

# **Nickel-Catalyzed Silylation of Aryl Thianthrenium Salts with Silylzinc Pivalates**

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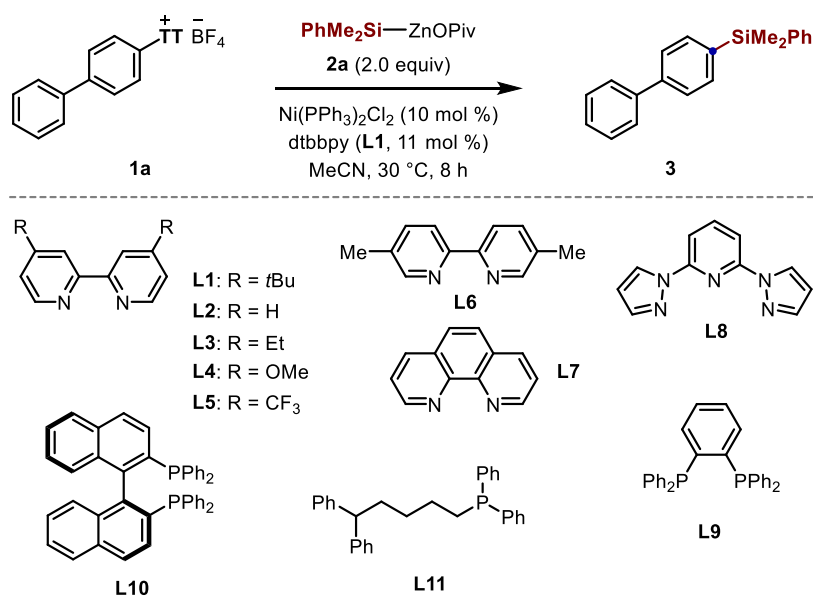
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## 1. General Remarks

All reactions were carried out under nitrogen atmosphere and anhydrous conditions unless otherwise indicated. Syringes used to transfer reagents and solvents were purged with N<sub>2</sub> prior to use. Superdry solvents, THF, MeCN, 1,4-dioxane, NMP, DMA, DMSO were purchased from commercial sources. Yields refer to isolated compounds, estimated to be > 95% pure as determined by <sup>1</sup>H-NMR and GC-analysis. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC were performed using aluminum plates covered with SiO<sub>2</sub> (Merck 60, F-254) and visualized by UV detection. Purification *via* column chromatography was performed using Merck silica gel 60 (40–63 mm 230–400 mesh ASTM from Merck). NMR spectra were recorded in CDCl<sub>3</sub> and chemical shifts ( $\delta$ ) are reported in parts per million (ppm). High-resolution mass spectra (HRMS) were recorded on an Agilent 1290 mass spectrometer using ESI-TOF (electrospray ionization time-of-flight).

## 2. Optimization for Ni-Catalyzed Thianthrenium Salts Silylation



| Entry | Modified conditions                                  | Yield (%) <sup>b</sup> |
|-------|--|------------------------|
| 1     | <b>none</b>  | 72 (70) <sup>c</sup>   |
| 2     | w/o ligand or [Ni]                                   | trace                  |
| 3     | <b>L2</b> instead of <b>L1</b>                       | 68                     |
| 4     | <b>L3</b> instead of <b>L1</b>                       | 59                     |
| 5     | <b>L4</b> instead of <b>L1</b>                       | 67                     |
| 6     | <b>L5</b> instead of <b>L1</b>                       | 48                     |
| 7     | <b>L6</b> instead of <b>L1</b>                       | 65                     |
| 8     | <b>L7</b> instead of <b>L1</b>                       | 67                     |
| 9     | <b>L8</b> instead of <b>L1</b>                       | 69                     |
| 10    | <b>L9</b> instead of <b>L1</b>                       | 46 <sup>d</sup>        |
| 11    | <b>L10</b> instead of <b>L1</b>                      | 34 <sup>d</sup>        |
| 12    | <b>L11</b> instead of <b>L1</b>                      | 57 <sup>d</sup>        |
| 13    | DMSO/NMP/DMA instead of MeCN                         | 17/19/20               |
| 14    | 1,4-dioxane/THF instead of MeCN                      | 13/52                  |
| 15    | Ni(acac) <sub>2</sub> as the catalyst                | 39                     |
| 16    | NiCl <sub>2</sub> •DME as the catalyst               | 52                     |
| 17    | NiBr <sub>2</sub> •DME as the catalyst               | 48                     |
| 18    | Ni(COD) <sub>2</sub> as the catalyst                 | 54                     |
| 19    | CoCl <sub>2</sub> as the catalyst                    | 0 <sup>d</sup>         |
| 20    | Co(acac) <sub>2</sub> as the catalyst                | 0 <sup>d</sup>         |
| 21    | FeCl <sub>2</sub> as the catalyst                    | 0 <sup>d</sup>         |
| 22    | Fe(acac) <sub>3</sub> as the catalyst                | 0 <sup>d</sup>         |
| 23    | <b>2a</b> (1.5 equiv) was used                       | <b>76</b>              |
| 24    | PhMe <sub>2</sub> Si-ZnX (X= Cl or Br or I) was used | 40/45/49               |

[a] Reaction conditions: **1a** (0.15 mmol, 1.0 equiv), **2a** (0.3 mmol, 2.0 equiv), Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol %), ligand (11 mol %), anhydrous MeCN (1.5 mL), 30 °C, 8 h. [b] Isolated yield. [c] under 50 °C for 8 h. [d] **2a** (0.225 mmol, 1.5 equiv).

### 3. Preparation of Starting Materials

#### 3.1 Preparation of Thianthrenium Salts.

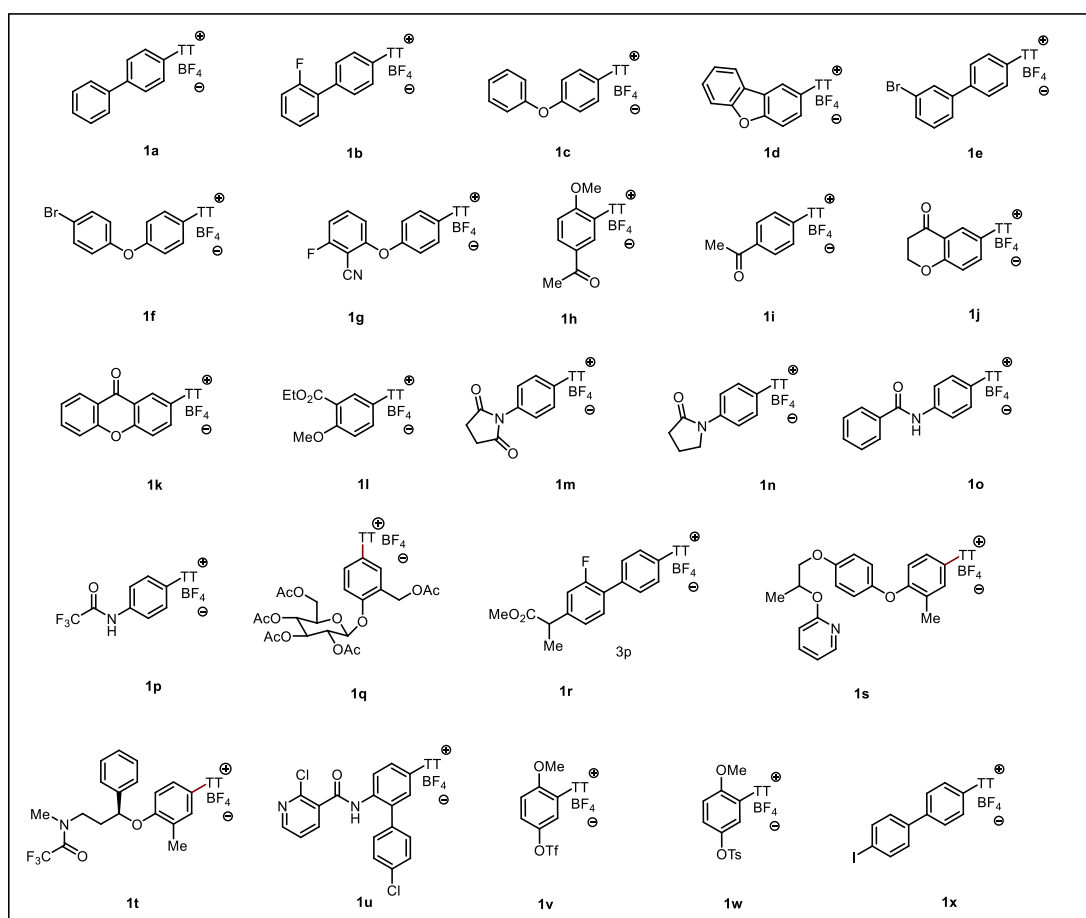


Figure S1. The Thianthrenium salts scoop

Thianthrenium salts **1a**, **1c~1m**, **1o~1u** were synthesized according to the reported procedures<sup>[1]</sup>. Thianthrenium salts **1b** were synthesized according to the reported procedures<sup>[2]</sup>. Thianthrenium salts **1n** were synthesized according to the reported procedures<sup>[3]</sup>.

#### 3.2 Preparation of Silylzinc Pivalates Reagents **2a–2d**

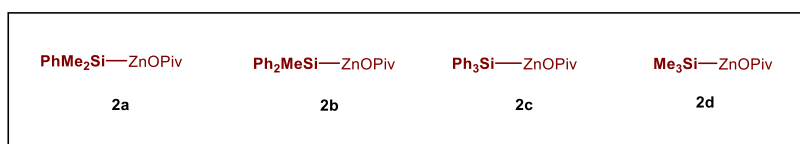


Figure S2. Silylzinc reagents

The organosilylzinc pivalates **2a**, **2b**, **2c**, **2d** were synthesized according to the reported procedures<sup>[4]</sup>.

#### Preparation of $\text{Zn}(\text{OPiv})_2$ :

### Typical Procedure 1 (TP1) for the Preparation of Zn(OPiv)<sub>2</sub><sup>[4]</sup>:

Pivalic acid (10.2 g, 100 mmol) was placed in a dry and nitrogen-flushed 250 mL three-necked round bottom flask, equipped with a magnetic stirring bar, a septum and a pressure equalizer, and was dissolved in dry THF (30 mL). The mixture was cooled to 0 °C, and a solution of Et<sub>2</sub>Zn (50 mL, 50 mmol, 1.0 M in heptane) was added over a period of 30 minutes under vigorous stirring. Then, the ice-bath was removed and stirring was continued at 25 °C for one additional hour at which point bubbling has ceased (a thick slurry was formed). The solvent was removed in vacuo and the solid residue was dried for at least 4 hours longer. Zn(OPiv)<sub>2</sub> was obtained in quantitative yield as a puffy amorphous white solid.

### Preparation of Aryl Organosilylzinc Pivalates

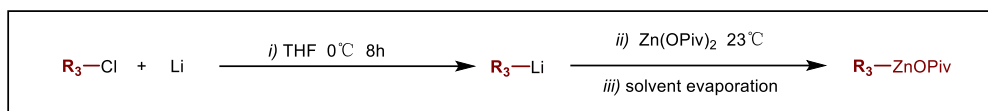


Figure S3. Preparation of aryl organosilylzinc pivalates

### Typical Procedure 2 (TP2) for the Preparation of Organosilylzinc Pivalates<sup>[4]</sup>:

A 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar and was charged with naphthalene (64 mg, 0.5 mmol), lithium clippings (174 mg, 25 mmol) and dry THF (10.0 mL). The resulting mixture started turning dark green and was stirred at room temperature for 1 h under an argon atmosphere. Then chlorosilane (10 mmol, 1.0 equiv) was added dropwise at 0 °C and the mixture was stirred at same temperature for 8 h. The silyllithium was titrated against iodine. Next, this solution was added via syringe into a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring and Zn(OPiv)<sub>2</sub> (1.2 equiv with respect to titrated silyllithium) at 0 °C, and the reaction mixture was stirred at rt for 15 min. The silylzinc solution (routinely formed as a ~0.5 M solution) was titrated using Knochel's method. The organosilylzinc pivalate in THF was removed under reduced pressure resulting in corresponding solid organosilylzinc pivalates reagent **2a**, **2b**, **2c**.

### Preparation of Trimethyl Substituted Silylzinc Pivalates

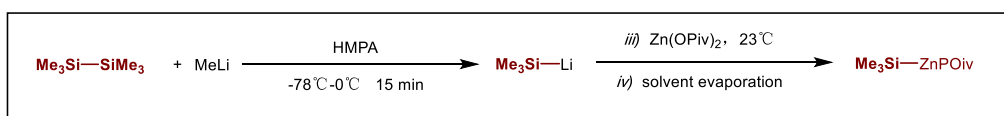


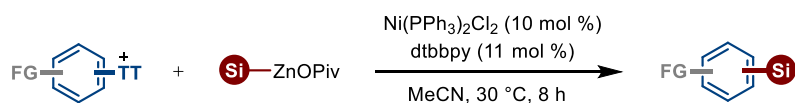
Figure S4. Preparation of trimethyl substituted silylzinc pivalates

### Typical Procedure 3 (TP3) for the Preparation of Organosilylzinc Pivalates<sup>[4]</sup>:

A 30-mL two-necked round-bottomed flask equipped with a magnetic stirring bar and was charged with hexamethyldisilane (1.00 mL, 4.88 mmol) and HMPA (2.00 mL). The reaction mixture was cooled to -78 °C. To the white solid was added to MeLi (1.07 M in Et<sub>2</sub>O, 3.65 mL, 3.91 mmol) and dry THF (8.0 mL) at -78 °C, which was warmed to 0 °C. After stirring at 0 °C for 15 min, the silyllithium was titrated against iodine. Next, this solution was added via syringe into a 30 mL two-necked round-bottomed flask equipped with a magnetic stirring and Zn(OPiv)<sub>2</sub> (1.2 equiv with respect to titrated silyllithium) at 0 °C, then the reaction mixture was stirred at rt for 15 min to afford a solution of the corresponding zinc reagent **2d**. The colorless silylzinc solution (routinely formed as a ~0.2 M solution) was titrated using Knochel's method.

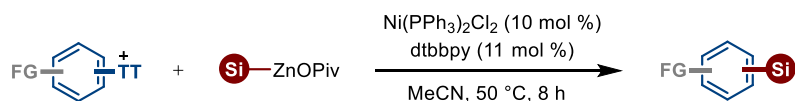
#### 4. General Procedure for General Procedure for Ni-Catalyzed Thianthrenium Salts Silylation

##### Typical procedure 4 (TP4) for General Procedure for Ni-Catalyzed Thianthrenium Salts Silylation



An oven-dried tube was charged with Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%), **L1** (11 mol%), thianthrenium salts **1** (0.15 mmol, 1.0 equiv). Then the tube was evacuated and backfilled with N<sub>2</sub>. Anhydrous MeCN (1.0 mL) was added and stirred for 3 minutes. Then **2** (0.225 mmol, 1.5 equiv) resolved in MeCN (0.5 mL) was added dropwise over 1 minutes. The reaction mixture was stirred at 30 °C for 8 hours. When the reaction was completed, the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products.

##### Typical Procedure 5 (TP5) for General Procedure for Ni-Catalyzed Thianthrenium Salts Silylation

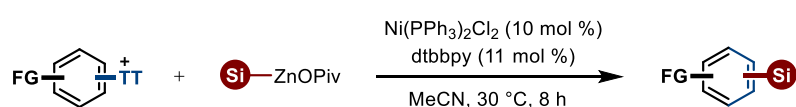


An oven-dried tube was charged with Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%), **L1** (11 mol%), thianthrenium salts **1** (0.15 mmol, 1.0 equiv). Then the tube was evacuated and backfilled with N<sub>2</sub>. Anhydrous MeCN (1.5 mL) was added and stirred for 3 minutes. Then **2** (0.225 mmol, 1.5 equiv) resolved in MeCN

(0.5 mL) was added dropwise over 1 minute. The reaction mixture was stirred at 50 °C for 8 hours. When the reaction was completed, the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) yield products.

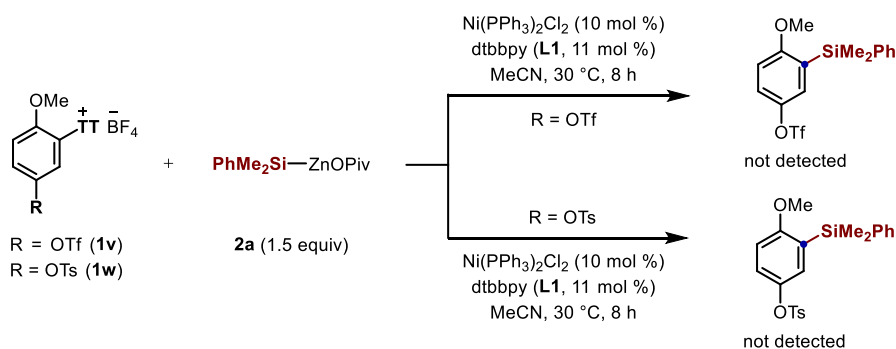
## 5. Expansion of the Nickel-Catalyzed Silylation of Aryl Thianthrenium Salts Using Silylzinc Pivalates

### Aryl Thianthrenium Salts (1a-1u) as the Electrophiles in the Nickel-Catalyzed Silylation Reaction



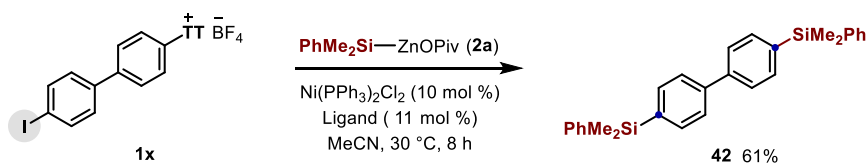
The general procedure **TP4** or **TP5** was followed using **1a-1u** (0.15 mmol), **2a-2d** (0.225 mmol) for 8 h. When the reaction was completed, the resulting residue was purified by column chromatography on silica gel.

### Aryl Thianthrenium Salts **1v** and **1w** as the Electrophiles in the Nickel-Catalyzed Silylation Reaction



The general procedure **TP4** was followed using **1v** or **1w** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Although the starting materials were completely consumed, the reaction outcome was mess, and the target product was not observed.

### Aryl Thianthrenium Salts **1x** as the Electrophiles in the Nickel-Catalyzed Silylation Reaction



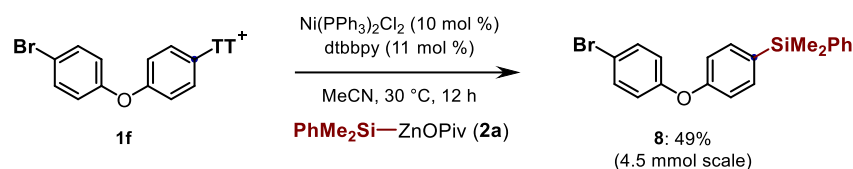
The general procedure **TP4** was followed using **1x** (0.15 mmol), **2a** (0.225 mmol) for 8 h. we



observed the formation of a disilylated product **42** with a 61% yield.

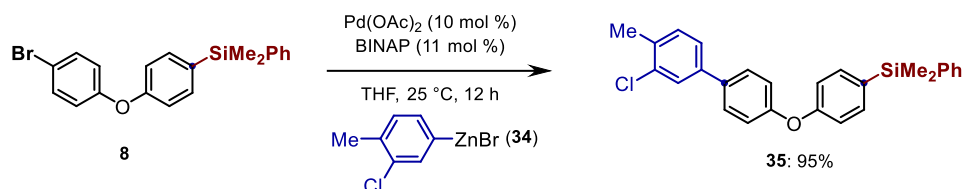
## 6. Synthetic Applications by Sequential Couplings

### Typical Procedure 4 (TP4) for Silylation of Aryls with Silyzinc Pivalates Enabled by Nickel-Catalysis



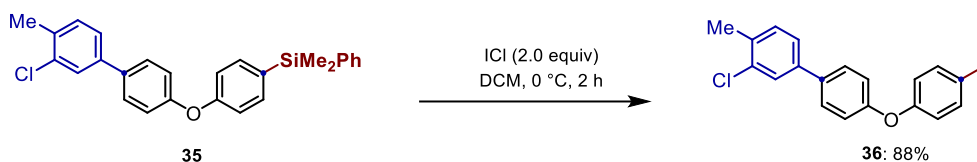
An oven-dried tube was charged with Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%), dtbbpy (11 mol%), thianthrenium salts **1f** (4.5 mmol, 1.0 equiv). Then the tube was evacuated and backfilled with N<sub>2</sub>. Anhydrous MeCN (20 mL) was added and stirred for 10 minutes vigorously. Then **2a** (6.75 mmol, 1.5 equiv) resolved in MeCN (5 mL) was added dropwise over 5 minutes. The reaction mixture was stirred at 30 °C for 12 hours. When the reaction was completed, the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 100:1) to yield **8** (842mg, 49%).

### Typical Procedure 6 (TP6) for Negishi-Type Arylation with Arylzinc Bromide.



An oven-dried tube was charged with Pd<sub>2</sub>(OAc)<sub>3</sub> (10 mol %), (S)-(-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (11 mol %). **8** (2 mmol, 1.0 equiv). Then the tube was evacuated and backfilled with N<sub>2</sub>. Anhydrous THF (8 mL) was added and stirred for 5 minutes vigorously. Then **34** (4 mmol, 2.0 equiv) resolved in THF (4 mL) was added dropwise over 5 minutes. The reaction mixture was stirred at 25°C for 12 hours. When the reaction was completed, the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 100:1) to yield **35** (813mg, 95%).

### Typical Procedure 7 (TP7) for Silyl Group Transformed into the Aryl Iodide



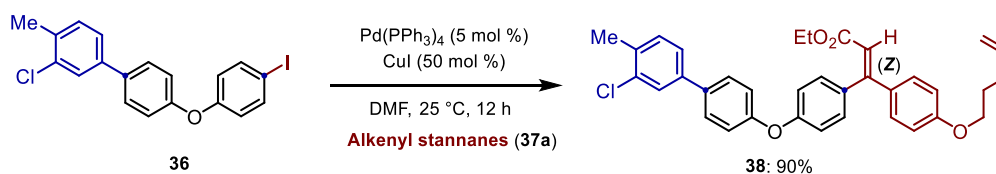
An oven-dried tube was charged with **35** (1 mmol, 1.0 equiv). Then the tube was evacuated and backfilled with  $\text{N}_2$ . Anhydrous  $\text{CH}_2\text{Cl}_2$  (2 mL) was added and stirred for 5 minutes. Then **ICl** (2 mmol, 2.0 equiv) was added dropwise over 1 minutes. The reaction mixture was stirred at  $0\text{ }^\circ\text{C}$  for 2 hours. When the reaction was completed, the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 100:1) to yield **36** (370mg, 88%).



**Figure S5.** The Alkenyl Stannanes scoop

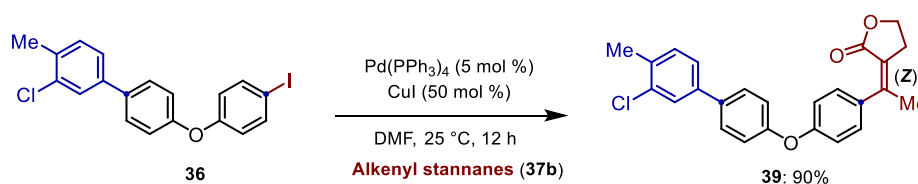
Alkenyl Stannanes **37a**, **37b** were synthesized according to the reported procedures<sup>[1]</sup>.

### Typical Procedure 8 (TP8) for Stille-Coupling Reaction with Stereodefined Trisubstituted Alkenyl Stannanes



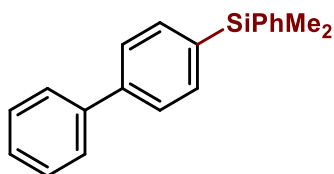
An oven-dried tube was charged with  $\text{Pd(PPh}_3)_4$  (5 mmol%), **CuI** (50 mmol%), **37a** (0.1 mmol, 1.0 equiv) and **36** (0.12 mmol, 1.2 equiv) Then the tube was evacuated and backfilled with  $\text{N}_2$ . Anhydrous DMF (2 mL) was added. The reaction mixture was stirred at  $30\text{ }^\circ\text{C}$  for 12 hours. When the reaction was completed, the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 40:1) to yield **38** (50mg, 90%).

### Typical Procedure 8 (TP8) for Stille-Coupling Reaction with Stereodefined Tetrasubstituted Alkenyl Stannanes



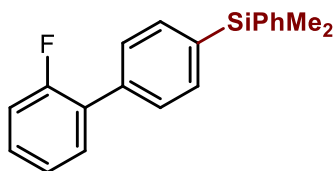
An oven-dried tube was charged with Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mmol%), CuI (50 mmol%), **37b** (0.1 mmol, 1.0 equiv) and **36** (0.12 mmol, 1.2 equiv) Then the tube was evacuated and backfilled with N<sub>2</sub>. Anhydrous DMF (2 mL) was added. The reaction mixture was stirred at 30 °C for 12 hours. When the reaction was completed, the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 40:1) to yield **39** (36mg, 90%).

## 7. Characterization Data



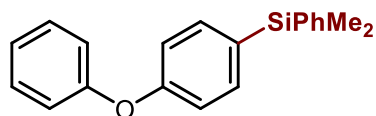
### (1,1'-Biphenyl)-4-yl dimethyl(phenyl)silane (**3**)<sup>[6]</sup>.

The general procedure TP4 was followed using **1a** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **3** (33 mg, 76%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.65 – 7.58 (m, 8H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 5.2, 1.7 Hz, 3H), 7.36 (d, *J* = 7.4 Hz, 1H), 0.62 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 141.9, 141.1, 138.1, 137.0, 134.7, 134.2, 129.1, 128.8, 127.8, 127.4, 127.2, 126.6, -2.7.



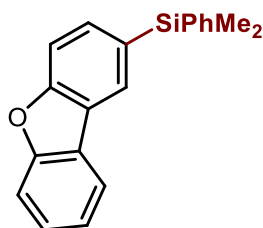
### [2'-Fluoro-(1,1'-biphenyl)-4-yl] dimethyl(phenyl)silane (**4**).

The general procedure TP4 was followed using **1b** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **4** (40 mg, 87%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.63 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.57 (m, 3H), 7.56 (s, 1H), 7.51 – 7.42 (m, 1H), 7.42 – 7.36 (m, 3H), 7.35 – 7.30 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.20 – 7.14 (m, 1H), 0.62 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ = 161.0 (d, *J*<sub>C-F</sub> = 246.6 Hz), 138.2, 137.8, 136.6, 134.5, 134.4, 130.9 (d, *J*<sub>C-F</sub> = 3.5 Hz), 129.3, 129.2, 129.1, 128.5 (d, *J*<sub>C-F</sub> = 3.9 Hz), 128.0, 116.2 (d, *J*<sub>C-F</sub> = 22.6 Hz), -2.2. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>): δ = -117.84. HR-MS (ESI) *m/z* calcd for C<sub>20</sub>H<sub>19</sub>FSi [M+H<sup>+</sup>] 307.1313, found 307.1314.



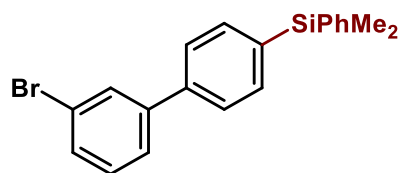
#### Dimethyl(4-phenoxyphenyl)(phenyl)silane (**5**)<sup>[7]</sup>.

The general procedure **TP4** was followed using **1c** (0.15 mmol), **2e** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **5** (27 mg, 60%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55 – 7.51 (m, 2H), 7.47 (d,  $J$  = 8.5 Hz, 2H), 7.40 – 7.31 (m, 5H), 7.12 (t,  $J$  = 7.4 Hz, 1H), 7.03 (d,  $J$  = 7.7 Hz, 2H), 6.98 (d,  $J$  = 8.5 Hz, 2H), 0.55 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.6, 156.9, 138.5, 135.9, 134.28, 132.3, 129.9, 129.3, 128.0, 123.7, 119.5, 118.1, -2.1.



#### Dibenzob[d,f]furan-2-yl(dimethylphenyl)silane (**6**).

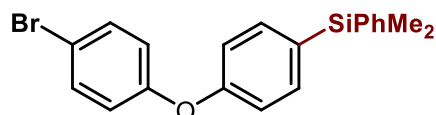
The general procedure **TP4** was followed using **1d** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 150:1) yielded **6** (36 mg, 80%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.15 (s, 1H), 7.97 (d,  $J$  = 7.6 Hz, 1H), 7.61 (dd,  $J$  = 19.1, 8.1 Hz, 5H), 7.47 (t,  $J$  = 7.7 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.35 (d,  $J$  = 7.3 Hz, 1H), 0.67 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.2, 156.3, 138.6, 134.4, 133.2, 131.9, 129.3, 128.0, 127.3, 126.8, 124.2, 124.1, 122.9, 120.8, 111.8, 111.5, -1.8. **HR-MS** (ESI)  $m/z$  calcd for C<sub>20</sub>H<sub>18</sub>OSi [M+H<sup>+</sup>] 303.1200, found 303.1203.



#### [3'-Bromo-(1,1'-biphenyl)-4-yl]dimethyl(phenyl)silane (**7**).

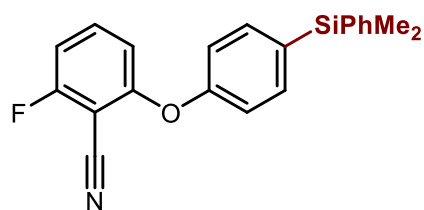
The general procedure **TP4** was followed using **1e** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **7** (36 mg, 66%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.74 (s, 1H), 7.61 (d,  $J$  = 8.0 Hz, 2H), 7.57 – 7.46 (m, 6H), 7.40 – 7.35 (m, 3H), 7.30 (t,  $J$  = 7.9 Hz, 1H), 0.59 (s, 6H). <sup>13</sup>C-NMR (100 MHz,

CDCl<sub>3</sub>):  $\delta$  = 143.4, 140.5, 138.1, 134.9, 134.3, 130.5, 130.4, 130.4, 129.4, 128.9, 128.0, 127.8, 126.6, 125.9, 123.1, -2.3. **HR-MS** (ESI)  $m/z$  calcd for C<sub>20</sub>H<sub>19</sub>BrSi [M+H<sup>+</sup>] 367.0512, found 367.0511.



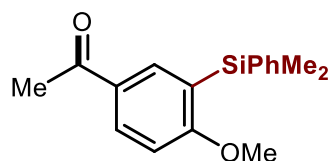
**[4'-Bromo-(1,1'-biphenyl)-4-yl]dimethyl(phenyl)silane (8)**<sup>[8]</sup>.

The general procedure **TP4** was followed using **1f** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **8** (31 mg, 54%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.56 – 7.51 (m, 2H), 7.49 (d,  $J$  = 8.3 Hz, 2H), 7.44 (d,  $J$  = 8.8 Hz, 2H), 7.41 – 7.33 (m, 3H), 6.97 (d,  $J$  = 8.3 Hz, 2H), 6.91 (d,  $J$  = 8.8 Hz, 2H), 0.55 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 158.0, 156.2, 138.3, 136.1, 134.3, 133.0, 132.9, 129.3, 128.0, 121.0, 118.3, 116.1, -2.1.



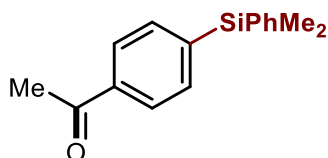
**2-{4-[Dimethyl(phenyl)silyl]phenoxy}-6-fluorobenzonitrile (9)**.

The general procedure **TP4** was followed using **1g** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **9** (44 mg, 85%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.63 – 7.51 (m, 4H), 7.41 (q,  $J$  = 7.1, 5.6 Hz, 4H), 7.09 (d,  $J$  = 6.6 Hz, 2H), 6.90 (d,  $J$  = 8.4 Hz, 1H), 6.65 (d,  $J$  = 8.6 Hz, 1H), 0.58 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.5, 162.9 (d,  $J_{C-F}$  = 3.9), 160.9, 155.6, 137.8, 136.3, 135.8, 134.9 (d,  $J_{C-F}$  = 9.2), 134.3, 129.4, 128.1, 119.7, 112.3 (d,  $J_{C-F}$  = 3.2), 111.2, 109.8 (d,  $J_{C-F}$  = 19.6), -2.2. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  = -104.67. **HR-MS** (ESI)  $m/z$  calcd for C<sub>21</sub>H<sub>18</sub>FNOSi [M+H<sup>+</sup>] 348.1214, found 348.1217



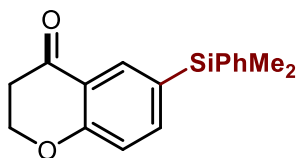
**1-{3-[Dimethyl(phenyl)silyl]-4-methoxyphenyl}Ethan-1-one (10)**<sup>[8]</sup>.

The general procedure **TP5** was followed using **1h** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 150:1) yielded **10** (23 mg, 55%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.01 (dd,  $J$  = 8.6, 2.3 Hz, 1H), 7.93 (d,  $J$  = 2.3 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.36 (dd,  $J$  = 5.1, 1.8 Hz, 3H), 6.84 (s, 1H), 3.80 (s, 3H), 2.49 (s, 3H), 0.59 (s, 6H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.2, 168.3, 138.3, 137.0, 134.3, 134.2, 132.6, 130.2, 129.1, 127.8, 127.8, 126.6, 109.4, 55.5, 26.4, -2.2.



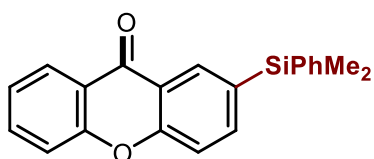
#### 1-{4-[Dimethyl(phenyl)silyl]phenyl}ethan-1-one (**11**)<sup>[7]</sup>.

The general procedure **TP4** was followed using **1i** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **11** (20 mg, 53%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.91 (d,  $J$  = 8.1 Hz, 1H), 7.62 (d,  $J$  = 8.1 Hz, 1H), 7.51 (dd,  $J$  = 7.3, 1.8 Hz, 2H), 7.37 (q,  $J$  = 5.9 Hz, 2H), 2.60 (s, 2H), 0.58 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.4, 145.1, 137.4, 137.2, 134.4, 134.14, 129.4, 128.0, 127.3, 26.7, -2.6.



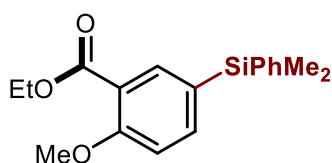
#### 6-[Dimethyl(phenyl)silyl]chroman-4-one (**12**).

The general procedure **TP4** was followed using **1j** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 40:1) yielded **12** (30 mg, 71%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.11 (s, 1H), 7.58 (d,  $J$  = 8.2 Hz, 1H), 7.50 (d,  $J$  = 7.4 Hz, 2H), 7.36 (d,  $J$  = 6.1 Hz, 3H), 6.95 (d,  $J$  = 8.2 Hz, 1H), 4.54 (t,  $J$  = 6.4 Hz, 2H), 2.81 (t,  $J$  = 6.4 Hz, 2H), 0.56 (s, 6H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.0, 162.8, 141.8, 137.9, 134.2, 133.4, 130.8, 129.4, 128.0, 121.0, 117.6, 67.1, 38.0, -2.3. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{18}\text{O}_2\text{Si}$  [ $\text{M}+\text{H}^+$ ] 283.1149, found 283.1147.



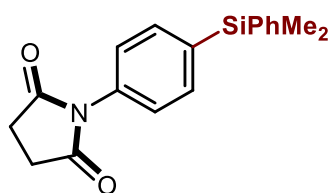
### 2-[Dimethyl(phenyl)silyl]-9H-xanthen-9-one (13).

The general procedure **TP4** was followed using **1k** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 30:1) yielded **13** (38 mg, 77%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.56 (d,  $J$  = 1.5 Hz, 1H), 8.35 (dd,  $J$  = 8.0, 1.6 Hz, 1H), 7.82 (dd,  $J$  = 8.3, 1.6 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.57 – 7.52 (m, 2H), 7.48 (d,  $J$  = 8.5 Hz, 1H), 7.46 (d,  $J$  = 8.3 Hz, 1H), 7.42 – 7.33 (m, 4H), 0.65 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.4, 157.1, 156.3, 140.5, 137.6, 134.9, 134.3, 133.1, 129.5, 128.1, 127.0, 124.1, 122.3, 121.3, 118.1, 117.6, -2.2. **HR-MS** (ESI)  $m/z$  calcd for C<sub>21</sub>H<sub>18</sub>O<sub>2</sub>Si [M+H<sup>+</sup>] 331.1149, found 331.1151.



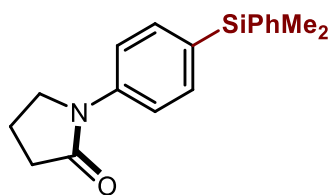
### Ethyl 5-[dimethyl(phenyl)silyl]-2-methoxybenzoate (14)<sup>18</sup>.

The general procedure **TP4** was followed using **1l** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 40:1) yielded **14** (41 mg, 86%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.92 (s, 1H), 7.58 (d,  $J$  = 9.8 Hz, 1H), 7.51 (d,  $J$  = 7.5 Hz, 2H), 7.40 – 7.33 (m, 3H), 6.97 (d,  $J$  = 8.3 Hz, 1H), 4.36 (q,  $J$  = 7.1 Hz, 2H), 3.90 (s, 3H), 1.37 (t,  $J$  = 7.1 Hz, 3H), 0.56 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.8, 159.9, 139.4, 138.2, 137.2, 134.2, 129.3, 128.9, 128.0, 120.5, 111.7, 60.9, 56.0, 14.4, -2.2.



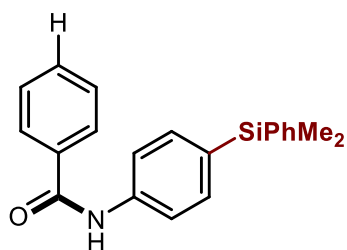
### 1-{4-[Dimethyl(phenyl)silyl]phenyl}pyrrolidine-2,5-dione(15)

The general procedure **TP4** was followed using **1m** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 3:1) yielded **15** (23 mg, 50%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.62 (d,  $J$  = 8.3 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.36 (dd,  $J$  = 4.6, 2.2 Hz, 3H), 7.25 (d,  $J$  = 8.3 Hz, 2H), 2.85 (s, 4H), 0.55 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.3, 139.5, 137.5, 135.1, 134.3, 132.6, 129.4, 128.0, 125.7, 28.5, -2.4. **HR-MS** (ESI)  $m/z$  calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>Si [M+H<sup>+</sup>] 310.1258, found 310.1257.



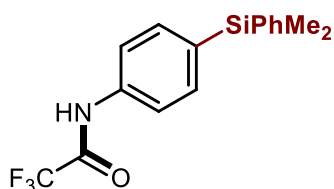
#### 1-{4-[Dimethyl(phenyl)silyl]phenyl}pyrrolidin-2-one(16) <sup>18</sup>

The general procedure **TP4** was followed using **1n** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 8:1) yielded **16** (40 mg, 90%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.59 (d, *J* = 8.5 Hz, 2H), 7.54 – 7.45 (m, 4H), 7.41 – 7.29 (m, 3H), 3.84 (t, *J* = 7.0 Hz, 2H), 2.60 (t, *J* = 8.1 Hz, 2H), 2.14 (p, *J* = 7.5 Hz, 2H), 0.53 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 174.4, 140.2, 138.3, 134.9, 134.2, 134.0, 129.21, 127.9, 119.3, 48.7, 32.9, 18.1, -2.3.



#### *N*-{4-[Dimethyl(phenyl)silyl]phenyl}benzamide (17).

The general procedure **TP4** was followed using **1o** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **17** (46 mg, 93%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.97 (s, 1H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.50 (m, 5H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.38 (q, *J* = 7.0, 5.0 Hz, 3H), 0.57 (s, 6H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.9, 138.8, 138.3, 135.2, 135.0, 134.2, 134.1, 131.9, 129.2, 128.8, 127.9, 127.1, 119.6, -2.3. **HR-MS** (ESI) *m/z* calcd for C<sub>21</sub>H<sub>21</sub>NOSi [M+H<sup>+</sup>] 332.1465, found 332.1466.

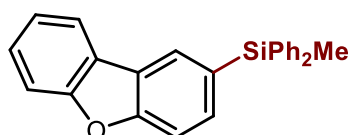


#### *N*-(4-(Dimethyl(phenyl)silyl)phenyl)-2,2,2-trifluoroacetamide (18).

The general procedure **TP4** was followed using **1p** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **18** (36 mg, 75%)

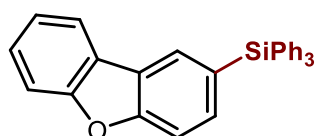


as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.00$  (s, 1H), 7.59 – 7.50 (m, 6H), 7.42 – 7.33 (m, 3H), 0.57 (s, 6H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 155.0$  (q,  $J_{\text{C-F}} = 37.0$  Hz), 137.8, 136.9, 136.0, 135.4, 134.2, 129.4, 128.0, 119.9, 115.8 (q,  $J_{\text{C-F}} = 286.9$  Hz), -2.3.  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -75.69$ . **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{16}\text{F}_3\text{NOSi}$  [ $\text{M}+\text{H}^+$ ] 324.1026, found 324.1024.



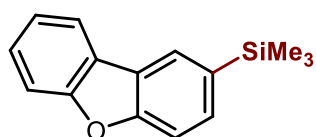
#### Dibenzo[b,d]furan-2-yl(methyl)diphenylsilane (**19**).

The general procedure **TP4** was followed using **1d** (0.15 mmol), **2b** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **19** (40 mg, 74%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.13$  (s, 1H), 7.92 (d,  $J = 7.7$  Hz, 1H), 7.62 – 7.54 (m, 6H), 7.46 – 7.38 (m, 6H), 7.37 – 7.29 (m, 3H), 0.94 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 157.4$ , 156.3, 136.4, 135.5, 134.3, 134.0, 133.8, 129.9, 129.6, 128.9, 128.7, 128.1, 128.0, 127.3, 124.3, 124.1, 122.9, 120.9, 111.8, 111.6, -2.8. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{20}\text{OSi}$  [ $\text{M}+\text{H}^+$ ] 365.1356, found 365.1353.



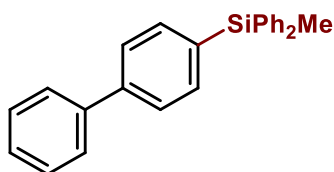
#### Dibenzo[b,d]furan-2-yltriphenylsilane (**20**).

The general procedure **TP4** was followed using **1d** (0.15 mmol), **2c** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **20** (42 mg, 65%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.16$  (s, 1H), 7.88 (d,  $J = 7.2$  Hz, 1H), 7.62 (dd,  $J = 8.0, 1.5$  Hz, 7H), 7.61 – 7.56 (m, 2H), 7.49 – 7.44 (m, 4H), 7.41 (d,  $J = 7.4$  Hz, 5H), 7.38 (d,  $J = 1.5$  Hz, 1H), 7.31 (t,  $J = 7.5$  Hz, 1H), 1.55 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 157.5$ , 156.3, 136.6, 135.4, 134.5, 129.8, 129.2, 128.1, 127.9, 127.4, 124.4, 124.0, 123.0, 121.0, 111.8, 111.6. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{30}\text{H}_{22}\text{OSi}$  [ $\text{M}+\text{H}^+$ ] 427.1513, found 427.1516.



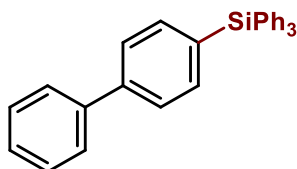
### Dibenzo[b,d]furan-2-yltrimethylsilane (**21**).

The general procedure **TP4** was followed using **1d** (0.15 mmol), **2d** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **21** (20 mg, 56%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.12 (s, 1H), 8.00 (d,  $J$  = 7.6 Hz, 1H), 7.63 – 7.55 (m, 3H), 7.48 – 7.43 (m, 1H), 7.36 (t,  $J$  = 7.5 Hz, 1H), 0.36 (s, 9H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 157.1, 156.2, 134.2, 132.3, 127.2, 125.8, 124.2, 124.1, 122.9, 120.7, 111.8, 111.3, -0.6. **HR-MS** (ESI)  $m/z$  calcd for C<sub>15</sub>H<sub>16</sub>OSi [M+H<sup>+</sup>] 241.1043, found 241.1045.



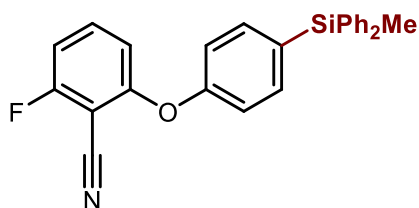
### [1,1'-Biphenyl]-4-yl(methyl)diphenylsilane (**22**)<sup>[9]</sup>.

The general procedure **TP4** was followed using **1a** (0.15 mmol), **2b** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **22** (30 mg, 57%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.65 – 7.59 (m, 6H), 7.57 (dd,  $J$  = 7.7, 1.6 Hz, 4H), 7.48 – 7.42 (m, 3H), 7.40 (d,  $J$  = 7.2 Hz, 4H), 7.37 – 7.34 (m, 2H), 0.89 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.2, 141.1, 136.2, 135.9, 135.4, 135.0, 129.6, 128.9, 128.0, 127.6, 127.3, 126.7, -3.2.



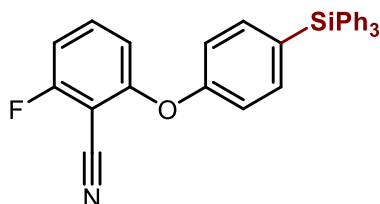
### [1,1'-Biphenyl]-4-yltriphenylsilane (**23**)<sup>[7]</sup>.

The general procedure **TP4** was followed using **1a** (0.15 mmol), **2c** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **23** (39 mg, 63%) as a white powder. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.63 (td,  $J$  = 8.0, 3.0 Hz, 12H), 7.41 (tt,  $J$  = 16.0, 6.8 Hz, 12H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.2, 140.9, 136.9, 136.4, 134.2, 133.0, 129.7, 128.8, 127.9, 127.5, 127.2, 126.6.



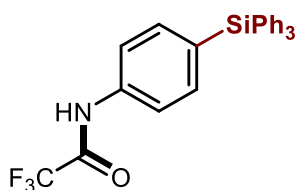
### 2-Fluoro-6-[4-(methyldiphenylsilyl)phenoxy]benzonitrile (24).

The general procedure **TP4** was followed using **1g** (0.15 mmol), **2b** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **24** (52 mg, 84%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.57 (d,  $J$  = 8.5 Hz, 2H), 7.57 – 7.50 (m, 4H), 7.46 – 7.37 (m, 7H), 7.10 (d,  $J$  = 8.5 Hz, 2H), 6.90 (t,  $J$  = 8.4 Hz, 1H), 6.69 (d,  $J$  = 8.6 Hz, 1H), 0.87 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.5, 162.9, 160.8 (d,  $J$  = 3.9 Hz), 155.9, 137.5, 135.8, 135.3, 135.0 (d,  $J$  = 10.2 Hz), 133.7, 129.7, 128.1, 119.7, 112.5, 112.4 (d,  $J$  = 3.5 Hz), 111.2, 109.9 (d,  $J$  = 19.1 Hz), -3.2.  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -104.57. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{26}\text{H}_{20}\text{FNOSi}$  [ $\text{M}+\text{H}^+$ ] 410.1371, found 410.1375.



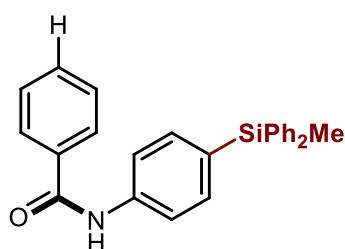
### 2-Fluoro-6-[4-(triphenylsilyl)phenoxy]benzonitrile (25).

The general procedure **TP4** was followed using **1g** (0.15 mmol), **2c** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **25** (37 mg, 52%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.63 (d,  $J$  = 8.5 Hz, 2H), 7.58 (dd,  $J$  = 7.9, 1.4 Hz, 6H), 7.49 – 7.43 (m, 4H), 7.41 (d,  $J$  = 7.3 Hz, 5H), 7.38 (d,  $J$  = 1.5 Hz, 1H), 7.12 (d,  $J$  = 8.5 Hz, 2H), 6.90 (t,  $J$  = 8.2 Hz, 1H), 6.71 (d,  $J$  = 8.6 Hz, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 165.5, 162.9, 160.7 (d,  $J$  = 3.8 Hz), 156.1, 138.6, 136.5, 135.0 (d,  $J$  = 10.1 Hz), 134.9, 133.9, 131.8, 129.9, 128.1, 119.7, 112.6 (d,  $J$  = 4.4 Hz), 111.2, 110.1 (d,  $J$  = 19.5 Hz).  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -104.49. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{31}\text{H}_{22}\text{FNOSi}$  [ $\text{M}+\text{H}^+$ ] 472.1527, found 472.1529.



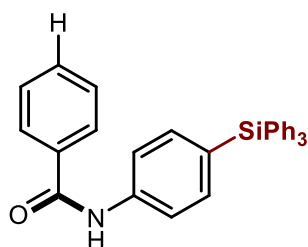
### 2,2,2-Trifluoro-*N*-[4-(triphenylsilyl)phenyl]acetamide (**26**).

The general procedure **TP4** was followed using **1p** (0.15 mmol), **2c** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **26** (33 mg, 49%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.92$  (s, 1H), 7.63 – 7.58 (m, 4H), 7.58 – 7.53 (m, 6H), 7.47 – 7.42 (m, 3H), 7.39 (d,  $J = 7.4$  Hz, 5H), 7.37 (d,  $J = 1.4$  Hz, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 154.9$  (d,  $J_{\text{C-F}} = 36.9$  Hz), 137.7, 137.1, 136.5, 135.9, 133.9, 132.9, 130.1 (d,  $J_{\text{C-F}} = 23.4$  Hz), 128.3 (d,  $J_{\text{C-F}} = 17.9$  Hz), 119.9 (d,  $J_{\text{C-F}} = 18.5$  Hz).  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -75.68$ . **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{26}\text{H}_{20}\text{F}_3\text{NOSi}$  [ $\text{M}+\text{H}^+$ ] 448.1339, found 448.1337.



### *N*-[4-(Methyldiphenylsilyl)phenyl]benzamide (**27**).

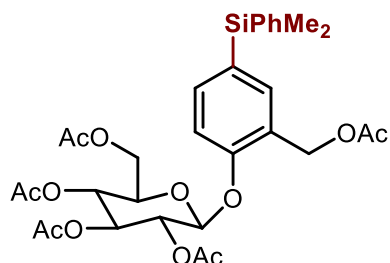
The general procedure **TP4** was followed using **1o** (0.15 mmol), **2b** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 30:1) yielded **27** (39 mg, 66%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.95$  (s, 1H), 7.88 – 7.84 (m, 2H), 7.66 (d,  $J = 8.3$  Hz, 2H), 7.56 – 7.50 (m, 7H), 7.48 (d,  $J = 7.7$  Hz, 2H), 7.42 – 7.34 (m, 6H), 0.85 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 166.0$ , 139.2, 136.4, 136.2, 135.4, 135.0, 132.0, 129.5, 128.9, 128.0, 127.2, 119.6, -3.2. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{26}\text{H}_{23}\text{NOSi}$  [ $\text{M}+\text{H}^+$ ] 394.1622, found 394.1626.



### *N*-[4-(Triphenylsilyl)phenyl]benzamide (**28**)

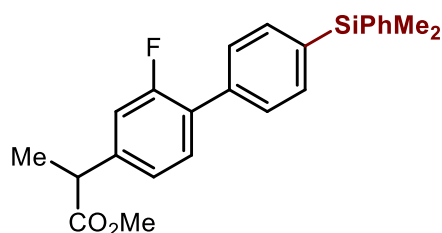
The general procedure **TP4** was followed using **1p** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 1:1) yielded **28** (40 mg, 59%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.87$  (d,  $J = 7.0$  Hz, 3H), 7.65 (d,  $J = 7.6$  Hz,

3H), 7.60 – 7.53 (m, 3H), 7.50 (d,  $J = 7.6$  Hz, 2H), 7.48 – 7.35 (m, 5H), 7.16 (t,  $J = 7.4$  Hz, 1H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 166.0, 139.3, 137.5, 136.5, 135.1, 134.3, 132.1, 130.2, 129.8, 129.0, 128.0, 127.2, 119.5$ . **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{31}\text{H}_{25}\text{NOSi}$   $[\text{M}+\text{H}^+]$  456.1778, found 456.1775.



**(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(Acetoxymethyl)-6-{2-(acetoxymethyl)-4-dimethyl(phenyl)silyl}phenoxy}tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (**29**)**

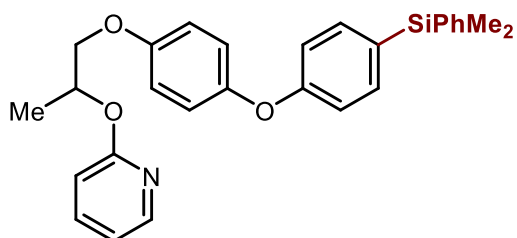
The general procedure **TP4** was followed using **1q** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 1:1) yielded **29** (44 mg, 47%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.49$  (dd,  $J = 7.5, 2.0$  Hz, 3H), 7.35 (td,  $J = 9.7, 3.5$  Hz, 4H), 6.98 (d,  $J = 8.2$  Hz, 1H), 5.45 – 5.28 (m, 2H), 5.26 – 5.09 (m, 2H), 4.49 (dd,  $J = 14.4, 7.1$  Hz, 1H), 4.31 (dd,  $J = 12.4, 5.3$  Hz, 1H), 4.23 – 4.04 (m, 2H), 3.86 (ddd,  $J = 10.0, 5.2, 2.3$  Hz, 1H), 2.11 – 2.01 (m, 12H), 1.96 (s, 3H), 0.53 (s, 6H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 170.7, 170.2, 170.0, 170.0, 169.6, 155.8, 136.6, 135.3, 134.2, 133.4, 129.3, 128.0, 127.5, 114.0, 98.7, 72.4, 72.3, 71.3, 68.3, 61.8, 39.6, 23.3, 2.9, 20.8, 20.7, -2.3$ . **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{31}\text{H}_{38}\text{O}_{12}\text{Si}$   $[\text{M}+\text{H}^+]$  631.2205, found 631.2209.



**Methyl 2-{4'-[dimethyl(phenyl)silyl]-2-fluoro-[1,1'-biphenyl]-4-yl}propanoate (**30**).**

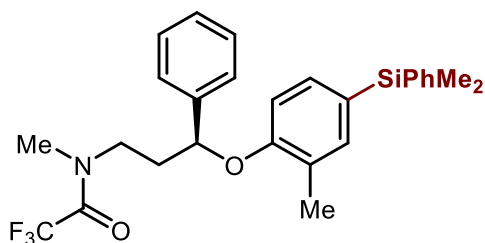
The general procedure **TP5** was followed using **1r** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **30** (51 mg, 86%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.65 - 7.57$  (m, 4H), 7.54 (d,  $J = 8.0$  Hz, 2H), 7.46 – 7.34 (m, 4H), 7.19 – 7.12 (m, 2H), 3.78 (q,  $J = 7.2$  Hz, 1H), 3.72 (s, 3H), 1.56 (d,  $J = 7.2$  Hz, 3H), 0.61 (s, 6H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 174.6, 161.1, 158.6, 142.0$  (d,  $J_{\text{C-F}} =$

8.0 Hz), 138.13, 137.82, 136.28, 134.4 (d,  $J_{C-F} = 12.7$  Hz), 130.93, 130.89, 129.31, 128.41, 128.38, 128.0, 127.8 (d,  $J_{C-F} = 12.1$  Hz), 123.7 (d,  $J_{C-F} = 3.5$  Hz), 115.4 (d,  $J_{C-F} = 23.4$  Hz), 52.3, 45.1, 18.6, -2.3.  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -117.37$ . **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{25}\text{FO}_2\text{Si}$  [ $\text{M}+\text{H}^+$ ] 393.1681, found 393.1685.



**2-((1-(4-(4-(Dimethyl(phenyl)silyl)phenoxy)phenoxy)propan-2-yl)oxy)pyridine (31)** <sup>[8]</sup>.

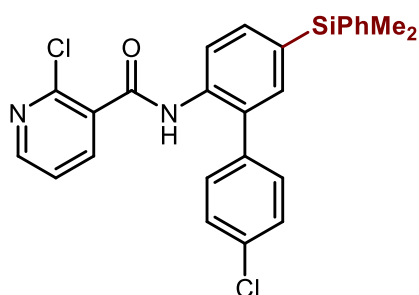
The general procedure **TP4** was followed using **1s** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **31** (47 mg, 69%) as a white powder.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.15$  (d,  $J = 3.9$  Hz, 1H), 7.59 – 7.50 (m, 3H), 7.43 (d,  $J = 8.3$  Hz, 2H), 7.38 – 7.33 (m, 3H), 6.99 – 6.90 (m, 6H), 6.88 – 6.84 (m, 1H), 6.74 (d,  $J = 8.3$  Hz, 1H), 5.59 (q,  $J = 5.5$  Hz, 1H), 4.22 – 4.15 (m, 1H), 4.11 – 4.04 (m, 1H), 1.48 (d,  $J = 6.4$  Hz, 3H), 0.53 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 163.3, 159.8, 155.6, 149.8, 146.9, 138.9, 138.6, 135.8, 134.3, 131.3, 129.2, 127.9, 121.3, 116.9, 116.0, 111.8, 71.2, 69.4, 17.2, -2.1$ .



**(S)-N-3-4-[Dimethyl(phenyl)silyl]-2-methylphenoxy-3-phenylpropyl-2,2,2-trifluoro-N-methylacetamide(32)**

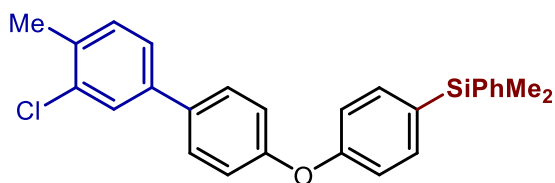
The general procedure **TP4** was followed using **1t** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 15:1) yielded **32** (40 mg, 55%) as a white powder.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.43$  (dd,  $J = 14.8, 7.4$  Hz, 2H), 7.31 (d,  $J = 6.1$  Hz, 4H), 7.24 – 7.17 (m, 3H), 6.97 (d,  $J = 4.2$  Hz, 1H), 6.94 – 6.84 (m, 1H), 6.61 (d,  $J = 8.5$  Hz, 1H), 6.53 (dd,  $J = 16.2, 8.6$  Hz, 1H), 5.39 – 4.95 (m, 1H), 4.12 – 3.45 (m, 2H), 2.31 (d,  $J = 3.9$  Hz, 3H), 2.23 (dd,  $J = 15.1, 7.5$  Hz, 5H), 0.53 (d,  $J = 2.6$  Hz, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 155.8, 155.8$  (q,  $J_{C-F} = 26.5$  Hz), 155.6, 155.6 (q,  $J_{C-F} = 26.0$  Hz), 142.9, 142.8, 140.8, 140.7, 138.7, 138.4, 136.7, 135.7, 134.5, 134.5, 130.8 (q,  $J_{C-F} = 241.4$  Hz), 130.7 (q,  $J_{C-F} = 242.7$  Hz),

130.5, 129.0, 129.0 (d,  $J_{C-F}$  = 21.7 Hz), 128.3, 128.3 (d,  $J_{C-F}$  = 21.0 Hz), 127.7, 127.0, 126.9, 126.5, 126.4, 125.7, 125.5, 124.6, 124.4, 113.6, 113.4, 77.6, 77.4, 47.2, 46.8, 35.7, 34.9, 29.6, 29.5, 16.6, 16.5, -1.3, -2.9.  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -68.95, -69.85. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{30}\text{F}_3\text{NO}_2\text{Si}$  [ $\text{M}+\text{H}^+$ ] 486.2071, found 486.2077.



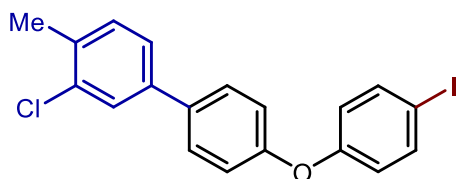
**2-Chloro-N-{4'-chloro-5-[dimethyl(phenyl)silyl]-[1,1'-biphenyl]-2-yl}nicotinamide (33)** <sup>[8]</sup>.

The general procedure **TP4** was followed using **1u** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 15:1) yielded **33** (41.4 mg, 58%) as a white powder.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.47 – 8.40 (m, 2H), 8.18 (s, 1H), 8.15 (d,  $J$  = 7.6 Hz, 1H), 7.61 (d,  $J$  = 8.1 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.43 (d,  $J$  = 8.4 Hz, 2H), 7.38 (d,  $J$  = 1.4 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.35 – 7.31 (m, 3H), 0.57 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 162.6, 151.5, 146.8, 140.4, 137.9, 136.5, 136.0, 135.5, 135.3, 135.1, 134.6, 134.3, 131.5, 131.2, 131.0, 129.5, 129.4, 128.1, 123.1, 121.2, -2.2.



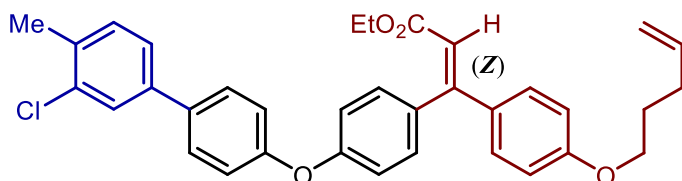
**4-[(3'-Chloro-4'-methyl-[1,1'-biphenyl]-4-yl)oxy]phenyl dimethyl(phenyl)silane (35)**.

The general procedure **TP6** was followed using **8** (2 mmol), **34** (4 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **35** (813 mg, 95%) as a white powder.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.57 – 7.52 (m, 4H), 7.51 (dd,  $J$  = 6.7, 1.9 Hz, 3H), 7.37 (dd,  $J$  = 5.1, 1.9 Hz, 3H), 7.35 (d,  $J$  = 2.0 Hz, 1H), 7.28 (d,  $J$  = 7.9 Hz, 1H), 7.09 (d,  $J$  = 8.7 Hz, 2H), 7.03 (d,  $J$  = 8.4 Hz, 2H), 2.42 (s, 3H), 0.56 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 158.4, 156.7, 139.9, 138.4, 136.0, 135.2, 134.9, 134.8, 134.3, 132.6, 131.4, 129.3, 128.4, 128.0, 127.5, 125.2, 119.7, 118.3, 19.8, -2.1. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{27}\text{H}_{25}\text{ClOSi}$  [ $\text{M}+\text{H}^+$ ] 429.1436, found 429.1439.



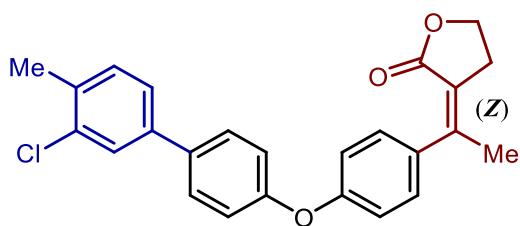
### 3-Chloro-4'-(4-iodophenoxy)-4-methyl-1,1'-biphenyl (**36**).

The general procedure **TP7** was followed using **35** (1 mmol), **IC1** (2 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **36** (370 mg, 88%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.64 (d,  $J$  = 8.9 Hz, 2H), 7.55 (d,  $J$  = 1.8 Hz, 1H), 7.52 (d,  $J$  = 8.7 Hz, 2H), 7.35 (dd,  $J$  = 7.9, 1.9 Hz, 1H), 7.28 (d,  $J$  = 7.9 Hz, 1H), 7.06 (d,  $J$  = 8.7 Hz, 2H), 6.82 (d,  $J$  = 8.9 Hz, 2H), 2.41 (s, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 157.4, 156.5, 139.7, 138.9, 135.5, 134.9, 131.4, 128.5, 127.5, 125.2, 121.1, 119.5, 86.3, 19.9. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{19}\text{H}_{14}\text{ClIO}$  [ $\text{M}+\text{H}^+$ ] 420.9851, found 420.9856.



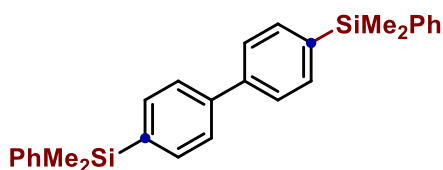
**Ethyl (Z)-3-{4-[(3'-Chloro-4'-methyl-[1,1'-biphenyl]-4-yl)oxy]phenyl}-3-[4-(pent-4-en-1-yloxy)phenyl]acrylate (**38**)**. The general procedure **TP8** was followed using **36** (0.12 mmol), **4a** (0.1 mmol) for 12 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **38** (50 mg, 90%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.57 – 7.51 (m, 3H), 7.36 (dd,  $J$  = 7.9, 1.9 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.21 – 7.17 (m, 2H), 7.16 – 7.12 (m, 2H), 7.06 – 7.01 (m, 2H), 6.88 – 6.82 (m, 2H), 6.27 (s, 1H), 5.91 – 5.79 (m, 1H), 5.10 – 5.03 (m, 1H), 5.03 – 4.95 (m, 1H), 4.08 (q,  $J$  = 7.1 Hz, 2H), 3.98 (t,  $J$  = 6.4 Hz, 2H), 2.41 (s, 3H), 1.94 – 1.84 (m, 2H), 1.18 (t,  $J$  = 7.1 Hz, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.4, 160.4, 157.3, 156.5, 155.9, 139.7, 137.7, 135.2, 134.8, 134.7, 134.0, 133.3, 131.3, 131.0, 129.9, 128.3, 127.4, 125.0, 119.6, 117.8, 115.3, 115.3, 114.3, 67.3, 60.0, 30.1, 28.3, 19.7, 14.2. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{35}\text{H}_{33}\text{ClO}_4$  [ $\text{M}+\text{H}^+$ ] 553.2140, found 553.2144.





**(Z)-3-{1-[4-(3'-Chloro-4'-methyl-[1,1'-biphenyl]-4-**

**yl)oxy]phenyl}ethylidene}dihydrofuran-2(3H)-one (39).** The general procedure **TP8** was followed using **36** (0.12 mmol), **4b** (0.1 mmol) for 12 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **39** (36 mg, 90%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.55 (d,  $J$  = 1.9 Hz, 1H), 7.52 (d,  $J$  = 8.7 Hz, 2H), 7.36 (dd,  $J$  = 7.9, 1.9 Hz, 1H), 7.28 (d,  $J$  = 8.2 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.14 – 7.10 (m, 2H), 7.03 – 6.98 (m, 2H), 4.37 (t,  $J$  = 7.4 Hz, 2H), 3.10 – 3.01 (m, 2H), 2.41 (s, 3H), 2.19 (t,  $J$  = 1.8 Hz, 3H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 168.9, 157.1, 156.5, 149.9, 139.8, 135.1, 134.8, 134.7, 134.5, 131.3, 129.3, 128.3, 127.4, 125.0, 119.9, 119.7, 117.9, 64.0, 28.6, 25.2, 19.7. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{21}\text{ClO}_3$  [ $\text{M}+\text{H}^+$ ] 405.1252, found 405.1255.



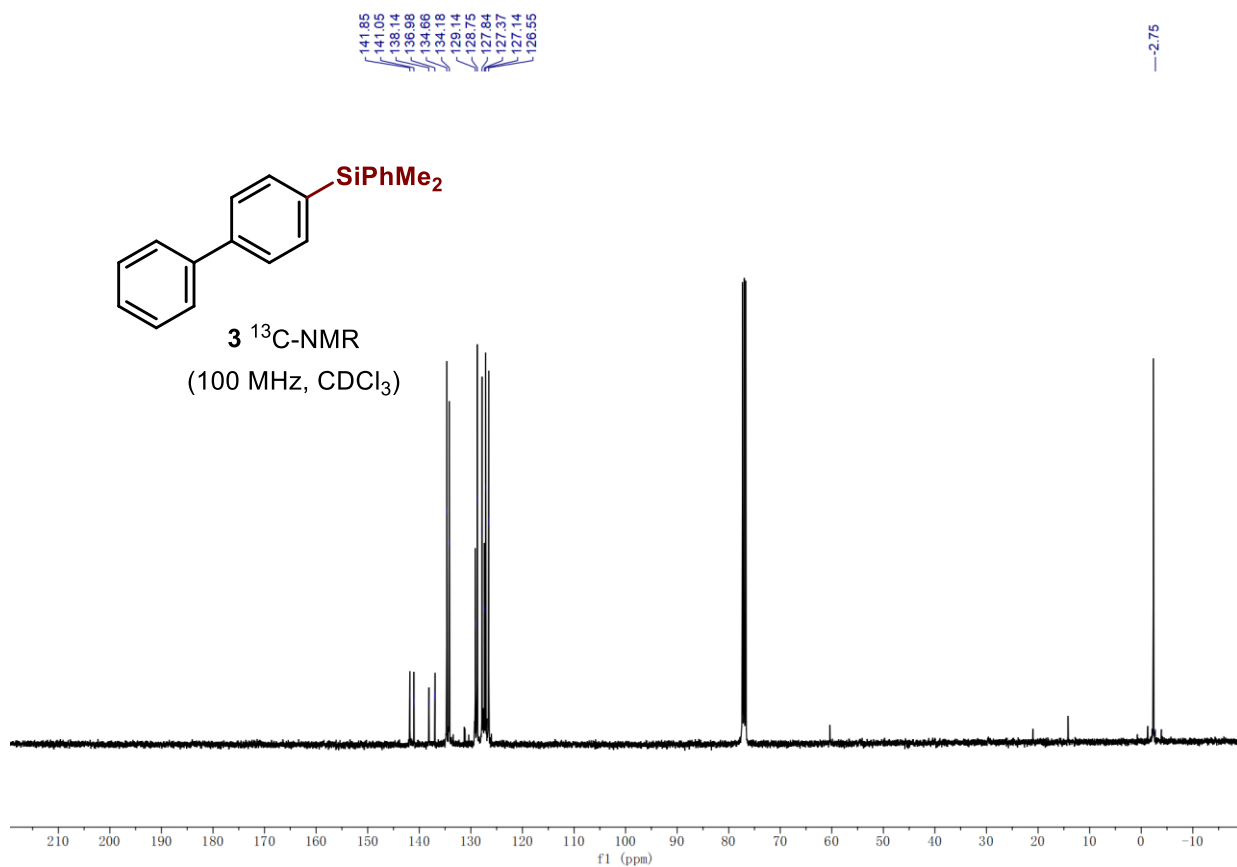
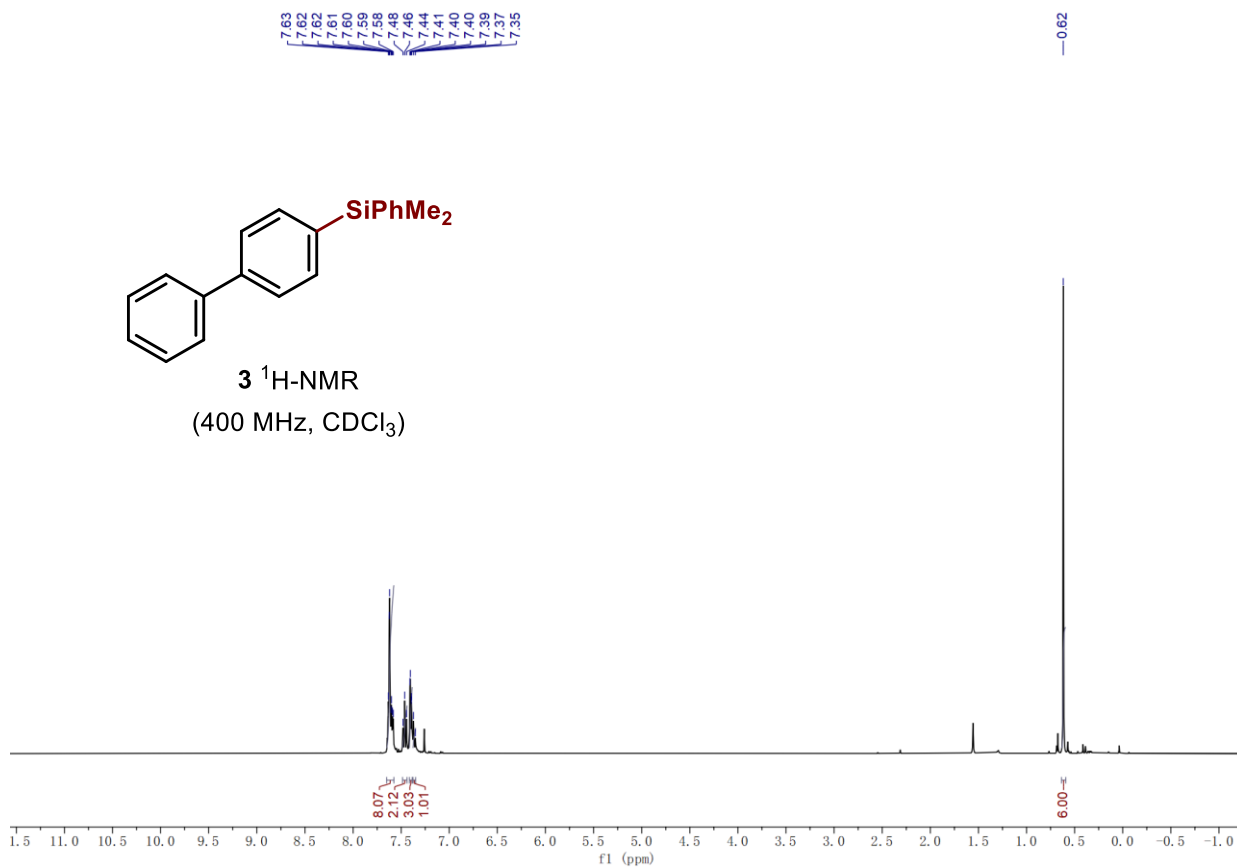
**4,4'-Bis(dimethyl(phenyl)silyl)-1,1'-biphenyl (42)**

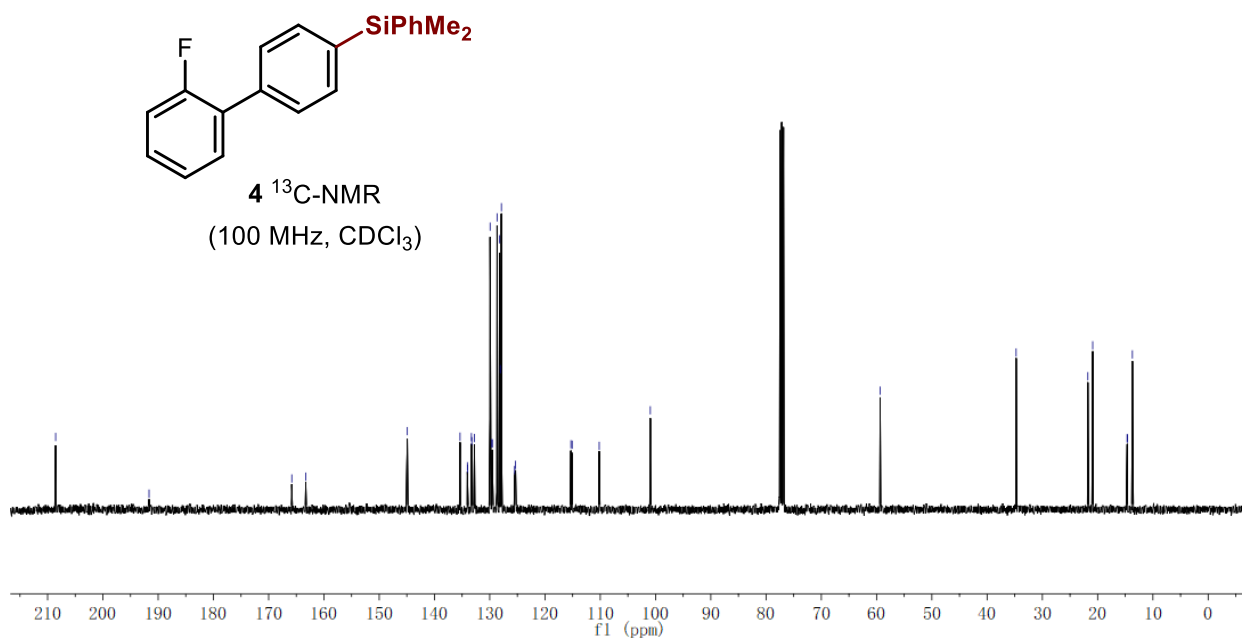
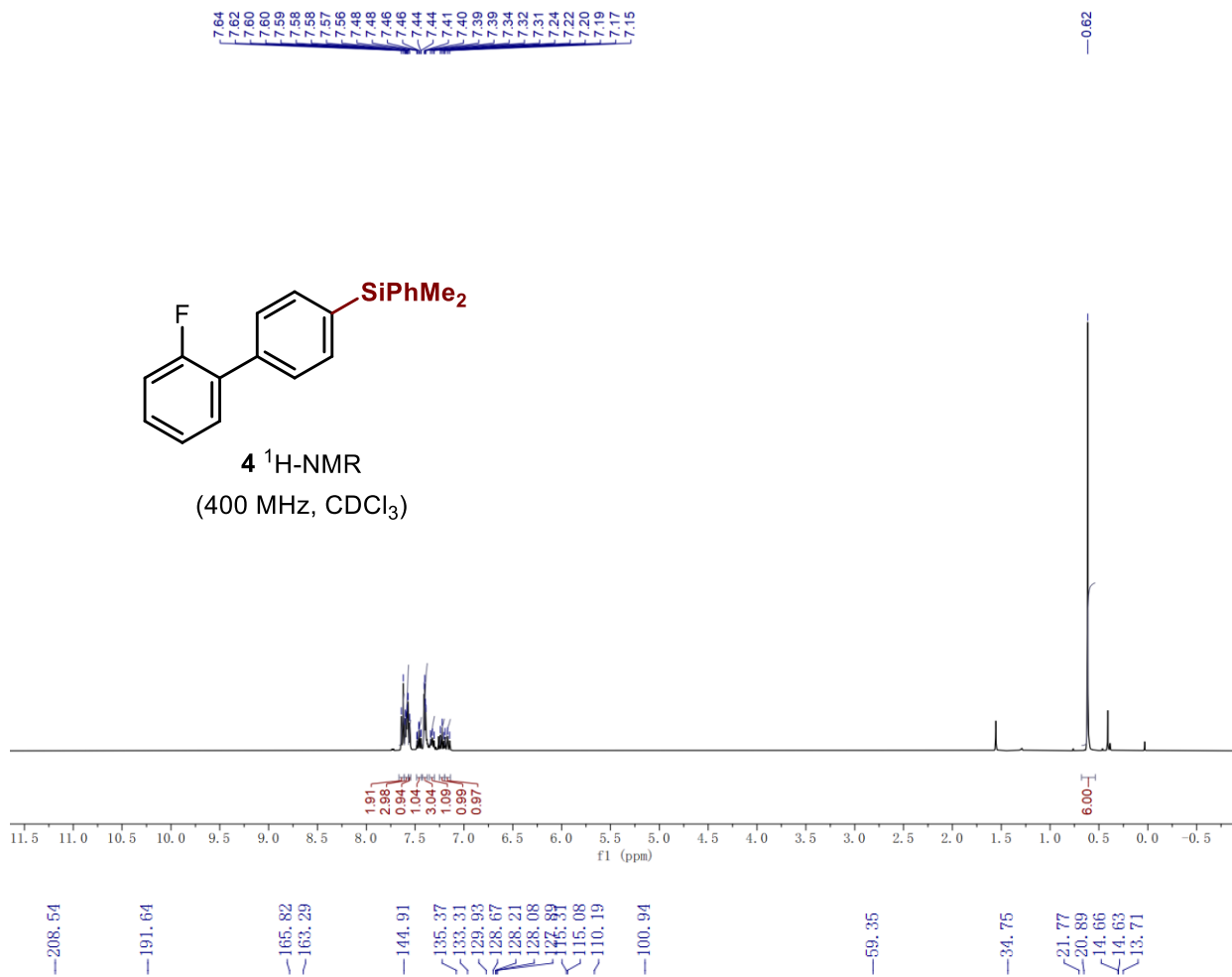
The general procedure **TP4** was followed using **1x** (0.15 mmol), **2a** (0.225 mmol) for 8 h. Purification by column chromatography (petroleum ether/EtOAc 200:1) yielded **42** (39 mg, 61%) as a white powder.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.63 – 7.54 (m, 13H), 7.38 (dd,  $J$  = 5.1, 1.9 Hz, 6H), 0.59 (s, 12H).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 141.9, 138.3, 137.3, 134.8, 134.3, 129.3, 128.0, 126.7, -2.2. **HR-MS** (ESI)  $m/z$  calcd for  $\text{C}_{28}\text{H}_{30}\text{Si}_2$  [ $\text{M}+\text{H}^+$ ] 423.1959, found 423.1956.

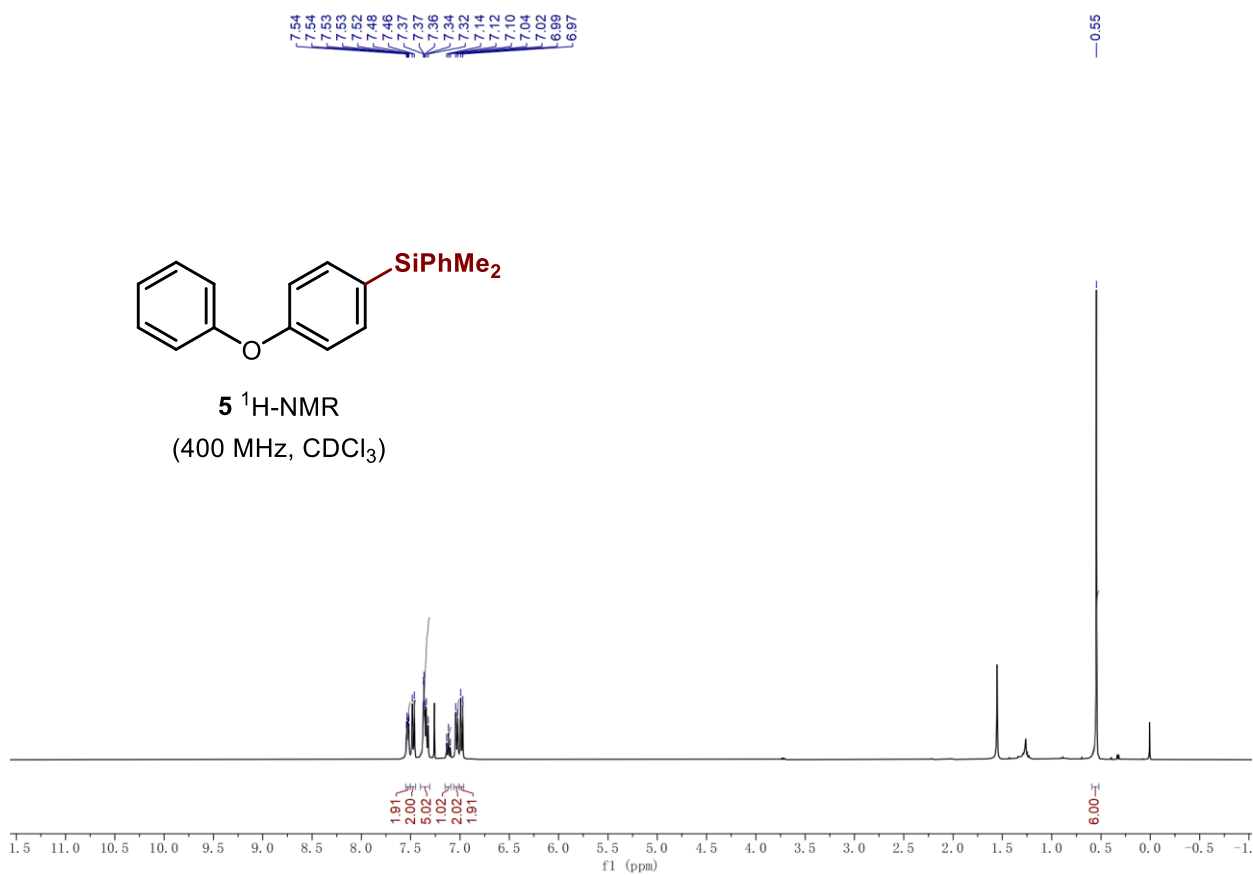
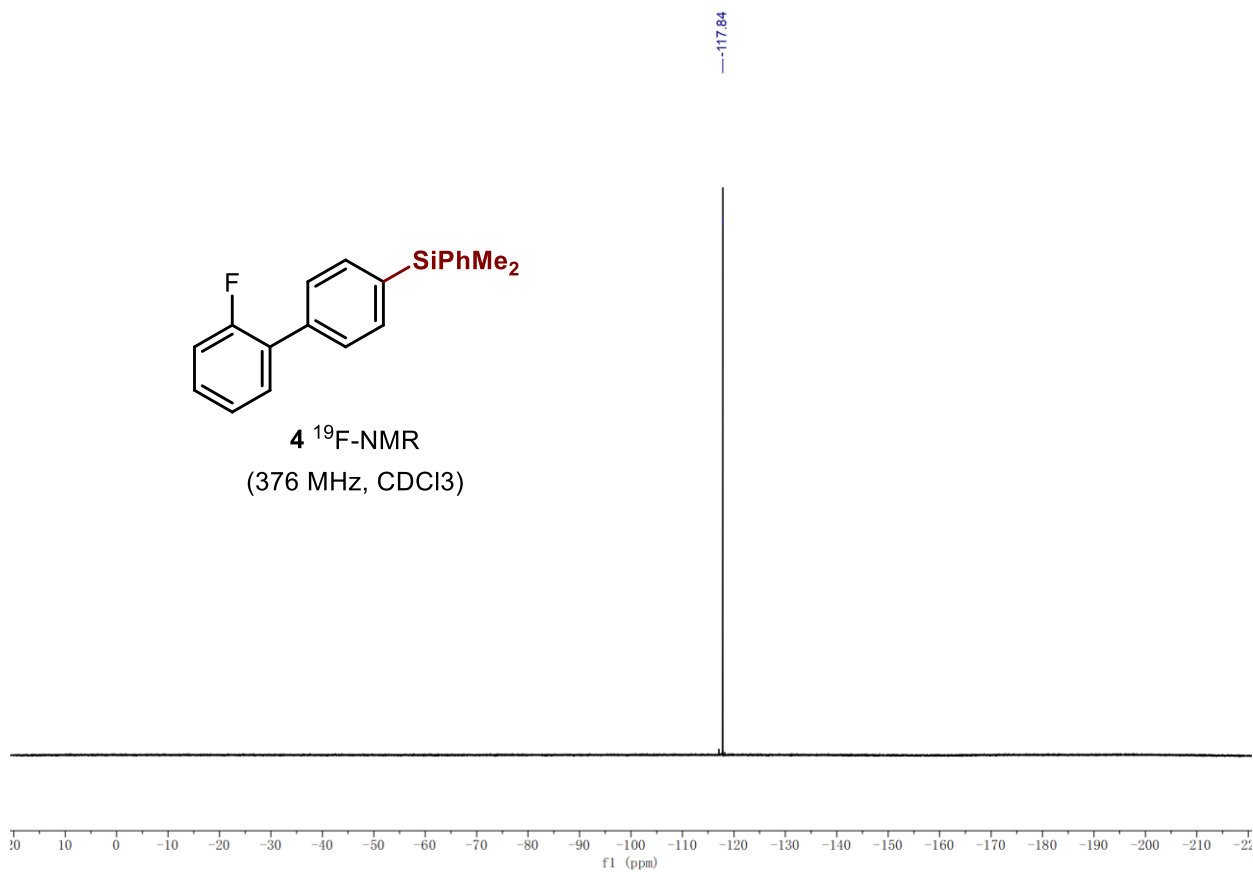
## 8. References:

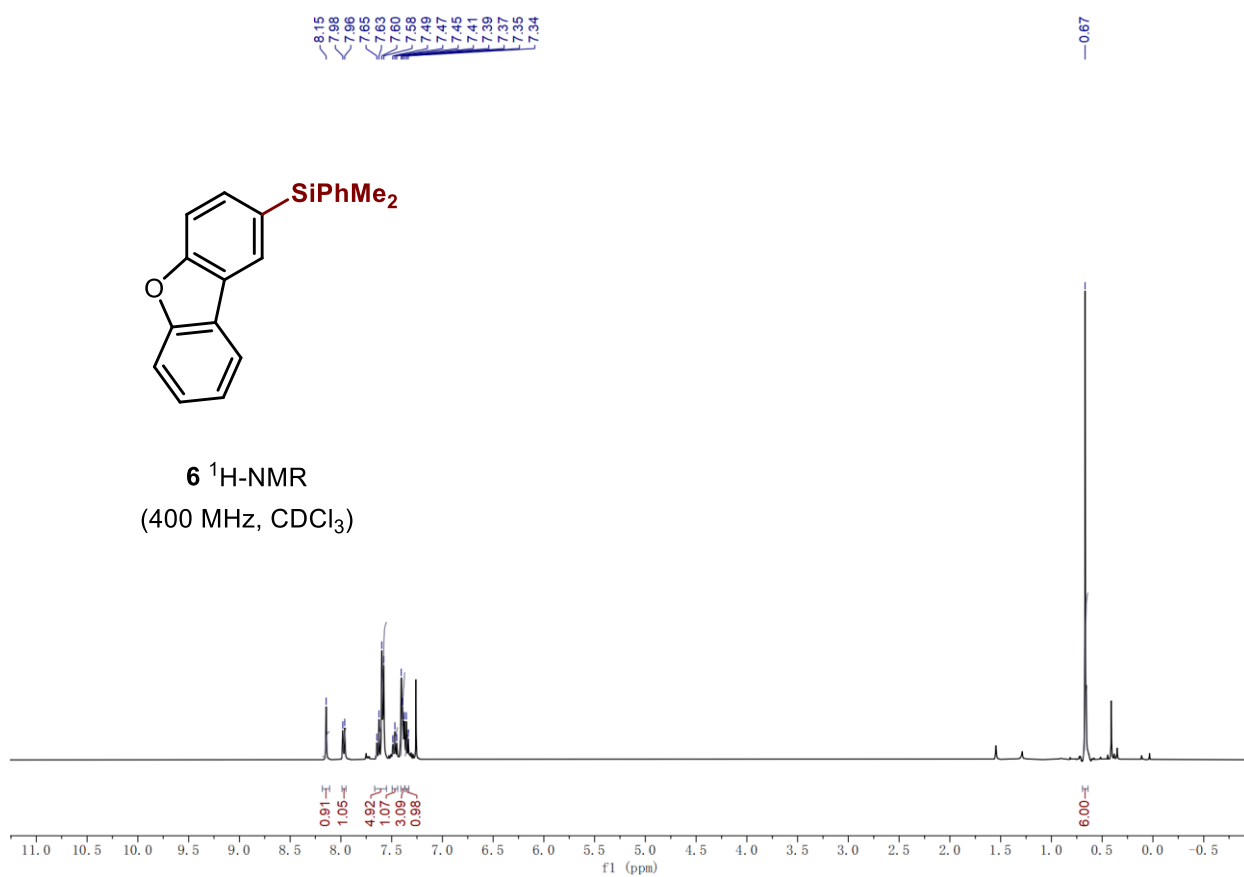
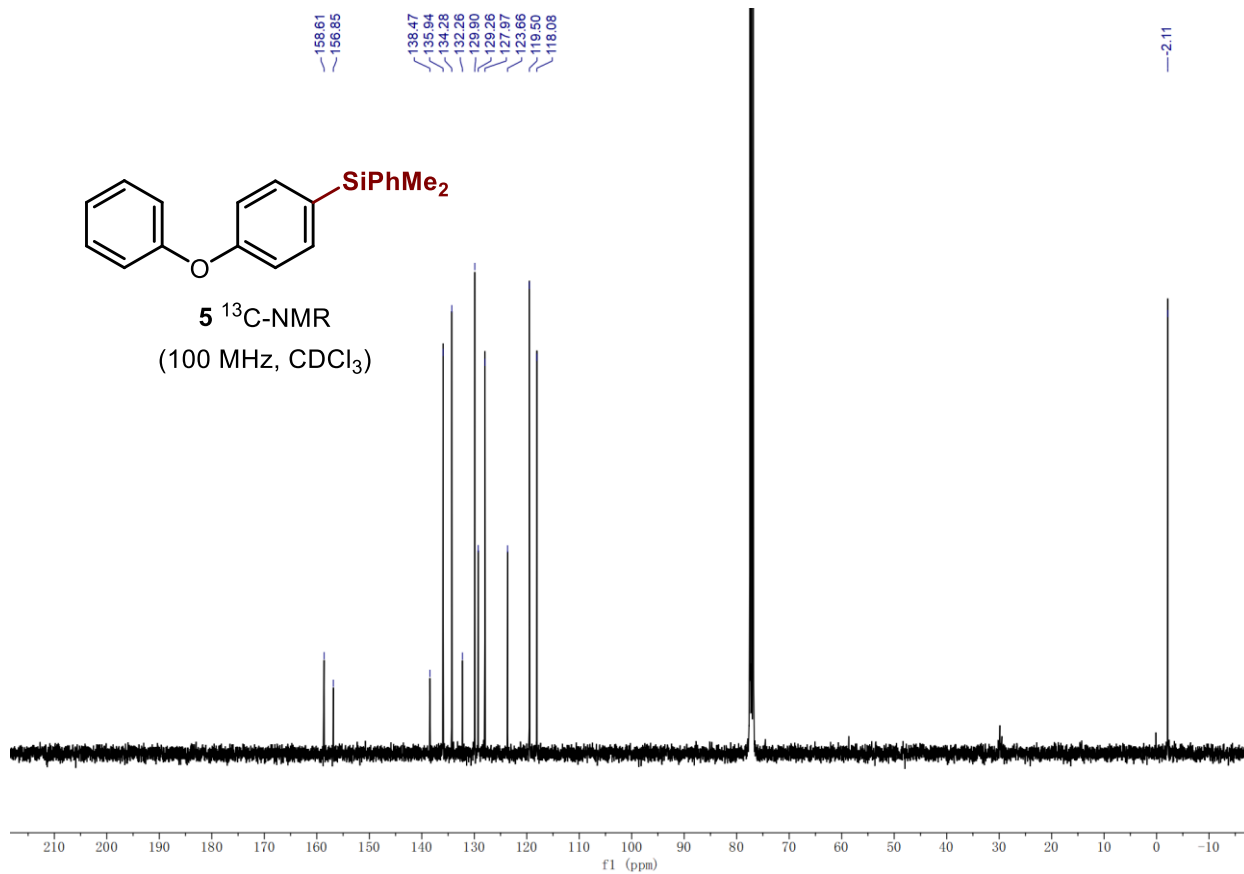
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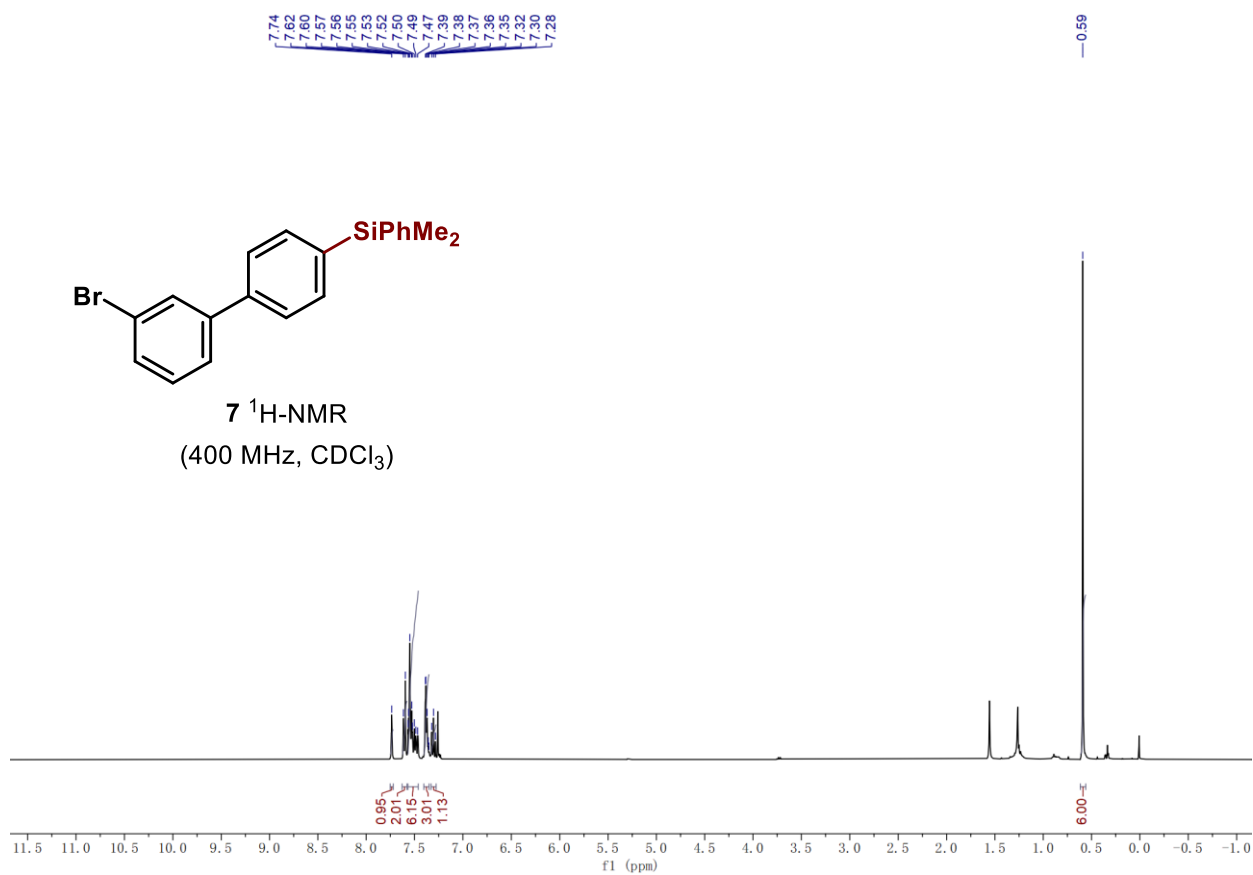
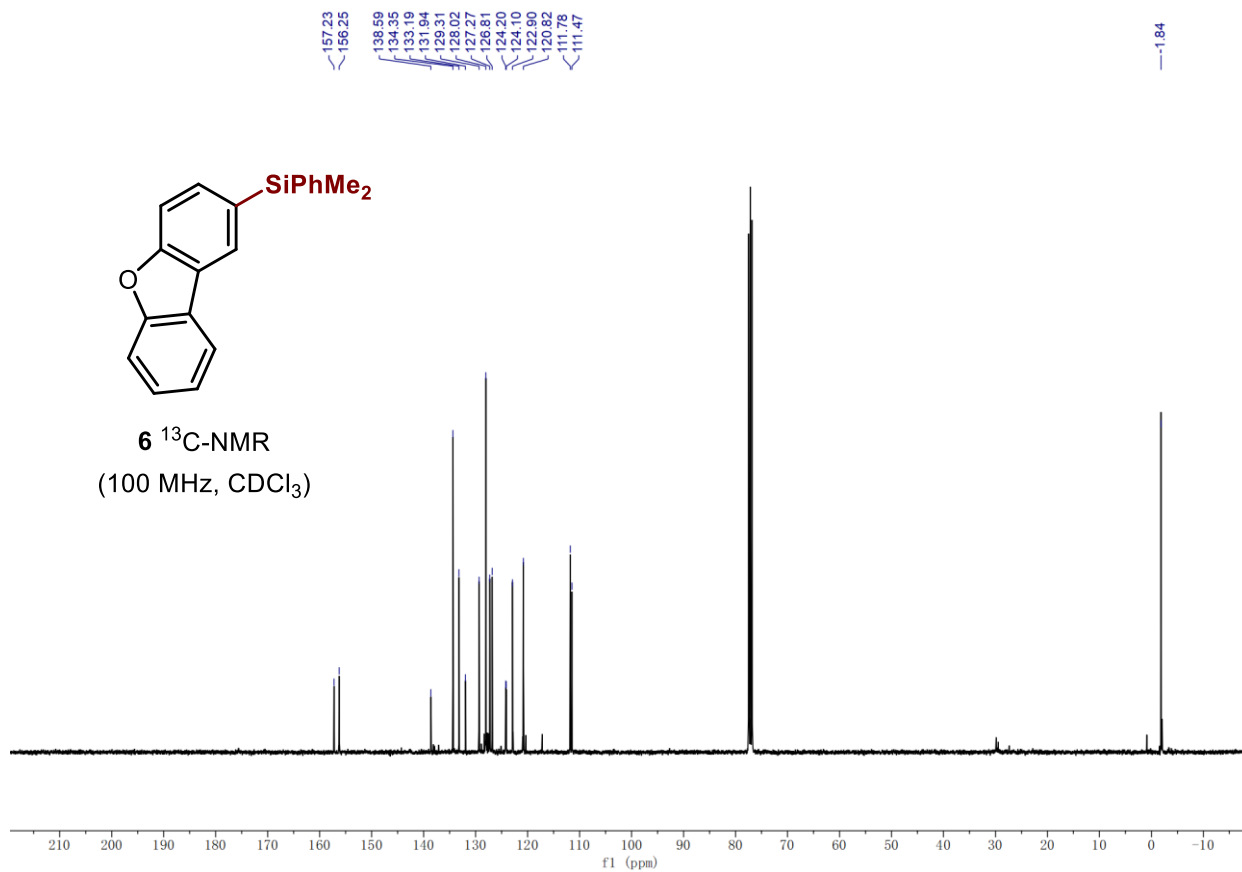
## 9. NMR Spectra

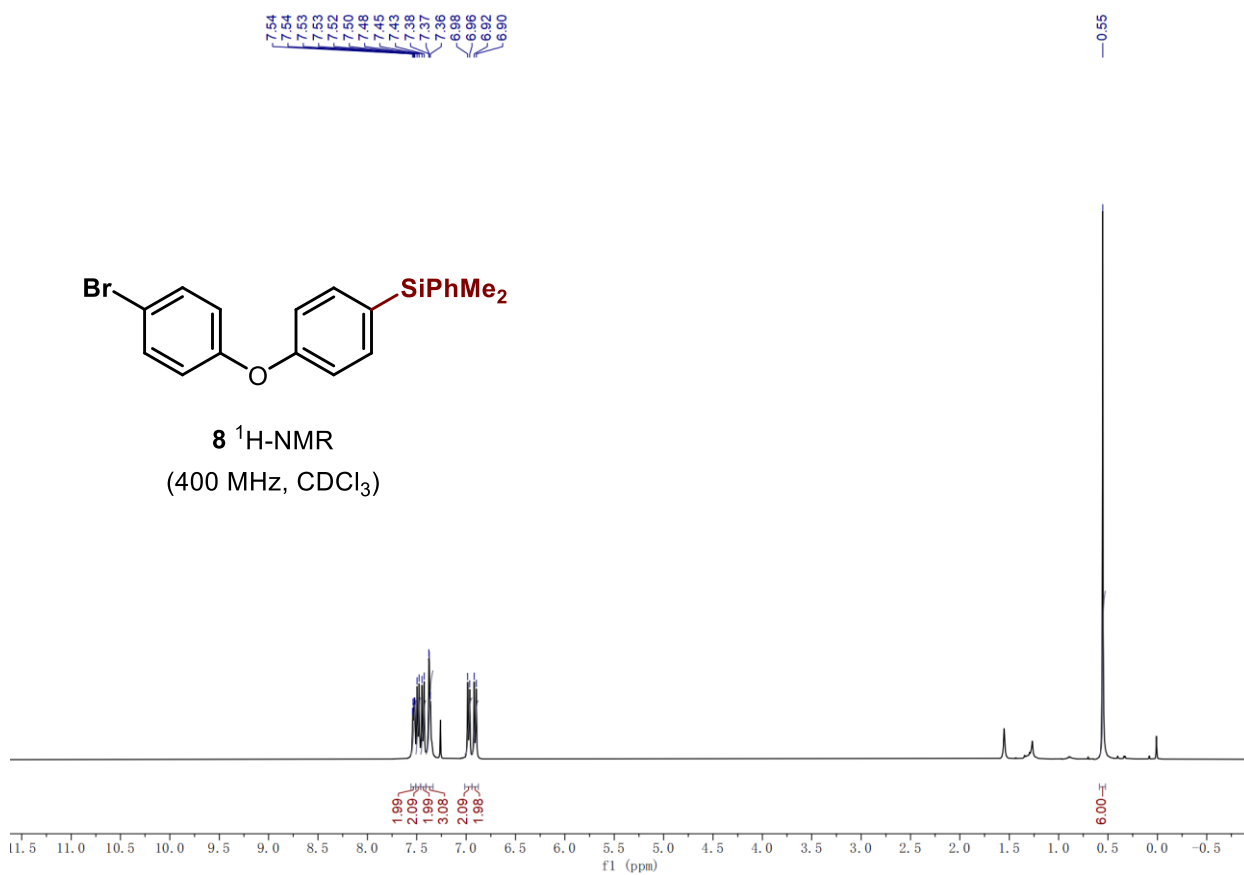
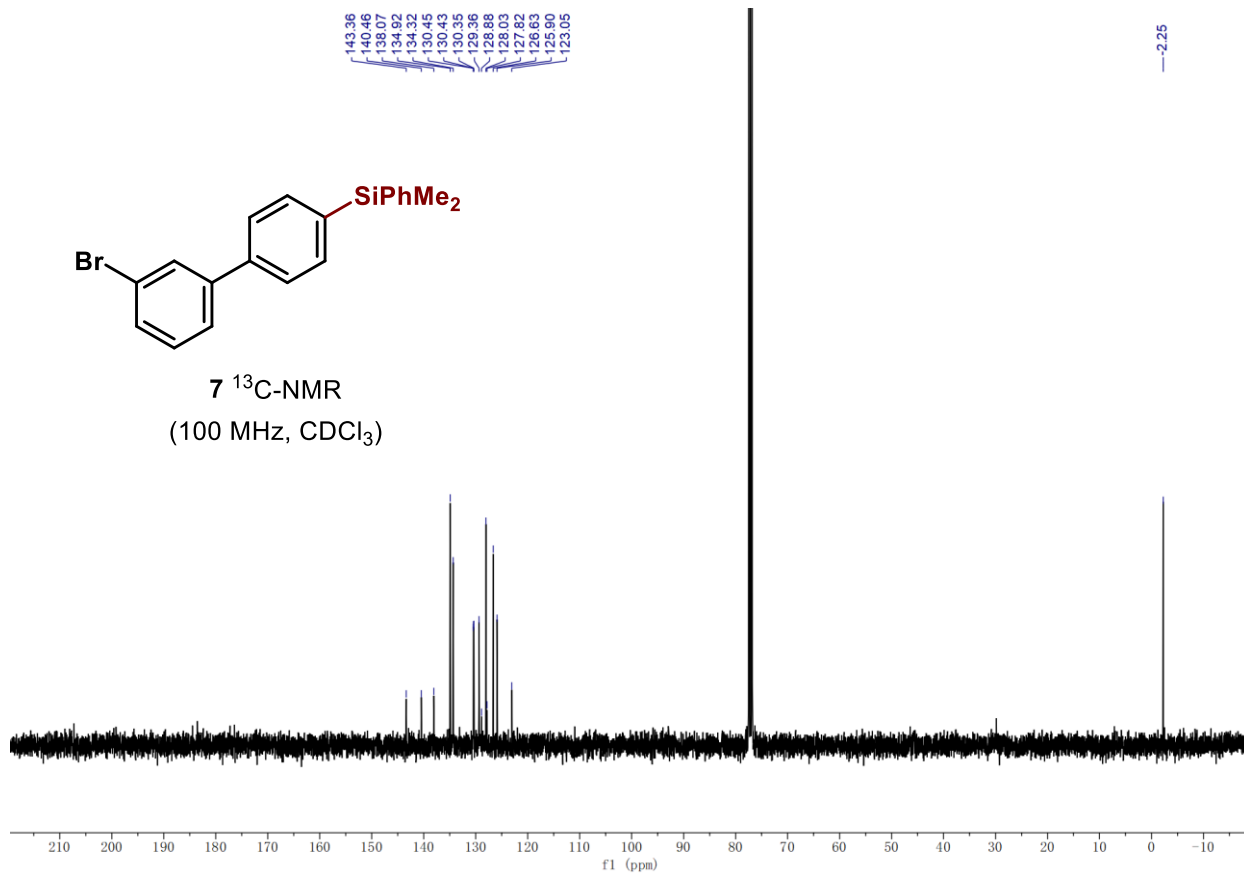




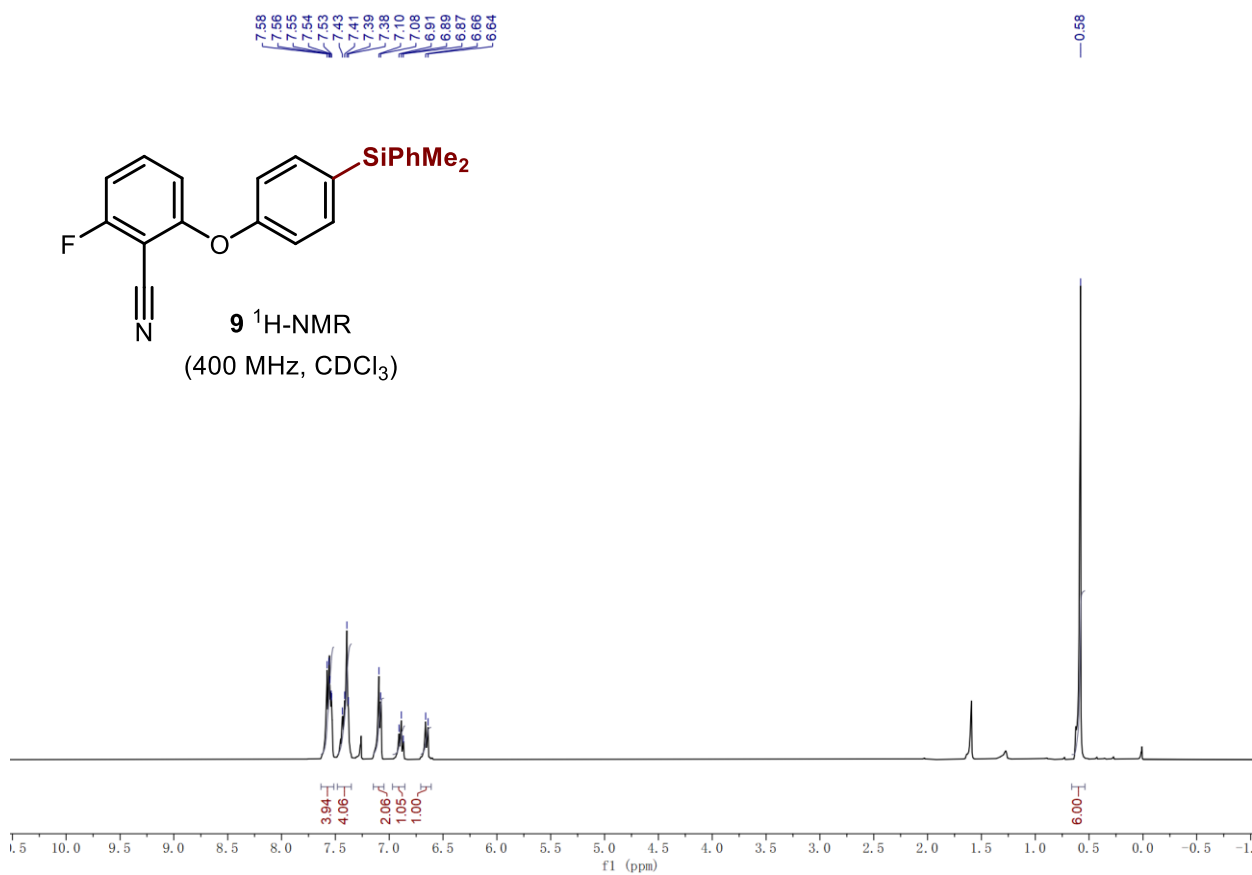
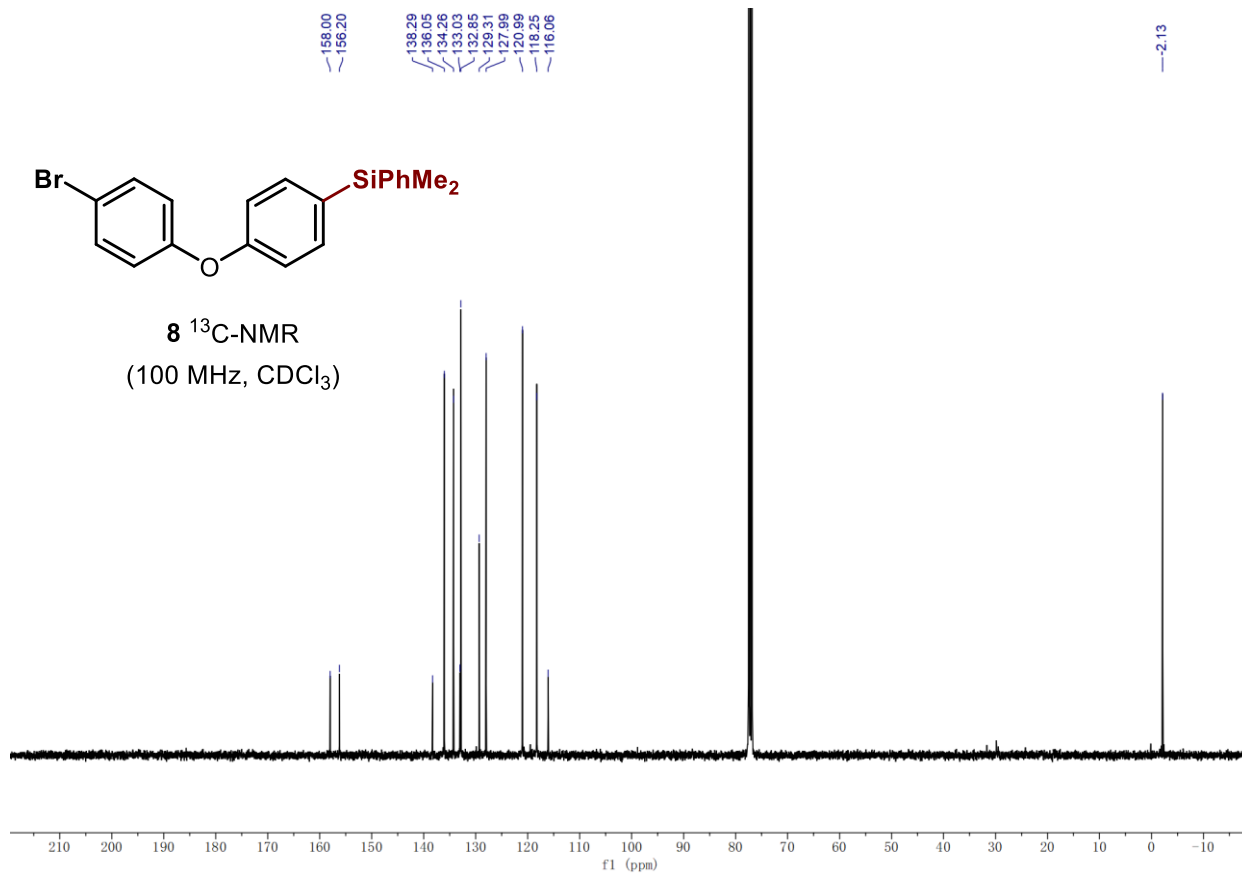


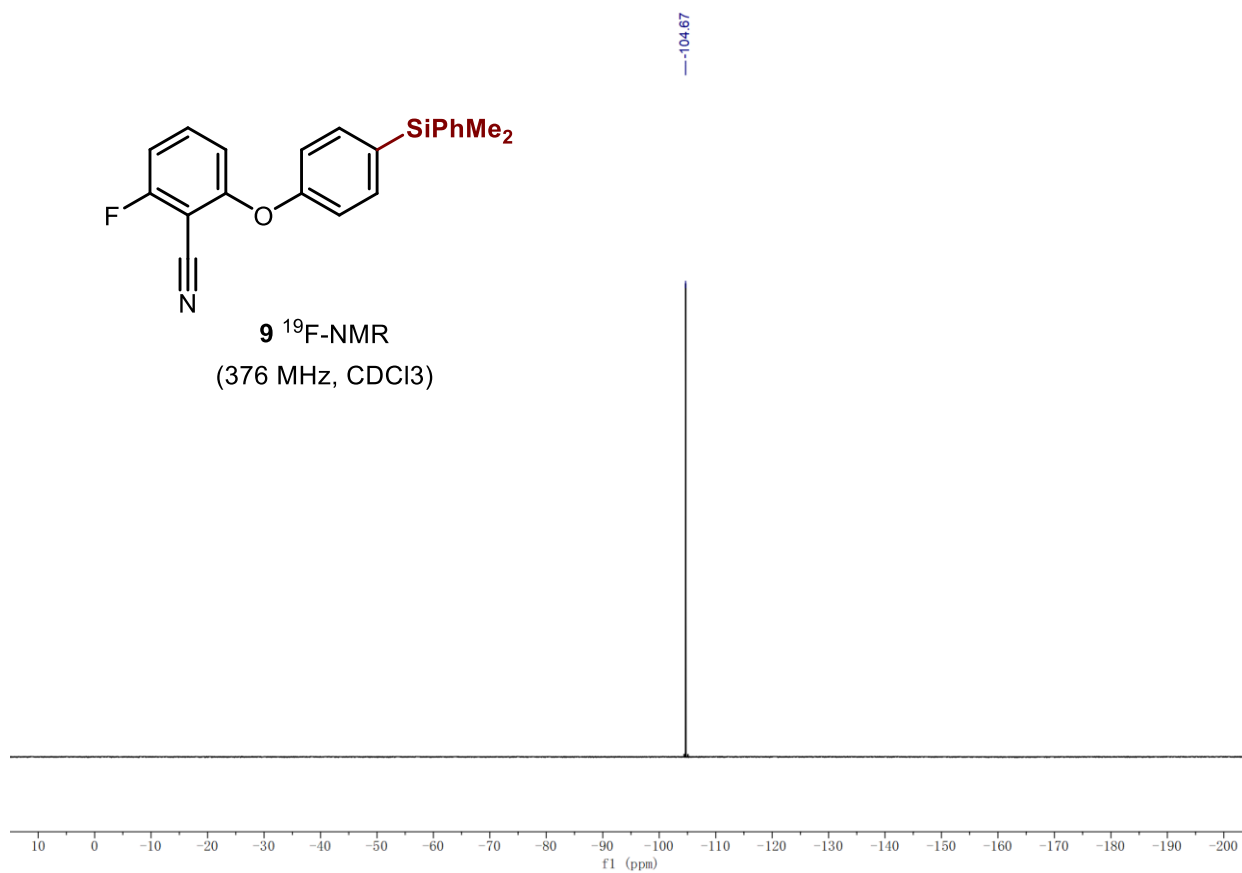
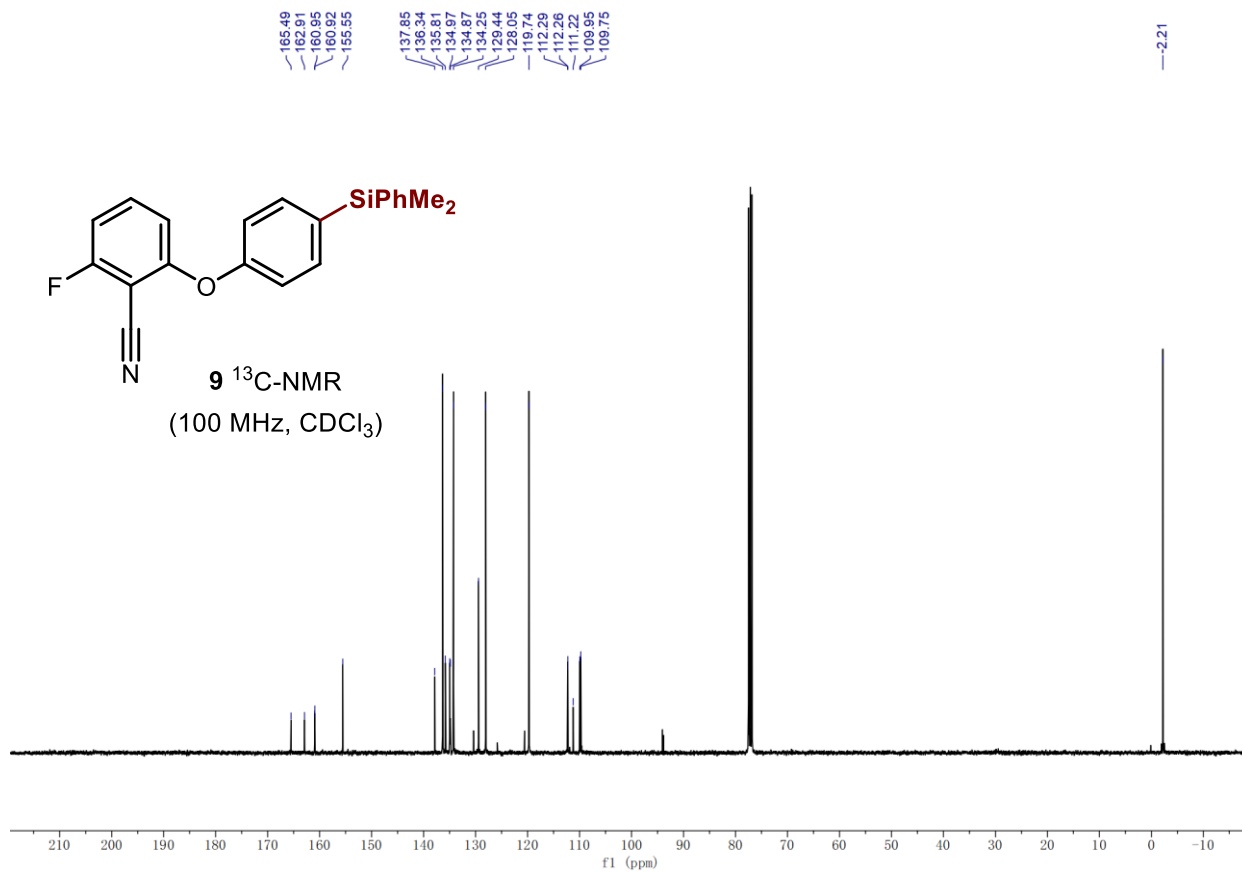


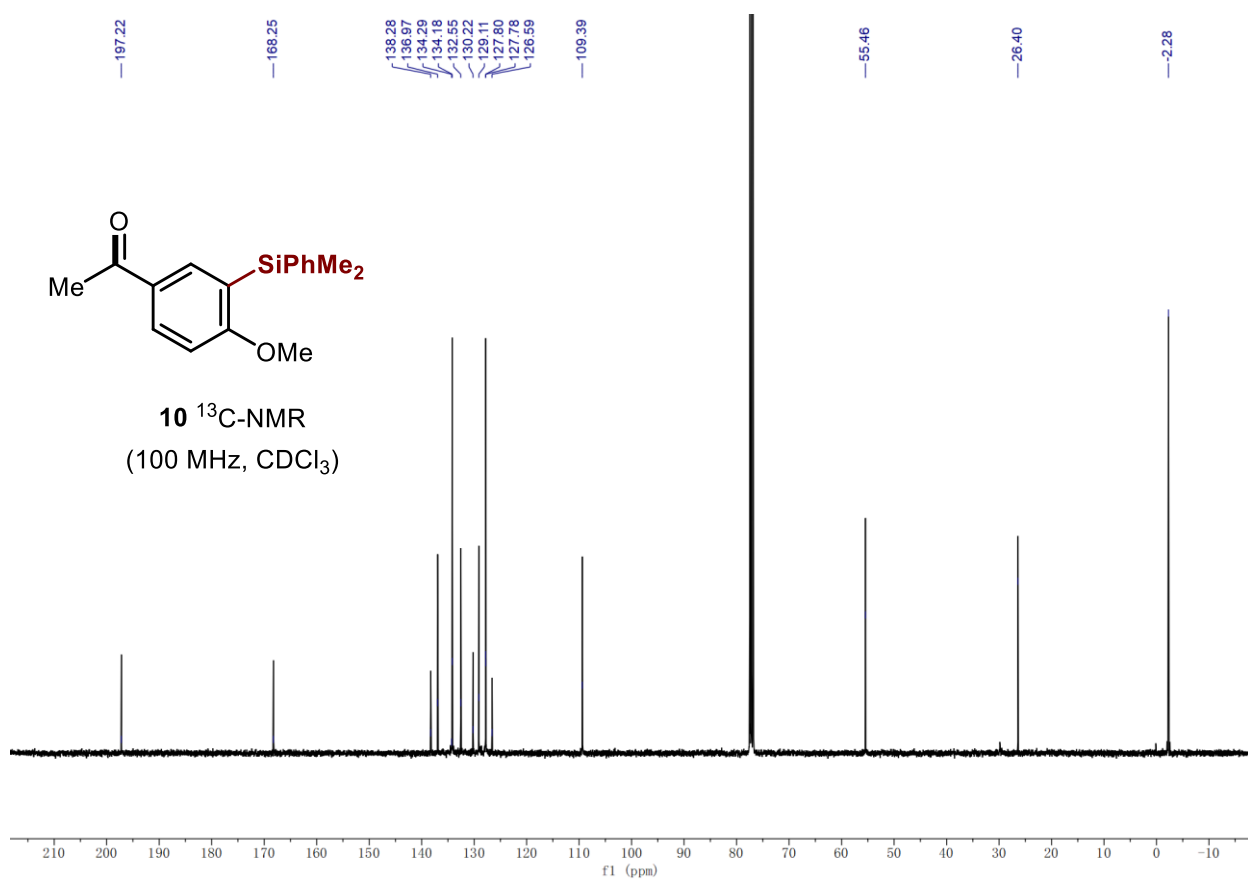
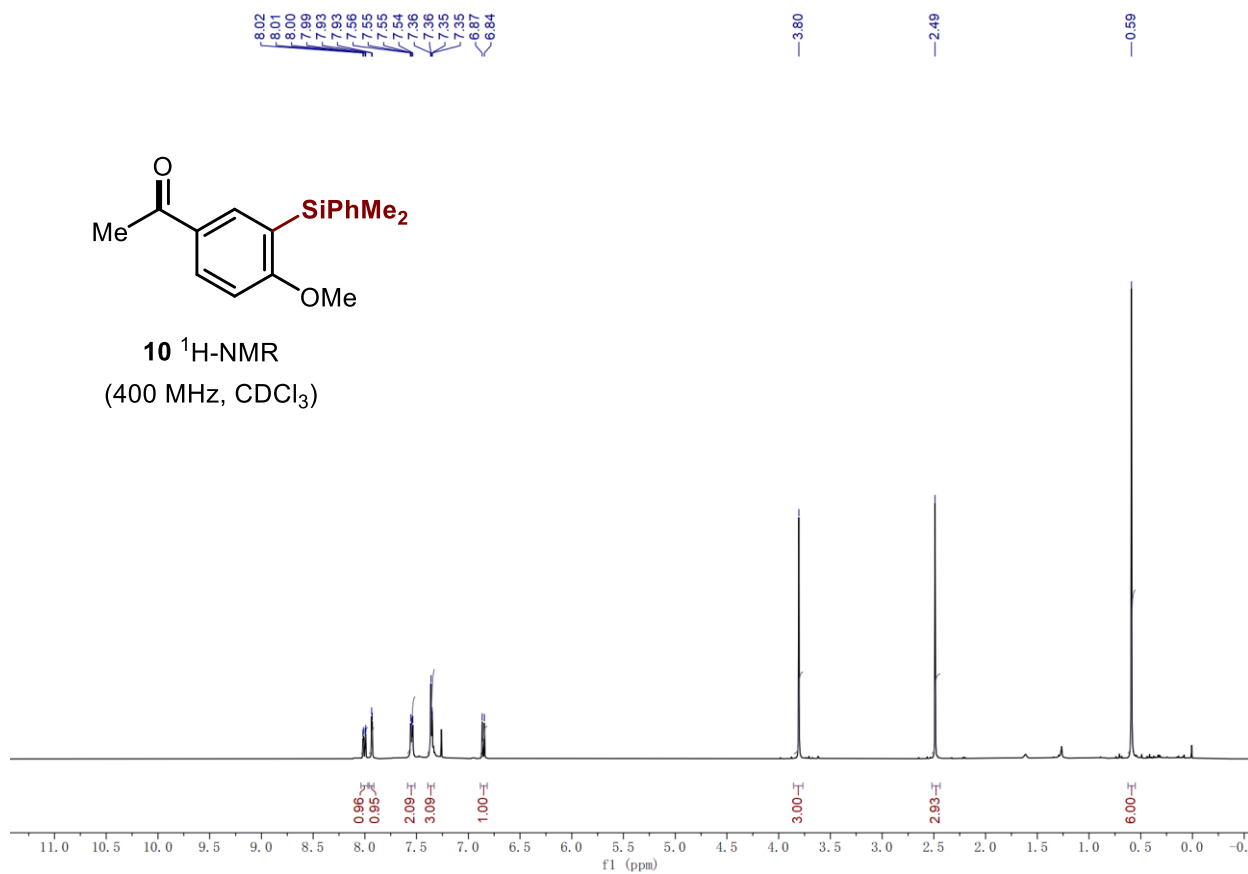


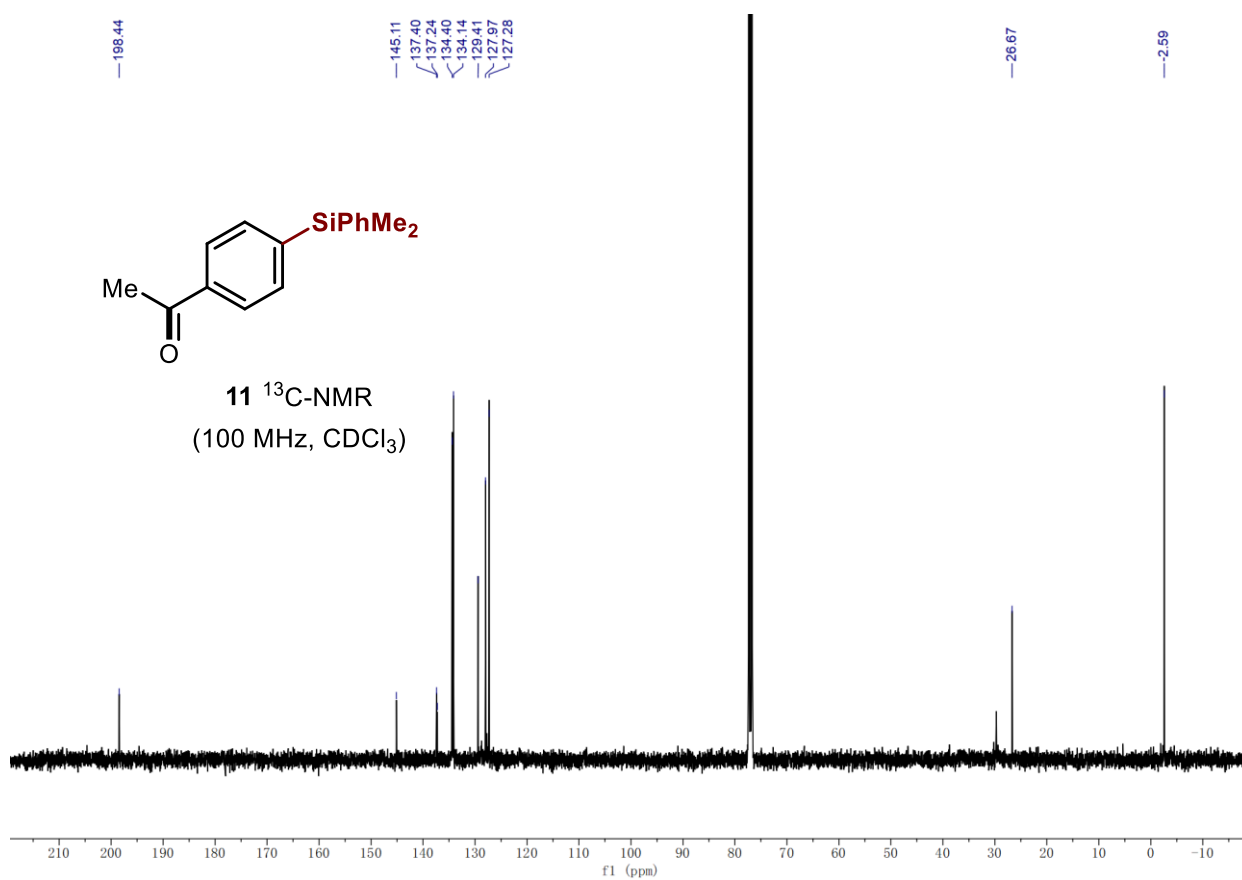
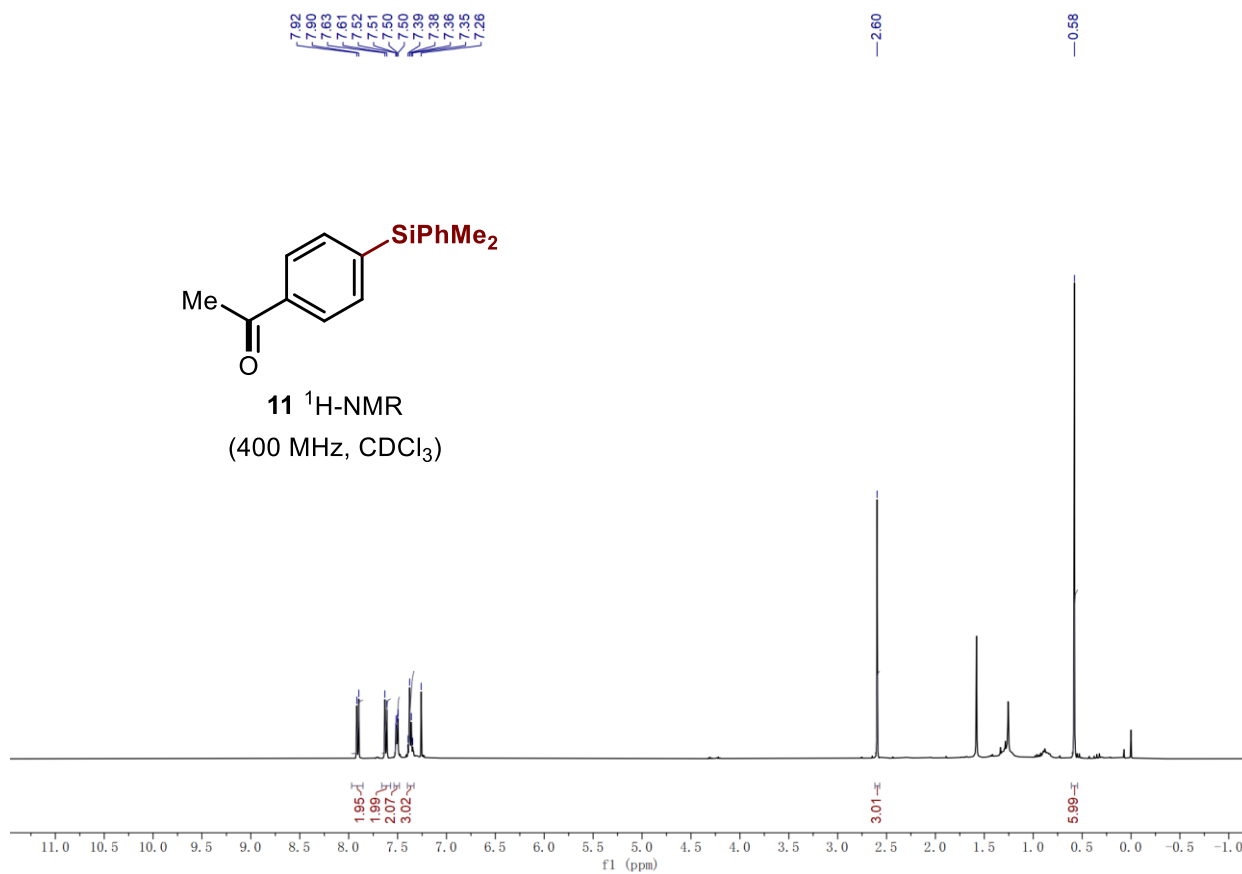


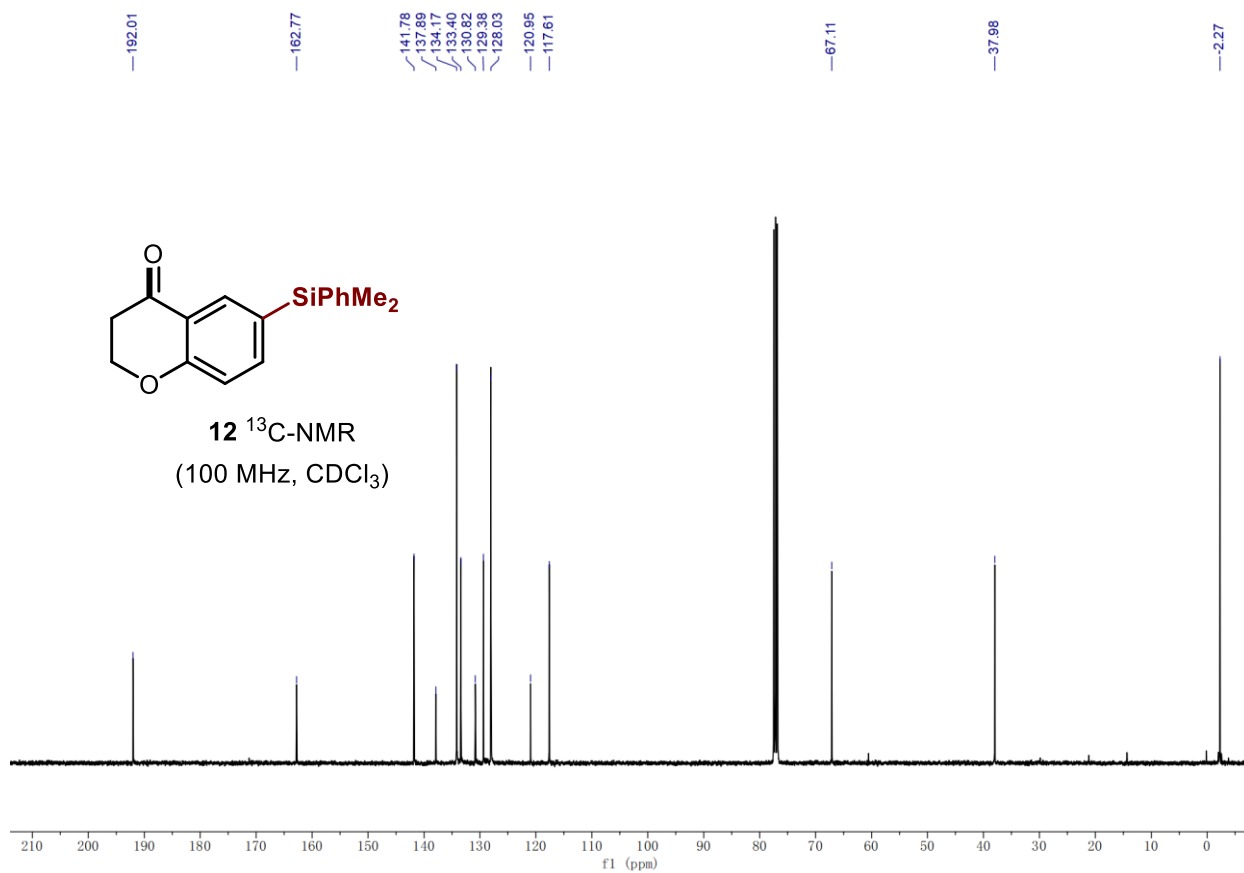
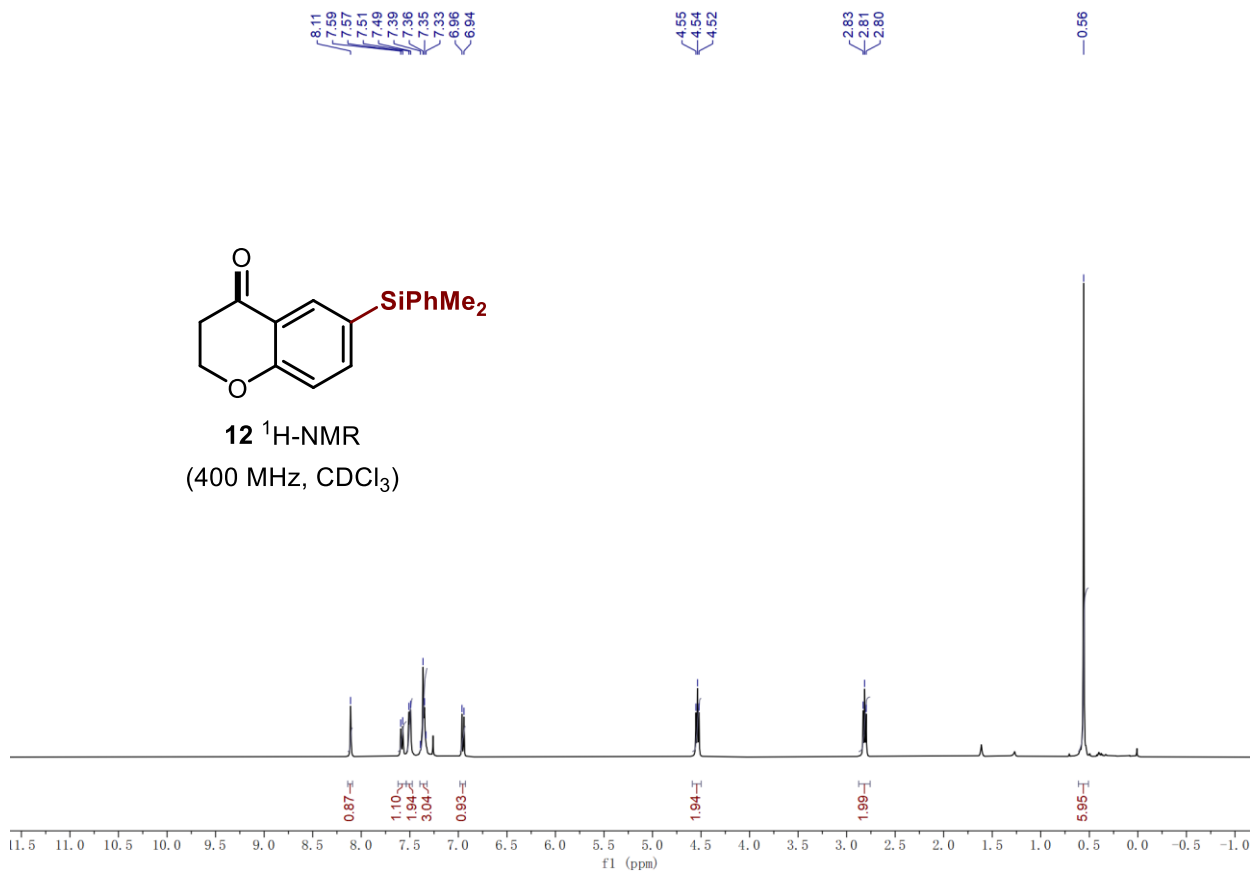


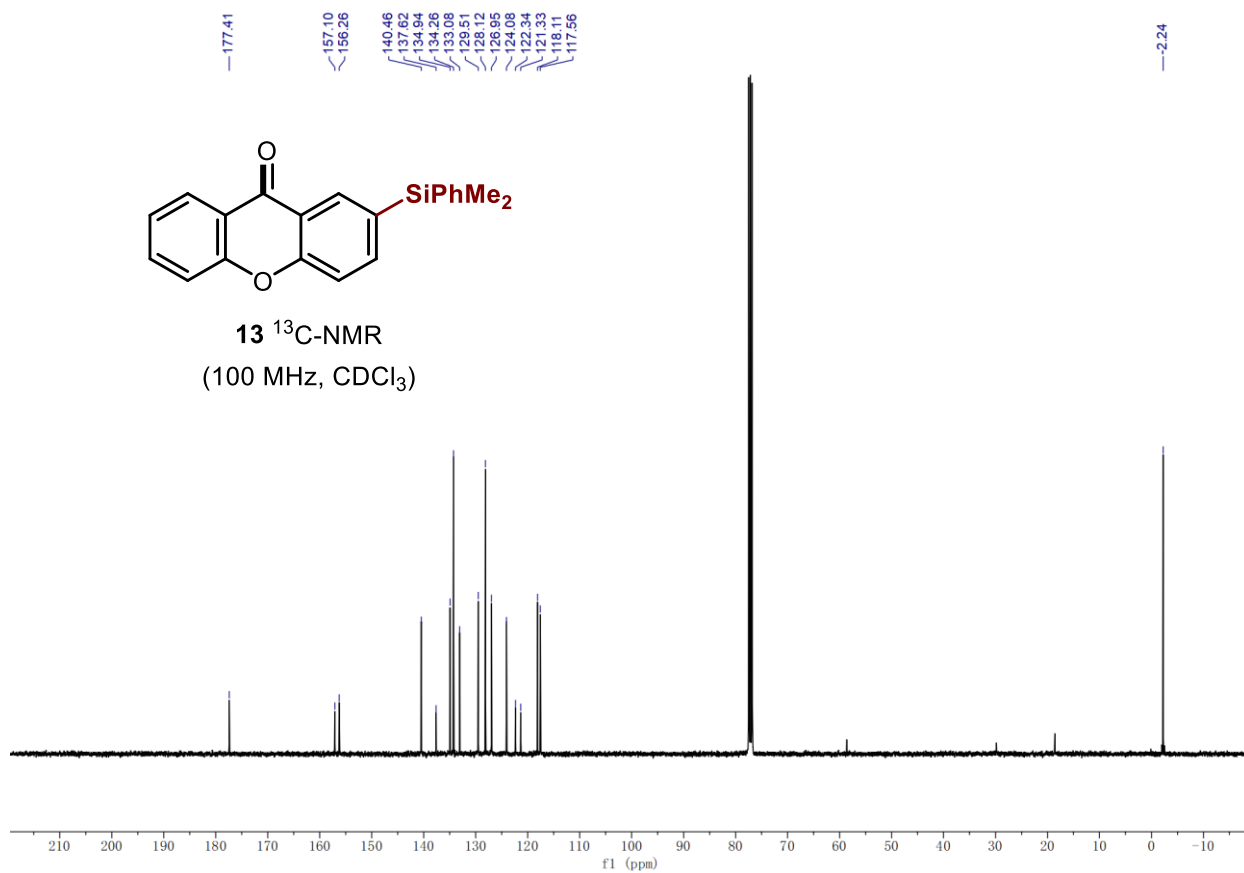
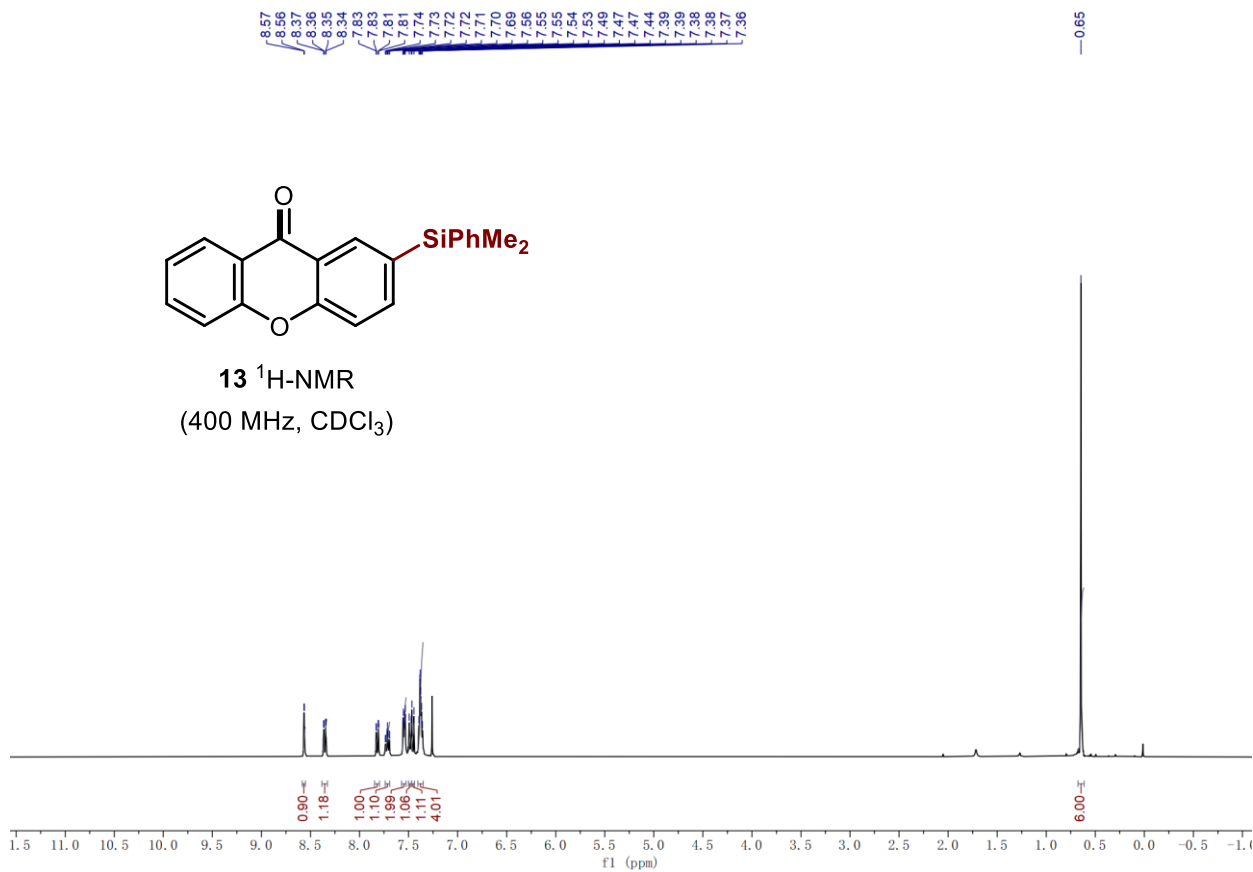


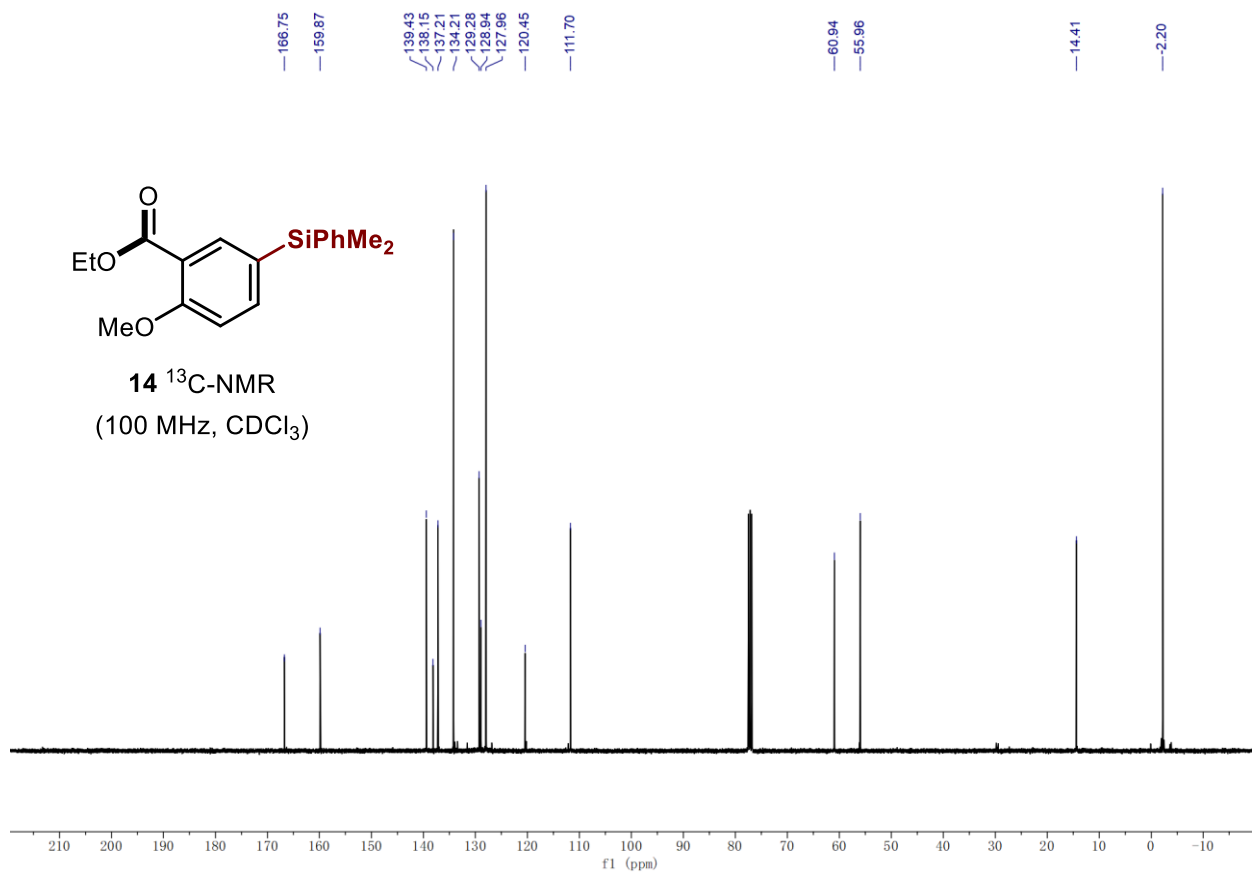
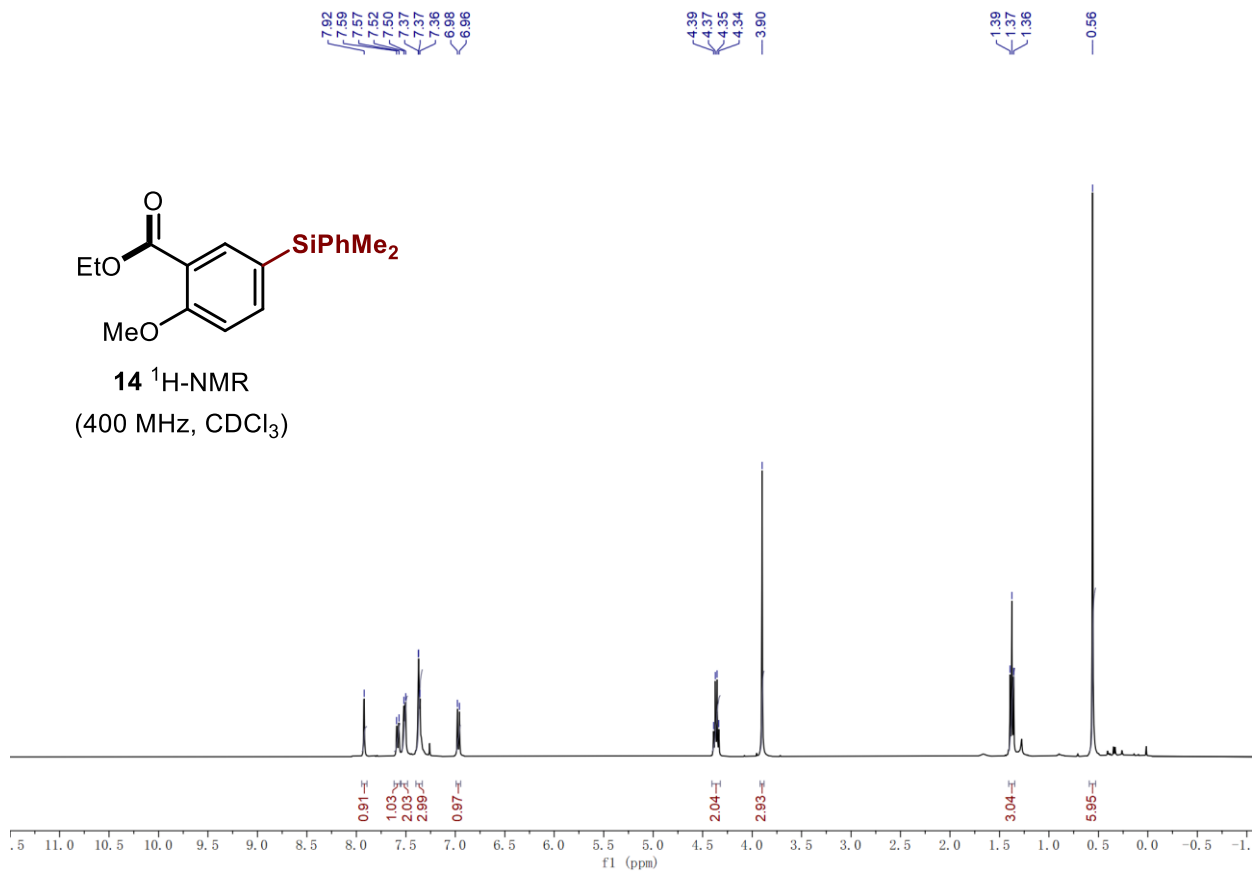


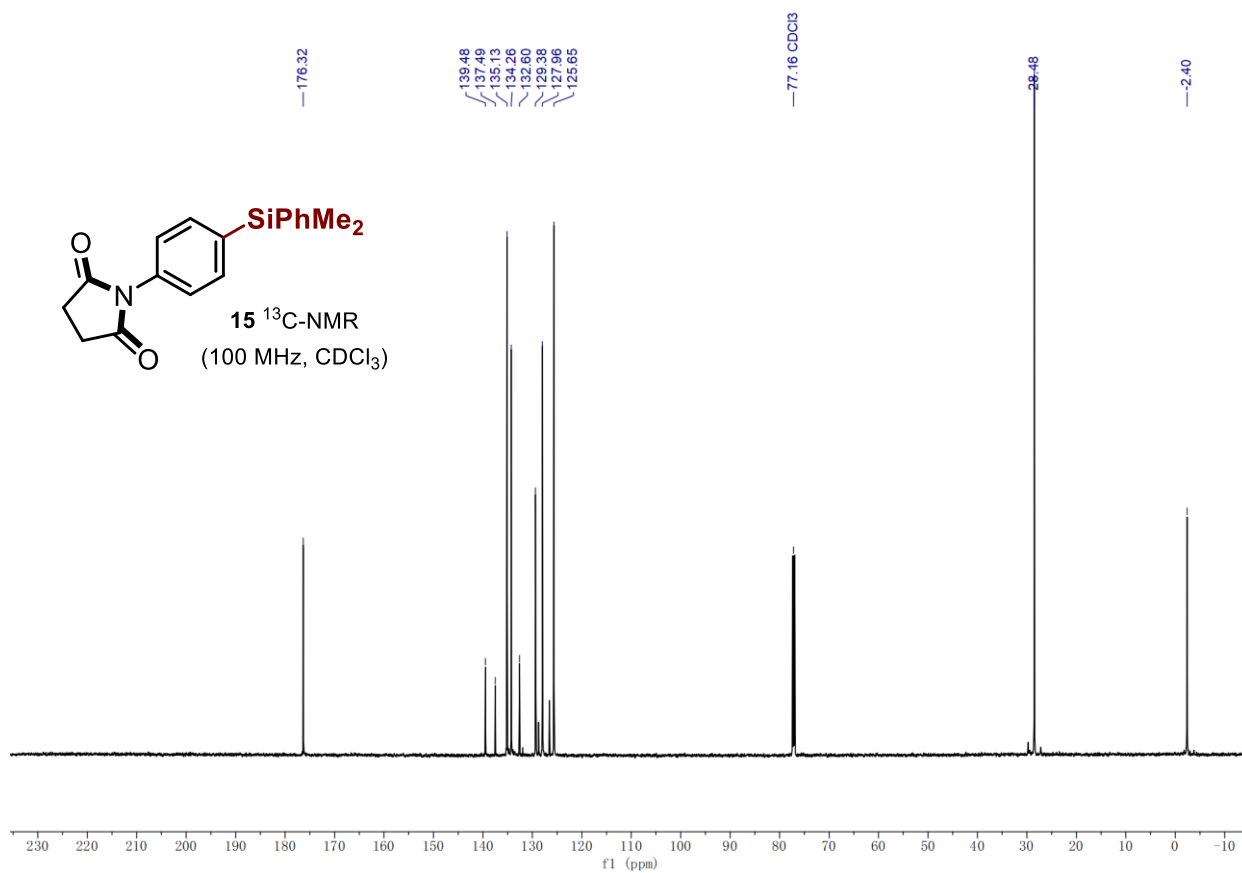
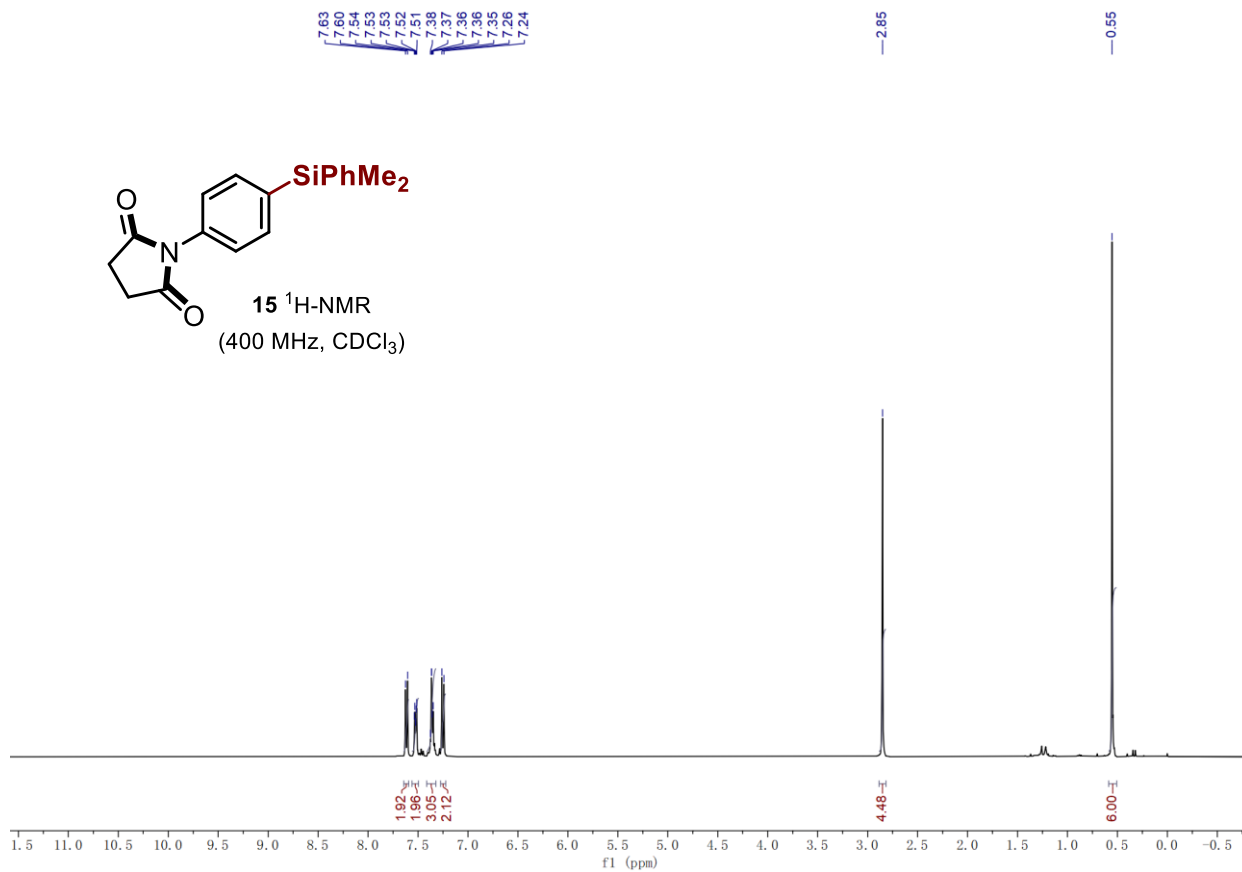




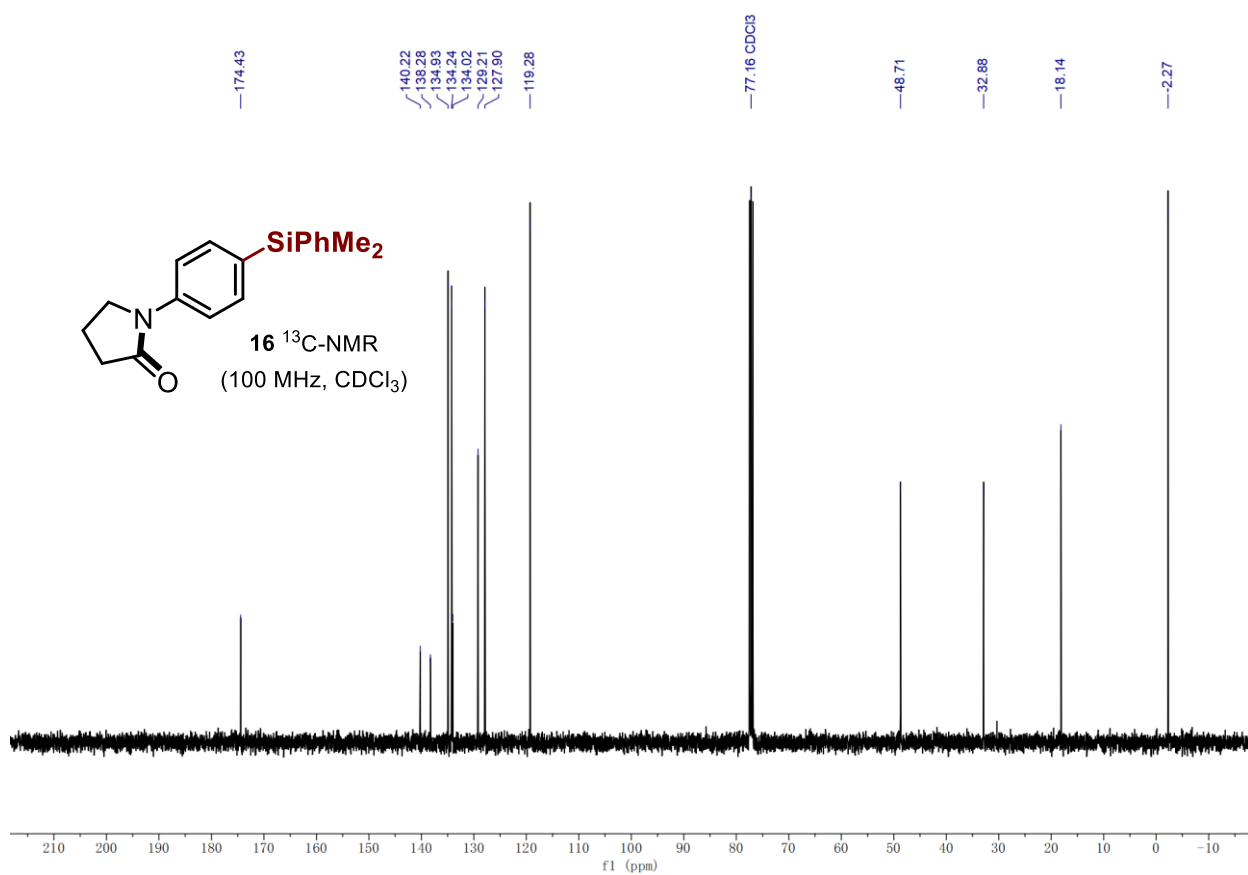
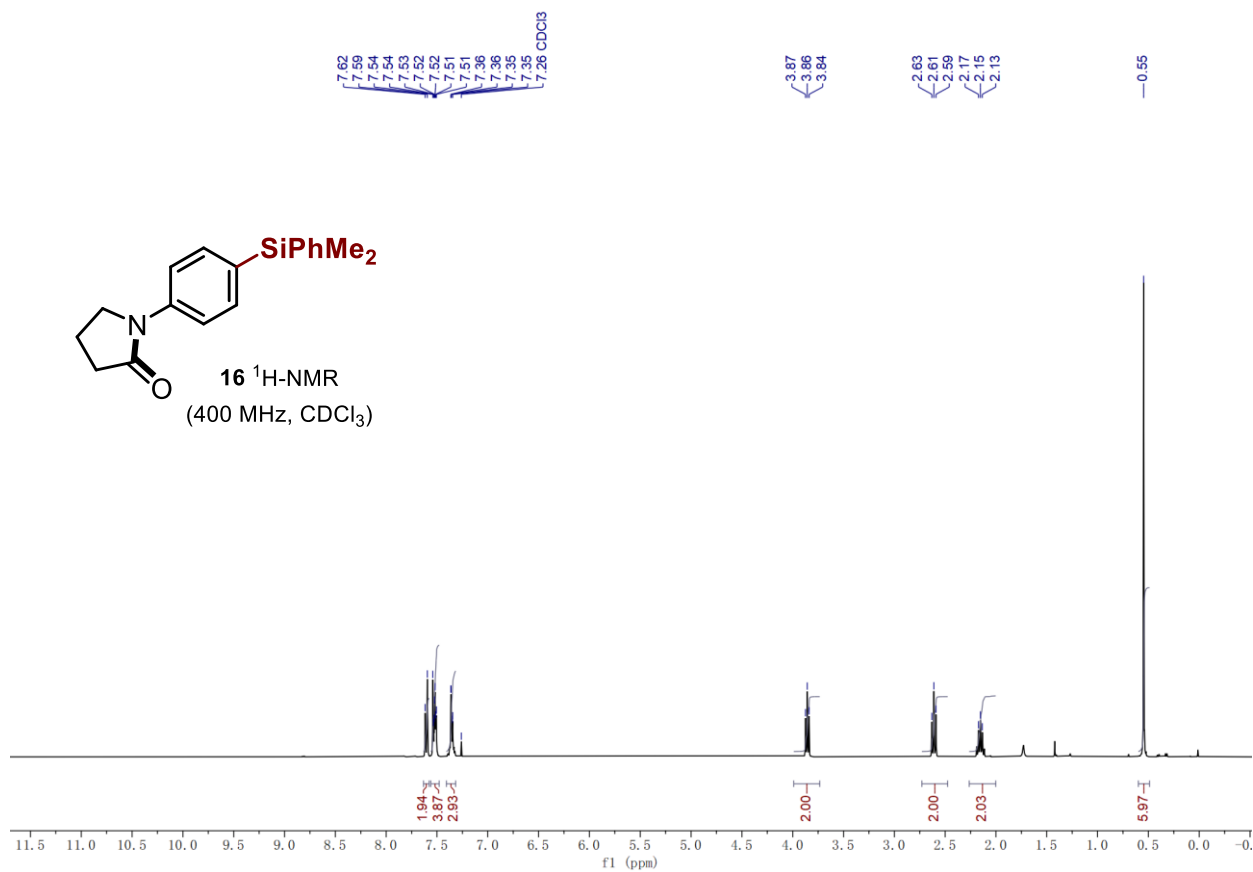


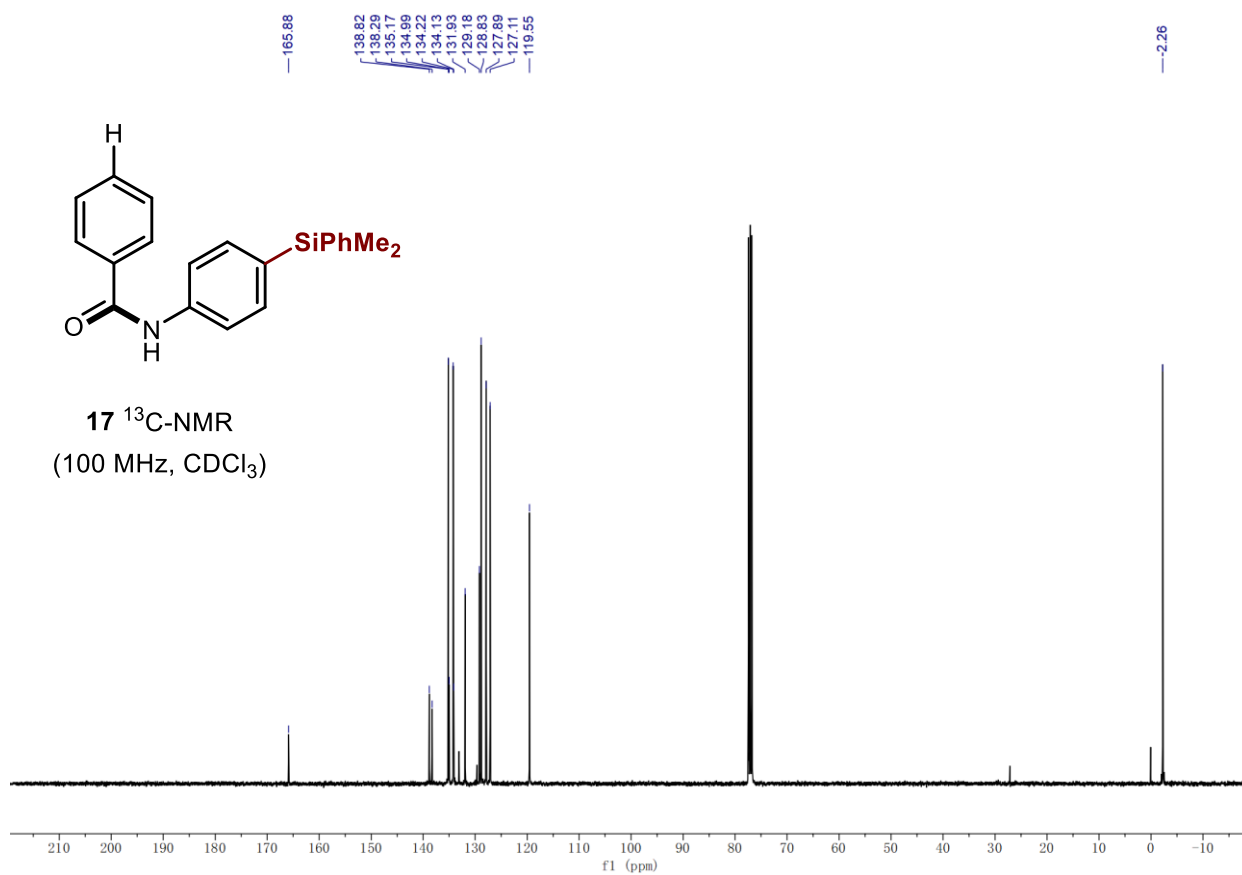
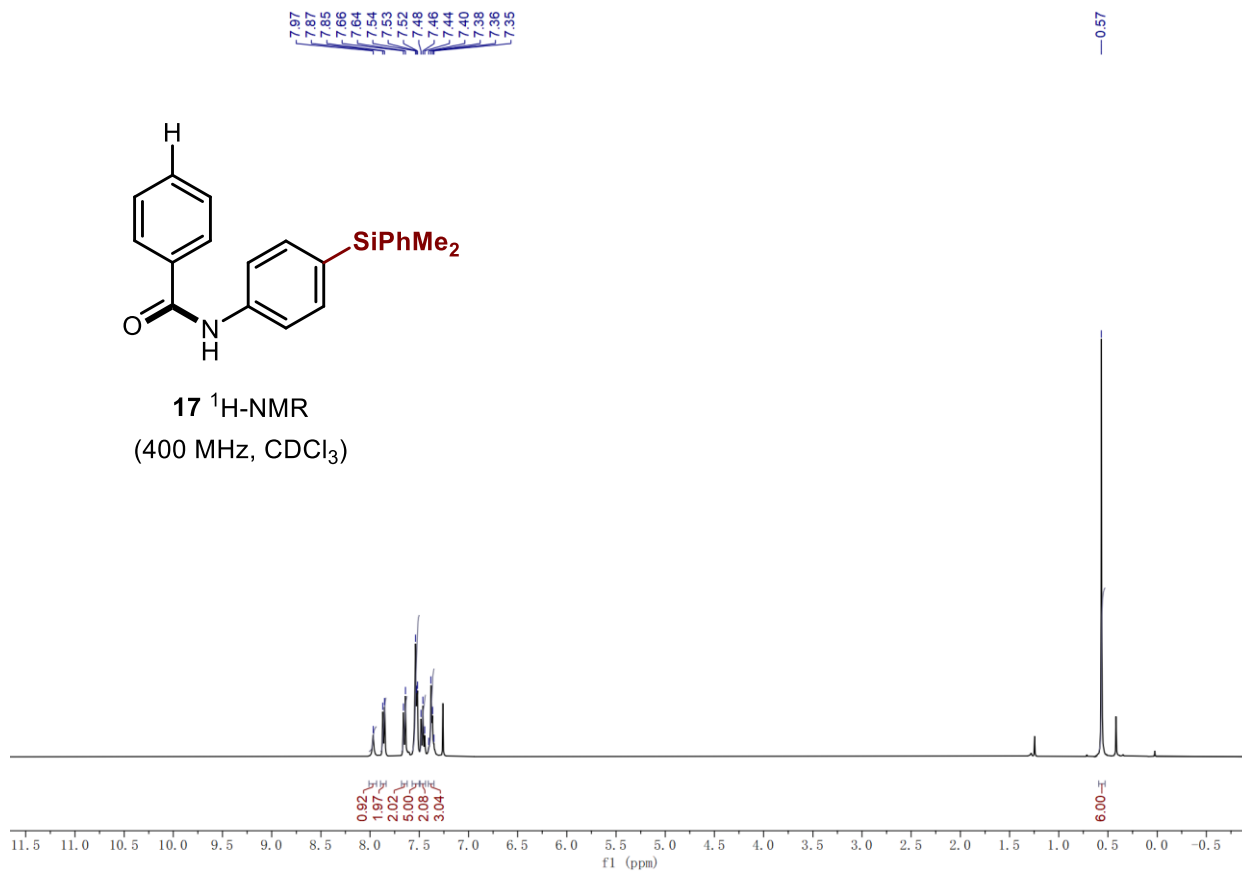


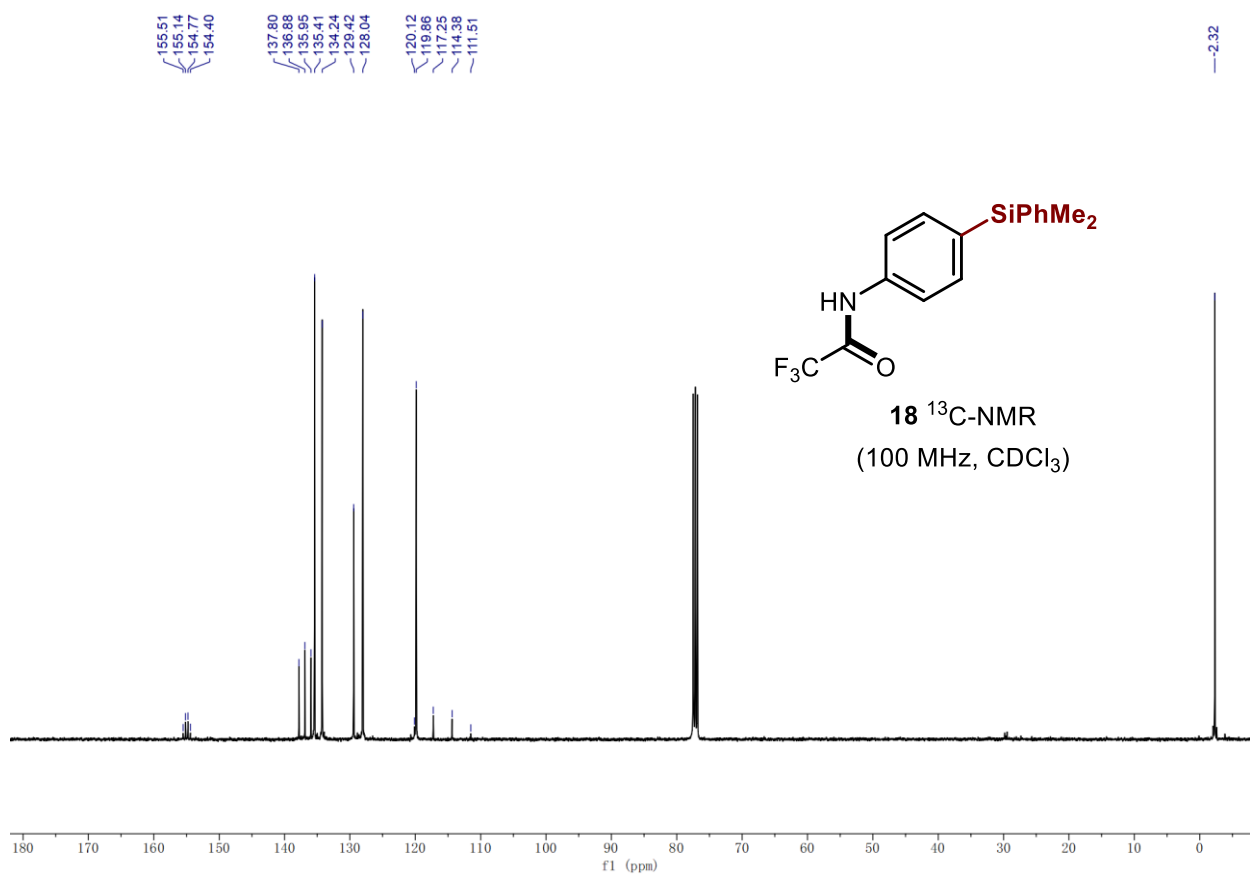
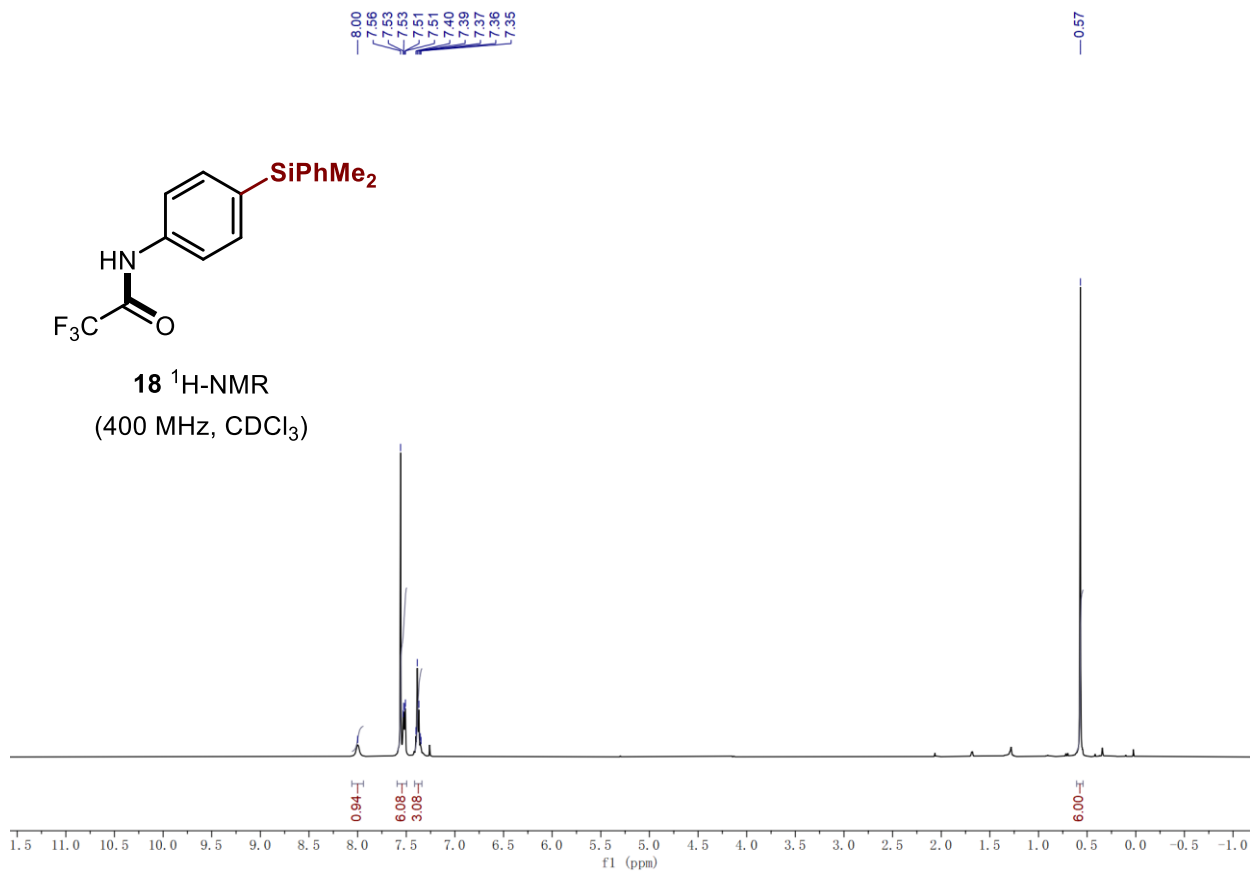


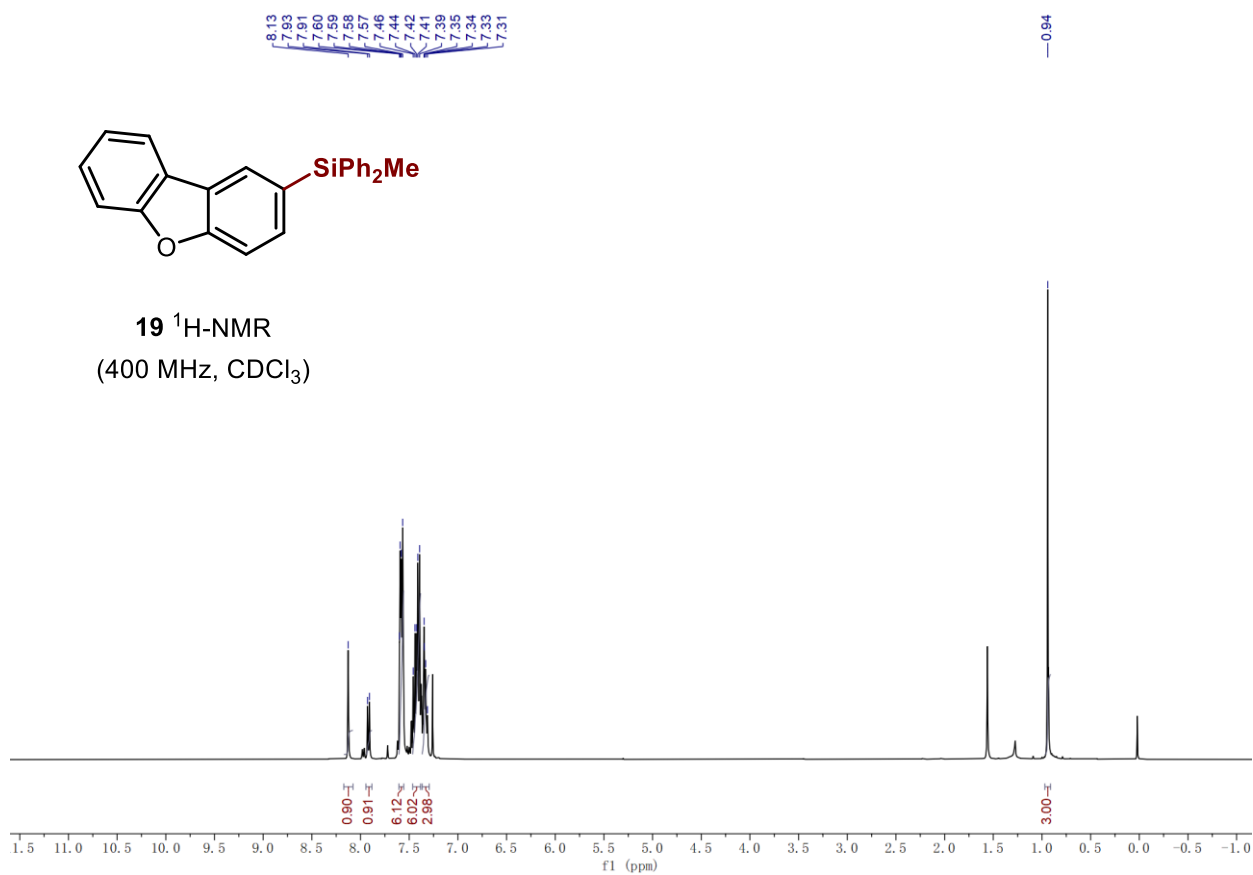
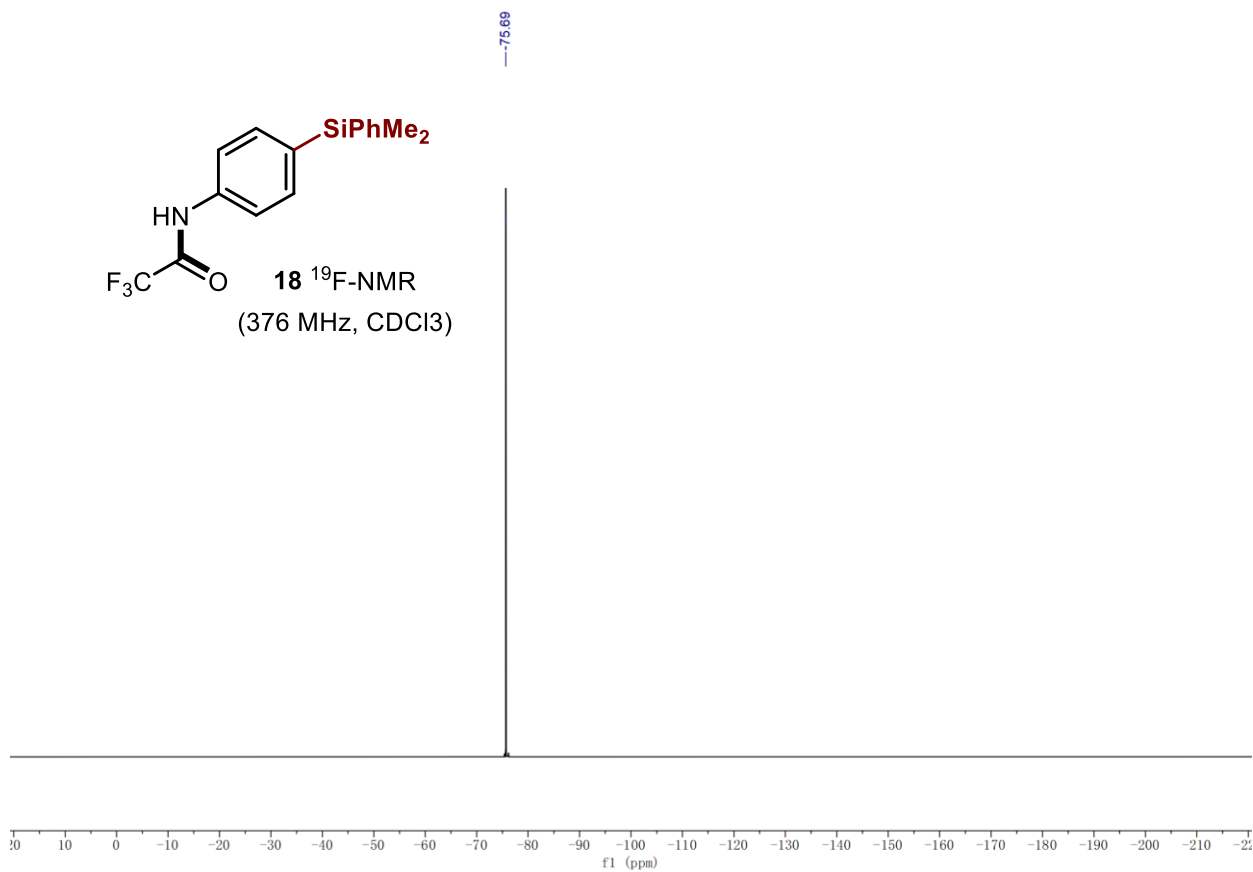


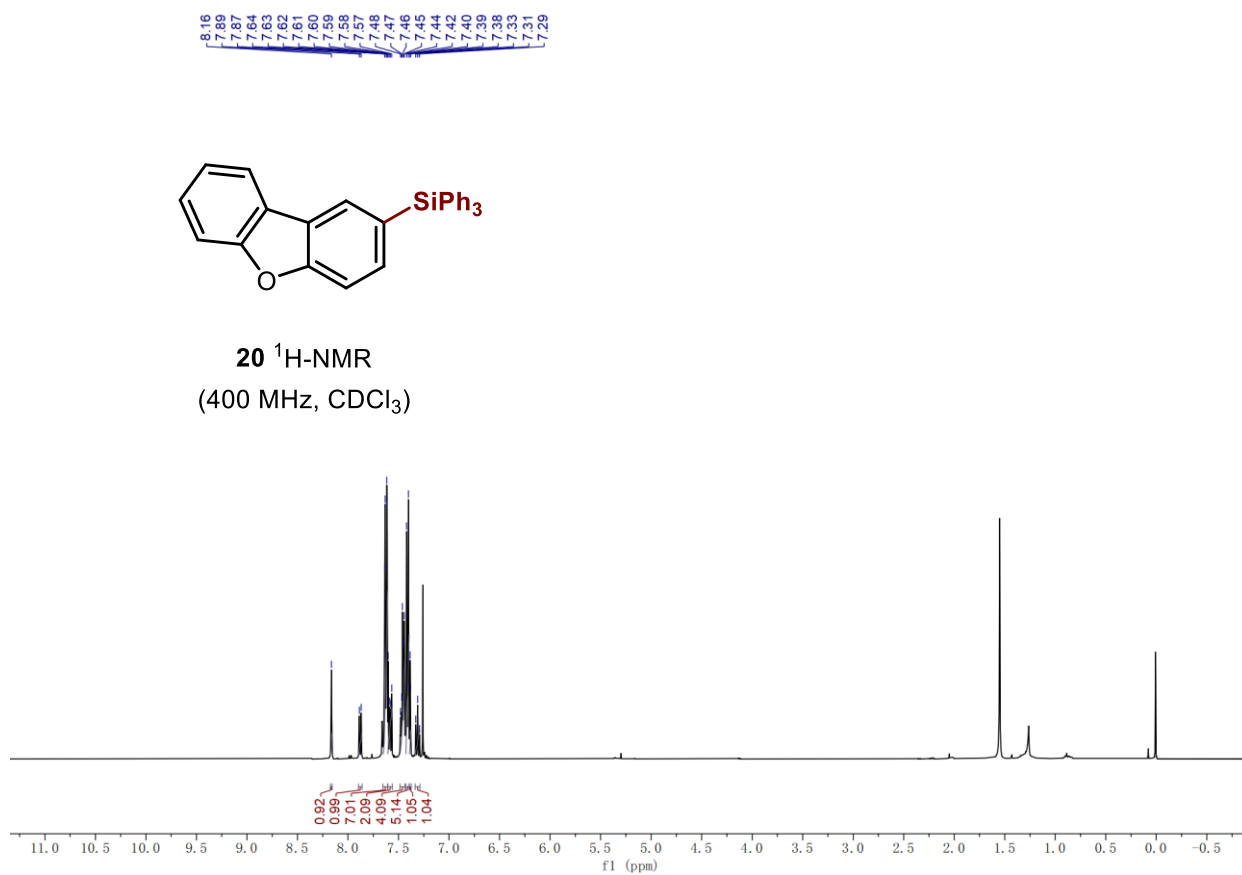
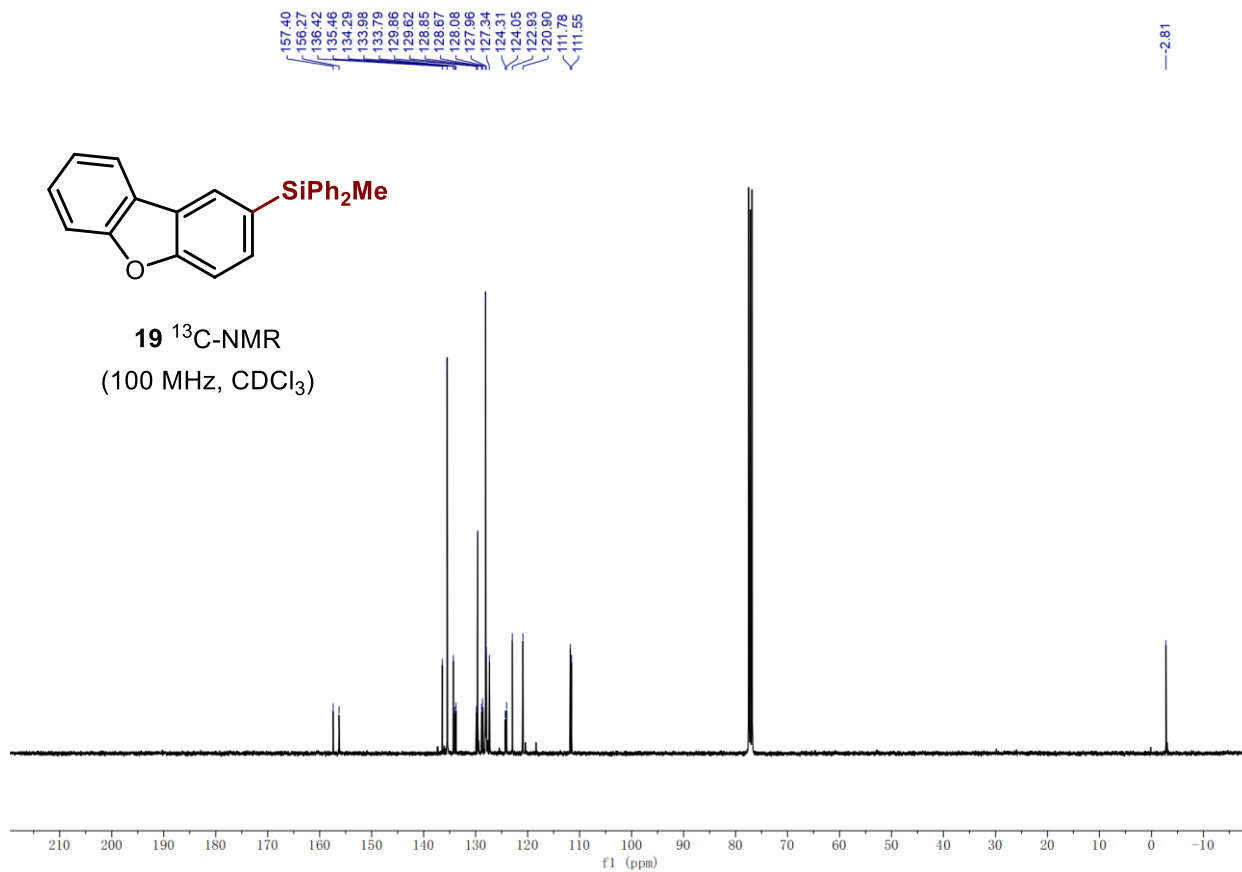


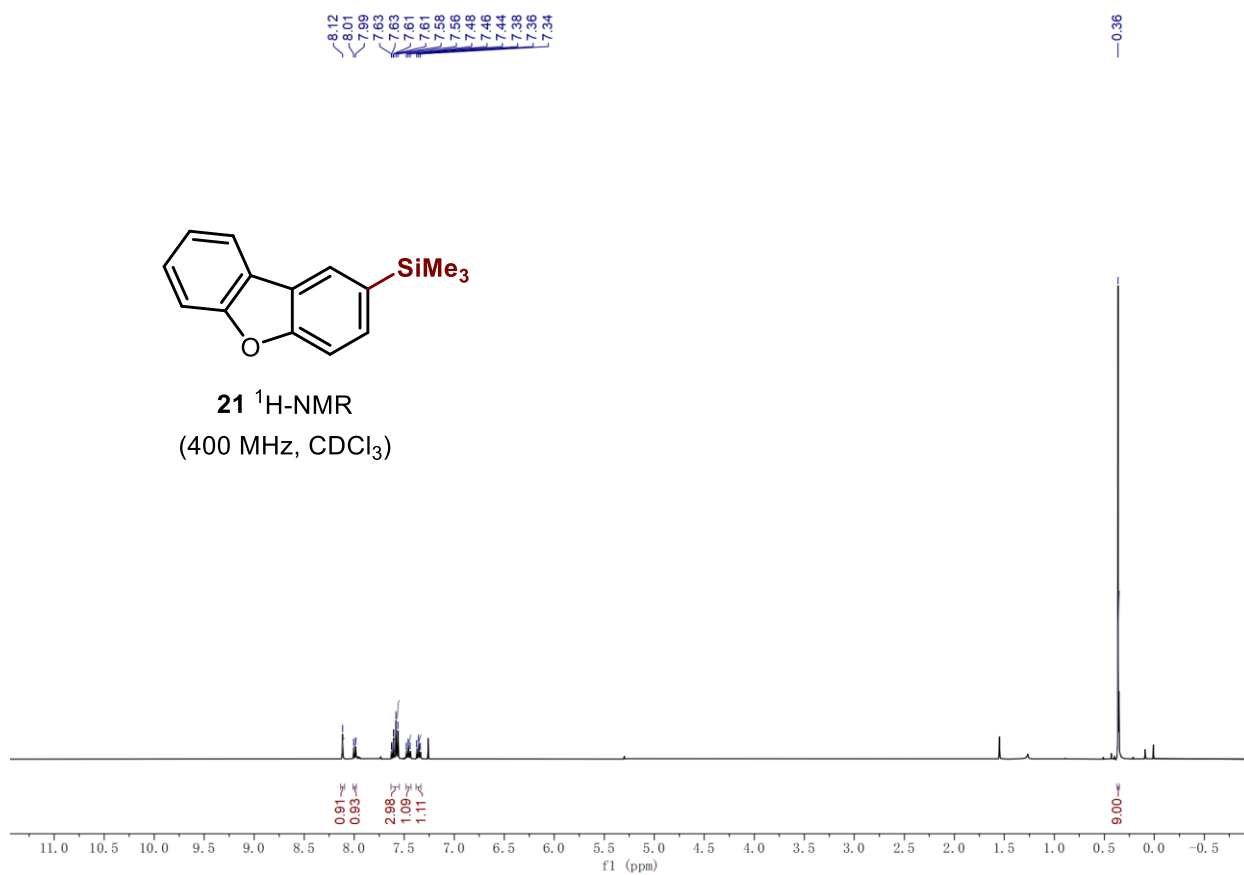
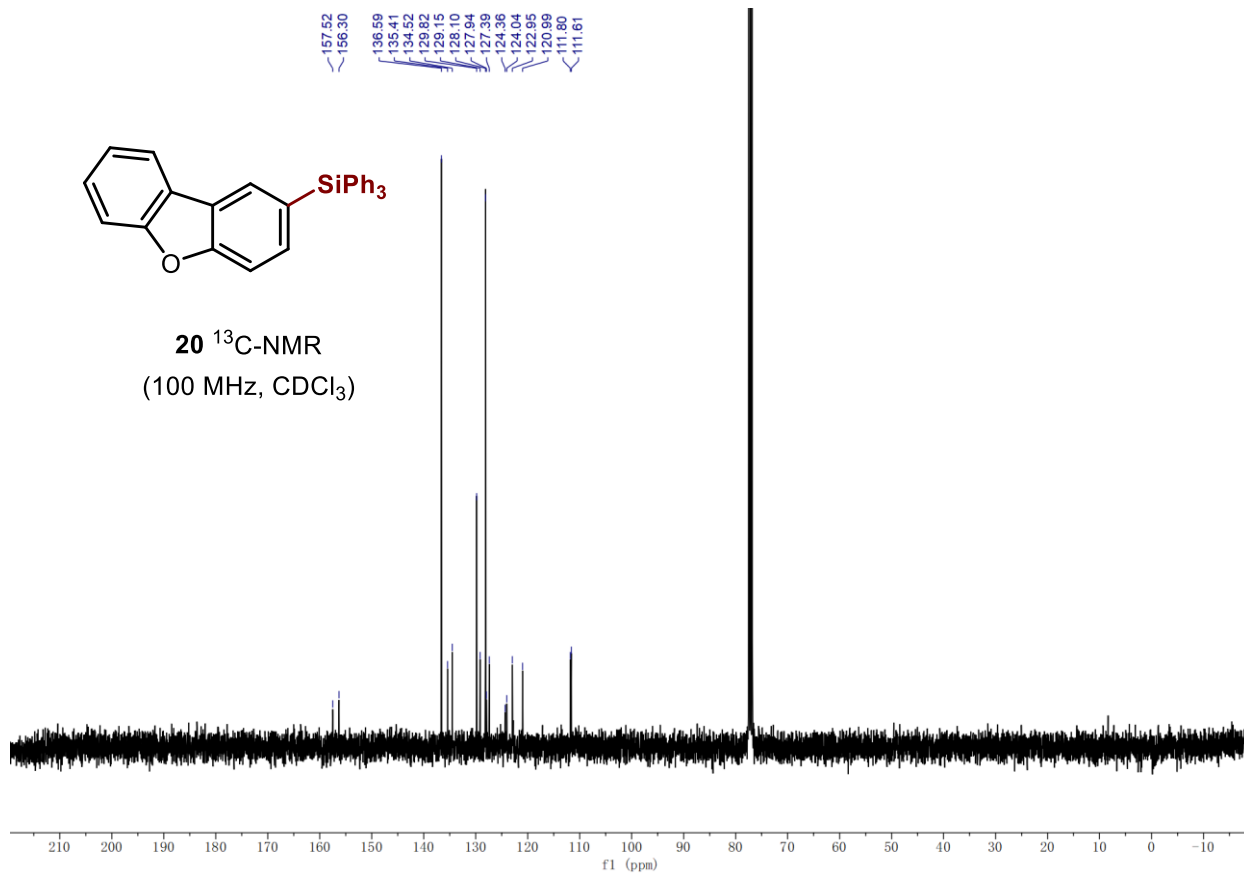


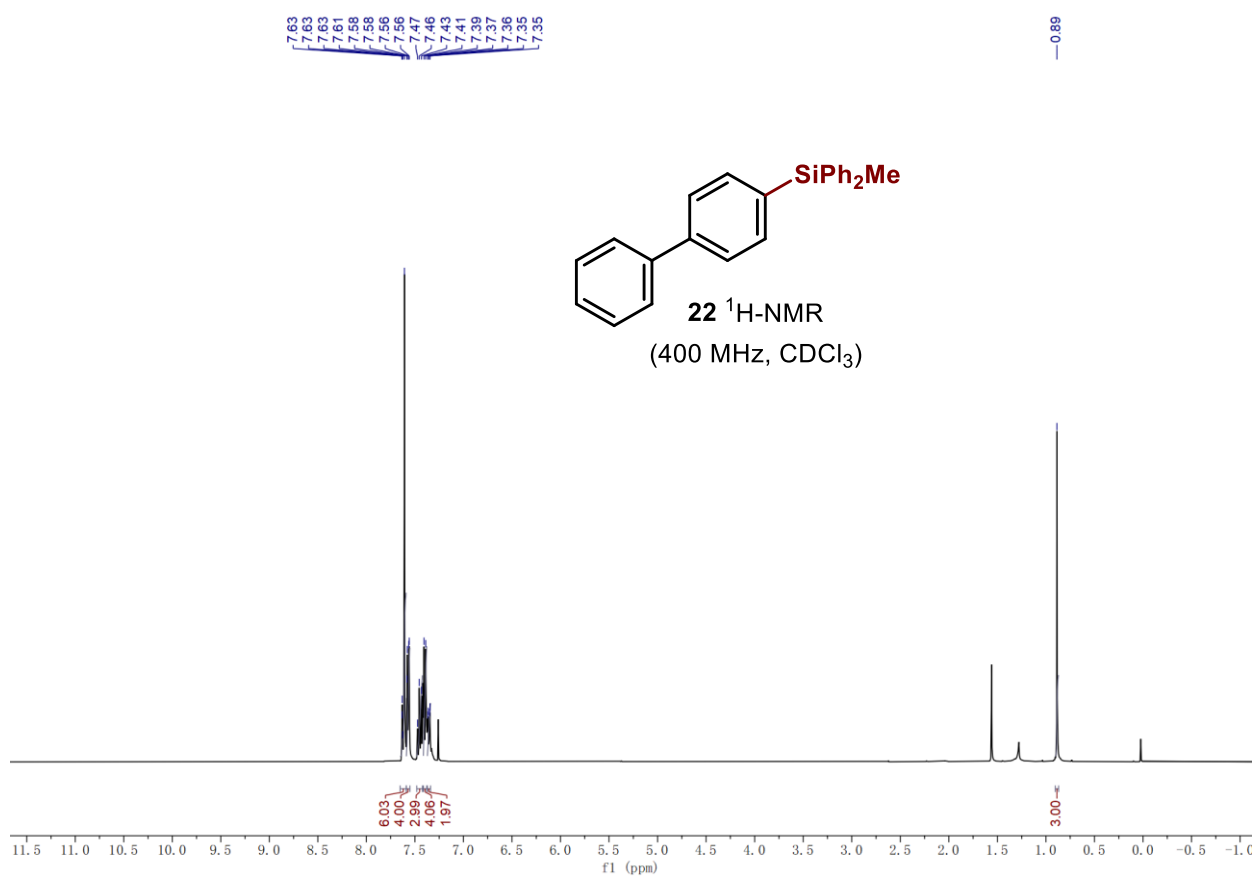
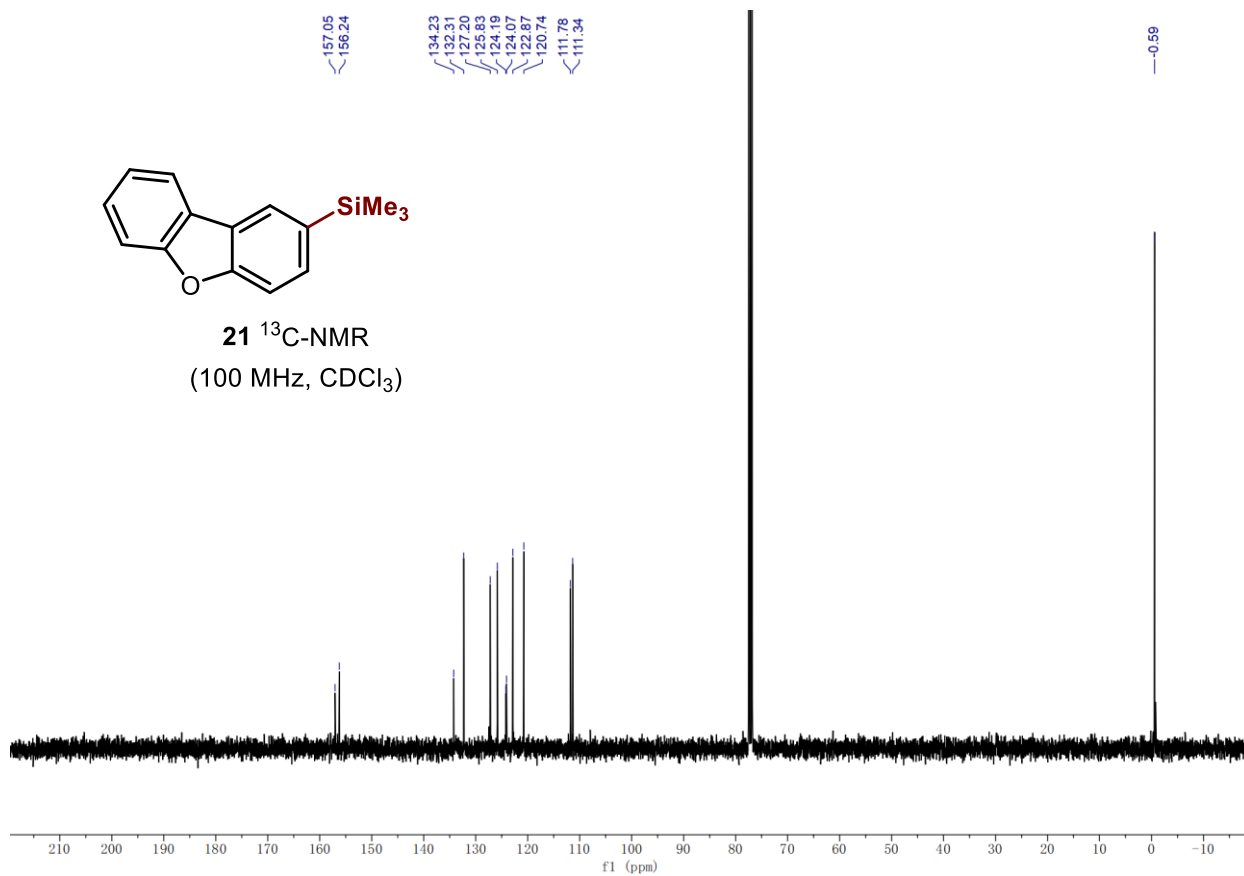


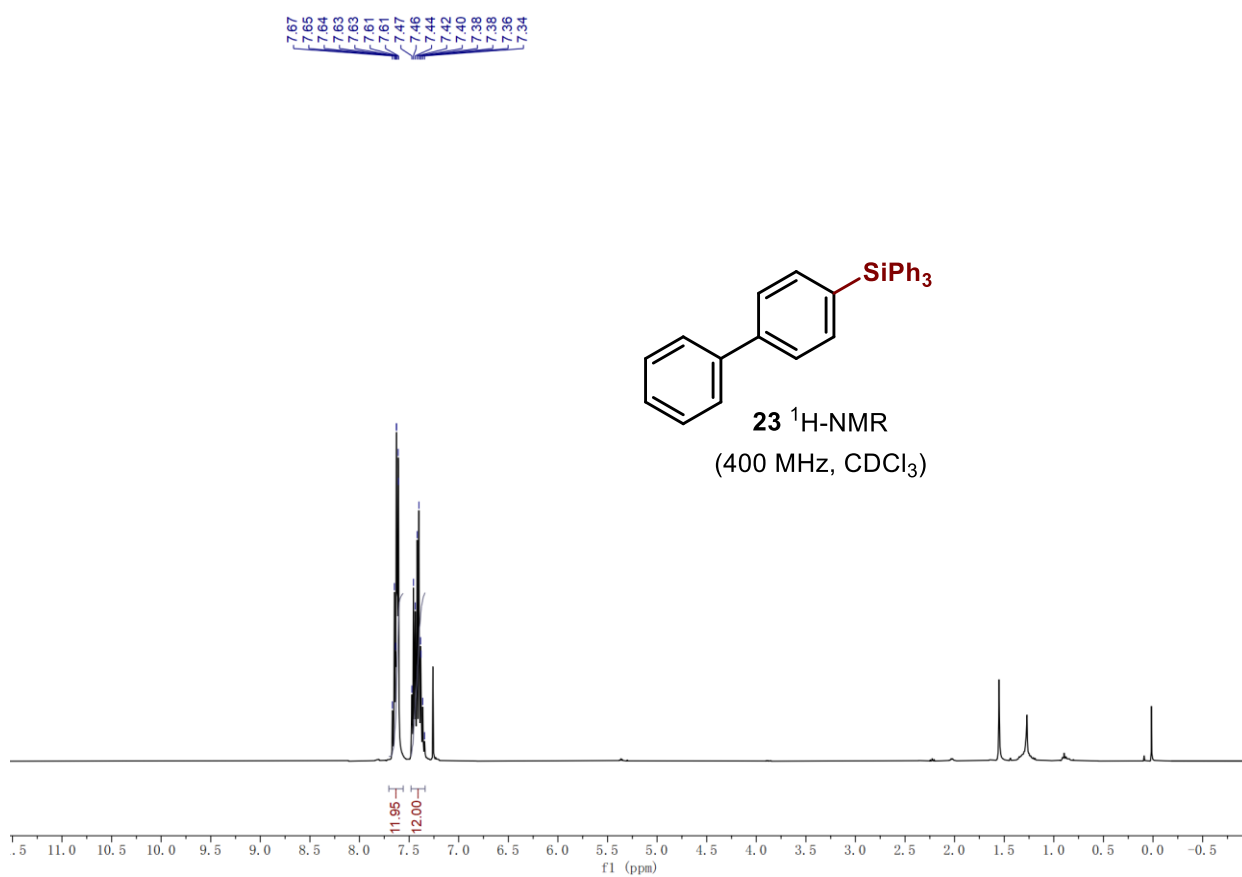
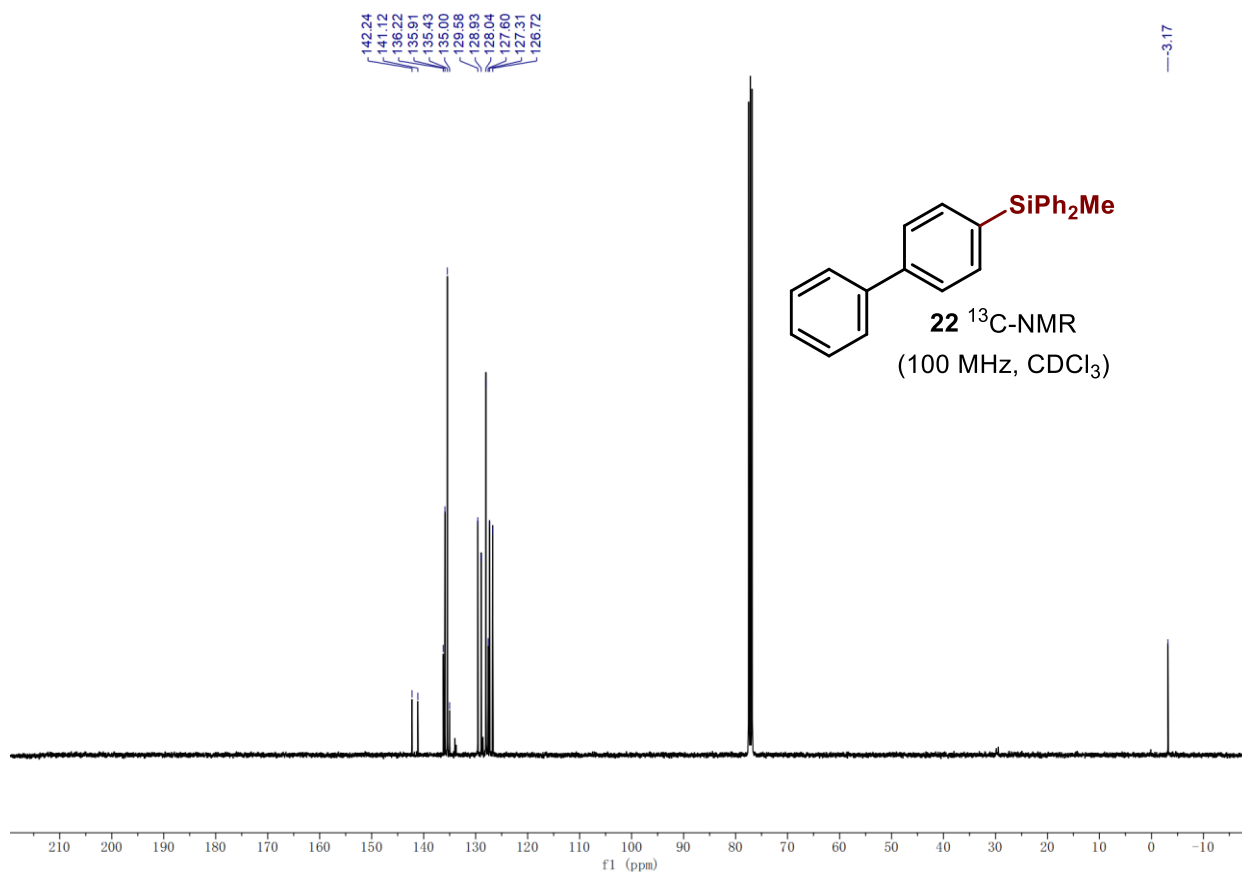




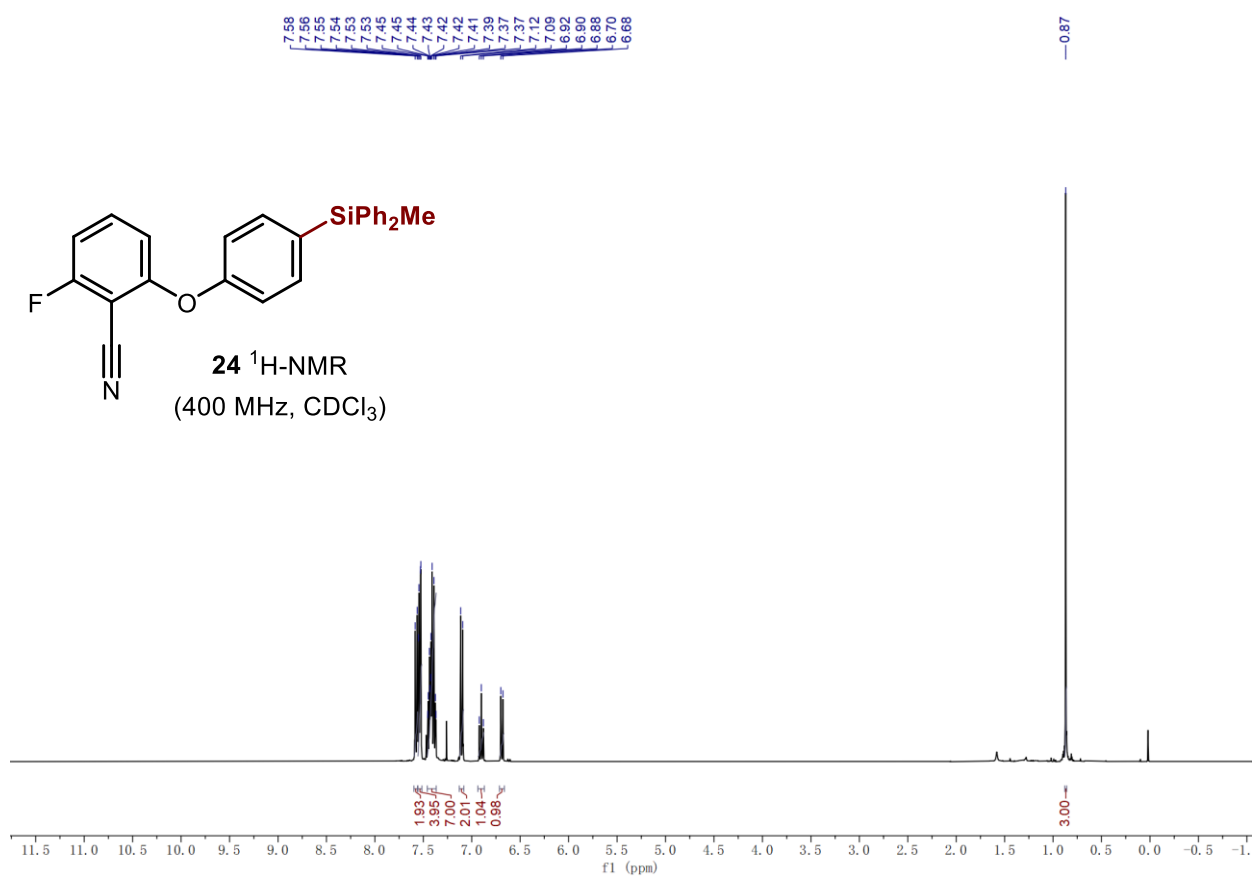
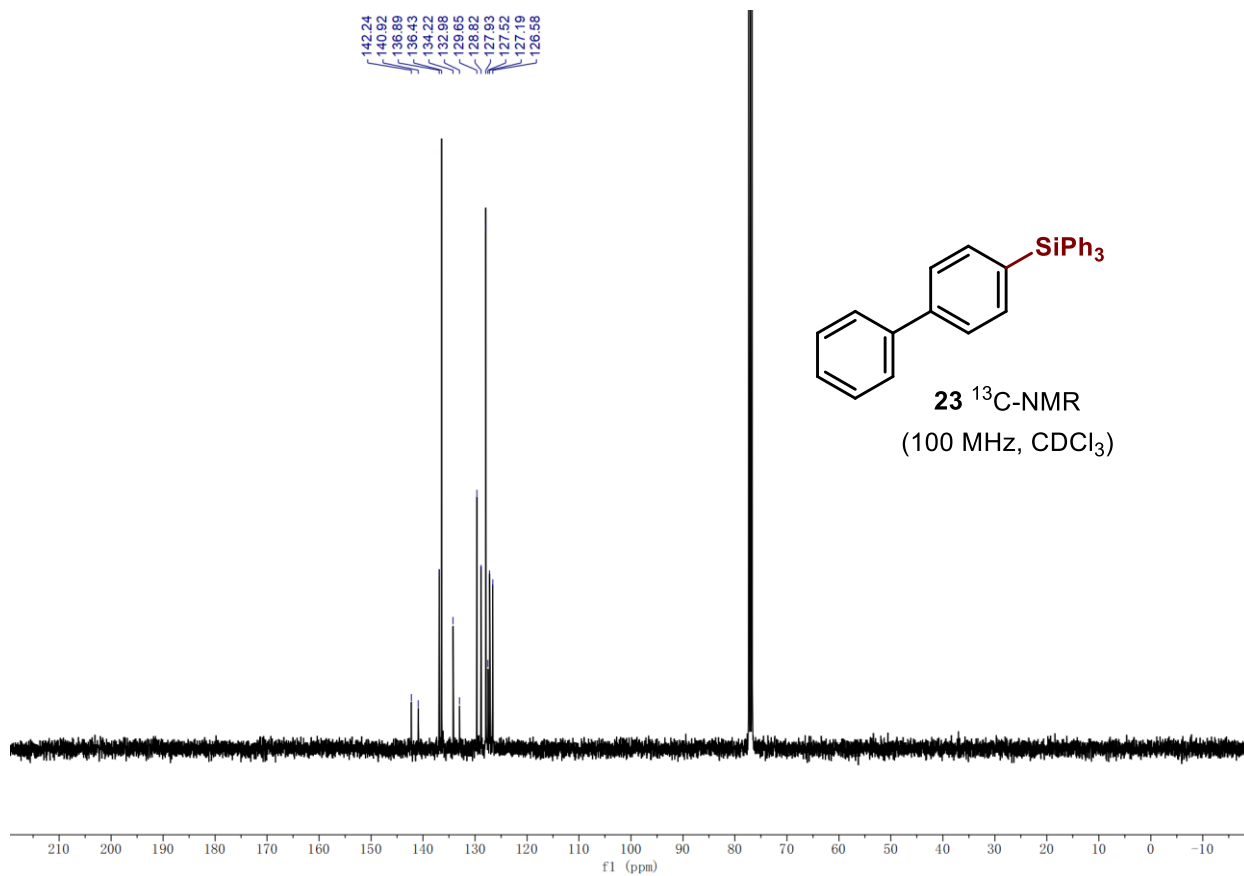


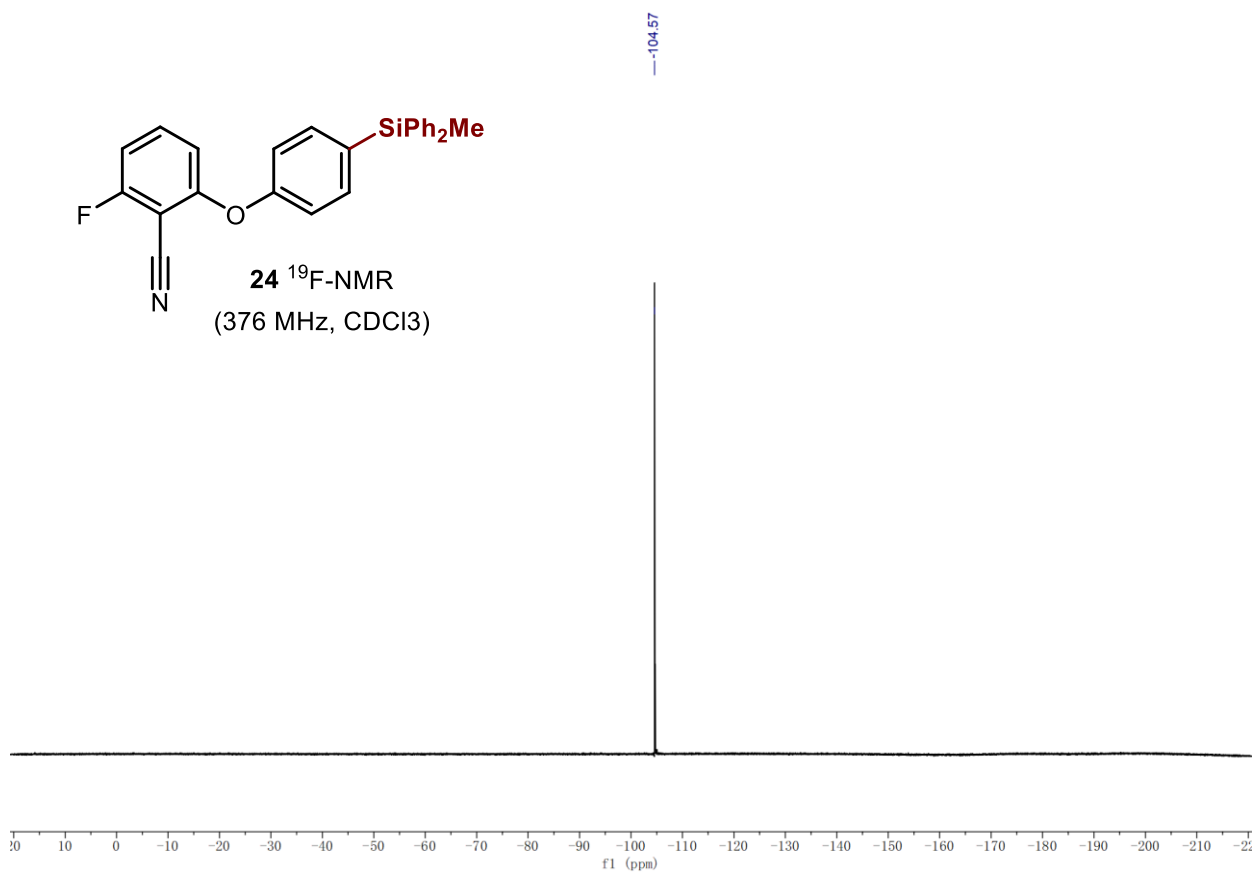
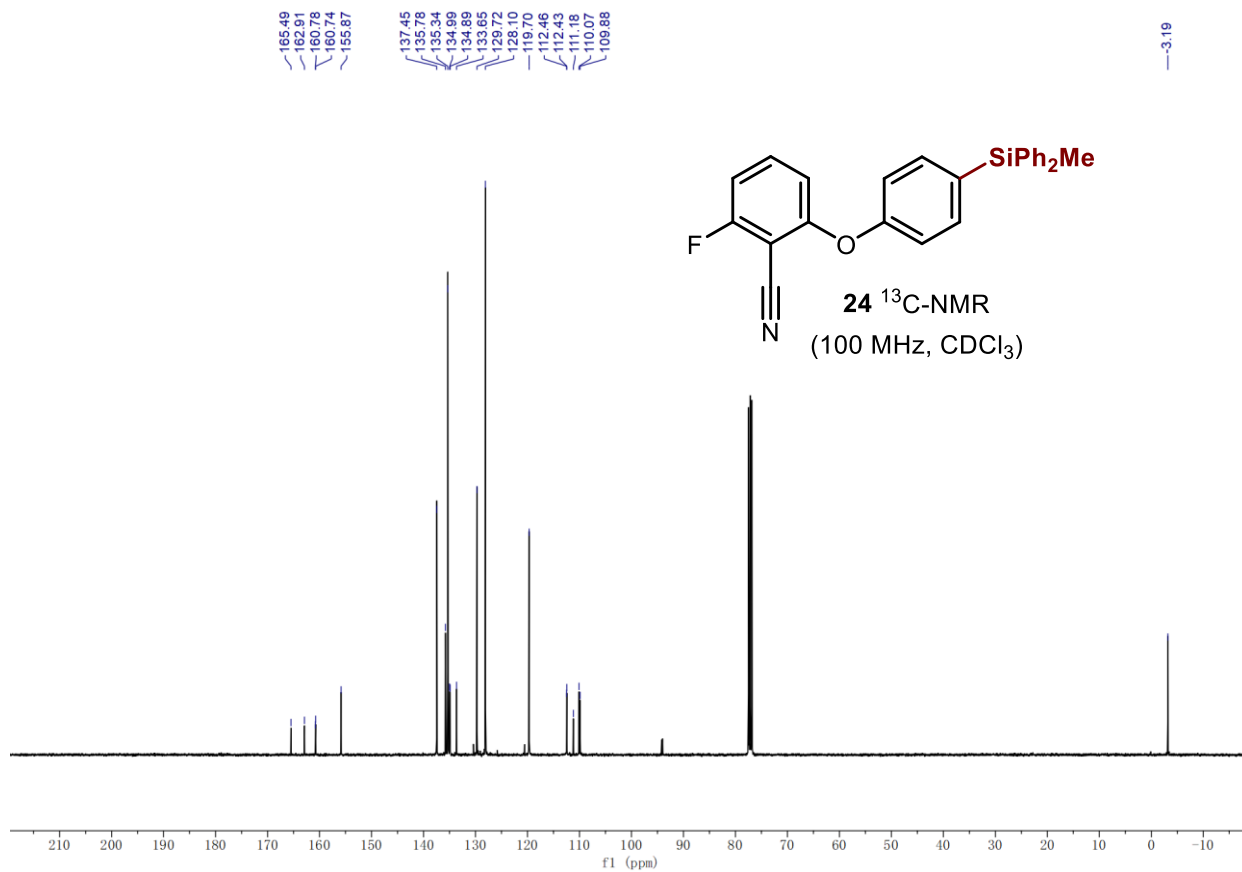




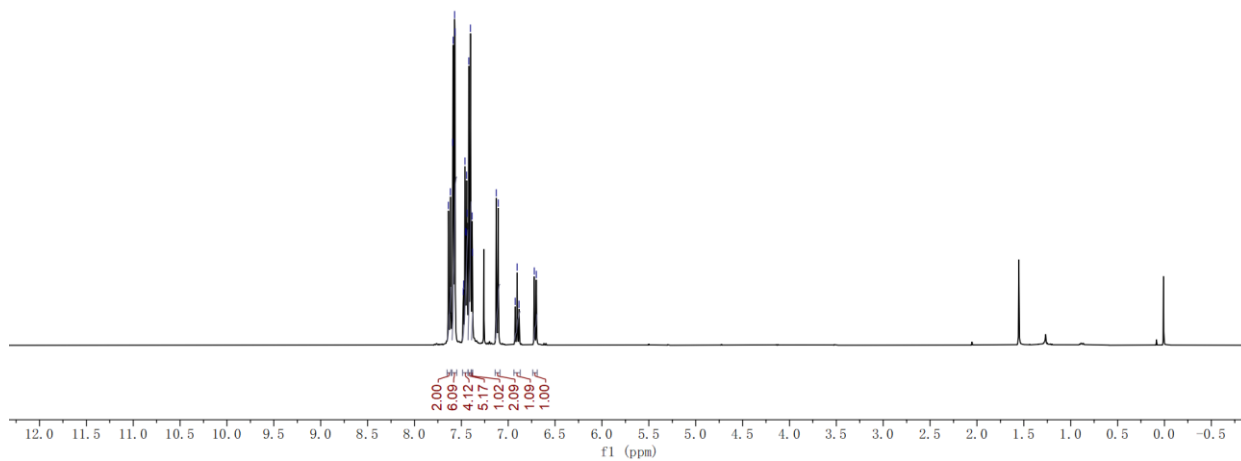
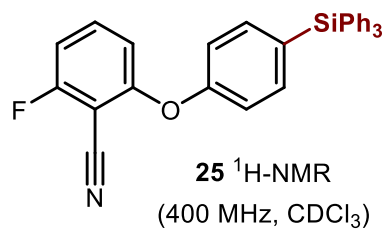








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