuration to give rise to the two enantiomers of **1a**. The scope of this procedure was then explored to other fluoroalkylated compounds and enabled the isolation of optically pure **1b** and **1c**. The enantiomerically pure version of the Shibata reagent **21** [11a] was also prepared from (*S*)-**1a** with an 85% global yield (Scheme 12).

3. Application

3.1. Application of perfluorinated sulfoximines in catalytic systems

Some bis-sulfoximines and sulfoximine thioureas prepared by our group [17] (Section 2.1.1) were investigated through model reactions, already described with nonfluorinated sulfoximine: a hetero Diels–Alder (HDA) reaction [25], a Mukaiyama-type aldol reaction [26], and a Biginelli reaction [27]. The HDA reaction was performed between cyclohexadiene **22** and the α-ketoester **23** catalyzed by a copper catalyst in the presence of **8a** as ligand

(Scheme 13). The adducts **24a** and **24b** were isolated in 51% and 55% yield, respectively. They are slightly lower to those obtained with the nonfluorinated bis-sulfoximine **25** (62% and 95% yield).

The sulfoximine **10** associated with Cu(OTf)$_2$ proved to be efficient to catalyze a Mukaiyama-type aldol reaction. The compound **28** was isolated with 50% yield, which is comparable to the one obtained with the nonfluorinated bis-sulfoximine **29** (Scheme 14).

The potential of **9a** and **9b** as organocatalysts was also compared to their nonfluorinated analogues in a Biginelli reaction between the benzaldehyde, the β-ketoester **30**, and the urea **31** (Scheme 15). This reaction enabled to set out **32** with a good yield.

Finally, the efficiency of these ligands was performed with a Friedel–Crafts reaction between the indole **33** and the β-(*E*)-nitrostyrene **34** (Scheme 16). Without catalyst, the product **35** was obtained in a 34% yield, compared to a 65% yield, in the presence of sulfoximine **9b**, demonstrating for the very first time the catalytic effect of a perfluoroalkylated sulfoximine for such a transformation. The same reaction with the enantiomerically pure sulfoximine (*R*)-(+)-**9b** delivered any asymmetric induction.

3.2. Biologically active compound

To increase the chemical diversity of the family of glucokinase-glucokinase regulatory protein (GK-GKRP) disruptors, the sulfoximine group was introduced as a bioisostere of the trifluoromethyl carbinol group of the bioactive compound **36** [28]. First, the carbinol moiety was replaced with sulfones and sulfonamides because of their three-dimensional features, important for the interactions with the targeted protein GKRP. A wide range of derivatives such as molecules **37a** and **37b** were synthesized, but revealed only weak to moderate disruptor properties (Fig. 2). The sulfoximine moiety was afterward evaluated. Its mildly basic nitrogen function and chiral sulfur center could indeed mimic the chiral trifluoromethyl carbinol group of compounds **36**. Although the nonfluorinated sulfoximine **38a** gave disappointing results, the *N*H-*S*-
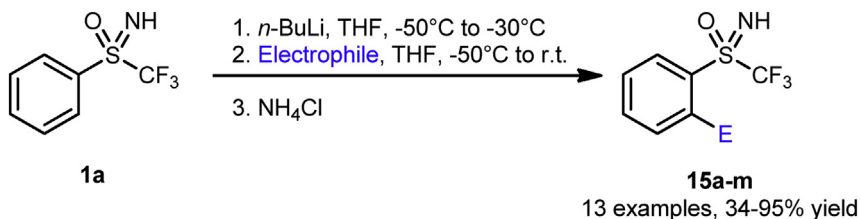

Scheme 9. *Ortho*-functionalization of **1a**.
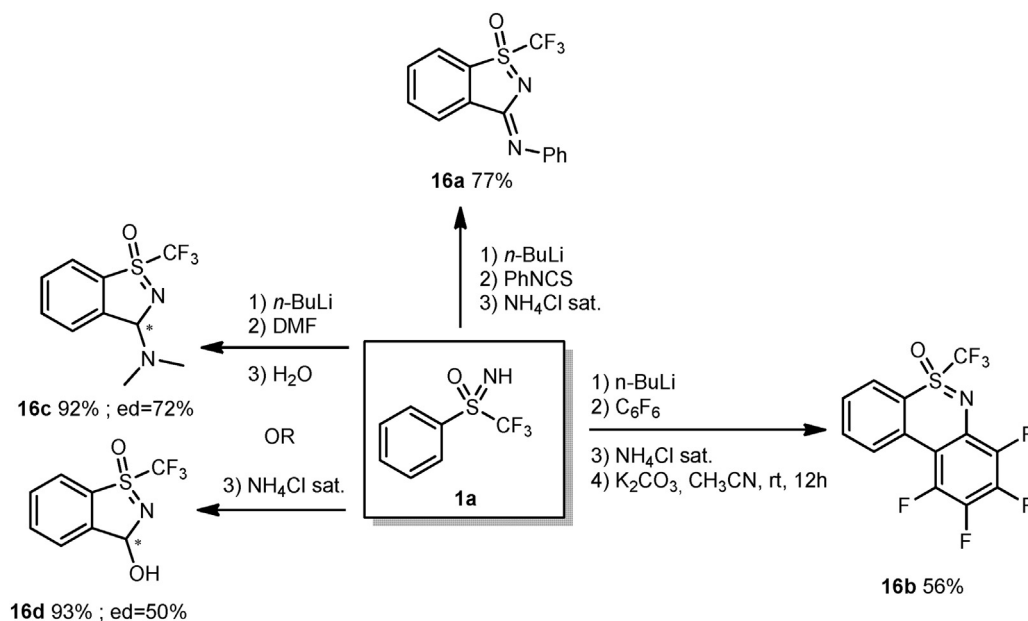
Scheme 10. Synthesis of cyclic sulfoximines 16.

trifluoromethyl sulfoximine 38b was approximately seven times more potent than the parent molecules 36. The (S)-NH-S-trifluoromethyl sulfoximine (S)-38b was found to have favorable in vivo pharmacokinetic properties in rodents and produced a significant reduction in blood glucose levels (about 40—58%, 6 h after dose at 100 mg/kg) when dosed orally in db/db mice.

3.3. Perfluorinated sulfoximines as perfluoroalkylating reagent

The introduction of fluoroalkyl groups into molecules is a modern and very important challenge. In the past decades, fluorinated sulfoximines have emerged as promising and efficient fluoroalkylating reagents through the work of
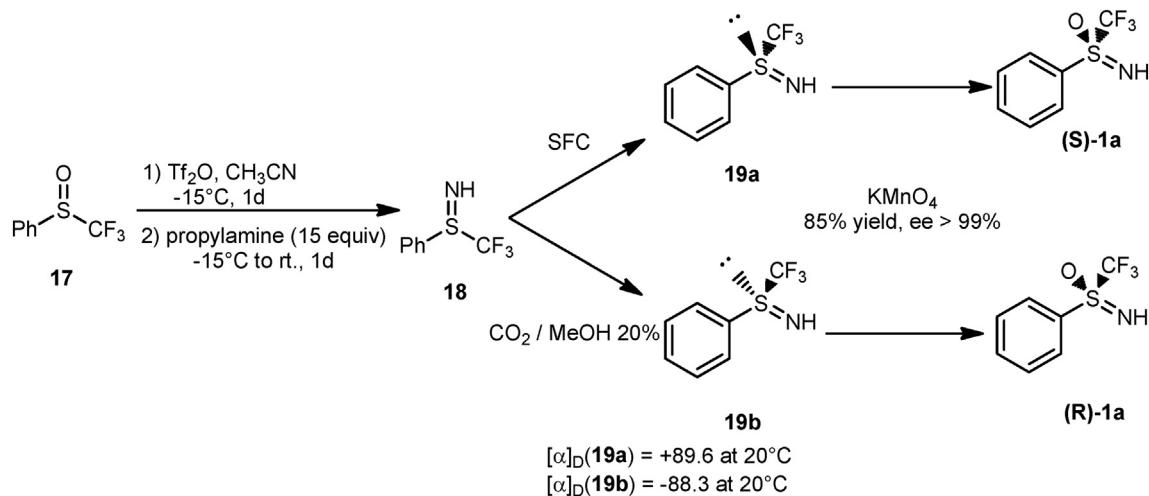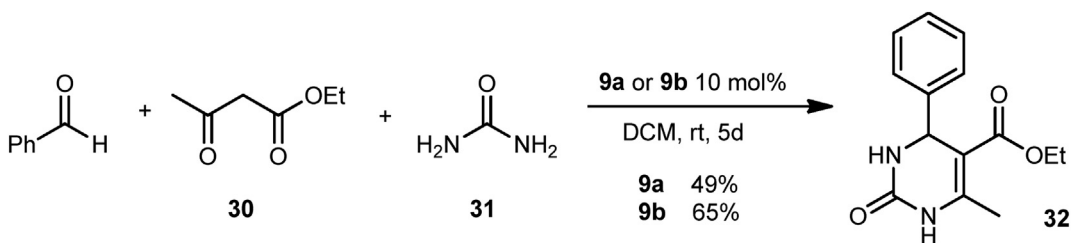

Scheme 11. Preparation of enantiomerically pure sulfoximines. SFC, supercritical fluid chromatography.
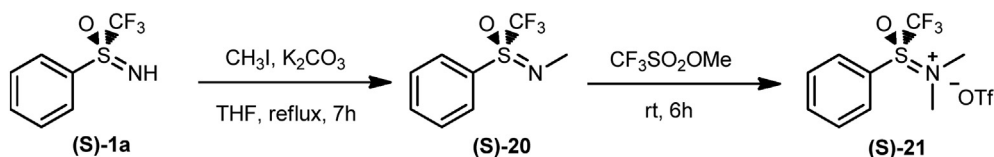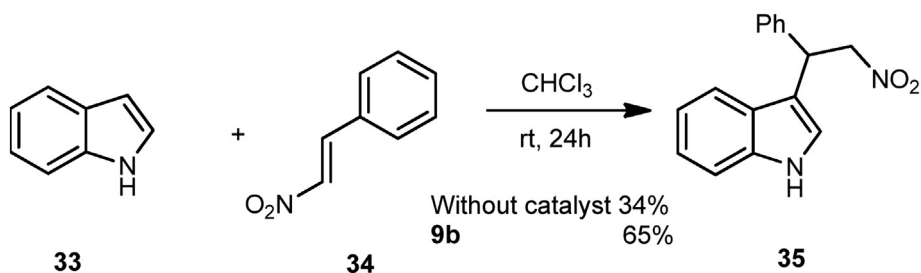

Scheme 12. Preparation of the enantiopure Shibata reagent 21.
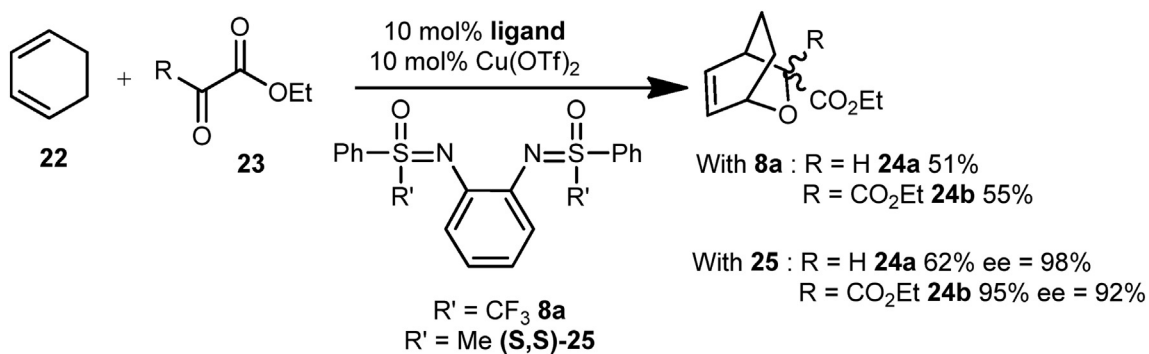
Scheme 13. HDA reaction copper-catalyzed with bis-sulfoximine **8a** as ligand.
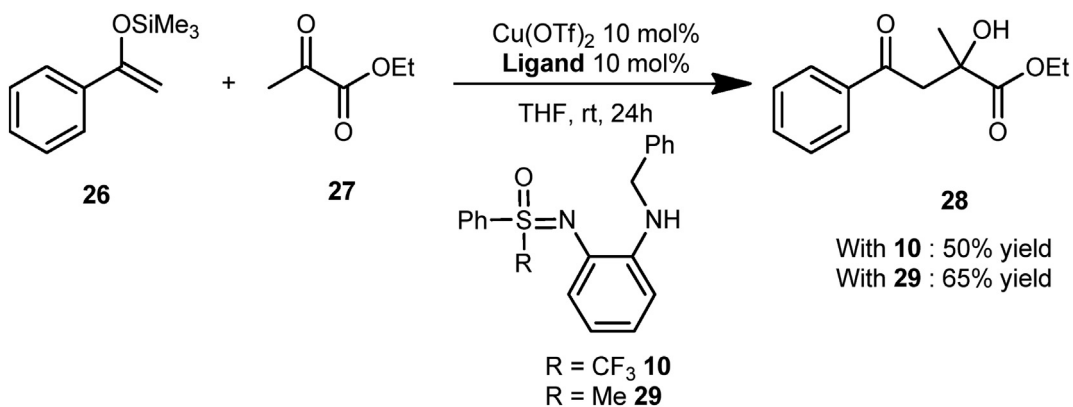
Scheme 14. Mukaiyama-type aldol reaction.

Scheme 15. Biginelli's reaction.

Scheme 16. Friedel−Crafts reaction.

36a X=CF$_3$ IC$_{50}$ = 4 nM
36b X = CH$_3$ IC$_{50}$ = 9 nM

37a X=CH$_3$ IC$_{50}$ = 0.401 μM
37b X = NH$_2$ IC$_{50}$ = 0.035 μM

38a X=CH$_3$ IC$_{50}$ = 0.301 μM
(R)-38b X = CF$_3$ IC$_{50}$ = 0.0182 μM
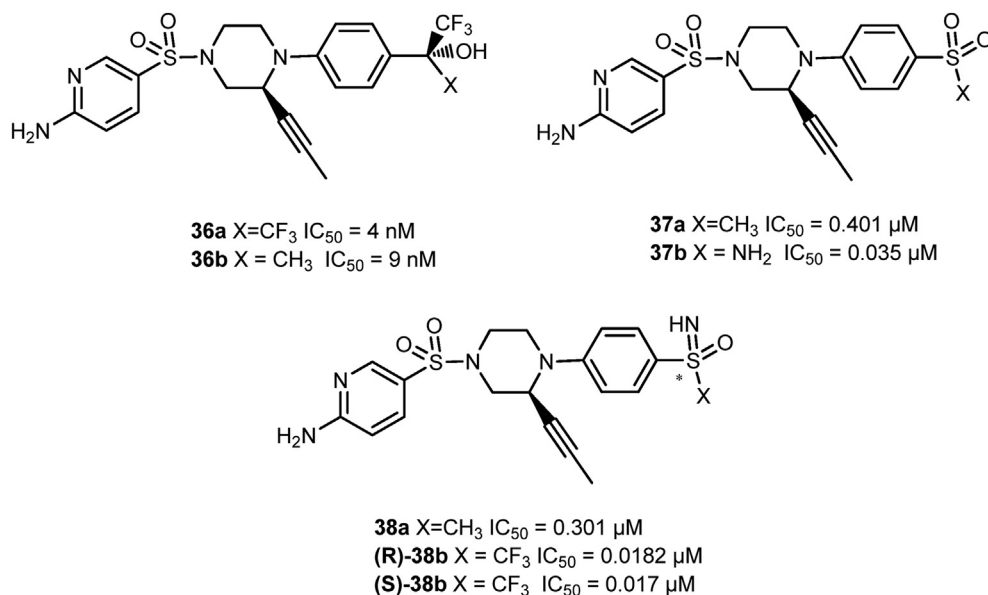**(S)-38b** X = CF$_3$ IC$_{50}$ = 0.017 μM

Fig. 2. Analogues of GK-GKRP disruptors.

Shibata and co-workers [11a,c,g], Hu and co-workers [11b,12], and Prakash et al. [11e] and also by our group [11f] (Fig. 3).
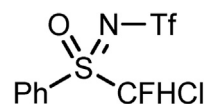
3.3.1. Electrophilic pathway

Sulfoximines were described as electrophilic perfluoroalkylating reagent [11]. Our group proposed recent extension. We reported the first example of electrophilic chlorofluoromethylation [29], thanks to a new sulfoximine **41** reagent (Fig. 4).

Its electrophilic activity was compared to Hu's reagent **39** in the perfluoroalkylation of the β-ketoester **42**. In the reaction conditions previously described by Shibata et al. [11c], Hu's reagent **39** gave a mixture of C-alkylated **43a** and O-alkylated **44a** derivatives whereas reagent **41** reacted to give the C-alkylated compound **43b** as the sole product with 40% yield (Scheme 17). It is noteworthy that a study of this C/O-selectivity was carried out in 2014 by Shibata et al. [11d].

We proposed a carbenic pathway for this transformation based on previous mechanistic studies from Hu's group and our own (Scheme 18).

The carbenic pathway A was proved to be the most plausible, even if the pathway B could not be totally excluded.

41

Fig. 4. New electrophilic reagent **41**.

3.3.2. Nucleophilic pathway

In 2014, Hu et al. [30] developed a new efficient and regioselective nucleophilic ring-opening difluoromethylation of epoxides using a difluoromethyl sulfoximine **46**. This strategy was successfully applied to a wide variety of three- and four-membered oxacycles **45** as substrates, leading to compounds **47** in good to excellent yields (Scheme 19). This regioselective reaction took place at the less hindered position of the oxacycles.

The difluorinated species **47** can be engaged in further transformation to form β-difluoromethyl alcohol **48** by reductive desulfoximination or β-difluoromethylenyl alcohol **49** by elimination process (Scheme 20).

More recently, Hu et al. described the preparation of a wide range of arylfluoroepoxides **52** (Scheme 21) using perfluoroalkyl sulfoximines [31]. These fluoroepoxides
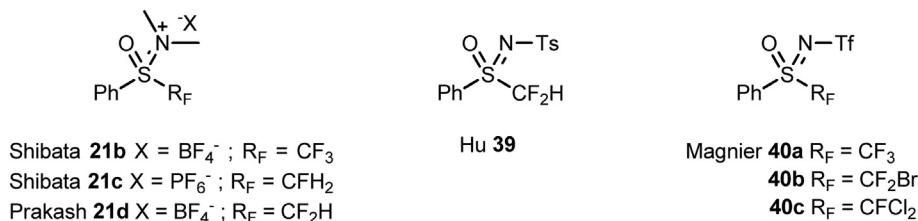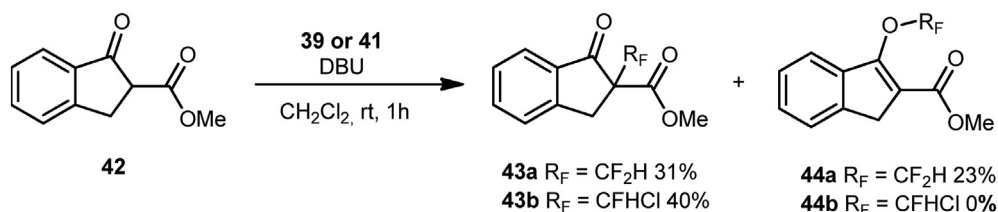

Shibata **21b** X = BF$_4^-$; R$_F$ = CF$_3$
Shibata **21c** X = PF$_6^-$; R$_F$ = CFH$_2$
Prakash **21d** X = BF$_4^-$; R$_F$ = CF$_2$H

Hu **39**

Magnier **40a** R$_F$ = CF$_3$
40b R$_F$ = CF$_2$Br
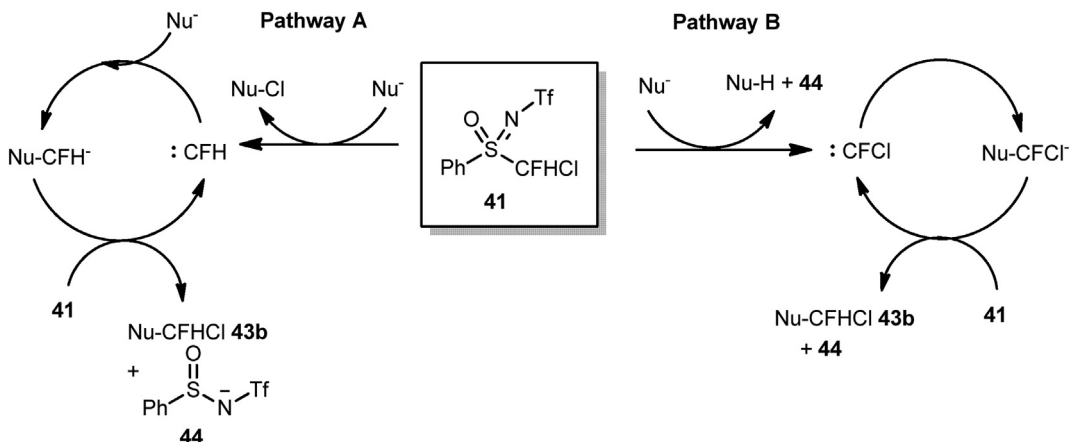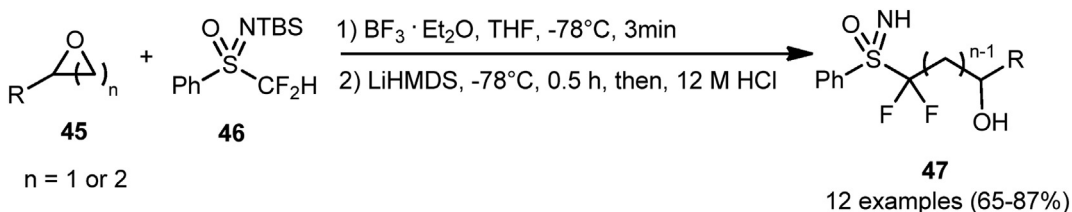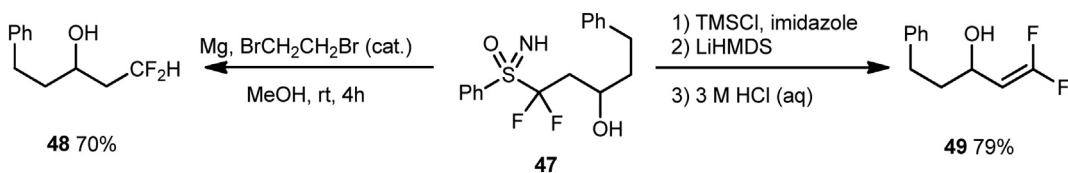**40c** R$_F$ = CFCl$_2$

Fig. 3. Overview of sulfoximines as fluoroalkylating reagents.

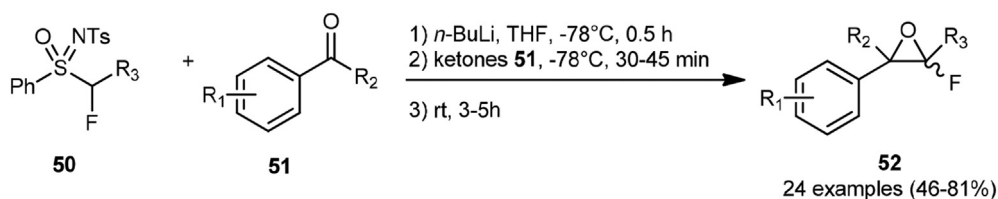**Scheme 17.** Reactivity of **39** and **41** toward β-ketoesters.

Scheme 18. Proposed mechanism.

Scheme 19. Nucleophilic difluoromethylation of three- and four-membered oxacycles.

Scheme 20. Synthetic utility of ring-opened compounds.

Scheme 21. Synthesis of arylfluoroepoxides.

could be isolated without significant decomposition and were next engaged in a Brønsted acid–catalyzed 1,2-fluorine migration.

In 2017, the same group reported a stereoselective synthesis of terminal monofluoroalkenes [32] through a Julia-Kocienski–type reaction. A wide variety of aromatic carbonyl compounds **54** were successfully transformed into monofluoroalkenes **55** in the presence of the sulfoximine **53** (Scheme 22).

The reaction tolerated many substituents on the aromatic ring, such as bromine, methoxy, benzoxy, methylthio groups, and heteroaromatic groups.

3.3.3. Radical—Advent of the photoredox-catalyzed fluoroalkylation

In recent years, the visible light photoredox catalysis has emerged as one of the most promising strategies for the introduction of fluorinated moiety into organic molecules. In 2016, Akita et al. described the direct hydroxydifluoromethylation of alkenes by photoredox catalysis [13] using Hu's reagent **39** at room temperature with visible light irradiation (Scheme 23).

The reaction conditions were successfully applied to a wide range of styrenes. Various functional groups, such as halogens, boronic acid esters, and cyanomethyl- and Boc-protected amino groups, are well tolerated

delivering a set of alcohols with yields up to 88%. The reaction was also carried out on the aliphatic dicyclohexylethene leading to the corresponding alcohol **57** with a 32% yield. Moreover, the hydroxydifluoromethylation of internal and trisubstituted alkenes was also possible with this photocatalytic reaction. Alcohols and carboxylic acids ROH were tested as nucleophiles, leading to the CF_2H-containing ethers **58a,b** and esters **58c** (Scheme 24).

Akita et al. proposed a radical pathway for this transformation (Scheme 25). The photocatalyst is excited by blue light to the species *Ir^III able to reduce Hu's reagent **39** delivering then the CF_2H radical. Its addition, alkene **56** generates an intermediate, which is then oxidized by Ir^IV. The resulting carbocationic intermediate is finally trapped by a nucleophile to give rise to the oxydifluoromethylated products **57** or **58**.

The same year, Akita et al. extended the previous reaction to the synthesis of CF_2H-spiroethers **60**, using Hu's reagent **39** and *fac*-[Ir(ppy)₃], under similar reaction conditions [33]. These CF_2H-spiroethers were synthesized in moderate yield, but with good diastereoselectivities in an *anti*-fashion (Scheme 26).
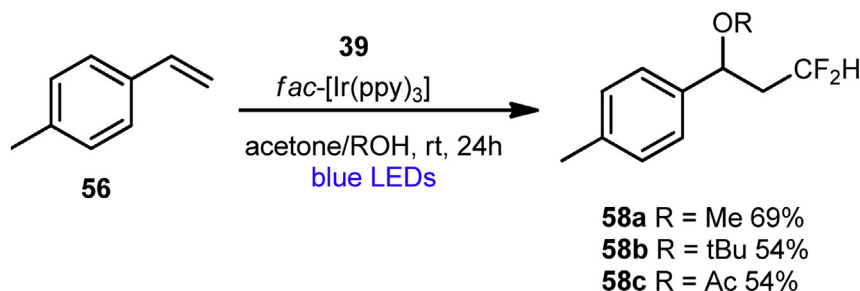
The authors proposed that the alcohol attacks in an *anti*-fashion because of the electronegativity of the fluoromethyl group.
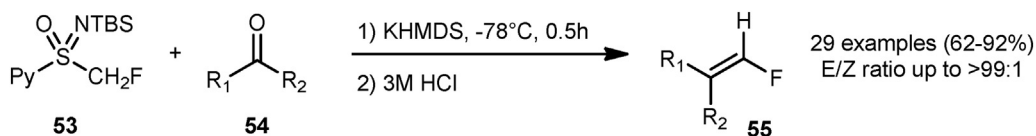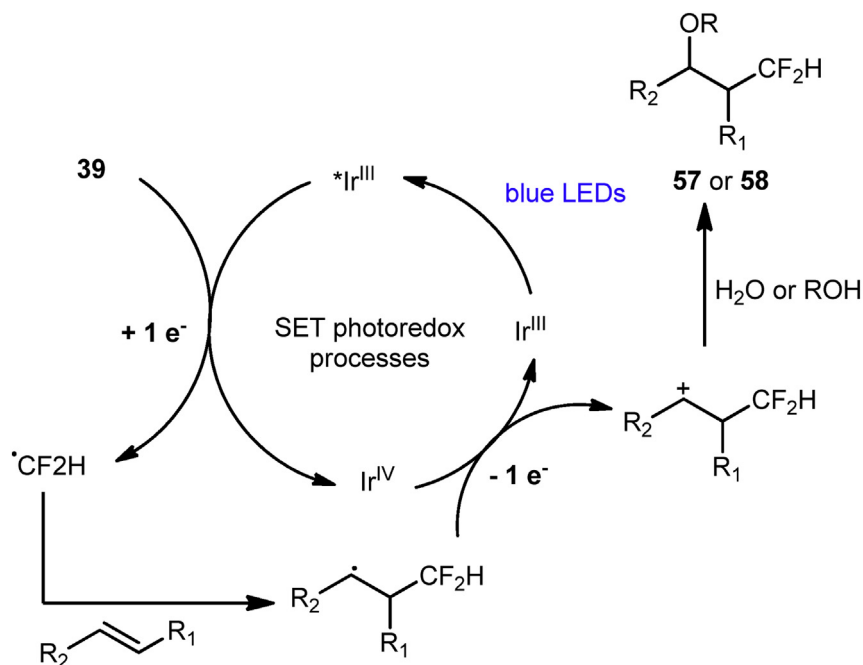

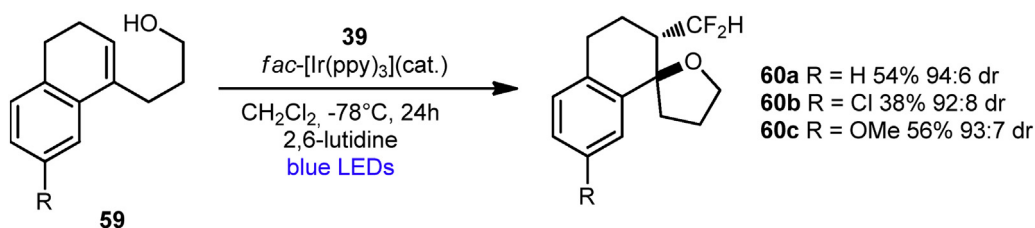**Scheme 22.** Stereoselective synthesis of terminal monofluoroalkenes.
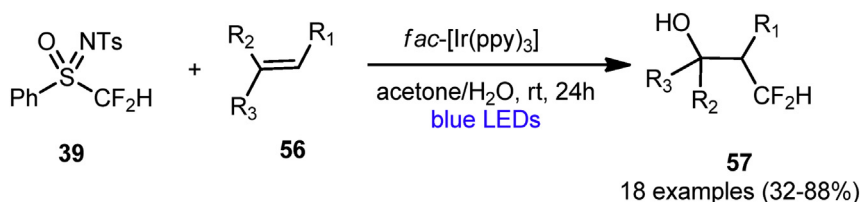
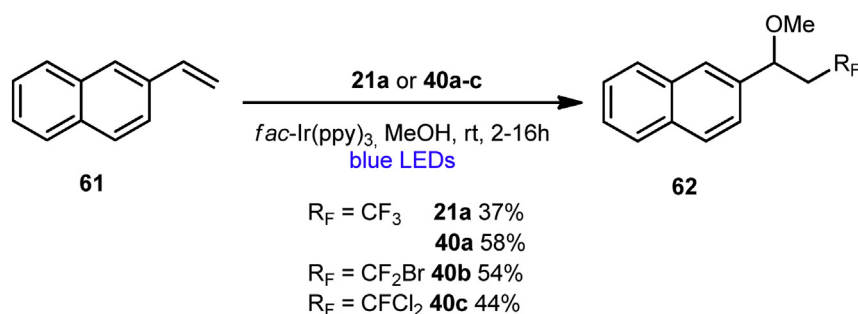**Scheme 23.** Hydroxydifluoromethylation of alkenes via photoredox catalysis.

Scheme 24. Oxydifluoromethylation of styrenes.

Scheme 25. Proposed mechanism for the oxydifluoromethylation.

60a R = H 54% 94:6 dr
60b R = Cl 38% 92:8 dr
60c R = OMe 56% 93:7 dr

Scheme 26. Synthesis of CF$_2$H-containing spiroethers.

R$_F$ = CF$_3$ **21a** 37%
          40a 58%
R$_F$ = CF$_2$Br **40b** 54%
R$_F$ = CFCl$_2$ **40c** 44%

Scheme 27. Methoxyperfluoroalkylation of vinylnaphthalene **61**.

More recently, our group has developed a new oxy-perfluoroalkylation method by photoredox catalysis using sulfoximines **21a** and **40a** as sources of trifluoromethyl radicals [34]. With optimized reaction conditions, using *fac*-Ir(ppy)$_3$ as the photocatalyst and methanol as both solvent and nucleophile, under blue LED irradiation, methoxyfluorinated compound **62** have been synthesized with moderate yield (Scheme 27). During the same work,

we demonstrated the potential of sulfoximines **40b** and **40c** for the methoxy mono- and di-fluoromethylation of vinylnaphthalene.

4. Conclusions

After a long period of latency, the chemistry of *S*-per-fluoroalkylated sulfoximines is rising up. This could be

explained by both the extended availability of the starting materials, thanks to the progress realized for their preparation, and by the increasing applications offered by these uncommon moieties. We have summarized in this short review all the recent developments, and we are fully convinced that they will exponentially grow in close future.

Acknowledgments

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