

# Supporting Information

## Visible Light-Induced Regioselective/Dehydrogenative Silylation of (Thio)chromones via Tricatalytic Process

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## A. General Information

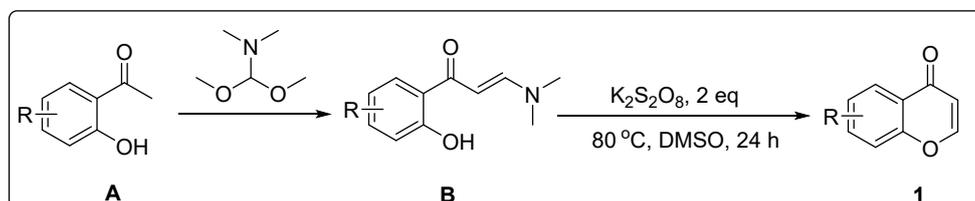
All purchased reagents and solvents were used without further purification unless otherwise noted. Melting points were measured with a melting point instrument and were uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker DRX-500 spectrometer using  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). Melting points were determined with a Büchi Melting Point B-545 instrument. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. The blue light source (460-465 nm) was provided by Shanghai 3S Technology Co., LtdSSSTECH-AL2 parallel reactor (Figure S1)



Figure S1. Photoreactor used in this study.

## B. Experimental Procedure

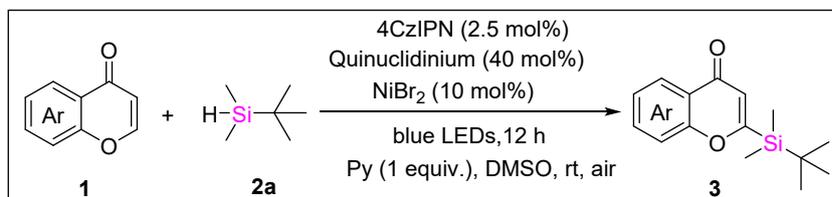
### B1. General Procedure for the Synthesis of 1



An oven dried sealed tube equipped with a stirring bar, filled with ketones (0.5 mmol), followed by of *N,N*-Dimethylformamide dimethyl acetal (DMF-DMA) (2.0 mmol) in toluene (5 mL). The reaction was allowed to stir at  $80\text{ }^\circ\text{C}$  for 6-8 h until the complete conversion of starting material as monitored by TLC. The reaction mixture was then concentrated and was purified by flash column chromatography (silica gel, pet. ether/EtOAc) to afford the desired products **B**. Add 4

mmol **B** and 2equiv of potassium persulfate to a 50ml round-bottomed flask, DMSO was used as solvent, the reaction was allowed to stir at 80 °C for 24 h, The reaction mixture was then concentrated and was purified by flash column chromatography (silica gel, pet. ether/EtOAc) to afford the desired products **1**.

## B2. General Procedure for the Synthesis of **3**



To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 4CzIPN (0.0025 mmol), NiBr<sub>2</sub> (0.01 mmol), and quinuclidine (0.04 mmol). Dry dimethyl sulfoxide (2.0 mL) was added, after which the alkene (0.1 mmol), silane (0.5 mmol) and pyridine (0.1 mmol) were added respectively at room temperature. Then placed in the irradiation apparatus equipped with a 12 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at 25 °C until the starting material was completely consumed as monitored by TLC. After the reaction was completed, the resulting mixture was extracted with ethyl acetate, dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated in vacuo. The desired products were obtained in the corresponding yields after being purified by column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate.

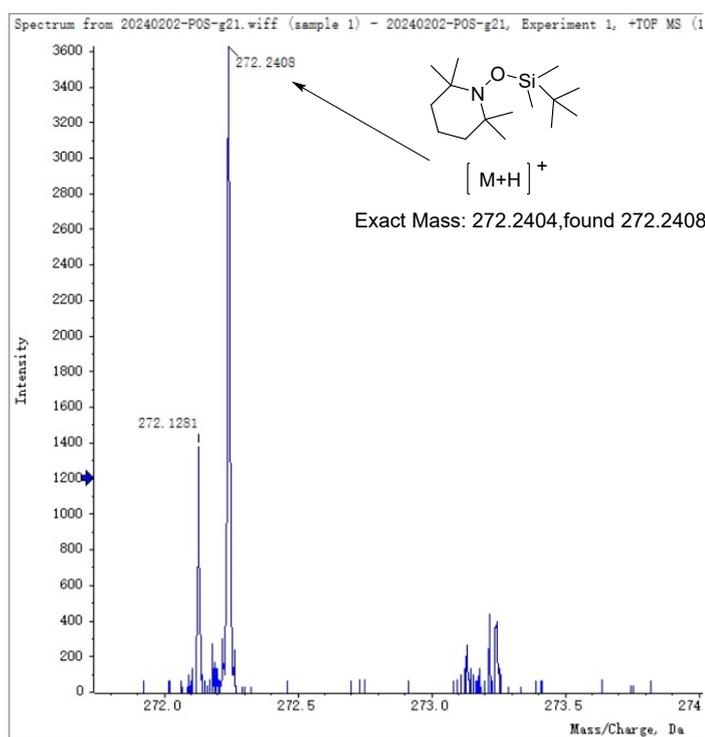
## C. Experimental Procedure for Gram Scale Reaction

To a 250 mL round-bottom flask equipped with a magnetic stir bar was added 4CzIPN (0.15 mmol), NiBr<sub>2</sub> (0.6 mmol), and quinuclidine (2.4 mmol). Dry dimethyl sulfoxide (100 mL) was added, after which **1a** (6 mmol), **2a** (30 mmol) and pyridine (6 mmol) were added to the mixture at room temperature, respectively. Then placed in the irradiation apparatus equipped with a 25 W blue light-emitting diode (LED) strip. The resulting mixture was stirred at 25 °C until the starting material was completely consumed as monitored by TLC. After the reaction was completed, the resulting mixture was extracted with ethyl acetate, dried over anhydrous MgSO<sub>4</sub>, filtered and evaporated in vacuo. The desired products were obtained in the corresponding yields after being purified by column chromatography on silica gel with a mixture of petroleum ether and ethyl acetate.

## D. Light On-off Experiment for the Synthesis of **3a**

To a 10 mL Schlenk tube equipped with a magnetic stir bar was added 4CzIPN (0.0025 mmol), NiBr<sub>2</sub> (0.01 mmol), and quinuclidine (0.04 mmol). Dry dimethyl sulfoxide (2.0 mL) was added, after which the alkene (0.1 mmol), silane (0.5 mmol) and pyridine (0.1 mmol) were added respectively at room temperature. Then placed in the irradiation apparatus equipped with a 25 W blue light-emitting diode (LED) strip. The reaction mixture was stirred for 0, 2, 4, 6, 8, 10, 12 and 14 hours respectively. Meanwhile, the setting time span for 2 hours, and only stirred without light. The yield of the product was determined by GC and dodecane as internal standard.

## E. The adduct of TEMPO and silicon radical detected by HRMS



## F. H<sub>2</sub> Detection Experiment

### F1. H<sub>2</sub> Detection Experiment for the Synthesis of 3a

In order to demonstrate the release of H<sub>2</sub> during this photoreaction procedure for the synthesis of **3a**, the model reaction of chromones (**1a**) and tert-butyldimethylsilane (**2a**) was monitored by a H<sub>2</sub> detector under standard conditions. Just as shown in Figure S1, as the reaction proceeded, the H<sub>2</sub> was observed clearly and the concentration increased gradually.

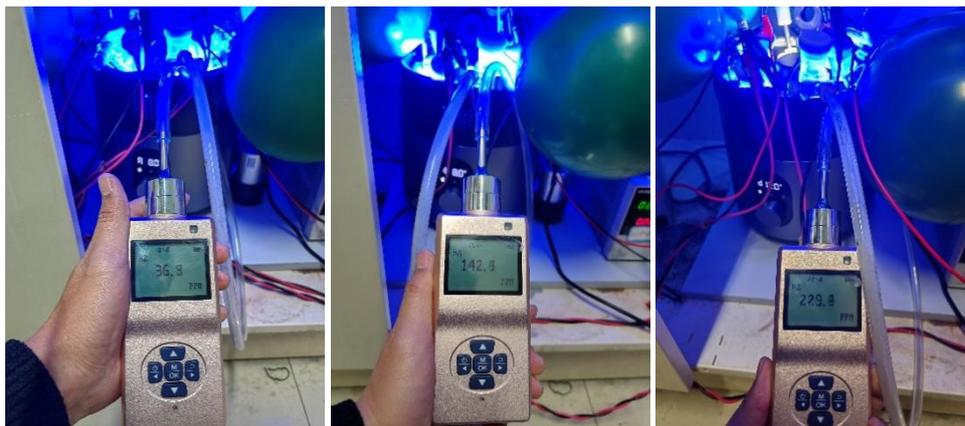
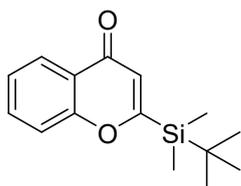


Figure S1. H<sub>2</sub> detection experiment by a H<sub>2</sub> detector for the synthesis of **3a**.

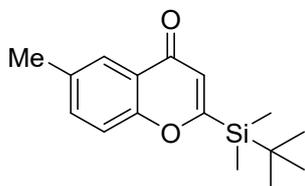
## G. Characterization Data of Products

### 2-(*tert*-butyldimethylsilyl)-4*H*-chromen-4-one (**3a**)



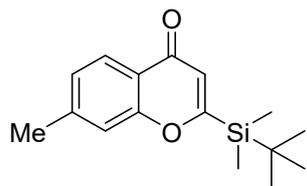
Yield 18.7 mg (72%, colorless liquid); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.06-7.98 (m, 1H), 7.80-7.74 (m, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 6.49 (s, 1H), 0.95 (s, 9H), 0.31 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sub>6</sub>) δ 176.27, 175.34, 157.88, 134.62, 125.67, 125.31, 124.42, 121.12, 118.93, 26.67, 16.91, -6.96. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>21</sub>O<sub>2</sub>Si 261.1311; Found 261.1313.

### 2-(*tert*-butyldimethylsilyl)-6-methyl-4*H*-chromen-4-one (**3b**)



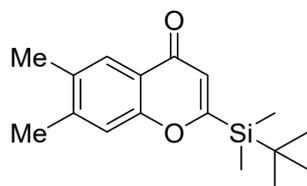
Yield 18.6 mg (68%, yellow liquid); <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.45 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 6.54-6.48 (m, 1H), 2.44 (s, 3H), 0.99 (s, 9H), 0.31 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, Chloroform-*d*) δ 176.65, 176.11, 156.42, 134.75, 134.69, 124.88, 124.21, 121.05, 118.04, 26.38, 20.93, 16.85, -7.15. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>23</sub>O<sub>2</sub>Si 275.1467; Found 275.1457.

### 2-(*tert*-butyldimethylsilyl)-7-methyl-4*H*-chromen-4-one (**3c**)



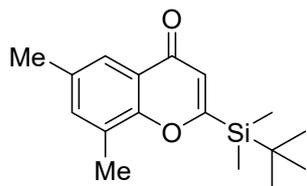
Yield 18.1 mg (66%, white solid); mp 111-114 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.78 (d,  $J$  = 5.6 Hz, 1H), 7.48 (s, 1H), 7.26 (s, 1H), 6.28 (d,  $J$  = 5.8 Hz, 1H), 2.49 (s, 3H), 0.96 (s, 9H), 0.39 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  177.81, 157.61, 153.98, 143.21, 139.76, 135.78, 126.78, 119.08, 112.97, 28.60, 21.81, 18.69, -1.29. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{23}\text{O}_2\text{Si}$  275.1467; Found 275.1459.

**2-(*tert*-butyldimethylsilyl)-6,7-dimethyl-4*H*-chromen-4-one (3d)**



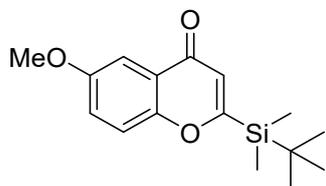
Yield 19 mg (66%, white solid); mp 96-99 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.93 (s, 1H), 7.25 (s, 1H), 6.49 (s, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 0.99 (s, 9H), 0.31 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  176.57, 175.72, 156.74, 143.94, 134.06, 125.16, 122.43, 121.07, 118.37, 26.40, 20.38, 19.31, 16.85, -7.15. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{25}\text{O}_2\text{Si}$  289.1624; Found 289.1618.

**2-(*tert*-butyldimethylsilyl)-6,8-dimethyl-4*H*-chromen-4-one (3e)**



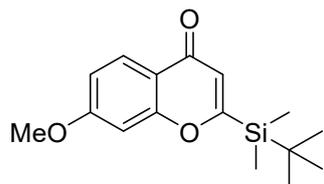
Yield 20.5 mg (71%, white solid); mp 92-95 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.84 (s, 1H), 7.32 (s, 1H), 6.54 (s, 1H), 2.46 (s, 3H), 2.41 (s, 3H), 1.01 (s, 9H), 0.34 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  177.04, 175.48, 155.01, 135.72, 134.13, 127.27, 124.11, 122.49, 120.92, 26.38, 20.90, 16.67, 15.77, -7.11. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{25}\text{O}_2\text{Si}$  289.1624; Found 289.1614.

**2-(*tert*-butyldimethylsilyl)-6-methoxy-4*H*-chromen-4-one (3f)**



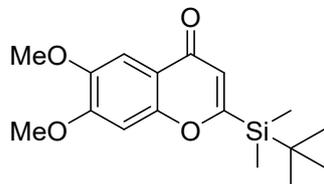
Yield 20.3 mg (70%, yellow liquid);  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.57 (d,  $J = 3.1$  Hz, 1H), 7.41 (d,  $J = 9.1$  Hz, 1H), 7.29-7.24 (m, 1H), 6.54 (s, 1H), 3.91 (s, 3H), 1.00 (s, 9H), 0.33 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  176.42, 175.99, 156.66, 153.18, 125.09, 123.79, 120.36, 119.77, 104.44, 55.94, 26.39, 16.88, -7.12. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{23}\text{O}_3\text{Si}$  291.1416; Found 291.1410.

**2-(*tert*-butyldimethylsilyl)-7-methoxy-4*H*-chromen-4-one (3g)**



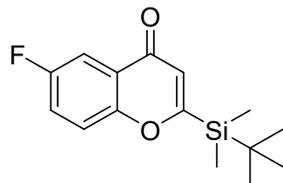
Yield 18.3 mg (63%, white solid); mp 88-91 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.11 (d,  $J = 8.8$  Hz, 1H), 6.95 (dd,  $J = 8.9, 2.4$  Hz, 1H), 6.83 (d,  $J = 2.4$  Hz, 1H), 6.49 (s, 1H), 3.92 (s, 3H), 1.01 (s, 9H), 0.32 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  175.96, 175.62, 163.96, 159.89, 127.07, 121.33, 118.52, 114.41, 100.12, 55.81, 26.42, 16.84, -7.12. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{23}\text{O}_3\text{Si}$  291.1416; Found 291.1412.

**2-(*tert*-butyldimethylsilyl)-6,7-dimethoxy-4*H*-chromen-4-one (3h)**



Yield 24.3 mg (76%, yellow solid); mp 143-145 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.53 (s, 1H), 6.86 (s, 1H), 6.52 (s, 1H), 3.99 (d,  $J = 14.8$  Hz, 6H), 1.00 (s, 9H), 0.32 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  175.63, 175.23, 154.47, 154.36, 147.43, 120.76, 117.99, 104.16, 99.74, 56.46, 56.37, 26.42, 16.85, -7.10. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{25}\text{O}_4\text{Si}$  321.1522; Found 321.1516.

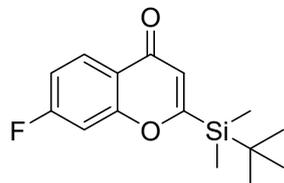
**2-(*tert*-butyldimethylsilyl)-6-fluoro-4*H*-chromen-4-one (3i)**



Yield 16.1 mg (58%, white solid); mp 91-94 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.84 (dd,  $J = 8.1, 3.1$  Hz, 1H), 7.48 (dd,  $J = 9.4, 4.3$  Hz, 1H), 7.38 (dq,  $J = 9.5, 3.1$  Hz, 1H), 6.53 (s, 1H), 1.01 (s, 9H), 0.33 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  176.73, 175.78 (d,  $J_{\text{C-F}} = 2.5$  Hz), 159.27 (d,  $J_{\text{C-F}} =$

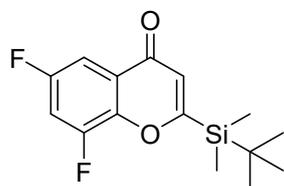
245 Hz), 154.40, 125.63 (d,  $J_{C-F}$  = 6.3 Hz), 121.77 (d,  $J_{C-F}$  = 25 Hz), 120.41, 120.40 (d,  $J_{C-F}$  = 8.8 Hz), 110.37 (d,  $J_{C-F}$  = 23.8 Hz), 26.37, 16.87, -7.15.  $^{19}\text{F}$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -115.59. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{20}\text{FO}_2\text{Si}$  279.1217; Found 279.1213.

**2-(*tert*-butyldimethylsilyl)-7-fluoro-4*H*-chromen-4-one (3j)**



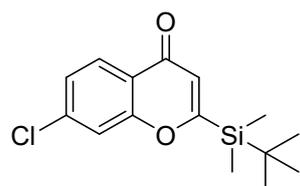
Yield 17.2 mg (62%, white solid); mp 64-66 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.22 (ddd,  $J$  = 8.5, 6.3, 1.8 Hz, 1H), 7.20-7.08 (m, 2H), 6.52 (d,  $J$  = 1.8 Hz, 1H), 1.01 (s, 9H), 0.33 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  176.73, 175.63, 166.55 (d,  $J_{C-F}$  = 253.8 Hz), 159.08 (d,  $J_{C-F}$  = 13.8 Hz), 128.29 (d,  $J_{C-F}$  = 10.0 Hz), 121.45 (d,  $J_{C-F}$  = 2.5 Hz), 121.38, 113.68 (d,  $J_{C-F}$  = 22.5 Hz), 104.75 (d,  $J_{C-F}$  = 25.0 Hz), 26.37, 16.85, -7.16.  $^{19}\text{F}$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -103.17, -103.19. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{20}\text{FO}_2\text{Si}$  279.1217; Found 279.1209.

**2-(*tert*-butyldimethylsilyl)-6,8-difluoro-4*H*-chromen-4-one (3k)**



Yield 11 mg (37%, white solid); mp 128-131 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.90 (d,  $J$  = 5.9 Hz, 1H), 7.63-7.50 (m, 1H), 6.37 (d,  $J$  = 6.0 Hz, 1H), 0.97 (s, 9H), 0.45 (t,  $J$  = 2.5 Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  175.80, 163.21 (d,  $J_{C-F}$  = 13.8 Hz), 161.27 (d,  $J_{C-F}$  = 15.0 Hz), 155.24 (dd,  $J_{C-F}$  = 235.0 Hz), 155.01, 141.92 (d,  $J_{C-F}$  = 15.0 Hz), 127.75 (d,  $J_{C-F}$  = 8.8 Hz), 112.70, 105.25 (dd,  $J_{C-F}$  = 25.0 Hz), 26.24, 17.74, -3.81, -3.85, -3.89.  $^{19}\text{F}$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -96.58, -113.26. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{19}\text{F}_2\text{O}_2\text{Si}$  297.1122; Found 297.1114.

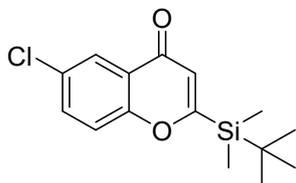
**2-(*tert*-butyldimethylsilyl)-7-chloro-4*H*-chromen-4-one (3l)**



Yield 16.8 mg (57%, white solid); mp 89-92 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.14 (d,  $J$  = 8.5 Hz, 1H), 7.51 (d,  $J$  = 2.0 Hz, 1H), 7.36 (dd,  $J$  = 8.6, 1.9 Hz, 1H), 6.53 (s, 1H), 1.01 (s, 9H), 0.33 (s, 6H).

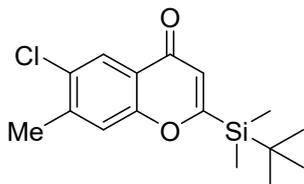
$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  176.71, 175.71, 158.15, 139.56, 127.14, 125.68, 123.10, 121.50, 118.30, 26.38, 16.87, -7.16. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{20}\text{ClO}_2\text{Si}$  295.0921; Found 295.0914.

**2-(*tert*-butyldimethylsilyl)-6-chloro-4*H*-chromen-4-one (3m)**



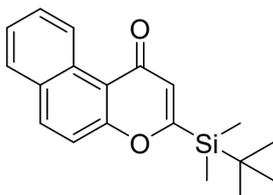
Yield 12.3 mg (42%, white solid); mp 91-94 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.17 (d,  $J$  = 2.6 Hz, 1H), 7.60 (dd,  $J$  = 9.0, 2.6 Hz, 1H), 7.44 (d,  $J$  = 9.0 Hz, 1H), 6.54 (s, 1H), 1.01 (s, 9H), 0.33 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  176.83, 175.31, 156.42, 133.73, 130.70, 125.54, 125.07, 121.12, 120.06, 26.38, 16.88, -7.15. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{20}\text{ClO}_2\text{Si}$  295.0921; Found 295.0916.

**2-(*tert*-butyldimethylsilyl)-6-chloro-7-methyl-4*H*-chromen-4-one (3n)**



Yield 16.6 mg (54%, white solid); mp 95-98 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.21-8.10 (m, 1H), 7.37 (s, 1H), 6.56-6.46 (m, 1H), 2.50 (s, 3H), 1.03-0.98 (m, 9H), 0.36-0.30 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  176.48, 175.38, 156.39, 142.73, 131.47, 125.30, 123.61, 121.02, 120.12, 26.38, 20.78, 16.87, -7.16. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{22}\text{ClO}_2\text{Si}$  309.1078; Found 309.1071.

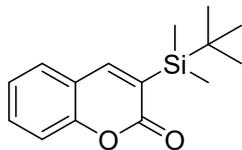
**3-(*tert*-butyldimethylsilyl)-1*H*-benzo[*f*]chromen-1-one (3o)**



Yield 10 mg (32%, colorless liquid);  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  10.06 (d,  $J$  = 8.6 Hz, 1H), 8.08 (d,  $J$  = 9.0 Hz, 1H), 7.91 (d,  $J$  = 8.1 Hz, 1H), 7.77 (t,  $J$  = 7.7 Hz, 1H), 7.63 (t,  $J$  = 7.5 Hz, 1H), 7.53 (d,  $J$  = 8.9 Hz, 1H), 6.72 (s, 1H), 1.04 (s, 9H), 0.38 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  178.32, 172.78, 159.33, 135.27, 130.60, 130.35, 129.14, 128.11, 127.31, 126.49, 124.58, 118.02, 117.86,

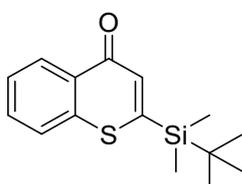
26.42, 16.89, -7.09. HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{19}H_{23}O_2Si$  311.1467; Found 311.1460.

**3-(*tert*-butyldimethylsilyl)-2*H*-chromen-2-one (3p)**



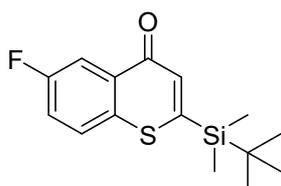
Yield 12.2 mg (47%, white solid); mp 98-100 °C.  $^1H$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.82 (d,  $J = 2.1$  Hz, 1H), 7.56-7.45 (m, 2H), 7.34-7.23 (m, 2H), 0.98 (s, 9H), 0.34 (s, 6H).  $^{13}C\{^1H\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  162.75, 154.79, 151.56, 131.75, 128.01, 127.68, 123.97, 119.22, 116.57, 27.03, 17.35, -5.66.

**2-(*tert*-butyldimethylsilyl)-4*H*-thiochromen-4-one (3q)**



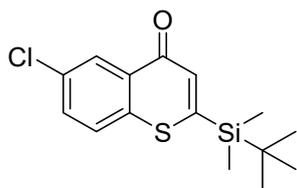
Yield 17.1 mg (62%, white solid); mp 121-124 °C.  $^1H$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.56 (d,  $J = 8.1$  Hz, 1H), 7.68-7.59 (m, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.21 (s, 1H), 1.00 (s, 9H), 0.39 (s, 6H).  $^{13}C\{^1H\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  178.36, 153.87, 140.32, 132.00, 131.75, 131.18, 128.52, 127.78, 126.02, 26.45, 17.15, -6.25. HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{15}H_{21}OSSi$  277.1082; Found 277.1071.

**2-(*tert*-butyldimethylsilyl)-6-fluoro-4*H*-thiochromen-4-one (3r)**



Yield 14.4 mg (49%, white solid); mp 86-89 °C.  $^1H$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.22 (dd,  $J = 9.5, 2.6$  Hz, 1H), 7.64 (dd,  $J = 9.1, 4.8$  Hz, 1H), 7.42-7.34 (m, 1H), 7.17 (s, 1H), 1.00 (s, 9H), 0.39 (s, 6H).  $^{13}C\{^1H\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  177.52, 162.11 (d,  $J_{C-F} = 248.8$  Hz), 153.84, 135.74 (d,  $J_{C-F} = 2.5$  Hz), 133.68 (d,  $J_{C-F} = 7.5$  Hz), 130.94, 128.29 (d,  $J_{C-F} = 7.5$  Hz), 120.11 (d,  $J_{C-F} = 25.0$  Hz), 113.91 (d,  $J_{C-F} = 22.5$  Hz), 26.42, 17.15, -6.25.  $^{19}F$  NMR (471 MHz, Chloroform-*d*)  $\delta$  -111.14. HRMS (ESI-TOF)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{15}H_{20}FOSSi$  295.0988; Found 295.0982.

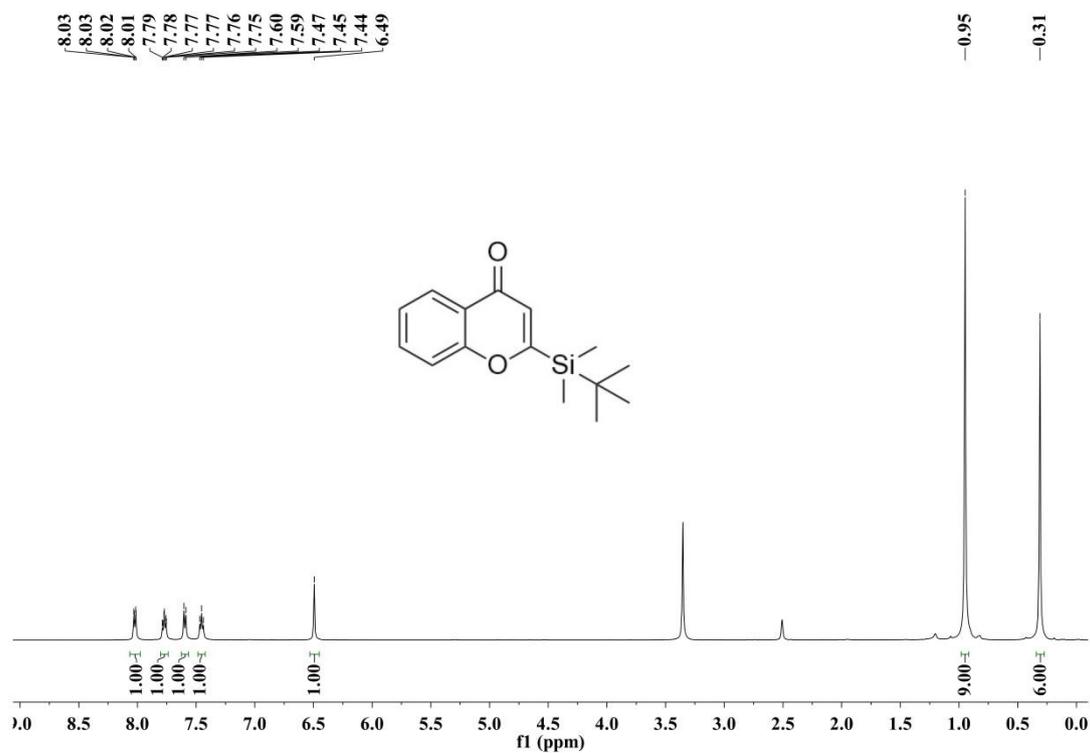
**2-(*tert*-butyldimethylsilyl)-6-chloro-4*H*-thiochromen-4-one (3s)**



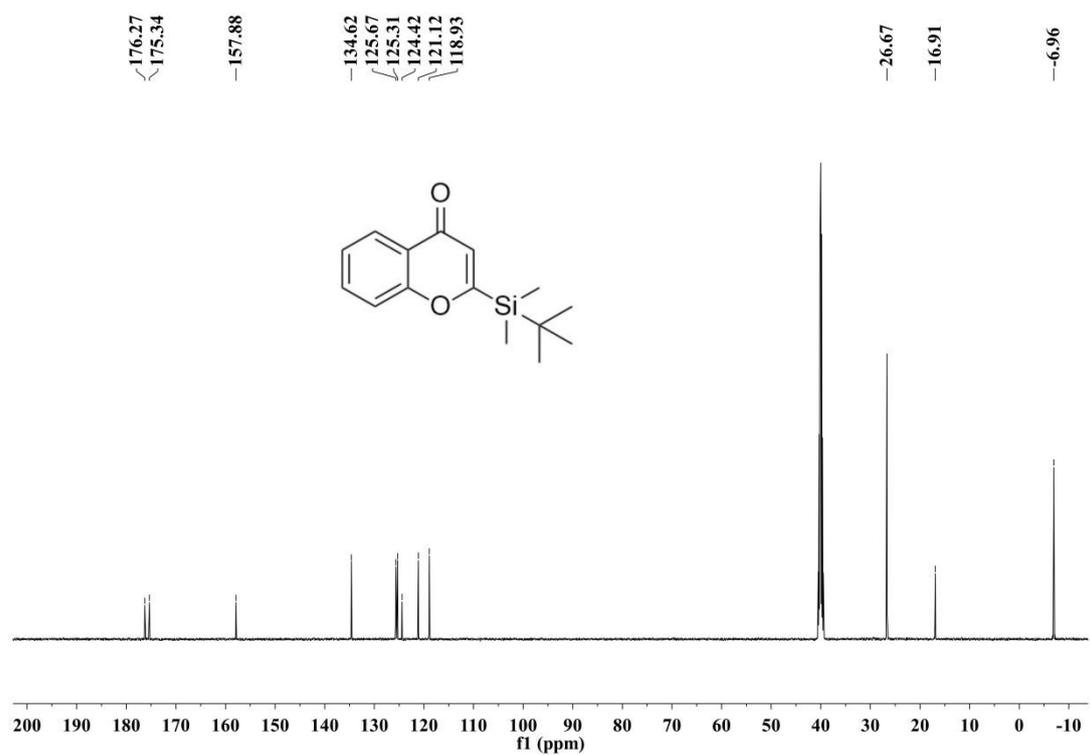
Yield 14.2 mg (46%, yellow solid); mp 99-101 °C.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.54 (s, 1H), 7.58 (s, 2H), 7.22-7.15 (m, 1H), 1.00 (s, 9H), 0.38 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, Chloroform-*d*)  $\delta$  177.18, 153.86, 138.36, 134.22, 132.88, 131.80, 131.59, 128.08, 127.57, 26.42, 17.16, -6.27. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{20}\text{ClO}\text{Si}$  311.0693; Found 311.0689.

## H. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

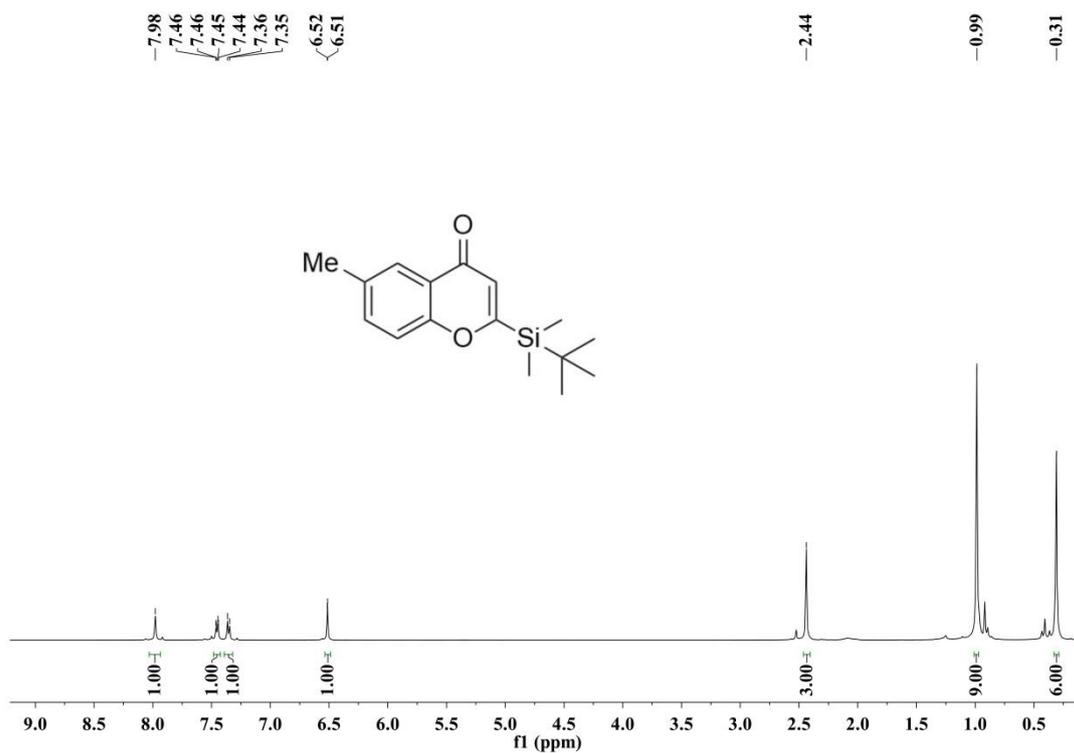
$^1\text{H}$  NMR spectrum of 3a (500 MHz,  $\text{DMSO-}d_6$ )



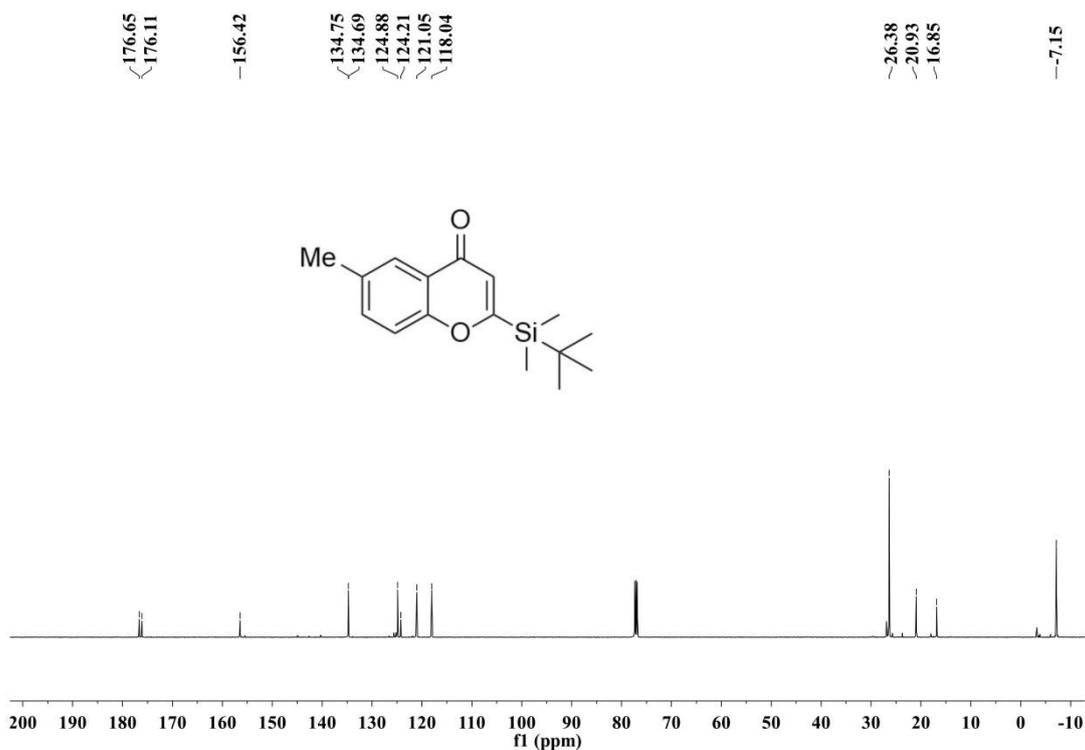
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3a (125 MHz,  $\text{DMSO-}d_6$ )



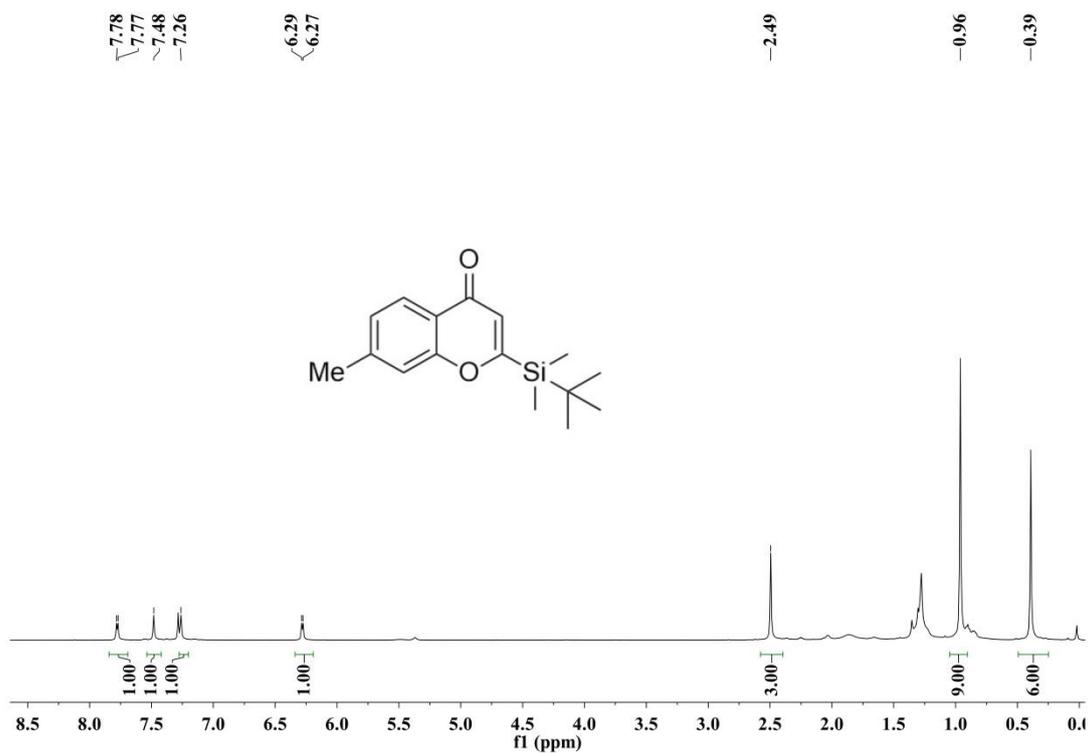
**$^1\text{H}$  NMR spectrum of 3b (500 MHz,  $\text{CDCl}_3$ )**



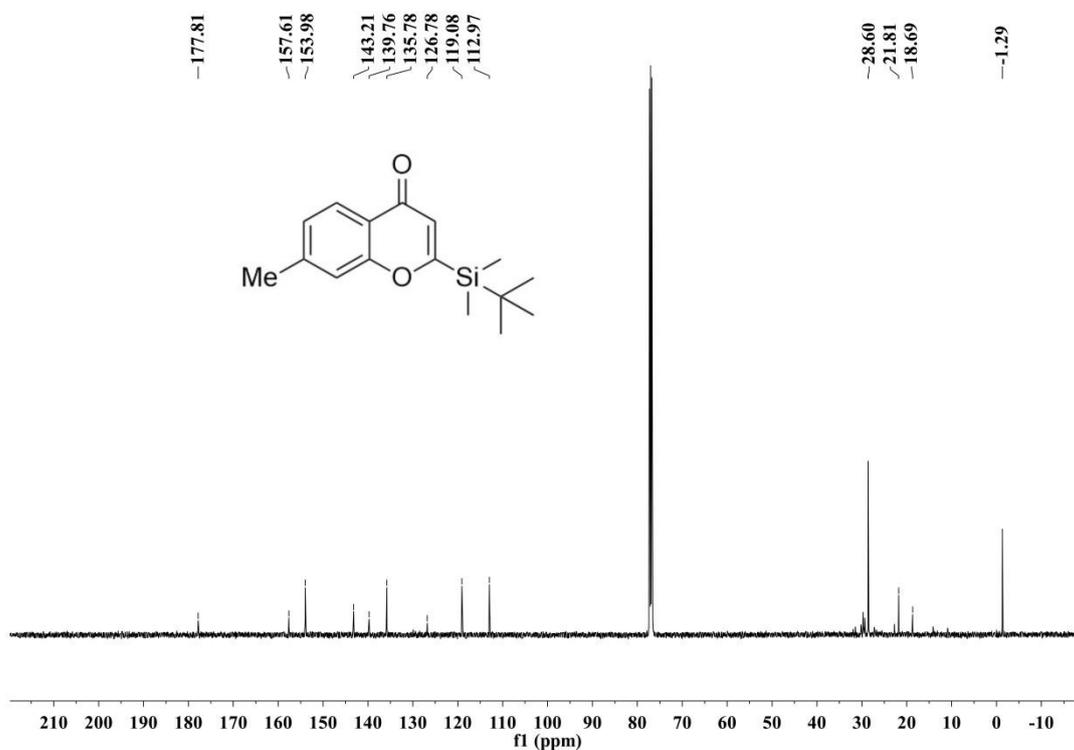
**$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3b (125 MHz,  $\text{CDCl}_3$ )**



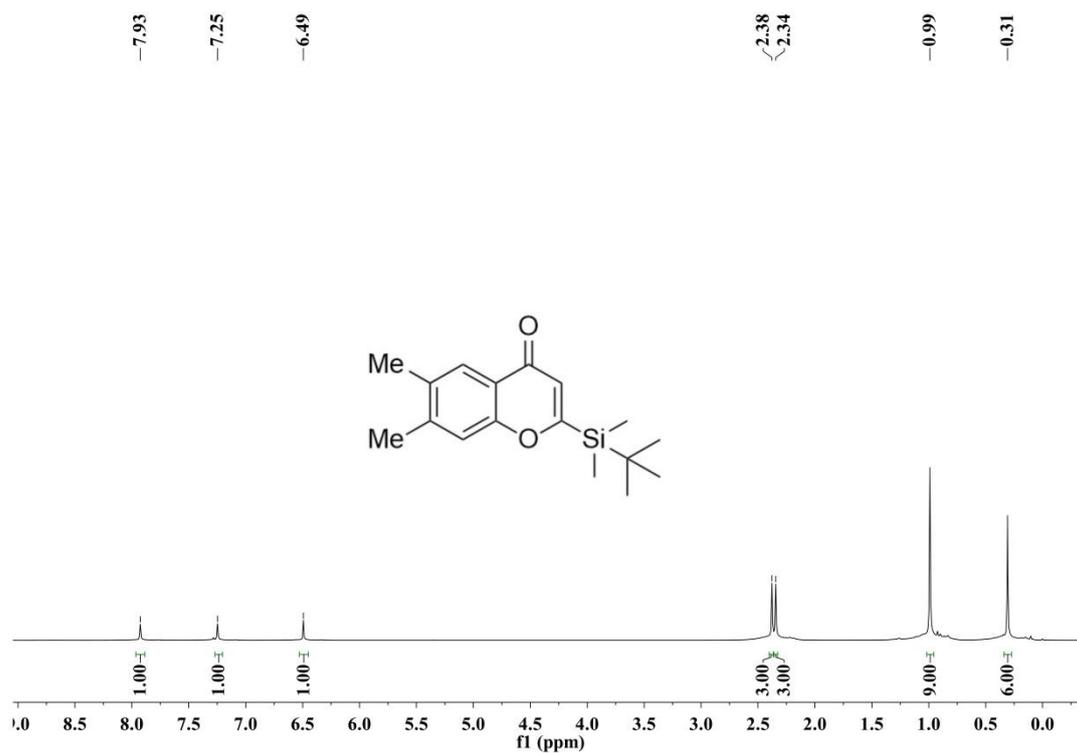
**<sup>1</sup>H NMR spectrum of 3c (500 MHz, CDCl<sub>3</sub>)**



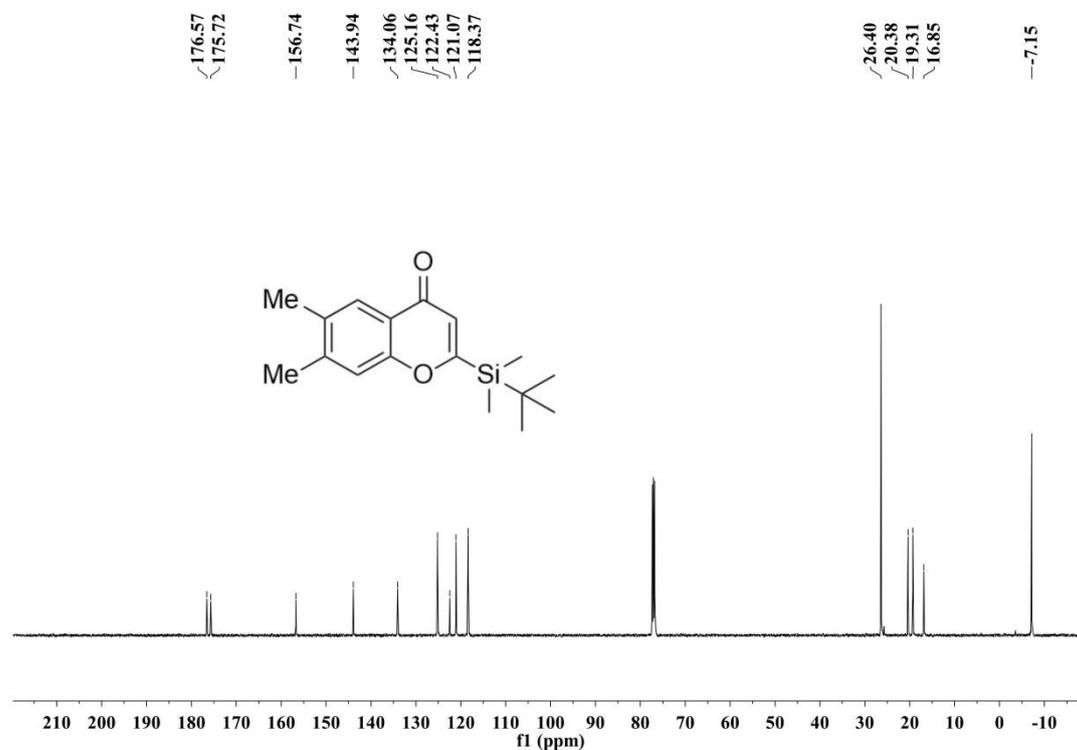
**<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3c (125 MHz, CDCl<sub>3</sub>)**



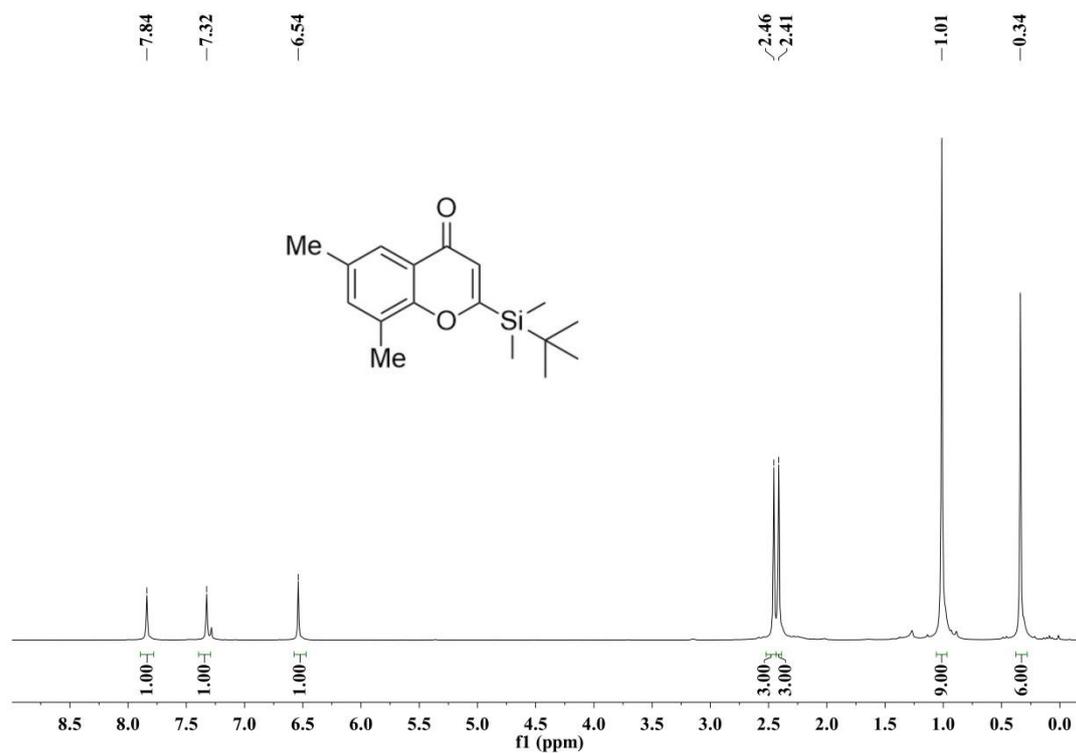
**<sup>1</sup>H NMR spectrum of 3d (500 MHz, CDCl<sub>3</sub>)**



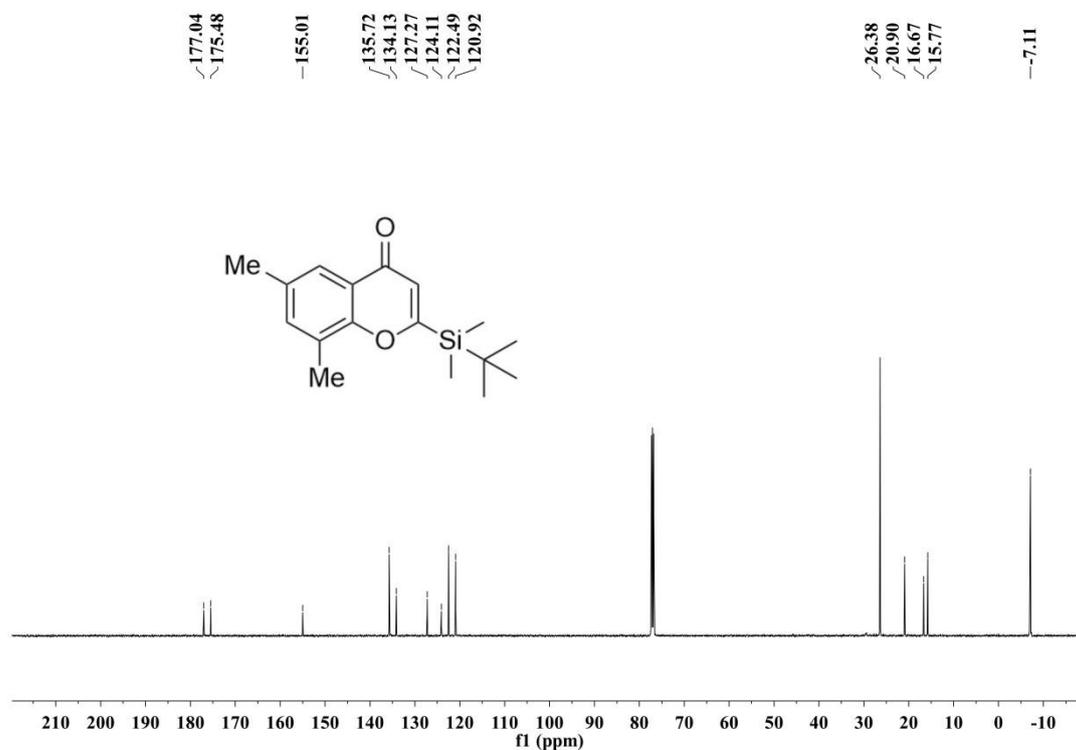
**<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3d (125 MHz, CDCl<sub>3</sub>)**



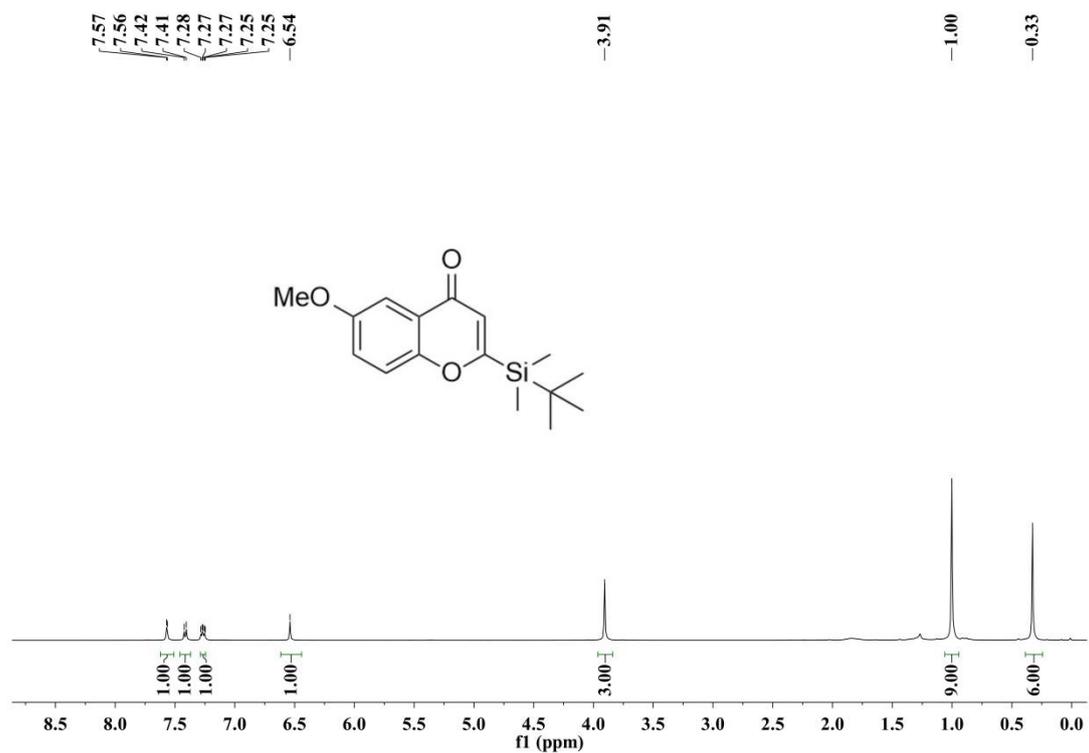
**<sup>1</sup>H NMR spectrum of 3e (500 MHz, CDCl<sub>3</sub>)**



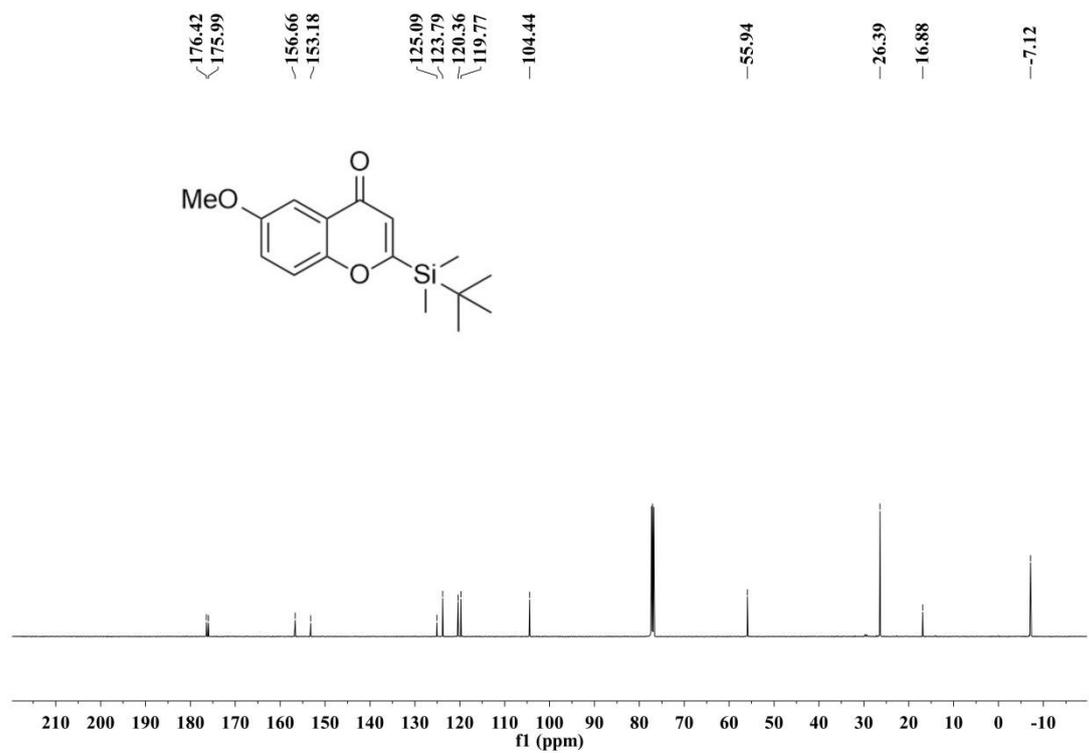
**<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3e (125 MHz, CDCl<sub>3</sub>)**



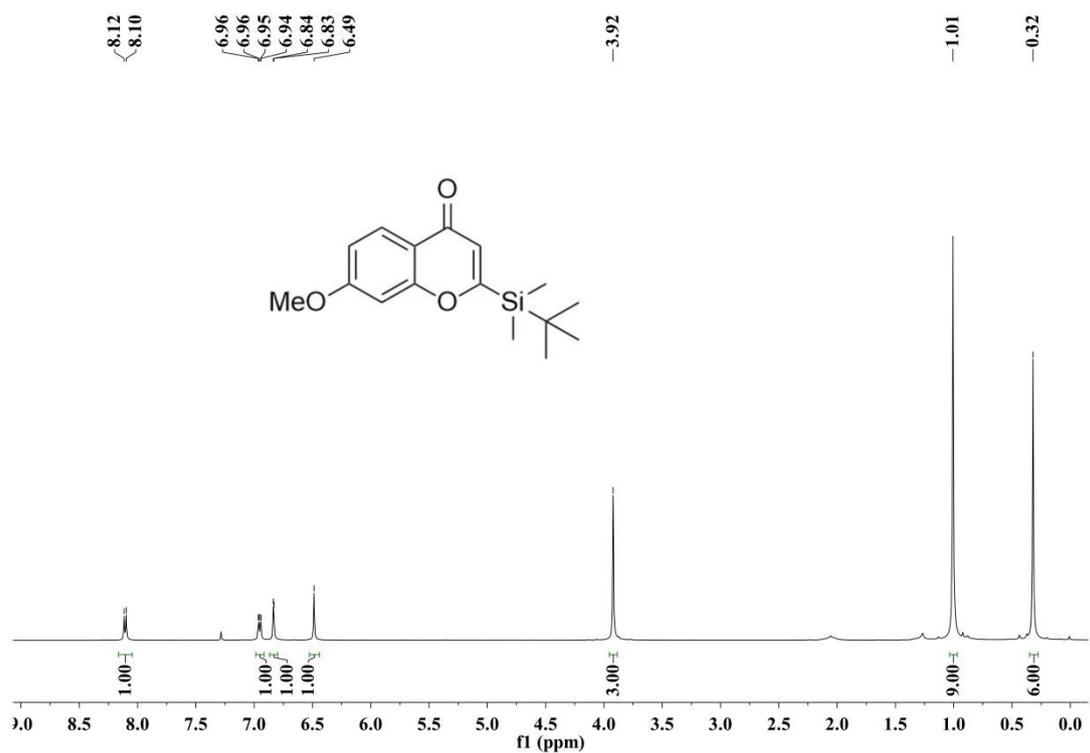
**<sup>1</sup>H NMR spectrum of 3f (500 MHz, CDCl<sub>3</sub>)**



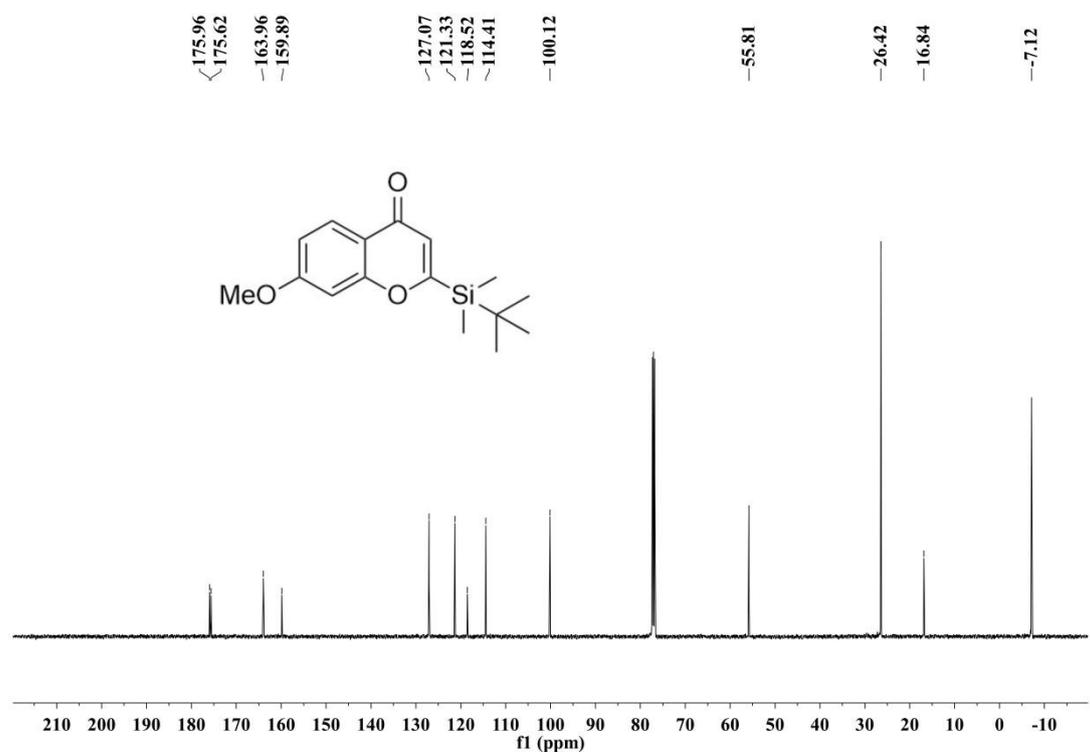
**<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3f (125 MHz, CDCl<sub>3</sub>)**



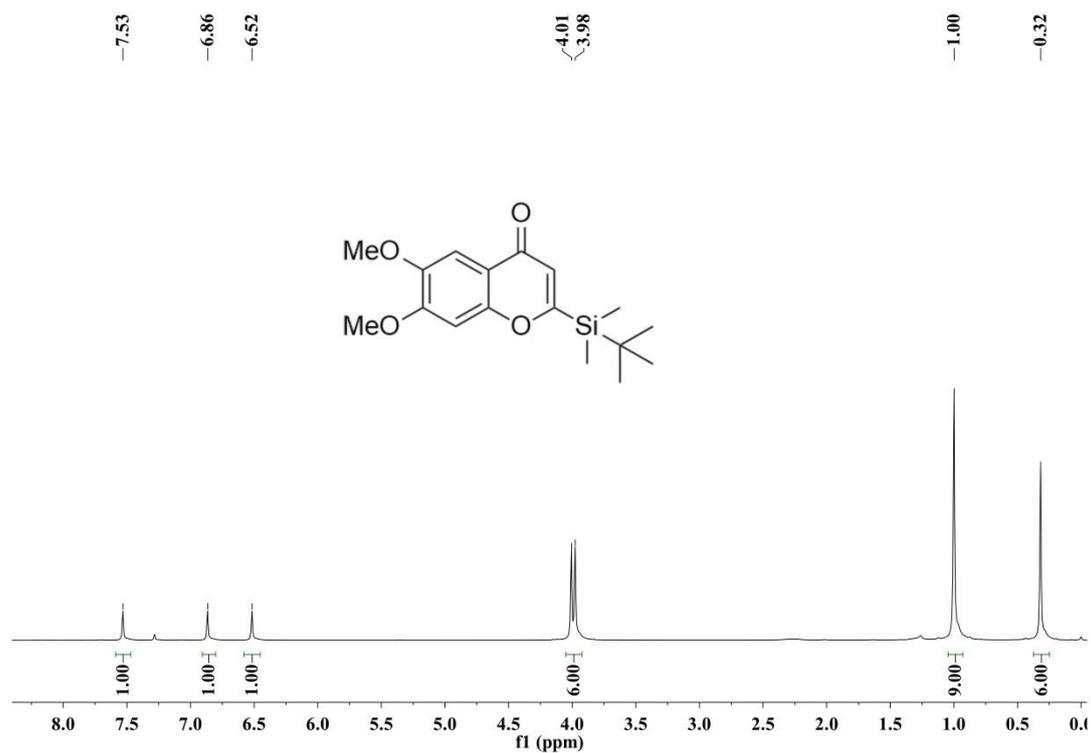
**$^1\text{H}$  NMR spectrum of 3g (500 MHz,  $\text{CDCl}_3$ )**



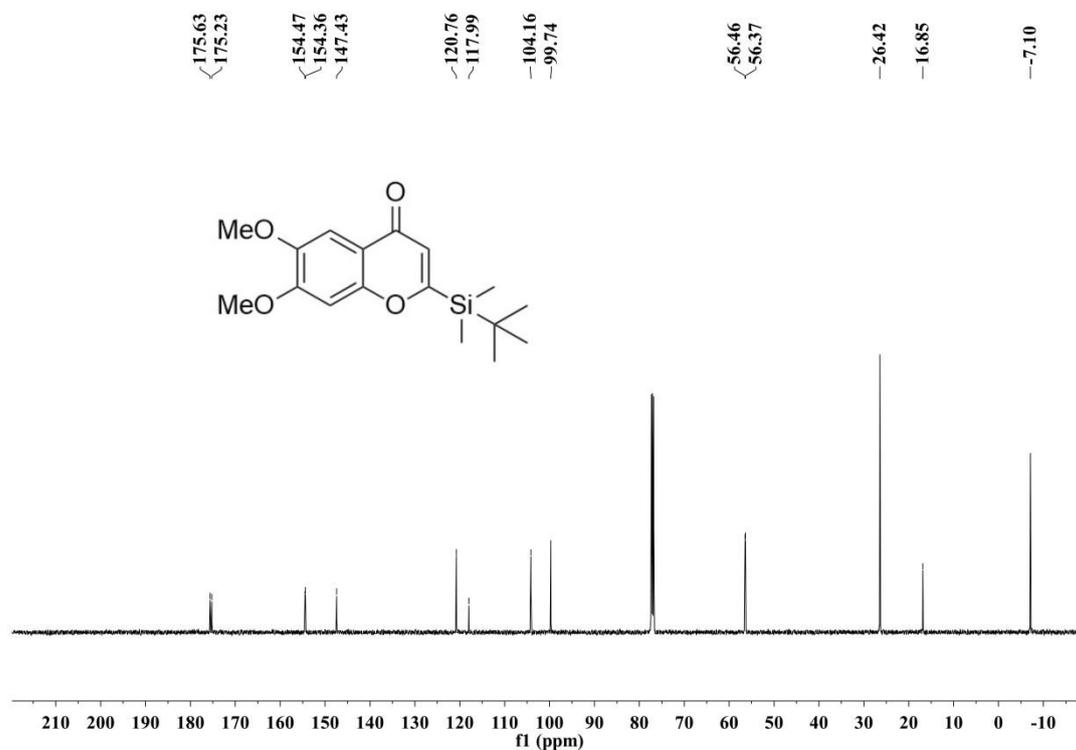
**$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3g (125 MHz,  $\text{CDCl}_3$ )**



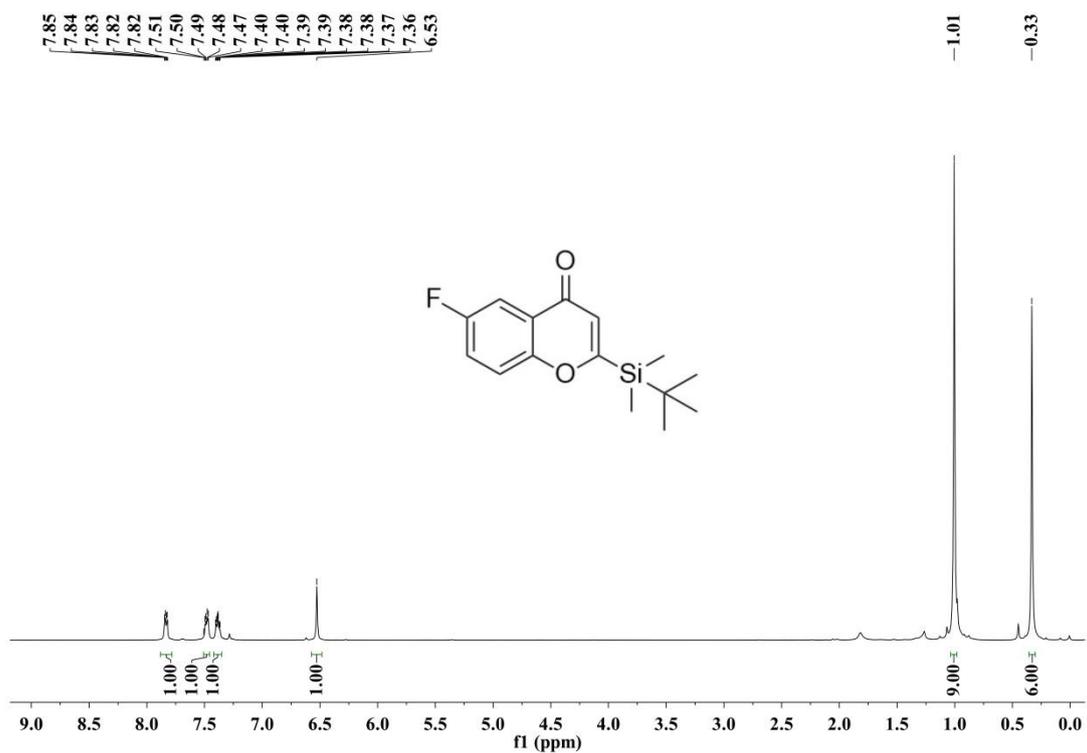
**$^1\text{H}$  NMR spectrum of 3h (500 MHz,  $\text{CDCl}_3$ )**



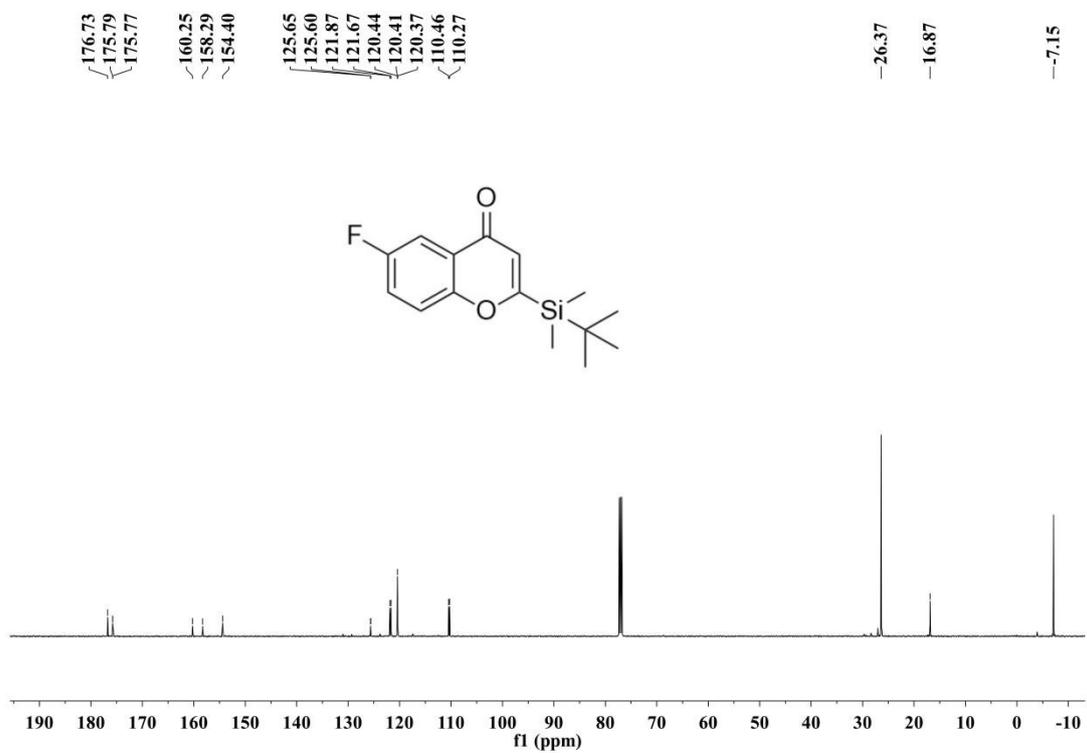
**$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3h (125 MHz,  $\text{CDCl}_3$ )**



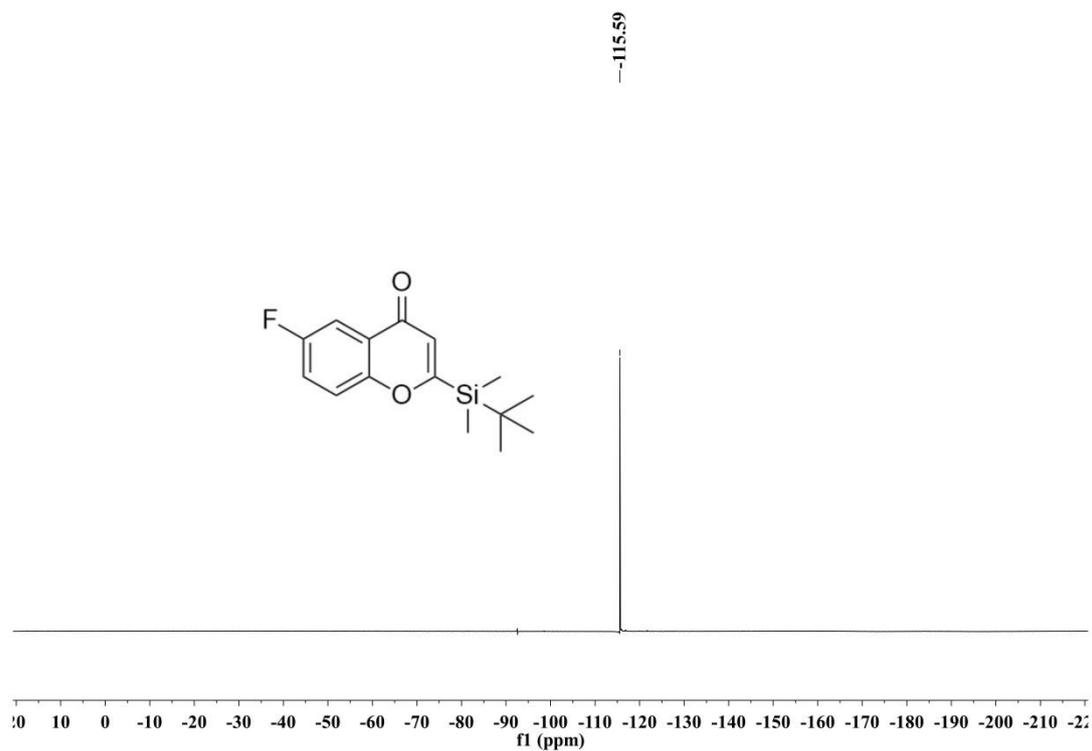
**<sup>1</sup>H NMR spectrum of 3i (500 MHz, CDCl<sub>3</sub>)**



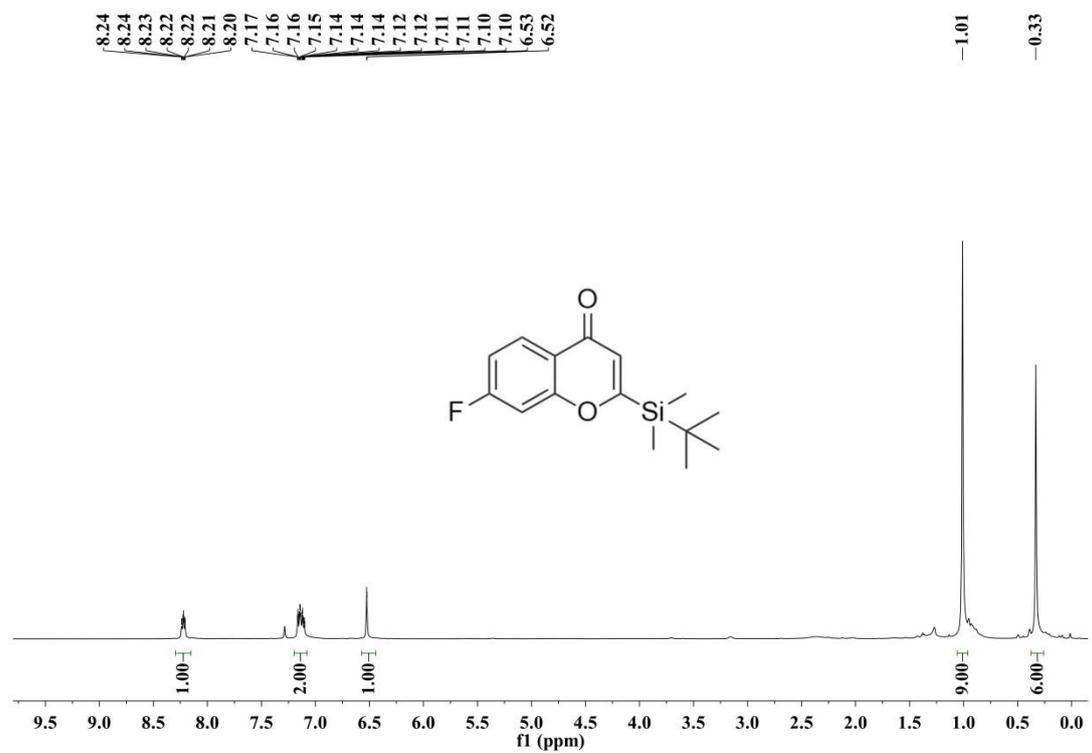
**<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3i (125 MHz, CDCl<sub>3</sub>)**



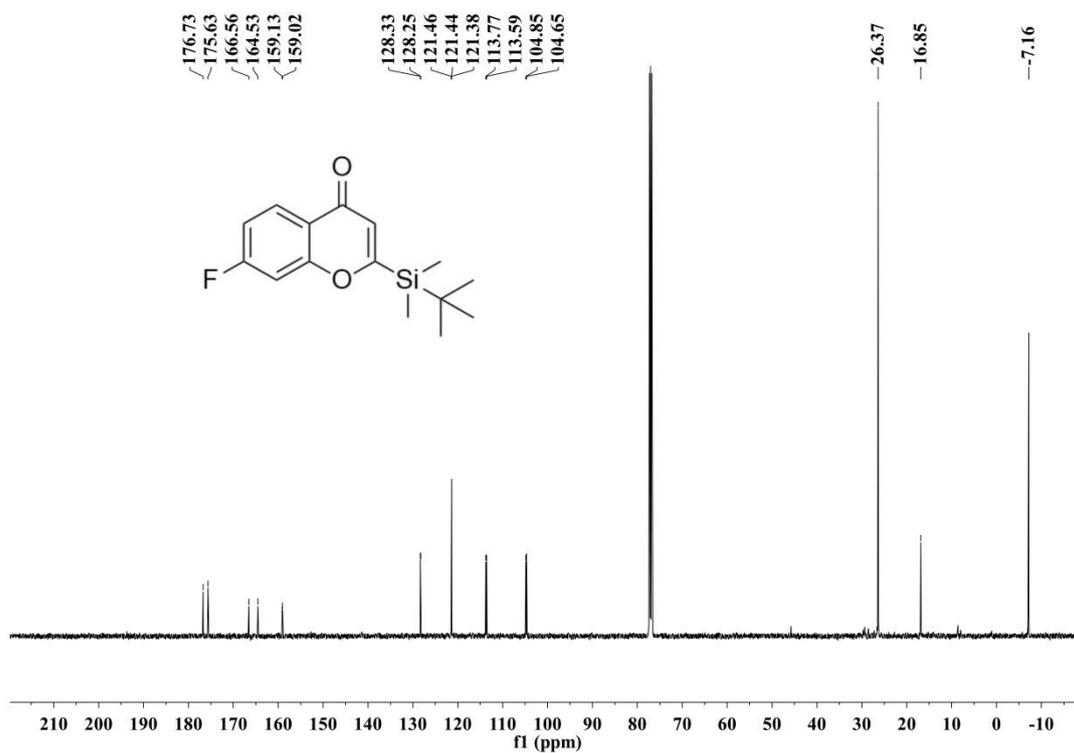
**<sup>19</sup>F NMR spectrum of 3i (125 MHz, CDCl<sub>3</sub>)**



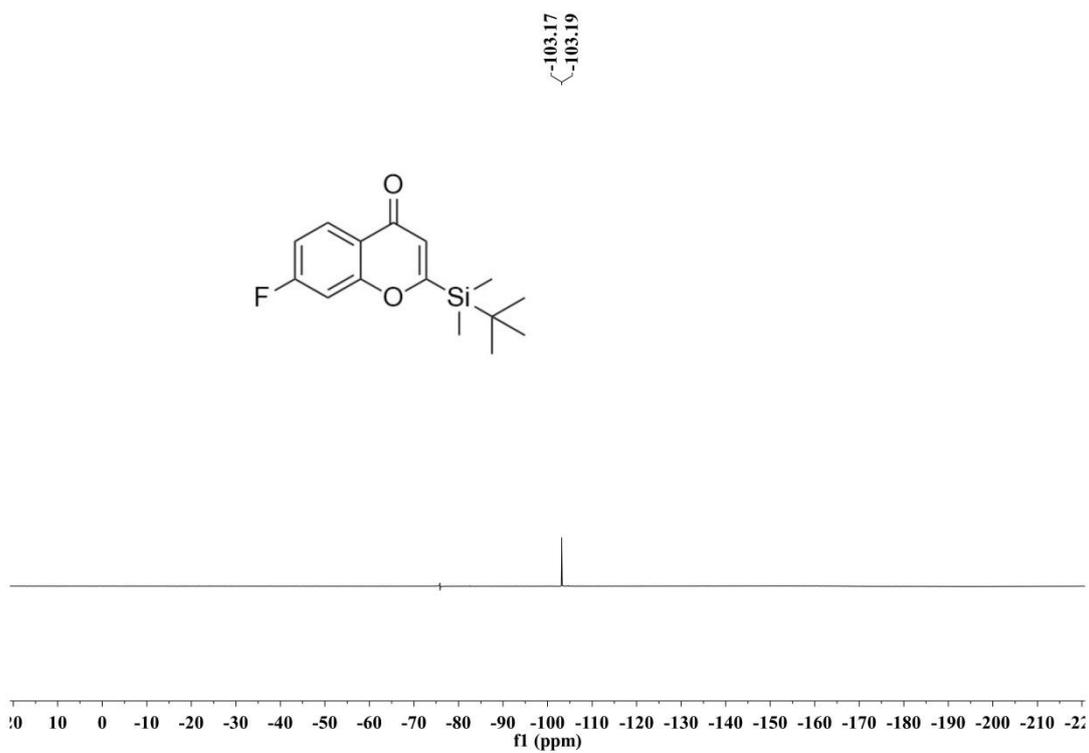
**<sup>1</sup>H NMR spectrum of 3j (500 MHz, CDCl<sub>3</sub>)**



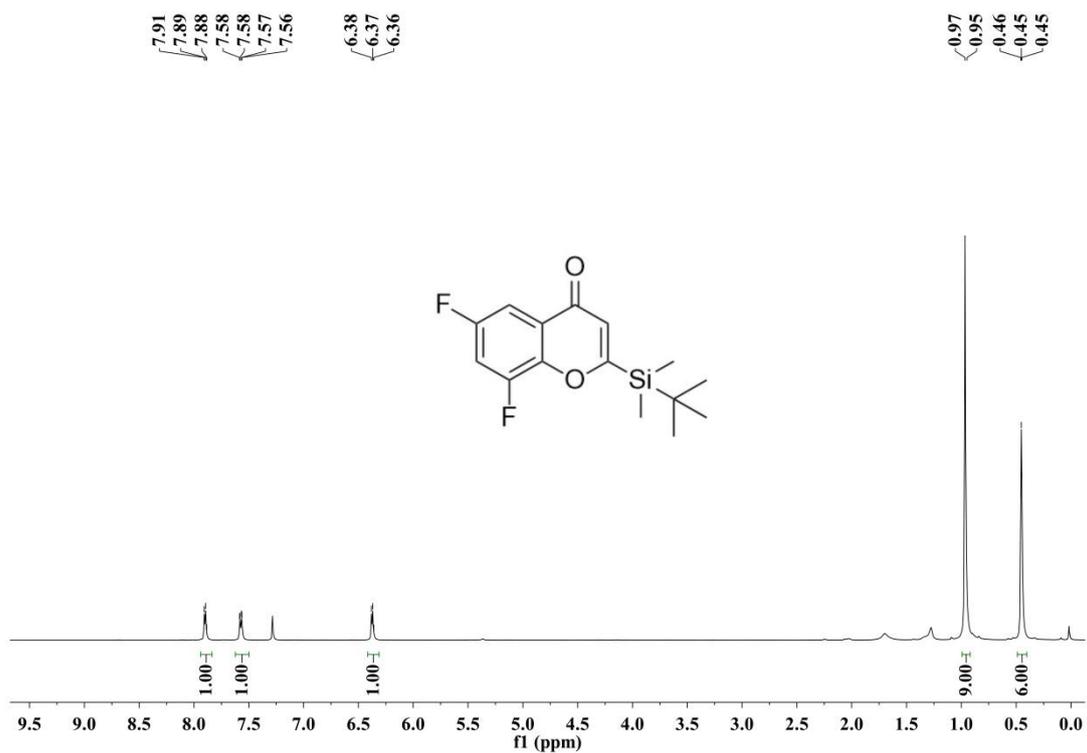
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3j (125 MHz,  $\text{CDCl}_3$ )



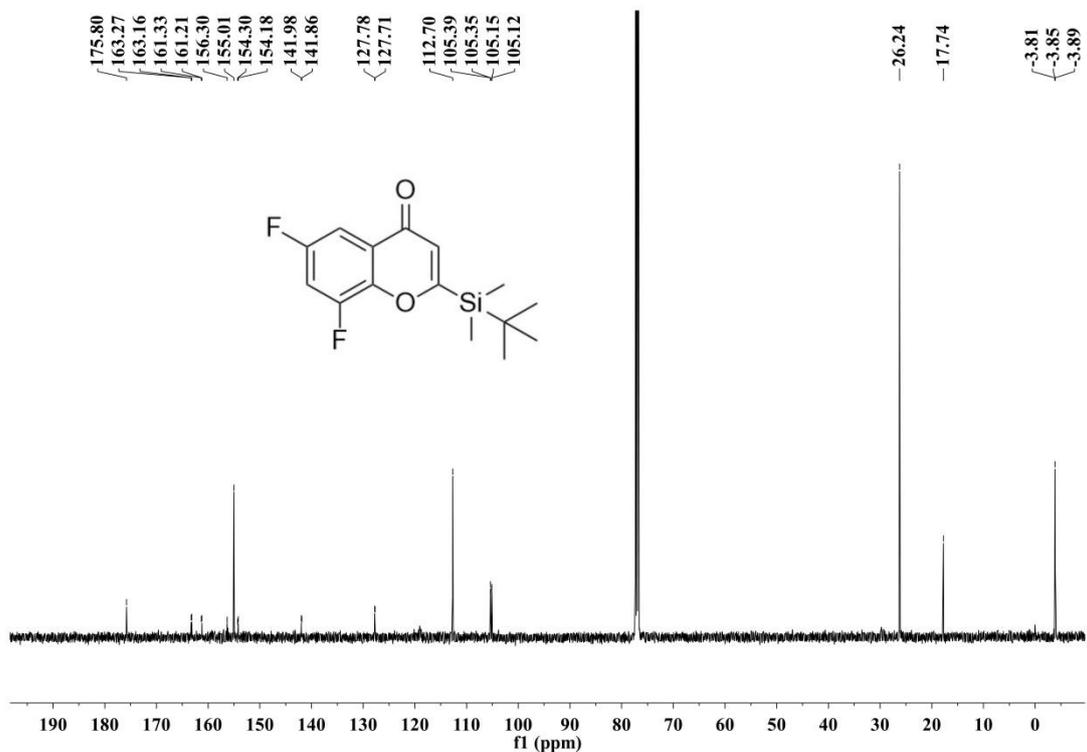
$^{19}\text{F}$  NMR spectrum of 3i (125 MHz,  $\text{CDCl}_3$ )



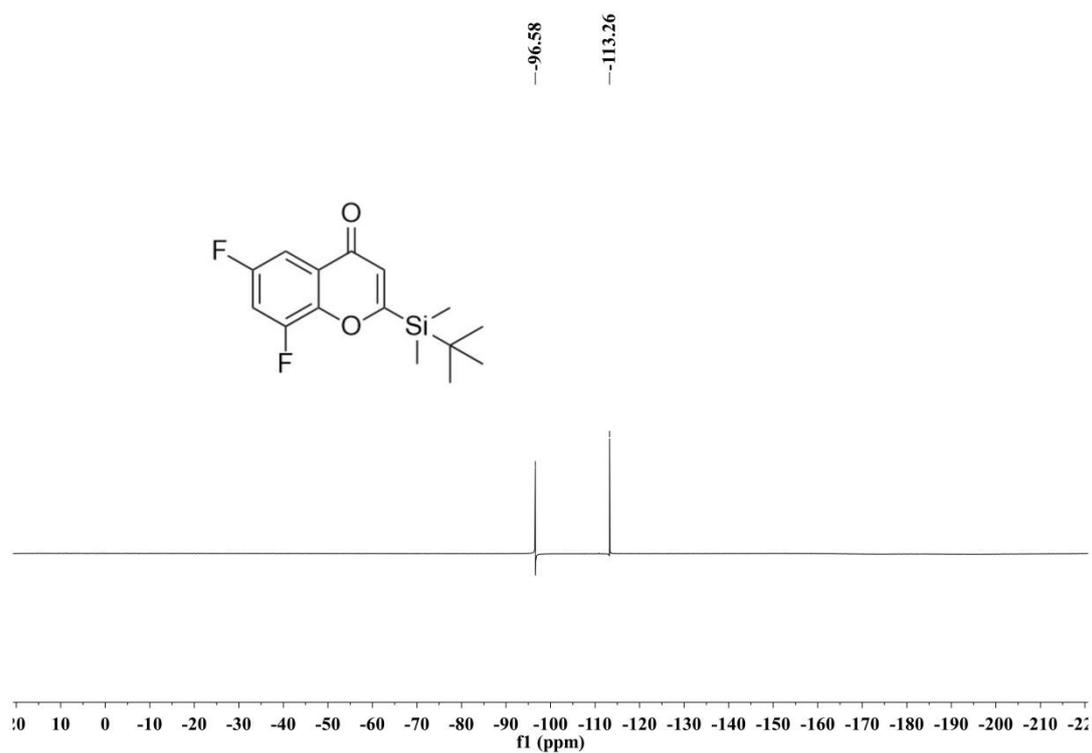
**<sup>1</sup>H NMR spectrum of 3k (500 MHz, CDCl<sub>3</sub>)**



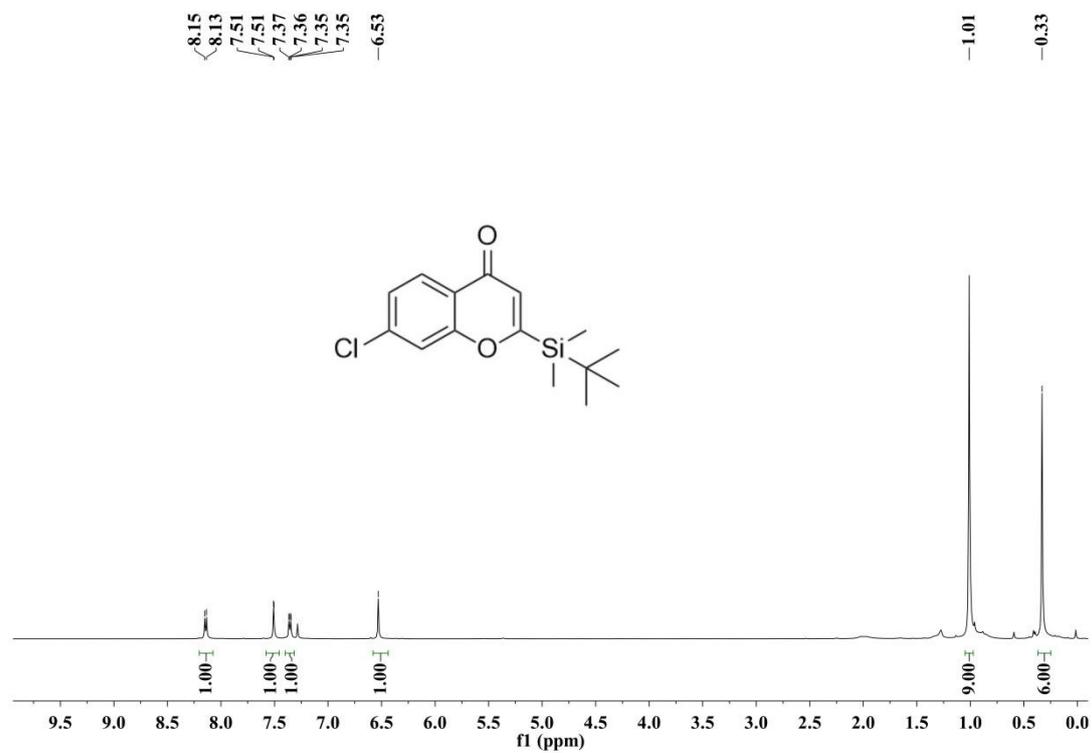
**<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3k (125 MHz, CDCl<sub>3</sub>)**



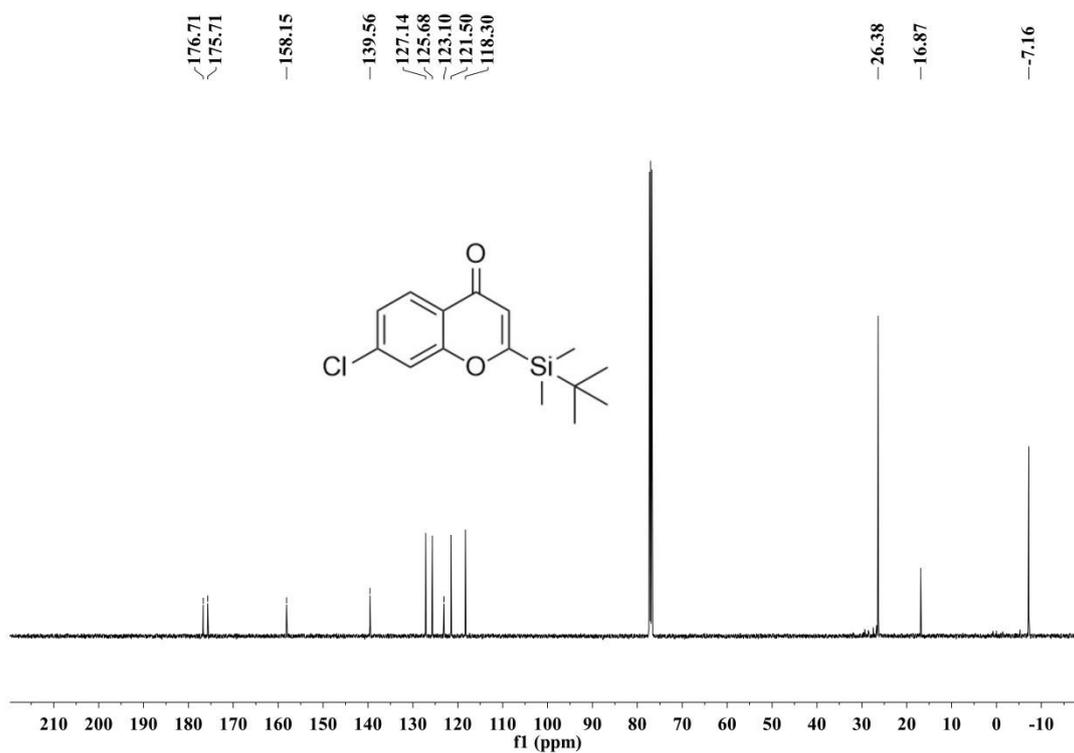
<sup>19</sup>F NMR spectrum of 3k (125 MHz, CDCl<sub>3</sub>)



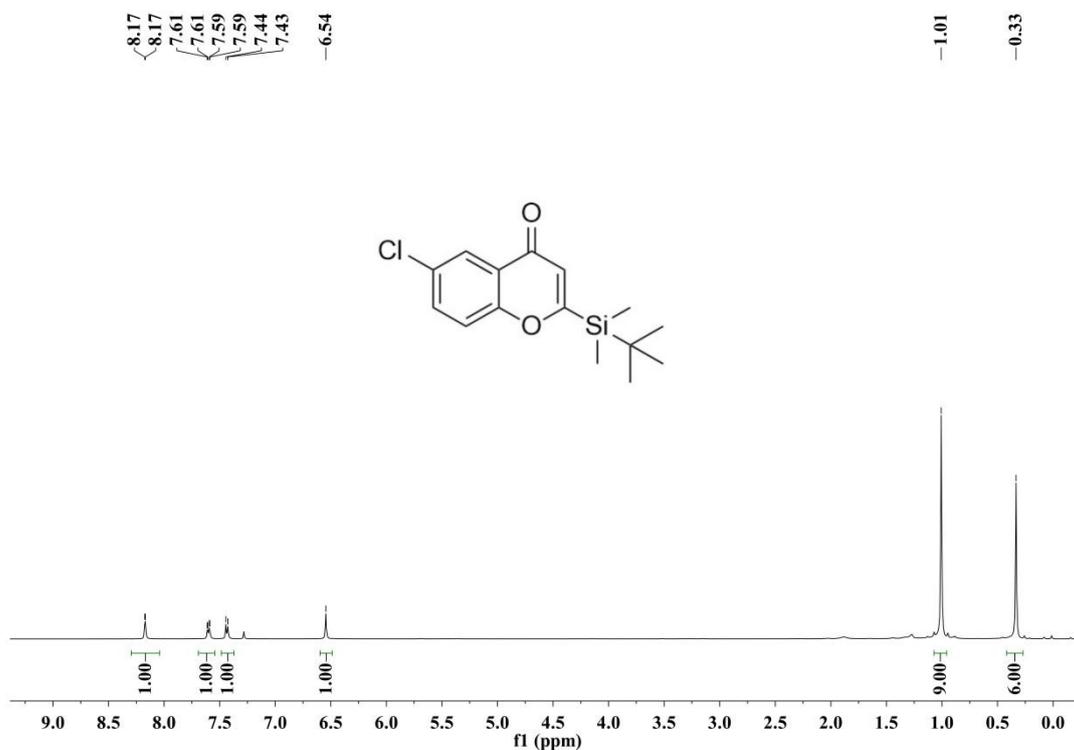
<sup>1</sup>H NMR spectrum of 3l (500 MHz, CDCl<sub>3</sub>)



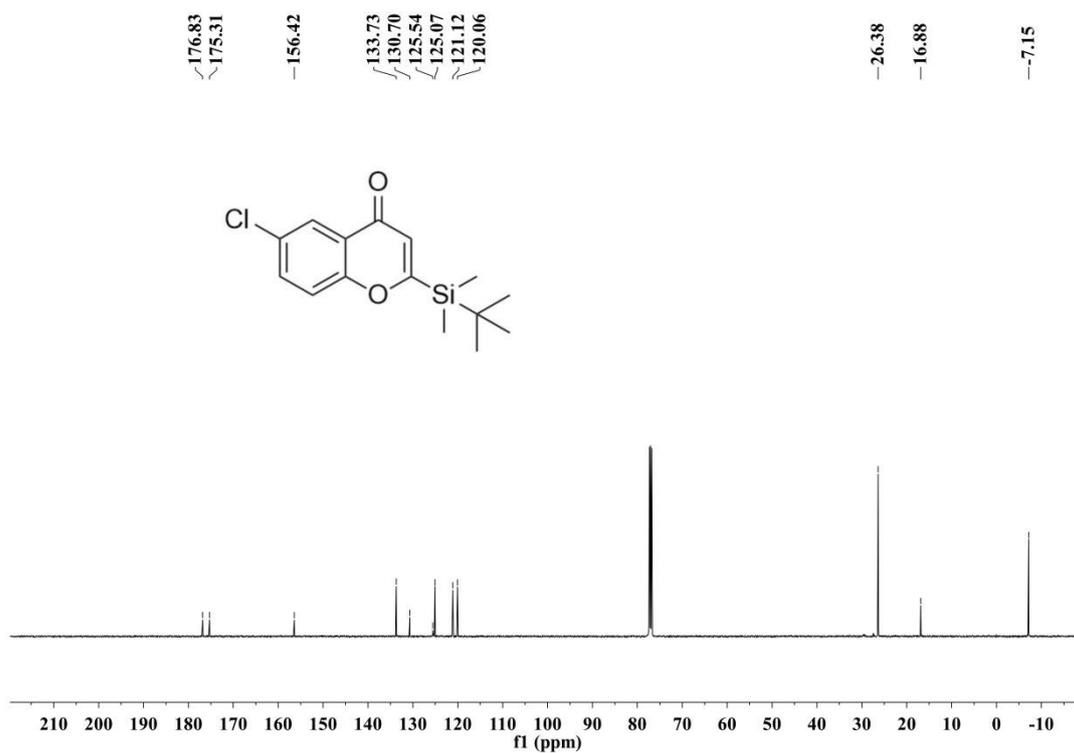
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3l (125 MHz,  $\text{CDCl}_3$ )



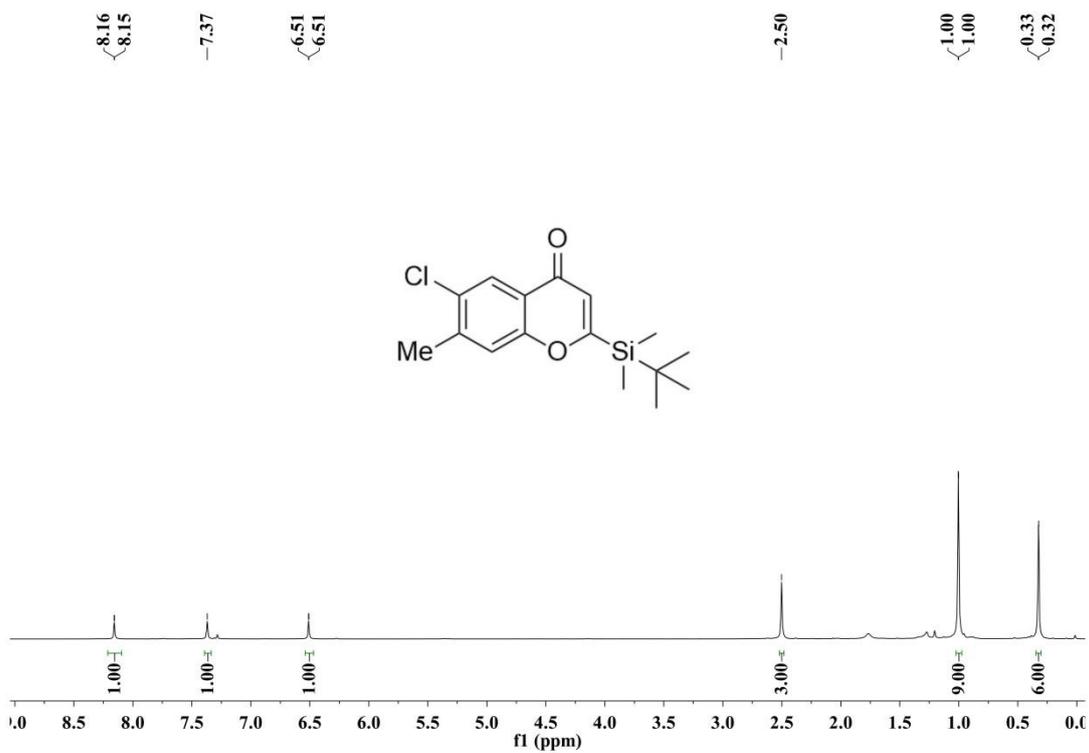
$^1\text{H}$  NMR spectrum of 3m (500 MHz,  $\text{CDCl}_3$ )



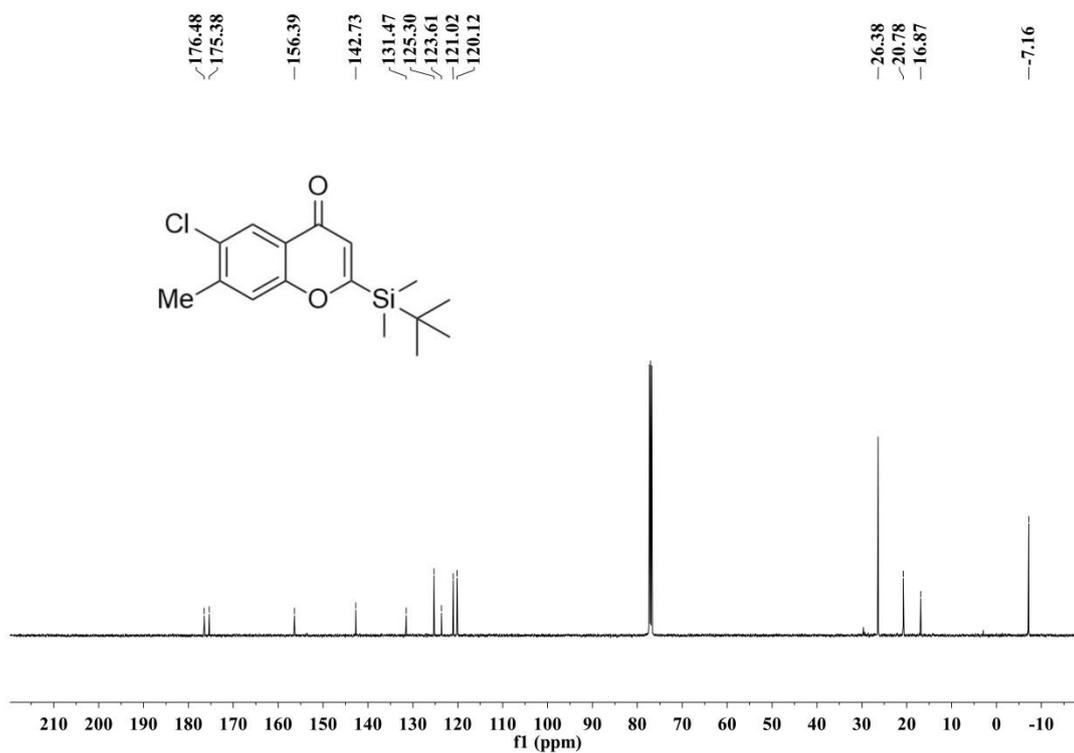
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3m (125 MHz,  $\text{CDCl}_3$ )



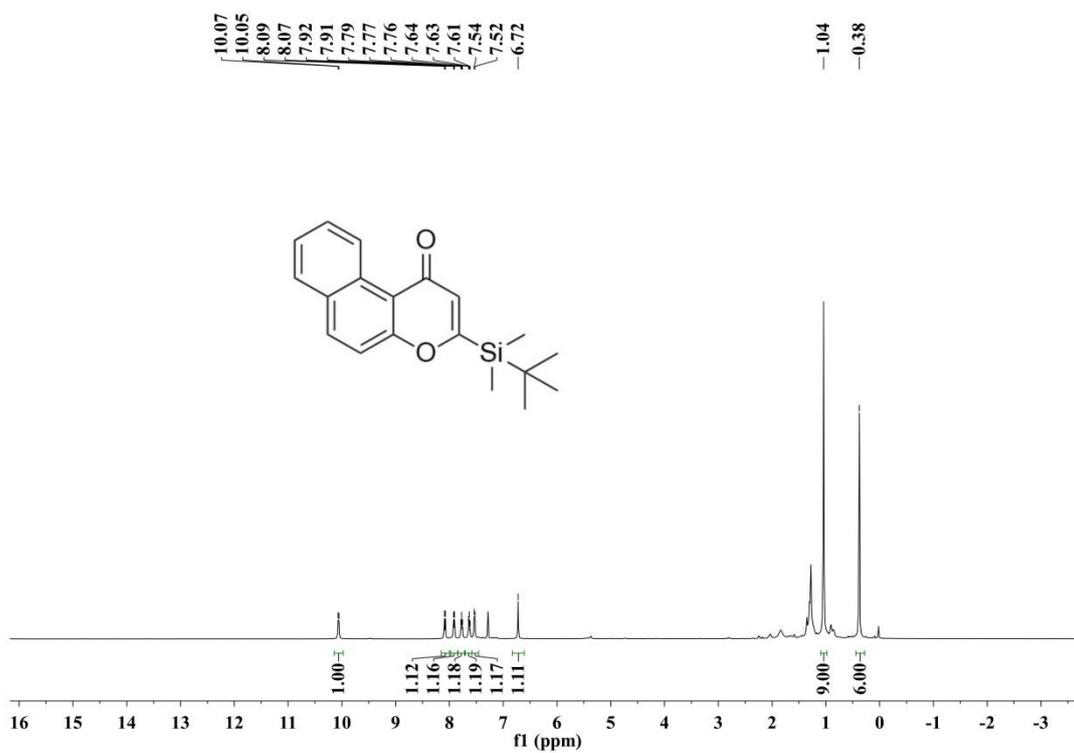
$^1\text{H}$  NMR spectrum of 3n (500 MHz,  $\text{CDCl}_3$ )



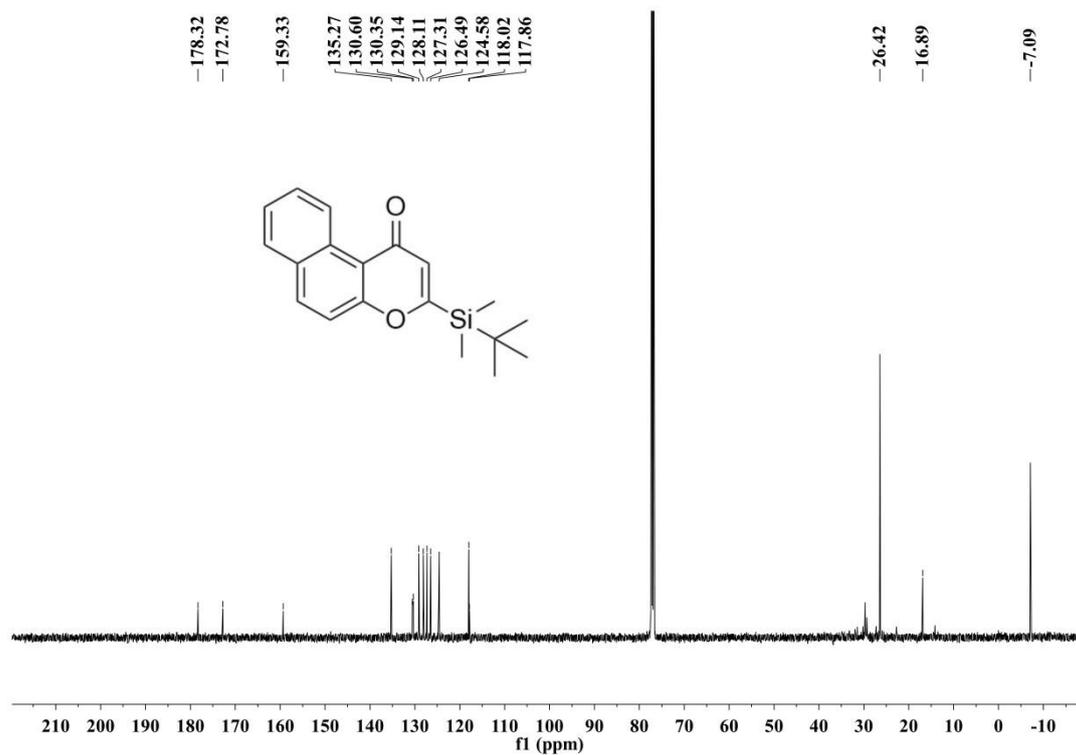
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3n (125 MHz,  $\text{CDCl}_3$ )



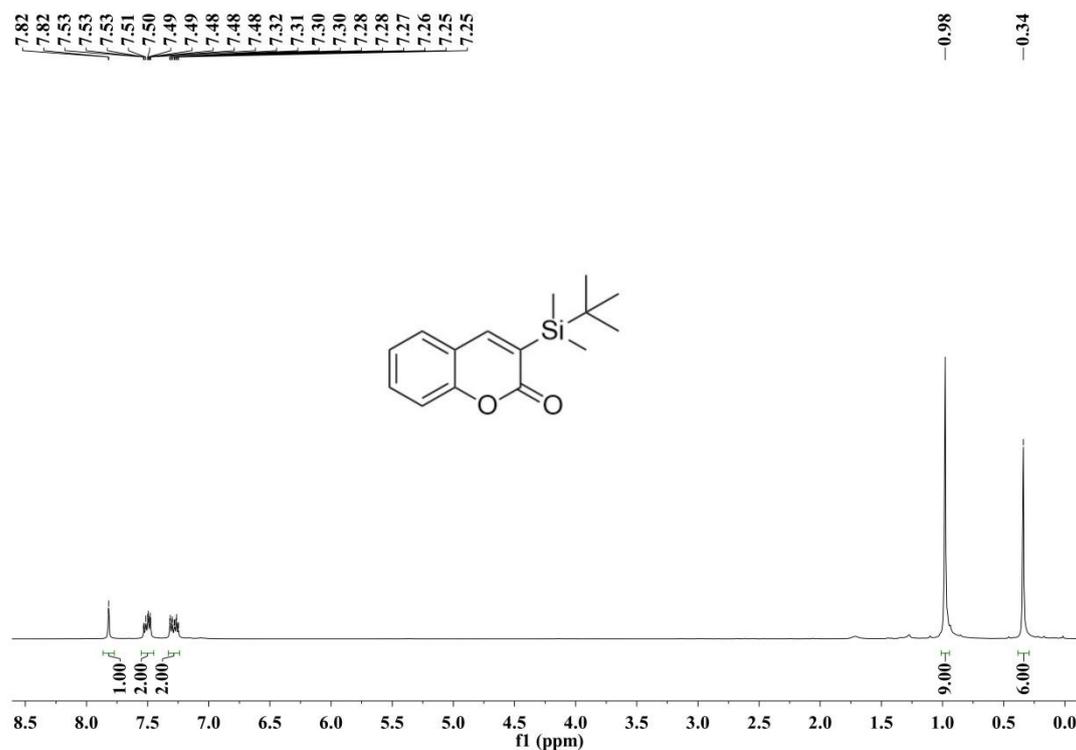
$^1\text{H}$  NMR spectrum of 3o (500 MHz,  $\text{CDCl}_3$ )



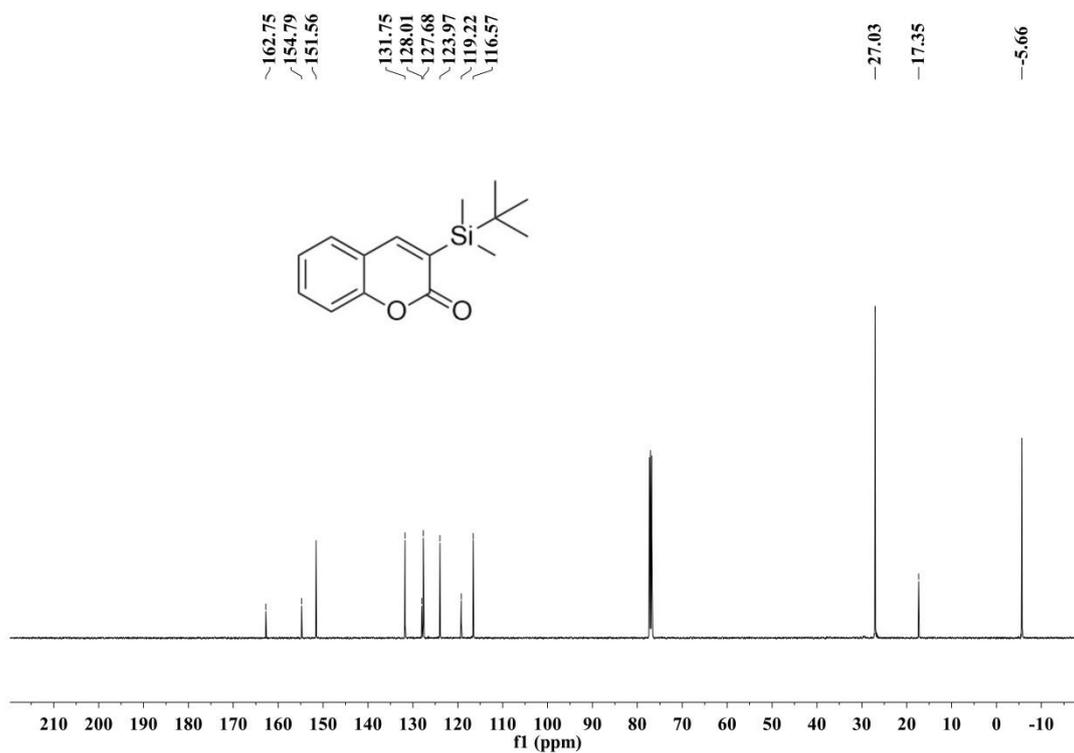
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3o (125 MHz,  $\text{CDCl}_3$ )



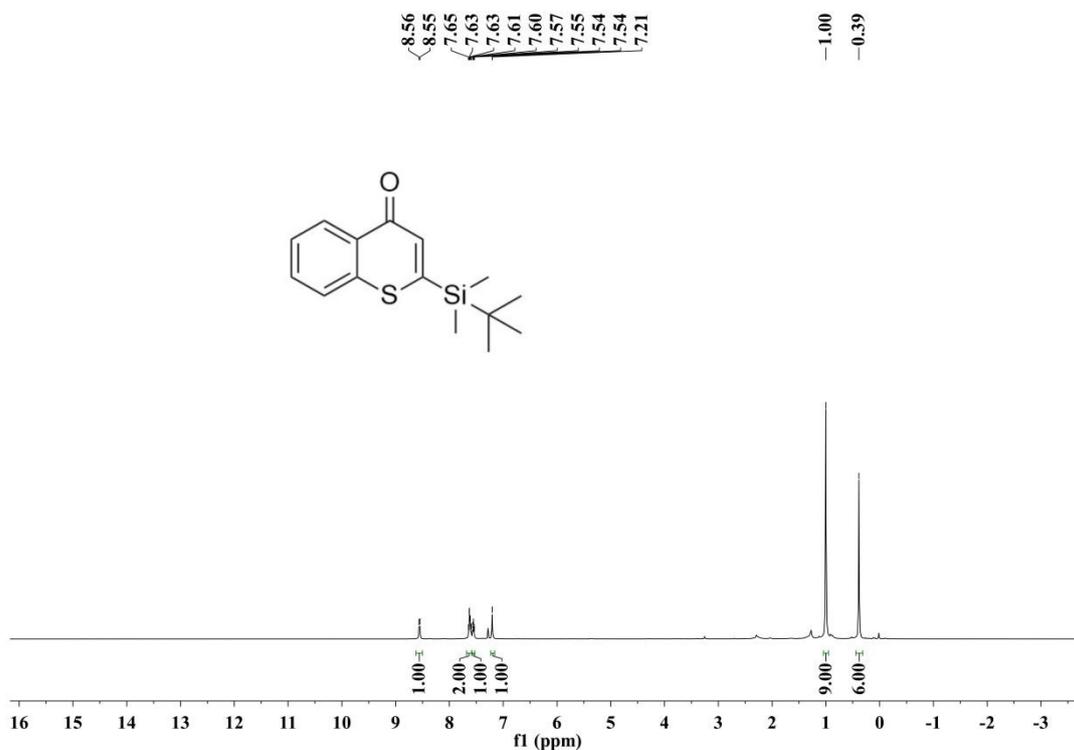
$^1\text{H}$  NMR spectrum of 3p (500 MHz,  $\text{CDCl}_3$ )



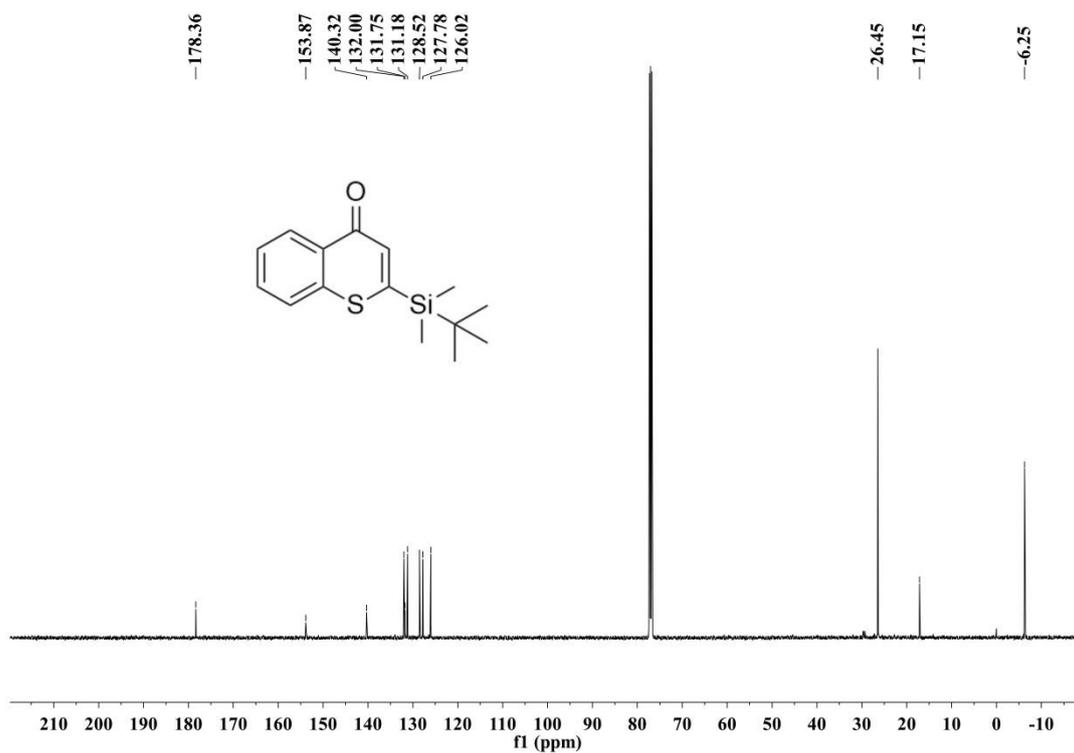
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3p (125 MHz,  $\text{CDCl}_3$ )



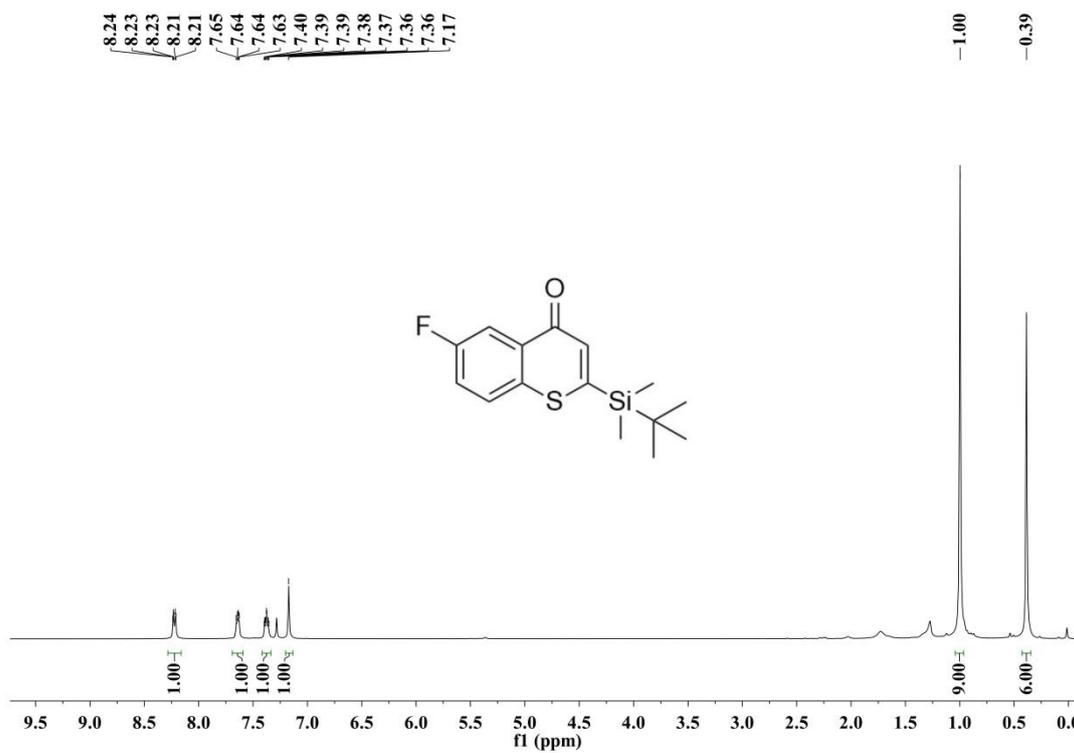
$^1\text{H}$  NMR spectrum of 3q (500 MHz,  $\text{CDCl}_3$ )



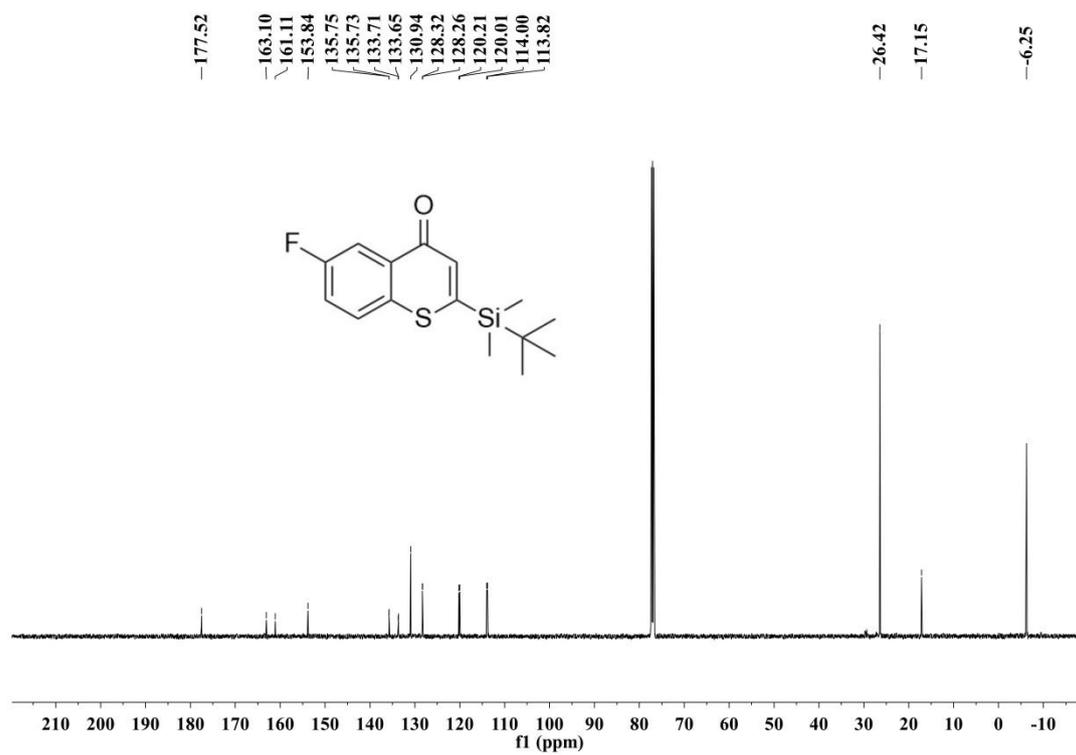
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3q (125 MHz,  $\text{CDCl}_3$ )



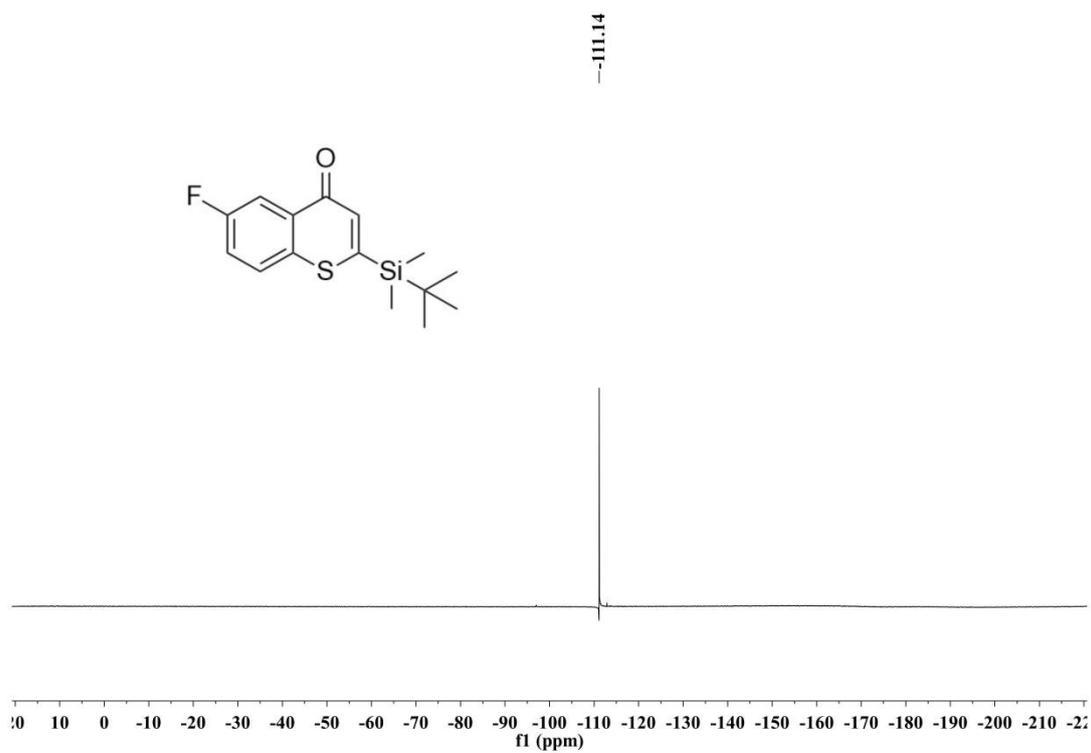
$^1\text{H}$  NMR spectrum of 3r (500 MHz,  $\text{CDCl}_3$ )



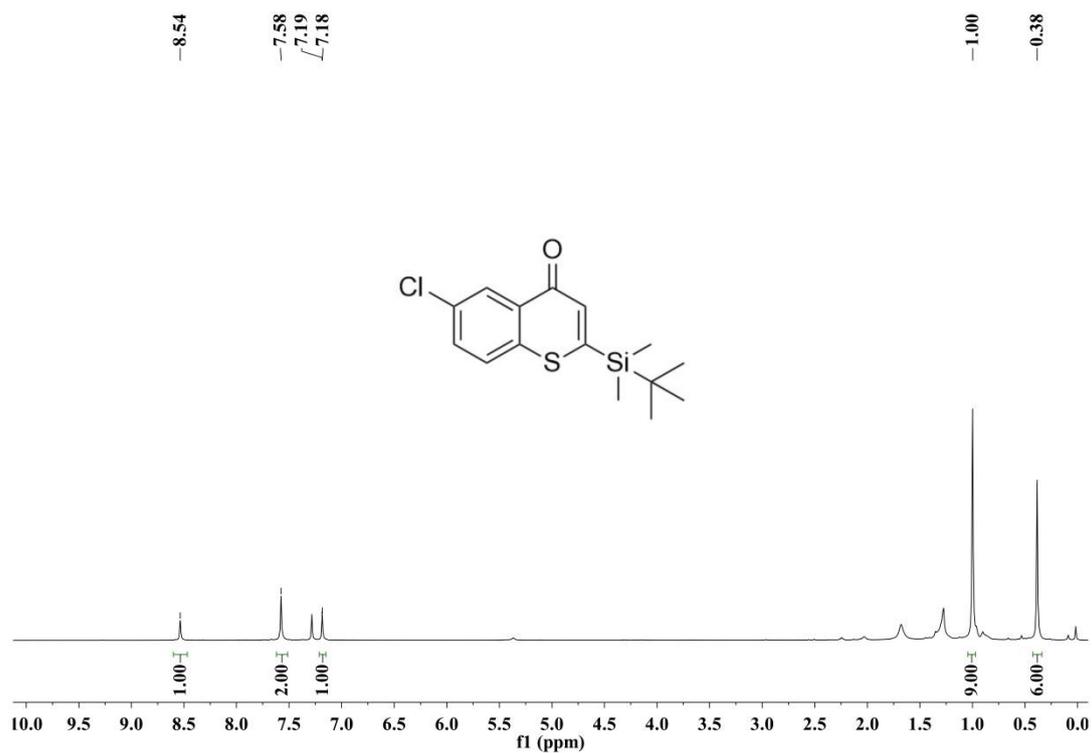
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 3r (125 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR spectrum of 3r (125 MHz,  $\text{CDCl}_3$ )



**<sup>1</sup>H NMR spectrum of 3s (500 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 3s (125 MHz, CDCl<sub>3</sub>)**

