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PAPER

Palladium-catalyzed silyl C(sp^3)–H bond activation†

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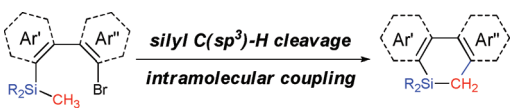
The first transition-metal-catalyzed activation of silyl C(sp^3)–H bond was realized and synthetically applied. A variety of organic skeletons substituted with $SiMe_3$ groups could undergo the Pd-catalyzed intramolecular coupling reaction, resulting in an unprecedented synthetic method for yielding six-membered silacycles. It was found that the adjacent Si atom played an essential role for the activation of the C(sp^3)–H bond of the $SiMe_3$ group; no activation reaction of the C(sp^3)–H bond of the CMe_3 group took place under the same reaction conditions.

Introduction

Transition-metal-catalyzed activation and synthetic application of C(sp^3)–H bond is a great challenge and has significant synthetic potential.[1,2] Silyl C(sp^3)–H bonds in trialkylsilyl groups such as $SiMe_3$ are among the most common C(sp^3)–H bonds because many compounds are substituted with trialkylsilyl groups. Although remarkable achievements have been realized on the activation and synthetic application of tertiary C(sp^3)–H bonds,[3] the activation of C(sp^3)–H bonds adjacent to a functional group, such as oxime,[4] oxazolne,[5] pyridine,[6] amide,[7] carboxyl,[8] and C(sp^3)–H bonds adjacent to hetero-atoms, such as N,[9] O,[10] S,[11] is unknown in the literature and remains a great challenge. In this paper, we report the first example of transition-metal-catalyzed activation and synthetic application of silyl C(sp^3)–H bonds (Scheme 1). A wide variety of organic skeletons substituted with a $SiMe_3$ group could undergo a Pd-catalyzed cleavage of the silyl C(sp^3)–H bond, providing an unprecedented synthetic method for yielding six-membered silacycles, which are not readily accessible *via* known methods.[12]

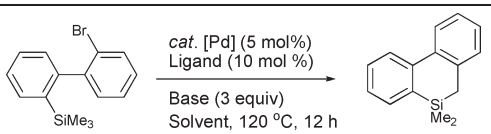


Scheme 1 Silyl C(sp^3)–H bond cleavage and intramolecular silyl C(sp^3)–C(sp^2) coupling leading to six-membered silacycles.

Results and discussion

Initially, we tested the compound **1a** possessing a $SiMe_3$ substituent as a model example (Table 1). After screening various reaction conditions, an optimal reaction condition was realized:

Table 1 Optimization of reaction conditions (see ESI† for details)



1a **2a**

Entry	[Pd]	Ligand	Base	Solvent	Yield of **2a** (%)[a]
1	$Pd(OAc)_2$	P*t*-Bu_3	NaO*t*-Bu	Dioxane	45
2	$Pd_2(dba)_3$	P*t*-Bu_3	NaO*t*-Bu	Dioxane	13
3	$[PdCl(\pi\text{-allyl})]_2$	P*t*-Bu_3	NaO*t*-Bu	Dioxane	45
4	$Pd(PPh_3)_4$		NaO*t*-Bu	Dioxane	63
5	$Pd(PPh_3)_4$	P*t*-Bu_3	NaO*t*-Bu	Dioxane	75 (64)
6	$Pd(PPh_3)_4$	PCy_3	NaO*t*-Bu	Dioxane	41
7	$Pd(PPh_3)_4$	PPh_3	NaO*t*-Bu	Dioxane	28
8	$Pd(PPh_3)_4$	P*t*-Bu_3	LiO*t*-Bu	Dioxane	9
9	$Pd(PPh_3)_4$	P*t*-Bu_3	KO*t*-Bu	Dioxane	trace
10	$Pd(PPh_3)_4$	P*t*-Bu_3	K_2CO_3	Dioxane	trace
11	$Pd(PPh_3)_4$	P*t*-Bu_3	Cs_2CO_3	Dioxane	trace
12	$Pd(PPh_3)_4$	P*t*-Bu_3	CsF	Dioxane	trace
13	$Pd(PPh_3)_4$	P*t*-Bu_3	KOH	Dioxane	trace
14	$Pd(PPh_3)_4$	P*t*-Bu_3	NaO*t*-Bu	Toluene	77 (70)
15	$Pd(PPh_3)_4$	P*t*-Bu_3	NaO*t*-Bu	Toluene	83 (74)[b]

[a] GC yields. Isolated yields are given in parenthesis. [b] 20 mol% of TBAB was added.

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†Electronic supplementary information available: Materials including experimental procedures, NMR spectra of all new products and X-ray data for **6e**, **8a**. CCDC reference numbers 823538 and 824123. For electronic supplementary information and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob06941e

Table 2 Formation of benzo- and dibenzo-fused six-membered silacycles

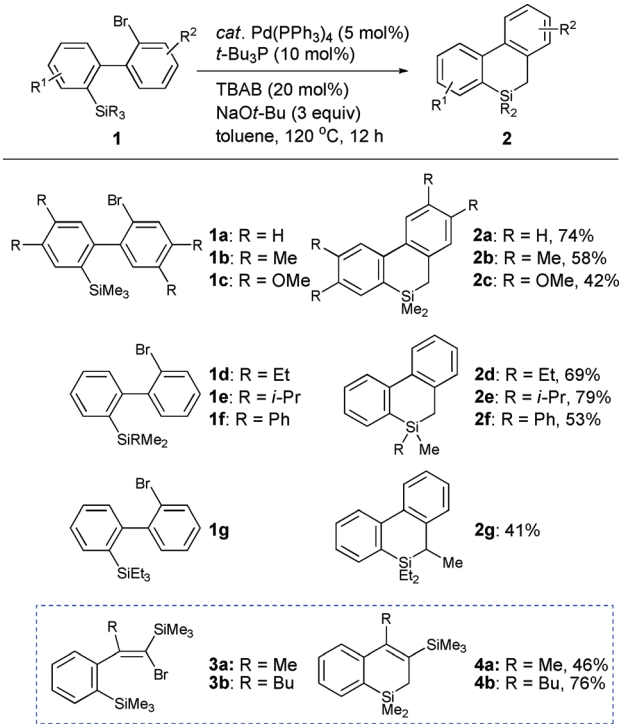
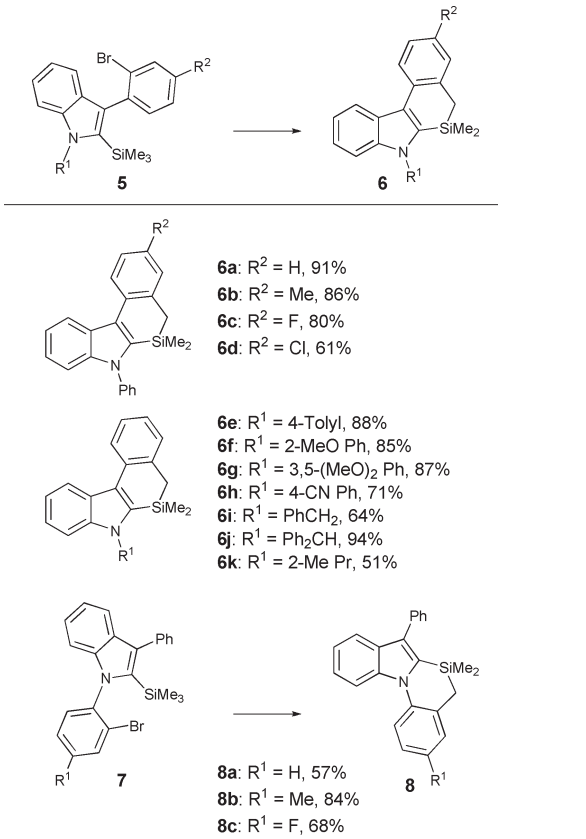


Table 3 Formation of heteroarene-fused silacycles **6** and **8** from their corresponding Me_3Si-substituted compounds **5** and **7**



$Pd(PPh_3)_4$ (5 mol%), P*t*-Bu_3 (10 mol%), TBAB (20 mol%), NaO*t*-Bu (3 equiv), in toluene, 120 °C, 12 h. Notably, in addition to the remarkable effect of different catalysts and ligands, the base was found to be very sensitive for this transformation. NaO*t*-Bu was found to be the most effective base, while most other bases such as LiO*t*-Bu, KO*t*-Bu, K_2CO_3, Cs_2CO_3, CsF, KOH afforded very low yields of products, or no products at all (see ESI† for details). With the optimized reaction condition, the dibenzo-fused six-membered silacycle **2a** was obtained in 74% isolated yield (entry 15, Table 1).

Similarly, as given in Table 2, the substituted derivatives **1b** and **1c** could afford their corresponding dibenzo-fused silacycles **2b** and **2c** in moderate yields.

Investigation into the effect of substituents on the silicon center disclosed, from which, as demonstrated in the cases of **1d** ($SiMe_2Et$), **1e** ($SiMe_2$*i*-Pr) and **1f** ($SiMe_2Ph$), the methyl C(sp^3)–H bond was selectively cleaved to afford their corresponding silacycles **2d**, **2e**, and **2f** in good isolated yields (Table 2). The reaction of **1g** ($SiEt_3$) is of particular interest, affording the methylated six-membered silacycle **2g** in 41% isolated yield. In this case, the methylene C(sp^3)–H bond was selectively cleaved; The methyl C(sp^3)–H bond was not involved.

The above silyl C(sp^3)–H bond cleavage and consequent intramolecular silyl C(sp^3)–C(aryl sp^2) coupling was also successfully applied to the vinylic bromide derivatives **3a** and **3b** (Table 2). Their corresponding benzo-fused silacycles **4a** and **4b** were obtained in 46% and 76% isolated yields, respectively.

It should be mentioned that, as given in Table 2, in most cases no Si–Me bond cleavage was observed.[13,14] For the cases of **1g** and the vinylic bromide derivatives **3**, small amounts of their corresponding siloles formed, *via* cleavage of the Si–Me bond,[13,14] and de-brominated products were detected by GC-MS.

As further demonstration of the usefulness of the above-mentioned reaction, we subjected Me_3Si-substituted-heteroarenes **5** and **7** to the reaction conditions, expecting the formation of complex structures containing six-membered silacyclic skeletons. As shown in Table 3, a variety of silyl[2,3-*b*]indoles **6** could be obtained in good isolated yields from their corresponding 3-(2-bromoaryl)-2-(trialkylsilyl)-1*H*-indoles **5** under the optimal reaction condition *via* the silyl C(sp^3)–H bond cleavage and consequent intramolecular silyl C(sp^3)–C(aryl sp^2) coupling. The substituent of the aryl moiety could be H (**6a**), Me (**6b**), F (**6c**) and Cl (**6d**) groups, and the yield of their corresponding products was 91%, 86%, 80%, 61%, respectively. The *N*-substituent of the indole moiety could be aryl (**6a–h**), benzyl (**6i**, **6j**), and an alkyl (**6k**) groups. The *N*-aryl could be substituted with both electron-donating groups such as OMe, Me (**6e–g**) and electron-withdrawing group such as CN (**6h**). The structure of product **6e** was determined by single-crystal X-ray structural analysis (Fig. 1, on the left).

Under the optimal reaction condition, the benzo[*e*][1,3]azasilanes **8a**, **8b**, and **8c** (Table 3) could be also efficiently obtained in 57%, 84%, 68% isolated yields, respectively, from their corresponding indole derivatives, **7**. The structure of product **8a** was determined by single-crystal X-ray structural analysis and is given in Fig. 1.

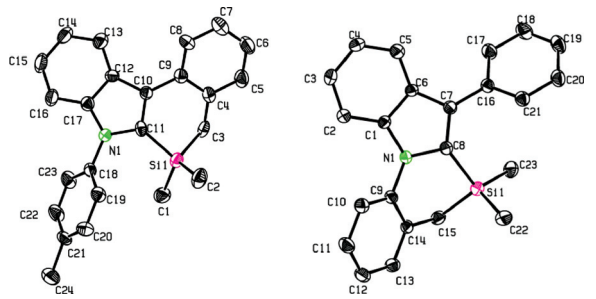
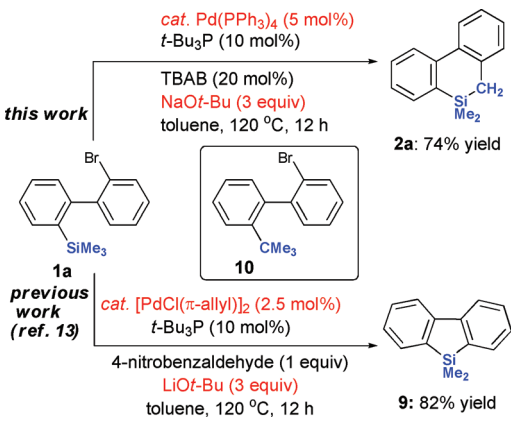


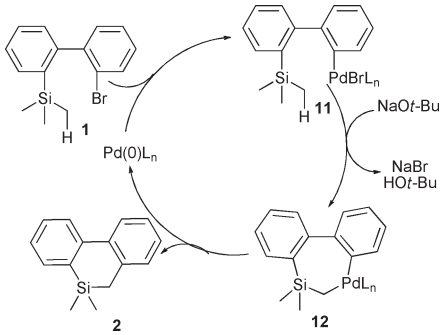
Fig. 1 ORTEP drawings of **6e** (left) and **8a** (right) with 30% thermal ellipsoids. Selected bond lengths [*Å*] for **6e**: Si(1)–C(3) 1.851(4), Si(1)–C(11) 1.847(4), C(3)–C(4) 1.500(5), C(10)–C(11) 1.376(5), C(11)–N(1) 1.396(4); for **8a**: Si(1)–C(8) 1.869(2), Si(1)–C(15) 1.872(2), C(7)–C(8) 1.380(3), C(8)–N(1) 1.415(2), C(14)–C(15) 1.496(3).



Scheme 2 Selective activation of the silyl C(sp^3)–H bond *vs* selective activation of the C(sp^3)–Si bond of a $SiMe_3$ group. No reaction took place in the case of the Me_3C-substituted compound.**10**.

The reaction mechanism for the selective cleavage of the silyl C(sp^3)–H bond is intriguing. It is interesting to compare the selective activation of the silyl C(sp^3)–H bond described in this work with the selective activation of the Si–Me bond of the $SiMe_3$ group reported previously by us[13] and by others.[14] As shown in Scheme 2, the major differences of these two reactions are the Pd catalysts and the bases used.[13] Although it is frequently reported in the literature that NaO*t*-Bu and KO*t*-Bu demonstrate remarkably different effects from those of LiO*t*-Bu, it is not clear yet what the major reason for this is. In our case, no remarkable change was observed when **1a** was treated in toluene with 3 equivalents of LiO*t*-Bu or NaO*t*-Bu, even at 120 °C, as followed by *in situ* NMR spectra. Furthermore, the addition of an aldehyde did not show remarkable effect on the selective activation of the silyl C(sp^3)–H bond.[13]

There are many examples of the activation of tertiary C(sp^3)–H bonds in the literature.[3] In order to know if the silicon atom plays a key role in the activation of the C(sp^3)–H bond of the $SiMe_3$ group, the analogue compound **10**, with a CMe_3 substituent instead of the $SiMe_3$ group, was synthesized and evaluated (Scheme 2). Experimental results showed that no reaction took place when the compound **10** was subjected to the reaction conditions described in Scheme 2. Most of the starting compound, **10**, was recovered. These results indicate that the silyl group is not innocent and not equivalent to simple alkyl groups.



Scheme 3 A proposed reaction mechanism for the formation of the six-membered silacycles, **2**, from **1**.

Based on all the above preliminary experimental results, a proposed catalytic cycle for the formation of the six-membered silacycles **2** from **1** is given in Scheme 3. A seven-membered palladacycle intermediate, **12**, might be formed *via* the NaO*t*-Bu-mediated proton abstraction of **11**. This process might be facilitated by the α-carboanion stabilizing effect of the Si atom[15] or by the hypervalent Si enter formation.[16] The palladacycle, **12**, would then give rise to the six-membered silacycle derivative, **2**, *via* reductive elimination.

Conclusions

In summary, the first Pd-catalyzed selective cleavage of the silyl C(sp^3)–H bond in a $SiMe_3$ group and consequent intramolecular silyl C(sp^3)–C(sp^2) bond forming process was developed. It was found that the silicon atom played a key role in the activation of the silyl C(sp^3)–H bond, making the $SiMe_3$ group remarkably different from the CMe_3 group. This finding would open a new way for the selective cleavage of the silyl C(sp^3)–H bond in a trialkylsilyl group and for the synthesis of silacycles.

Experimental

General information

Unless otherwise noted, all starting materials are commercially available and were used without further purification. Solvents were purified using an M-Braun SPS-800 Solvent Purification System. *n*-BuLi and PhLi were obtained from Acros. All reactions were carried out under a dry and oxygen-free nitrogen atmosphere in slight positive pressure by using Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (FT, 300 MHz for ^1H; 75 MHz for ^{13}C), or a Bruker ARX400 spectrometer (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) at room temperature. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using electrospray ionization (ESI).

Typical procedure for the preparation and characterization of 2, 4, 6, 8. Under the protection of nitrogen, $Pd(PPh_3)_4$ (5 mol%), P*t*-Bu_3 (10 mol%) and NaO*t*-Bu (0.9 mmol), were added to 2 mL of toluene. After this, reaction mixture was stirred at room temperature for 15 min, **1**, **3**, **5**, or **7** (0.3 mmol), TBAB (20 mol %) were added and this reaction mixture was stirred at 120 °C for 12 h. The reaction mixture was quenched with water and

extracted with Et_2O. The extraction was washed with brine and dried over $MgSO_4$. The solvent was then evaporated *in vacuo* and the residue was purified by using silicon gel column with petroleum ether and ethyl acetate as eluent, to afford the final products **2**, **4**, **6**, or **8**.

2a: Colorless oil, isolated yield 74% (50 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.26–7.16 (m, 3H), 2.17 (s, 2H), 0.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −4.35, 21.25, 126.11 (2C), 126.56, 127.45, 127.93, 130.19, 131.21, 132.52, 135.48, 136.17, 137.55, 144.44; HRMS (ESI, m/z) calcd for $[C_{15}H_{16}Si]H^+$: 225.1094; found 225.1093.

2b: Colourless solid, isolated yield 58% (49 mg); mp: 94.2–94.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (s, 1H), 7.37 (s, 1H), 7.27 (s, 1H), 6.94 (s, 1H), 2.32 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.23 (s, 3H), 2.06 (s, 2H), 0.19 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −4.09, 19.26, 19.31, 19.45, 20.12, 20.60, 127.12, 128.80, 132.29, 132.70, 133.07, 133.78, 133.88, 134.52, 134.96, 135.32, 138.48, 142.32; HRMS (ESI, m/z) calcd for $[C_{19}H_{24}Si]H^+$: 281.1720; found 281.1716.

2c: Colourless solid, isolated yield 42% (43 mg); mp: 155.2–155.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (s, 1H), 7.09 (s, 1H), 6.99 (s, 1H), 6.71 (s, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H), 2.06 (s, 2H), 0.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −4.16, 20.70, 55.78, 55.89, 55.95, 56.19, 109.63, 111.31, 114.43, 114.82, 126.46, 128.35, 129.77, 137.95, 147.05, 147.51, 147.71, 150.51; HRMS (ESI, m/z) calcd for $[C_{19}H_{24}O_4Si]H^+$: 345.1517; found 345.1522.

2d: Colourless oil, isolated yield 69% (49 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 7.2 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.24–7.13 (m, 3H), 2.20–2.12 (m, 2H), 0.89 (t, J = 7.8 Hz, 3H), 0.70–0.64 (m, 2H), 0.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −6.46, 4.37, 7.33, 19.50, 126.09, 126.14, 126.47, 127.43, 127.94, 130.17, 131.16, 132.81, 134.66, 136.18, 137.68, 144.70; HRMS (ESI, m/z) calcd for $[C_{16}H_{18}Si]H^+$: 239.1251; found 239.1247.

2e: Colourless oil, isolated yield 79% (60 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.23–7.14 (m, 3H), 2.22–2.14 (m, 2H), 0.90–0.87 (m, 7H), 0.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −8.21, 11.37, 17.39, 17.54, 18.64, 126.09, 126.16, 126.42, 127.46, 127.96, 130.14, 131.08, 133.22, 134.21, 136.22, 137.87, 144.90; HRMS (ESI, m/z) calcd for $[C_{17}H_{20}Si]H^+$: 253.1407; found 253.1407.

2f: Colourless oil, isolated yield 53% (46 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.50–7.43 (m, 4H), 7.35–7.14 (m, 7H), 2.54–2.32 (m, 2H), 0.51 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −5.90, 20.55, 126.17, 126.34, 126.62, 127.61, 127.82, 127.98, 129.55, 130.51, 131.45, 133.63, 133.77, 134.44, 135.22, 135.49, 137.67, 144.90; HRMS (ESI, m/z) calcd for $[C_{20}H_{18}Si]H^+$: 287.1251; found 287.1251.

2g: Colourless oil, isolated yield 41% (33 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 9.6 Hz, 1H), 7.50–7.43 (m, 2H), 7.29–7.21 (m, 4H), 2.34–2.28 (m, 1H), 1.21 (d, J = 7.2 Hz, 3H), 0.97 (t, J = 7.8 Hz, 3H), 0.85 (d, J = 7.8 Hz, 3H), 0.81–0.65 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 0.91, 2.21, 7.35, 7.42, 14.65, 21.82, 126.05, 126.08, 126.46, 127.74, 128.30, 128.67, 130.13, 132.80, 133.62, 137.46, 141.95, 144.73; HRMS (ESI, m/z) calcd for $[C_{18}H_{22}Si]H^+$: 267.1564; found 267.1558.

4a: Colourless oil, isolated yield 46% (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J = 7.2 Hz, 1H), 7.37–7.35 (m, 2H), 7.20–7.17 (m, 1H), 2.23 (s, 3H), 1.52 (s, 2H), 0.23 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −4.46, 0.66, 17.07, 23.01, 124.84, 126.02, 129.53, 131.73, 133.07, 135.61, 141.17, 145.91; HRMS (ESI, m/z) calcd for $[C_{15}H_{24}Si_2]H^+$: 259.1333; found 259.1330.

4b: Colourless oil, isolated yield 76% (69 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, J = 6.8 Hz, 1H), 7.37–7.35 (m, 2H), 7.20–7.16 (m, 1H), 2.66 (t, J = 7.4 Hz, 2H), 1.48 (s, 2H), 1.32–1.26 (m, 4H), 0.86 (t, J = 6.8 Hz, 3H), 0.23 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −4.61, 0.88, 14.08, 16.99, 22.91, 32.49, 35.26, 124.84, 125.90, 129.47, 131.91, 134.81, 136.76, 144.15, 146.87; HRMS (ESI, m/z) calcd for $[C_{18}H_{30}Si_2]H^+$: 303.1959; found 303.1967.

6a: Pale yellow solid, isolated yield 91% (93 mg); mp: 110.5–111.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18–8.15 (m, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.50–7.46 (m, 2H), 7.42–7.38 (m, 3H), 7.34–7.32 (m, 1H), 7.29–7.20 (m, 4H), 7.08 (t, J = 7.4 Hz, 1H), 2.20 (s, 2H), −0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.55, 22.64, 110.63, 120.42, 120.54, 122.79, 125.01, 125.53, 125.70, 126.15, 126.29, 127.21, 127.72, 129.34, 131.07, 134.49, 134.60, 138.05, 140.26, 140.34; HRMS (ESI, m/z) calcd for $[C_{23}H_{21}NSi]H^+$: 340.1516; found 340.1520.

6b: Colourless solid, isolated yield 86% (91 mg); mp: 133.8–134.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16–8.13 (m, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.4 Hz, 2H), 7.42–7.40 (m, 3H), 7.33–7.31 (m, 1H), 7.21–7.19 (m, 2H), 7.09 (d, J = 7.6 Hz, 2H), 2.33 (s, 3H), 2.16 (s, 2H), −0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.48, 21.06, 22.56, 110.58, 120.41, 120.45, 122.71, 125.58, 126.17, 126.33, 127.20, 127.64, 128.36, 129.32, 131.71, 132.00, 134.38, 134.45, 137.57, 140.29, 140.32; HRMS (ESI, m/z) calcd for $[C_{24}H_{24}NSi]H^+$: 354.1673; found 354.1676.

6c: Colourless solid, isolated yield 80% (86 mg); mp: 155.2–156.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.45–7.41 (m, 3H), 7.35–7.31 (m, 1H), 7.23–7.21 (m, 2H), 6.98 (d, J = 8.8 Hz, 2H), 2.18 (s, 2H), −0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.63, 22.98, 110.72, 112.14 (d, J = 20.4 Hz), 117.75 (d, J = 20.4 Hz), 120.10, 120.63, 122.93, 124.80, 125.96, 127.18, 127.32 (d, J = 32.1 Hz), 127.8, 129.41, 130.67 (d, J = 3.1 Hz), 137.21 (d, J = 7.4 Hz), 137.44, 140.19, 140.26, 160.24 (d, J = 242.3 Hz); HRMS (ESI, m/z) calcd for $[C_{23}H_{21}FNSi]H^+$: 358.1422; found 358.1429.

6d: Pale yellow solid, isolated yield 61% (68 mg); mp: 156.7–158.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10–8.08 (m, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.53 (t, J = 7.4 Hz, 2H), 7.48–7.42 (m, 3H), 7.35–7.33 (m, 1H), 7.26–7.22 (m, 4H), 2.18 (s, 2H), −0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.60, 22.70, 110.79, 120.15, 120.77, 123.02, 124.59, 125.68, 125.95, 127.27 (2C), 127.93, 129.45, 130.00, 130.77, 133.19, 136.67, 138.11, 140.15, 140.40; HRMS (ESI, m/z) calcd for $[C_{23}H_{21}ClNSi]H^+$: 374.1126; found 374.1121.

6e: Colourless solid, isolated yield 88% (93 mg); mp: 165.8–167.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.18 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.34–7.27 (m, 7H), 7.23 (t, J = 5.4 Hz, 2H), 7.11 (t, J = 7.4 Hz, 1H), 2.46 (s, 3H), 2.23 (s, 2H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.47, 21.19, 22.67, 110.71, 120.39, 120.43, 122.68, 124.93, 125.24, 125.68, 126.06, 126.26, 127.04, 129.92, 131.08, 134.50, 134.71, 137.63, 138.19, 140.49; HRMS (ESI, m/z) calcd for $[C_{24}H_{23}NSi]H^+$: 354.1673; found 354.1675.

6f: Pale yellow solid, isolated yield 85% (94 mg); mp: 118.2–119.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (d, J = 6.8 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.30–7.22 (m, 3H), 7.20–7.17 (m, 2H), 7.08–7.01 (m, 4H), 3.66 (s, 3H), 2.25–2.16 (m, 2H), −0.04 (s, 3H), −0.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −4.56, −3.56, 22.66, 55.42, 110.98, 111.89, 120.22, 120.33, 120.60, 122.45, 124.74, 124.91, 125.61, 125.79, 126.15, 128.54, 129.64, 129.94, 131.09, 134.54, 134.88, 138.77, 140.83, 155.80; HRMS (ESI, m/z) calcd for $[C_{24}H_{23}NOSi]H^+$: 370.1622; found 370.1623.

6g: Yellow oil, isolated yield 87% (104 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.45–7.42 (m, 1H), 7.29–7.20 (m, 4H), 7.08 (d, J = 7.4 Hz, 1H), 6.61 (s, 2H), 6.54 (s, 1H), 3.79 (s, 6H), 2.21 (s, 2H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.49, 22.75, 55.53, 99.91, 105.44 (2C), 110.86, 120.43, 120.59, 122.85, 125.07, 125.58, 125.70, 126.21, 126.32, 131.07, 134.56, 137.80, 140.08, 141.92, 161.21; HRMS (ESI, m/z) calcd for $[C_{25}H_{25}NO_2Si]H^+$: 400.1727; found 400.1728.

6h: Colourless solid, isolated yield 71% (78 mg); mp: 238.9–239.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17–8.14 (m, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.39–7.35 (m, 1H), 7.32–7.25 (m, 4H), 7.14 (t, J = 7.4 Hz, 1H), 2.21 (s, 2H), 0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.36, 22.42, 110.13, 110.92, 118.17, 120.71, 121.32, 123.51, 125.59, 125.83, 126.48, 126.75, 127.38, 127.44, 131.08, 133.43, 133.91, 134.41, 137.14, 139.65, 144.33; HRMS (ESI, m/z) calcd for $[C_{24}H_{20}N_2Si]H^+$: 365.1469; found 365.1469.

6i: Pale yellow solid, isolated yield 64% (68 mg); mp: 109.4–110.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19–8.16 (m, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.27–7.16 (m, 8H), 7.05 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 6.4 Hz, 1H), 5.41 (s, 2H), 2.23 (s, 2H), 0.11 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.25, 22.45, 49.74, 109.96, 120.13, 120.77, 122.59, 124.66, 124.77, 125.71, 125.87, 126.09, 126.13, 127.33, 128.67, 131.08, 134.03, 134.73, 137.65, 138.01, 140.10; HRMS (ESI, m/z) calcd for $[C_{24}H_{24}NSi]H^+$: 354.1673; found 354.1671.

6j: Pale yellow solid, isolated yield 94% (121 mg); mp: 129.7–130.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.14 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 7.2 Hz, 1H), 7.31–7.23 (m, 8H), 7.17 (t, J = 3.8 Hz, 4H), 7.10–7.04 (m, 2H), 7.00 (s, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 8.8 Hz, 1H), 2.27 (s, 2H), 0.17 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −2.81, 22.58, 66.57, 113.26, 119.83, 120.72, 122.08, 124.82, 124.88, 125.65, 126.32, 127.41, 127.73, 128.14, 128.56, 130.99, 134.01, 134.65, 139.17, 139.21, 139.51; HRMS (ESI, m/z) calcd for $[C_{30}H_{28}NSi]H^+$: 430.1986; found 430.1988.

6k: Pale yellow oil, isolated yield 51% (49 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.25–7.21 (m, 3H), 7.16 (t, J = 7.6 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 4.01 (d, J = 7.6 Hz, 2H), 2.28–2.17 (m, 3H), 0.93 (d, J = 6.4 Hz, 6H), 0.36 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −2.75, 20.41, 22.64, 30.30, 53.97, 110.23, 119.76, 120.56, 122.15, 124.14, 124.67, 125.67, 125.98, 126.25, 130.88, 134.12, 134.85, 137.14, 139.90; HRMS (ESI, m/z) calcd for $[C_{21}H_{26}NSi]H^+$: 320.1829; found 320.1831.

8a: Yellow solid, isolated yield 57% (58 mg); mp: 129.1–130.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 6.8 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.30–7.26 (m, 3H), 7.17 (t, J = 7.0 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 2.13 (s, 2H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.37, 20.36, 111.76, 119.84, 120.60, 121.52, 123.16, 124.83, 125.98, 126.81, 128.34, 128.53, 128.67, 129.76, 130.44, 131.56, 134.95, 136.01, 137.67, 137.83; HRMS (ESI, m/z) calcd for $[C_{23}H_{22}NSi]H^+$: 340.1516; found 340.1519.

8b: Pale yellow oil, isolated yield 84% (89 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.6 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 7.6 Hz, 1H), 7.28 (t, J = 7.0 Hz, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.11 (s, 1H), 7.08 (d, J = 8.0 Hz, 1H), 2.36 (s, 3H), 2.09 (s, 2H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.33, 20.26, 20.89, 111.73, 119.79, 120.42, 121.35, 123.05, 126.52, 126.75, 128.25, 128.32, 128.51, 129.78, 130.17, 132.21, 134.35, 135.01, 135.39, 136.11, 137.65; HRMS (ESI, m/z) calcd for $[C_{24}H_{24}NSi]H^+$: 354.1673; found 354.1675.

8c: Yellow solid, isolated yield 68% (73 mg); mp: 135.6–136.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82–7.77 (m, 2H), 7.70–7.67 (m, 1H), 7.53 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.22–7.16 (m, 1H), 7.03–6.95 (m, 2H), 2.12 (s, 2H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: −3.45, 20.76, 111.35, 112.44 (d, J = 21.6 Hz), 117.87 (d, J = 21.6 Hz), 119.94, 120.66, 122.67 (d, J = 8.7 Hz), 123.32, 126.90, 128.38, 128.49, 128.67, 129.71, 133.12 (d, J = 8.0 Hz), 133.92 (d, J = 2.5 Hz), 134.60, 135.85, 137.66, 159.46 (d, J = 242.3 Hz); HRMS (ESI, m/z) calcd for $[C_{24}H_{24}FNSi]H^+$: 358.1422; found 358.1427.

X-ray crystallographic studies for 6e and 8a

The single crystals of **6e** and **8a** suitable for X-ray analysis were grown in mixed solvent of hexane, diethyl ether and ethyl acetate. Data collections were performed at 20 °C on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the Rapid-AUTO (Rigaku 2000) program package. The raw frame data were processed using Crystal Structure (Rigaku/MSC 2000) to yield the reflection data file. The structure was solved by use of the SHELXTL program.[17] Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **6e** and **8a** were given only in the ESI†. Crystallographic data (excluding structure factors) have been deposited with the Cambridge

Crystallographic Data Centre as supplementary publication nos. CCDC-823538 (**6e**), and CCDC-824123 (**8a**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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