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DOI: 10.1039/C9OB00609E

ARTICLE

Ruthenium(II) / Acetate Catalyzed Intermolecular Dehydrogenative Ortho C-H Silylation of 2-Aryl N-Containing Heterocycles

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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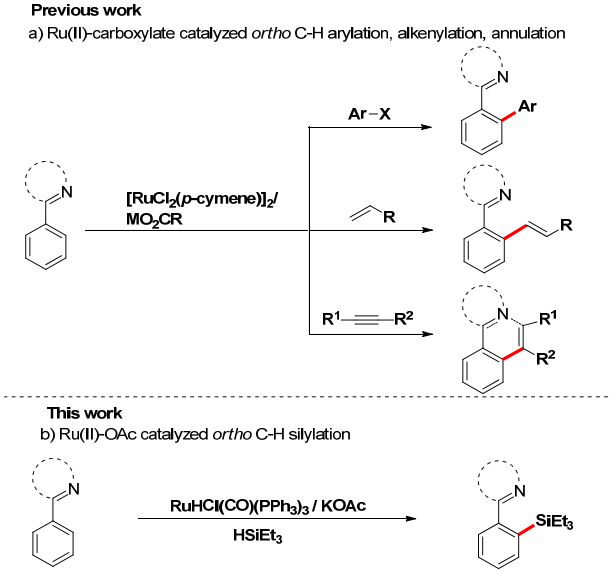
The first application of RuHCl(CO)(PPh$_3$)$_3$-OAc catalytic system on selective intermolecular mono C-H silylation of 2-aryl *N*-heterocycles using HSiEt$_3$ as the silylating reagent has been described. This protocol features good functional group tolerance, high regioselectivity, gram scale-up ability, which provides a convenient and practical pathway for the synthesis of versatile organosilane compounds. This catalytic system can be also applied to the silylation of challenging sp^3 C-H bonds.

Organosilane compounds are important molecules due to their unique properties of C-Si bonds,[1] and they are not only widely existing in advance materials and pharmaceuticals,[2] but also as valuable key synthetic intermediates for a variety of chemical transformations in modern organic synthesis.[3] Among the most useful methods for the synthesis of organosilanes, even classical electrophilic silylation by reagents such as TMSOTf or TMSCl is well established to be a simple way to prepare functional organosilane compounds, the limitations of this method still exist, such as the low functional group tolerance, waste inorganic salts production, and a multistep synthetic sequence.[4] Recently, the transition-metal catalyzed direct C-H bond silylation has attracted much attention as a straightforward method to synthesize functional organosilane compounds because of their atom- and step-economy.[5] Hartwig's group reported Rh and Ir systems which can efficiently catalyze the C-H silylation of C=O bond as directing group.[6] Choi,[7] Huang,[8] and Pilarski[9] developed the C-H silylation on heteroarenes using Rh or Ru precatalysts.

N-containing heterocycles are important structural motif as ligands in material science and drug discoveries,[10] Moreover, *N*-containing heterocycles including pyridine, oxazoline, quinoline, thiazole, pyrazole etc are efficient directing groups for *ortho* C-H bond functionalization.[11] However, only few reports deal with the synthesis of silyl-functionalized *N*-containing heterocycles *via* intermolecular C-H *ortho*-silylation with *N*-containing heterocycles as directing groups. Kakiuchi reported the first C-H *ortho*-silylation of pyridine derivatives by using Ru$_3$(CO)$_{12}$ catalyst, but affording mono silyl-pyridine and di silyl-pyridine products.[12] Murata reported the first [RuCl$_2$(*p*-cymene)]$_2$ catalyzed *ortho* C-H silylation but at 200 °C.[13] Recently, Mashima[14] and Oro[15] have succeeded to perform *ortho* C-H silylation of pyridine derivatives with good chemoselective by using (C^C)(C^N)Ir-OAc catalyst or NHC-Ir catalyst [Ir(H)$_2$(IPr)(py)$_3$][BF$_4$].

The commercial ruthenium(II) complex [RuCl$_2$(*p*-cymene)]$_2$ with carboxylate as co-catalyst has shown advantages in Ru(II) catalyzed C-H bond functionalizations, such as arylation,[16] alkenylation,[17] annulation[18] etc. However, RuHCl(CO)(PPh$_3$)$_3$-carboxylate catalytic system has never been reported for the direct C-H silylation reaction. Based on our previous contribution on Ru(II) catalyzed C-H silylation,[19] herein, we report an efficient selective mono C-H silylation of *N*-containing heterocycles by using commercially available RuHCl(CO)(PPh$_3$)$_3$/KOAc catalytic system. (Scheme 1)



Scheme 1. Ru(II)-OAc Catalyzed *Ortho* C-H Activation

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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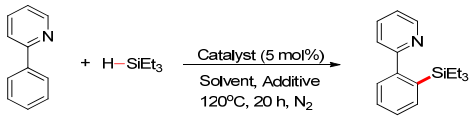
Optimization of reaction conditions was initiated by examining the coupling reaction of 2-phenylpyridine (**1a**) with triethylsilane (**2a**) using ruthenium catalysts (Table **1**). The product **3a** was obtained in 13% GC-yield, in the presence of 5 mol% of $[RuCl_2(p\text{-cymene})]_2$ as catalyst, 4 equiv. of cyclohexene as hydrogen acceptor in toluene at 120 °C under N_2 atmosphere (Table 1, entry 1). Upon addition of 20 mol% of KOAc as co-catalyst, the yield of product **3a** increased to 25% (Table 1, entry 2). When this reaction was performed in DMF or NMP, no conversion of product **3a** was detected (Table1, entries 3 and 4). The yield of product **3a** was slightly improved when using $RuCl_2(PPh_3)_3$ as catalyst instead of $[RuCl_2(p\text{-cymene})]_2$ (Table 1, entry 5). It is worthy to mention that the use of KPF_6, $AgSbF_6$, KO*t*Bu, or KBF_4, inhibits the formation of the C-H silylation product **3a** (Table 1, entries 6-9). When norbornylene (nbe) was chosen as hydrogen acceptor, the yield of C-H silylation product **3a** increased to 35% (Table 1, entry 10). Fortunately, among the tested ruthenium catalysts, such as $Ru_3(CO)_{12}$, $RuHCl(CO)(PPh_3)_3$, $RuH_2(CO)(PPh_3)_3$, $RuCl_2(2,2'\text{-bipyridyl})_3.6H_2O$ and $[RuCl_2(COD)]_n$, the best catalyst for this C-H silylation was found to be $RuHCl(CO)(PPh_3)_3$, and the yield of product **3a** reached 82% (Table 1, entries 12-16). Finally, when the amount of KOAc was increased to 30 mol%, up to 95% yield of silyl-functionalized pyridine product **3a** was obtained, while only 10% yield of product **3a** was observed with the absence of KOAc. (Table 1, entries 17 and 18) These results indicated that KOAc plays an important role as the co-catalyst for the selective C-H silylation.

Table 1. Optimization of Ru(II)-Catalyzed *ortho* C-H Silylation of 2-Phenylpyridine[a]



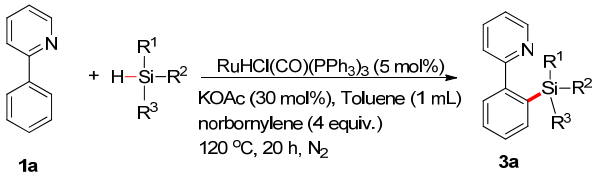
1a **3a**

entry	catalyst	additive	alkene	yield (%)
1	$[RuCl_2(p\text{-cymene})]_2$	----	cyclohexene	13
2	$[RuCl_2(p\text{-cymene})]_2$	KOAc	cyclohexene	25
3	$[RuCl_2(p\text{-cymene})]_2$	KOAc	cyclohexene	---[b]
4	$[RuCl_2(p\text{-cymene})]_2$	KOAc	cyclohexene	---[c]
5	$RuCl_2(PPh_3)_3$	KOAc	cyclohexene	29
6	$RuCl_2(PPh_3)_3$	KPF_6	cyclohexene	13
7	$RuCl_2(PPh_3)_3$	$AgSbF_6$	cyclohexene	---
8	$RuCl_2(PPh_3)_3$	KO^{t}Bu	cyclohexene	5
9	$RuCl_2(PPh_3)_3$	KBF_4	cyclohexene	3
10	$RuCl_2(PPh_3)_3$	KOAc	norbornylene	35
11	$RuCl_2(PPh_3)_3$	KOAc	methyl acrylate	7
12	$Ru_3(CO)_{12}$	KOAc	norbornylene	30
13	$RuHCl(CO)(PPh_3)_3$	KOAc	norbornylene	82
14	$RuH_2(CO)(PPh_3)_3$	KOAc	norbornylene	9
15	$RuCl_2(2,2'\text{-bipyridyl})_3.6H_2O$	KOAc	norbornylene	13
16	$[RuCl_2(COD)]_n$	KOAc	norbornylene	48
17	$RuHCl(CO)(PPh_3)_3$	KOAc	norbornylene	95[d] (85[e])
18	$RuHCl(CO)(PPh_3)_3$	----	norbornylene	10

[a] Reaction conditions: 2-phenylpyridine **1a** (0.5 mmol), triethylsilane (2.0 mmol), catalyst (5 mol%), additive (20 mol%), alkene (2.0 mmol), and toluene (1 mL) at 120 °C for 20 h under N_2. The product yield was determined by GC. [b]In DMF. [c]In NMP. [d]30 mol% of KOAc was used. [e]Isolated yield.

Furthermore, the variety of silanes, such as Et_3SiH, $Et(Me)_2SiH$, $(MeO)_3SiH$, Et_2SiH_2, $(EtO)_3SiH$, $(Me)_2PhSiH$, $(Me)_2EtOSiH$ and $Me(EtO)_2SiH$, were tested in toluene at 120 °C for 20 h in the presence of 5 mol% of $RuHCl(CO)(PPh_3)_3$, 30 mol% of KOAc, and 4 equiv. of nbe. However, only Et_3SiH as coupling reagent could lead to desired product in good yield, other silanes give the low yields and seem not favor this *ortho* C-H silylation. (Table 2)

Table 2. Ru(II)-Catalyzed *ortho* C-H Silylation of 2-Phenylpyridine with different silanes[a]



1a **3a**

Entry	Silane	Yield (%)
1	Et_3SiH	95
2	$Et(Me)_2SiH$	12
3	$(MeO)_3SiH$	30
4	Et_2SiH_2	15
5	$(EtO)_3SiH$	26
6	$(Me)_2PhSiH$	5
7	$(Me)_2EtOSiH$	20
8	$Me(EtO)_2SiH$	9

[a] Reaction conditions: 2-phenylpyridine **1a** (0.5 mmol), silane (2.0 mmol), $RuHCl(CO)(PPh_3)_3$ (5 mol%), KOAc (30 mol%), nbe (2.0 mmol), and toluene (1 mL) at 120 °C for 20 h under N_2. The product yield was determined by GC-MS.

To evaluate the scope of this catalytic reaction, the optimized reaction conditions were applied to a range of 2-aryl *N*-containing heterocycles **3a-m** (Scheme 2). The *ortho* C-H silylation of 2-aryl pyridine derivatives (**1b-d**) occurred on aryl ring bearing Me-, MeO- and CF_3- at the 4-position to afford **3b-d** in 84%, 73% and 52% yields, respectively. These results indicated that the electron-donating groups provided more reactive substrates for this C-H silylation than electron-deficient ones (**3b-d**). The pyridine ring bearing 3-methyl group or 5-phenyl group were compatible in this transformation as well (**3e-f**). Moreover, quinoline derivatives were also applicable to the catalytic system, and the silylated products **3g-i** were obtained in 75-81% yields. It is noteworthy that the silylation of 4-chloro-2-phenylquinoline **1h** was successfully silylated to afford the corresponding product **3h** without the dehalogenation of the chloro group. Interestingly, the C-H silylation was located on the thiophen ring with the reaction of 2-(thiophen-2-yl)pyridine **1j**. Other 2-phenyl *N*-containing heterocycles, such as thiazole, pyrazole and oxazoline derivatives, also proceeded smoothly in the C-H silylation catalytic system, giving the desired silylated products **3k-p** in moderate to good yields. Furthermore, this C-H silylation could tolerate ester group on the oxazoline aryl ring, and the corresponding silylated oxazoline product **3q** was directly obtained without the reduction of the carbonyl moiety.

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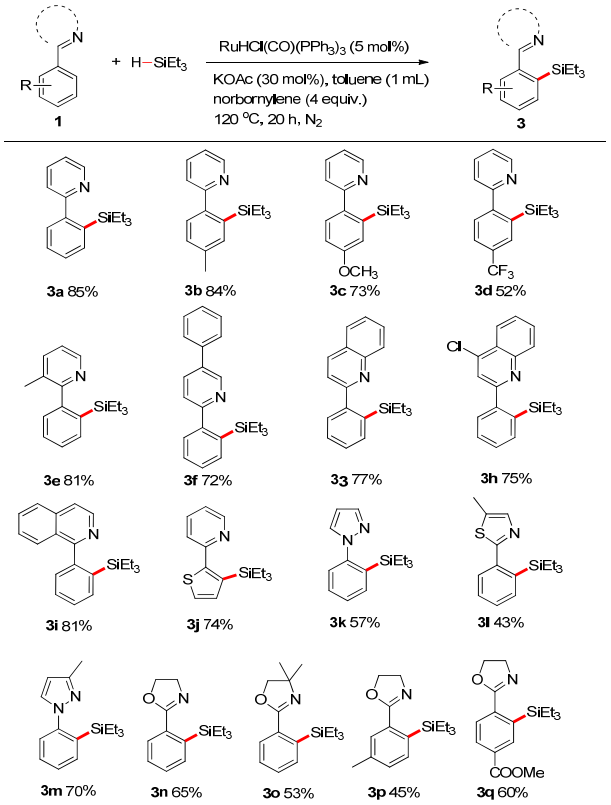
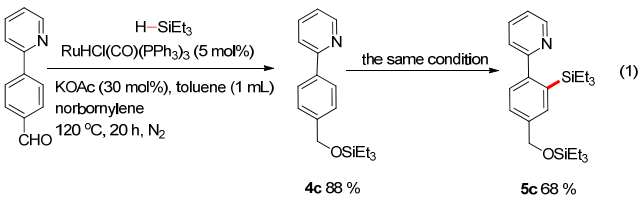


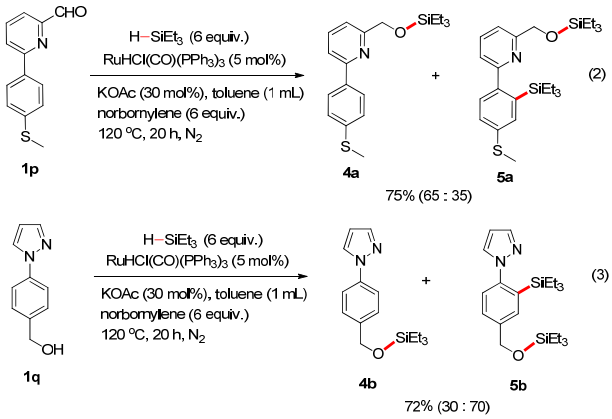
Reaction conditions: **1** (0.5 mmol), triethylsilane (2.0 mmol), $RuHCl(CO)(PPh_3)_3$ (5 mol%), KOAc (30 mol%), nbe (2.0 mmol), and toluene (1 mL) at 120 °C for 20 h under N_2.

Scheme 2. Ru(II)-OAc Catalyzed *ortho* C-H Silylation of 2-Aryl heterocycles.

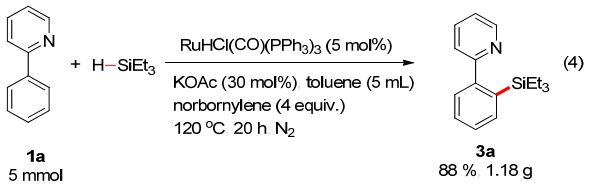
Hydrosilanes have been shown to be an excellent reductants for the reduction of C=O bond. In order to test the reaction rate and the aldehyde group tolerance, the reaction of 4-(pyridin-2-yl)benzaldehyde with triethylsilane was performed under similar conditions (eq 1). Interestingly, only the hydrosilylation product of aldehyde **4c** was produced in 88% isolated yield.[20] Under the same reaction conditions, 68% isolated yield of *ortho* C-H silylation product **5c** was obtained using silyl ether **4c** as the substrate. These results indicated that: (1) the reaction rate of hydrosilylation of aldehyde is much faster than the C-H silylation. (2) silyl-group could be used as a potential hydroxyl protection group in C-H silylation process.



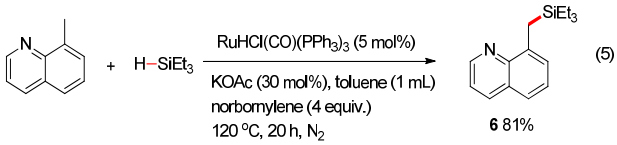
Increasing the quantity of triethylsilane and norbonylene to 6 equivalents under similar conditions, 75% yield of a mixture of silyl-compounds **4a** and **5a** with a ratio of 65 : 35 was obtained from the reaction of 6-(4-(methylthio)phenyl)picolinaldehyde **1p** (eq 2). Similarly, mixed oxidative O-Si coupling products 4b and double silylated compound **5b** were observed in 72% yield with a ratio of 30:70 (eq 3). These results indicated that both hydrosilation of C=O bond and oxidative O-Si coupling are more favored than the C-H silylation process.



The synthetic potential of this C-H silylation was further demonstrated by a gram-scale synthesis (eq 4). 5 mmol of 2-phenylpyridine **1a** was silylated under the standard conditions to generate 1.18 g of the desired silylation product **3a** (88% yield).



Intermolecular sp^3 C-H silylation is usually more challenging than the silylation of sp^2 C-H bonds. This catalytic system also displayed good reactivity for sp^3 C-H bond silylation of 8-methylquinoline, and the corresponding silyl-compound **6** was isolated in 81 % yield.(eq 5)



The easiness and reversibility of the *ortho* C-H bond cleavage were studied by H/D exchanges. First, the reaction of **1a** in the presence of KOAc (30 mol%) and D_2O (0.2 mL) was carried out under the previous reaction conditions at 120 °C for 12 h. 93% of H/D exchange took place at the *ortho* C-H bond (Scheme 3). The same reaction performed without KOAc led to an decreased H/D exchange at *ortho* position (68%) at 120 °C for 12 h. However, decreasing the temperature to 80 °C and giving lower H/D exchange under the similar conditions. These results indicated that the KOAc plays an important role to promote this C-H silylation.

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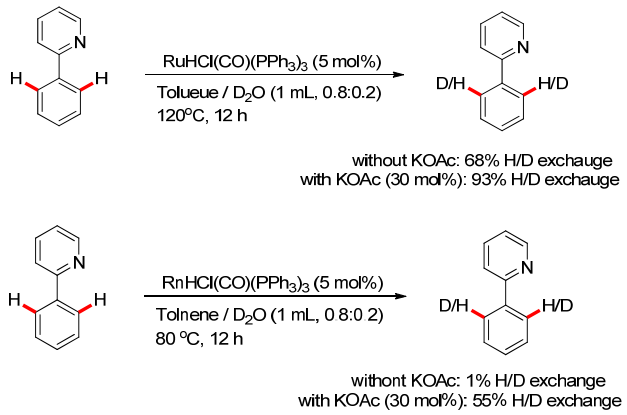
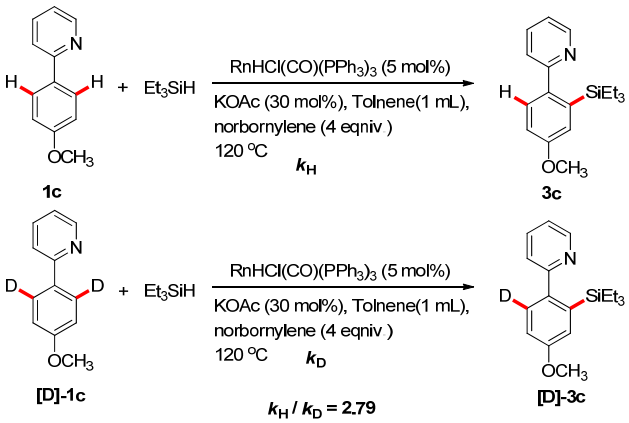


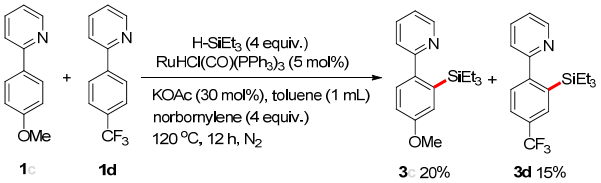
Scheme 3. H/D Exchange Experiments in 2-Phenylpyridine **1a**.

Furthermore, to gather more information, *ortho*-deuterium labeled pyridine derivative (**[D]-1c**) was used to study the kinetic isotopic effects (KIE) during the C-H silylation. Two separate, parallel reactions of triethylsilane with pyridine derivative **1c** and **[D]-1c** were performed to determine the KIE value (Scheme 4), and a significant KIE value (k_H/k_D = 2.79) was observed. This result indicated that C-H bond cleavage step is the rate determining step in $RuHCl(CO)(PPh_3)_3$ catalyzed *ortho* C-H silylation.



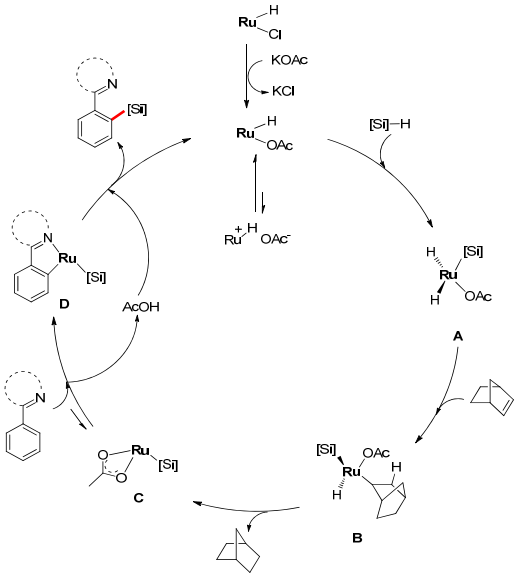
Scheme 4. Isotope Effect of Deuterium-Labeled Substrates.

Moreover, to test the selectivities of our catalytic system, we conducted competitive experiments with different subtituted 2-aryl pyridines **1**, which revealed that the electron-rich arenes gave slight higher reactivity in this $RuHCl(CO)(PPh_3)_3$/KOAc catalyzed C-H silylation, and these results could explain this C-H bond cleavage process could be an acetate-assisted electrophilic substitution (IES)-type mechanism[19,21] (Scheme 5).



Scheme 5. Competitive C−H Silylation Reaction.

Based on the previous results, a proposed catalytic cycle for the Ru-OAc catalyzed *ortho* C-H silylation is illustrated in Scheme 6. First, the Ru-Cl bond of Ru catalyst would be converted to Ru-OAc bond by the salt metathesis with KOAc. Next, Ru(IV) species **B** could be easily generated by the hydrosilylation of triethylsilane, as it was well demonstrated by Gunanathan[20] and Murata[13]. Then, after norbornylene insertion, reductive elimination, the active species **C** would be formed and release bicyclo[2,2,1]heptane. And the subsequent acetate promoted C-H bond cleavage gave the intermediate **D**, as Ru-OAc catalyst was found the efficiency for C-H bond activation via C-H bond cleavage as demonstrated by Jutand and Dixneuf[22]. Finally, a new Si-C bond was generated to produce the desired silylated product **3** after reductive elimination of **D**, and the active Ru-OAc species would be regenerated by the coordination of HOAc for the next catalytic cycle.



Scheme 6. Proposed Mechanism.

Experimental

1) **General Remarks**. 1H NMR spectra were recorded in $CDCl_3$ at ambient temperature on Bruker AVANCE I 300 or 500 spectrometers at 300.1 MHz or 500.1 MHz, using the solvent as internal standard (7.26 ppm). 13C NMR spectra were obtained at 75 or 125 MHz and referenced to the internal solvent signals (central peak is 77.2 ppm). Chemical shift (δ) and coupling constants (J) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad. GC analyses were performed with GC-14C (Shimadzu) equipped with a 30-m capillary column (Supelco, SPB-5, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with N_2/air as vector gas. GCMS were measured by GCMS-7890A-5975C (Agilent) with GC-7890A equipped with a 30-m capillary column (HP-5ms, fused silica capillary column, 30 M*0.25 mm*0.25 mm film thickness), was used with helium as vector gas. HRMS were measured by MAT 95XP (Termol) (LCMS-IT-TOF).

2) **General procedure.** $Ru(PPh_3)_3(CO)HCl$ (0.025 mmol, 23.8 mg), pyridines (0.5 mmol), hydrosilane (2.0 mmol), KOAc (0.15 mmol,

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15 mg), norbornylene (2.0 mmol, 197 μL) and toluene (1 mL) were introduced in a tube under N_2, equipped with magnetic stirring bar and was stirred at 120 °C. After 20 h, the conversion of the reaction was analyzed by gas chromatography. The solvent was then evaporated under vacuum and the desired product was purified by using a silica gel chromatography column and a mixture of petrol ether/ethyl acetate as eluent.

Conclusions

In summary, we have developed a new Ru(II)-OAc catalytic system and its application in the *ortho* C-H silylation of 2-aryl heterocycles using $HSiEt_3$ as the silylating reagent. Many heterocycles such as pyridine, quinoline, thiazole, pyrazole and oxazoline were converted into mono-silylated compounds successfully in moderate to good yields. Moreover, this catalytic system could be applied to the silylation of more challenging sp^3 C-H bonds.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the Support of the National Natural Science Foundation of China (No: 21702148), the Foundation of Department of Education of Guangdong Province.

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DOI: 10.1039/C9OB00609E

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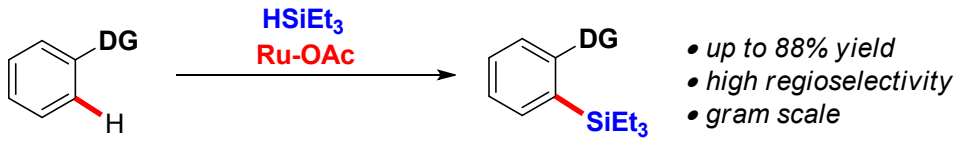

DG = pyridine, quinoline, thiazole, pyrazole, oxazoline etc

The application of $RuHCl(CO)(PPh_3)_3$-OAc catalytic system on selective intermolecular mono C-H silylation of 2-aryl heterocycles using $HSiEt_3$ as the silylating reagent has been described for the first time