

## Supporting Information

### Visible-light-induced transition-metal-free defluorosilylation of $\alpha$ -trifluoromethylalkenes via hydrogen atom transfer of silanes

Wengang Xu,<sup>\*a</sup> Congjian Xia,<sup>b</sup> Qi Shao,<sup>b</sup> Qiao Zhang,<sup>b</sup> Mingrui Liu,<sup>a</sup> Hongwei Zhang,<sup>b</sup> and Mingbo Wu<sup>\*a, b</sup>

#### Affiliations:

<sup>a</sup> Dr. W. Xu, Dr. M. Wu, College of New Energy, China University of Petroleum (China East), 266580, Qingdao, P. R. China

E-mail: [chmxw@upc.edu.cn](mailto:chmxw@upc.edu.cn); [wumb@upc.edu.cn](mailto:wumb@upc.edu.cn).

<sup>b</sup> Q. Zhang, Q. Shao, C. Xia, Dr. M. Wu, College of Chemical Engineering, State Key Laboratory of Heavy Oil Processing, China University of Petroleum (China East), 266580, Qingdao, P. R. China.

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## 1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR,  $^{19}\text{F}$  NMR spectra were recorded on a Bruker AV-III400 (400 MHz) spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ( $\text{CDCl}_3$ : 7.26 ppm  $^1\text{H}$  NMR, 77.0 ppm  $^{13}\text{C}$  NMR). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), q (quartet). High-resolution mass spectra (HRMS) were obtained on an Agilent 7200 GC-QTOF spectrometer (EI). Cyclic voltammetry was performed using a CHI660E Chenhua (China).  $\alpha$ -(Trifluoromethyl)styrenes (**1**) were according to literature procedure.<sup>1-2</sup> Silanes (**2i**, **2j**, **2k**) were prepared according to literature.<sup>3</sup> Bioactive compounds **1u** was prepared with 3-(3,3,3-trifluoroprop-1-en-2-yl)benzoic acid and Menthol; **1v** with 3-(1,1-difluoro-3-(triphenylsilyl)prop-1-en-2-yl)aniline and Probenecid according to literature process.<sup>4</sup>

## 2. Complementary Reaction Optimization Data

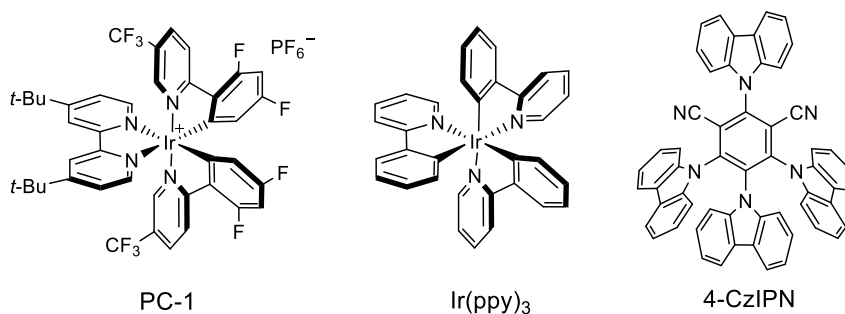
### 2.1 Reaction Optimization for Defluoroborylation of Trifluoromethylalkenes

**Table S1.** Screening of photocatalysts



entry	PC.	yield% <sup>a</sup>
1	4-CzIPN	65
2	Ir(ppy) <sub>2</sub> (dtbpy)PF <sub>6</sub>	25
3	PC-1	22
4	Ir(ppy) <sub>3</sub>	6

<sup>a</sup> The yields were obtained with <sup>1</sup>H-NMR using trimethoxybenzene as the internal standard.

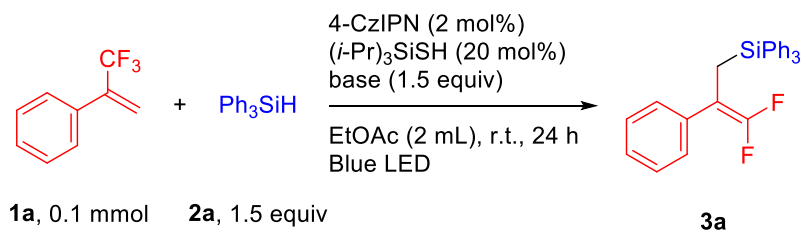


**Table S2.** Screening of HAT cat.



entry	HAT Cat.	yield% <sup>a</sup>
1	quinuclidine	16
2	<i>t</i> -Dodecyl Mercaptan	70
3	( <i>i</i> -Pr) <sub>3</sub> SiSH	73

<sup>a</sup> The yields were obtained with <sup>1</sup>H-NMR using trimethoxybenzene as the internal standard.

**Table S3.** Screening of bases

entry	base	yield% <sup>a</sup>
1	$\text{K}_2\text{CO}_3$	37
2	$\text{KH}_2\text{PO}_4$	44
3	$\text{K}_3\text{PO}_4$	trace
4	$\text{K}_2\text{HPO}_4$	12
5	NaOAc	65
6 <sup>b</sup>	$\text{PhCO}_2\text{Na}$	19
7 <sup>b</sup>	$\text{NaHCO}_3$	73
8 <sup>b</sup>	DIPEA	12
9 <sup>b</sup>	TEA	trace
10	DABCO	31
11	Pyridine	25
12	2,6-Lutidine	25
13	TEMP	0
14	DBU	0

<sup>a</sup> The yields were obtained with  $^1\text{H-NMR}$  using trimethoxybenzene as the internal standard.

<sup>b</sup> Solvent:  $\text{CH}_3\text{CN}$

**Table S4.** Screening of solvents

entry	solvent	yield% <sup>a</sup>
1	CH <sub>3</sub> CN	65
2	THF	14
3	EtOAc	68
4	DCM	trace
5	DCE	34
6	1,4-Dioxane	22
7	DMA	trace
8	DMSO	trace
9	DMF	trace
10	2-methyl-THF	14

<sup>a</sup> The yields were obtained with <sup>1</sup>H-NMR using trimethoxybenzene as the internal standard.

**Table S5.** Control experiments

entry	deviation	yield% <sup>a</sup>
1 <sup>b</sup>	no	84
2	without light	0
3	without 4-CzIPN	0
4	without (i-Pr) <sub>3</sub> SiSH	0
5	without NaHCO <sub>3</sub>	12

<sup>a</sup> The yields were obtained with <sup>1</sup>H-NMR using trimethoxybenzene as the internal standard.

<sup>b</sup> The reaction time was 48 h.

### 3. General Procedures

#### 3.1 General Procedure for Defluorosilylation of Trifluoromethyl alkenes



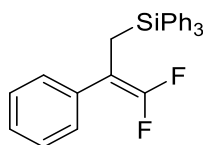
In a 20 mL Schlenk tube with a magnetic stir bar were placed 4-CzIPN (**PC**, 1.6 mg, 0.002 mmol, 2 mol%), NaHCO<sub>3</sub> (12.6 mg, 0.15 mmol, 1.5 equiv), and Ph<sub>3</sub>SiH (**2**, 0.15 mmol, 1.5 equiv). Under nitrogen atmosphere, trifluoromethyl alkenes (**1**, 0.1 mmol, 1 equiv), (*i*-Pr)<sub>3</sub>SiSH (4 μL, 0.02 mmol, 20 mol%), EtOAc (2 mL) were added, subsequently. The resulting mixture was sealed and degassed via freeze-pump-thaw for three times. Then, the reaction was placed under a blue LED (2-meter strips, 20 W) and irradiated for 48 hrs at rt. The solvent was removed under vacuum. Silica gel chromatography (eluent: PE) of the crude product afforded the desired compound.

#### 3.2 Gram-scale preparation of 3a



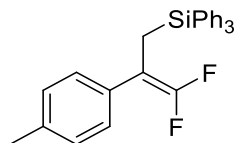
In a 100 mL Schlenk tube with a magnetic stir bar were placed 4-CzIPN (**PC**, 32 mg, 0.02 mmol, 2 mol%), NaHCO<sub>3</sub> (252 mg, 3 mmol, 1.5 equiv), and Ph<sub>3</sub>SiH (**2a**, 781 mg, 1.5 equiv). Under nitrogen atmosphere, (3,3,3-trifluoroprop-1-en-2-yl)benzene (**1a**, 344 mg, 1 equiv), (*i*-Pr)<sub>3</sub>SiSH (80 μL, 0.4 mmol, 20 mol%), EtOAc (20 mL) were added, subsequently. The resulting mixture was sealed and degassed via freeze-pump-thaw for three times. Then, the reaction was placed under a blue LED (2-meter strips, 20 W) and irradiated for 48 hrs at rt. The solvent was removed under vacuum. Silica gel chromatography (eluent: PE) of the crude product afforded (3,3-Difluoro-2-phenylallyl)triphenylsilane (**3a**, 0.47 g) as white solid.

#### 4. Analytical Data of the Products

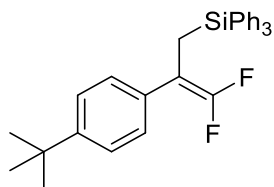


(3,3-Difluoro-2-phenylallyl)triphenylsilane (**3a**): white solid (35 mg, 84%); Mp. 45-46 °C. <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36-7.26 (m, 9H), 7.29 – 7.24 (m, 6H), 7.13 – 7.09 (m, 3H), 7.00 (ddd, *J* = 7.2, 3.1, 1.3 Hz, 2H), 2.59 (dd, *J* = 2.9, 2.1 Hz, 2H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -90.35 (d, *J* = 45.4 Hz), -93.95 (d, *J* = 45.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.50 (dd, *J* = 297.7, 285.1 Hz), 135.63, 134.52 (dd, *J* = 4.7, 3.4 Hz), 133.93, 129.49, 128.55 (t, *J* = 3.6 Hz), 128.04, 127.70, 127.03, 89.57 (dd, *J* = 22.3, 16.1 Hz), 14.68. HRMS (EI): Calcd for C<sub>27</sub>H<sub>22</sub>F<sub>2</sub>Si [M+H]<sup>+</sup> 413.1537, found 413.1537.

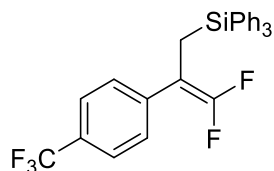


**(3,3-Difluoro-2-(p-tolyl)allyl)triphenylsilane (3b):** white solid (21 mg, 49%); Mp. 45-46 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.26 (m, 9H), 7.22 – 7.18 (m, 6H), 6.85 – 6.79 (m, 4H), 2.50 (t, *J* = 2.5 Hz, 2H), 2.19 (s, 3H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -90.68 (d, *J* = 45.2 Hz), -94.22 (d, *J* = 45.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.59 (dd, *J* = 287.5, 285.2 Hz), 136.74, 135.71, 134.14, 131.58 (dd, *J* = 4.7, 3.0 Hz) 129.47, 128.77, 128.47 (t, *J* = 3.1, Hz), 127.73, 89.46 (dd, *J* = 22.2, 16.3 Hz), 21.08, 14.87. HRMS (EI): Calcd for C<sub>28</sub>H<sub>25</sub>F<sub>2</sub>Si [M+H]<sup>+</sup> 427.1694, found 427.1701.

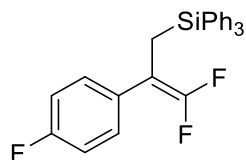


**(2-(4-(Tert-butyl)phenyl)-3,3-difluoroallyl)triphenylsilane (3c):** white solid (31 mg, 66%); Mp. 48-50 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.32 (m, 9H), 7.25 (t, *J* = 7.3 Hz, 6H), 7.14 – 7.08 (m, 2H), 6.97 – 6.91 (m, 2H), 2.58 (t, *J* = 2.5 Hz, 2H), 1.27 (s, 9H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -90.84 (d, *J* = 47.6 Hz), -94.23 (d, *J* = 48.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.52 (t', *J* = 285.6 Hz), 149.82, 135.64, 134.03, 131.39 (t', *J* = 3.6 Hz), 129.43, 128.17 (t, *J* = 3.0 Hz), 127.66, 124.93, 89.26 (dd, *J* = 22.1, 16.3 Hz), 34.39, 31.27, 14.76. HRMS (EI): Calcd for C<sub>31</sub>H<sub>31</sub>F<sub>2</sub>Si [M+H]<sup>+</sup> 469.2163, found 469.2169.

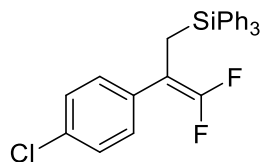




**(3,3-Difluoro-2-(4-(trifluoromethyl)phenyl)allyl)triphenylsilane (3d):** white solid (32 mg, 67%). Mp. 81-82 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 – 7.25 (m, 9H), 7.24 – 7.21 (m, 2H), 7.19 – 7.15 (m, 6H), 6.99 (d, *J* = 7.9 Hz, 2H), 2.52 (t, *J* = 2.5 Hz, 2H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -62.73, -88.74 (d, *J* = 42.3 Hz), -92.15 (d, *J* = 42.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.81 (dd, *J* = 287.4, 285.7 Hz), 138.29, 135.57, 133.61, 129.73 (t, *J* = 4.1 Hz), 128.87 (t, *J* = 3.1 Hz), 127.88, 125.18 (q, *J* = 3.8 Hz), 124.93 (q, *J* = 3.9 Hz), 124.04 (d, *J* = 270.3 Hz), 89.21 (dd, *J* = 23.0, 15.0 Hz), 14.51. HRMS (EI): Calcd for C<sub>28</sub>H<sub>22</sub>F<sub>5</sub>Si [M+H]<sup>+</sup> 481.1411, found 481.1417.

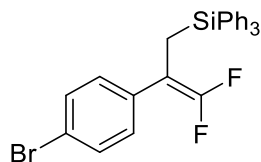


**(3,3-Difluoro-2-(4-fluorophenyl)allyl)triphenylsilane (3e):** white solid (27 mg, 62%); Mp. 108-109 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.34 (m, 9H), 7.27 (m, 6H), 6.93 (ddd, *J* = 8.8, 5.4, 1.2 Hz, 2H), 6.76 (t, *J* = 8.7 Hz, 2H), 2.56 (t, *J* = 2.5 Hz, 2H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -89.80 – -91.59 (m), -93.04 – -95.08 (m), -114.36 – -115.63 (m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.70 (d, *J* = 246.6 Hz), 152.60 (t', *J* = 286.6 Hz), 135.61, 133.85, 130.24 (dt, *J* = 8.1, 3.0 Hz), 129.61, 128.10 (t, *J* = 2.3 Hz), 127.81, 114.95 (d, *J* = 21.6 Hz), 88.88 (dd, *J* = 23.0, 16.2 Hz), 14.87. HRMS (EI): Calcd for C<sub>27</sub>H<sub>22</sub>F<sub>3</sub>Si [M+H]<sup>+</sup> 431.1443, found 431.1446.

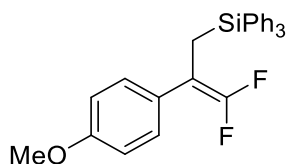


**(2-(4-Chlorophenyl)-3,3-difluoroallyl)triphenylsilane (3f):** white solid (21 mg, 46%); Mp. 59-60 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (dd, *J* = 6.8, 2.2 Hz, 9H), 7.28 (dd, *J* = 8.5, 6.3 Hz, 6H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.89 (dd, *J* = 8.5, 1.3 Hz, 2H), 2.56 (t, *J* = 2.5 Hz, 2H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -89.72 (d, *J* = 45.0 Hz), -93.13 (d, *J* = 45.1 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.56 (dd, *J* = 286.7, 284.4 Hz), 135.60, 133.74, 132.92 (dd, *J* = 4.7, 3.3 Hz), 132.82, 129.86 (t,

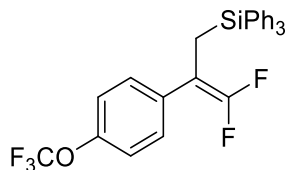
$J = 3.1$  Hz), 129.64, 128.19, 127.84, 88.94 (dd,  $J = 23.1, 16.1$  Hz), 14.61. HRMS (EI): Calcd for  $C_{27}H_{22}F_2SiCl$   $[M+H]^+$  447.1147, found 447.1144.



**(2-(4-Bromophenyl)-3,3-difluoroallyl)triphenylsilane (3g):** white solid (27 mg, 54%); Mp. 65-66 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.31 – 7.27 (m, 9H), 7.22 – 7.17 (m, 6H), 7.11 – 7.08 (m, 2H), 6.75 (dd,  $J = 8.6, 1.3$  Hz, 2H), 2.48 (t,  $J = 2.5$  Hz, 2H);  $^{19}F$  NMR (377 MHz,  $CDCl_3$ )  $\delta$  -89.57 (d,  $J = 44.3$  Hz), -92.96 (d,  $J = 44.3$  Hz);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  152.52 (dd,  $J = 287.0, 284.3$  Hz), 135.60, 133.73, 133.41 (dd,  $J = 5.2, 3.4$  Hz), 131.15, 130.19 (t,  $J = 3.1$  Hz), 129.65, 127.86, 121.01, 89.02 (dd,  $J = 23.3, 15.9$  Hz), 14.58. HRMS (EI): Calcd for  $C_{27}H_{22}F_2SiBr$   $[M+H]^+$  491.0642, found 491.0641.

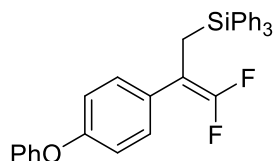


**(3,3-difluoro-2-(4-methoxyphenyl)allyl)triphenylsilane (3h):** white solid (18 mg, 40%); Mp. 119-120 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40 – 7.34 (m, 9H), 7.27 (t,  $J = 7.3$  Hz, 6H), 6.91 (dd,  $J = 8.7, 1.3$  Hz, 2H), 6.63 (d,  $J = 8.8$  Hz, 2H), 3.74 (s, 3H), 2.56 (t,  $J = 2.6$  Hz, 2H);  $^{19}F$  NMR (377 MHz,  $CDCl_3$ )  $\delta$  -91.28 (d,  $J = 48.6$  Hz), -94.76 (d,  $J = 48.6$  Hz);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  158.52 (t',  $J = 285.9$  Hz), 135.66, 135.01 (dd,  $J = 5.8, 4.1$  Hz), 134.09, 129.68 (t,  $J = 3.1$  Hz), 129.47, 127.71, 126.75, 113.53, 88.98 (dd,  $J = 23.3, 15.6$  Hz), 55.25, 14.86. HRMS (EI): Calcd for  $C_{28}H_{25}OF_2Si$   $[M+H]^+$  443.1643, found 443.1647.

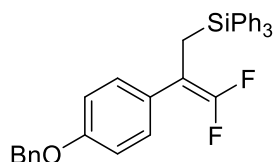


**(3,3-Difluoro-2-(4-(trifluoromethoxy)phenyl)allyl)triphenylsilane (3i):** white solid (46 mg, 93%); Mp. 91-92 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.39 – 7.34 (m, 9H), 7.29 – 7.24 (m, 6H), 7.01

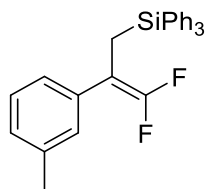
– 6.97 (m, 2H), 6.93 – 6.89 (m, 2H), 2.58 (t,  $J = 2.5$  Hz, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  - 57.77, -89.76 (d,  $J = 44.9$  Hz), -93.12 (d,  $J = 44.6$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.63 (dd,  $J = 286.9, 284.2$  Hz), 147.91 (d,  $J = 2.3$  Hz), 135.58, 133.66, 133.25 (dd,  $J = 5.1, 3.4$  Hz), 129.96 (t,  $J = 3.6$  Hz), 129.68, 127.80, 120.59, 120.43 (q,  $J = 257.5$  Hz), 88.82 (dd,  $J = 23.4, 16.0$  Hz), 14.72. HRMS (EI): Calcd for  $\text{C}_{28}\text{H}_{21}\text{OF}_5\text{SiNa}$   $[\text{M}+\text{Na}]^+$  519.1180, found 519.1171.



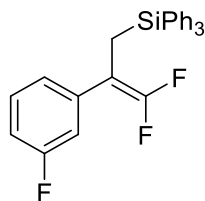
**(3,3-Difluoro-2-(4-phenoxyphenyl)allyl)triphenylsilane (3j):** white solid (24 mg, 47%); Mp. 101-102 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.34 (m, 11H), 7.29 (t,  $J = 7.2$  Hz, 6H), 7.10 (t,  $J = 7.4$  Hz, 1H), 6.99 – 6.92 (m, 4H), 6.74 (d,  $J = 8.7$  Hz, 2H), 2.58 (t,  $J = 2.6$  Hz, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -90.52 (d,  $J = 46.8$  Hz), -94.03 (d,  $J = 46.8$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.03 (d,  $J = 108.6$  Hz), 152.56 (t',  $J = 284.5$  Hz), 135.64, 133.90, 129.91 (t,  $J = 3.1$  Hz), 129.68, 129.54, 129.34 (dd,  $J = 4.9, 3.0$  Hz), 128.07, 127.74, 123.24, 118.78, 118.43, 88.94 (dd,  $J = 22.7, 16.2$  Hz), 14.72. HRMS (EI): Calcd for  $\text{C}_{33}\text{H}_{27}\text{OF}_2\text{Si}$   $[\text{M}+\text{H}]^+$  505.1799, found 505.1798.



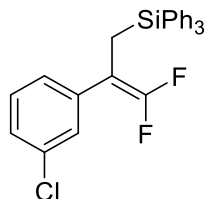
**(2-(4-(Benzyloxy)phenyl)-3,3-difluoroallyl)triphenylsilane (3k):** white solid (16 mg, 30%). Mp. 82-83 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.33 (m, 14H), 7.28 – 7.24 (m, 6H), 6.93 – 6.87 (m, 2H), 6.70 (d,  $J = 8.8$  Hz, 2H), 5.00 (s, 2H), 2.55 (t,  $J = 2.5$  Hz, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -91.14 (d,  $J = 48.3$  Hz), -94.59 (d,  $J = 48.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.65, 152.47 (t',  $J = 284.7$  Hz), 136.95, 135.61, 134.00, 129.66 (t,  $J = 2.9$  Hz), 129.44, 128.58, 127.96, 127.68, 127.38, 126.92 (dd,  $J = 3.1, 4.3$  Hz), 114.40, 88.99 (dd,  $J = 22.6, 16.3$  Hz), 69.86, 14.77. HRMS (EI): Calcd for  $\text{C}_{34}\text{H}_{29}\text{OF}_2\text{Si}$   $[\text{M}+\text{H}]^+$  519.1956, found 519.1954.



**(3,3-Difluoro-2-(m-tolyl)allyl)triphenylsilane (3l):** white solid (33 mg, 77%). Mp. 45-46 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.34 (m, 9H), 7.30 – 7.25 (m, 6H), 7.02 (t,  $J = 7.6$  Hz, 1H), 6.91 (d,  $J = 7.5$  Hz, 1H), 6.85 (dd,  $J = 7.7, 1.6$  Hz, 1H), 6.71 (s, 1H), 2.57 (dd,  $J = 2.9, 2.1$  Hz, 2H), 2.12 (s, 3H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -90.56 (d,  $J = 46.7$  Hz), -93.82 (d,  $J = 46.6$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.59 (dd,  $J = 285.9, 283.6$  Hz), 137.60, 135.71, 134.42 (dd,  $J = 4.7, 3.0$  Hz), 134.08, 129.54, 129.42 (t,  $J = 2.8$  Hz), 127.98, 127.84, 127.73, 125.61 (t,  $J = 3.4$  Hz), 89.67 (dd,  $J = 22.3, 16.2$  Hz), 21.27, 14.81. HRMS (EI): Calcd for  $\text{C}_{28}\text{H}_{25}\text{F}_2\text{Si}$   $[\text{M}+\text{H}]^+$  427.1694, found 427.1701.

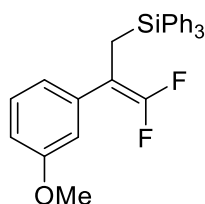


**(3,3-Difluoro-2-(3-fluorophenyl)allyl)triphenylsilane (3m):** white solid (37 mg, 87%). Mp. 108-109 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.34 (m, 9H), 7.28 (t,  $J = 7.2$  Hz, 6H), 7.04 (td,  $J = 8.0, 6.1$  Hz, 1H), 6.82 – 6.74 (m, 2H), 6.67 (ddt,  $J = 10.3, 2.7, 1.4$  Hz, 1H), 2.57 (t,  $J = 2.5$  Hz, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -89.14 (d,  $J = 43.3$  Hz), -92.44 (d,  $J = 42.1$  Hz), -113.58;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.37 (d,  $J = 245.5$  Hz), 152.68 (dd,  $J = 289.4, 286.2$  Hz), 136.73 – 136.56 (m), 135.58, 133.69, 129.64, 129.44 (d,  $J = 4.7$  Hz), 127.78, 124.18 (t,  $J = 3.1$  Hz), 116.40 – 114.85 (m), 113.91 (d,  $J = 21.1$  Hz), 89.26 – 88.85 (m), 14.50. HRMS (EI): Calcd for  $\text{C}_{27}\text{H}_{22}\text{F}_3\text{Si}$   $[\text{M}+\text{H}]^+$  431.1443, found 431.1446.

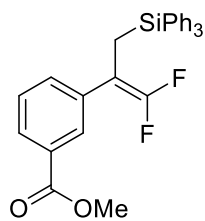


**(2-(3-Chlorophenyl)-3,3-difluoroallyl)triphenylsilane (3n):** white solid (38 mg, 85%). Mp. 59-60 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.26 (m, 9H), 7.21 (dd,  $J = 7.7, 6.6$  Hz, 6H), 6.99 –

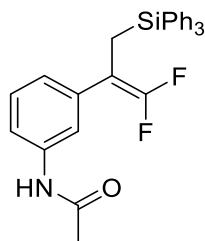
6.89 (m, 2H), 6.84 – 6.79 (m, 2H), 2.48 (t,  $J = 2.5$  Hz, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -89.20 (d,  $J = 43.1$  Hz), -92.42 (d,  $J = 43.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.74 (dd,  $J = 289.2$ , 286.5 Hz), 136.34 (dd,  $J = 4.9$ , 3.2 Hz), 135.62, 133.93, 133.70, 129.73, 129.25, 128.79 (t,  $J = 3.2$  Hz), 127.85, 127.19, 126.66 (t,  $J = 3.1$  Hz), 89.04 (dd,  $J = 23.3$ , 15.7 Hz), 14.50. HRMS (EI): Calcd for  $\text{C}_{27}\text{H}_{22}\text{F}_2\text{SiCl}$   $[\text{M}+\text{H}]^+$  447.1147, found 447.1144.



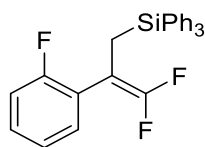
**(3,3-Difluoro-2-(3-methoxyphenyl)allyl)triphenylsilane (3o):** white solid (34 mg, 76%); Mp. 119-120 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.26 (m, 9H), 7.22 – 7.18 (m, 6H), 6.96 (t,  $J = 8.0$  Hz, 1H), 6.62 – 6.55 (m, 2H), 6.40 (dt,  $J = 2.7$ , 1.3 Hz, 1H), 3.51 (s, 3H), 2.50 (dd,  $J = 3.0$ , 2.1 Hz, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -90.09 (d,  $J = 45.5$  Hz), -93.18 (d,  $J = 45.6$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.24, 151.59 (dd,  $J = 288.2$ , 285.4 Hz), 134.89 (dd,  $J = 4.8$ , 3.1 Hz), 134.63, 133.02, 128.48, 128.01, 126.70, 120.04 (t,  $J = 3.2$  Hz), 113.02 (t,  $J = 2.9$  Hz), 112.12, 88.52 (dd,  $J = 22.7$ , 16.1 Hz), 54.00, 13.77. HRMS (EI): Calcd for  $\text{C}_{28}\text{H}_{25}\text{OF}_2\text{Si}$   $[\text{M}+\text{H}]^+$  443.1643, found 443.1647.



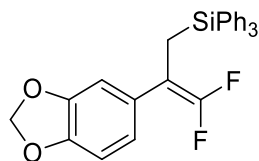
**Methyl 3-(1,1-difluoro-3-(triphenylsilyl)prop-1-en-2-yl)benzoate (3p):** white solid (25 mg, 52%); Mp. 102-103 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (dt,  $J = 7.2$ , 1.7 Hz, 1H), 7.59 (td,  $J = 1.9$ , 0.9 Hz, 1H), 7.30 – 7.22 (m, 9H), 7.15 (dd,  $J = 7.9$ , 6.6 Hz, 6H), 7.08 – 7.02 (m, 2H), 3.76 (s, 3H), 2.53 (t,  $J = 2.4$  Hz, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -89.49 (d,  $J = 43.7$  Hz), -92.84 (d,  $J = 44.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.57, 151.72 (dd,  $J = 288.8$ , 286.2 Hz), 134.53, 133.73 (dd,  $J = 4.8$ , 3.1 Hz), 132.69, 131.92 (t,  $J = 3.3$  Hz), 128.93, 128.69 (t,  $J = 3.1$  Hz), 128.53, 127.14, 127.04, 126.74, 88.14 (dd,  $J = 23.1$ , 15.8 Hz), 50.96, 13.39. HRMS (EI): Calcd for  $\text{C}_{29}\text{H}_{24}\text{OF}_2\text{NaSi}$   $[\text{M}+\text{Na}]^+$  493.1411, found 493.1415.



**N-(3-(1,1-difluoro-3-(triphenylsilyl)prop-1-en-2-yl)phenyl)acetamide (3q):** white solid (26 mg, 56%); Mp. 105-106 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.44 (m, 1H), 7.40 – 7.33 (m, 9H), 7.26 (dd, *J* = 6.7, 1.5 Hz, 6H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.81 – 6.76 (m, 1H), 2.55 (t, *J* = 2.5 Hz, 2H), 2.07 (s, 3H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -89.45 (d, *J* = 44.7 Hz), -92.65 (d, *J* = 45.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.30, 152.75 (dd, *J* = 289.0, 285.9 Hz), 137.78, 135.73, 134.01, 130.87, 129.59, 128.76, 127.81, 124.43 (t, *J* = 3.7 Hz), 119.88, 118.73, 89.42 (dd, *J* = 22.7, 15.7 Hz), 24.51, 14.69. HRMS (EI): Calcd for C<sub>29</sub>H<sub>26</sub>NOF<sub>2</sub>Si [M+H]<sup>+</sup> 470.1752, found 470.1754.

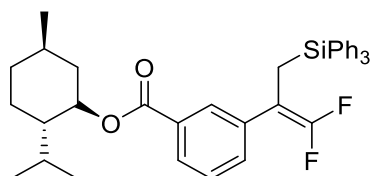


**(3,3-Difluoro-2-(2-fluorophenyl)allyl)triphenylsilane (3r):** white solid (21 mg, 48%); Mp. 108-109 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.25 (m, 9H), 7.19 (dd, *J* = 7.3, 1.1 Hz, 6H), 7.01 (ddt, *J* = 9.2, 8.1, 3.8 Hz, 1H), 6.81 – 6.76 (m, 2H), 6.74 – 6.66 (m, 1H), 2.54 – 2.50 (m, 2H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -90.23 – -90.47 (m), -90.74 – -91.01 (m), -112.67 – -112.85 (m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.07 (d, *J* = 247.8 Hz), 152.45 (t', *J* = 287.0 Hz), 135.54, 133.85, 130.96 (dd, *J* = 4.8, 3.1 Hz), 129.52, 129.30 (d, *J* = 8.4 Hz), 127.75, 123.69 (d, *J* = 3.6 Hz), 122.40 – 122.08 (m), 115.51 (d, *J* = 22.2 Hz), 84.28 (dd, *J* = 25.4, 18.6 Hz), 14.37. HRMS (EI): Calcd for C<sub>27</sub>H<sub>22</sub>F<sub>3</sub>Si [M+H]<sup>+</sup> 431.1443, found 431.1446.

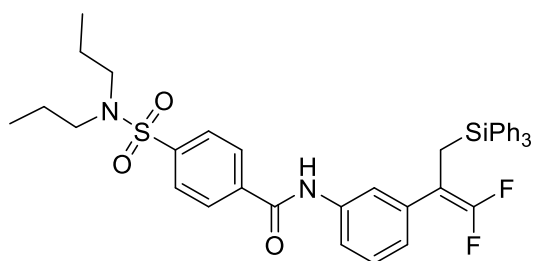


**(2-(Benzo[d][1,3]dioxol-5-yl)-3,3-difluoroallyl)triphenylsilane (3s):** white solid (10 mg, 21%). Mp. 56-58 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.25 (m, 9H), 7.22 – 7.17 (m, 6H), 6.46 – 6.32

(m, 3H), 5.75 (s, 2H), 2.45 (q,  $J = 2.2$  Hz, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -91.03 (d,  $J = 47.6$ ), -93.88 (d,  $J = 47.6$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.53 (t',  $J = 284.2$  Hz), 145.83 (d,  $J = 69.7$  Hz), 134.58, 132.99, 128.46, 127.14 (dd,  $J = 4.7, 3.1$  Hz), 126.69, 121.16 (t,  $J = 2.8$  Hz), 108.16 (t,  $J = 3.1$  Hz), 106.84, 99.85, 88.33 (dd,  $J = 22.8, 16.4$  Hz), 14.04. HRMS (EI): Calcd for  $\text{C}_{28}\text{H}_{22}\text{O}_2\text{F}_2\text{NaSi}$   $[\text{M}+\text{Na}]^+$  479.1255, found 479.1247.

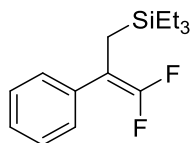


**(1S,2S,5R)-2-isopropyl-5-methylcyclohexyl 3-(1,1-difluoro-3-(triphenylsilyl)prop-1-en-2-yl)benzoate (3t):** white solid (27 mg, 46%); Mp. 78-79 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (td,  $J = 4.5, 1.6$  Hz, 1H), 7.72 – 7.70 (m, 1H), 7.64 (ddd,  $J = 7.9, 6.1, 1.5$  Hz, 1H), 7.39 – 7.32 (m, 9H), 7.27 – 7.23 (m, 6H), 7.14 (d,  $J = 4.6$  Hz, 1H), 4.89 (d,  $J = 4.4$  Hz, 1H), 2.63 (s, 2H), 2.12 – 2.07 (m, 1H), 1.91 (td,  $J = 7.0, 2.7$  Hz, 1H), 1.73 (dt,  $J = 12.8, 2.9$  Hz, 3H), 1.55 (d,  $J = 12.9$  Hz, 4H), 0.95 – 0.91 (m, 6H), 0.80 (d,  $J = 7.0$  Hz, 3H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -89.78 (d,  $J = 44.4$  Hz), -93.07 (d,  $J = 44.5$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.62, 152.72 (dd,  $J = 286.8, 284.5$  Hz), 135.58, 135.01, 134.72 (dd,  $J = 4.8, 3.0$  Hz), 133.72, 132.82 (t,  $J = 3.1$  Hz), 130.65, 130.14, 129.58, 127.93 (d,  $J = 3.2$  Hz), 127.77, 89.17 (dd,  $J = 23.0, 16.0$  Hz), 74.82, 47.23, 40.99, 34.34, 31.46, 26.57, 23.72, 22.11, 20.77, 16.65, 14.44. HRMS (EI): Calcd for  $\text{C}_{38}\text{H}_{41}\text{O}_2\text{F}_2\text{Si}$   $[\text{M}+\text{H}]^+$  595.2844, found 595.2845.

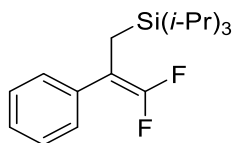


**N-(3-(1,1-difluoro-3-(triphenylsilyl)prop-1-en-2-yl)phenyl)-4-(N,N-dipropylsulfamoyl)benzamide (3u):** white solid (29 mg, 45%); Mp. 236-239 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.4$  Hz, 2H), 7.68 – 7.65 (m, 2H), 7.34 – 7.26 (m, 11H), 7.21 – 7.17 (m, 6H), 7.03 (s, 1H), 6.76 (dq,  $J = 7.8, 1.4$  Hz, 1H), 3.00 – 2.97 (m, 4H), 2.52 (t,  $J = 2.5$  Hz, 2H), 1.46 – 1.41 (m, 4H), 0.77 (d,  $J = 1.3$  Hz, 6H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -89.60 (d,  $J = 44.2$

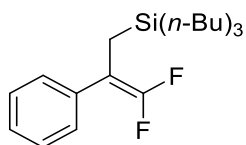
Hz), -92.63 (d,  $J = 44.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.49, 152.76 (dd,  $J = 288.8, 285.9$  Hz), 142.83, 138.81, 137.61, 135.72, 135.39 (dd,  $J = 4.4, 3.5$  Hz), 134.94, 133.98, 129.58, 128.80, 127.95 (t,  $J = 3.1$  Hz), 127.79, 127.29, 125.07, 119.10, 89.44 (dd,  $J = 23.0, 15.5$  Hz), 50.01, 21.95, 14.60, 11.16. HRMS (EI): Calcd for  $\text{C}_{40}\text{H}_{40}\text{N}_2\text{O}_3\text{F}_2\text{NaSiS}$   $[\text{M}+\text{Na}]^+$  717.2395, found 717.2386.



**(3,3-Difluoro-2-phenylallyl)triethylsilane (4a):** colorless oil (15 mg, 57%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 (d,  $J = 5.4$  Hz, 3H), 7.19 (s, 2H), 1.67 (dd,  $J = 3.2, 2.1$  Hz, 2H), 0.75 (t,  $J = 7.9$  Hz, 9H), 0.32 (q,  $J = 7.9$  Hz, 6H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -92.63 (d,  $J = 50.1$  Hz), -94.95 (d,  $J = 50.1$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.32 (dd,  $J = 281.7, 278.9$  Hz), 135.44 (dd,  $J = 4.9, 3.4$  Hz), 128.32 (t,  $J = 4.1$  Hz), 128.20, 127.12, 90.28 (dd,  $J = 23.5, 16.3$  Hz), 12.16, 7.05, 3.44. HRMS (EI): Calcd for  $\text{C}_{15}\text{H}_{23}\text{F}_2\text{Si}$   $[\text{M}+\text{H}]^+$  269.1537, found 269.1529.



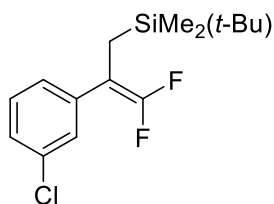
**(3,3-Difluoro-2-phenylallyl)triisopropylsilane (4b):** colorless oil (16 mg, 50%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 4.5$  Hz, 4H), 7.25 (q,  $J = 4.4$  Hz, 1H), 1.82 (dd,  $J = 3.1, 2.1$  Hz, 2H), 0.93 (m, 21H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -91.82 (d,  $J = 49.7$  Hz), -94.68 (d,  $J = 49.7$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.73 (t',  $J = 281.8$  Hz), 135.39 (dd,  $J = 4.6, 3.1$  Hz), 128.60 (t,  $J = 3.4$  Hz), 128.16, 127.20, 90.79 (dd,  $J = 22.2, 15.8$  Hz), 18.40, 11.31, 9.88. HRMS (EI): Calcd for  $\text{C}_{18}\text{H}_{28}\text{F}_2\text{NaSi}$   $[\text{M}+\text{Na}]^+$  333.1826, found 333.1830.



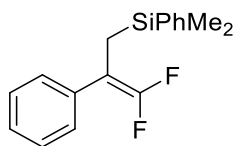
**Tributyl(3,3-difluoro-2-phenylallyl)silane (4c):** colorless oil (20 mg, 58%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (d,  $J = 5.2$  Hz, 4H), 7.25 (d,  $J = 8.0$  Hz, 1H), 1.74 (dd,  $J = 3.2, 2.1$  Hz, 2H), 1.22 – 1.12 (m, 12H), 0.81 (t,  $J = 7.1$  Hz, 9H), 0.43 – 0.35 (m, 6H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -92.80



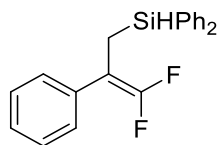
(d,  $J = 50.2$  Hz),  $-95.12$  (d,  $J = 50.2$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.31 (dd,  $J = 287.5$ , 284.1 Hz), 135.38 (dd,  $J = 4.9$ , 3.2 Hz), 128.39 (t,  $J = 3.0$  Hz), 128.19, 127.10, 90.48 (dd,  $J = 23.3$ , 14.4 Hz), 26.70, 25.78, 13.65, 13.03, 12.18. HRMS (EI): Calcd for  $\text{C}_{21}\text{H}_{35}\text{F}_2\text{Si}$   $[\text{M}+\text{H}]^+$  353.2476, found 353.2485.



**tert-butyl(2-(3-chlorophenyl)-3,3-difluoroallyl)dimethylsilane (4d):** colorless oil (12 mg, 40%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (q,  $J = 1.7$  Hz, 1H), 7.27 – 7.18 (m, 4H), 1.72 (dd,  $J = 3.2$ , 2.1 Hz, 2H), 0.87 (s, 9H),  $-0.21$  (s, 6H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$   $-90.67$  (dd,  $J = 46.3$ , 3.4 Hz),  $-93.14$  (d,  $J = 46.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.8 (dd,  $J = 285.7$ , 283.2 Hz), 137.23 (dd,  $J = 5.1$ , 3.4 Hz), 134.19, 129.51, 128.37 (t,  $J = 3.1$  Hz), 127.28, 126.47 (t,  $J = 3.4$  Hz), 89.65 (dd,  $J = 23.1$ , 14.8 Hz), 26.27, 16.63, 12.57,  $-5.29$ . HRMS (EI): Calcd for  $\text{C}_{15}\text{H}_{22}\text{ClF}_2\text{Si}$   $[\text{M}+\text{H}]^+$  303.1147, found 303.1149.

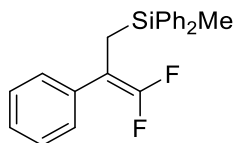


**(3,3-Difluoro-2-phenylallyl)dimethyl(phenyl)silane (4e):** colorless oil (22 mg, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.32 (m, 2H), 7.28 – 7.12 (m, 8H), 1.90 (dd,  $J = 3.1$ , 2.1 Hz, 2H), 0.07 (s, 6H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$   $-91.79$  (d,  $J = 48.3$  Hz),  $-94.40$  (d,  $J = 48.1$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.97 (dd,  $J = 287.4$ , 283.8 Hz), 138.45, 135.23 (dd,  $J = 4.9$ , 3.2 Hz), 133.72, 129.40, 128.62 (t,  $J = 3.1$  Hz), 128.53, 128.03, 127.42, 90.26 (dd,  $J = 23.9$ , 15.6 Hz), 16.50,  $-2.93$ . HRMS (EI): Calcd for  $\text{C}_{17}\text{H}_{19}\text{F}_2\text{Si}$   $[\text{M}+\text{H}]^+$  289.1224, found 289.1231.

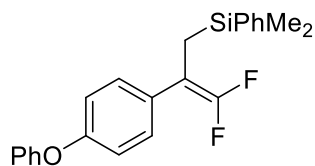


**(3,3-Difluoro-2-phenylallyl)diphenylsilane (4f):** colorless oil (17 mg, 50%).  $^1\text{H}$  NMR (400 MHz,

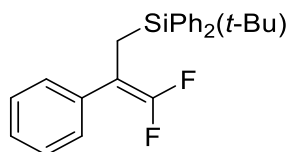
CDCl<sub>3</sub>) δ 7.34 – 7.28 (m, 2H), 7.26 (s, 4H), 7.23 – 7.17 (m, 4H), 7.17 – 7.13 (m, 3H), 6.94 (ddd, *J* = 6.0, 3.2, 1.4 Hz, 2H), 5.35 (t, *J* = 4.8 Hz, 1H), 2.13 (t, *J* = 2.5 Hz, 2H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -90.56 (d, *J* = 45.2 Hz), -92.96 (d, *J* = 45.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.77 (dd, *J* = 289.2, 285.2 Hz), 135.08, 134.37 (t', *J* = 4.0 Hz), 133.14, 129.86, 128.38 (t, *J* = 3.5 Hz), 128.27, 128.01, 127.25, 89.28 (dd, *J* = 22.7, 15.7 Hz), 13.48. HRMS (EI): Calcd for C<sub>21</sub>H<sub>19</sub>F<sub>2</sub>Si [M+H]<sup>+</sup> 337.1224, found 337.1223.



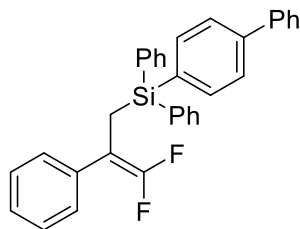
**(3,3-Difluoro-2-phenylallyl)(methyl)diphenylsilane (4g):** colorless oil (19 mg, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.33 (m, 4H), 7.30 – 7.19 (m, 6H), 7.16 – 7.08 (m, 3H), 7.08 – 7.03 (m, 2H), 2.22 (dd, *J* = 3.0, 2.1 Hz, 2H), 0.27 (s, 3H); <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -91.26 (d, *J* = 47.5 Hz), -93.58 (d, *J* = 47.3 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.69 (dd, *J* = 288.3, 285.0 Hz), 136.08, 134.75 (dd, *J* = 4.7, 3.2 Hz), 134.41, 129.39, 128.48 (t, *J* = 3.1 Hz), 128.20, 127.82, 127.17, 89.69 (dd, *J* = 22.9, 15.5 Hz), 15.29, -4.23. HRMS (EI): Calcd for C<sub>22</sub>H<sub>21</sub>F<sub>2</sub>Si [M+H]<sup>+</sup> 351.1381, found 351.1379.



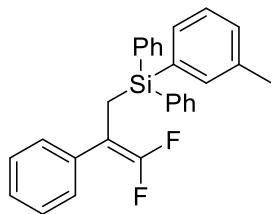
**(3,3-difluoro-2-(4-phenoxyphenyl)allyl)(methyl)diphenylsilane (4h):** colorless oil (16 mg, 42%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.21 – 7.14 (m, 5H), 7.03 (dd, *J* = 8.7, 1.4 Hz, 2H), 6.97 – 6.93 (m, 1H), 6.87 – 6.83 (m, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 1.83 – 1.78 (m, 2H), 0.04 (s, 6H); <sup>19</sup>F NMR (377MHz, CDCl<sub>3</sub>) δ -91.97 (d, *J* = 49.5 Hz), -94.47 (d, *J* = 49.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.53, 158.63, 155.16 (dd, *J* = 288.0, 284.4 Hz), 140.52, 135.91, 132.98 (t, *J* = 4.2 Hz) 132.21, 132.14 (t, *J* = 3.3 Hz), 131.56, 130.19, 125.80, 121.36, 121.02, 91.88 (dd, *J* = 23.5, 14.6 Hz), 19.07, -0.47. HRMS (EI): Calcd for C<sub>23</sub>H<sub>23</sub>F<sub>2</sub>OSi [M+H]<sup>+</sup> 381.5137, found 381.5139.



**Tert-butyl(3,3-difluoro-2-phenylallyl)diphenylsilane (4i):** colorless oil (18 mg, 47%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.39 (m, 4H), 7.33 – 7.28 (m, 2H), 7.21 (t,  $J = 7.4$  Hz, 4H), 7.09 – 7.01 (m, 3H), 6.94 – 6.88 (m, 2H), 2.36 (t,  $J = 2.5$  Hz, 2H), 1.02 (s, 9H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -90.98 (d,  $J = 47.7$  Hz), -94.61 (d,  $J = 47.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.26 (dd,  $J = 286.3, 284.0$  Hz), 136.07, 134.51 (dd,  $J = 8.1, 4.3$  Hz), 133.77, 129.02, 128.55 (t,  $J = 2.9$  Hz), 127.88, 127.27, 126.89, 90.08 (dd,  $J = 22.2, 16.0$  Hz), 27.63, 18.33, 11.55. HRMS (EI): Calcd for  $\text{C}_{25}\text{H}_{26}\text{F}_2\text{SiNa}$   $[\text{M}+\text{Na}]^+$  415.1670, found 415.1664.

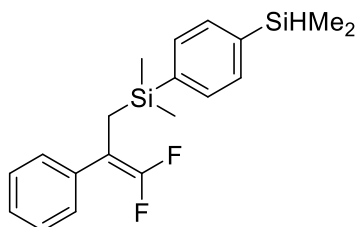


**[1,1'-Biphenyl]-4-yl(3,3-difluoro-2-phenylallyl)diphenylsilane (4j):** white solid (21 mg, 42%); Mp. 48-50 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 7.5$  Hz, 2H), 7.48 – 7.36 (m, 14H), 7.29 (s, 3H), 7.13 – 7.08 (m, 3H), 7.04 – 6.99 (m, 2H), 2.62 (s, 2H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -90.29 (d,  $J = 45.7$  Hz), -93.86 (d,  $J = 45.9$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.55 (dd,  $J = 286.1, 283.7$  Hz), 142.03, 140.86, 136.09, 135.61, 134.48 (dd,  $J = 5.1, 3.3$  Hz), 133.92, 132.62, 129.54, 128.77, 128.55 (t,  $J = 2.9$  Hz), 128.04, 127.75, 127.47, 127.10, 127.00, 126.35, 89.57 (dd,  $J = 22.3, 16.1$  Hz), 14.71. HRMS (EI): Calcd for  $\text{C}_{33}\text{H}_{27}\text{F}_2\text{Si}$   $[\text{M}+\text{H}]^+$  489.1850, found 489.1855.



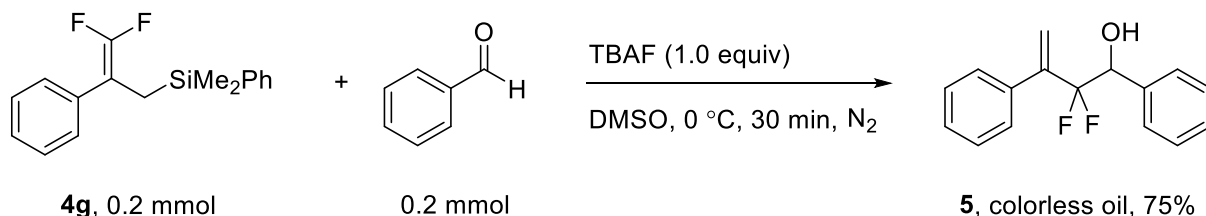
**(3,3-Difluoro-2-phenylallyl)diphenyl(m-tolyl)silane (4k):** white solid (42 mg, 98%); Mp. 68-69 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.44 (m, 7H), 7.41 – 7.32 (m, 6H), 7.23 – 7.19 (m, 4H), 7.11 (ddd,  $J = 5.5, 3.4, 1.8$  Hz, 2H), 2.68 (t,  $J = 2.5$  Hz, 2H), 2.33 (s, 3H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -90.43 (d,  $J = 46.1$  Hz), -94.11 (d,  $J = 46.4$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$

152.58 (dd,  $J = 285.7, 283.9$  Hz), 137.04, 136.22, 135.67, 134.63 (dd,  $J = 4.1, 3.0$  Hz), 134.16, 133.74, 132.78, 130.36, 129.48, 128.62 (t,  $J = 2.9$  Hz), 128.04, 127.72, 127.62, 127.06, 89.66 (dd,  $J = 22.3, 16.3$  Hz), 21.51, 14.78. HRMS (EI): Calcd for  $C_{28}H_{25}F_2Si$   $[M+H]^+$  427.1694, found 427.1690.

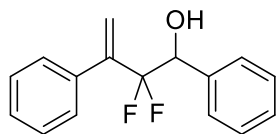


**(3,3-Difluoro-2-phenylallyl)(4-(dimethylsilyl)phenyl)dimethylsilane (4l):** colorless oil (14 mg, 40%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.20 (d,  $J = 7.7$  Hz, 2H), 7.13 (d,  $J = 7.8$  Hz, 2H), 7.01 – 6.92 (m, 5H), 4.13 (m, 1H), 1.69 (dd,  $J = 3.1, 2.1$  Hz, 2H), 0.06 (d,  $J = 3.7$  Hz, 6H), -0.14 (s, 6H);  $^{19}F$  NMR (377 MHz,  $CDCl_3$ )  $\delta$  -91.77 (d,  $J = 48.5$  Hz), -94.32 (d,  $J = 47.7$  Hz);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  152.66 (dd,  $J = 288.6, 284.4$  Hz), 149.20, 138.36, 134.88 (t,  $J = 4.1$  Hz), 133.24, 132.77, 128.30 (dd,  $J = 4.1, 3.0$  Hz), 128.21, 127.10, 89.91 (dd,  $J = 23.2, 14.6$  Hz), 16.35, -3.06, -3.89. HRMS (EI): Calcd for  $C_{19}H_{25}F_2Si_2$   $[M+H]^+$  347.1463, found 347.1472.

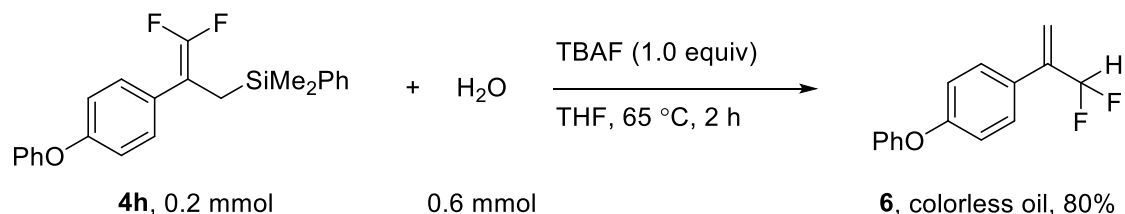
## 5. Transformations of the Products



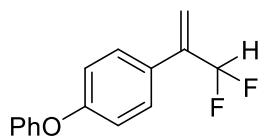
According to literature report,<sup>5</sup> an Schlenk tube was charged with **4g** (57.6 mg, 0.2 mmol), benzaldehyde (41  $\mu$ L, 0.2 mmol) and DMSO (2.0 mL) under nitrogen atmosphere. After the resultant solution was cooled to 0 °C, TBAF (0.2 mL, 1 M in THF, 0.2 mmol) was added dropwise *via* a syringe. Then, the reaction mixture was continued to stir at 0 °C for 30 minutes and the crude product were purified by column chromatography (PE/EA = 10/1) on silica gel to afford colorless oil **5** (39 mg, 75% yield).



**2,2-Difluoro-1,3-diphenylbut-3-en-1-ol (5):** colorless oil (39 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (m, 5H), 7.24 (m, 5H), 5.58 (s, 1H), 5.41 (s, 1H), 4.79 (t,  $J = 11.7$  Hz, 1H), 2.30 (s, 1H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -106.47 (d,  $J = 11.0$  Hz), -107.13 (d,  $J = 11.0$  Hz), -108.07 (d,  $J = 12.3$  Hz), -108.73 (d,  $J = 12.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.60 (t,  $J = 22.2$  Hz), 136.74, 135.90 (d,  $J = 2.7$  Hz), 128.78, 128.43, 128.39, 128.13, 127.99, 122.87, 120.85 (t,  $J = 9.0$  Hz), 117.92, 74.78 (t,  $J = 28.1$  Hz). HRMS (EI): Calcd for  $\text{C}_{16}\text{H}_{15}\text{F}_2\text{O}$   $[\text{M}+\text{H}]^+$  261.2817, found 261.2815.



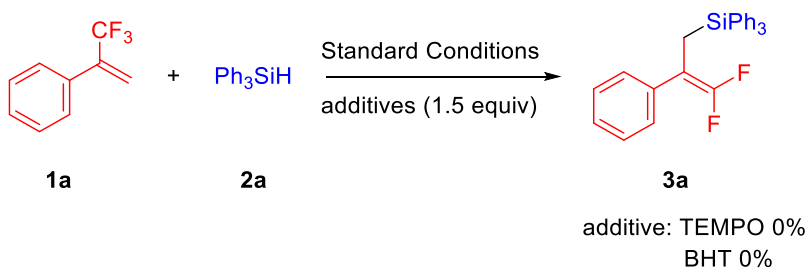
According to literature report,<sup>5</sup> to a THF solution (1 mL) of (3,3-difluoro-2-(4-phenoxyphenyl)allyl)dimethyl(phenyl)silane (**4h**) (76.4 mg, 0.2 mmol) and  $\text{H}_2\text{O}$  (3.0 equiv, 0.6 mmol) was added TBAF (0.6 mL, 1 M in THF, 0.6 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 10 minutes and then continued to stir at 65 °C for 2 hours. The reaction mixture was concentrated under vacuo, and the residue was purified by flash chromatography (petroleum ether as the eluent) using silica to afford colorless oil **6** (19.7 mg, 80% yield).



**1-(3,3-Difluoroprop-1-en-2-yl)-4-phenoxybenzene (6):** colorless oil (19.7 mg, 80%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 8.7$  Hz, 2H), 7.27 (dd,  $J = 8.6, 7.3$  Hz, 2H), 7.10 – 7.01 (m, 1H), 6.97 – 6.87 (m, 4H), 6.28 (t,  $J = 55.3$  Hz, 1H), 5.56 (d,  $J = 28.3$  Hz, 1H);  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.03 (d,  $J = 55.3$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.34, 159.10, 143.68 (t,  $J = 20.2$  Hz), 132.30, 130.90, 126.17, 121.77, 120.93, 120.74 (t,  $J = 9.6$  Hz), 118.10, 115.72. HRMS (EI): Calcd for  $\text{C}_{15}\text{H}_{13}\text{F}_2\text{O}$   $[\text{M}+\text{H}]^+$  247.2613, found 247.2611.

## 6. Additional Experiments to Elucidate the Mechanism

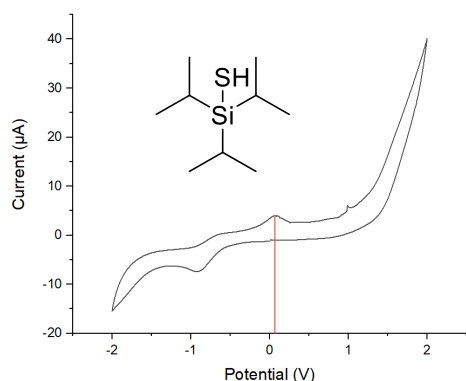
### 6.1 Radical Inhibition Experiments



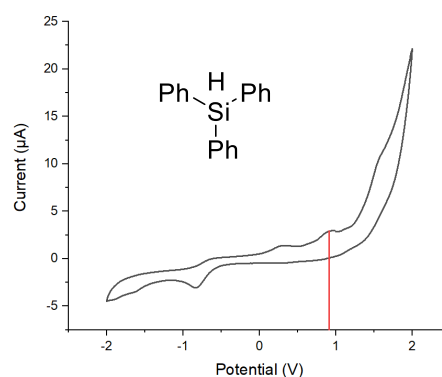
The radical initiator, TEMPO or BHT, can totally inhibit the formation of product, **3a**, thus supporting a radical-based mechanism.

## 6.2 Cyclic Voltammetry Experiments

Cyclic Voltammograms were collected using a Vertex. C. EIS (Ivium Technologies BV, Netherlands) with a typical three-electrode cell which contained 0.5 M sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) aqueous solution ( $\text{pH} \approx 7$ ) as electrolyte. The KCl-saturated Ag/AgCl and Pt net were used as the reference electrode and counter electrode, respectively. Sample 0.01 M and tetrabutylammonium tetrafluoroborate 0.1 M in ethyl acetate were used for tests. Measurements were performed using glassy carbon working electrode, platinum wire counter electrode, and KCl-saturated Ag/AgCl reference electrode in a scan rate of 0.1 V/s.



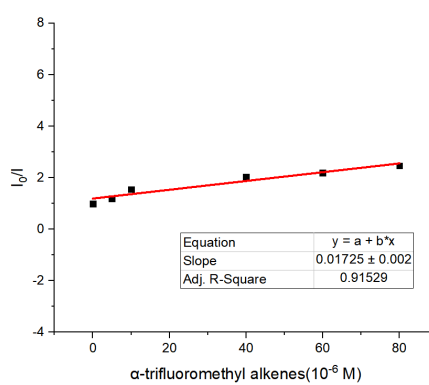
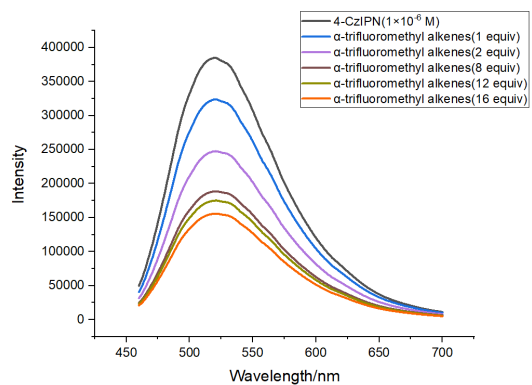
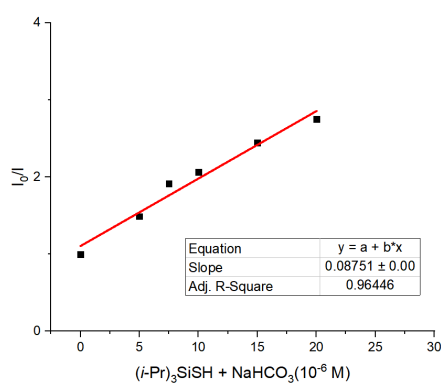
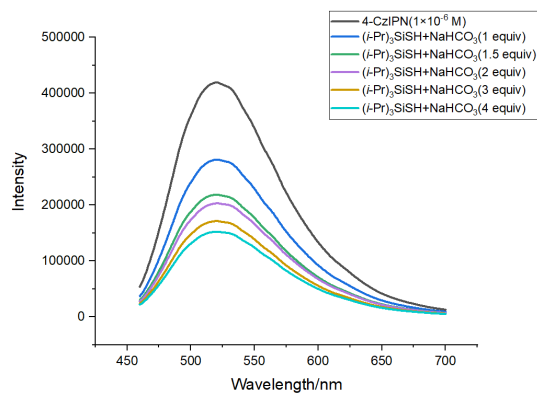
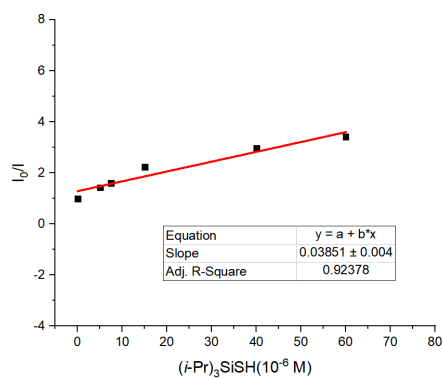
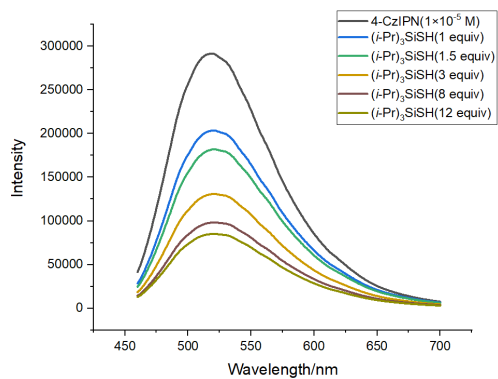
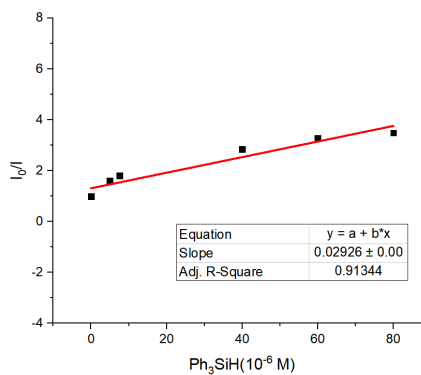
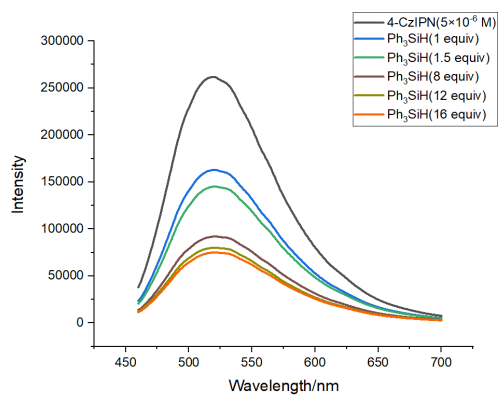
$E^{\text{ox}} = +0.07 \text{ V vs SCE in EA}$



$E^{\text{ox}} = +0.93 \text{ V vs SCE in EA}$

## 6.3 Stern-Volmer Fluorescence Quenching Experiments

In a typical experiment, a solution of 4CzIPN in anhydrous reaction solvent (EtOAc) ( $5.0 \times 10^{-6}$  M) was added with an appropriate amount of quencher in a quartz cuvette. Then the emission of the sample was collected. The emission intensity was collected with excited wavelength of photocatalysts, respectively.



## 6.4 Quantum Yield Measurement

Determination of the light intensity at 470 nm: Following Yoon's protocol,<sup>6</sup> the photon flux of the

spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H<sub>2</sub>SO<sub>4</sub>. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub>. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at  $\lambda = 470$  nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq (1).

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \epsilon} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline,  $\Delta A$  is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and  $\epsilon$  is the molar absorptivity at 510 nm (11,100 L mol<sup>-1</sup> cm<sup>-1</sup>). The photon flux can be calculated using eq (2).

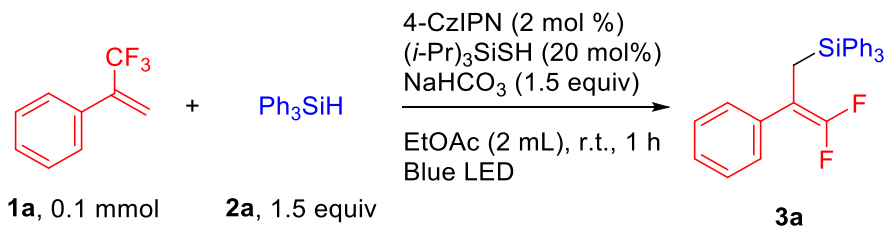
$$\text{Photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} \quad (2)$$

Where  $\Phi$  is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at  $\lambda = 468$  nm),<sup>7</sup> t is the time (90.0 s), and f is the fraction of light absorbed at  $\lambda = 470$  nm (0.14, vide infra).<sup>8</sup> The photon flux was calculated (average of three experiments) to be  $3.22 \times 10^{-8}$  einstein s<sup>-1</sup>.

$$\text{mol Fe}^{2+} = \frac{0.00235 \text{ L} \cdot 1.76}{1.000 \text{ cm} \cdot 11100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 3.73 \times 10^{-7} \text{ mol}$$

$$\text{Photon flux} = \frac{3.73 \times 10^{-7} \text{ mol}}{0.92 \cdot 90.0 \text{ s} \cdot 0.14} = 3.22 \times 10^{-8} \text{ mol}$$

#### Determination of quantum yield:



A cuvette was charged with **1a** (15  $\mu$ L, 0.1 mmol), **2a** (39 mg, 0.15mmol), 4-CzIPN (1.6 mg, 0.02



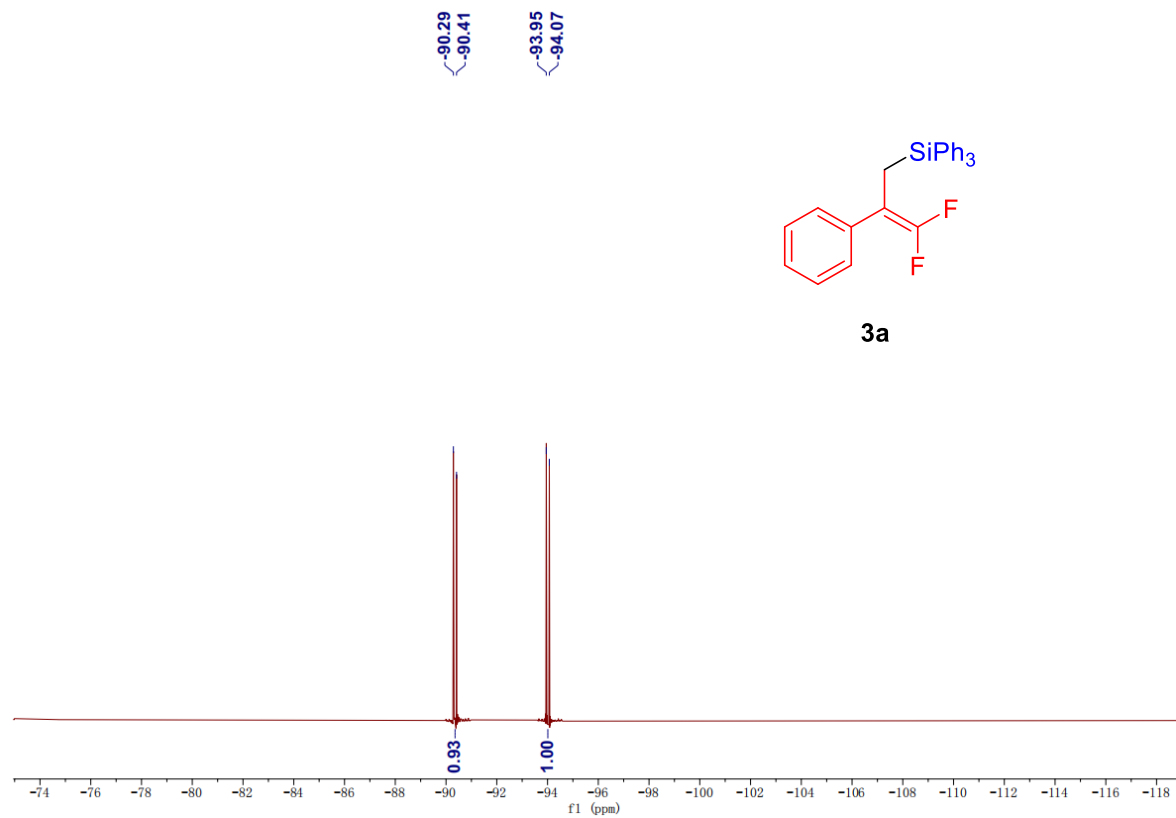
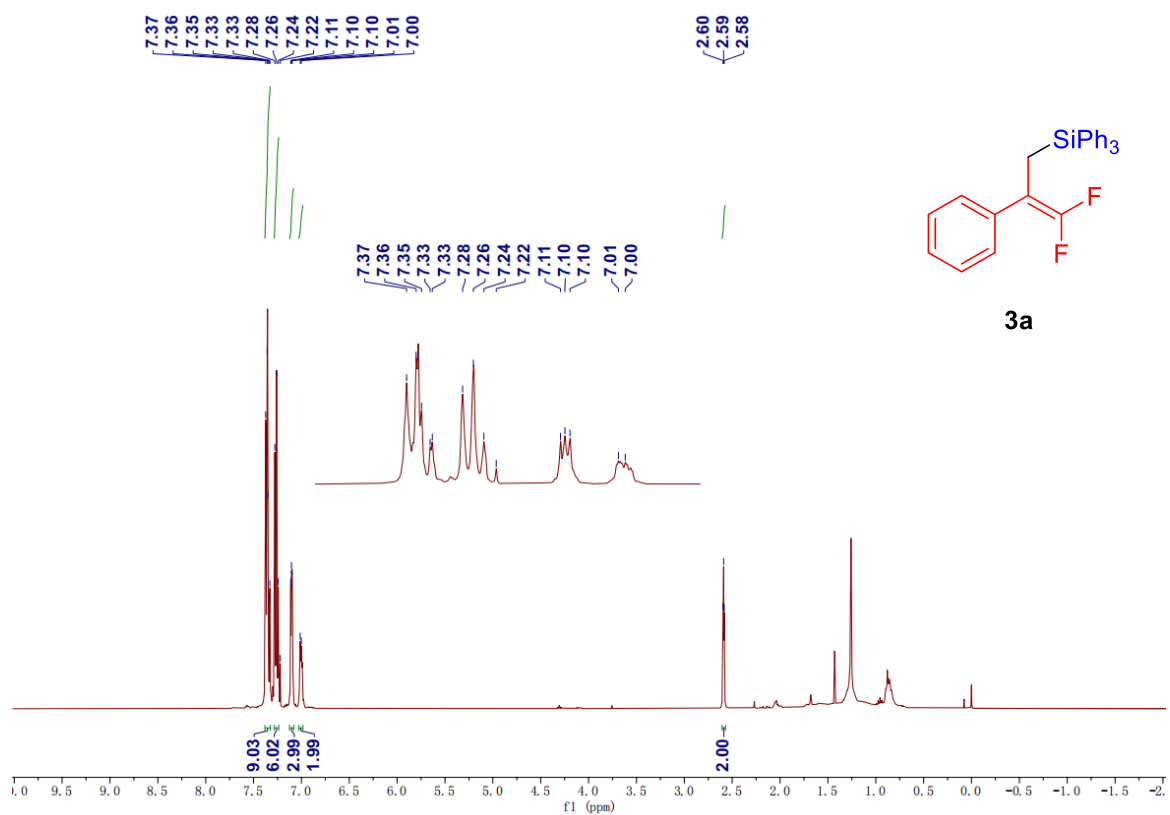
mmol, 2 mol%), NaHCO<sub>3</sub> (12.6 mg, 0.15 mmol, 1.5 equiv), (*i*-Pr)<sub>3</sub>SiSH (4 μL, 0.02 mmol, 20 mol%), and EtOAc (2 mL). The cuvette was then capped with a PTFE stopper. The sample was stirred and irradiated ( $\lambda = 470$  nm, slit width = 10.0 nm) for 3600 s (1 h). After irradiation, the solvent was removed. The yield of product formed was determined as 7% by crude <sup>1</sup>H NMR using a 1,3,5-trimethoxybenzene as the internal standard. The quantum yield was determined using eq (3). Essentially all incident light ( $f > 0.999$ , vide infra) is absorbed by the 4-CzIPN at the reaction conditions described above.  $\Phi$  (7%) = 0.07.

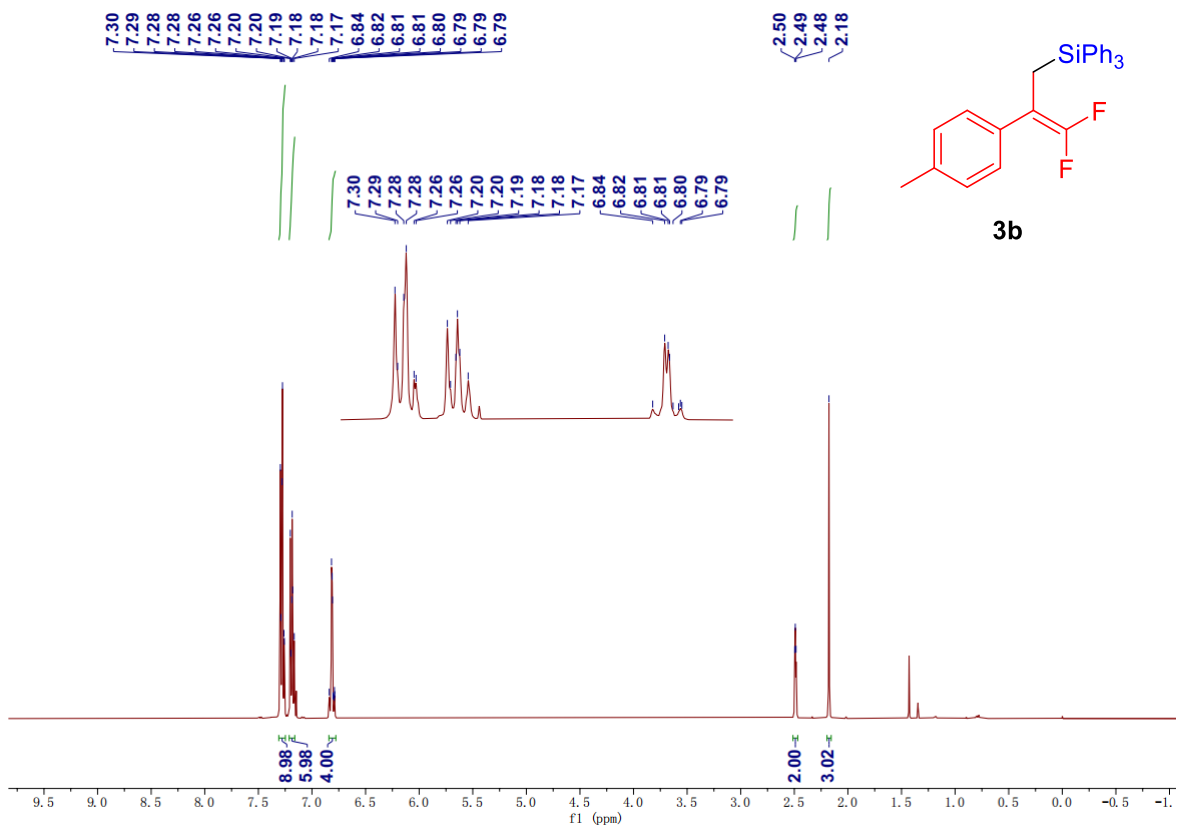
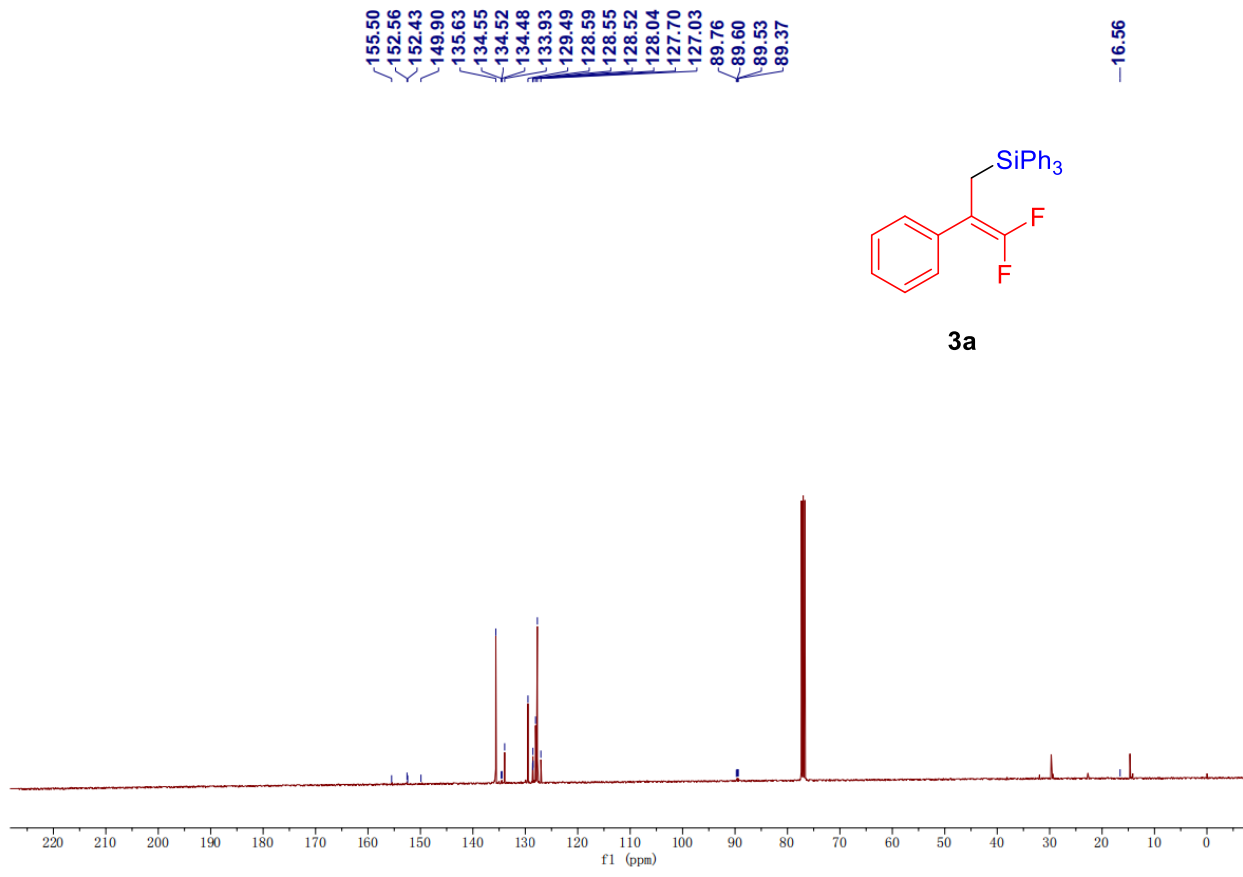
$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot t \cdot f} \quad (3)$$
$$\Phi = \frac{0.07 \times 10^{-3} \text{ mol}}{3.22 \times 10^{-8} \text{ mol} \cdot 3600 \text{ s} \cdot 1.00} = 0.07$$

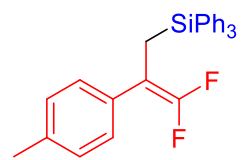
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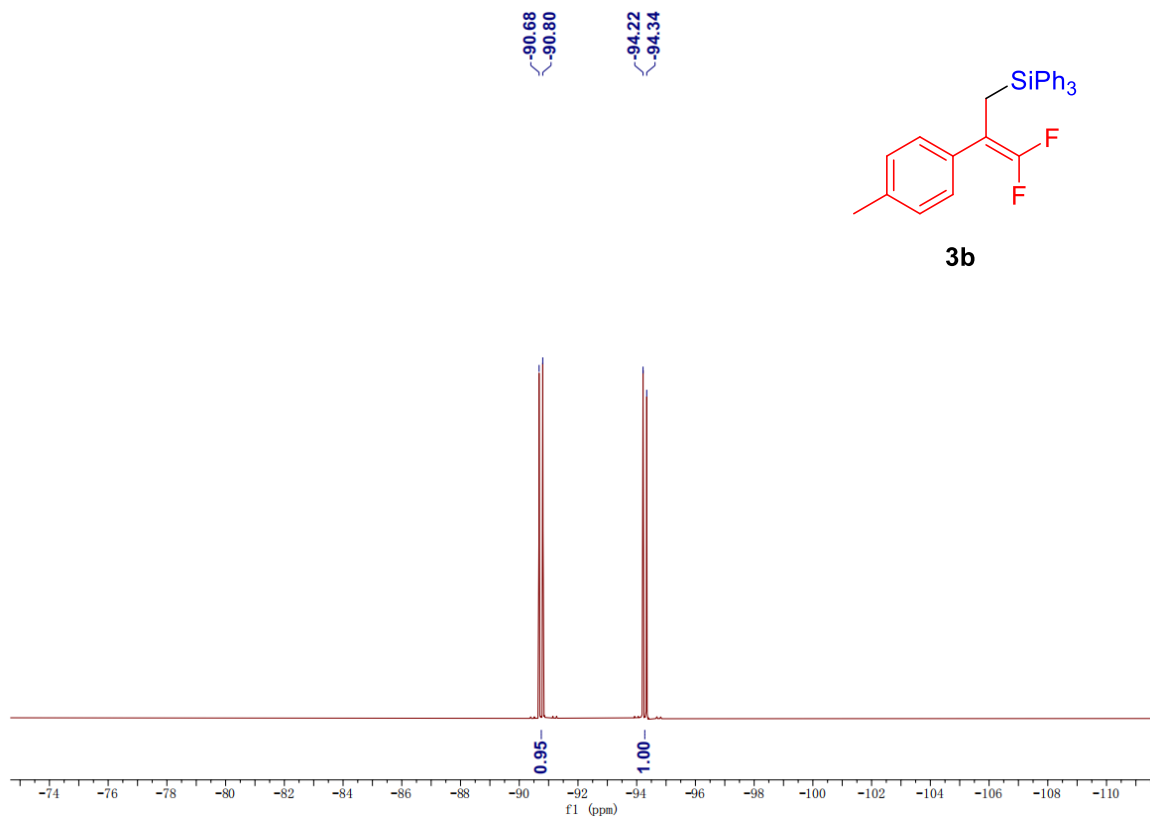
# $^1\text{H}$ , $^{19}\text{F}$ , $^{13}\text{C}$ -NMR Spectra





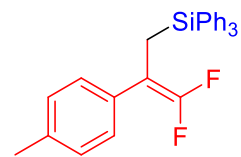


**3b**

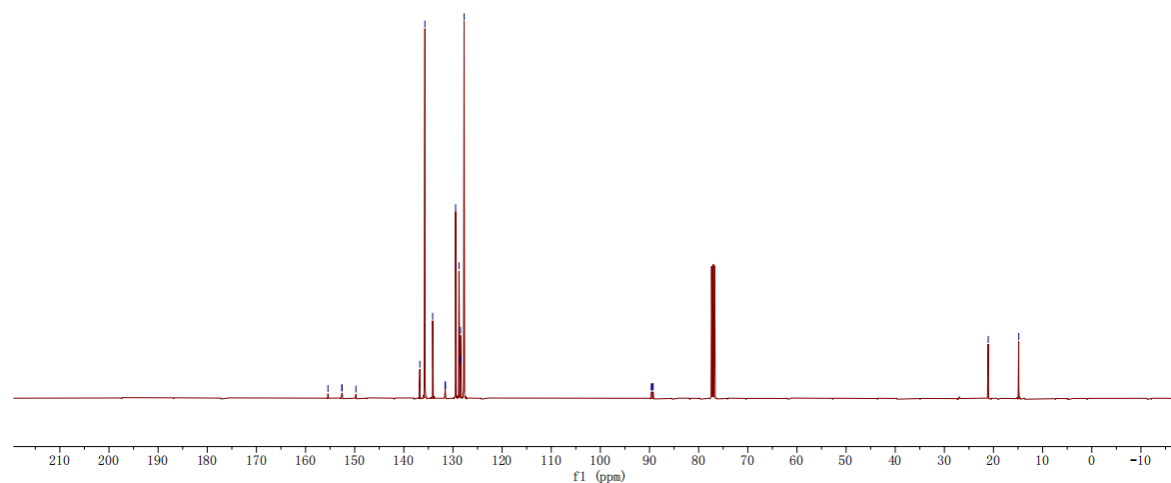


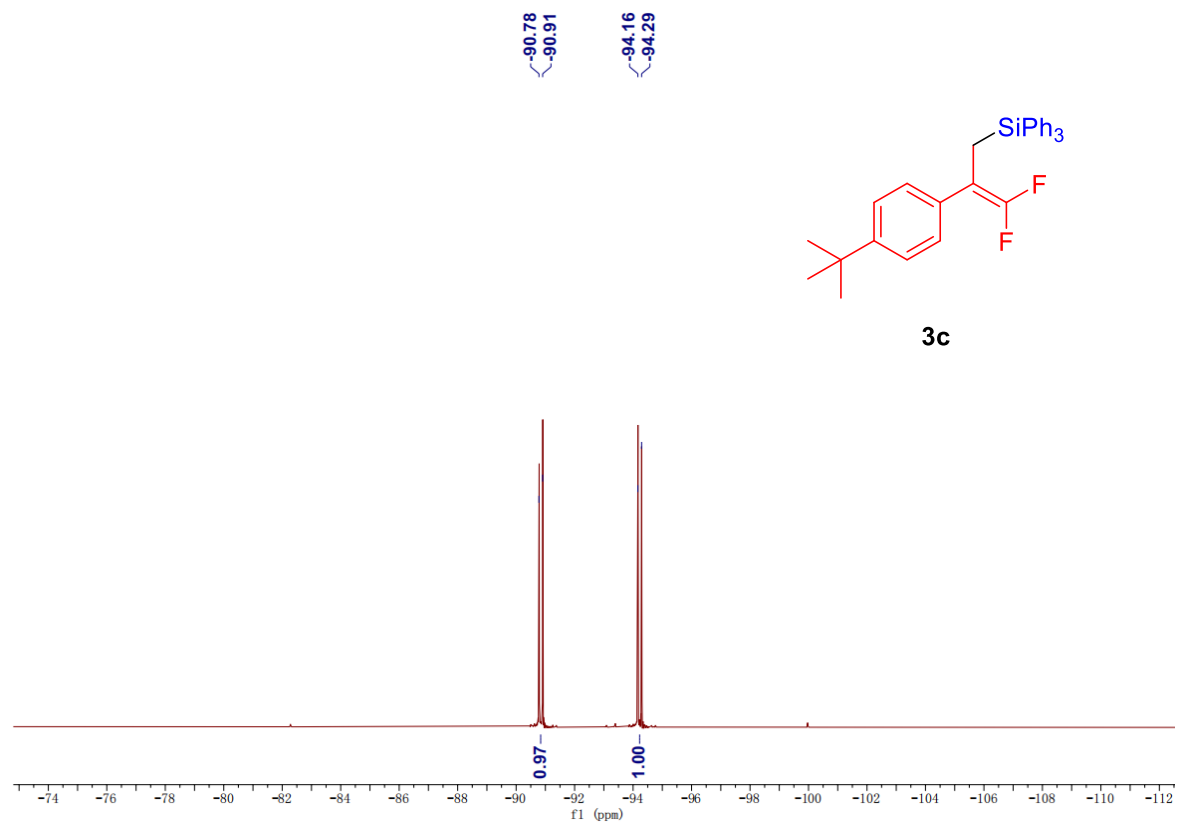
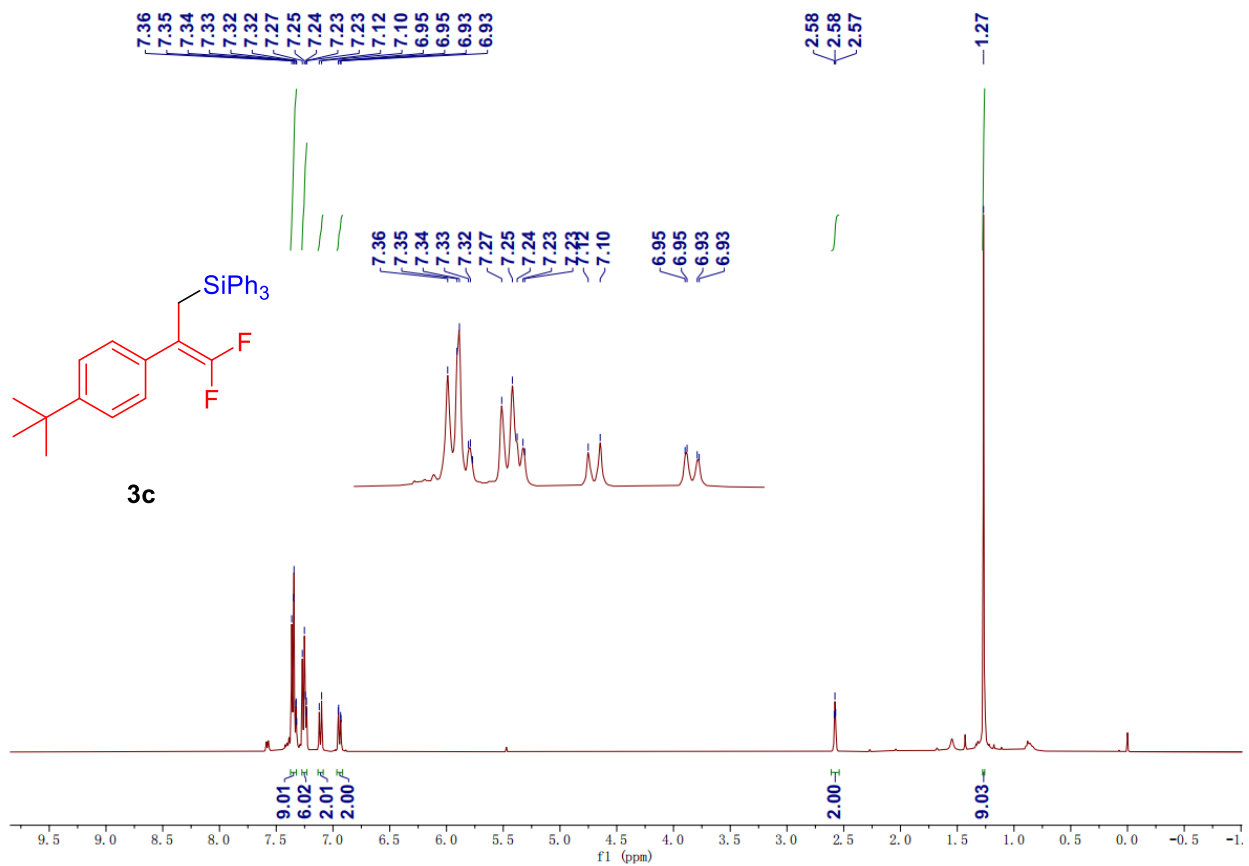
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152.60  
152.58  
149.75  
136.74  
135.71  
134.14  
131.62  
131.59  
131.57  
131.54  
129.47  
128.77  
128.50  
128.47  
128.43  
127.73  
89.65  
89.48  
89.43  
89.26

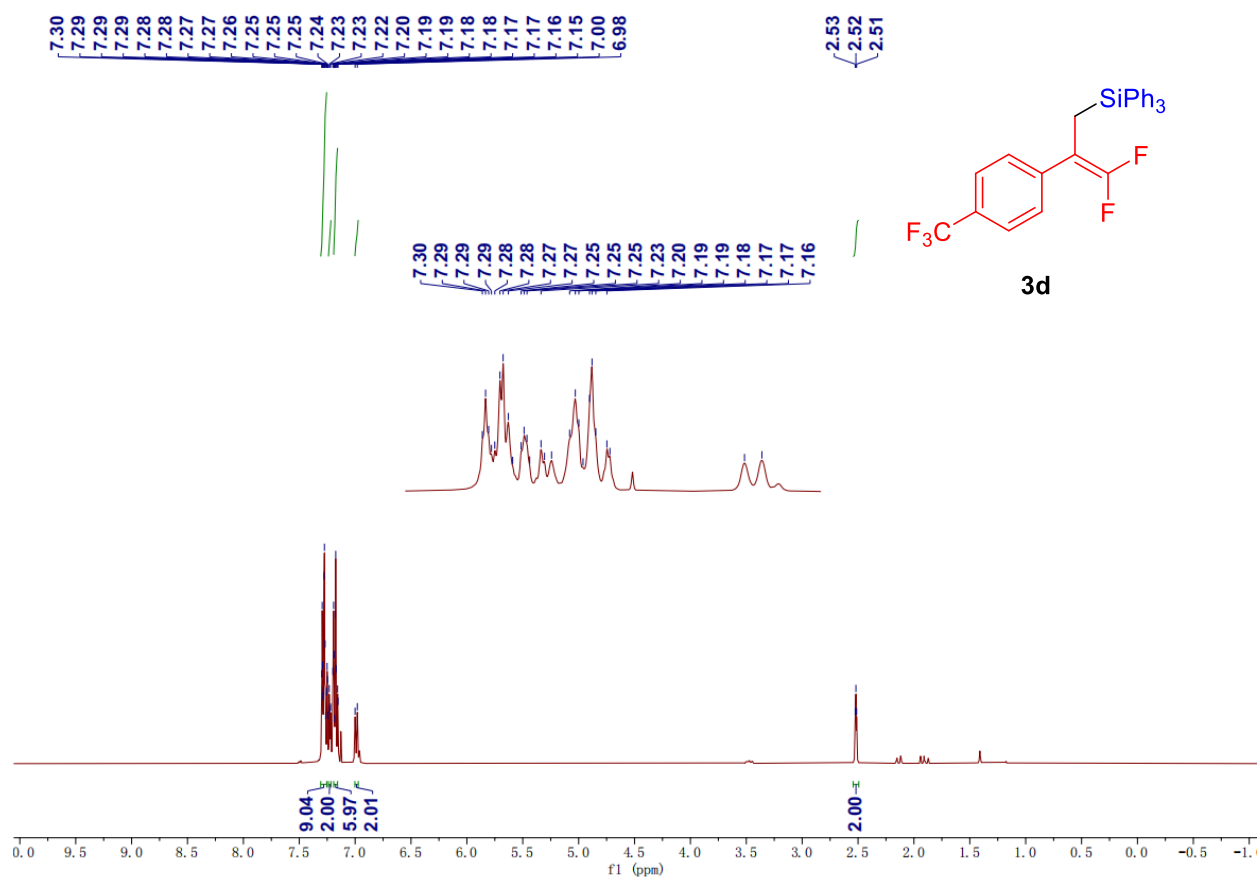
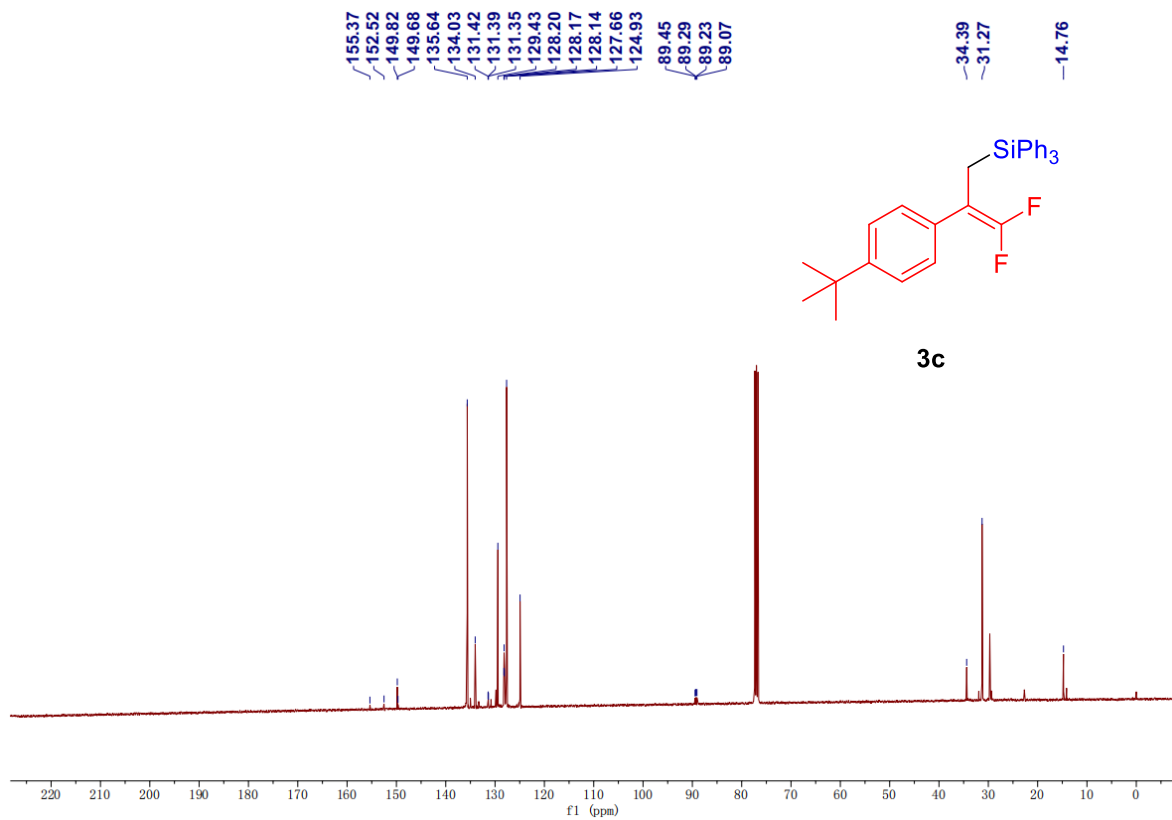
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14.87

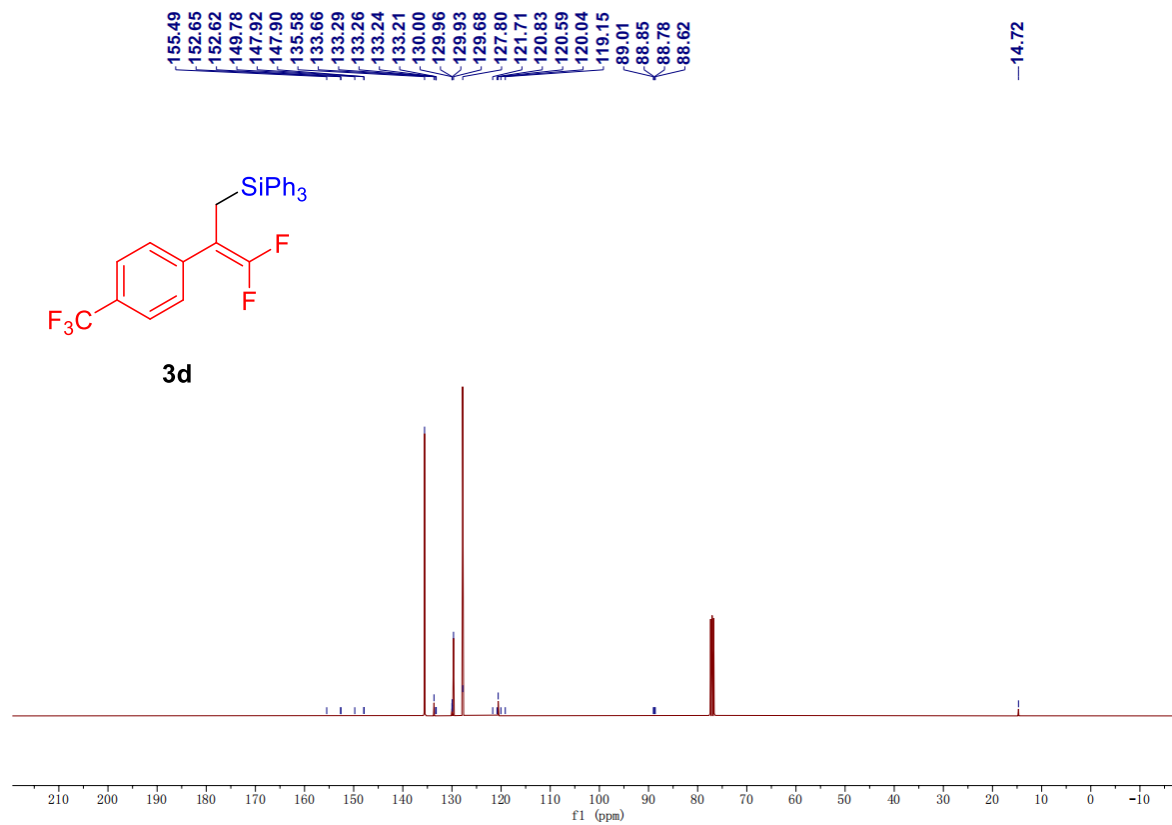
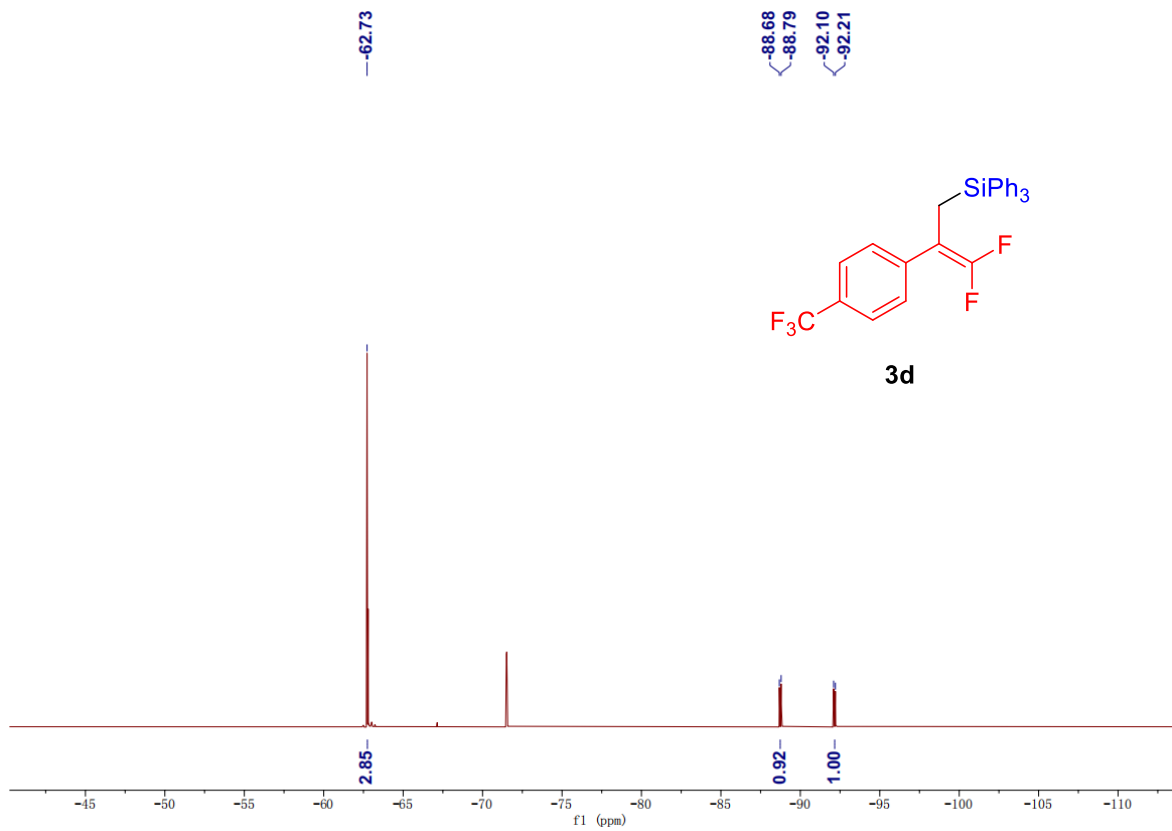


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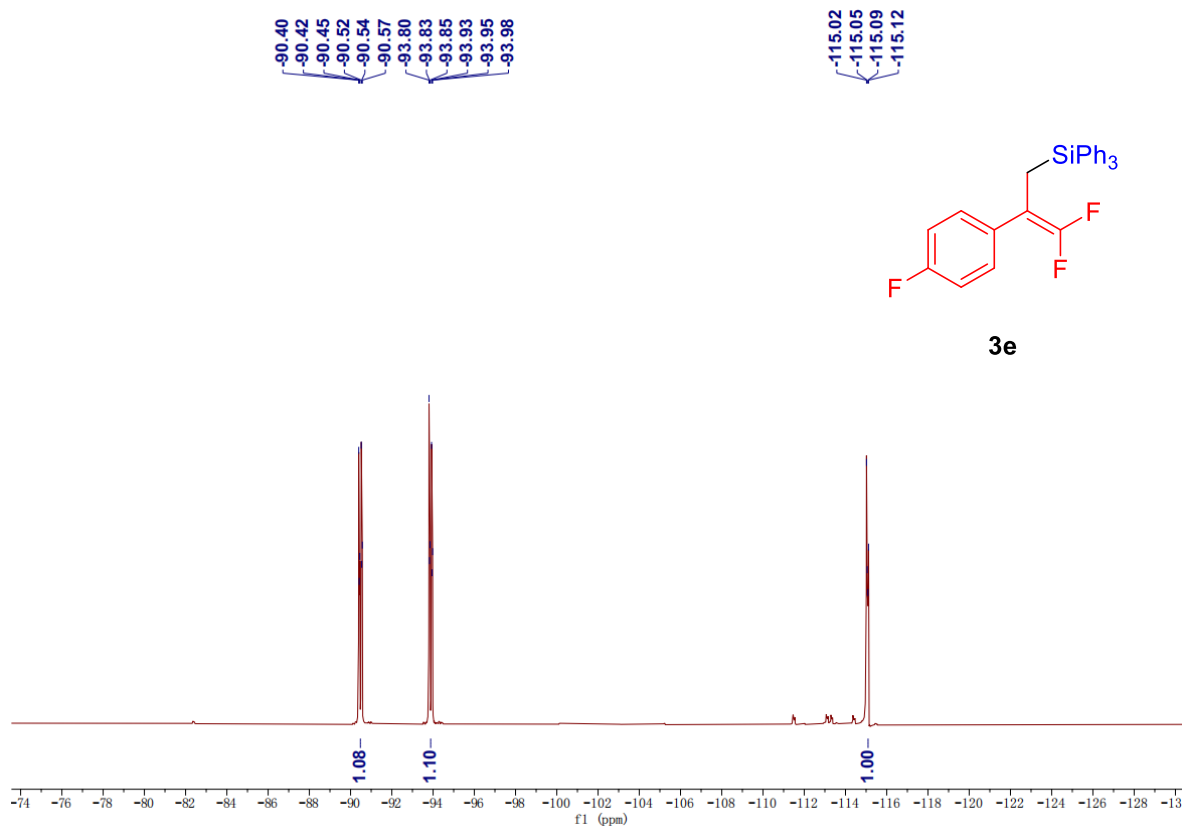
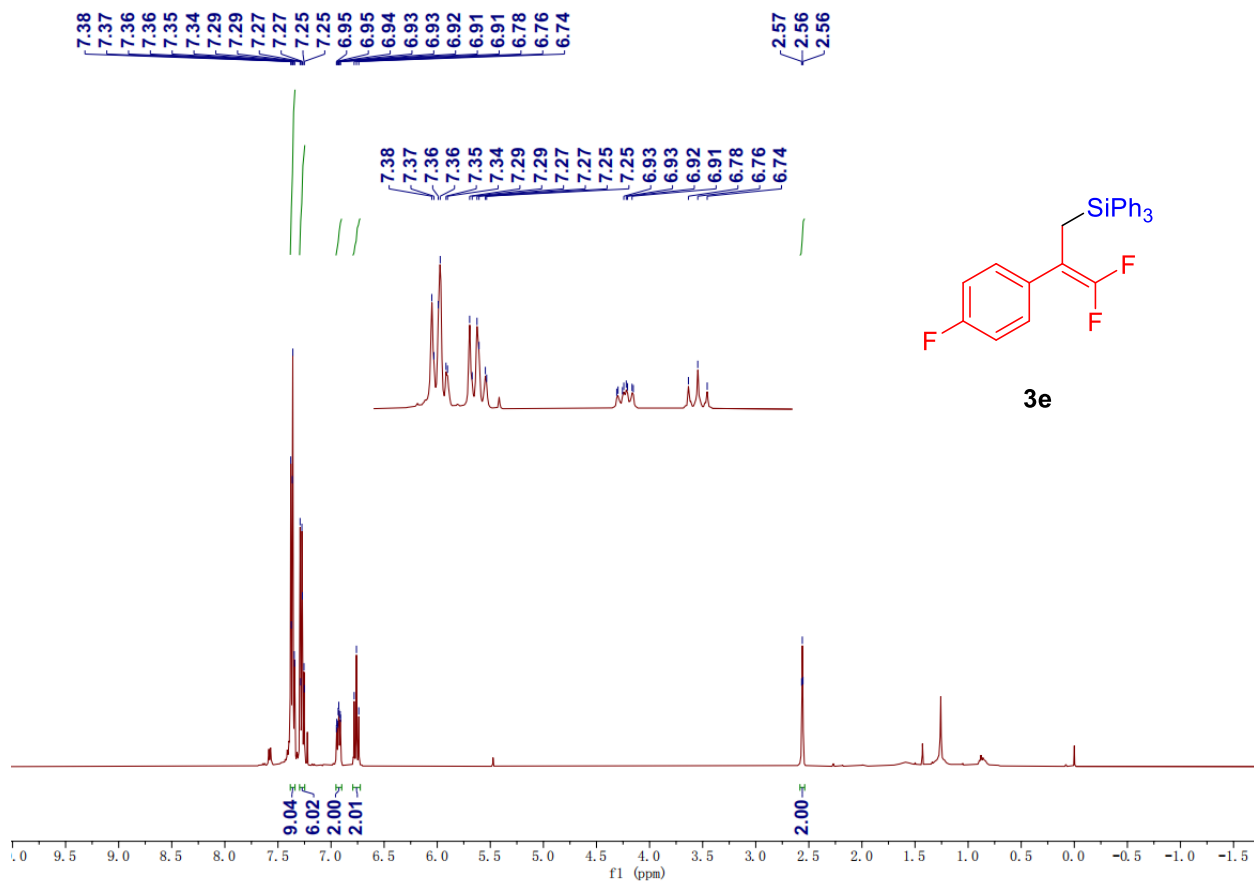


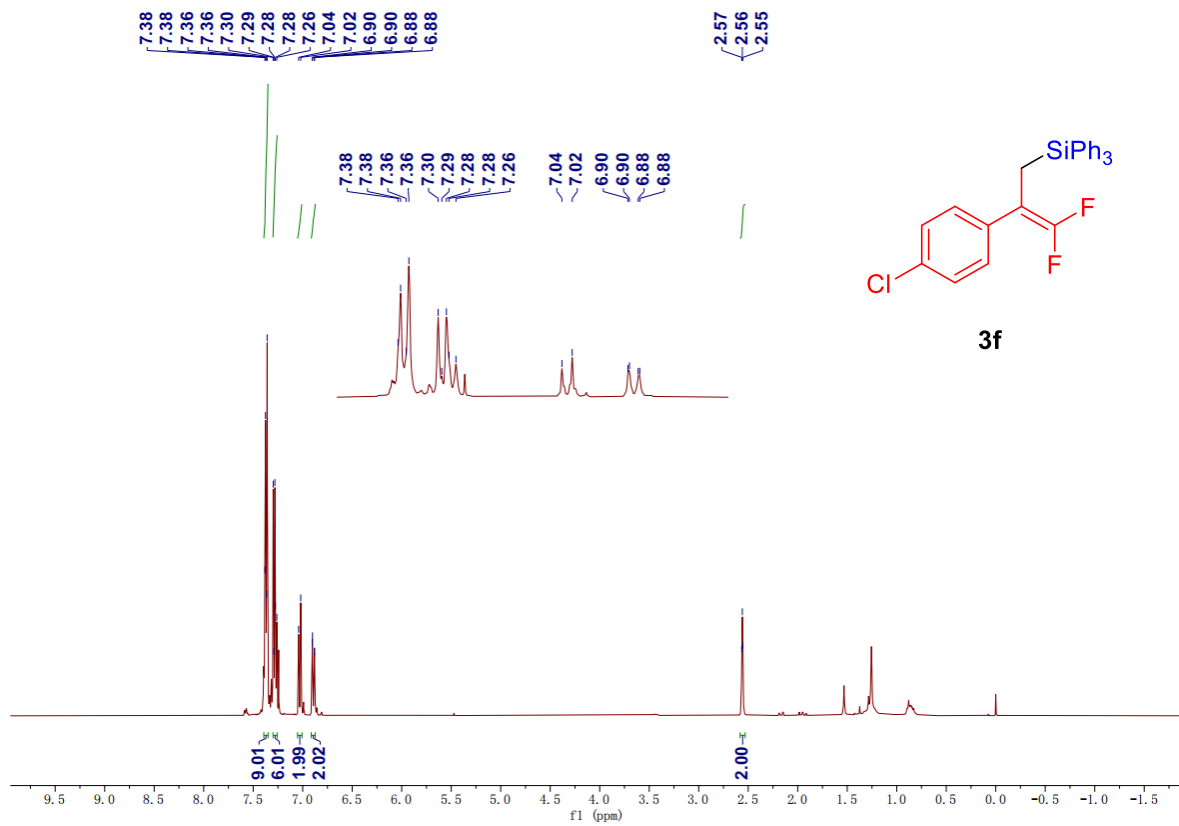
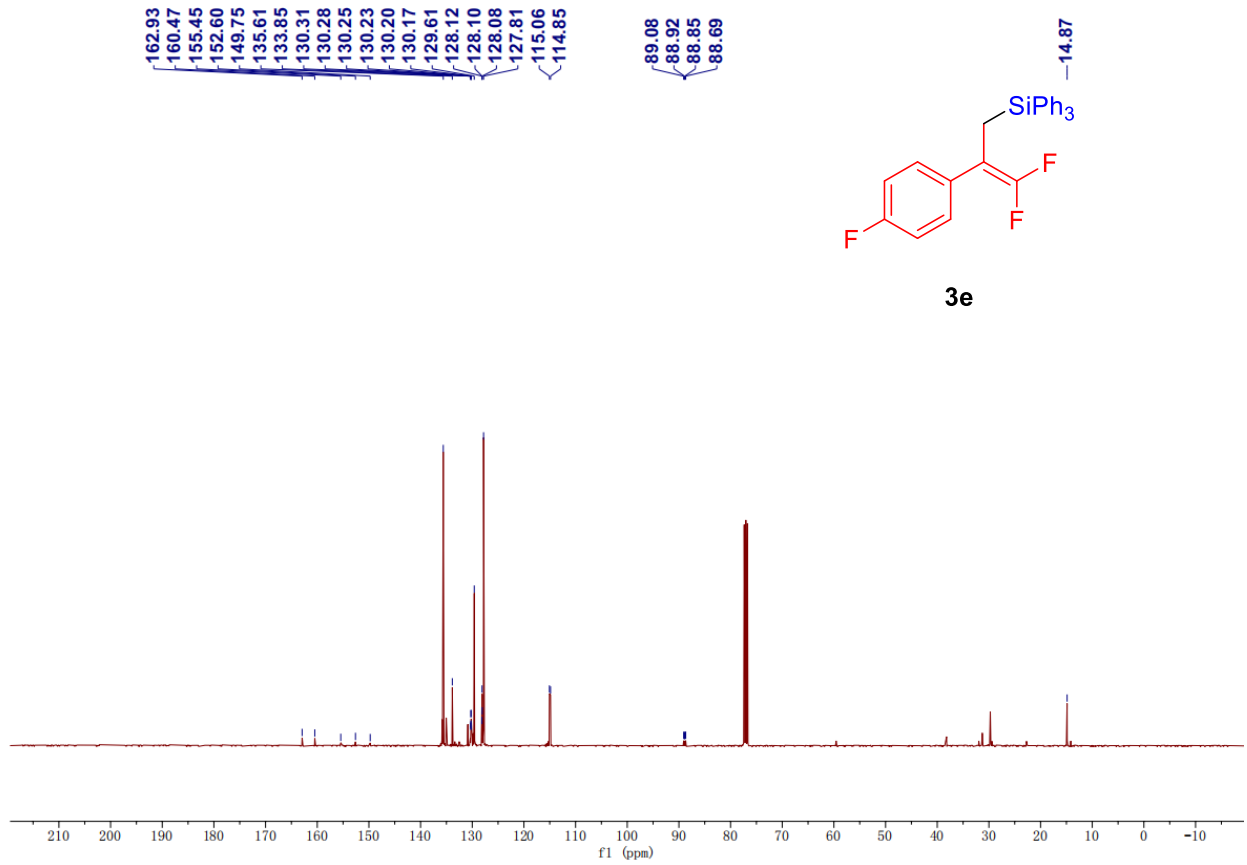


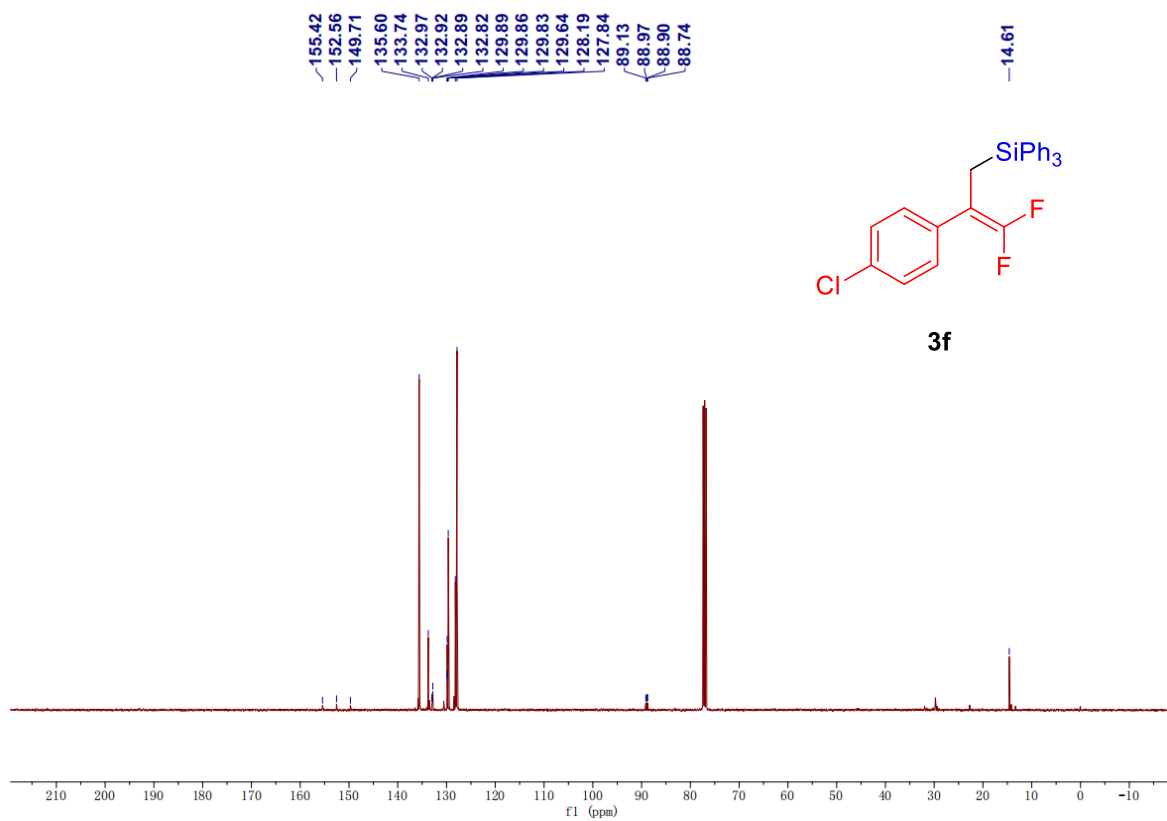
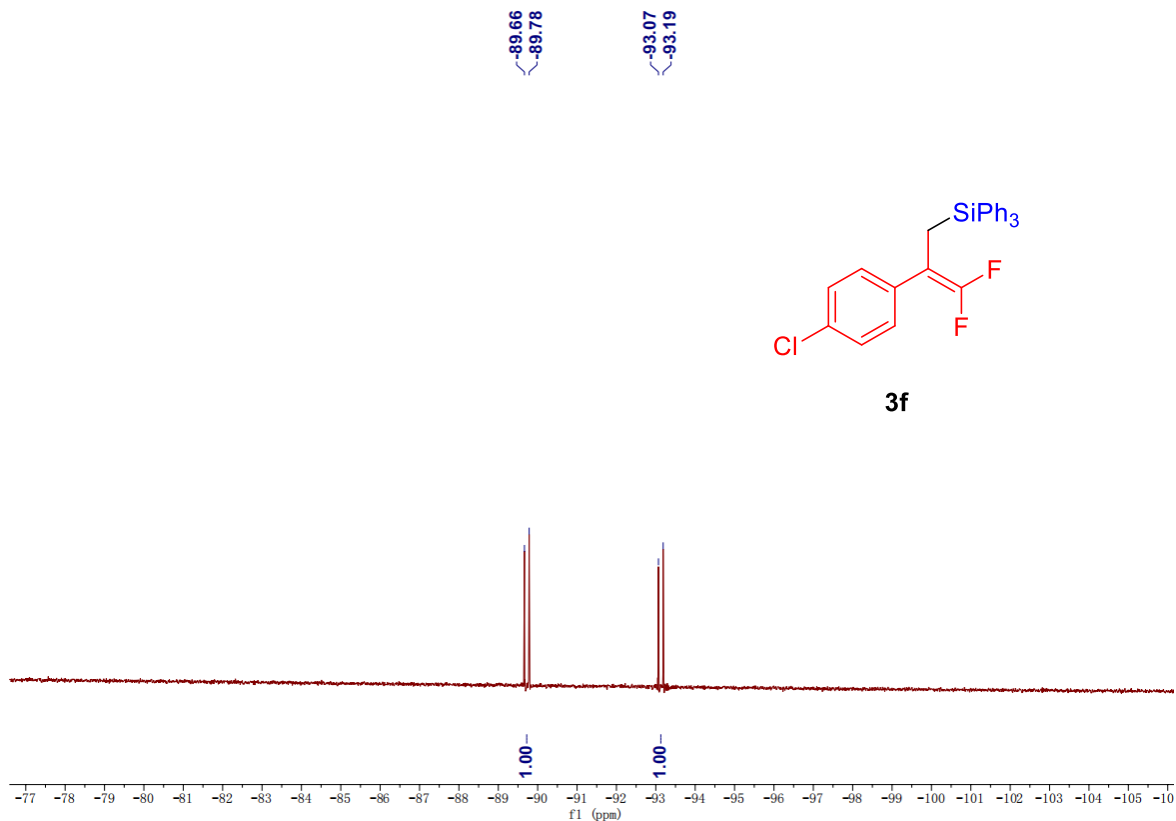


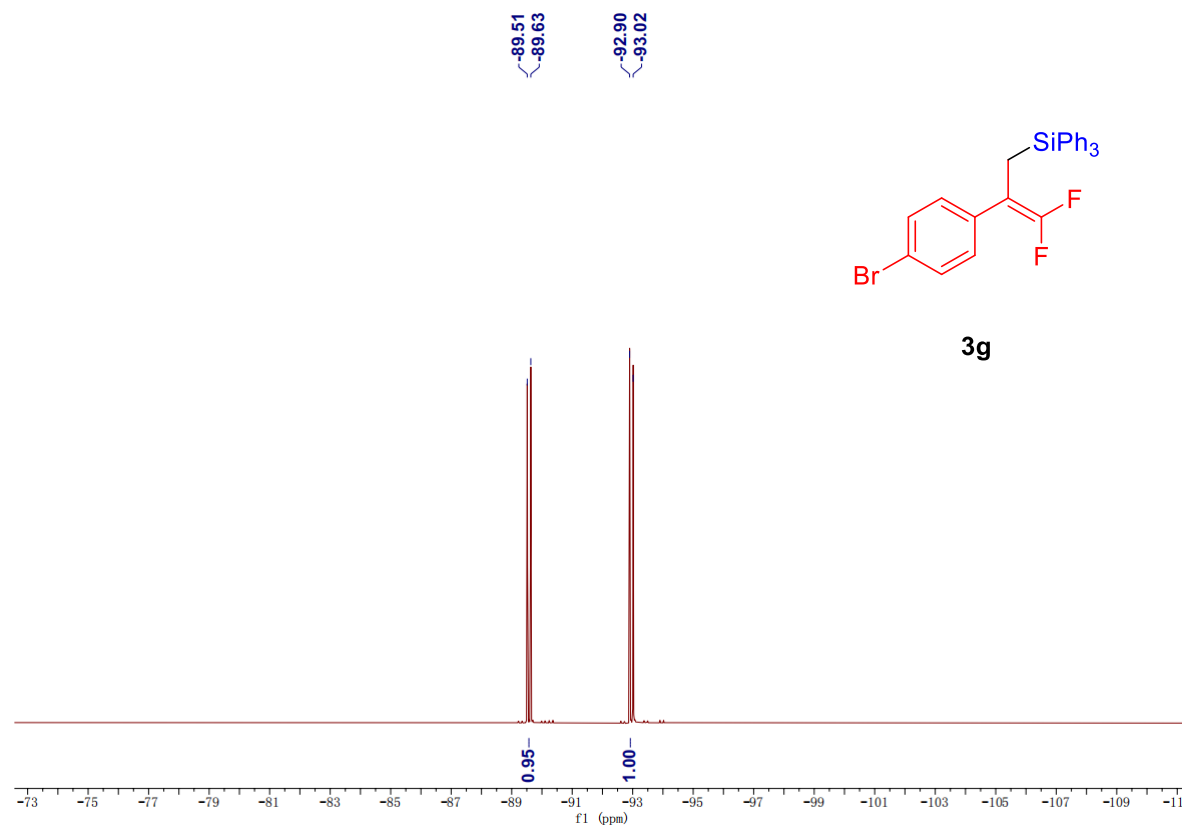
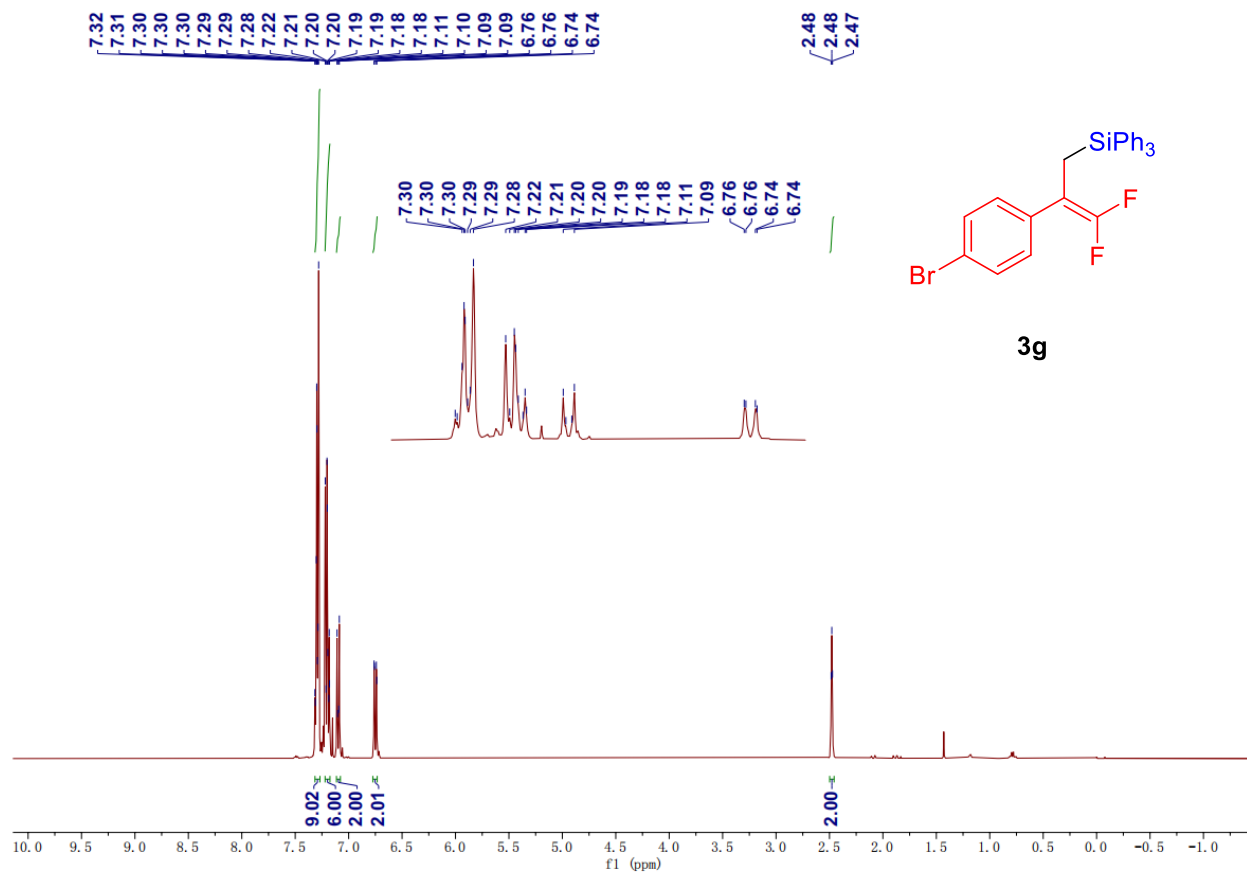


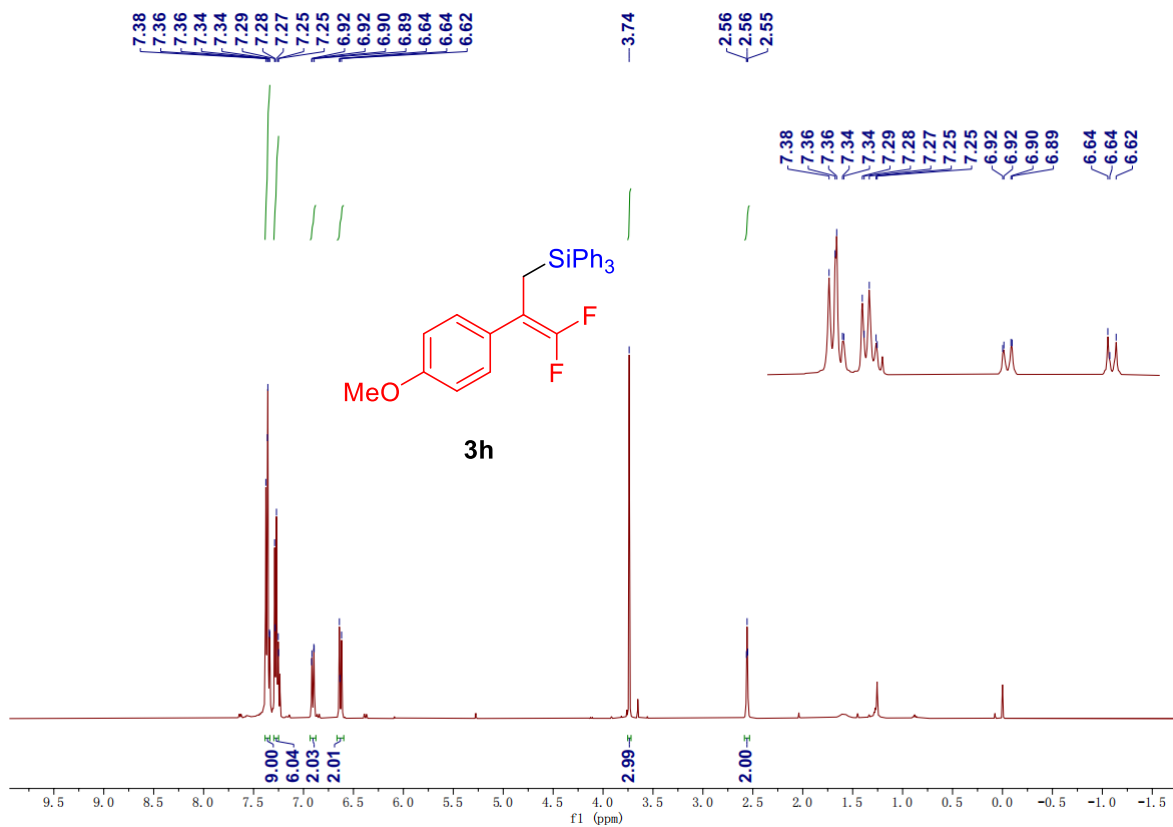
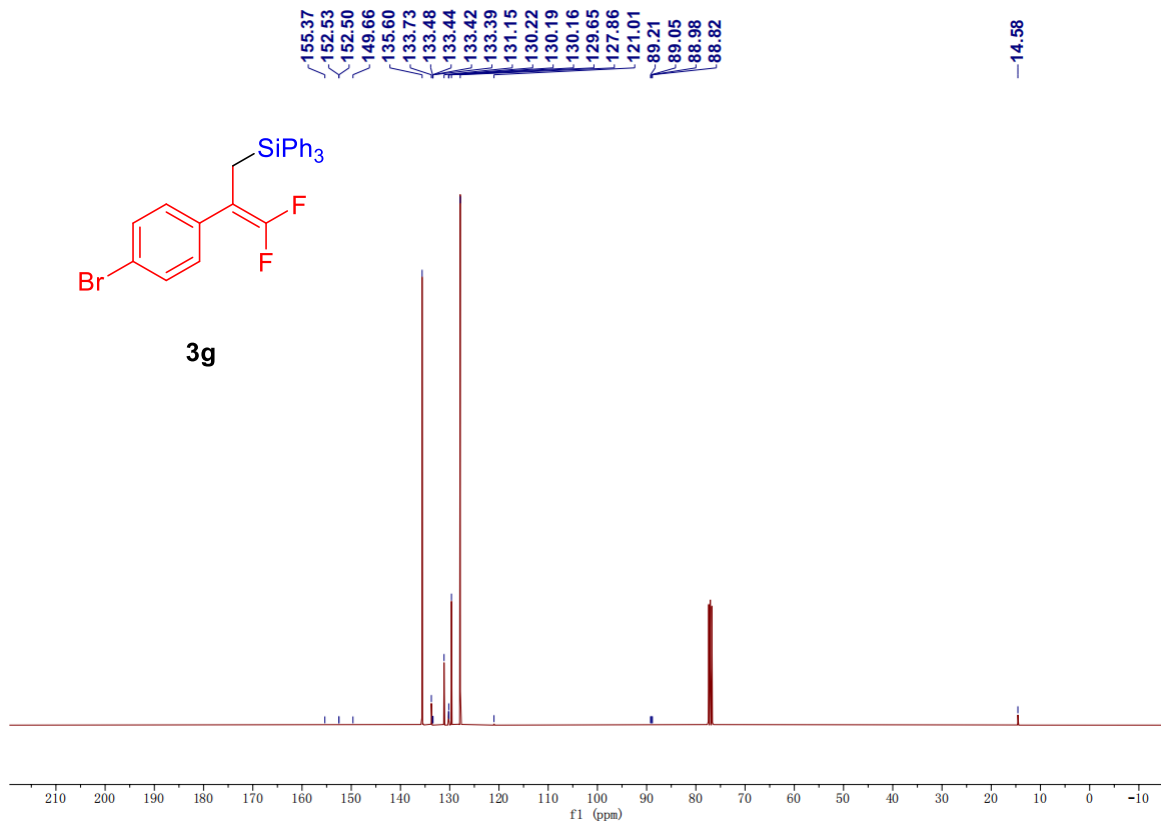


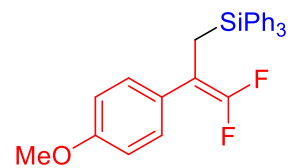




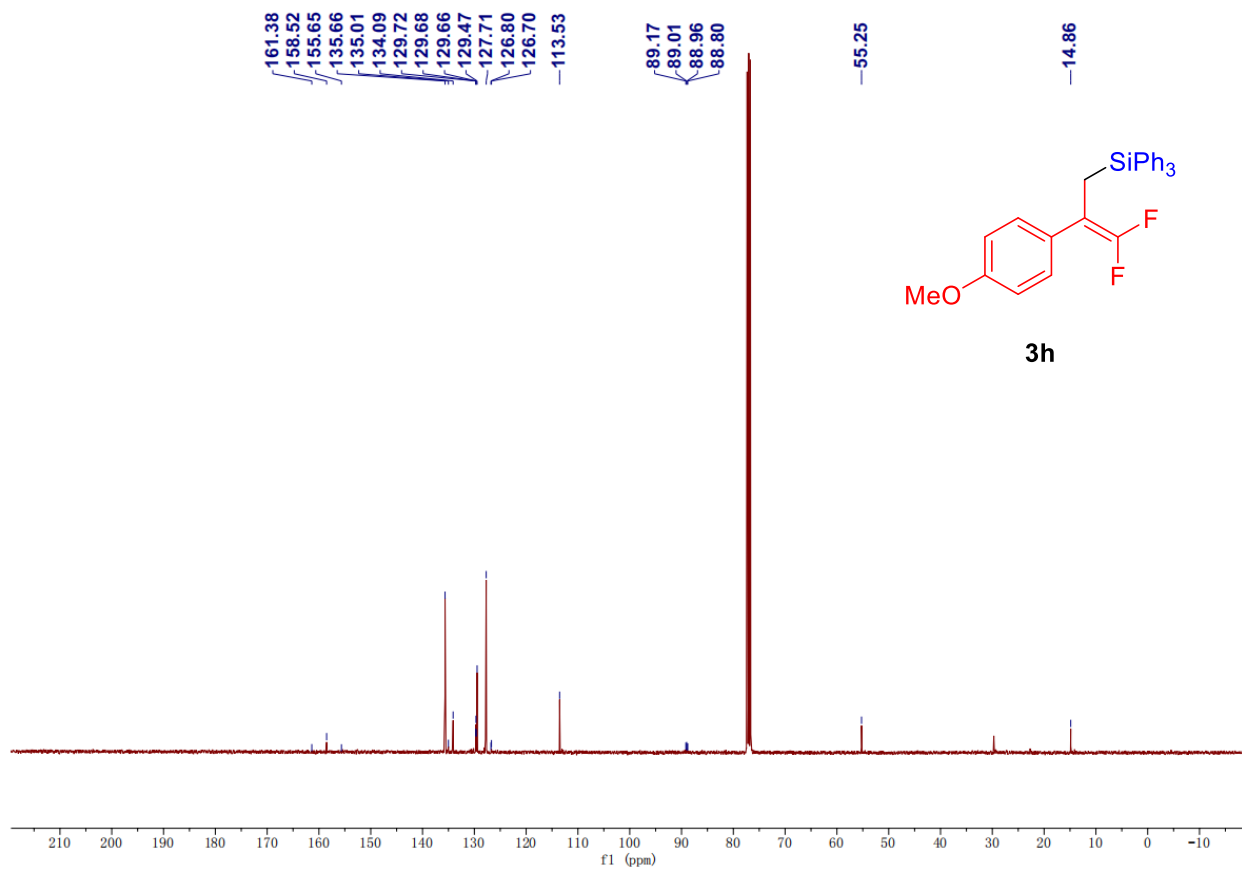
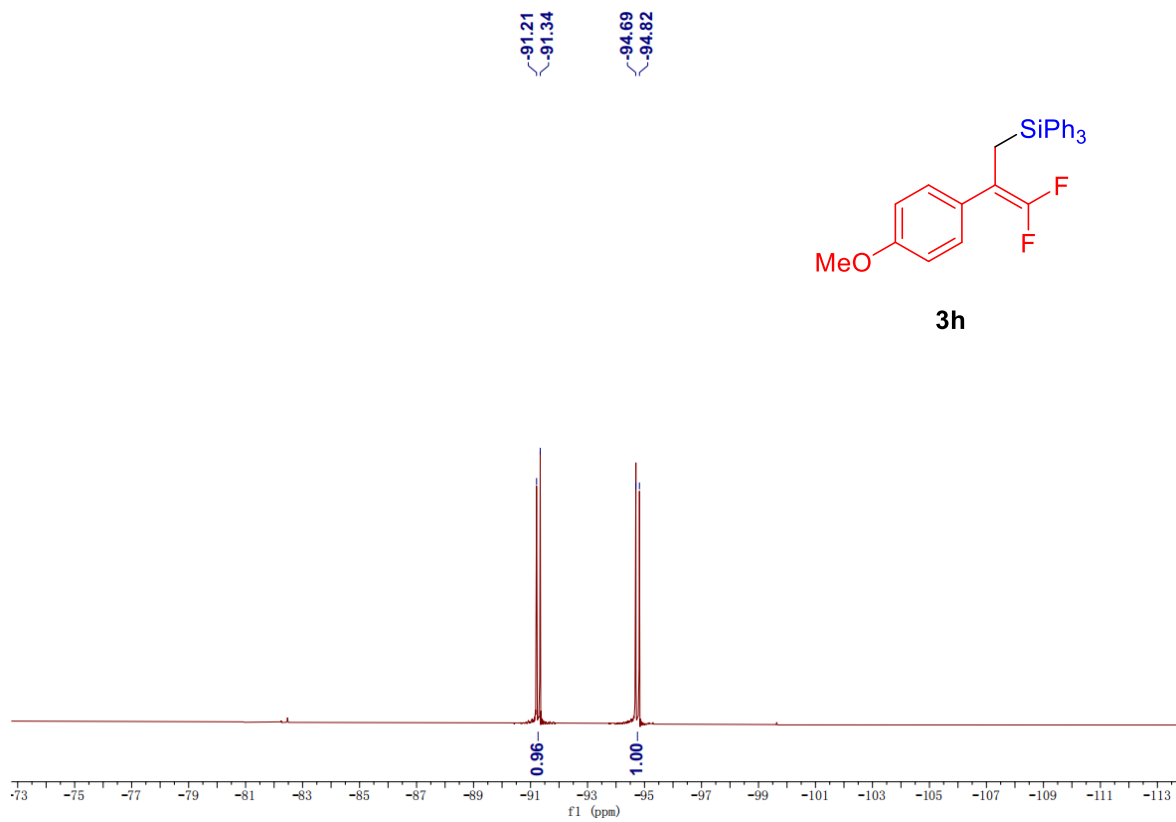


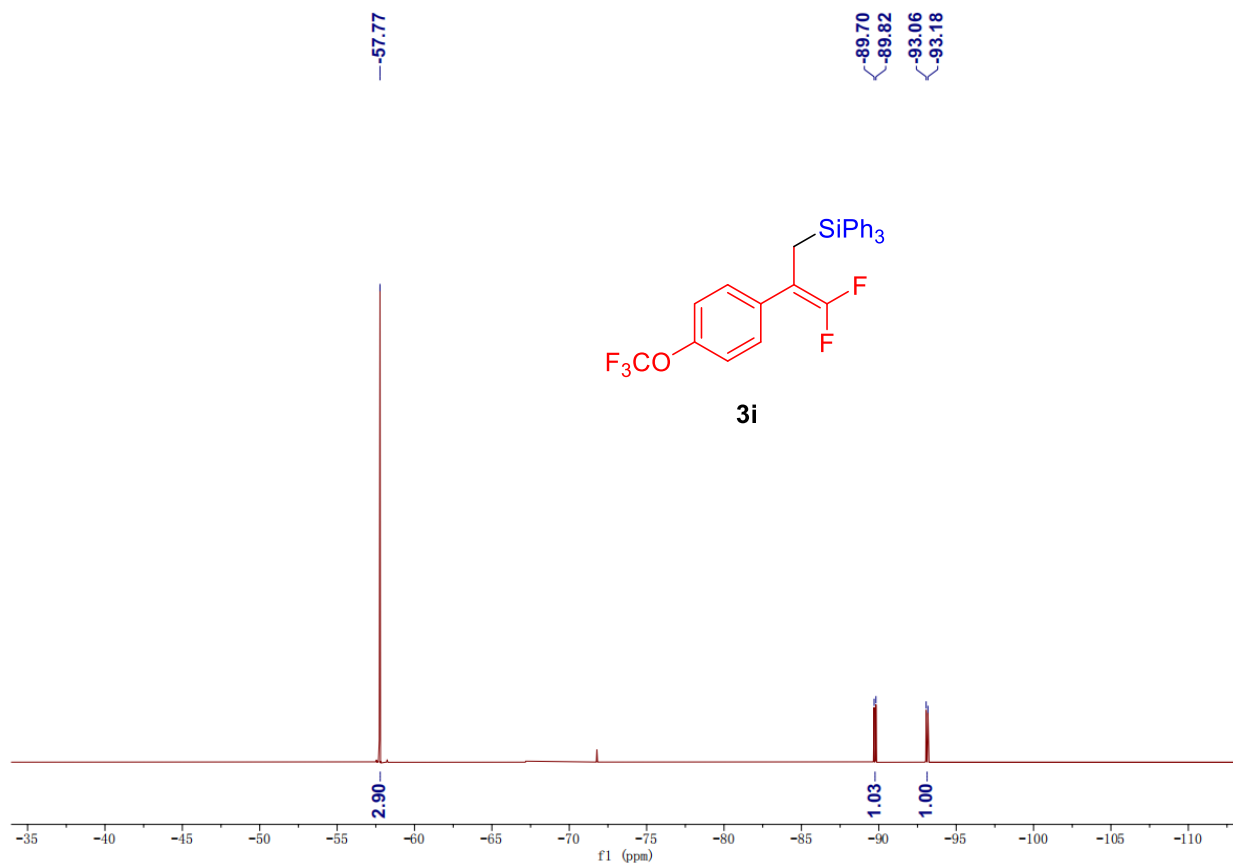
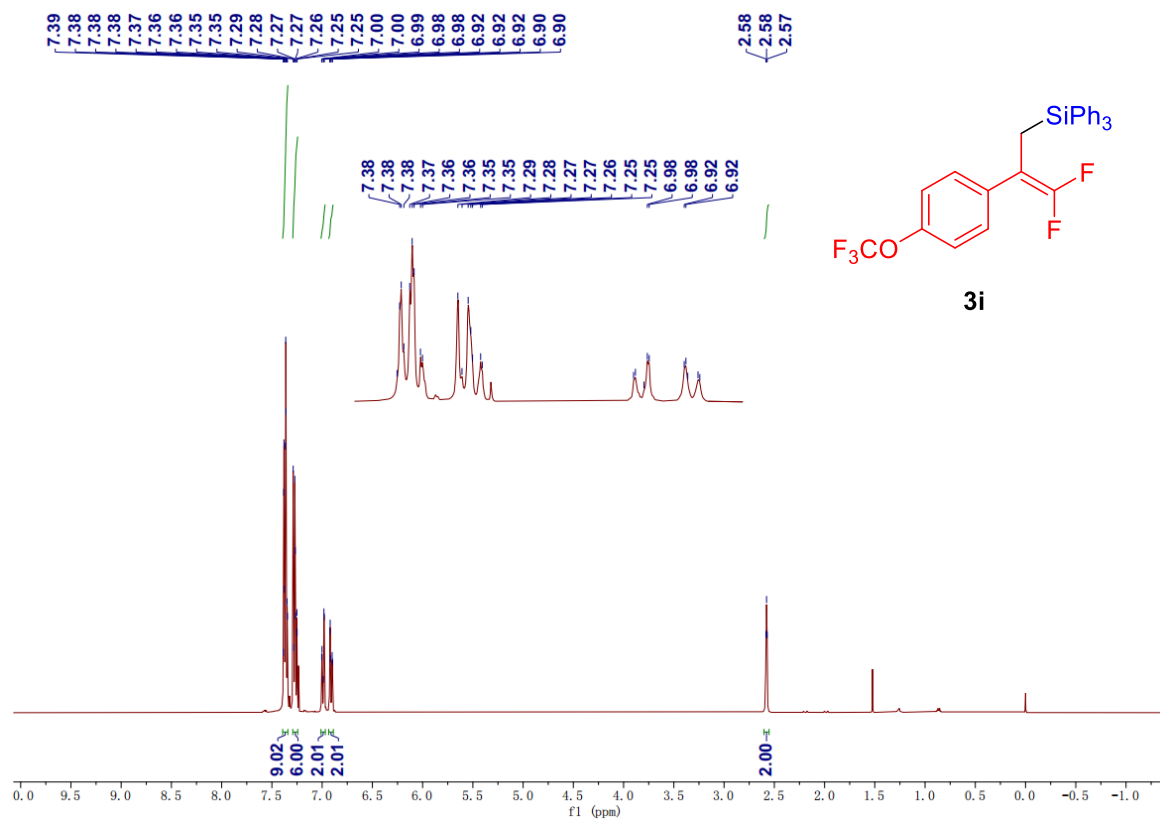


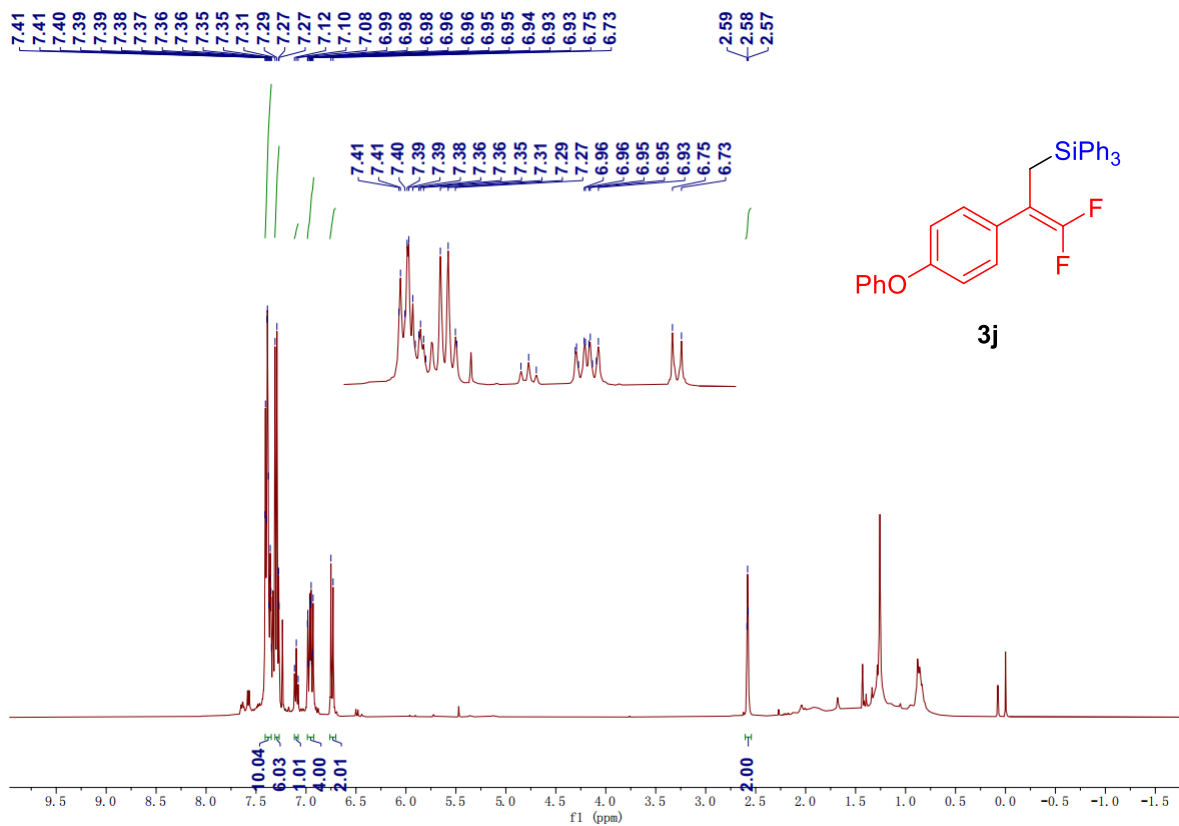
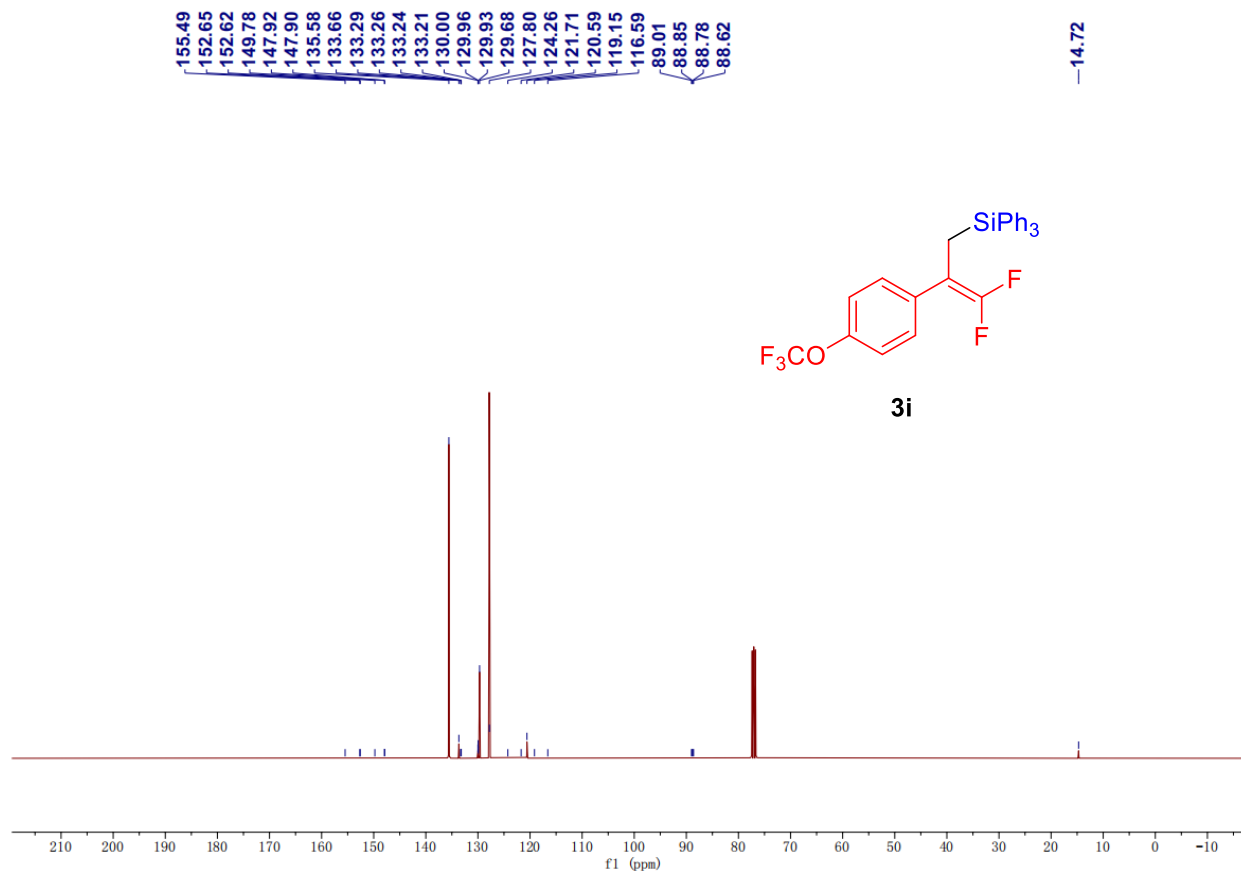




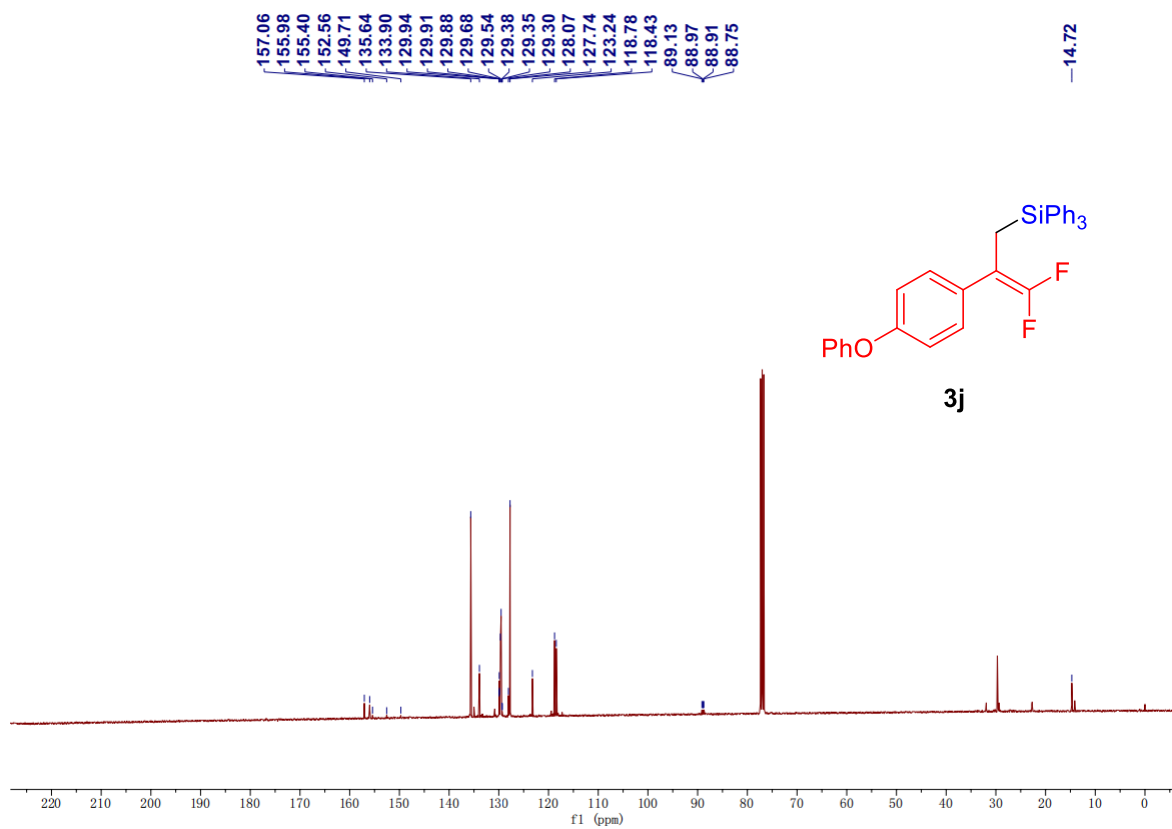
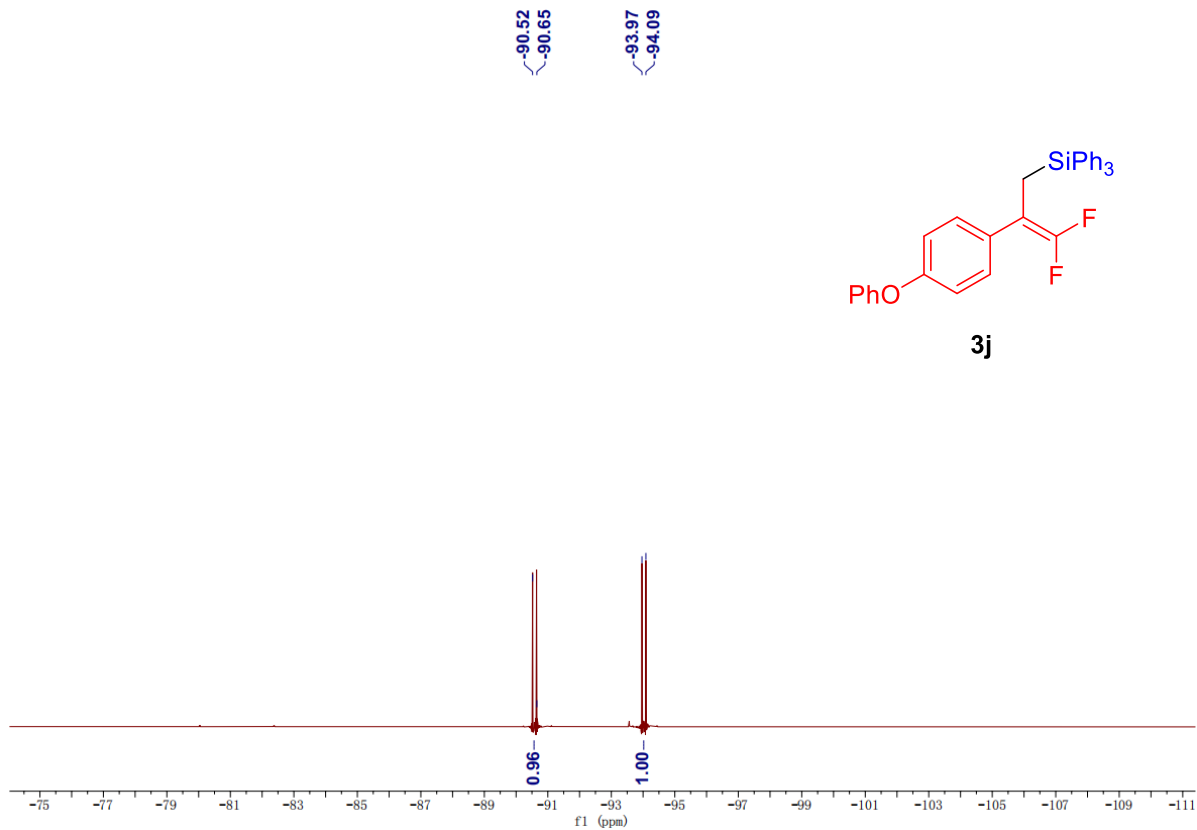
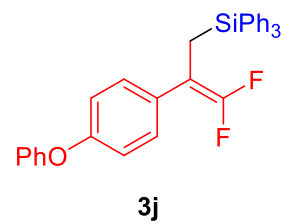
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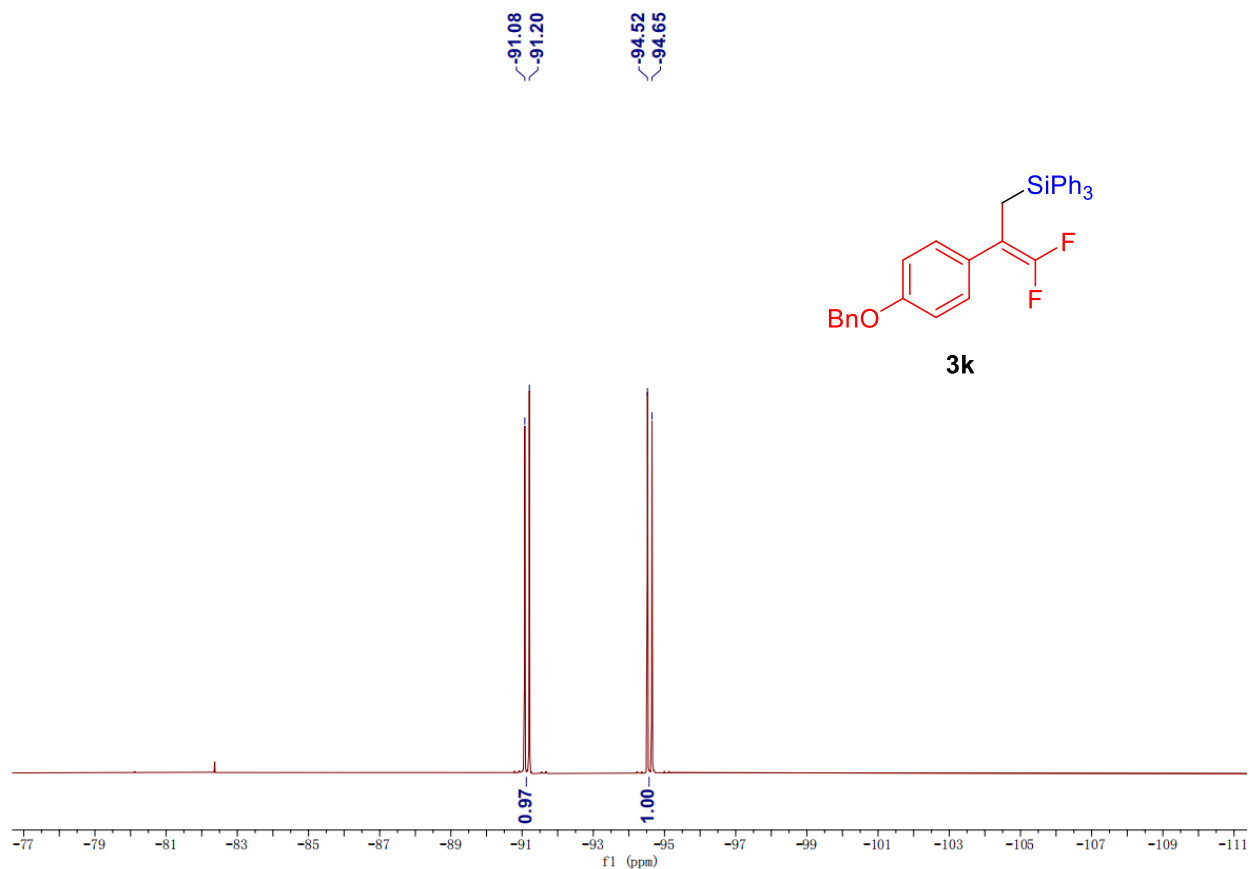
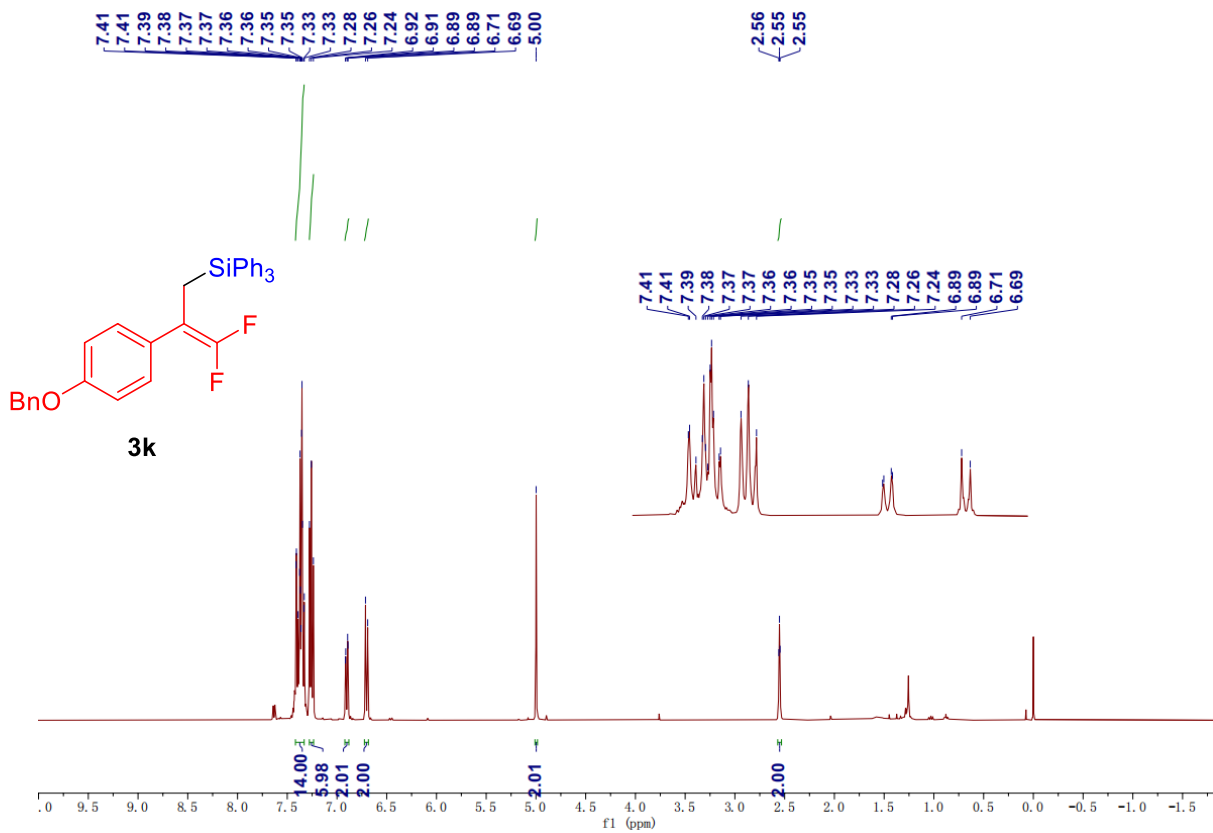


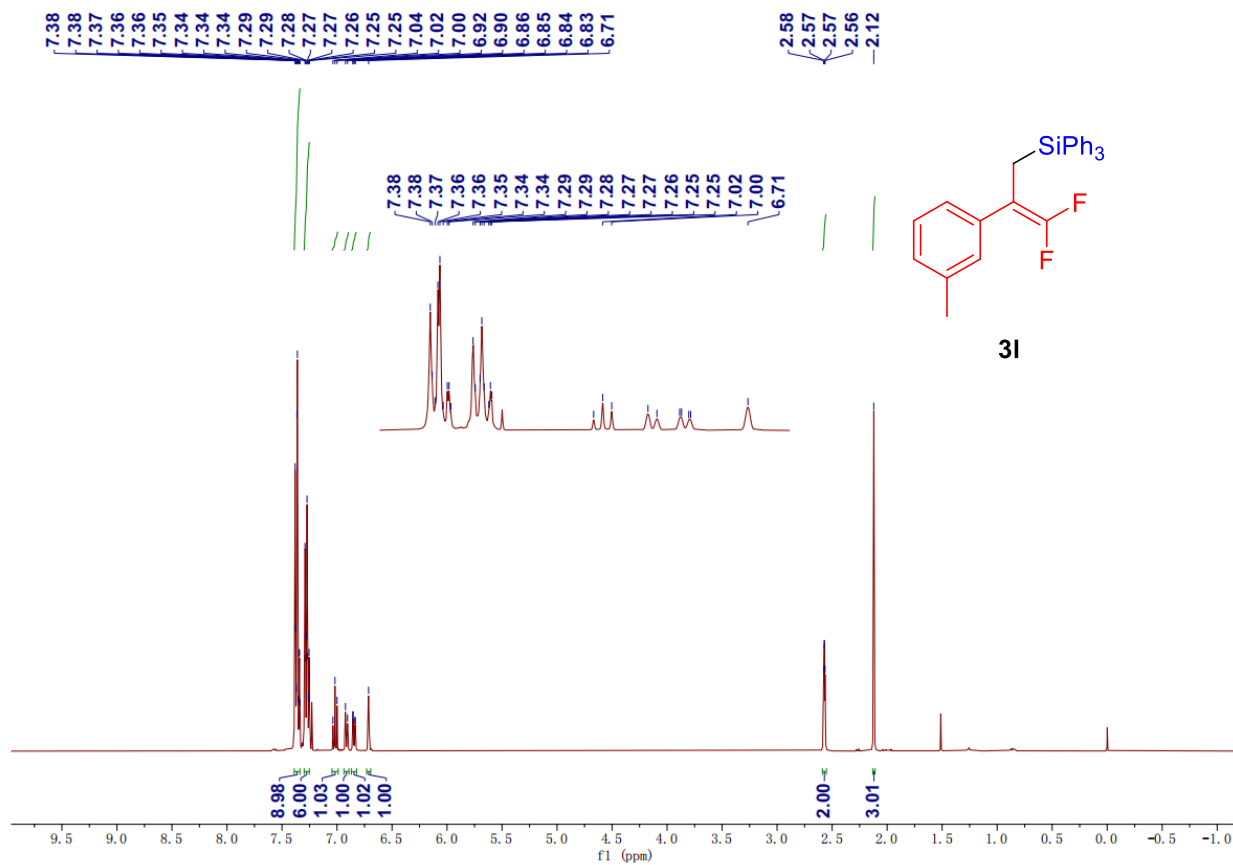
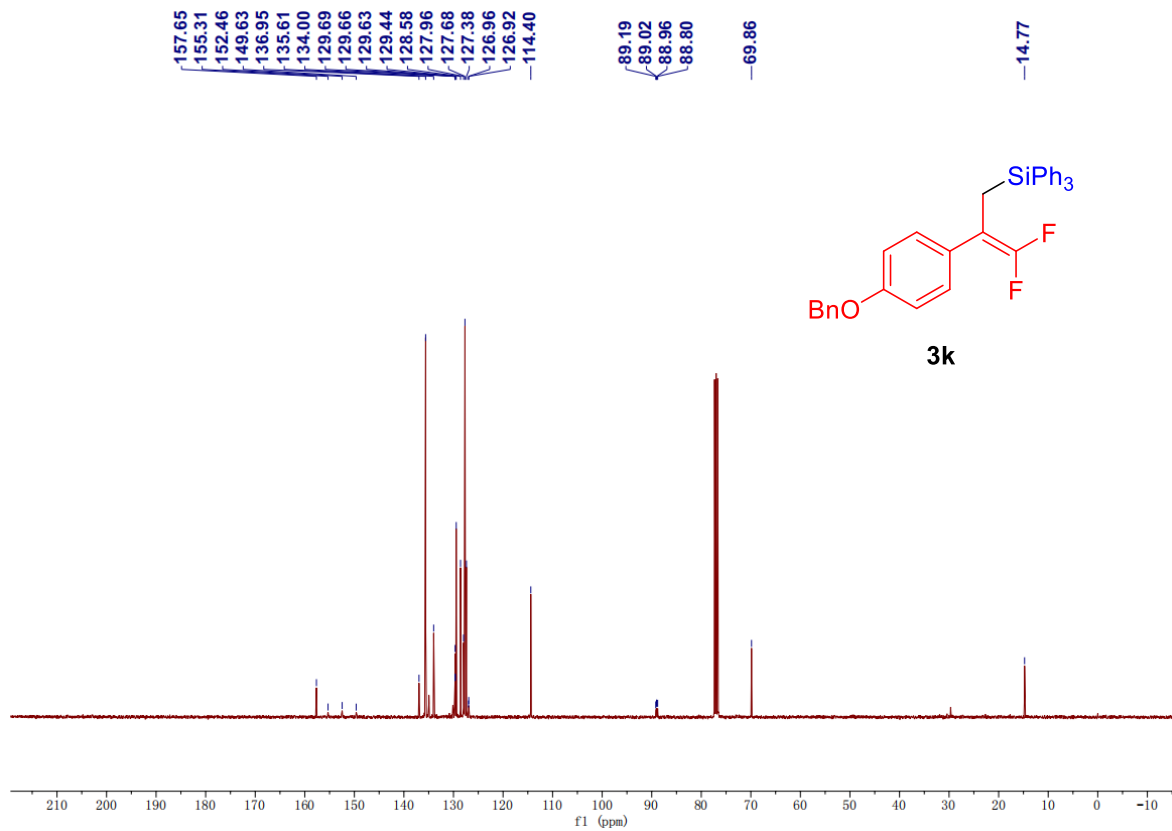


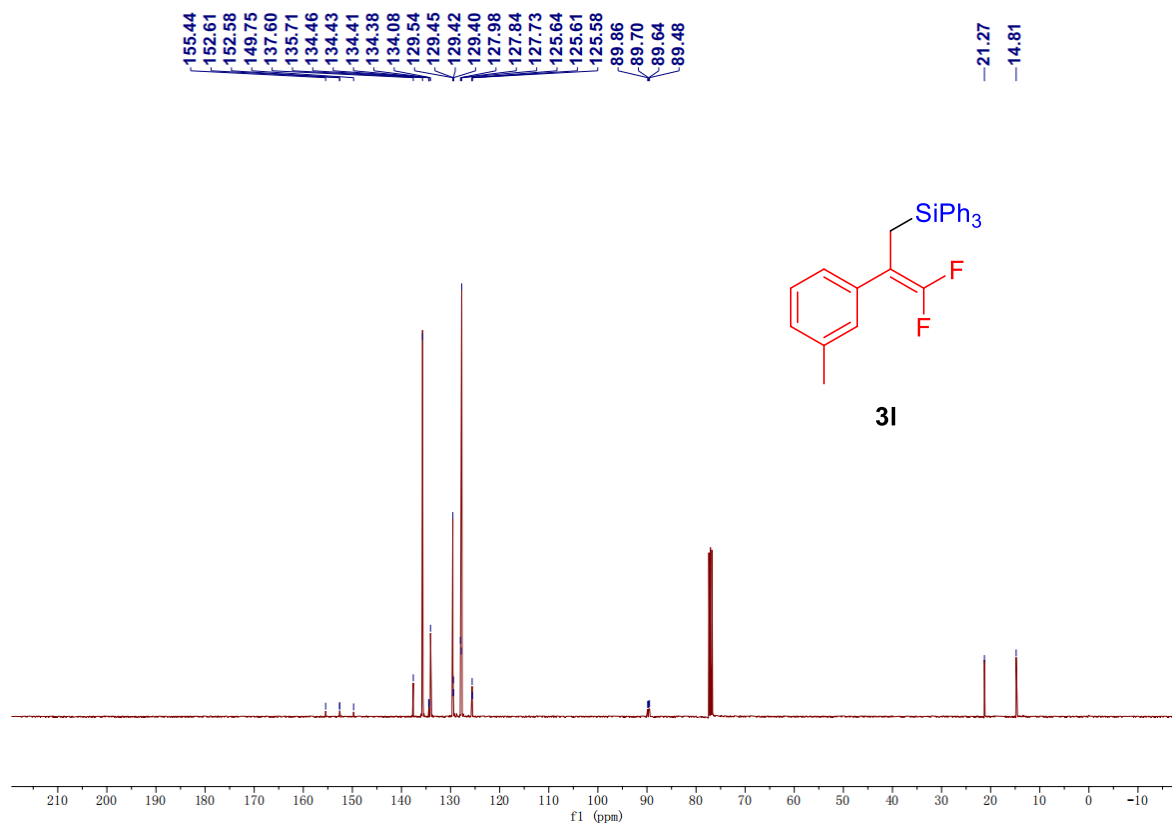
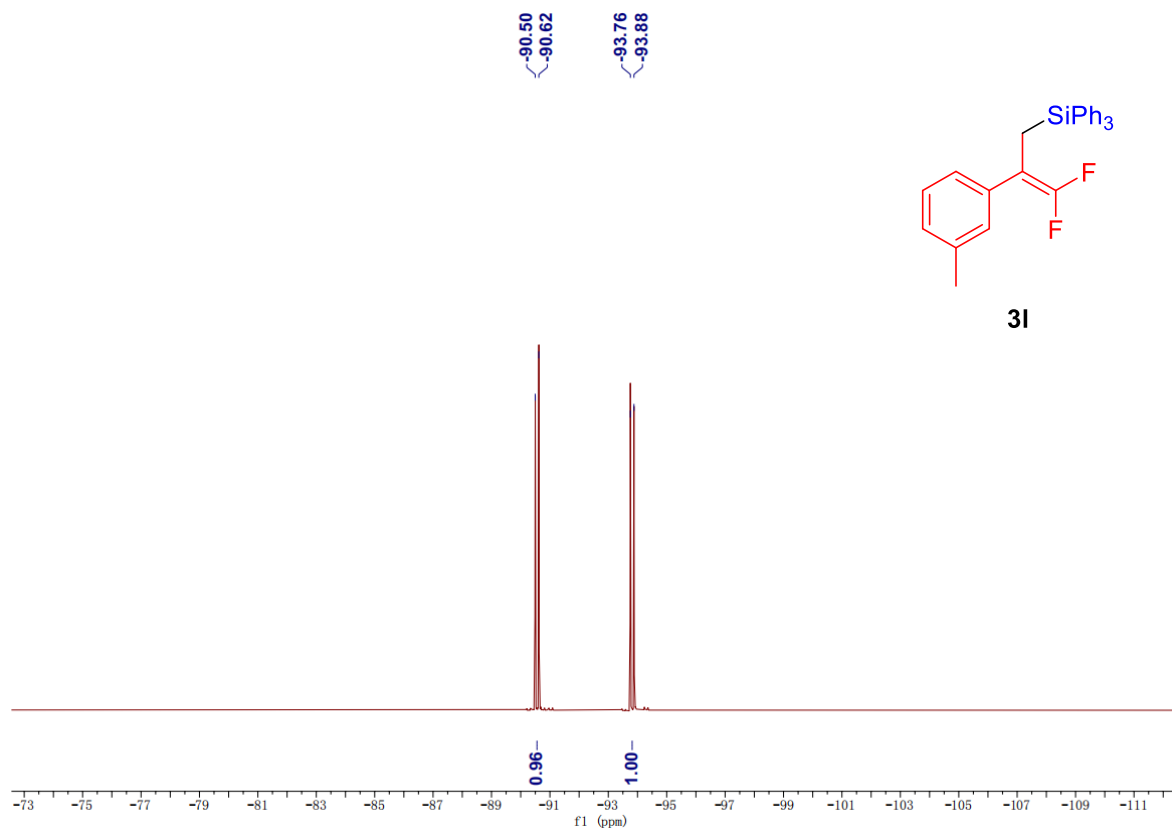


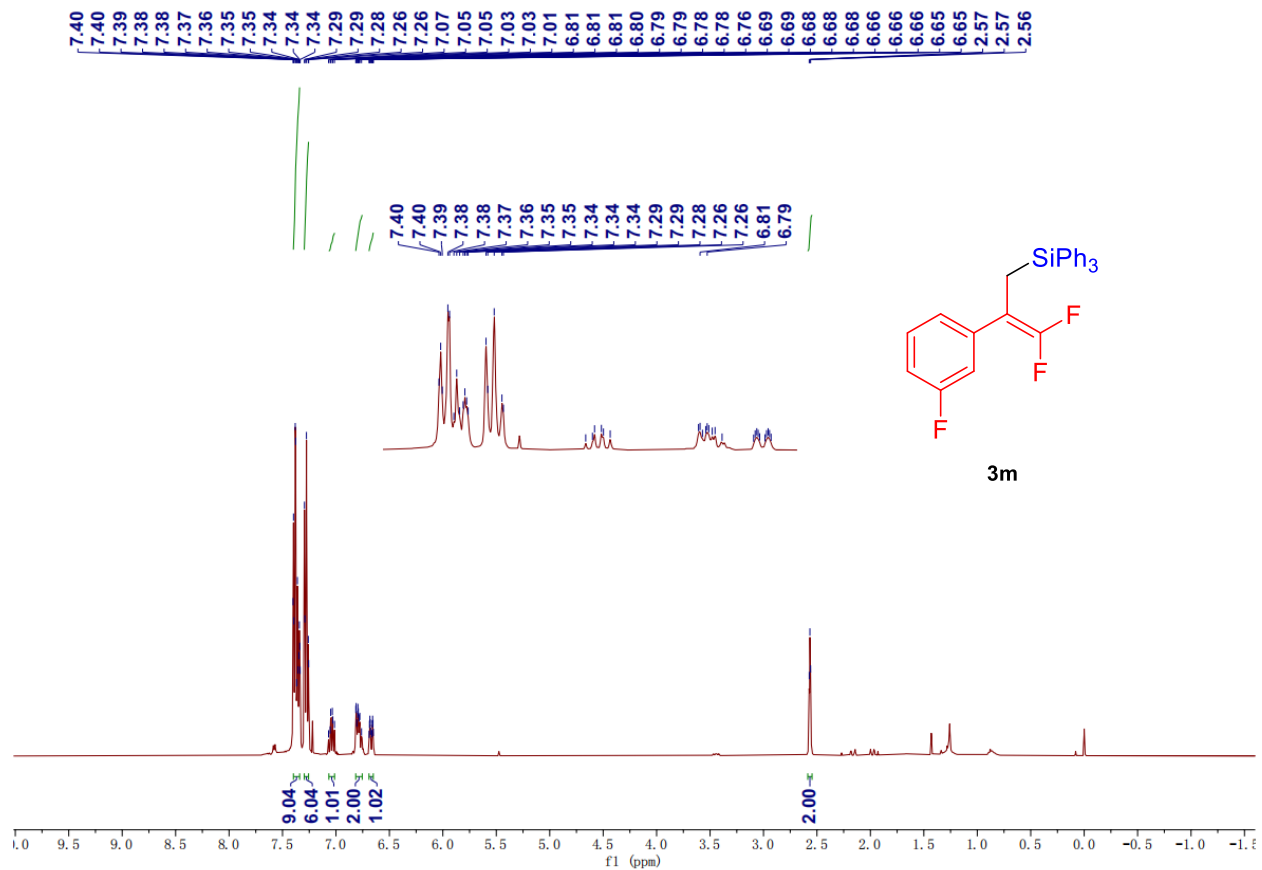






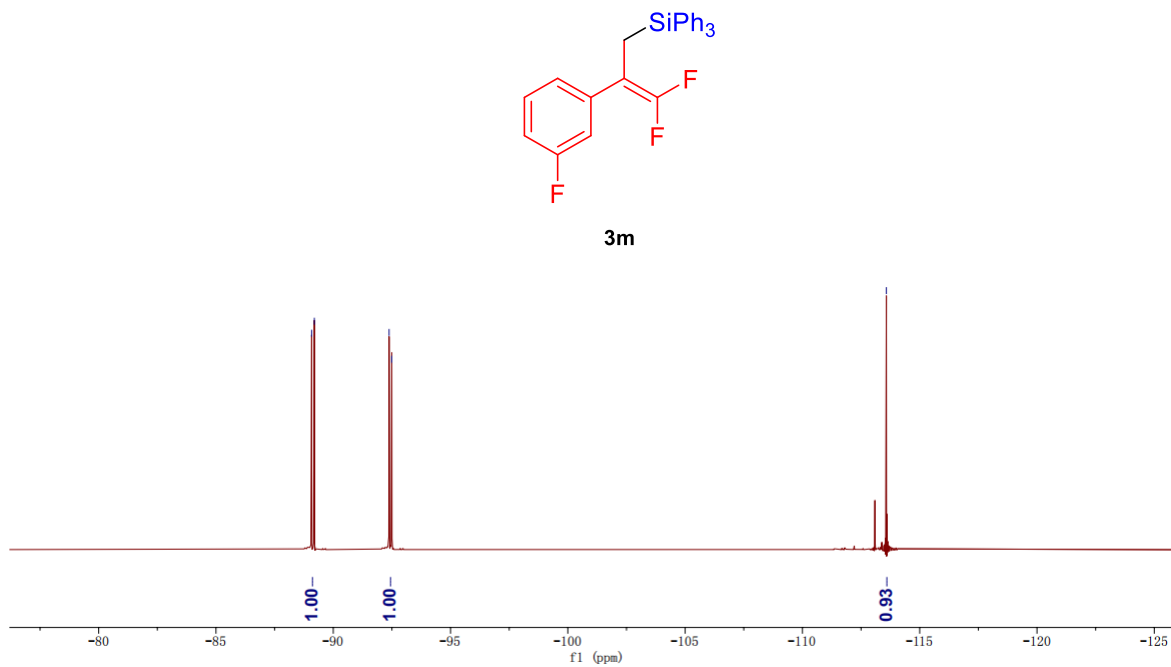


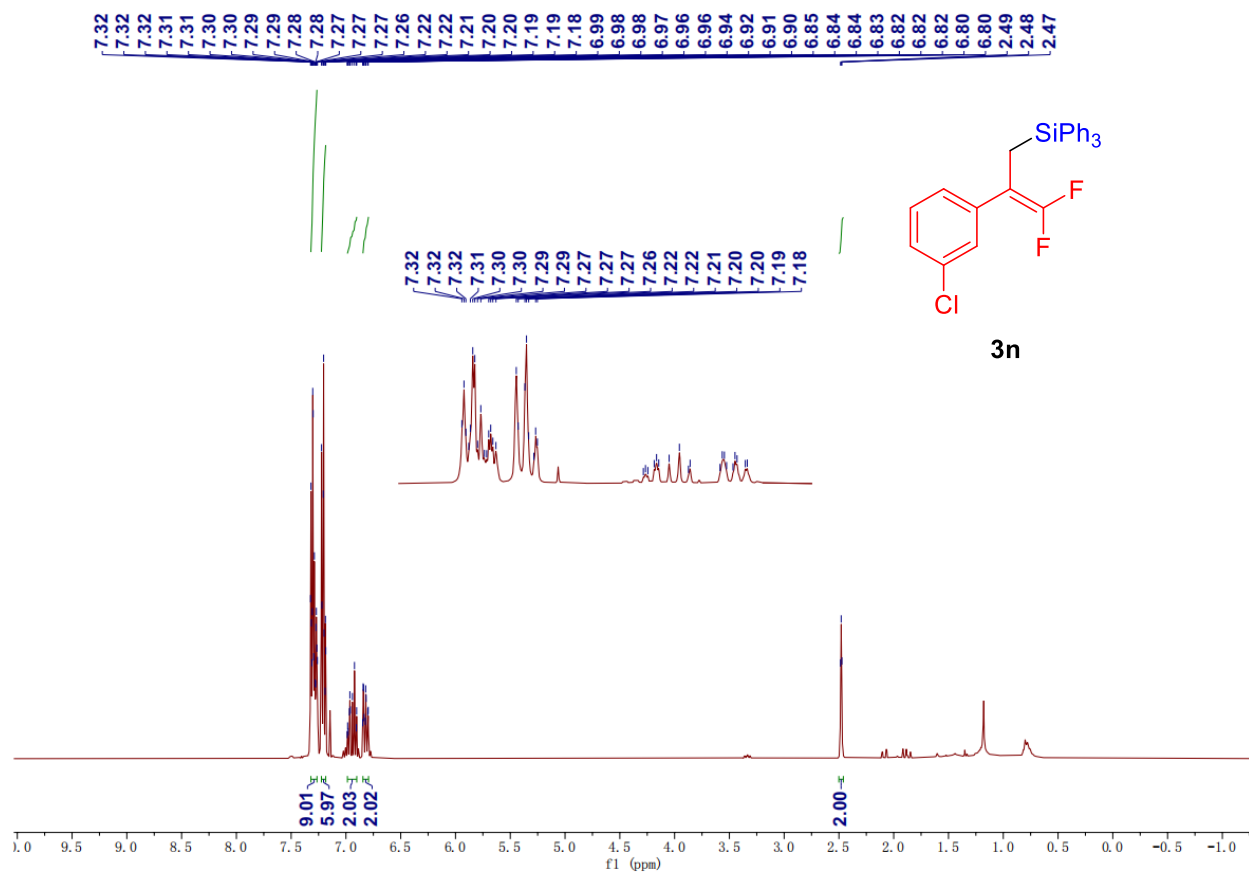
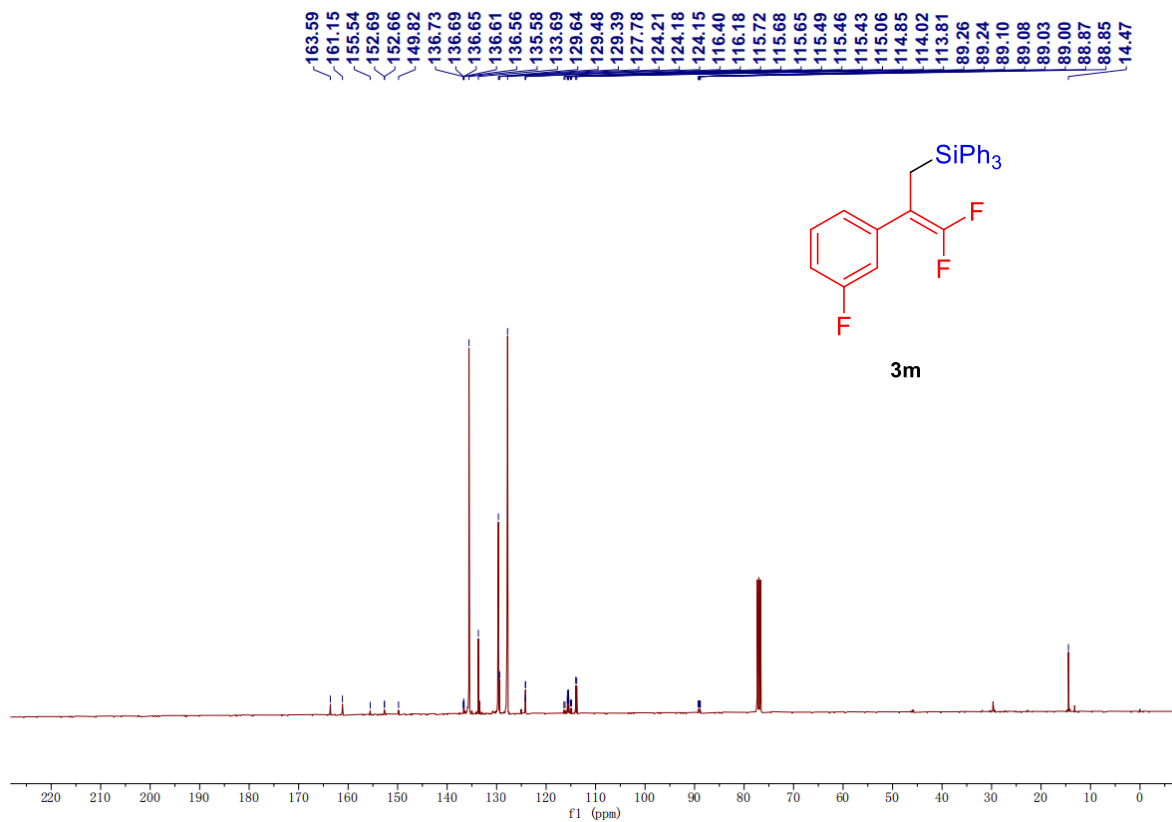


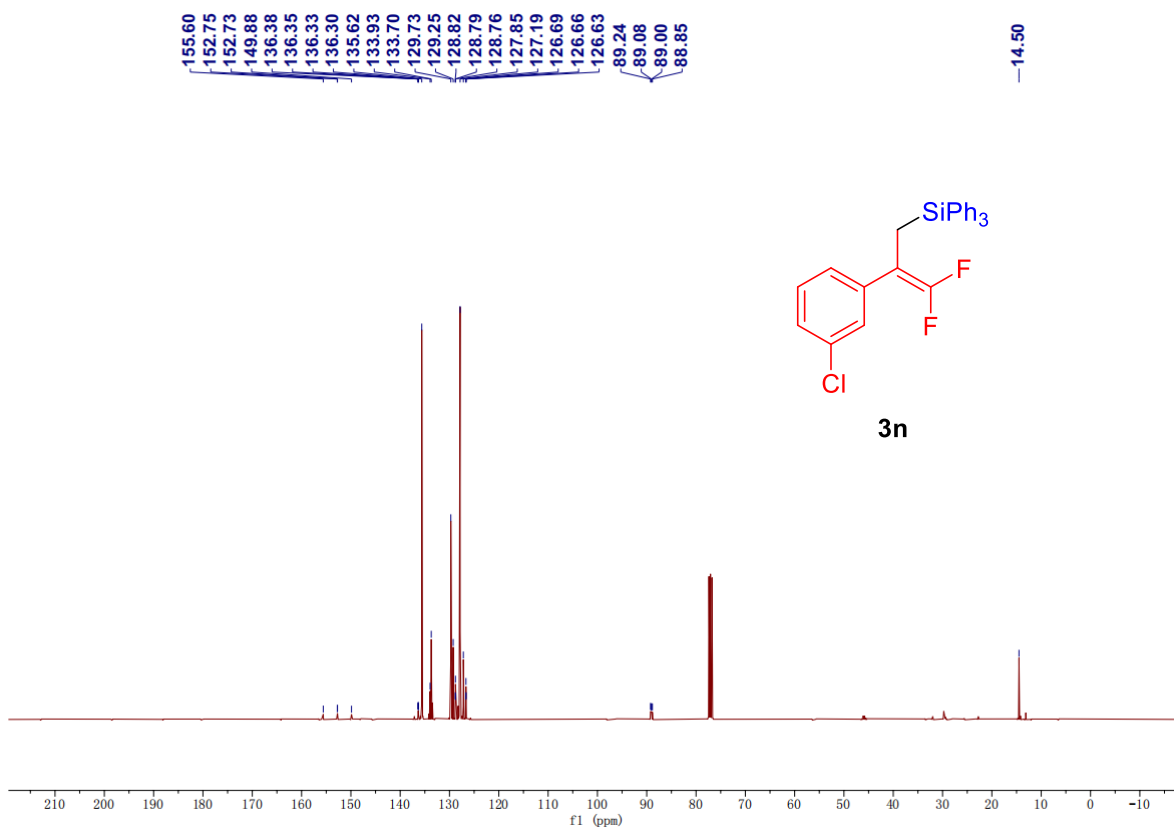
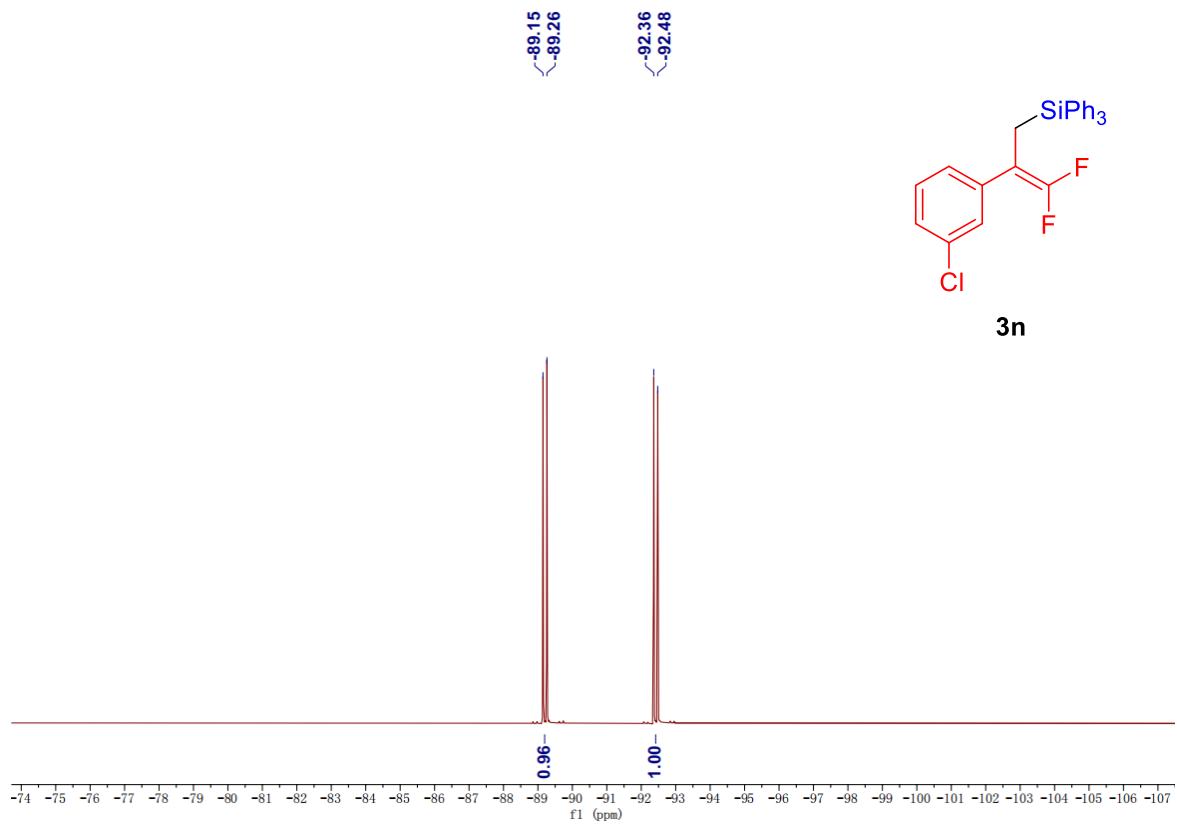


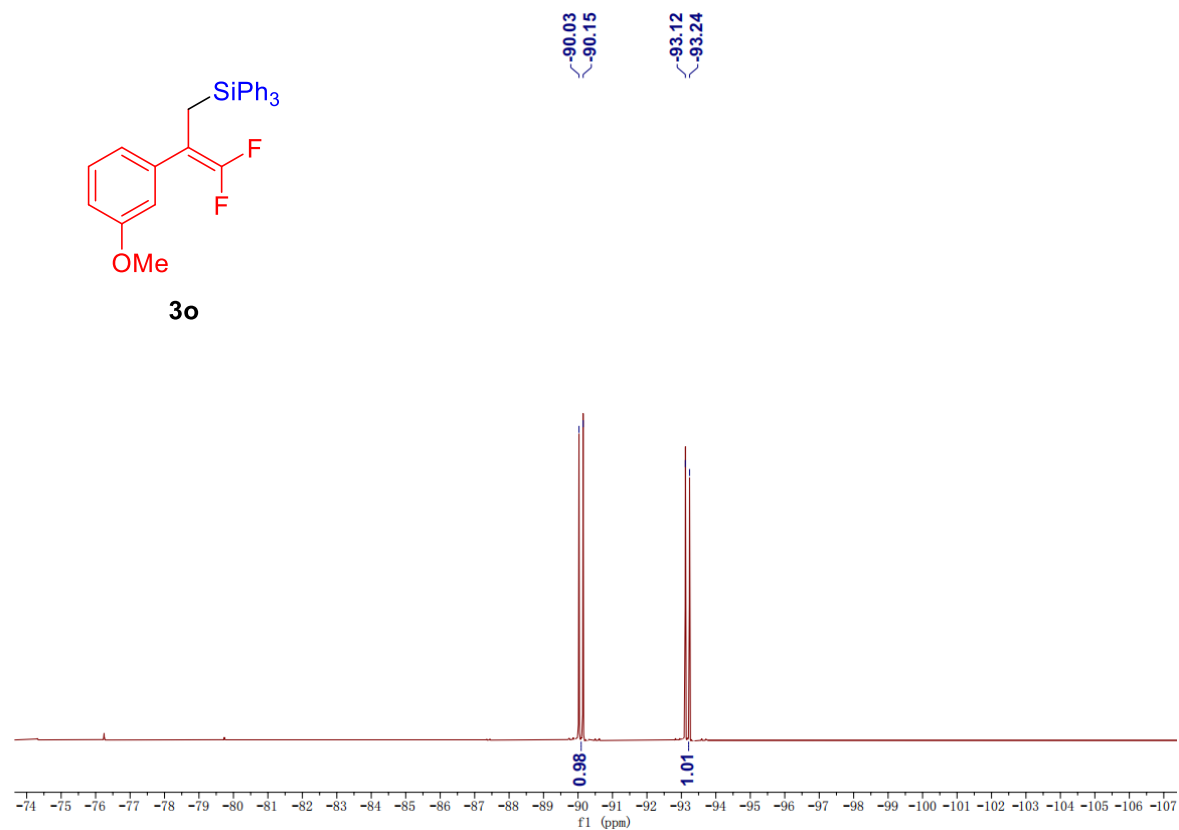
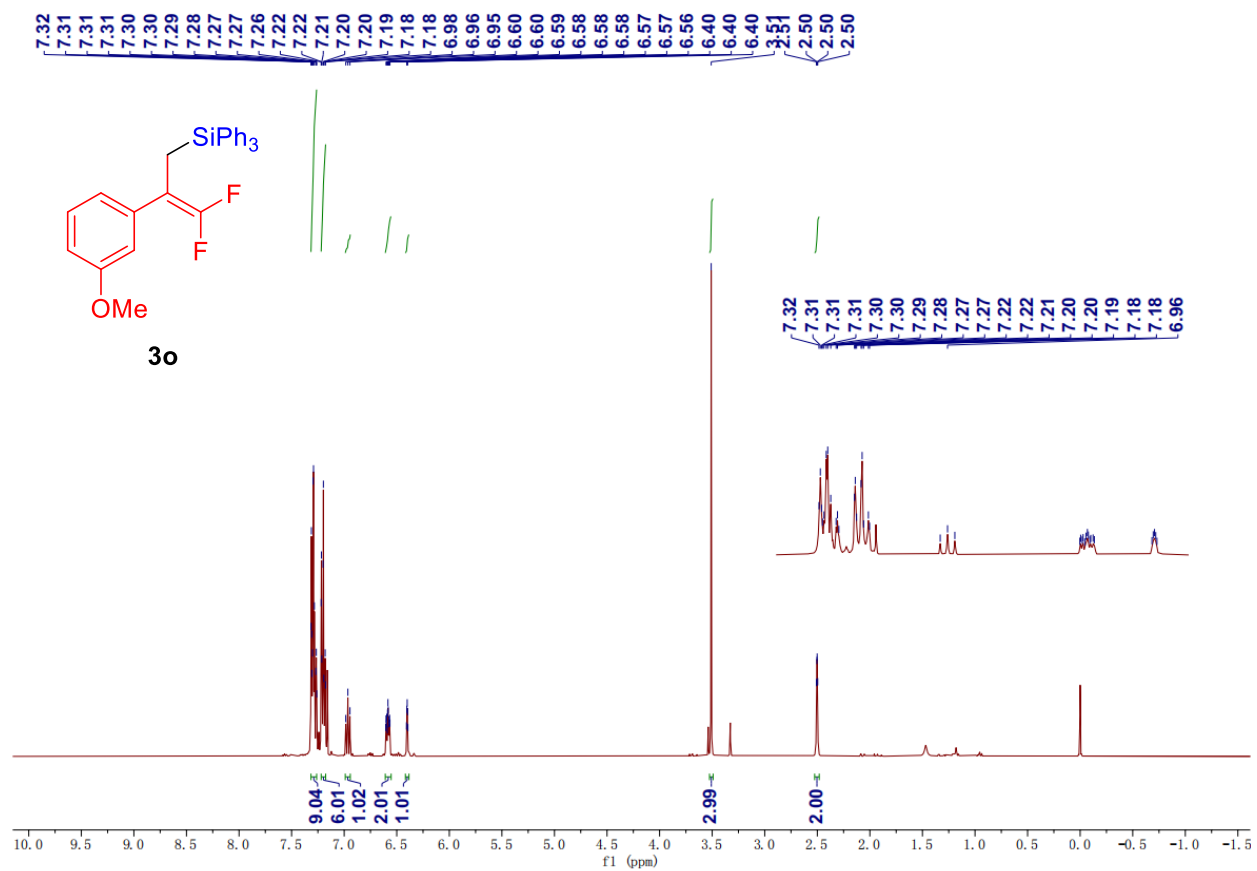
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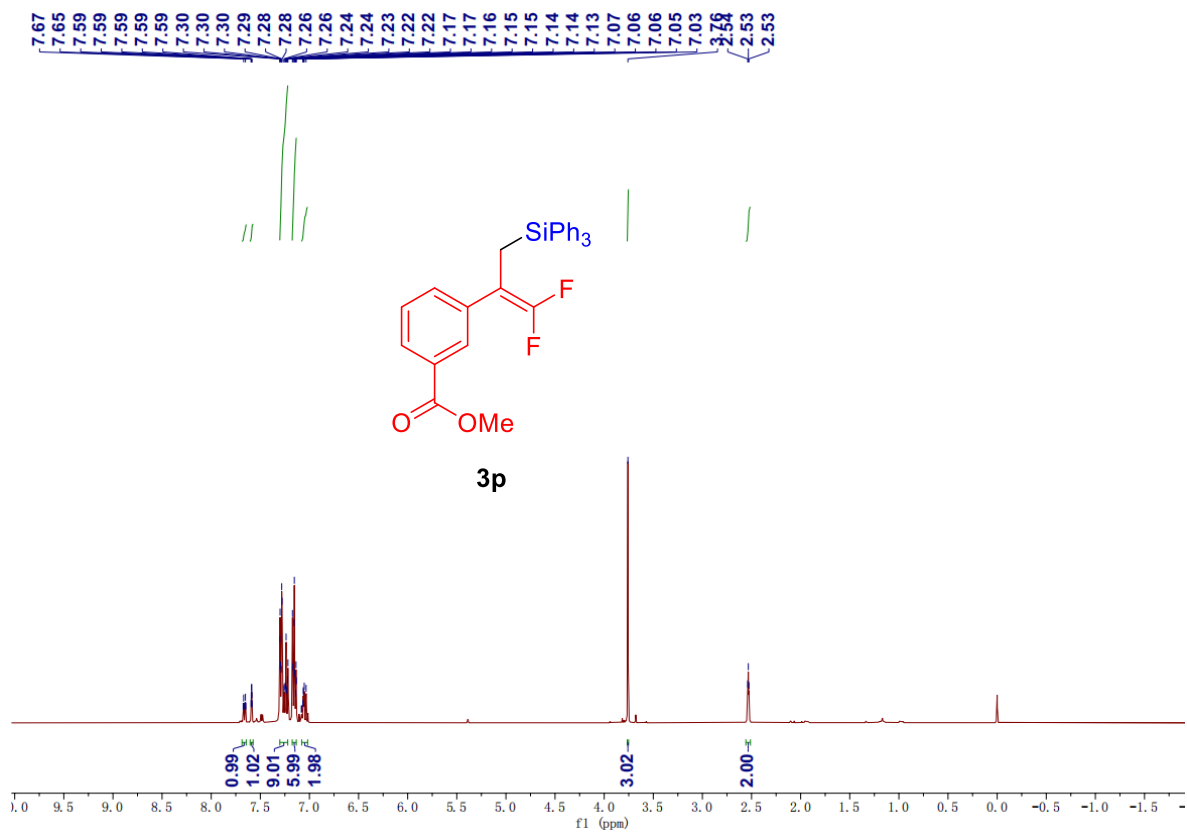
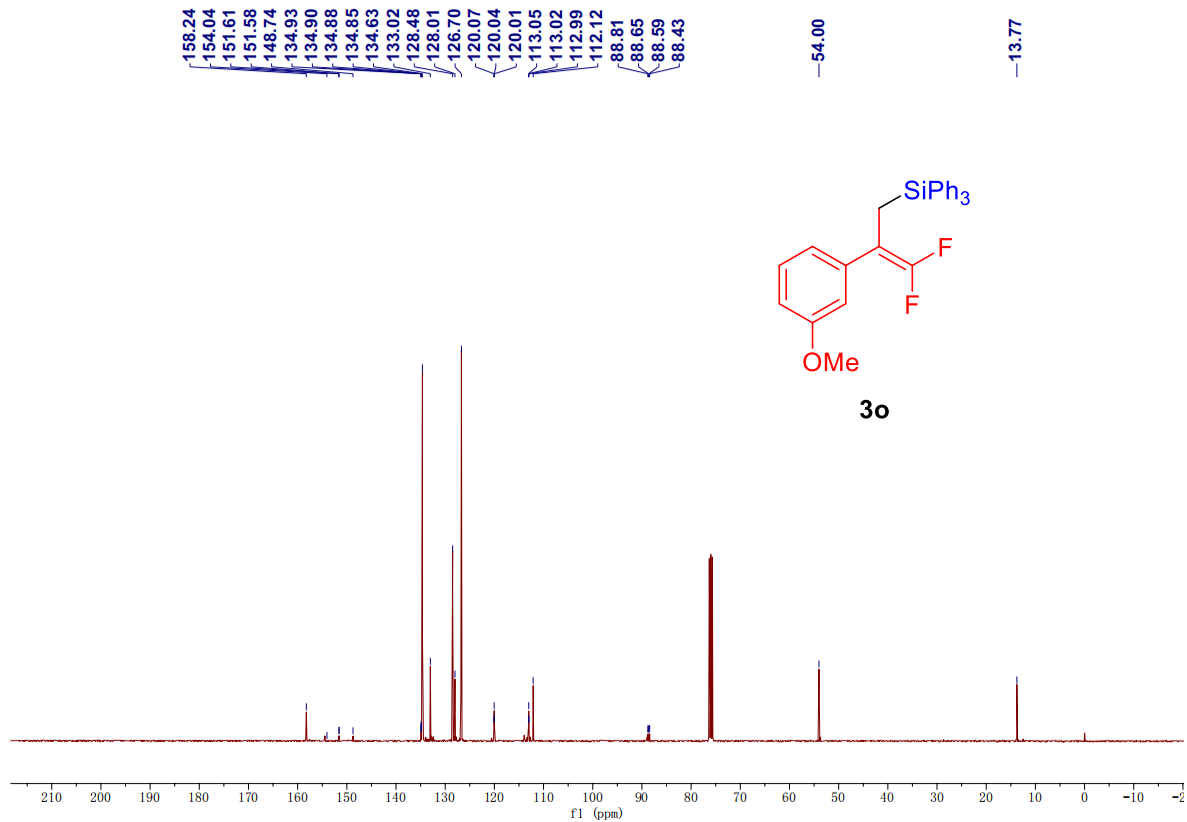


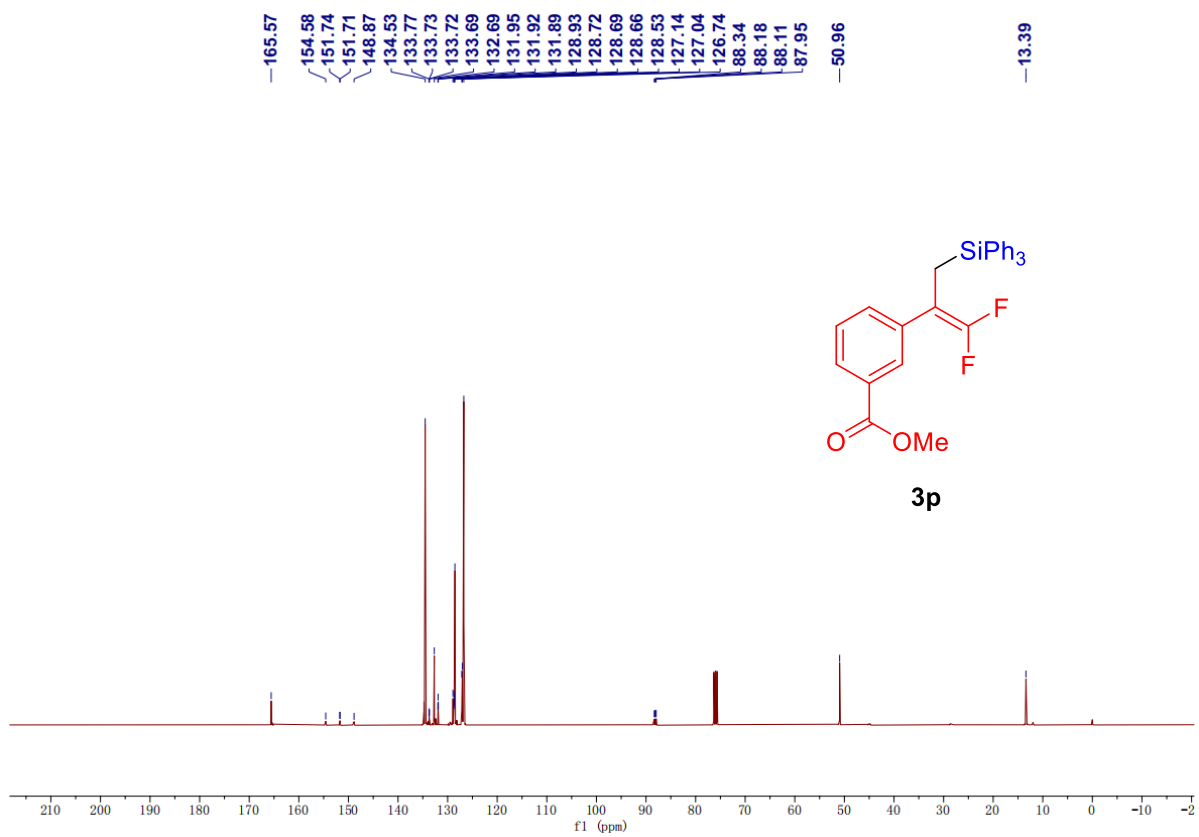
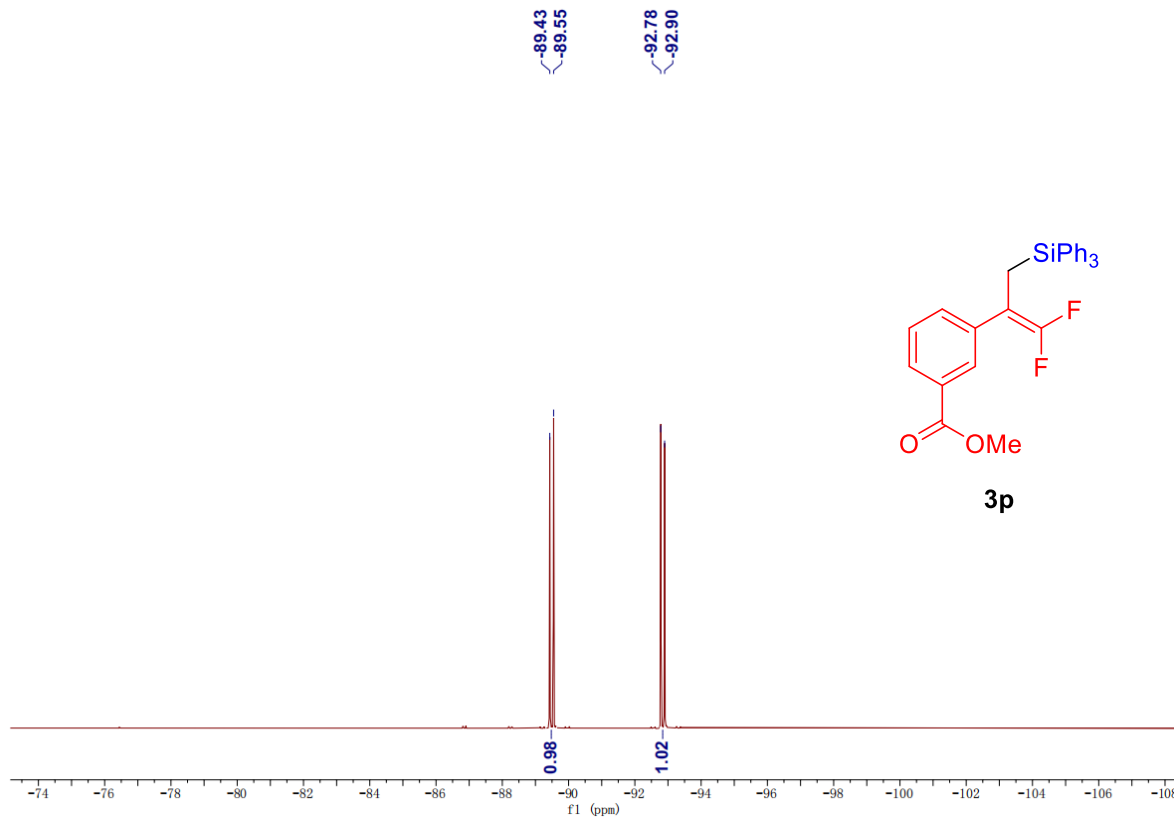


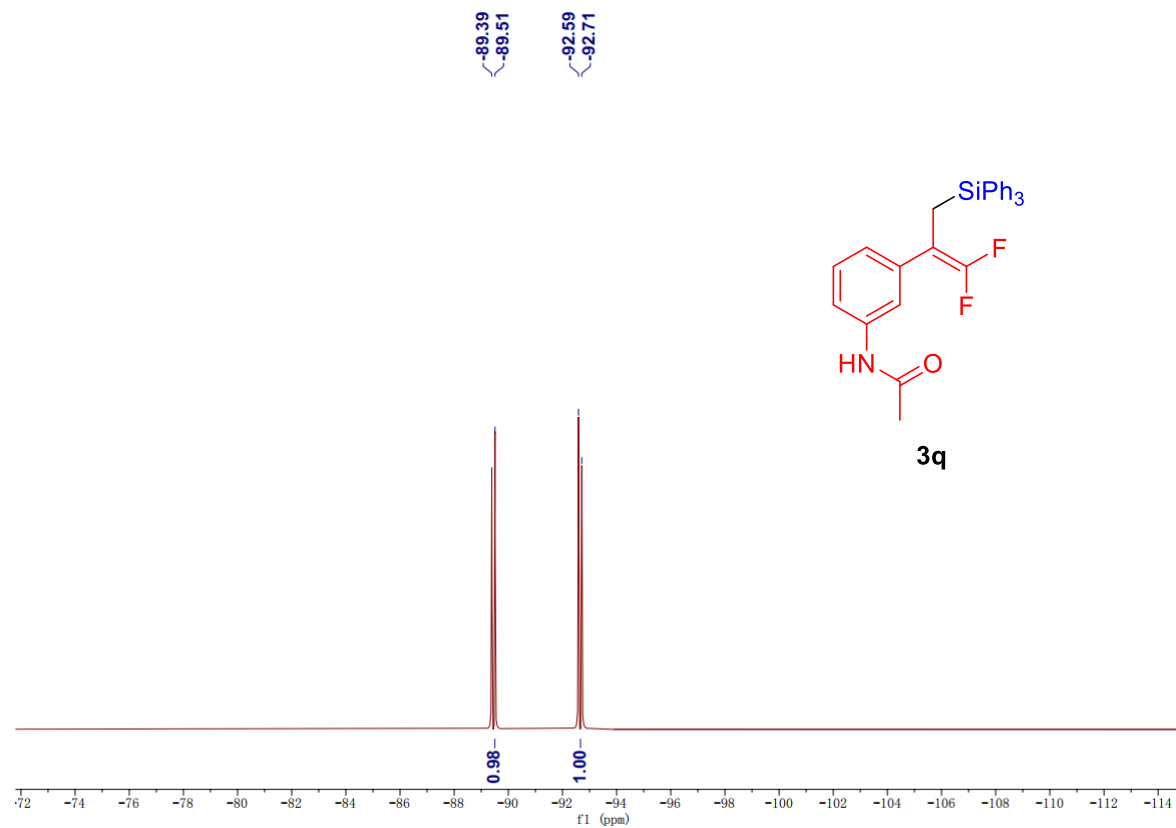
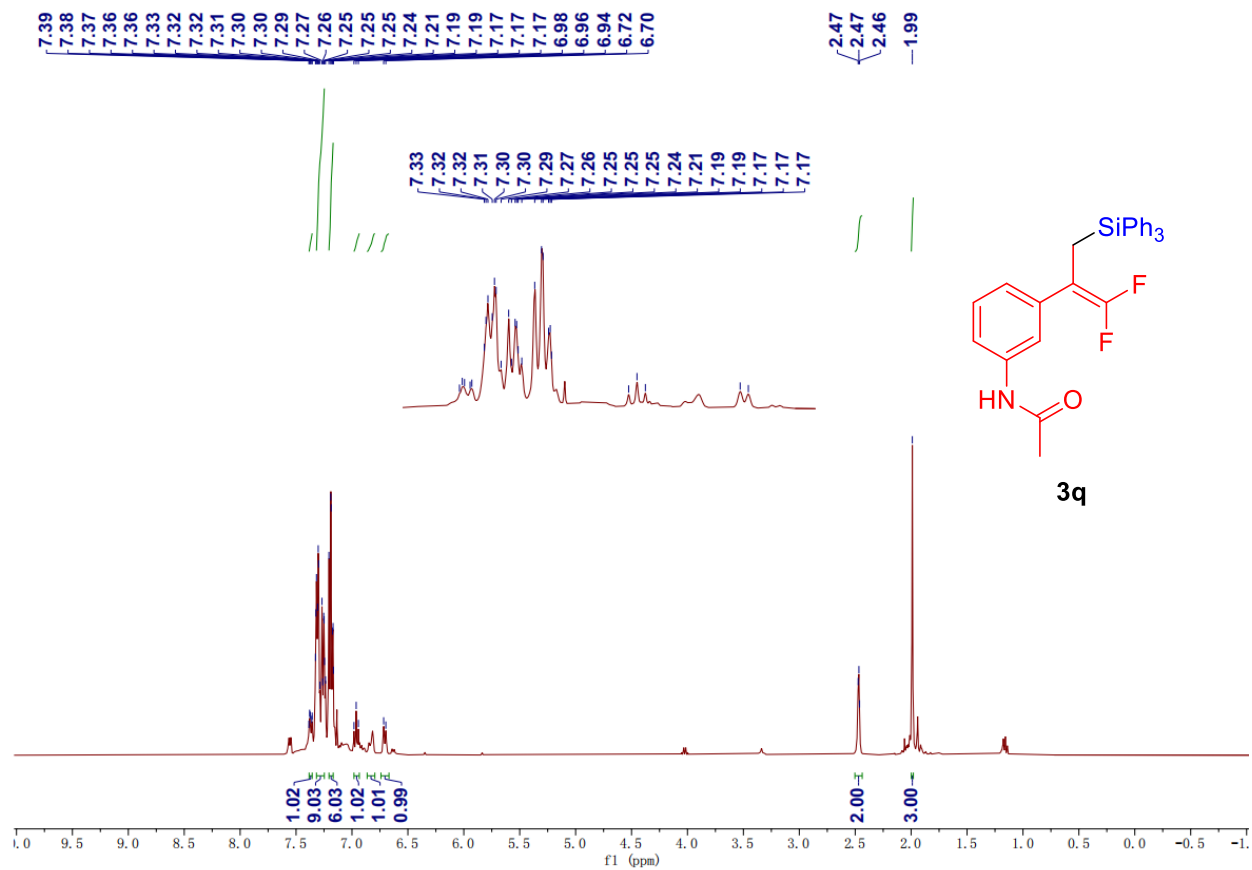


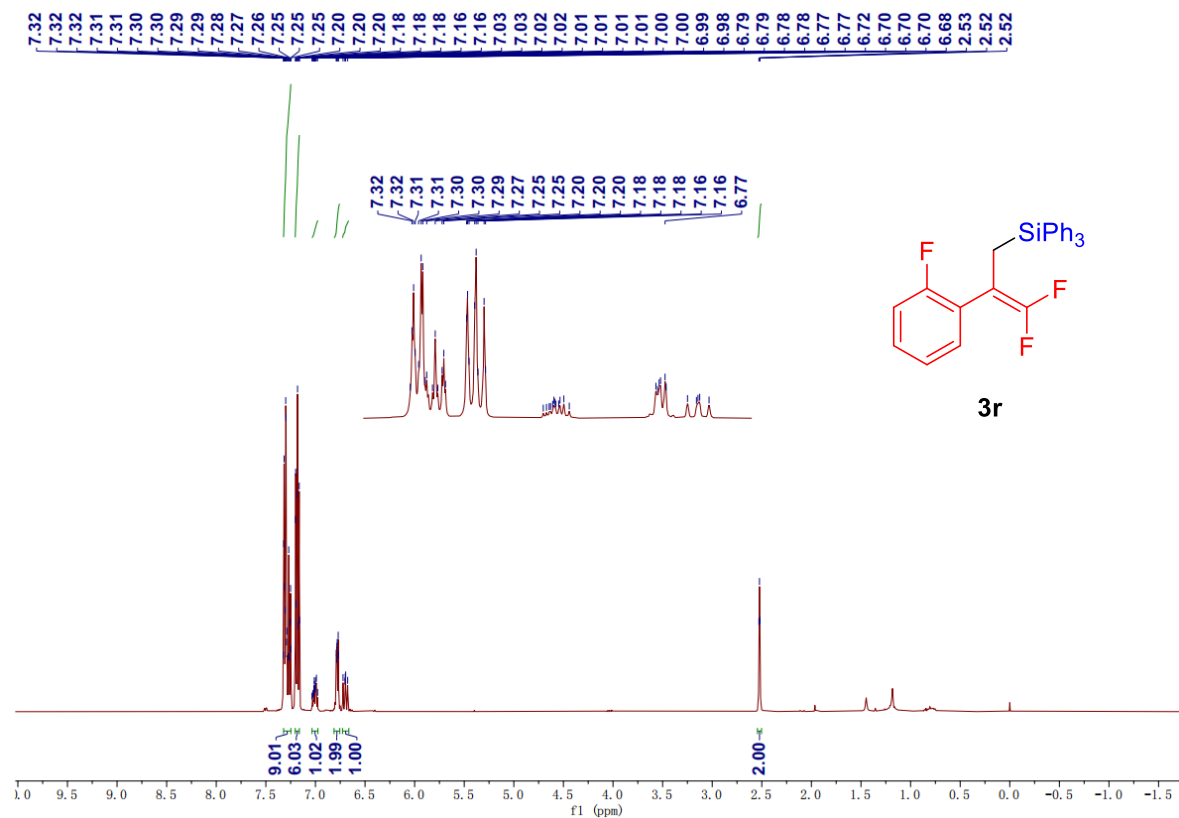
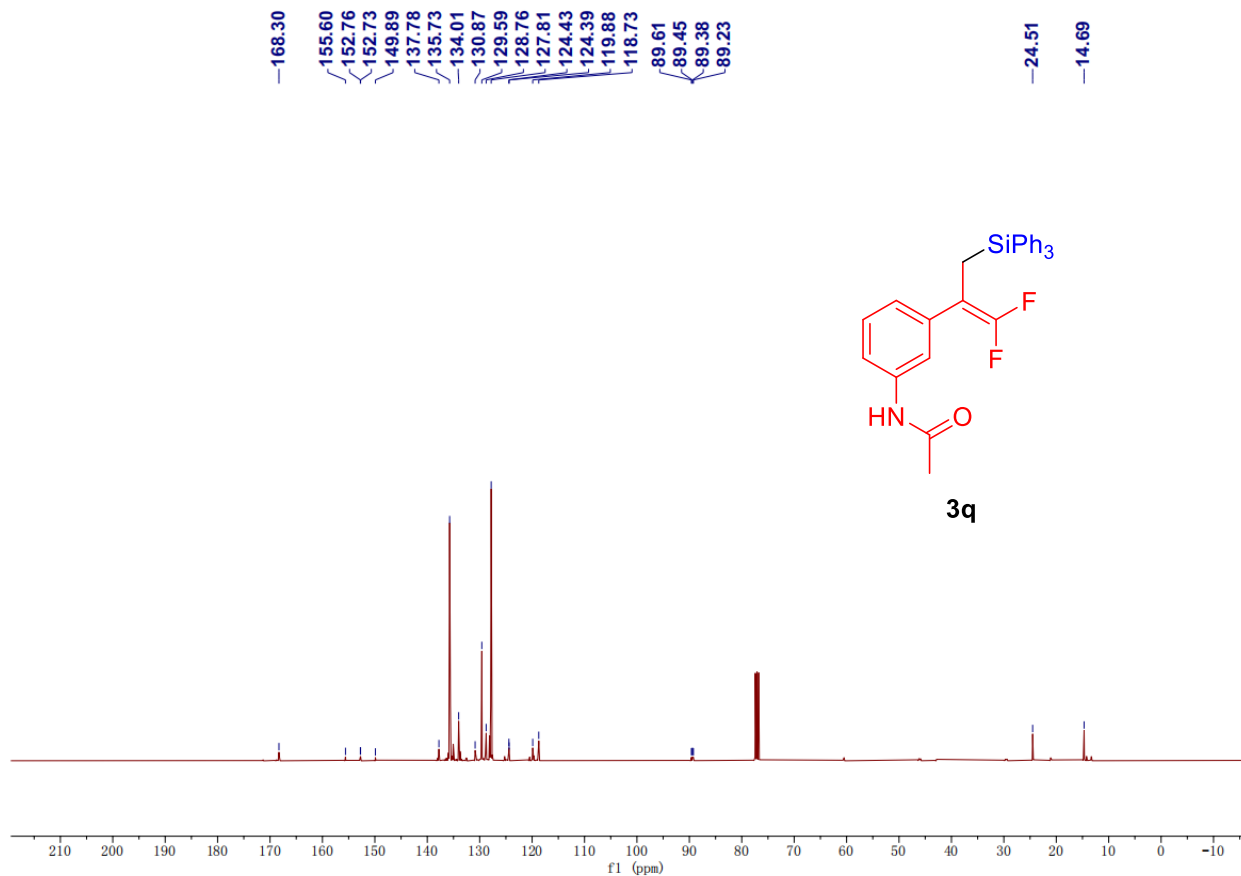


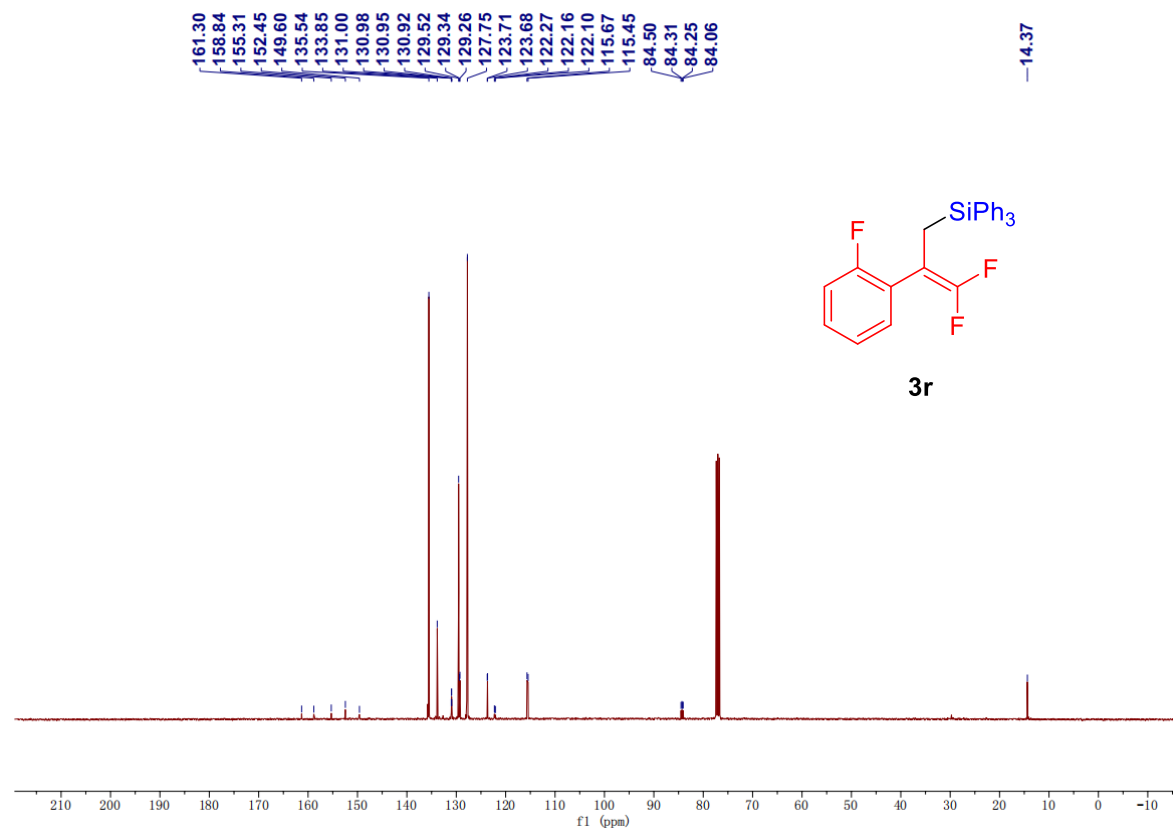
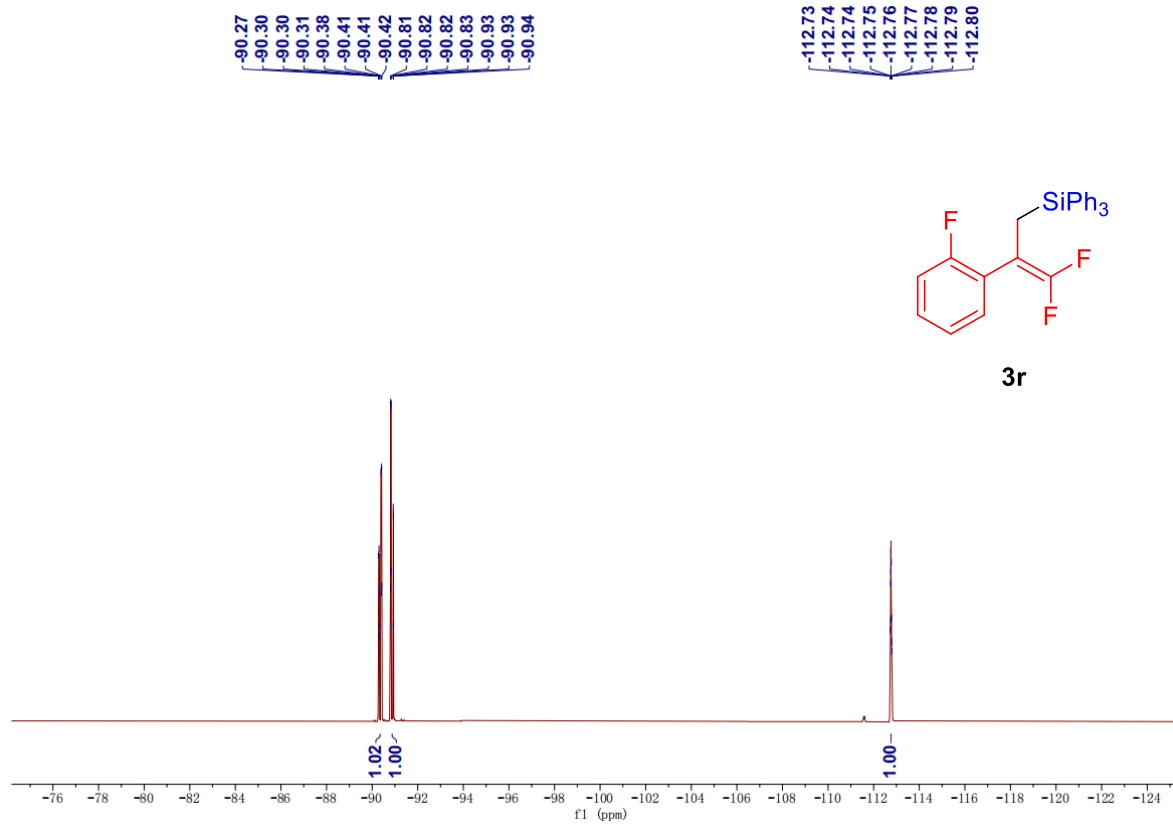


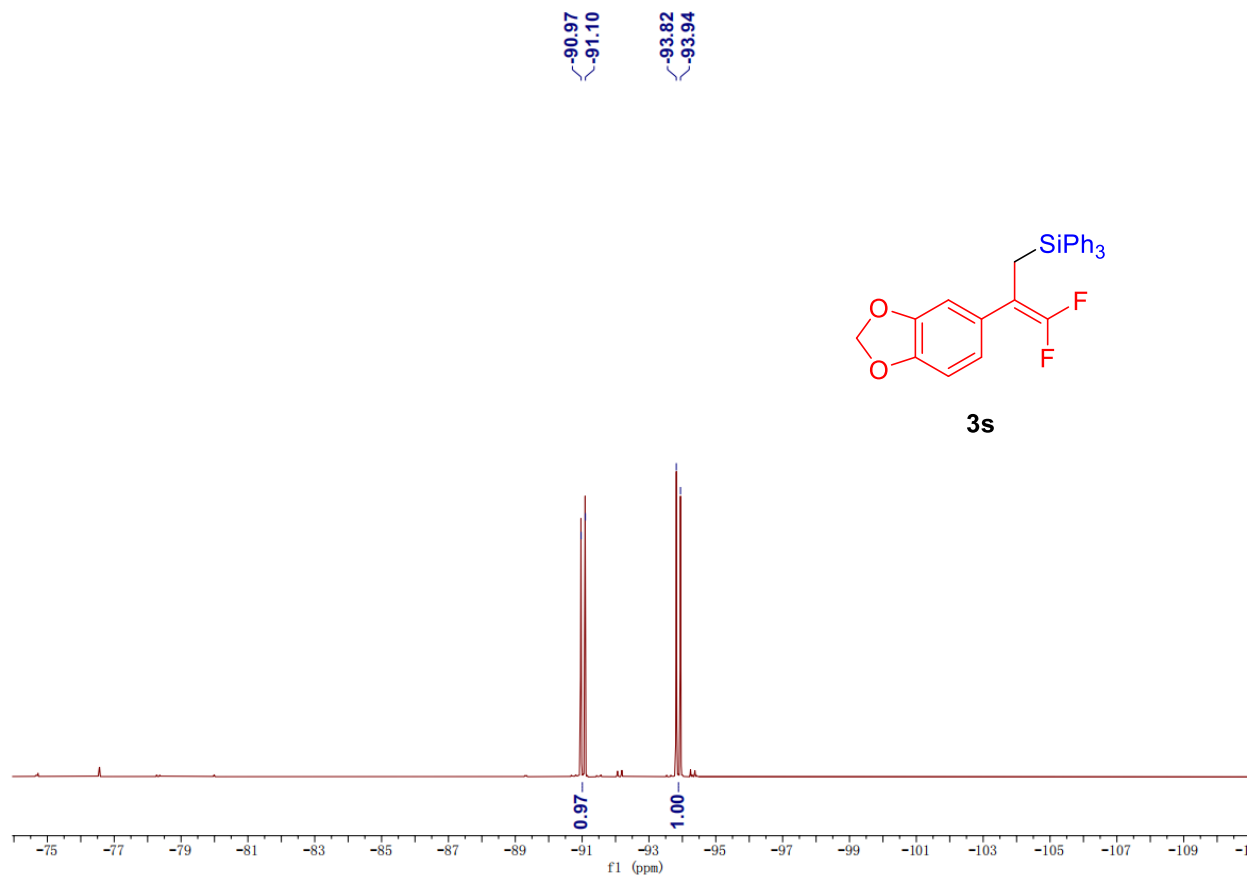
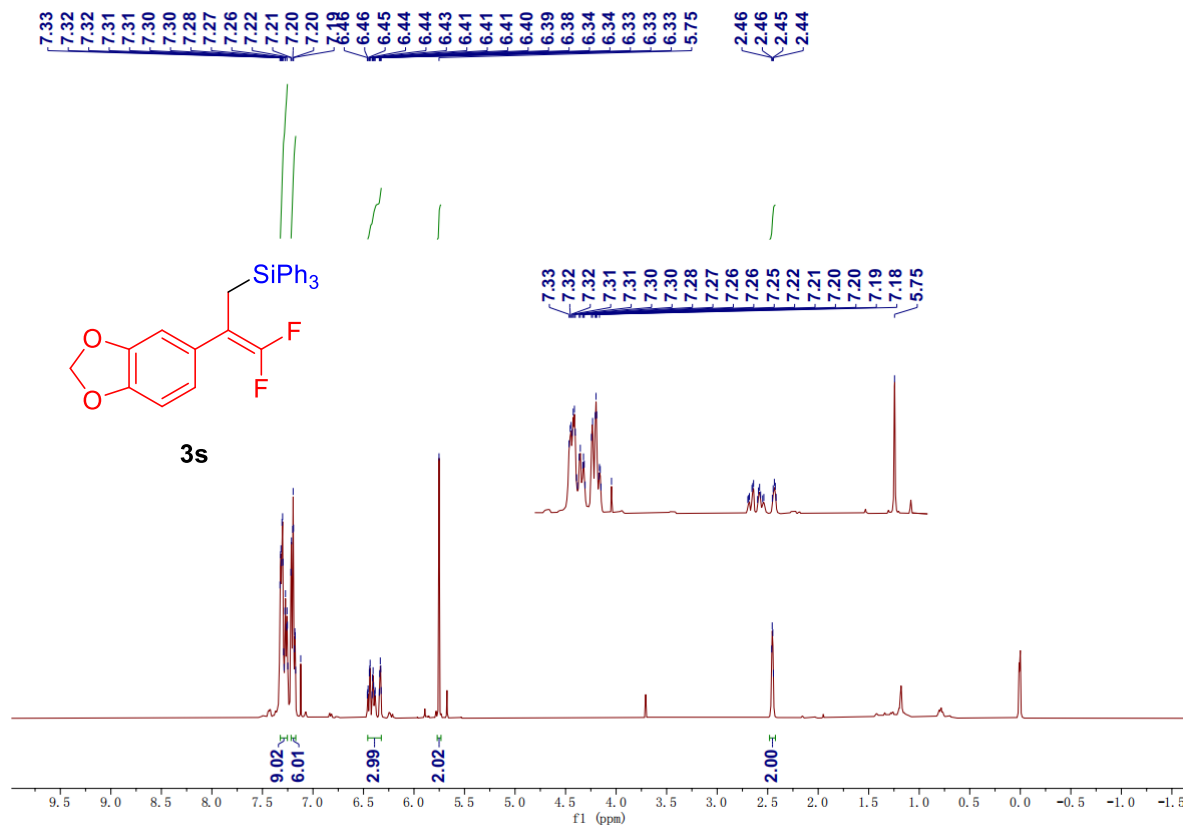


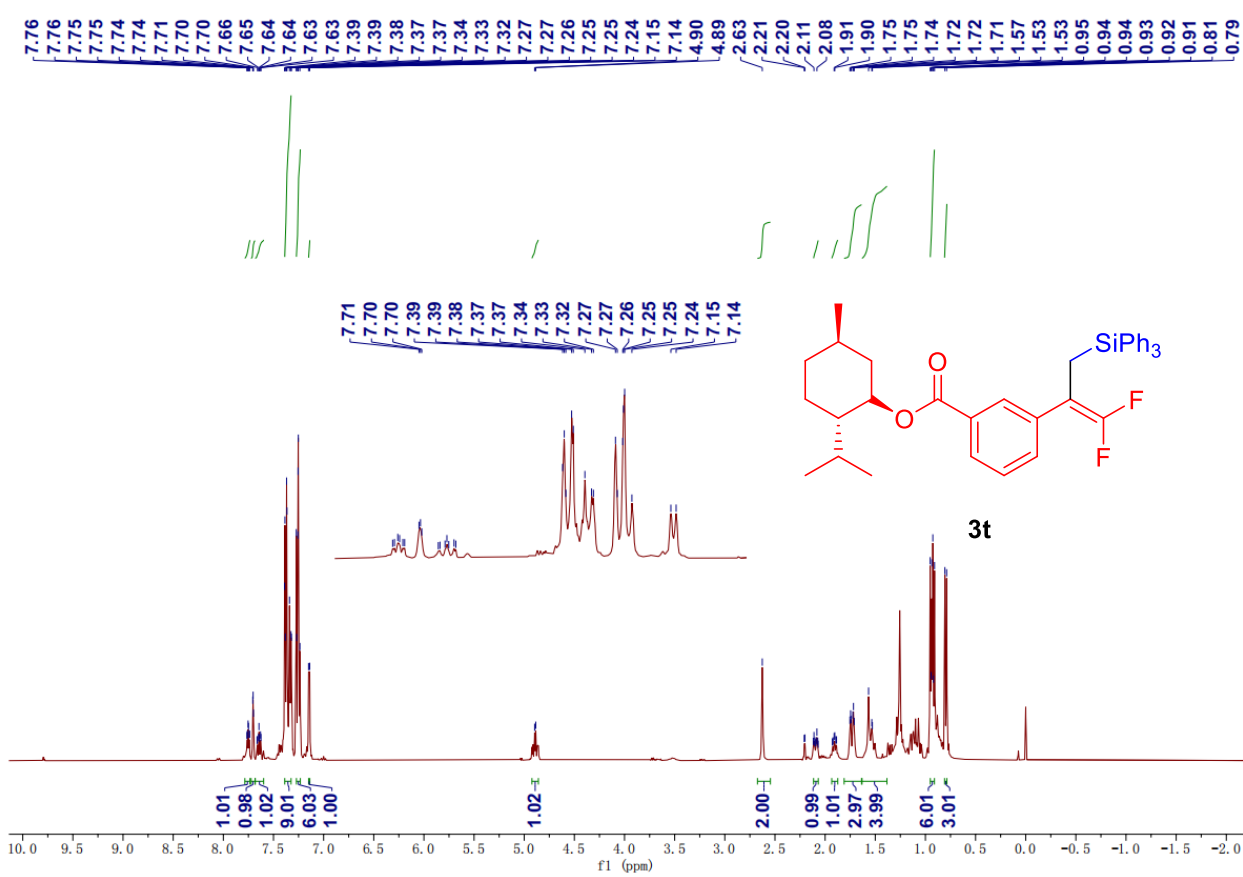
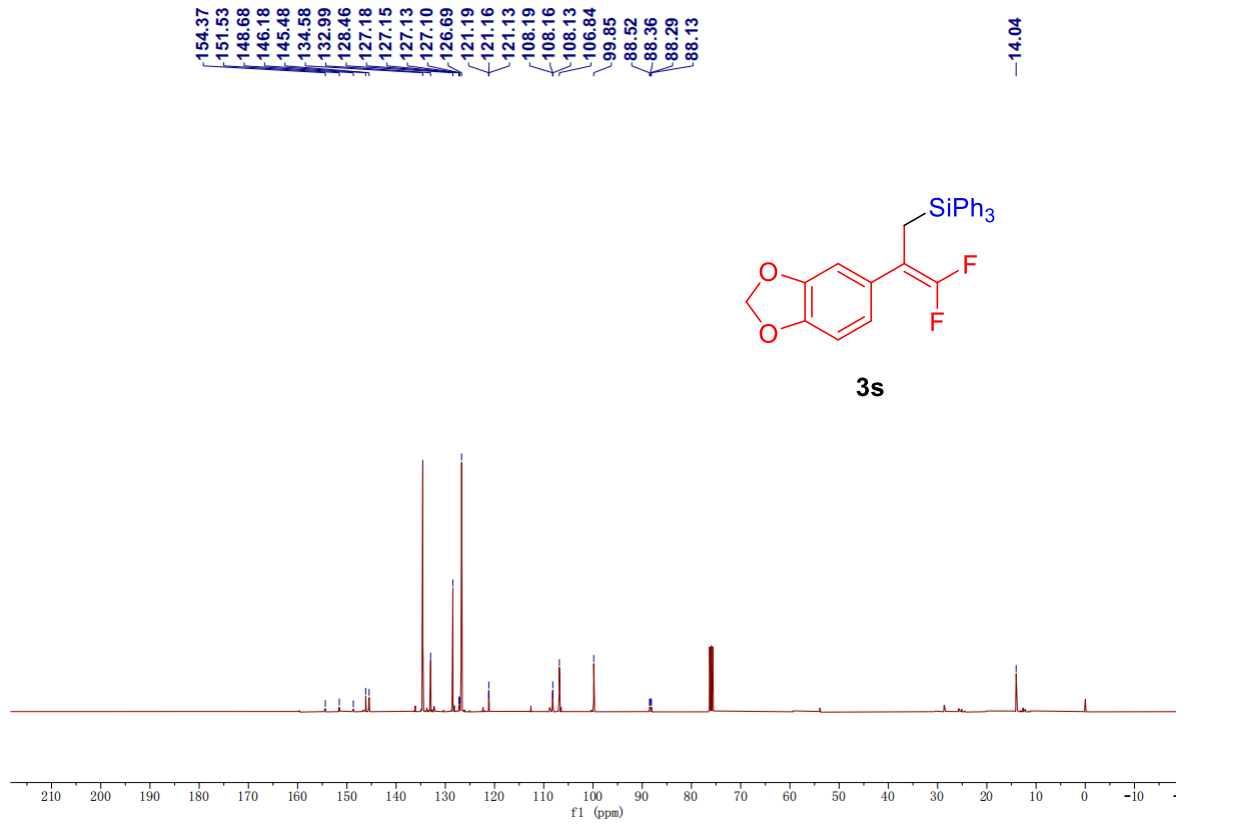


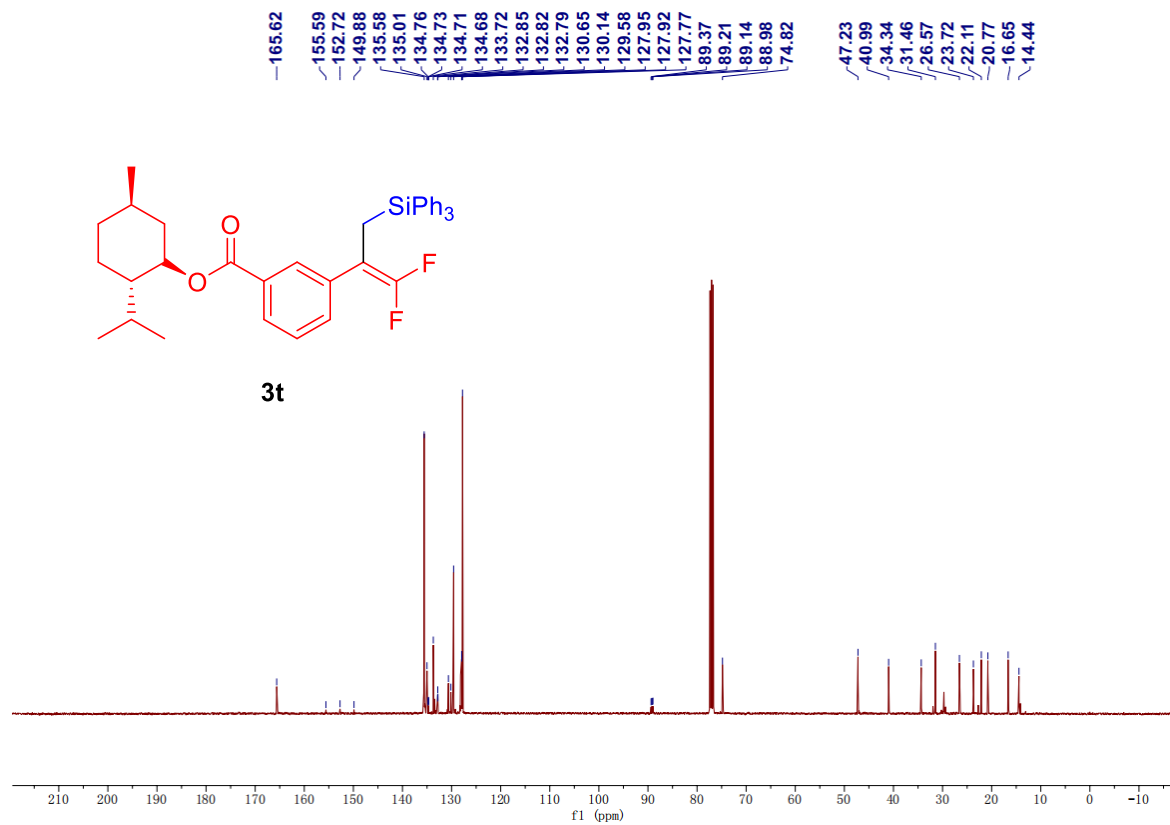
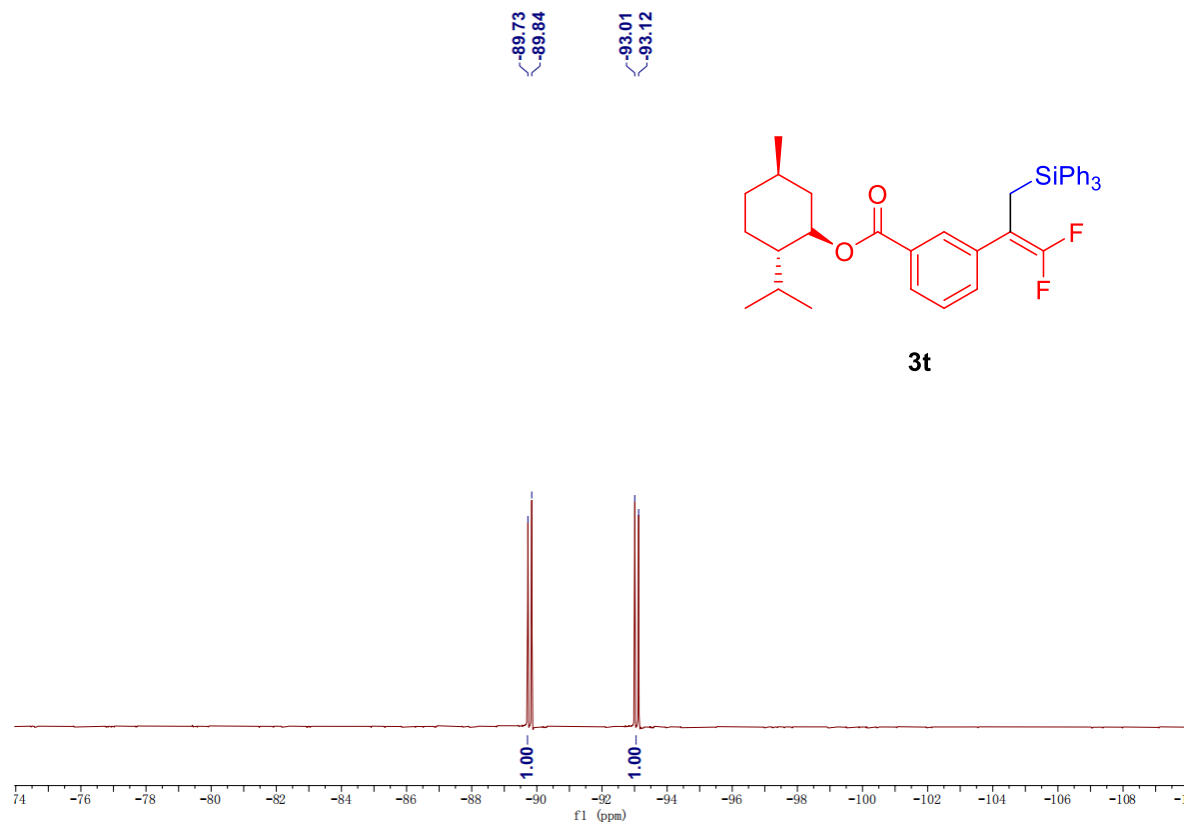




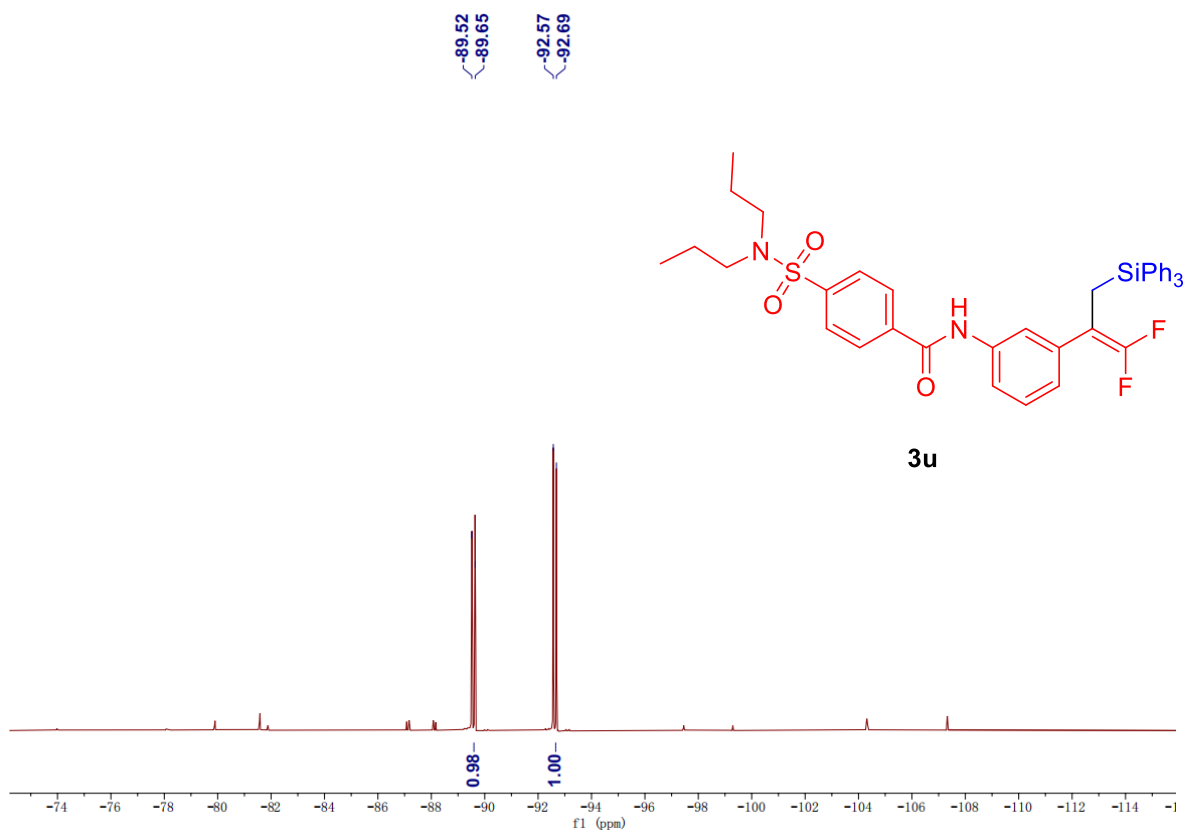
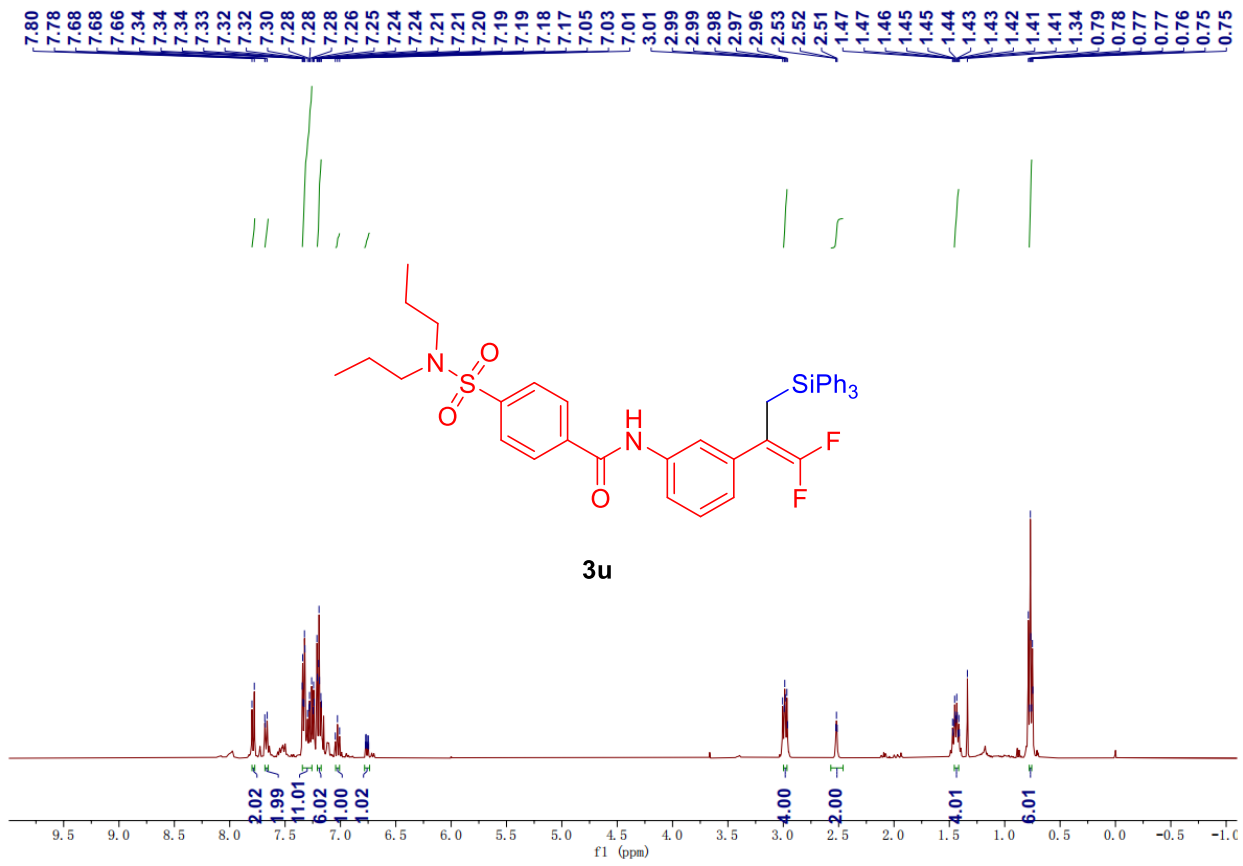


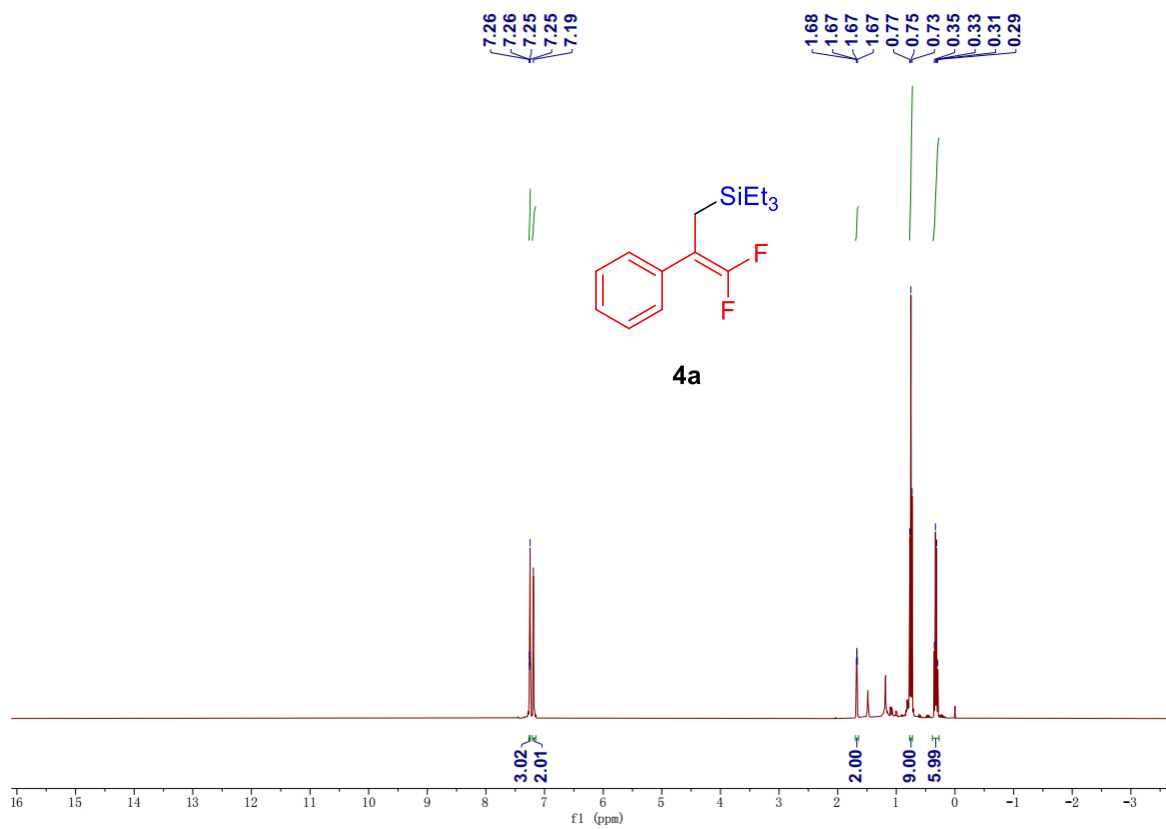
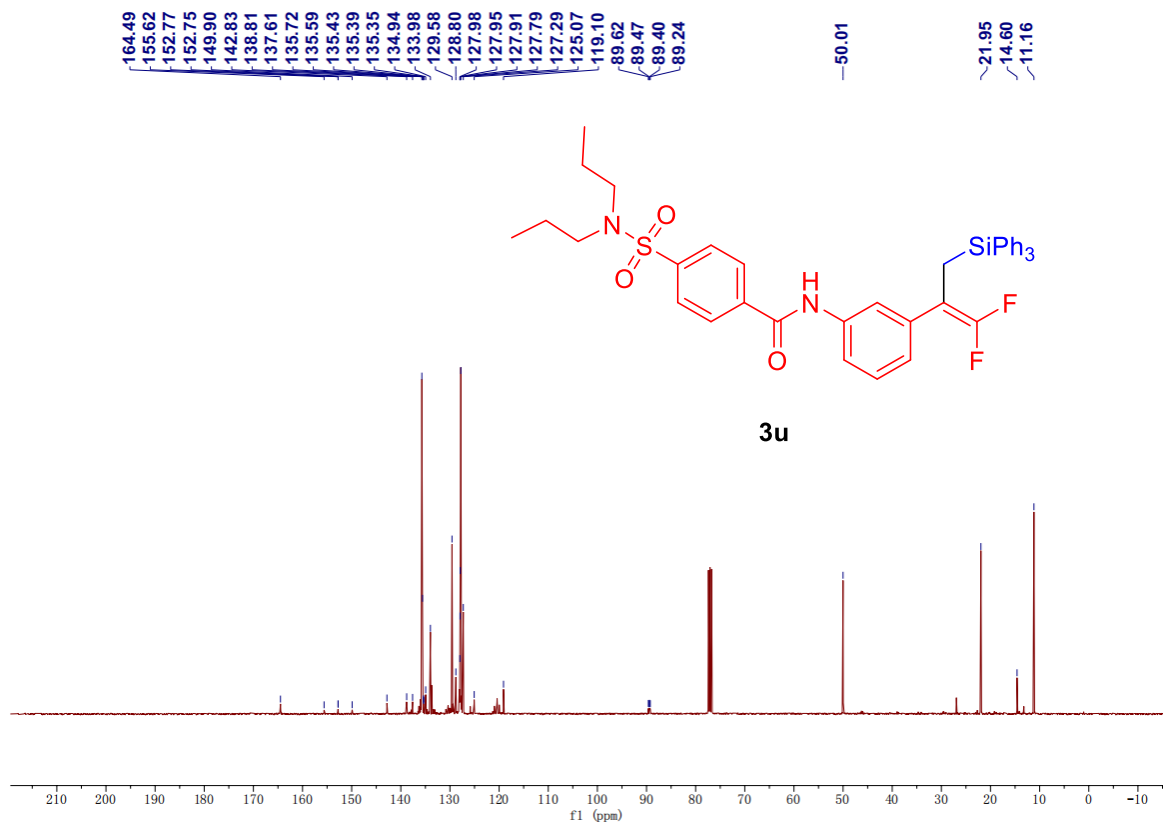


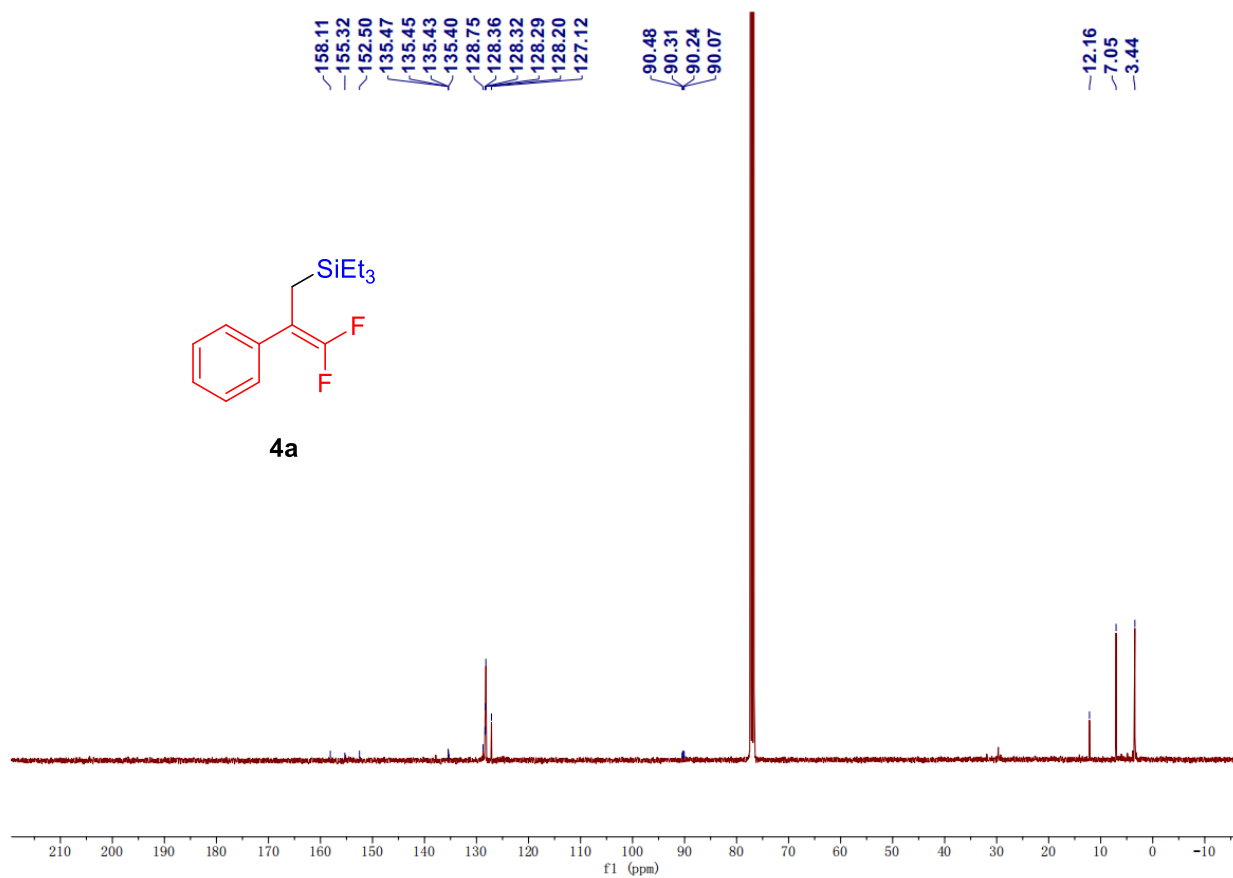
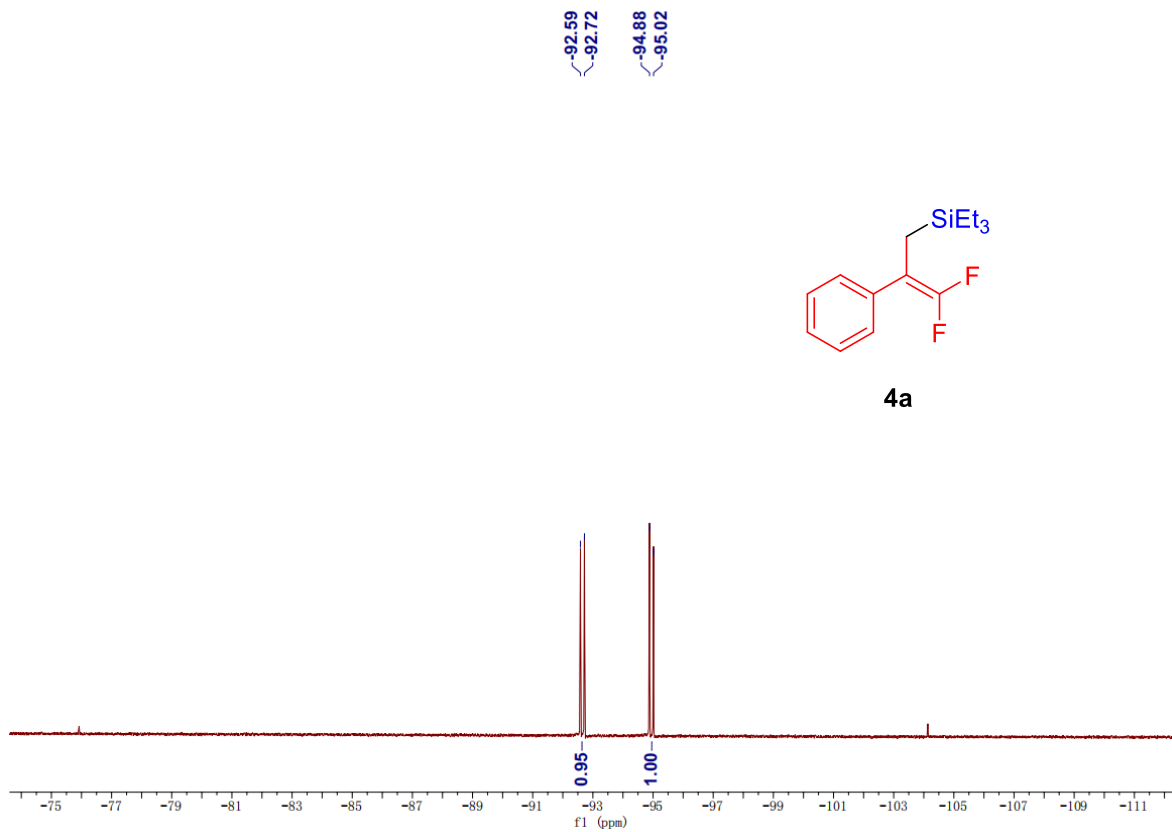


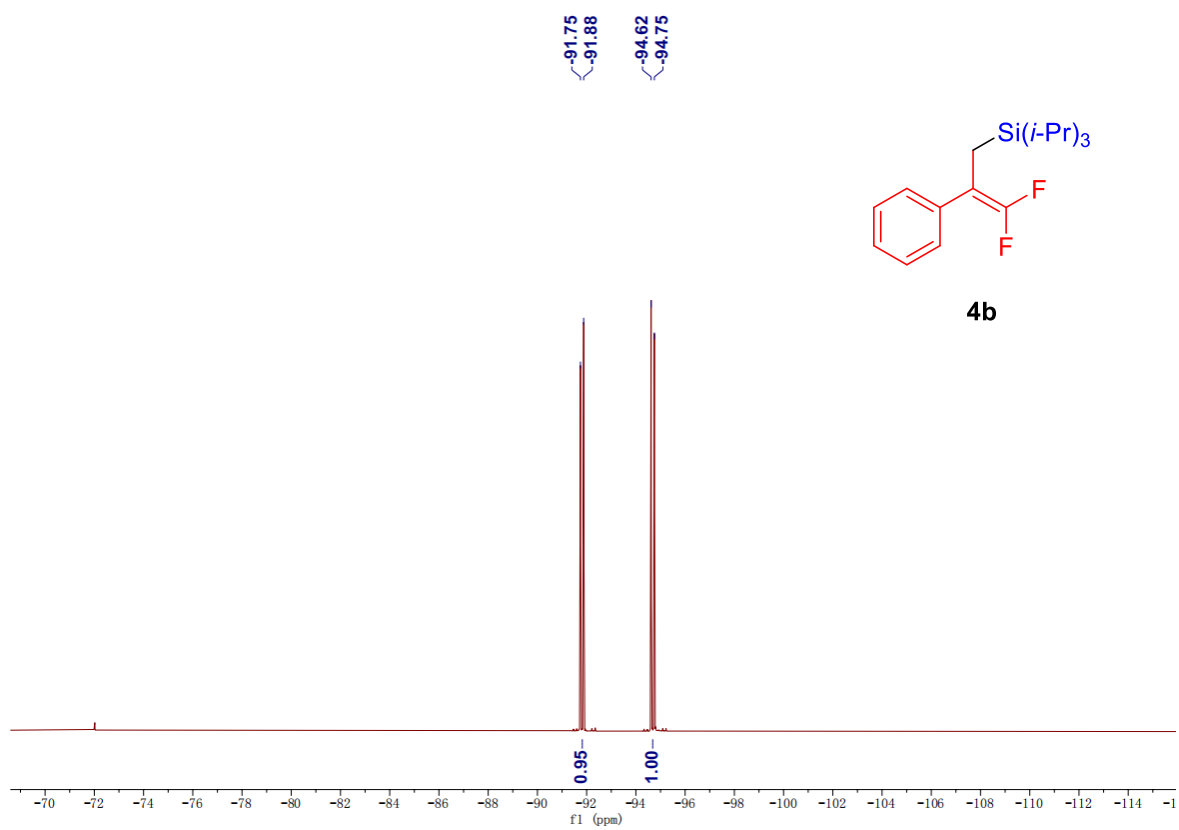
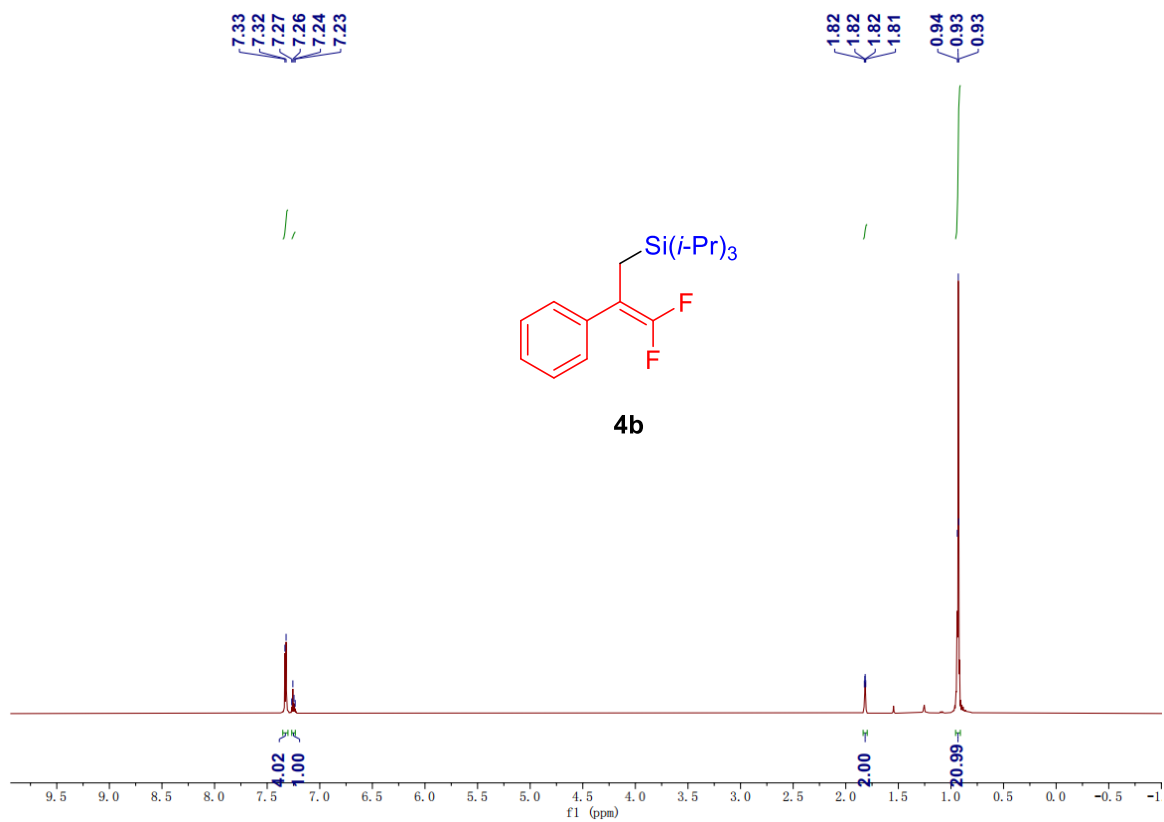


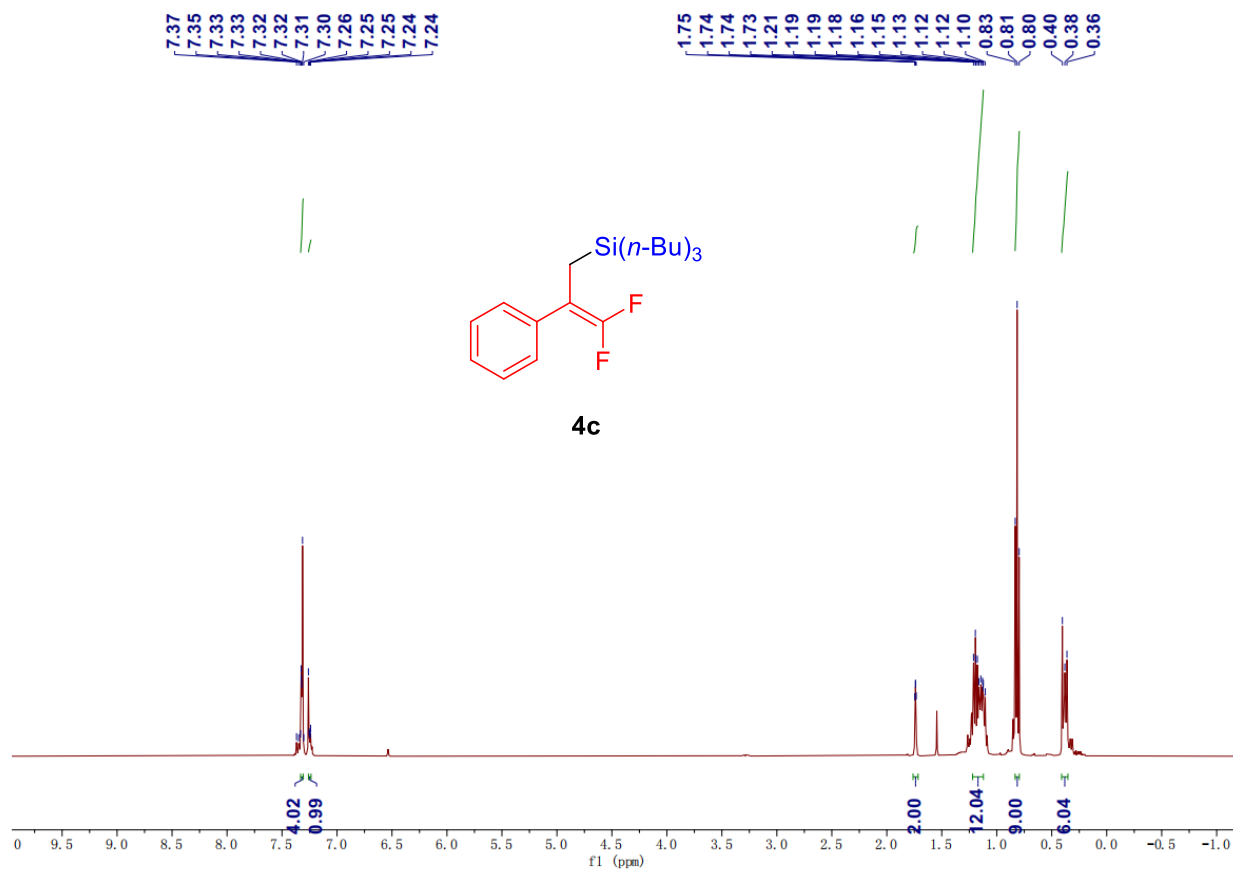
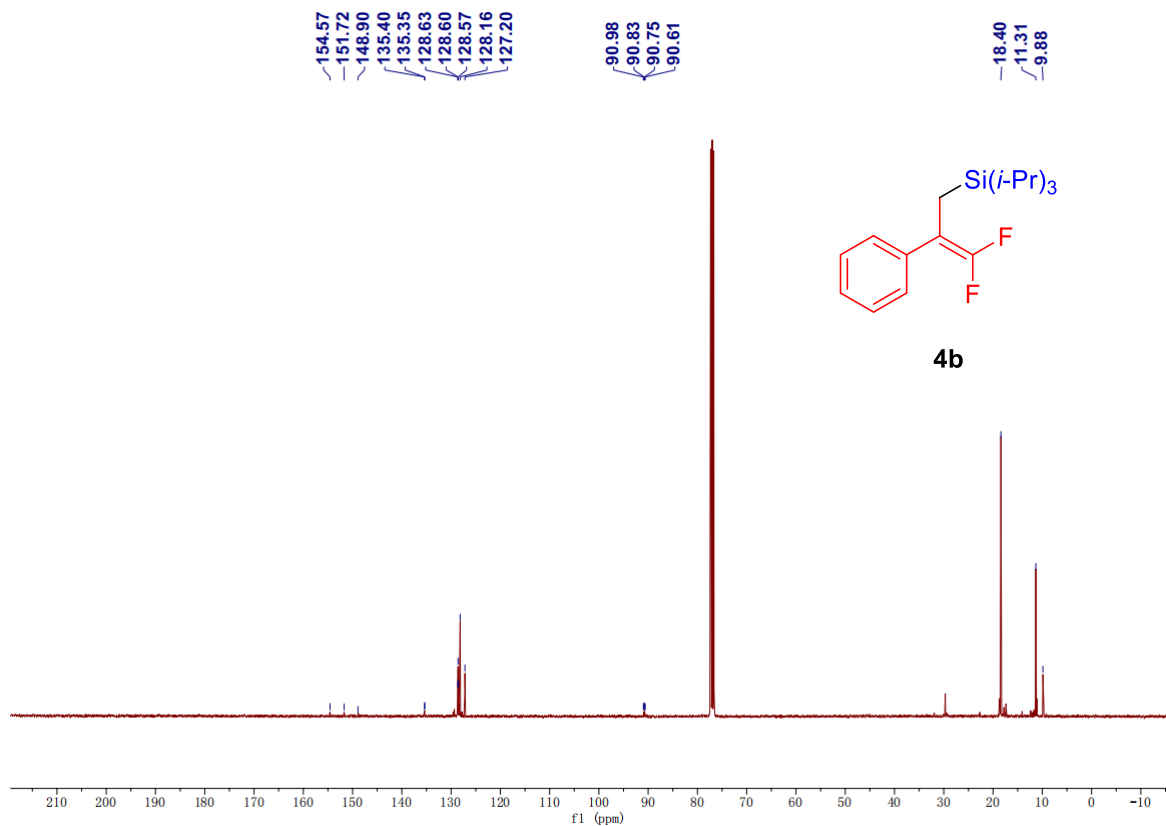


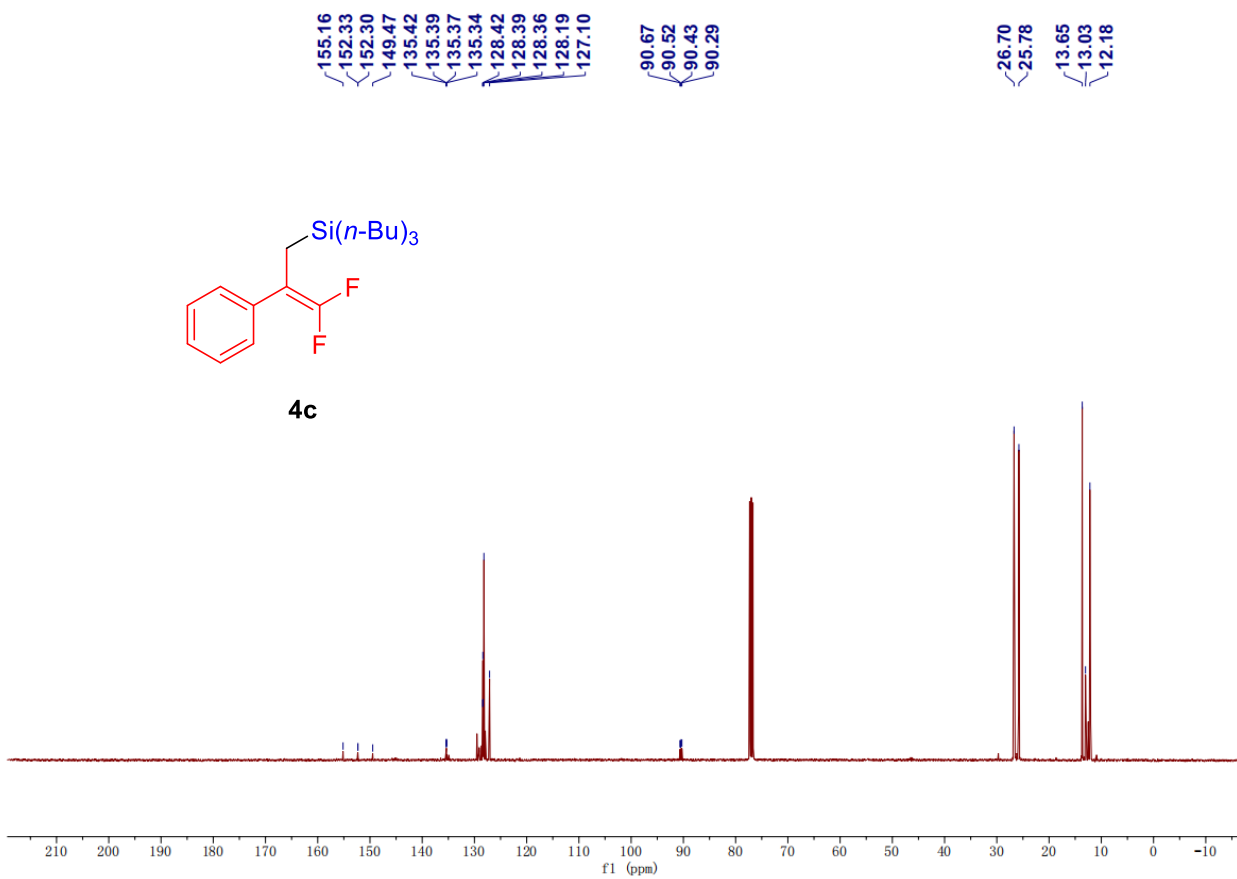
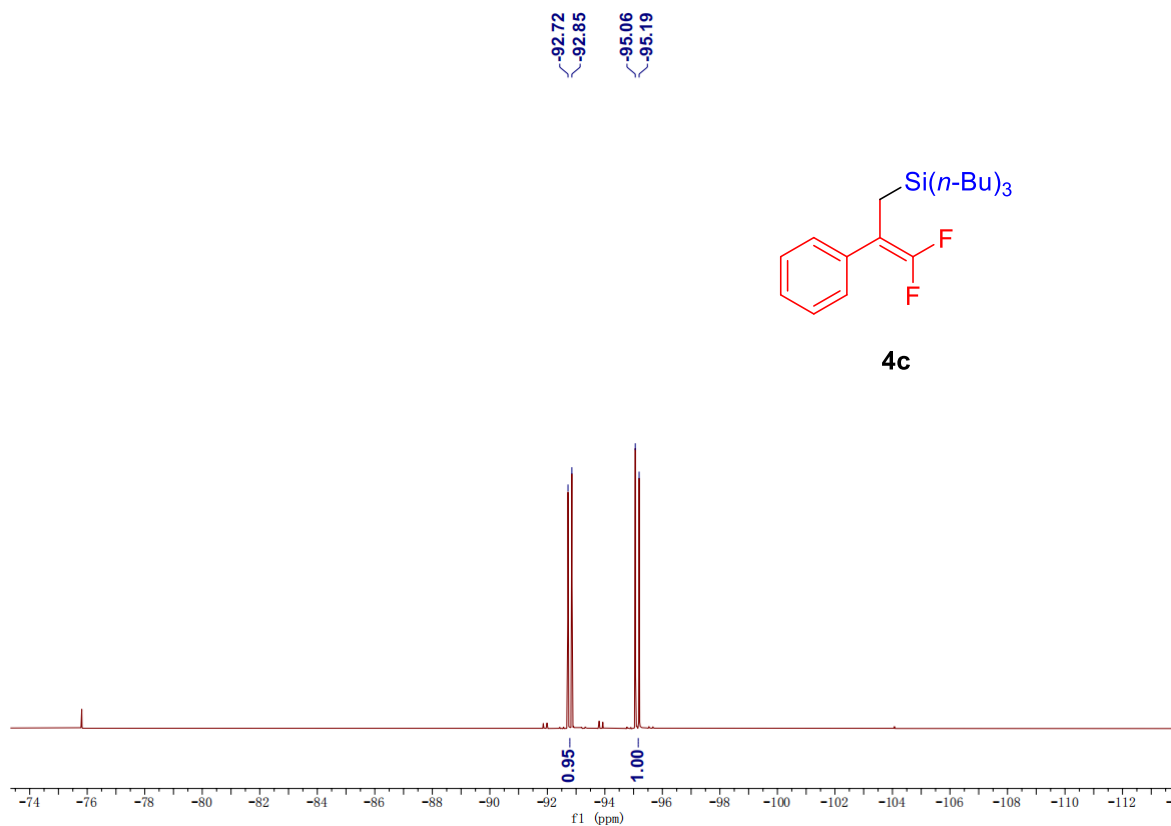


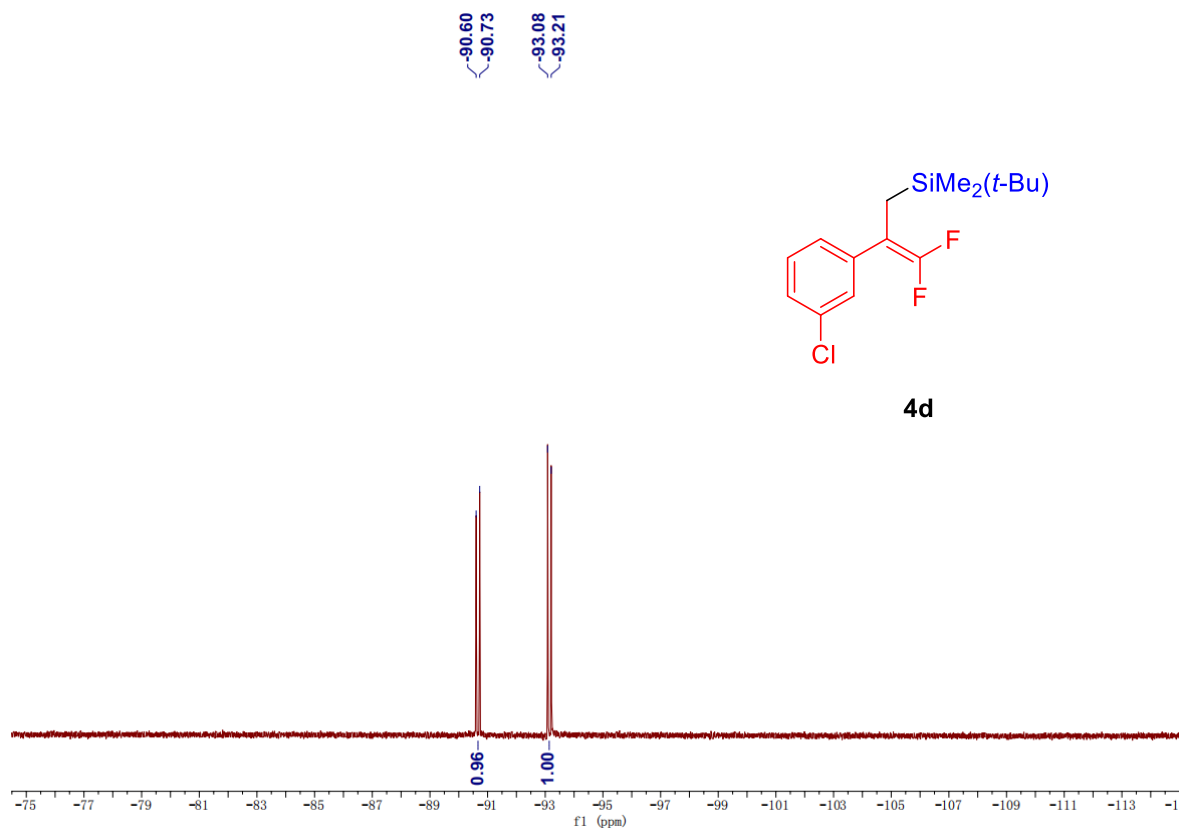
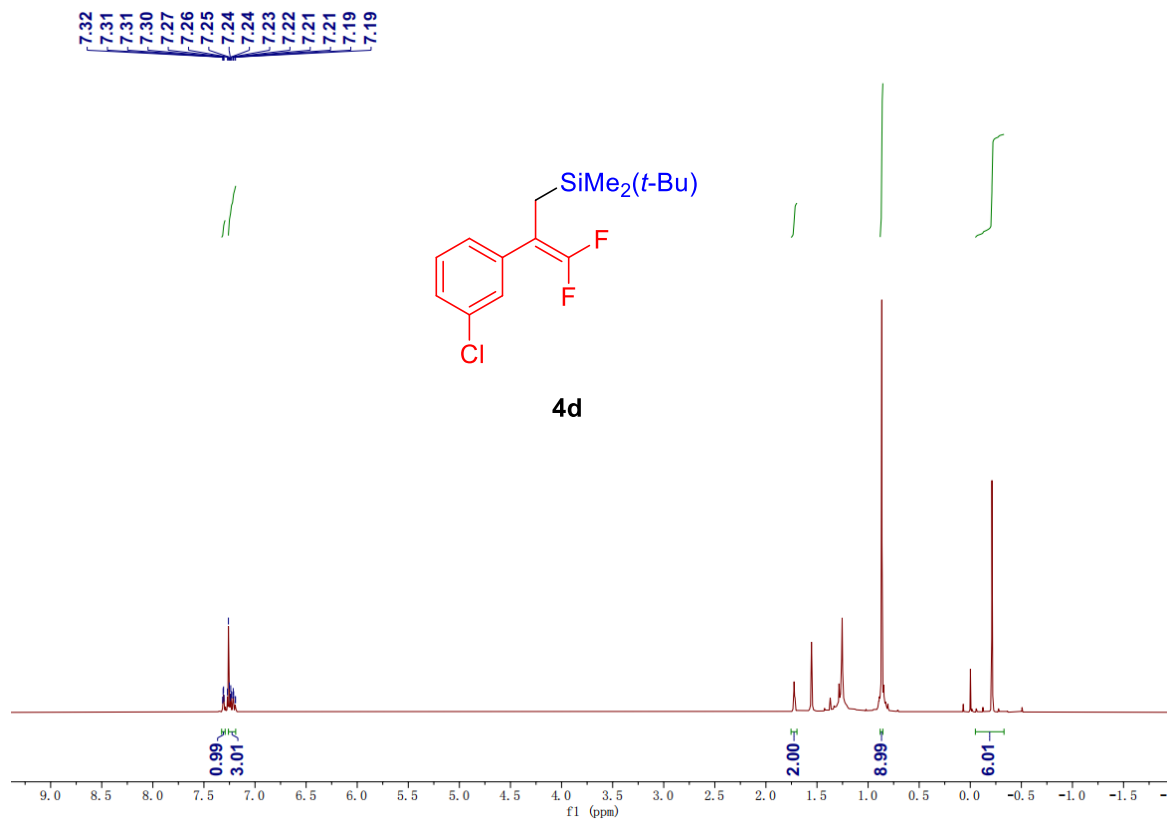


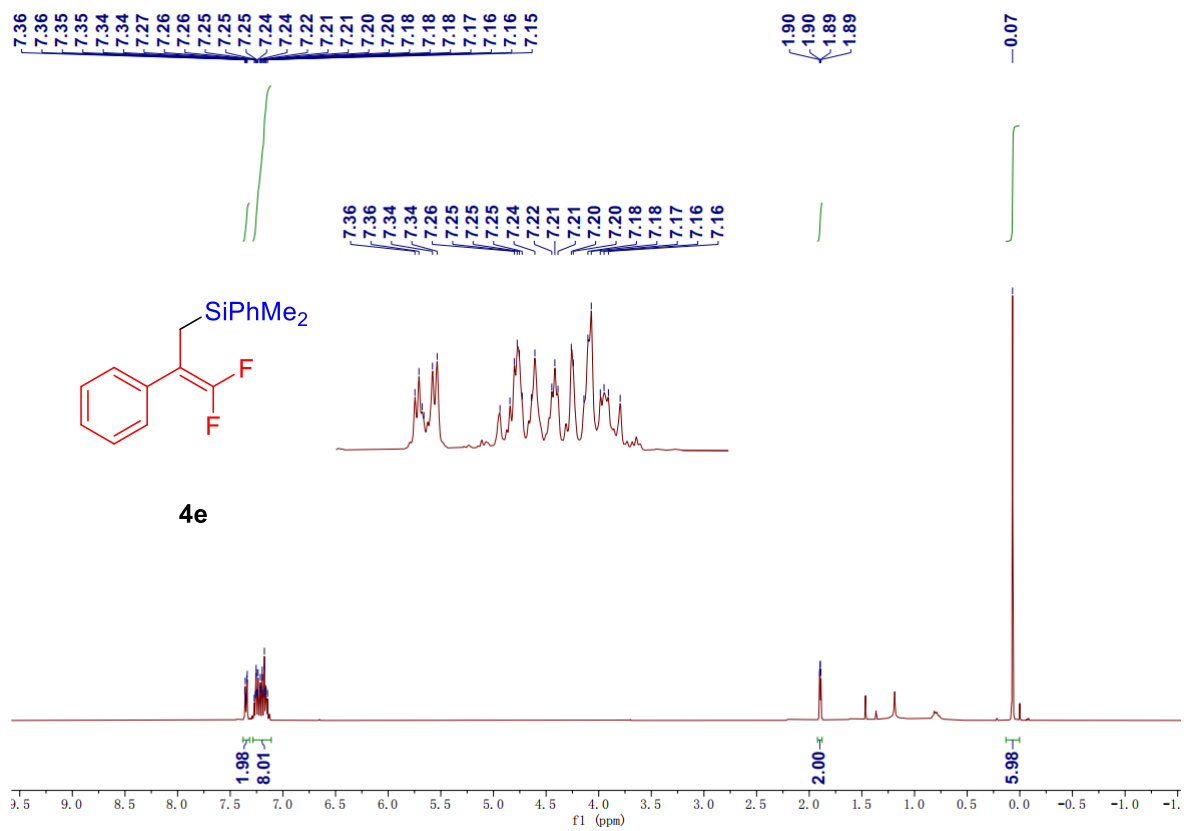
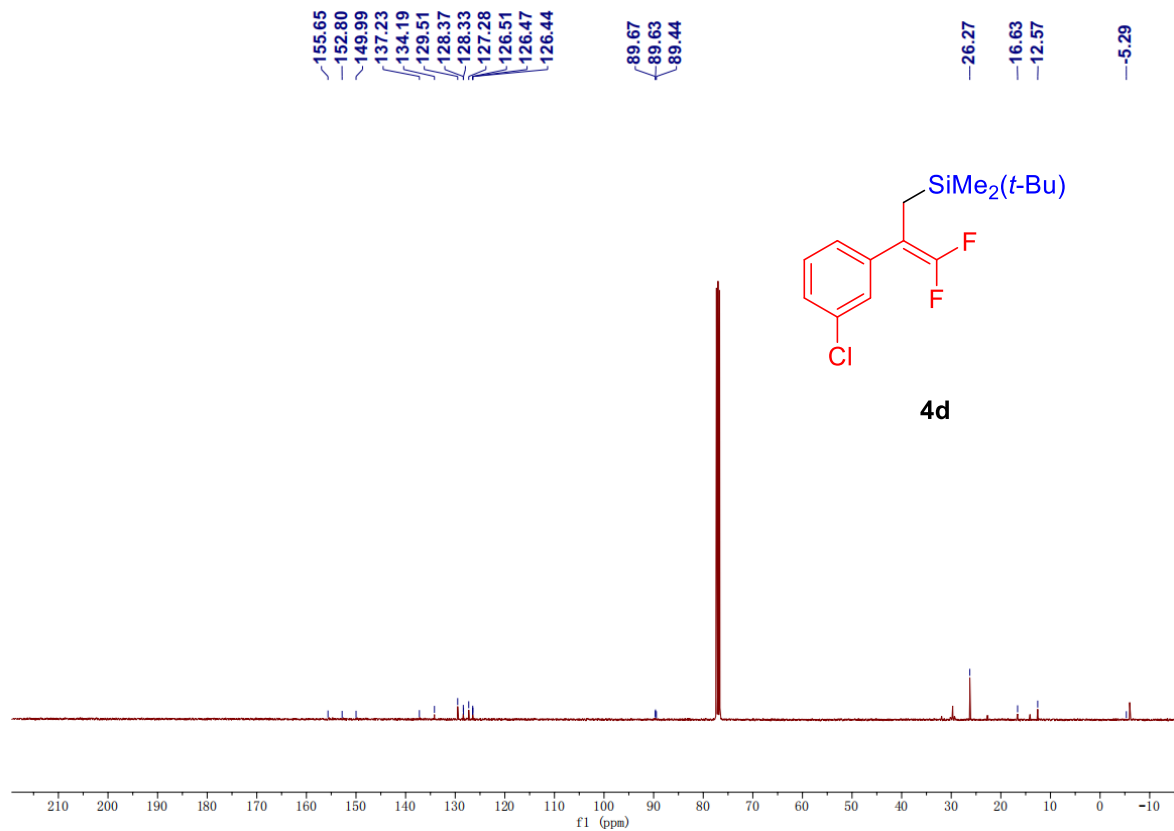




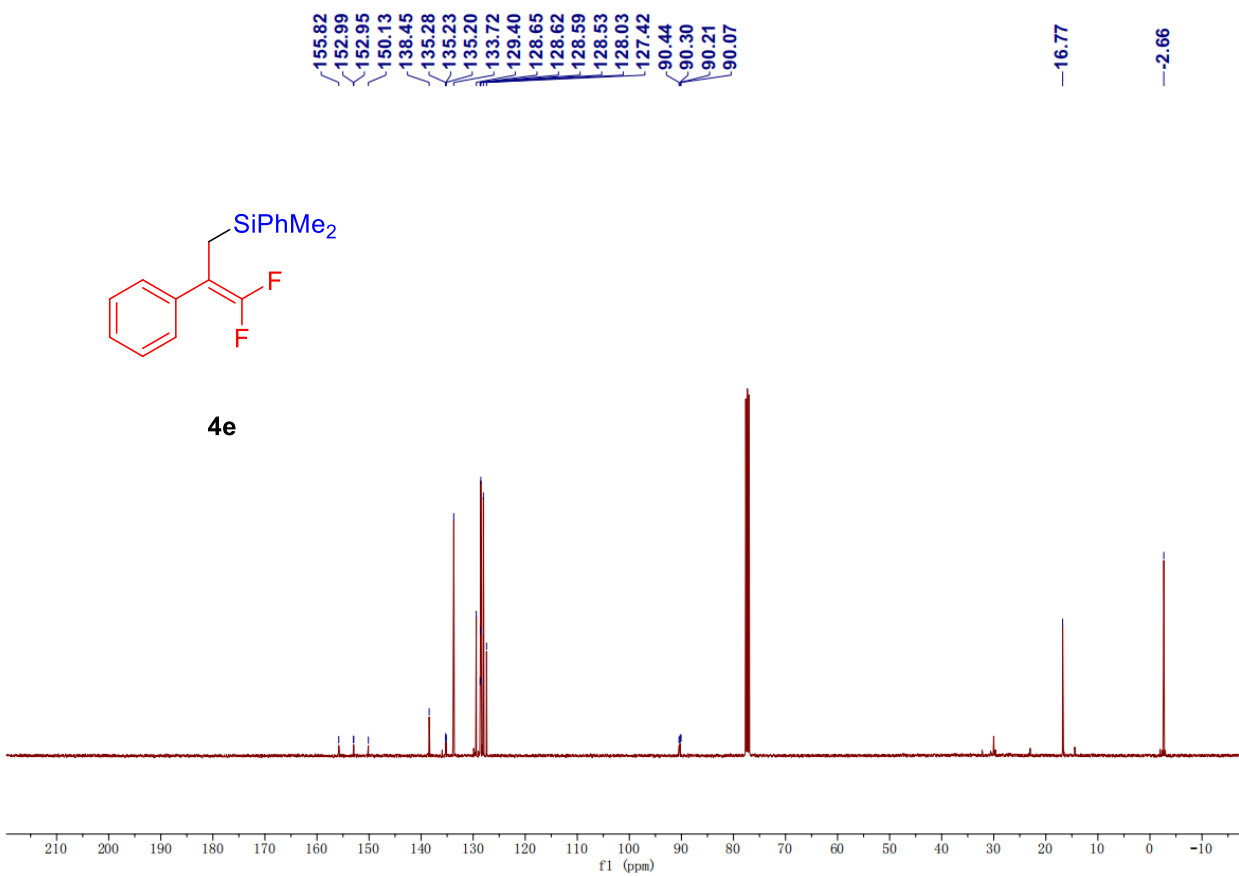
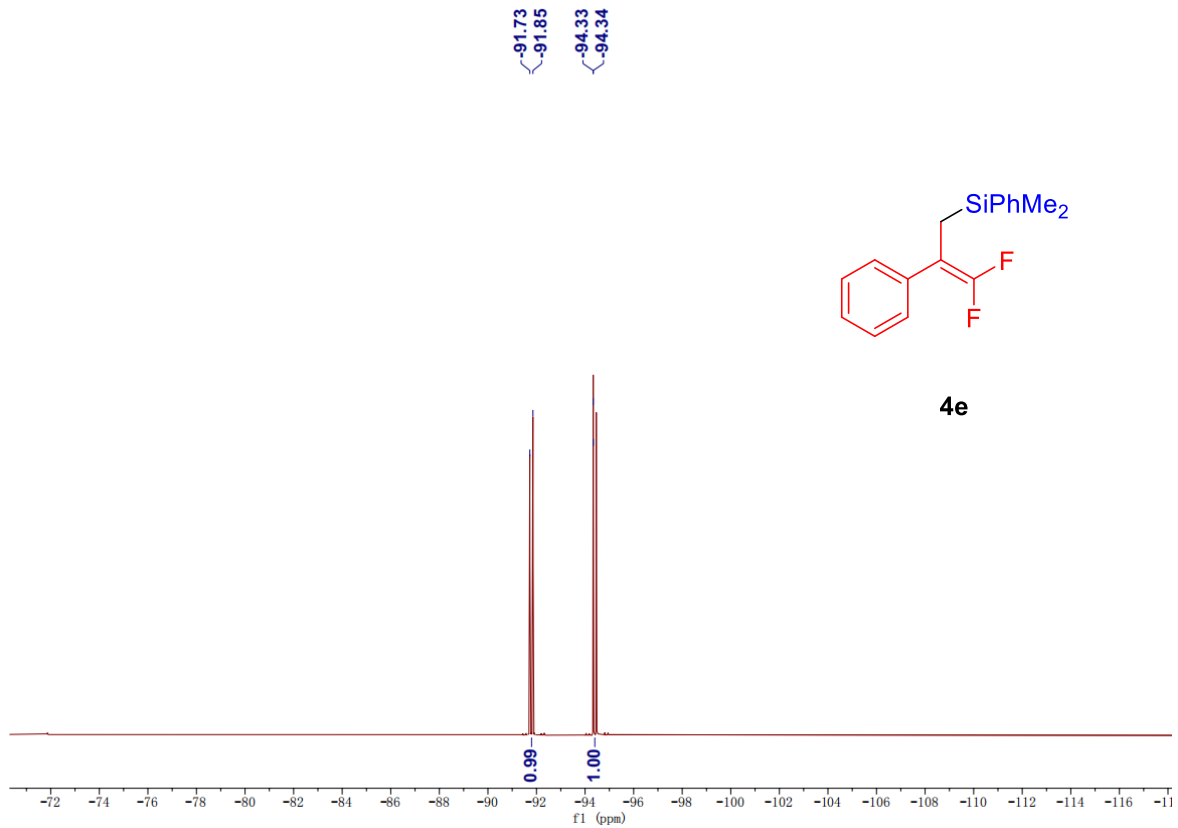


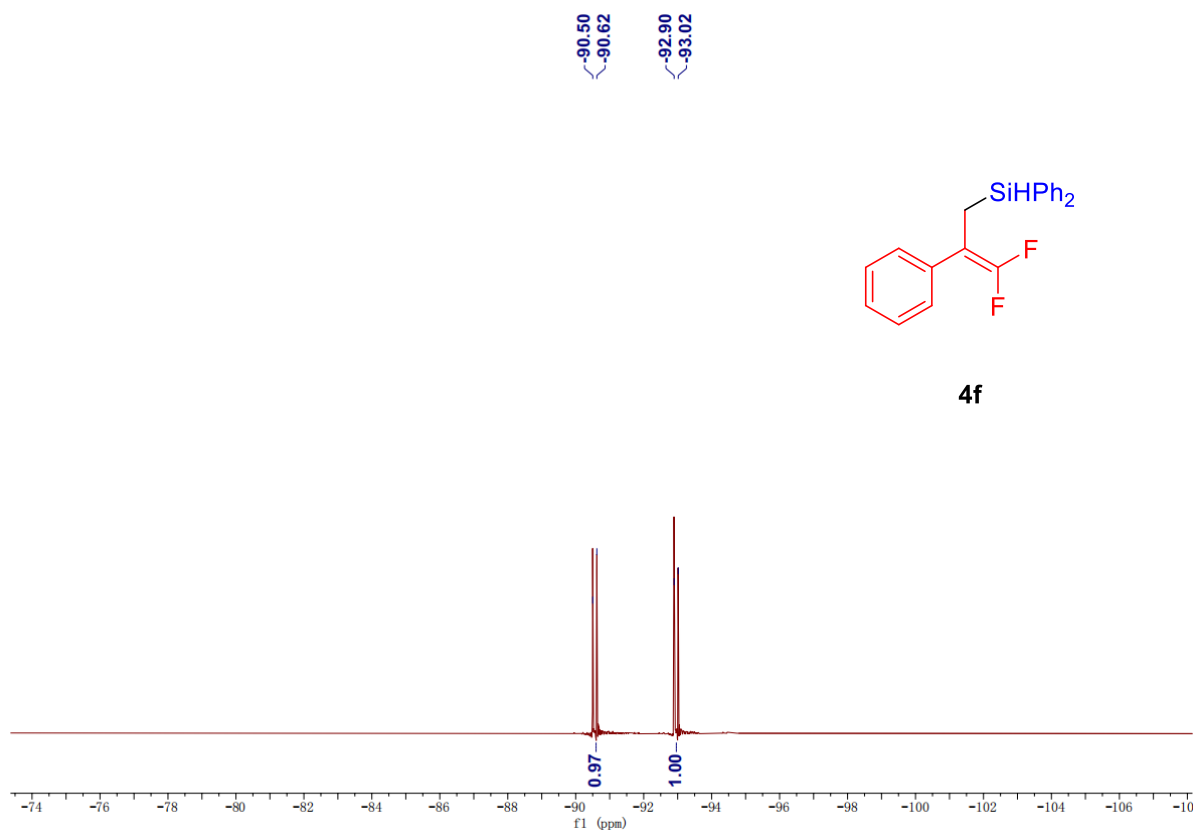
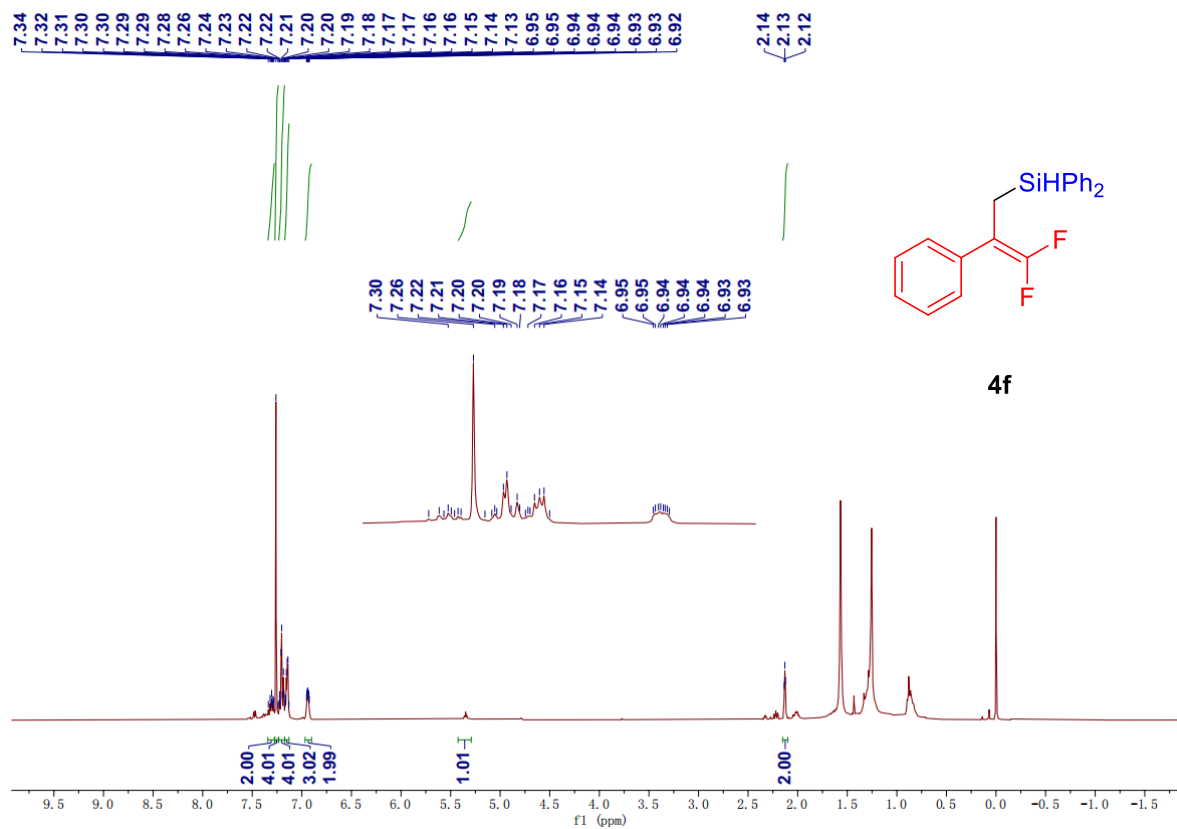


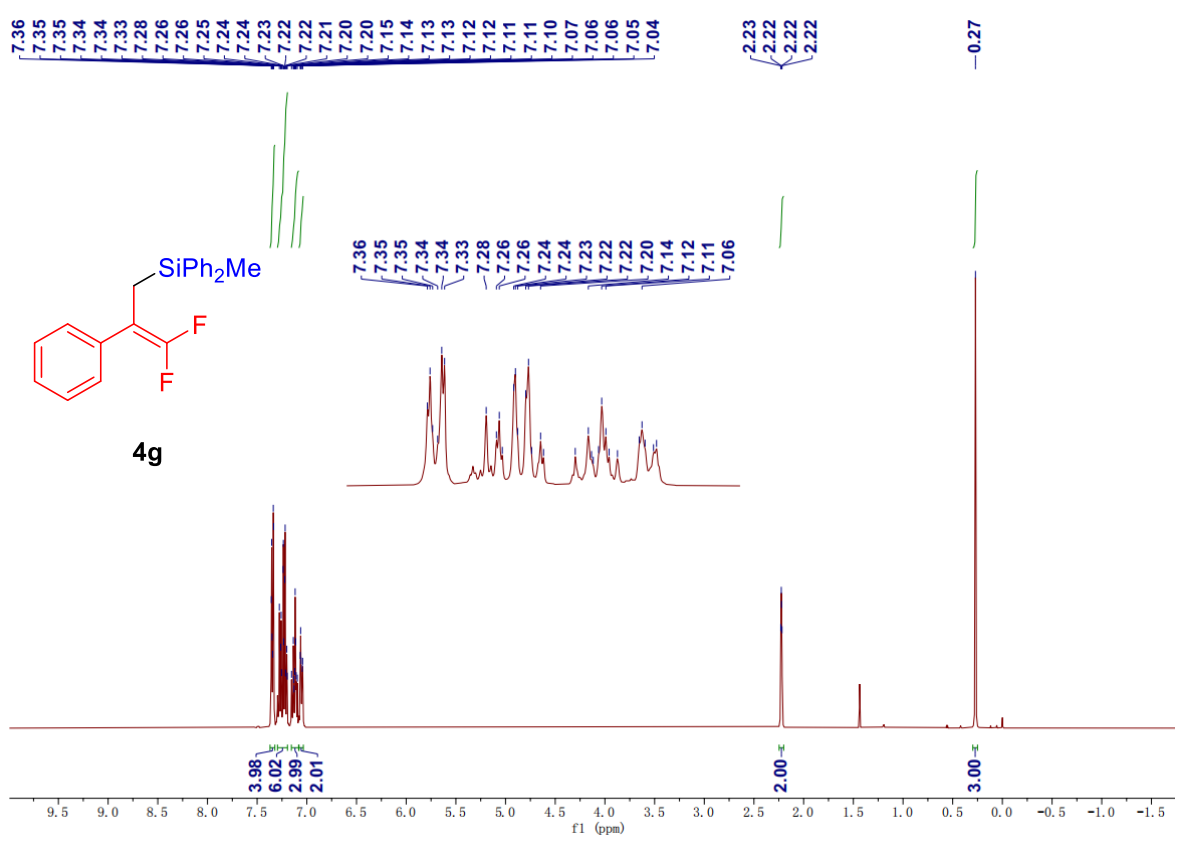
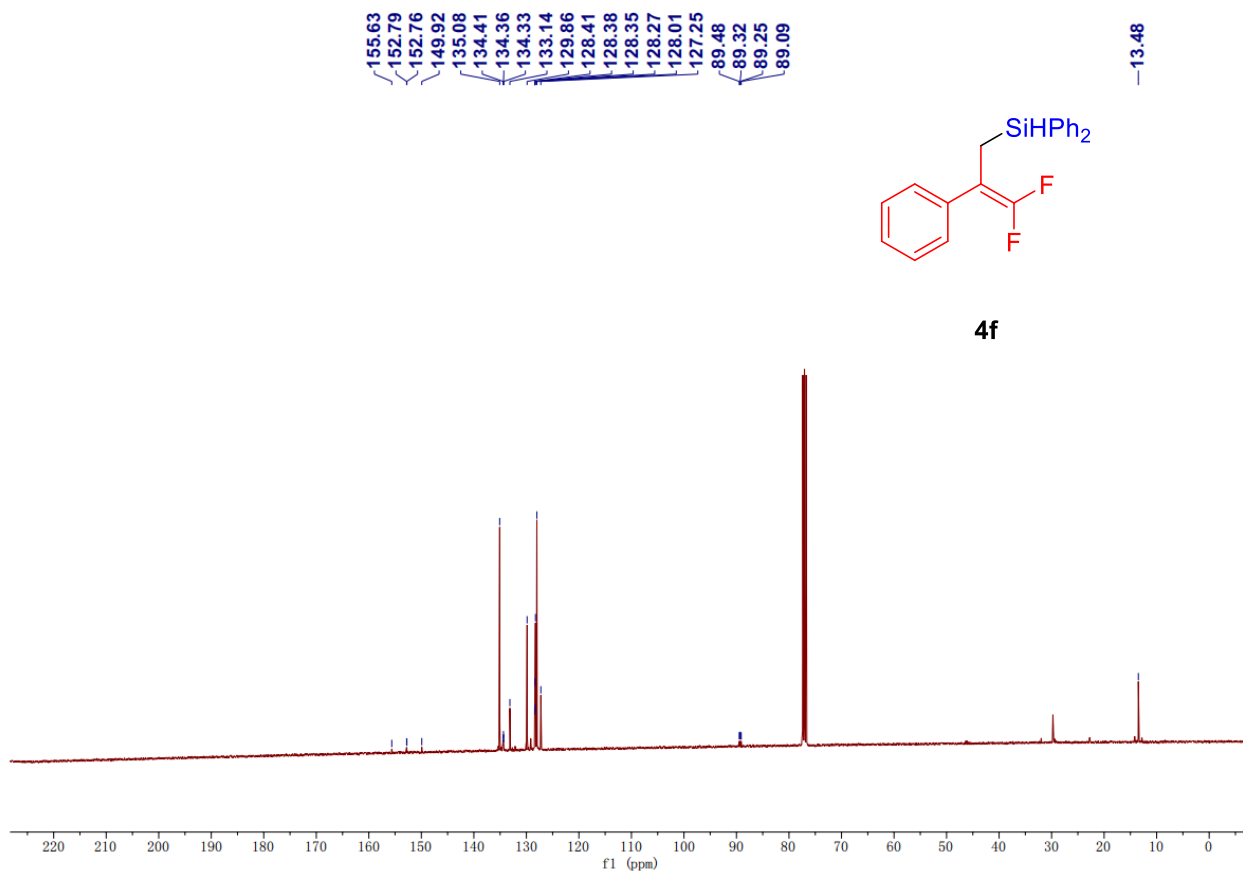


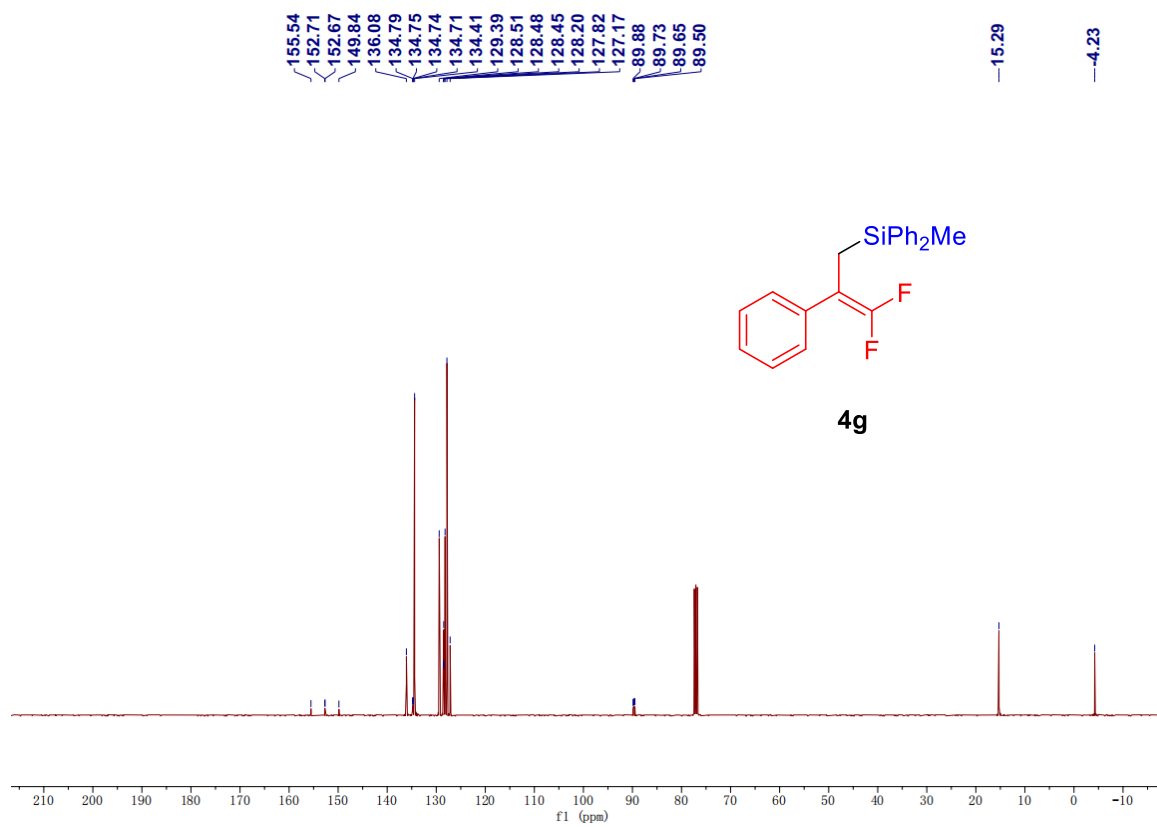
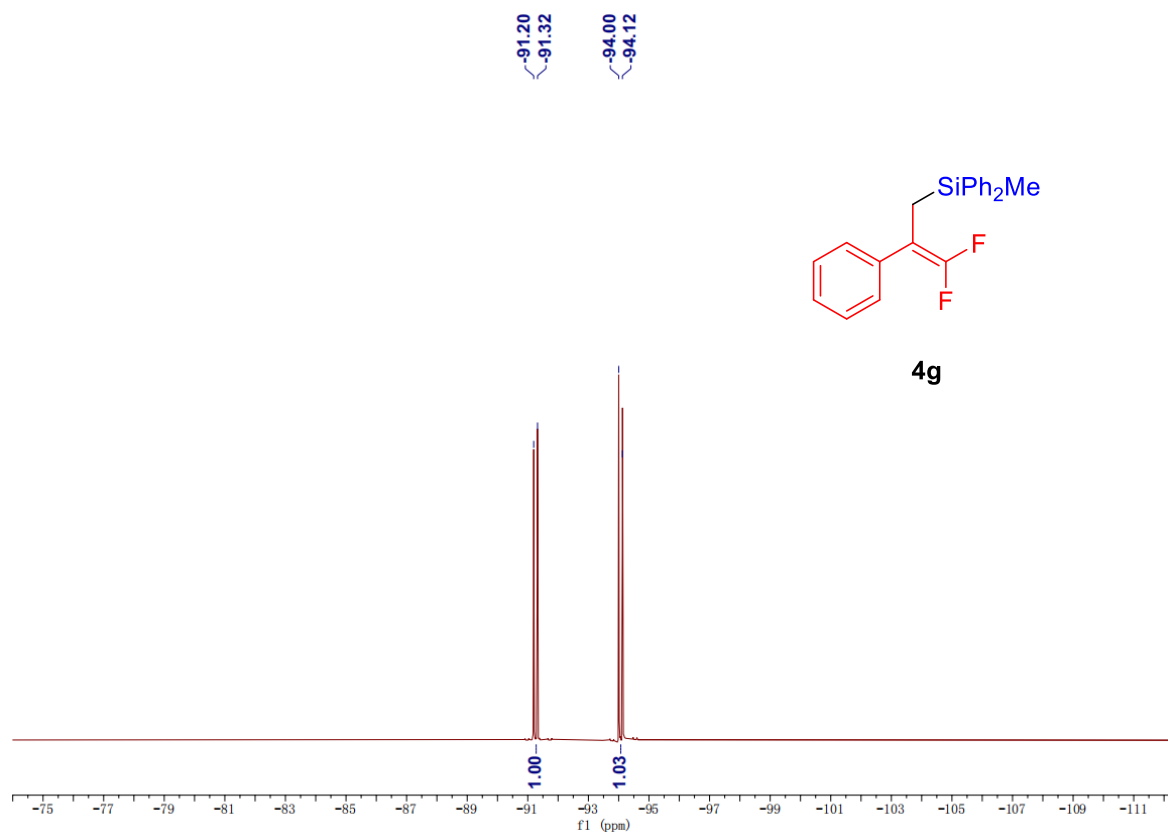


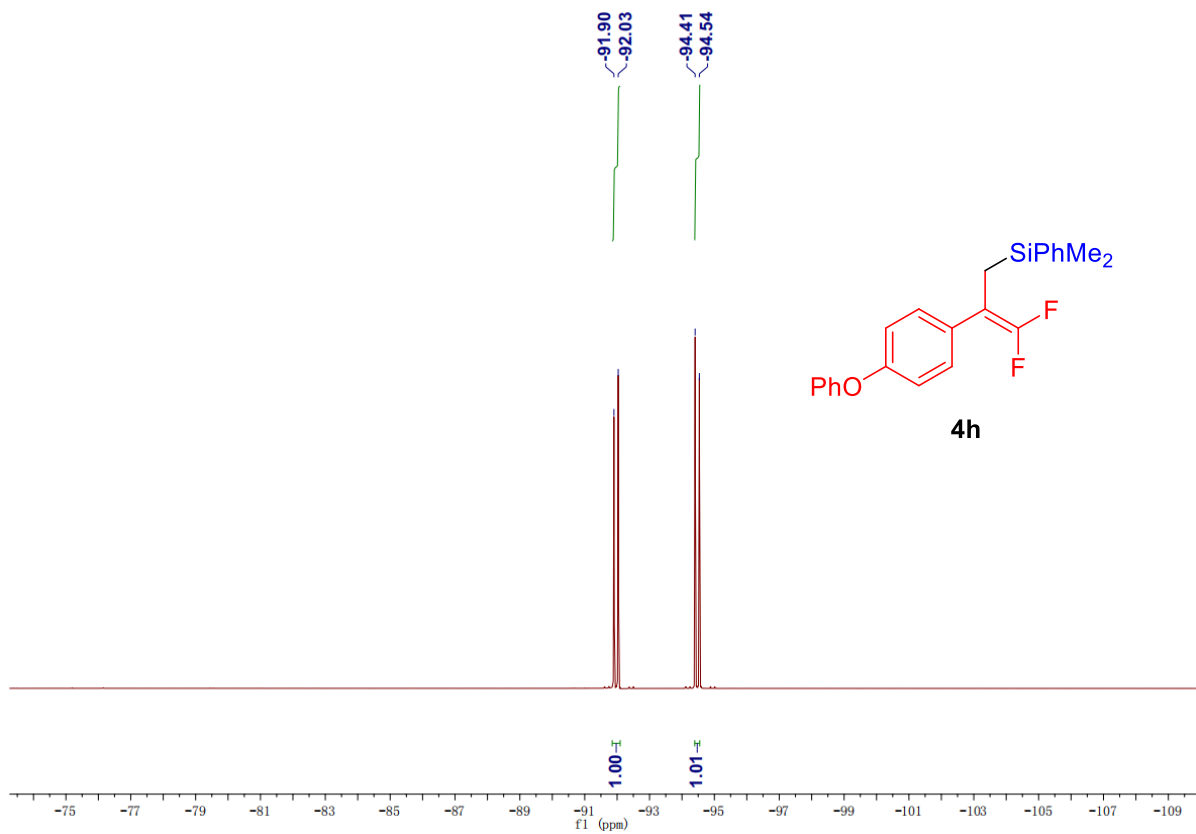
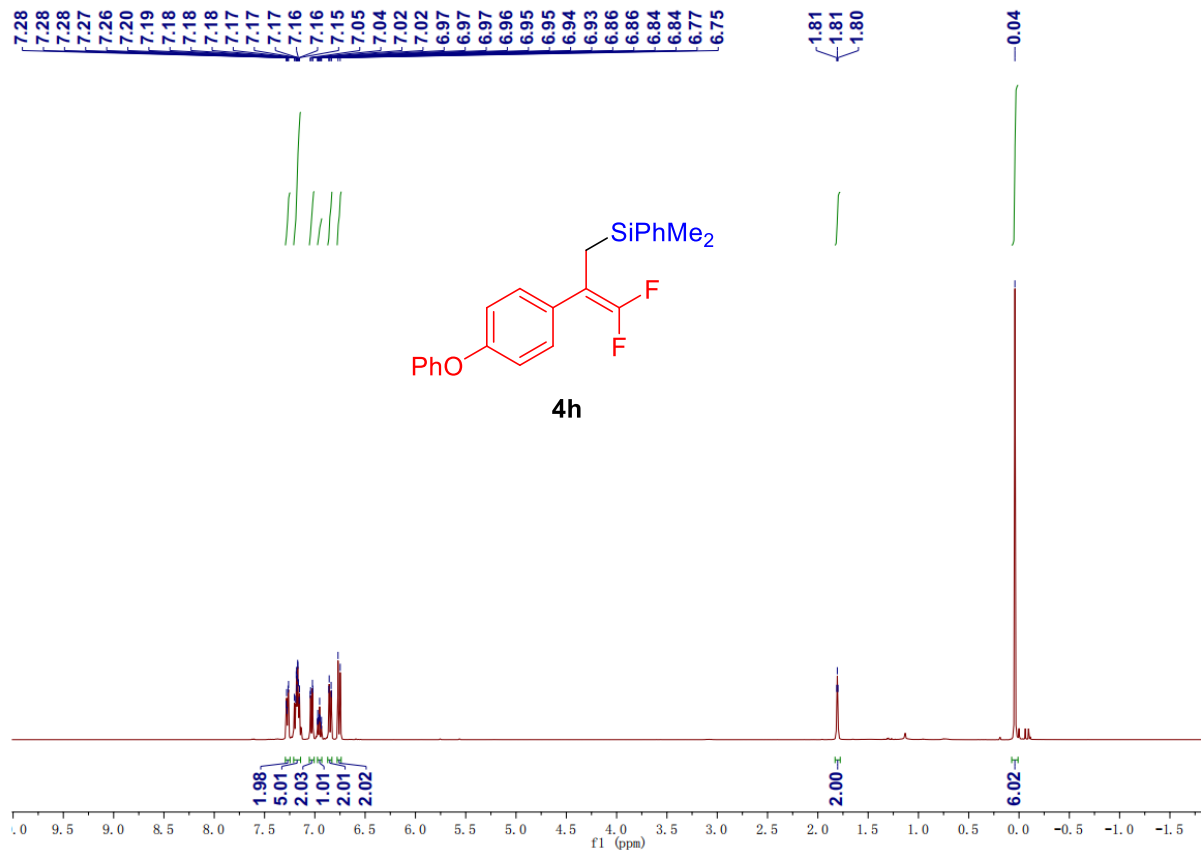


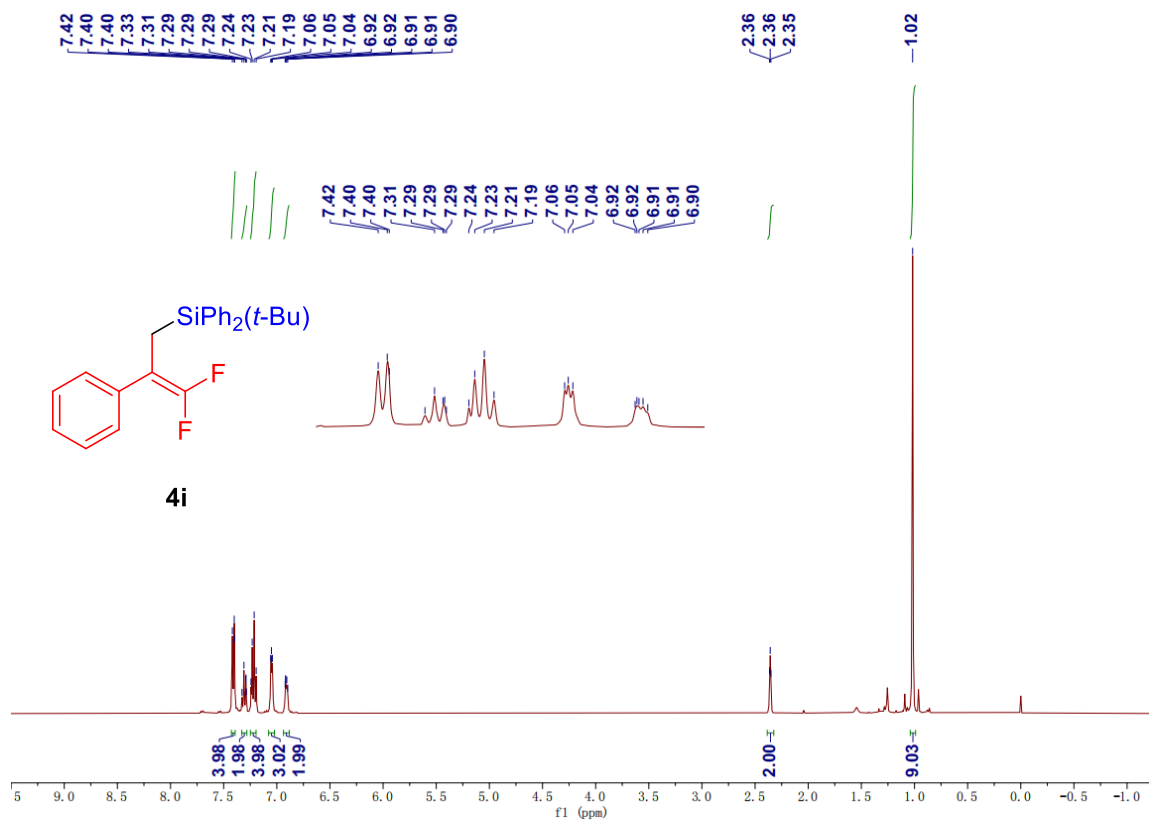
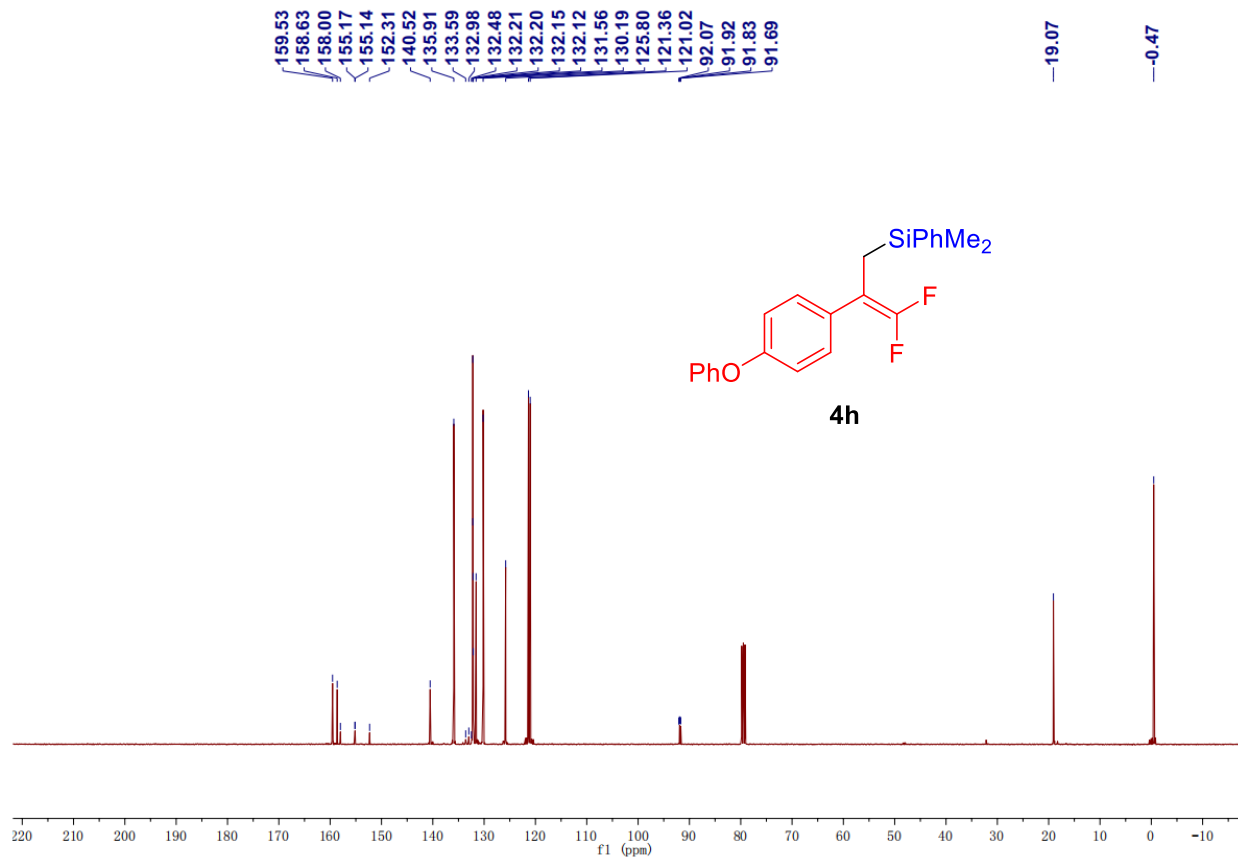


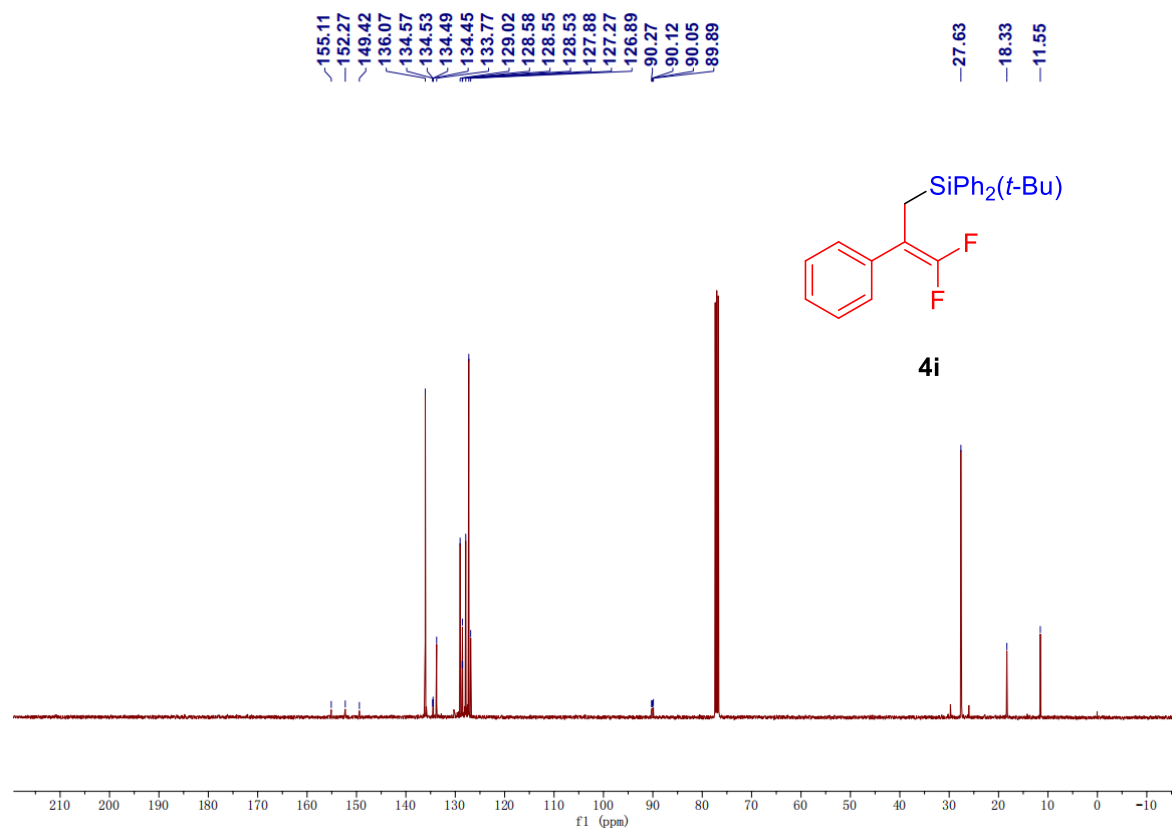
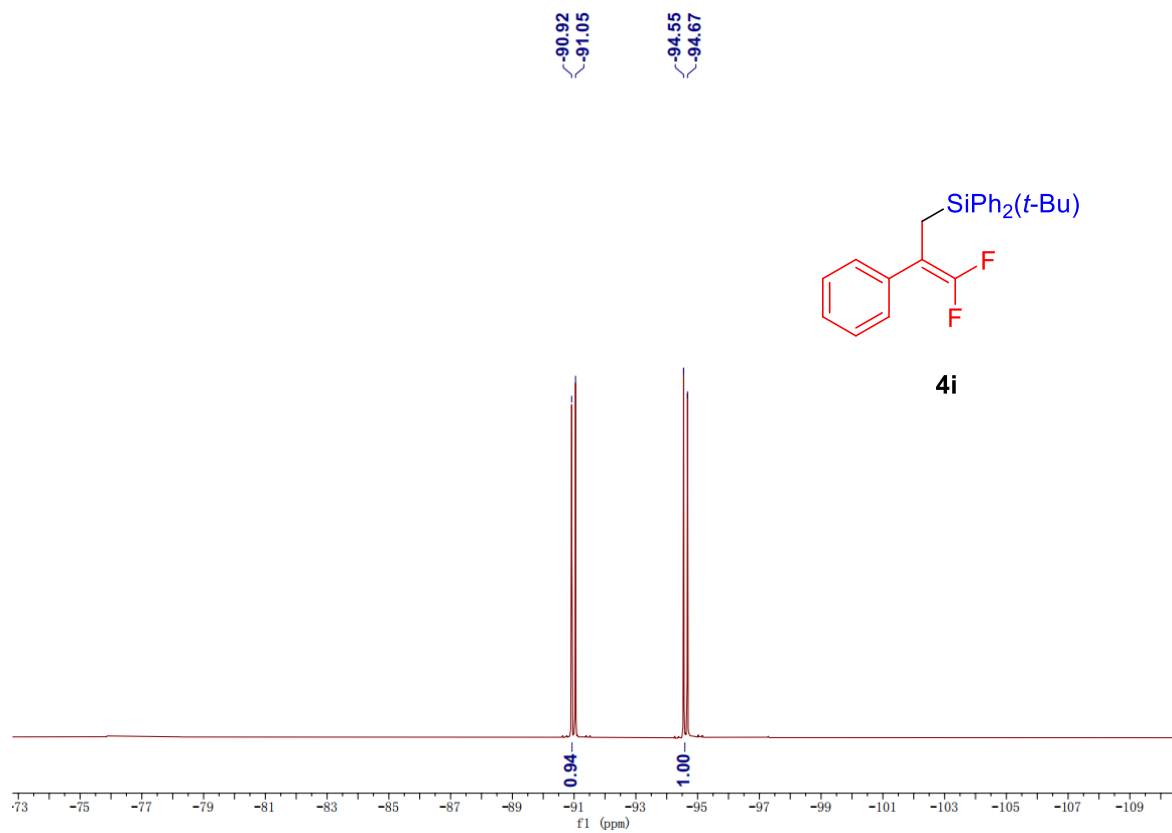


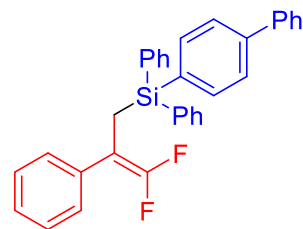
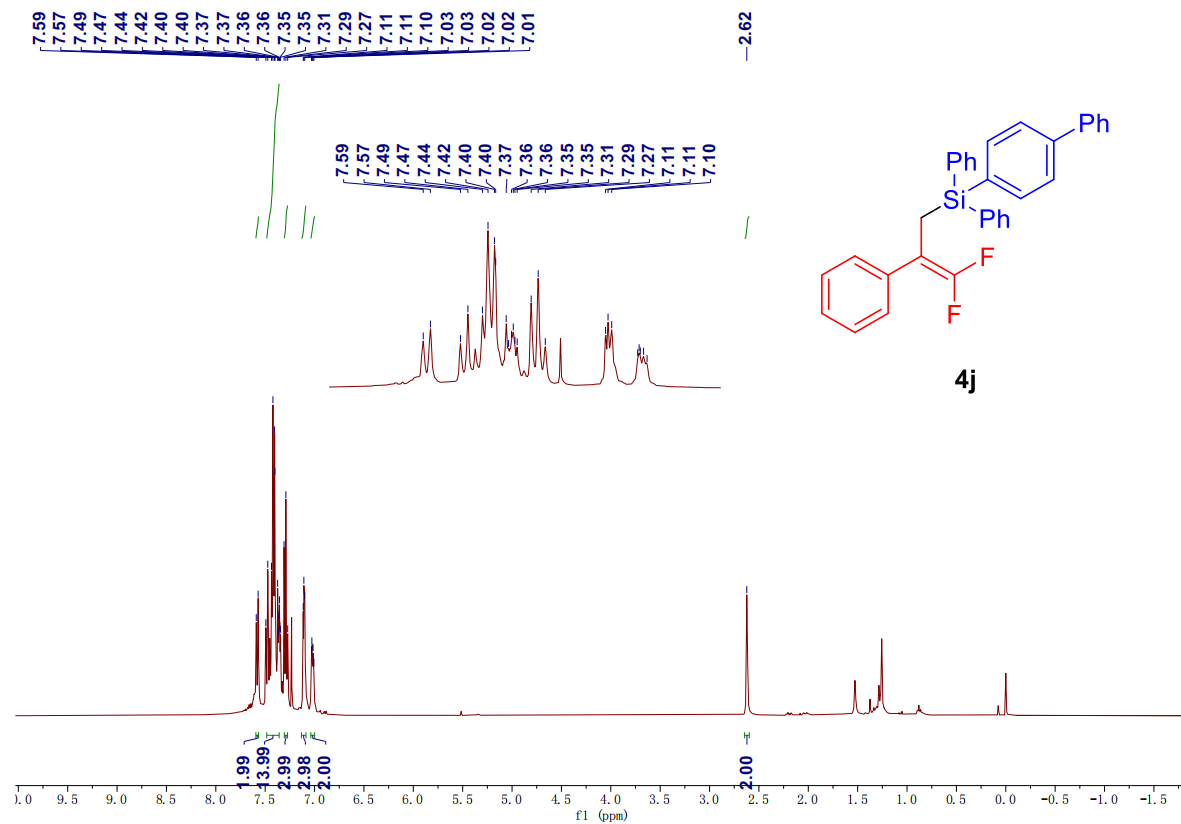




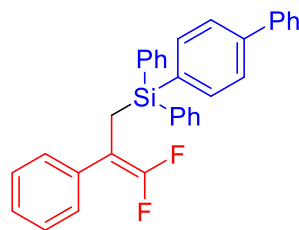
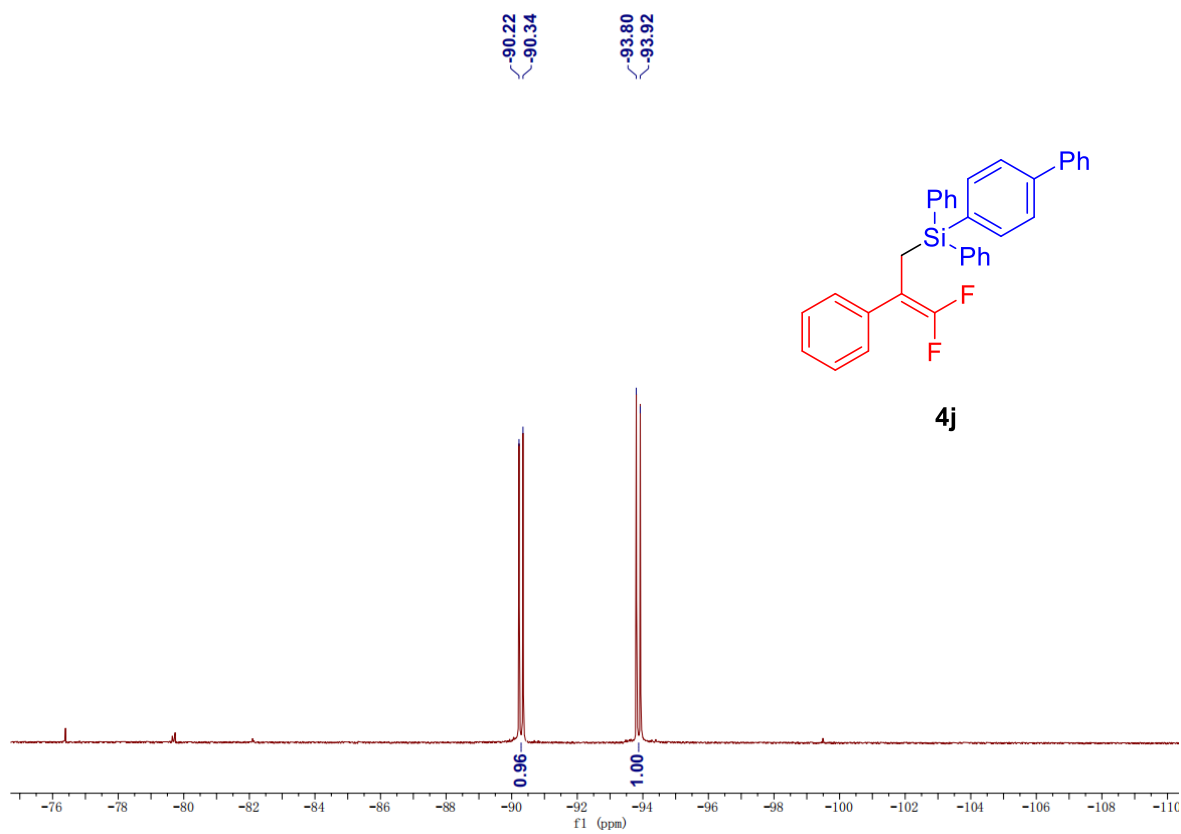








4j



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