## Supporting Information

# Efficient Access to 5-Acylated Benzoxasilepines Enabled by NHC/Pd Cooperative Catalysis

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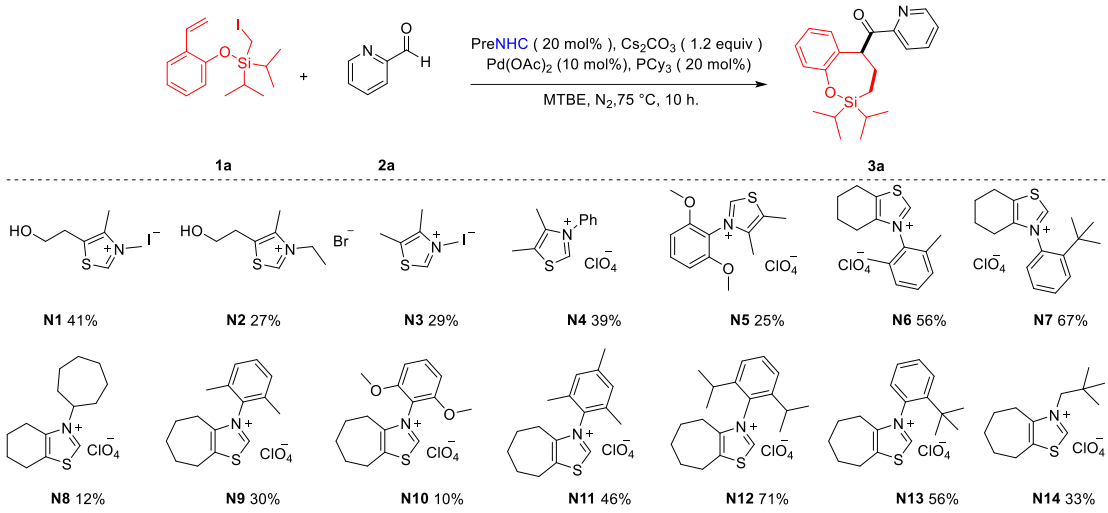
# 1. General information

All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a Brüker ASCEND 400 (400 MHz) spectrometer ($^{1}$H: 400 MHz, $^{13}$C: 101 MHz, $^{19}$F: 377 MHz), and deuterated $CDCl_3$ was used as solvent. Chemical shifts (δ) for $^{1}$H and $^{13}$C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for $^{1}$H and $^{13}$C NMR spectra, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.0 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). High-resolution mass spectrometer analysis (HRMS) was performed on a Thermo Fisher Q Exactive mass spectrometer. Analytical thin-layer chromatography (TLC) was carried out on a pre-coated silica gel plate (0.2 mm thickness). All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh).

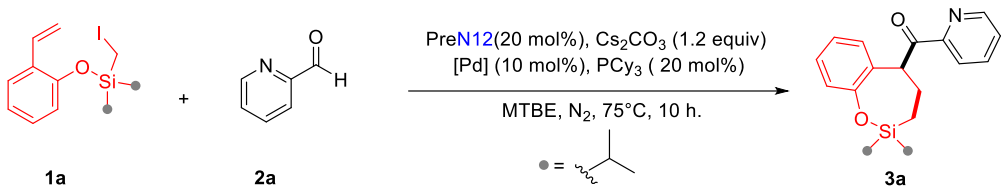
## 2. Condition optimizations

**Table S1. Optimization studies of preNHC[a]**




[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), $Pd(OAc)_2$ (10 mol%), $PCy_3$(20 mol%), pre**NHC** (20 mol%), $Cs_2CO_3$ (0.12 mmol), 2.0 mL MTBE, 75 °C, under $N_2$; NMR yield with 1,3,5-Trimethoxybenzene used as internal standard.

**Table S2. Optimization studies of Palladium catalyst.**[a]



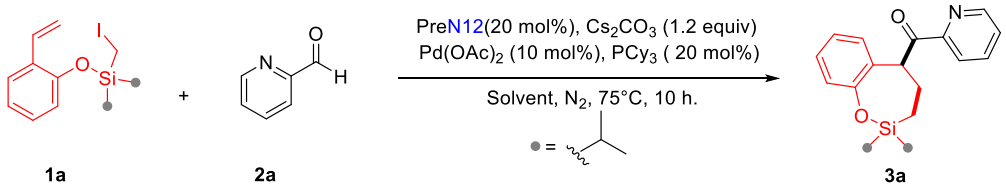

**1a** **2a** **3a**

| Entry | [Pd] | Yield (%)[b] |
|---|---|---|
| 1 | $Pd(OAc)_2$ | 71 |
| 2 | $Pd(PPh_3)_4$ | 68 |
| 3 | $Pd(TFA)_2$ | 67 |
| 4 | $Pd2(dba)_3$ | 64 |
| 5 | $PdCl_2$ | 57 |
| 6 | $PdCl2(MeCN)_2$ | 65 |
| 7 | $PdBr_2$ | 63 |

a) The reactions were performed with **1a** (0.1 mmol), **2a** (0.1 mmol), **N12** (20 mol%), $Cs_2CO_3$ (0.12 mmol), [Pd](10 mol%), $PCy_3$ (20 mol%), MTBE (2.0 mL), and $N_2$ atmosphere at 75 ℃ for 10 h.

b) NMR yield with 1,3,5-Trimethoxybenzene used as internal standard.

**Table S3. Optimization studies of solvent.**[a]




**1a** **2a** **3a**

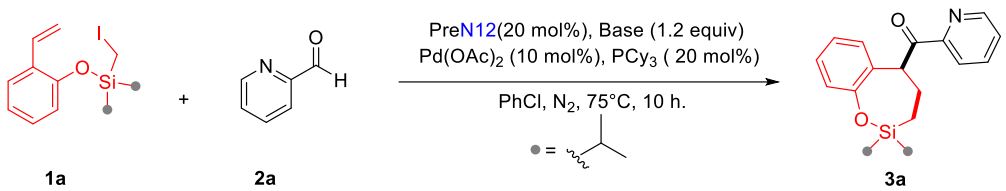
| Entry | Solvent | Yield (%)[b] |
|---|---|---|
| 1 | EA | 48 |
| 2 | THF | 33 |
| 3 | DCM | 45 |
| 4 | MeCN | ND |
| 5 | DMSO | Trace |
| 6 | DMF | Trace |
| 7 | NMP | Trace |
| 8 | Acetone | Trace |
| 9 | 1,4-Dioxane | 74 |
| 10 | PhMe | 74 |
| 11 | PhCl | 77 |
| 12 | $CH_3OH$ | Trace |
| 13 | $CHCl_3$ | Trace |
| 14 | $PhCF_3$ | 32 |
| 15 | 1,2-dimethoxy-ethan | 31 |

a) The reactions were performed with **1a** (0.1 mmol), **2a** (0.1 mmol), **N12** (20 mol%), $Cs_2CO_3$ (0.12 mmol), $Pd(OAc)_2$ (10 mol%), $PCy_3$ (20 mol%), sovent (2.0 mL), and $N_2$ atmosphere at

75 °C for 10 h.

b) NMR yield with 1,3,5-Trimethoxybenzene used as internal standard.

**Table S4. Optimization studies of Base.**[a]



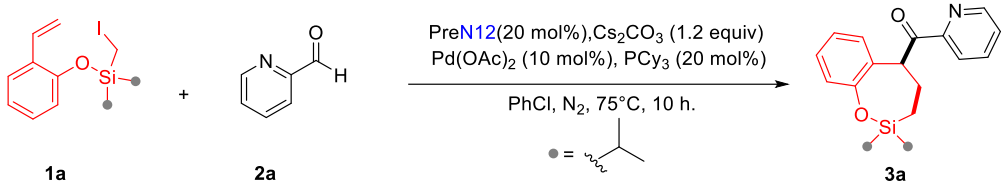

1a 2a 3a

| Entry | Base | Yield (%)[b] |
|---|---|---|
| 1 | DIPEA | 34 |
| 2 | DBU | 29 |
| 3 | $Et_3N$ | 31 |
| 4 | $K_3PO_4$ | 39 |
| 5 | $K_2CO_3$ | Trace |
| 6 | $Ag_2CO_3$ | ND |
| 7 | TBuOK | 33 |
| 8 | DMAP | 45 |
| 9 | AcONa | Trace |
| 10 | $CF_3OONa$ | Trace |
| 11 | DIPEA | 34 |
| 12 | DBU | 29 |

a) The reactions were performed with **1a** (0.1 mmol), **2a** (0.1 mmol), **N12** (20 mol%), $Cs_2CO_3$ (0.12 mmol), $Pd(OAc)_2$ (10 mol%), $PCy_3$ (20 mol%), PhCl (2.0 mL), and $N_2$ atmosphere at 75 °C for 10 h.

b) NMR yield with 1,3,5-Trimethoxybenzene used as internal standard.

**Table S5. Optimization studies of the stoichiometric ratio.**[a]




1a 2a 3a

| Entry | 1a/2a | Yield (%)[b] |
|---|---|---|
| 1[c] | 1/1 | 56 |
| 2[d] | 1/1 | 53 |
| 3[e] | 1/1 | 54 |
| 4 | 1/1.2 | 82 |
| 5 | 1/1.5 | 84 |
| 6 | 1/2.0 | 92(87)[f] |

| | | |
|---|---|---|
| 7 | 1/2.5 | 92 |
| 8[g] | 1/2.0 | ND |
| 9[h] | 1/2.0 | ND |
| 10[i] | 1/2.0 | 89 |

a) The reactions were performed with **1a** (0.1 mmol), **2a** (x mmol), **N12** (20 mol%), $Cs_2CO_3$ (0.12 mmol), $Pd(OAc)_2$ (10 mol%), $PCy_3$ (20 mol%), PhCl (2.0 mL), and $N_2$ atmosphere at 75 °Cfor 10 h.

b) NMR yield with 1,3,5-Trimethoxybenzene used as internal standard.

c) Base (0.15 mmol).

d) Base (0.2 mmol).

e) Base (0.25 mmol).

f) Isolated yield.

g) Without Palladium catalyst

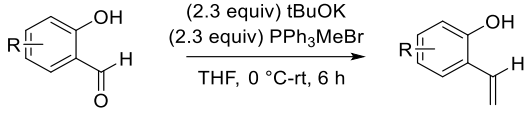
h) Without NHC.

i) In the dark.

# 3. Supplemental Methods

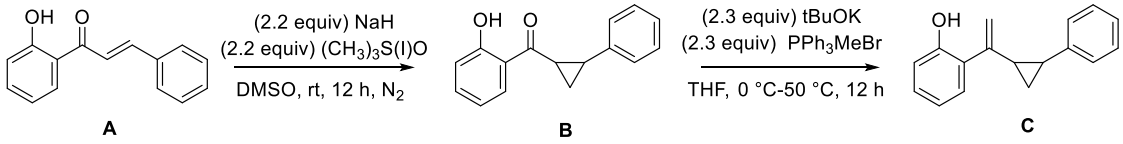
## 3.1 Preparation of Starting Materials

### 3.1.1 Synthesis of vinyl phenols:




**General Procedure A[1,2]:** To a suspension of $MePPh_3$ Br (2.3 equiv) ($EtPPh_3Br$ and $iPrPPh_3Br$) in THF (50 mL) was added tBuOK in one portion (2.3 equiv), and the resulting mixture was stirred at room temperature for 0.5 h. The reaction mixture was cooled to 0 °C, and salicylaldehyde derivatives (1.0 equiv) were added over 10 min. The mixture was stirred for 6h at room temperature. A saturated ammonium chloride solution was added, and the aqueous phase was extracted with ethyl acetate (3 x 50 mL). The organic phase was dried over $Na_2SO_4$, filtered, and concentrated. The compound was purified by flash column chromatography (20:1 PE: EA) to give a clear/yellow oil. Identity and purity were assessed by $^1H$ NMR and were compared to the literature reports.

### 3.1.2 Synthesis of complex phenols:



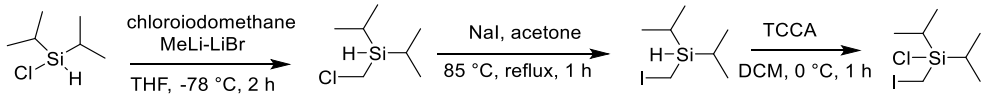

A B C

**Step 1[2]:** To a 100 mL flask equipped with a magnetic stir bar, argon inlet, and septum, NaH 60% (0.88 g, 22 mmol) and trimethylsulfoxonium iodide (4.84 g, 22 mmol) were added. Followed by the slow addition of DMSO (30 mL), and stirred at room temperature for 30 min. After $H_2$ evolution, 2'-Hydroxychalcone (2.24 g, 10 mmol) in 10 mL DMSO was added slowly. The reaction was stirred overnight at room temperature. Then, the reaction was quenched by the addition of 50 mL $H_2O$ and extracted with $Et_2O$ (3 x 30 mL). The organic phase was dried over $Na_2SO_4$, filtered, and concentrated. The compound was purified by column chromatography (20:1 PE: EA) to give **B** as a clear/yellow oil (50%, 1.20 g)

**Step 2:** To a suspension of $MePPh_3$ Br (2.2 equiv,11 mmol,3.9 g) in THF (30 mL) was added tBuOK in one portion (2.2 equiv,11 mmol,1.23 g), and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was cooled to 0 °C, and **B** (1.0 equiv, 1.2 g, 5 mmol) in 10 mL THF was added over 10 min. The mixture was stirred overnight at 55 °C. A saturated ammonium chloride solution was added, and the aqueous phase was extracted with ether (3 x 50 mL). The organic phase

was dried over $Na_2SO_4$, filtered, and concentrated. The compound was purified by flash column chromatography (20:1 PE: EA) to give **C** clear/yellow oil (52%).**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.31-7.27 (m, 2H), 7.24 – 7.13 (m, 3H), 7.13 – 7.09 (m, 2H), 6.95 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.90 (td, *J* = 7.5, 1.2 Hz, 1H), 5.56 (s, 1H), 5.40 (s, 1H), 5.14 (d, *J* = 1.3 Hz, 1H), 2.04-1.99 (m, 1H), 1.98 – 1.92 (m, 1H), 1.32 – 1.21 (m, 2H).

**3.1.3 Synthesis of chloro (iodomethyl) diisopropylsilane:**

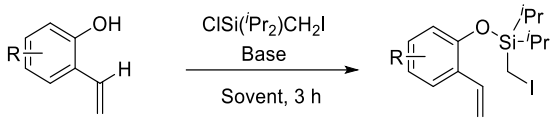



**Step 1**[1-3]**:** To a solution of dichlorodiisopropylsilane (6.8 mL, 1.0 equiv, 40 mmol) and chloroiodomethane (4.4 mL, 1.5 equiv, 60 mmol) in THF (50 mL) was added a solution of MeLi-LiBr complex (1.5 M in ether, 40 mL, 60 mmol) dropwise at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and then allowed to warm to room temperature before quenching with saturated ammonium chloride solution. The aqueous layer was extracted with hexane. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product, (chloromethyl)diisopropylsilane, was used for the next step without further purification.

**Step 2:**To a solution of NaI (18 g, 3.0 equiv, 120 mmol) in ACS standard acetone (40 mL) was added crude (chloromethyl)diisopropylsilane in acetone (5 mL). The reaction mixture was refluxed at 85 °C for 1h. The reaction was allowed to cool to room temperature before quenching with a saturated solution of $Na_2S_2O_3$. The aqueous layer was extracted with hexane. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product, 5.1 g (50% yield) (iodomethyl)diisopropylsilane, was used for the next step without further purification.

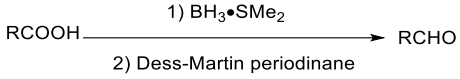
**Step 3:**To a solution of TCCA (1.67 g, 0.36 equiv, 7.2 mmol) in dry DCM (40 mL) under argon was added crude (chloromethyl)diisopropylsilane (5.1 g, 1.0 equiv, 20 mmol) in DCM(5mL) dropwise at 0 °C for 1 h. The mixture was allowed to warm to room temperature. and was then filtered through celite and concentrated. The residue was then dissolved in hexane and re-filtered through celite and then concentrated to yield chloro(iodomethyl)diisopropylsilane (quantitative, 5.8 g) as a pink/purple oil. The crude product, >95% purity, chloro(iodomethyl)diisopropylsilane, was used for the next step without further purification. Yield = 50% over three steps.**$^1$H NMR (400 MHz, $CDCl_3$)** δ 2.22 (s, 1H), 1.43 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.13 (dd, *J* = 7.4, 2.3 Hz, 6H).

### 3.1.4 Synthesis of silyl tethered phenols and alcohols:

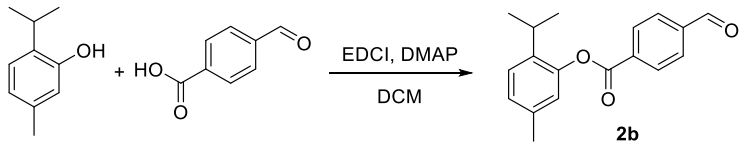



**General Procedure B[1,2]:** To a stirred solution of alcohol (1.0 equiv.) and imidazole (2.0 equiv.) in THF, chloro(iodomethyl)diisopropylsilane (1.2 equiv.) was added at room temperature under $N_2$ atmosphere. After being stirred until completion of the reaction, as judged by TLC analysis. The filtrate was then concentrated under reduced pressure. The residue was purified by column chromatography in petroleum ether to afford the desired product, alkyl silyl ether. The other several alkylsilyl ethers were also prepared by this method.

### 3.1.5 Synthesis of complex aldehydes:

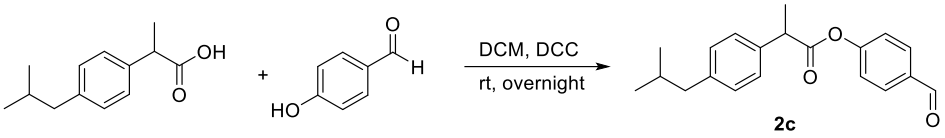



**General Procedure C for the Synthesis of Compounds 2a and 2e [4,6]:** To a stirring solution of carboxylic acid (1.0 mmol, 1.0 equiv.) in THF (3.0 mL) at 0 °C under argon was dropwise added $BH_3$•$SMe_2$ (4.0 mmol, 4.0 equiv.). Then the reaction was allowed to warm to room temperature and kept stirring for 18 h. After quenching by the addition of water (5.0 mL), the alcohol intermediate was extracted with $CH_2Cl_2$ (3 × 10.0 mL), dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The obtained crude residue was redissolved in $CH_2Cl_2$ (20.0 mL), and Dess-Martin periodinane (1.0 mmol, 1.0 equiv.) was added at 0 °C. Subsequently, the reaction mixture was warmed to room temperature and stirred for 1 h. After dilution with saturated aqueous $NaHCO_3$ (10.0 mL), the product was extracted with $CH_2Cl_2$ (3 × 10 mL), dried over $Na_2SO_4$, filtered, then concentrated in vacuo to give the crude residue. Purification by flash column chromatography (PE: DCM = 4:1) furnished the aldehyde derivative.

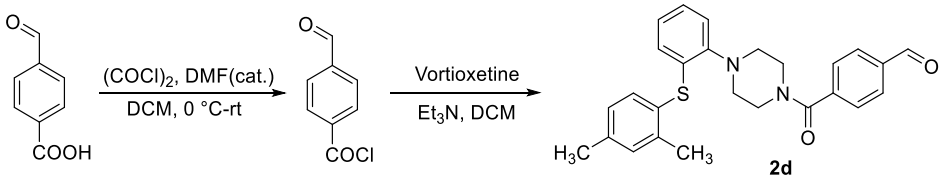



**Synthesis of 2b[4,6]:** To a solution of the 4-carboxybenzaldehyde (6 mmol, 1.2 equiv.) in DCM (0.02 mmol/mL) was added EDCI (13 mmol, 2.6 equiv.) at rt under an Ar atmosphere. Then, the resulting mixture was stirred for 5 min. Then the DMAP (2.5 mmol, 0.5 equiv.) and the corresponding alcohol (5 mmol, 1.0 equiv.) were added. After stirring overnight at rt, the mixture

was washed with $Na_2CO_3$, $H_2O$, and brine. The combined organic phases were dried over anhydrous $Na_2SO_4$, filtered, and concentrated in a vacuum, and the crude residue was then purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1 to 1:1).




**Synthesis of 2c [5]:** To a stirred solution of ibuprofen (1 mmol, 1.0 equiv.) in DCM (5 mL) was added 4-hydroxybenzaldehyde (1.2 mmol, 1.2 equiv.) and Dicyclohexylcarbodiimide (DCC, 1.5 mmol, 1.5 equiv.). The mixture was stirred at room temperature overnight. After the filtration through Celite, the filtrate was concentrated and purified on a silica gel column (petroleum ether/ethyl acetate = 10:1 - 4:1) to afford the 4-formylphenyl 2-(4-isobutylphenyl) propanoate, which furnished the aldehyde derivative as a colorless oil.

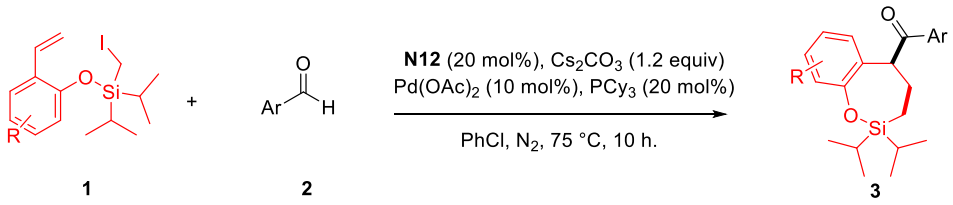



**Synthesis of 2d [4,6]:**

**Step 1:** To a solution of 4-formylbenzoic acid (5 mmol, 1.0 equiv.) in DCM (50 mL) was added oxalyl chloride (7.5 mmol, 1.5 equiv.) dropwise at 0 ℃, and one drop of DMF was subsequently added to the solution. Then the mixture was transferred to room temperature and stirred at the same temperature overnight. After the indicated time, the mixture was evaporated to dry under reduced pressure, and the crude acyl chloride was used directly for the next step without further purification.

**Step 2:** A solution of vortioxetine (4 mmol, 1 equiv.) and $Et_3N$ (12 mmol, 3.0 equiv.) in DCM (50 mL) was added dropwise with acyl chloride at 0 ℃ and then kept at room temperature for another 10 h. The reaction mixture was quenched by adding 20 mL $H_2O$, then the solution was extracted with DCM (2 × 30 mL). The combined organic layer was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel. To gain the corresponding compounds.

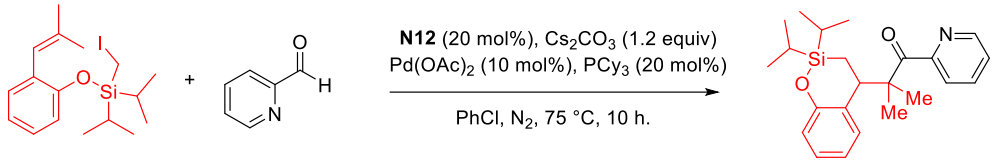
### 3.2 Synthesis of 5-Acylated Benzoxasilepines




**Scheme S1**. Model reaction for computation.

In an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1** (0.1 mmol), **2** (0.2 mmol), $Pd(OAc)_2$ (10 mol%, 2.2 mg), Pre**N12** (20 mol%, 8.2 mg ), $PCy_3$(20 mol%, 5.6 mg), and $Cs_2CO_3$ (0.12 mmol, 39 mg) were added to degassed PhCl (2 mL) under a nitrogen atmosphere. Then, the reaction mixture was stirred at 75 ℃ for 10 h. The residue was then purified by column chromatography on silica gel using hexane as eluent to give pure cyclization products.

### 3.3 Applicability for trisubstituted alkenes



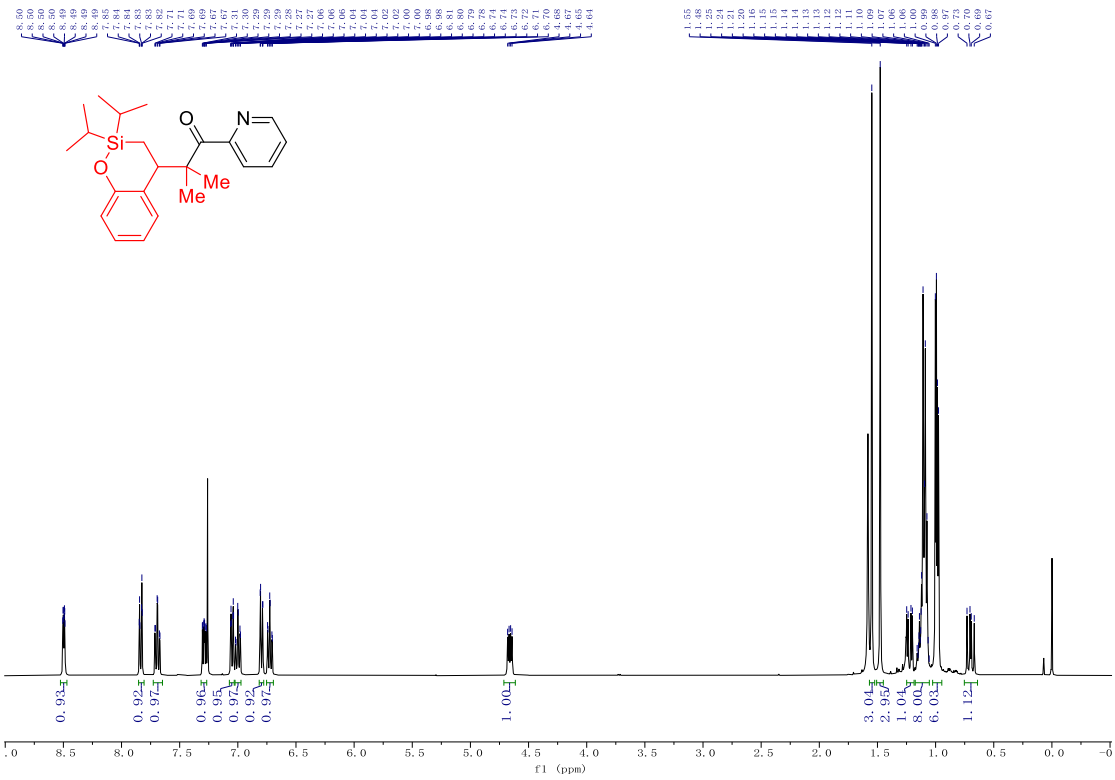

**1o** **2a** **5**

In an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1o** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%, 2.2 mg), Pre**N12** (20 mol%, 8.2 mg ), $PCy_3$(20 mol%, 5.6 mg), and $Cs_2CO_3$ (0.12 mmol, 39 mg) were added to degassed PhCl (2 mL) under a nitrogen atmosphere. Then, the reaction mixture was stirred at 75 °C for 10 h. The residue was then purified by column chromatography on silica gel using hexane as eluent to give pure cyclization product **5,** which was isolated in 21% yield (8.0 mg) as a colorless liquid.

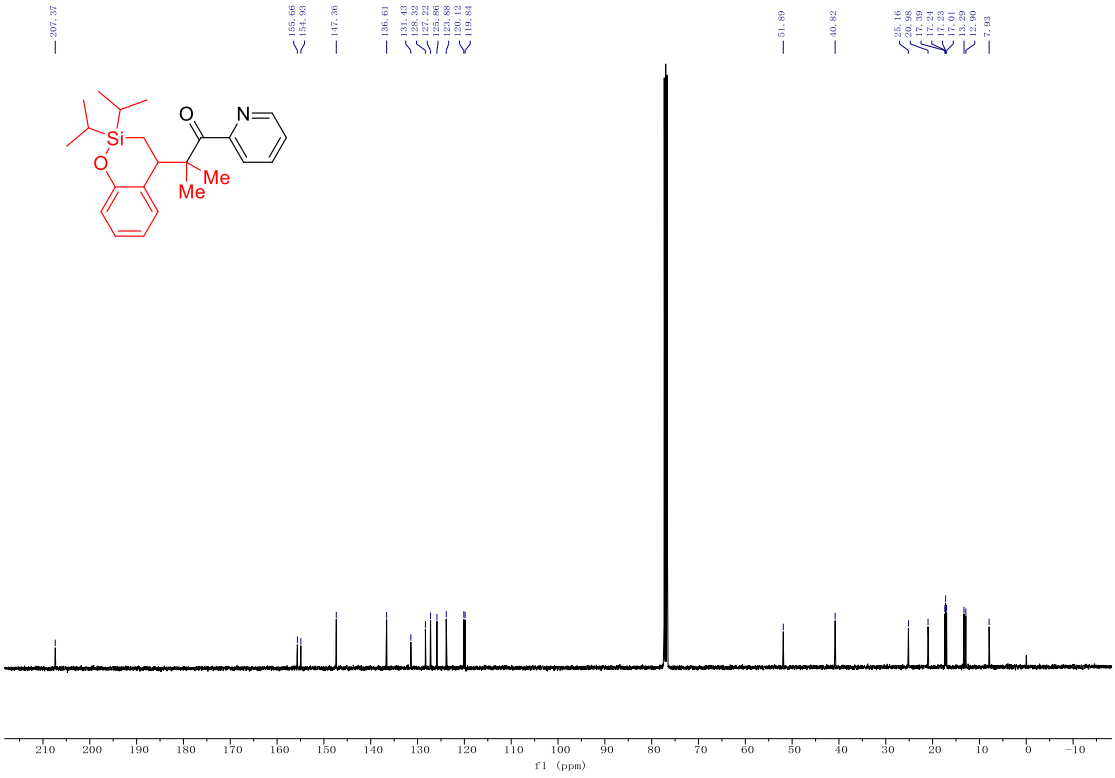
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.50 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H), 7.83 (dt, J = 7.9, 1.1 Hz, 1H), 7.69 (td, J = 7.8, 1.8 Hz, 1H), 7.29 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H), 7.05 (dt, J = 7.6, 1.2 Hz, 1H), 7.00 (td, J = 7.7, 1.7 Hz, 1H), 6.80 (dd, J = 7.9, 1.4 Hz, 1H), 6.72 (td, J = 7.5, 1.4 Hz, 1H), 4.66 (dd, J = 10.3, 4.9 Hz, 1H), 1.55 (s, 3H), 1.48 (s, 3H), 1.22 (dd, J = 14.7, 4.9 Hz, 1H), 1.17 – 1.05 (m, 8H), 0.99 (dd, J = 7.3, 3.6 Hz, 6H), 0.70 (dd, J = 14.6, 10.3 Hz, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 207.4, 155.7, 154.9, 147.4, 136.6, 131.4, 128.3, 127.2, 125.9, 123.9, 120.1, 119.8, 51.9, 40.8, 25.2, 21.0, 17.4, 17.2, 17.2, 17.0, 13.3, 12.9, 7.9.

**HRMS (ESI-TOF, m/z)**: Calc'd for $C_{23}H_{31}NO$**2**Si H+[M+ H]$^+$, 382.219682; found: 382.2192

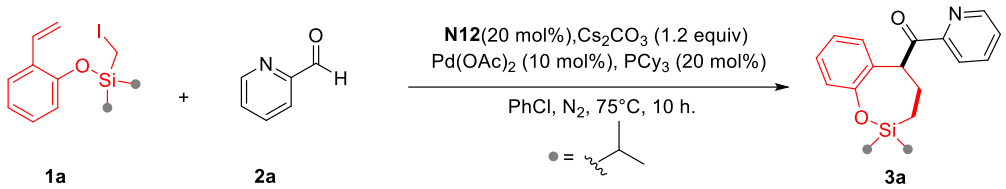



**$^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **5**




**$^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **5**

### 3.4 Gram-scale synthesis

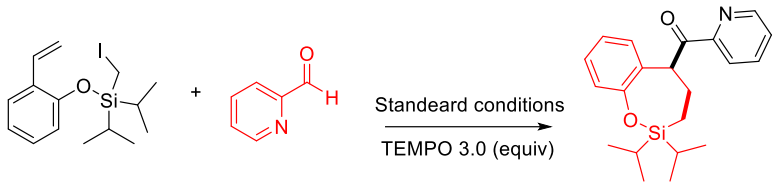



**1a** **2a** **3a**

In an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar, substrates **1a** (4 mmol, 1.5 g), **2a** (8 mmol, 0.86 g), $Pd(OAc)_2$ (10 mol%, 89.6 mg), Pre**N12** (20 mol%, 328 mg), $PCy_3$(20 mol%, 224 mg), and $Cs_2CO_3$ (4.8 mmol, 1.56 g) were added to degassed PhCl (15 mL) under a nitrogen atmosphere. Then, the reaction mixture was stirred at 75 °C for 16 h. The residue was then purified by column chromatography on silica gel using hexane as eluent to give pure cyclization product **3a** in 1.0291 g, 73% total yield.

### 3.5 Mechanistic studies

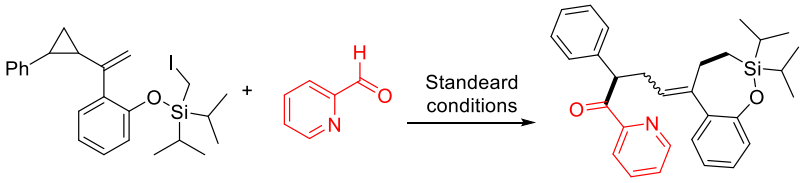
#### 3.4.1 Radical trapping experiment:




**1a** **2a** **3a:** Trace

In an oven dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1** (0.1 mmol), **2** (0.2 mmol), $Pd(OAc)_2$ (10 mol%, 2.2 mg), Pre**N12** (20 mol%, 8.2 mg), $PCy_3$(20 mol%, 5.6 mg) and $Cs_2CO_3$(0.12 mmol, 39 mg), Tempo (0.3 mmol, 46.9 mg) were added to degassed PhCl (2 mL) under the nitrogen atmosphere. Then, the reaction mixture was stirred at 75 ℃ for 10 h.

#### 3.4.2 Radical clock experiment:




**1q** **2a** **4f**: 93%

In an oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar, substrates **1q** (0.1 mmol), **2a** (0.2 mmol), $Pd(OAc)_2$ (10 mol%, 2.2 mg), Pre**N12** (20 mol%, 8.2 mg), $PCy_3$(20 mol%, 5.6 mg) and $Cs_2CO_3$(0.12 mmol, 39 mg) were added to degassed PhCl (2 mL) under a nitrogen atmosphere. Then, the reaction mixture was stirred at 75 ℃ for 10 h. The residue was then purified by column chromatography on silica gel using hexane as eluent to give pure cyclization products.

# 4. X-ray Crystallographic data

**Table S6. Crystallographic data for compound 3t**

| **Compound** | **3t** |
|---|---|
| **Empirical formula** | $C_{28}H_{29}Cl_3N_2O_3S_2Si$ |
| **Formula weight** | 640.09 |
| **Temperature/K** | 302.00 |
| **Crystal system** | triclinic |
| **Space group** | P-1 |
| **a/Å** | 10.0331(2) |
| **b/Å** | 11.8736(2) |
| **c/Å** | 14.2336(2) |
| **α/°** | 100.4090(10) |
| **β/°** | 98.8060(10) |
| **γ/°** | 104.1300(10) |
| **Volume/Å$^3$** | 1582.33(5) |
| **Z** | 2 |
| **$\rho_{calc}$g/cm$^3$** | 1.343 |
| **μ/mm$^{-1}$** | 4.477 |
| **F(000)** | 664.0 |
| **Crystal size/mm$^3$** | 0.2 × 0.15 × 0.1 |
| **Radiation** | CuKα (λ = 1.54178) |
| **2Θ range for data collection/** | 7.884 to 136.654 |
| **Index ranges** | $-12 \le h \le 11$, $-14 \le k \le 14$, $-17 \le l \le 17$ |
| **Reflections collected** | 24705 |
| **Independent reflections** | 5667 [$R_{int}$ = 0.0408, $R_{sigma}$ = 0.0368] |
| **Data/restraints/parameters** | 5667/1/357 |
| **Goodness-of-fit on F$^2$** | 1.066 |
| **Final R indexes [I>=2σ (I)]** | $R_1$= 0.0835, w$R_2$= 0.2522 |

| | |
|---|---|
| **Final R indexes [all data]** | $R_1$= 0.0884, $wR_2$= 0.2580 |
| **Largest diff. peak/hole / e Å$^{-3}$** | 1.08/-0.98 |
| **CCDC Number** | **2481818** |

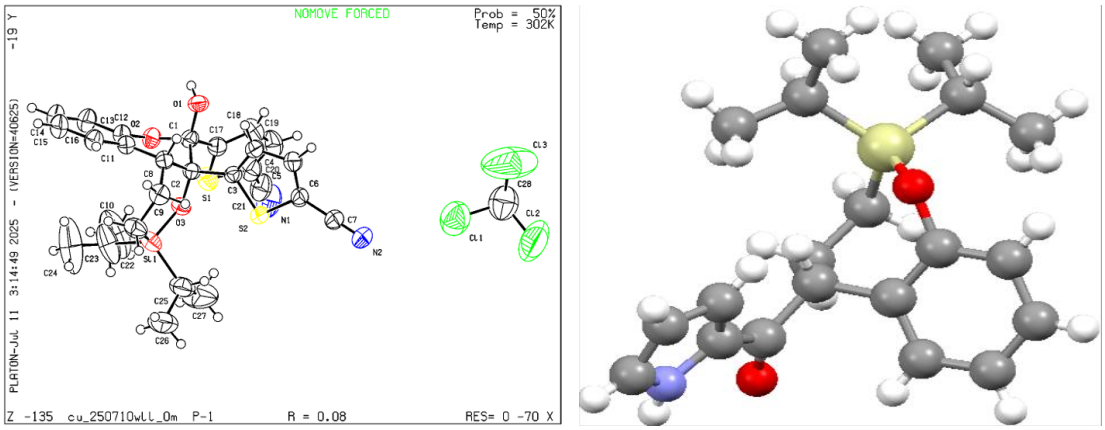



**Figure S1. ORTEP diagram of 3t**

## 5. Antifungal studies of the products

**Table S7.** ***In vitro*** **antifungal activities of the new compounds against** ***Phomopsis sp*** **(0.1 mg/mL)**

| Compounds | Ps inhibition rates at 0.1 mg/ml (%) | Compounds | Ps inhibition rates at 0.1 mg/ml (%) |
|---|---|---|---|
| 3a | 62.67±2.98 | 3u | 68.2±1.33 |
| 3b | 17.97±2.94 | 3v | 58.53±3.07 |
| 3c | 5.53±3.59 | 3y | 60.37±2.94 |
| 3d | 20.74±2.51 | 3z | 65.9±1.98 |
| 3e | 48.85±3.35 | 3ac | 9.22±1.83 |
| 3f | 40.09±2.51 | 3ad | 20.28 ±3.89 |
| 3g | 34.56 ±3.32 | 3ae | 14.29 ±3.1 |
| 3h | 47.93±3.41 | 3af | 13.36±3.02 |
| 3i | 9.68±4.25 | 3ag | -8.29±3.59 |
| 3j | 18.43±3.35 | 3ah | 21.66±3.66 |
| 3k | 68.66 ±3.66 | 3ai | 28.11±3.1 |
| 3l | 60.37±2.94 | 3aj | 63.13±3.66 |
| 3m | 19.35±3.58 | 3ak | 20.28±1.83 |
| 3n | 48.39±2.51 | 3al | 23.96±2.55 |
| 3o | 46.54±1.25 | 3am | 32.26±2.03 |
| 3p | 6.91±4.78 | 3an | 36.41±3.07 |
| 3q | 18.43±2.03 | 3ao | 8.76±4.06 |
| 3r | 35.02 ±2.55 | Fbjxa | 48.85±1.33- |
| 3s | 45.16±3.14 | Ck | 0 |
| 3t | 86.64±0.99 | | |

**Table S8. *In vitro* antifungal activities of the new compounds against *Rhizoctonia solani* (0.1 mg/mL)**

| Compounds | Rs inhibition rates at 0.1 mg/ml (%) | Compounds | Rs inhibition rates at 0.1 mg/ml (%) |
|---|---|---|---|
| 3a | 43.98±2.32 | 3t | 56.85±1.14 |
| 3b | 32.78±2.29 | 3u | 52.7±3.07 |
| 3c | 71.78±2.95 | 3v | 51.04±3.59 |
| 3d | 76.76±2.29 | 3y | 70.12±2.43 |
| 3e | 41.91±2.58 | 3z | 61.00±3.56 |
| 3f | 49.38±4.78 | 3ac | 59.75±8.33 |
| 3g | 53.94±1.21 | 3ad | 70.12 ±1.98 |
| 3h | 54.36±3.88 | 3ae | 46.06±4.12 |
| 3i | 53.53±2.29 | 3af | 48.13±4.73 |
| 3j | 63.9±3.64 | 3ag | 60.17±2.43 |
| 3k | 44.81±2.94 | 3ah | 18.26±3.2 |
| 3l | 54.77±4.52 | 3ai | 38.59±3.33 |
| 3m | 60.17±2.8 | 3aj | 36.93±2.29 |
| 3n | 55.19±3.97 | 3al | 61.83±3.33 |
| 3o | 78.42±2.41 | 3am | 29.46±4.57 |
| 3p | 52.7±2.8 | 3an | 48.96±2.32 |
| 3q | 46.06±3.62 | Fbjxa | 63.49±2.68 |
| 3r | 68.05±2.59 | Ck | 0 |
| 3s | 51.45±3.24 | | |

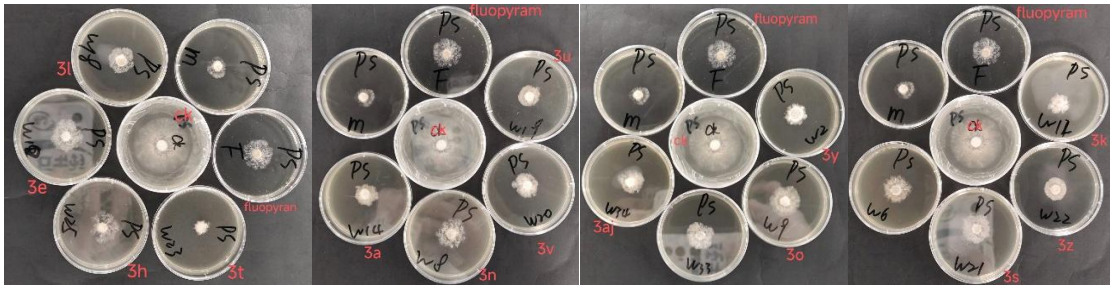



**Figure S2.** Selected compounds showed inhibitory effects on Ps in *vitro* at 0.1 mg/mL.

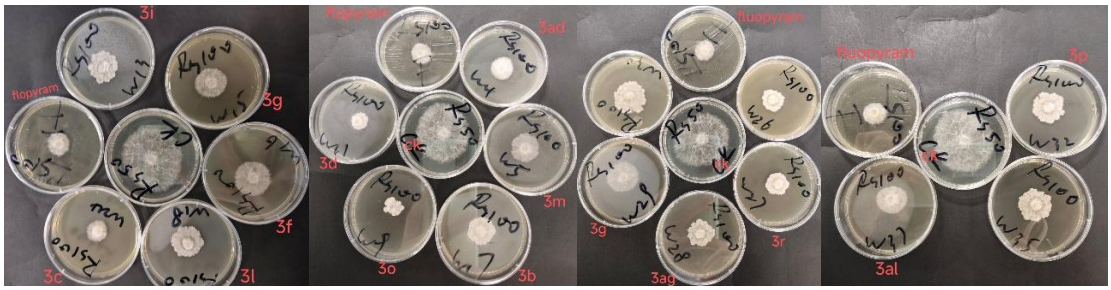
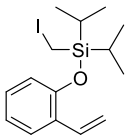



**Figure S3.** Selected compounds showed inhibitory effects on Rs in *vitro* at 0.1 mg/mL.

# 6. Characterizations of new compounds.

**(iodomethyl)diisopropyl(2-vinylphenoxy)silane (1a)**

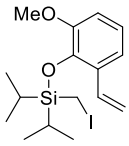


According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.50 (dd, J = 7.8, 1.8 Hz, 1H), 7.18 – 7.04 (m, 2H), 6.96 (td, J = 7.3, 1.0 Hz, 1H), 6.84 (dd, J = 8.0, 1.2 Hz, 1H), 5.69 (dd, J = 17.8, 1.4 Hz, 1H), 5.26 (dd, J = 11.1, 1.4 Hz, 1H), 2.24 (s, 2H), 1.43 (p, J = 7.5 Hz, 2H), 1.14 (dd, J = 8.6, 7.5 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values. [1,2]

**(iodomethyl)diisopropyl(3-methoxy-2-vinylphenoxy)silane (1b)**

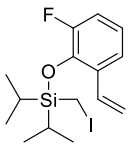


According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.17 – 7.08 (m, 2H), 6.88 (t, *J* = 8.0 Hz, 1H), 6.76 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.66 (dd, *J* = 17.8, 1.5 Hz, 1H), 5.26 (dd, *J* = 11.1, 1.4 Hz, 1H), 3.80 (s, 3H), 2.26 (s, 2H), 1.40 (dt, *J* = 15.1, 7.6 Hz, 2H), 1.11 (dd, *J* = 8.2, 7.5 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values. [2]

**(3-fluoro-2-vinylphenoxy)(iodomethyl)diisopropylsilane (1c)**



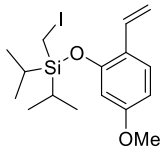
According to the general procedure **B**;

**1H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.22 (m, 1H), 7.06 (dd, J = 17.7, 11.1 Hz, 1H), 6.96 (ddd, J = 10.5, 8.1, 1.7 Hz, 1H), 6.87 (td, J = 8.0, 5.2 Hz, 1H), 5.70 (dd, J = 17.8, 1.3 Hz, 1H), 5.31 (dd, J = 11.0, 1.2 Hz, 1H), 2.26 (d, J = 1.8 Hz, 2H), 1.44 (hept, J = 7.6 Hz, 2H), 1.13 (dd, J = 14.3, 7.5 Hz,

12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[2]

**(iodomethyl)diisopropyl(5-methoxy-2-vinylphenoxy)silane (1d)**

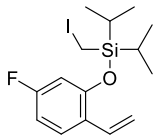



According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.42 (d, *J* = 8.7 Hz, 1H), 6.99 (dd, *J* = 17.8, 11.1 Hz, 1H), 6.54 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 5.57 (dd, *J* = 17.8, 1.5 Hz, 1H), 5.14 (dd, *J* = 11.1, 1.4 Hz, 1H), 3.78 (s, 3H), 2.25 (s, 2H), 1.43 (dq, *J* = 14.9, 7.5 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[1,2]

**(5-fluoro-2-vinylphenoxy)(iodomethyl)diisopropylsilane (1e)**

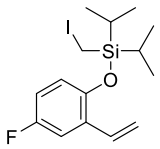



According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.44 (dd, J = 8.7, 6.9 Hz, 1H), 6.99 (dd, J = 17.7, 11.1 Hz, 1H), 6.69 (d, J = 2.6 Hz, 1H), 6.57 (dd, J = 10.1, 2.6 Hz, 1H), 5.61 (dd, J = 17.7, 1.3 Hz, 1H), 5.22 (dt, J = 11.2, 0.9 Hz, 1H), 2.23 (s, 2H), 1.49 – 1.35 (m, 2H), 1.13 (dd, J = 8.8, 7.4 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[2]

**(4-fluoro-2-vinylphenoxy)(iodomethyl)diisopropylsilane (1f)**

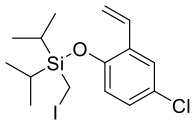


According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.17 (dd, J = 9.5, 3.0 Hz, 1H), 7.02 (ddd, J = 17.8, 11.0, 1.8 Hz, 1H), 6.87 – 6.73 (m, 2H), 5.67 (dd, J = 17.7, 1.2 Hz, 1H), 5.30 (dd, J = 11.1, 1.1 Hz, 1H), 2.21 (s, 2H), 1.40 (dt, J = 15.2, 7.6 Hz, 2H), 1.12 (dd, J = 9.6, 7.5 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[1]

**(4-chloro-2-vinylphenoxy)(iodomethyl)diisopropylsilane (1g)**

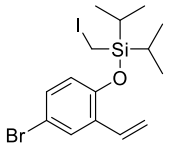


According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.44 (d, J = 2.7 Hz, 1H), 7.08 (dd, J = 8.6, 2.7 Hz, 1H), 6.99 (dd, J = 17.8, 11.1 Hz, 1H), 6.77 (d, J = 8.6 Hz, 1H), 5.69 (dd, J = 17.7, 1.2 Hz, 1H), 5.30 (dd, J = 11.1, 1.1 Hz, 1H), 2.21 (s, 2H), 1.46 – 1.36 (m, 2H), 1.12 (dd, J = 8.6, 7.5 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[1,2]

**(4-bromo-2-vinylphenoxy)(iodomethyl)diisopropylsilane (1h)**

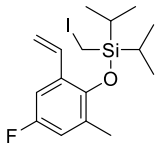


According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, J = 2.5 Hz, 1H), 7.22 (dd, J = 8.6, 2.5 Hz, 1H), 6.98 (dd, J = 17.7, 11.1 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 5.68 (dd, J = 17.8, 1.1 Hz, 1H), 5.30 (dd, J = 11.1, 1.1 Hz, 1H), 2.21 (s, 2H), 1.40 (p, J = 7.5 Hz, 2H), 1.12 (t, J = 7.9 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[1]

**(4-fluoro-2-methyl-6-vinylphenoxy)(iodomethyl)diisopropylsilane (1i)**




According to the general procedure **B**;

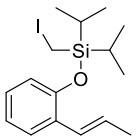
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.00 – 6.90 (m, 2H), 6.76 (dd, J = 8.7, 3.2 Hz, 1H), 5.62 (dd, J = 17.7, 1.1 Hz, 1H), 5.30 (dd, J = 10.9, 1.2 Hz, 1H), 2.25 (s, 3H), 2.22 (s, 2H), 1.44 – 1.32 (m, 2H), 1.13 (d, J = 7.5 Hz, 6H), 1.07 (d, J = 7.5 Hz, 6H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 157.8 (d, *J* = 239.3 Hz), 147.7 (d, *J* = 2.4 Hz), 132.8 (d, *J* = 2.3 Hz), 130.7 (d, *J* = 8.2 Hz), 130.5 (d, *J* = 8.0 Hz), 117.2 (d, *J* = 22.9 Hz), 115.8, 110.1 (d, *J* = 23.2 Hz), 18.2 (d, *J* = 1.5 Hz), 18.1, 17.7, 13.6.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -122.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{16}H_{24}FIOSi$ H+$[M+H]^+$, 407.0698; found: 407.0694.

**(iodomethyl)diisopropyl(2-(prop-1-en-1-yl)phenoxy)silane (1j)**

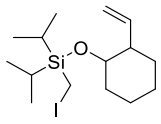



According to the general procedure **B**;

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.40 (dd, J = 7.7, 1.8 Hz, 1H), 7.06 (td, J = 7.7, 1.8 Hz, 1H), 6.92 (td, J = 7.6, 1.2 Hz, 1H), 6.81 (dd, J = 8.2, 1.2 Hz, 1H), 6.75 (dq, J = 15.9, 1.9 Hz, 1H), 6.16 (dq, J = 15.9, 6.6 Hz, 1H), 2.23 (s, 2H), 1.89 (dd, J = 6.6, 1.8 Hz, 3H), 1.42 (dt, J = 15.0, 7.5 Hz, 2H), 1.13 (t, J = 7.8 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[2]

**(iodomethyl)diisopropyl((2-vinylcyclohexyl)oxy)silane (1k)**

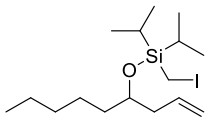


According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 3.96 (dddt, J = 14.9, 11.1, 7.6, 3.8 Hz, 2H), 2.36 – 2.26 (m, 1H), 2.14 (s, 2H), 2.13 – 2.06 (m, 1H), 1.86 – 1.62 (m, 3H), 1.51 – 1.41 (m, 1H), 1.41 – 1.31 (m, 2H), 1.30 – 1.20 (m, 3H), 1.10 (td, J = 7.1, 4.6 Hz, 14H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[2]

**(iodomethyl)diisopropyl(non-1-en-4-yloxy)silane (1l)**

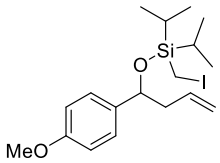


According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 5.83 (ddt, J = 17.3, 10.3, 7.1 Hz, 1H), 5.11 – 5.01 (m, 2H), 3.91 (p, J = 5.8 Hz, 1H), 2.35 – 2.18 (m, 2H), 2.08 (s, 2H), 1.47 (ddt, J = 13.5, 11.8, 6.9 Hz, 2H), 1.38 – 1.15 (m, 9H), 1.08 (t, J = 6.7 Hz, 12H), 0.89 (t, J = 6.9 Hz, 3H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[2]

**(iodomethyl)(isopropyl)((1-(4-methoxyphenyl)but-3-en-1-yl)oxy)(methyl)silane (1m)**



According to the general procedure **B**;

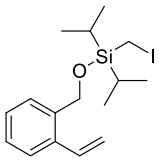
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.24 – 7.19 (m, 2H), 6.87 – 6.82 (m, 2H), 5.79 – 5.67 (m, 1H), 5.03 – 5.00 (m, 1H), 4.98 (t, *J* = 1.2 Hz, 1H), 4.81 (t, *J* = 6.3 Hz, 1H), 3.80 (s, 3H), 2.59 – 2.47 (m, 1H), 2.46 – 2.34 (m, 1H), 1.92 (d, *J* = 2.4 Hz, 2H), 1.26 – 1.12 (m, 2H), 1.07 (dd, *J* = 11.9, 7.4 Hz, 6H), 0.97 (dd, *J* = 17.8, 7.4 Hz, 6H).

**$^3$C NMR (101 MHz, $CDCl_3$)** δ 158.76, 136.75, 134.79, 127.14, 117.17, 113.39, 75.14, 55.18, 45.50,

17.89, 17.57, 17.46, 17.31, 12.47, 12.33.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{18}H_{29}IO_2SiNa$+[M+Na]$^+$, 455.0874; found: 455.0874.

**(iodomethyl)diisopropyl((2-vinylbenzyl)oxy)silane (1n)**

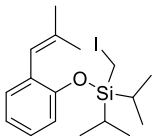



According to the general procedure **B**;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.48 (td, J = 6.5, 2.0 Hz, 2H), 7.29 – 7.25 (m, 2H), 6.95 (dd, J = 17.4, 11.0 Hz, 1H), 5.65 (dd, J = 17.4, 1.4 Hz, 1H), 5.31 (dd, J = 11.0, 1.4 Hz, 1H), 4.94 (s, 2H), 2.12 (s, 2H), 1.38 – 1.23 (m, 2H), 1.12 – 1.07 (m, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[2]

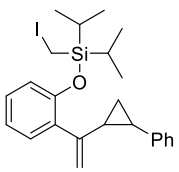
**(iodomethyl)diisopropyl(2-(2-methylprop-1-en-1-yl)phenoxy)silane (1o)**




**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.16 (dd, J = 7.6, 1.8 Hz, 1H), 7.08 (td, J = 7.7, 1.9 Hz, 1H), 6.93 (td, J = 7.5, 1.2 Hz, 1H), 6.85 (dd, J = 8.0, 1.2 Hz, 1H), 6.30 (s, 1H), 2.18 (s, 2H), 1.90 (d, J = 1.4 Hz, 3H), 1.78 (d, J = 1.4 Hz, 3H), 1.46 – 1.29 (m, 1H), 1.10 (dd, J = 10.6, 7.4 Hz, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[2]

**(iodomethyl)diisopropyl(2-(1-(2-phenylcyclopropyl)vinyl)phenoxy)silane (1q)**

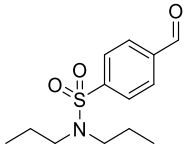



**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.3 – 7.2 (m, 2H), 7.2 – 7.1 (m, 3H), 7.1 – 7.0 (m, 2H), 6.9 (td, *J* = 7.5, 1.2 Hz, 1H), 6.8 (dd, *J* = 8.6, 1.2 Hz, 1H), 5.2 – 5.1 (m, 1H), 5.0 (d, *J* = 1.6 Hz, 1H), 2.2 (s, 2H),

2.1 – 2.0 (m, 1H), 2.0 – 1.9 (m, 1H), 1.4 – 1.3 (m, 2H), 1.2 – 1.2 (m, 2H), 1.1 – 1.0 (m, 12H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[2]

**4-formyl-*N*,*N*-dipropylbenzenesulfonamide (2a)**

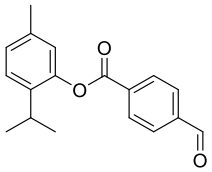


According to the synthesis method of complex aldehydes;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.09 (s, 1H), 8.15 – 7.82 (m, 4H), 3.19 – 3.03 (m, 4H), 1.62 – 1.47 (m, 4H), 0.86 (t, *J* = 7.4, 6H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[4,5]

**2-isopropyl-5-methylphenyl 4-formylbenzoate (2b)**

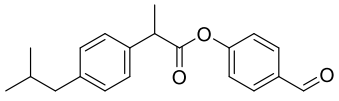


According to the synthesis method of complex aldehydes;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.15 (s, 1H), 8.45 – 8.32 (m, 2H), 8.09 – 7.99 (m, 2H), 7.26 (d, *J* = 7.7, 1H), 7.14 – 7.05 (m, 1H), 6.95 (d, *J* = 1.8, 1H), 3.09 – 2.99 (m, 1H), 2.35 (s, 3H), 1.22 (d, *J* = 6.8, 6H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[4,5]

**4-formylphenyl 2-(4-isobutylphenyl)propanoate (2c)**



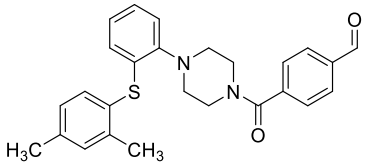
According to the synthesis method of complex aldehydes;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.0 (s, 1H), 7.9 – 7.9 (m, 2H), 7.3 – 7.3 (m, 2H), 7.2 – 7.1 (m, 4H), 4.0 (q, *J* = 7.1 Hz, 1H), 2.5 (d, *J* = 7.2 Hz, 2H), 1.9 (dh, *J* = 13.6, 6.7 Hz, 1H), 1.6 (d, *J* = 7.1 Hz,

3H), 0.9 (d, *J* = 6.6 Hz, 6H).

The title compound was prepared according to a known procedure. T The NMR data are consistent with the literature values.[5,6]

**4-(4-(2-((2,4-dimethylphenyl)thio)phenyl)piperazine-1-carbonyl)benzaldehyde (2d)**

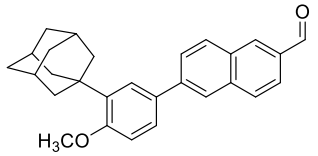



According to the synthesis method of complex aldehydes;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.06 (s, 1H), 7.98 – 7.93 (m, 2H), 7.65 – 7.58 (m, 2H), 7.35 (d, *J* = 7.8, 1H), 7.15 (d, *J* = 2.0, 1H), 7.11 – 7.07 (m, 1H), 7.05 – 7.02 (m, 2H), 6.92 – 6.88 (m, 1H), 6.54 (dd, *J* = 8.0, 1.5, 1H), 4.00 (s, 2H), 3.57 (s, 2H), 3.17 (s, 2H), 3.02 (s, 2H), 2.36 (s, 3H), 2.30 (s, 3H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[4,5]

**6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthaldehyde (2e)**

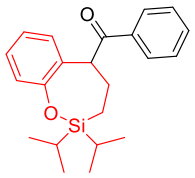



According to the synthesis method of complex aldehydes;

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 10.16 (s, 1H), 8.34 (d, *J* = 1.2, 1H), 8.04 (dd, *J* = 5.1, 3.3, 2H), 7.97 (d, *J* = 1.1, 2H), 7.84 (dd, *J* = 8.6, 1.8, 1H), 7.61 (d, *J* = 2.4, 1H), 7.56 (dd, *J* = 8.4, 2.3, 1H), 7.01 (d, *J* = 8.5, 1H), 3.91 (s, 3H), 2.19 (d, *J* = 3.0, 6H), 2.14 – 2.08 (m, 3H), 1.81 (t, *J* = 3.1, 6H).

The title compound was prepared according to a known procedure. The NMR data are consistent with the literature values.[4,5]

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(phenyl)methanone (3a)**



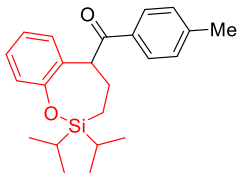
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3a** was isolated in 74% yield (26.06 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.85 – 7.78 (m, 2H), 7.49 – 7.40 (m, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.10 (m, 1H), 7.03 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.80 (td, *J* = 7.4, 1.3 Hz, 1H), 6.75 (dd, *J* = 7.7, 1.9 Hz, 1H), 5.01 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.16 – 2.07 (m, 1H), 1.38 – 1.25 (m, 1H), 1.21 (dd, *J* = 7.3, 4.6 Hz, 6H), 1.06 – 0.99 (m, 7H), 0.92 – 0.84 (m, 1H), 0.78 – 0.69 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.4, 154.0, 136.3, 132.8, 129.9, 128.7, 128.5, 128.4, 127.6, 122.4, 120.99, 48.0, 23.9, 17.8, 17.4, 17.4, 13.6, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{28}O_2SiNa$+[M+Na]$^+$, 375.1751; found: 375.1751.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(p-tolyl)methanone (3b)**



According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3b** was isolated in 69% yield (25.26 mg) as a colorless liquid.

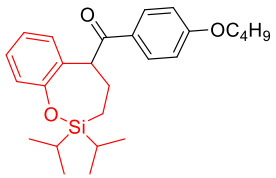
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.14-7.10 (m, 3H), 7.03 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.80 (td, *J* = 7.3, 1.3 Hz, 1H), 6.76 (dd, *J* = 7.7, 2.0 Hz, 1H), 4.99 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.38 – 2.33 (m, 1H), 2.33 (s, 3H), 2.15 – 2.06 (m, 1H), 1.38 – 1.25 (m, 1H), 1.21 (dd, *J* = 7.3, 5.2 Hz, 6H), 1.06 – 0.99 (m, 7H), 0.91 – 0.83 (m, 1H), 0.77 – 0.69 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.1, 153.9, 143.5, 133.8, 130.1, 129.2, 128.8, 128.3, 127.6, 122.4, 120.9, 47.8, 23.9, 21.6, 17.78, 17.4, 17.4, 13.6, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{23}H_{30}O_2SiNa$+[M+Na]$^+$, 389.1907; found: 389.1907.

**(4-butoxyphenyl)(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)methanone**

**(3c)**



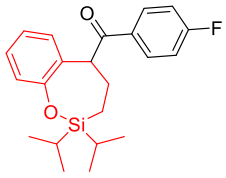

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3c** was isolated in 52% yield (22.06 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.81 – 7.73 (m, 2H), 7.12 (ddd, *J* = 7.9, 6.8, 2.1 Hz, 1H), 7.02 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.83 – 6.74 (m, 4H), 4.95 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.95 (t, *J* = 6.5 Hz, 2H), 2.36-2.28 (m, 1H), 2.14 – 2.04 (m, 1H), 1.77-1.70 (m, 2H), 1.52 – 1.39 (m, 2H), 1.37 – 1.27 (m, 1H), 1.20 (dd, *J* = 7.3, 4.9 Hz, 6H), 1.06 – 0.99 (m, 7H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.89 – 0.83 (m, 1H), 0.76 – 0.68 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.0, 162.8, 153.9, 131.0, 130.3, 129.1, 128.2, 127.7, 122.4, 120.9, 114.08, 67.8, 47.6, 31.1, 23.9, 19.1, 17.8, 17.5, 17.4, 13.8, 13.6, 12.9, 5.6.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{26}H_{36}O_3SiNa$+[M+Na]$^+$, 447.2326; found: 447.2329.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(4-fluorophenyl)methanone (3d)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3d** was isolated in 50% yield (18.51 mg) as a colorless liquid.

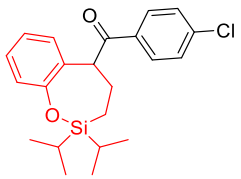
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.77 (m, 2H), 7.14 (td, *J* = 7.7, 1.8 Hz, 1H), 7.07 – 6.94 (m, 3H), 6.81 (td, *J* = 7.5, 1.3 Hz, 1H), 6.72 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.94 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.16 – 2.06 (m, 1H), 1.37 – 1.25 (m, 1H), 1.20 (dd, *J* = 7.2, 4.1 Hz, 6H), 1.04-0.99 (m, 7H), 0.91 – 0.83 (m, 1H), 0.77 – 0.69 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 198.9, 165.4 (d, *J* = 254.7 Hz), 154.0, 132.7 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 9.3 Hz), 129.8, 128.5, 127.6, 122.5, 121.1, 115.6 (d, *J* = 21.9 Hz), 48.1, 23.9, 17.7, 17.4, 17.4, 13.6, 12.9, 5.6.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -105.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{27}FO_2SiNa$+[M+Na]$^+$, 393.1657; found: 393.1655.

**(4-chlorophenyl)(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)methanone (3e)**



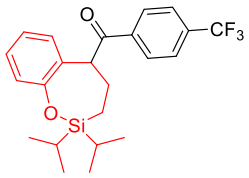

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3e** was isolated in 66% yield (25.49mg) as a white/yellow solid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.14 (ddd, *J* = 9.0, 7.4, 1.7 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.80 (td, *J* = 7.5, 1.3 Hz, 1H), 6.70 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.93 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.16 – 2.06 (m, 1H), 1.37 – 1.24 (m, 1H), 1.20 (dd, *J* = 7.2, 4.2 Hz, 6H), 1.04-0.99 (m, 7H), 0.90 – 0.83 (m, 1H), 0.78 – 0.68 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.2, 154.0, 139.2, 134.6, 130.1, 129.7, 128.8, 128.6, 127.6, 122.5, 121.1, 48.2, 23.9, 17.7, 17.4, 17.4, 13.6, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{27}ClO_2SiNa$+[M+Na]$^+$, 409.1361; found: 409.1362.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(4-(trifluoromethyl)phenyl) methanone (3f)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3f** was isolated in 61% yield (25.63 mg) as a colorless liquid.

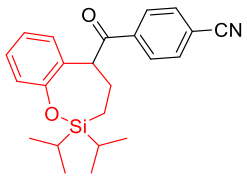
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.81 (td, *J* = 7.5, 1.3 Hz, 1H), 6.70 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.97 (dd, *J* = 11.4, 4.8 Hz, 1H), 2.40 – 2.30 (m, 1H), 2.17 – 2.08 (m, 1H), 1.40 – 1.25 (m, 1H), 1.20 (dd, *J* = 7.3, 4.0 Hz, 6H), 1.06 – 0.99 (m, 7H), 0.93 – 0.85 (m, 1H), 0.79 – 0.71 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.4, 154.0, 138.9, 134.0 (q, *J* = 32.7 Hz), 129.3, 129.0, 128.7, 127.5, 125.6 (q, *J* = 3.8 Hz), 122.6,123.6 (q, *J* = 272.7 Hz), 121.2, 48.5, 23.8, 17.7, 17.4, 17.4, 13.5, 12.9, 5.5.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -63.2.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{23}H_{27}F_3O_2SiNa$+[M+Na]$^+$, 443.1625; found: 443.1626.

**4-(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine-5-carbonyl)benzonitrile (3g)**



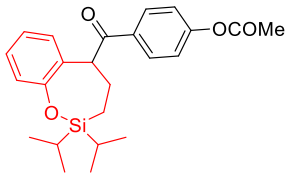

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3g** was isolated in 73% yield (27.53 mg) as a white/yellow solid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.80 (td, *J* = 7.5, 1.3 Hz, 1H), 6.66 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.92 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.17 – 2.08 (m, 1H), 1.36 – 1.24 (m, 1H), 1.19 (dd, *J* = 7.2, 3.2 Hz, 6H), 1.05 – 0.98 (m, 7H), 0.91 – 0.84 (m, 1H), 0.79 – 0.70 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.0, 154.0, 139.3, 132.4, 129.1, 129.1, 128.9, 127.5, 122.6, 121.3, 117.90, 116.0, 48.7, 23.8, 17.7, 17.4, 17.3, 13.5, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{23}H_{27}NO_2SiNa$+[M+Na]$^+$, 400.1703; found: 400.1702.

**4-(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine-5-carbonyl)phenyl acetate (3h)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3h** was isolated in 46% yield (18.87 mg) as a colorless liquid.

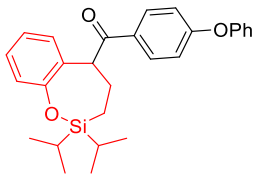
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.87 – 7.79 (m, 2H), 7.13 (ddd, *J* = 8.0, 7.2, 1.8 Hz, 1H), 7.09 – 7.00 (m, 3H), 6.81 (td, *J* = 7.5, 1.4 Hz, 1H), 6.74 (dd, *J* = 7.7, 1.8 Hz, 1H), 4.96 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.37 – 2.29 (m, 1H), 2.28 (s, 3H), 2.14 – 2.05 (m, 1H), 1.40 – 1.25 (m, 1H), 1.20 (dd, *J* =

7.2, 4.0 Hz, 6H), 1.07 – 0.99 (m, 7H), 0.90 – 0.83 (m, 1H), 0.76 – 0.68 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.1, 168.8, 154.0, 153.9, 133.8, 130.4, 129.7, 128.5, 127.6, 122.5, 121.6, 121.0, 48.0, 23.9, 21.1, 17.7, 17.4, 17.4, 17.4, 13.6, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{24}H_{30}O_4SiNa$+[M+Na]$^+$, 433.1806; found: 433.1800.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(4-phenoxyphenyl)methanone (3i)**



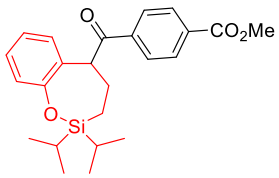

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3i** was isolated in 75% yield (33.32 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.36 (dd, *J* = 8.5, 7.4 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.14 – 7.10 (m, 1H), 7.02 (d, *J* = 8.5, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.82 (td, *J* = 7.4, 1.3 Hz, 1H), 6.78 (dd, *J* = 7.6, 1.9 Hz, 1H), 4.96 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.15 – 2.05 (zm, 1H), 1.37 – 1.26 (m, 1H), 1.20 (dd, *J* = 7.3, 4.3 Hz, 6H), 1.05 – 0.98 (m, 7H), 0.91 – 0.83 (m, 1H), 0.77 – 0.69 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.0, 161.7, 155.3, 154.0, 131.0, 130.9, 130.1, 130.0, 128.3, 127.6, 124.6, 122.4, 121.0, 120.3, 117.1, 47.8, 24.0, 17.7, 17.4, 17.4, 13.6, 12.9, 5.6.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{28}H_{32}O_3SiNa$+[M+Na]$^+$, 467.2013; found: 467.2010.

**methyl4-(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine-5-carbonyl)benzoate (3j)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3j** was isolated in 68% yield (27.89 mg) as a colorless liquid.

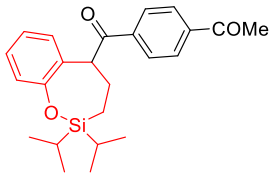
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.13 (ddd, *J* = 9.1, 7.3, 1.7 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.79 (td, *J* = 7.4, 1.3 Hz, 1H), 6.70 (dd, *J* = 7.6,

1.7 Hz, 1H), 4.98 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.89 (s, 3H), 2.38 – 2.29 (m, 1H), 2.17 – 2.08 (m, 1H), 1.37 – 1.24 (m, 1H), 1.20 (dd, *J* = 7.3, 4.2 Hz, 6H), 1.02 (dq, *J* = 11.7, 2.1 Hz, 7H), 0.91 – 0.84 (m, 1H), 0.78 – 0.70 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.0, 166.2, 154.0, 139.5, 133.5, 129.7, 129.4, 128.6, 128.6, 127.6, 122.47, 121.1, 52.4, 48.5, 23.8, 17.7, 17.4, 17.4, 13.5, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{24}H_{30}O_4SiNa^+$[M+Na]$^+$, 433.1806; found: 433.1803.

**1-(4-(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine-5-carbonyl)phenyl)ethan-1-one (3k)**



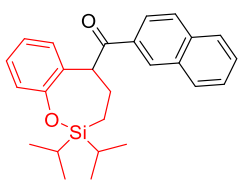

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3k** was isolated in 67% yield (26.41 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.92 – 7.82 (m, 4H), 7.18 – 7.09 (m, 1H), 7.03 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.79 (td, *J* = 7.5, 1.3 Hz, 1H), 6.70 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.98 (dd, *J* = 11.4, 4.8 Hz, 1H), 2.56 (s, 3H), 2.39 – 2.29 (m, 1H), 2.17 – 2.08 (m, 1H), 1.38 – 1.25 (m, 1H), 1.20 (dd, *J* = 7.3, 4.2 Hz, 6H), 1.06 – 0.99 (m, 7H), 0.92 – 0.84 (m, 1H), 0.80 – 0.70 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.8, 197.4, 154.0, 139.8, 139.5, 129.4, 128.8, 128.6, 128.4, 127.6, 122.5, 121.2, 48.6, 26.8, 23.8, 17.7, 17.4, 17.4, 13.5, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{24}H_{30}O_3SiNa^+$[M+Na]$^+$, 417.1856; found: 417.1855.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(naphthalen-2-yl)methanone (3l)**



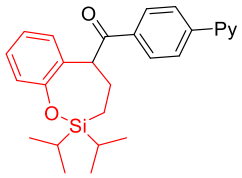

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3l** was isolated in 73% yield (29.36 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.33 (s, 1H), 7.89 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.86 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.53 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.47 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.12 (ddd, *J* = 8.1, 6.8, 2.1 Hz, 1H), 7.06 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.82 (dd, *J* = 7.7, 2.1 Hz, 1H), 6.80 – 6.76 (m, 1H), 5.17 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.46 – 2.36 (m, 1H), 2.22 – 2.14 (m, 1H),1.44-1.32 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 6H), 1.09 – 1.01 (m, 7H), 0.95 – 0.87 (m, 1H), 0.83 – 0.74 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.5, 154.0, 135.4, 133.6, 132.5, 130.3, 130.0, 129.7, 128.4, 128.3, 128.3, 127.7, 127.6, 126.5, 124.4, 122.4, 121.0, 48.1, 24.1, 17.8, 17.46, 17.4, 13.6, 12.9, 5.6.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{26}H_{30}O_2SiNa$+$[M+Na]^+$, 425.1907; found: 425.1905.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(4-(pyridin-2-yl)phenyl) methanone (3m)**



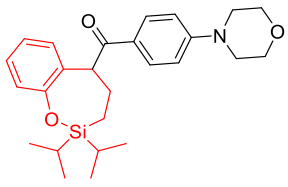

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3m** was isolated in 50% yield (30.47 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.71 – 8.65 (m, 1H), 8.48 (d, *J* = 1.9 Hz, 1H), 8.17 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.77-7.73 (m, 2H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.25-7.22 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 4.4 Hz, 2H), 5.07 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.20 – 2.09 (m, 1H), 1.41 – 1.28 (m, 1H), 1.22 (dd, *J* = 7.3, 5.1 Hz, 6H), 1.07 – 0.99 (m, 7H), 0.93 – 0.85 (m, 1H), 0.81 – 0.71 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.3, 156.4, 154.1, 149.7, 139.8, 136.9, 136.7, 131.3, 129.8, 129.2, 129.0, 128.4, 127.7, 126.9, 122.5, 122.4, 121.0, 120.5, 48.2, 24.0, 17.8, 17.5, 17.4, 17.4, 13.6, 12.9, 5.6.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{27}H_{31}NO_2SiH$+[M+H]$^+$, 430.2197; found: 430.2205.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(4-morpholinophenyl) methanone (3n)**



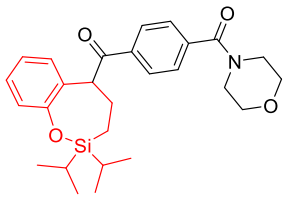

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3n** was isolated in 41% yield (17.92 mg) as a white/yellow solid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 9.0 Hz, 2H), 7.14-7.08 (m, 1H), 7.01 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.83 – 6.77 (m, 2H), 6.74 (d, *J* = 9.1 Hz, 2H), 4.94 (dd, *J* = 11.7, 4.9 Hz, 1H), 3.81 – 3.79 (m, 4H), 3.24-3.22 (m, 4H), 2.37 – 2.27 (m, 1H), 2.13 – 2.04 (m, 1H), 1.37 – 1.25 (m, 1H), 1.20 (dd, *J* = 7.3, 5.4 Hz, 6H), 1.07 – 0.98 (m, 7H), 0.90 – 0.82 (m, 1H), 0.77 – 0.68 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 198.7, 153.9, 153.8, 130.7, 130.5, 128.1, 127.7, 127.1, 122.4, 120.8, 113.2, 66.5, 47.4, 23.9, 17.8, 17.5, 17.4, 13.6, 12.9, 5.6.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{26}H_{35}NO_3SiH+[M+H]^+$, 438.2459; found: 438.2461.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(4-(morpholine-4-carbonyl) phenyl) methanone (3o)**



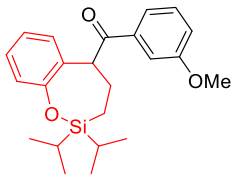

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3o** was isolated in 74% yield (37.42 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.13 (td, *J* = 7.6, 1.7 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.80 (td, *J* = 7.4, 1.3 Hz, 1H), 6.70 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.96 (dd, *J* = 11.5, 4.8 Hz, 1H), 3.89 – 3.23 (m, 8H), 2.39 – 2.28 (m, 1H), 2.16 – 2.01 (m, 1H), 1.35-1.26 (m, 1H), 1.19 (dd, *J* = 7.3, 4.9 Hz, 6H), 1.04-0.99 (m, 7H), 0.90 – 0.83 (m, 1H), 0.77 – 0.68 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.6, 169.3, 153.9, 139.2, 137.1, 129.5, 129.0, 128.6, 127.5, 127.2, 122.5, 121.1, 66.8, 48.2, 23.8, 17.7, 17.4, 17.4, 17.3, 13.5, 12.8, 5.4.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{27}H_{35}NO_4SiNa+[M+Na]^+$, 488.2228; found: 488.2228.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(3-methoxyphenyl)methanone (3p)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3p** was isolated in 62% yield (23.69 mg) as a colorless liquid.

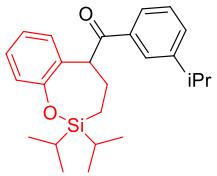
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.42 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.32 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.1, 1.9 Hz, 1H), 7.05 – 6.97 (m, 2H), 6.81 (td, *J* = 7.4, 1.3

Hz, 1H), 6.75 (dd, *J* = 7.6, 1.9 Hz, 1H), 4.99 (dd, *J* = 11.6, 4.9 Hz, 1H), 3.77 (s, 3H), 2.39 – 2.29 (m, 1H), 2.15 – 2.06 (m, 1H), 1.38 – 1.25 (m, 1H), 1.20 (dd, *J* = 7.3, 5.2 Hz, 6H), 1.06 – 0.99 (m, 7H), 0.90 – 0.83 (m, 1H), 0.78 – 0.69 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.6, 159.6, 154.0, 137.6, 129.9, 129.5, 128.4, 127.6, 122.4, 121.4, 121.0, 119.5, 112.7, 55.3, 48.1, 24.0, 17.8, 17.4, 17.4, 13.6, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{23}H_{30}O_3SiNa$+[M+Na]$^+$, 405.1856; found: 405.1854.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(3-isopropylphenyl) methanone (3q)**



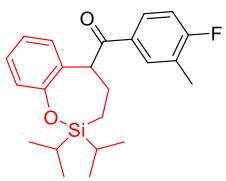

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3q** was isolated in 66% yield (26.01 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.75 (t, *J* = 1.9 Hz, 1H), 7.56 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.32 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.12 (ddd, *J* = 8.1, 6.6, 2.3 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.83 – 6.76 (m, 2H), 5.01 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.93-2.83 (m, 1H), 2.39 – 2.30 (m, 1H), 2.14 – 2.05 (m, 1H), 1.38 – 1.25 (m, 1H), 1.23 – 1.15 (m, 12H), 1.06 – 0.99 (m, 7H), 0.90 – 0.84 (m, 1H), 0.78 – 0.70 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.6, 154.0, 149.1, 136.3, 131.1, 130.0, 128.4, 128.3, 127.6, 126.7, 126.4, 122.4, 120.9, 48.0, 33.9, 24.0, 23.8, 23.7, 17.8, 17.5, 17.4, 17.4, 13.6, 12.9, 5.5, 1.0.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{25}H_{34}O_2SiNa$+[M+Na]$^+$, 417.2220; found: 417.2226.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(4-fluoro-3-methylphenyl) methanone (3r)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3r** was isolated

in 74% yield (28.43 mg) as a colorless liquid.

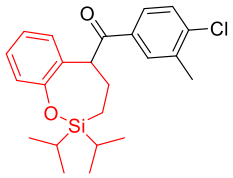
**$^1$H NMR (400 MHz, $CDCl_3$)** δ7.74 (dd, *J* = 7.8, 2.4 Hz,1H), 7.56 (ddd, *J* = 7.8, 5.0, 2.4 Hz, 1H), 7.13 (ddd, *J* = 8.0, 7.2, 1.8 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.91 (t, *J* = 8.9 Hz, 1H), 6.81 (td, *J* = 7.4, 1.3 Hz, 1H), 6.73 (dd, *J* = 7.6, 1.8 Hz, 1H), 4.94 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.37 – 2.27 (m, 1H), 2.23 (d, *J* = 2.0 Hz, 3H), 2.14 – 2.05 (m, 1H), 1.37 – 1.25 (m, 1H), 1.20 (dd, *J* = 7.3, 5.3 Hz, 6H), 1.06 – 0.98 (m, 7H), 0.90 – 0.83 (m, 1H), 0.77 – 0.69 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.2, 164.1 (d, *J* = 253.3 Hz), 153.9, 132.4 (d, *J* = 2.6 Hz), 132.3, 129.8, 128.7 (d, *J* = 9.3 Hz), 128.4, 127.6, 125.3 (d, *J* = 17.8 Hz), 122.4, 121.0, 115.1 (d, *J* = 22.9 Hz), 47.9, 24.0, 17.8, 17.4, 17.4, 14.5 (d, *J* = 3.4 Hz), 13.6, 12.9, 5.5, 1.0.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -109.6.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{23}H_{29}FO_2SiNa$+[M+Na]$^+$, 407.1813; found: 407.1810.

**(4-chloro-3-methylphenyl)(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl) methanone (3s)**



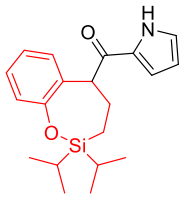

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3s** was isolated in 63% yield (25.20 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 2.2 Hz, 1H), 7.46 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.25 (d, *J* = 4.8 Hz, 1H), 7.12 (ddd, *J* = 8.8, 7.3, 1.8 Hz, 1H), 7.02 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.80 (td, *J* = 7.5, 1.3 Hz, 1H), 6.71 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.92 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.33 (s, 3H), 2.32 – 2.25 (m, 1H), 2.13 – 2.04 (m, 1H), 1.36 – 1.23 (m, 1H), 1.19 (dd, *J* = 7.3, 5.4 Hz, 6H), 1.05 – 0.98 (m, 7H), 0.89 – 0.82 (m, 1H), 0.76 – 0.67 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.6, 154.0, 139.3, 136.5, 134.7, 131.0, 129.7, 129.2, 128.5, 127.5, 127.5, 122.5, 121.1, 48.0, 23.9, 20.1, 17.8, 17.4, 17.4, 13.6, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{23}H_{29}ClO_2SiNa$+[M+Na]$^+$, 423.1518; found: 423.1512.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(1H-pyrrol-2-yl)methanone (3t)**



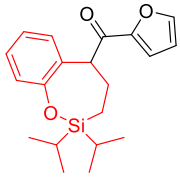
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3t** was isolated in 49% yield (16.72 mg) as a white/yellow solid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.52 (s, 1H), 7.12 (td, *J* = 7.6, 1.7 Hz, 1H), 7.00-6.97 (m, 3H), 6.87-6.83 (m, 1H), 6.66 – 6.59 (m, 1H), 6.16-6.14 (m, 1H), 4.81 (dd, *J* = 11.7, 4.9 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.12 – 2.03 (m, 1H), 1.34 – 1.25 (m, 1H), 1.20 (t, *J* = 7.0 Hz, 6H), 1.05 – 0.98 (m, 7H), 0.88 – 0.77 (m, 1H), 0.77 – 0.68 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 190.7, 154.1, 131.8, 130.3, 128.1, 127.5, 124.2, 122.2, 120.8, 116.5, 110.7, 47.7, 24.1, 17.8, 17.4, 17.4, 13.5, 12.9, 5.7.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{20}H_{27}NO_2SiNa$+$[M+Na]^+$, 364.1703; found: 364.1706.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(furan-2-yl)methanone (3u)**



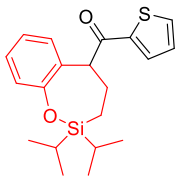
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3u** was isolated in 58% yield (19.84 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.47 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.13 (ddd, *J* = 8.9, 7.2, 1.9 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.90 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.85 (td, *J* = 7.4, 1.3 Hz, 1H), 6.40 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.83 (dd, *J* = 11.6, 4.9 Hz, 1H), 2.35 – 2.26 (m, 1H), 2.13 – 2.04 (m, 1H), 1.34 – 1.25 (m, 1H), 1.20 (t, *J* = 6.8 Hz, 6H), 1.04 – 0.97 (m, 7H), 0.89 – 0.81 (m, 1H), 0.78 – 0.70 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 189.4, 154.3, 152.3, 146.4, 129.5, 128.3, 127.3, 122.3, 120.9, 117.9, 112.0, 48.1, 23.7, 17.7, 17.4, 17.4, 13.5, 12.8, 5.6.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{20}H_{26}O_3SiNa$+$[M+Na]^+$, 365.1543; found: 365.1548.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(thiophen-2-yl)methanone (3v)**



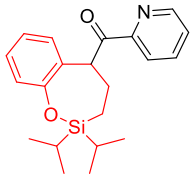
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3v** was isolated in 68% yield (24.36 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.53 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.42 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.14 (ddd, *J* = 8.1, 7.2, 1.9 Hz, 1H), 7.01 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.97 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.91 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.85 (td, *J* = 7.4, 1.3 Hz, 1H), 4.90 (dd, *J* = 11.5, 4.9 Hz, 1H), 2.36 – 2.27 (m, 1H), 2.16 – 2.08 (m, 1H), 1.37 – 1.25 (m, 1H), 1.20 (t, *J* = 6.7 Hz, 6H), 1.05 – 0.98 (m, 7H), 0.89 – 0.82 (m, 1H), 0.78 – 0.69 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 193.5, 154.1, 144.0, 133.3, 132.5, 129.9, 128.4, 128.1, 127.5, 122.4, 120.9, 49.3, 24.0, 17.8, 17.4, 17.4, 13.5, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{20}H_{26}O_2SSiNa$+[M+Na]$^+$, 381.1315; found: 381.1313.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl)methanone (3w)**



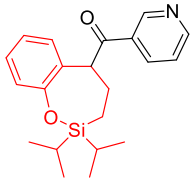
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3w** was isolated in 87% yield (30.73 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.54 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.04 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.76 (td, *J* = 7.7, 1.7 Hz, 1H), 7.34 (ddd, *J* = 7.6, 4.7, 1.3 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.0, 1.9 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.82 (dd, *J* = 7.7, 1.9 Hz, 1H), 6.77 (td, *J* = 7.4, 1.4 Hz, 1H), 5.73 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.39-2.30 (m, 1H), 2.15-2.06 (m,1H), 1.42-1.28 (m, 1H), 1.23-1.17 (m, 6H), 1.12 – 0.92 (m, 7H), 0.90-0.83 (m, 1H), 0.80-0.71 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 202.3, 154.6, 153.2, 149.1, 136.7, 129.8, 128.0, 127.5, 126.7, 122.4, 121.86, 121.1, 46.3, 24.2, 17.7, 17.4, 17.4, 13.4, 12.9, 6.0.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{21}H_{27}NO_2SiH$+[M+H]$^+$, 354.1884; found: 354.1894.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-3-yl)methanone (3x)**



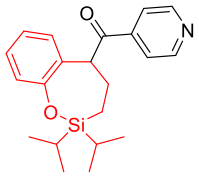
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3x** was isolated in 59% yield (20.84 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.01 – 8.96 (m, 1H), 8.64 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.04 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.28 (ddd, *J* = 8.1, 4.9, 0.9 Hz, 1H), 7.14 (td, *J* = 7.6, 1.7 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.80 (td, *J* = 7.5, 1.4 Hz, 1H), 6.70 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.93 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.38-2.29 (m, 1H), 2.17-2.08 (m, 1H), 1.35-1.25 (m,1H), 1.19 (dd, *J* = 7.2, 3.2 Hz, 6H), 1.05 – 0.99 (m, 7H), 0.90-0.83 (m, 1H), 0.77-0.69 m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.4, 154.2, 153.0, 150.3, 136.0, 131.5, 129.1, 128.8, 127.6, 123.4, 122.50, 121.3, 48.6, 23.6, 17.7, 17.4, 17.4 , 17.4, 13.5, 12.9, 5.4.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{21}H_{27}NO_2SiH$+$[M+H]^+$, 354.1884; found: 354.1878.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-4-yl)methanone (3y)**



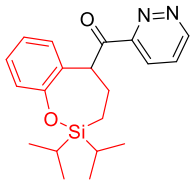
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3y** was isolated in 57% yield (20.13 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.69 – 8.62 (m, 2H), 7.57 – 7.51 (m, 2H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1H), 7.04 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.81 (td, *J* = 7.5, 1.3 Hz, 1H), 6.66 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.91 (dd, *J* = 11.3, 4.8 Hz, 1H), 2.37-2.27(m,1H), 2.16-2.07 (m, 1H), 1.35-1.27 (m, 1H), 1.19 (dd, *J* = 7.2, 3.3 Hz, 6H), 1.07 – 0.95 (m, 7H), 0.90-0.83 (m, 1H), 0.78-0.69(m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.9, 154.1, 150.8, 142.2, 128.9, 128.9, 127.5, 122.6, 121.6, 121.3, 48.7, 23.6, 17.7, 17.4, 17.3, 13.5, 12.9, 5.4.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{21}H_{27}NO_2SiH$+$[M+H]^+$, 354.1884; found: 354.1881.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridazin-3-yl)methanone (3z)**



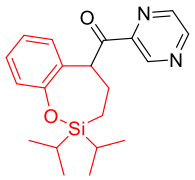
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3z** was isolated in 38% yield (13.46 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 9.21 (dd, *J* = 5.1, 1.8 Hz, 1H), 8.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.58 (dd, *J* = 8.4, 5.0 Hz, 1H), 7.09 (ddd, *J* = 8.0, 7.1, 1.9 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.84 (dd, *J* = 7.6, 1.9 Hz, 1H), 6.78 (td, *J* = 7.4, 1.3 Hz, 1H), 5.81 (dd, *J* = 10.7, 4.5 Hz, 1H), 2.50-2.41 (m, 1H), 2.23-2.14 (m, 1H), 1.34 – 1.26 (m, 1H), 1.18 (dd, *J* = 7.3, 1.7 Hz, 6H), 1.05 – 0.99 (m, 7H), 0.91 – 0.83 (m, 1H), 0.82 – 0.75 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.9, 155.9, 154.8, 152.9, 129.0, 128.3, 127.9, 127.1, 125.3, 121.8, 121.5, 47.89, 24.2, 17.6, 17.4, 13.2, 12.9, 6.0.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{20}H_{26}N_2O_2SiH^+[M+H]^+$, 355.1836; found: 355.1826.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyrazin-2-yl)methanone (3aa)**



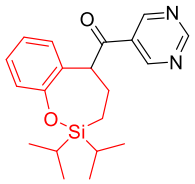
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3aa** was isolated in 63% yield (22.31 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 9.23 (d, *J* = 1.5 Hz, 1H), 8.62 (d, *J* = 2.5 Hz, 1H), 8.49 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.10 (ddd, *J* = 8.1, 5.9, 3.1 Hz, 1H), 7.02 – 6.97 (m, 1H), 6.80 – 6.76 (m, 2H), 5.58 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.39-2.30 (m, 1H), 2.15-2.06 (m, 1H),1.37-1.28 m, 1H), 1.20 (dd, *J* = 7.3, 6.0 Hz, 6H), 1.05 – 0.99 (m, 7H), 0.90-0.84 (m, 1H), 0.81-0.72 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.5, 154.5, 147.6, 147.3, 144.1, 143.7, 129.1, 128.3, 127.3, 122.1, 121.2, 46.7, 23.7, 17.7, 17.4, 17.4, 13.5, 12.9, 5.8.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{20}H_{26}N_2O_2SiH^+[M+H]^+$, 355.1836; found: 355.1838.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyrimidin-5-yl)methanone (3ab)**



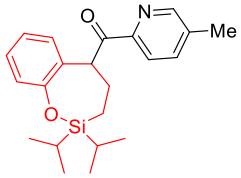
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ab** was isolated in 31% yield (10.98 mg) as a white/yellow solid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 9.23 (s, 1H), 9.02 (s, 2H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.83 (td, *J* = 7.5, 1.3 Hz, 1H), 6.69 (dd, *J* = 7.6, 1.7 Hz, 1H), 4.83 (dd, *J* = 11.1, 4.8 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.18 – 2.09 (m, 1H), 1.35 – 1.25 (m, 1H), 1.17 (dd, *J* = 7.1, 1.8 Hz, 6H), 1.05 – 0.97 (m, 7H), 0.90-0.83 (m, 1H), 0.79-0.71 , 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 197.9, 160.8, 157.2, 154.3, 129.2, 129.0, 128.3, 127.6, 122.7, 121.6, 49.3, 23.3, 17.7, 17.4, 17.3, 13.4, 12.9, 5.3.

**HRMS (ESI-TOF, m/z):** Calc'd for C20H26N2O2SiH+[M+H]$^+$, 355.1836; found: 355.1831.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(5-methylpyridin-2-yl) methanone (3ac)**



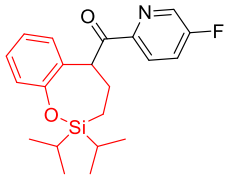
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ac** was isolated in 75% yield (27.54 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.36 (d, *J* = 2.1 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.08 (td, *J* = 7.6, 1.9 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.83 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.77 (td, *J* = 7.4, 1.3 Hz, 1H), 5.72 (dd, *J* = 11.6, 4.7 Hz, 1H), 2.40 – 2.33 (m, 1H), 2.32 (s, 3H), 2.14 – 2.05 (m, 1H), 1.38-1.32(m, 1H), 1.22 (t, *J* = 7.0 Hz, 6H), 1.06 – 0.99 (m, 7H), 0.90 – 0.83 (m, 1H), 0.80 – 0.72 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 202.1, 154.6, 150.9, 149.7, 137.1, 137.0, 130.0, 127.9, 127.5, 122.1, 121.8, 121.0, 46.2, 24.2, 18.6, 17.7, 17.4, 17.4, 13.5, 12.9, 6.0.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{29}NO_2SiH+[M+H]^+$, 368.2040; found: 368.2040.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(5-fluoropyridin-2-yl) methanone (3ad)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ad** was isolated in 69% yield (23.42 mg) as a colorless liquid.

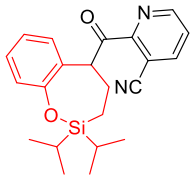
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.35 (d, *J* = 2.8 Hz, 1H), 8.12 (dd, *J* = 8.7, 4.6 Hz, 1H), 7.44 (td, *J* = 8.4, 2.9 Hz, 1H), 7.09 (ddd, *J* = 8.0, 5.6, 3.4 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.80 – 6.75 (m, 2H), 5.68 (dd, *J* = 11.6, 4.7 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.14 – 2.05 (m, 1H), 1.39 – 1.28 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 6H), 1.06 – 0.99 (m, 7H), 0.90 – 0.83 (m, 1H), 0.81 – 0.72 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.6, 161.1 (d, *J* = 263.3 Hz), 154.5, 149.6, 137.5 (d, *J* = 24.4 Hz), 129.6, 128.0, 127.3, 124.3 (d, *J* = 5.5 Hz), 123.2 (d, *J* = 18.6 Hz), 121.9, 121.1, 46.3, 24.1, 17.7, 17.4, 17.4, 13.5, 12.9, 5.9.

**$^{19}$F NMR (377 MHz, $CDCl_3$) δ** -120.3.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{21}H_{26}FNO_2SiNa+[M+Na]^+$, 394.1609; found:394.1612.

**2-(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine-5-carbonyl)nicotinonitrile (3ae)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ae** was isolated in 53% yield (20.04 mg) as a colorless liquid.

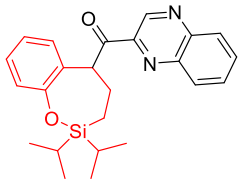
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.23 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.95 (t, *J* = 7.8 Hz, 1H), 7.76 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.11 (ddd, *J* = 8.0, 7.2, 1.8 Hz, 1H), 6.98 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.89 (dd, *J* = 7.6, 1.8 Hz, 1H), 6.80 (td, *J* = 7.4, 1.3 Hz, 1H), 5.68 (dd, *J* = 11.1, 4.7 Hz, 1H), 2.40 – 2.31 (m, 1H),

2.15 – 2.06 (m, 1H), 1.40-1.32 (m, 1H), 1.22 (t, *J* = 7.3 Hz, 6H), 1.07 – 0.99 (m, 7H), 0.90 – 0.82 (m, 1H), 0.81 – 0.74 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.3, 154.9, 154.3, 138.3, 133.0, 131.1, 128.4, 128.4, 127.6, 125.2, 121.8, 121.3, 116.5, 46.3, 24.5, 17.7, 17.4 ,17.4 17.4, 13.4, 12.8, 5.9.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{26}N_2O_2SiNa^+$[M+Na]$^+$, 401.1656; found: 401.1658.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(quinoxalin-2-yl)methanone (3af)**



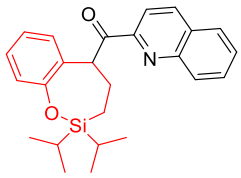

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3af** was isolated in 69% yield (27.89 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 9.51 (s, 1H), 8.10 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.05 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.82 (tdd, *J* = 6.9, 1.6, 0.8 Hz, 1H), 7.76 (ddd, *J* = 8.5, 6.7, 1.5 Hz, 1H), 7.11 – 7.06 (m, 1H), 6.98 (ddd, *J* = 9.7, 7.6, 1.5 Hz, 2H), 6.80 (td, *J* = 7.5, 1.3 Hz, 1H), 5.94 (dd, *J* = 11.6, 4.7 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.21 – 2.12 (m, 1H), 1.47 – 1.36 (m, 1H), 1.28 (dd, *J* = 11.5, 7.4 Hz, 6H), 1.10 – 1.00 (m, 7H), 0.95 – 0.85 (m, 1H), 0.85 – 0.77 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.9, 154.8, 146.3, 143.7, 143.6, 140.9, 132.1, 130.7, 130.5, 129.2, 128.8, 128.3, 127.4, 122.0, 121.1, 46.0, 24.3, 17.8, 17.5, 17.4, 17.4, 13.6, 12.9, 5.8.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{24}H_{28}N_2O_2SiNa^+$[M+Na]$^+$, 427.1812; found: 427.1811.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(quinolin-2-yl)methanone (3ag)**



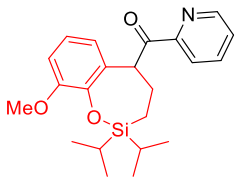
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ag** was isolated in 59% yield (23.79 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.22 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.07 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.79 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.69 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.57 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.07 (td, *J* = 7.6, 1.7 Hz, 1H), 7.00 (ddd, *J* = 7.7, 5.5, 1.5 Hz, 2H), 6.79 (td, *J* = 7.4, 1.3 Hz, 1H), 6.14 (dd, *J* = 11.8, 4.8 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.20 – 2.12 (m, 1H), 1.52 – 1.43 (m, 1H), 1.31 (dd, *J* = 10.6, 7.4 Hz, 6H), 1.11 – 1.01 (m, 7H), 0.94 – 0.85 (m, 1H), 0.84 – 0.76 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 202.7, 154.9, 152.6, 147.1, 136.8, 130.8, 129.7, 129.4, 129.4, 128.4, 127.9, 127.5, 127.4, 121.8, 121.0, 118.6, 45.5, 24.6, 17.9, 17.5, 17.5, 17.4, 13.6, 12.9, 5.9.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{25}H_{29}NOSiH^+$[M+H]$^+$, 404.2040; found: 404.2058.

**(2,2-diisopropyl-9-methoxy-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl) methanone (3ah)**



According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ah** was isolated in 76% yield (29.12 mg) as a colorless liquid.

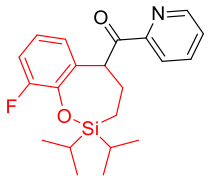
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.50 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 1H), 8.00 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.31 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 6.73 – 6.70 (m, 2H), 6.41 (q, *J* = 4.5 Hz, 1H), 5.77 (dd, *J* = 11.8, 4.9 Hz, 1H), 3.81 (s, 3H), 2.38 – 2.29 (m, 1H), 2.13 – 2.04 (m, 1H), 1.44-1.34 (m, 1H), 1.23 (dd, *J* = 21.1, 7.4 Hz, 6H), 1.07 – 0.98 (m, 7H), 0.90 – 0.83 (m, 1H), 0.80

– 0.72 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 202.2, 153.1, 151.2, 149.1, 143.6, 136.6, 130.6, 126.6, 122.3, 121.6, 119.1, 110.6, 55.4, 46.1, 23.8, 17.9, 17.5, 17.0, 16.9, 13.8, 12.7, 5.9.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{29}NO_3SiH$+[M+H]$^+$, 384.1989; found: 384.1992.

**(9-fluoro-2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl) methanone (3ai)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ai** was isolated in 81% yield (30.07 mg) as a colorless liquid.

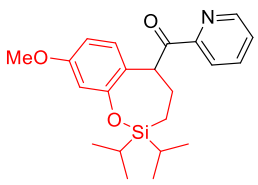
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.54 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.05 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.78 (td, *J* = 7.7, 1.7 Hz, 1H), 7.36 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 6.91 (ddd, *J* = 10.0, 8.1, 1.6 Hz, 1H), 6.70 (td, *J* = 8.0, 5.0 Hz, 1H), 6.59 (dt, *J* = 7.8, 1.4 Hz, 1H), 5.74 (dd, *J* = 11.5, 4.6 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.17 – 2.08 (m, 1H), 1.42-1.33(m, 1H), 1.22 (t, *J* = 7.6 Hz, 6H), 1.07 – 1.00 (m, 7H), 0.94 – 0.87 (m, 1H), 0.84 – 0.76 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.8, 154.5 (d, *J* = 244.5 Hz), 152.9, 149.1, 142.6 (d, *J* = 12.0 Hz), 136.7, 132.4, 126.9, 122.6 (d, *J* = 3.2 Hz), 122.3, 121.5 (d, *J* = 7.5 Hz), 115.0 (d, *J* = 19.2 Hz), 46.3 (d, *J* = 2.1 Hz), 24.1, 17.7, 17.4, 17.0 (d, *J* = 1.3 Hz), 16.9 (d, *J* = 1.5 Hz), 13.5, 12.83, 6.1.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -131.8.

**HRMS (ESI-TOF, m/z):** Calc'd for C21H26FNO2SiH+[M+H]$^+$, 372.1790; found: 372.1797.

**(2,2-diisopropyl-8-methoxy-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl) methanone (3aj)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3aj** was

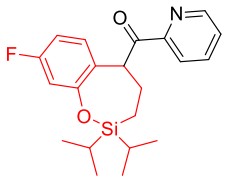
isolated in 58% yield (22.23 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.55 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.02 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.76 (td, *J* = 7.7, 1.7 Hz, 1H), 7.34 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 2.6 Hz, 1H), 6.35 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.63 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.71 (s, 3H), 2.38 – 2.28 (m, 1H), 2.11 – 2.02 (m, 1H), 1.38-1.25 (m, 1H), 1.20 (dd, *J* = 7.3, 4.4 Hz, 6H), 1.07 – 0.99 (m, 7H), 0.90 – 0.80 (m, 1H), 0.80 – 0.72 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 202.4, 159.5, 155.6, 153.3, 149.1, 136.7, 128.0, 126.7, 122.3, 122.0, 107.2, 107.1, 55.2, 45.9, 24.3, 17.7, 17.5, 17.6, 17.4, 13.4, 12.9, 6.0.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{29}NO_3SiH+[M+H]^+$, 384.1989; found: 384.1996.

**(8-fluoro-2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl) methanone (3ak)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ak** was isolated in 58% yield (21.53 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.55 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 8.04 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.36 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 6.79 (dd, *J* = 8.6, 6.7 Hz, 1H), 6.71 (dd, *J* = 10.0, 2.7 Hz, 1H), 6.50 (td, *J* = 8.4, 2.6 Hz, 1H), 5.66 (dd, *J* = 11.4, 4.6 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.12 – 2.03 (m, 1H), 1.43 – 1.26 (m, 1H), 1.20 (dd, *J* = 7.3, 2.7 Hz, 6H), 1.07 – 0.99 (m, 7H), 0.91 – 0.84 (m, 1H), 0.81 – 0.73 (m, 1H).

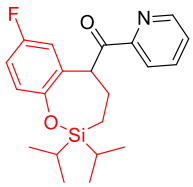
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 202.0, 162.2 (d, *J* = 245.1 Hz), 155.9 (d, *J* = 11.6 Hz), 153.0, 149.1, 136.7, 128.3 (d, *J* = 10.0 Hz), 126.9, 125.6 (d, *J* = 3.3 Hz), 122.4, 108.7 (d, *J* = 5.2 Hz), 108.5 (d, *J* = 3.4 Hz), 45.9, 24.2, 17.6, 17.4, 17.4, 13.4, 12.9, 5.9.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -114.5 (dt, *J* = 9.7, 7.3 Hz).

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{21}H_{26}FNO_2SiH+[M+H]^+$, 372.1790; found: 372.1806.

**(7-fluoro-2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl)**

**methanone (3al)**



According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3al** was isolated in 82% yield (30.44 mg) as a colorless liquid.

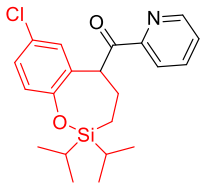
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.55 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.07 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.79 (td, *J* = 7.7, 1.7 Hz, 1H), 7.37 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 6.92 (dd, *J* = 8.8, 5.1 Hz, 1H), 6.76 (ddd, *J* = 8.8, 8.0, 3.1 Hz, 1H), 6.61 (dd, *J* = 9.4, 3.1 Hz, 1H), 5.73 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.37 – 2.28 (m, 1H), 2.14 – 2.05 (m, 1H), 1.39-1.29(m, 1H), 1.21 (dd, *J* = 7.3, 6.3 Hz, 6H), 1.06 – 0.98 (m, 7H), 0.91 – 0.84 (m, 1H), 0.80 – 0.72 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.8, 157.6 (d, *J* = 239.2 Hz), 152.8, 150.5 (d, *J* = 2.4 Hz), 149.1, 136.8, 131.0 (d, *J* = 7.4 Hz), 127.0, 122.4, 121.6 (d, *J* = 8.3 Hz), 114.2 (d, *J* = 10.2 Hz), 114.0 (d, *J* = 9.0 Hz), 46.0, 24.2, 17.7, 17.4, 17.4, 13.4, 12.8, 5.9.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -121.8.

**HRMS (ESI-TOF, m/z):** Calc'd for C21H26FNO2SiH+[M+H]$^{+}$, 372.1790; found: 372.1789.

**(7-chloro-2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl) methanone (3am)**



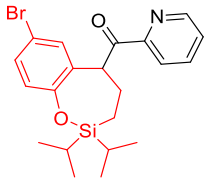
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3am** was isolated in 61% yield (23.62 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.55 (dt, *J* = 4.8, 1.2 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.80 (td, *J* = 7.7, 1.8 Hz, 1H), 7.38 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 7.04 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.87 (d, *J* = 2.6 Hz, 1H), 5.72 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.13 – 2.04 (m, 1H), 1.39 – 1.29 (m, 1H), 1.20 (dd, *J* = 7.4, 4.3 Hz, 6H), 1.06 – 0.97 (m, 7H), 0.91 – 0.84 (m, 1H), 0.81 – 0.73 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.6, 153.4, 152.7, 149.1, 136.8, 131.4, 127.8, 127.5, 127.0, 126.6, 122.5, 122.2, 45.9, 24.2, 17.7, 17.4, 17.4, 13.4, 12.8, 5.8.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{21}H_{26}ClNO_2SiH$+[M+H]$^+$, 388.1494; found: 388.1504.

**(7-bromo-2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl) methanone (3an)**



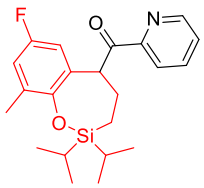

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3an** was isolated in 56% yield (24.14 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.56 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.07 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.80 (td, *J* = 7.7, 1.7 Hz, 1H), 7.38 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 7.19 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 5.72 (dd, *J* = 11.5, 4.7 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.12 – 2.03 (m, 1H), 1.38-1.29(m, 1H), 1.20 (dd, *J* = 7.3, 3.9 Hz, 6H), 1.06 – 0.97 (m, 7H), 0.90 – 0.83 (m, 1H), 0.82 – 0.72 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.6, 154.0, 152.7, 149.1, 136.8, 131.9, 130.8, 130.4, 127.0, 122.8, 122.5, 114.1, 45.9, 24.3, 17.7, 17.4, 17.4, 13.4, 12.8, 5.8.

**HRMS (ESI-TOF, m/z):** Calc' d. for $C_{21}H_{26}BrNO_2SiH$+[M+H]$^+$, 432.0989; found: 432.0989.

**(7-fluoro-2,2-diisopropyl-9-methyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl)methanone (3ao)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ao** was isolated in 74% yield (28.5 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.55 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.05 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.78 (td, *J* = 7.7, 1.7 Hz, 1H), 7.36 (ddd, *J* = 7.6, 4.7, 1.3 Hz, 1H), 6.67 (dd, *J* = 8.8, 3.1 Hz, 1H),

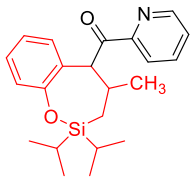
6.44 (dd, *J* = 9.3, 3.1 Hz, 1H), 5.70 (dd, *J* = 11.5, 4.4 Hz, 1H), 2.37 – 2.28 (m, 1H), 2.27 (s, 3H), 2.17-2.09 (m, 1H), 1.39 – 1.30 (m, 1H), 1.22 (dd, *J* = 7.3, 2.1 Hz, 6H), 1.06 – 0.95 (m, 7H), 0.93 – 0.86 (m, 1H), 0.84 – 0.76 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 202.0, 156.9 (d, *J* = 238.4 Hz), 152.9, 149.1, 148.8 (d, *J* = 2.5 Hz), 136.8, 130.2 (d, *J* = 5.1 Hz), 130.1 (d, *J* = 4.8 Hz), 126.9, 122.4, 115.6 (d, *J* = 22.2 Hz), 111.6 (d, *J* = 23.7 Hz), 46.4 (d, *J* = 1.3 Hz), 24.5, 17.7, 17.5, 17.4, 17.3, 17.2 (d, *J* = 1.5 Hz), 14.2, 13.0, 6.4.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -122.7.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{28}FNO_2SiH^+[M+H]^+$, 386.1946; found: 386.1952.

**(2,2-diisopropyl-4-methyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl) methanone (3ap)**



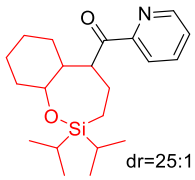

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3at** was isolated in 23% yield (8.5 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.67 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.10 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.85 (td, *J* = 7.7, 1.8 Hz, 1H), 7.46 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.90 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.86 (td, *J* = 7.4, 1.3 Hz, 1H), 4.56-4.49 (m, 1H), 3.51-3.46 (m, 1H), 1.19-1.12 (m, 2H), 1.00 (dd, *J* = 7.2, 3.3 Hz, 8H), 0.88 (d, *J* = 7.2 Hz, 6H), 0.71 (d, *J* = 7.6 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 205.7, 155.3, 153.0, 148.9, 136.9, 131.5, 130.4, 128.0, 127.0, 122.3, 120.4, 120.1, 43.2, 40.5, 18.0, 17.2, 17.1, 16.5, 13.6, 13.2, 10.9.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{29}NO_2SiH^+[M+H]^+$, 368.2040; found: 368.20434.

**(2,2-diisopropyldecahydrobenzo[f][1,2]oxasilepin-5-yl)(pyridin-2-yl)methanone (3aq)**



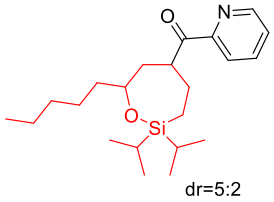

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3aq** was isolated in 53% yield (19.0 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.67 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.04 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 4.03-3.99 (m, 1H), 3.94-3.90 (m, 1H), 3.27 (d, *J* = 10.5 Hz, 1H), 3.17 (d, *J* = 10.6 Hz, 1H), 2.18-2.11 (m, 1H), 2.07-2.00 (m, 1H), 1.76-1.68 (m, 1H), 1.61 (s, 3H), 1.38-1.24 (m, 4H), 1.12 – 0.97 (m, 15H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.0, 154.2, 148.6, 136.8, 126.7, 121.6, 73.8, 56.8, 32.7, 31.8, 26.8, 23.5, 21.8, 17.4, 17.4, 17.3, 13.8, 13.7.

**HRMS (ESI-TOF, m/z):** Calc'd for C21H33NO2SiNa+[M+Na]$^+$, 382.2173; found: 382.2180.

**(2,2-diisopropyl-7-pentyl-1,2-oxasilepan-6-yl)(pyridin-2-yl)methanone (3ar)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ar** was isolated in 40% yield (15.0 mg) as a colorless liquid.

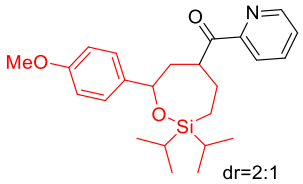
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.69-8.66 (m, 1H), 8.04-8.00 (m, 1H), 7.85-7.80 (m, 1H), 7.49 – 7.40 (m, 1H), 4.28 – 4.10 (m, 1H), 3.96 – 3.86 (m, 1H), 2.14 – 1.79 (m, 3H), 1.75 – 1.58 (m, 3H), 1.56 – 1.36 (m, 3H), 1.33 – 1.22 (m, 6H), 1.05 – 1.02 (m, 12H), 0.89 – 0.84 (m, 4H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 204.5, 152.7, 148.9, 137.0, 126.9, 122.7, 74.2, 48.0, 41.0, 39.6, 31.9, 26.4, 25.6, 22.7, 17.8, 17.6, 17.6, 13.6, 13.0, 9.7.

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 205.0, 153.1, 148.8,136.9, 126.8, 122.5, 71.0, 42.3, 38.4, 37.6, 31.9, 25.8, 24.4, 18.0, 17.7, 17.7, 14.1, 13.7, 13.1, 8.0.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{37}NO_2SiH$+[M+H]$^+$, 376.2666; found: 376.2671.

**(2,2-diisopropyl-7-(4-methoxyphenyl)-1,2-oxasilepan-5-yl)(pyridin-2-yl)methanone (3as)**




According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), **3as** was isolated in 50% yield (20.56 mg) as a colorless liquid.

**Major product:$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.61 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.00 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.81 (td, *J* = 7.7, 1.8 Hz, 1H), 7.42 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.37 (dd, *J* = 8.1, 2.6 Hz, 1H), 4.23-4.17 (m, 1H), 3.79 (s, 3H), 2.26 (ddd, *J* = 15.0, 6.9, 2.7 Hz, 1H), 2.17 – 2.01 (m, 3H), 1.16 – 1.08 (m, 8H), 1.02 (d, *J* = 6.4 Hz, 6H), 0.90 – 0.83 (m, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 205.0, 158.2, 153.0, 148.9, 138.1, 136.9, 126.8, 126.3, 122.4, 113.4, 71.8, 55.2, 42.5, 40.5, 24.2, 17.8, 17.8, 17.7, 17.6, 13.6, 13.0, 7.8.

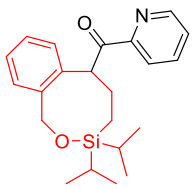
**HRMS (ESI-TOF, m/z):** Calc'd for $C_{24}H_{33}NO_3SiH$+[M+H]$^+$, 412.2302; found: 412.2304.

**Minor product:$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.71 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.02 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.82 (td, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.02 (d, *J* = 9.7 Hz, 1H), 4.11 (tt, *J* = 10.8, 2.1 Hz, 1H), 3.77 (s, 3H), 2.21 – 2.10 (m, 2H), 1.93 – 1.75 (m, 2H), 1.13-1.10 (m, 7H), 1.05 – 0.98 (m, 9H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 204.0, 158.3, 152.6, 148.9, 138.6, 137.0, 126.9, 126.3, 122.7, 113.4, 75.6, 55.2, 48.5, 44.4, 26.2, 18.0, 17.8, 17.7, 17.5, 13.6, 13.0, 9.8.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{24}H_{33}NO_3SiH$+[M+H]$^+$, 412.2302; found: 412.2305.

**(3,3-diisopropyl-3,4,5,6-tetrahydro-1H-benzo[f][1,2]oxasilocin-6-yl)(pyridin-2-yl)methanone (3at)**



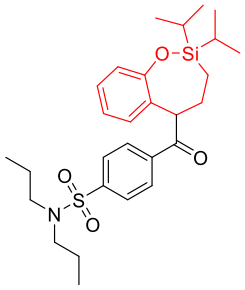

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **3ap** was isolated in 14% yield (5.14 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.51 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 1H), 8.02 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.73 (td, *J* = 7.7, 1.7 Hz, 1H), 7.31 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.20 – 7.10 (m, 2H), 7.08 (dd, *J* = 7.4, 1.6 Hz, 1H), 5.85 (dd, *J* = 12.3, 4.7 Hz, 1H), 5.70 (d, *J* = 12.2 Hz, 1H), 4.76 (d, *J* = 12.3 Hz, 1H), 2.40-2.32(m, 1H), 2.16-2.07 (m, 1H), 1.22 – 1.13 (m, 1H), 1.09 (t, *J* = 6.2 Hz, 6H), 0.85 (dd, *J* = 7.4, 3.1 Hz, 6H), 0.72 – 0.58 (m, 2H), 0.18-0.10(m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.6, 153.1, 149.0, 139.8, 139.3, 136.6, 130.4, 128.7, 126.7, 126.7, 126.5, 122.3, 66.6, 47.4, 26.6, 17.8, 17.6, 17.6, 17.6, 13.6, 13.3, 7.8.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{22}H_{29}NO_2SiH$+[M+H]$^+$, 368.2040; found: 368.2038.

**4-(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine-5-carbonyl)-N,N-dipropyl benzene sulfonamide (4a)**



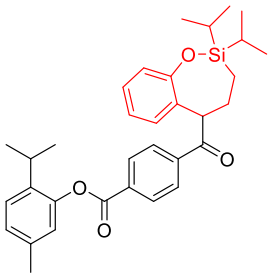

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **4a** was isolated in 68% yield (34.83 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.91 – 7.83 (m, 2H), 7.78 – 7.71 (m, 2H), 7.14 (ddd, *J* = 9.0, 7.4, 1.7 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.80 (td, *J* = 7.5, 1.3 Hz, 1H), 6.68 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.94 (dd, *J* = 11.3, 4.8 Hz, 1H), 3.08 – 3.00 (m, 4H), 2.35-2.88 (m,1H), 2.16-2.07 (m, 1H), 1.57 – 1.44 (m, 4H), 1.32 – 1.23 (m, 1H), 1.19 (dd, *J* = 7.2, 3.2 Hz, 6H), 1.04 – 0.98 (m, 7H), 0.90-0.87 (m, 1H), 0.83 (t, *J* = 7.4 Hz, 6H), 0.76 – 0.66 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.43, 154.00, 143.73, 138.99, 129.21, 128.72, 127.58, 127.11, 122.50, 121.22, 49.94, 48.60, 23.82, 21.96, 17.73, 17.41, 17.35, 13.50, 12.88, 11.09, 5.45.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{28}H_{41}NO_4SSiH$+[M+H]$^+$, 516.2598; found: 516.2603.

**2-isopropyl-5-methylphenyl 4- (2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine-5-carbonyl) benzoate (4b)**



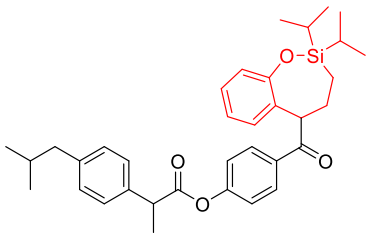
According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **4b** was isolated in 72% yield (38.04 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.20 – 8.13 (m, 2H), 7.96 – 7.88 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.16 (td, *J* = 7.7, 1.8 Hz, 1H), 7.06 (dt, *J* = 8.1, 1.9 Hz, 2H), 6.89 (d, *J* = 1.8 Hz, 1H), 6.83 (td, *J* = 7.5, 1.3 Hz, 1H), 6.74 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.02 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.04-2.93 (m, 1H), 2.41 – 2.34 (m, 1H), 2.33 (s, 3H), 2.19-2.10 (m, 1H), 1.37 – 1.28 (m, 1H), 1.25 – 1.15 (m, 12H), 1.07 – 1.00 (m, 7H), 0.92-0.85 (m, 1H), 0.79-0.71 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.9, 164.5, 154.0, 147.9, 140.0, 137.0, 136.7, 133.0, 130.3, 129.4, 128.8, 128.7, 127.6, 127.3, 126.5, 122.6, 122.5, 121.2, 48.6, 27.2, 23.8, 23.0, 23.0, 20.8, 17.8, 17.4, 17.4, 13.5, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{33}H_{40}O_4SiH^+[M+H]^+$, 529.2769; found: 529.2767.

**4-(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepine-5-carbonyl)phenyl2-(4-isobutylphenyl)propanoate (4c)**



According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **4c** was isolated in 81% yield (45.06 mg) as a colorless liquid.

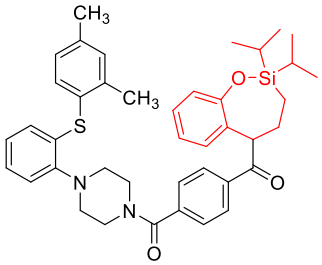
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.82 – 7.76 (m, 2H), 7.27 – 7.22 (m, 2H), 7.15 – 7.09 (m, 3H), 7.01 (dt, *J* = 8.1, 1.5 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.79 (tt, *J* = 7.3, 1.7 Hz, 1H), 6.71 (dt, *J* = 7.6, 2.0 Hz, 1H), 4.93 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.90 (q, *J* = 7.1 Hz, 1H), 2.45 (d, *J* = 7.1 Hz, 2H), 2.35 – 2.26 (m, 1H), 2.13 – 2.04 (m, 1H), 1.89 – 1.83 (m, 1H), 1.57 (dd, *J* = 7.2, 1.3 Hz, 3H), 1.31 (dd, *J* = 8.2,

6.5 Hz, 1H), 1.21 – 1.16 (m, 6H), 1.04 – 0.98 (m, 7H), 0.90 (d, *J* = 6.6 Hz, 6H), 0.88 – 0.82 (m, 1H), 0.75 – 0.67 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.2, 172.6, 154.2, 153.9, 141.0, 136.8, 133.7, 130.3, 129.7 , 129.5, 128.5, 127.6, 127.1, 122.5, 121.5, 121.0, 48.0, 45.2, 45.0, 30.1, 23.9, 22.4, 18.3, 17.74, 17.4, 17.4, 17.4, 13.6, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{35}H_{44}O_4SiH^+$[M+H]$^+$, 557.3082; found: 557.3086.

**(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo[f][1,2]oxasilepin-5-yl)(4-(4-(2-((2,4-dimethylphenyl) thio) phenyl) piperazine-1-carbonyl) phenyl) methanone (4d)**



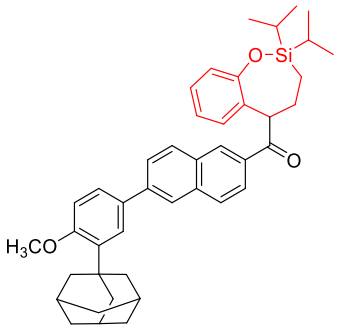

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **4d** was isolated in 71% yield (48.02 mg) as a colorless liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.89 – 7.82 (m, 2H), 7.43 – 7.38 (m, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.10 – 6.98 (m, 4H), 6.89 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 6.81 (td, *J* = 7.4, 1.3 Hz, 1H), 6.73 (dd, *J* = 7.7, 1.7 Hz, 1H), 6.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 4.99 (dd, *J* = 11.5, 4.8 Hz, 1H), 3.95 (s, 2H), 3.51 (s, 2H), 3.13 (s, 2H), 2.96 (s, 2H), 2.35 (s, 3H), 2.35-2.31(m,1H), 2.29 (s, 3H), 2.16-2.07(Mm,1H), 1.35-1.30 (m, 1H), 1.20 (dd, *J* = 7.3, 5.2 Hz, 6H), 1.07 – 0.99 (m, 7H), 0.89 – 0.85 (m, 1H), 0.78-0.69 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 199.8, 169.4, 154.0, 148.3, 142.3, 139.9, 139.4, 137.0, 136.1, 134.6, 131.8, 129.6, 129.0, 128.6, 127.9, 127.6, 127.6, 127.2, 126.4, 125.6, 125.0, 122.6, 121.1, 120.0, 48.3, 23.9, 21.2, 20.6, 17.8, 17.5, 17.4, 13.6, 12.9, 5.5.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{41}H_{48}N_2O_3SSiH^+$[M+H]$^+$, 677.3228; found: 677.3230.

**(6-(3-(adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)(2,2-diisopropyl-2,3,4,5-tetrahydrobenzo [f] [1,2] oxasilepin-5-yl) methanone (4e)**



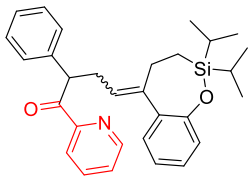

According to the synthesis method of 5-acylbenzoxasilole (0.1 mmol scale), product **4e** was isolated in 61% yield (41.11 mg) as a colorless liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.33 (d, *J* = 1.7 Hz, 1H), 7.93 (d, *J* = 1.7 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.73 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.51 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.13 (ddd, *J* = 8.8, 6.9, 2.0 Hz, 1H), 7.07 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.85 – 6.76 (m, 2H), 5.17 (dd, *J* = 11.5, 4.8 Hz, 1H), 3.89 (s, 3H), 2.45-2.36 (m,1H), 2.24 – 2.14 (m, 7H), 2.13 – 2.07 (m, 3H), 1.80 (d, *J* = 3.1 Hz, 6H), 1.41-1.35 (m,1H), 1.25 (t, *J* = 7.4 Hz, 6H), 1.11 – 1.01 (m, 7H), 0.95 – 0.89 (m, 1H), 0.82-0.74 (m, 1H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 200.4, 158.9, 154.0, 141.5, 139.0, 135.8, 133.2, 132.5, 131.2, 130.1, 130.1, 130.1, 128.4, 128.3, 127.7, 126.3, 125.9, 125.7, 124.8, 124.5, 122.5, 121.0, 112.1, 55.1, 48.1, 40.5, 37.2, 37.1, 29.1, 24.1, 17.8, 17.5, 17.4, 13.6, 12.9, 5.7.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{43}H_{50}O_3SiH$+$[M+H]^+$, 643.3602; found: 643.3611.

**(R)-4-(2,2-diisopropyl-3,4-dihydrobenzo[f][1,2]oxasilepin-5(2H)-ylidene)-2-phenyl-1-(pyridin-2-yl)butan-1-one (4f)**




**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.64 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 1H), 8.01 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.74 (td, *J* = 7.7, 1.7 Hz, 1H), 7.44 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.37 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.19 – 7.14 (m, 1H), 7.06 (ddd, *J* = 8.1, 7.2, 1.9 Hz, 1H), 6.83 (ddd, *J* = 12.9,

7.8, 1.6 Hz, 2H), 6.77 (td, *J* = 7.4, 1.3 Hz, 1H), 5.55 (t, *J* = 7.6 Hz, 1H), 5.42 (t, *J* = 7.2 Hz, 1H), 3.10,3.02 (m, 1H), 2.82,8.75 (m, 1H), 2.62 – 2.48 (m, 2H), 1.06 – 0.94 (m, 16H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 201.0, 153.1, 152.9, 148.8, 142.0, 138.8, 136.8, 135.0, 129.6, 128.9, 128.5, 128.1, 128.0, 126.9, 126.9, 122.7, 121.0, 120.5, 50.7, 31.4, 25.4, 17.2, 17.1 13.0, 9.1.

**HRMS (ESI-TOF, m/z):** Calc'd for $C_{30}H_{35}NO_2SiH+[M+H]^+$, 470.2510; found: 470.2520.

## Supplementary references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(3) Wang, H.-Y.; Wang, X.-H.; Zhou, B.-A.; Zhang, C.-L.; Ye, S. Ketones from aldehydes via alkyl C(sp3)−H functionalization under photoredox cooperative NHC/palladium catalysis. *Nat. Commun.* **2023**, *14*, 4044.

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(6) Li, Q.-Z.; Zou, W.-L.; Yu, Z.-Y.; Kou, X.-X.; Liu, Y.-Q.; Zhang, X.; He, Y.; Li, J.-L. Remote site-selective arene C–H functionalization enabled by N-heterocyclic carbene organocatalysis. *Nat. Catal.* **2024**, *7*, 900-911.

# Appendix: $^{1}H$, $^{13}C$, and $^{19}F$ NMR spectra for new compounds

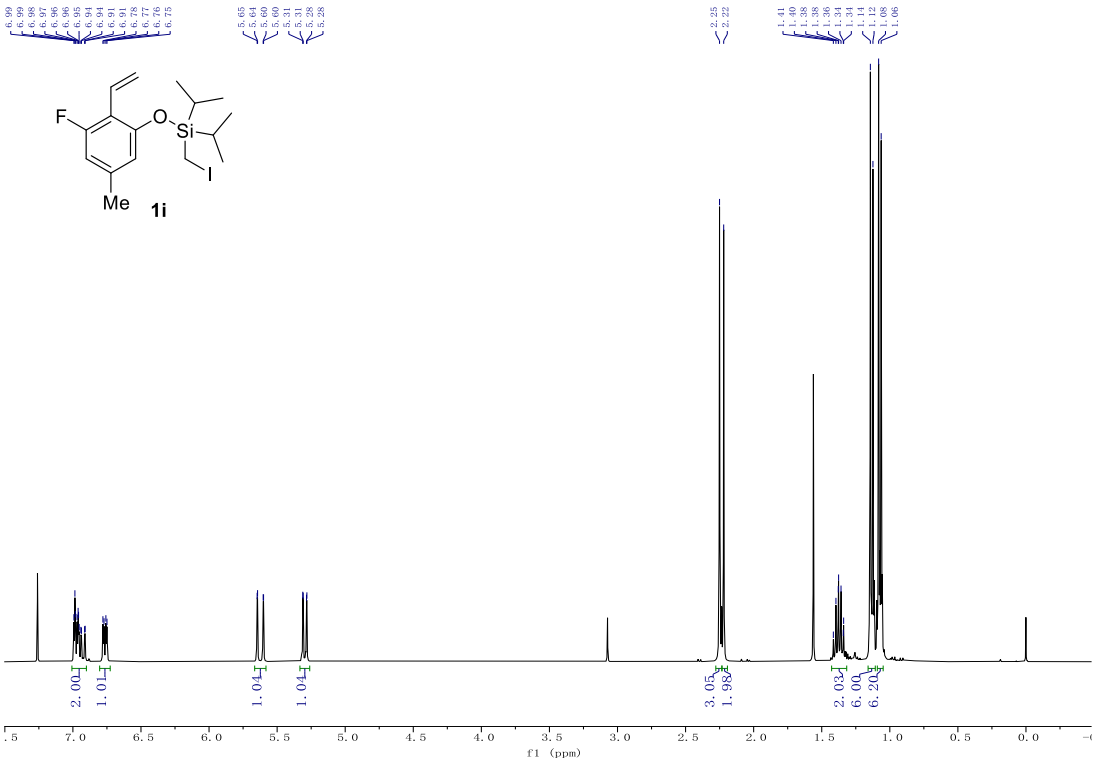


**Figure S4.** $^{1}H$ **NMR** (400 MHz, $CDCl_3$) spectrum of **1i**

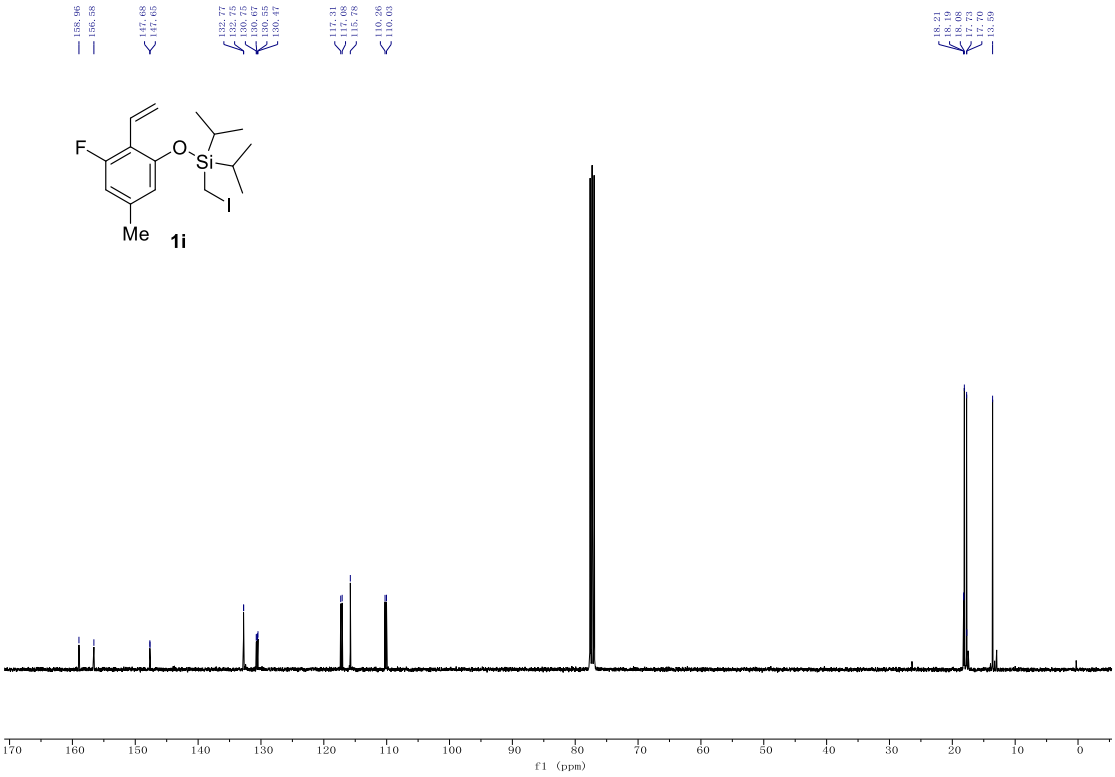


**Figure S5.** $^{13}C$ **NMR** (101 MHz, $CDCl_3$) spectrum of **1i**

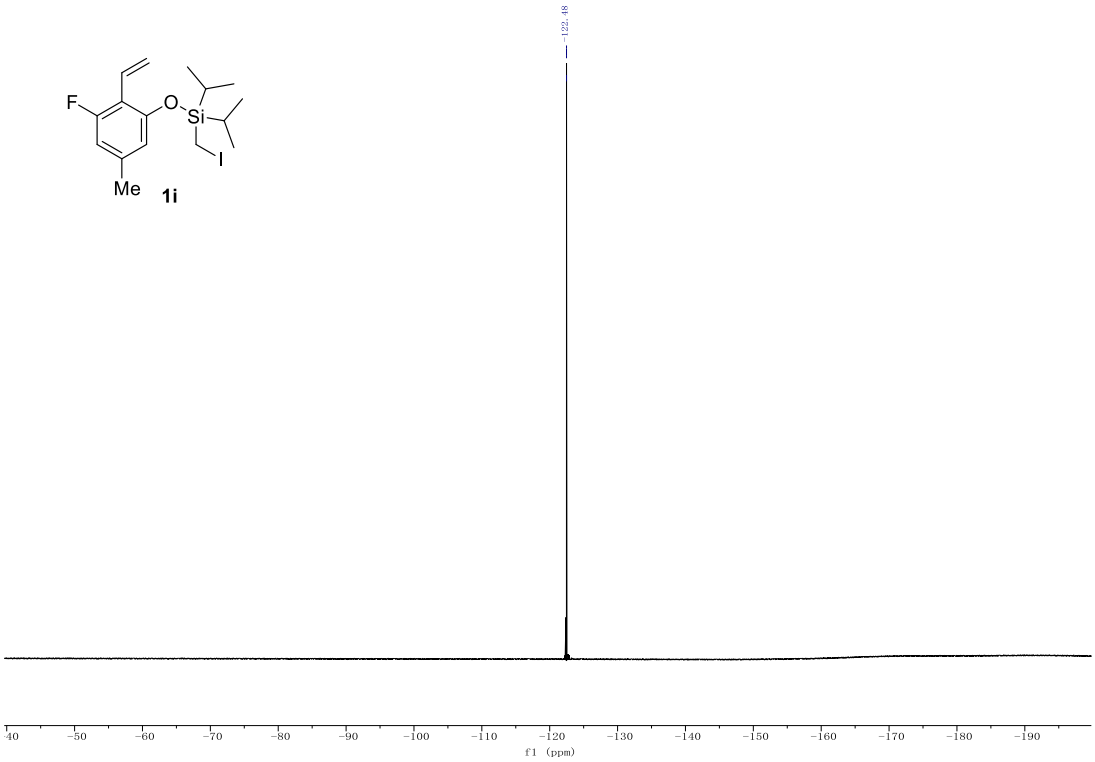


**Figure S6. $^{19}$F NMR** (377 MHz, $CDCl_3$) spectrum of **1i**

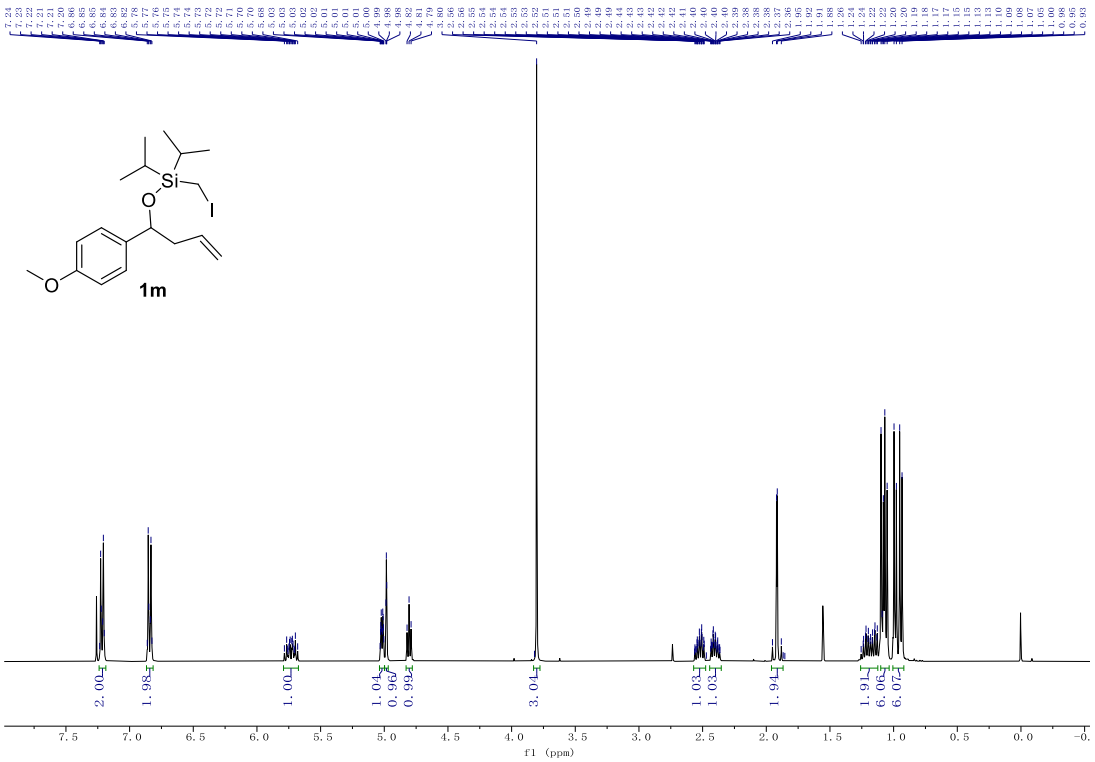


**Figure S7.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **1m**

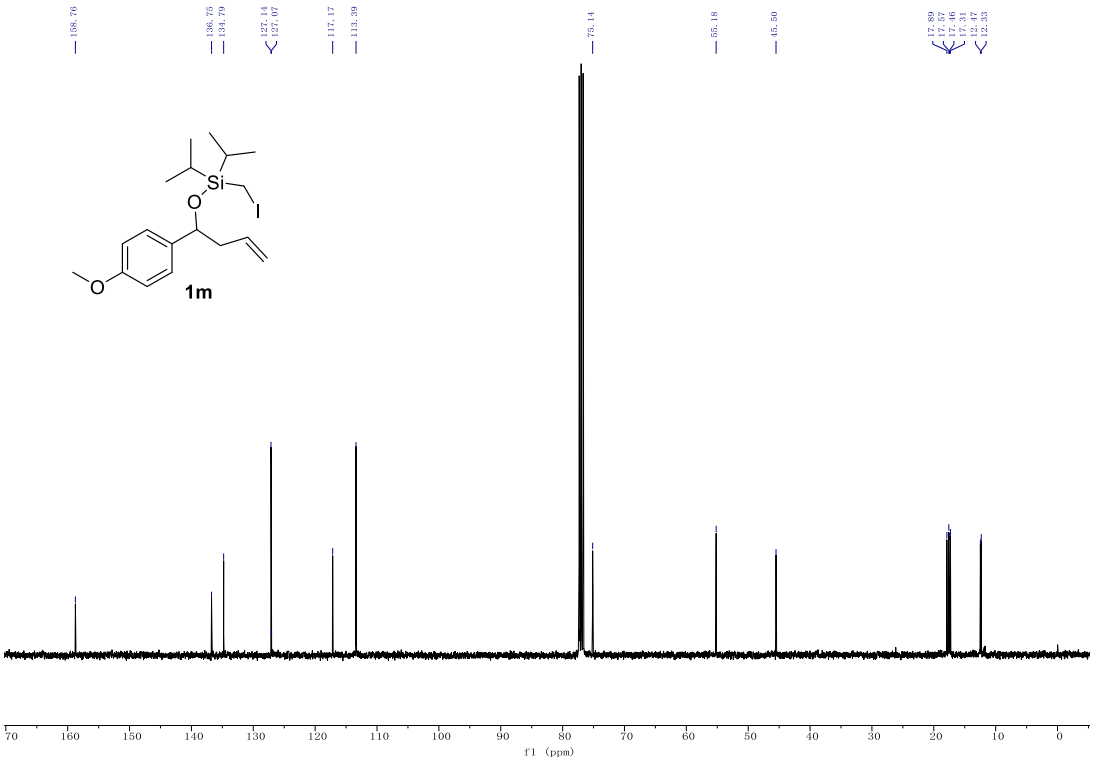


**Figure S8.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **1m**

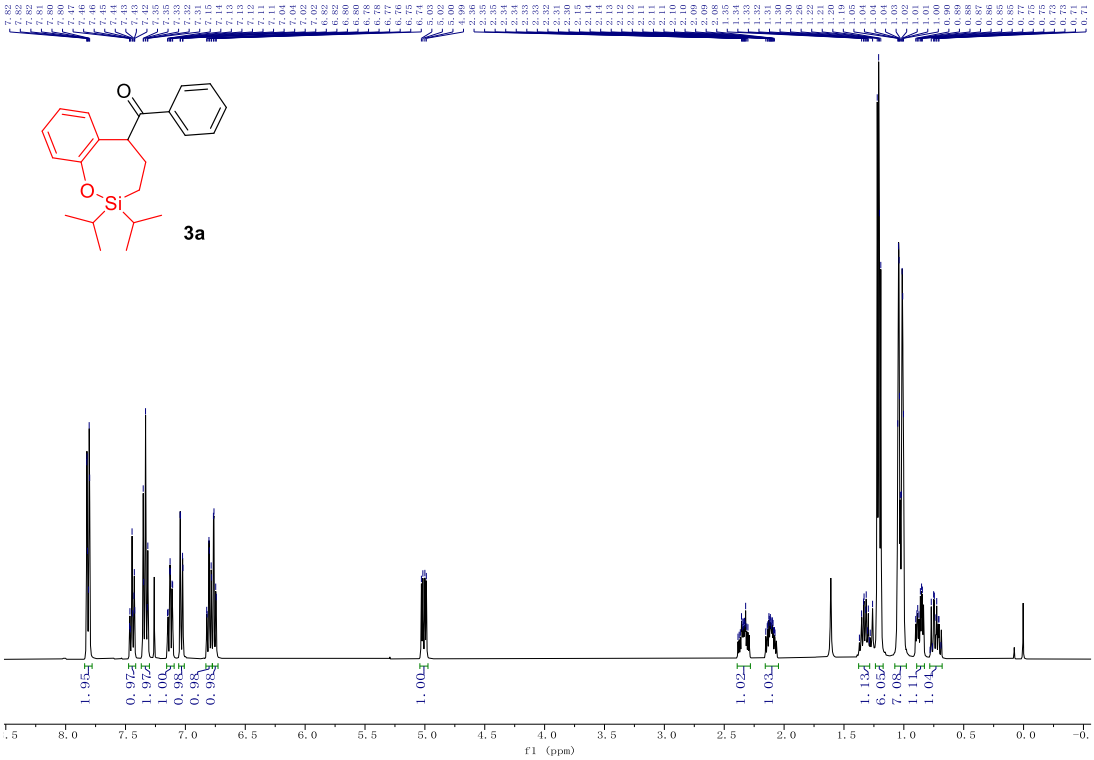


**Figure S9.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3a**

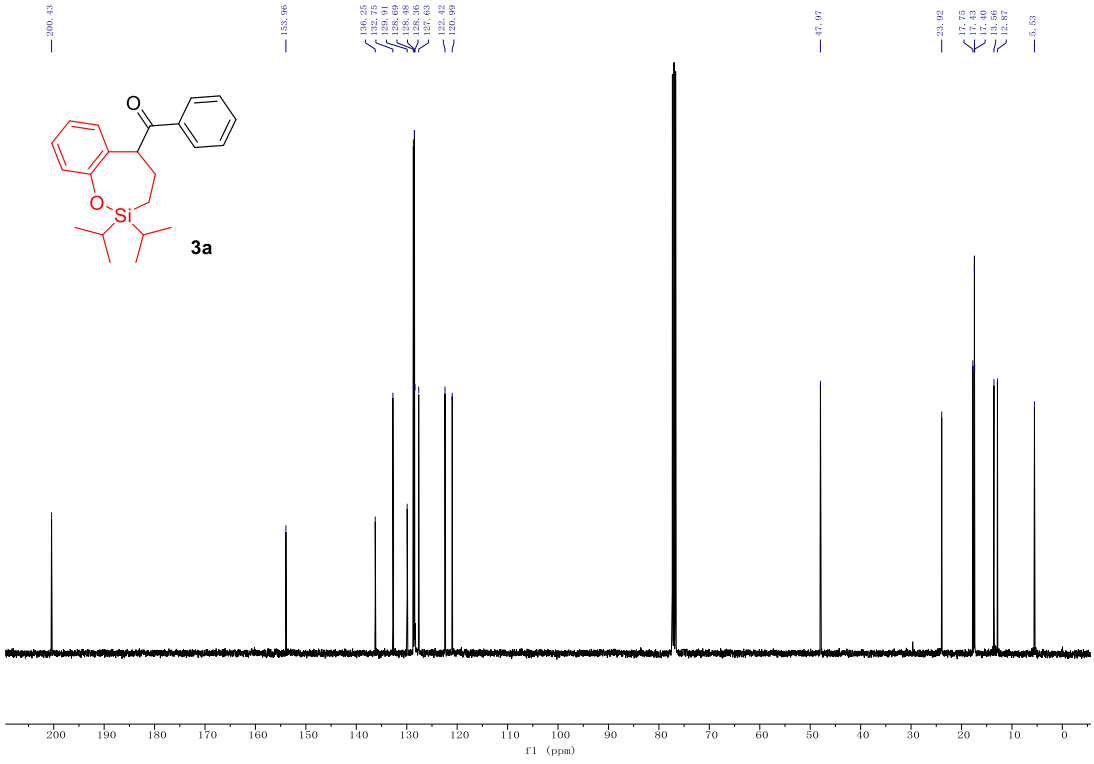


**Figure S10.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3a**

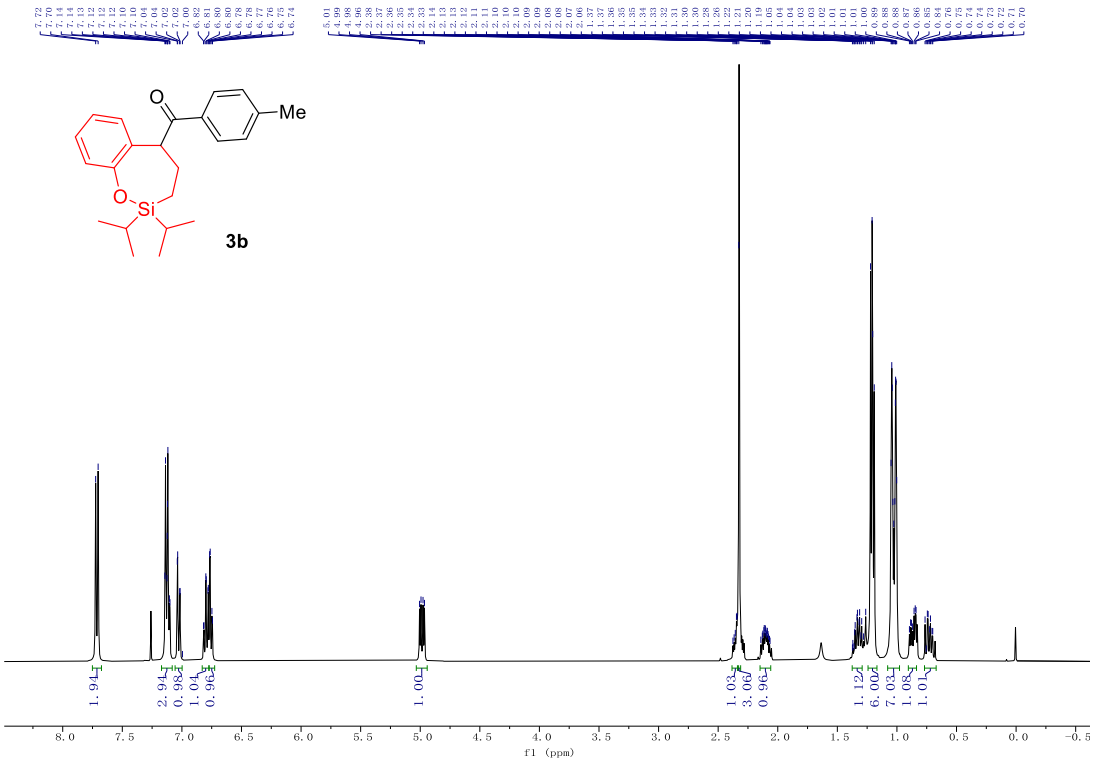


**Figure S11.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3b**

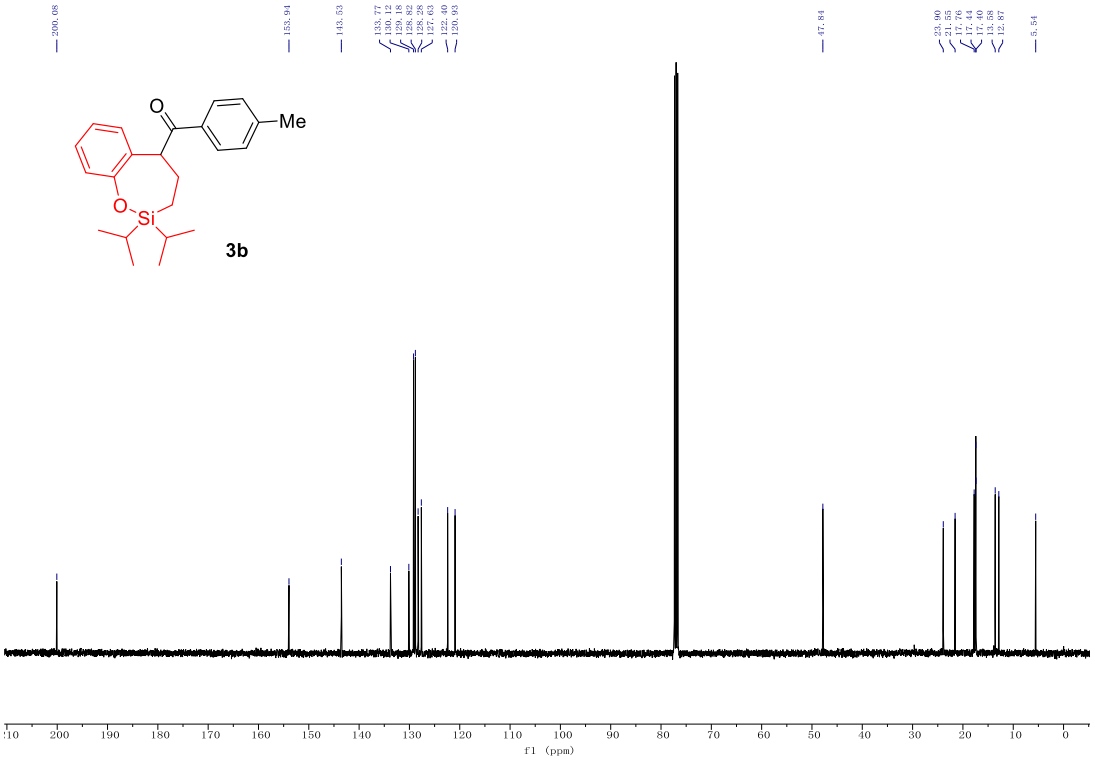


**Figure S12.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3b**

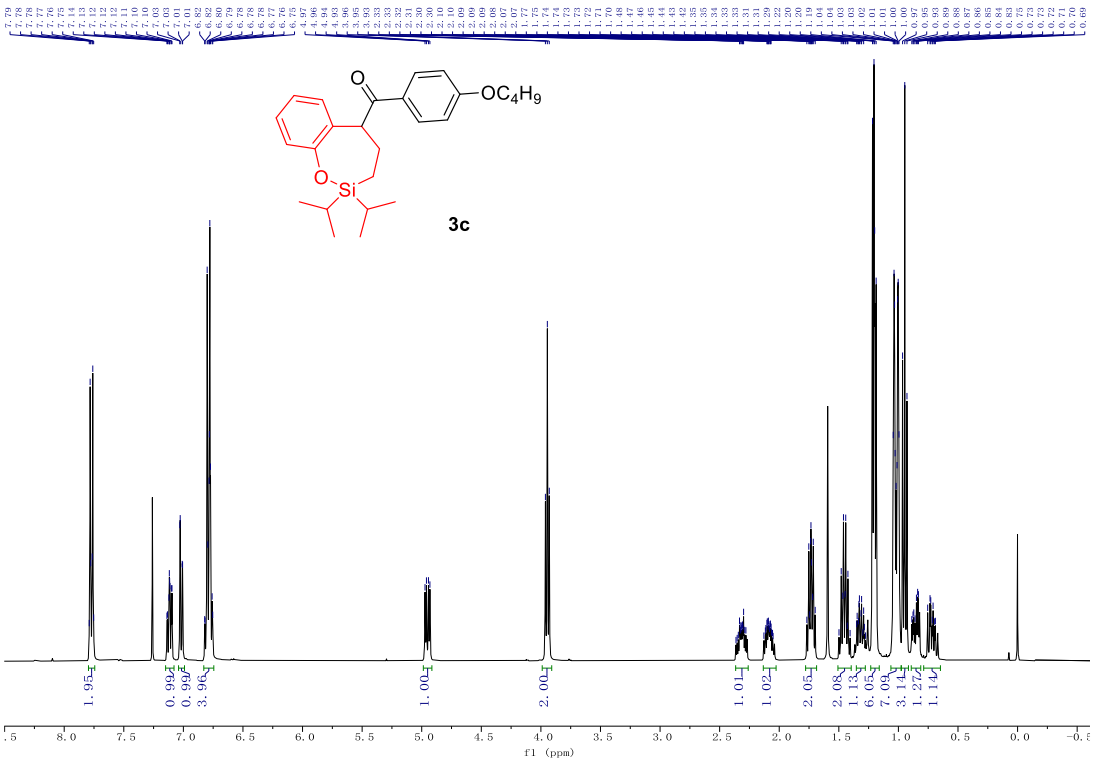


**Figure S13.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3c**

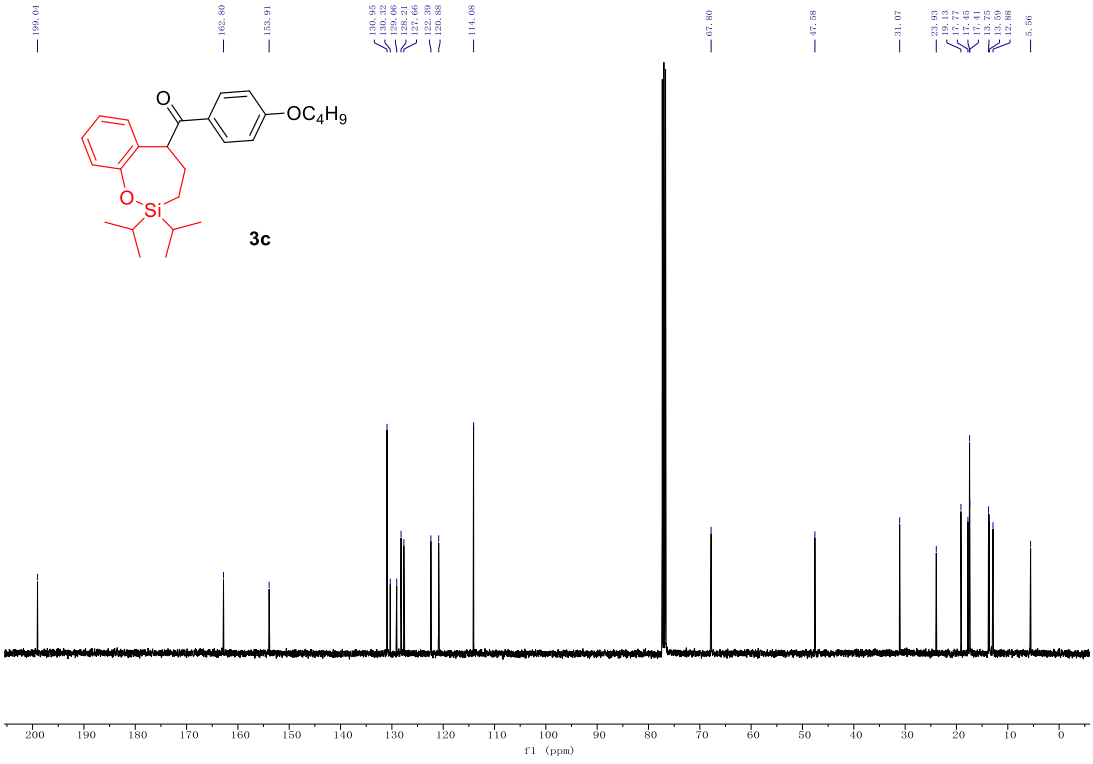


**Figure S14.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3c**

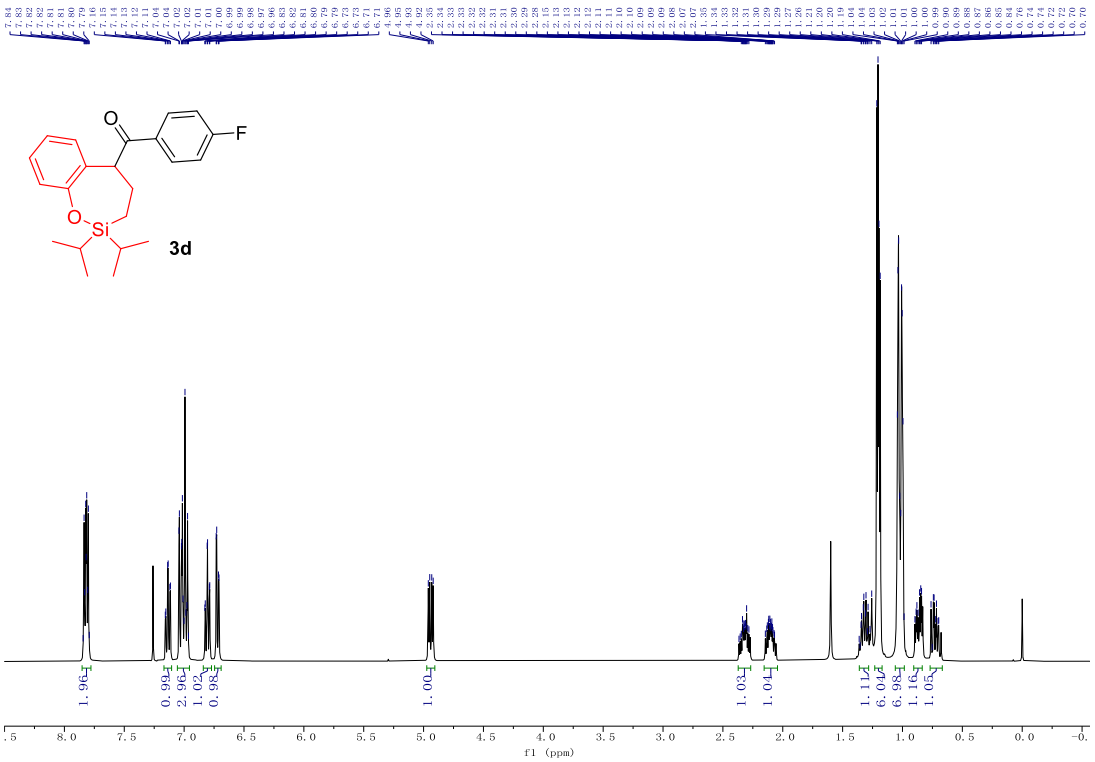


**Figure S15.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3d**

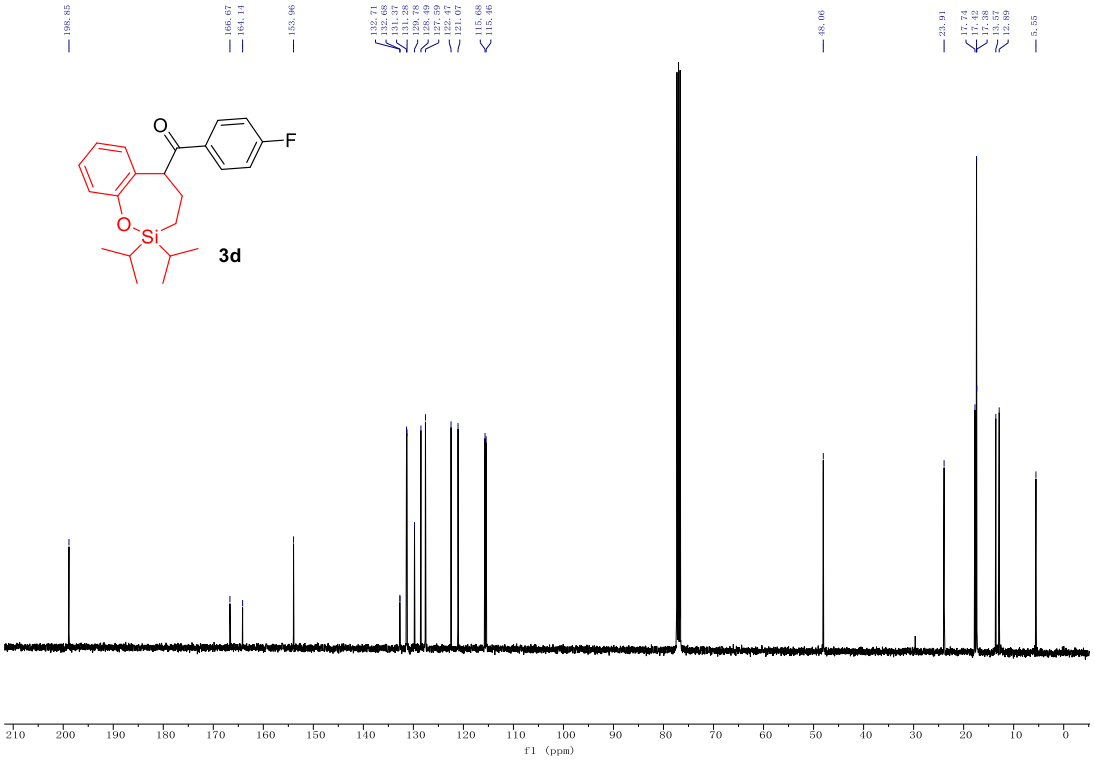


**Figure S16.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3d**

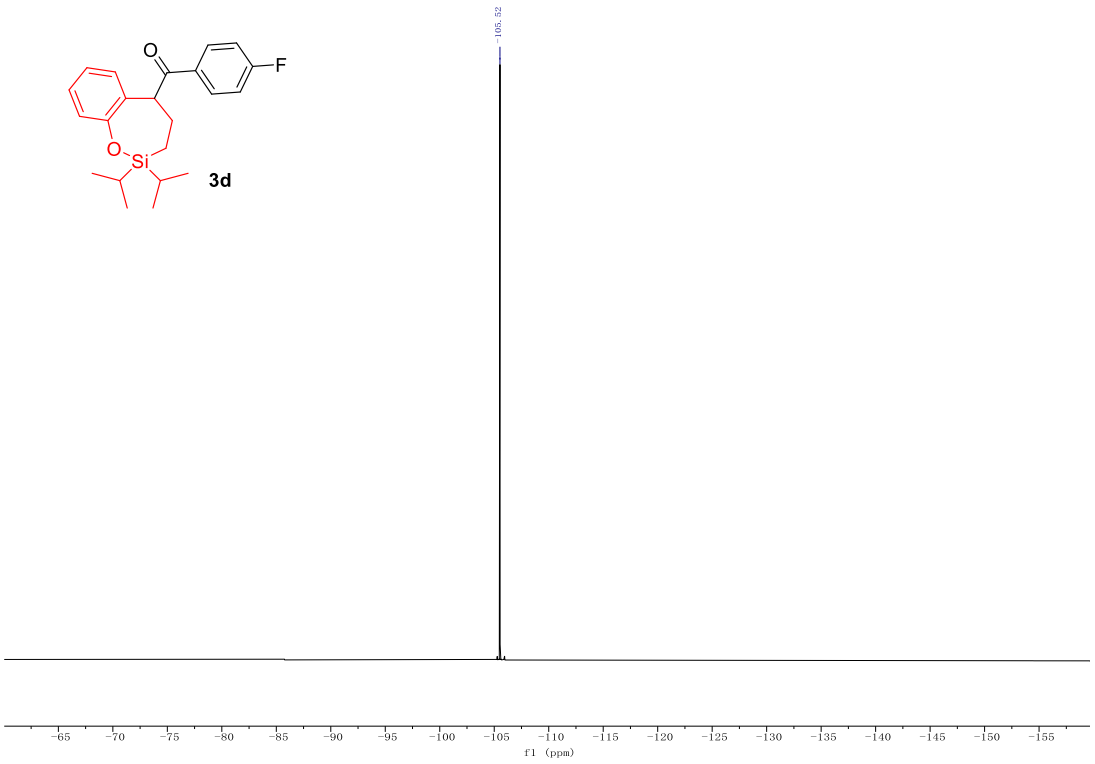


**Figure S17. $^{19}$F NMR** (377 MHz, $CDCl_3$) spectrum of **3d**

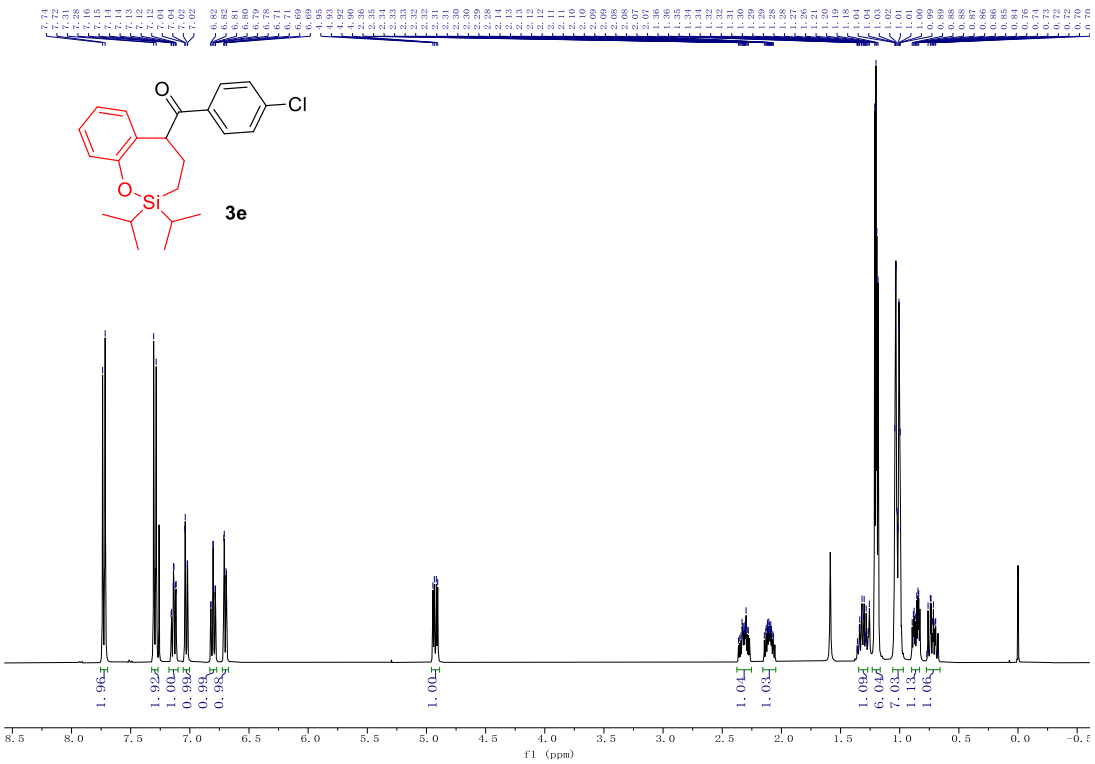


**Figure S18.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3e**

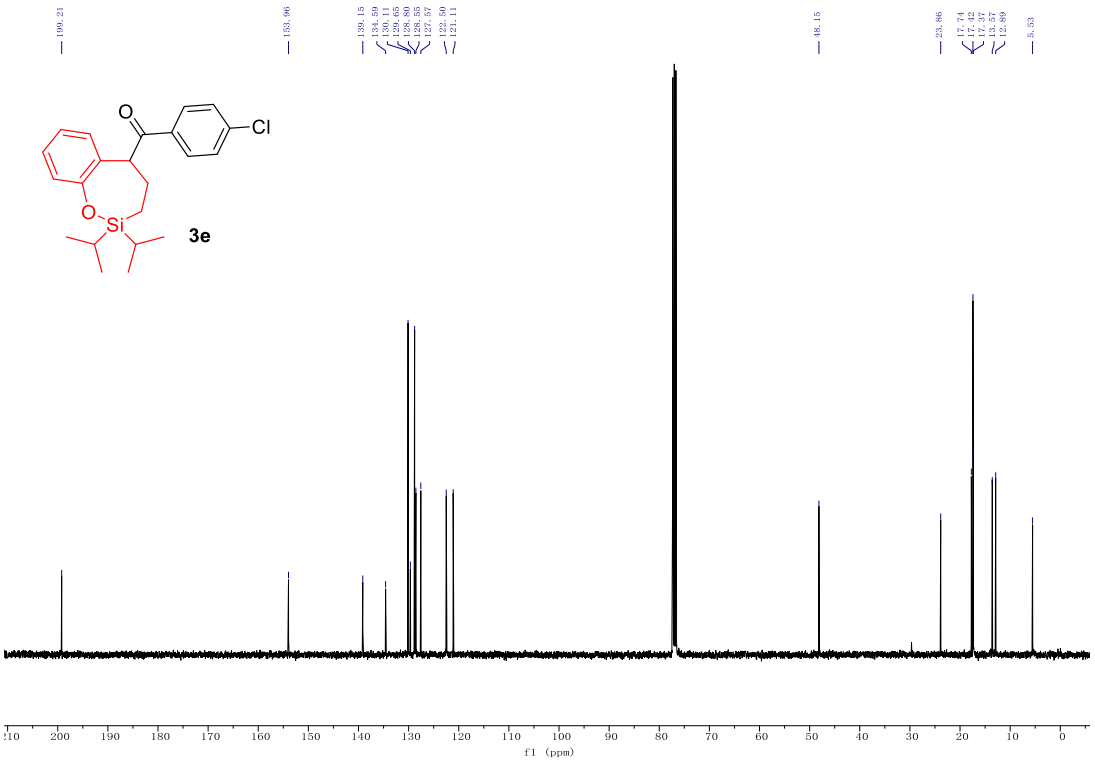


**Figure S19.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3e**

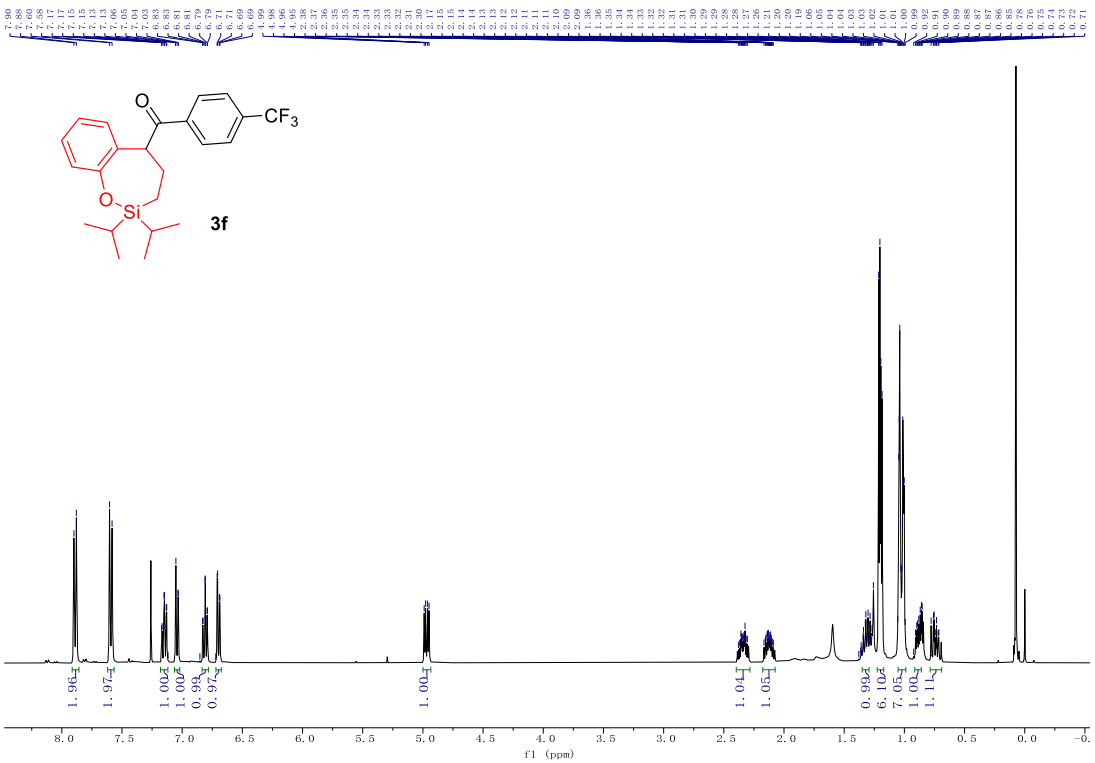


**Figure S20.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3f**

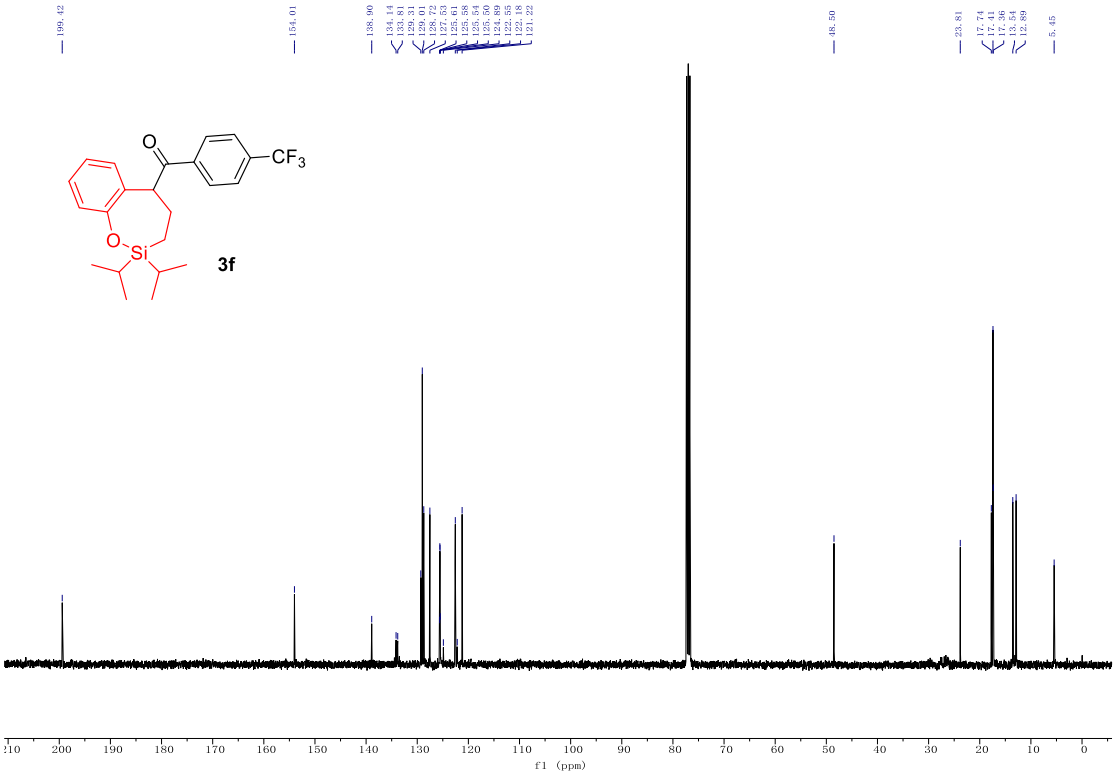


**Figure S21.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3f**

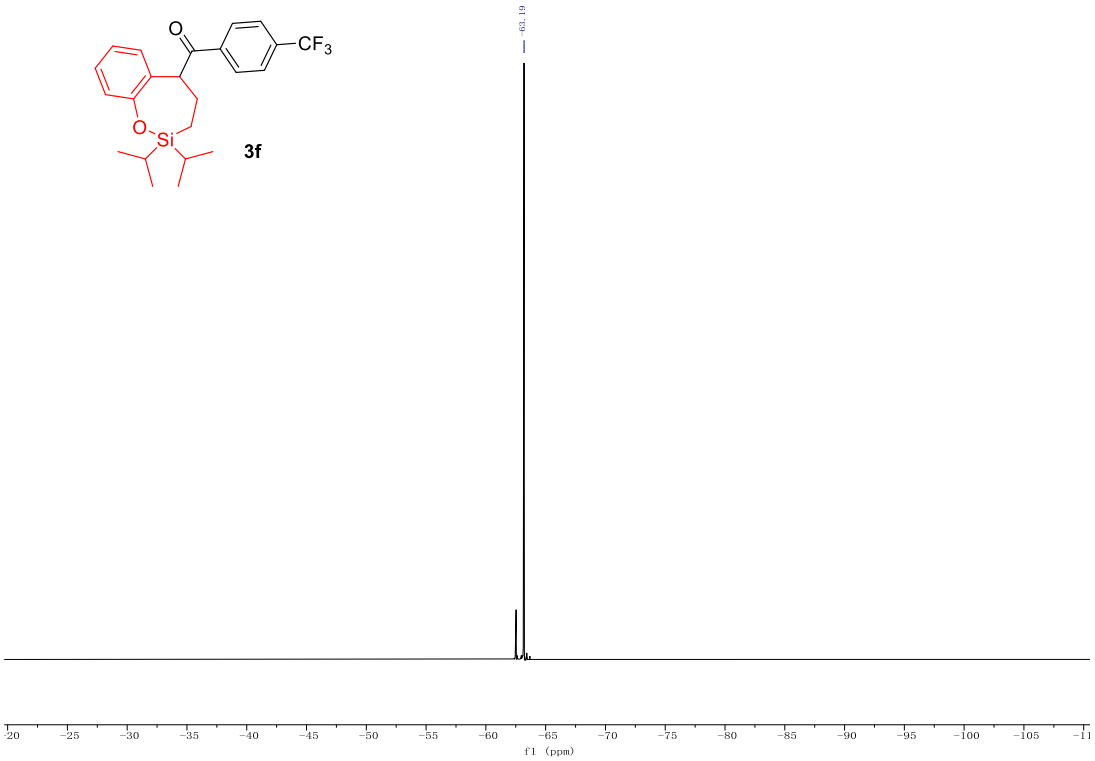


**Figure S22.** $^{19}$**F NMR** (377 MHz, $CDCl_3$) spectrum of **3f**

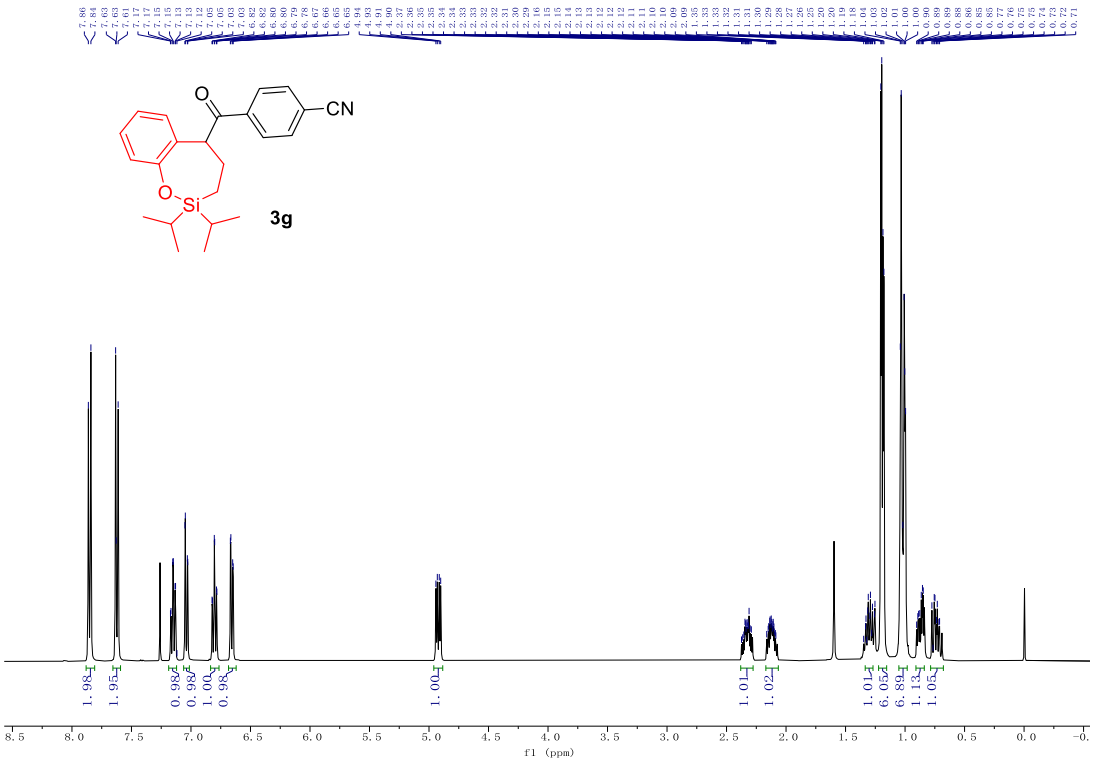


**Figure S23. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3g**

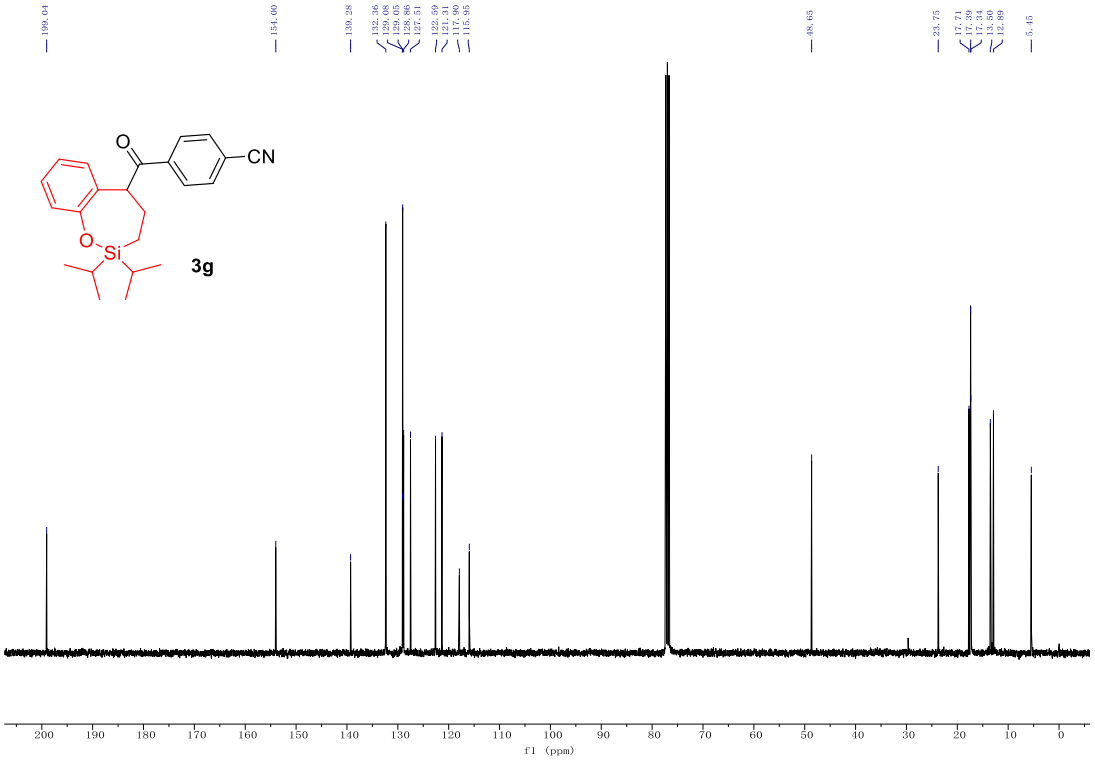


**Figure S24. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3g**

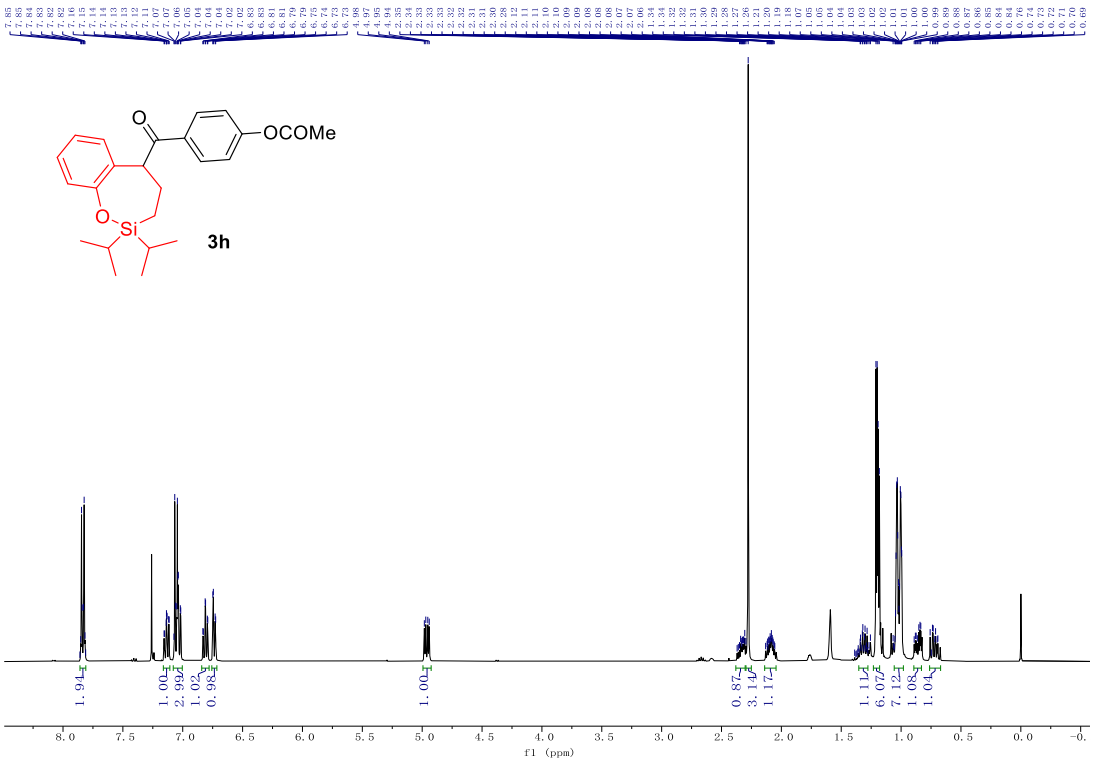


**Figure S25.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3g**

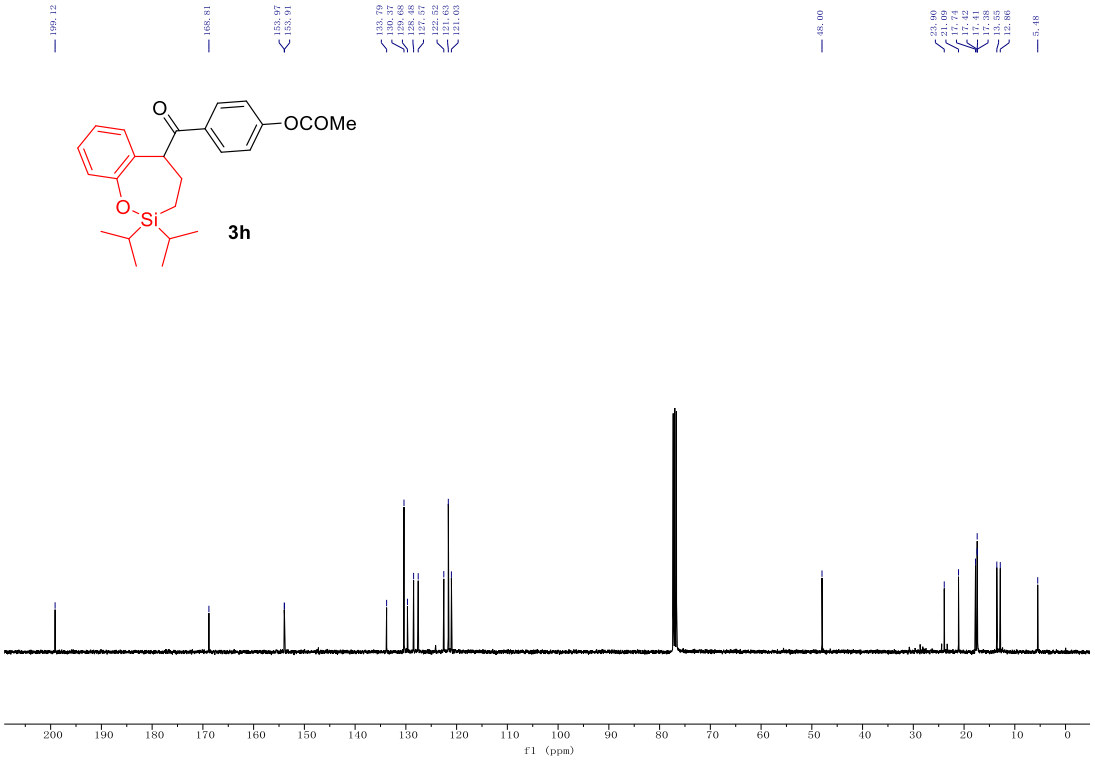


**Figure S26.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3g**

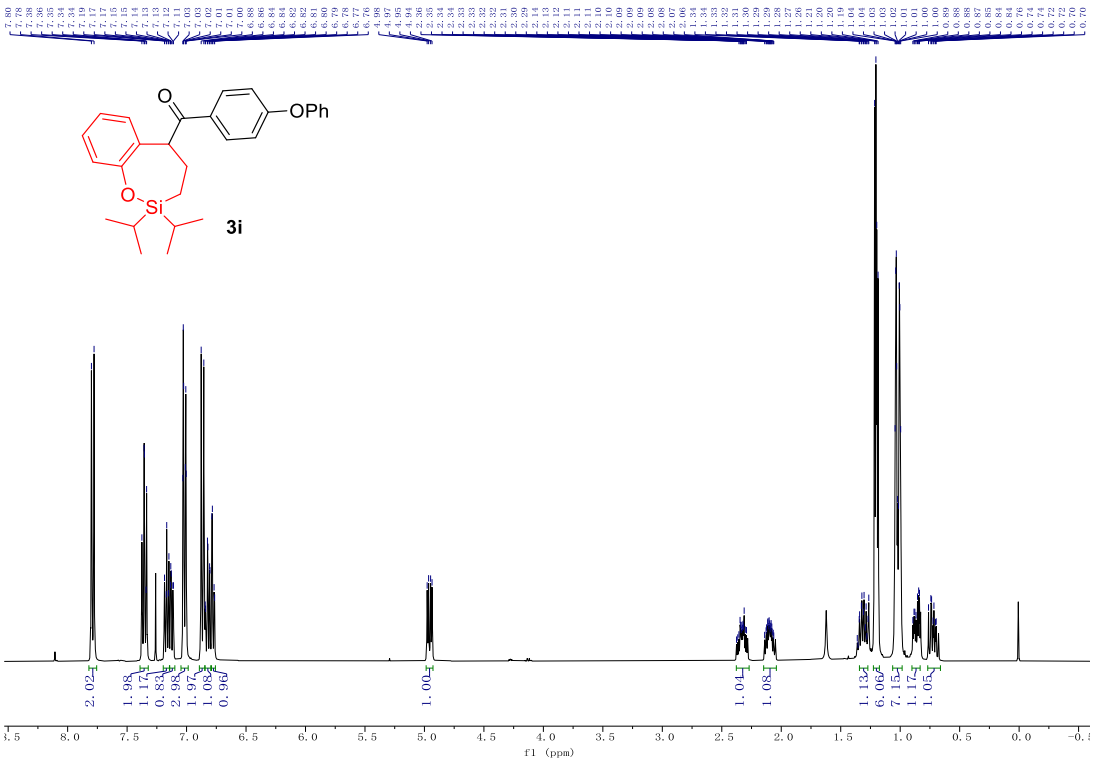


**Figure S27.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3i**

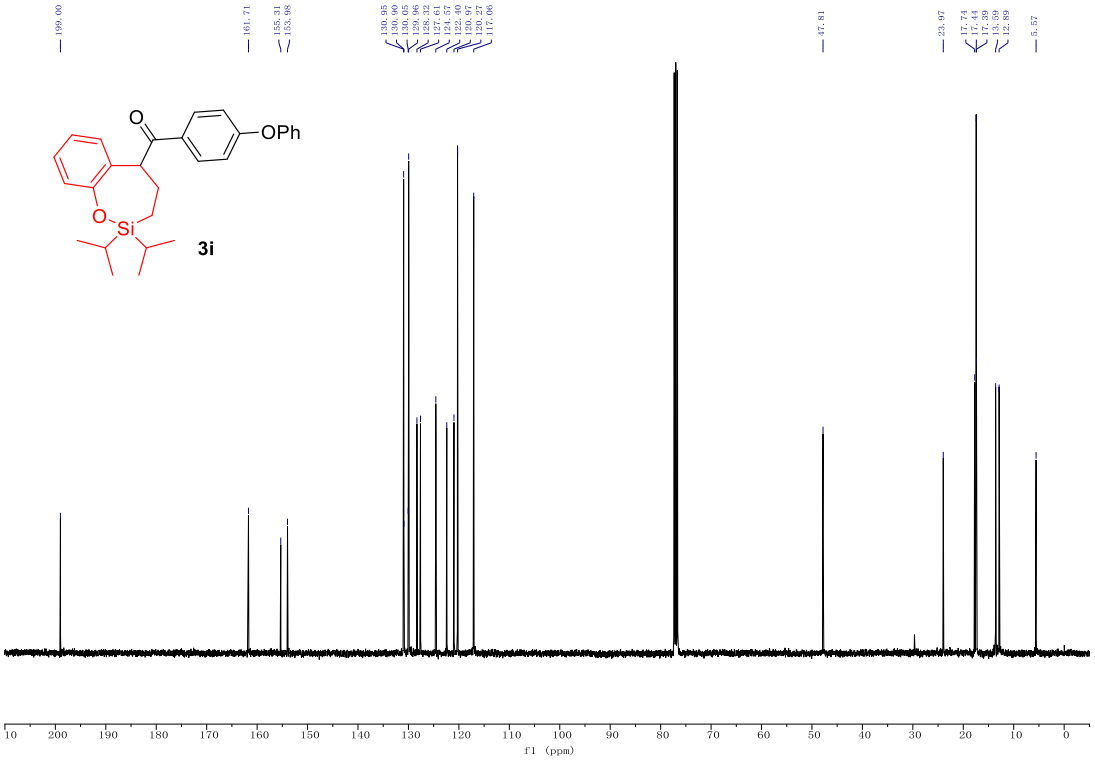


**Figure S28.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3i**

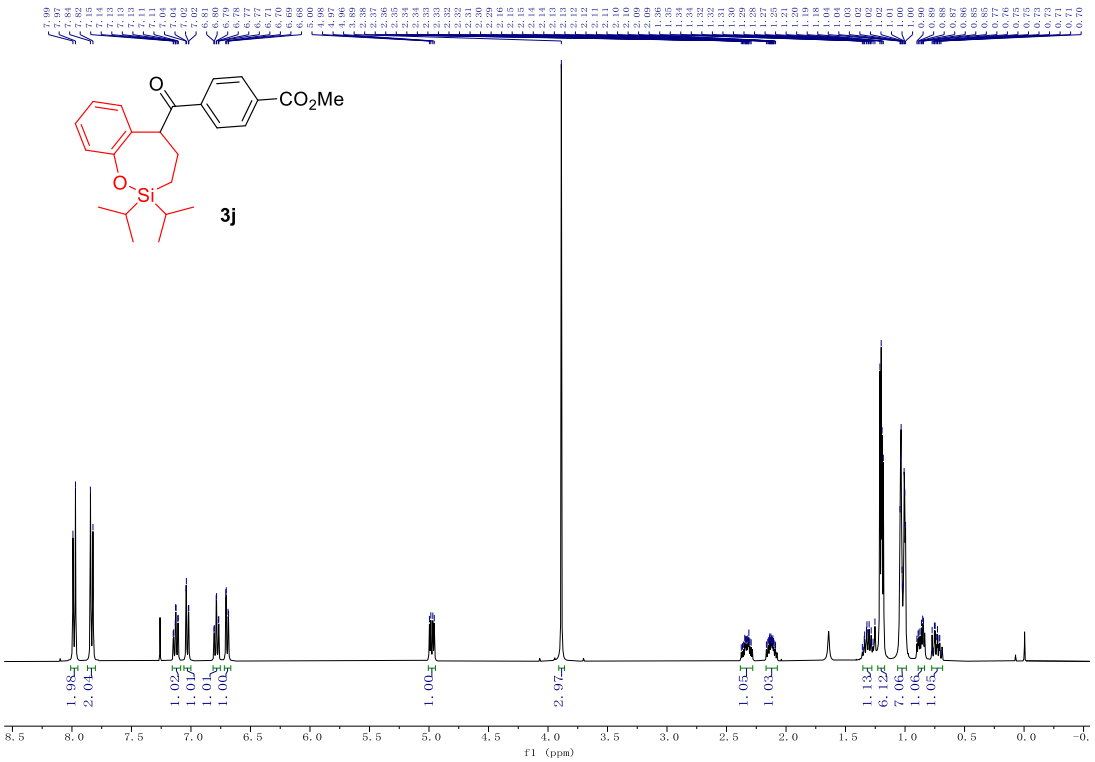


**Figure S29.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3j**

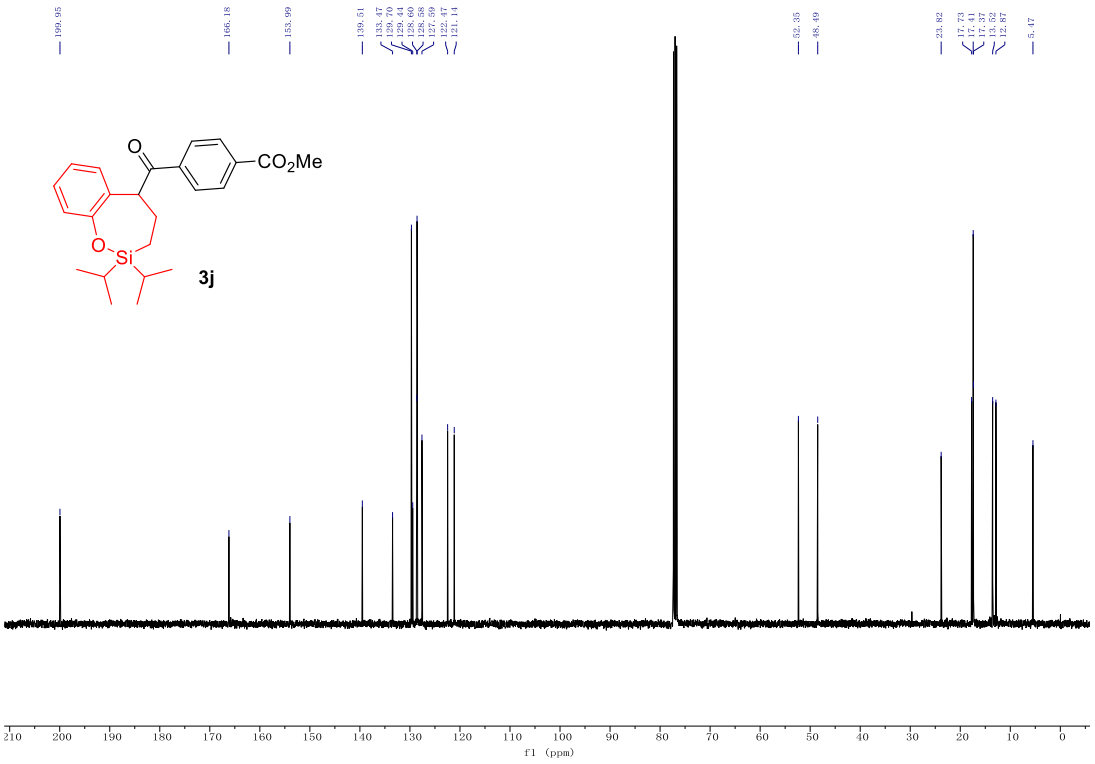


**Figure S30.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3j**

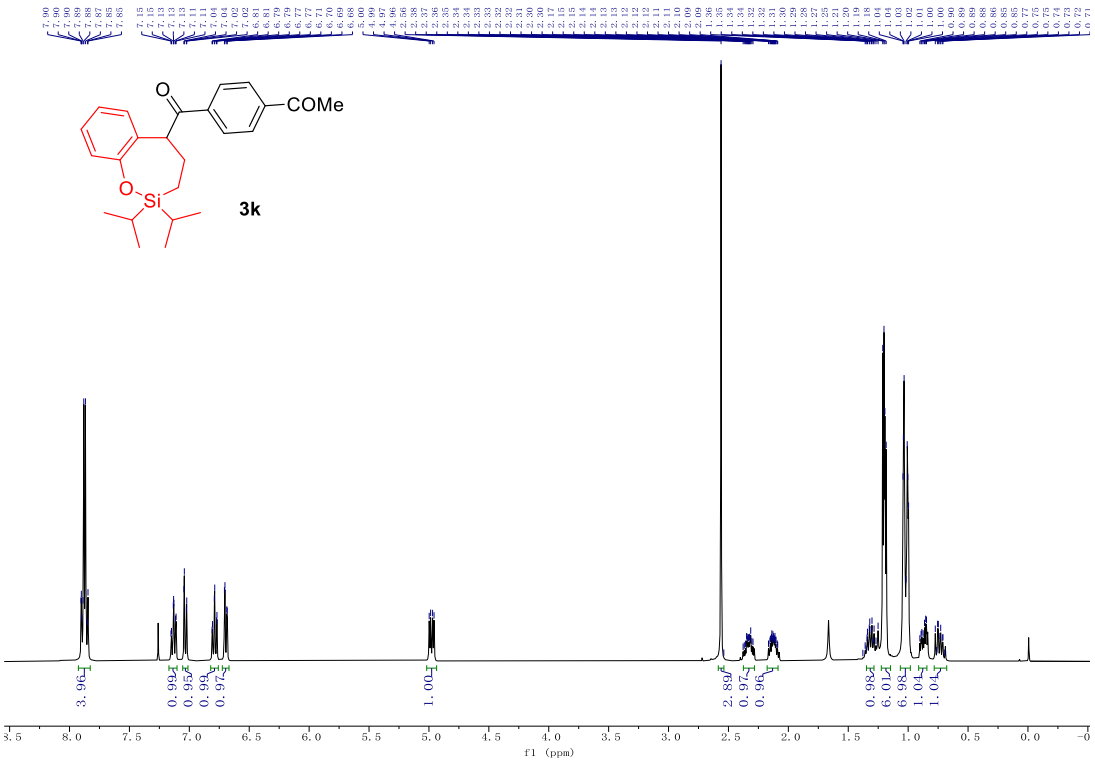


**Figure S31.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3k**

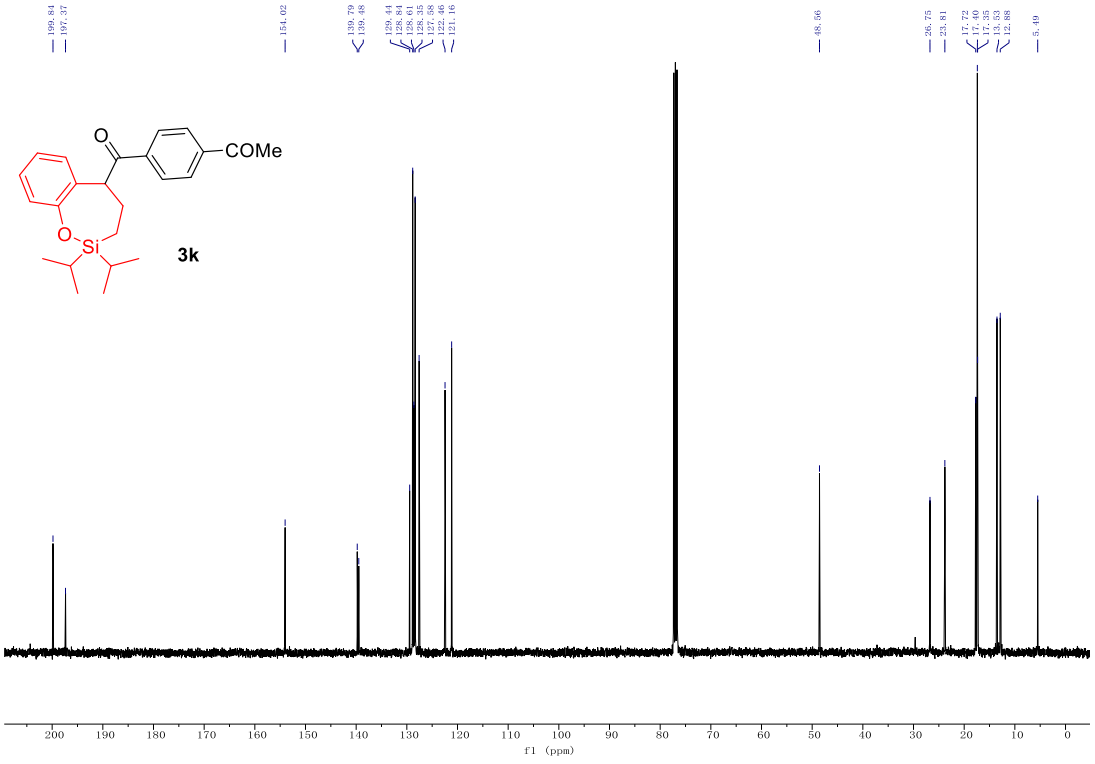


**Figure S32.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3k**

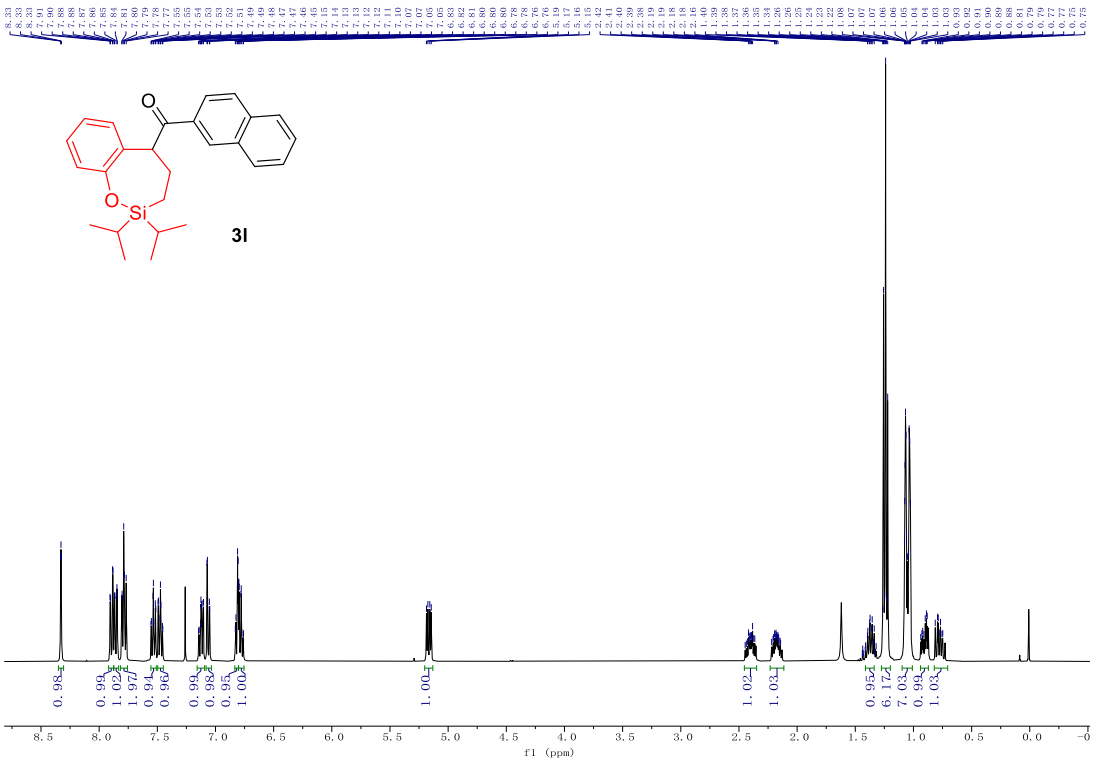


**Figure S33.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3l**

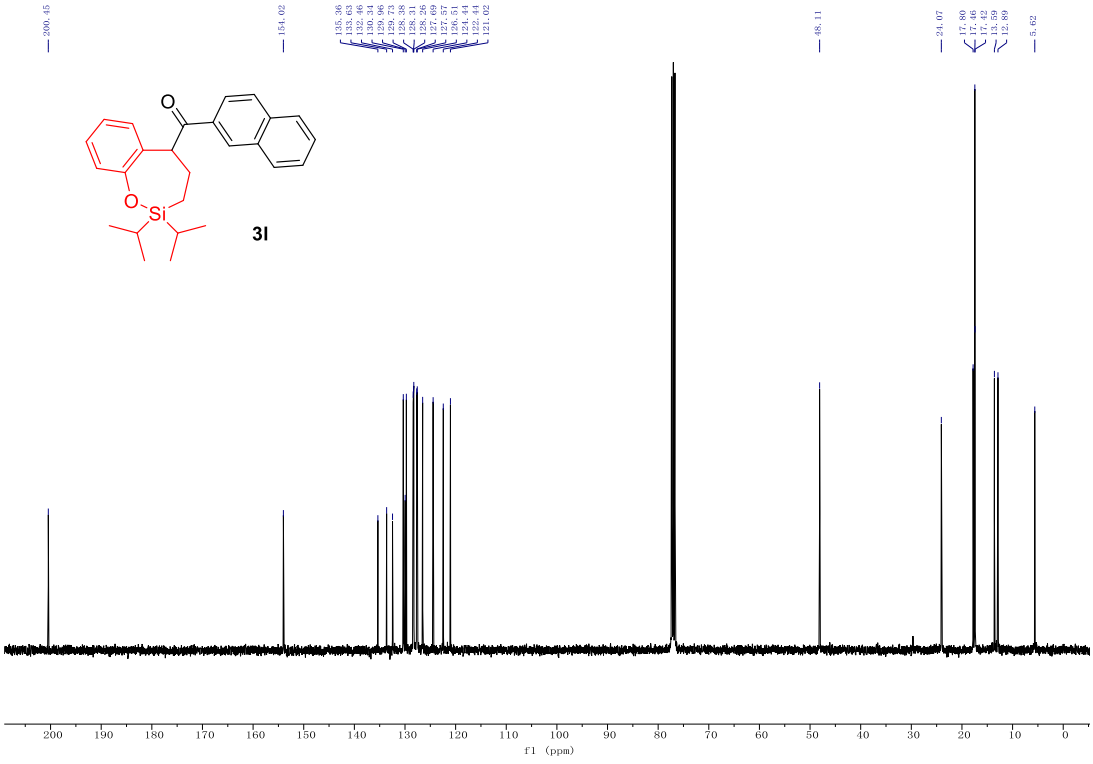


**Figure S34.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3l**

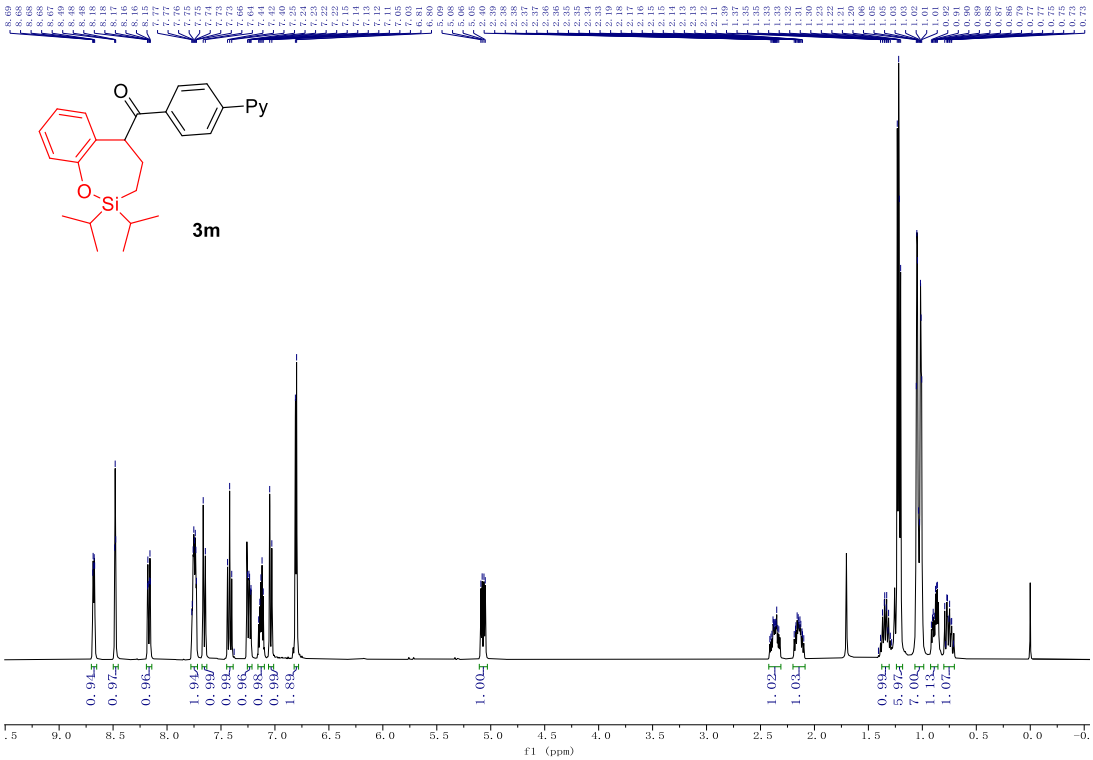


**Figure S35.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3m**

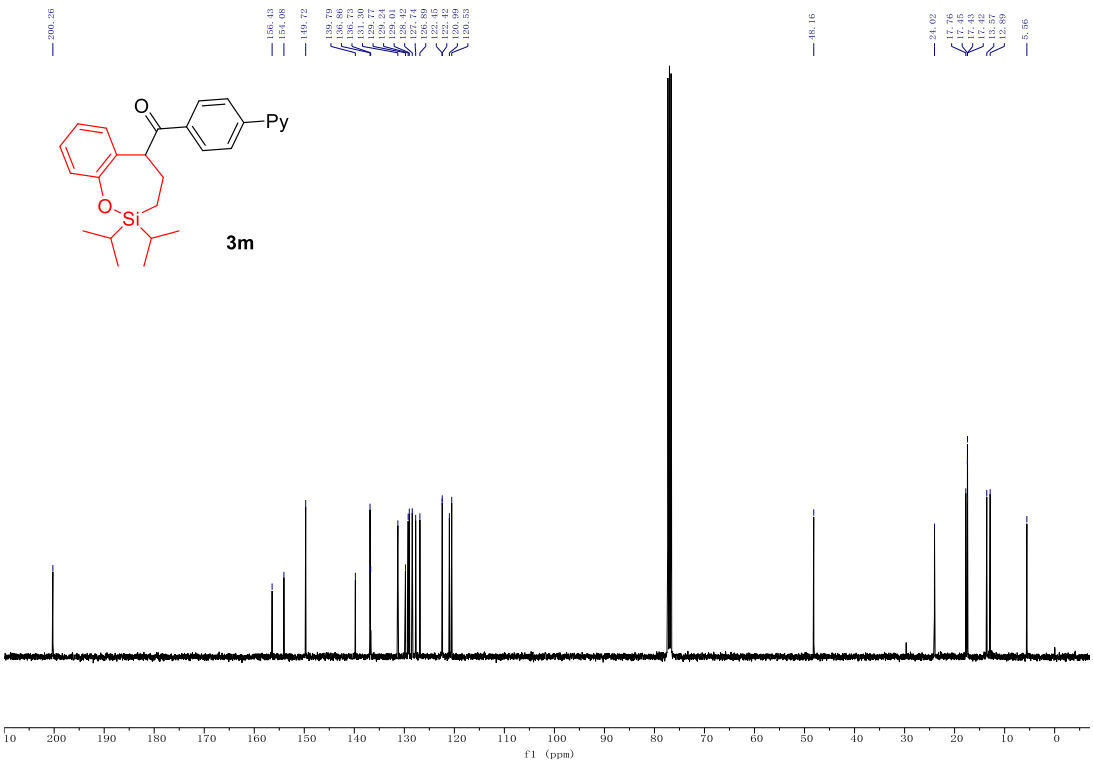


**Figure S36.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3m**

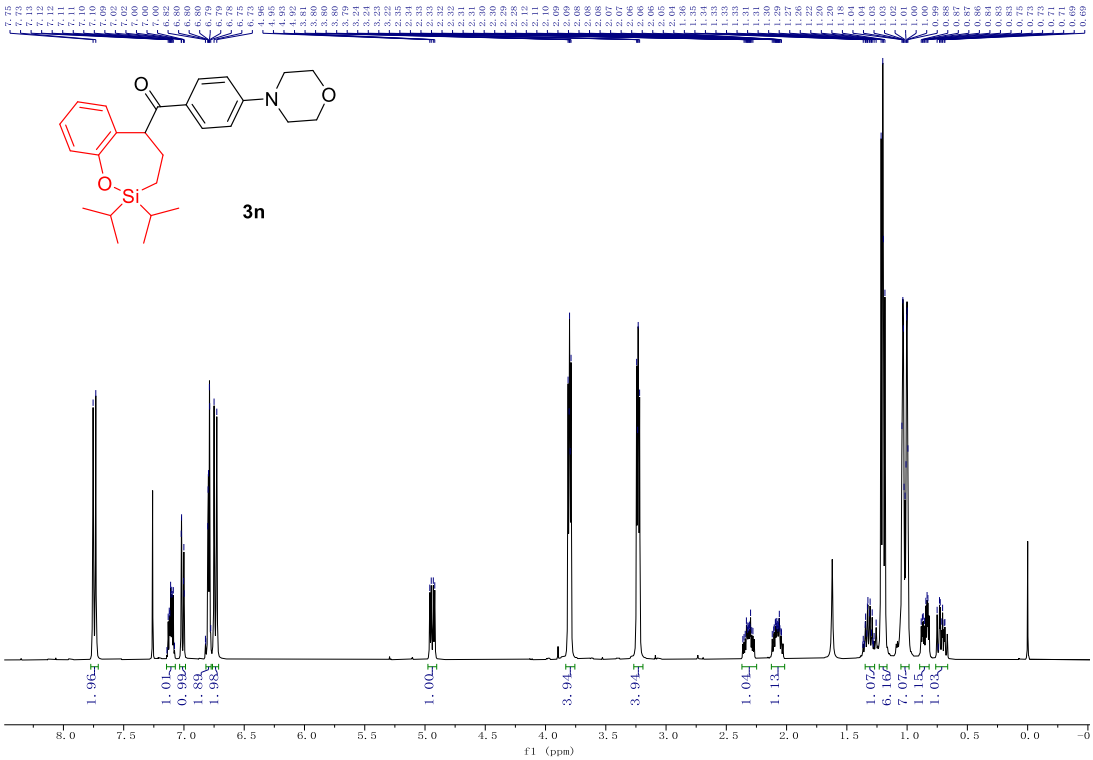


**Figure S37.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3n**

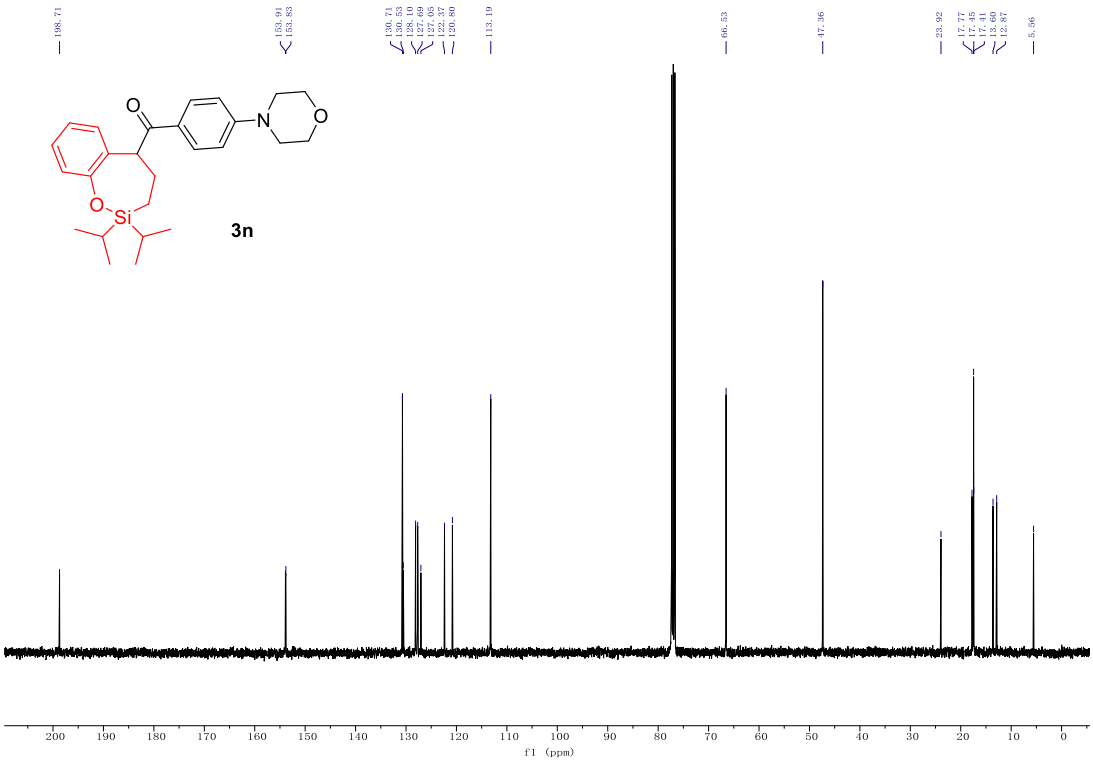


**Figure S38.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3n**

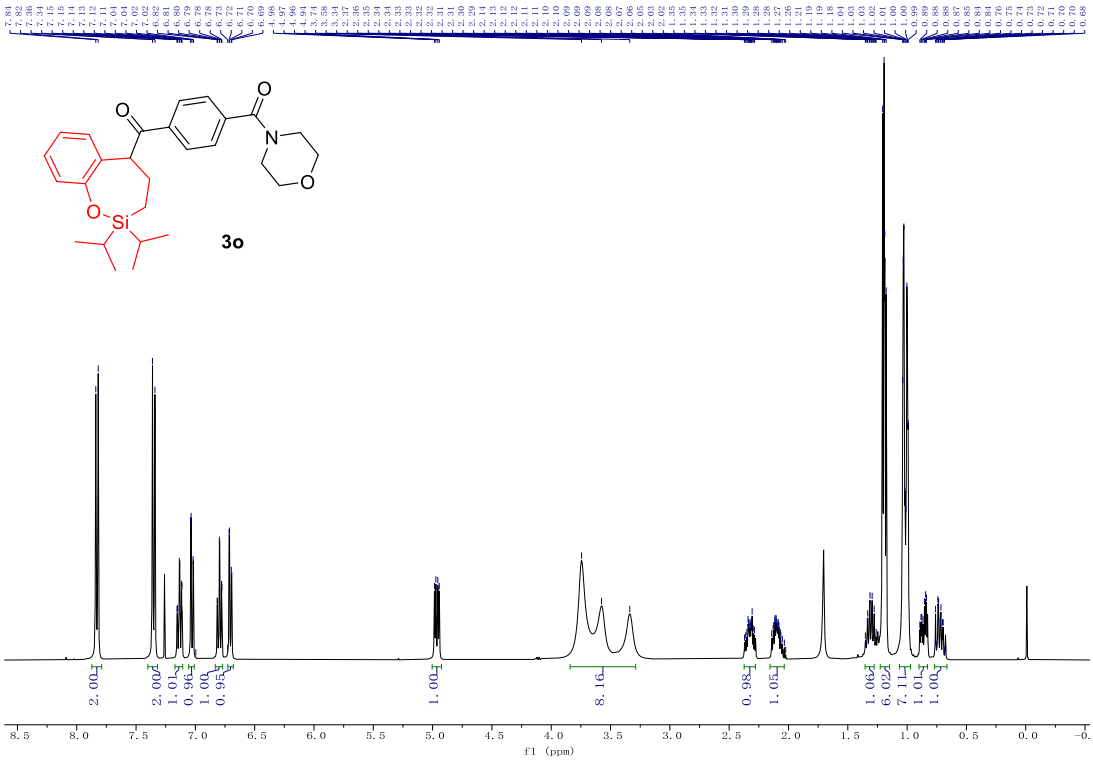


**Figure S39.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3o**

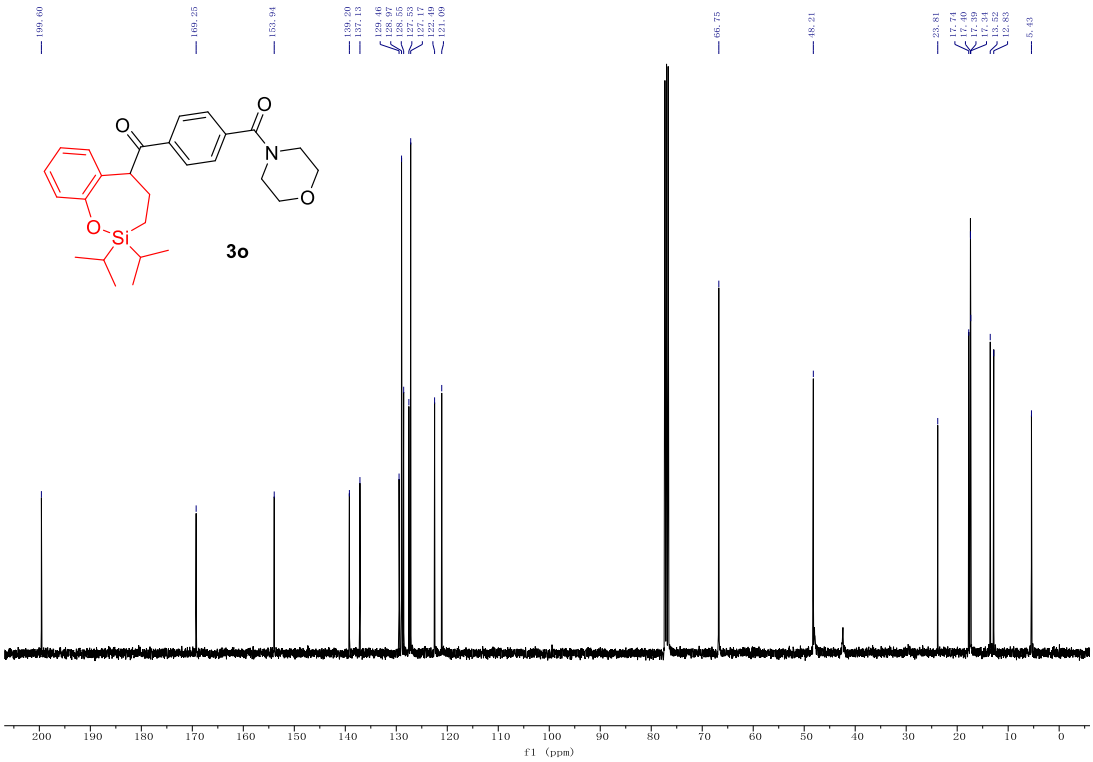


**Figure S40.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3o**

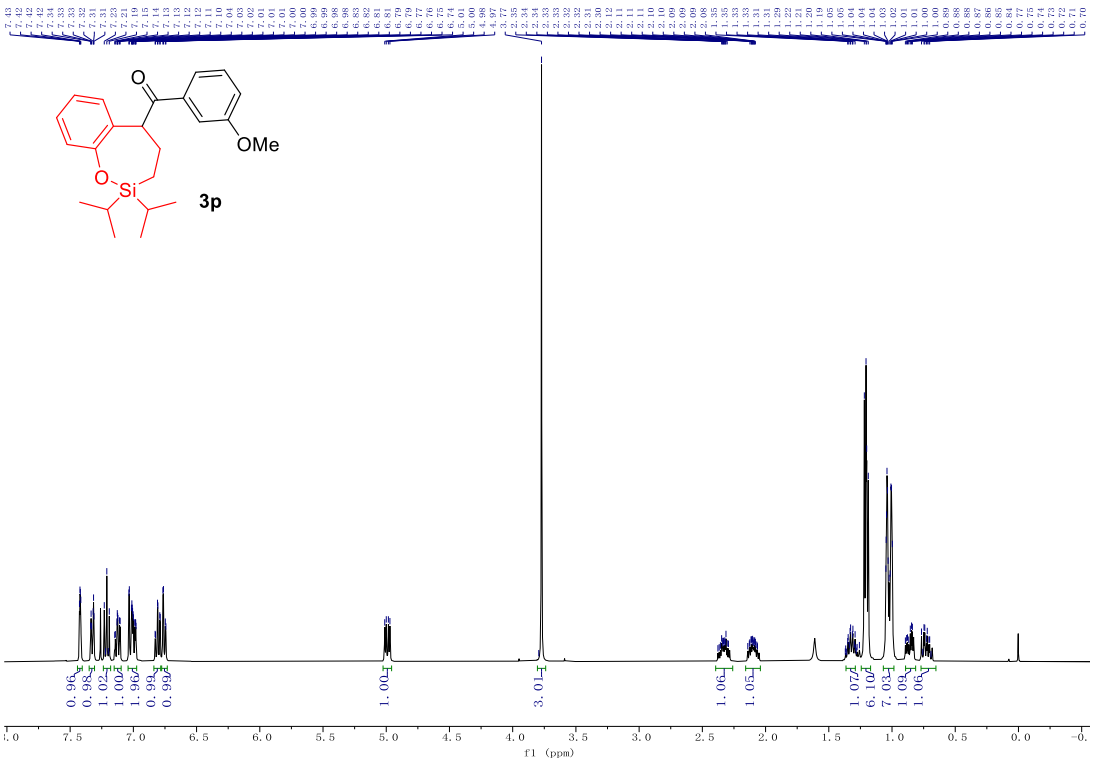


**Figure S41.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3p**

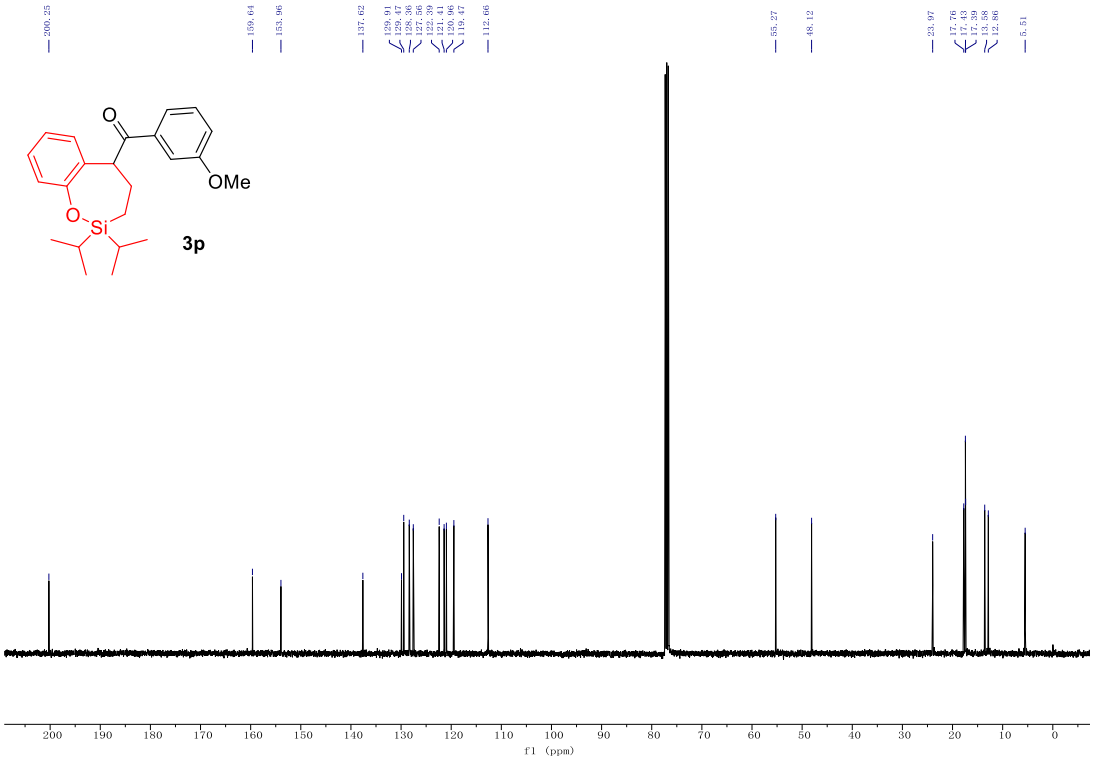


**Figure S42.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3p**

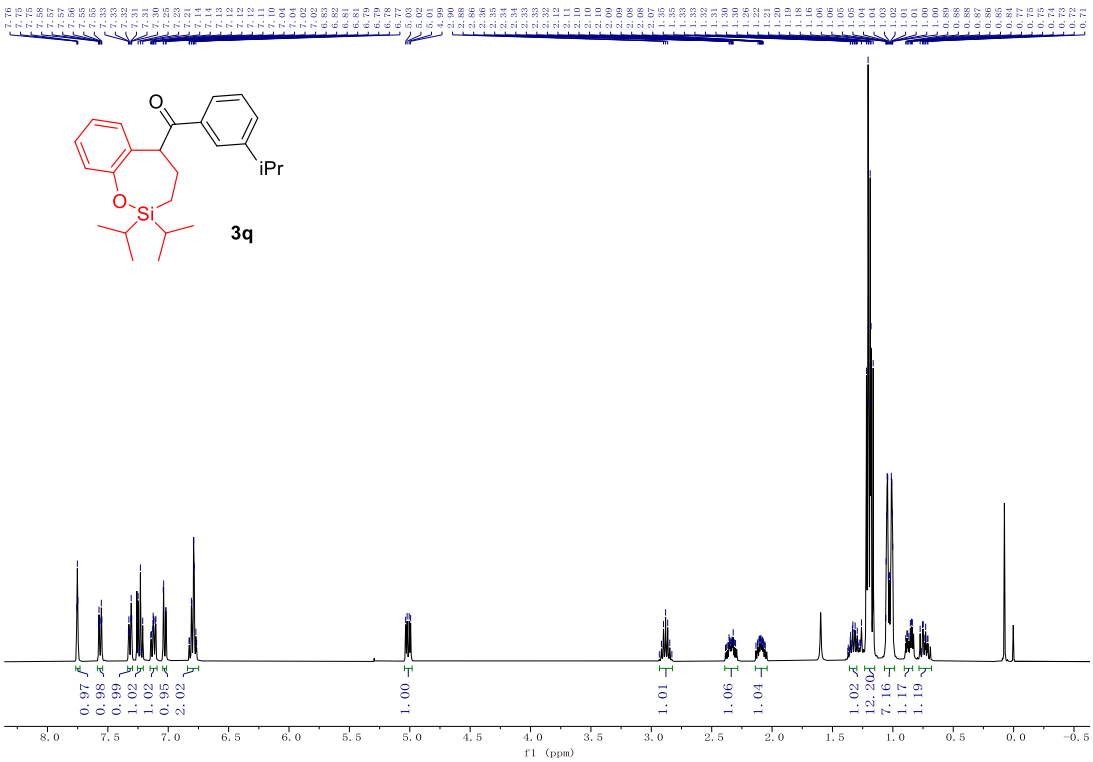


**Figure S43.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3q**

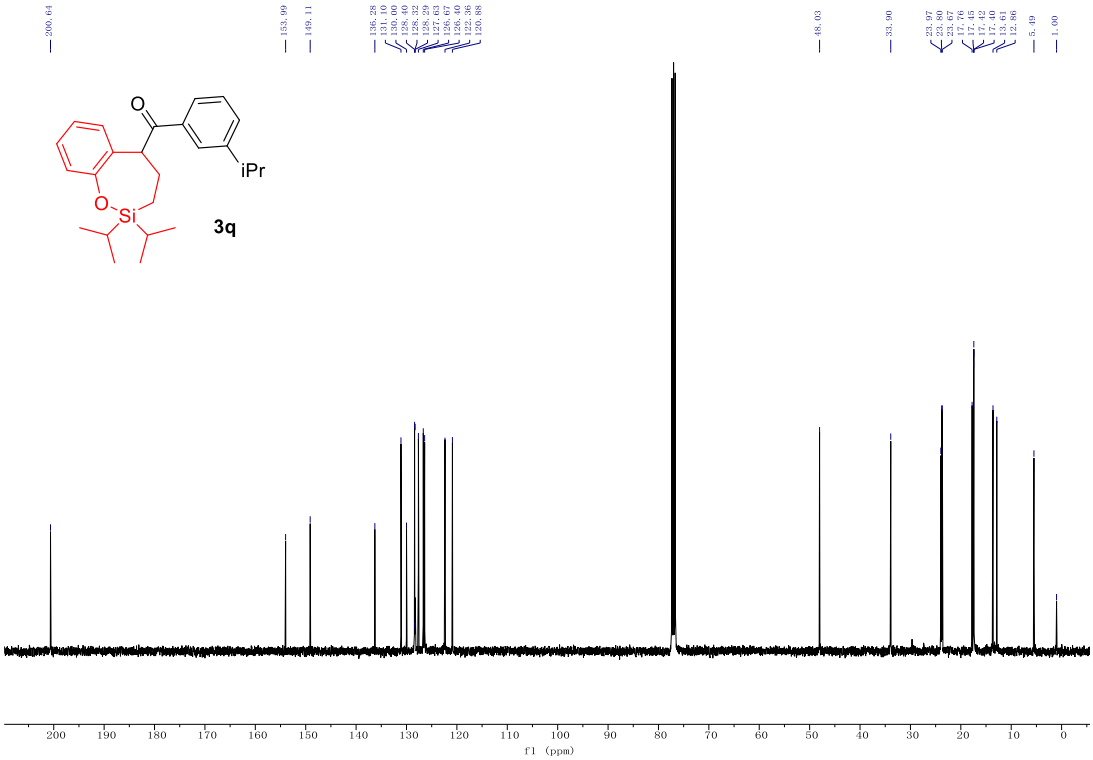


**Figure S44.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3q**

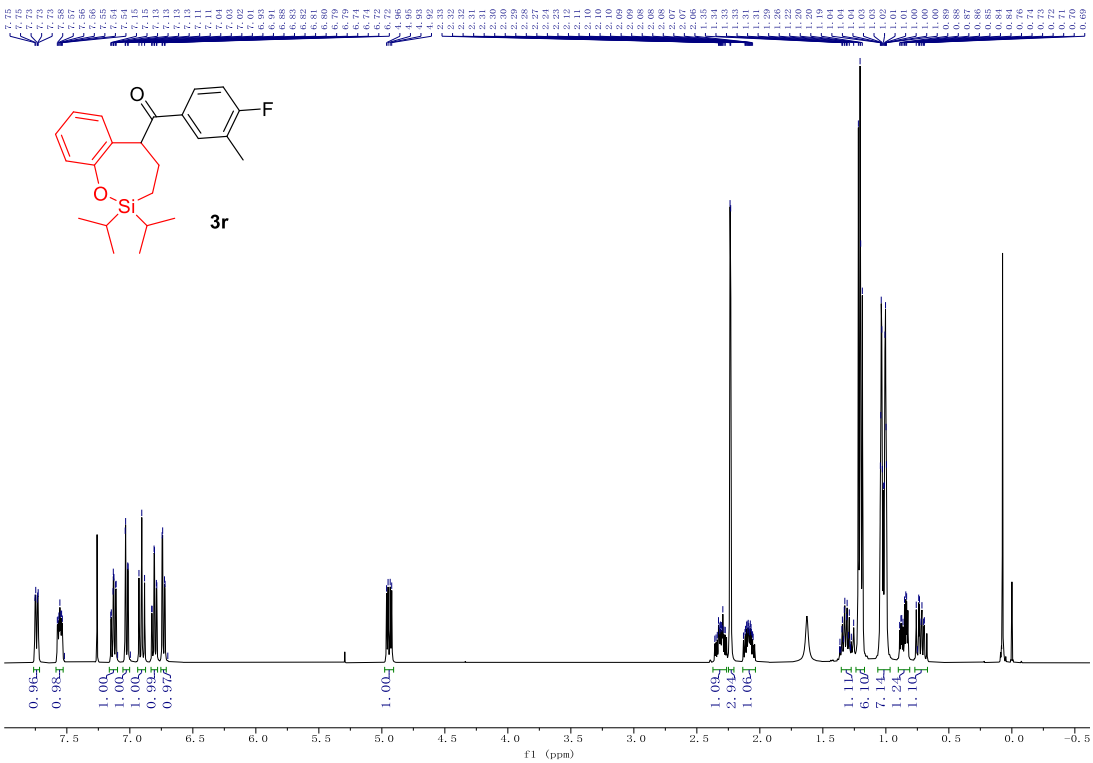


**Figure S45.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3r**

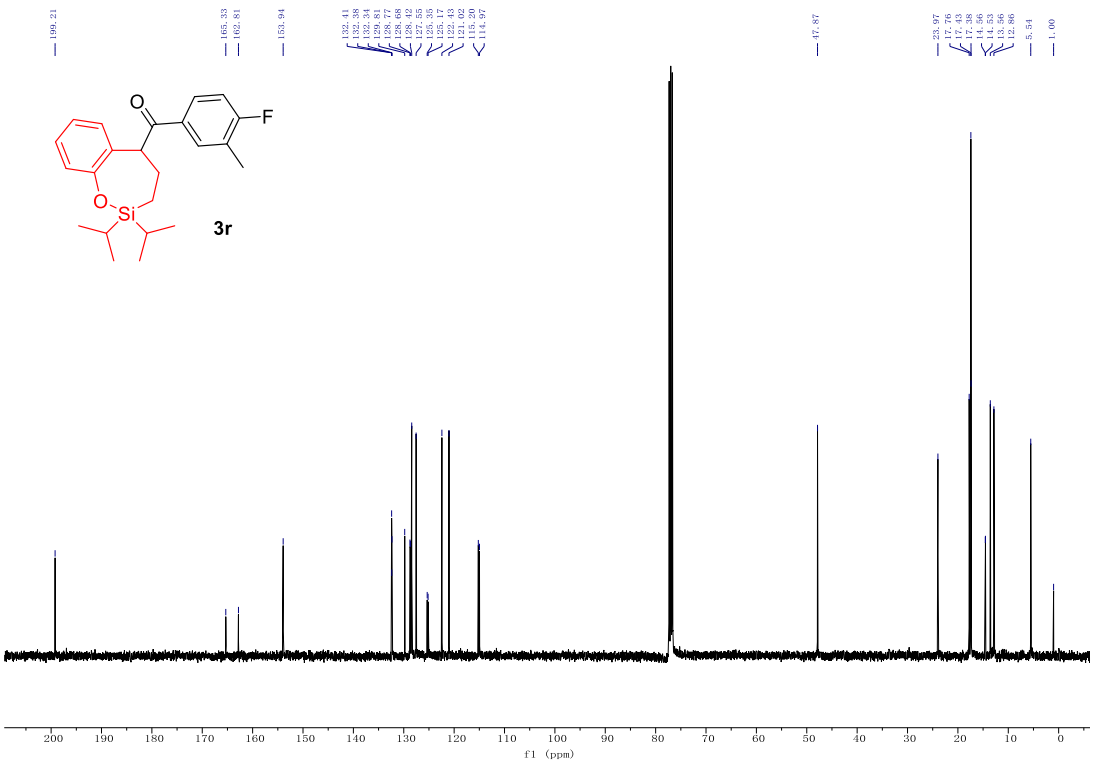


**Figure S46.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3r**


**Figure S47.** $^{19}$**F NMR** (377 MHz, $CDCl_3$) spectrum of **3r**

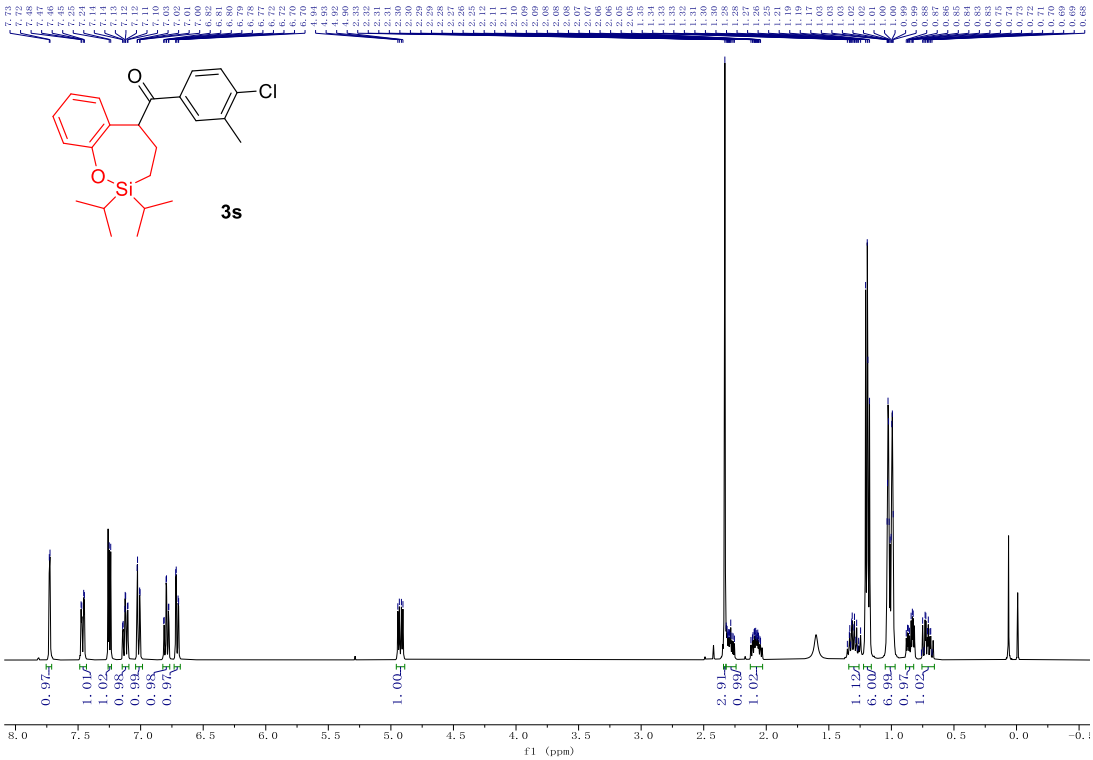


**Figure S48.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3s**

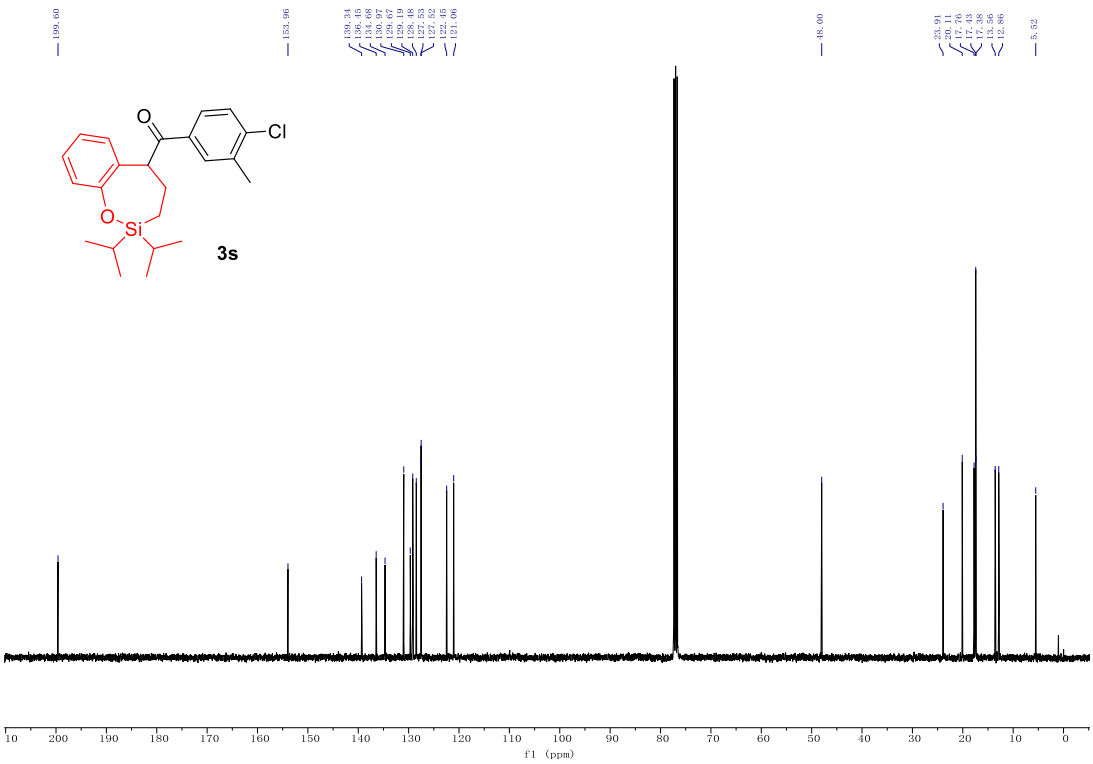


**Figure S49.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3s**

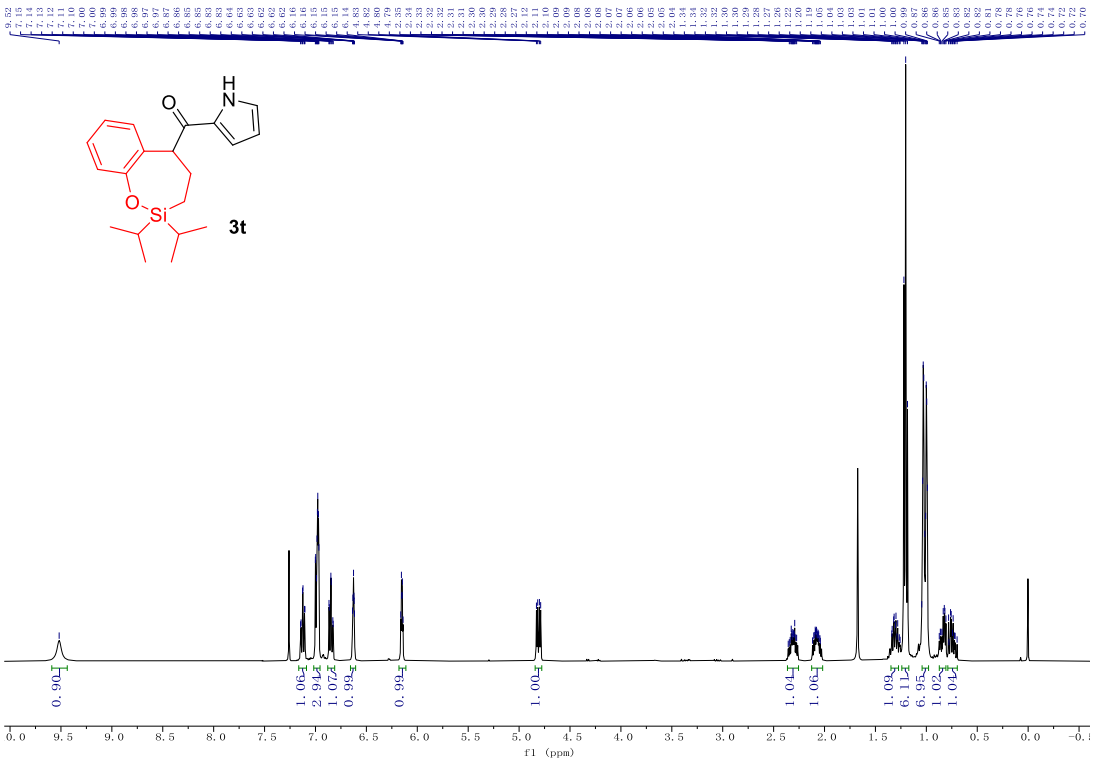


**Figure S50.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3t**

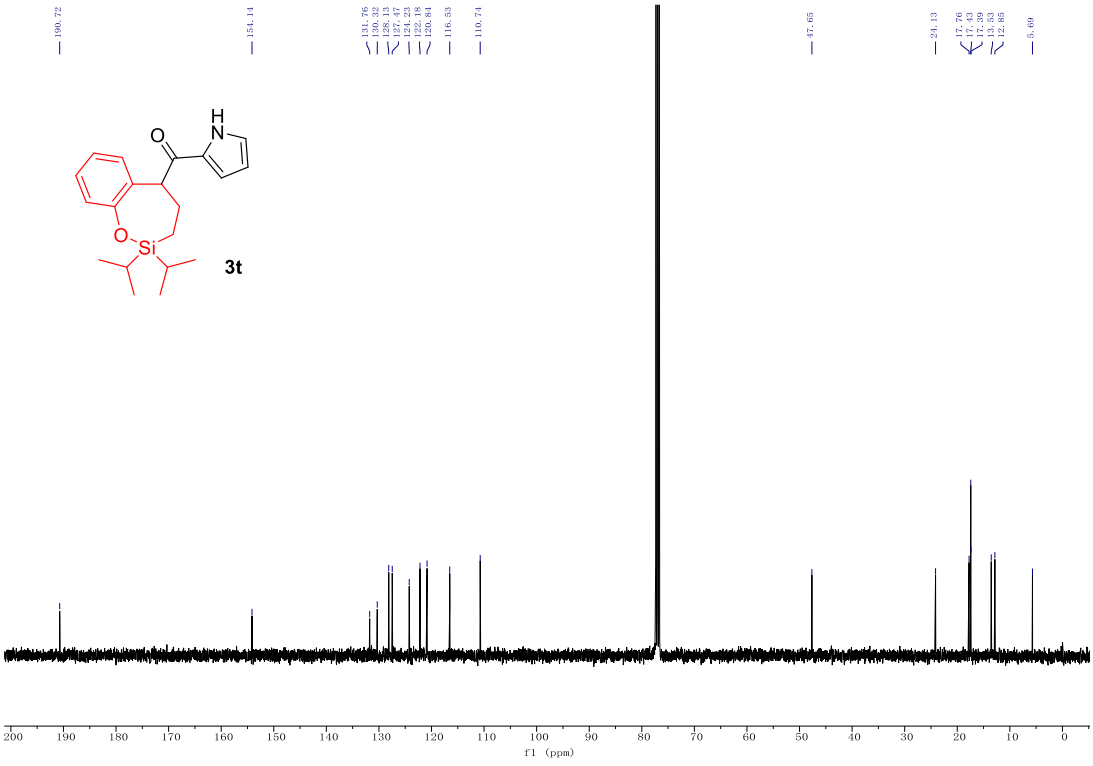


**Figure S51.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3t**

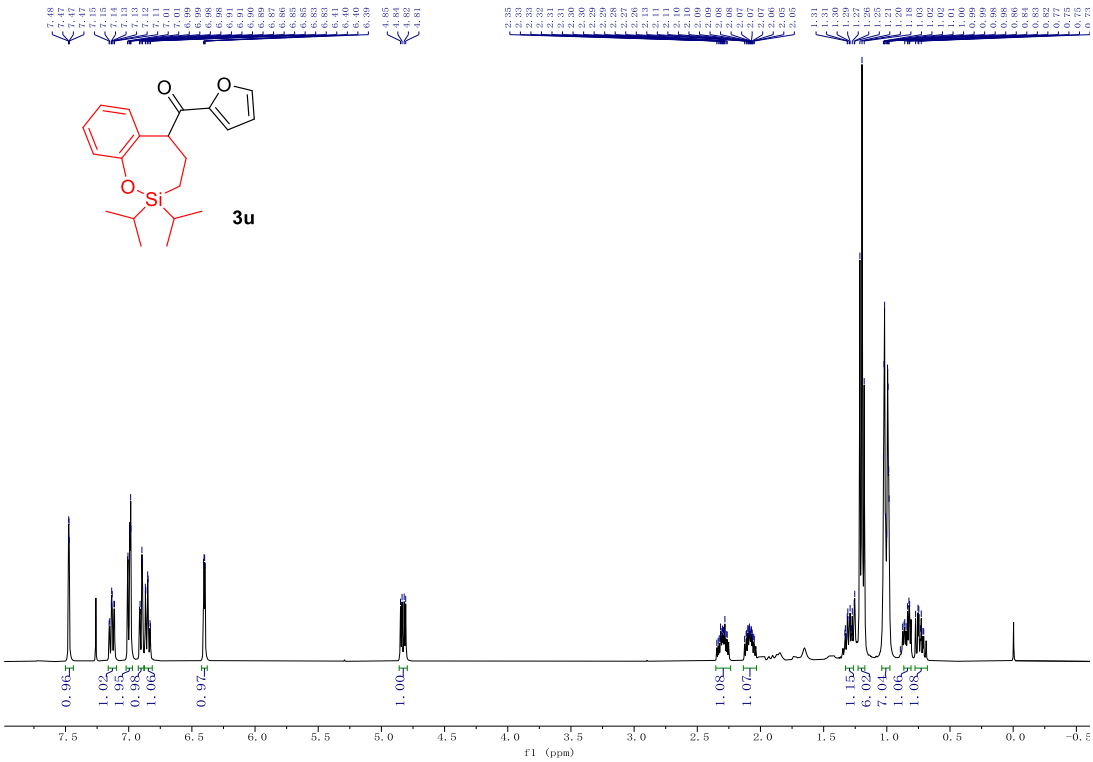


**Figure S52.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3u**

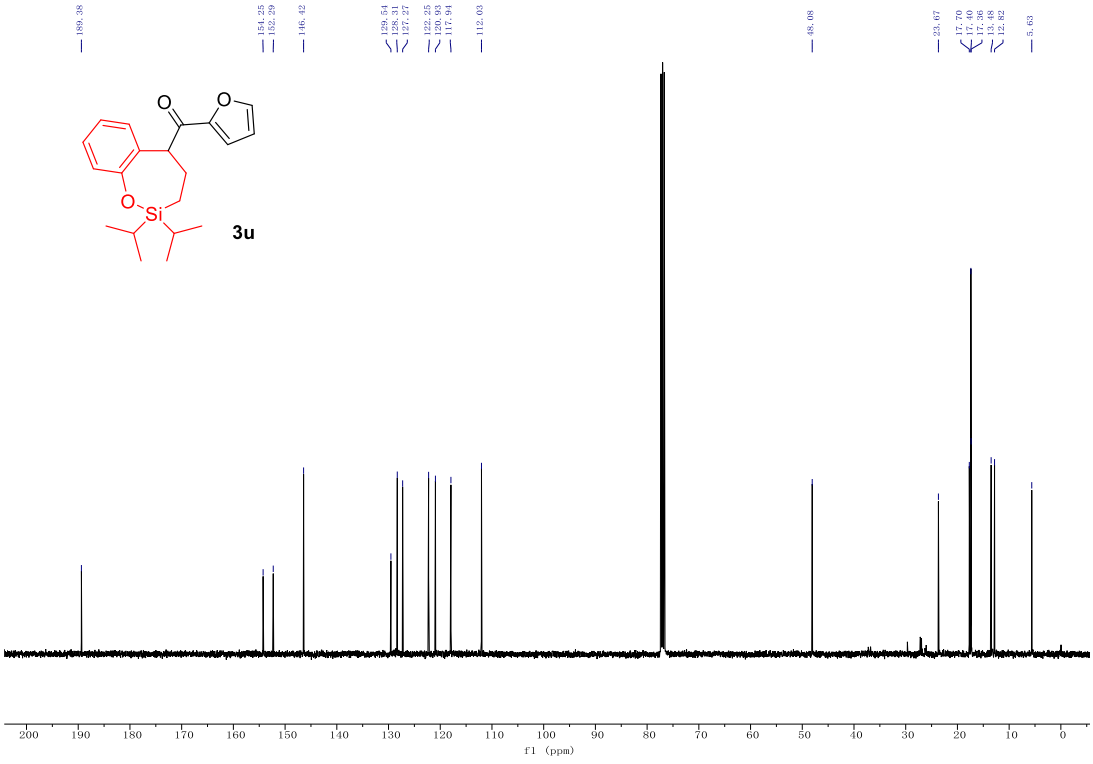


**Figure S53.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3u**

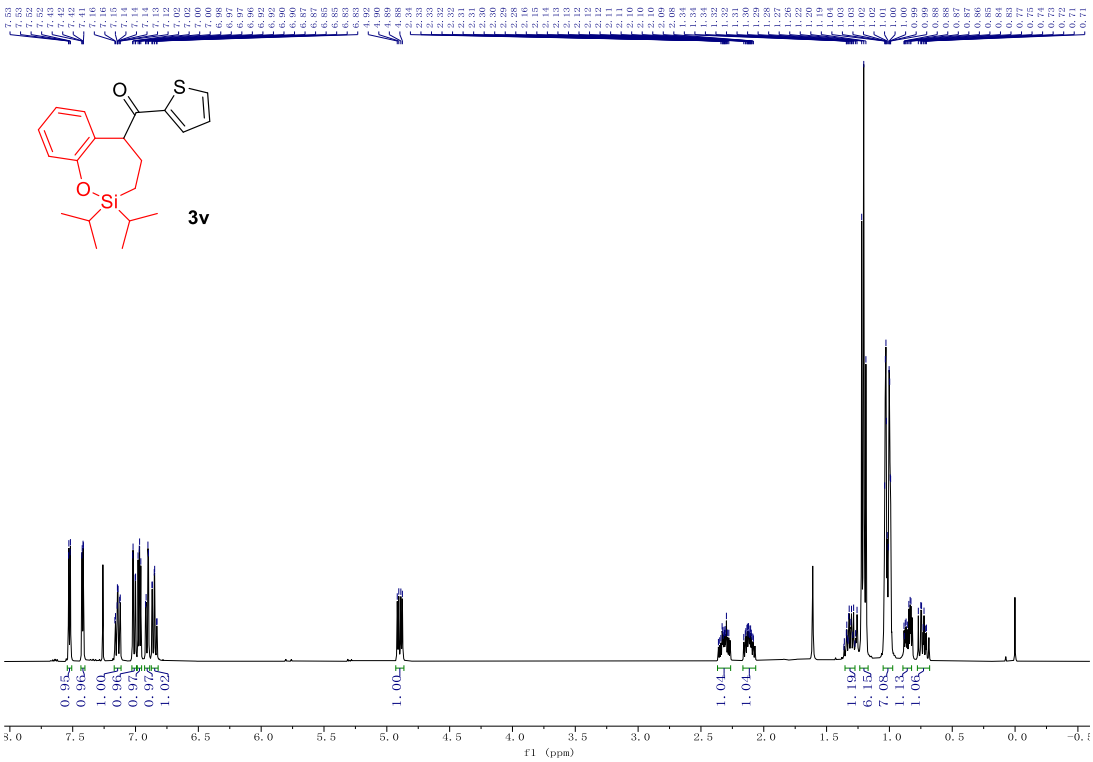


**Figure S54. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3v**

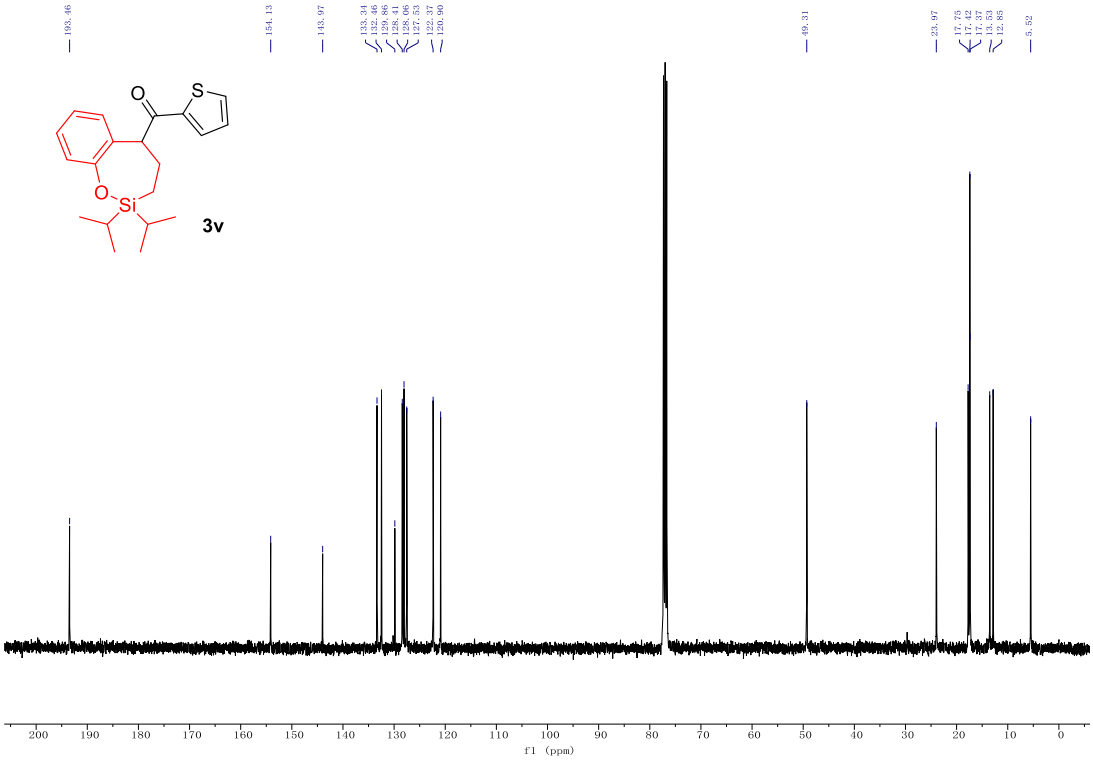


**Figure S55. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3v**

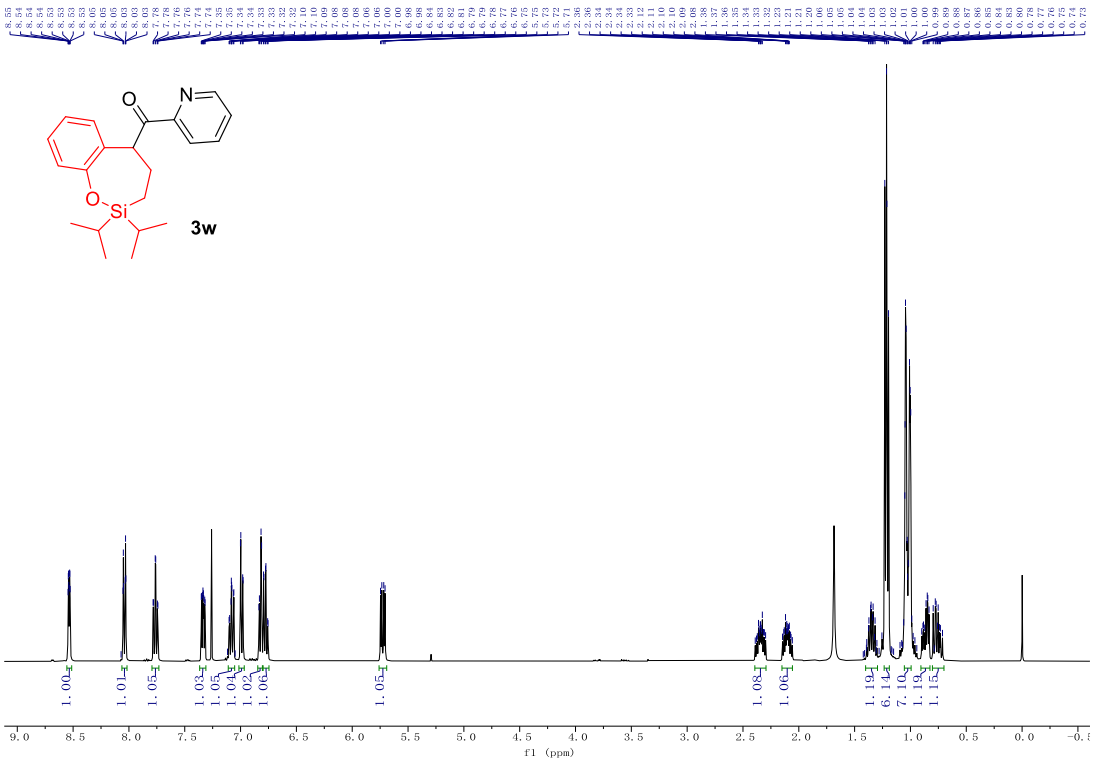


**Figure S56. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3w**

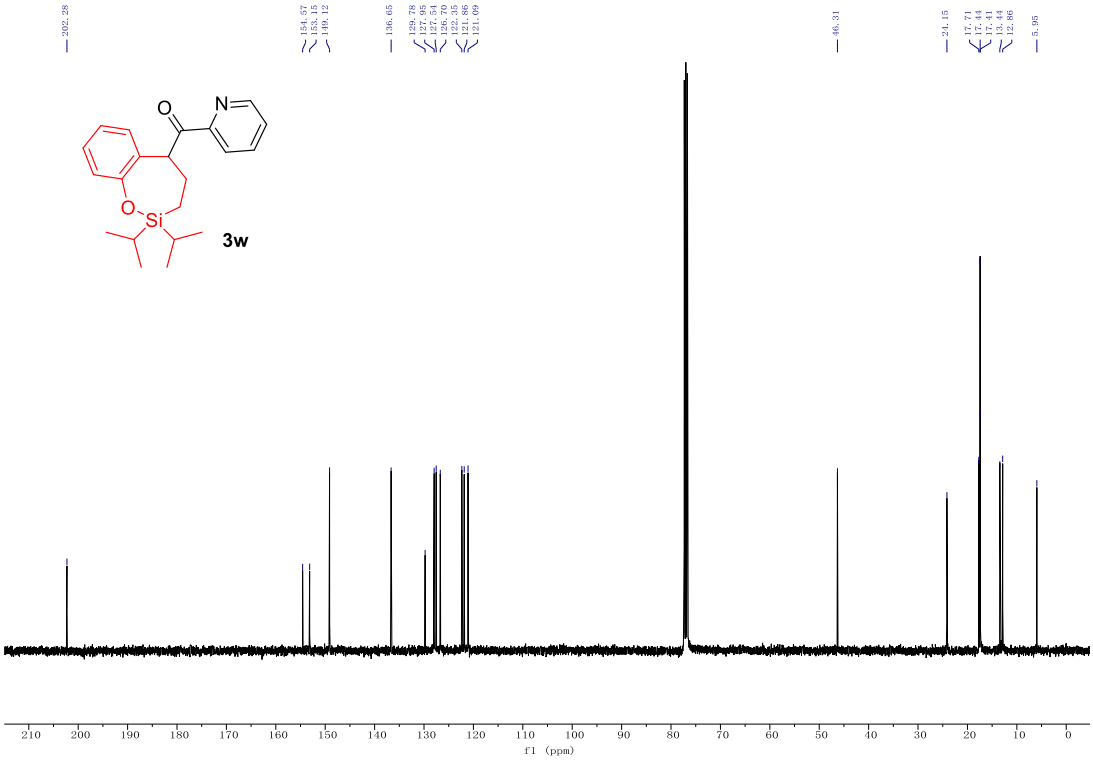


**Figure S57. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3w**

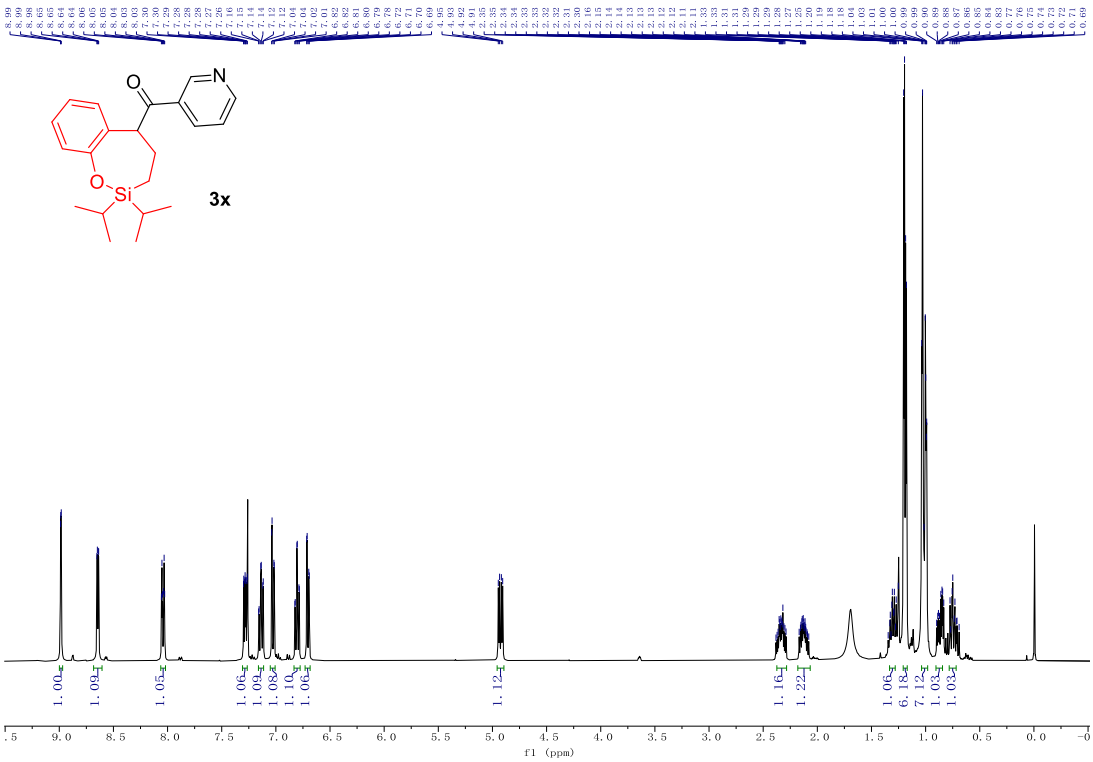


**Figure S58. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3x**

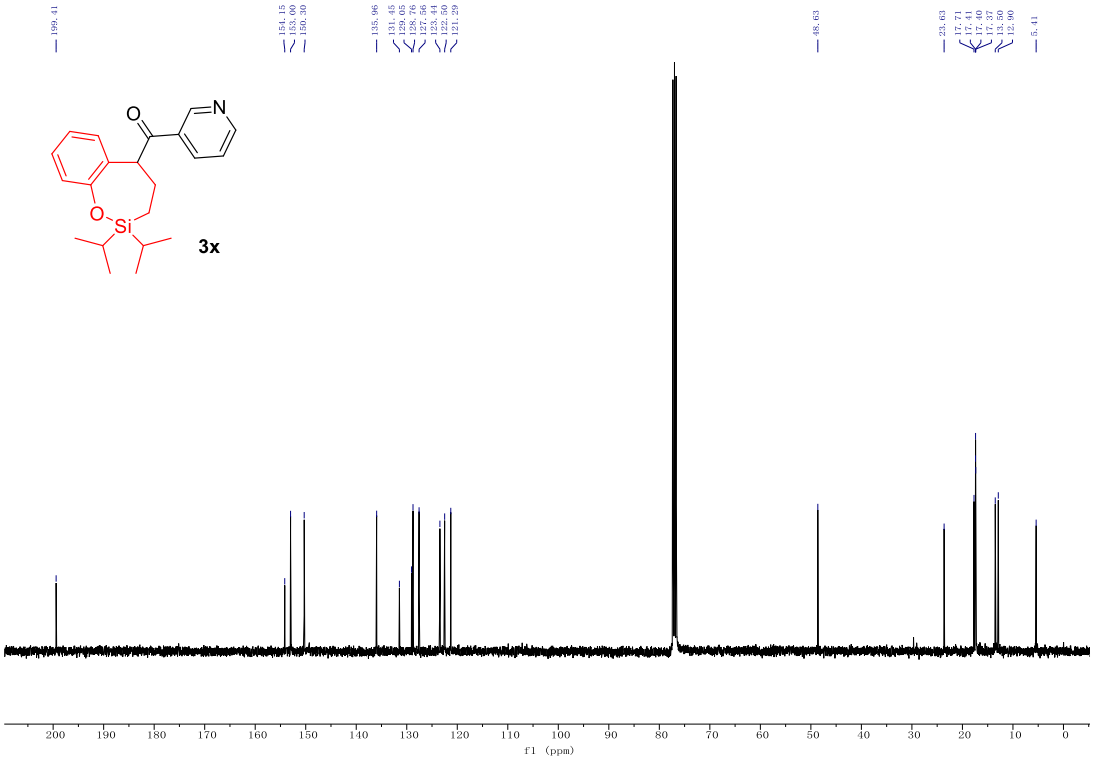


**Figure S59. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3x**

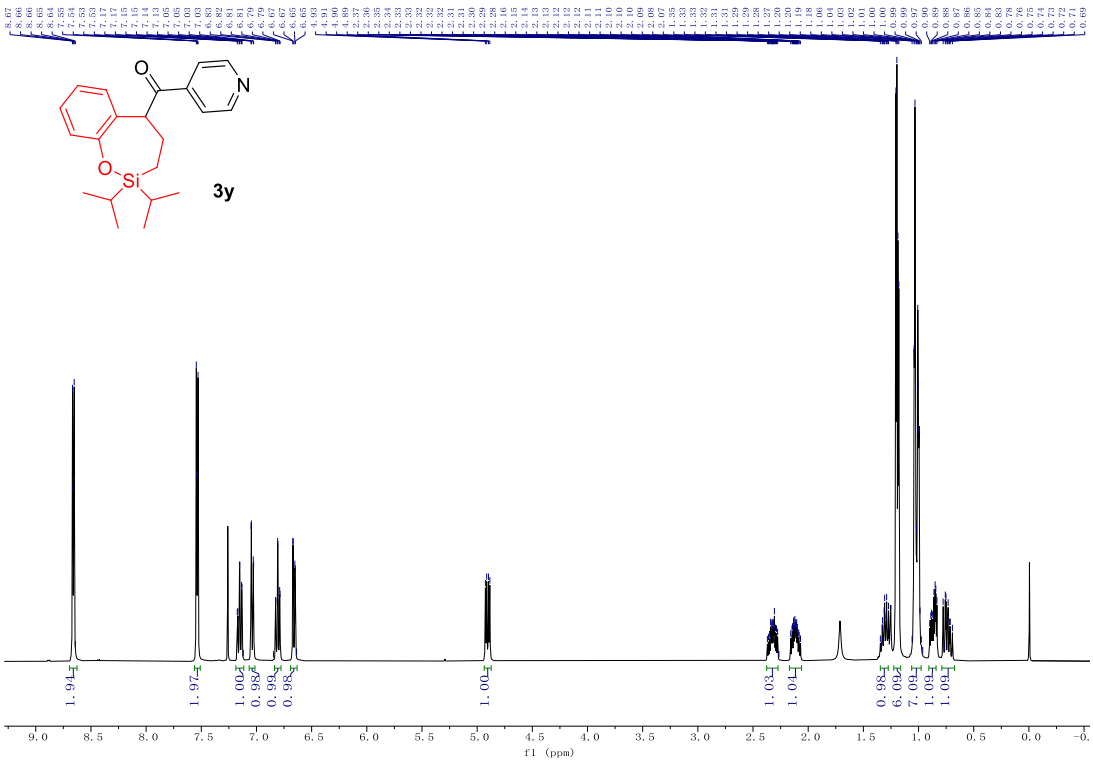


**Figure S60. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3y**

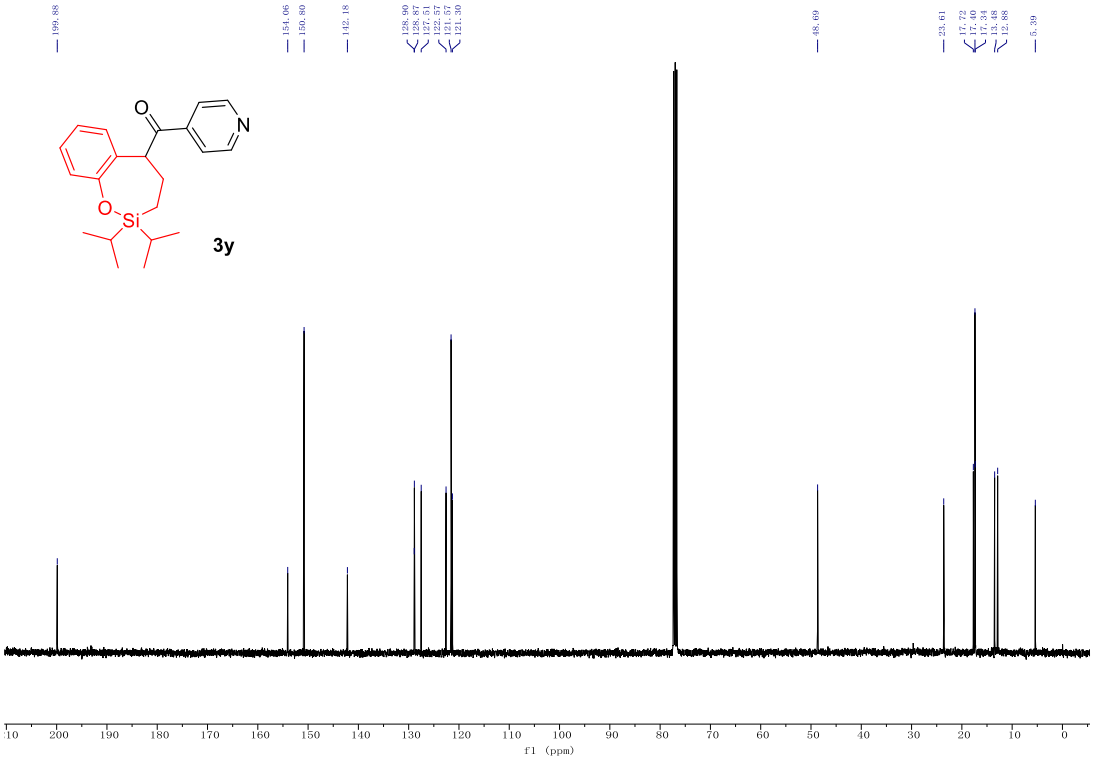


**Figure S61. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3y**

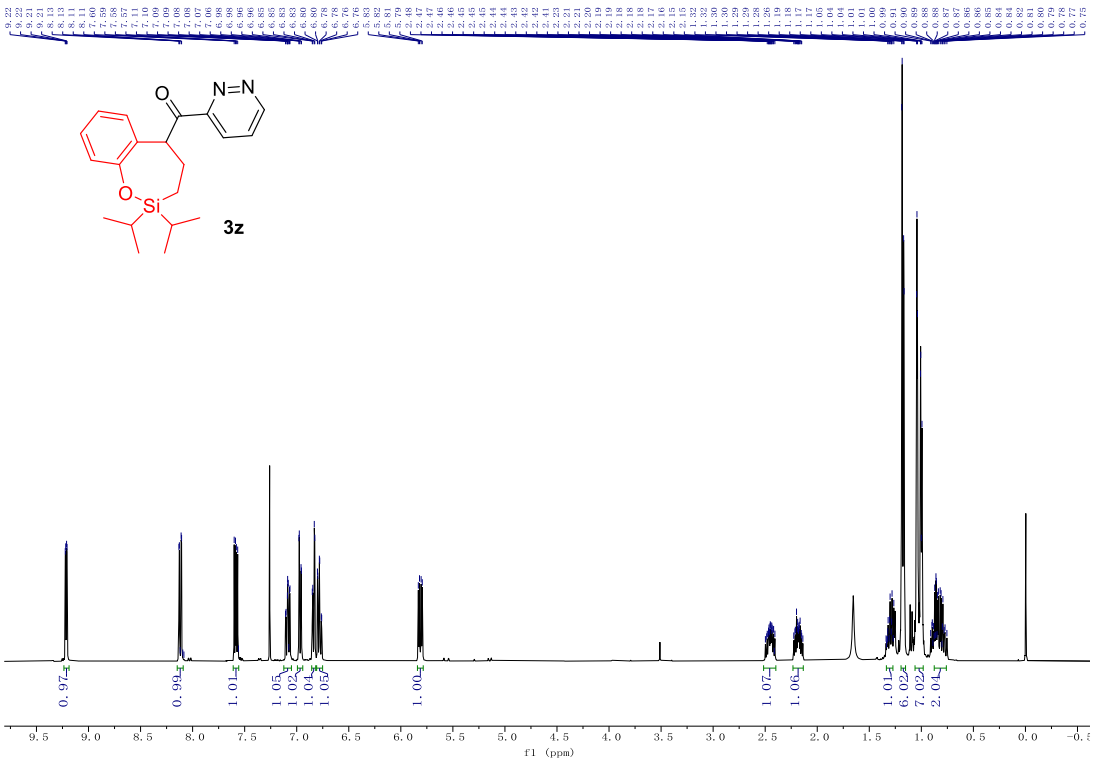


**Figure S62. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3z**

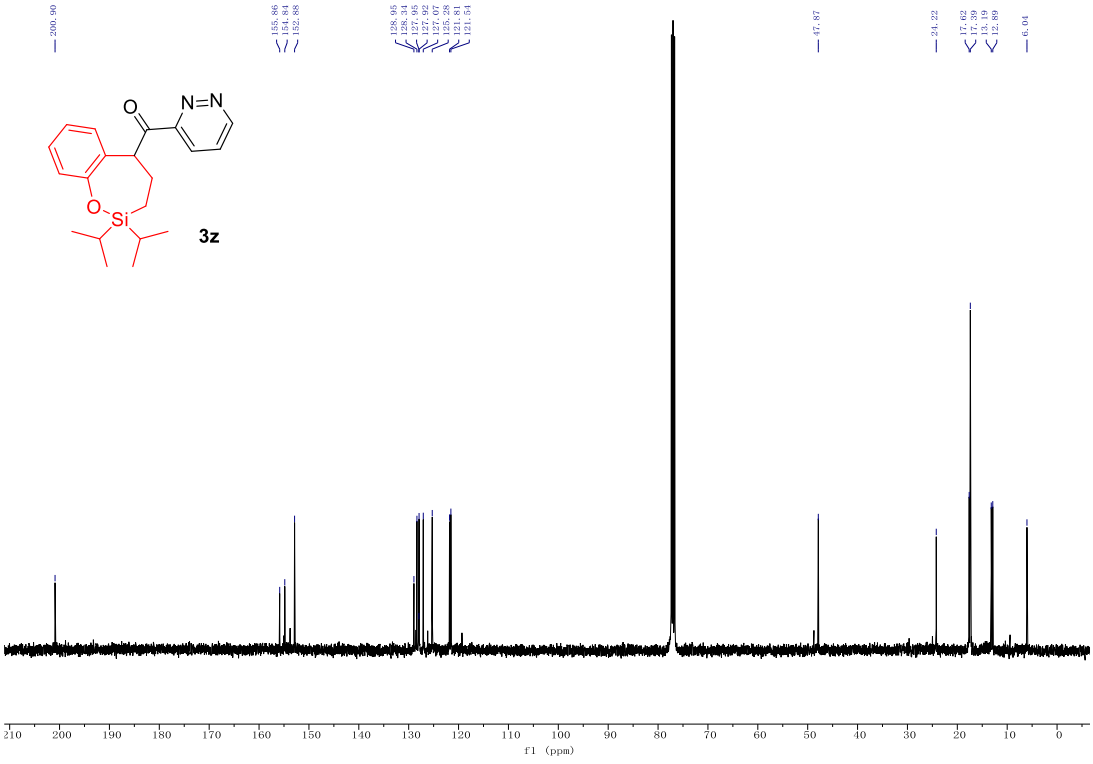


**Figure S63. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3z**

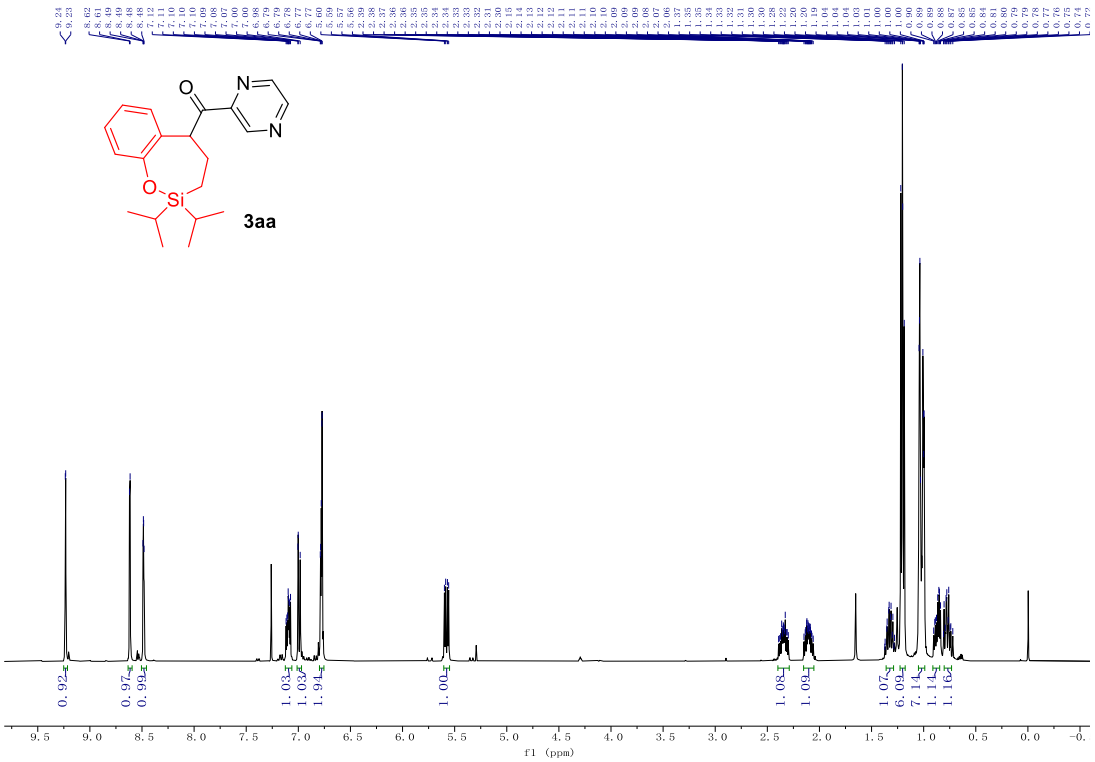


**Figure S64.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3aa**

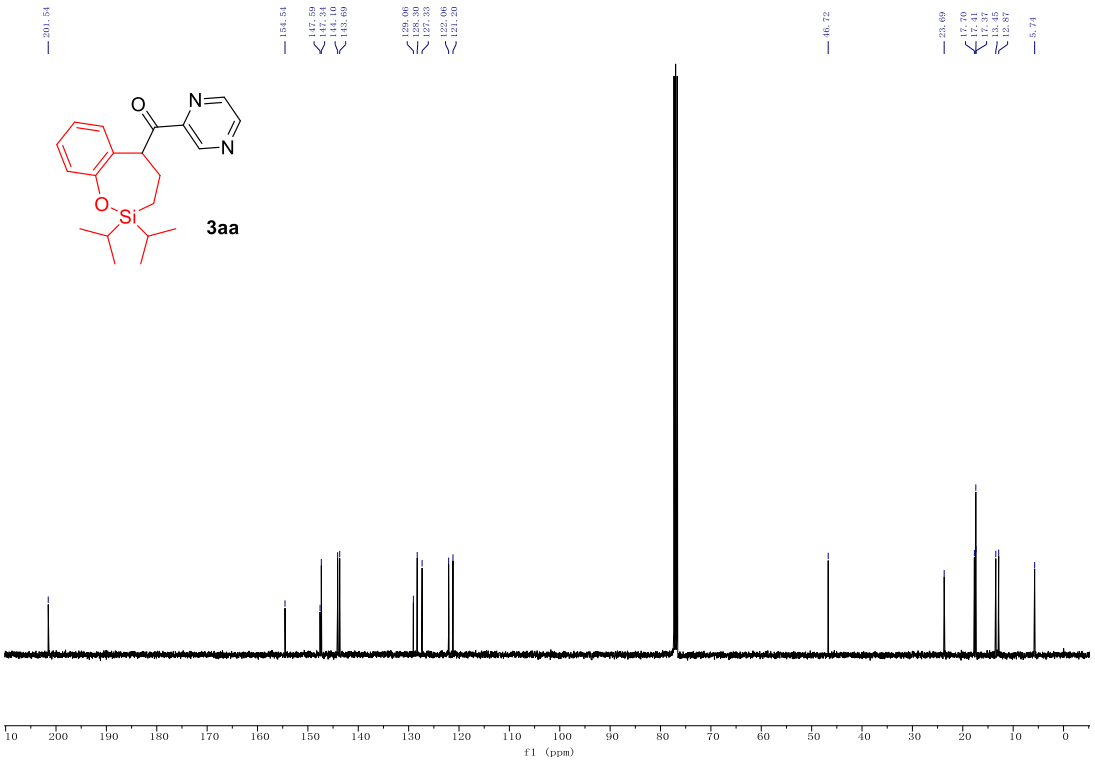


**Figure S65.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3aa**

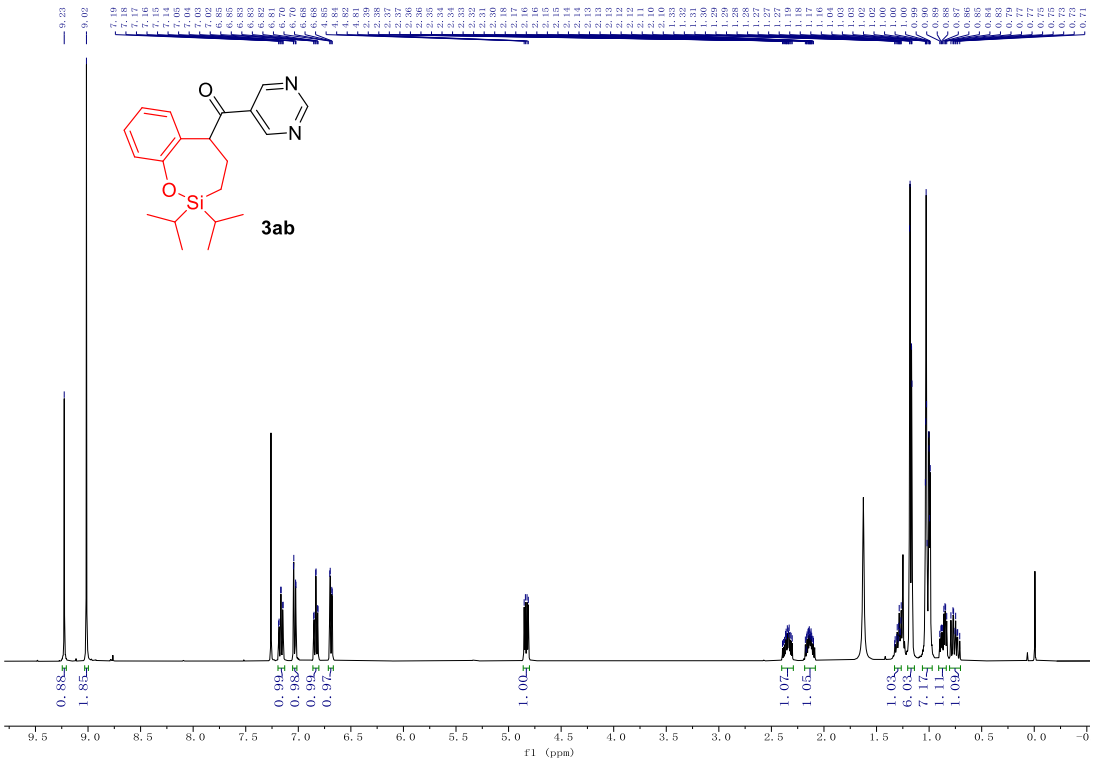


**Figure S66.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ab**

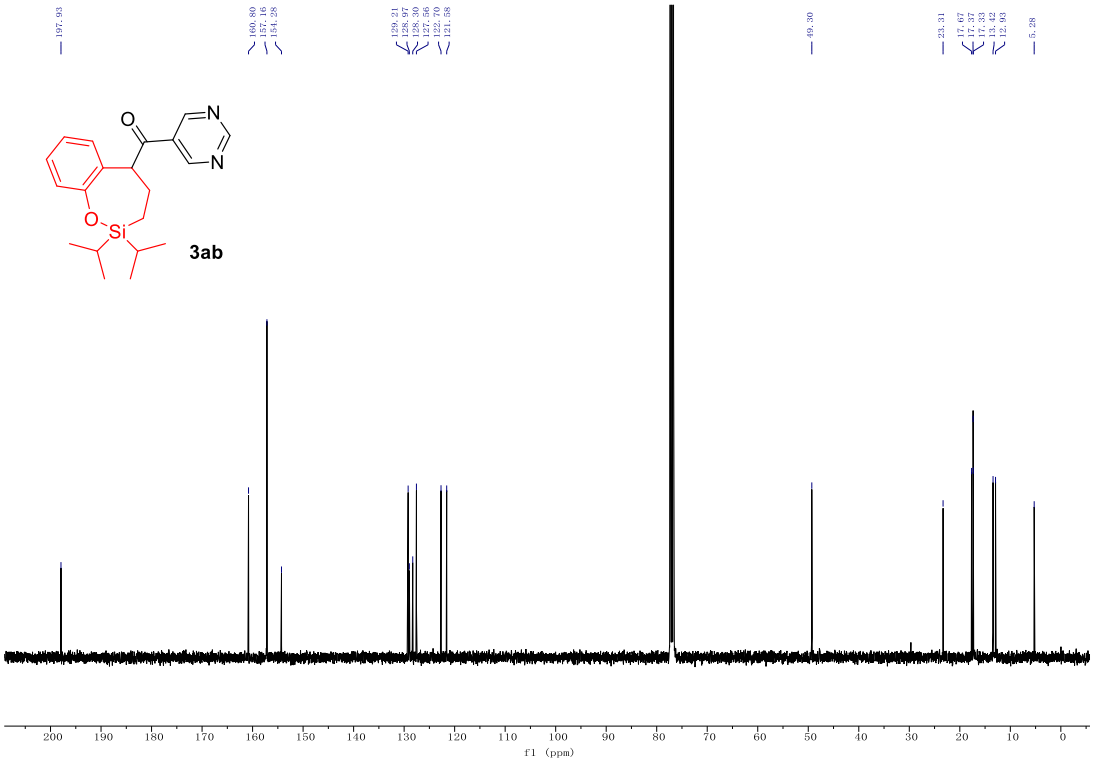


**Figure S67.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ab**

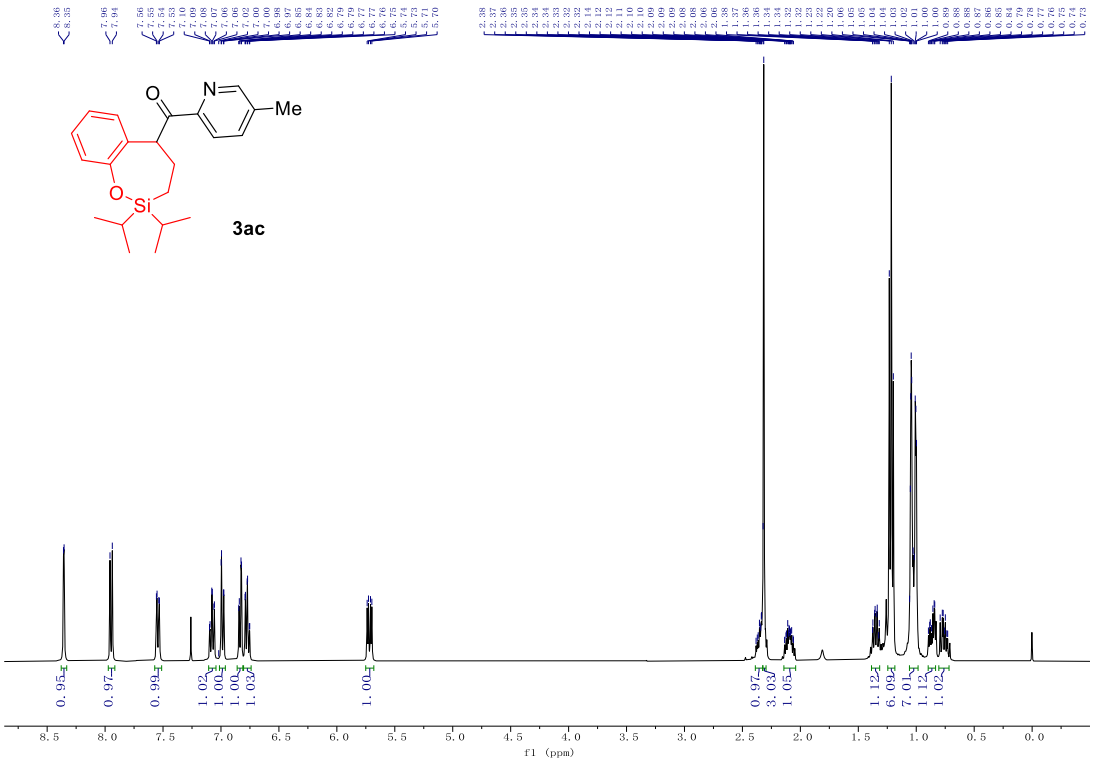


**Figure S68. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3ac**

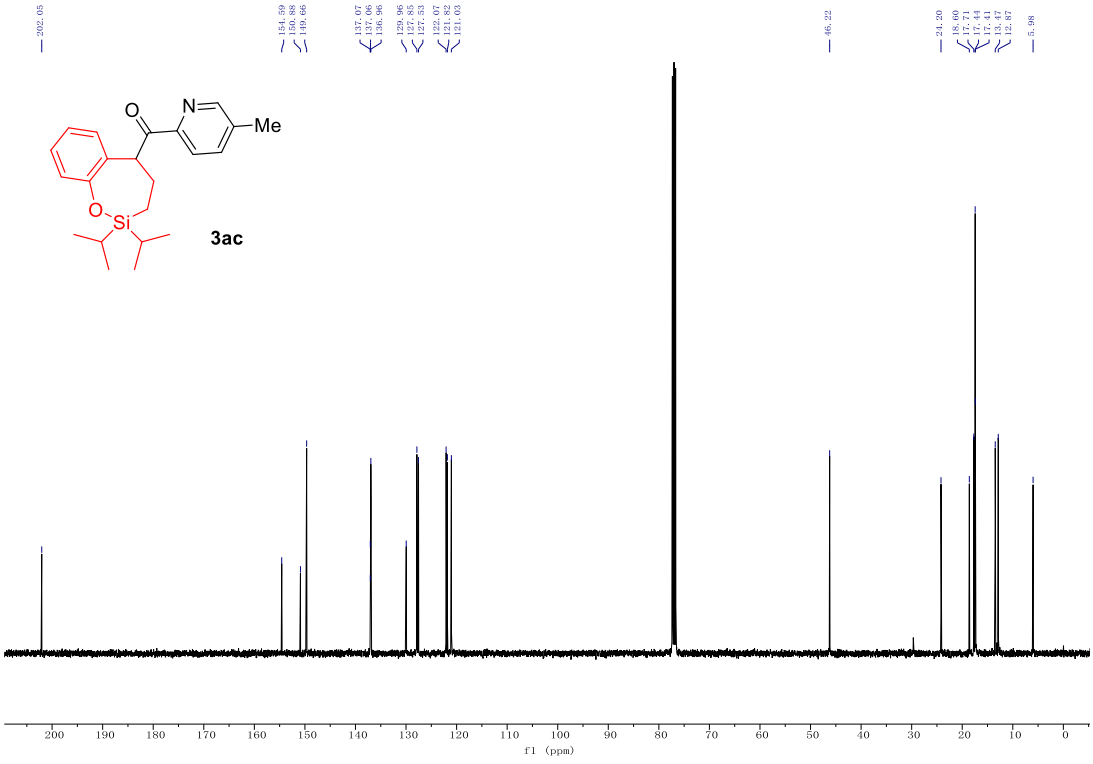


**Figure S69. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3ac**

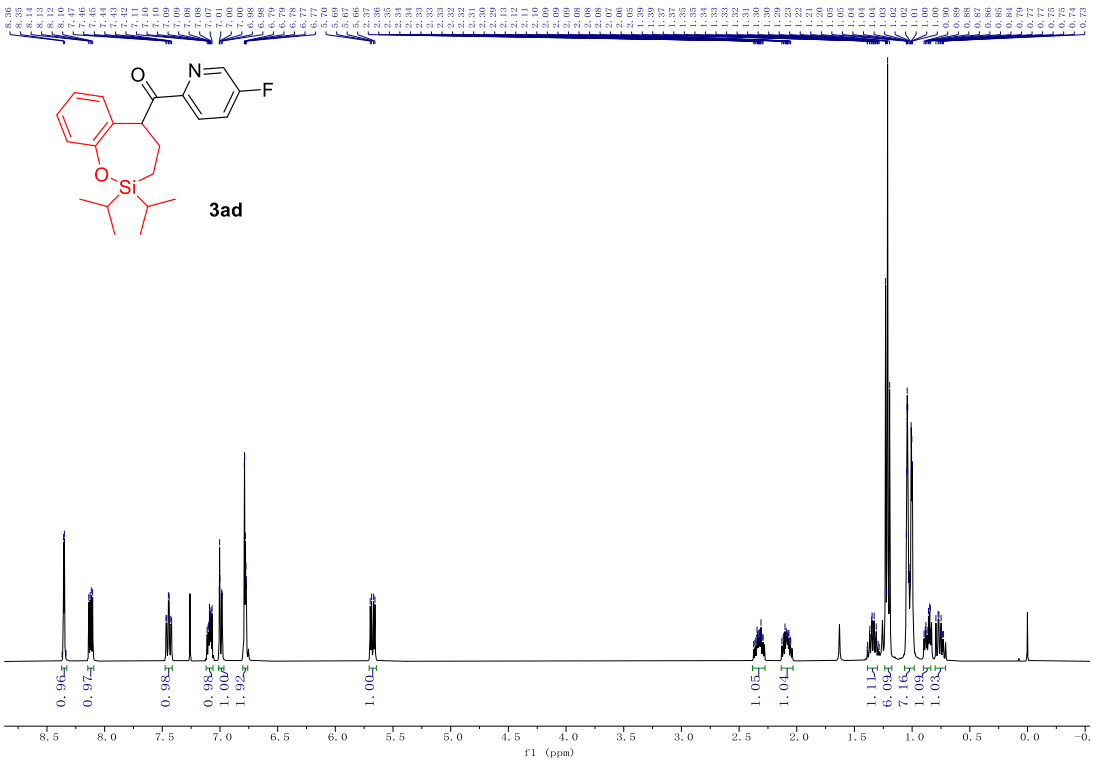


**Figure S70.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ad**

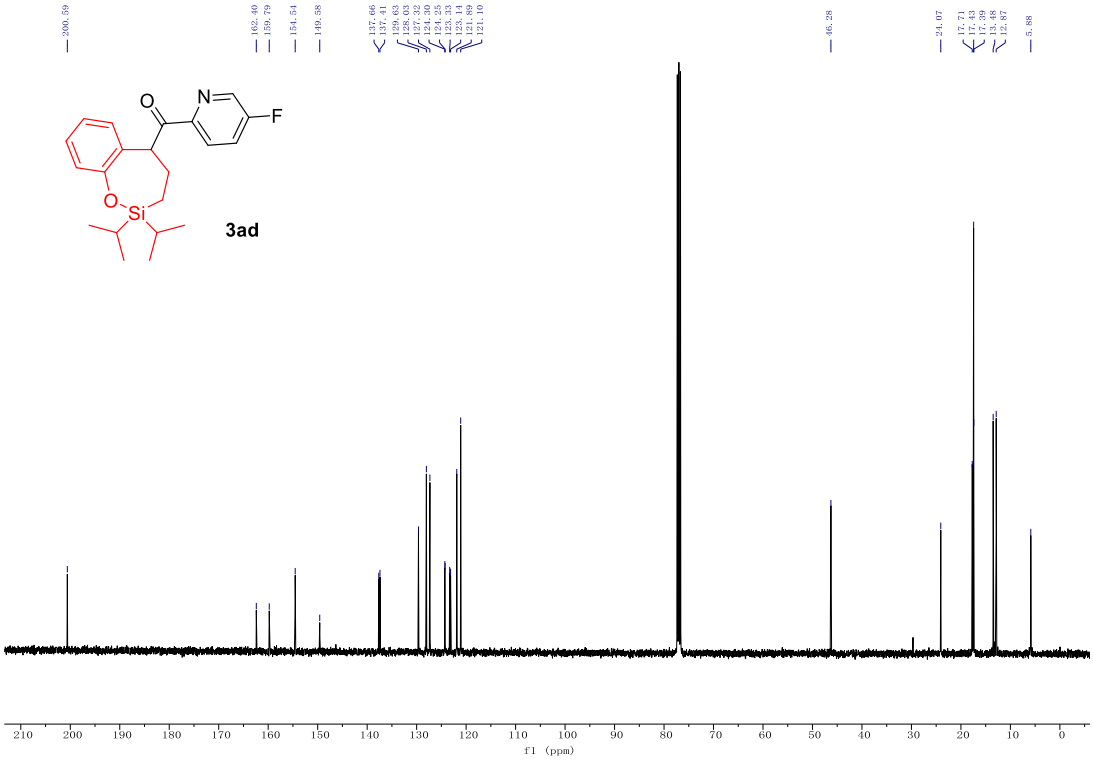


**Figure S71.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ad**


**Figure S72.** $^{19}$**F NMR** (377 MHz, $CDCl_3$) spectrum of **3ad**

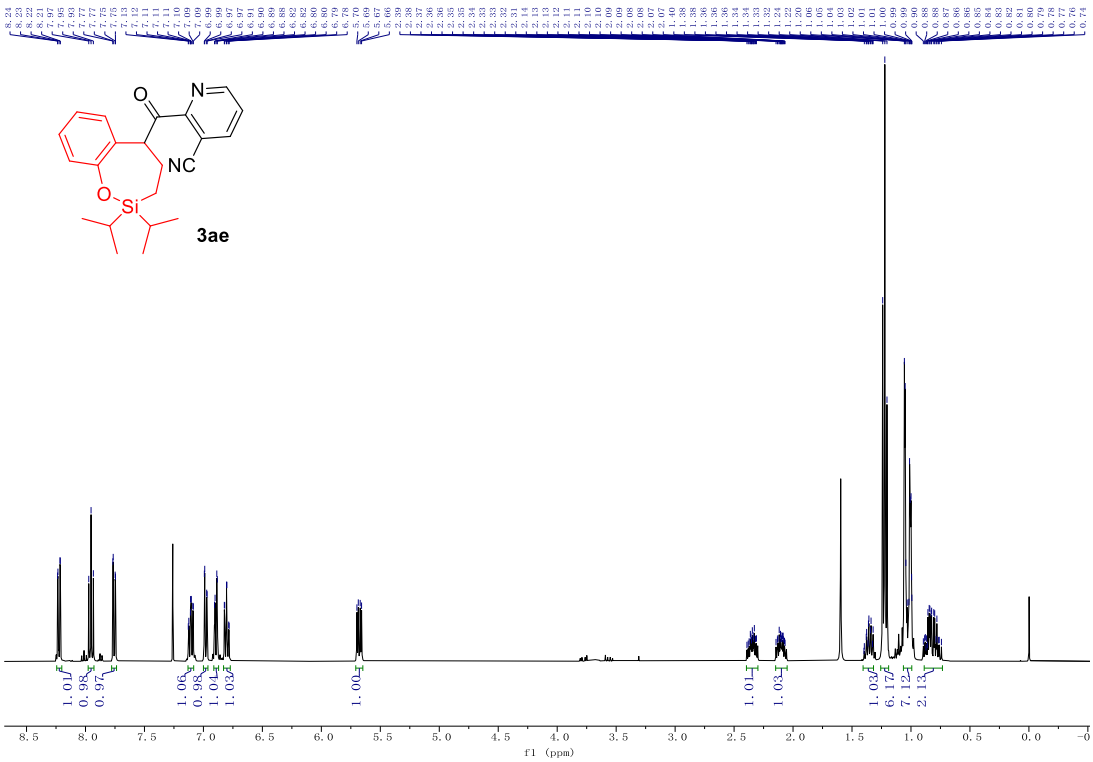


**Figure S73.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ae**

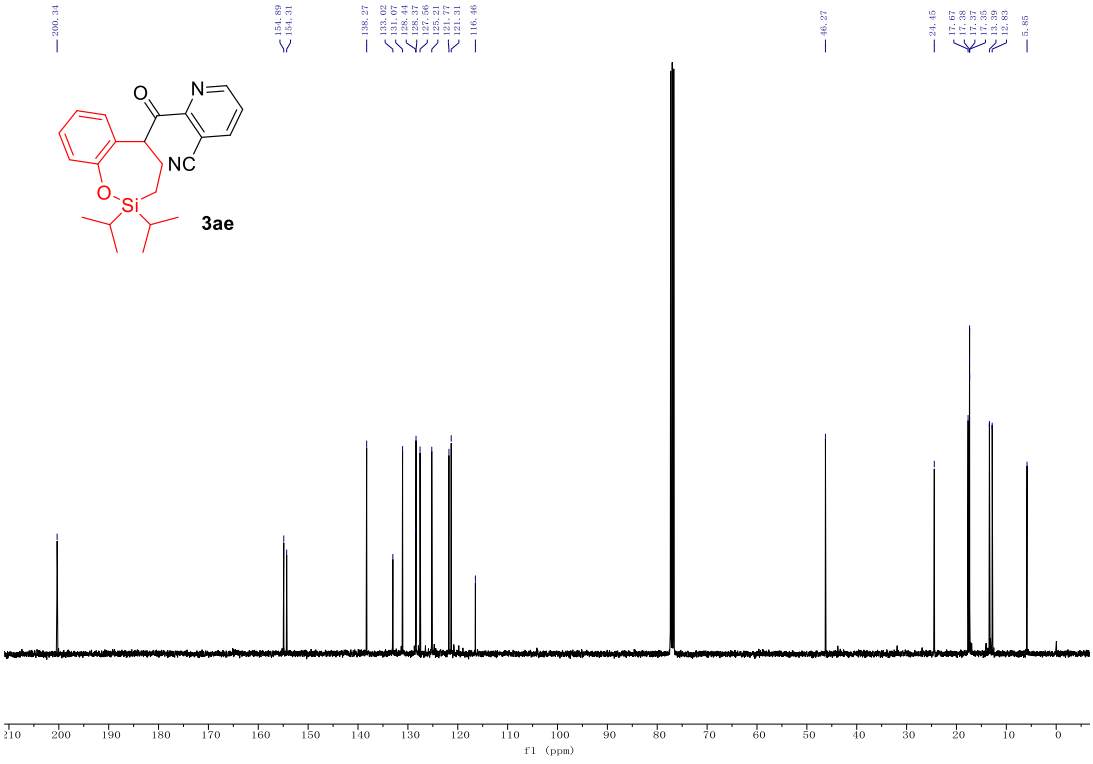


**Figure S74.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ae**

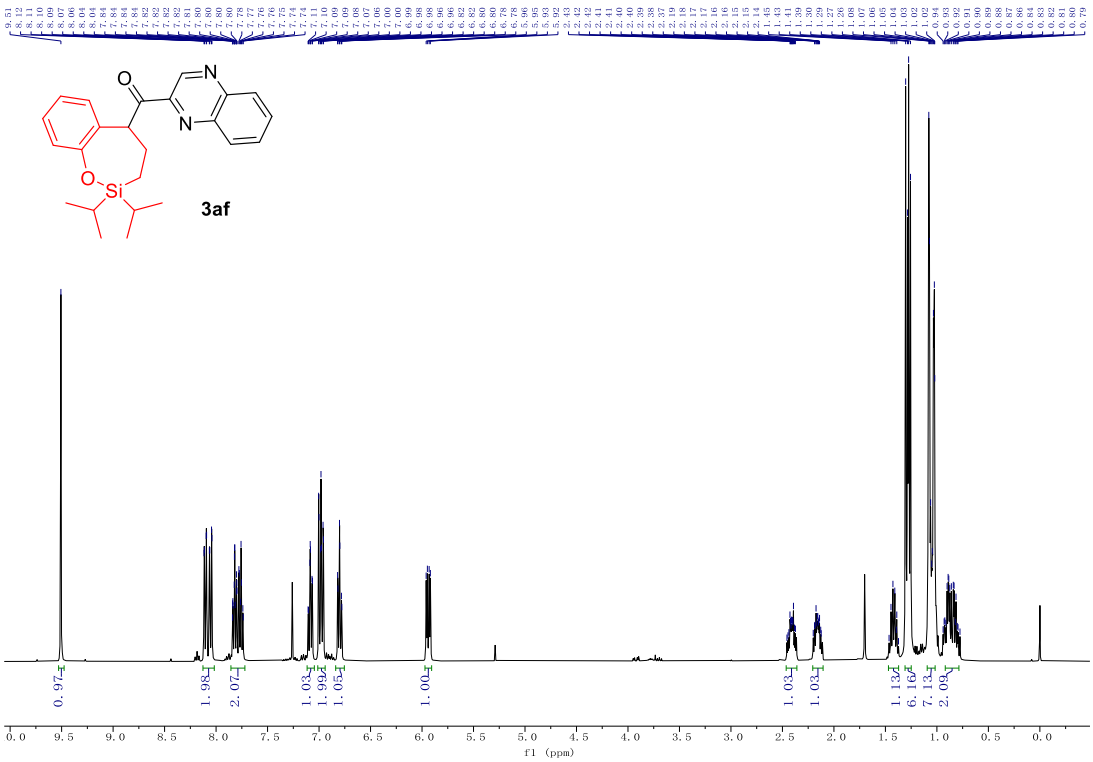


**Figure S75. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3af**

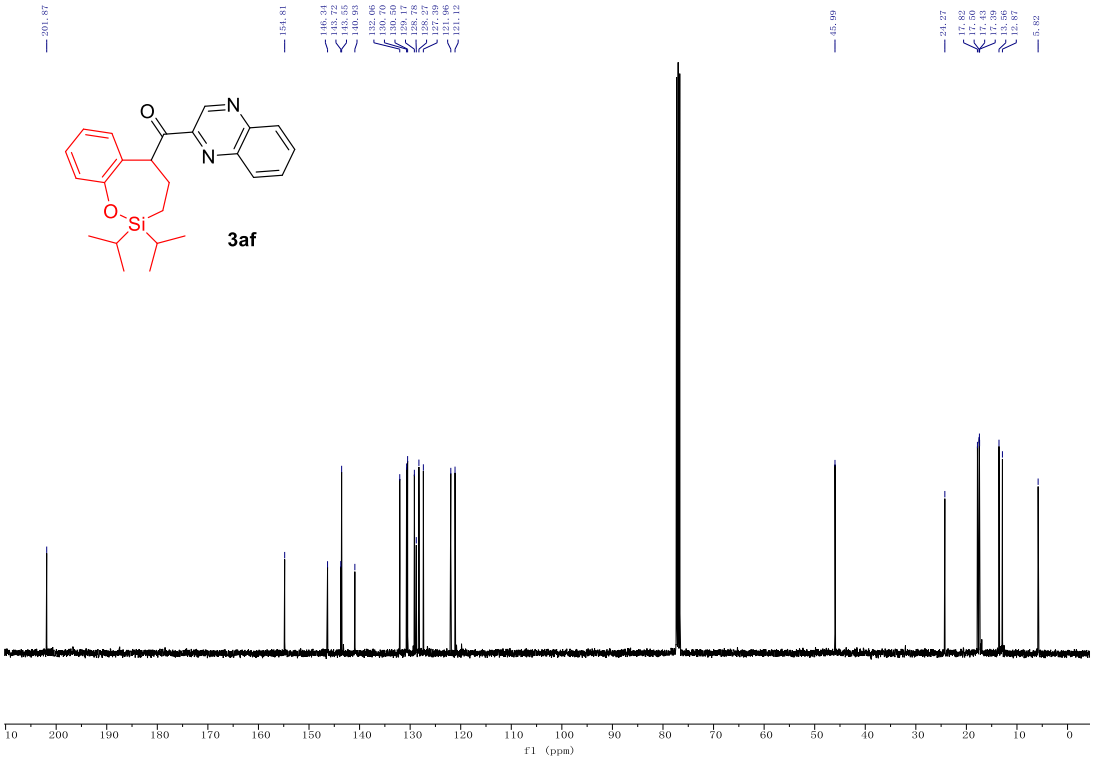


**Figure S76. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3af**

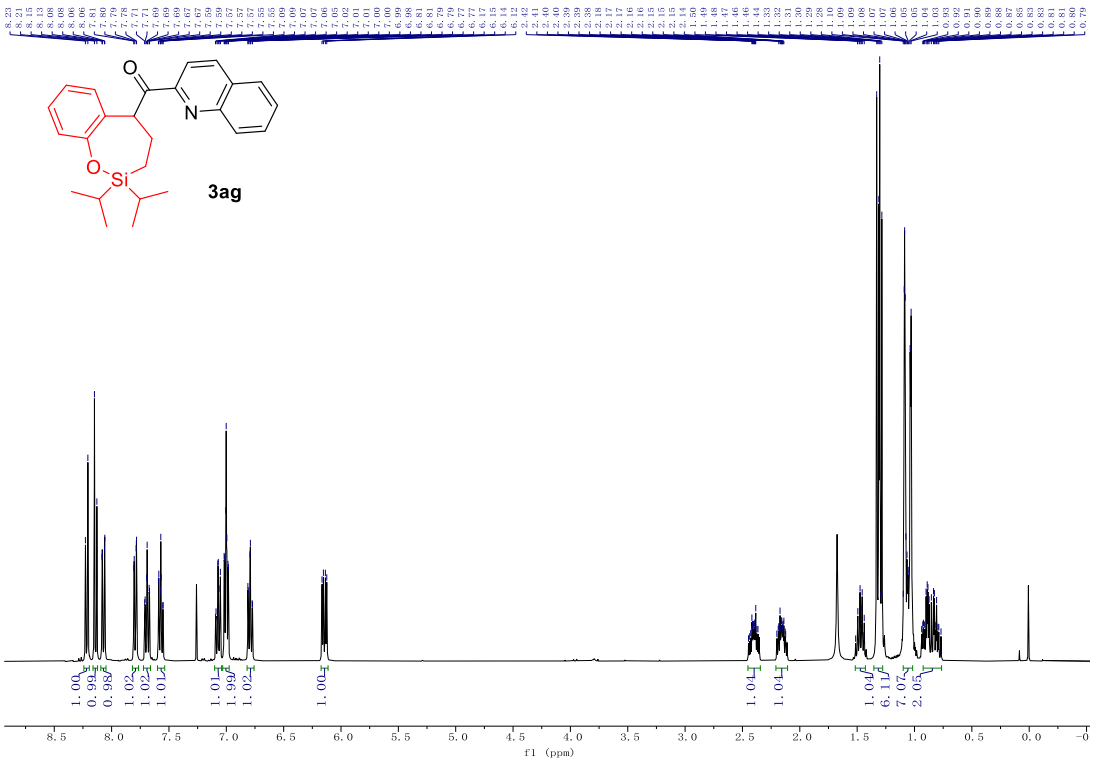


**Figure S77.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ag**

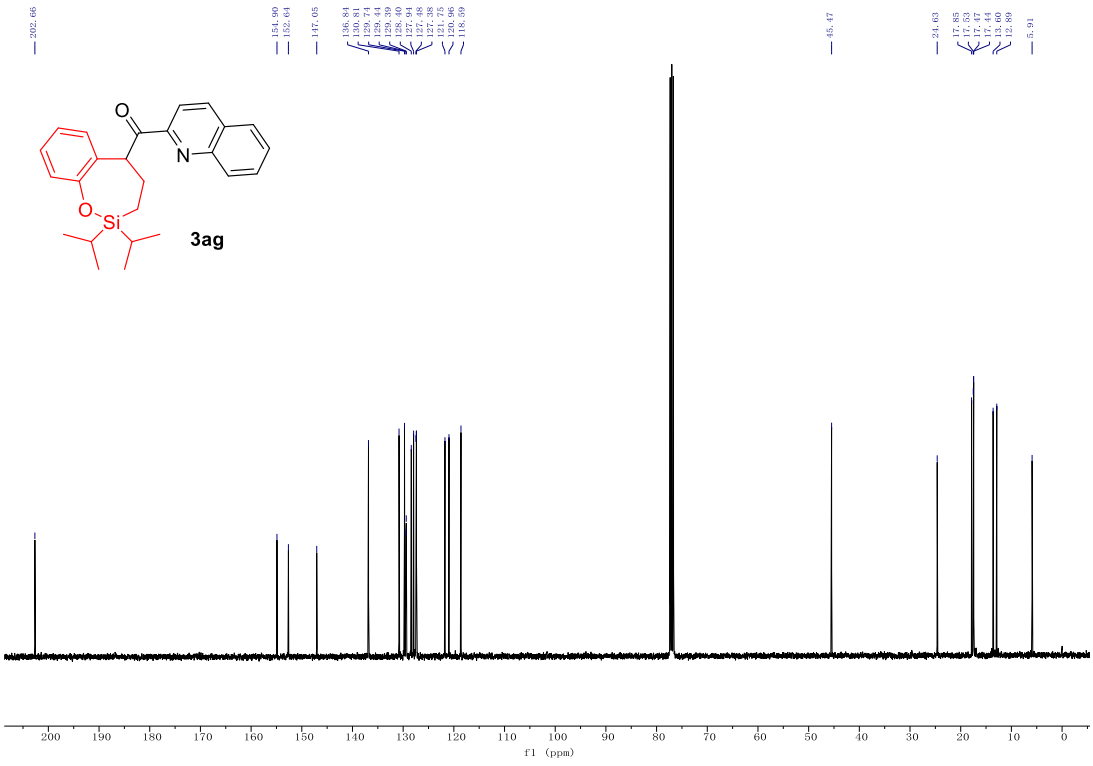


**Figure S78.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ag**

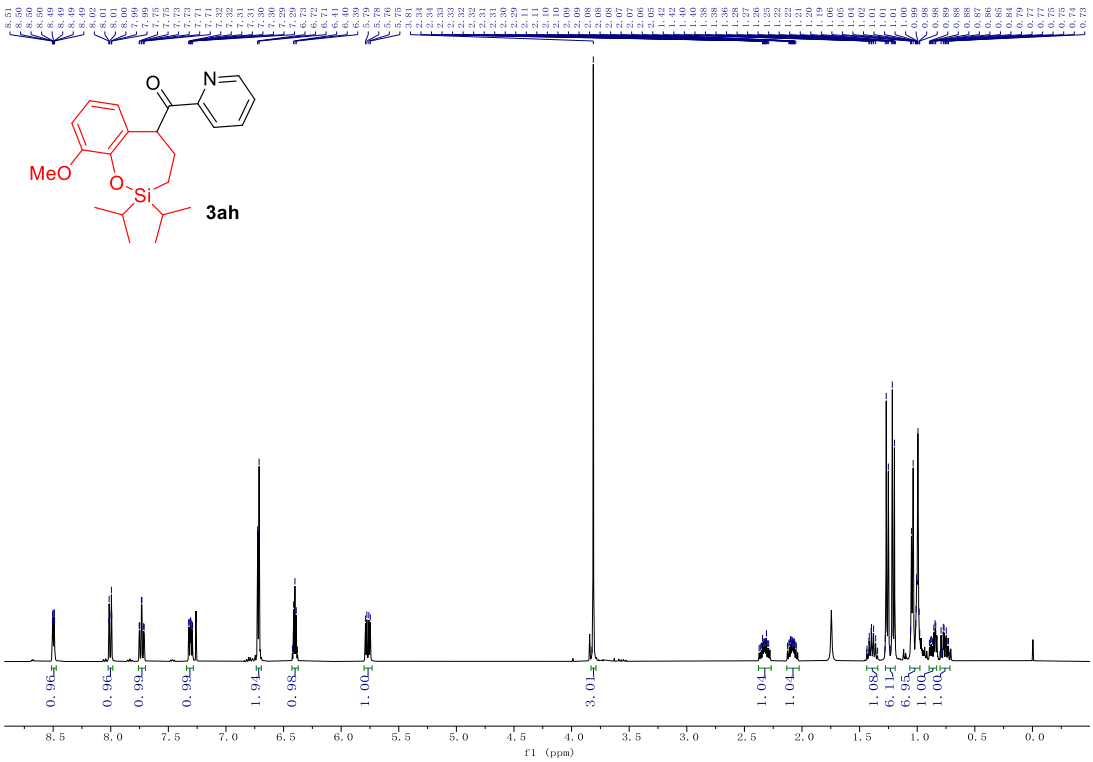


**Figure S79.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ah**

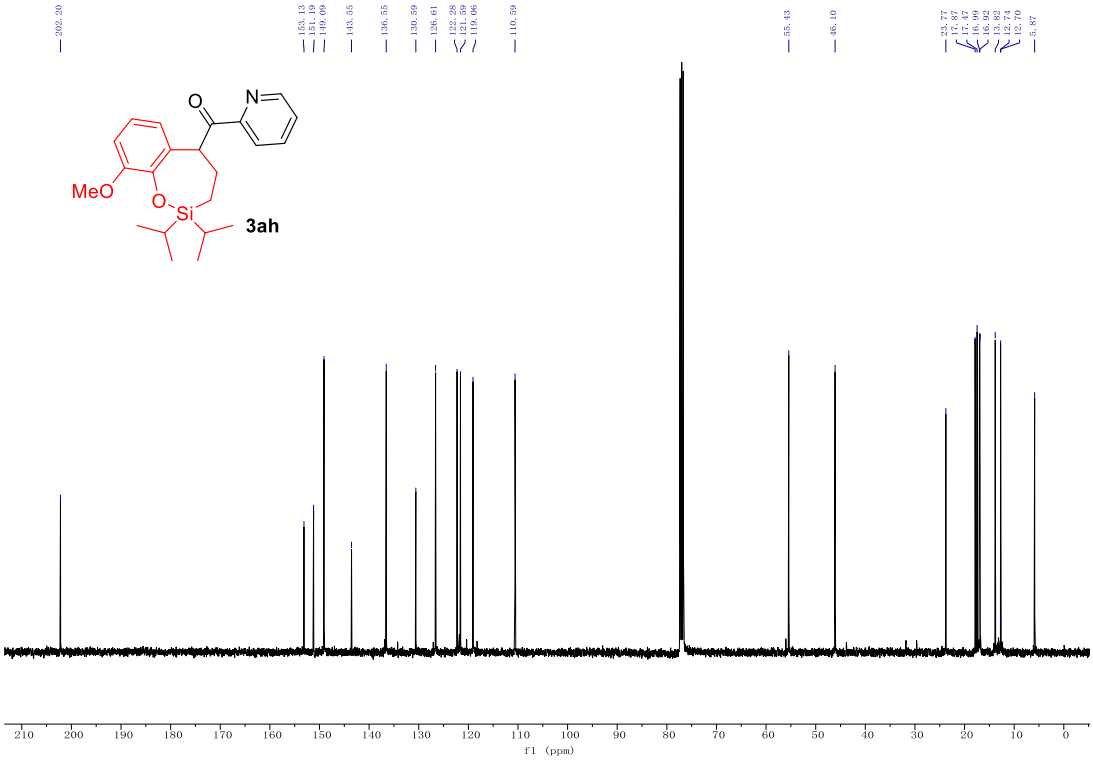


**Figure S80.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ah**

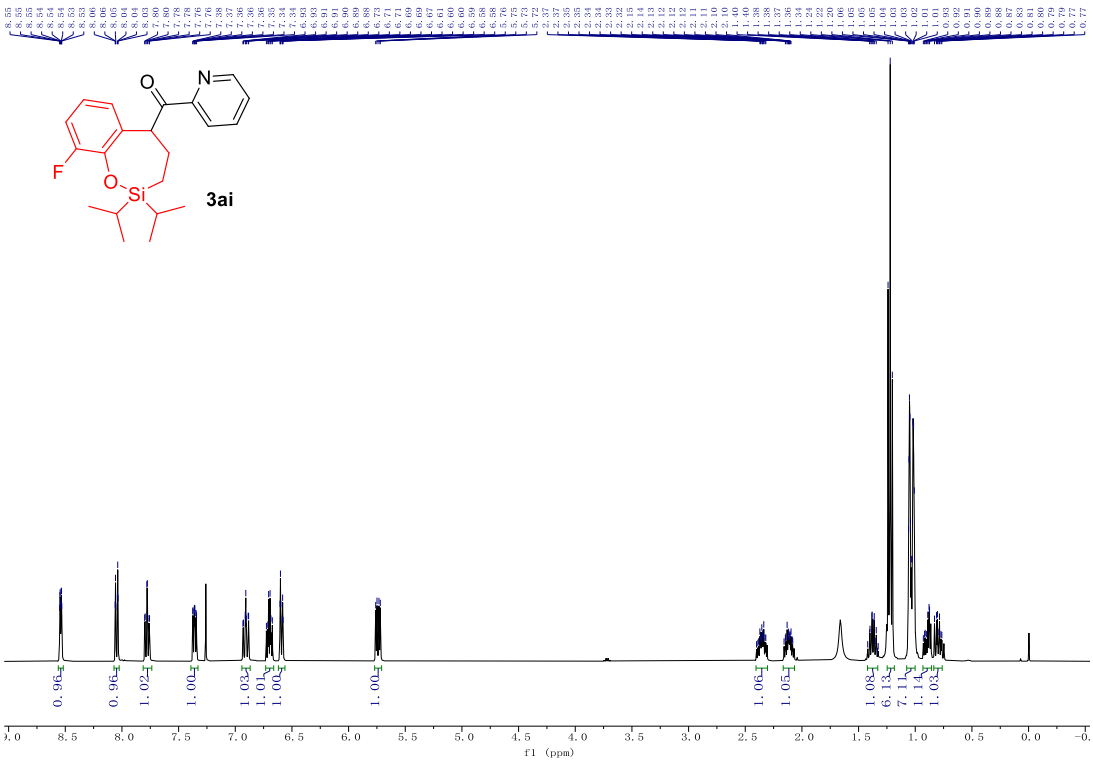


**Figure S81.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ai**

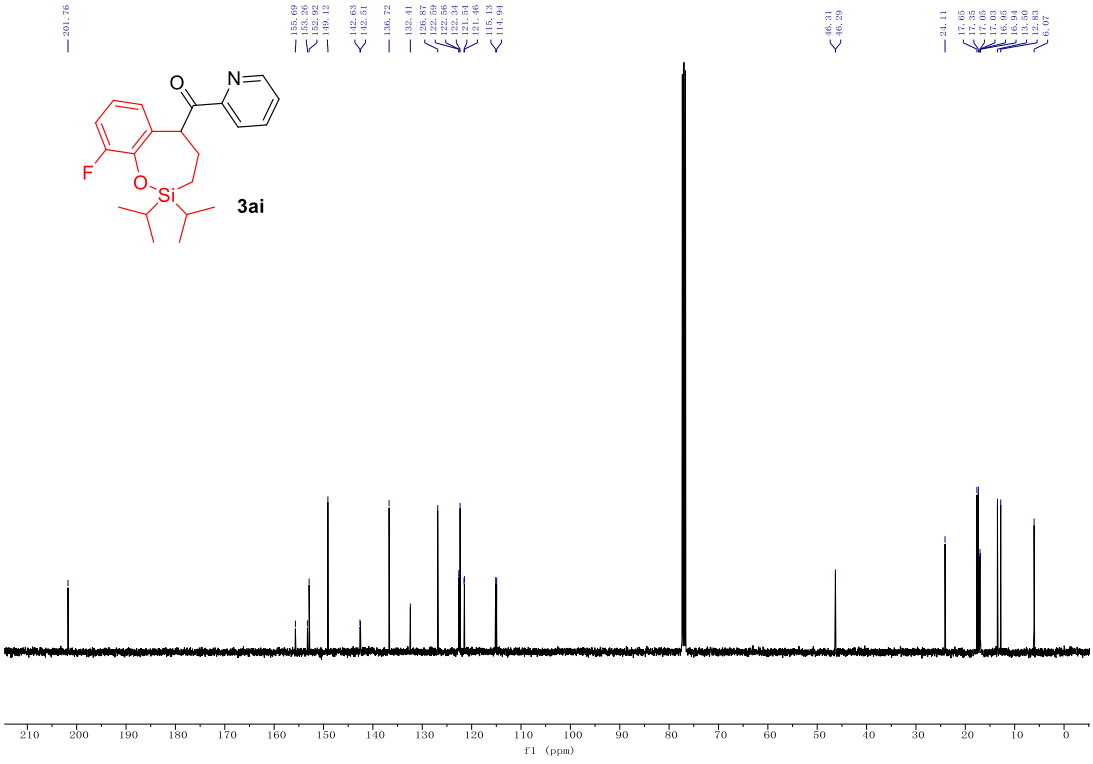


**Figure S82.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ai**

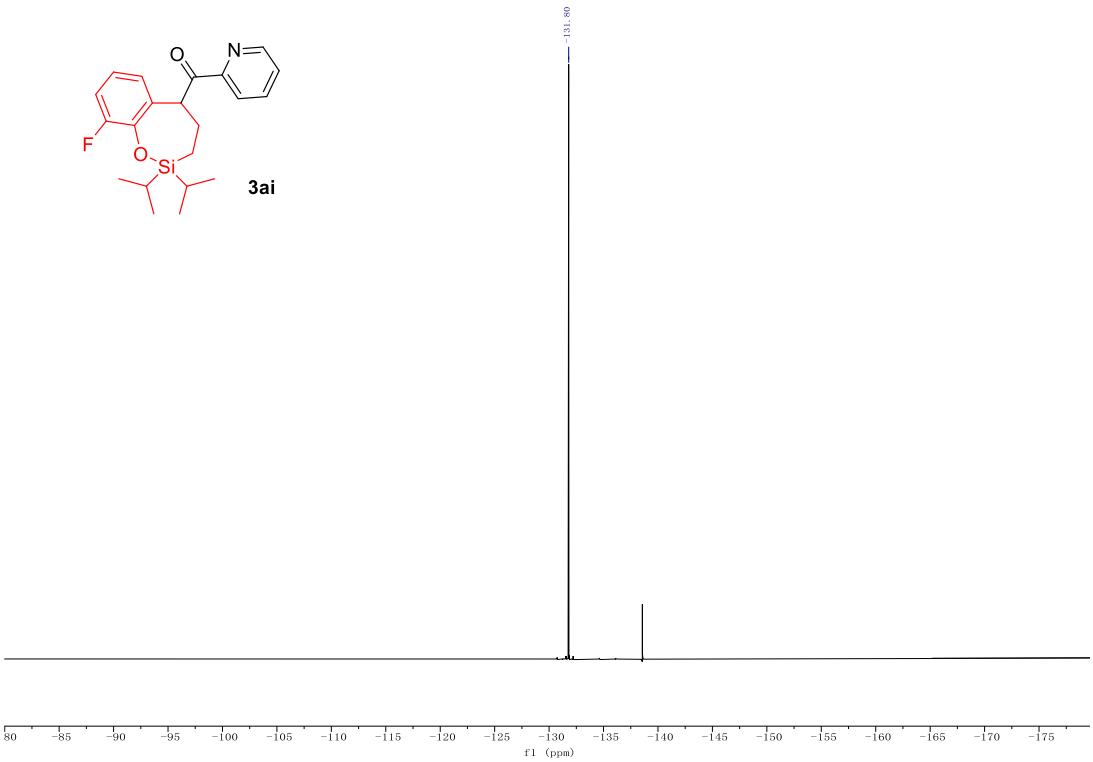


**Figure S83.** $^{19}$**F NMR** (377 MHz, $CDCl_3$) spectrum of **3ai**

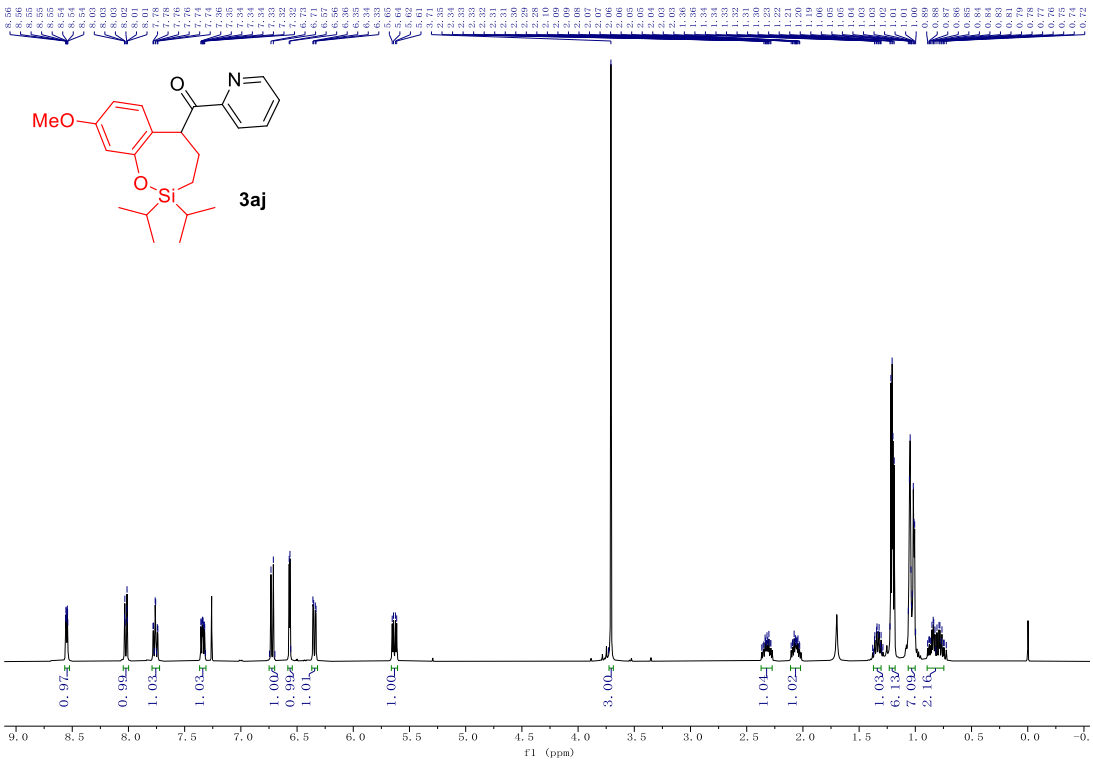


**Figure S84. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3aj**

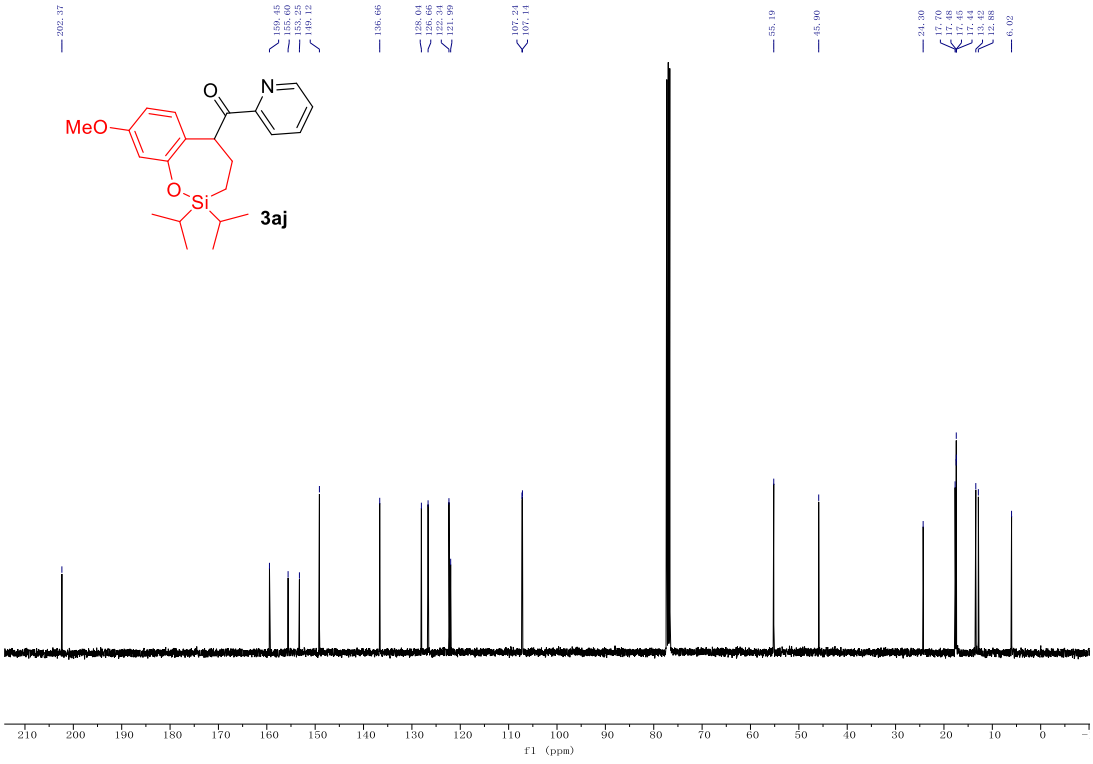


**Figure S85. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3aj**

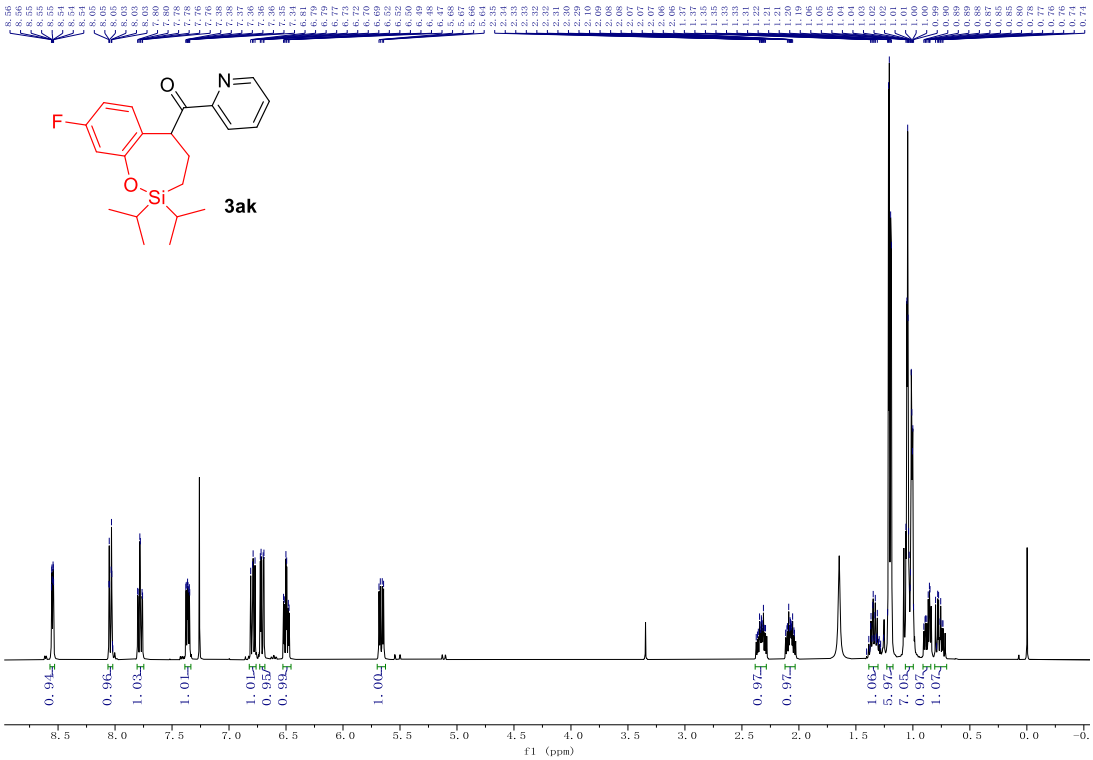


**Figure S86.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ak**

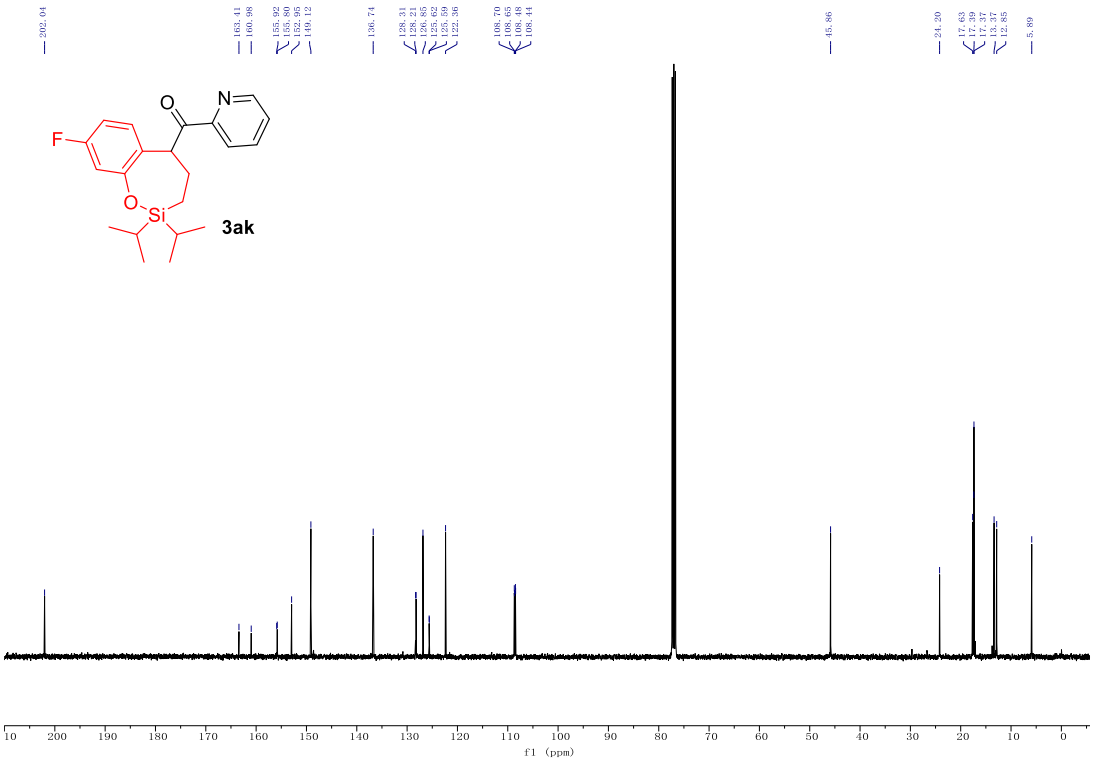


**Figure S87.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ak**

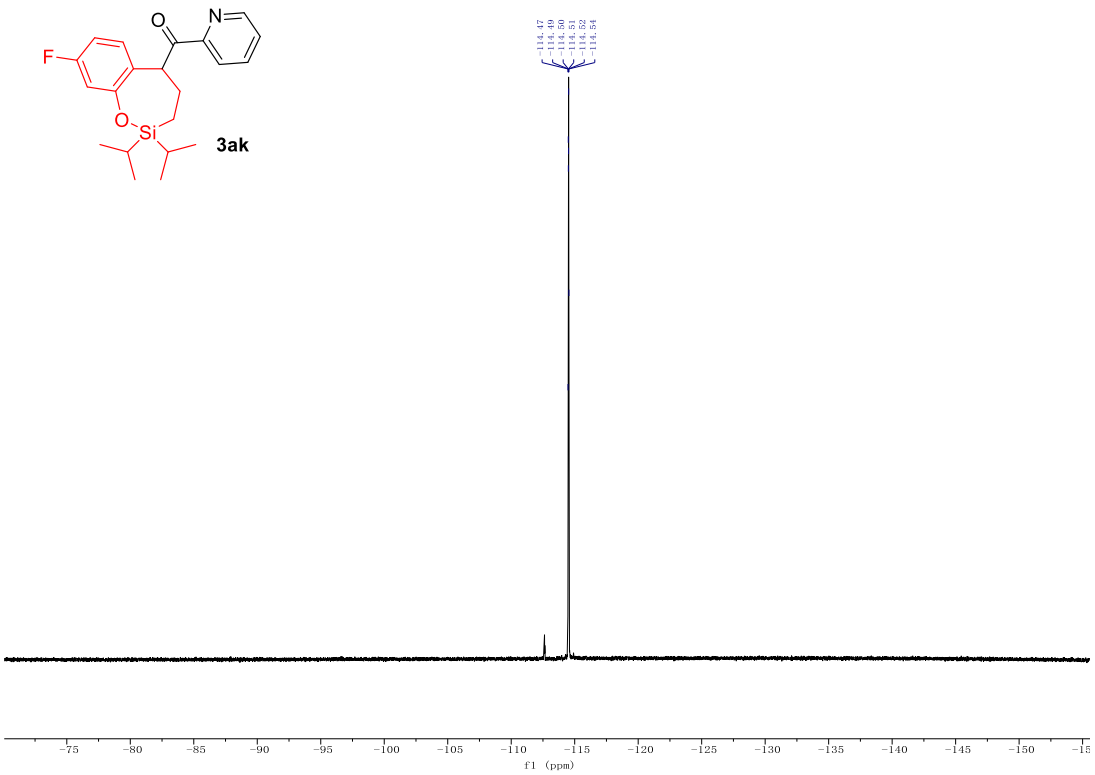


**Figure S88.** $^{19}$**F NMR** (377 MHz, $CDCl_3$) spectrum of **3ak**

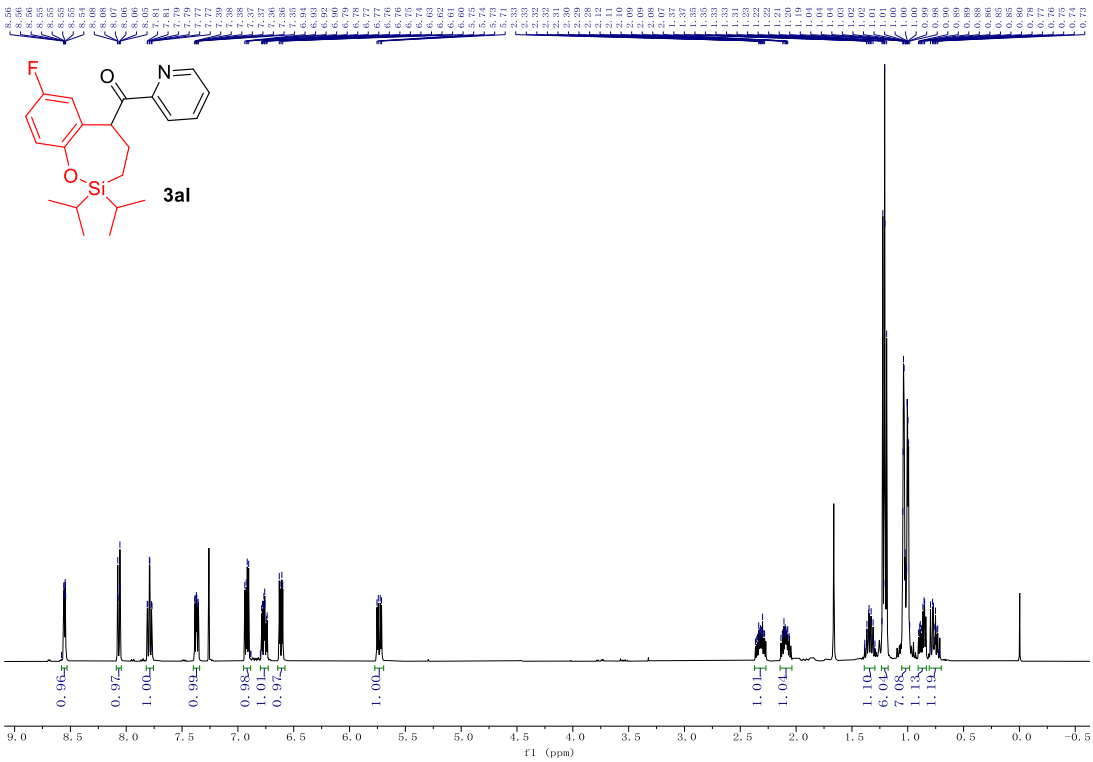


**Figure S89. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3al**

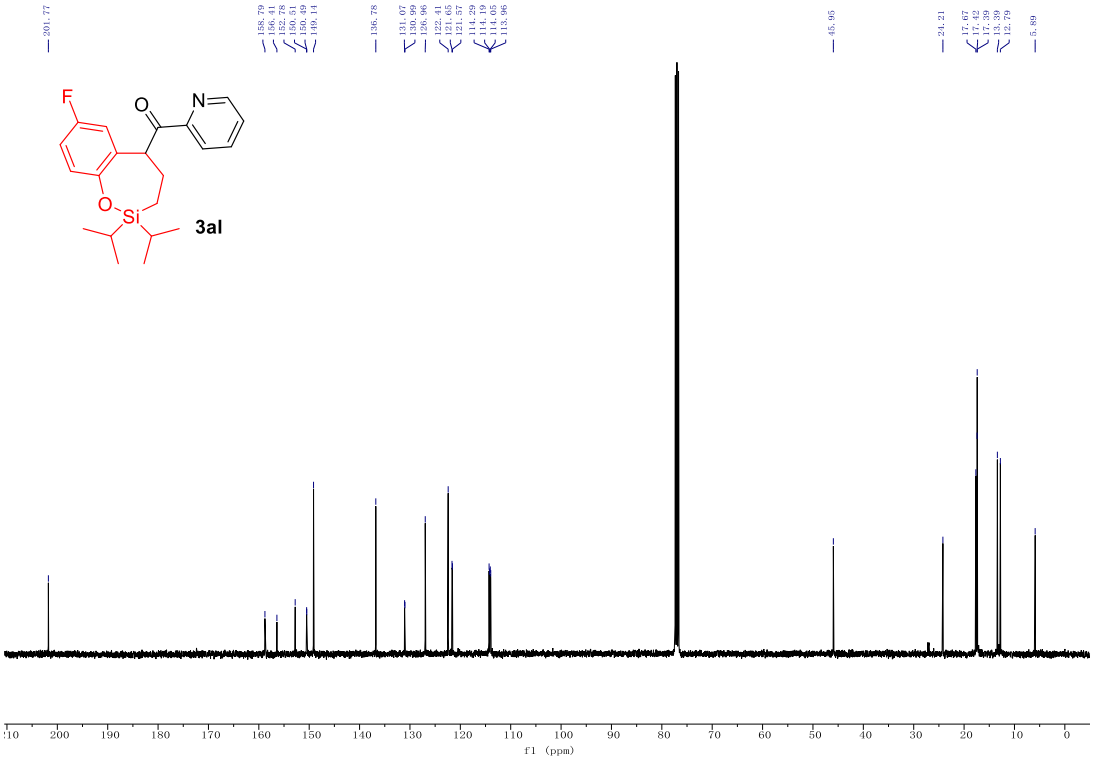


**Figure S90. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3al**

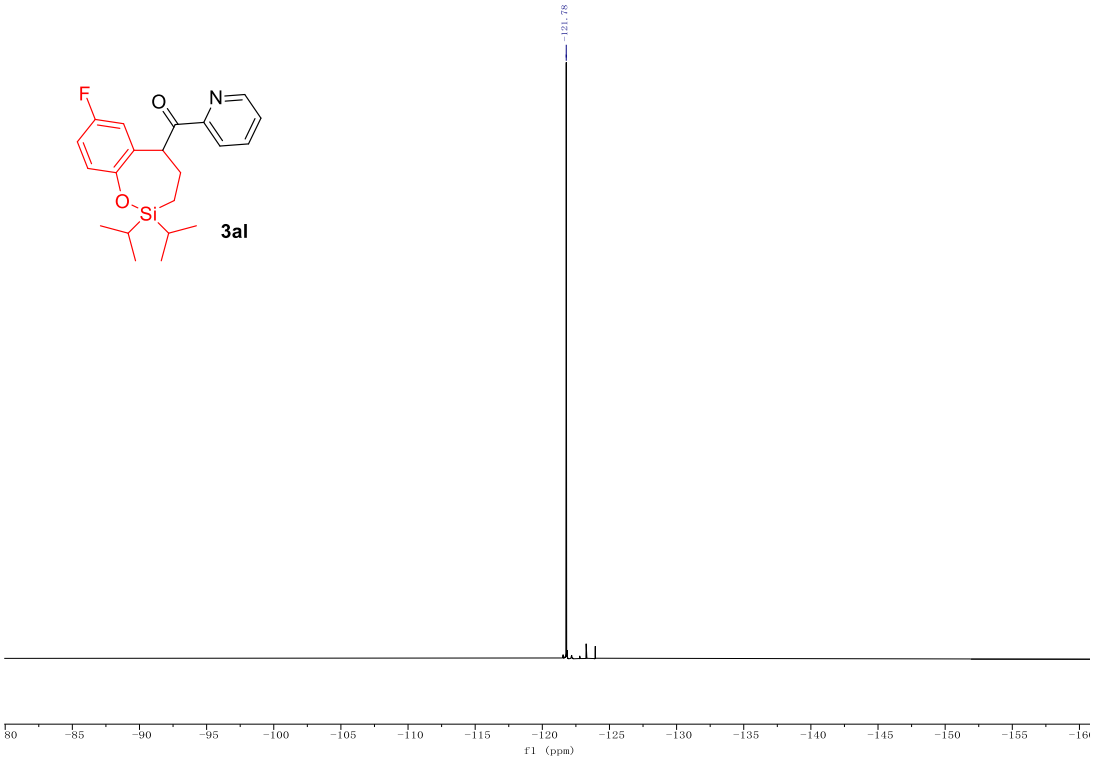


**Figure S91.** $^{19}$**F NMR** (377 MHz, $CDCl_3$) spectrum of **3al**

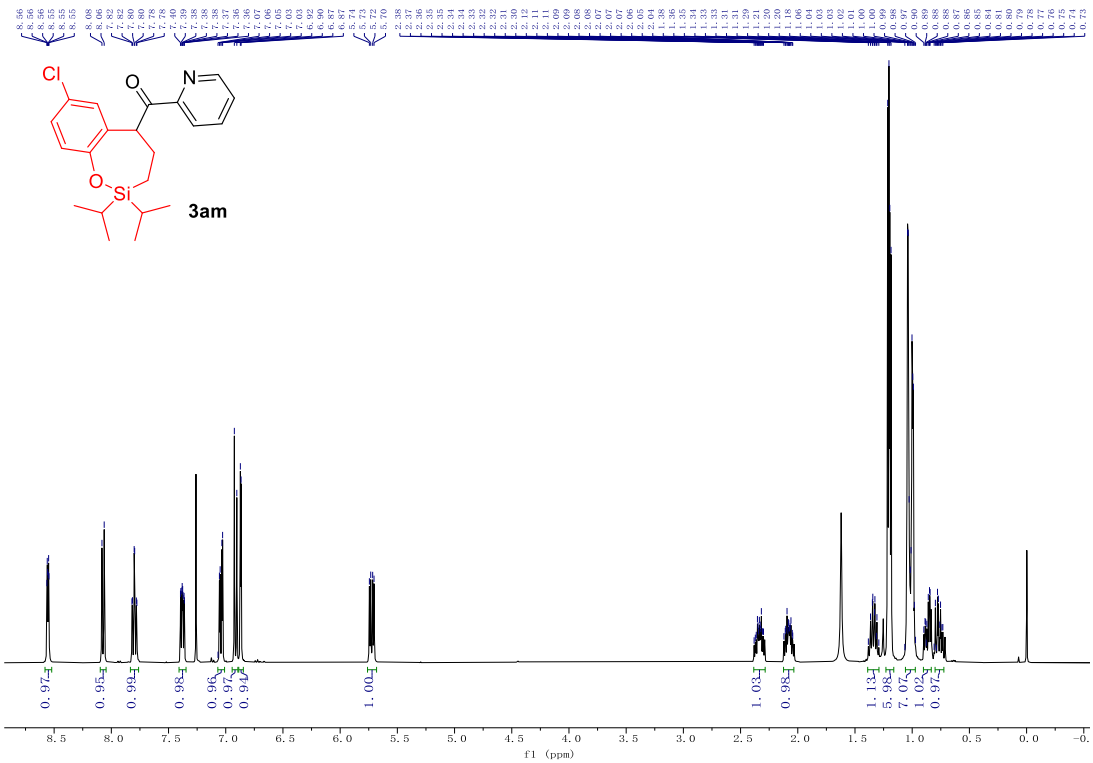


**Figure S92.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3am**

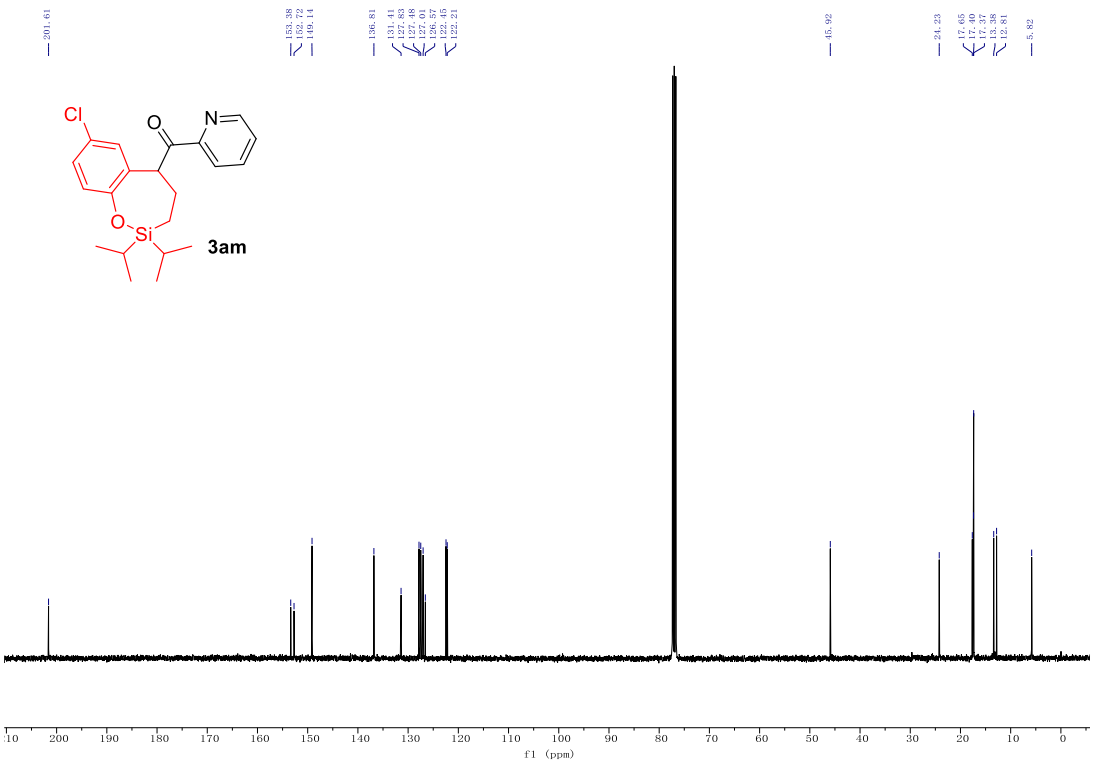


**Figure S93.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3am**

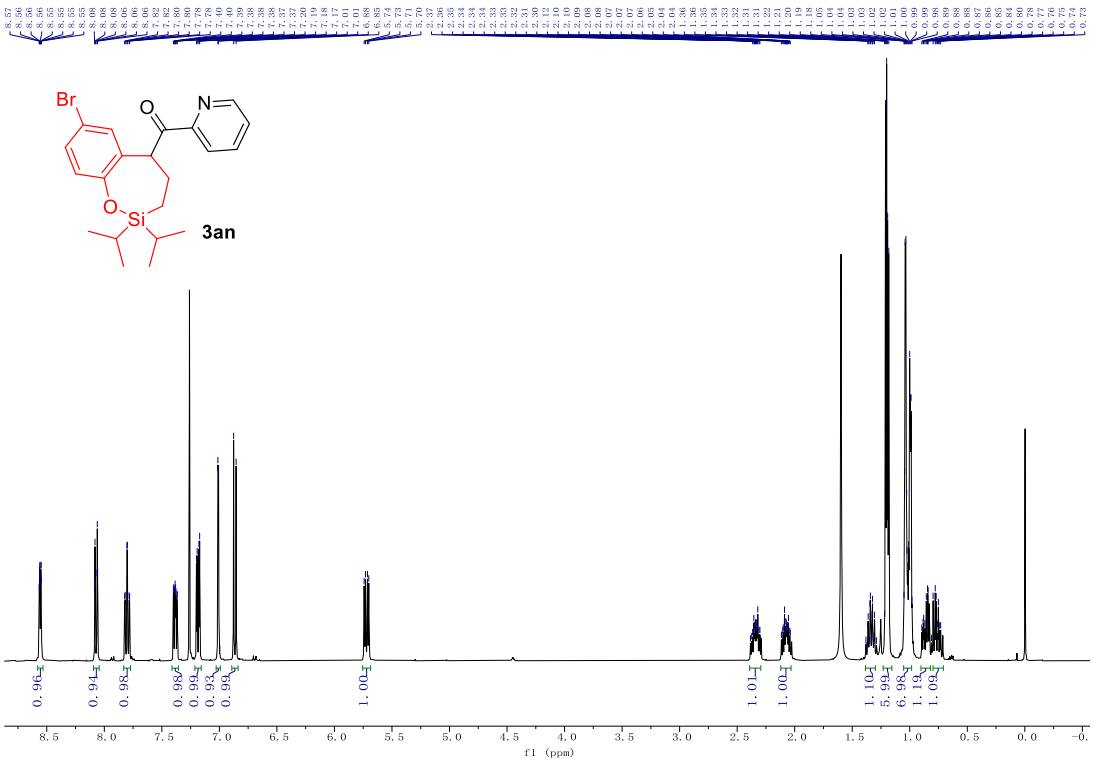


**Figure S94.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3an**

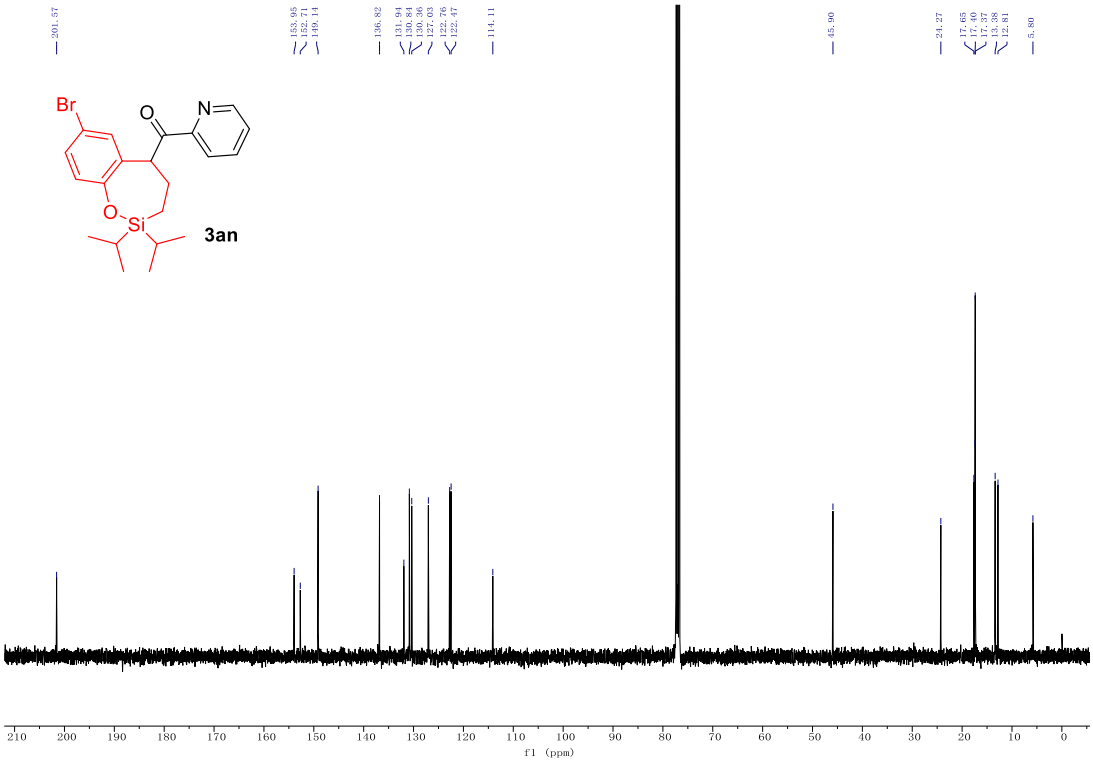


**Figure S95.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3an**

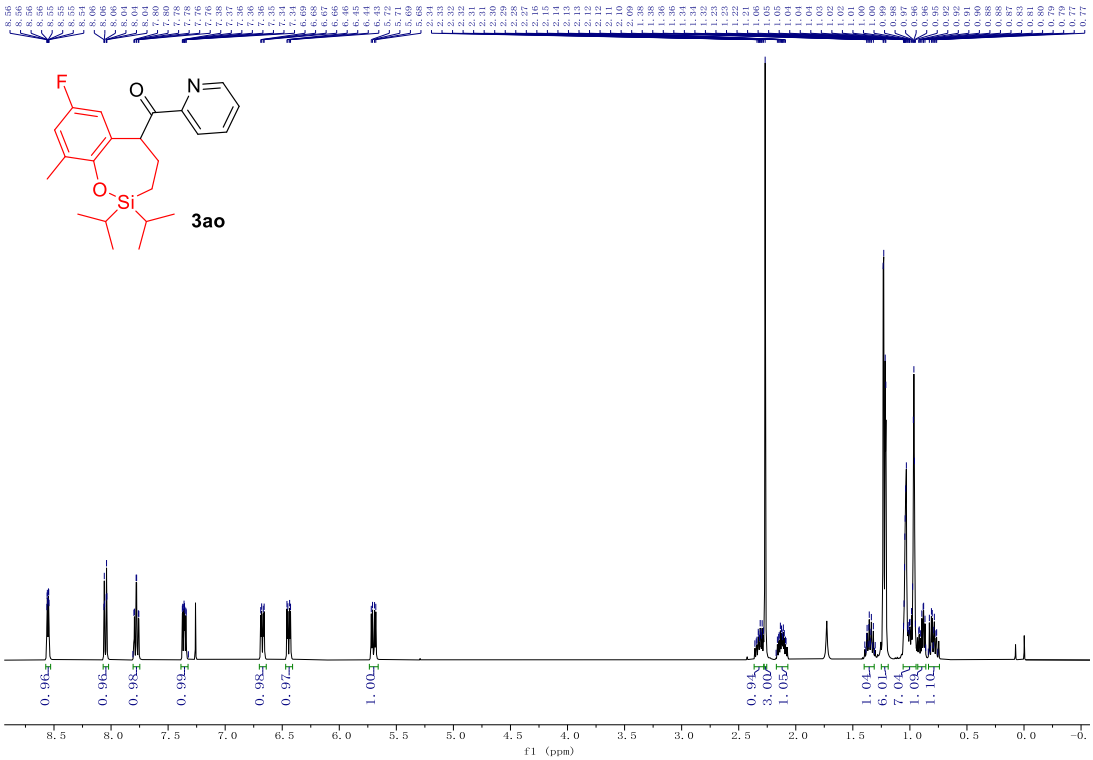


**Figure S96.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ao**

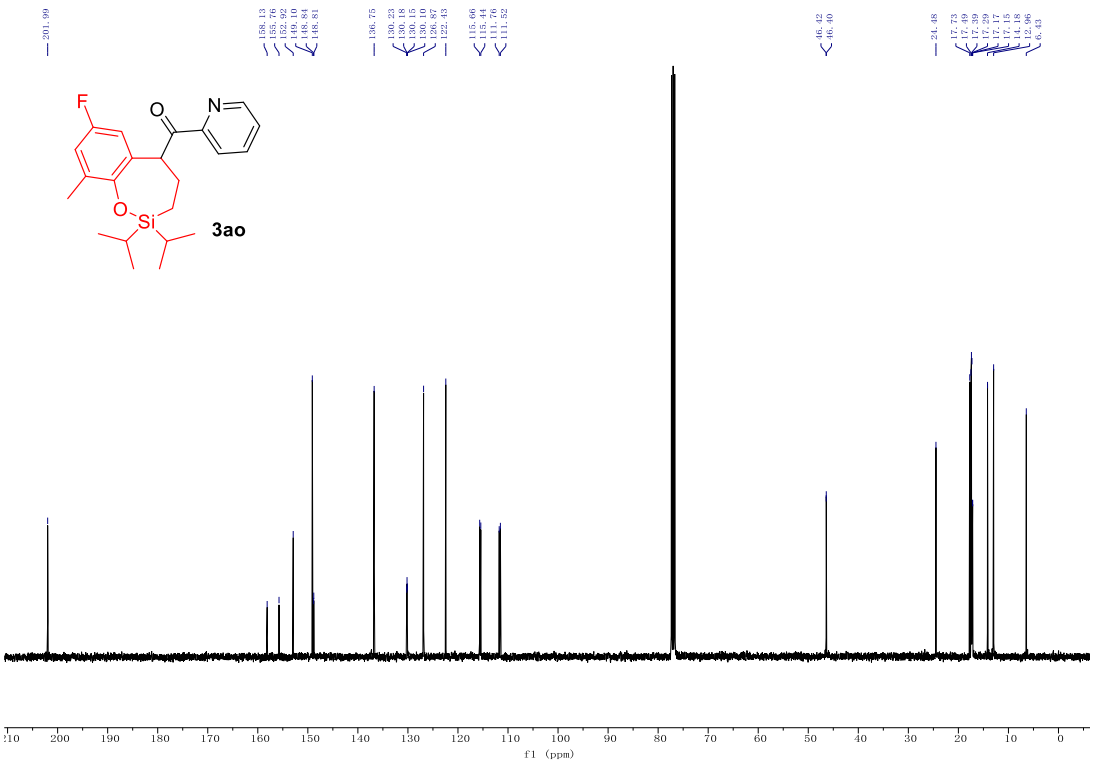


**Figure S97.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ao**

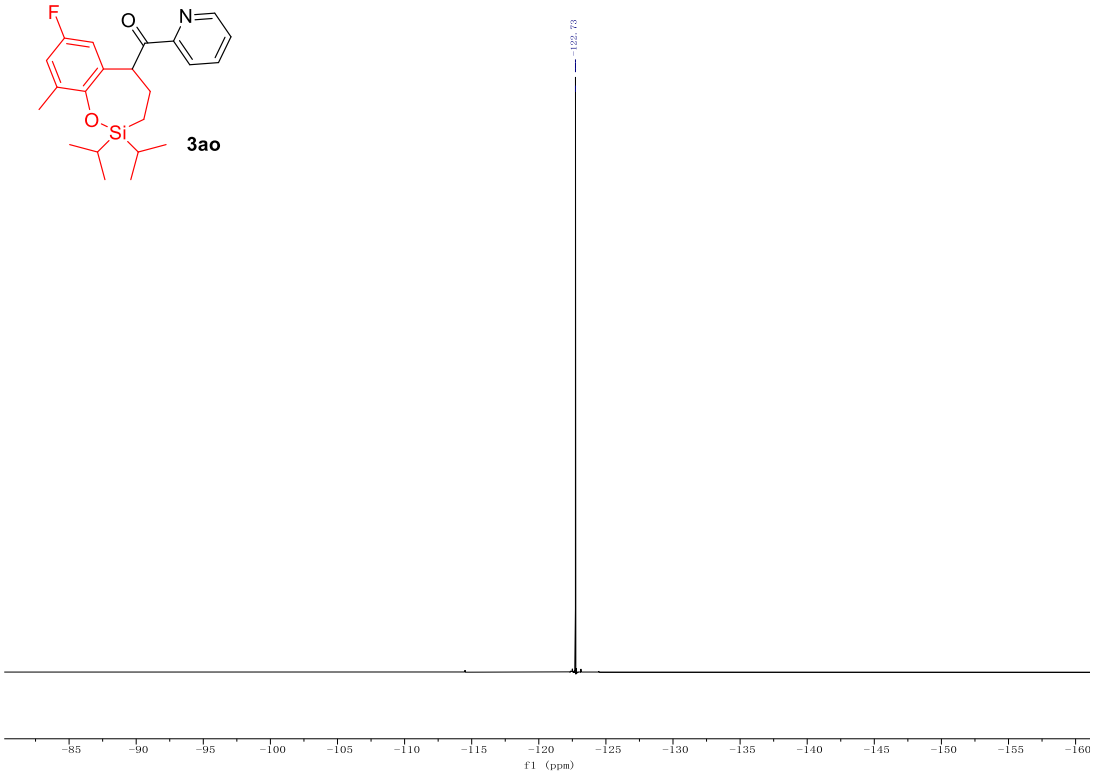


**Figure S98.** $^{19}$**F NMR** (377 MHz, $CDCl_3$) spectrum of **3ao**

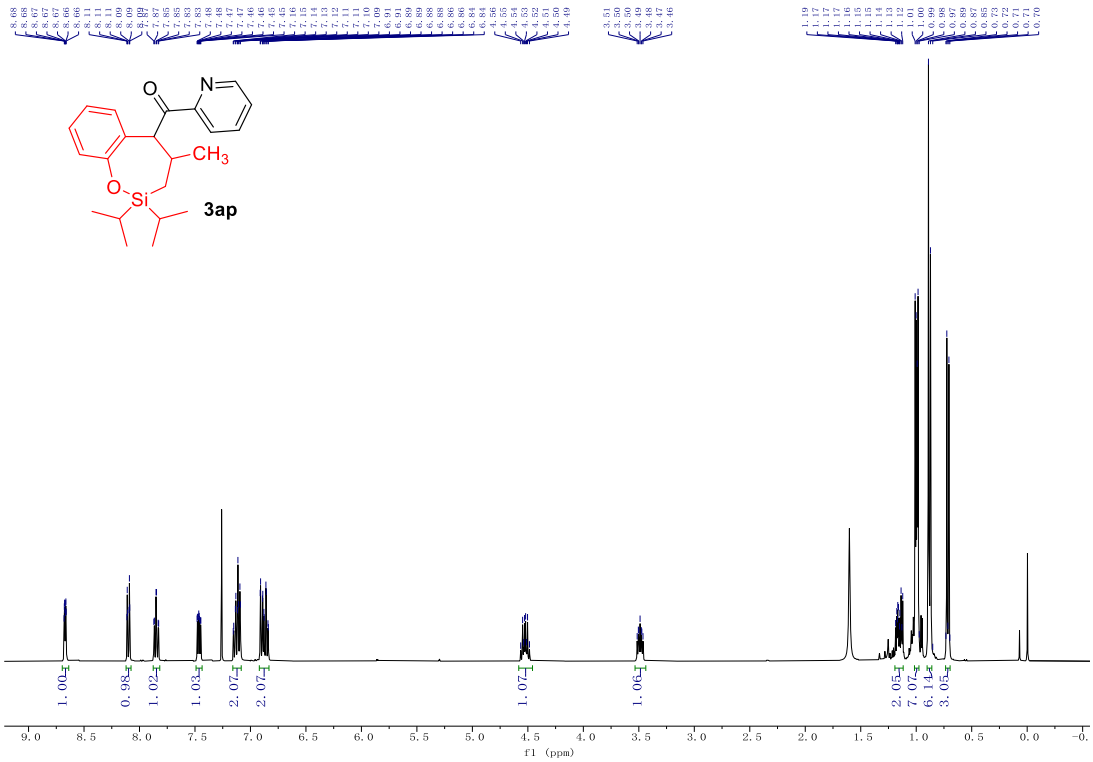


**Figure S99.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ap**

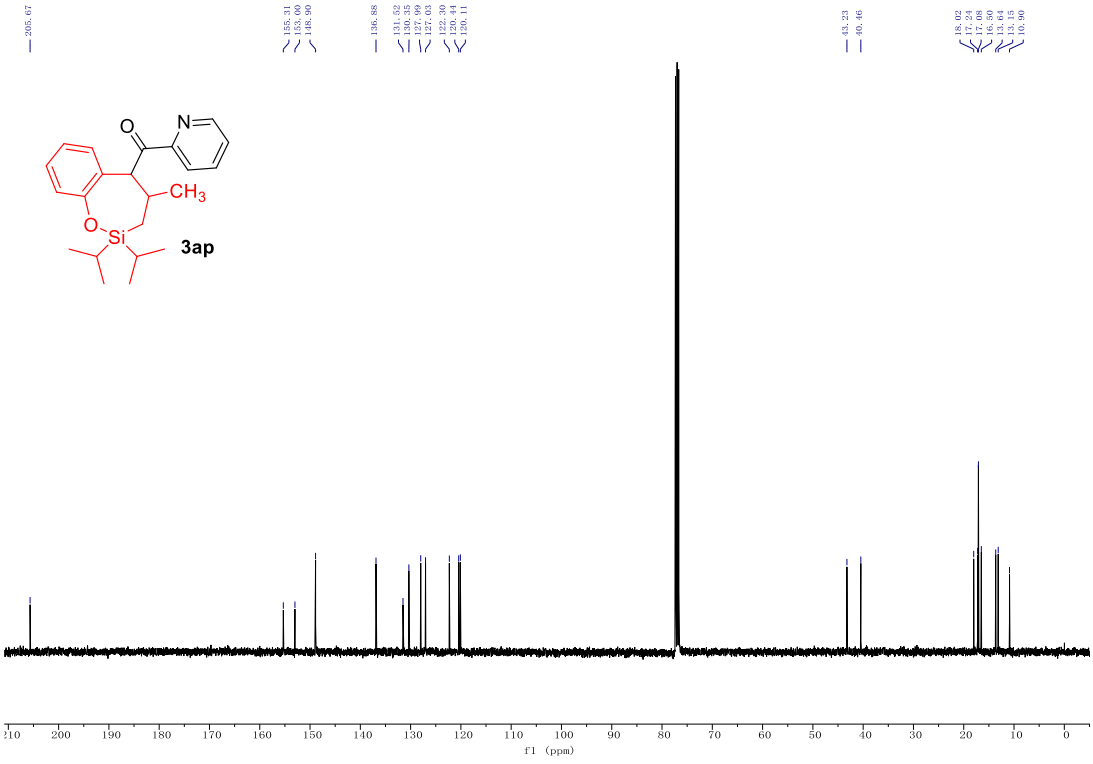


**Figure S100.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ap**

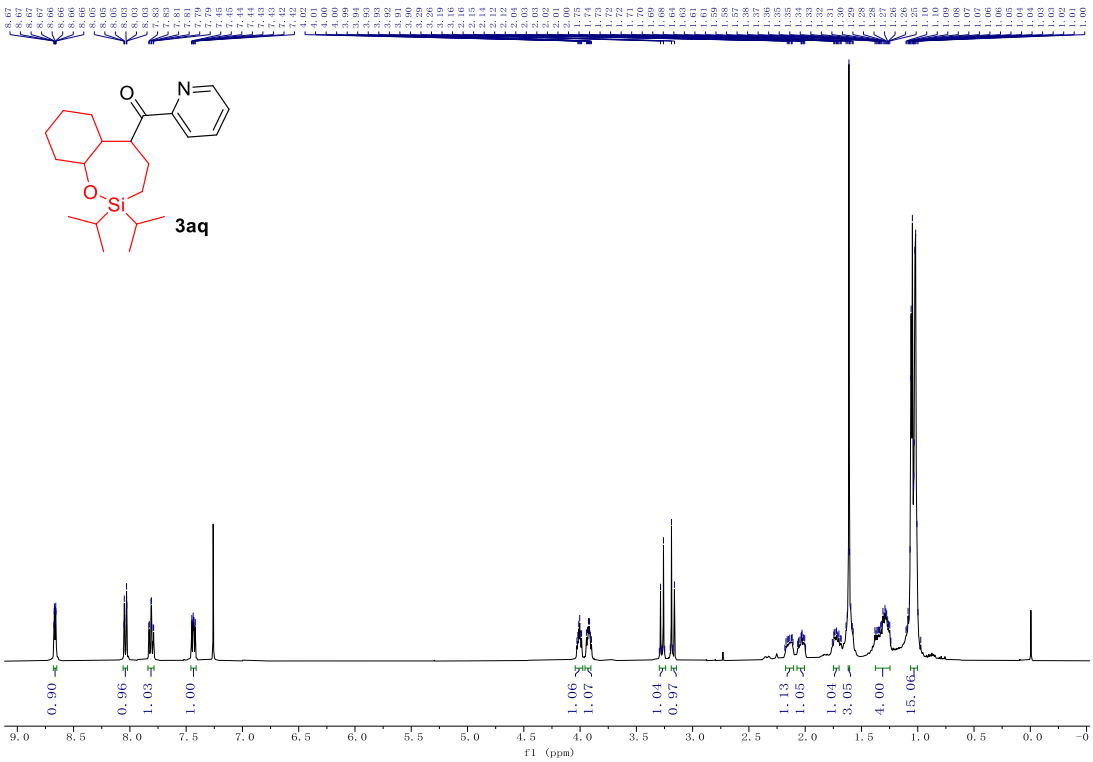


**Figure S101.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3aq**

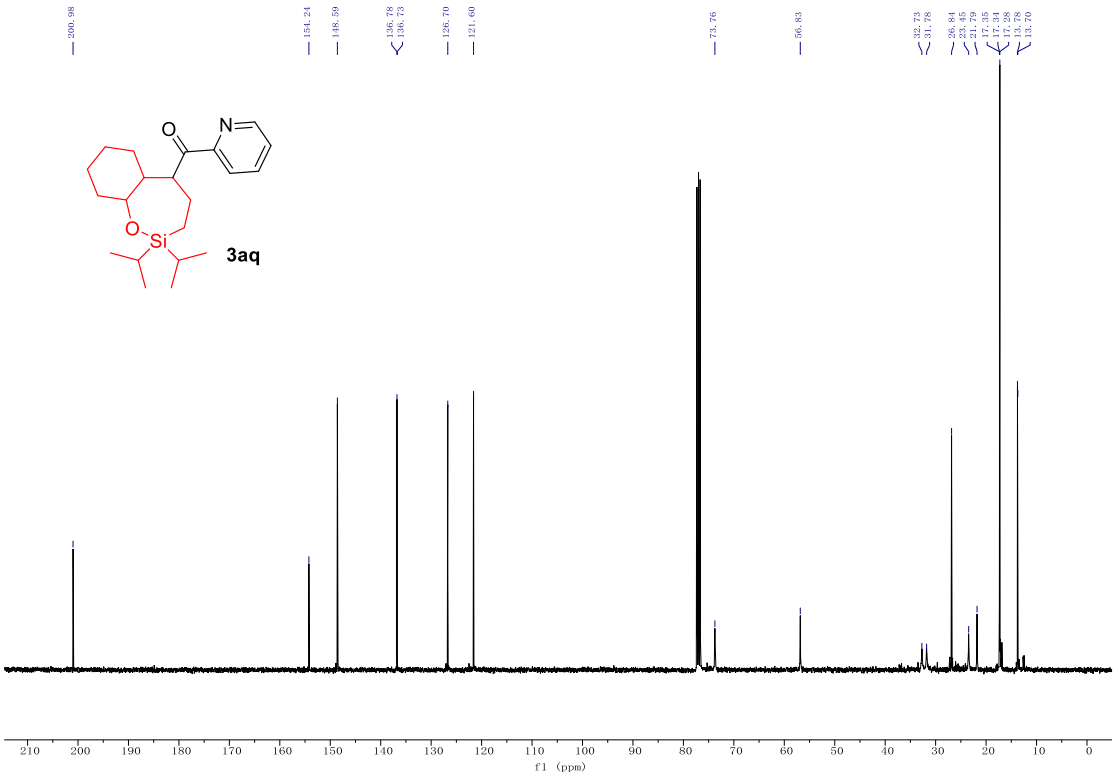


**Figure S102.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3aq**

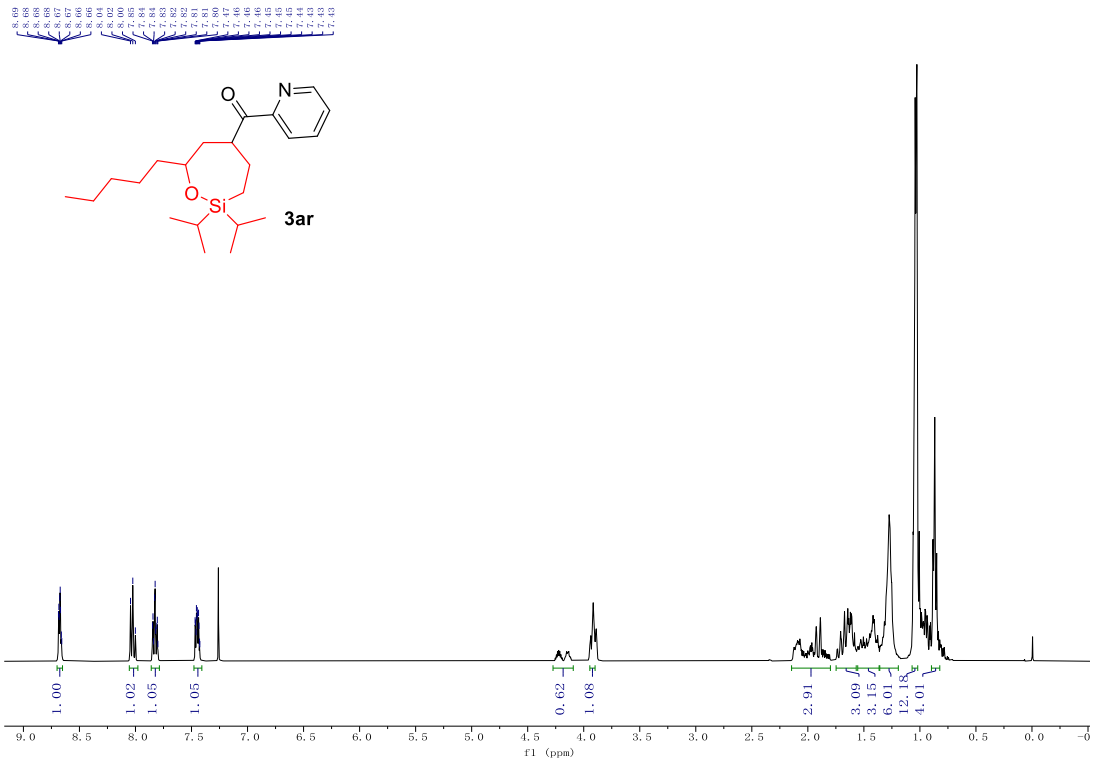


**Figure S103.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3ar**

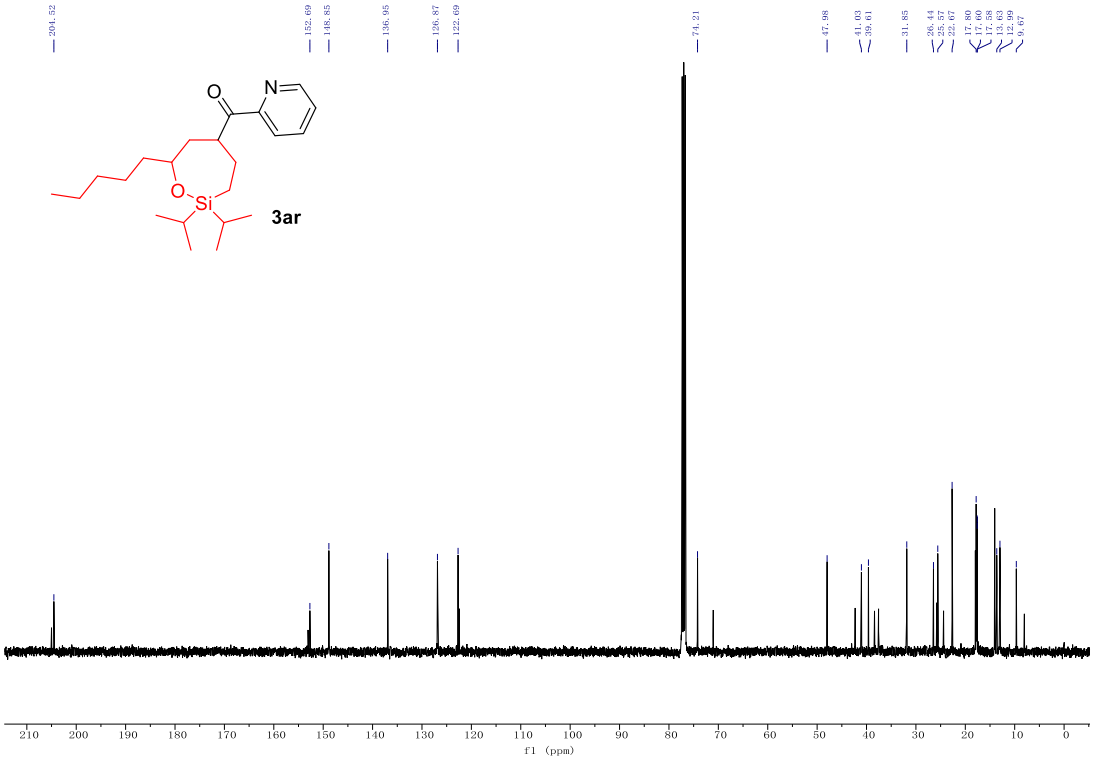


**Figure S104.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3ar**

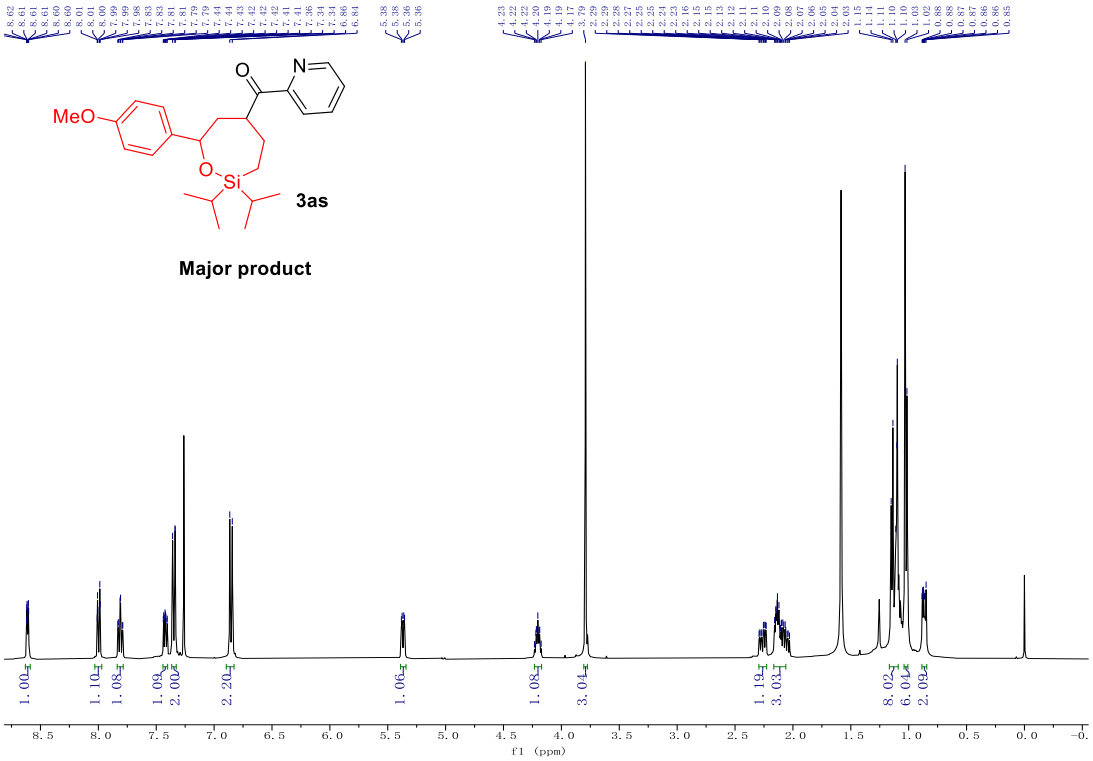


**Figure S105. $^{1}$H NMR** (400 MHz, $CDCl_3$) spectrum of **3as**

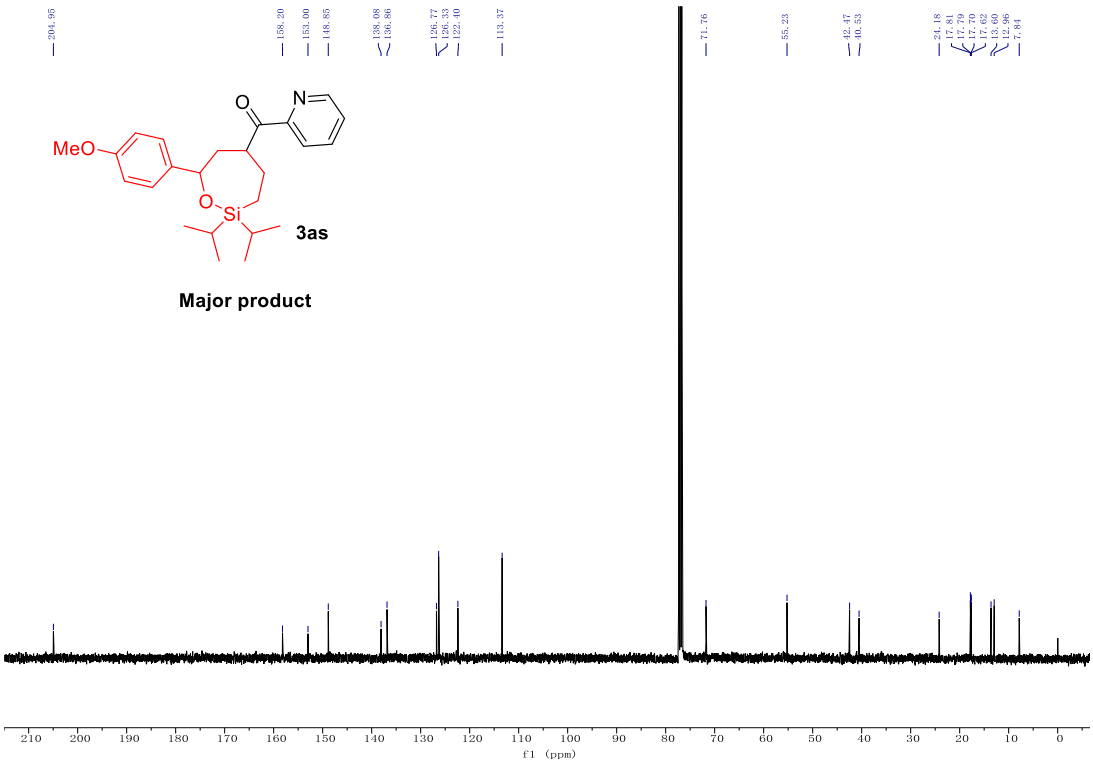


**Figure S106. $^{13}$C NMR** (101 MHz, $CDCl_3$) spectrum of **3as**

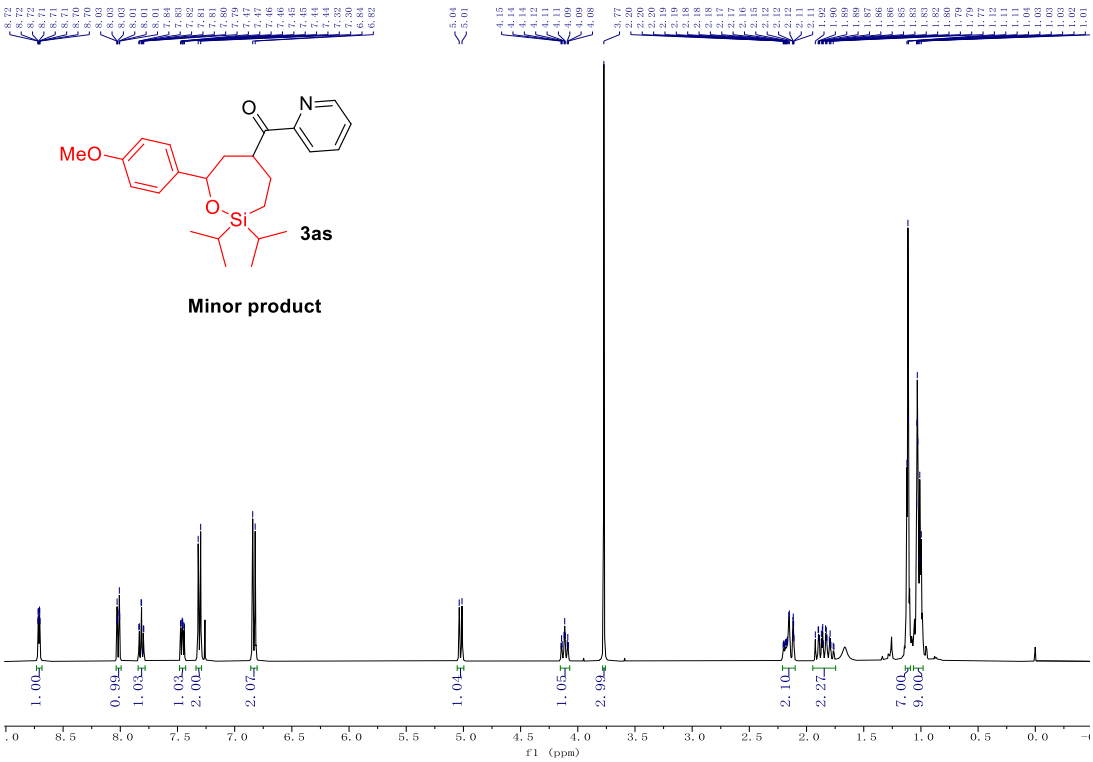


**Figure S107.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3as**

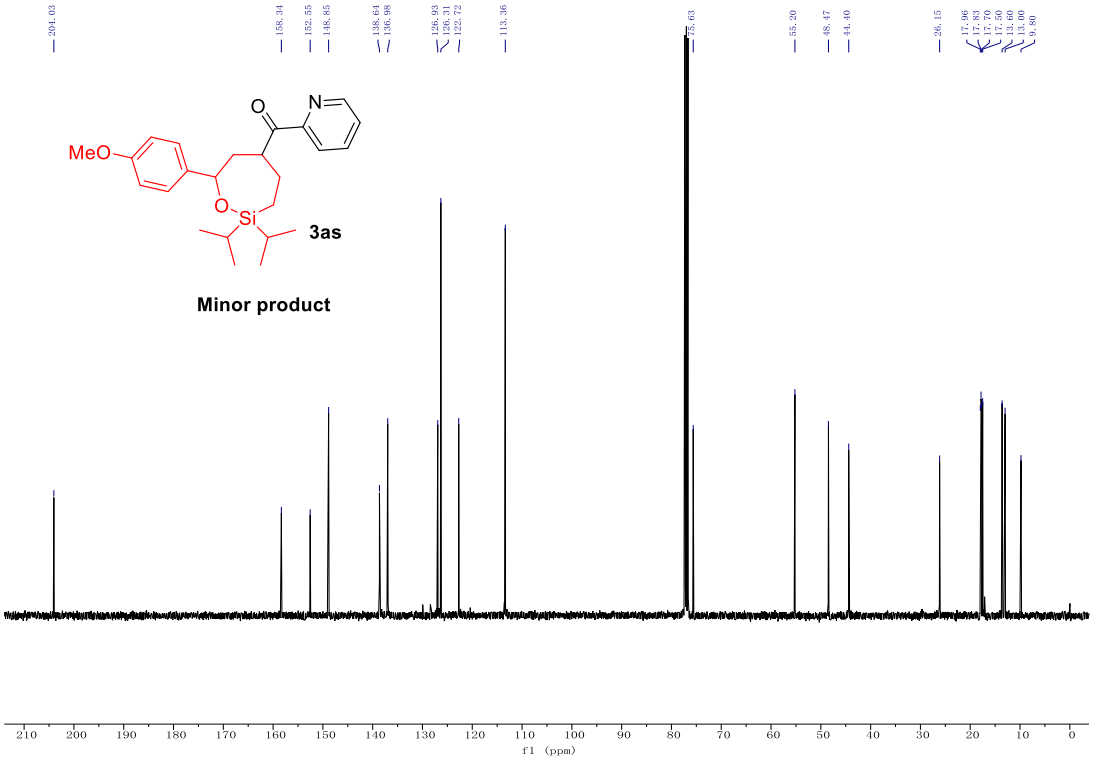


**Figure S108.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3as**

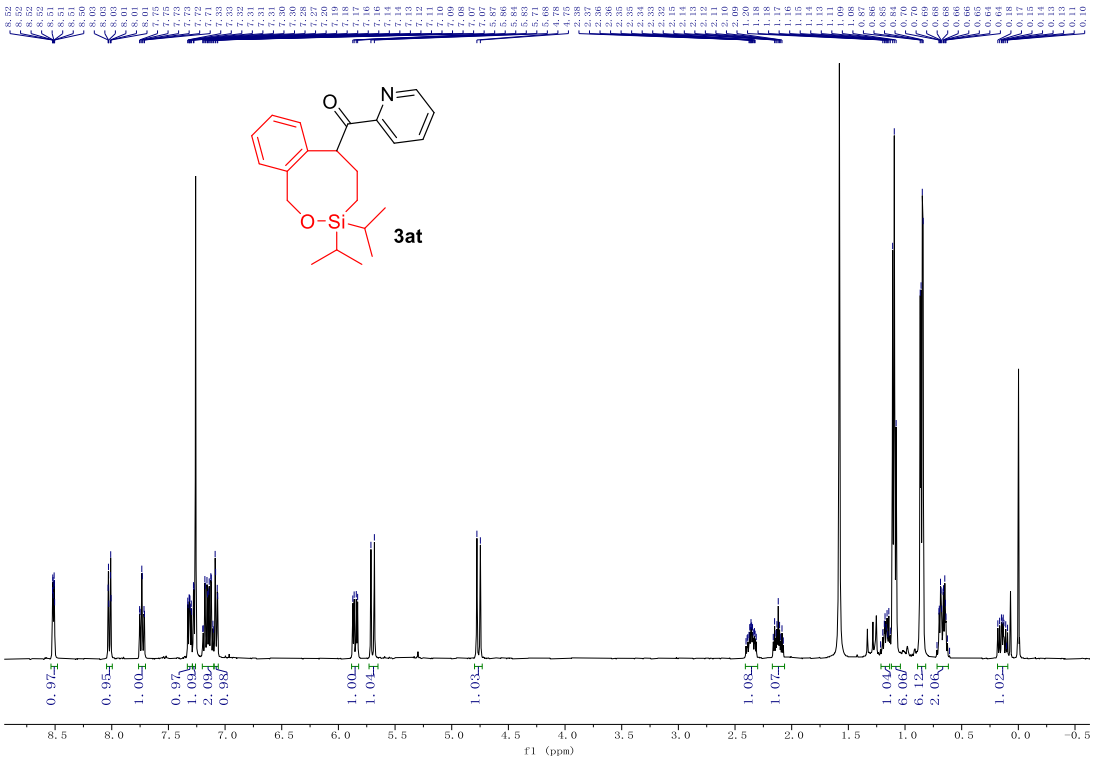


**Figure S109.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **3at**

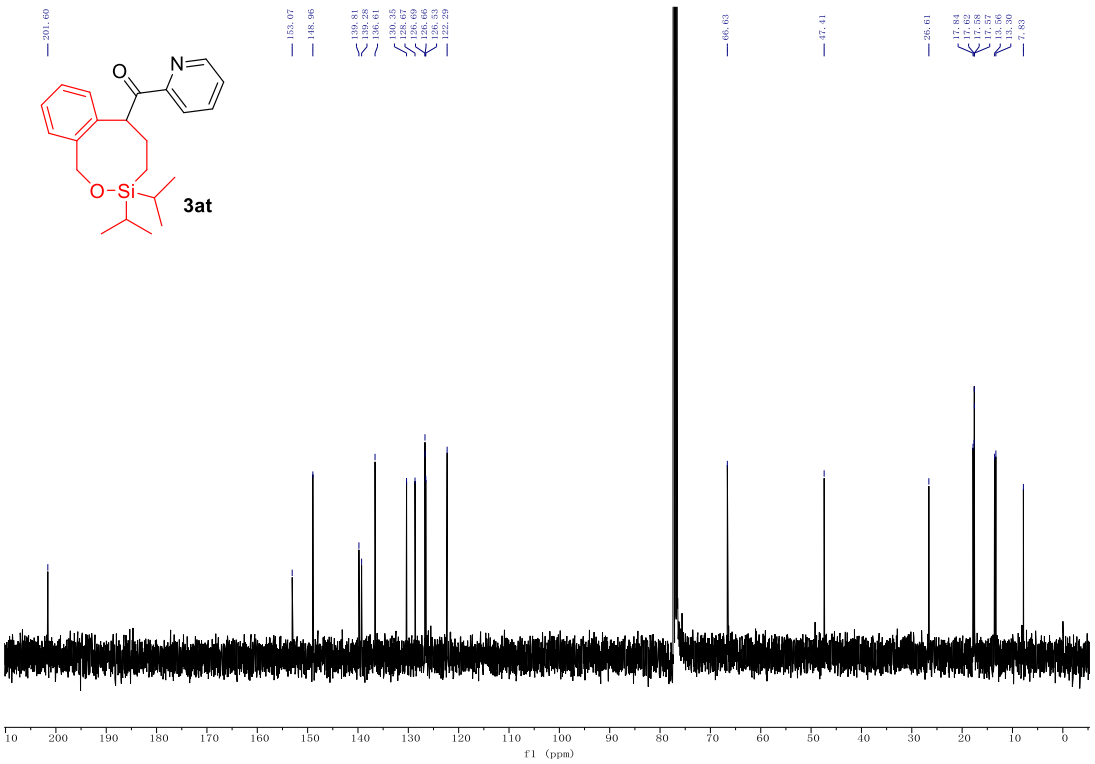


**Figure S110.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **3at**

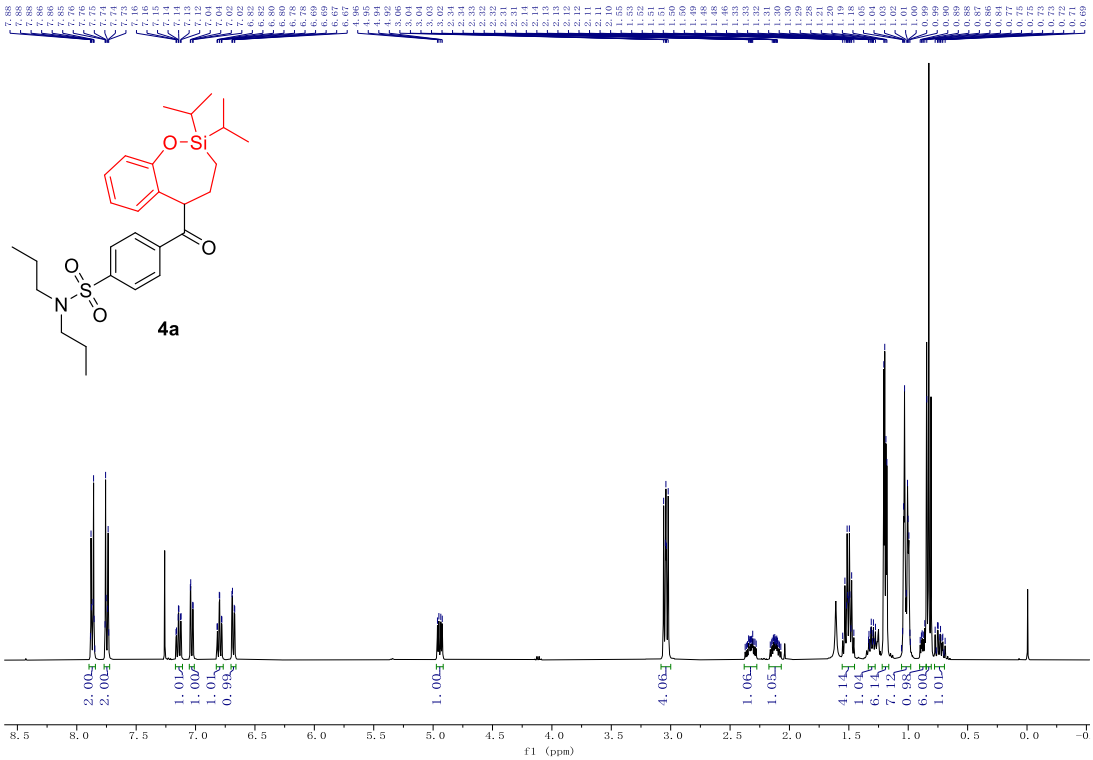


**Figure S111.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **4a**

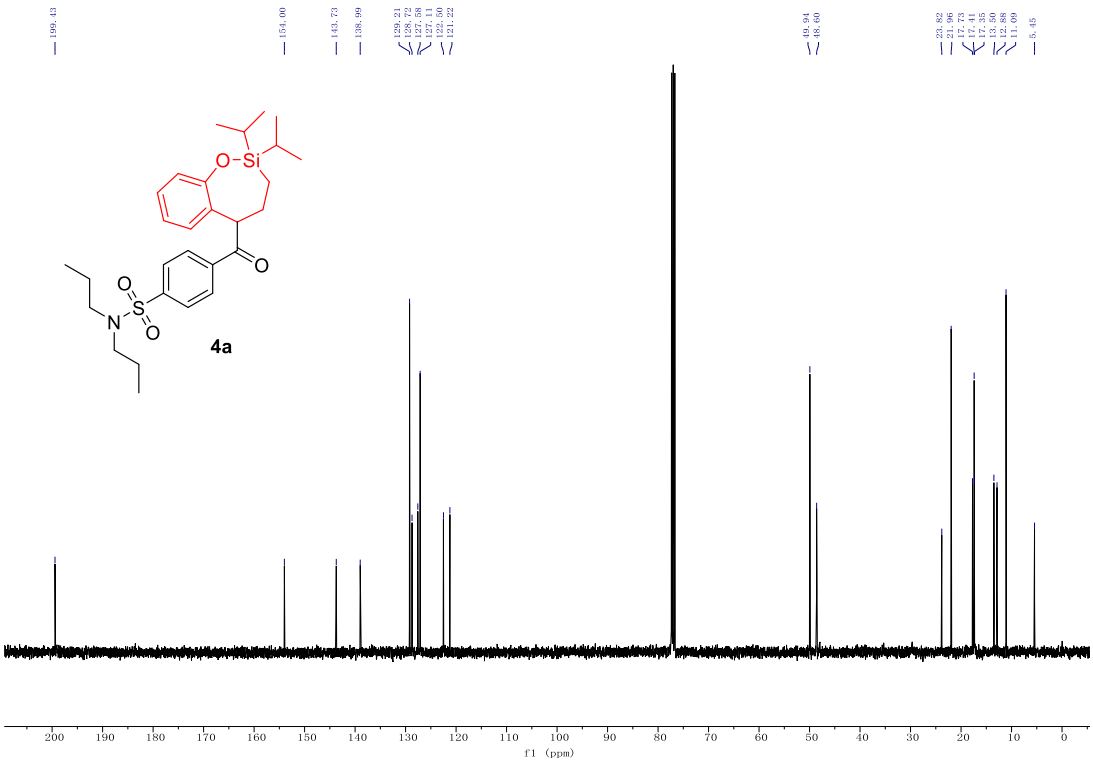


**Figure S112.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **4a**

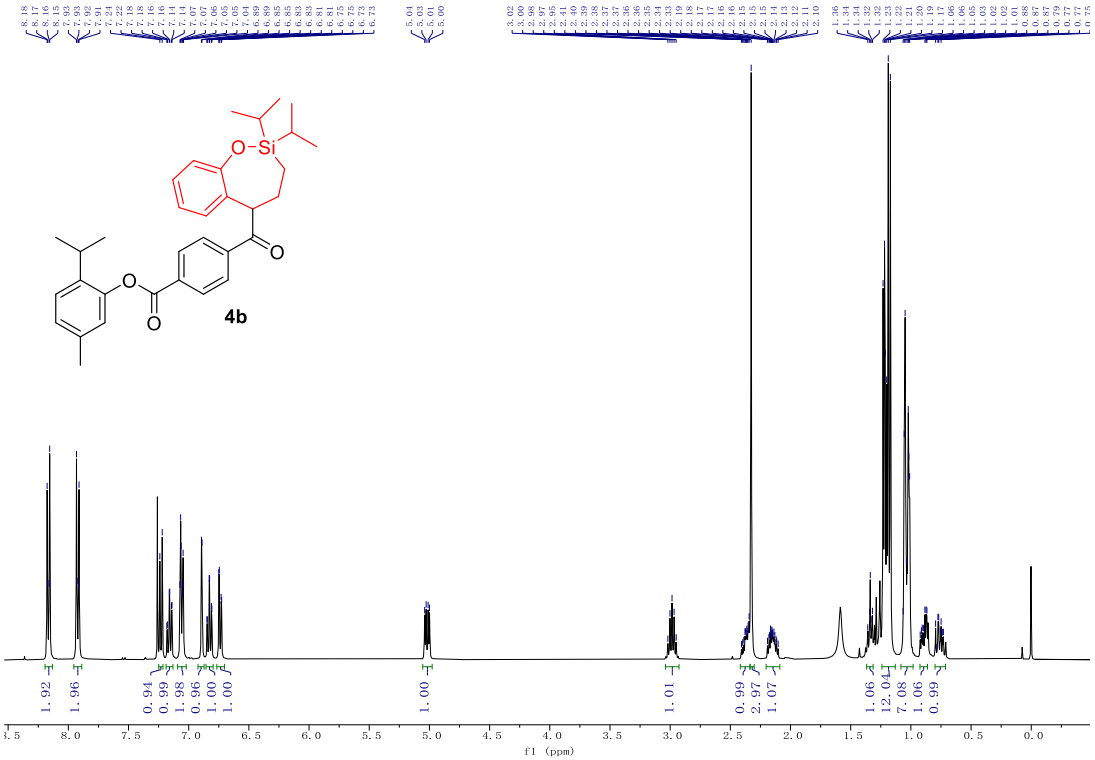


**Figure S113.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **4b**

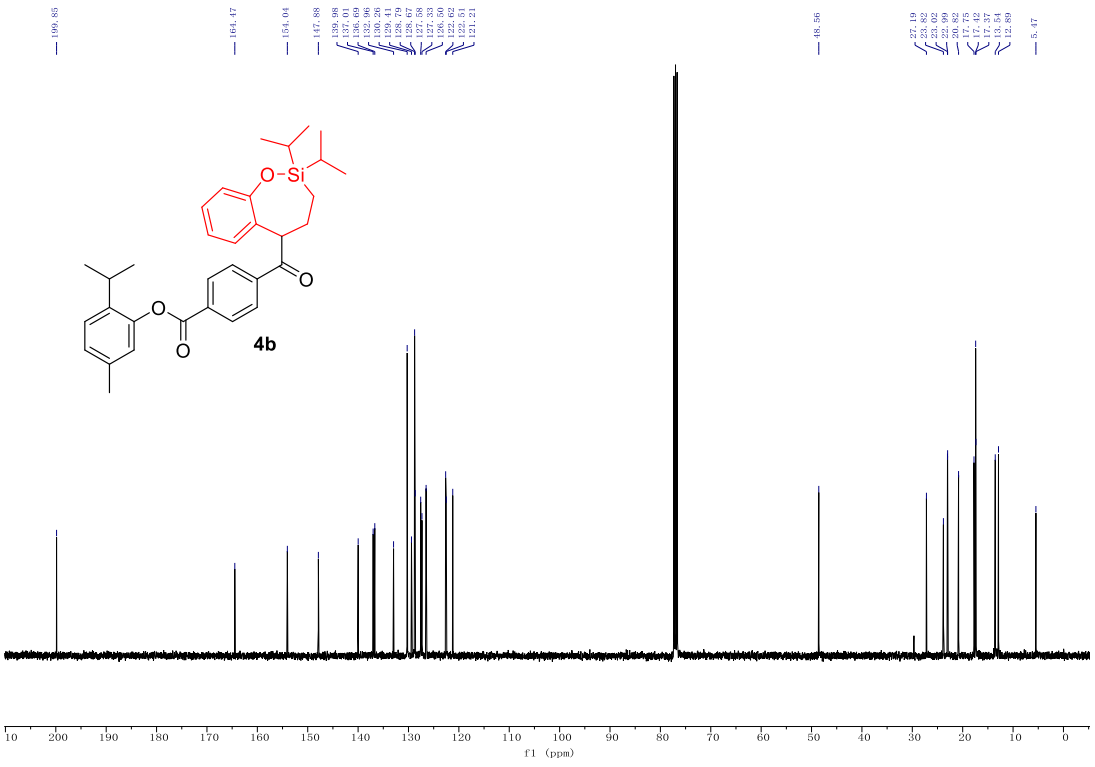


**Figure S114.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **4b**

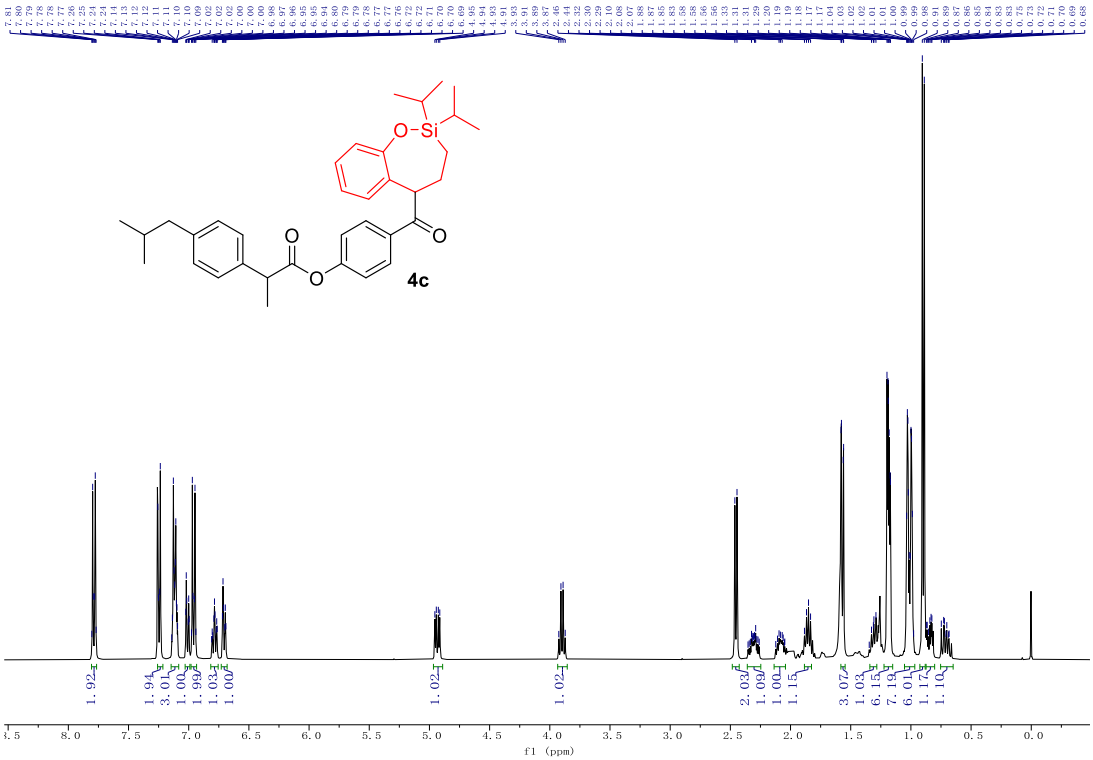


**Figure S115.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **4c**

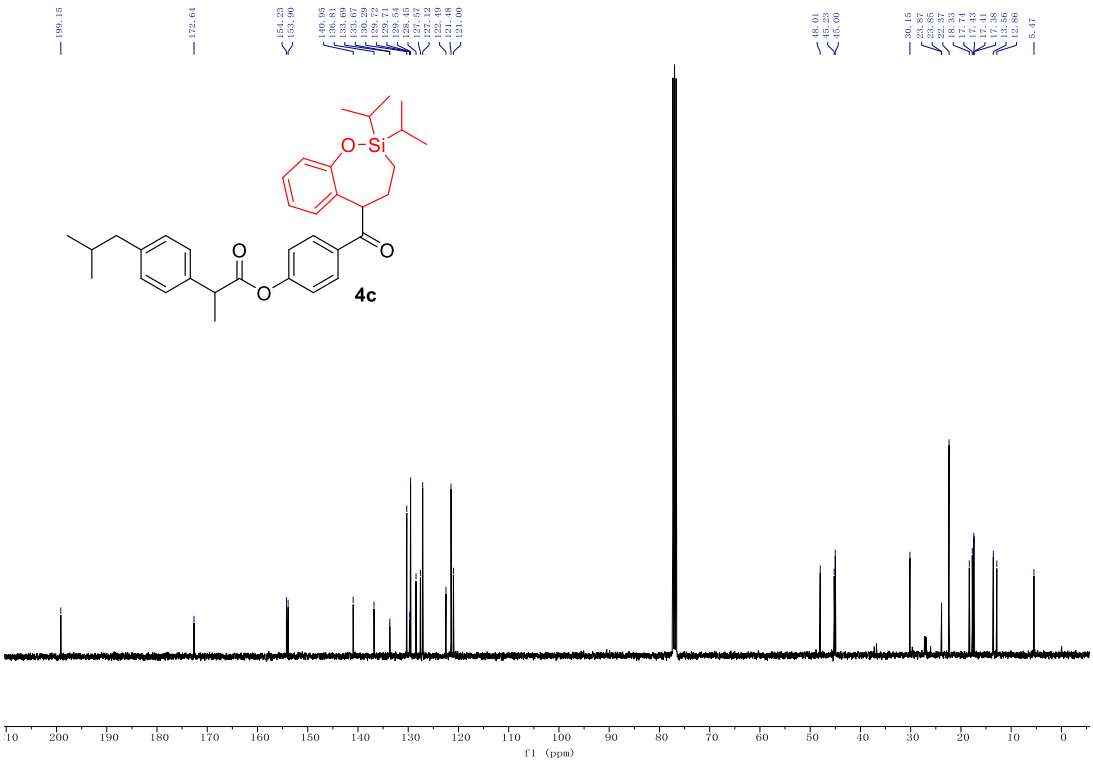


**Figure S116.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **4c**

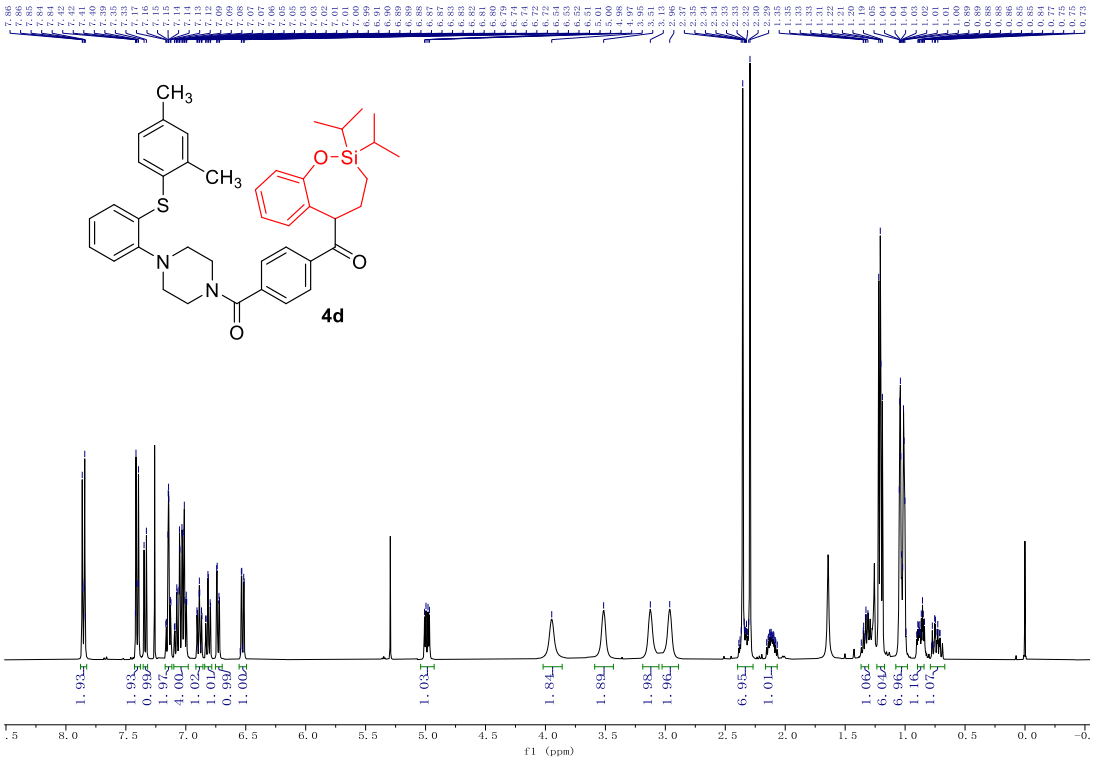


**Figure S117.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **4d**

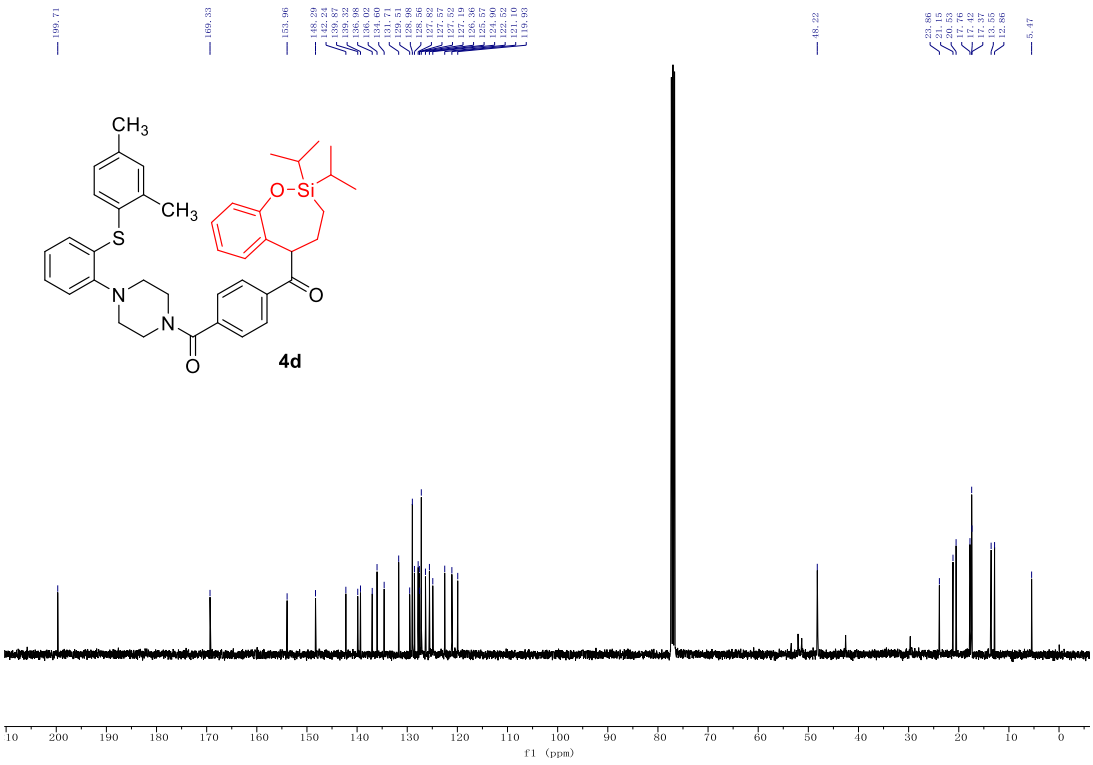


**Figure S118.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **4d**

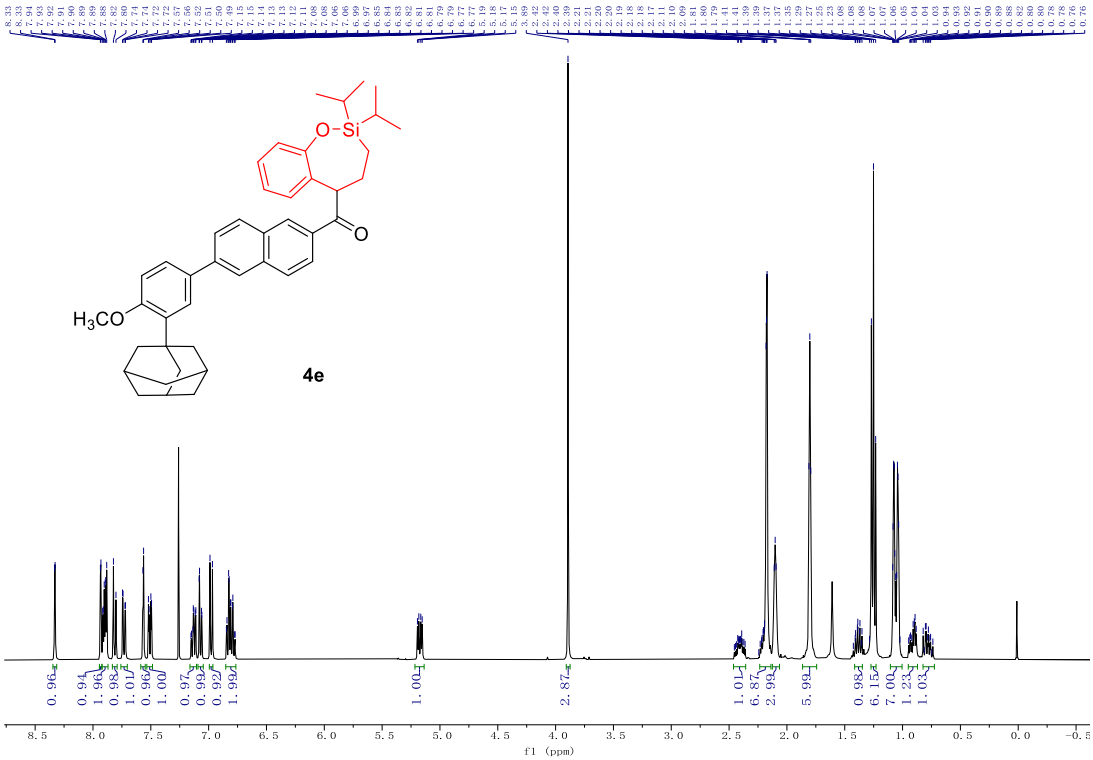


**Figure S119.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **4e**

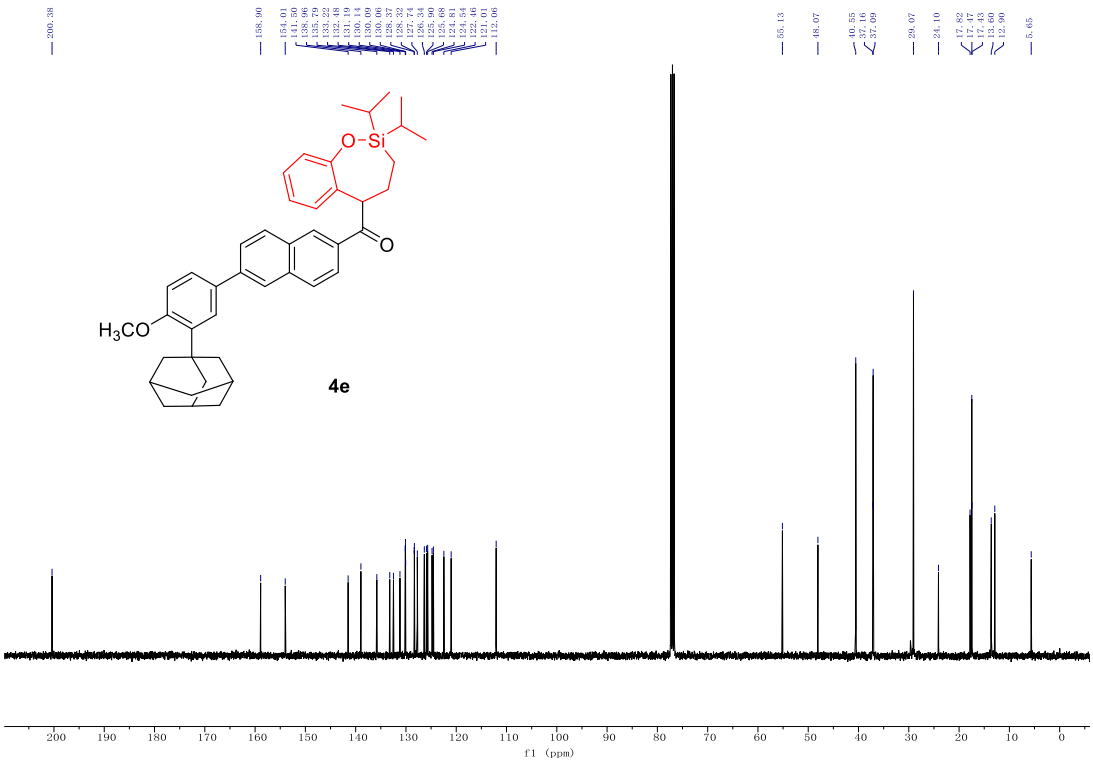


**Figure S120.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **4e**

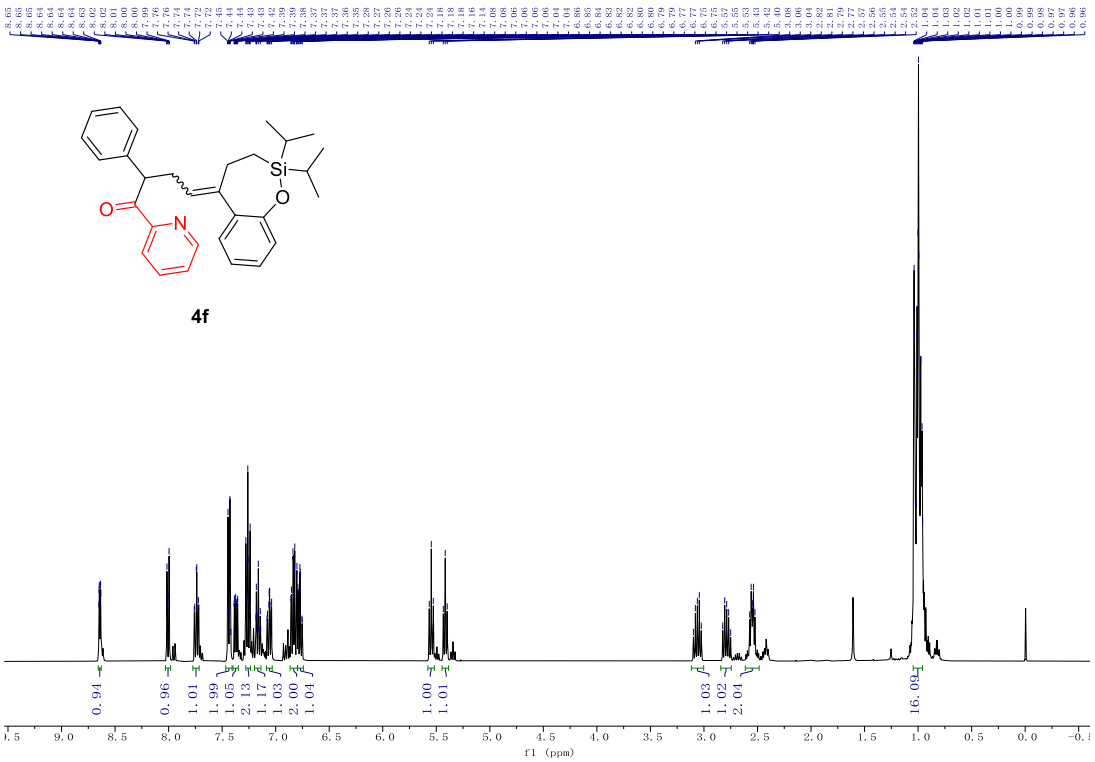


**Figure S121.** $^{1}$**H NMR** (400 MHz, $CDCl_3$) spectrum of **4f**

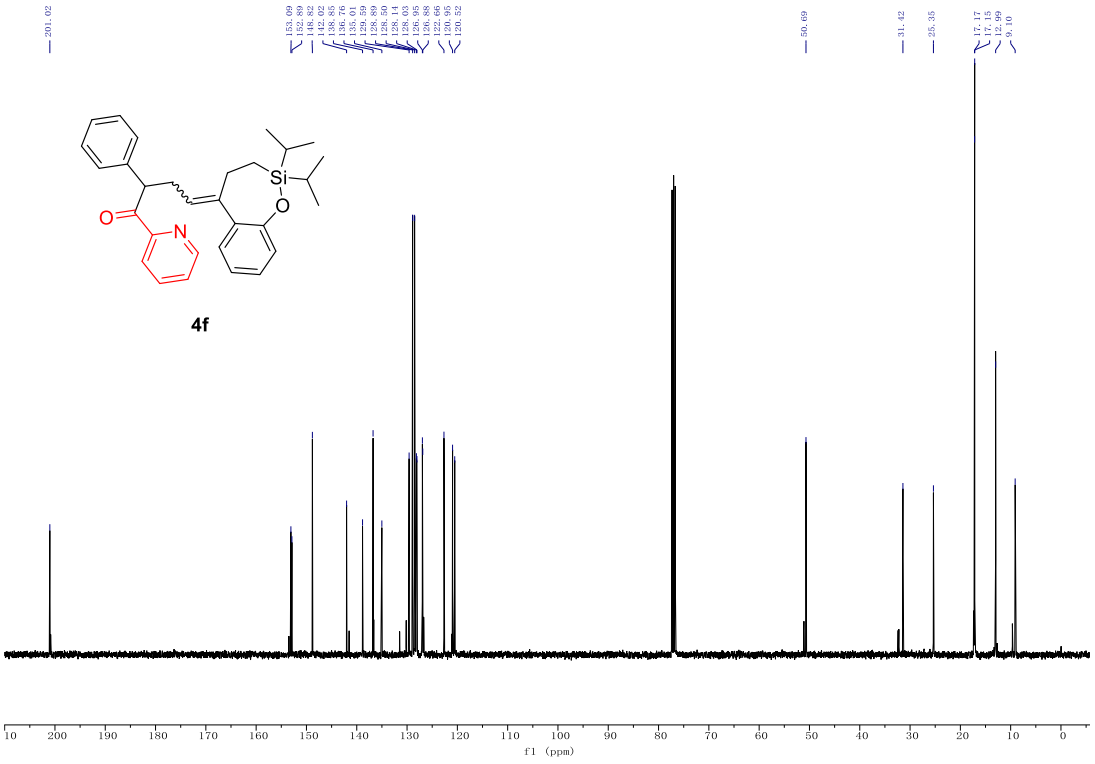


**Figure S122.** $^{13}$**C NMR** (101 MHz, $CDCl_3$) spectrum of **4f**