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Redox-Convertible Groups to Expand the Substrate Scope for Pentafluorosulfanylation of Styrenes by Photocatalytic Activation of Sulfur Hexafluoride

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The photocatalytic activation of sulfur hexafluoride, SF_6, is an important synthetic method to access pentafluorosulfanylated organic compounds because of the nontoxic properties of this gas. However, the redox properties of the organic substrates must fit to the photoredox cycle for the activation of SF_6. Strong electron-donating groups turned α-phenyl styrenes into a redox-inactive state. These substrates has to be converted into redox-active derivatives by reversible modifications of the critical substituents. This concept of redox-convertible substituents has been successfully applied to expand the substrate scope for the pentafluorosulfanylation of α-phenyl and α-methyl styrenes by using SF_6.

1. Introduction

The interest in fluorinated compounds rises due to the tremendous impact of fluorinated substituents on the physicochemical properties. This leads to a broad application of fluorinated molecules in pharmaceutical chemistry,[1] agrochemistry[2] and dye chemistry.[3] The $-CF_3$, $-OCF_3$, and the $-SCF_3$ groups are well explored.[4] In particular, the trifluoromethyl group (CF_3) is the most often used fluorinated substituent.[5] In contrast, the pentasulfanyl group (SF_5) is much less explored, although it seems to be a good candidate for applications mentioned above. In contrast to the CF_3 group, the SF_5 group shows—besides its octahedral symmetry and the resulting steric demand—a high substituent electronegativity and lipophilicity.[6] Highly beneficial properties have been proposed for the SF_5 group, especially as CF_3 replacement in pharmaceutically active drugs,[7] metal complexes,[8] and biologically active compounds.[9] For instance, trifluoralin has a fivefold enhanced activity as pesticide if the CF_3 group is replaced by SF_5, fenfluramine (an appetite suppressant) shows tenfold stronger binding to the receptor.[10] The synthetic access to pentafluorosulfanylated molecules is limited and often includes working with dangerous and toxic compounds, like elemental fluorine or SF_5Br/Cl.[11] Not much safer is the method in the report of Umemoto et al. on the synthesis of SF_5-aryl compounds from disulfides by chlorine oxidation in the presence of fluoride salts, as chlorine gas is also dangerous.[12] Most recently, Pitts and Togni et al. turned this method into a gas-free approach by in situ chlorine formation from trichloroisocyanuric acid.[13] The accessibility of SF_5-alkyl compounds is still restricted to methods based on the use of mixed or low sulfur fluorides.

The photocatalytic activation of sulfur hexafluoride, SF_6, poses an important alternative based on the nontoxic properties of this gas, but it is also an ongoing challenge for the application in organic synthesis. The fluorination by photocatalytic activation of SF_6 was shown in two examples with a diverse substrate scope: Nagorny et al. converted glycosides with SF_6 to glycosyl fluorides.[14] Deoxyfluorinations of small allyl compounds from alcohols were achieved by Jamison et al. and Xie et al.[15] Jin and Wang used SF_6 as a reagent for the photocatalytic deoxyfluorination of benzyl alcohols and as an electrophilic fluorinating reagent for the photocatalyzed conversion of phosphine oxides.[16] We showed that the photoredox activated transfer of the pentafluorosulfanyl group from SF_6 is possible, but the reaction was limited to two styrenes as substrates.[17] The substrate scope was expanded by the use of alcohols[18] and 1-alkynols as nucleophiles.[19] Herein, we expand the substrate scope of pentafluorosulfanylations by substituted α-phenyl and α–methyl styrenes (**Figure 1**). In particular, strong electron-donating groups ($-NH_2$, -OH) turned these substrates into a redox-inactive state for pentafluorosulfanylation. We converted them into redox-active derivatives by reversible modifications of the substituents.

2. Results and Discussion

All substrates **2–21** were subjected to the same reaction conditions for the photocatalytic conversion with SF_6. This includes the use of 5 mol% *N*-phenyl phenothiazine (**1**) as an organophotoredox catalyst together with 10 mol% $Cu(acac)_2$ as a radical stabilizer in MeCN as solvent. This catalyst loading is the optimum for the conversion of substrate **2** into product **22**.[17] Solid and highly viscous substrates were directly placed into the reaction vessel (**Figure 2**). The liquid substrates were added in dry MeCN under

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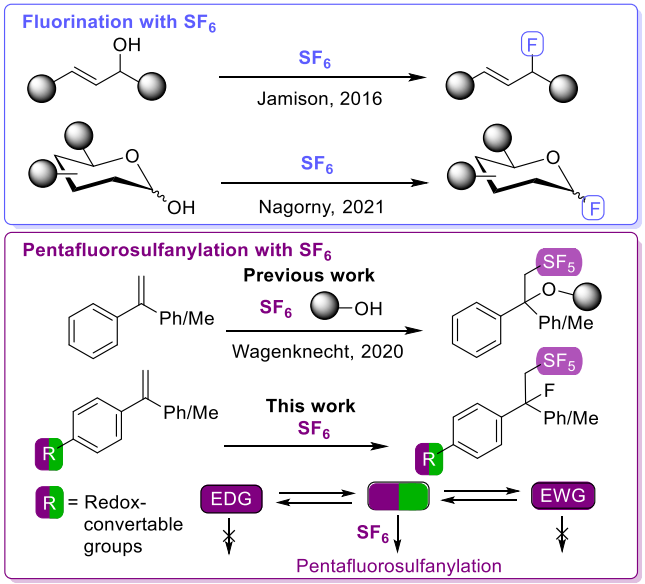

Figure 1. Photocatalytic activation of SF_6 for fluorination (top) and pentafluorosulfanylation (bottom) of substrates from previous work. In this work, the substrate scope is expanded by redox-convertible groups (EDG = electron-donating groups, EWG = electron-withdrawing groups).

an argon atmosphere. The reaction mixtures were degassed using the "freeze-pump-thaw" method, but the vessels were not flushed with argon after the final thawing.[20] Instead, the vessel was freezed again, and SF_6 gas (25 equiv.) was introduced as layer on top of the reaction mixtures. The mixture was then allowed to thaw and irradiated for 21 h using both 365 nm and 525 nm LEDs. The obtained SF_5 compounds show a specific pattern in the ^{19}F nuclear magnetic resonance (NMR) spectra, a combination of a low-field doublet at 70.8 ppm and a pentet at 83.4 ppm (values of **3** as an example) as signature caused by the axial and equatorial fluorine atoms in the SF_5 group. Further fine splitting through the coupling with neighboring protons provides additional structural information. Using deuterated acetonitrile, the yields of the pentafluorosulfanylated products **22**–**37** were determined via ^{19}F NMR spectroscopy and are given as an average of triplicates based on the internal standard α,α,α–trifluorotoluene. Due to small scale of the photocatalytic experiments, only compounds with a yield higher than 30% were isolated.

We assume that the photoredox catalytic pentafluorosulfanylation of substrates **2**–**21** (*vide infra*) follows the established mechanism with two consecutive photoinduced electron transfer steps.[16] Accordingly, the catalytic cycle starts with the oxidative quenching of the excited state of **1** by SF_6 generating the radical anion $SF_6^{\cdot-}$ in an excited state that favors the decay into a fluoride anion and the desired radical $SF_5^{\cdot}$. The subsequent reaction with the substrate, for instance **2**, does not involve a direct Giese-type addition of the radical $SF_5^{\cdot}$ to the double bond of the substrate, because the generated phenothiazine radical cation $\mathbf{1}^{\cdot+}$ cannot oxidize the substrate **2** directly. This electron transfer would be endergonic by about 100 kJ mol^{-1}. Only the second excitation of the radical cation $\mathbf{1}^{\cdot+}$ by light at 365 nm or preferably by 525 nm, where $\mathbf{1}^{\cdot+}$ has significant absorption and initiates a charge shift in the radical cation $\mathbf{1}^{\cdot+*}$ generating its strongly

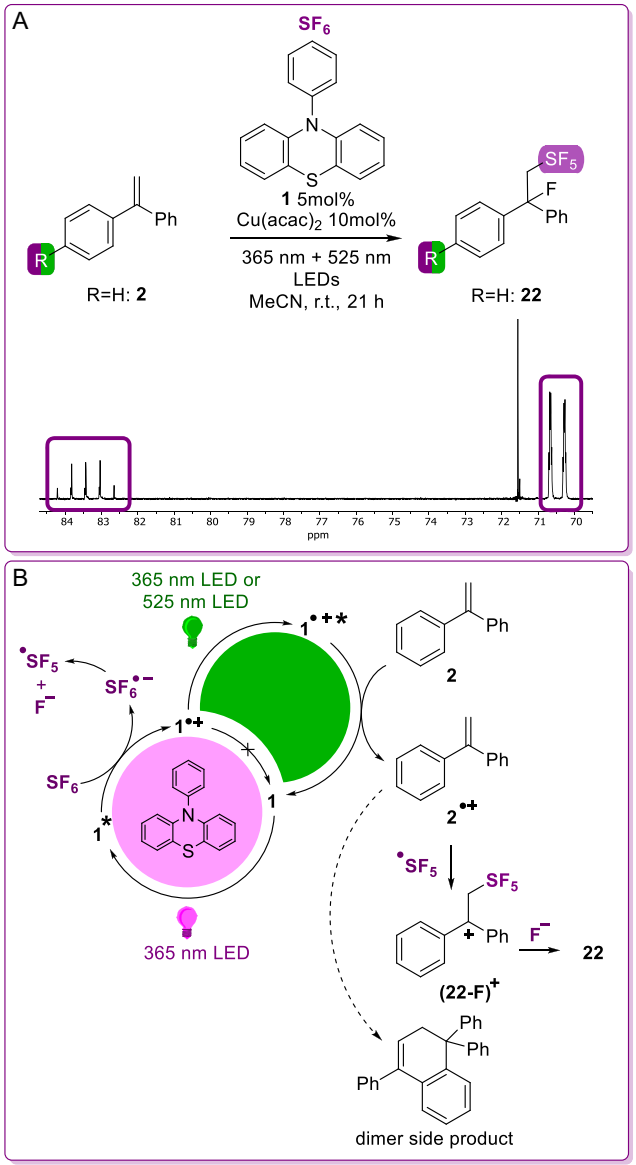

Figure 2. A) General reaction conditions for the SF_6 activation by α-phenyl styrenes, representatively shown for **2** using the organophotocatalyst *N*-phenylphenothiazine (**1**) together with $Cu(acac)_2$ in MeCN. The product, here **3**, was identified by the typical ^{19}F NMR signature of the SF_5 group. B) Photocatalytic mechanism including two consecutive excitations by light at 365 nm (LED) and at 525 nm (LED). The dimer of **2** is observed as main side product.[16]

oxidizing excited state $\mathbf{1}^{\cdot+*}$,[21] capable to oxidize the substrate **2** to its radical cation $\mathbf{2}^{\cdot+}$. This closes the photoredox catalytic cycle. The oxidized substrate $\mathbf{2}^{\cdot+}$ is so electron deficient that it cannot be oxidized by the radical $SF_5^{\cdot}$, although the latter has a high electron affinity, and instead the C—S bond is formed by radical–radical coupling. The mesomerically stabilized cation $\mathbf{(22\text{-}F)}^+$ can then be captured by the fluoride ion generated in situ to form the product **22**.

The pentafluorosulfanylation of the initial smaller library of substrates **2**–**10** (**Figure 3**) reveals that the mechanism for the pentafluorosulfanylation limits the substrate scope by the redox-active window. The critical step in the photocatalytic cycle

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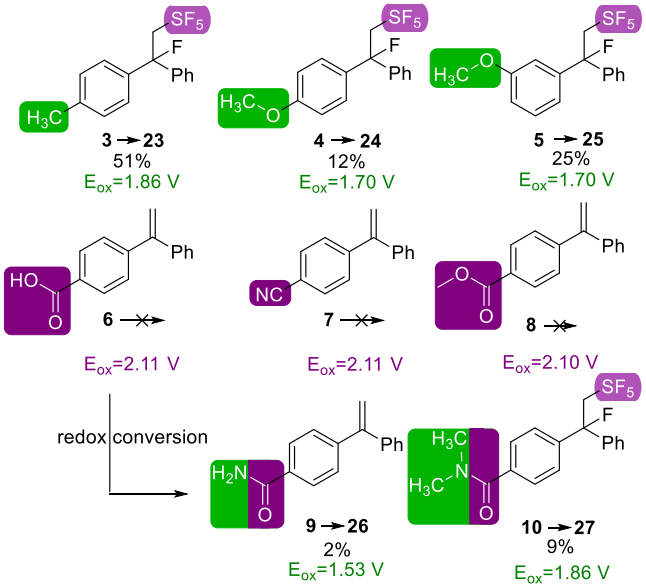

Figure 3. First substrate scope **2**–**10** with electron-withdrawing (purple), electron-donating substituents (green) and redox-convertible groups (purple–green). Yields were determined by ^{19}F NMR spectroscopy.

is the oxidation of the substrate, like **2**, by the excited state of the phenothiazine radical cation $\mathbf{1}^{\cdot+*}$. Its potential was estimated to be $E_{red}^*=(\mathbf{1}^{\cdot+*}/\mathbf{1}) = 2.06$ V versus SCE (standard calomel electrode, changed from 2.31 V versus normal hydrogen electrode (NHE)) using $E_{oo} = 1.39$ V.[22] The unsubstituted α-phenyl styrene **2** has an oxidation potential of $E_{ox}(\mathbf{2}^{\cdot+*}/\mathbf{2}) = 1.73$ V.[23] The driving force for this electron transfer is $\Delta G_{ET} = E_{ox}\text{-}E_{red}^* = -0.3$ V and clearly exergonic. Accordingly, **2** can be converted to the product **22** in a yield of 63%. Substrates with electron-donating groups should be -in principle- applicable to broaden the substrate scope for pentafluorosulfanylation because they show reduced oxidation potentials. We determined the oxidation potential $E_{ox}(\mathbf{3}^{\cdot+}/\mathbf{3})$ of this substrate as well as all further substrates **4**–**21** by cyclic voltammetry (see Supporting Information). The methyl group in *para* position to one of the phenyl rings in substrate **3** gives a yield of 51% for product **23** which is an only slightly reduced yield compared to the unsubstituted product **22** (63%). The yield for the conversion of the 4-methoxy substituted substrate **4** is around 12% for product **24** if this group is shifted to the 3-postion in substrate **5**, the yield of product **25** increases to 25%. Both yields are below the expectation based on the discussion above. We have to take into consideration, that the dimerization of the substrates by the reaction of the oxidized substrates is the most significant side reaction of this photocatalytic method. As lower the oxidation potential gets as more dimerized substrate is obtained as side product. Obviously, as more efficiently the substrate oxidation occurs due the higher driving force ΔG_{ET} in the photocatalytic cycle as higher the stationary concentration of the substrate radical cation gets which increases the substrate dimerization as side reaction. Interestingly, the position of the methoxy group has also a rather strong effect on the yield of the reaction. Since the substrates **4** and **5** both have identical oxidation potentials of $E_{ox}(\mathbf{4}^{\cdot+}/\mathbf{4}) = E_{ox}(\mathbf{5}^{\cdot+}/\mathbf{5}) = 1.70$ V versus SCE, the difference in yield cannot be explained by the different driving force ΔG_{ET} for the electron retransfer. Apparently, there is a steric or electronic effect that has an impact on the yield. Possibly, a substituent in the 3-position hinders electrophilic attack during dimerization. This would make the substrate radical cation $\mathbf{5}^{\cdot+}$more durable less reactive than $\mathbf{4}^{\cdot+}$ due to the higher steric hindrance and allow trapping of more SF_5 radicals with subsequent product formation. Electron-deficient substrates, especially those with a carboxy group (**6**) and a cyano group (**7**), do not show any reaction which can be explained by their high redox potential, $E_{ox}(\mathbf{6}^{\cdot+}/\mathbf{6}) = E_{ox}(\mathbf{7}^{\cdot+}/\mathbf{7}) = 2.11$ V versus SCE, that are above the threshold value 2.06 V set by the photocatalyst radical cation in the excited state $\mathbf{1}^{\cdot+*}$. Thus, the catalysis cycle is not closed, and the catalyst is not regenerated. In addition, the SF_5 radical generated in the first step cannot be captured because the substrate is not present as a radical cation. This results in larger amounts of unreacted reactant in the crude reaction mixture. If the electron-withdrawing effect is reduced by synthetic modification, the substrate oxidation potentials should be shifted back in the redox-active range below 2.06 V. The methyl ester in substrate **8** does not provide enough electron-donating power for this purpose. The amide in substrate **9** significantly lowers the oxidation potential to $E_{ox}(\mathbf{9}^{\cdot+}/\mathbf{9}) = 1.53$ V but induces significant substrate dimerization. As a result, product **26** is formed, but only in traces (2%). The dimethylamido group in substrate **10** provides the best compromise by its oxidation potential of $E_{ox}(\mathbf{10}^{\cdot+}/\mathbf{10}) = 1.86$ V. The pentafluorosulfanylation reactivity is regained, and product **27** is formed in a small yield of 9%. This shows that redox-inactive substrates, like the carboxy-substituted substrate **6**, can be converted into a redox-active one by small synthetic modifications that alter the electronic effects of the substituents. We call them redox-convertible groups and followed this concept to broaden the substrate scope for photocatalytic pentafluorosulfanylation of α-phenyl styrenes.

Strongly electron-donating groups, especially the amino and dimethylamino substituents in substrates **11** and **17**, were not converted into the desired products under the photocatalytic pentafluorosulfanylation conditions due to the dimerization of these substrates because of their very low oxidation potential of $E_{ox}(\mathbf{11}^{\cdot+}/\mathbf{11}) = 0.88$ V and $E_{ox}(\mathbf{17}^{\cdot+}/\mathbf{17}) = 1.15$ V. The protons of the amino group are not a problem for the pentafluorosulfanylation because the dimethylamino-substituted substrate **13** also shows a low oxidation potential of $E_{ox}(\mathbf{13}^{\cdot+}/\mathbf{13}) = 0.72$ V, and therefore no pentafluorosulfanylation activity in the photocatalytic experiments. Applying our concept of redox-convertible groups (**Figure 4**), the electron-donating character of the amino group in substrate **11** is reduced by a Boc group in substrate **12**, yielding an oxidation potential of $E_{ox}(\mathbf{12}^{\cdot+}/\mathbf{12}) = 2.09$ V, a trifluoroacetyl group in **14**, $E_{ox}(\mathbf{14}^{\cdot+}/\mathbf{14}) = 1.95$ V, or by the succinimide in substrate **15**, $E_{ox}(\mathbf{15}^{\cdot+}/\mathbf{15}) = 1.92$ V. Accordingly, the pentafluorosulfanylated product **29** is formed in 27% yield, the product **30** in 22% yield, and product **31** in 18% yield. A simple acetyl group shifts substrate **16** to the oxidation potential $E_{ox}(\mathbf{16}^{\cdot+}/\mathbf{16}) = 2.08$ V close to the threshold value of −2.06 V, and is convertible into product **32** in a yield of 12%.

The concept was also applied to the phenolic substrate **17** (**Figure 5**) which cannot directly be pentafluorosulfanylated to product **33** due to the low oxidation potential of

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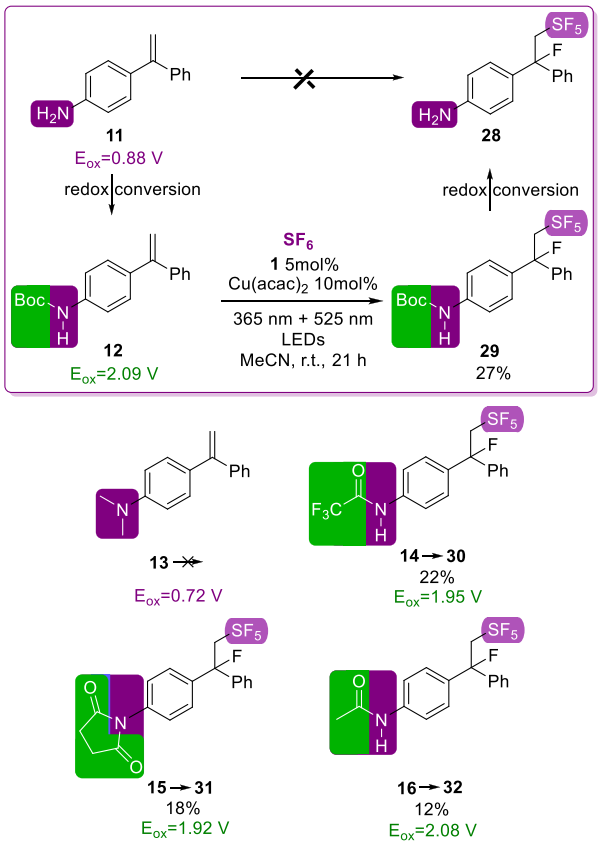

Figure 4. Photocatalytic pentafluorosulfanylation of the amino-substituted substrate **11** can only be achieved by redox conversion into the modified substrate **12** and redox conversion of the pentafluorosulfanylated product **29** back into the final product **28**. The pentafluorosulfanylation works also with the modified substrates **14**–**16**, but not with **13**. Yields were determined by ^{19}F NMR spectroscopy.

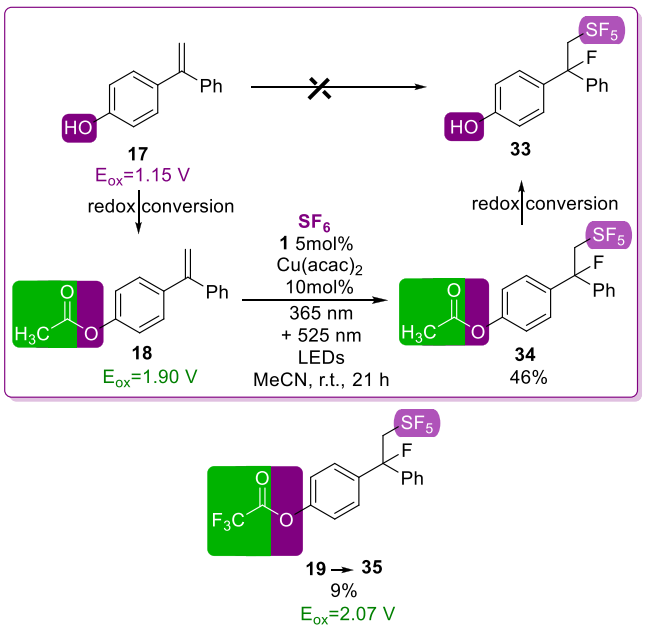

Figure 5. Photocatalytic pentafluorosulfanylation of the hydroxy-substituted substrate **17** can only be achieved by redox conversion into the modified substrate **18** and redox conversion of the pentafluorosulfanylated product **34** back into the final product **35**. This works also with the modified substrate **19**. Yields were determined by ^{19}F NMR spectroscopy.

E_{ox}(**17**$^{\cdot+}$/**17**) = 1.54 V. If the hydroxy group is acetylated into substrate **18**, the redox potential is converted to E_{ox}(**18**$^{\cdot+}$/**18**) = 1.90 V. As a result, this substrate can be pentafluorosulfanylated to product **34** in a yield of 46%. A reduction of the electron-donating character by trifluoroacetylation in substrate **19** shifts the oxidation potential to E_{ox}(**19**$^{\cdot+}$/**19**) = 2.07 V, which is again a borderline case with respect to the threshold potential of 2.06 V and drops the yield to 9% for product **35**. Due to the low yield and the lack of hydrolysis stability of compound **35**, it was not considered in the following deprotection experiments. The similarity of the oxidation potentials of substrates **12**, **16,** and **19** does not explain the higher yield observed for product **29**. We assume that the shielding of the sterically demanding Boc group in substrate **12** prevents dimerization of this substrate as side reaction and therefore gives a higher yield of the pentafluorosulfanylated product **29**. Hence, the Boc group is not only preferred by the induced redox change but also by its steric hindrance.

α-Methyl styrene is also a substrate suitable for the photocatalytic pentafluorosulfanylation with SF_6. The hydroxylated substrate **20**, however, fails due to the low redox potential of E_{ox}(**20**$^{\cdot+}$/**20**) = 0.95 V (**Figure 6**). This potential can be tuned into the right range by acetylation of **20** into substrate **21** with E_{ox}(**21**$^{\cdot+}$/**21**) = 1.95 V. This substrate can be pentafluorosulfanylated to product **37** in a yield of 31% and is another example for the concept of redox-convertible groups.

To obtain the final amino- and hydroxy-SF_5 compounds **28**, **33,** and **36**, the redox converting groups had to be removed (**Figure 7**). The deprotection of the Boc moiety of **29** was carried out by treatment with trifluoroacetic acid and product **28** was obtained in a yield of 75%. The trifluoroacetyl group of **30** was removed in a solution of sodium hydroxide (5 M) in methanol. The hydrolysis of the esters **35** and **37**, respectively, gave an E/Z mixture of the alkenes, **33** and **36**, because HF is also eliminated in addition to the ester cleavage. In case of the α-phenyl derivative **33**, the cleavage proceeds quantitatively giving an E/Z ratio of 10:1 (**33a/b**). For the α-methyl product **36**, the cleavage of the ester group after pentafluorosulfanylations gave also an E/Z mixture of 10:1, but a lower yield of 40%.

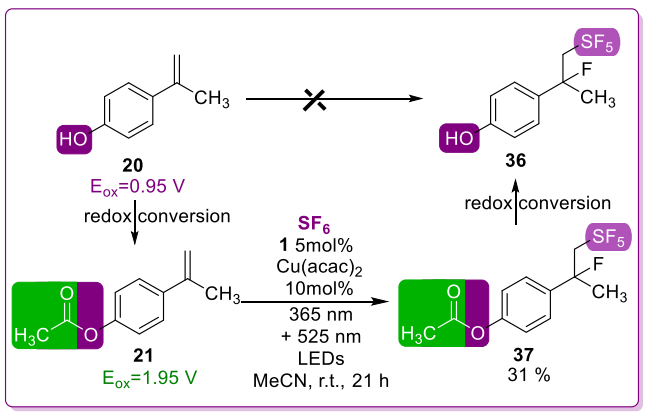

Figure 6. Photocatalytic pentafluorosulfanylation of the hydroxy-substituted substrate **20** can only be achieved by redox conversion into the modified substrate **21** and redox conversion of the pentafluorosulfanylated product **37** back into the final product **36.** Yields were determined by ^{19}F NMR spectroscopy.

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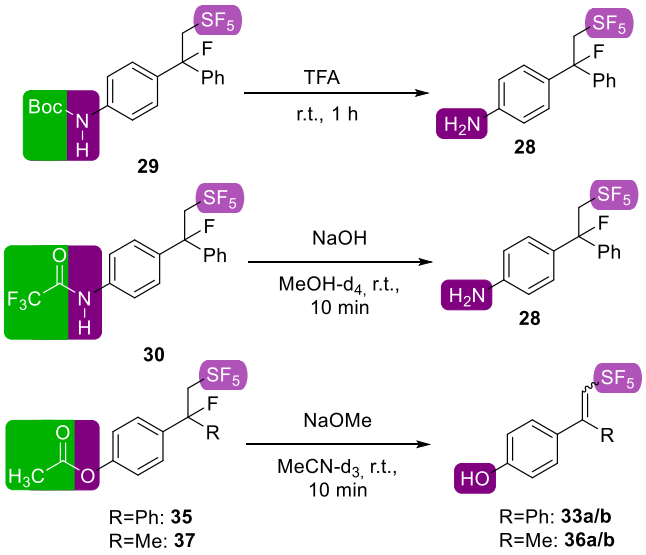

Figure 7. "Reconversion" of the protected groups in products **29**, **30**, **35,** and **37** into the final pentafluorosulfanylated products **28**, **33,** and **36**.

3. Conclusion

The photocatalytic activation of sulfur hexafluoride, SF_6, is an important method for the pentafluorosulfanylation of organic compounds because of the nontoxic properties of this gas compared to conventional and extremely toxic reagents, like SF_5Cl. However, the redox properties of α-phenyl and α-methyl styrenes as substrates must fit to the photoredox activated transfer of the pentafluorosulfanyl group from SF_6. Strong electron-withdrawing and -donating groups, in particular the –COOH, -OH, and NH_2 groups, turned these substrates into a redox-inactive state for pentafluorosulfanylation. These substrates had to be converted into redox-active derivatives by reversible modifications of the substituents (**Figure 8**). This concept has been successfully applied to expand the substrate scope for the pentafluorosulfanylation of styrenes by using SF_6. Although the catalytic yields are low to moderate, in the range of 9% to 46%, it is important to note that these compounds are novel and were not yet synthesized by any other method. Furthermore, this advanced method shows proof of concept that even complex transformations could be realized under SF_6 activating conditions by precise fine-tuning of the photoredox catalytic activity. The concept therefore expands the scope of accessible SF_5-containing chemical space.

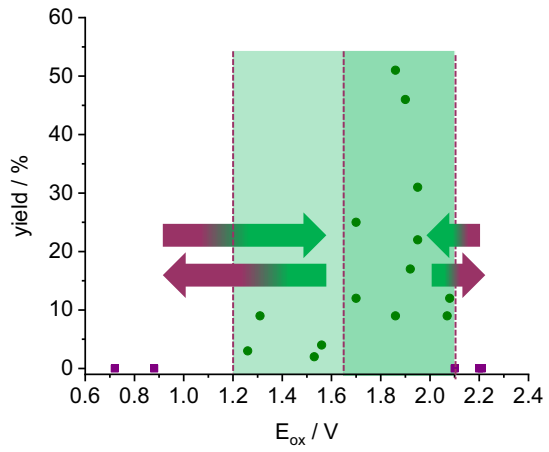

Figure 8. The concept of redox-convertible groups: The redox-active range for pentafluorosulfanylations of α-phenyl styrenes lies in the range between $E_{ox} = 1.2$ V (better above 1.6 V) and 2.1 V. Substrates with oxidation potentials outside this range need to chemically converted into substrates derivatives in the range and back after the pentafluorosulfanylation.

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Conflict of Interest

The authors declare no conflict of interest

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: electron transfer · phenothiazine · photocatalysis · photochemistry · sulfur hexafluorides

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