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Palladium-Catalyzed Coupling of Azoles or Thiazoles with Aryl Thioethers via C−H/C−S Activation

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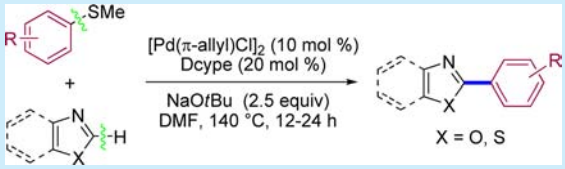
Supporting Information

ABSTRACT: Palladium-catalyzed cross-coupling via the C_{sp^2}−S bond activation of aryl thioethers and the C−H bond activation of azoles or thiazoles was carried out. Electron-deficient and -rich aryl methyl thioethers and diaryl thioethers can be employed as the coupling partners and the reaction tolerates a range of functional groups including MeO, CF_3, CN, PhCO, $CONEt_2$, and Py groups.



2-Aryl oxazoles or thiazoles are important structural units found in natural products, functional materials, agrochemicals, and pharmaceutically active compounds.[1] Among many different synthetic approaches, the direct C−H bond arylation of oxazoles or thiazoles is a significant alternative to traditional cross-coupling reactions such as Kumada, Negishi, and Suzuki couplings from an environmental and economical viewpoint.[2,3] In recent years, significant progress has been achieved in the development of the direct C−H bond arylation of oxazoles or thiazoles through oxidative coupling or using aryl electrophiles such as aryl halides and phenol derivatives including triflates, tosylates, mesylates, sulfamates, esters, and carbamates.[4−8] Among the electrophiles, relatively expensive aryl iodides, bromides, and triflates were largely employed because of the high strength of aryl C−Cl or C−OR bonds. The search for new aryl electrophiles and improving the catalytic efficiency of current systems are still active research topics.

The use of organosulfur compounds such as aryl sulfides as electrophiles in transition metal catalyzed cross-coupling reactions has received less attention because (1) C_{sp^2}−S bonds are rather strong to retard oxidative addition,[9] and (2) the sulfur atom can be strongly bound to transition metals, which poison the catalysts and lead to deactivation.[10] Even so some successful trials have been carried out.[11] For example, aryl methyl sulfides have been used in transition metal catalyzed C−C coupling[11−13] and C−N coupling as electrophiles,[14] and the carbothiolation of terminal alkynes.[15] Herein, we present the first example of the construction of C−C bonds through cleavage of an unreactive aryl C−S bond and the C−H bond activation of oxazoles or thiazoles.

We screened catalysts and reaction conditions using methyl-(naphthalen-2-yl)sulfane and benzoxazole as the model substrates (Table 1). Pd−NHC systems were first examined on the basis of several recent reports.[7e,13a,b] However, the Pd/NHC-catalyzed reaction in DMF at 120 °C using NaO*t*Bu as base gave only a trace amount of cross-coupling product (Table 1, entries 1−3). We then screened the combination of $[Pd(\pi\text{-allyl})Cl]_2$ and some common monodentate and bidentate phosphine ligands including PCy_3, TFP (trifurylphosphine), Xphos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl), Dppe, Xantphos (4,5-bis(diphenyl-phosphino)-9,9-dimethyl-xanthene), DPEphos (bis[2-(diphenylphosphino)phenyl] ether), and Dcype (1,2-bis(dicyclohexylphosphino)ethane). Among them a 1:2 $[Pd(\pi\text{-allyl})Cl]_2$-Dcype combination gave the best result. A higher Dcype loading resulted in a decrease of the yield (Table 1, entries 4−11). Next we examined the effect of solvent, temperature, and base. Both toluene and 1,4-dioxane were as effective as DMF as solvent (Table 1, entries 12 and 13). Yet, enhancing the reaction temperature to 140 °C resulted in an increase of yield. The reaction could be further improved by lengthening the reaction time to 24 h, achieving a 70% yield (Table 1, entries 14 and 15). Two alternative bases, LiO*t*Bu and KO*t*Bu, were demonstrated to be less effective than NaO*t*Bu (Table 1, entries 16 and 17). We also tried to use $Pd(OAc)_2$ and $Pd_2(dba)_3$ as the Pd source or use Dcypm (bis(dicyclohexyl-phosphino)methane) and Dcypp (1,3-bis(dicyclohexylphos-phino)propane) as diphosphine ligands. However, these combinations behaved with lower catalytic activity than the $[Pd(\pi\text{-allyl})Cl]_2$-Dcype system (Table 1, entries 18−21). Dramatic improvement was observed when the $[Pd(\pi\text{-allyl})Cl]_2$ loading was increased to 10 mol %, achieving an 86% yield. Further optimization revealed that the reaction reached completion furnishing the desired product in 98% yield when 2.0 equiv of benzoxazole and 2.5 equiv of NaO*t*Bu were employed. Under the same conditions, a 6 mmol scale of methyl(naphthalen-2-yl)sulfane could be completely transformed to afford a 96% yield of the desired product. Finally, we tried to reduce the catalyst loading to 7.5 mol %, resulting in a marked decrease in yield (Table 1, entries 22−25).

With the optimized reaction conditions in hand, we first examined the scope of aryl thioethers. Aryl methyl thioethers

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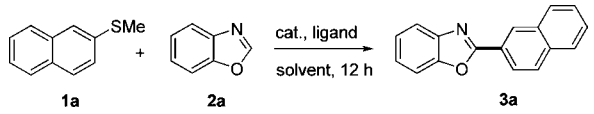
Table 1. Optimization of Reaction Conditions[a]

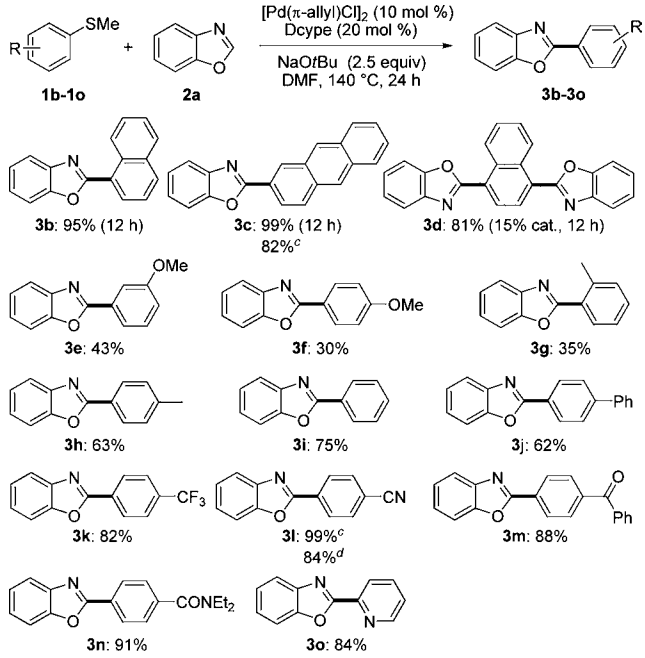


entry	Pd cat. (mol %)	ligand (mol %)	t (°C)	yield (%)[b]
1	Pd-PEPPSI-IPr (10)	none	120	trace
2	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	IPr·HCl (20)	120	trace
3	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	IMes·HCl (20)	120	trace
4	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	PCy_3 (20)	120	11
5	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	TFP (20)	120	trace
6	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Xphos (20)	120	trace
7	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dppe (10)	120	10
8	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Xantphos (10)	120	trace
9	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	DPEphos (10)	120	trace
10	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcype (10)	120	54
11	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcype (20)	120	14
12[c]	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcype (10)	120	54
13[d]	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcype (10)	120	50
14	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcype (10)	140	65
15[e]	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcype (10)	140	70
16[f]	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcype (10)	140	41
17[g]	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcype (10)	140	65
18	$Pd(OAc)_2$ (10)	Dcype (10)	140	42
19	$Pd_2(dba)_3$ (5)	Dcype (10)	140	52
20	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcypm (10)	140	18
21	$[Pd(\pi\text{-allyl})Cl]_2$ (5)	Dcypp (10)	140	48
22	$[Pd(\pi\text{-allyl})Cl]_2$ (10)	Dcype (20)	140	86
23[h]	$[Pd(\pi\text{-allyl})Cl]_2$ (10)	Dcype (20)	140	98
24[h,i]	$[Pd(\pi\text{-allyl})Cl]_2$ (10)	Dcype (20)	140	96
25[h]	$[Pd(\pi\text{-allyl})Cl]_2$ (7.5)	Dcype (15)	140	75

[a]Unless otherwise stated, reactions were run in DMF (5 mL) for 12 h; 0.5 mmol of 2-methylthionaphthalene, 1.5 equiv of benzoxazole, and 2 equiv of NaO*t*Bu were employed. [b]Isolated yield. [c]Toluene was used as solvent. [d]1,4-Dioxane was used as solvent. [e]Reaction time was 24 h. [f]2.0 equiv of LiO*t*Bu were used as base. [g]2.0 equiv of KO*t*Bu were used as base. [h]2.0 equiv of benzoxazole and 2.5 equiv of NaO*t*Bu were employed. [i]6 mmol scale of 2-methylthionaphthalene was used.

1b−**1o** were found to be suitable reaction partners with benzoxazole to provide the corresponding 2-aryl substituted benzoxazoles as shown in Scheme 1. Similar to **1a**, methyl(naphthalen-2-yl)sulfane (**1b**) and anthracen-2-yl(methyl)sulfane (**1c**) were successfully coupled with benzoxazole to afford products **3b** and **3c**, respectively, in excellent yields. When $[Pd(\pi\text{-allyl})Cl]_2$ and Dcype loadings were respectively decreased to 5 and 10 mol % in the reaction of anthracene-2-thiol with benzoxazole, the coupling product yield decreased to 82%. The two methylthio groups of 1,4-bis(methylthio)naphthalene (**1d**) could be smoothly transformed using a 15 mol % catalyst loading, affording 1,4-di(benzoxazol-2-yl)naphthalene (**3d**) in 81% yield. These thioethers exhibited high reactivity, and the reactions could reach completion in 12 h. To install substituted phenyl groups onto benzoxazole, we found that prolonging the reaction time to 24 h was necessary. Electron-rich or sterically hindered aryl thioethers such as (3-methoxyphenyl)(methyl)-sulfane (**1e**), (4-methoxyphenyl)(methyl)sulfane (**1f**), and methyl(*o*-tolyl)sulfane (**1g**) showed slightly lower reactivity and resulted in relatively low yields (30−43%). Unactivated and activated aryl methyl thioethers gave moderate to high product yields (**3i**−**3n**). Among them, 4-mercaptobenzonitrile exhibited especially high reactivity. 5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ led to a 99% product yield, and 2.5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ resulted in an 84% product yield.

Scheme 1. Scope of Aryl Thioethers[a,b]

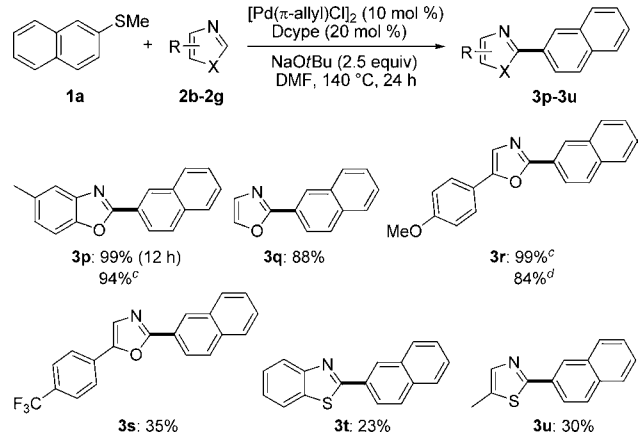


[a]Unless otherwise stated, reactions were performed with 0.5 mmol of aryl methyl thioethers and 1 mmol of benzoxazole in DMF (5 mL) according to the conditions indicated by the above equation. [b]Isolated yield. [c]5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ and 10 mol % Dcype were employed. [d]2.5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ and 5 mol % Dcype were employed.

Meanwhile, the functional groups on the aromatic rings such as CF_3, CN, COPh, and $CONEt_2$ were well tolerated. Furthermore, 2-methylthiopyridine was also demonstrated to react smoothly with benzoxazole, forming 2-(pyridin-2-yl)benzoxazole (**3o**) in 84% yield.

Next we examined the scope of azoles and thioazoles using methyl(naphthalen-2-yl)sulfane (Scheme 2). 5-Methyl-benzoxazole exhibited slightly higher reactivity than benzoxazole. 10 mol % $[Pd(\pi\text{-allyl})Cl]_2$ resulted in the coupling product in

Scheme 2. Scope of Azoles or Thiazoles[a,b]



[a]Unless otherwise stated, the reactions were performed with 0.5 mmol of 2-methylthio-naphthalene and 1 mmol of azoles or thioazoles in DMF (5 mL) according to the conditions indicated by the above equation. [b]Isolated yield. [c]5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ and 10 mol % Dcype were employed. [d]2.5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ and 5 mol % Dcype were employed.

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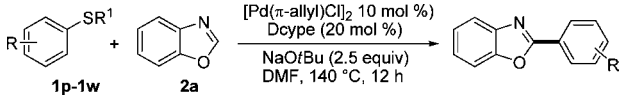
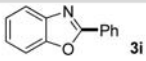
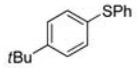
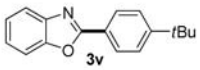
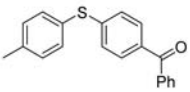
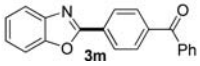
quantitative yield in 12 h, and 5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ led to a 94% product yield in 24 h (**3p**). Oxazole also reacted smoothly with methyl(naphthalen-2-yl)sulfane under standard conditions. Its 2-position C−H bond was activated and arylated, affording the corresponding product in 88% yield. Two 5-aryloxazoles were tested for the cross-coupling. Reaction of 5-(4-methoxyphenyl)oxazole afforded the arylating product in 99% yield using 5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ as the catalyst and in 84% yield using 2.5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ as the catalyst (**3r**), whereas reaction of 5-(4-(trifluoromethyl)phenyl)oxazole gave the product in 35% yield under standard conditions. The experimental facts clearly showed that an electron-rich aryl group facilitated the reaction and an electron-deficient aryl group was disadvantageous to the reaction. Benzothiazole and 5-methylthiazole could also react with methyl(naphthalen-2-yl)sulfane, but the product yields were much lower than those using benzoxazole and oxazole (**3t** and **3u**).

To expand the substrate scope and study the reactivity of various thioethers, a series of nonmethyl aryl thioethers were evaluated using the reaction with benzoxazole, and the results are presented in Table 2. Phenyl(trifluoromethyl)sulfane, trimethyl-

Table 2. Reaction of Non-methyl Aryl Thioethers[a]



1p-1w 2a

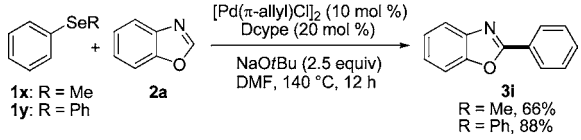
entry	sulfide	product	yield (%)[b]
1	$PhS\text{-}CF_3$	 3i	13
2	$PhS\text{-}SiMe_3$	**3i**	trace
3	$PhS\text{-}CH_2CH{=}CH_2$	**3i**	16
4	$PhS\text{-}CH_2Ph$	**3i**	12
5	$PhS\text{-}CH{=}CH_2$	**3i**	17
6	PhSPh	**3i**	99 (96[c])
7[d]		**3i**	53[c,e]
		 3v	44[c,e]
8[d]		**3h**	19[c]
		 3m	78[c]

[a]Unless otherwise stated, the reactions were performed with 0.5 mmol of thioethers and 1.0 mmol of benzoxazole in DMF (5 mL) according to the conditions indicated by the above equation. [b]Isolated yield. [c]5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ and 10 mol % Dcype were employed; the reaction was run for 24 h. [d]Two products were obtained, and the yields were calculated based on the amount of the sulfides. [e]The two components cannot be separated, and the yields were calculated based on the integral resulting from the ^1H NMR spectrum of the mixture of **3i** and **3v**.

(phenylthio)silane, allyl(phenyl)sulfane, phenyl(vinyl)sulfane, and benzyl(phenyl)sulfane were respectively reacted with benzoxazole to result in a trace amount or low yield of 2-phenylbenzoxazole (Table 2, entries 1−5). Most of the raw materials remained under the reaction conditions. This showed that the reactivity of these thioethers was lower than that of thioanisole (Scheme 1, **3i**). In each case cleavage of the C_{Ar}−S bond was observed. No products via C_{sp^3}−S bonds or vinyl C_{sp^2}−S bond cleavage were obtained. Diphenylsulfane exhibited high reactivity, and its reaction resulted in 2-phenylbenzoxazole in 99% yield under standard conditions and in 96% yield when using 5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ as the catalyst. Reaction of unsymmetrical diaryl thioethers required a 5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ loading and gave a product mixture. For example, in the presence of 5 mol % $[Pd(\pi\text{-allyl})Cl]_2$ and 10 mol % Dcype reaction of (4-*tert*-butylphenyl)(phenyl)sulfane generated a mixture of 2-phenylbenzoxazole and 2-(4-*tert*-butylphenyl)-benzoxazole in a ratio of 53 to 44 (Table 2, entry 7); reaction of phenyl(4-*p*-tolylthiophenyl)methanone resulted in a mixture of 2-(*p*-tolyl)benzoxazole and (4-benzoxazol-2-ylphenyl)-(phenyl)methanone in a ratio of 19 to 78 (Table 2, entry 8). It seems that an electron-withdrawing group on the phenyl ring promotes the C_{Ar}−S bond cleavage. This observation is consistent with the results listed in Scheme 1.

We noted that the C_{Ar}−Se bond of an aryl selenide could be similarly activated under the conditions mentioned above. For example, reaction of benzoxazole with methyl(phenyl)selane afforded 2-phenylbenzoxazole in 66% yield, and the reaction with diphenylselane resulted in the same product in 88% yield (Scheme 3). Compared with corresponding aryl thioethers, the

Scheme 3. C−Se Bond Cleavage of Phenylselenides



1x: R = Me
1y: R = Ph
2a
3i
R = Me, 66%
R = Ph, 88%

reactivity of methyl(phenyl)selane is close to that of thioanisole, whereas the reactivity of diphenylselane is slightly lower than that of diphenylsulfane.

To gain preliminary mechanistic information about this transformation, several control experiments were carried out under the standard conditions. When an equimolar amount of free-radical inhibitor 1,1-diphenylethylene or TEMPO was added to the reaction mixture, the product yields were not affected. It seems that the reaction did not proceed via a free-radical process. As shown in Table 1 (entry 19), the $Pd_2(dba)_3$-Dcype system showed comparable catalytic activity with the combination of $[Pd(\pi\text{-allyl})Cl]_2$ or $Pd(OAc)_2$ and Dcype. Hence, the active catalyst in the catalytic cycle may be a Pd(0) species. Based on the above-mentioned experimental facts and literature information,[8a,16] a possible mechanism is outlined in Scheme 4. Thus, a Pd(0) species, LPd(0) (**A**), is first generated under the reaction conditions. The Pd(0) species reacts with ArSMe to generate an oxidative addition product LPd(SMe)Ar (**B**). Base-assisted C−H palladation of azoles with LPd(SMe)Ar occurs to form an aryl(heteroaryl) palladium intermediate (**C**), which undergoes reductive elimination to give a cross-coupling product along with regeneration of the starting Pd(0) complex (**A**) to close the catalytic cycle. The role of Dcype may involve (1) promotion of the oxidative addition of C−S bonds by providing suitable electron effect, (2) stabilization of the intermediate of oxidative addition **B**, and (3) facilitation of the reductive elimination of the C−H palladation species **C** by offering the appropriate steric effect (Table 1, entries 20 and 21).[16a]

In conclusion, we have developed a palladium-catalyzed arylation of azoles and thiozaoles with aryl thioethers via C−H/C−S activation. The method displays a broad substrate scope.

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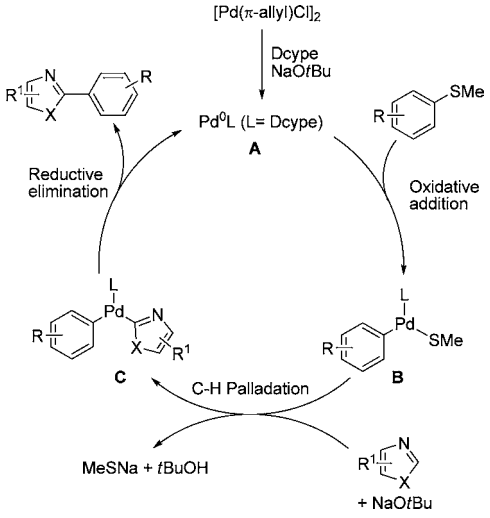
Scheme 4. A Proposed Mechanism



Various aryl methyl sulfides and diaryl sulfides including electron-rich and -poor ones can be used as arylating reagents. Electron-deficient aryl sulfides and electron-rich azoles show higher reactivity rather than vice versa. The reaction gives good to excellent yields in most cases and shows good functional group compatibility. We believe that this methodology would provide a valuable complement to the direct C−H arylation of azoles and thiazoles.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details of the coupling reaction, characterization data, and the copies of NMR spectra of the cross-coupling products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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