

## $\alpha$ -Methylpyridine 유도체의 국지 선택적 리튬화 반응과 $\text{Me}_2\text{RSiCl}$ ( $\text{R}=\text{Me}$ , $t\text{-BuCH}_2(\text{Me}_3\text{Si})\text{CH}$ )을 이용한 반응생성물의 확인반응

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## Regioselective Lithiation of $\alpha$ -Methylpyridine Analogue and Its Trapping Reactions with $\text{Me}_2\text{RSiCl}$ ( $\text{R}=\text{Me}$ , $t\text{-BuCH}_2(\text{Me}_3\text{Si})\text{CH}$ )

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**요 약.**  $\alpha$ -Methylpyridine 유도체 **1(a~f)**는  $n\text{-BuLi}$ 과의 반응에서  $\alpha$ -methylene pyridinium 염 **3(a~f)**을 형성한다. **3(a~f)**와  $\text{Me}_3\text{SiCl}$  및  $\text{Me}_2\text{SiClCH}(\text{SiMe}_3)\text{CH}_2t\text{-Bu}$ 의 반응에서 생성물 **4(a~f)**와 **5(a~f)**을 형성한다. 화합물 **4(a~f)**에 있는 규소원자와 결합된 methylene기의 수소원자는 화합물 **4(a~f)**의  $\text{CH}_3$ 기 보다  $n\text{-BuLi}$ 과의 반응에서 반응성이 큰 것으로 확인되었다.

**ABSTRACT.** The metallation of  $\alpha$ -methylpyridine **1(a~f)** with  $n\text{-BuLi}$  produced  $\alpha$ -methylene pyridinium salt **3(a~f)** by elimination of butane. The trapping reactions of **3(a~f)** with  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_2\text{SiClCH}(\text{SiMe}_3)\text{CH}_2t\text{-Bu}$  produced only **4(a~f)** and **5(a~f)**. The  $\alpha$ -hydrogen atom of silylated methylene group in **4(a~f)** is more reactive than unreacted  $\text{CH}_3$  of **4(b~f)** itself and **1(a~f)** toward  $n\text{-BuLi}$  at low temperature in pentane medium.

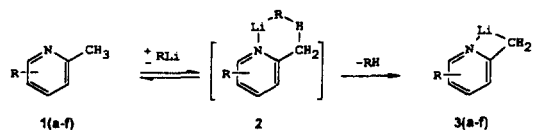
### INTRODUCTION

In recent years, the metallation of aromatic systems has been successfully developed as a powerful functionalization method<sup>1</sup>, and the reactions of pyridine, diazine, and triazine with organolithium have appeared<sup>2</sup> on the many articles. But only a few cases about the metallation of  $\alpha$ -methyl substituted pyridine have been reported<sup>3</sup> previously. Our interests have been focused on the reaction of  $\alpha$ -methyl substituted pyridine with  $n\text{-BuLi}$  and  $t\text{-BuLi}$  at low temperature via direct ortho metallation (DoM-process)<sup>3</sup>.

### RESULTS AND DISCUSSION

The reactions of  $\alpha$ -picoline and its analogue ( $\alpha$ -methyl substituted lutidine and 2,5,5-collidine) with  $n\text{-BuLi}$  have provided a  $\alpha$ -lithiomethylene pyridine complex (**3**)<sup>4</sup> by the elimination of butane. The reaction pathway of formation of **3** is shown Scheme 1.

The lithiations of **1(a~f)** were performed by using on equivalent amount of  $n\text{-BuLi}$  at low temperature in pentane medium. The lithiated compounds **3(a~f)** were trapped by  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_2\text{SiClCH}(\text{SiMe}_3)\text{CH}_2t\text{-Bu}$ <sup>5</sup>, to give **4(a~f)** and **5(a~f)**,



1a: 2-picoline; 1b: 2,3-lutidine; 1c: 2,4-lutidine;  
1d: 2,5-lutidine; 1e: 1,6-lutidine; 1f: 2,4,6-collidine

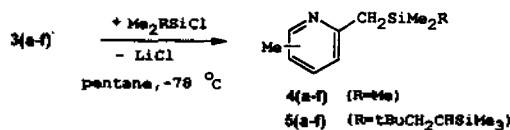
Scheme 1.

Table 1. Yields and boiling points of compounds 4(a~f) and 5(a~f)

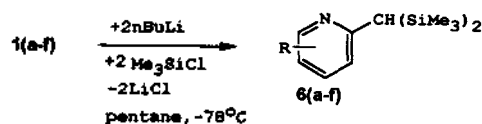
	3-	4-	5-	6-	Yields	bp.
4a	H	H	H	H	18(%)	30 ( $^{\circ}\text{C}/10^{-1}$ torr)
b	Me	H	H	H	52	40
c	H	Me	H	H	46	40
d	H	H	Me	H	50	40
e	H	H	H	Me	50	40
f	H	Me	H	Me	45	45
5a	H	H	H	H	66	90
b	Me	H	H	H	53	110
c	H	Me	H	H	46	120
d	H	H	Me	H	72	110
e	H	H	H	Me	60	110
f	H	Me	H	Me	70	120

respectively. We found strong evidences of regioselective characters in these metallation processes. Because we did not observe methylenyl group at the other position of pyridine ring by trapping reactions. This regioselective character of the reaction depends on the reaction medium, since the formation of intermediate 3(a~f) is favored in nonpolar medium, whereas THF or  $\text{Et}_2\text{O}$  leads many products<sup>6</sup> unconsiderably.

When if the metallation of  $\alpha$ -methylpyridine (1 a) and its analogues 1(b~f) was carried out in the presence of  $\text{Me}_3\text{SiCl}$  (one pot reaction), compounds 6(a~f) were only formed. The remarkable difference in this reaction path between reaction Scheme 2 and 3 could be explained on the basis of reactivities of compounds 1 and 4. The  $\alpha$ -hydrogen atom of mono silylated group is more reactive than unreacted methyl group in compound 4 itself (in the case of compounds 4(b~f)) and 1(a~f) toward  $n$ -BuLi. This regioselective functionalization methods are performed at low temperature in pentane. Therefore, the reactions of 4



Scheme 2.



Scheme 3.

Table 2. Yields and boiling points of compounds 6(a~f)

	3-	4-	5-	6-	Yields	bp.
6a	H	H	H	H	45(%)	55
b	Me	H	H	H	35	60
c	H	Me	H	H	35	60
d	H	H	Me	H	50	60
e	H	H	H	Me	31	60
f	H	Me	H	Me	42	70

( $^{\circ}\text{C}/10^{-1}$  torr)

(a~f) with organolithium produce  $\alpha$ -lithiated compounds at mono silylated position, which are reacted with  $\text{Me}_3\text{SiCl}$  to give the compounds 6(a~f). The metallations of 1(a~f) with organolithium in the presence of  $\text{Me}_2\text{SiClCH}(\text{SiMe}_3)\text{CH}_2/\text{Bu}$  (one pot condition) provided only compound 5(a~f).

The structure of compounds 4(a~f), 5(a~f) and 6(a~f) was confirmed by  $^1\text{H-NMR}$  spectrum which showed a hyperfine signal between 6.00~8.00 ppm (aromatic CH) and  $\alpha$ -methylene group and another methyl group in compounds 4(b~f), 5(b~f) and 6(b~f) showed between 1.5~3.5 ppm, with integral 3 to 2 (compounds 4(b~f) and 5(b~f)), with 3 to 1 (compounds 6(b~f)). Another assignments of the structure 4, 5 and 6 are based on the  $^{13}\text{C-NMR}$ , DEPT spectra of the same derivatives of prepared compounds, which the compounds 4(a~f) and 5(a~f)  $\text{CH}_2$  are negative signal but compounds 6(a~f) are positive. All mass spectra by 70 eV were showed molecular ion peaks.

## EXPERIMENTAL

All reactions were carried out under dried  $\text{N}_2$

atmosphere. All solvents were freshly distilled (THF and Et<sub>2</sub>O were dried by boiling with Ph<sub>2</sub>C=O/Na; pentane was dried by boiling with Na metal). <sup>1</sup>H-NMR spectra were recorded of solution in CDCl<sub>3</sub> on a JEOL 90(90 MHz) and Bruker AC 200 (200 MHz) spectrometer using the solvent proton signal as standard. <sup>13</sup>C-NMR spectra were recorded on a JEOL 90 (22.5 MHz) and Bruker AC 200 (50.32 MHz) spectrometer using the solvent proton signal as standard. Mass spectra were measured with a VG-70-SEG mass spectrometer. Mass spectra and elemental analyses (measured with CE2400 elemental analyzer) were performed by Korean Basic Science Center (in Seoul). Materials such as α-picoline, lutidine and collidine were freshly distilled and stored over molecular sieve (3 Å).

**General procedure for synthesis of 4(a~f) and 5(a~f).** A solution of 15 mmol of 1(a~f) in 100 ml of pentane was slowly treated with an equivalent amount of *n*-BuLi in 10 ml of pentane at -78 °C, and resulting solution was stirred for 1 hr at this temperature. About 10% excess of RMe<sub>2</sub>SiCl (R=Me, <sup>t</sup>BuCH<sub>2</sub>(Me<sub>3</sub>Si)CH) was added to the stirred solution and the mixture was allowed to stir for 12 hrs. White precipitate was filtered off and then pentane and unreacted RMe<sub>2</sub>SiCl was removed by reduced distillation. The residue was subjected to short path distillation. <sup>1</sup>H-, <sup>13</sup>C-NMR spectroscopic data and their mass spectroscopic fragmentations is might have been expected.

**General procedure for synthesis of 6(a~f).** A solution of 1(a~f) and 2.1 equivalent of Me<sub>3</sub>SiCl in 100 ml pentane was treated with 2 equivalent of *n*-BuLi in 10 ml of pentane at -78 °C. Other procedures for handling and isolation are the same as before.

**2-(2,2-Dimethyl-2-silapropyl)pyridine (4a).** Colorless liquid, bp. (30°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>); δ=0.00(s, 9H, Me<sub>3</sub>Si), 2.35(s, 2H, CH<sub>2</sub>), 6.90(t, 1H), 6.85(d, 1H), 7.45(m, 1H), 8.40(t, 1H), <sup>13</sup>C-NMR(22.5 MHz, CDCl<sub>3</sub>); δ=-0.20(Me<sub>3</sub>Si), 30.00(CH<sub>2</sub>), 119.10(CH), 122.00(CH), 135.50(CH), 148.60(CH), 161.50(C). Mass(70 eV); m/z=165(M<sup>+</sup>, 16), 150((M-Me)<sup>+</sup>, 70), 73(Me<sub>3</sub>Si<sup>+</sup>, 100).

Anal. Calcd. for C<sub>9</sub>H<sub>15</sub>NSi: C, 65.39; H, 9.57; N, 8.47. Found: C, 63.12; H, 10.29; N, 7.85.

**2-(2,2-Dimethyl-2-silapropyl)-3-methylpyridine (4b).** Colorless liquid, bp. (40°C/10<sup>-1</sup> torr) <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>); δ=-0.01(s, 9H, Me<sub>3</sub>Si), 2.18(s, 3H, CH<sub>3</sub>), 2.36(s, 2H, CH<sub>2</sub>), 6.70(m, 1H), 7.20(m, 1H), 8.20(m, 1H), <sup>13</sup>C-NMR(22.5 MHz, CDCl<sub>3</sub>); δ=-0.09(Me<sub>3</sub>Si), 19.90(CH<sub>3</sub>), 26.50(CH<sub>2</sub>), 119(CH), 137(CH), 146(CH), 160(C). Mass (70 eV)=179(M<sup>+</sup>, 4), 164((M-Me)<sup>+</sup>, 16), 73(Me<sub>3</sub>Si<sup>+</sup>, 100). Anal. Calc. for C<sub>10</sub>H<sub>17</sub>NSi: C, 66.97; H, 9.56; N, 7.81. Found: C, 67.26; H, 9.72; N, 7.90.

**2-(2,2-Dimethyl-2-silapropyl)-4-methylpyridine (4c).** Colorless liquid, bp. (40°C/10<sup>-1</sup> torr) <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>); δ=-0.05(s, 9H, Me<sub>3</sub>Si), 2.15(s, 3H, CH<sub>3</sub>), 2.22(s, 2H, CH<sub>2</sub>), 6.58(s, 1H), 6.80(m, 1H), 8.15(m, 1H), <sup>13</sup>C-NMR(22.5 MHz, CDCl<sub>3</sub>); δ=0.00(Me<sub>3</sub>Si), 20.90(CH<sub>3</sub>), 29.95(CH<sub>2</sub>), 119.20(CH), 123.00(CH), 148.50(CH), 160.00(C), 164.00(C). Mass (70 eV) m/z=179(M<sup>+</sup>, 4), 164((M-Me)<sup>+</sup>, 16), 73(Me<sub>3</sub>Si<sup>+</sup>, 100). Anal. Calcd. for C<sub>10</sub>H<sub>17</sub>NSi: C, 66.97; H, 9.56; N, 7.81. Found: C, 63.51; H, 9.67; N, 6.78.

**2-(2,2-Dimethyl-2-silapropyl)-5-methylpyridine (4d).** Colorless liquid, bp. (40°C/10<sup>-1</sup> torr) <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>); δ=0.03(s, 9H, Me<sub>3</sub>Si), 2.15(s, 3H, CH<sub>3</sub>), 2.20(s, 2H, CH<sub>2</sub>), 6.80(t, 1H), 7.20(m, 1H), 8.20(m, H). Mass (70 eV) m/z=179(M<sup>+</sup>, 4), 164((M-Me)<sup>+</sup>, 9), 73(Me<sub>3</sub>Si<sup>+</sup>, 100). Anal. Calcd. for C<sub>10</sub>H<sub>17</sub>NSi: C, 66.97; H, 9.56; N, 7.81. Found: C, 67.01; H, 10.91; N, 7.53.

**2-(2,2-Dimethyl-2-silapropyl)-6-methylpyridine (4e).** Colorless liquid, bp. (40°C/10<sup>-1</sup> torr) <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>); δ=0.09(s, 9H, Me<sub>3</sub>Si), 2.30(s, 3H, CH<sub>3</sub>), 2.45(s, 2H, CH<sub>2</sub>), 6.65(d, 1H), 6.80(d, 1H), 7.40(m, 1H), <sup>13</sup>C-NMR(22.5 MHz, CDCl<sub>3</sub>); δ=0.19(Me<sub>3</sub>Si), 24.50(CH<sub>3</sub>), 30.02(CH<sub>2</sub>), 118.50(CH), 119.00(CH), 135.60(CH), 157.00(C), 160.05(C). Mass (70 eV) m/z=179(M<sup>+</sup>, 2), 164((M-Me)<sup>+</sup>, 14), 73(Me<sub>3</sub>Si<sup>+</sup>, 100). Anal. Calcd. for C<sub>10</sub>H<sub>17</sub>NSi: C, 66.97; H, 9.56; N, 7.81. Found: C, 66.91; H, 10.23; N, 6.10.

**2-(2,2-Dimethyl-2-silapropyl)-4,6-dimethylpyridine (4f).** Colorless liquid, bp. (45°C/10<sup>-1</sup> torr) <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>); δ=0.14(s, 9H, Me<sub>3</sub>

Si), 2.47(s, 3H, *p*-CH<sub>3</sub>), 2.52(s, 2H, CH<sub>2</sub>), 2.69(s, 3H, *o*-CH<sub>3</sub>), 7.06(s, 1H, aromatic CH), 7.15(s, 1H, aromatic CH). <sup>13</sup>C-NMR (50.32 MHz, CDCl<sub>3</sub>);  $\delta = -5.91(\text{SiMe}_3)$ , 17.75(*o*-CH<sub>3</sub>), 21.46(*p*-CH<sub>3</sub>), 27.27(*o*-CH<sub>3</sub>), 121.77(*m*-CH), 121.96(*m*-CH), 150.26(*p*-C), 161.13(*o*-C), 164.48(*o*-C).

**2-(2,2,4,4-Tetramethyl-3-trimethyl-2-silapentyl)pyridine (5a).** Colorless liquid, bp. (90°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta = -0.08(\text{t}, 1\text{H}, \text{CH})$ ,  $-0.02(\text{s}, 6\text{H}, \text{Me}_2\text{Si})$ , 0.08(s, 9H, Me<sub>3</sub>Si), 0.82(s, 9H, 'Bu), 1.45(d, 2H, CH<sub>2</sub>), 2.40(s, 2H, CH<sub>2</sub>), 6.89(s, 1H), 7.36(d, 1H), 7.00(q, 1H), 7.41, 7.45, 7.57(m, 1H), 8.40, 8.45(d, 1H). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta = -1.50$ ,  $-1.00(\text{d}, \text{Me}_2\text{Si})$ , 1.00(Me<sub>3</sub>Si), 30.20(CH<sub>2</sub>), 31.50(C-'Bu), 37.60(CH<sub>2</sub>), 119.00(CH), 122.80(CH), 161.90(C), 122.80(CH), 135.80(CH), 149.00(CH), 161.90(C). Mass (70 eV)  $m/z = 307(\text{M}^+, 6)$ , 292((M-Me)<sup>+</sup>, 55), 250((M-'Bu)<sup>+</sup>, 58), 234((M-Me<sub>3</sub>Si)<sup>+</sup>, 30), 215('BuCH<sub>2</sub>(Me<sub>3</sub>Si)CHMe<sub>2</sub>Si<sup>+</sup>, 16), 176((M-Me<sub>3</sub>Si, 'Bu)<sup>+</sup>, 16), 150((M-'BuCH<sub>2</sub>(SiMe<sub>3</sub>)CH)<sup>+</sup>, 100), 141('BuCH<sub>2</sub>CHSiMe<sub>2</sub><sup>+</sup>, 70), 73(Me<sub>3</sub>Si<sup>+</sup>, 75). Anal. Calcd. for C<sub>17</sub>H<sub>33</sub>NSi<sub>2</sub>: C, 66.38; H, 10.75; N, 4.55. Found: C, 66.32; H, 10.76; N, 4.80.

**2-(2,2,4,4-Tetramethyl-3-trimethylsilyl-2-silapentyl)-3-methylpyridine (5b).** Colorless liquid, bp. (110°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta = 0.00(\text{s}, 6\text{H}, \text{Me}_2\text{Si})$ , 0.05(s, 9H, Me<sub>3</sub>Si), 0.85(s, 9H, 'Bu), 1.45(d, 2H, CH<sub>2</sub>), 2.21(s, 1H, CH), 2.40(s, 2H, CH<sub>2</sub>), 6.88(t, 1H), 7.29(d, 1H), 8.27(d, 1H). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta = -3.00(\text{d}, \text{Me}_2\text{Si})$ , 1.40(Me<sub>3</sub>Si), 7.30(CH), 27.00(CH<sub>2</sub>), 30.01('Bu), 31.09(C), 38.00(CH<sub>2</sub>), 119.50(CH), 130.00(CH), 137.20(CH), 147.00(CH), 152.00(C). Mass (70 eV)  $m/z = 321(\text{M}^+, 4)$ , 306((M-Me)<sup>+</sup>, 10), 264((M-'Bu)<sup>+</sup>, 23), 248((M-Me<sub>3</sub>Si)<sup>+</sup>, 10), 215('BuCH<sub>2</sub>(Me<sub>3</sub>Si)CHMe<sub>2</sub>-Si<sup>+</sup>, 4), 176((M-Me<sub>3</sub>Si, 'Bu)<sup>+</sup>, 8), 164((M-'BuCH<sub>2</sub>-CHSiMe<sub>3</sub>)<sup>+</sup>, 100), 141('BuCH<sub>2</sub>CHSiMe<sub>2</sub><sup>+</sup>, 25), 73(Me<sub>3</sub>Si<sup>+</sup>, 76). Anal. Calcd. for C<sub>18</sub>H<sub>35</sub>NSi<sub>2</sub>: C, 67.21; H, 10.97; N, 4.35. Found: C, 66.23; H, 11.79; N, 4.51.

**2-(2,2,4,4-Tetramethyl-3-trimethylsilyl-2-silapentyl)-4-methylpyridine (5c).** Colorless liquid, bp. (120°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta = -0.01(\text{s}, 6\text{H}, \text{Me}_2\text{Si})$ , 0.02(t, 1H, CH), 0.05(s, 9H, Me<sub>3</sub>Si), 0.80(s, 9H, 'Bu), 1.40(d, 2H, CH<sub>2</sub>), 2.24

(d, 2H, CH<sub>2</sub>), 6.70(d, 1H), 6.75(d, 1H), 8.22(d, 1H). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta = -1.00(\text{d}, \text{Me}_2\text{Si})$ , 1.50(Me<sub>3</sub>Si), 6.80(CH), 30.00('Bu), 31.50(C), 21.60(CH<sub>2</sub>), 38.00(CH<sub>2</sub>), 120.05(CH), 123.50(CH), 149.00(CH), 161.50(C). Mass (70 eV)  $m/z = 321(\text{M}^+, 5)$ , 306((M-Me)<sup>+</sup>, 10), 264((M-'Bu)<sup>+</sup>, 25), 248((M-Me<sub>3</sub>-Si)<sup>+</sup>, 10), 164((M-'BuCH<sub>2</sub>CHSiMe<sub>3</sub>)<sup>+</sup>, 100), 141('BuCH<sub>2</sub>CHSiMe<sub>2</sub><sup>+</sup>, 23), 73(Me<sub>3</sub>Si<sup>+</sup>, 79). Anal. Calcd. for C<sub>18</sub>H<sub>35</sub>NSi<sub>2</sub>: C, 67.21; H, 10.97; N, 4.35. Found: C, 66.07; H, 11.83; N, 4.47.

**2-(2,2,4,4-Tetramethyl-3-trimethylsilyl-2-silapentyl)-5-methylpyridine (5d).** Colorless liquid, bp. (110°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta = -0.02(\text{s}, 6\text{H}, \text{Me}_2\text{Si})$ , 0.05(s, 9H, Me<sub>3</sub>Si), 0.08(s, 9H, 'Bu), 1.40(d, 2H, CH<sub>2</sub>), 2.21(s, 1H, CH), 2.35(s, 2H, CH<sub>2</sub>), 6.83(d, 1H, CH), 7.20(d, 1H, CH), 8.21(d, 1H, CH). <sup>13</sup>C-NMR (22.5 Hz, CDCl<sub>3</sub>);  $\delta = -1.00(\text{d}, \text{Me}_2\text{Si})$ , 1.50(Me<sub>3</sub>Si), 6.80(CH), 17.50(CH<sub>3</sub>), 29.50(CH<sub>2</sub>), 30.00('Bu), 31.50(C), 38.00(CH<sub>2</sub>), 122.00(CH), 136.20(CH), 149.00(CH), 158.50(C). Mass (70 eV)  $m/z = 321(\text{M}^+, 5)$ , 306((M-Me)<sup>+</sup>, 10), 264((M-'Bu)<sup>+</sup>, 23), 248((M-Me<sub>3</sub>Si)<sup>+</sup>, 10), 215('BuCH<sub>2</sub>(Me<sub>3</sub>Si)CH-SiMe<sub>2</sub><sup>+</sup>, 4), 164((M-'BuCH<sub>2</sub>CHSiMe<sub>3</sub>)<sup>+</sup>, 100), 73(Me<sub>3</sub>Si<sup>+</sup>, 79). Anal. Calcd. for C<sub>18</sub>H<sub>35</sub>NSi<sub>2</sub>: C, 67.21; H, 10.97; N, 4.35. Found: C, 66.60; H, 11.97; N, 4.27.

**2-(2,2,4,4-Tetramethyl-3-trimethylsilyl-2-silapentyl)-6-methylpyridine (5e).** Colorless liquid, bp. (110°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta = 0.00(\text{s}, 6\text{H}, \text{Me}_2\text{Si})$ , 0.05(t, 1H, CH), 0.08(s, 9H, Me<sub>3</sub>Si), 0.81(s, 9H, 'Bu), 1.41(d, 2H, CH<sub>2</sub>), 2.49(s, 3H, CH<sub>3</sub>), 6.75(d, 1H, CH), 6.83(d, 1H, CH), 7.38(t, 1H, CH). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta = -0.09(\text{d}, \text{Me}_2\text{Si})$ , 1.00(Me<sub>3</sub>Si), 6.30(CH), 24.50(CH<sub>3</sub>), 19.90('Bu), 30.01(CH<sub>2</sub>), 31.60(C), 37.50(CH<sub>2</sub>), 118.90(CH), 119.60(CH), 135.40(CH), 157.10(C), 161.00(CH). Mass (70 eV)  $m/z = 321(\text{M}^+, 6)$ , 306((M-Me)<sup>+</sup>, 60), 264((M-'Bu)<sup>+</sup>, 55), 248((M-Me<sub>3</sub>Si)<sup>+</sup>, 21), 215('BuCH<sub>2</sub>(Me<sub>3</sub>Si)CHSiMe<sub>2</sub><sup>+</sup>, 55), 176((M-Me<sub>3</sub>Si, 'Bu)<sup>+</sup>, 22), 164((M-'BuCH<sub>2</sub>CHSiMe<sub>3</sub>)<sup>+</sup>, 100), 73(Me<sub>3</sub>-Si<sup>+</sup>, 81). Anal. Calcd. for C<sub>18</sub>H<sub>35</sub>NSi<sub>2</sub>: C, 67.21; H, 10.97; N, 4.35. Found: C, 66.54; H, 11.88; N, 4.37.

**2-(2,2,4,4-Tetramethyl-3-trimethylsilyl-2-silapentyl)-4,6-dimethylpyridine (5f).** Colorless liquid, bp. (120°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (200 MHz,

CDCl<sub>3</sub>);  $\delta$  = -0.17(t, 1H, CH), -0.14, -0.13(d, 6H, Me<sub>2</sub>Si), -0.05(s, 9H, Me<sub>2</sub>Si), 0.79(s, 9H, <sup>t</sup>Bu), 1.45(t, 2H, -CH<sub>2</sub>/<sup>t</sup>Bu), 2.12(s, 3H, *p*-CH<sub>3</sub>), 2.18, 2.21(d, 2H, *o*-CH<sub>2</sub>), 2.31(s, 3H, *o*-CH<sub>3</sub>), 6.46(s, 1H, *m*-aromatic CH), 6.53(s, 1H, *m'*-aromatic CH). <sup>13</sup>C-NMR (50.32 MHz, CDCl<sub>3</sub>);  $\delta$  = -1.61, -1.06(d, Me<sub>2</sub>Si), 0.89(Me<sub>3</sub>Si), 6.13(CH), 20.66(CH<sub>2</sub>), 24.20(*o*-CH<sub>2</sub>), 29.62(*p*-CH<sub>3</sub>), 29.73(<sup>t</sup>Bu), 31.39(C<sub>quartet</sub>), 37.48(*o*-CH<sub>3</sub>), 119.45(*m*-aromatic CH), 120.20(*m*-aromatic CH), 146.41(*p*-aromatic C<sub>quartet</sub>), 156.92(*o*-aromatic C<sub>quartet</sub>), 160.45(*o*-C<sub>quartet</sub>).

**2-(Bistrimethylsilylmethyl)pyridine (6a).** Colorless liquid, bp. (55°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.00(s, 18H, Me<sub>3</sub>Si), 1.82(s, 1H, CH), 6.80(d, 1H, CH), 6.80(d, 1H, CH), 7.40(m, 1H, CH), 8.37(m, 1H, CH). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.00(Me<sub>3</sub>Si), 33.00(CH), 118.00(CH), 122.40(CH), 135.00(CH), 135.50(C), 148.50(CH). Mass (70 eV) *m/z* = 237(M<sup>+</sup>, 37), 222((M-Me)<sup>+</sup>, 100), 164((M-Me<sub>3</sub>Si)<sup>+</sup>, 8), 14((M-Me<sub>3</sub>Si, Me)<sup>-</sup>, 37), 73(Me<sub>3</sub>Si<sup>+</sup>, 48). Anal. Calcd. for C<sub>12</sub>H<sub>23</sub>NSi<sub>2</sub>: C, 60.69; H, 9.76; N, 5.90(%). Found: C, 61.43; H, 10.90; N, 5.86.

**2-(Bistrimethylsilylmethyl)-3-methylpyridine (6b).** Colorless liquid, bp. (60°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.05(s, 18H, Me<sub>3</sub>Si), 1.95(s, 1H, CH), 2.20(s, 3H, CH<sub>3</sub>), 6.80(q, 1H, CH), 7.24(q, 1H, CH), 8.25(t, 1H, CH). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.50(Me<sub>3</sub>Si), 20.00(CH<sub>3</sub>), 28.50(CH), 118.00(CH), 129.50(C), 137.00(CH), 146.50(CH), 164.00(C). Mass (70 eV) *m/z* = 251 (M<sup>+</sup>, 11), 236((M-Me)<sup>+</sup>, 22), 178((M-Me<sub>3</sub>Si)<sup>+</sup>, 3), 163((M-Me<sub>3</sub>Si, Me)<sup>+</sup>, 13), 73(Me<sub>3</sub>Si<sup>+</sup>, 100). Anal. Calcd. for C<sub>13</sub>H<sub>25</sub>NSi<sub>2</sub>: C, 62.08; H, 10.02; N, 5.57(%). Found: C, 63.85; H, 10.05; N, 6.03.

**2-(Bistrimethylsilylmethyl)-4-methylpyridine (6c).** Colorless liquid, bp. (60°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.00(s, 18H, Me<sub>3</sub>Si), 1.75(s, 1H, CH), 2.18(s, 3H, CH<sub>3</sub>), 6.60(d, 1H, CH), 6.75(q, 1H, CH), 8.20(q, 1H, CH). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.05(Me<sub>3</sub>Si), 17.70(CH<sub>3</sub>), 32.50(CH), 121.10(CH), 127.60(C), 136.50(CH), 154.50(C). Mass (70 eV) *m/z* = 251(M<sup>+</sup>, 11), 236(M-Me)<sup>-</sup>, 22), 178((M-Me<sub>3</sub>Si)<sup>+</sup>, 3), 163(M-Me<sub>3</sub>Si, Me)<sup>+</sup>, 13), 73(Me<sub>3</sub>Si<sup>+</sup>, 100). Anal. Calcd. for C<sub>13</sub>H<sub>25</sub>NSi<sub>2</sub>: C, 62.08; H, 10.02; N, 5.57(%). Found: C, 63.68; H, 10.53; N, 5.25.

**2-(Bistrimethylsilylmethyl)-5-methylpyridine (6d).** Colorless liquid, bp. (60°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.01(s, 18H, Me<sub>3</sub>Si), 1.80(s, 1H, CH), 2.20(s, 3H, CH<sub>3</sub>), 6.80(d, 1H, CH), 7.19(q, 1H, CH), 8.21(q, 1H, CH). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.50(Me<sub>3</sub>Si), 18.50(CH), 32.50(CH<sub>3</sub>), 122.50(CH), 129.50(C), 136.50(CH), 149.50(CH), 164.50(C). Mass (70 eV) *m/z* = 251(M<sup>+</sup>, 2), 236((M-Me)<sup>-</sup>, 97), 178((M-Me<sub>3</sub>Si)<sup>+</sup>, 7), 163((M-Me<sub>3</sub>Si, Me)<sup>+</sup>, 31), 73(Me<sub>3</sub>Si<sup>+</sup>, 100). Anal. Calcd. for C<sub>13</sub>H<sub>25</sub>NSi<sub>2</sub>: C, 62.08; H, 10.02; N, 5.57(%). Found: C, 62.43; H, 11.64; N, 5.62.

**2-(Bistrimethylsilylmethyl)-6-methylpyridine (6e).** Colorless liquid, bp. (60°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (90 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.00(s, 18H, Me<sub>3</sub>Si), 1.80(s, 1H, CH), 2.38(s, 3H, CH<sub>3</sub>), 6.64(d, 1H, CH), 6.69(d, 1H, CH), 7.26(t, 1H, CH). <sup>13</sup>C-NMR (22.5 MHz, CDCl<sub>3</sub>);  $\delta$  = 0.50(Me<sub>3</sub>Si), 30.05(CH), 33.00(CH<sub>3</sub>), 117.50(CH), 119.10(CH), 136.00(CH), 157.5(C), 163.50(C). Mass (70 eV) *m/z* = 251(M<sup>+</sup>, 8), 236((M-Me)<sup>-</sup>, 35), 178((M-Me<sub>3</sub>Si)<sup>-</sup>, 5), 163((M-Me<sub>3</sub>Si, Me)<sup>+</sup>, 21), 73(Me<sub>3</sub>Si<sup>+</sup>, 100). Anal. Calcd. for C<sub>13</sub>H<sub>25</sub>NSi<sub>2</sub>: C, 62.08; H, 10.02; N, 5.57(%). Found: C, 61.60; H, 11.04; N, 5.50.

**2-(1-Trimethylsilyl-2,2-dimethyl-2-sila-propyl)-4,6-methylpyridine (6f).** Colorless liquid, bp. (70°C/10<sup>-1</sup> torr). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>);  $\delta$  = -0.02(s, 18H, 2Me<sub>3</sub>Si), 1.75(s, 1H, CH), 2.16(s, 3H, *p*-CH<sub>3</sub>), 2.34(s, 3H, *o*-CH<sub>3</sub>), 6.44(s, 1H, aromatic CH), 6.54(s, 1H, aromatic CH). <sup>13</sup>C-NMR (50.32 MHz, CDCl<sub>3</sub>);  $\delta$  = -5.78(Me<sub>3</sub>Si), 18.01(*o*-CH), 21.62(*p*-CH<sub>3</sub>), 30.29(*o*-CH<sub>3</sub>), 120.90(*m*-aromatic CH), 121.90(*o*-aromatic C<sub>quart</sub>), 122.08(*p*-C<sub>quart</sub>), 122.32(*m*-aromatic CH), 149.74(*o*-aromatic C<sub>quart</sub>).

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4. Lithiation of all reactions with butyllithium at  $-78^\circ\text{C}$  proceeds smoothly, generating a yellow solution, which becomes slowly brown on room temperature. Quenching with  $\text{Me}_2\text{RSiCl}$  at  $-78^\circ\text{C}$  produced unchanged color, but on RT produced slowly colorless solution and insoluble white  $\text{LiCl}$  salt.
5.  $\text{Me}_2\text{SiClCH}(\text{SiMe}_3)\text{CH}_2\text{Bu}$  were prepared by the reaction of  $\text{Me}_3\text{SiCH}=\text{CH}_2$  with  $t\text{-BuLi}$  and  $\text{Me}_2\text{SiCl}_2$  in pentane:
- $$\begin{aligned} \text{Me}_3\text{SiCH}=\text{CH}_2 + t\text{-BuLi} &\longrightarrow \text{Me}_3\text{SiCHCH}_2\text{Bu} \\ &\quad \text{Li} \\ &\xrightarrow{+\text{Me}_2\text{SiCl}_2 - \text{LiCl}} \text{Me}_2\text{SiClCH}(\text{SiMe}_3)\text{CH}_2\text{Bu} \end{aligned}$$
- Colorless liquid, bp. ( $60^\circ\text{C}/10^{-1}$  torr), yield (35%),  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta=0.097$ (s, 9H,  $\text{Me}_3\text{-Si}$ ), 0.435, 0.442(d, 6H,  $\text{Me}_2\text{Si}$ ,  $J=0.01$ ), 0.863(s, 9H,  $t\text{-Bu}$ ), 1.415, 1.427, 1.463, 1.475, 1.519, 1.535, 1.568, 1.583(qq, 2H,  $\text{CH}_2$ ).
6. Many experimental results in polar solvent such as THF and  $\text{Et}_2\text{O}$  have been reviewed; see ref. 1 and 2, (a) Mallet, M.; Que'guiner, G. *Tetrahedron.* **1985**, 41, 3433~3440; (b) Quesnelle, C.; Iihama, T.; Aubert, T.; Perrier, H.; Snieckus, V. *Tetrahedron. Lett.* **1992**, 33, 2625~2628; (c) Mallet, M.; Que'guiner, G. *Tetrahedron.* **1986**, 42, 2253~2262, in nonpolar medium; (d) Francis, R. F.; Crews, C. D.; Scott, B. S. *J. Org. Chem.* **1978**, 43, 3227~3230.