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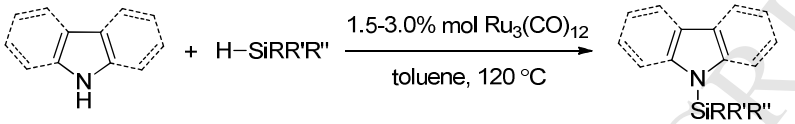

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- Base free
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$Ru_3(CO)_{12}$-catalyzed dehydrogenative Si–N coupling of indoles with hydrosilanes without additive

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ABSTRACT

An efficient $Ru_3(CO)_{12}$-catalyzed dehydrogenative Si–N coupling reaction of indoles, pyrrole, and carbazole with hydrosilanes is reported. The reaction does not need any external additive. This catalytic reaction has a wide substrate range, excellent functional group tolerance, and high to excellent reaction efficiency. Gram-scale synthesis demonstrates the practicability of this synthetic method.

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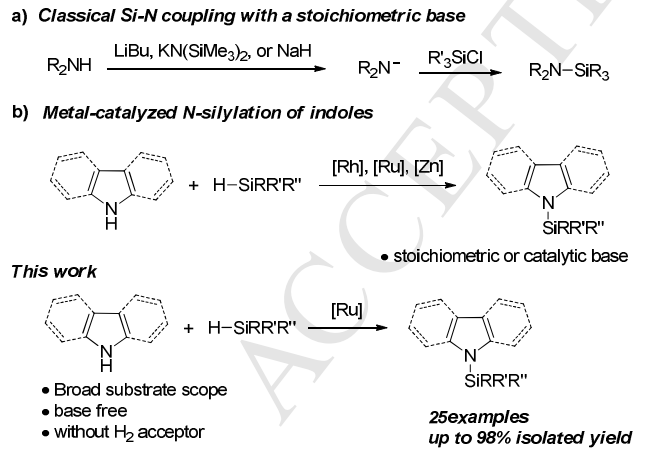
1. Introduction

Much attention has been paid to develop efficient routes for the functionalization of indoles,[1] because the indole ring is one of the most important skeletons ubiquitously existing in many natural products and bioactive compounds.[2] *N*-Protected indoles, in particular, *N*-silylated indoles are considered as very crucial synthetic platforms which can be used to build significant indole-based natural products and pharmaceuticals.[3] For example, Hartwig and co-workers reported that *N*-silylated indoles generated in situ can achieve the selective borylation of indoles.[4a] Minami and co-workers reported Nickel-catalyzed *N*-arylation reaction of *N*-trimethylsilyl-carbazole with aryl bromides, giving *N*-aryl-carbazoles in high yields.[4b]

The conventional methods to synthesize *N*-silylated indoles generally include preactivation of indoles and subsequent coupling of the deprotonated indoles with a halosilane (Scheme 1a).[3,5] However, this antique method requires a stoichiometric strong metallic base and a halosilane which in most cases is sensitive to moisture and hard to handle. The ambient of strong base is prejudice to some functional groups.[6] In light of this, the direct dehydrogenative coupling of N–H of indoles with hydrosilanes is an attractive alternative transformation which generates dihydrogen as the sole by-product. Until now, several procedures for the dehydrogenative Si–N coupling of indoles with hydrosilanes have been reported (Scheme 1b). Tsuchimoto et al.[7] reported zinc-catalyzed dehydrogenative *N*-silylation of indoles with hydrosilanes with the addition of a catalytic amount base and a nitrile solvent as the H_2 acceptor. Mizuno et al.[8] developed rhodium acetate catalyzed dehydrogenative Si–N coupling of indoles with hydrosilanes in the presence of stoichiometric base. Oestreich et al.[9] reported a base-free dehydrogenative Si–N coupling of hydrosilanes with indoles as well as indolines and anilines with a sulfur-bridged Ru-arene complex as catalyst. Paradies developed a metal-free $B(C_6F_5)_3$ catalyzed dehydrogenative Si–N coupling of hydrosilanes with anilines, carbazoles, and indoles.[10] Here, we developed a commercially available $Ru_3(CO)_{12}$ catalyzed base-free dehydrogenative Si–N coupling of indoles with hydrosilanes.

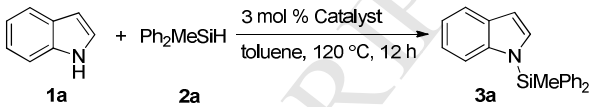


Scheme 1. Synthetic strategies for *N*-silylated indoles.

2. Results and discussion

Firstly, we examined different ruthenium catalysts for the Si–N dehydrogenative coupling reaction of indole (**1a**) with Ph_2MeSiH (**2a**) (Table 1). Fortunately, $Ru_3(CO)_{12}$ was found to show the best catalytic activity, affording **3a** in 97% yield when the reaction was done in toluene at 120 °C with 3 mol % of catalyst (Table 1, entry 1). $[(p\text{-cymene})RuCl_2]_2$ and $H_2Ru(CO)(PPh_3)_3$ were totally inactive (Table 1, entries 2–3). With $Ru_3(CO)_{12}$ as the catalyst, the effect of various solvents was investigated. It showed that dioxane and CH_3CN gave **3a** in 51 % and 10% yields, respectively (Table 1, entries 4–5), while the reaction hardly proceeded in DMF (Table 1, entry 6). Decreasing the reaction temperature led to lower yield (Table 1, entry 7). It is worth to note that when the loading of catalyst decreased to 1.5 mol %, **3a** was still obtained in 95% yield (Table 1, entry 8). Adding norbornene as an additive decreased the yield of **3a** to 25%. This result implied that the use of a H_2 acceptor cannot improve the reaction efficiency. In the absence of $Ru_3(CO)_{12}$ no target compound was detected (Table 1, entry 10).

Table 1 Optimization of ruthenium-catalyzed dehydrogenative Si–N coupling of indoles with hydrosilanes.[a]



1a 2a 3a

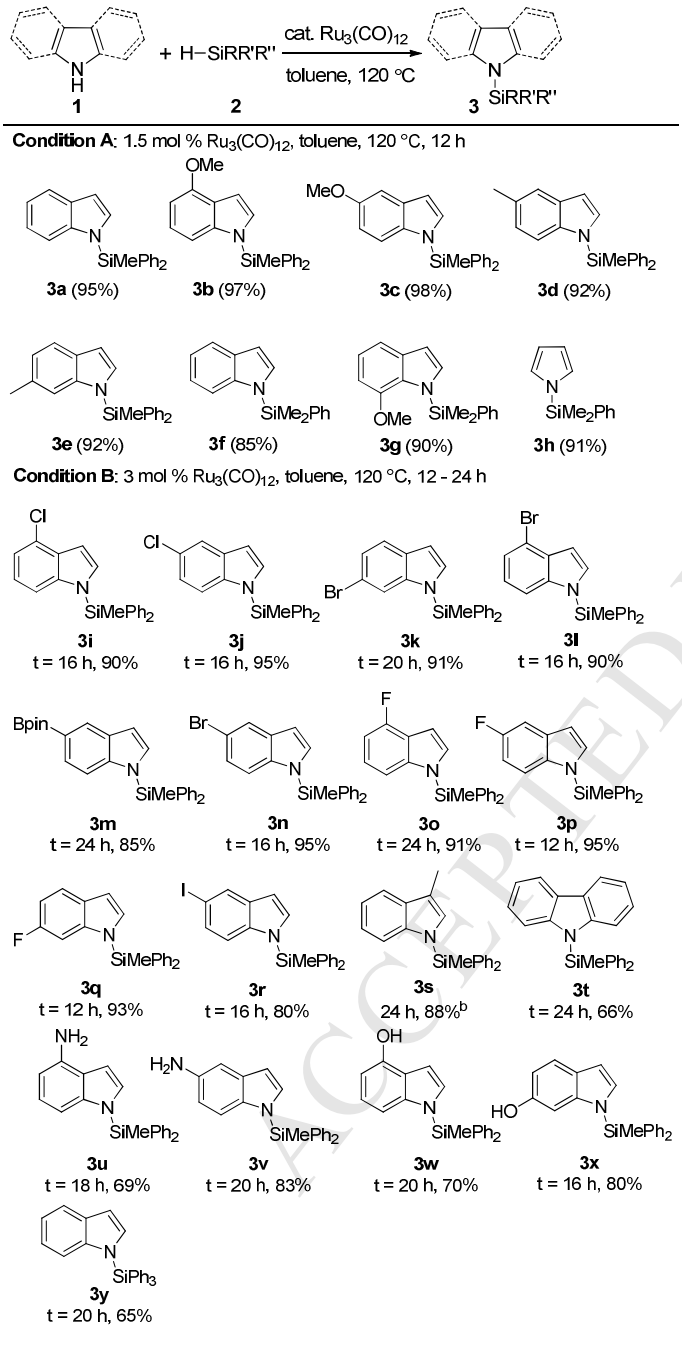
entry	catalyst	solvent	yield [%]
1	$Ru_3(CO)_{12}$	toluene	97
2	$[(p\text{-cymene})RuCl_2]_2$	toluene	N.R
3	$H_2Ru(CO)(PPh_3)_3$	toluene	N.R
4	$Ru_3(CO)_{12}$	CH_3CN	10
5	$Ru_3(CO)_{12}$	dioxane	51
6	$Ru_3(CO)_{12}$	DMF	N.R
7[b]	$Ru_3(CO)_{12}$	toluene	83
8[c]	$Ru_3(CO)_{12}$	toluene	95
9[d]	$Ru_3(CO)_{12}$	toluene	25
10	No	toluene	N.R

[a]Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $Ru_3(CO)_{12}$ (3 mol %), solvent (2 mL), 120 °C, 12 h. Isolated yield.
[b]The reaction proceeded in 100 °C.
[c]1.5 mol % of $Ru_3(CO)_{12}$ was used.
[d]2 equiv of norbornene were added.

With the optimal reaction conditions in hand, we tested functional-group compatibilities of indoles and the scope of different hydrosilane for the reaction. The results showed that indoles with electron-donating (-Me, -OMe) and electron-withdrawing groups (-F, -Cl, -Br, -I) all proceeded well, giving the corresponding products in 80–98% yields (Table 2, **3a**–**3e**, **3i**–**3s**). Especially, indoles with electron-donating groups could afford the target compounds using half amount of catalyst loading of optimized conditions in excellent yields over 90 % (Table 2, **condition A**). Indoles with electron-withdrawing groups at C5 also afforded the corresponding *N*-silylated indoles in great yields (Table 2, **3j, 3m, 3n, 3p and 3r**). These results could compare well with the previous reports.[7,8,9] Indoles with electron-withdrawing groups (-F, -Cl, -Br) at C4 and C6 are also eligible in these conditions, affording corresponding target compounds in excellent yields after proper extension of time (Table 2, **3i, 3k, 3l, 3o**, and **3q**). It would be possible to utilize these functional groups to achieve the further modification of the indole molecules. It required an increased amount of catalyst (5 mol %) and longer time to get a high yield for indole with C3-Me (Table 2, **3s**). However, indoles with strong electron-withdrawing groups (^-CN, $^-NO_2$, $-COCH_3$) and methyl ester group at C2 position did not work in these reaction conditions while indoles with methyl ester group at C4 or C5 position could only afford trace of target products along with the decomposition of indole substrates. 7-Methoxy-1*H*-indole can be converted to 1-

(dimethyl(phenyl)silyl)-7-methoxy-1*H*-indole (**3g**) in 90% yield, indicating the steric hindrance at C7 position is tolerable. The site selectivity of the present method by testing -NH_2 or -OH-substituted indoles was also investigated. The results showed that the -NH_2 or -OH group in different position of indole cannot couple with hydrosilanes, and only *N*-silylated indoles were obtained in 69% to 83% yields (Table 2, **3u**-**3x**). This unique selectivity may offer potentials in further modification of the indole molecules in organic synthesis.

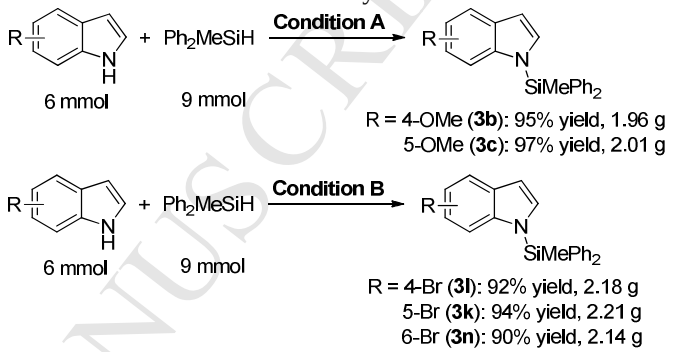
Table 2 $Ru_3(CO)_{12}$-catalyzed dehydrogenative *N*-silylation of indoles, pyrrole, and carbazole with hydrosilanes.[a]



[a]Conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), toluene (2 mL), isolated yields are given.
[b]5 mol % of $Ru_3(CO)_{12}$ wad used.

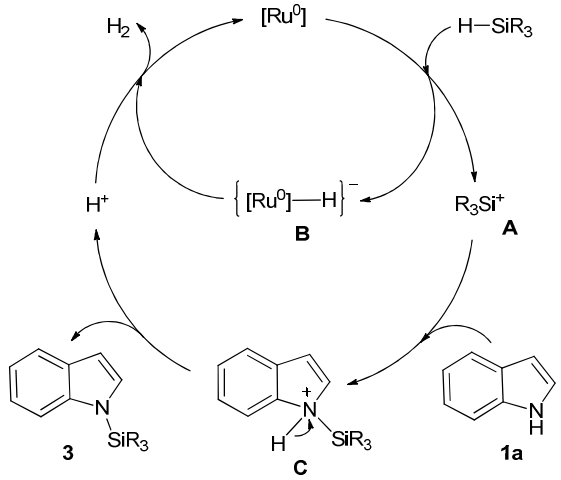
Besides indole derivatives, pyrrole and carbazole were also silylated to afford the corresponding *N*-silylated products in moderate to high yields (Table 2, **3h** and **3t**). Subsequently, we investigated the effect of different hydrosilanes as silylating reagents for the coupling reaction. The results showed that dimethylphenylsilane and triphenylsilane could also afford the corresponding *N*-silylated indoles in moderate to high yields (Table 2, **3f, 3g**, and **3y**), whereas triethylsilane did not react even at higher temperature. It illustrated that an aromatic group at silicon is essential for the reaction. Triphenylsilane conducted in a depressed yield likely due to the steric hindrance.

With the extensive functional groups adaptability in hand, we did several gram-scale transformation for indoles with C4, C5, and C6 bromo/methoxy-substituents to further demonstrate the practicability of this catalytic reaction, which afforded the corresponding target products **3** in 90–97% yields (Scheme 2). The further C–C bond formation reactions have been proved feasible,[7] which demonstrates that *N*-($SiMePh_2$)indoles can serve as useful intermediates for further synthetic transformations.



Scheme 2. Gram-scale preparation of *N*-silylated indoles.

According to our results and the previous reports,[7,8,9,11] a plausible mechanism for this coupling reaction is described in Scheme 3. Initially, silyl cation (**A**) and [Ru]–H intermediate (**B**) would be formed by the reaction of $Ru_3(CO)_{12}$ with a hydrosilane. Subsequently, a nucleophilic attack of the nitrogen atom of indole to **A** happened, and followed by deprotonation to afford the target compound **3**. Meanwhile, complex **B** would react with H^+ to regenerate Ru(0) catalyst by release a H_2. It explained why the aromatic group in the hydrosilanes is important to the reaction, because the silyl cation with an aromatic group is more stable and easily to be formed.[12]



Scheme 3 A plausible reaction mechanism for the dehydrogenative *N*-silylation of indoles; [Ru^0] = $Ru_3(CO)_{12}$.

3. Conclusions

In summary, we developed an efficient $Ru_3(CO)_{12}$-catalyzed dehydrogenative Si–N coupling of indoles with hydrosilanes. This catalytic reaction has a broad substrate range including indole derivatives, pyrrole, and carbazole, excellent functional group tolerance, and high to excellent reaction efficiency. Gram-scale preparation of *N*-silylated indoles with various bromo/methoxy-substituents demonstrated the practicability of this synthetic method. A plausible mechanism involving Ru–H species and silyl cation is proposed.

4. Experimental

4.1. General information

All reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H (400 MHz), ^{19}F (376 MHz), and ^{13}C NMR (100 MHz) NMR spectra were recorded on a Bruker AV400 NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{19}F, and ^{13}C NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities were reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Column chromatography was performed on silica gel 200–300 mesh. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High-resolution mass spectrometry (HRMS) was done on a Varian 7.0 T FTICR-mass spectrometer. $Ru_3(CO)_{12}$ was prepared from $RuCl_3.xH_2O$ following a literature procedure.[13] Indoles, pyrrole, carbazole, and silanes are commercially available from Alfa Aesar China (Tianjin) Chemical Co., Ltd. and used as received without any further purification.

4.2 General Procedure for $Ru_3(CO)_{12}$-Catalyzed Dehydrogenative Si–N Coupling.

Condition A: A mixture of indole (**1**) (0.2 mmol, 1 equiv), hydrosilane (**2**) (0.3 mmol, 1.5 equiv), $Ru_3(CO)_{12}$ (1.9 mg, 0.003 mmol, 1.5 mol %), were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (2.0 mL) was added and the mixture was stirred at 120 °C for 12 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a 50 mL round bottom flask. Silica was added to the flask and solvents were evaporated under reduced pressure. Flash column chromatography on silica gel with EtOAc:petroleum ether = 1:100 as eluent afforded the *N*-silylated indole.

Condition B: A mixture of indole (**1**) (0.2 mmol, 1equiv), hydrosilanes (**2**) (0.3 mmol, 1.5 equiv), $Ru_3(CO)_{12}$ (3.8 mg, 0.006 mmol, 3.0 mol %), were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (2.0 mL) was added and the mixture was stirred at 120 °C for 12–24 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a 50 mL round bottom flask. Silica was added to the flask and solvents were evaporated under reduced pressure. Flash column chromatography on silica gel with EtOAc:petroleum ether = 1:100 as eluent afforded the *N*-silylated indole.

*4.2.1 1-(Methyldiphenylsilyl)-1H-indole (**3a**)*

White solid, 95% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 4H), 7.56 – 7.51 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 4H), 7.24 – 7.15 (m, 2H), 7.11 – 7.04 (m, 2H), 6.68 (d, *J* = 3.1 Hz, 1H), 1.13 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.5, 134.8, 133.2, 131.7, 131.4, 130.5, 128.2, 121.4, 120.6, 120.1, 113.8, 105.1, –2.5. The NMR data were in agreement with reported results.[7]

*4.2.2 4-Methoxy-1-(methyldiphenylsilyl)-1H-indole (**3b**)*

White solid, 97% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 – 7.50 (m, 4H), 7.50 – 7.44 (m, 2H), 7.42 – 7.37 (m, 4H), 6.98 – 6.88 (m, 2H), 6.78 – 6.69 (m, 2H), 6.53 (d, *J* = 7.8 Hz, 1H), 3.95 (s, 3H), 1.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.2, 142.0, 134.9, 133.3, 130.5, 130.0, 128.2, 122.2, 122.1, 107.3, 102.2, 100.0, 55.2, –2.5. The NMR data were in agreement with reported results.[7]

*4.2.3 5-Methoxy-1-(methyldiphenylsilyl)-1H-indole (**3c**)*

White solid, 98% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 – 7.56 (m, 4H), 7.55 – 7.49 (m, 2H), 7.48 – 7.40 (m, 4H), 7.17 (d, *J* = 2.5 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.73 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.60 (d, *J* = 3.1 Hz, 1H), 3.87 (s, 3H), 1.10 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.3, 135.5, 134.8, 133.3, 132.2, 130.5, 128.2, 114.3, 111.3, 105.0, 102.4, 55.6, –2.5. The NMR data were in agreement with reported results.[7]

*4.2.4 5-Methyl-1-(methyldiphenylsilyl)-1H-indole (**3d**)*

White solid, 92% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (dd, *J* = 6.5, 1.4 Hz, 4H), 7.56 – 7.48 (m, 3H), 7.48 – 7.40 (m, 4H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 3.1 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 2.5 Hz, 1H), 2.47 (s, 3H), 1.10 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.8, 134.8, 133.8, 132.0, 131.5, 130.4, 129.3, 128.2, 123.0, 120.4, 113.4, 104.7, 21.3, –2.5. The NMR data were in agreement with reported results.[7]

*4.2.5 6-Methyl-1-(methyldiphenylsilyl)-1H-indole (**3e**)*

White solid, 92% yield. Mp: 98–100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 – 7.52 (m, 5H), 7.52 – 7.47 (m, 2H), 7.45 – 7.39 (m, 4H), 7.00 – 6.89 (m, 3H), 6.57 (dd, *J* = 3.2, 0.7 Hz, 1H), 2.31 (s, 3H), 1.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.0, 134.9, 133.4, 131.0, 130.9, 130.4, 129.4, 128.2, 121.8, 120.2, 113.8, 104.9, 21.8, –2.4. HRMS (ESI): Calcd for $C_{22}H_{21}NSi$ $[M+H]^+$ 328.1522, found: 328.1516.

*4.2.6 1-(Dimethyl(phenyl)silyl)-1H-indole (**3f**)*

White solid, 85% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (dd, *J* = 6.9, 1.4 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.46 – 7.36 (m, 3H), 7.29 – 7.26 (m, 1H), 7.16 (d, *J* = 3.2 Hz, 1H), 7.14 – 7.03 (m, 2H), 6.63 (dd, *J* = 3.2, 0.7 Hz, 1H), 0.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.2, 135.2, 133.8, 131.6, 130.4, 130.2, 128.2, 121.4, 120.7, 119.9, 113.3, 104.9, –1.3. The NMR data were in agreement with reported results.[7]

*4.2.7 1-(Dimethyl(phenyl)silyl)-7-methoxy-1H-indole (**3g**)*

White solid, 90% yield. Mp: 55–57 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.42 – 7.31 (m, 3H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.60 – 6.52 (m, 2H), 3.60 (s, 3H), 0.77 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.4, 137.9, 133.4, 133.2, 131.7, 130.7, 129.3, 127.7, 120.7, 113.3, 104.6, 102.1, 54.1, 0.3. HRMS (ESI): Calcd for $C_{17}H_{19}NOSi$ $[M+H]^+$ 282.1314, found: 282.1311.

*4.2.8 1-(Dimethyl(phenyl)silyl)-1H-pyrrole (**3h**)*

White solid, 91% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 – 7.46 (m, 2H), 7.45 – 7.34 (m, 3H), 6.81 (s, 2H), 6.41 – 6.30 (m, 2H), 0.70 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.5, 133.6, 130.2, 128.0, 123.7, 111.0, –1.7. The NMR data were in agreement with reported results.[8]

*4.2.9 4-Chloro-1-(methyldiphenylsilyl)-1H-indole (**3i**)*

White solid, 91% yield. Mp: 75–77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 – 7.48 (m, 6H), 7.46 – 7.39 (m, 4H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.08 – 7.00 (m, 2H), 6.93 (t, *J* = 7.9 Hz, 1H), 6.74 (d, *J* = 3.2 Hz, 1H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.2, 134.8, 132.7, 132.0, 130.7, 130.5, 128.3, 125.8, 122.0, 119.9, 112.3, 103.7, –2.6. HRMS (ESI): Calcd for $C_{21}H_{18}ClNSi$ $[M+H]^+$ 348.0975, found: 348.0969.

*4.2.10 5-Chloro-1-(methyldiphenylsilyl)-1H-indole (**3j**)*

White solid, 95% yield. Mp: 99–101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, *J* = 1.9 Hz, 1H), 7.57 – 7.47 (m, 6H), 7.45 – 7.39 (m, 4H), 7.05 – 6.99 (m, 2H), 6.95 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.56 (d, *J* = 3.2 Hz, 1H), 1.06 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.9, 134.8, 132.9, 132.8, 130.7, 128.3, 125.9, 121.7, 120.0, 114.6, 104.8, –2.6. HRMS (ESI): Calcd for $C_{21}H_{18}ClNSi$ $[M+H]^+$ 348.0975, found: 348.0961.

*4.2.11 6-Bromo-1-(methyldiphenylsilyl)-1H-indole (**3k**)*

White solid, 91% yield. Mp: 123–125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 – 7.48 (m, 7H), 7.46 – 7.40 (m, 4H), 7.25 – 7.19 (m, 2H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.58 (d, *J* = 2.5 Hz, 1H), 1.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.4, 134.8, 132.7, 132.2, 130.7, 130.5, 128.3, 123.4, 121.7, 116.5, 115.0, 105.1, –2.5. HRMS (ESI): Calcd for $C_{21}H_{18}BrNSi$ $[M+H]^+$ 392.0470, found: 392.0460.

4.2.12 4-Bromo-1-(methyldiphenylsilyl)-1H-indole (**3l**)

White solid, 90% yield. Mp: 120–122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 – 7.45 (m, 6H), 7.42 – 7.37 (m, 4H), 7.24 (d, *J* = 1.9 Hz, 1H), 7.03 (dd, *J* = 5.8, 2.5 Hz, 2H), 6.84 (t, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 3.2 Hz, 1H), 1.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.7, 134.8, 132.7, 132.4, 132.0, 130.7, 128.3, 123.0, 122.4, 114.4, 112.9, 105.4, –2.5. HRMS (ESI): Calcd for $C_{21}H_{18}BrNSi$ $[M+H]^+$ 392.0470, found: 392.0459.

*4.2.13 1-(Methyldiphenylsilyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (**3m**)*

White solid, 85% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (s, 1H), 7.56 – 7.50 (m, 4H), 7.47 (t, *J* = 7.4 Hz, 3H), 7.39 (t, *J* = 7.5 Hz, 4H), 7.11 (d, *J* = 8.3 Hz, 1H), 6.98 (d, *J* = 3.2 Hz, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 1.34 (s, 12H), 1.06 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.7, 134.8, 133.1, 131.4, 130.5, 128.4, 128.2, 127.5, 113.3, 105.5, 83.3, 24.8, –2.5. The NMR data were in agreement with reported results.[7]

*4.2.14 5-Bromo-1-(methyldiphenylsilyl)-1H-indole (**3n**)*

White solid, 95% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 1.9 Hz, 1H), 7.55 – 7.47 (m, 6H), 7.45 – 7.38 (m, 4H), 7.09 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.01 (d, *J* = 3.2 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.55 (d, *J* = 3.2 Hz, 1H), 1.06 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.2, 134.8, 133.5, 132.7, 130.7, 128.3, 124.3, 123.2, 115.1, 113.5, 104.7, –2.6. The NMR data were in agreement with reported results.[7]

*4.2.15 4-Fluoro-1-(methyldiphenylsilyl)-1H-indole (**3o**)*

White solid, 91% yield. Mp: 76–78 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 – 7.47 (m, 6H), 7.46 – 7.39 (m, 4H), 6.98 – 6.95 (m, 1H), 6.95 – 6.86 (m, 2H), 6.82 – 6.74 (m, 1H), 6.70 (d, *J* = 3.2 Hz, 1H), 1.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.5, 155.1, 143.2, 143.1, 134.8, 133.9, 132.8, 131.3, 130.7, 128.3, 121.9, 121.8, 120.8, 120.6, 109.9, 105.0, 104.9, 100.9, –2.6. ^{19}F NMR ($CDCl_3$, 376 MHz): δ –126.64. HRMS (ESI): Calcd for $C_{21}H_{18}FNSi$ $[M+H]^+$ 332.1271, found: 332.1261.

*4.2.16 5-Fluoro-1-(methyldiphenylsilyl)-1H-indole (**3p**):*

White solid, 95% yield. Mp: 92–94 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 – 7.49 (m, 6H), 7.49 – 7.39 (m, 4H), 7.33 – 7.28 (m, 1H), 7.07 (d, *J* = 3.2 Hz, 1H), 7.03 (dd, *J* = 8.9, 4.4 Hz, 1H), 6.78 (td, *J* = 9.1, 2.5 Hz, 1H), 6.60 (d, *J* = 3.2 Hz, 1H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.2, 156.9, 137.0, 134.8, 133.3, 132.9, 132.2, 132.1, 130.6, 128.3, 114.3, 114.2, 109.8, 109.5, 105.6, 105.3, 105.2, 105.2, –2.5. ^{19}F NMR ($CDCl_3$, 376 MHz): δ –124.25. HRMS (ESI): Calcd for $C_{21}H_{18}FNSi$ $[M+H]^+$ 332.1271, found: 332.1265.

*4.2.17 6-Fluoro-1-(methyldiphenylsilyl)-1H-indole (**3q**)*

Colorless liquid, 93% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 – 7.46 (m, 7H), 7.45 – 7.38 (m, 4H), 6.98 (d, *J* = 3.2 Hz, 1H), 6.92 – 6.82 (m, 1H), 6.77 (dd, *J* = 10.5, 1.7 Hz, 1H), 6.58 (d, *J* = 3.1 Hz, 1H), 1.06 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.4, 158.1, 140.6, 140.5, 134.8, 133.9, 132.7, 131.7, 130.7, 128.3, 121.0, 120.9, 108.9, 108.6, 105.0, 100.3, 100.1, –2.6. ^{19}F NMR ($CDCl_3$, 376 MHz): δ –120.81. HRMS (ESI): Calcd for $C_{21}H_{18}FNSi$ $[M+H]^+$ 332.1271, found: 332.1263.

*4.2.18 5-Iodo-1-(methyldiphenylsilyl)-1H-indole (**3r**)*

White solid, 80% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, *J* = 1.6 Hz, 1H), 7.56 – 7.46 (m, 6H), 7.45 – 7.38 (m, 4H), 7.26 – 7.23 (m, 1H), 6.97 (d, *J* = 3.2 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.57 – 6.50 (m, 1H), 1.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.7, 134.8, 134.3, 132.7, 132.3, 130.7, 129.8, 129.5, 128.3, 115.7, 104.4, 84.0, –2.6. The NMR data were in agreement with reported results.[7]

*4.2.19 3-Methyl-1-(methyldiphenylsilyl)-1H-indole (**3s**)*

White solid, 88% yield. Mp: 98–100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 – 7.56 (m, 5H), 7.54 – 7.48 (m, 2H), 7.47 – 7.38 (m, 4H), 7.20 – 7.10 (m, 2H), 7.08 – 7.02 (m, 1H), 6.80 (s, 1H), 2.33 (s, 3H), 1.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 134.8, 133.6, 132.2, 130.4, 128.5, 128.2, 121.4, 119.5, 118.8, 114.0, 113.7, 9.6, –2.4. HRMS (ESI): Calcd for $C_{22}H_{21}NSi$ $[M+H]^+$ 328.1522, found: 328.1516.

*4.2.20 9-(Methyldiphenylsilyl)-9H-carbazole (**3t**)*

White solid, 65% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 – 8.11 (m, 2H), 7.71 – 7.64 (m, 4H), 7.59 – 7.53 (m, 2H), 7.50 – 7.44 (m, 4H), 7.29 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 1.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.4, 134.9, 134.2, 133.9, 130.5, 128.4, 127.7, 126.4, 125.2, 119.7, 114.1, –1.3. The NMR data were in agreement with reported results.[7]

*4.2.21 1-(Methyldiphenylsilyl)-1H-indol-4-amine (**3u**)*

Colorless liquid, 69% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62 – 7.52 (m, 4H), 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 4H), 6.91 (d, *J* = 3.3 Hz, 1H), 6.89 – 6.83 (m, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 3.3 Hz, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 3.95 (s, 2H), 1.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.6, 138.9, 134.8, 133.2, 130.4, 129.8, 128.2, 122.5, 120.9, 105.5, 104.9, 101.3, -2.6. HRMS (ESI): Calcd for $C_{21}H_{20}N_2Si$ $[M+H]^+$ 328.1396, found: 329.1472

*4.2.22 1-(Methyldiphenylsilyl)-1H-indol-5-amine (**3v**)*

White solid, 83% yield. Mp: 113–115 °C ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 – 7.51 (m, 4H), 7.50 – 7.45 (m, 2H), 7.43 – 7.36 (m, 4H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.48 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.45 (d, *J* = 3.1 Hz, 1H), 3.49 (s, 2H), 1.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.5, 135.2, 134.8, 133.4, 132.6, 132.0, 130.4, 128.2, 114.2, 112.1, 105.7, 104.3, -2.5. HRMS (ESI): Calcd for $C_{21}H_{20}N_2Si$ $[M+H]^+$ 328.1396, found: 329.1473

*4.2.23 1-(Methyldiphenylsilyl)-1H-indol-4-ol (**3w**)*

Colorless liquid, 70% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (s, 1H), 7.74 (d, *J* = 6.4 Hz, 4H), 7.49 – 7.37 (m, 6H), 7.12 – 7.07 (m, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.98 – 6.90 (m, 1H), 6.61 (s, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 0.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.4, 137.7, 136.0, 134.3, 129.9, 127.9, 122.7, 122.5, 121.4, 108.7, 104.9, 100.3, -2.6. HRMS (ESI): Calcd for $C_{21}H_{19}NOSi$ $[M+H]^+$ 329.1236, found: 330.1310

*4.2.24 1-(Methyldiphenylsilyl)-1H-indol-6-ol (**3x**)*

Colorless liquid, 80% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 1H), 7.70 (dd, *J* = 7.8, 1.6 Hz, 4H), 7.46 – 7.37 (m, 7H), 7.10 – 7.01 (m, 1H), 6.83 (d, *J* = 1.9 Hz, 1H), 6.74 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.48 – 6.42 (m, 1H), 0.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.1, 135.8, 134.4, 133.9, 130.0, 127.9, 123.3, 122.8, 120.9, 114.2, 102.4, 101.5, -2.5. HRMS (ESI): Calcd for $C_{21}H_{19}NOSi$ $[M+H]^+$ 329.1236, found:330.1310

*4.2.25 1-(Triphenylsilyl)-1H-indole (**3y**)*

White solid, 65% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 6.7 Hz, 6H), 7.57 – 7.48 (m, 3H), 7.43 (t, *J* = 7.2 Hz, 6H), 7.15 (t, *J* = 6.9 Hz, 1H), 7.05 – 6.92 (m, 3H), 6.67 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 135.9, 132.2, 131.7, 131.6, 130.6, 128.2, 121.4, 120.5, 120.2, 114.7, 105.4. The NMR data were in agreement with reported results.[8]

*4.3 Gram-scale synthesis of **3b** and **3c***

A mixture of indole (6 mmol, 1 equiv), hydrosilane (**2**) (9 mmol, 1.5 equiv), $Ru_3(CO)_{12}$ (57 mg, 0.09 mmol, 1.5 mol %), were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (20 mL) was added and the mixture was stirred at 120 °C for 12 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a 100 mL round bottom flask. Silica was added to the flask and solvents were evaporated under reduced pressure. Flash column chromatography on silica gel with EtOAc:petroleum ether = 1:100 as eluent afforded the *N*-silylated indole. in.95–97% yield.

*4.4 Gram-scale synthesis of **3l**, **3k**, and **3n***

A mixture of indole (6 mmol, 1 equiv), hydrosilane (2) (9 mmol, 1.5 equiv), $Ru_3(CO)_{12}$ (114 mg, 0.18 mmol, 3.0 mol %), were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (20 mL) was added and the mixture was stirred at 120 °C for 12 h under Ar atmosphere. Afterwards, it was diluted with CH_2Cl_2 and transferred to a 100 mL round bottom flask. Silica was added to the flask and solvents were evaporated under reduced pressure. Flash column chromatography on silica gel with EtOAc:petroleum ether = 1:100 as eluent afforded the *N*-silylated indole in 90–94% yields.

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