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Photoredox Fluoroalkylation of Hydrazones in Neutral and Reductive Modes

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Abstract. Visible light promoted fluoroalkylation of hydrazones using 4-perfluoropyridine sulfides as fluoroalkyl radical sources is described. The process can proceed in neutral and reductive modes delivering either hydrazones or hydrazines, respectively, depending on structure of starting substrates and reaction conditions. For the reductive process, ascorbic acid is used as a terminal reductant, which recycles the photocatalyst and serves as a source of hydrogen towards nitrogen-centered radicals.

Keywords: fluorine; photocatalysis; hydrazones; radical reactions; fluoroalkylation

Addition to carbon-nitrogen (azomethine) double bonds is a fundamental transformation in organic synthesis.[1,2] While the most widely used reactions of azomethines are based on addition of nucleophiles,[1] emerging radical approaches[2,3] provided an elegant solution for a number of innate anionic chemistry problems e.g. substrate enolization and low C=N bond electrophilicity. Among various azomethines, hydrazones have one of the highest rates of radical addition[2a] and therefore they became the most suitable substrates for this process.[3]

Hydrazone and hydrazine scaffolds are common motifs in structures of a number of bioactive compounds and even commercial top selling drugs[4] (Figure 1). Moreover, hydrazones are often used as valuable intermediates in organic synthesis,[5] such as equivalents of carbonyl compounds[6] or precursors of heterocycles.[7] Therefore, radical processes involving hydrazones gained significant attention over the last decades.

Due to unceasing demand of organofluorine compounds in pharmaceutical and agrochemical industries,[8] addition of fluorinated radicals to hydrazones represents a transformation of great importance. While addition of alkyl radicals to hydrazones was very well studied, first successful

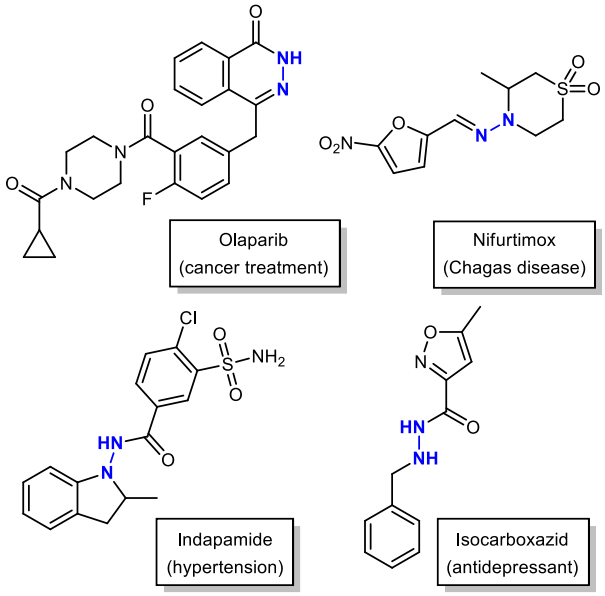

Figure 1. Commercial drugs containing hydrazone and hydrazine motif.

attempt of perfluoroalkyl radical addition was reported only in 2013 using Togni reagent,[9] which was followed by a surge of papers[3b,c,10] (Scheme 1, path a). Transition metals such as copper,[10a-c] silver[10d] and palladium[10e] in combination with activated fluoroalkyl halides, Togni, Langlois or Ruppert-Prakash reagents were employed for the generation of fluorinated radicals, though metal-free conditions were also reported.[10f]

Since visible light photoredox catalysis can provide very mild conditions for the radical formation,[11] hydrazone fluoroalkylation using iridium[12a,b] and gold[12c] metal complexes, as well as organic photocatalysts,[12d-f] was also documented. Noteworthy, certain hydrazones were reported to react with perfluoroalkyl iodides by direct photoinduced single electron transfer in the absence

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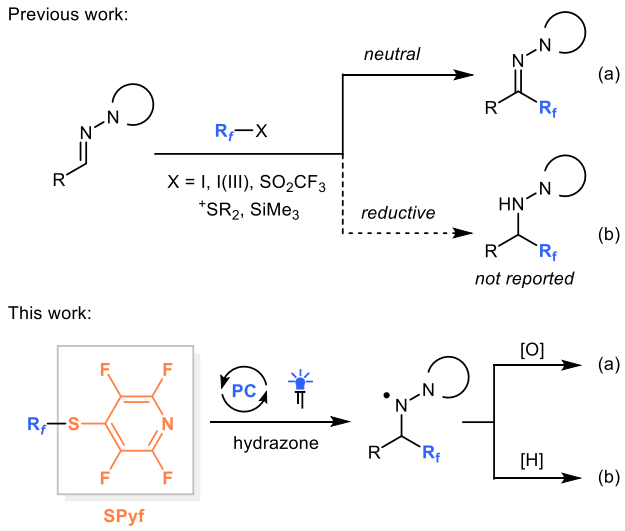

Scheme 1. Radical reactions of hydrazones.

of any sensitizer.[13] In all these cases, radical perfluoroalkylation of hydrazones generally leads to formal sp^2-functionalization product, which corresponds to electron neutral process (Scheme 1, path a). To the best of our knowledge, no reductive addition of fluorinated radicals to hydrazones leading to hydrazines has been reported (path b). It is noteworthy that visible light induced reductive addition of non-fluorinated radicals derived from redox-active esters[14a] or bis(catecholato)silicates[14b,c] to C=N double bond was extensively studied. In those approaches, Hantzsch ester or DIPEA were applied as hydrogen atom donors.

Recently, we introduced reagents bearing 4-tetrafluoropyridinylthio group as precursors of radicals under photoredox conditions, and they were coupled with silyl enol ethers, nitrones and alkenes.[15] In this work we present our findings on their reactions with most common types of hydrazones. We demonstrate that by choice of conditions, the process may be directed to either neutral or reductive pathway.

Hydrazone **1a** derived from 4-chlorobenzaldehyde and *N*-aminomorpholine and difluoromethyl sulfide **2b**, which can be readily obtained starting from pentafluoropyridine,[15a] were selected as model substrates, and their reaction was evaluated under blue LED irradiation (Scheme 2, Optimization). The reaction was best performed in the presence of *fac*-$Ir(ppy)_3$ (0.25% mol) as photocatalyst leading to product **3b** corresponding to the neutral mode of addition. The reaction did not proceed without light, but, surprisingly, noticeable yield 45% of **3b** was observed in the absence of photocatalyst. For **3h**, single X-ray structure was determined.[16]

Variation of solvents revealed that polar aprotic solvents are preferable for the reaction, with dimethyl sulfoxide affording the best results. Addition of water (10 equiv) did not shut down the reaction, though led to a reduced yield (54%). Base is important for scavenging the produced acid with 1 equiv of zinc acetate providing the highest yield of **3b**. Use of 0.6 equiv of the zinc salt gave small decrease in the yield, while other bases such as collidine and sodium bicarbonate gave inferior results. Highly nucleophilic DABCO led to degradation of starting sulfide, presumably, owing to aromatic fluorine substitution in the pyridine ring. The beneficial effect of zinc salts for reactions of PyS-compounds may be ascribed to its ability to tightly bind thiolate by-product.

With optimal conditions in hand, we evaluated the applicability of the method to various types of fluorinated groups and hydrazones (Scheme 2, Overview). Thus, a range of PyfS-reagents **2a-d**, differing in a number of fluorines and serving as sources of radicals CF_nH_{3-n} (n = from 3 to 0) was prepared. As azomethines, besides N-aminomorpholine hydrazone **1a**, we also considered conventional N-benzoylhydrazone **1c**, as well as amidrazone **1b**, which has recently been introduced by our group.[17] The addition of trifluoromethyl and difluoromethyl radicals was quite effective for morpholine derived hydrazone **1a** and amidrazone **1b**. Addition of fluoromethyl radical to **1a** did not proceed, and only in case of **1b** the expected product was observed by ^{19}F NMR (around 17% yield). Non-fluorinated methyl radical was unreactive; however, traces of methylated products were detected by GC-MS analysis. As for benzoyl hydrazone **1c**, it did not give products with all set of radicals under standard conditions.

Next, the method was tested with the scope of more complex fluorinated radical precursors and hydrazone acceptors (Scheme 2, Scope). Thus, *gem*-difluorinated radicals (RCF_2) generated from the PyfS-reagents accessible from 1,1-difluoroalkenes[15a] were found to be of reactivity similar to that of difluoromethyl radical, significantly expanding the area of the approach. Perfluorinated *n*-propyl radical reacted smoothly furnishing product **3g**. The reaction is tolerant to electron-rich and electron-poor aromatic rings both in hydrazone and radical counterparts with product yields ranging from 53% to 91%. Pyridine ring, which is amenable to Minisci-type radical alkylations,[18] remained unaffected with the corresponding product **3f** obtained in 76% yield. Isobutyraldehyde derived hydrazone gave the desired product **3k** in a decreased yield of 41%.

Further, we investigated the reactions of hydrazones under reductive conditions. We focused on a photocatalytic system involving ascorbic acid as a stoichiometric reductant recently developed by our group.[19] When combined with difluoromethyl reagent **2b**, *N*-benzoylhydrazone **1c** was found to be the most appropriate substrate leading to hydrazine **4a** in excellent yield (Scheme 3, Optimization). Besides ascorbic acid, various sources of hydrogen such as Hantzsch ester, boron hydrides and silanes were ineffective. Under the optimized reductive conditions, we evaluated other sulfides **2a,c,d** with hydrazones **1a-c** (Scheme 3, Overview). Thus, hydrazones **1a,b** effectively reacted with trifluoromethyl and difluoromethyl radicals, but

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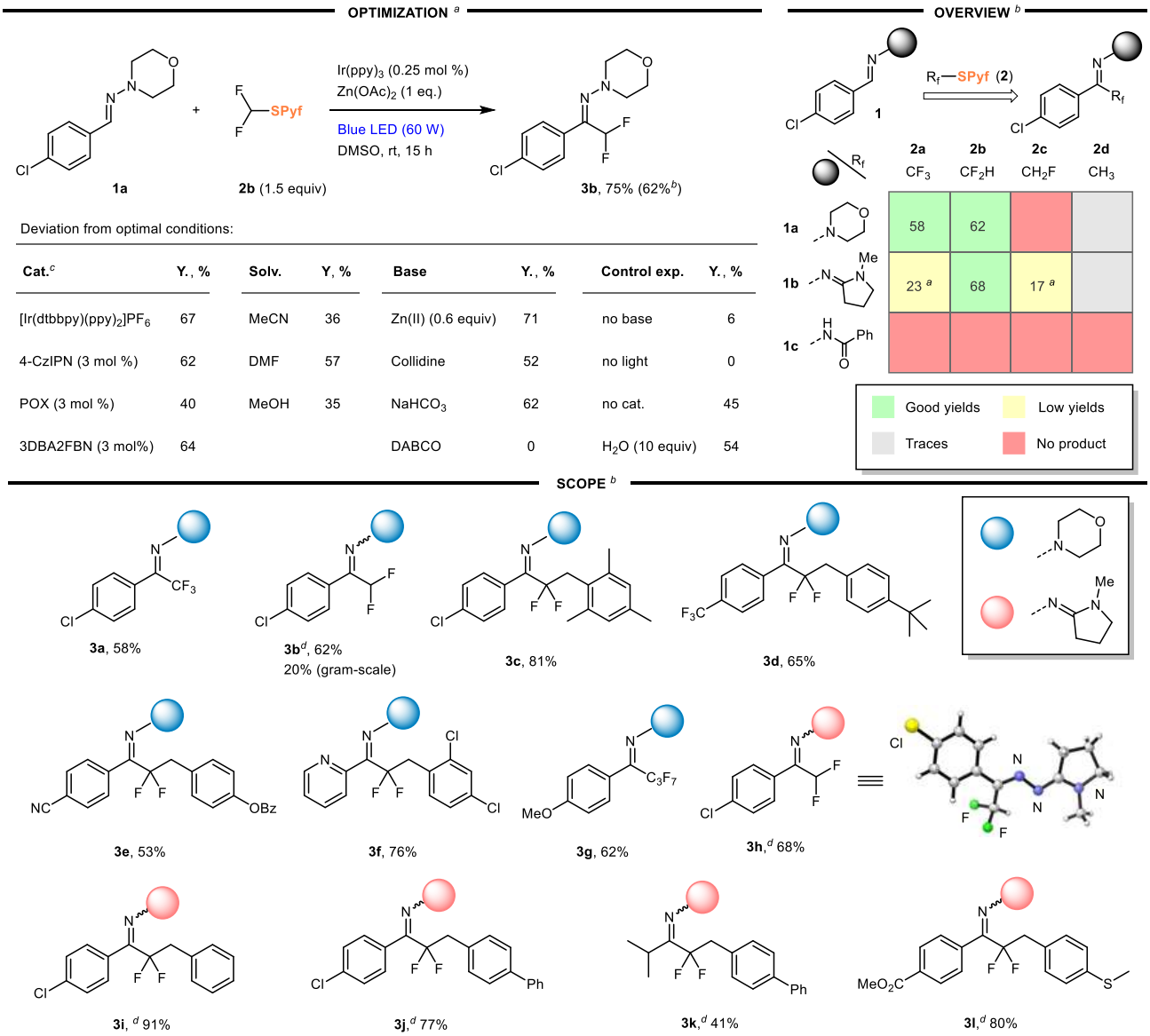


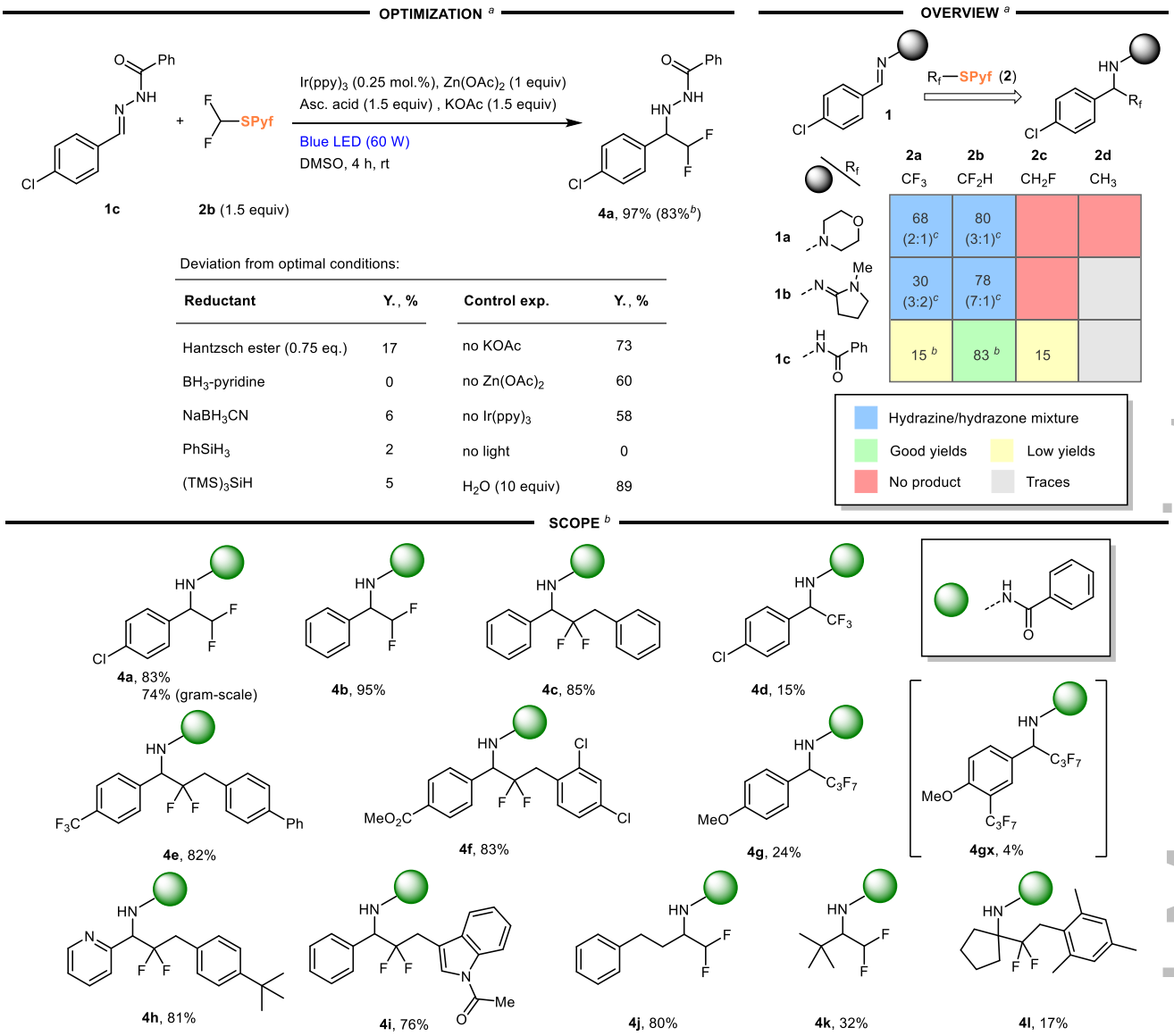
[a] ^{19}F NMR yields using $PhCF_3$ as internal standard. [b] Isolated yield. [c] Abbreviations: dtbbpy, 4,4'-di-tert-butyl-2,2'-bipyridine; ppy, 2-phenylpyridinato-C^2; 4-CzIPN, 2,4,5,6- tetra(9*H*-carbazol-9-yl)isophthalonitrile; POX, 3,7-dibiphenyl-4-yl-10-(1-naphthyl)-10*H*-phenoxazine; 3DPA2FBN, 2,4,6-tris(diphenylamino)-3,5-difluorobenzonitrile. [d] Isolated as a mixture of two C=N isomers (see SI for details).

Scheme 2. Fluoroalkylation of hydrazones under redox neutral conditions.

mixtures of products originating from neutral and reductive pathways were formed. Fluoromethyl and methyl sulfides **2c,d** reacted poorly with hydrazones of all types.

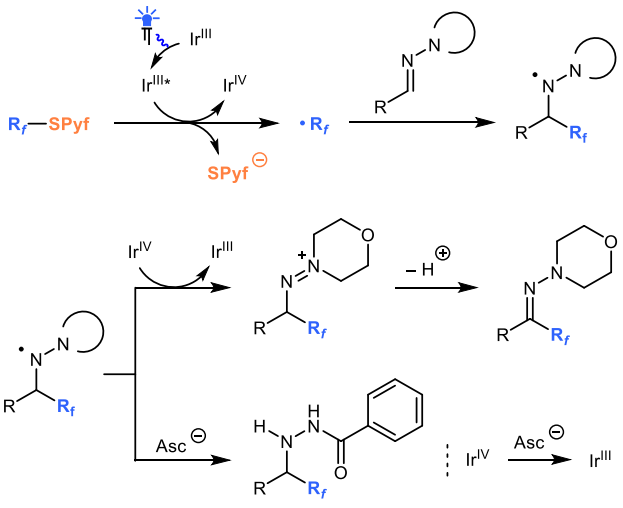
Since combination **1c**/**2b** was most effective, a series of *N*-benzoyl hydrazones were coupled with sulfide **2b**, as well as with other difluorinated PyS-reagents[15] (Scheme 3, Scope). The reaction proceeded with excellent yields with substrates containing halogenated or electron-withdrawing groups. In the presence of donor substituents, considerable amounts of by-products originating from radical attack on the aromatic ring were observed (by-product **4gx** was isolated and characterized). Though, product **4g** can still be isolated in moderate yield. Fortunately, pyridine and even *N*-acetyl indole fragments were tolerated (products **4h**,**i**). Hydrazone derived from hydrocinnamic aldehyde furnished good yield (product **4j**), but sterically hindered aliphatic hydrazones gave noticeably decreased yields (products **4k**,**l**). In contrast to difluoroalkylations, trifluoromethylation proceeded poorly presumably due to radical addition on aromatics (product **4d**, see SI for analysis of by-products).

A unified mechanism of the reactions of hydrazones is shown in Scheme 4. The process starts from single electron reduction of the sulfide by photoexcited iridium complex generating the fluorinated radical. It is believed that zinc acetate facilitates cleavage of the PyfS-reagents either by



[a] ^{19}F NMR yields using $PhCF_3$ as internal standard. [b] Isolated yield. [c] Ratio of hydrazine/hydrazone.

Scheme 3. Fluoroalkylation of hydrazones under reductive conditions.

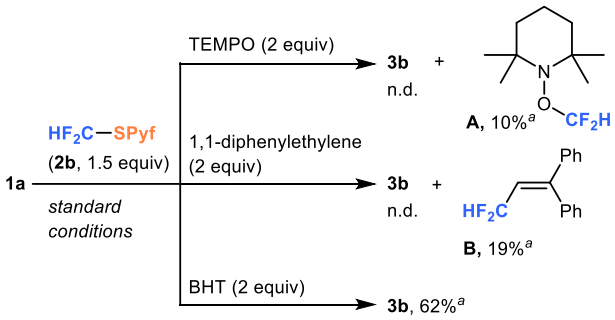


Scheme 4. Proposed mechanism.

coordinating the starting substrate or by scavenging PyfS-anion. Subsequent radical addition at the C=N bond provides nitrogen-centered radical, which reactivity depends on structural features and reaction conditions. For morpholine substituted hydrazones, as well as for amidrazones, oxidation by Ir(IV) is possible and is followed by a loss of proton. On the other hand, for *N*-benzoyl hydrazones, the oxidation is problematic, but instead the hydrogen atom transfer can be realized in the presence of ascorbic acid.[20] In the latter case, ascorbate can also serve as single electron reductant to convert Ir(IV) into Ir(III). Low quantum yield for redox neutral reaction (0.04) makes alternative chain mechanism less favorable.

To support our mechanistic hypothesis, we conducted the model redox neutral reaction in the presence of common radical traps (Scheme 5). Thus, TEMPO completely inhibited the reaction, and the trapping product A was detected. 1,1-Diphenylethylene also impeded the process giving radical addition product **B**. Surprisingly, the presence

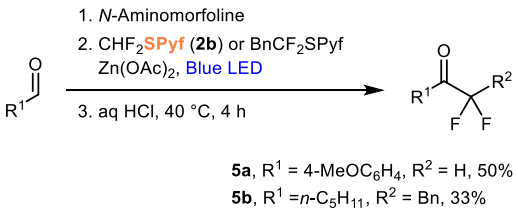
of 2,6-di-*tert*-butyl-4-methylphenol (BHT) had almost no effect on the reaction.



[a] ^{19}F NMR yield using $PhCF_3$ as internal standard. [b] Abbreviations: TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl; BHT, 2,6-di-*tert*-butyl-4-methylphenol.

Scheme 5. Mechanistic experiments.

To demonstrate synthetic utility of our method, 10 mmol scale reactions were conducted using the same power of light source (60W). The reductive alkylation was suitable for scale-up affording 74% yield of product **4a** after 42 h of irradiation. At the same time, for the synthesis of **3b** (neutral conditions), the reaction proceeded very slowly delivering full conversion after 144 h of irradiation with the yield of **3b** being only 20%. Also, a conversion of aldehydes to difluorinated ketones was performed (Scheme 6). Thus, hydrazones generated using *N*-aminomorpholine were difluoroalkylated under standard conditions followed by an acidic hydrolysis of the hydrazone fragment. Though the overall yields of ketones **5a,b** were moderate, the reactions were performed in a one-pot fashion without isolation of intermediate products.



Scheme 6. Conversion of aldehydes to difluorinated ketones.

In summary, a visible light promoted fluoroalkylation of hydrazones was developed. Easily accessible 4-perfluoropyridine sulfides were used as convenient sources of difluorinated radicals. The method enables fluoroalkylation in both neutral and reductive modes providing fluorinated hydrazones or hydrazines, respectively.

Experimental Section

Reactions under redox neutral conditions; synthesis of compounds 3 (general procedure 1).

A tube equipped with a stirring bar was evacuated, backfilled with argon and successively charged with hydrazone **1** (0.5 mmol), sulfide **2** (0.75 mmol), anhydrous $Zn(OAc)_2$ (92 mg, 0.5 mmol) and *fac*-Ir(ppy)$_3$ (0.8 mg, 1.25 µmol), and DMSO (1 mL). The tube was evacuated, refilled with argon, and closed with a screw cap. The reaction vessel was irradiated with blue light (60 W/455 nm LED) for 15 h; during irradiation the mixture was cooled with room temperature water. For the work-up, the mixture was treated with a saturated aqueous solution of K_2CO_3 (1 mL), diluted with water (3 mL) and extracted with ethyl acetate (4×2 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

Reactions under reductive conditions; synthesis of compounds 4 (general procedure 2).

A tube equipped with a stirring bar was evacuated, backfilled with argon and successively charged with hydrazone **1** (0.5 mmol), sulfide **2** (0.75 mmol), freshly dried KOAc (73.6 mg, 0.75 mmol), anhydrous $Zn(OAc)_2$ (92 mg, 0.5 mmol), ascorbic acid (132.1 mg, 0.75 mmol) and *fac*-Ir(ppy)$_3$ (0.8 mg, 1.25 µmol), and DMSO (1 mL) The tube was evacuated, refilled with argon, and closed with a screw cap. The reaction vessel was irradiated with blue light (60 W/455 nm LED) for 4 h; during irradiation the mixture was cooled with room temperature water. For the workup, the mixture was diluted with water (5 mL) and extracted with ethyl acetate (4×2 mL). The combined organic phase was dried over Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

One-pot difluoroalkylation of aldehydes (general procedure 3).

A tube equipped with a stirring bar was charged with DMSO (1 mL), and then evacuated and backfilled with argon. Aldehyde (0.5 mmol) and *N*-aminomopholine (53 mg, 525 mmol) were successively added and the mixture was stirred for 1 hour at 25 °C. Anhydrous $Zn(OAc)_2$ (92 mg, 0.5 mmol) and *fac*-Ir(ppy)$_3$ (0.8 mg, 1.25 µmol) were added into the reaction tube. The reaction vessel was irradiated with blue light (60 W/455 nm LED) for 15 h; during irradiation the mixture was cooled with room temperature water. The mixture was diluted with 2M HCl (1 mL) and stirred for additional 2 h at 50 °C. After the completion of hydrazone hydrolysis (monitored by GC-MS), the reaction mixture was extracted with diethyl ether (4×2 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

Acknowledgements

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