

*Supporting Information*

**Regio- and Stereoselective Hydrosilylation of Alkynes  
with Alkoxysilanes for  $\beta$ -(Z) Vinylsilanes Catalyzed  
by Dirhodium (II)/XantPhos Complex**

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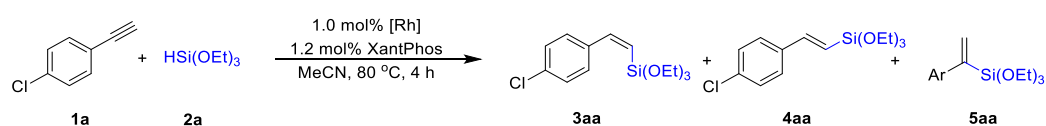
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## 1. General Information

Unless otherwise noted, all hydrosilylation reactions were carried out under an atmosphere of N<sub>2</sub>. Materials were purchased from commercial suppliers and used without further purification. <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F and <sup>31</sup>P NMR spectra were recorded on 400 MHz, 500 MHz, 600 MHz or 700 MHz spectrometers. The chemical shifts for <sup>1</sup>H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for <sup>13</sup>C NMR were recorded in ppm downfield using the central peak of deuteriochloroform (77.16 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. HRMS were obtained on an ESI-TOF mass spectrometer. Flash column chromatography was performed on silica gel.

## 2. Optimization of the Reaction Conditions

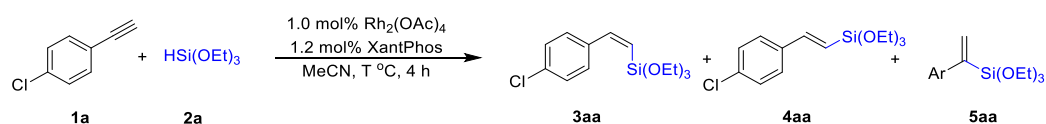
**Table S1.** The effects of solvent on the formation  $\beta$ -(*Z*) vinylsilanes <sup>a</sup>



entry	solvent	conv.%	yield%	
			<b>3aa+4aa</b>	<b>5aa</b>
1	1,4-dioxane	19	8 (25:75)	6
2	DCE	40	31 (44:56)	5
3	Toluene	69	54 (36:64)	10

<sup>a</sup> Rh<sub>2</sub>(OAc)<sub>4</sub> (2.2 mg, 1.0 mol%), XantPhos (3.5 mg, 1.2 mol%), **1a** (0.50 mmol, 68.3 mg, 1.0 equiv), **2a** (0.6 mmol, 98.5 mg, 1.2 equiv) in solvent (2 mL) at 80 °C for 4 h, and yields were determined by GC (1,2,4,5-tetramethylbenzene as an internal standard).

**Table S2.** The effects of temperature on the formation  $\beta$ -(*Z*) vinylsilanes <sup>a</sup>

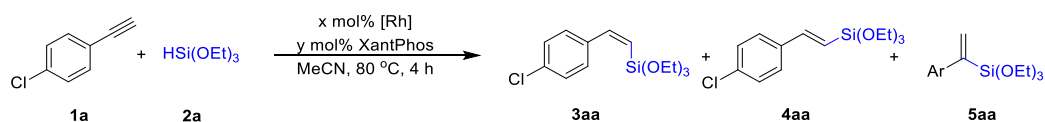


entry	Temperature/ °C	conv.%	yield%	
			<b>3aa+4aa</b>	<b>5aa</b>
1	80	85	80 (97:3)	trace

2	70	44	31 (97:3)	trace
3	90	99	91 (91:9)	trace

<sup>a</sup> Rh<sub>2</sub>(OAc)<sub>4</sub> (2.2 mg, 1.0 mol%), XantPhos (3.5 mg, 1.2 mol %), **1a** (0.50 mmol, 68.3 mg, 1.0 equiv), **2a** (0.6 mmol, 98.5 mg, 1.2 equiv) in MeCN (2 mL) at T °C for 4 h, and yields were determined by GC (1,2,4,5-tetramethylbenzene as an internal standard).

**Table S3.** The effects of catalyst loading on the formation β-(Z) vinylsilanes <sup>a</sup>



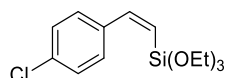
entry	x	y	conv.%	yield%	
				<b>3aa+4aa</b>	<b>5aa</b>
1	1.0	1.2	85	80 (97:3)	trace
2	1.0	2.4	84	84 (92:8)	trace
3	2.0	2.4	99	93 (97:3)	trace
4	0.5	0.6	34	32 (93:7)	trace

<sup>a</sup> **1a** (0.50 mmol, 68.3 mg, 1.0 equiv), **2a** (0.6 mmol, 98.5 mg, 1.2 equiv), 80 °C, in MeCN (2 mL); and yields were determined by GC (1,2,4,5-tetramethylbenzene as an internal standard).

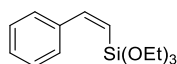
### 3. General Procedures of Hydrosilylation for β-(Z) Vinylsilanes and the

#### Analytical Data for Products

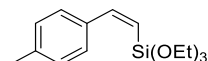
In an oven-dried 25 mL sealed tube containing a stirring bar, Rh<sub>2</sub>(OAc)<sub>4</sub> (4.4 mg, 1.0 mol %), XantPhos (6.9 mg, 1.2 mol %), alkynes (1.2 mmol) and R<sub>3</sub>SiH (1.0 mmol) were added in MeCN (2.0 mL). Then the above mixture was reacted for 6 h at 80 °C. After the reaction, the resulting red brown mixture was cooled to room temperature and the solvent was concentrated. Then the crude production was purified by column chromatography to afford the corresponding products **3**.



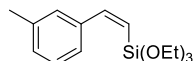
**(Z)-(4-Chlorostyryl)triethoxysilane (3aa).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate: Et<sub>3</sub>N = 100:2:1) obtained **3aa** as light yellow liquid (240.0 mg, 80% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.34 (d, *J* = 15.6 Hz, 1H), 7.32 – 7.28 (m, 2H), 5.61 (d, *J* = 15.6 Hz, 1H), 3.76 (q, *J* = 7.0 Hz, 6H), 1.16 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.7, 137.1, 134.2, 129.9, 128.4, 121.3, 58.6, 18.2. HRMS-ESI (*m/z*): Calcd for C<sub>14</sub>H<sub>21</sub><sup>35</sup>ClO<sub>3</sub>Si Na [M + Na]<sup>+</sup>: 323.0835, Found: 323.0842.



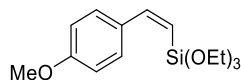
**(Z)-Triethoxy(styryl)silane (3ba).**<sup>1</sup> Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate: Et<sub>3</sub>N = 100:1:1) obtained **3ba** as light yellow liquid (204.8 mg, 77% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H), 7.43 (d, *J* = 15.6 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 5.59 (d, *J* = 15.6 Hz, 1H), 3.76 (q, *J* = 7.0 Hz, 6H), 1.15 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.3, 138.6, 128.5, 128.4, 128.2, 120.2, 58.5, 18.2.



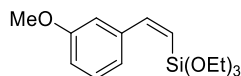
**(Z)-Triethoxy(4-methylstyryl)silane (3ca).**<sup>2</sup> Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3ca** as light yellow liquid (218.4 mg, 78% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 15.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.52 (d, *J* = 15.2 Hz, 1H), 3.77 (q, *J* = 7.2 Hz, 6H), 2.35 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.3, 138.3, 135.8, 128.9, 128.5, 118.8, 58.5, 21.4, 18.2.



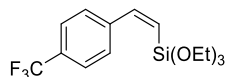
**(Z)-Triethoxy(3-methylstyryl)silane (3da).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3da** as light yellow liquid (243.8 mg, 87% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.35 (m, 3H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 5.56 (d, *J* = 15.6 Hz, 1H), 3.76 (q, *J* = 7.0 Hz, 6H), 2.36 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.5, 138.6, 137.7, 129.2, 129.1, 128.1, 125.6, 119.9, 58.5, 21.5, 18.2. HRMS-ESI (m/z): Calcd for C<sub>15</sub>H<sub>24</sub>O<sub>3</sub>Si Na [M + Na]<sup>+</sup>: 303.1387, Found: 303.1388.



**(Z)-Triethoxy(4-methoxystyryl)silane (3ea).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3ea** as light yellow liquid (157.1 mg, 53% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.53 (m, 2H), 7.35 (d, *J* = 15.6 Hz, 1H), 6.89 – 6.84 (m, 2H), 5.44 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 3H), 3.77 (q, *J* = 7.0 Hz, 6H), 1.16 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C NMR {<sup>1</sup>H} (100 MHz, CDCl<sub>3</sub>) δ 160.3, 148.8, 130.7, 128.3, 114.8, 114.0, 58.7, 55.4, 18.4. HRMS-ESI (m/z): Calcd for C<sub>15</sub>H<sub>24</sub>O<sub>4</sub>Si Na [M + Na]<sup>+</sup>: 319.1336, Found: 319.1342.

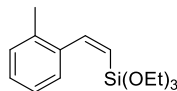


**(Z)-Triethoxy(3-methoxystyryl)silane (3fa).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3fa** as light yellow liquid (234.2 mg, 79% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 15.6 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.85 (dd, *J* = 8.0, 2.8 Hz, 1H), 5.59 (d, *J* = 15.6 Hz, 1H), 3.84 (s, 3H), 3.77 (q, *J* = 7.0 Hz, 6H), 1.15 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 159.6, 151.2, 140.0, 129.2, 121.4, 120.4, 115.0, 112.8, 58.5, 55.5, 18.2. HRMS-ESI (m/z): Calcd for C<sub>15</sub>H<sub>24</sub>O<sub>4</sub>Si Na [M + Na]<sup>+</sup>: 319.1336, Found: 319.1340.

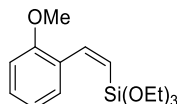


**(Z)-Triethoxy(4-(trifluoromethyl)styryl)silane (3ga).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3ga** as light yellow liquid

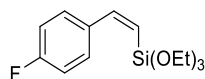
(200.6 mg, 60% yield).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.67 (d,  $J = 8.0$  Hz, 2H), 7.59 (d,  $J = 8.0$  Hz, 2H), 7.42 (d,  $J = 15.6$  Hz, 1H), 5.74 (d,  $J = 15.6$  Hz, 1H), 3.75 (q,  $J = 7.0$  Hz, 6H), 1.14 (t,  $J = 7.0$  Hz, 9H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 142.1, 130.0 (q,  $^2J_{\text{C-F}} = 32.1$  Hz), 128.8, 125.1 (q,  $^3J_{\text{C-F}} = 3.9$  Hz), 124.3 (q,  $^1J_{\text{C-F}} = 272.0$  Hz), 123.7, 58.6, 18.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.6. HRMS-ESI (*m/z*): Calcd for  $\text{C}_{15}\text{H}_{21}\text{F}_3\text{O}_3\text{Si Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 357.1104, Found: 357.1104.



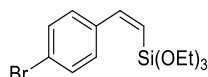
**(Z)-Triethoxy(2-methylstyryl)silane (3ha).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate :  $\text{Et}_3\text{N} = 100:2:1$ ) obtained **3ha** as light yellow liquid (235.5 mg, 84% yield).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.63 – 7.50 (m, 2H), 7.22 – 7.10 (m, 3H), 5.66 (d,  $J = 15.2$  Hz, 1H), 3.67 (q,  $J = 7.0$  Hz, 6H), 2.30 (s, 3H), 1.10 (t,  $J = 7.0$  Hz, 9H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.3, 138.6, 135.9, 129.6, 128.5, 128.4, 125.9, 121.4, 58.5, 20.0, 18.2. HRMS-ESI (*m/z*): Calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_3\text{Si Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 303.1387, Found: 303.1384.



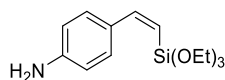
**(Z)-Triethoxy(2-methoxystyryl)silane (3ia).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate :  $\text{Et}_3\text{N} = 100:2:1$ ) obtained **3ia** as light yellow liquid (82% yield).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.73 – 7.60 (m, 2H), 7.31 – 7.23 (m, 1H), 6.94 (t,  $J = 7.5$  Hz, 1H), 6.84 (d,  $J = 8.4$  Hz, 1H), 5.60 (d,  $J = 15.6$  Hz, 1H), 3.83 (s, 3H), 3.72 (q,  $J = 7.0$  Hz, 6H), 1.12 (t,  $J = 7.0$  Hz, 9H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.3, 146.7, 129.7, 129.4, 127.9, 120.3, 120.0, 110.1, 58.4, 55.6, 18.2. HRMS-ESI (*m/z*): Calcd for  $\text{C}_{15}\text{H}_{24}\text{O}_4\text{Si Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 319.1336, Found: 319.1335.



**(Z)-Triethoxy(4-fluorostyryl)silane (3ja).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate :  $\text{Et}_3\text{N} = 100:2:1$ ) obtained **3ja** as light yellow liquid (224.6 mg, 79% yield).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.60 – 7.53 (m, 2H), 7.37 (d,  $J = 15.6$  Hz, 1H), 7.05 – 6.98 (m, 2H), 5.56 (d,  $J = 15.6$  Hz, 1H), 3.76 (q,  $J = 7.0$  Hz, 6H), 1.15 (t,  $J = 7.0$  Hz, 9H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9 (d,  $^1J_{\text{C-F}} = 248.9$  Hz), 149.9, 134.8 (d,  $^4J_{\text{C-F}} = 3.2$  Hz), 130.4 (d,  $^3J_{\text{C-F}} = 8.3$  Hz), 120.0, 115.1 (d,  $^2J_{\text{C-F}} = 21.7$  Hz), 58.6, 18.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.43. HRMS-ESI (*m/z*): Calcd for  $\text{C}_{14}\text{H}_{21}\text{FO}_3\text{Si Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 307.1136, Found: 307.1138.

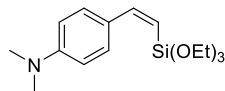


**(Z)-(4-Bromostyryl)triethoxysilane (3ka).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate :  $\text{Et}_3\text{N} = 100:2:1$ ) obtained **3ka** as light yellow liquid (252.0 mg, 73% yield).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.46 (s, 4H), 7.32 (d,  $J = 15.6$  Hz, 1H), 5.63 (d,  $J = 15.6$  Hz, 1H), 3.76 (q,  $J = 7.0$  Hz, 6H), 1.16 (t,  $J = 7.0$  Hz, 9H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8, 137.5, 131.3, 130.2, 122.5, 121.4, 58.6, 18.2. HRMS-ESI (*m/z*): Calcd for  $\text{C}_{14}\text{H}_{21}^{79}\text{BrO}_3\text{Si Na}$  [ $\text{M} + \text{Na}$ ] $^+$ : 367.0336, Found: 367.0336.

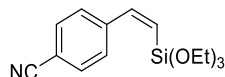


**(Z)-4-(2-(Triethoxysilyl)vinyl)aniline (3la).** Purified by flash column chromatography (300-400 mesh

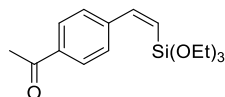
silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:10:1) obtained **3la** as light yellow liquid (247.1 mg, 88% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.29 (d, *J* = 15.6 Hz, 1H), 6.67 – 6.61 (m, 2H), 5.32 (d, *J* = 15.6 Hz, 1H), 3.78 (q, *J* = 7.0 Hz, 6H), 1.17 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.4, 146.9, 130.1, 129.2, 114.7, 114.6, 58.4, 18.2. HRMS-ESI (*m/z*): Calcd for C<sub>14</sub>H<sub>23</sub>NO<sub>3</sub>Si Na [M + Na]<sup>+</sup>: 304.1339, Found: 304.1340.



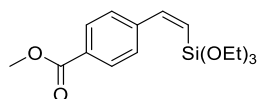
**(Z)-N,N-Dimethyl-4-(2-(triethoxysilyl)vinyl)aniline (3ma)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:10:1) obtained **3ma** as light yellow liquid (229.0 mg, 88% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.49 (m, 2H), 7.31 (d, *J* = 15.6 Hz, 1H), 6.72 – 6.65 (m, 2H), 5.28 (d, *J* = 15.6 Hz, 1H), 3.79 (q, *J* = 7.0 Hz, 6H), 2.98 (s, 7H), 1.18 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.5, 130.0, 128.1, 113.5, 111.8, 58.4, 40.5, 18.3. HRMS-ESI (*m/z*): Calcd for C<sub>16</sub>H<sub>27</sub>NO<sub>3</sub>Si H [M + H]<sup>+</sup>: 310.1833, Found: 310.1833.



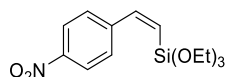
**(Z)-4-(2-(Triethoxysilyl)vinyl)benzonitrile (3na)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:5:1) obtained **3na** as light yellow liquid (183.6 mg, 63% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 15.6 Hz, 1H), 5.80 (d, *J* = 15.6 Hz, 1H), 3.75 (q, *J* = 7.0 Hz, 6H), 1.14 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 148.8, 143.0, 132.0, 129.1, 125.2, 119.1, 111.6, 58.7, 18.2. HRMS-ESI (*m/z*): Calcd for C<sub>15</sub>H<sub>21</sub>NO<sub>3</sub>Si Na [M + Na]<sup>+</sup>: 314.1183, Found: 314.1183.



**(Z)-1-(4-(2-(Triethoxysilyl)vinyl)phenyl)ethan-1-one (3oa)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:10:1) obtained **3oa** as light yellow liquid (182.0 mg, 59% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.91 (m, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 15.6 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 3.76 (q, *J* = 7.0 Hz, 6H), 2.60 (s, 3H), 1.15 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.7, 143.2, 136.5, 128.7, 128.3, 123.8, 58.6, 26.8, 18.2. HRMS-ESI (*m/z*): Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub>Si Na [M + Na]<sup>+</sup>: 331.1336, Found: 331.1337.

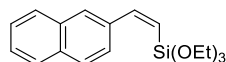


**Methyl (Z)-4-(2-(triethoxysilyl)vinyl)benzoate (3pa)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:10:1) obtained **3pa** as colorless liquid (152.5 mg, 47% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.98 (m, 2H), 7.66 – 7.61 (m, 2H), 7.42 (d, *J* = 15.6 Hz, 1H), 5.73 (d, *J* = 15.6 Hz, 1H), 3.92 (s, 3H), 3.76 (q, *J* = 7.0 Hz, 6H), 1.14 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 167.1, 149.8, 143.1, 129.6, 129.5, 128.5, 123.5, 58.6, 52.2, 18.2. HRMS-ESI (*m/z*): Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>5</sub>Si Na [M + Na]<sup>+</sup>: 347.1285, Found: 347.1286.

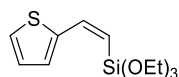


**(Z)-Triethoxy(4-nitrostyryl)silane (3qa)**. Purified by flash column chromatography (300-400 mesh

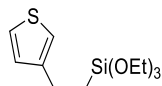
silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3na** as light yellow liquid (73.4 mg, 23% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.17 (m, 2H), 7.76 – 7.70 (m, 2H), 7.43 (d, *J* = 15.6 Hz, 1H), 5.85 (d, *J* = 15.6 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 6H), 1.15 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 148.2, 147.4, 145.0, 129.3, 126.1, 123.4, 58.7, 18.2. HRMS-ESI (m/z): Calcd for C<sub>14</sub>H<sub>21</sub>NO<sub>5</sub>Si Na [M + Na]<sup>+</sup>: 334.1081, Found: 334.1084.



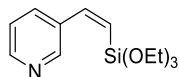
**(Z)-Triethoxy(2-(naphthalen-2-yl)vinyl)silane (3ra)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3na** as light yellow liquid (269.0 mg, 85% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.86 – 7.78 (m, 4H), 7.57 (d, *J* = 15.6 Hz, 1H), 7.47 (dd, *J* = 6.4, 3.2 Hz, 2H), 5.68 (d, *J* = 15.6 Hz, 1H), 3.79 (q, *J* = 7.0 Hz, 6H), 1.15 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 151.2, 136.2, 133.3, 128.5, 128.4, 127.7 (2 C), 126.4, 126.2, 126.1, 120.6, 58.6, 18.2. HRMS-ESI (m/z): Calcd for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>Si Na [M + Na]<sup>+</sup>: 339.1387, Found: 339.1387.



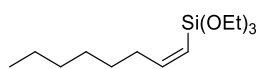
**(Z)-Triethoxy(2-(thiophen-2-yl)vinyl)silane (3sa)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:5:1) obtained **3na** as light yellow liquid (185.1 mg, 68% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 6.94 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.38 (d, *J* = 15.6 Hz, 1H), 3.76 (q, *J* = 7.0 Hz, 6H), 1.14 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 142.3, 141.9, 128.3, 127.4, 126.9, 117.7, 58.5, 18.1. HRMS-ESI (m/z): Calcd for C<sub>12</sub>H<sub>20</sub>O<sub>3</sub>SSi Na [M + Na]<sup>+</sup>: 295.0795, Found: 295.0795.



**(Z)-Triethoxy(2-(thiophen-3-yl)vinyl)silane (3ta)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained as light yellow liquid (171.7 mg, 63% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 1H), 7.46 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.36 (d, *J* = 15.6 Hz, 1H), 7.24 (dd, *J* = 5.2, 3.2 Hz, 1H), 5.48 (d, *J* = 15.6 Hz, 1H), 3.80 (q, *J* = 7.2 Hz, 6H), 1.18 (t, *J* = 6.8 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 144.4, 140.9, 128.1, 125.8, 125.3, 118.2, 58.6, 18.2. HRMS-ESI (m/z): Calcd for C<sub>12</sub>H<sub>20</sub>O<sub>3</sub>SSi Na [M + Na]<sup>+</sup>: 295.0795, Found: 295.0795.



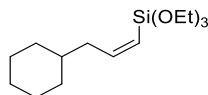
**(Z)-3-(2-(Triethoxysilyl)vinyl)pyridine (3ua)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:10:1) obtained **3ua** as light yellow liquid (195.1 mg, 73% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 2.2 Hz, 1H), 8.51 (dd, *J* = 5.0, 1.8 Hz, 1H), 8.02 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.38 (d, *J* = 15.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 5.77 (d, *J* = 15.6 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 6H), 1.16 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.8, 149.1, 145.5, 133.2, 133.1, 123.6, 121.2, 58.8, 18.4. HRMS-ESI (m/z): Calcd for C<sub>13</sub>H<sub>21</sub>NO<sub>3</sub>Si H [M + H]<sup>+</sup>: 268.1363, Found: 268.1363.



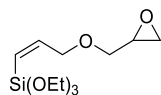
**(Z)-Triethoxy(oct-1-en-1-yl)silane (3va)**.<sup>3</sup> Purified by flash column chromatography (300-400 mesh



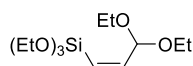
silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3va** as light yellow liquid (233.3 mg, 85% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.51 (dt, *J* = 14.4, 7.6 Hz, 1H), 5.28 (d, *J* = 14.0 Hz, 1H), 3.81 (q, *J* = 7.0 Hz, 6H), 2.27 (q, *J* = 7.2 Hz, 2H), 1.44 – 1.26 (m, 8H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.88 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 155.3, 118.4, 58.3, 34.0, 31.9, 29.6, 29.2, 22.7, 18.4, 14.2.



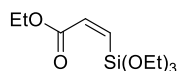
**(Z)-(3-Cyclohexylprop-1-en-1-yl)triethoxysilane (3va)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3va** as light yellow liquid (249.3 mg, 87% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.53 (dt, *J* = 14.6, 7.4 Hz, 1H), 5.31 (dt, *J* = 14.2, 1.4 Hz, 1H), 3.80 (q, *J* = 7.0 Hz, 6H), 2.18 (td, *J* = 7.2, 1.4 Hz, 2H), 1.75 – 1.57 (m, 6H), 1.40 – 1.28 (m, 1H), 1.22 (t, *J* = 7.0 Hz, 9H), 1.19 – 1.10 (m, 2H), 0.99 – 0.87 (m, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 154.1, 119.1, 58.3, 41.4, 38.2, 33.2, 26.6, 26.5, 18.3. HRMS-ESI (*m/z*): Calcd for C<sub>15</sub>H<sub>30</sub>O<sub>3</sub>Si Na [M + Na]<sup>+</sup>: 309.1856, Found: 309.1856.



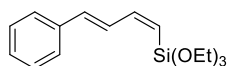
**(Z)-Triethoxy(3-(oxiran-2-ylmethoxy)prop-1-en-1-yl)silane (3xa)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3xa** as light yellow liquid (171.3 mg, 62% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.60 (dt, *J* = 14.8, 6.2 Hz, 1H), 5.54 (dt, *J* = 14.8, 1.6 Hz, 1H), 4.31 – 4.20 (m, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 3.71 (dd, *J* = 11.4, 3.2 Hz, 1H), 3.43 (dd, *J* = 11.4, 5.8 Hz, 1H), 3.19 – 3.14 (m, 1H), 2.80 (dd, *J* = 5.2, 4.2 Hz, 1H), 2.62 (dd, *J* = 5.0, 2.8 Hz, 1H), 1.23 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.9, 122.2, 71.7, 71.1, 58.6, 50.8, 44.7, 18.3. HRMS-ESI (*m/z*): Calcd for C<sub>12</sub>H<sub>24</sub>O<sub>5</sub>Si Na [M + Na]<sup>+</sup>: 299.1285, Found: 299.1285.



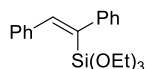
**(Z)-(3,3-Diethoxyprop-1-en-1-yl)triethoxysilane (3ya)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:4:1) obtained **3ya** as colorless liquid (193.1 mg, 66% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 6.45 (dd, *J* = 15.0, 8.0 Hz, 1H), 5.59 (dd, *J* = 15.0, 1.0 Hz, 1H), 5.21 (dd, *J* = 8.0, 1.0 Hz, 1H), 3.83 (q, *J* = 7.0 Hz, 6H), 3.69 (dq, *J* = 9.5, 7.0 Hz, 2H), 3.55 (dq, *J* = 9.5, 7.0 Hz, 2H), 1.23 (q, *J* = 7.0 Hz, 15H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 149.4, 123.0, 101.1, 61.9, 58.6, 18.3, 15.4. HRMS-ESI (*m/z*): Calcd for C<sub>13</sub>H<sub>28</sub>O<sub>5</sub>Si Na [M + Na]<sup>+</sup>: 315.1598, Found: 315.1599.



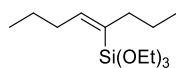
**Ethyl (Z)-3-(triethoxysilyl)acrylate (3za)**. Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:4:1) obtained **3ya** and **4ya** as colorless liquid (52.0 mg, 20% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 6.96 (d, *J* = 3.5 Hz, 1H), 6.42 (d, *J* = 3.5 Hz, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 3.86 (q, *J* = 7.0 Hz, 6H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.22 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 168.3, 145.0, 136.1, 60.7, 58.9, 18.2, 14.2. HRMS-ESI (*m/z*): Calcd for C<sub>11</sub>H<sub>22</sub>O<sub>5</sub>Si Na [M + Na]<sup>+</sup>: 285.1129, Found: 285.1130.



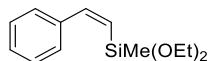
**Triethoxy((1Z,3E)-4-phenylbuta-1,3-dien-1-yl)silane (3a'a).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:4:1) obtained **3a'a** and **4a'a** as yellow liquid (169.7 mg, 58% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.42 (m, 2H), 7.35 – 7.30 (m, 3H), 7.28 – 7.25 (m, 1H), 7.12 (dd, *J* = 14.0, 11.2 Hz, 1H), 6.64 (d, *J* = 15.6 Hz, 1H), 5.48 (d, *J* = 14.0 Hz, 1H), 3.87 (q, *J* = 7.0 Hz, 6H), 1.27 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 150.3, 137.1, 136.6, 129.5, 128.8, 128.2, 126.9, 121.4, 58.6, 18.4. HRMS-ESI (*m/z*): Calcd for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>Si Na [M + Na]<sup>+</sup>: 315.1387, Found:315.1392.



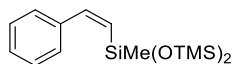
**(Z)-(1,2-Diphenylvinyl)triethoxysilane (3b'a).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3b'a** as light yellow liquid (308.2 mg, 90% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 7.23 – 7.14 (m, 4H), 7.13 – 7.08 (m, 3H), 7.06 – 7.00 (m, 2H), 3.83 (q, *J* = 7.0 Hz, 6H), 1.20 (t, *J* = 7.0 Hz, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 142.6, 140.9, 137.2, 137.0, 130.0, 128.6, 128.4, 128.0, 127.6, 126.2, 59.0, 18.3. HRMS-ESI (*m/z*): Calcd for C<sub>20</sub>H<sub>26</sub>O<sub>3</sub>Si Na [M + Na]<sup>+</sup>: 365.1543, Found: 365.1543.



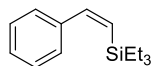
**(Z)-Triethoxy(oct-4-en-4-yl)silane (3c'a).**<sup>4</sup> Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3c'a** as light yellow liquid (200.5 mg, 73% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 6.09 (t, *J* = 7.0 Hz, 1H), 3.80 (q, *J* = 7.0 Hz, 6H), 2.15 – 2.05 (m, 4H), 1.45 – 1.35 (m, 4H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.95 – 0.87 (m, 6H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 146.0, 132.9, 58.4, 31.5, 30.5, 23.1, 22.6, 18.3, 14.4, 14.0.



**(Z)-Diethoxy(methyl)(styryl)silane (3bb).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate : Et<sub>3</sub>N = 100:2:1) obtained **3bb** as light yellow liquid (153.8 mg, 65% yield). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.48 (m, 2H), 7.40 (d, *J* = 15.6 Hz, 1H), 7.36 – 7.25 (m, 4H), 5.71 (d, *J* = 15.6 Hz, 1H), 3.76 (qd, *J* = 7.0, 3.2 Hz, 4H), 1.20 (t, *J* = 7.0 Hz, 6H), 0.10 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 149.8, 139.1, 128.4, 128.2, 128.2, 125.7, 58.4, 18.4, -3.4. HRMS-ESI (*m/z*): Calcd for C<sub>13</sub>H<sub>20</sub>O<sub>2</sub>Si Na [M + Na]<sup>+</sup>: 259.1125, Found: 259.1126.

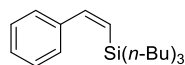


**(Z)-1,1,1,3,5,5,5-Heptamethyl-3-styryltrisiloxane (3bc).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : Et<sub>3</sub>N = 100:1) obtained **3bc** as light yellow liquid (191.0 mg, 59% yield). <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.46 (m, 2H), 7.33 – 7.26 (m, 3H), 7.26 – 7.23 (m, 1H), 5.65 (d, *J* = 15.6 Hz, 1H), 0.13 (s, 3H), 0.06 (s, 18H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 147.3, 139.4, 129.9, 128.6, 128.0, 127.8, 1.9, 1.3. HRMS-ESI (*m/z*): Calcd for C<sub>15</sub>H<sub>28</sub>O<sub>2</sub>Si<sub>3</sub> Na [M + Na]<sup>+</sup>: 347.1289, Found: 347.1291.

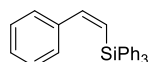


**(Z)-Triethyl(styryl)silane (3bd).**<sup>1</sup> Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : Et<sub>3</sub>N = 100:1) obtained **3bd** as light-yellow liquid (113.6 mg, 52% yield). <sup>1</sup>H NMR

(400 MHz, Chloroform-*d*)  $\delta$  7.45 (d,  $J = 15.2$  Hz, 1H), 7.34 – 7.21 (m, 5H), 5.76 (d,  $J = 15.2$  Hz, 1H), 0.87 (t,  $J = 8.0$  Hz, 9H), 0.55 (q,  $J = 8.0$  Hz, 6H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.8, 140.5, 129.5, 127.9, 127.3, 126.3, 7.5, 4.8.



**(Z)-Tributyl(styryl)silane (3be).** Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether :  $\text{Et}_3\text{N} = 100:1$ ) obtained **3be** as light-yellow liquid (221.0 mg, 73% yield).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.41 (d,  $J = 15.2$  Hz, 1H), 7.32 – 7.22 (m, 5H), 5.76 (d,  $J = 15.2$  Hz, 1H), 1.26 – 1.14 (m, 12H), 0.80 (t,  $J = 6.8$  Hz, 9H), 0.57 – 0.48 (m, 6H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.4, 140.7, 130.5, 128.0, 128.0, 127.4, 26.8, 26.3, 13.9, 13.6. HRMS-ESI ( $m/z$ ): Calcd for  $\text{C}_{20}\text{H}_{34}\text{Si}$   $[\text{M} + \text{H}]^+$ : 303.2503, Found: 303.2490.

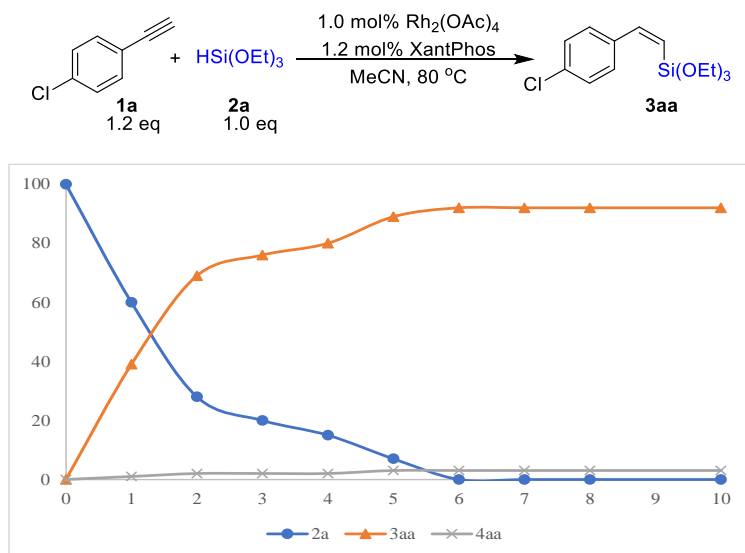


**(Z)-Triphenyl(styryl)silane (3bf).**<sup>1</sup> Purified by flash column chromatography (300-400 mesh silica gel, petroleum ether : ethyl acetate :  $\text{Et}_3\text{N} = 100:1:1$ ) obtained **3bf** as light yellow liquid (210.3 mg, 58% yield).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.73 (d,  $J = 15.2$  Hz, 1H), 7.59 – 7.52 (m, 6H), 7.38 – 7.34 (m, 2H), 7.34 (t,  $J = 1.5$  Hz, 1H), 7.32 – 7.30 (m, 2H), 7.30 – 7.28 (m, 3H), 7.28 – 7.27 (m, 1H), 7.18 – 7.14 (m, 2H), 7.03 – 6.97 (m, 1H), 6.95 – 6.88 (m, 2H), 6.34 (d,  $J = 15.2$  Hz, 1H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 138.1, 135.9, 135.1, 129.5, 128.8, 127.9, 127.8, 127.6, 125.4.

## 4. Mechanism Experiments

### 4.1 Time monitoring

**Figure S1.** Time monitoring for hydrosilylation of **1a** in MeCN (nine parallel reactions).



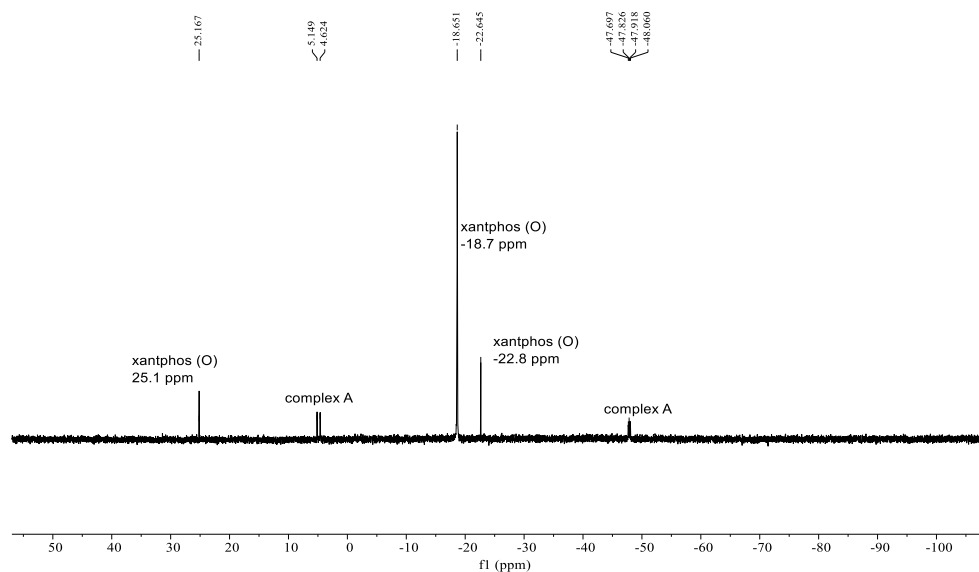
Curve 2a: the concentration of **2a** in the reaction system. Curve 3aa: the concentration of **3aa** in the reaction system. Curve 4aa: the concentration of **4aa** in the reaction system.

### 4.2 The complexes of $\text{Rh}_2(\text{OAc})_4$ and XantPhos in MeCN

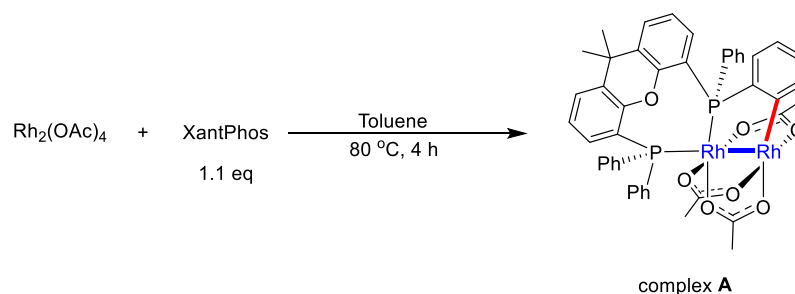
In an oven-dried 25 mL sealed tube containing a stirring bar,  $\text{Rh}_2(\text{OAc})_4$  (4.4 mg, 2.0 mol %), XantPhos (6.9 mg, 2.4 mol %) and  $\text{CD}_3\text{CN}$  (1.0 mL) were added. The reaction mixture was measured after 2 h and

monitored via  $^{31}\text{P}$  NMR as Figure S2.

**Figure S2.**  $^{31}\text{P}$  NMR for the reaction mixture of  $\text{Rh}_2(\text{OAc})_4/\text{XantPhos}$  in  $\text{CD}_3\text{CN}$



### 4.3 Synthesis of dirhodium complexes and crystallographic data



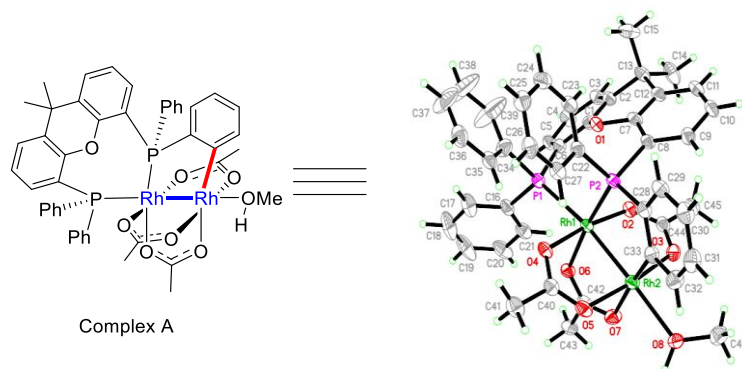
$\text{Rh}_2(\text{OAc})_4$  (44.2 mg, 0.10 mol, 1.0 equiv.) and XantPhos (63.6 mg, 0.11 mol, 1.1 equiv.) were placed in a Schlenk tube under a nitrogen atmosphere followed by the addition of degassed toluene (5 mL). After the reaction mixture was stirred at 80 °C for 4 hours, the resulting red brown mixture was allowed to cool to room temperature and then the solvent was concentrated. The residue was purified by column chromatography with eluent (DCM/AcOH = 30:1) under nitrogen atmosphere to afford the corresponding green solid A (61.2 mg, 64% yield).  $^1\text{H}$  NMR (700 MHz, Chloroform-*d*)  $\delta$  8.21 (dd,  $J$  = 8.4, 4.2 Hz, 1H), 7.55 (dd,  $J$  = 8.4, 1.4 Hz, 1H), 7.47 (d,  $J$  = 7.7 Hz, 1H), 7.40 – 7.44 (m, 1H), 7.35 – 7.30 (m, 4H), 7.19 (t,  $J$  = 9.1 Hz, 2H), 7.17 – 7.13 (m, 2H), 7.11 – 7.06 (m, 2H), 7.04 – 6.98 (m, 3H), 6.94 (td,  $J$  = 7.7, 2.1 Hz, 2H), 6.84 (td,  $J$  = 7.7, 2.1 Hz, 2H), 6.81 – 6.78 (m, 1H), 6.78 – 6.74 (m, 2H), 6.34 (ddd,  $J$  = 9.8, 7.7, 1.4 Hz, 1H), 2.13 (s, 3H), 1.85 (s, 3H), 1.74 (s, 3H), 1.52 (s, 3H), 0.47 (s, 3H).  $^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ )  $\delta$  190.5, 189.8 (d,  $J$  = 2.6 Hz), 182.3 (t,  $J$  = 3.7 Hz), 171.2 – 170.7 (m), 154.9 (d,  $J$  = 4.0 Hz), 154.8 (d,  $J$  = 9.3 Hz), 147.7 (d,  $J$  = 73.9 Hz), 137.5 (d,  $J$  = 15.5 Hz), 135.5 (d,  $J$  = 9.2 Hz), 132.8 (d,  $J$  = 9.7 Hz), 132.6, 132.5 (d,  $J$  = 40.8 Hz), 132.49 (d,  $J$  = 6.5 Hz), 132.42 (d,  $J$  = 41.7

Hz), 131.9, 131.6 (d,  $J = 3.7$  Hz), 131.3 (d,  $J = 3.5$  Hz), 130.9 (d,  $J = 25.3$  Hz), 130.2 (d,  $J = 22.4$  Hz), 129.4 (d,  $J = 2.3$  Hz), 129.1 (d,  $J = 42.7$  Hz), 128.2 (d,  $J = 9.0$  Hz), 127.7 (d,  $J = 10.9$  Hz), 127.4 (d,  $J = 2.8$  Hz), 127.2 (d,  $J = 8.8$  Hz), 126.8 (d,  $J = 114.4$  Hz), 124.6 (d,  $J = 8.8$  Hz), 124.3 (d,  $J = 5.1$  Hz), 121.7 (d,  $J = 8.8$  Hz), 120.4 (d,  $J = 51.4$  Hz), 118.5 (d,  $J = 26.2$  Hz), 35.9, 33.2, 25.0, 23.74, 23.70 (d,  $J = 4.6$  Hz), 22.0.  $^{31}\text{P}$  NMR (283 MHz, Chloroform-*d*)  $\delta$  1.6 (dd,  $J = 140.4, 8.2$  Hz), -58.4 (dd,  $J = 80.4, 69.0$  Hz). HRMS-ESI ( $m/z$ ): Calcd for  $\text{C}_{45}\text{H}_{40}\text{O}_7\text{P}_2\text{Rh}_2 \text{Na} [\text{M} + \text{Na}]^+$ : 983.0252, Found: 983.0259.

The relative configuration of the complex **A** was determined by X-ray. The crystal was obtained by slow evaporation of the solution of complex **A** in MeOH/ DCM (3:1) at room temperature. The single-crystal X-ray diffraction data were collected on a Bruker D8 VENTURE CMOS Photon II diffractometer with helios mx multilayer monochromator Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) in the Instrumental Analysis Center of Shanghai Jiao Tong University. Data collection, unit cell refinement and data reduction were performed using APEX3 v2019.11-0. The structure was solved by Intrinsic Phasing method and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXTL program package. The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to nitrogen were located in a  $\Delta F$  map and refined with isotropic displacement parameters.

CCDC number of **A**: 2194134

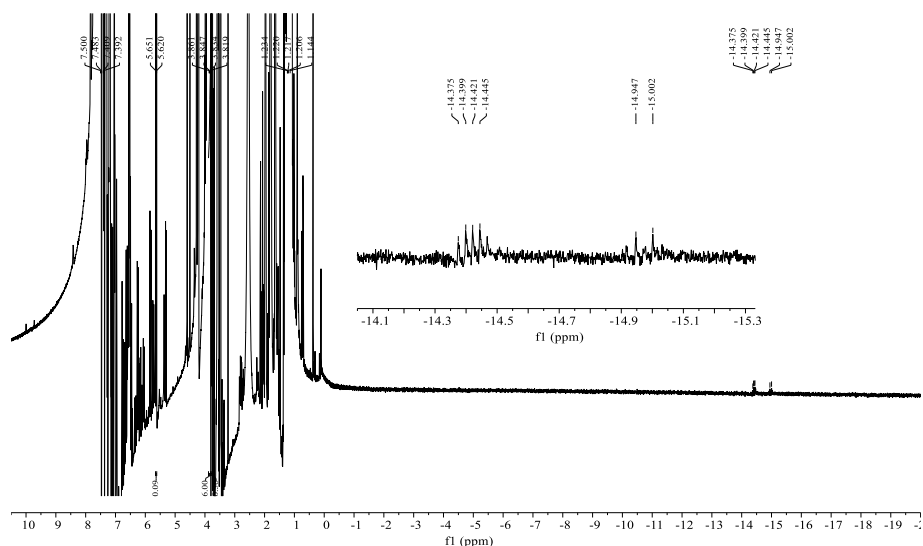
**Figure S3.** X-ray Crystal Diffraction of Complex **A**



**Table S5.** Crystal Data and Structure Refinement for Complex **A**

Empirical formula	$\text{C}_{47}\text{H}_{46}\text{Cl}_2\text{O}_8\text{P}_2\text{Rh}_2$
Formula weight	1077.50
Temperature/K	173(2)
Crystal system	Monoclinic
space group	$C2/c$
$a/\text{\AA}$	27.2748(8)
$b/\text{\AA}$	19.7988(6)
$c/\text{\AA}$	20.4678(5)
$\alpha/^\circ$	90
$\beta/^\circ$	119.2820(10)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	9640.5(5)

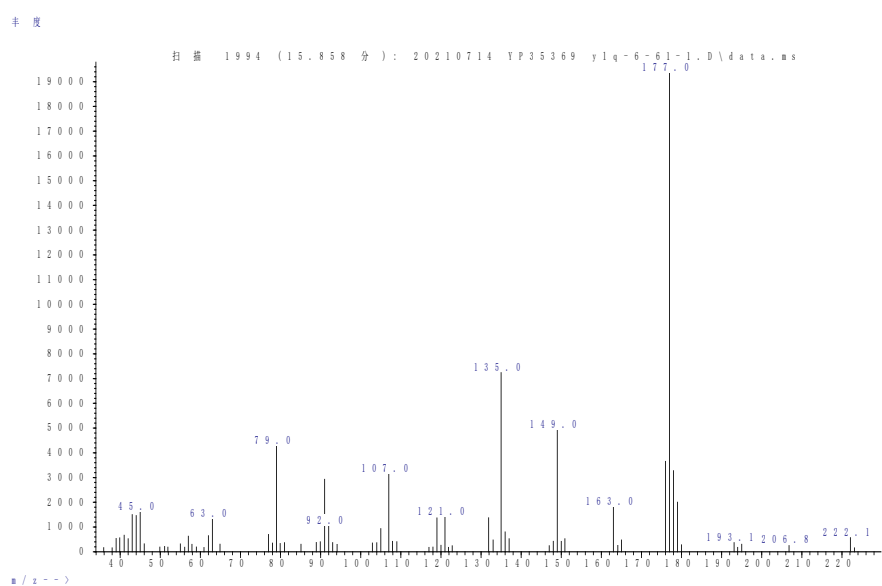




#### 4.6 The capture of $(\text{EtO})_3\text{SiOAc}$ and alkene

After the reaction under standard condition, the resulting mixture was allowed to cool to room temperature and then monitored by GC-MS. It is confirmed that  $(\text{EtO})_3\text{SiOAc}$  and alkene was observed in the reaction mixture.

**Figure S5.** The mass of  $(\text{EtO})_3\text{SiOAc}$  monitored by GC-MS.



$m/z=222.1$ : Chemical Formula:  $(\text{EtO})_3\text{SiOAc}$ , Exact Mass: 222.0924

$m/z=179.1$ : Chemical Formula:  $(\text{EtO})_3\text{SiO}$ , Exact Mass: 179.0740

$m/z=177.0$ : Chemical Formula:  $(\text{EtO})_2\text{SiOAc}$ , Exact Mass: 177.0583

$m/z=163.0$ : Chemical Formula:  $(\text{EtO})_3\text{Si}$ , Exact Mass: 163.0790

$m/z=149.0$ : Chemical Formula:  $(\text{EtO})\text{SiO}_3\text{CO}$ , Exact Mass: 148.9906

$m/z=135.0$ : Chemical Formula:  $\text{O}_3\text{SiOAc}$ , Exact Mass: 134.9750

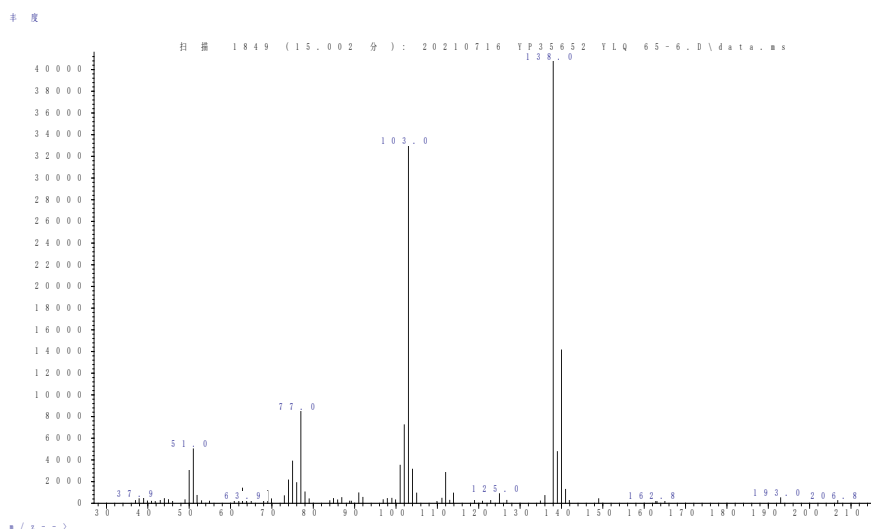
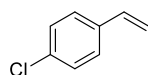
$m/z=121.0$ : Chemical Formula:  $(\text{EtO})\text{O}_3\text{Si}$ , Exact Mass: 120.9957

$m/z=107.0$ : Chemical Formula:  $\text{CH}_2\text{O}_4\text{Si}$ , Exact Mass: 106.9801

$m/z=92.0$ : Chemical Formula:  $\text{O}_4\text{Si}$ , Exact Mass: 91.9566

$m/z=45.0$ : Chemical Formula:  $\text{EtO}$ , Exact Mass: 45.0340

**Figure S6.** The mass of alkene monitored by GC-MS.

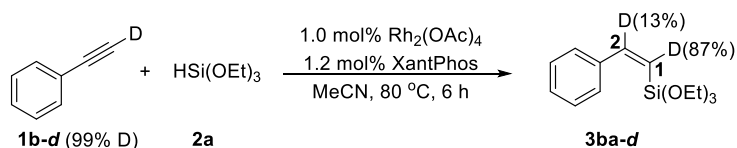


$m/z=138.0$ : Chemical Formula:  $C_8H_7^{35}Cl$ , Exact Mass: 138.0236

$m/z=140.0$ : Chemical Formula:  $C_8H_7^{37}Cl$ , Exact Mass: 138.0236

## 4.7 Deuterium labeling experiments

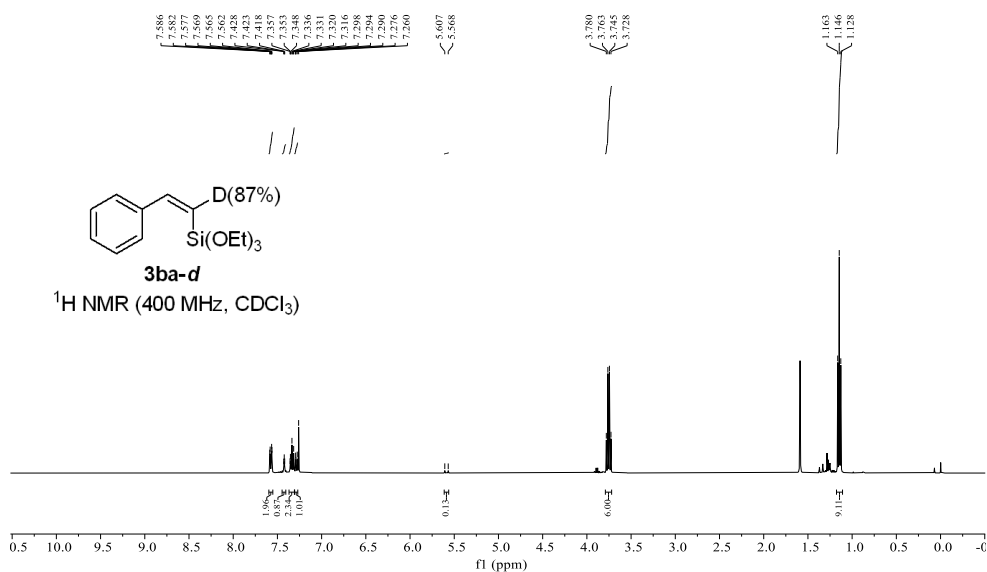
4.7.1 In an oven-dried 25 mL sealed tube containing a stirring bar,  $Rh_2(OAc)_4$  (2.2 mg, 1.0 mol %), XantPhos (3.5 mg, 1.2 mol %), **1a-d** (61.9 mg, 0.6 mmol, 1.2 eq),  $(EtO)_3SiH$  (82.1 mg, 0.5 mmol, 1.0 eq) and dried MeCN (2.0 mL) were and the above mixture and reacted for 6 h at 80 °C. After the reaction, the resulting red brown mixture was allowed to cool to room temperature and the solvent was concentrated. Then the crude production was purified by column chromatography to afford the corresponding products **3ba-d** (122.0 mg, 91% yield).



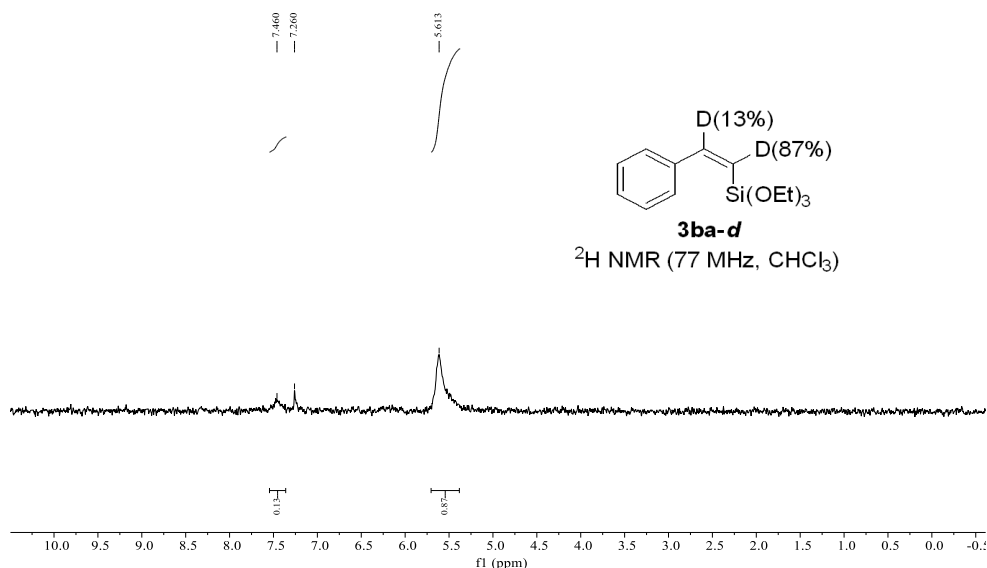
**3ba-d**:  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.60 – 7.55 (m, 2H), 7.41 – 7.45 (m,  $J = 2.2$  Hz, 0.87 H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 5.59 (d,  $J = 15.6$  Hz, 0.13H), 3.75 (q,  $J = 7.0$  Hz, 6H), 1.15 (t,  $J = 7.0$  Hz, 9H).  $^2H$  NMR (77 MHz, Chloroform-*d*) 5.61 (br, 0.87 D), 7.46 (br, 0.13 D).

**Figure S7.** The  $^1H$  NMR of **3ba-d**.

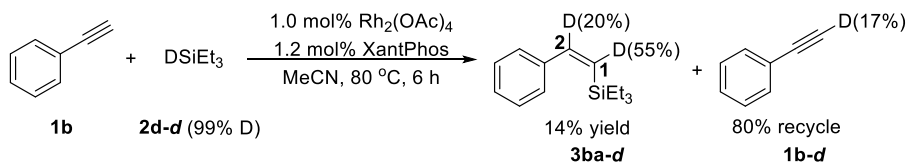




**Figure S8.** The  $^1\text{H}$  NMR of **3ba-d**.

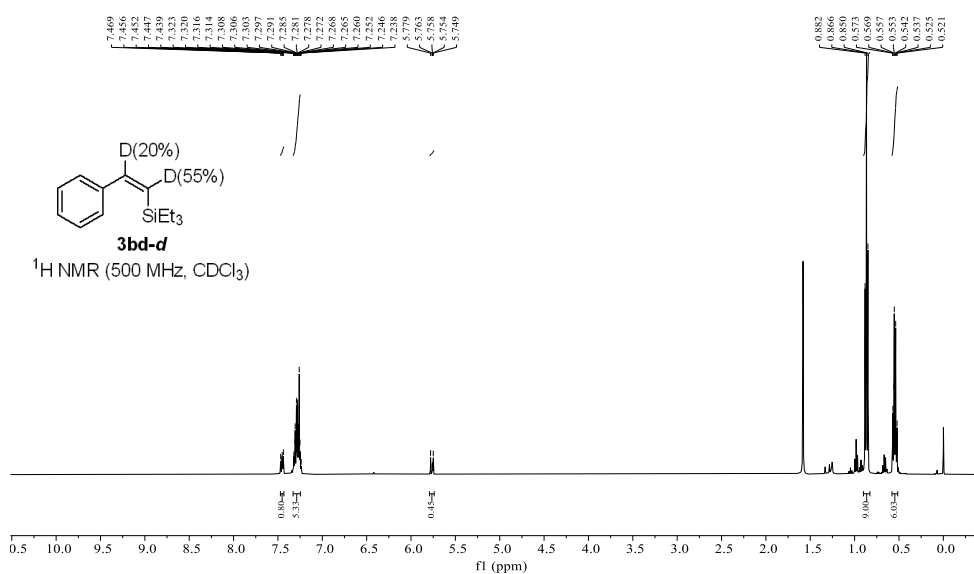


4.7.2 In an oven-dried 25 mL sealed tube containing a stirring bar,  $\text{Rh}_2(\text{OAc})_4$  (2.2 mg, 1.0 mol %), XantPhos (3.5 mg, 1.2 mol %), **1b** (61.3 mg, 0.6 mmol, 1.2 eq), **2d-d**  $\text{Et}_3\text{SiD}$  (58.8 mg, 0.5 mmol, 1.0 eq) and dried MeCN (2.0 mL) were and the above mixture and reacted for 6 h at 80 °C. After the reaction, the resulting red brown mixture was allowed to cool to room temperature and the solvent was concentrated. Then the crude production was purified by column chromatography to afford the corresponding products **3bd-d** (15.0 mg, 14% yield), accompanied by 80% **1b-d**.

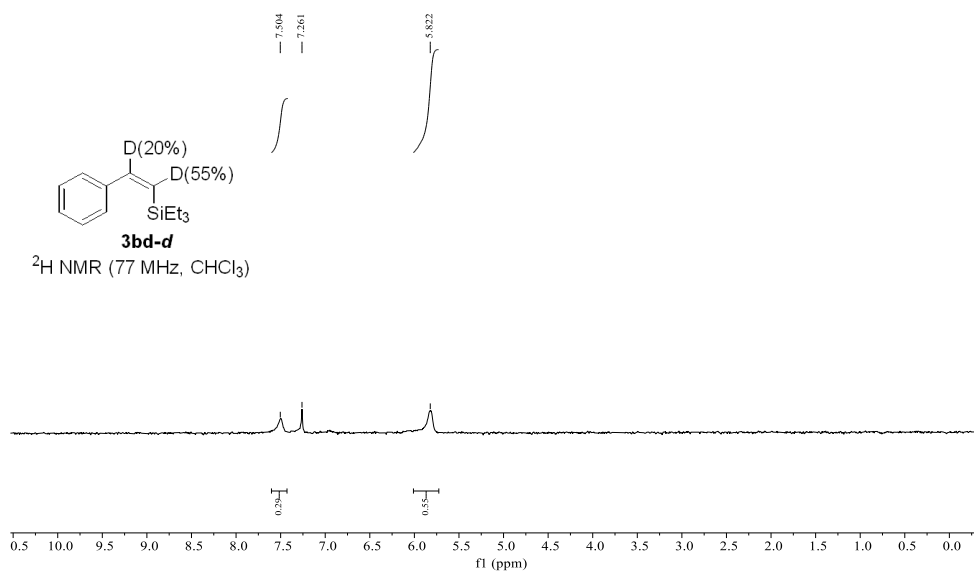


**3bd-d**:  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.48 – 7.43 (m, 0.8H), 7.33 – 7.25 (m, 5H), 5.79 – 5.74 (m, 0.45H), 0.87 (t,  $J = 8.0$  Hz, 9H), 0.58 – 0.52 (m, 6H).  $^2\text{H}$  NMR (77 MHz, Chloroform-*d*) 7.50 (br, 0.29 D), 5.82 (br, 0.55 D).

**Figure S9.** The  $^1\text{H}$  NMR of **3bd-d**.

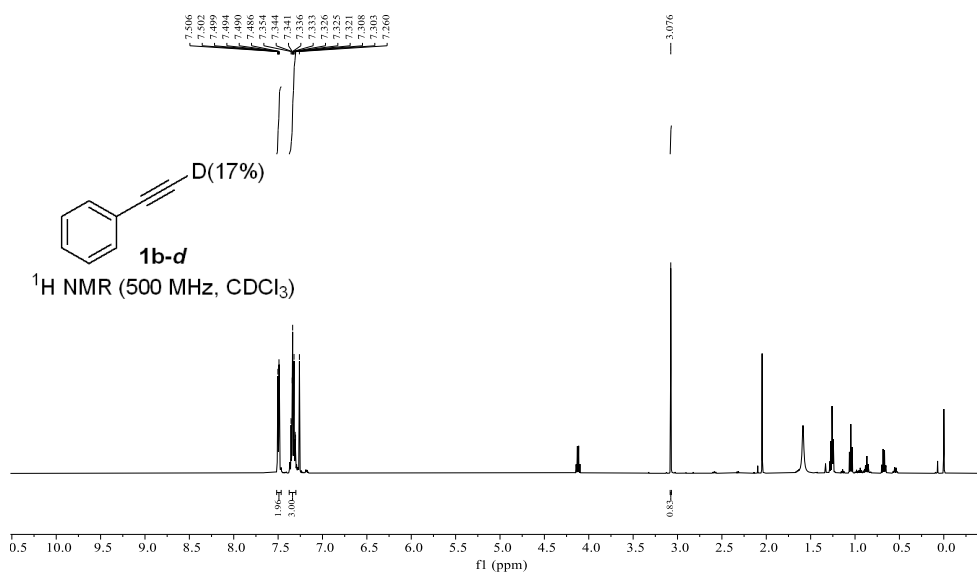


**Figure S10.** The  $^2\text{H}$  NMR of **3bd-d**.

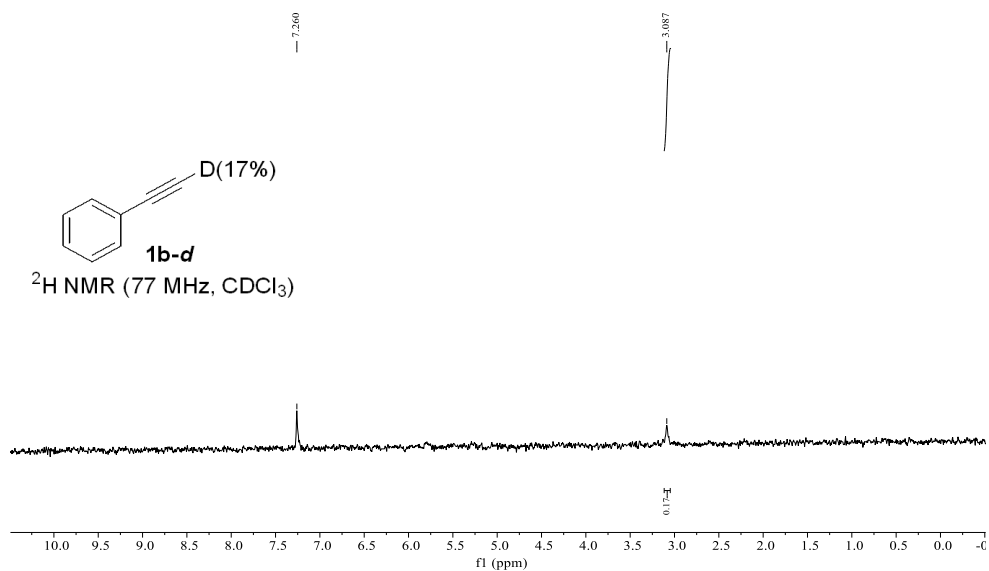


**The recycled 1b-d:**  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  7.52 – 7.47 (m, 2H), 7.37 – 7.30 (m, 3H), 3.08 (s, 0.83H).  $^2\text{H}$  NMR (77 MHz, Chloroform-*d*) 3.09 (br, 0.17 D).

**Figure S11.** The  $^1\text{H}$  NMR of recycled **1b-d**.

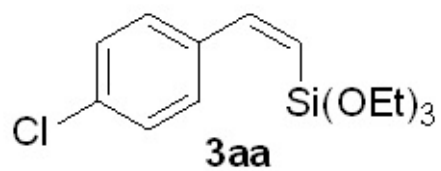


**Figure S12.** The <sup>2</sup>H NMR of recycled **1b-d**.

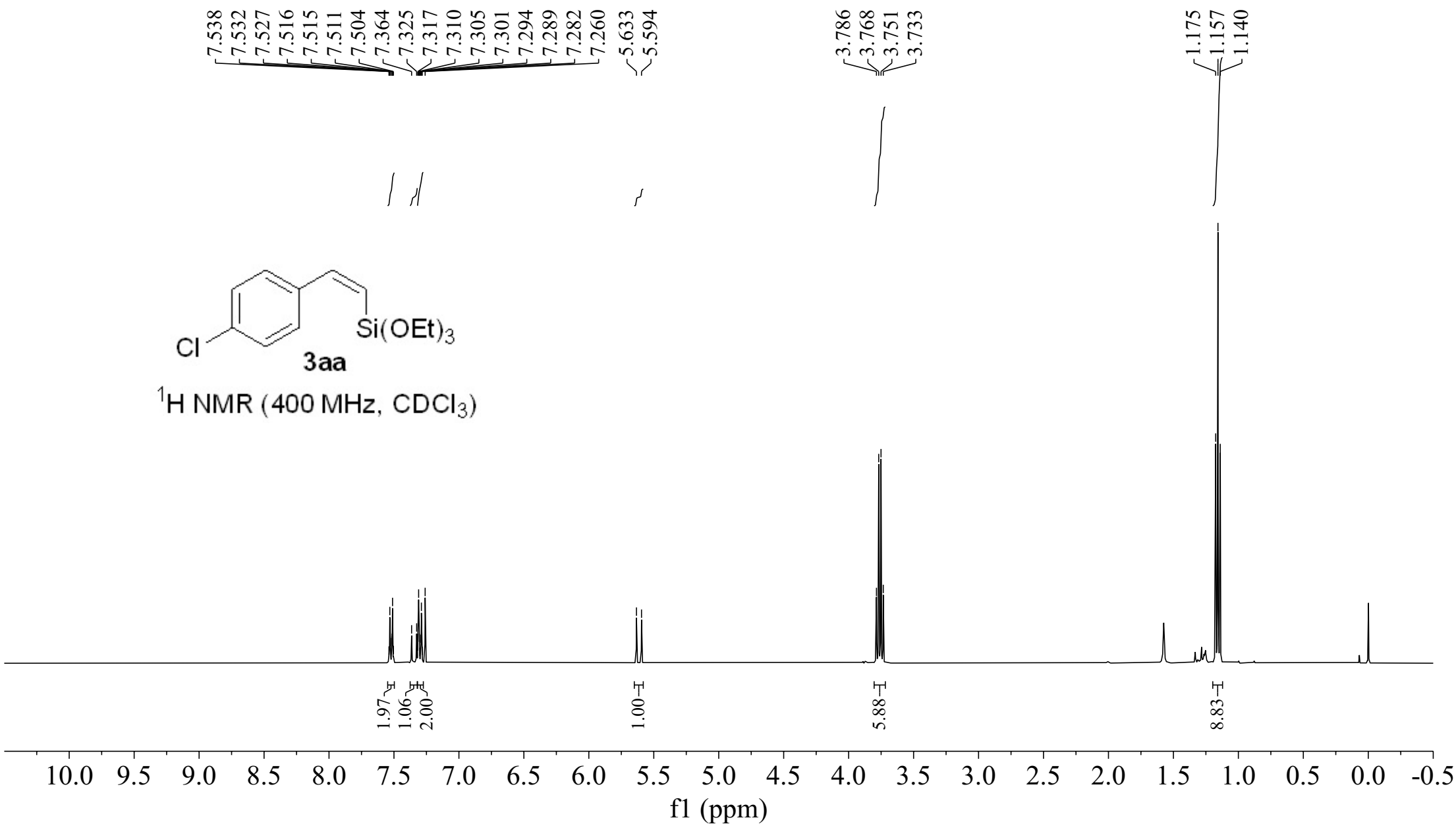


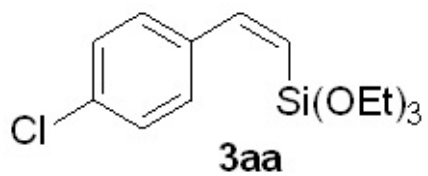
## References

1. X. Zhao, D. Yang, Y. Zhang, B. Wang and J. Qu, *Org. Lett.*, **2018**, *20*, 5357.
2. J. Dong, X. A. Yuan, Z. Yan, L. Mu, J. Ma, C. Zhu and J. Xie, *Nat. Chem.*, **2021**, *13*, 182.
3. A. Monge-Marcet, R. Pleixats, X. Cattoën and M. Wong Chi Man, *Tetrahedron*, **2013**, *69*, 341.
4. B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, **2001**, *123*, 12726.



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





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

—149.721

~137.085

~134.182

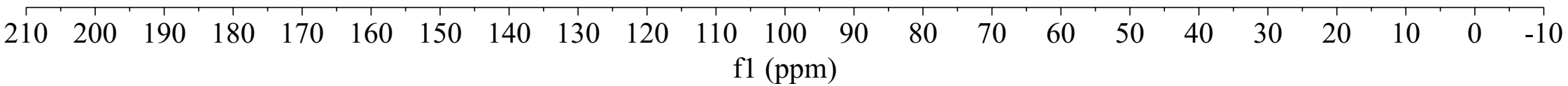
~129.916

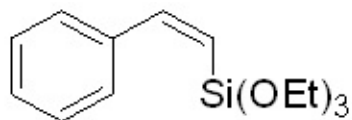
~128.358

~121.261

—58.596

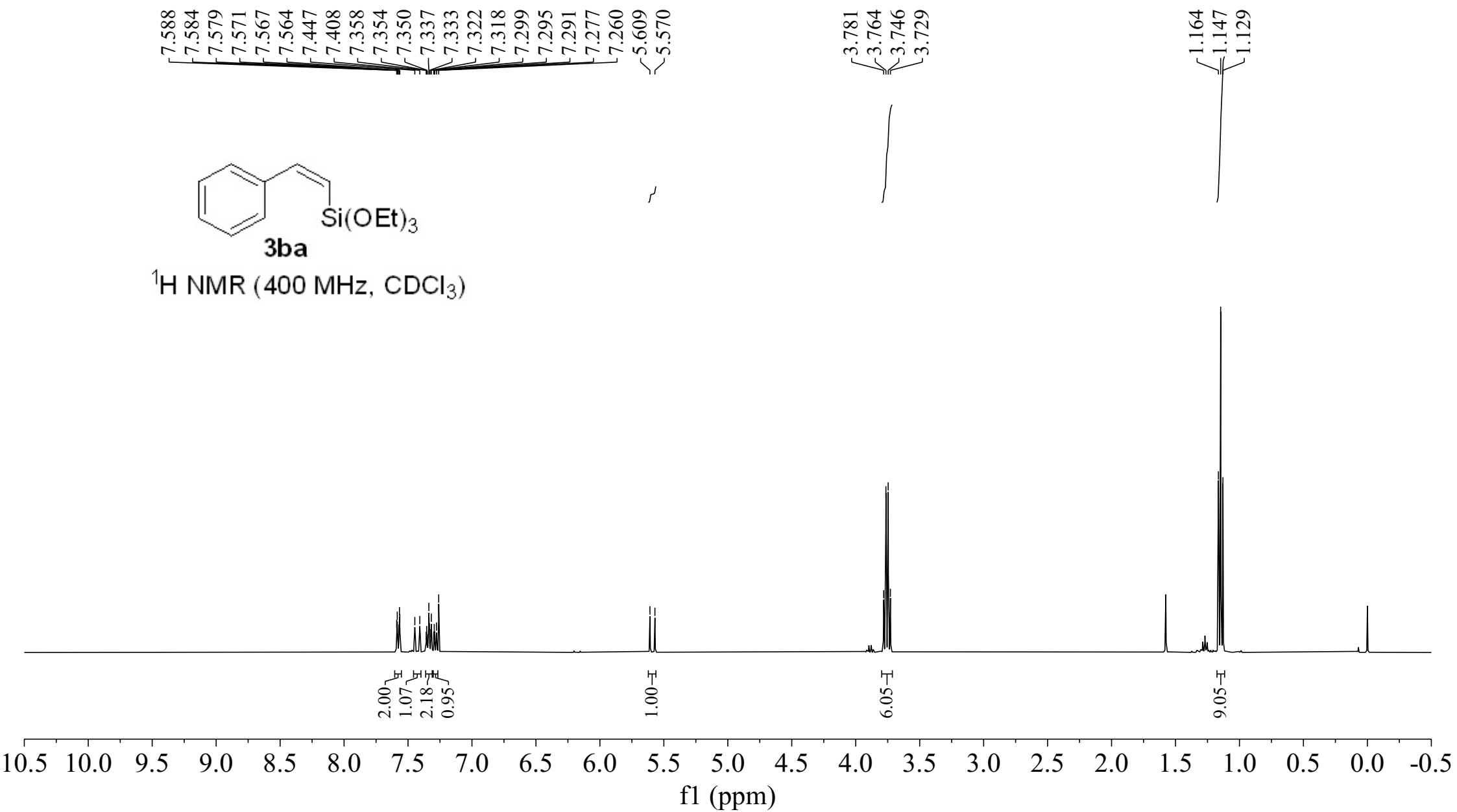
—18.194

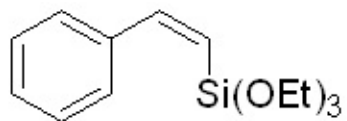




**3ba**

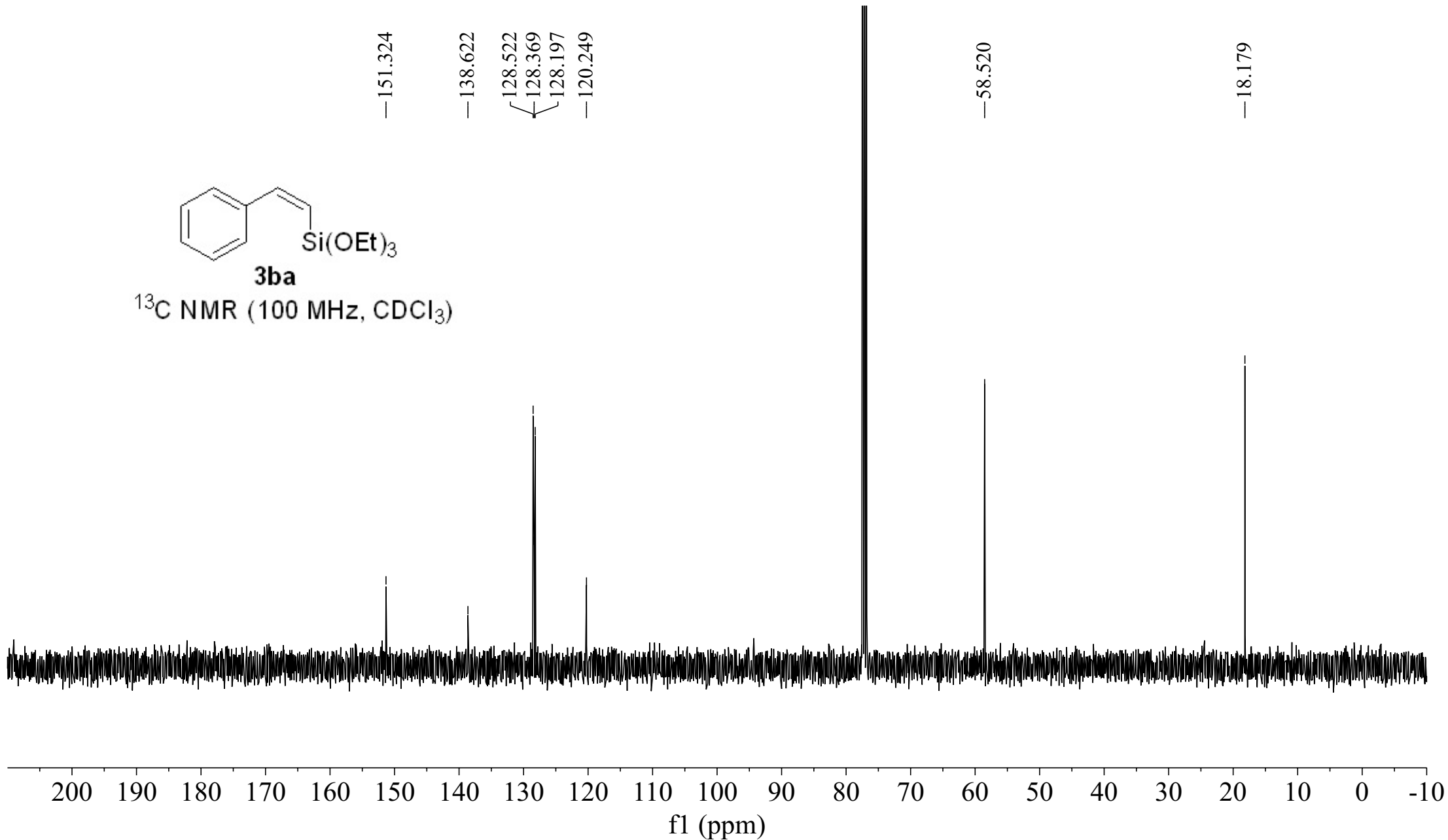
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

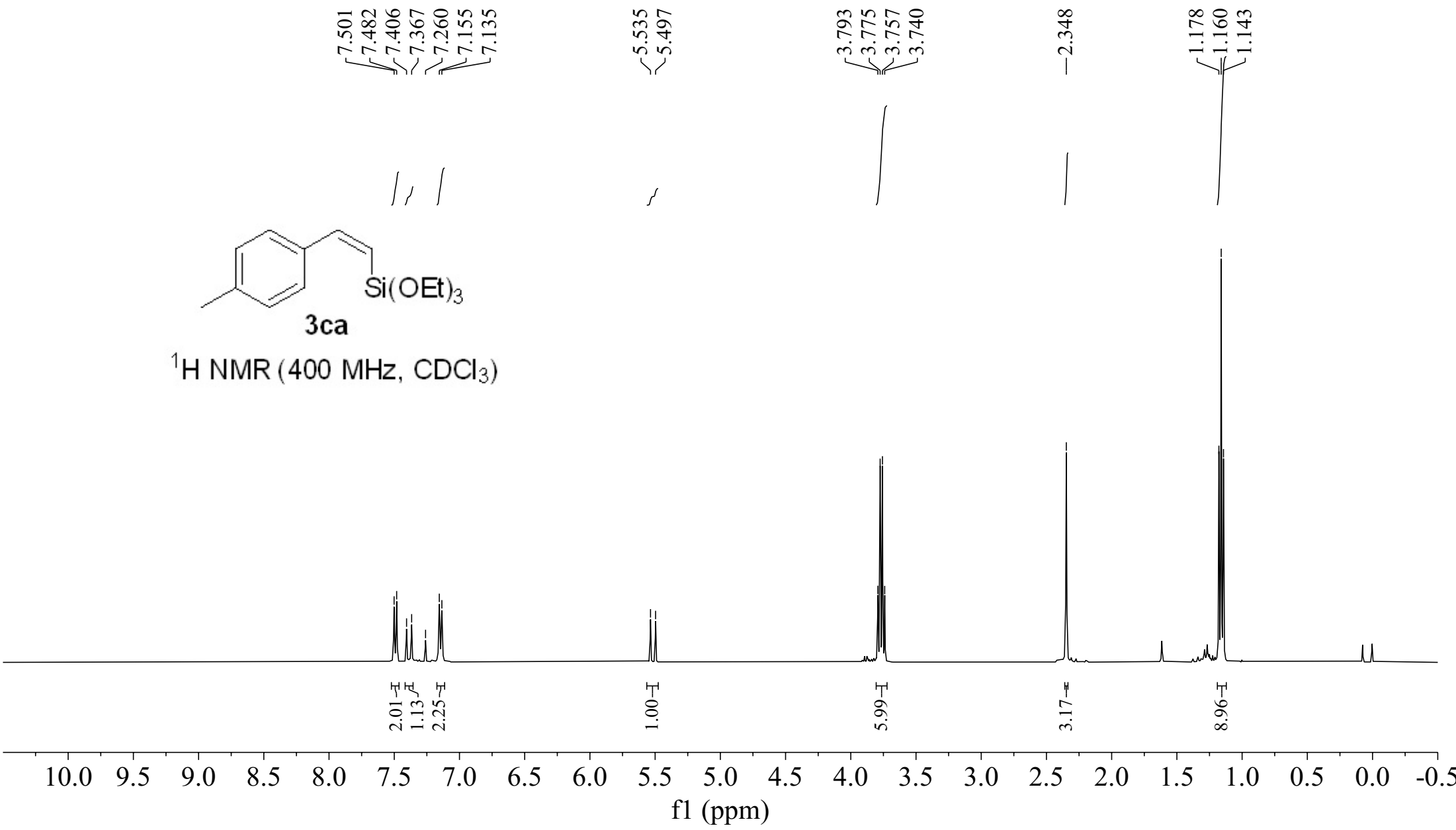
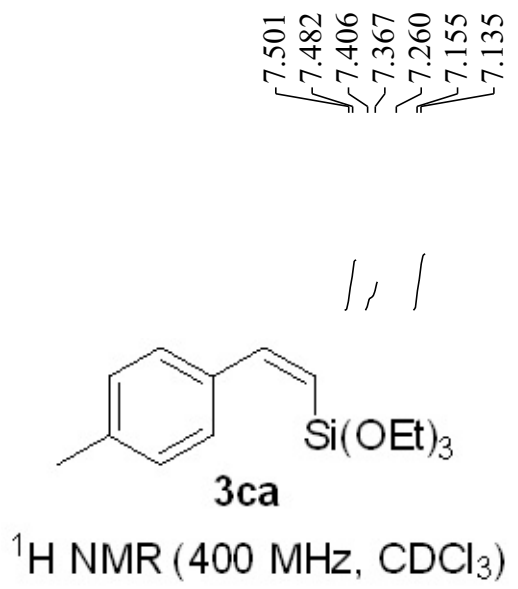




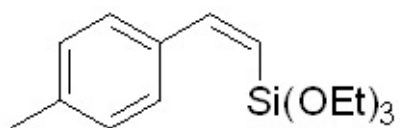
**3ba**

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )









**3ca**

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

— 151.298

~ 138.332

~ 135.801

~ 128.910

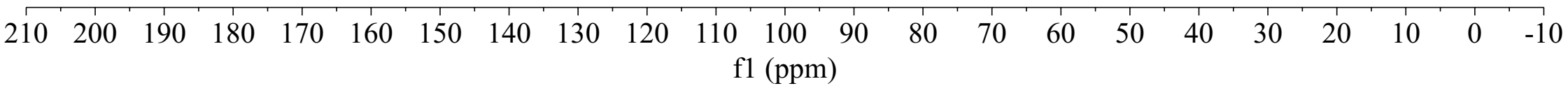
~ 128.533

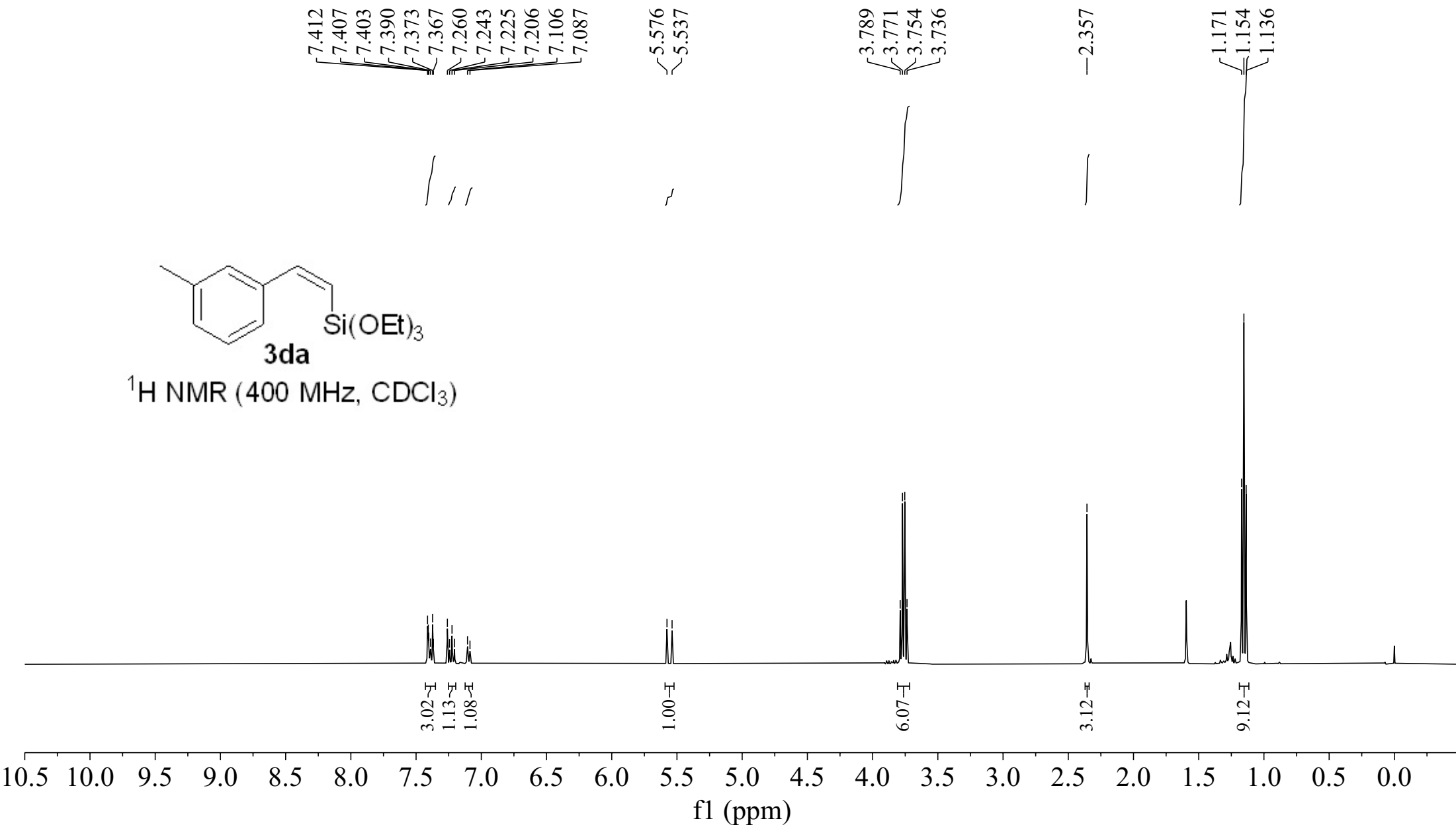
— 118.751

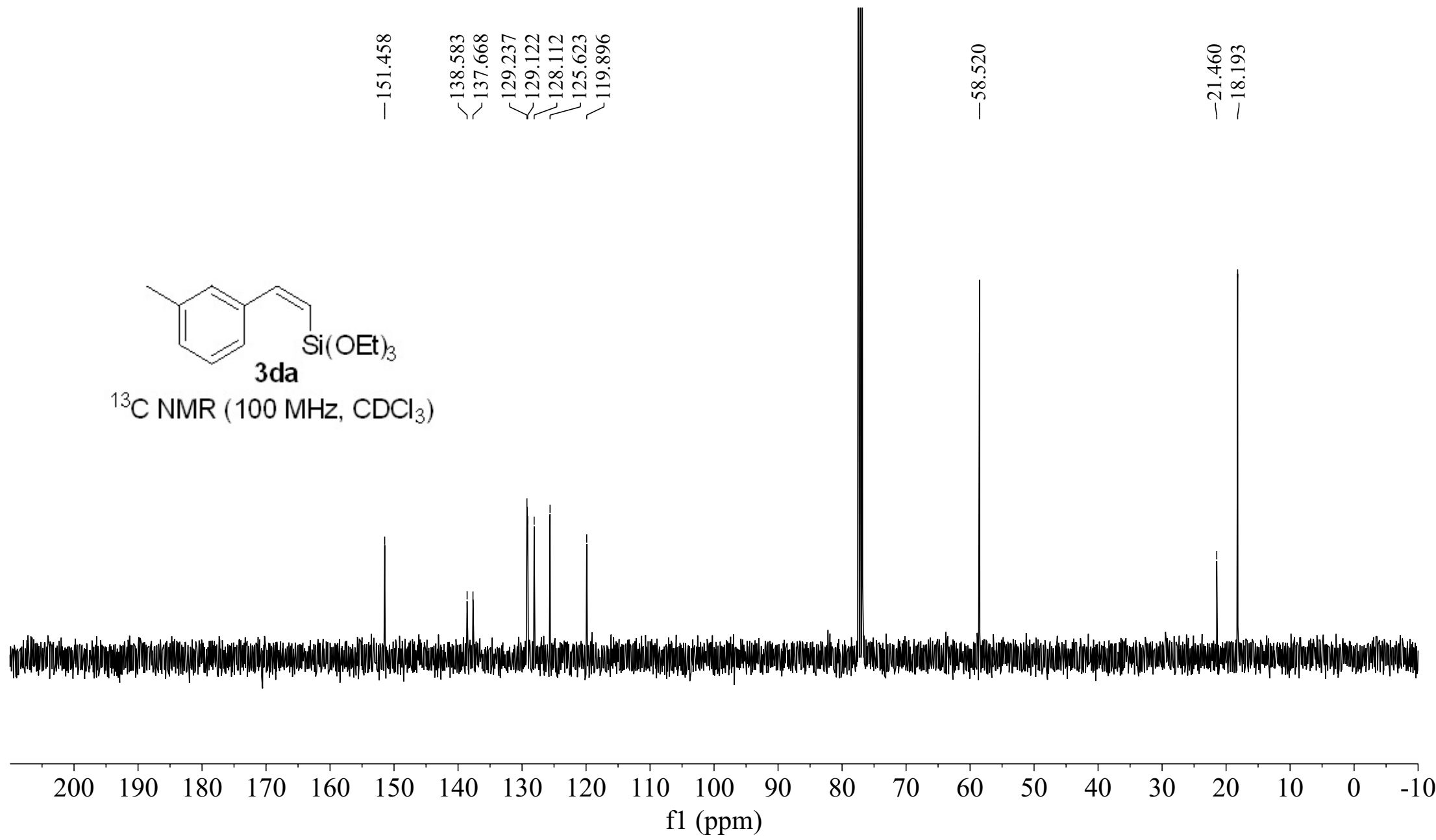
— 58.489

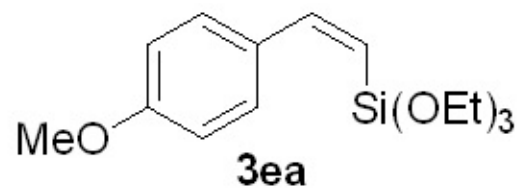
~ 21.409

~ 18.187

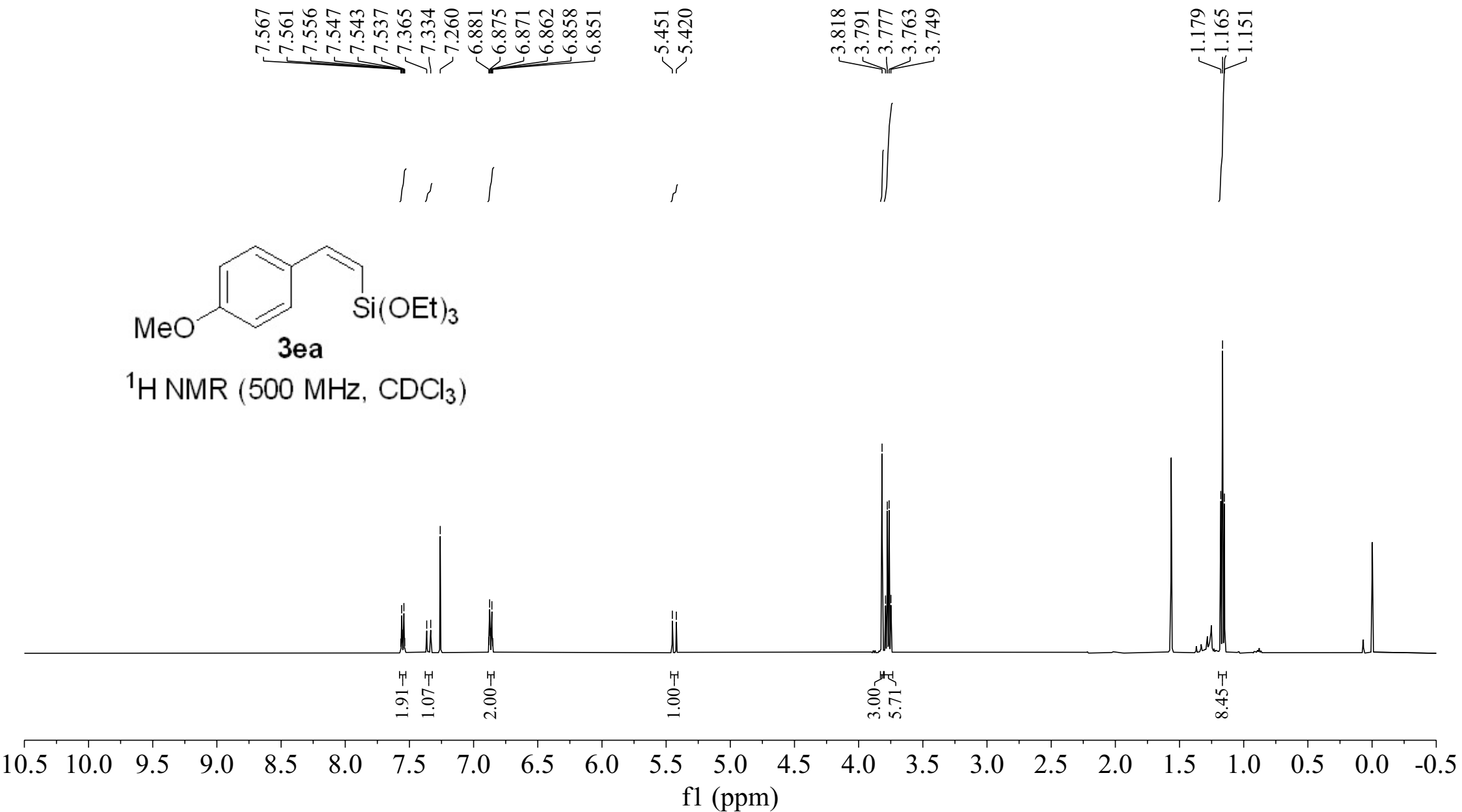


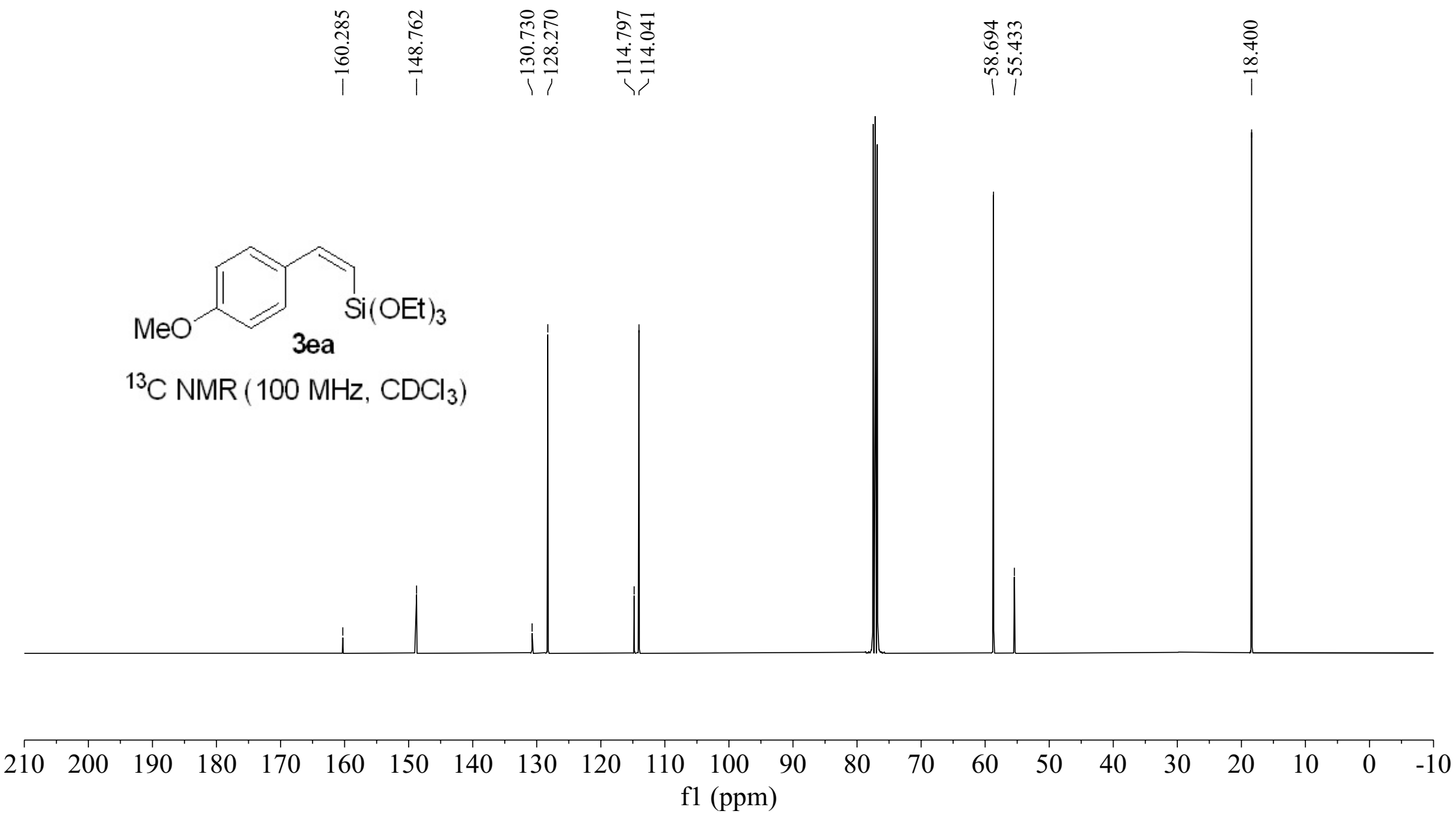


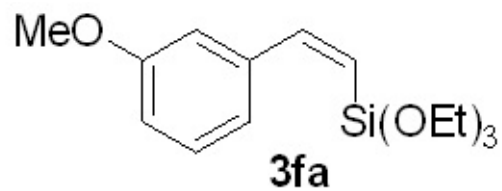




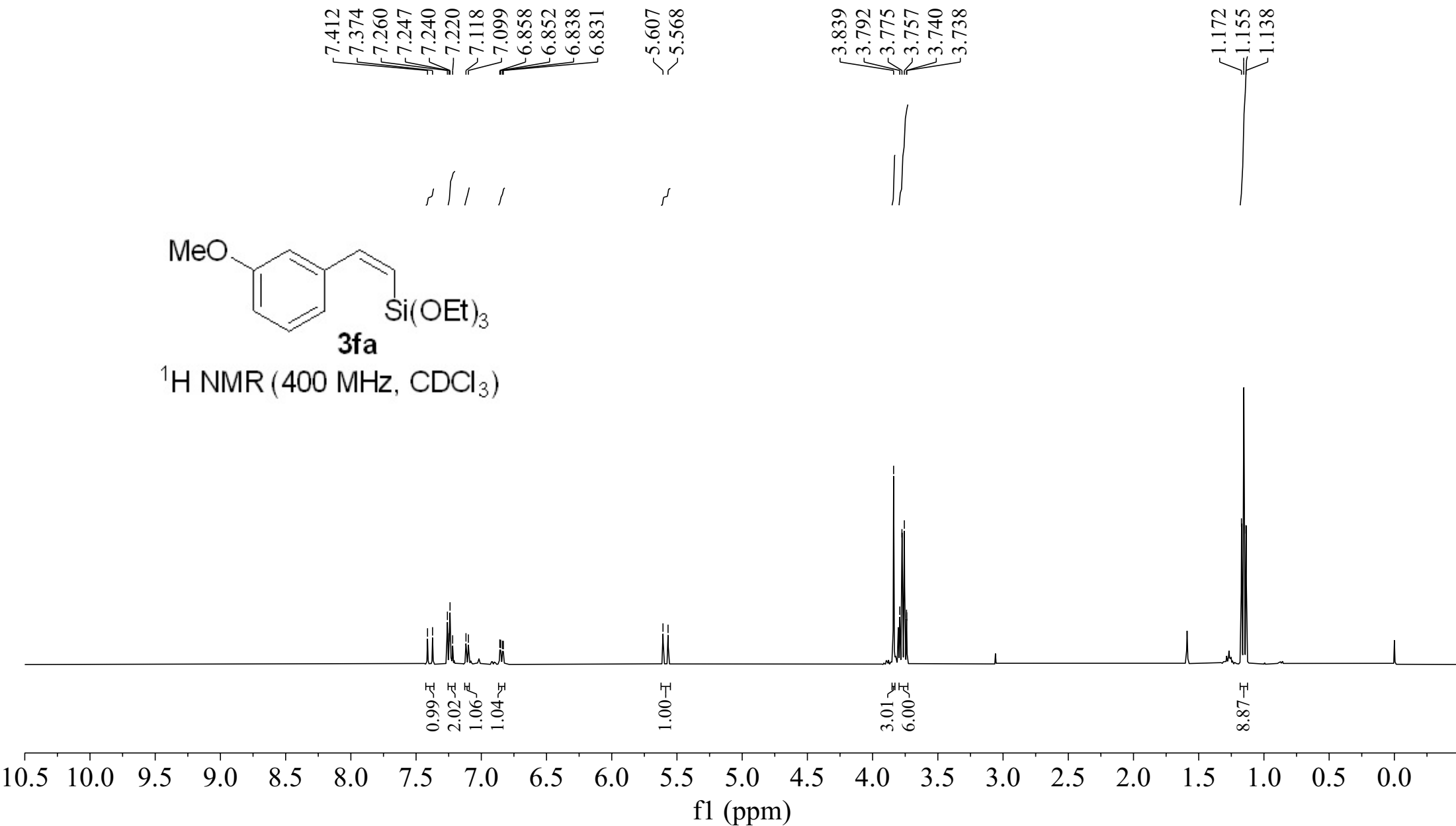
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

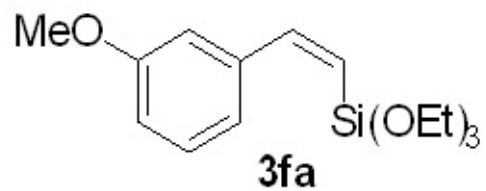




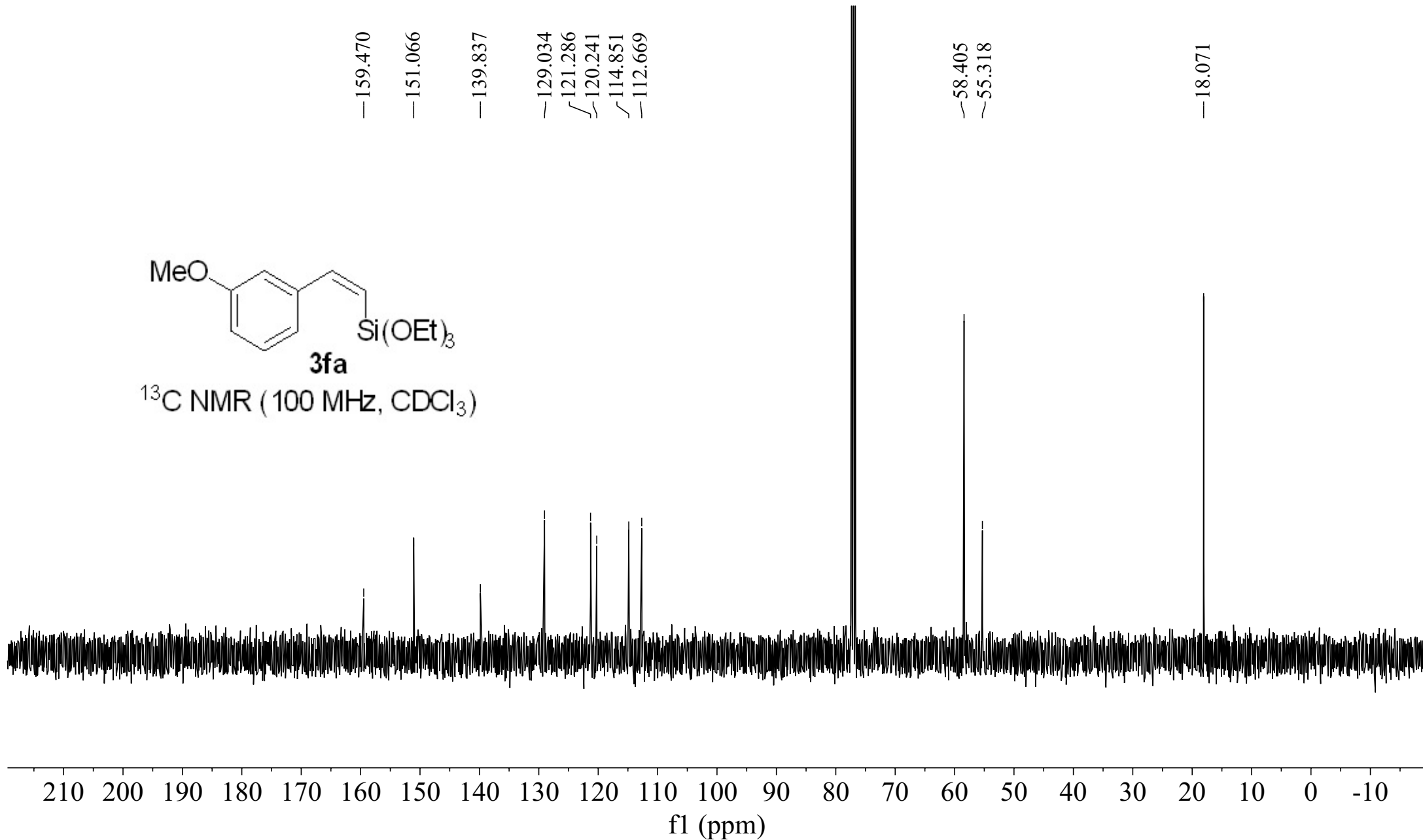


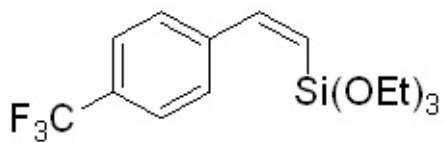
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





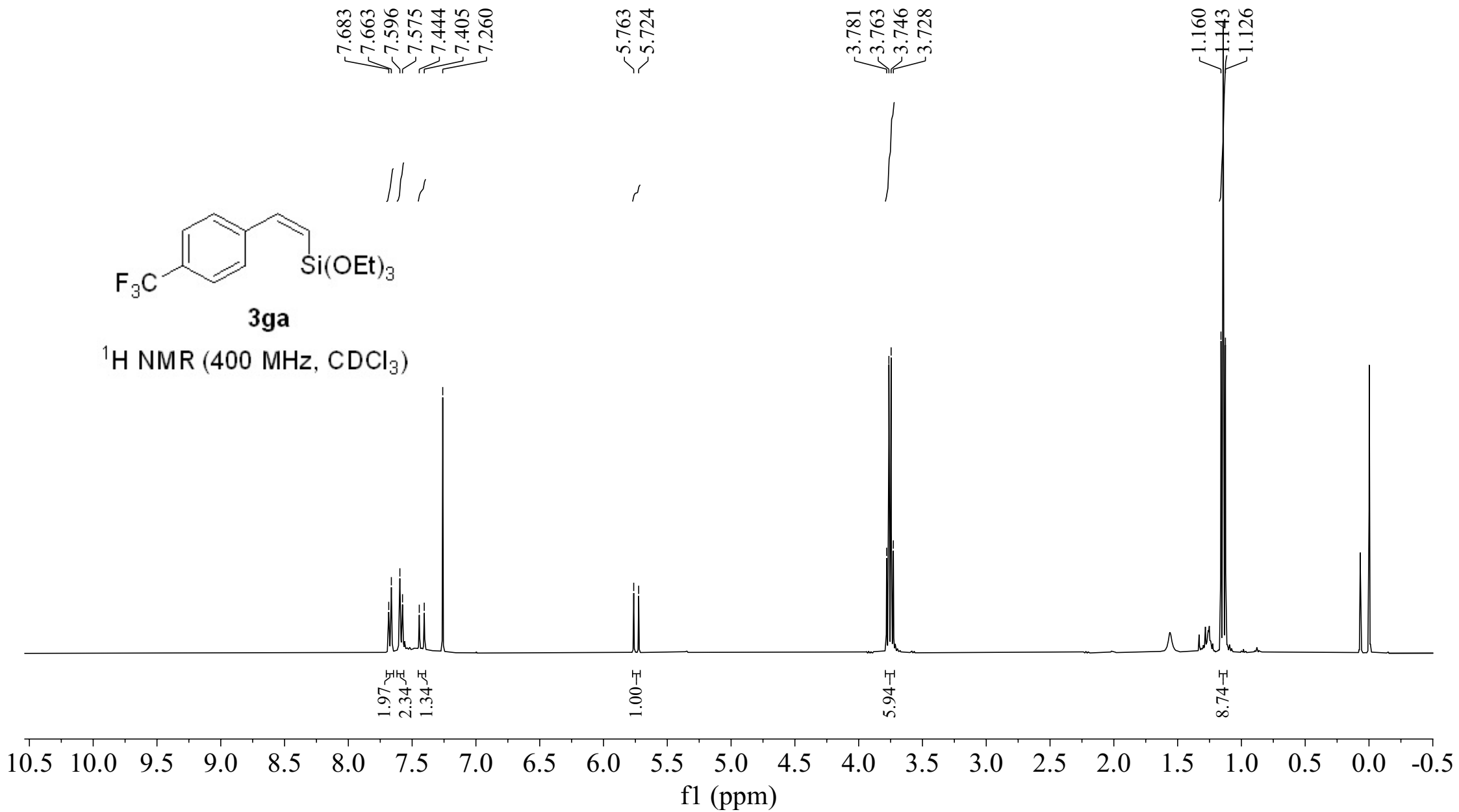
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



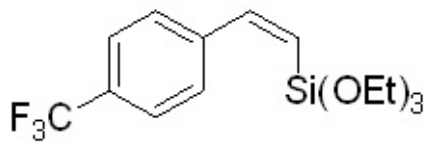


**3ga**

$^1H$  NMR (400 MHz,  $CDCl_3$ )



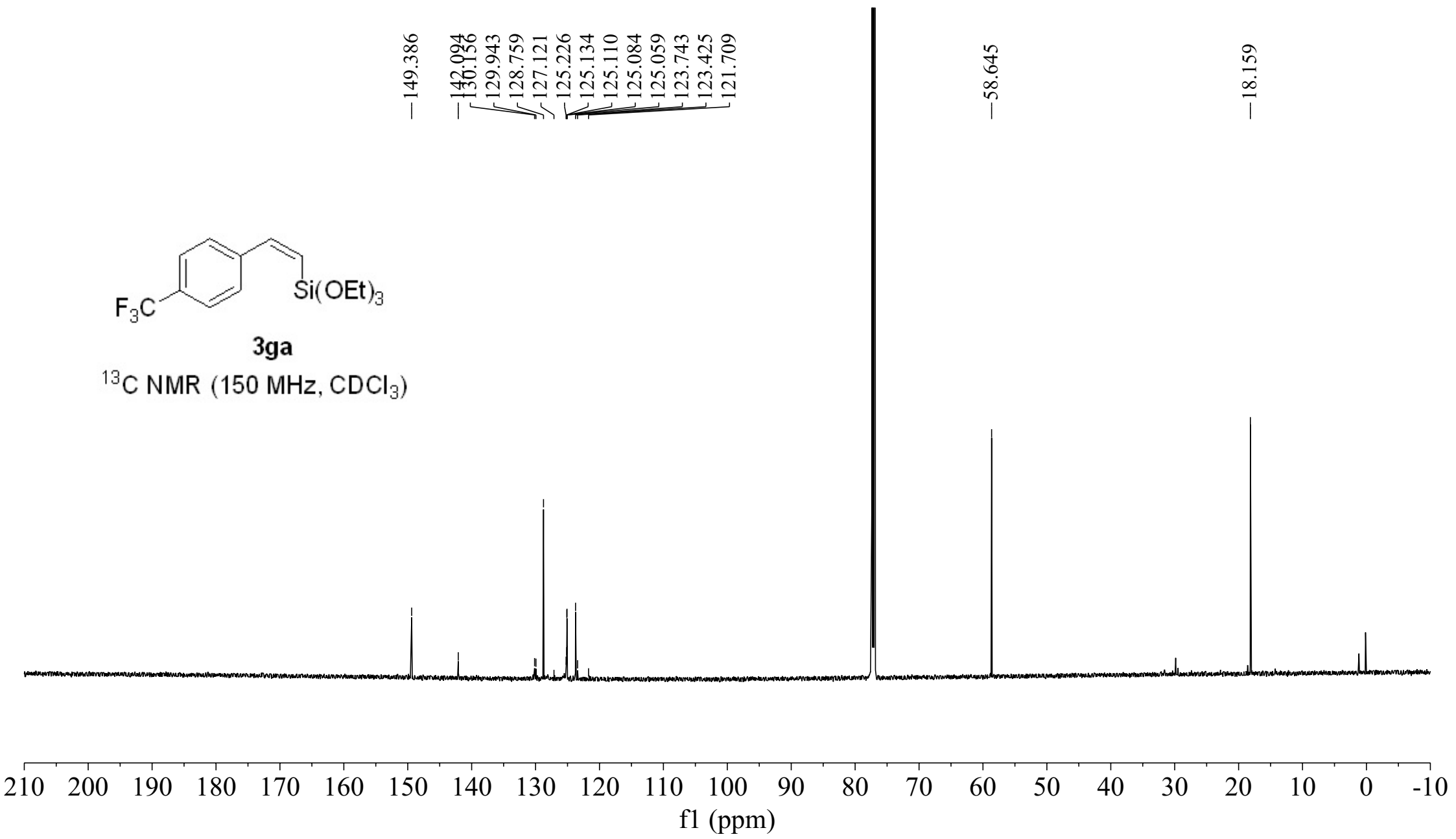


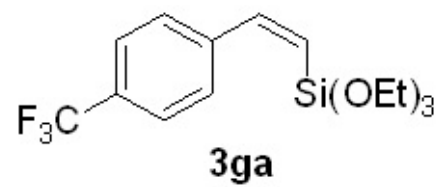


**3ga**

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)

- 149.386
- 142.094
- 136.136
- 129.943
- 128.759
- 127.121
- 125.226
- 125.134
- 125.110
- 125.084
- 125.059
- 123.743
- 123.425
- 121.709





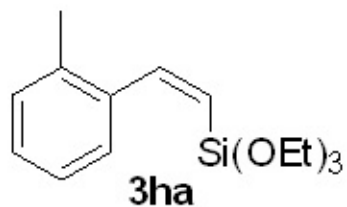
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

---62.590

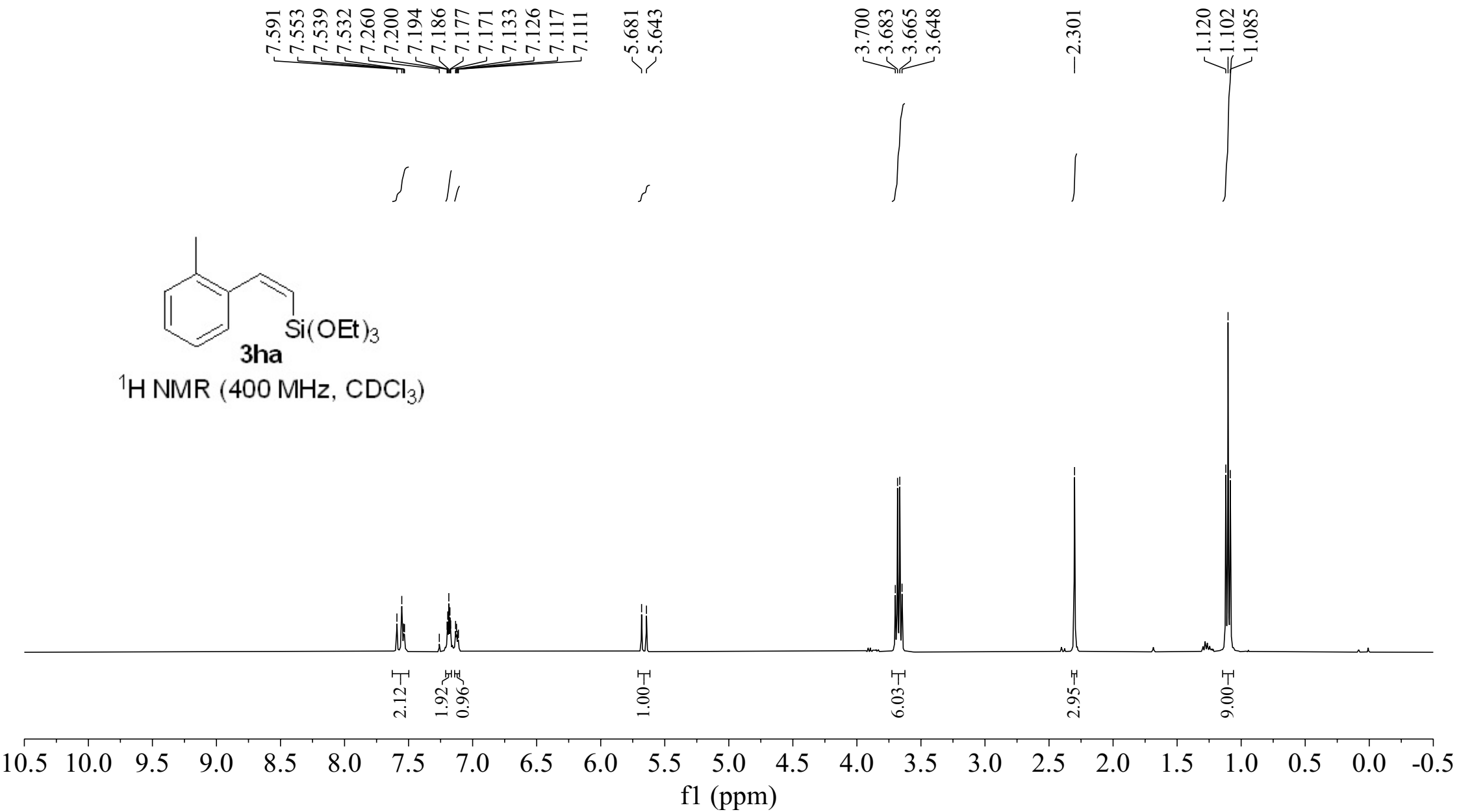


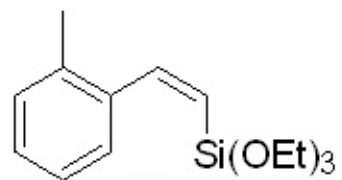
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)



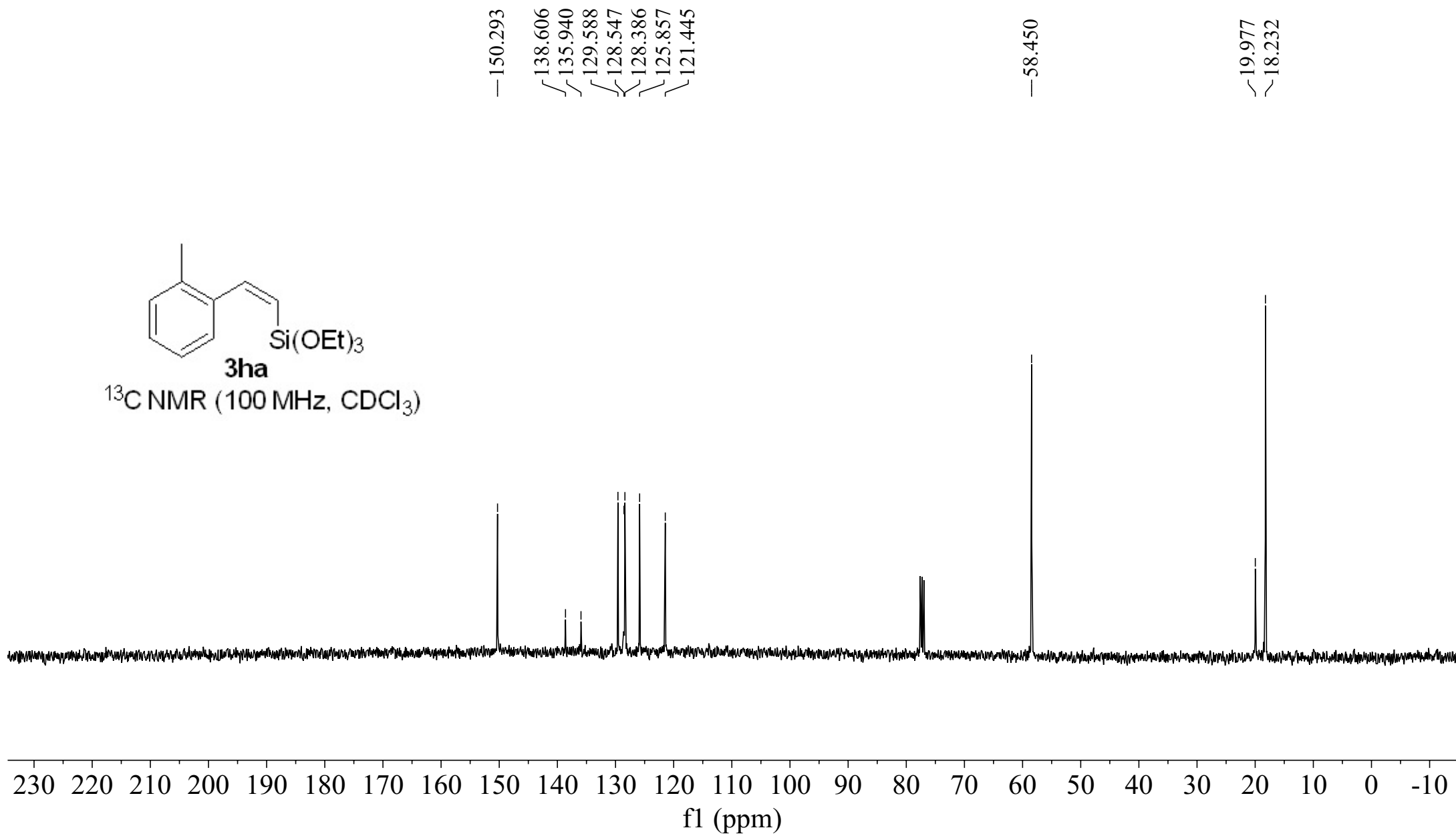
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

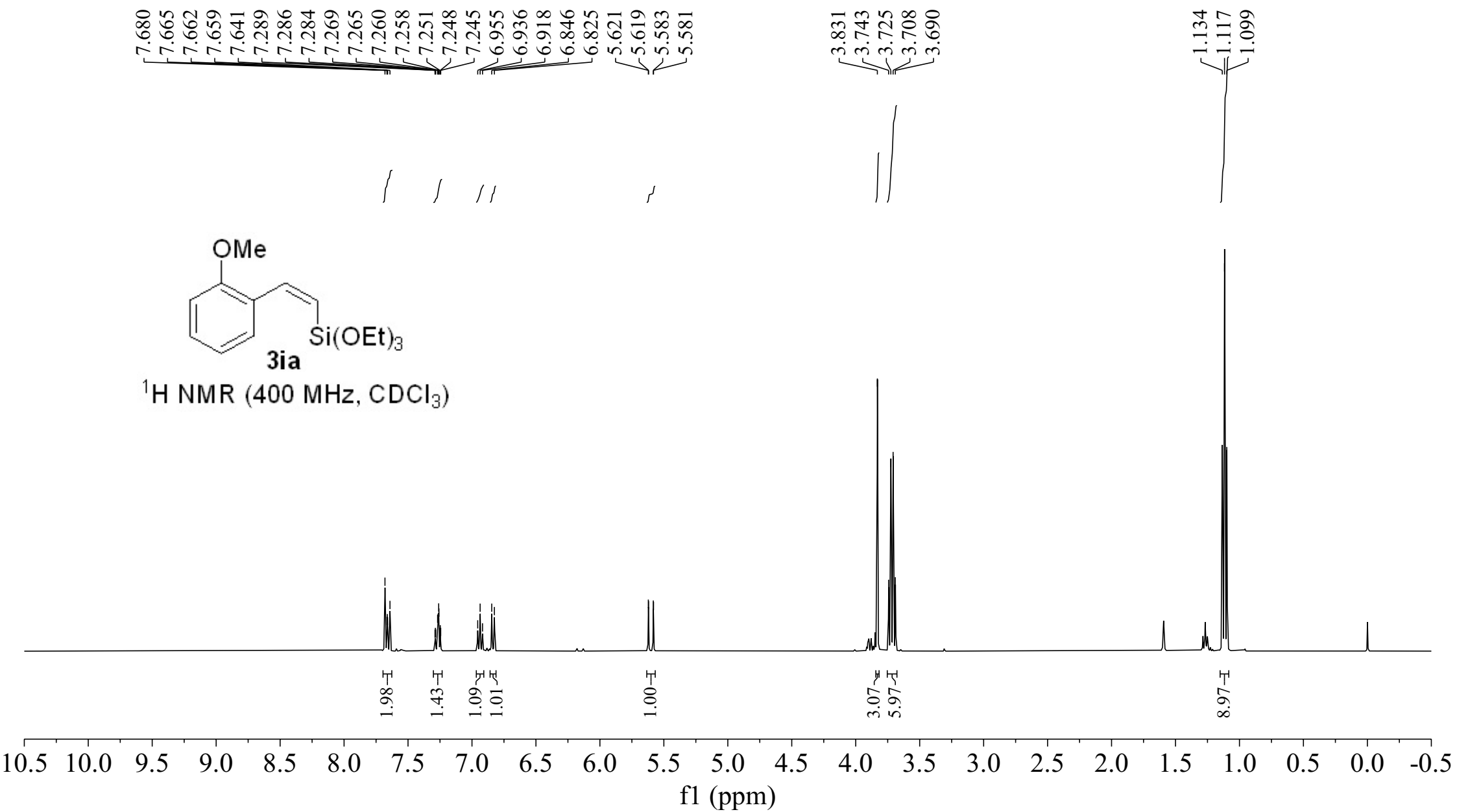


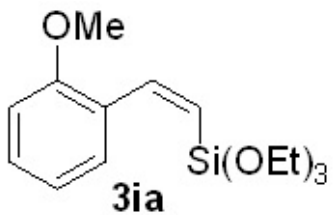


**3ha**

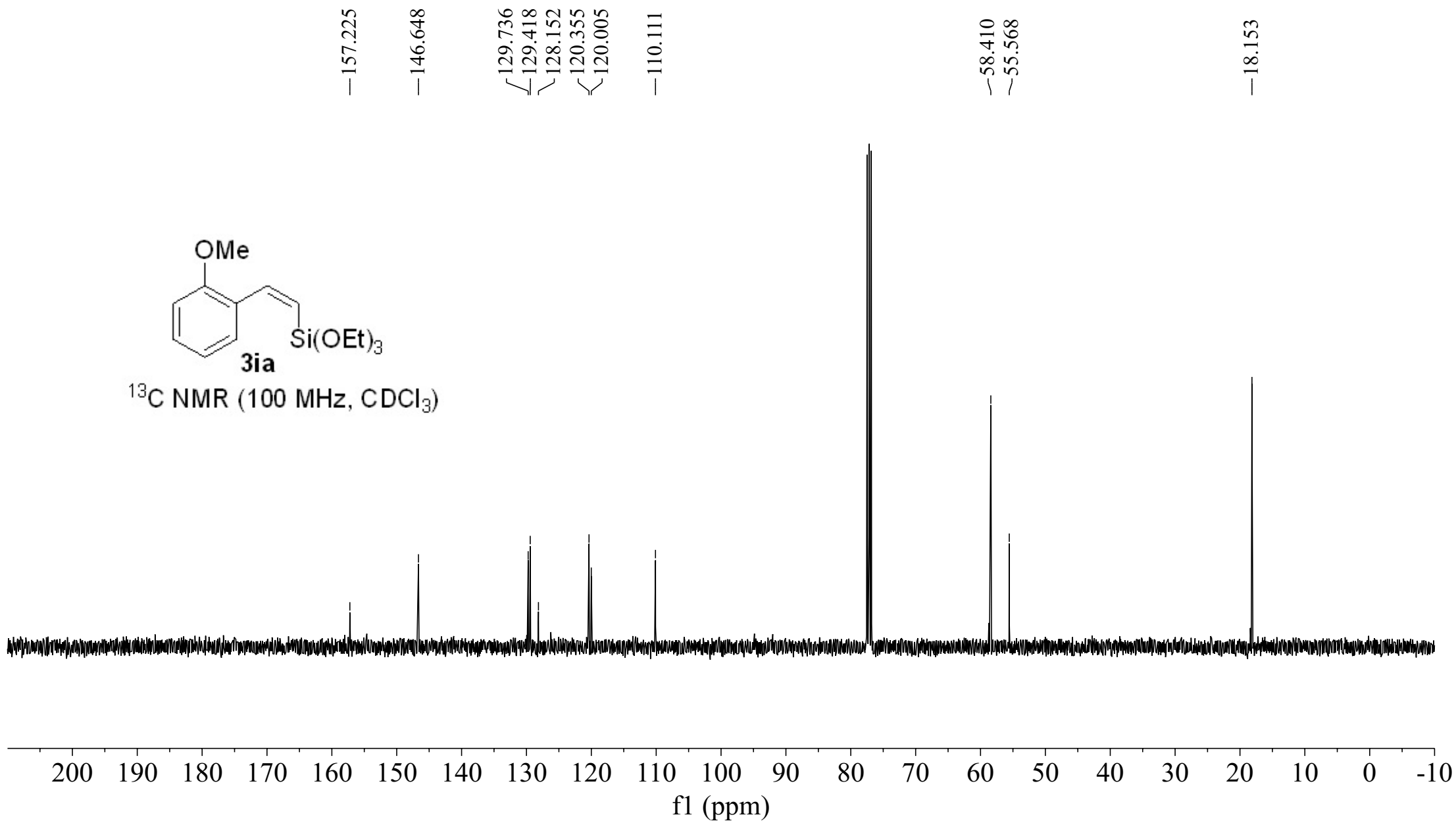
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

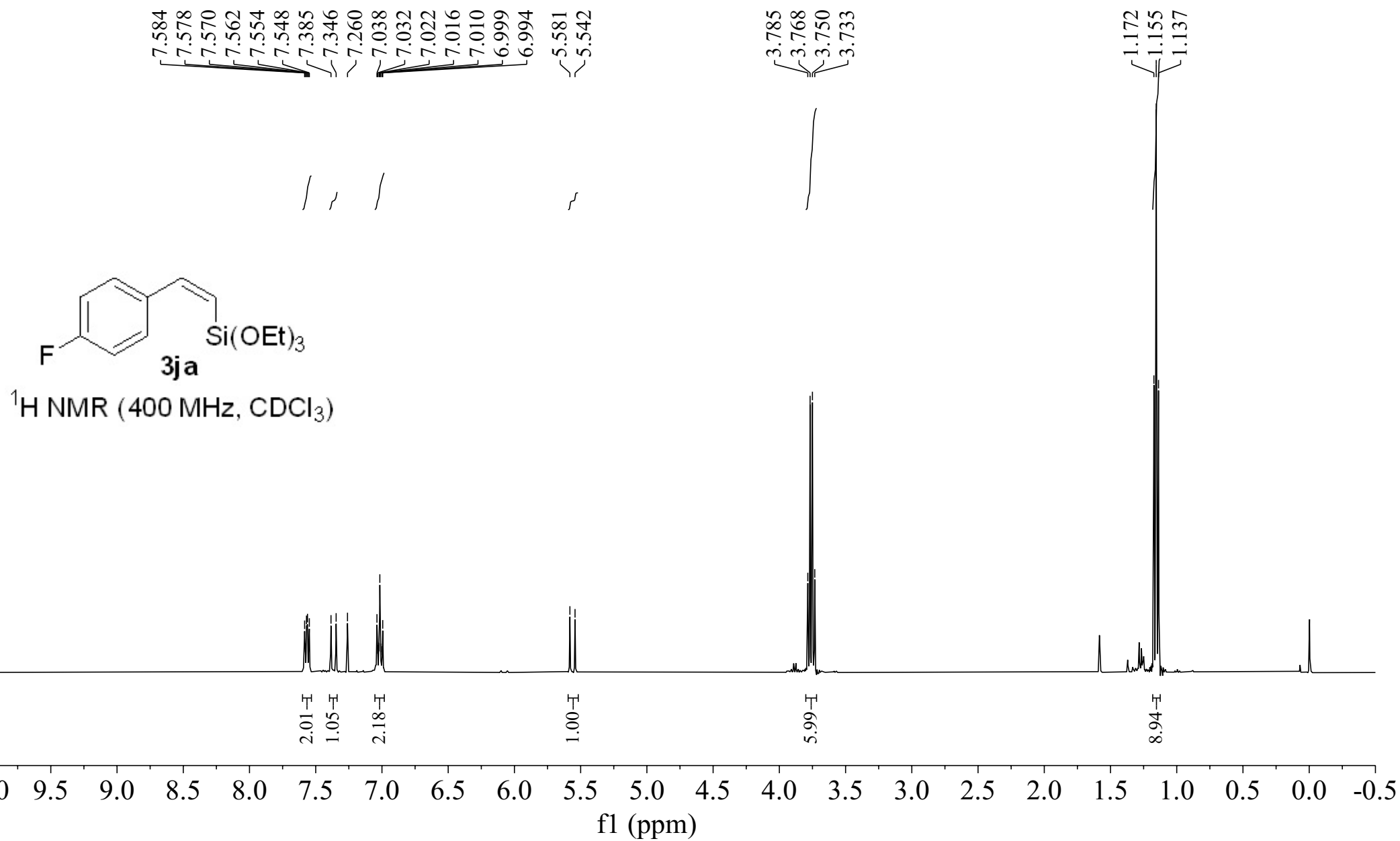






$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



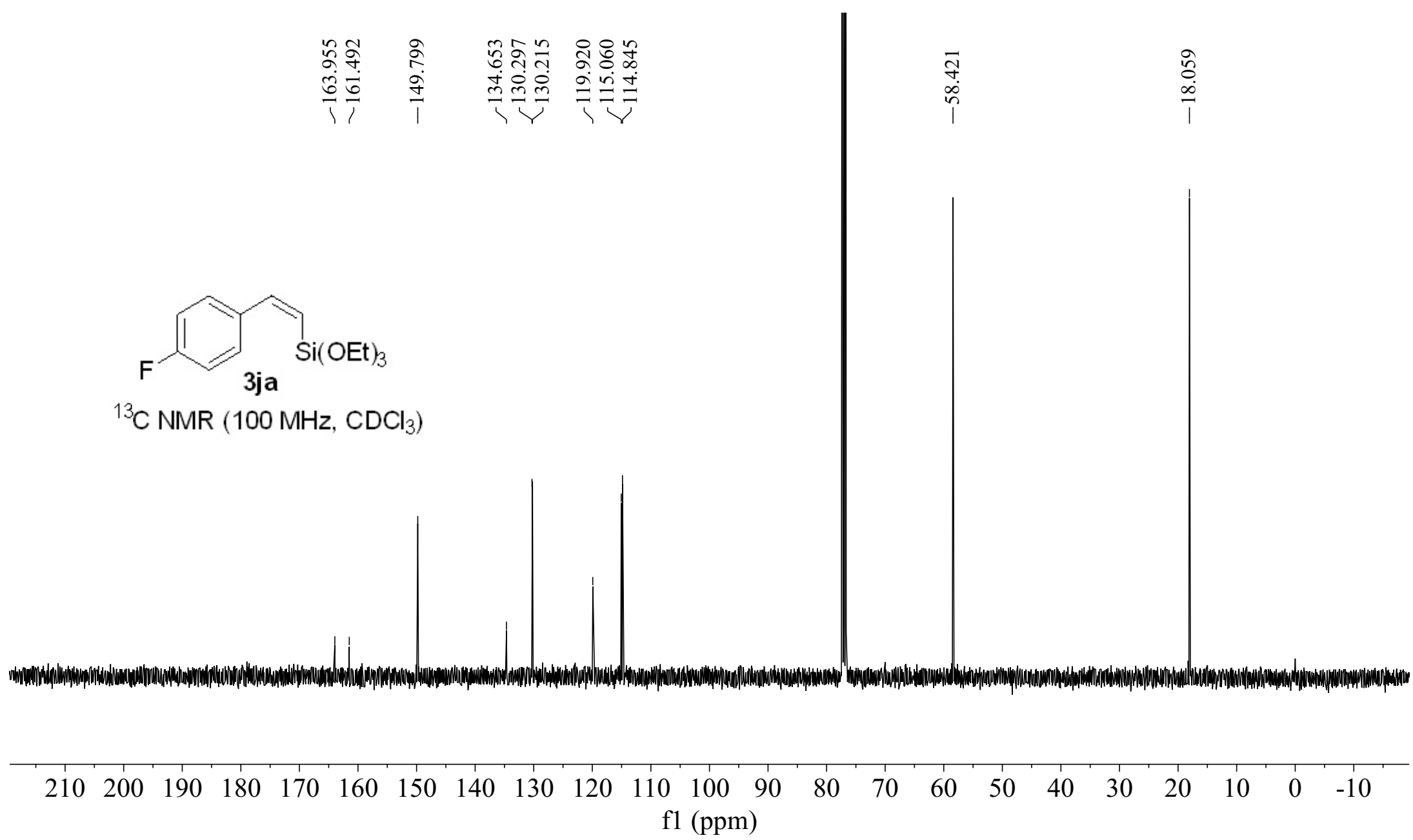




~163.955  
~161.492  
—149.799  
/ 134.653  
\ 130.297  
/ 130.215  
/ 119.920  
\ 115.060  
\ 114.845

—58.421

—18.059





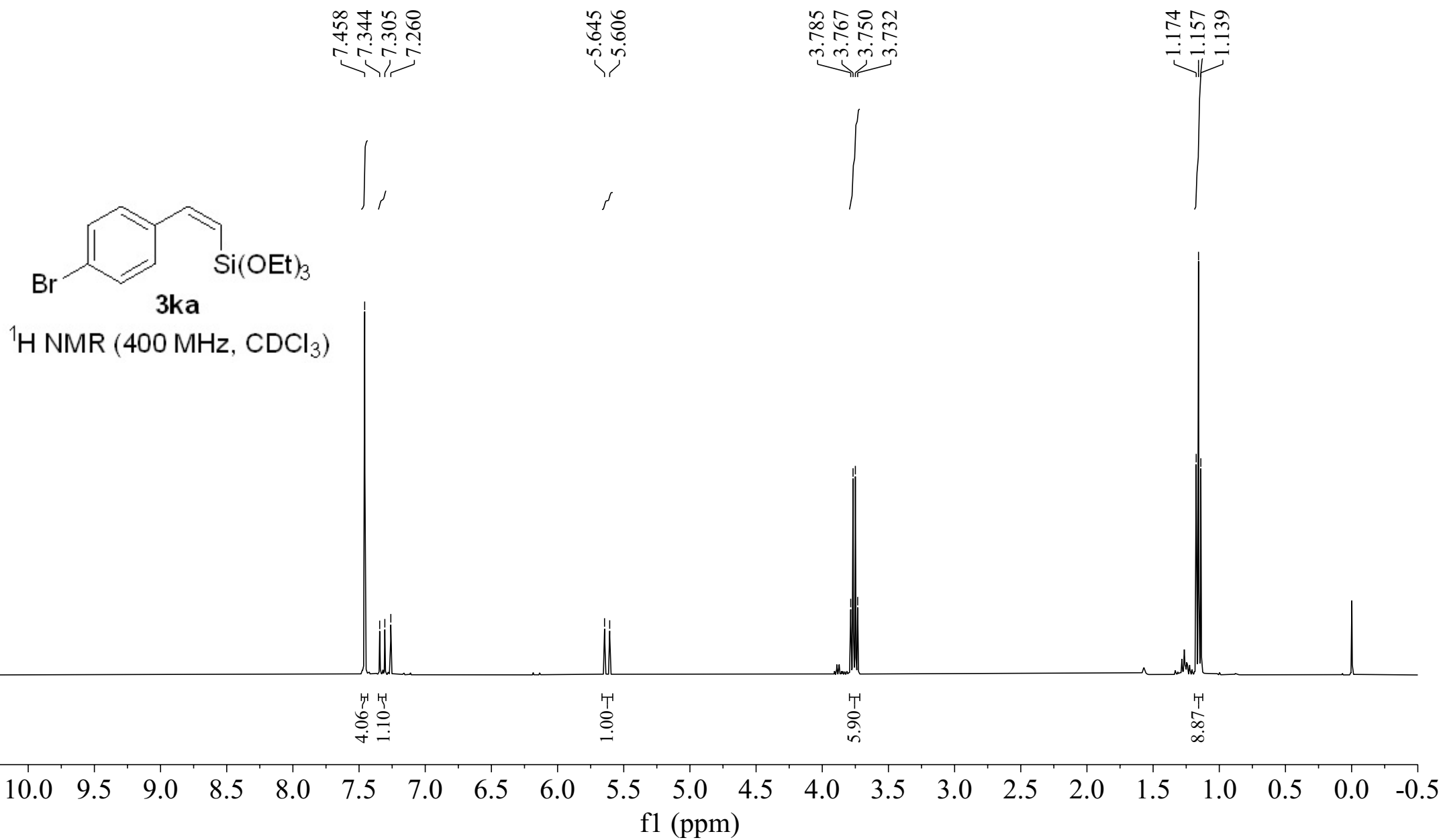


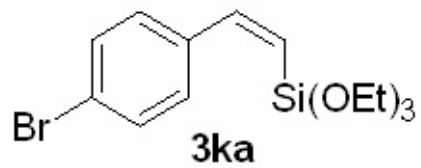
— -113.431



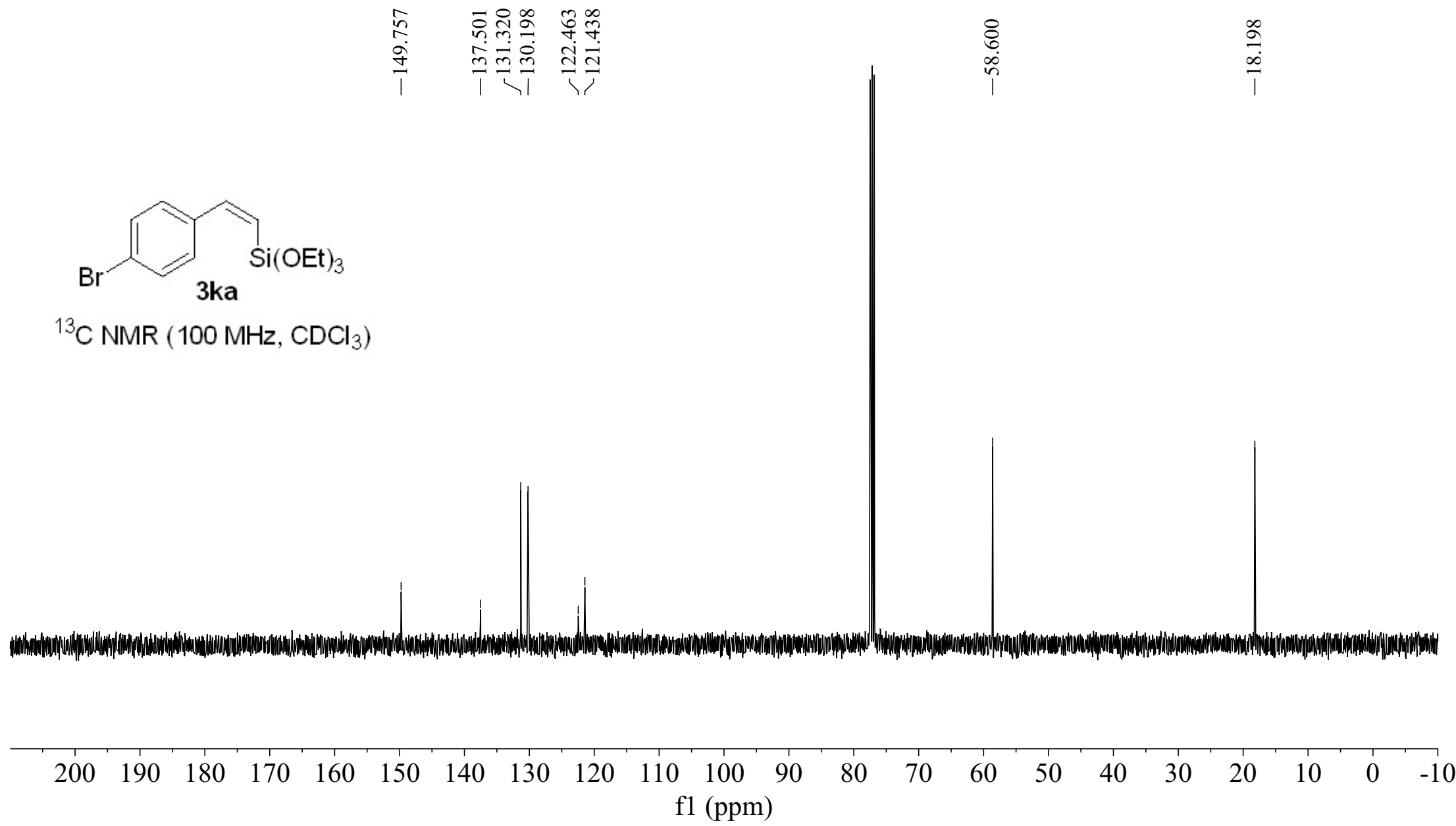
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

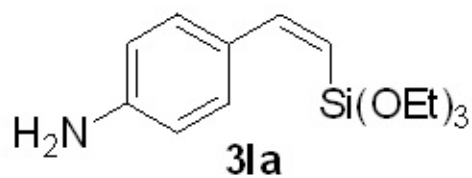
f1 (ppm)



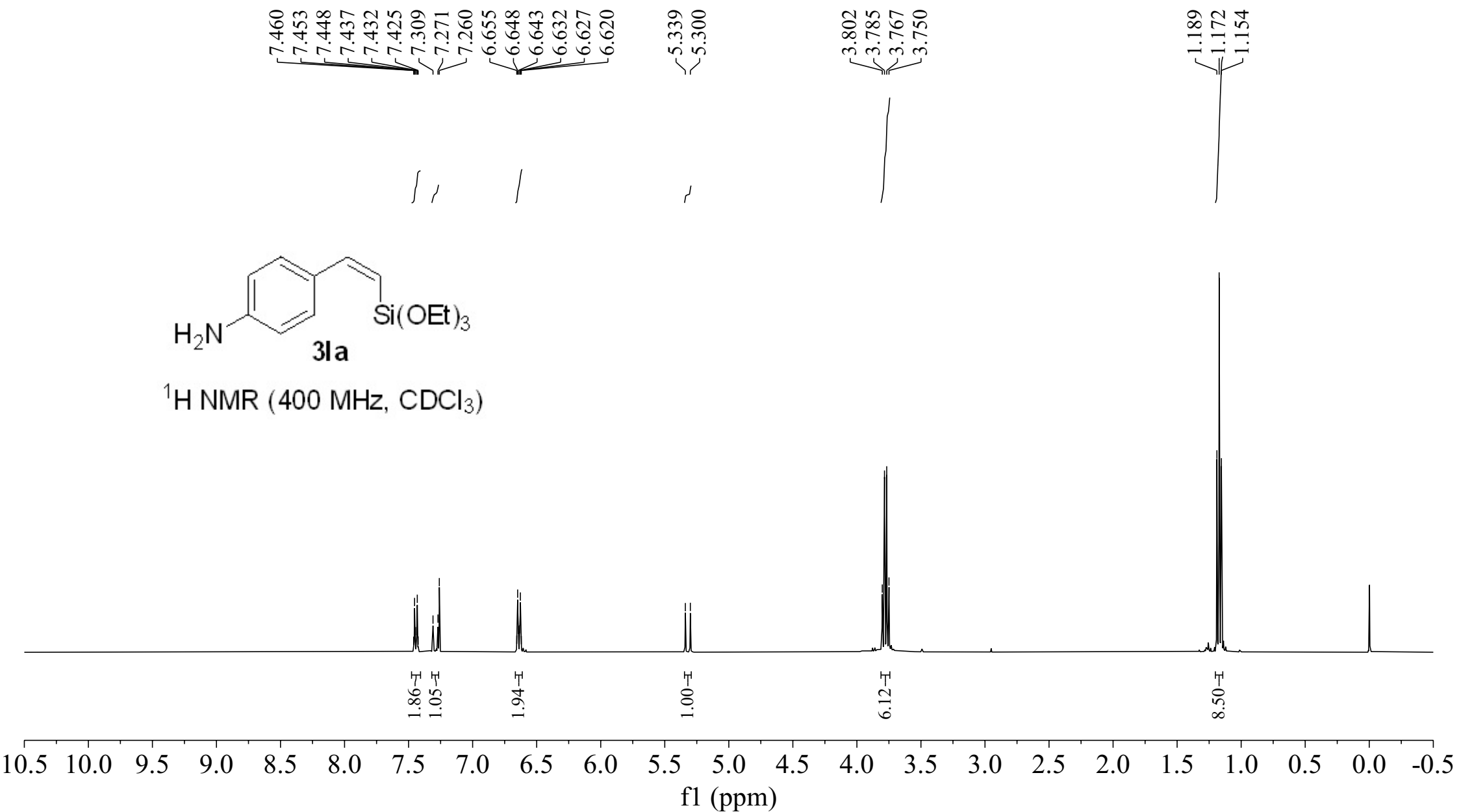


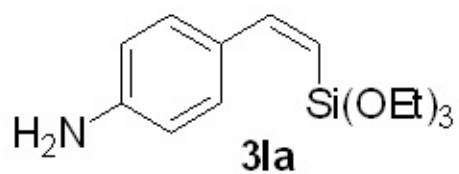
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



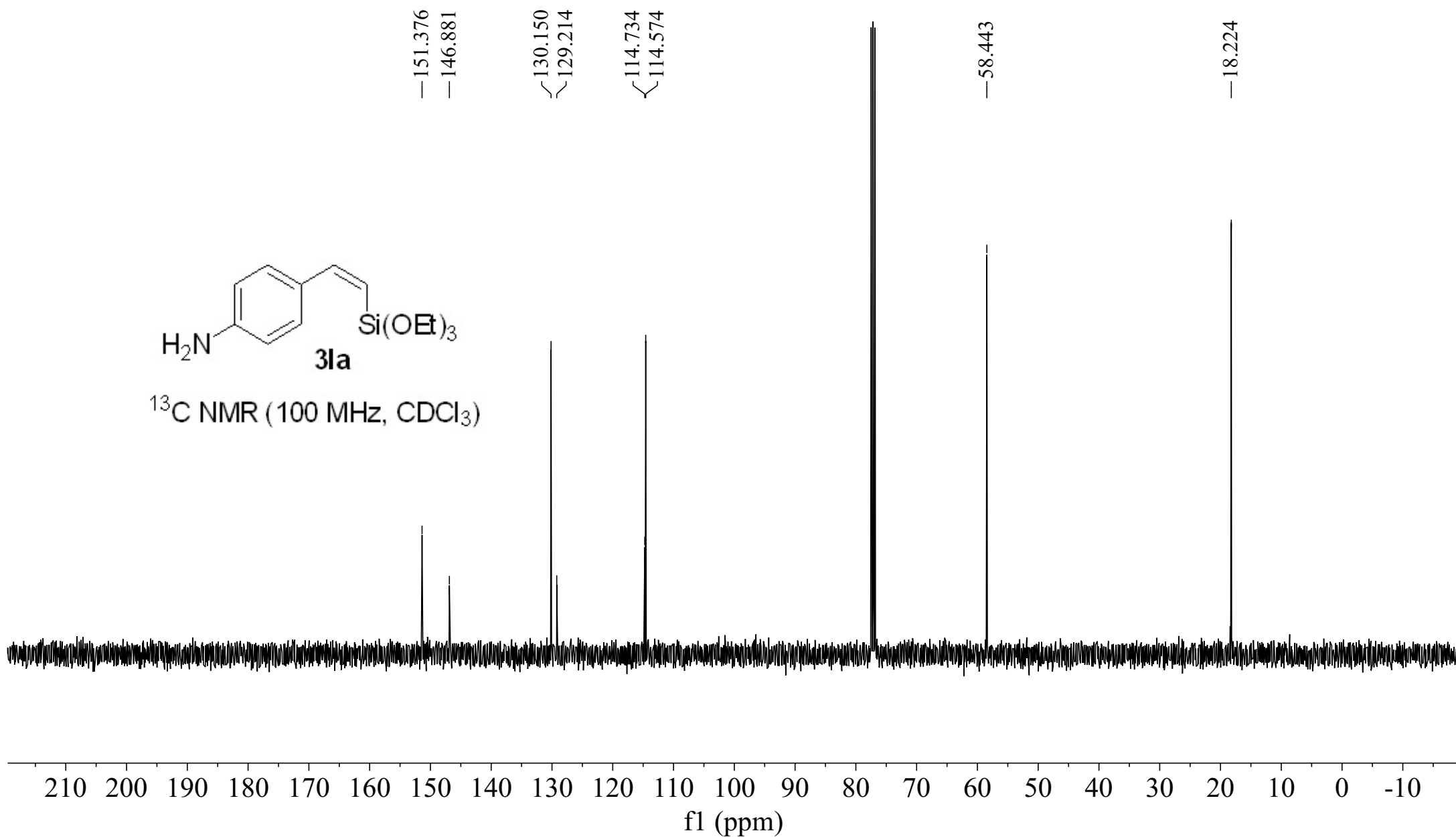


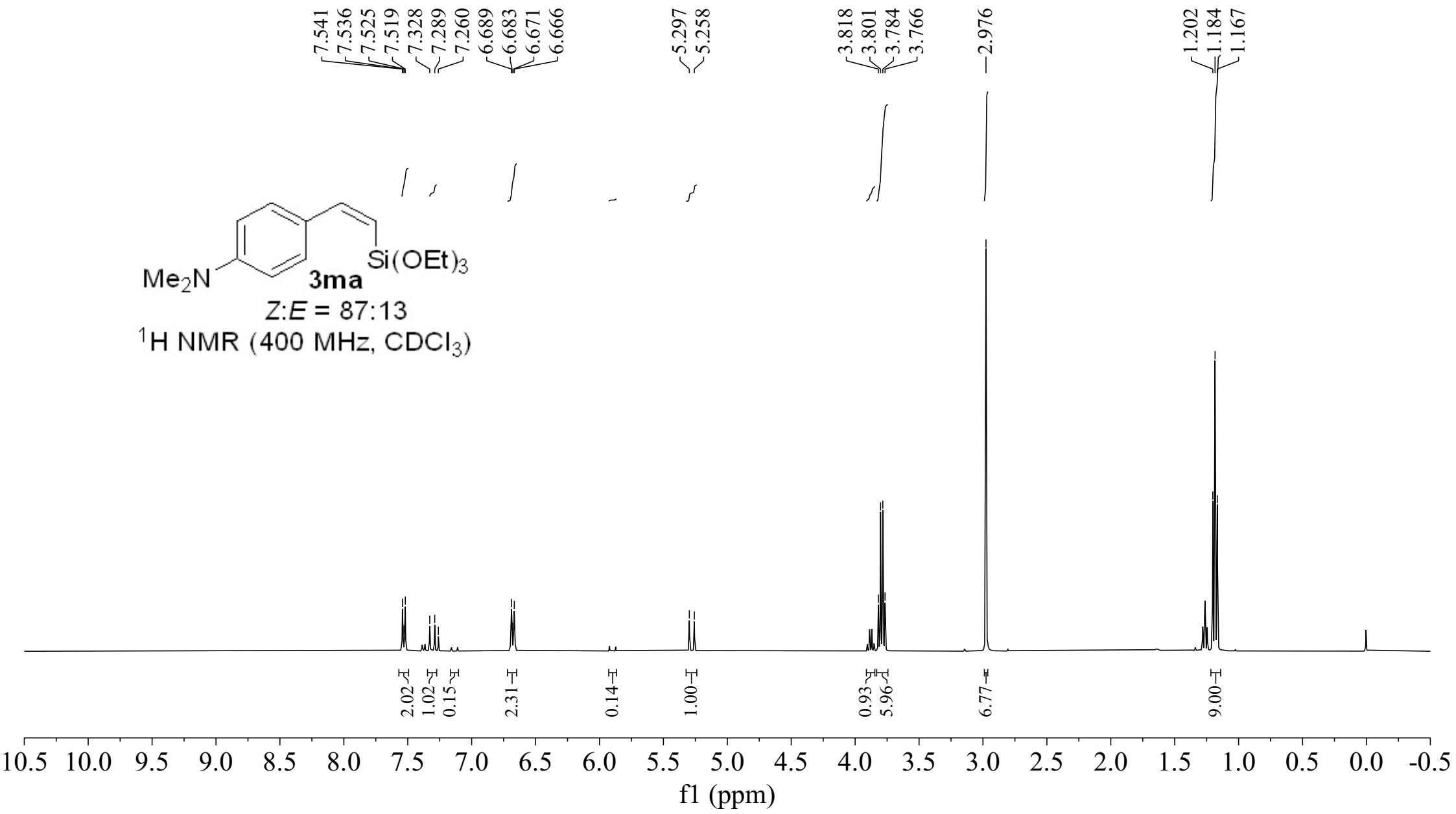
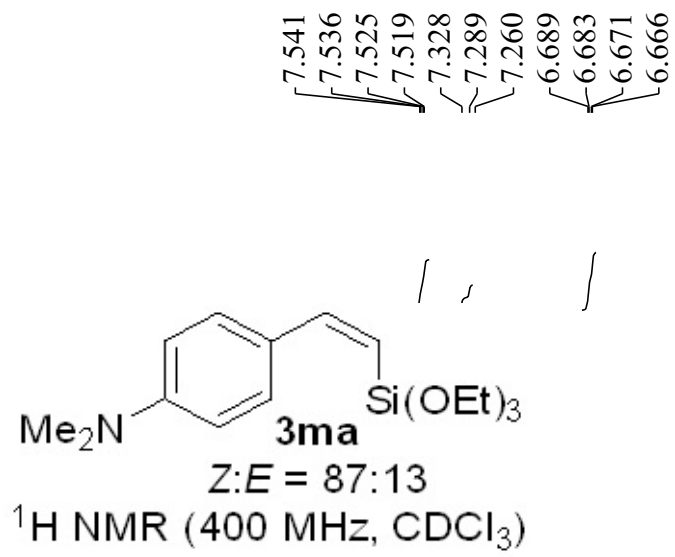
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

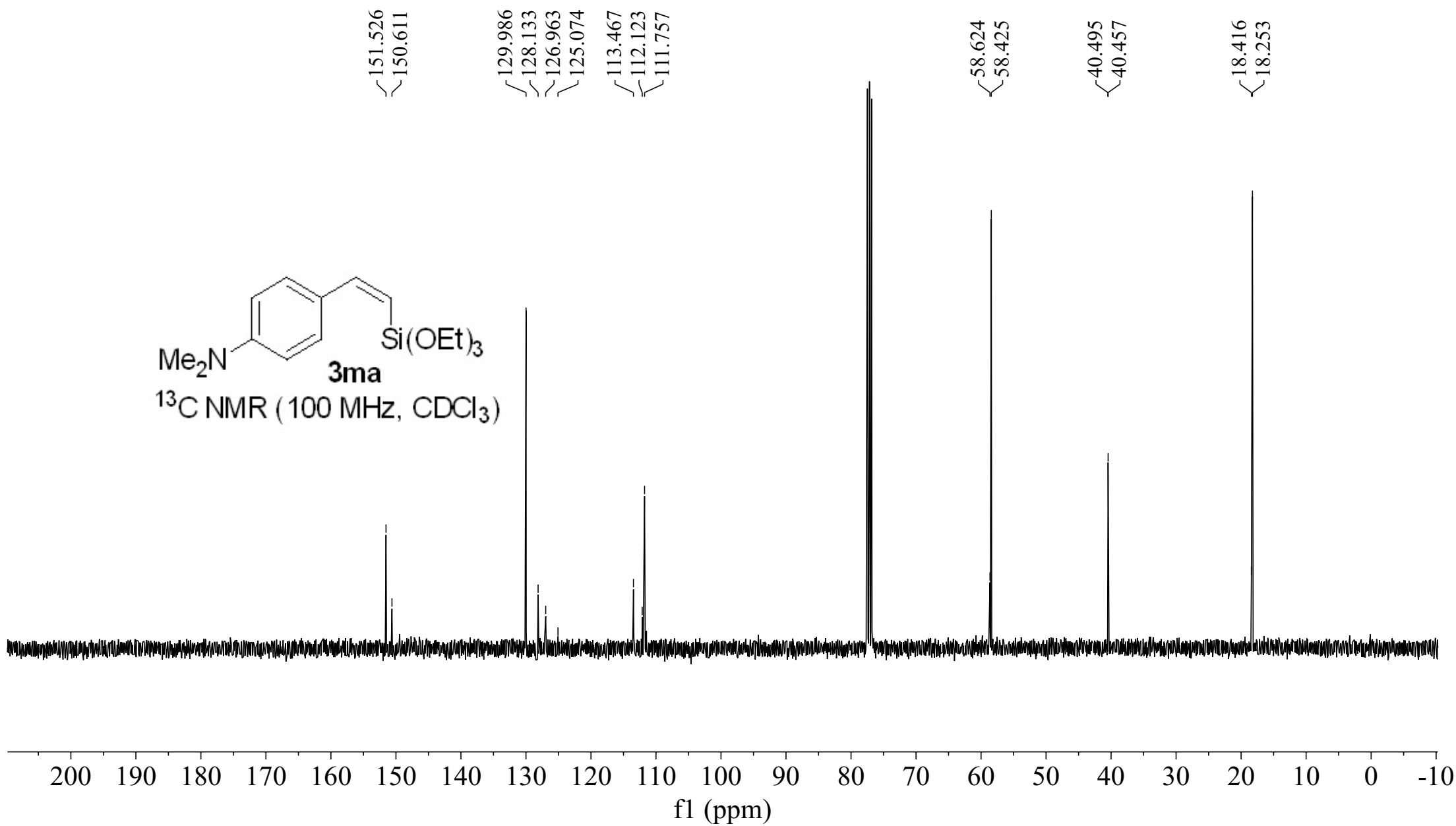


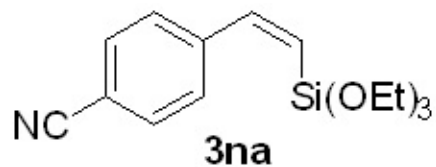


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

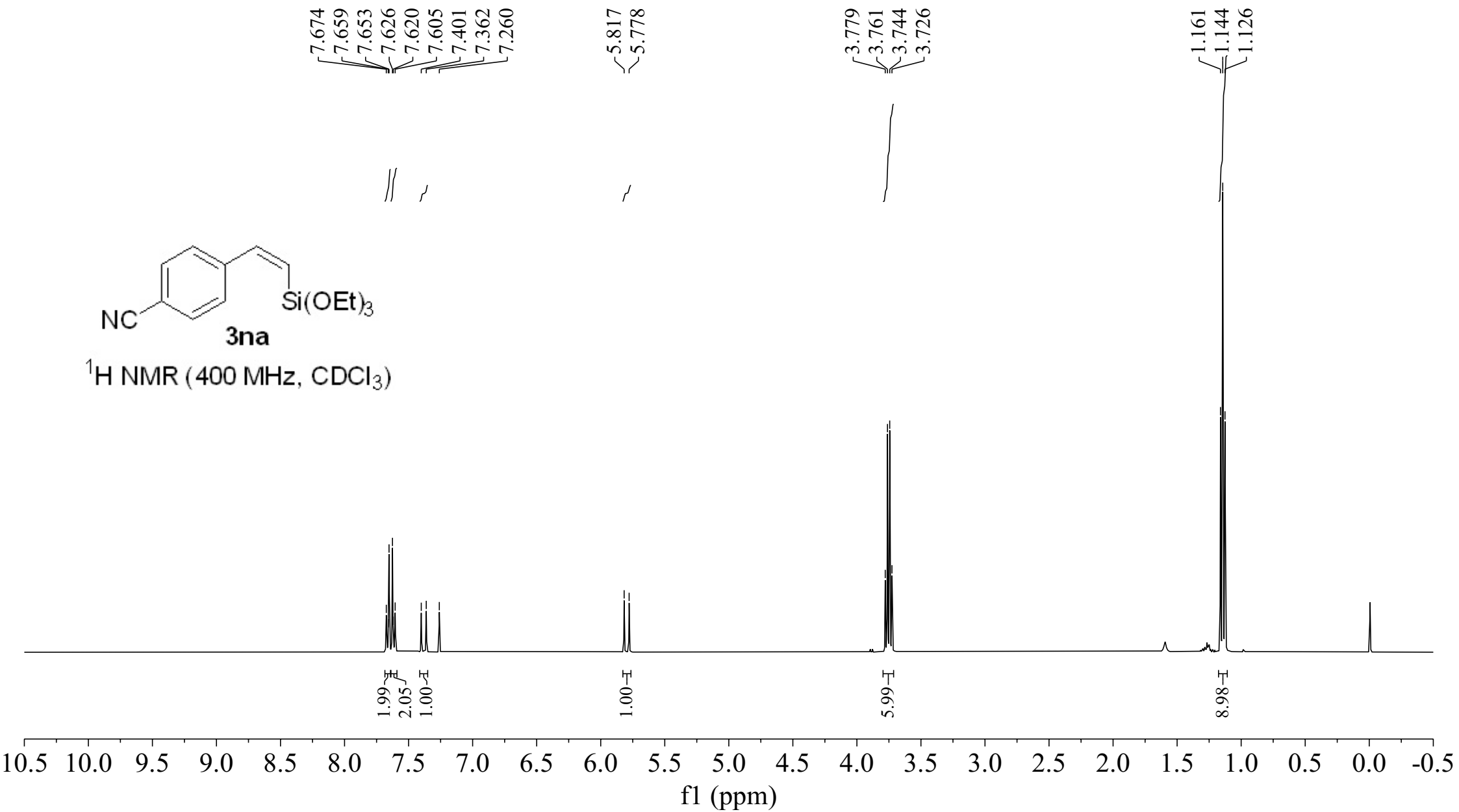




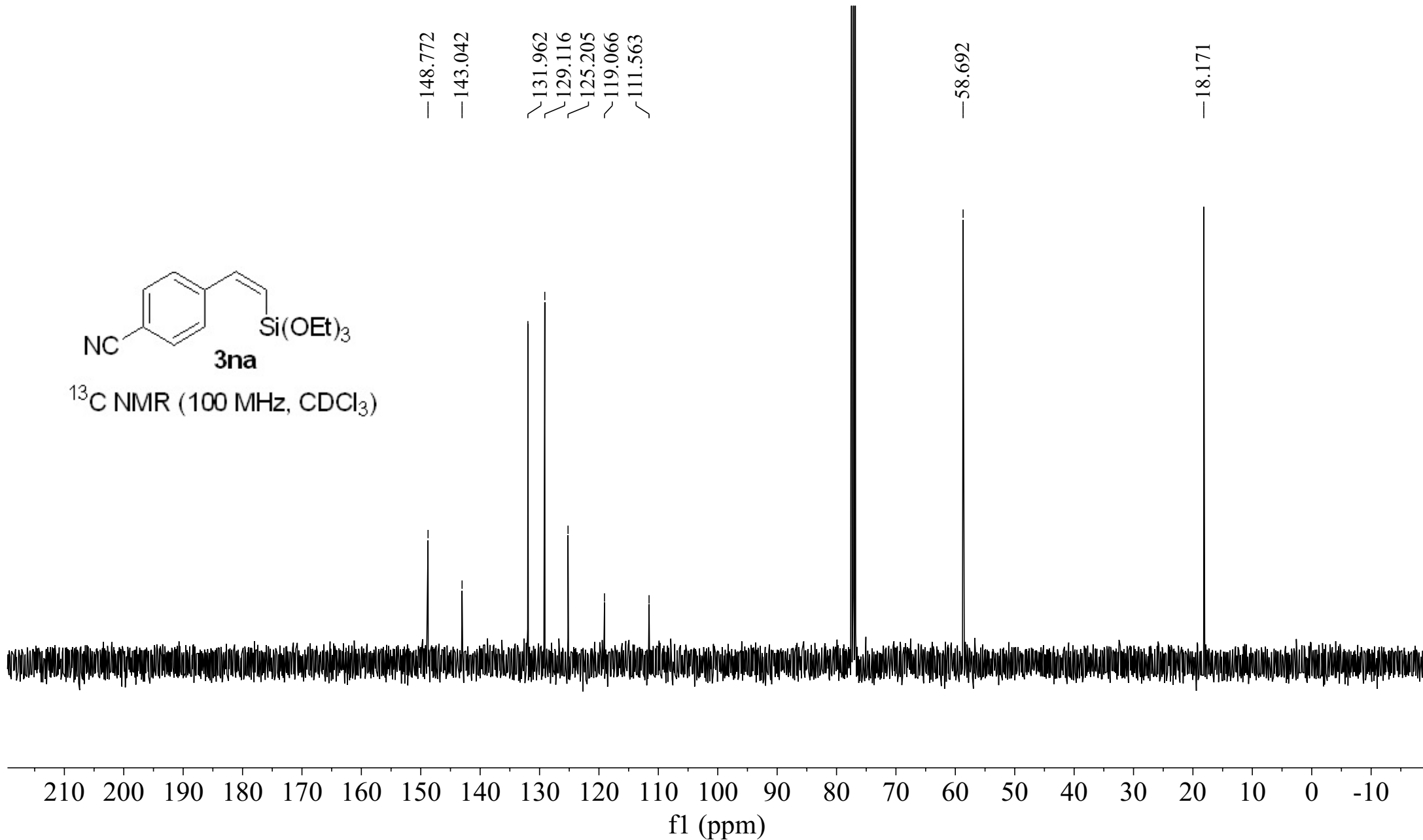
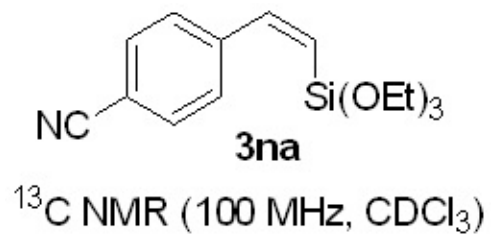


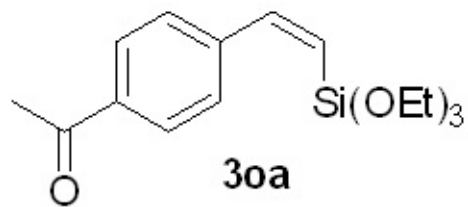


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

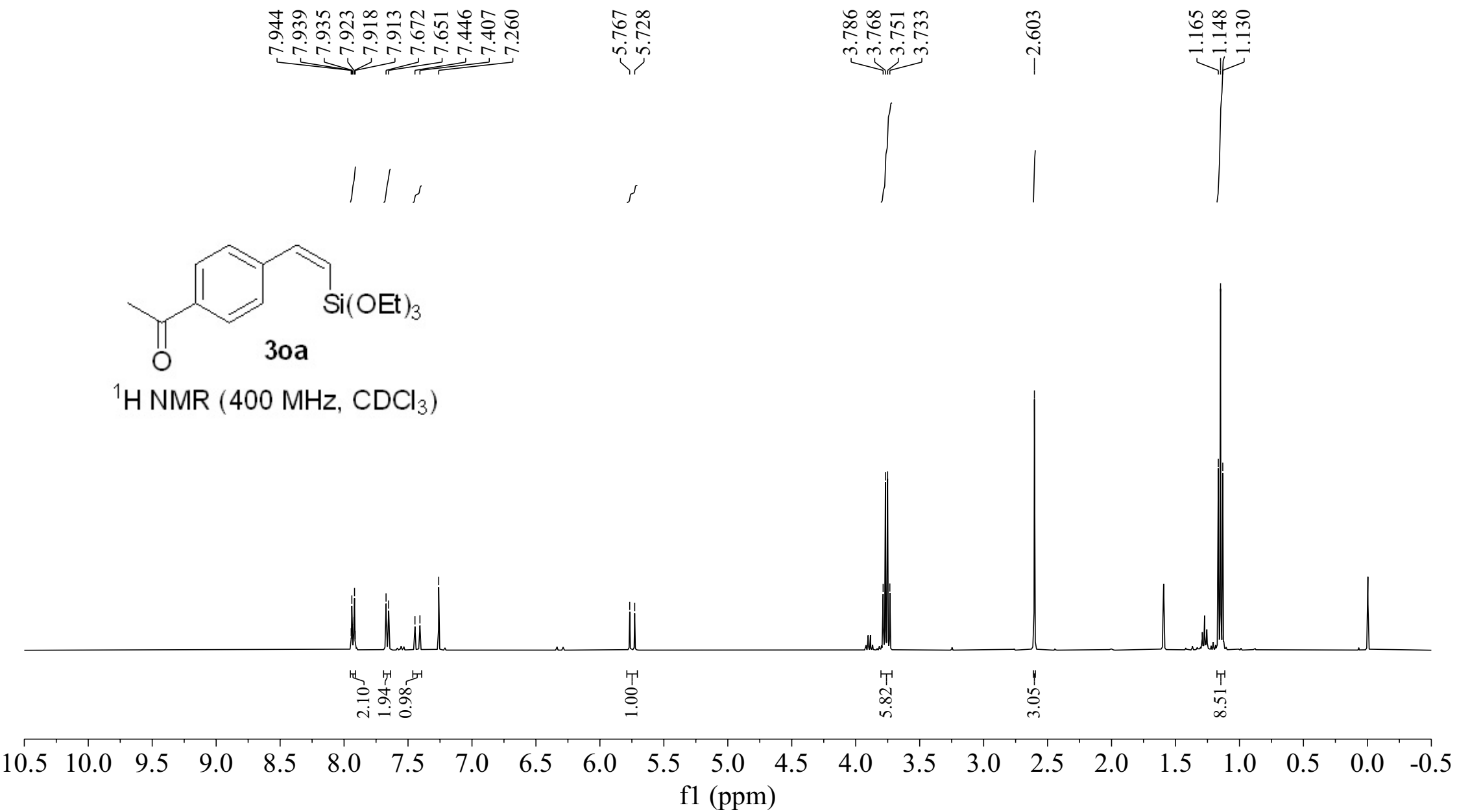


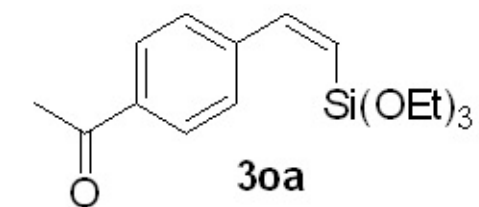




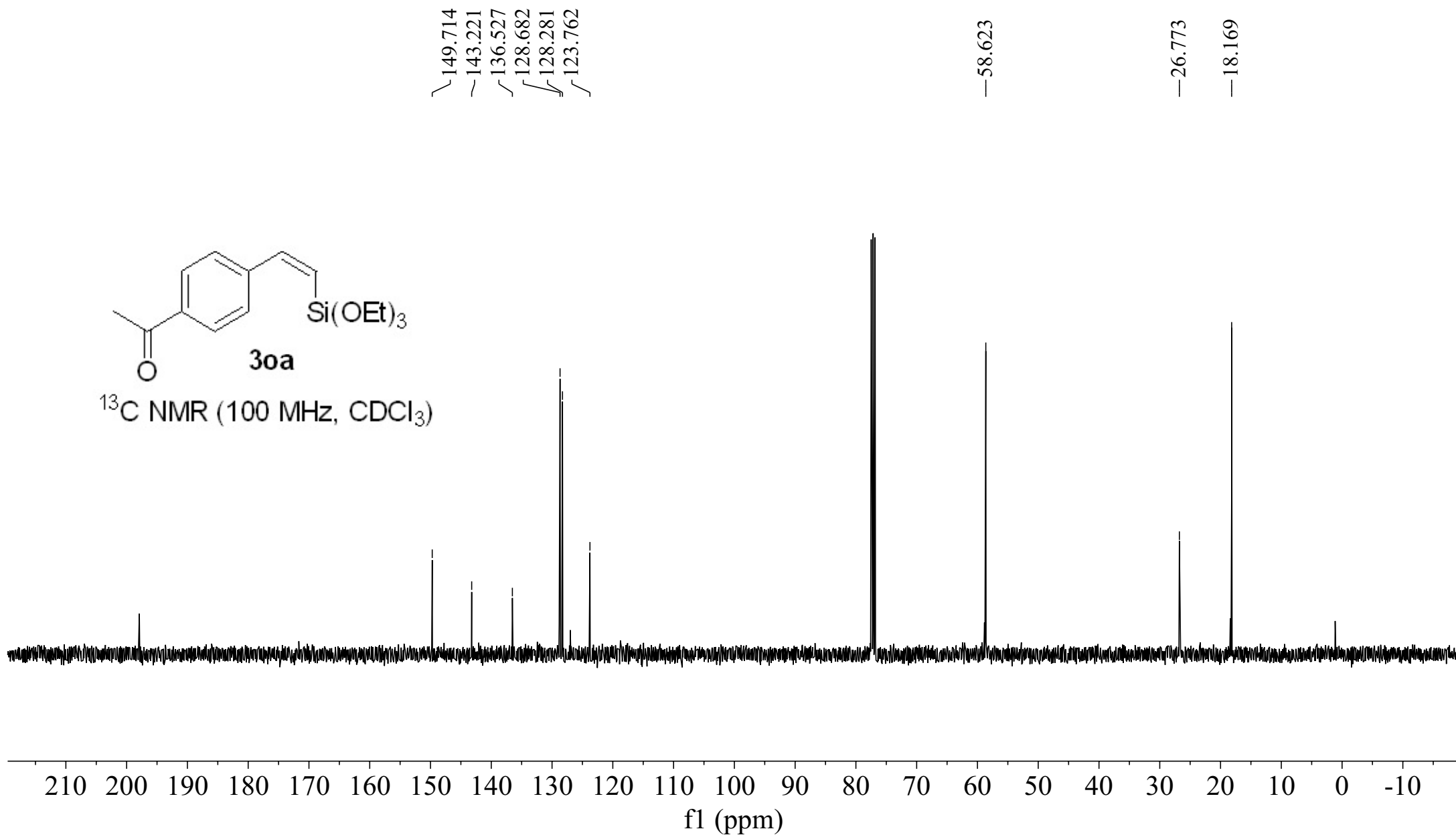


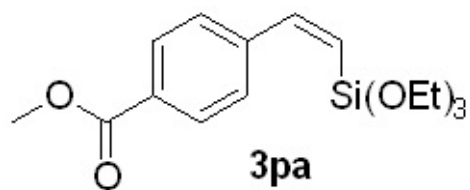
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )



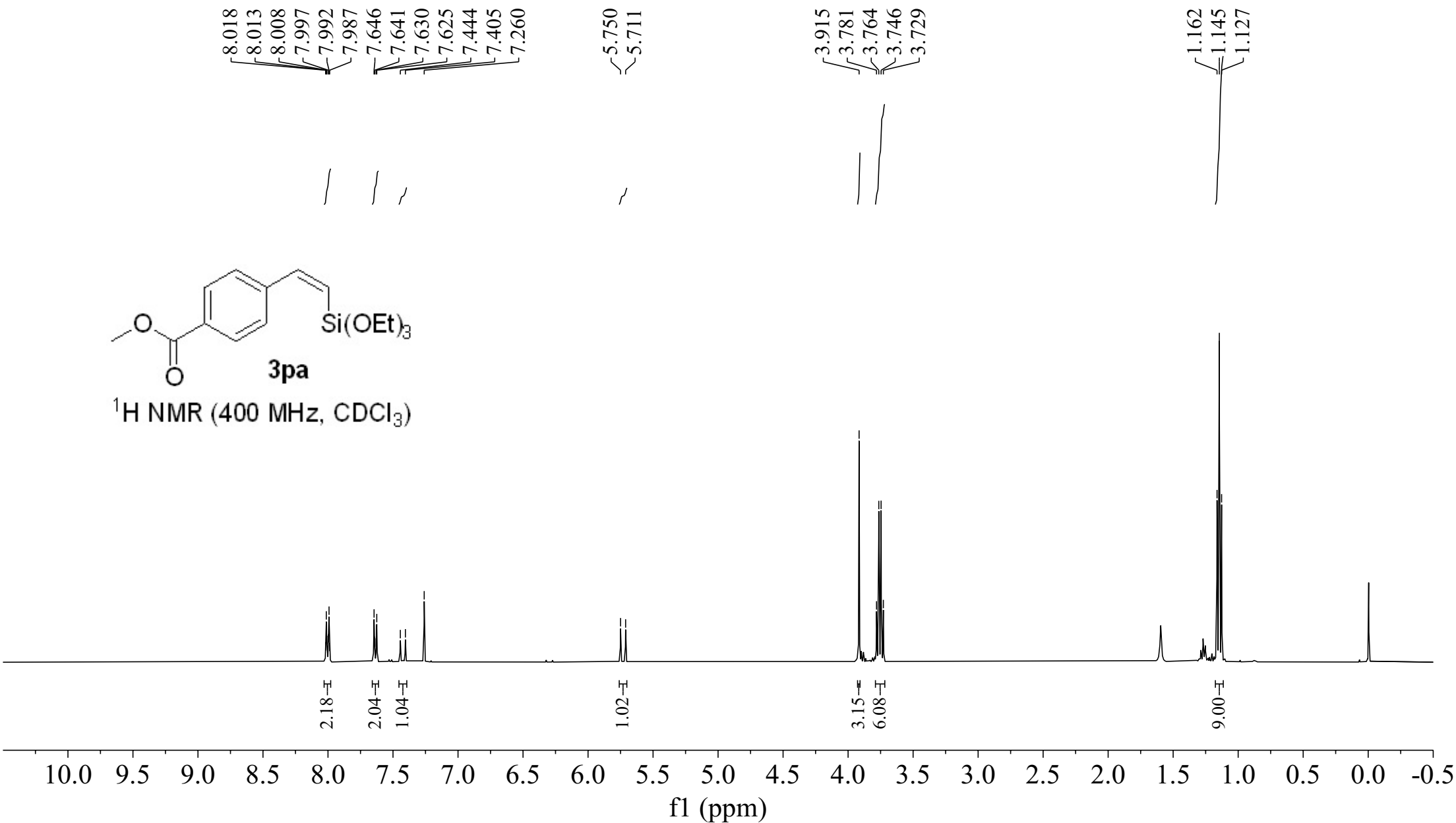


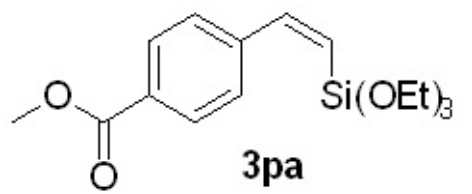
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )





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





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

—167.080

—149.843

—143.079

—129.618

—129.492

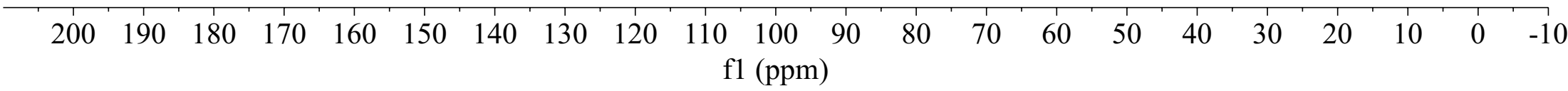
—128.491

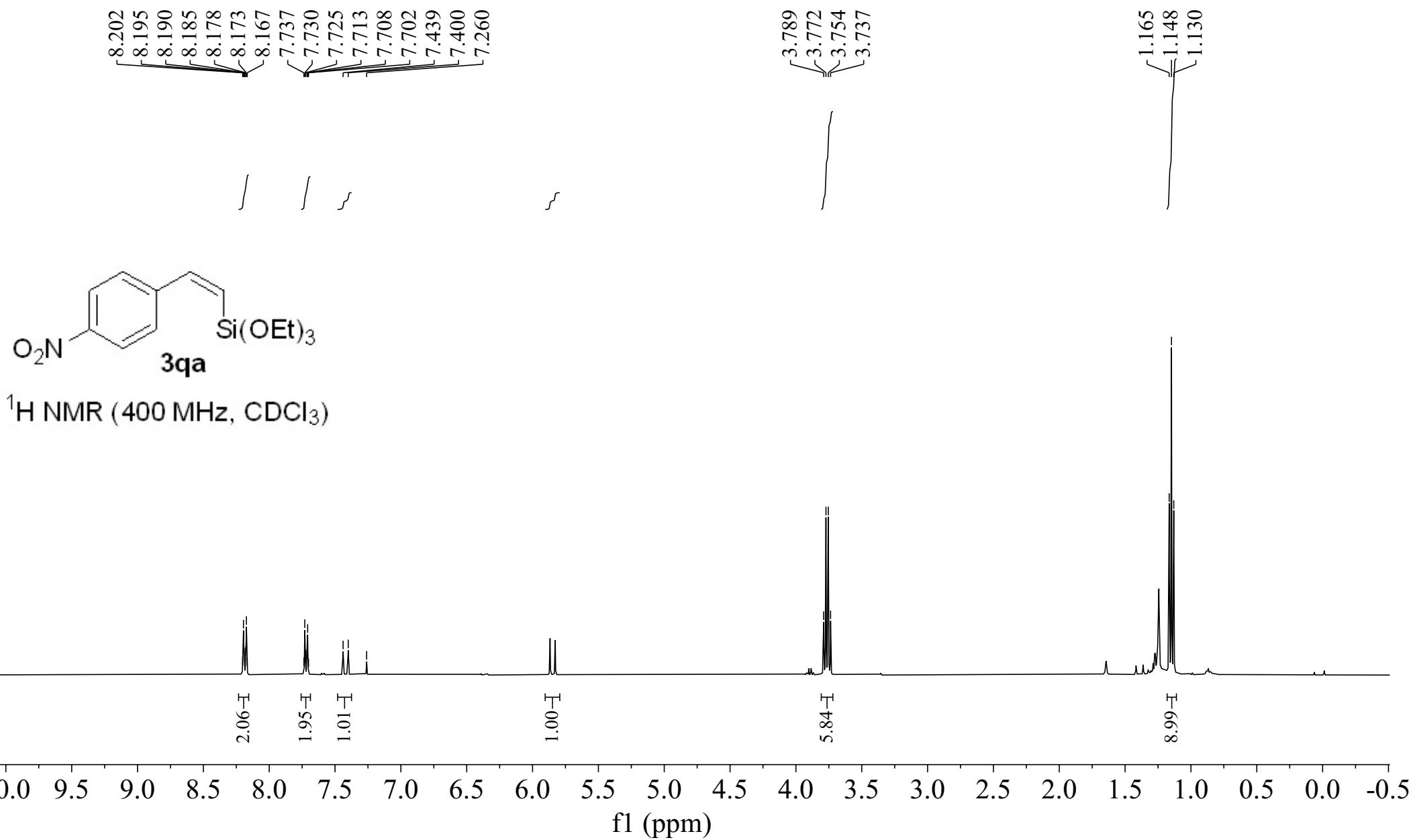
—123.526

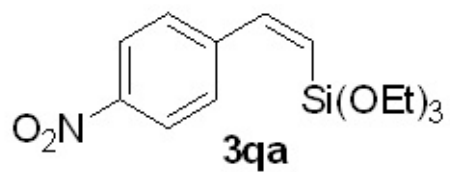
—58.634

—52.234

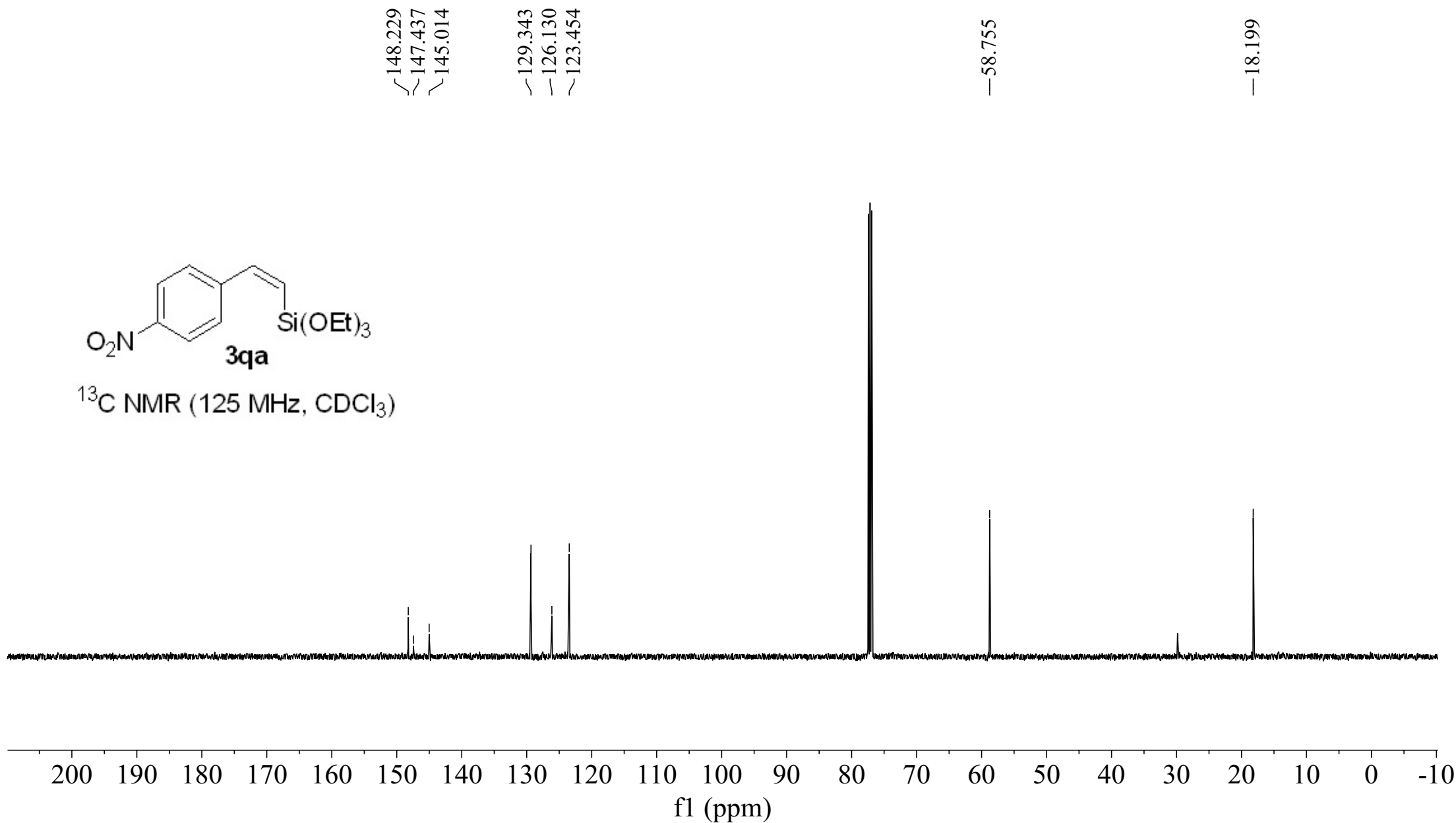
—18.180







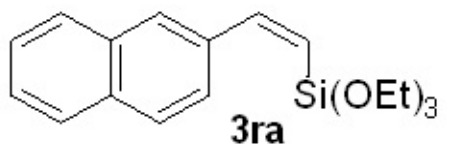
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )



8.023  
7.857  
7.849  
7.843  
7.840  
7.834  
7.826  
7.823  
7.820  
7.817  
7.815  
7.811  
7.800  
7.796  
7.792  
7.594  
7.555  
7.478  
7.470  
7.462  
7.454  
7.260  
5.695  
5.656

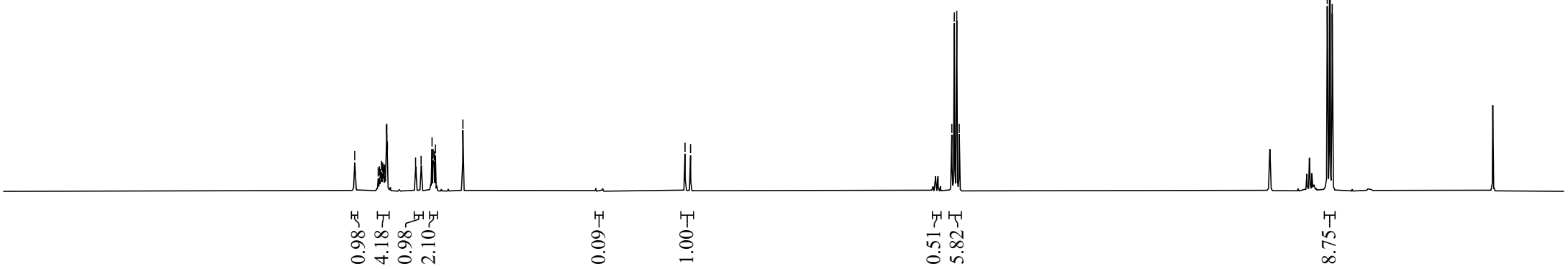
3.815  
3.797  
3.780  
3.762

1.168  
1.151  
1.134



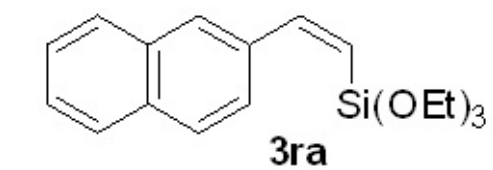
Z:E = 92:8

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

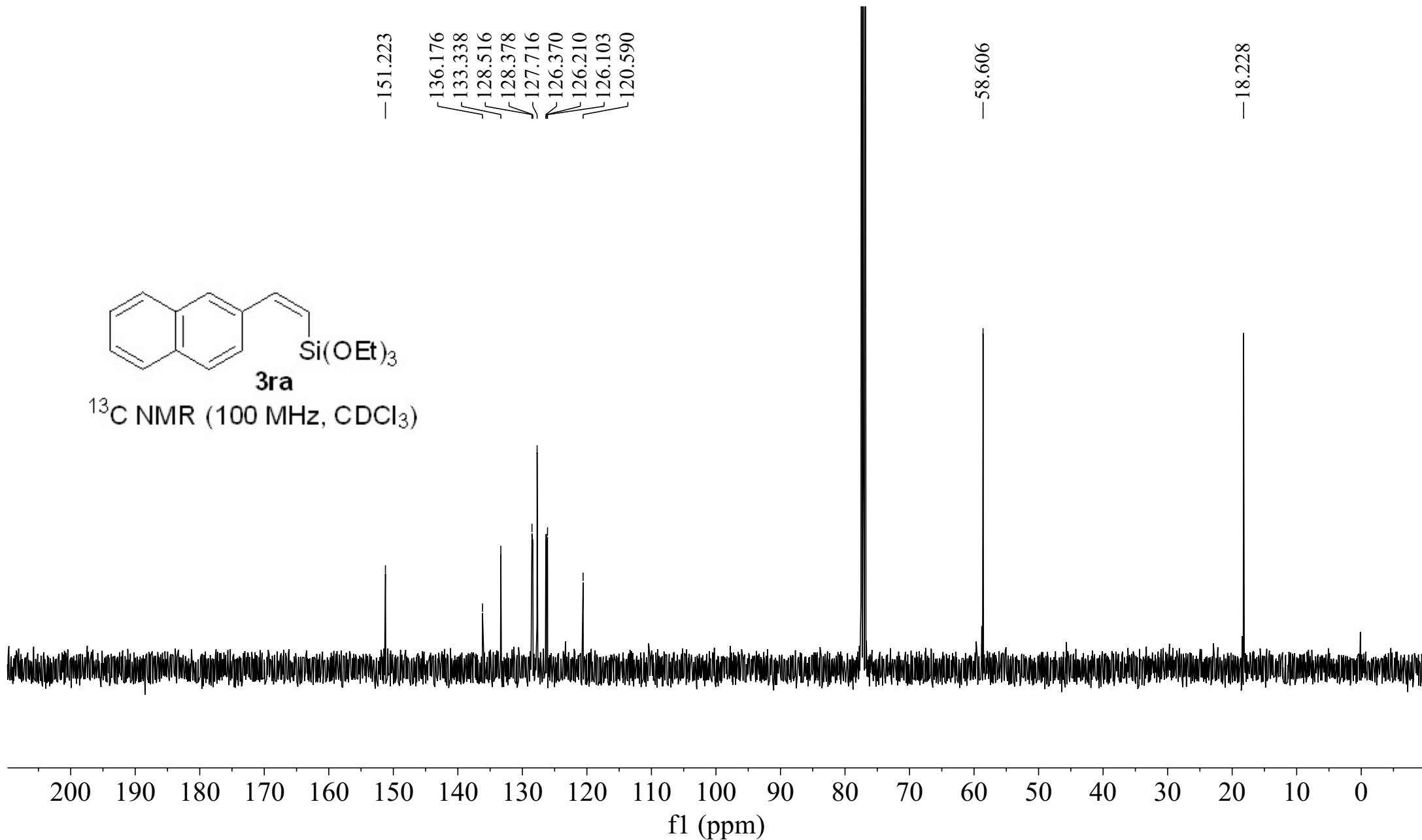


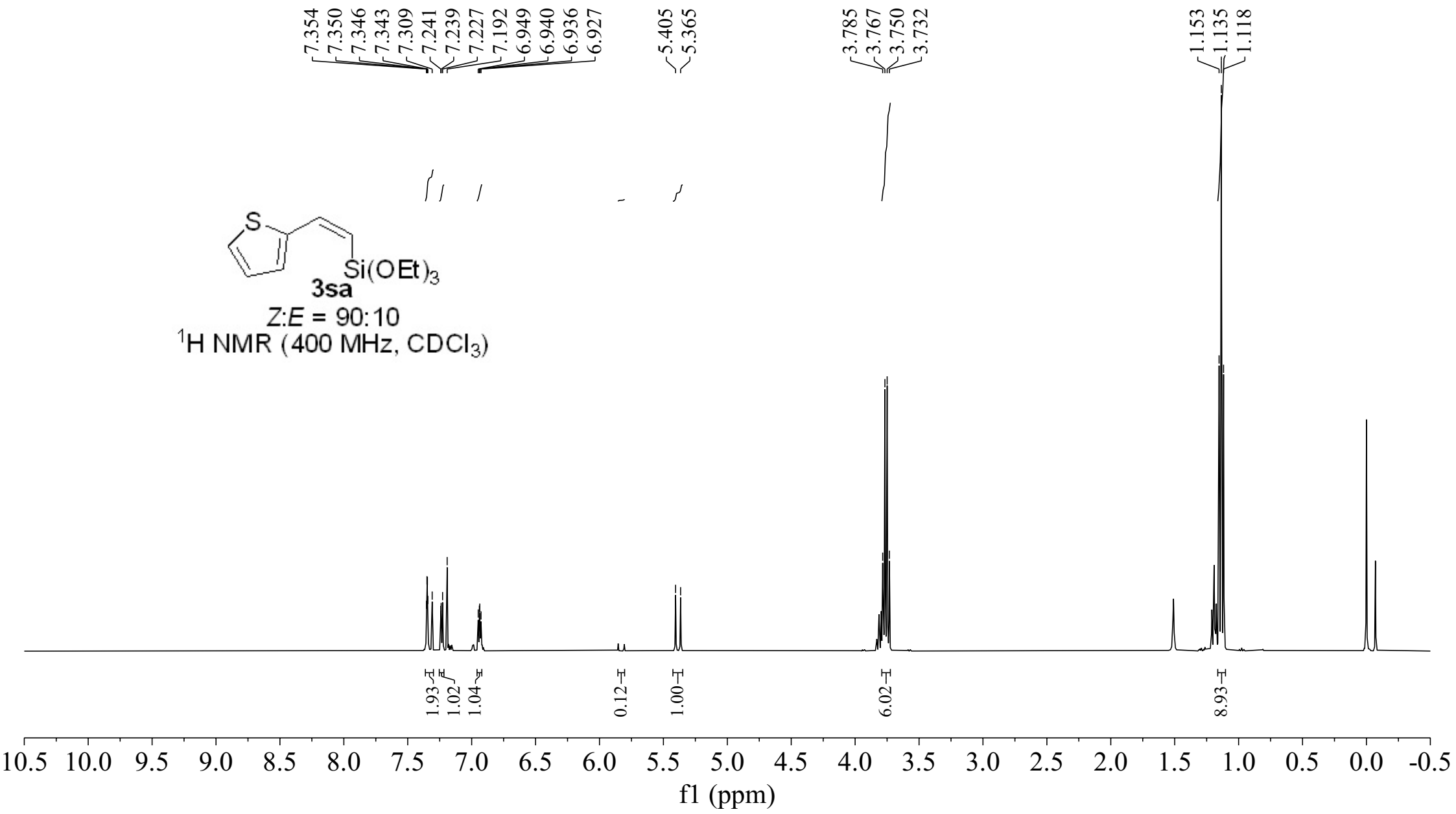
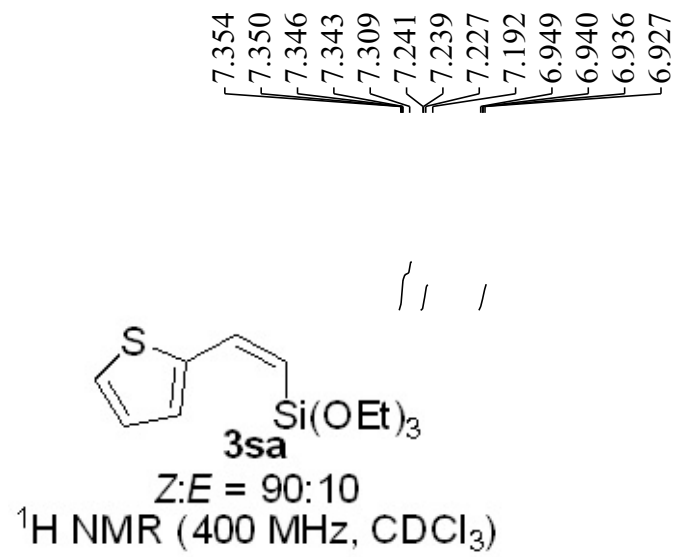
f1 (ppm)

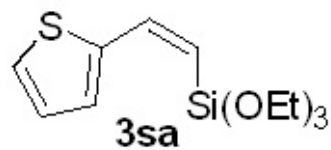




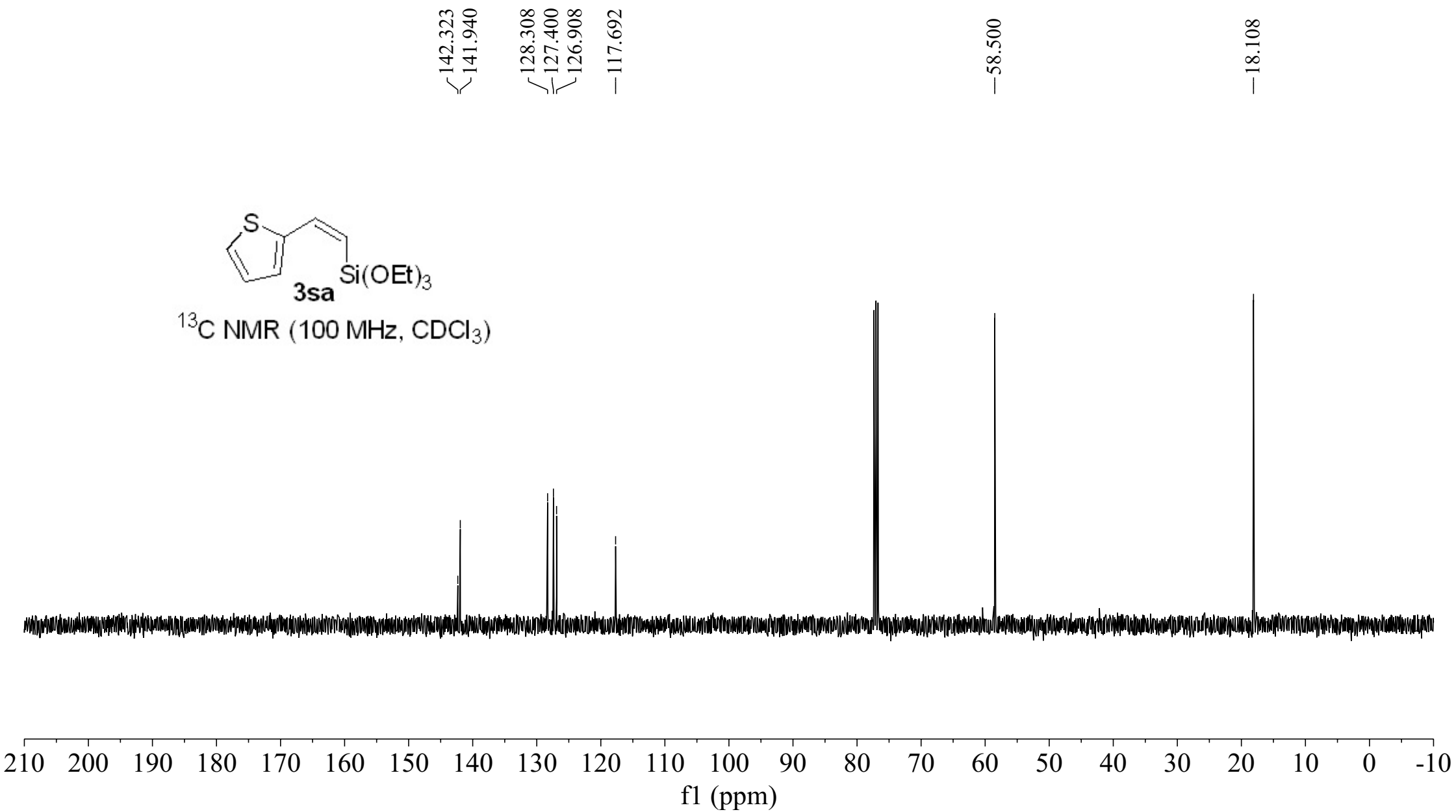
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

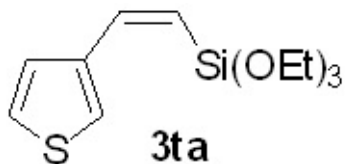




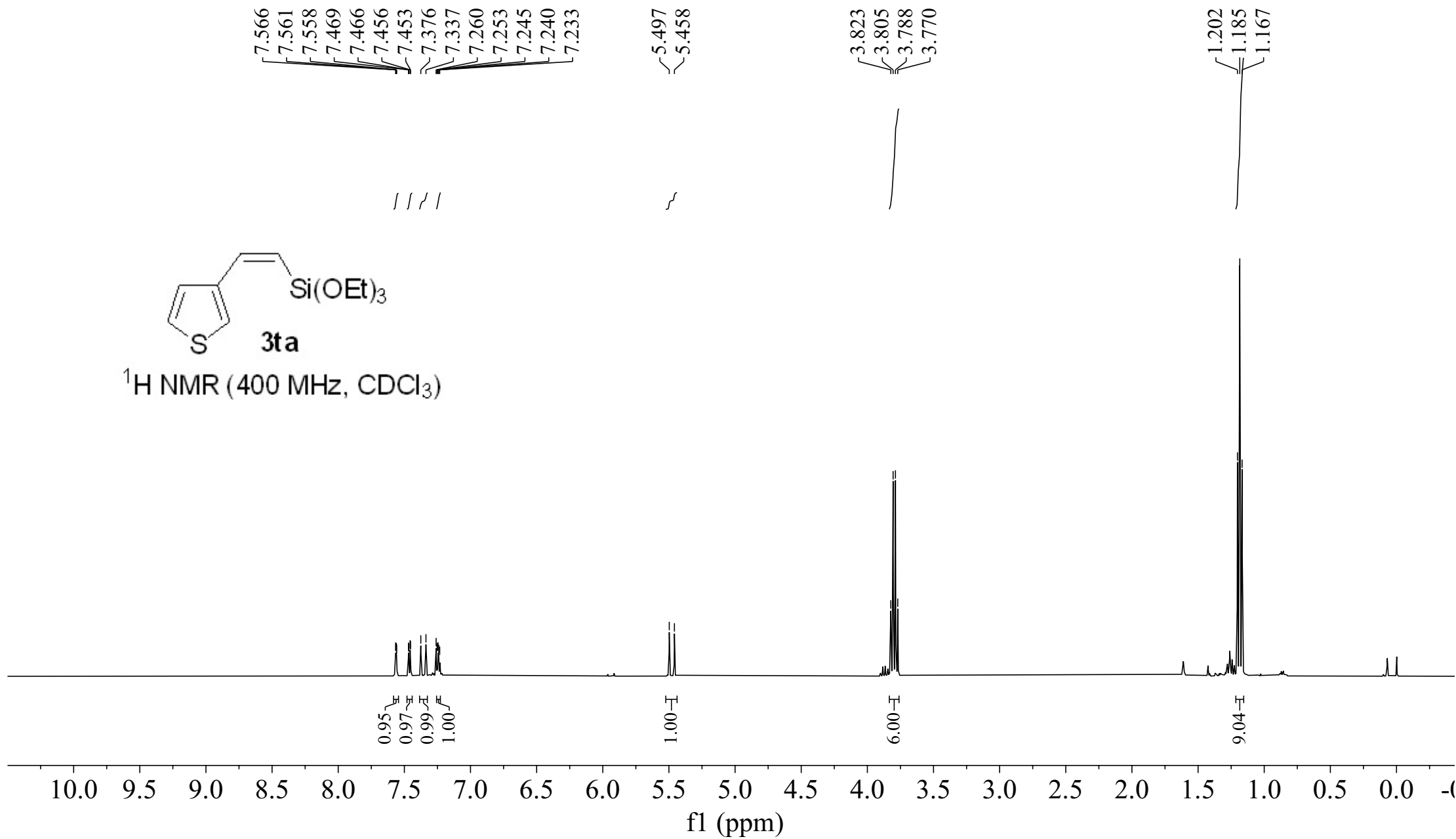


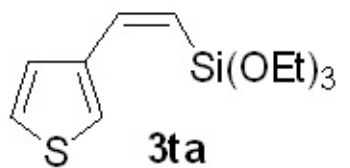
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)





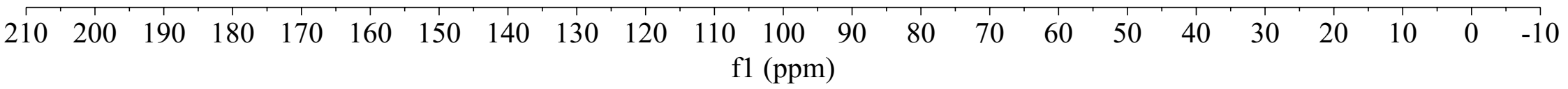
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

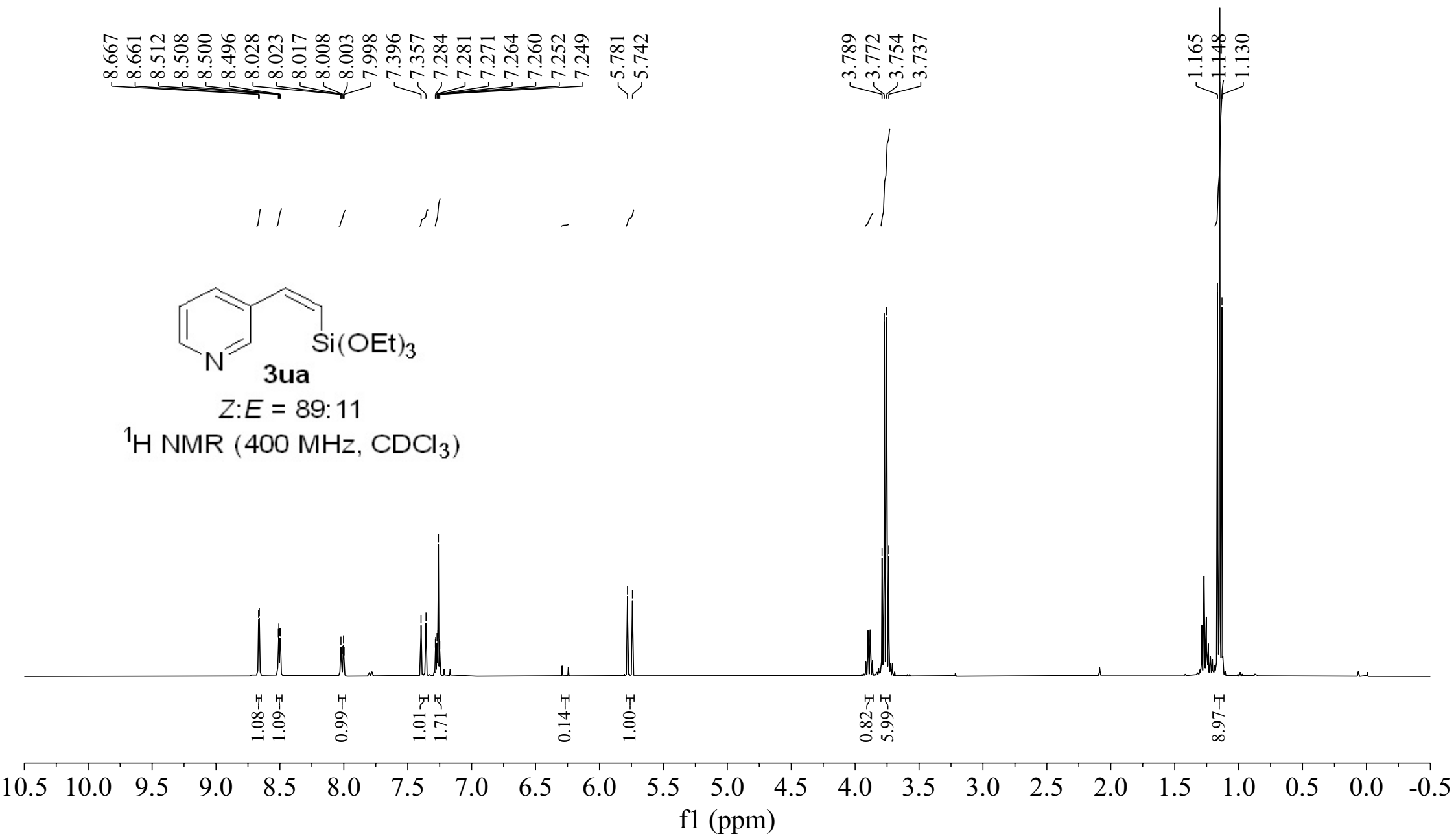


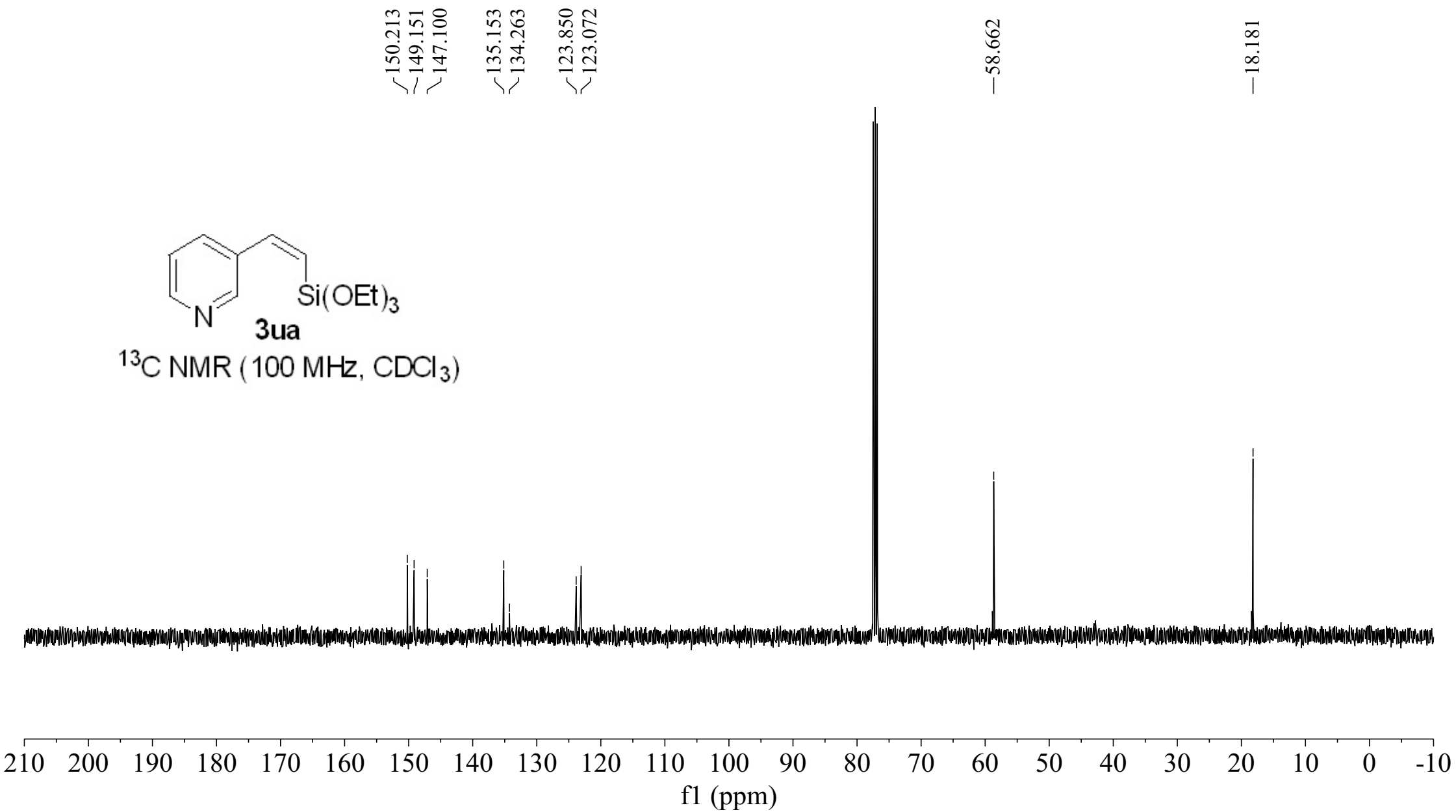
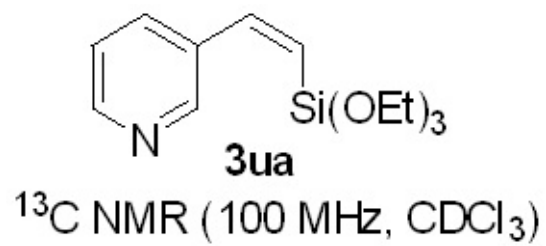


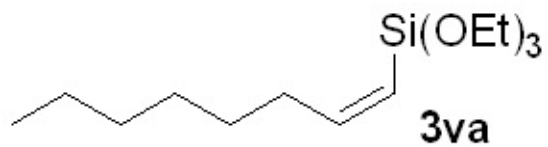
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

- ~144.395
- ~140.887
- ~128.053
- ~125.804
- ~125.282
- ~118.156
- 58.550
- 18.212

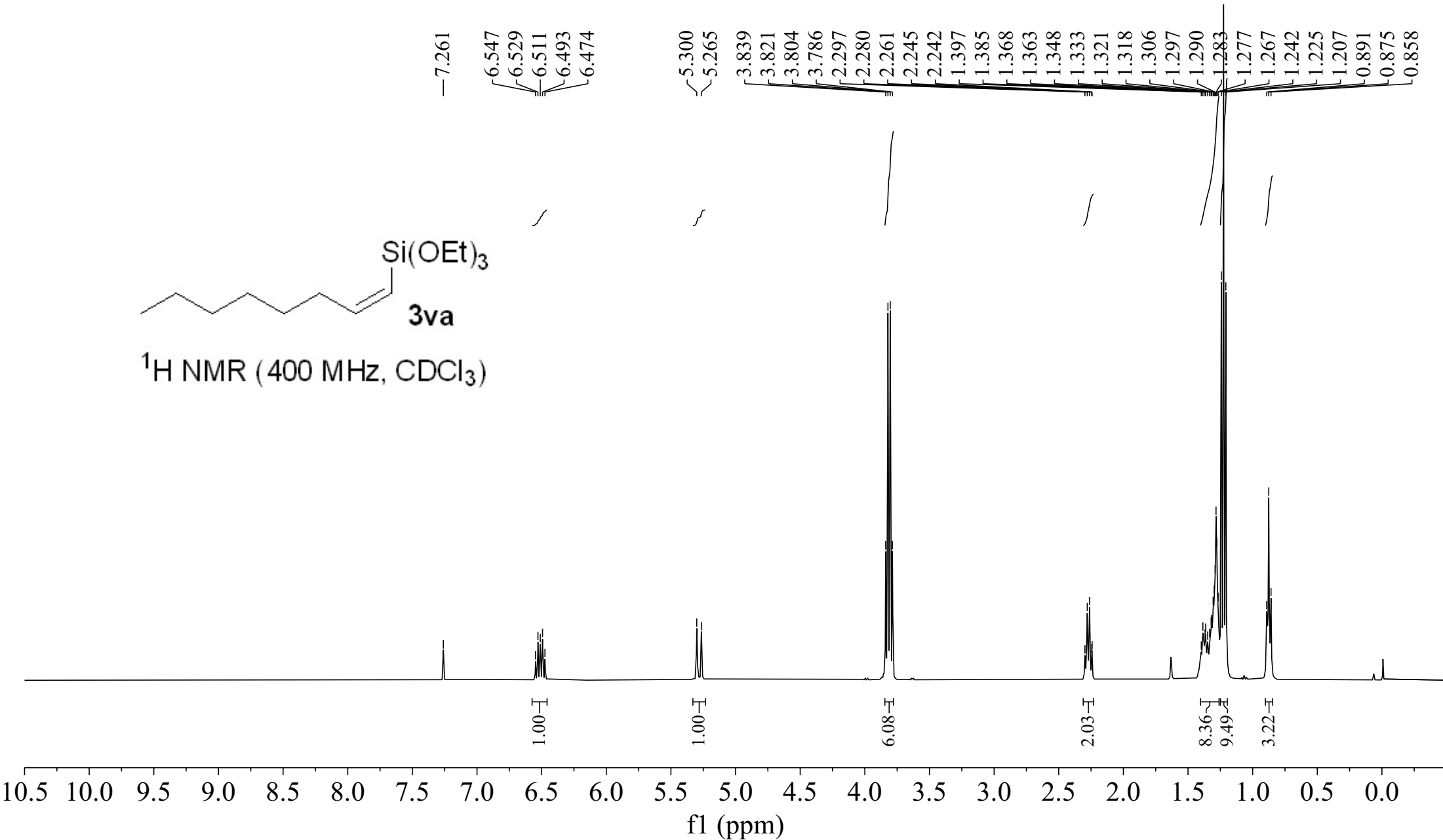




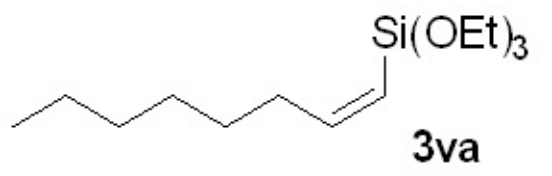




$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )







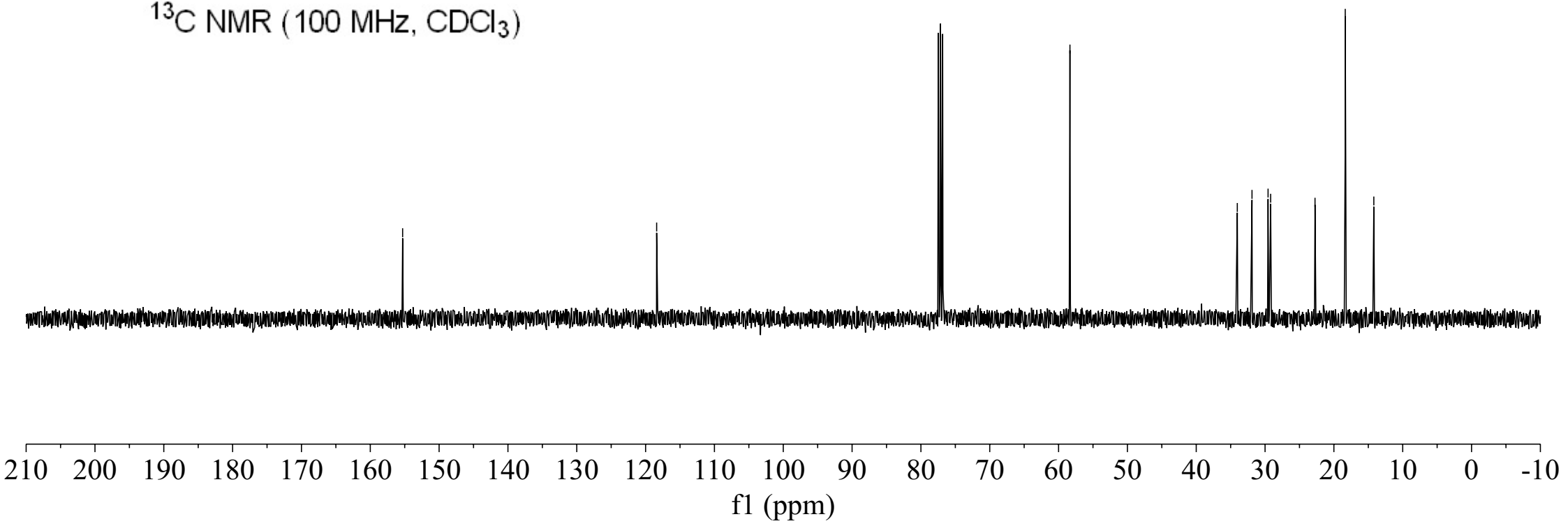
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

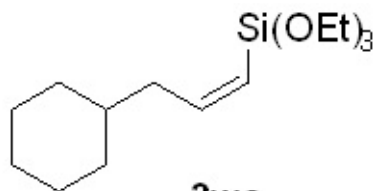
—155.300

—118.395

—58.348

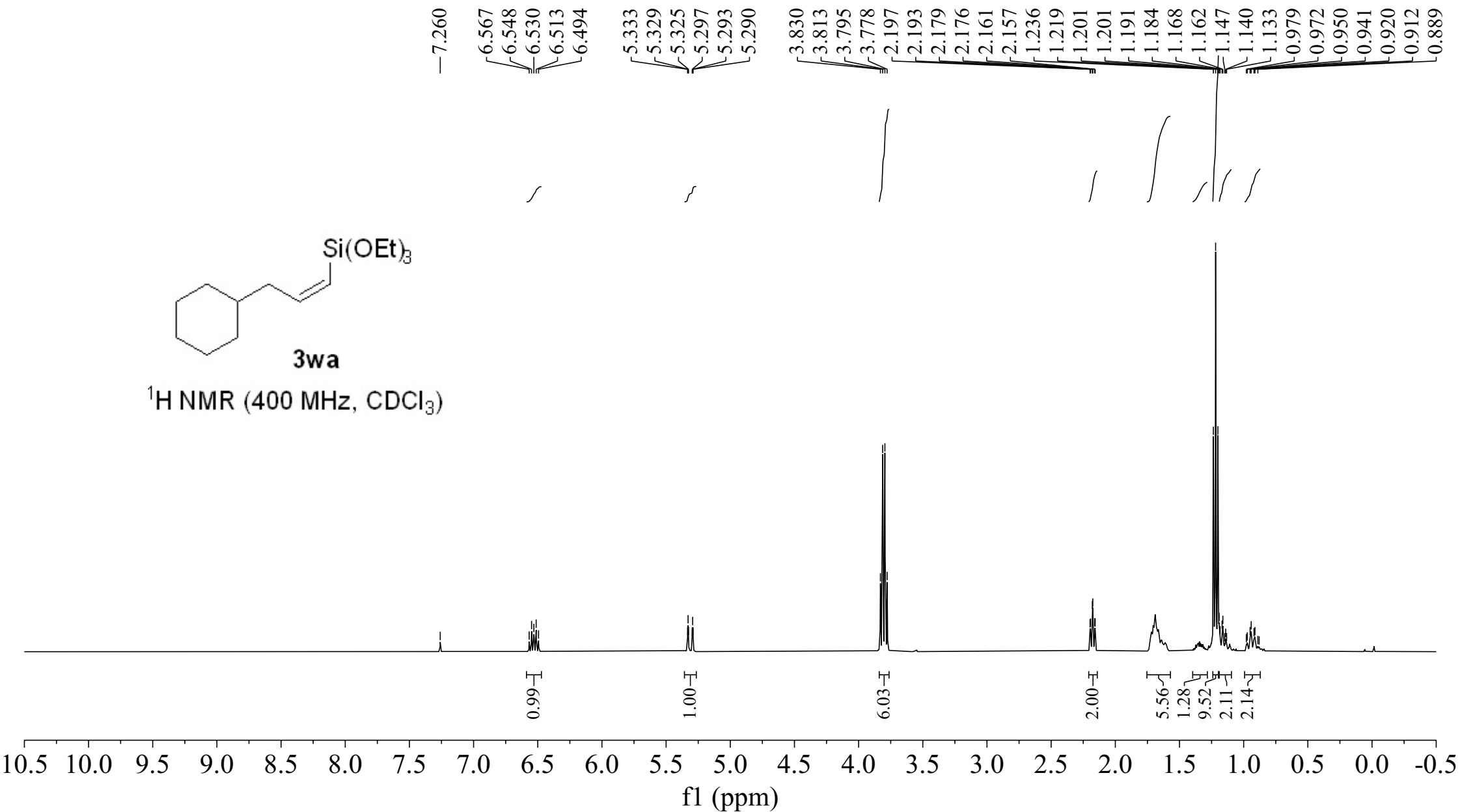
~34.034  
~31.897  
~29.564  
~29.188  
~22.742  
~18.351  
~14.198

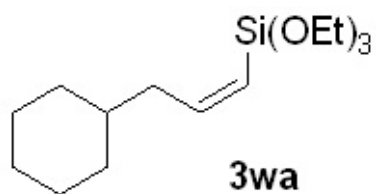




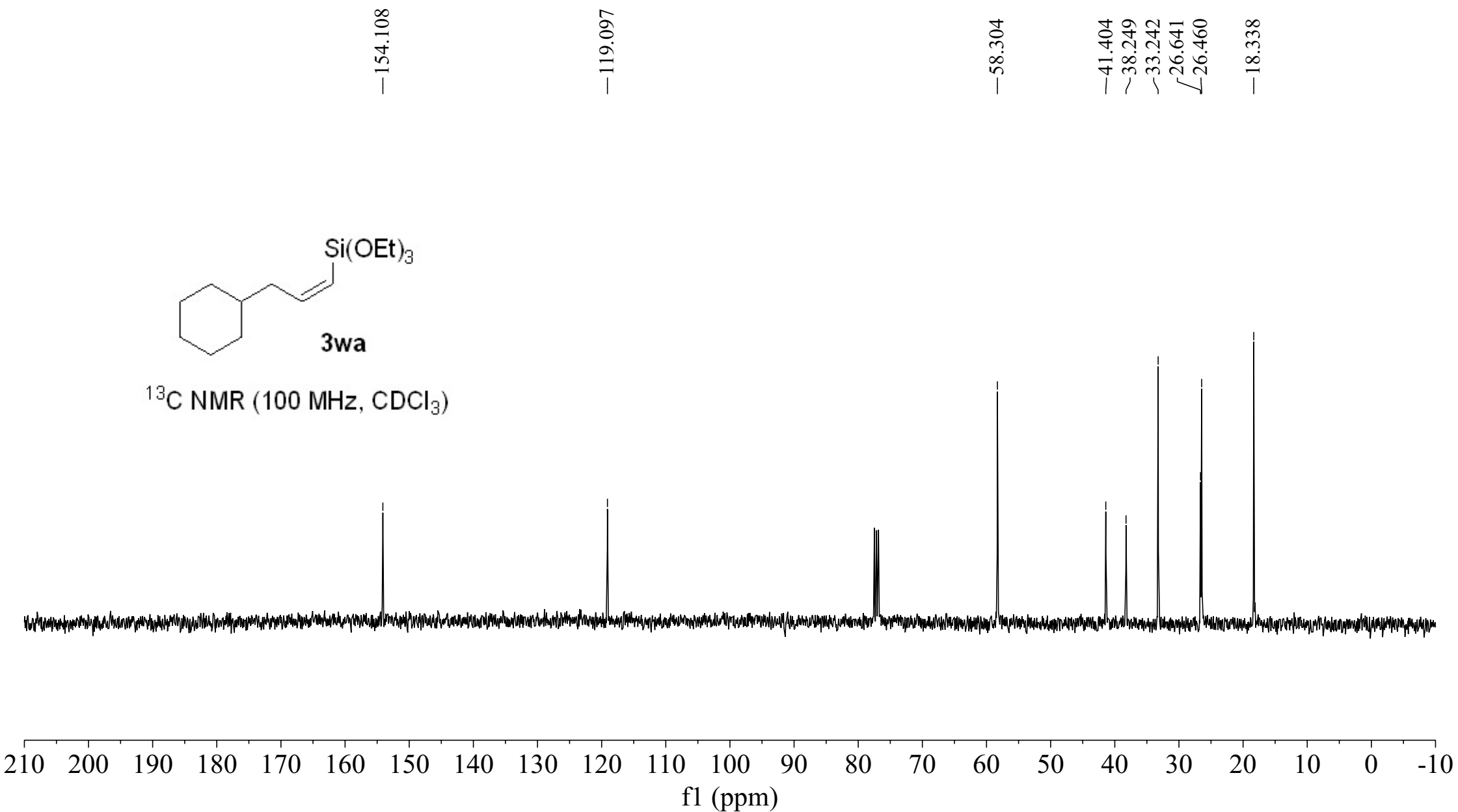
3wa

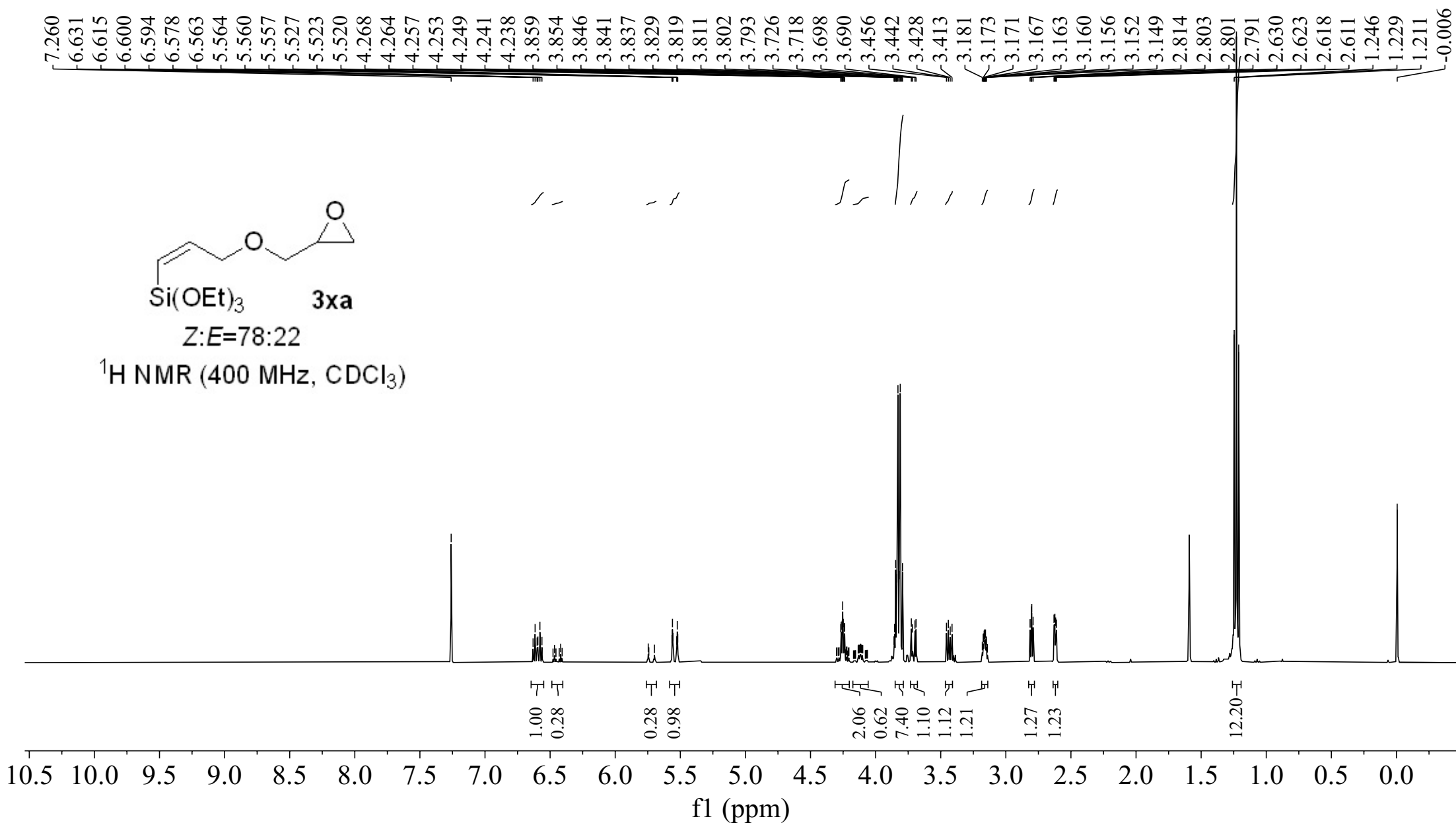
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

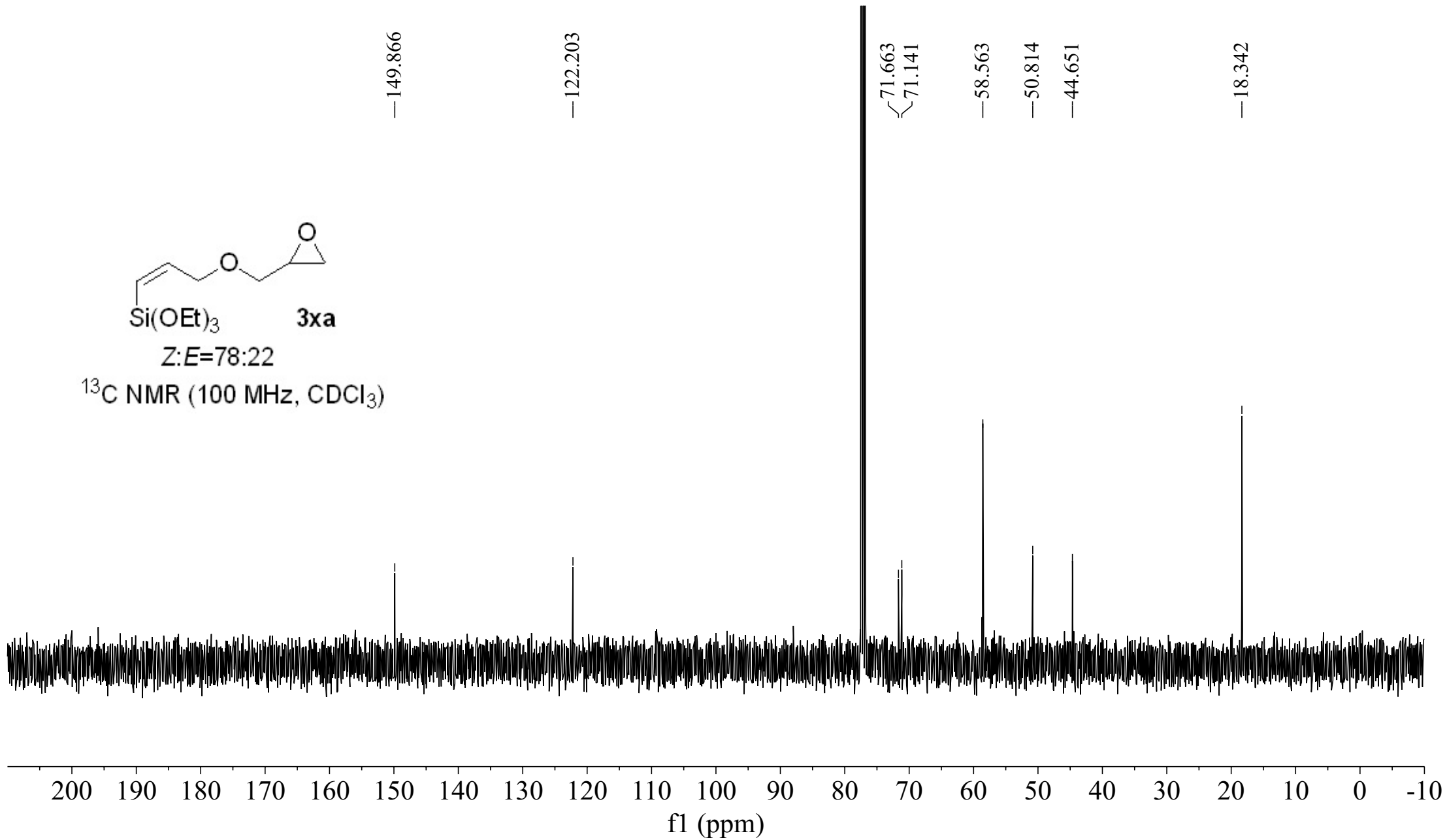
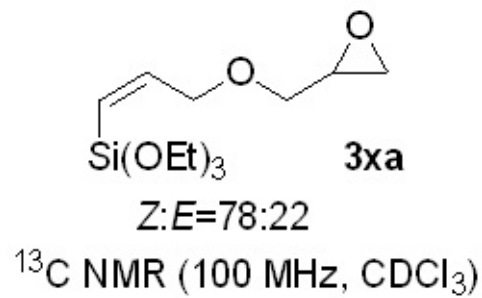


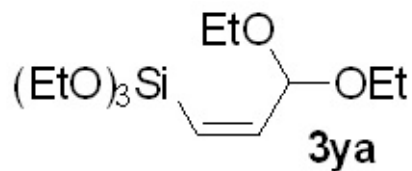


$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

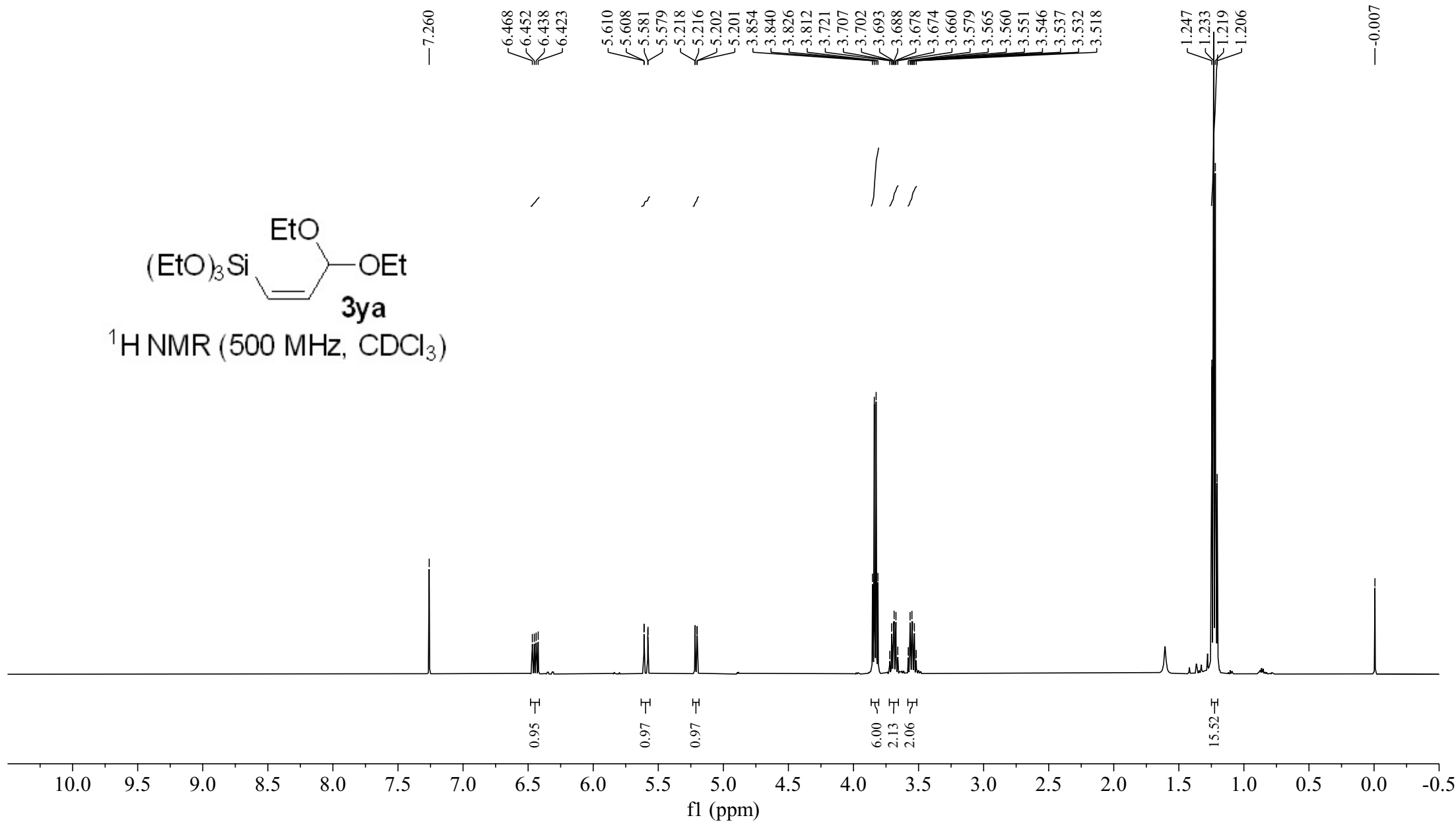


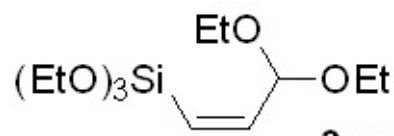






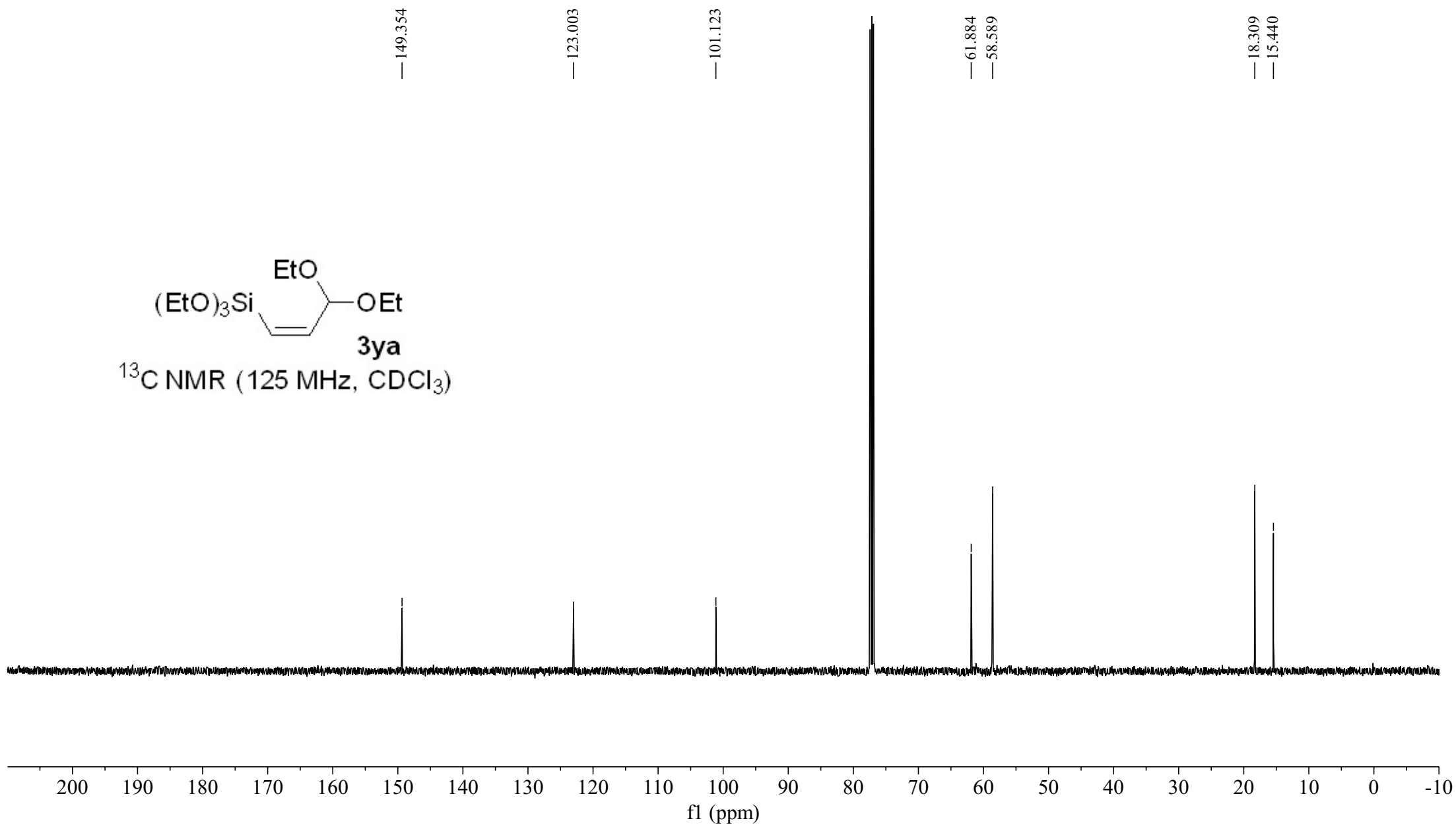
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

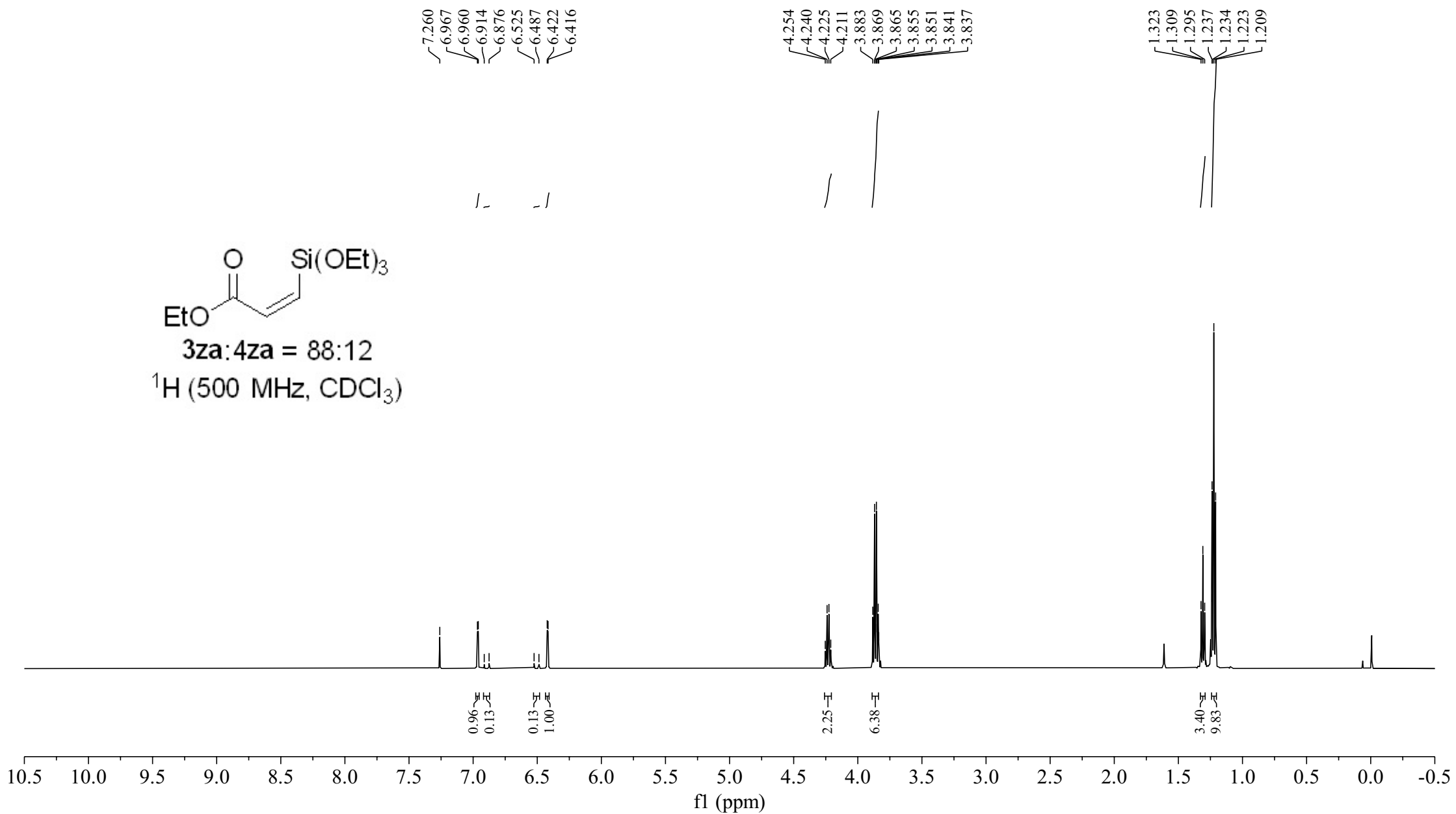
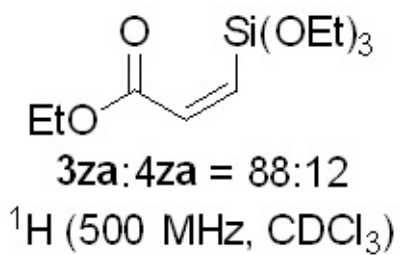




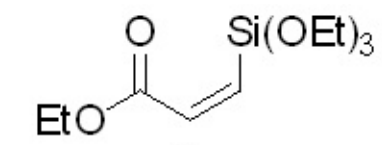
3ya

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )



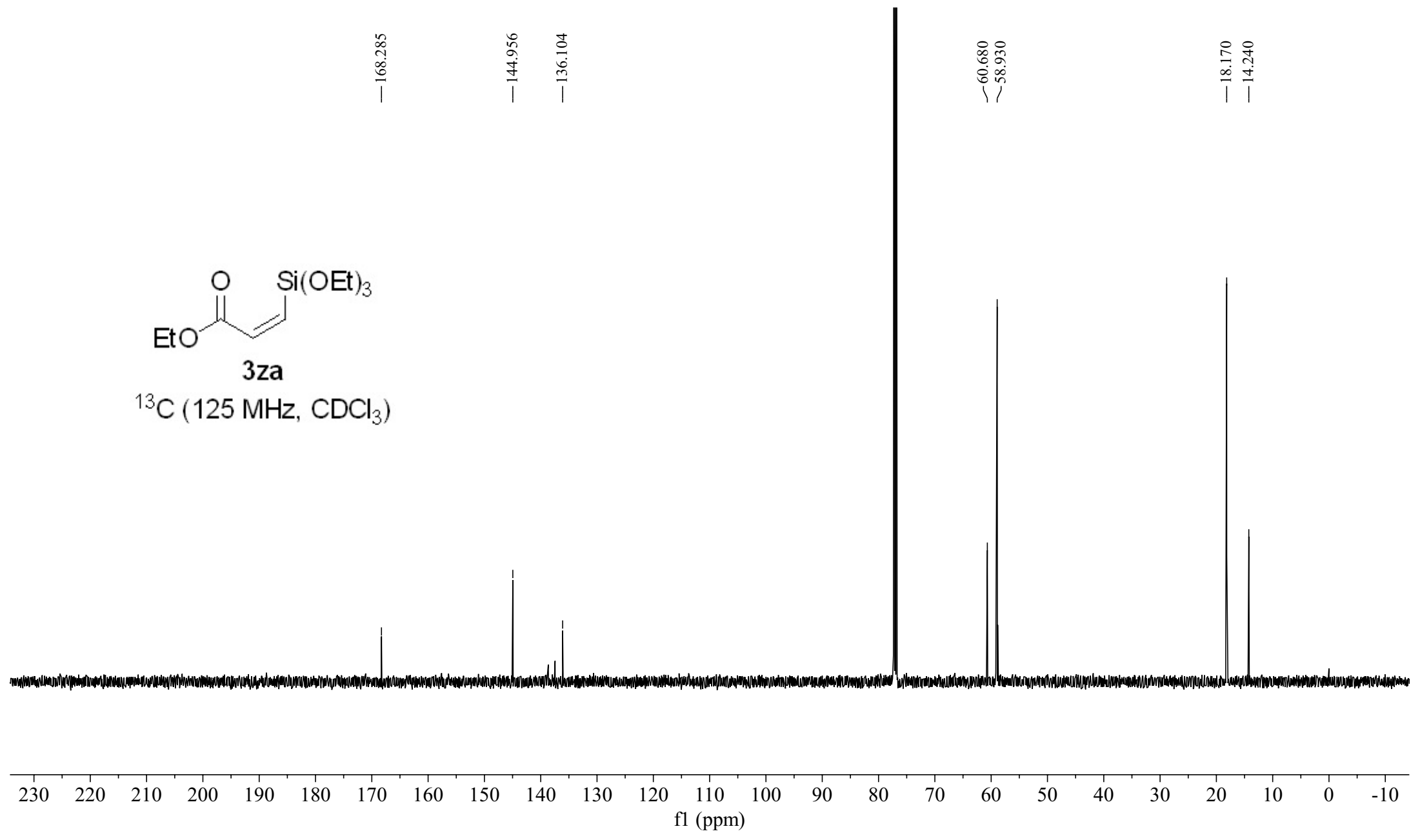


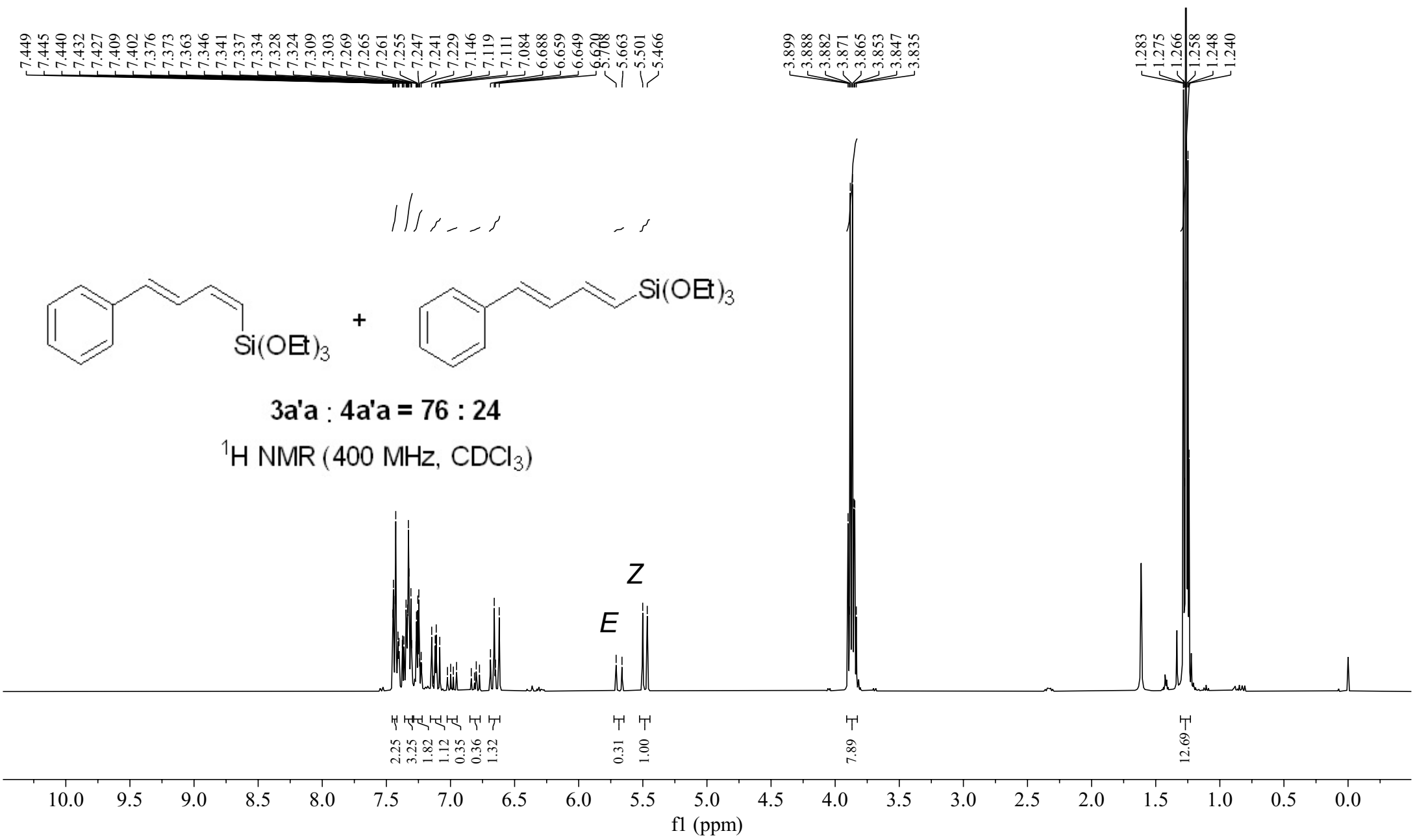


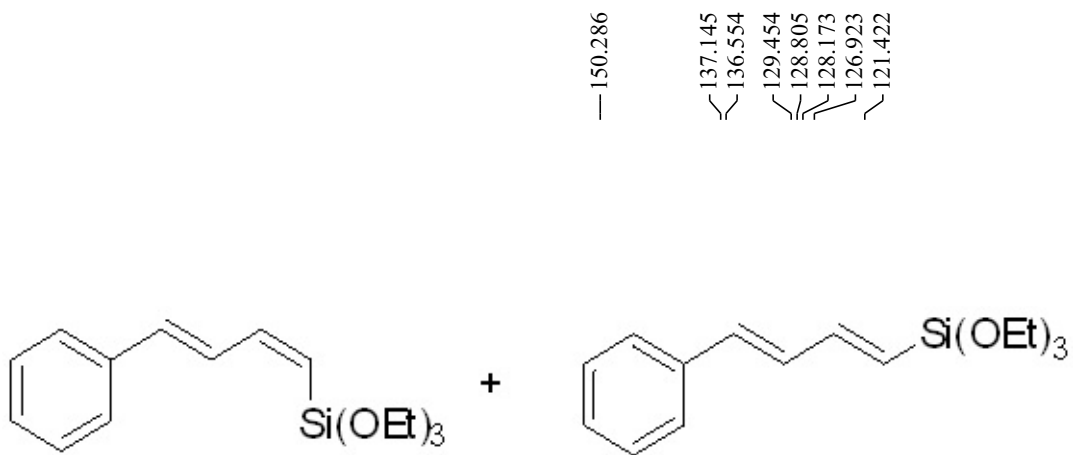


3za

<sup>13</sup>C (125 MHz, CDCl<sub>3</sub>)



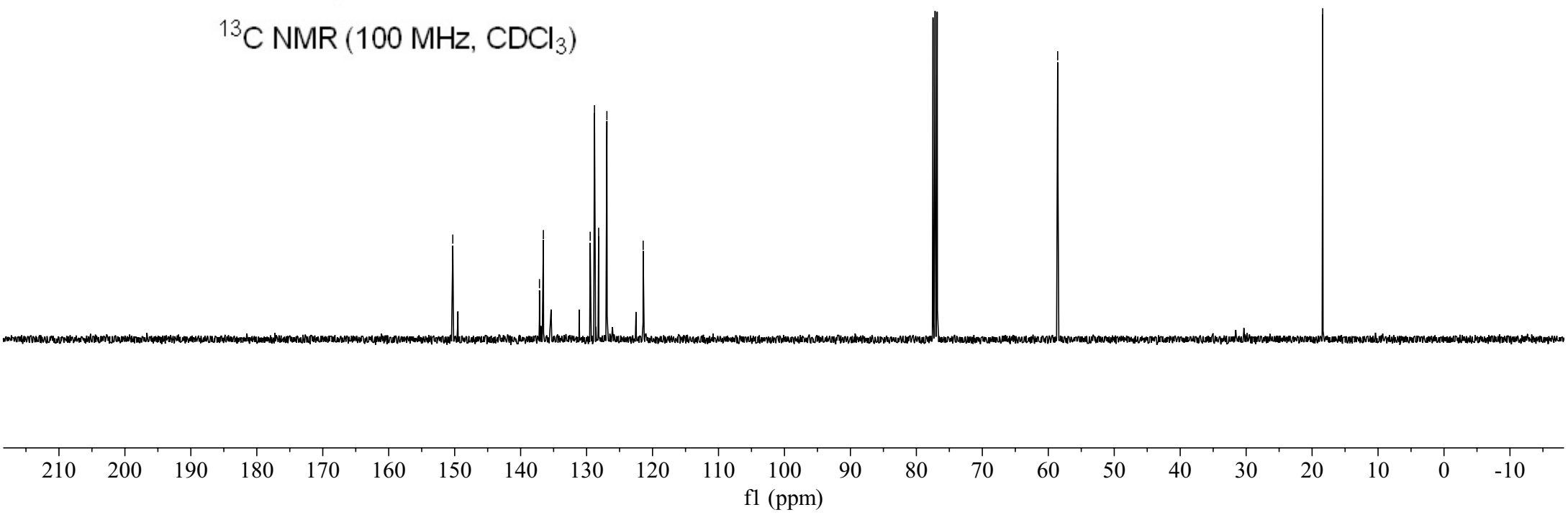


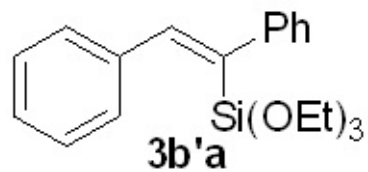


**3a'a : 4a'a = 76 : 24**

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

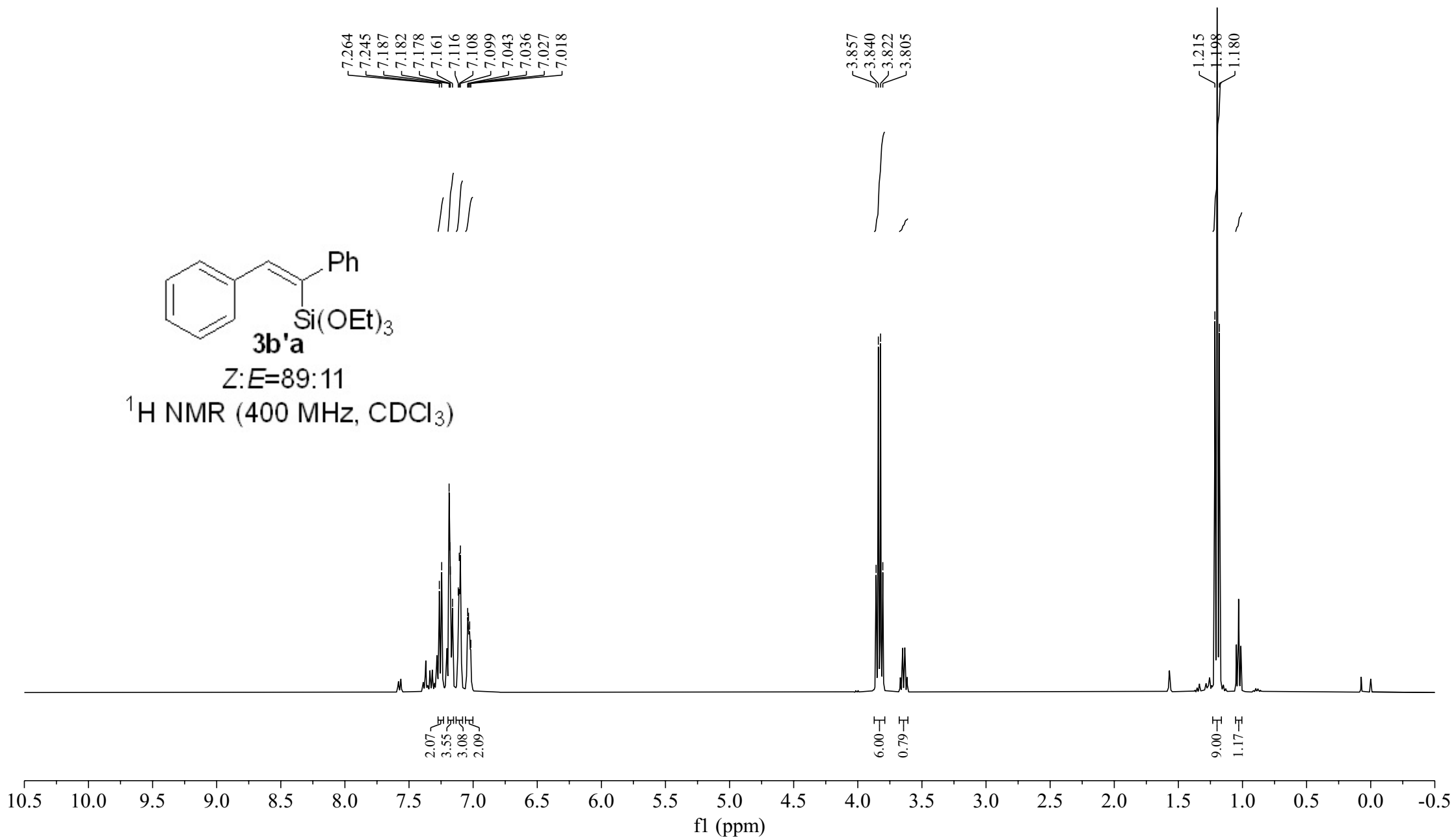
— 150.286  
 { 137.145  
 { 136.554  
 { 129.454  
 { 128.805  
 { 128.173  
 { 126.923  
 { 121.422  
 — 58.574  
 — 18.397

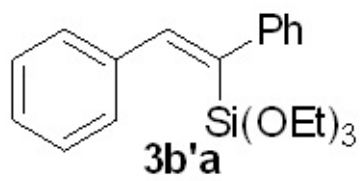




Z:E=89:11

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





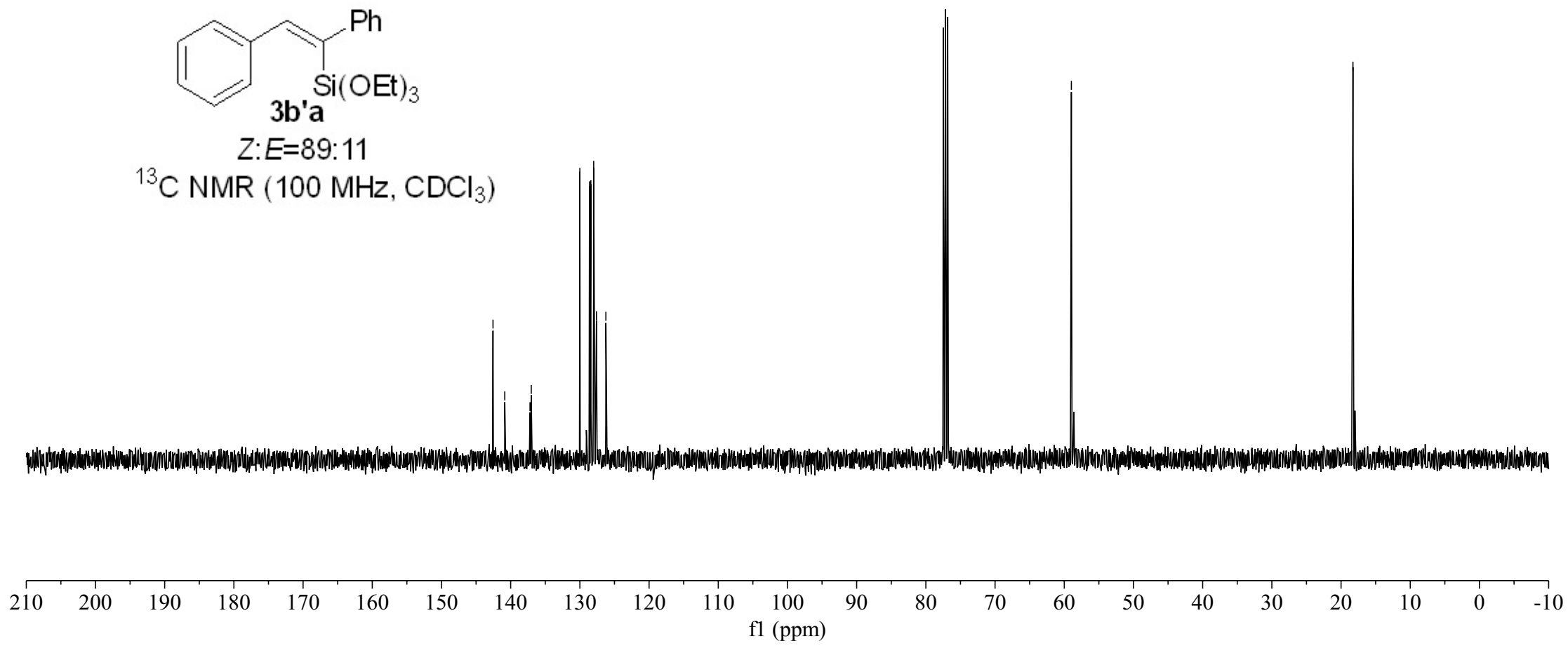
Z:E=89:11

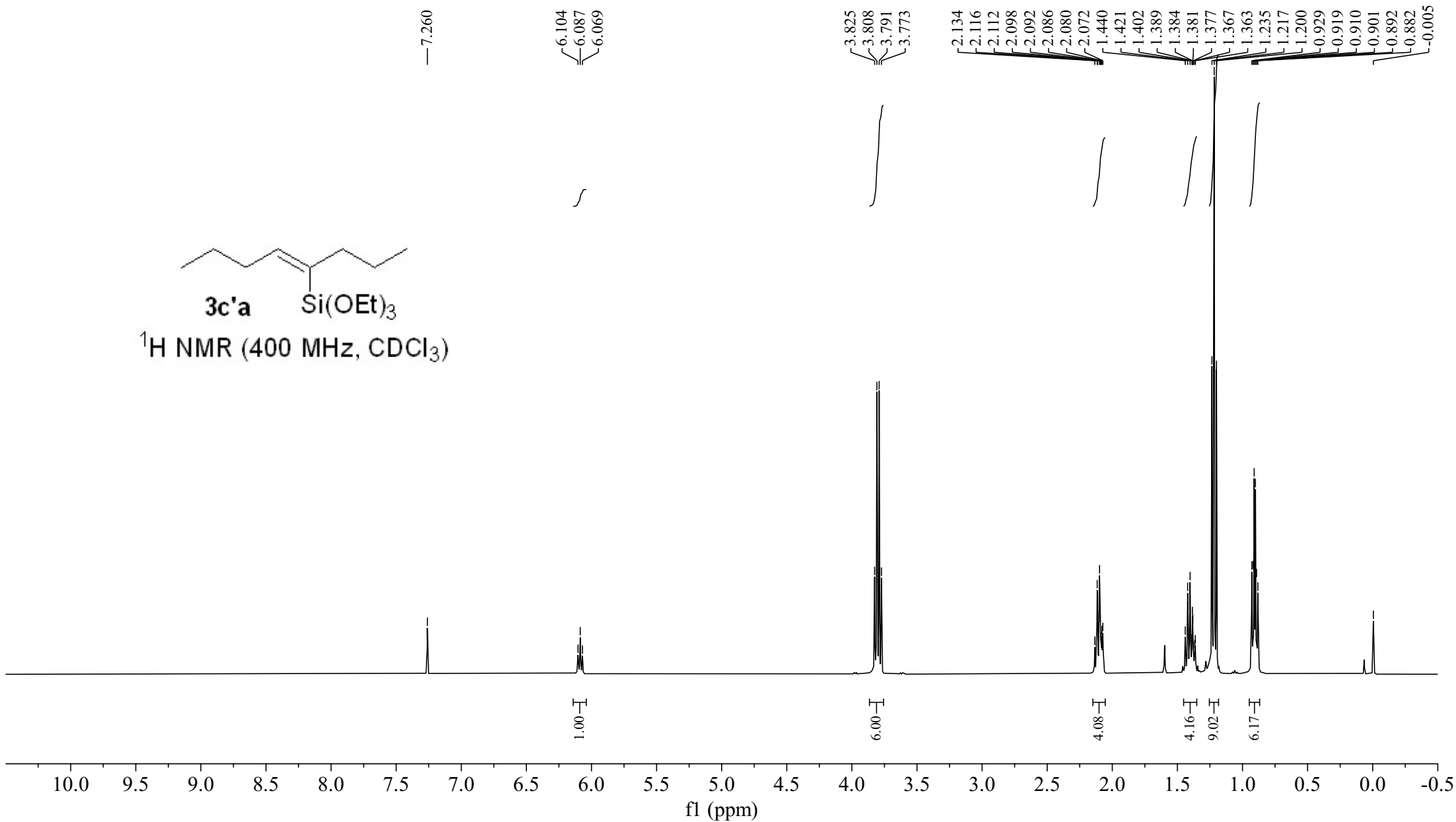
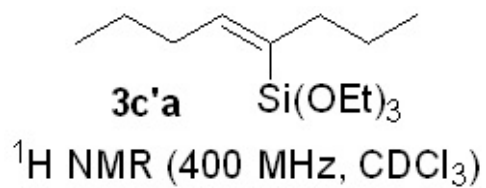
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

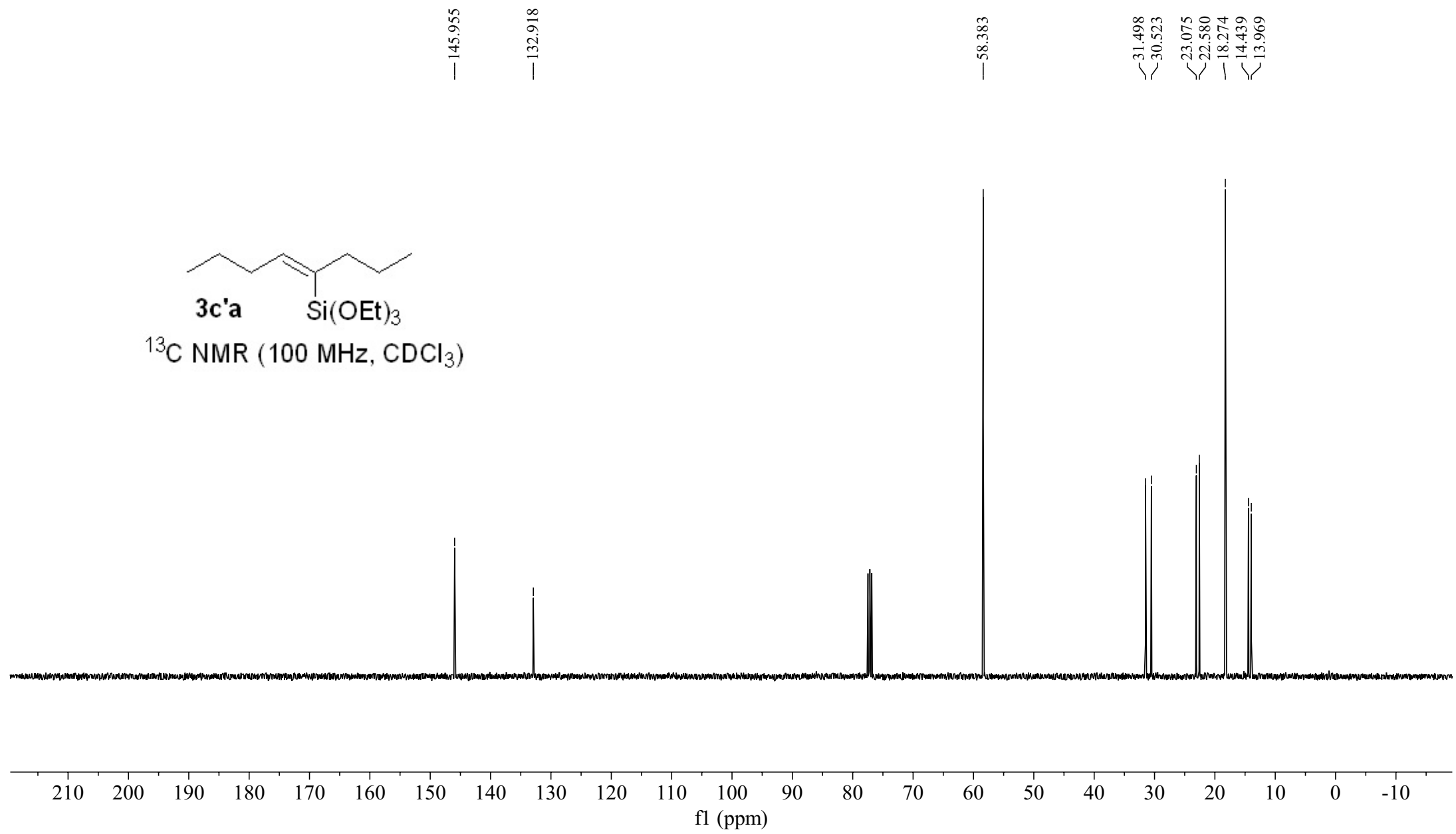
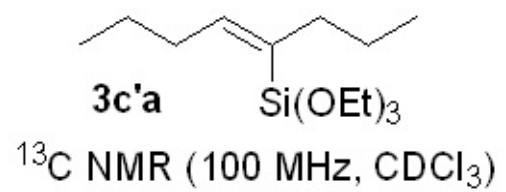
142.553  
140.851  
137.204  
137.028  
130.005  
128.609  
128.412  
128.002  
127.603  
126.240

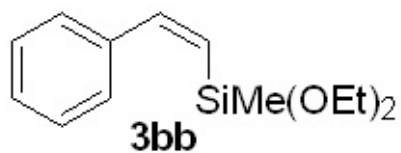
58.973

18.282

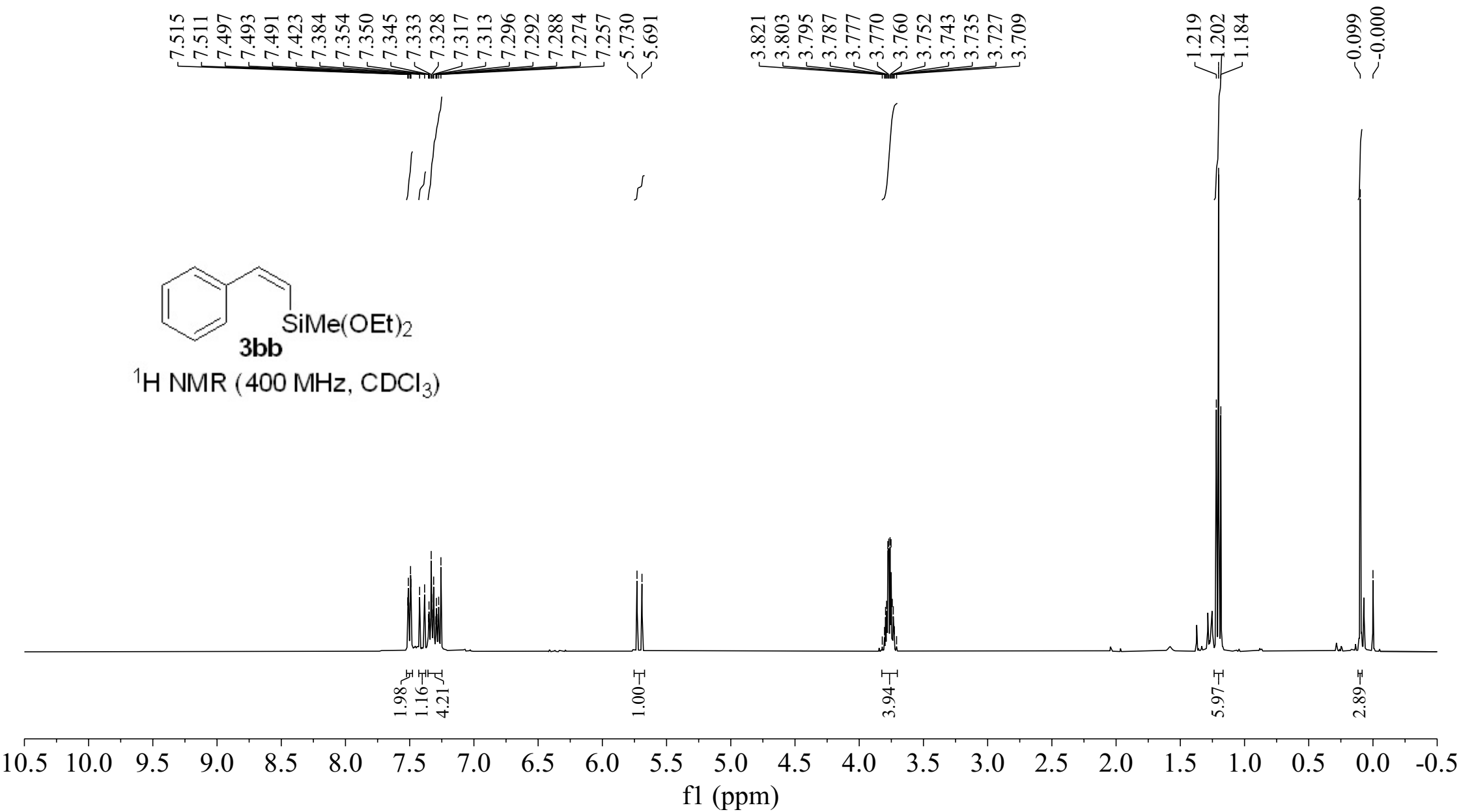




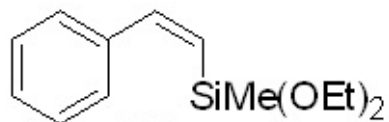




<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

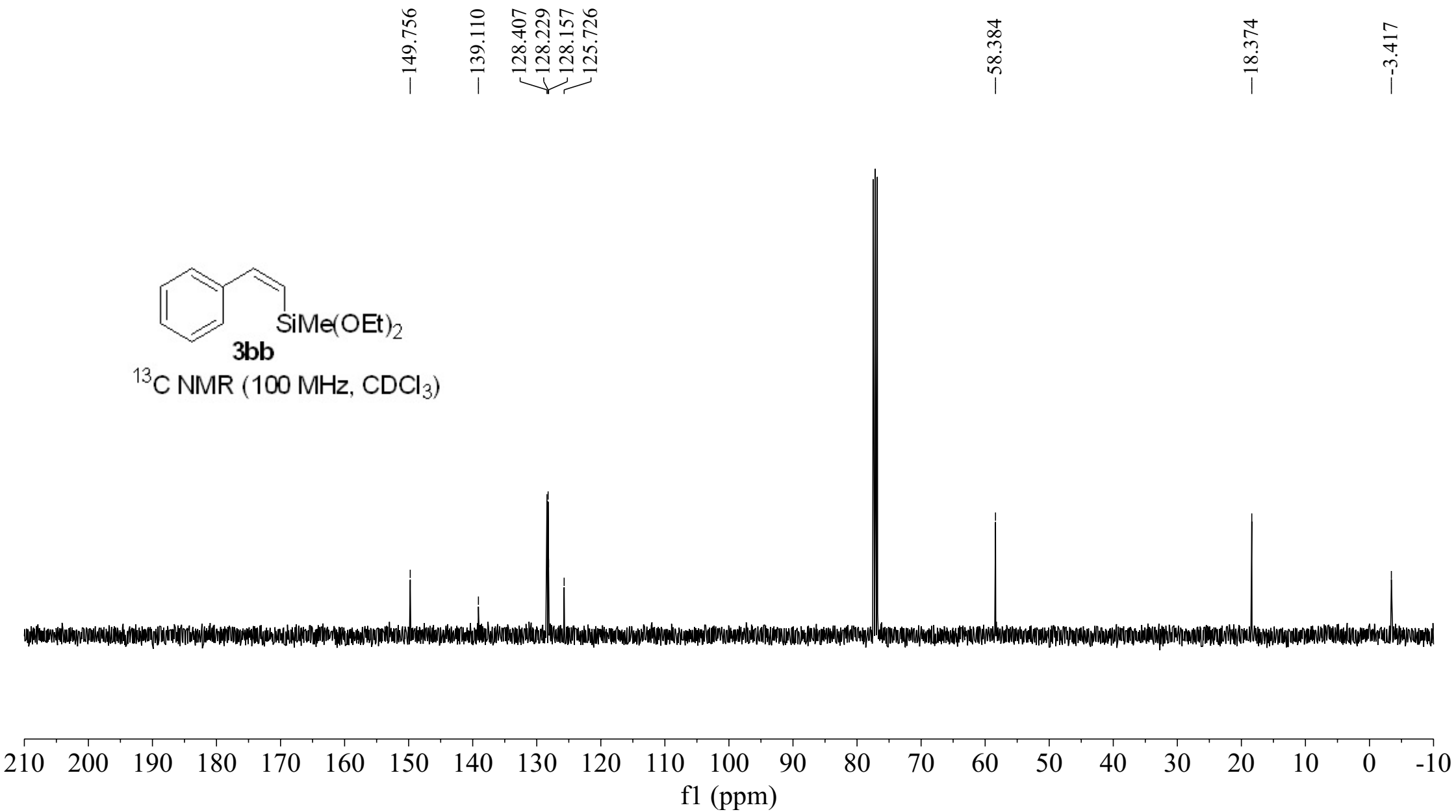


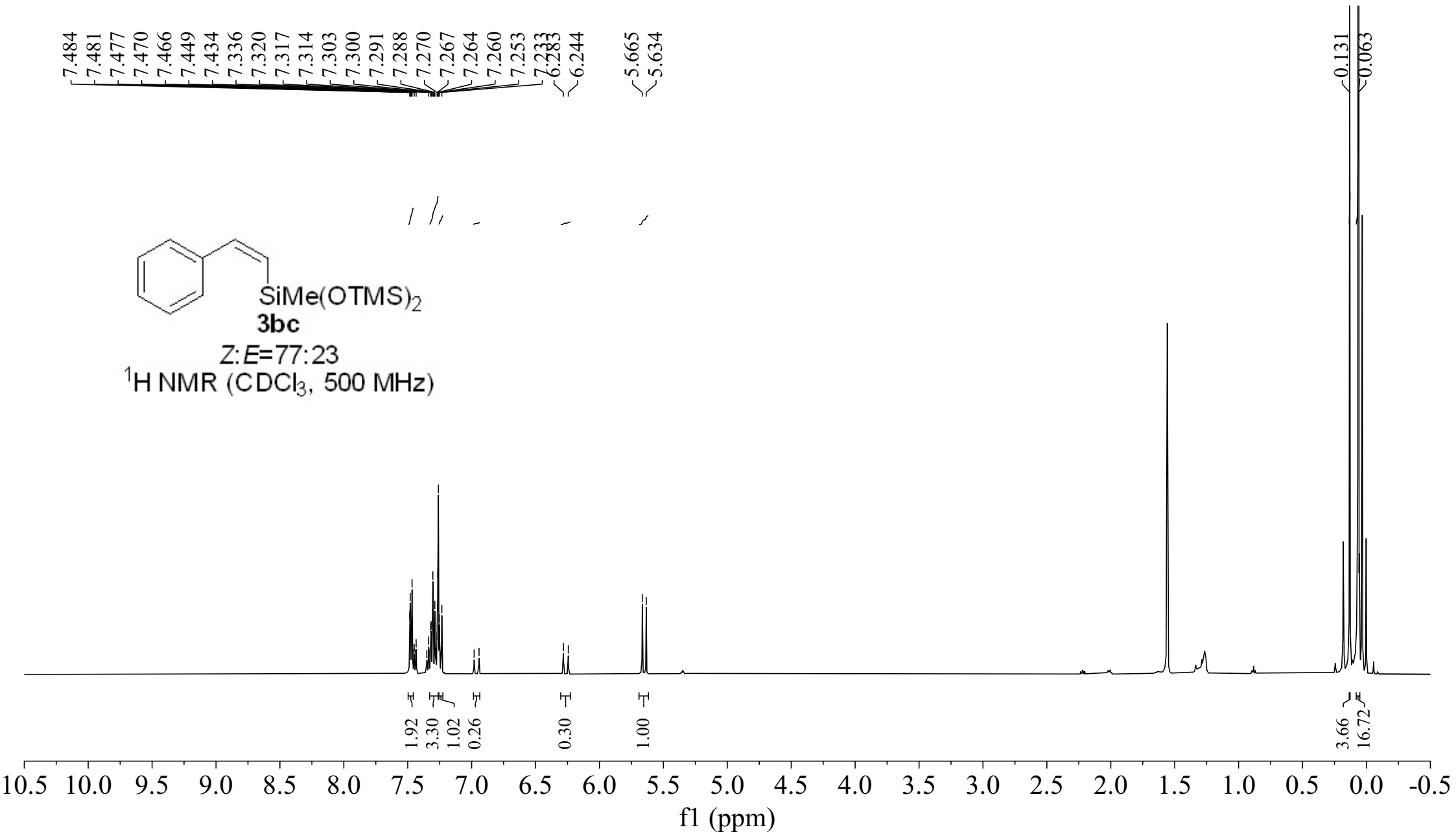


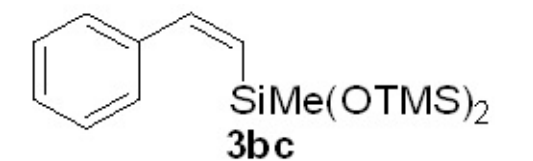


**3bb**

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





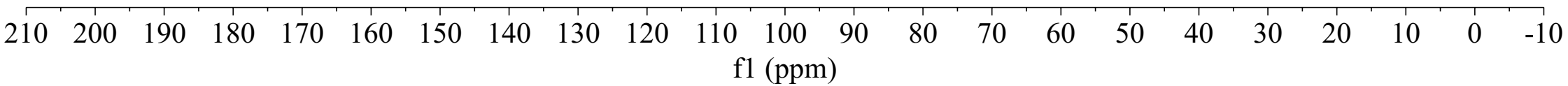


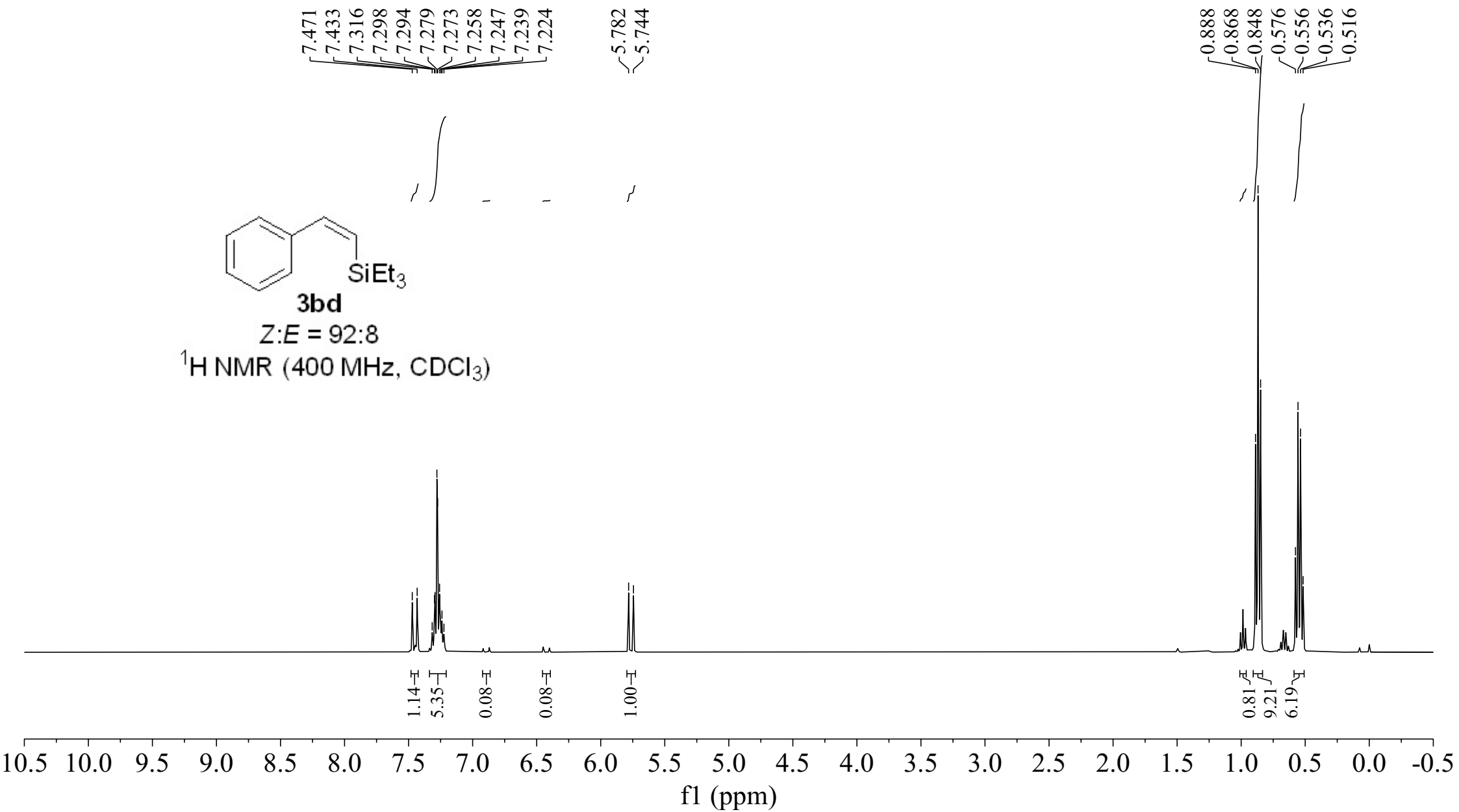
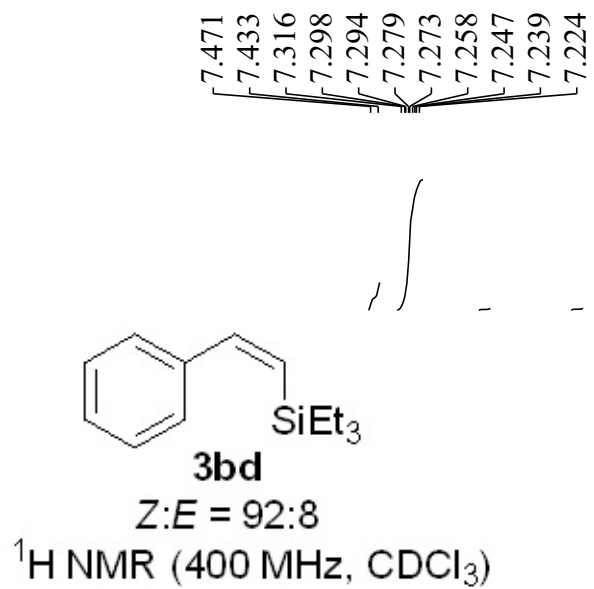
Z:E=77:23

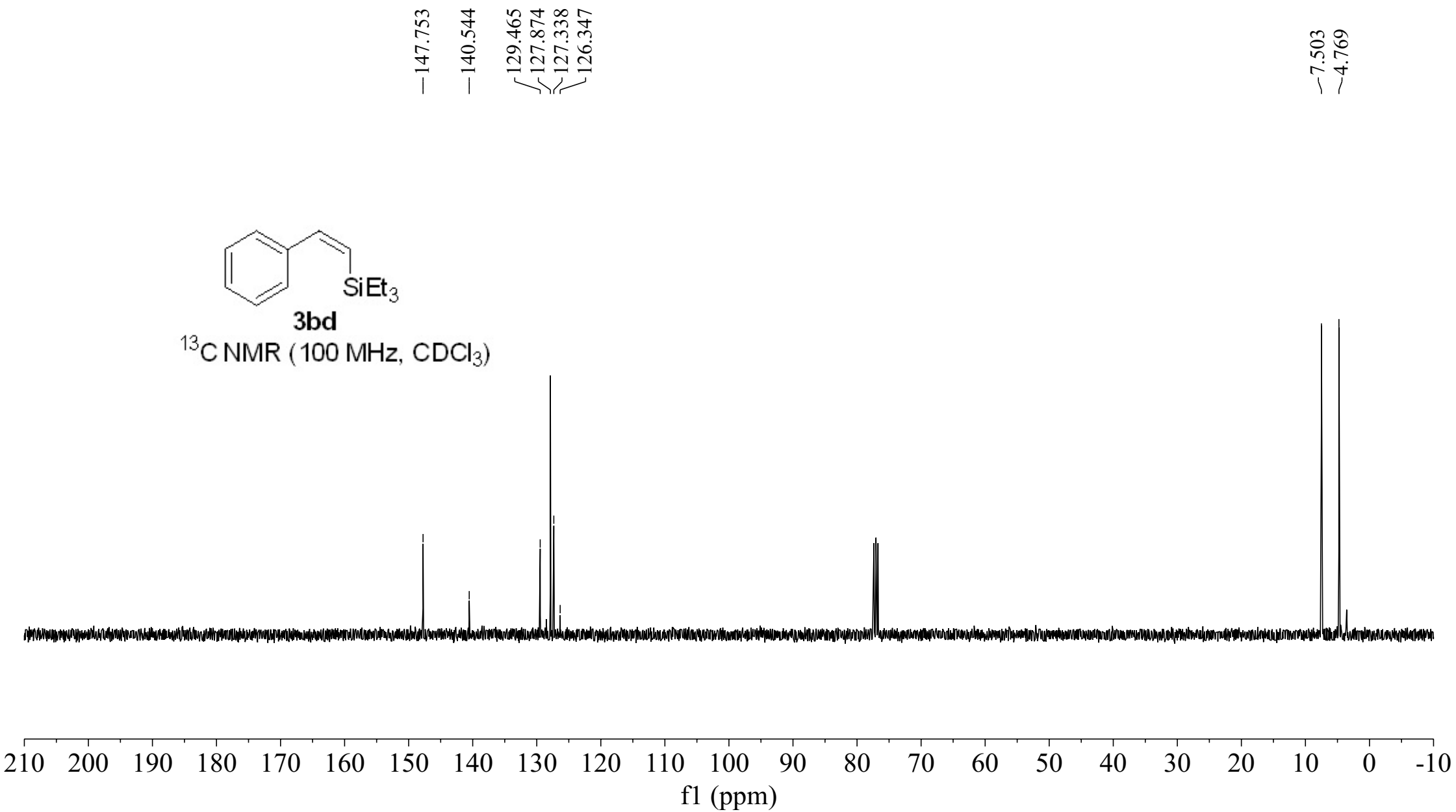
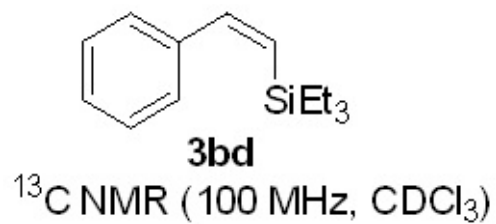
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz)

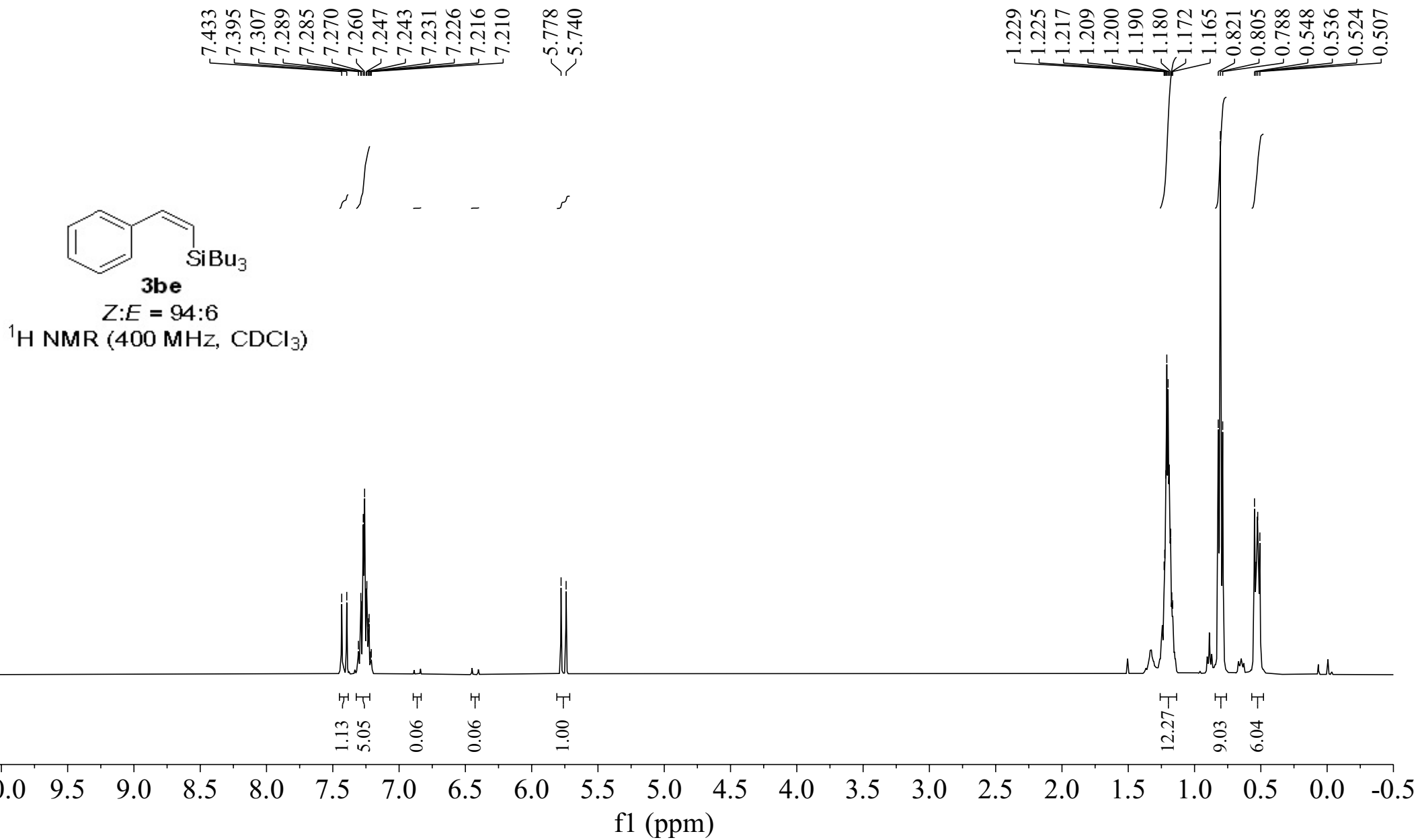
— 147.289  
— 139.440  
— 129.949  
— 128.608  
— 128.043  
— 127.788

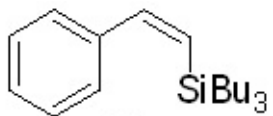
— 1.871  
— 1.298





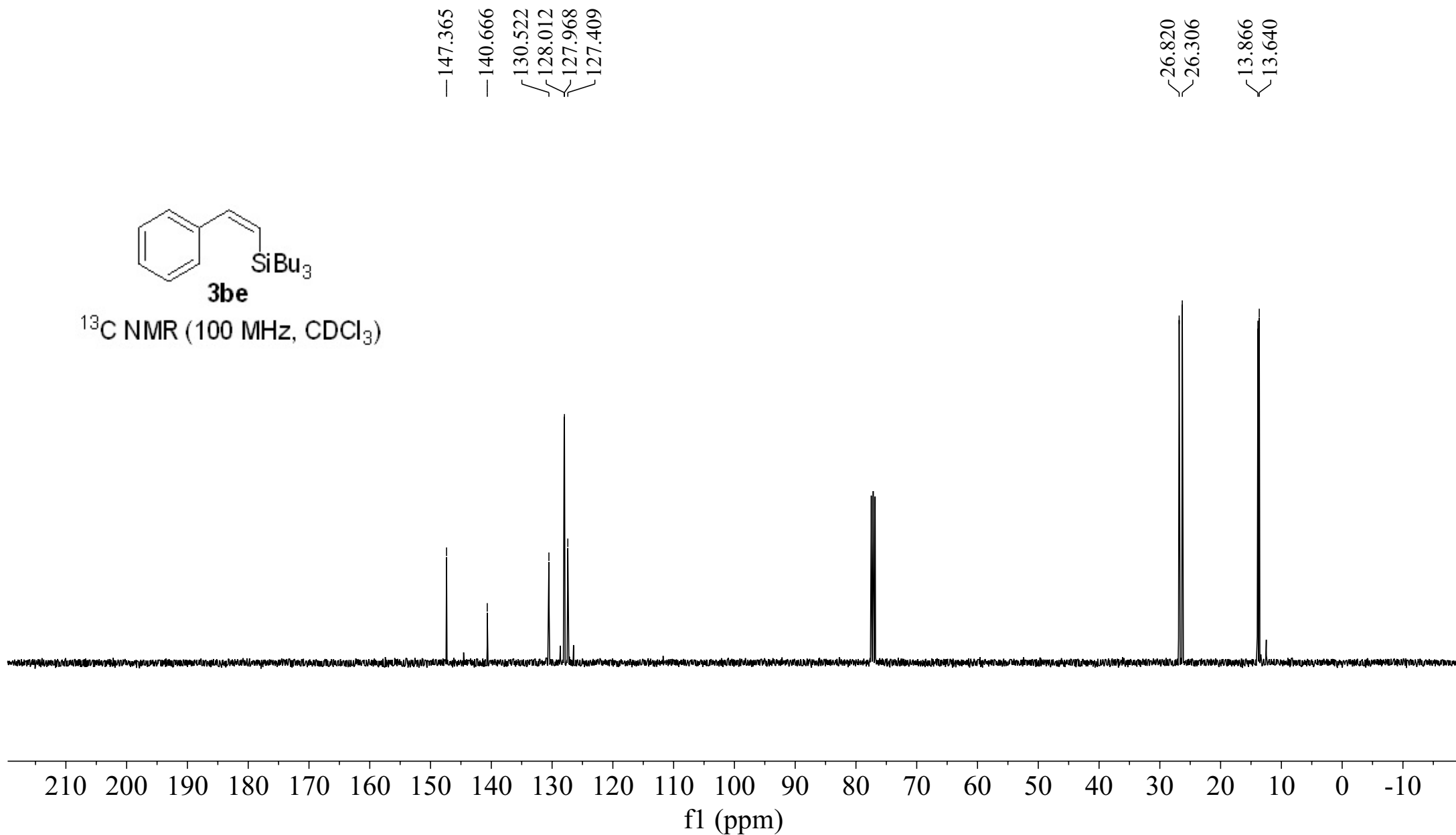


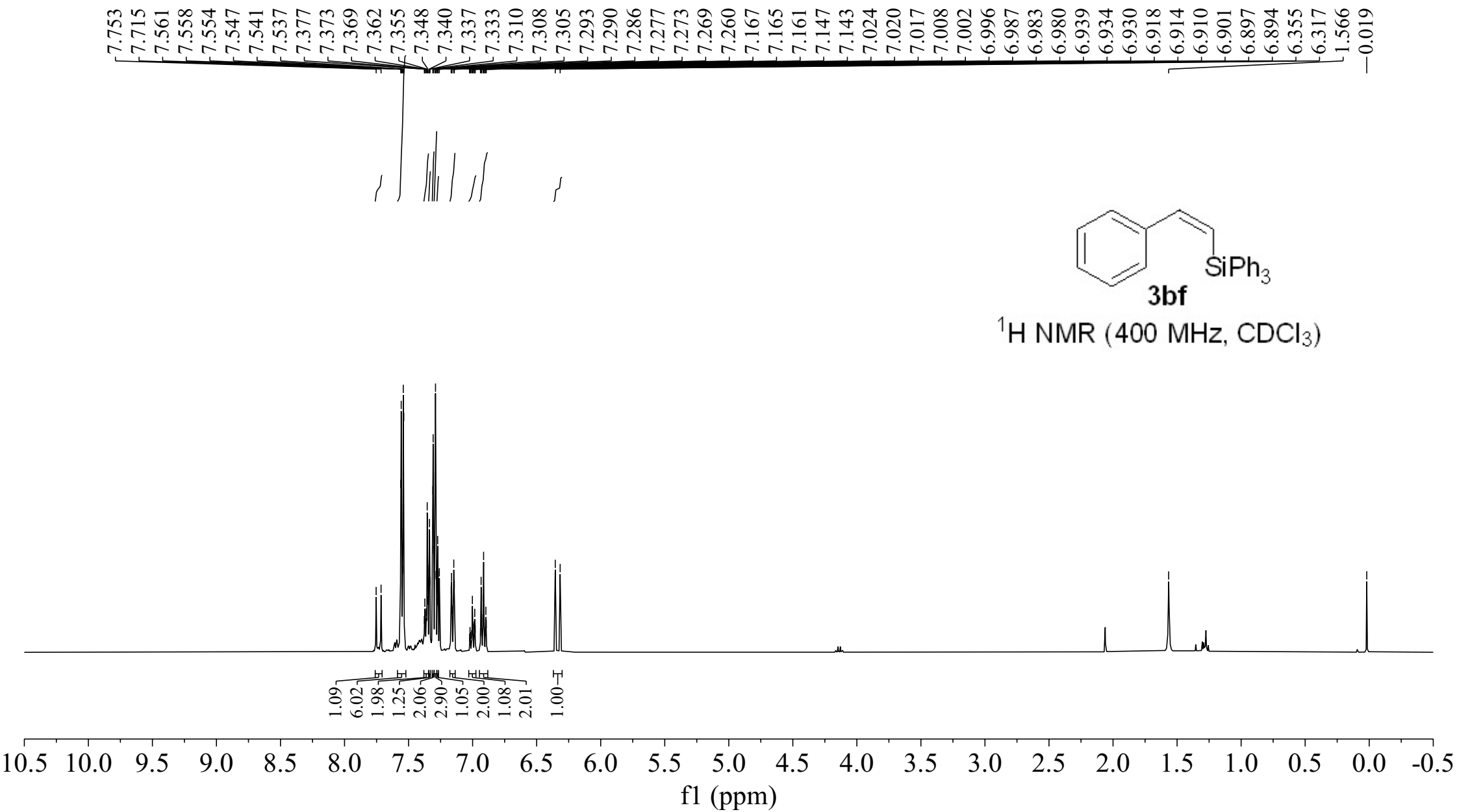




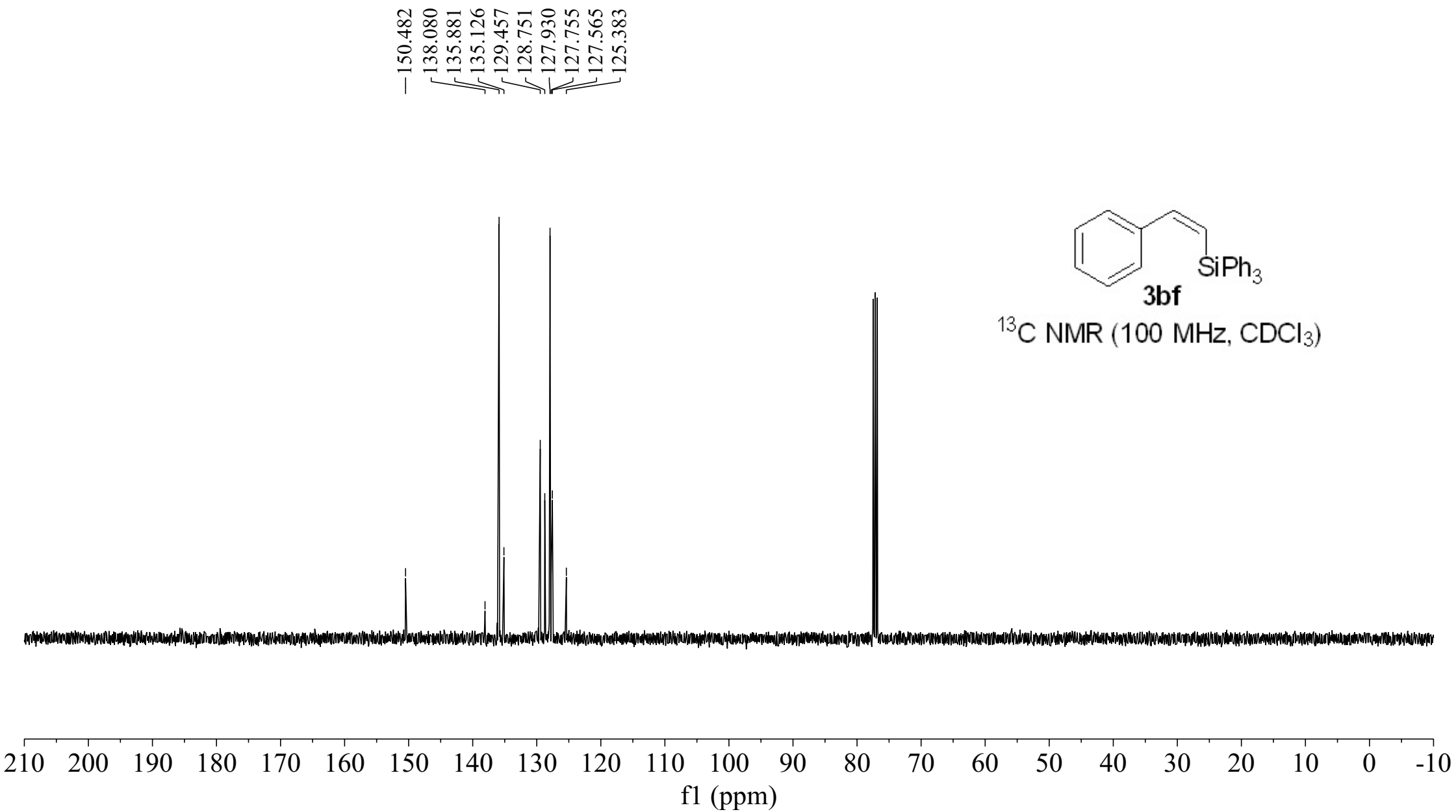
**3be**

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

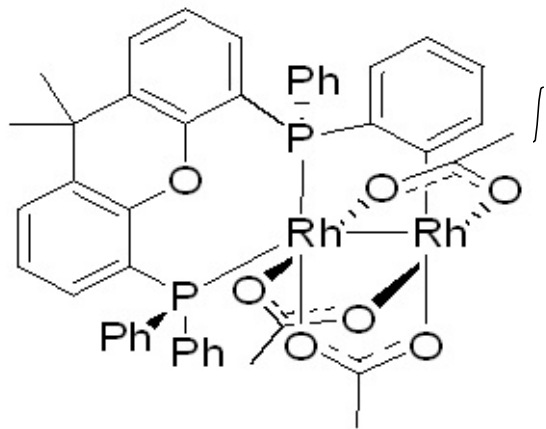






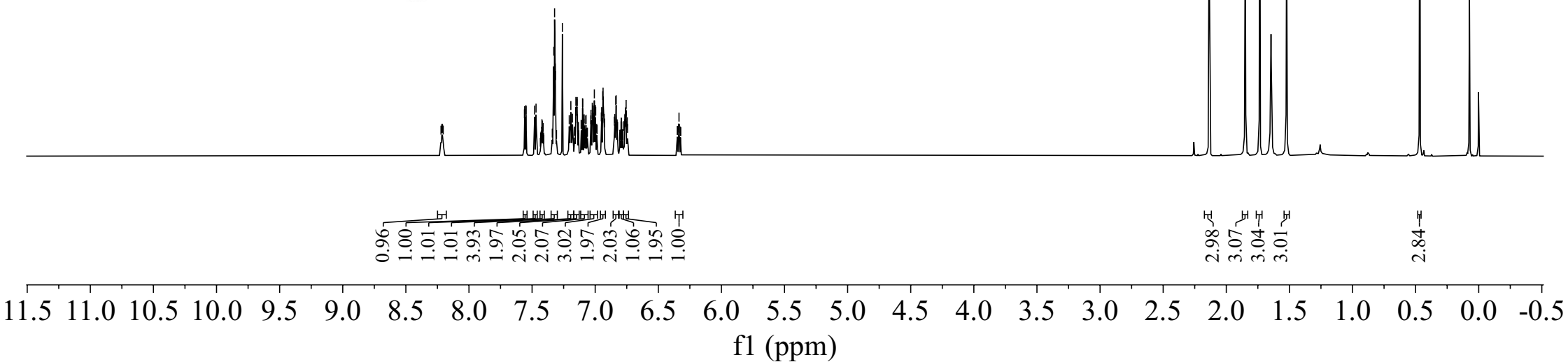


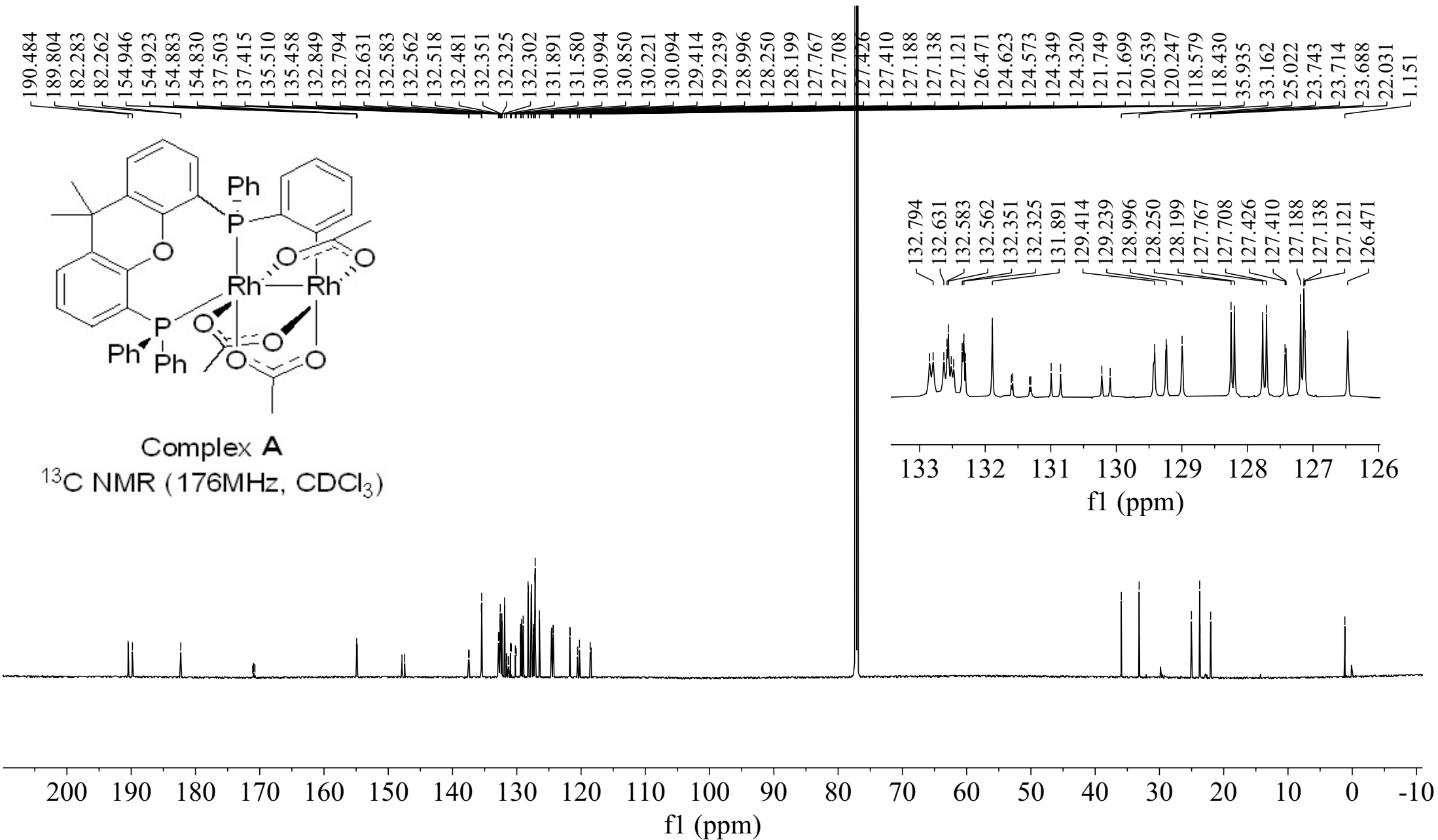
7.561  
7.559  
7.549  
7.547  
7.480  
7.469  
7.331  
7.328  
7.322  
7.318  
7.316  
7.315  
7.260  
7.206  
7.193  
7.180  
7.155  
7.153  
7.151  
7.144  
7.143  
7.141  
7.100  
7.099  
7.088  
7.075  
7.072  
7.035  
7.033  
7.023  
7.021  
7.019  
7.017  
7.010  
7.007  
7.005  
6.999  
6.996  
6.952  
6.949  
6.941  
6.938  
6.929  
6.848  
6.845  
6.837  
6.834  
6.765  
6.763  
6.760  
6.758  
6.755  
6.746  
6.336  
2.135  
1.849  
1.735  
1.522  
0.467

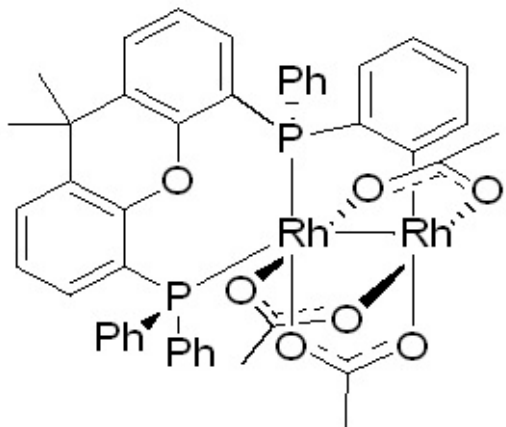


Complex A

$^1\text{H}$  NMR (700MHz,  $\text{CDCl}_3$ )







Complex A

$^{31}\text{P}$  NMR (283MHz,  $\text{CDCl}_3$ )

1.839  
1.810  
1.340

-58.093  
-58.337  
-58.377  
-58.618

