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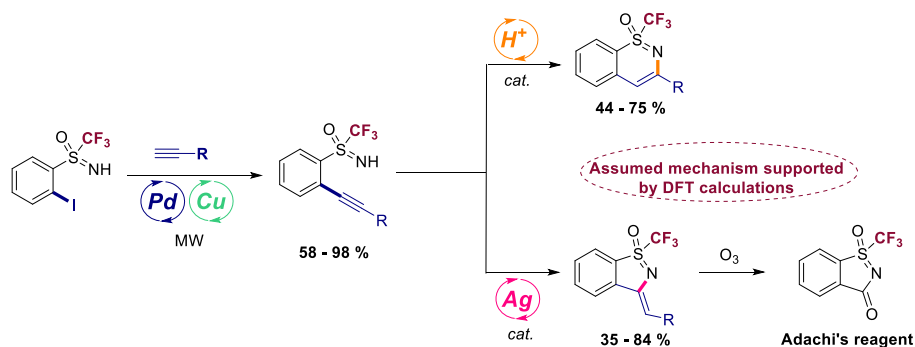
Divergent synthesis of 1,2-benzo[*e*]thiazine and benzo[*d*]thiazole analogs containing a *S*-trifluoromethyl sulfoximine group. Preparation and new properties of the Adachi reagent.

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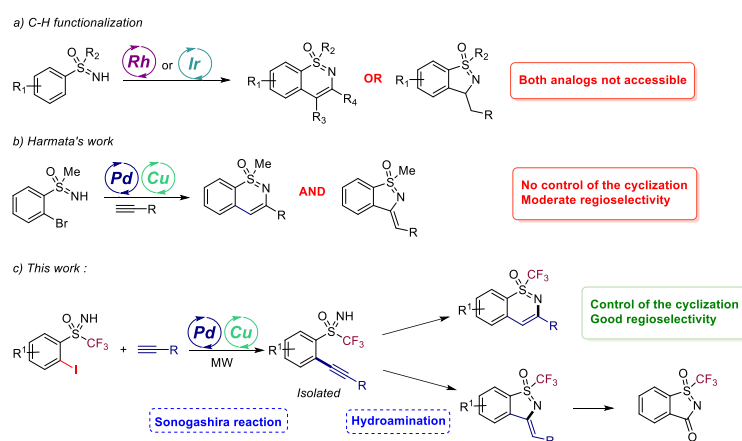
Abstract

We report here the preparation of unprecedented analogs of 1,2-benzothiazine and benzoisothiazole incorporating the *S*-trifluoromethyl sulfoximine group in their core. Starting from a stable precursor, cyclization occurs via a catalytic controlled process. The choice of the catalyst is crucial for selectivity towards the 5- or the 6-membered ring. Interestingly, one of the benzothiazines can be converted on a gram-scale into the trifluoromethylating Adachi reagent. We also disclose the first use of this reagent as a source of radical CF₃ under photoredox catalysis. DFT calculations were performed to clarify the cyclization mechanism.

Introduction

Sulfoximine, the mono-aza analog of sulfone, is an emerging and promising group for pharmaceutical, agrochemical and bioactive purposes.¹ The *S*-trifluoromethyl sulfoximines are unique members of this family, owing to the peculiar properties brought by this moiety.² On the other hand, benzothiazines and benzoisothiazoles are also promising frameworks for the structural diversity they offer and their applications in medicinal chemistry.³ Various benzothiazine containing compounds exhibit biological activities such as anticancer, antimicrobial or anti-inflammatory properties.⁴ Among them, the oxicam family has already been marketed (Meloxicam, Piroxicam, etc.). Likewise, 1,2-benzoisothiazoles are involved in the design of central nervous stimulants, hypertensive agents, antidepressants or HLE (Human Leukocyte elastase) inhibitors.⁵ The inclusion of the sulfoximine group in a heterocyclic ring allows the creation of original analogs of benzothiazine and benzoisothiazole. Limited examples of building 1,2-benzothiazines or 1,2-benzoisothiazoles on a sulfoximine moiety, via rhodium- or iridium-catalyzed C-H functionalization, have been reported (Scheme 1a).⁶ However, the coupling partners reacting with the sulfoximines in these reports can lead to only one of the possible cyclic products. A single example of the synthesis of 1,2-benzothiazines and benzoisothiazoles was reported in 2005 by Harmata *et al.*, via a palladium-catalyzed cross-coupling reaction between *ortho*-bromo sulfoximines and alkynes (Scheme 1b).⁷ Although efficient, this synthetic approach exhibits substrate-dependent cyclization (R = alkyl favors 6-*endo*-dig cyclization while R = aryl favors 5-*exo*-dig cyclization). The absence of control of the hydroamination step leads to moderate regioselectivities (around 3 to 1 in most cases).

Scheme 1. General approach for the preparation of 1,2-benzothiazine and benzoisothiazole analogs.



As part of our ongoing research program devoted to *S*-perfluoroalkyl sulfoximines, we were intrigued by the extension of the methodology of Harmata to our peculiar systems, *i.e.* *S*-trifluoromethyl sulfoximines. Unfortunately, our attempts to apply these conditions failed, pointing out the dramatic modification of reactivity induced by the fluorine atoms, and also the need for an alternative, general and selective method.

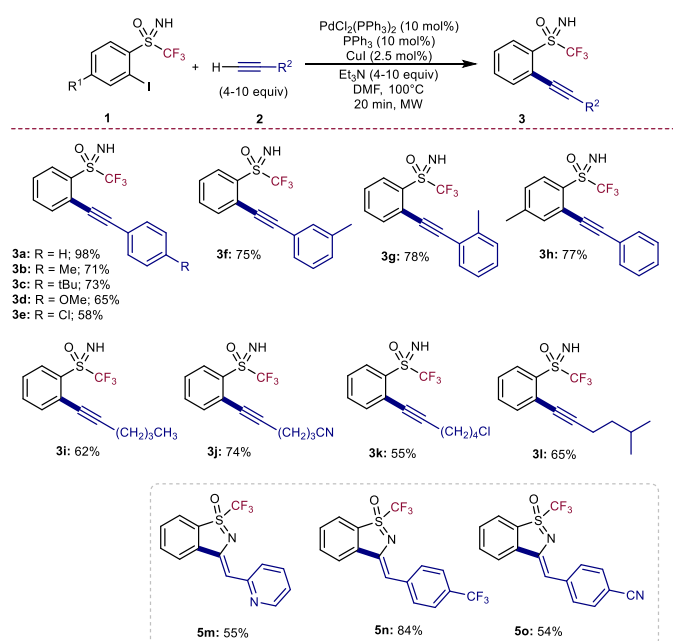
We recently reported the preparation of *o*-vinylaryl *S*-trifluoromethylated sulfoximines *via* Stille and Suzuki cross-coupling reactions, starting from iodo aryl sulfoximines.⁸ The obtained compounds proved to be stable and no further cyclization occurred between the nitrogen and the double bonds. We then postulated that a Sonogashira cross-coupling reaction, followed by a controlled hydroamination process towards a five- or six-membered ring could be an efficient and general entry to 1,2-benzothiazines or benzoisothiazoles bearing a fluorinated sulfoximine moiety (Scheme 1c). We wish to report herein these simple and general catalysed cyclization protocols, delivering either the 5- or the 6- membered core, starting from a common stable precursor. This procedure proved to be compatible with *S*-trifluoromethyl sulfoximines, resulting in original frameworks. Computational studies allowed us to propose a comprehensive mechanism.

Results and Discussion

The Sonogashira cross-coupling reaction conditions were optimized using 1-hexyne as a model substrate with the sulfoximine **1a** under microwave activation (for details see ESI, section 1). The desired *o*-functionalized sulfoximine was isolated, without cyclization, in a 62 % yield as the sole product using PdCl₂(PPh₃)₂ (10 mol%), PPh₃ (10 mol%) and CuI (2.5 mol%) in the presence of a large

excess of triethylamine and 1-hexyne. With these optimized conditions in hand, the scope of the Sonogashira cross-coupling reaction was next investigated (Scheme 2). This transformation proved to be compatible with a variety of alkynes, delivering molecules bearing either aromatic (**3a-h**) or aliphatic (**3i-l**) moieties in moderate to good yields. The presence of a heteroatom on the aromatic ring (**3d-e**) or on the aliphatic chain (**3j-k**) was not deleterious to the conversion. The transformation was also efficient with a tolyl sulfoximine (**3h**). Importantly, all the compounds **3a-l** were fully characterized, stable, and no cyclized product was obtained during the Sonogashira coupling reaction. Surprisingly, the results were reversed with 2-ethynylpyridine, or with an aromatic ring possessing an electronwithdrawing group. In these particular cases, the major isolated products were the benzoisothiazoles **5m-o**. The latter were formed during the purification process for molecule **5m**, or directly during the Sonogashira reaction (**5n-o**).

Scheme 2. Sonogashira coupling reactions.



We then assumed that the palladium and/or the copper catalyst could assist this process. We also noticed a propensity for some compounds **3** to cyclize in a 6-*endo*-dig manner in deuterated chloroform, certainly due to its acidity. These observations encouraged us to develop selective conditions to control the cyclization towards either the 6- or the 5-membered ring, with emphasis on either acid or metal

catalyzed reaction conditions. Our complete study is available in the ESI (Section 2), and Table 1 summarizes some relevant results. Compound **3a** was used as a model substrate.

A set of catalysts was first tested in toluene (Table 1, entries 1-8). A pronounced tendency clearly appeared. Brønsted acids favored 6-*endo*-dig cyclization, whereas Lewis acids gave preferentially 5-*exo*-dig cyclization. The regioselectivity of the hydroamination also appeared to be dependent on the solvent. Triflic acid was identified as the best reagent to favor the formation of compound **4a** (entries 1-4) and silver trifluoroacetate for the sulfoximine **5a** (entries 5-8). The structures **4a** and **5a** were determined by X-ray diffraction analysis (see ESI). The optimized reaction conditions (entries 4 and 19) were then applied to *o*-alkynyl aryl sulfoximines **3**. They were successfully cyclized in a 6-*endo*-dig manner with moderate to good yields and excellent selectivities of up to 100:0 (Scheme 3, left) by simply heating in toluene in the presence of a catalytic amount of TfOH (10 mol%).

Table 1. Screening of conditions for the regioselective cyclization of **3a**.

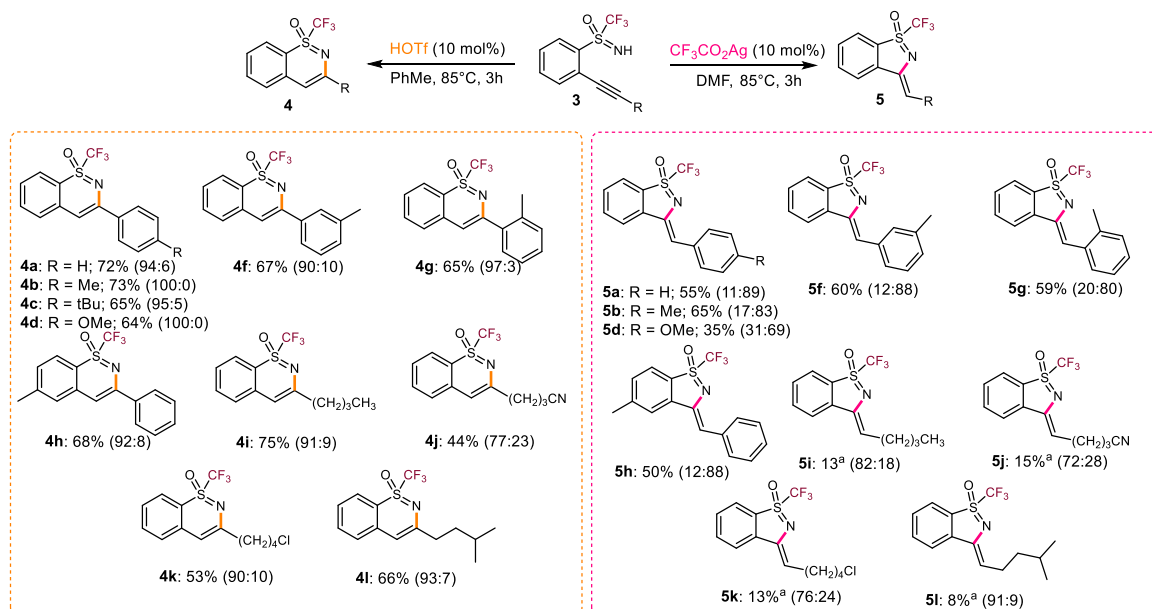
Entry	Catalyst ^a	Solvent	Ratio 4a/5a	4a/5a (%) ^b
1	H ₂ SO ₄	PhMe	84/16	48/10
2	CF ₃ CO ₂ H	PhMe	80/20	51/13
3	HOTf	PhMe	88/12	51/7
4^c	HOTf	PhMe	90/10	78/7(77)
5	CuI	PhMe	70/30	32/13
6	Pd(PPh ₃) ₄	PhMe	24/76	3/9
7	Ag(OTf)	PhMe	44/56	34/43
8	CF ₃ CO ₂ Ag	PhMe	27/73	19/52
9	CuI	DMF	40/60	2/4
10	Pd(PPh ₃) ₄	DMF	2/98	1/45
11	Ag(OTf)	DMF	27/73	16/42
12	CF ₃ CO ₂ Ag	DMF	11/89	7/56
13	HOTf	DMF	60/40	13/8
14	HOTf	MeCN	90/10	23/3
15	HOTf	CH ₂ Cl ₂	77/23	48/15
16	HOTf	C ₆ H ₄ Cl	78/22	14/4

17	CF ₃ CO ₂ Ag	MeCN	19/81	9/38
18	CF ₃ CO ₂ Ag	CH ₂ Cl ₂	30/70	17/40
19^c	CF₃CO₂Ag	DMF	11/89	8/65 (52)

^a 10 mol% of catalyst were used. ^b ¹⁹F NMR yield using trifluoromethoxybenzene as internal standard, isolated yields of the major products are in brackets. ^c The reaction was heated at 85°C during 3h. Conversions are available in the Supporting Information.

1,2-Benzothiazine analogs **4a-l** are stable compounds and were fully characterized. Interestingly, the presence of a substituent on the aromatic ring of the alkyne (**4b-d**, **4f-g**) or the sulfoximine (**4h**) did not have any negative impact on the selectivity which was always in favor of the six-membered ring. This methodology was also successful in the aliphatic series, giving rise to compounds **4i-l**.

Scheme 3. Regioselective synthesis of 1,2-benzothiazines **4** and benzoisothiazoles **5**.



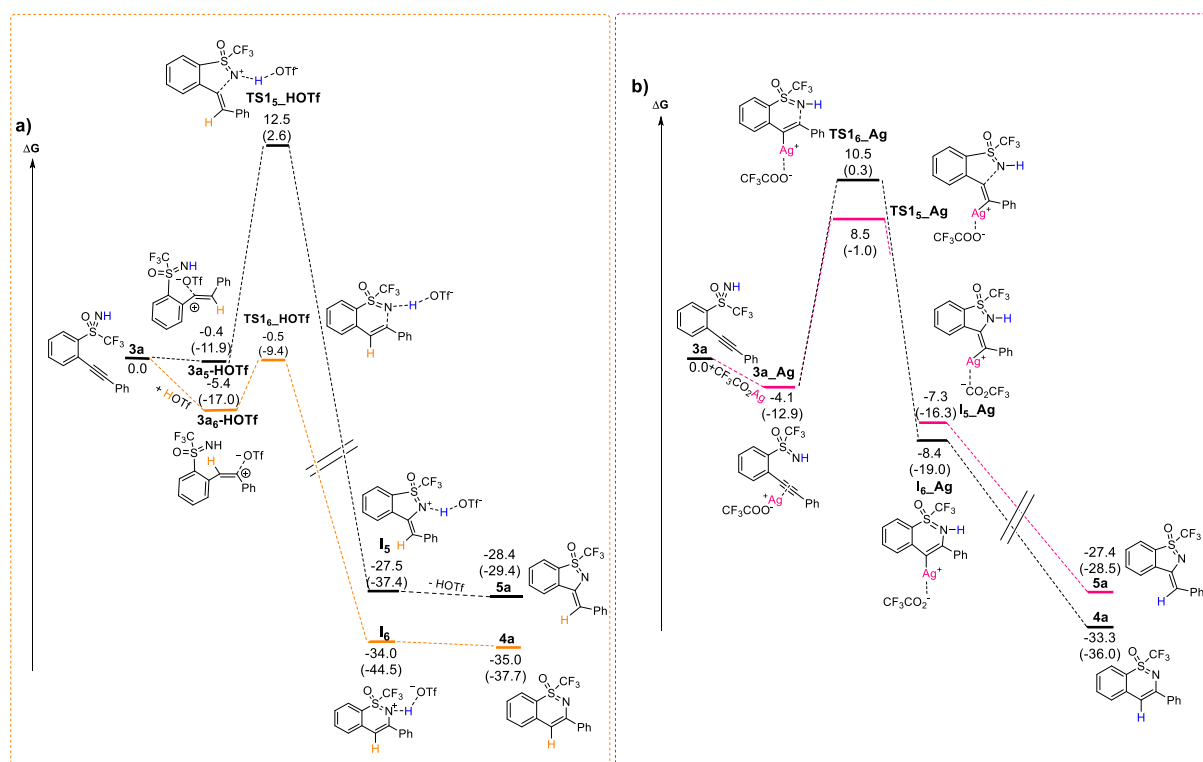
Isolated yields of the major product are given. Ratio **4:5** specified in brackets was measured by ¹⁹F NMR analysis of the crude mixture. ^a ¹⁹F NMR yields of the 5-membered compounds (minor products) are given using trifluoromethoxybenzene as internal standard.

The preparation of 1,2-benzoisothiazole derivatives **5a-l** proved to be both successful and surprising. Heating the substrates **3** in DMF with a catalytic amount of CF₃CO₂Ag resulted in total conversion and gave rise to benzoisothiazoles **5a-l** (Scheme 3, right). With substrates possessing an aromatic ring attached to the triple bond, the molecules **5a-b**, **d**, **f-h** were isolated with good regioselectivities in favor of the 5-membered ring (up to 89/11 d.r.). Surprisingly, in the aliphatic series,

cyclization occurred in favour of the 6-membered ring, accounting for the very low yield of sulfoximines **5i-l**. The treatment of compound **4a** with $\text{CF}_3\text{CO}_2\text{Ag}$ gave no conversion, while treatment of molecule **5a** under acidic conditions led to total decomposition. We can therefore assert that the sulfoximines **5** are not in equilibrium with the bicyclic compounds **4**.

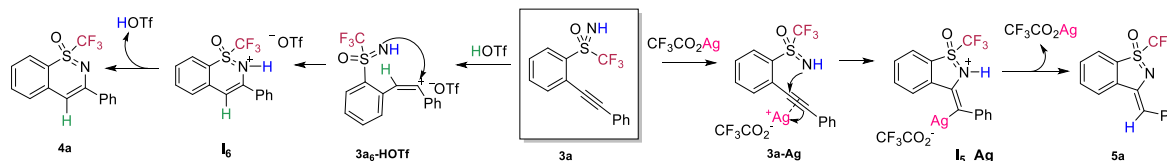
At this stage, the mechanisms of these two intriguing catalytic pathways were far from obvious. Consequently, to gain insight into this transformation, computational studies were initiated in order to rationalize our results.⁹ Two catalysts were selected, HOTf with toluene as solvent and $\text{CF}_3\text{CO}_2\text{Ag}$ with DMF, which favor respectively the formation of compounds **4a** or **5a**. The compound **4a** corresponds to the thermodynamic product of the cyclization. It is more stable than compound **5a** by around 6-8 kcal/mol in the two solvents. With triflic acid, the energy profiles involving assistance of the catalyst (Figure 1a) are the most favored (Figure S3 for other mechanisms). The two processes (5 and 6-membered cyclization), computed in toluene, were predicted to be highly exergonic ($\Delta G < -28.0$ kcal/mol). In these processes, a first adduct **3a_x-HOTf** (x: 5, 6) is formed. It corresponds to the activation of the triple bond by HOTf, with the protonation of the C₁ atom of the π_{CC} orbital being slightly favored (**3a₆-HOTf**). The activation barrier was found to be 7-8 kcal/mol lower in energy than that for **TS1₅-HOTf**. The N...C distance in the TSs varies from 1.890 Å to 2.030 Å, suggesting a later transition state for the 5-membered ring. These theoretical data are consistent with the experimental results, and show that the cyclization in favor of **4a** is kinetically controlled.

Figure 1. Energy profile (ΔG in kcal/mol) for cyclization of **3a** in the presence of : **a)** HOTf computed at SMD(Toluene)-B3LYP/6-31G** level of theory; **b)** $\text{CF}_3\text{CO}_2\text{Ag}$ computed at SMD(DMF)-B3LYP/SDD+f(Ag),6-31G**(other atoms) level of theory. B3LYP-D3 values are in brackets.



Considering now the $\text{CF}_3\text{CO}_2\text{Ag}$ catalyst, the reaction (Figure 1b), calculated in DMF, proceeds through the formation of the cyclic intermediate $\text{I}_x\text{-Ag}$ (cyclization step, $x = 5, 6$). A final prototropy followed by the regeneration of $\text{CF}_3\text{CO}_2\text{Ag}$ gives rise to the compounds **5a/4a** (Scheme 4). For modelling the process, we focused on the key step of the mechanism, the cyclization step (Figure 1b and Figure S4), going from $\text{I}_x\text{-Ag}$ to **4a/5a** corresponding to a straightforward prototropic shift (Figure S5). As previously observed in toluene, the overall reaction is strongly exergonic ($\Delta G > -27$ kcal/mol for **5a** and > -33 kcal/mol for **4a**) and the 6-membered ring is the thermodynamically privileged compound. DFT calculations revealed that $\text{CF}_3\text{CO}_2\text{Ag}$ first weakly activates the triple bond of **3a**. The formation of **3a-Ag** is exergonic ($\Delta G = -4.1$ kcal/mol, -12.9 in B3LYP-D3). Cyclization then occurs. The two cyclization transition states $\text{TS1}_x\text{-Ag}$ ($x = 5$ or 6) are close in energy, with a lower activation barrier found for the formation of the 5-membered ring **I5-Ag** (12.6 kcal/mol vs. 14.6 kcal/mol without dispersion and 11.9 vs. 13.2 kcal/mol with dispersion). The C...N distances are quite similar in the two TSs, 2.076 ($x = 5$) and 2.090 Å ($x = 6$) and Ag...O distances are around 2.14 Å. Thus, the theoretical results indicate that the selective formation of **5a**, observed experimentally, is under kinetic control. Conversely, the 6-membered ring cyclization results from thermodynamic control. The computational studies are clearly in favor of the mechanisms proposed in Scheme 4.

Scheme 4. Proposed privileged mechanism for the cyclization steps from **3a** in the presence of HOTf or CF₃CO₂Ag.

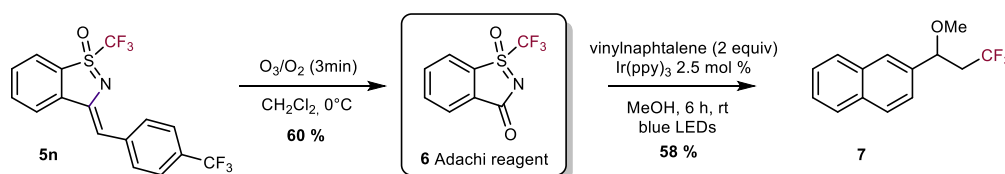


They also account for the observed regioselectivities. Indeed, despite 6-*endo*-dig cyclization being largely favored, the activation barrier for **TS1₅-HOTf** remains accessible in the experimental conditions ($\Delta G^\ddagger = 12.9$ kcal/mol, 14.5 in B3LYP-D3), which can explain the formation of a tiny fraction of **5a**. Regarding the 5-*exo*-dig cyclization, the difference between the activation barriers is even less significant, and leads to the formation of a small amount of benzothiazine. Finally, the impact of the substituents (alkyl *versus* aryl) was studied. The comparison of the two energy profiles for cyclization of **3a** and **3i** [R : Ph or (CH₂)₃CH₃, respectively on the triple bond of **3**] has shown that the formation of the intermediate **I₅-Ag**, essential for the cyclization step, is quasi thermoneutral for **3i** [ΔG : -0.2 kcal/mol and 0.5 kcal/mol in B3LYP-D3] and slightly exergonic for **3a** [ΔG : -3.2 kcal/mol and -3.4 kcal/mol in B3LYP-D3] (Figure S6). As a result, this intermediate is not enough stabilized with aliphatic chains, which is in line with the poor yields for **5i**. Moreover, in contrary to the results described for aromatic compound **3a** (lower activation barrier for **TS1₅-Ag**), DFT calculations indicated that the activation barrier for the formation of the 6-membered ring **4i** from **3i** is computed lower in energy than that for the 5 membered-ring **5i** [ΔG^\ddagger : 12.5 kcal/mol and 11.2 kcal/mol in B3LYP-D3 for **TS1₆-Ag_{Alkyl}** *versus* 13.4 kcal/mol and 14 kcal/mol in B3LYP-D3 for **TS1₅-Ag_{Alkyl}**], consistent with the experimental results. All these data point out that the formation of the major product with CF₃CO₂Ag (5-membered ring **5a** or 6-membered ring **4i**) is driven by the height of the activation barrier of the cyclization step and the relative stability of the intermediate **I₅-Ag** towards initial reactant **3**, whatever the substitution of the triple bond in compound **3**.

All the new molecules prepared in this work could have various and interesting applications. Among them, the most direct and obvious one is the opportunity to prepare the Adachi reagent **6** by simple oxidation of a five-membered ring derivative (scheme 5). This cyclic sulfoximine is known as an electrophilic source of the trifluoromethyl group and can be compared to the Shibata reagent.¹⁰ Adachi and Ishihara reported compound **6** in a patent and prepared it by Yagupolskii's method.¹¹ To the best of our knowledge no other synthesis has been proposed in the literature.¹² We chose the molecule **5n** as a model substrate owing to its high yielding and straightforward synthesis starting from iodo sulfoximine

1. Ozonolysis of the exocyclic double bond of **5n** gave rise to the target compound **6** in a reasonable yield. The transformation could be performed on a gram scale. In the highly challenging scientific context of the use of electrophilic trifluoromethylating reagents as a source of radicals¹³ as well as our own expertise in this domain,¹⁴ the sulfoximine **6** was tested under photoredox catalysis. We were pleased that methoxy trifluoromethylation of vinylnaphthalene was successful under these conditions. The isolation of compound **7** is the first example of the use of the Adachi reagent for the generation of the CF₃ radical.

Scheme 5. Preparation of the Adachi reagent and its use under photoredox catalysis



Conclusion

In conclusion, we have described the first and efficient preparation of *ortho*-alkynyl *S*-trifluoromethyl *S*-arylsulfoximines through a Sonogashira reaction under microwave activation. The non-cyclized sulfoximines were isolated in moderate to excellent yields and allowed us to control the hydroamination cyclization reaction in a second step. DFT calculations enabled us to propose a consistent mechanism for the cyclization and to understand its regioselectivity. Lastly, an efficient synthesis of the Adachi reagent is described for the first time. Potential further developments are currently being studied in our laboratory.

Experimental Section

General techniques: All cross-coupling reactions were carried out in microwave glassware previously dried in an oven at 80°C, under an atmosphere of argon. Dry DMF was purchased from Sigma-Aldrich. Triethylamine was distilled under nitrogen from CaH₂. Commercial starting materials were used without further purification. Preparative chromatography plates were prepared using silica gel. Nuclear magnetic resonance (¹H NMR, ¹⁹F NMR and ¹³C NMR) spectra were recorded on a Bruker AC-200 or AC-300 spectrometer in CD₃CN and CDCl₃.

Reported coupling constants and chemical shifts were based on a first order analysis. Internal references were the residual peak of CHCl₃ (7.26 ppm) or CH₃CN (1.94 ppm) for ¹H (200 or 300 MHz) NMR spectra, central peak of CDCl₃ (77.16 ppm) or peak of CD₃CN (118.26 ppm) for ¹³C (75 or 50 MHz) NMR spectra, and CFCl₃ (0.00 ppm) as internal reference for ¹⁹F (188 MHz or 282 MHz) NMR spectra. High Resolution Mass Spectrometry (HRMS) was recorded on a Mass Spectrometer XEVO-QTOF in Institut Lavoisier of Versailles – University of Versailles Saint-Quentin. Microwave experiments were conducted in an Anton Paar Monowave 300 instrument using the following method: P = 600W, Full air cooling ON, Stirring ON. The imino(2-iodophenyl)(trifluoromethyl)-λ⁶-sulfanone (**1a**) and the imino(2-iodo-4-methylphenyl) (trifluoromethyl)-λ⁶-sulfanone (**1b**) were prepared following the literature procedure.^{6k-8} An ozone generator BMT 802X was used to produce ozone from pure oxygen.

General procedure for the Sonogashira cross-coupling reaction: To a mixture of *o*-iodine sulfoximine **1a** (100 mg, 0.3 mmol) and PPh₃ (8 mg, 0.03 mmol) in dry and degassed DMF (5 mL) in a microwave tube, was added the alkyne (1.2-3 mmol)¹⁵ and Et₃N (418 μL, 3 mmol). Pd(PPh₃)₂Cl₂ (21 mg, 0.03 mmol) was added and the solution was stirred at room temperature for 10 minutes under an inert atmosphere. Then, CuI (1.4 mg, 0.0075 mmol) was added, the tube was sealed and the solution was stirred for 20 minutes at room temperature. The tube was then placed in the microwave for 20 minutes at 100°C. Et₂O (10 mL) was added and the mixture was washed with a solution of NaHCO₃ (5%) (3 x 10 mL). The organic phase was concentrated under reduced pressure. The crude product was purified on a preparative silica plate using petroleum ether/ether = 7/3 as eluent to give the desired *ortho*-functionalized sulfoximine **3**.

Imino(2-(phenylethynyl)phenyl)(trifluoromethyl)-λ⁶-sulfanone (3a): 91 mg - 98% yield as yellow oil. ¹⁹NMR (188 MHz, CD₃CN): δ (ppm) = -76.65 (s, CF₃). ¹H NMR (200 MHz, CD₃CN): δ (ppm) = 8.20 (d, *J* = 7.6 Hz, 1H), 7.78-7.66 (m, 2H), 7.60-7.48 (m, 3H), 7.36-7.33 (m, 3H), 4.89 (s, brs, 1H). ¹³C{¹H} NMR (50 MHz, CD₃CN): δ (ppm) = 136.5, 136.2, 133.7, 132.5, 130.5, 130.1, 129.7, 125.5, 123.2, 122.3 (q, *J* = 332.6 Hz), 98.7, 86.4. **HRMS** (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₅H₁₁F₃NOS 310.0513; Found 310.0524.

Imino(2-(*p*-tolylethynyl)phenyl)(trifluoromethyl)-λ⁶-sulfanone (3b): 69 mg – 71 % yield as yellow oil. ¹⁹F NMR (188 MHz, CD₃CN): δ (ppm) = -76.66 (s, CF₃). ¹H NMR (200 MHz, CD₃CN): δ (ppm) = 8.29 (d, *J* = 8.4 Hz, 1H), 7.76-7.73 (m, 2H), 7.62-7.64 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.89 (s, brs, 1H), 2.31 (s, 3H). ¹³C{¹H} NMR (50 MHz, CD₃CN): δ (ppm) = 141.1, 136.4, 136.2, 133.7, 133.3, 132.4, 130.4,

129.9, 125.7, 121.9 (q, $J = 332.4$ Hz), 120.1, 99.1, 85.9, 21.58. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NOS$ 324.0670; Found 324.0675.

Imino(2-((4-(tert-butyl)phenyl)ethynyl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3c): 80 mg – 73 % yield as yellow oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.63 (s, CF_3). **1H NMR** (300 MHz, CD_3CN): δ (ppm) = 8.25 (d, $J = 8.0$ Hz, 1H), 7.82-7.74 (m, 2H), 7.64-7.59 (m, 1H), 7.50-7.43 (m, 4H), 4.92 (s, brs, 1H), 1.28 (s, 9H). **$^{13}C\{^1H\}$ NMR** (75 MHz, CD_3CN): δ (ppm) = 154.0, 136.4, 136.3, 133.7, 133.4, 132.3, 130.0, 126.8, 125.7, 122.3 (q, $J = 332.8$ Hz), 120.2, 99.0, 85.9, 35.5, 31.3. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{19}H_{19}F_3NOS$ 366.1139; Found 366.1141.

Imino(2-((4-methoxyphenyl)ethynyl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3d): 67 mg – 65 % yield as yellow oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.66 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.20 (d, $J = 8.1$ Hz, 1H), 7.74-7.71 (m, 2H), 7.61-7.51 (m, 1H), 7.45 (d, $J = 8.9$ Hz, 2H), 6.91 (d, $J = 8.9$ Hz, 2H), 4.89 (s, brs, 1H), 3.75 (s, 3H). **$^{13}C\{^1H\}$ NMR** (50 MHz, CD_3CN): δ (ppm) = 161.6, 136.2, 136.1, 134.1, 133.6, 133.0, 129.7, 125.9, 122.2 (q, $J = 332.4$ Hz), 115.3, 115.1, 99.2, 85.4, 56.1. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NO_2S$ 340.0619; Found 340.0611.

Imino(2-((4-chlorophenyl)ethynyl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3e): 60 mg – 58 % yield as yellow solid. **Mp** = 86°C. **^{19}F NMR** (282 MHz, CD_3CN): δ (ppm) = -76.70 (s, CF_3). **1H NMR** (300 MHz, CD_3CN): δ (ppm) = 8.29 (d, $J = 8.0$ Hz, 1H), 7.88-7.77 (m, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.55 (d, $J = 8.3$ Hz, 2H), 7.44 (d, $J = 8.3$ Hz, 2H), 4.96 (s, brs, 1H). **$^{13}C\{^1H\}$ NMR** (75 MHz, CD_3CN): δ (ppm) = 136.5, 136.3, 135.9, 134.0, 133.8, 133.4, 130.4, 130.0, 125.2, 122.2 (q, $J = 333.4$ Hz), 122.0, 97.3, 87.4. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{15}H_{10}ClF_3NOS$ 344.0124; Found 344.0120.

Imino(2-(*m*-tolylethynyl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3f): 75 mg – 77 % yield as orange oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.66 (s, CF_3). **1H NMR** (300 MHz, CD_3CN): δ (ppm) = 8.21 (d, $J = 8.2$ Hz, 1H), 7.77-7.70 (m, 2H), 7.61-7.55 (m, 1H), 7.33-7.18 (m, 4H), 4.90 (s, brs, 1H), 2.28 (s, 3H). **$^{13}C\{^1H\}$ NMR** (75 MHz, CD_3CN): δ (ppm) = 139.6, 136.5, 136.2, 133.7, 133.3, 132.8, 131.3, 130.1, 129.6, 129.5, 125.6, 123.1, 122.3 (q, $J = 332.7$ Hz), 98.9, 86.1, 21.2. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NOS$ 324.0670; Found 324.0679.

Imino(2-(*o*-tolylethynyl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3g): 76 mg – 78 % yield as orange oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.75 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.25 (d, $J = 8.0$ Hz, 1H), 7.87-7.73 (m, 2H), 7.68-7.56 (m, 1H), 7.51 (d, $J = 7.4$ Hz), 7.36-7.14 (m, 3H), 4.92 (s, brs, 1H), 2.49 (s, 3H). **$^{13}C\{^1H\}$ NMR** (50 MHz, CD_3CN): δ (ppm) = 141.7, 136.9, 136.2, 133.7, 133.2, 132.8, 130.7, 130.5, 130.1,

126.8, 125.9, 123.0, 122.3 (q, $J = 332.6$ Hz), 97.9, 90.1, 20.7. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NOS$ 324.0670; Found 324.0670.

Imino(4-methyl-2-(phenylethynyl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3h): 75 mg – 77 % yield as orange oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.92 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.15 (d, $J = 8.3$ Hz, 1H), 7.66 (s, 1H), 7.58 (m, 2H), 7.50 – 7.37 (m, 4H), 4.90 (s, brs, 1H), 2.44 (s, 3H). **$^{13}C\{^1H\}$ NMR** (50 MHz, CD_3CN): δ (ppm) = 148.0, 136.9, 133.8, 132.4, 130.9, 130.4, 129.7, 125.3, 123.3, 122.3 (q, $J = 331.9$ Hz), 98.1, 86.6, 21.4. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NOS$ 324.0670; Found 324.0675.

Imino(2-(hex-1-yn-1-yl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3i): 52 mg – 60 % yield as yellow oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.88 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.18 (d, $J = 8.0$ Hz, 1H), 7.75-7.52 (m, 3H), 4.85 (s, brs, 1H), 2.45 (t, $J = 6.7$ Hz, 2H), 1.69-1.32 (m, 4H), 0.90 (t, $J = 7.1$ Hz, 3H). **$^{13}C\{^1H\}$ NMR** (50 MHz, CD_3CN): δ (ppm) = 136.8, 136.1, 133.5 (q, $J = 1.3$ Hz), 133.2, 129.4, 126.3, 122.4 (q, $J = 332.8$ Hz), 101.9, 77.5, 30.9, 22.6, 19.9, 13.8. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{13}H_{15}F_3NOS$ 290.0826; Found 290.0833.

Imino(2-(hex-5-yne nitrile)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3j): 67 mg – 74 % yield as yellow oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.73 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.18 (d, $J = 7.8$ Hz, 1H), 7.69 (m, 2H), 7.61 – 7.49 (m, 1H), 4.84 (s, brs, 1H), 2.65 – 2.47 (m, 4H), 1.98 – 1.76 (m, 2H). **$^{13}C\{^1H\}$ NMR** (50 MHz, CD_3CN): δ (ppm) = 136.9, 136.2, 133.4, 133.3 (q, $J = 1.1$ Hz), 129.7, 125.7, 122.2 (q, $J = 332.4$ Hz), 98.9, 78.7, 24.9, 19.3, 16.5. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{13}H_{12}F_3N_2OS$ 301.0622; Found 301.0625.

Imino(2-(6-chlorohex-1-yn-1-yl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3k): 54 mg – 56 % yield as yellow oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.78 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.17 (d, $J = 7.8$ Hz, 1H), 7.80-7.48 (m, 3H), 4.82 (s, brs, 1H), 3.60 (t, $J = 6.5$ Hz, 2H), 2.48 (t, $J = 6.8$ Hz, 2H), 2.03-1.81 (m, 2H), 1.70 (m, 2H). **$^{13}C\{^1H\}$ NMR** (50 MHz, CD_3CN): δ (ppm) = 136.88, 136.1, 133.4 (q, $J = 1.4$ Hz), 133.3, 129.5, 126.2, 122.2 (q, $J = 332.7$ Hz), 101.0, 77.9, 45.7, 32.3, 26.1, 18.5. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{13}H_{14}ClF_3NOS$ 324.0437; Found 324.0436.

Imino(2-(5-methylhex-1-yn-1-yl)phenyl)(trifluoromethyl)- λ^6 -sulfanone (3l): 59 mg – 65 % yield as yellow oil. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -76.87 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.16 (d, $J = 8.1$ Hz, 1H), 7.75 – 7.48 (m, 3H), 4.83 (s, brs, 1H), 2.44 (t, $J = 7.3$ Hz, 2H), 1.73 (m, 1H), 1.45 (q, $J = 7.1$ Hz, 2H), 0.88 (d, $J = 6.6$ Hz, 6H). **$^{13}C\{^1H\}$ NMR** (50 MHz, CD_3CN): δ (ppm) = 136.8, 136.1, 133.4 (q, $J = 1.3$ Hz), 133.2,

129.4, 126.3, 122.3 (q, $J = 333.3$ Hz), 101.9, 77.5, 37.7, 27.9, 22.3, 18.2. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{14}H_{17}F_3NOS$ 304.0983; Found 304.0974.

(Z)-3-(pyridin-2-ylmethylene)-1-(trifluoromethyl)benzothiazole-1-oxide (5m): 51 mg – 55 % yield as brownish solid. **Mp** = 93 °C. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -75.58 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.62 (d, $J = 8.2$ Hz, 2H), 8.22 (d, $J = 7.9$ Hz, 1H), 8.09 (d, $J = 7.7$ Hz, 1H), 7.94 (d, $J = 7.5$ Hz, 1H), 7.82 – 7.71 (m, 2H), 7.22 – 7.16 (m, 1H), 6.98 (s, 1H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ (ppm) = 154.7, 149.2, 144.9, 141.4, 136.8, 135.4, 130.6, 129.5, 128.7, 125.8, 124.1, 122.3, 120.9 (q, $J = 331.8$ Hz), 120.1. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{14}H_{10}F_3N_2OS$ 311.0466; Found 311.0463.

(Z)-1-oxido-1-(trifluoromethyl)-3-(4-(trifluoromethyl)benzylidene)benzothiazole (5n): 95 mg – 84 % yield as brownish solid. **Mp** = 126 °C. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -61.76 (s, 3F) and -75.62 (s, 3F). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.13 (dd, $J = 8.0$ and 5.4 Hz, 3H), 8.03 (d, $J = 7.8$ Hz, 1H), 7.95-7.82 (m, 1H), 7.76-7.68 (m, 1H), 7.64 (d, $J = 8.3$ Hz, 2H), 6.87 (s, 1H). **$^{13}C\{^1H\}$ NMR** (50 MHz, CD_3CN): δ (ppm) = 145.2, 142.8, 140.3, 137.3, 131.8, 131.0, 128.8, 128.2, 126.2 (q, $J = 3.9$ Hz), 126.1 (q, $J = 335.2$), 126.0, 125.3, 123.7, 112.0. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{10}F_6NOS$ 378.0387; Found 378.0379.

(Z)-4-((1-oxido-1-(trifluoromethyl)benzothiazol-3-ylidene)methyl)benzotrile (5o): 54 mg – 54 % yield as yellow solid. **Mp** = 74 °C. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -75.53 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 8.15 (d, $J = 8.3$ Hz, 3H), 8.08 (d, $J = 7.8$ Hz, 1H), 8.02-7.88 (m, 1H), 7.82-7.65 (m, 3H), 6.88 (s, 1H). **$^{13}C\{^1H\}$ NMR** (75 MHz, CD_3CN): δ (ppm) = 145.1, 143.5, 141.1, 137.4, 133.2, 132.0, 131.0, 126.2, 125.5, 123.8, 121.7 (q, $J = 329.9$ Hz), 119.9, 111.8, 110.9. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{10}F_3N_2OS$ 335.0466; Found 335.0464.

General procedure for the synthesis of benzothiazines 4: Sulfoximine **3** (0.16 mmol) was dissolved in toluene (3 mL) and HOTf (1.4 μ L, 0.016 mmol) was added. The mixture was heated at 85°C for 3 hours. Then, the reaction was allowed to cool to room temperature, diluted with Et_2O (5 mL) and washed with a saturated $NaHCO_3$ solution (3 x 5 mL). The organic phase was concentrated under reduced pressure. The crude product was purified on a preparative silica plate using petroleum ether/ether = 7/3 as eluent to isolate the desired product **4** (Compounds **4** and **5** can be perfectly separated by preparative thin-layer chromatography).

3-phenyl-1-(trifluoromethyl)benzo[e][1,2]thiazine-1-oxide (4a): 38 mg – 77 % yield as yellow solid. **Mp** = 101 °C. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -79.89 (s, CF_3). **1H NMR** (300 MHz, CD_3CN): δ (ppm) = 7.91 (m, 3H), 7.82 (t, $J = 7.7$ Hz, 1H), 7.67 – 7.49 (m, 2H), 7.43 (m, 3H), 6.95 (s, 1H). **$^{13}C\{^1H\}$ NMR** (75 MHz,

CD₃CN): δ (ppm) = 147.3, 141.9, 137.7, 137.5, 130.7, 129.7, 129.5, 129.2, 127.3, 127.1, 121.7 (q, J = 332.9 Hz), 115.6, 101.4. **HRMS** (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₅H₁₁F₃NOS 310.0513; Found 310.0520.

3-(*p*-tolyl)-1-(trifluoromethyl)benzo[*e*][1,2]thiazine-1-oxide (4b): 37 mg – 73 % yield as orange solid. **Mp** = 100 °C. **¹⁹F NMR** (282 MHz, CDCl₃): δ (ppm) = -80.25 (s, CF₃). **¹H NMR** (300 MHz, CDCl₃): δ (ppm) = 7.83 (d, J = 7.9 Hz, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.69 – 7.60 (m, 1H), 7.40 (m, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.65 (s, 1H), 2.34 (s, 3H). **¹³C{¹H} NMR** (75 MHz, CDCl₃): δ (ppm) = 147.6, 141.3, 140.0, 135.8, 134.2, 129.4, 127.8, 127.5, 126.7, 126.5, 120.8 (q, J = 333.4 Hz), 110.9, 99.5, 21.4. **HRMS** (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₆H₁₃F₃NOS 324.0670; Found 324.0669.

3-(*p*-*tert*-butyl)-1-(trifluoromethyl)benzo[*e*][1,2]thiazine-1-oxide (4c): 38 mg – 65 % yield as yellow solid. **Mp** = 116 °C. **¹⁹F NMR** (188 MHz, CDCl₃): δ (ppm) = -80.31 (s, CF₃). **¹H NMR** (200 MHz, CDCl₃): δ (ppm) = 7.96 – 7.84 (m, 3H), 7.78 – 7.66 (m, 1H), 7.53 – 7.41 (m, 4H), 6.74 (s, 1H), 1.36 (s, 9H). **¹³C{¹H} NMR** (50 MHz, CDCl₃): δ (ppm) = 153.2, 147.5, 141.3, 135.8, 134.2, 127.8, 127.5, 126.7, 126.3, 125.7, 120.8 (q, J = 333.1 Hz), 110.9 (q, J = 1.1 Hz), 99.56, 34.9, 31.36. **HRMS** (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₉H₁₉F₃NOS 366.1139; Found 366.1136.

3-(*p*-methoxy)-1-(trifluoromethyl)benzo[*e*][1,2]thiazine-1-oxide (4d): 35 mg – 64 % yield as yellow solid. **Mp** = 93 °C. **¹⁹F NMR** (188 MHz, CD₃CN): δ (ppm) = -79.98 (s, CF₃). **¹H NMR** (200 MHz, CD₃CN): δ (ppm) = 7.95 – 7.71 (m, 4H), 7.53 (m, 2H), 6.96 (d, J = 8.8 Hz, 2H), 6.83 (s, 1H), 3.79 (s, 3H). **¹³C{¹H} NMR** (75 MHz, CD₃CN): δ (ppm) = 162.1, 147.3, 142.2, 137.4, 130.1, 128.9, 128.6, 127.2, 121.7 (q, J = 332.5 Hz), 115.0, 111.0, 99.9, 56.1. **HRMS** (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₆H₁₃F₃NO₂S 340.0616; Found 340.0619.

3-(*m*-tolyl)-1-(trifluoromethyl)benzo[*e*][1,2]thiazine-1-oxide (4f): 35 mg – 67 % yield as yellow solid. **Mp** = 68 °C. **¹⁹F NMR** (188 MHz, CDCl₃): δ (ppm) = -80.21 (s, CF₃). **¹H NMR** (300 MHz, CDCl₃): δ (ppm) = 7.91 (d, J = 7.8 Hz, 1H), 7.74 (m, 3H), 7.49 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 6.75 (s, 1H), 2.43 (s, 3H). **¹³C{¹H} NMR** (75 MHz, CDCl₃): δ (ppm) = 147.6, 141.1, 138.4, 136.9, 135.8, 130.6, 128.6, 127.9, 127.7, 127.2, 126.7, 123.6, 120.8 (q, J = 333.3 Hz), 100.1, 21.6. **HRMS** (ESI-TOF) m/z : [M+H]⁺ Calcd for C₁₆H₁₃F₃NOS 324.0670; Found 324.0664.

3-(*o*-tolyl)-1-(trifluoromethyl)benzo[*e*][1,2]thiazine-1-oxide (4g): 34 mg – 65 % yield as orange solid. **Mp** = 75 °C. **¹⁹F NMR** (188 MHz, CD₃CN): δ (ppm) = -79.76 (s, CF₃). **¹H NMR** (300 MHz, CD₃CN): δ (ppm) = 7.92 (d, J = 8.1 Hz, 1H), 7.85 – 7.75 (m, 1H), 7.63 – 7.50 (m, 2H), 7.36 (d, J = 7.5 Hz, 1H), 7.31 – 7.14 (m, 3H), 6.41 (s, 1H), 2.38 (s, 3H). **¹³C{¹H} NMR** (75 MHz, CD₃CN): δ (ppm) = 150.1, 141.7, 139.4, 137.6, 137.1, 131.8, 129.9,

129.8, 129.6, 128.9, 127.2, 126.9, 121.7 (q, $J = 332.7$ Hz), 111.0, 105.1, 20.4. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NOS$ 324.0670; Found 324.0676.

6-methyl-3-phenyl-1-(trifluoromethyl)-1 λ^4 -benzo[*e*][1,2]thiazine 1-oxide (4h): 35 mg – 68 % yield as orange solid. **Mp** = 75 °C. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -80.40 (s, CF_3). **1H NMR** (300 MHz, CD_3CN): δ (ppm) = 7.94 (dd, $J = 7.9, 1.8$ Hz, 2H), 7.80 (d, $J = 8.3$ Hz, 1H), 7.48 – 7.39 (m, 3H), 7.31 (d, $J = 7.5$ Hz, 1H), 6.69 (s, 1H), 2.49 (s, 3H). **$^{13}C\{^1H\}$ NMR** (75 MHz, CD_3CN): δ (ppm) = 147.5, 147.3, 141.3, 137.2, 129.7, 129.3, 128.7, 127.7, 126.6, 126.5, 120.8 (q, $J = 332.8$ Hz), 108.6, 100.1, 22.2. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NOS$ 324.0670; Found 324.0677.

3-butyl-1-(trifluoromethyl)benzo[*e*][1,2]thiazine-1-oxide (4i): 35 mg – 75 % yield as yellow solid. **Mp** = 50 °C. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -80.65 (s, CF_3). **1H NMR** (200 MHz, $CDCl_3$): δ (ppm) = 7.83 (d, $J = 8.0$ Hz, 1H), 7.75 – 7.61 (m, 1H), 7.50 – 7.29 (m, 2H), 6.04 (s, 1H), 2.47 (t, $J = 7.5$ Hz, 2H), 1.78 – 1.57 (m, 2H), 1.35 (ddd, $J = 18.8, 13.2, 6.0$ Hz, 2H), 0.93 (t, $J = 7.2$ Hz, 3H). **$^{13}C\{^1H\}$ NMR** (50 MHz, $CDCl_3$): δ (ppm) = 153.2, 141.2, 135.7, 127.7, 126.8, 126.6, 120.7 (q, $J = 332.9$ Hz). **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{13}H_{15}F_3NOS$ 290.0826; Found 290.0827.

4-(1-oxido-1-(trifluoromethyl)benzo[*e*][1,2]thiazin-3-yl)butanenitrile (4j): 21 mg – 44 % yield as white solid. **Mp** = 44 °C. **^{19}F NMR** (188 MHz, CD_3CN): δ (ppm) = -80.13 (s, CF_3). **1H NMR** (200 MHz, CD_3CN): δ (ppm) = 7.87 – 7.60 (m, 2H), 7.53 – 7.26 (m, 2H), 6.14 (s, 1H), 2.45 (t, $J = 7.3$ Hz, 2H), 2.30 (t, $J = 7.2$ Hz, 2H), 1.87 (q, $J = 7.2$ Hz, 2H). **$^{13}C\{^1H\}$ NMR** (75 MHz, CD_3CN): δ (ppm) = 150.8, 141.6, 137.5, 129.1, 128.1, 127.2, 121.5 (q, $J = 332.3$ Hz), 120.8, 111.0, 102.9, 37.3, 24.4, 16.6. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{13}H_{12}F_3N_2OS$ 301.0622; Found 301.0630.

3-(4-chlorobutyl)-1-(trifluoromethyl)benzo[*e*][1,2]thiazine-1-oxide (4k): 27 mg – 53 % yield as yellow oil. **^{19}F NMR** (188 MHz, $CDCl_3$): δ (ppm) = -80.55 (s, CF_3). **1H NMR** (200 MHz, $CDCl_3$): δ (ppm) = 7.84 (d, $J = 8.1$ Hz, 1H), 7.77 – 7.63 (m, 1H), 7.52 – 7.39 (m, 1H), 7.34 (d, $J = 8.1$ Hz, 1H), 6.06 (s, 1H), 3.56 (t, $J = 6.2$, 2H), 2.50 (t, $J = 6.9$ Hz, 2H), 1.94 – 1.75 (m, 4H). **$^{13}C\{^1H\}$ NMR** (50 MHz, $CDCl_3$): δ (ppm) = 152.0, 140.9, 135.9, 127.4, 126.9, 126.6, 120.7 (q, $J = 333.2$ Hz), 110.4 (q, $J = 1.0$ Hz), 101.4, 44.9, 37.6, 31.9, 25.2. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{13}H_{14}ClF_3NOS$ 324.0437; Found 324.0428.

3-isopentyl-1-(trifluoromethyl)benzo[*e*][1,2]thiazine 1-oxide (4l): 32 mg – 66 % yield as yellow oil. **^{19}F NMR** (188 MHz, $CDCl_3$): δ (ppm) = -80.63 (s, CF_3). **1H NMR** (200 MHz, $CDCl_3$): δ (ppm) = 7.82 (d, $J = 8.1$ Hz, 1H), 7.73 – 7.60 (m, 1H), 7.48 – 7.36 (m, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 6.04 (s, 1H), 2.52 – 2.40 (t, 2H), 1.64 – 1.48 (m, 3H), 0.92 (d, $J = 6.2$ Hz, 6H). **$^{13}C\{^1H\}$ NMR** (50 MHz, $CDCl_3$): δ (ppm) = 153.4, 141.2, 135.7, 127.1,

126.8, 126.5, 120.7 (q, $J = 333.5$ Hz), 110.2 (q, $J = 1.1$ Hz), 100.9, 37.1, 36.5, 27.7, 22.6, 22.5. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{14}H_{17}F_3NOS$ 304.0983; Found 304.0983.

General procedure for the synthesis of benzoisothiazoles 5: Sulfoximine **3** (0.16 mmol) was dissolved in DMF (3 mL) and CF_3COOAg (3.5 mg, 0.016 mmol) was added. The mixture was heated at 85°C for 3 hours. Then, the reaction was allowed to cool to room temperature and filtered through a Celite pad. The filtrate was extracted with Et_2O (10 mL) and washed with a solution of $NaHCO_3$ (5%) (3 x 10 mL). The organic phase was concentrated under reduced pressure. The crude product was purified on preparative silica plate, pre-treated by Et_3N , using petroleum ether/dichloromethane = 7/3 as eluent to give the desired compound **5**. The eluent was changed from the previous procedure to prevent any degradation of product **5** during the purification process.

(Z)-3-benzylidene-1-(trifluoromethyl) benzo[d]isothiazole 1-oxide (5a): 27 mg – 55 % yield as yellow solid. **Mp** = 87 °C. **^{19}F NMR** (188 MHz, $CDCl_3$): δ (ppm) = -75.99 (s, CF_3). **1H NMR** (200 MHz, $CDCl_3$): δ (ppm) = 8.07 (d, $J = 7.7$ Hz, 2H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 7.9$ Hz, 1H), 7.81 (t, $J = 7.5$ Hz, 1H), 7.66 – 7.55 (m, 1H), 7.41 (t, $J = 7.7$ Hz, 3H), 6.69 (s, 1H). **$^{13}C\{^1H\}$ NMR** (50 MHz, $CDCl_3$): δ (ppm) = 145.2, 139.9, 135.2, 135.1, 130.3, 129.6, 128.6, 128.0, 124.2, 122.1, 121.5 (q, $J = 334.4$ Hz), 113.4. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{15}H_{11}F_3NOS$ 310.0513; Found 310.0512.

(Z)-3-(4-methylbenzylidene)-1-(trifluoromethyl) benzo[d]isothiazole 1-oxide (5b): 34 mg – 65 % yield as yellow solid. **Mp** = 72 °C. **^{19}F NMR** (282 MHz, $CDCl_3$): δ (ppm) = -76.07 (s, CF_3). **1H NMR** (300 MHz, $CDCl_3$): δ (ppm) = 7.97 (dd, $J = 8.1, 2.2$ Hz, 3H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.79 (t, $J = 7.6$ Hz, 1H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 2H), 6.67 (s, 1H), 2.38 (s, 3H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ (ppm) = 145.3, 139.2, 138.1, 135.1, 132.5, 130.2, 129.4, 129.3, 125.5, 124.1, 122.0, 120.9 (q, $J = 331.7$ Hz), 113.6, 21.6. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NOS$ 324.0670; Found 324.0673.

(Z)-3-(4-methoxybenzylidene)-1-(trifluoromethyl)benzo[d]isothiazole 1-oxide (5d): 19 mg – 35 % yield as yellow solid. **Mp** = 74 °C. **^{19}F NMR** (188 MHz, $CDCl_3$): δ (ppm) = -76.13 (s, CF_3). **1H NMR** (200 MHz, $CDCl_3$): δ (ppm) = 8.03 (d, $J = 8.7$ Hz, 2H), 7.92 (m, 2H), 7.77 (t, $J = 7.5$ Hz, 1H), 7.56 (t, $J = 7.5$ Hz, 1H), 6.95 (d, $J = 8.6$ Hz, 2H), 6.66 (s, 1H), 3.85 (s, 3H). **$^{13}C\{^1H\}$ NMR** (75 MHz, $CDCl_3$): δ (ppm) = 159.5, 145.3, 138.2, 135.0, 131.8, 129.1, 128.1, 124.1, 121.8, 120.9 (q, $J = 333.3$ Hz), 114.5, 114.1, 113.4, 55.5. **HRMS** (ESI-TOF) m/z : $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NO_2S$ 340.0619; Found 340.0616.

(Z)-3-(3-methylbenzylidene)-1-(trifluoromethyl) benzo[d]isothiazole 1-oxide (5f): 31 mg – 60 % yield as yellow solid. **Mp** = 75 °C. **^{19}F NMR** (188 MHz, $CDCl_3$): δ (ppm) = -75.97 (s, CF_3). **1H NMR** (200 MHz, $CDCl_3$): δ (ppm) = 7.94 (m, 4H), 7.79 (t, $J = 7.5$ Hz, 1H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 7.8$ Hz, 1H), 7.11 (d, $J = 7.5$

Hz, 1H), 6.66 (s, 1H), 2.41 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) = 145.1, 139.7, 138.0, 135.0, 130.8, 129.4, 128.8, 128.4, 125.5, 124.0, 121.9, 120.8 (q, $J = 332.4$ Hz), 113.5, 21.6. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NOS}$ 324.0670; Found 324.0661.

(Z)-3-(2-methylbenzylidene)-1-(trifluoromethyl) benzo[*d*]isothiazole 1-oxide (5g): 30 mg – 59 % yield as yellow solid. **Mp** = 102 °C. ^{19}F NMR (188 MHz, CDCl_3): δ (ppm) = -75.88 (s, CF_3). ^1H NMR (200 MHz, CDCl_3): δ (ppm) = 8.57 (d, $J = 7.8$ Hz, 1H), 8.03 (d, $J = 7.8$ Hz, 1H), 7.92 (d, $J = 7.9$ Hz, 1H), 7.82 (t, $J = 7.6$ Hz, 1H), 7.61 (t, $J = 7.6$ Hz, 1H), 7.37 – 7.27 (m, 1H), 7.20 (m, 2H), 6.90 (s, 1H), 2.48 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) = 145.2, 140.1, 136.7, 135.1, 133.6, 130.6, 130.2, 129.6, 127.9, 126.3, 125.9, 124.2, 122.1, 120.9 (q, $J = 331.9$ Hz), 110.2, 20.4. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NOS}$ 324.0670; Found 324.0671.

(Z)-3-benzylidene-5-methyl-1-(trifluoromethyl)-3*H*-1 λ^4 -benzo[*d*]isothiazole 1-oxide (5h): 26 mg – 50 % yield as yellow solid. **Mp** = 99 °C. ^{19}F NMR (188 MHz, CDCl_3): δ (ppm) = -76.17 (s, CF_3). ^1H NMR (200 MHz, CDCl_3): δ (ppm) = 8.07 (dd, $J = 7.2, 1.7$ Hz, 2H), 7.83 – 7.73 (m, 2H), 7.45 – 7.37 (m, 3H), 7.33 – 7.27 (m, 1H), 6.64 (s, 1H), 2.58 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) = 146.9, 145.7, 140.0, 135.4, 131.0, 130.2, 128.6, 127.9, 123.9, 123.1, 122.3, 112.8, 22.41. HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{NOS}$ 324.0670; Found 324.0670.

Procedure for the synthesis of Adachi's reagent 6: A flow of O_3 diluted in oxygen (0.5 L/min) was bubbled into a solution of benzoisothiazole **5n** (1.92 g, 5.1 mmol) in dichloromethane (100 mL) at 0 °C during 3 min. A solution of $\text{Na}_2\text{S}_2\text{O}_4$ (50 mL, 10 % w/w) was then added and the solution was extracted with dichloromethane (3 x 20 mL). The organic phase was dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified by chromatography on silica using petroleum ether/ethyl acetate = 8/2 as eluent to isolate the desired product **6**.

1-(trifluoromethyl)benzo[*d*]isothiazol-3-one 1-oxide (6): 708 mg – 60 % yield as white solid. **Mp** = 60 °C. ^{19}F NMR (282 MHz, CDCl_3): δ (ppm) = -74.00 (s, CF_3). ^1H NMR (300 MHz, CDCl_3): δ (ppm) = 8.19 (d, $J = 7.5$ Hz, 1H), 8.07 (dd, $J = 14.4, 7.5$ Hz, 2H), 7.95 (t, $J = 7.5$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ (ppm) = 169.3, 138.2, 138.1, 134.5, 133.7, 126.7, 125.1, 120.6 (q, $J = 328.4$ Hz, CF_3). HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_8\text{H}_5\text{F}_3\text{NO}_2\text{S}$ 235.9993; Found 235.9995. ^1H and ^{19}F NMR values are in agreement with those reported (^{13}C NMR analysis not available).¹¹

Procedure for the photocatalytic methoxytrifluoromethylation of vinyl naphthalene: In a dry tube, under argon, were added Adachi reagent **6** (71 mg, 0.3 mmol), $\text{Ir}(\text{ppy})_3$ (5 mg, 0.0075 mmol, 2.5 mol%) and vinyl naphthalene (93 mg, 0.6 mmol). MeOH (6 mL) was added and the solution was stirred at room temperature under blue LEDs for 6h. Dichloromethane (15 mL) and brine (15 mL) were added and the solution was extracted with

dichloromethane (2 x 15 mL). The combined organic layers were dried with MgSO₄ and concentrated under reduced pressure. The crude was then purified on a preparative silica plate using petroleum ether/ethyl acetate = 95/5 as eluent to isolate the desired product **7**.

2-(3,3,3-trifluoro-1-methoxypropyl)naphthalene (7): 44 mg – 58 % yield as oil. ¹⁹F NMR (282 MHz, CDCl₃): δ (ppm) = - 64.13 (t, *J* = 10.6 Hz, CF₃). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.89 (m, 3H), 7.80 (s, 1H), 7.53 (m, 2H), 7.47 (dd, *J* = 8.5, 1.3 Hz, 1H), 4.66 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.29 (s, 3H), 2.90 – 2.65 (m, 1H), 2.65 – 2.34 (m, 1H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ (ppm) = 137.4, 133.5, 133.3, 129.0, 128.1, 127.9, 126.6, 126.5, 126.2, 125.8 (q, *J* = 276.7 Hz, CF₃), 123.9, 78.1, 56.9, 42.3 (q, *J* = 26.7 Hz). These values are in agreement with those reported.¹⁴

Supporting information

Optimization of the Sonogashira cross-coupling reaction conditions, screening of conditions for the regioselective cyclization of **3a** and computational details, some theoretical data, Z-matrices are available in the supporting information. X-Ray analysis and NMR spectra are also available in the supporting information.

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