

## Supporting Information for

### Amino Acid-Promoted C-H Alkylation with Alkylboronic Acids Using a Removable

#### Directing Group

Yu Zhang, Hang Jiang, Dushen Chen, Yanghui Zhang\*

*Department of Chemistry, and Shanghai Key Lab of Chemical Assessment and Sustainability, Tongji*

*University, 1239 Siping Road, Shanghai, 200092, P. R. China.*

\*To whom correspondence should be addressed. Email: zhangyanghui@tongji.edu.cn

#### Table of Contents

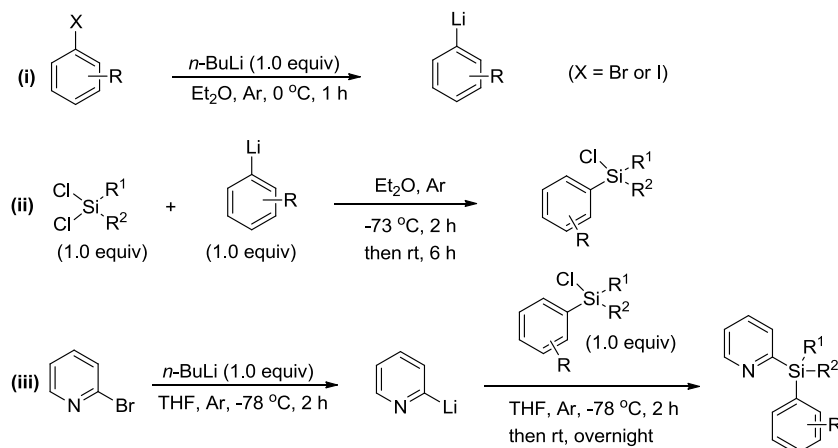
<b>I. General information</b>	<b>S2</b>
<b>II. Synthesis of pyridyl silanes and alkylboronic acids</b>	<b>S2</b>
<b>III. General procedure for the optimization of reaction conditions</b>	<b>S15</b>
<b>IV. General procedure for the C-H alkylation with alkylboronic acids</b>	<b>S16</b>
<b>V. Characterization of synthesized compounds</b>	<b>S17</b>
<b>VI. Removal of directing group</b>	<b>S27</b>
<b>VII. NMR spectra</b>	<b>S28</b>

## I. General information

All the solvents were purified by distillation prior to use. Unless otherwise noted, the other commercial chemicals were used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker ARX400. High resolution mass spectra were measured on Bruker MicroTOFII ESI-TOF or EI-TOF (Agilent 6538 UHD) mass spectrometer.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$ , or  $(\text{CD}_3)_2\text{SO}$  and referenced to residual  $\text{CHCl}_3$  at 7.26 ppm,  $\text{CH}_3\text{OH}$  at 3.31 ppm, or  $(\text{CH}_3)_2\text{SO}$  at 2.50 ppm, respectively.  $^{13}\text{C}$  NMR spectra are referenced to the central peak of  $\text{CDCl}_3$  at 77.0 ppm,  $\text{CD}_3\text{OD}$  at 49.00 ppm, and  $(\text{CD}_3)_2\text{SO}$  at 39.52 ppm, respectively. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance.

## II. Synthesis of pyridyl silanes and alkylboronic acids

### 1. General procedure for the preparation of aryl pyridyl silanes<sup>[1][2][3]</sup>



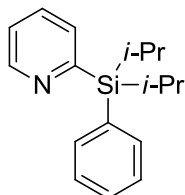
To a solution of aryl bromide or -iodide (10 mmol) in  $\text{Et}_2\text{O}$  (10 mL) was added dropwise a solution of *n*-butyllithium (4.0 mL, 2.5 M in hexane, 10 mmol) at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h.

The prepared phenyllithium was added slowly via syringe to a solution of dichlorosilane (10 mmol) in solution of  $\text{Et}_2\text{O}$  (20 mL) at -73 °C under argon atmosphere. After 30 min, precipitation of salts was observed. After the addition was complete, the mixture was allowed to warm to room temperature over 2 h and was stirred for an additional 6 h. Hexane was added, and the slurry was Schlenk-filtered. The filtrate was concentrated *in vacuo* to afford chlorophenylsilane without further purification.

To a solution of 2-bromopyridine (0.98 mL, 10 mmol) in dry THF (20 mL) was added dropwise a solution of *n*-butyllithium (4.0 mL, 2.5 M in hexane, 10 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred at -78 °C for 2 h and then prepared chlorophenylsilane (10 mmol) was added dropwise. The resulting solution was allowed to warm to room temperature and was stirred overnight. The mixture was quenched with 10 mL of saturated  $\text{NH}_4\text{Cl}$  solution and extracted with ethyl acetate three times. The combined organic extracts were washed with brine, dried over the

anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford corresponding pyridyl silanes.

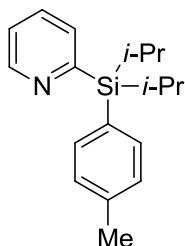
### 2-(diisopropyl(phenyl)silyl)pyridine (1a)



The product was prepared using the general procedure above and was isolated as a colorless liquid (2.31 g, 86% yield from iodobenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (ddd,  $J = 4.9, 1.7, 1.1$  Hz, 1H), 7.53 - 7.58 (m, 3H), 7.50 (dt,  $J = 7.5, 1.3$  Hz, 1H), 7.34 - 7.41 (m, 3H), 7.23 (ddd,  $J = 7.5, 4.9, 1.4$  Hz, 1H), 1.68 (sept,  $J = 7.4$  Hz, 2H), 1.01 (dd,  $J = 7.4, 5.0$  Hz, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 149.9, 135.7, 133.2, 132.8, 131.7, 128.9, 127.4, 122.5, 17.4, 17.4, 9.9. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{23}\text{NNaSi}^+$ : 292.1492 ( $\text{M} + \text{Na}$ ) $^+$ , found: 292.1492.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

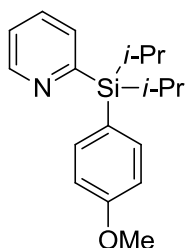
### 2-(diisopropyl(*p*-tolyl)silyl)pyridine (1b)



The product was prepared using the general procedure above and was isolated as a colorless liquid (2.32 g, 82% yield from 1-iodo-4-methylbenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.93 - 8.88 (m, 1H), 7.61 (td,  $J = 7.5, 1.7$  Hz, 1H), 7.57 - 7.54 (m, 1H), 7.52 (d,  $J = 7.9$  Hz, 2H), 7.29 - 7.24 (m, 3H), 2.43 (s, 3H), 1.73 (sept,  $J = 7.38$  Hz, 2H), 1.07 (t,  $J = 7.5$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 150.0, 138.8, 135.9, 133.2, 131.9, 129.1, 128.4, 122.5, 21.4, 17.6, 17.5, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{25}\text{NNaSi}^+$ : 306.1648 ( $\text{M} + \text{Na}$ ) $^+$ , found: 306.1648.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

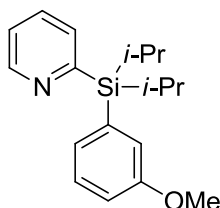
### 2-(diisopropyl(4-methoxyphenyl)silyl)pyridine (1c)



The product was prepared using the general procedure above and was isolated as a white solid (2.45 g, 82% yield from 1-iodo-4-methoxybenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 – 8.83 (m, 1H), 7.56 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.49 (d,  $J = 8.6$  Hz, 3H), 7.23 – 7.18 (m, 1H), 6.94 (d,  $J = 8.6$  Hz, 2H), 3.82 (s, 3H), 1.65 (sept,  $J = 7.4$  Hz, 2H), 1.00 (t,  $J = 6.9$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 160.5, 150.0, 137.3, 133.2, 131.8, 123.5, 122.5, 113.4, 54.9, 17.6, 17.5, 10.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{25}\text{NNaOSi}^+$ : 322.1598 ( $\text{M} + \text{Na}$ ) $^+$ , found: 322.1615.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

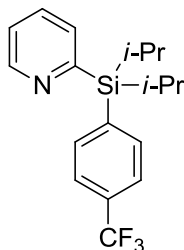
### 2-(diisopropyl(3-methoxyphenyl)silyl)pyridine (1d)



The product was prepared using the general procedure above and was isolated as a colorless liquid (2.45 g, 82% yield from 1-iodo-3-methoxybenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (d,  $J = 4.7$  Hz, 1H), 7.56 (t,  $J = 7.5$  Hz, 1H), 7.51 (d,  $J = 7.4$  Hz, 1H), 7.32 (t,  $J = 7.7$  Hz, 1H), 7.24 – 7.19 (m, 1H), 7.12 (dd,  $J = 13.0, 4.8$  Hz, 2H), 6.94 (dd,  $J = 8.1, 2.3$  Hz, 1H), 3.79 (s, 3H), 1.67 (sept,  $J = 7.34$  Hz, 2H), 1.01 (dd,  $J = 7.4, 3.7$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 158.7, 150.0, 134.5, 133.3, 131.9, 128.7, 128.2, 122.6, 121.6, 114.1, 54.9, 17.6, 17.5, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{25}\text{NNaOSi}^+$ : 322.1598 ( $\text{M} + \text{Na}$ ) $^+$ , found: 322.1583.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

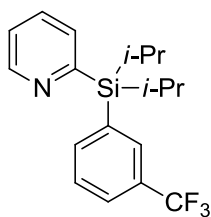
### 2-(diisopropyl(4-(trifluoromethyl)phenyl)silyl)pyridine (1e)



The product was prepared using the general procedure above and was isolated as a colorless liquid (2.43 g, 85% yield from 1-iodo-4-(trifluoromethyl)benzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.90 (ddd,  $J = 4.8, 1.5, 1.0$  Hz, 1H), 7.73 (d,  $J = 7.8$  Hz, 2H), 7.69 – 7.61 (m, 3H), 7.54 (dd,  $J = 6.5, 1.1$  Hz, 1H), 7.33 – 7.27 (m, 1H), 1.74 (sept,  $J = 7.34$  Hz, 2H), 1.05 (dd,  $J = 7.4, 3.6$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 150.3, 138.3, 136.1, 132.7 (q,  $J_{\text{CF}} = 15.6$  Hz), 131.0 (q,  $J_{\text{CF}} = 32.2$  Hz), 125.6, 124.2 (q,  $J_{\text{CF}} = 270.6$  Hz), 124.0 (q,  $J_{\text{CF}} = 3.7$  Hz), 122.9, 17.5, 17.4, 10.05. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{22}\text{F}_3\text{NNaSi}^+$ : 360.1366 ( $\text{M} + \text{Na}$ ) $^+$ , found: 360.1366.

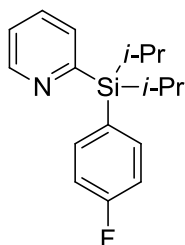
### 2-(diisopropyl(3-(trifluoromethyl)phenyl)silyl)pyridine (1f)





The product was prepared using the general procedure above and was isolated as a colorless liquid (2.70 g, 80% yield from 1-iodo-3-(trifluoromethyl)benzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (d,  $J = 4.6$  Hz, 1H), 7.85 (d,  $J = 6.5$  Hz, 1H), 7.78 (t,  $J = 7.2$  Hz, 1H), 7.74 – 7.62 (m, 2H), 7.54 (d,  $J = 5.3$  Hz, 2H), 7.36 – 7.25 (m, 1H), 1.75 (sept,  $J = 7.5$  Hz, 2H), 1.06 (dt,  $J = 8.0, 4.3$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 150.3, 139.2, 134.6, 133.6, 132.1 (q,  $J_{\text{CF}} = 15.2$  Hz), 131.8, 130.3, 129.8 (q,  $J_{\text{CF}} = 31.5$  Hz), 127.8 (q,  $J_{\text{CF}} = 212.4$  Hz), 125.8 (d,  $J_{\text{CF}} = 13.2$  Hz), 123.0, 17.5, 17.4, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{22}\text{F}_3\text{NNaSi}^+$ : 360.1366 (M + Na) $^+$ , found: 360.1360.

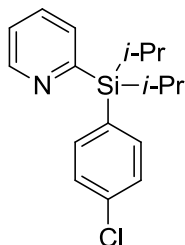
### 2-((4-fluorophenyl)diisopropylsilyl)pyridine (1g)



The product was prepared using the general procedure above and was isolated as a colorless liquid (1.88 g, 85% yield from 1-fluoro-4-iodobenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (dd,  $J = 3.4, 1.1$  Hz, 1H), 7.58 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.53 (ddd,  $J = 6.2, 5.2, 2.0$  Hz, 2H), 7.50 – 7.46 (m, 1H), 7.23 (ddd,  $J = 7.6, 4.9, 1.3$  Hz, 1H), 7.08 (t,  $J = 9.0$  Hz, 2H), 1.70 – 1.61 (sept,  $J = 7.36$  Hz, 2H), 0.99 (dd,  $J = 7.4, 4.0$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 162.8 (d,  $J_{\text{CF}} = 247.7$  Hz), 150.1, 137.7 (d,  $J_{\text{CF}} = 7.3$  Hz), 133.4, 131.8, 128.3 (d,  $J_{\text{CF}} = 3.9$  Hz), 122.7, 114.8 (d,  $J_{\text{CF}} = 19.5$  Hz), 17.5, 17.4, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{22}\text{FNNaSi}^+$ : 310.1398 (M + Na) $^+$ , found: 310.1398.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

### 2-((4-chlorophenyl)diisopropylsilyl)pyridine (1h)

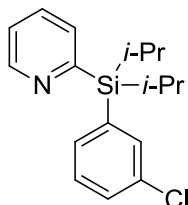


The product was prepared using the general procedure above and was isolated as a colorless liquid (2.36 g, 78% yield from 1-chloro-4-iodobenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.86 – 8.82 (m, 1H), 7.57 (td,  $J = 7.6, 1.4$  Hz, 1H), 7.48 (dd,  $J = 7.3, 5.8$  Hz, 3H), 7.36 (d,  $J = 8.3$  Hz, 2H), 7.25 –

7.19 (m, 1H), 1.65 (sept,  $J = 7.4$  Hz, 2H), 0.99 (dd,  $J = 7.4, 4.5$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7, 150.1, 137.1, 135.5, 133.4, 131.7, 131.3, 127.8, 122.8, 17.5, 17.4, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{22}\text{ClNNaSi}^+$ : 326.1102 ( $\text{M} + \text{Na}$ ) $^+$ , found: 326.1094.

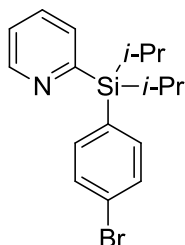
The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

### 2-((3-chlorophenyl)diisopropylsilyl)pyridine (1i)



The product was prepared using the general procedure above and was isolated as a white solid (2.30 g, 76% yield from 1-chloro-3-iodobenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (d,  $J = 4.8$  Hz, 1H), 7.59 (td,  $J = 7.6, 1.1$  Hz, 1H), 7.50 (dd,  $J = 8.8, 4.5$  Hz, 2H), 7.42 (d,  $J = 7.2$  Hz, 1H), 7.39 – 7.35 (m, 1H), 7.33 – 7.27 (m, 1H), 7.23 (dd,  $J = 4.5, 3.1$  Hz, 1H), 1.72 – 1.60 (sept,  $J = 7.34$  Hz, 2H), 1.00 (dd,  $J = 7.4, 2.1$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 150.2, 135.9, 135.3, 134.0, 133.8, 133.5, 131.8, 129.2, 129.0, 122.8, 17.5, 17.4, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{22}\text{ClNNaSi}^+$ : 326.1102 ( $\text{M} + \text{Na}$ ) $^+$ , found: 326.1100.

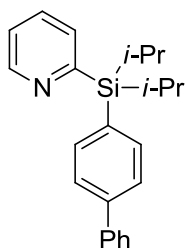
### 2-((4-bromophenyl)diisopropylsilyl)pyridine (1j)



The product was prepared using the general procedure above and was isolated as a white solid (2.81 g, 81% yield from 1-bromo-4-iodobenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 (d,  $J = 4.7$  Hz, 1H), 7.56 (dd,  $J = 7.6, 1.3$  Hz, 1H), 7.51 (d,  $J = 8.2$  Hz, 2H), 7.47 (d,  $J = 7.5$  Hz, 1H), 7.42 (d,  $J = 8.2$  Hz, 2H), 7.25 – 7.18 (m, 1H), 1.72 – 1.58 (sept,  $J = 7.36$  Hz, 2H), 0.99 (dd,  $J = 7.4, 4.6$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.6, 150.1, 137.4, 133.5, 131.8, 131.8, 130.7, 124.1, 122.8, 17.5, 17.4, 9.9. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{17}\text{H}_{23}\text{BrNSi}^+$ : 348.0778 ( $\text{M} + \text{H}$ ) $^+$ , found: 348.0758.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

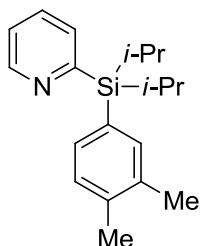
### 2-([1,1'-biphenyl]-4-yl)diisopropylsilyl)pyridine (1k)



The product was prepared using the general procedure above and was isolated as a white solid (2.93 g, 85% yield from 4-bromo-1,1'-biphenyl).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (d,  $J = 4.8$  Hz, 1H), 7.75 – 7.68 (m, 7H), 7.64 (qd,  $J = 7.2, 1.3$  Hz, 2H), 7.52 (t,  $J = 7.6$  Hz, 2H), 7.45 – 7.40 (m, 1H), 7.30 (ddd,  $J = 6.9, 4.9, 2.2$  Hz, 1H), 1.88 – 1.73 (sept,  $J = 7.36$  Hz, 2H), 1.13 (dd,  $J = 7.3, 3.8$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.3, 150.1, 141.7, 141.0, 136.3, 133.3, 131.9, 131.6, 128.6, 127.2, 127.0, 126.2, 122.6, 17.6, 17.5, 10.1. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{27}\text{NNaSi}^+$ : 368.1805 ( $\text{M} + \text{Na}$ ) $^+$ , found: 368.1805.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

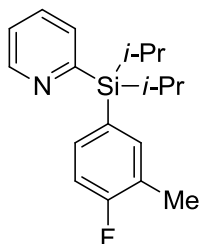
#### 2-((3,4-dimethylphenyl)diisopropylsilyl)pyridine (1n)



The product was prepared using the general procedure above and was isolated as a colorless liquid (2.43 g, 82% yield from 4-iodo-1,2-dimethylbenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (d,  $J = 4.8$  Hz, 1H), 7.57 (td,  $J = 7.5, 1.6$  Hz, 1H), 7.53 (t,  $J = 6.9$  Hz, 1H), 7.32 (d,  $J = 7.6$  Hz, 2H), 7.25 – 7.20 (m, 1H), 7.18 (d,  $J = 7.3$  Hz, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 1.78 – 1.61 (sept,  $J = 7.35$  Hz, 2H), 1.03 (t,  $J = 7.5$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 150.0, 137.6, 137.1, 135.6, 133.6, 133.2, 131.9, 129.6, 128.9, 122.5, 19.8, 19.7, 17.6, 17.5, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{27}\text{NNaSi}^+$ : 320.1805 ( $\text{M} + \text{Na}$ ) $^+$ , found: 320.1805.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

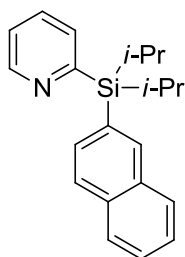
#### 2-((4-fluoro-3-methylphenyl)diisopropylsilyl)pyridine (1o)



The product was prepared using the general procedure above and was isolated as a colorless liquid (2.23 g, 74% yield from 1-fluoro-4-iodo-2-methylbenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 – 8.82 (m, 1H), 7.58 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.49 (d,  $J = 7.5$  Hz, 1H), 7.34 (t,  $J = 6.9$  Hz, 2H), 7.25 – 7.18 (m, 1H), 7.02 (dd,  $J = 9.9, 8.3$  Hz, 1H), 2.27 (d,  $J = 1.4$  Hz, 3H), 1.65 (sept,  $J = 7.34$  Hz, 2H), 0.99 (dd,  $J = 7.4, 3.7$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 163.2, 161.2, 150.1, 139.1 (d,  $J_{\text{CF}} = 4.9$  Hz), 135.1 (d,  $J_{\text{CF}} = 7.5$  Hz), 132.6 (d,  $J_{\text{CF}} = 162.3$  Hz), 128.0 (d,  $J_{\text{CF}} = 4.6$  Hz), 124.0 (d,  $J_{\text{CF}} = 15.8$  Hz), 122.7, 114.4 (d,  $J_{\text{CF}} = 20.7$  Hz), 17.5, 17.4, 14.5 (d,  $J_{\text{CF}} = 3.8$  Hz), 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{18}\text{H}_{24}\text{FNNaSi}^+$ : 324.1554 ( $\text{M} + \text{Na}$ ) $^+$ , found: 324.1550.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

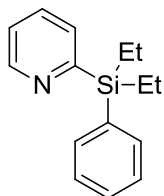
### 2-(diisopropyl(naphthalen-2-yl)silyl)pyridine (1p)



The product was prepared using the general procedure above and was isolated as a white solid (2.68 g, 84% yield from 2-bromonaphthalene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.96 (dd,  $J = 3.4, 1.1$  Hz, 1H), 8.17 (s, 1H), 7.94 – 7.87 (m, 3H), 7.72 – 7.67 (m, 1H), 7.67 – 7.62 (m, 1H), 7.63 – 7.60 (m, 1H), 7.58 – 7.54 (m, 2H), 7.31 (ddd,  $J = 6.9, 4.9, 1.9$  Hz, 1H), 1.86 (sept,  $J = 7.34$  Hz, 2H), 1.14 (t,  $J = 7.7$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 150.1, 136.9, 133.7, 133.2, 132.8, 131.9, 130.6, 128.1, 127.6, 126.6, 126.3, 125.7, 122.7, 17.7, 17.6, 10.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{25}\text{NNaSi}^+$ : 342.1648 ( $\text{M} + \text{Na}$ ) $^+$ , found: 342.1623.

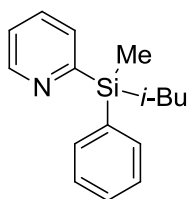
The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

### 2-(diethyl(phenyl)silyl)pyridine (4a)



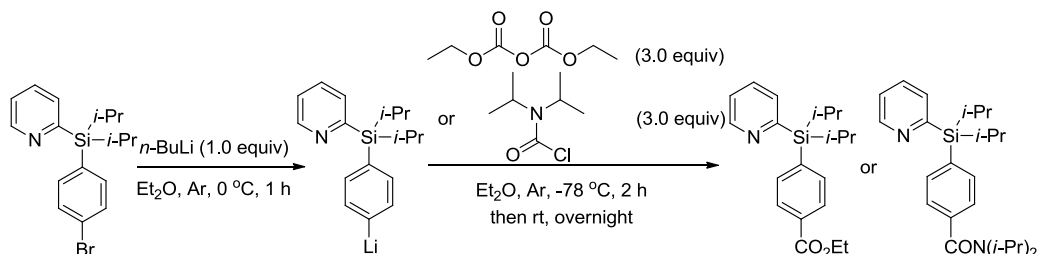
The product was prepared using the general procedure above and was isolated as a colorless liquid (1.93 g, 80% yield from iodobenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 – 8.81 (m, 1H), 7.61 – 7.57 (m, 2H), 7.55 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.46 (d,  $J = 7.5$  Hz, 1H), 7.40 – 7.35 (m, 3H), 7.19 (ddd,  $J = 7.5, 4.9, 1.3$  Hz, 1H), 1.20 (dt,  $J = 9.8, 6.8$  Hz, 4H), 1.06 (t,  $J = 7.7$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 150.1, 135.3, 134.7, 133.6, 130.4, 129.1, 127.7, 122.6, 7.3, 3.4. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{20}\text{NSi}^+$ : 242.1360 ( $\text{M} + \text{H}$ ) $^+$ , found: 242.1353.

### 2-(isobutyl(methyl)(phenyl)silyl)pyridine (4b)



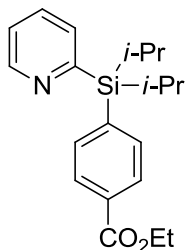
The product was prepared using the general procedure above and was isolated as a colorless liquid (2.01 g, 79% yield from iodobenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.8$  Hz, 1H), 7.62 (dd,  $J = 6.4, 3.0$  Hz, 2H), 7.53 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.44 (d,  $J = 7.5$  Hz, 1H), 7.40 – 7.32 (m, 3H), 7.18 (ddd,  $J = 7.5, 4.9, 1.3$  Hz, 1H), 1.90 (dt,  $J = 13.4, 6.7$  Hz, 1H), 1.22 (qd,  $J = 14.9, 7.0$  Hz, 2H), 0.92 (dd,  $J = 6.6, 2.9$  Hz, 6H), 0.69 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 150.1, 137.0, 134.4, 133.8, 129.8, 129.0, 127.7, 122.6, 26.2, 26.1, 24.7, 23.8, -4.4. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{16}\text{H}_{21}\text{NNaSi}^+$ : 278.1335 ( $\text{M} + \text{Na}$ ) $^+$ , found: 278.1351.

## 2. Procedure for the preparation of 1l and 1m<sup>[4]</sup>



To a solution of aryl bromide (1.04 g, 3 mmol) in  $\text{Et}_2\text{O}$  (8 mL) was added dropwise a solution of *n*-butyllithium (1.2 mL, 2.5 M in hexane, 3 mmol) at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h and then was added via cannula a solution of an appropriate electrophile (9 mmol) in  $\text{Et}_2\text{O}$  (8 mL) at -78 °C. After being stirred for 2 h at -78 °C, the solution was allowed to warm to room temperature overnight. The reaction was quenched with 10 mL of saturated  $\text{NH}_4\text{Cl}$  solution and extracted with ethyl acetate three times. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to provide the corresponding *para*-substituted aryl pyridyl silane.

### ethyl 4-(diisopropyl(pyridin-2-yl)silyl)benzoate (1l)

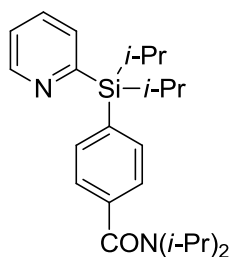


The product was prepared using the procedure above and was isolated as a white solid (0.94 g, 92% yield from 2-((4-bromophenyl)diisopropylsilyl)pyridine).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (d,  $J = 4.3$  Hz, 1H), 8.02 (d,  $J = 8.1$  Hz, 2H), 7.63 (d,  $J = 8.1$  Hz, 2H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.45 (d,  $J =$

7.5 Hz, 1H), 7.22 (dd,  $J = 6.6, 5.7$  Hz, 1H), 4.36 (q,  $J = 7.1$  Hz, 2H), 1.67 (dt,  $J = 14.7, 7.3$  Hz, 2H), 1.36 (t,  $J = 7.1$  Hz, 3H), 0.98 (dd,  $J = 7.3, 4.5$  Hz, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 162.5, 150.1, 139.5, 135.7, 133.4, 131.8, 130.9, 128.1, 122.8, 60.8, 17.4, 17.4, 14.2, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{27}\text{NNaO}_2\text{Si}^+$ : 364.1703 ( $\text{M} + \text{Na}$ ) $^+$ , found: 364.1703.

The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

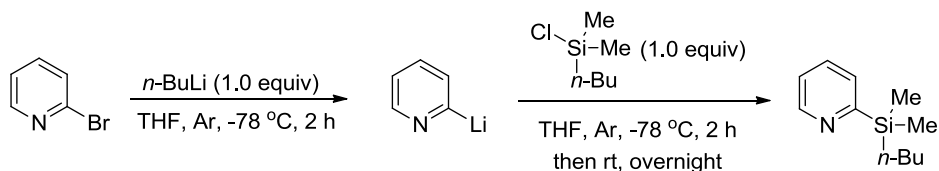
#### 4-(diisopropyl(pyridin-2-yl)silyl)-*N,N*-diisopropylbenzamide (1m)



The product was prepared using the procedure above and was isolated as a white solid (1.07 g, 90% yield from 2-((4-bromophenyl)diisopropylsilyl)pyridine).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 – 8.81 (m, 1H), 7.60 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.54 (d,  $J = 8.1$  Hz, 2H), 7.51 (d,  $J = 7.5$  Hz, 1H), 7.30 (d,  $J = 8.0$  Hz, 2H), 7.25 – 7.21 (m, 1H), 3.97 (s, 1H), 3.51 (s, 1H), 1.65 (dt,  $J = 14.7, 7.4$  Hz, 2H), 1.54 (s, 6H), 1.16 (s, 6H), 0.99 (m, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.0, 162.9, 150.1, 139.3, 136.0, 133.8, 133.5, 131.9, 124.8, 122.8, 20.7, 17.5, 17.4, 10.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{24}\text{H}_{37}\text{N}_2\text{OSi}^+$ : 397.2670 ( $\text{M} + \text{H}$ ) $^+$ , found: 397.2661.

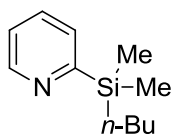
The NMR data are identical to: Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.

### 3. Procedure for the preparation of 2-(butyldimethylsilyl)pyridine **6a**<sup>[3]</sup>



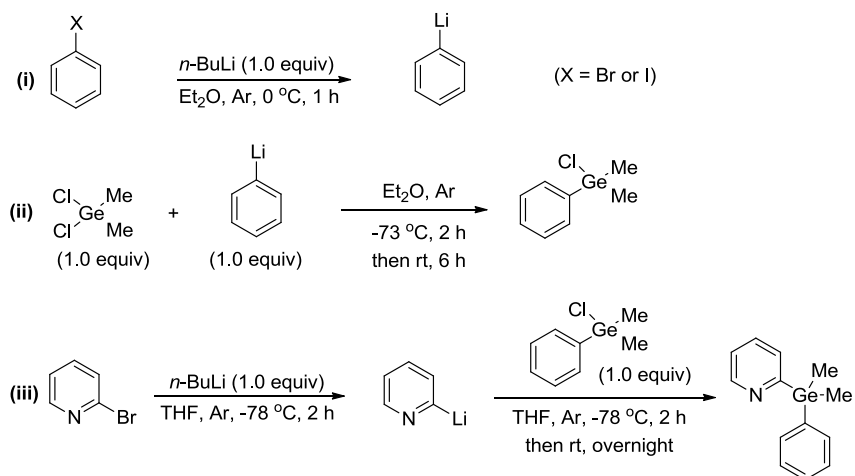
To a solution of 2-bromopyridine (0.98 mL, 10 mmol) in dry THF (20 mL) was added dropwise a solution of *n*-butyllithium (4.0 mL, 2.5 M in hexane, 10 mmol) at  $-78$  °C under argon atmosphere. The reaction mixture was stirred at  $-78$  °C for 2 h and then neat butylchlorodimethylsilane (0.95 mL, 10 mmol) was added dropwise. The resulting solution was allowed to warm to room temperature and was stirred overnight. The mixture was quenched with 10 mL of saturated  $\text{NH}_4\text{Cl}$  solution and extracted with ethyl acetate three times. The combined organic organic extracts were washed with brine, dried over the anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford 2-(butyldimethylsilyl)pyridine.

#### 2-(butyldimethylsilyl)pyridine (**6a**)



The product was prepared using the procedure above and was isolated as a colorless liquid (1.39 g, 72% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (d,  $J = 4.8$  Hz, 1H), 7.55 (t,  $J = 7.6$  Hz, 1H), 7.46 (d,  $J = 7.5$  Hz, 1H), 7.18 – 7.13 (m, 1H), 1.34 – 1.26 (m, 4H), 0.87 – 0.77 (m, 5H), 0.29 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 150.0, 133.7, 128.9, 122.5, 26.4, 25.9, 14.5, 13.6, -3.6. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{11}\text{H}_{20}\text{NSi}^+$ : 194.1360 ( $M + \text{H}$ ) $^+$ , found: 194.1357.

#### 4. Procedure for the preparation of 2-(dimethyl(phenyl)germyl)pyridine **8a**<sup>[1][2][3]</sup>

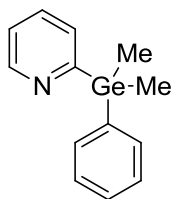


To a solution of aryl bromide or -iodide (6 mmol) in  $\text{Et}_2\text{O}$  (10 mL) was added dropwise a solution of *n*-butyllithium (2.4 mL, 2.5 M in hexane, 6 mmol) at 0 °C under argon atmosphere. The reaction mixture was stirred at 0 °C for 1 h.

The prepared phenyllithium was added slowly via syringe to a solution of dichlorodimethylgermane (0.69 mL, 6 mmol) in solution of  $\text{Et}_2\text{O}$  (10 mL) at -73 °C under argon atmosphere. After 30 min, precipitation of salts was observed. After the addition was complete, the mixture was allowed to warm to room temperature over 2 h and was stirred for an additional 6 h. Hexane was added, and the slurry was Schlenk-filtered. The filtrate was concentrated to afford chlorodimethyl(phenyl)germane without further purification.

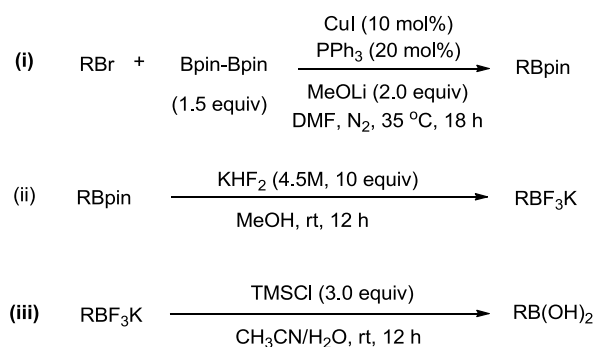
To a solution of 2-bromopyridine (0.58 mL, 6 mmol) in dry THF (10 mL) was added dropwise a solution of *n*-butyllithium (2.4 mL, 2.5 M in hexane, 6 mmol) at -78 °C under argon atmosphere. The reaction mixture was stirred at -78 °C for 2 h and then prepared chlorodimethyl(phenyl)germane (6 mmol) was added dropwise. The resulting solution was allowed to warm to room temperature and was stirred overnight. The mixture was quenched with 10 mL of saturated  $\text{NH}_4\text{Cl}$  solution and extracted with ethyl acetate three times. The combined organic extracts were washed with brine, dried over the anhydrous sodium sulfate, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford 2-(dimethyl(phenyl)germyl)pyridine.

## 2-(dimethyl(phenyl)germyl)pyridine (8a)



The product was prepared using the procedure above and was isolated as a colorless liquid (1.43 g, 92% yield from iodobenzene).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.6$  Hz, 1H), 7.60 – 7.58 (m, 1H), 7.57 (d,  $J = 1.9$  Hz, 1H), 7.54 (td,  $J = 7.6, 1.8$  Hz, 1H), 7.45 – 7.41 (m, 1H), 7.41 – 7.35 (m, 3H), 0.75 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.6, 150.2, 139.3, 134.0, 133.5, 129.0, 128.5, 128.0, 122.5, -3.7. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{13}\text{H}_{16}\text{GeN}^+$ : 260.0489 ( $M + \text{H}$ ) $^+$ , found: 260.0488.

## 5. General procedure for the preparation of alkylboronic acids<sup>[5]</sup>



CuI (0.1905 g, 1.0 mmol),  $\text{PPh}_3$  (0.5246 g, 2.0 mmol), LiOMe (0.7594 g, 20.0 mmol), and bis(pinacolato)diboron (3.80 g, 15.0 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three times). DMF (20 mL), the corresponding alkyl bromide (10.0 mmol) were added in turn by syringe under an argon atmosphere (if the alkyl bromide is a solid, it was added along with the CuI). The resulting reaction mixture was stirred vigorously at  $35^\circ\text{C}$  for 18 h. The reaction mixture was then diluted with EtOAc, filtered through silica gel with copious washings ( $\text{Et}_2\text{O}$  or EtOAc), concentrated, and purified by column chromatography to afford corresponding alkylboronic esters.

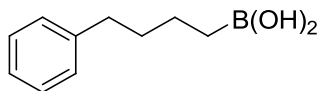
To a solution of prepared pinacol ester in methanol (18 mL) was added 4.5 M  $\text{KHF}_2$  (aq) (10 equiv.) {NOTE:  $\text{KHF}_2$  is corrosive and discolours glassware after prolonged exposure.} The resulting mixture was stirred for 12 h, and then concentrated to dryness. The residue, a white solid, was extracted with hot acetone (20 mL) two times, and the combined filtered extracts were concentrated to a volume of ca. 4 mL. Ether (50 mL) was added and the resultant precipitate was collected and dried to afford corresponding potassium trifluoroborate as a white solid.

The prepared potassium trifluoroborate was dissolved in acetonitrile (20 mL) and water (9 mL) before addition of trimethylsilylchloride (3 equiv.). The resultant mixture was stirred for 12 h, before concentrating to a volume of ca. 4 mL. Saturated sodium bicarbonate solution (2 mL) and water (10 mL) were added to the residue, before extraction with ethyl acetate (10 mL) for two times. The



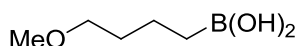
combined extracts were washed with near saturated brine, dried ( $\text{Na}_2\text{SO}_4$ ), and the solvent was removed to provide corresponding alkylboronic acids as a white solid.

**(4-phenylbutyl)boronic acid (2d)**



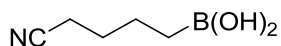
The product was prepared using the general procedure above and was isolated as a white solid (1.48 g, 83% yield).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.38 (s, 2H), 7.26 (t,  $J = 7.4$  Hz, 2H), 7.20 – 7.12 (m, 3H), 2.57 – 2.51 (m, 2H), 1.51 (dt,  $J = 15.3, 7.5$  Hz, 2H), 1.34 (dt,  $J = 15.2, 7.6$  Hz, 2H), 0.66 – 0.55 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  142.5, 128.2, 128.1, 125.4, 35.1, 34.1, 23.9. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{10}\text{H}_{15}\text{BNaO}_2^+$ : 201.1057 ( $\text{M} + \text{Na}$ ) $^+$ , found: 201.1100.

**(4-methoxybutyl)boronic acid (2e)**



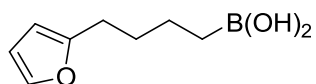
The product was prepared using the general procedure above and was isolated as a white solid (0.95 g, 72% yield).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.38 (s, 2H), 3.27 (t,  $J = 6.5$  Hz, 2H), 3.19 (s, 3H), 1.48 – 1.39 (m, 2H), 1.32 (dt,  $J = 14.8, 7.4$  Hz, 2H), 0.57 (t,  $J = 7.7$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  71.9, 57.7, 31.9, 20.8. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_5\text{H}_{13}\text{BNaO}_3^+$ : 155.0850 ( $\text{M} + \text{Na}$ ) $^+$ , found: 155.0851.

**(4-cyanobutyl)boronic acid (2f)**



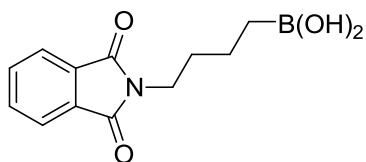
The product was prepared using the general procedure above and was isolated as a white solid (0.75 g, 77% yield).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.47 (s, 2H), 2.44 (t,  $J = 6.9$  Hz, 2H), 1.54 – 1.45 (m, 2H), 1.44 – 1.34 (m, 2H), 0.59 (t,  $J = 7.7$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  120.7, 27.4, 23.4, 16.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_5\text{H}_{10}\text{BNNaO}_2^+$ : 150.0697 ( $\text{M} + \text{Na}$ ) $^+$ , found: 150.0718.

**(4-(furan-2-yl)butyl)boronic acid (2g)**



The product was prepared using the general procedure above and was isolated as a white solid (1.37 g, 82% yield).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.47 (d,  $J = 1.0$  Hz, 1H), 7.40 (s, 2H), 6.32 (dd,  $J = 2.9, 1.9$  Hz, 1H), 6.05 (d,  $J = 2.5$  Hz, 1H), 2.55 (t,  $J = 7.5$  Hz, 2H), 1.52 (dt,  $J = 15.2, 7.5$  Hz, 2H), 1.40 – 1.30 (m, 2H), 0.62 – 0.57 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  157.6, 141.7, 110.9, 105.5, 31.9, 28.7, 24.4.

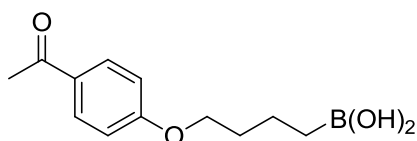
**4-(1,3-dioxoisindolin-2-yl)butylboronic acid (2h)**



The product was prepared using the general procedure above and was isolated as a white solid (1.83 g, 74% yield).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.88 – 7.80 (m, 4H), 7.40 (s, 2H), 3.54 (t,  $J$  = 7.0 Hz, 2H), 1.53 – 1.47 (m, 2H), 1.31 – 1.27 (m, 2H), 0.59 (t,  $J$  = 7.8 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  167.9, 134.3, 131.6, 122.9, 37.4, 30.8, 21.5. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{12}\text{H}_{14}\text{BNaO}_4^+$ : 270.0908 ( $M + \text{Na}$ ) $^+$ , found: 270.0908.

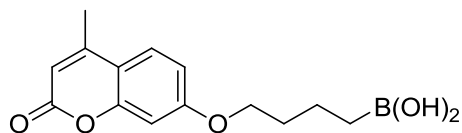
The data are identical to: Shao, X.; Liu, T.; Lu, L.; Shen, Q.-L. *Org. Lett.* **2014**, *16*, 4738.

#### (4-(4-acetylphenoxy)butyl)boronic acid (2i)



The product was prepared using the general procedure above and was isolated as a white solid (1.58 g, 67% yield).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.90 (d,  $J$  = 8.9 Hz, 2H), 7.44 (s, 2H), 7.01 (d,  $J$  = 8.9 Hz, 2H), 4.02 (t,  $J$  = 6.5 Hz, 2H), 2.50 (s, 3H), 1.74 – 1.63 (m, 2H), 1.46 (dt,  $J$  = 15.3, 7.7 Hz, 2H), 0.63 (t,  $J$  = 7.9 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  196.2, 162.6, 130.4, 129.6, 114.1, 67.8, 31.2, 26.3, 20.6. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{12}\text{H}_{17}\text{BNaO}_4^+$ : 259.1112 ( $M + \text{Na}$ ) $^+$ , found: 259.1114.

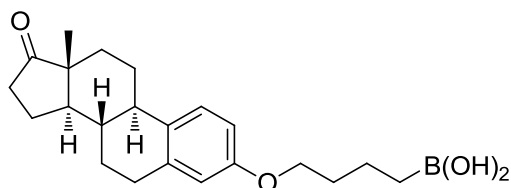
#### (4-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)butyl)boronic acid (2j)



The product was prepared using the general procedure above and was isolated as a white solid (1.68 g, 61% yield).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.67 (d,  $J$  = 9.5 Hz, 1H), 7.45 (s, 2H), 6.97 – 6.93 (m, 2H), 6.20 (d,  $J$  = 1.0 Hz, 1H), 4.05 (t,  $J$  = 6.5 Hz, 2H), 2.39 (s, 3H), 1.74 – 1.64 (m, 2H), 1.52 – 1.43 (m, 2H), 0.64 (t,  $J$  = 7.8 Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  161.8, 160.1, 154.7, 153.4, 126.4, 112.9, 112.4, 110.9, 101.0, 68.2, 31.2, 20.6, 18.1. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{14}\text{H}_{17}\text{BNaO}_5^+$ : 299.1061 ( $M + \text{Na}$ ) $^+$ , found: 299.1053.

The data are identical to: Shao, X.; Liu, T.; Lu, L.; Shen, Q.-L. *Org. Lett.* **2014**, *16*, 4738.

#### (4-(((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)butyl)boronic acid (2k)



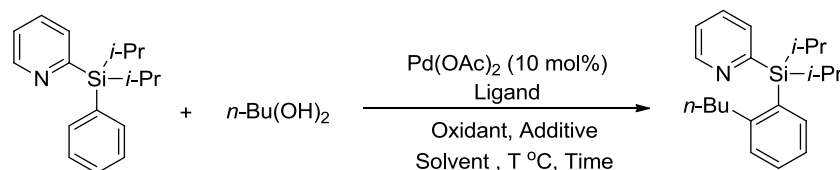
The product was prepared using the general procedure above and was isolated as a white solid (2.11 g, 57% yield).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  7.42 (s, 2H), 7.15 (d,  $J = 8.6$  Hz, 1H), 6.66 (dd,  $J = 8.5, 2.6$  Hz, 1H), 6.60 (d,  $J = 2.3$  Hz, 1H), 3.87 (t,  $J = 6.5$  Hz, 2H), 2.84 – 2.76 (m, 2H), 2.43 (dd,  $J = 18.7, 8.2$  Hz, 1H), 2.33 (s, 1H), 2.17 (s, 1H), 2.11 – 2.00 (m, 1H), 1.94 (m, 2H), 1.75 (d,  $J = 6.9$  Hz, 1H), 1.68 – 1.57 (m, 2H), 1.57 – 1.40 (m, 5H), 1.41 – 1.29 (m, 3H), 0.82 (s, 3H), 0.62 (t,  $J = 7.8$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  219.7, 156.6, 137.3, 131.5, 126.2, 114.1, 112.0, 67.2, 60.5, 49.6, 47.3, 43.4, 37.9, 35.4, 31.6, 31.4, 29.2, 26.1, 25.5, 21.2, 20.8, 13.5. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{31}\text{BNaO}_4^+$ : 393.2208 ( $\text{M} + \text{Na}$ ) $^+$ , found: 393.2213.

The data are identical to: Shao, X.; Liu, T.; Lu, L.; Shen, Q.-L. *Org. Lett.* **2014**, *16*, 4738.

### Reference:

- [1] Huang, W.-L.; Dulong, F.; Khan, S. I.; Cantat, T.; Diaconescu, P. L. *J. Am. Chem. Soc.* **2014**, *136*, 17410.  
 [2] Denmark, S. E.; Hurd, A. R.; Sacha, H. J. *J. Org. Chem.* **1997**, *62*, 1668.  
 [3] Itami, K.; Mitsudo, K.; Fujita, K.; Ohashi, Y.; Yoshida, J. *J. Am. Chem. Soc.* **2004**, *126*, 11058.  
 [4] Dudnik, A. S.; Chernyak, N.; Huang, C.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 8729.  
 [5] Xu, J.; Xiao, B.; Xie, C.-Q.; Luo, D.-F.; Liu, L.; Fu, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 12551.

### III. General procedure for the optimization of the reaction conditions



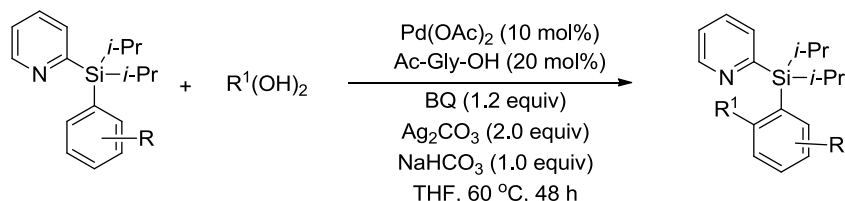
A 35 mL tube, equipped with a magnetic stir bar, was charged with  $\text{Pd(OAc)}_2$  (0.0045 g, 0.02 mmol, 10 mol%) followed by 2-(diisopropyl(phenyl)silyl)pyridine (54  $\mu\text{L}$ , 0.2 mmol), butylboronic acid, ligand, oxidant, additives, and solvent. The tube was placed into an oil bath under desired temperature. After the reaction was completed, it was allowed to cool to room temperature. The reaction mixture was diluted with ethyl acetate and then filtered through a small pad of Celite. The filtrate was concentrated *in vacuo*. The yield was determined by  $^1\text{H}$  NMR analysis of crude product using  $\text{Cl}_2\text{CHCHCl}_2$  as the internal standard.

**Table 1. Ligand Survey for PyrDipSi-Directed C–H alkylation with Alkylboronic Acid**

entry	Ligand	yield (%) <sup>b</sup>	entry	Ligand	yield (%) <sup>b</sup>
1	Ac-Gly-OH	89	11	L-Proline	0
2	Ac-Leu-OH	32	12	Boc-Ser-OH	32
3	Ac-Ile-OH	17	13	N-Cbz-O-tBu-Ser-OH	trace
4	Boc-Leu-OH	trace	14	Ac-Glu-OH	0
5	Boc-Ile-OH	18	15	Boc-Glu-OH	55
6	Boc-Gly-OH	trace	16	Ac-Cys-OH	0
7	Cbz-Gly-OH	42	17	Ac-Tyr-OH	trace
8	Ac-Ala-OH	31	18	PivOH	22
9	Ac-Val-OH	47			
10	Boc-Abu-OH	32			

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol, 3.0 equiv), Pd(OAc)<sub>2</sub> (0.02 mmol, 10 mol%), ligand (0.04 mmol, 20 mol%), BQ (0.24 mmol, 1.2 equiv), Ag<sub>2</sub>CO<sub>3</sub> (0.4 mmol, 2.0 equiv), NaHCO<sub>3</sub> (0.2 mmol, 1.0 equiv), THF (1.0 mL), air, 60 °C, 48 h. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis of the crude reaction mixtures using CHCl<sub>2</sub>CHCl<sub>2</sub> as an internal standard.

#### IV. General procedure for the C-H alkylation with alkylboronic acids

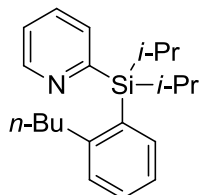


A 35 mL tube, equipped with a magnetic stir bar, was charged with Pd(OAc)<sub>2</sub> (0.0045 g, 0.02 mmol, 10 mol%) followed by pyridyl silanes (0.2 mmol), alkylboronic acid (0.0612 g, 0.6 mmol), Ac-Gly-OH (0.0046 g, 0.04 mmol), BQ (0.0218 g, 0.24 mmol), Ag<sub>2</sub>CO<sub>3</sub> (0.1102 g, 0.4 mmol), NaHCO<sub>3</sub> (0.0168g, 0.2 mmol) and THF (1.0 mL). The tube was placed into an oil bath preheated to 60 °C. After the reaction mixture was stirred for 48 h, it was allowed to cool to room temperature. The reaction mixture was diluted with ethyl acetate and then filtered through a small pad of Celite.

The filtrate was concentrated *in vacuo* and the residue was purified by silica gel column chromatography affording the corresponding products.

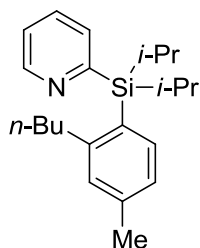
## V. Characterization of synthesized compounds

### 2-((2-butylphenyl)diisopropylsilyl)pyridine (3aa)



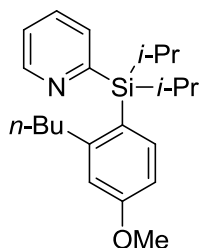
Colorless liquid (58.5 mg, 90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.6$  Hz, 1H), 7.56 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.48 (dd,  $J = 7.4, 1.4$  Hz, 2H), 7.36 – 7.31 (m, 1H), 7.26 – 7.14 (m, 3H), 2.42 – 2.34 (m, 2H), 1.73 – 1.70 (m, 2H), 1.45 – 1.36 (m, 2H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.03 – 0.97 (m, 8H), 0.71 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 149.9, 149.8, 136.8, 133.3, 131.3, 131.1, 129.2, 128.6, 124.6, 122.4, 36.8, 33.6, 22.9, 18.2, 17.9, 13.8, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{31}\text{NNaSi}^+$ : 348.2118 ( $\text{M} + \text{Na}$ ) $^+$ , found: 348.2118.

### 2-((2-butyl-4-methylphenyl)diisopropylsilyl)pyridine (3ba)



Colorless liquid (56.3 mg, 83%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.7$  Hz, 1H), 7.56 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.47 (d,  $J = 7.5$  Hz, 1H), 7.38 (d,  $J = 7.6$  Hz, 1H), 7.21 (ddd,  $J = 7.5, 4.9, 1.3$  Hz, 1H), 7.08 (s, 1H), 7.01 (d,  $J = 7.6$  Hz, 1H), 2.38 – 2.30 (m, 5H), 1.73 – 1.70 (m, 2H), 1.50 – 1.31 (m, 2H), 1.05 (d,  $J = 7.4$  Hz, 6H), 1.03 – 0.97 (m, 8H), 0.72 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 149.8, 139.0, 136.9, 133.3, 132.0, 131.2, 129.5, 127.7, 125.6, 122.4, 36.7, 33.6, 22.9, 21.4, 18.2, 18.0, 13.7, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{33}\text{NNaSi}^+$ : 362.2274 ( $\text{M} + \text{Na}$ ) $^+$ , found: 362.2265.

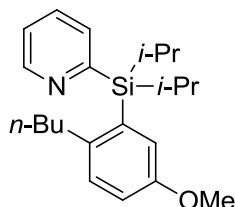
### 2-((2-butyl-4-methoxyphenyl)diisopropylsilyl)pyridine (3ca)



Colorless liquid (29.8 mg, 42%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.5$  Hz, 1H), 7.55 (t,  $J = 7.0$  Hz, 1H), 7.47 (d,  $J = 7.4$  Hz, 1H), 7.40 (d,  $J = 8.3$  Hz, 1H), 7.23 – 7.16 (m, 1H), 6.81 (d,  $J = 2.0$

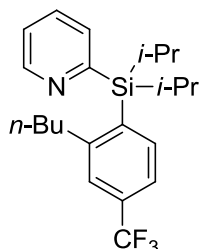
Hz, 1H), 6.78 – 6.71 (m, 1H), 3.81 (s, 3H), 2.41 – 2.32 (m, 2H), 1.71 – 1.67 (m, 4H), 1.47 – 1.36 (m, 2H), 1.05 (d,  $J = 7.4$  Hz, 6H), 1.02 – 0.95 (m, 8H), 0.71 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 160.5, 151.8, 149.9, 138.2, 133.2, 131.2, 122.4, 114.5, 110.2, 54.8, 36.8, 33.4, 22.9, 18.2, 17.9, 13.8, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{33}\text{NNaOSi}^+$ : 378.2224 ( $\text{M} + \text{Na}$ ) $^+$ , found: 378.2230.

### 2-((2-butyl-5-methoxyphenyl)diisopropylsilyl)pyridine (3da)



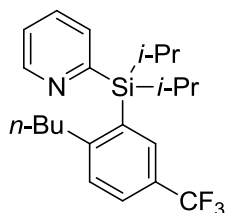
Colorless liquid (36.2 mg, 51%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 – 8.77 (m, 1H), 7.56 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.51 – 7.45 (m, 1H), 7.23 – 7.15 (m, 2H), 7.03 (d,  $J = 2.8$  Hz, 1H), 6.89 (dd,  $J = 8.5, 2.8$  Hz, 1H), 3.77 (s, 3H), 2.36 – 2.26 (m, 2H), 1.73 – 1.69 (m, 2H), 1.37 (ddd,  $J = 11.7, 10.1, 6.5$  Hz, 2H), 1.08 (d,  $J = 7.4$  Hz, 6H), 1.05 – 0.95 (m, 8H), 0.71 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 156.4, 149.9, 141.8, 133.3, 133.0, 131.2, 129.5, 122.5, 122.4, 114.3, 55.1, 35.8, 33.8, 22.8, 18.2, 18.0, 13.8, 11.3. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{33}\text{NNaOSi}^+$ : 378.2224 ( $\text{M} + \text{Na}$ ) $^+$ , found: 378.2216.

### 2-((2-butyl-4-(trifluoromethyl)phenyl)diisopropylsilyl)pyridine (3ea)



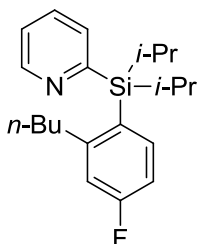
Colorless liquid (59.7 mg, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.6$  Hz, 1H), 7.59 (dt,  $J = 7.5, 3.9$  Hz, 2H), 7.48 (d,  $J = 7.6$  Hz, 2H), 7.41 (d,  $J = 7.9$  Hz, 1H), 7.24 (ddd,  $J = 7.6, 4.9, 1.3$  Hz, 1H), 2.47 – 2.40 (m, 2H), 1.75 – 1.69 (m, 2H), 1.47 – 1.36 (m, 2H), 1.07 (d,  $J = 7.4$  Hz, 6H), 1.04 – 0.96 (m, 8H), 0.73 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.2, 150.6, 150.1, 137.1, 136.8, 133.5, 132.6, 131.0 (q,  $J_{\text{CF}} = 10.1$  Hz), 124.9 (q,  $J_{\text{CF}} = 11.6$  Hz), 122.7 (q,  $J_{\text{CF}} = 220.1$  Hz), 121.1 (q,  $J_{\text{CF}} = 10.2$  Hz), 99.9, 36.6, 33.3, 22.8, 18.1, 17.9, 13.7, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{31}\text{F}_3\text{NSi}^+$ : 394.2172 ( $\text{M} + \text{H}$ ) $^+$ , found: 394.2176.

### 2-((2-butyl-5-(trifluoromethyl)phenyl)diisopropylsilyl)pyridine (3fa)



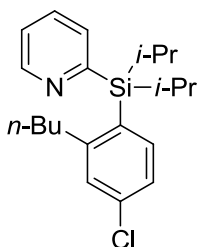
Colorless liquid (47.2 mg, 60%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.8$  Hz, 1H), 7.72 (s, 1H), 7.63 – 7.54 (m, 2H), 7.48 (d,  $J = 7.5$  Hz, 1H), 7.35 (d,  $J = 8.1$  Hz, 1H), 7.26 – 7.21 (m, 1H), 2.45 – 2.36 (m, 2H), 1.76 – 1.72 (m, 2H), 1.43 – 1.35 (m, 2H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.01 (d,  $J = 7.3$  Hz, 6H), 0.99 – 0.94 (m, 2H), 0.70 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 154.0, 150.1, 133.6, 133.1 (q,  $J_{\text{CF}} = 8.4$  Hz), 132.8, 131.0, 129.4, 128.8, 128.5 (q,  $J_{\text{CF}} = 9.6$  Hz), 125.9 (q,  $J_{\text{CF}} = 15.1$  Hz), 122.8 (q,  $J_{\text{CF}} = 274.2$  Hz), 36.7, 33.3, 22.8, 18.1, 17.8, 13.7, 11.1. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{30}\text{F}_3\text{NNaSi}^+$ : 416.1992 ( $\text{M} + \text{Na}$ ) $^+$ , found: 416.1986.

### 2-((2-butyl-4-fluorophenyl)diisopropylsilyl)pyridine (3ga)



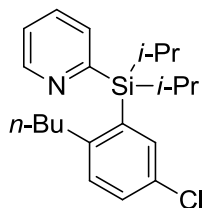
Colorless liquid (59.7 mg, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.84 – 8.79 (m, 1H), 7.58 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.50 – 7.41 (m, 2H), 7.22 (ddd,  $J = 7.6, 4.9, 1.3$  Hz, 1H), 6.96 (dd,  $J = 11.1, 2.5$  Hz, 1H), 6.88 (td,  $J = 8.5, 2.6$  Hz, 1H), 2.42 – 2.34 (m, 2H), 1.72 – 1.67 (m, 2H), 1.45 – 1.35 (m, 2H), 1.05 (d,  $J = 7.4$  Hz, 6H), 1.03 – 0.96 (m, 8H), 0.72 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 164.8, 162.8, 152.8, 150.0, 138.5 (d,  $J_{\text{CF}} = 7.6$  Hz), 133.4 (d,  $J_{\text{CF}} = 233.0$  Hz), 131.1, 122.6, 115.3 (d,  $J_{\text{CF}} = 19.4$  Hz), 111.9 (d,  $J_{\text{CF}} = 19.5$  Hz), 36.6, 33.1, 22.8, 18.2, 17.9, 13.7, 11.3. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{30}\text{FNNaSi}^+$ : 366.2024 ( $\text{M} + \text{Na}$ ) $^+$ , found: 366.2002.

### 2-((2-butyl-4-chlorophenyl)diisopropylsilyl)pyridine (3ha)



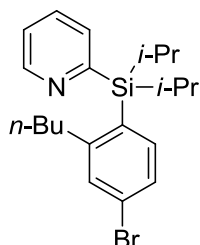
Colorless liquid (51.7 mg, 72%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.8$  Hz, 1H), 7.58 (t,  $J = 7.6$  Hz, 1H), 7.47 (d,  $J = 7.5$  Hz, 1H), 7.40 (d,  $J = 8.1$  Hz, 1H), 7.23 (t,  $J = 6.0$  Hz, 2H), 7.16 (dd,  $J = 8.0, 1.5$  Hz, 1H), 2.40 – 2.32 (m, 2H), 1.73 – 1.67 (m, 2H), 1.44 – 1.37 (m, 2H), 1.05 (d,  $J = 7.4$  Hz, 6H), 1.03 – 0.96 (m, 8H), 0.72 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.5, 151.9, 150.0, 138.0, 135.6, 133.5, 131.1, 130.0, 128.7, 124.9, 122.6, 36.5, 33.2, 22.8, 18.1, 17.9, 13.7, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{30}\text{ClNNaSi}^+$ : 382.1728 ( $\text{M} + \text{Na}$ ) $^+$ , found: 382.1721.

### 2-((2-butyl-5-chlorophenyl)diisopropylsilyl)pyridine (3ia)



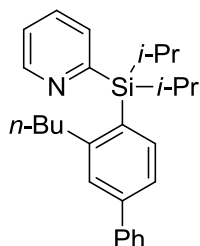
Colorless liquid (57.5 mg, 80%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (dd,  $J = 3.3, 1.1$  Hz, 1H), 7.58 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.47 (d,  $J = 7.6$  Hz, 1H), 7.41 (d,  $J = 2.3$  Hz, 1H), 7.28 (dd,  $J = 8.3, 2.3$  Hz, 1H), 7.22 (ddd,  $J = 7.6, 4.9, 1.3$  Hz, 1H), 7.18 (d,  $J = 8.3$  Hz, 1H), 2.37 – 2.29 (m, 2H), 1.74 – 1.68 (m, 2H), 1.40 – 1.31 (m, 2H), 1.07 (d,  $J = 7.4$  Hz, 6H), 1.04 – 0.96 (m, 8H), 0.70 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3, 150.1, 148.1, 136.0, 134.5, 133.5, 131.0, 130.9, 130.1, 129.2, 122.7, 36.1, 33.5, 22.8, 18.2, 17.9, 13.7, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{30}\text{ClNNaSi}^+$ : 383.1728 ( $\text{M} + \text{Na}$ ) $^+$ , found: 382.1718.

### 2-((4-bromo-2-butylphenyl)diisopropylsilyl)pyridine (3ja)



Colorless liquid (41.1 mg, 51%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.6$  Hz, 1H), 7.57 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.46 (d,  $J = 7.5$  Hz, 1H), 7.39 (d,  $J = 1.2$  Hz, 1H), 7.35 – 7.28 (m, 2H), 7.22 (dd,  $J = 6.4, 5.2$  Hz, 1H), 2.40 – 2.31 (m, 2H), 1.73 – 1.65 (m, 2H), 1.44 – 1.34 (m, 2H), 1.05 (d,  $J = 7.4$  Hz, 6H), 1.02 – 0.98 (m, 8H), 0.72 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.5, 152.1, 150.1, 138.2, 133.4, 131.6, 131.1, 130.6, 127.8, 124.3, 122.6, 36.5, 33.3, 22.8, 18.1, 17.9, 13.7, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{30}\text{BrNNaSi}^+$ : 426.1223 ( $\text{M} + \text{Na}$ ) $^+$ , found: 426.1224.

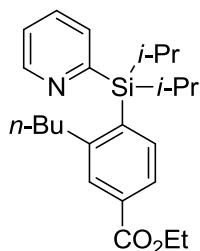
### 2-((3-butyl-[1,1'-biphenyl]-4-yl)diisopropylsilyl)pyridine (3ka)



Colorless liquid (65.8 mg, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (d,  $J = 4.7$  Hz, 1H), 7.65 – 7.58 (m, 3H), 7.55 (dt,  $J = 10.5, 4.6$  Hz, 2H), 7.48 (d,  $J = 1.5$  Hz, 1H), 7.46 – 7.39 (m, 3H), 7.34 (t,  $J = 7.3$  Hz, 1H), 7.25 – 7.20 (m, 1H), 2.50 – 2.40 (m, 2H), 1.82 – 1.74 (m, 2H), 1.48 (ddd,  $J = 11.9, 10.1, 6.6$  Hz, 2H), 1.10 (d,  $J = 7.4$  Hz, 6H), 1.08 – 1.01 (m, 8H), 0.74 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 150.3, 150.0, 141.8, 141.2, 137.3, 133.3, 131.2, 130.3, 128.6, 127.4, 127.2, 127.1, 123.4, 122.5, 36.9, 33.7, 23.0, 18.9, 18.0, 13.8, 11.3. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{27}\text{H}_{35}\text{NNaSi}^+$ : 424.2431 ( $\text{M} + \text{Na}$ ) $^+$ , found: 424.2430.

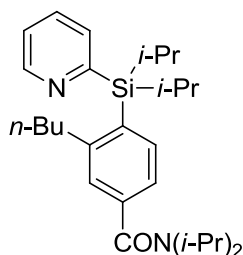


### ethyl 3-butyl-4-(diisopropyl(pyridin-2-yl)silyl)benzoate (3la)



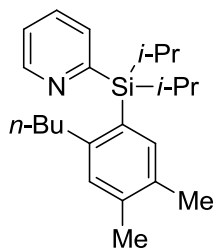
Colorless liquid (77.1 mg, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.8$  Hz, 1H), 7.90 (d,  $J = 1.3$  Hz, 1H), 7.81 (dd,  $J = 7.8, 1.5$  Hz, 1H), 7.58 (td,  $J = 7.8, 1.9$  Hz, 2H), 7.46 (d,  $J = 7.6$  Hz, 1H), 7.22 (ddd,  $J = 7.6, 4.9, 1.3$  Hz, 1H), 4.37 (q,  $J = 7.1$  Hz, 2H), 2.47 – 2.39 (m, 2H), 1.76 – 1.72 (m, 2H), 1.50 – 1.36 (m, 5H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.03 – 0.95 (m, 8H), 0.72 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 164.4, 150.2, 150.1, 138.1, 136.8, 133.4, 131.1, 131.0, 129.2, 125.2, 122.6, 60.8, 36.6, 33.5, 22.9, 18.1, 17.9, 14.3, 13.7, 11.3. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{24}\text{H}_{35}\text{NNaO}_2\text{Si}^+$ : 420.2329 ( $\text{M} + \text{Na}$ ) $^+$ , found: 420.2333.

### 3-butyl-4-(diisopropyl(pyridin-2-yl)silyl)-*N,N*-diisopropylbenzamide (3ma)



Colorless liquid (67.8 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.5$  Hz, 1H), 7.59 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.51 (d,  $J = 7.5$  Hz, 1H), 7.46 (d,  $J = 7.6$  Hz, 1H), 7.22 (ddd,  $J = 7.5, 4.9, 1.3$  Hz, 1H), 7.18 (d,  $J = 1.2$  Hz, 1H), 7.10 (dd,  $J = 7.6, 1.5$  Hz, 1H), 3.96 (s, 1H), 3.50 (s, 1H), 2.42 – 2.34 (m, 2H), 1.69 (d,  $J = 7.4$  Hz, 2H), 1.49 (s, 6H), 1.44 – 1.38 (m, 2H), 1.15 (s, 6H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.03 – 0.94 (m, 8H), 0.71 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 164.7, 150.2, 150.0, 139.4, 136.9, 133.5, 132.3, 131.1, 125.8, 122.6, 121.8, 36.7, 33.4, 29.6, 22.9, 20.7, 18.1, 17.8, 13.7, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{28}\text{H}_{44}\text{N}_2\text{NaOSi}^+$ : 475.3115 ( $\text{M} + \text{Na}$ ) $^+$ , found: 475.3113.

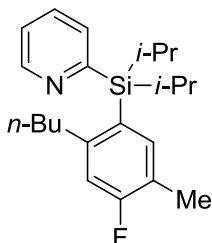
### 2-((2-butyl-4,5-dimethylphenyl)diisopropylsilyl)pyridine (3na)



Colorless liquid (54.4 mg, 77%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.5$  Hz, 1H), 7.54 (d,  $J = 1.7$  Hz, 1H), 7.47 (s, 1H), 7.22 (s, 1H), 7.19 (ddd,  $J = 7.4, 4.9, 1.3$  Hz, 1H), 7.03 (s, 1H), 2.34 – 2.27

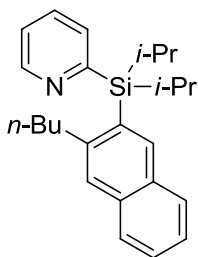
(m, 2H), 2.25 (s, 3H), 2.23 (s, 3H), 1.74 – 1.69 (m, 2H), 1.42 – 1.35 (m, 2H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.03 – 0.94 (m, 8H), 0.71 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 149.8, 147.3, 138.0, 137.6, 133.1, 132.5, 131.2, 130.1, 128.2, 122.3, 36.3, 33.8, 22.9, 19.7, 19.4, 18.3, 18.0, 13.8, 11.3. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{35}\text{NNaSi}^+$ : 376.2431 ( $\text{M} + \text{Na}$ ) $^+$ , found: 376.2422.

### 2-((2-butyl-4-fluoro-5-methylphenyl)diisopropylsilyl)pyridine (30a)



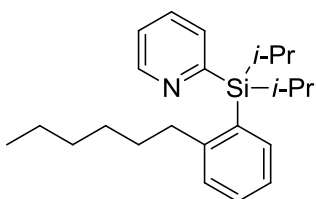
Colorless liquid (37.2 mg, 52%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J = 4.6$  Hz, 1H), 7.57 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.47 (d,  $J = 7.5$  Hz, 1H), 7.21 (ddd,  $J = 7.5, 6.6, 3.5$  Hz, 2H), 6.90 (d,  $J = 11.8$  Hz, 1H), 2.37 – 2.28 (m, 2H), 2.23 (s, 3H), 1.73 – 1.69 (m, 2H), 1.42 – 1.32 (m, 2H), 1.05 (d,  $J = 7.4$  Hz, 6H), 0.99 (d,  $J = 7.4$  Hz, 6H), 0.94 (dd,  $J = 12.7, 5.5$  Hz, 2H), 0.71 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 163.7, 161.3, 150.0, 139.9 (d,  $J_{\text{CF}} = 5.4$  Hz), 133.3 (d,  $J_{\text{CF}} = 232.0$  Hz), 131.0, 126.5 (d,  $J_{\text{CF}} = 4.4$  Hz), 122.5, 120.8 (d,  $J_{\text{CF}} = 15.9$  Hz), 115.0 (d,  $J_{\text{CF}} = 20.3$  Hz), 36.2, 33.2, 22.8, 18.2, 17.9, 14.3 (d,  $J_{\text{CF}} = 3.2$  Hz), 13.7, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{22}\text{H}_{33}\text{FNSi}^+$ : 358.2361 ( $\text{M} + \text{H}$ ) $^+$ , found: 358.2356.

### 2-((3-butyl-naphthalen-2-yl)diisopropylsilyl)pyridine (3pa)



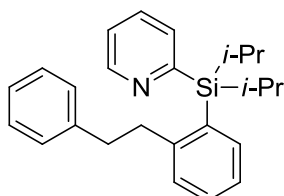
Colorless liquid (37.5 mg, 49%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (dd,  $J = 3.5, 1.3$  Hz, 1H), 8.04 (s, 1H), 7.82 – 7.72 (m, 2H), 7.69 (d,  $J = 10.2$  Hz, 1H), 7.61 – 7.53 (m, 1H), 7.52 – 7.37 (m, 3H), 7.23 (ddd,  $J = 7.5, 4.9, 1.4$  Hz, 1H), 2.59 – 2.51 (m, 2H), 1.86 – 1.81 (m, 2H), 1.52 (ddd,  $J = 12.3, 10.3, 6.6$  Hz, 2H), 1.15 – 1.10 (m, 6H), 1.10 – 1.01 (m, 8H), 0.76 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 150.0, 145.7, 137.9, 134.0, 133.3, 131.6, 131.2, 131.0, 127.9, 126.9, 126.4, 126.0, 124.8, 122.5, 36.4, 33.3, 22.8, 18.4, 18.2, 13.8, 11.5. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{25}\text{H}_{33}\text{NNaSi}^+$ : 398.2274 ( $\text{M} + \text{Na}$ ) $^+$ , found: 398.2283.

### 2-((2-hexylphenyl)diisopropylsilyl)pyridine (3ab)



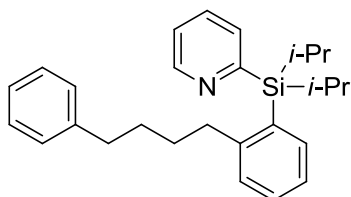
Colorless liquid (57.9 mg, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.5$  Hz, 1H), 7.56 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.51 – 7.45 (m, 2H), 7.36 – 7.30 (m, 1H), 7.26 – 7.14 (m, 3H), 2.42 – 2.34 (m, 2H), 1.76 – 1.69 (m, 2H), 1.47 – 1.37 (m, 2H), 1.19 (dd,  $J = 14.6, 7.3$  Hz, 2H), 1.12 – 1.05 (m, 8H), 1.04 – 0.95 (m, 8H), 0.82 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 149.9, 149.9, 136.8, 133.3, 131.5, 131.1, 129.2, 128.6, 124.6, 122.4, 37.1, 31.6, 31.5, 29.5, 22.5, 18.2, 18.0, 14.0, 11.3. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{23}\text{H}_{35}\text{NNaSi}^+$ : 376.2431 ( $\text{M} + \text{Na}$ ) $^+$ , found: 376.2419.

### 2-(diisopropyl(2-phenethylphenyl)silyl)pyridine (3ac)



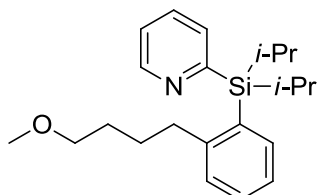
Colorless liquid (43.3 mg, 58%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (d,  $J = 4.6$  Hz, 1H), 7.59 – 7.50 (m, 3H), 7.38 (d,  $J = 6.6$  Hz, 2H), 7.21 – 7.09 (m, 5H), 6.82 (d,  $J = 7.0$  Hz, 2H), 2.76 (s, 4H), 1.74 – 1.70 (m, 2H), 1.09 (d,  $J = 7.4$  Hz, 6H), 1.01 (d,  $J = 7.3$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 150.1, 148.6, 141.9, 136.9, 133.5, 131.7, 131.1, 129.4, 128.9, 128.1, 128.0, 125.6, 125.0, 122.6, 38.4, 37.5, 18.3, 18.0, 11.3. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{25}\text{H}_{31}\text{NNaSi}^+$ : 396.2118 ( $\text{M} + \text{Na}$ ) $^+$ , found: 396.2115.

### 2-(diisopropyl(2-(4-phenylbutyl)phenyl)silyl)pyridine (3ad)



Colorless liquid (52.1 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (d,  $J = 4.8$  Hz, 1H), 7.48 (dd,  $J = 14.2, 7.4$  Hz, 3H), 7.37 – 7.30 (m, 1H), 7.28 – 7.23 (m, 2H), 7.23 – 7.12 (m, 4H), 7.08 (d,  $J = 7.1$  Hz, 2H), 2.41 (dd,  $J = 14.9, 7.2$  Hz, 4H), 1.75 – 1.70 (m, 2H), 1.47 (dd,  $J = 8.1, 3.6$  Hz, 2H), 1.27 (d,  $J = 6.6$  Hz, 2H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.01 (t,  $J = 6.2$  Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 149.9, 149.5, 142.5, 136.7, 133.3, 131.4, 131.1, 129.3, 128.6, 128.3, 128.1, 125.5, 124.7, 122.5, 37.0, 35.7, 31.7, 31.1, 18.2, 17.9, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{27}\text{H}_{35}\text{NNaSi}^+$ : 424.2431 ( $\text{M} + \text{Na}$ ) $^+$ , found: 424.2437.

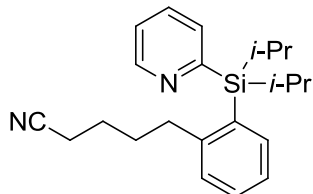
### 2-(diisopropyl(2-(4-methoxybutyl)phenyl)silyl)pyridine (3ae)



Colorless liquid (49.7 mg, 70%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.4$  Hz, 1H), 7.56 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.51 – 7.46 (m, 2H), 7.36 – 7.30 (m, 1H), 7.26 (t,  $J = 3.5$  Hz, 1H), 7.23 – 7.14 (m, 2H), 3.26 (s, 3H), 3.17 (t,  $J = 6.7$  Hz, 2H), 2.44 – 2.37 (m, 2H), 1.75 – 1.69 (m, 2H), 1.54 – 1.44 (m, 2H), 1.26 (dd,  $J = 9.3, 5.5$  Hz, 2H), 1.08 – 1.05 (m, 6H), 1.00 (d,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (100

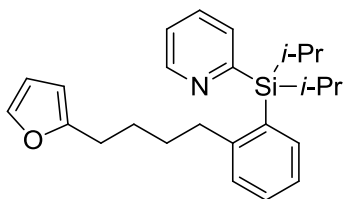
MHz, CDCl<sub>3</sub>) δ 171.3, 164.7, 150.0, 139.4, 136.9, 133.5, 132.3, 131.1, 125.8, 122.6, 121.8, 36.7, 33.4, 22.9, 20.7, 18.1, 17.8, 13.7, 11.2. HRMS (ESI-TOF) m/z: calcd for C<sub>22</sub>H<sub>33</sub>NNaOSi<sup>+</sup>: 378.2224 (M + Na)<sup>+</sup>, found: 378.2225.

### 5-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)pentanenitrile (3af)



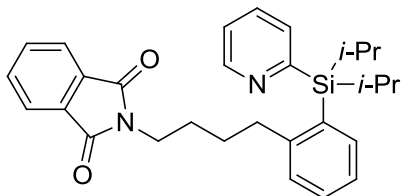
Colorless liquid (49.7 mg, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.82 (d, *J* = 4.7 Hz, 1H), 7.61 (td, *J* = 7.6, 1.7 Hz, 1H), 7.51 (dd, *J* = 11.3, 7.6 Hz, 2H), 7.38 – 7.31 (m, 1H), 7.26 – 7.19 (m, 3H), 2.42 – 2.35 (m, 2H), 2.10 (t, *J* = 7.2 Hz, 2H), 1.74 – 1.69 (m, 2H), 1.53 (ddd, *J* = 11.7, 10.1, 6.5 Hz, 2H), 1.26 (dd, *J* = 15.2, 7.4 Hz, 2H), 1.06 (d, *J* = 7.4 Hz, 6H), 1.01 (d, *J* = 7.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.2, 150.0, 148.1, 136.8, 133.6, 131.6, 131.0, 129.4, 128.5, 125.1, 122.6, 119.4, 36.0, 30.4, 25.4, 18.2, 17.9, 16.8, 11.2. HRMS (ESI-TOF) m/z: calcd for C<sub>22</sub>H<sub>30</sub>N<sub>2</sub>NaSi<sup>+</sup>: 373.2070 (M + Na)<sup>+</sup>, found: 373.2045.

### 2-((2-(4-(furan-2-yl)butyl)phenyl)diisopropylsilyl)pyridine (3ag)



Colorless liquid (17.2 mg, 22%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.80 (d, *J* = 4.7 Hz, 1H), 7.54 (td, *J* = 7.6, 1.6 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 1.0 Hz, 1H), 7.25 – 7.16 (m, 3H), 6.29 – 6.23 (m, 1H), 5.89 (d, *J* = 2.6 Hz, 1H), 2.45 – 2.38 (m, 4H), 1.72 – 1.68 (m, 2H), 1.47 (ddd, *J* = 11.5, 10.2, 6.4 Hz, 2H), 1.32 – 1.26 (m, 2H), 1.06 (d, *J* = 7.4 Hz, 6H), 1.00 (d, *J* = 7.3 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 156.2, 150.0, 149.4, 140.5, 136.8, 133.3, 131.5, 131.1, 129.3, 128.6, 124.7, 122.5, 110.0, 104.5, 36.8, 31.0, 28.2, 27.7, 18.2, 18.0, 11.3. HRMS (ESI-TOF) m/z: calcd for C<sub>25</sub>H<sub>33</sub>NNaOSi<sup>+</sup>: 414.2224 (M + Na)<sup>+</sup>, found: 414.2226.

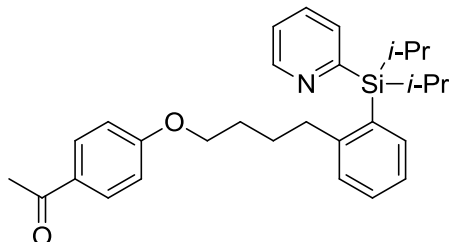
### 2-(4-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)butyl)isoindoline-1,3-dione (3ah)



Colorless liquid (43.2 mg, 46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.78 (d, *J* = 4.5 Hz, 1H), 7.83 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.14 (m, 3H), 3.49 (t, *J* = 7.2 Hz, 2H), 2.43 – 2.34 (m, 2H), 1.74 – 1.66 (m, 2H), 1.43 (dt, *J* = 15.9, 9.0 Hz, 2H), 1.29 (d, *J* = 7.2 Hz, 2H), 1.04 (d, *J* = 7.4 Hz, 6H), 0.98 (d, *J* = 7.3 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.2, 150.0, 149.0, 136.7, 133.8, 133.4, 132.1,

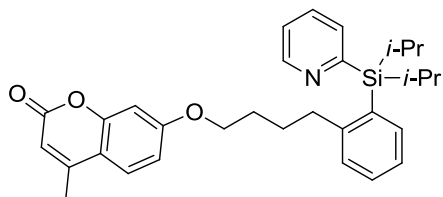
131.5, 131.0, 129.7, 129.3, 128.7, 124.9, 123.1, 122.7, 37.7, 36.6, 29.6, 28.8, 18.2, 17.9, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $C_{29}H_{34}N_2NaO_2Si^+$ : 493.2282 ( $M + Na$ )<sup>+</sup>, found: 493.2282.

**1-(4-(4-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)butoxy)phenyl)ethanone (3ai)**



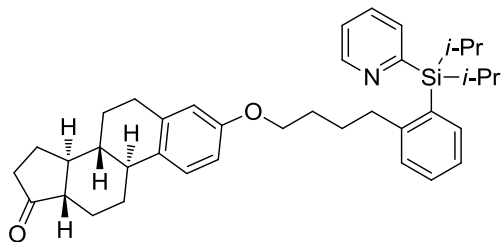
Colorless liquid (47.7 mg, 52%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.80 (d,  $J = 4.6$  Hz, 1H), 7.92 (d,  $J = 8.8$  Hz, 2H), 7.53 (dt,  $J = 16.6, 7.2$  Hz, 3H), 7.35 (t,  $J = 7.4$  Hz, 1H), 7.27 (d,  $J = 4.7$  Hz, 1H), 7.19 (dd,  $J = 12.3, 5.1$  Hz, 2H), 6.85 (d,  $J = 8.8$  Hz, 2H), 3.82 (t,  $J = 6.4$  Hz, 2H), 2.56 (s, 3H), 2.49 – 2.42 (m, 2H), 1.75 – 1.69 (m, 4H), 1.53 – 1.45 (m, 2H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.00 (d,  $J = 7.3$  Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.8, 165.1, 162.9, 162.4, 150.0, 149.0, 136.8, 133.4, 131.5, 131.1, 130.5, 129.3, 128.5, 124.9, 122.5, 114.0, 67.7, 36.6, 29.1, 27.8, 26.3, 18.2, 17.9, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $C_{29}H_{37}NNaO_2Si^+$ : 482.2486 ( $M + Na$ )<sup>+</sup>, found: 482.2493.

**7-(4-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)butoxy)-4-methyl-2H-chromen-2-one (3aj)**



Colorless liquid (68.8 mg, 69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.81 (d,  $J = 4.6$  Hz, 1H), 7.57 (t,  $J = 7.0$  Hz, 1H), 7.49 (dd,  $J = 14.9, 8.4$  Hz, 3H), 7.35 (t,  $J = 7.4$  Hz, 1H), 7.28 (s, 1H), 7.20 (t,  $J = 7.5$  Hz, 2H), 6.79 (dd,  $J = 8.8, 2.3$  Hz, 1H), 6.72 (d,  $J = 2.2$  Hz, 1H), 6.13 (s, 1H), 3.80 (t,  $J = 6.3$  Hz, 2H), 2.51 – 2.42 (m, 2H), 2.40 (s, 3H), 1.75 – 1.71 (m, 2H), 1.62 (dd,  $J = 10.2, 5.8$  Hz, 2H), 1.51 (dd,  $J = 13.8, 6.6$  Hz, 2H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.01 (d,  $J = 7.3$  Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 162.0, 161.3, 155.2, 152.5, 150.0, 148.9, 136.8, 133.4, 131.5, 131.1, 129.4, 128.5, 125.4, 124.9, 122.6, 113.3, 112.6, 111.8, 101.2, 68.1, 36.6, 29.0, 27.7, 18.6, 18.2, 17.9, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $C_{31}H_{37}NNaO_3Si^+$ : 522.2435 ( $M + Na$ )<sup>+</sup>, found: 522.2430.

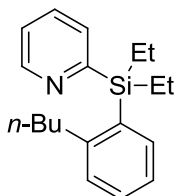
**(8S,9S,13S,14S)-3-(4-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)butoxy)-7,8,9,11,12,13,15,16-octa-hydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3ak)**



Colorless liquid (82.2 mg, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.80 (d,  $J = 4.6$  Hz, 1H), 7.55 (t,  $J = 7.5$  Hz, 1H), 7.49 (t,  $J = 6.8$  Hz, 2H), 7.34 (t,  $J = 7.2$  Hz, 1H), 7.27 (s, 1H), 7.19 (t,  $J = 7.1$  Hz, 3H),

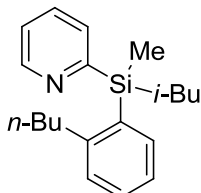
6.64 (d,  $J = 8.4$  Hz, 1H), 6.58 (s, 1H), 3.74 (t,  $J = 6.5$  Hz, 2H), 2.88 (d,  $J = 9.4$  Hz, 2H), 2.55 – 2.48 (m, 1H), 2.48 – 2.42 (m, 2H), 2.39 (d,  $J = 9.6$  Hz, 1H), 2.23 (d,  $J = 11.8$  Hz, 1H), 2.06 (dddd,  $J = 23.4, 20.4, 12.2, 3.6$  Hz, 6H), 1.74 – 1.70 (m, 3H), 1.47 – 1.42 (m, 3H), 1.06 (d,  $J = 7.4$  Hz, 6H), 1.00 (t,  $J = 7.0$  Hz, 6H), 0.97 (d,  $J = 7.5$  Hz, 1H), 0.91 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 156.9, 156.7, 150.0, 149.2, 137.6, 136.8, 133.4, 131.8, 131.4, 131.1, 129.3, 128.6, 126.2, 124.8, 122.5, 114.4, 112.0, 67.4, 50.3, 48.0, 43.9, 38.3, 36.7, 35.8, 31.5, 29.6, 29.4, 27.8, 26.5, 25.9, 21.5, 18.2, 17.9, 13.8, 11.2. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{38}\text{H}_{50}\text{NO}_2\text{Si}^+$ : 580.3605 ( $\text{M} + \text{H}$ ) $^+$ , found: 580.3630.

### 2-((2-butylphenyl)diethylsilyl)pyridine (5aa)



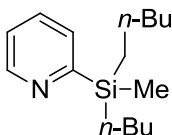
Colorless liquid (17.8 mg, 30%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J = 4.8$  Hz, 1H), 7.56 – 7.49 (m, 2H), 7.41 (d,  $J = 7.5$  Hz, 1H), 7.36 – 7.30 (m, 1H), 7.23 – 7.15 (m, 3H), 2.50 – 2.42 (m, 2H), 1.26 – 1.15 (m, 6H), 1.08 (dd,  $J = 14.9, 7.4$  Hz, 2H), 0.97 (t,  $J = 7.8$  Hz, 6H), 0.72 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 150.1, 149.4, 135.9, 133.7, 133.2, 130.3, 129.5, 128.5, 124.9, 122.5, 36.2, 34.1, 22.8, 13.8, 7.4, 4.0. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{27}\text{NNaSi}^+$ : 320.1805 ( $\text{M} + \text{Na}$ ) $^+$ , found: 320.1778.

### 2-((2-butylphenyl)(isobutyl)(methyl)silyl)pyridine (5ba)



Colorless liquid (24.9 mg, 40%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J = 4.8$  Hz, 1H), 7.56 – 7.49 (m, 2H), 7.40 (d,  $J = 7.5$  Hz, 1H), 7.35 – 7.30 (m, 1H), 7.21 – 7.15 (m, 3H), 2.54 – 2.46 (m, 2H), 1.80 (dt,  $J = 13.3, 6.6$  Hz, 1H), 1.25 (dd,  $J = 6.8, 2.7$  Hz, 4H), 1.16 – 1.08 (m, 2H), 0.88 (t,  $J = 6.1$  Hz, 6H), 0.74 (t,  $J = 7.2$  Hz, 3H), 0.66 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 150.0, 149.1, 135.5, 134.8, 133.8, 129.9, 129.5, 128.5, 125.0, 122.5, 36.2, 34.0, 26.3, 26.2, 24.8, 24.2, 22.8, 13.9. HRMS (ESI-TOF)  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{29}\text{NNaSi}^+$ : 334.1961 ( $\text{M} + \text{Na}$ ) $^+$ , found: 334.1956.

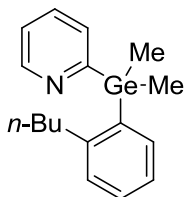
### 2-(butyl(methyl)(pentyl)silyl)pyridine (7aa)



Colorless liquid (17.9 mg, 36%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J = 4.7$  Hz, 1H), 7.58 (t,  $J = 7.5$  Hz, 1H), 7.47 (d,  $J = 7.5$  Hz, 1H), 7.21 – 7.15 (m, 1H), 1.29 (dd,  $J = 11.8, 4.2$  Hz, 14H), 0.85 (d,  $J = 6.1$  Hz, 6H), 0.30 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.1, 133.7, 130.8, 129.3, 122.5, 35.8,

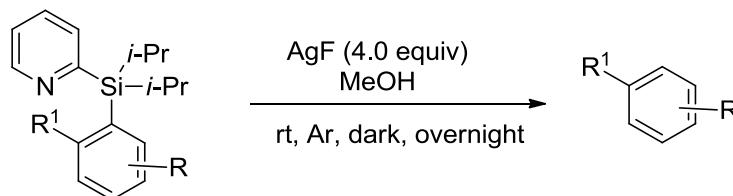
26.5, 26.0, 23.4, 22.2, 13.9, 13.7, 13.3, 13.2, -5.6. HRMS (ESI-TOF)  $m/z$ : calcd for  $C_{15}H_{28}NSi^+$ : 250.1986 ( $M + H$ )<sup>+</sup>, found: 250.1981.

### 2-((2-butylphenyl)dimethylgermyl)pyridine (9aa)



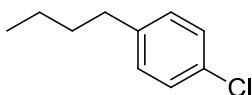
Colorless liquid (16.4 mg, 26%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.76 (d,  $J = 4.8$  Hz, 1H), 7.53 (td,  $J = 7.6, 1.7$  Hz, 1H), 7.45 (t,  $J = 6.6$  Hz, 1H), 7.38 (d,  $J = 7.5$  Hz, 1H), 7.30 (dd,  $J = 11.2, 3.8$  Hz, 1H), 7.18 (ddd,  $J = 7.8, 7.2, 5.3$  Hz, 3H), 2.59 – 2.50 (m, 2H), 1.37 – 1.32 (m, 2H), 1.22 – 1.16 (m, 2H), 0.78 (t,  $J = 7.3$  Hz, 3H), 0.74 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.2, 148.3, 137.6, 134.4, 134.2, 132.0, 129.2, 129.0, 128.6, 125.2, 122.5, 36.5, 34.3, 29.6, 22.7, 13.9, -1.9. HRMS (ESI-TOF)  $m/z$ : calcd for  $C_{17}H_{24}GeN^+$ : 316.1115 ( $M + H$ )<sup>+</sup>, found: 316.1122.

### VI. Removal of directing group



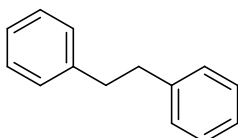
An oven dried 10 ml Wheaton V-vial was charged with **3ia** or **3ac** (0.20 mmol), AgF (104 mg, 0.80 mmol), and regular MeOH (1.0 ml) under argon atmosphere. The mixture was stirred overnight in the dark at room temperature. After completion, the mixture was filtered through celite and concentrated. The residue was purified by silica gel chromatography to afford the product.

### 1-butyl-4-chlorobenzene (10ia)



Colorless liquid (32 mg, 96%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (d,  $J = 8.2$  Hz, 2H), 7.16 (d,  $J = 8.2$  Hz, 2H), 2.64 (t,  $J = 7.7$  Hz, 2H), 1.70 – 1.59 (m, 2H), 1.48 – 1.36 (m, 2H), 1.01 (td,  $J = 7.2, 0.9$  Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.2, 131.2, 129.6, 128.2, 34.9, 33.5, 22.2, 13.8.

### 1,2-diphenylethane (10ac)

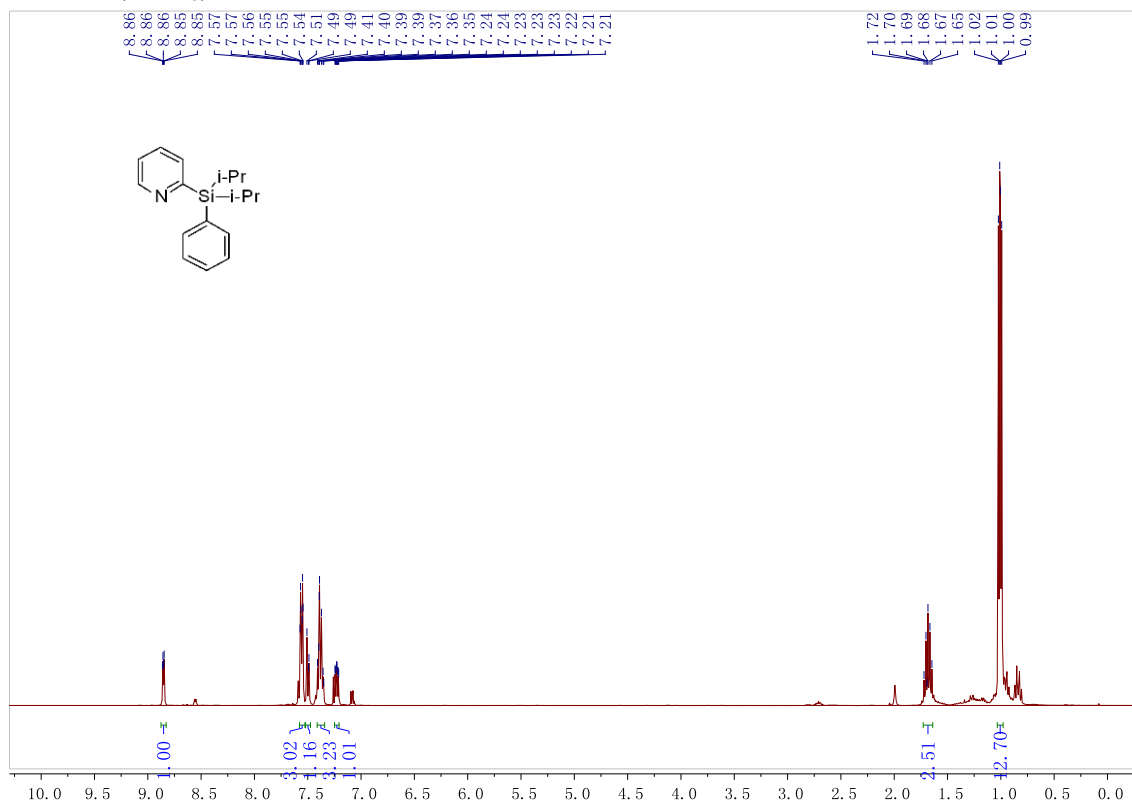


White solid (33 mg, 91%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (dd,  $J = 6.5, 2.8$  Hz, 4H), 7.36 – 7.27 (m, 6H), 3.05 (d,  $J = 3.0$  Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.7, 128.4, 128.2, 125.8, 37.9.

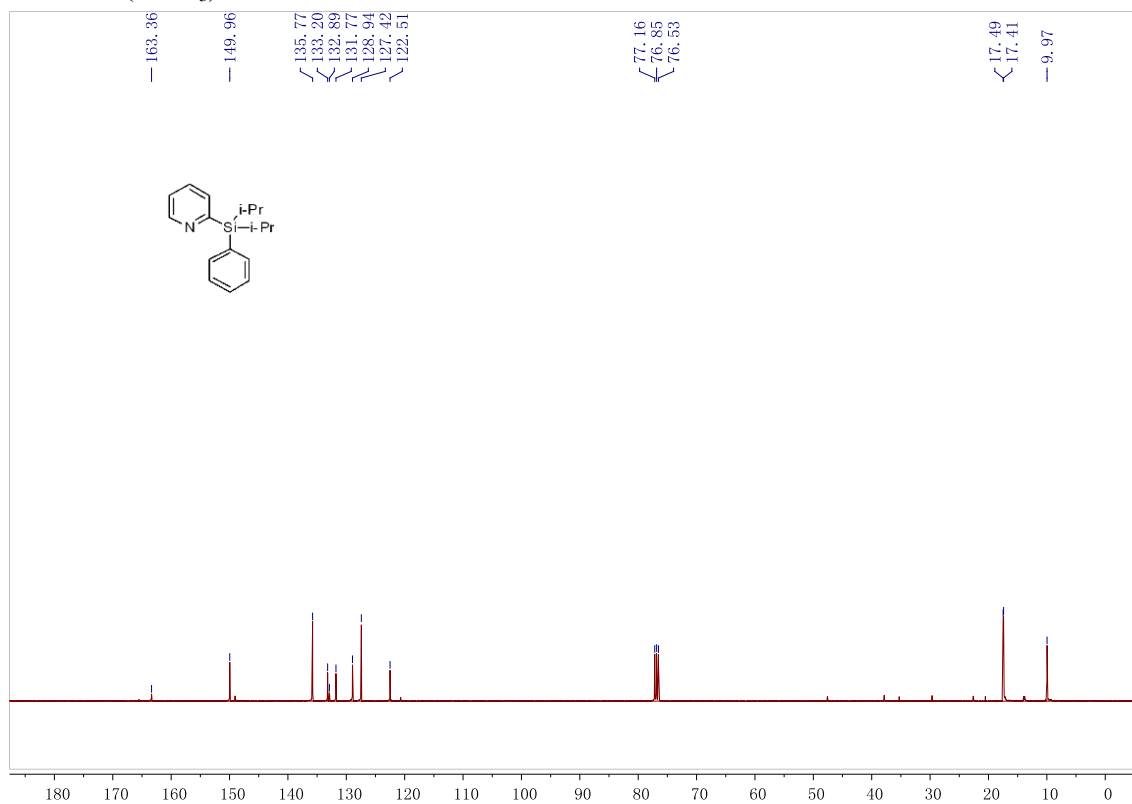
## VII. NMR Spectra

### 2-(diisopropyl(phenyl)silyl)pyridine (1a)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )



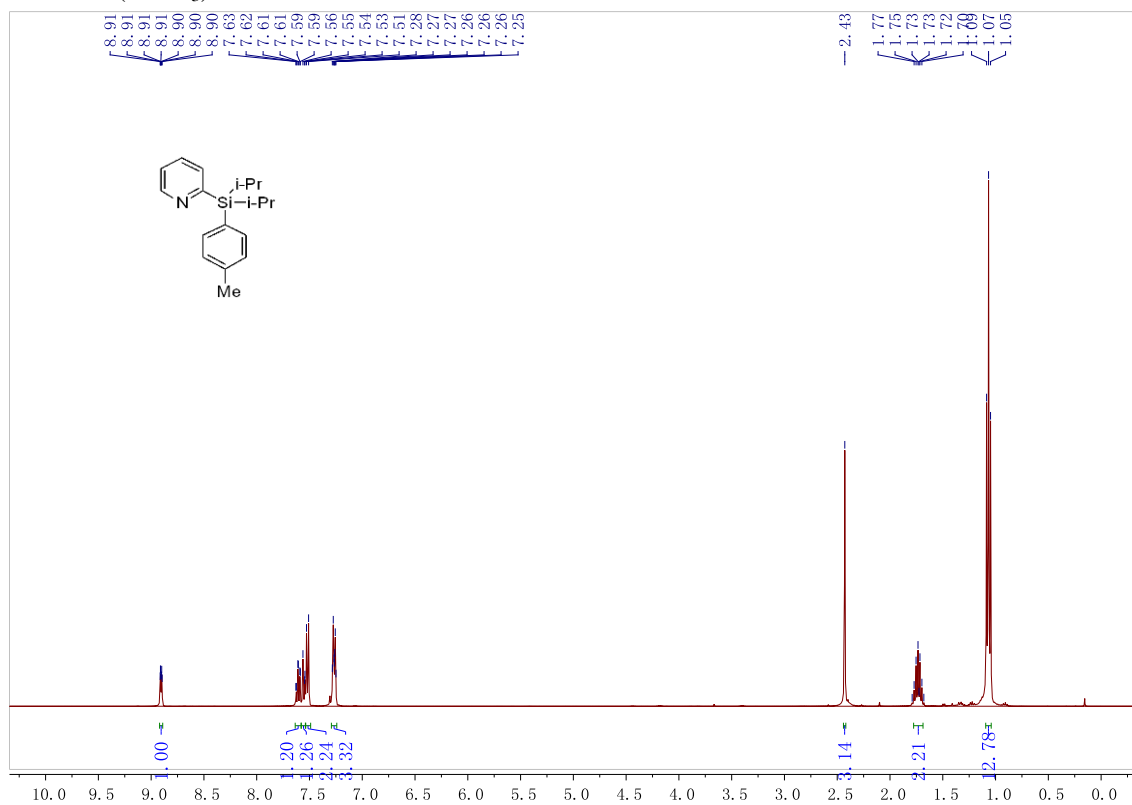
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )



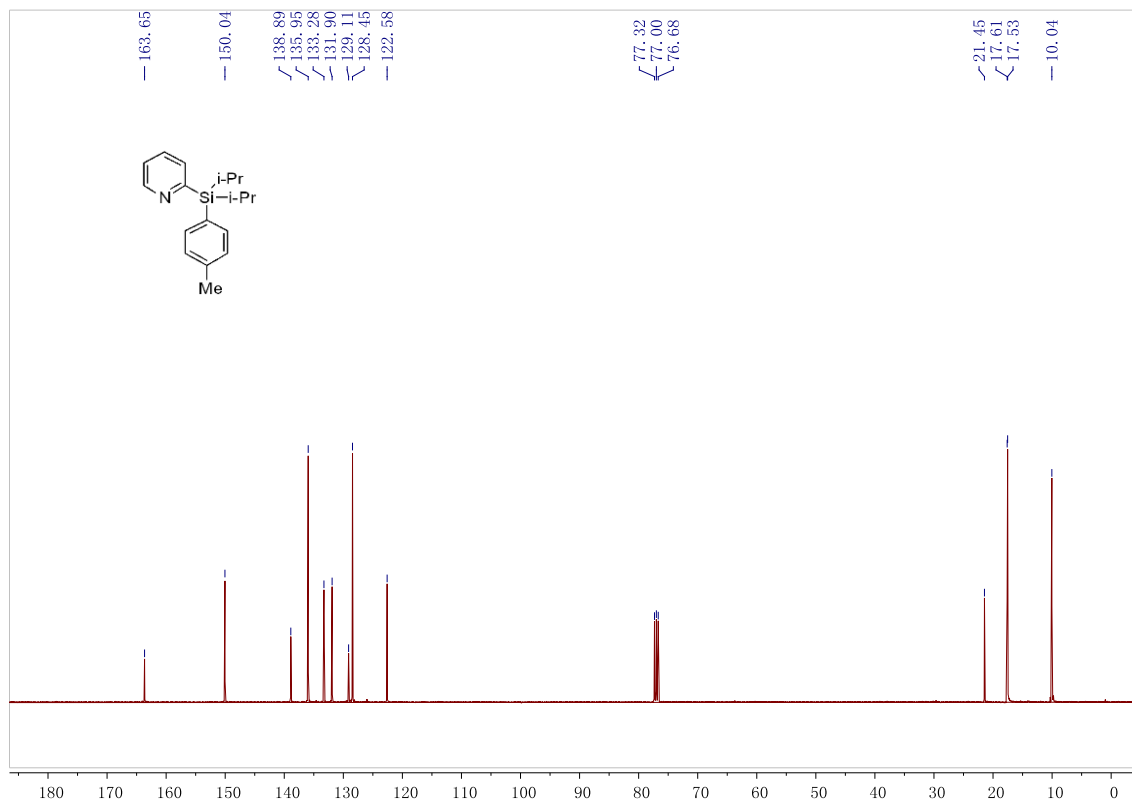


## 2-(diisopropyl(*p*-tolyl)silyl)pyridine (1b)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

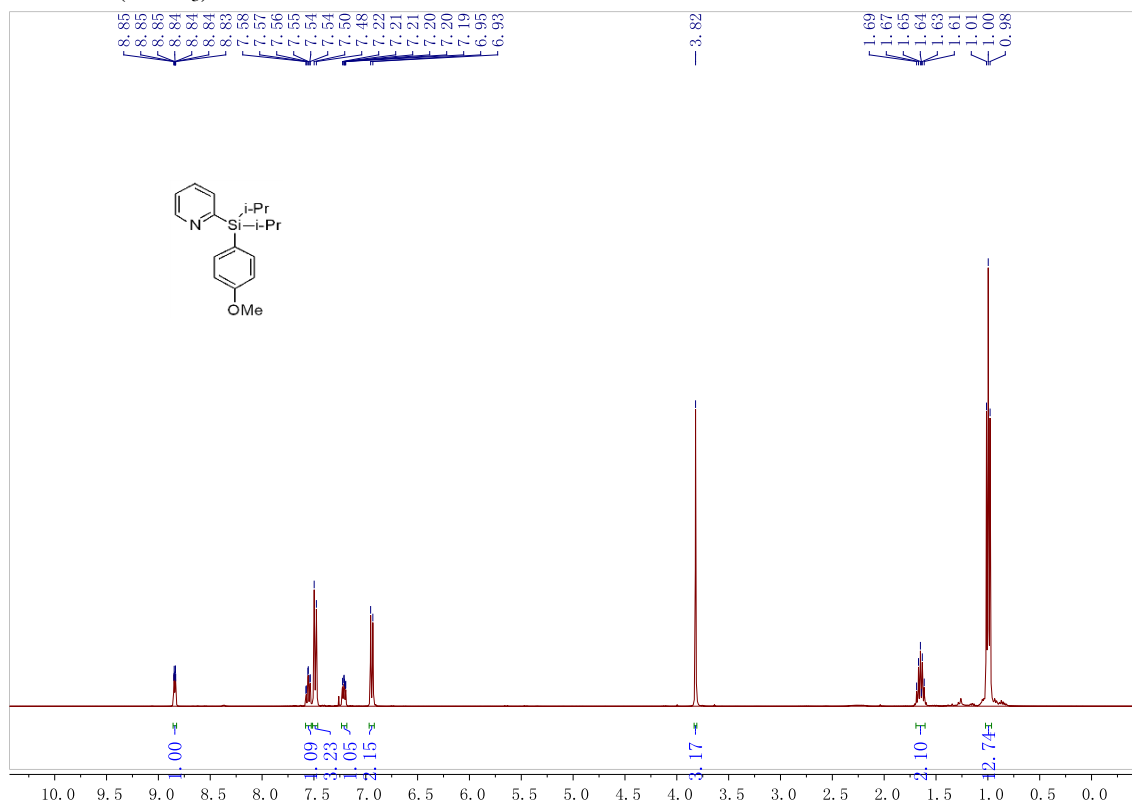


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

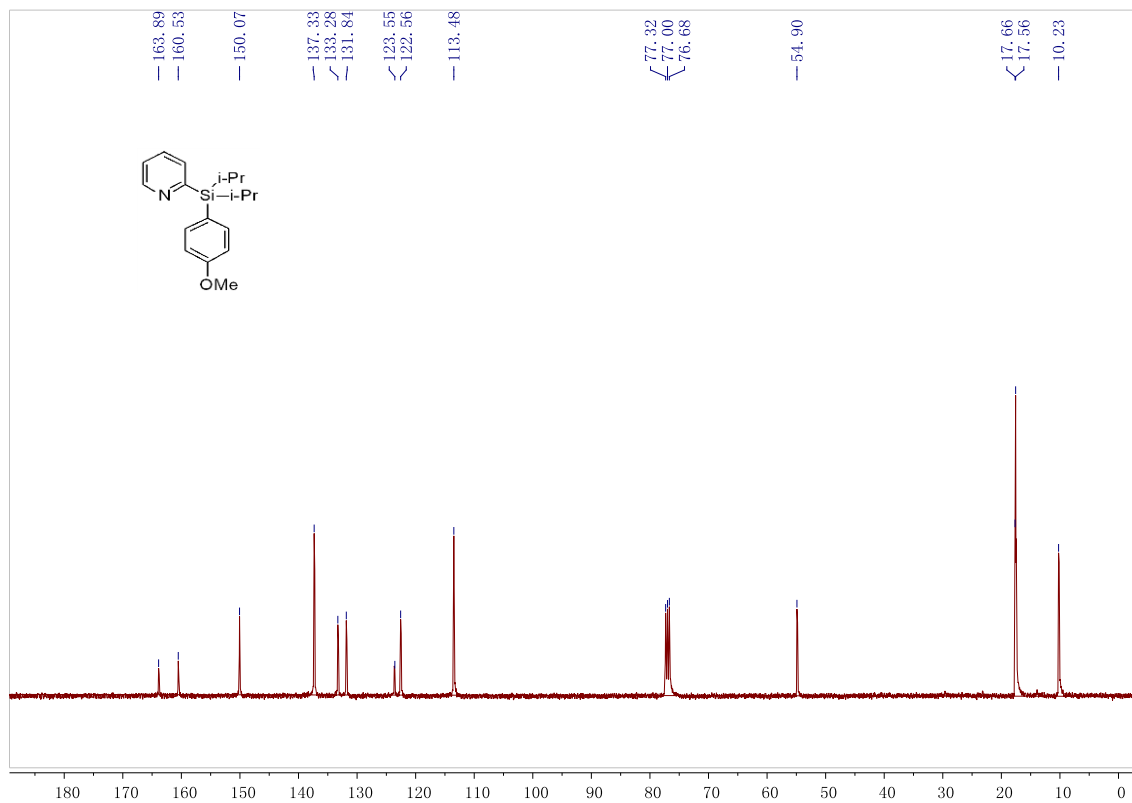


## 2-(diisopropyl(4-methoxyphenyl)silyl)pyridine (1c)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

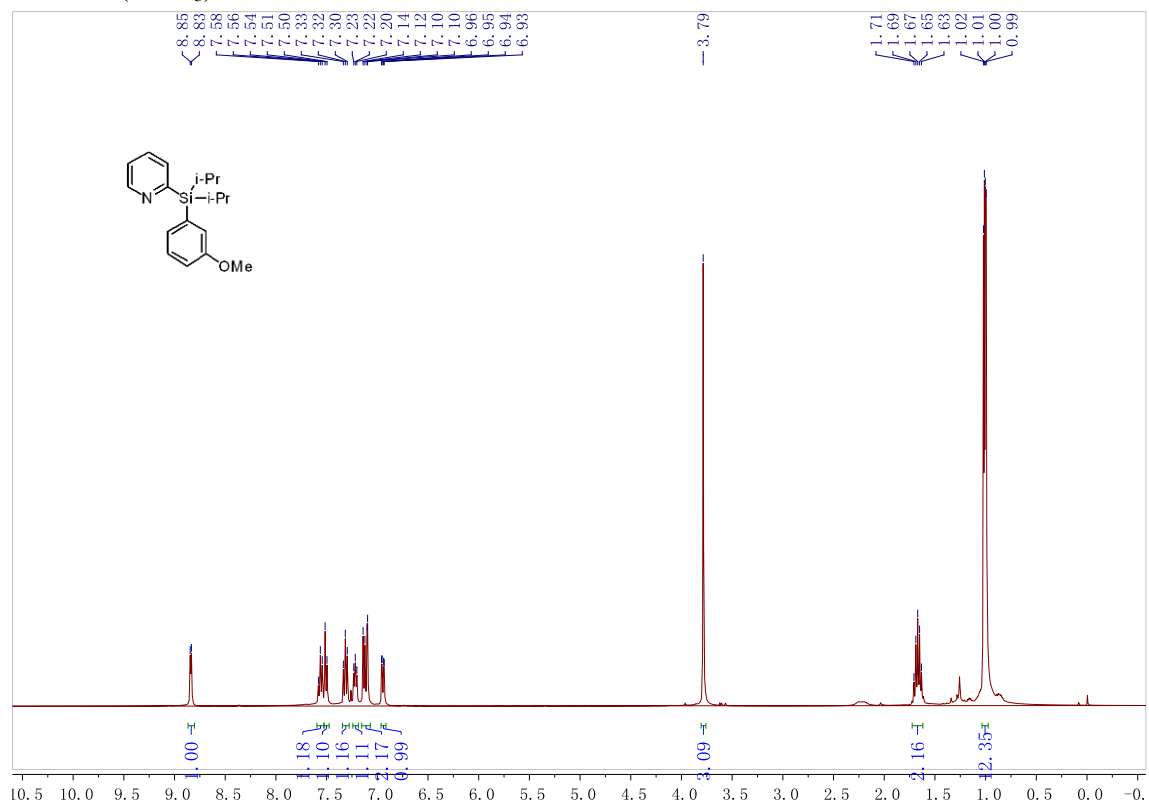


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

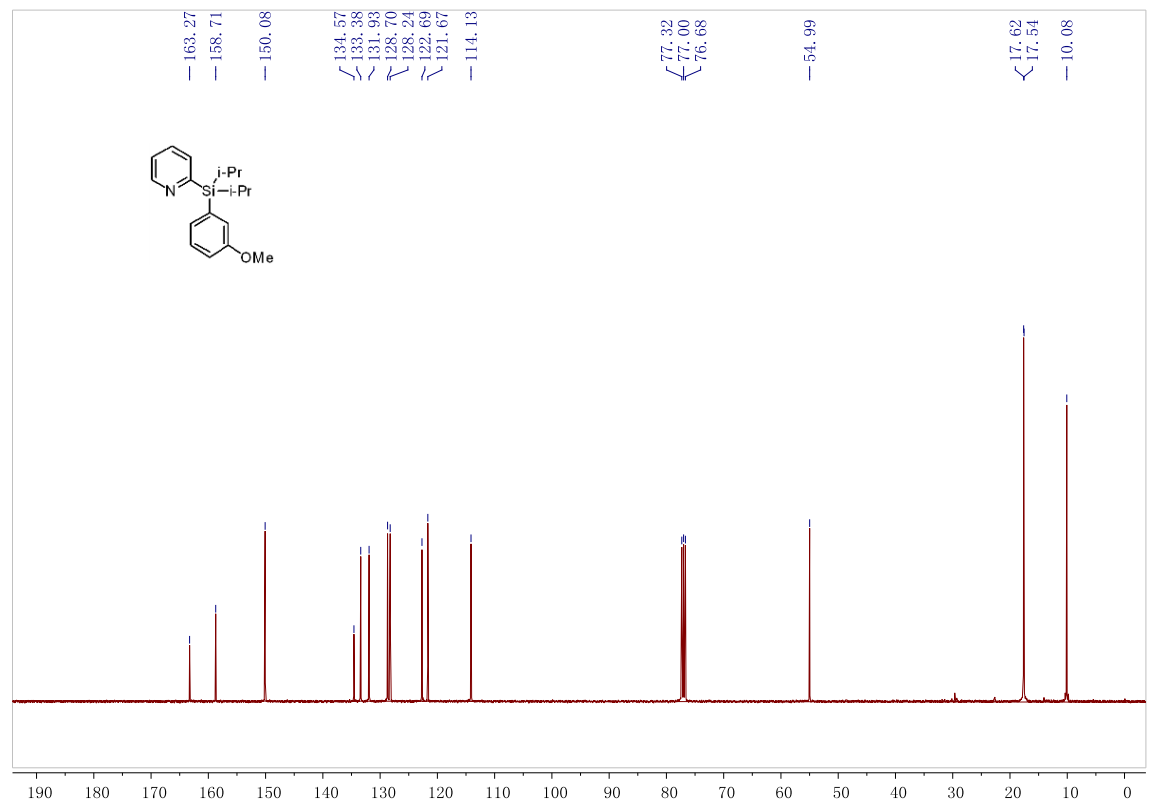


## 2-(diisopropyl(3-methoxyphenyl)silyl)pyridine (1d)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

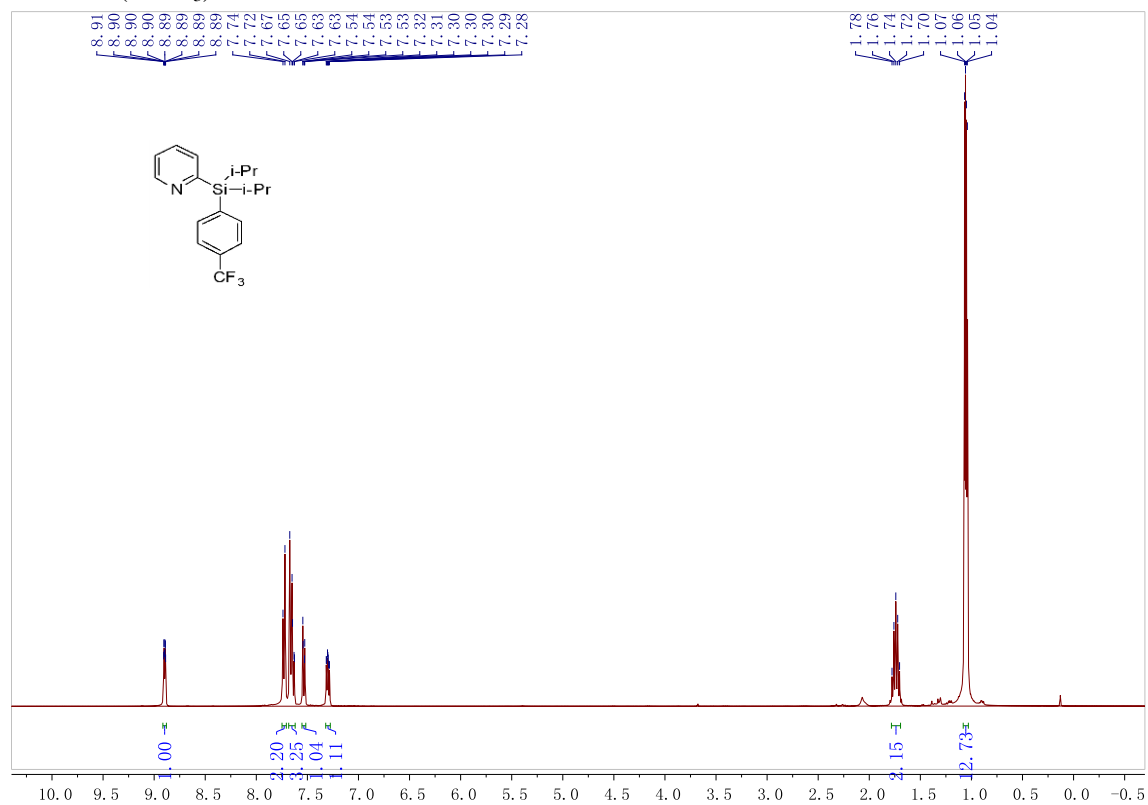


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

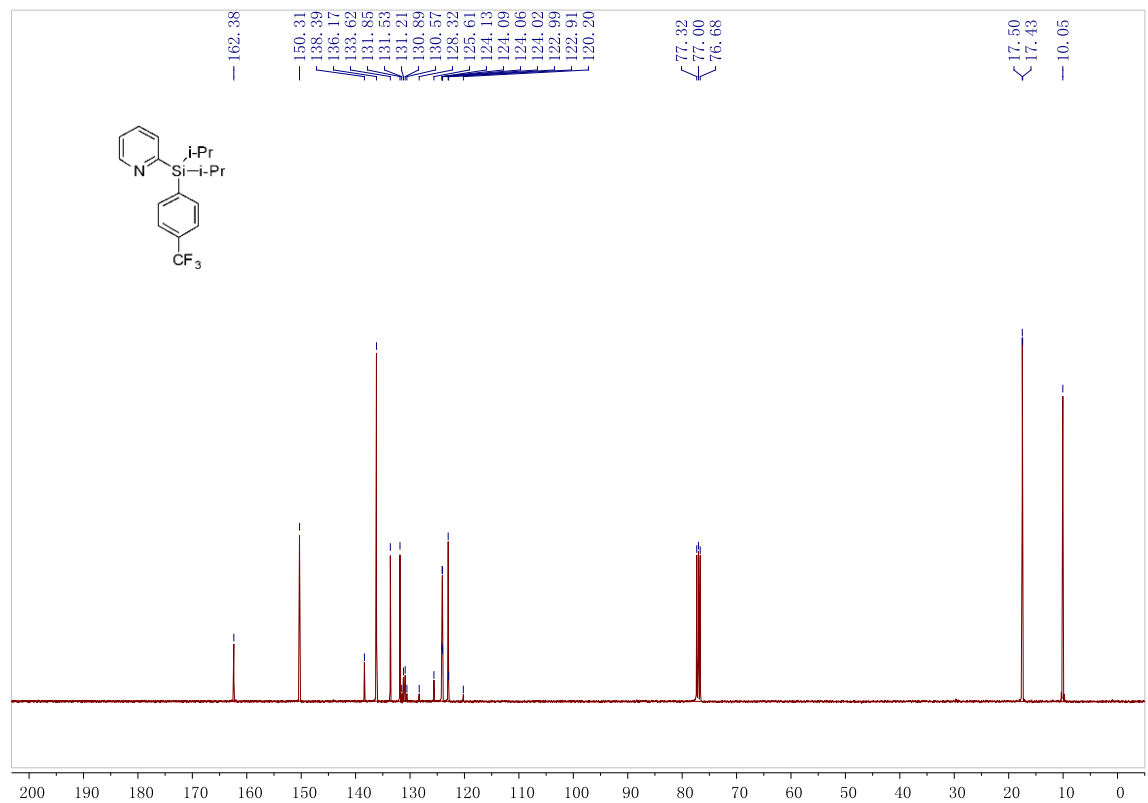


## 2-(diisopropyl(4-(trifluoromethyl)phenyl)silyl)pyridine (1e)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

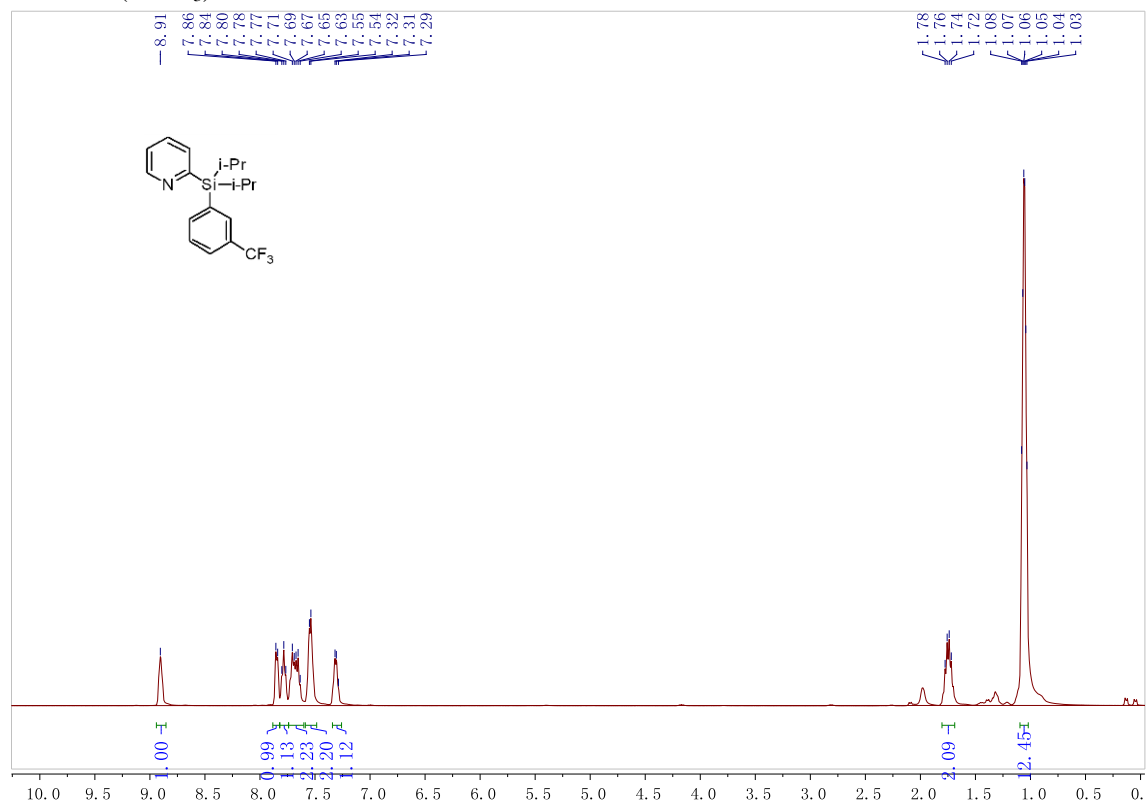


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

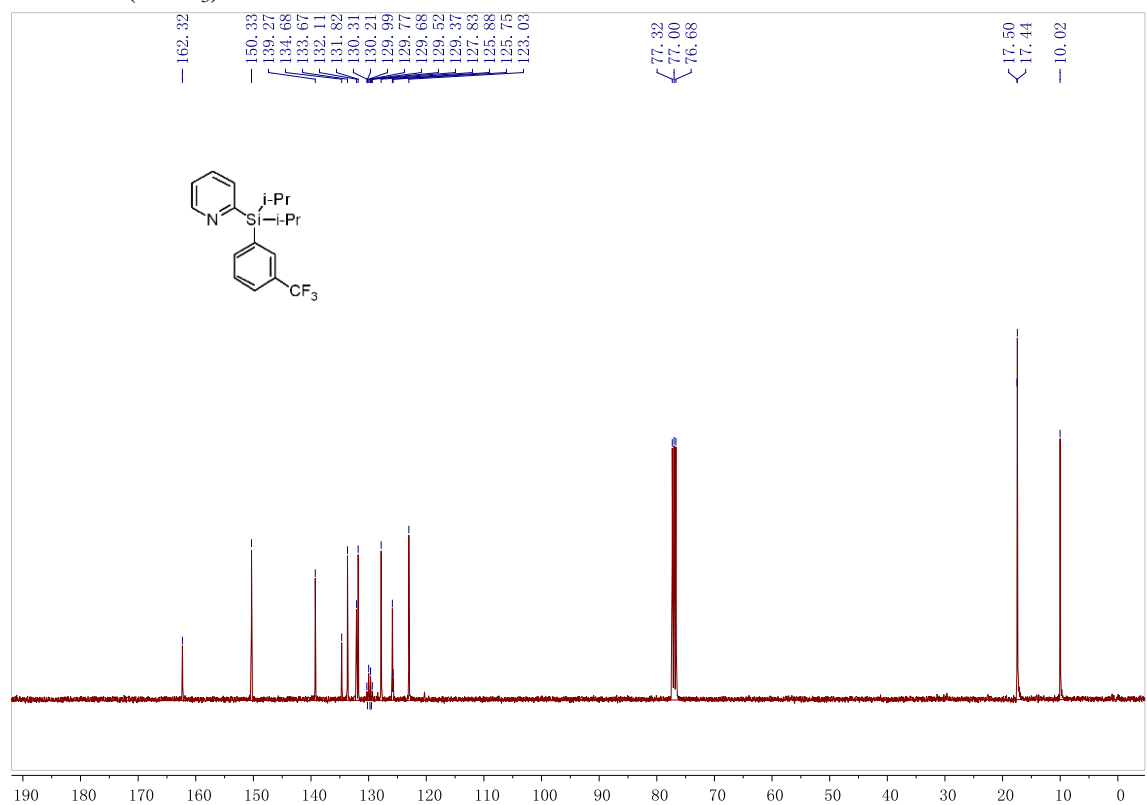


## 2-(diisopropyl(3-(trifluoromethyl)phenyl)silyl)pyridine (1f)

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )

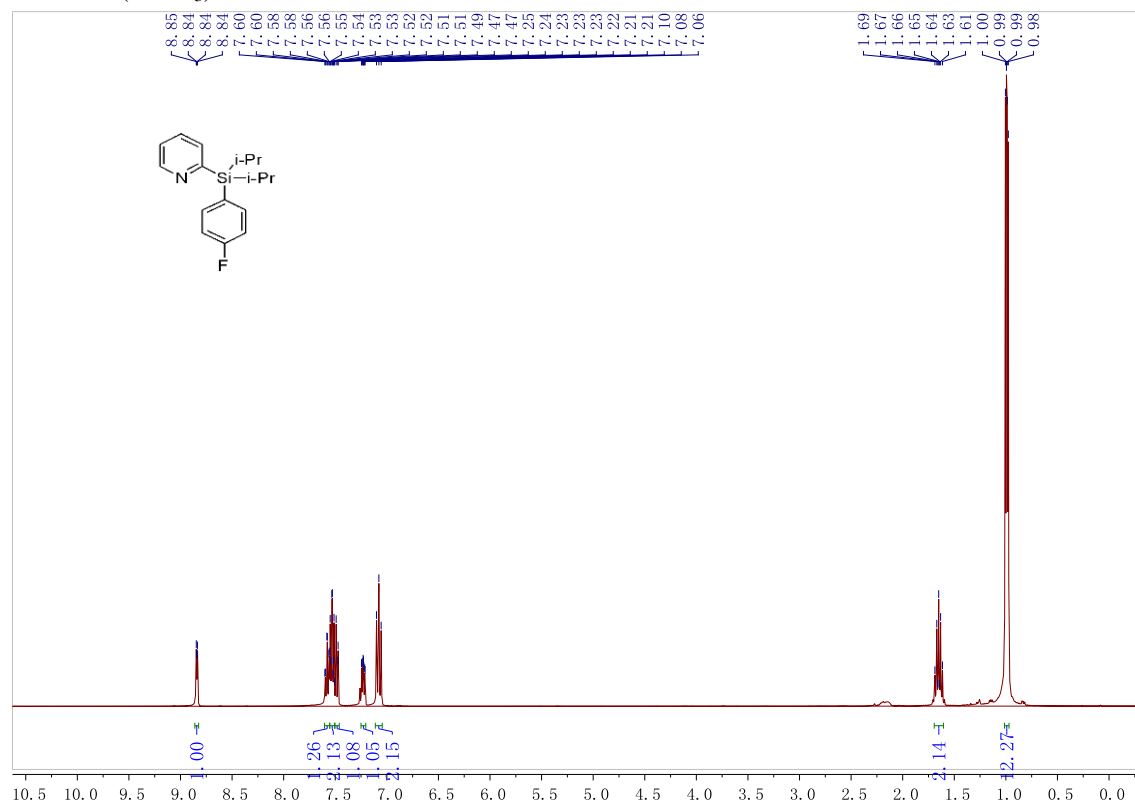


$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )

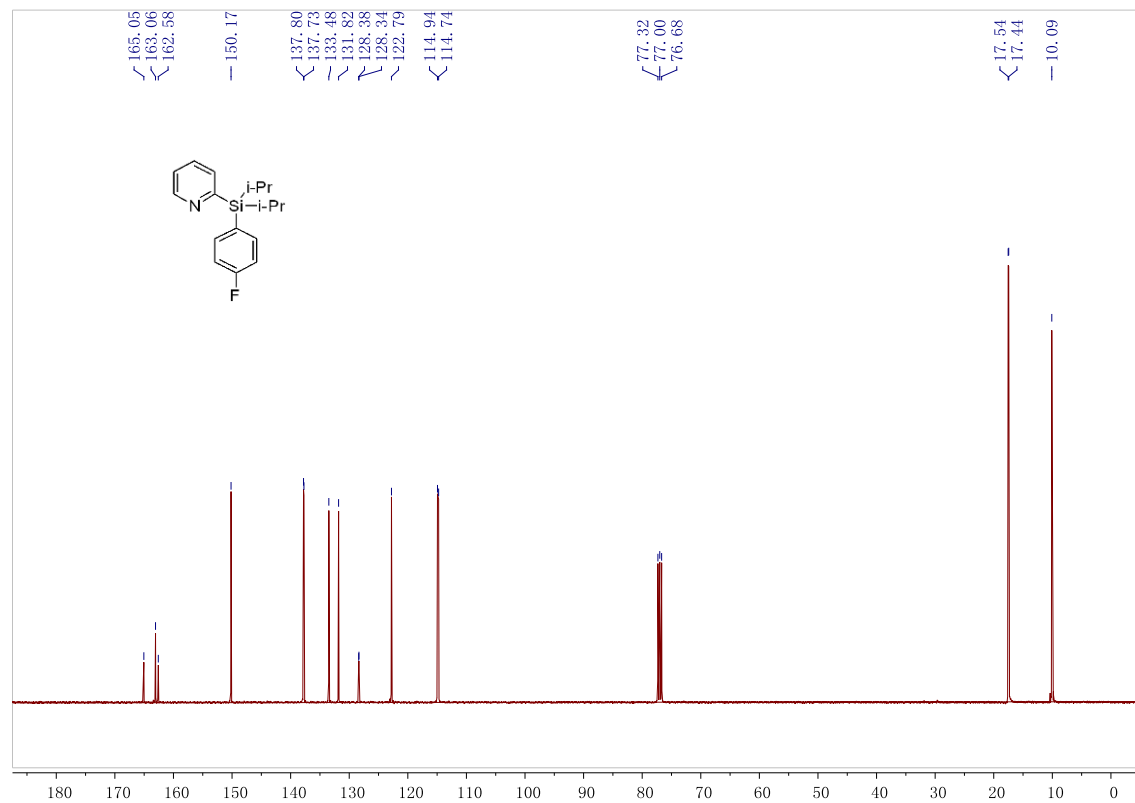


## 2-((4-fluorophenyl)diisopropylsilyl)pyridine (1g)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

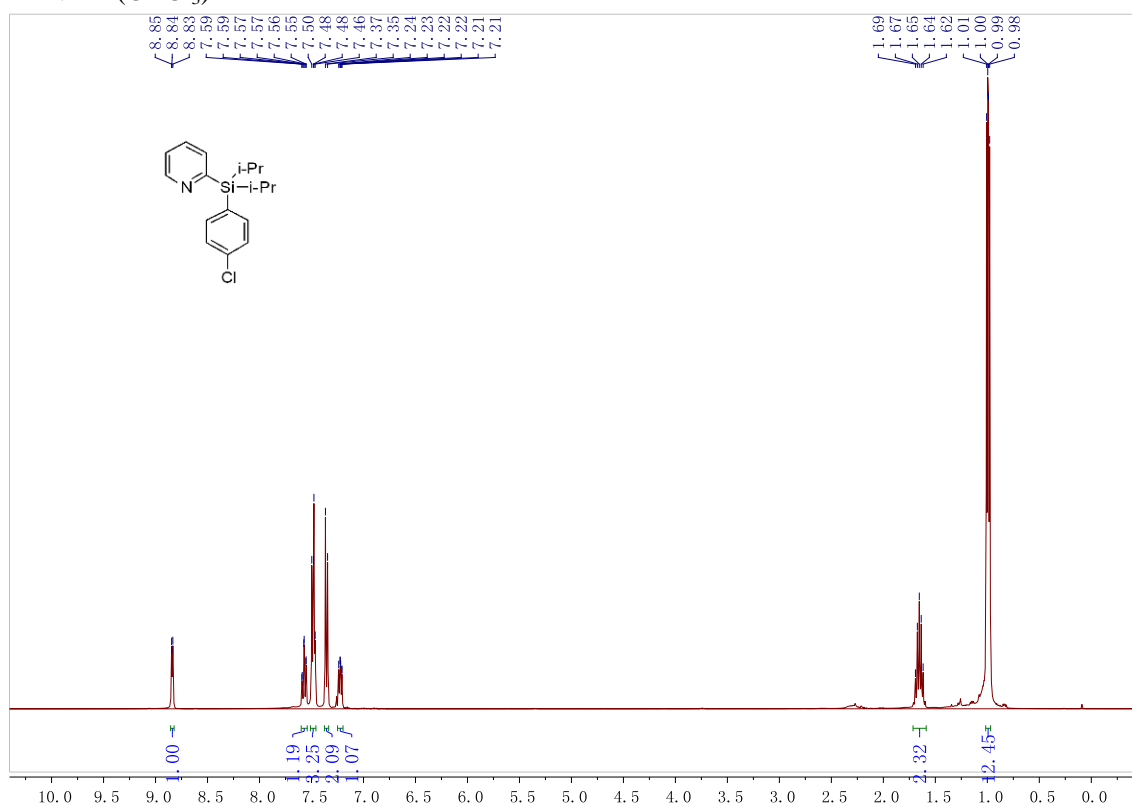


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

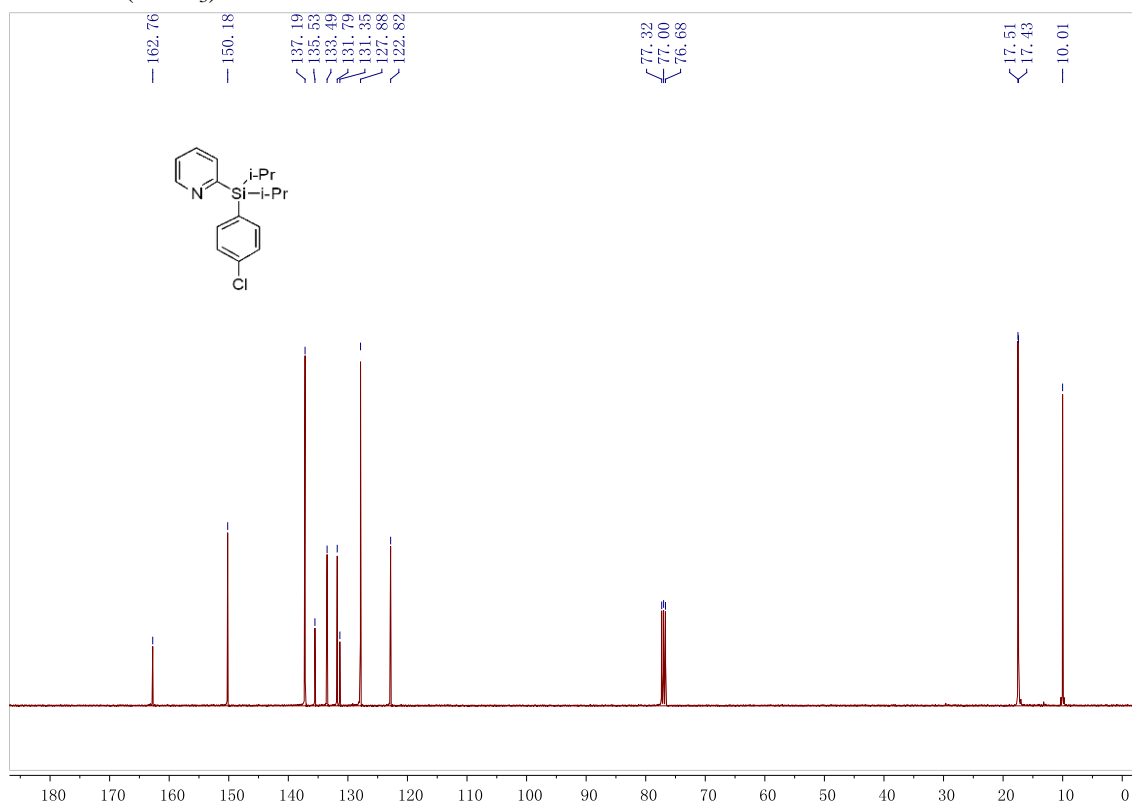


## 2-((4-chlorophenyl)diisopropylsilyl)pyridine (1h)

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )

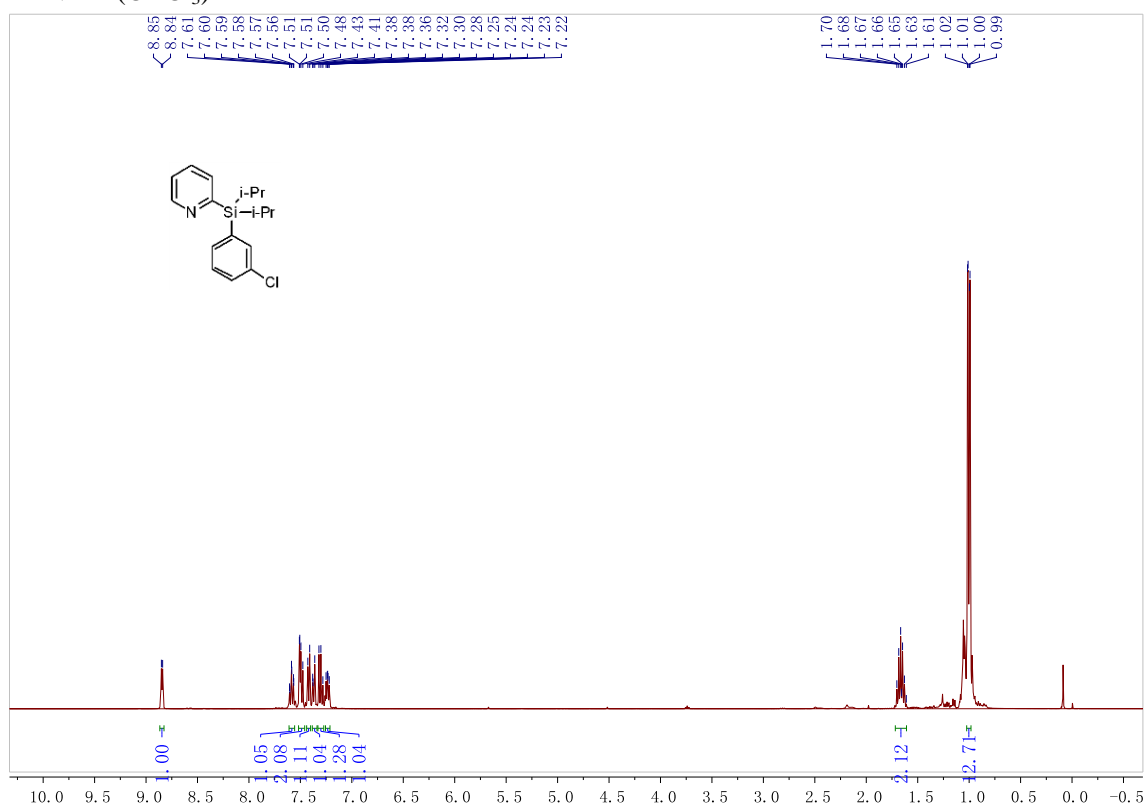


$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )

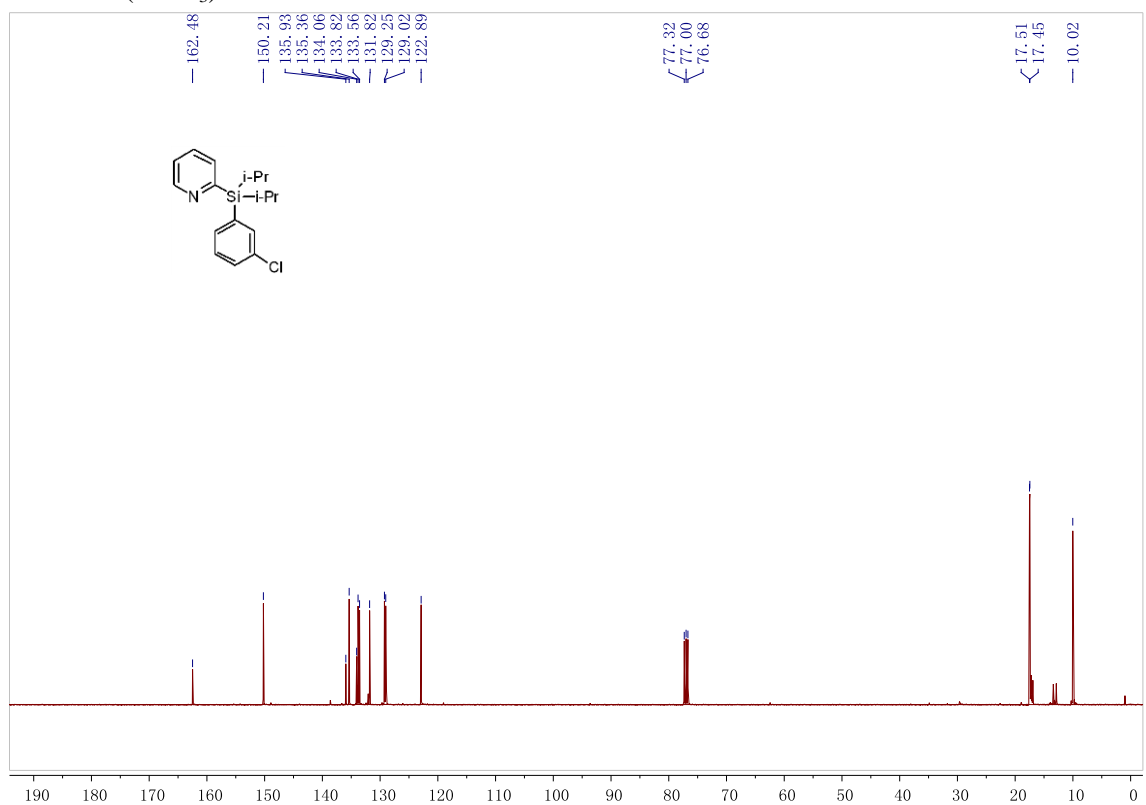


## 2-((3-chlorophenyl)diisopropylsilyl)pyridine (1i)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )



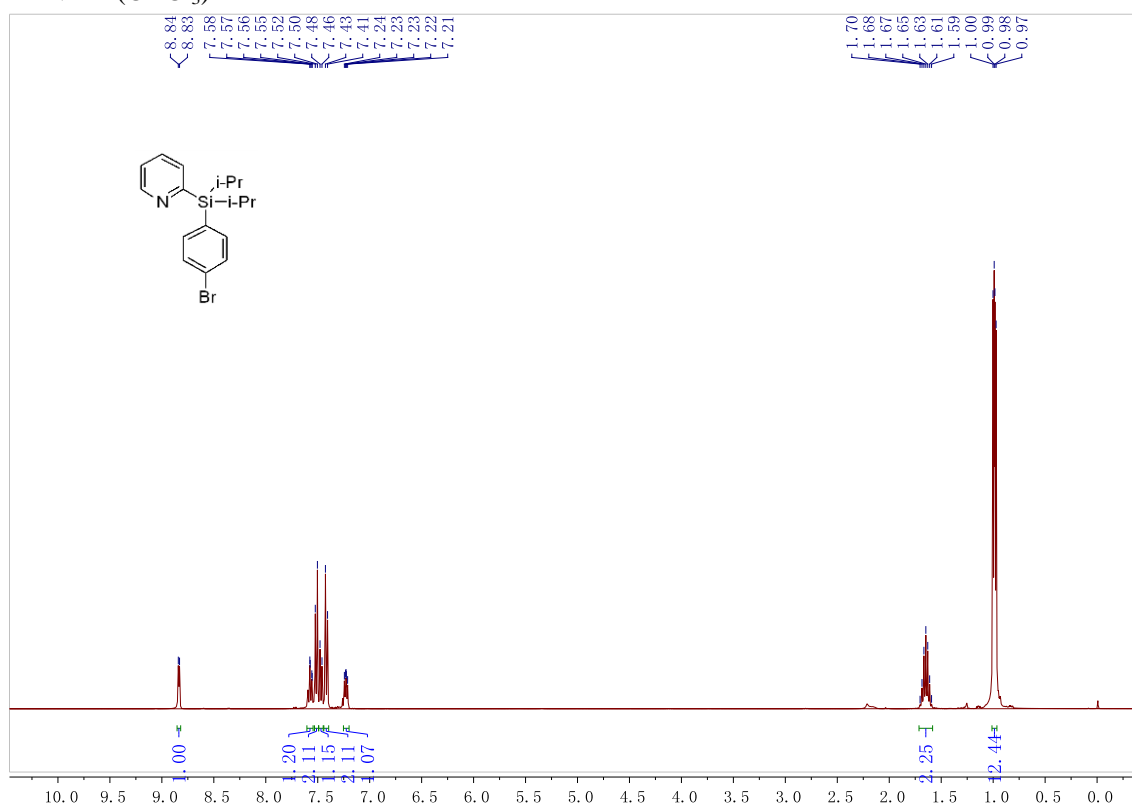
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )



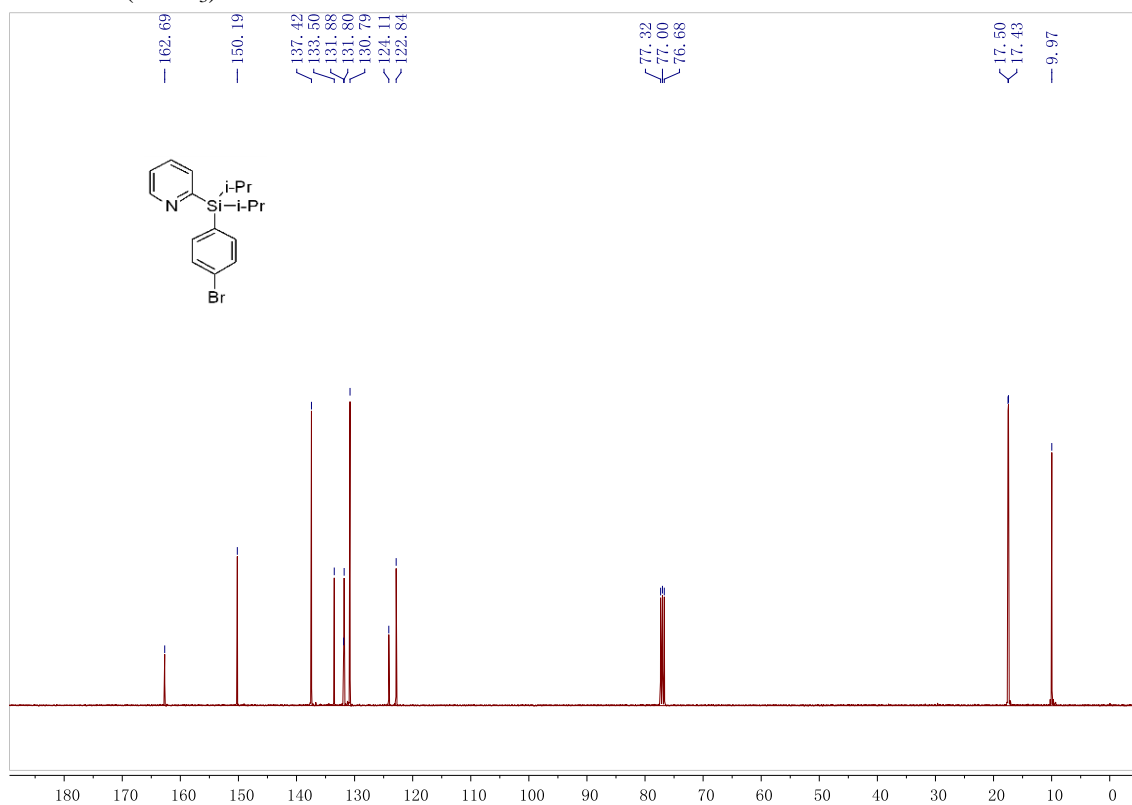


## 2-((4-bromophenyl)diisopropylsilyl)pyridine (1j)

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )

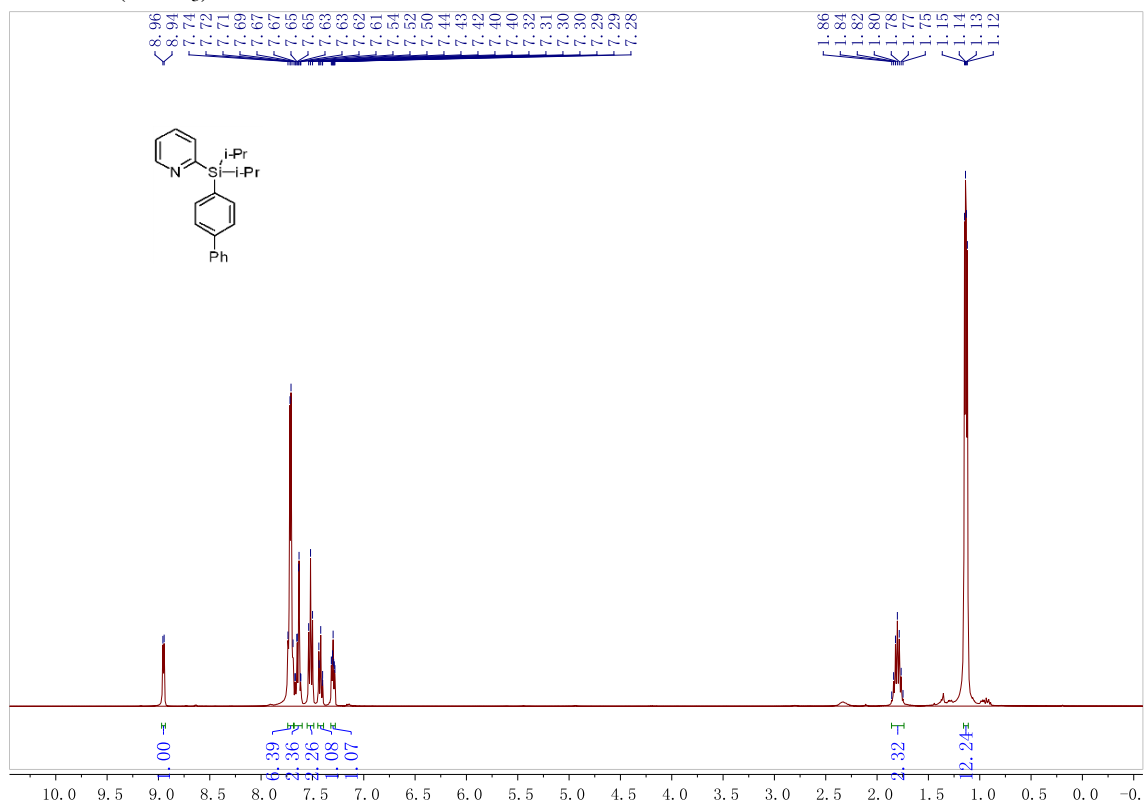


$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )

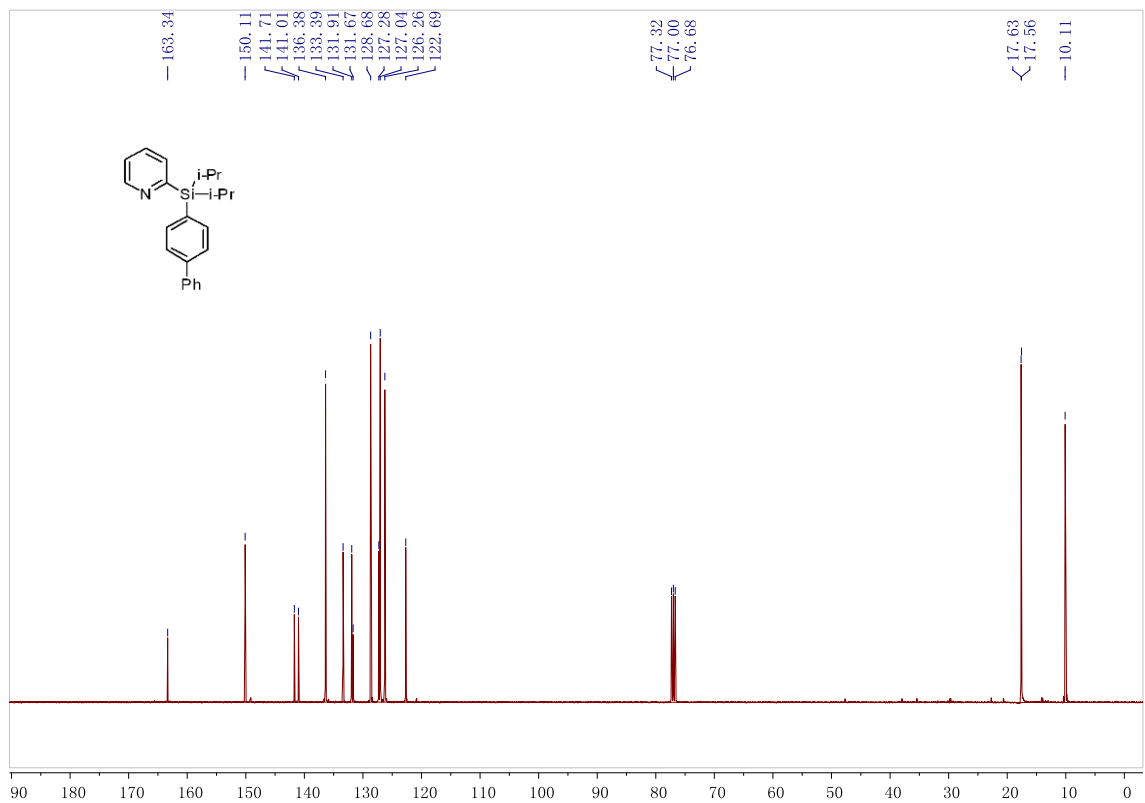


## 2-([1,1'-biphenyl]-4-yl)diisopropylsilylpyridine (1k)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

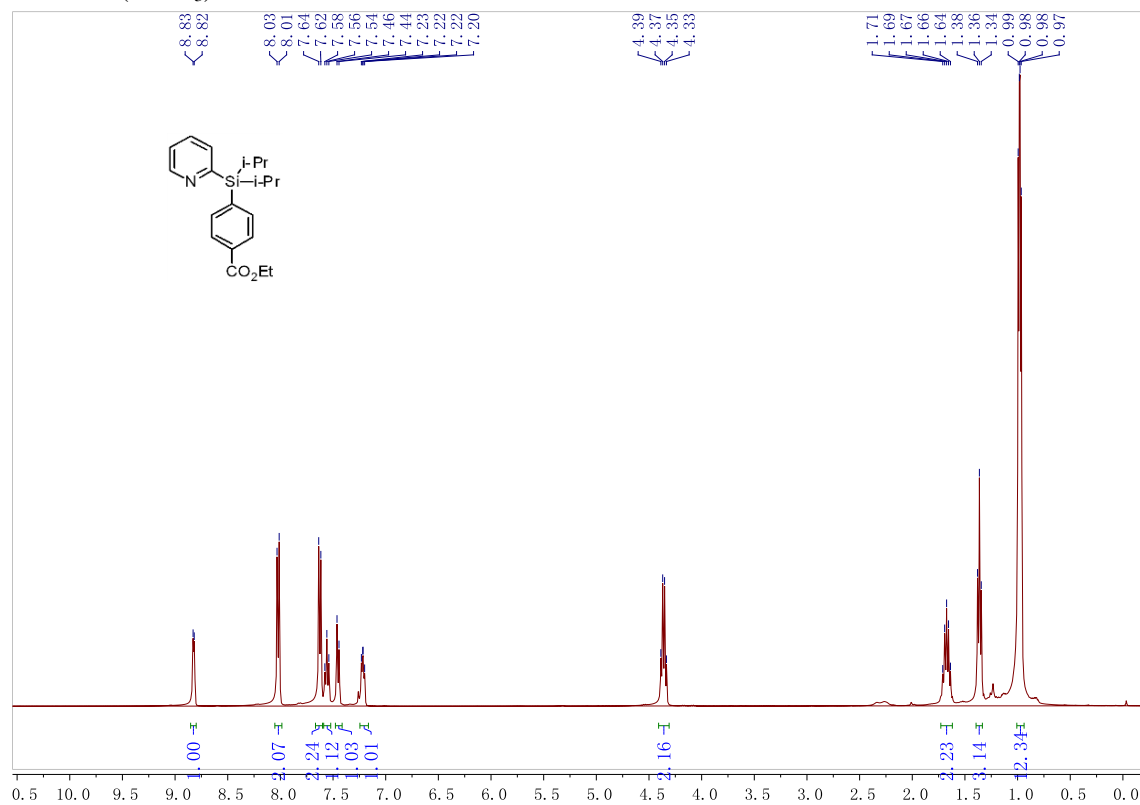


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

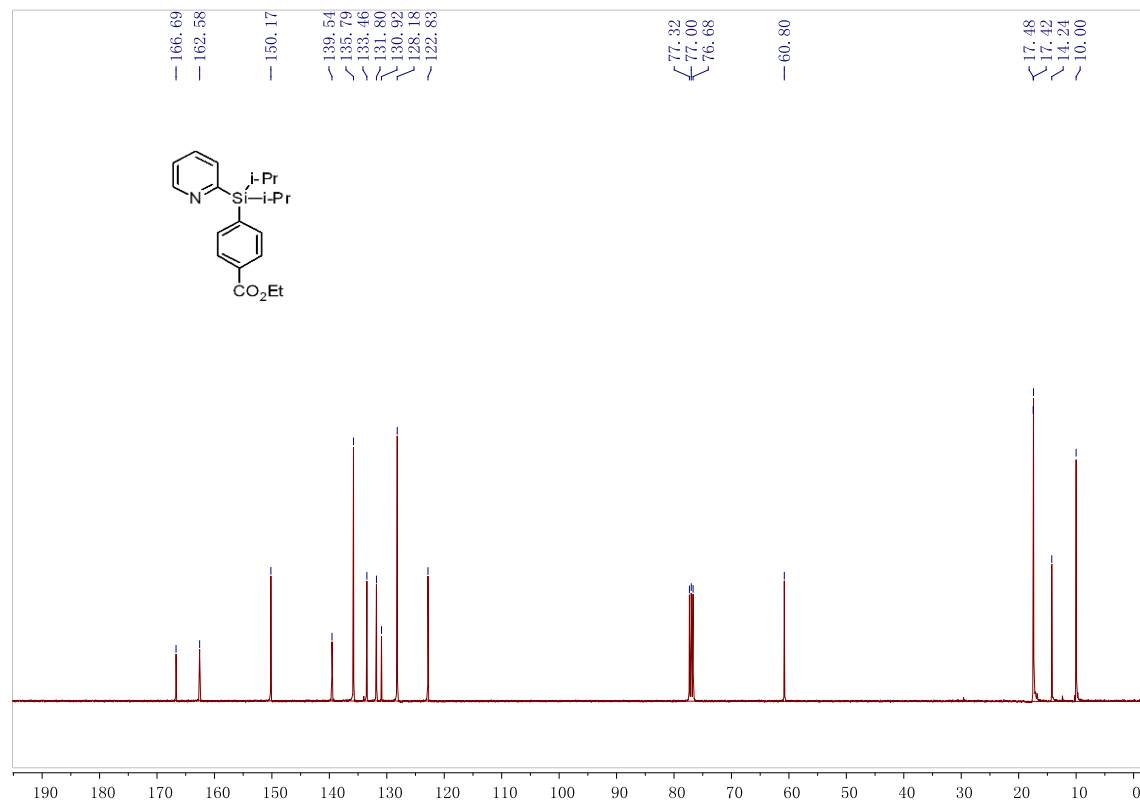


**ethyl 4-(diisopropyl(pyridin-2-yl)silyl)benzoate (11)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

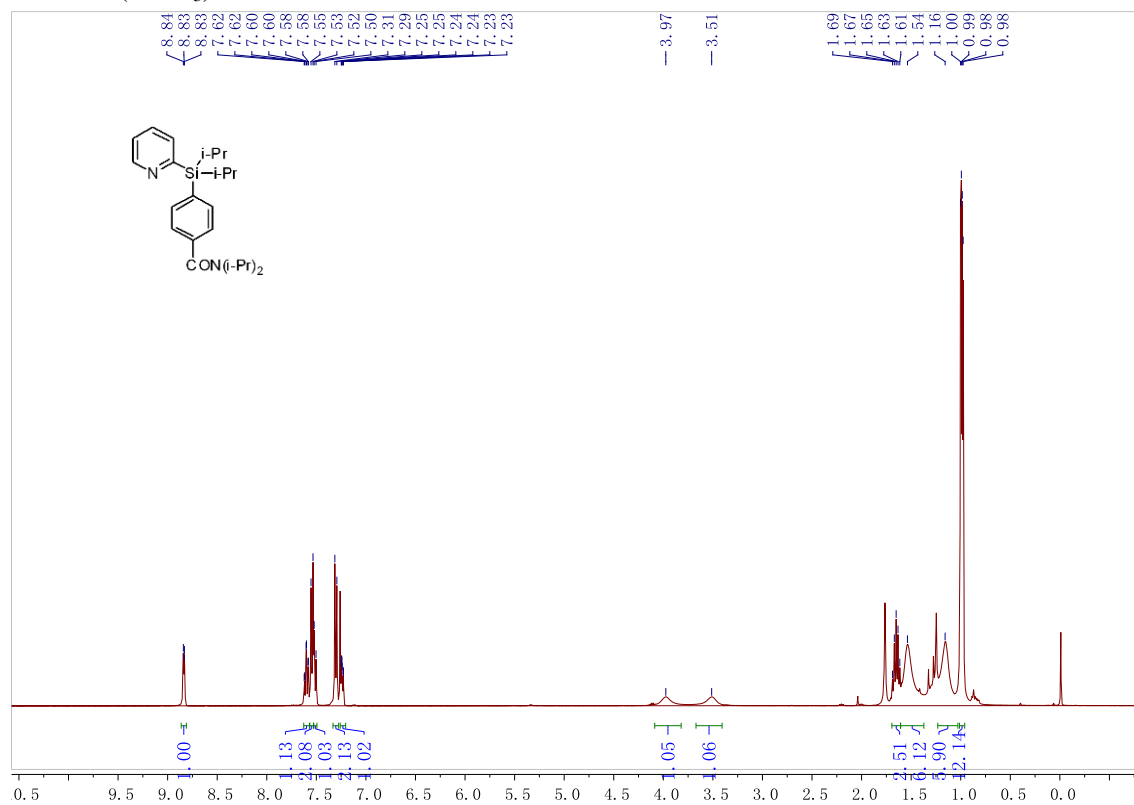


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

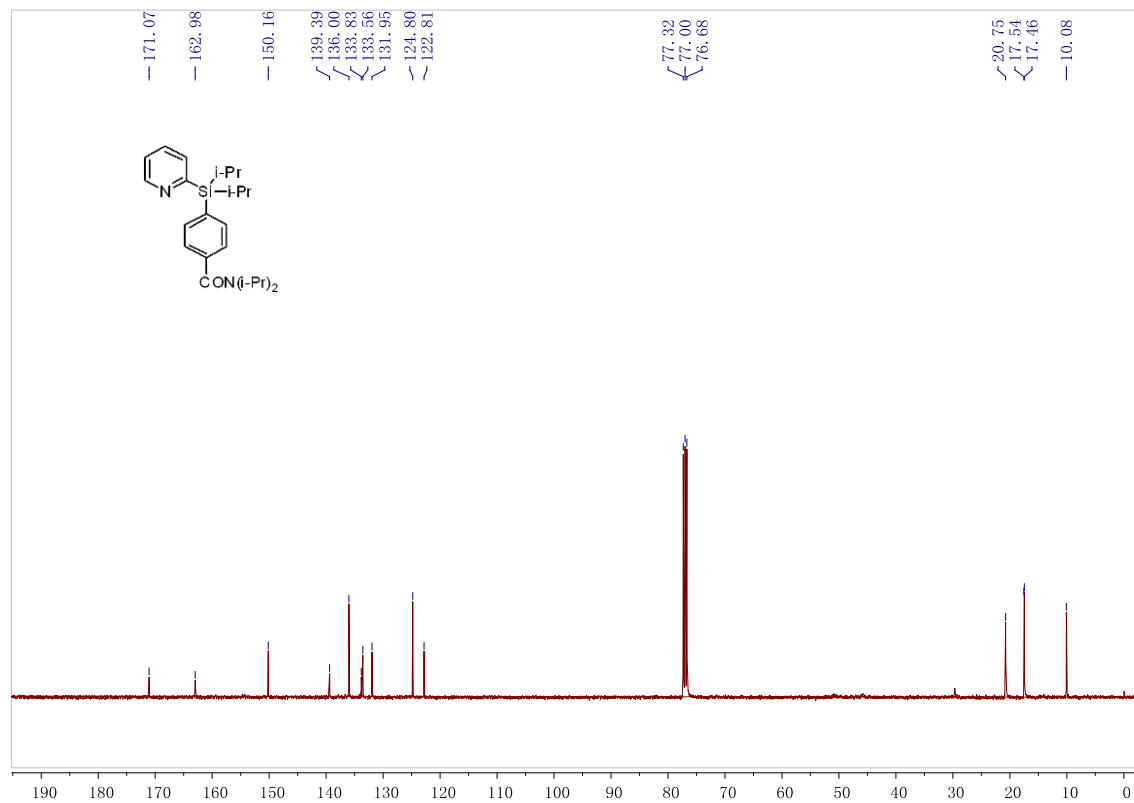


### 4-(diisopropyl(pyridin-2-yl)silyl)-*N,N*-diisopropylbenzamide (1m)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

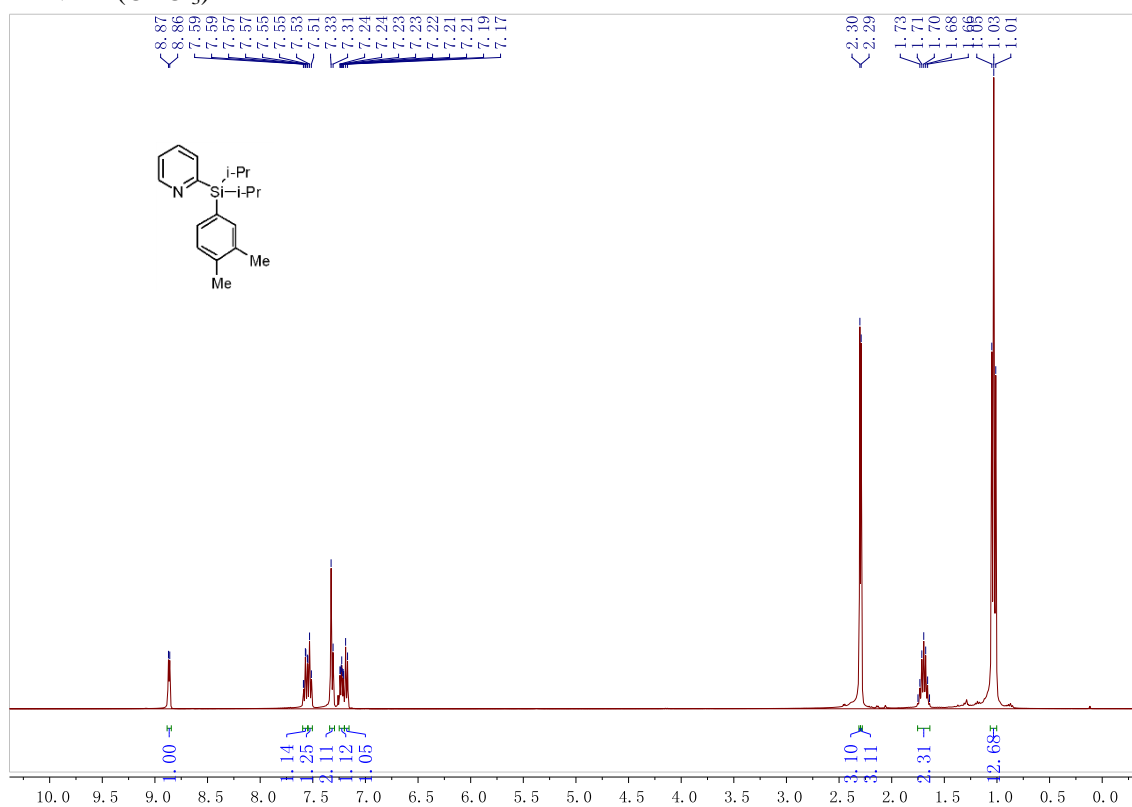


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

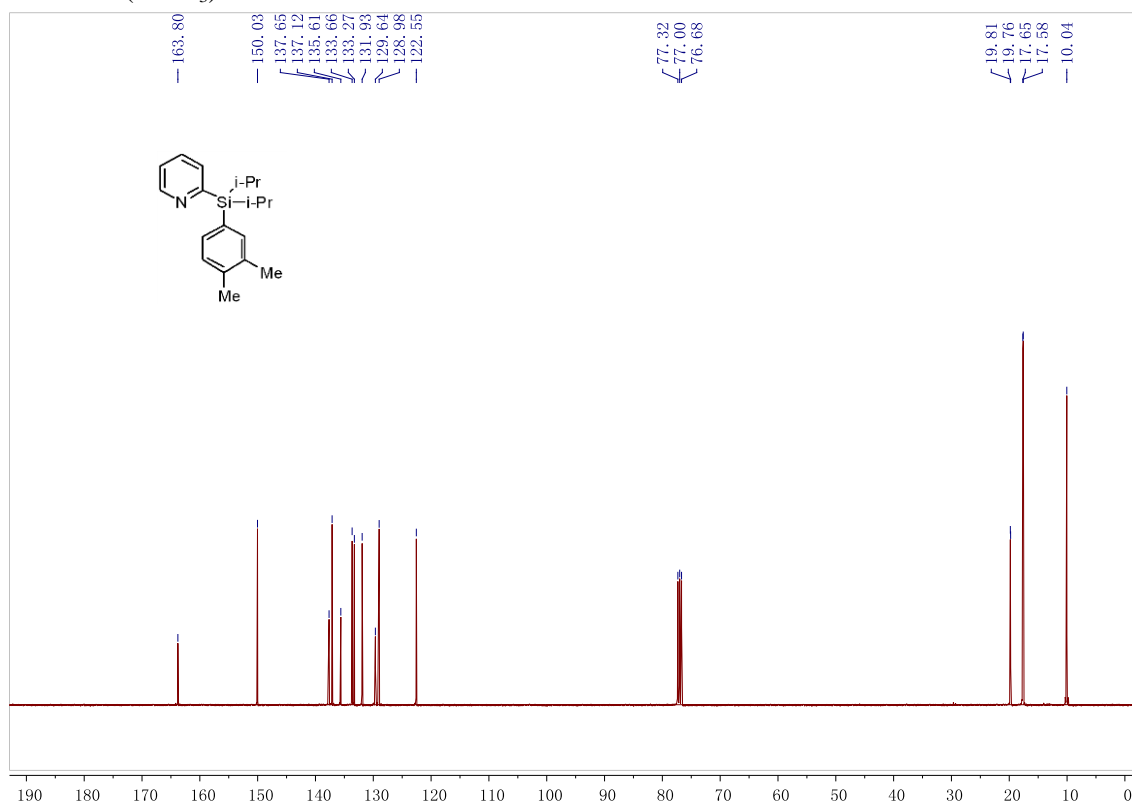


## 2-((3,4-dimethylphenyl)diisopropylsilyl)pyridine (1n)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

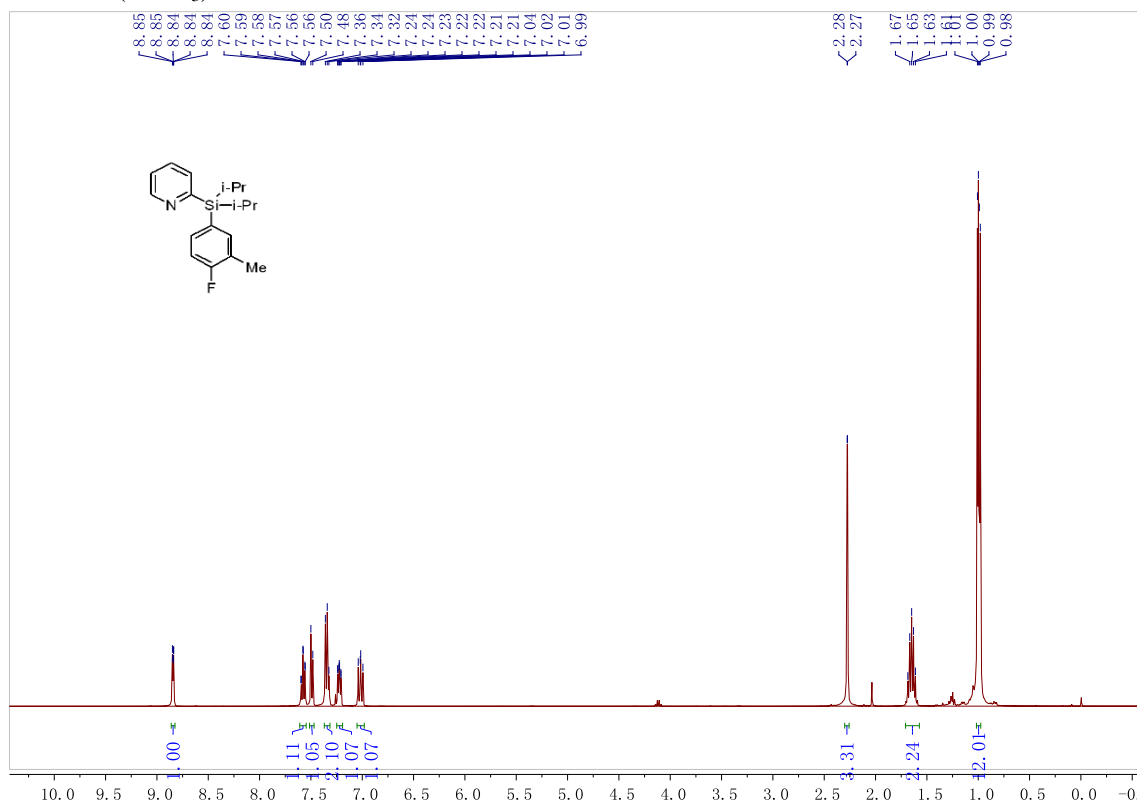


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

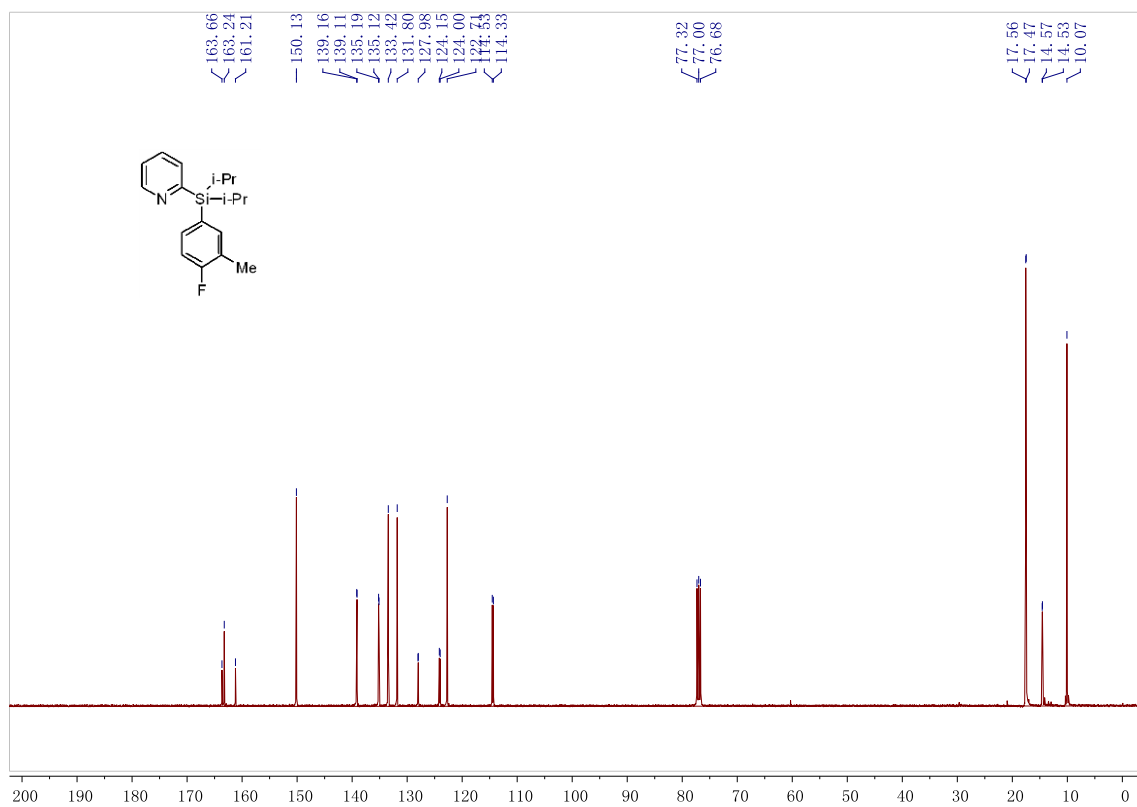


## 2-((4-fluoro-3-methylphenyl)diisopropylsilyl)pyridine (1o)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

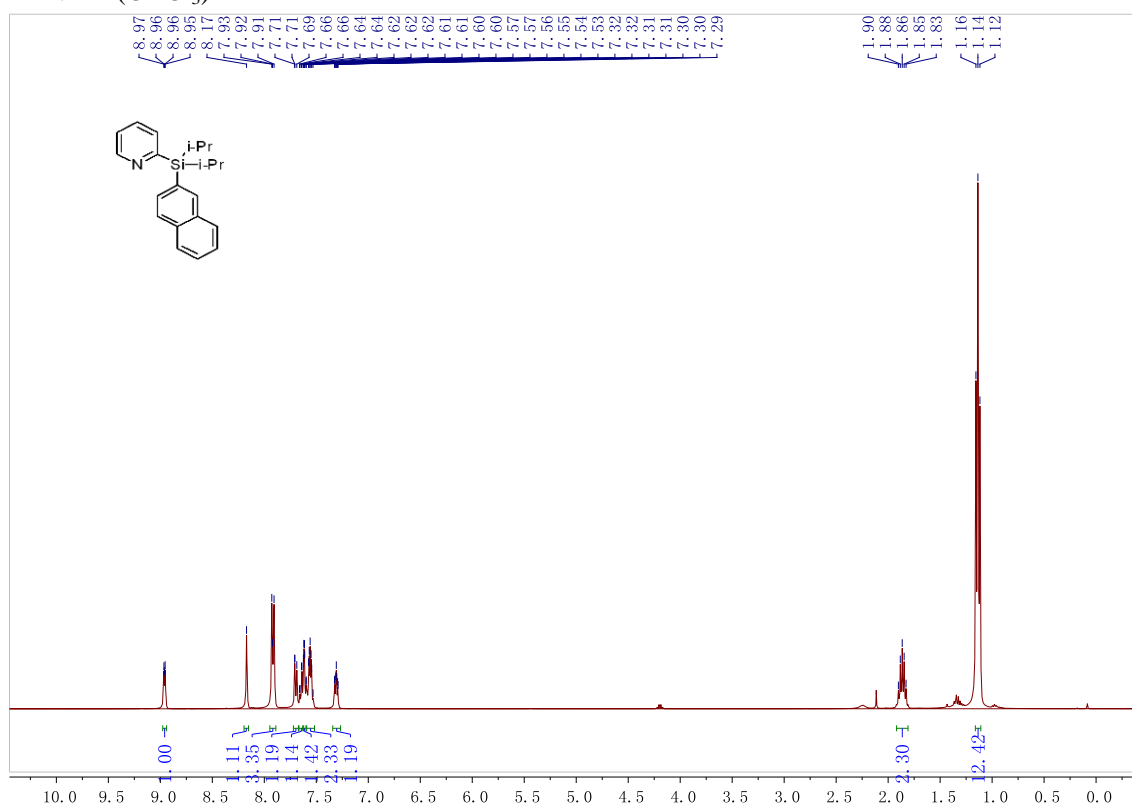


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

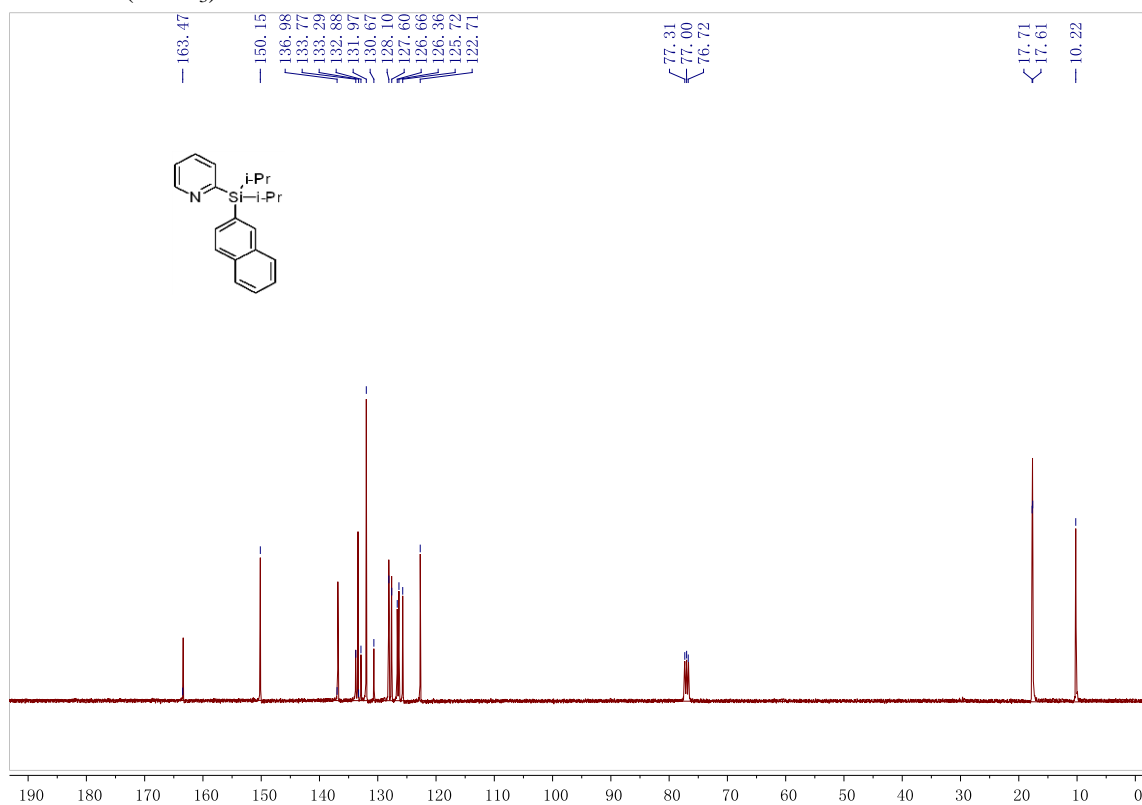


## 2-(diisopropyl(naphthalen-2-yl)silyl)pyridine (1p)

$^1\text{H NMR}$  ( $\text{CDCl}_3$ )

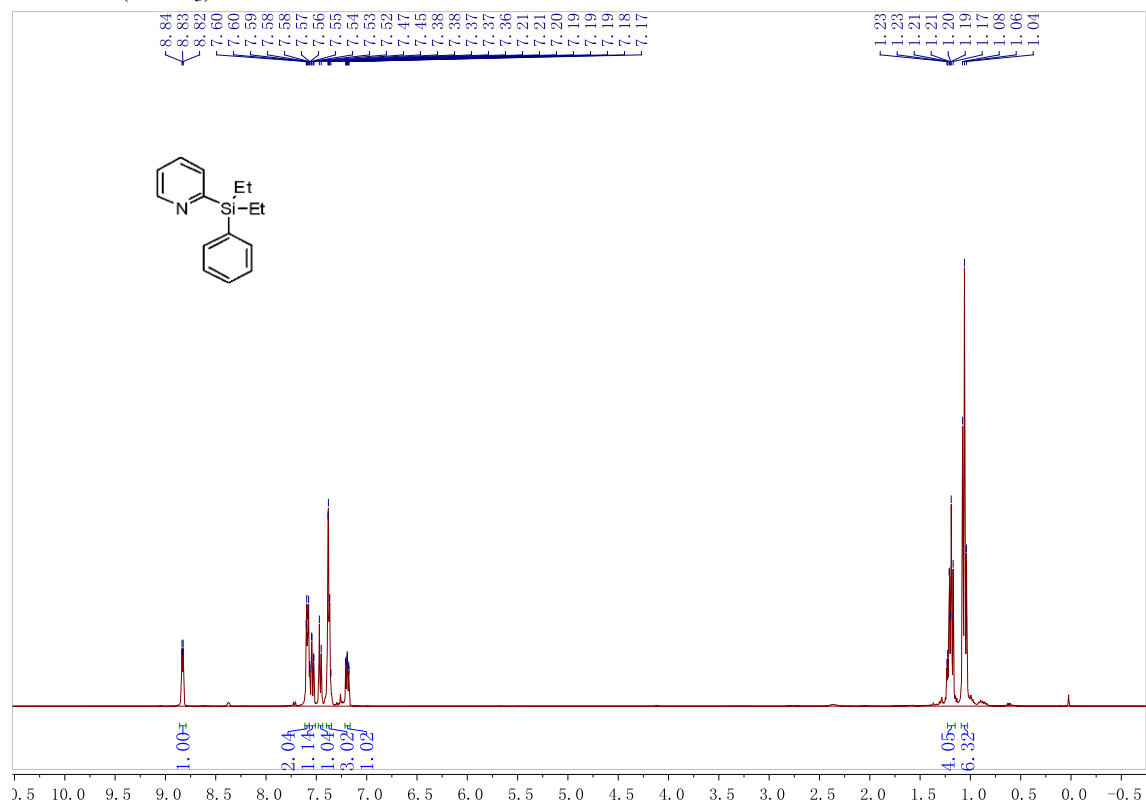


$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )

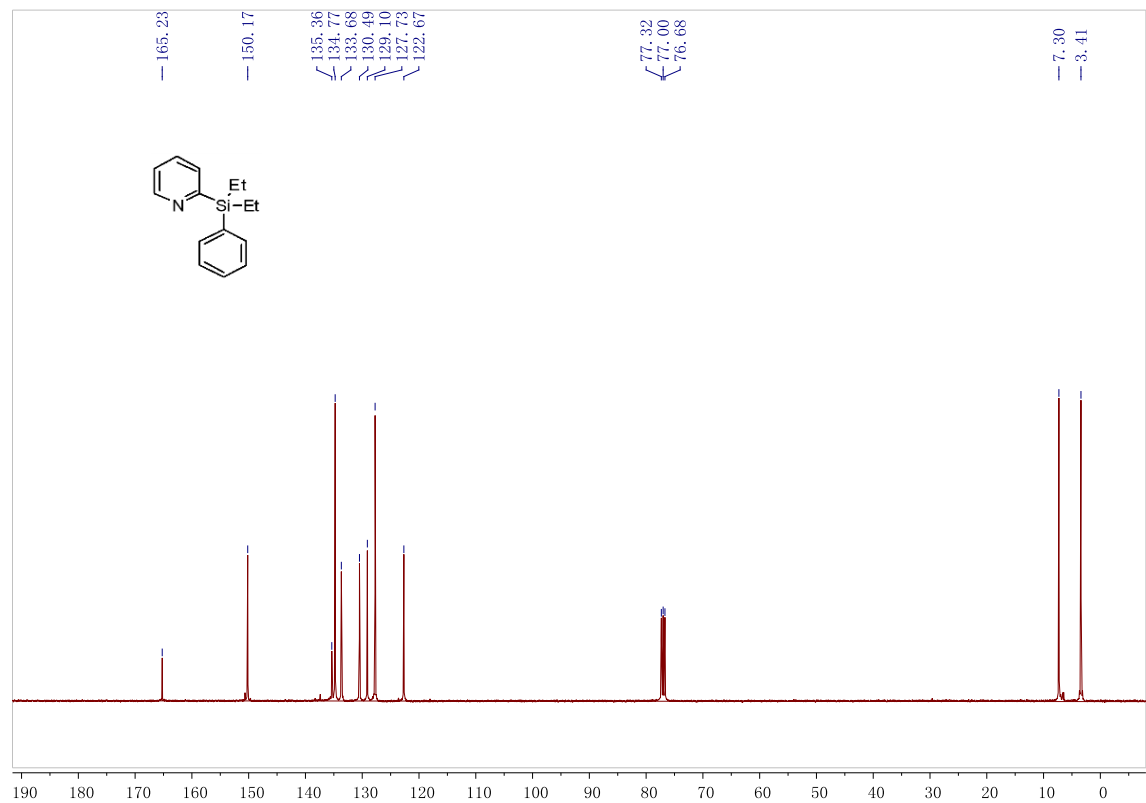


## 2-(diethyl(phenyl)silyl)pyridine (4a)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )



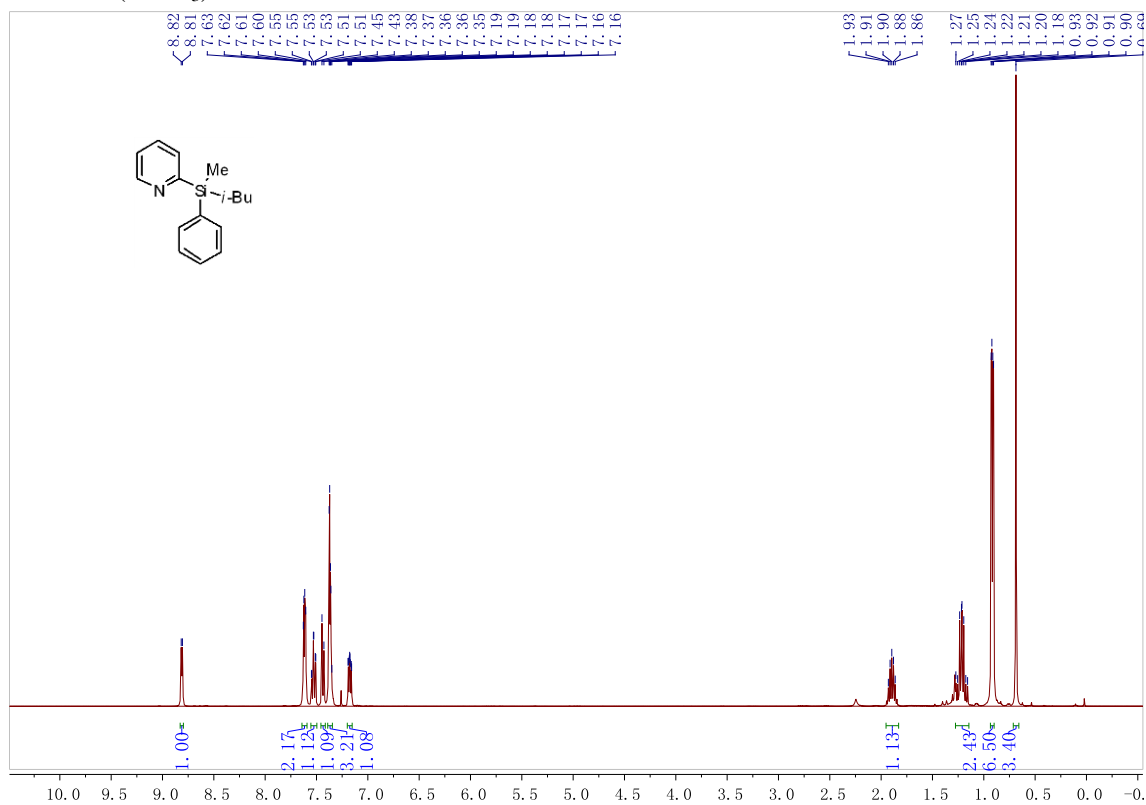
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )



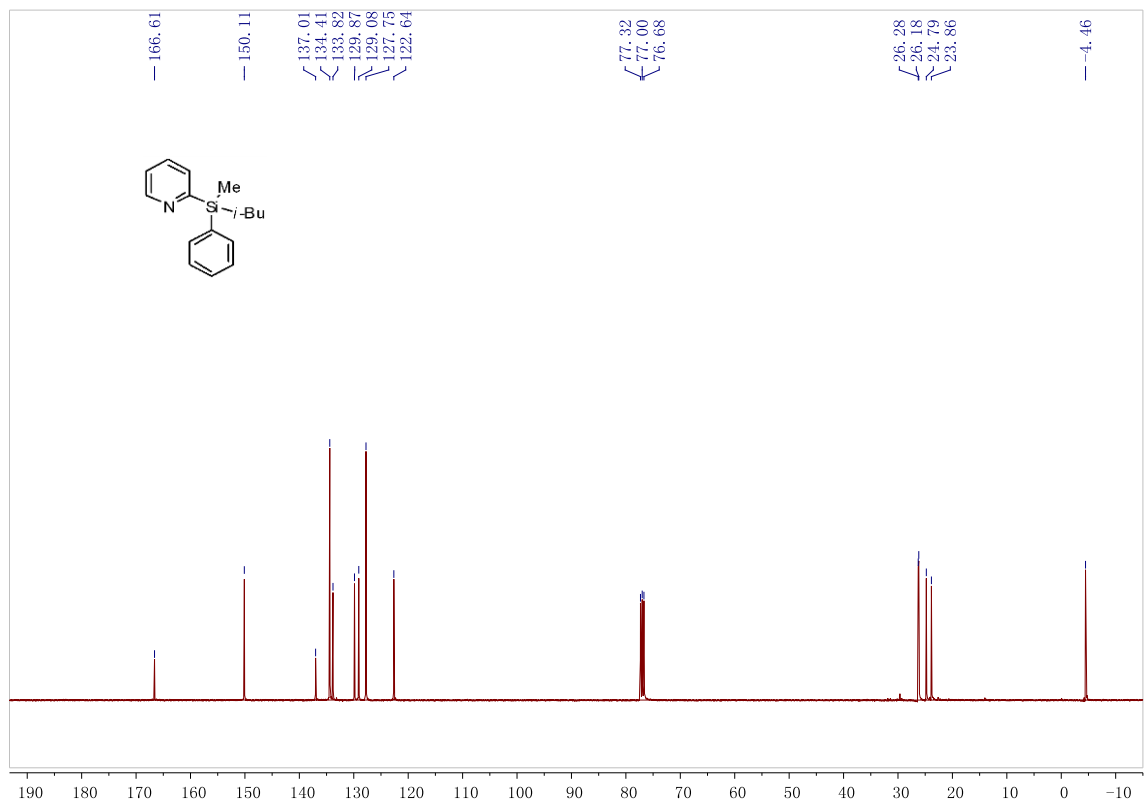


## 2-(isobutyl(methyl)(phenyl)silyl)pyridine (4b)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

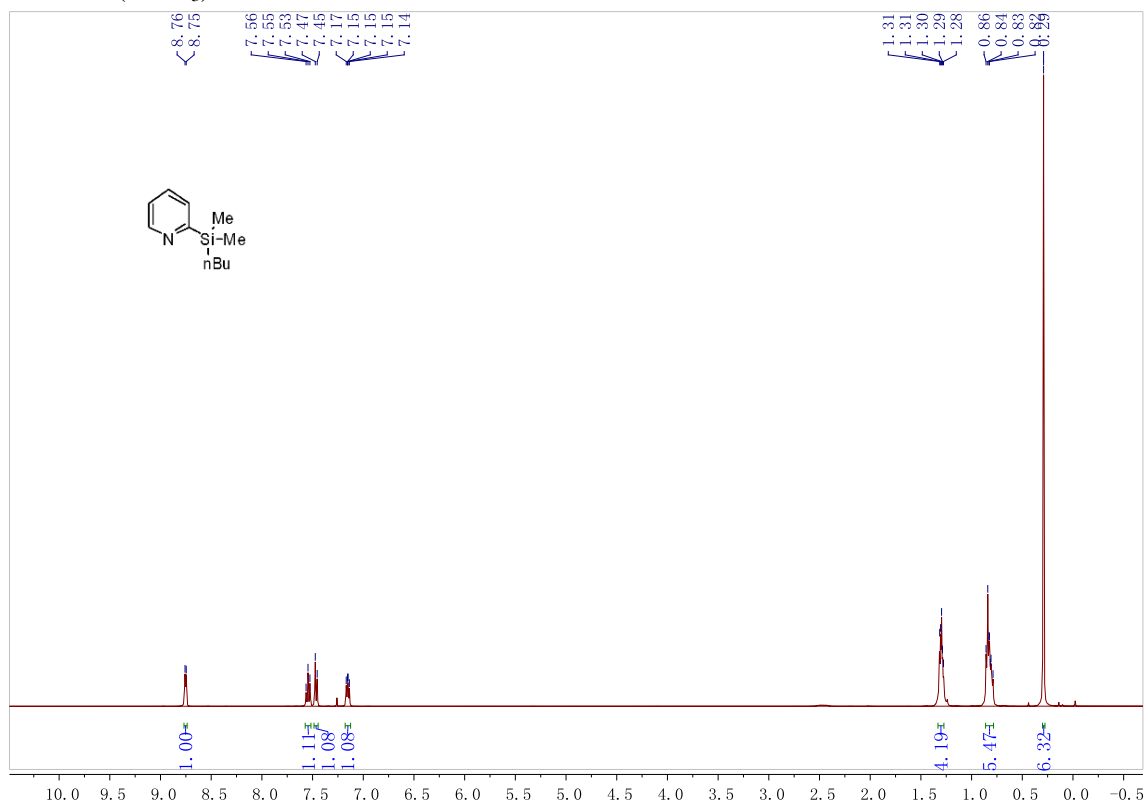


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

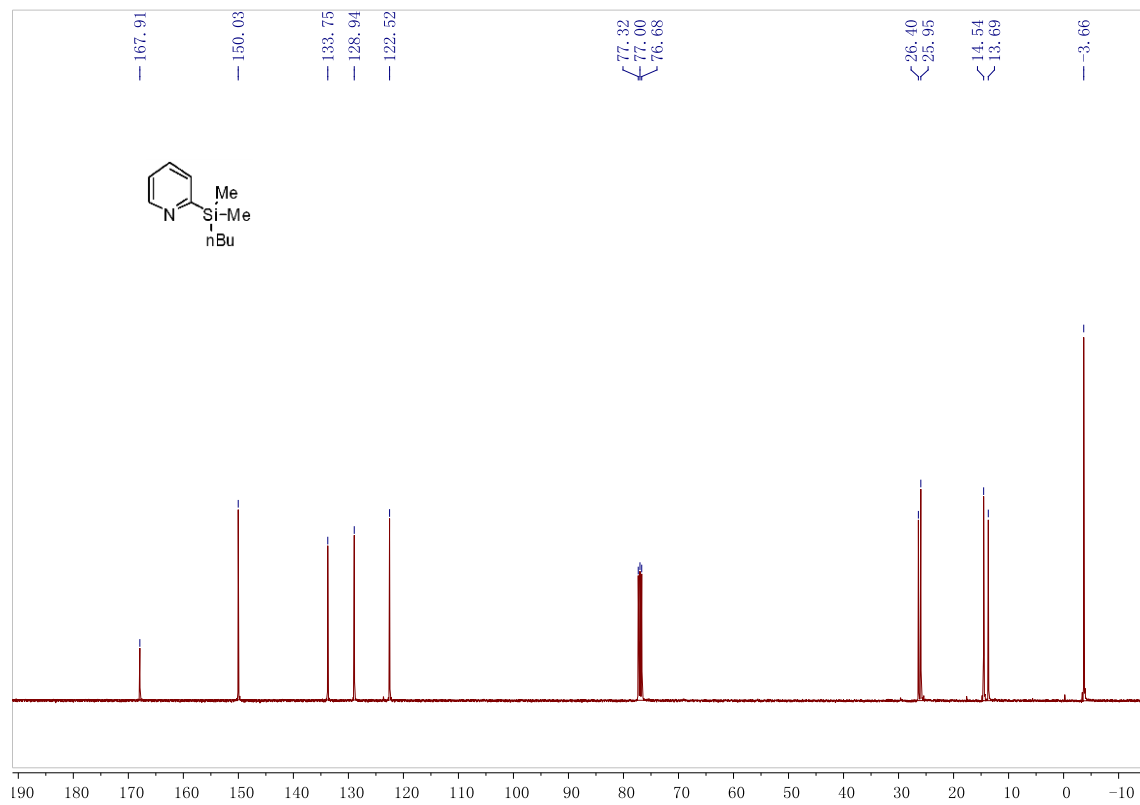


## 2-(butyldimethylsilyl)pyridine (6a)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

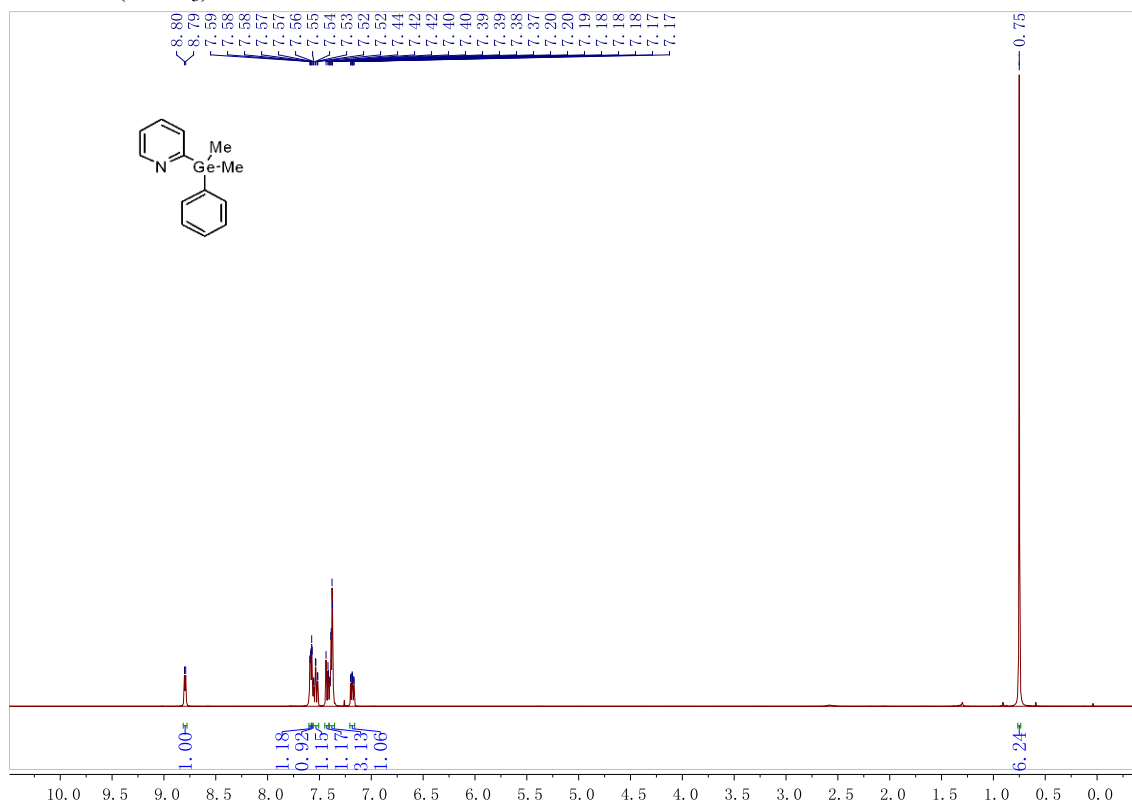


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

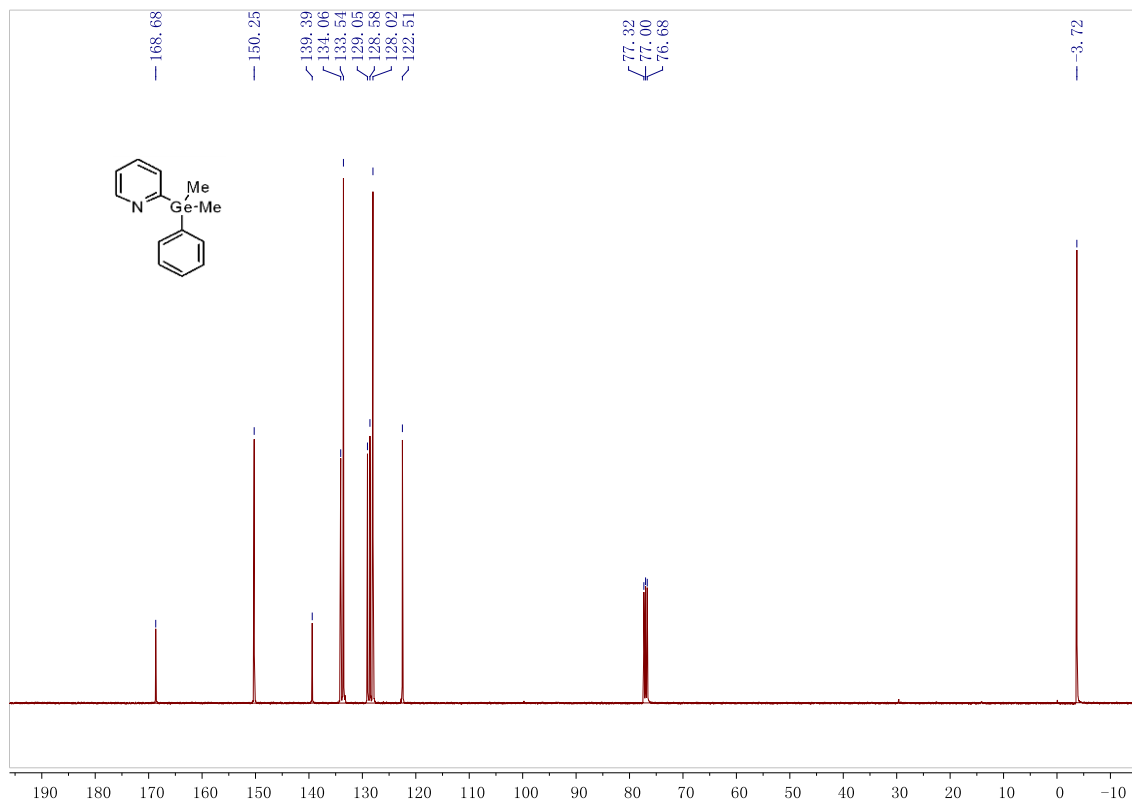


## 2-(dimethyl(phenyl)germyl)pyridine (8a)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

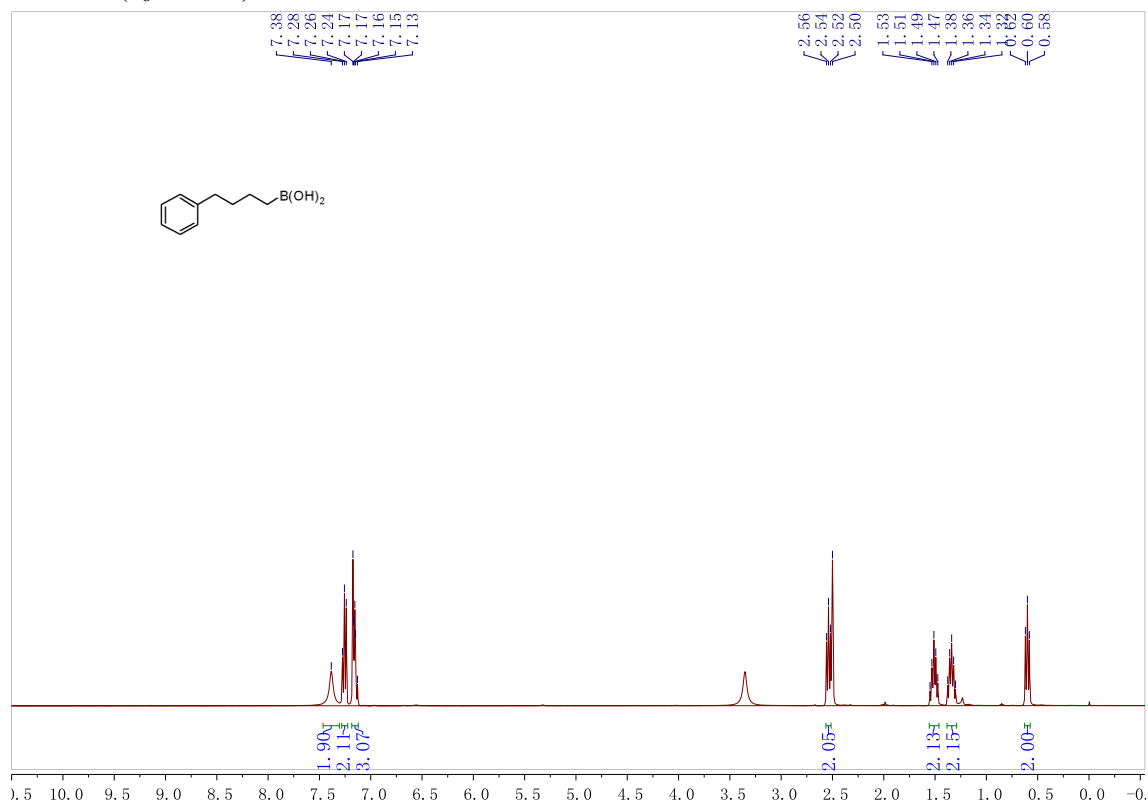


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

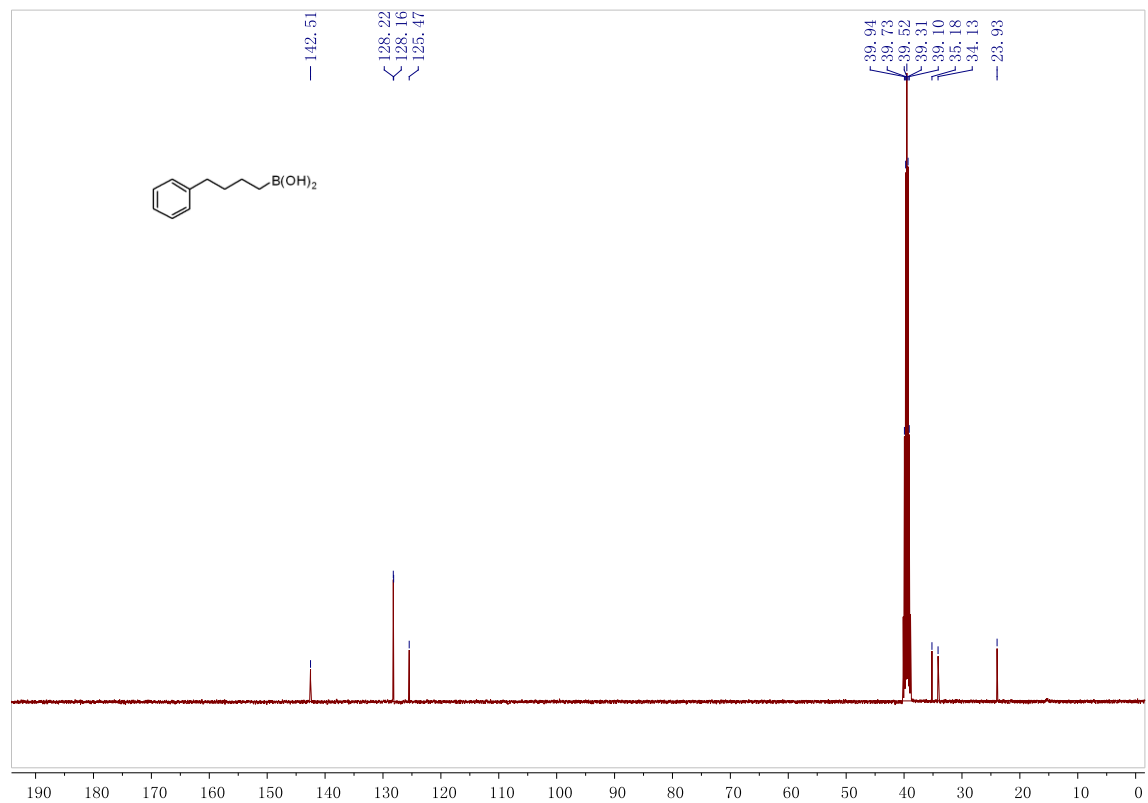


(4-phenylbutyl)boronic acid (2d)

$^1\text{H}$  NMR ( $d_6$ -DMSO)

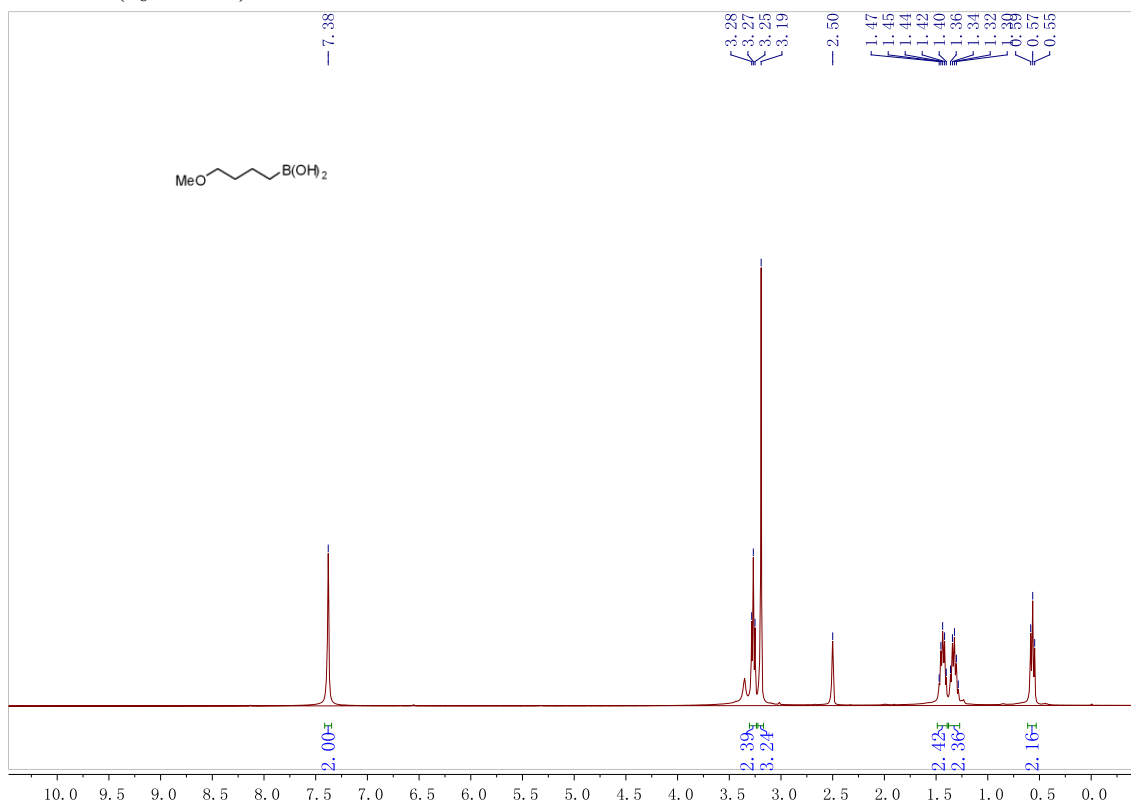


$^{13}\text{C}$  NMR ( $d_6$ -DMSO)

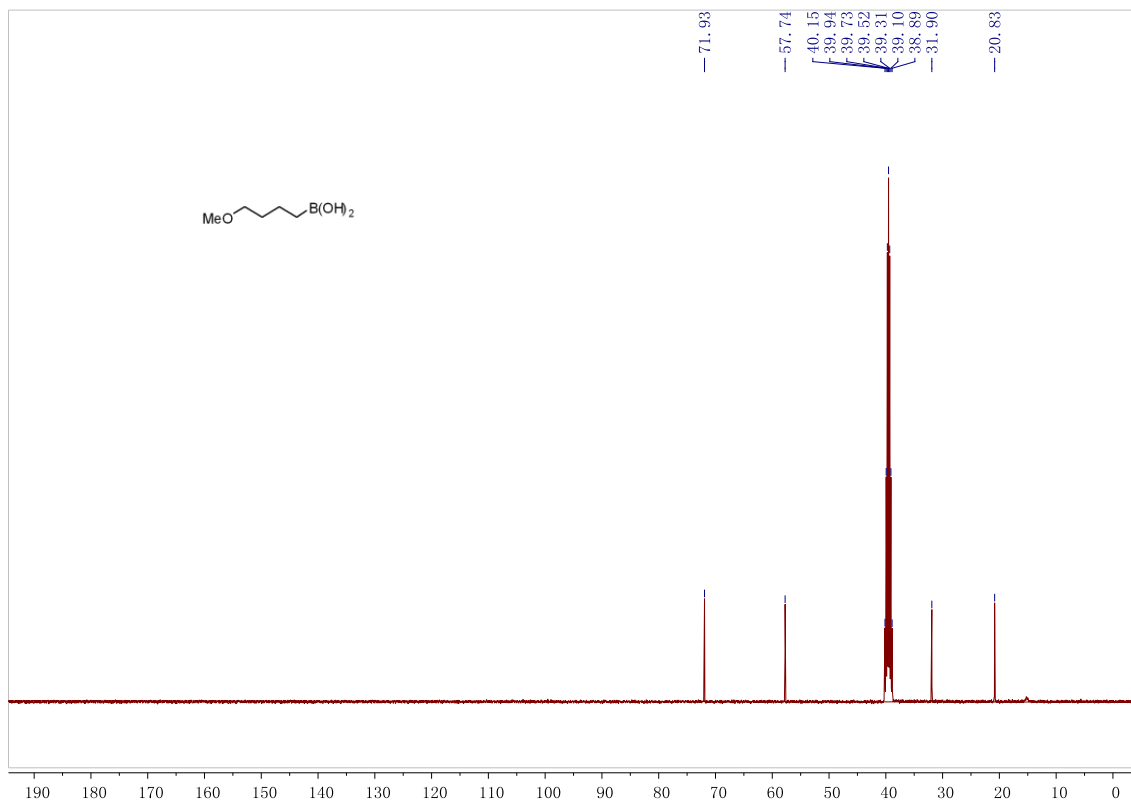


**(4-methoxybutyl)boronic acid (2e)**

$^1\text{H NMR}$  ( $d_6$ -DMSO)

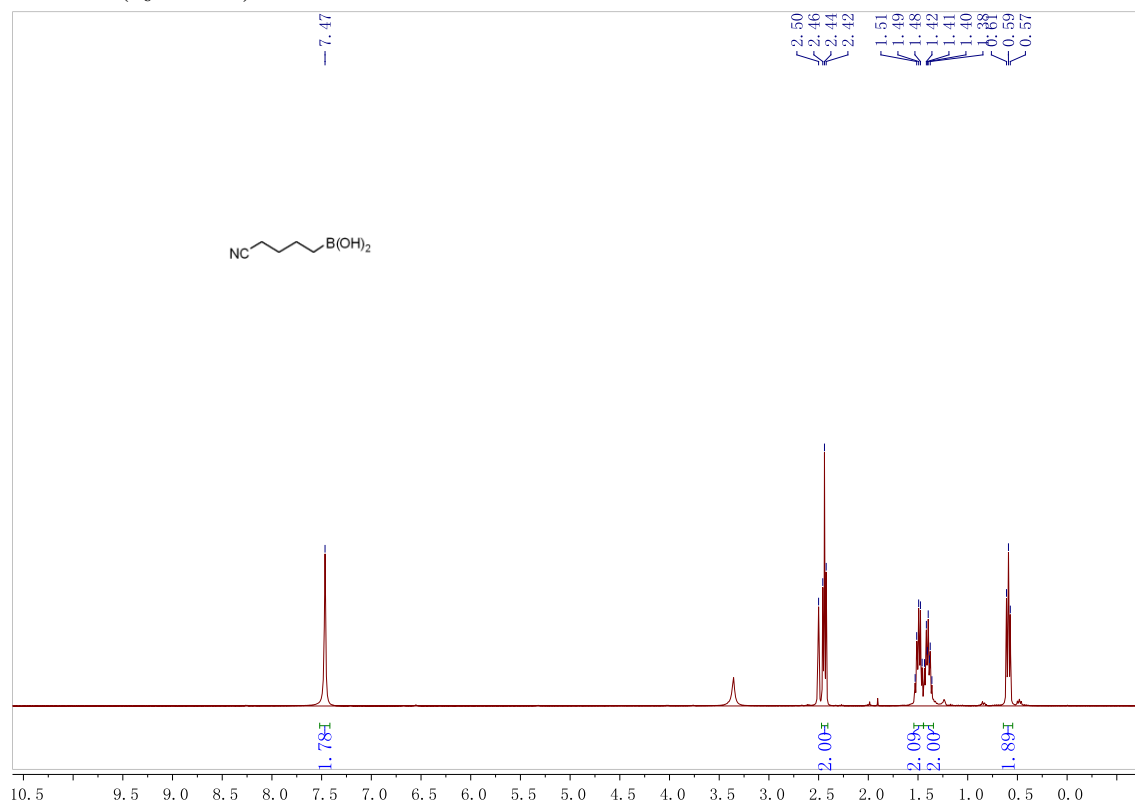


$^{13}\text{C NMR}$  ( $d_6$ -DMSO)

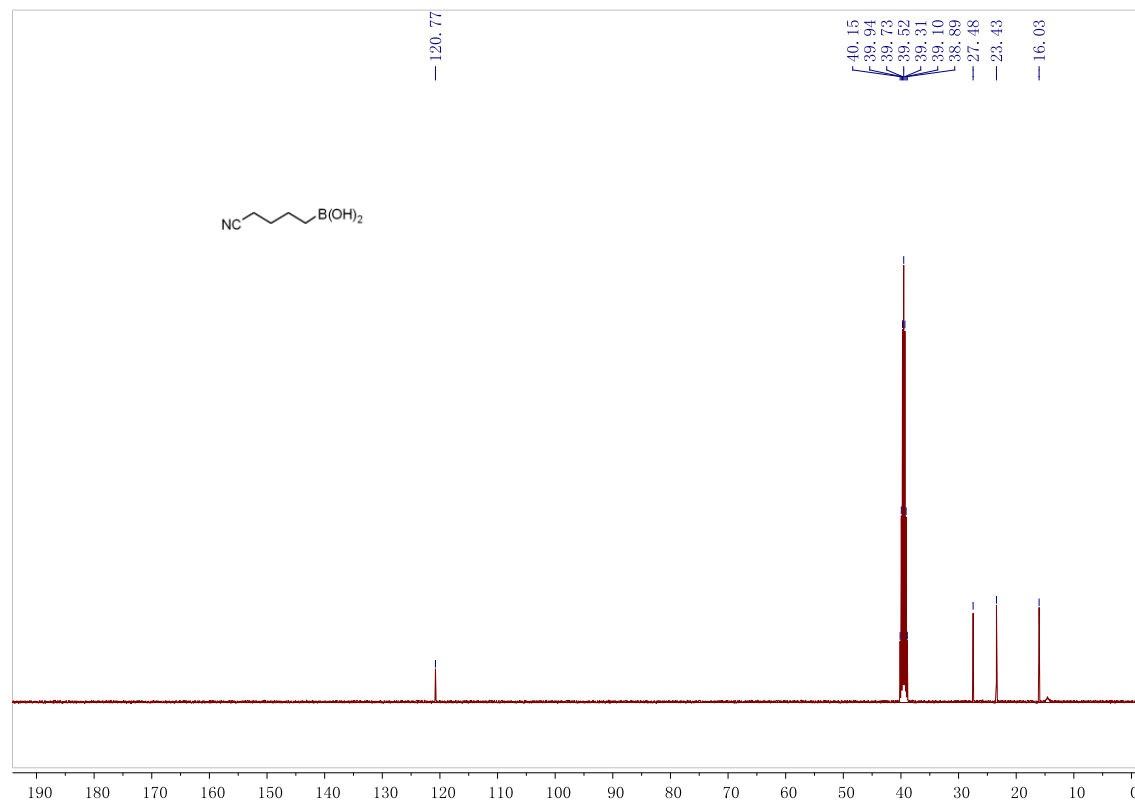


**(4-cyanobutyl)boronic acid (2f)**

$^1\text{H}$  NMR ( $d_6$ -DMSO)

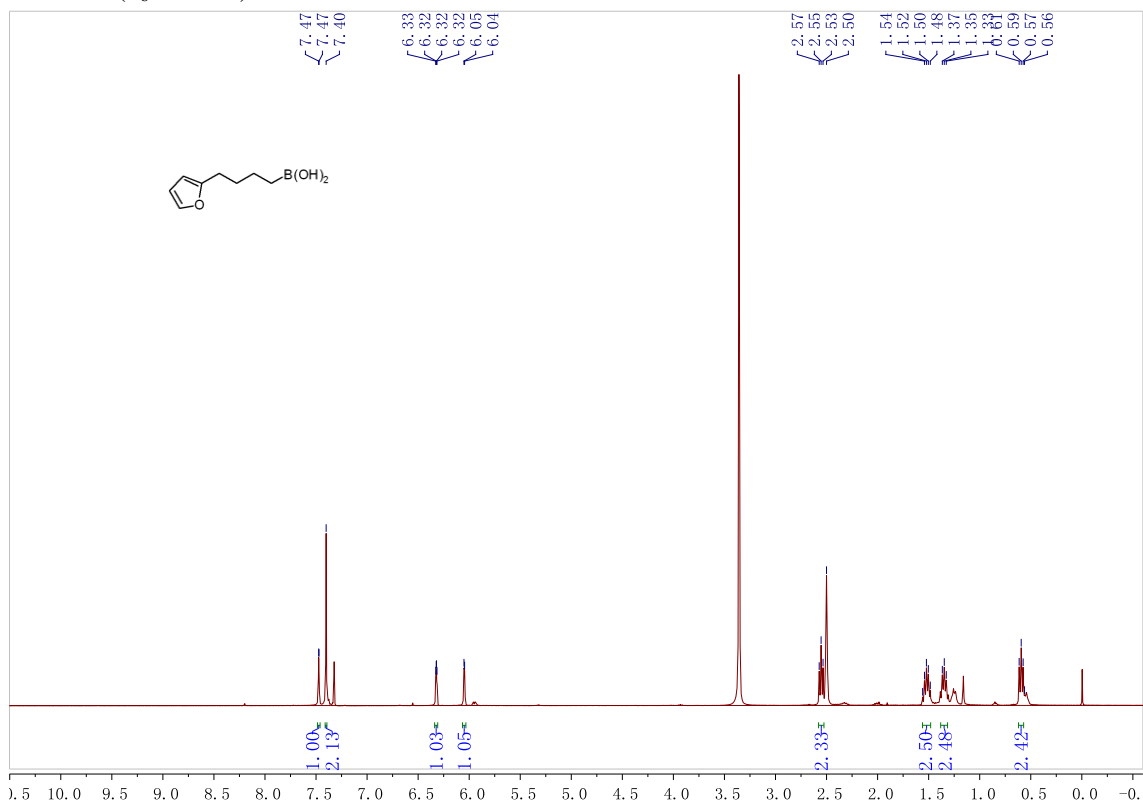


$^{13}\text{C}$  NMR ( $d_6$ -DMSO)

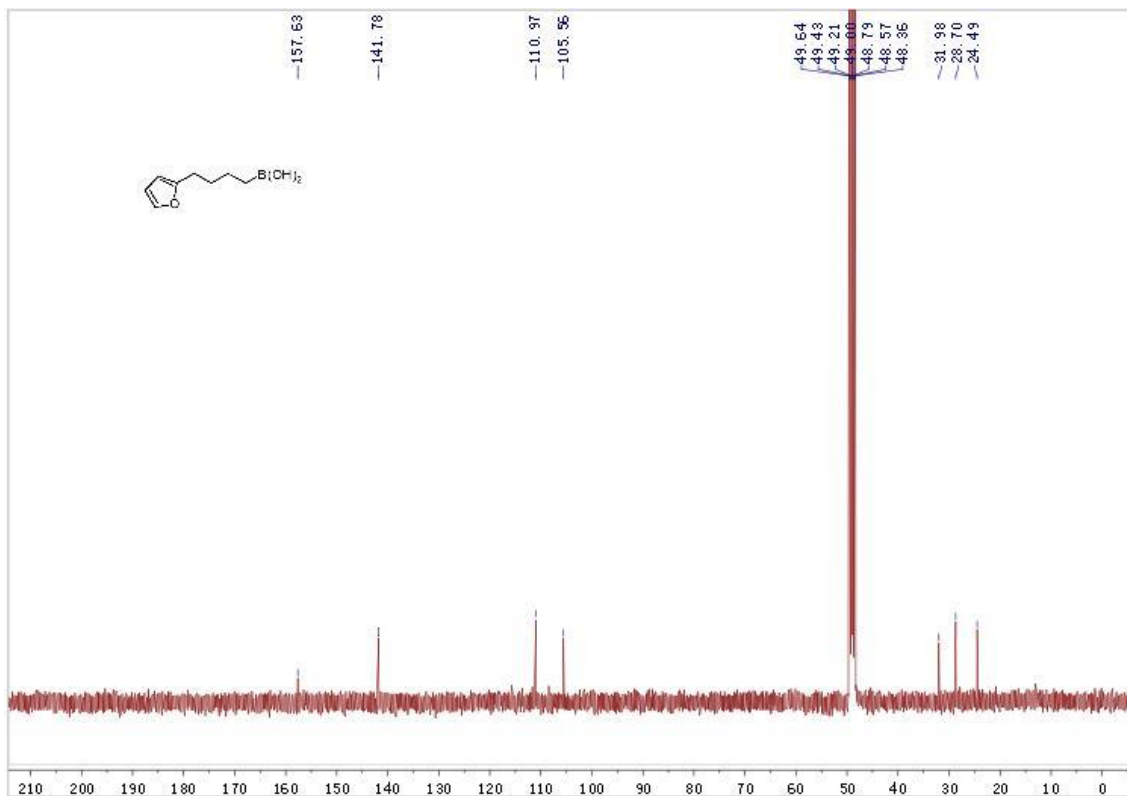


**(4-(furan-2-yl)butyl)boronic acid (2g)**

<sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO)

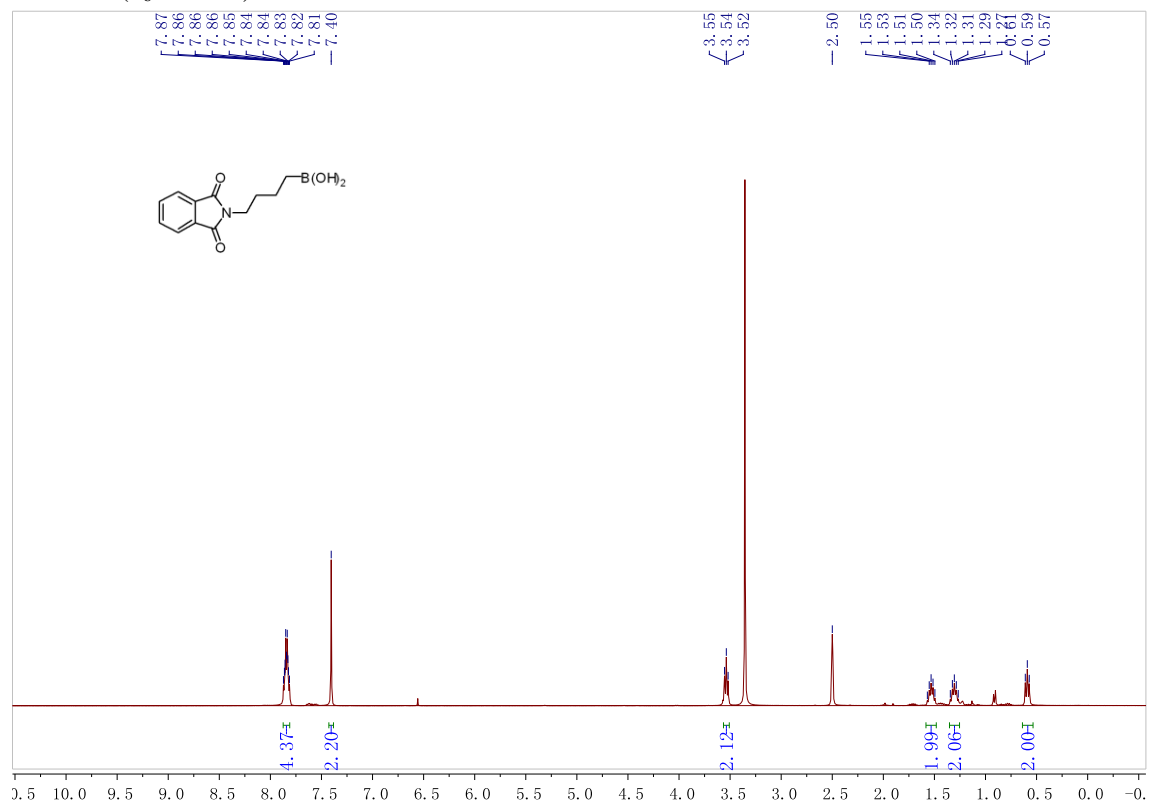


<sup>13</sup>C NMR (CD<sub>3</sub>OD)

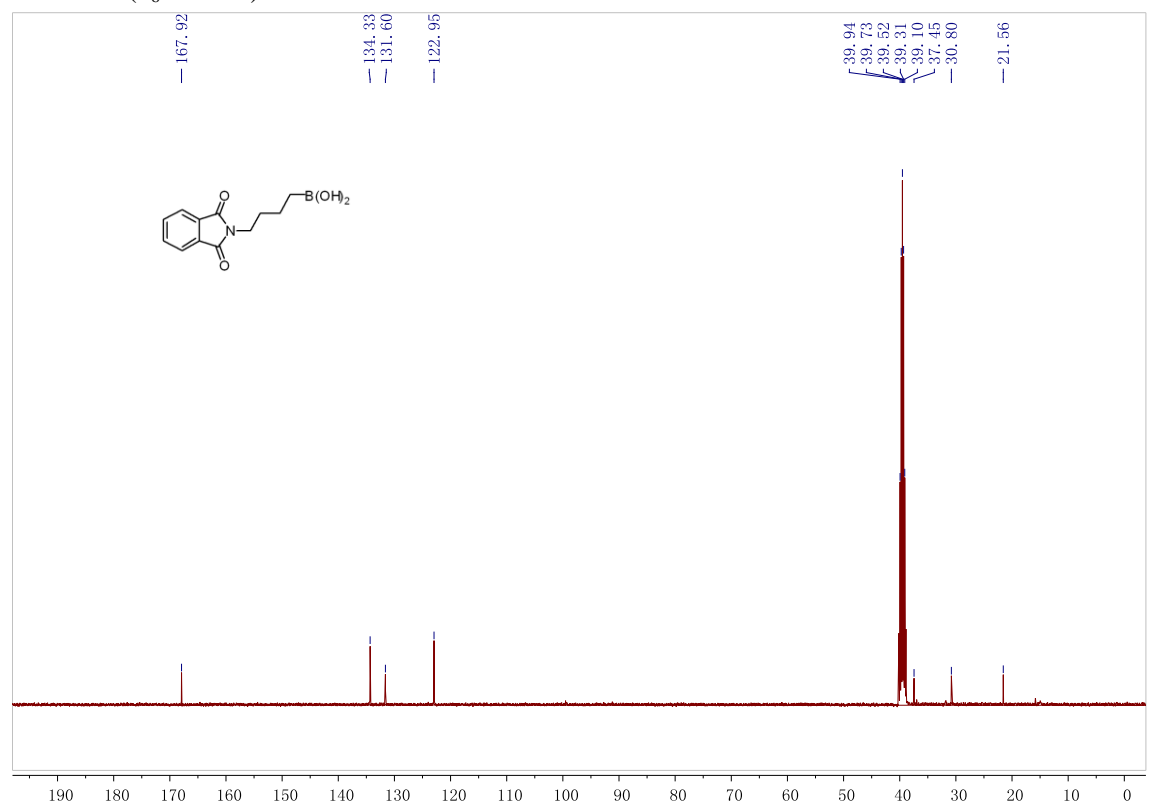


### 4-(1,3-dioxisoindolin-2-yl)butylboronic acid (2h)

$^1\text{H}$  NMR ( $d_6$ -DMSO)



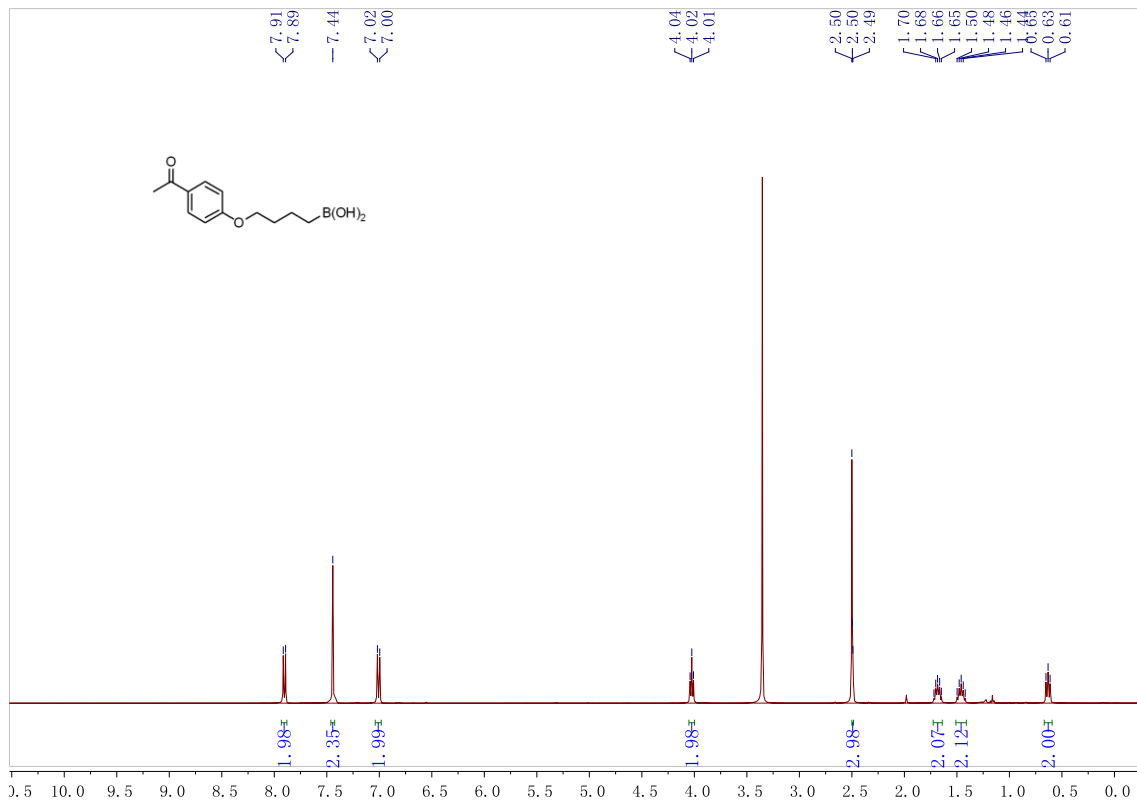
$^{13}\text{C}$  NMR ( $d_6$ -DMSO)



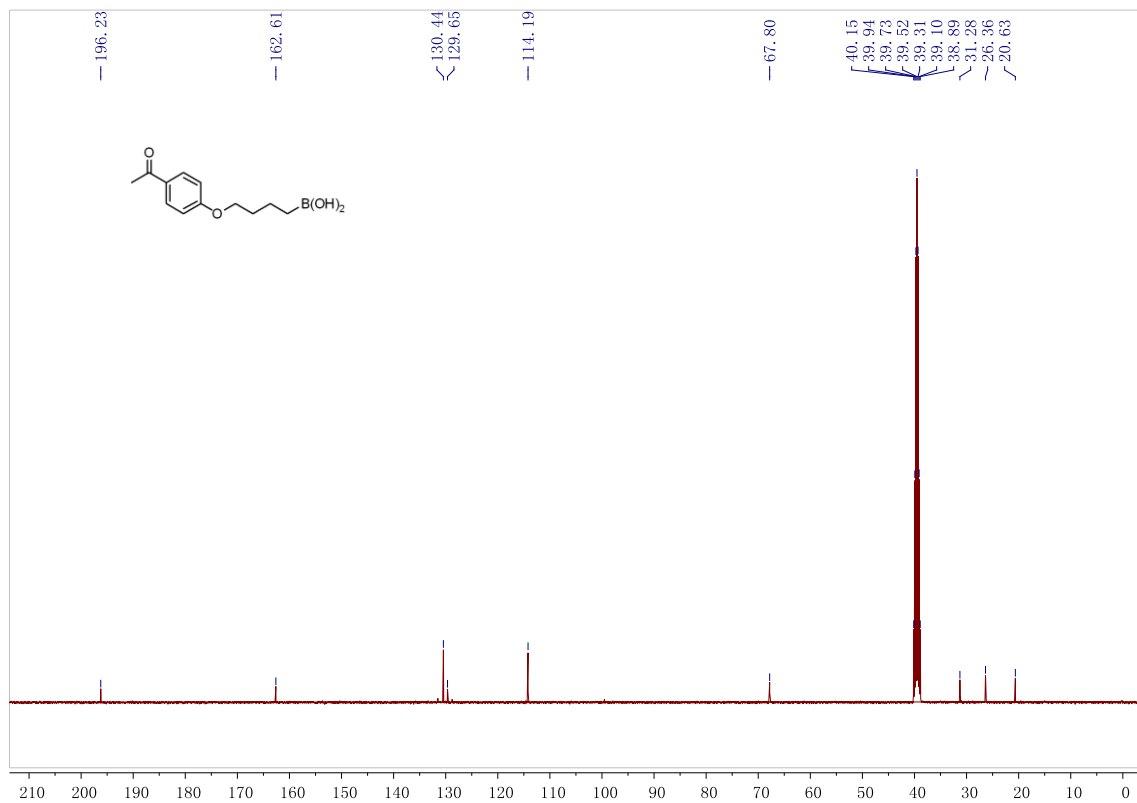


**(4-(4-acetylphenoxy)butyl)boronic acid (2i)**

$^1\text{H NMR}$  ( $d_6$ -DMSO)

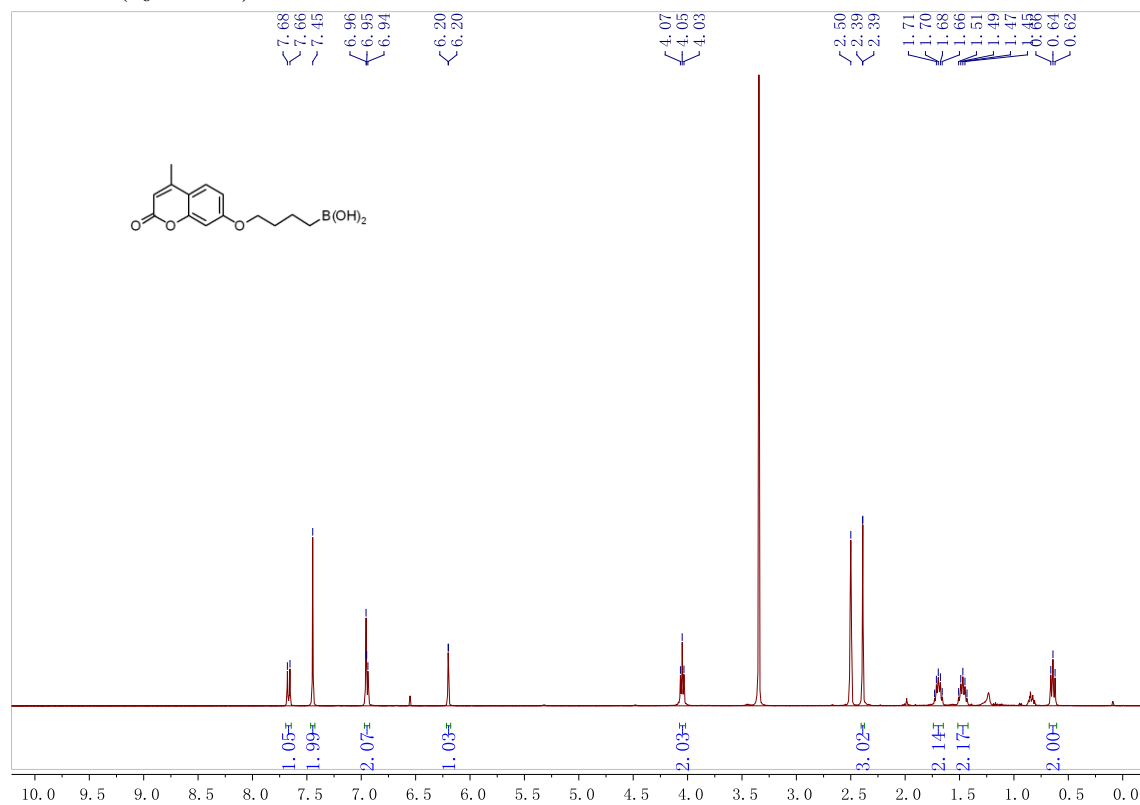


$^{13}\text{C NMR}$  ( $d_6$ -DMSO)

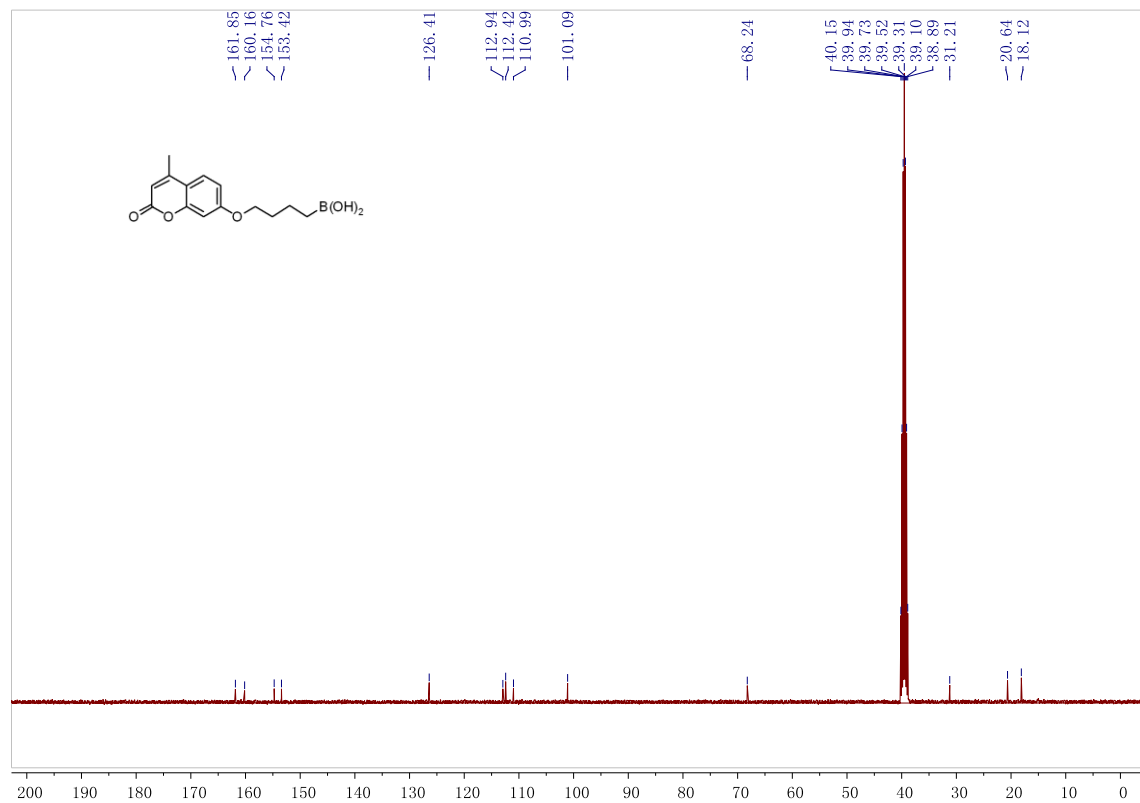


**(4-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)butyl)boronic acid (2j)**

$^1\text{H}$  NMR ( $d_6$ -DMSO)

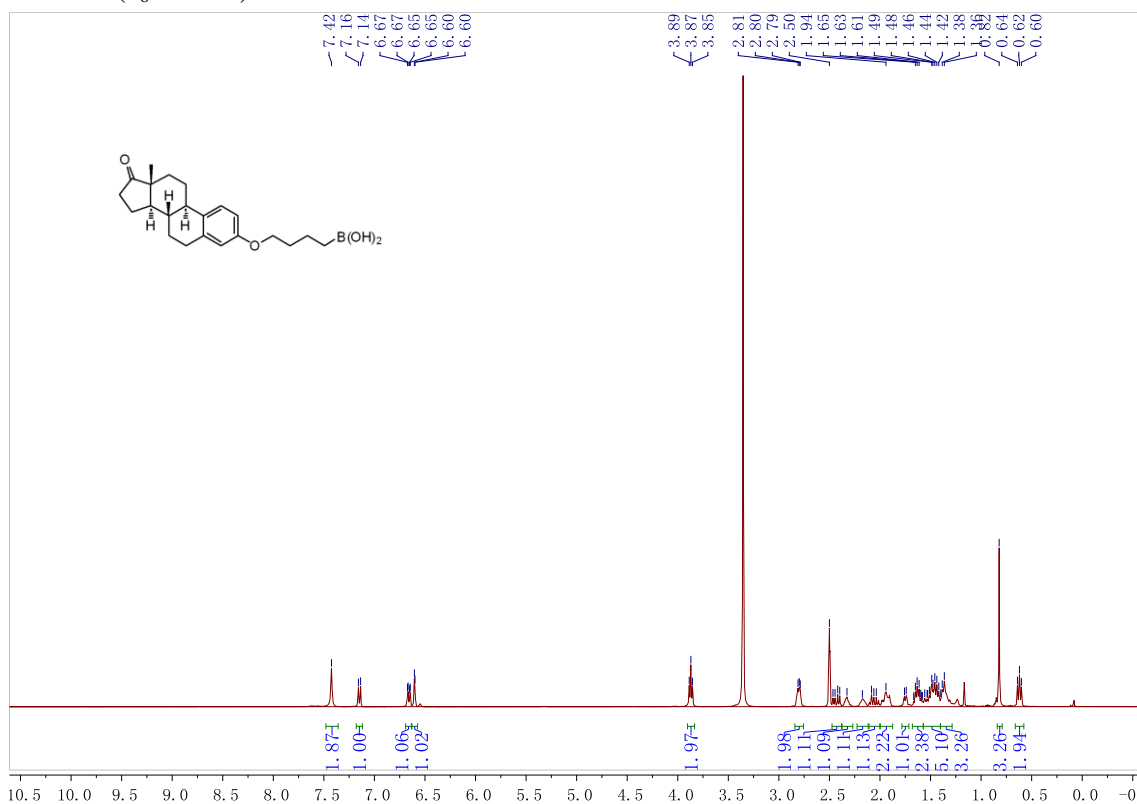


$^{13}\text{C}$  NMR ( $d_6$ -DMSO)

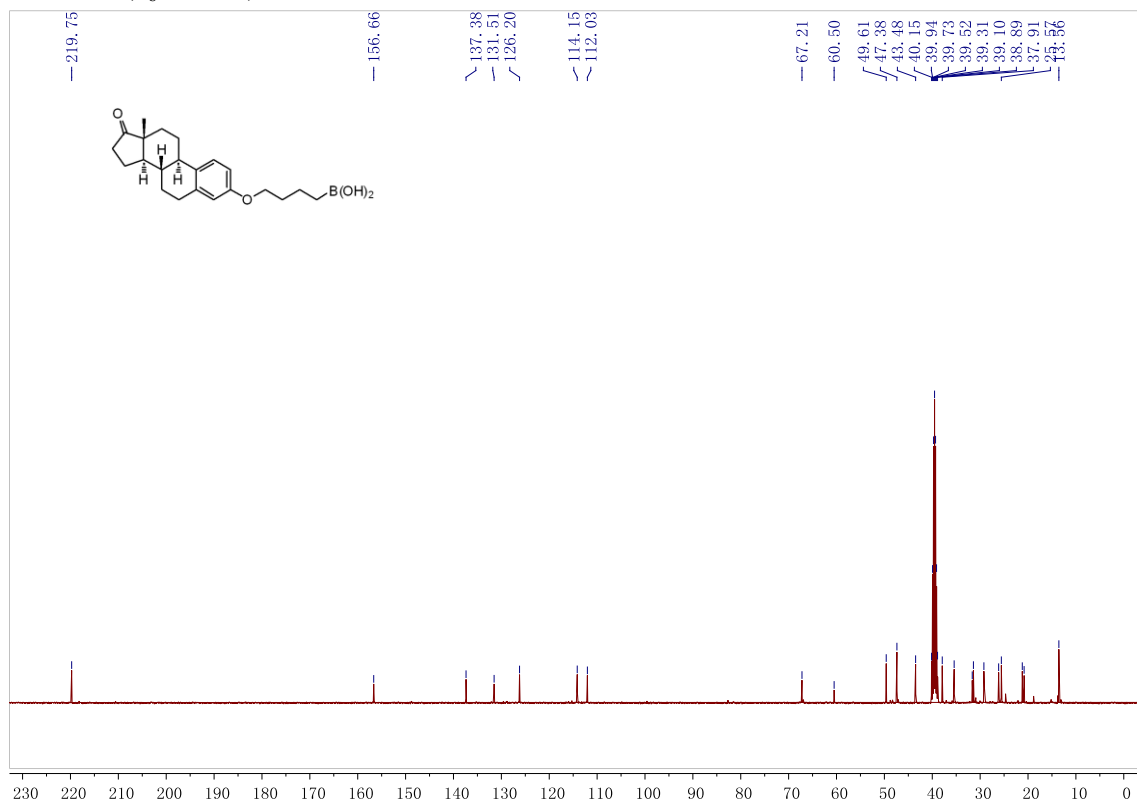


**(4-(((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)butyl)boronic acid (2k)**

<sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO)

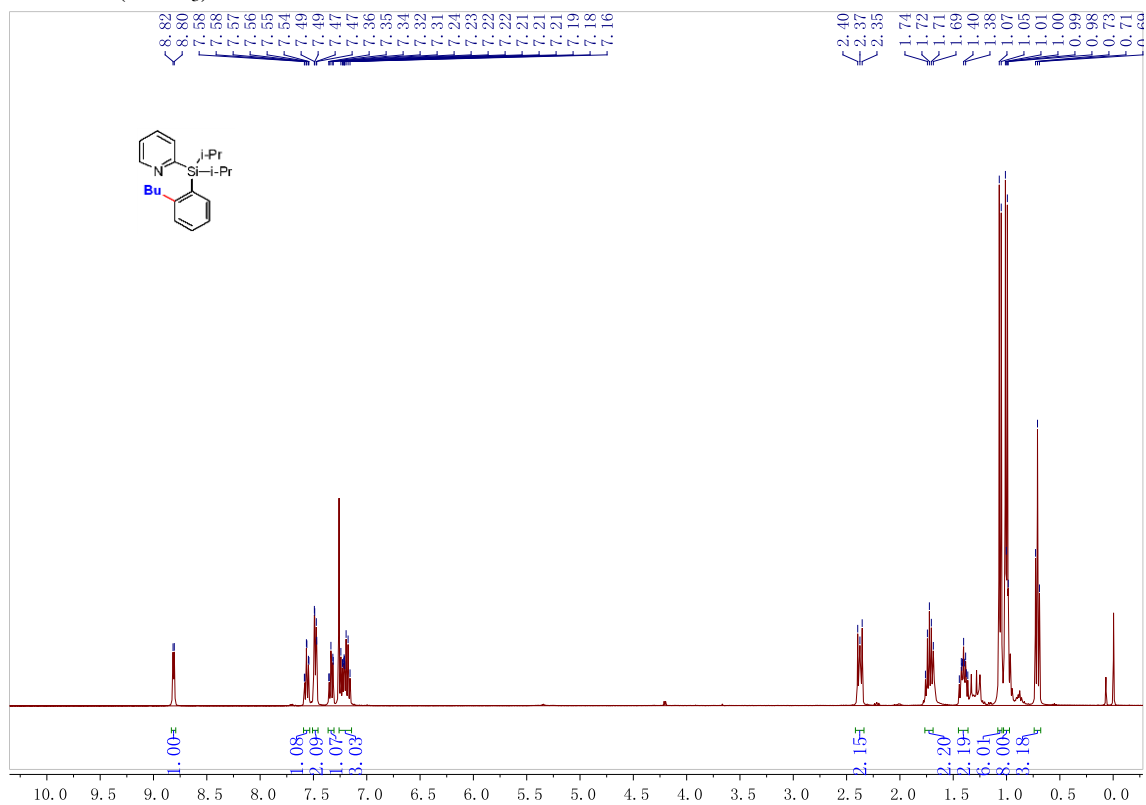


<sup>13</sup>C NMR (*d*<sub>6</sub>-DMSO)

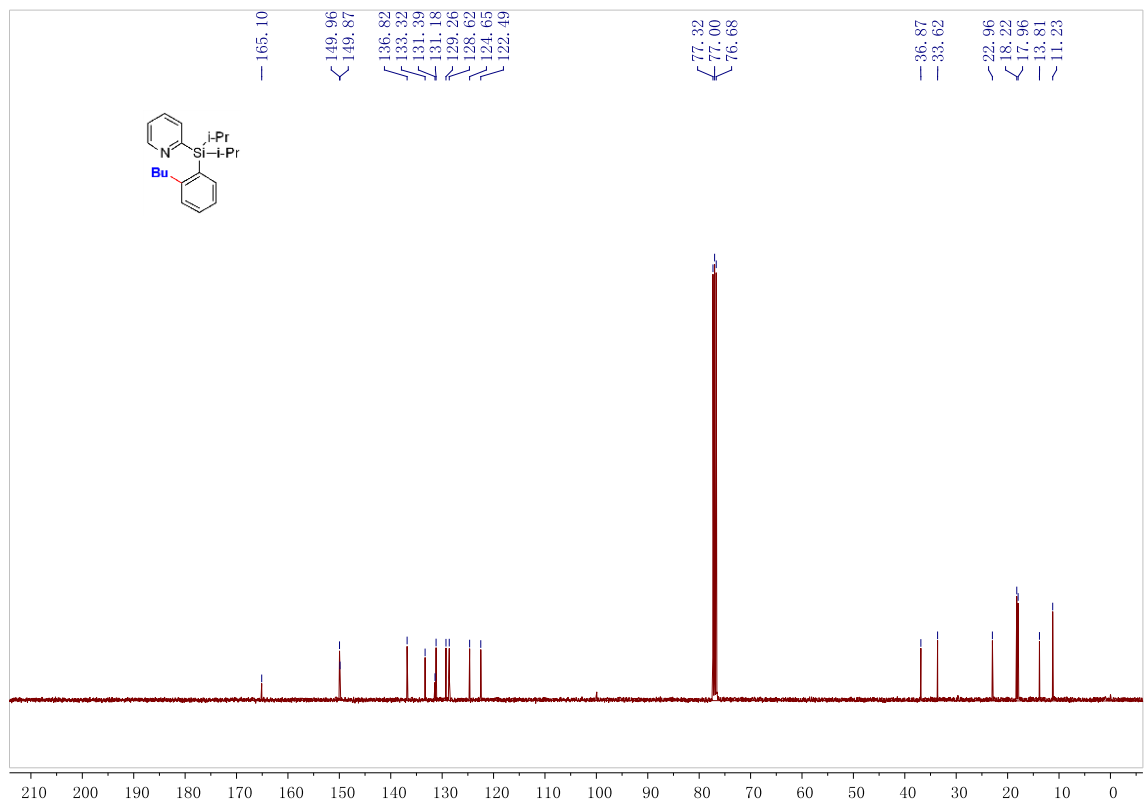


## 2-((2-butylphenyl)diisopropylsilyl)pyridine (3aa)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

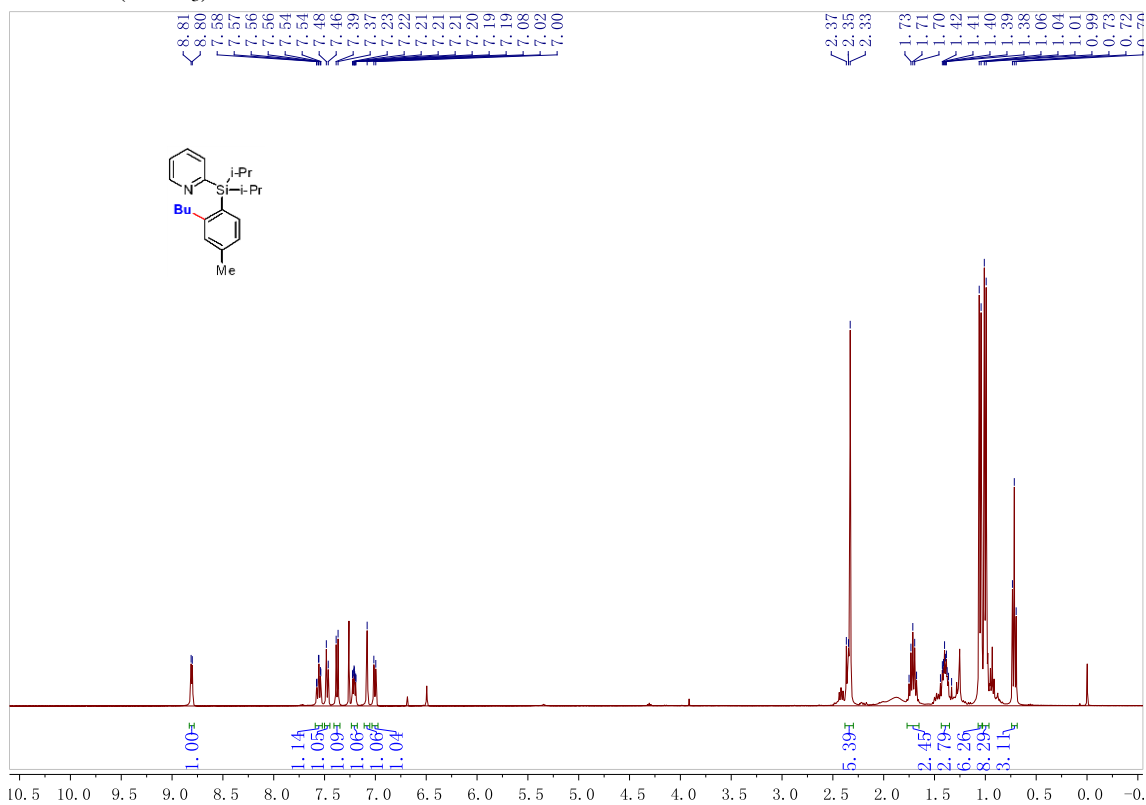


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

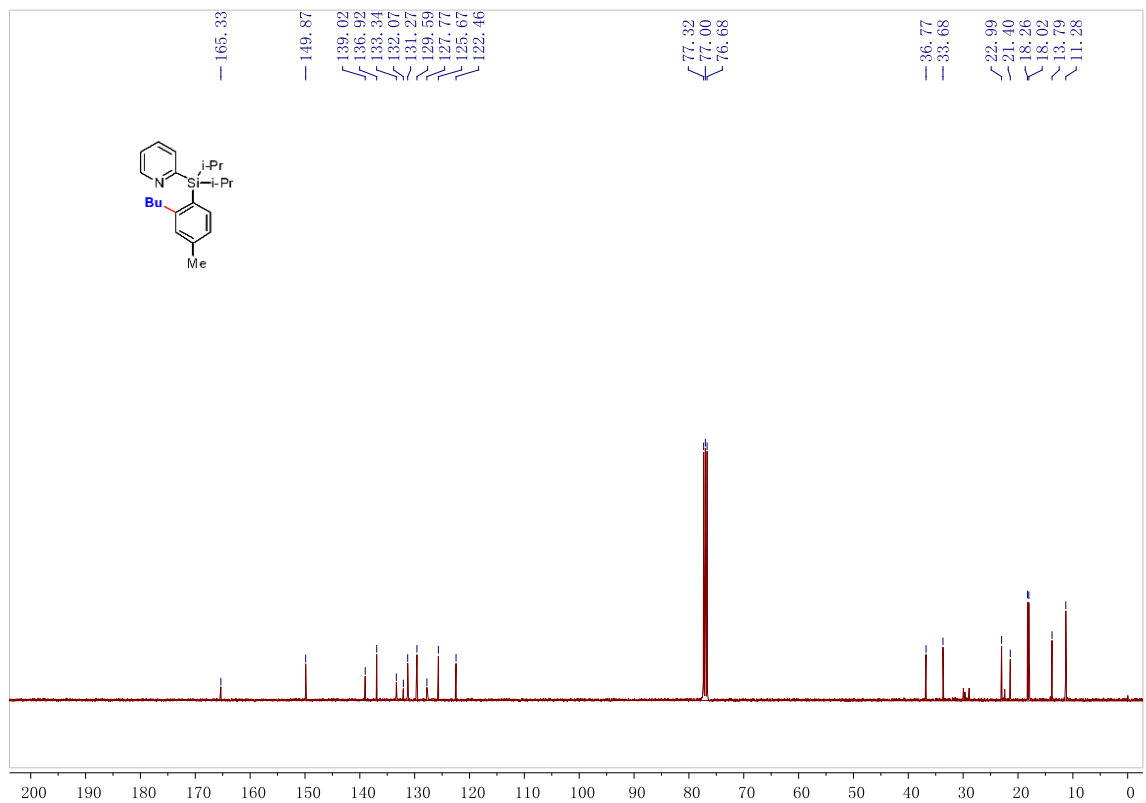


## 2-((2-butyl-4-methylphenyl)diisopropylsilyl)pyridine (3ba)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

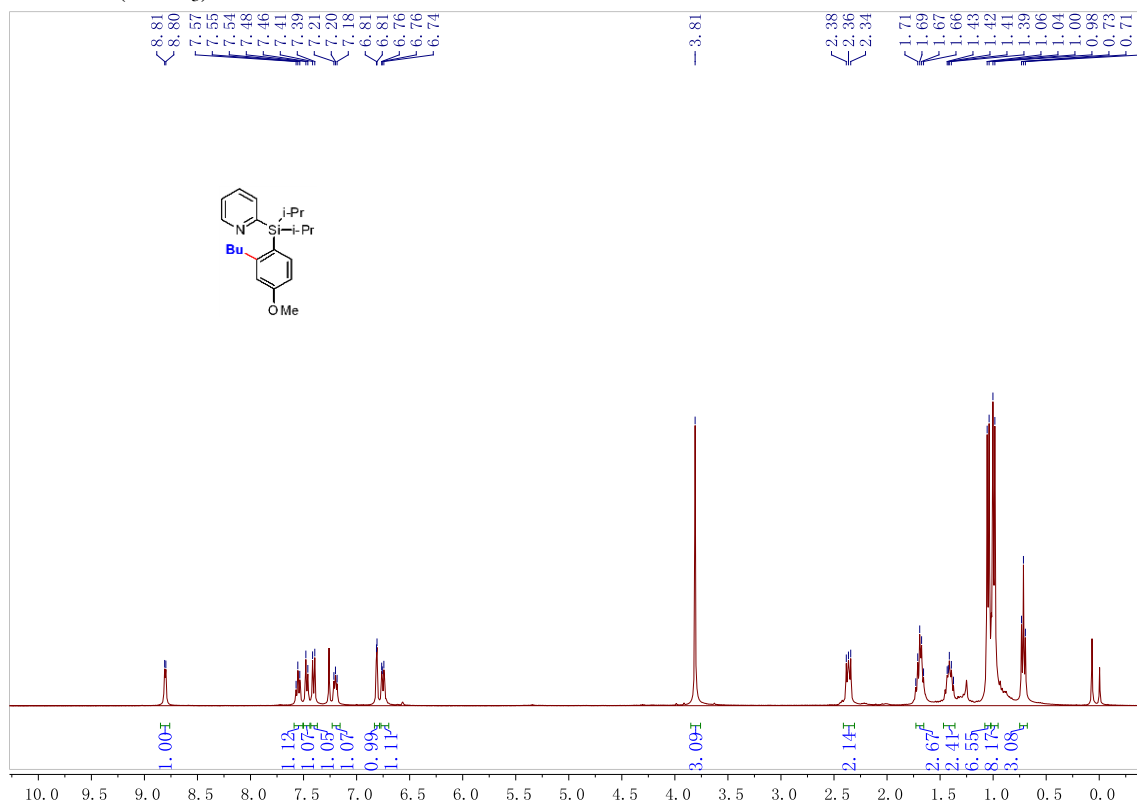


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

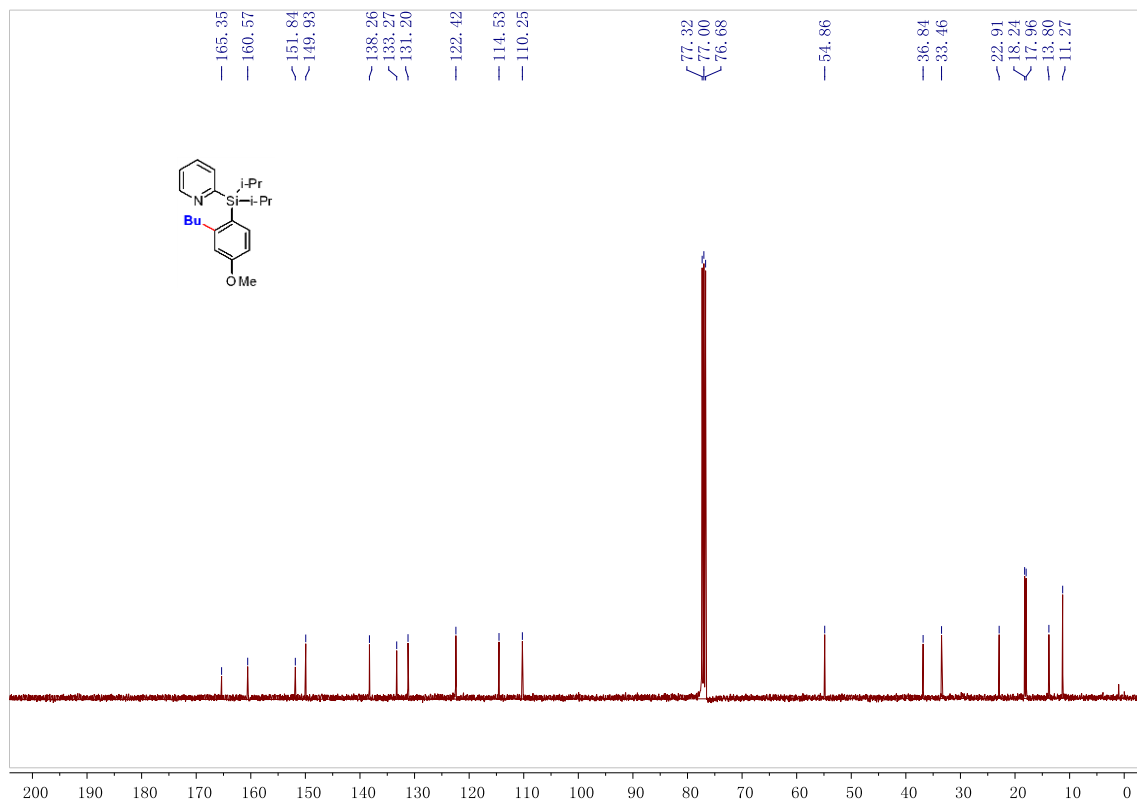


2-((2-butyl-4-methoxyphenyl)diisopropylsilyl)pyridine (3ca)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

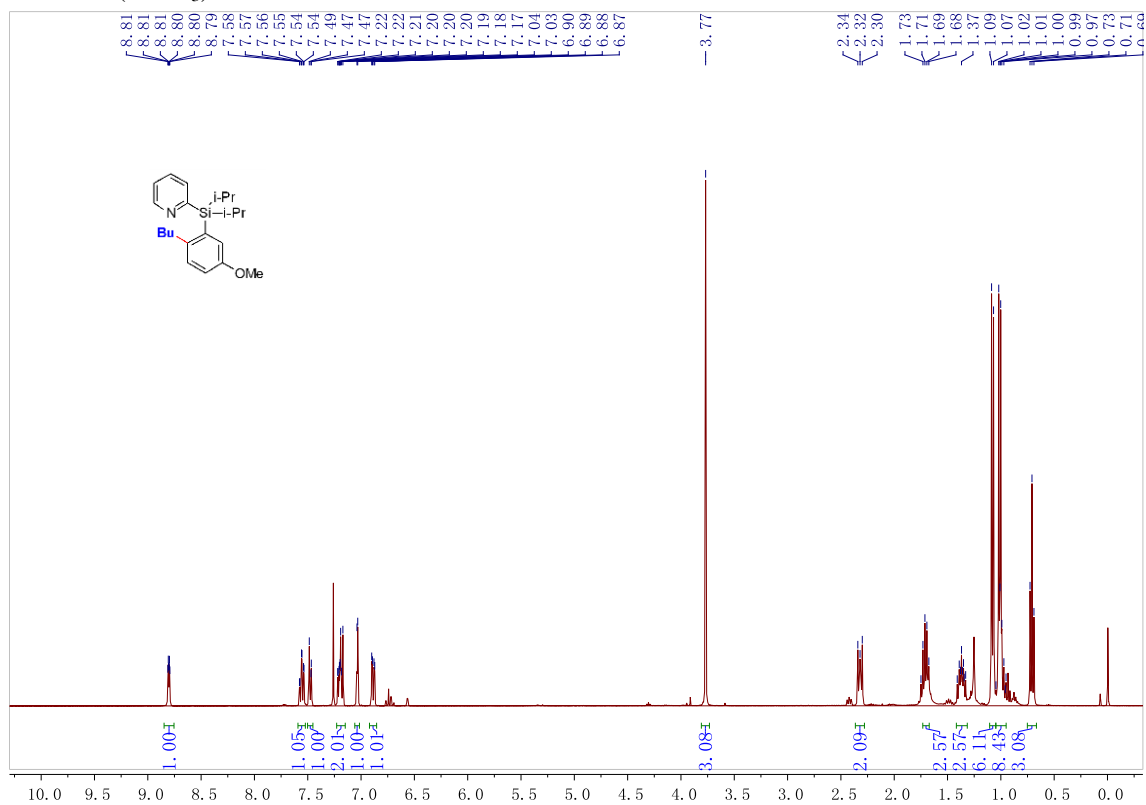


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

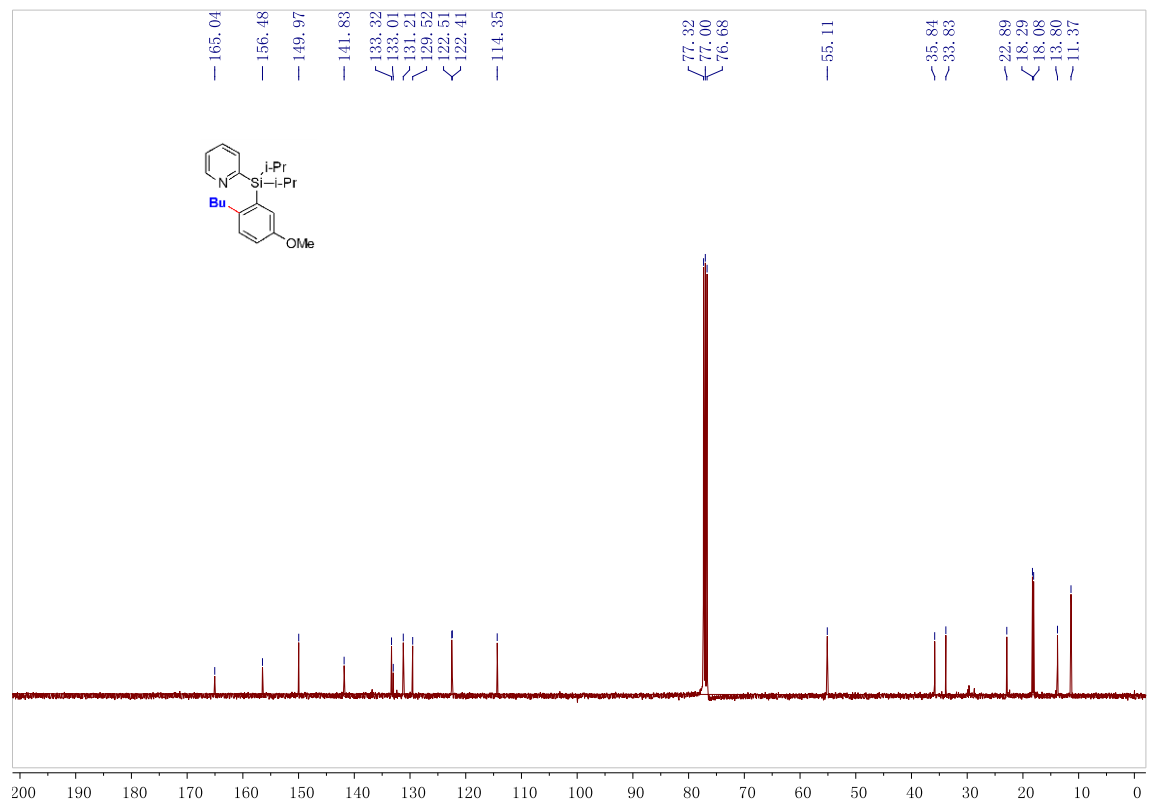


### 2-((2-butyl-5-methoxyphenyl)diisopropylsilyl)pyridine (3da)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)



<sup>13</sup>C NMR (CDCl<sub>3</sub>)

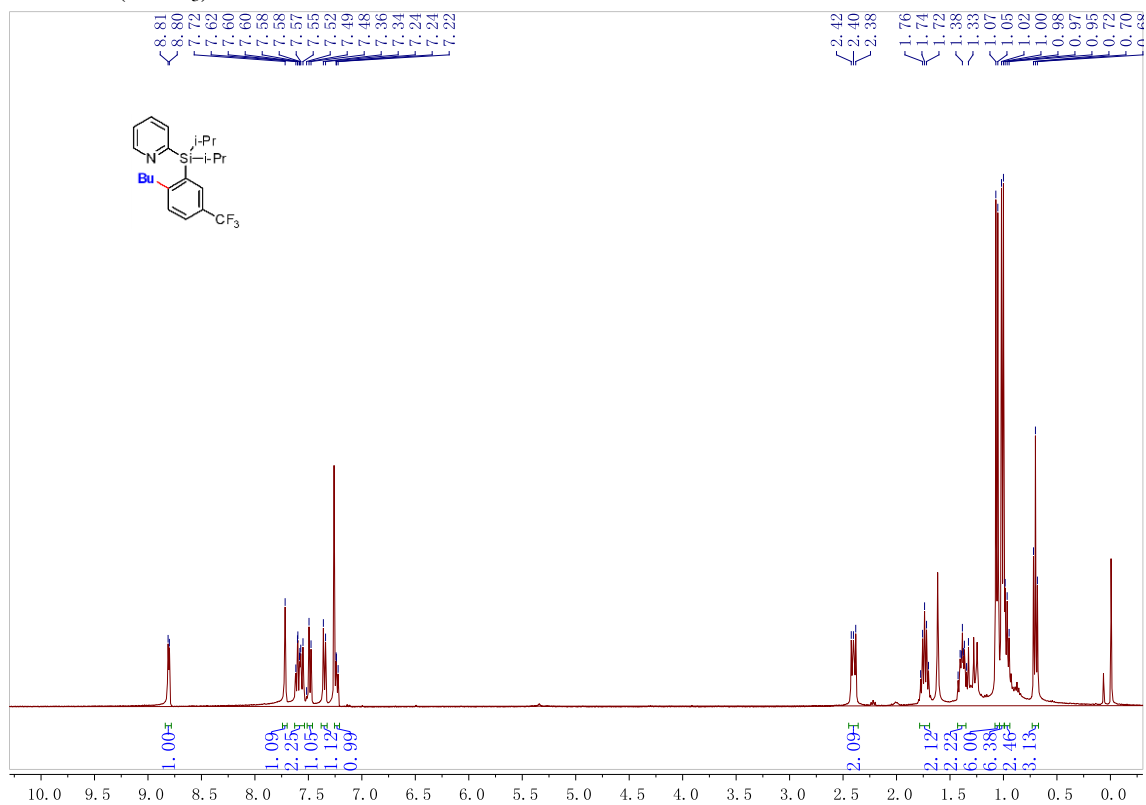




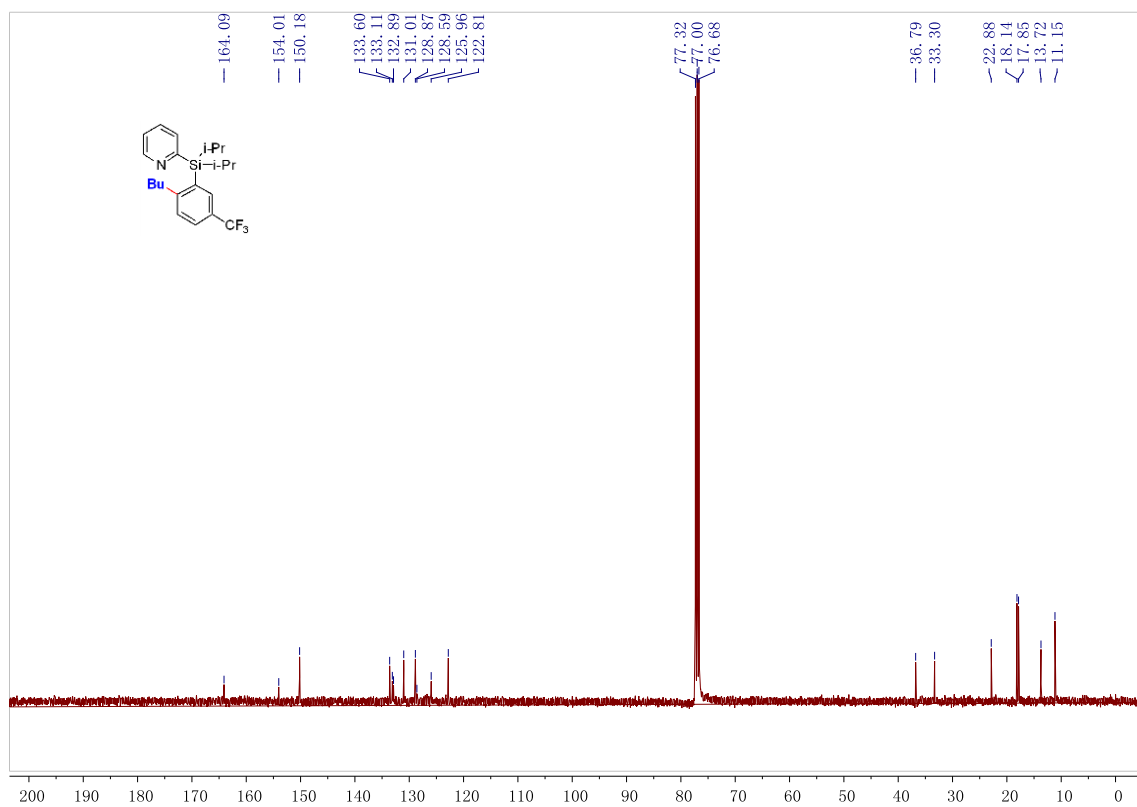


## 2-((2-butyl-5-(trifluoromethyl)phenyl)diisopropylsilyl)pyridine (3fa)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

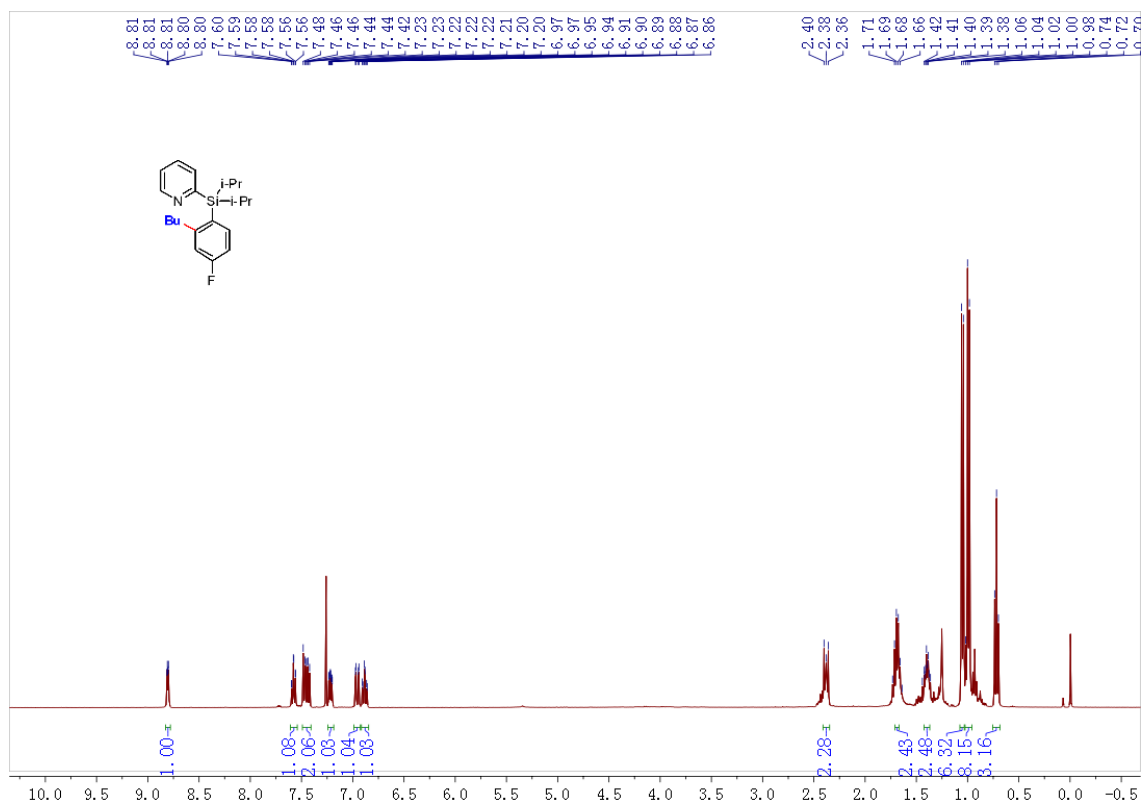


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

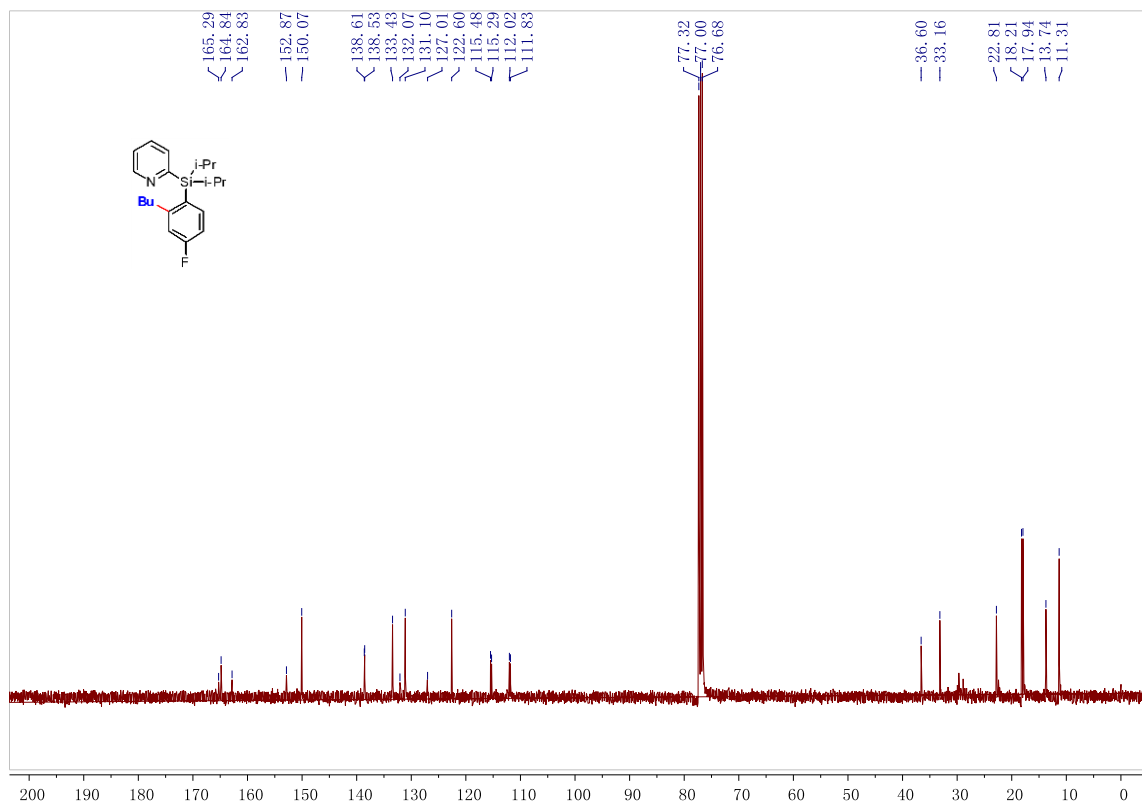


## 2-((2-butyl-4-fluorophenyl)diisopropylsilyl)pyridine (3ga)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

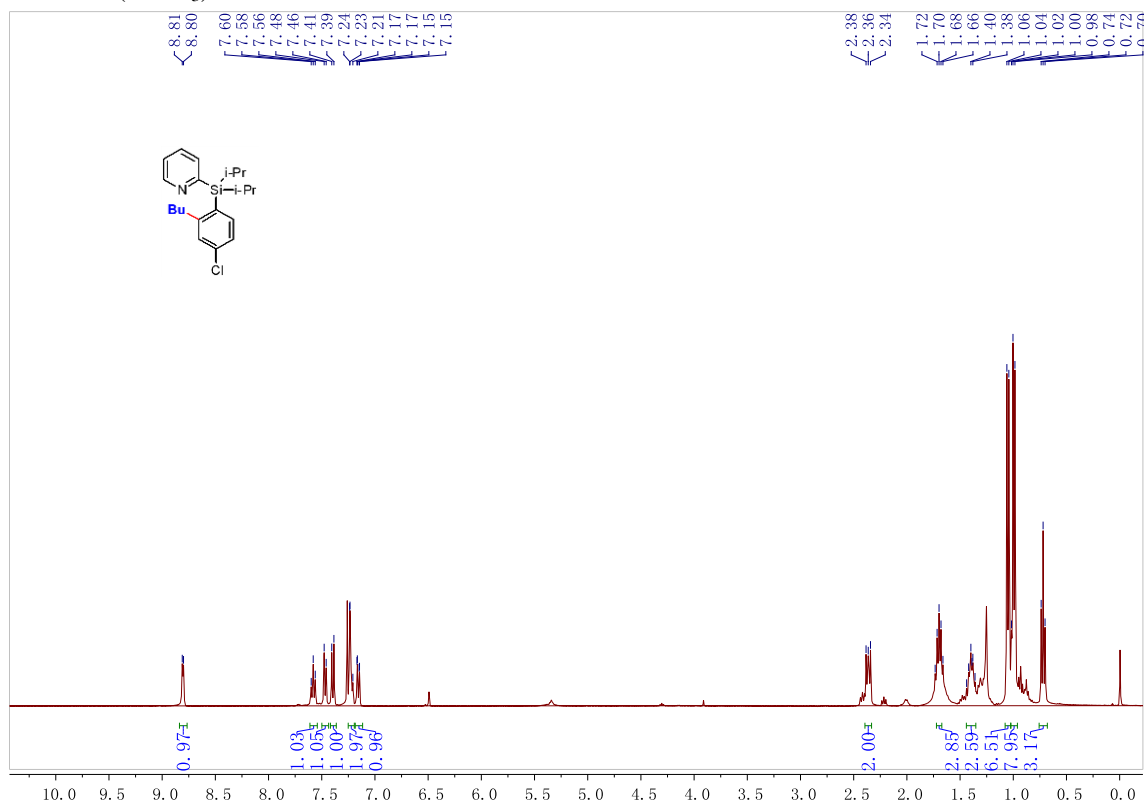


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

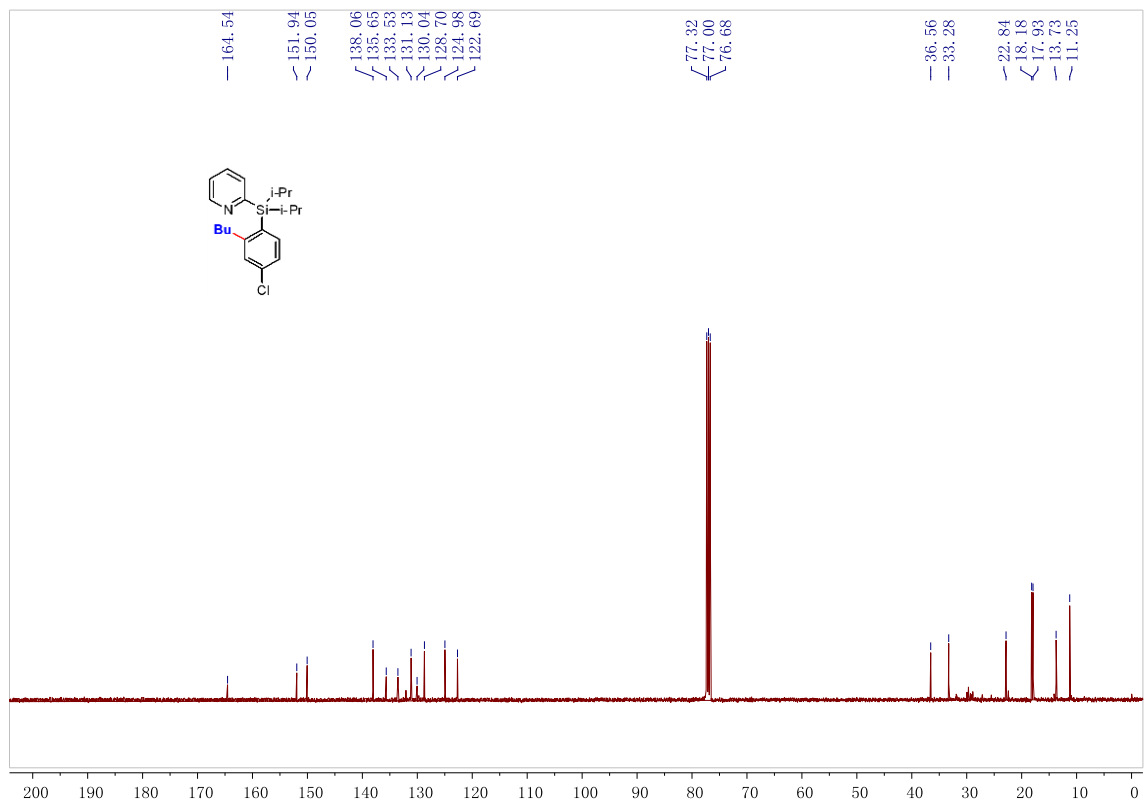


## 2-((2-butyl-4-chlorophenyl)diisopropylsilyl)pyridine (3ha)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

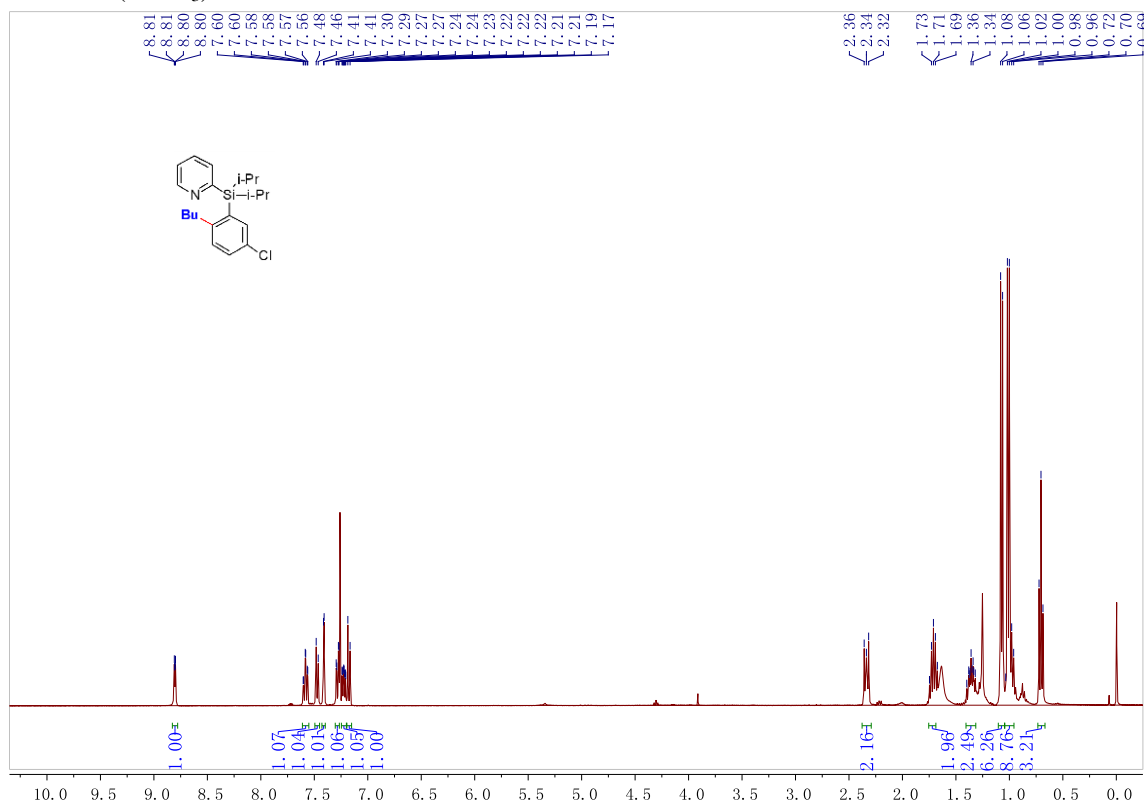


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

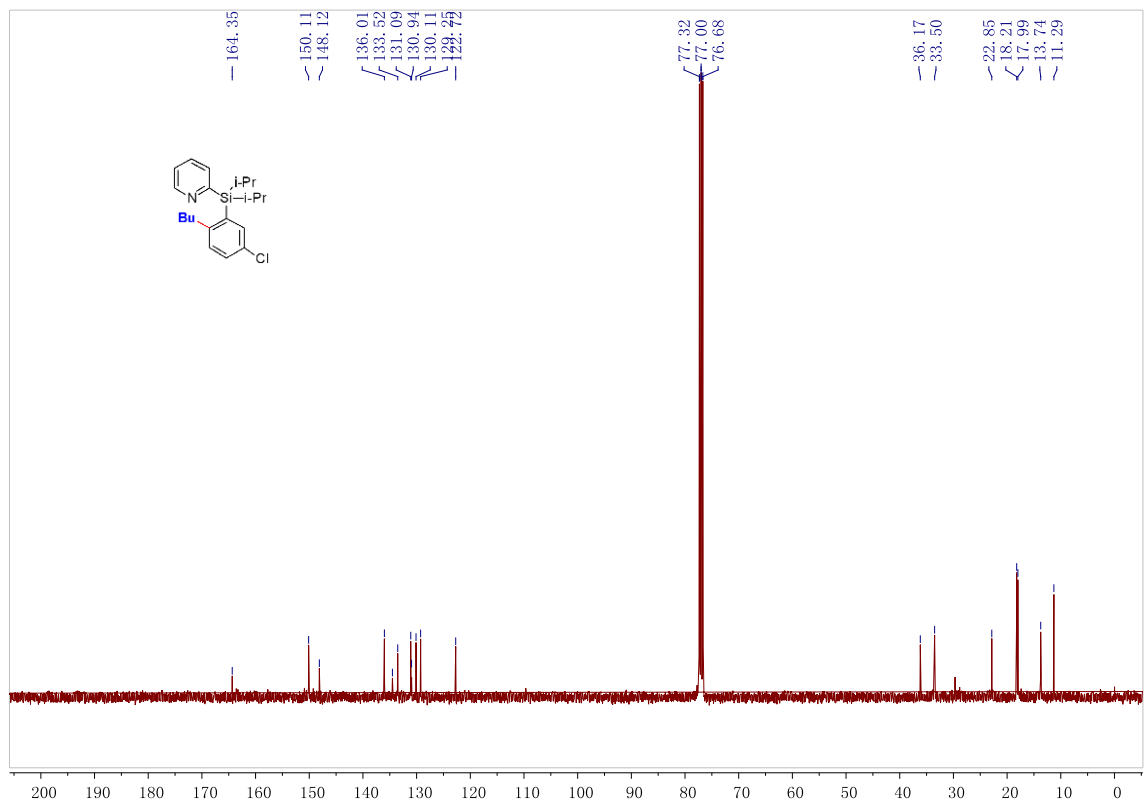


## 2-((2-butyl-5-chlorophenyl)diisopropylsilyl)pyridine (3ia)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

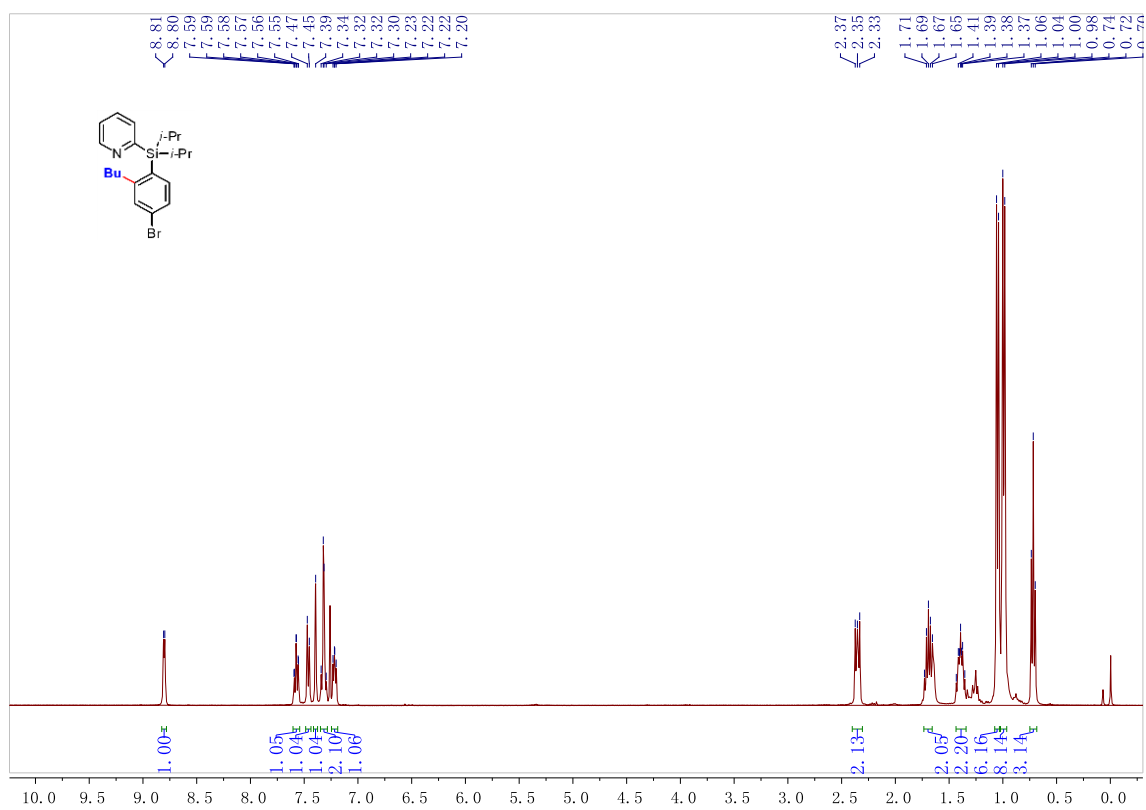


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

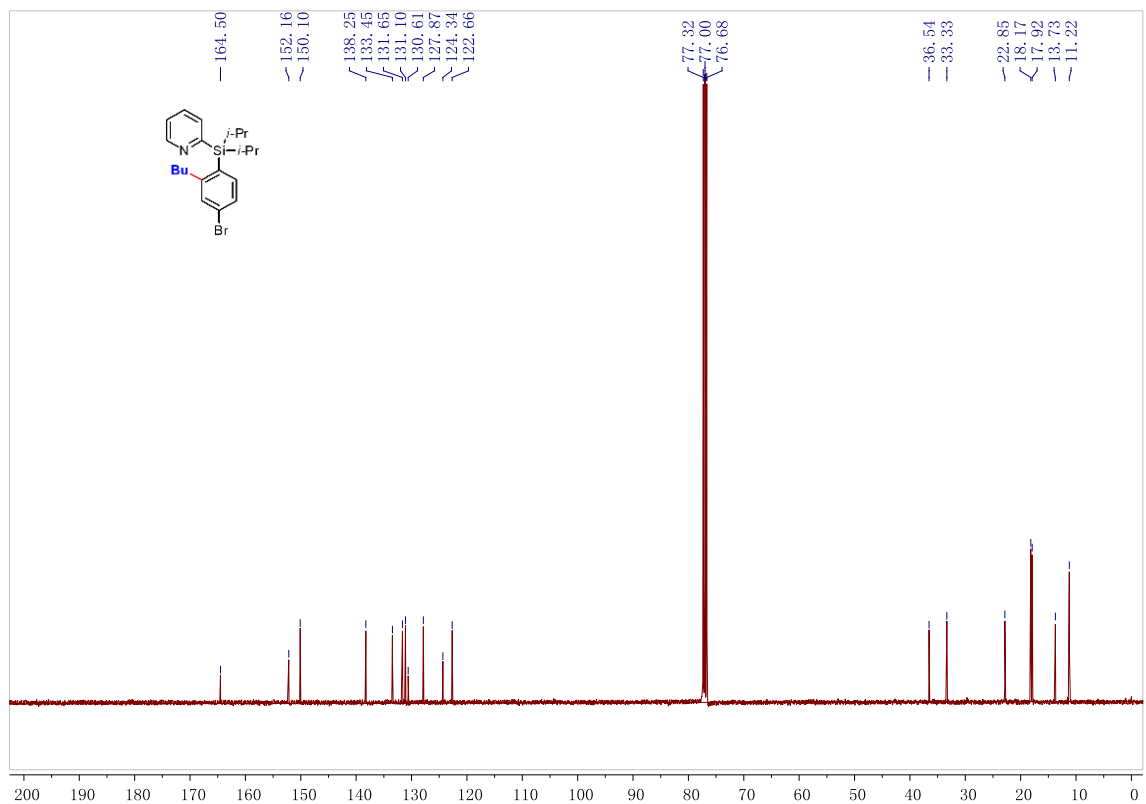


## 2-((4-bromo-2-butylphenyl)diisopropylsilyl)pyridine (3ja)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

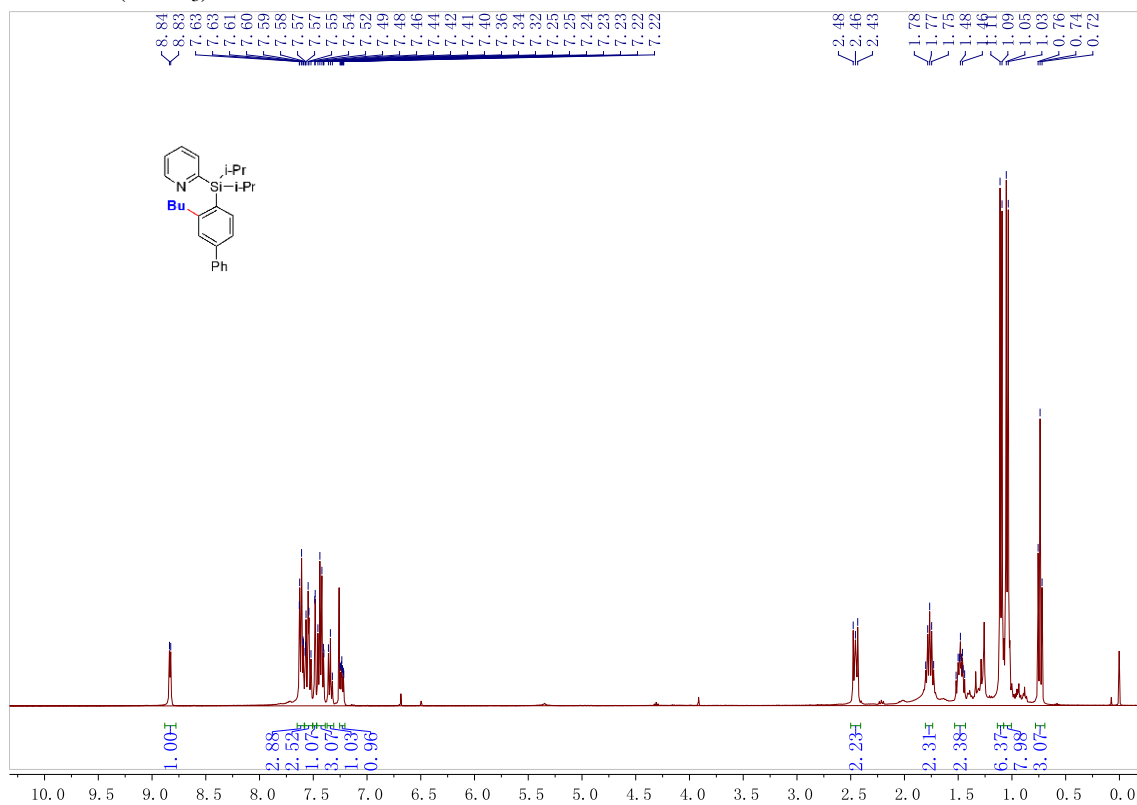


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

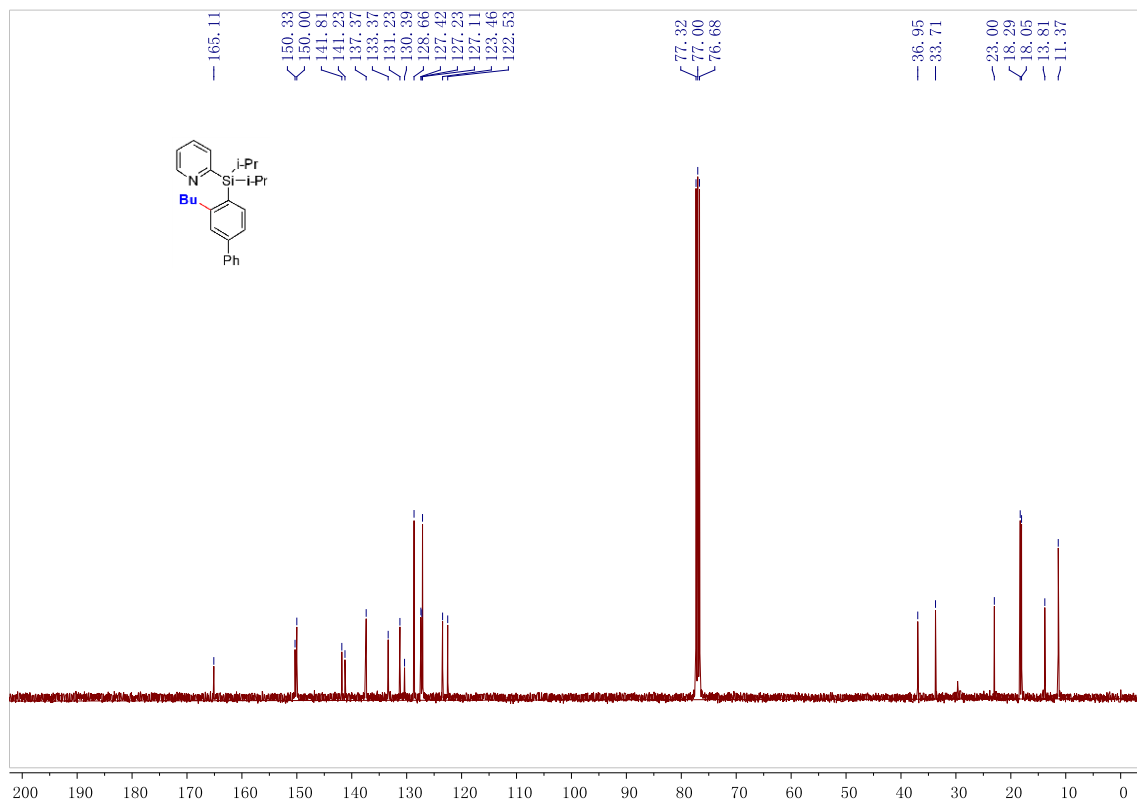


2-((3-butyl-[1,1'-biphenyl]-4-yl)diisopropylsilyl)pyridine (3ka)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

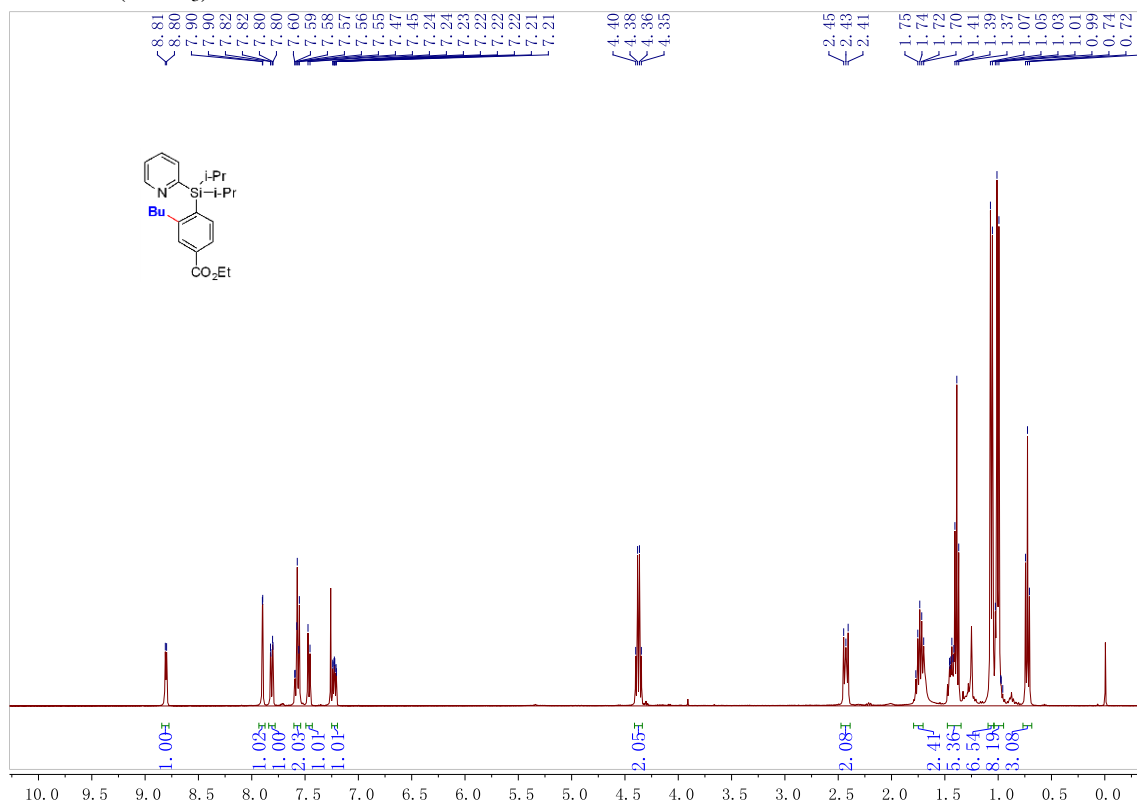


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

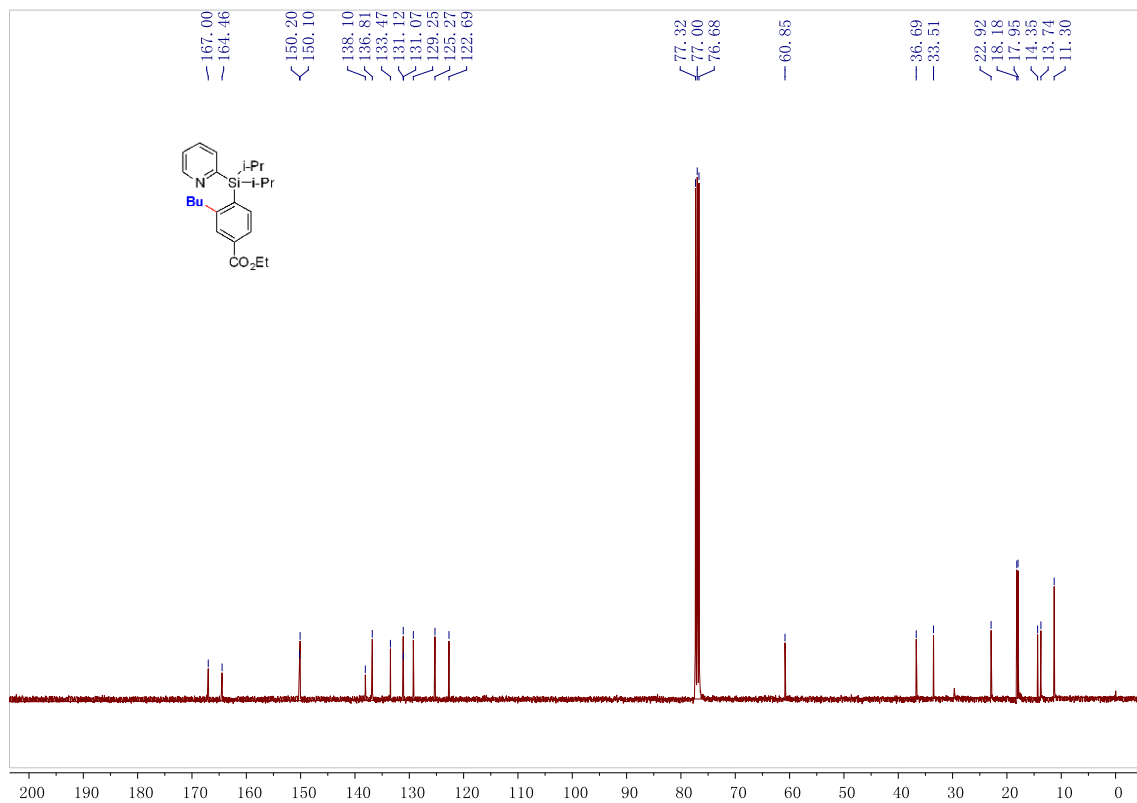


ethyl 3-butyl-4-(diisopropyl(pyridin-2-yl)silyl)benzoate (3la)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

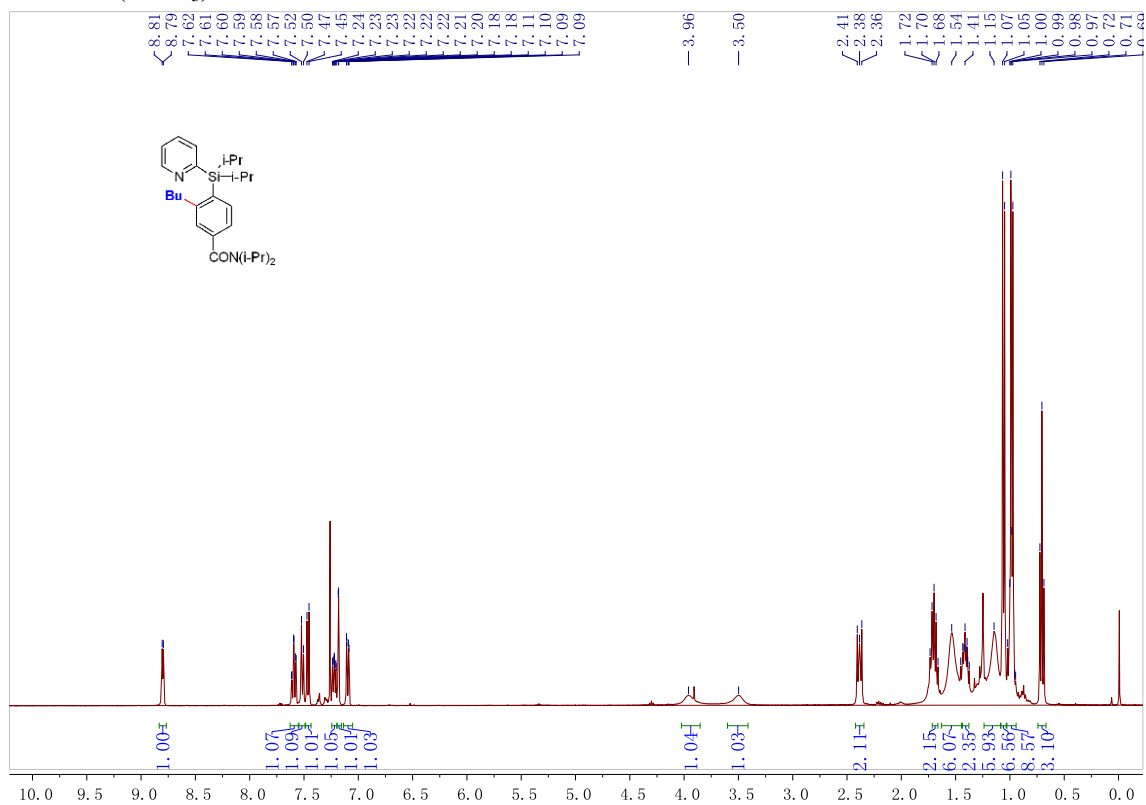


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

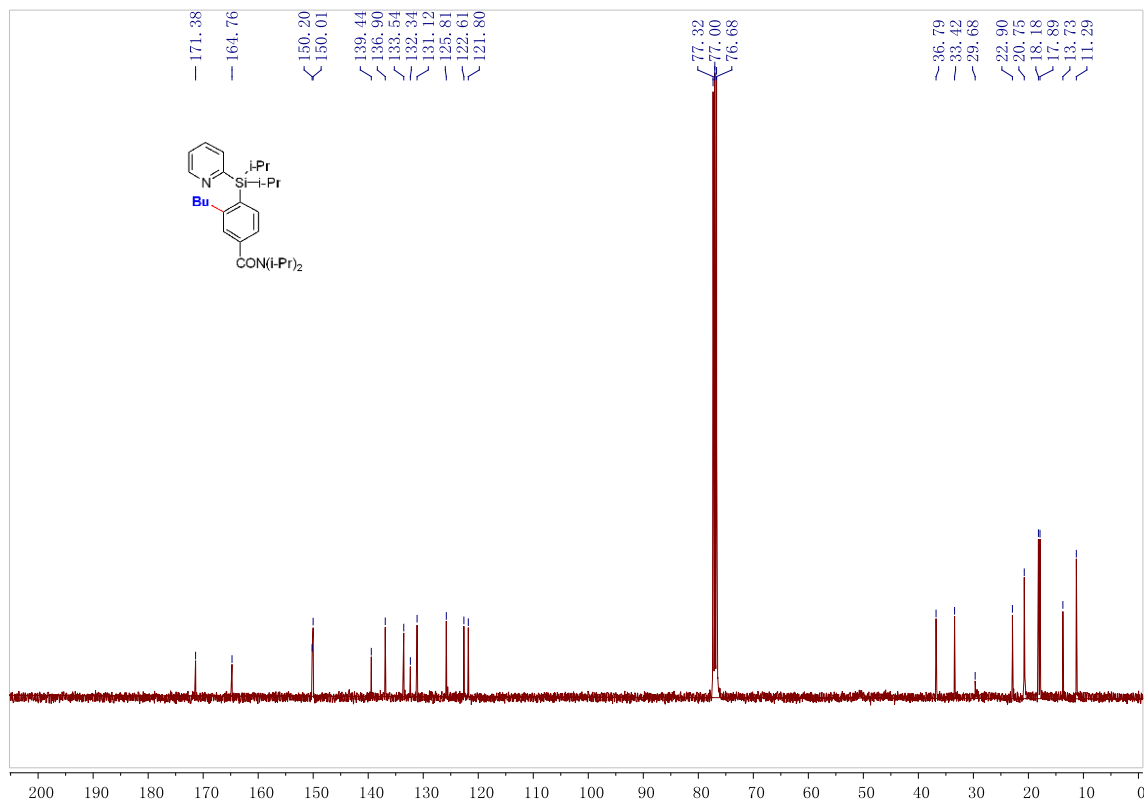


### 3-butyl-4-(diisopropyl(pyridin-2-yl)silyl)-*N,N*-diisopropylbenzamide (3ma)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )



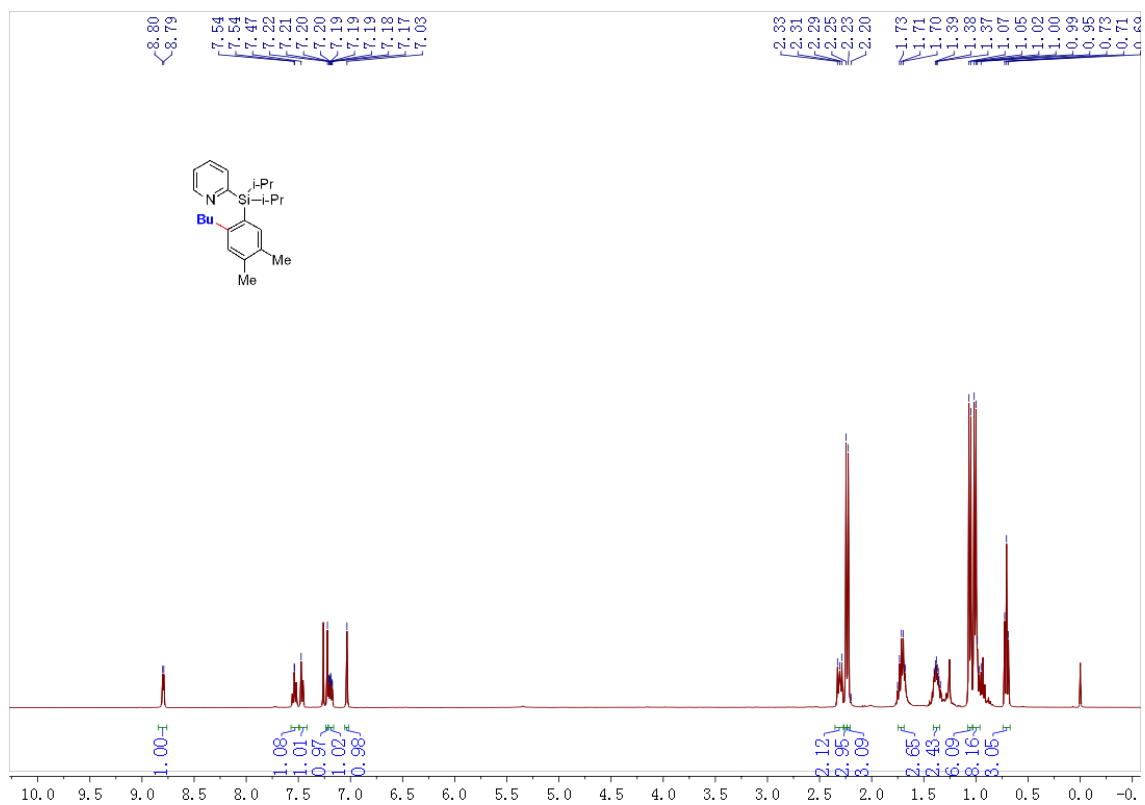
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )



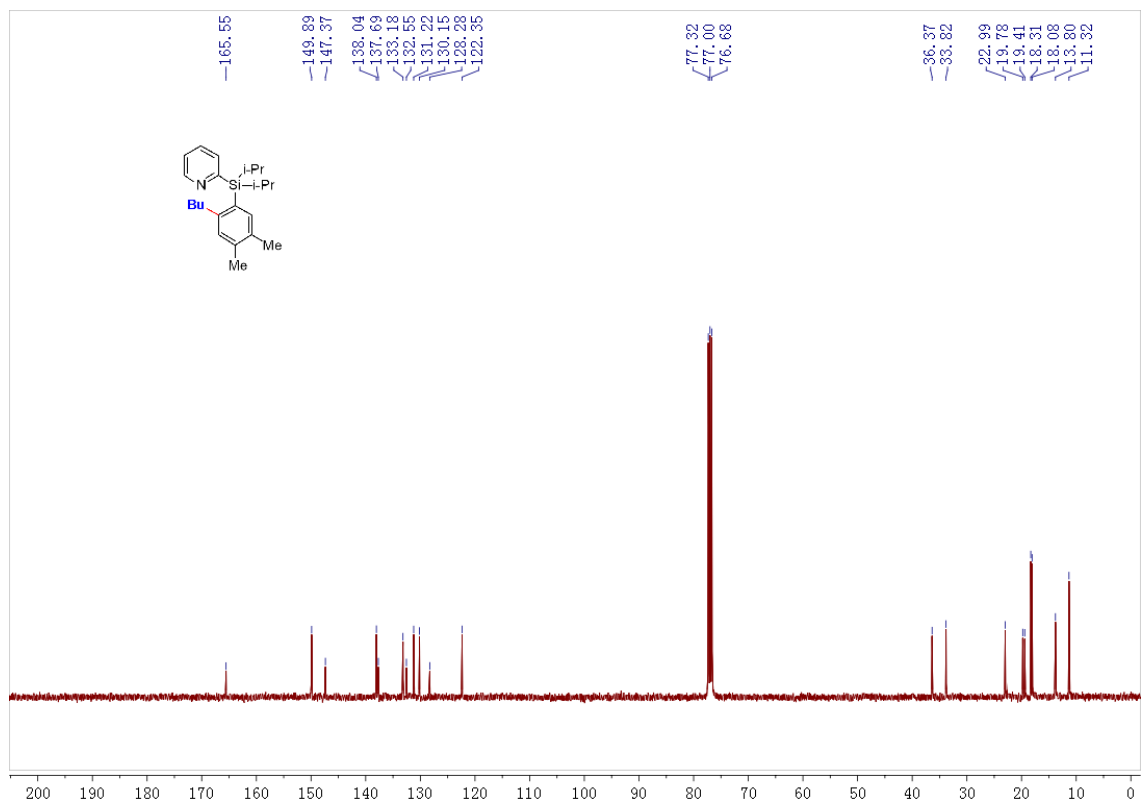


## 2-((2-butyl-4,5-dimethylphenyl)diisopropylsilyl)pyridine (3na)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

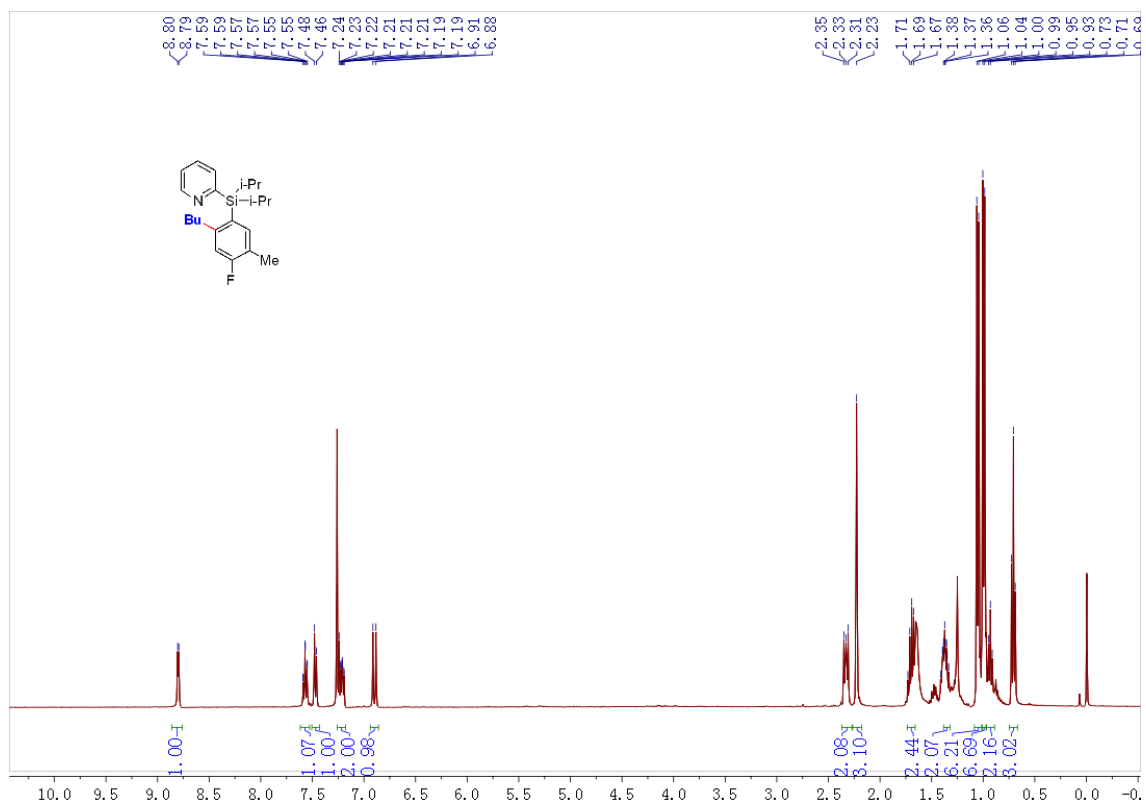


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

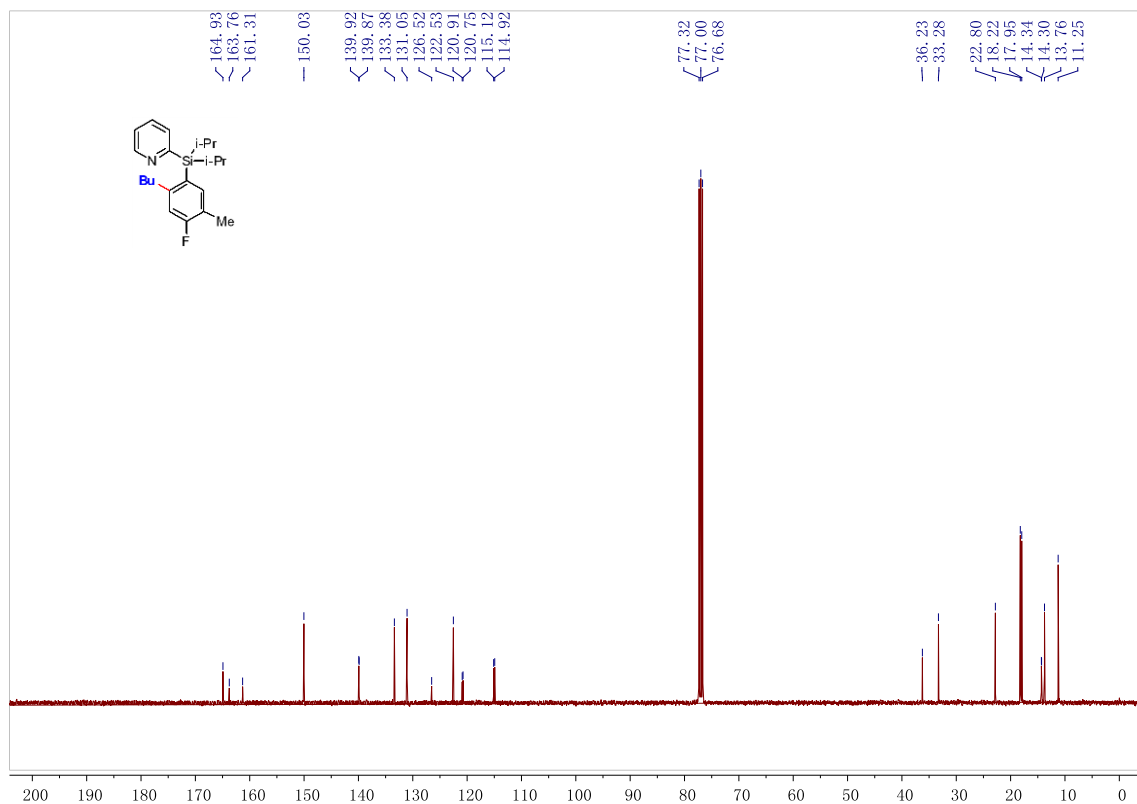


## 2-((2-butyl-4-fluoro-5-methylphenyl)diisopropylsilyl)pyridine (30a)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

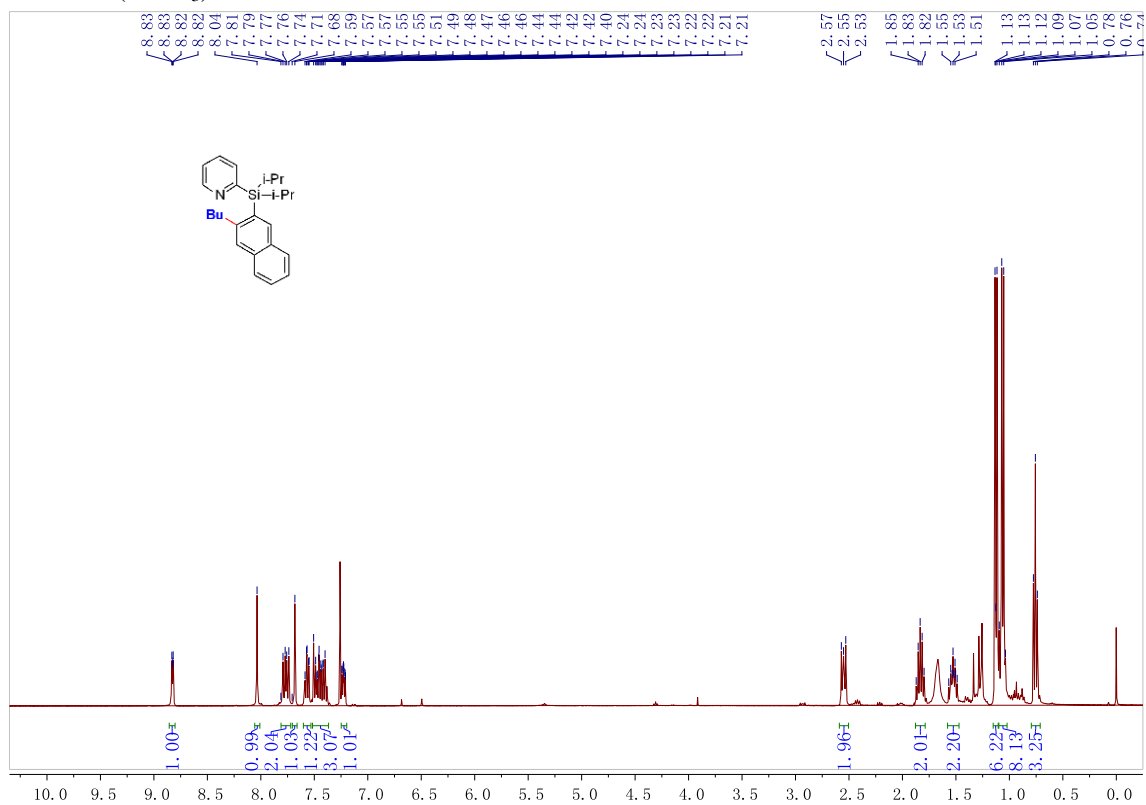


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

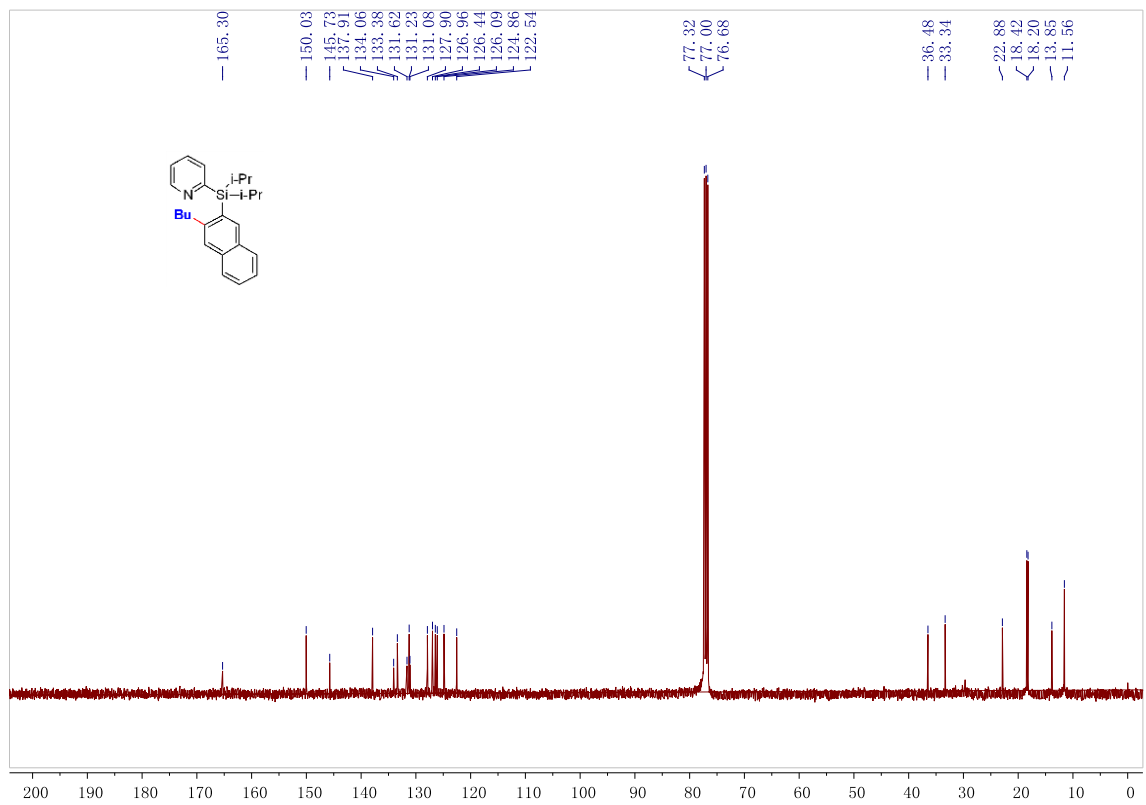


## 2-((3-butyl-naphthalen-2-yl)diisopropylsilyl)pyridine (3pa)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

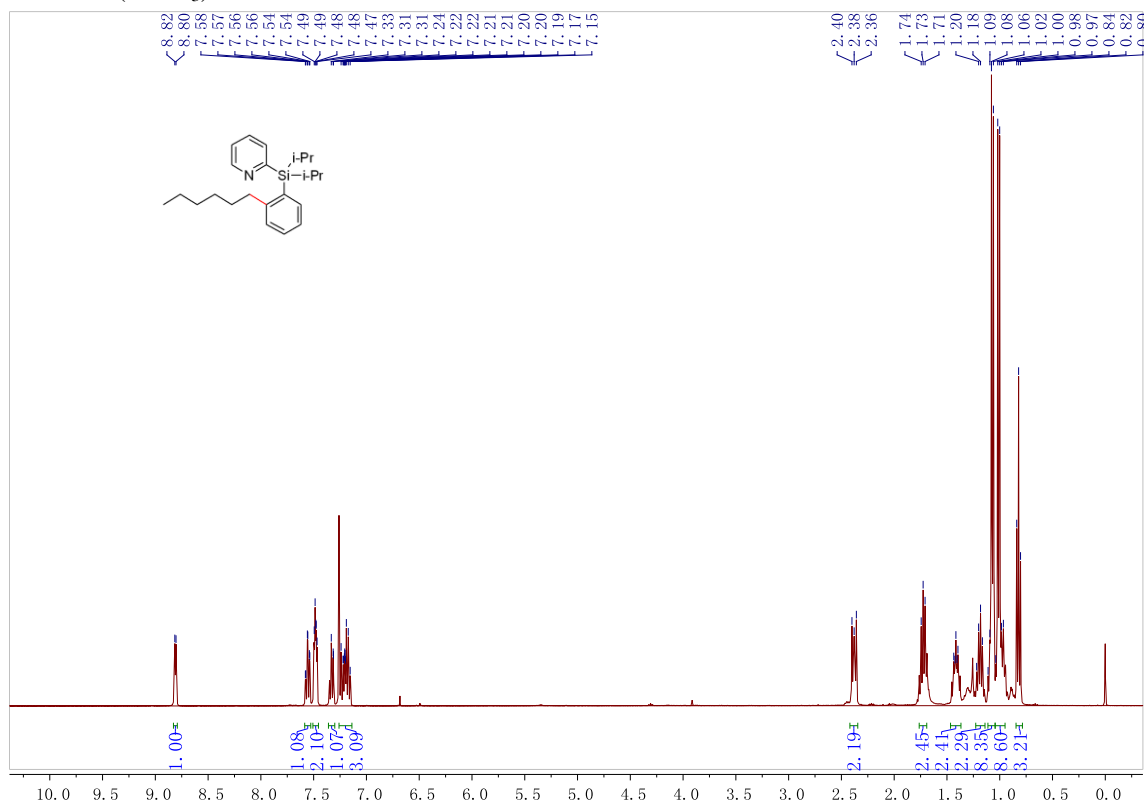


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

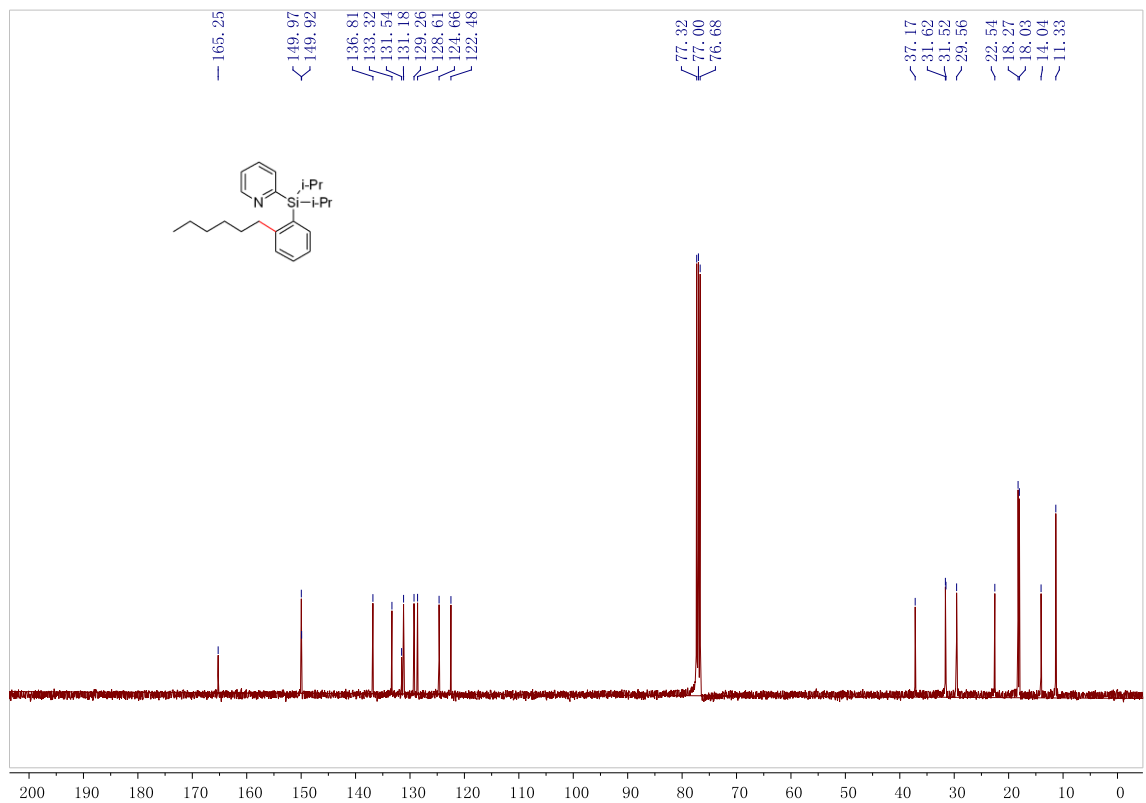


## 2-((2-hexylphenyl)diisopropylsilyl)pyridine (3ab)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

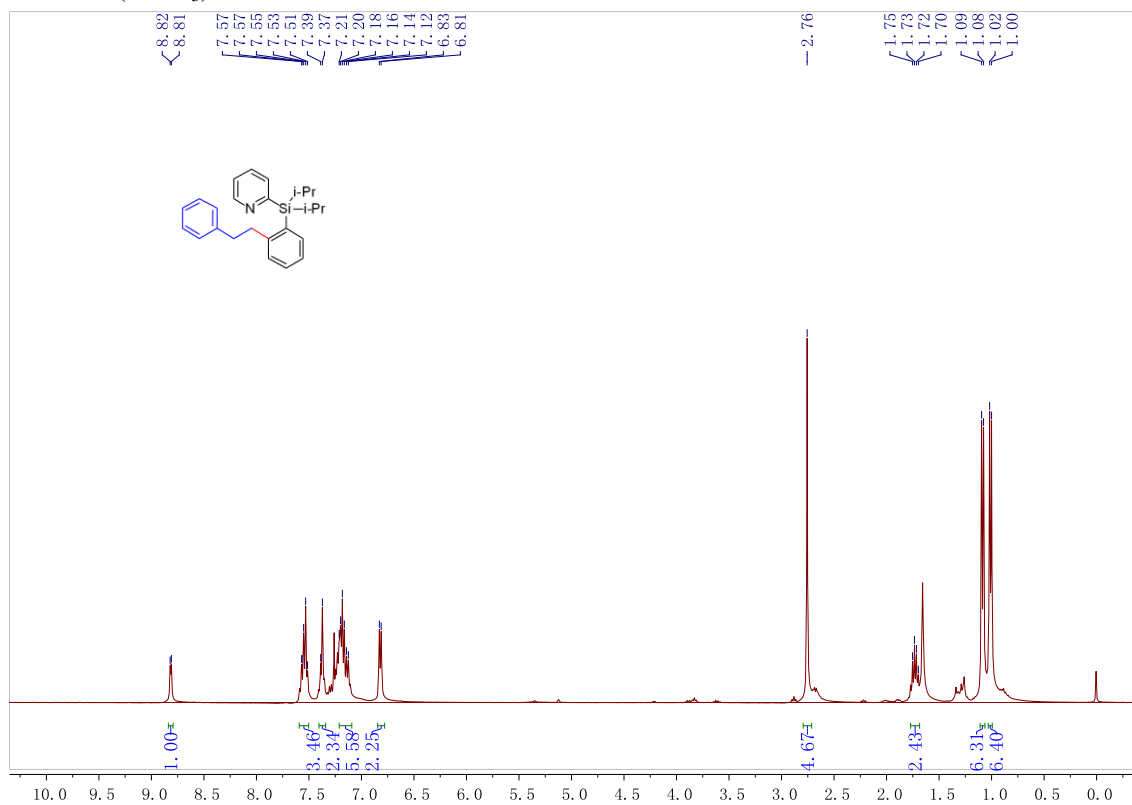


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

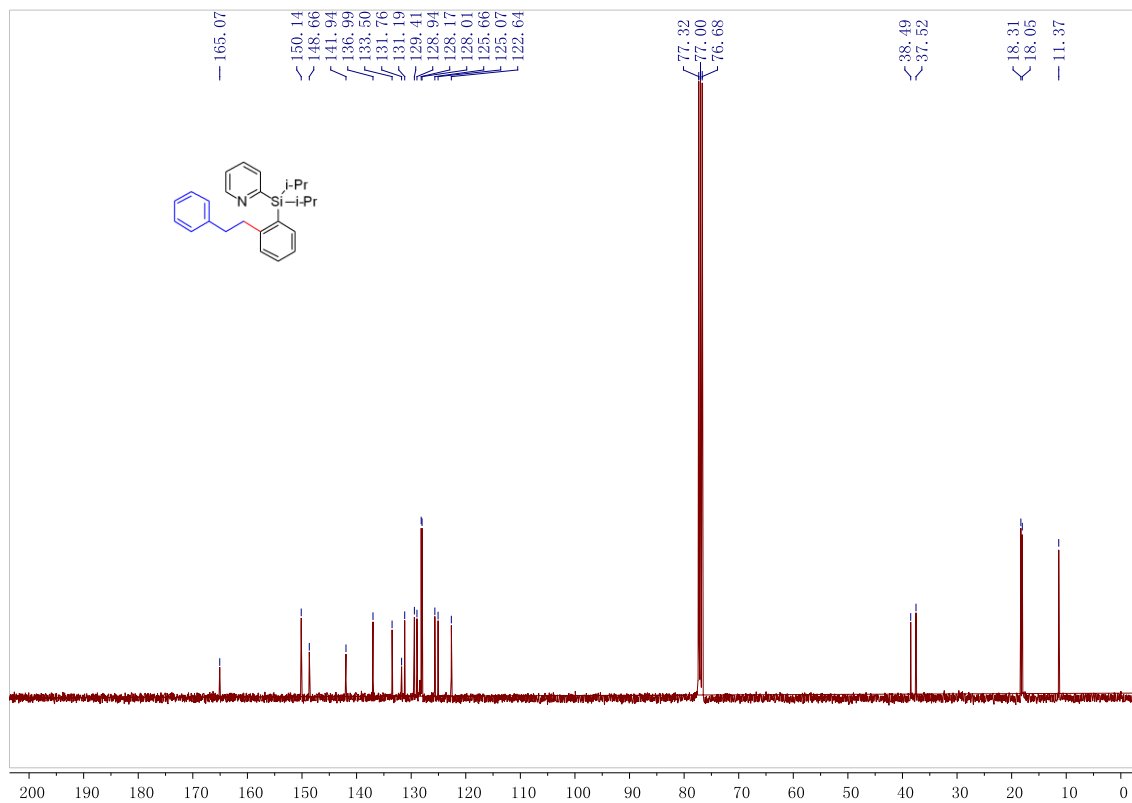


## 2-(diisopropyl(2-phenethylphenyl)silyl)pyridine (3ac)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

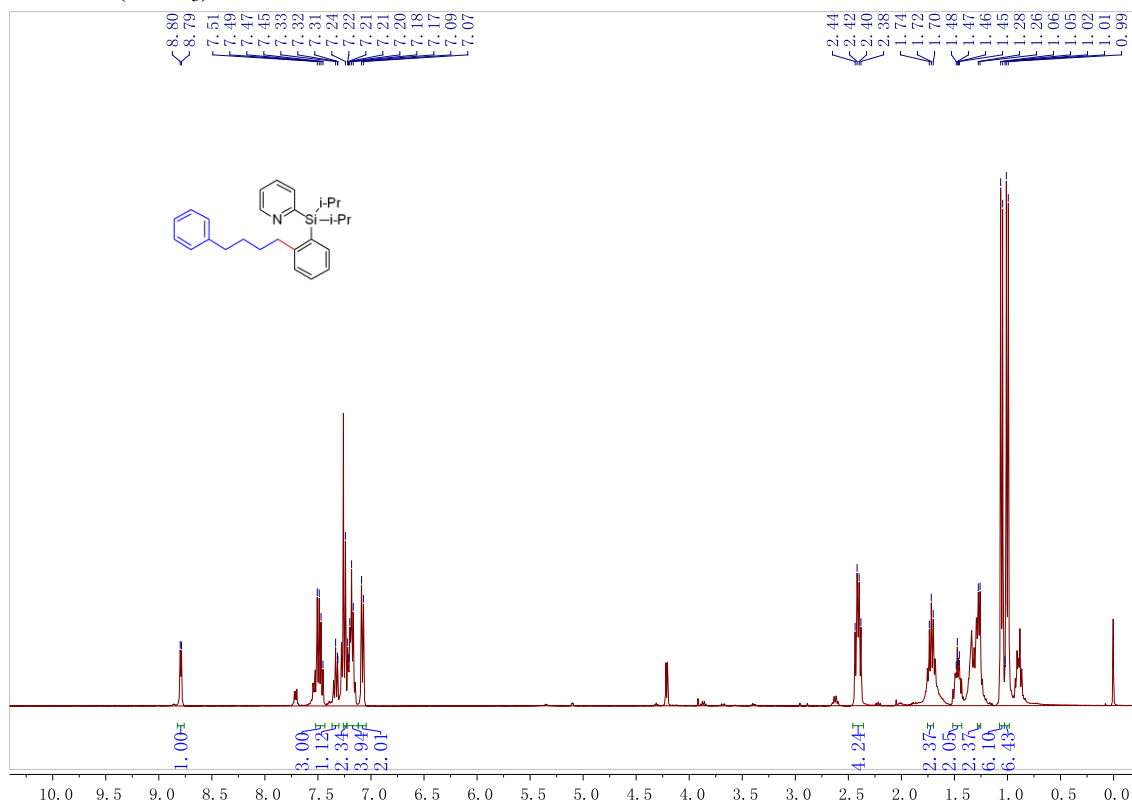


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

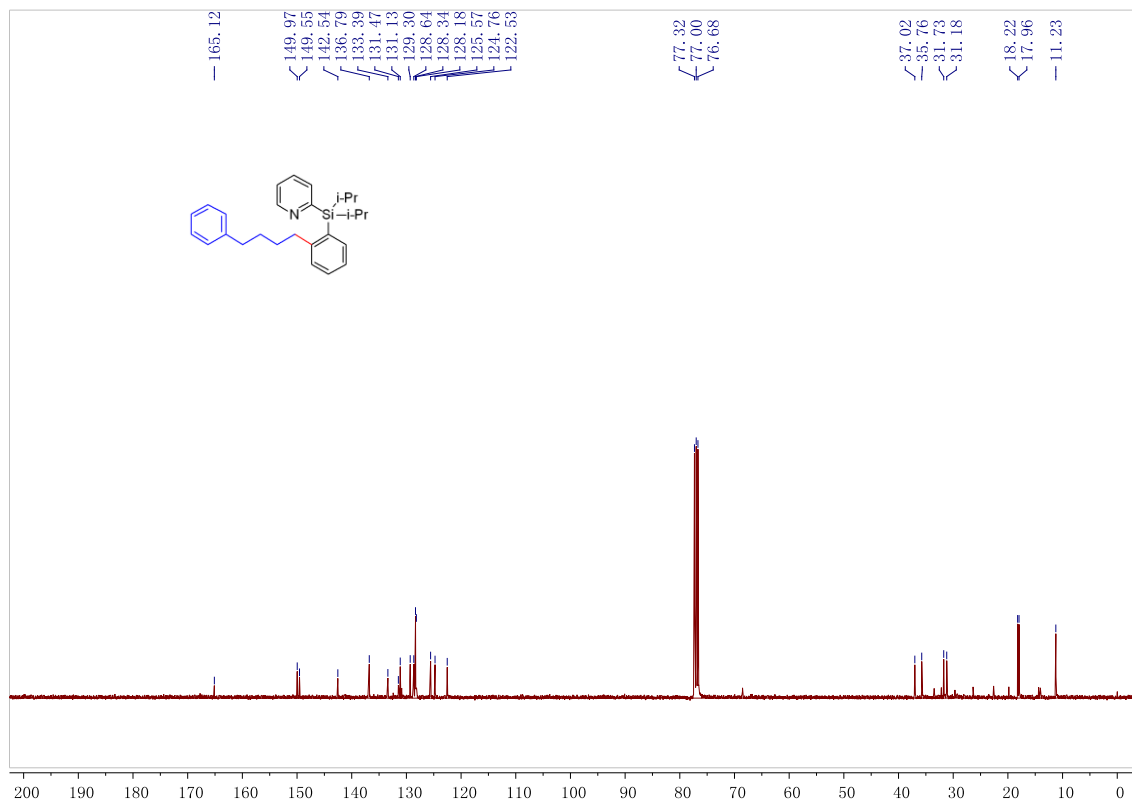


## 2-(diisopropyl(2-(4-phenylbutyl)phenyl)silyl)pyridine (3ad)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

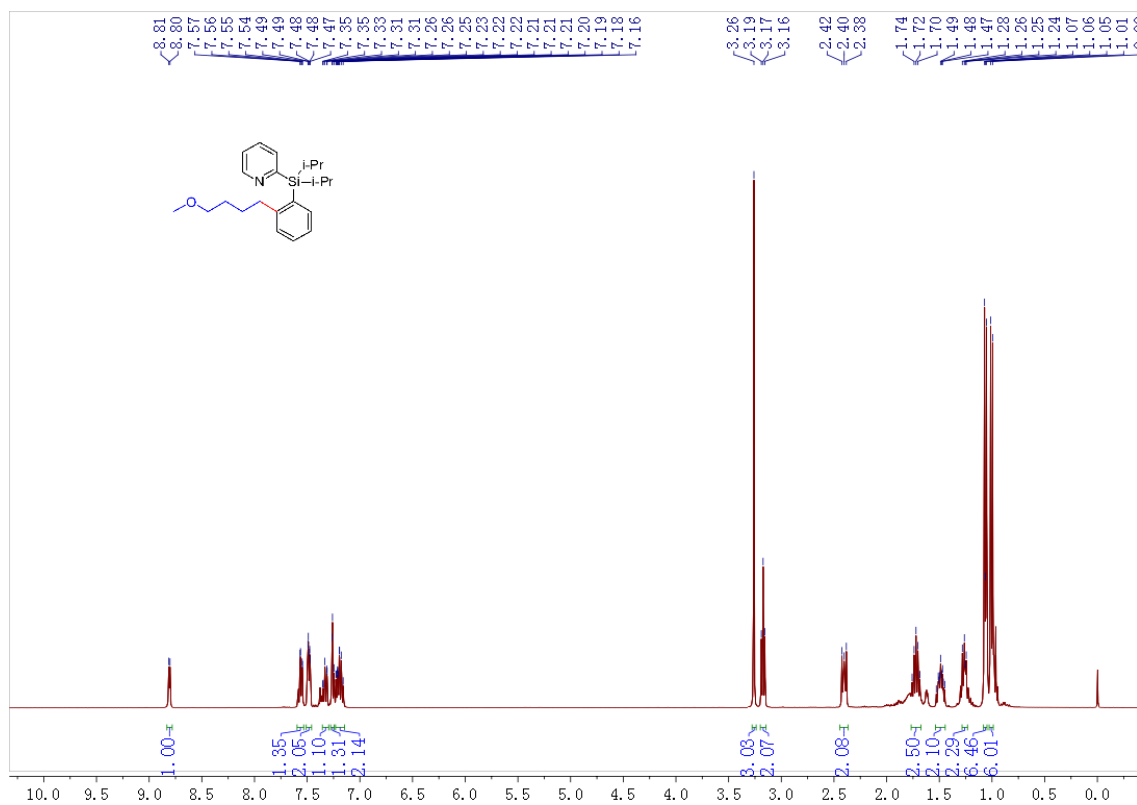


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

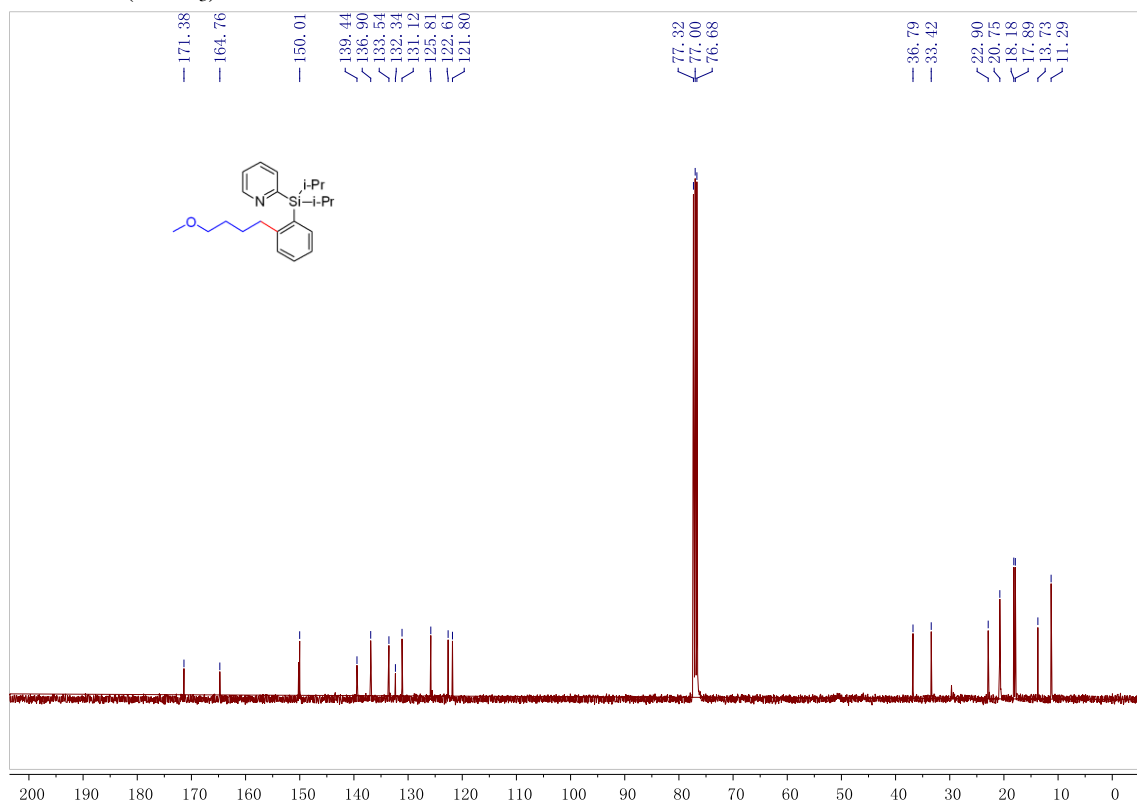


## 2-(diisopropyl(2-(4-methoxybutyl)phenyl)silyl)pyridine (3ae)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

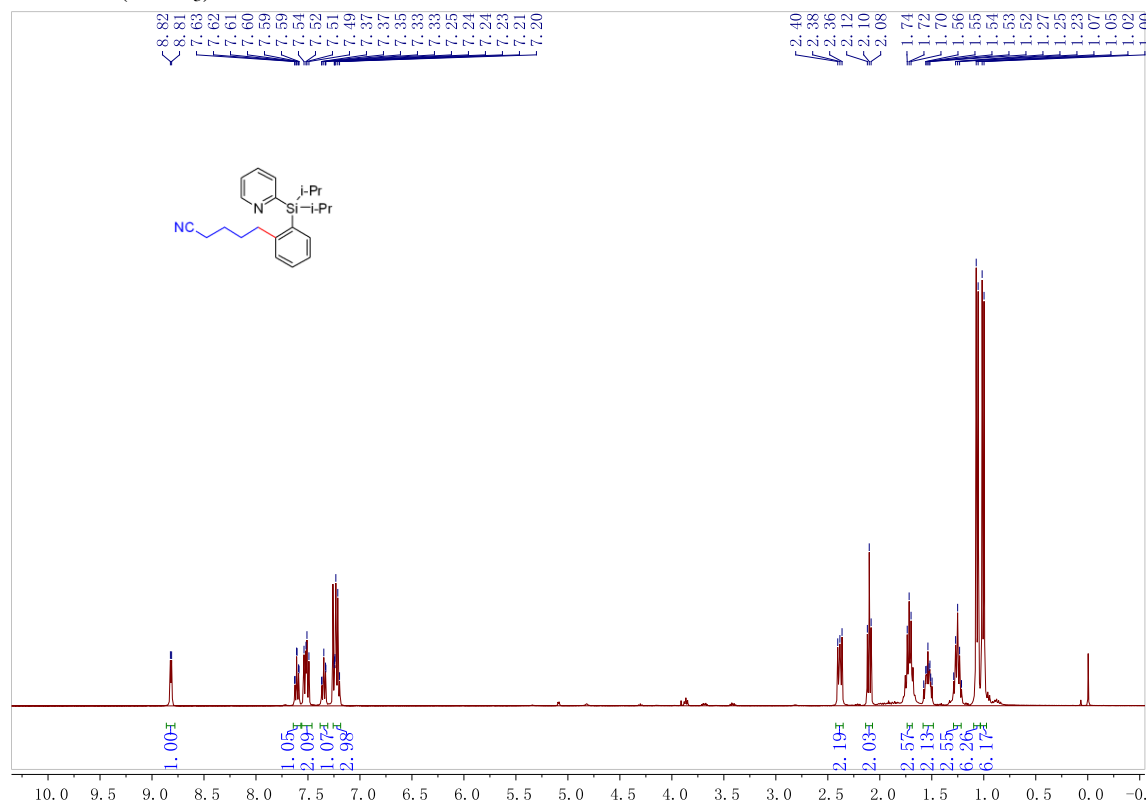


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

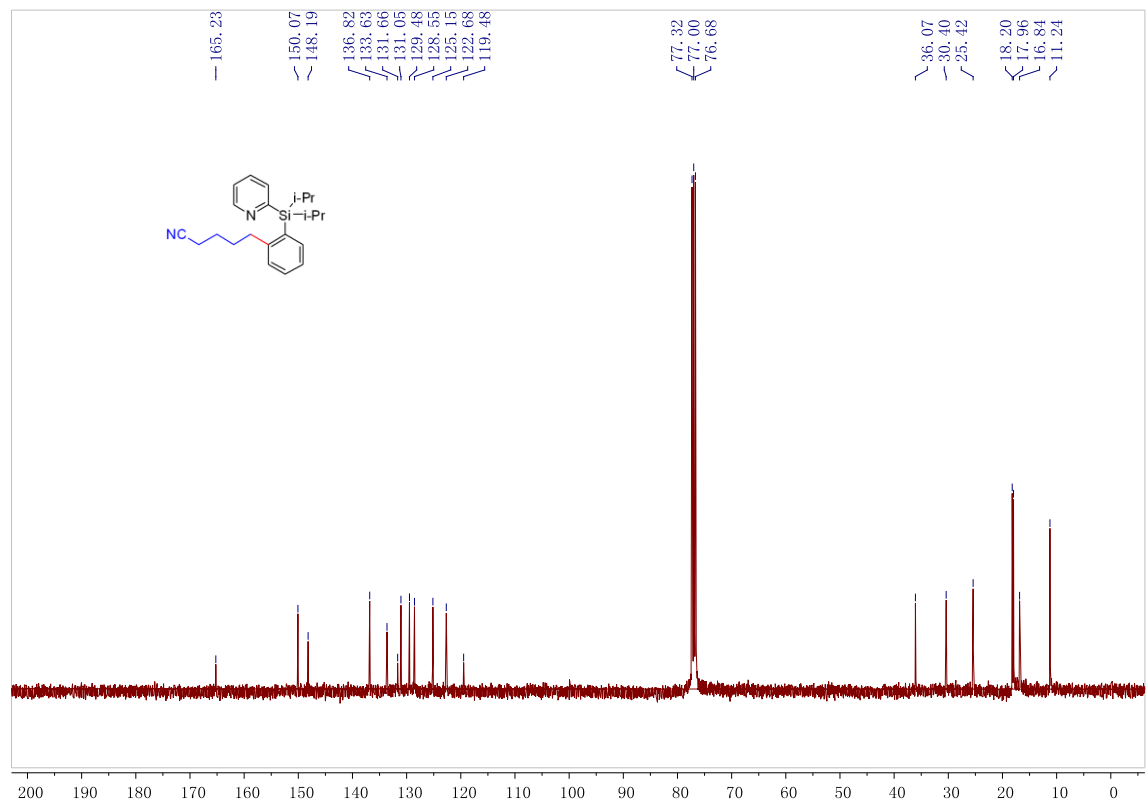


### 5-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)pentanenitrile (3af)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )



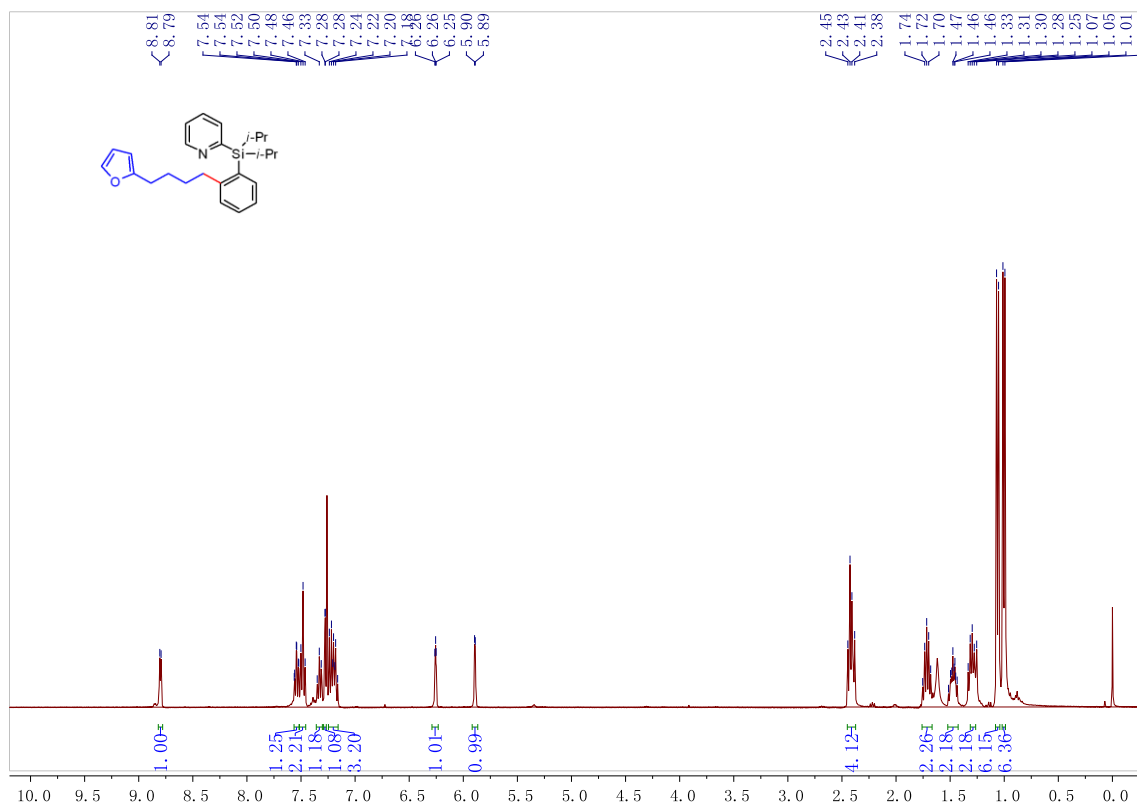
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )



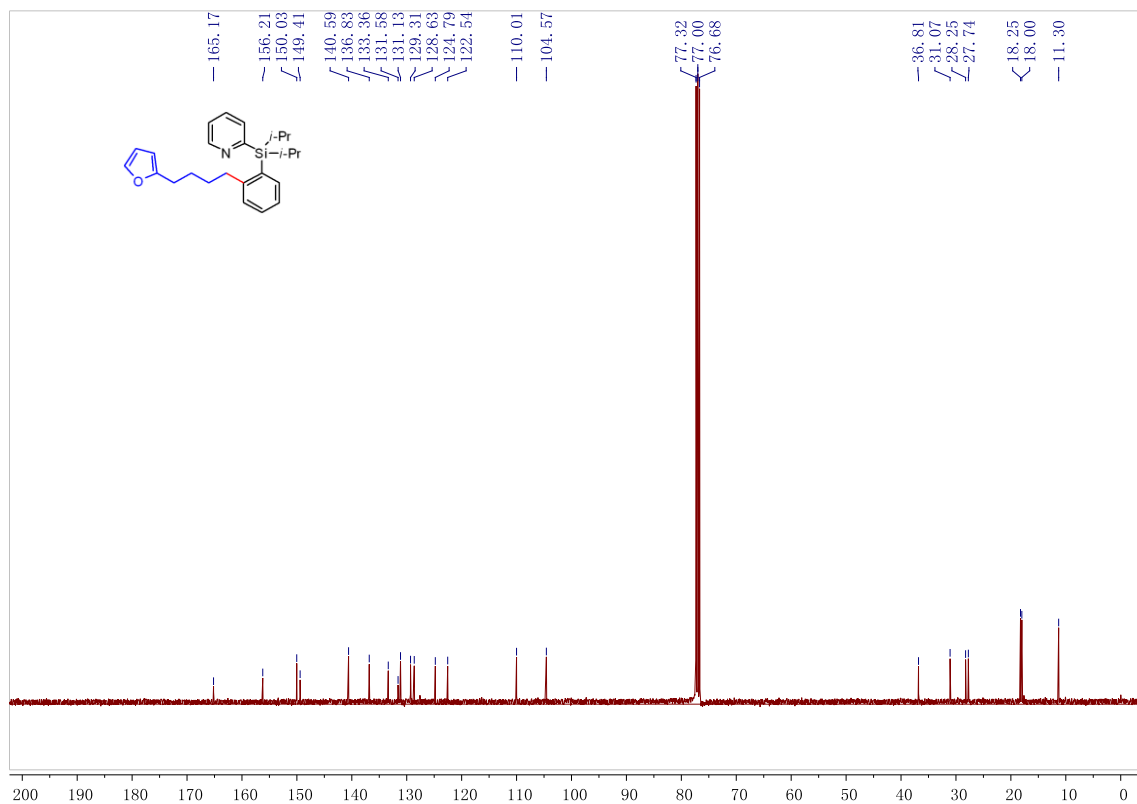


## 2-((2-(4-(furan-2-yl)butyl)phenyl)diisopropylsilyl)pyridine (3ag)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

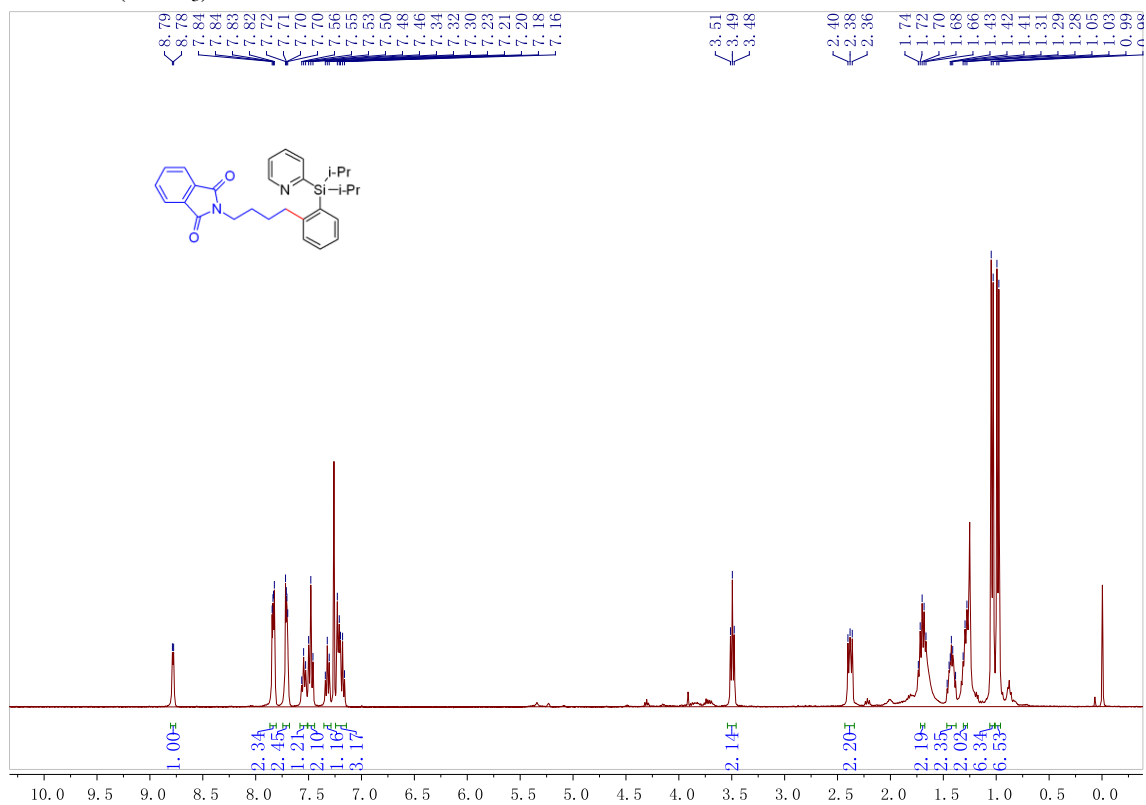


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

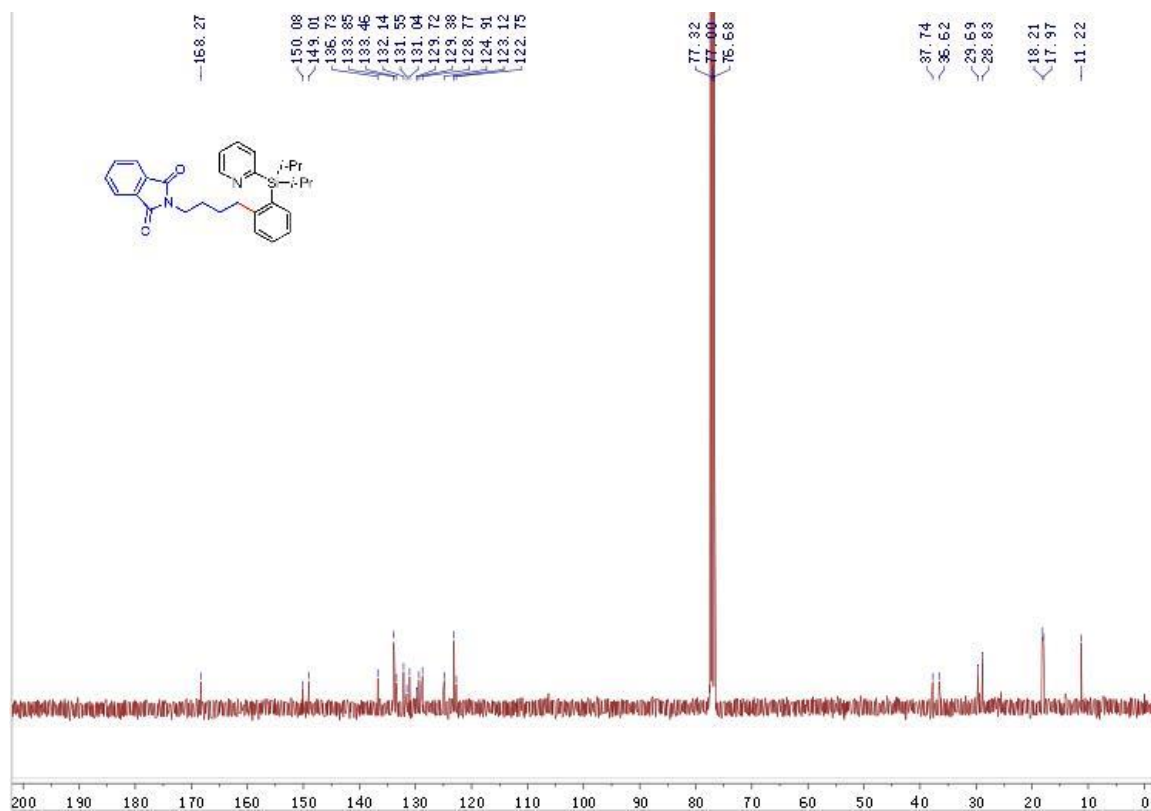


## 2-(4-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)butyl)isoindoline-1,3-dione (3ah)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

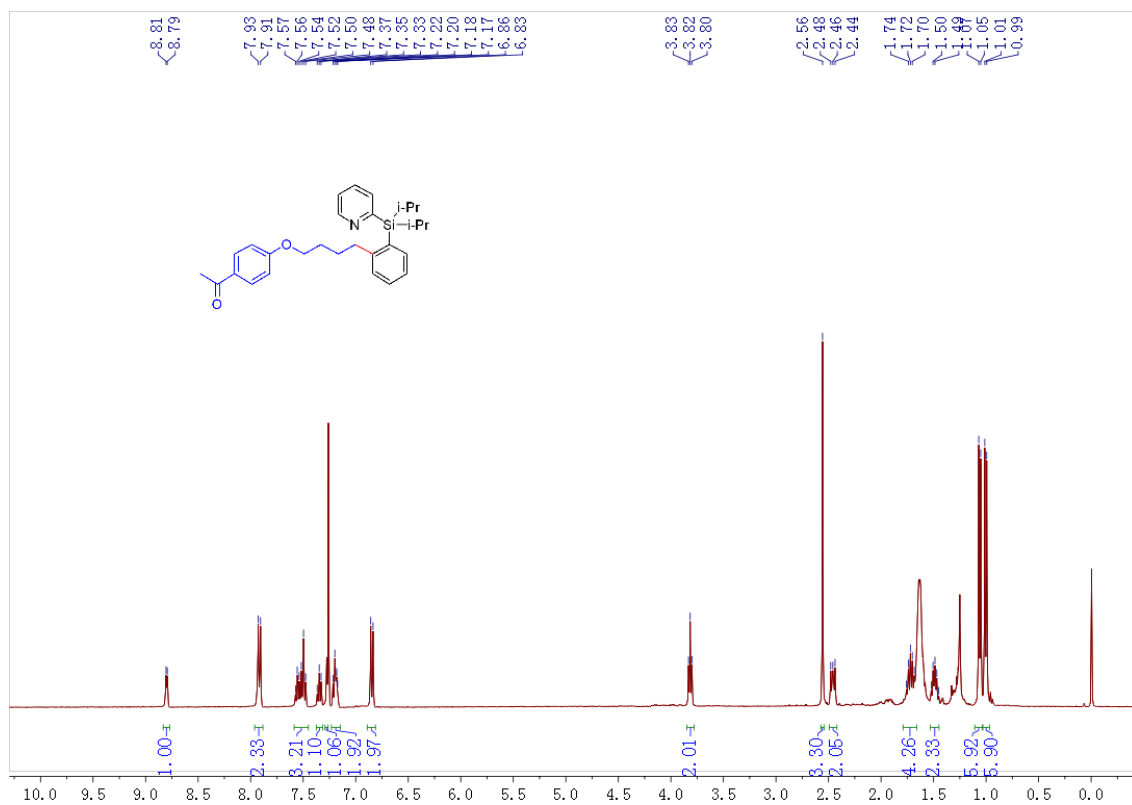


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

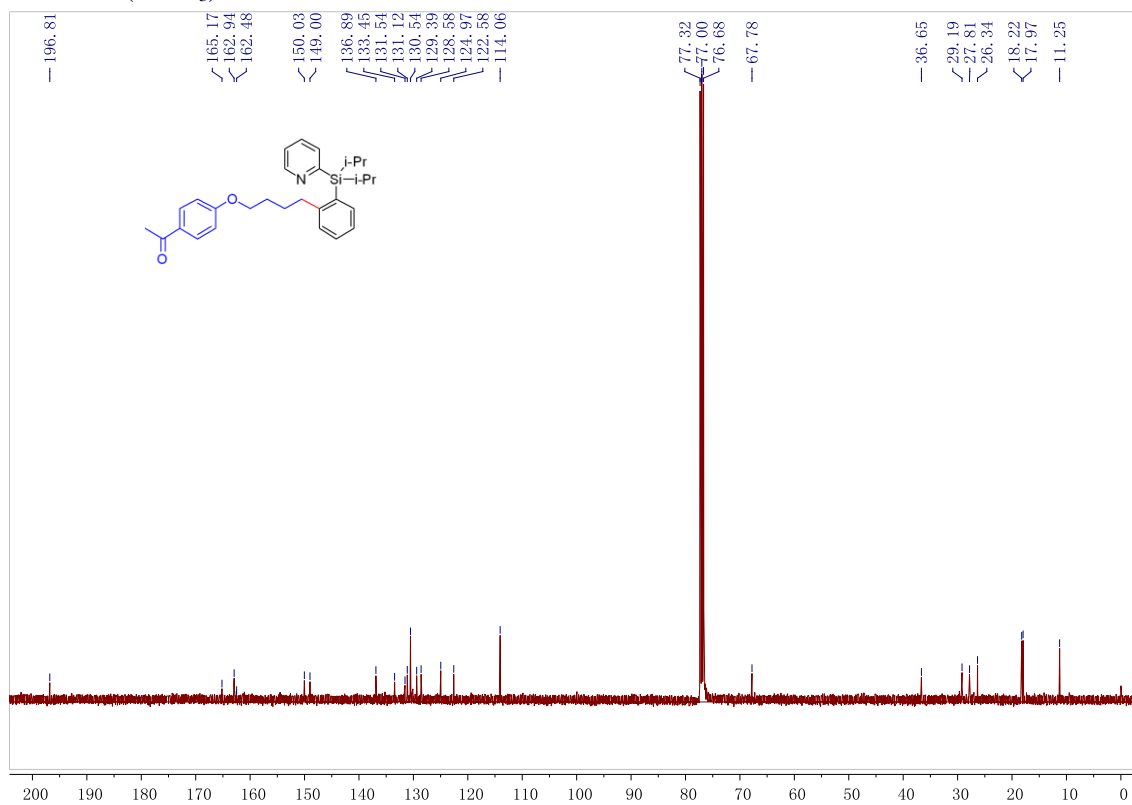


### 1-(4-(4-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)butoxy)phenyl)ethanone (3ai)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

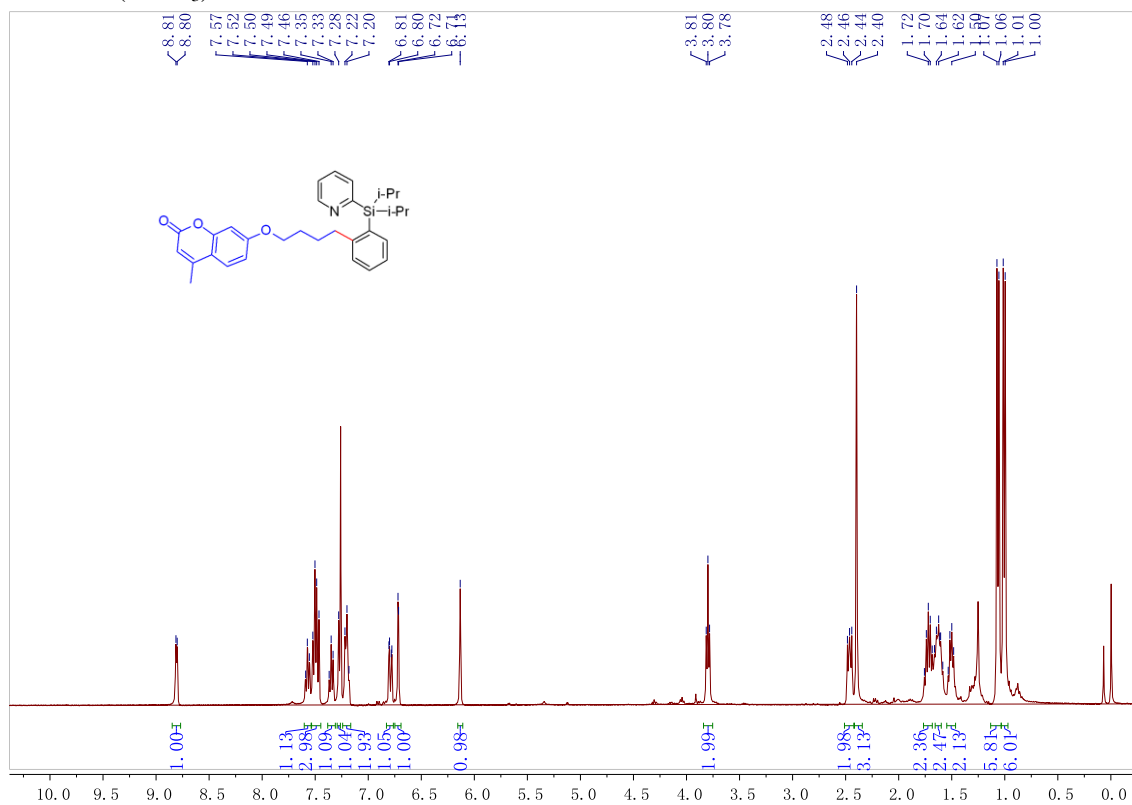


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

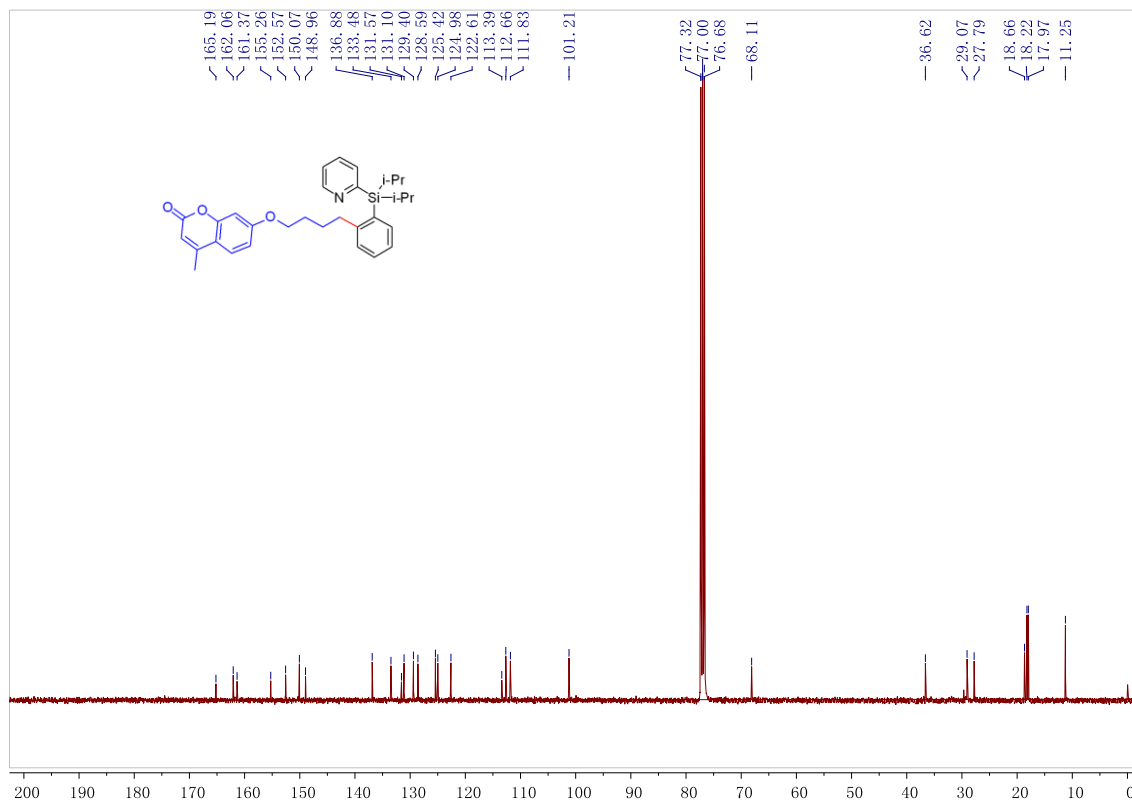


7-(4-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)butoxy)-4-methyl-2H-chromen-2-one (3aj)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

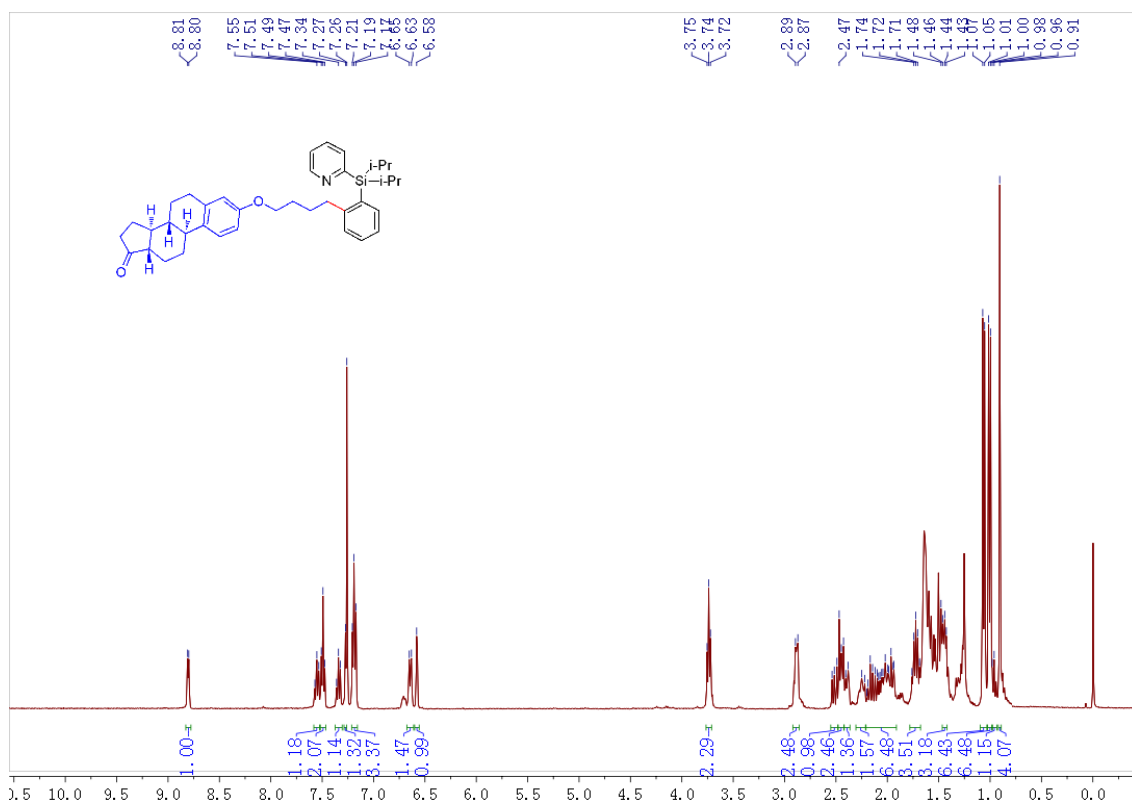


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

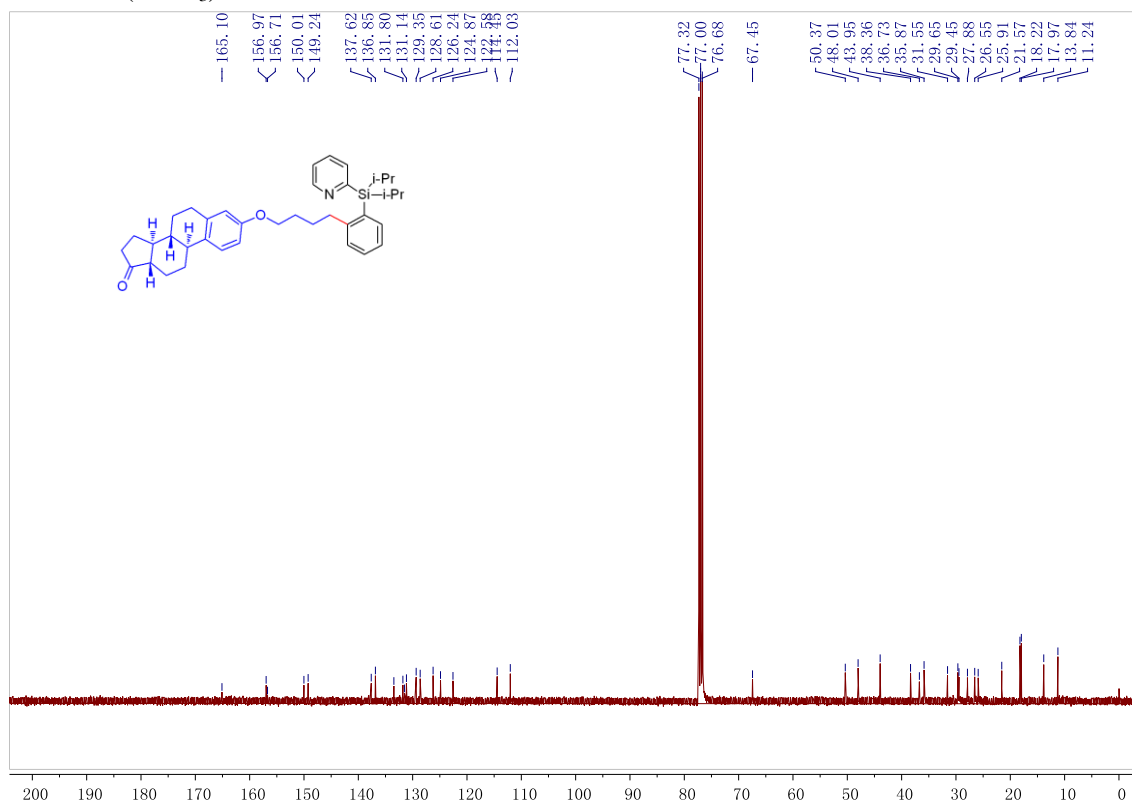


**(8S,9S,13S,14S)-3-(4-(2-(diisopropyl(pyridin-2-yl)silyl)phenyl)butoxy)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (3ak)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>)

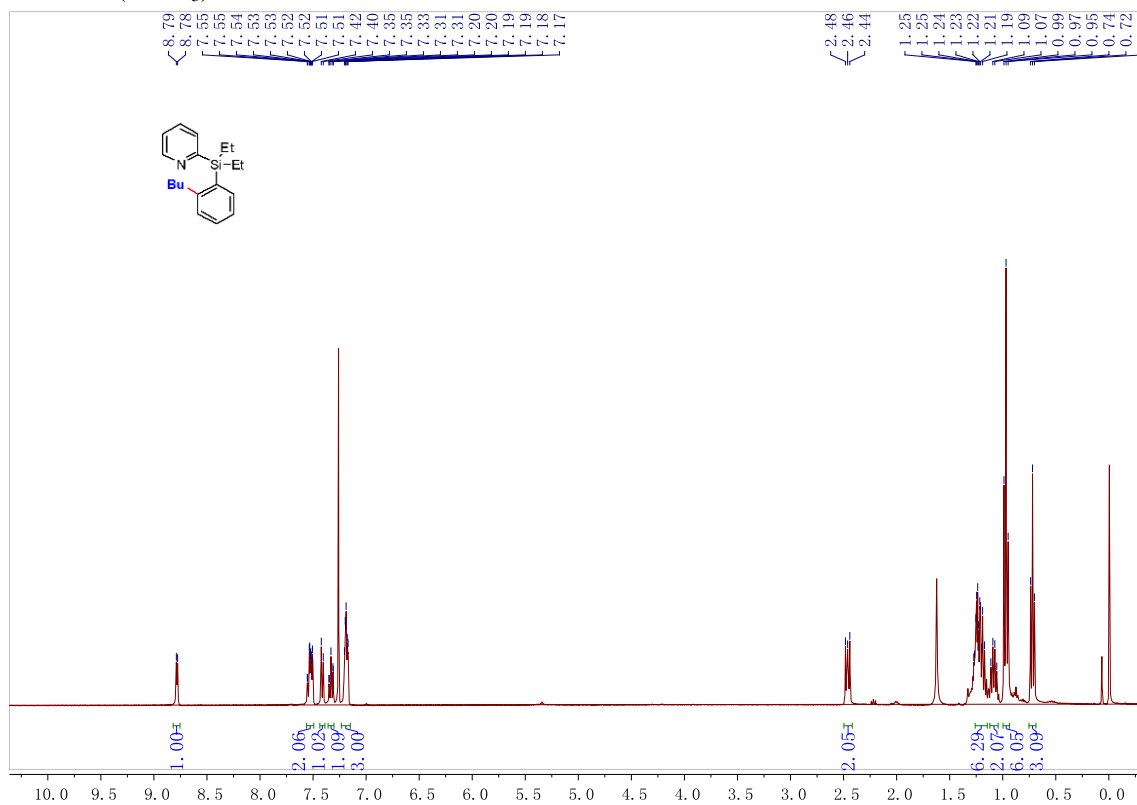


<sup>13</sup>C NMR (CDCl<sub>3</sub>)

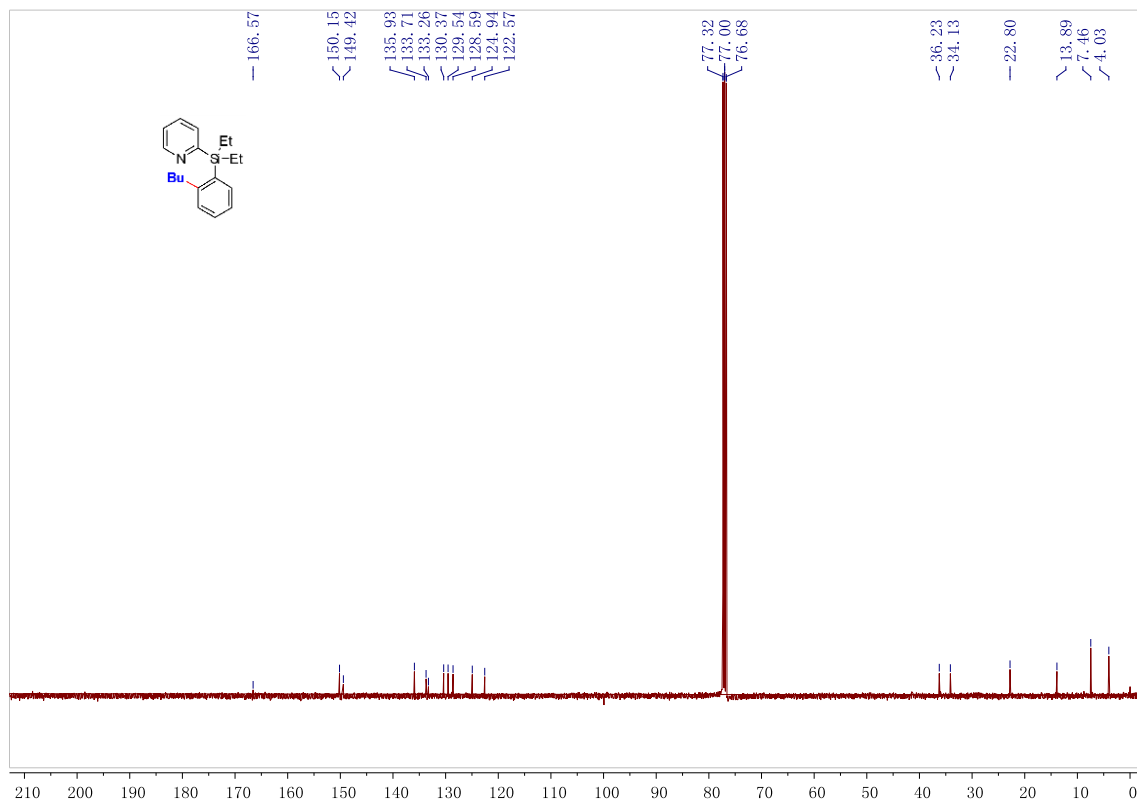


## 2-((2-butylphenyl)diethylsilyl)pyridine (5aa)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

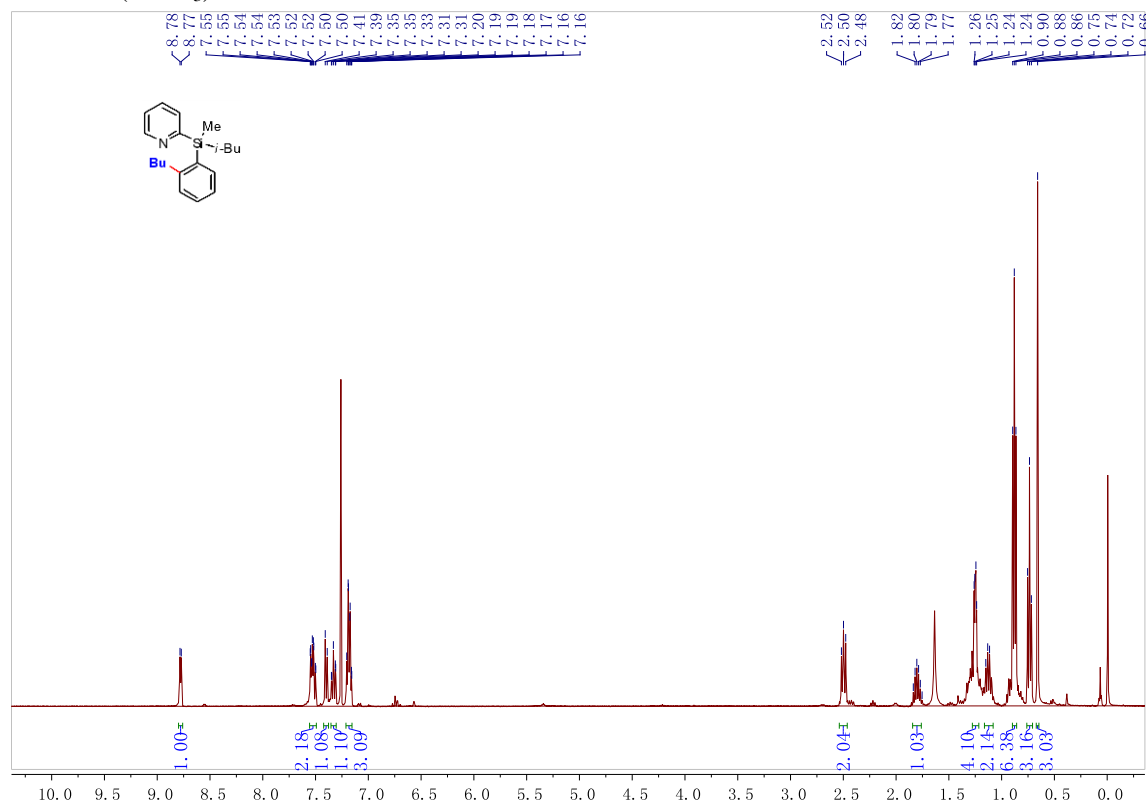


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

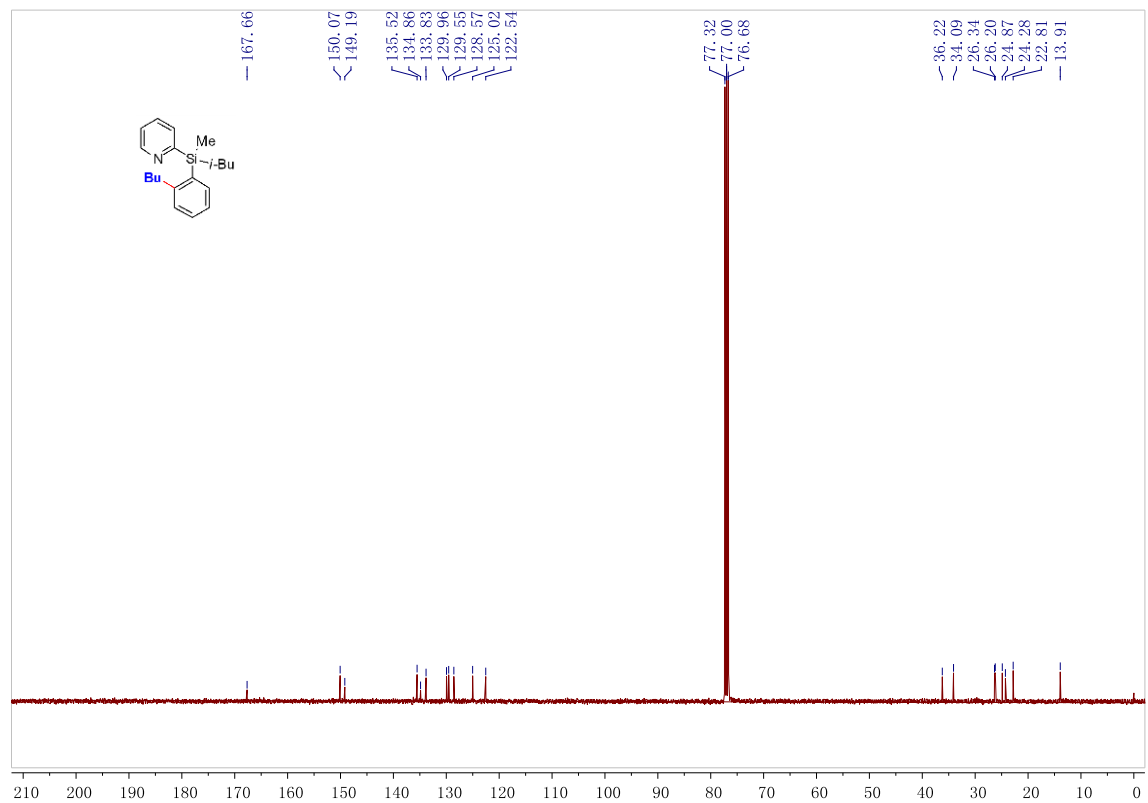


## 2-((2-butylphenyl)(isobutyl)(methyl)silyl)pyridine (5ba)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

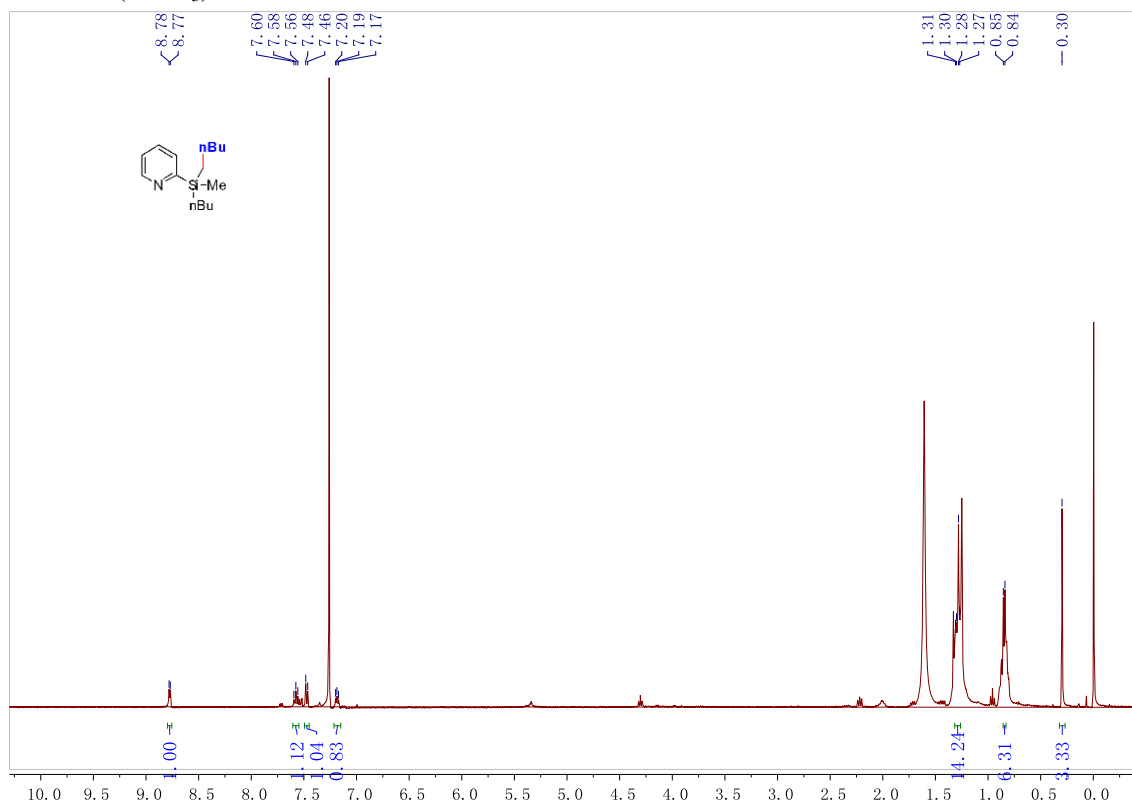


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

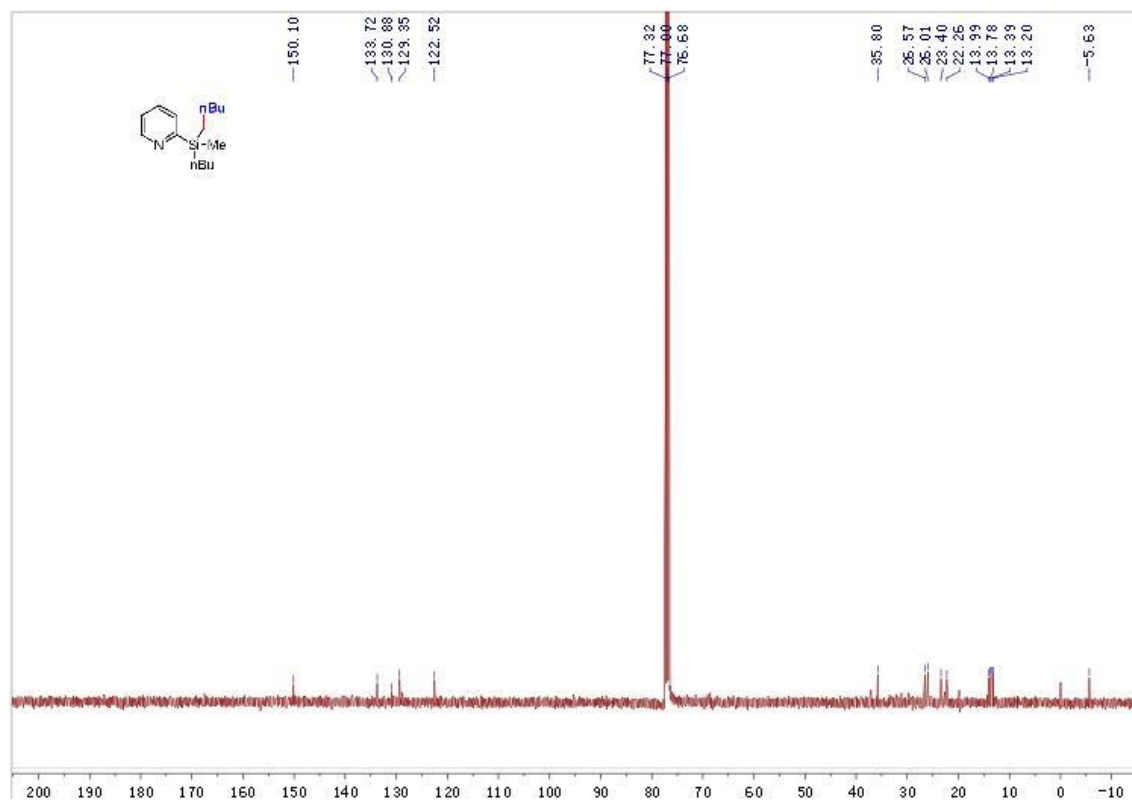


## 2-(butyl(methyl)(pentyl)silyl)pyridine (7aa)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )



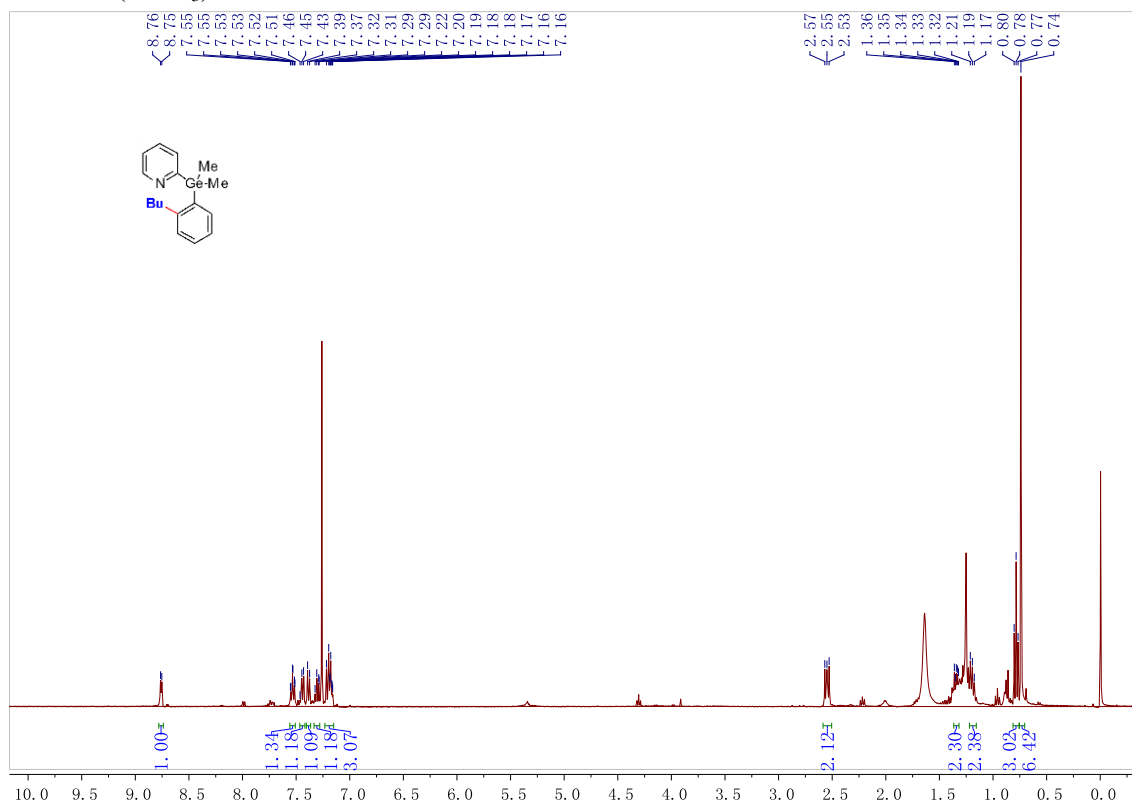
$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )



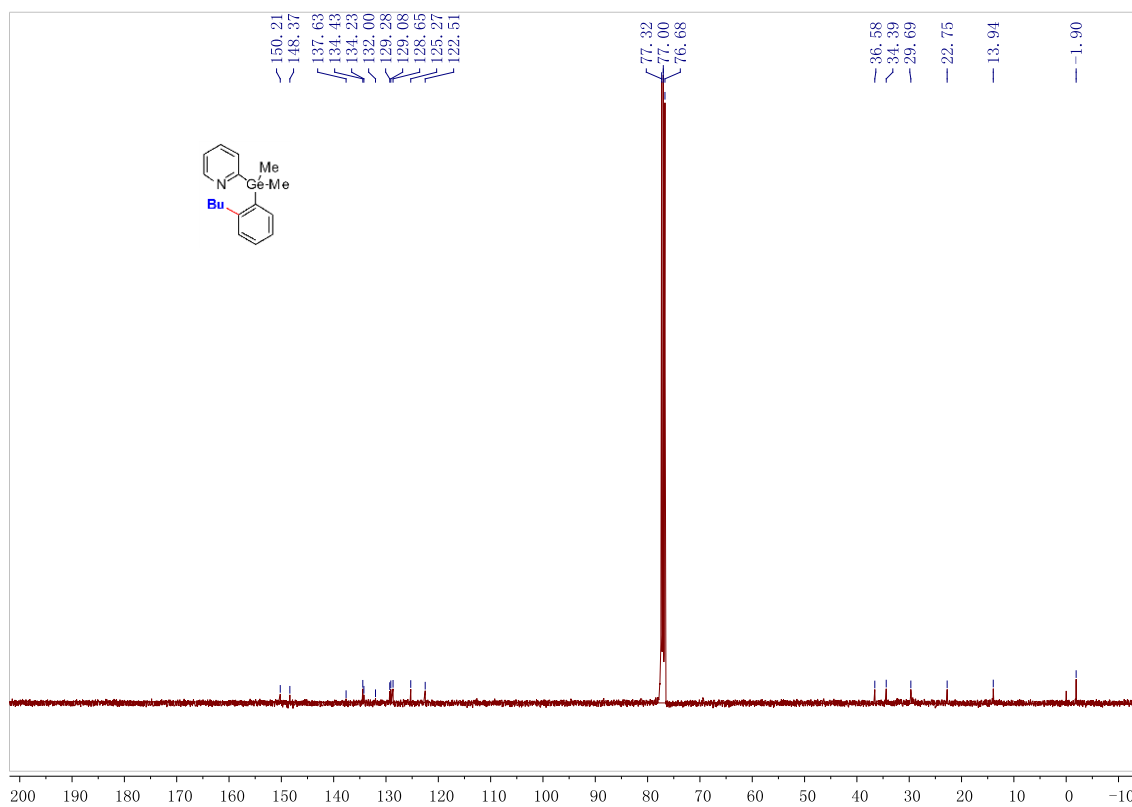


## 2-((2-butylphenyl)dimethylgermyl)pyridine (9aa)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

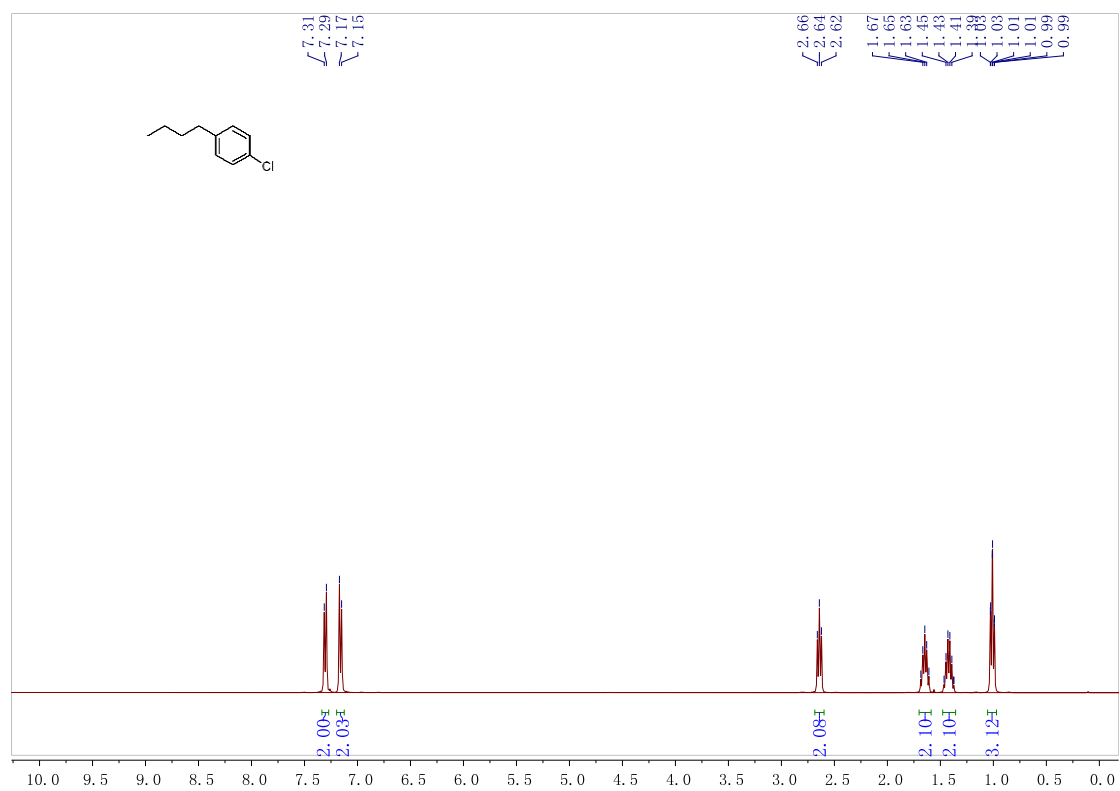


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

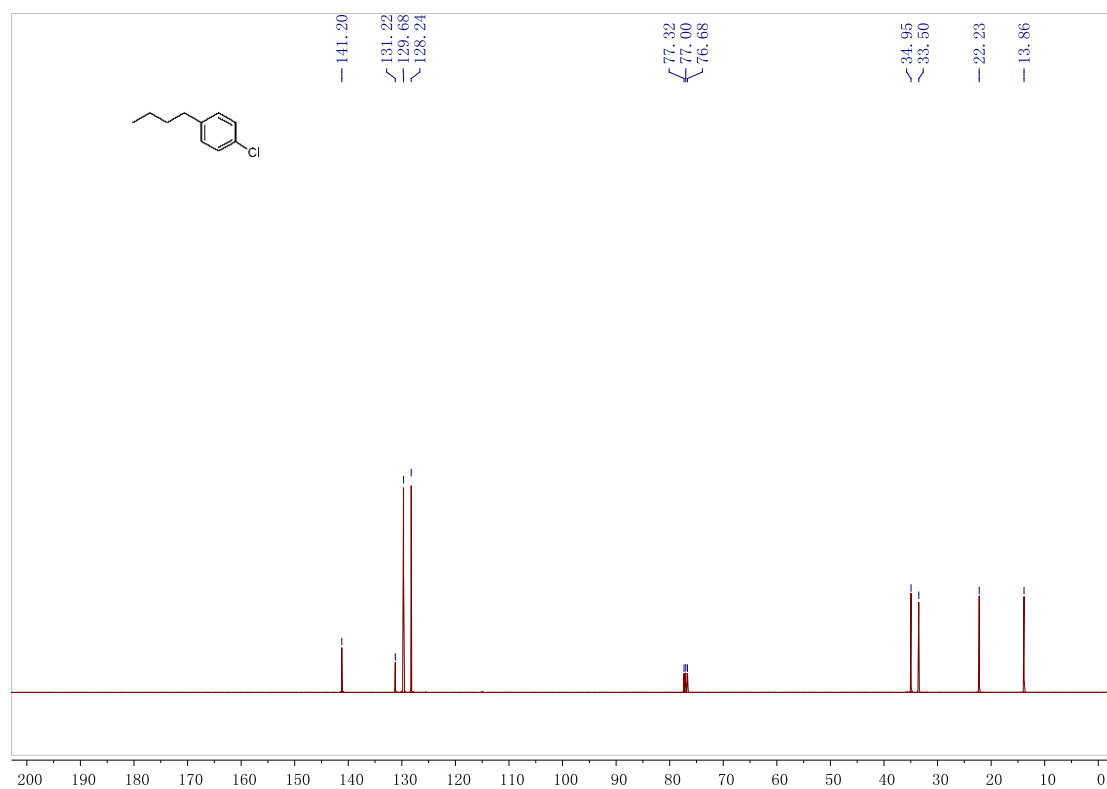


### 1-butyl-4-chlorobenzene (10ia)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )

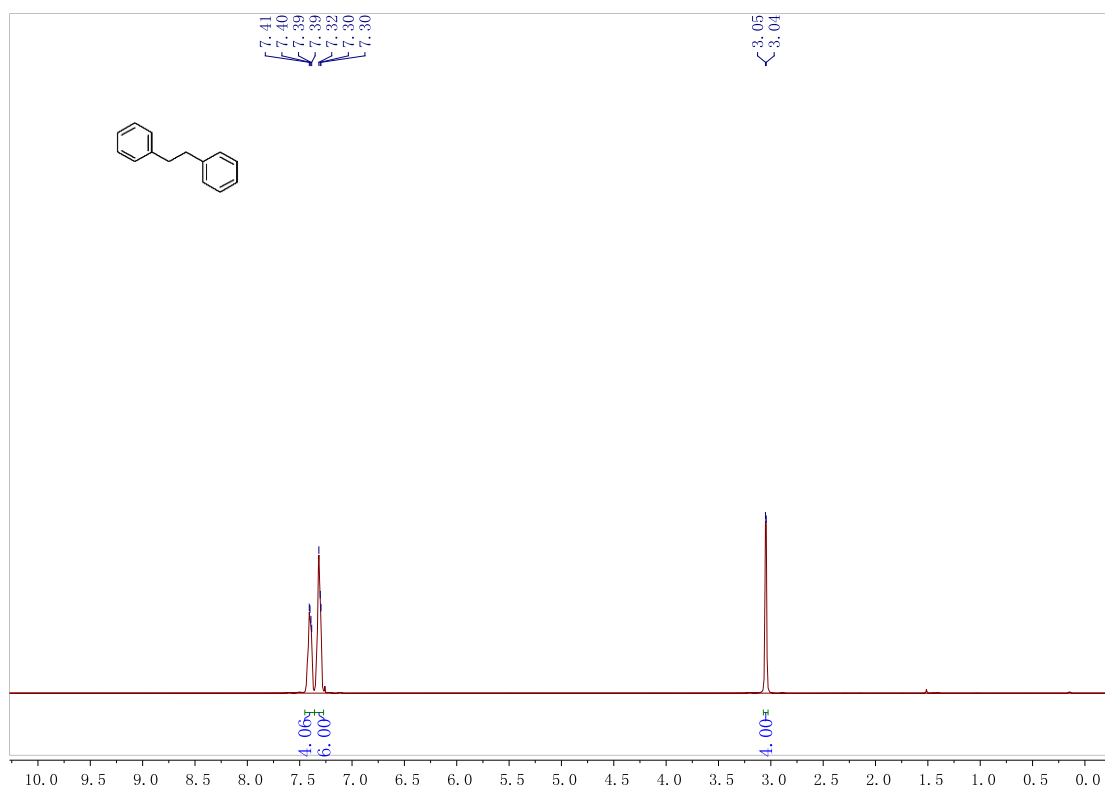


$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )



### 1,2-diphenylethane (10ac)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )

