

Palladium(0)-Catalyzed Si—Si Bond Insertion by the Terminal Nitrogen of Diazo Compounds†

Zhenxing Liu,^a Tianren Fu,^a Jingfeng Huo,^a Sheng Feng,^a and Jianbo Wang^{*,a}

ABSTRACT The palladium(0)-catalyzed nitrogen insertion into cyclic Si—Si bonds has been realized by using *N*-tosylhydrazones/diazo compounds as the nitrogen source. The palladium(II) nitrene formation and subsequent migratory insertion process are proposed as the key steps for this reaction.

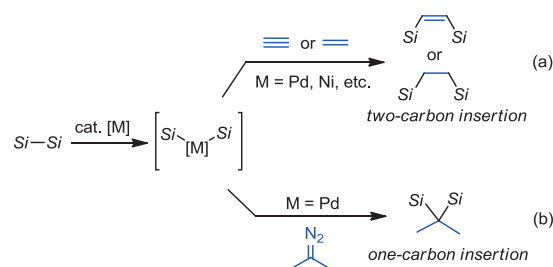
KEYWORDS insertion, diazo compounds, Si—Si bond, palladium catalysts, palladium(II) nitrene, carbenes

Introduction

The activation of inert σ bonds represents one of the most exciting fields in modern organic chemistry.^[1] Among the various inert σ bond activations developed in recent years, the transition-metal-catalyzed Si—Si bond activation followed by subsequent addition to unsaturated organic molecules has emerged as a useful way to synthesize various organosilicon compounds.^[2] This type of transformation follows the common mechanism which includes: 1) oxidative addition of Si—Si bond to transition-metal catalysts; 2) coordination of the organometallic species followed by migratory insertion to unsaturated organic molecules; 3) reductive elimination to complete the catalytic cycle (Scheme 1, a). These reactions have been extensively studied and have found applications in organic synthesis.^[3] However, the coupling partners with Si—Si bonds are limited to alkynes or alkenes, which affords two-carbon unit insertion products. Recently, we have reported a Pd(0)-catalyzed carbene insertion into Si—Si bonds, from which geminal bis(silane) derivatives could be obtained efficiently under mild conditions (Scheme 1, b).^[4] In contrast to the classic Si—Si bonds insertion into alkyne or alkene bonds, the one-carbon unit insertion with diazo compounds is featured by the formation of Pd carbene, followed by similar migratory insertion and reductive elimination.

In our previous investigation, the Si—Si reagent was limited to $\text{FMe}_2\text{Si-SiMe}_2\text{F}$.^[4] To further demonstrate the generality of this type of carbene insertion reactions, we have conceived to extend the Si—Si reagent to cyclic Si—Si compounds, with the expectation that ring-enlargement products will be obtained. However, to our surprise the reaction afforded the products which are generated from Si—Si bond insertion by the terminal nitrogen of diazo substrate,^[5] rather than the anticipated carbene insertion. Herein we report the details of this investigation.

Scheme 1 Transition-metal-catalyzed Si—Si bond insertions



Results and Discussion

Initially, we intended to develop the Pd(0)-catalyzed carbene insertion into the cyclic Si—Si bonds. However, when we carried out the reaction of *N*-tosylhydrazone **1a**^[6] with cyclic disilane **2a** in the presence of $\text{Pd}(\text{PPh}_3)_4$ catalyst and 3 equiv. of Cs_2CO_3 , the nitrogen insertion product **3a** instead of the carbene insertion product was obtained in 93% yield (eq. 1). The structure of **3a** was established by spectroscopic data and was unambiguously confirmed by X-ray diffraction of single crystal (Figure 1).^[7]

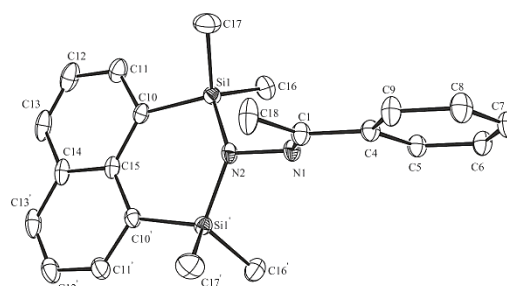
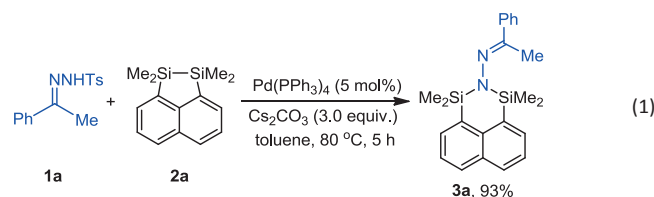
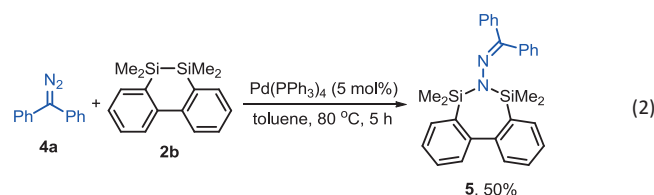


Figure 1 X-ray structure of **3a**. Thermal ellipsoids shown at 30% probability.

Furthermore, we found that the reaction was also applicable to the six-membered cyclic disilane and diazo substrate. Thus, diaryldiazomethane **4a** was subjected to the reaction with **2b** in the presence of $\text{Pd}(\text{PPh}_3)_4$ catalyst. The reaction afforded the seven-membered disilaheterocycle **5** in 50% yields (eq. 2).



Based on our previous investigation on carbene Si—Si bond

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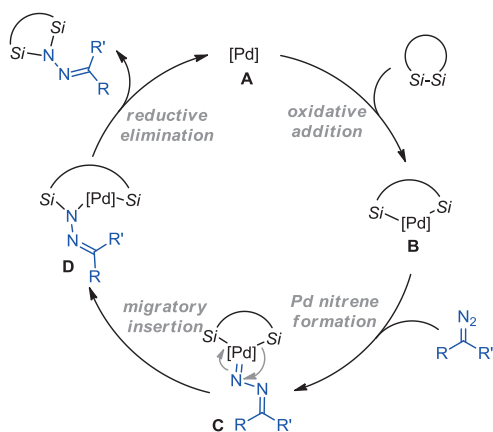
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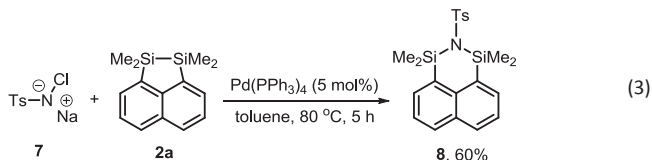
† Dedicated to Professor Xiyan Lu on the occasion of his 90th birthday.

insertion,^[4] we proposed a similar mechanism as shown in Scheme 2. Oxidative addition of Si—Si bond to Pd(0) generates intermediate **B**. Subsequently, **B** reacts with diazo compound to generate a Pd(II) nitrene species **C**. Finally, silyl migratory insertion followed by reductive elimination affords the Si—Si bond insertion product and regenerates the catalyst.

Scheme 2 Proposed reaction mechanism

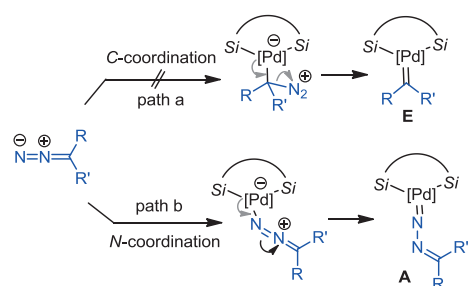


In this proposed mechanism, the first and last step have been known before,^[4] while the Pd(II) nitrene formation and subsequent silyl migratory insertion process are unprecedented for catalytic reactions.^[8] To substantiate the proposed mechanism, we carried out the reaction with a generally used nitrene precursor **7** (Chloramine-T) under the similar conditions. The reaction indeed afforded the anticipated Si—Si bond nitrogen insertion product **8** in 60% yield (eq. 3). This result provides supportive evidence for the proposed reaction mechanism and indicates that palladium nitrene insertion into Si—Si bonds may be a general process.



An intriguing question is why the reaction shown in eq. 1 and eq. 2 only affords nitrogen insertion products without any carbene insertion products, given the fact that Pd(II) carbene formation from diazo compounds and subsequent migratory insertion has been established as a general type of transformations.^[9–11] We have reasoned that the exclusive nitrogen insertion in the current reaction may be attributed to steric effects. As shown in Scheme 3, the Pd(II) complex generated from the oxidative addition of Si—Si bond to Pd(0) has crowded surroundings, which may hinder the approach of the carbon attached to the dinitrogen to undergo further Pd(II) carbene formation through dinitrogen

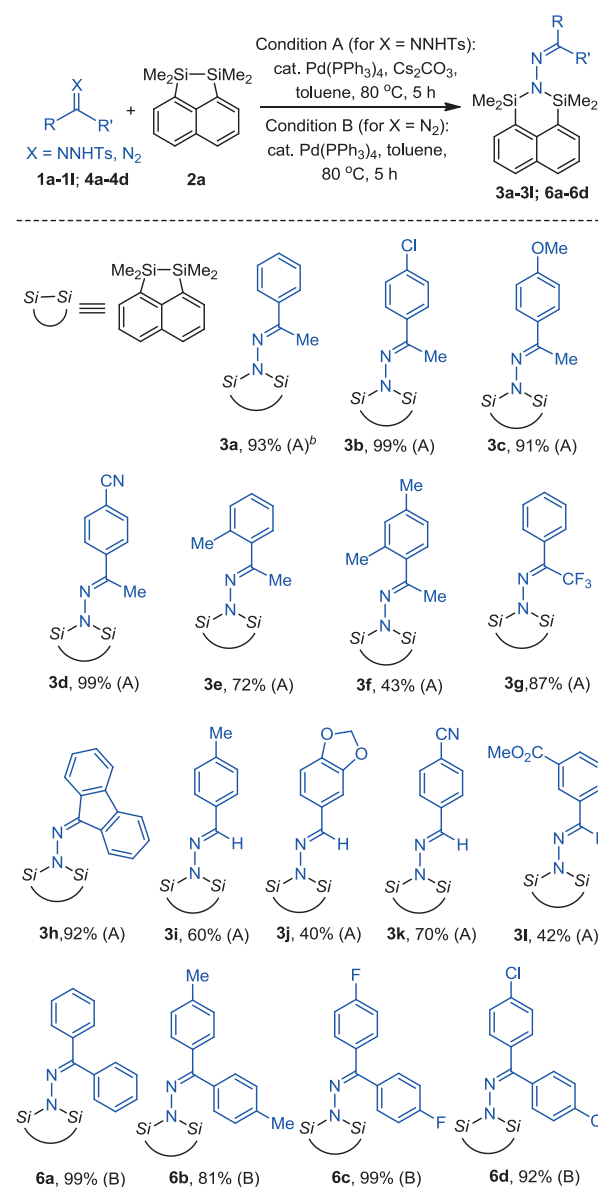
Scheme 3 Rationalization of exclusive nitrogen insertion



extrusion (path a). Instead, the sterically less crowded terminal nitrogen coordinates to the Pd(II), generating Pd(II) nitrene intermediate with the retention of dinitrogen moiety (path b).^[12] However, further theoretical and experimental studies are needed to substantiate this reasoning.

Since this transformation is a new type of Si—Si bond insertion reactions, we then proceeded to study the generality of the reaction by examining a series of *N*-tosylhydrazones and diazo substrates (Scheme 4). It turned out that *N*-tosylhydrazones derived from acetophenones bearing *para*-substituents (**1b–1d**) were excellent substrates. However, the insertion reaction showed low efficiency for *ortho*-substituted acetophenone *N*-tosylhydrazones (**1e–1f**), presumably due to steric hindrance. This is consistent with the rationalization of the nitrogen insertion as shown in Scheme 3. Notably, *N*-tosylhydrazones derived from trifluoroac-

Scheme 4 Scope of the reaction^a



^a Condition A: *N*-tosylhydrazone **1a–1f** (0.1 mmol), **2a** (0.1 mmol), Pd(PPh₃)₄ (0.005 mmol) and Cs₂CO₃ (0.3 mmol) in toluene (1.0 mL) at 80 °C for 5 h; Condition B: Diazo substrate **4a–4d** (0.1 mmol), **2a** (0.1 mmol), and Pd(PPh₃)₄ (0.005 mmol) in toluene (1.0 mL) at 80 °C for 5 h. All the yields refer to the products isolated by silica gel column chromatography.
^b The reaction conditions are indicated in the parenthesis.

tophenone (**1g**) and fluorenone (**1h**) reacted smoothly under the current conditions to afford the corresponding products **3g** and **3h** in excellent yields. The *N*-tosylhydrazones derived from aromatic aldehydes (**1i**–**1l**) were highly reactive under the basic conditions. The diminished yields in these cases are due to the increased side reactions.

In addition to *N*-tosylhydrazones, diaryldiazomethanes (**4a**–**4d**) were also subjected to the current reaction. The corresponding Si—Si insertion products **6a**–**6d** were isolated in excellent yields. The reaction with donor-acceptor diazo compounds is also tested, but they gave the corresponding Si—Si insertion products in diminished yields together with unidentified side products. The structure of **6a** was also confirmed by X-ray diffraction (Figure 2).^[7]

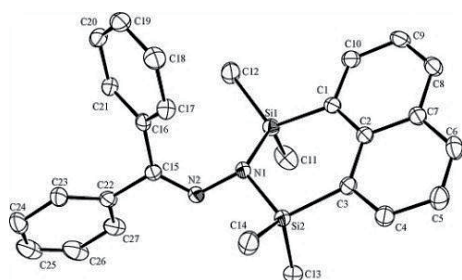


Figure 2 X-ray structure of **6a**. Thermal ellipsoids shown at 30% probability.

Conclusions

In conclusion, we have reported the first Pd(0)-catalyzed nitrogen insertion into Si—Si bonds. This reaction further highlights the insertion reaction as a unique method to functionalize σ bonds, such as Si—Si bonds. Furthermore, this study demonstrates that *N*-tosylhydrazones and diazo compounds may serve as nitrene sources in palladium-catalyzed reactions, which may open up new possibilities in the future studies.^[13]

Experimental

General

All the reactions were performed under nitrogen atmosphere in an oven-dried reaction flask. 1,4-Dioxane, toluene and THF were distilled over Na with benzophenone-ketyl intermediate as indicator. 200–300 mesh silica gels for the chromatography (Qingdao, China) were used. Melting points were measured on a SGW X-4 microscopic melting point instrument and were uncorrected. ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as the internal standard and CDCl₃ as the solvent. IR spectra were recorded with a Nicolet 5MX-S infrared spectrometer. HRMS were obtained on a Bruker Apex IV FTMS. The aldehydes and ketones were purchased from commercial sources and were used without further purification.

N-Tosylhydrazones **1a**–**1l**, diazo compounds **4a**–**4d**, and the cyclic disilanes **2a** and **2b** were prepared according to literature procedures.

1,1,2,2-Tetramethyl-1,2-dihydronaphtho[1,8-*cd*][1,2]disilole (2a).^[14] ¹H NMR (400 MHz, CDCl₃) δ : 7.84 (dd, J =1.0, 8.2 Hz, 2H), 7.74 (dd, J =1.1, 6.6 Hz, 2H), 7.50 (dd, J =6.7, 8.2 Hz, 2H), 0.41 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ : 143.73, 138.39, 132.48, 131.48, 128.86, 125.68, –3.34.

5,5,6,6-Tetramethyl-5,6-dihydrodibenzo[*c,e*][1,2]disilane (2b).^[14] ¹H NMR (400 MHz, CDCl₃) δ : 7.50 (d, J =7.2 Hz, 2H), 7.43 (d, J =3.9 Hz, 1H), 7.30–7.28 (m, 2H), 7.60–7.49 (m, 3H), 0.22 (s, 12H);

¹³C NMR (100 MHz, CDCl₃) δ : 147.35, 135.50, 133.27, 129.85, 129.75, 126.49, –5.42.

General procedure for the Pd(0)-catalyzed nitrogen insertion into cyclic Si—Si bonds with *N*-tosylhydrazones or diazo compounds as nitrogen source

Condition A: To a mixture of cyclic disilane (0.1 mmol), *N*-tosylhydrazone^[15] (0.1 mmol), LiO^tBu (0.3 mmol) and Pd(PPh₃)₄ (0.005 mmol) in 10 mL Schlenk tube was added dry toluene (1.0 mL) under N₂ atmosphere. The solution was stirred for 5 h at 80 °C. The crude mixture was purified by silica gel (saturated with NEt₃) column chromatography to give the nitrogen insertion product.

Condition B: To a mixture of cyclic disilane (0.1 mmol), diazo compound (0.1 mmol) and Pd(PPh₃)₄ (0.005 mmol) in 10 mL Schlenk tube was added dry toluene (1.0 mL) under N₂ atmosphere. The solution was stirred for 5 h at 80 °C. The crude mixture was purified by silica gel (saturated with NEt₃) column chromatography to give the nitrogen insertion product.

Phenyl-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]-azadisilin-2(3*H*)-yl)ethan-1-imine (3a). 93%, white solid, m.p. 193–196 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.92–7.89 (m, 4H), 7.72 (dd, J =1.3, 6.7 Hz, 2H), 7.52 (dd, J =6.8, 8.1 Hz, 2H), 7.45–7.43 (m, 3H), 2.37 (s, 3H), 0.37 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ : 172.52, 139.85, 139.12, 137.82, 133.23, 132.85, 130.38, 129.66, 128.26, 126.65, 124.98, 15.73, 0.17.

1-(4-Chlorophenyl)-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)ethan-1-imine (3b). 99%, white solid, m.p. 208–211 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.91 (d, J =7.6 Hz, 2H), 7.84 (d, J =8.6 Hz, 2H), 7.72–7.70 (m, 2H), 7.54–7.50 (m, 2H), 7.40 (d, J =8.5 Hz, 2H), 2.34 (s, 3H), 0.36 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ : 171.37, 139.84, 137.63, 137.41, 135.77, 133.25, 132.88, 130.44, 128.44, 127.92, 125.00, 15.50, 0.16; HRMS (ESI, m/z): calcd for C₂₂H₂₆³⁵ClN₂Si₂[M+H]⁺ 409.1318, found 409.1327; IR (film) ν : 788, 824, 1007, 1066, 1253 cm^{–1}.

1-(4-Methoxyphenyl)-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)ethan-1-imine (3c). 91%, white solid, m.p. 196–198 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.91–7.86 (m, 4H), 7.71 (dd, J =1.2, 6.7 Hz, 2H), 7.51 (dd, J =6.9, 8.0 Hz, 2H), 6.95 (d, J =8.9 Hz, 2H), 3.86 (s, 3H), 2.33 (s, 3H), 0.36 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ : 171.56, 160.93, 139.90, 137.99, 133.21, 132.88, 131.83, 130.34, 128.06, 124.97, 113.55, 55.36, 15.43, 0.16; HRMS (ESI, m/z): calcd for C₂₃H₂₉N₂O₂Si₂ [M+H]⁺ 405.1812, found 405.1824; IR (film) ν : 791, 934, 1253, 1514, 1609, 2081 cm^{–1}.

4-(1-((1,1,3,3-Tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)imino)ethyl)benzotrile (3d). 99%, yellow solid; m.p. 249–251 °C; ¹H NMR (400 MHz, CDCl₃) δ : 8.00 (d, J =8.5 Hz, 2H), 7.91 (dd, J =1.0, 8.2 Hz, 2H), 7.72 (d, J =8.2 Hz, 2H), 7.53 (dd, J =6.9, 8.1 Hz, 4H), 2.37 (s, 3H), 0.36 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ : 171.04, 142.90, 139.76, 137.25, 133.28, 132.88, 132.09, 130.54, 127.15, 125.04, 118.73, 113.12, 15.54, 0.17; HRMS (ESI, m/z): calcd for C₂₃H₂₆N₃Si₂ [M+H]⁺ 400.1660, found 400.1669; IR (film) ν : 734, 790, 908, 1252, 2231 cm^{–1}.

1-(2-Methylphenyl)-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)ethan-1-imine (3e). 72%, white solid; m.p. 135–137 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.91 (dd, J =0.8, 8.1 Hz, 2H), 7.73 (dd, J =1.0, 6.7 Hz, 2H), 7.52 (dd, J =7.0, 7.9 Hz, 2H), 7.26–7.25 (m, 4H), 2.46 (s, 3H), 2.28 (s, 3H), 0.43 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ : 177.31, 140.73, 139.85, 137.73, 134.72, 133.25, 132.88, 130.73, 130.41, 128.34, 127.66, 125.89, 125.01, 20.41, 19.89, 0.46; HRMS (ESI, m/z): calcd for C₂₃H₂₉N₂Si₂ [M+H]⁺ 389.1864, found 389.1870; IR (film) ν : 787, 824, 933, 1249 cm^{–1}.

1-(2,4-Dimethylphenyl)-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)ethan-1-imine (3f). 43%, white solid; m.p. 126–129 °C; ¹H NMR (400 MHz, CDCl₃) δ : 7.91 (dd, J =1.2, 8.2 Hz, 2H), 7.73 (dd, J =1.2, 6.7 Hz, 2H), 7.52 (dd, J =6.8, 8.1 Hz,

2H), 7.16 (d, $J=7.5$ Hz, 1H), 7.06 (d, $J=7.7$ Hz, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.27 (s, 3H), 0.42 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 177.09, 139.87, 138.12, 137.83, 134.71, 133.23, 132.88, 131.54, 130.38, 127.68, 126.48, 125.00, 21.11, 20.48, 19.82, 0.43; HRMS (ESI, m/z): calcd for $\text{C}_{24}\text{H}_{31}\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 403.2020, found 403.2027; IR (film) ν : 788, 818, 916, 942, 1248 cm^{-1} .

***N*-(1,1,3,3-Tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)-1-(2-(trifluoromethyl)phenyl)ethan-1-imine (3g).** 87%, pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.86–7.84 (m, 2H), 7.63–7.61 (m, 2H), 7.54 (d, $J=3.7$ Hz, 2H), 7.46 (dd, $J=7.1$, 7.9 Hz, 2H), 7.40–7.39 (m, 3H), 0.18 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 151.67 (q, $J=31.3$ Hz), 139.58, 137.44, 133.02, 132.62, 130.73, 130.44, 130.37, 129.89, 128.80, 125.12, 121.06 (q, $J=276.2$ Hz), 0.27; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{24}\text{F}_3\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 429.1425, found 429.1428; IR (film) ν : 789, 983, 1125, 1190, 1253, 1330 cm^{-1} .

***N*-(1,1,3,3-Tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)-9*H*-fluoren-9-imine (3h).** 92%, yellow solid; m.p. 210–212 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.54 (d, $J=7.7$ Hz, 1H), 8.01 (d, $J=7.4$ Hz, 1H), 7.96–7.94 (m, 2H), 7.75–7.73 (m, 2H), 7.62–7.52 (m, 4H), 7.46–7.42 (m, 1H), 7.33–7.28 (m, 2H), 6.99 (t, $J=7.6$ Hz, 1H), 0.37 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 169.08, 142.48, 141.03, 140.00, 137.71, 137.63, 133.36, 132.92, 131.32, 130.74, 130.52, 129.47, 128.04, 127.95, 125.09, 122.53, 119.61, 119.48, –0.01; HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{27}\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 435.1707, found 435.1703; IR (film) ν : 669, 731, 907, 988, 1254 cm^{-1} .

***N*-(1,1,3,3-Tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)-1-(*p*-tolyl)methanimine (3i).** 60% yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 8.22 (s, 1H), 7.90 (dd, $J=0.9$, 8.2 Hz, 2H), 7.76 (dd, $J=1.1$, 6.8 Hz, 2H), 7.59–7.51 (m, 4H), 7.20 (d, $J=7.9$ Hz, 2H), 2.38 (s, 3H), 0.56 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 145.63, 139.52, 138.50, 137.85, 133.65, 133.58, 132.73, 130.38, 129.23, 126.07, 125.06, 21.37, 1.43; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 375.1707, found 375.1714; IR (film) ν : 787, 823, 982, 1047, 1252 cm^{-1} .

1-(Benzo[d][1,3]dioxol-5-yl)-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)methanimine (3j). 40%, pale yellow solid; m.p. 164–166 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.16 (s, 1H), 7.90 (dd, $J=1.1$, 8.2 Hz, 2H), 7.75 (dd, $J=1.2$, 6.8 Hz, 2H), 7.53 (dd, $J=6.9$, 8.0 Hz, 2H), 7.36 (d, $J=1.4$ Hz, 1H), 6.98 (dd, $J=1.5$, 8.0 Hz, 1H), 6.82 (d, $J=7.9$ Hz, 1H), 5.99 (s, 2H), 0.55 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 148.16, 145.11, 139.50, 137.77, 133.58, 132.73, 131.13, 130.39, 125.06, 121.57, 108.04, 104.90, 101.13, 45.76, 1.42; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 405.1449, found 405.1454; IR (film) ν : 787, 1039, 1252, 1447, 1491 cm^{-1} .

4-(((1,1,3,3-Tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)imino)methyl)benzotrile (3k). 70%, white solid; m.p. 216–218 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.19 (s, 1H), 7.92 (d, $J=8.1$ Hz, 2H), 7.78–7.73 (m, 4H), 7.66 (m, 2H), 7.57–7.53 (t, $J=7.5$ Hz, 2H), 0.58 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 142.02, 140.59, 139.33, 137.01, 133.72, 132.75, 132.35, 130.65, 126.22, 125.15, 119.07, 111.19, 1.29; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{24}\text{N}_3\text{Si}_2$ $[\text{M}+\text{H}]^+$ 386.1503, found 386.1514; IR (film) ν : 779, 984, 1045, 1249, 1591, 2231 cm^{-1} .

Methyl 3-(((1,1,3,3-Tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)imino)methyl)benzoate (3l). 42%, white solid; m.p. 129–131 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.27 (s, 1H), 8.21 (s, 1H), 7.99 (dd, $J=1.5$, 7.8 Hz, 2H), 7.91 (dd, $J=0.9$, 8.2 Hz, 2H), 7.77 (dd, $J=1.1$, 6.8 Hz, 2H), 7.54 (dd, $J=6.8$, 8.0 Hz, 2H), 7.47 (t, $J=7.7$ Hz, 1H), 3.96 (s, 3H), 0.59 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 166.99, 143.70, 139.43, 137.50, 136.76, 133.66, 132.74, 130.49, 129.58, 129.37, 128.64, 127.76, 125.10, 52.21, 1.37; HRMS (ESI, m/z): calcd for $\text{C}_{23}\text{H}_{27}\text{N}_2\text{O}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 419.1606, found 419.1611; IR (film) ν : 788, 1051, 1209, 1286, 1724 cm^{-1} .

1,1-Diphenyl-*N*-(5,5,7,7-tetramethyl-5,7-dihydro-6*H*-dibenzo-

[*c,e*][1,2,7]azadisilepin-6-yl)methanimine (5). 50%, yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.60–7.58 (m, 2H), 7.54–7.52 (m, 2H), 7.50–7.46 (m, 5H), 7.40–7.38 (m, 4H), 7.31–7.26 (m, 5H), 0.50 (s, 6H), –0.33 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 149.44, 137.99, 133.02, 130.59, 130.03, 129.40, 128.90, 128.79, 128.11, 126.45, 126.43, 0.11, –0.67; IR (film) ν : 696, 752, 787, 835, 977, 1254 cm^{-1} .

1,1-Diphenyl-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)methanimine (6a). 99%, yellow solid; m.p. 139–141 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.85 (dd, $J=0.9$, 9.1 Hz, 2H), 7.65–7.56 (m, 4H), 7.50–7.45 (m, 4H), 7.40–7.32 (m, 6H), 0.22 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 166.95, 140.22, 139.89, 138.51, 135.85, 132.84, 132.62, 130.81, 130.08, 129.29, 128.98, 128.64, 127.95, 127.91, 124.99, 0.45; HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 437.1863, found 437.1879; IR (film) ν : 788, 823, 955, 1250, 1491 cm^{-1} .

***N*-(1,1,3,3-Tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)-1,1-di-*p*-tolylmethanimine (6b).** 81%, pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.85–7.83 (m, 2H), 7.63 (dd, $J=1.0$, 6.7 Hz, 2H), 7.50–7.44 (m, 4H), 7.38 (d, $J=8.1$ Hz, 2H), 7.15 (d, $J=8.0$ Hz, 2H), 7.11 (d, $J=7.9$ Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H), 0.22 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 167.40, 139.95, 139.31, 138.81, 138.67, 137.73, 132.95, 132.82, 132.64, 130.74, 130.04, 128.67, 128.60, 128.48, 124.96, 21.36, 21.29, 0.47; HRMS (ESI, m/z): calcd for $\text{C}_{29}\text{H}_{33}\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 465.2176, found 465.2187; IR (film) ν : 787, 822, 932, 1249 cm^{-1} .

1,1-Bis(4-fluorophenyl)-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)methanimine (6c). 99%, pale yellow solid; m.p. 156–158 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.86 (dd, $J=1.0$, 8.2 Hz, 2H), 7.64 (dd, $J=0.9$, 6.7 Hz, 2H), 7.57–7.54 (m, 2H), 7.51–7.46 (m, 4H), 7.07–7.00 (m, 4H), 0.23 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 165.49, 164.53 (d, $J=97.5$ Hz), 162.05 (d, $J=97.7$ Hz), 139.85, 138.02, 136.16 (d, $J=3.1$ Hz), 132.94, 132.77 (d, $J=8.3$ Hz), 132.66, 131.37 (d, $J=3.6$ Hz), 130.47, 130.43 (d, $J=8.2$ Hz), 125.03, 115.15 (d, $J=14.7$ Hz), 114.94 (d, $J=14.9$ Hz), 0.44; HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{27}\text{F}_2\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 473.1675, found 473.1681; IR (film) ν : 840, 954, 1156, 1504, 1601 cm^{-1} .

1,1-Bis(4-chlorophenyl)-*N*-(1,1,3,3-tetramethyl-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilin-2(3*H*)-yl)methanimine (6d). 92%, yellow solid; m.p. 155–157 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.86 (d, $J=8.1$ Hz, 2H), 7.63 (d, $J=6.7$ Hz, 2H), 7.51–7.42 (m, 6H), 7.32 (dd, $J=6.3$, 8.3 Hz, 4H), 0.23 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 165.44, 139.82, 138.19, 137.83, 135.71, 135.08, 133.44, 132.96, 132.66, 132.10, 130.29, 129.80, 128.39, 128.28, 125.04, 0.49; HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{27}\text{Cl}_2\text{N}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 505.1084, found 505.1093; IR (film) ν : 734, 787, 934, 1249, 1488 cm^{-1} .

1,1,3,3-Tetramethyl-2-tosyl-2,3-dihydro-1*H*-naphtho[1,8-*cd*][1,2,6]azadisilene (8). 60%, white solid; m.p. 163–165 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 7.93 (dd, $J=1.0$, 8.2 Hz, 2H), 7.75 (d, $J=8.3$ Hz, 2H), 7.71 (dd, $J=1.0$, 6.8 Hz, 2H), 7.53 (dd, $J=7.0$, 8.1 Hz, 2H), 7.21 (d, $J=8.2$ Hz, 2H), 2.37 (s, 3H), 0.64 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ : 142.51, 141.66, 138.92, 136.08, 133.25, 132.68, 130.88, 129.29, 126.24, 125.26, 21.38, 2.22; HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 412.1217, found 412.1222; IR (film) ν : 793, 940, 1150, 1256, 1313, 1494 cm^{-1} .

Supporting Information

The supporting information for this article is available on the WWW under <https://doi.org/10.1002/cjoc.201800292>.

Acknowledgement

The project is supported by the National Basic Research Program of China (973 Program, No. 2015CB856600) and the National Natural Science Foundation of China (Grant 21332002, 21472004).

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Manuscript received: June 25, 2018

Manuscript revised: July 25, 2018

Manuscript accepted: July 26, 2018

Accepted manuscript online: July 29, 2018

Version of record online: August 22, 2018