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Benzodithiazoles-Sulfoximines: Preparation, Properties and Reactivities as Radical Perfluoroalkylating Agents

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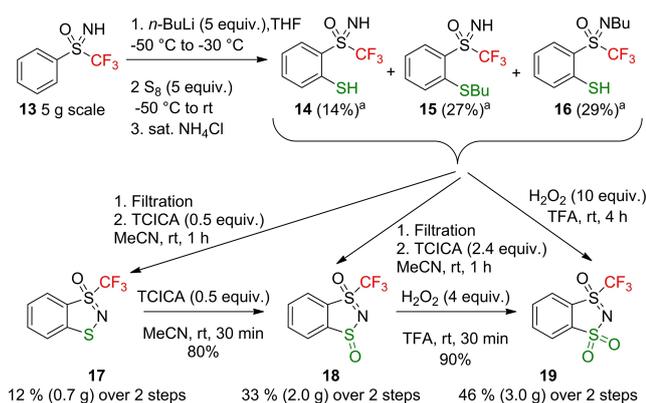
Abstract: We describe the preparation of S-perfluoroalkyl benzodithiazole trioxides as radical perfluoroalkylating reagents. Their syntheses were performed on a multi-gram scale by an oxidative cyclization connecting the nitrogen of a sulfoximine and a sulfur atom previously introduced in the *ortho* position of this group. The structures and properties of these new molecules were carefully examined by X-Ray diffraction, DFT calculations and cyclic voltammetry. These data clearly highlight the enhanced reactivity of these cyclic sulfoximines compared to their open analogues. This was confirmed by photoredox catalysis experiments that revealed interesting reactivity, most especially for the introduction of di- and monofluoroalkyl chains.

Keywords: Sulfur heterocycles; Fluorine; Photocatalysis; Sulfoximines; Radicals

Introduction

Increasing the molecular space is a central concern for organic chemists and a daily challenge for innovation in life and materials sciences.^[1] To push the limits of the chemical world, the invention of selective and robust reagents is the focus of much attention.^[2] In this context, the selective introduction of a trifluoromethyl or perfluoroalkyl group is amongst the most sought-after goals.^[3] The reason is the unique and profound modifications induced in a molecule by these halogenated groups, such as lipophilicity, electronic perturbation, conformational changes and metabolic stability.^[4] The chemist's toolbox has recently been enriched by easy-to-use reagents for the introduction of the CF₃ group to various scaffolds.^[5] The most emblematic of these compounds are the Ruppert-Prakash **1**^[6], Umemoto **2**^[7] or Togni **3–4**^[8] reagents (Figure 1a). The first allows the generation of the synthetic equivalent of the trifluoromethyl anion, while

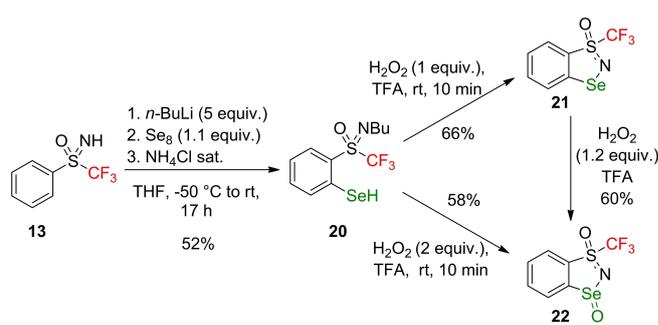
the other three react with nucleophiles and are qualified as electrophilic reagents. In addition, the renaissance of photoredox catalysis linked with these reagents by making them sources of CF₃ radicals.^[9] A more recent family of compounds, the S-perfluoroalkyl sulfoximines have also shown great potential both as electrophilic and radical reagents.^[10] These groups show an advantage over the previous reagents: the variation of the perfluorinated chain linked to the sulfur atom is fully mastered. Adachi and Ishihara were the first to describe, in a patent in 2005, a cyclic sulfoximine **5** as an electrophilic trifluoromethylating agent (Figure 1a).^[11] In 2008, Shibata and coworkers described the non-cyclic fluorinated version **6** (R_F=CF₃) of the Johnson reagent, a sulfoximine able to transfer a trifluoromethyl group to carbon nucleophiles.^[12] Hu and coworkers were the first to demonstrate that the neutral non-cyclic sulfoximine **7** (R_F=CF₂H, R=Ts) was also a good candidate for the transfer of difluoromethylated groups.^[13] Inspired by



Scheme 2. *Ortho*-thiolation of *S*-trifluoromethyl *S*-phenylsulfoximine **13** and selective oxidation to benzodithiazoles. [a] ¹⁹F NMR proportions.

be astonishing. A thorough analysis of the reaction medium revealed that the desired compound **14** bearing the –SH function was accompanied by two *S*- and *N*-butylated derivatives **15** and **16** in equal proportions (for a mechanistic discussion of the butylation process by electrophilic synthons see SI1). These three compounds are separable and accounted for 70% of the quantity engaged in the reaction. The next step was the formation of the nitrogen-sulfur bond to achieve the desired cyclisation. Some preliminary oxidative attempts were conducted independently on each isolated compound **14**, **15** and **16** that allowed us to ensure the feasibility of our strategy *i.e.* oxidative ring closing (see SI1 for details). To our delight, we managed to identify reaction conditions that selectively led to three cyclic compounds **17–19**, with different degrees of oxidation on the sulfur atom, starting directly from the mixture of the three intermediates **14–16** (Scheme 2). The crude mixture resulting from the *ortho*-lithiation was filtered through Celite® (to remove the excess sulfur) and subjected to the action of trichloroisocyanuric acid (TCICA) to give rise to benzodithiazole **17**. An increase in the quantity of TCICA allowed the preparation on a two-gram scale of the monooxidized sulfur analogue **18** in an acceptable yield calculated over two steps. The treatment of pure product **17** by TCICA provided the oxidized form **18** in very good yield. Lastly, when an excess of hydrogen peroxide in trifluoroacetic acid (TFA) was added to the crude mixture, the fully oxidized sulfur skeleton **19** was isolated on a three-gram scale in a reasonable yield. This benzodithiazole **19** can also be prepared by oxidation of **18**. Mechanistic discussions for these quite uncommon cyclizations are proposed in SI1 (Schemes S2–4).

Stimulated by the previous results, we considered synthesizing the corresponding selenium scaffolds (Scheme 3). For this purpose, we replaced elemental sulfur by elemental selenium during the first *ortho*-



Scheme 3. Syntheses of selenium analogues.

lithiation step. In this case, the analysis of the crude mixture by NMR showed fewer products than in the sulfur series. In fact, this transformation led quite exclusively to product **20** (85% by ¹⁹F NMR) resulting from the incorporation of selenium in the *ortho* position and of a butyl group on the sulfoximine nitrogen atom. This new skeleton **20** was isolated in a moderate yield of 52%. Oxidation of selenol **20** with only one equivalent of hydrogen peroxide in TFA led to the formation of **21** in good yield, while the use of two equivalents gave rise to the oxidized skeleton **22** in 58% yield. The latter can also be synthesized by oxidation of the molecule **21**. Unfortunately, the use of a large excess of hydrogen peroxide or even any other oxidant did not allow us to obtain a selenone analogue. This result highlights the important difference in reactivity between a sulfur and a selenium atom.

All these new products have been fully characterized by NMR (see SI6) as well as by X-ray diffraction (see SI3, except for **17** and **21** that are liquids at room temperature, Figure 2).^[21]

Among the most relevant structural information, no significant difference between the S₇–CF₃ bond lengths was observed (Table 1). They are all close to 1.85 Å, in agreement with the value obtained for sulfoximine **13** (1.867 Å). The lengths of the X₉–N₈ (X=C, S, Se) bonds vary logically with the nature of the X atom. This bond is the shortest with molecule **5** (1.405 Å),



Figure 2. Structures of Adachi's reagent **5** and the new perfluorinated benzodithiazoles **18**, **19** and **22**.

Table 1. Relevant structural information for compounds **5**, **13**, **18**, **19** and **22**.

	5	13	18	19	22
Length (Å)	1.846	1.867	1.852	1.858	1.850
S ₇ -C ₁₂					
Length (Å)	1.405	–	1.689	1.635	1.876
R ₉ -N ₈					
Torsion (°)	-0.44	–	0.82	6.72	-0.42
C ₆ -C ₅ -R ₉ -N ₈					

raised by the same order of magnitude for molecules **18** and **19**. The highest value is obtained in molecule **19** (1.876 Å). The C₆-C₅-C₉-N₈/C₆-C₅-S₉-N₈ torsion angles are between 0 and 7°, showing the (almost) coplanarity of the two rings in all the molecules.

In order to quantify and evaluate their reactivity in photoredox catalyzed transformations, we undertook to evaluate the redox properties of all these new benzodithiazoles by cyclic voltammetry, in acetonitrile (Table 2).

Cyclic voltammetry curves for each compound (see SI4) at the same scan rate, allowed us to evaluate the reversibility and the position of the peak potential E_p as well as the peak width ($|E_p - E_{p/2}|$) indicating the value of the electronic transfer coefficient α ($\alpha = 47.5/|E_p - E_{p/2}|$). The more oxidized trifluoromethyl compound **19** has a peak potential very close to the carbon analogue **5** while compound **18** exhibited a more negative value (Table 2). Interestingly, the peak potential for the selenium analogue **22** appeared very similar to that of compound **18**. The data for open sulfoximines **11** and **12** are given in Table 2 for comparison. It clearly appears that cyclic sulfoximines are easier to reduce than their acyclic analogues, with a potential gap of around 0.5 V in each case (−1.26 V vs −1.73 V in sulfur series and −1.24 V vs −1.78 V in carbon series).

In order to explain this discrepancy, the mechanism of the reduction in the homogeneous phase (Ir(III)*/Ir(II)) or heterogeneous phase (electrochemistry) must be considered. Two pathways have to be differentiated. The dissociative electron transfer can either be concerted (electron transfer and bond breaking are simultaneous) or stepwise (electron transfer and bond break-

ing are successive steps with the presence of an intermediate radical anion). A first indication of the mechanism is given by the value of the electronic transfer coefficient α . The small value of the latter (less than or around 0.5) clearly indicates that the reduction is kinetically controlled by the electron transfer step and is concerted.

DFT calculations were then undertaken to get more insight into the mechanism.^[22] We first evaluated the S-CF₃ bond dissociation energy (BDE) of our compounds. All the values are in the same range of 40 kcal.mol⁻¹ except the benzodithiazole **17** for which the BDE is somewhat smaller around 23 kcal.mol⁻¹ (see SI5). These data are therefore not sufficiently discriminating. We then turned our attention to modelling of the radical anions. The clear-cut information obtained by calculations are as follows (see SI5 for values): *i*) the lengths of the S-CF₃ bonds increased by around 1 Å after the seminal reduction; *ii*) spin density is localized on the carbon of the radical CF₃; *iii*) the charge on the anion is localized on the nitrogen; *iv*) the energy difference between the cluster radical/anion and the sum (energy of radical CF₃ + anion R⁻) is negative. These results clearly account for the existence of a cluster radical/anion in the gas phase for all the trifluoromethyl compounds and not a true radical-anion. The mechanism involved herein is in accordance with the recent extension of the theory of dissociative electron transfer (ET) for which a “sticky” dissociative electron transfer formed by interaction between the produced fragments was postulated.^[22] It is important to notice that the electrostatic interactions between the two fragments influences the electrochemical reaction. Moreover, the peak potential (E_p) position in cyclic voltammetry adjusts according to the reorganization energy and the standard potential energy E° of the reduction. We can speculate that the reorganization energy is lower for the rigid cyclic compounds **5** or **19** than for the more flexible and heavier acyclic analogs **11** and **12** respectively. Consequently, it could explain why their peak potentials are reached at more negative potentials and that a gap of about 500 mV is observed between them. It suggests that our new entities **18** and **19** could be more efficient than their acyclic analogue **12** in photoredox catalysis.

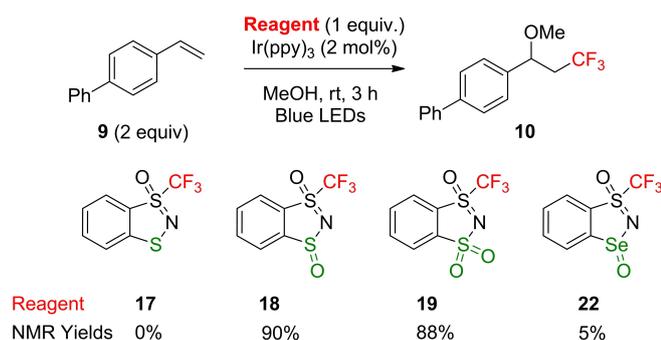
The reactivity of these new molecules was then evaluated in the methoxytrifluoromethylation of 4-vinylbiphenyl (Scheme 4). Contrasting results were obtained. Derivatives **17** and **22** did not give any conversion and seem quite stable under the reaction conditions. More than the half of the compound **17** was still present after 24 h reaction. This value rose to 80% with the selenoxide **22**. On the other hand, both sulfoximines **18** and **19** showed excellent reactivity in our standard transformation. The radical mechanism was unambiguously proved with *in operando* ST/EPR

Table 2. Electrochemical characteristics of new trifluoromethylated sulfoximines.^[a]

	5	18	19	22	11	12
E_p (V vs SCE)	-1.24	-1.41	-1.26	-1.39	-1.78	-1.73
α^b	0.48	0.32	0.41	0.28	0.40	0.40

^[a] At $v = 200$ mV/s;

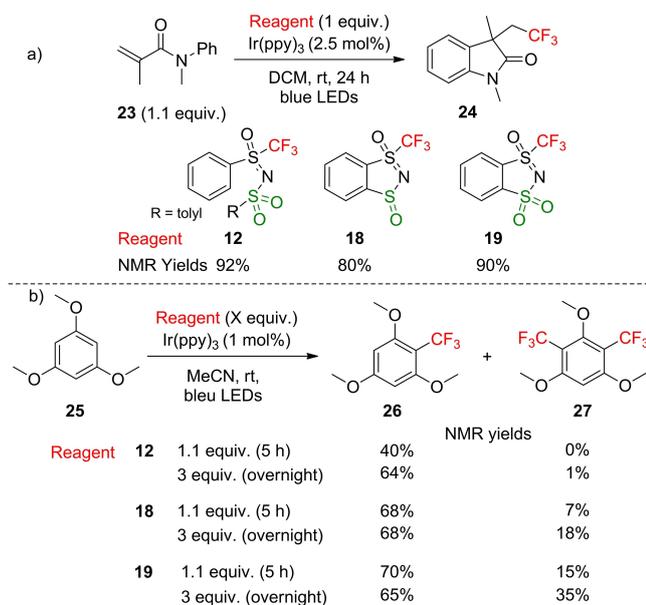
^[b] From $|E_p - E_{p/2}|$.



Scheme 4. Reactivity of reagents **17**, **18**, **19** and **22**.

experiments (see SI5 for details and spectra). Target **10** was obtained in very high yield in both cases after three hours reaction, which is in line with the yields shown in Scheme 1.

Based on these promising results, the reactivity of the perfluorinated benzodithiazoles **18** and **19** in photoredox catalysis was pursued (Scheme 5a). Radical trifluoromethylation of the *N*-aryl-acrylamide **23** was explored. The reagents **18** and **19** showed excellent reactivity, leading to the desired compound **24** in very good yields (80% and 90% respectively). The acyclic analogue **12** gave a comparable yield of 92%. The advantage of a cyclic form *versus* an open one was nevertheless more prominent for a more challenging reaction, the trifluoromethylation of 1,3,5-trimethoxybenzene **25** (Scheme 5b). The presence of the three donor groups on the aromatic ring could favor

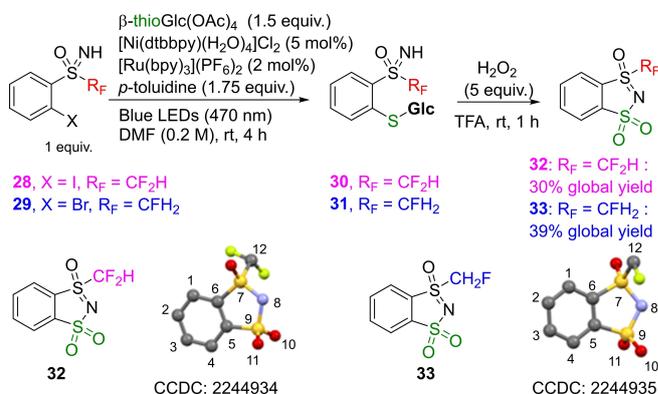


Scheme 5. Radical reactivity of the benzodithiazoles on *N*-aryl-acrylamide **23** and on an electro-enriched aromatic compound **25**.

the formation of mono-trifluoromethylated product **26**, but also bis-trifluoromethylated compound **27**. While sulfoximine **12** only led to the mono trifluoromethylated compound **26** even when used in excess (three equivalents), reagents **18** and **19** allowed bis-trifluoromethylation. A slight excess of reagent **18** gave rise to the product **26** with a good yield of 70% with a limited formation of the compound **27** (only 7%), whereas in the same conditions, reagent **19** delivered a higher yield of compound **27**. The use of three equivalents of reagents **18** or **19** provided a better yield of difunctionalized target **27**, of up to 35%. These positive results strongly encouraged us to continue this study.

As a logical follow-up to this work, it seemed to us essential to explore the possibility of extending this new family of compounds to mono- and difluoroalkylated entities. This choice was motivated by two opposing observations: the growing interest in these two moieties, in particular because of their unique properties, which contrasts with the limited number of reagents allowing their introduction into molecular scaffolds.^[24] The *ortho*-lithiation methodology is unfortunately not compatible with S–CF₂H and S–CFH₂ sulfoximines. To circumvent this limitation, a new synthetic approach was developed. In a recent work, we disclosed the introduction of thiosugars at the *ortho* position of sulfoximines by the help of dual photocatalysis.^[25] Compounds **28** and **29** appeared then as substrates of choice for the synthesis of the cyclic targets (Scheme 6). To our delight, with the oxidation conditions described in the CF₃ series (excess hydrogen peroxide), we were able to isolate the fully oxidized benzodithiazoles **32** and **33** without purification of the intermediates **30** and **31**.

These two new compounds **32** and **33** were fully characterized and obtained as single crystals. X-ray diffraction allowed us to have structural information on our new products, which were logically compared to the data of compound **19** (Table 3). We noticed that



Scheme 6. Syntheses of di- and monofluorinated benzodithiazoles and their structures.

Table 3. Relevant structural information about compounds **32** and **33**, compared to those of compounds **19** as reference.

	19	32	33
Length S ₇ –C ₁₂ (Å)	1.858	1.822	1.761
Length S ₉ –N ₈ (Å)	1.635	1.632	1.611
Torsion C ₆ –C ₅ –S ₉ –N ₈ (°)	6.72	-0.61	4.79

the S₇–C₁₂ as well as the S₉–N₈ bond lengths decreased with the number of fluorine atoms. This suggests that the molecule **33** could be the most difficult to reduce (vide infra). The torsion angles are not really changed, with the two rings still almost in the same plane.

As in the CF₃ series, the peak potentials were measured for further applications in photoredox catalysis (Table 4). The values for the cyclic sulfoximines **32** and **33** are more negative than the compound **19** (which is consistent with the bond lengths and the less electron-withdrawing radical CF₂H· and CFH₂·) but not to the same extent than their acyclic analogs **34** and **35** (table 4), with the potential gap still around 0.5 V in each case (–1.45 V vs –1.94 V in CF₂H series and –1.56 V vs an undefined potential below –1.97 V for the CFH₂ series). As previously, the reorganization energy seems to be greater in the case of acyclic sulfoximines **34** and **35** than for the rigid and smaller **32** and **33**. Moreover, the mechanism of the dissociative electron transfer could change in the case of sulfoximines **34** and **35** as α , the electronic transfer coefficient, is greater than 0.5 indicating a possible stepwise dissociative electron transfer, leading to E_p values more negative and higher than their standard potential E° .

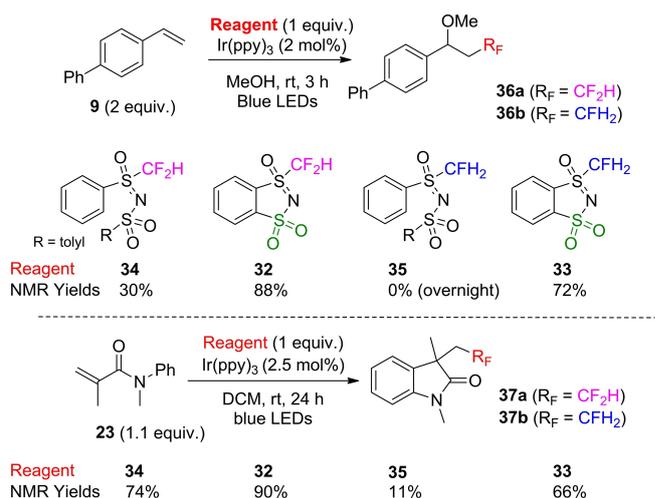
The reactivity of compounds **32** and **33** in photoredox catalysis was tested with the same model reaction described in the CF₃ series, the methoxy perfluoroalkylation of 4-vinylbiphenyl **9** (Scheme 7). Pleasingly, the target **36a** was obtained with an excellent yield after only three hours using the benzodithiazole **32**. The same reaction with the Hu reagent **34** delivered the compound **36a** in only 30% yield. In the monofluoroalkyl series, the result was even more striking. The use of cyclic sulfoximine **33** allowed the preparation of the derivative **36b** in 70%

Table 4. Electrochemical characteristics of new di- and monofluoromethyl sulfoximines.^[a]

	19	32	33	34	35	
E_p (V vs SCE)	-1.26	-1.45	-1.56	-1.73	-1.94	< -1.97
α^b	0.41	0.40	0.53	0.40	0.60	> 0.50

^[a] At $v = 200$ mV/s;

^[b] From $|E_p - E_{p/2}|$.



Scheme 7. Radical reactivity of the benzodithiazoles **32**, **33** and the sulfoximines **34**, **35**. Reactions performed with 0.1 mmol of perfluorinating agent.

yield in only three hours whereas the open reagent **35** was inefficient whatever the reaction time. It is of importance to highlight that this transformation occurred without the need of a non-commercially available strongly reducing compound.^[14g] Finally, the di- and monofluoroalkylation of the N-aryl acrylamide **23** was examined with our new reagents **32** and **33**. To our delight, a very high yield of 90% of CF₂H-product **37a** was obtained with the reagent **32** as difluoromethyl source, which outperformed the corresponding non-cyclic sulfoximine **34**. The difference in reactivity was even more clear-cut for the monofluoroalkylation of **23**: while the non-cyclic sulfoximine **35** showed very poor efficiency (11% yield), our new cyclic reagent **33** delivered the target compound **37b** in a good yield of 66%. These results clearly highlight the importance of the cyclic form of the sulfoximine compared to the open form.

These reactivity tests unequivocally validate our hypothesis and unambiguously show the major interest of a ring system for the smooth generation of mono- and difluorinated radicals. The scope and limitations of these reagents are under development in our group.

Conclusion

In conclusion, we have synthesized new cyclic reagents for perfluoroalkylation with an original scaffold based on cyclic sulfoximines and with enhanced reactivity compared to the existing ones. In particular, we have shown that compound **19** is a trifluoromethylation agent, as well as compounds **32** and **33** for di- and monofluoromethylation reactions. The latter are interesting in view of the few examples of mono- and difluoromethylation reagents in the

literature, and an extensive study of their scope is underway in our laboratory.

Experimental Section

Typical Procedure for Synthesis of 3-(trifluoromethyl)benzo[d][1,3,2]dithiazole 1,1,3-trioxide **19** from **13**

A round-bottomed flask was charged with (*S*-(trifluoromethyl)sulfonylimidoyl)benzene **13** (5.0 g, 23.9 mmol, 1 equiv.) in THF at -50°C under Argon. *n*-BuLi in a 2.5 M solution in hexane (48 mL, 120 mmol, 5 equiv.) was added dropwise at -50°C and the reaction medium stirred for 5 h at -30°C . The temperature was then decreased to -50°C again and solid elemental sulfur (30 g, 120 mmol, 5 equiv.) was added by portion and carefully in order to stay under -30°C . The resulting mixture was stirred for 1 h at room temperature and the reaction was quenched with aqueous NH_4Cl (sat.). The organic and aqueous phases were separated and the aqueous phase extracted with Et_2O (x3). The combined organic phases were then washed with aqueous NaCl (sat.), dried over MgSO_4 and concentrated under vacuum. The resulting crude was then diluted in trifluoroacetic acid (200 mL) and H_2O_2 in a 10 M solution in water (30 mL, 10 equiv.) was carefully added by portion at 0°C . The resulting mixture was stirred at room temperature for 4 h and then diluted with 200 mL of water. The reaction was then carefully quenched with a dilution aqueous NaHCO_3 (sat) and the organic and aqueous phases were separated. The aqueous phase was extracted with CH_2Cl_2 (x3) and the combined organic phases washed with aqueous NaHCO_3 (sat), dried over MgSO_4 and concentrated under vacuum. This crude was purified by column chromatography on silica gel (pentane/ethyl acetate 9/1) and **19** isolated as a white solid in 46% yield (3.0 g, 11.1 mmol).

General Procedure for the Methoxytrifluoromethylation of 4-vinylbiphenyl **9**

A sealed tube purged with argon was charged with 4-vinylbiphenyl **9** (36.0 mg, 0.2 mmol, 2 equiv.), the desired reagent (0.1 mmol, 1 equiv.) and $\text{Ir}(\text{ppy})_3$ (1.3 mg, 0.002 mmol, 0.02 equiv.). Dry MeOH (2 mL, 0.05 M) was added and the reaction medium was purged with argon again. The mixture was placed in the photoreactor vessel $\sim 5\text{--}7$ cm away from the blue LEDs, and allowed to stirred vigorously for 3 h at room temperature. The yield of the desired product **10** was determined by comparing the integration of the ^{19}F NMR resonance of the product with trifluoromethoxybenzene as internal reference.

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