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Transition Metal Catalyzed C–H bond Activation as a Sustainable Strategy for The Synthesis of Fluorinated Molecules: An overview

Louis Monsigny,^{a, #} Floriane Doche,^{a, #} Tatiana Besset^{*a}

^a *Normandie Univ., INSA Rouen, UNIROUEN, CNRS, COBRA (UMR 6014), 76000 Rouen, France).*

[#] *Both authors contributed equally.*

Abstract

The last decade has witnessed the emergence of innovative synthetic tools for the synthesis of fluorinated molecules. Among these approaches, the transition metal catalyzed functionalization of various scaffolds with a panel of fluorinated groups (XR_F, X = S, Se, O) offered straightforward access to high added-value compounds. This review will highlight the main advances made in the field with the transition metal catalyzed functionalization of C(sp²)- and C(sp³)-centers with SCF₃, SeCF₃, or OCH₂CF₃ groups among others, by C–H bond activation. The scope and limitations of these transformations are discussed in this review.

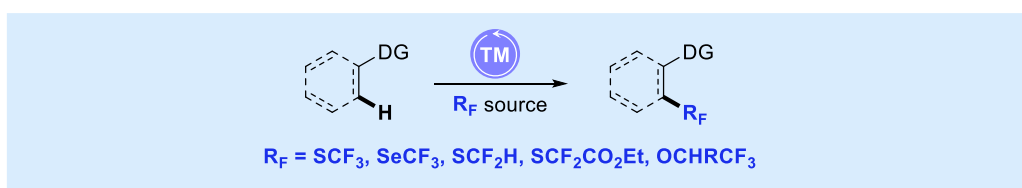
Keywords

Homogeneous catalysis, C–H bond activation, Emergent Fluorinated groups, Organofluorine chemistry, Palladium, Synthetic method

Introduction

Nowadays, fluorinated molecules represent an unavoidable class of molecules in chemistry and in chemical biology. Thanks to the unique properties of the fluorine atom or the fluorinated groups to modulate the biological and physicochemical properties of the parent non-fluorinated molecules [1, 2], their incorporation in various scaffolds afforded high value-added compounds as demonstrated by their numerous applications in the industrial sector such as drugs, agrochemicals and materials. To further illustrate the ubiquity of fluorinated compounds, almost 20% of pharmaceuticals and 30-40% of agrochemicals [3-5] contain at least one fluorine atom. Because of the exceptional features of fluorinated derivatives, tremendous developments and discoveries have been made in this blossoming research area, with a high interest for fundamental research as well as the industry [6-11]. Among them [2, 5, 12-18], the direct functionalization of a simple C–H bond by transition metal catalysis [19-43] became an important tool offering new retrosynthetic disconnections. In this context, a strong interest from the scientific community was shown towards the challenging synthesis of fluorinated molecules by transition-metal catalyzed C–H bond activation [44-50], allowing the functionalization of complex molecules and even for late-stage functionalization strategy [51-53] for the synthesis of natural products [42, 54-59].

The goal of this review is to highlight and discuss the recent approaches for the synthesis of fluorinated derivatives by the direct incorporation of a fluorinated group of XR_F type (e.g., SCF_3 , SeCF_3 , $\text{SCF}_2\text{CO}_2\text{Et}$, OCH_2CF_3) by transition metal catalyzed C–H bond activation (Scheme 1). The review will be organized in two main parts, dedicated to the construction of a C– $\text{SCF}_2\text{R}/\text{SeCF}_3$ and C– OCH_2CF_3 bond. This review does not aim to be exhaustive and key examples were carefully chosen to provide the reader a nice overview. Since reviews dealing with transition metal catalyzed functionalization of compounds by C–H bond activation with fluorinated reagents [60-77] and vinylic, allylic or propargylic fluorinated building blocks [49] have been already reported, these reactions will not be depicted.



Scheme 1: Transition metal catalyzed C– XR_F bond by C–H bond activation: an overview.

I) Transition metal catalyzed directed C–Chalcogen bond formation (C–S, C–Se) by C–H bond activation

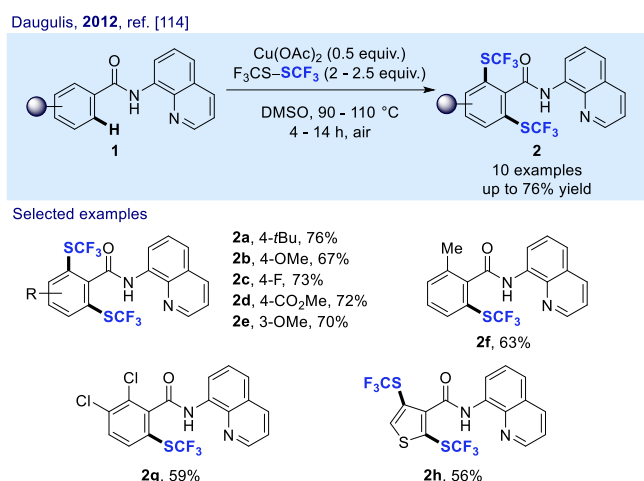
In the past decade, a particular attention was paid to the development of new methodologies for the incorporation of sulfur-containing fluorinated groups. Although transition metal catalyzed direct C–H bond functionalization appeared to be a powerful tool for C–C, C–N or C–O bond formation, the direct formation of a $\text{C}(\text{sp}^2)\text{--SR}_F$ or a $\text{C}(\text{sp}^3)\text{--SR}_F$ bond remains a challenging transformation. In this context, key players in the field have been interested in the design of original methodologies for the trifluoromethylthiolation and more recently difluoromethylthiolation of various compounds by transition metal catalysis [78]. Moreover, a recent interest was devoted to the trifluoromethylselenolation reaction as depicted in this section.

I.1) Transition metal catalyzed C–H trifluoromethylthiolation of aromatic $\text{C}(\text{sp}^2)$ -centers.

Thanks to its unique feature such as an interesting lipophilicity (Hansch parameter = 1.44) [79, 80] and a strong withdrawing character, the development of new methodologies for the incorporation of the SCF_3 residue on various molecules has known a tremendous expansion [81-113].

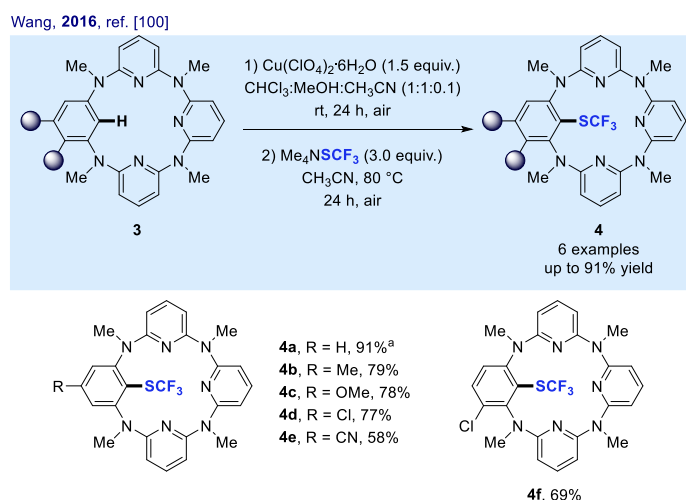
Copper Catalysis: In 2012, Daugulis and co-workers reported the copper-promoted trifluoromethylthiolation of benzamide derivatives **1** at the *ortho* position by C–H bond activation [114]. Indeed, using a bidentate directing group (amide derived from the 8-

aminoquinoline), the mono- and di-functionalized compounds were obtained when $\text{Cu}(\text{OAc})_2$ (0.5 equiv.) and the toxic and volatile disulfide $\text{F}_3\text{CS}-\text{SCF}_3$ were employed (Scheme 2, 10 examples, up to 76% yield). With this approach, derivatives bearing an aromatic part substituted at the *para* position with electron donating substituents (**1a-1b**), halogens (**1c**) as well as electron withdrawing groups (**1d**) were difunctionalized in good yields. The substitution pattern on the aromatic ring did not affect the reaction efficiency, the *meta* substituted derivative **2e** as well as the *ortho* substituted derivative **2f** were obtained in high yields (70% and 63% yields, respectively). It should be noted that the presence of *ortho*-substituents on the aryl residue allowed the mono-functionalization to occur selectively. Also, amide bearing a poly-substituted arene **1g** was successfully functionalized in 59% yield. Finally, the di-functionalized thiophene derivative **2h** was obtained in 56% yield.



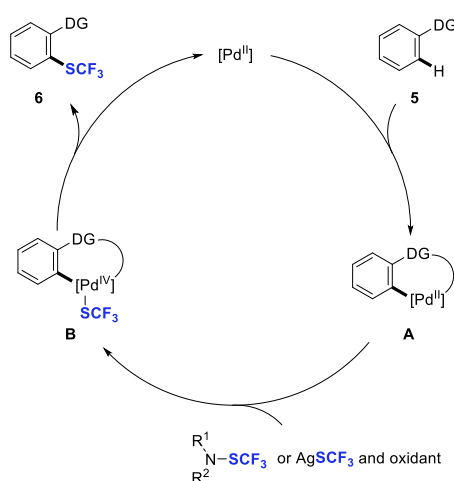
Scheme 2: $\text{Cu}(\text{OAc})_2$ promoted mono- and di-trifluoromethylthiolation of benzamide derivatives derived from 8-aminoquinoline reported by the group of Daugulis [114].

In 2016, Wang's group developed another methodology for the trifluoromethylthiolation of azacalix[1]arene[3]pyridines by C–H bond activation using a complex of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and the shelf stable Me_4NSCF_3 [115, 116] as a nucleophilic source of SCF_3 (Scheme 3) [100]. Within these conditions, 6 azacalix[1]arene[3]pyridines bearing electron donating groups, halogens or electron withdrawing groups were functionalized and the expected products were isolated in moderate to high yields (**4a-4f**, 58%-91%).



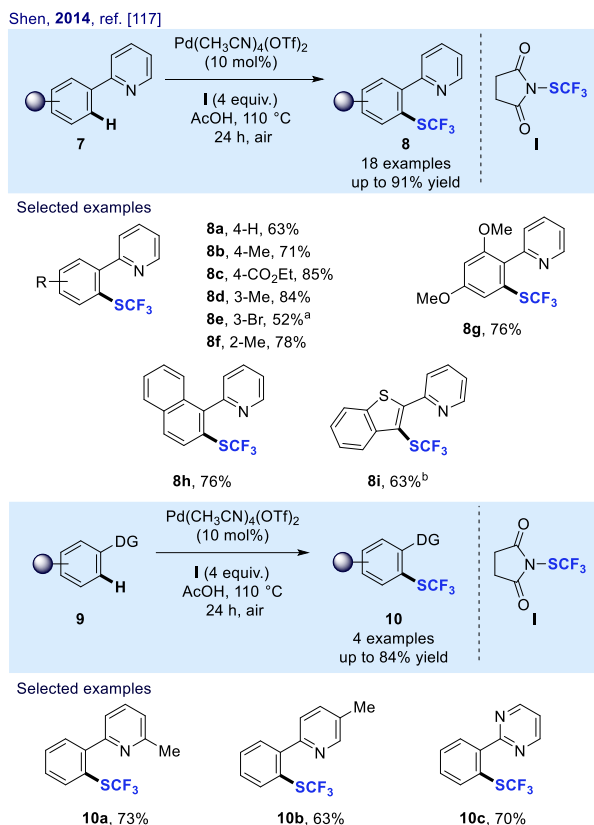
Scheme 3: Trifluoromethylthiolation of azacalix[1]arene[3]pyridines using copper salts and a nucleophilic source of SCF_3 reported by Wang and co-workers [100]. ^a A mixture of $\text{CHCl}_3:\text{MeOH}$ (1:1) was used as solvent.

Palladium Catalysis: Several works have been reported for the palladium catalyzed trifluoromethylthiolation reaction of various compounds **5** by C–H bond activation and involved in most cases an electrophilic SCF_3 source ($\text{R}^1\text{R}^2\text{NSCF}_3$). For these transformations, the following working hypothesis was generally suggested (Scheme 4). After coordination of the palladium catalyst to the directing group, the metallacycle **A** would be formed. This latter would undergo an oxidative addition in the presence of an electrophilic source or an oxidation/ligand exchange in the presence of a nucleophilic source (i.e., AgSCF_3) and oxidant (**B** in scheme 4). Finally, after a reductive elimination step, the expected functionalized product **6** would be obtained and the palladium catalyst would be regenerated.



Scheme 4: Working hypothesis for the palladium catalyzed C–H trifluoromethylthiolation reaction.

In 2014, Shen and co-workers [117] developed a new methodology for the selective functionalization of 2-arylpyridine derivatives using an electrophilic SCF_3 reagent, the Haas reagent **I** (Scheme 5) [118]. A broad range of 2-arylpyridine derivatives were trifluoromethylthiolated in good to high yields (18 examples, from 52 to 91% yields). The substitution pattern of the aromatic ring had no impact on the outcome of the reaction as illustrated with substrates substituted by a methyl group (**7b**, **7d** and **7f**) at the *para*-, *meta*- and *ortho*-positions, which were readily functionalized in 71%, 84% and 78% yields, respectively. This reaction was also tolerant of a 2-naphthyl group, the palladium catalyzed trifluoromethylthiolation afforded the corresponding product **8h** in 76% yield. The polysubstituted compound **7g** and the benzothiophene derivative **7i** have been also successfully trifluoromethylthiolated in 76% and 63% yields, respectively. This reaction proved to be compatible to the presence of an ester (**8c**) or a halogen (**8e**). Other directing groups, such as substituted pyridines (**9a** and **9b**) and pyrimidine (**9c**) turned out to be also efficient in this transformation (Scheme 5, 4 examples, up to 84% yield).

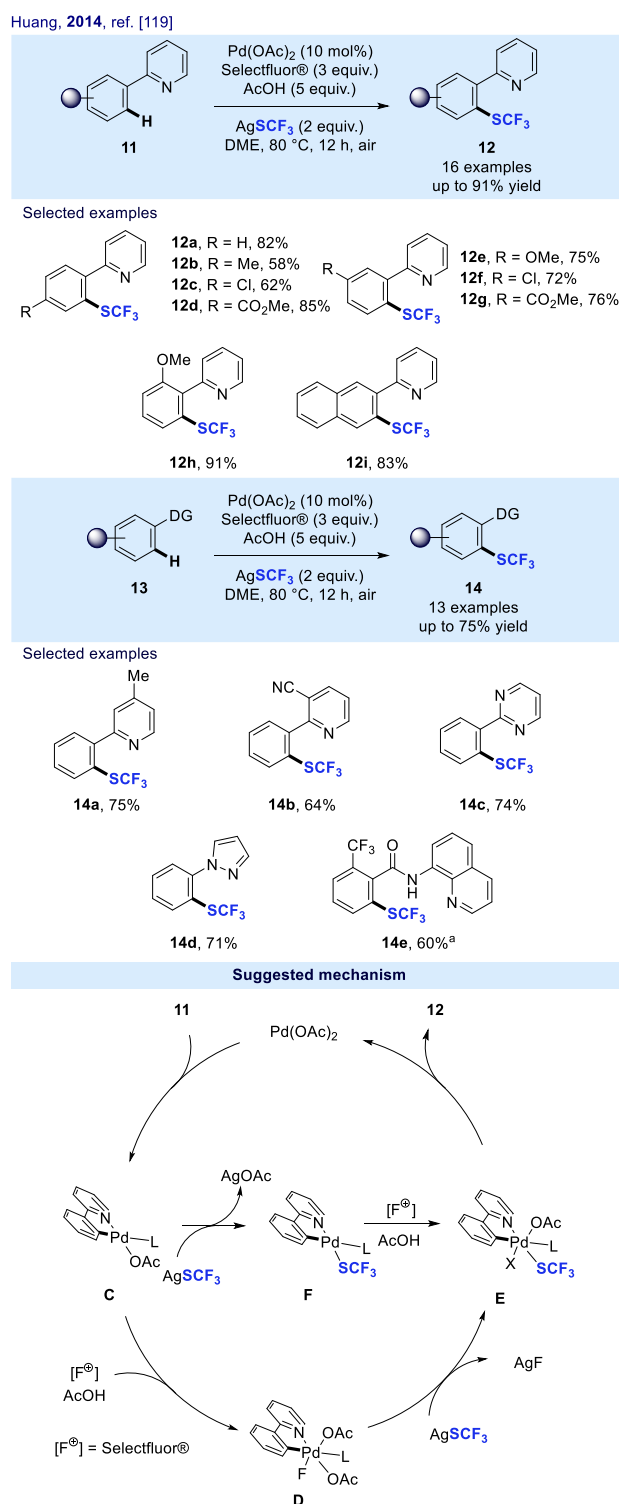


Scheme 5: Trifluoromethylthiolation of 2-arylpyridine derivatives and analogs by means of palladium catalyzed C–H activation reported by the group of Shen [117]. ^a 6 equiv. of **I** were used at 150 °C for 24 h. ^b The reaction was conducted at 150 °C for 24 h.

The same year, the group of Huang reported an elegant and straightforward pallado-catalyzed *ortho*-selective trifluoromethylthiolation of arenes bearing various directing groups using the nucleophilic trifluoromethylthiolated source AgSCF₃ in combination with Selectfluor® as oxidant (Scheme 6, 29 examples, up to 91% yield) [119]. 2-arylpyridine derivatives bearing electron-donating groups, electron-withdrawing groups or halogen at the *para* and *meta*-positions were readily functionalized (**11a–11g**, 58%–85% yields). The 2-(2-methoxyphenyl)pyridine **11h** and the 2-(3-naphthyl)pyridine **11i** were found to be suitable substrates leading to the corresponding products **12h** and **12i** in 91% and 83% yields, respectively. The use of other directing groups was also suitable for this transformation such as methyl-, and cyano-substituted pyridines (**13a–13b**), pyrimidine (**13c**), pyrazole (**13d**), as well as the amide derived from the 8-aminoquinoline **13e** (Scheme 6, 13 examples, up to 75% yield).

In this study, two mechanisms were reported. The first one suggested that the palladacycle **C** would be formed after the irreversible chelation of 2-phenylpyridine with palladium, which was the rate-determining step (KIE = 2.7). **C** would then be oxidized by Selectfluor® to form a palladium(IV) complex **D**. After a ligand exchange with AgSCF₃, the intermediate **E** would be obtained, which, after reductive elimination, would release the desired product **12** and regenerate the catalyst. Alternatively, a ligand exchange with AgSCF₃ would occur before the oxidation step, generating the palladium(II) complex **F**. After an oxidative addition in the presence of Selectfluor®, the palladium(IV) **E** would be generated. Finally, after reductive elimination step, the desired product **12** would be released and the catalyst would be regenerated. Note that, in this process, the Selectfluor® was playing a key role. Indeed, using this electrophilic fluorinating source as oxidant would generate a Pd(IV)(ppy)F(OAc)₂ (ppy = 2-phenylpyridine) complex as intermediate. As the competitive C–F bond formation was disfavored (slow reductive elimination step), the desired trifluoromethylthiolated product **12**

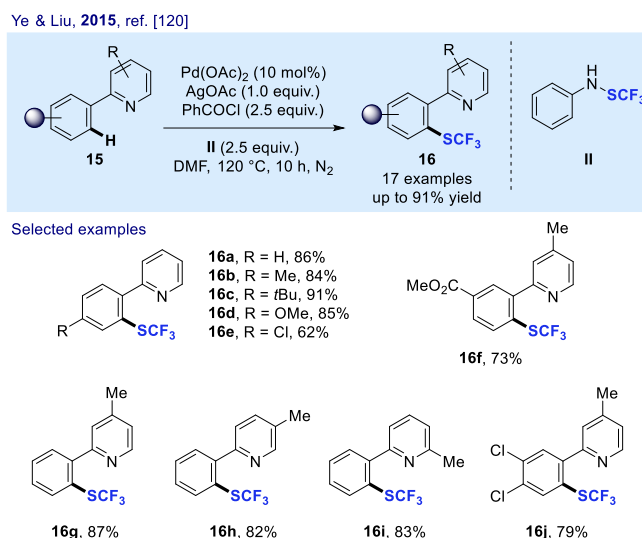
would be selectively afforded after a F/SCF₃ ligand exchange.



Scheme 6: C(sp²)-SCF₃ bond formation by Pd-catalyzed C–H bond activation using AgSCF₃ and Selectfluor[®] as reported by the group of Huang [119]. ^a 20 equiv. of Cl₂CHCOOH were used instead of AcOH.

In 2015, Ye and Liu reported the palladium catalyzed trifluoromethylthiolation of 2-arylpyridine derivatives using the Billard reagent **II** (Scheme 7) [120]. Unlike Shen's methodology (Scheme 5), the use of benzoyl chloride was necessary to activate the trifluoromethylthiolated reagent [120]. Non-substituted and substituted pyridines as directing

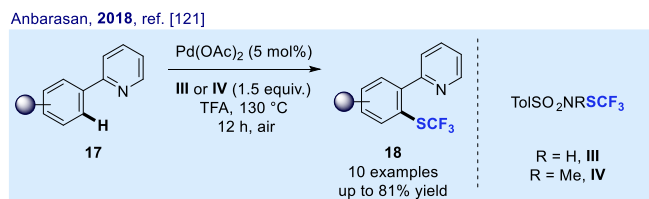
groups were very efficient for the *ortho*-trifluoromethylthiolation reaction (17 examples, up to 91% yield). This methodology was tolerant to electron donating and electron withdrawing groups as well as halogens (**16b-16f**, 62%-91% yields). The *meta*-substituted **16f** and disubstituted **16j** were obtained in high yield (73% and 79%, respectively).



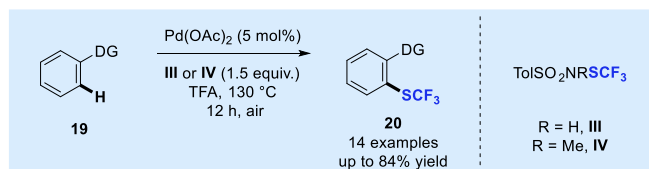
Scheme 7: Palladium catalyzed *ortho*-trifluoromethylthiolation of 2-arylpyridine derivatives reported by the group of Ye and Liu [120].

In 2018, Anbarasan and co-workers described a palladium catalyzed trifluoromethylthiolation of arenes by C–H bond activation bearing several directing groups (Scheme 8) [121]. With this methodology, the functionalization of 2-phenylpyridine derivatives was possible (10 examples, up to 81% yield) using the Billard reagents **III** or **IV** [122]. The trifluoromethylthiolation of 2-arylpyridines substituted by electron donating groups such as methyl, methoxy or methylthio groups (**17b-17d**) or by halogen (**17e**) was achieved (Scheme 8, up to 77% yield). Note that in case of the poly-substituted 2-phenylpyridine **17h**, the expected product **18h** was isolated in 31% yield. Moreover, selective oxidation of the SCF₃ residue into the corresponding sulfoxide and the sulfone was possible and the corresponding products were obtained in 98% and 95% yields, respectively.

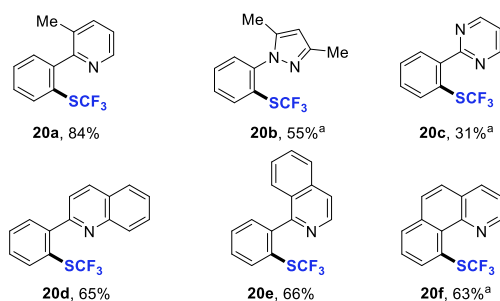
This reaction was successfully applied to the trifluoromethylthiolation of derivatives bearing various directing groups such as substituted pyridines (4 examples, up to 84% yield, **19a**, 84% yield), substituted pyrazole derivatives (6 examples, up to 55% yield, **19b**, 55% yield), pyrimidine (**19c**, 31% yield) as well as quinoline and isoquinoline (**19d** and **19e**, 65% and 66% yields, respectively). In addition, the trifluoromethylthiolated benzo[h]quinoline **20f** was obtained in good yield (63%).



Selected examples



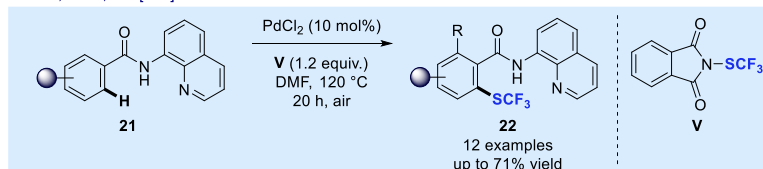
Selected examples



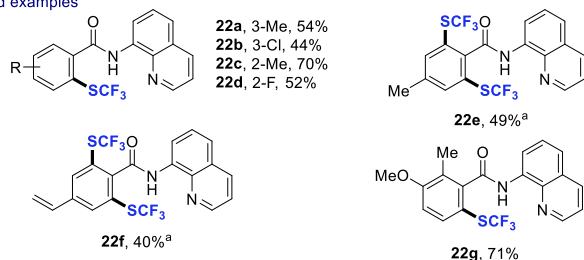
Scheme 8: Palladium catalyzed *ortho*-trifluoromethylthiolation of 2-arylpyridine and analogs reported by Anbarasan [121]. ^a The reaction was conducted at 120 °C using 1.1 equiv. of **IV** (R = Me).

The same year, Besset and co-workers reported a palladium catalyzed C(sp²)-SCF₃ bond formation on amides derived from the 8-aminoquinoline as a cleavable directing group in the presence of the Munavalli reagent **V** (Scheme 9, 12 examples, up to 71% yield) [106]. Depending on the substitution pattern on the aromatic ring, the amides were mono- or difunctionalized. Indeed, *meta*- and *ortho*-substituted derivatives (**21a-21d**) were selectively trifluoromethylthiolated while *para*-substituted ones led to the difunctionalized products **22e** and **22f**. Within these reaction conditions, the polysubstituted derivative **21g** was also functionalized in high yield (71%).

Besset, 2018, ref. [106]



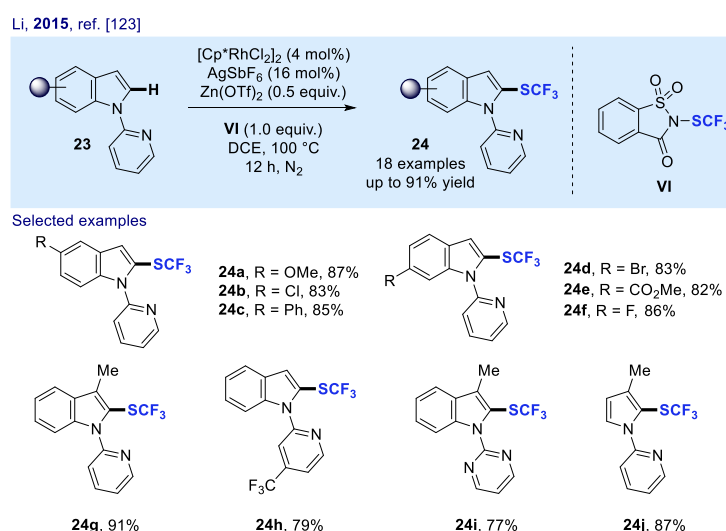
Selected examples



Scheme 9: Mono- and di-trifluoromethylthiolation of benzamide derivatives derived from *N*-8-aminoquinoline using PdCl₂ as catalyst reported by Besset and co-workers [106]. ^a 2.2 equiv. of the fluorinated source **V** were used.

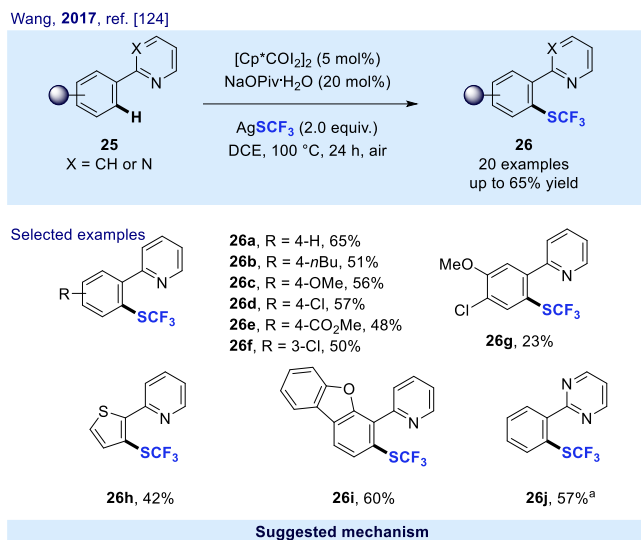
Pleasingly, other metals have been also successfully applied for the trifluoromethylthiolation of aromatic derivatives by C(sp²)-H bond activation such as Rh(III)- and Co(III)-based catalysts as depicted below.

Rhodium Catalysis: In 2015, the group of Li disclosed the Cp^{*}Rh(III)-catalyzed regioselective trifluoromethylthiolation of *N*-substituted indoles with (substituted) pyridines or pyrimidine as the directing groups (Scheme 10) [123]. The selective trifluoromethylthiolation of indoles at the C2 position was achieved in the presence of the *N*-trifluoromethylthiosaccharine **VI** (Shen's reagent) as both oxidant and electrophilic source (18 examples, up to 91% yield). Indoles bearing various electron donating and electron withdrawing groups as well as halogens at the C5-position and at the C6-position were functionalized in high yields (**24a-24f**, 82%-87% yields). The substitution of the indole at the 3-position did not impact the reaction and **24g** was obtained in 91% yield. Substituted pyridines and pyrimidine (**24h-24i**) were also used as directing groups (7 examples, up to 86% yield). This methodology was extended to the functionalization of other heteroaromatic derivatives (**24j**, 87% yield). It should be noted that the presence of zinc triflate, a Lewis acid, was used for the activation of the electrophilic source **VI**.



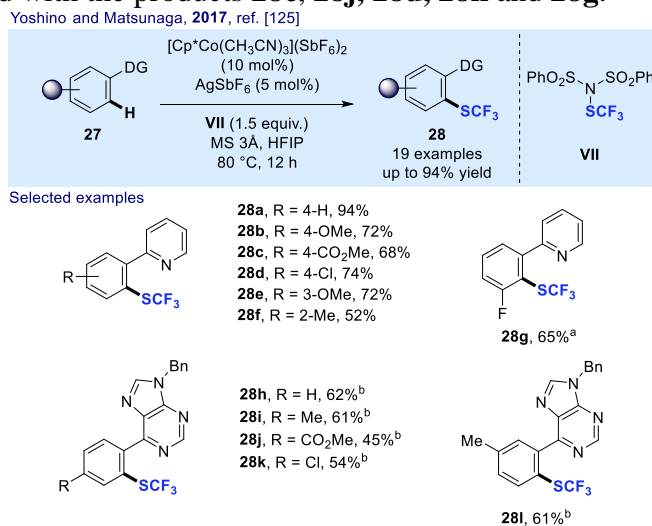
Scheme 10: Regioselective Cp^{*}Rh(III)-catalyzed directed trifluoromethylthiolation reported by the group of Li [123]. Cp^{*} = pentamethylcyclopentadienyl.

Cobalt Catalysis: In 2017, Wang described the Cp^{*}Co(III)-catalyzed trifluoromethylthiolation of 2-phenylpyridine derivatives using AgSCF₃ (Scheme 11) [124]. This methodology allowed the functionalization of several aromatic compounds bearing a pyridine or a pyrimidine as a directing group (20 examples, up to 65% yield). The reaction proceeded smoothly with substrates bearing an electron donating group (**25b-25c**), halogen (**25d**) or withdrawing group (**25e**) and the desired SCF₃-containing products were obtained in moderate to good yields. The functionalization of polysubstituted arene **25g** and heteroarene **25h** were also possible leading to the corresponding products (**26g** and **26h**) in moderate yields (23% and 42% yields, respectively). Regarding the reaction mechanism, the active Co(III) complex **G** was obtained from the dimer catalyst [Cp^{*}CoI₂]₂ in the presence AgSCF₃ and/or NaOPiv·H₂O. Then, the reversible formation of the metallacycle **H** would occur, which after a transmetallation step, in the presence of AgSCF₃ would lead to the formation of **J**. The product **26** would be released *via* a reductive elimination step, generating at the same time the reduced cobalt Cp^{*}Co(I), which would be regenerated after oxidation.



Scheme 11: Cp*Co(III)-catalyzed *ortho*-trifluoromethylthiolation of 2-phenylpyridine and 2-phenylpyrimidine derivatives reported by Wang and co-workers [124]. ^a CH₂Cl₂ was used as solvent.

The same year, Yoshino and Matsunaga described a similar methodology, using a cobalt (III) complex, [Cp*Co(CH₃CN)₃](SbF₆)₂ and *N*-trifluoromethylthiodibenzenesulfonimide **VII** as electrophilic SCF₃ source (Scheme 12) [125]. Within these reaction conditions, 2-arylpyridine (9 examples, up to 94% yield) or 6-arylpyrimidine (10 examples, up to 72% yield) were *ortho*-trifluoromethylthiolated. The substitution pattern of the aryl part did not impact the outcome of the reaction. This methodology was also tolerant to a large range of functional groups (ester, halogen) as illustrated with the products **28c**, **28j**, **28d**, **28k** and **28g**.

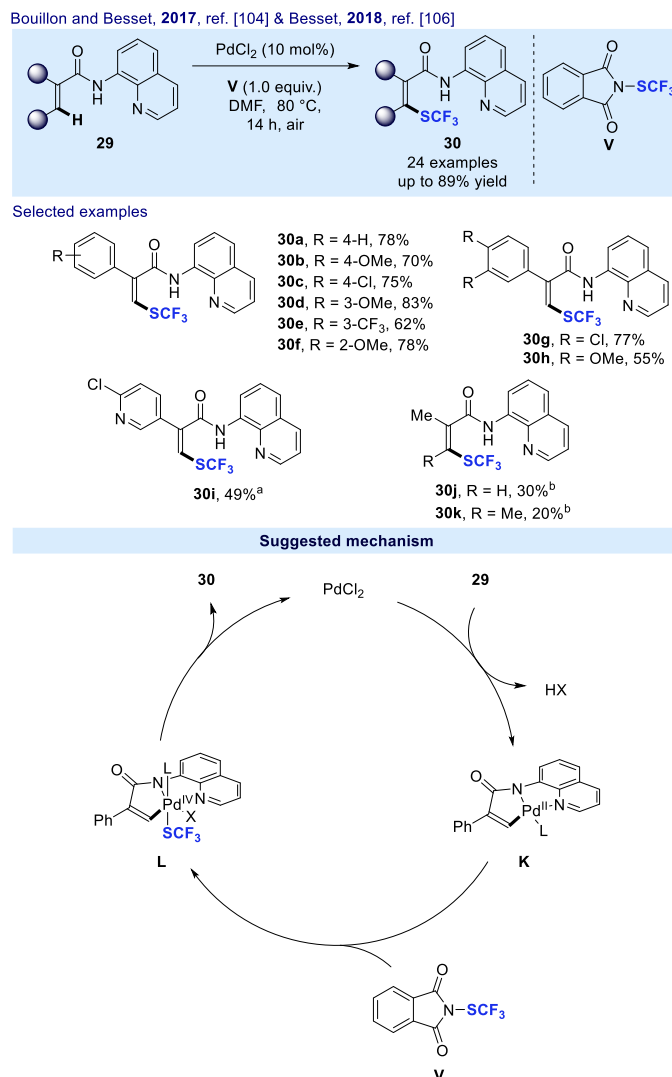


Scheme 12: Cp*Co(III)-catalyzed *ortho*-trifluoromethylthiolation of 2-phenylpyridine and 6-phenylpurine derivatives described by Yoshino and Matsunaga [125]. ^a Without AgSbF₆. ^b 2.0 equiv. of **VII**, 10 mol% of AgOAc and 30 mol% of Gd(OTf)₃ were used instead of AgSbF₆.

I.2) Transition metal catalyzed C–H trifluoromethylthiolation of vinylic C(sp²)-centers.

Several research groups have been interested in the development of strategies for the formation of vinylic C(sp²)–SCF₃ bond, offering an efficient tool towards the synthesis of challenging *Z*-isomers.

Palladium catalysis: In 2018, Bouillon and Besset described the first example of selective palladocatalyzed trifluoromethylthiolation of α -aryl acrylamides derived from 8-aminoquinoline **29** by C–H bond activation (Scheme 13) [104]. Using the Munavalli reagent **V** as an electrophilic SCF₃ source, this diastereoselective method selectively led to the formation of *Z*-isomers and turned out to be robust (no air or moisture sensitive). Under these mild reaction conditions, a panel of α -(hetero)aryl acrylamides were trifluoromethylthiolated in good to high yields. Acrylamides substituted at the α -position by an aryl bearing electron donating group (OMe) and halogen (Cl) at the *para* position were readily functionalized (**30b**, **30c**, 70% and 75% yields, respectively). The substitution of the arene with a CF₃ residue at the *meta* position or with a methoxy group at the *ortho* position did not have any impact to the outcome of the reaction (**30e**, **30f**, 62% and 78% yields, respectively). It should be noted that acrylamides bearing a disubstituted arene (**29g-29h**) and an heteroaryl (**29i**) at the α position were also suitable substrate in this reaction. Finally, an acrylamide bearing a methyl at the α -position (**29j**) or α,β -dimethylsubstituted acrylamide (**29k**) was possible substrate albeit the corresponding products were obtained in 30% and 20% yields, respectively. Several mechanistic experiments revealed that the C(sp²)–H bond activation step was reversible and was the rate-determining step (KIE = 2.4). First, the chelation of the palladium (II) catalyst with the bidentate directing group, followed by the C(sp²)–H bond activation involving a concerted metalation-deprotonation pathway would afford the metallacycle **K**. After an oxidative addition in the *N*-SCF₃ bond of the Munavalli reagent **V**, the palladium(IV) species **L** would be obtained. Finally, the catalyst would be regenerated, and the product released by a reductive elimination. The same year, Besset and co-workers extended this methodology to a larger class of acrylamides [106].



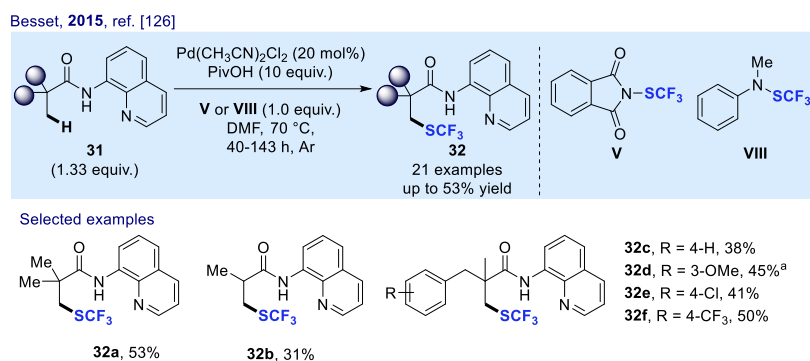
Scheme 13: Diastereoselective trifluoromethylthiolation of acrylamide derivatives derived from the 8-aminoquinoline using PdCl₂ reported by Bouillon & Besset [104, 106]. ^a 20 mol% of PdCl₂ and 2.0 equiv. of **V** were used for 36. ^b The reaction was conducted with 30 mol% of PdCl₂ and 2.0 equiv. of **V** were used.

I.3) Transition metal catalyzed trifluoromethylthiolation of aliphatic C(sp³)-H bond

Despite the important progresses presented in the previous section, some limitations of the trifluoromethylthiolation persist. In particular, the functionalization of a C(sp³)-H bond with a trifluoromethylthiolated moiety by transition metal catalyzed C-H activation remains a challenging task both in term of reactivity and selectivity.

In 2015, Besset reported the first C(sp³)-SCF₃ bond formation on unactivated primary C(sp³) -centers by transition metal catalyzed C-H activation and the Munavalli or the Billard reagents as the trifluoromethylation source (Scheme 14) [126]. Using a bidentate directing group, this methodology allowed the functionalization of a large range of aliphatic amides with a primary β-C(sp³)-H bond (21 examples, up to 53% yield). The methodology was applied to the functionalization of a series of amides having an α-quaternary center (α, α-dialkyl (**31a**) or α-alkyl (**31b**), α-benzyl derivatives (**31c-31f**) as well as amides with a α-tertiary center (**31b**)

as pleasingly, the presence of α -C–H bonds did not have a significant impact on the outcome of the reaction. It should be noted that this methodology afforded a high regioselectivity, no incorporation of the SCF_3 moiety on the benzylic or at the C5 position of the quinoline part of the directing group was observed. since the aromatic $\text{C}(\text{sp}^2)$ –H bond activation was not observed. Note that in 2018, Besset and Lebel developed a more efficient process for the palladium -catalyzed trifluoromethylthiolation by C–H bond activation under continuous flow [127].

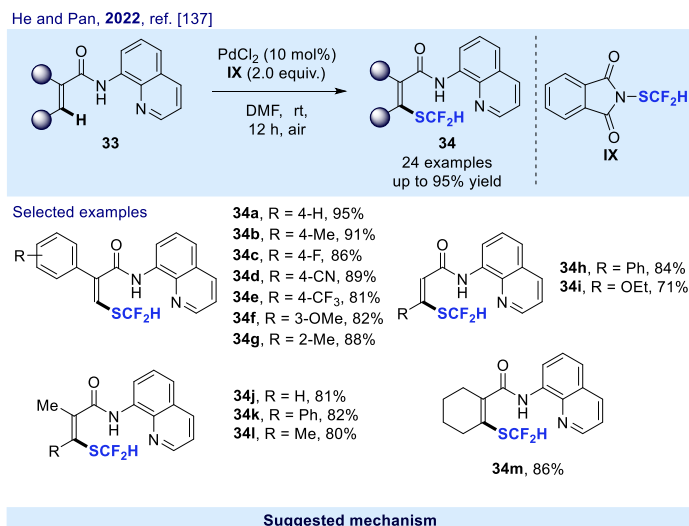


Scheme 14: $\text{C}(\text{sp}^3)$ – SCF_3 bond formation on aliphatic amide derivatives derived from 8-aminoquinoline by palladium catalyzed C–H bond activation described by Besset and co-workers [126]. **32d** was contaminated with 10% of an inseparable impurity.

I.4) Difluoromethylthiolation of aromatic and vinylic $\text{C}(\text{sp}^2)$ –H bond (C – SCF_2H and C – $\text{SCF}_2\text{CO}_2\text{Et}$ bonds)

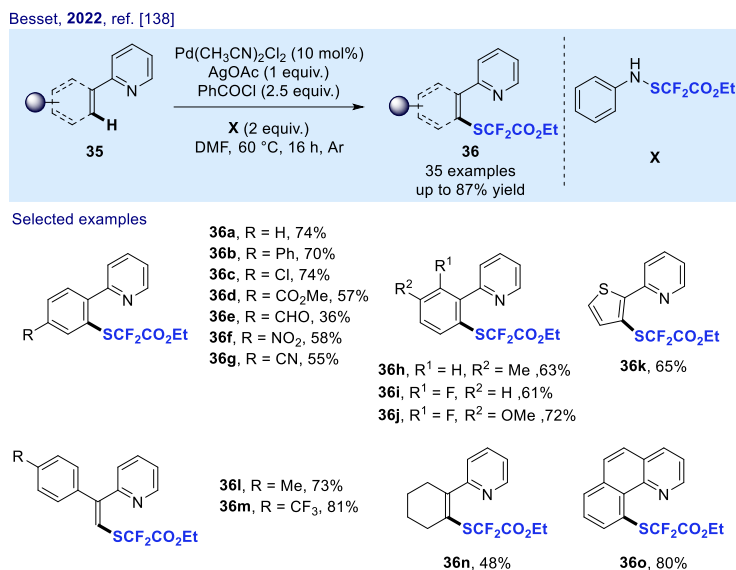
More recently, a strong interest has been shown on the synthesis of molecules substituted with original and functionalized fluorinated moieties such as SCF_2FG [128-136] (FG = functional group). In sharp contrast with the trifluoromethylthiolation reaction, only a handful of reports dealt with the incorporation of such high-value added fluorinated moieties onto a $\text{C}(\text{sp}^2)$ centers by transition metal catalyzed C–H bond activation.

In 2022, He and Pan reported the first example of difluoromethylthiolation using transition metal catalyzed C–H bond activation (Scheme 15) [137]. Using the reagent **IX** and a catalytic amount of PdCl_2 , they functionalized acrylamides derived from 8-aminoquinoline **33**. Within these mild conditions, α -aryl acrylamides substituted at *para*, *meta* and *ortho* positions were readily difluoromethylthiolated (**34a-34g**, 81%-95% yields). This reaction was also tolerant to a large class of functional groups (halogens, cyano, trifluoromethyl), **34c**, **34d** and **34e** were obtained in high yields (86%, 89% and 81%, respectively). α -Methylsubstituted acrylamide **34j** was also isolated in 81% yield. α,β - and β -substituted acrylamides were functionalized in high yields (**34h-34i** and **34k-34m**, 71%-86%). The plausible mechanism is similar as the one reported by Besset with the trifluoromethylthiolation of acrylamides derived from 8-aminoquinoline (Scheme 13).



Scheme 15: Regio- and diastereoselective difluoromethylthiolation of acrylamides under palladium catalysis reported by He and Pan [137].

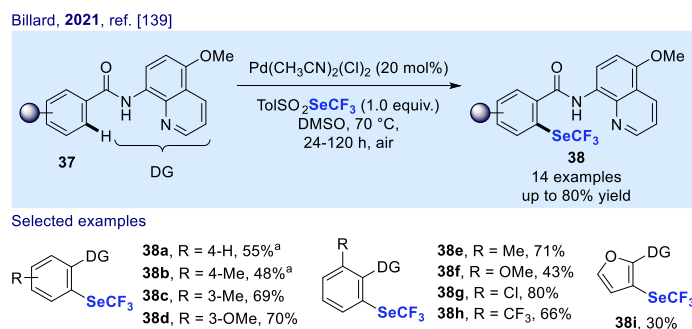
The same year, Besset and co-workers reported the first palladium catalyzed C(sp²)–SCF₂CO₂Et bond formation by C–H bond activation (Scheme 16) [138]. In the presence of an electrophilic SCF₂CO₂Et source **X**, the methodology was successfully applied for the functionalization of 2-arylpyridine derivatives (**35a–35i**) as well as 2-vinylpyridine derivatives (**35j–35m**, 35 examples, up to 87% yield). The substitution pattern of the aryl of the 2-phenylpyridine derivatives did not influence the reaction as for instance **36b**, **36h** and **36i** were obtained in good yields (70%, 63% and 61% yields, respectively). This reaction was tolerant to many functional groups such as halogens, ester, aldehyde, cyano, nitro (**36c–36g**, 36%–74% yields). It is noteworthy that a disubstituted compound **35j** and a thiophene derivative **35k** were also efficiently difluoromethylthiolated (**36j** and **36k**, 72% and 65%, respectively). α -Substituted-vinylpyridines with electron donating or electron withdrawing groups on the aromatic ring were functionalized and **36l** and **36m** were easily isolated in 73% and 81% yields, respectively. Even a α,β -disubstituted-vinylpyridine **35n** and the benzoquinoline **35o** were smoothly functionalized showing the efficiency of the approach. Of high interest, the modularity of the SCF₂CO₂Et was highlighted by its conversion in various other fluorinated residues (amide, carboxylic acid) and its selective oxidation into the corresponding sulfoxide and sulfone.



Scheme 16: Palladium catalyzed (ethoxycarbonyl)difluoromethylthiolation reaction of 2-(hetero)aryl and 2-(α -aryl-vinyl)pyridine derivatives reported by Beset [138].

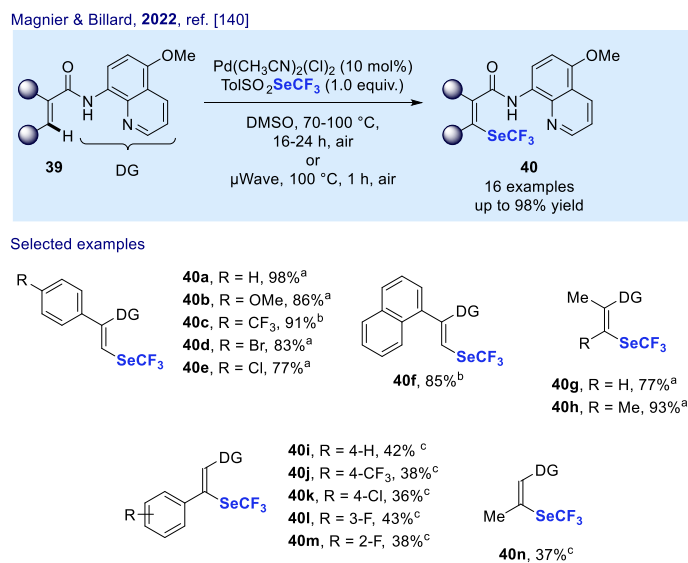
I.5) Trifluoromethylselenolation of aromatic and vinylic C(sp²)-H bonds by palladium catalysis

Very recently, the palladium catalyzed trifluoromethylselenolation of (hetero)aromatic and olefinic derivatives was investigated by the group of Billard using similar catalytic systems as those depicted for the trifluoromethylthiolation reactions. Indeed, using amides derived from the 5-methoxy-8-aminoquinoline **37**, the functionalization of (hetero)aromatic compounds was achieved using 20 mol% of Pd(CH₃CN)₄Cl₂ in the presence of the TolSO₂SeCF₃ as the fluorinated source (14 examples, Scheme 17) [139]. Of note, when the reaction was carried out on derivatives bearing substituents at the *meta* (**37c** and **37d**) as well as at the *para* (**37a** and **37b**) positions, the corresponding products **38a-38d** were obtained as a mixture of mono- and di-substituted trifluoromethylselenolated derivatives with global yields ranging from 48% to 70%. When one of the *ortho* position of the aromatic ring was substituted with a Me (**37e**), a OMe (**37f**), a Cl (**37g**) and a CF₃ (**37h**) group, the corresponding compounds **38e**, **38f**, **38g** and **38h** were isolated in moderate to high yields (43% to 80%). The methodology also allowed the trifluoromethylselenolation of the furan derivative **37i**, which led to the compound **38i** in 30% yield. A careful monitoring of the reaction unveiled the rapid formation of the CF₃SeSeCF₃ dimer, which could be the active trifluoromethylselenolating reagent in this transformation.



Scheme 17: Pd(II)-catalyzed trifluoromethylselenolation of benzamides derivatives derived from the 5-methoxy-8-aminoquinoline reported by the group of Billard [139]. ^a The yields given are the sum of the yields of mono- and di-trifluoromethylselenolated products.

Then, in 2022, Magnier, Billard and co-workers applied the previous methodology to the trifluoromethylselenolation of acrylamide derivatives [140]. Using the same directing group, a panel of α -arylacrylamide derivatives **39a-39f** was successfully functionalized with a high Z-selectivity (yields up to 98%, scheme 18). Both thermal reaction conditions (DMSO at 70 °C for 16 h) or upon microwave irradiation (100 °C using microwaves in only 1 h) turned out to be efficient in the process. α -Methyl and α,β -dimethyl acrylamides (**39g** and **39h**) were also functionalized. Furthermore, a series of β -substituted acrylamides **39i-39m** with various substituents readily undergoes the trifluoromethylselenolation with high selectivity in moderate yields. Finally, the SeCF₃-containing β -methylacrylamide **40n** was also obtained in 37% yield.



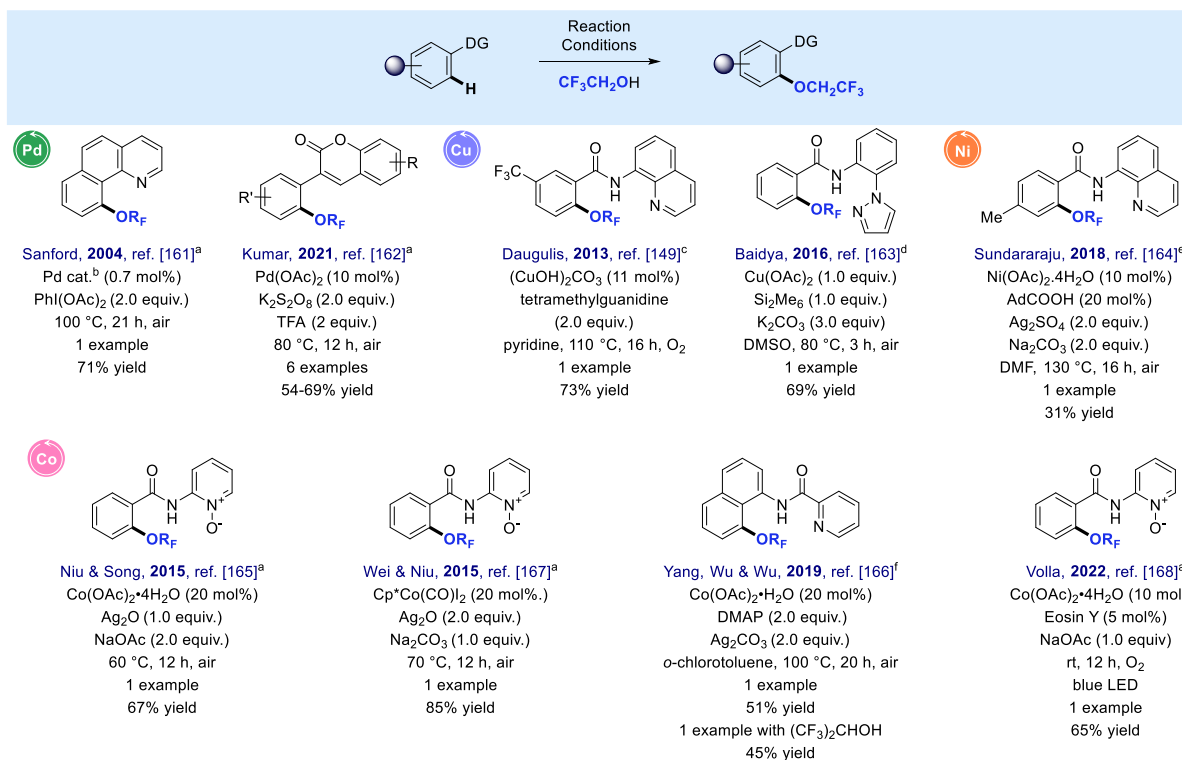
Scheme 18: Pd(II)-catalyzed trifluoromethylselenolation of acrylamide derivatives derived from the 5-methoxy-8-aminoquinoline reported by the groups of Magnier and Billard [140]. ^aMicrowave, 100 °C, 1 h. ^b70 °C for 16 h. ^c20 mol% of Pd(CH₃CN)₂(Cl)₂, 100 °C for 24 h.

Transition metal catalyzed fluoroalkoxylation of (hetero)arenes by C–H bond activation

II.1) Fluoroalkoxylation of aromatic C(sp²)–H bonds by transition metal catalysis

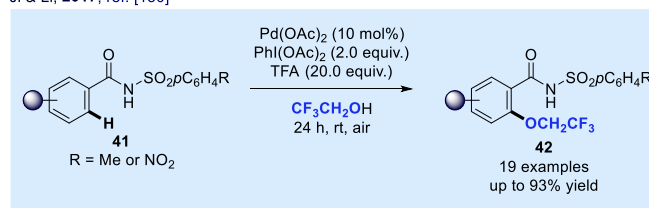
Over the last years, key advances have been made for the formation of a C(sp²)–OCH₂CF₃ bond by transition metal catalyzed C–H bond activation. Indeed, fluorinated ethers [71, 141-153] are key compounds, with especially molecules substituted with the 2,2,2-trifluoroethoxy moiety (OCH₂CF₃), an important fluorinated group found in several bioactive compounds such as Flecanide [154, 155] and Lansoprazole [156], as flagship molecules. Although the transition metal catalyzed hydroxylation and alkoxylation have been studied especially under palladium catalysis [157, 158], the direct dehydrogenative 2,2,2-trifluoroethoxylation of (hetero)arenes, often using the 2,2,2-trifluoroethanol as a readily available, inexpensive and green fluorinated source [159, 160], is still underexplored.

In 2004, Sanford and co-workers reported the dehydrogenative 2,2,2-trifluoroethoxylation of benzo[h]quinoline under palladium catalysis in the presence of PhI(OAc)₂ as oxidant (Scheme 19) [161]. Since this seminal work and in the course of their investigation towards the development of new methods for the alkoxylation of C(sp²)-centers by transition metal catalysis, few examples of transition metal catalyzed dehydrogenative 2,2,2-trifluoroethoxylation reaction were reported. In 2021, the palladium catalyzed *ortho*-2,2,2-trifluoroethoxylation of 3-arylcoumarins was depicted by the group of Kumar (6 examples, up to 69% yields) [162]. Further developments unveiled the use of copper catalysts for such functionalization. In 2013, the group of Daugulis described the copper-catalyzed *ortho*-2,2,2-trifluoroethoxylation of 3-trifluoromethylated benzamide derived from 8-aminoquinoline, giving the corresponding product in 73% yield [149]. The group of Baidya showed that the dehydrogenative 2,2,2-trifluoroethoxylation of benzamide with another bidentate directing group was also possible in the presence of Cu(OAc)₂ and hexamethyldisilane [163]. Using *N,N*- and *N,O*-bidentate directing groups, the construction of C(sp²)–OCH₂CF₃ by C–H bond activation was also reported using Ni- [164] and Co-catalysis [165-167]. In 2022, Volla and co-workers depicted the *ortho*-2,2,2-trifluoroethoxylation of the benzamide using a *N,O*-bidentate directing group by merging Co- and visible light organophotocatalysis [168].

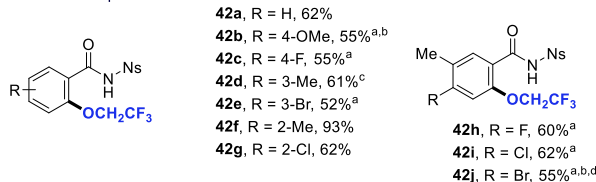


Scheme 19: Transition metal catalyzed dehydrogenative 2,2,2-trifluoroethoxylation of (hetero)aromatic derivatives by C–H bond activation [149]. ^a CF₃CH₂OH used as solvent. ^b Pd cat. = [Pd(μ-κ¹-OAc)(κ²-N,C₁₀-benzo[*h*]quinoline)]₂ ^c 5 equiv. of CF₃CH₂OH. ^d 15 equiv. of CF₃CH₂OH. ^e 50 equiv. of CF₃CH₂OH. ^f CF₃CH₂OH or (CF₃)₂CHOH used as solvent with *o*-chlorotoluene with a ratio of 1:1. AdCOOH = Adamantanecarboxylic acid, DMAP = 4-(dimethylamino)pyridine, OR_F = OCH₂CF₃.

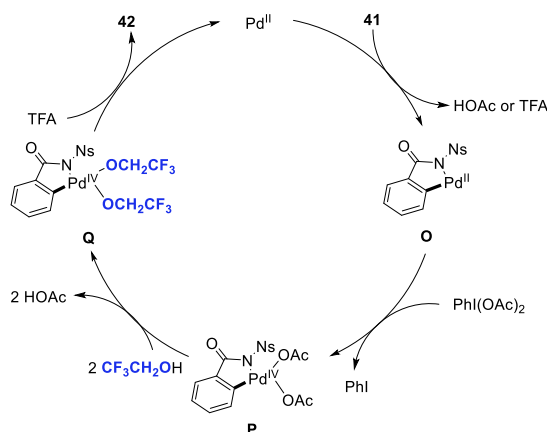
Palladium Catalysis: In 2017, Ji, Li and co-workers reported a thorough study of the Pd-catalyzed 2,2,2-trifluoroethoxylation of *N*-sulfonylbenzamides in the presence of PhI(OAc)₂ as oxidant and an excess of TFA (Scheme 20) [150]. The functionalization of diversely substituted derivatives bearing either electron donating groups (**41b**, **41d** and **41f**) and electron withdrawing groups (**41c**, **41e** and **41g**) was achieved (19 examples, up to 93% yield). Of note, the transformation was also efficient with disubstituted products such as **41h-41j**. The authors suggested the following mechanism. After formation of the metallacycle **O**, the latter would be oxidized leading to the Pd(IV) species **P**. After a ligand exchange, the intermediate **Q** would be generated. Finally, a reductive elimination step would afford the expected functionalized product **42** and would regenerate the catalyst.



Selected examples



Suggested mechanism

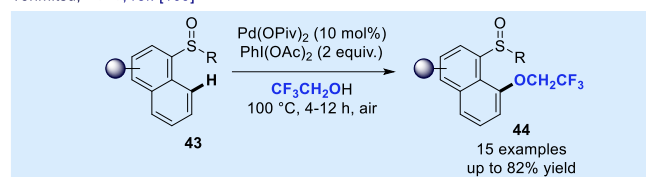


Scheme 20: Pd(II)-catalyzed *ortho*-2,2,2-trifluoroethoxylation of *N*-sulfonylbenzamides reported by the group of Ji and Li [150]. ^a 50 °C. ^b 15 equiv. TFA. ^c 5 equiv. TFA. ^d *N*-acetylglycine (60 mol %). Ns: 4-nitrobenzensulfonyl.

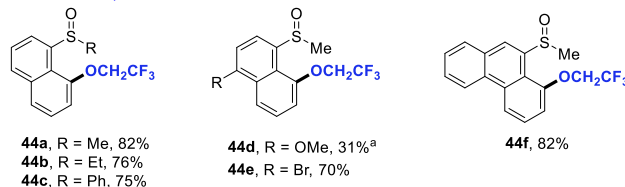
The reaction of 2,2,2-trifluoroethoxylation was not restricted to amides, since in 2020 Yorimitsu and co-workers developed a methodology allowing the formation of a C(sp²)–OR_F by palladium catalyzed C–H bond activation [169]. Using Pd(OPiv)₂ as the catalyst in presence of PhI(OAc)₂ (PIDA), the naphthalene sulfoxide **43a** was 2,2,2-trifluoroethoxylated in 82% yield (Scheme 21). The substituent of the sulfoxide part does not impact the efficiency of the reaction as illustrated with the compounds **44b** and **44c**. The presence of an electron donating substituent at the *para* position of the directing groups was found to be deleterious for the reaction since **44d** was obtained in 31% yield while its brominated analog **44e** was isolated in 70% yield.

Mechanistic studies indicated that the C–H bond activation event was the rate limiting step and the authors suggested a similar mechanism to the one depicted in scheme 20: formation of a palladacycle thanks to a CMD process followed by an oxidation, ligand exchange with CF₃CH₂OH, which would afford the expected product and regeneration of the catalyst. Gratifyingly, the approach was applied to the incorporation of other fluorinated moieties such as OCH₂CF₂H and OCH₂(CF₂)_nH (n = 2 or 4) and gave compounds **46a-46c**.

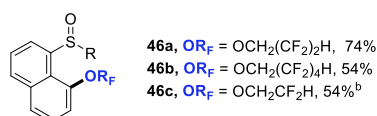
Yorimitsu, 2020, ref. [169]



Selected examples



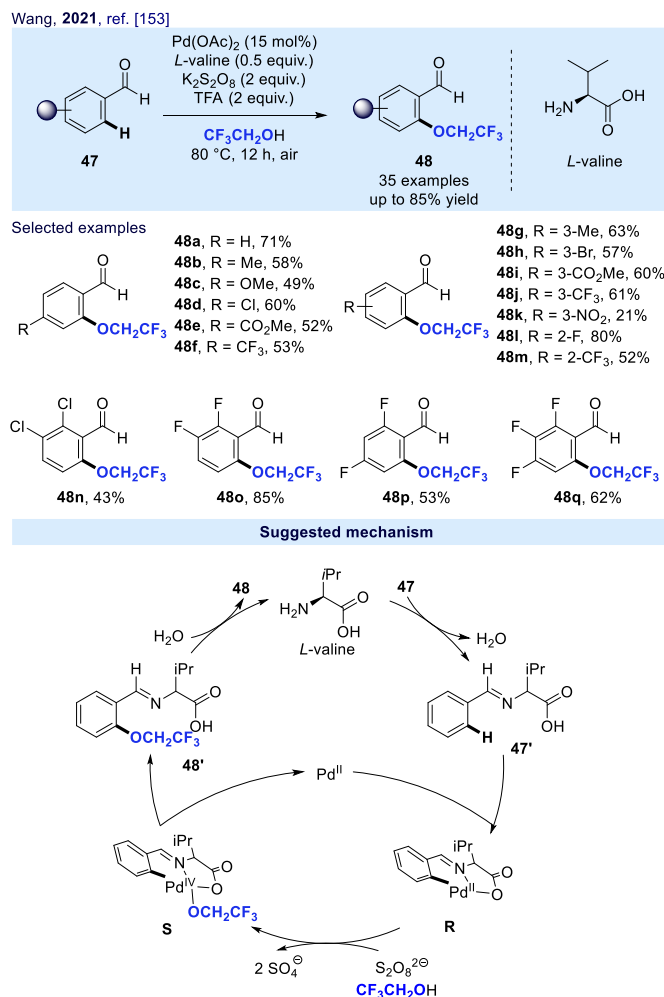
Selected examples



Scheme 21: Pd(II)-catalyzed selective 2,2,2-trifluoroethoxylation and other fluoroalkoxylation of naphthalene sulfoxide derivatives reported by the group of Yorimitsu [169]. ^a 80 °C for 1 h. ^b R_FOH/AcOH (1:7).

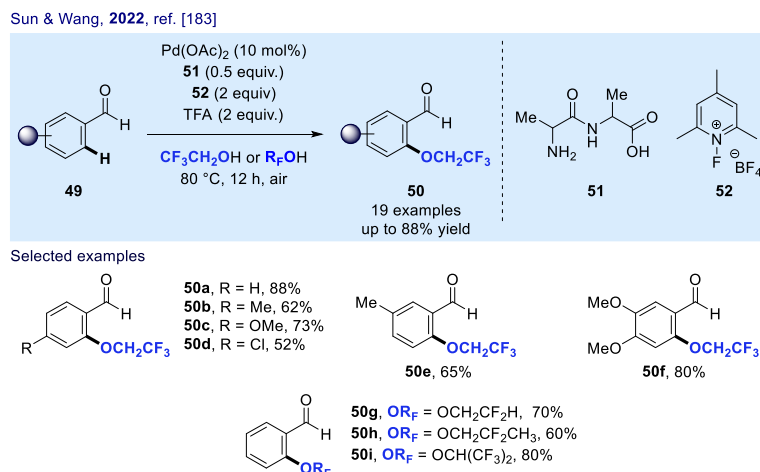
Thanks to the transient directing group strategy [35, 170-182], efficient methodologies for the functionalization of previously reluctant compounds such as benzaldehyde derivatives were developed, and key advances are depicted below.

In 2021, Wang and co-workers described the selective palladium catalyzed *ortho*-2,2,2-trifluoroethoxylation of a series of benzaldehydes (Scheme 22, 35 examples) using the amino acid *L-valine* in the presence of K₂S₂O₈ and TFA at 80 °C [153]. This reaction proved to be highly tolerant to various substituents including a CF₃ group (at the *ortho*, *meta* and *para* positions, **48m**, **48j** and **48f**, respectively), halogens (**48d**, **48h** and **48l**), an ester moiety (**48e** and **48i**) and a methoxy group (**48c**). Note that even di- and tri-substituted benzaldehydes **47n-47q** were smoothly functionalized. A plausible mechanism was suggested by the authors. The amino acid would act as an organic catalyst and would first react with the benzaldehyde **47** to generate the transient directing group (**47'**). Then, formation of the palladacycle (species **R**) followed by its oxidation to a Pd(IV) intermediate and a ligand exchange with 2,2,2-trifluoroethanol would lead to the formation of the species **S**. The latter complex **S** would undergo a reductive elimination leading to the compound **48'** along with the regeneration of the palladium catalyst. Finally, after hydrolysis of **48'**, the expected product **48** would be afforded with the organo-catalyst.



Scheme 22: Pd(II)-catalyzed selective *ortho*-2,2,2-trifluoroethoxylation of benzaldehyde derivatives by means of the transient directing group strategy as reported by the group of Wang [153].

Then, the group of Sun and Wang used a similar approach for the 2,2,2-trifluoroethoxylation of benzaldehydes under palladium catalysis using the amino acid **51** as organic catalyst in the presence of the fluoropyridinium **52** (19 examples, up to 88 % yield, Scheme 23) [183]. Pleasingly, the methodology was extended to the formation of C(sp²)-OR_F bond starting from benzaldehyde (OR_F = 2,2,-difluoroethoxy **50g**, 2,2,-difluoropropoxy **50h** and 1,1,1,3,3,3-hexafluoroisopropoxy **50i**).

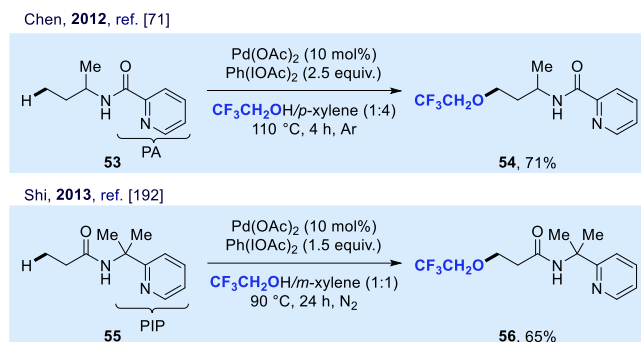


Scheme 23: Pd(II)-catalyzed selective *ortho*-2,2,2-trifluoroethoxylation (and other fluoroalkoxylation) of

benzaldehyde derivatives via the assistance of a transient directing group reported by the group of Sun and Wang [183].

II.2) Fluoroalkoxylation of aliphatic C(sp³)-H bonds by transition metal catalysis

The functionalization of C(sp³)-centers by transition metal catalyzed C-H bond activation remains highly challenging [24, 184-191]. In particular, the 2,2,2-trifluoroethoxylation of aliphatic derivatives is still limited to a handful of examples as illustrated by the two examples depicted in Scheme 24 [71, 192]. Using a bidentate directing group (namely NHPA and CONHPIP for **53** and **55** respectively), the groups of Chen [71] and Shi [192] independently reported the palladium catalyzed selective 2,2,2-trifluoroethoxylation of aliphatic amines and amides at the γ and β positions, respectively, using the trifluoroethanol as fluorinated source in the presence of PIDA. Hence, an efficient access to the corresponding monoether derivatives **54** and **56** in 71 and 65%, respectively, was obtained.



Scheme 24: Pd(II)-catalyzed selective 2,2,2-trifluoroethoxylation of aliphatic amides using a bidentate directing group reported by the group of Chen [71] and Shi [192].

Conclusion

In summary, this review provides an overview of the major developments made over the last years for the synthesis of fluorinated compounds by transition metal catalyzed C-H bond activation. This review focused on the construction of C(sp²)-XR_F bond and C(sp³)-XR_F bond with an emphasis on the trifluoromethylation reaction and transformations using emergent fluorinated residues (SCF₃, SeCF₃, SCF₂H, SCF₂CO₂Et or OCH₂CF₃ groups). Well-designed catalytic systems and suitable fluorinated sources were the key of success for these major developments.

Despite these advances, synthetic challenges still need to be overcome. These synthetic tools are so far still restricted to some fluorinated moieties and extension to other high value-added fluorinated residues [131, 136, 193-208] is of high importance. Besides, in comparison with the functionalization of C(sp²)-centers on aromatic and vinylic derivatives, transition metal catalyzed functionalization of C(sp³)-H bonds remains largely underexplored to date. Furthermore, the development of enantioselective transformations allowing the synthesis of enantioenriched fluorine-containing compounds by transition metal catalyzed C-H bond activation will have a significant impact as for instance an access to pharmaceutically relevant

derivatives. Finally, the use of abundant non-noble transition metals [209-211] in such reactions combined or not with modern technologies (photocatalysis and electrocatalysis) is still underexplored and any advances will be of high importance especially from a sustainability point of view aiming at developing greener synthetic routes towards fluorinated molecules.

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