

## Supporting Information

### **Palladium-Catalysed Regioselective [4+2] Annulation to Access Silatetralin-1-amines**

Yan Sun,<sup>a‡</sup> Ruiqiang Lu,<sup>a‡</sup> Hang Zhou,<sup>a</sup> Liuzhou Gao,<sup>a,b,\*</sup> Yidong Wang<sup>a,b,\*</sup>

<sup>a</sup>School of Chemistry & Materials, Yangzhou University, Yangzhou, Jiangsu, 225002, P. R. China.

<sup>b</sup>Jiangsu Provincial Key Laboratory of Green & Functional Materials and Environmental Chemistry, Yangzhou, Jiangsu 225002, China

Corresponding authors: gaoliuzhou@yzu.edu.cn; wangyd021@yzu.edu.cn

<sup>‡</sup>These authors contributed equally.

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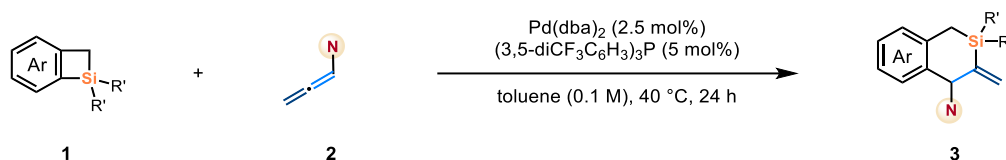
## General Information

**General Reagent Information:** Unless mentioned otherwise, all manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques. All the dry solvents were purchased from Adamas, Energy Chemical company, and used directly unless otherwise stated. Commercially available chemicals were purchased from Adamas, Bide Pharmatech, LeYan Pharmatech and Energy Chemical and used as received unless otherwise stated.

**General Analytical Information:** New compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, HRMS, and, where appropriate, other analytical techniques as indicated. Copies of the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were processed with MestReNova Software and can be found at the end of the Supporting Information.  $^1\text{H}$ , and  $^{13}\text{C}$  NMR spectra were recorded on Agilent 400 MHz or Bruker 400 MHz instruments. All  $^1\text{H}$  NMR data are reported in  $\delta$  units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm ( $\text{CDCl}_3$ ). All  $^{13}\text{C}$  NMR spectra are  $^1\text{H}$  decoupled and reported in ppm relative to the solvent signal at 77.06 ppm ( $\text{CDCl}_3$ ). High-resolution mass spectra (HRMS) were recorded on the Thermo Fisher Q Exactive system equipped with an ESI and a TOF detector mass spectrometer. X-ray crystallographic studies were carried out on a Bruker D8 QUEST diffractometer. Unless otherwise stated, Pyrazine was used as the internal standard for yields determined by  $^1\text{H}$  NMR. Thin-layer chromatography (TLC) was performed on Silicycle 250  $\mu\text{m}$  (analytical) or 1000  $\mu\text{m}$  (preparative) silica gel plates. Compounds were purified by flash column chromatography using silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China). Compounds were visualized by irradiation with UV light, or by staining with iodine/silica gel, potassium permanganate, or phosphomolybdic acid (PMA). Yields refer to isolated compounds, unless otherwise indicated.

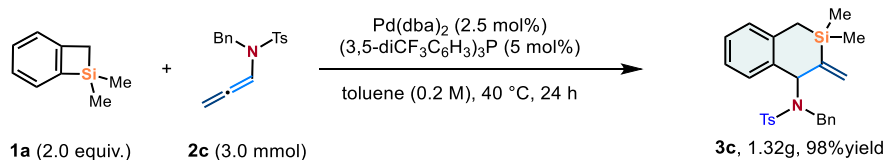


## General Procedure for Palladium-Catalysed Synthesis of Silatetralin-1-amines via Regioselective [4+2] Annulation



**General Procedure A:** In a nitrogen-filled glove-box, an oven-dried 15 mL sealed tube equipped with a magnetic stir bar was charged with Pd(dba)<sub>2</sub> (2.5 mol%), P(3,5-diCF<sub>3</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (5 mol%) and toluene (1.0 mL). The mixture was stirred at r.t. for 10 minutes. Then *N*-allenamides (**2**, 0.2 mmol, 1.0 equiv), benzosilacyclobutenes (**1**, 0.4 mmol, 2.0 equiv) and toluene (1.0 mL) were added to the above solution in rapid succession. The reaction tube was sealed, removed from the glovebox and stirred at 40 °C for 24 h. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel to provide the desired product **3**.

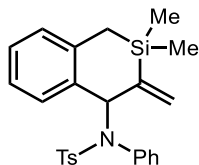
### Gram-Scale Experiments



**Synthetic Procedure:** In a nitrogen-filled glove-box, an oven-dried 50 mL sealed tube equipped with a magnetic stir bar was charged with Pd(dba)<sub>2</sub> (42.5 mg, 2.5 mol%), P(3,5-diCF<sub>3</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (100.5 mg, 5 mol%) and toluene (5 mL). The mixture was stirred at r.t. for 10 minutes. Then *N*-allenamide (**2c**, 3.0 mmol, 1.0 equiv), benzosilacyclobutenes (**1a**, 6.0 mmol, 2.0 equiv) and toluene (10 mL) were added to the above solution in rapid succession. The reaction tube was sealed, removed from the glovebox and stirred at 40 °C for 24 h. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography on silica gel to provide the desired product **3c** (1.32 g, 98% yield).

## Characterization data for products:

### 1. *N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methyl-*N*-phenylbenzenesulfonamide (**3a**)



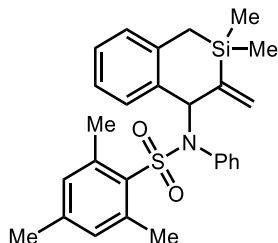
The title compound **3a** was isolated as pale-yellow solid (78.1 mg, 90% yield) following the above general procedure A. m.p. = 96-97 °C.  $R_f$  = 0.4 (Petroleum Ether:EtOAc = 30:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.58 – 7.48 (m, 2H), 7.33 – 7.27 (m, 1H), 7.23 – 7.04 (m, 7H), 6.85 – 6.76 (m, 1H), 6.76 – 6.63 (m, 2H), 6.27 (s, 1H), 6.01 (s, 1H), 5.79 – 5.65 (m, 1H), 2.39 (s, 3H), 1.45 (d,  $J$  = 14.4 Hz, 1H), 0.81 (d,  $J$  = 14.8 Hz, 1H), 0.08 (s, 3H), -0.24 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  148.6, 142.9, 139.1, 137.5, 137.3, 136.4, 132.8, 131.6, 131.4, 131.1, 129.1, 128.28, 128.26, 128.2, 127.9, 125.5, 68.9, 21.5, 19.4, -2.1, -2.3.

**HRMS** (ESI) calcd for C<sub>25</sub>H<sub>27</sub>NNaO<sub>2</sub>SSi [M+Na]<sup>+</sup>: 456.1424, found: 456.1423.

### 2. *N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-2,4,6-trimethyl-*N*-phenylbenzenesulfonamide (**3b**)



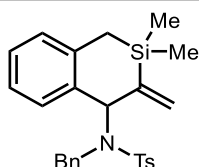
The title compound **3b** was isolated as white solid (91.2 mg, 99% yield) following the above general procedure A. m.p. = 81-82 °C.  $R_f$  = 0.3 (Petroleum Ether:EtOAc = 20:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.57 – 7.45 (m, 1H), 7.23 – 7.08 (m, 3H), 7.09 – 6.99 (m, 2H), 6.91 – 6.77 (m, 3H), 6.73 (s, 2H), 6.54 – 6.47 (m, 1H), 6.27 (s, 1H), 5.91 – 5.81 (m, 1H), 2.44 (s, 6H), 2.18 (s, 3H), 1.36 (d,  $J$  = 15.2 Hz, 1H), 0.46 (d,  $J$  = 15.2 Hz, 1H), 0.05 (s, 3H), -0.24 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  148.1, 142.3, 140.4, 139.4, 137.1, 136.3, 133.4, 133.0, 132.8, 132.3, 131.5, 131.3, 128.5, 128.31, 128.29, 125.6, 67.2, 23.0, 20.9, 19.1, -1.6, -2.2.

**HRMS** (ESI) calcd for C<sub>27</sub>H<sub>31</sub>NNaO<sub>2</sub>SSi [M+Na]<sup>+</sup>: 484.1737, found: 484.1736.

### 3. *N*-benzyl-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3c**)



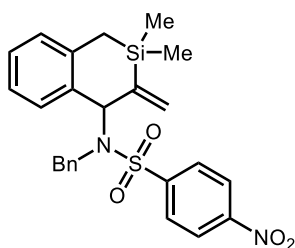
The title compound **3c** was isolated as colorless gum (87.5 mg, 98% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 20:1).

**$^1\text{H NMR}$**  (400 MHz, Chloroform-*d*)  $\delta$  7.53 – 7.36 (m, 2H), 7.22 – 7.11 (m, 5H), 7.11 – 6.89 (m, 5H), 6.79 – 6.62 (m, 1H), 5.76 – 5.66 (m, 1H), 5.48 – 5.39 (m, 1H), 5.32 (s, 1H), 4.65 (d,  $J = 16.0$  Hz, 1H), 4.15 (d,  $J = 16.0$  Hz, 1H), 2.39 (s, 3H), 1.85 (d,  $J = 14.8$  Hz, 1H), 1.67 (d,  $J = 15.2$  Hz, 1H), 0.18 (s, 3H), -0.19 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz, Chloroform-*d*)  $\delta$  147.3, 142.7, 139.0, 137.9, 137.2, 136.0, 131.2, 130.9, 129.3, 129.1, 128.2, 128.1, 127.8, 127.4, 126.8, 125.2, 69.4, 51.3, 21.5, 20.7, -2.4, -2.6.

**HRMS** (ESI) calcd for  $\text{C}_{26}\text{H}_{30}\text{NO}_2\text{SSi}$   $[\text{M}+\text{H}]^+$ : 448.1761, found: 448.1761.

#### 4. *N*-benzyl-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-nitrobenzenesulfonamide (**3d**)



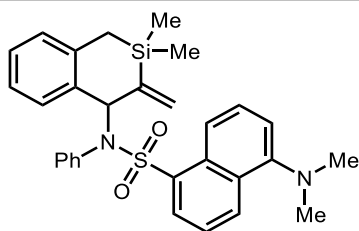
The title compound **3d** was isolated as colorless gum (90.3 mg, 94% yield) following the above general procedure A.  $R_f = 0.3$  (Petroleum Ether:EtOAc = 20:1).

**$^1\text{H NMR}$**  (400 MHz, Chloroform-*d*)  $\delta$  8.12 – 7.95 (m, 2H), 7.51 – 7.43 (m, 2H), 7.25 – 7.14 (m, 6H), 7.11 – 7.01 (m, 2H), 6.70 – 6.60 (m, 1H), 5.64 – 5.56 (m, 1H), 5.46 – 5.42 (m, 1H), 5.41 (s, 1H), 4.82 (d,  $J = 16.1$  Hz, 1H), 4.32 (d,  $J = 16.1$  Hz, 1H), 1.81 (d,  $J = 14.6$  Hz, 1H), 1.71 (d,  $J = 14.7$  Hz, 1H), 0.27 (s, 3H), -0.20 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz, Chloroform-*d*)  $\delta$  149.1, 146.8, 145.8, 138.8, 136.6, 135.4, 131.7, 130.9, 130.7, 128.8, 128.2, 128.0, 127.9, 127.2, 125.5, 123.3, 69.7, 51.8, 20.8, -2.4, -2.6.

**HRMS** (ESI) calcd for  $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_4\text{SSi}$   $[\text{M}+\text{H}]^+$ : 479.1455, found: 479.1449.

#### 5. *N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-5-(dimethylamino)-*N*-phenylphthalene-1-sulfonamide (**3e**)



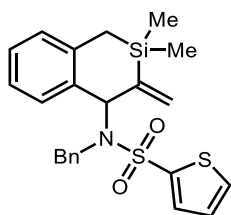
The title compound **3e** was isolated as yellow solid (101.0 mg, 98% yield) following the above general procedure A. m.p. = 149-150 °C.  $R_f$  = 0.4 (Petroleum Ether:EtOAc = 30:1).

**$^1\text{H NMR}$**  (400 MHz, Chloroform- $d$ )  $\delta$  8.55 – 8.28 (m, 2H), 8.06 – 7.87 (m, 1H), 7.48 – 7.41 (m, 1H), 7.37 – 7.25 (m, 2H), 7.21 – 7.11 (m, 2H), 7.10 – 7.00 (m, 4H), 6.88 – 6.75 (m, 2H), 6.75 – 6.64 (m, 1H), 6.26 – 6.18 (m, 1H), 6.08 (s, 1H), 5.70 – 5.60 (m, 1H), 2.86 (s, 6H), 1.29 (d,  $J$  = 15.2 Hz, 1H), 0.64 (d,  $J$  = 15.2 Hz, 1H), 0.01 (s, 3H), -0.30 (s, 3H).

**HRMS** (ESI) calcd for  $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_2\text{SSi}$   $[\text{M}+\text{H}]^+$ : 513.2027, found: 513.2026.

The data is consistent with the reported literature.<sup>[1]</sup>

#### 6. *N*-benzyl-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)thiophene-2-sulfonamide (**3f**)



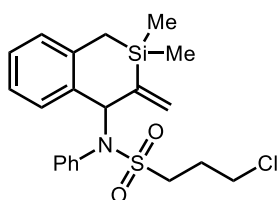
The title compound **3f** was isolated as colorless gum (87.3 mg, 99% yield) following the above general procedure A.  $R_f$  = 0.3 (Petroleum Ether:EtOAc = 30:1).

**$^1\text{H NMR}$**  (400 MHz, Chloroform- $d$ )  $\delta$  7.59 – 7.45 (m, 1H), 7.25 (s, 1H), 7.18 – 7.10 (m, 3H), 7.10 – 6.94 (m, 6H), 6.80 (d,  $J$  = 7.3 Hz, 1H), 5.85 – 5.73 (m, 1H), 5.52 – 5.42 (m, 1H), 5.34 (s, 1H), 4.58 (d,  $J$  = 16.4 Hz, 1H), 4.10 (d,  $J$  = 16.0 Hz, 1H), 1.90 (d,  $J$  = 15.2 Hz, 1H), 1.71 (d,  $J$  = 14.8 Hz, 1H), 0.18 (s, 3H), -0.17 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz, Chloroform- $d$ )  $\delta$  147.5, 141.1, 139.2, 136.8, 135.8, 132.3, 131.3, 131.12, 131.10, 129.2, 128.4, 128.2, 127.8, 126.95, 126.93, 125.4, 70.0, 51.3, 20.7, -2.4, -2.6.

**HRMS** (ESI) calcd for  $\text{C}_{23}\text{H}_{25}\text{NNaO}_2\text{S}_2\text{Si}$   $[\text{M}+\text{Na}]^+$ : 462.0988, found: 462.0987.

#### 7. 3-chloro-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-*N*-phenylpropane-1-sulfonamide (**3g**)



The title compound **3g** was isolated as colorless gum (57.0 mg, 68% yield) following the above general

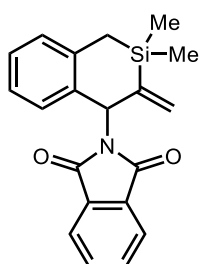
procedure A.  $R_f = 0.3$  (Petroleum Ether:EtOAc = 20:1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.50 – 7.41 (m, 1H), 7.35 – 7.28 (m, 1H), 7.27 – 7.15 (m, 4H), 7.02 – 6.81 (m, 3H), 6.49 – 6.39 (m, 1H), 6.12 (s, 1H), 5.91 – 5.76 (m, 1H), 3.68 – 3.57 (m, 2H), 3.17 – 3.03 (m, 2H), 2.38 – 2.19 (m, 2H), 1.50 (d,  $J = 14.8$  Hz, 1H), 0.70 (d,  $J = 14.8$  Hz, 1H), 0.06 (s, 3H), -0.22 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  148.4, 139.2, 136.8, 136.3, 132.75, 132.67, 131.6, 131.5, 128.9, 128.8, 128.6, 126.0, 68.2, 50.3, 43.0, 26.8, 19.2, -2.0, -2.4.

**HRMS** (ESI) calcd for  $\text{C}_{21}\text{H}_{27}\text{ClNO}_2\text{SSi}$   $[\text{M}+\text{H}]^+$ : 420.1215, found: 420.1217.

## 8. 2-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)isoindoline-1,3-dione (3h)



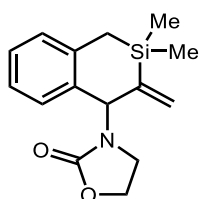
The title compound **3h** was isolated as colorless gum (60.1 mg, 90% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 20:1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.93 – 7.79 (m, 2H), 7.77 – 7.64 (m, 2H), 7.21 – 7.10 (m, 3H), 7.10 – 7.01 (m, 1H), 6.17 (t,  $J = 2.4$  Hz, 1H), 5.67 (t,  $J = 1.8$  Hz, 1H), 5.60 – 5.49 (m, 1H), 2.58 (d,  $J = 14.8$  Hz, 1H), 2.11 (d,  $J = 14.8$  Hz, 1H), 0.21 (s, 3H), 0.13 (s, 3H).

$^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  167.8, 146.3, 137.9, 135.3, 134.0, 132.0, 131.4, 128.1, 127.7, 125.5, 124.7, 123.4, 56.4, 21.2, -2.6, -3.1.

**HRMS** (ESI) calcd for  $\text{C}_{20}\text{H}_{20}\text{NO}_2\text{Si}$   $[\text{M}+\text{H}]^+$ : 334.1258, found: 334.1256.

## 9. 3-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)oxazolidin-2-one (3i)



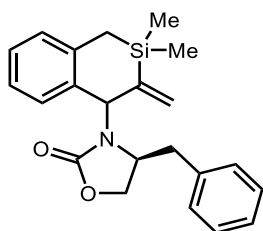
The title compound **3i** was isolated as pale-yellow solid (49.5 mg, 91% yield) following the above general procedure A. m.p. = 79-80 °C.  $R_f = 0.3$  (Petroleum Ether:EtOAc = 20:1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.38 – 7.01 (m, 4H), 5.97 (t,  $J = 2.0$  Hz, 1H), 5.67 (t,  $J = 2.0$  Hz, 1H), 5.65 – 5.56 (m, 1H), 4.40 – 4.15 (m, 2H), 3.50 – 3.35 (m, 1H), 3.33 – 3.17 (m, 1H), 2.22 – 2.00 (m, 2H), 0.18 (s, 3H), 0.04 (s, 3H).

$^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  158.7, 146.0, 137.5, 135.5, 131.6, 129.4, 128.1, 128.0, 126.0, 61.8, 61.5, 41.3, 21.0, -2.8, -3.1.

**HRMS** (ESI) calcd for  $C_{15}H_{20}NO_2Si$   $[M+H]^+$ : 274.1258, found: 274.1252.

**10. (4R)-4-benzyl-3-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)oxazolidin-2-one (3j)**



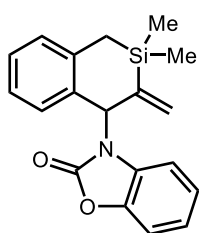
The title compound **3j** was isolated as colorless gum (59.5 mg, 82% yield, dr = 1:1) following the above general procedure A. m.p. = 79-80 °C.  $R_f$  = 0.3 (Petroleum Ether:EtOAc = 20:1).

**$^1H$  NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.38 – 7.32 (m, 1H), 7.32 – 7.08 (m, 13H), 7.00 – 6.87 (m, 2H), 6.75 – 6.65 (m, 2H), 6.14 – 6.05 (m, 1H), 6.05 – 5.98 (m, 1H), 5.72 – 5.65 (m, 1H), 5.65 – 5.60 (m, 1H), 5.60 – 5.55 (m, 1H), 5.34 (s, 1H), 4.08 – 3.91 (m, 4H), 3.82 – 3.69 (m, 1H), 3.57 – 3.46 (m, 1H), 3.13 – 3.04 (m, 1H), 2.88 – 2.77 (m, 1H), 2.64 – 2.38 (m, 2H), 2.35 – 2.23 (m, 1H), 2.21 – 2.03 (m, 3H), 0.39 – 0.19 (m, 6H), 0.11 – -0.06 (m, 6H).

**$^{13}C$  NMR** (100 MHz, Chloroform-*d*)  $\delta$  158.1, 157.4, 147.4, 146.5, 138.2, 137.4, 136.7, 136.23, 136.21, 135.3, 131.9, 131.8, 130.3, 130.0, 129.1, 129.0, 128.96, 128.95, 128.86, 128.85, 128.3, 128.0, 127.13, 127.10, 127.0, 126.1, 126.0, 66.7, 66.0, 65.3, 62.6, 57.5, 57.0, 39.2, 38.0, 21.3, 21.1, -1.3, -2.73, -2.75, -3.1.

**HRMS** (ESI) calcd for  $C_{22}H_{26}NO_2Si$   $[M+H]^+$ : 364.1727, found: 364.1722.

**11. 3-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)benzo[d]oxazol-2(3H)-one (3k)**



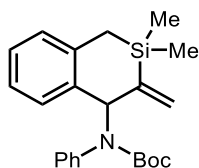
The title compound **3k** was isolated as pale-yellow solid (87.8 mg, 91% yield) following the above general procedure A on a 0.3 mmol scale.  $R_f$  = 0.3 (Petroleum Ether:EtOAc = 20:1).

**$^1H$  NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.34 – 7.24 (m, 1H), 7.23 – 7.06 (m, 3H), 7.06 – 6.92 (m, 2H), 6.88 – 6.73 (m, 1H), 6.55 – 6.38 (m, 1H), 6.29 (s, 1H), 5.53 (s, 1H), 5.41 (s, 1H), 2.36 – 2.13 (m, 2H), 0.33 (s, 3H), 0.02 (s, 3H).

**$^{13}C$  NMR** (100 MHz, Chloroform-*d*)  $\delta$  155.0, 143.0, 142.5, 137.1, 133.5, 130.9, 129.4, 127.8, 125.4, 125.2, 125.0, 123.3, 122.3, 113.3, 110.1, 59.6, 21.4, -2.5, -2.9.

**HRMS** (ESI) calcd for  $C_{19}H_{19}NNaO_2Si$   $[M+Na]^+$ : 344.1077, found: 344.1076.

**12. tert-butyl (2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)(phenyl)carbamate (3l)**



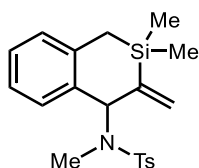
The title compound **3l** was isolated as colorless gum (66.5 mg, 88% yield) following the above general procedure A.  $R_f = 0.5$  (Petroleum Ether:EtOAc = 30:1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.52 – 7.40 (m, 1H), 7.26 – 7.08 (m, 5H), 7.05 – 6.91 (m, 3H), 6.23 (t,  $J = 2.2$  Hz, 1H), 5.98 (s, 1H), 5.69 (t,  $J = 2.3$  Hz, 1H), 1.67 (d,  $J = 14.9$  Hz, 1H), 1.36 (s, 9H), 1.27 (d,  $J = 5.4$  Hz, 1H), 0.01 (d,  $J = 5.6$  Hz, 6H).

$^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  155.0, 148.5, 142.1, 137.7, 137.4, 130.8, 129.1, 128.6, 128.3, 127.3, 126.6, 126.3, 125.3, 80.2, 66.3, 28.3, 20.2, -2.3, -2.7.

**HRMS** (ESI) calcd for  $\text{C}_{23}\text{H}_{29}\text{NNaO}_2\text{Si}$   $[\text{M}+\text{Na}]^+$ : 402.1860, found: 402.1860.

**13. N-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)-N,4-dimethylbenzenesulfonamide (3m)**



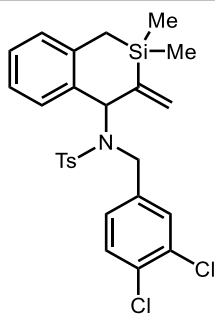
The title compound **3m** was isolated as colorless gum (64.2 mg, 86% yield) following the above general procedure A.  $R_f = 0.3$  (Petroleum Ether:EtOAc = 20:1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.79 – 7.61 (m, 2H), 7.33 – 7.25 (m, 2H), 7.20 – 6.97 (m, 3H), 6.97 – 6.85 (m, 1H), 5.71 – 5.65 (m, 1H), 5.61 – 5.53 (m, 1H), 5.53 – 5.44 (m, 1H), 2.64 (s, 3H), 2.42 (s, 3H), 2.25 – 2.16 (m, 1H), 2.07 – 1.98 (m, 1H), 0.13 (s, 3H), 0.02 (s, 3H).

$^{13}\text{C NMR}$  (150 MHz, Chloroform-*d*)  $\delta$  146.9, 143.1, 137.9, 136.35, 136.33, 130.9, 129.4, 127.7, 127.54, 127.49, 126.4, 125.4, 67.3, 32.2, 21.5, 21.3, -2.6, -2.7.

**HRMS** (ESI) calcd for  $\text{C}_{20}\text{H}_{25}\text{NNaO}_2\text{SSi}$   $[\text{M}+\text{Na}]^+$ : 394.1267, found: 394.1267.

**14. N-(3,4-dichlorobenzyl)-N-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)-4-methylbenzenesulfonamide (3n)**



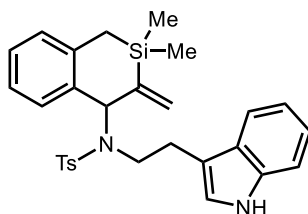
The title compound **3n** was isolated as pale-yellow solid (97.9 mg, 95% yield) following the above general procedure A. m.p. = 72-73 °C.  $R_f$  = 0.4 (Petroleum Ether:EtOAc = 30:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.45 (m, 2H), 7.24 – 7.14 (m, 3H), 7.12 – 6.98 (m, 3H), 6.98 – 6.91 (m, 1H), 6.91 – 6.83 (m, 1H), 6.83 – 6.67 (m, 1H), 5.72 – 5.65 (m, 1H), 5.50 – 5.41 (m, 1H), 5.27 (s, 1H), 4.50 (d,  $J$  = 16.2 Hz, 1H), 4.05 (d,  $J$  = 16.2 Hz, 1H), 2.40 (s, 3H), 1.83 (d,  $J$  = 14.9 Hz, 1H), 1.71 (d,  $J$  = 15.0 Hz, 1H), 0.23 (s, 3H), -0.18 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 147.6, 143.4, 138.9, 137.8, 137.3, 136.0, 131.8, 131.3, 131.2, 130.9, 130.1, 129.8, 129.5, 129.2, 128.66, 127.68, 127.5, 125.6, 70.0, 50.4, 21.6, 20.8, -2.3, -2.6.

**HRMS** (ESI) calcd for C<sub>26</sub>H<sub>27</sub>Cl<sub>2</sub>NNaO<sub>2</sub>SSi [M+Na]<sup>+</sup>: 538.0801, found: 538.0805.

#### 15. *N*-(2-(1H-indol-3-yl)ethyl)-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3o**)



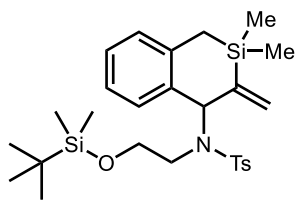
The title compound **3o** was isolated as colorless gum (65.3 mg, 65% yield) following the above general procedure A.  $R_f$  = 0.4 (Petroleum Ether:EtOAc = 20:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.49 (m, 3H), 7.33 – 7.27 (m, 1H), 7.24 – 7.18 (m, 3H), 7.18 – 7.11 (m, 2H), 7.10 – 7.00 (m, 3H), 6.84 – 6.75 (m, 1H), 6.46 – 6.37 (m, 1H), 5.68 – 5.58 (m, 1H), 5.55 – 5.47 (m, 1H), 5.46 – 5.37 (m, 1H), 4.27 – 3.98 (m, 2H), 3.50 – 3.25 (m, 2H), 2.40 (s, 3H), 2.28 – 2.15 (m, 1H), 2.06 – 1.91 (m, 1H), 0.21 (s, 3H), -0.05 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 147.5, 143.3, 138.4, 137.1, 136.2, 135.7, 131.5, 131.0, 129.4, 128.6, 128.3, 128.0, 127.5, 127.4, 125.9, 121.6, 120.8, 119.4, 109.3, 101.5, 69.1, 46.9, 46.1, 21.5, 21.1, -2.7, -3.0.

**HRMS** (ESI) calcd for C<sub>29</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub>SSi [M+H]<sup>+</sup>: 501.2027, found: 501.2025.

#### 16. *N*-(2-((tert-butyldimethylsilyl)oxy)ethyl)-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3p**)



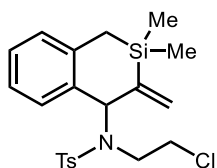
The title compound **3p** was isolated as colorless gum (75.1 mg, 73% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 20:1).

**$^1\text{H NMR}$**  (400 MHz, Chloroform-*d*)  $\delta$  7.65 – 7.53 (m, 2H), 7.24 – 7.14 (m, 3H), 7.13 – 6.97 (m, 2H), 6.91 (d,  $J = 7.4$  Hz, 1H), 5.68 (t,  $J = 1.9$  Hz, 1H), 5.50 (t,  $J = 1.9$  Hz, 1H), 5.49 – 5.45 (m, 1H), 3.62 – 3.53 (m, 1H), 3.48 – 3.38 (m, 1H), 3.30 – 3.19 (m, 1H), 3.17 – 3.06 (m, 1H), 2.39 (s, 3H), 2.12 (d,  $J = 14.9$  Hz, 1H), 1.89 (d,  $J = 14.9$  Hz, 1H), 0.80 (s, 9H), 0.22 (s, 3H), -0.08 (s, 9H).

**$^{13}\text{C NMR}$**  (100 MHz, Chloroform-*d*)  $\delta$  147.5, 142.8, 138.2, 137.7, 136.4, 131.2, 130.8, 129.3, 128.2, 128.1, 127.3, 125.5, 67.9, 61.7, 48.4, 25.9, 21.5, 21.0, 18.2, -2.8, -3.0, -5.39, -5.41.

**HRMS** (ESI) calcd for  $\text{C}_{27}\text{H}_{41}\text{NNaO}_3\text{SSi}_2$   $[\text{M}+\text{Na}]^+$ : 538.2238, found: 538.2236.

#### 17. *N*-(2-chloroethyl)-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3q**)



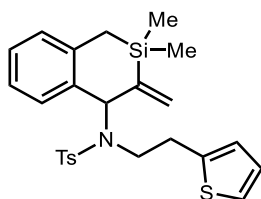
The title compound **3q** was isolated as colorless gum (52.9 mg, 63% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

**$^1\text{H NMR}$**  (400 MHz, Chloroform-*d*)  $\delta$  7.61 – 7.51 (m, 2H), 7.23 – 7.14 (m, 3H), 7.14 – 7.01 (m, 2H), 6.96 – 6.87 (m, 1H), 5.73 – 5.65 (m, 1H), 5.59 – 5.51 (m, 1H), 5.51 – 5.45 (m, 1H), 3.56 – 3.21 (m, 4H), 2.40 (s, 3H), 2.10 – 2.02 (m, 1H), 1.97 – 1.85 (m, 1H), 0.22 (s, 3H), -0.10 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz, Chloroform-*d*)  $\delta$  147.4, 143.3, 138.1, 137.2, 135.9, 131.4, 130.8, 129.4, 128.8, 128.4, 127.2, 125.7, 67.7, 48.2, 41.6, 21.5, 20.9, -2.8, -3.1.

**HRMS** (ESI) calcd for  $\text{C}_{21}\text{H}_{27}\text{ClNO}_2\text{SSi}$   $[\text{M}+\text{H}]^+$ : 420.1215, found: 420.1217.

#### 18. *N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methyl-*N*-(2-(thiophen-2-yl)ethyl)benzenesulfonamide (**3r**)



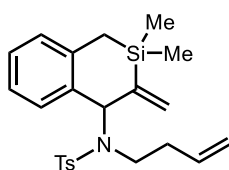
The title compound **3r** was isolated as colorless gum (91.7 mg, 98% yield) following the above general procedure A.  $R_f = 0.3$  (Petroleum Ether:EtOAc = 50:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.64 – 7.45 (m, 2H), 7.28 – 7.21 (m, 1H), 7.21 – 7.14 (m, 2H), 7.14 – 6.99 (m, 3H), 6.96 – 6.79 (m, 2H), 6.72 – 6.56 (m, 1H), 5.89 – 5.81 (m, 1H), 5.60 – 5.52 (m, 1H), 5.47 (s, 1H), 3.55 – 3.42 (m, 1H), 3.35 – 3.24 (m, 1H), 3.10 – 2.98 (m, 1H), 2.98 – 2.85 (m, 1H), 2.39 (s, 3H), 2.12 (d, *J* = 14.8 Hz, 1H), 1.89 (d, *J* = 14.8 Hz, 1H), 0.23 (s, 3H), -0.07 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 147.8, 142.9, 141.2, 138.5, 138.0, 136.3, 131.2, 131.0, 129.3, 128.7, 128.4, 127.3, 127.0, 125.7, 125.1, 123.7, 68.6, 49.6, 30.2, 21.6, 21.1, -2.3, -2.7.

**HRMS** (ESI) calcd for C<sub>25</sub>H<sub>29</sub>NNaO<sub>2</sub>S<sub>2</sub>Si [M+Na]<sup>+</sup>: 490.1301, found: 490.1301.

### 19. *N*-(but-3-en-1-yl)-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3s**)



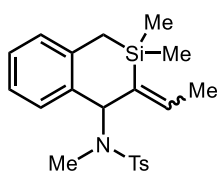
The title compound **3s** was isolated as colorless gum (62.6 mg, 76% yield) following the above general procedure A. *R<sub>f</sub>* = 0.4 (Petroleum Ether:EtOAc = 30:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.45 (m, 2H), 7.22 – 7.10 (m, 3H), 7.11 – 6.98 (m, 2H), 6.89 – 6.81 (m, 1H), 5.82 (t, *J* = 1.7 Hz, 1H), 5.61 – 5.46 (m, 1H), 5.51 (t, *J* = 1.9 Hz, 1H), 5.41 (d, *J* = 1.6 Hz, 1H), 4.97 – 4.81 (m, 2H), 3.28 (ddd, *J* = 14.7, 11.4, 5.2 Hz, 1H), 3.07 (ddd, *J* = 14.7, 11.3, 5.0 Hz, 1H), 2.37 (s, 3H), 2.32 – 2.10 (m, 2H), 2.07 (d, *J* = 14.7 Hz, 1H), 1.84 (d, *J* = 14.8 Hz, 1H), 0.20 (s, 3H), -0.09 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 147.7, 142.6, 138.4, 138.2, 136.2, 135.0, 130.9, 130.7, 129.1, 128.4, 128.1, 127.2, 125.4, 116.5, 68.3, 47.0, 33.8, 21.5, 21.0, -2.5, -2.8.

**HRMS** (ESI) calcd for C<sub>23</sub>H<sub>30</sub>NO<sub>2</sub>SSi [M+H]<sup>+</sup>: 412.1761, found: 412.1760.

### 20. (*Z*)-*N*-(3-ethylidene-2,2-dimethyl-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-*N*,4-dimethylbenzenesulfonamide (**3ma**)



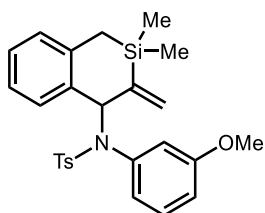
The title compound **3ma** was isolated as colorless gum (69.9 mg, 91% yield, *Z/E* = 1:1) following the above general procedure A. *R<sub>f</sub>* = 0.4 (Petroleum Ether:EtOAc = 20:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 2H), 7.50 – 7.44 (m, 2H), 7.26 – 6.88 (m, 12H), 6.19 (qd, *J* = 6.9, 1.2 Hz, 1H), 6.01 (qd, *J* = 6.7, 1.2 Hz, 1H), 5.29 (d, *J* = 1.2 Hz, 1H), 4.94 (s, 1H), 2.70 (s, 3H), 2.67 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H), 2.33 (d, *J* = 7.5 Hz, 1H), 2.30 (d, *J* = 8.1 Hz, 1H), 1.92 (d, *J* = 6.3 Hz, 1H), 1.88 (d, *J* = 5.8 Hz, 1H), 1.85 – 1.68 (m, 6H), 0.30 (s, 3H), 0.24 (s, 3H), 0.04 (s, 3H), -0.14 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 142.9, 140.7, 138.9, 138.8, 138.7, 138.5, 137.4, 137.2, 136.4, 136.1, 135.4, 130.9, 130.5, 130.2, 129.2, 129.1, 128.6, 128.3, 127.78, 127.75, 127.6, 125.0, 124.9, 71.2, 63.3, 34.5, 34.4, 21.6, 21.49, 21.47, 20.9, 18.2, 15.0, -1.2, -1.9, -2.1, -2.3.

**HRMS** (ESI) calcd for C<sub>21</sub>H<sub>27</sub>NNaO<sub>2</sub>SSi [M+Na]<sup>+</sup>: 408.1424, found: 408.1425.

**21. *N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-*N*-(3-methoxyphenyl)-4-methylbenzenesulfonamide (3t)**



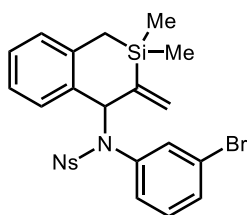
The title compound **3t** was isolated as colorless gum (66.2 mg, 71% yield) following the above general procedure A. *R<sub>f</sub>* = 0.4 (Petroleum Ether:EtOAc = 30:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.63 – 7.57 (m, 2H), 7.36 – 7.31 (m, 1H), 7.26 – 7.19 (m, 2H), 7.13 – 7.02 (m, 3H), 6.89 – 6.79 (m, 2H), 6.44 – 6.36 (m, 1H), 6.34 – 6.26 (m, 1H), 6.23 – 6.16 (m, 1H), 6.09 – 6.00 (m, 1H), 5.78 – 5.70 (m, 1H), 3.54 (s, 3H), 2.42 (s, 3H), 1.51 (d, *J* = 15.2 Hz, 1H), 0.88 (d, *J* = 15.2 Hz, 1H), 0.12 (s, 3H), -0.20 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 159.2, 148.6, 143.0, 139.4, 138.2, 137.7, 136.4, 131.7, 131.5, 131.1, 129.1, 128.7, 128.3, 128.0, 125.6, 125.0, 117.9, 114.9, 68.9, 55.1, 21.5, 19.5, -2.0, -2.2.

**HRMS** (ESI) calcd for C<sub>26</sub>H<sub>30</sub>NO<sub>3</sub>SSi [M+H]<sup>+</sup>: 464.1710, found: 464.1709.

**22. *N*-(3-bromophenyl)-*N*-(2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-nitrobenzenesulfonamide (3u)**



The title compound **3u** was isolated as colorless gum (65.2 mg, 60% yield) following the above general procedure A. *R<sub>f</sub>* = 0.4 (Petroleum Ether:EtOAc = 30:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.33 – 8.13 (m, 2H), 7.80 – 7.73 (m, 2H), 7.48 – 7.42 (m, 1H), 7.35 – 7.28 (m, 1H), 7.15 – 7.09 (m, 2H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.99 (t, *J* = 2.0 Hz, 1H), 6.84 – 6.77 (s, 1H), 6.66 – 6.56 (m, 1H), 6.23 (t, *J* = 1.5 Hz, 1H), 6.01 (s, 1H), 5.73 (t, *J* = 1.5 Hz, 1H), 1.54 (d, *J* = 15.0 Hz, 1H), 0.85 (d, *J* = 15.0 Hz, 1H), 0.10 (s, 3H), -0.24 (s, 3H).

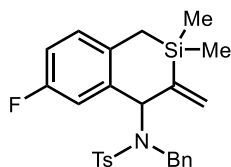
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.31 – 8.13 (m, 2H), 7.80 – 7.73 (m, 2H), 7.47 – 7.42 (m, 1H), 7.34 – 7.28 (m, 1H), 7.14 – 7.02 (m, 3H), 7.01 – 6.95 (m, 1H), 6.82 – 6.76 (m, 1H), 6.64 – 6.55 (m, 1H), 6.22

(s, 1H), 6.00 (s, 1H), 5.80 – 5.64 (m, 1H), 1.56 – 1.49 (m, 1H), 0.83 (d,  $J = 15.2$  Hz, 1H), 0.09 (s, 3H), -0.25 (s, 3H).

**$^{13}\text{C}$  NMR** (100 MHz, Chloroform-*d*)  $\delta$  149.8, 147.8, 145.9, 139.1, 138.0, 135.5, 135.1, 132.8, 132.1, 131.43, 131.40, 131.1, 129.9, 129.0, 128.8, 126.0, 123.8, 121.9, 70.2, 19.6, -2.1, -2.5.

**HRMS** (ESI) calcd for  $\text{C}_{24}\text{H}_{23}\text{BrN}_2\text{NaO}_4\text{SSi}$  [ $\text{M}+\text{Na}$ ] $^+$ : 565.0223, found: 565.0220.

### 23. *N*-benzyl-*N*-(6-fluoro-2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3v**)



The title compound **3v** was isolated as colorless gum (90.2 mg, 97% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

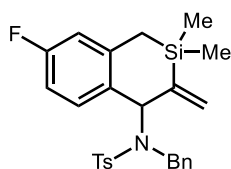
**$^1\text{H}$  NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.59 – 7.50 (m, 2H), 7.25 – 7.15 (m, 5H), 7.14 – 7.06 (m, 2H), 6.87 – 6.66 (m, 3H), 5.77 – 5.69 (m, 1H), 5.55 – 5.46 (m, 1H), 5.42 – 5.35 (m, 1H), 4.65 (d,  $J = 16.0$  Hz, 1H), 4.23 (d,  $J = 16.0$  Hz, 1H), 2.43 (s, 3H), 1.90 – 1.79 (m, 1H), 1.70 (d,  $J = 15.2$  Hz, 1H), 0.20 (s, 3H), -0.14 (s, 3H).

**$^{13}\text{C}$  NMR** (100 MHz, Chloroform-*d*)  $\delta$  160.7 (d,  $J = 241.7$  Hz), 146.3, 143.1, 137.9, 137.7 (d,  $J = 6.6$  Hz), 137.0, 134.3 (d,  $J = 3.0$  Hz), 132.1 (d,  $J = 7.4$  Hz), 129.8, 129.3, 128.2, 127.9, 127.3, 127.0, 117.7 (d,  $J = 21.8$  Hz), 114.9 (d,  $J = 20.5$  Hz), 68.3, 51.1, 21.5, 19.9, -2.66, -2.72.

**$^{19}\text{F}$  NMR** (376 MHz, Chloroform-*d*)  $\delta$  -118.4.

**HRMS** (ESI) calcd for  $\text{C}_{26}\text{H}_{28}\text{FNNaO}_2\text{SSi}$  [ $\text{M}+\text{Na}$ ] $^+$ : 488.1486, found: 488.1485.

### 24. *N*-benzyl-*N*-(7-fluoro-2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3w**)



The title compound **3w** was isolated as colorless gum (82.1 mg, 88% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

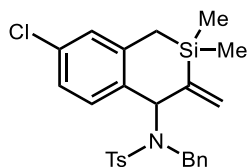
**$^1\text{H}$  NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.52 – 7.46 (m, 2H), 7.25 – 7.17 (m, 5H), 7.16 – 7.07 (m, 3H), 6.78 – 6.66 (m, 1H), 6.53 – 6.37 (m, 1H), 5.70 – 5.59 (m, 1H), 5.50 – 5.42 (m, 1H), 5.33 (s, 1H), 4.72 (d,  $J = 16.4$  Hz, 1H), 4.22 (d,  $J = 16.0$  Hz, 1H), 2.43 (s, 3H), 1.90 (d,  $J = 14.8$  Hz, 1H), 1.66 (d,  $J = 14.8$  Hz, 1H), 0.23 (s, 3H), -0.15 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  162.4 (d,  $J = 245.3$  Hz), 146.8, 142.9, 141.7 (d,  $J = 8.0$  Hz), 137.9, 137.2, 132.9 (d,  $J = 8.5$  Hz), 132.0 (d,  $J = 3.0$  Hz), 129.7, 129.2, 127.99, 127.97, 127.3, 126.9, 117.0 (d,  $J = 20.6$  Hz), 111.9 (d,  $J = 21.0$  Hz), 68.7, 51.4, 21.5, 21.1, -2.50, -2.6.

**<sup>19</sup>F NMR** (376 MHz, Chloroform-*d*)  $\delta$  -115.1.

**HRMS** (ESI) calcd for C<sub>26</sub>H<sub>28</sub>FNNaO<sub>2</sub>SSi [M+Na]<sup>+</sup>: 488.1486, found: 488.1487.

## 25. *N*-benzyl-*N*-(7-chloro-2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3x**)



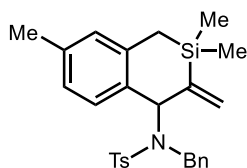
The title compound **3x** was isolated as colorless gum (89.6 mg, 93% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.49 – 7.37 (m, 2H), 7.23 – 7.01 (m, 8H), 7.01 – 6.91 (m, 1H), 6.72 – 6.60 (m, 1H), 5.65 – 5.56 (m, 1H), 5.45 – 5.37 (m, 1H), 5.27 (s, 1H), 4.69 (d,  $J = 16.4$  Hz, 1H), 4.16 (d,  $J = 16.4$  Hz, 1H), 2.39 (s, 3H), 1.84 (d,  $J = 14.4$  Hz, 1H), 1.61 (d,  $J = 14.8$  Hz, 1H), 0.20 (s, 3H), -0.18 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  146.3, 142.9, 141.0, 137.7, 137.0, 134.6, 133.7, 132.5, 130.2, 129.9, 129.1, 129.0, 128.0, 127.2, 126.9, 125.2, 68.6, 51.3, 21.5, 20.8, -2.5, -2.6.

**HRMS** (ESI) calcd for C<sub>26</sub>H<sub>28</sub>ClNNO<sub>2</sub>SSi [M+Na]<sup>+</sup>: 504.1191, found: 504.1190.

## 26. *N*-benzyl-4-methyl-*N*-(2,2,7-trimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)benzenesulfonamide (**3y**)



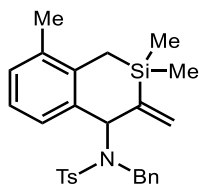
The title compound **3y** was isolated as colorless gum (90.5 mg, 98% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.53 – 7.38 (m, 2H), 7.24 – 6.99 (m, 7H), 6.96 – 6.88 (m, 1H), 6.86 – 6.73 (m, 1H), 6.55 (s, 1H), 5.82 – 5.68 (m, 1H), 5.50 – 5.38 (m, 1H), 5.33 (s, 1H), 4.63 (d,  $J = 16.0$  Hz, 1H), 4.13 (d,  $J = 16.0$  Hz, 1H), 2.40 (s, 3H), 2.21 (s, 3H), 1.83 (d,  $J = 14.8$  Hz, 1H), 1.68 – 1.59 (m, 1H), 0.17 (s, 3H), -0.17 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*)  $\delta$  147.5, 142.6, 138.7, 137.92, 137.88, 137.3, 133.0, 131.7, 131.1, 129.1, 129.0, 128.2, 127.8, 127.4, 126.7, 126.0, 69.0, 51.1, 21.5, 20.9, 20.6, -2.4, -2.5.

**HRMS** (ESI) calcd for C<sub>27</sub>H<sub>31</sub>NO<sub>2</sub>SSi [M+H]<sup>+</sup>: 462.1918, found: 462.1916.

**27. N-benzyl-4-methyl-N-(2,2,8-trimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)benzenesulfonamide (3z)**

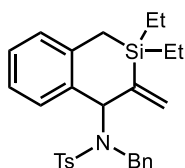


The title compound **3z** was isolated as colorless gum (91.8 mg, 99% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

**$^1\text{H NMR}$**  (400 MHz, Chloroform-*d*)  $\delta$  7.44 – 7.32 (m, 2H), 7.23 – 7.04 (m, 7H), 7.04 – 6.84 (m, 3H), 5.62 – 5.48 (m, 1H), 5.39 – 5.29 (m, 1H), 5.06 (s, 1H), 4.85 (d,  $J = 16.0$  Hz, 1H), 4.08 (d,  $J = 16.4$  Hz, 1H), 2.37 (s, 3H), 1.93 (s, 3H), 1.74 (d,  $J = 14.8$  Hz, 1H), 1.51 (d,  $J = 14.8$  Hz, 1H), 0.26 (s, 3H), -0.25 (s, 3H).  
 **$^{13}\text{C NMR}$**  (100 MHz, Chloroform-*d*)  $\delta$  147.5, 142.5, 138.0, 137.54, 137.51, 136.2, 135.9, 129.9, 129.4, 129.1, 128.8, 127.9, 127.8, 127.3, 126.7, 124.6, 71.7, 52.1, 21.4, 20.5, 15.3, -2.0, -2.4.

**HRMS** (ESI) calcd for  $\text{C}_{27}\text{H}_{31}\text{NNaO}_2\text{SSi}$   $[\text{M}+\text{Na}]^+$ : 484.1737, found: 484.1735.

**28. N-benzyl-N-(2,2-diethyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)-4-methylbenzenesulfonamide (3aa)**



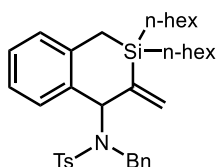
The title compound **3aa** was isolated as colorless gum (91.5 mg, 96% yield) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

**$^1\text{H NMR}$**  (400 MHz, Chloroform-*d*)  $\delta$  7.56 – 7.38 (m, 2H), 7.24 – 7.07 (m, 8H), 7.06 – 6.96 (m, 2H), 6.80 – 6.69 (m, 1H), 5.76 (t,  $J = 1.7$  Hz, 1H), 5.44 (t,  $J = 1.7$  Hz, 1H), 5.37 (s, 1H), 4.70 (d,  $J = 16.2$  Hz, 1H), 4.18 (d,  $J = 16.2$  Hz, 1H), 2.39 (s, 3H), 1.80 (d,  $J = 14.9$  Hz, 1H), 1.71 (d,  $J = 14.9$  Hz, 1H), 0.98 (t,  $J = 7.9$  Hz, 3H), 0.77 – 0.65 (m, 2H), 0.62 (t,  $J = 7.9$  Hz, 3H), 0.44 – 0.24 (m, 2H).

**$^{13}\text{C NMR}$**  (100 MHz, Chloroform-*d*)  $\delta$  145.0, 142.6, 139.2, 138.0, 137.3, 136.1, 131.3, 130.8, 130.2, 129.1, 128.2, 128.1, 127.9, 127.4, 126.8, 125.2, 69.4, 51.2, 21.5, 17.5, 7.3, 7.0, 4.4, 4.0.

**HRMS** (ESI) calcd for  $\text{C}_{28}\text{H}_{33}\text{NNaO}_2\text{SSi}$   $[\text{M}+\text{Na}]^+$ : 498.1893, found: 498.1893.

**29. N-benzyl-N-(2,2-dihexyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)-4-methylbenzenesulfonamide (3ab)**



The title compound **3ab** was isolated as colorless gum (114.2 mg, 97% yield) following the above general

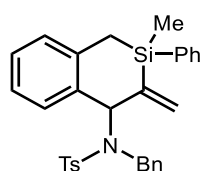
procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.54 – 7.38 (m, 2H), 7.23 – 7.06 (m, 8H), 7.06 – 6.88 (m, 2H), 6.86 – 6.60 (m, 1H), 5.88 – 5.67 (m, 1H), 5.43 (d,  $J = 2.2$  Hz, 1H), 5.41 (s, 1H), 4.68 (d,  $J = 16.0$  Hz, 1H), 4.19 (d,  $J = 16.4$  Hz, 1H), 2.38 (s, 3H), 1.87 – 1.75 (m, 1H), 1.75 – 1.64 (m, 1H), 1.39 – 1.23 (m, 8H), 1.21 – 1.02 (m, 6H), 1.00 – 0.85 (m, 5H), 0.85 – 0.74 (m, 3H), 0.74 – 0.56 (m, 2H), 0.47 – 0.19 (m, 2H).

$^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  145.5, 142.6, 139.2, 138.2, 137.3, 136.0, 131.4, 130.9, 130.3, 129.1, 128.2, 128.1, 127.9, 127.3, 126.8, 125.2, 69.0, 51.0, 33.3, 32.9, 31.5, 31.3, 23.7, 23.3, 22.6, 22.4, 21.5, 18.4, 14.2, 14.0, 12.9, 12.6.

**HRMS** (ESI) calcd for  $\text{C}_{36}\text{H}_{49}\text{NNaO}_2\text{SSi}$  [ $\text{M}+\text{Na}$ ] $^+$ : 610.3145, found: 610.3140.

### 30. *N*-benzyl-4-methyl-*N*-(2-methyl-3-methylene-2-phenyl-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)benzenesulfonamide (**3ac**)



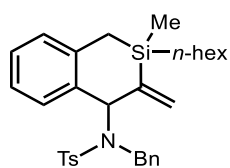
The title compound **3ac** was isolated as colorless gum (97.2 mg, 95% yield, dr = 3:1) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

$^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.54 – 7.31 (m, 6H), 7.24 – 6.97 (m, 11H), 6.82 – 6.75 (m, 0.75H), 6.75 – 6.63 (m, 0.25H), 5.85 (s, 0.25H), 5.75 – 5.66 (m, 0.75H), 5.64 – 5.43 (m, 1.5H), 5.43 – 5.32 (m, 0.5H), 4.78 – 4.69 (m, 0.25H), 4.69 – 4.60 (m, 0.75H), 4.20 – 4.13 (m, 0.25H), 4.11 – 4.02 (m, 0.75H), 2.40 (s, 0.8H), 2.37 (s, 2.2H), 2.21 – 2.14 (m, 0.7H), 2.09 – 2.00 (m, 0.3H), 1.95 – 1.83 (m, 1H), 0.47 (s, 0.75H), 0.09 (s, 2.35H).

$^{13}\text{C NMR}$  (100 MHz, Chloroform-*d*)  $\delta$  146.0, 144.8, 142.9, 142.5, 138.7, 138.5, 138.1, 137.6, 137.3, 137.2, 136.5, 136.2, 136.0, 135.4, 134.1, 133.9, 132.0, 131.8, 131.5, 131.3, 131.14, 131.11, 129.8, 129.23, 129.19, 129.0, 128.4, 128.3, 128.2, 128.0, 127.94, 127.92, 127.90, 127.6, 127.5, 127.1, 126.9, 126.7, 125.6, 125.4, 69.9, 67.9, 51.5, 50.9, 21.49, 21.46, 20.2, 19.0, -3.78, -3.84.

**HRMS** (ESI) calcd for  $\text{C}_{31}\text{H}_{31}\text{NNaO}_2\text{SSi}$  [ $\text{M}+\text{Na}$ ] $^+$ : 532.1737, found: 532.1734.

### 31. *N*-benzyl-*N*-((4*R*)-2-hexyl-2-methyl-3-methylene-1,2,3,4-tetrahydrobenzo[*c*]silin-4-yl)-4-methylbenzenesulfonamide (**3ad**)



The title compound **3ad** was isolated as colorless gum (102.7 mg, 99% yield, dr = 1.5:1) following the above general procedure A.  $R_f = 0.4$  (Petroleum Ether:EtOAc = 30:1).

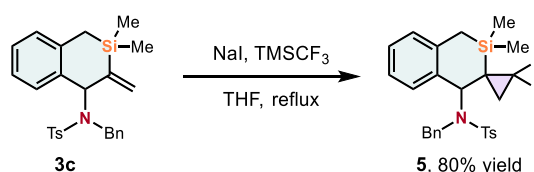
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.53 – 7.39 (m, 2H), 7.23 – 6.94 (m, 10H), 6.82 – 6.65 (m, 1H), 5.79 – 5.73 (m, 0.6H), 5.71 (s, 0.4H), 5.55 – 5.25 (m, 2H), 4.79 – 4.59 (m, 1H), 4.26 – 4.11 (m, 1H), 2.39 (s, 3H), 1.91 – 1.61 (m, 2H), 1.56 – 0.84 (m, 10H), 0.85 – 0.60 (m, 2H), 0.39 – 0.20 (m, 1H), 0.15 (s, 1.8H), -0.19 (s, 1.2H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 146.7, 146.4, 142.6, 139.1, 139.0, 138.1, 138.0, 137.33, 137.29, 136.0, 131.4, 131.3, 130.9, 129.83, 129.80, 129.12, 129.10, 128.2, 128.14, 128.09, 128.0, 127.7, 127.4, 127.3, 126.81, 126.76, 125.24, 125.18, 69.6, 69.1, 51.3, 51.1, 33.2, 32.8, 31.6, 31.3, 23.6, 23.3, 22.6, 22.4, 21.5, 19.62, 19.59, 14.20, 14.18, 14.1, 14.0, -4.2, -4.4.

**HRMS** (ESI) calcd for C<sub>31</sub>H<sub>40</sub>NO<sub>2</sub>SSi [M+H]<sup>+</sup>: 518.2544, found: 518.2540.

## Synthetic transformations

### *N*-benzyl-*N*-(2',2'-difluoro-2,2-dimethyl-1,4-dihydro-2H-spiro[benzo[*c*]siline-3,1'-cyclopropan]-4-yl)-4-methylbenzenesulfonamide (**5**)



A Schlenk flask containing NaI (37.5 mg, 2.5 equiv) was dried under vacuum with a heat gun. After cooling to room temperature, the flask was transferred into an inert-atmosphere glovebox, where compound **3c** (44.8 mg, 1.0 equiv), TMSCF<sub>3</sub> (44.3 μL, 3.0 equiv), and dry THF (0.5 mL) were added. The reaction mixture was stirred under reflux, and the progress was monitored by TLC until complete consumption of **3c** was observed. After cooling to room temperature, the mixture was quenched with water and extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by preparative silica gel plate with EtOAc/Petroleum ether (1:20) to give the pure product **5** as a colorless gum (39.8 mg, 80% yield).

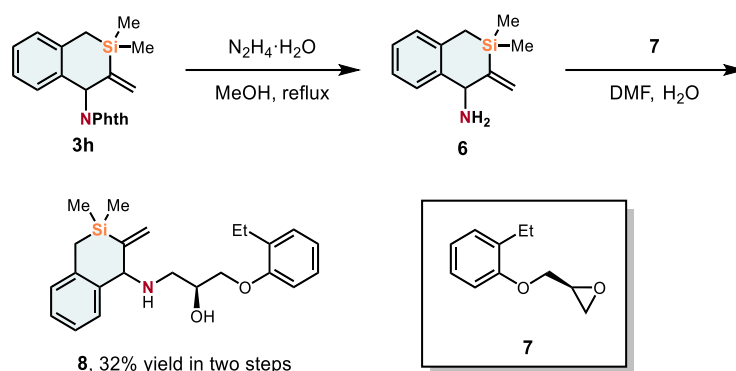
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.57 (m, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.13 (m, 4H), 7.11 – 6.99 (m, 3H), 6.97 – 6.89 (m, 2H), 5.26 (s, 1H), 4.52 (d, *J* = 17.6 Hz, 1H), 4.37 (d, *J* = 17.6 Hz, 1H), 2.44 (s, 3H), 2.03 (d, *J* = 15.3 Hz, 1H), 1.71 (d, *J* = 15.3 Hz, 1H), 1.62 – 1.51 (m, 1H), 1.48 – 1.39 (m, 1H), -0.08 (s, 3H), -0.18 (s, 2H).

**<sup>13</sup>C NMR** (100 MHz, Chloroform-*d*) δ 143.4, 137.9, 137.6, 137.5, 135.7, 131.5, 131.46, 129.50, 128.8, 128.0, 127.6, 126.9, 126.9, 125.9, 116.5 (dd, *J* = 287.6, 277.3 Hz), 60.8 (d, *J* = 6.6 Hz), 49.4, 21.5, 20.6, 20.2 (dd, *J* = 16.4, 6.5 Hz), 19.6 (t, *J* = 9.8 Hz), -2.9 (d, *J* = 4.6 Hz), -4.2.

**<sup>19</sup>F NMR** (376 MHz, Chloroform-*d*) δ -118.1 (d, *J* = 145.5 Hz), -135.7 (d, *J* = 145.9 Hz).

**HRMS** (ESI) calcd for C<sub>27</sub>H<sub>29</sub>F<sub>2</sub>NNaO<sub>2</sub>SSi [M+Na]<sup>+</sup>: 520.1549, found: 520.1546.

**(2R)-1-((2,2-dimethyl-3-methylene-1,2,3,4-tetrahydrobenzo[c]silin-4-yl)amino)-3-(2-ethylphenoxy)propan-2-ol (8)**



A reaction flask equipped with a magnetic stir bar was sequentially charged with **3h** (0.2 mmol, 66.7 mg), MeOH (1.0 mL), and hydrazine hydrate (25  $\mu\text{L}$ , 2.5 equiv.). The mixture was refluxed under an inert atmosphere for 2 hours. After cooling, the mixture was filtered. The filtrate was concentrated, dissolved in DCM, and saturated potassium bicarbonate solution was added until the solution became clear. The mixture was then extracted with DCM three times. The crude product was concentrated under vacuum and used directly in the next step.

The crude product **6** from the previous step was placed in a vessel containing compound **7** (35.6 mg, 1.0 equiv.), DMF (1.0 mL), and water (0.18 mL, 50 equiv.). The mixture was refluxed under a nitrogen atmosphere for 15 hours. After the reaction was complete, the mixture was extracted with EA. The organic phase was washed sequentially with water and brine, dried, and concentrated. The residue was purified by preparative silica gel plate to afford the desired product **8** as a colorless gum (24.2 mg, 32% yield).

**$^1\text{H NMR}$**  (400 MHz, Chloroform-*d*)  $\delta$  7.22 – 7.08 (m, 6H), 6.97 – 6.89 (m, 1H), 6.86 – 6.75 (m, 1H), 5.89 – 5.80 (m, 1H), 5.49 – 5.40 (m, 1H), 4.24 (d,  $J = 4.8$  Hz, 1H), 4.13 – 3.93 (m, 3H), 2.98 – 2.52 (m, 5H), 2.03 (brs, 3H), 1.21 (t,  $J = 7.6$  Hz, 1.5H), 1.15 (t,  $J = 7.6$  Hz, 1.5H), 0.31 (s, 1.5H), 0.30 (s, 1.5H), 0.03 (s, 3H).

**$^{13}\text{C NMR}$**  (100 MHz, Chloroform-*d*)  $\delta$  156.3, 156.2, 151.3, 151.1, 140.1, 138.3, 138.2, 132.6, 132.6, 131.2, 129.0, 128.9, 128.8, 127.84, 127.82, 126.82, 126.81, 125.80, 125.7, 125.22, 125.20, 120.9, 111.1, 111.0, 72.94, 72.88, 70.6, 70.5, 69.0, 68.9, 49.62, 49.57, 23.31, 23.29, 20.6, 14.2, 14.1, -0.5, -2.3.

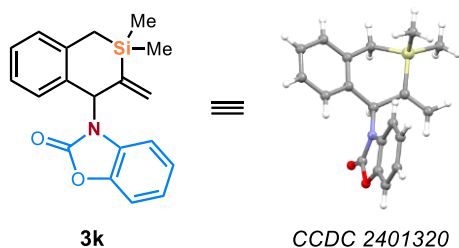
**HRMS** (ESI) calcd for  $\text{C}_{23}\text{H}_{32}\text{NO}_2\text{Si}$   $[\text{M}+\text{H}]^+$ : 382.2197, found: 382.2190.

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## Single crystal X-ray analysis data

The molecular structure of products **3k** were unambiguously determined by single-crystal X-ray diffraction analysis. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

The purified solid sample (15.0 mg) was dissolved in dichloromethane (1.0 mL) in a 5 mL glass vial. Petroleum ether (2.0 mL) was then slowly added along the inner wall of the vial using a syringe to facilitate controlled mixing and prevent rapid precipitation. To enable controlled solvent evaporation, the vial was partially sealed with Parafilm perforated by a needle, creating a small vapor diffusion aperture. The crystallization setup was maintained under ambient conditions ( $25 \pm 2$  °C) in a vibration-isolated environment. Well-defined block-shaped colorless crystals suitable for X-ray analysis were obtained within 24-48 hours through this slow diffusion method. A suitable crystal was selected and mounted on a Bruker D8 QUEST diffractometer for data collection at 293(2) K.



## Datablock: 1

Bond precision: C-C = 0.0033 Å

Wavelength=0.71073

Cell: a=9.4569 (11)  
alpha=90

b=19.015 (2)  
beta=90

c=19.421 (2)  
gamma=90

Temperature: 273 K

	Calculated	Reported
Volume	3492.3 (7)	3492.4 (7)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C19 H19 N O2 Si	C19 H19 N O2 Si
Sum formula	C19 H19 N O2 Si	C19 H19 N O2 Si
Mr	321.44	321.44
Dx, g cm <sup>-3</sup>	1.223	1.223
Z	8	8
Mu (mm <sup>-1</sup> )	0.143	0.143
F000	1360.0	1360.0
F000'	1361.17	
h, k, lmax	12, 24, 25	12, 24, 25
Nref	4021	4002
Tmin, Tmax	0.997, 0.999	0.662, 0.746
Tmin'	0.996	

Correction method= # Reported T Limits: Tmin=0.662 Tmax=0.746

AbsCorr = MULTI-SCAN

Data completeness= 0.995

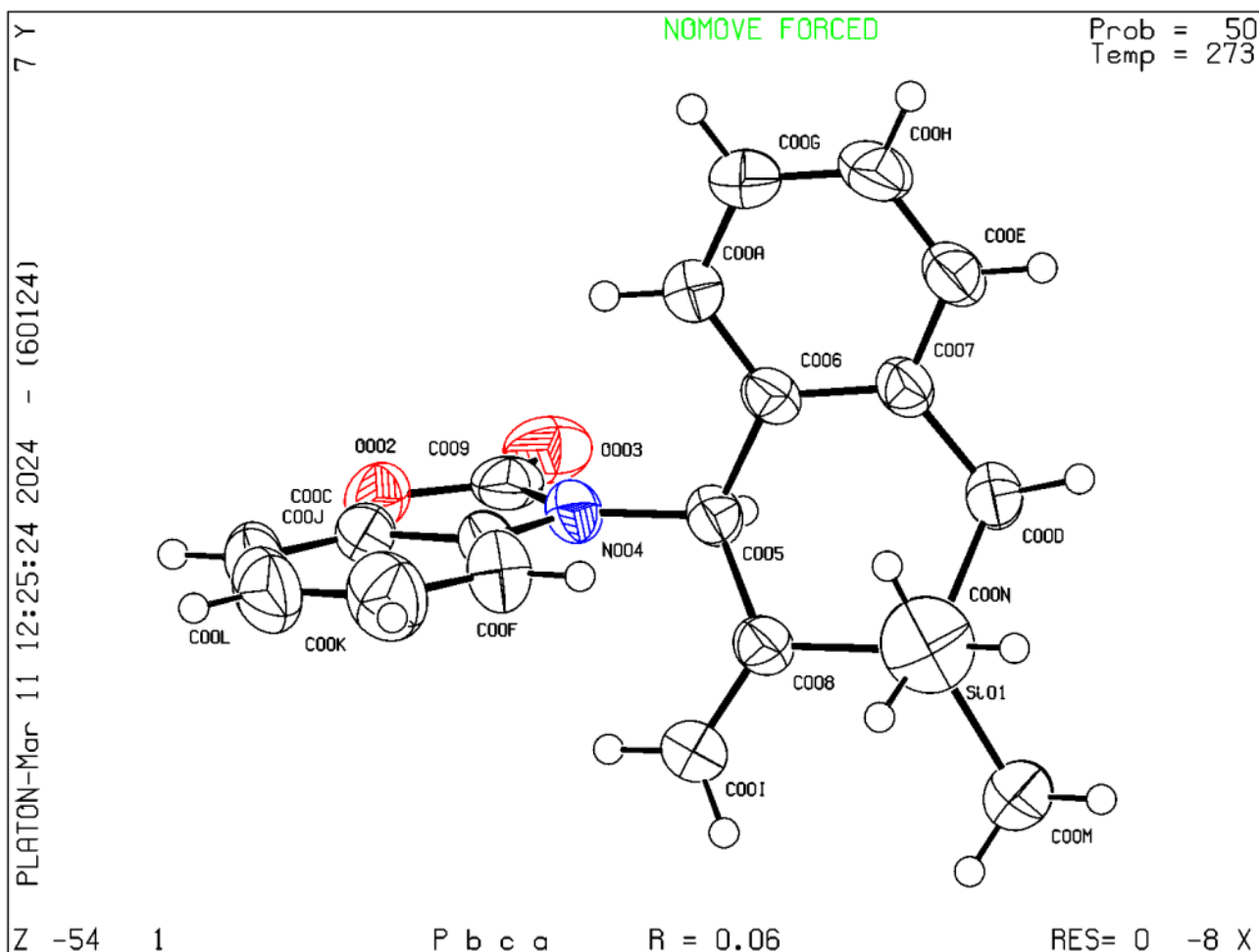
Theta(max)= 27.502

R(reflections)= 0.0562 ( 2321)

wR2(reflections)=  
0.1310 ( 4002)

S = 1.011

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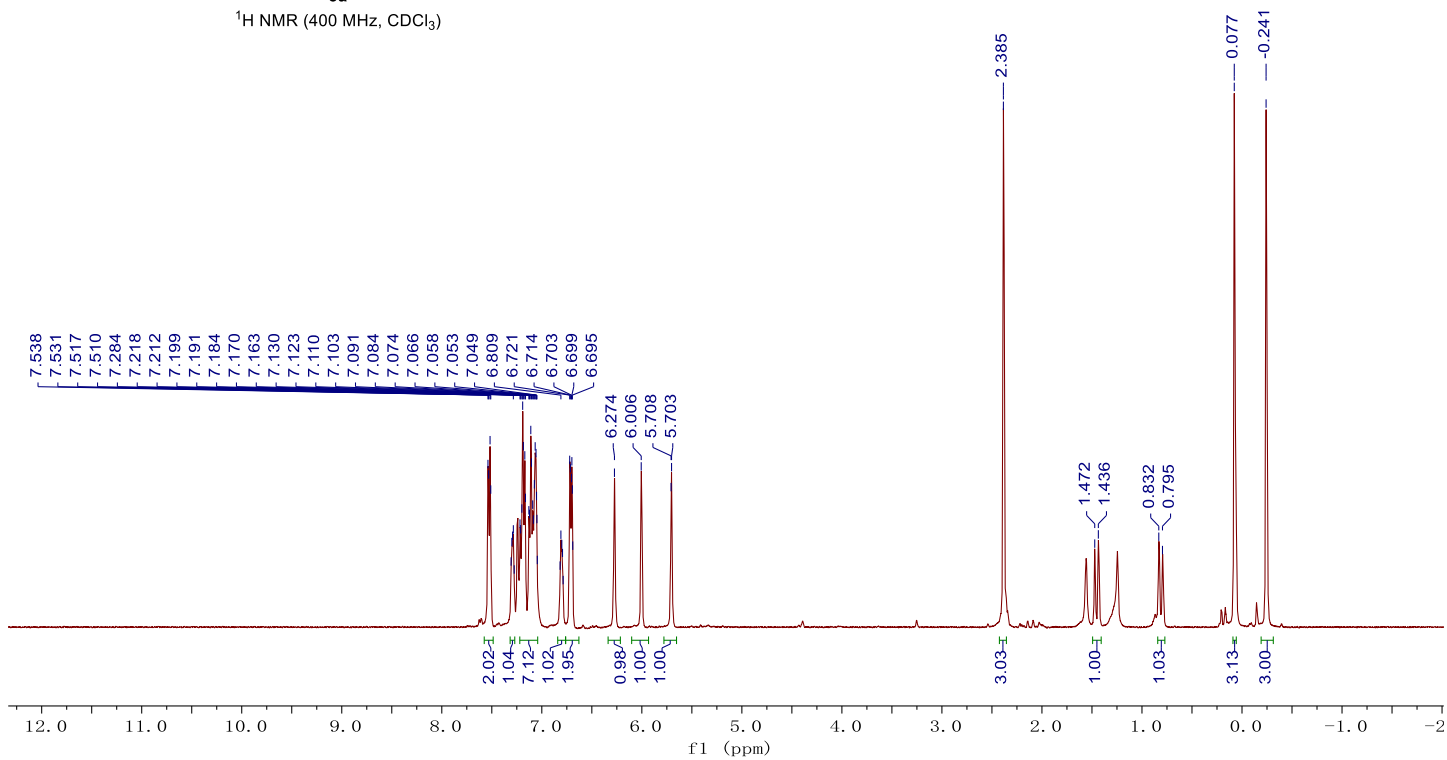
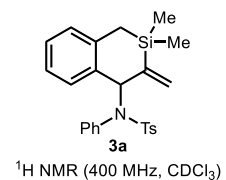


## Reference

1. Y. Sun, R. Lu, H. Zhou, T. Chen, L. Gao, J. Zhang and Y. Wang, *ACS Catal.* 2026, **16**, 8022–8031.

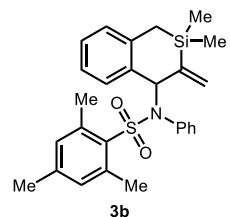
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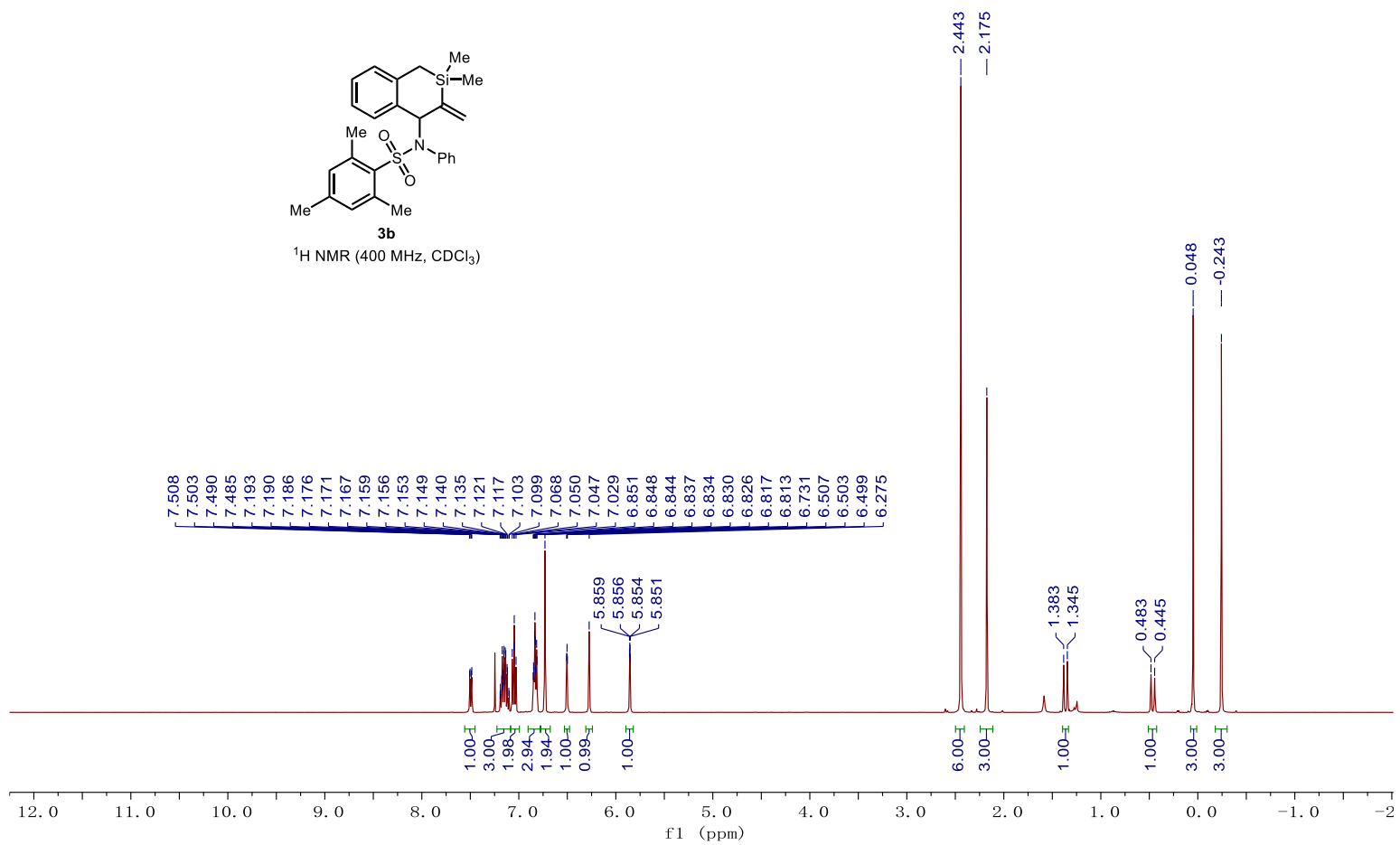




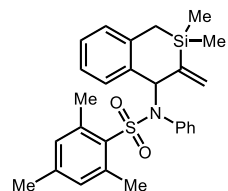
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<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

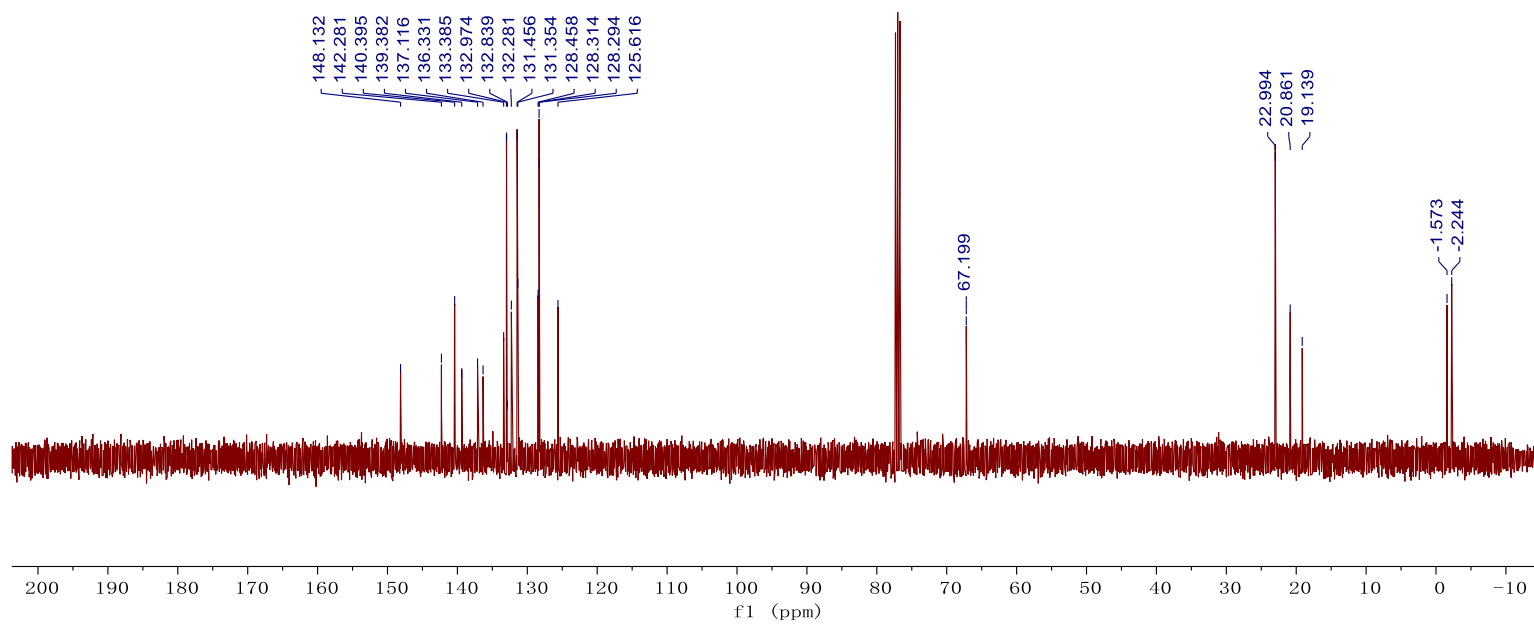


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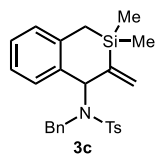


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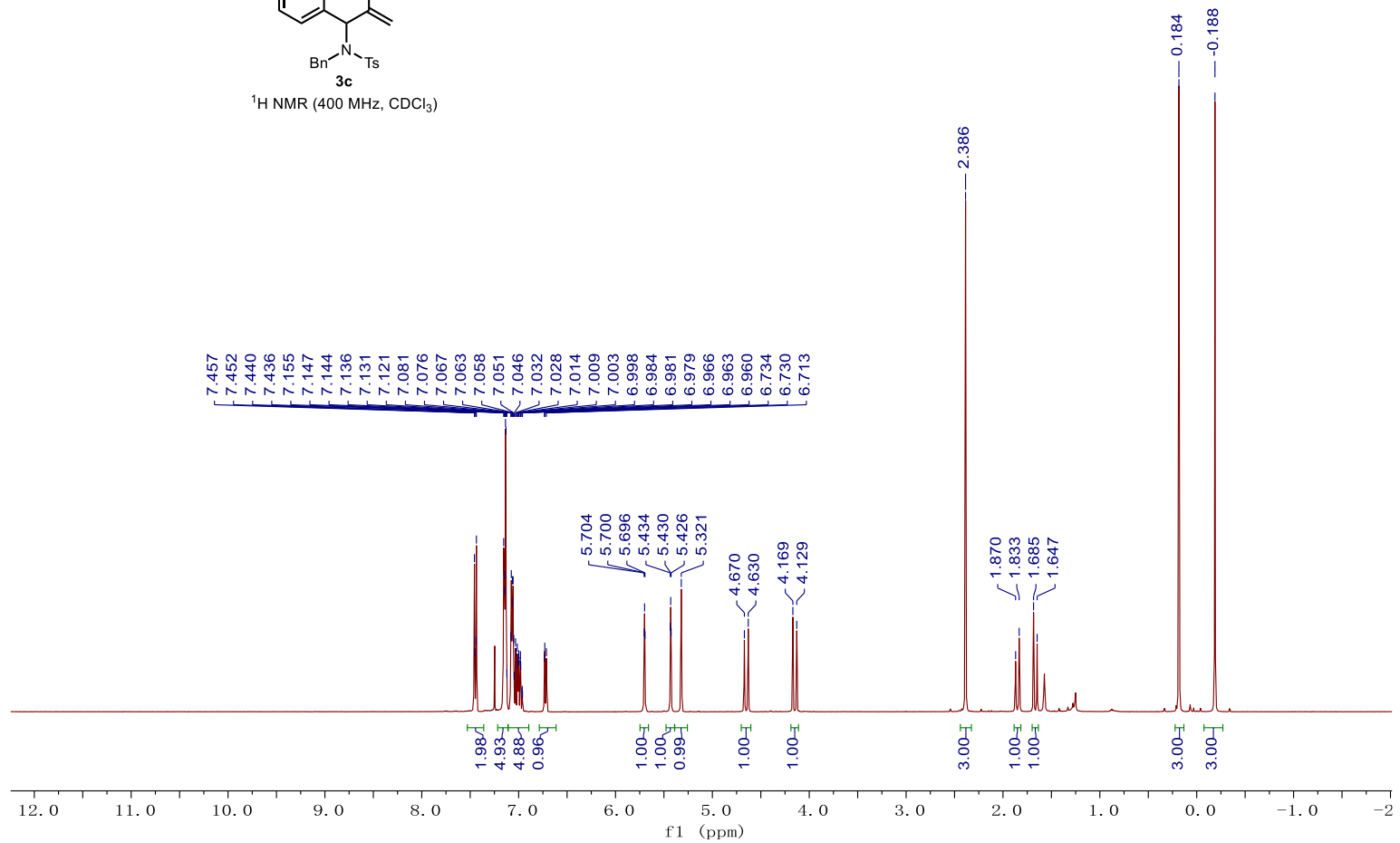
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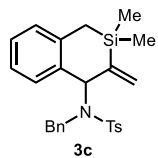
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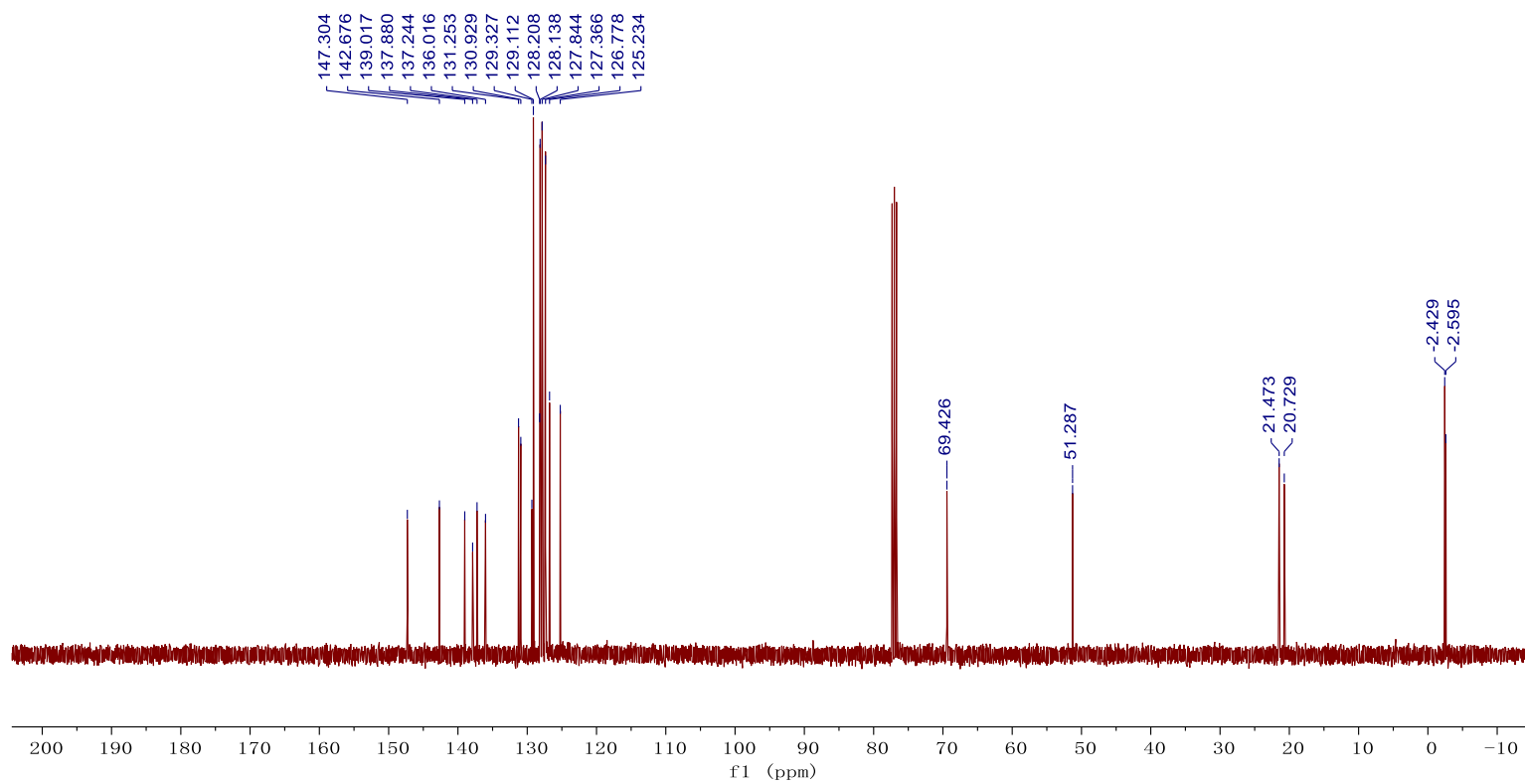
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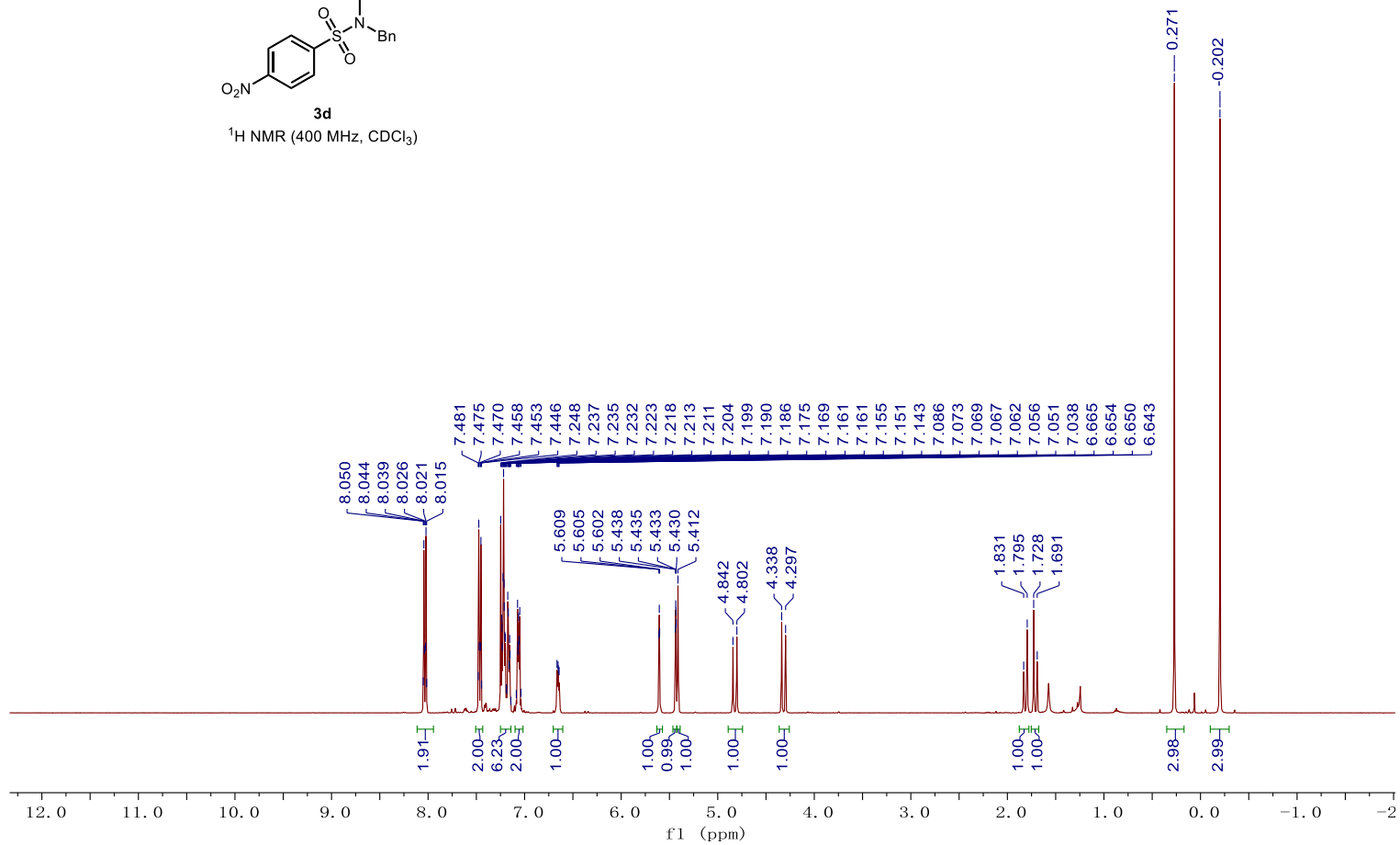
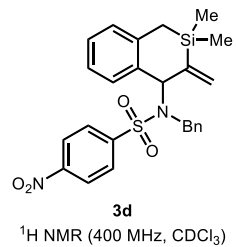
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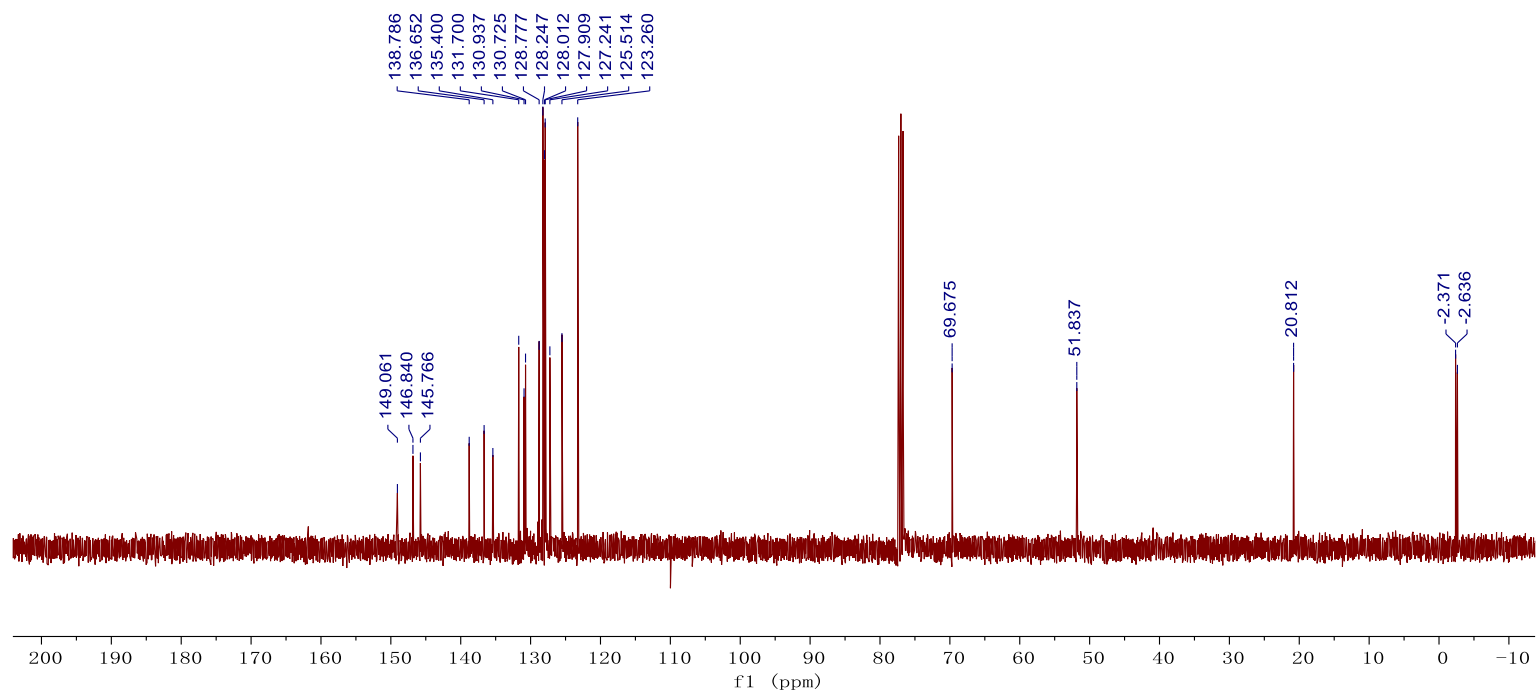
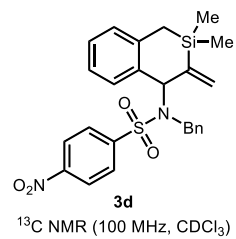
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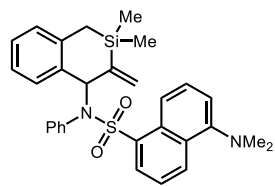
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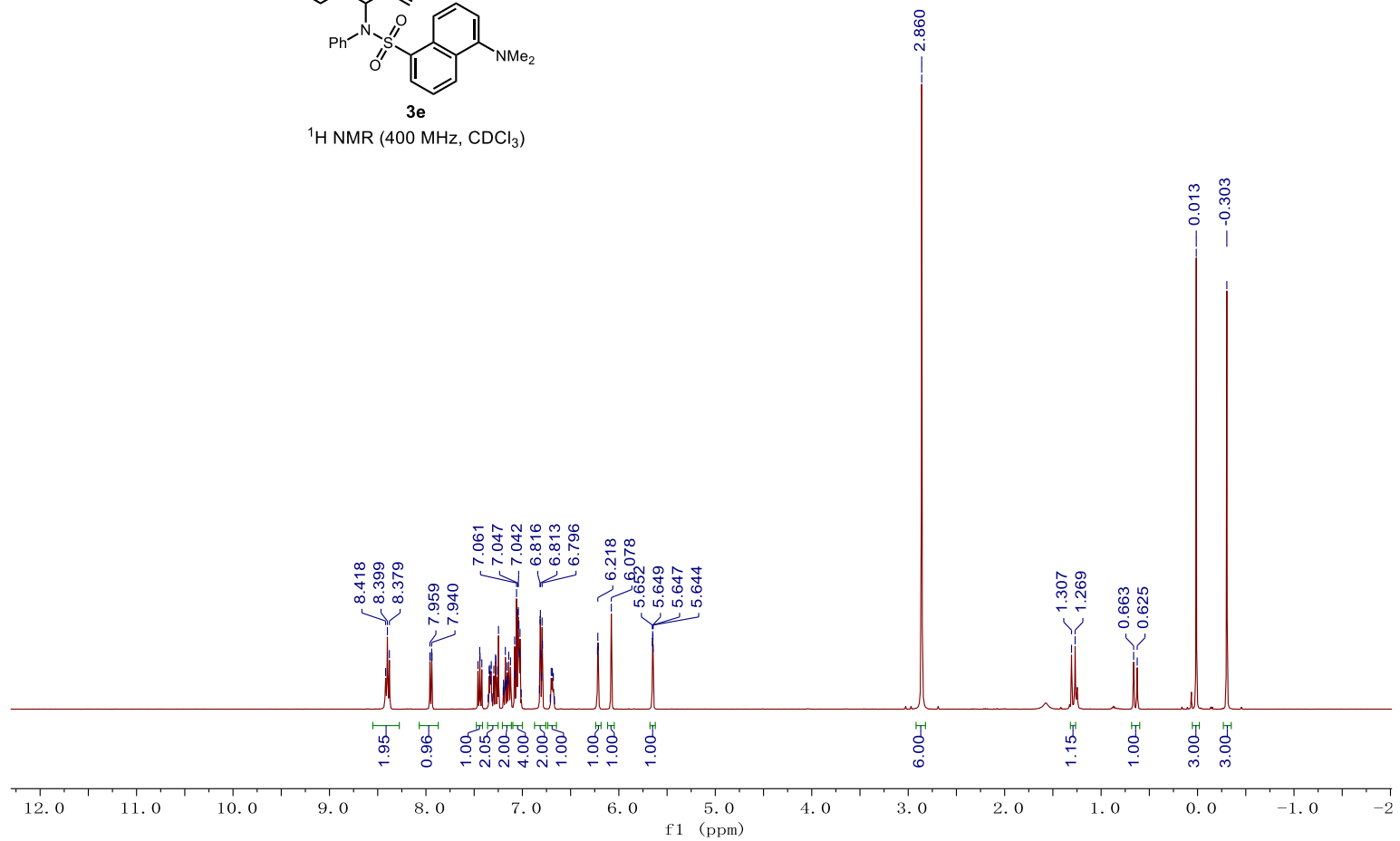
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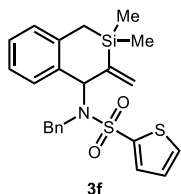
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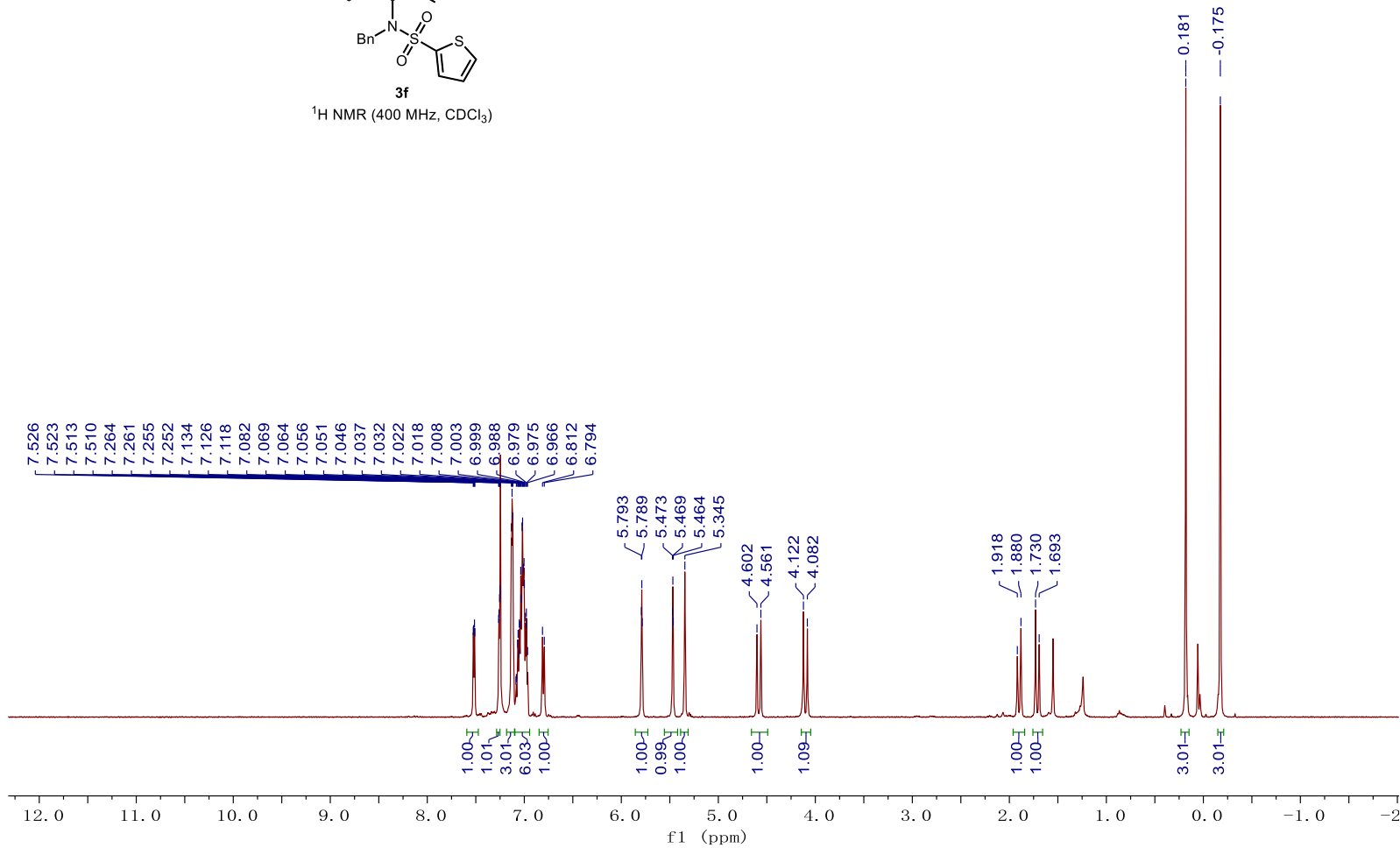
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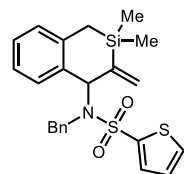
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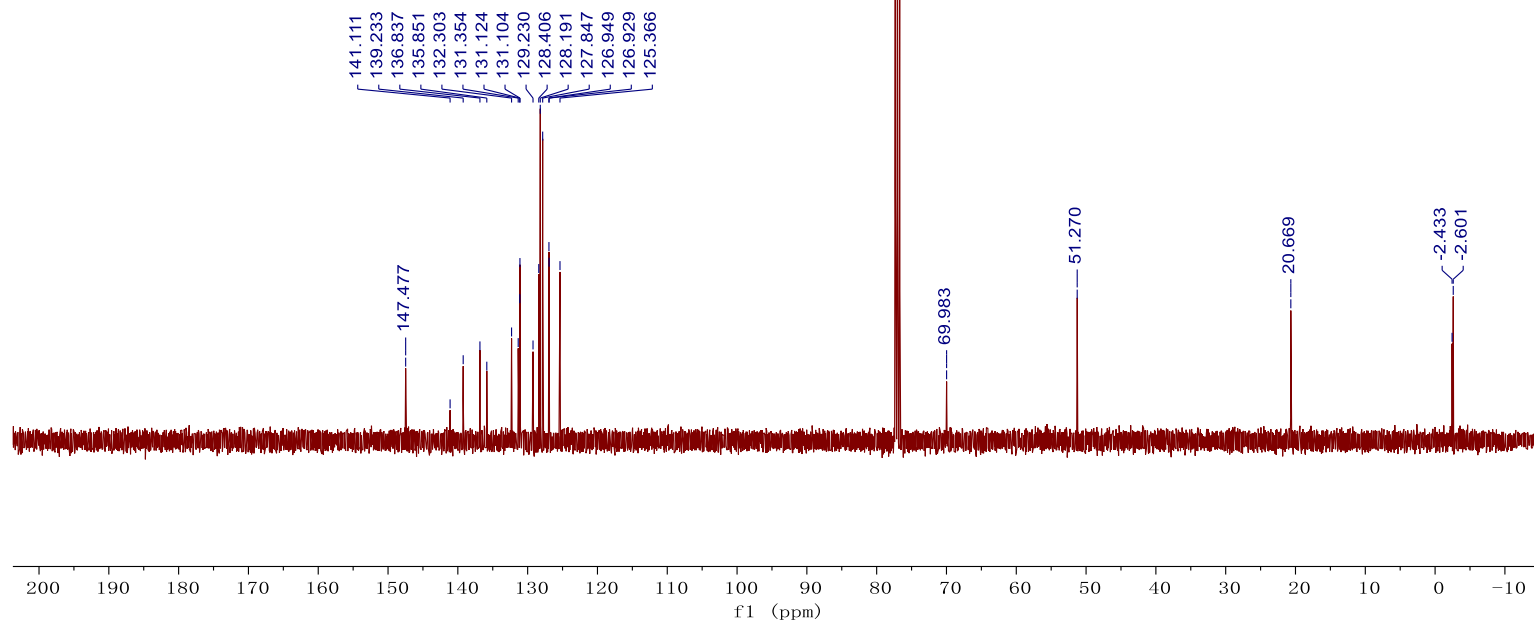


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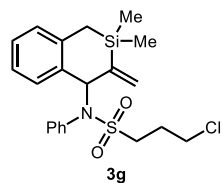


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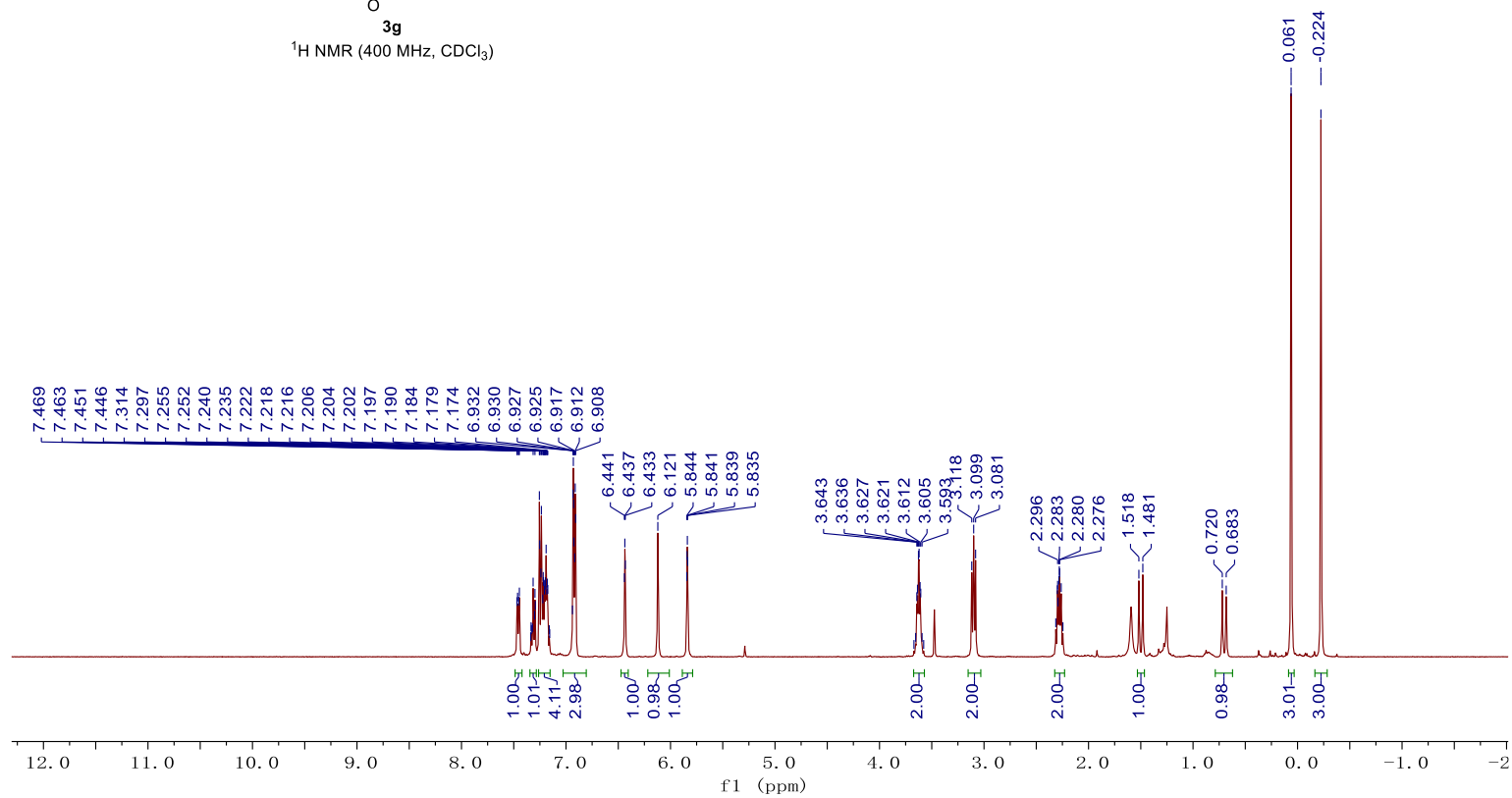
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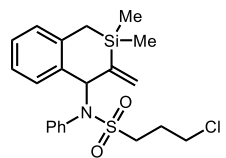
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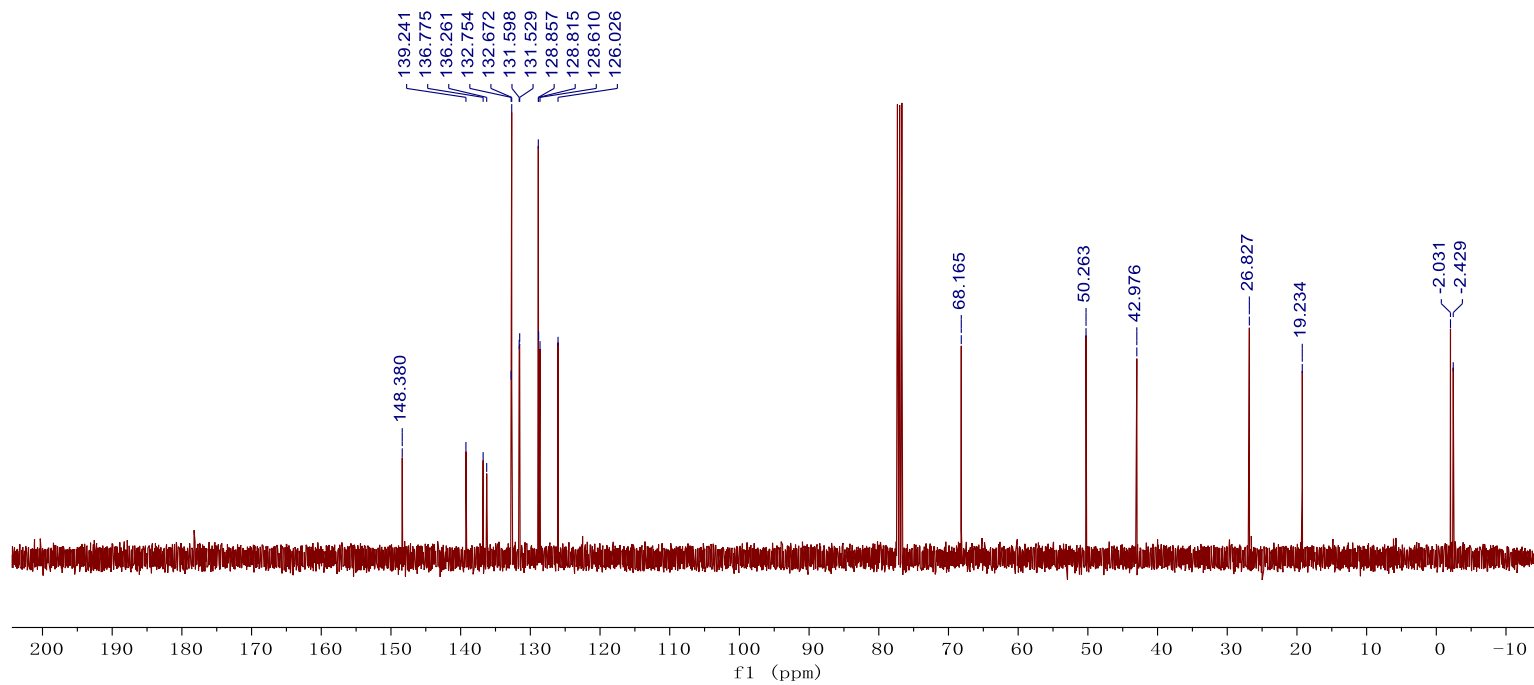
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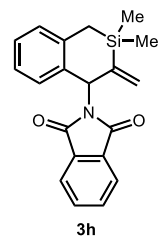
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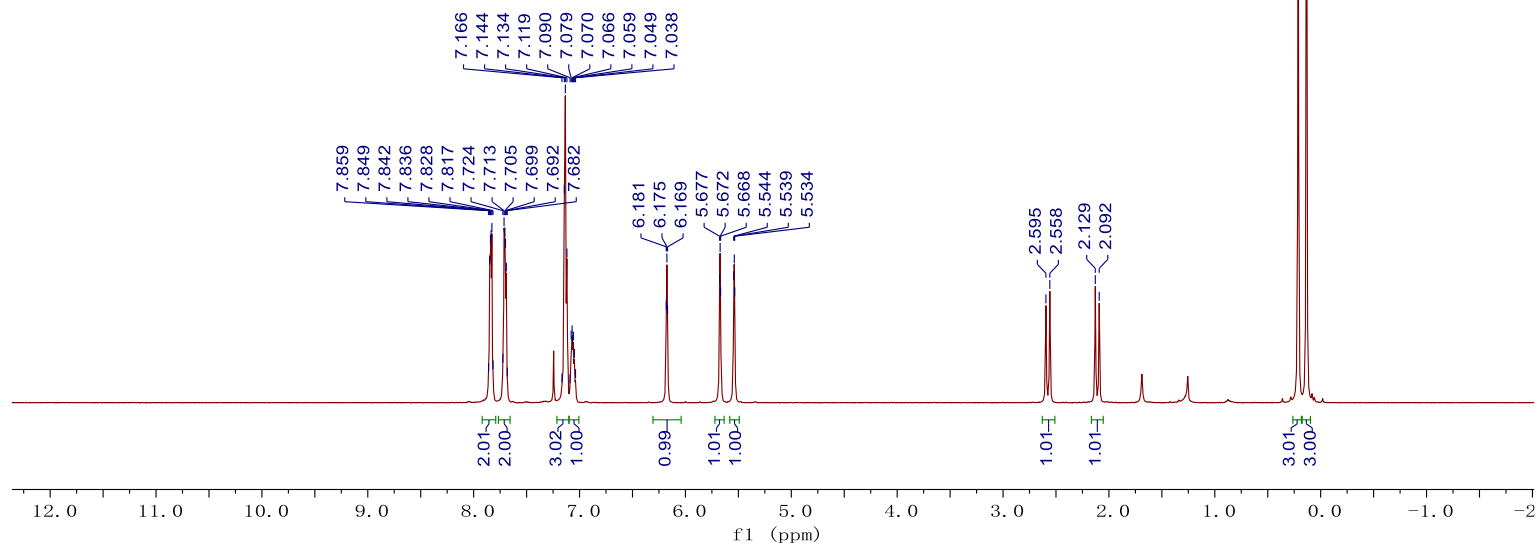
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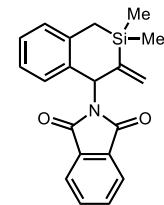
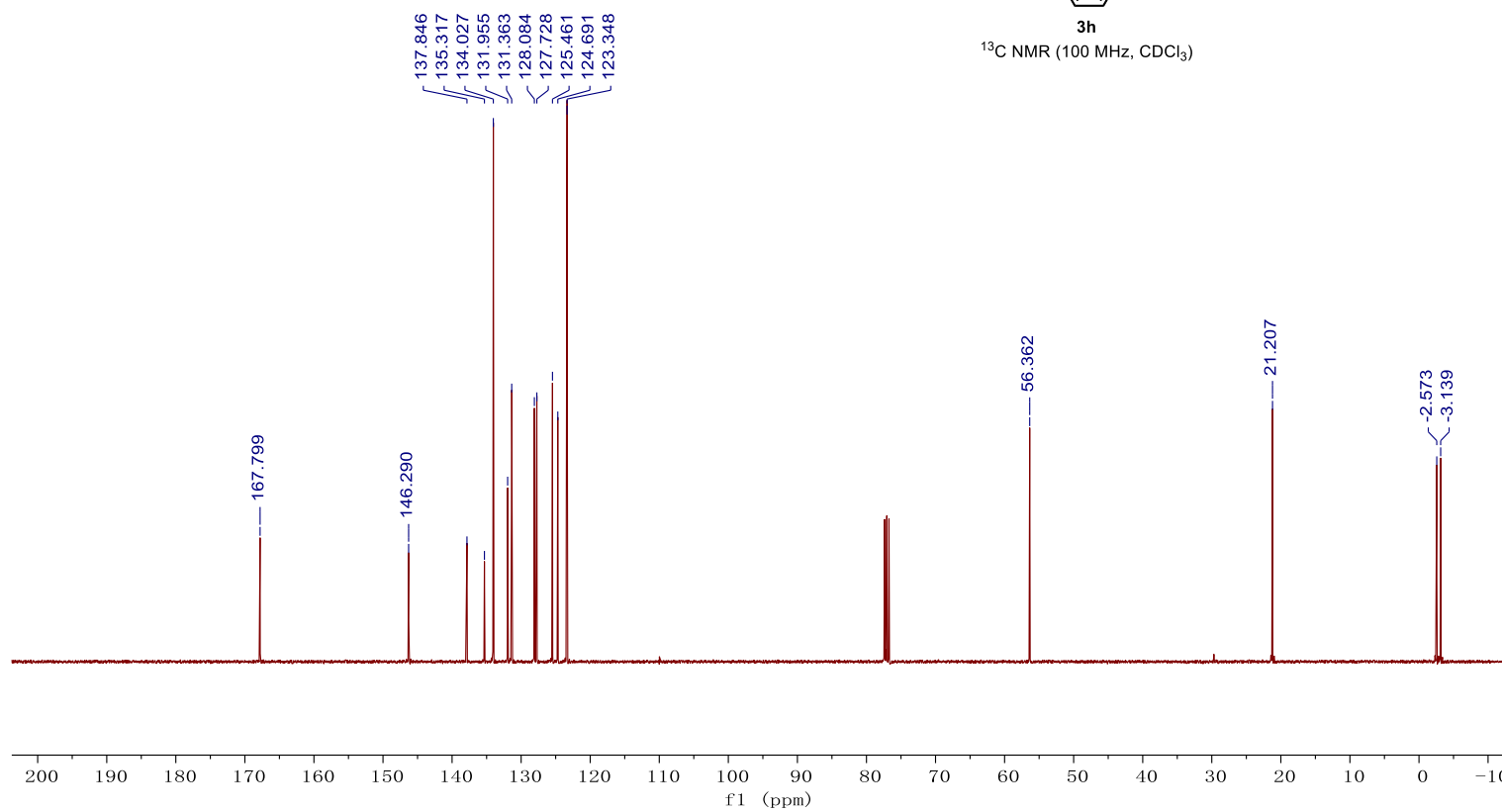
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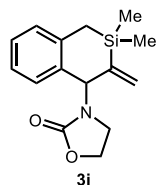
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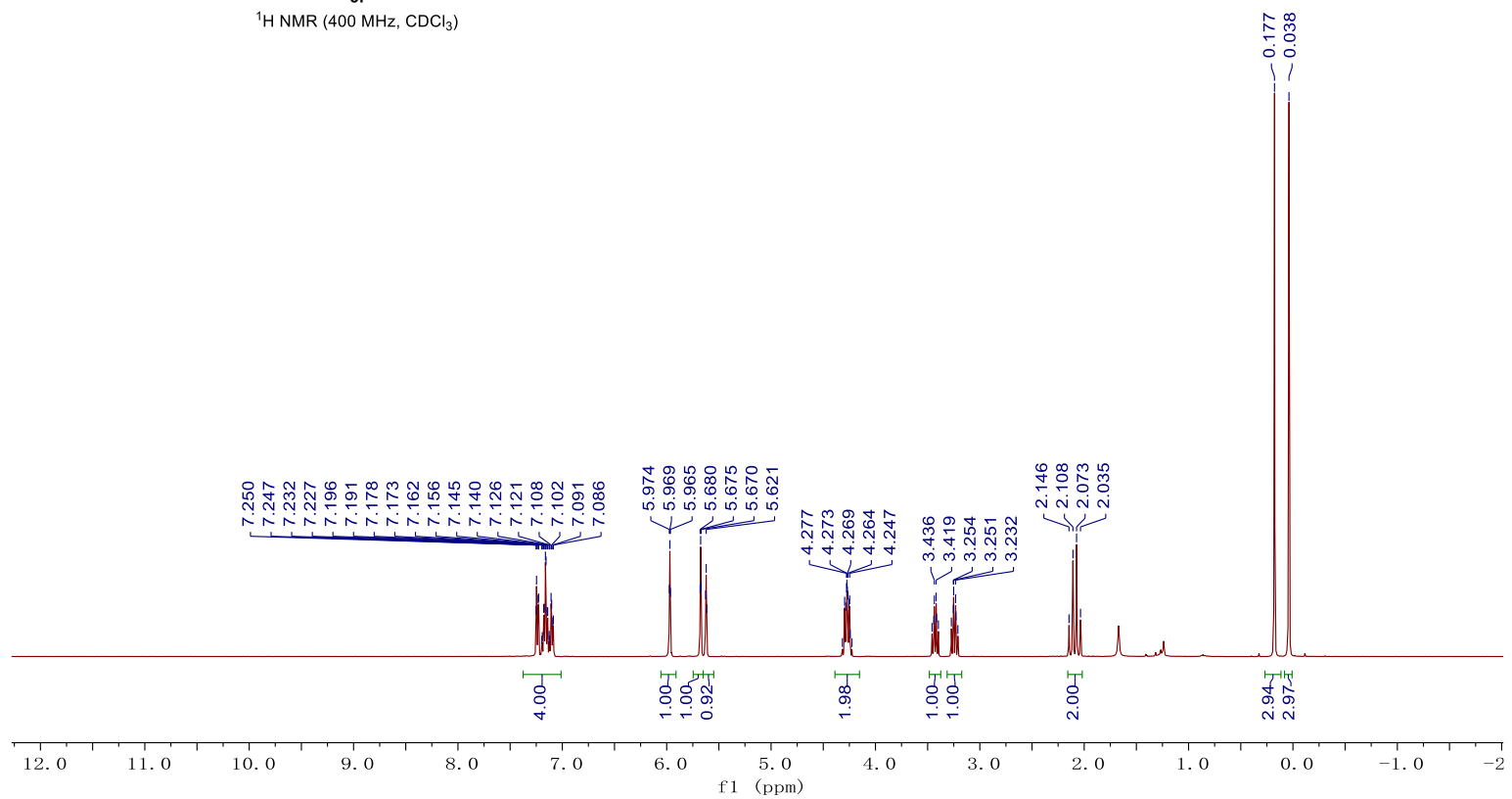
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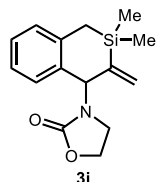
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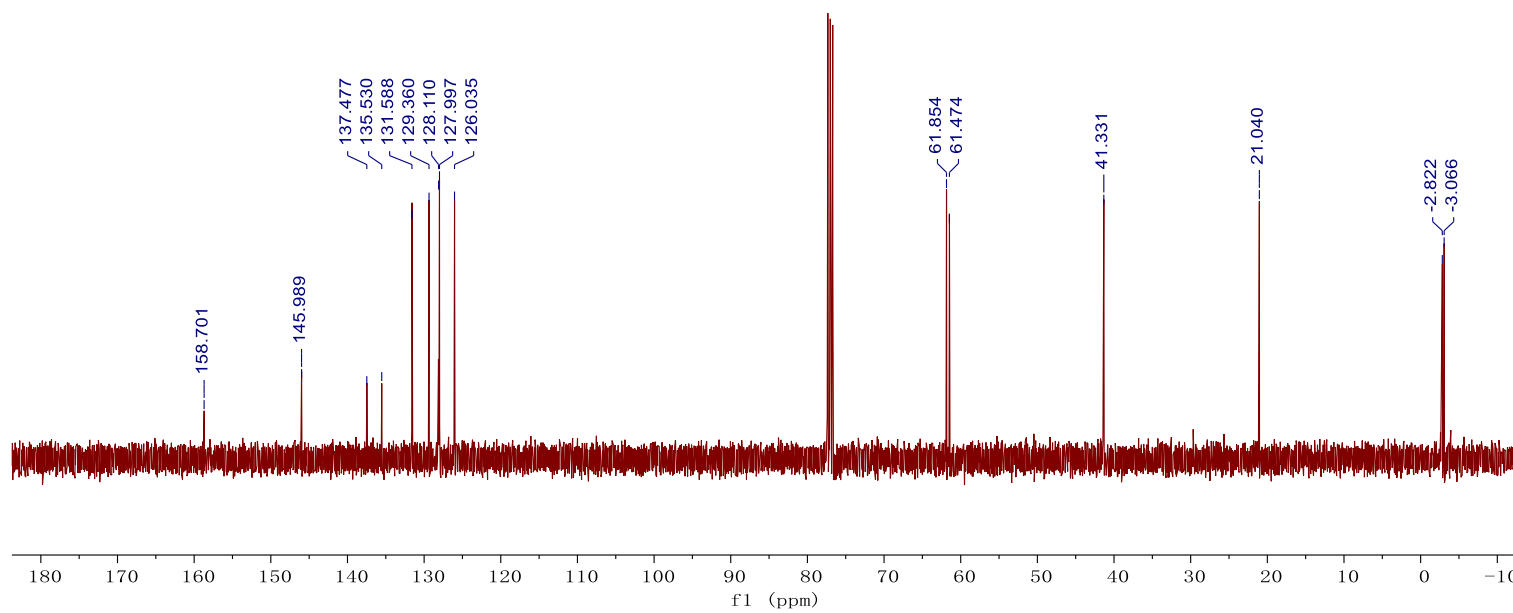
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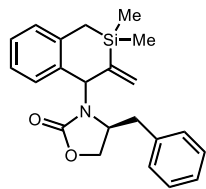
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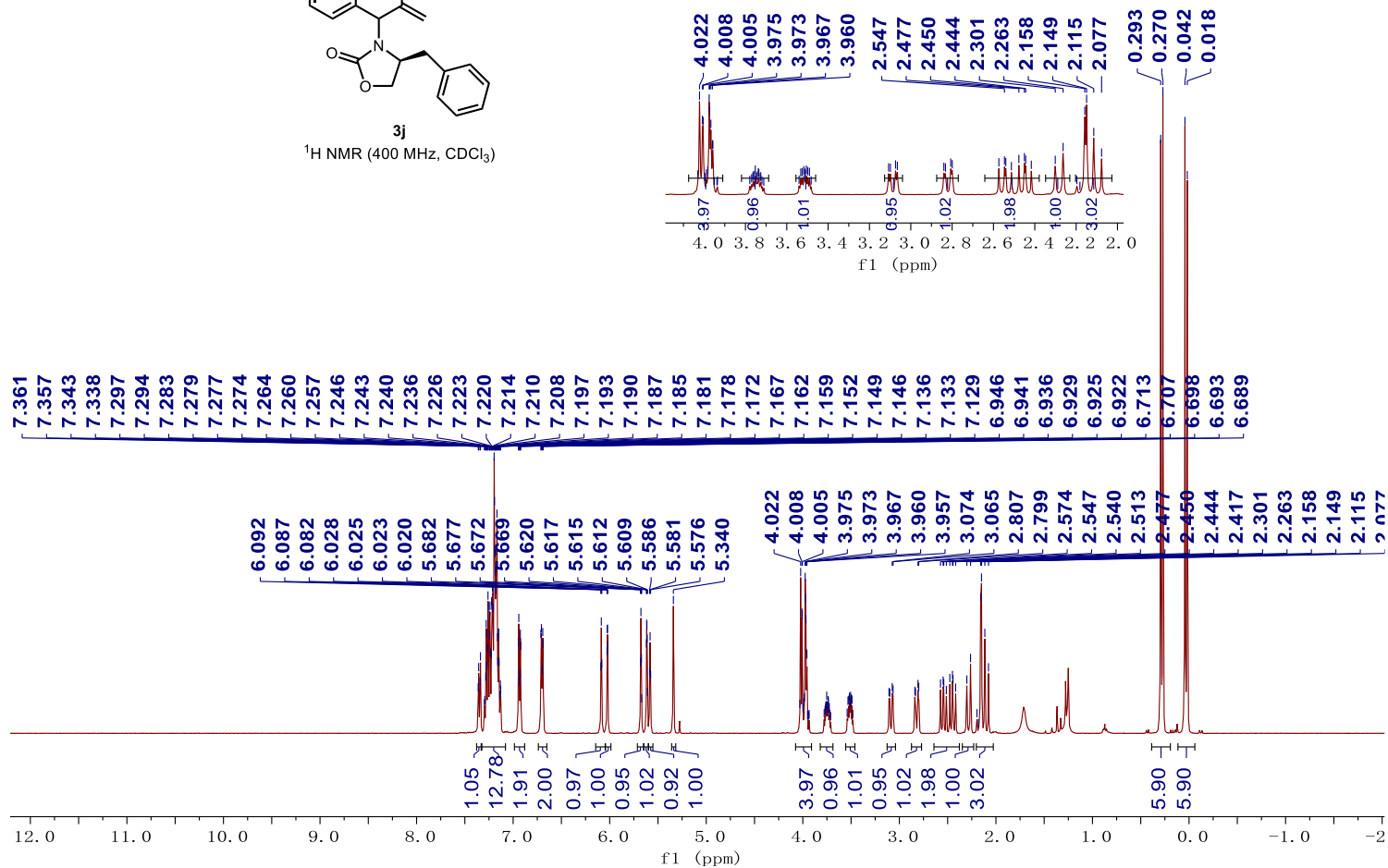
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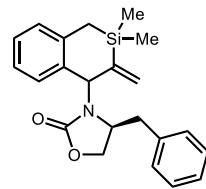
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3j  
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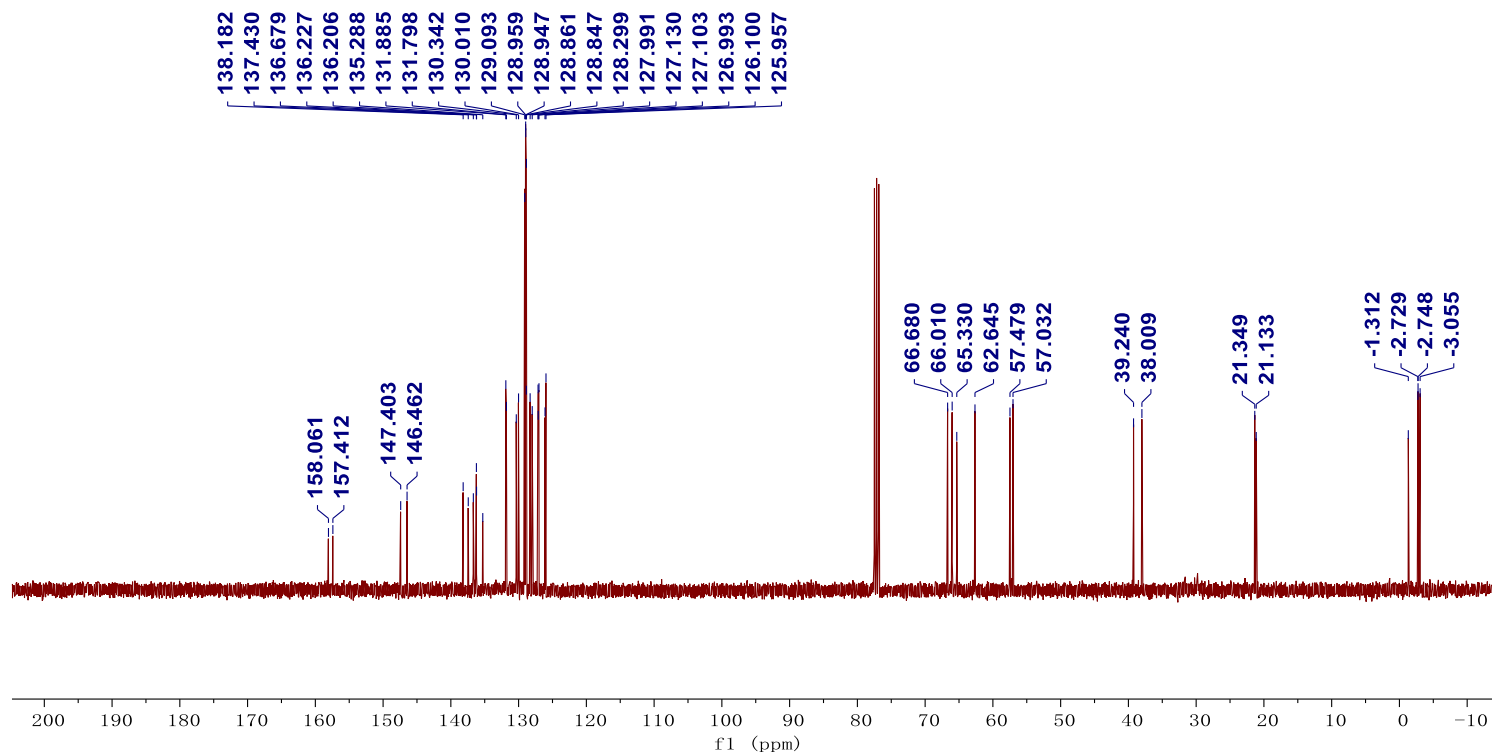


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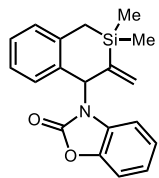


3j

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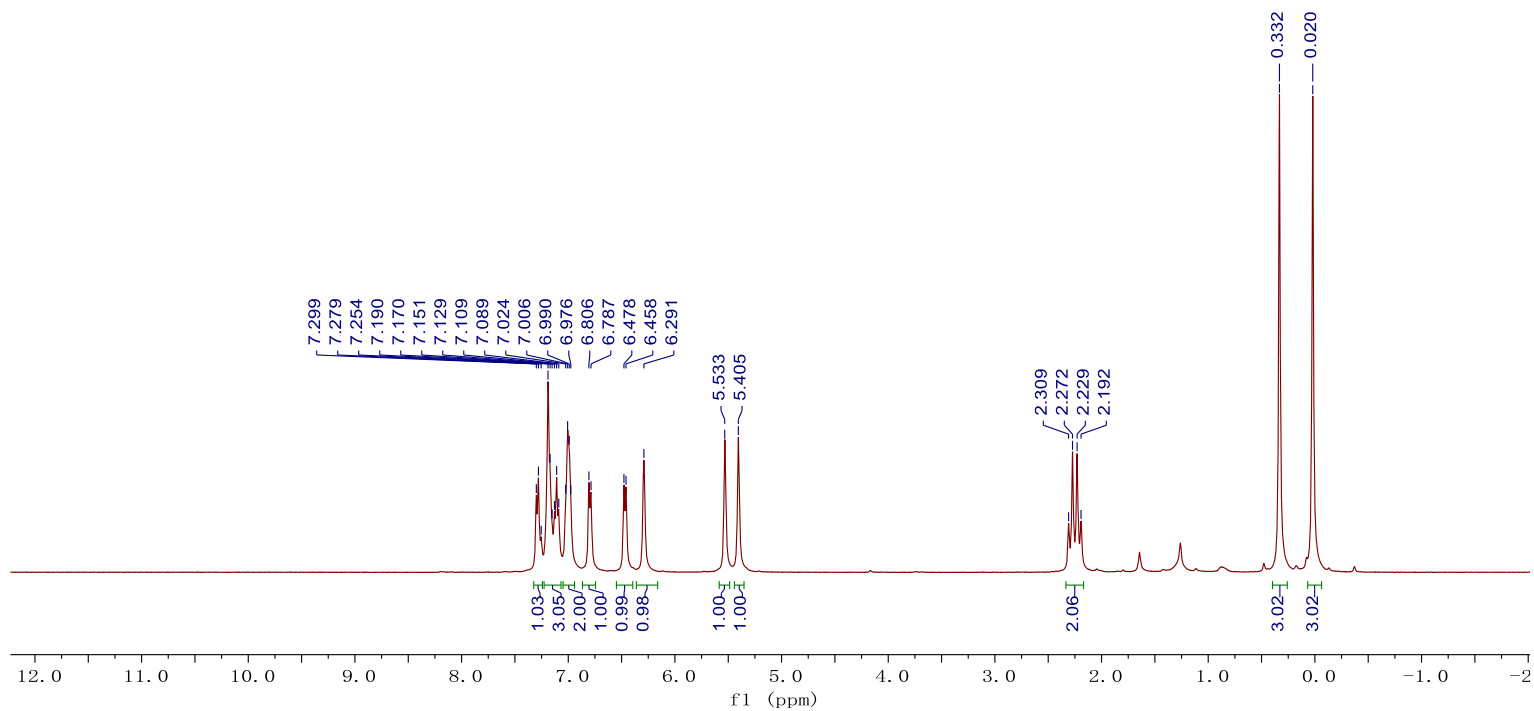


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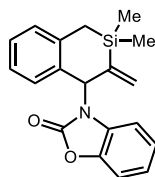


**3k**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

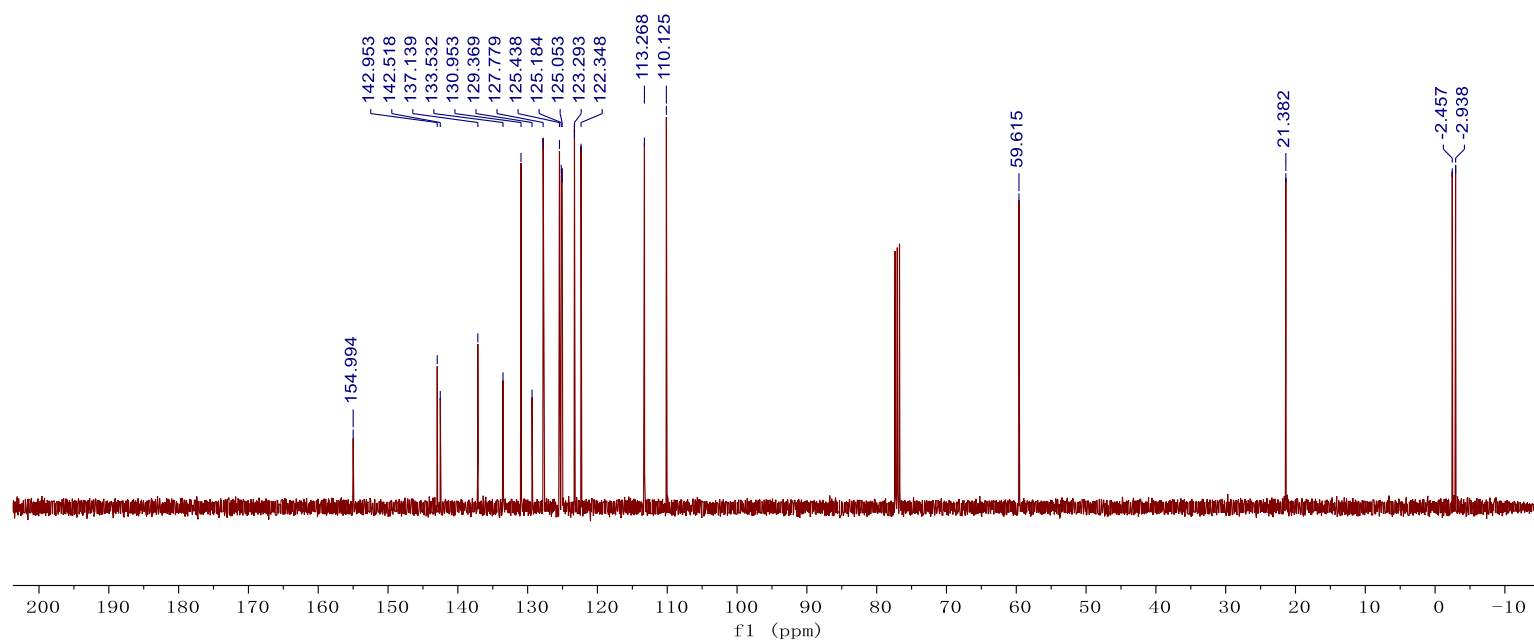


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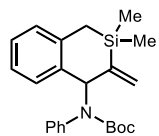


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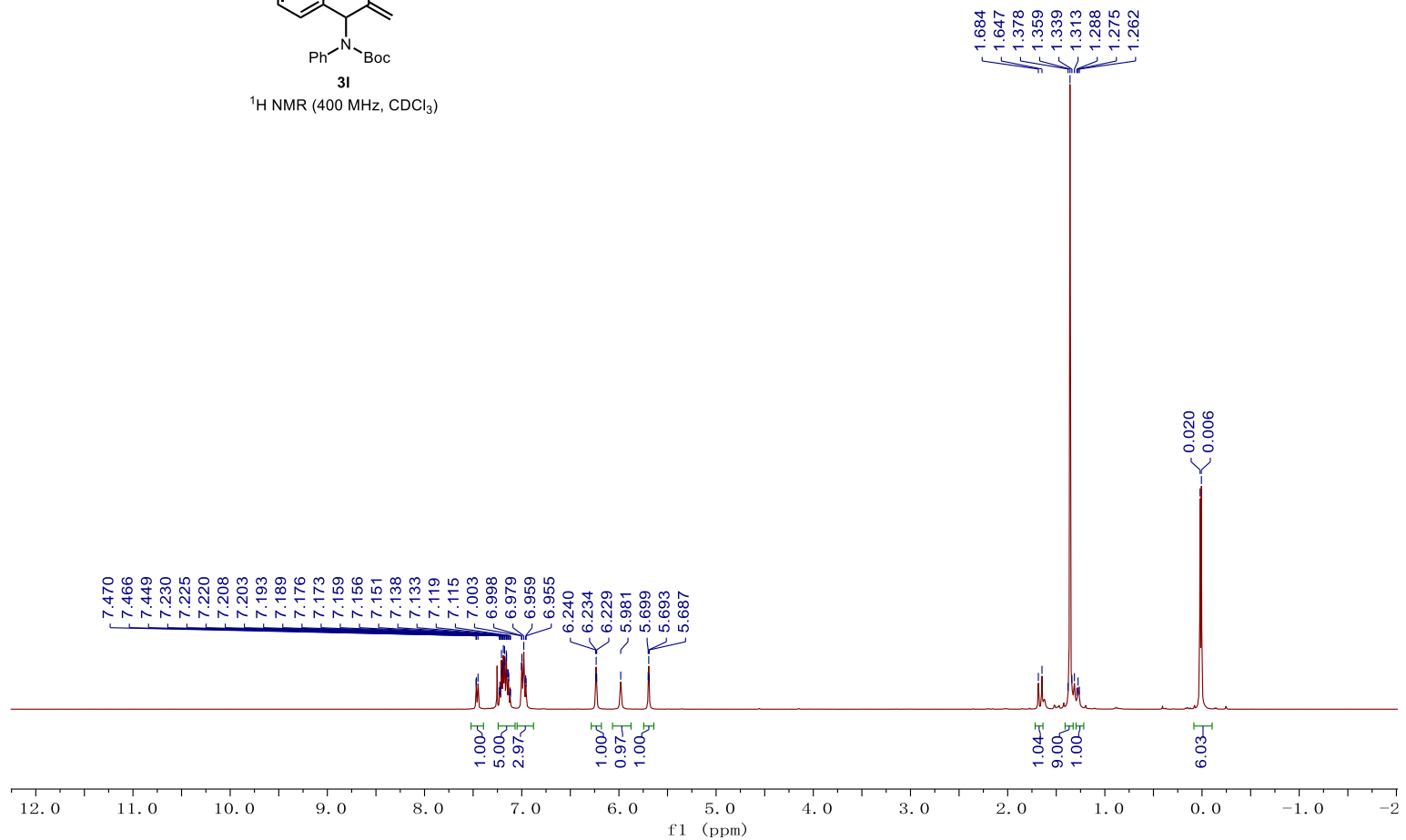
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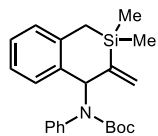
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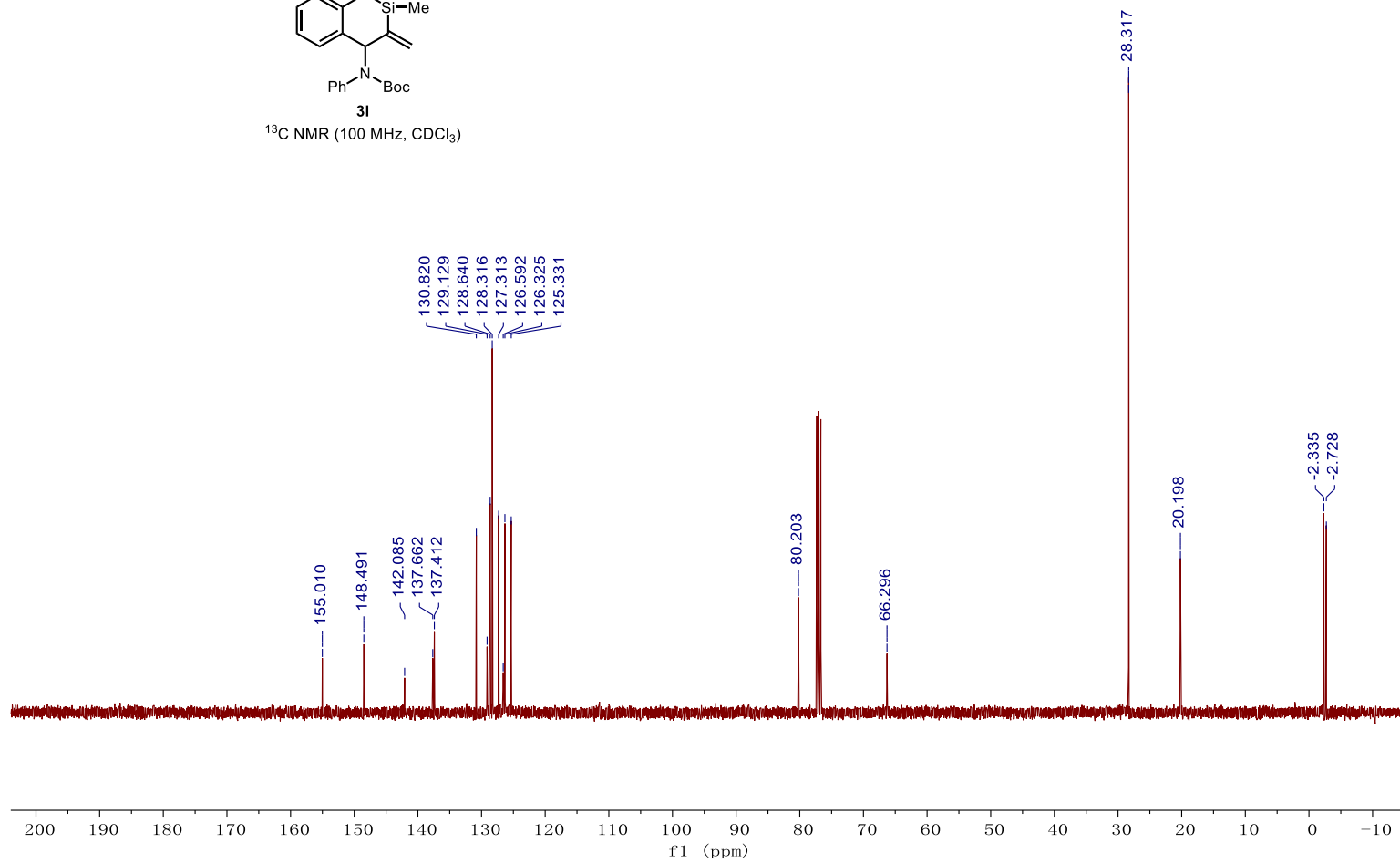
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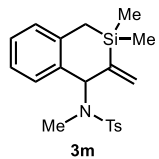
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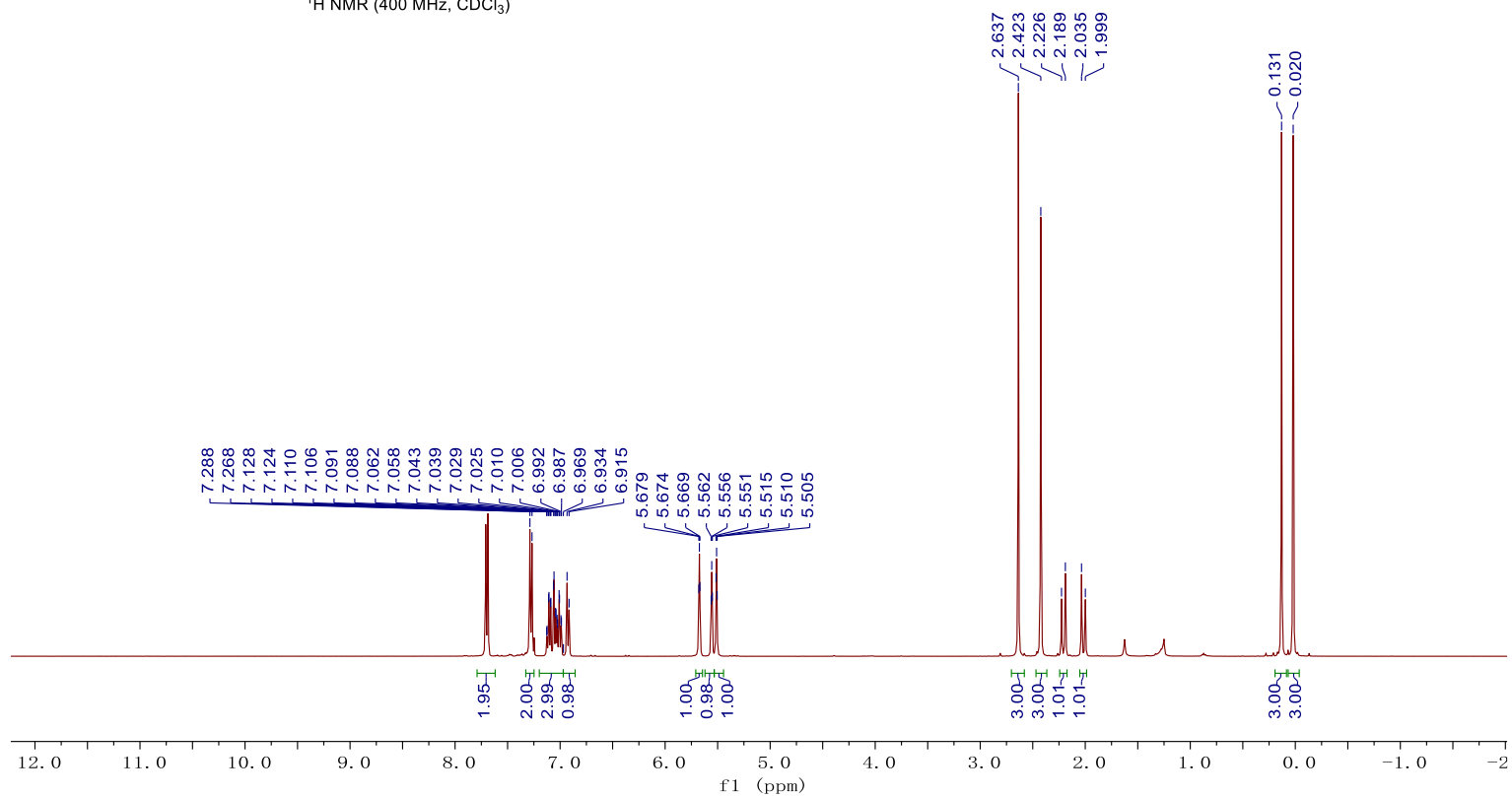
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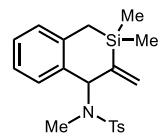
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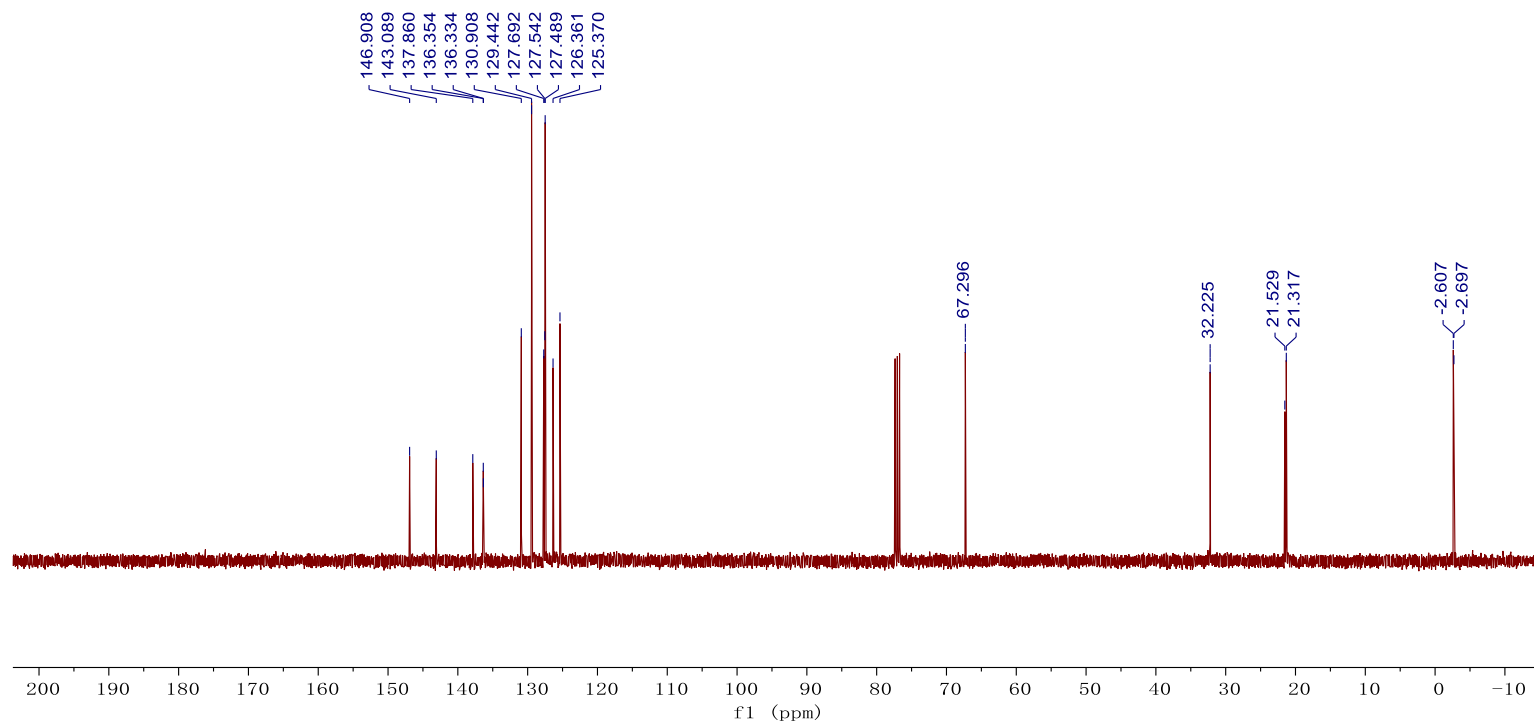
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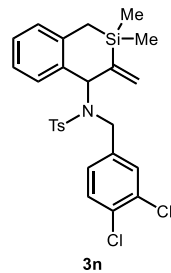
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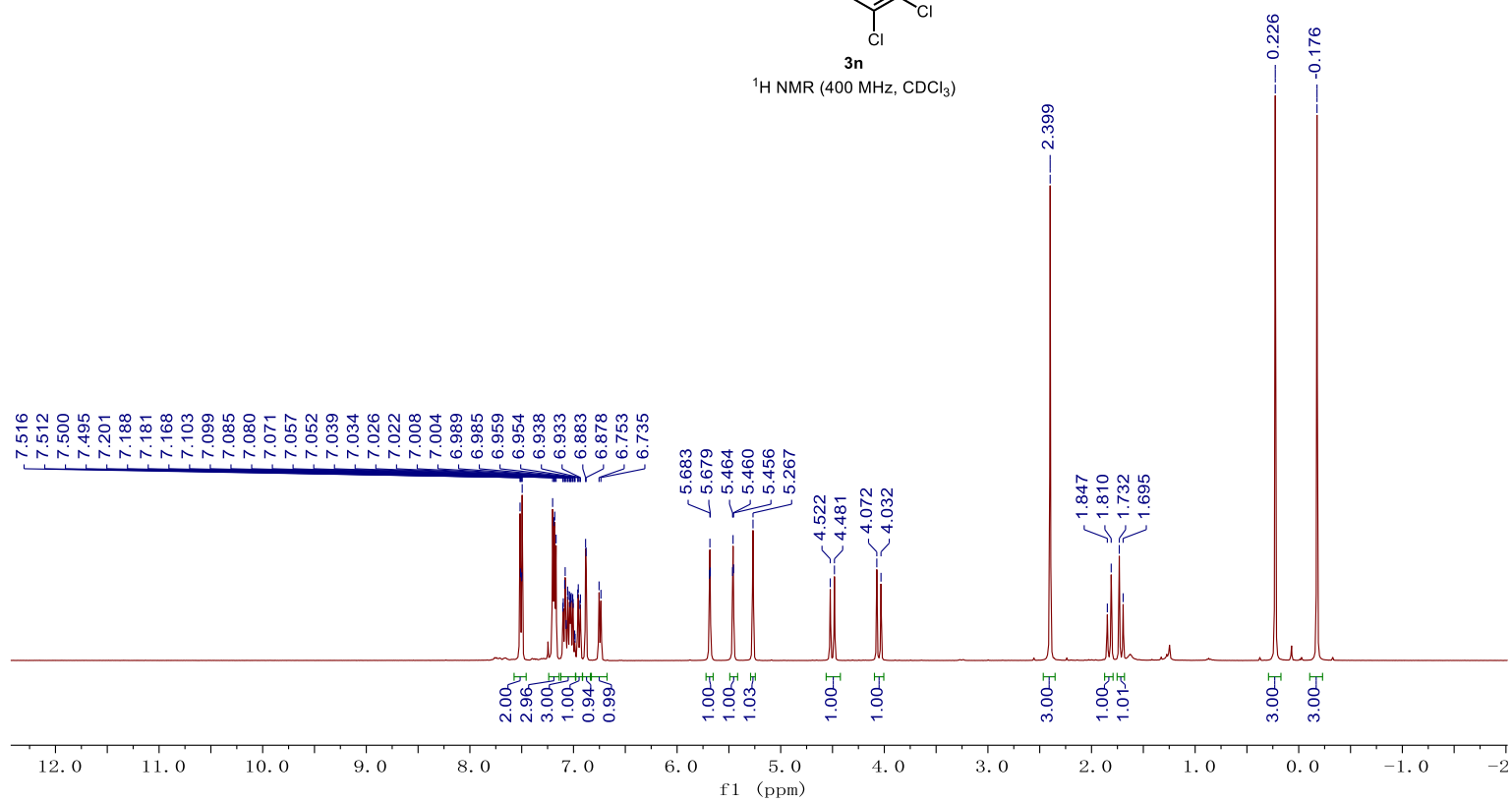
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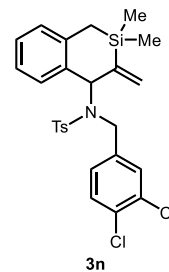
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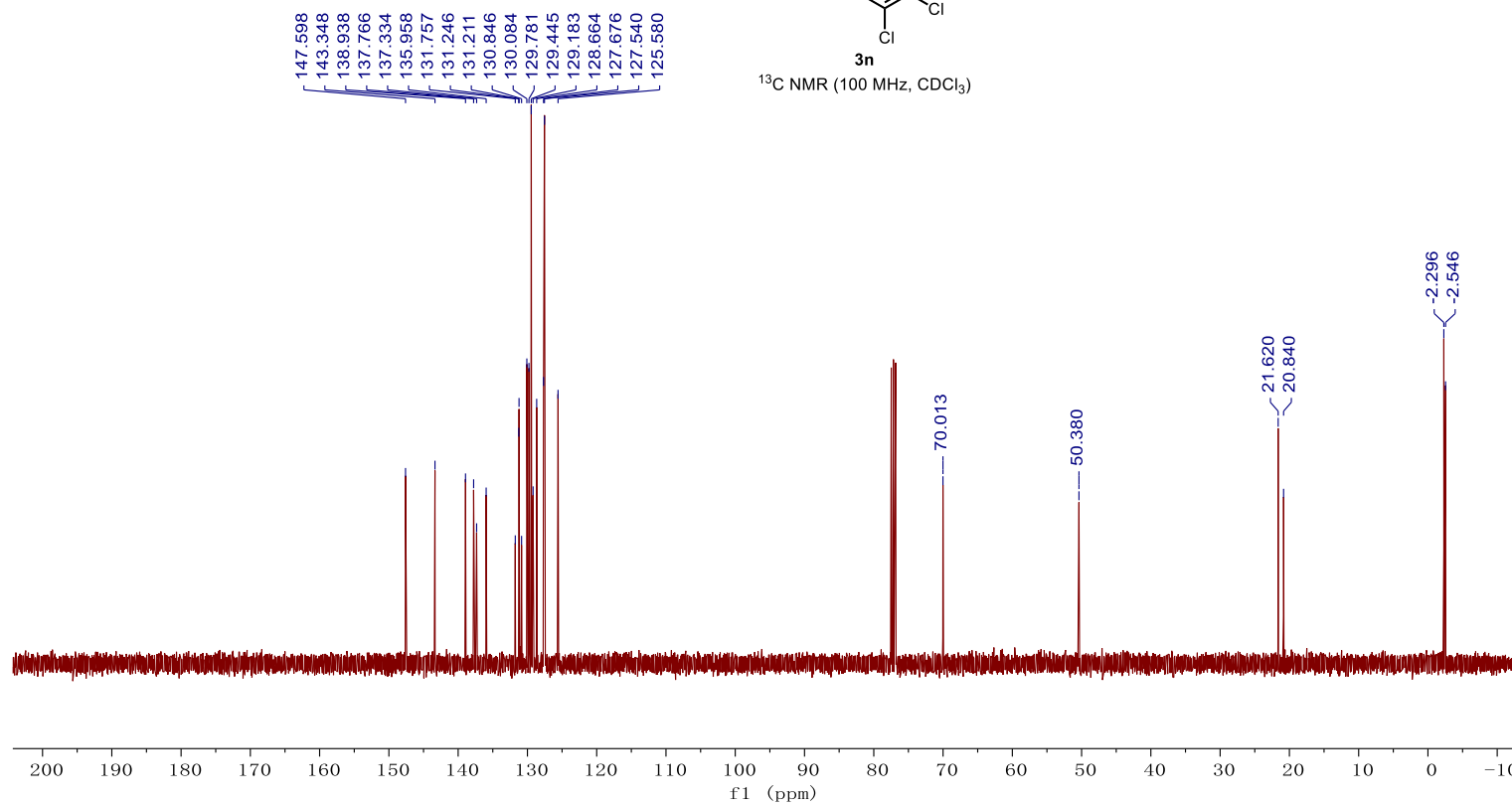
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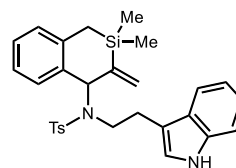


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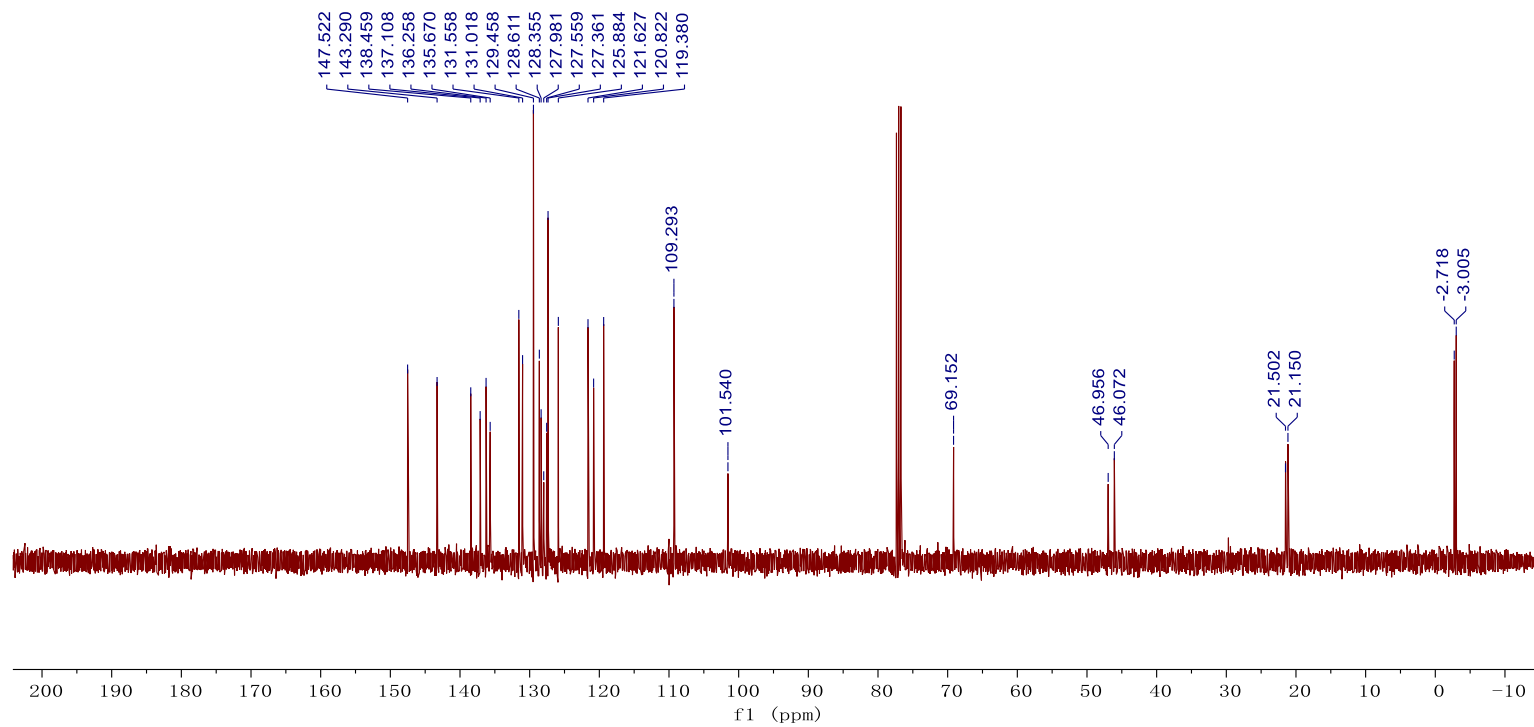




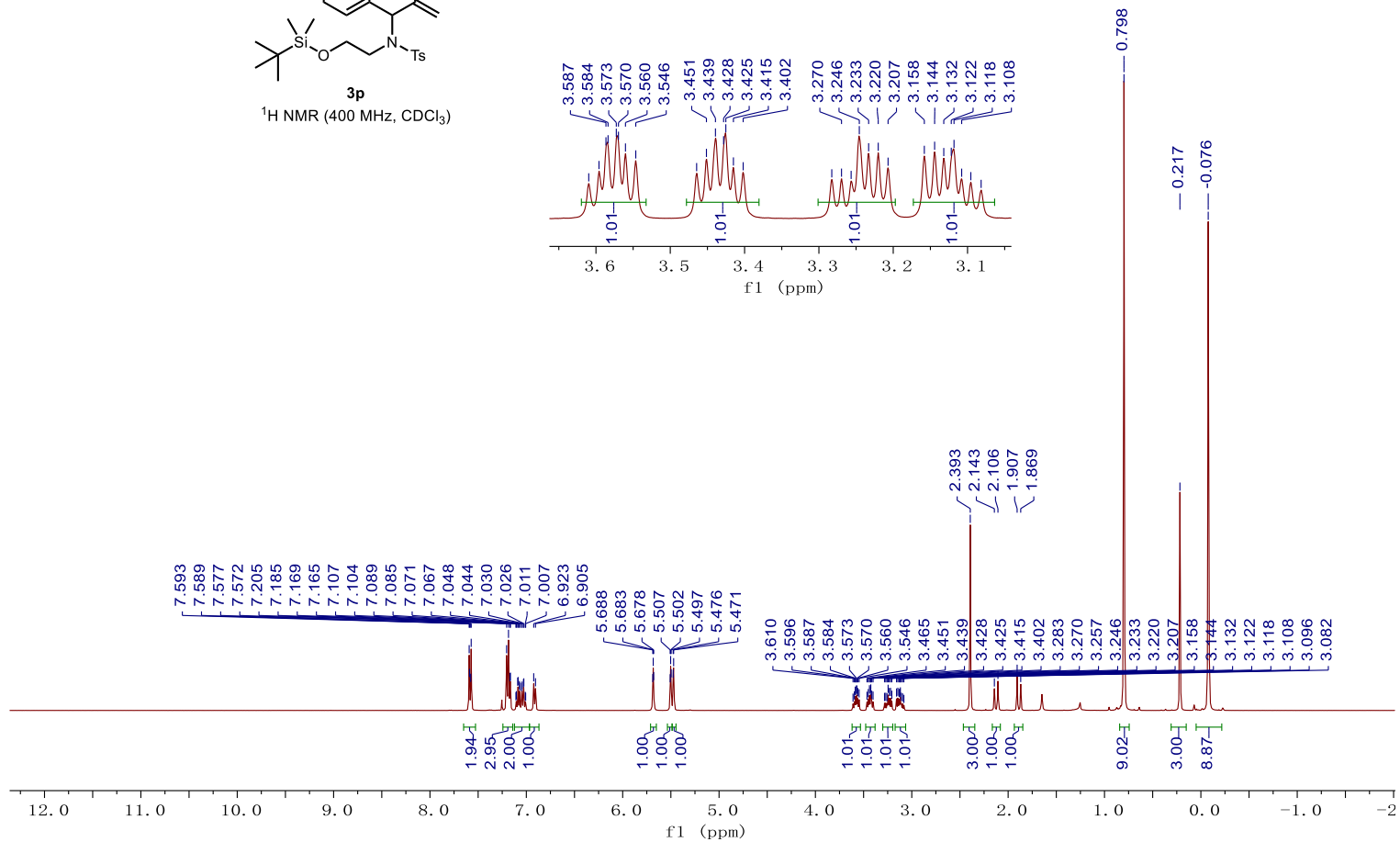
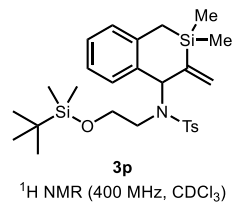
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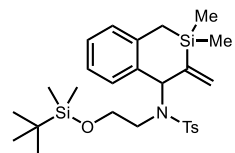
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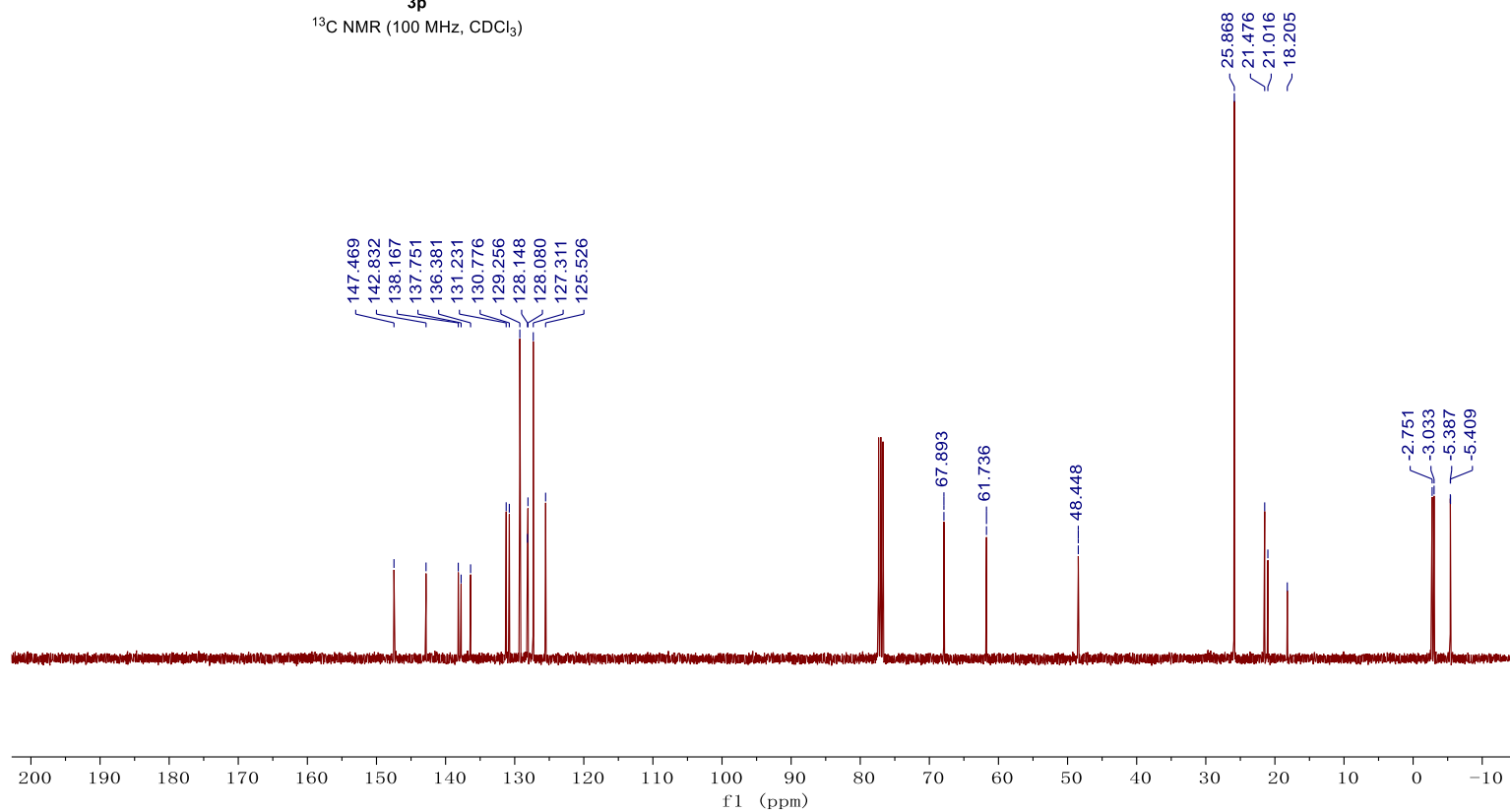
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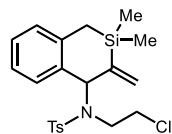


**3p**  
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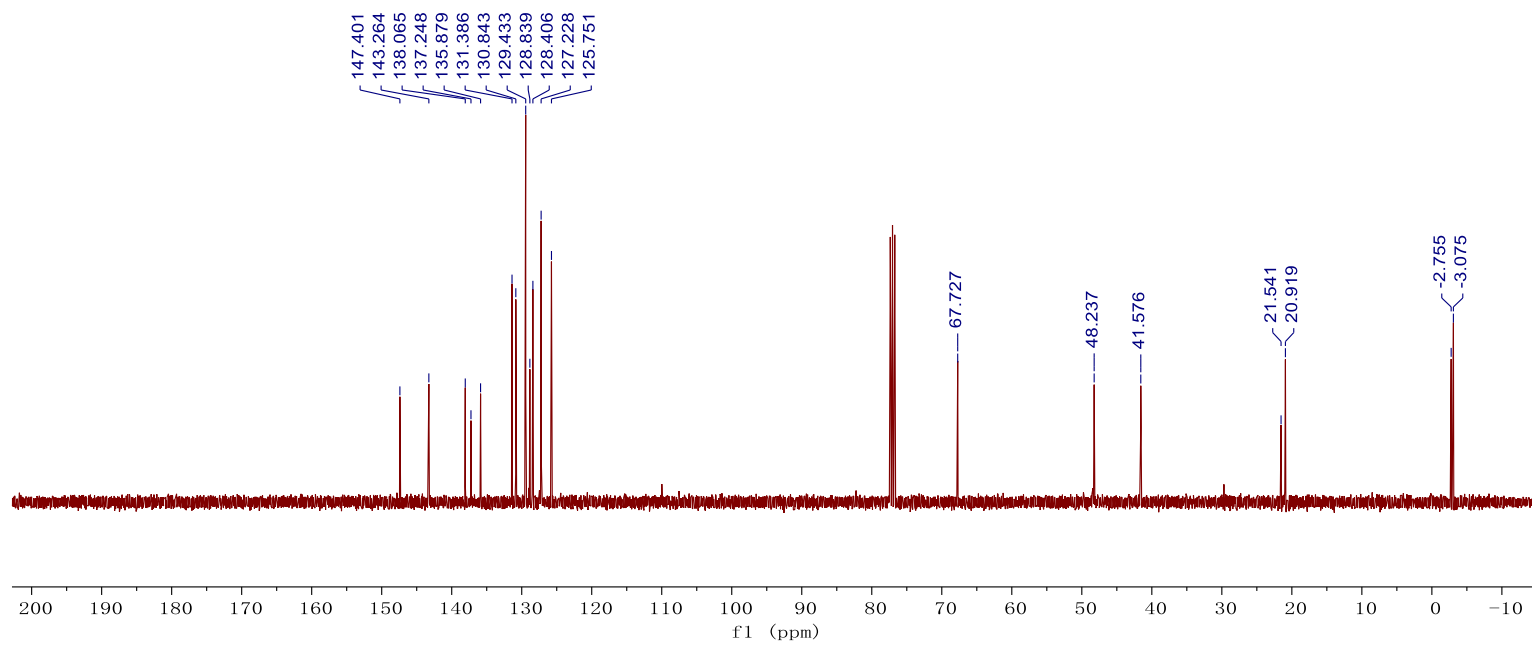


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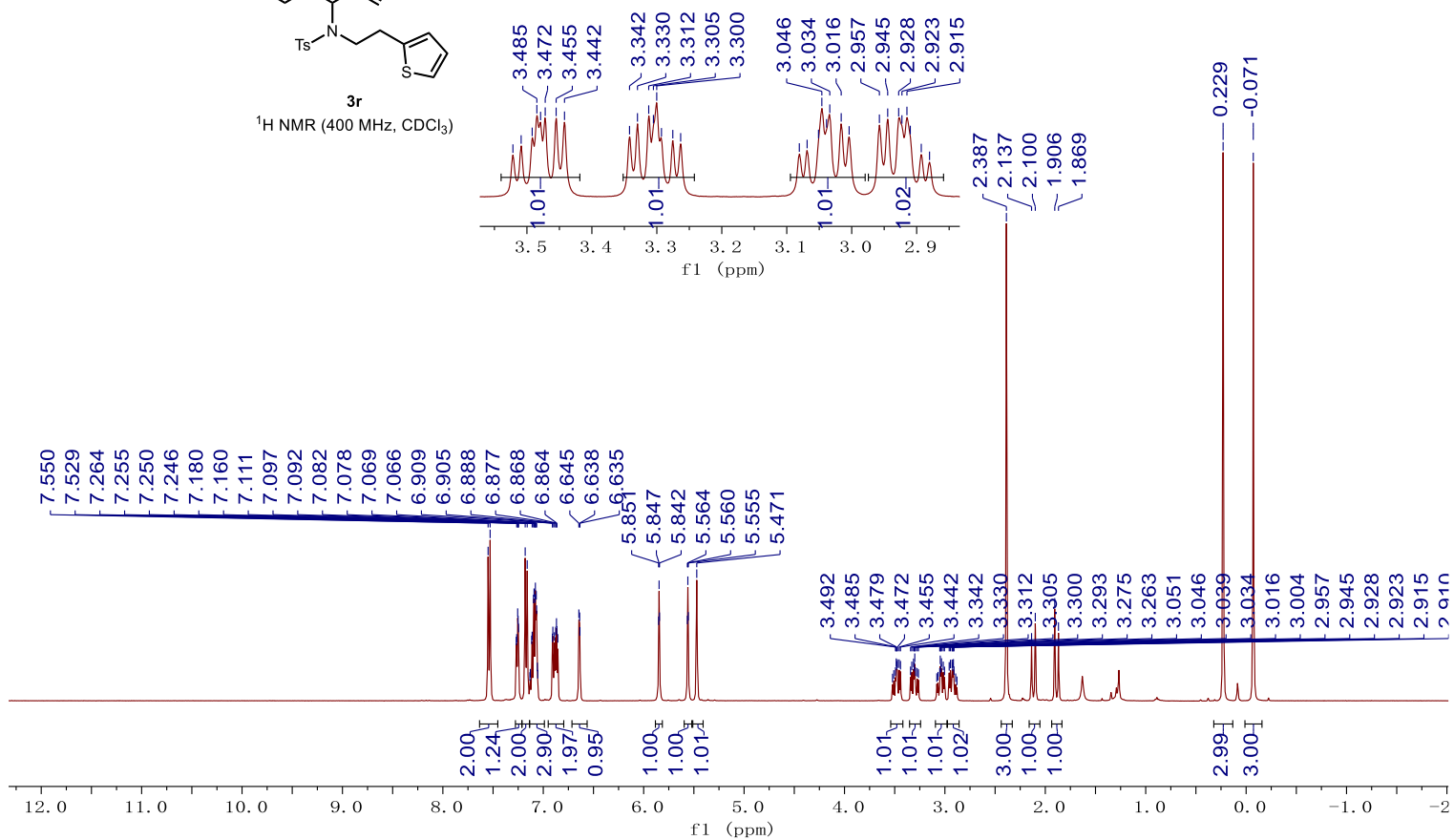
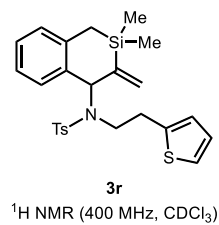


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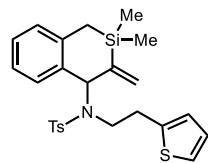
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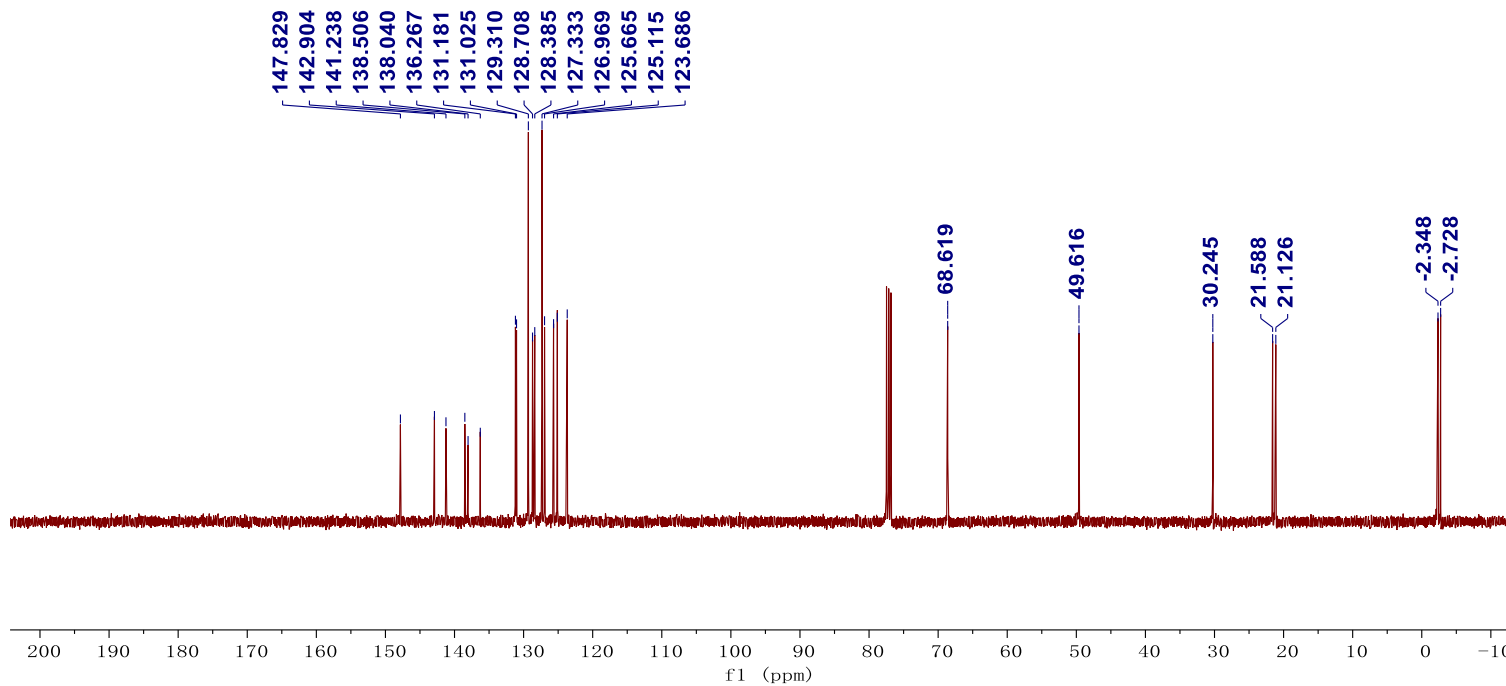


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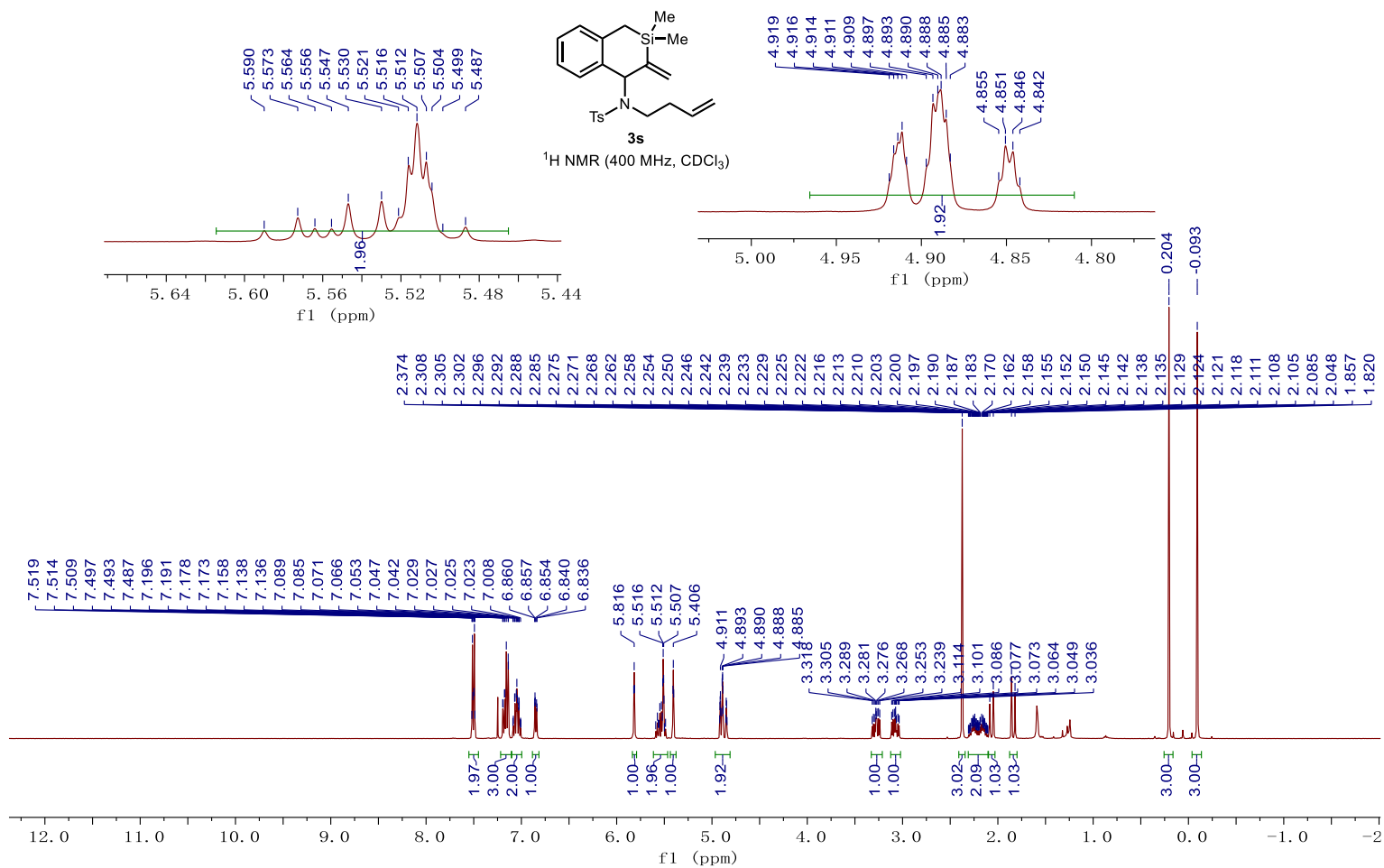


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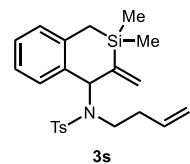
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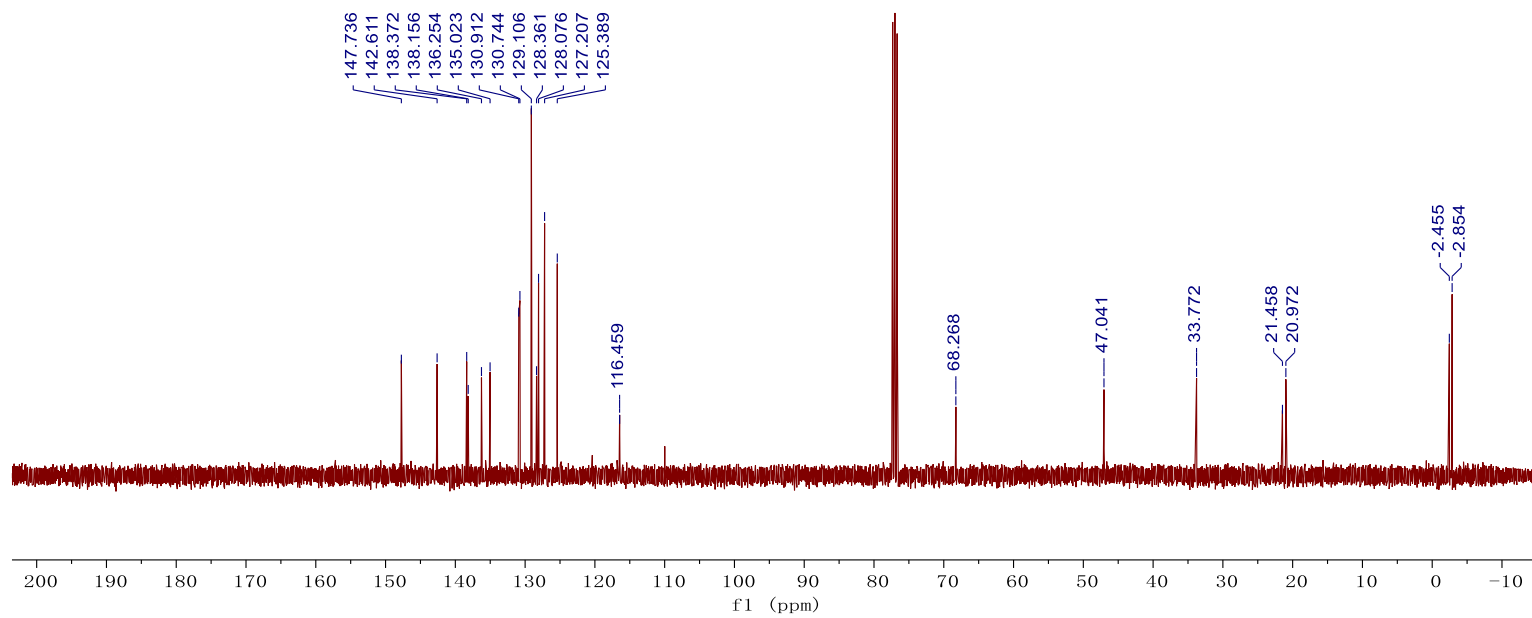
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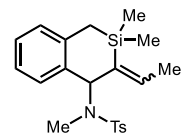
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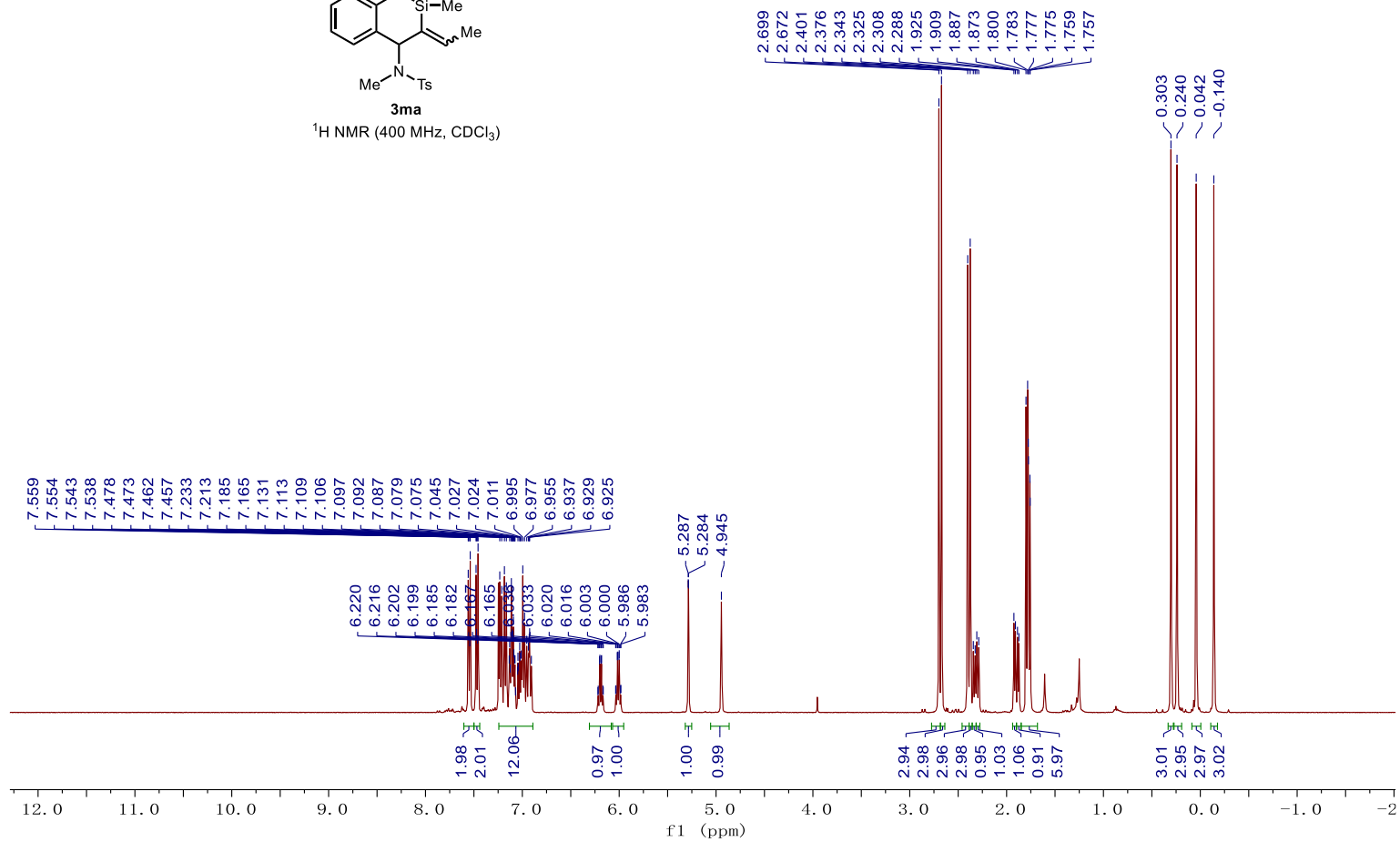
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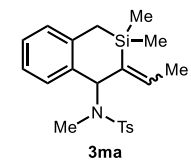
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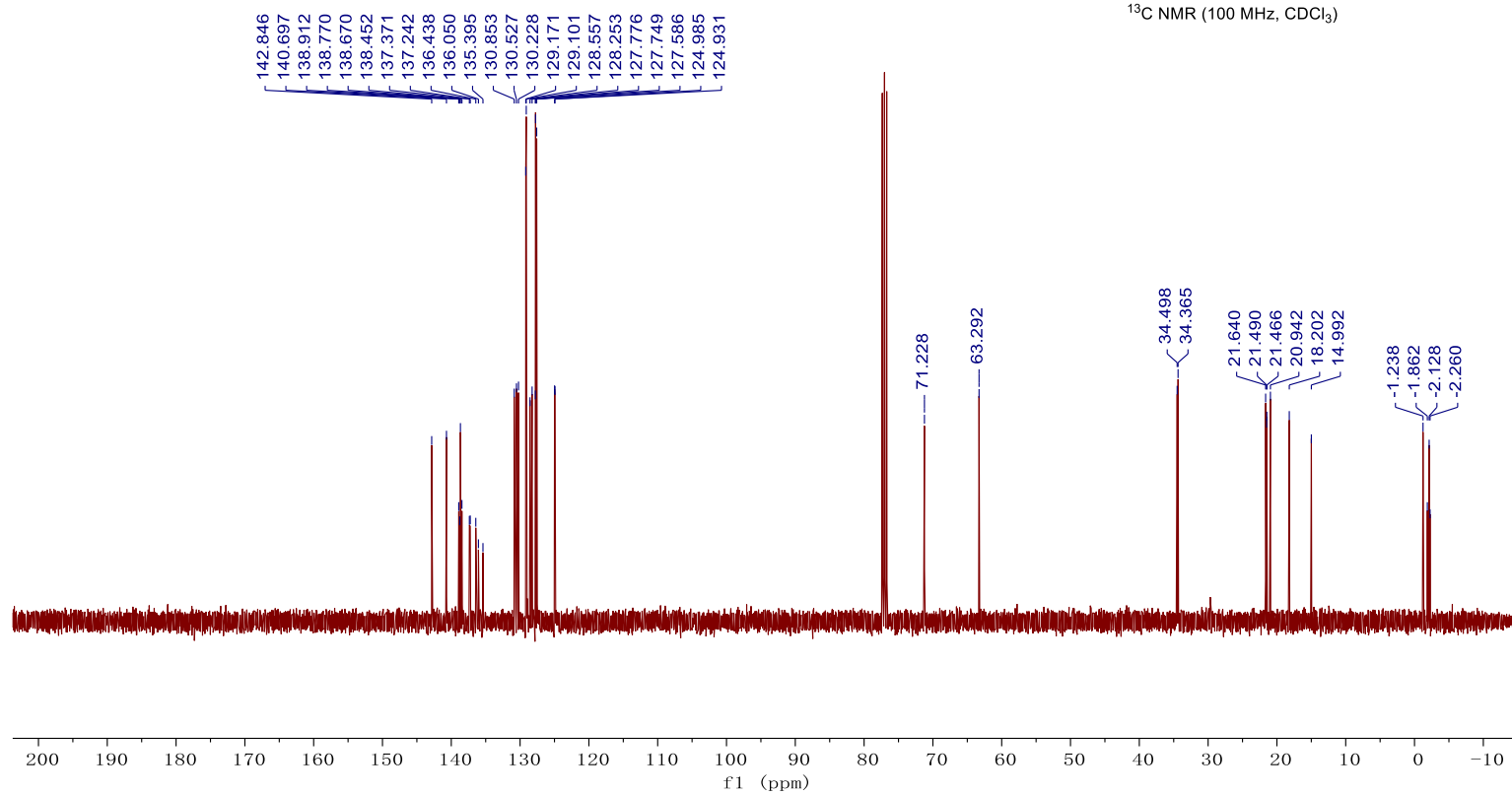
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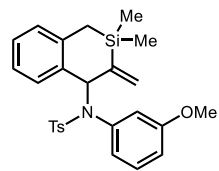
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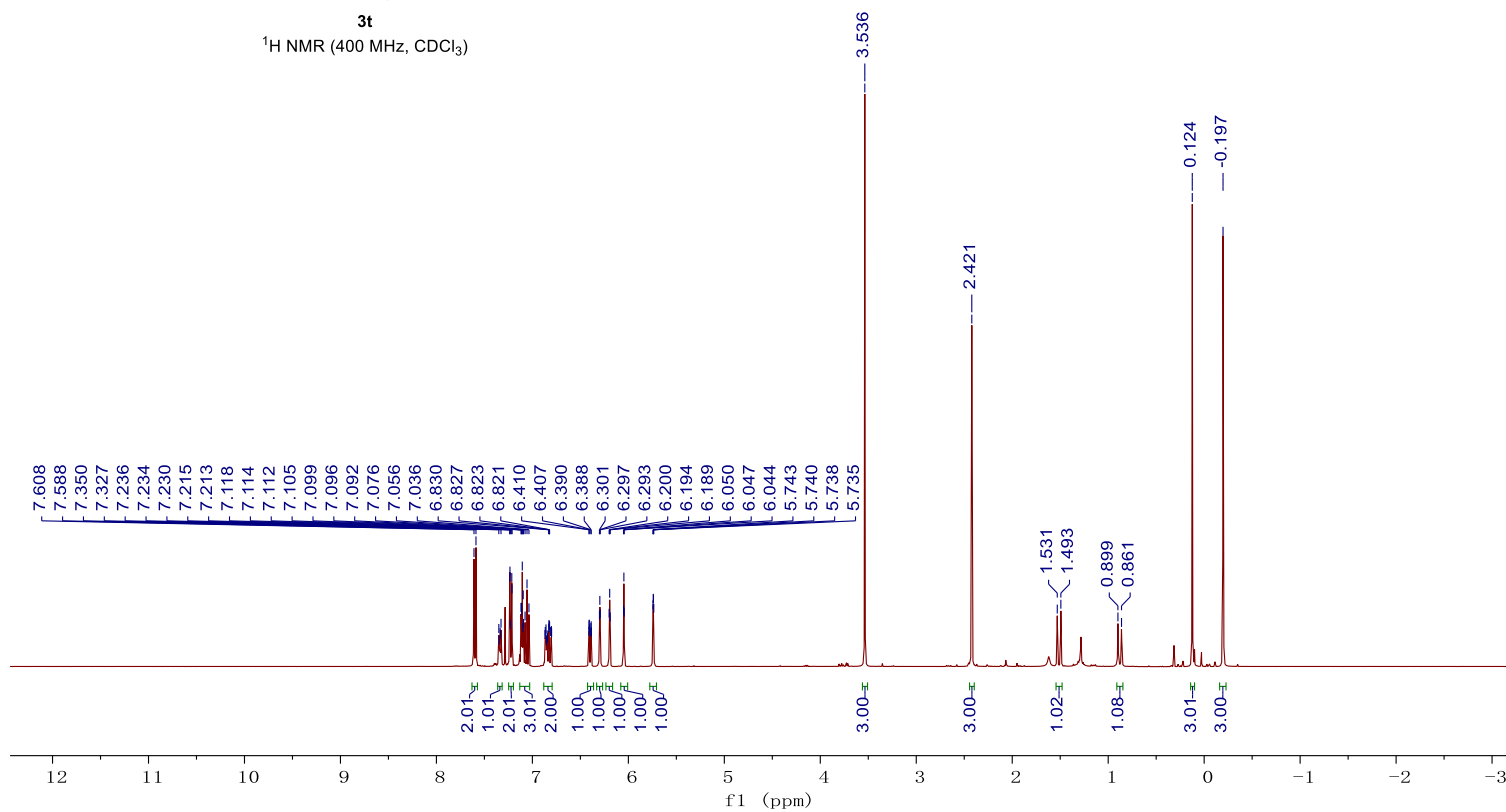
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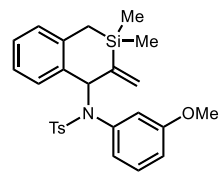
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SY-260-1 1H CDCL3



**3t**  
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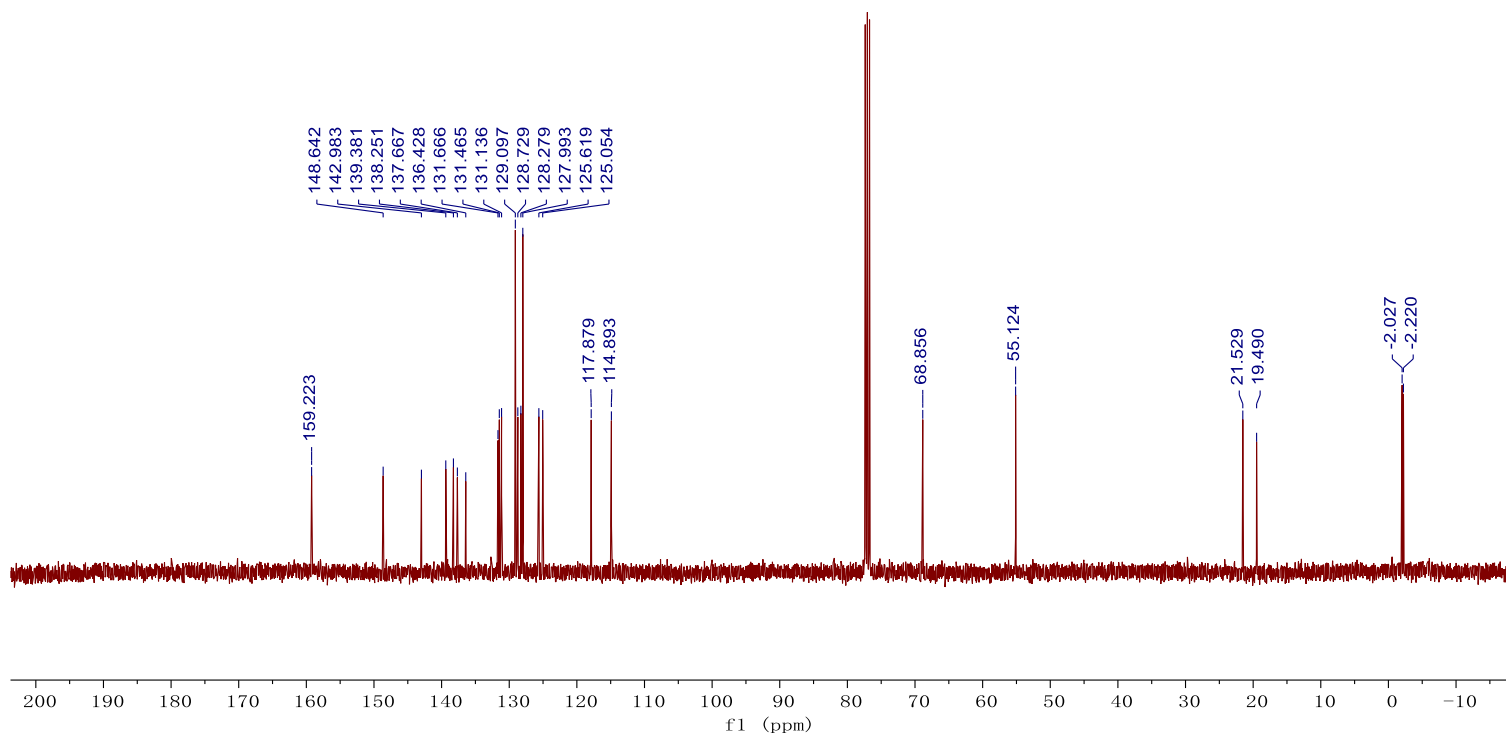


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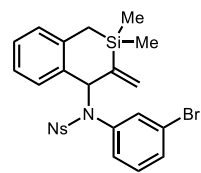


3t

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

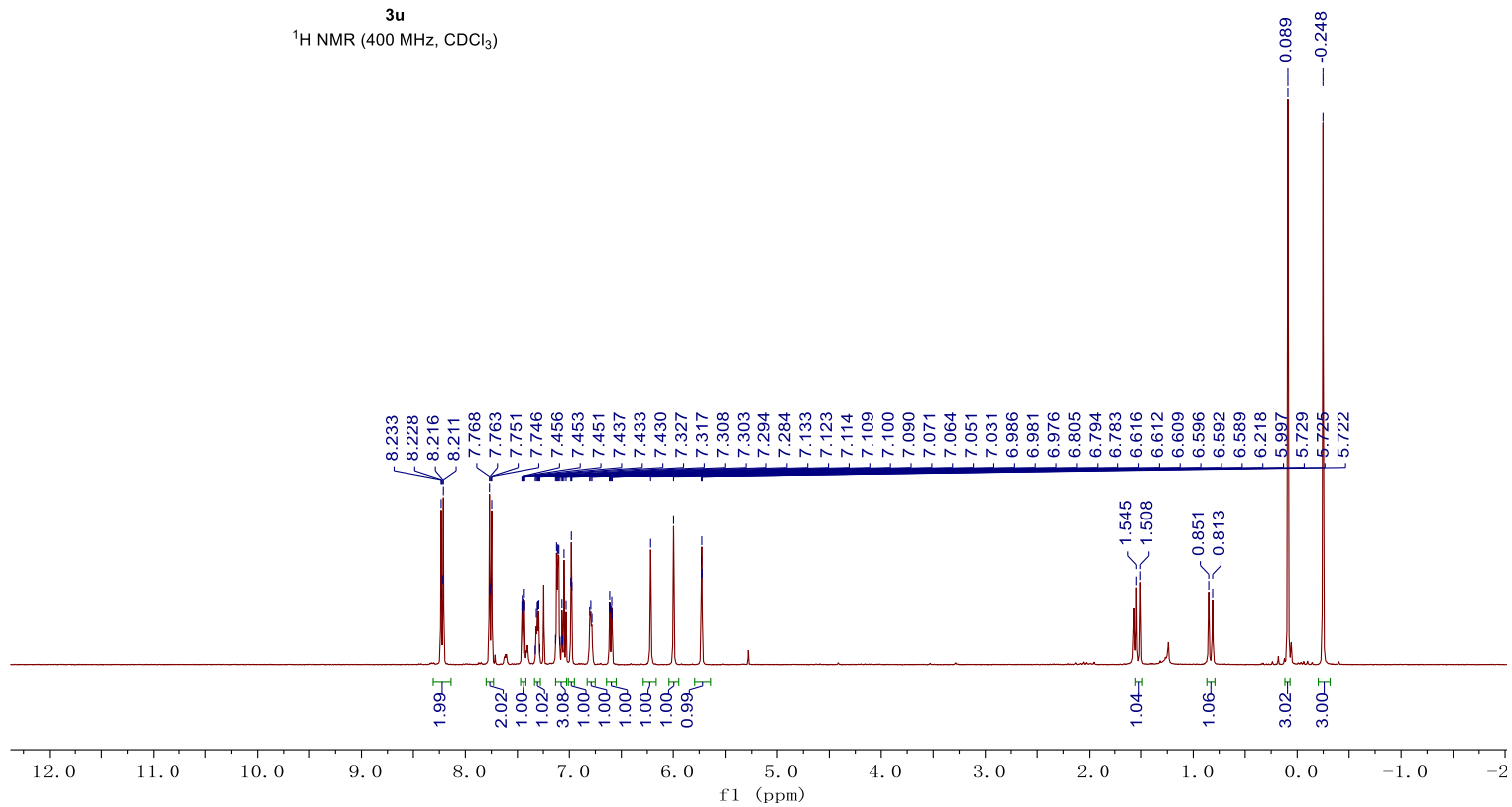


20260306-SY-260-2H  
Gradient Shimming

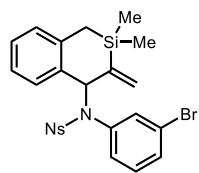


3u

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

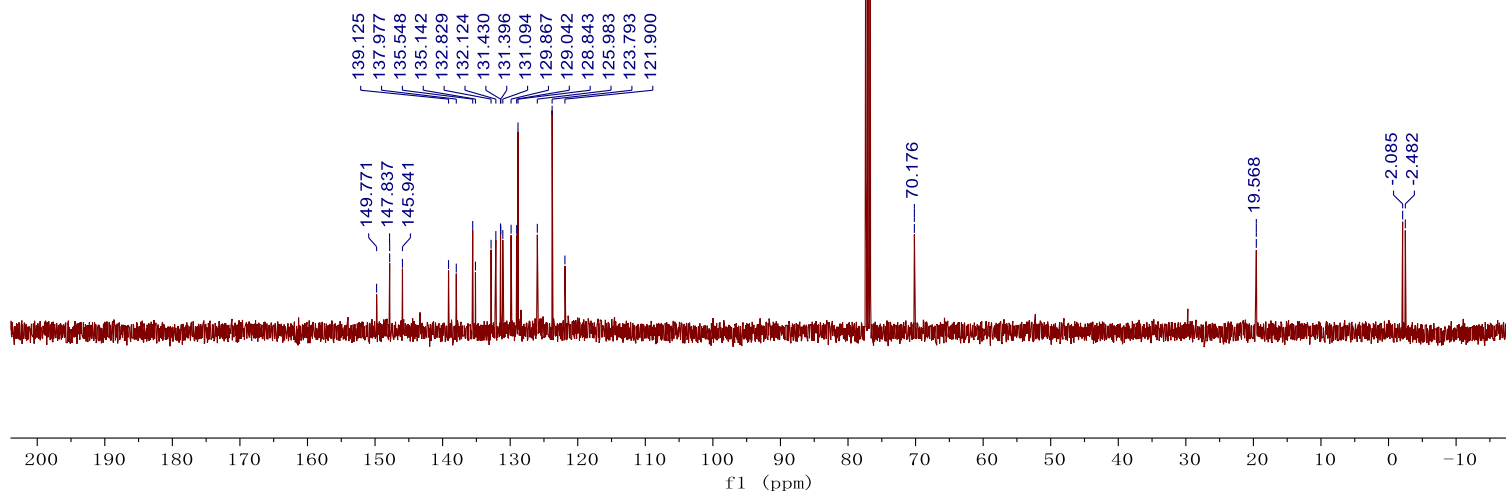


360\$4/1  
SY-260-2 13C CDCL3

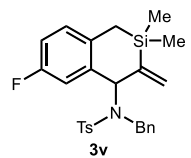


**3u**

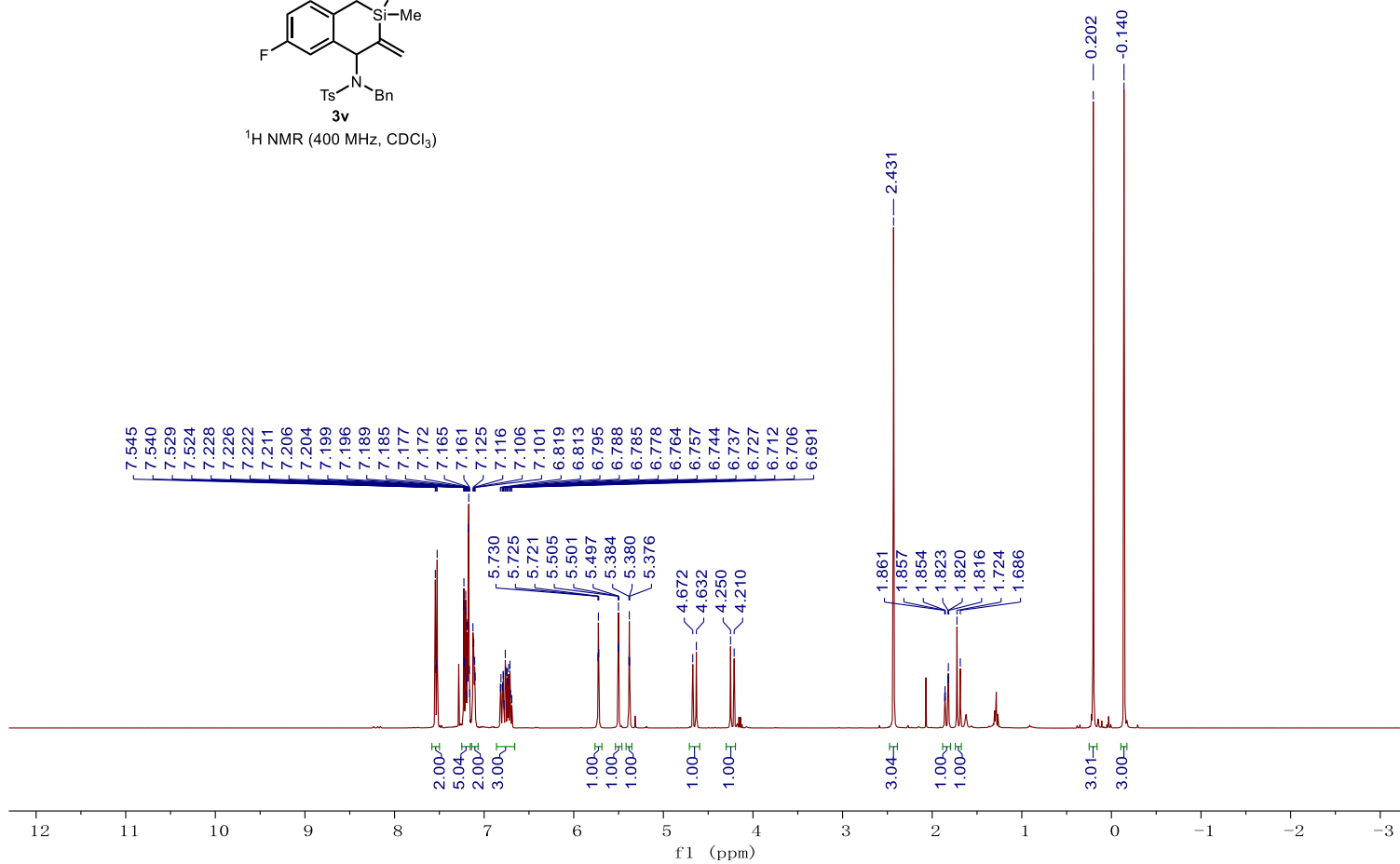
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



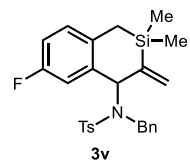
36088/3  
SY-263-2 1H CDCL3



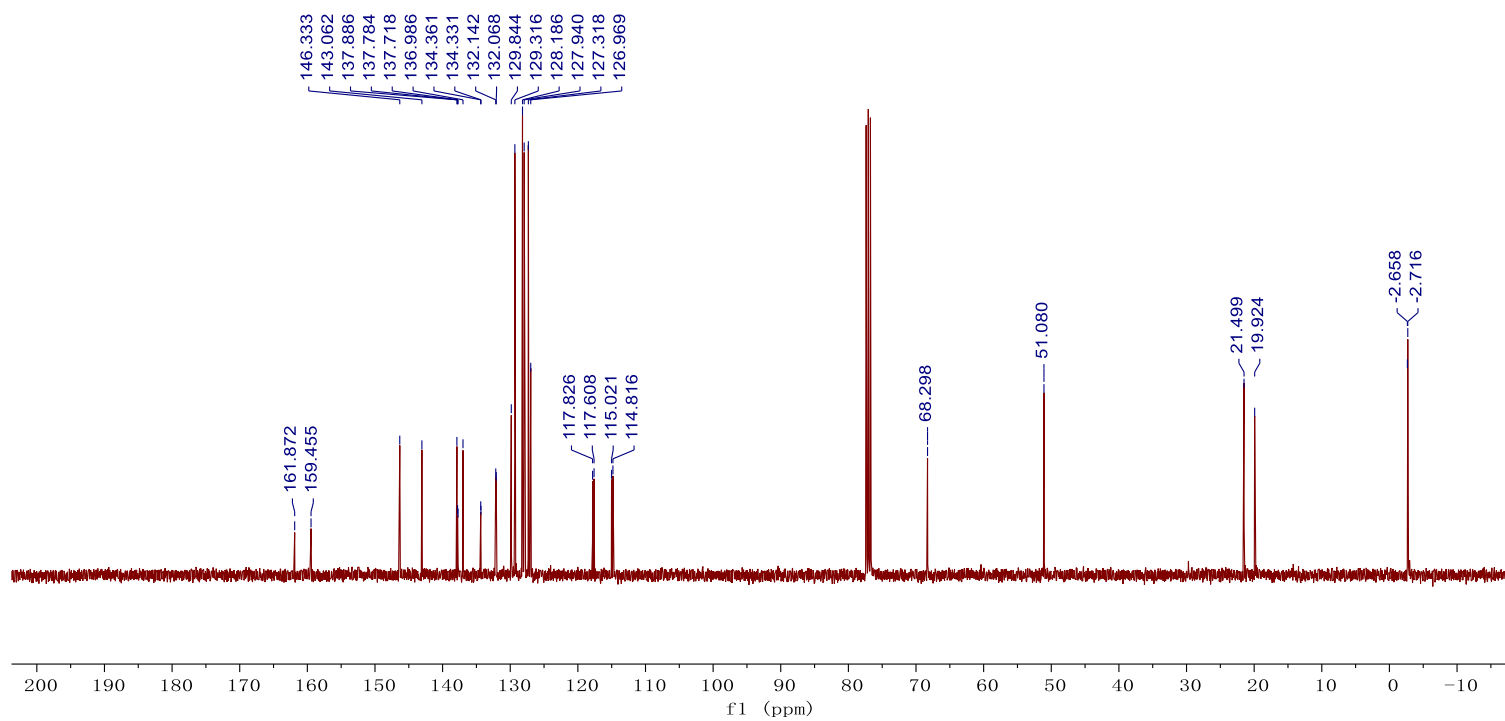
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



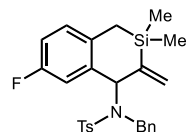
36088/2  
SY-263-2 13C CDCL3



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

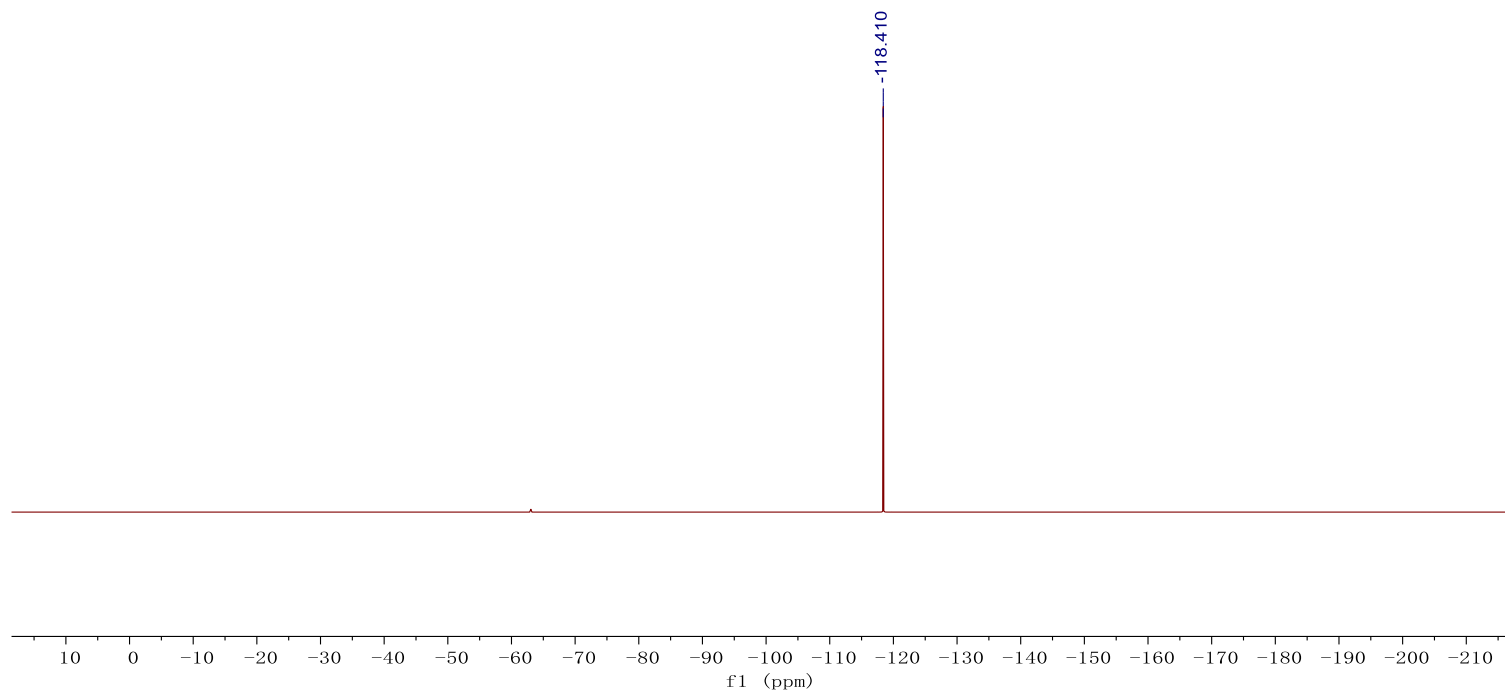


36088/1  
SY-263-2 19F CDCL3

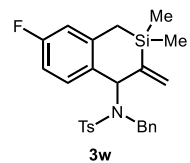


**3v**

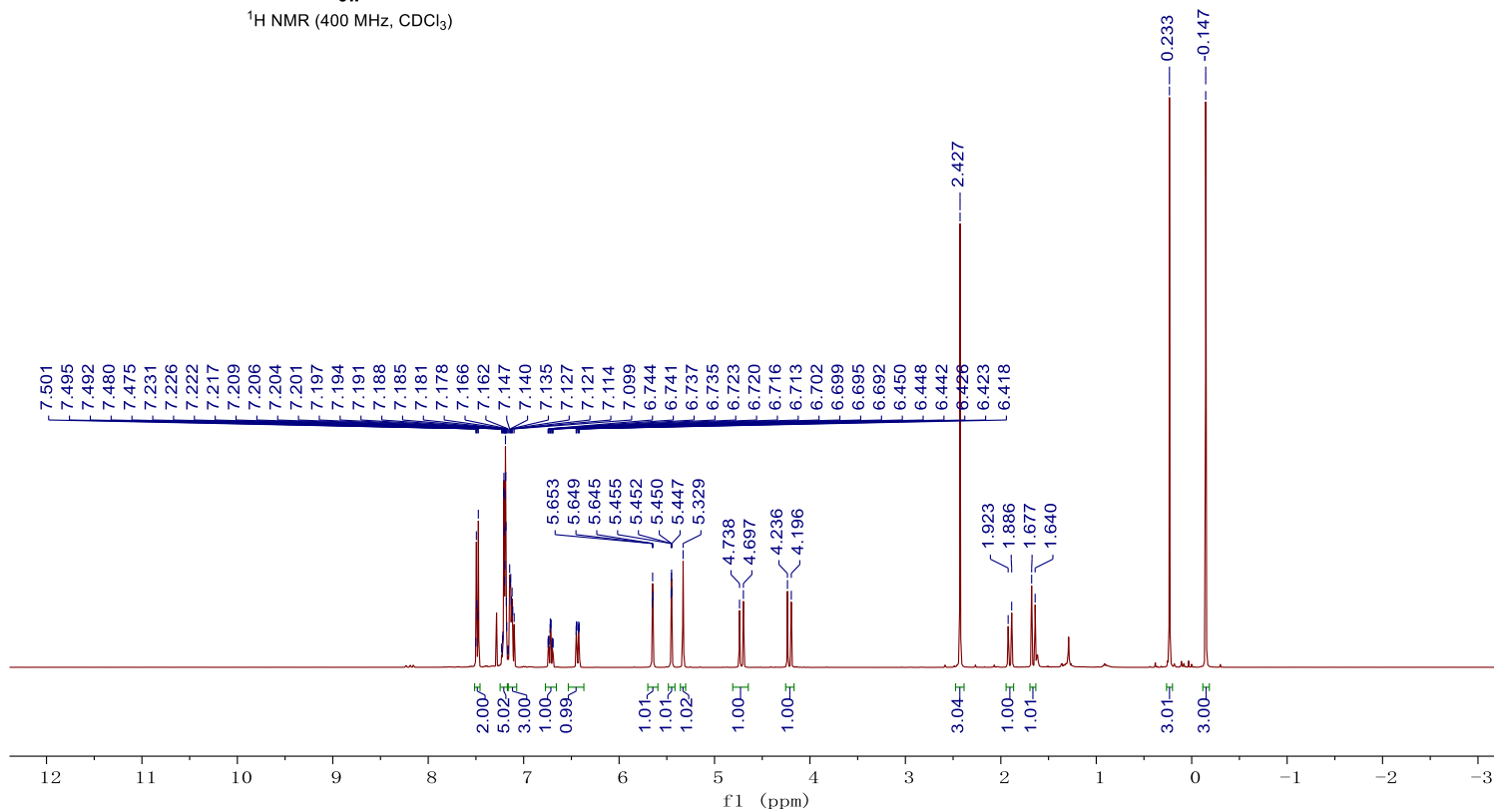
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)



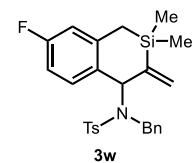
360\$6/1  
SY-263-1 1H CDCL3



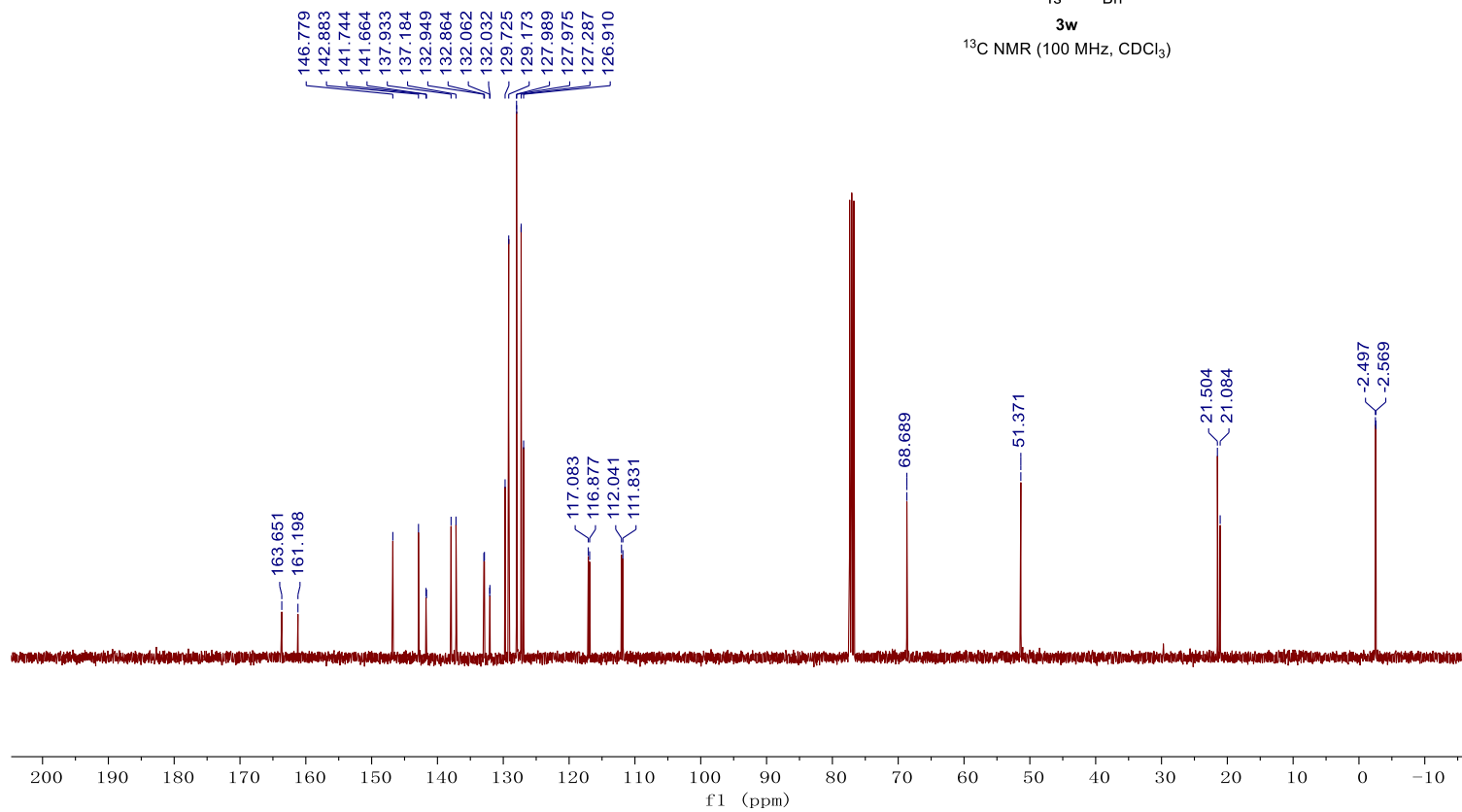
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



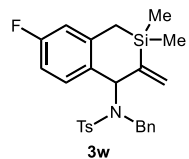
360\$7/2  
SY-263-1 13C CDCL3



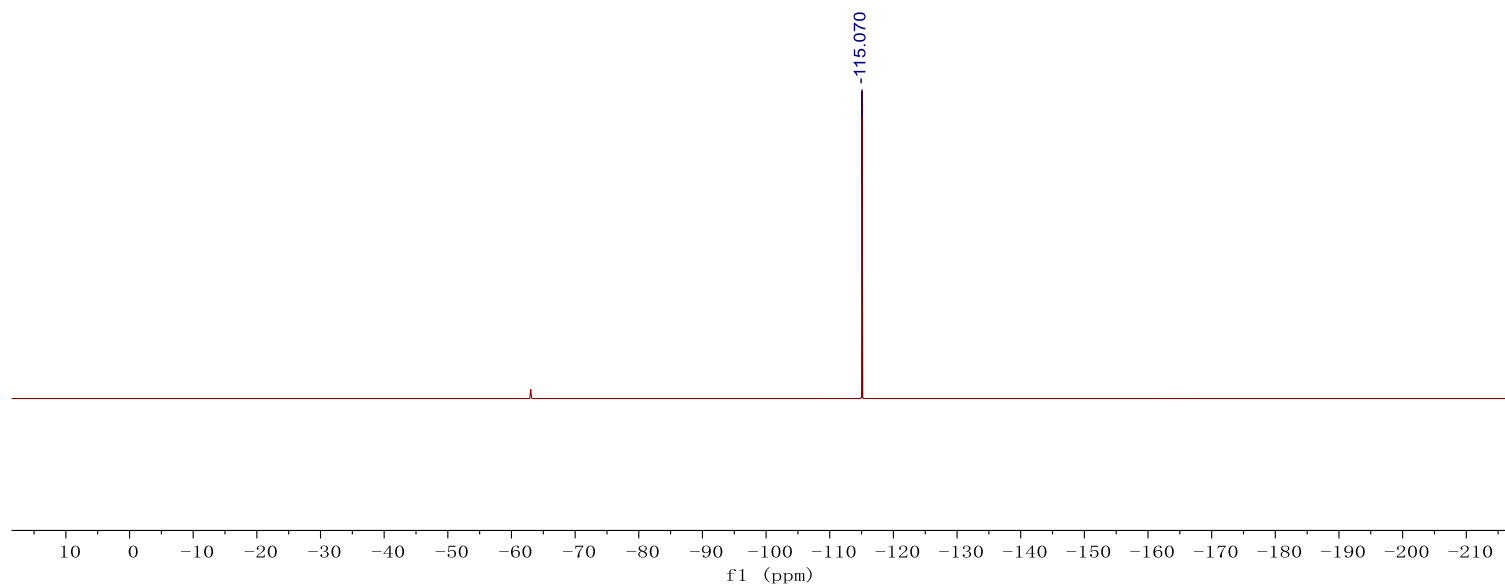
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



360\$7/3  
SY-263-1 19F CDCL3

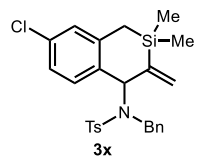


<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

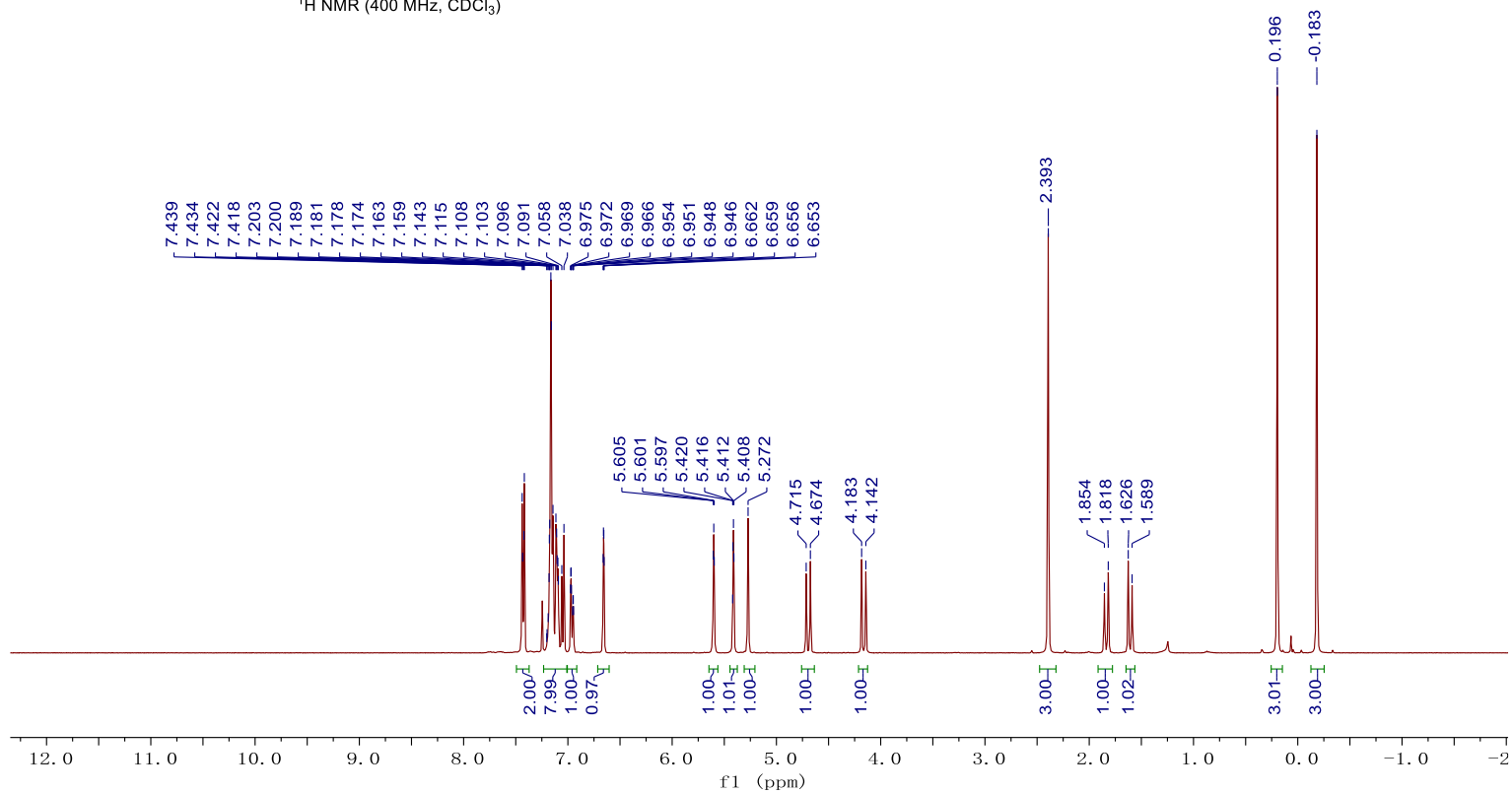


S73

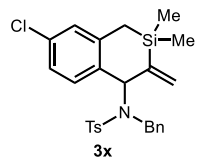
20251231-SY-227-1H  
Gradient Shimming



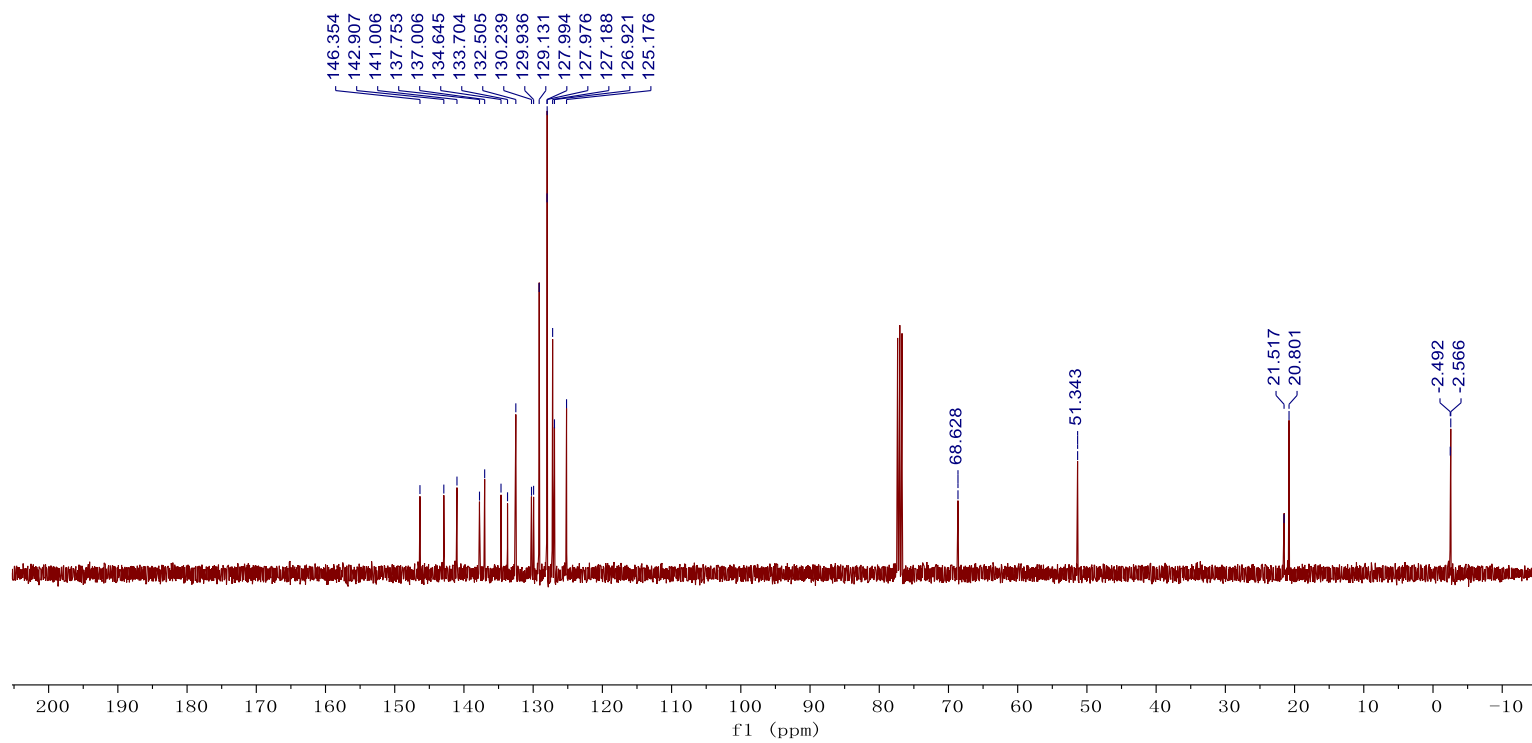
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



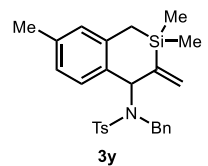
20251231-SY-227-1C  
Gradient Shimming



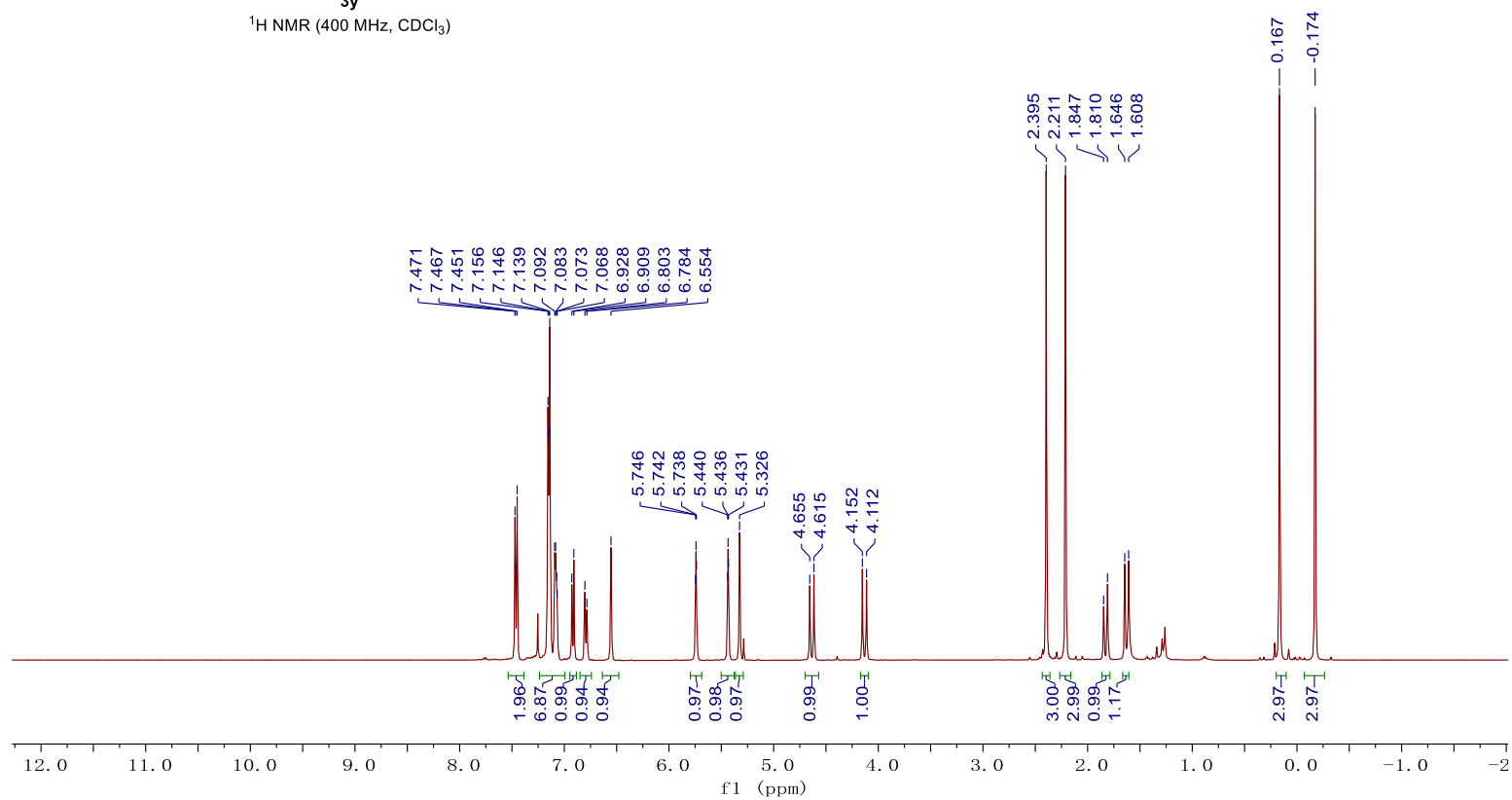
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



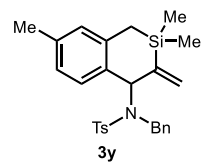
2024-10-18-SY-2-212H  
Gradient Shimming



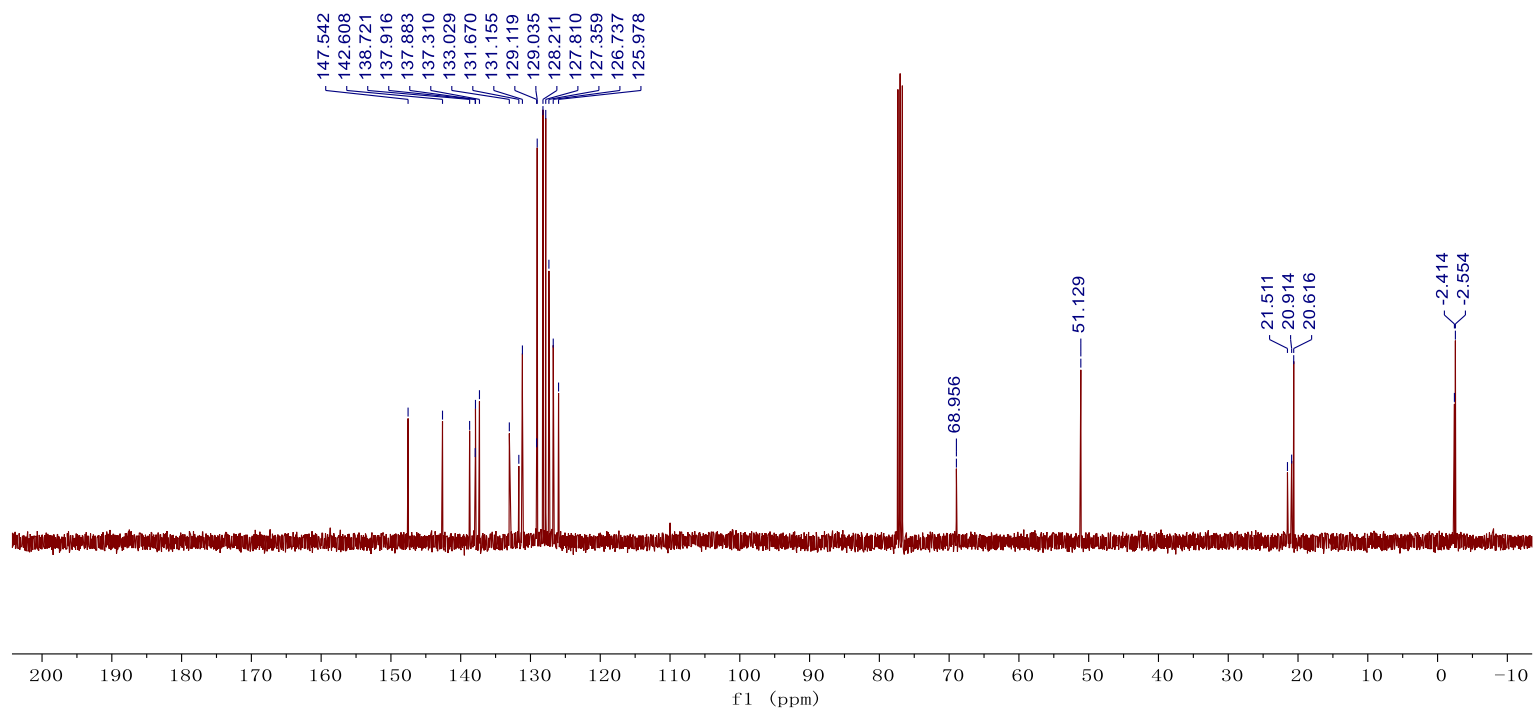
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



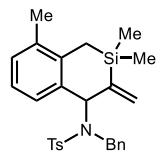
20251231-SY-212C  
Gradient Shimming



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

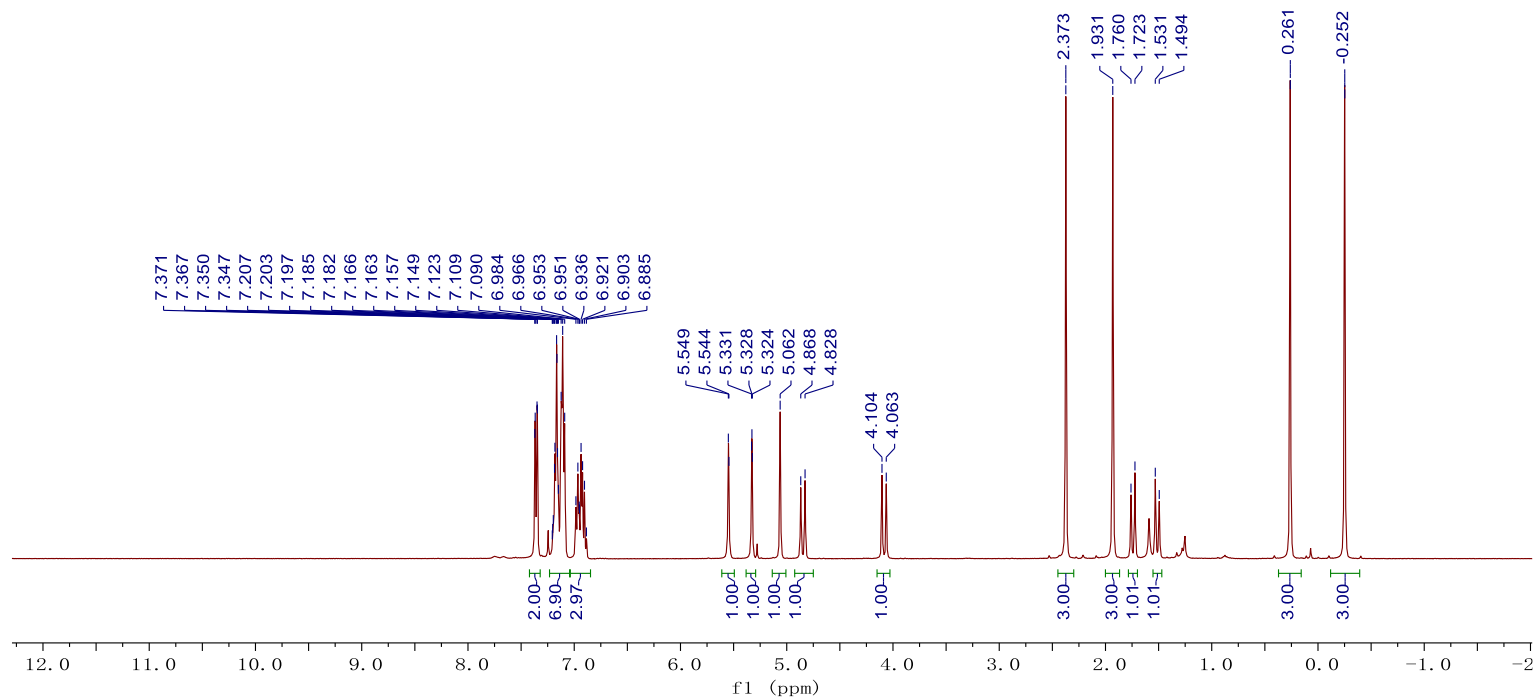


20251029-SY-44-4H  
Gradient Shimming

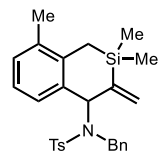


**3z**

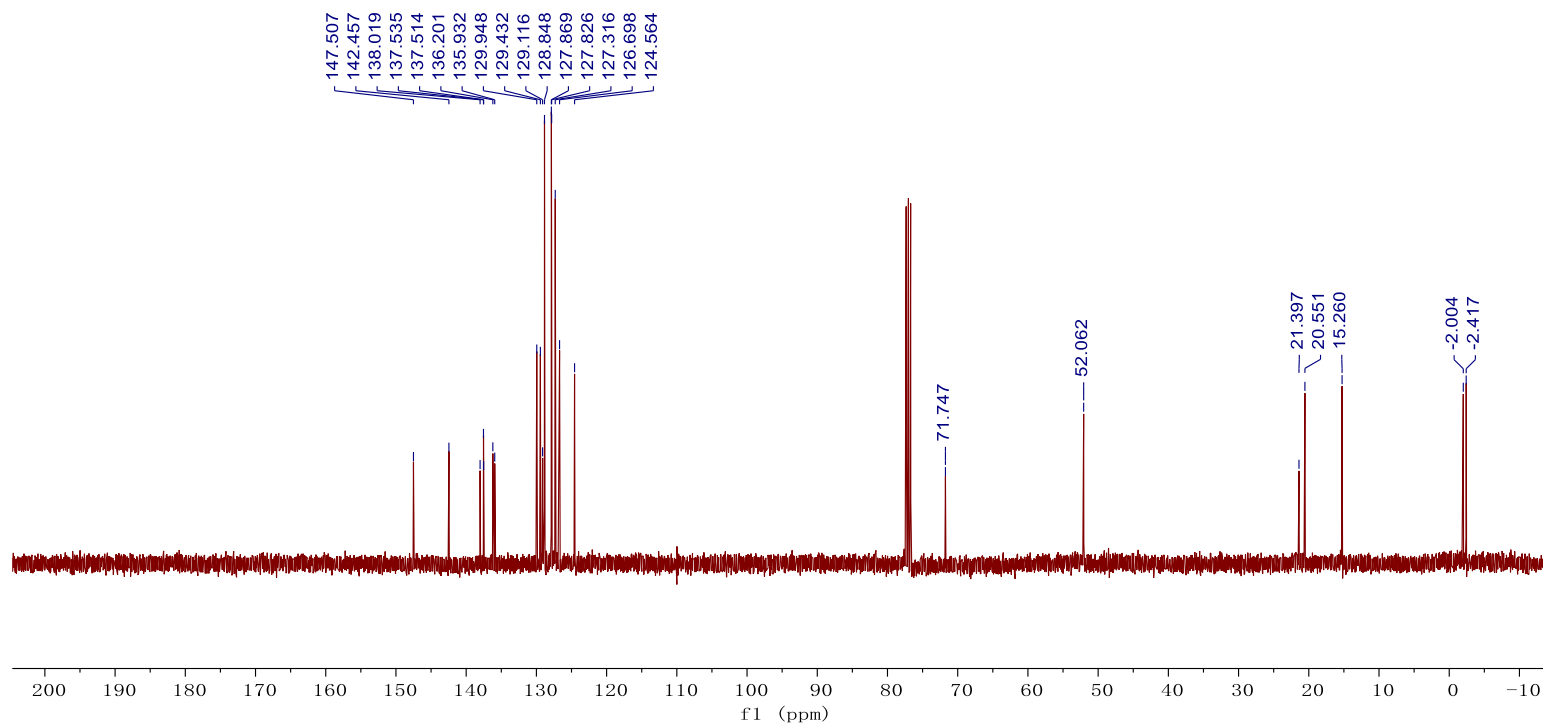
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



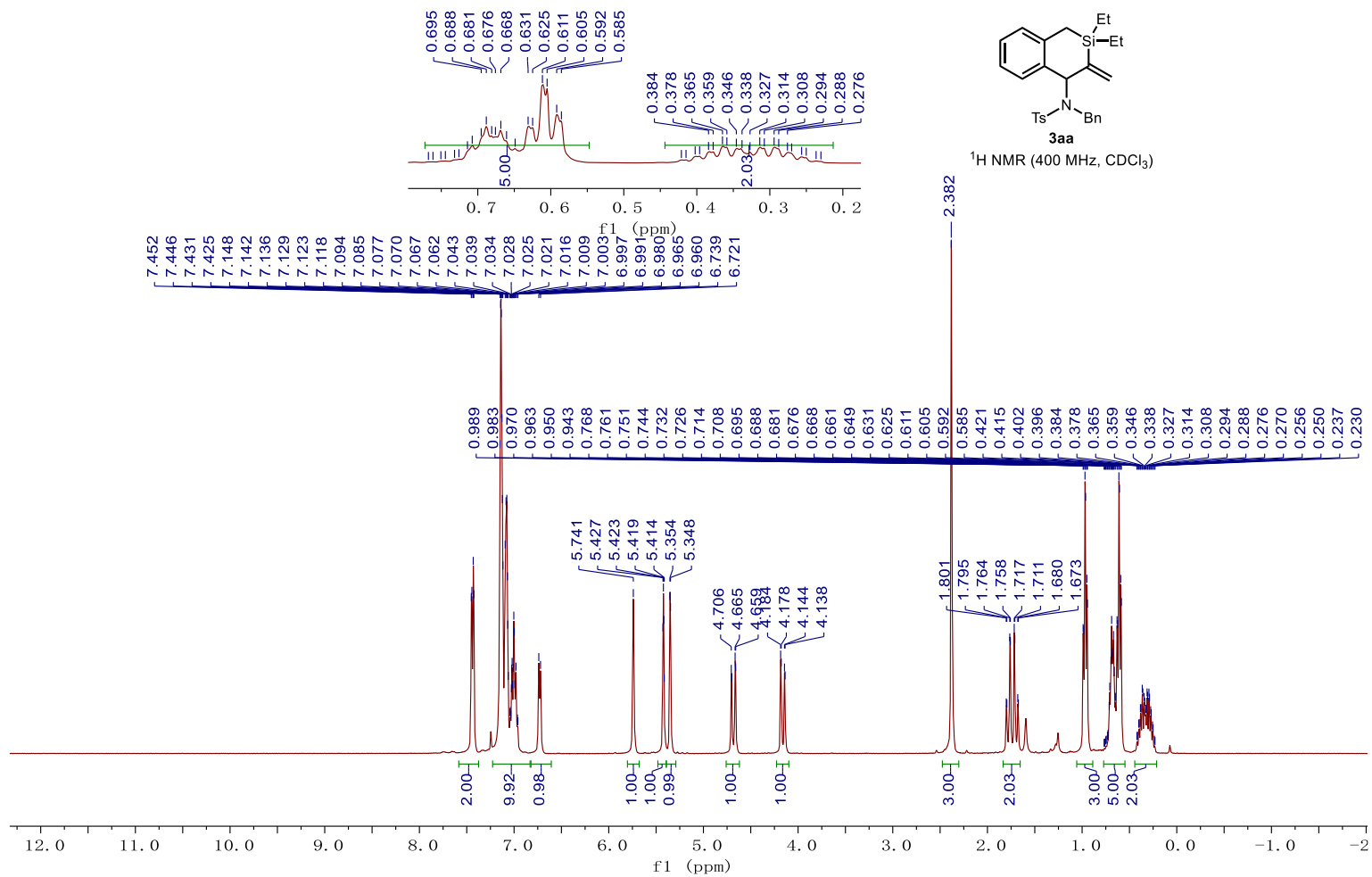
20251029-SY-44-4C  
Gradient Shimming



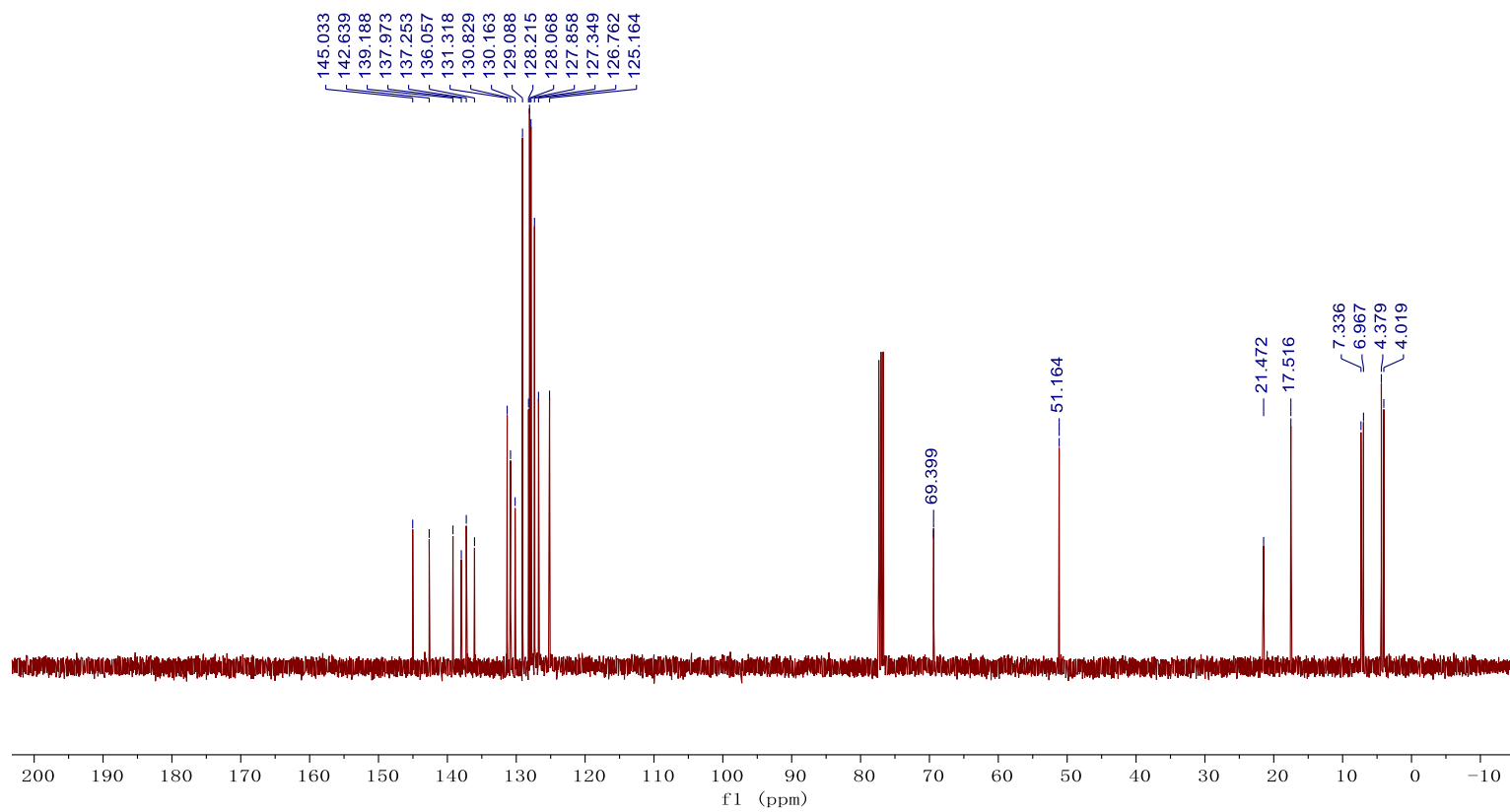
3z  
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



20251029-L-29-4H  
Gradient Shimming

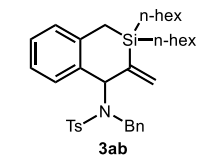


20251029-L-29-4C  
Gradient Shimming

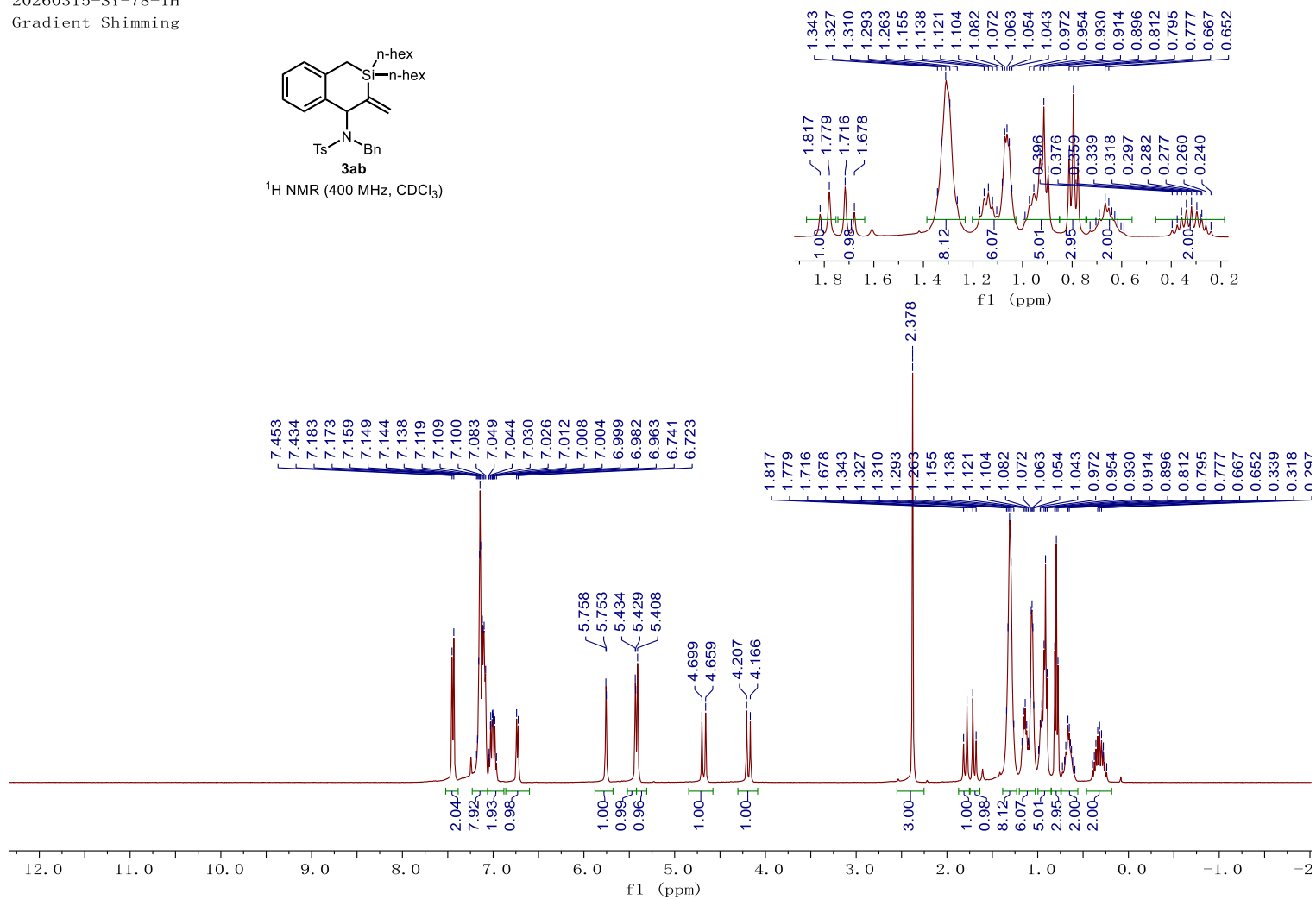


S81

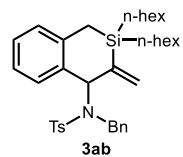
20260315-SY-78-1H  
Gradient Shimming



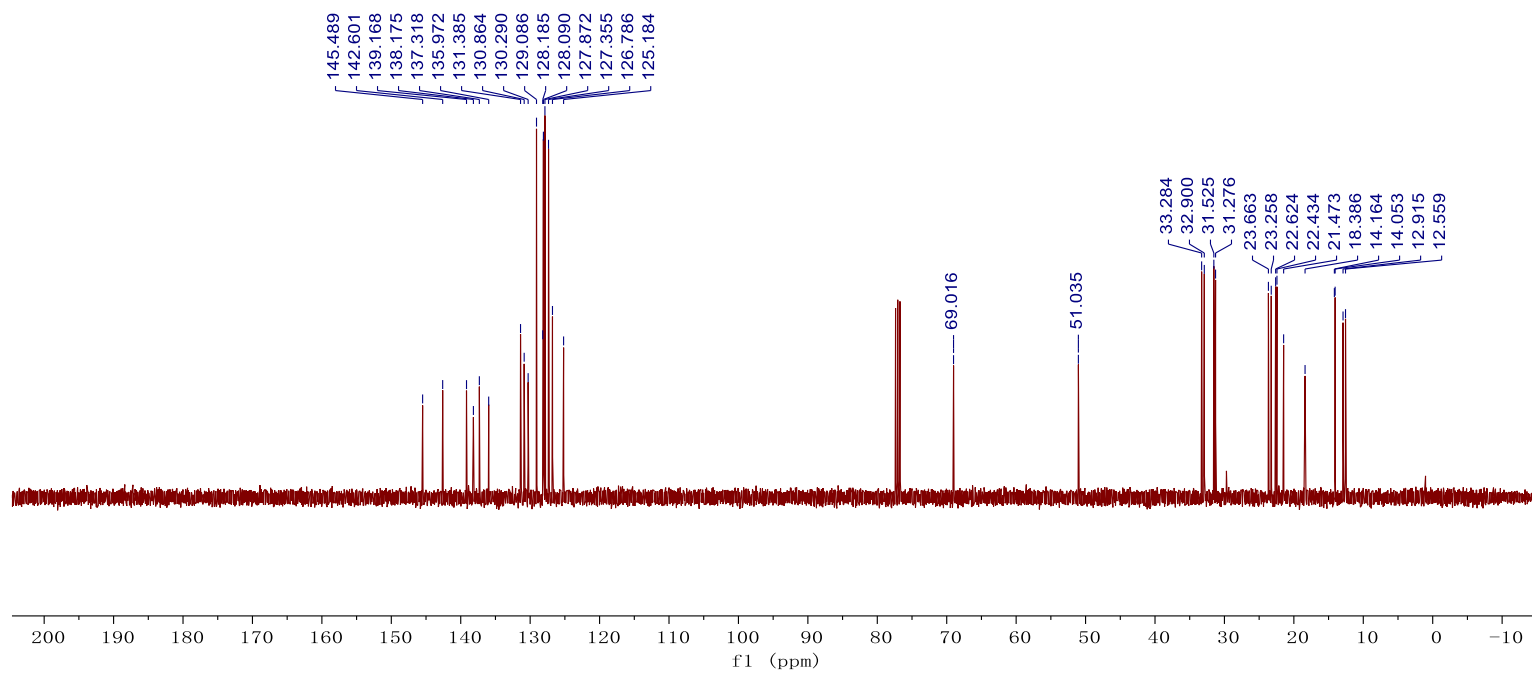
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )



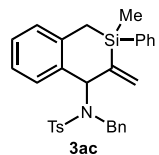
2025-6.01-SY-78-1C  
Gradient Shimming



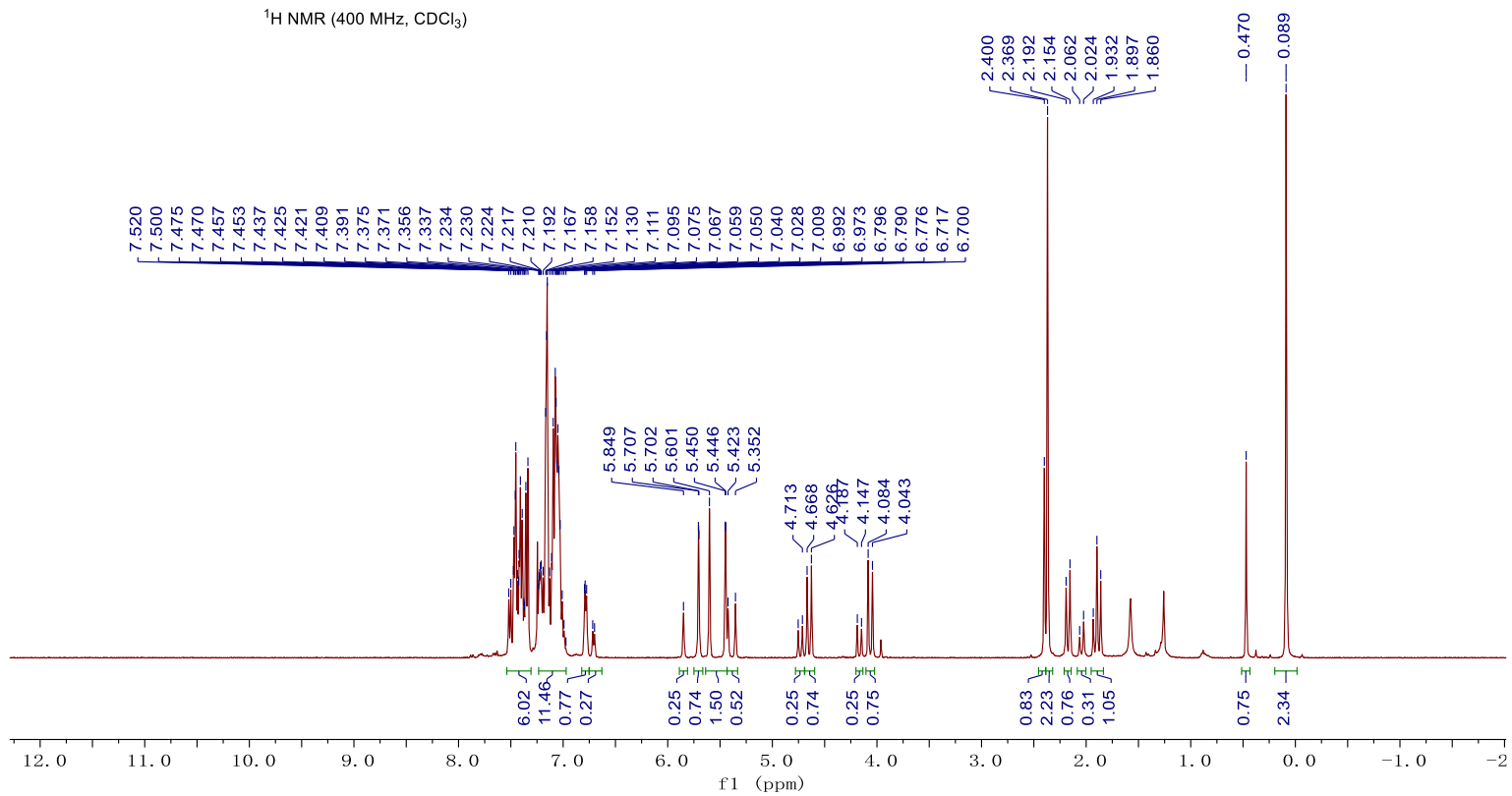
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



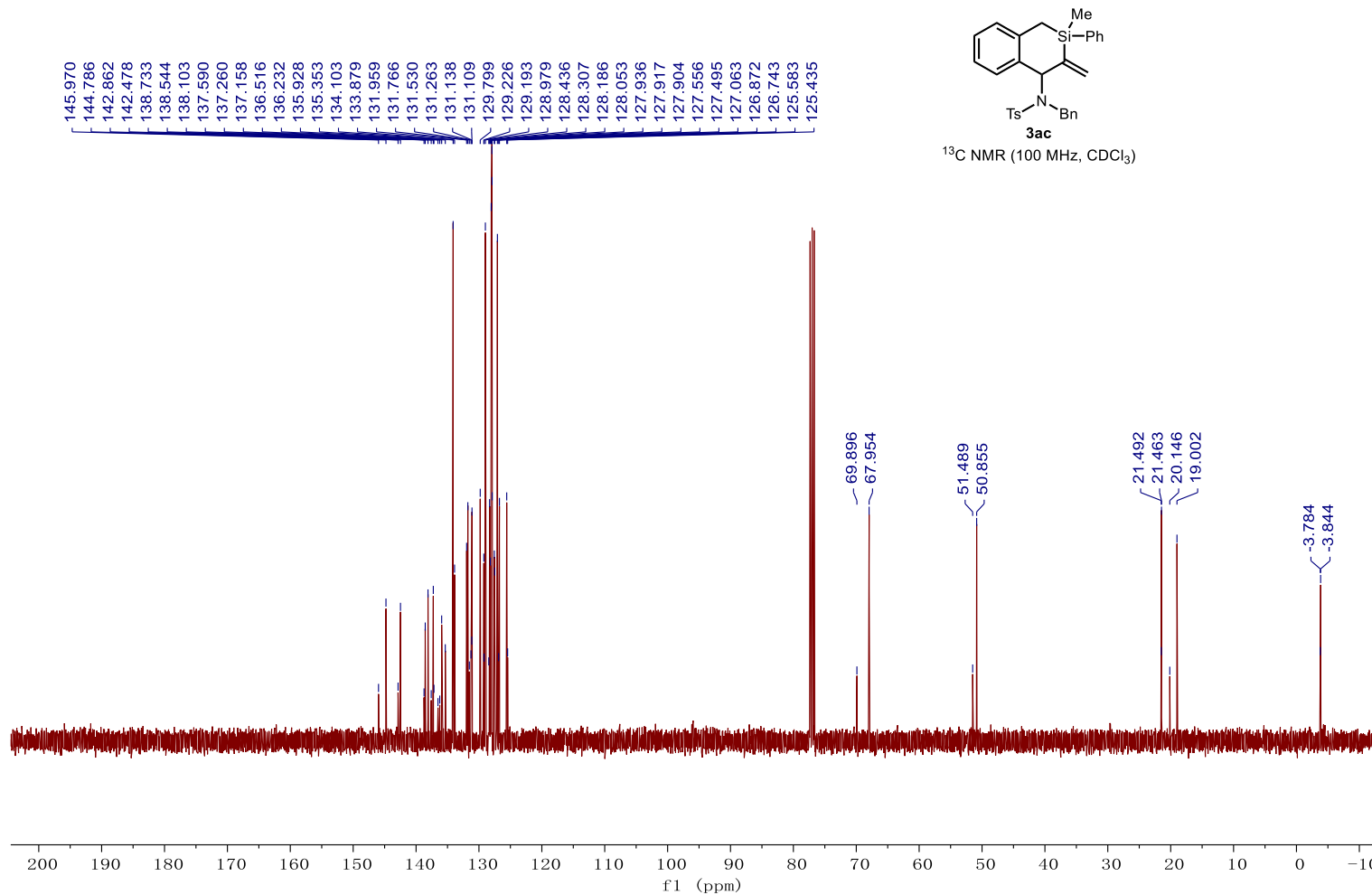
20260430-SUNYAN-219H-32  
Gradient Shimming



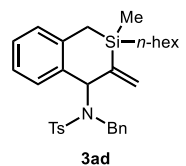
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



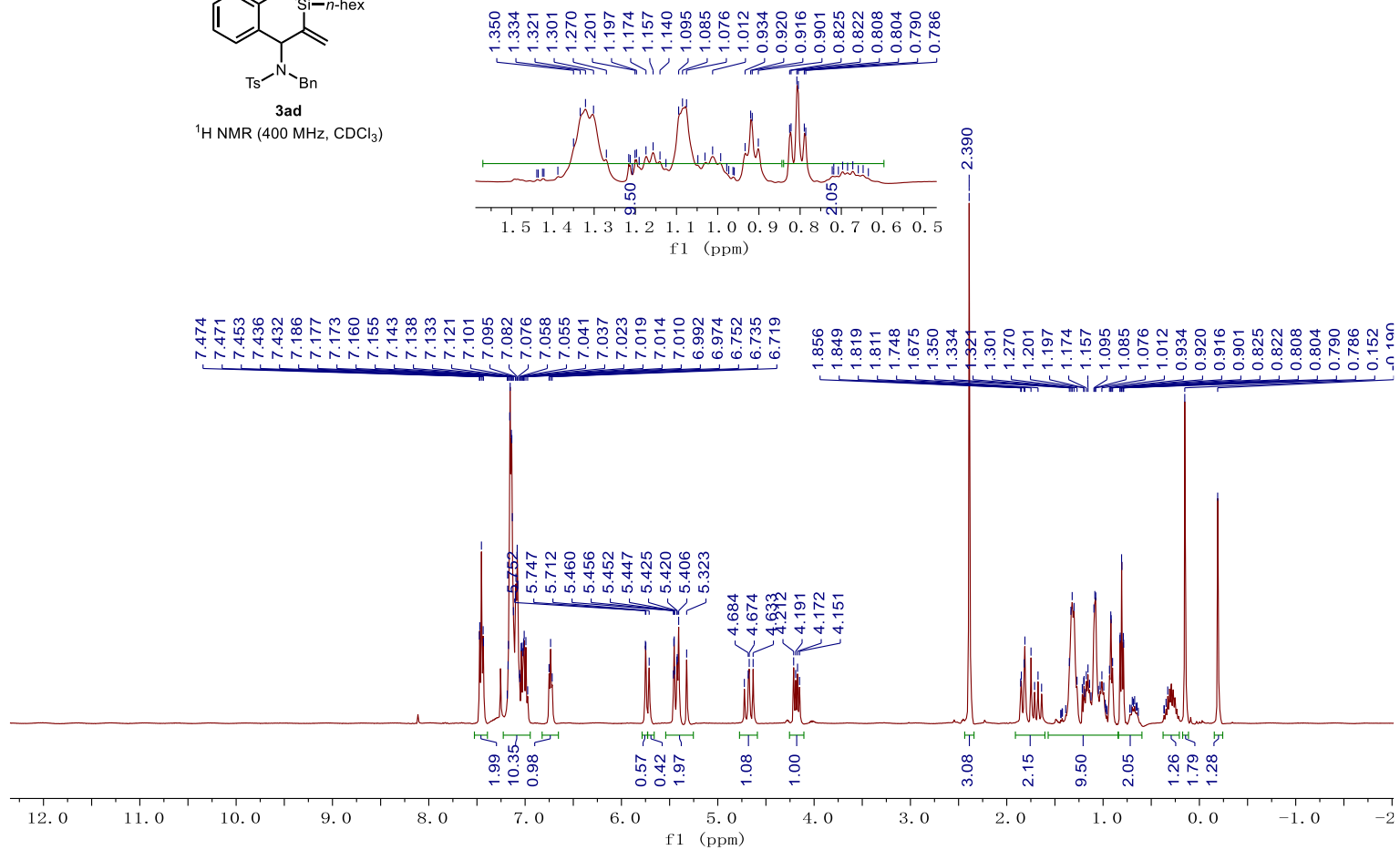
20260430-SUNYAN-219C-34  
Gradient Shimming



20241201-SY-251H  
Gradient Shimming

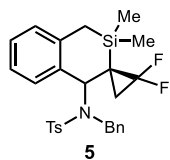


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

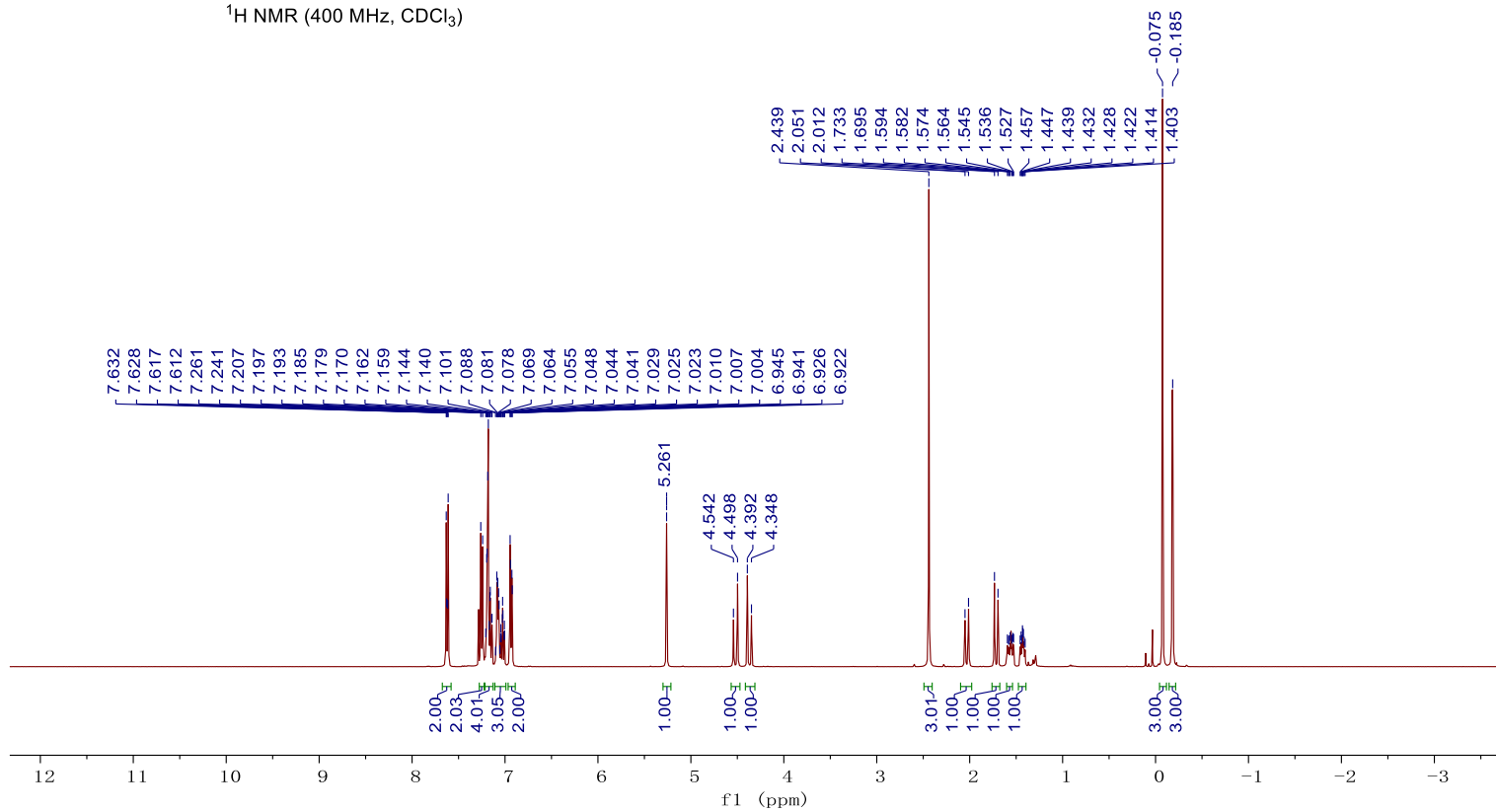




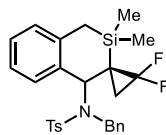
360\$8/3  
SY-147 1H CDCL3



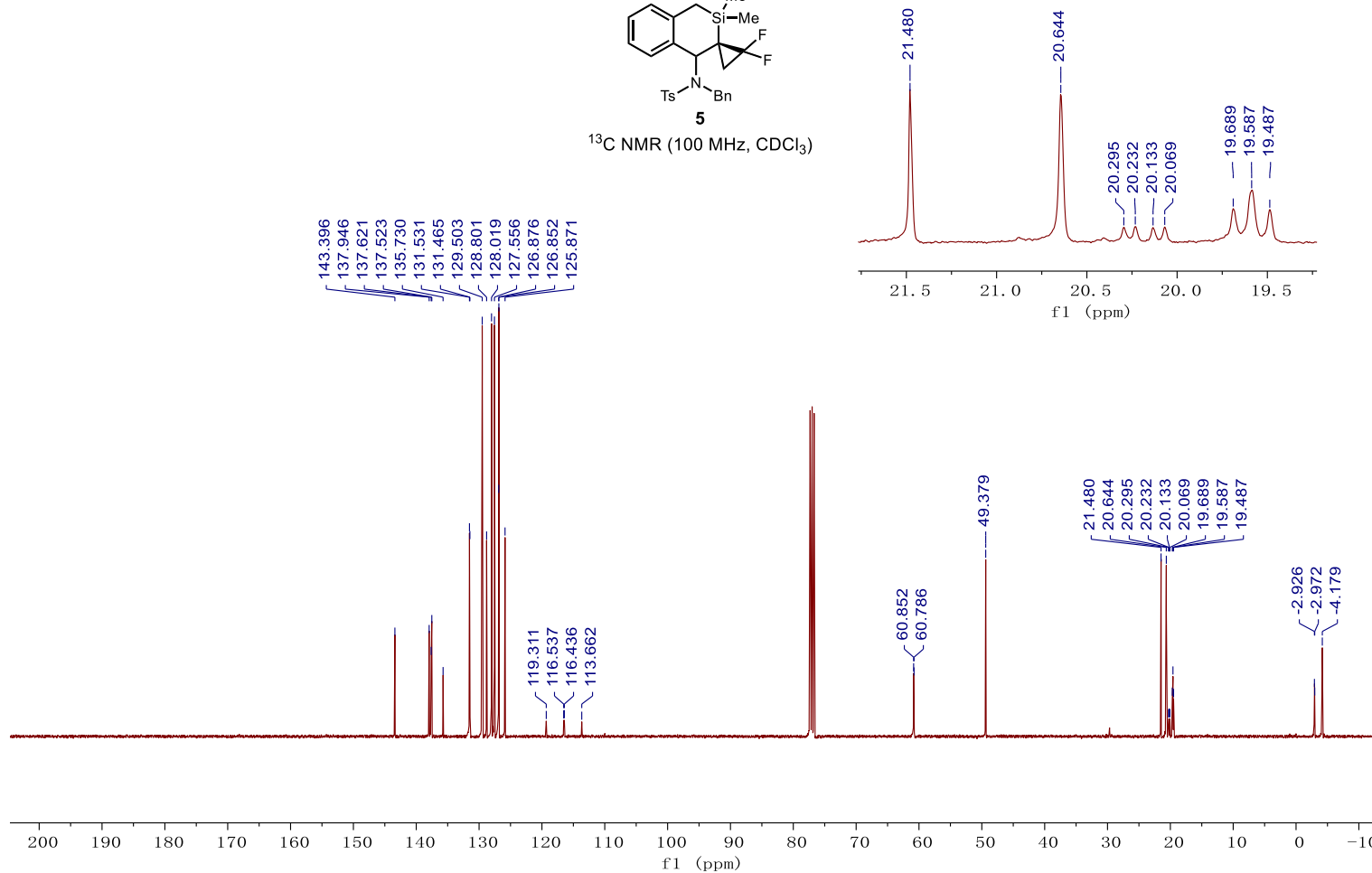
5  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



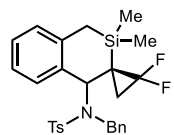
20260506-SUNYAN-1C-106  
Gradient Shimming



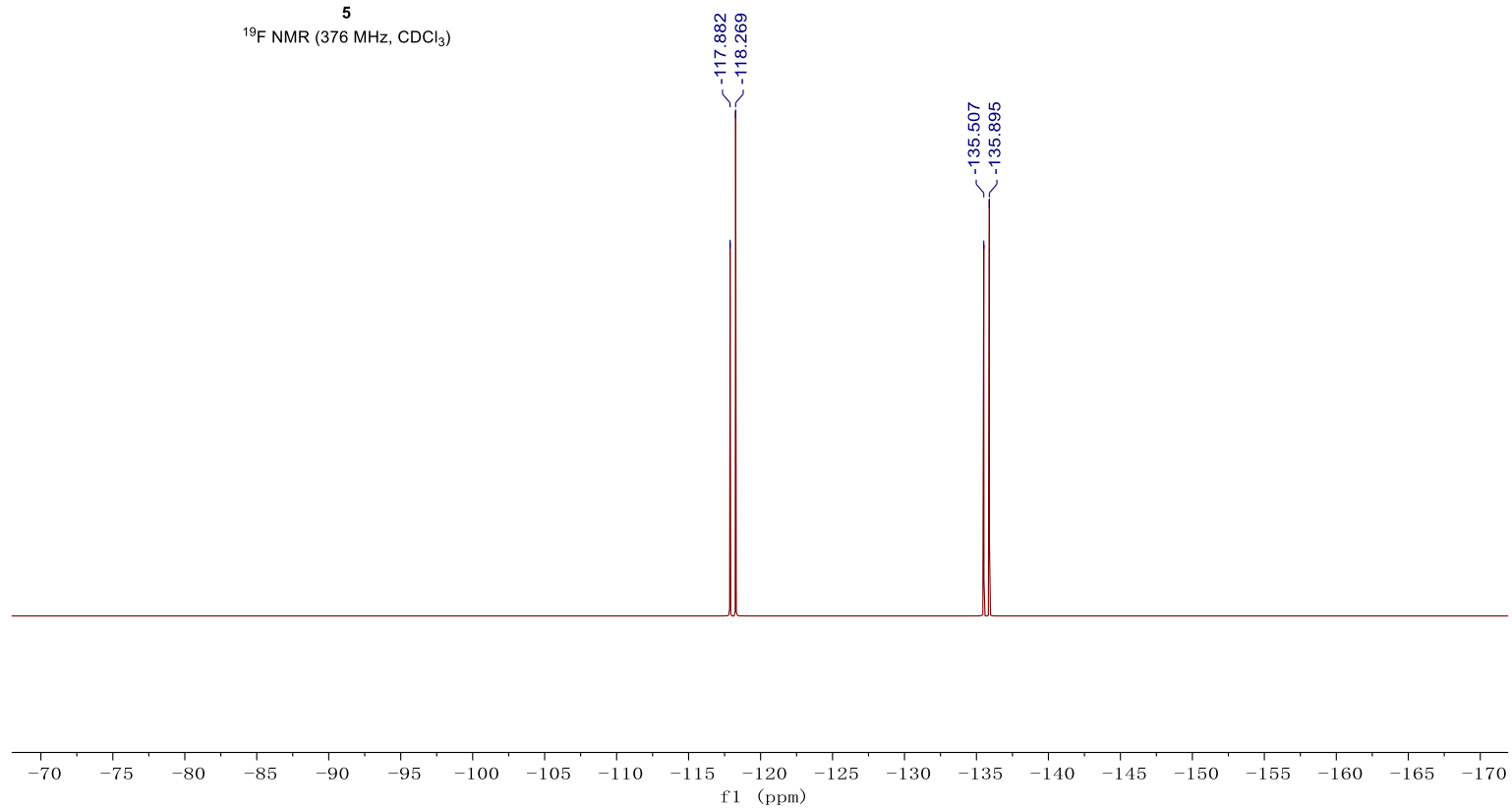
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



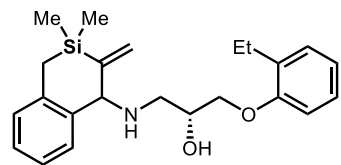
360\$6/1  
SY-147 19F CDCL3



**5**  
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

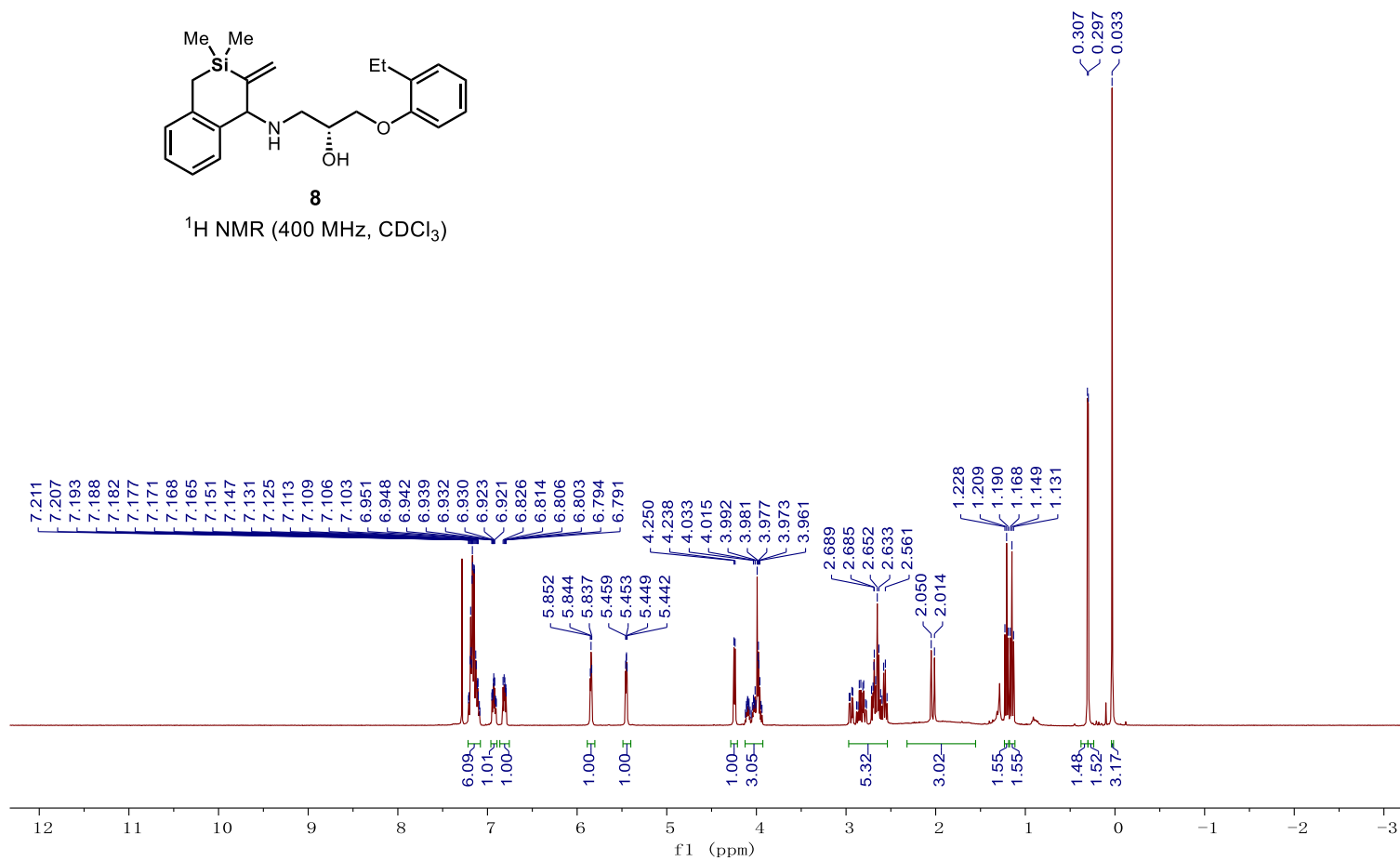


360\$1/2  
L-79 1H CDCL3

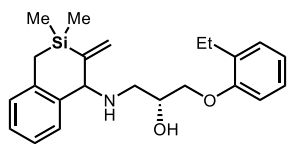


**8**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



360\$1/2  
L-79-2 13C CDCL3



**8**

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

