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Regioselective *lateral* or vinyl C–H lithiation/1,5-retro-Brook rearrangement via quinolyl or pyridyl ring directed deprotonation

Yongping He [a], Bin Ma [a], Juan Yang [a], Xingang Xie [a], Xuegong She [a,b,*]

[a] State Key Laboratory of Applied Organic Chemistry, Department of Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China
[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

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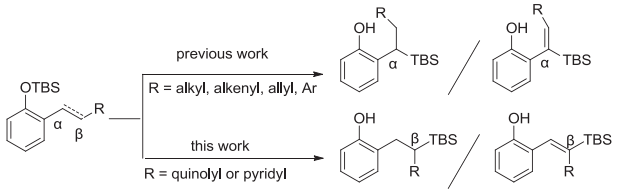
ABSTRACT

A regioselective *lateral* or vinyl C–H lithiation/1,5-retro-Brook rearrangement via quinolyl or pyridyl ring directed deprotonation has been developed. 16 examples were tested and the corresponding alkyl silanes and *E*-vinyl silanes were obtained in moderate to good yields.

1. Introduction

Silanes are usually inexpensive, nontoxic, and environmentally benign, and appropriately substituted organosilanes can undergo a variety of transformations to form useful derivatives. Among the strategies for the preparation of silanes, the silylation of C–H bonds is particularly attractive.[1] The complex-induced proximity effect (CIPE) in deprotonations may serve as a heuristic to discover new modes for C–H activation, which could be extended to carbanion chemistry.[2] In order to establish a CIPE, the direct metallation groups (DMGs) should be able to effectively coordinate the alkyllithium species. The relative strength of common DMGs in directing metallation has already been demonstrated.[2a] Very recently, our group have developed a sequence of *lateral* C–H lithiation/1, 4-retro-Brook rearrangement via direct deprotonation for preparing benzyl silanes and *trans*-vinyl silanes (Scheme 1).[3] In our proposal, when the β-position was substituted by a sDMG (strong direct metallation group), the adjacent β-carbon will be deprotonated and form a carbanion accordingly, which may initiate a 1,5-retro-Brook reaction to give the corresponding alkyl or vinyl silanes (Scheme 1).[4] Herein we report the preliminary research result, which led to a new regioselective *lateral* or vinyl C–H lithiation/1,5-retro-Brook rearrangement via quinolyl or pyridyl ring directed deprotonation.



Scheme 1. Lithiation/retro-Brook rearrangement of aryloxysilanes.

2. Results and discussion

Initially, several strong directed metallation groups were investigated in the presence of aryloxysilanes. When sDMGs, such as thioether, sulfone were introduced, trace of desired products were detected (Table 1, entries 1 and 2). Indeed, the best directing groups tend to have a mixture of the basic properties required for good coordination to lithium and the acidic properties required for rapid and efficient deprotonation-it might be called as 'amphoteric'.[5] The quinolyl or pyridyl ring containing the nitrogen atom functions as a directing group both for lithium coordination and C–H activation.

* Corresponding author. Tel.: +86 931 8912276; fax: +86 931 8912583; e-mail address: shexg@lzu.edu.cn (X. She).

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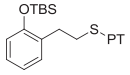
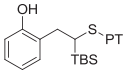
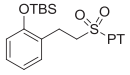
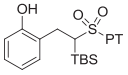
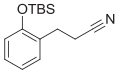
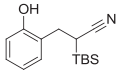
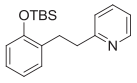
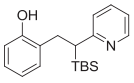
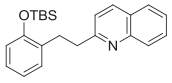
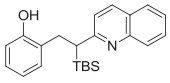
Table 1
Investigation about directed metallation group

Entry	Substrate	Product	Yield (%)
1			<10
2			<10
3			<10
4			—[a]
5			75

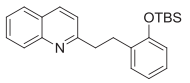
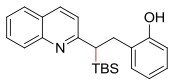
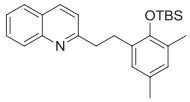
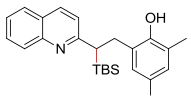
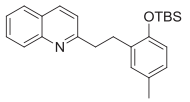
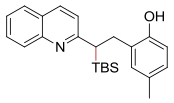
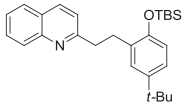
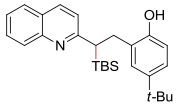
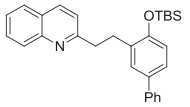
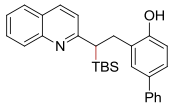
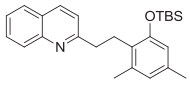
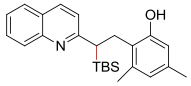
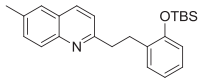
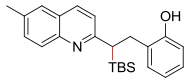
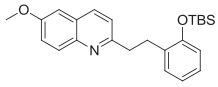
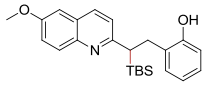
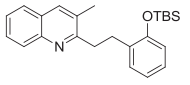
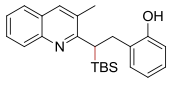
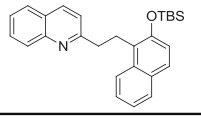
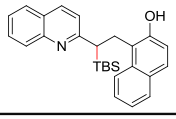
[a] No product was observed. PT=1-phenyl-1*H*-tetrazole-5-yl.

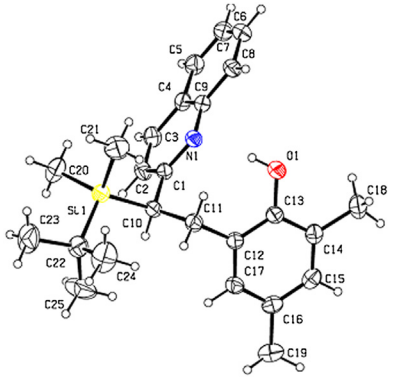
But there was competition reaction between *ortho*-lithiation of the pyridyl ring and lateral-lithiation (Table 1, entry 4).[6] When the substrate with a quinolyl ring was treated with 4 equiv of LDA from −78 °C to reflux for 24 h, the desired product was obtained in 75% yield through a lateral C–H lithiation/1,5-retro-Brook rearrangement sequence (Table 1, entry 5).

The scope and limitation of the reaction was examined and the results were shown in Table 2. Aryloxysilane **2a** with *ortho*-methyl substituent gave the product **2b** in 62% yield (Table 2, entry 2), which structure was confirmed by the X-ray single crystal diffraction experiment (Fig. 1). It was also found that there was complete selectivity for the *lateral* position of quinolyl ring rather than that of the phenolic group. Reactions of aryloxysilanes containing *meta*-, *para*-substituents, such as methyl, *tert*-butyl and phenyl on the phenolic group gave the expected products in satisfactory yields (Table 2, entries 3–6). The substrate **8a** with 6-methoxy quinolyl ring, the directed *ortho*-metallation group methoxy hardly had any effect on deprotonation at the *lateral* position of the quinolyl ring, reacted well affording **8b** in 85% yield (Table 2, entry 8). In the case of substrate with 3-methyl substituted quinolyl ring, **9b** was obtained in 65% yield presumably due to a slight steric hindrance of methyl group (Table 2, entry 9). The *lateral* C–H lithiation/1,5-retro-Brook rearrangement sequence was also proceeded smoothly when the phenolic ring was replaced by the naphtholic ring (Table 2, entry 10).

Encouraged by the results of the lateral C–H lithiation/1,5-retro-Brook rearrangement in the series of substrates A, our attention was turned to the vinyl C–H lithiation/1,5-retro-Brook rearrangement.[7] The result was shown in Table 3. It was found that the reaction was performed smoothly to give **1d** in 62% yield at 0 °C for 1 h, and the process was prompted by increasing the reaction time and temperature (Table 3, entry 1). Fluorine substituent was also tolerated herein.[8] Fluorine-substituted aryloxysilane **2c** underwent a high-yielding transformation to afford **2d** (Table 3, entry 2). It indicated that the vinyl lithiation process had been much easier. The X-ray experiment of **2d** was confirmed that the substrates did undergo vinyl C–H lithiation at the vicinal position of quinolyl ring to provide an *E*-vinyl silane, which was the thermodynamic product (Fig. 2). Examination of chloro-substituted aryloxysilane **3c** gave diisopropylamide-substituted product **3d** in 45% yield through a nucleophilic substitution of chlorine/vinyl lithiation/1,5-retro-Brook rearrangement sequence (Table 3, entry 3).[9] Reaction of

Table 2
Regioselective *lateral* C–H Lithiation/1,5-retro-Brook rearrangement of aryloxysilanes

Entry	Substrate (A)	Product (B)	Yield (%)
1		**1a**  **1b**	75
2		**2a**  **2b**	62
3		**3a**  **3b**	81
4		**4a**  **4b**	78
5		**5a**  **5b**	85
6		**6a**  **6b**	84
7		**7a**  **7b**	83
8		**8a**  **8b**	85
9		**9a**  **9b**	65
10		**10a**  **10b**	54



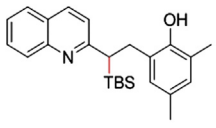
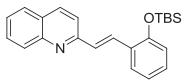
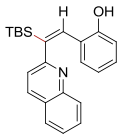
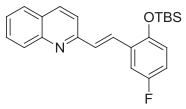
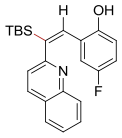
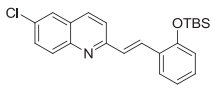
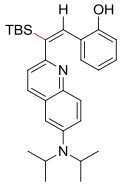
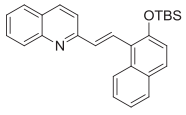
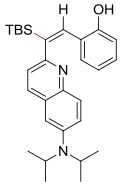


Fig. 1. X-ray of **2b** (CCDC 915675).

Table 3
Regioselective vinyl C–H lithiation/1,5-retro-Brook rearrangement of substrates

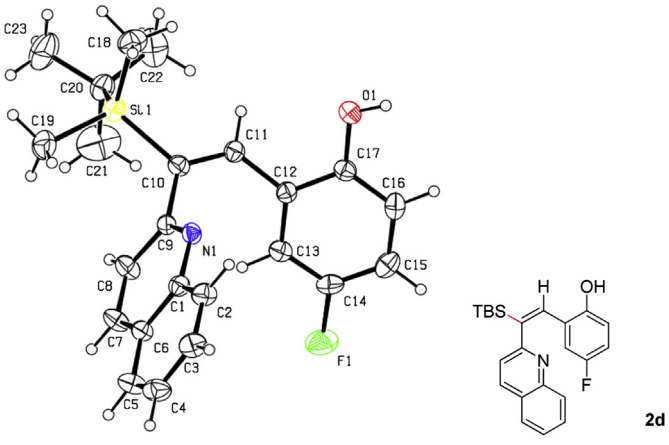
Entry	Substrate (C)		Product (D)		Yield (%)
1		1c		1d	80 62[a]
2		2c		2d	82
3		3c		3d	45
4		4c		3d	70

[a] Reaction was performed at 0 °C for 1 h.

naphthyloxysilane **4c** also proceeded well to afford **4d** in 70% yield (Table 3, entry 4).

As mentioned above (Table 1, entry 4), the *lateral* C–H lithiation/1,5-retro-Brook rearrangement did not take place at all because of the *ortho*-lithiation at the pyridyl ring. Then substrate **1e** containing 1, 6-di-substituent pyridyl ring was designed, the expected product **1f** was received in 78% yield, which structure was confirmed by the X-ray experiment (Table 4, entry 1).[10] Furthermore, reaction of substrate **2e** proceeded well to provide the desired product **2f** in 72% yield. The result suggested that the vinyl-lithiation was given preference over *ortho*-lithiation (Table 4, entry 2).

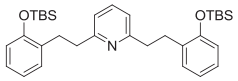
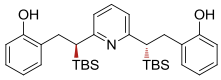
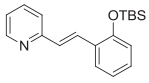
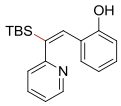
Considering the strong fluorescence intensity of the *E*-vinyl silanes, such product as **3d** was taken as an example to demonstrate its fluorescence behaviour (Fig. 3). It showed the strong emission



2d

Fig. 2. X-ray of **2d** (CCDC 915671).

Table 4
Regioselective lithiation/1,5-retro-Brook rearrangement of substrates with pyridyl ring

Entry	Substrate (E)		Product (F)		Yield (%)
1		1e		1f	78
2		2e		2f	72

peak at 489 nm, and the fluorescence intensity decreased remarkably in the presence of Al^{3+} or Fe^{3+} ion. The preliminary result demonstrated that such vinyl silanes might have potential in fluorescence probes.[11]

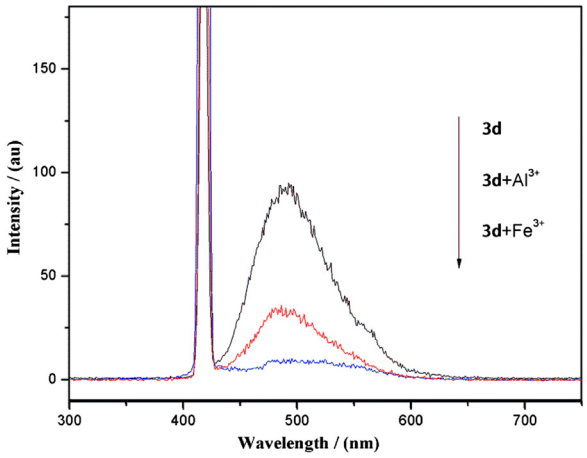


Fig. 3. Fluorescence spectra of **3d** (7 μM) in MeOH; at 25 °C; λ_{ex}=418 nm; black, free **3d**; red, **3d**+Al^{3+}, in the presence of Al^{3+} ion (33 μM); blue, **3d**+Fe^{3+}, in the presence of Fe^{3+} ion (17 μM).

3. Conclusion

In conclusion, we report a regioselective *lateral* or vinyl C–H lithiation/1,5-retro-Brook rearrangement via quinolyl or pyridyl ring directed deprotonation. Various benzyl silanes and *E*-vinyl silanes have been prepared directly. Fluorescence behaviour of **3d** has been measured for potential application. Further investigation and application of the methodology are under way in our lab.

4. Experimental

4.1. General

All commercially available reagents were used without further purification unless otherwise noted. Solvents were purified and dried by standard methods prior to use. Column chromatography was generally performed on silica gel (200–300 mesh). Melting points were determined with a digital Koffer apparatus and were uncorrected. The ^1H and ^{13}C NMR data were recorded on a *Mercury Plus*-300 MHz spectrometer or *Bruker* AM-400 MHz instrument using $CDCl_3$ as solvent at room temperature. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.27 for ^1H

NMR and 77.0 for ^{13}C NMR). High-resolution mass spectra (HRMS) were obtained on a *Bruker Daltonics* APEXII47e FT-ICR mass spectrometer. Fluorescence responses were recorded on FL2500.

4.2. General procedure for lithiation/retro-Brook rearrangement

A solution of aryloxysilane (0.1 mmol) in anhydrous THF (5 mL) was cooled to −78 °C under Ar. LDA (0.4 mmol, 4 equiv, 2 M) was added at −78 °C slowly under stirring. The mixture was allowed to warm up to room temperature slowly, then heated to reflux and refluxed for 24 h and monitored by TLC. When the starting material was consumed, the resulting mixture was cooled to room temperature and quenched with NH_4Cl. The layers were separated and the aqueous layer was extracted with ethyl acetate (three times). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and filtered. Concentration under reduced pressure gave a residue, which was purified by flash column chromatography to afford the product.

*4.2.1. 2-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)ethyl)phenol (**1b**).* White solid, mp 160–164 °C. Yield: 75% (22 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.21 (d, J=8.6 Hz, 1H), 8.01 (d, J=8.5 Hz, 1H), 7.78–7.71 (m, 2H), 7.50 (t, J=7.5 Hz, 1H), 7.25–7.17 (m, 2H), 7.02–6.96 (m, 1H), 6.92 (dd, J=8.0, 1.3 Hz, 1H), 6.80 (td, J=7.5, 1.3 Hz, 1H), 3.65 (d, J=17.5 Hz, 1H), 3.45 (dt, J=17.6, 12.1 Hz, 2H), 0.82 (s, 9H), 0.22 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 154.8, 146.5, 136.7, 132.7, 129.9, 128.9, 127.8, 127.4, 127.0, 126.3, 126.2, 122.1, 120.3, 118.3, 41.9, 27.0, 17.6, −5.5, −6.1; HRMS (ESIMS) calcd for $C_{23}H_{30}NOSi^+$ $[M+H]^+$ 364.2091, found 364.2083.

4.2.2. 2-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)ethyl)-4,6-dimethylphenol (2b). White solid, mp 145–147 °C. Yield: 62% (24 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.14 (d, J=8.6 Hz, 1H), 7.89 (d, J=8.5 Hz, 1H), 7.72 (dd, J=11.7, 4.6 Hz, 2H), 7.46 (t, J=7.5 Hz, 1H), 7.03 (d, J=8.6 Hz, 1H), 6.79 (s, 1H), 6.66 (s, 1H), 3.89–3.74 (m, 1H), 3.15 (dd, J=13.0, 3.2 Hz, 1H), 2.86 (dd, J=14.3, 3.1 Hz, 1H), 2.18 (s, 3H), 2.06 (s, 3H), 0.99 (s, 9H), 0.14 (s, 3H), −0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 150.7, 146.7, 135.8, 129.7, 129.6, 129.2, 128.5, 127.6, 127.5, 127.4, 126.4, 126.3, 125.5, 123.5, 41.9, 27.6, 27.2, 27.0, 20.5, 18.2, 16.4, −5.1, −6.7; HRMS (ESIMS) calcd for $C_{25}H_{34}NOSi^+$ $[M+H]^+$ 392.2404, found 392.2410.

*4.2.3. 2-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)ethyl)-4-methylphenol (**3b**).* White solid; mp 182–185 °C. Yield: 81% (30 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.30–8.15 (m, 1H), 8.23–8.17 (m, 1H), 8.00 (d, J=8.5 Hz, 1H), 8.00 (d, J=8.5 Hz, 1H), 7.74 (d, J=7.5 Hz, 2H), 7.74 (d, J=7.5 Hz, 2H), 7.49 (td, J=7.3, 1.0 Hz, 1H), 7.49 (td, J=7.3, 1.0 Hz, 1H), 7.23 (d, J=8.5 Hz, 1H), 7.23 (d, J=8.5 Hz, 1H), 7.00 (d, J=1.8 Hz, 1H), 7.00 (d, J=1.8 Hz, 1H), 6.85–6.73 (m, 2H), 6.84–6.77 (m, 2H), 3.64 (d, J=17.0 Hz, 1H), 3.44 (m, 2H), 2.22 (s, 3H), 0.83 (s, 9H), 0.22 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 152.4, 146.6, 136.6, 132.4, 130.9, 129.8, 129.2, 127.8, 127.4, 127.0, 126.8, 126.1, 122.1, 118.0, 41.8, 29.7, 27.0, 19.7, 17.6, −5.5, −6.1; HRMS (ESIMS) calcd for $C_{24}H_{32}NOSi^+$ $[M+H]^+$ 378.2248, found 378.2243.

*4.2.4. 4-(tert-Butyl)-2-(2-(tert-butyldimethylsilyl)-2-(quinolin-2-yl)ethyl)phenol (**4b**).* White solid, mp 184–187 °C. Yield: 78% (32 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J=9.0 Hz, 1H), 7.96 (d, J=8.5 Hz, 1H), 7.12–7.68 (m, 2H), 7.47 (td, J=6 Hz, 1H), 7.25–7.19 (m, 2H), 6.85–6.73 (dd, J=3.0, 9.0 Hz, 2H), 6.86 (d, J=5.7 Hz, 1H), 3.64 (d, J=17.0 Hz, 1H), 3.52–3.40 (m, 2H), 1.28 (s, 9H), 0.80 (s, 9H), 0.21 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 152.3, 146.5, 142.6, 136.6, 132.0, 129.8, 127.7, 127.4, 127.0, 126.1, 123.1, 122.1, 117.5, 41.9, 34.0, 31.7,27.0, 19.9, 17.5, −5.4, −6.0; HRMS (ESIMS) calcd for $C_{27}H_{38}NOSi^+$ $[M+H]^+$ 420.2717, found 420.2712.

*4.2.5. 3-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)ethyl)-[1,1′-biphenyl]-4-ol (**5b**).* White solid, mp 195–197 °C. Yield: 85% (38 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.24 (d, J=8.7 Hz, 1H), 8.02 (d, J=8.5 Hz, 1H), 7.78–7.72 (m, 2H), 7.56–7.49 (m, 3H), 7.46 (d, J=1.2 Hz, 1H), 7.40 (t, J=7.6 Hz, 2H), 7.31–7.26 (m, 2H), 7.24 (d, J=8.5 Hz, 2H), 6.99 (dd, J=8.3, 0.7 Hz, 1H), 3.69 (d, J=17.3 Hz, 1H), 3.50 (dt, J=17.3, 11.7 Hz, 2H), 0.85 (d, J=0.5 Hz, 9H), 0.26 (s, 3H), 0.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 154.6, 146.5, 141.6, 136.7, 133.3, 132.9, 129.9, 128.6, 127.8, 127.7, 127.5, 127.1, 126.5, 126.3, 126.2, 125.3, 122.1, 118.7, 41.9, 29.7, 27.0, 17.6, −5.4, −5.9; HRMS (ESIMS) calcd for $C_{29}H_{34}NOSi^+$ $[M+H]^+$ 440.2404, found 440.2409.

*4.2.6. 2-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)ethyl)-3,5-dimethylphenol (**6b**).* White solid, mp 193–195 °C. Yield: 84% (33 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.14 (d, J=8.4 Hz, 1H), 7.89 (d, J=8.8 Hz, 1H), 7.75 (t, J=6.8 Hz, 2H), 7.46 (t, J=7.6 Hz, 3H), 7.04 (d, J=8.8 Hz, 1H), 6.49 (d, J=7.6 Hz, 2H), 3.89 (t, J=14.4 Hz, 1H), 3.24 (dd, J=13.2, 3.6 Hz, 1H), 2.99 (dd, J=14.8, 2.8 Hz, 1H), 2.41 (s, 3H), 2.13 (s, 3H), 0.98 (s, 9H), 0.19 (s, 3H), −0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.2, 146.5, 136.9, 136.6, 135.9, 129.9, 128.4, 127.4, 126.3, 125.6, 125.3, 123.5, 123.0, 116.4, 39.4, 27.3, 25.9, 24.8, 20.8, 20.0, 18.2, −5.3, −6.6; HRMS (ESIMS) calcd for $C_{25}H_{34}NOSi^+$ $[M+H]^+$ 392.2404, found 392.2409.

*4.2.7. 2-(2-(tert-Butyldimethylsilyl)-2-(6-methylquinolin-2-yl)ethyl)phenol (**7b**).* White solid, mp 184–186 °C. Yield: 83% (31 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.10 (d, J=8.6 Hz, 1H), 7.91 (d, J=8.5 Hz, 1H), 7.56 (dd, J=8.6, 1.7 Hz, 1H), 7.50 (s, 1H), 7.20 (dd, J=13.6, 4.8 Hz, 2H), 7.03–6.95 (m, 1H), 6.94–6.89 (m, 1H), 6.85–6.76 (m, 1H), 3.64 (d, J=17.6 Hz, 1H), 3.52 (d, J=11.8 Hz, 1H), 3.39 (dd, J=17.6, 11.6 Hz, 1H), 2.52 (s, 3H), 0.83 (s, 9H), 0.23 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 154.9, 145.1, 136.0, 135.9, 132.8, 132.0, 128.9, 127.4, 127.1, 126.3, 126.3, 122.0, 120.2, 118.4, 41.7, 27.0, 21.4, 17.6, 14.1, −5.5, −6.1; HRMS (ESIMS) calcd for $C_{24}H_{32}NOSi^+$ $[M+H]^+$ 378.2248, found 378.2246.

*4.2.8. 2-(2-(tert-Butyldimethylsilyl)-2-(6-methoxyquinolin-2-yl)ethyl)phenol (**8b**).* White solid, mp 167–170 °C. Yield: 85% (33 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 10.51 (s, 1H), 8.10 (d, J=9.2 Hz, 1H), 7.89 (d, J=8.5 Hz, 1H), 7.37 (dd, J=9.2, 2.7 Hz, 1H), 7.19 (dd, J=12.0, 4.8 Hz, 2H), 7.04–6.95 (m, 2H), 6.91 (d, J=7.1 Hz, 1H), 6.80 (t, J=7.3 Hz, 1H), 3.91 (s, 3H), 3.61 (d, J=17.5 Hz, 1H), 3.48 (d, J=12.0 Hz, 1H), 3.36 (dd, J=17.5, 11.7 Hz, 1H), 0.82 (s, 9H), 0.21 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 157.5, 154.8, 142.5, 135.5, 132.8, 129.1, 128.9, 128.0, 126.3, 122.3, 122.1, 120.2, 118.3, 105.4, 55.5, 41.5, 27.0, 19.7, 17.6, −5.5, −6.1; HRMS (ESIMS) calcd for $C_{24}H_{32}NO_2Si^+$ $[M+H]^+$ 394.2197, found 394.2201.

*4.2.9. 2-(2-(tert-Butyldimethylsilyl)-2-(3-methylquinolin-2-yl)ethyl)phenol (**9b**).* White solid, mp 144–146 °C. Yield: 65% (25 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.25 (d, J=8.5 Hz, 1H), 7.76 (s, 1H), 7.73–7.60 (m, 2H), 7.46 (t, J=7.5 Hz, 1H), 7.27 (d, J=7.5 Hz, 1H), 7.09–6.97 (m, 2H), 6.86 (t, J=7.3 Hz, 1H), 3.61 (d, J=11.2 Hz, 1H), 3.49 (d, J=18.4 Hz, 1H), 3.31 (dd, J=18.4, 11.4 Hz, 1H), 2.41 (s, 3H), 0.87 (s, 9H), 0.27 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 155.0, 145.1, 136.1, 132.9, 130.1, 128.9, 128.8, 127.4, 127.2, 126.6, 126.4, 126.0, 120.1, 118.3, 39.7, 27.0, 19.1, 18.9, 17.6, −5.5, −6.1; HRMS (ESIMS) calcd for $C_{24}H_{32}NOSi^+$ $[M+H]^+$ 378.2248, found 378.2250.

*4.2.10. 1-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)ethyl)naphthalen-2-ol (**10b**).* White solid, mp 97–101 °C. Yield: 54% (22 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.29 (d, J=8.4 Hz, 1H), 8.01 (t, J=8.5 Hz, 2H), 7.74 (dd, J=11.5, 4.5 Hz, 3H), 7.53 (t, J=8.2 Hz, 3H),

7.38 (d, *J*=7.7 Hz, 1H), 7.23 (dd, *J*=8.5, 4.6 Hz, 2H), 4.21 (dd, *J*=11.2, 1.8 Hz, 1H), 3.93 (dd, *J*=18.4, 11.2 Hz, 1H), 3.76 (dd, *J*=18.3, 1.6 Hz, 1H), 0.87 (s, 9H), 0.46 (s, 3H), −0.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 153.0, 146.4, 136.8, 133.9, 129.9, 129.8, 128.9, 128.5, 127.7, 127.5, 127.0, 126.2, 124.8, 124.5, 123.8, 122.3, 122.2, 120.9, 40.1, 26.5, 18.1, 17.3, −4.5, −5.5; HRMS (ESIMS) calcd for $C_{27}H_{32}NOSi^+$ $[M+H]^+$ 414.2248, found 414.2243.

*4.2.11. (E)-2-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)vinyl)phenol (**1d**).* White solid, mp 142–144 °C. Yield: 80% (29 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.11 (d, *J*=8.4 Hz, 1H), 8.02 (d, *J*=8.5 Hz, 1H), 7.77–7.67 (m, 2H), 7.50 (t, *J*=7.5 Hz, 1H), 7.16 (d, *J*=8.5 Hz, 1H), 7.11 (s, 1H), 7.01 (t, *J*=7.7 Hz, 1H), 6.96 (d, *J*=7.8 Hz, 1H), 6.84 (d, *J*=8.1 Hz, 1H), 6.72 (t, *J*=7.4 Hz, 1H), 0.90 (s, 9H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 152.9, 145.8, 139.8, 137.6, 136.5, 133.8, 129.9, 129.2, 128.7, 128.0, 127.5, 126.5, 126.3, 121.6, 119.7, 119.3, 26.9, 17.6, −5.0; HRMS (ESIMS) calcd for $C_{23}H_{28}NOSi^+$ $[M+H]^+$ 362.1935, found 362.1937.

*4.2.12. (E)-2-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)vinyl)-4-fluorophenol (**2d**).* Red solid, mp 163–165 °C. Yield: 82% (31 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 8.09 (d, *J*=8.4 Hz, 2H), 7.78 (d, *J*=8.0 Hz, 1H), 7.71 (t, *J*=7.2 Hz, 1H), 7.52 (t, *J*=7.7 Hz, 1H), 7.24 (d, *J*=8.5 Hz, 1H), 7.11 (s, 1H), 6.63–6.53 (m, 3H), 0.91 (s, 9H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 157.2, 154.8, 150.4, 146.3, 145.8, 138.8, 136.6, 131.1, 130.1, 128.8, 127.8, 127.6, 126.6, 126.5, 121.7, 119.7, 119.6, 115.2, 115.0, 114.9, 114.6, 26.8, 17.7, −5.1; HRMS (ESIMS) calcd for $C_{23}H_{27}FNOSi^+$ $[M+H]^+$ 380.1846, found 380.1846.

*4.2.13. (E)-2-(2-(tert-Butyldimethylsilyl)-2-(6-(diisopropylamino) quinolin-2-yl)vinyl)phenol (**3d**).* Yellow solid, mp 133–135 °C. Yield: 45% (20 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J*=9.3 Hz, 1H), 7.78 (d, *J*=8.5 Hz, 1H), 7.42 (dd, *J*=9.3, 2.7 Hz, 1H), 7.06–7.01 (m, 3H), 7.00–6.95 (m, 1H), 6.88 (dd, *J*=9.5, 5.4 Hz, 2H), 6.72 (t, *J*=7.4 Hz, 1H), 3.92 (dt, *J*=13.6, 6.8 Hz, 2H), 1.31 (d, *J*=6.8 Hz, 12H), 0.89 (s, 9H), 0.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 154.8, 146.5, 136.7, 132.7, 129.9, 128.9, 128.4, 128.3, 127.7, 127.4, 127.0, 126.3, 126.2, 122.1, 120.3, 118.4, 49.1, 29.7, 27.0, 14.1, −5.0, −6.2; HRMS (ESIMS) calcd for $C_{29}H_{41}N_2OSi^+$ $[M+H]^+$ 461.2983, found 461.2987.

*4.2.14. (E)-1-(2-(tert-Butyldimethylsilyl)-2-(quinolin-2-yl)vinyl) naphthalen-2-ol (**4d**).* White solid, mp 85–88 °C. Yield: 70% (28 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J*=8.5 Hz, 1H), 7.81 (d, *J*=8.1 Hz, 1H), 7.68 (d, *J*=8.9 Hz, 1H), 7.65–7.55 (m, 4H), 7.41 (t, *J*=7.7 Hz, 3H), 7.03 (d, *J*=8.8 Hz, 1H), 6.94 (t, *J*=7.5 Hz, 1H), 6.45 (d, *J*=7.9 Hz, 1H), 1.12 (s, 9H), 0.41 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 144.8, 141.2, 134.6, 131.6, 130.1, 129.0, 128.7, 128.2, 127.6, 126.8, 126.6, 126.1, 126.0, 123.8, 123.5, 120.8, 119.0, 118.8, 114.8, 113.9, 27.3, 17.6, −3.0, −3.8; HRMS (ESIMS) calcd for $C_{27}H_{30}NOSi^+$ $[M+H]^+$ 412.2091 found 412.2095.

*4.2.15. 2,2′-(Pyridine-2,6-diylbis(2-(tert-butyldimethylsilyl)ethane-2,1-diyl))diphenol (**1f**).* White solid, mp 136–138 °C. Yield: 78% (42 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 1H), 7.04–6.96 (m, 4H), 6.74 (dd, *J*=11.7, 4.3 Hz, 4H), 6.65 (d, *J*=7.7 Hz, 2H), 3.39–3.29 (m, 2H), 3.06 (d, *J*=14.4 Hz, 2H), 2.98 (d, *J*=12.8 Hz, 2H), 1.06 (s, 18H), 0.14 (s, 6H), −0.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 153.9, 135.9, 129.8, 129.0, 127.1, 120.7, 120.2, 116.6, 37.5, 29.9, 27.4, 17.9, −5.6, −7.2; HRMS (ESIMS) calcd for $C_{33}H_{50}NO_2Si_2^+$ $[M+H]^+$ 548.3375, found 548.3367.

*4.2.16. (E)-2-(2-(tert-Butyldimethylsilyl)-2-(pyridin-2-yl)vinyl)phenol (**2f**).* White solid, mp 143–145 °C. Yield: 72% (22 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.48 (d, *J*=4.0 Hz, 1H), 7.62 (t, *J*=7.7 Hz, 1H), 7.13 (dd, *J*=14.2, 7.2 Hz, 3H), 6.88 (s, 1H), 6.73 (s, 1H), 6.58 (d, *J*=3.7 Hz, 2H), 0.89 (s, 9H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 154.4, 147.8, 143.5, 134.0, 136.5, 129.2, 128.5, 126.5, 123.8, 121.3, 119.0, 117.9, 26.8, 17.6, −5.2; HRMS (ESIMS) calcd for $C_{19}H_{26}NOSi^+$ $[M+H]^+$ 312.1778, found 312.1774.

Acknowledgements

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Supplementary data

NMR spectra (^{1}H and ^{13}C) for all products. X-ray ORTEP illustration of **2b**, **2d** and **1f**, fluorescence spectra of **3d**. This material is available free of charge. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.04.065. These data include MOL files and InChiKeys of the most important compounds described in this article.

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