Advanced Synthesis & Catalysis

Accepted Article

Title: Nickel-Catalyzed Reaction of Aryl 2-Pyridyl Ethers with Silylzinc Chlorides: Silylation of Aryl 2-Pyridyl Ethers via Cleavage of the Carbon-Oxygen Bond

Authors: Ying-Ying Kong and Zhong-Xia Wang

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201900949

Link to VoR: http://dx.doi.org/10.1002/adsc.201900949

10.1002/adsc.201900949

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Nickel-Catalyzed Reaction of Aryl 2-Pyridyl Ethers with Silylzinc Chlorides: Silylation of Aryl 2-Pyridyl Ethers via Cleavage of the Carbon–Oxygen Bond

Ying-Ying Kong[a] and Zhong-Xia Wang[a,b,*]

[a] CAS Key Laboratory of Soft Matter Chemistry and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China. E-mail: zxwang@ustc.edu.cn.
[b] Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, People's Republic of China.

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. Ni-catalyzed C–O(Py) bond activation and silylation of aryl 2-pyridyl ethers with silylzinc chlorides were carried out. This protocol allowed the 2-pyridyloxy group to be substituted by a silyl group with short reaction times, mild reaction conditions, and good compatibility of functional groups.

Keywords: C-O bond activation; nickel catalysis; silylation; aryl 2-pyridyl ether; silylzinc reagent

Introduction

2-Pyridyloxy (OPy) group has been demonstrated to be an excellent *ortho* directing group in transition-metal-catalyzed C−H bond functionalization reactions of aromatic systems.[1] However, the existence of the pyridyloxy group in the functionalized products might limit the utility of the products. Hence, developing methodology to remove or functionalize the OPy moiety after directing C−H functionalization is of great significance. Chatani et al. reported first example of the OPy group conversion from an aryl 2-pyridyl ether via rhodium- or nickel-catalyzed C-OPy bond activation and borylation.[2] Subsequently, we carried out amination,[3] alkylation[4] and reduction[5] of aryl 2-pyridyl ethers via nickel-catalyzed C-OPy bond cleavage. Zeng et al. reported chromium-catalyzed Kumada arylation of aryl 2-pyridyl ethers via C–OPy bond activation.[6] Li et al. reported an example of cross-coupling reaction of naphthyl 2-pyridyl ether with $Sc(CH_2SiMe_3)_3(THF)_2$ under $Ni(COD)_2/PCy_3$ catalysis.[7] Although these significant achievements have been made, the methods to remove or convert the OPy group are still very limited.

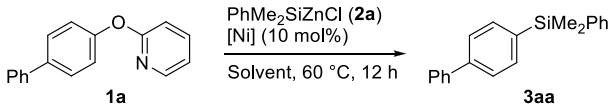
On the other hand, aryl silanes are important building blocks or synthetic intermediates in medicinal chemistry and materials science.[8] Some methodologies for the synthesis of arylsilanes have been developed. The classic method for the synthesis of arylsilanes is via the reaction of chlorosilanes with arylmagnesium or aryllithium reagents.[9] Reaction of silyllithium with aryl halides was reported recently.[10] Transition-metal-catalyzed reaction of aromatic electrophiles with silylation reagents also attracts considerable attention. Representative examples include the coupling of aryl halides or esters with silylboranes,[11] the coupling of aryl halides with hydrosilanes or disilanes,[12] and aromatic C−H silylation of arenes.[13] It is interesting to explore silylation of aryl 2-pyridyl ethers with appropriate silicon nucleophiles. Silylzinc reagents have better compatibility of functional groups than silylmagnesium and lithium reagents and showed good reactivity in the reaction with alkyl or alkenyl electrophiles.[14] Hence they were chosen as the silylation reagents to perform the transformation of aryl 2-pyridyl ethers. Herein we report the results.

Results and Discussion

2-([1,1'-Biphenyl]-4-yloxy)pyridine (**1a**) and (dimethyl-(phenyl)silyl)zinc chloride (**2a**) were used as the model substrates to screen the reaction conditions. Nickel complexes have been demonstrated to be effective in activation of the C-O bonds of aryl pyridyl ethers. We also tested a series of nickel complexes in this study. The readily available nickel complexes including $NiCl_2(DME)$, $NiCl_2(PPh_3)_2$, and $NiCl_2(PMe_3)_2$ were found to be almost ineffective in THF at 60 °C (Table 1, entries 1-3). However, $NiCl_2(PCy_3)_2$ showed good catalytic activity in this transformation at the same solvent and temperature as above, leading to the silylated product **3a** in 84% yield (Table 1, entry 4). The nickel complexes with didentate phosphine ligands such as $NiCl_2(dppp)$ and $NiCl_2(dppf)$ exhibited very low catalytic activity under the same conditions (Table 1,

10.1002/adsc.201900949

Table 1. Optimization of reaction conditions[a]



1a 3aa

Entry	[Ni]	Solvent	Yield (%)[b]
1	$NiCl_2(DME)$	THF	3
2	$NiCl_2(PPh_3)_2$	THF	trace
3	$NiCl_2(PMe_3)_2$	THF	trace
4	$NiCl_2(PCy_3)_2$	THF	84
5	$NiCl_2$(dppp)	THF	6
6	$NiCl_2$(dppf)	THF	3
7	$NiCl_2(PCy_3)_2$	Et_2O	trace
8	$NiCl_2(PCy_3)_2$	dioxane	4
9	$NiCl_2(PCy_3)_2$	toluene	trace
10	$NiCl_2(PCy_3)_2$	DMSO	trace
11	$NiCl_2(PCy_3)_2$	NMP	20
12	$NiCl_2(PCy_3)_2$	DMA	25
13	$NiCl_2(PCy_3)_2$	NMP/THF(1:1)	24
14	$NiCl_2(PCy_3)_2$	DMA/THF(1:1)	27
15	$NiCl_2(PCy_3)_2$	THF	78[c]
16	$NiCl_2(PCy_3)_2$	THF	69[d]
17	$NiCl_2(PCy_3)_2$	THF	85[e]
18	$NiCl_2(PCy_3)_2$	THF	70[f]
19	$NiCl_2(PCy_3)_2$	THF	73[g]
20	$NiCl_2(PCy_3)_2$	THF	85[h]
21	$NiCl_2(PCy_3)_2$	THF	84[i]
22	$NiCl_2(PCy_3)_2$	THF	85(82)[j]
23	$NiCl_2(PCy_3)_2$	THF	85[c,k]
24	$NiCl_2(PCy_3)_2$	THF	27[l]
25	-	THF	trace

[a] Unless otherwise stated, the reactions were carried out according to the conditions indicated by the above equation; 0.2 mmol of **1a** and 0.22 mmol of $PhMe_2SiZnCl$ (**2a**) were employed. **2a** was prepared by reaction of $PhMe_2SiLi$ with an equimolar of $ZnCl_2$ in THF. [b] GC yield using dodecane as an internal standerd; isolated yield is shown in parentheses. [c] 1.25 equiv of **2a** were employed. [d] 1.5 equiv of **2a** were employed. [e] The reaction was carried out at 100 °C. [f] The reaction was carried out at 40 °C. [g] The reaction was carried out at 25 °C. [h] The reaction time was 24 h. [i] The reaction time was 4 h. [j] The reaction time was 1 h. [k] 15 mol% of $NiCl_2(PCy_3)_2$ was employed. [l] 5 mol% of $NiCl_2(PCy_3)_2$ was employed.

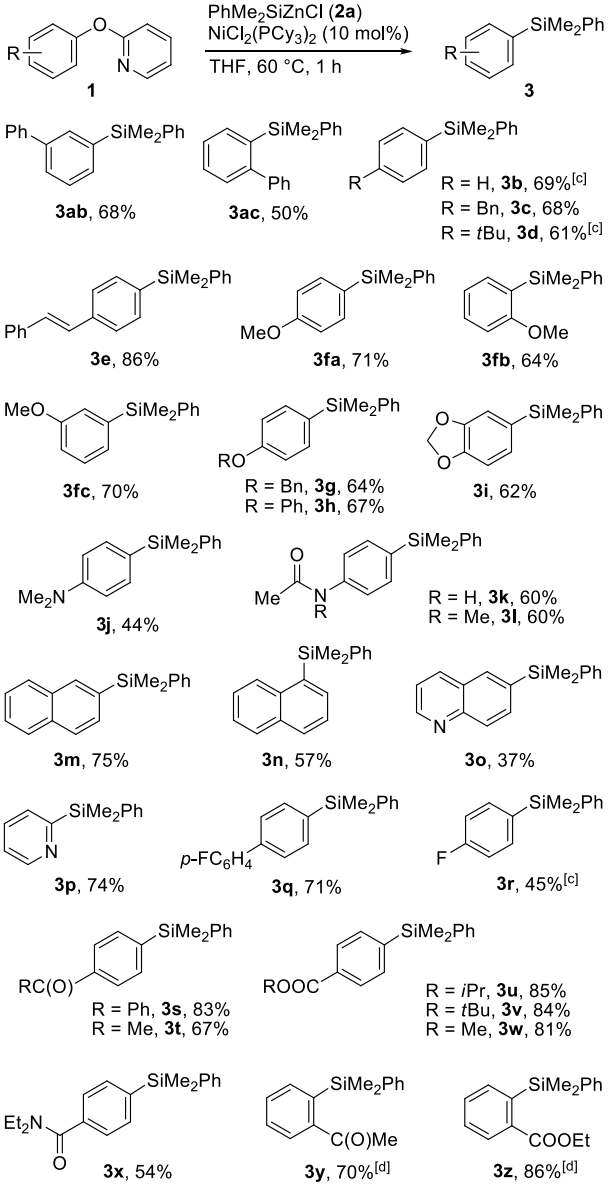
entries 5 and 6). Next, solvents were screened. Et_2O, 1,4-dioxane, toluene and DMSO were not suitable solvents for this reaction. Only trace amount of products were observed when the reaction was run in these solvents (Table 1, entries 7-10). When the reaction was respectively carried out in NMP, DMA, or mixed solvents NMP/THF (1:1) and DMA/THF (1:1), the desired product were achieved in 20-27% yields (Table 1, entries 11-14). Then we demonstrated that higher **2a** loading than 1.1 equivalents cannot increase the product yield (Table 1, entries 15 and 16). The reaction performed at 100 °C gave almost same yield as that at 60 °C. However, when the reaction was run at lower temperature than 60 °C, the product yields decreased (Table 1, entries 17-19). The reaction time was also examined. Longer reaction time than 12 h did not improve the reaction results. Further tests demonstrated that the reaction can be completed in 1 h (Table 1, entries 20-22). Attempt to further improve the product yield, 15 mol% catalyst were employed. The result showed that the reaction gave the same product yield as that employing 10 mol% catalyst. When 5 mol% catalyst was used, a marked yield decrease was observed (Table 1, entries 23 and 24). Finally, in the absence of any nickel catalysts, the reaction gave only trace amount of product (Table 1, entry 25).

Under the optimized conditions, reaction of various aryl 2-pyridyl ethers with $PhMe_2SiZnCl$ (**2a**) was tested. Like 2-(biphenyl-4-yloxy)pyridine, both 2-(biphenyl-3-yloxy)pyridine and 2-(biphenyl-2-yloxy)pyridine also reacted smoothly with **2a**, but they led to the corresponding products in lower yields than 2-(biphenyl-4-yloxy)pyridine (Table 2, **3ab** and **3ac**). 2-Phenoxypyridine and 4-alkyl-substituted phenyl 2-pyridyl ethers including 2-(4-benzyl phenoxy)pyridine and 2-(4-*tert*-butylphenoxy) pyridine displayed similar reactivity to 2-(biphenyl-3-yloxy)pyridine. Their reaction with $PhMe_2SiZnCl$ gave the desired products in 61% to 69% yields (Table 2, **3b**-**3d**). (*E*)-2-(4-Styrylphenoxy)pyridine showed markedly higher reactivity than the 4-alkyl-substituted phenyl 2-pyridyl ethers (Table 2, **3e**). A series of alkoxy-substituted phenyl 2-pyridyl ethers were also tested (Table 2, **3e**-**3h**). They showed similar reactivity to the alkyl-substituted phenyl 2-pyridyl ethers. In the reactions the alkoxy groups on the aromatic rings were tolerated. Reaction of 2-(2-methoxyphenoxy)pyridine gave the product in lower yield compared with that of 2-(3-methoxy phenoxy)pyridine and 2-(4-methoxyphenoxy) pyridine (Table 2, **3fa**-**3fc**). This is ascribed to steric hindrance of the *ortho*-MeO group in 2-(2-methoxyphenoxy)pyridine. *N*,*N*-Dimethyl-4-(pyridin-2-yloxy)aniline exhibited lower reactivity than the alkoxy-substituted phenyl 2-pyridyl ethers possibly due to strong electron donating property of the Me_2N group in *N*,*N*-dimethyl-4-(pyridin-2-yloxy)aniline (Table 2, **3j**). Acetamido-substituted phenyl 2-pyridyl ethers including *N*-(4-(pyridin-2-yloxy)phenyl) acetamide and *N*-methyl-*N*-(4-(pyridin-2-yloxy)-phenyl)acetamide also showed higher reactivity than *N*,*N*-dimethyl-4-(pyridin-2-yloxy)aniline (Table 2, **3k** and **3l**). It seems that the acidic proton of the MeC(O)NH group in *N*-(4-(pyridin-2-yloxy)phenyl) acetamide did not have an effect on the coupling reaction. Three aryl 2-pyridyl ethers with a fused aromatic system including 2-(naphthalen-2-yloxy) pyridine, 2-(naphthalen-1-yloxy)pyridine and 6-(pyridin-2-yloxy)quinoline were tested and their reaction with **2a** resulted in the corresponding products in 75%, 57% and 37% yields, respectively (Table 2, **3m**-**3o**). It is a little surprise that reaction of 6-(pyridin-2-yloxy)quinoline gave the lowest product yield for unclear reason. 2,2'-Oxydipyridine was demonstrated to react with **2a** to afford 2-(dimethyl(phenyl)silyl)pyridine in 74% yield (Table 2,

10.1002/adsc.201900949

3p). However, in the reaction of aryl 2-pyridyl ethers with **2a** no products via C(Py)-O bond cleavage were observed. Other electron-poor aryl 2-pyridyl ethers including 2-((4'-fluoro-[1,1'-biphenyl]-4-yl)oxy) pyridine, 2-(4-fluorophenoxy)pyridine, phenyl(4-(pyridin-2-yloxy)phenyl)methanone, 1-(4-(pyridin-2-yloxy)phenyl)ethan-1-one, isopropyl 4-(pyridin-2-yloxy)benzoate, *tert*-butyl 4-(pyridin-2-yloxy) benzoate, methyl 4-(pyridin-2-yloxy)benzoate and N,N-diethyl-4-(pyridin-2-yloxy)benzamide were examined under the same conditions (Table 2, **3q**-**3x**).

Table 2. Scope of aryl 2-pyridyl ethers[a,b]



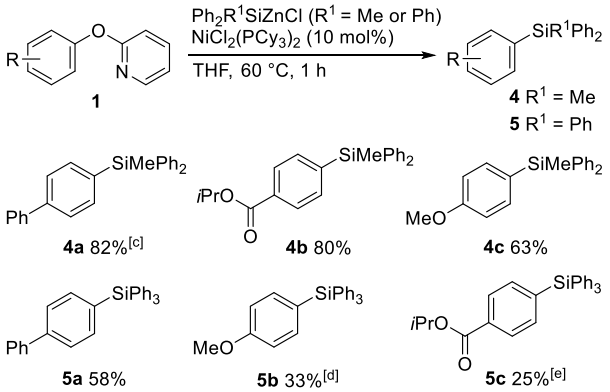
[a] The reactions were carried out according to the conditions indicated by the above equation. 0.2 mmol 2-([1,1′-biphenyl]-4-yloxy)pyridine and 1.1 equiv of $PhMe_2SiZnCl$ (**2a**) were employed; **2a** was prepared by reaction of $PhMe_2SiLi$ with an equimolar of $ZnCl_2$ in THF. [b] Isolated yield was reported. [c] The yield was calculated based on the weight of the mixture of dimethyldiphenylsilane and the desired product and the integral ratio of ^1H NMR spectrum of the mixture. [d] Reaction time was 2 h.

2-(4-Fluorophenoxy)pyridine, 1-(4-(pyridin-2-yloxy) phenyl)ethan-1-one and *N*,*N*-diethyl-4-(pyridin-2-yloxy)benzamide led to relatively low product yields. The other compounds led to good or very good yield in the transformation. The relatively low product yield of reaction of 1-(4-(pyridin-2-yloxy)phenyl) ethan-1-one with **2a** was probably due to side reaction of MeC(O) group with **2a**. The reaction of 2-(4-fluorophenoxy)pyridine and N,N-diethyl-4-(pyridin-2-yloxy)benzamide with **2a** led to low product yields for unclear reasons. Two *ortho*-electron-withdrawing-group-substituted phenyl 2-pyridyl ethers, 1-(2-(pyridin-2-yloxy)phenyl) ethanone and ethyl 2-(pyridin-2-yloxy)benzoate, also reacted smoothly with **2a** to afford the desired products in 71% and 86% yields, respectively (Table 2, **3y** and **3z**). From above reaction data it seems that the ethers with large conjugated aromatic systems or electron-poor aromatic systems have better reactivity in the coupling. The steric effect plays some role. The ethers with sterically hindered aryl groups led to low product yields (Table 2, **3ac**, **3fc** and **3n**). In addition, in each reaction small amounts of homocoupling products of the aryl groups and other unidentified byproducts could be observed by TLC. We could hardly find remained starting materials.

Other silylzinc reagents were also tested. $Me_3SiZnCl$ was not a suitable nucleophilic reagent in this transformation. $Ph_2MeSiZnCl$ showed similar reactivity to $PhMe_2SiZnCl$ under the same conditions as above. Reaction of $Ph_2MeSiZnCl$ with conjugated aryl 2-pyridyl ether, 2-([1,1'-biphenyl]-4-yloxy) pyridine, or electron-poor aryl 2-pyridyl ether, isopropyl 4-(pyridin-2-yloxy)benzoate, resulted in the desired products in very good yields (Table 3, **4a** and **4b**). Reaction of $Ph_2MeSiZnCl$ with electron-rich aryl 2-pyridyl ether, 2-(4-methoxyphenoxy)pyridine, led to the coupling product in markedly lower yield (Table 3, **4c**). In the reactions of $Ph_2MeSiZnCl$ we also observed small amounts of homocoupling byproducts. Under the same conditions, $Ph_3SiZnCl$ exhibited different reactivity. Reaction of $Ph_3SiZnCl$ with 2-([1,1'-biphenyl]-4-yloxy)pyridine gave the desired coupling product in 58% yield (Table 3, **5a**). A small amount of homocoupling product of 2-([1,1'-biphenyl]-4-yloxy)pyridine was observed. Reaction of $Ph_3SiZnCl$ with 2-(4-methoxy-phenoxy)pyridine or isopropyl 4-(pyridin-2-yloxy)benzoate gave the desired products in 33% and 25% yields, respectively, along with homocoupling species of the aryl 2-pyridyl ethers in 32% and 30% yields, respectively (Table 3, **5b** and **5c**). Attempts to improve the reaction by using Ph_3SiLi, $(Ph_3Si)_2Zn$ or $(Ph_3Si)_3ZnLi$ as the nucleophiles were unsuccessful. Reaction of these nucleophilic reagents with 2-(4-methoxy phenoxy)pyridine or 2-(biphenyl-4-yloxy)pyridine under the optimized conditions gave the corresponding silylated products in low yields (11-29%) (Table S1 in the Supporting Information).

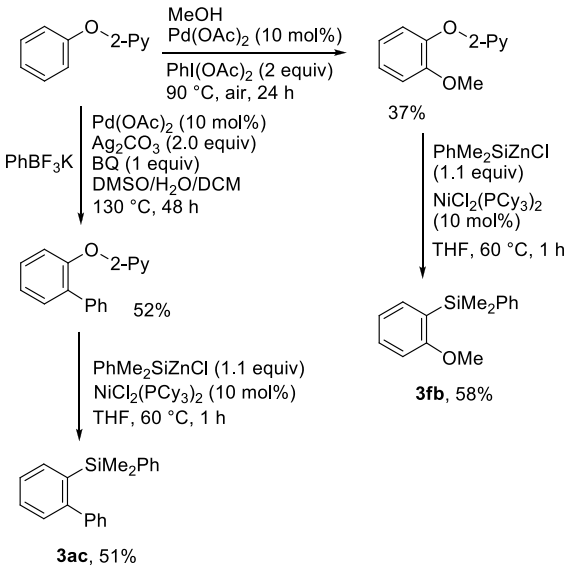
As indicated in the introduction, 2-pyridyloxy group is one of the most effective directing groups which could facilitate various aromatic functionaliza-

Table 3. Reaction of aryl 2-pyridyl ethers with $Ph_2MeSiZnCl$ and $Ph_3SiZnCl$[a,b]



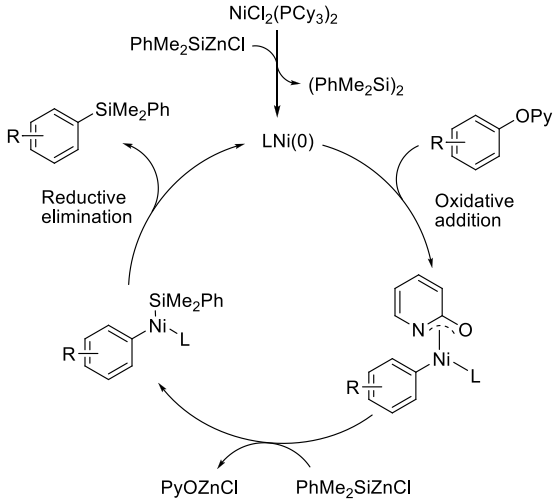
[a] Unless otherwise stated, the reactions were carried out according to the conditions indicated by the above equation; 0.2 mmol 2-([1,1'-biphenyl]-4-yloxy)pyridine and 1.1 equiv of **2a** were employed. $Ph_2MeSiZnCl$ and $Ph_3SiZnCl$ were prepared by reaction of the corresponding silyllithium with an equimolar amount of $ZnCl_2$. [b] Unless otherwise stated, yield reported was isolated yield. [c] The yield was calculated based on the weight of the mixture of [1,1'-biphenyl]-4-yl(methyl)diphenylsilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane and the integral ratio of ^1H NMR spectrum of the mixture. [d] 4,4'-Dimethoxy-1,1'-biphenyl was formed in 32% yield. [e] Diisopropyl [1,1'-biphenyl]-4,4'-dicarboxylate was formed in 30% yield.

tion reactions. In this study we performed the sequential OPy-directed *ortho* C-H functionalization and removal of the directing group to demonstrate the practicability of the methodology developed in this work. Both 2-(2-methoxyphenoxy)pyridine and 2-(biphenyl-2-yloxy)pyridine prepared according to literature procedures[1b,h] can be successfully silylated via nickel-catalyzed reaction of $PhMe_2SiZnCl$ with the corresponding aryl 2-pyridyl ethers (Scheme 1).



Scheme 1. The sequential reaction.

Preliminary study on the plausible reaction pathway was carried out. Under the standard conditions, 1 equiv of 1,1-diphenylethylene additive had no influence on the reaction results of 2-(biphenyl-4-yloxy)pyridine with **2a**; 80% yield of the coupling product was isolated. This ruled out the possibility of a free radical process. A combination of $Ni(COD)_2$ (10 mol%) and PCy_3 (20 mol%) was demonstrated to be as effective as $Ni(PCy_3)_2Cl_2$ (10 mol%) to catalyze the reaction of 2-(biphenyl-4-yloxy)pyridine with **2a**. Hence we surmised that the catalytic reaction proceeded through a Ni(0)/Ni(II) cycle. We also studied the reaction process by ^{31}P NMR spectroscopy. Reaction of $Ni(COD)_2$ with 2 equiv of PCy_3 formed a nickel complex which displayed a ^{31}P NMR signal at δ 45.3 ppm, along with a signal of PCy_3 at δ 9.77 ppm.[15] After reaction of above solution with an equiv of 2-(biphenyl-4-yloxy) pyridine a new ^{31}P NMR spectral signal at δ 30.3 ppm appeared. This new signal might be that of the oxidative addition intermediate of the Ni-PCy_3 complex with 2-(biphenyl-4-yloxy)pyridine.[16] The results further supported a Ni(0)/Ni(II) process. In addition, reaction of 3-([1,1'-biphenyl]-4-yloxy) pyridine with **2a** cannot occur under the standard conditions. This experimental fact implies that the chelation assistance of pyridine might help the catalyst to exclusively break the C–OPy bond. Based on the above experimental facts, a possible catalytic cycle is proposed in Scheme 2.

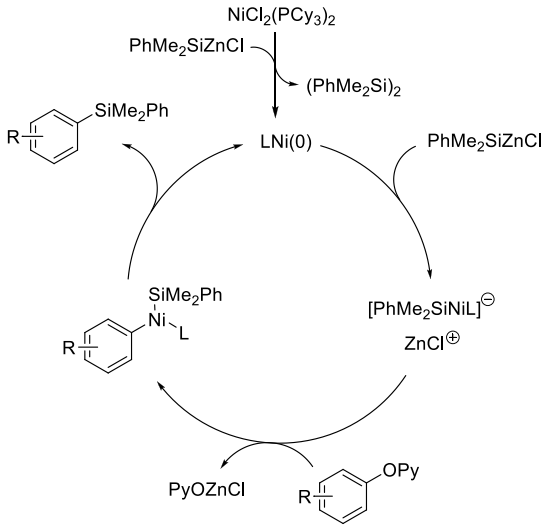


Scheme 2. Proposed catalytic cycle.

On the other hand, the solution formed from the reaction of $Ni(COD)_2$ with 2 equiv of PCy_3 was treated with an equiv of $PhMe_2SiZnCl$ to lead to disappearance of the signal of $Ni(COD)_2$-PCy_3 complex and appearance of two new ^{31}P NMR signals at δ 52.6 and 0.75 ppm, respectively. The emerging signals might result from nickel(0) ate complexes such as $[PhMe_2SiNi(PCy_3)_2]^-ZnCl^+$ and $[PhMe_2SiNi(PCy_3)(COD)]^-ZnCl^+$.[17,18] Hence it is possible that another catalytic cycle operates concurrently (Scheme 3).[19]

Conclusion

In summary, we carried out the reaction of aryl 2-pyridyl ethers with silylzinc reagents via Ni-catalyzed C-O(Py) bond cleavage under mild conditions, providing the corresponding silylated arenes in moderate to good yields. The method suits for a wide scope of aryl 2-pyridyl ethers including those with electron-poor and electron-rich aryl groups and nitrogen-containing heteroaryl groups. A range of functional groups on the aromatic rings including alkoxy, alkenyl, Me_2N, F, C(O)R, COOR, $C(O)NEt_2$ and MeC(O)NH groups can be tolerated. Both $PhMe_2SiZnCl$ and $Ph_2MeSiZnCl$ were suitable silylation reagents. Reaction of $Ph_3SiZnCl$ resulted in low yields due to homocoupling of aryl 2-pyridyl ethers and $Me_3SiZnCl$ cannot be used in this transformation.



Scheme 3. Another possible reaction pathway.

Experimental Section

General

All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Toluene, THF and Et_2O were purified by JC Meyer Phoenix Solvent Systems. 1,4-Dioxane was distilled under nitrogen over sodium and degassed prior to use. DMSO, DMAc and NMP were dried over 4 Å molecular sieves, fractionally distilled under reduced pressure, and stored under nitrogen atmosphere. $PhMe_2SiCl$, $Ph_2MeSiCl$, Ph_3SiCl, $NiCl_2(PPh_3)_2$, and $NiCl_2(PCy_3)_2$ were purchased from Energy Chemical. $Ni(COD)_2$ was purchased from Alfa Aesar. PCy_3 was purchased from J&K Scientific Ltd. Aryl 2-pyridyl ethers,[2a,20] $NiCl_2(PMe_3)_2$,[21] $NiCl_2$(dppp),[21] $NiCl_2$(dppf),[21] and silylzinc reagents[14b] were prepared according to the literature procedures. The concentration of the silylzinc solution was titrated using Knochel's method.[22] Other chemicals were obtained from commercial vendors. NMR spectra were recorded on a Bruker av400 spectrometer at 25 °C. The chemical shifts of the ^1H NMR spectra were referenced to TMS or internal solvent resonances and the chemical shifts of the ^{13}C NMR spectra were referenced to internal solvent resonances. High-resolution mass spectra (HRMS) were acquired on a Thermo Fisher LTQ Orbitrap XL mass spectrometer.

General procedure for the catalytic coupling of aryl 2-pyridyl ethers with silylzinc reagents

A Schlenk tube was charged with $NiCl_2(PCy_3)_2$ (13.8 mg, 0.020 mmol), aryl 2-pyridyl ethers (0.20 mmol) and THF (1.4 mL). To the stirred mixture was added $PhMe_2SiZnCl$ solution (0.6 mL, 0.37 M solution in THF, 0.22 mmol). The resultant mixture was stirred at 60 °C for 1 h and then cooled to room temperature. A 20% aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

[1,1'-Biphenyl]-4-yldimethyl(phenyl)silane (3aa):[23] Yield: 47.5 mg (82%); white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.73-7.60 (m, 8H), 7.54-7.48 (m, 2H), 7.47-7.37 (m, 4H), 0.67 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.0, 141.2, 138.3, 137.1, 134.8, 134.3, 129.3, 128.9, 128.0, 127.5, 127.3, 126.3, –2.2.

[1,1'-Biphenyl]-3-yldimethyl(phenyl)silane (3ab):[10b] Yield: 39.1 mg (68%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.63-7.54 (m, 5H), 7.53 (d, J = 7.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 3H), 7.40-7.32 (m, 4H), 0.60 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.6, 140.7, 138.9, 138.3, 134.3, 133.3, 133.1, 129.3, 128.9, 128.3, 128.2, 128.0, 127.4, 127.3, –2.2. HR-MS (ESI): m/z = 288.1330, calcd. for $C_{20}H_{20}Si$ ($[M]^+$): 288.1329.

[1,1'-Biphenyl]-2-yldimethyl(phenyl)silane (3ac):[24] Yield: 28.6 mg (50%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.4 Hz, 1H), 7.44-7.17 (m, 11H) 7.11-7.05 (m, 2H), 0.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.7, 144.2, 140.2, 136.6, 135.9, 134.1, 130.0, 129.8, 129.6, 129.1, 128.8, 128.0, 127.8, 127.7, 127.1, 126.4, –1.1.

(4-Benzylphenyl)dimethyl(phenyl)silane (3c): Yield: 41.1 mg (68%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57-7.51 (m, 2H), 7.46 (d, J = 7.9 Hz, 2H), 7.39-7.33 (m, 3H), 7.31-7.27 (m, 2H), 7.25-7.17 (m, 5H), 3.99 (s, 2H), 0.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.2, 141.0, 138.5, 135.6, 134.5, 134.3, 129.2, 129.1, 128.6, 128.5, 127.9, 126.2, 42.1, –2.2. HR-MS (ESI): m/z = 302.1486, calcd. for $C_{21}H_{22}Si$ ($[M]^+$): 302.1485.

(*E*)-Dimethyl(phenyl)(4-styrylphenyl)silane (3e): Yield: 54.1 mg (86%); white solid. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63-7.52 (m, 8H), 7.45-7.37 (m, 5H), 7.34-7.27 (m, 1H), 7.20 (d, J = 16.4 Hz, 1H), 7.15 (d, J = 16.4 Hz, 1H), 0.62 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.3, 138.1, 137.8, 137.4, 134.7, 134.3, 129.3, 129.2, 128.8, 128.7, 128.0, 127.8, 126.7, 126.0, –2.2. HR-MS (ESI): m/z = 314.1484, calcd. for $C_{22}H_{22}Si$ ($[M]^+$): 314.1485 .

(4-Methoxyphenyl)dimethyl(phenyl)silane (3fa):[12b] Yield: 34.9 mg (71%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.39-7.32 (m, 3H), 6.92 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H), 0.53 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.6, 138.8, 135.8, 134.3, 129.1, 127.9, 113.7, 55.2, –2.1.

(2-Methoxyphenyl)dimethyl(phenyl)silane (3fb): Yield: 31.3 mg (64%); colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.61-7.53 (m, 2H), 7.40-7.32 (m, 4H), 7.28 (dd, J = 7.2, 1.6 Hz, 1H), 6.93 (t, J = 7.3 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 3.75 (s, 3H), 0.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.6, 139.1, 136.1, 134.3, 131.2, 128.8, 127.7, 126.2, 120.6, 109.9, 55.2, -2.1. HR-MS (ESI): m/z = 243.1196, calcd. for $C_{15}H_{19}OSi$ ($[M+H]^+$): 243.1200.

(3-Methoxyphenyl)dimethyl(phenyl)silane (3fc):[11a,25] Yield: 34.8 mg (70%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.50 (m, 2H), 7.39-7.27 (m, 4H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 2.6 Hz, 1H), 6.91 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.80 (s, 3H), 0.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 140.0, 138.2, 134.3, 129.3, 129.2, 127.9, 126.6, 120.0, 114.3, 55.2, –2.3.

(4-(Benzyloxy)phenyl)dimethyl(phenyl)silane (3g): Yield: 40.6 mg (64%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.51 (m, 2H), 7.49-7.30 (m, 10H), 7.00 (d, *J* = 8.6 Hz, 2H), 5.09 (s, 2H), 0.55 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9, 138.8, 137.1, 135.8, 134.3, 129.5, 129.2, 128.7, 128.1, 127.9, 127.6, 114.6, 69.9, –2.1. HR-MS (ESI): *m/z* = 319.1513, calcd. for $C_{21}H_{23}OSi$ ($[M+H]^+$): 319.1513.

Dimethyl(4-phenoxyphenyl)(phenyl)silane (3h):[10b] Yield: 40.5 mg (67%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.53 (m, 2H), 7.49 (d, *J* = 8.5 Hz), 7.42-7.32 (m, 5H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.09-7.03 (m, 2H), 7.00 (d, *J* = 8.5 Hz), 0.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 156.8, 138.4, 135.9, 134.3, 132.2, 129.9, 129.2, 128.0, 123.6, 119.5, 118.1, –2.1. HR-MS (ESI): *m/z* = 305.1351, calcd. for $C_{20}H_{21}OSi$ ($[M+H]^+$): 319.1513.

Benzo[*d*][1,3]dioxol-5-yldimethyl(phenyl)silane (3i): Yield: 31.7 mg (62%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.49 (m, 2H), 7.42-7.32 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 1H) , 6.98 (s, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 5.94 (s, 2H), 0.54 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.6, 147.5, 138.4, 134.2, 131.3, 129.2, 128.4, 128.0, 113.6, 108.7, 100.7, –2.0. HR-MS (ESI): *m/z* = 257.0989, calcd for $C_{15}H_{17}O_2Si$ ($[M+H]^+$): 257.0992.

4-(Dimethyl(phenyl)silyl)-*N*,*N*-dimethylaniline (3j):[26] Yield: 22.3 mg (44%); pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.52 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.38-7.32 (m, 3H), 6.75 (d, *J* = 8.5 Hz, 2H), 2.97 (s, 6H), 0.53 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.2, 139.5, 135.4, 134.3, 128.9, 127.8, 123.1, 112.0, 40.3, –2.0.

***N*-(4-(Dimethyl(phenyl)silyl)phenyl)acetamide (3k):**[12g] Yield: 31.8 mg (60%); white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.43 (m, 6H), 7.40-7.30 (m, 3H), 7.21 (b, 1H), 2.17 (s, 3H), 0.53 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4, 138.8, 138.4, 135.2, 134.3, 133.9, 129.2, 127.9, 119.2, 24.8, –2.2.

***N*-(4-(Dimethyl(phenyl)silyl)phenyl)-*N*-methylacetamide (3l):** Yield: 33.8 mg (60%); white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.50 (m, 4H), 7.42-7.33 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 3.26 (s, 3H), 1.89 (s, 3H), 0.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 145.3, 138.3, 137.6, 135.6, 134.2, 129.5, 128.0, 126.4, 37.2, 22.6, –2.3. HR-MS (ESI): *m/z* = 284.1464, calcd for $C_{17}H_{22}ONSi$ ($[M+H]^+$): 284.1465.

Dimethyl(naphthalen-2-yl)(phenyl)silane (3m):[27] Yield: 39.3 mg (75%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.88-7.81 (m, 3H), 7.64-7.56 (m, 3H), 7.53-7.47 (m, 2H), 7.42-7.35 (m, 3H), 0.66 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.3, 135.8, 135.0, 134.4, 133.9, 133.0, 130.5, 129.3, 128.2, 128.0, 127.8, 127.2, 126.5, 126.0, –2.2.

Dimethyl(naphthalen-1-yl)(phenyl)silane (3n): Yield: 29.9 mg (57%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.85 (m, 3H), 7.76 dd, *J* = 6.8, 1.0 Hz, 1H), 7.60-7.55 (m, 2H), 7.53-7.43 (m, 2H), 7.42-7.33 (m, 4H), 0.74 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.0, 137.1, 135.9, 134.8, 134.3, 133.6, 130.4, 129.2, 129.1, 128.7, 128.0, 125.8, 125.5, 125.2, –0.8. HR-MS (ESI): *m/z* = 262.1172, calcd. for $C_{18}H_{18}Si$ ($[M]^+$): 262.1172.

6-(Dimethyl(phenyl)silyl)quinolone (3o): Yield: 19.7 mg (37%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (d, *J* = 3.0 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 7.98 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.59-7.52 (m, 2H), 7.44-7.34 (m, 4H), 0.65 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.0, 148.8, 137.8, 137.3, 136.3, 134.9, 134.4, 134.3, 129.5, 128.6, 128.1, 127.9, 121.3, –2.2. HR-MS (ESI): *m/z* = 264.1195, calcd. for $C_{17}H_{18}NSi$ ($[M+H]^+$): 264.1203.

2-(Dimethyl(phenyl)silyl)pyridine (3p):[28] Yield: 31.6 mg (74%); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (dt, *J* = 4.8, 1.2 Hz, 1H), 7.63-7.58 (m, 2H), 7.55 (dt, *J* = 7.6, 1.7 Hz, 1H), 7.44 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.40-7.35 (m, 3H), 7.22-7.17 (m, 1H), 0.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 150.4, 137.4, 134.4, 134.1, 129.9, 129.4, 128.0, 123.0, –3.0.

(4'-Fluoro-[1,1'-biphenyl]-4-yl)dimethyl(phenyl)silane (3q): Yield: 43.3 mg (71%); white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.51 (m, 8H), 7.41-7.36 (m, 3H), 7.13 (t, *J* = 8.7 Hz, 2H), 0.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.7 (d, *J* = 245.0 Hz), 141.0, 138.2, 137.3 (d, *J* = 3.1 Hz), 137.2, 134.9, 134.3, 129.3, 128.8 (d, *J* = 8.1 Hz), 128.0, 126.5, 115.8 (d, *J* = 21.5 Hz), –2.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ –115.54. HR-MS (ESI): *m/z* = 306.1235, calcd. for $C_{20}H_{19}FSi$ ($[M]^+$): 306.1235.

(4-(Dimethyl(phenyl)silyl)phenyl)(phenyl)methanone (3s): Yield: 52.4 mg (84%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.80 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.62-7.53 (m, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.44-7.35 (m, 3H), 0.62 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.0, 144.2, 138.1, 137.6, 137.4, 134.3, 134.2, 132.6, 130.2, 129.5, 129.2, 128.4, 128.1, –2.4. HR-MS (ESI): *m/z* = 317.1352, calcd. for $C_{21}H_{21}OSi$ ($[M+H]^+$): 317.1356.

1-(4-(Dimethyl(phenyl)silyl)phenyl)ethan-1-one (3t):[29] Yield: 33.6 mg (67%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz 2H), 7.54-7.49 (m, 2H), 7.42-7.34 (m, 3H), 2.60 (s, 3H), 0.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 145.2, 137.5, 137.3, 134.5, 134.3, 129.5, 128.1, 127.4, 26.8, –2.5.

Isopropyl 4-(dimethyl(phenyl)silyl)benzoate (3u): Yield: 50.5 mg (85%); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.55-7.49 (m, 2H), 7.41-7.34 (m, 3H), 5.32-5.23 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 6H), 0.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 144.4, 137.5, 134.3, 134.2, 131.5, 129.5, 128.6, 128.0, 68.4, 22.1, –2.4. HR-MS (ESI): *m/z* = 299.1453, calcd. for $C_{18}H_{23}O_2Si$ ($[M+H]^+$): 299.1462.

***tert*-Butyl 4-(dimethyl(phenyl)silyl)benzoate (3v):** Yield: 52.3 mg (84%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.53-7.47 (m, 2H), 7.40-7.32 (m, 3H), 1.59 (s, 9H), 0.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.0, 144.1, 137.6, 134.3, 134.2, 132.6, 129.4, 128.5, 128.0, 81.1, 28.3, –2.4. HR-MS (ESI): *m/z* = 313.1609, calcd. for $C_{19}H_{25}O_2Si$ ($[M+H]^+$): 313.1618.

Methyl 4-(dimethyl(phenyl)silyl)benzoate (3w):[11a] Yield: 43.4 mg (81%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.54-7.48 (m, 2H), 7.41-7.33 (m, 3H), 3.92 (s, 3H), 0.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.4, 144.8, 137.5, 134.29, 134.27, 130.7, 129.5, 128.7, 128.1, 52.3, –2.4.

4-(Dimethyl(phenyl)silyl)-N,N-diethylbenzamide (3x): Yield: 33.6 mg (54%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.49 (m, 4H), 7.40-7.31 (m, 5H), 3.62-3.49 (m, 2H), 3.32-3.19 (m, 2H), 1.32-1.19 (m, 3H), 1.17-1.05 (m, 3H), 0.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4, 139.7, 137.9, 137.8, 134.32, 134.29, 129.4, 128.0, 125.6, 43.3, 39.3, 14.4, 13.0, –2.4. HR-MS (ESI): *m/z* = 312.1768, calcd for $C_{19}H_{25}NOSi$ ($[M+H]^+$): 312.1778.

1-(2-(Dimethyl(phenyl)silyl)phenyl)ethanone (3y): Yield: 35.6 mg (70%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.84 (m, 1H), 7.65-7.60 (m, 1H), 7.54-7.45 (m, 4H), 7.34-7.28 (m, 3H), 2.49 (s, 3H), 0.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 200.0, 142.9, 140.6, 140.1, 137.5, 134.0, 131.7, 129.8, 129.3, 128.4, 127.6, 27.1, –0.9. HR-MS (EI): *m/z* = 239.0887, calcd for $C_{15}H_{15}OSi$ ([M-Me]$^+$): 239.0887.

Ethyl 2-(dimethyl(phenyl)silyl)benzoate (3z): Yield: 48.7 mg (86%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.96 (m, 1H), 7.60-7.55 (m, 1H), 7.52-7.41 (m, 4H), 7.36-7.28 (m, 3H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.60 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 140.1, 136.8, 134.0, 131.3, 130.0, 129.3, 128.6, 127.7, 61.1, 14.2, –0.7. HR-MS (EI): *m/z* = 241.0679, calcd for $C_{14}H_{13}O_2Si$ ([M-Me]$^+$): 241.0679.

Isopropyl 4-(methyldiphenylsilyl)benzoate (4b): Yield: 57.5 mg (80%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.54-7.48 (m, 4H), 7.46-7.34 (m, 6H), 5.32-5.23 (m, 1H), 1.38 (d, *J* = 6.2 Hz, 6H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 142.4, 135.5, 135.4, 135.3, 131.8, 129.8, 128.7, 128.1, 68.5, 22.1, –3.4. HR-MS (ESI): *m/z* = 361.1625, calcd for $C_{23}H_{25}O_2Si$ ([M+H]$^+$): 361.1618.

(4-Methoxyphenyl)(methyl)diphenylsilane (4c):[12c] Yield: 38.2 mg (63%); white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.53 (m, 4H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.45-7.35 (m, 6H), 6.96 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.8, 136.9, 136.7, 135.4, 129.4, 128.0, 126.9, 113.8, 55.1, –3.0.

[1,1'-Biphenyl]-4-yltriphenylsilane (5a):[10b] Yield: 47.8 mg (58%); white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72-7.58 (m, 12H), 7.51-7.32 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.4, 141.0, 137.0, 136.6, 134.3, 133.1, 129.8, 128.9, 128.1, 127.6, 127.3, 126.7. HR-MS (ESI): *m/z* = 412.1646, calcd for $C_{30}H_{24}Si$ ([M]$^+$): 412.1642.

(4-Methoxyphenyl)triphenylsilane (5b):[12b] Yield: 24.0 mg (33%); white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.54 (m, 6H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.46-7.34 (m, 9H), 6.94 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.0, 138.1, 136.5, 134.7, 129.6, 128.0, 125.0, 113.8, 55.2.

Isopropyl 4-(triphenylsilyl)benzoate (5c): Yield: 21.0 mg (25%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.61-7.52 (m, 6H), 7.50-7.34 (m, 9H), 5.31-5.22 (m, 1H), 1.37 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.3, 140.5, 136.48, 136.45, 133.6, 131.9, 130.0, 128.6, 128.1, 68.6, 22.1. HR-MS (ESI): *m/z* = 423.1783, calcd for $C_{28}H_{27}O_2Si$ ([M+H]$^+$): 423.1775.

The sequential reaction

Synthesis of [1,1'-biphenyl]-2-yldimethyl(phenyl)silane from 2-phenoxypyridine.

Synthesis of 2-([1,1'-biphenyl]-2-yloxy)pyridine follows a literature procedure.[1b] 2-Phenoxypyridine (85.5 mg, 0.5 mmol), potassium phenyltrifluoroborates (230 mg, 1.25 mmol), Ag_2CO_3 (276 mg, 1.0 mmol), *p*-benzoquinone (54.1 mg, 0.5 mmol), $Pd(OAc)_2$ (11.3 mg, 0.05 mmol), DMSO (142 μL, 2.0 mmol) H_2O (72 μL, 4.0 mmol) and CH_2Cl_2 (15 mL) was added to a Schlenk tube. The mixture was stirred at 130 °C for 48 h and then cooled to room temperature. The solution was filtered through a plug of silica gel which was rinsed with EtOAc (20 mL). The filtrate was concentrated and purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 100:1 to 60:1) to give 2-([1,1'-biphenyl]-2-yloxy)pyridine, yield: 64.3 mg (52%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (dd, *J* = 1.4, 4.9 Hz, 1H), 7.56-7.49 (m, 1H), 7.49-7.42 (m, 3H), 7.37 (dt, *J* = 1.7, 7.6 Hz, 1H), 7.32-7.25 (m, 3H), 7.25-7.19 (m, 1H), 7.17 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.88-6.81 (m, 1H), 6.73 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.9, 151.0, 147.7, 139.2, 137.9, 134.8, 131.3, 129.2, 128.7, 128.1, 127.2, 125.4, 122.8, 118.1, 111.4.

A Schlenk tube was charged with $NiCl_2(PCy_3)_2$ (13.8 mg, 0.020 mmol), 2-([1,1'-biphenyl]-2-yloxy)pyridine (49.4 mg, 0.20 mmol) and THF (1.52 mL). To the stirred mixture was added $PhMe_2SiZnCl$ solution (0.48 mL, 0.46 M solution in THF, 0.22 mmol). The resultant mixture was stirred at 60 °C for 2 h and then cooled to room temperature. A 20% aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by silica gel column chromatography (eluent: petroleum ether) to give [1,1'-biphenyl]-2-yldimethyl (phenyl)silane, yield: 29.1 mg (51%), colorless oil.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.2 Hz, 1H), 7.45-7.17 (m, 11H), 7.09 (d, *J* = 7.2 Hz, 2H), 0.17 (s, 6H).

Synthesis of (2-methoxyphenyl)dimethyl(phenyl)silane from 2-phenoxypyridine.

Synthesis of 2-(2-methoxyphenoxy)pyridine follows a literature procedure.[1h] 2-Phenoxypyridine (85.5 mg, 0.5 mmol), $PhI(OAc)_2$ (322.1 mg, 1.0 mmol), Pd(OAc)2 (11.3 mg, 0.05 mmol) and methanol (4 mL) was added to a Schlenk tube. The mixture was stirred at 90 °C for 24 h and then cooled to room temperature. Solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 60:1 to 15:1) to give 2-(2-methoxyphenoxy) pyridine, yield: 37.2 mg (37%), white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, *J* = 1.3, 4.9 Hz, 1H), 7.68-7.61 (m, 1H), 7.23-7.17 (m, 1H), 7.14 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.04-6.96 (m, 2H), 6.96-6.89 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 163.83, 151.90, 147.65, 142.64, 139.26, 126.10, 123.21, 121.19, 118.10, 112.97, 110.76, 55.99.

A Schlenk tube was charged with $NiCl_2(PCy_3)_2$ (13.8 mg, 0.020 mmol), 2-(2-methoxyphenoxy)pyridine (40.2 mg, 0.20 mmol) and THF (1.52 mL). To the stirred mixture was added $PhMe_2SiZnCl$ solution (0.48 mL, 0.46 M solution in THF, 0.22 mmol). The resultant mixture was stirred at 60 °C for 2 h and then cooled to room temperature. A 20% aqueous solution of NH_4Cl (10 mL) was added. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, concentrated by rotary evaporation, and purified by silica gel column chromatography (eluent: petroleum ether) to afford (2-methoxyphenyl)dimethyl (phenyl)silane, yield: 28.1 mg (58%), colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.51 (m, 2H), 7.39-7.30 (m, 4H), 7.29-7.22 (m, 1H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 3.73 (s, 3H), 0.55 (s, 6H).

Acknowledgements

This work was supported by the National Basic Research Program of China (Grant No. 2015CB856600).

References

[1] a) F. Kakiuchi, K. Igi, M. Matsumoto, T. Hayamizu, N. Chatani, S. Murai, *Chem. Lett.* **2002**, 396; b) J.-H. Chu, P.-S. Lin, M.-J. Wu, *Organometallics* **2010**, *29*, 4058; c) L. Ackermann, E. Diers, A. Manvar, *Org. Lett.* **2012**,

14, 1154; d) L. Niu, H. Yang, R. Wang, H. Fu, *Org. Lett.* **2012**, *14*, 2618; e) J. Yao, R. Feng, Z. Wu, Z. Liu, Y. Zhang, *Adv. Synth. Catal.* **2013**, *355*, 1517; f) Y.-F. Liang, X. Li, X. Wang, Y. Yan, P. Feng, N. Jiao, *ACS Catal.* **2015**, *5*, 1956; g) S.-J. Lou, Q. Chen, Y.-F. Wang, D.-Q. Xu, X.-H. Du, J.-Q. He, Y.-J. Mao, Z.-Y. Xu, *ACS Catal.* **2015**, *5*, 2846; h) C. Zhang, P. Sun, *J. Org. Chem.* **2014**, *79*, 8457.

[2] a) H. Kinuta, M. Tobisu, N. Chatani, *J. Am. Chem. Soc.* **2015**, *137*, 1593; b) M. Tobisu, J. Zhao, H. Kinuta, T. Furukawa, T. Igarashi, N. Chatani, *Adv. Synth. Catal.* **2016**, *358*, 2417.

[3] J. Li, Z.-X. Wang, *Org. Lett.* **2017**, *19*, 3723.

[4] J. Li, Z.-X. Wang, *Synthesis* **2018**, *50*, 3217.

[5] J. Li, Z.-X. Wang, *Chem. Commun.* **2018**, *54*, 2138.

[6] F. Fan, J. Tang, M. Luo, X. Zeng, *J. Org. Chem.* **2018**, *83*, 13549.

[7] X. Yan, F. Yang, G. Cai, Q. Meng. X. Li, *Org. Lett.* **2018**, *20*, 624.

[8] a) G. K. Min, D. Hernández, T. Skrydstrup, *Acc. Chem. Res.* **2013**, *46*, 457; b) D. Sun, Z. Ren, M. R. Bryce, S. Yan, *J. Mater. Chem. C*, **2015**, *3*, 9496; c) M. J. Barnes, R. Conroy, D. J. Miller, J. S. Mills, J. G. Montana, P. K. Pooni, G. A. Showell, L. M. Walsh, J. B. H. Warneck, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 354; d) J. Wang, C. L. Ma, Y. B. Wu, R. A. Lamb, L. H. Pinto, W. F. DeGrado, *J. Am. Chem. Soc.* **2011**, *133*, 13844; e) A. K. Franz, S. O. Wilson, *J. Med. Chem.* **2013**, *56*, 388; f) N. Fukaya, H. Haga, T. Tsuchimoto, S. Onozawa, T. Sakakura, H. Yasuda, *J. Organomet. Chem.* **2010**, *695*, 2540.

[9] a) *The Chemistry of Organic Silicon Compounds*, (Eds. S. Patai, Z. Rappoport), Wiley & Sons, New York, **2000**; b) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley-Interscience, New York, 1st ed. **2000**; c) T. Hiyama, in *Organometallics in Synthesis Third Manual*, (Ed. M. Schlosser), Wiley, Hoboken, **2013**, pp373.

[10] a) E. Yamamoto, S. Ukigai, H. Ito, *Synlett* **2017**, *28*, 2460; b) S. Mallick, P. Xu, E.-U. Würthwein, A. Studer, *Angew. Chem. Int. Ed.* **2019**, *58*, 283.

[11] a) H. Guo, X. Chen, C. Zhao, W. He, *Chem. Commun.* **2015**, *51*, 17410; b) C. Zarate, R. Martin, *J. Am. Chem. Soc.* **2014**, *136*, 2236.

[12] a) A. Hamze, O. Provot, M. Alami, J.−D. Brion, *Org. Lett.* **2006**, *8*, 931; b) Y. Yamanoi, *J. Org. Chem.* **2005**, *70*, 9607; c) Y. Yamanoi, H. Nishihara, *J. Org. Chem.* **2008**, *73*, 6671; d) E. McNeill, T. E. Barder, S. L. Buchwald, *Org. Lett.* **2007**, *9*, 3785; e) S. E. Denmark, J. M. Kallemeyn, *Org. Lett.* **2003**, *5*, 3483; f) Y. Minami, K. Shimizu, C. Tsuruoka, T. Komiyama, T. Hiyama, *Chem. Lett.* **2014**, *43*, 201; g) Y. Yamamoto, H. Matsubara, K. Murakami, H. Yorimitsu, A. Osuka, *Chem. Asian J.* **2015**, *10*, 219.

[13] a) C. Cheng, J. F. Hartwig, *Chem. Rev.* **2015**, *115*, 8946; b) S. C. Richter, M. Oestreich, *Trends Chem.* DOI:10.1016/j.trechm.2019.07.003; c) J. F. Hartwig, *Acc. Chem. Res.* **2012**, *45*, 864; d) L. Omann, C. D. F. Kçnigs, H. F. T. Klare, M. Oestreich, *Acc. Chem. Res.* **2017**, *50*, 1258.

[14] a) L. Zhang, M. Oestreich, *Org. Lett.* **2018**, *20*, 8061; b) C. K. Chu, Y. Liang, G. C. Fu, *J. Am. Chem. Soc.* **2016**, *138*, 6404; c) H. Azuma, K. Okano, H. Tokuyama, *Chem. Lett.* **2011**, *40*, 959; d) A. Hensel, M. Oestreich, *Chem. Eur. J.* **2015**, *21*, 9062; e) M. Yonehara, S. Nakamura, A. Muranaka, M. Uchiyama, *Chem. Asian J.* **2010**, *5*, 452; f) S. Hayashi, T. Endo, T. Takanami, *Heterocycles* **2018**, *97*, 1082; g) Y. Nagashima, D. Yukimori, C. Wang, M. Uchiyama, *Angew. Chem. Int. Ed.* **2018**, *57*, 8053; h) M. Oestreich, B. Weiner, *Synlett* **2004**, 2139; i) W. Xue, R. Shishido, M. Oestreich, *Angew. Chem. Int. Ed.* **2018**, *57*, 12141.

[15] a) A. Chardon, O. Maubert, J. Rouden, J. Blanchet, *ChemCatChem* **2017**, *9*, 4460; b) E. Moser, E. Jeanneau, N. Mézailles, H. Olivier-Bourbigou, P.-A. R. Breuil, *Dalton Trans.* **2019**, *48*, 4101; c) G. D. Jones, D. A. Vicic, *Organometallics* **2005**, *24*, 3821.

[16] S. Y. Desjardins, K. J. Cavell, H. Jin, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **1996**, *515*, 233.

[17] O. Kühl, *Phosphorus-31 NMR Spectroscopy: A Concise Introduction for the Synthetic Organic and Organometallic Chemist*, Springer-Verlag, Heidelberg, **2008**, pp 99-101.

[18] Th. Kruck, E. Job, U. Klose, *Angew. Chem. Int. Ed.* **1968**, *7*, 374.

[19] a) M. Tobisu, N. Chatani, *Acc. Chem. Res.* **2015**, *48*, 1717; b) J. Terao, N. Kambe, *Acc. Chem. Res.* **2008**, *41*, 1545.

[20] D. Maiti, S. L. Buchwald, *J. Org. Chem.* **2010**, *75*, 1791.

[21] E. A. Standley, S. J. Smith, P. Müller, T. F. Jamison, *Organometallics* **2014**, *33*, 2012.

[22] A. Krasovskiy, P. Knochel, *Synthesis* **2006**, 890.

[23] M. Yoshida, S. Tsuzuki, M. Goto, F. Nakanishi, *J. Chem. Soc., Dalton Trans.* **2001**, 1498.

[24] T. Matsuda, H. Kirikae, *Organometallics* **2011**, *30*, 3923.

[25] M. Uchiyama, Y. Kobayashi, T. Furuyama, S. Nakamura, Y. Kajihara, T. Miyoshi, T. Sakamoto, Y. Kondo, K. Morokuma, *J. Am. Chem. Soc.* **2008**, *130* 472.

[26] Q. Yin, H. F. T. Klare, M. Oestreich, *Angew. Chem. Int. Ed.* **2016**, *55*, 3204.

[27] M. Tobisu, Y. Kita, N. Chatani, *J. Am. Chem. Soc.* **2006**, *128*, 8152.

[28] K. Itami, T. Kamei, K. Mitsudo, T. Nokami, J.-i. Yoshida, *J. Org. Chem.* **2001**, *66*, 3970.

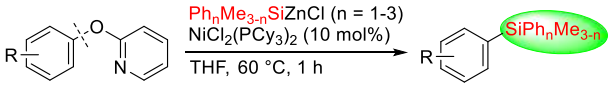
[29] M. Iizuka, Y. Kondo, *Eur. J. Org. Chem.* **2008**, 1161.

10.1002/adsc.201900949

FULL PAPER

Nickel-Catalyzed Reaction of Aryl 2-Pyridyl Ethers with Silylzinc Chlorides: Silylation of Aryl 2-Pyridyl Ethers via Cleavage of the Carbon–Oxygen Bond

Adv. Synth. Catal. **Year**, *Volume*, Page – Page



Ying-Ying Kong, Zhong-Xia Wang*