

## Supporting Information

# Palladium-catalyzed olefination of aryl/alkyl halides with trimethylsilyldiazomethane via carbene migratory insertion

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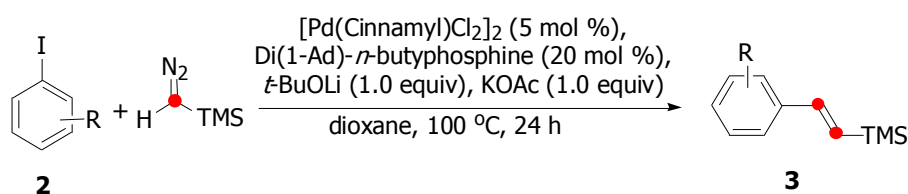
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## 1. General Considerations

Unless other noted, all experiments were carried out under N<sub>2</sub> atmosphere. Reactions were monitored by thin layer chromatography using silica gel. Most solvents were purified according to the standard procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories. The other regular chemicals were obtained from commercial suppliers with purity over 98% and used without further purification. Nuclear magnetic resonance spectra (<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR) were recorded using a Bruker 400 MHz spectrometer. The chemical shifts were reported ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CHCl<sub>3</sub> at 7.26). <sup>13</sup>C NMR was recorded at 100 MHz: chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CHCl<sub>3</sub> at 76). <sup>19</sup>F NMR spectra were recorded at 376 MHz. GC/MS data was collected using an Agilent 7890A series GC and 5975C Ms detector. High-resolution mass spectral data were recorded by an Agilent instrument with ESI-MS technique.

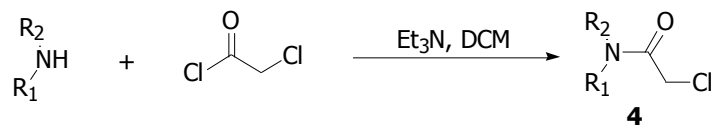
## 2. Typical procedure for the synthesis of (E)-Vinylsilane

### 2.1 General procedure for (E)-Vinylsilane using Aryl iodides



To a dried vial was added [Pd(Cinnamyl)Cl<sub>2</sub>]<sub>2</sub> (5 mol %), Di(1-Ad)-*n*-butylphosphine (20 mol %), *t*-BuOLi (0.75 mmol, 1.0 equiv) and KOAc (0.75 mol, 1.0 equiv), then dry dioxane (1.5 mL) was added. The mixture was stirred at room temperature under N<sub>2</sub> atmosphere for 1 h. Then a solution of **2** (0.75 mmol, 1.0 equiv) in dioxane (1 mL) was added, followed by TMSCHN<sub>2</sub> (1.1 mL, 2M/L, 3.0 equiv). The reaction mixture was stirred at 100 °C for 24 hours. After cooling, the mixture was diluted with water and extracted with EA, the combined organic layer was washed with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, the filtrate was concentrated under vacuum and purified by column chromatography on silica gel to afford the corresponding **3**.

## 2.2 General procedure for (E)-Vinylsilane using $\alpha$ -chloroacetamides



**4** ( $\alpha$ -chloroacetamides) synthesized according to the literature methods:

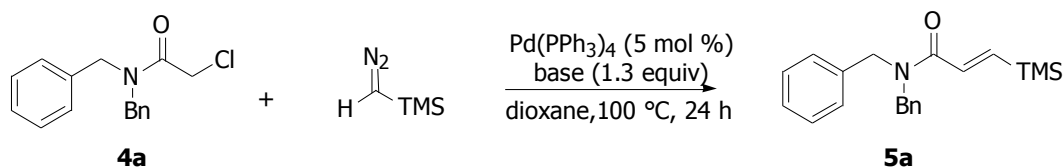
**4a, 4c, 4d, 4e** (J. Pedroni, M. Boghi, T. Saget, N. Cramer, *Angew. Chem. Int. Ed.* 2014, **53**, 9064-9067.)

**4b, 4g, 4h** (E. J. Hennessy, S. L. Buchwald, *J. Am. Chem. Soc.* 2003, **125**, 12084-12085.)

**4i** (M. C. Joshi, K. J. Wicht, D. Taylor, R. Hunter, P. J. Smith, T. J. Egan, *Eur. J. Med. Chem.* 2013, **69**, 338-347.)

### General optimization procedure

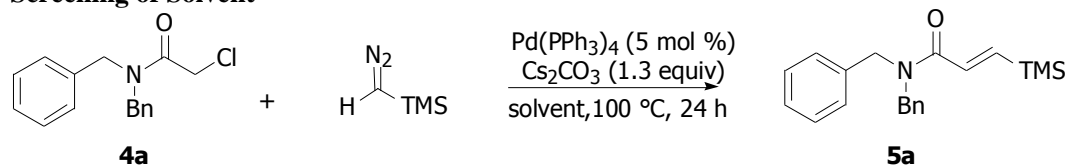
#### Screening of Base



Entry <sup>a</sup>	Pd salt	Solvent	Base/Additive	Product <sup>b</sup>
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	K <sub>2</sub> CO <sub>3</sub> /KOAc	15
2	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	CsPiv/KOAc	no
3	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	K <sub>2</sub> CO <sub>3</sub>	54
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	Na <sub>2</sub> CO <sub>3</sub>	38
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	Li <sub>2</sub> CO <sub>3</sub>	trace
6	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	KHCO <sub>3</sub>	22
7	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	90
8	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	Ag <sub>2</sub> CO <sub>3</sub>	trace
9	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	Et <sub>3</sub> N	no
10	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	<i>t</i> -BuOLi	trace
11	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	<i>t</i> -BuONa	trace
12	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	<i>t</i> -BuOK	trace
13	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	K <sub>3</sub> PO <sub>4</sub>	no
14	[Pd(Cinnamyl)Cl <sub>2</sub> ] <sub>2</sub> , Di(1-Ad)- <i>n</i> -butylphosphine, <i>t</i> -BuOLi, KOAc			no
15	[Pd(Cinnamyl)Cl <sub>2</sub> ] <sub>2</sub> , Di(1-Ad)- <i>n</i> -butylphosphine, <i>t</i> -BuOLi			10

<sup>a</sup>**4a** (0.1 mmol, 1.0 equiv), TMSD (3.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), Base (1.3 equiv), dioxane (1.0 mL), 100 °C, 24 hours. <sup>b</sup>Determined by GC-MS.

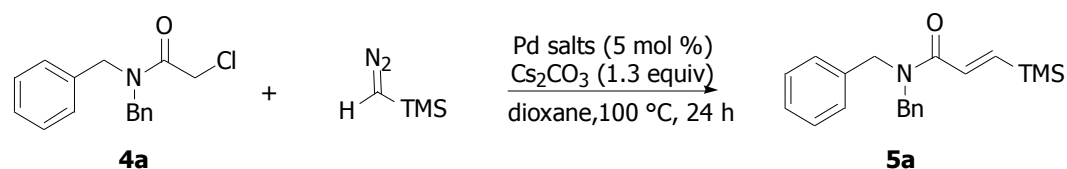
### Screening of Solvent



Entry <sup>a</sup>	Pd salt	Solvent	Base	Product <sup>b</sup>
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	90
2	Pd(PPh <sub>3</sub> ) <sub>4</sub>	toluene	Cs <sub>2</sub> CO <sub>3</sub>	no
3	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DMF	Cs <sub>2</sub> CO <sub>3</sub>	messy
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DCE	Cs <sub>2</sub> CO <sub>3</sub>	54

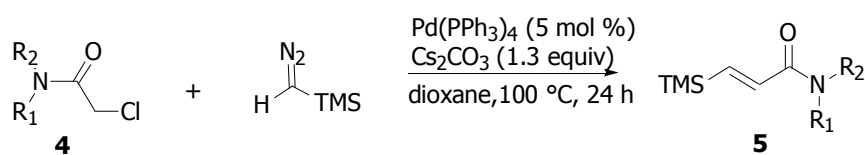
<sup>a</sup>4a (0.1 mmol, 1.0 equiv), TMSD (3.0 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), Cs<sub>2</sub>CO<sub>3</sub> (1.3 equiv), Solvent (1.0 mL), 100 °C, 24 hours. <sup>b</sup>Determined by GC-MS.

### Screening of Palladium salt



Entry <sup>a</sup>	Pd salt	Solvent	Base	Product <sup>b</sup>
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	90
2	Pd(OAc) <sub>2</sub>	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	no
3	Pd <sub>2</sub> dba <sub>3</sub>	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	no
4	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	trace
5	Pd <sub>2</sub> dba <sub>3</sub> +Sphos	dioxane	Cs <sub>2</sub> CO <sub>3</sub>	trace

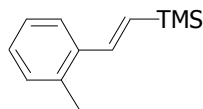
<sup>a</sup>4a (0.1 mmol, 1.0 equiv), TMSD (3.0 equiv), Pd salt (5 mol %), Cs<sub>2</sub>CO<sub>3</sub> (1.3 equiv), dioxane (1.0 mL), 100 °C, 24 hours. <sup>b</sup>Determined by GC-MS.



To a dried vial was added Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), Cs<sub>2</sub>CO<sub>3</sub> (1.3 equiv) and **4** ( $\alpha$ -chloroacetamides) (1.0 mmol, 1.0 equiv), dry dioxane (1.0 mL) was then added. The mixture was stirred at 80 °C under N<sub>2</sub> atmosphere for 20 mins. Then TMSCHN<sub>2</sub> (1.50 mL, 2M/L, 3.0 equiv) was added slowly and the reaction mixture was stirred at 100 °C for 24 hours. After cooling, the mixture was diluted with water and extracted with EA, the combined organic layer was washed with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, the filtrate was concentrated under vacuum and purified by column chromatography on silica gel to afford the corresponding **5**.

### 3. Synthesis and characterization of products

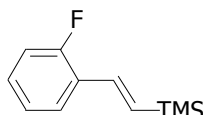
#### (E)-trimethyl(2-methylstyryl)silane (**3a**)<sup>1</sup>



**3a**

**3a** (62 mg, 65 %, E/Z = 99:1) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.22-7.16 (m, 4H), 6.46 (d, *J* = 16.0 Hz, 1H), 2.43 (s, 3H), 0.23 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.4, 137.8, 135.3, 130.4, 127.8, 126.2, 125.4, 19.7, -1.0; GC/MS (EI) 190.1 (M)<sup>+</sup>, 175.1 (M-Me)<sup>+</sup>.

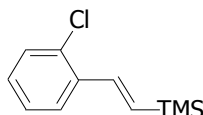
#### (E)-trimethyl[2-(2-fluorophenyl)ethenyl]silane (**3b**)<sup>4</sup>



**3b**

**3b** (44 mg, 30%, E/Z = 82:18) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56-7.52 (m, 1H), 7.24-7.17 (m, 1H), 7.12-7.09 (m, 1H), 7.07-7.04 (m, 1H), 7.02-6.99 (m, 1H), 6.57 (d, *J* = 12.0 Hz, 1H), 0.17 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.5, 159.0, 146.3, 135.3 (d, *J* = 250.0 Hz), 132.5 (d, *J* = 3.0 Hz), 126.7 (d, *J* = 4.0 Hz), 124.0 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 22.0 Hz), -1.3; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -119.6; GC/MS (EI) 194.1 (M)<sup>+</sup>, 179.1 (M-Me)<sup>+</sup>.

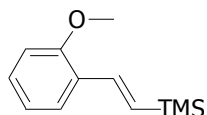
#### (E)-trimethyl[2-(2-chlorophenyl)ethenyl]silane (**3c**)<sup>5</sup>



**3c**

**3c** (73 mg, 69%, E/Z = 99:1) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55-7.53 (m, 1H), 7.29-7.22 (m, 1H), 7.16-7.10 (m, 3H), 6.46 (d, *J* = 20.0 Hz, 1H), 0.13 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.4, 136.3, 133.1, 129.6, 128.7, 126.7, 126.6, -1.2; GC/MS (EI) 210.1 (M)<sup>+</sup>, 195.1 (M-Me)<sup>+</sup>.

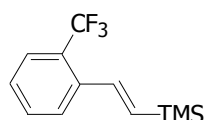
**(E)-(2-methoxystyryl)trimethylsilane (3d)**<sup>6</sup>



**3d**

**3d** (70 mg, 45%, E/Z = 99:1) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 (m, 1H), 7.32-7.20 (m, 2H), 6.95-6.85 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 0.17 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.7, 139.9, 131.9, 131.0, 129.6, 128.3, 122.7, 113.0, 57.5, 0.9; GC/MS (EI) 206.1 (M)<sup>+</sup>, 191.1 (M-Me)<sup>+</sup>.

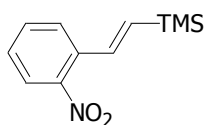
**(E)-trimethyl[2-(2-trifluoromethylphenyl)ethenyl]silane (3e)**



**3e**

**3e** (70 mg, 38%, E/Z = 88:12) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 4.0 Hz 8.0 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.17 (s, 1H), 0.02 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.8, 149.1, 133.6, 131.0, 128.3, 126.3, 125.5, 0.8; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -57.0; GC/MS (EI) 244.1 (M)<sup>+</sup>, 229.1 (M-Me)<sup>+</sup>.

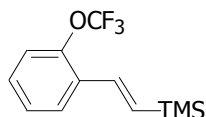
**(E)-trimethyl[2-(2-nitrophenyl)ethenyl]silane (3f)**<sup>8</sup>



**3f**

**3f** (53 mg, 32%, E/Z = 88:12) was isolated as a brown oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00-7.98 (m, 1H), 7.77-7.69 (m, 1H), 7.67 (m, 1H), 7.51 (m, 1H), 7.42 (d, *J* = 20.0 Hz, 1H), 6.64 (d, *J* = 20.0 Hz, 1H), 0.29 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.5, 141.4, 137.1, 135.2, 133.0, 131.6, 127.2 (d, *J* = 31.0 Hz), 123.0 (d, *J* = 6.0 Hz), -2.6; GC/MS (EI) 221.1 (M)<sup>+</sup>, 206.1 (M-Me)<sup>+</sup>.

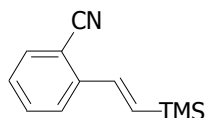
**(E)-trimethyl[2-(2-trifluoromethoxyphenyl)ethenyl]silane (3g)**



**3g**

**3g** (70 mg, 36%, E/Z = 74:26) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55-7.53 (m, 1H), 7.17 (m, 2H), 7.07 (m, 2H), 6.46 (d,  $J = 20.0$  Hz, 1H), 0.06 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8, 149.6, 145.2, 134.8, 132.3, 130.7, 127.6, 125.7 (d,  $J = 32.0$  Hz), 120.2, -2.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.3; GC/MS (EI) 260.1 (M) $^+$ , 245.1 (M-Me) $^+$ .

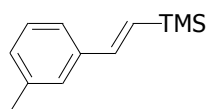
**(E)-trimethyl[2-(2-cyanophenyl)ethenyl]silane (3h)**



**3h**

**3h** (84 mg, 56%, E/Z = 88:12) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (m, 1H), 7.50 (m, 1H), 7.44 (m, 1H), 7.25 (t,  $J = 8.0$  Hz, 1H), 7.16 (d,  $J = 20.0$  Hz, 1H), 6.66 (d,  $J = 20.0$  Hz, 1H), 0.11 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 137.7, 135.2, 131.7 (d,  $J = 30.0$  Hz, 1H), 126.7, 124.3, 116.5, 109.9, -2.6; GC/MS (EI) 201.1 (M) $^+$ , 186.1 (M-Me) $^+$ .

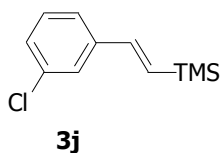
**(E)-trimethyl[2-(3-methylphenyl)ethenyl]silane (3i)**



**3i**

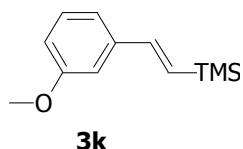
**3i** (50 mg, 53%, E/Z = 91:9) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20-7.14 (m, 3H), 7.00 (d,  $J = 8.0$  Hz, 1H), 6.81 (d,  $J = 20.0$  Hz, 1H), 6.42 (d,  $J = 16.0$  Hz, 1H), 2.28 (s, 3H), 0.09 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 137.6, 137.3, 128.5, 128.0, 127.1, 126.3, 122.8, 20.6, -1.9; GC/MS (EI) 190.1 (M) $^+$ , 175.1 (M-Me) $^+$ .

**(E)-trimethyl[2-(2-chlorophenyl)ethenyl]silane (3j)**<sup>10</sup>



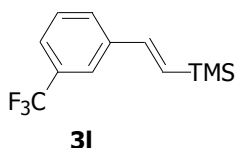
**3j** (44 mg, 42%, E/Z = 83:17) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23-7.11 (m, 4H), 6.76 (d, *J* = 20.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 0.10 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.2, 139.3, 133.6, 130.7, 128.8, 126.9, 125.4, 123.7, -2.1; GC/MS (EI) 210.1 (M)<sup>+</sup>, 195.1 (M-Me)<sup>+</sup>.

**(E)-(3-methoxystyryl)trimethylsilane (3k)**<sup>5</sup>



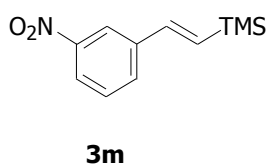
**3k** (71 mg, 49%, E/Z = 99:1) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29-7.25 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 4.0 Hz, 1H), 6.85-6.82 (m, 2H), 6.53 (d, *J* = 20.0 Hz, 1H), 3.85 (s, 3H), 0.19 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 143.6, 140.0, 130.0, 129.6, 119.2, 114.0, 111.4, 55.3, -1.1; GC/MS (EI) 206.1 (M)<sup>+</sup>, 191.1 (M-Me)<sup>+</sup>.

**(E)-trimethyl[2-(3-trifluoromethylphenyl)ethenyl]silane (3l)**<sup>5</sup>



**3l** (80 mg, 44%, E/Z = 87:13) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 20.0 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 0.17 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.7, 142.0, 139.1, 132.1, 129.4, 128.9, 124.3 (d, *J* = 4.0 Hz), 123.0 (d, *J* = 4.0 Hz), -1.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.6; GC/MS (EI) 244.1 (M)<sup>+</sup>, 229.1 (M-Me)<sup>+</sup>.

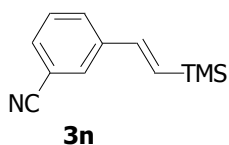
**(E)-trimethyl[2-(3-nitrophenyl)ethenyl]silane (3m)**<sup>8</sup>





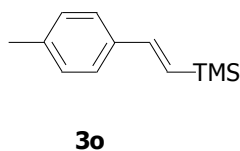
**3m** (60 mg, 36%, E/Z = 88:12) was isolated as a brown oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (s, 1H), 8.09-8.06 (m, 1H), 7.73 (d,  $J = 8.0$  Hz, 1H), 7.50 (t,  $J = 8.0$  Hz, 1H), 6.93 (d,  $J = 20.0$  Hz, 1H), 6.68 (d,  $J = 20.0$  Hz, 1H), 0.19 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.5, 140.8, 139.9, 133.7, 132.1, 129.3, 122.2, 120.7, -1.5; GC/MS (EI) 221.1 (M) $^+$ , 206.1 (M-Me) $^+$ .

**(E)-trimethyl[2-(3-cyanophenyl)ethenyl]silane (3n)**



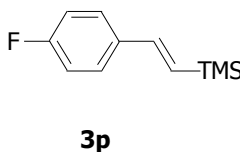
**3n** (91 mg, 60%, E/Z = 99:1) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (s, 1H), 7.55 (d,  $J = 8.0$  Hz, 1H), 7.42 (d,  $J = 12.0$  Hz, 1H), 7.35-7.29 (m, 1H), 6.77 (d,  $J = 20.0$  Hz, 1H), 6.51 (d,  $J = 20.0$  Hz, 1H), 0.09 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 138.4, 132.2, 129.9 (d,  $J = 54.0$  Hz), 128.7 (d,  $J = 5.0$  Hz), 128.2, 117.6, 111.7, -2.4; GC/MS (EI) 201.1 (M) $^+$ , 186.1 (M-Me) $^+$ .

**(E)-trimethyl[2-(4-methylphenyl)ethenyl]silane (3o) $^2$**



**3o** (52 mg, 59%, E/Z = 95:5) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 8.0$  Hz, 2H), 7.20 (d,  $J = 8.0$  Hz, 1H), 6.94 (d,  $J = 20.0$  Hz, 1H), 6.50 (d,  $J = 20.0$  Hz, 1H), 2.40 (s, 3H), 0.22 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.6, 136.9, 134.8, 128.3, 127.3, 125.4, 20.4, -2.0; GC/MS (EI) 190.1 (M) $^+$ , 175.1 (M-Me) $^+$ .

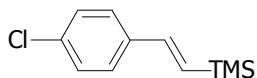
**(E)-(4-fluorostyryl)trimethylsilane (3p) $^3$**



**3p** (45 mg, 31%, E/Z = 81:19) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43-7.40 (m, 2H), 7.04 (t,  $J = 8.0$  Hz, 2H), 6.82 (d,  $J = 20.0$  Hz, 1H), 6.42 (d,  $J = 20.0$  Hz, 1H), 0.17 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 164.0, 161.6, 142.5, 134.8 (d,  $J = 3.0$

Hz), 129.4 (d,  $J = 2.0$  Hz), 128.1 (d,  $J = 8.0$  Hz), 115.7 (d,  $J = 21.0$  Hz), -1.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.0; GC/MS (EI) 194.1 (M) $^+$ , 179.1 (M-Me) $^+$ .

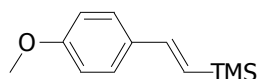
**(E)-(4-chlorostyryl)trimethylsilane (3q)**<sup>3</sup>



**3q**

**3q** (57 mg, 54%, E/Z = 85:15) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 12.0$  Hz, 2H), 7.30 (d,  $J = 8.0$  Hz, 2H), 6.84 (d,  $J = 20.0$  Hz, 1H), 6.48 (d,  $J = 20.0$  Hz, 1H), 0.16 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 144.9, 142.4, 137.0, 133.7, 130.6, 128.8, 127.7, -1.1; GC/MS (EI) 210.1 (M) $^+$ , 195.1 (M-Me) $^+$ .

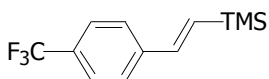
**(E)-(4-methoxystyryl)trimethylsilane (3r)**<sup>5</sup>



**3r**

**3r** (79 mg, 51%, E/Z = 99:1) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J = 12.0$  Hz, 2H), 6.84-6.79 (m, 3H), 6.32 (d,  $J = 20.0$  Hz, 1H), 3.76 (s, 3H), 0.14 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 143.2, 131.5, 127.7, 126.7, 114.0, 55.3, -1.0; GC/MS (EI) 206.1 (M) $^+$ , 191.1 (M-Me) $^+$ .

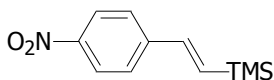
**(E)-trimethyl[2-(4-trifluoromethylphenyl)ethenyl]silane (3s)**<sup>7</sup>



**3s**

**3s** (90 mg, 49%, E/Z = 92:8) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 8.0$  Hz, 2H), 7.44 (d,  $J = 8.0$  Hz, 2H), 6.85 (d,  $J = 20$  Hz, 1H), 6.56 (d,  $J = 20.0$  Hz, 1H), 0.12 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.6, 143.2, 134.6, 129.0, 128.0, 127.0, 126.9, 124.4, 0.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.2; GC/MS (EI) 244.1 (M) $^+$ , 229.1 (M-Me) $^+$ .

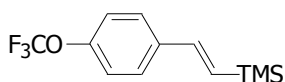
**(E)-trimethyl[2-(4-nitrophenyl)ethenyl]silane (3t)**<sup>8</sup>



**3t**

**3t** (52 mg, 31%, E/Z = 86:14) was isolated as a brown oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J = 8.0$  Hz, 2H), 7.56 (d,  $J = 8.0$  Hz, 2H), 6.95 (d,  $J = 20.0$  Hz, 1H), 6.74 (d,  $J = 20.0$  Hz, 1H), 0.19 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.0, 144.3, 141.1, 136.1, 129.3, 126.8, 123.9, -1.5; GC/MS (EI) 221.1 (M) $^+$ , 206.1 (M-Me) $^+$ .

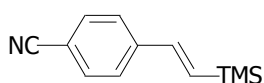
**(E)-trimethyl[2-(4-trifluoromethoxyphenyl)ethenyl]silane (3u)**



**3u**

**3u** (80 mg, 41%, E/Z = 85:15) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J = 8.0$  Hz, 2H), 7.12 (d,  $J = 8.0$  Hz, 2H), 6.81 (d,  $J = 20.0$  Hz, 1H), 6.43 (d,  $J = 20.0$  Hz, 1H), 0.10 (s, 9H);  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta$  164.1, 147.8, 144.0, 140.9, 130.0, 127.4, 126.5, 119.9, -2.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.7; GC/MS (EI) 260.1 (M) $^+$ , 245.1 (M-Me) $^+$ .

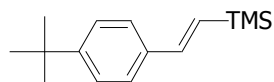
**(E)-trimethyl[2-(4-cyanophenyl)ethenyl]silane (3v) $^4$**



**3v**

**3v** (86 mg, 57%, E/Z = 99:1) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 8.0$  Hz, 1H), 7.50 (d,  $J = 8.0$  Hz, 1H), 6.88 (d,  $J = 16.0$  Hz, 1H), 6.66 (d,  $J = 20.0$  Hz, 1H), 0.17 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.4, 140.6, 133.8, 131.2, 125.7, 117.8, 110.0, 111.0, -2.5; GC/MS (EI) 201.1 (M) $^+$ , 186.1 (M-Me) $^+$ .

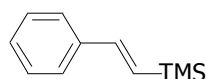
**(E)-(4-Tert-butylstyryl)trimethylsilane (3w) $^3$**



**3w**

**3w** (62 mg, 36%, E/Z = 99:1) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.33 (m, 4H), 6.89 (d,  $J = 20.0$  Hz, 1H), 6.45 (d,  $J = 20.0$  Hz, 1H), 1.31 (s, 9H), 0.15 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.2, 143.5, 135.9, 128.6, 126.2, 125.5, 34.7, 31.4, -1.0; GC/MS (EI) 232.1 (M) $^+$ , 217.1 (M-Me) $^+$ .

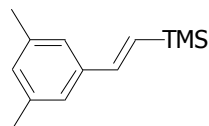
**(E)-trimethyl(styryl)silane (3x)<sup>3</sup>**



**3x**

**3x** (44 mg, 50%, E/Z = 85:15) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 4.0 Hz, 2H), 6.94 (d, *J* = 20.0 Hz, 1H), 6.55 (d, *J* = 20.0 Hz, 1H), 0.20 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.8, 138.5, 129.7, 128.7, 128.1, 126.5, -1.0; GC/MS (EI) 176.1 (M)<sup>+</sup>, 161.1 (M-Me)<sup>+</sup>.

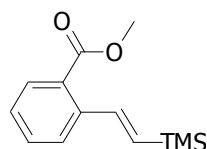
**(E)-(3,5-Dimethylstyryl)trimethylsilane (3y)<sup>9</sup>**



**3y**

**3y** (63 mg, 41%, E/Z = 99:1) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.06 (s, 2H), 6.89 (m, 2H), 6.47 (d, *J* = 20.0 Hz, 1H), 2.30 (s, 6H), 0.15 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.9, 138.4, 137.9, 129.7, 129.0, 124.3, 21.3, -1.1; GC/MS (EI) 204.1 (M)<sup>+</sup>, 189.1 (M-Me)<sup>+</sup>.

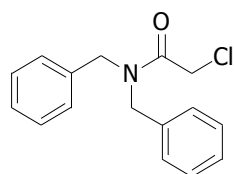
**(E)-trimethyl[2-(2-carbomethoxyphenyl)ethenyl]silane (3z)<sup>8</sup>**



**3z**

**3z** (79 mg, 45%, E/Z = 88:12) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (m, 1H), 7.65 (m, 2H), 7.48 (m, 1H), 7.31-7.27 (m, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 0.18 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.5, 142.0, 140.0, 132.6, 131.5, 129.8, 128.0, 126.8, 126.6, 51.5, -1.6; GC/MS (EI) 234.1 (M)<sup>+</sup>, 219.1 (M-Me)<sup>+</sup>.

**N,N-dibenzyl-2-chloroacetamide (4a)<sup>11</sup>**

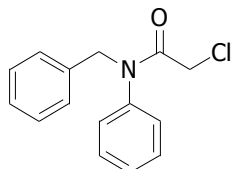


**4a**

**4a** (2.49 g, 91%) was isolated as a colourless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31-7.23 (m,

6H), 7.17 (t,  $J = 8.0$  Hz, 2H), 7.09 (d,  $J = 8.0$  Hz, 2H), 4.53 (s, 2H), 4.43 (s, 2H), 4.06 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 136.4, 135.7, 129.1, 128.7, 128.2, 128.0, 127.7, 126.4, 50.3, 48.6, 41.4; HRMS (ESI): calculated for  $[\text{C}_{16}\text{H}_{16}\text{ClNO}+\text{Na}]^+$  296.0813, found 296.0823.

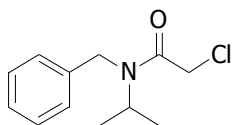
#### N-benzyl-2-chloro-N-phenyl-acetamide (4b)<sup>12</sup>



**4b**

**4b** (2.10 g, 81%) was isolated as a white powder;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (t,  $J = 4.0$  Hz, 3H), 7.19 (t,  $J = 4.0$  Hz, 3H), 7.13 (t,  $J = 4.0$  Hz, 2H), 6.95 (t,  $J = 4.0$  Hz, 2H), 4.82 (s, 2H), 3.77 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 140.8, 136.5, 129.8, 129.0, 128.7, 128.5, 128.2, 127.7, 53.7, 42.0; HRMS (ESI): calculated for  $[\text{C}_{15}\text{H}_{14}\text{ClNO}+\text{Na}]^+$  282.0656, found 282.0668.

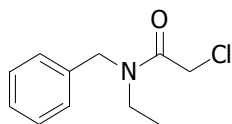
#### N-benzyl-2-chloro-N-isopropylacetamide (4c)<sup>11</sup>



**4c**

**4c** (1.70 g, 75%) was isolated as a colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (mixture of rotamers in ratio 1/0.8, \* stands for the major rotamer)  $\delta$  7.30-7.13 (m, 10 (H+H\*)), 4.73 (t,  $J = 8.0$  Hz, 1H\*), 4.46 (s, 4 (H+H\*)), 4.15 (s, 1H), 4.12 (s, 2H\*), 3.84 (s, 2H), 1.13 (d,  $J = 8.0$  Hz, 3H), 1.08 (d,  $J = 8.0$  Hz, 3H\*);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 166.8, 138.6, 137.7, 129.0, 128.4, 127.5, 126.8, 125.7, 49.8, 46.9, 46.3, 44.1, 42.2, 41.6, 21.5, 20.0; HRMS (ESI): calculated for  $[\text{C}_{12}\text{H}_{16}\text{ClNO}+\text{Na}]^+$  248.0813, found 248.0824.

#### N-benzyl-2-chloro-N-ethylacetamide (4d)<sup>11</sup>

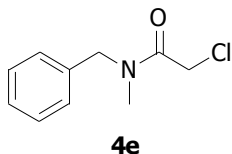


**4d**

**4d** (1.80 g, 85%) was isolated as a colourless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (mixture of rotamers in ratio 1/0.8, \* stands for the major rotamer)  $\delta$  7.29-7.10 (m, 10 (H+H\*)), 4.52 (s, 2H\*), 4.49 (s, 2H), 4.06 (s, 2H\*), 3.96 (s, 2H), 3.35 (d,  $J = 4.0$  Hz, 2H), 3.26-3.22 (m, 2H\*), 1.11-1.08 (m, 3H\*), 1.05-1.02 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 136.9, 136.2,

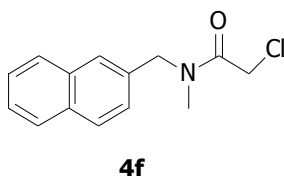
129.0, 128.6, 127.9, 127.8, 127.5, 126.3, 50.9, 48.0, 41.9, 41.6, 41.5, 41.2, 13.8, 12.2; HRMS (ESI): calculated for  $[C_{11}H_{14}ClNO+Na]^+$  234.0656, found 234.0666.

#### **N-benzyl-2-chloro-N-methylacetamide (4e)<sup>11</sup>**



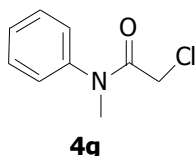
**4e** (1.88 g, 95%) was isolated as a colorless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ ) (mixture of rotamers in ratio 1/0.6, \* stands for the major rotamer)  $\delta$  7.38-7.18 (m, 10 (H+H\*)), 4.60 (s, 4 (H+H\*)), 4.15 (s, 2H\*), 4.11 (s, 2H), 2.99 (s, 3H\*), 2.97 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.9, 166.7, 136.4, 135.7, 129.0, 128.7, 128.0, 127.9, 127.6, 126.4, 53.6, 51.3, 41.4, 41.1, 35.0, 34.3; HRMS (ESI): calculated for  $[C_{10}H_{12}ClNO+Na]^+$  220.0500, found 220.0509.

#### **2-chloro-N-methy-N-(naphthalene-2-ylmethyl)acetamide (4f)<sup>11</sup>**



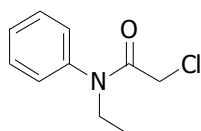
**4f** (1.68 g, 68%) was isolated as a colourless oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ ) (mixture of rotamers in ratio 1/0.5, \* stands for the major rotamer)  $\delta$  7.96-7.74 (m, 6(H+H\*)), 7.53-7.13 (m, 8(H+H\*)), 5.01 (s, 4H), 4.09 (s, 2H\*), 3.98 (s, 2H), 3.03 (s, 3H), 2.84 (s, 3H\*);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  167.5, 166.4, 133.8, 131.7, 131.6, 128.7, 127.1, 126.7, 126.1, 125.1, 123.7, 51.4, 49.4, 41.6, 41.0, 35.4, 34.9; HRMS (ESI): calculated for  $[C_{14}H_{14}ClNO+Na]^+$  270.0656, found 270.0657.

#### **2-chloro-N-methy-N-benzyl-acetamide (4g)<sup>12</sup>**



**4g** (1.43 g, 78%) was isolated as a white powder;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.40-7.31 (m, 3H), 7.20 (t, J=4.0 8.0 Hz, 2H), 3.78 (s, 2H), 3.25 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.3, 142.6, 130.1, 128.6, 127.0, 41.5, 38.0; HRMS (ESI): calculated for  $[C_9H_{10}ClNO+Na]^+$  206.0343, found 206.0349.

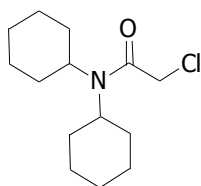
### N-ethyl-chloroacetanilide (**4h**)<sup>12</sup>



**4h**

**4h** (1.68 g, 85%) was isolated as a colourless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.41 (t, *J* = 4.0 Hz, 3H), 7.19 (d, *J* = 4.0, 2H), 3.76-3.73 (m, 4H), 1.11 (d, *J* = 4.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.6, 140.8, 129.9, 128.6, 128.1, 44.8, 42.0, 12.7; HRMS (ESI): calculated for [C<sub>10</sub>H<sub>12</sub>ClNO+Na]<sup>+</sup> 220.0500, found 220.0504.

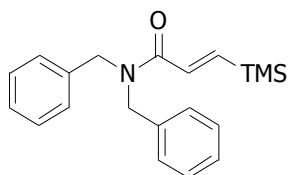
### 2-chloro-N,N-dicyclohexylacetamide (**4i**)<sup>13</sup>



**4i**

**4i** (2.11 g, 82%) was isolated as a Brown-solid powder; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.96 (s, 2H), 3.37 (s, 1H), 2.89 (s, 1H), 2.34 (s, 2H), 1.79-1.70 (m, 6H), 1.62-1.53 (m, 3H), 1.47-1.28 (m, 3H), 1.25 (m, 2H), 1.07 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.4, 58.9, 56.4, 43.5, 31.2, 29.5, 26.4, 25.8, 25.1; HRMS (ESI): calculated for [C<sub>14</sub>H<sub>24</sub>ClNO+Na]<sup>+</sup> 280.1439, found 280.1448.

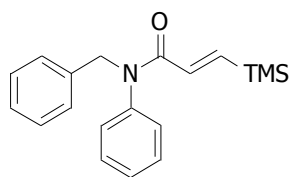
### (E)-3-(trimethylsilyl)-N,N-Dibenzyl-acrylamide (**5a**)



**5a**

**5a** (162 mg, 50%, E/Z = 99:1) was isolated as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31-7.25 (m, 5H), 7.23-7.18 (m, 4H), 7.11 (s, 1H), 7.09 (s, 1H), 6.65 (d, *J*=16.0, 1H), 4.58 (s, 2H), 4.45 (s, 2H), 0.00 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.24, 146.47, 136.49, 136.01, 132.38, 128.14, 127.84, 127.66, 126.93, 126.67, 125.94, 49.26, 48.02, -2.48; HRMS (ESI): calculated for [C<sub>20</sub>H<sub>25</sub>NOSi+Na]<sup>+</sup> 346.1598, found 346.1607.

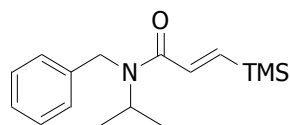
**(E)-3-(trimethylsilyl)-N-Benzyl-N-phenyl-acrylamide (5b)**



**5b**

**5b** (124 mg, 40%, E/Z = 99:1) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.25 (m, 4H), 7.24-7.18 (m, 5H), 6.97 (d,  $J = 8.0$ , 2H), 6.11 (d,  $J = 20.0$ , 1H), 4.94 (s, 2H), -0.07 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.24, 146.47, 136.49, 136.01, 132.38, 128.14, 127.84, 127.66, 126.93, 126.67, 125.94, 49.26, 48.02, -2.48; HRMS (ESI): calculated for  $[\text{C}_{19}\text{H}_{23}\text{NOSi}+\text{Na}]^+$  332.1441, found 332.1451.

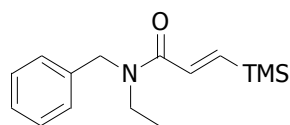
**(E)-3-(trimethylsilyl)-N-Benzyl-N-isopropyl-acrylamide (5c)**



**5c**

**5c** (120 mg, 43%, E/Z = 67:33) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.18 (m, 12(H+H\*)), 6.49 (d,  $J = 20.0$ , 1H), 4.95 (t,  $J = 8.0$ , 1H), 4.64-4.40 (m, 4(H+H\*)), 1.21-1.13 (m, 12(H+H\*)), 0.00 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 167.1, 146.3, 145.9, 139.9, 139.3, 135.2, 134.4, 129.0, 128.6, 127.5, 127.0, 126.4, 49.3, 46.5, 46.4, 44.8, 22.1, 20.6, -1.4; HRMS (ESI): calculated for  $[\text{C}_{16}\text{H}_{25}\text{NOSi}+\text{Na}]^+$  298.1598, found 298.1607.

**(E)-3-(trimethylsilyl)-N-Benzyl-N-ethyl-acrylamide (5d)**

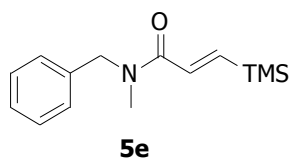


**5d**

**5d** (112 mg, 43%, E/Z = 50:50) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21-7.02 (m, 12 (H+H\*)), 6.59 (d,  $J = 20.0$ , 1H), 4.51 (s, 2H), 3.25-3.20 (m, 2H), 1.02-0.99 (t,  $J = 8.0$ , 6 (H+H\*)), 0.00 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 165.2, 145.4, 145.1, 136.8, 136.4, 132.7, 132.0, 127.8, 127.5, 127.1, 126.6, 126.3, 125.5, 49.8, 47.8, 40.8, 40.6, 13.3, 11.7, -2.5, -2.6; HRMS (ESI): calculated for  $[\text{C}_{15}\text{H}_{23}\text{NOSi}+\text{Na}]^+$  284.1441, found 284.1451.

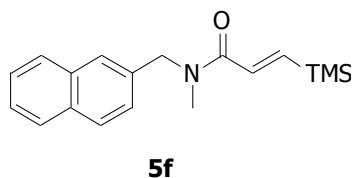


**(E)-3-(trimethylsilyl)-N-Benzyl-N-methyl-acrylamide (5e)**



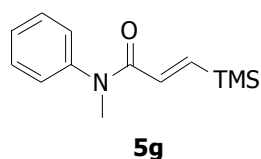
**5e** (72 mg, 30%, E/Z = 50:50) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23-7.10 (m, 12(H+H\*)), 6.61 (t,  $J = 20.0$  16.0, 1H), 4.51 (s, 2H), 2.86 (s, 3H), -0.07 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 168.0, 149.8, 148.0, 147.7, 138.9, 138.5, 134.9, 134.8, 130.5, 130.2, 129.7, 129.6, 129.3, 129.0, 128.2, 128.0, 55.1, 52.9, 43.4, 36.4, 35.9, 31.3, -0.06; HRMS (ESI): calculated for  $[\text{C}_{14}\text{H}_{21}\text{NOSi}+\text{Na}]^+$  270.1285, found 270.1294.

**(E)-3-(trimethylsilyl)-N-Methyl-N-naphthalen-2-ylmethyl-acrylamide (5f)**



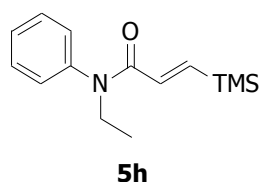
**5f** (96 mg, 32%, E/Z = 60:40) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.0$ , 1H), 7.75-7.64 (m, 5(H+H\*)), 7.40-7.09 (m, 10(H+H\*)), 6.60 (d,  $J = 20.0$ , 1H), 4.49 (s, 2H), 2.78 (s, 3H), 0.00 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.1, 167.9, 150.0, 148.1, 135.5, 135.0, 134.7, 134.1, 133.4, 132.3, 130.6, 130.2, 130.1, 129.7, 128.7, 127.5, 127.2, 126.7, 125.6, 125.1, 123.6, 52.7, 50.6, 36.3, 35.9, 2.6, 1.2; HRMS (ESI): calculated for  $[\text{C}_{18}\text{H}_{23}\text{NOSi}+\text{Na}]^+$  320.1441, found 320.1451.

**(E)-3-(trimethylsilyl)-N-Methyl-N-phenyl-acrylamide (5g)**



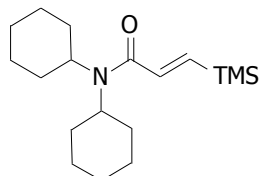
**5g** (94 mg, 40%, E/Z = 99:1) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (t,  $J = 8.0$ , 2H), 7.27 (d,  $J = 8.0$  1H), 7.11 (t,  $J = 8.0$ , 3H), 6.12 (d,  $J = 20.0$ , 1H), 3.29 (s, 3H), -0.09 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 145.5, 143.8, 134.6, 129.7, 127.8, 127.5, 37.8, -1.5; HRMS (ESI): calculated for  $[\text{C}_{13}\text{H}_{19}\text{NOSi}+\text{Na}]^+$  256.1128, found 256.1139.

**(E)-3-(trimethylsilyl)-N-ethyl-N-phenyl-acrylamide (5h)**



**5h** (100 mg, 38%, E/Z = 99:1) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 8.0$ , 2H), 7.29 (d,  $J = 8.0$ , 1H), 7.09 (d,  $J = 8.0$ , 3H), 6.02 (d,  $J = 16.0$ , 1H), 3.78 (d,  $J = 8.0$ , 2H), 1.08 (s, 3H), -0.11 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 145.3, 142.2, 135.0, 129.7, 128.6, 127.9, 44.8, -1.5; HRMS (ESI): calculated for  $[\text{C}_{14}\text{H}_{21}\text{NOSi}+\text{Na}]^+$  270.1285, found 270.1295.

**(E)-3-(trimethylsilyl)-N,N-Dicyclohexyl-acrylamide (5i)**



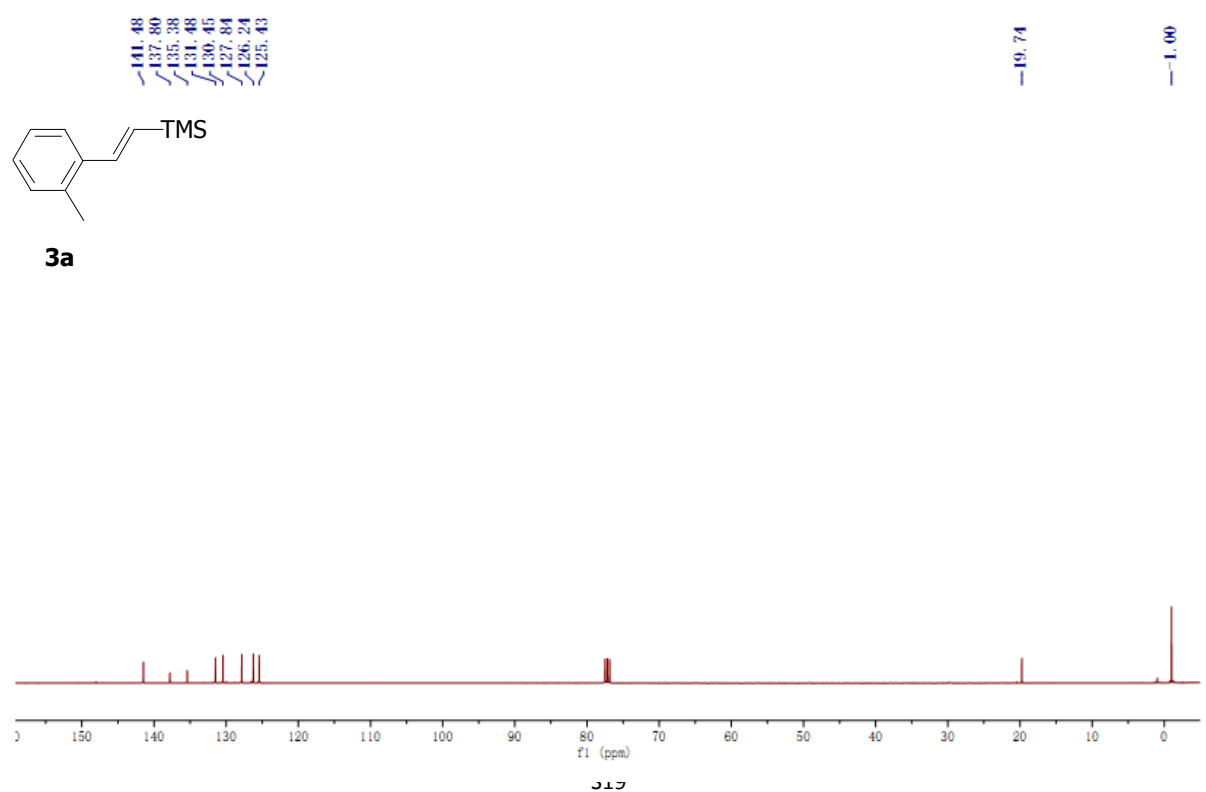
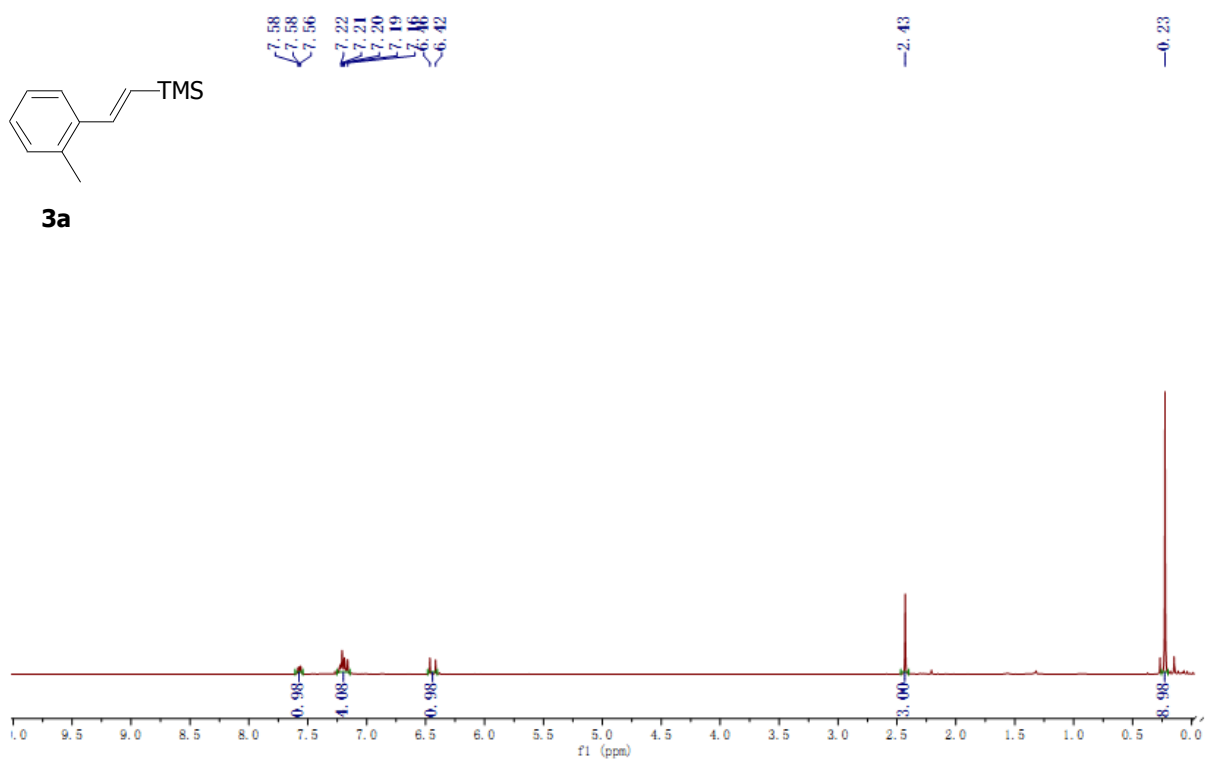
**5i**

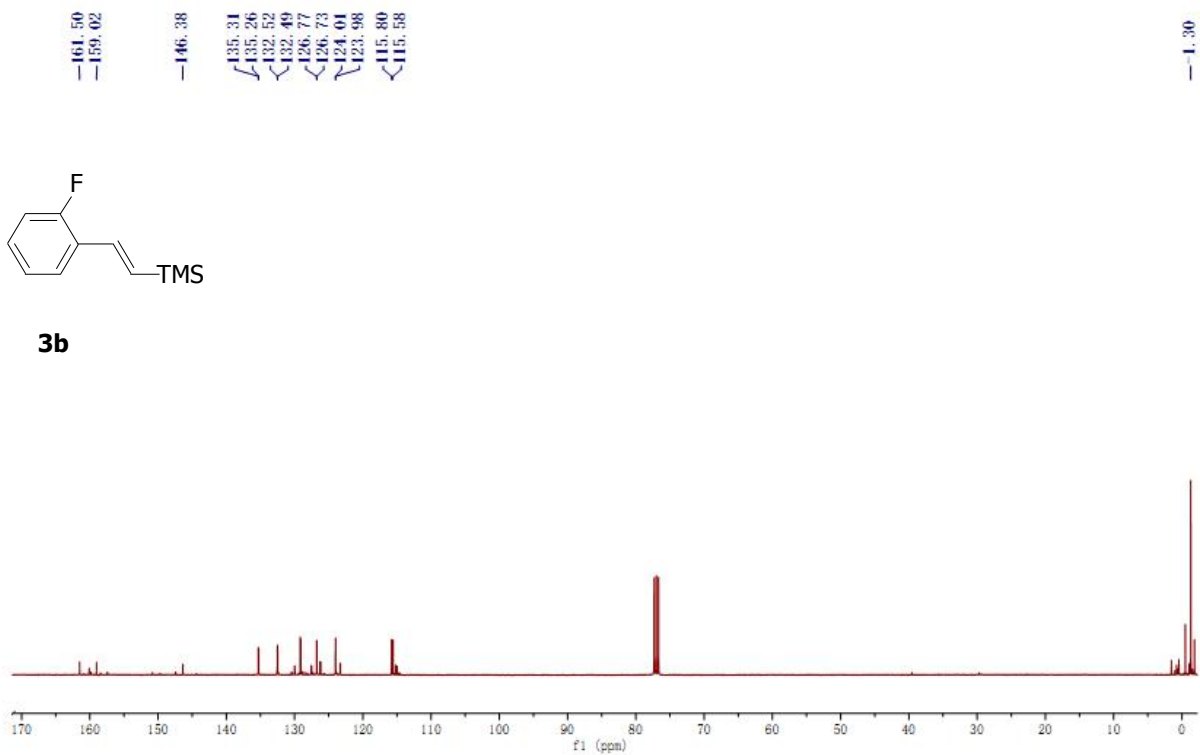
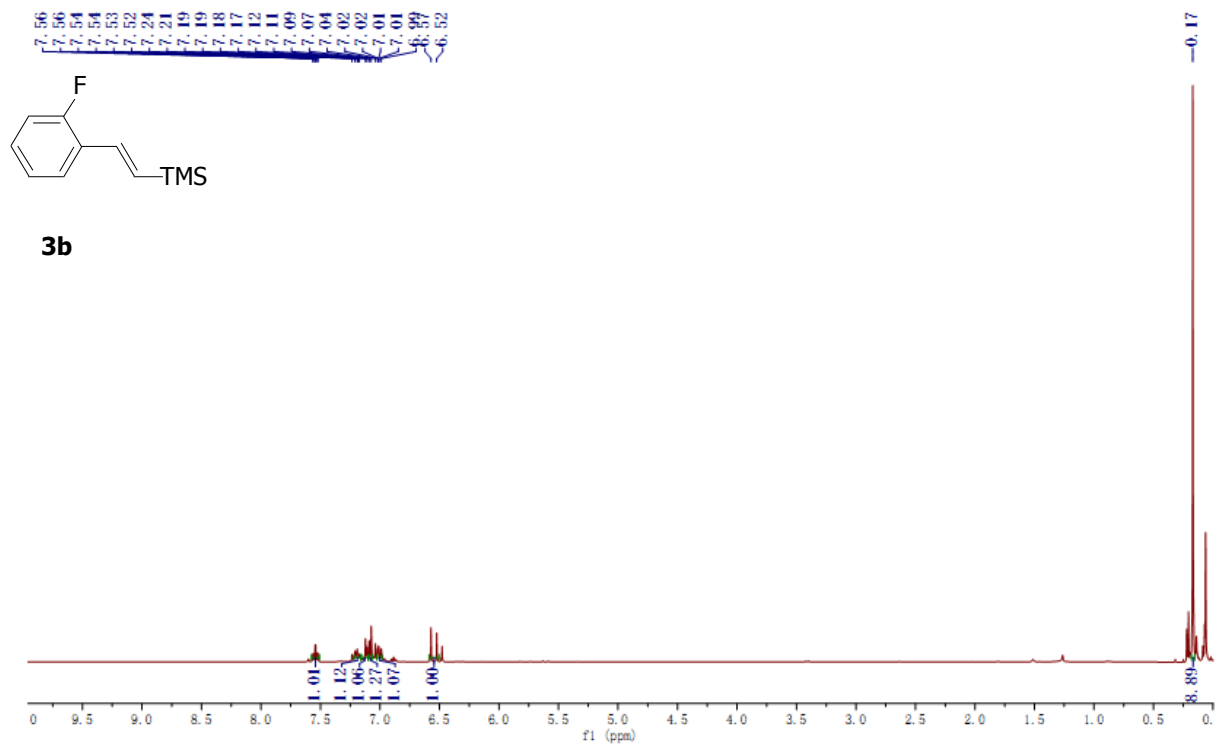
**5i** (108 mg, 35%, E/Z = 99:1) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.81 (d,  $J = 20.0$ , 1H), 6.53 (d,  $J = 20.0$ , 1H), 3.38 (s, 1H), 2.11 (s, 1H), 1.63 (d,  $J = 12.0$ , 6H), 1.49 (d,  $J = 28.0$ , 7H), 1.17 (d,  $J = 16.0$ , 7H), 0.00 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 141.4, 135.9, 56.4, 54.6, 30.9, 29.2, 25.4, 25.2, 24.4, -2.6; HRMS (ESI): calculated for  $[\text{C}_{18}\text{H}_{33}\text{NOSi}+\text{H}]^+$  308.2404, found 308.2419.

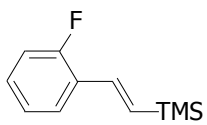
#### 4. Gram-Scale Preparation of 5a

To a dried vial was added  $\text{Pd}(\text{PPh}_3)_4$  (5 mol %),  $\text{Cs}_2\text{CO}_3$  (1.30 equiv) and **4a** (10.0 mmol, 1.0 equiv), dry dioxane (20 mL) was then added. The mixture was stirred at 80 °C under  $\text{N}_2$  atmosphere for 1.5 h. Then  $\text{TMSCHN}_2$  (15.0 mL, 2M/L, 3.0 equiv) was added slowly and the reaction mixture was stirred at 100 °C for 24 hours. After cooling, the mixture was diluted with water and extracted with EA, the combined organic layer was washed with brine solution, dried over  $\text{Na}_2\text{SO}_4$ , the filtrate was concentrated under vacuum and purified by column chromatography on silica gel to afford the corresponding **5a** (1.23 g 38%) as a yellow oil.

## 5. Copies of NMR spectra

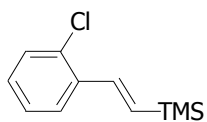
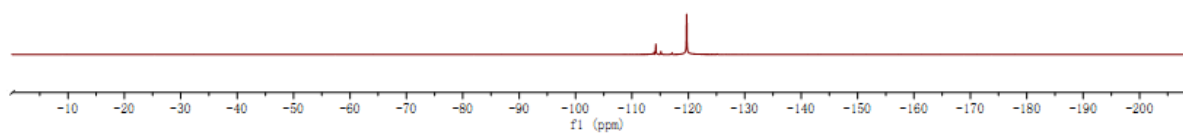






**3b**

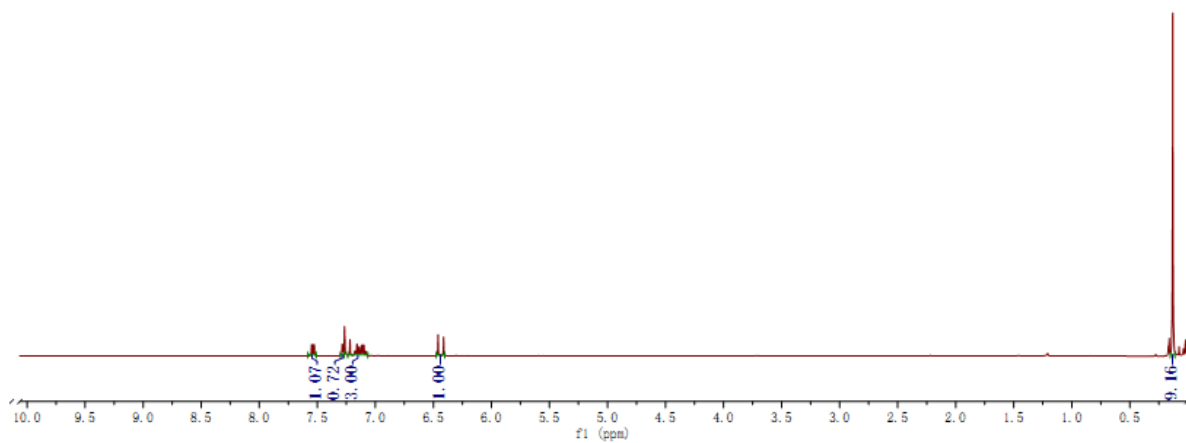
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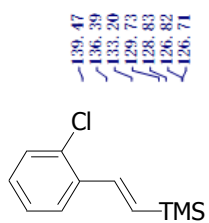


**3c**

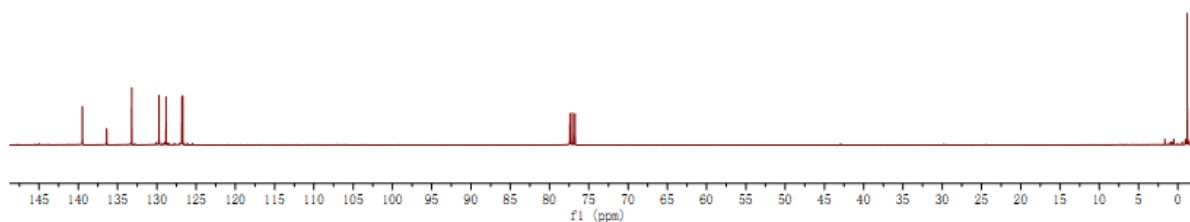
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6.41

0.13

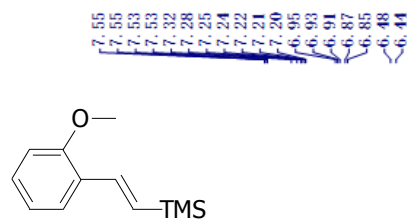




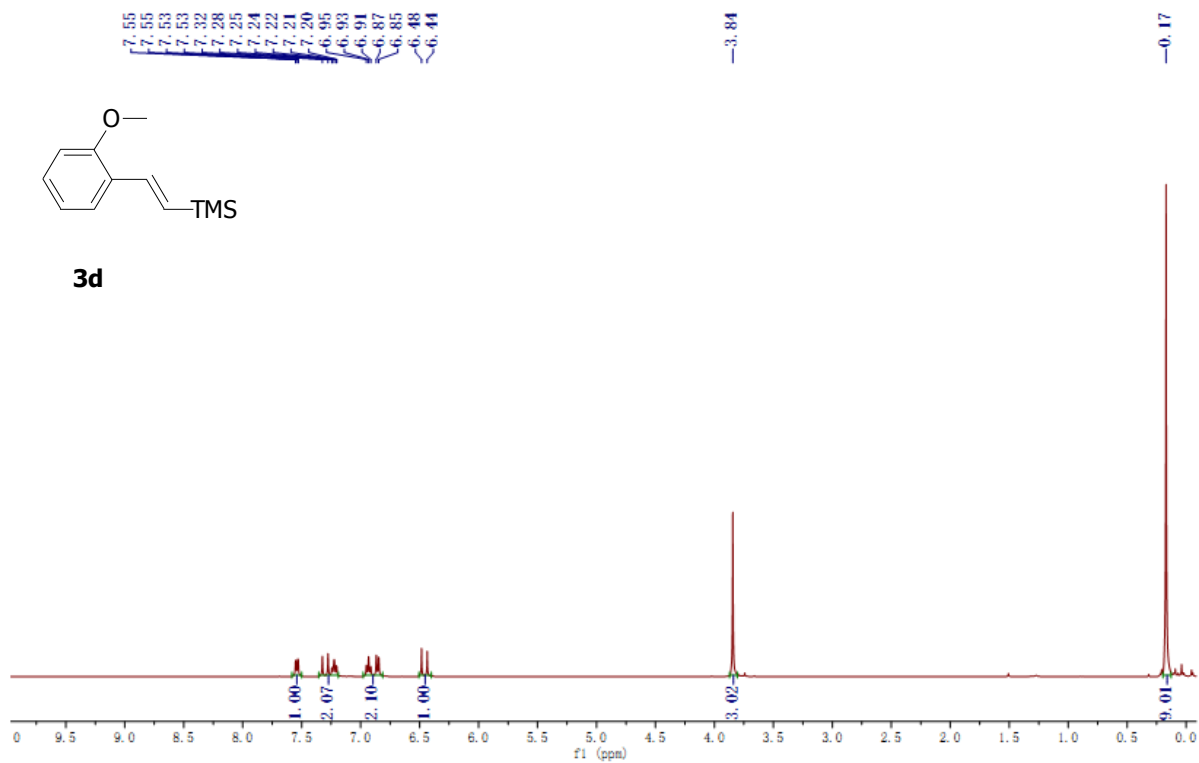
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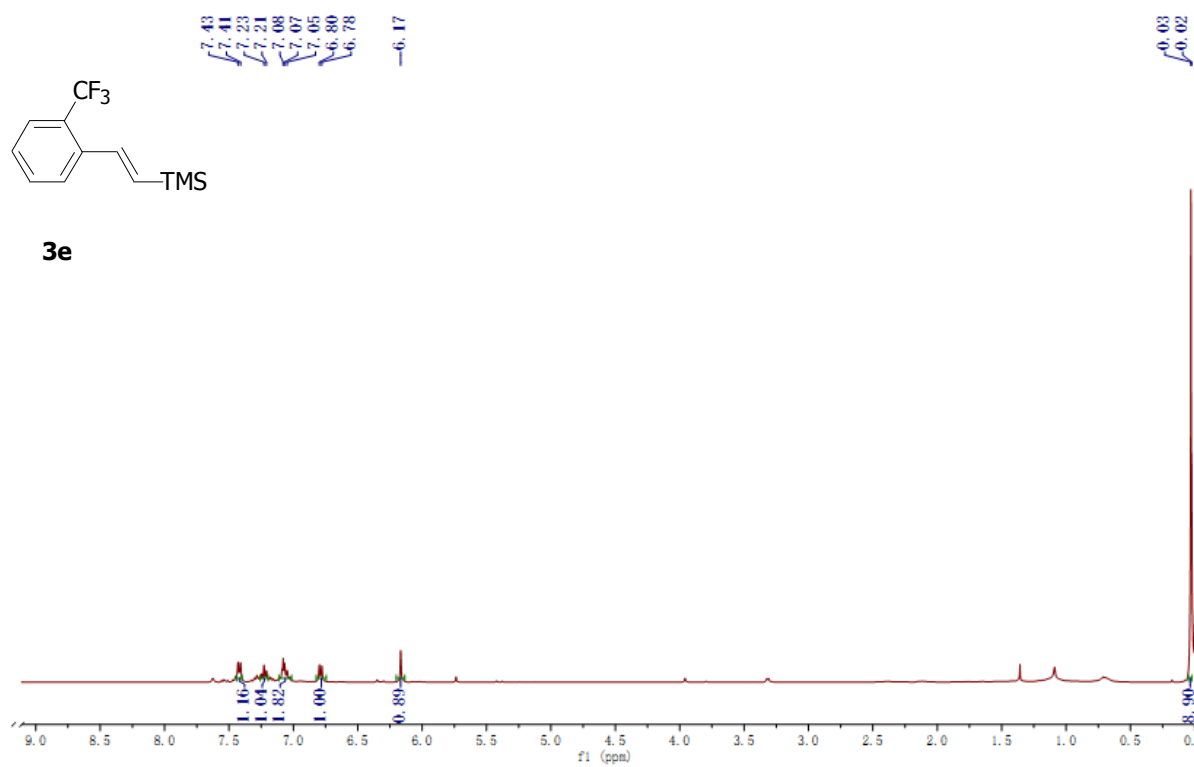
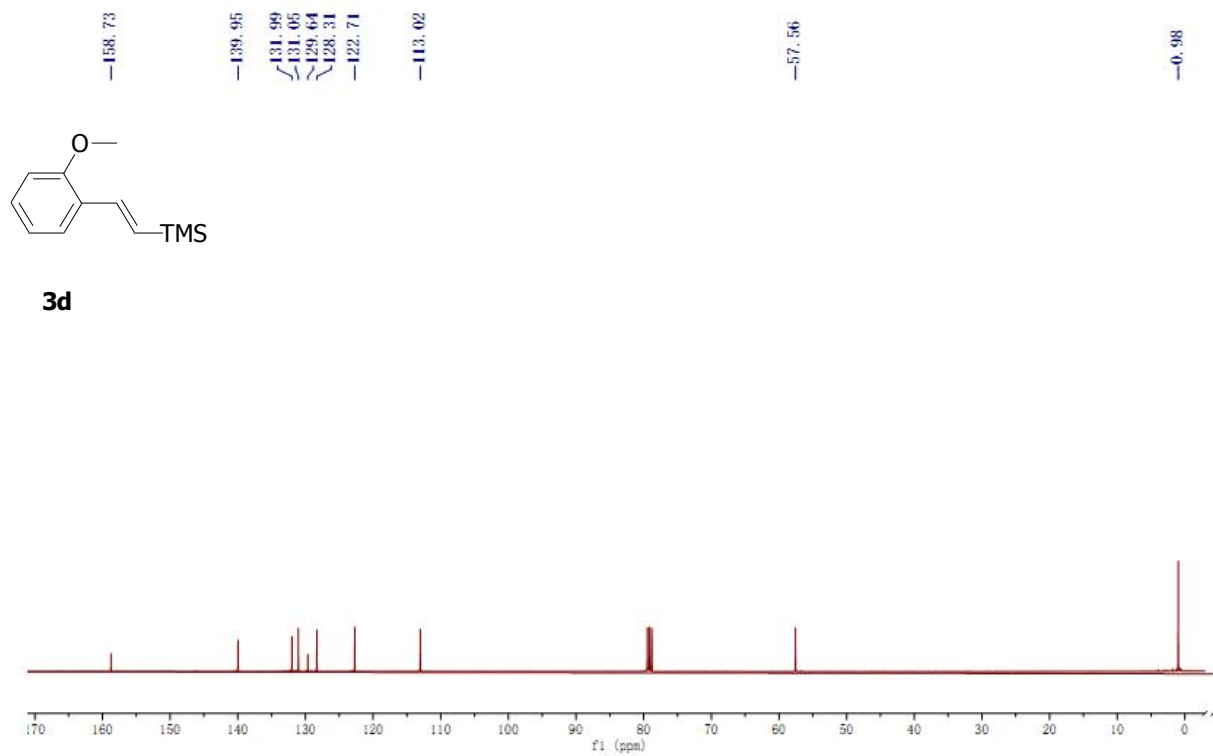


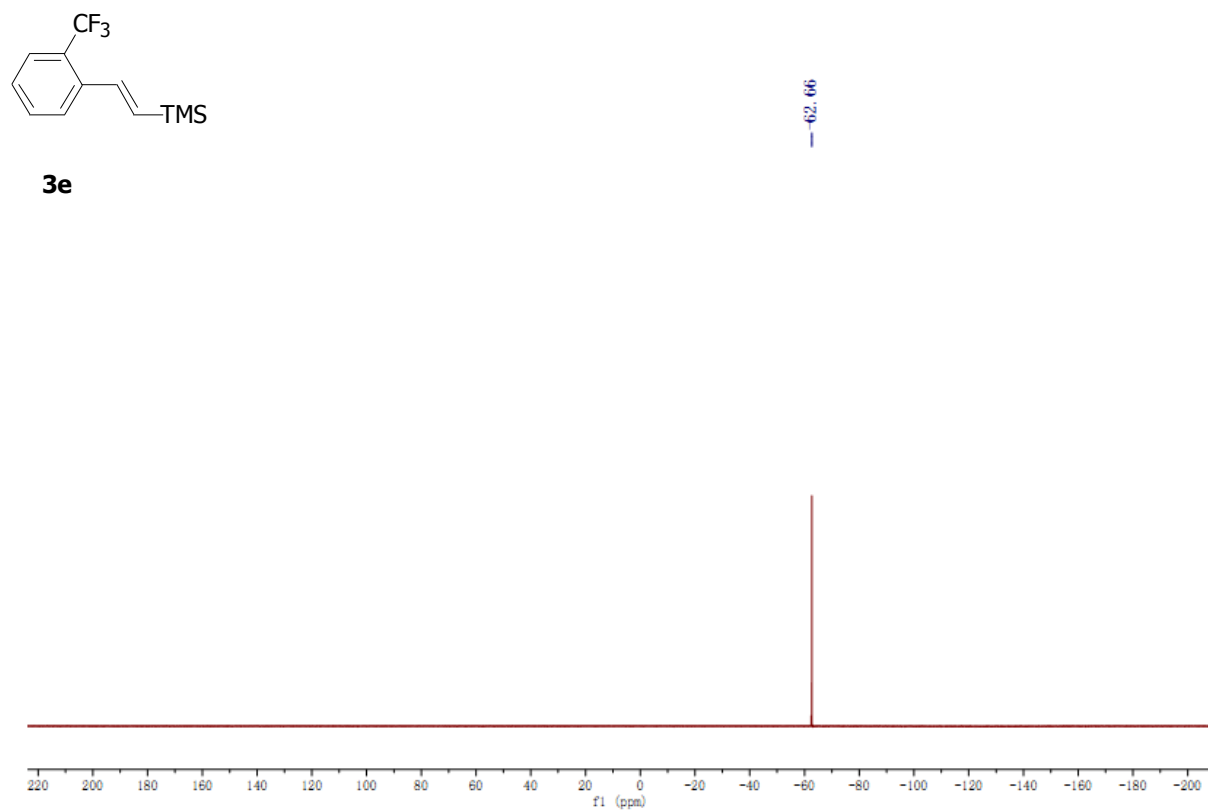
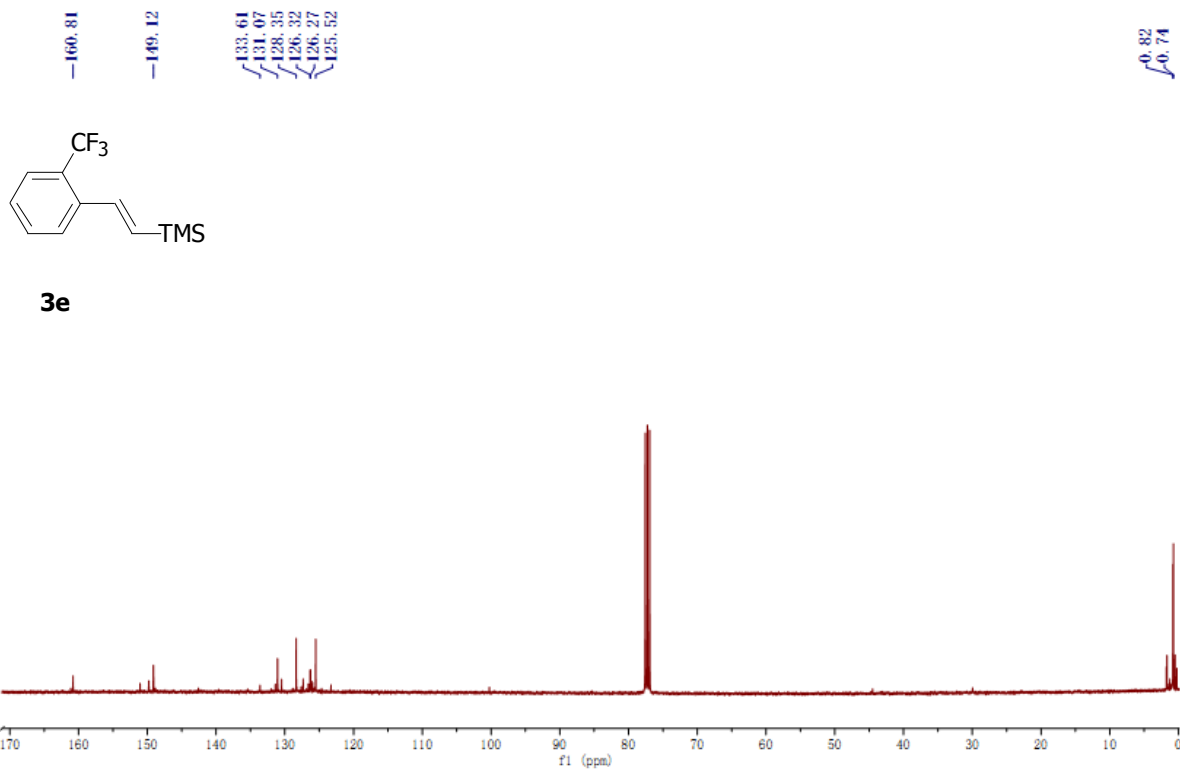
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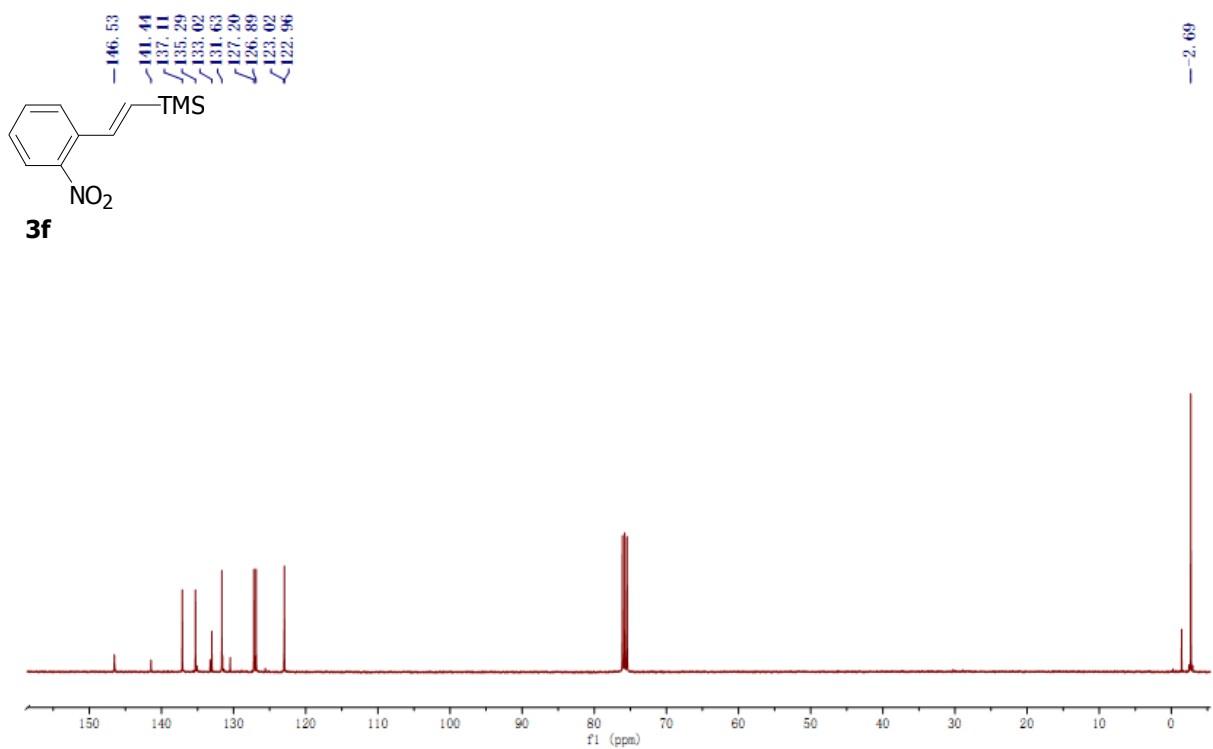
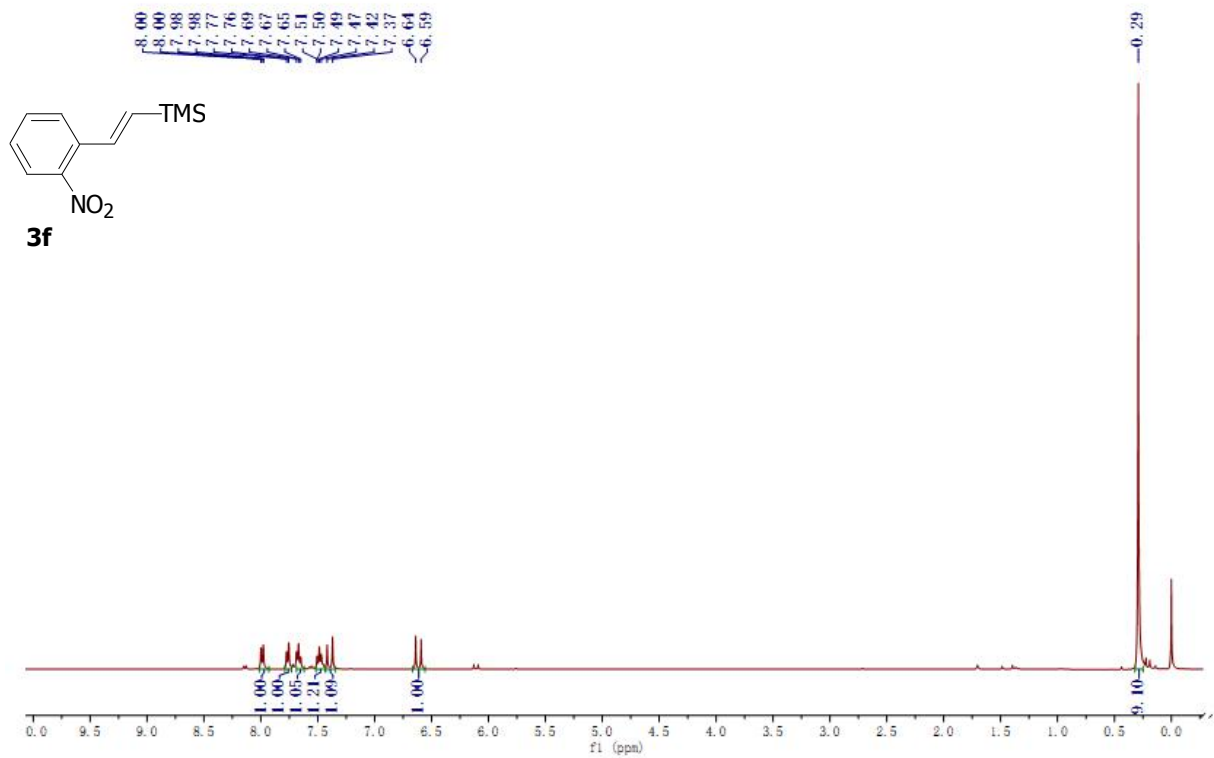
**3d**

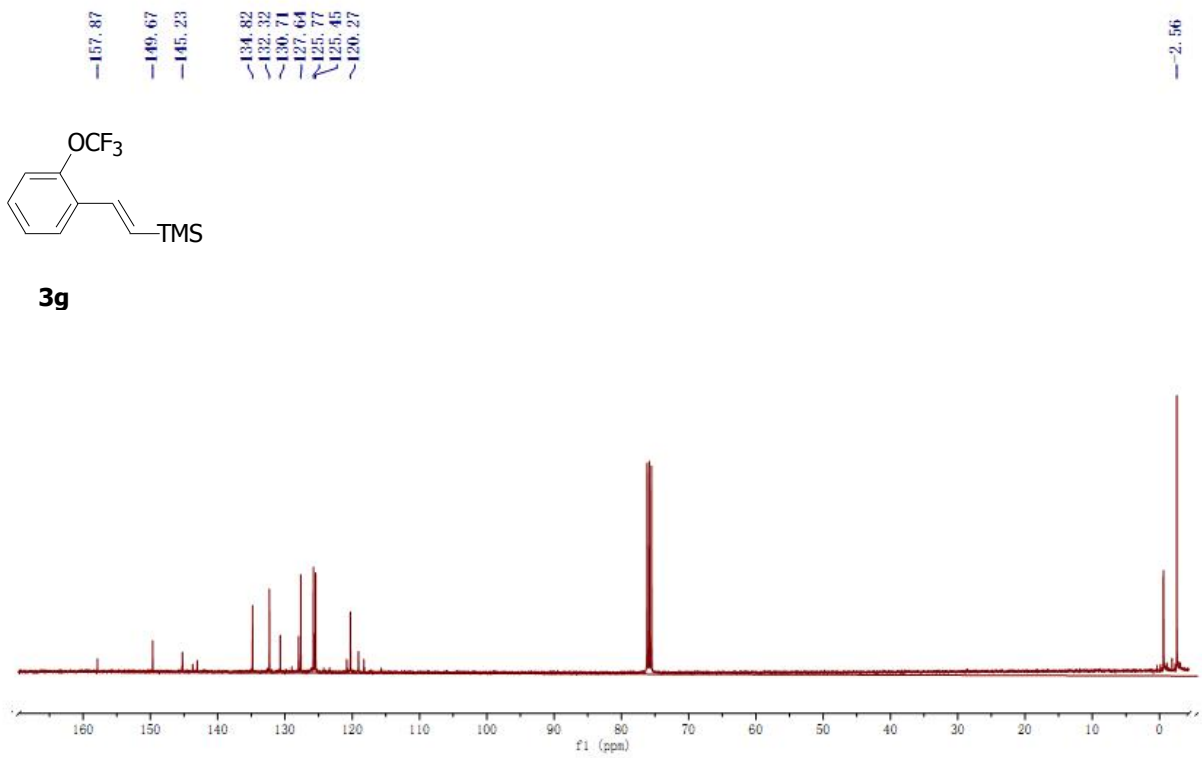
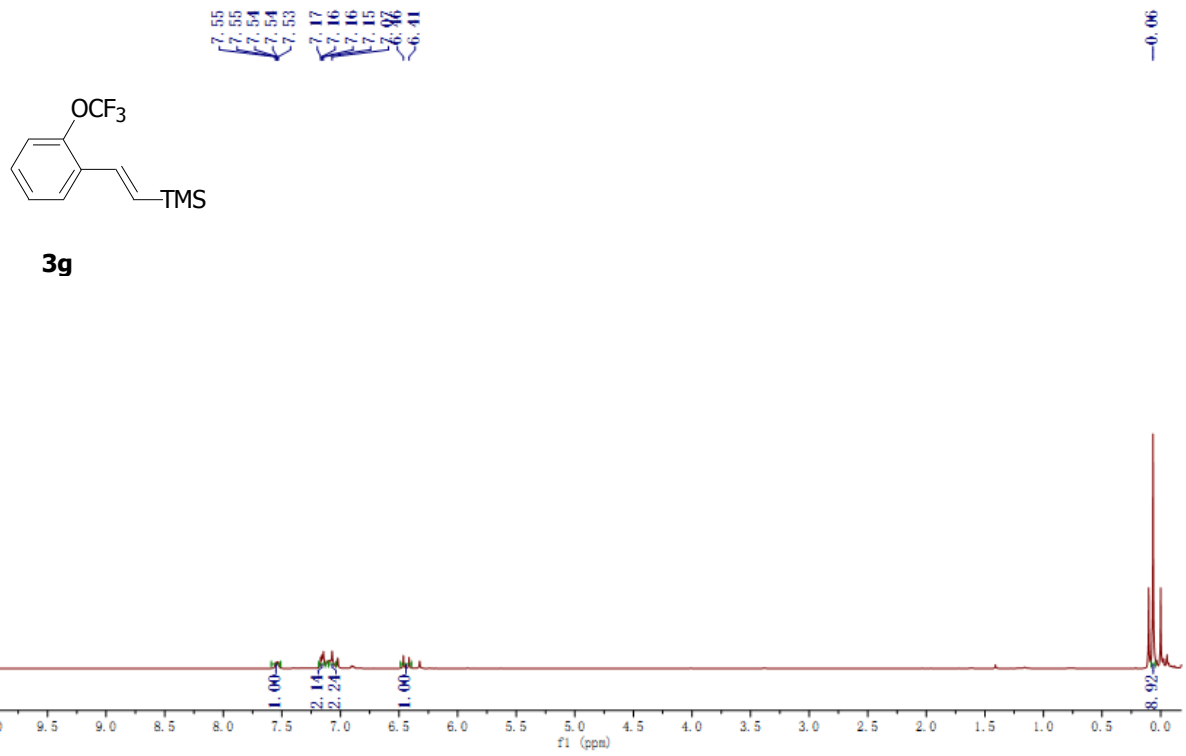


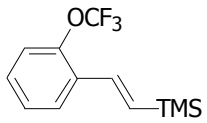




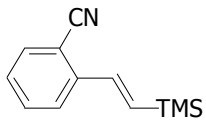
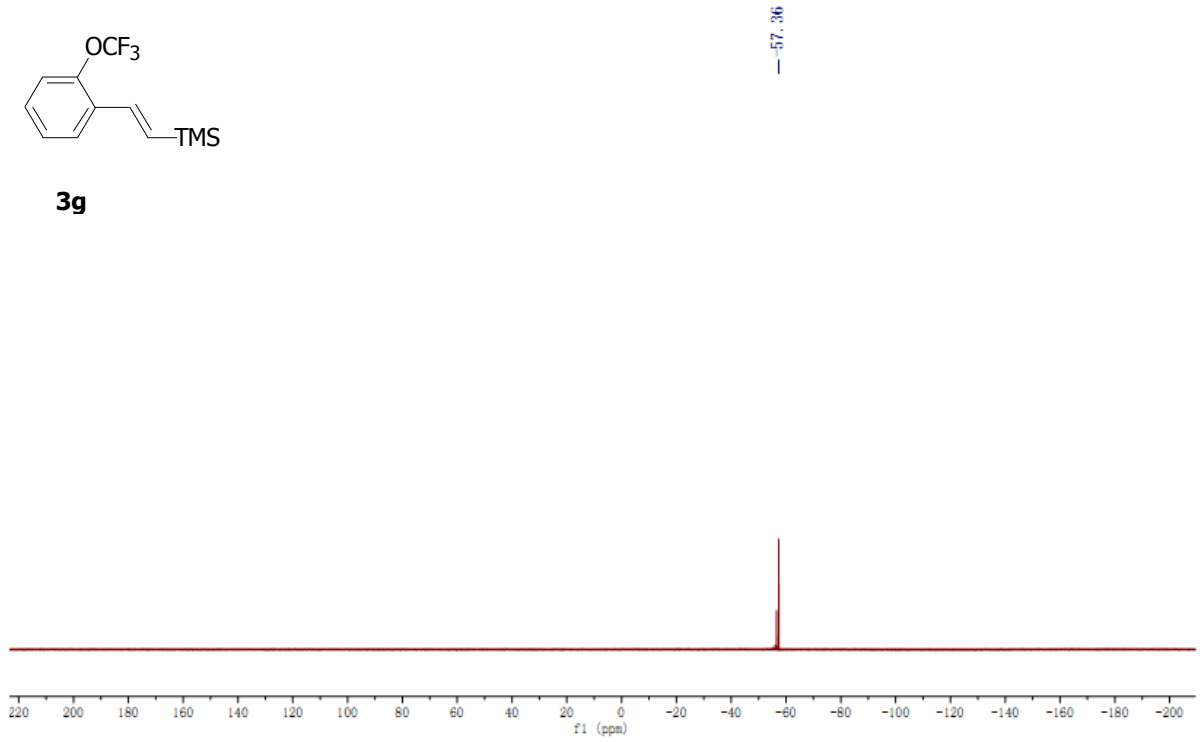




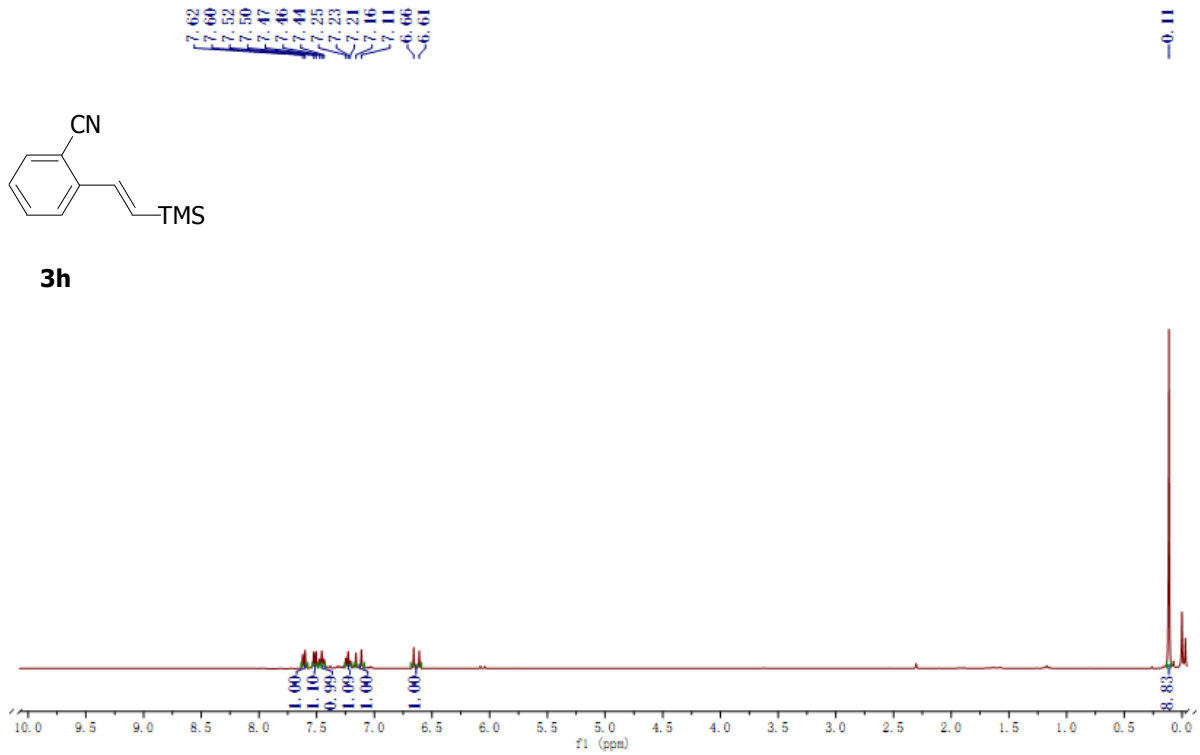


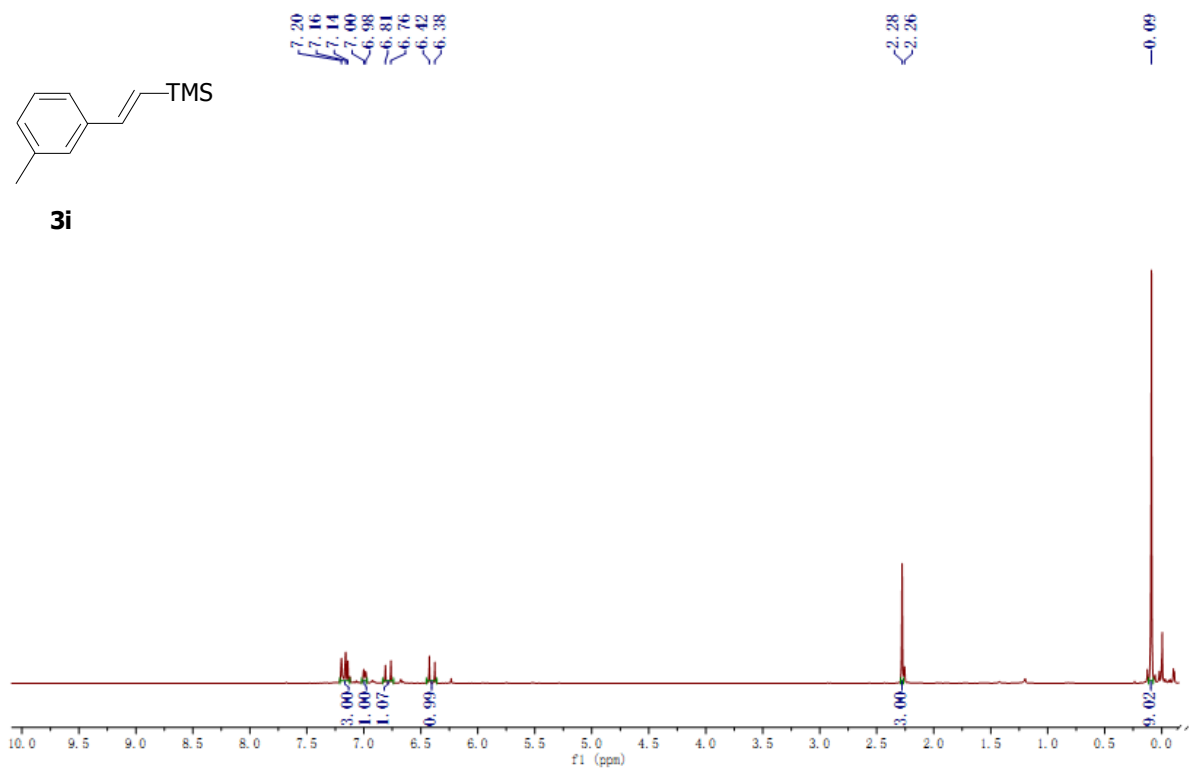
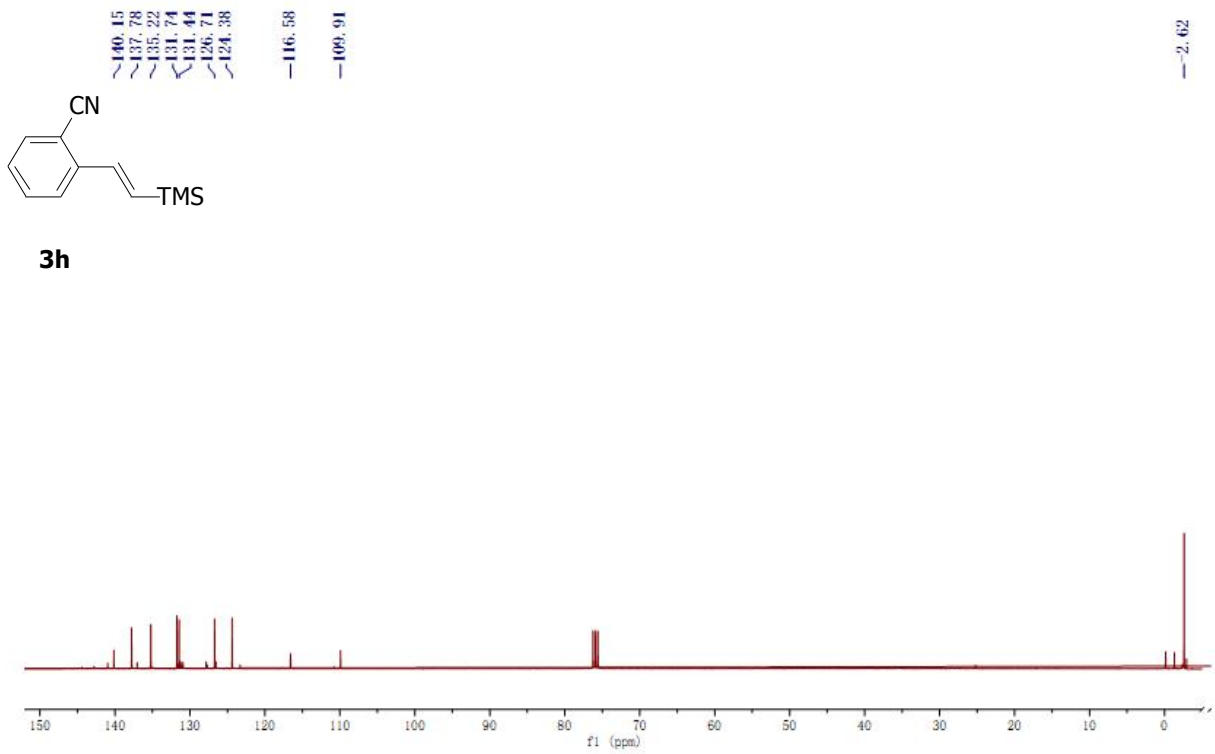


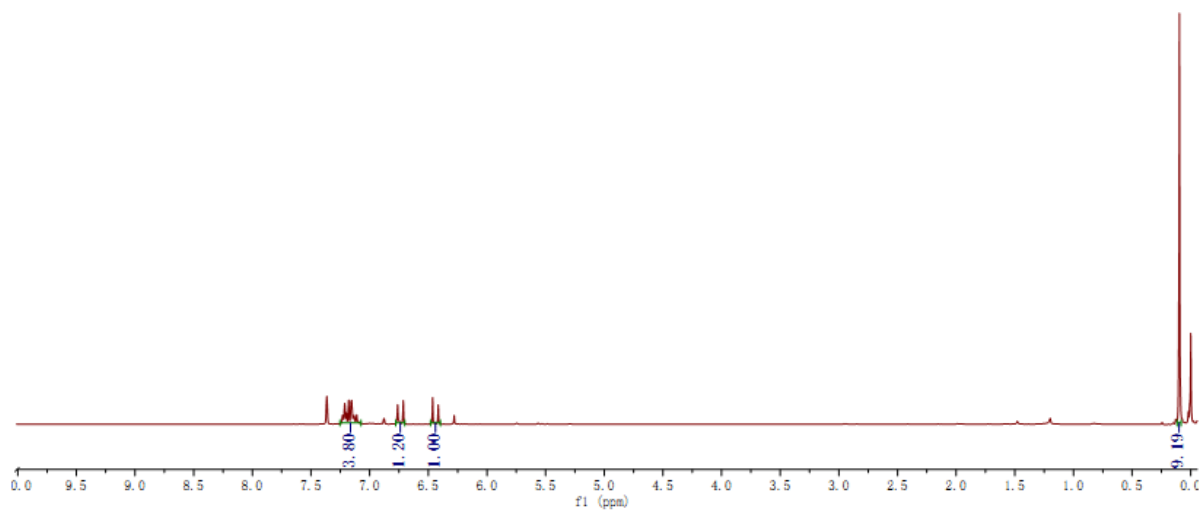
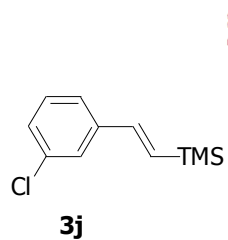
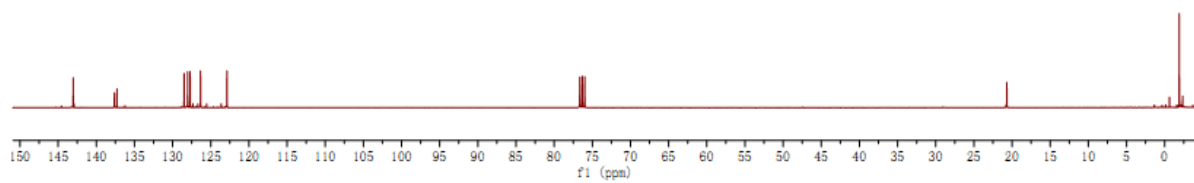
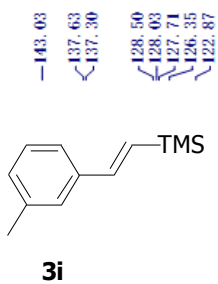
**3g**

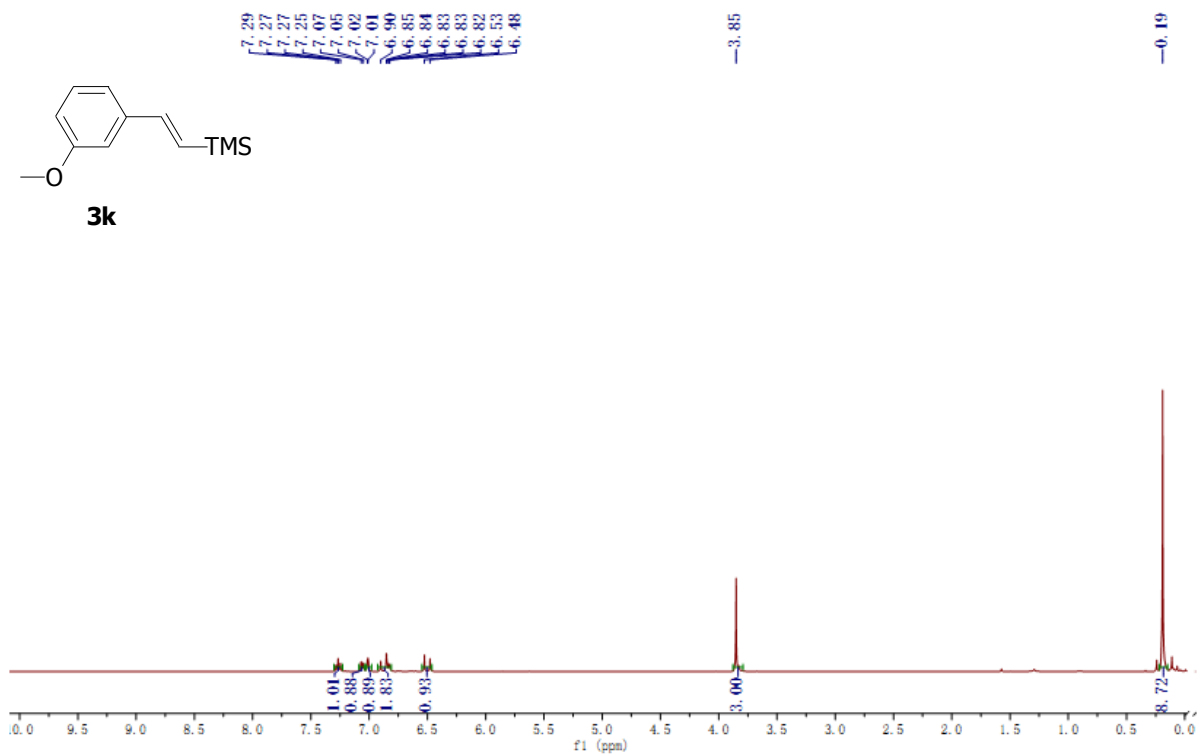
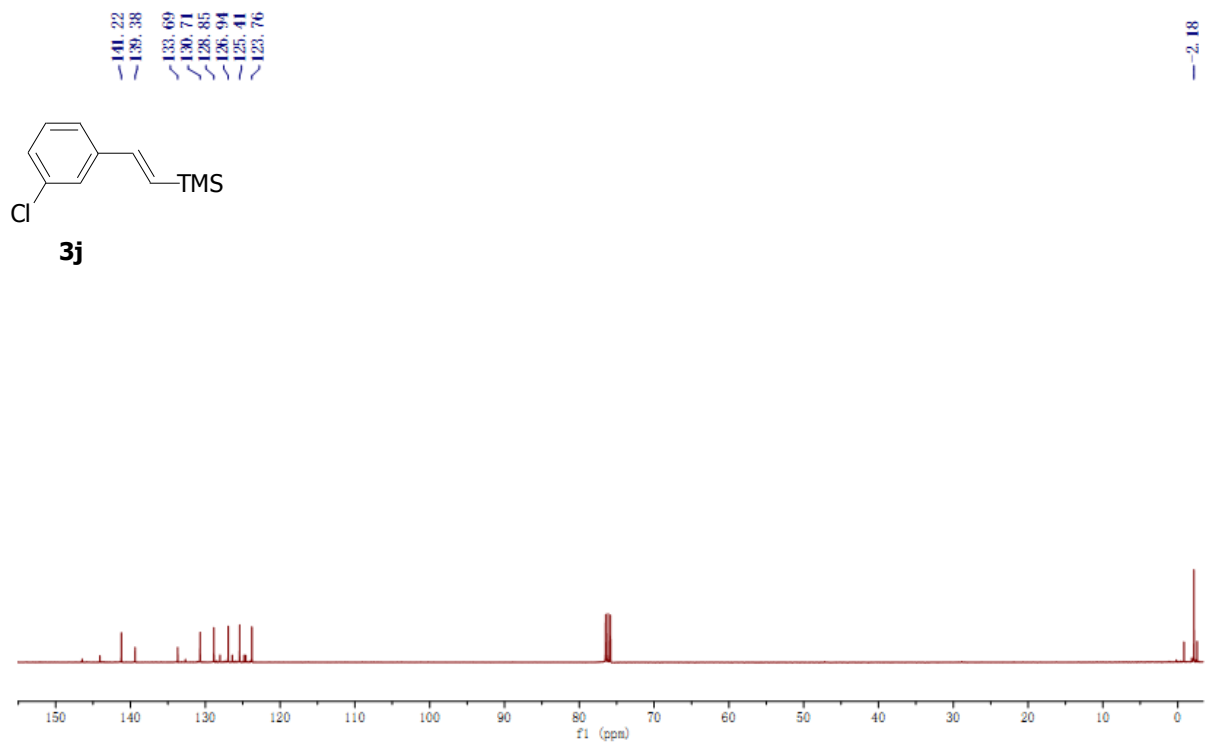


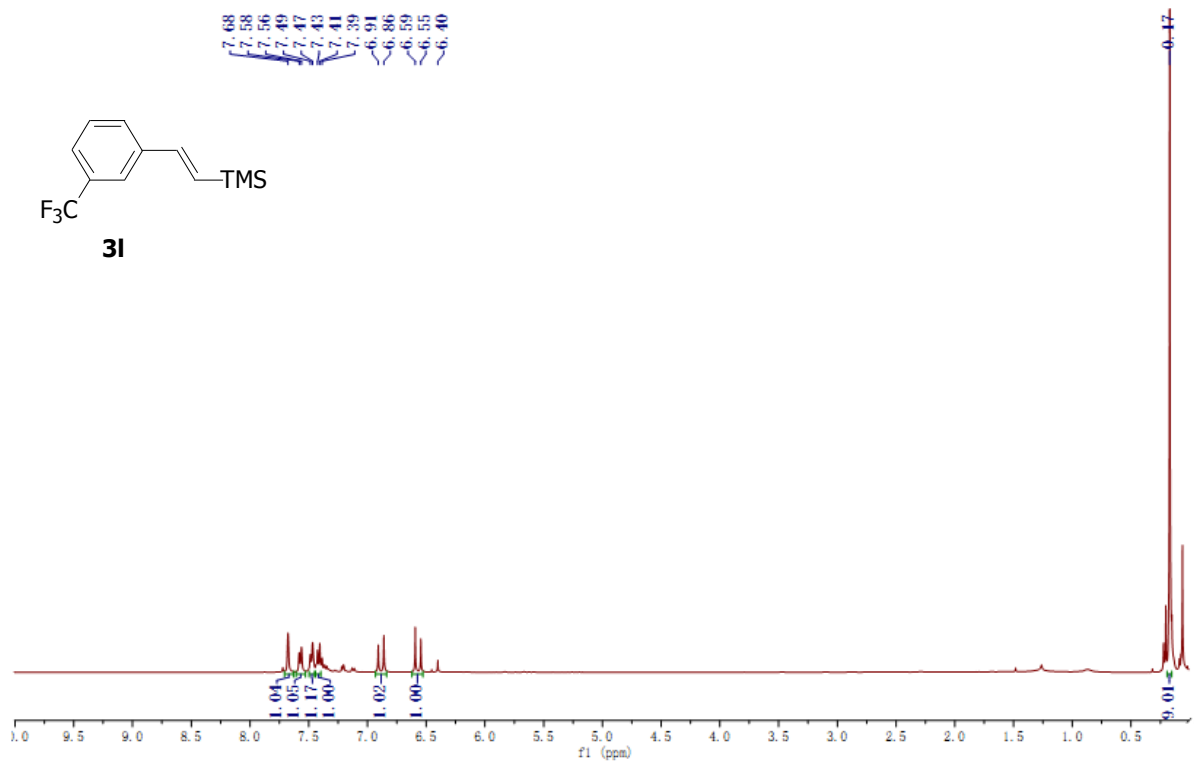
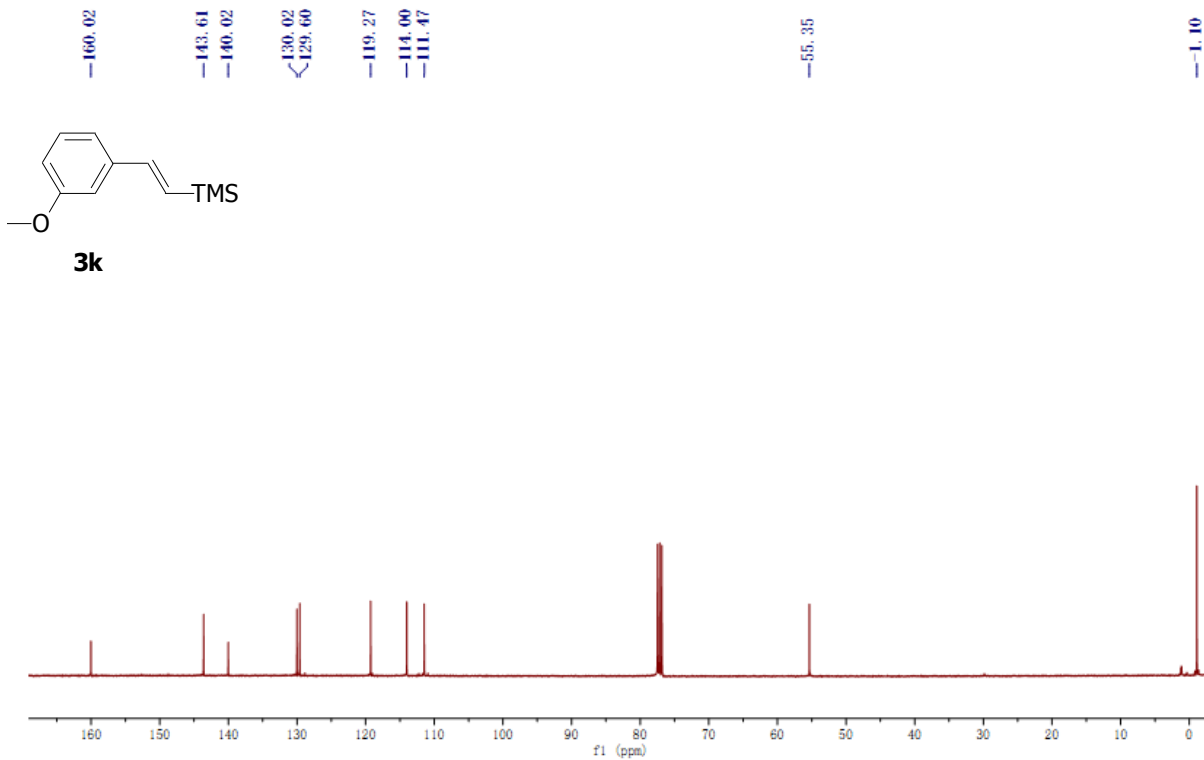
**3h**



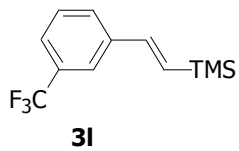




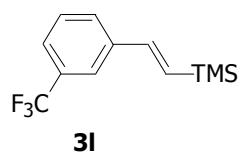
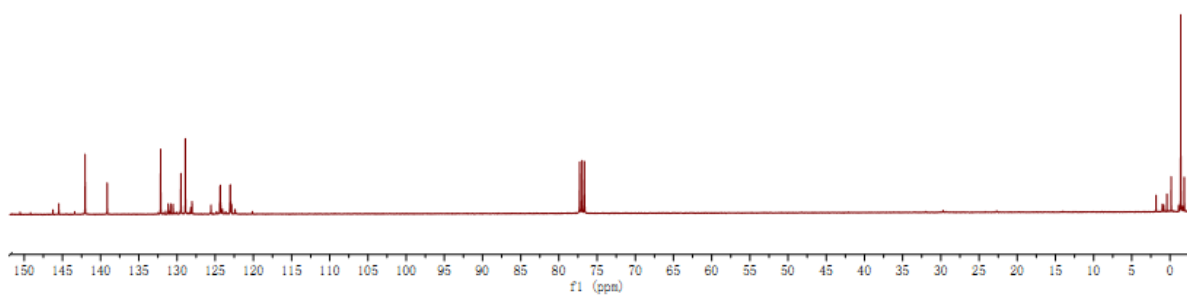




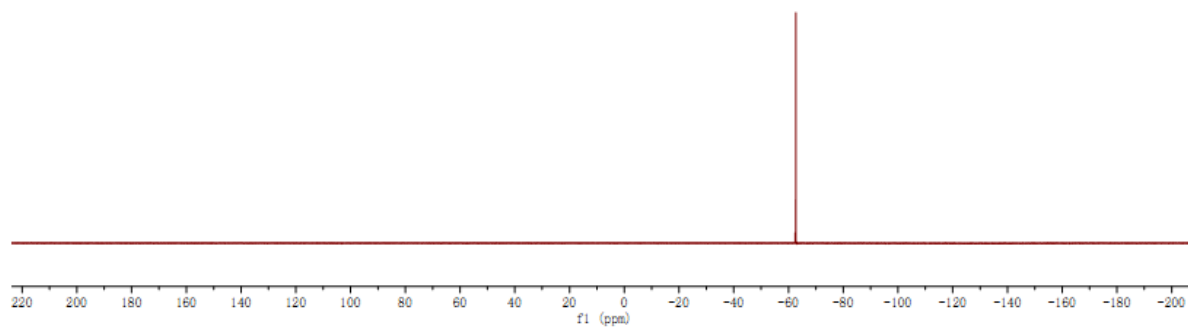
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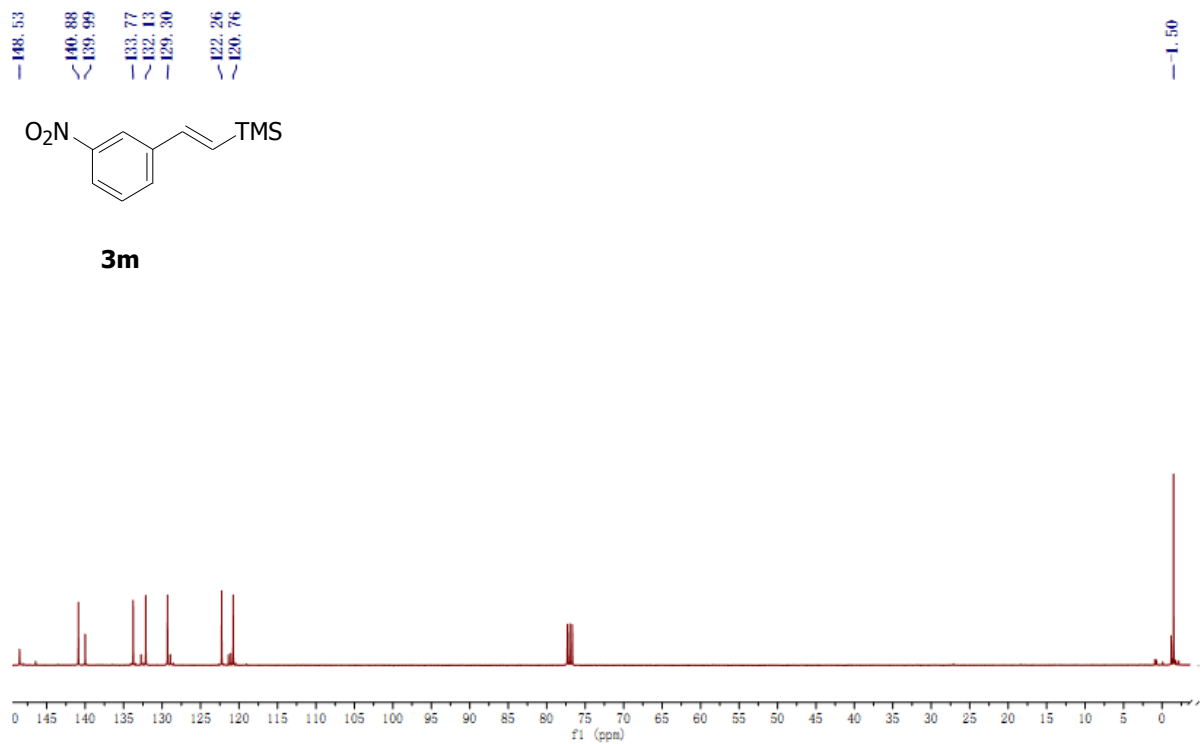
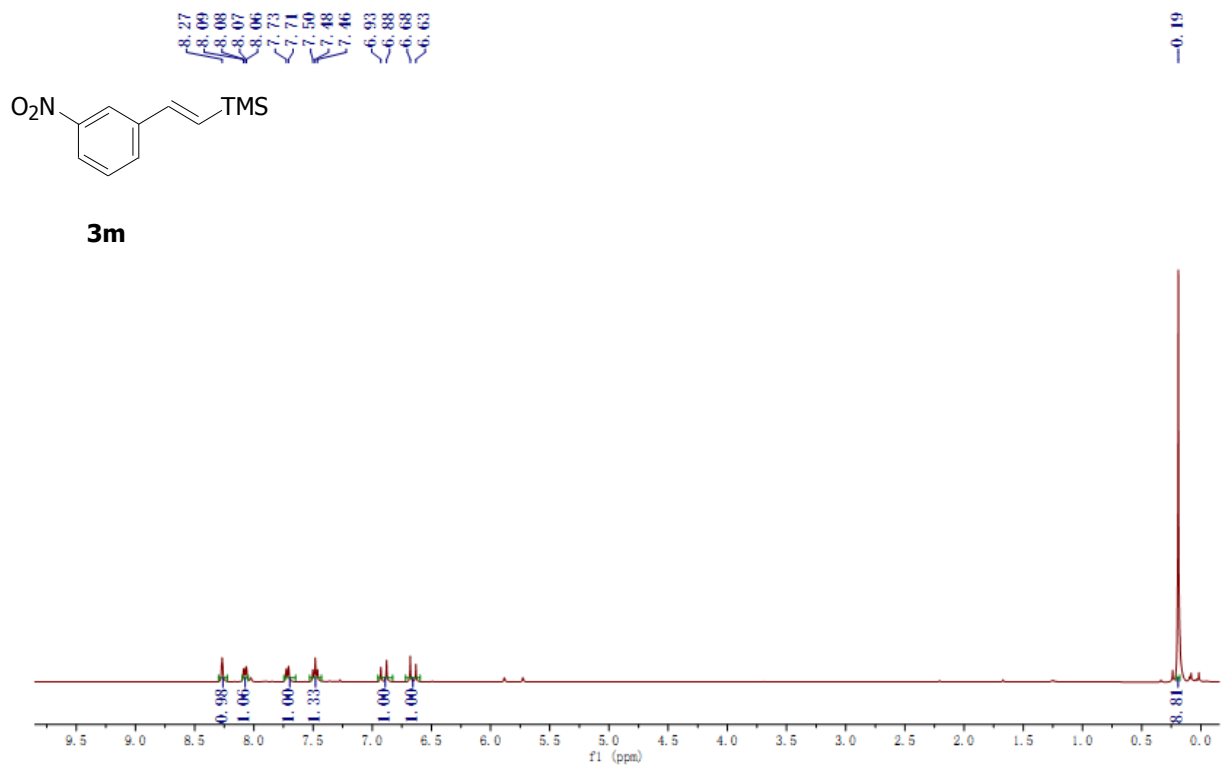
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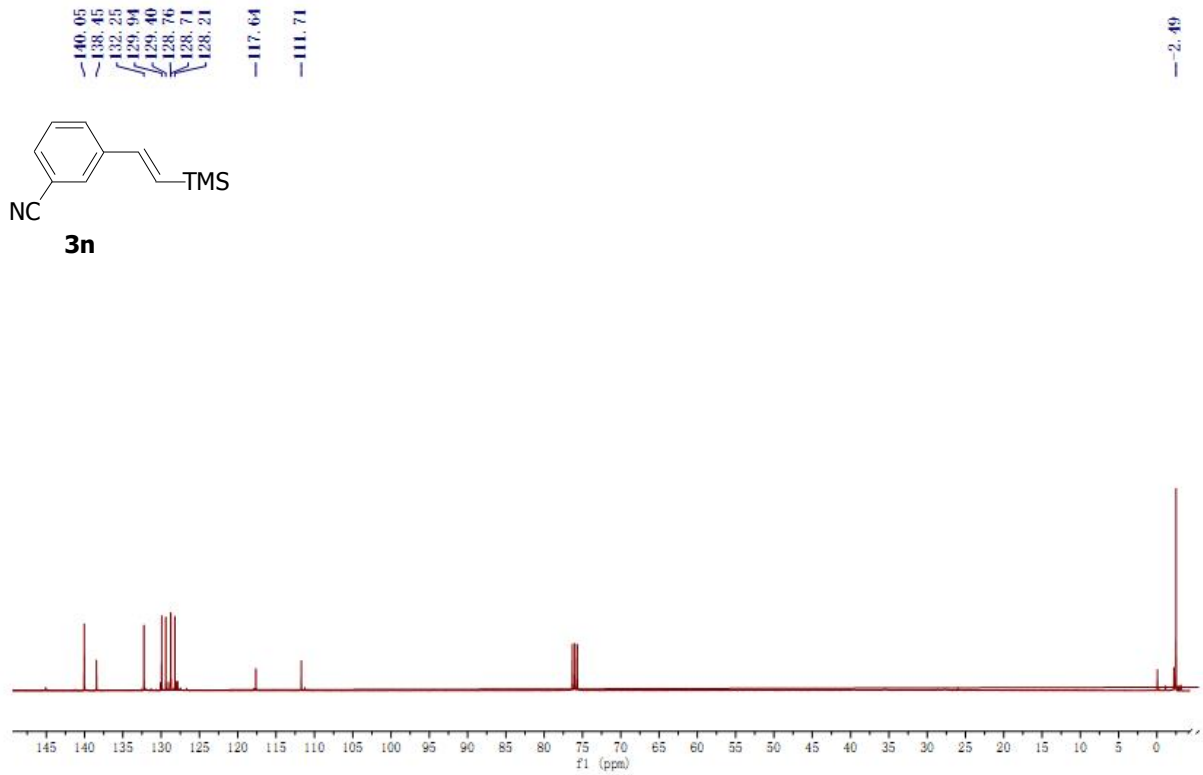
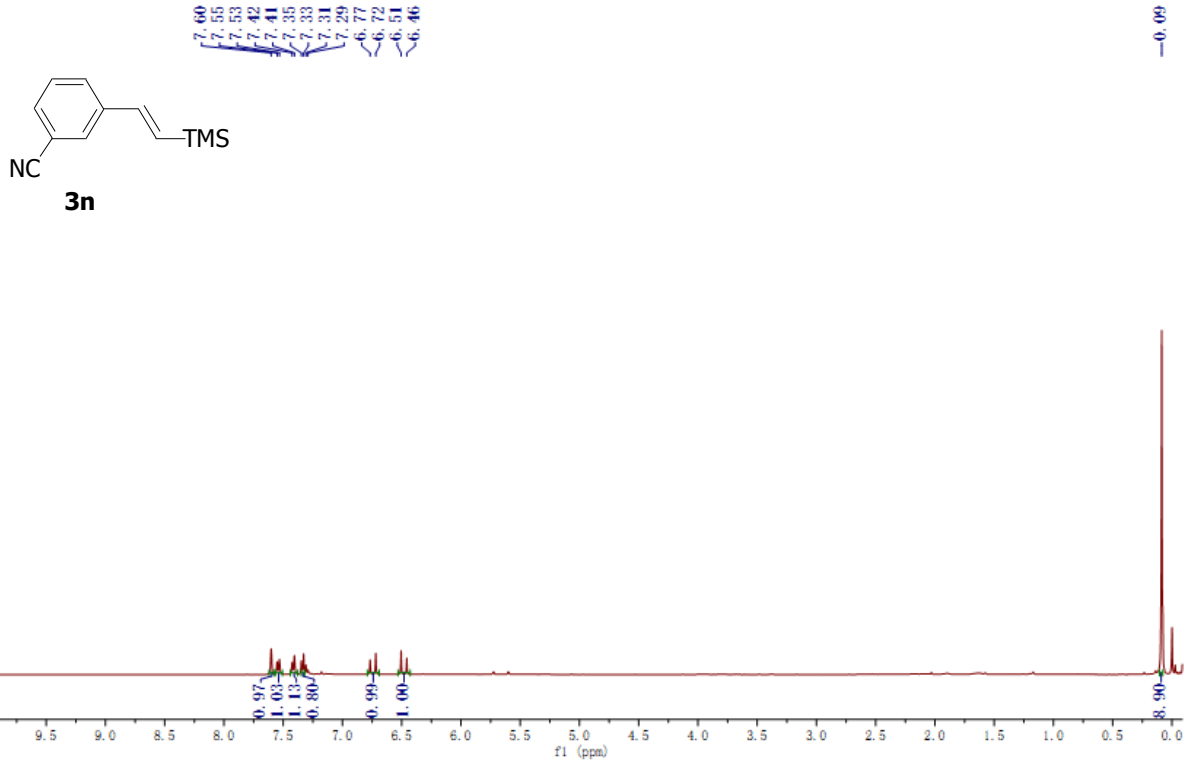


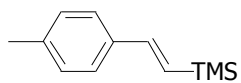
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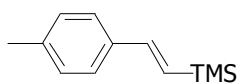
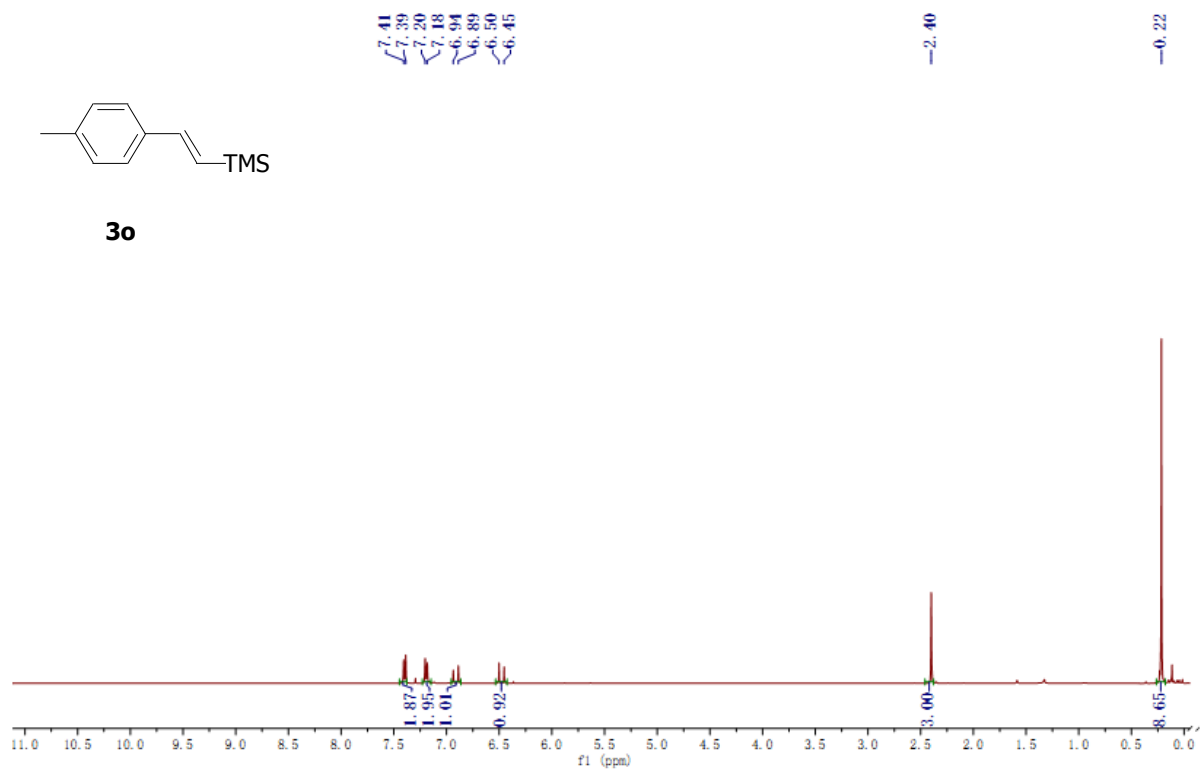




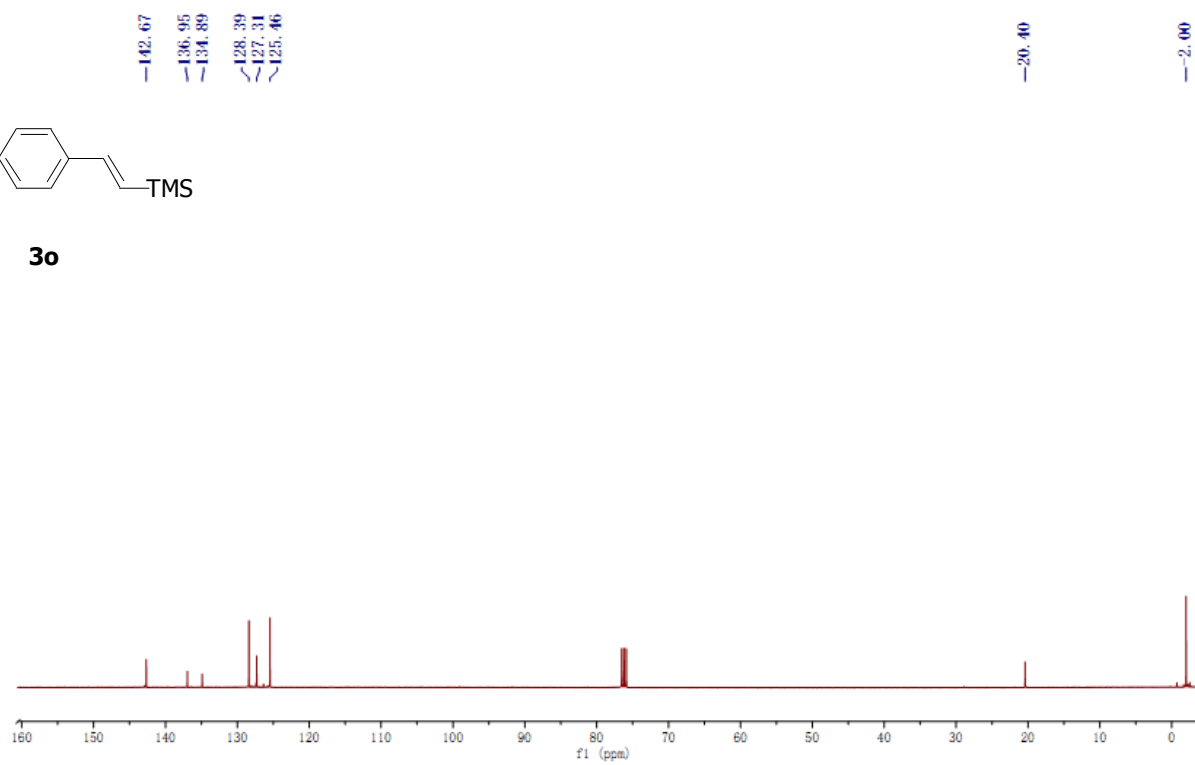


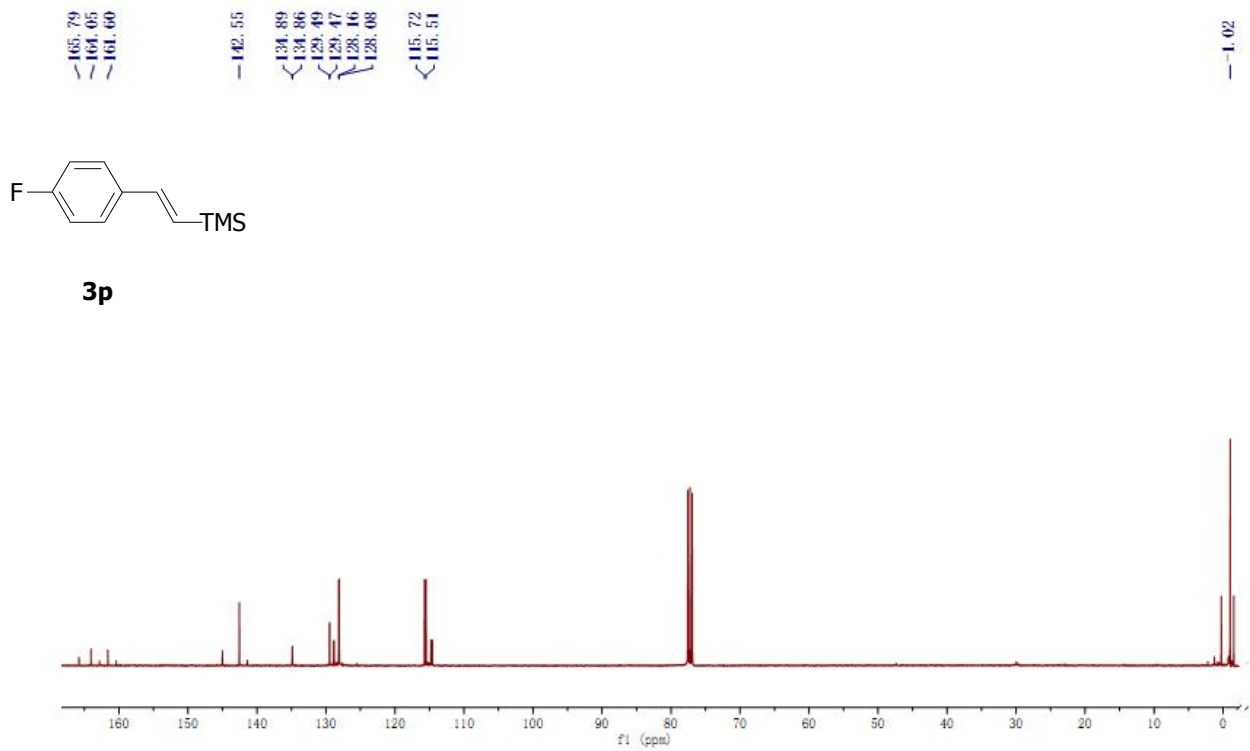
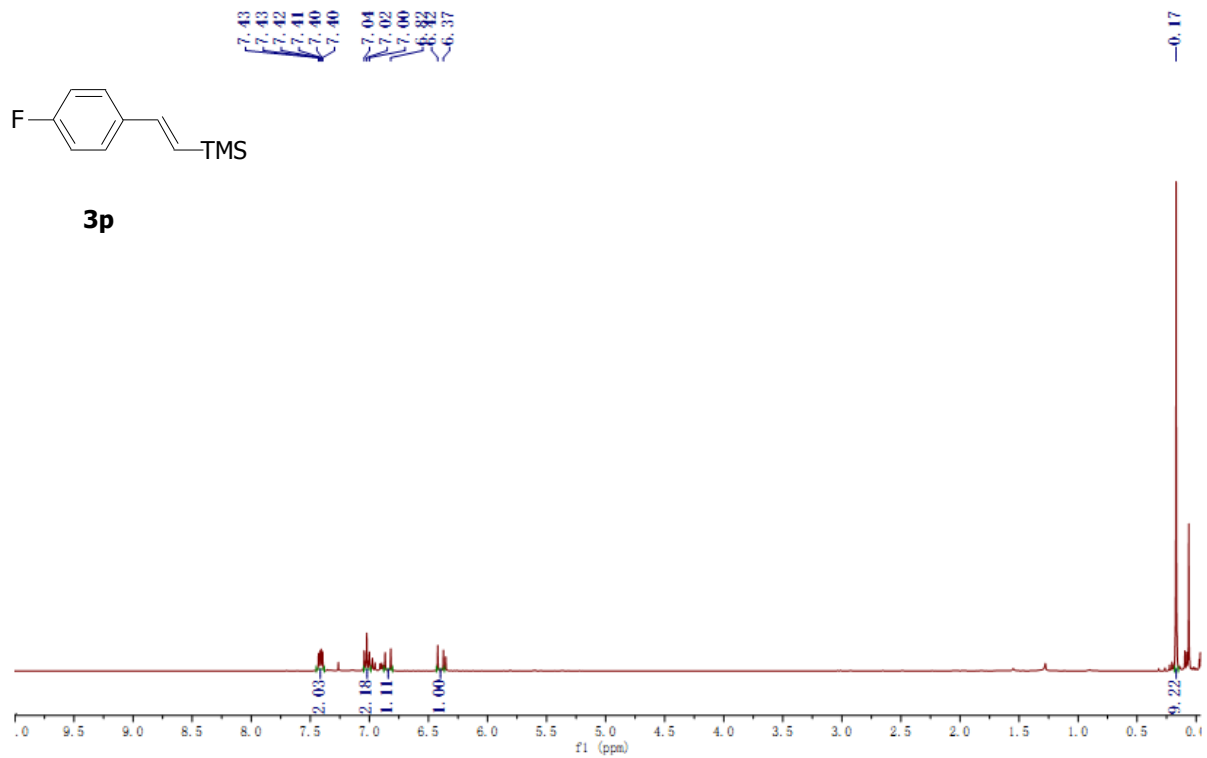


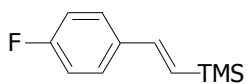
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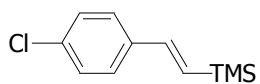
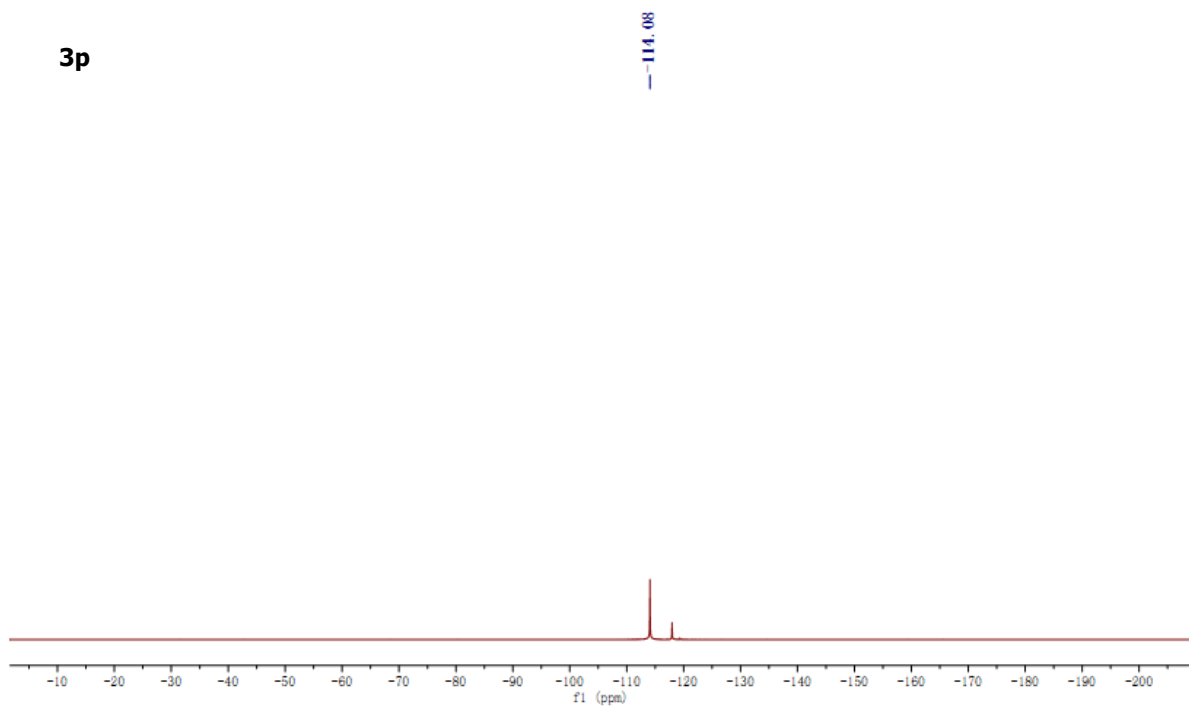
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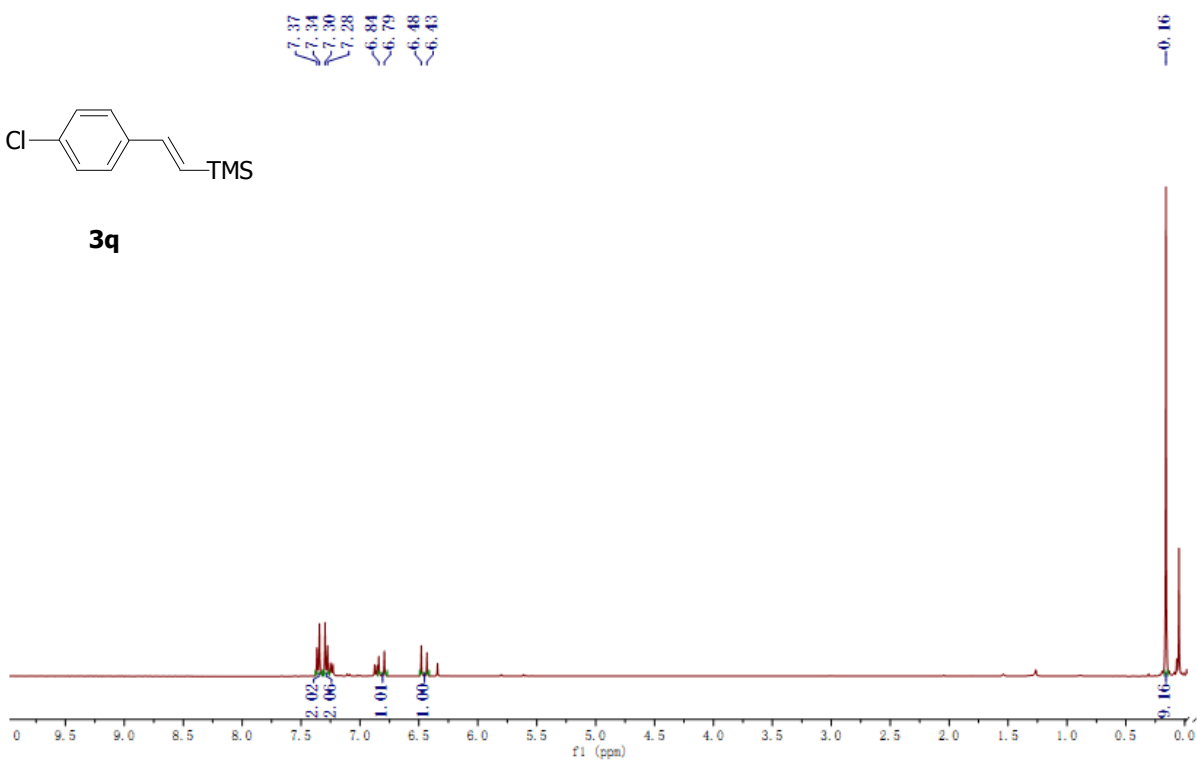




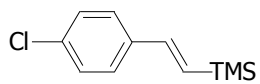
**3p**



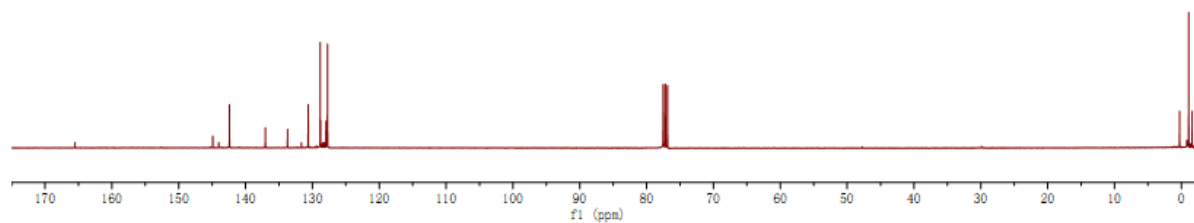
**3q**



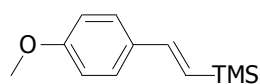
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142.41  
137.05  
133.72  
130.63  
128.84  
127.74



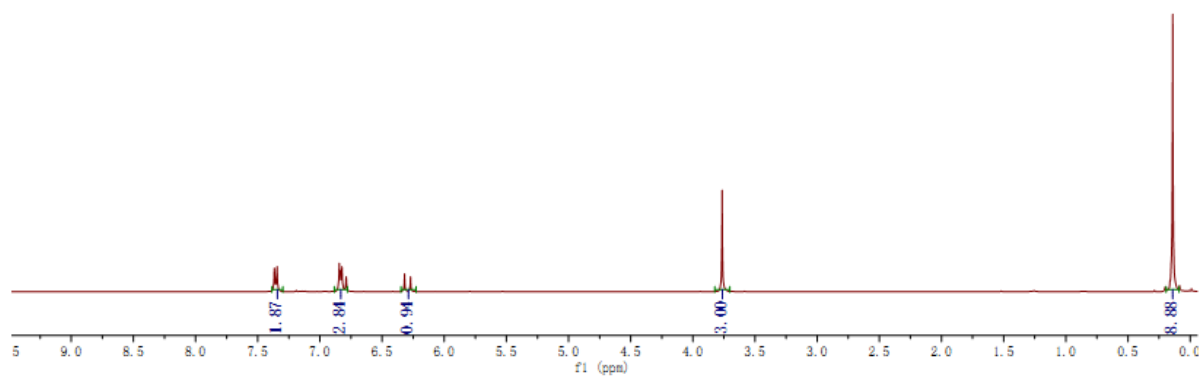
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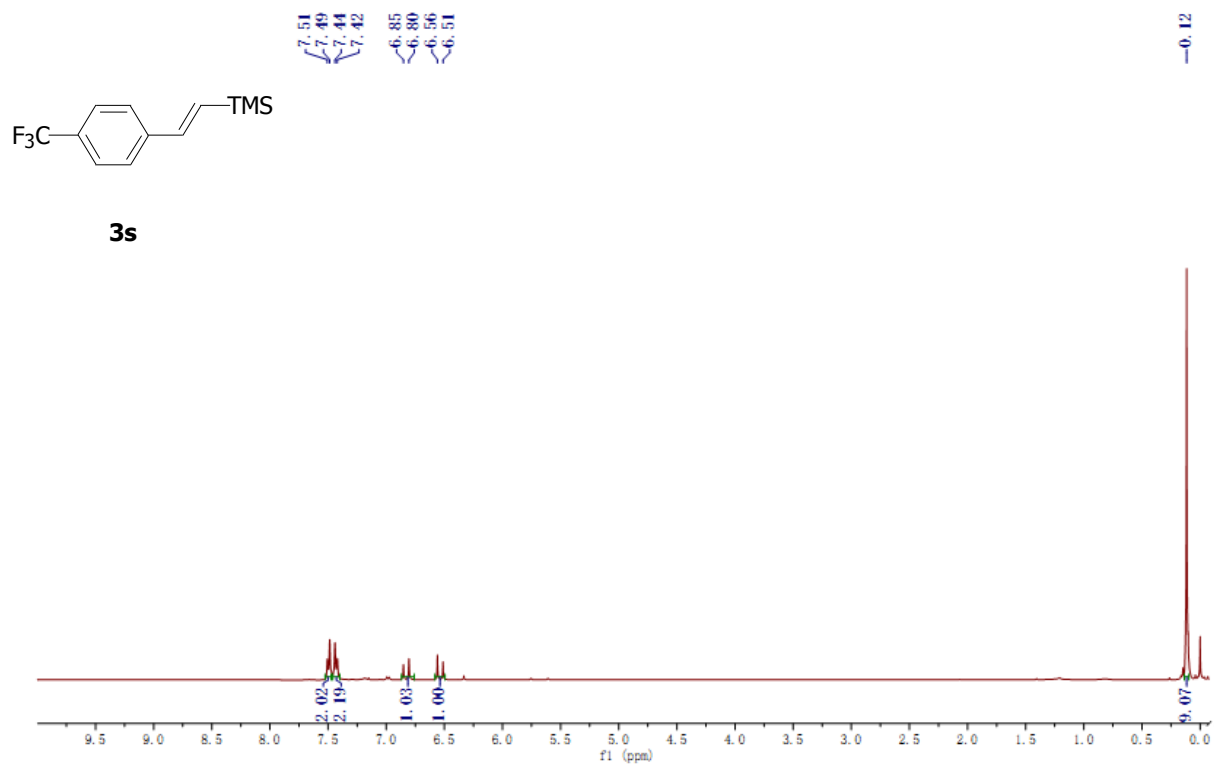
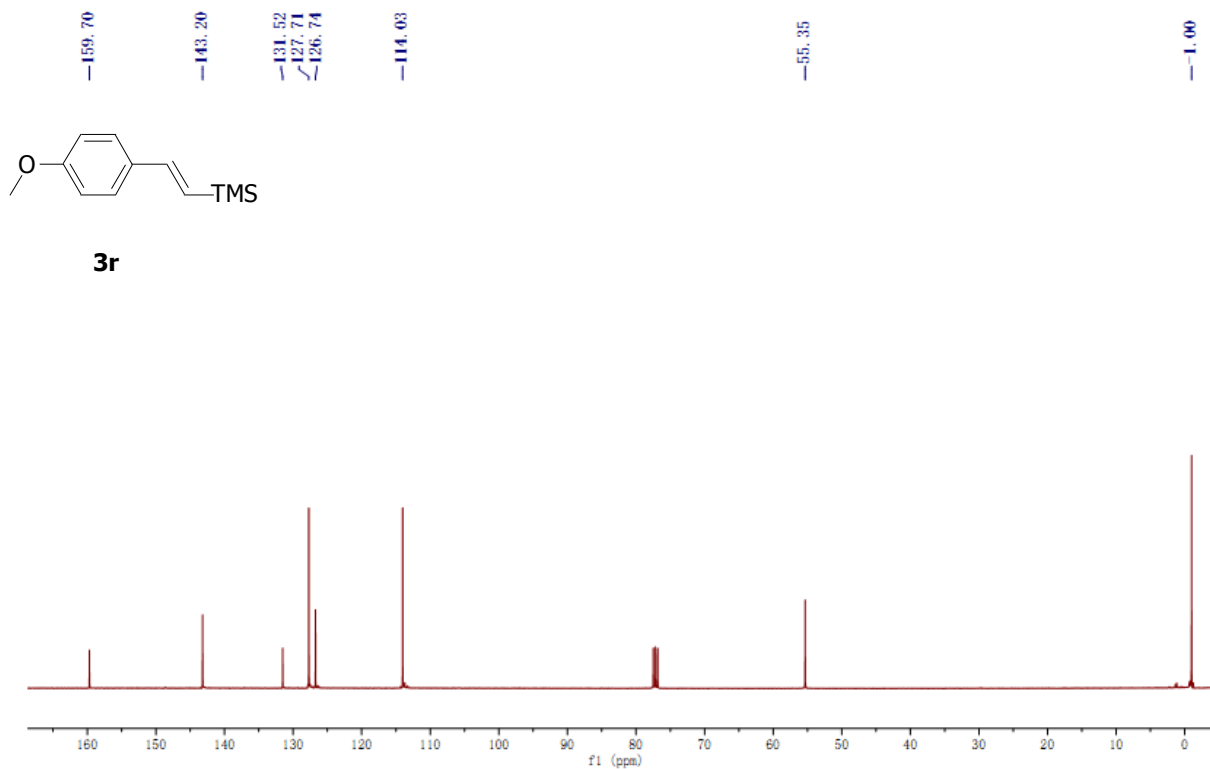


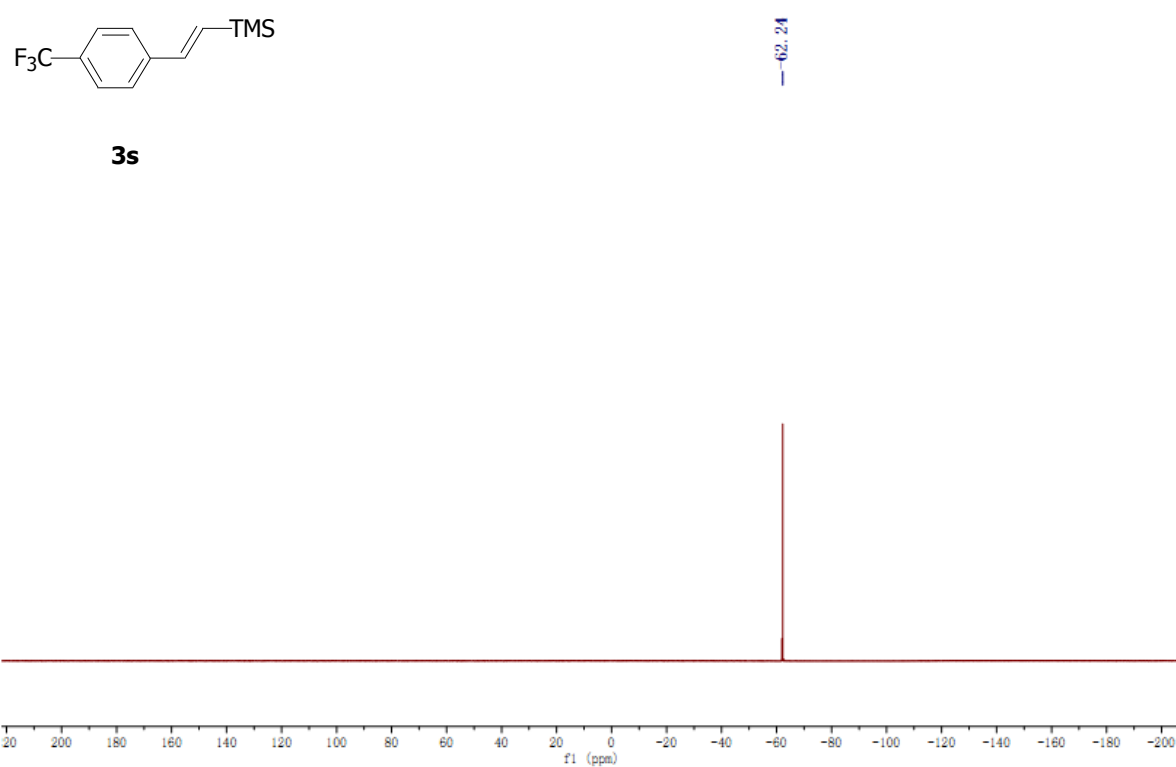
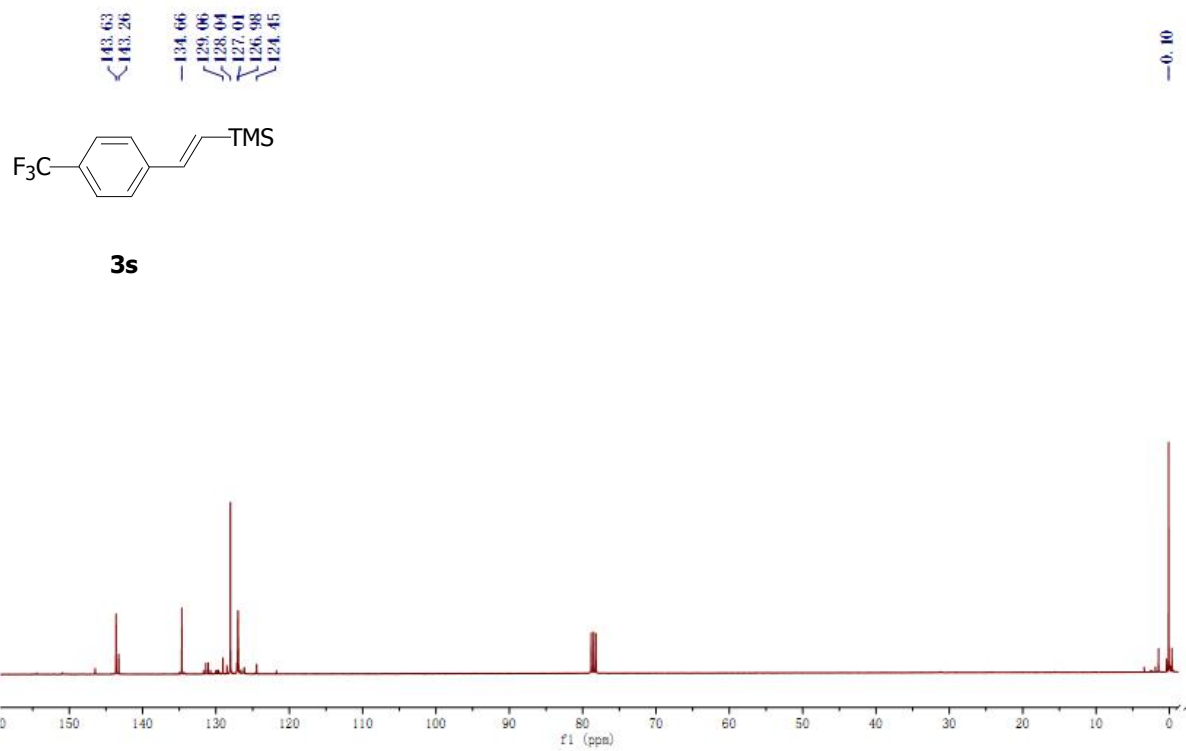
7.37  
7.34  
6.84  
6.84  
6.82  
6.79  
6.32  
6.27



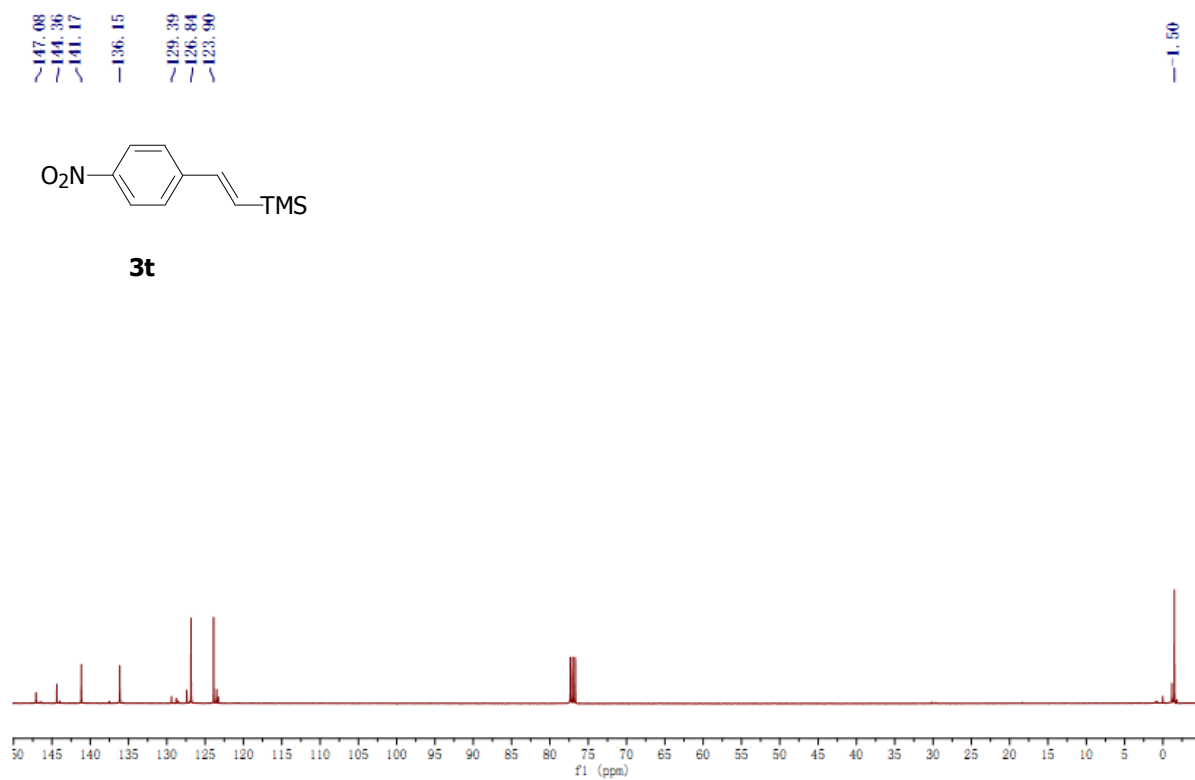
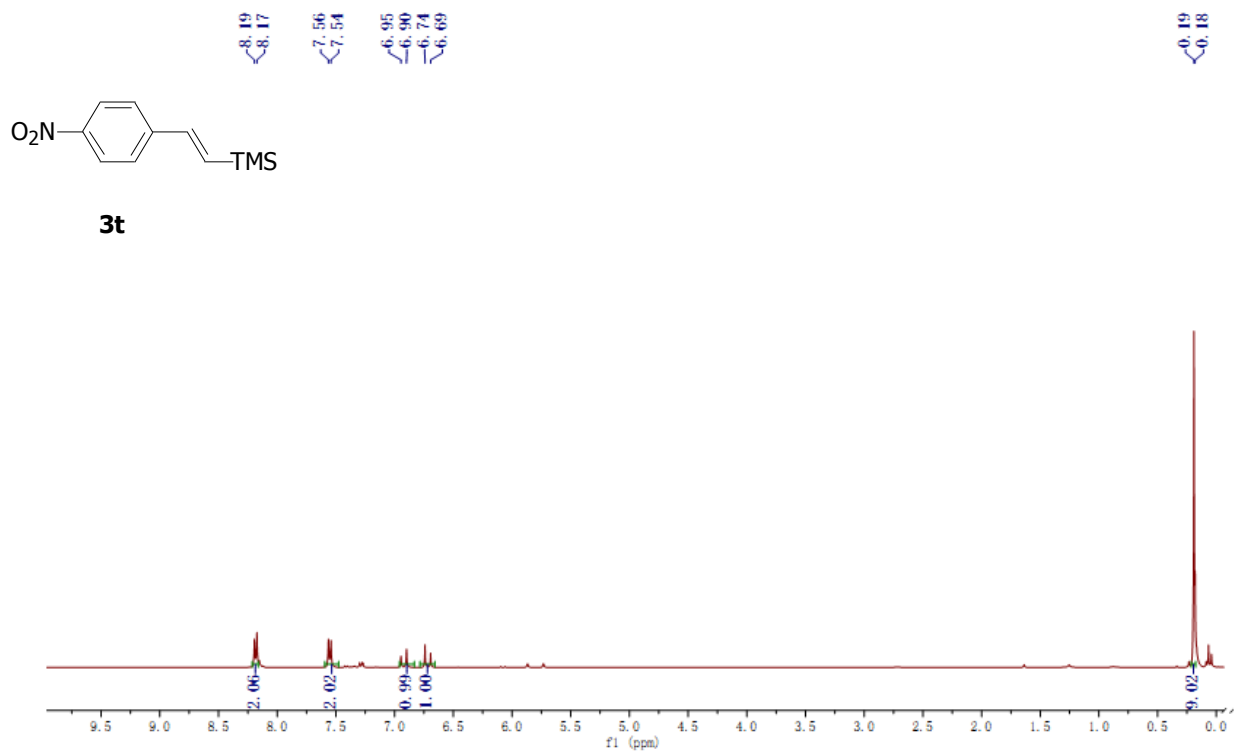
**3r**

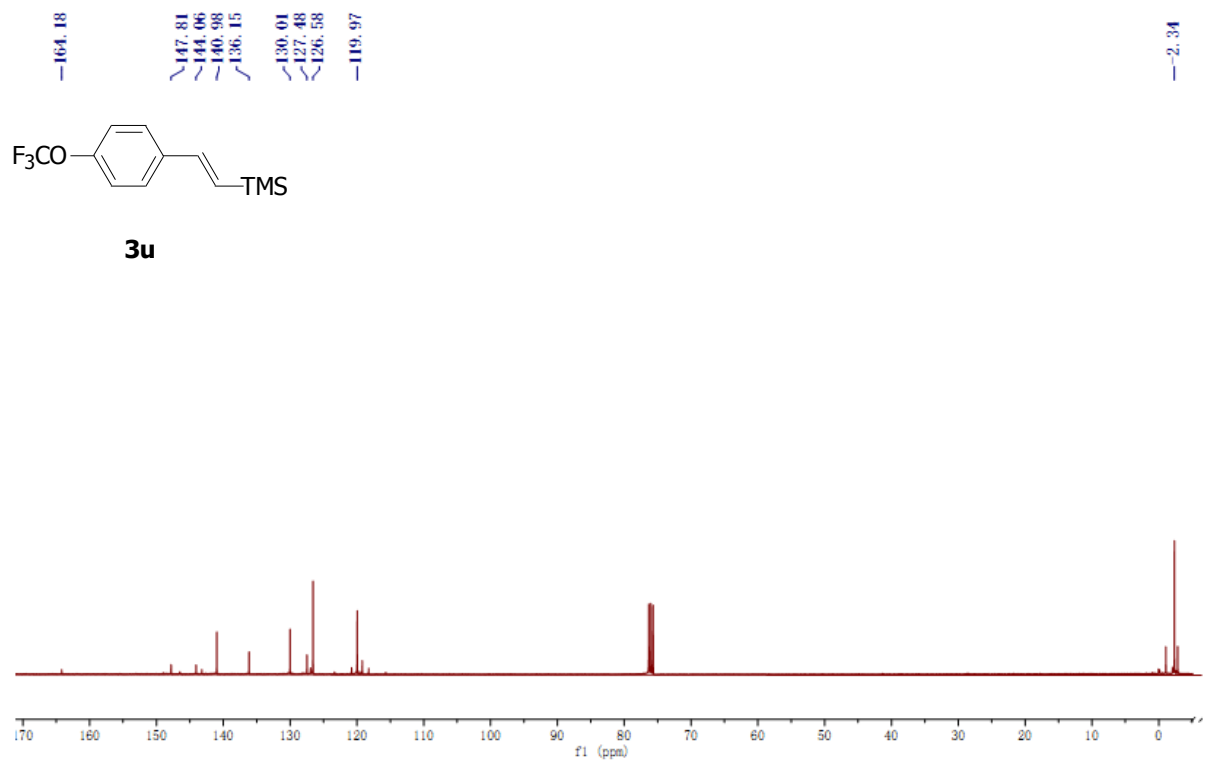
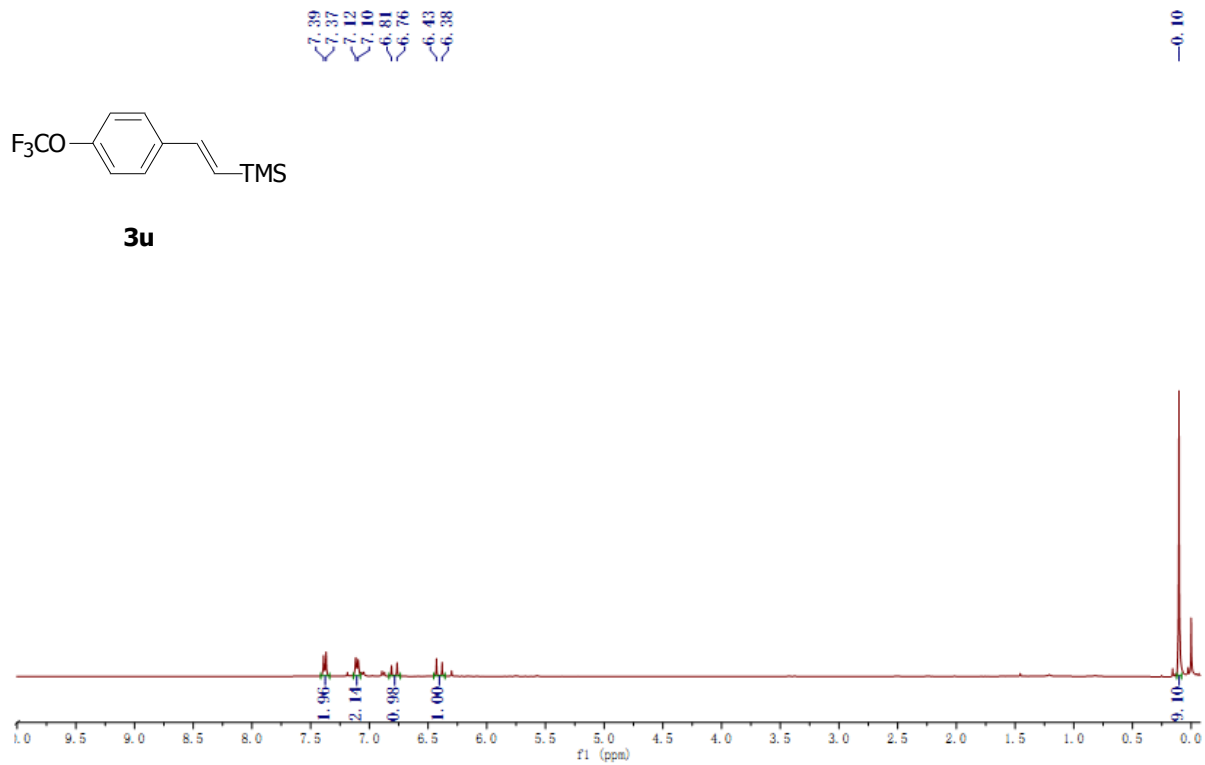


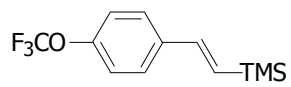




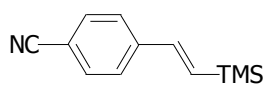
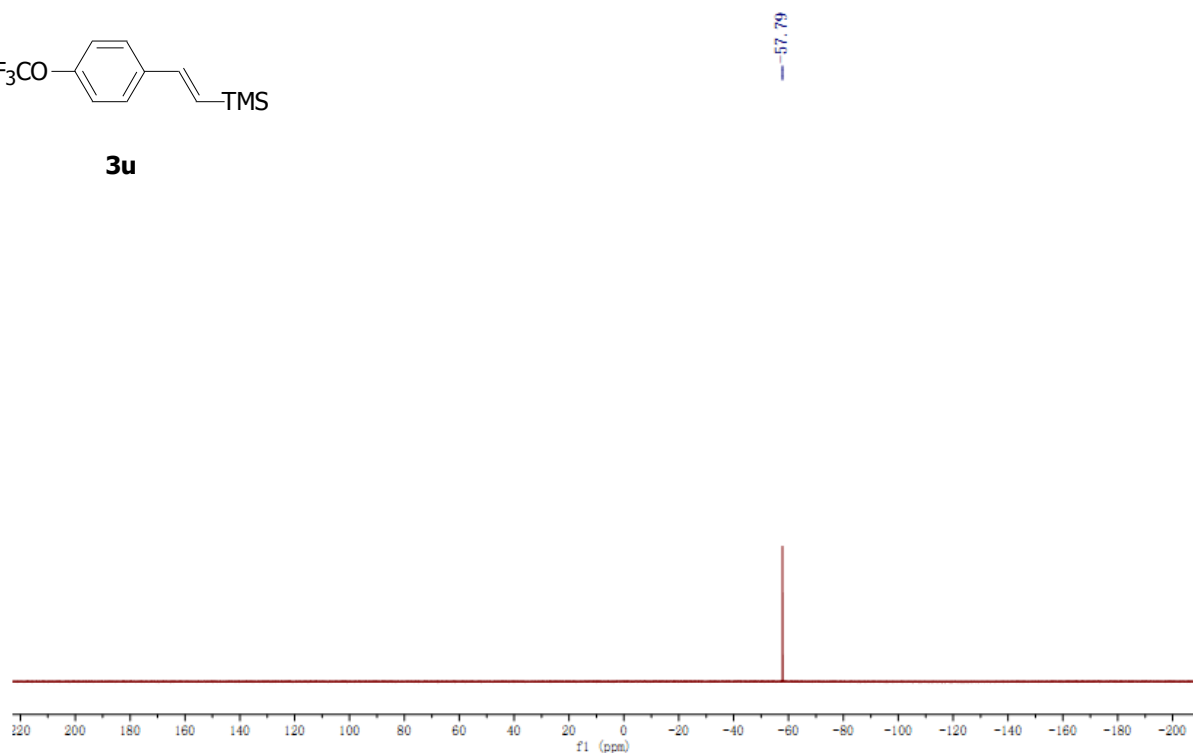




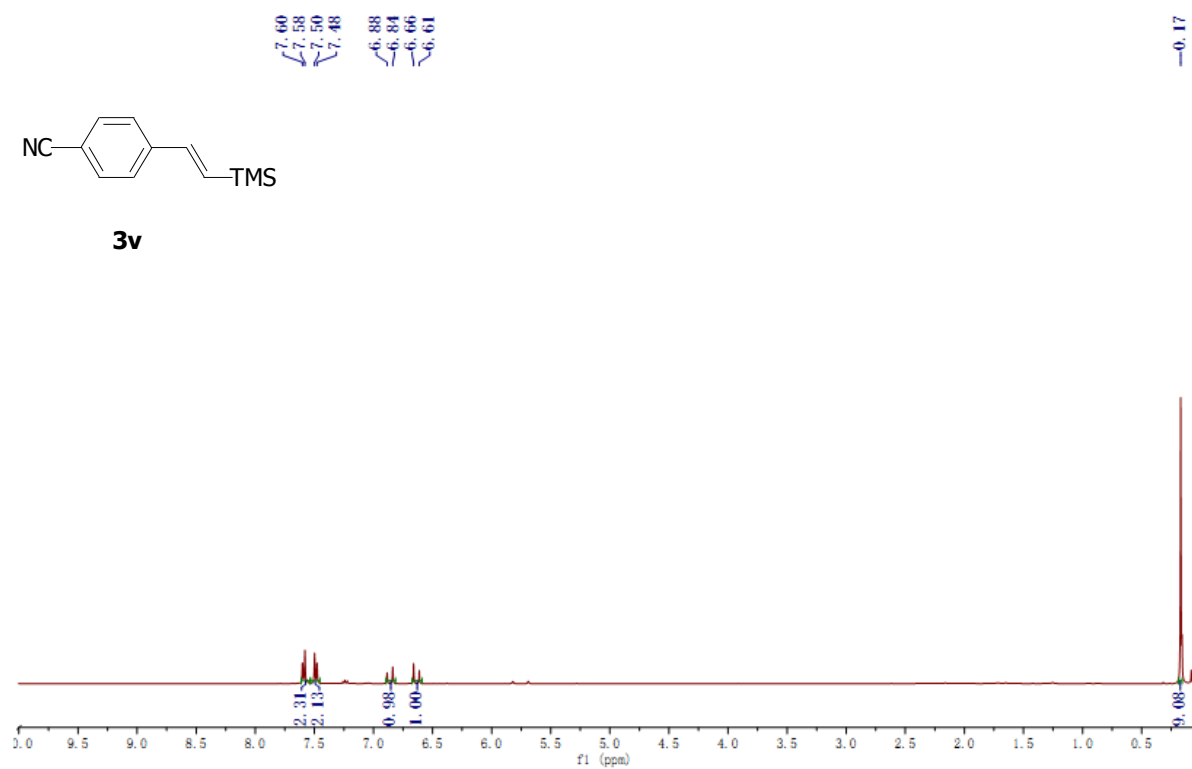


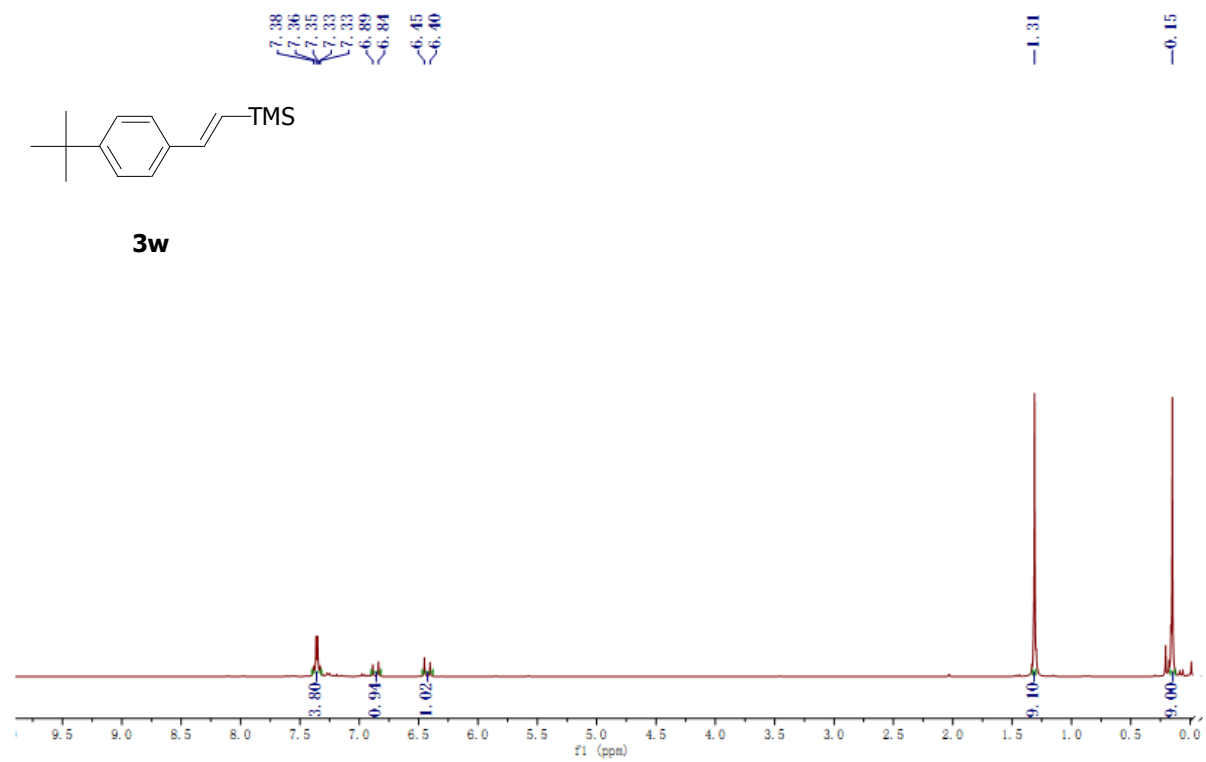
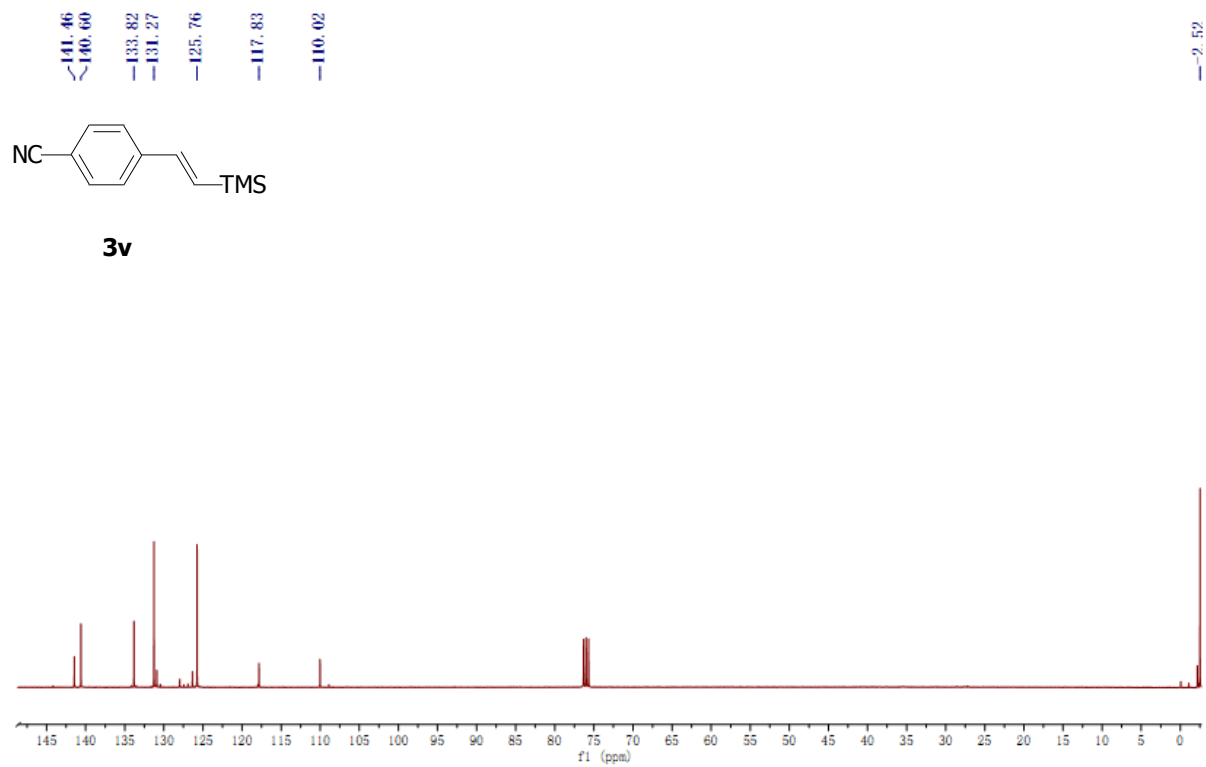


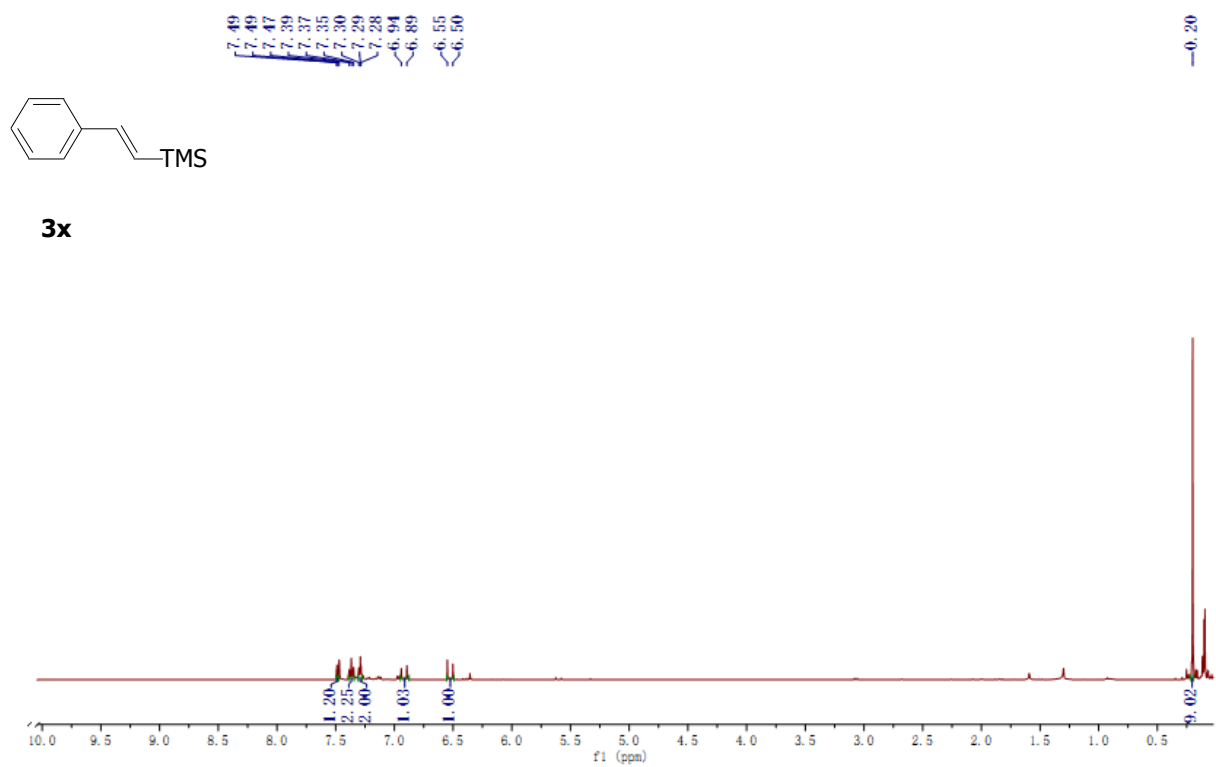
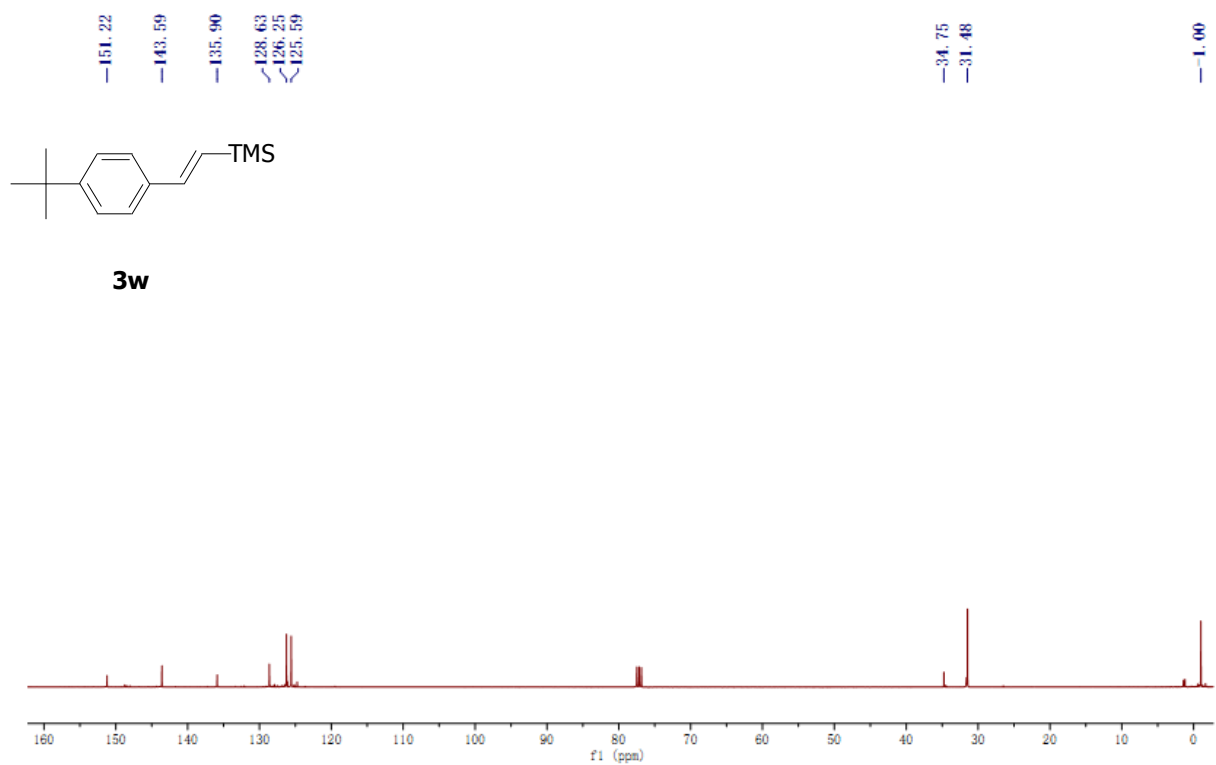
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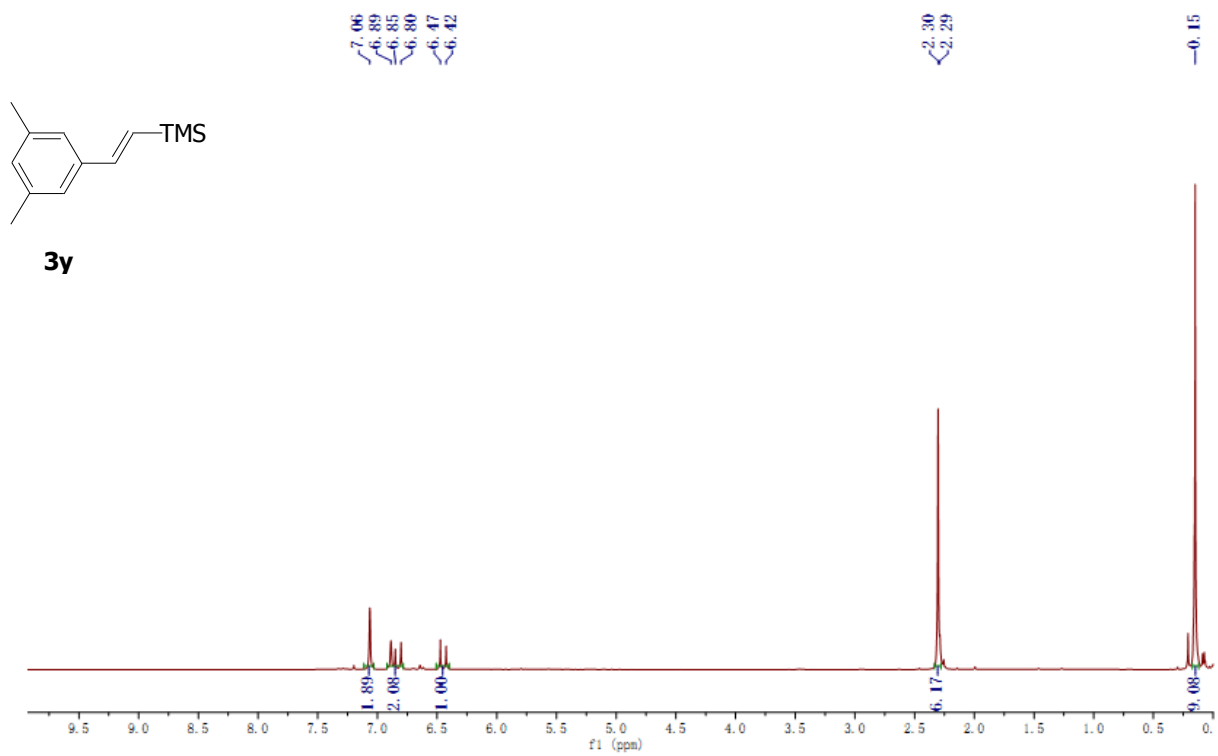
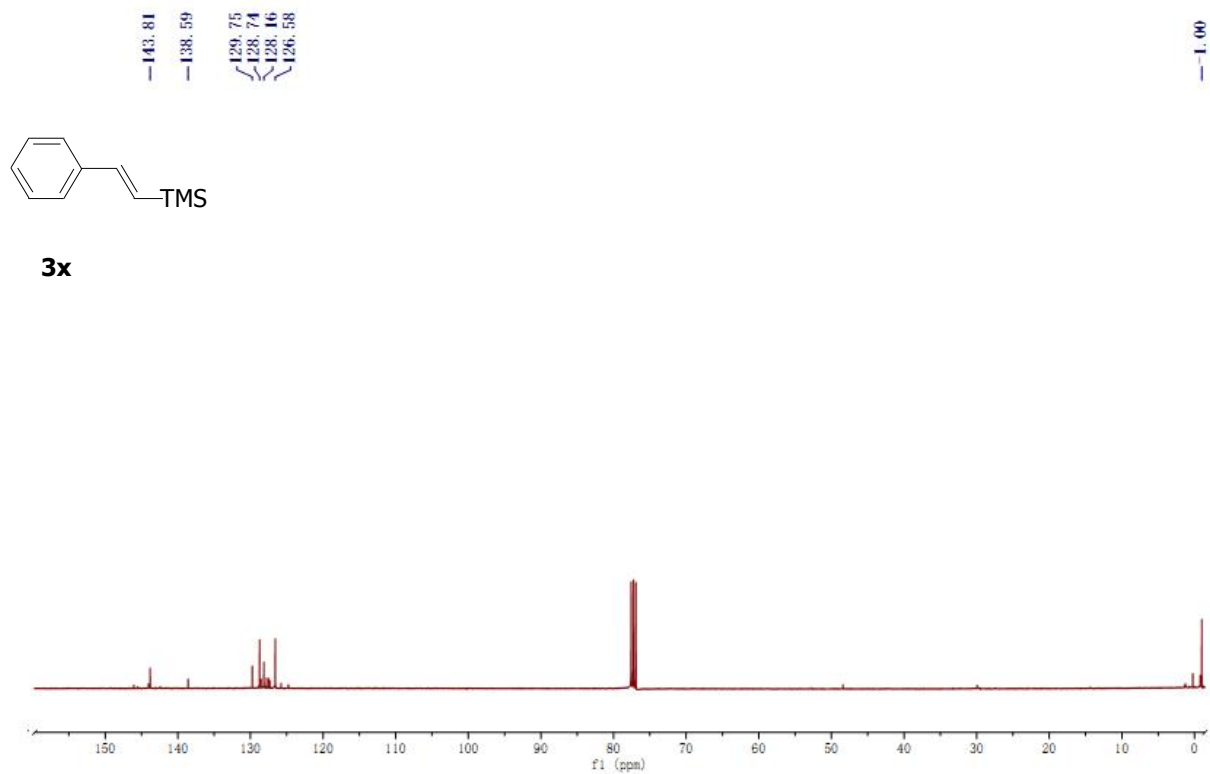


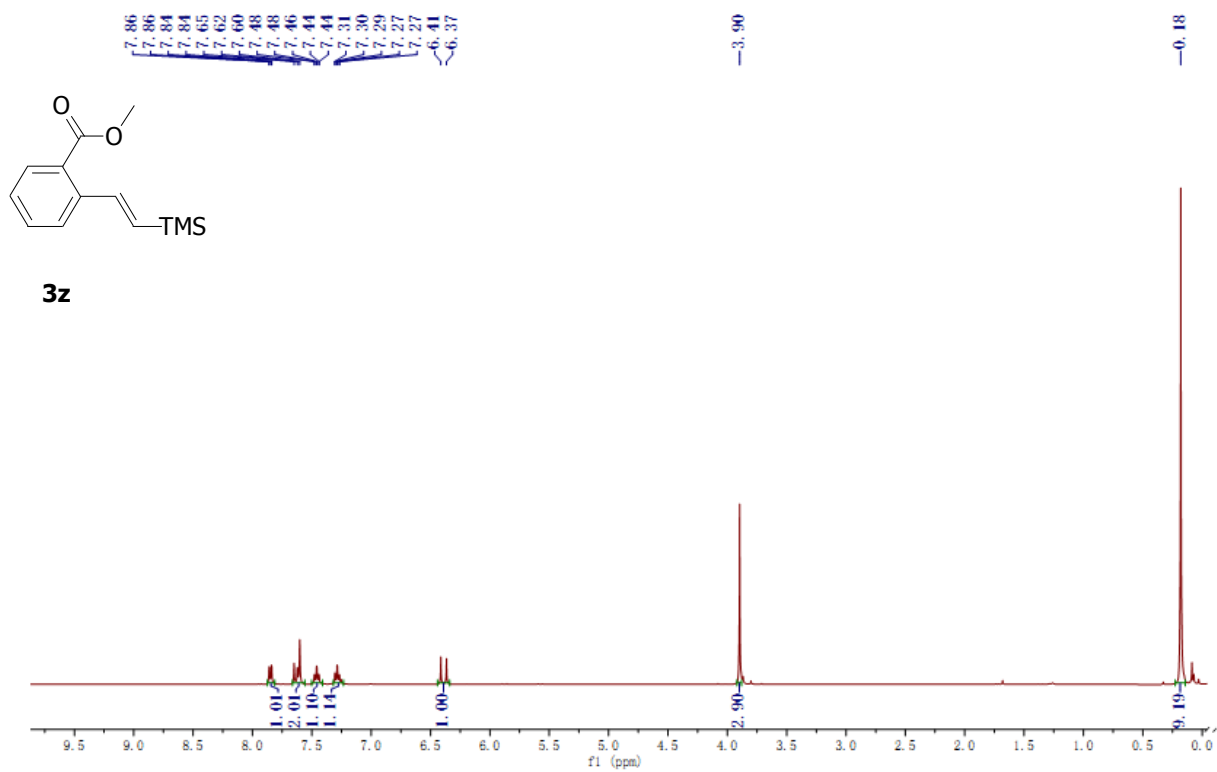
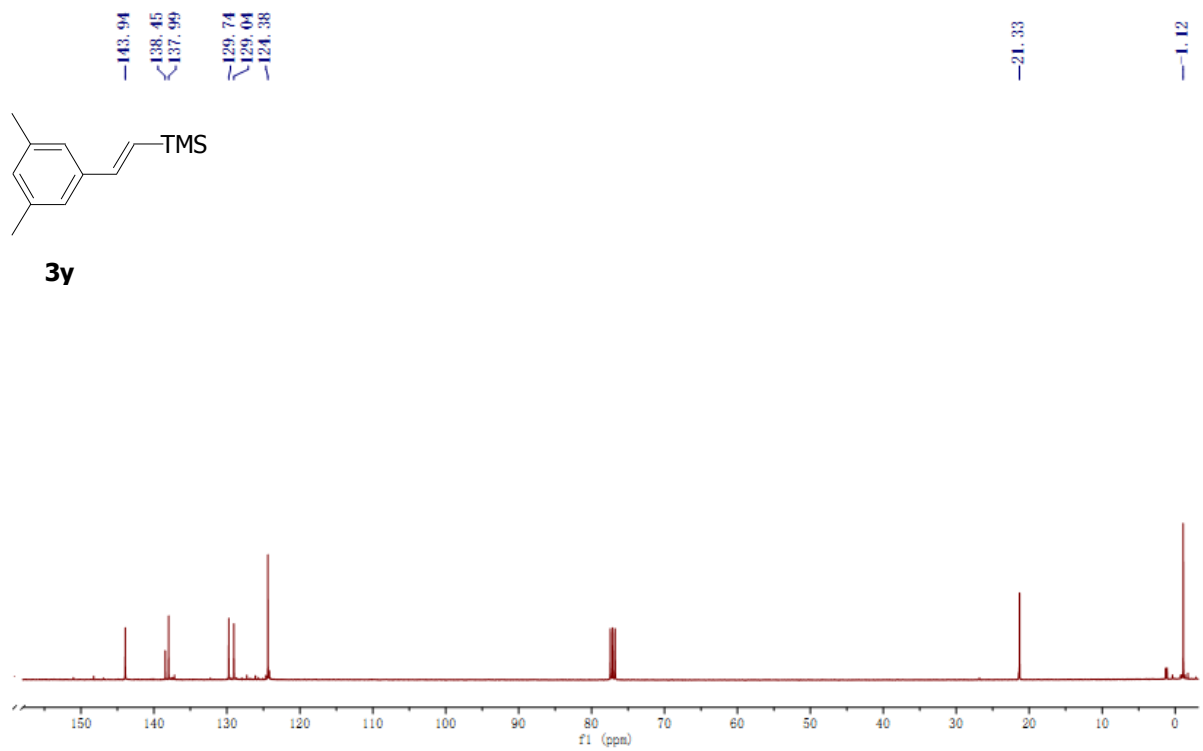
**3v**



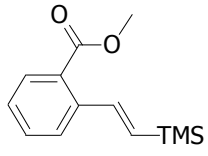








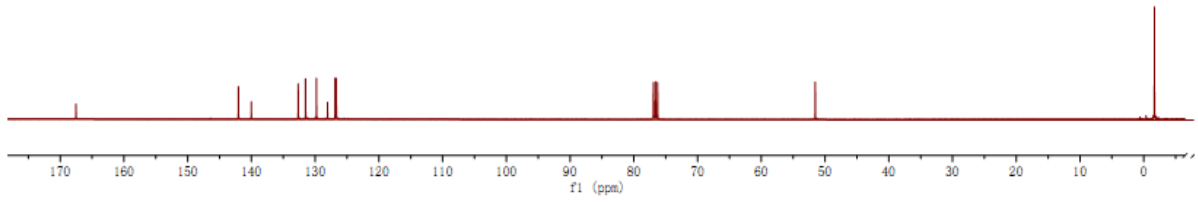
167.53  
 142.03  
 140.01  
 132.66  
 131.51  
 129.80  
 128.06  
 126.88



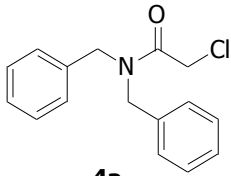
**3z**

51.55

1.67

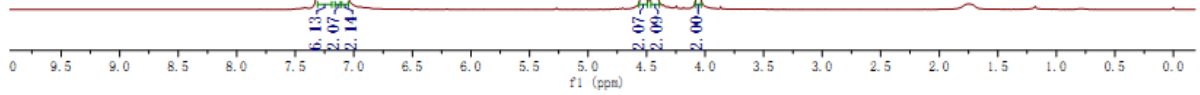


7.31  
 7.29  
 7.28  
 7.25  
 7.23  
 7.20  
 7.17  
 7.15  
 7.13  
 7.09  
 7.07

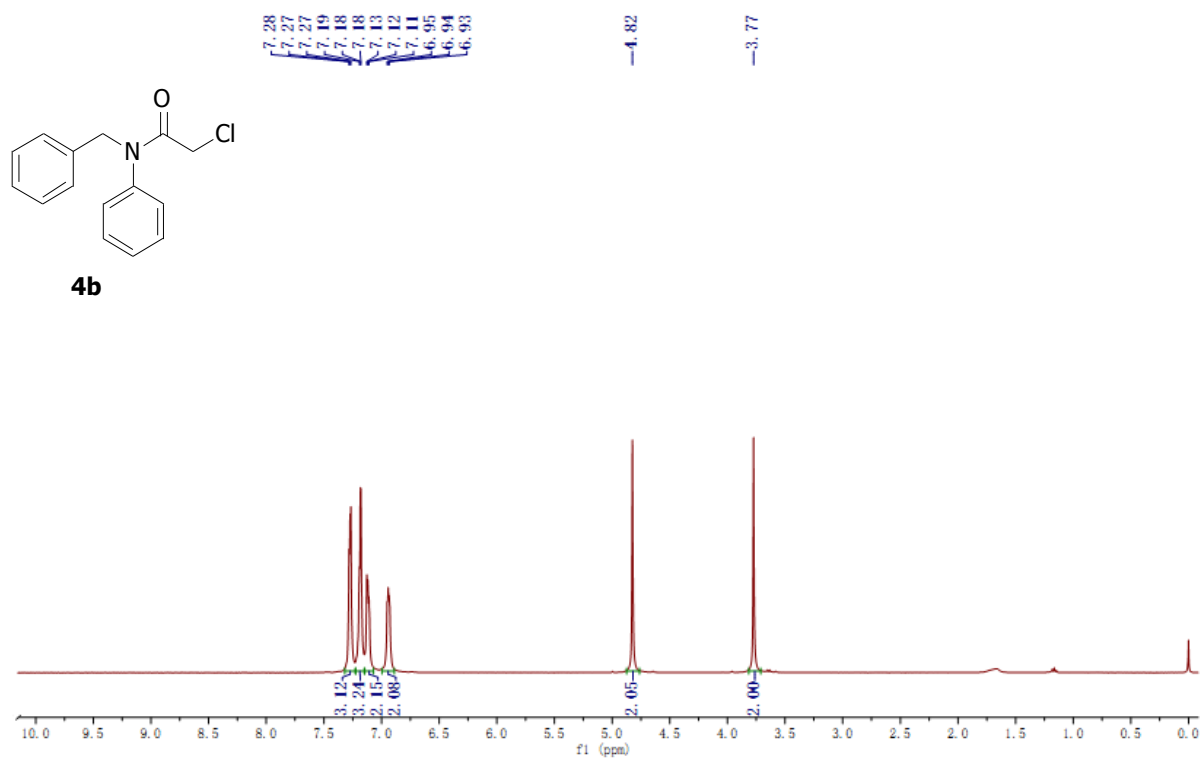
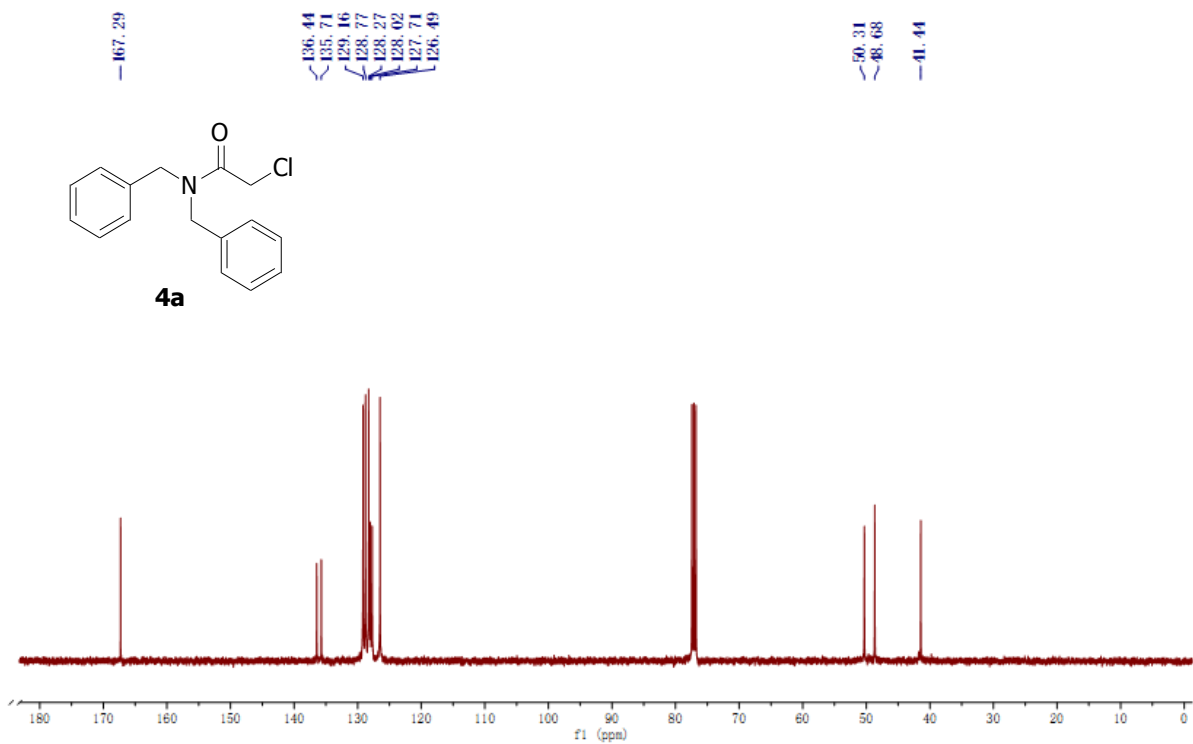


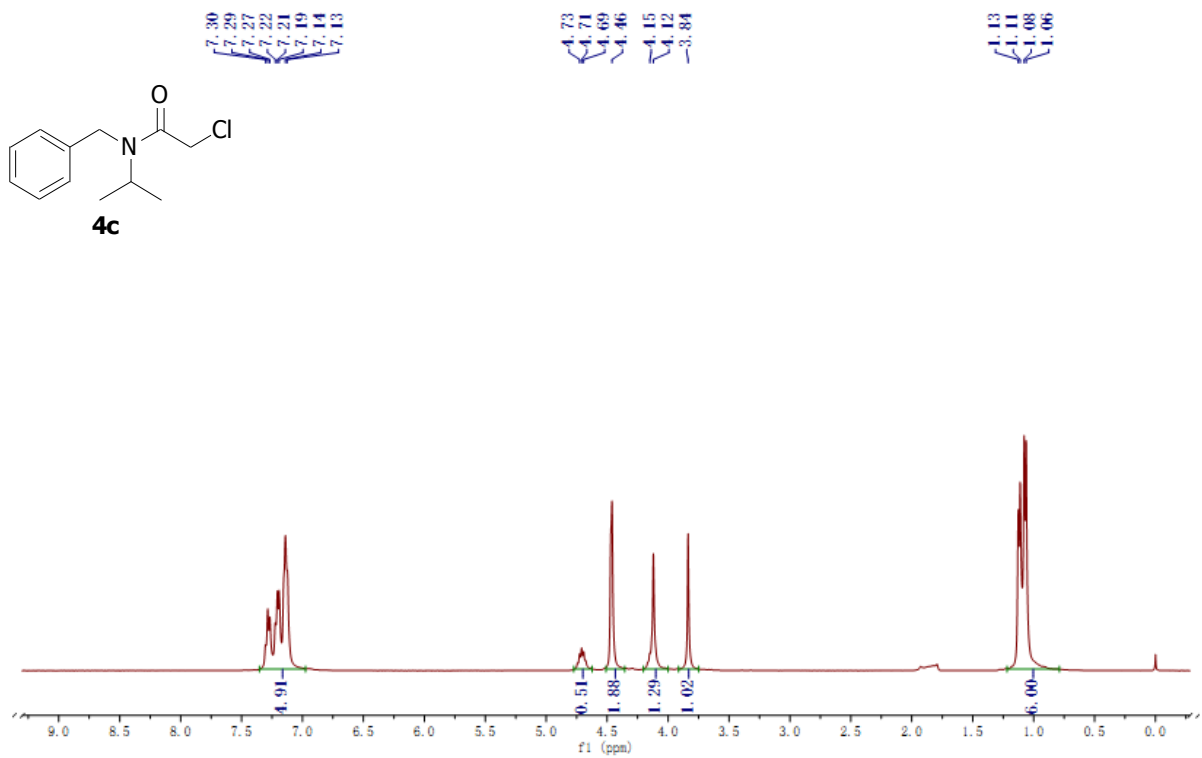
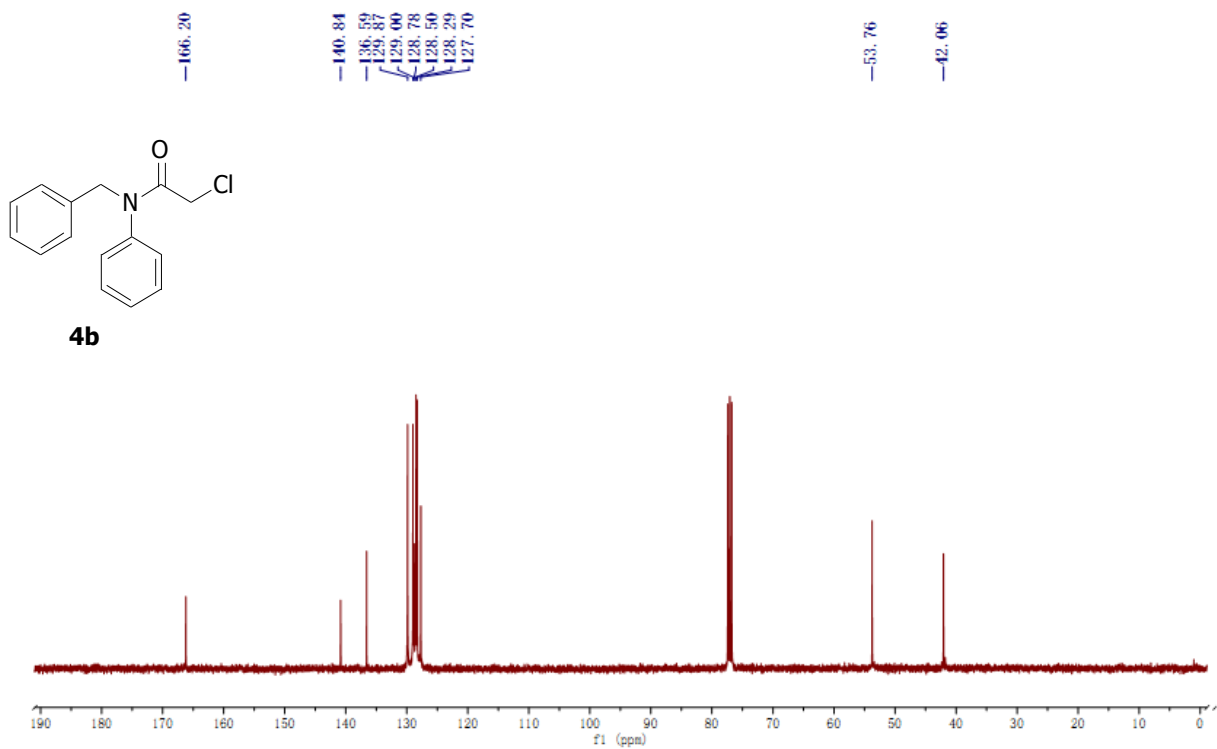
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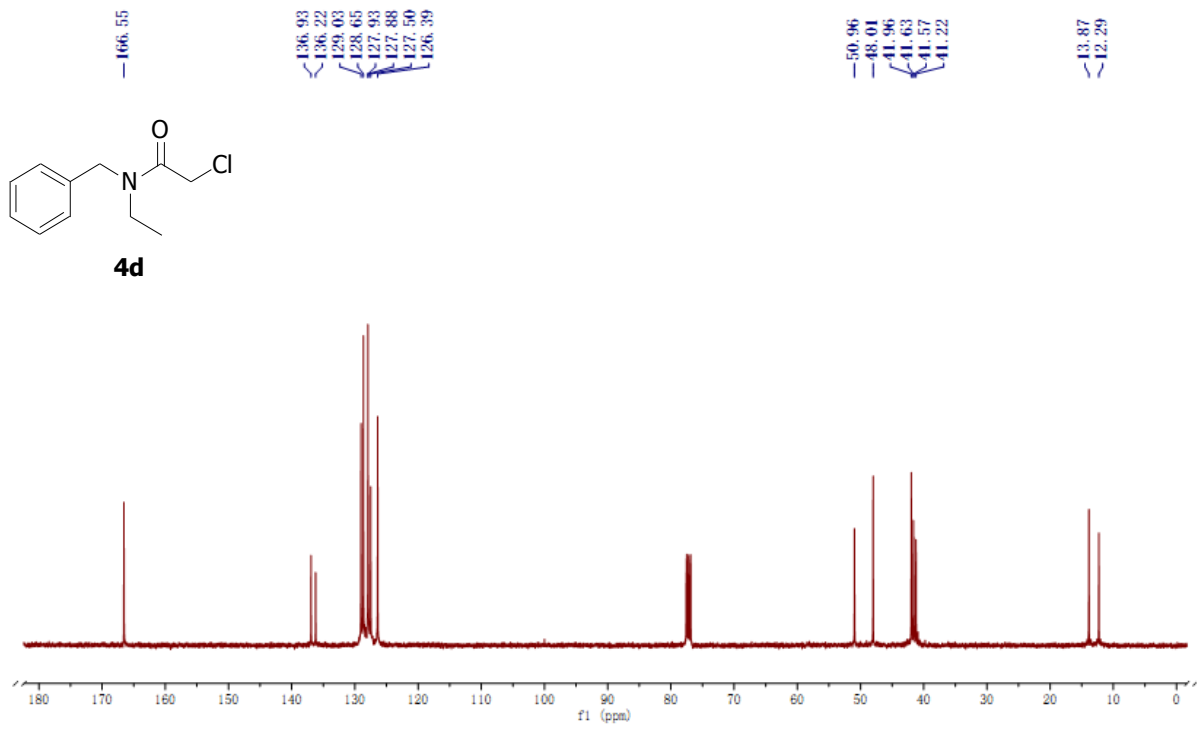
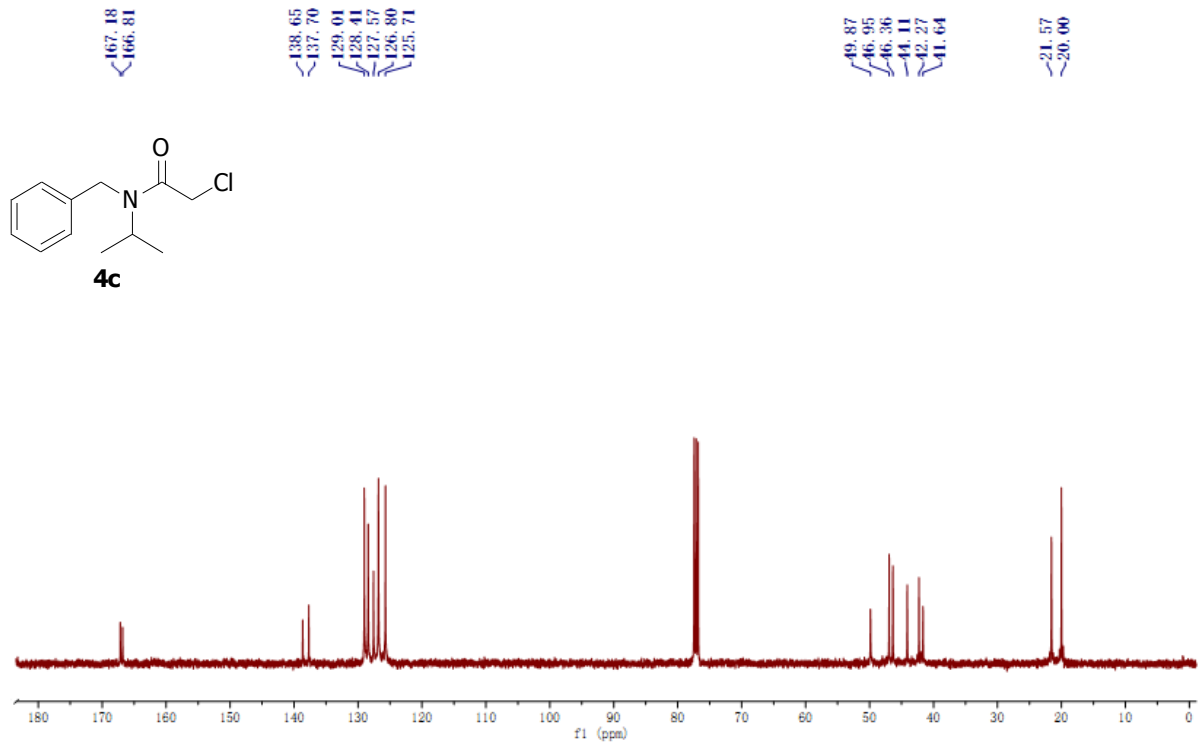
4.53  
 4.43  
 4.06

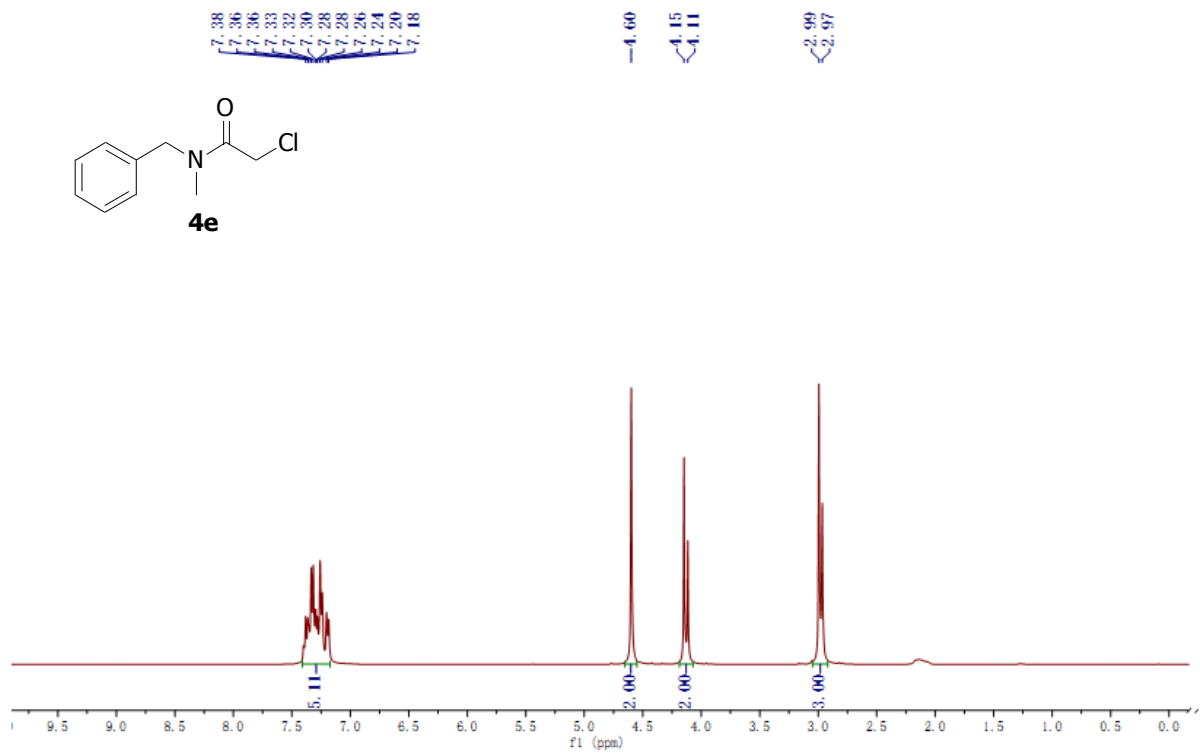
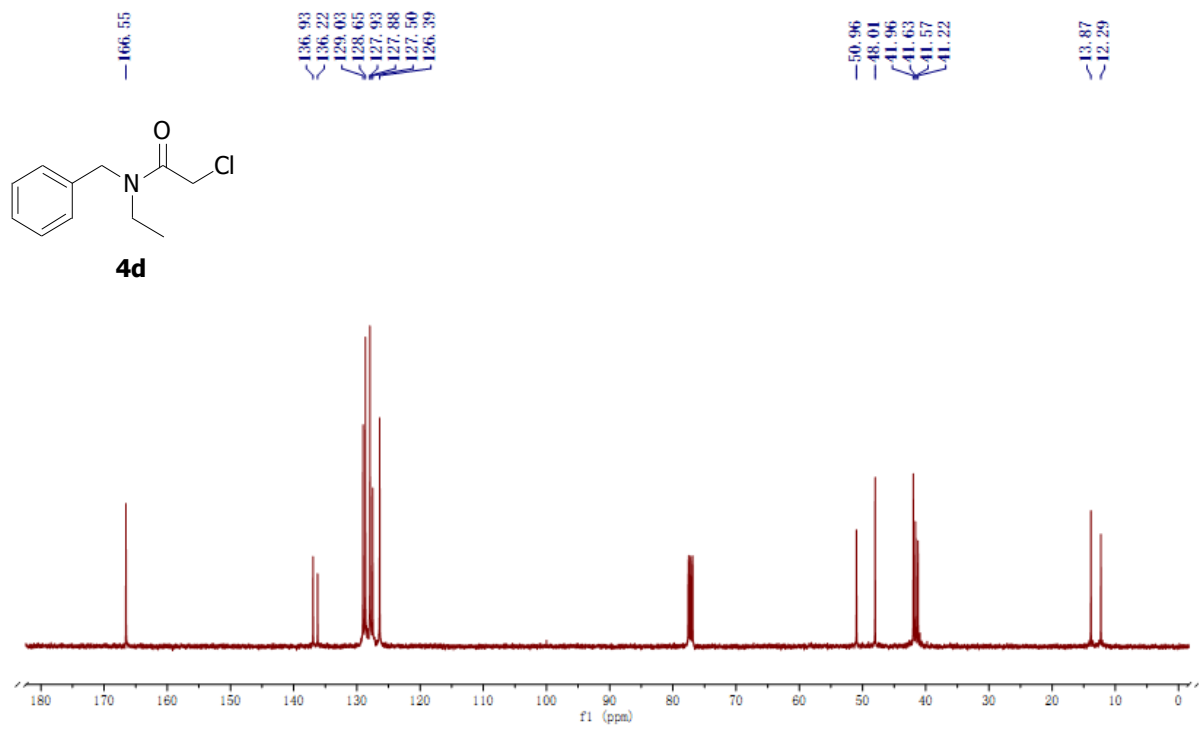


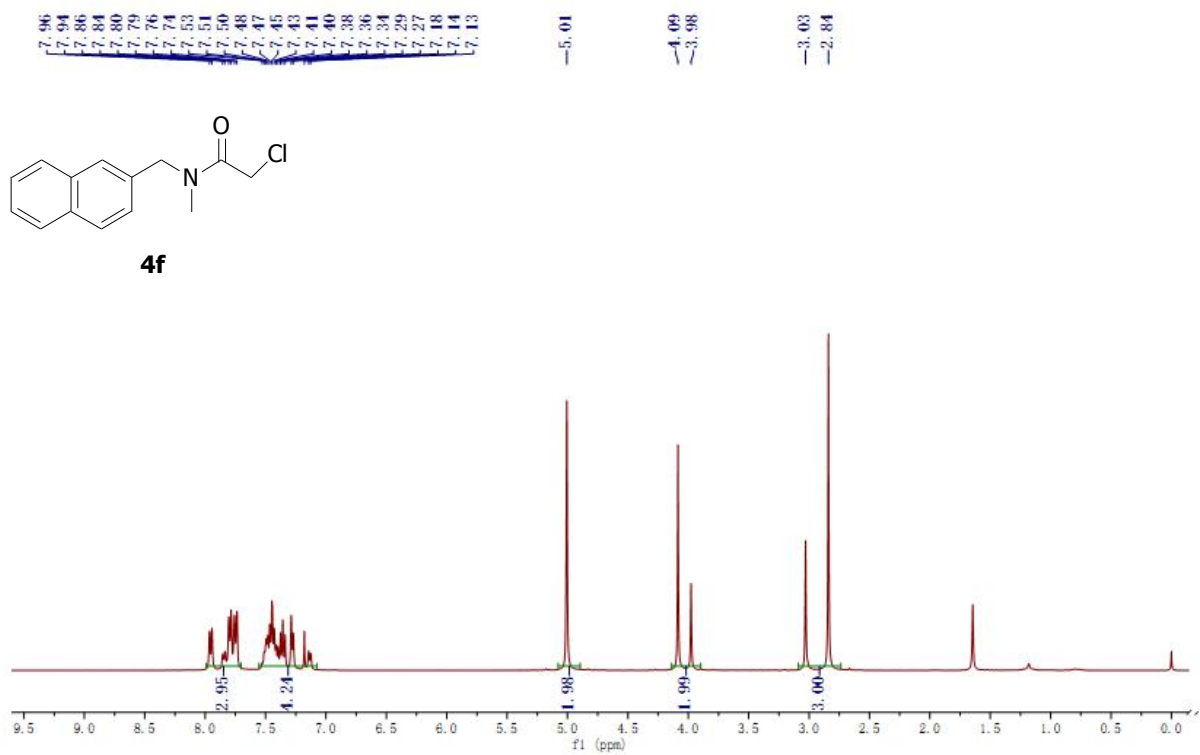
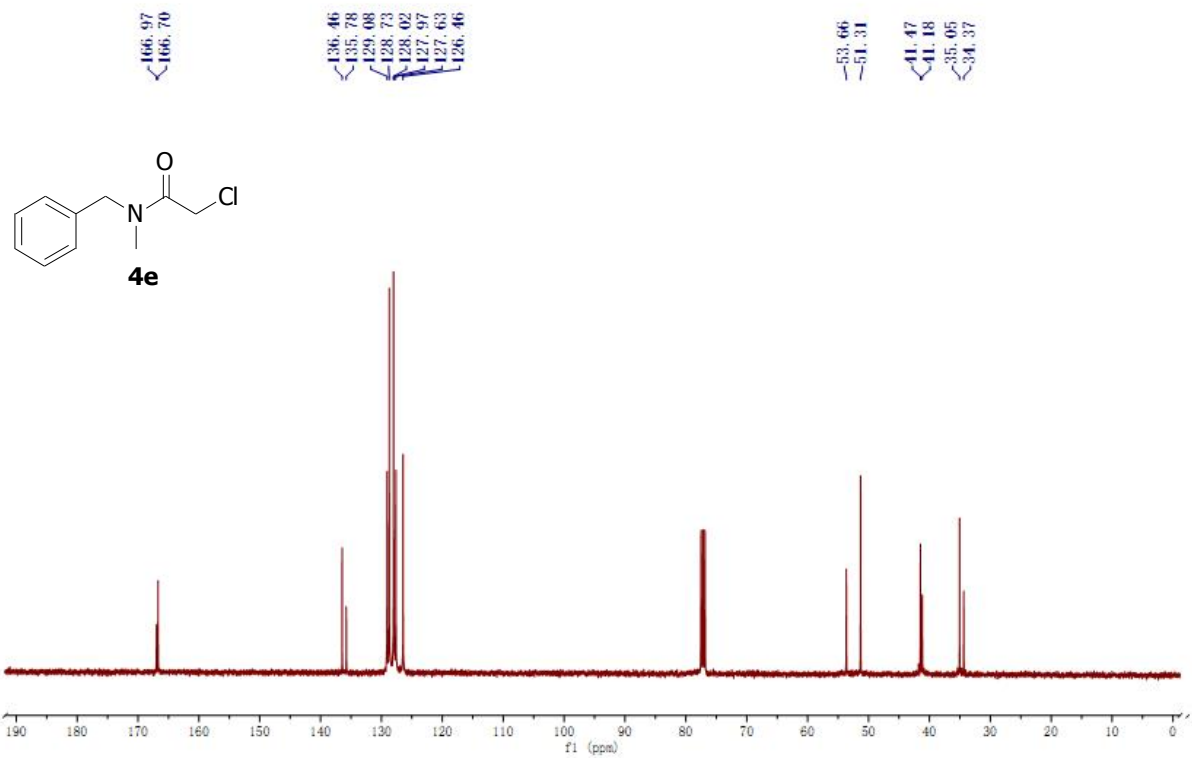


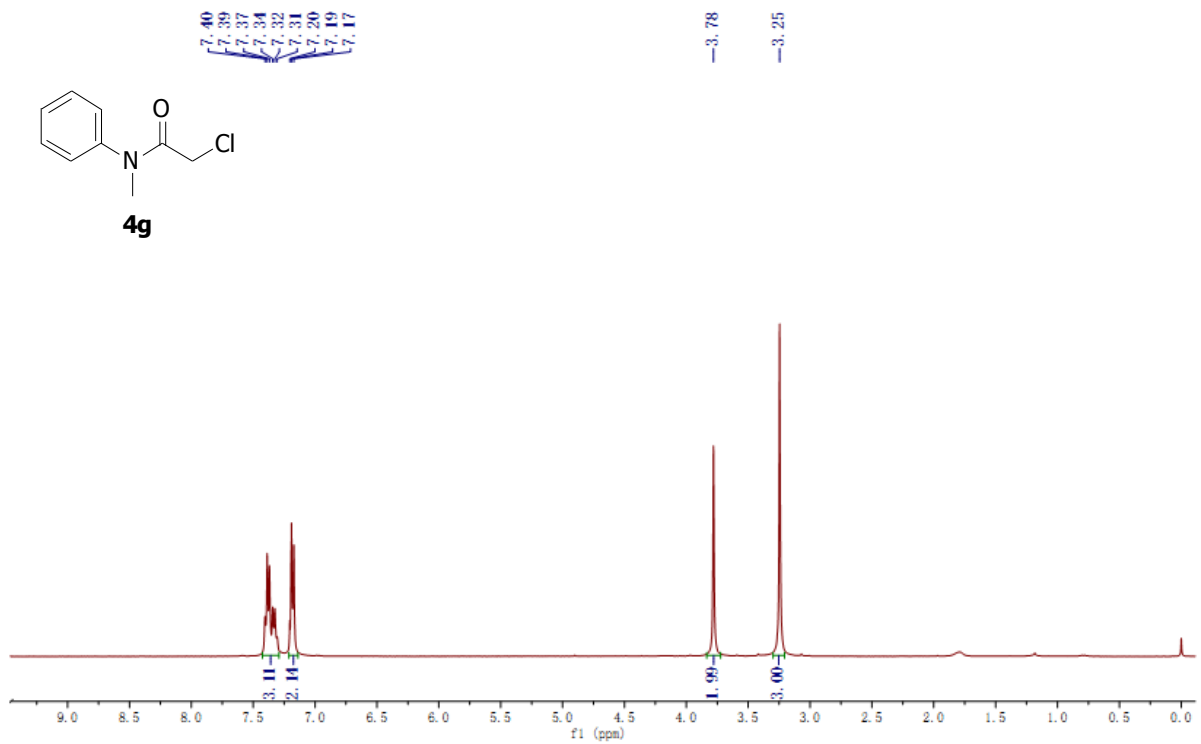
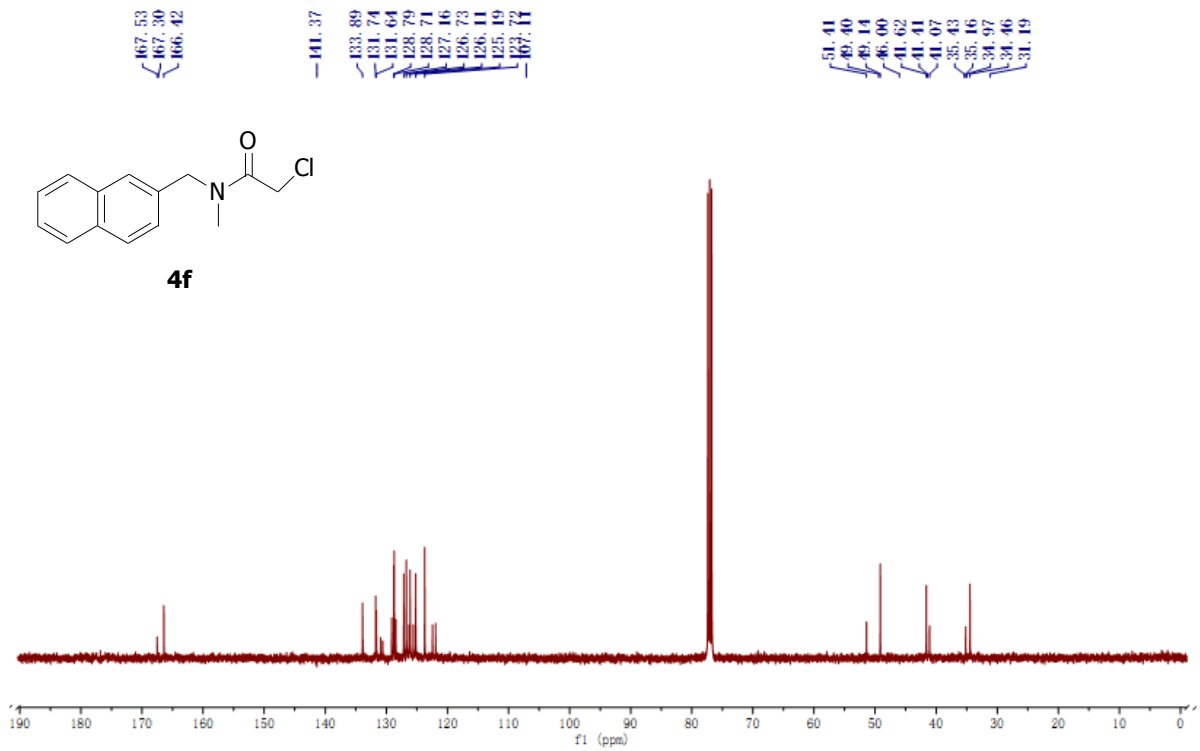


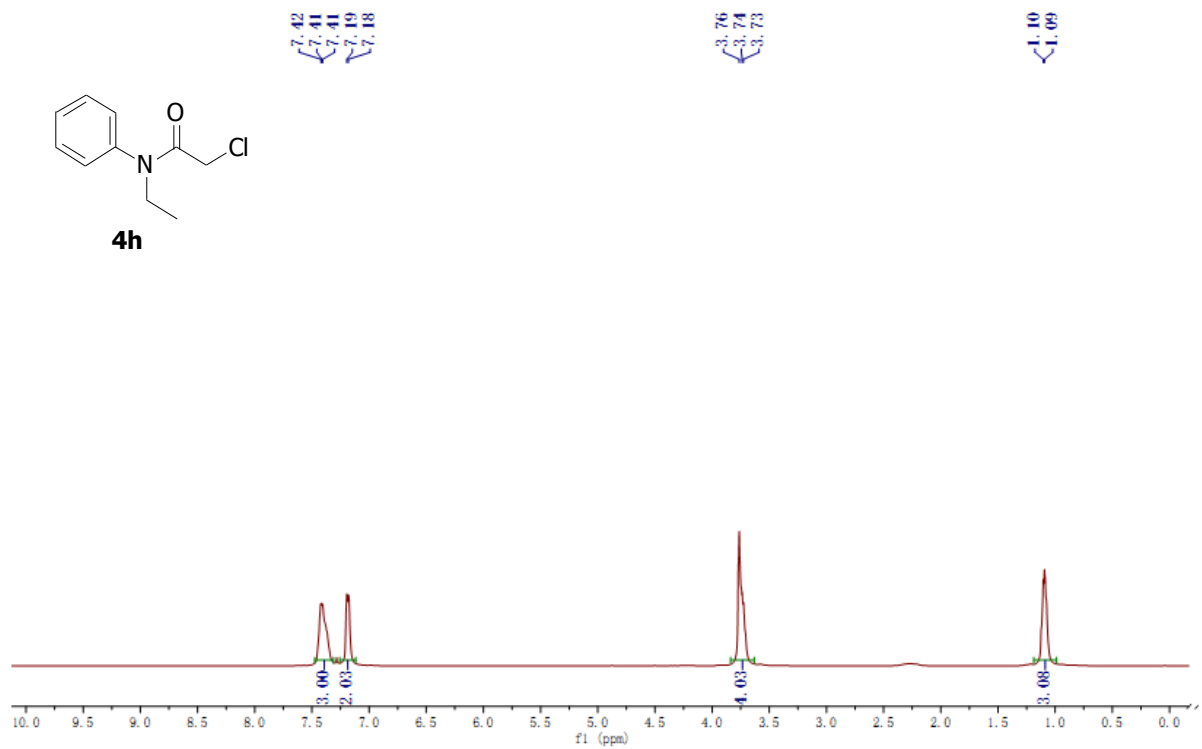
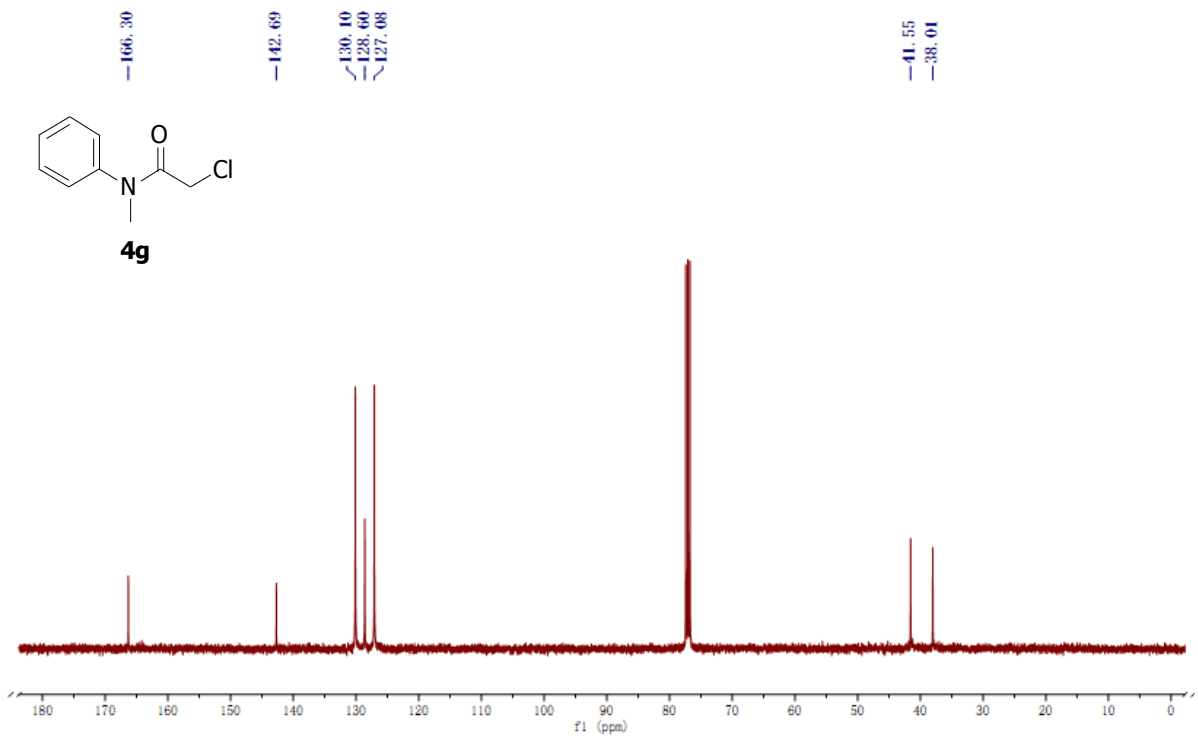


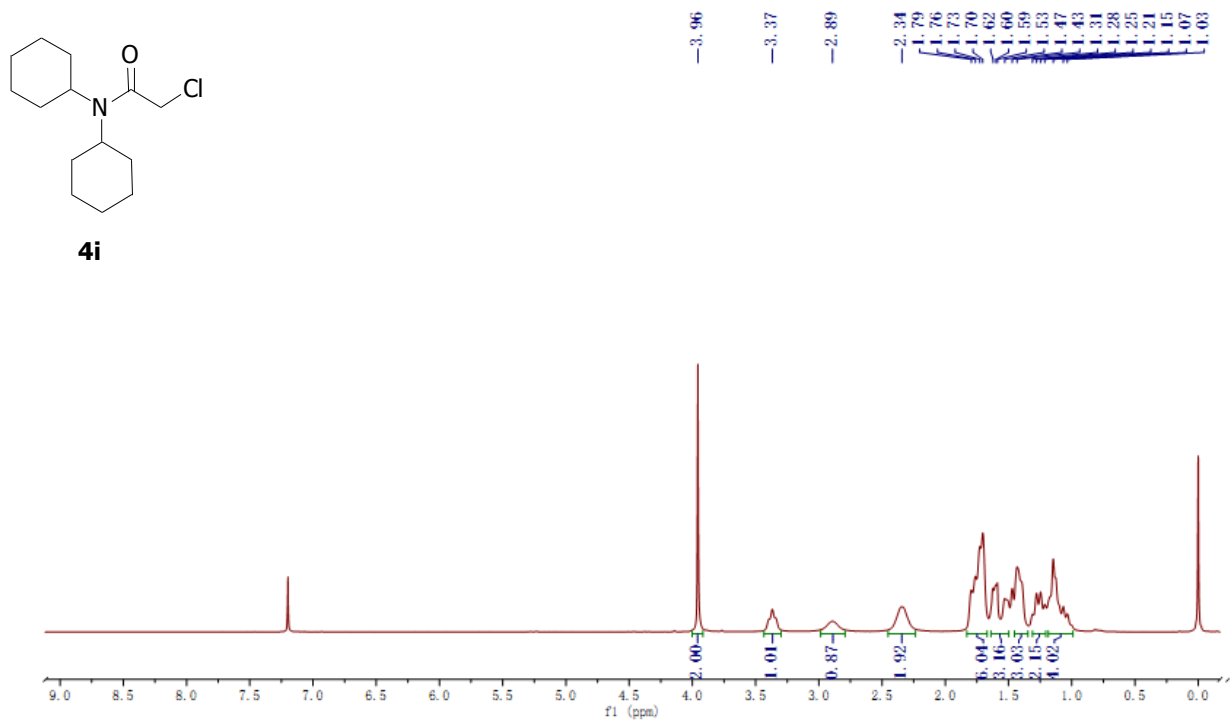
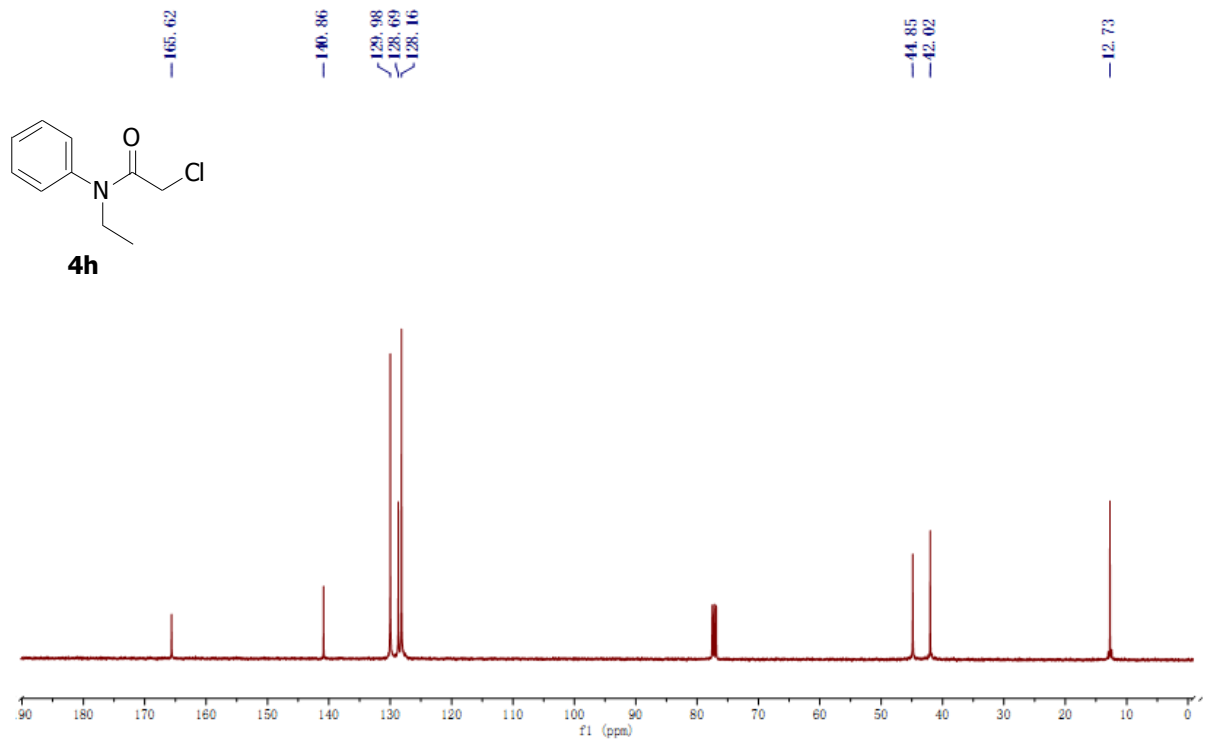




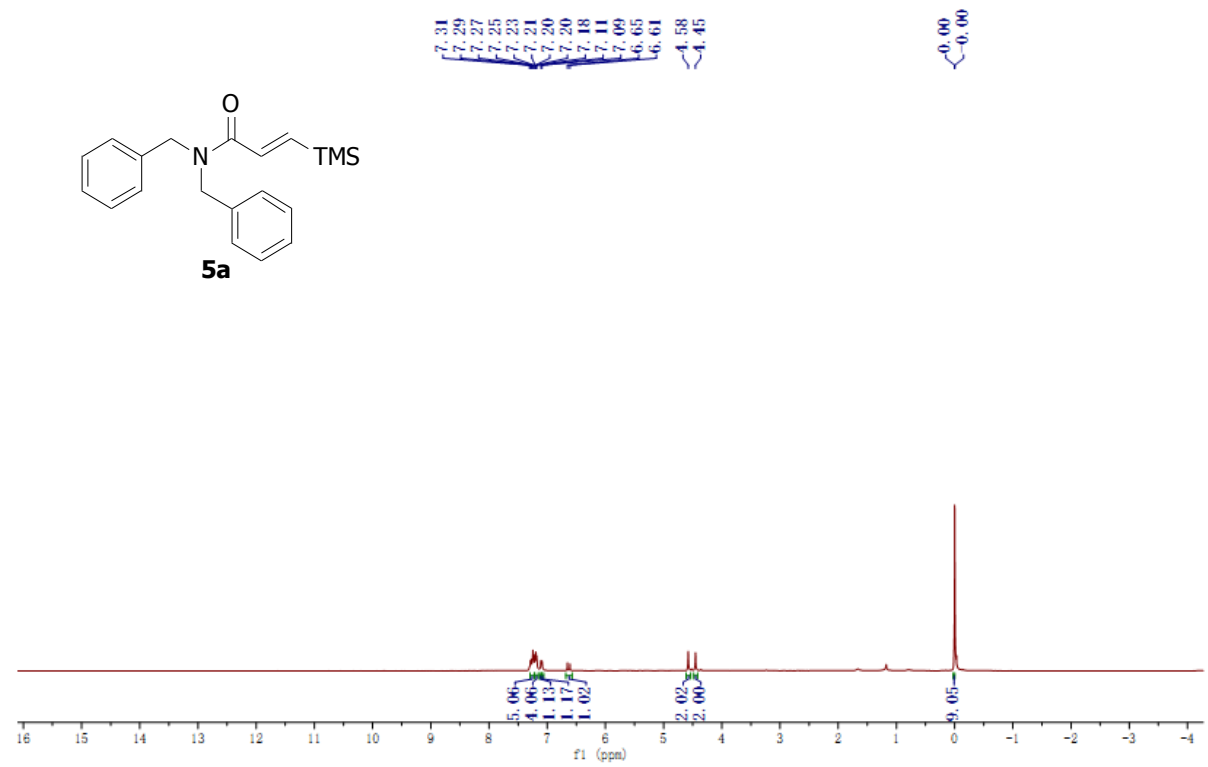
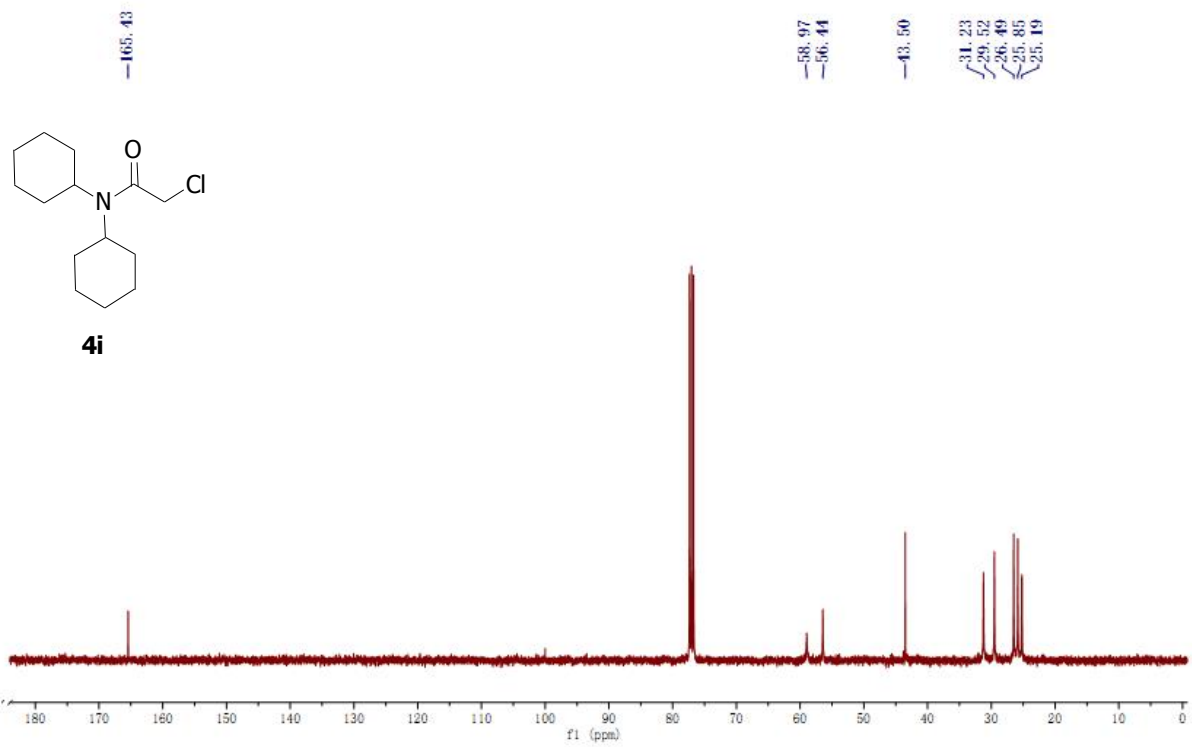


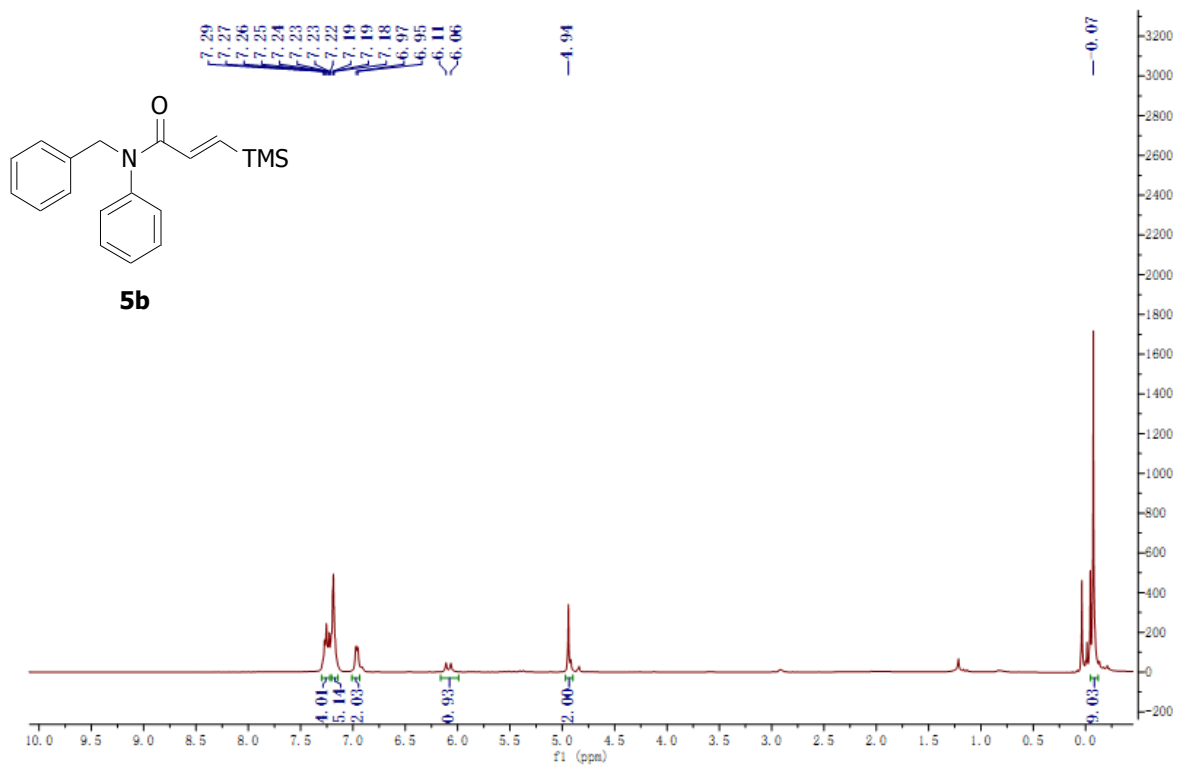
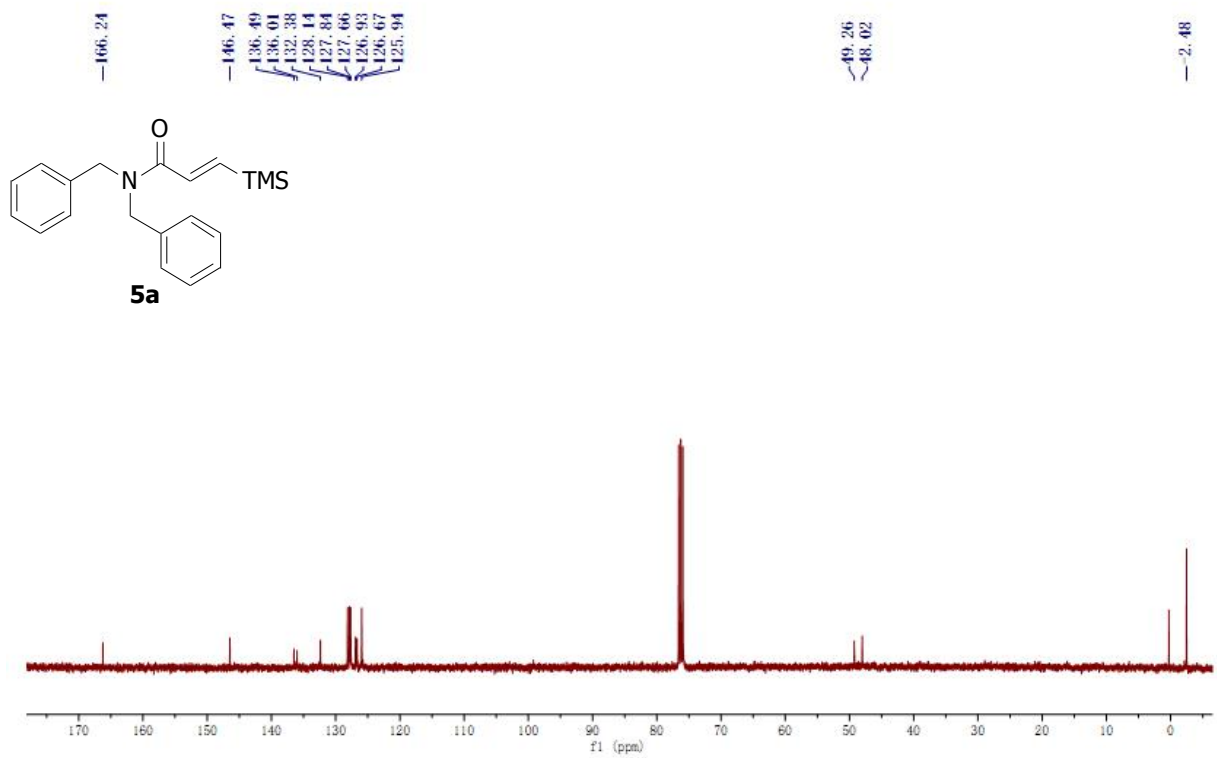


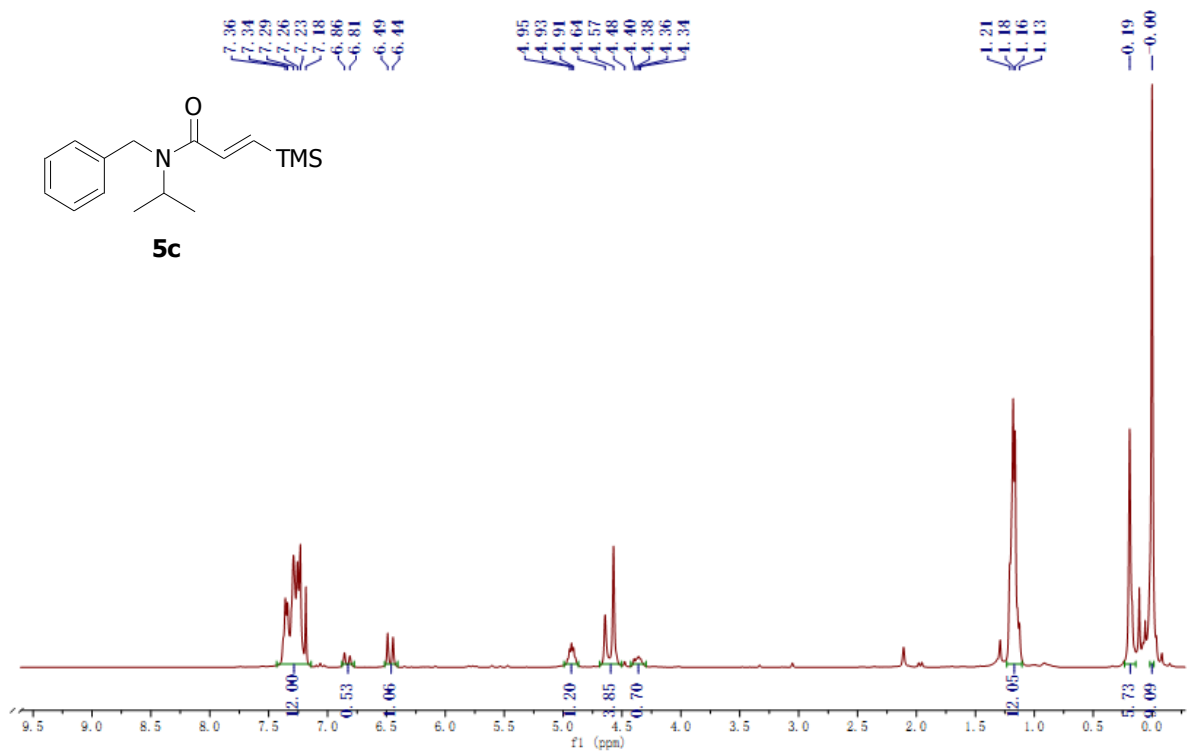
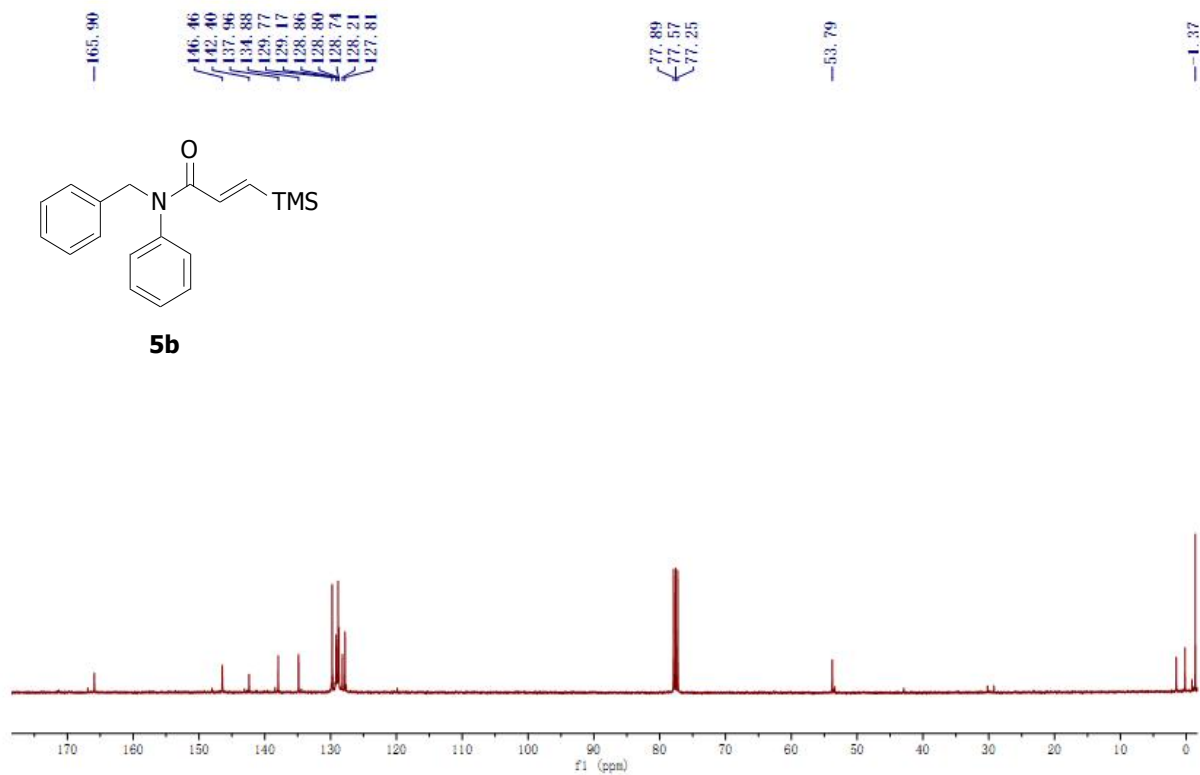


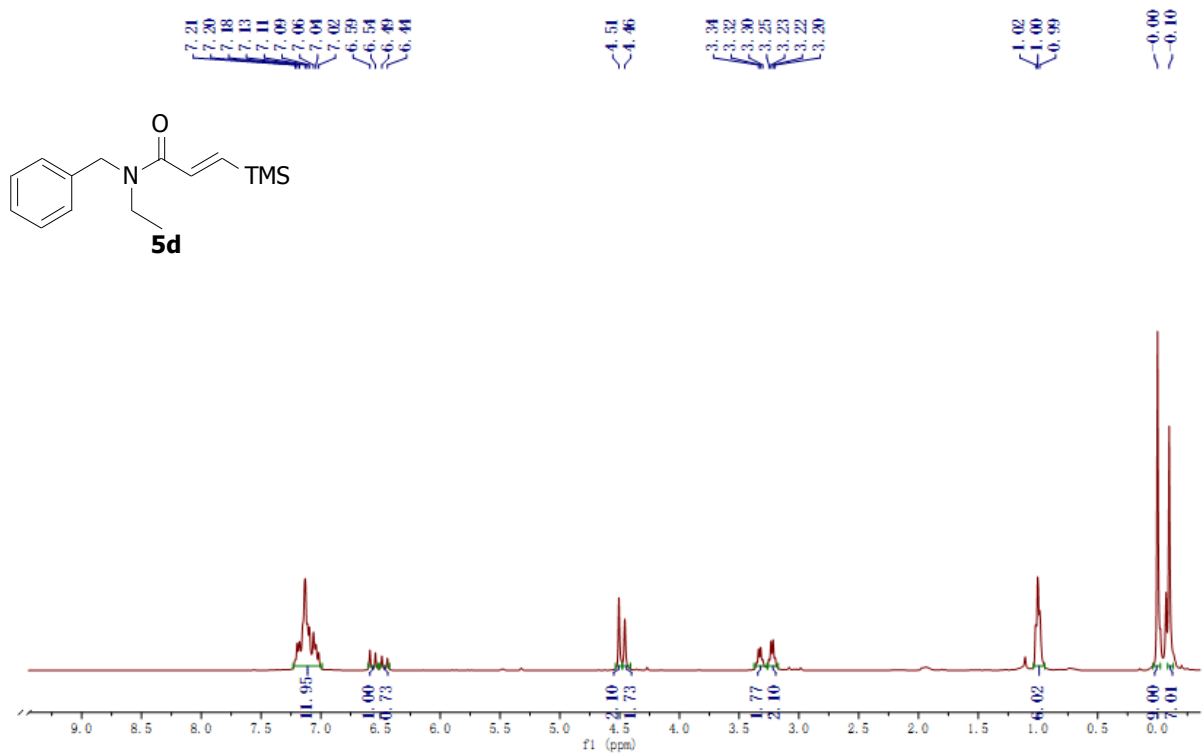
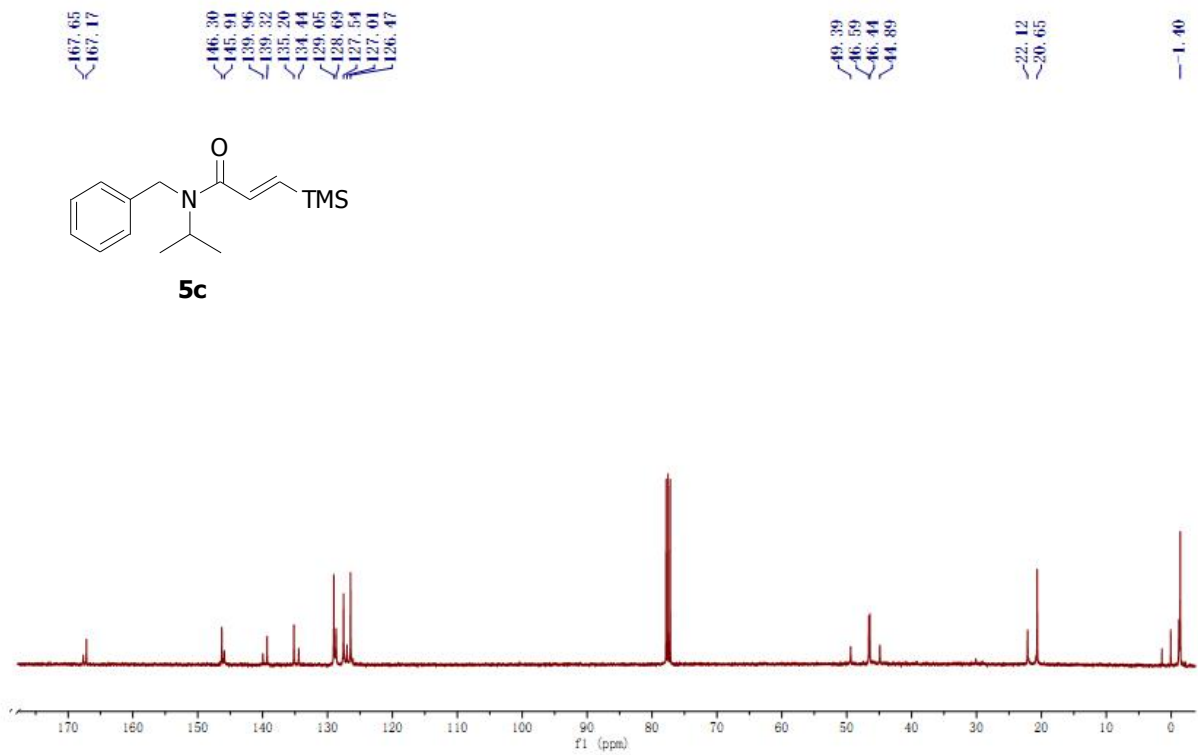


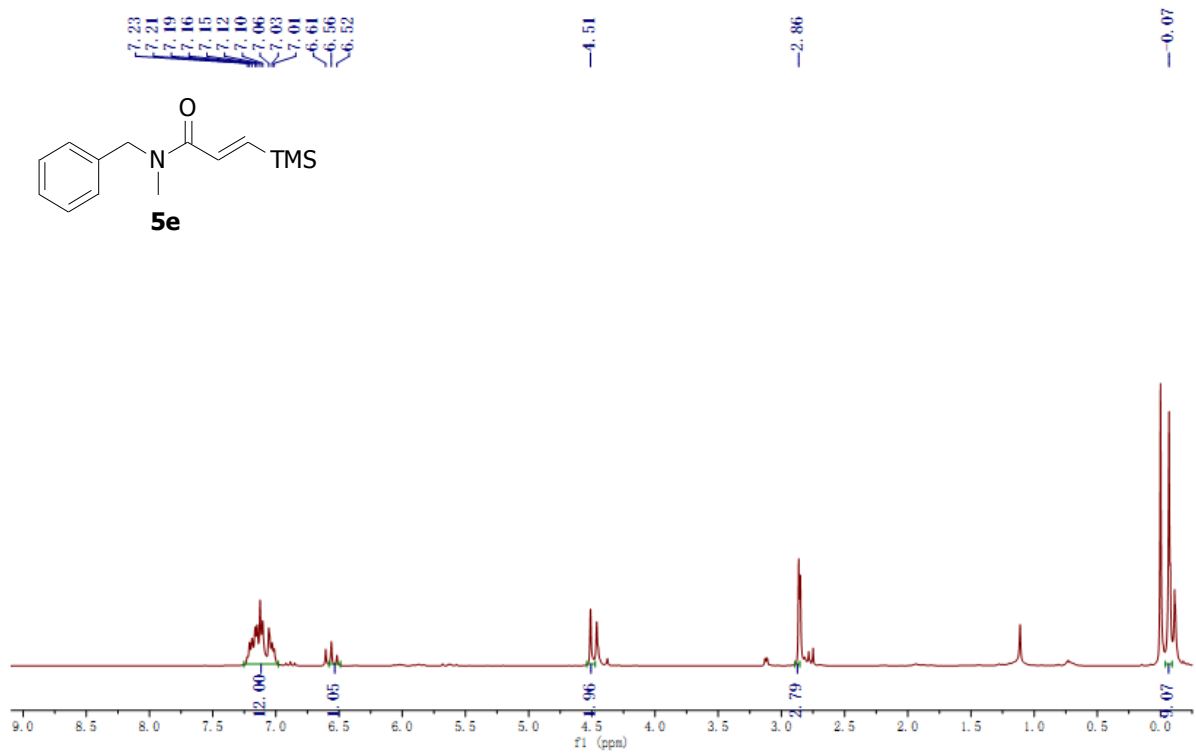
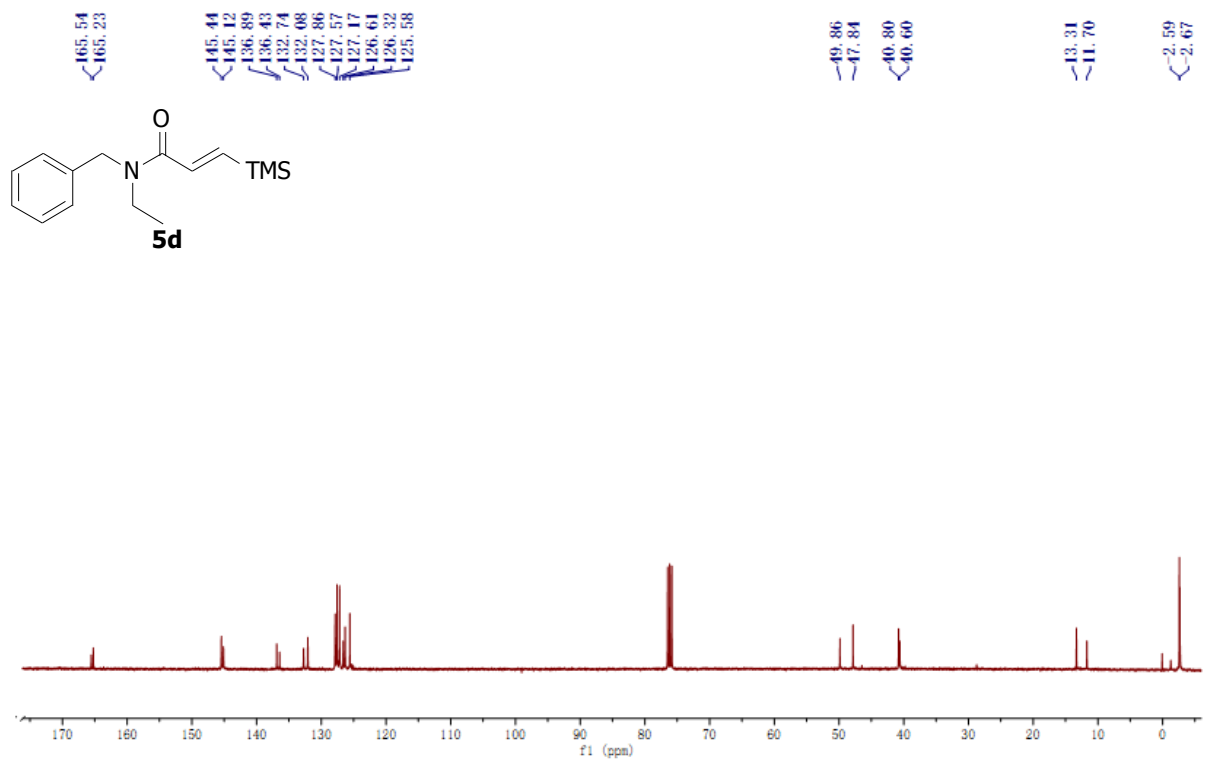


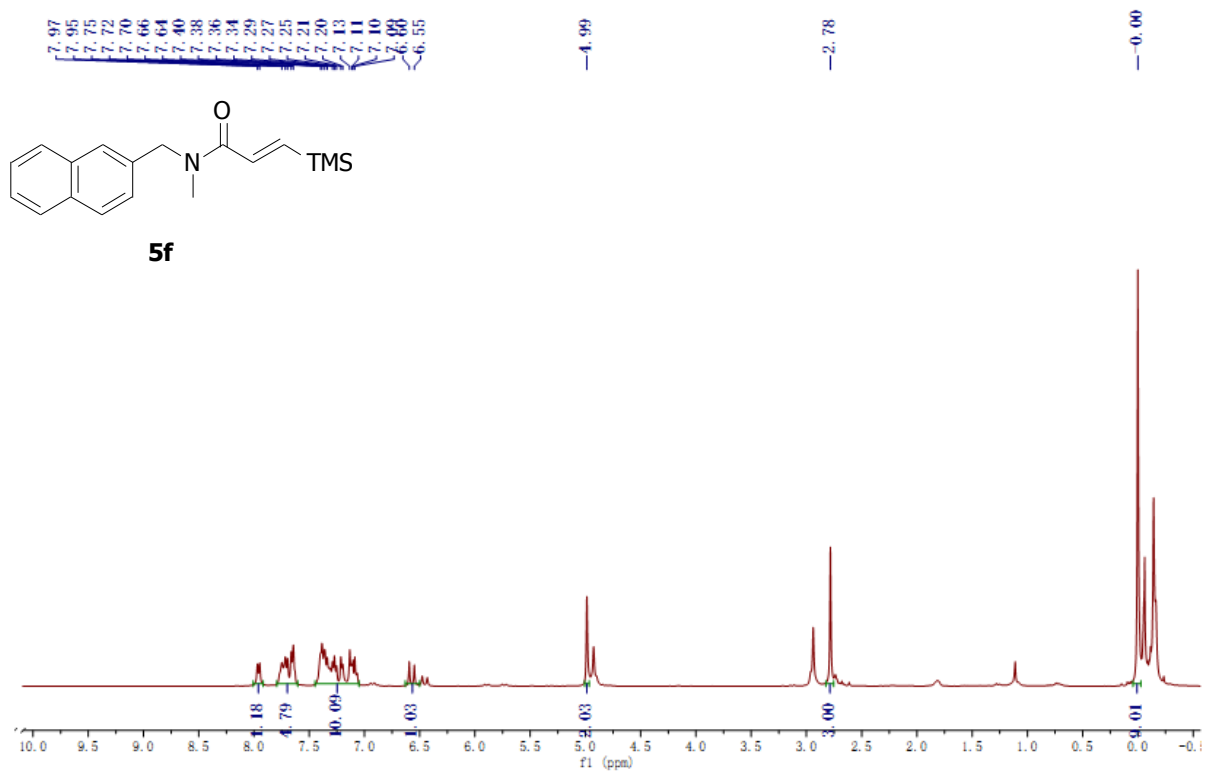
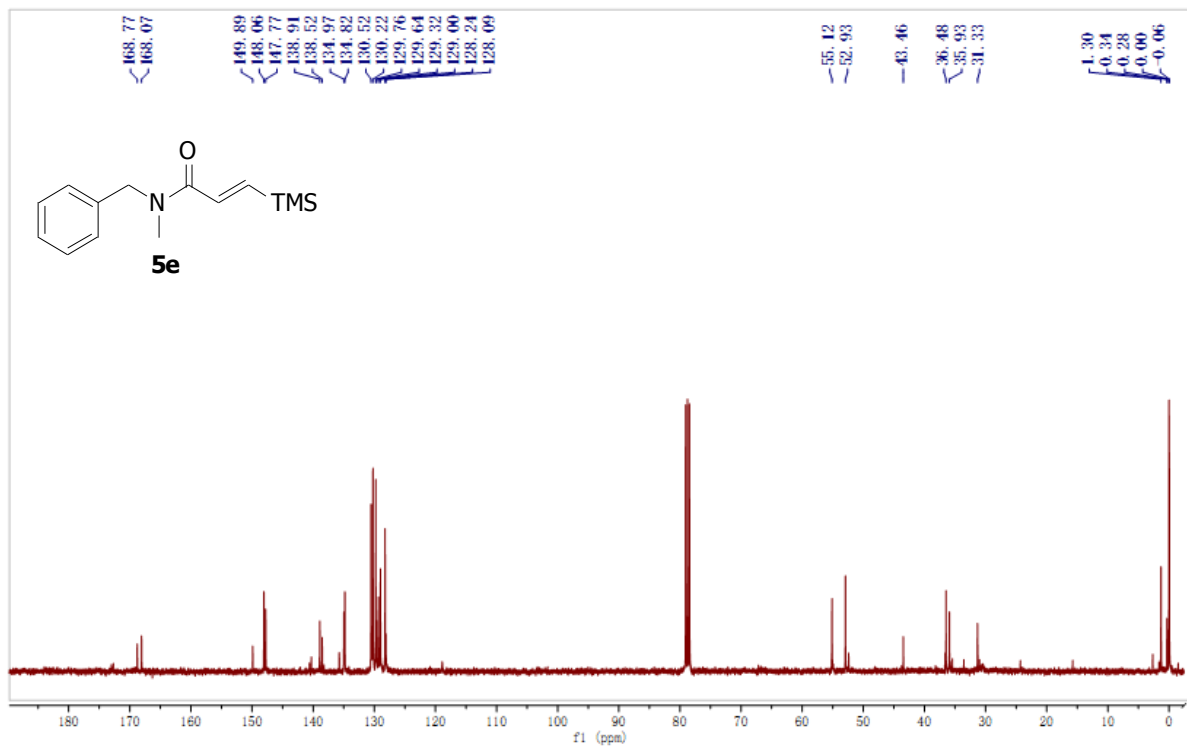


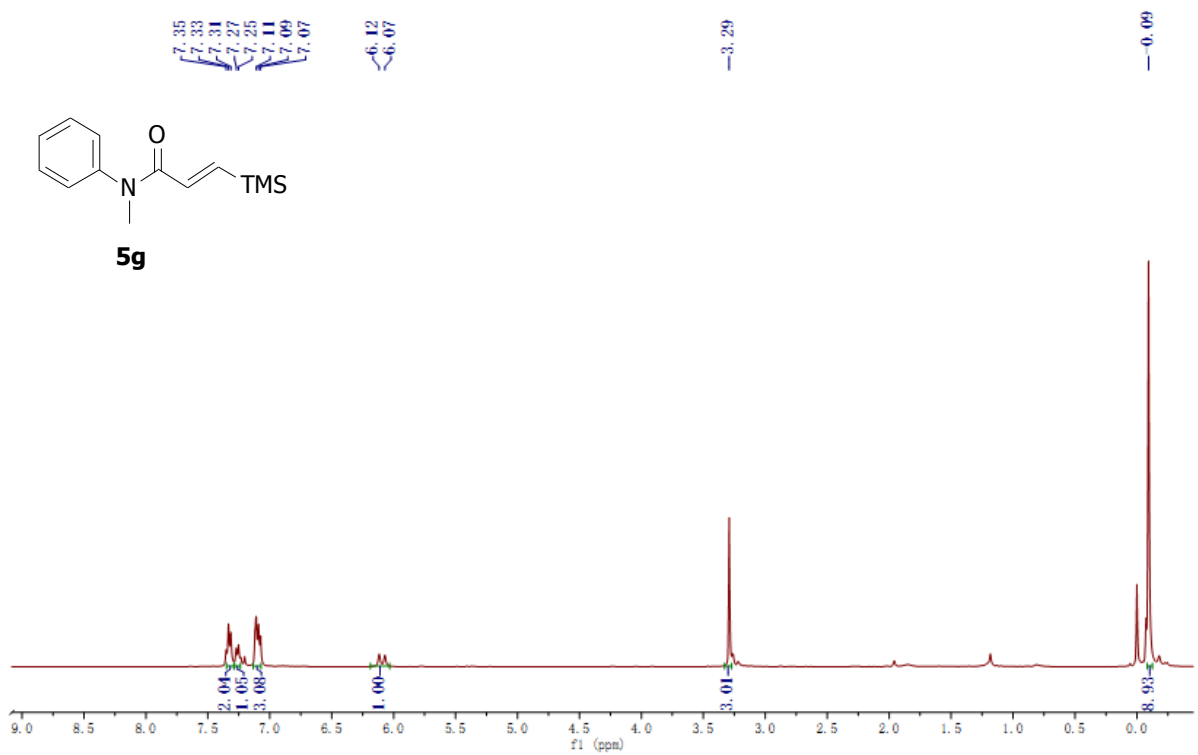
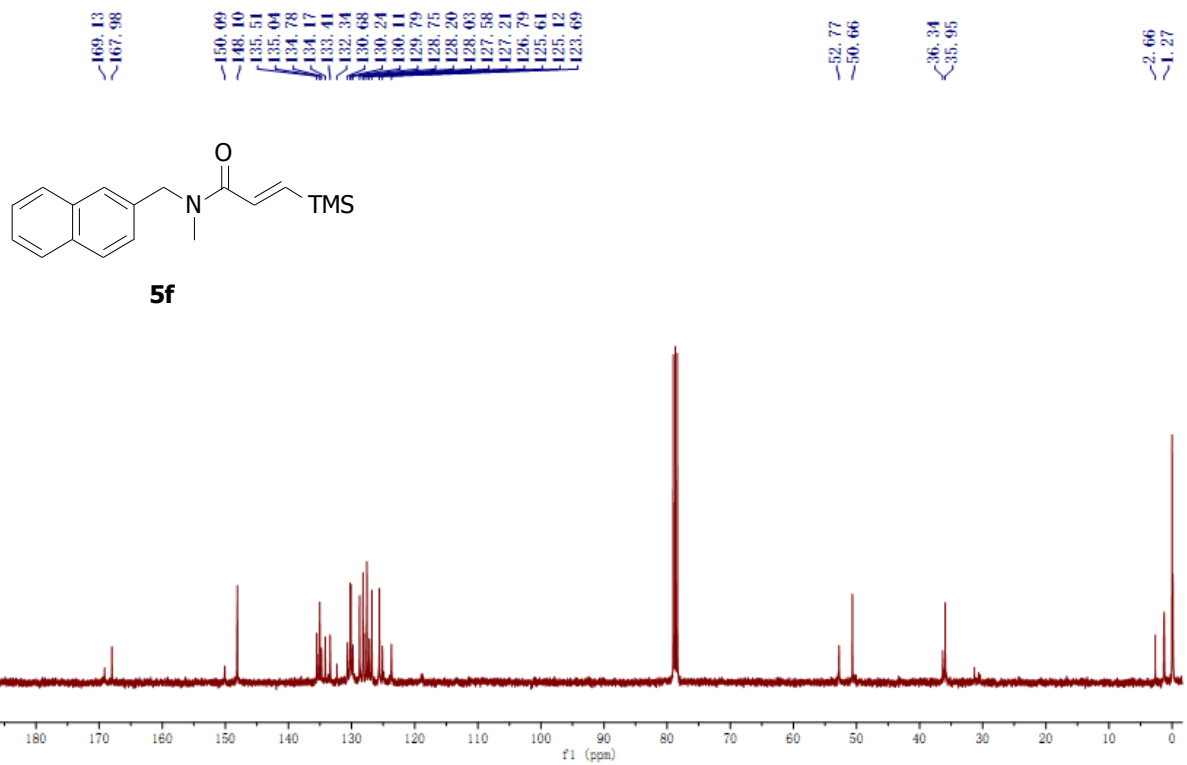


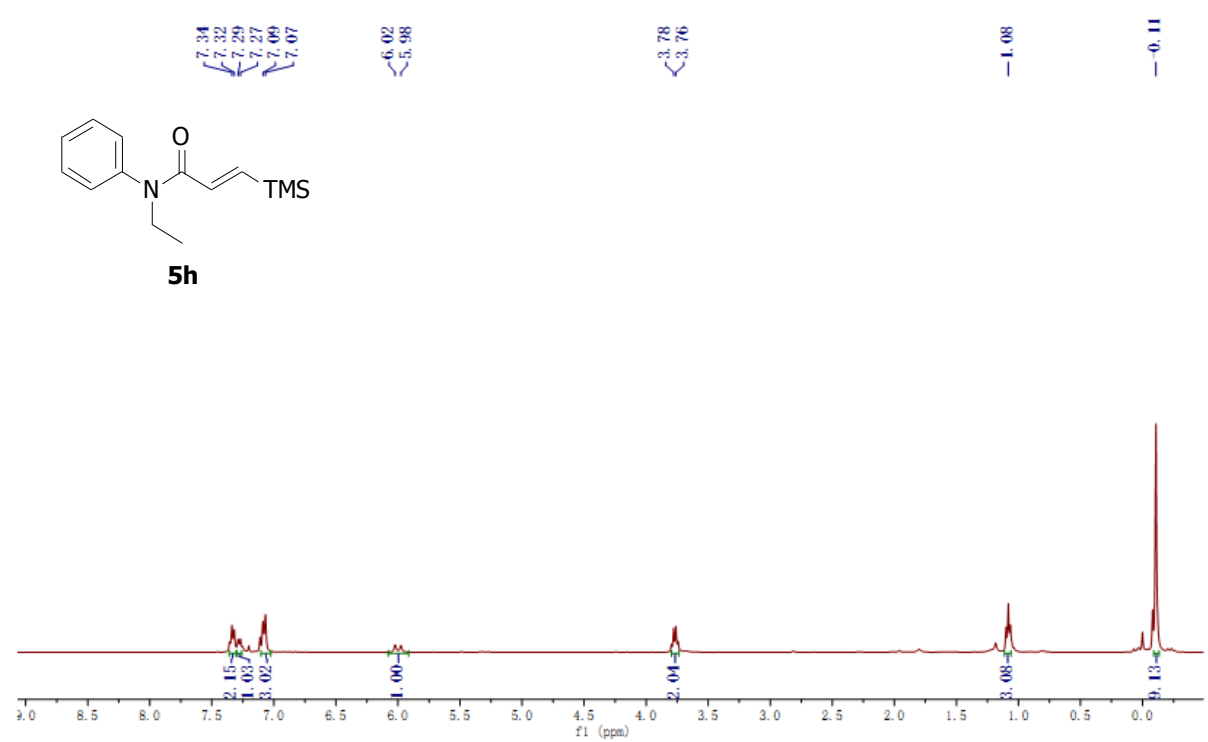
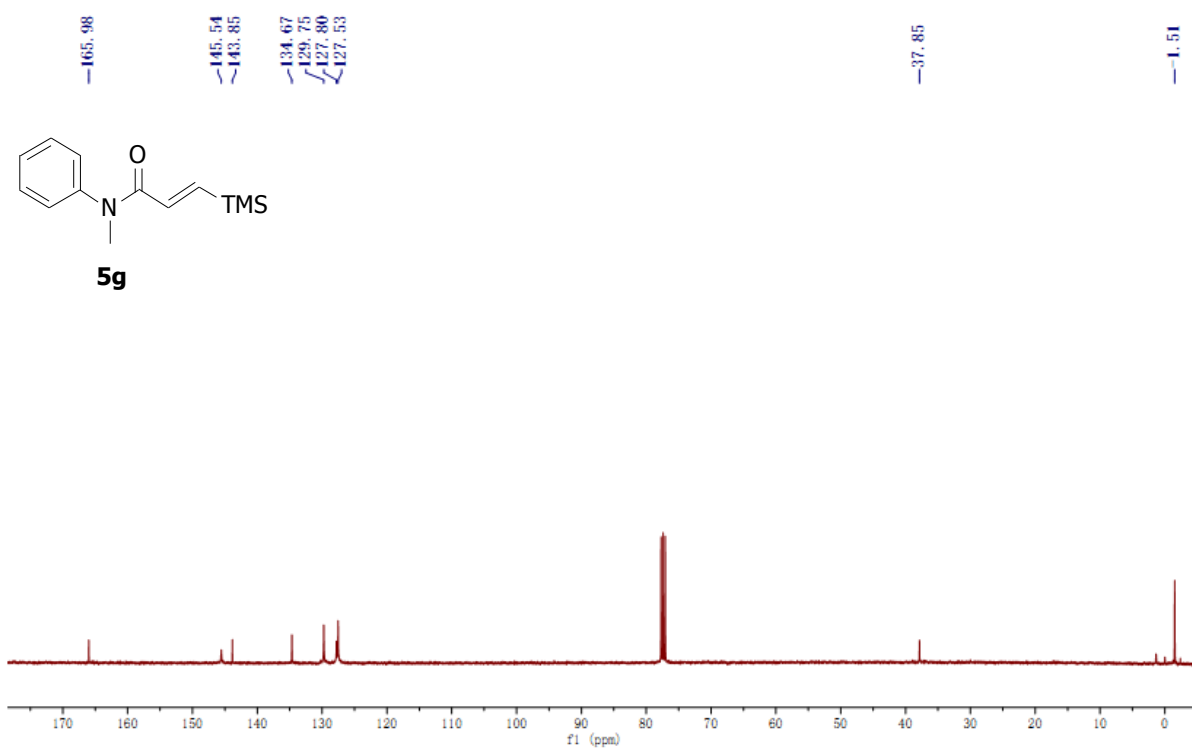




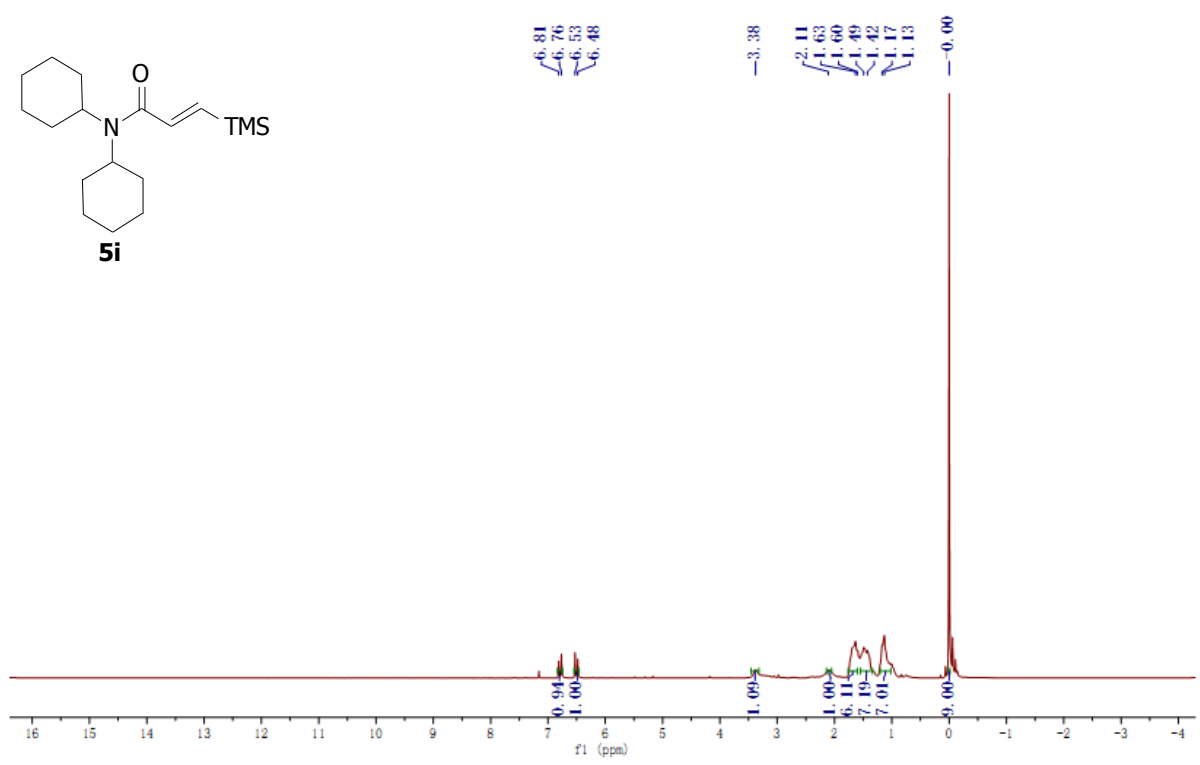
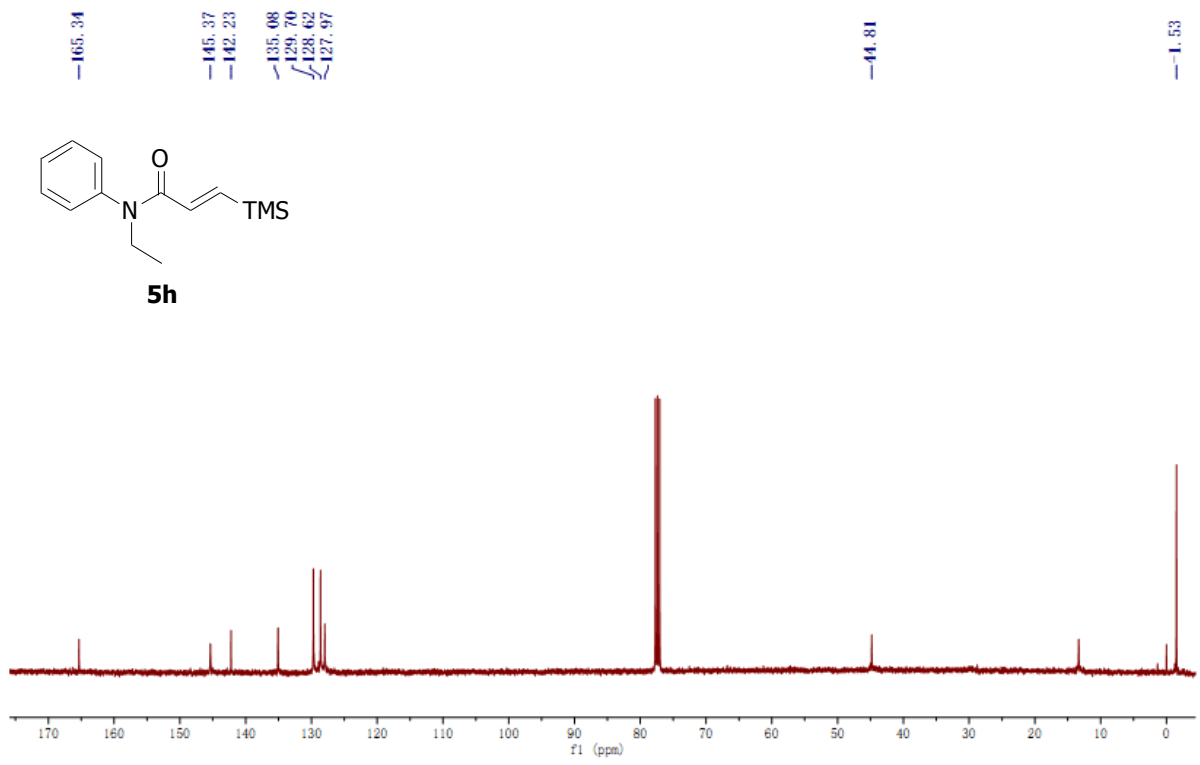


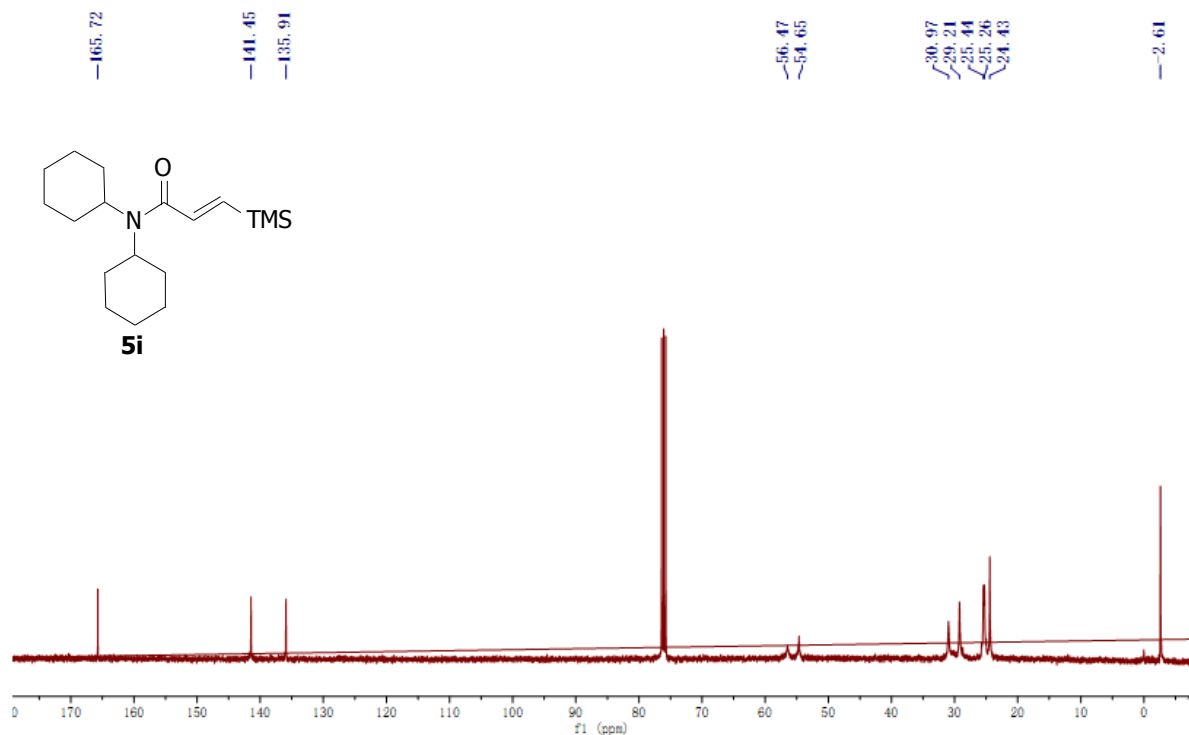












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