

钯催化芳香溴化物与三甲基硅基重氮甲烷的还原偶联及其在芳香化合物甲基化中的应用

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摘要 芳香化合物的甲基化反应是一类重要的转化。其中,由芳香卤化物出发的转化是在芳香体系中引入甲基基团的有效策略。已有的方法多需要使用预先制备的甲基金属试剂或高毒性的甲基亲电试剂作为甲基化试剂。本研究发展了一种利用三甲基硅基重氮化合物和芳香溴化物在钯催化下的还原偶联反应生成苄基硅化合物,再经过脱硅质子化过程实现的甲基化方法。此方法具有良好的官能团兼容性,是一种具有潜在应用价值的对芳香卤化物进行甲基化的新方法。同时,该方法也可应用于在有机分子中引入硅甲基基团。

关键词 甲基化; 三甲基硅基重氮甲烷; 金属卡宾; 转移插入; 还原偶联

Palladium-Catalyzed Reductive Coupling of Aromatic Bromides and Trimethylsilyldiazomethane: Its Application to Methylation of Aromatic Compounds

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Abstract The introduction of methyl group into aromatic compounds is a valuable transformation. A large number of known methods use organohalides as the starting materials. However, those methods require pre-synthesized methyl metal reagents or toxic methyl electrophiles. Herein, a palladium-catalyzed reductive coupling reaction between aryl bromides and trimethylsilyl-diazomethane is developed, and the following desilylification process can afford the methylated products. This transformation has broad functional group tolerance and allows methylation of (hetero)aryl halides in moderate to good yields. Thus, it has the potential to be an attractive approach for methylation of organic. In addition, this reductive coupling can also serve as an efficient way for the introduction of silylmethyl group.

Keywords methylation; trimethylsilyldiazomethane; metal carbene; migratory insertion; reductive coupling

1 Introduction

Methyl group (Me), as the smallest alkyl group, is ubiquitous in organic compounds, especially in a large number of bioactive molecules.^[1] The introduction of methyl groups has been demonstrated to have significant influence on the bioactivity of molecules, which is very important for drug discovery and development.^[2] The optimization of many properties by introducing various groups, which is referred as “magic methyl effect”, can be attributed to the change of solubility, hydrophilicity, and molecular conformation.^[3]

For this reason, the development of efficient methylation methods has attracted considerable attentions in recent years.^[4]

The traditional methylation methods involve nucleophilic substitution of *in situ* generated aryl lithium reagent and methyl electrophile, and Minisci-type reaction of electron-deficient arenes.^[5] These methods commonly suffered from rigorous conditions and limited substrate scope. In the past decades, transition-metal-catalyzed cross-coupling reactions have been widely studied and have emerged as a powerful tool for the construction of C—C bonds. In recent

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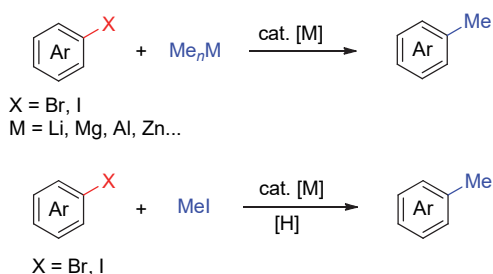
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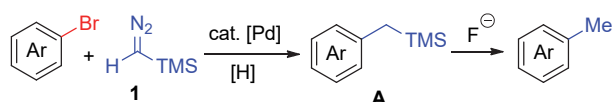
years, synthetic methods for both methylation of C—X bonds and directing-group promoted C—H methylation were developed with transition metal complexes as the catalysts (Scheme 1a).^[6] In general, the methylation reagents used in these transformations involve pre-synthesized methyl organometallic reagents and highly reactive, toxic methyl electrophiles.^[7] Thus, the employment of easily-handled methylation reagents is crucial for the further development of methylation methods. A few of new methylation reagents were reported in recent years. In 2016, Chatani and co-workers reported that phenyltrimethylammonium salts could be employed as methylation reagents in nickel-catalyzed C—H bond methylation reactions.^[8] In 2018, Hartwig and co-workers^[9] reported the copper-catalyzed methylation of arylboronic esters with trimethylphosphite as stable methylation reagent. In addition, several radical-based methylation reagents, such as *N*-hydroxyphthalimide esters and trimethyl orthoformate, have been reported by the groups of Weix^[10] and Doyle.^[11] While significant advances have been achieved, new and efficient methylation methods with easily-handled methylation reagents are still highly demanded.

On the other hand, transition-metal-catalyzed cross-coupling reactions involving metal carbene species have been actively explored in the past decade, and now emerged as powerful tool for the construction of C—C and C—X bonds.^[12] We conceived that trimethylsilyldiazomethane (TMSCHN₂, **1**), which is used as a stable alternative of diazomethane and widely employed in the synthesis of methyl esters from the corresponding acids, may be functioned as C1 carbene precursor undergoing reductive coupling with aryl bromides through migratory insertion process, giving silylmethylated arenes **A** as the intermediate products.^[13-14] Followed by desilicification step with fluoride, the methylated products are expected to be easily obtained (Scheme 1b).

(a) Methylation of aryl halides through cross-coupling reactions



(b) This work: trimethylsilyldiazomethane as the methyl source



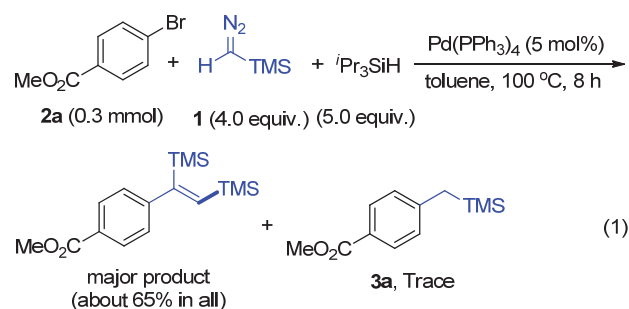
Scheme 1 Methylation of aromatic halides

Moreover, the benzyltrimethylsilane intermediate products **A** are also valuable compounds in organic synthesis.^[15] However, methodologies for the direct introduction of silylmethyl groups are limited.

In general, pre-synthesized silylmethyl metal compounds are employed as the silylmethylation reagents, which restrict the functional group tolerance.^[15a,16] In this context, the palladium-catalyzed reductive coupling we report herein can also be regarded as an efficient way for the direct introduction of silylmethyl group.

2 Results and discussion

To test our hypothesis, methyl 4-bromobenzoate (**2a**) was initially selected as the standard substrate in the Pd-catalyzed reductive coupling reaction. To our disappointment, the reaction of **1** and **2a** only gave trace of the desired product **3a** with 5 mol% Pd(PPh₃)₄ as catalyst and 5 equiv. of ^tPr₃SiH as the reductant in toluene (Eq. 1). This result indicates that the benzyl palladium intermediate generated from the migratory insertion process reacts faster with the second molecule of **1** rather than the reductant (*vide infra*). Thus, the optimization of the reaction conditions by investigating the reaction parameters was continued, with slow addition of **1** using syringe pump.



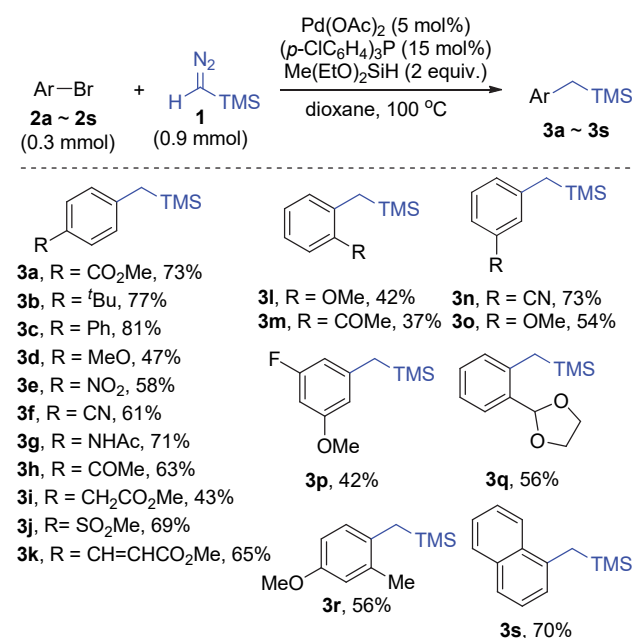
The study showed that 40% yield of **3a** could be obtained with 4.0 equiv. of **1** added slowly in 6 h (Table 1, Entry 1). Then the ratio of palladium catalyst and the ligand with weak-coordinated Pd₂(dba)₃ and PPh₃ instead of Pd(PPh₃)₄ was examined, and the 1 : 3 ratio (Pd : L) gave a better yield of 55% (Table 1, Entry 2). By testing several palladium catalysts and ligands, it was found that the combination of palladium acetate and tris(*p*-chlorophenyl)phosphane was more effective for this transformation (Table 1, Entries 3~5). Then several reductants were screened. To our delight, by using 3 equiv. of Me(EtO)₂SiH as the reductant instead of 6 equiv. of ^tPr₃SiH, both the loading and the addition time of **1** could be reduced (Table 1, Entry 6). Furthermore, solvent effect was then examined. Replacement of toluene with 1,4-dioxane slightly improved the yield to 73% (Table 1, Entry 7). When the reaction was carried out under a higher or lower temperature, the product **3a** was obtained in a lower yield (Table 1, Entries 8, 9).

With the optimized conditions in hand, the substrate scope of the aryl bromides was further investigated (Scheme 2). A variety of electron-donating and electron-withdrawing functional groups, including alkyl (**3b** and **3r**), phenyl (**3c**), methoxyl (**3d**, **3l**, **3p** and **3r**), nitro (**3e**), cyano (**3f** and **3n**), acetamido (**3g**), acetyl (**3h** and **3m**),

Table 1 Optimization of the reaction conditions^a

Entry	x/equiv.	y/equiv.	z/h	Cat. [Pd]	L	[H]	Solvent	T/°C	Yield ^b /%
1	4	5	6	Pd(PPh ₃) ₄	—	^t Pr ₃ SiH	Toluene	100	40
2	4	5	6	Pd ₂ (dba) ₃	PPh ₃	^t Pr ₃ SiH	Toluene	100	55
3	4	5	6	Pd ₂ (dba) ₃	(<i>p</i> -ClC ₆ H ₄) ₃ P	^t Pr ₃ SiH	Toluene	100	62
4	4	5	6	Pd(OAc) ₂	(<i>p</i> -ClC ₆ H ₄) ₃ P	^t Pr ₃ SiH	Toluene	100	68
5	4	5	6	Pd(OAc) ₂	(<i>p</i> -FC ₆ H ₄) ₃ P	^t Pr ₃ SiH	Toluene	100	54
6	3	2	3	Pd(OAc) ₂	(<i>p</i> -ClC ₆ H ₄) ₃ P	Me(EtO) ₂ SiH	Toluene	100	70
7	3	2	3	Pd(OAc) ₂	(<i>p</i> -ClC ₆ H ₄) ₃ P	Me(EtO) ₂ SiH	Dioxane	100	73
8	3	2	3	Pd(OAc) ₂	(<i>p</i> -ClC ₆ H ₄) ₃ P	Me(EtO) ₂ SiH	Dioxane	110	66
9	3	2	3	Pd(OAc) ₂	(<i>p</i> -ClC ₆ H ₄) ₃ P	Me(EtO) ₂ SiH	Dioxane	90	50

^a Reaction conditions: *p*-bromobenzoate **2a** (0.3 mmol), TMSCHN₂ **1** (2 mol/L in hexane, 1.2 mmol, 4 equiv.), ^tPr₃SiH (1.5 mmol, 5 equiv.), Pd(PPh₃)₄ (0.015 mmol, 5 mol%) in toluene (2 mL) under 100 °C for 8 h, in which **1** was added in 6 h. ^b All the yields refer to isolated products after silica gel column chromatography.



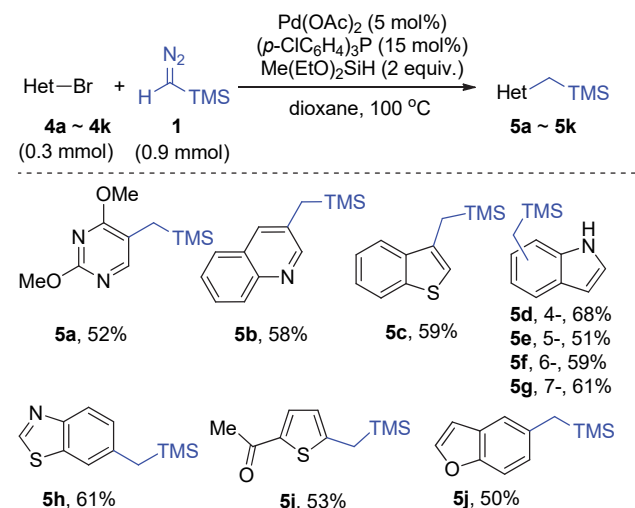
Reaction conditions: aryl bromide (0.3 mmol), TMSCHN₂ **1** (2 mol/L in hexane, 0.9 mmol, 3 equiv.), Me(EtO)₂SiH (0.6 mmol, 2 equiv.), Pd(OAc)₂ (0.015 mmol, 5 mol%), (*p*-ClC₆H₄)₃P (0.045 mmol, 15 mol%) in dioxane (2 mL) under 100 °C for 8 h. **1** was added slowly with a syringe pump over 3 h. All the yields refer to the isolated products after silica gel column chromatography.

Scheme 2 Substrate scope of aryl bromides

sulfonyl (**3j**), alkenyl (**3k**), fluorine (**3p**), 1,3-dioxolan-2-yl (**3q**), and naphthyl (**3s**), were all well-tolerated and gave the corresponding products in moderate to good yields, and the results showed that electron effect has obvious influence on the yields. In addition, the influence of steric effect was also observed. The *ortho*-substituted aryl bromide gave relatively lower yield as compared to the *meta*- and *para*-substituted substrates with the same functional group (**3l** compared to **3d** and **3o**). Notably, the reaction tolerates the

functional group bearing relatively active hydrogen (**3g**).

The substrate scope to heteroaromatic bromides under the standard conditions was then expanded, and the results are shown in Scheme 3. Substrates with a series of heteroaromatic rings, including pyrimidine (**5a**), quinoline (**5b**), indole (**5d** ~ **5g**), benzofuran (**5j**), thiophene (**5i**), benzothienophene (**5c**) and benzoxazole (**5h**), could undergo this transformation and give the corresponding products in moderate yields.

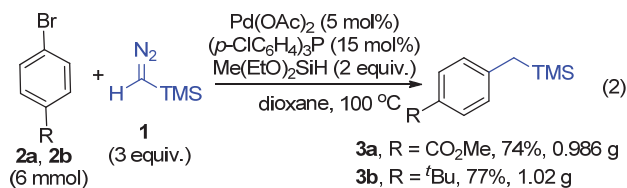


Reaction conditions: heteroaromatic bromide (0.3 mmol), TMSCHN₂ **1** (2 mol/L in hexane, 0.9 mmol, 3 equiv.), Me(EtO)₂SiH (0.6 mmol, 2 equiv.), Pd(OAc)₂ (0.015 mmol, 5 mol%), (*p*-ClC₆H₄)₃P (0.045 mmol, 15 mol%) in dioxane (2 mL) under 100 °C for 8 h. **1** was added slowly with a syringe pump over 3 h. All the yields refer to isolated products after silica gel column chromatography.

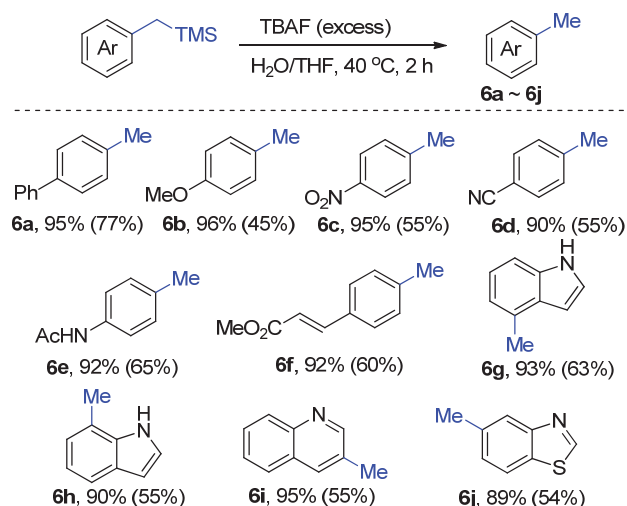
Scheme 3 Substrate scope of heteroaromatic bromides

For a further demonstration of the practical synthetic application of this method, the Pd-catalyzed reductive coupling reactions of **2a** and **2b** were carried out in 6 mmol

scale, and the corresponding products **3a** and **3b** were isolated in gram-scale in similar yields to those in the small scale reactions (Eq. 2).



Subsequently, the desilicification reactions were carried out to verify the feasibility of methylation process (Scheme 4). The desilicification process was efficient and easy to operate with excess amount of tetrabutylammonium fluoride (TBAF). The methylated products **6a**~**6j** could be isolated in moderate yields from the corresponding benzyltrimethylsilanes.

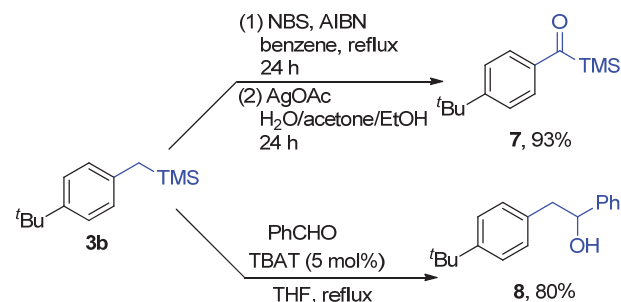


Reaction conditions: the purified benzyltrimethylsilanes (obtained from the 0.3 mmol-scale reductive coupling), TBAF (1 mol/L in THF, 0.4 mmol), H₂O (36 mg, 2 mmol) in THF (1 mL), 40 °C for 2 h. All the yields refer to isolated products after silica gel column chromatography; the number in the bracket refers to the overall yield of the two steps

Scheme 4 Substrate scope of the methylation reaction

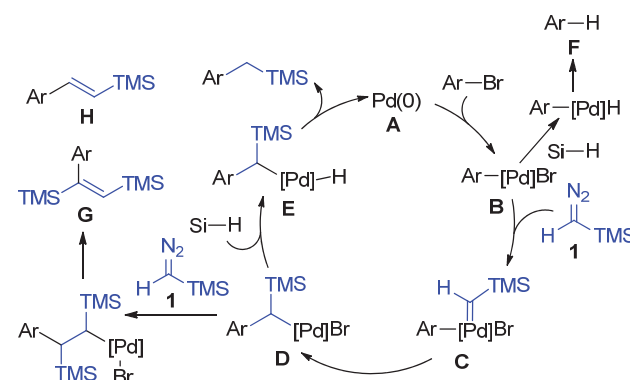
Furthermore, the benzyltrimethylsilane products obtained from the reductive cross-coupling are valuable compounds in organic synthesis. For examples, (*p*-*tert*-butyl)benzyltrimethylsilane (**3b**) could undergo oxidation reaction to afford **7**, while reaction of **3b** with benzaldehyde could afford addition product **8** in a moderate yield (Scheme 5).

The proposed mechanism is shown in Scheme 6. The catalytically active Pd(0) species is generated from the reduction of Pd(OAc)₂. The oxidative addition of the aryl halide to the Pd(0) **A** gives aryl palladium(II) complex **B**. Reaction of trimethylsilyldiazomethane **1** and **B** leads to the generation of metal carbene species **C**. Subsequently, migratory insertion occurs to afford the benzyl palladium



Scheme 5 The transformations of (*p*-*tert*-butyl)benzyltrimethylsilane **3b**

intermediate **D**. Intermediate **D** undergoes ligand exchange with Me(EtO)₂SiH to afford intermediate **E**, and the product is generated in a following reductive elimination process. Two side reactions may occur in this transformation: (1) the ligand exchange between **B** and Me(EtO)₂SiH, followed by reductive elimination provides arenes **F**, namely the direct reduction of arylbromide; (2) **D** may react with the second molecule of **1** to afford alkene by-products **G** and **H**. It is noteworthy that the latter process is reported as a synthetic method for silyl-substituted alkenes by Xu, Chen and co-workers.^[17] These two kinds of by-products are both observed in our reaction.



Scheme 6 Proposed mechanism

4 Conclusion

Overall, we have developed a new methylation strategy using a reductive coupling/desilicification cascade process with trimethylsilyldiazomethane as methylation reagent. A wide range of functional groups and heteroaromatic rings were well-tolerated in this reaction. The transformation provides a new method for the introduction of methyl group and silylmethyl group into aromatic rings.

4 Experimental section

4.1 Instruments and reagents

All necessary reagents were purchased from commercial suppliers and used without further purification. The solvents were all distilled prior to use. Purification of products were accomplished by flash chromatography on silica gel (200~300 mesh, from Qingdao, China). NMR spectra were

measured on a Bruker ARX400 (^1H NMR at 400 MHz, ^{13}C NMR at 100 MHz) magnetic resonance spectrometer. IR spectra were recorded on a Nicolet Avatar 330 Fourier transform spectrometer (FT-IR) and are reported in wave numbers (cm^{-1}). For HRMS measurements, the mass analyzer is FT-ICR.

4.2 General procedure for the reductive coupling reactions of aryl bromides and trimethylsilyldiazomethane 1

Under nitrogen atmosphere, aryl bromide (0.3 mmol), $\text{Pd}(\text{OAc})_2$ (0.015 mmol, 3.4 mg), $(p\text{-ClC}_6\text{H}_4)_3\text{P}$ (0.045 mmol, 16.5 mg), $\text{Me}(\text{EtO})_2\text{SiH}$ (0.3 mmol, 40 mg) and dioxane (1.6 mL) were mixed in a 10 mL reaction flask. The solution was stirred at 100°C , and the solution of TMSCHN_2 **1** (2 mol/L in hexane, 0.45 mL) and $\text{Me}(\text{EtO})_2\text{SiH}$ (0.3 mmol, 40 mg) in dioxane (0.4 mL) was added to this mixture through a syringe pump over 3 h. The reaction was stirred at 100°C for another 5 h. Then the mixture was cooled to room temperature and filtered through a short column filled with silica gel. Solvent was evaporated under reduced pressure, and the crude residue was purified by thin layer chromatography on silica gel to afford the product.

Methyl 4-((trimethylsilyl)methyl)benzoate (**3a**): 73% (48.6 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data were consistent with the literature.^[18]

(4-(*tert*-Butyl)benzyl)trimethylsilane (**3b**): 77% (50.8 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[16a]

([1,1'-Biphenyl]-4-ylmethyl)trimethylsilane (**3c**): 81% (58.3 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[16a]

(4-Methoxybenzyl)trimethylsilane (**3d**): 47% (27.4 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[16a]

Trimethyl(4-nitrobenzyl)silane (**3e**): 58% (36.4 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[19]

4-((Trimethylsilyl)methyl)benzonitrile (**3f**): 61% (34.6 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[16a]

N-(4-((Trimethylsilyl)methyl)phenyl)acetamide (**3g**): 71% (47.1 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[20]

1-(4-((Trimethylsilyl)methyl)phenyl)ethan-1-one (**3h**): 63% (38.9 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[16b]

Methyl 2-(4-((trimethylsilyl)methyl)phenyl)acetate (**3i**): 43% (30.4 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 6.92 (d, $J=8.0$ Hz, 2H), 6.75 (d, $J=8.0$ Hz, 2H), 3.49 (s, 3H), 3.37 (s, 2H), 1.86 (s, 2H), -0.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 172.4, 139.3, 129.3, 128.9, 128.2, 51.9, 40.7, 26.6, -2.0 ; IR (film) ν : 1741, 1436, 1259, 1161, 1013, 807 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{21}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 237.1305, found 237.1302.

Trimethyl(4-(methylsulfonyl)benzyl)silane (**3j**): 69% (50.1 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3)

δ : 7.77 (d, $J=8.4$ Hz, 2H), 7.16 (d, $J=8.3$ Hz, 2H), 3.04 (s, 3H), 2.20 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 148.1, 136.0, 128.5, 127.3, 44.6, 28.0, -2.0 ; IR (film) ν : 2957, 1593, 1304, 1146, 1091, 851 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{19}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 243.0870, found 243.0862.

Methyl (*E*)-3-(4-((trimethylsilyl)methyl)phenyl)acrylate (**3k**): 65% (48.4 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 7.66 (d, $J=16.0$ Hz, 1H), 7.38 (d, $J=8.1$ Hz, 2H), 7.01 (d, $J=8.1$ Hz, 2H), 6.37 (d, $J=16.0$ Hz, 1H), 3.79 (s, 3H), 2.12 (s, 2H), 0.00 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.7, 145.1, 143.9, 130.2, 128.4, 128.1, 115.8, 51.5, 27.6, -2.0 ; IR (film) ν : 2954, 1719, 1634, 1249, 1168, 850 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{21}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 249.1305, found 249.1302.

(2-Methoxybenzyl)trimethylsilane (**3l**): 42% (24.4 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data were consistent with the literature.^[21]

1-(2-((Trimethylsilyl)methyl)phenyl)ethan-1-one (**3m**): 37% (22.9 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data were consistent with the literature.^[22]

3-((Trimethylsilyl)methyl)benzonitrile (**3n**): 73% (41.4 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data were consistent with the literature.^[23]

(3-Methoxybenzyl)trimethylsilane (**3o**): 54% (31.4 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data were consistent with the literature.^[21]

(3-Fluoro-5-methoxybenzyl)trimethylsilane (**3p**): 42% (26.7 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 6.36~6.30 (m, 3H), 3.76 (s, 3H), 2.05 (s, 2H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 163.5 (d, $J=243.5$ Hz), 160.5 (d, $J=11.9$ Hz), 143.8 (d, $J=9.8$ Hz), 109.5, 107.1 (d, $J=21.5$ Hz), 97.1 (d, $J=25.4$ Hz), 55.3, 27.5, -1.91 ; IR (film) ν : 2956, 1612, 1249, 1156, 982, 850 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{18}\text{FOSi}$ $[\text{M}+\text{H}]^+$ 213.1111, found 213.1109.

(2-(1,3-Dioxolan-2-yl)benzyl)trimethylsilane (**3q**): 56% (39.6 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 7.53 (d, $J=7.6$ Hz, 1H), 7.22 (td, $J=8.4$, 1.0 Hz, 1H), 7.12 (t, $J=7.4$ Hz, 1H), 7.00 (d, $J=7.6$ Hz, 1H), 5.91 (s, 1H), 4.17~4.11 (m, 2H), 4.07~4.01 (m, 2H), 2.27 (s, 2H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 139.3, 133.7, 129.4, 128.7, 126.1, 124.2, 101.7, 65.2, 22.8, -1.4 ; IR (film) ν : 2954, 2894, 1249, 1087, 944, 846 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{21}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 237.1311, found 237.1307.

(4-Methoxy-2-methylbenzyl)trimethylsilane (**3r**): 56% (34.9 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 6.89 (d, $J=8.3$ Hz, 1H), 6.71~6.71 (m, 1H), 6.68~6.65 (m, 1H), 3.78 (s, 3H), 2.23 (s, 3H), 2.04 (s, 2H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 156.4, 135.6, 130.8, 129.4, 115.6, 111.0, 55.1, 22.4, 20.6, -1.4 ; IR (film) ν : 2955, 1609, 1501, 1254, 1203, 854 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{20}\text{OSi}$ $[\text{M}]^+$ 208.1283, found 208.1277.

Trimethyl(naphthalen-1-ylmethyl)silane (**3s**): 70% (44.9 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data were consistent with the literature.^[24]

2,4-Dimethoxy-5-((trimethylsilyl)methyl)pyrimidine (**5a**): 52% (35.3 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 7.83 (s, 1H), 3.93 (s, 6H), 1.84 (s, 2H), -0.04 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 168.5, 162.9, 155.3, 113.9, 54.4, 53.5, 15.6, -1.8; IR (film) ν : 2956, 1570, 1486, 1377, 1074, 844 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{19}\text{N}_2\text{O}_2\text{Si}$ $[\text{M} + \text{H}]^+$ 227.1216, found 227.1217.

3-((Trimethylsilyl)methyl)quinoline (**5b**): 58% (37.4 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 8.63 (d, $J=2.0$ Hz, 1H), 8.05 (d, $J=8.4$ Hz, 1H), 7.72~7.70 (m, 2H), 7.62~7.58 (m, 1H), 7.50~7.74 (m, 1H), 2.24 (s, 2H), 0.04 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 151.8, 145.7, 133.6, 132.5, 129.0, 128.3, 127.8, 126.9, 126.4, 24.3, -2.0; IR (film) ν : 2953, 1492, 1249, 1174, 904, 847, 748 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{18}\text{NSi}$ $[\text{M} + \text{H}]^+$ 216.1209, found 216.1209.

(Benzo[*b*]thiophen-3-ylmethyl)trimethylsilane (**5c**): 59% (38.9 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 7.86~7.84 (m, 1H), 7.67 (d, $J=7.4$ Hz, 1H), 7.40~7.31 (m, 2H), 6.86 (s, 1H), 2.33 (s, 2H), 0.04 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 140.2, 139.3, 134.3, 123.8, 123.4, 122.7, 122.1, 118.3, 18.6, -1.4; IR (film) ν : 2953, 1733, 1422, 1246, 838, 761 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{16}\text{OSi}$ $[\text{M}]^+$ 204.0970, found 204.0966.

4-((Trimethylsilyl)methyl)-1*H*-indole (**5d**): 68% (41.4 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 8.01 (s, 1H), 7.16~7.16 (m, 3H), 6.80 (d, $J=6.4$ Hz, 1H), 6.53~6.52 (m, 1H), 2.42 (s, 2H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 135.6, 133.0, 127.0, 122.9, 122.0, 118.8, 106.9, 101.8, 24.0, -1.3; IR (film) ν : 3415, 2955, 1248, 1078, 851, 749 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{NSi}$ $[\text{M} + \text{H}]^+$ 204.1209, found 204.1202.

5-((Trimethylsilyl)methyl)-1*H*-indole (**5e**): 51% (31.1 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data were consistent with the literature.^[16a]

6-((Trimethylsilyl)methyl)-1*H*-indole (**5f**): 59% (35.9 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 7.94 (s, 1H), 7.51 (s, $J=8.1$ Hz, 1H), 7.10 (t, $J=2.9$ Hz, 1H), 7.02 (s, 1H), 6.82 (d, $J=8.1$ Hz, 1H), 6.50 (s, 1H), 6.20 (s, 2H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 136.4, 134.4, 124.6, 122.9, 121.3, 120.1, 109.6, 102.3, 27.1, -1.8; IR (film) ν : 3408, 2955, 1454, 1247, 1089, 848 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{NSi}$ $[\text{M} + \text{H}]^+$ 204.1209, found 204.1199.

7-((Trimethylsilyl)methyl)-1*H*-indole (**5g**): 61% (37.1 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 7.92 (s, 1H), 7.44 (d, $J=7.9$ Hz, 1H), 7.18 (t, $J=2.9$ Hz, 1H), 7.05 (t, $J=7.4$ Hz, 1H), 6.87 (d, $J=7.1$ Hz, 1H), 6.56 (dd, $J=3.2, 2.1$ Hz, 1H), 2.27 (s, 2H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 134.6, 127.5, 123.5, 122.8, 121.4, 120.0, 116.7, 103.0, 21.8, -1.3; IR (film) ν : 3435, 1430, 1332, 1249, 1099, 854 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{18}\text{NSi}$ $[\text{M} + \text{H}]^+$ 204.1209, found 204.1197.

6-((Trimethylsilyl)methyl)benzo[*d*]thiazole (**5h**): 61% (40.4 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 8.94 (s, 1H), 7.79~7.77 (m, 2H), 7.10 (d, $J=8.3$ Hz,

1H), 2.25 (s, 1H), 0.02 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.9, 153.8, 139.2, 126.6, 122.1, 121.1, 27.0, -2.0; IR (film) ν : 3435, 2953, 1430, 1249, 1067, 854 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{16}\text{NSSi}$ $[\text{M} + \text{H}]^+$ 222.0773, found 222.0765.

1-(5-((Trimethylsilyl)methyl)thiophen-2-yl)ethan-1-one (**5i**): 53% (33.7 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 7.49 (d, $J=3.8$ Hz, 1H), 6.60 (d, $J=3.7$ Hz, 1H), 2.48 (s, 3H), 2.34 (s, 2H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 190.1, 154.2, 140.5, 133.5, 124.6, 26.3, 22.5, -2.0; IR (film) ν : 2956, 1655, 1446, 1281, 1250, 843 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{17}\text{OSSi}$ $[\text{M} + \text{H}]^+$ 213.0769, found 213.0758.

(Benzofuran-5-ylmethyl)trimethylsilane (**5j**): 50% (30.6 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 7.57 (d, $J=2.1$ Hz, 1H), 7.36 (d, $J=8.4$ Hz, 1H), 7.21 (d, $J=1.0$ Hz, 1H), 6.94 (dd, $J=8.4, 1.6$ Hz, 1H), 6.68 (dd, $J=2.0, 0.8$ Hz, 1H), 2.17 (s, 2H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.7, 144.8, 134.7, 127.5, 124.7, 119.5, 110.7, 106.2, 26.6, -1.9; IR (film) ν : 2955, 1467, 1247, 1198, 847, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{16}\text{SSi}$ $[\text{M}]^+$ 220.0742, found 220.0737.

4.3 Procedure for the gram-scale reductive coupling of aryl bromides and trimethylsilyldiazomethane 1

Under nitrogen atmosphere, aryl bromides (6 mmol), $\text{Pd}(\text{OAc})_2$ (0.3 mmol, 67.3 mg), $(p\text{-ClC}_6\text{H}_4)_3\text{P}$ (0.9 mmol, 329 mg), $\text{Me}(\text{EtO})_2\text{SiH}$ (6 mmol, 804 mg) and dioxane (32 mL) were mixed in a 100 mL reaction flask. The mixture was stirred at 100 $^\circ\text{C}$ and the solution of TMSCHN_2 **1** (2 mol/L in hexane, 18 mmol, 9 mL), $\text{Me}(\text{EtO})_2\text{SiH}$ (6 mmol, 804 mg) and dioxane (8 mL) was added into the reaction system through syringe pump over 3 h. Then the reaction was stirred at 100 $^\circ\text{C}$ for another 5 h. Then the mixture was cooled to room temperature and filtered through a short column filled with silica gel. Solvent was evaporated under reduced pressure, and the crude residue was purified by distillation under reduced pressure to give the product.

3.4 General procedure for the desilicification of benzyltrimethylsilanes

The purified benzyltrimethylsilanes, obtained by the 0.3 mmol-scale reductive coupling, was transferred into a 10 mL round bottom flask. Then THF (2 mL), TBAF (1 mol/L in THF, 0.3 mmol, 0.3 mL), H_2O (2 mmol, 36 mg) was added. The mixture was stirred at 40 $^\circ\text{C}$ for 2 h. Solvent was evaporated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel to give the product.

4-Methyl-1,1'-biphenyl (**6a**): 77% (38.8 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[7a]

1-Methoxy-4-methylbenzene (**6b**): 45% (16.5 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[11]

1-Methyl-4-nitrobenzene (**6c**): 55% (22.6 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[25]

4-Methylbenzonitrile (**6d**): 55% (19.3 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[11]

N-(*p*-tolyl)acetamide (**6e**): 65% (29.1 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[26]

Methyl (*E*)-3-(*p*-tolyl)acrylate (**6f**): 60% (31.7 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[27]

4-Methyl-1*H*-indole (**6g**): 63% (24.8 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[28]

7-Methyl-1*H*-indole (**6h**): 55% (21.6 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[28]

3-Methylquinoline (**6i**): 55% (23.6 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[28]

5-Methylbenzo[*d*]thiazole (**6j**): 54% (24.1 mg) yield, colorless oil. ^1H NMR (400 MHz, CDCl_3) δ : 8.95 (s, 1H), 7.94 (s, 1H), 7.83 (d, $J=8.2$ Hz, 1H), 7.27 (d, $J=8.6$ Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.9, 153.7, 136.3, 130.6, 127.2, 123.5, 121.3, 21.4; IR (film) ν : 3055, 2918, 1435, 1318, 849, 803 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_8\text{H}_8\text{NS}$ $[\text{M}+\text{H}]^+$ 150.0377, found 150.0371.

4.5 Procedure for the oxidation reaction of **3b** to afford **7**

Under nitrogen atmosphere, **3b** (0.5 mmol, 110 mg), *N*-bromosuccinimide (NBS) (1.1 mmol, 196 mg), 2,2'-azobis(2-methylpropionitrile) (AIBN) (0.025 mmol, 4.1 mg) and benzene (2.5 mL) were mixed in a 10 mL reaction flask and refluxed for 24 h. Then the mixture was cooled to room temperature and filtered. Solvent was evaporated under reduced pressure, and the crude residue was dissolved in dichloromethane (DCM) 10 mL and washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution 10 mL. The organic layer was washed with 10 mL brine for 3 times and then dried over Na_2SO_4 . The organic layer was separated and solvent was evaporated under reduced pressure to afford the α,α -dibromo-substituted intermediate product. This intermediate product was then transferred into a 10 mL reaction flask, to which the solvent (water/acetone/ethanol, $V:V:V=1:2:3$, 5 mL) and AgOAc (1 mmol, 167 mg) were added. The mixture was stirred for 24 h in dark. After the reaction was complete, the mixture was filtered and the solvent was evaporated under reduced pressure. The crude residue was dissolved in 20 mL petroleum ether and washed with 10 mL brine for 3 times. The combined aqueous layer was extracted with 10 mL petroleum ether for three times. The combined organic layer was dried over Na_2SO_4 . The organic layer was then filtered and solvent was evaporated under reduced pressure. The crude residue was purified by flash chromatography on silica gel, eluted with petroleum ether to give the product (4-(*tert*-butylphenyl)(trimethylsilyl)methanone (**7**)).^[29] 93% (108.8 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data were consistent with

the literature.^[30]

4.6 Procedure for the reaction addition reaction of **3b** with benzaldehyde to afford **8**

Under nitrogen atmosphere, **3b** (0.5 mmol, 110 mg), tetrabutylammonium difluorotriphenylsilicate (TBAT) (0.025 mmol, 13.5 mg), benzaldehyde (0.5 mmol, 53 mg) and THF (2 mL) were mixed in a 10 mL reaction flask and refluxed for 3 h. The mixture was cooled to room temperature. Then 10 mL ethyl acetate and 10 mL hydrochloric acid (2 mol/L) was added to the mixture. The water layer was extracted with 10 mL ethyl acetate for three times. The organic layer was combined and dried over Na_2SO_4 . Solvent was evaporated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, $V:V=100:1$) to give the product 2-(4-(*tert*-butylphenyl)-1-phenylethan-1-ol (**8**)).^[21] 80% (101.6 mg) yield, colorless oil. The ^1H NMR and ^{13}C NMR data are consistent with the literature.^[31]

Supporting Information ^1H NMR and ^{13}C NMR spectra of all the products. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn>.

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