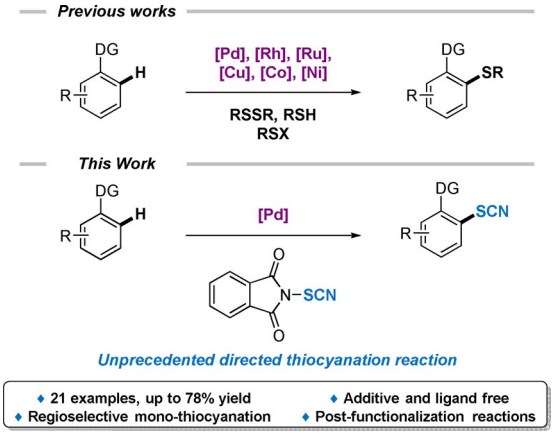
Synthetic Methods

Pd-Catalyzed Directed Thiocyanation Reaction by C–H Bond Activation

Mélissa Gao[+], Mu-Yi Chen[+], Xavier Pannecoucke, Philippe Jubault, and Tatiana Besset*[a]

Abstract: The Pd-catalyzed directed thiocyanation reaction of arenes and heteroarenes by C–H bond activation was achieved. In the presence of an electrophilic SCN source, this original methodology offered an efficient tool to access a panel of functionalized thiocyanated compounds (21 examples, up to 78% yield). Post-functionalization reactions further demonstrated the synthetic utility of the approach by converting the SCN-containing molecules into value-added scaffolds.

Over the years, the direct functionalization of a simple C–H bond by transition metal catalysis became an efficient and pivotal tool in organic chemistry, answering to the increasing demand for more sustainable chemical transformations.[1] Indeed, an array of methodologies was developed to build up a C–N, C–O, C–X or C–C bond. However, less attention was paid to the formation of the C–S bond by transition metal catalyzed C–H bond activation[2] as sulfur poisoning of the transition metal might be a problem to circumvent.[3] Nevertheless, key advances were made by several research groups using Pd-, Rh-, Ru-, Cu-, Co-, and Ni-catalysts, among others (Scheme 1).[2,4] These major contributions brought synthetic solutions for making C–S bonds generally using di(hetero)aryl disulfides as coupling partners. In sharp contrast, the directed thiocyanation reaction by transition metal catalysis is still elusive, and the existing methods are based on the functionalization of innate positions. Convinced about the key role of organothiocyanate compounds,[5a,b] for agrochemicals and medicinal chemistry along with the synthetic utility of the SCN residue as a linchpin[6] to access a large variety of sulfur-containing molecules,[5] we thought that the development of a new tool for the direct introduction of a SCN moiety by transition metal catalyzed C–H bond activation is of prime importance and constitutes today a challenge.



Scheme 1. State of the art on transition metal catalyzed directed C–S bond formation by C(sp^2)–H bond activation and the present work.

To this end, in course of our research program dedicated to the development of new methodologies to build up C–S bonds by transition metal catalyzed C–H bond activation,[7] we report herein an unprecedented directed Pd-catalyzed thiocyanation reaction by C–H bond activation.

At the outset of this study, the 2-phenylpyridine was selected as the model substrate (Table 1). Pleasingly, in the presence of *N*-(thiocyanato)phthalimide as the electrophilic SCN source and using a catalytic amount of $PdCl_2$, the mono-thiocyanation of **1a** occurred, affording the product **2a** in 67% yield (Table 1, entry 1). Then, several parameters were investigated to further improve the efficiency of the transformation. First, different catalysts were tested (Table 1, entries 2–5) and $PdCl_2$ turned out to be the best one. It must be noted that when the catalyst loading was decreased (Table 1, entry 6), a significant drop of the yield was observed (37% vs. 67%). The replacement of DMF by other solvents did not improve the reactivity (Table 1, entries 7–10) and the temperature as well as the time turned out to be key parameters in this transformation (Table 1, entries 11–14). When other electrophilic SCN sources (**II**–**IV**) were evaluated, no better result was obtained (Table 1, entries 15–17). Finally, the presence of additives (AcOH or CsOPiv) was not beneficial to the outcome of the reaction (Table 1, entries 18 and 19). Importantly, a control experiment was per-

[a] M. Gao,[+] M.-Y. Chen,[+] Prof. Dr. X. Pannecoucke, Prof. Dr. P. Jubault, Dr. T. Besset
Normandie Univ, INSA Rouen
UNIROUEN, CNRS, COBRA (UMR 6014)
76000 Rouen (France)
E-mail: tatiana.besset@insa-rouen.fr

[+] These authors contributed equally to this work.

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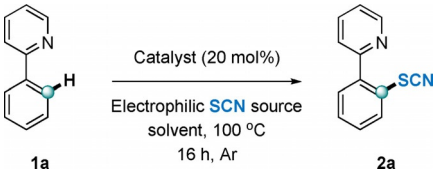
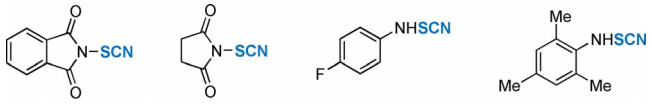
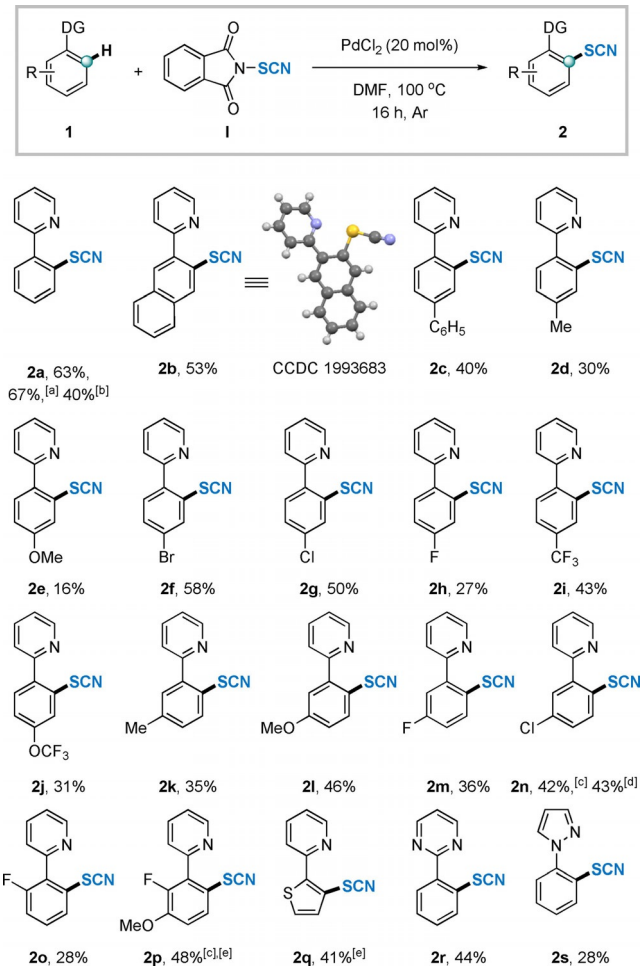
Table 1. Optimization studies for the thiocyanation of the 2-phenylpyridine **1a**.[a]



Entry	Catalyst	Solvent	SCN source	Yield [%]
1	**$PdCl_2$**	**DMF**	**I**	**67**
2	$PdBr_2$	DMF	I	18
3	$Pd(OAc)_2$	DMF	I	21
4	$Pd(MeCN)_2Cl_2$	DMF	I	36
5	$Pd(PPh_3)_4$	DMF	I	NR
6 [b]	$PdCl_2$	DMF	I	37
7	$PdCl_2$	DMSO	I	NR
8	$PdCl_2$	DCE	I	46
9	$PdCl_2$	toluene	I	27
10	$PdCl_2$	1,4-dioxane	I	28
11 [c]	$PdCl_2$	DMF	I	28
12 [d]	$PdCl_2$	DMF	I	20
13 [e]	$PdCl_2$	DMF	I	49
14 [f]	$PdCl_2$	DMF	I	32
15	$PdCl_2$	DMF	II	NR
16	$PdCl_2$	DMF	III	traces
17	$PdCl_2$	DMF	IV	NR
18[g]	$PdCl_2$	DMF	I	57
19[h]	$PdCl_2$	DMF	I	NR
20	–	DMF	I	NR



[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv), reagent **I** (2 equiv), catalyst (20 mol%), in solvent (0.1 M) at 100 °C for 16 h under argon. Isolated yields were given. [b] $PdCl_2$ (10 mol%). [c] 120 °C. [d] 80 °C. [e] 8 h. [f] 24 h. [g] AcOH (1 equiv) was used. [h] CsOPiv (1 equiv) was used. NR = No Reaction.



Scheme 2. Scope of the Pd-catalyzed thiocyanation reaction of 2-phenylpyridine derivatives. Reaction conditions: **1** (0.3 mmol), **I** (2 equiv), $PdCl_2$ (20 mol%), DMF (0.1 M), 100 °C, 16 h, Ar. Isolated yields were provided. [a] Reaction was run on 0.2 mmol scale. [b] Reaction was run on a gram scale. [c] The product was obtained with an inseparable impurity. [d] $PdCl_2$ (15 mol%), **I** (1.55 equiv). [e] No reaction occurred in the absence of $PdCl_2$.

formed without catalyst (Table 1, entry 20) and no product was observed, which confirmed the importance of the Pd^{II} catalyst in that transformation.

With the optimized reaction conditions in hand, a series of 2-phenylpyridine derivatives was evaluated (Scheme 2). The thiocyanation of the 2-phenylpyridine **1a** provided selectively an access to the mono-functionalized product **2a** in 63% yield and the reaction was easily scaled up on a gram scale, affording **2a** in 40% yield. When the naphthalene derivative **1b** was used, the expected product **2b** was obtained in 53% yield and its structure was further confirmed by X-ray analysis (CCDC 1993683).[8]

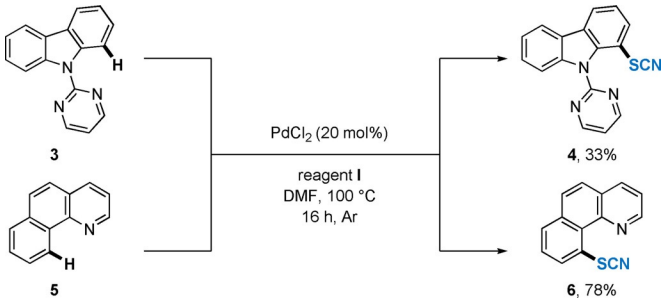
2-Aryl-pyridines with various electron-donating and electron-withdrawing substituents at the *para* position were thiocyanated (**2c**–**2j**). When arenes bearing a substituent at the *meta* position (**2k**–**2n**) were tested, the selective functionalization occurred at the less sterically hindered position.[9] In the case of **1n**, we were able to decrease the catalyst loading to 15 mol% without alteration of the efficiency of the catalytic system as the product **2n** was obtained in a similar yield (43% yield). Even *ortho*- (**1o**) and *ortho, meta*-disubstituted (**1p**) derivatives were suitable substrates. It must be noted that the transformation was tolerant to halogens (**2f**–**2h**, **2p**) and fluorinated groups (**2h**–**2j**), although no reaction was observed with compounds bearing more sensitive functional groups such as alcohol, amine, nitrile.[9] Pleasingly, when an heteroaromatic substrate namely the 2-(2-thienyl)pyridine was reacted, the methodology furnished the corresponding product **2q** in 41% yield. A control experiment was conducted in the absence of Pd-catalyst using **1p** and **1q** as starting materials and no product was observed, which allowed us to rule out a Friedel–Crafts type reaction. Finally, when substrates bearing a pyrimidine or a pyrazole as directing groups were used, the expected products **2r** and **2s** were obtained in lower yields (44% and 28% yields, respectively).[10]

We were pleased to see that our methodology was also applied to the thiocyanation of the *N*-pyrimidine carbazole **3** and the benzo[*h*]quinoline **5**, offering an access to the corresponding products **4** and **6** in 33% and 78% yields, respectively

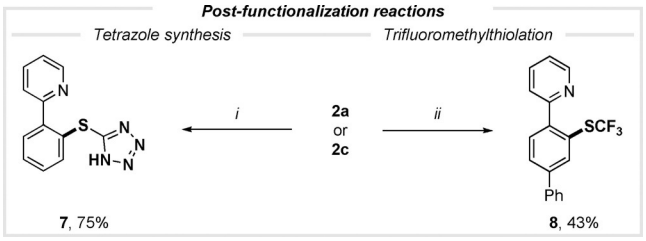
(Scheme 3). To further demonstrate the synthetic utility of the organothiocyanate compounds,[5] the SCN residue was easily converted into high value-added groups (Scheme 4).[9] The tetrazole **7** was synthesized by reacting **2a** with NaN_3 via a [3+2]-cycloaddition reaction.[11] Then, the trifluoromethylthiolation of the derivative **2c** was carried out using the conditions described by Gooβen,[12] leading to the corresponding product **8** in 43% yield.

Based on the literature data,[4d] the following mechanism was suggested (Scheme 5). The metallacycle formation (intermediate **A**) followed by an oxidative addition with the reagent **I**, would provide the Pd^{IV} intermediate **B**. Finally, a final reductive elimination would afford the expected product **2a** and regenerate the catalyst.

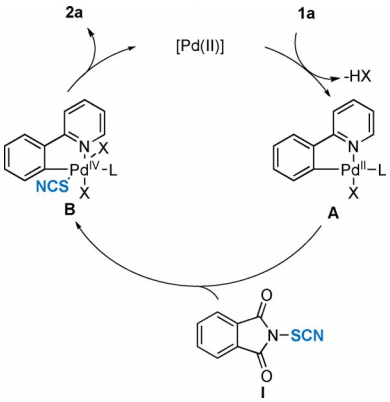
In summary, the regioselective Pd-catalyzed directed monothiocyanation of 2-phenylpyridine and heteroarene derivatives by C–H bond activation was developed. With this innovative methodology, a panel of aromatic derivatives was functionalized in moderate to good yields (21 examples, up to 78% yield). Finally, the introduction of the thiocyanate group as a "synthetic transformable handle" reinforced the synthetic utility of the depicted method as it opened several possibilities towards a large variety of high value-added compounds. To this end, post-functionalization reactions were smoothly achieved. We believe that this original approach to build up C–SCN bond by C–H bond activation will be useful for the organic chemistry community and will open new avenues towards further investigations regarding the potential of the SCN group.



Scheme 3. Extension to the thiocyanation of the *N*-pyrimidine carbazole **3** and the benzo[*h*]quinoline **5**. Reaction conditions: **3** or **5** (0.3 mmol), **I** (2 equiv), $PdCl_2$ (20 mol%), DMF (0.1 M), 100 °C, 16 h, Ar. Isolated yields were provided.



Scheme 4. Post-functionalization reactions. Conditions: *i.* NaN_3 (1.2 equiv), $ZnCl_2$ (1 equiv), *i*PrOH (0.2 M), 50 °C, 1.5 h. *ii.* $TMSCF_3$ (2 equiv), Cs_2CO_3 (2 equiv), MeCN (0.1 M), 40 °C, 20 h. See Supporting Information for more details.



Scheme 5. Plausible mechanism. L = ligand.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: C–H activation · homogeneous catalysis · palladium · synthetic methodology · thiocyanation

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