

## Preparation of silyl substituted crotylzinc reagents and their highly diastereoselective addition to carbonyl compounds

Matthew D. Helm, Peter Mayer and Paul Knochel\*

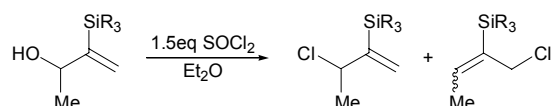
Department Chemie, Ludwig-Maximilians-Universität, Butenandtstrasse 5-13, 81377, München (Germany).

[Paul.Knochel@cup.uni-muenchen.de](mailto:Paul.Knochel@cup.uni-muenchen.de)

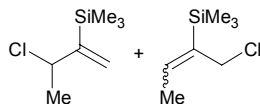
### 1. General

All reactions were carried out under argon using standard Schlenk techniques. Melting points are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX 300 or AMX 600 instrument. Chemical shifts are given as ppm relative to the residual solvent peak (chloroform-*d*1:7.26 ppm/77.0 ppm). IR spectra were recorded on a Perkin Elmer 1420 Infrared Spectrometer. Mass spectra were recorded on a Finnigan Mat 95 Q spectrometer. Column chromatography purification was performed on Merck silica gel 60 (230-400 mesh ASTM). THF was dried with sodium/benzophenone and distilled. Yields refer to isolated yields of compounds estimated to be > 95% pure as determined by  $^1\text{H}$ -NMR and capillary GC.

### 2. Formation of silyl substituted allylic chlorides

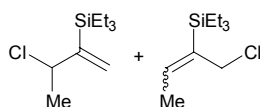


#### Formation of [1-(1-chloro-ethyl)-vinyl]-trimethyl-silane (**1a**) and (1-chloromethyl-propenyl)-trimethyl-silane (**1b**)



To a solution of 3-trimethylsilyl-but-3-en-2-ol<sup>1</sup> (28.9 g, 200 mmol) in dry diethyl ether (400 mL) at 25 °C was added thionyl chloride (21.9 mL, 300 mmol). The reaction was stirred for 16 hours at 25 °C before being quenched with water. The aqueous layer was extracted three times with diethyl ether, the combined organic fractions dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. The crude product was purified by distillation under vacuum to give a mixture of 1-(1-chloro-ethyl)-vinyl]-trimethyl-silane **1a** and (1-chloromethyl-propenyl)-trimethyl-silane **1b** (26.0 g, 80%).<sup>2</sup>

#### Formation of [1-(1-chloro-ethyl)-vinyl]-triethyl-silane (**13a**) and (1-chloromethyl-propenyl)-triethyl-silane (**13b**)



To a solution of 3-triethylsilyl-but-3-en-2-ol<sup>3</sup> (4 g, 21.5 mmol) in dry diethyl ether (43 mL) at 25 °C was added thionyl chloride (2.35 mL, 32.2 mmol). The reaction was stirred for 16 hours at 25 °C before being quenched with water. The aqueous layer was extracted three times with diethyl ether, the combined organic fractions dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel using pentane as the

eluent to give a mixture of [1-(1-chloro-ethyl)-vinyl]-triethylsilane **13a** and (1-chloromethyl-propenyl)-triethylsilane **13b** (3.35 g, 76%) as a colourless oil.

<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>) (major isomer): δ 0.54-0.84 (9H, m, CH<sub>3</sub>), 0.90-1.10 (8H, m, CH<sub>2</sub>), 1.81 (3H, dt, *J* = 7 Hz, *J* = 2 Hz, CH<sub>3</sub>), 4.11 (2H, br, CH<sub>2</sub>), 6.49 (1H, qt, *J* = 7 Hz, *J* = 1 Hz, CH).

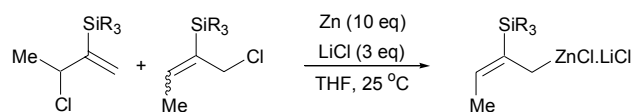
<sup>13</sup>C-NMR (75 MHz; CDCl<sub>3</sub>): (major isomer): δ 143.8, 134.3, 52.3, 17.6, 7.5, 3.8.

IR (neat): 2953 (m), 2912 (m), 2876 (m), 1612 (w), 1457 (w), 1416 (w), 1255 (w) cm<sup>-1</sup>.

MS (EI, 70 eV) *m/z* = 175 (M<sup>+</sup>-Et), 147, 121, 93.

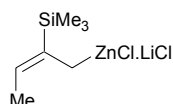
HRMS (EI): calcd. for C<sub>8</sub>H<sub>16</sub>SiCl [M<sup>+</sup>-Et]: 175.0710. Found: 175.0707.

### 3. Formation of silyl substituted crotyl zinc reagents from silyl substituted allylic chlorides



To a dry 50 mL argon flushed schlenk tube was added lithium chloride (1.27, 30 mmol) the flask was evacuated and the lithium chloride heated under vacuum until thoroughly dry. To this flask was then added zinc dust (6.54g, 100 mmol), the flask was again evacuated and the contents thoroughly dried by heating under vacuum. The cooled flask was purged with argon three times and THF (5 mL) was added before the zinc was activated using 1,2-dibromoethane (5 mol %) and chlorotrimethylsilane (1 mol %).<sup>4</sup> The allyl chloride (10 mmol) was then added in THF (10 mL) and the suspension vigorously stirred at 25 °C until complete consumption of the allyl chloride was observed (monitored by GC analysis of reaction aliquats). After allowing the excess zinc to settle at the bottom of the flask the allyl zinc reagent was titrated against iodine before use.

#### 2-trimethylsilylbut-2-enylzinc chloride **2**:

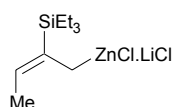


A mixture of [1-(1-chloro-ethyl)-vinyl]-trimethylsilane **1a** and (1-chloromethyl-propenyl)-trimethylsilane **1b** (1.63 g, 10 mmol) was used and the reaction was completed after 18 hours. The concentration of **2** and the yield were determined as follows:

Iodine (254 mg, 1 mmol) was placed into a dry 10 mL round-bottomed flask equipped with a magnetic stirrer bar and septum under argon. Dry THF (5 mL) was added and the solution of **2** in THF was added dropwise until the red colour disappeared. The volume of the solution of **2** added was determined and the following equation used to determine the molarity of the solution: molarity of zinc reagent **2** = 1/volume of zinc reagent **2**.

The concentration of **2** in THF was 0.51 molL<sup>-1</sup>; volume = 15.0 mL; yield: 78%.

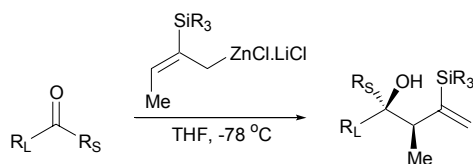
#### 2-triethylsilylbut-2-enylzinc chloride **14**:



A mixture of [1-(1-chloro-ethyl)-vinyl]-triethylsilane **13a** and (1-chloromethyl-propenyl)-triethylsilane **13b** (2.05 g, 10 mmol) was used and the reaction was completed after 24 hours. The concentration of **14** in THF was determined as above.

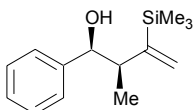
The concentration of **14** in THF was 0.39 molL<sup>-1</sup>; volume = 14.5 mL; yield: 57%.

#### 4. Addition of silyl substituted crotyl zinc reagents to aldehydes or ketones



To a solution of the aldehyde or ketone (1 mmol) in THF (2 mL) at -78 °C was added the silyl substituted crotyl zinc reagent (1.1 mmol) as a solution in THF. Upon complete conversion of the aldehyde or ketone (monitored by GC or TLC analysis of reaction aliquats) the reaction was diluted with diethyl ether and a minimum amount of water was added. After drying over magnesium sulfate, the solids were filtered and the solvents were removed *in vacuo* before the crude products were purified by chromatography on silica.

#### 2-methyl-1-phenyl-3-trimethylsilylbut-3-en-1-ol **3**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to benzaldehyde (0.10 mL, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 5 : 1 pentane/diethyl ether to give **3** (220 mg, 94%) as colourless oil.

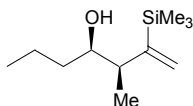
**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 0.00 (CH<sub>3</sub>, s, 9H), 0.89 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 1.78 (OH, br, 1H), 2.69 (CH, dq, *J* = 5 Hz, *J* = 7 Hz, 1H), 4.66 (CH, d, *J* = 5 Hz, 1H), 5.51 (CH, d, *J* = 2 Hz, 1H), 5.73 (CH, d, *J* = 2 Hz, 1H), 7.12- 7.31 (Ar, m, 5H).

**<sup>13</sup>C-NMR** (75 MHz; CDCl<sub>3</sub>): δ -1.3, 13.3, 44.8, 74.9, 125.6, 126.1, 127.0, 128.0, 143.1, 155.2. **IR** (neat): 3418 (br), 3032 (w), 2956 (m), 2895 (w), 1452 (w), 1404 (w) 1247 (m) cm<sup>-1</sup>.

**MS** (EI, 70 eV) *m/z* = 235 (M<sup>+</sup>+H), 219, 201, 179, 128.

**HRMS** (EI): calcd. for C<sub>14</sub>H<sub>22</sub>OSi: 234.1440. Found: 234.1414.

#### 3-methyl-2-trimethylsilylhept-1-en-4-ol **5**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to butyraldehyde (0.09 mL, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 10 : 1 pentane/diethyl ether to give **5** (180 mg, 90%) as colourless oil.

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 0.10 (CH<sub>3</sub>, s, 9H), 0.93 (CH<sub>3</sub>, t, *J* = 7 Hz, 3H), 1.03 (CH<sub>3</sub>, t, *J* = 7 Hz, 3H), 1.23-1.50 (CH<sub>2</sub>, m, 4H), 1.52 (OH, br, 1H), 2.42 (CH, m, 1H), 3.54 (CH, dt, *J* = 5 Hz, *J* = 12 Hz, 1H), 5.52 (CH, d, *J* = 2 Hz, 1H), 5.68 (CH, dd, *J* = 2 Hz, *J* = 1 Hz, 1H).

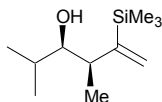
**<sup>13</sup>C-NMR** (75 MHz; CDCl<sub>3</sub>): δ -1.1, 13.6, 14.1, 19.5, 37.0, 43.1, 72.6, 124.9, 155.9.

**IR** (neat): 3335 (br), 3048 (w), 2957 (s), 2873 (m), 1458 (w), 1404 (w), 1248 (m) cm<sup>-1</sup>.

**MS** (EI, 70 eV) *m/z* = 185 (M<sup>+</sup>-Me), 167, 145, 129, 113.

**HRMS** (EI): calcd. for C<sub>11</sub>H<sub>23</sub>OSi [M<sup>+</sup>-H]: 199.1518. Found: 199.1529.

### 2,4-dimethyl-5-trimethylsilyl-hex-5-en-3-ol **6**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to isobutyraldehyde (0.08 mL, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 10 : 1 pentane/diethyl ether to give **6** (190 mg, 95%) as colourless oil.

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 0.11 (CH<sub>3</sub>, s, 9H), 0.91 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 0.98 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 1.00 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 1.54 (OH, br, 1H), 1.71 (CH, m, 1H), 2.66 (CH, m, 1H), 3.15 (CH, dd, *J* = 4 Hz, *J* = 7 Hz, 1H), 5.54 (CH, d, *J* = 2 Hz, 1H), 5.70 (CH, m, 1H).

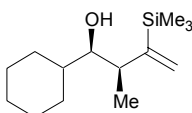
**<sup>13</sup>C-NMR** (75 MHz; CDCl<sub>3</sub>): δ -0.9, 12.6, 18.8, 19.4, 30.5, 40.5, 77.4, 125.3, 156.0.

**IR** (neat): 3421 (br), 2957 (s), 1463 (w), 1406 (w), 1248 (m) cm<sup>-1</sup>.

**MS** (EI, 70 eV) *m/z* = 185 (M<sup>+</sup>-Me), 167, 145, 128, 113.

**HRMS**: calcd. for C<sub>11</sub>H<sub>24</sub>OSi [M<sup>+</sup>-H]: 199.1518. Found: 199.1532.

### 1-cyclohexyl-2-methyl-3-trimethylsilyl-but-3-en-1-ol **7**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to cyclohexanecarboxaldehyde (0.12 mL, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 10 : 1 pentane/diethyl ether to give **7** (204 mg, 85%) as colourless oil.

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 0.11 (CH<sub>3</sub>, s, 9H), 0.93-1.30 (CH<sub>2</sub>, m, 5H), 0.99 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 1.39 (CH<sub>2</sub>, m, 1H), 1.53 (OH, br, 1H), 1.71 (CH<sub>2</sub>, m, 4H), 2.02 (CH, m, 1H), 2.69 (CH, dq, *J* = 4 Hz, *J* = 7 Hz, 1H), 3.18 (CH, dd, *J* = 4 Hz, *J* = 8 Hz, 1H), 5.56 (CH, d, *J* = 2 Hz, 1H), 5.71 (CH, dd, *J* = 1 Hz, *J* = 2 Hz, 1H).

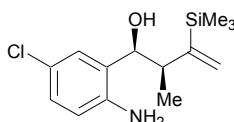
**<sup>13</sup>C-NMR** (75 MHz; CDCl<sub>3</sub>): δ -0.9, 12.2, 26.0, 26.3, 26.5, 29.4, 29.5, 39.5, 40.0, 76.2, 125.3, 156.3.

**IR** (neat): 3399 (br), 2923 (s), 2852 (m), 1449 (w), 1406 (w), 1247 (m) cm<sup>-1</sup>.

**MS** (EI, 70 eV) *m/z* = 225 (M<sup>+</sup>-Me), 207, 185, 169, 149, 129, 113.

**HRMS** (EI): calcd. for C<sub>14</sub>H<sub>28</sub>OSi: 240.1909. Found: 240.1885.

### 1-(2-amino-5-chloro-phenyl)-2-methyl-3-trimethylsilyl-but-3-en-1-ol **8**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to 2-amino-5-chlorobenzaldehyde (156 mg, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 3 : 1 pentane/diethyl ether to give **8** (263 mg, 93%) as light yellow solid mp 68-70 °C.

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ -0.01 (CH<sub>3</sub>, s, 9H), 1.13 (CH<sub>3</sub>, d, 3H), 2.97 (CH, dq, *J* = 7 Hz, *J* = 7 Hz, 1H), 4.62 (CH, d, *J* = 7 Hz, 1H), 5.55 (CH, d, *J* = 2 Hz, 1H), 5.80 (CH, dd, *J* = 1 Hz, *J* = 2 Hz, 1H), 6.50-6.56 (Ar, m, 1H), 6.95-7.01 (Ar, m, 2H).

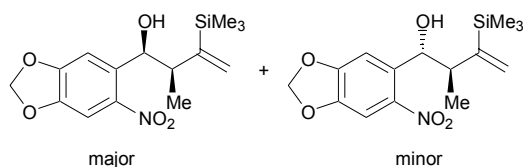
$^{13}\text{C-NMR}$  (75 MHz;  $\text{CDCl}_3$ ):  $\delta$  -1.5, 16.3, 41.4, 76.3, 117.9, 122.4, 125.7, 127.7, 128.0, 128.7, 143.4, 155.4.

**IR** (neat): 3395 (m), 3215 (br), 2955 (m), 2899 (w), 1618 (w), 1488 (m), 1413 (w), 1357 (w), 1248 (m)  $\text{cm}^{-1}$ .

**MS** (EI, 70 eV)  $m/z$  = 283 ( $\text{M}^+$ ), 266, 250, 156, 128.

**HRMS** (EI): calcd. for  $\text{C}_{14}\text{H}_{22}\text{NOClSi}$ : 283.1159. Found: 283.1137.

### 2-methyl-1-(6-nitro-benzo[1,3]dioxol-5-yl)-3-trimethylsilyl-but-3-en-1-ol **9**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to 6-nitropiperonal (195 mg, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 4 : 1 pentane/diethyl ether to give **9** (310 mg, 96%, dr 89 : 11) as yellow oil.

#### Major diastereoisomer:

$^1\text{H-NMR}$  (300 MHz;  $\text{CDCl}_3$ ):  $\delta$  0.13 ( $\text{CH}_3$ , s, 9H), 0.93 ( $\text{CH}_3$ , d,  $J$  = 7 Hz, 3H), 2.16 (OH, br, 1H), 2.98 (CH, m, 1H), 5.40 (CH, d,  $J$  = 5 Hz, 1H), 5.61 (CH, d,  $J$  = 2 Hz, 1H), 5.78 (CH, m, 1H), 6.10 ( $\text{CH}_2$ , s, 2H), 7.26 (Ar, s, 1H), 7.46 (Ar, s, 1H).

$^{13}\text{C-NMR}$  (75 MHz;  $\text{CDCl}_3$ ):  $\delta$  -1.2, 14.4, 42.2, 69.9, 102.8, 105.3, 108.2, 126.6, 135.9, 141.9, 146.7, 151.8, 155.2.

**IR** (neat): 3405 (br), 2957 (m), 1618 (w), 1520 (s), 1504 (s), 1420 (w), 1329 (m), 1246 (s)  $\text{cm}^{-1}$ .

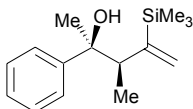
**MS** (EI, 70 eV)  $m/z$  = 308 ( $\text{M}^+ - \text{Me}$ ), 290, 268, 196, 165, 148, 129, 113.

**HRMS** (EI): calcd. for  $\text{C}_{15}\text{H}_{21}\text{NO}_5\text{Si}$  [ $\text{M}^+ - \text{H}$ ]: 322.1111. Found: 322.1101.

#### Minor diastereoisomer:

$^1\text{H-NMR}$  (300 MHz;  $\text{CDCl}_3$ ): 0.14 ( $\text{CH}_3$ , s, 9H), 0.90 ( $\text{CH}_3$ , d,  $J$  = 7 Hz, 3H), 2.16 (OH, br, 1H), 2.98 (CH, m, 1H), 5.45 (CH, d,  $J$  = 9 Hz, 1H), 5.66 (CH, d,  $J$  = 2 Hz, 1H), 5.80 (CH, m, 1H), 6.10 ( $\text{CH}_2$ , s, 2H), 7.14 (Ar, s, 1H), 7.39 (Ar, s, 1H). (Could not distinguish  $^{13}\text{C}$  signals for minor diastereomer).

### 3-methyl-2-phenyl-4-trimethylsilyl-pent-4-en-2-ol **10**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to acetophenone (0.12 mL, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 20 : 1 pentane/diethyl ether containing 2% triethylamine to give **10** (239 mg, 96%) as a colourless oil.

$^1\text{H-NMR}$  (600 MHz;  $\text{CDCl}_3$ ):  $\delta$  0.13 ( $\text{CH}_3$ , s, 9H), 0.81 ( $\text{CH}_3$ , d,  $J$  = 7 Hz, 3H), 1.46 ( $\text{CH}_3$ , s, 3H), 1.84 (OH, br, 1H), 2.77 (CH, q,  $J$  = 7 Hz, 1H), 5.62 (CH, d,  $J$  = 2 Hz, 1H), 5.94 (CH, d,  $J$  = 2 Hz, 1H), 7.20-7.25 (Ar, m, 1H), 7.31-7.36 (Ar, m, 2H), 7.41-7.46 (Ar, m, 2H).

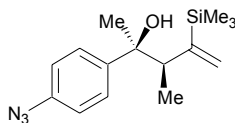
$^{13}\text{C-NMR}$  (150 MHz;  $\text{CDCl}_3$ ):  $\delta$  -0.8, 16.9, 30.5, 47.6, 76.6, 125.0, 126.2, 127.0, 127.9, 147.9, 155.6.

**IR** (neat): 3486 (w), 2957 (m), 1495 (w), 1445 (w), 1369 (w), 1247 (m)  $\text{cm}^{-1}$ .

**MS** (EI, 70 eV)  $m/z$  = 233 ( $\text{M}^+ - \text{Me}$ ), 215, 193, 156, 121.

**HRMS** (EI): calcd. for C<sub>15</sub>H<sub>24</sub>OSi [M<sup>+</sup>-H]: 247.1518. Found: 247.1519.

### 2-(4-azido-phenyl)-3-methyl-4-trimethylsilanyl-pent-4-en-2-ol **11**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to 1-(4-azido-phenyl)-ethanone<sup>5</sup> (161 mg, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 10 : 1 pentane/diethyl ether containing 2% triethylamine to give **11** (263 mg, 91%) as a light yellow oil.

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 0.13 (CH<sub>3</sub>, s, 9H), 0.81 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 1.44 (CH<sub>3</sub>, s, 3H), 1.84 (OH, br, 1H), 2.73 (CH, q, *J* = 7 Hz, 1H), 5.62 (CH, d, *J* = 2 Hz, 1H), 5.90 (CH, d, *J* = 2 Hz, 1H), 6.97-7.02 (Ar, m, 2H), 7.38-7.45 (Ar, m, 2H).

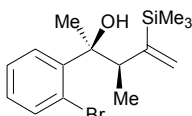
**<sup>13</sup>C-NMR** (75 Hz; CDCl<sub>3</sub>): δ -0.8, 16.9, 30.5, 47.5, 76.4, 118.5, 126.6, 127.1, 138.0, 144.7, 155.5.

**IR** (neat): 3488 (w), 2958 (m), 2116 (s), 2088 (s), 1604 (w), 1504 (m), 1453 (w), 1411 (w), 1369 (w), 1290 (m), 1247 (m) cm<sup>-1</sup>.

**MS** (EI, 70 eV) *m/z* = 261 (M<sup>+</sup>-N<sub>2</sub>), 245, 228, 172, 156, 136.

**HRMS** (EI): calcd. For C<sub>15</sub>H<sub>23</sub>N<sub>3</sub>OSi: 289.1610. Found: 289.1593.

### 2-(2-bromo-phenyl)-3-methyl-4-trimethylsilanyl-pent-4-en-2-ol **12**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to 2'-bromoacetophenone (199 mL, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 10 : 1 pentane/diethyl ether containing 2% triethylamine to give **12** (311 mg, 95%) as colourless oil.

**<sup>1</sup>H-NMR** (300 MHz; CDCl<sub>3</sub>): δ 0.18 (CH<sub>3</sub>, s, 9H), 0.74 (CH<sub>3</sub>, d, *J* = Hz, 3H), 1.66 (CH<sub>3</sub>, s, 3H), 2.12 (OH, br, 1H), 3.75 (CH, q, *J* = Hz, 1H), 5.69 (CH, d, *J* = Hz, 1H), 6.06 (CH, d, *J* = Hz, 1H), 7.08 (Ar, dt, *J* = 2 Hz *J* = 8 Hz, 1H), 7.31 (Ar, dt, *J* = 2 Hz *J* = 8 Hz, 1H), 7.58 (Ar, dd, *J* = 2 Hz *J* = 8 Hz, 1H), 7.92 (Ar, dd, *J* = 2 Hz *J* = 8 Hz, 1H).

**<sup>13</sup>C NMR** (75 MHz; CDCl<sub>3</sub>): δ -0.6, 17.0, 27.7, 41.9, 77.0, 119.4, 127.2, 127.8, 128.1, 128.9, 135.0, 145.6, 155.9.

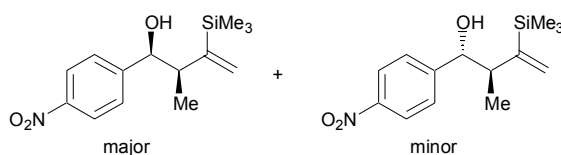
**IR** (neat): 3577 (w), 2957 (w), 1463 (w), 1424 (w), 1370 (w), 1247 (m) cm<sup>-1</sup>.

**MS** (EI, 70 eV) *m/z* = 313 (M<sup>+</sup>-Me), 311, 295, 293, 273, 271, 199, 183, 157.

**HRMS** (EI): calcd. for C<sub>14</sub>H<sub>20</sub>OSiBr [M<sup>+</sup>-Me] calcd: 311.0467. Found: 311.0436.

calcd. for C<sub>13</sub>H<sub>17</sub>OSiBr [M<sup>+</sup>-2Me] calcd: 296.0232. Found: 296.0236.

### 2-methyl-1-(4-nitro-phenyl)-3-trimethylsilyl-but-3-en-1-ol **15**:



A 0.51 M solution of **2** (2.2 mL, 1.1 mmol) was added to 4-nitrobenzaldehyde (151 mg, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 4 : 1 pentane/diethyl ether to give **15** (249 mg, 89%, dr 89 : 11) as colourless solid. Recrystallisation from ethyl acetate/pentane only the major isomer (200 mg, 71%) as a colourless solid mp 75-76 °C. (see CCDC 673535 and attached .cif file)

**Major diastereoisomer:**

<sup>1</sup>H-NMR (600 MHz; CDCl<sub>3</sub>): δ 0.11 (CH<sub>3</sub>, s, 9H), 0.90 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 2.07 (OH, br, 1H), 2.79 (CH, dq, *J* = 4 Hz, *J* = 7 Hz, 1H), 4.82 (CH, d, *J* = 4 Hz, 1H), 5.65 (CH, d, *J* = 2 Hz, 1H), 5.82 (CH, t, *J* = 2 Hz, 1H), 7.51 (Ar, d, *J* = 9 Hz, 2H), 8.19 (Ar, d, *J* = 9 Hz, 2H).

<sup>13</sup>C-NMR (150 MHz; CDCl<sub>3</sub>): δ -1.3, 12.7, 44.6, 73.8, 123.3, 126.4, 126.9, 147.0, 150.5, 154.6.

IR (neat): 3543 (m), 3110 (w), 3052 (w), 2957 (m), 2927 (w), 2888 (w), 1603 (w), 1512 (s), 1415 (w), 1343 (s) 1245 (m) cm<sup>-1</sup>.

MS (EI, 70 eV) *m/z* = 264 (M<sup>+</sup>-Me), 246, 225, 210, 152, 128, 113.

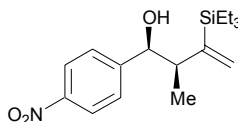
HRMS (EI): calcd. for C<sub>14</sub>H<sub>21</sub>NO<sub>3</sub>Si: 279.1291. Found: 279.1276.

**Minor diastereoisomer:**

<sup>1</sup>H-NMR (600 MHz; CDCl<sub>3</sub>): δ 0.17 (CH<sub>3</sub>, s, 9H), 0.83 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 2.32 (OH, br, 1H), 2.55 (CH, dq, *J* = 9 Hz, *J* = 7 Hz, 1H), 4.65 (CH, d, *J* = 9 Hz, 1H), 5.70 (CH, d, *J* = 2 Hz, 1H), 5.89 (CH, d, *J* = 2 Hz, 1H), 7.54 (Ar, d, *J* = 9 Hz, 2H), 8.21 (Ar, d, *J* = 9 Hz, 2H).

<sup>13</sup>C-NMR (150 MHz; CDCl<sub>3</sub>): δ -1.0, 18.3, 48.3, 123.4, 127.1, 127.9, 147.5, 150.0, 154.9. (1 carbon hidden by solvent or major diastereomer).

**2-methyl-1-(4-nitro-phenyl)-3-triethylsilyl-but-3-en-1-ol 16:**



A 0.51 M solution of **14** (2.2 mL, 1.1 mmol) was added to 4-nitrobenzaldehyde (151 mg, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 5 : 1 pentane/diethyl ether to give **16** (257 mg, 80%, dr 94 : 6) as a yellow oil.

**Major diastereoisomer:**

<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): δ 0.55-0.74 (CH<sub>2</sub>, m, 6H), 0.86 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 0.90-0.99 (CH<sub>3</sub>, m, 9H), 2.11 (OH, br, 1H), 2.83 (CH, dq, *J* = 4 Hz, *J* = 7 Hz, 1H), 4.80 (CH, d, *J* = 4 Hz, 1H), 5.65 (CH, d, *J* = 2 Hz, 1H), 5.93 (CH, m, 1H), 7.49-7.56 (Ar, m, 2H), 8.17-8.24 (Ar, m, 2H).

<sup>13</sup>C-NMR (75 MHz; CDCl<sub>3</sub>): δ 3.0, 7.3, 12.1, 44.4, 73.2, 123.3, 126.8, 127.6, 147.0, 150.4, 151.8.

IR (EI): 3559 (br), 2954 (m), 2876 (m), 1603 (w), 1518 (s), 1344 (s), 1235 (w) cm<sup>-1</sup>.

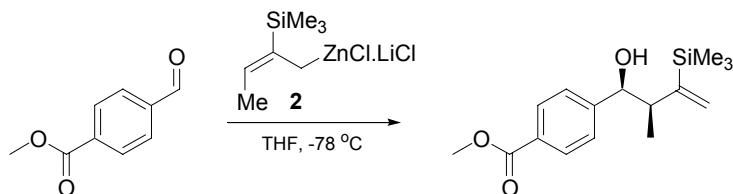
MS (EI, 70 eV) *m/z* = 292 (M<sup>+</sup>-EtH), 274, 238, 170, 141, 103.

HRMS (EI): calcd. for C<sub>17</sub>H<sub>27</sub>NO<sub>3</sub>Si: 321.1760. Found: 321.1754.

**Minor diastereoisomer:**

<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): 0.55-0.74 (CH<sub>2</sub>, m, 6H), 0.81 (CH<sub>3</sub>, d, *J* = 7 Hz, 3H), 0.90-0.99 (CH<sub>3</sub>, m, 9H), 2.53 (CH, dq, *J* = 9 Hz, *J* = 7 Hz, 1H), 4.67 (CH, d, *J* = 9 Hz, 1H), 5.68 (CH, d, *J* = 2 Hz, 1H), 5.97 (CH, m, 1H), 7.49-7.56 (Ar, m, 2H), 8.17-8.24 (Ar, m, 2H).

### Reaction of **2** with 4-formyl-benzoic acid methyl ester:



A 0.46 M solution of **2** (2.4 mL, 1.1 mmol) was added to 4-formyl-benzoic acid methyl ester (164 mg, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 3 : 1 pentane/diethyl ether to give 4-(1-hydroxy-2-methyl-3-trimethylsilylbut-3-enyl)-benzoic acid methyl ester (257 mg, 88%, dr 92 : 8) as colourless oil.

#### Major diastereoisomer:

<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): δ 0.09 (9H, s, CH<sub>3</sub>), 0.92 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 2.00 (1H, br, OH), 2.78 (1H, m, CH), 3.91 (3H, s, CH<sub>3</sub>), 4.78 (1H, d, *J* = 5 Hz, CH), 5.61 (1H, d, *J* = 2 Hz, CH), 5.81 (1H, dd, *J* = 1 Hz, *J* = 2 Hz, CH), 7.41 (2H, d, *J* = 8 Hz, CH), 8.00 (2H, d, *J* = 8 Hz, CH)

<sup>13</sup>C-NMR (75 MHz; CDCl<sub>3</sub>): δ -1.3, 13.0, 44.7, 52.0, 74.3, 126.0, 126.1, 128.8, 129.4, 148.3, 154.9, 167.0.

IR (EI): 3484 (br), 3048 (w), 2953 (w), 2895 (w), 1723 (s), 1706 (s), 1610 (m), 1436 (m), 1414 (m), 1276 (s), 1246 (s) cm<sup>-1</sup>.

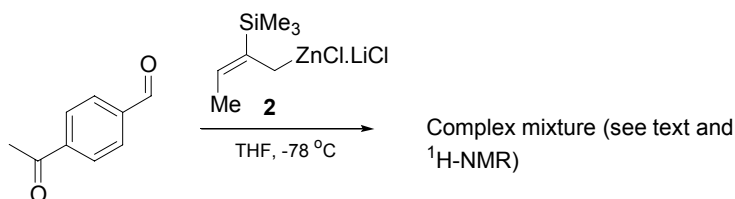
MS (EI, 70 eV) *m/z* = 277 (M<sup>+</sup>-Me), 261, 237, 165, 128, 113.

HRMS (EI): calcd. for C<sub>16</sub>H<sub>25</sub>O<sub>3</sub>Si [M<sup>+</sup>+Me]: 293.1573. Found: 293.1582.

#### Minor diastereoisomer:

<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): <sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): δ 0.17 (9H, s, CH<sub>3</sub>), 0.81 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 2.78 (1H, m, CH), 3.96 (3H, s, CH<sub>3</sub>), 4.60 (1H, d, *J* = 9 Hz, CH), 5.67 (1H, d, *J* = 2 Hz, CH), 5.88 (1H, d, *J* = 2 Hz, CH), 7.42-7.46 (2H, m, CH), 8.01-8.04 (2H, m, CH). (the two aromatic peaks are partially obscured by the major diastereomer).

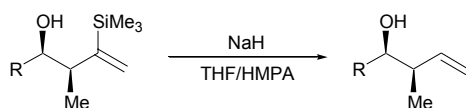
### Reaction of **2** with 4-acetyl-benzaldehyde:



A 0.46 M solution of **2** (2.4 mL, 1.1 mmol) was added to 4-acetyl-benzaldehyde (148 mg, 1 mmol) and the reaction was completed after 1 hour. The crude products were purified by chromatography on silica gel eluting with 2 : 1 pentane/diethyl ether to give a mixture of isomeric products (260 mg, 94%) as a colourless oil. Analysis of the <sup>1</sup>H-NMR and the GC-MS (see attached data) indicate the formation of the aldehyde allylation products (the  $\gamma$ -addition products) as well as the product of  $\alpha$ -addition to the aldehyde (characterised by the quartet at  $\delta$  6.07) as the major products with trace quantities of products derived from allylation of the ketone. It is interesting to note this is the only case in which the  $\alpha$ -addition product has been observed.

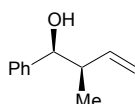


## 5. Protodesilylation of addition products



To the alcohol (0.5 mmol) in THF (0.6 mL) was added a 60% sodium hydride dispersion in paraffin oil (20 mg, 0.505 mmol) and HMPA (0.4 mL). The reaction was stirred at 25 °C until complete conversion of the starting material was observed. The reaction was quenched with water, extracted three times with Et<sub>2</sub>O and the combined organic phase dried over magnesium sulfate. Following removal of the volatiles in vacuo the crude products were purified by chromatography on silica gel using 10 : 1 pentan/Et<sub>2</sub>O as the eluent.<sup>6</sup>

### Formation of 2-methyl-1-phenyl-but-3-en-1-ol **4**:



The reaction using 2-methyl-1-phenyl-3-trimethylsilyl-but-3-en-1-ol **3** (117 mg, 0.5 mmol) was completed after 2 hours to give 2-methyl-1-phenyl-but-3-en-1-ol **4** (70 mg, 86%) as a colourless oil.

<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): δ 1.05 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 2.06 (1H, br, OH), 2.54-2.67 (1H, m, CH), 4.62 (1H, d, *J* = 6 Hz, CH), 5.02-5.15 (2H, m, CH), 5.71-5.87 (1H, m, CH), 7.23-7.41 (5H, m, CH).

<sup>13</sup>C-NMR (150 MHz; CDCl<sub>3</sub>): δ 14.0, 44.6, 77.3, 115.4, 126.5, 127.3, 128.0, 140.3, 142.5.

Previously reported values for **5**:<sup>8</sup>

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 1.01 (3H, d, *J* = 6.8 Hz), 1.90 (1H, br s), 2.55-2.62 (1H, m), 4.61 (1H, d, *J* = 5.5 Hz), 5.02-5.08 (2H, m), 5.70-5.81 (1H, m), 7.25-7.34 (5H, m).

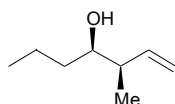
<sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 14.0, 44.6, 77.4, 115.5, 126.5, 127.3, 128.0, 140.2, 142.5.

Previously reported values for the *anti*-isomer:<sup>8</sup>

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.90 (3H, d, *J* = 6.8 Hz), 2.16 (1H, br s), 2.45-2.52 (1H, m), 4.34-4.37 (1H, dd, *J* = 6.8 Hz, *J* = 2.0 Hz), 5.17-5.23 (2H, m), 5.76-5.88 (1H, ddd, *J* = 17.2 Hz, *J* = 10.3 Hz, *J* = 8.1 Hz), 7.26-7.35 (5H, m).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 16.5, 46.2, 77.8, 116.7, 126.7, 127.5, 128.2, 140.6, 142.4.

### Formation of 3-methyl-hept-1-en-4-ol:



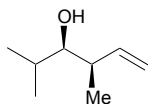
The reaction using 3-methyl-2-trimethylsilyl-hept-1-en-4-ol **5** (100 mg, 0.5 mmol) was completed after 2 hours to give 3-methyl-hept-1-en-4-ol (59 mg, 92%) as a colourless oil.

<sup>1</sup>H-NMR (200 MHz; CDCl<sub>3</sub>): δ 0.88 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 0.95 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 1.16-1.56 (4H, m, CH<sub>2</sub>), 2.23 (1H, apparent sextet from ddq, *J* = 7 Hz, CH), 3.35-3.51 (1H, m, CH), 4.95-5.09 (2H, m, CH), 5.63-5.86 (2H, m, 1H).

Previously reported values for *syn*-isomer:<sup>8</sup>

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.88 (3H, d, *J* = 6.8 Hz), 0.98 (3H, d, *J* = 6.8 Hz), 1.22-1.48 (4H, m), 1.86 (1H, s), 2.22 (1H, dq, *J* = 6.5 Hz), 3.43-3.47 (1H, m), 4.93-5.06 (2H, m), 5.66-5.81 (1H, m).

#### Formation of 2,4-dimethyl-hex-5-en-3-ol:



The reaction using 2,4-dimethyl-5-trimethylsilyl-hex-5-en-3-ol **6** (100 mg, 0.5 mmol) was completed after 2 hours to give 2,4-dimethyl-hex-5-en-3-ol (52 mg, 82%) as a colourless oil.

<sup>1</sup>H-NMR (200 MHz; CDCl<sub>3</sub>): δ 0.91 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 0.94 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 1.04 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 1.77 (1H, apparent sextet from dt, *J* = 7 Hz, CH), 2.39 (1H, apparent sextet from ddq, *J* = 7 Hz, CH), 3.19 (1H, apparent triplet from dd, *J* = 7 Hz, CH), 4.96-5.14 (2H, m, CH), 5.68-5.89 (2H, m, 1H).

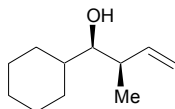
Previously reported values for *syn*-isomer:<sup>9</sup>

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.92 (3H, d, *J* = 7 Hz), 0.93 (3H, d, *J* = 7 Hz), 1.03 (3H, d, *J* = 7 Hz), 1.60 (1H, br s), 1.71 (1H, octet, *J* = 7 Hz), 2.37 (1H, sextet, *J* = 7 Hz), 3.17 (1H, t, *J* = 7 Hz), 4.88-5.21 (2H, m), 5.58-6.02 (1H, m).

Previously reported values for the *anti*-isomer:<sup>9</sup>

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 0.90 (3H, d, *J* = 7 Hz), 0.95 (3H, d, *J* = 7 Hz), 1.00 (3H, d, *J* = 6 Hz), 1.45-2.00 (2H, m), 2.32 (1H, sextet, *J* = 6 Hz), 3.00-3.33 (1H, m), 4.95-5.30 (2H, m), 5.55-6.00 (1H, m).

#### Formation of 1-cyclohexyl-2-methyl-but-3-en-1-ol:



The reaction using 1-cyclohexyl-2-methyl-3-trimethylsilyl-but-3-en-1-ol **7** (120 mg, 0.5 mmol) was completed after 2 hours to give 1-cyclohexyl-2-methyl-but-3-en-1-ol (72 mg, 85%) as a colourless oil.

<sup>1</sup>H-NMR (300 MHz; CDCl<sub>3</sub>): δ 1.01 (3H, d, *J* = 7 Hz, CH<sub>3</sub>), 0.96-2.03 (12H, m), 2.41 (1H, m, CH), 3.20 (1H, dd, *J* = 5 Hz, *J* = 6 Hz), 5.04-5.12 (2H, m, CH), 5.82 (1H, ddd, *J* = 7 Hz, *J* = 10 Hz, *J* = 18 Hz, CH).

Previously reported values for *syn*-isomer:<sup>10</sup>

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 1.01 (3H, d, *J* = 6.9 Hz), 0.98-1.95 (12H, m), 2.37-2.44 (1H, m), 3.19 (1H, t, *J* = 5.8 Hz), 5.07 (1H, d, *J* = 10.0 Hz), 5.08 (1H, d, *J* = 16.9 Hz), 5.81 (ddd, 1H, *J* = 6.9, *J* = 10.0, *J* = 16.9 Hz)

Previously reported values for the *anti*-isomer:<sup>10</sup>

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 1.03 (3H, d, *J* = 6.9 Hz), 1.00-1.85 (12H, m), 2.31-2.44 (1H, m), 3.10 (1H, t, *J* = 5.8 Hz), 5.09 (1H, d, *J* = 10.0 Hz), 5.10 (1H, d, *J* = 16.2 Hz), 5.78 (ddd, 1H, *J* = 8.1, *J* = 10.2, *J* = 16.2 Hz)

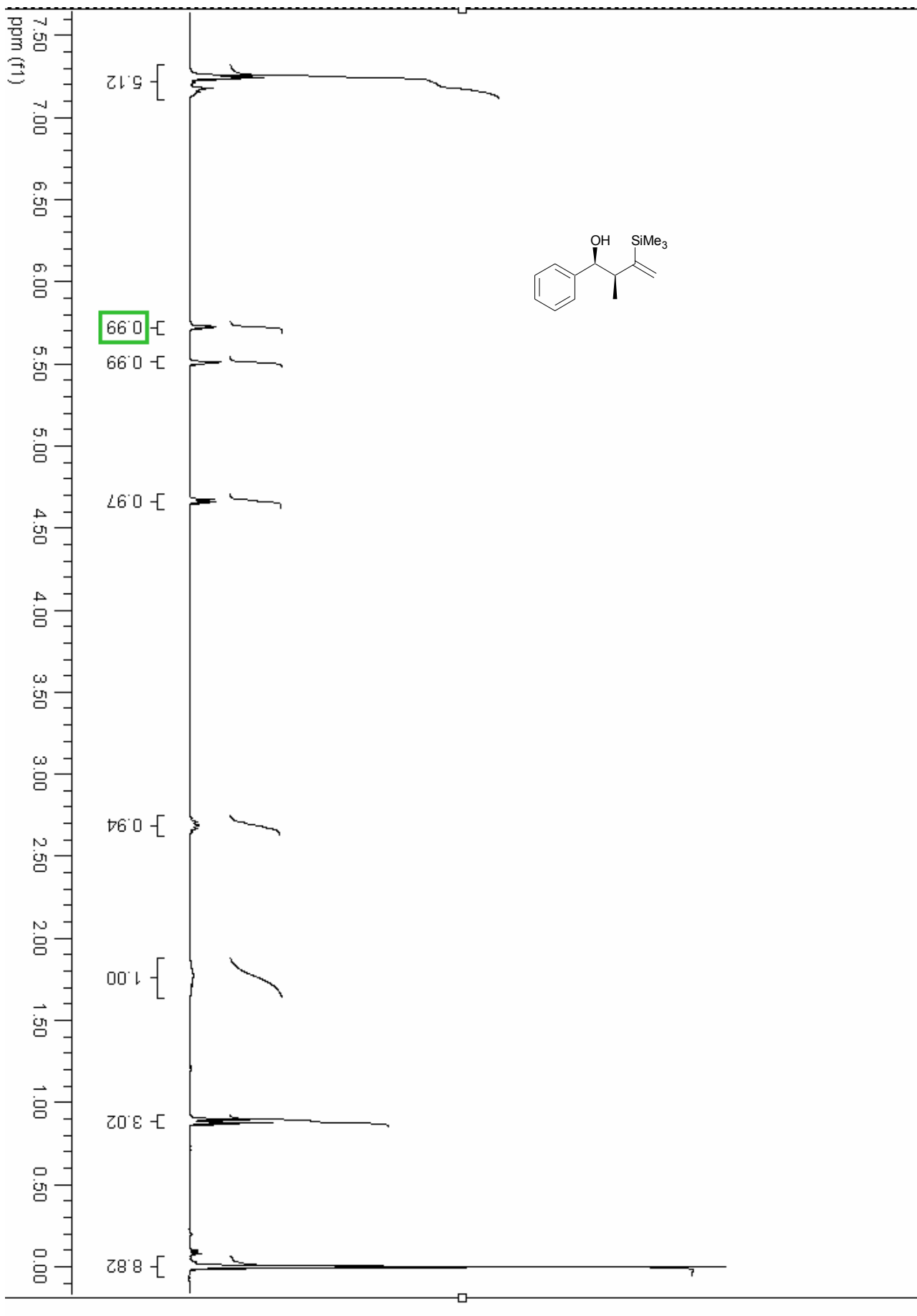
## 6. References

1. B. M. Trost and S. Mignani *J. Org. Chem.* 1986, **51**, 3435.

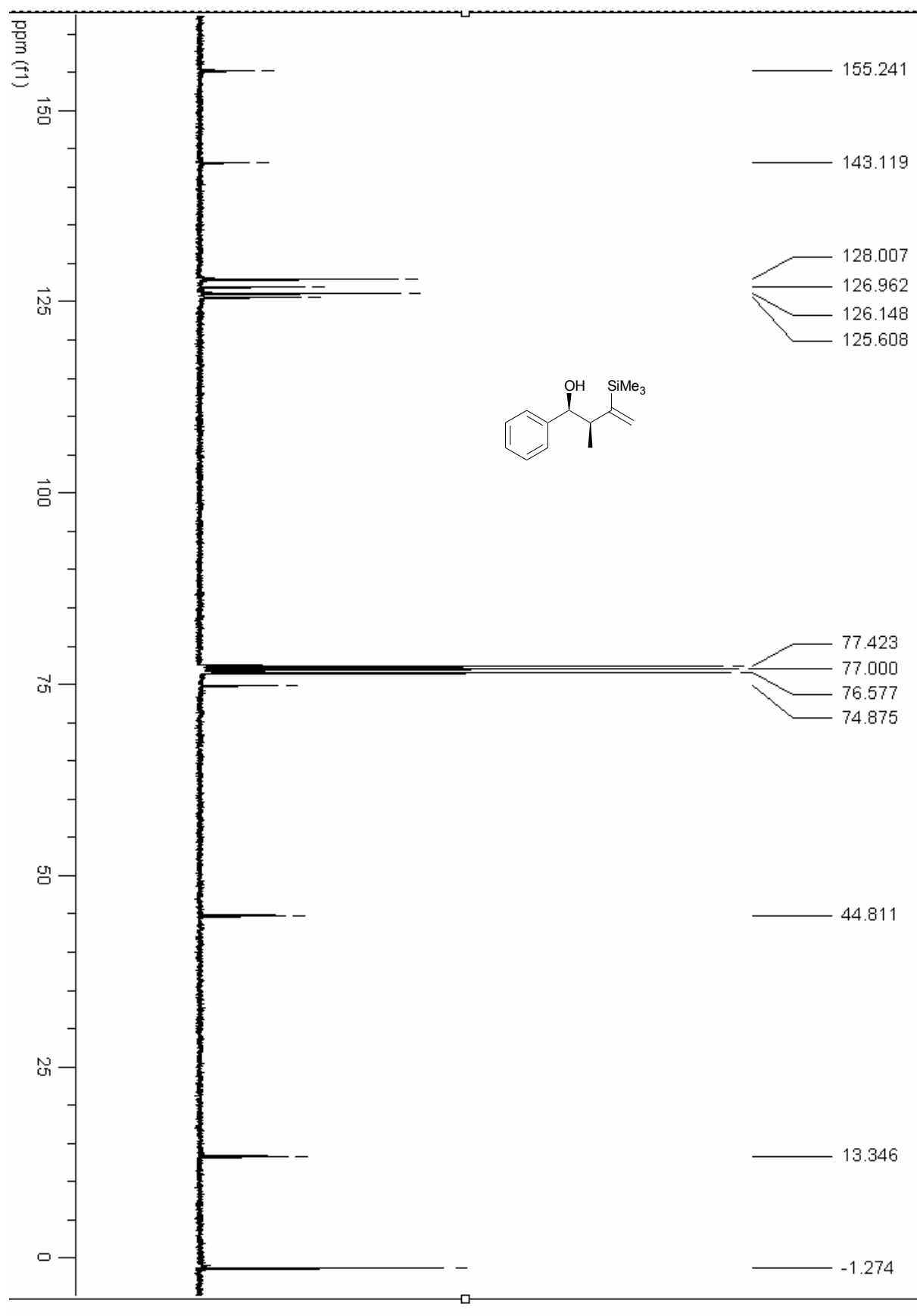
2. T. H. Chan and B. S. Ong *J. Org. Chem.* 1978, **43**, 2994.
3. G. Stork and B. Ganem *J. Am. Chem. Soc.* 1973, **95**, 6152.
4. The zinc powder was activated by treatment first with 1,2- dibromoethane and then with chlorotrimethylsilane; see: P. Knochel, M. J. Rozema and C. E. Tucker *Organocopper reagents* (Ed.: R. J. K. Taylor), Oxford University press, Oxford, 1994, p. 85.
5. K. Lamara and R. K. Smalley *Tetrahedron*, 1991, **47**, 2277.
6. F. Sato, M. Kusakabe and Y. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1984, 1130.
7. S. Hayashi, K. Hirano, H. Yorimitsu and K. Oshima *Org. Lett.* 2005, **7**, 3577.
8. C. H. Burgos, E. Canales, K. Matos and J. A. Soderquist *J. Am. Chem. Soc.* 2005, **127**, 8044.
9. R. W. Hoffmann and H.-J. Zeiß *J. Org. Chem.* 1981, **46**, 1309.
10. S. Kobayashi and K. Nishio *J. Org. Chem.* 1994, **59**, 6620.

## 7. NMR Spectra

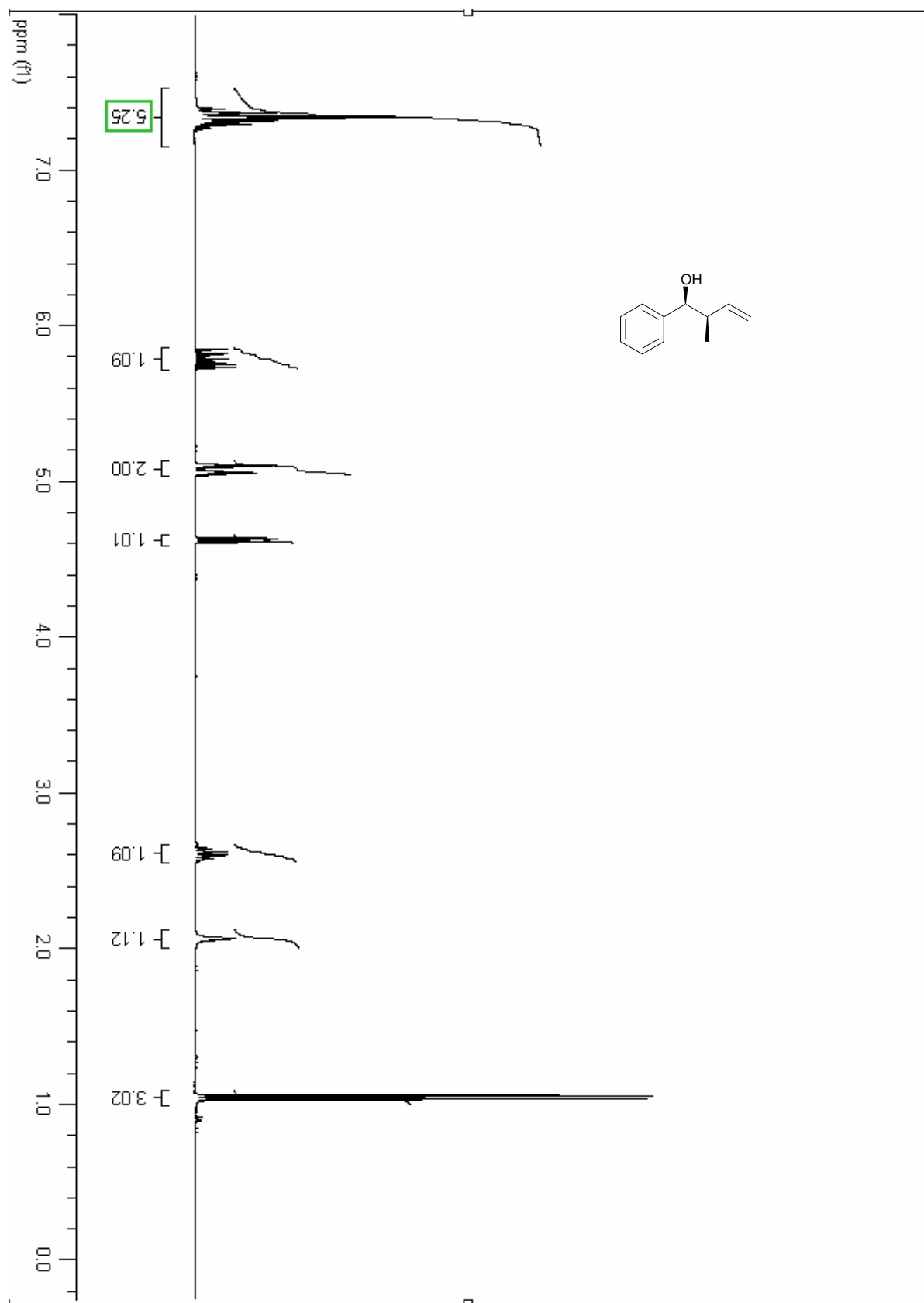
2-methyl-1-phenyl-3-trimethylsilanyl-but-3-en-1-ol **3**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):



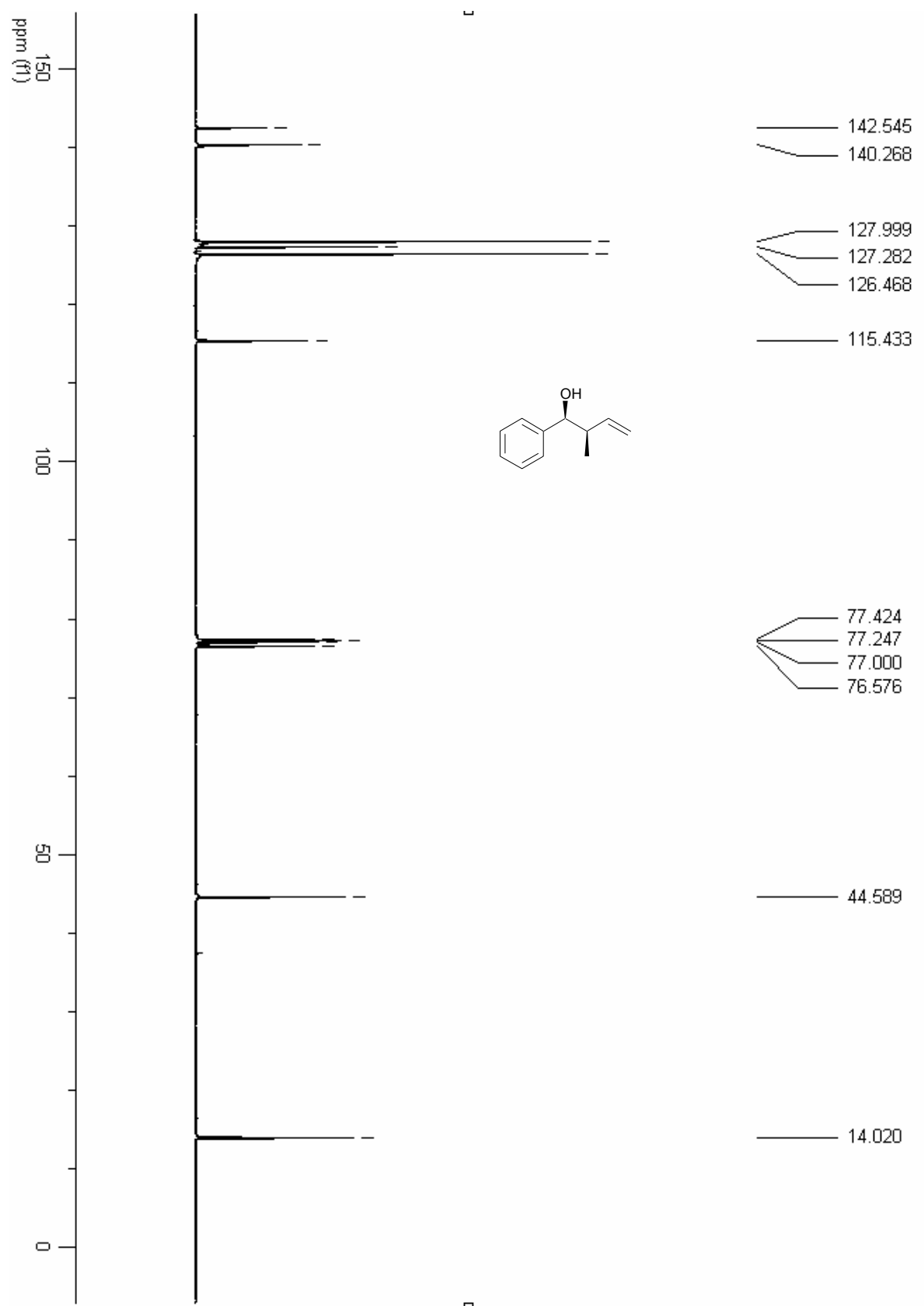
2-methyl-1-phenyl-3-trimethylsilyl-but-3-en-1-ol **3**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



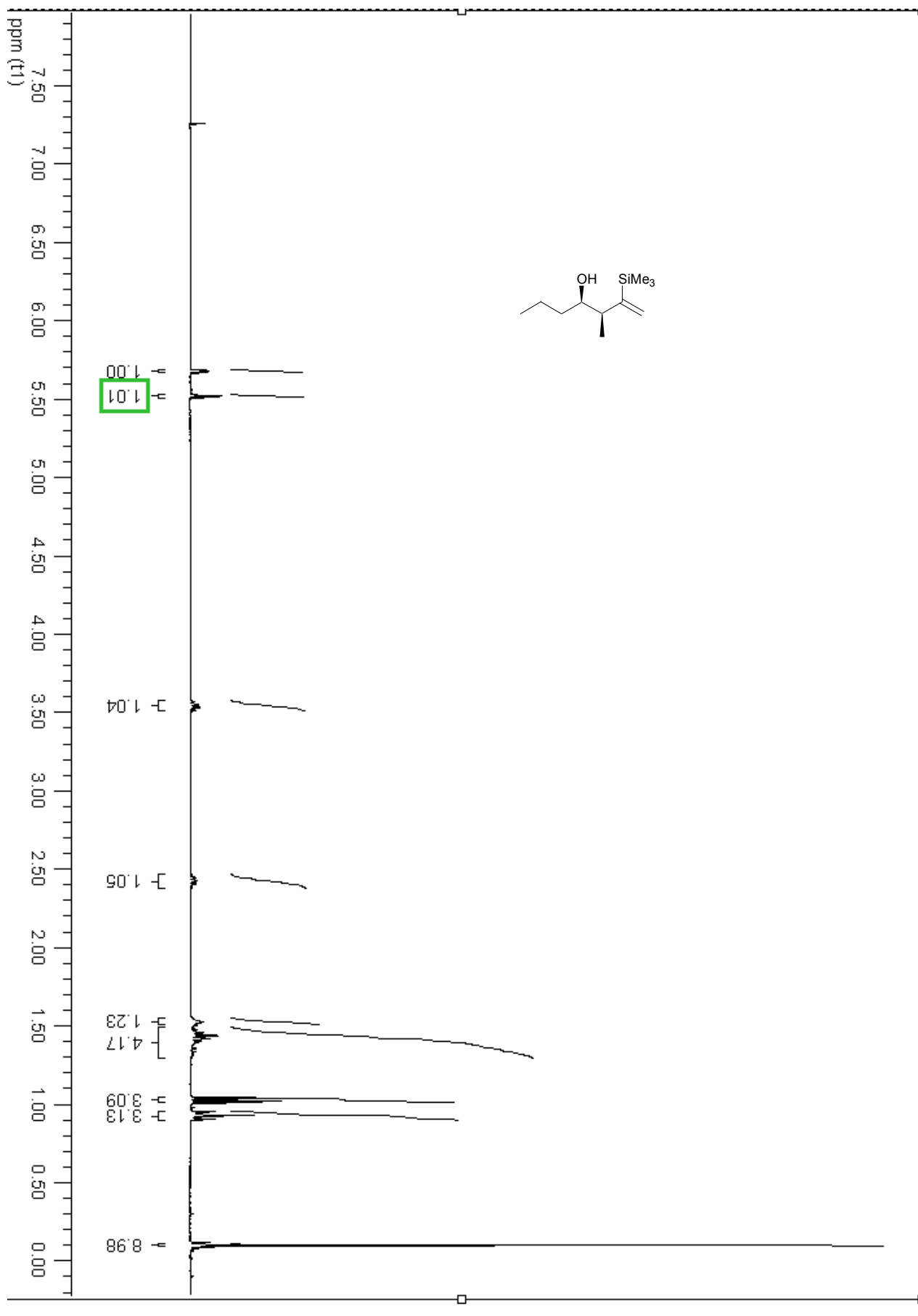
2-Methyl-1-phenyl-but-3-en-1-ol **4**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):



2-Methyl-1-phenyl-but-3-en-1-ol **4**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):

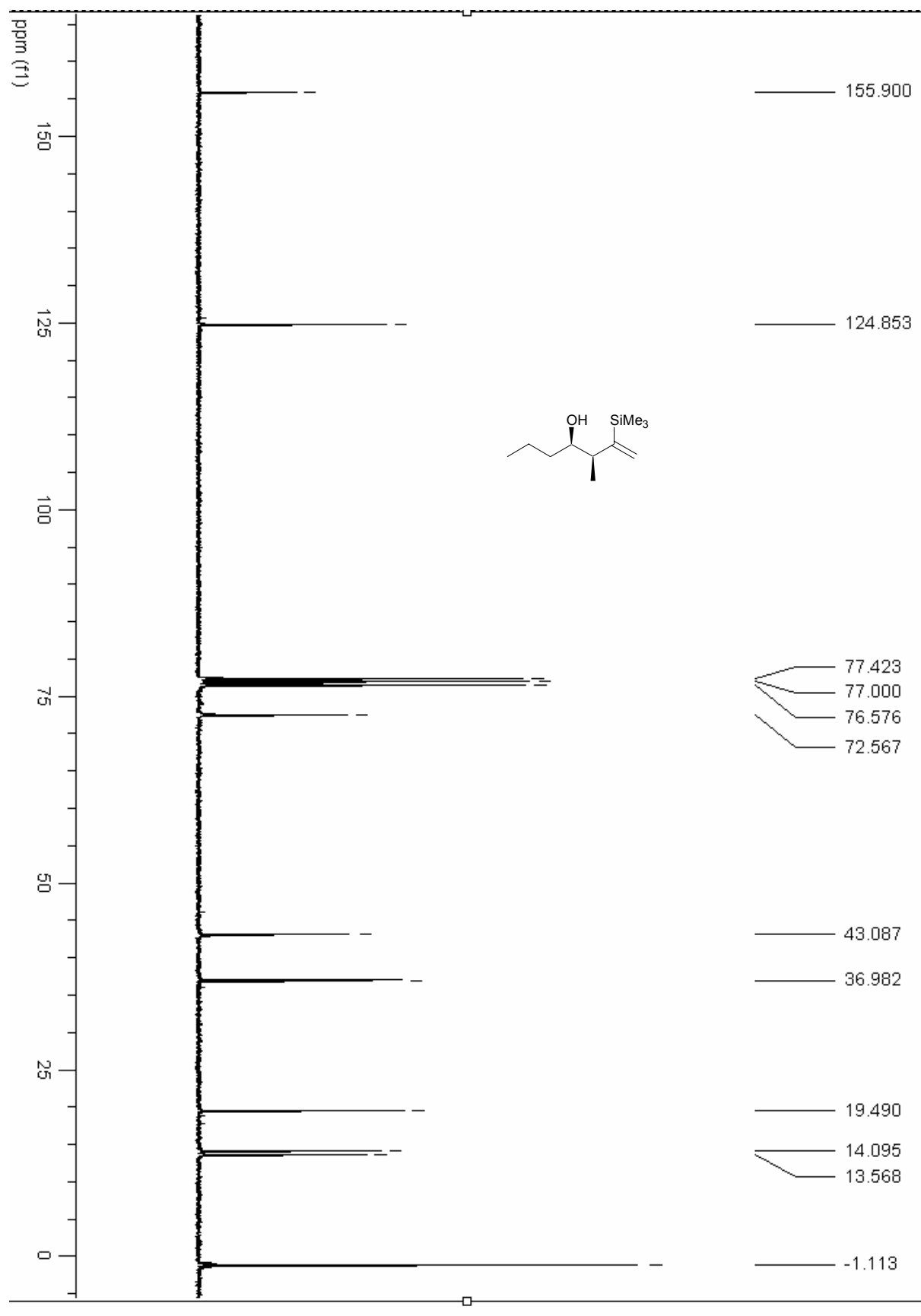


3-methyl-2-trimethylsilyl-hept-1-en-4-ol **5**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):

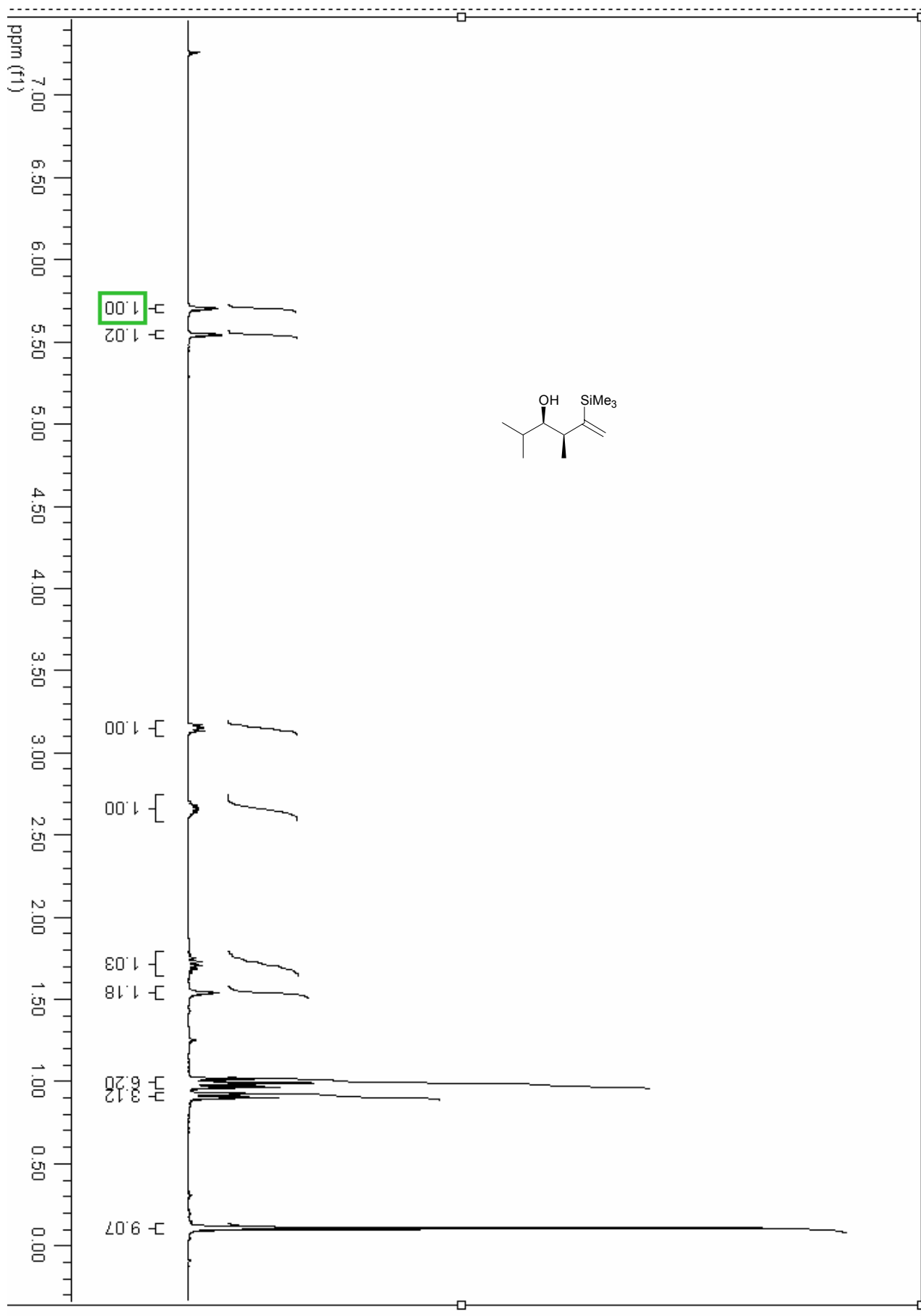




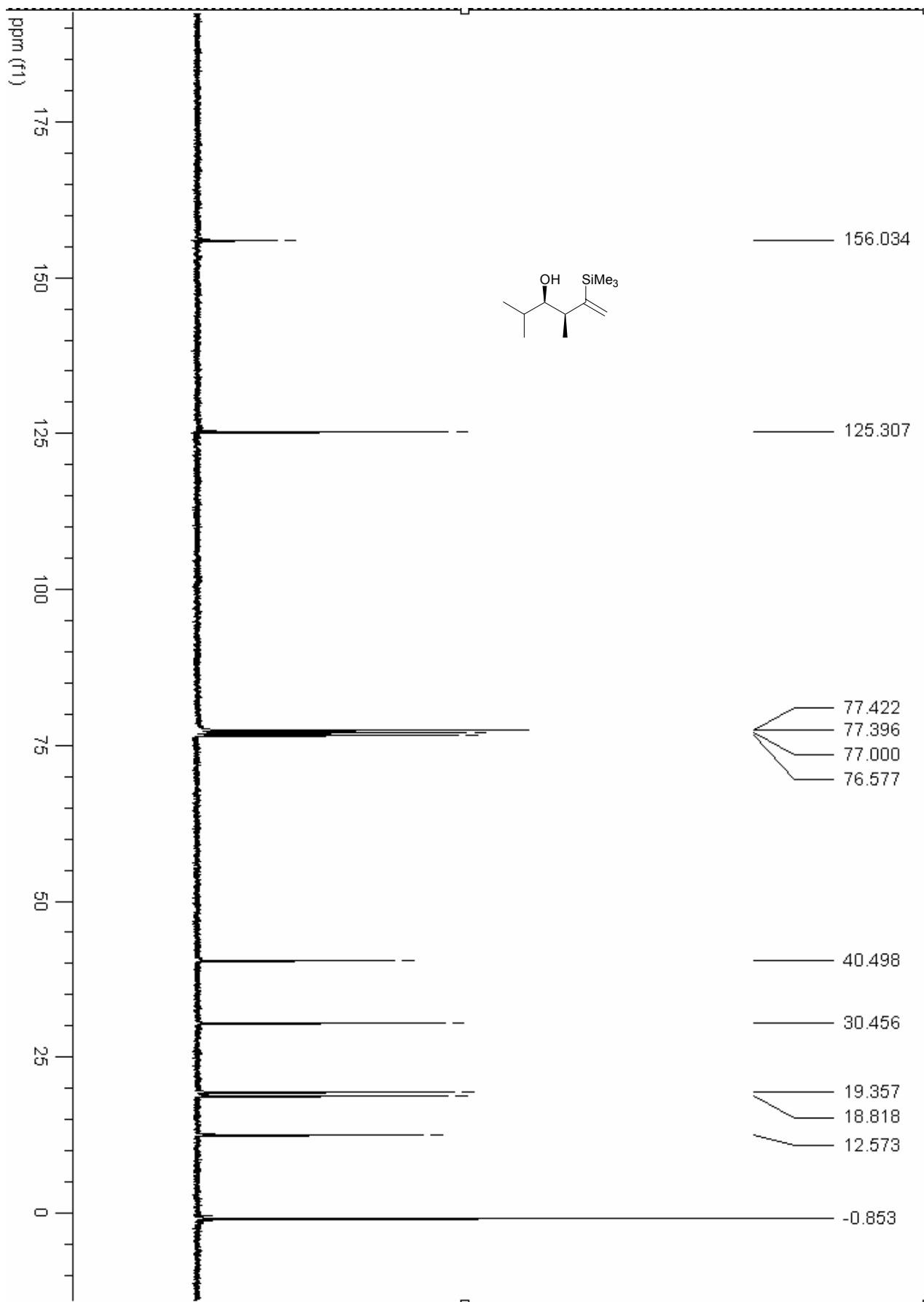
3-methyl-2-trimethylsilyl-hept-1-en-4-ol **5**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



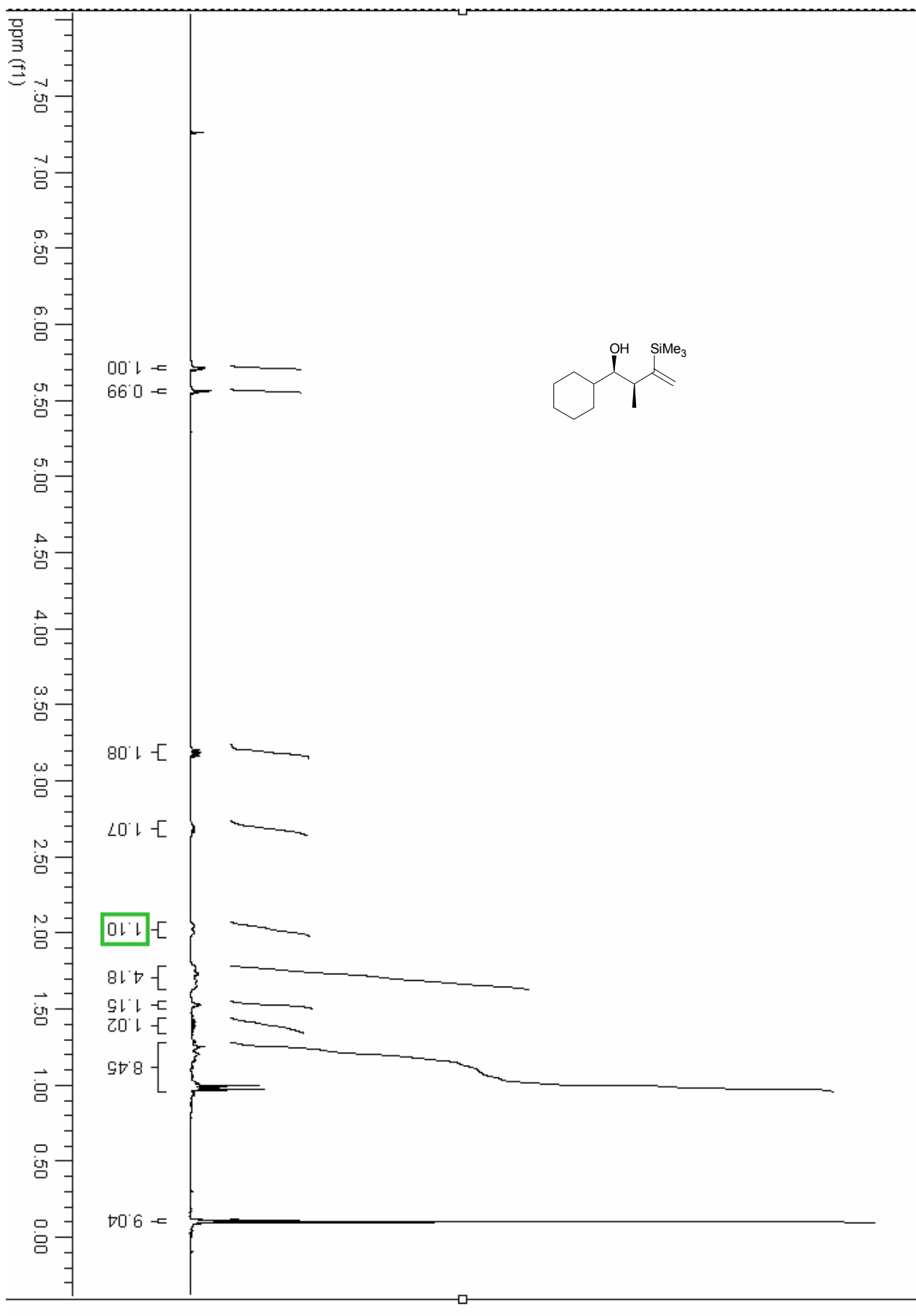
2,4-dimethyl-5-trimethylsilyl-hex-5-en-3-ol **6**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):



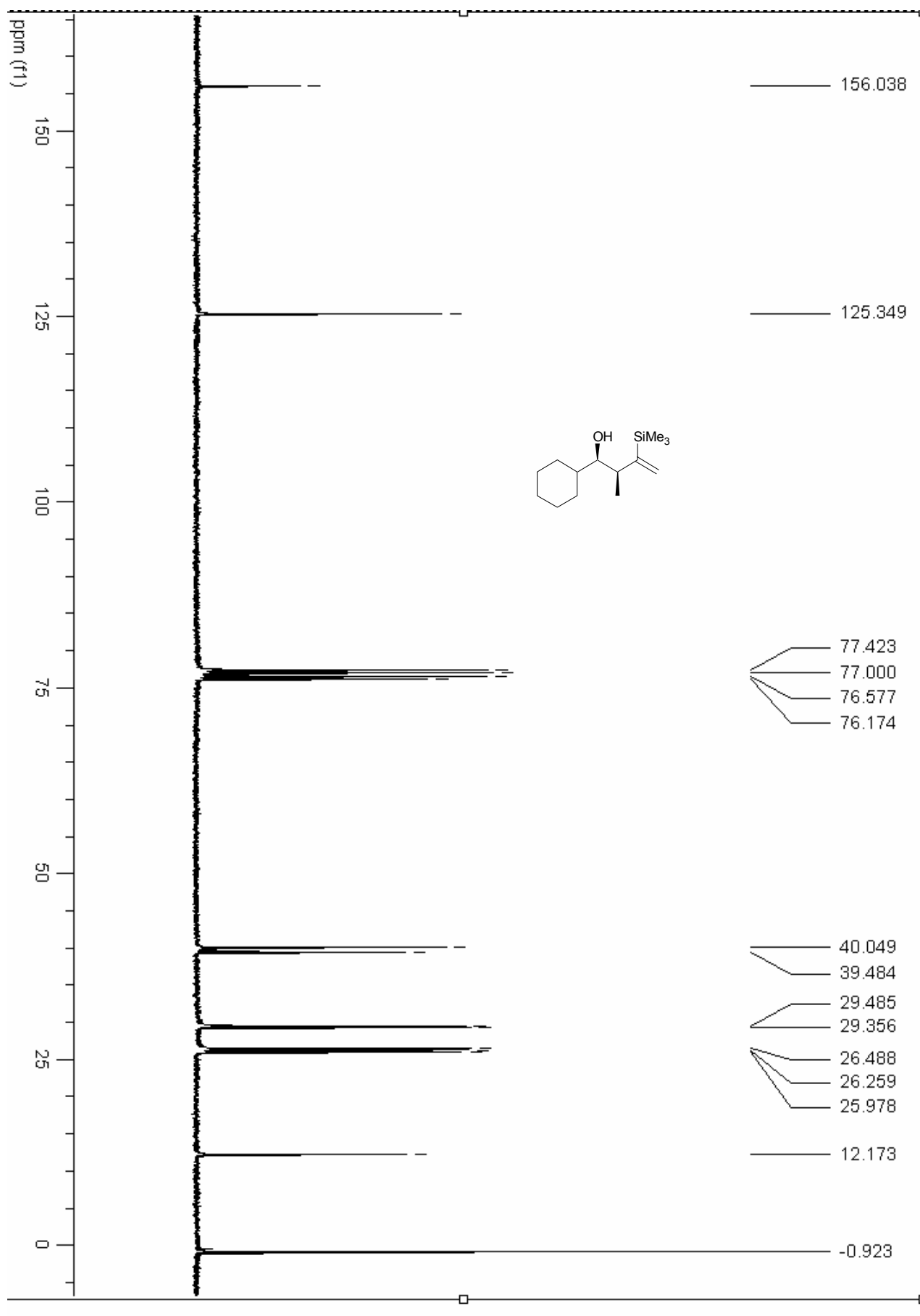
2,4-dimethyl-5-trimethylsilyl-hex-5-en-3-ol **6**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



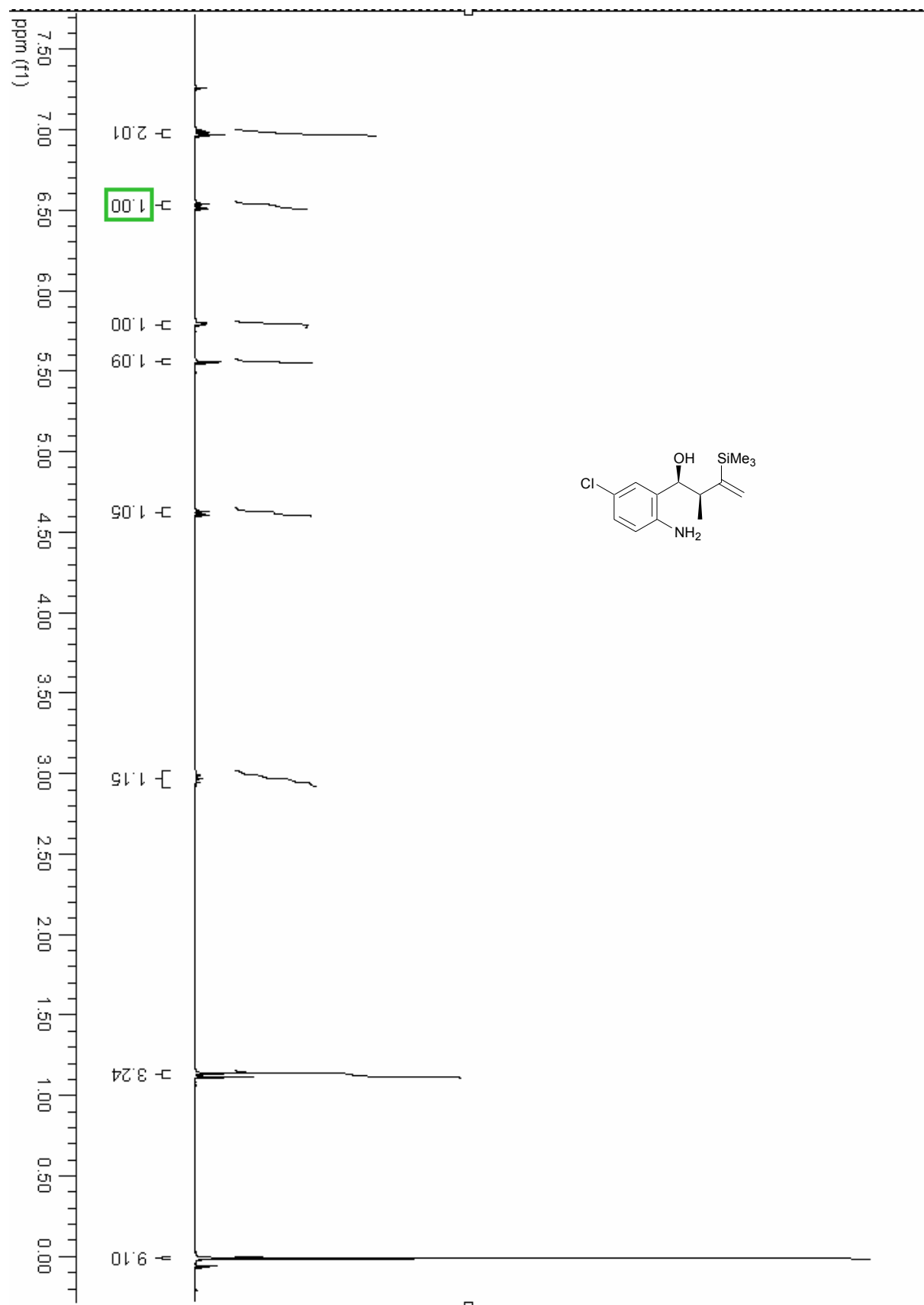
1-cyclohexyl-2-methyl-3-trimethylsilyl-but-3-en-1-ol **7**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):



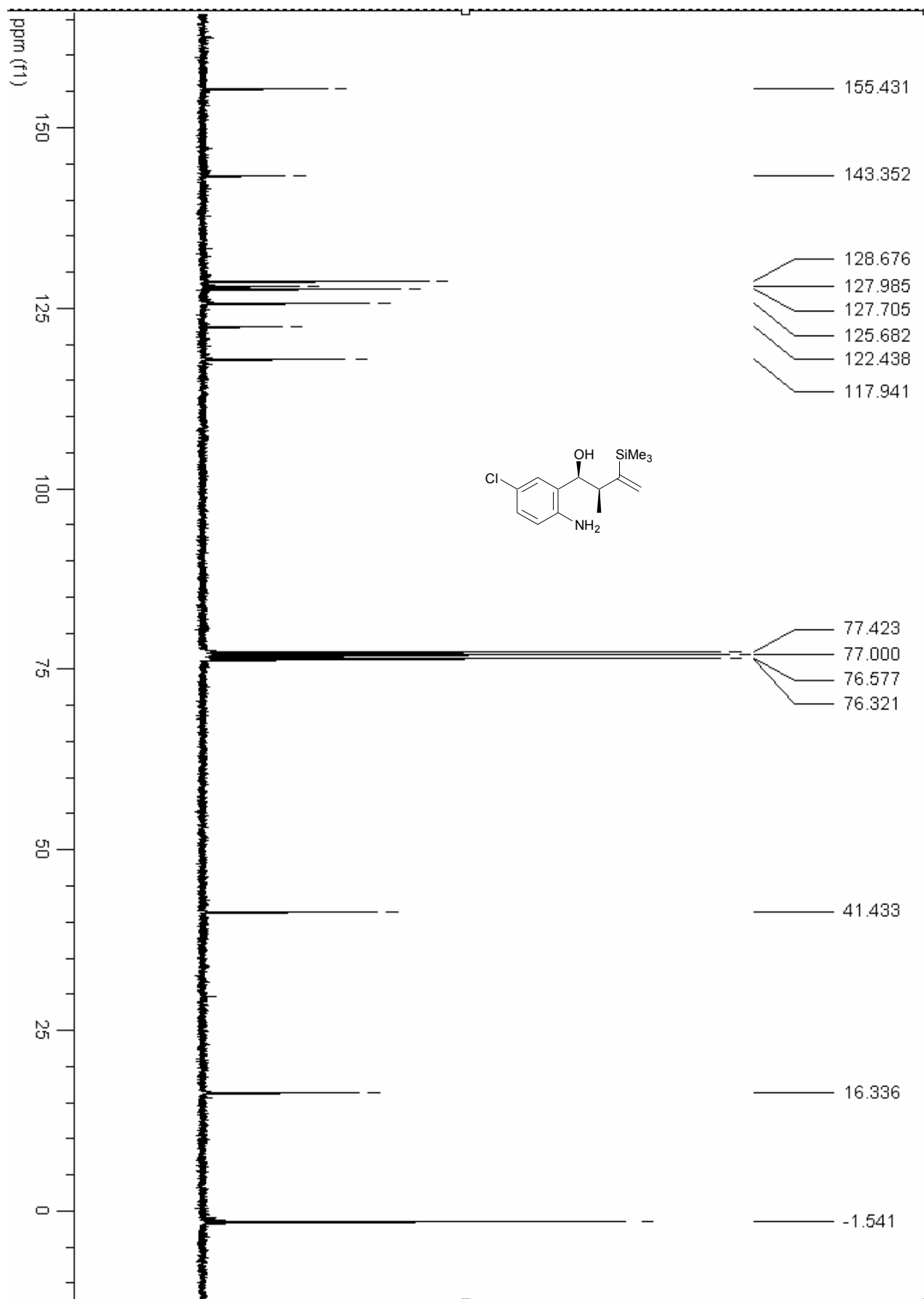
1-cyclohexyl-2-methyl-3-trimethylsilyl-but-3-en-1-ol **7**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



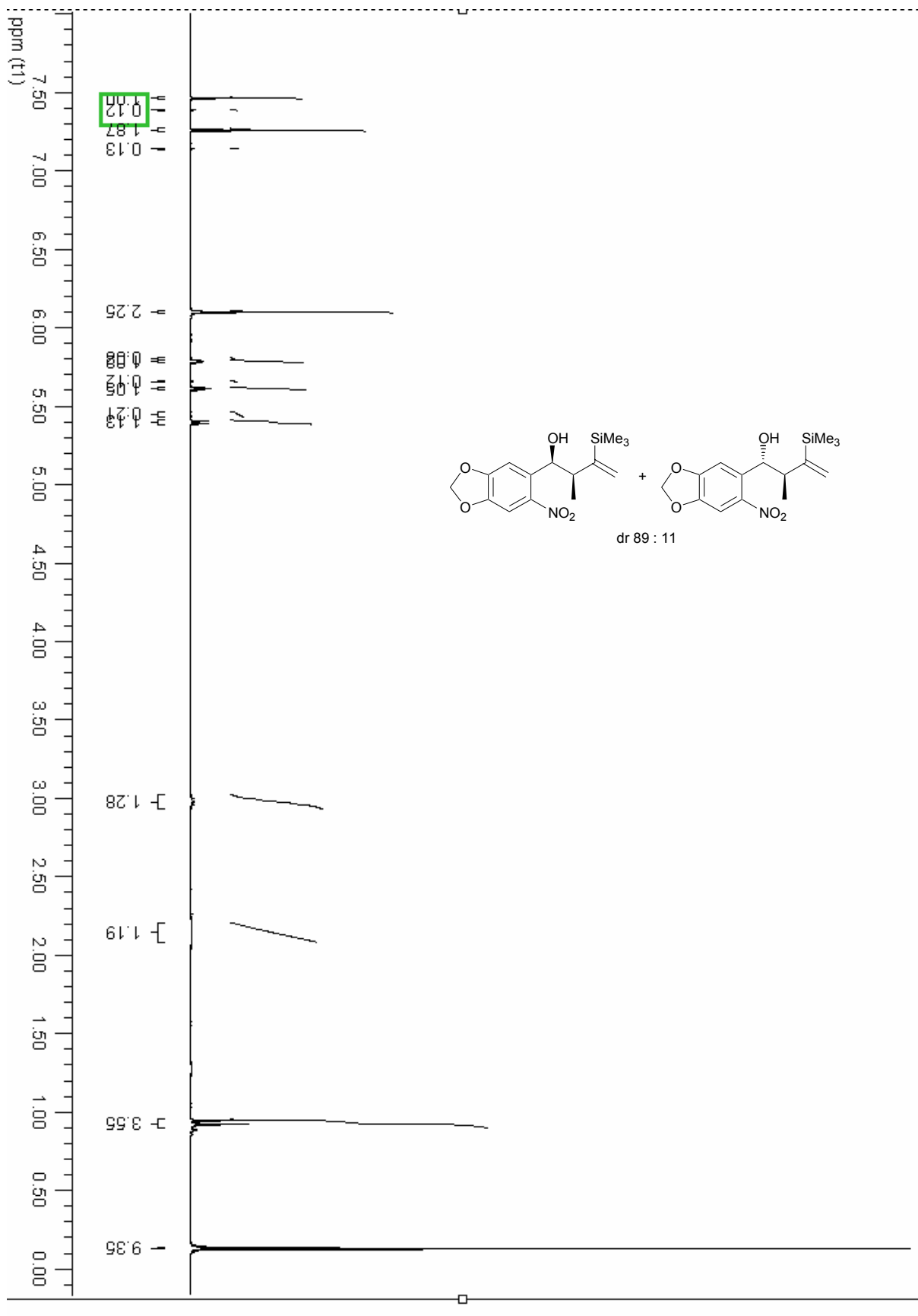
1-(2-amino-5-chloro-phenyl)-2-methyl-3-trimethylsilyl-but-3-en-1-ol **8**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):



1-(2-amino-5-chloro-phenyl)-2-methyl-3-trimethylsilyl-but-3-en-1-ol **8**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):

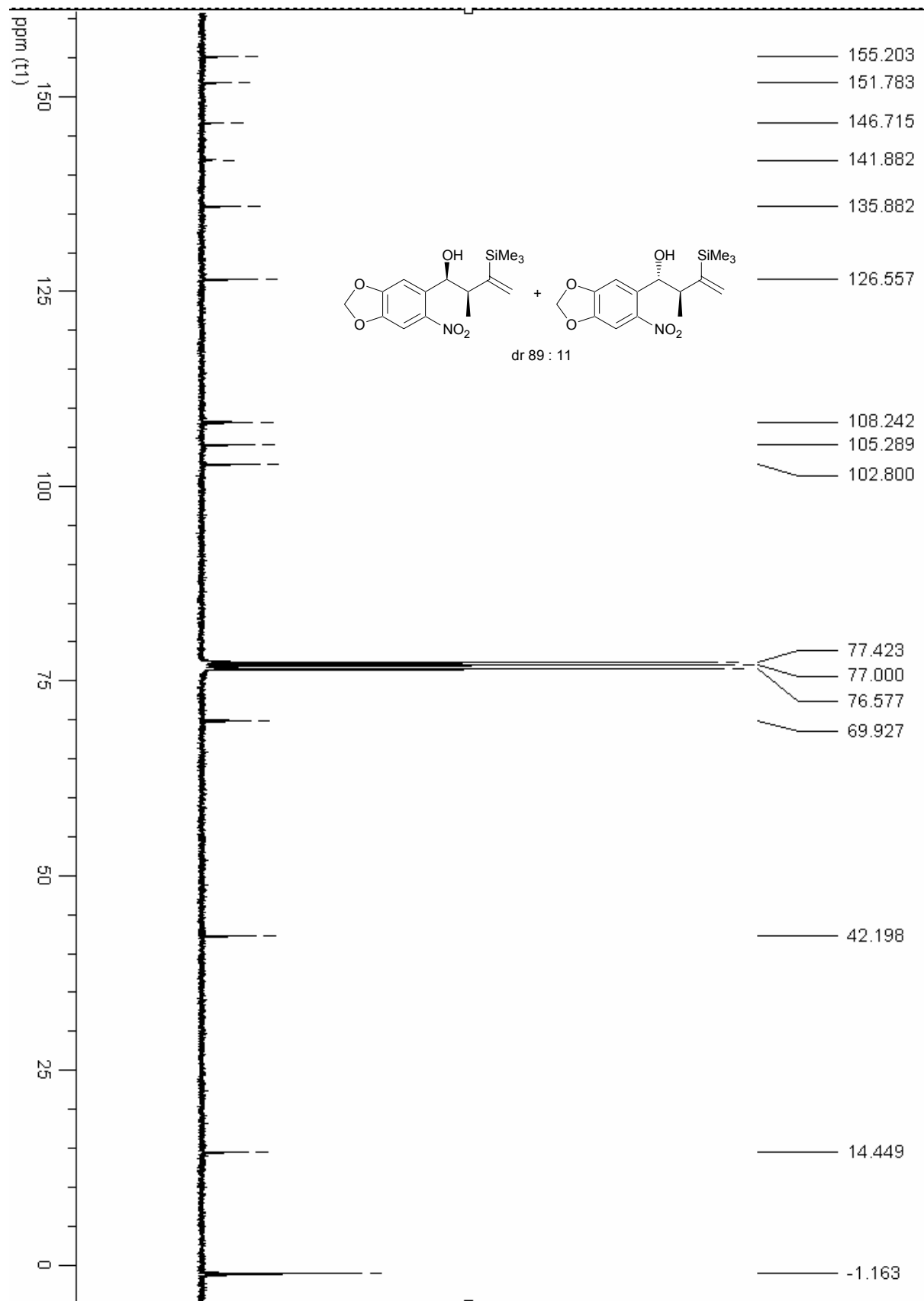


2-methyl-1-(6-nitro-benzo[1,3]dioxol-5-yl)-3-trimethylsilyl-but-3-en-1-ol **9**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):

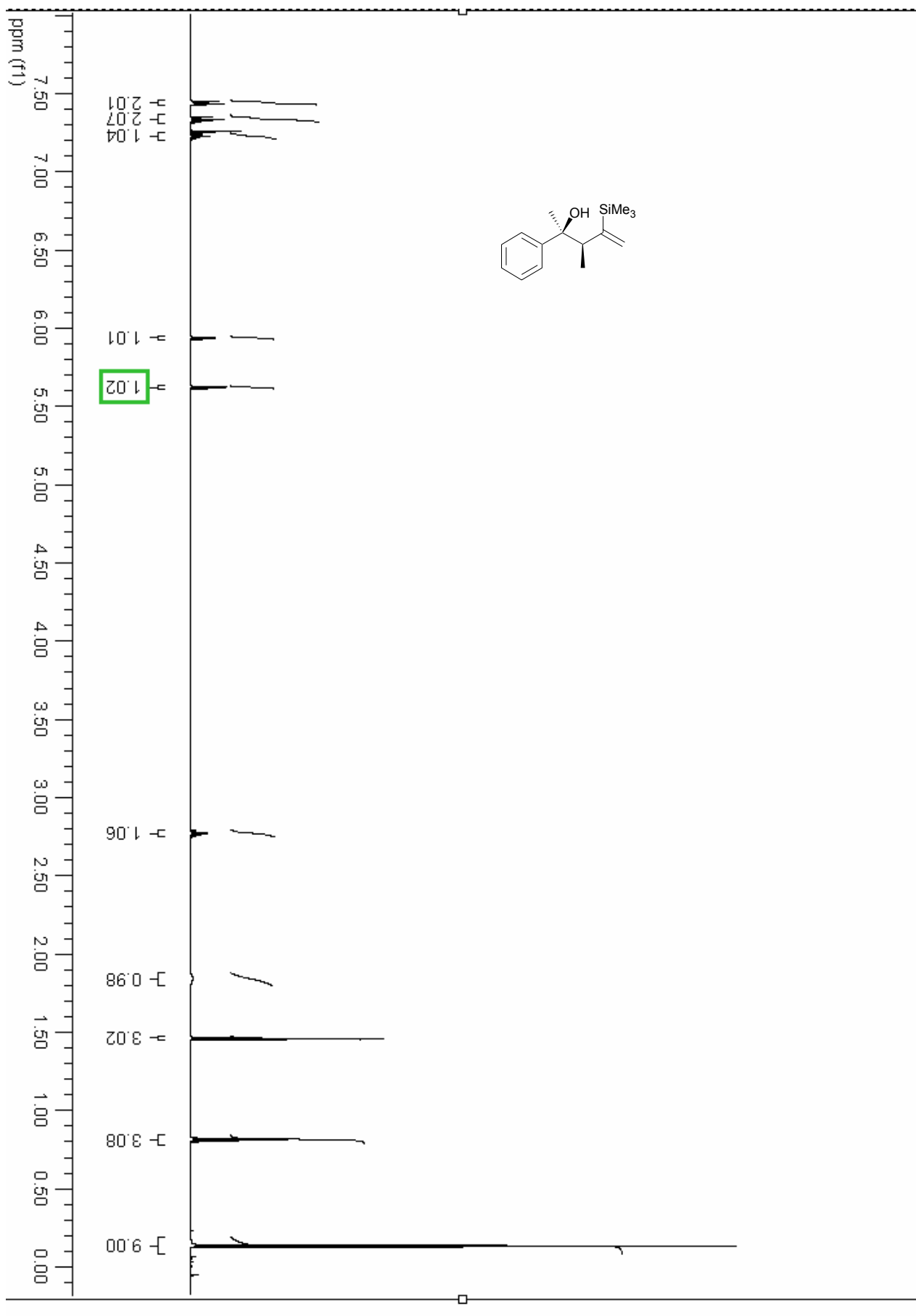




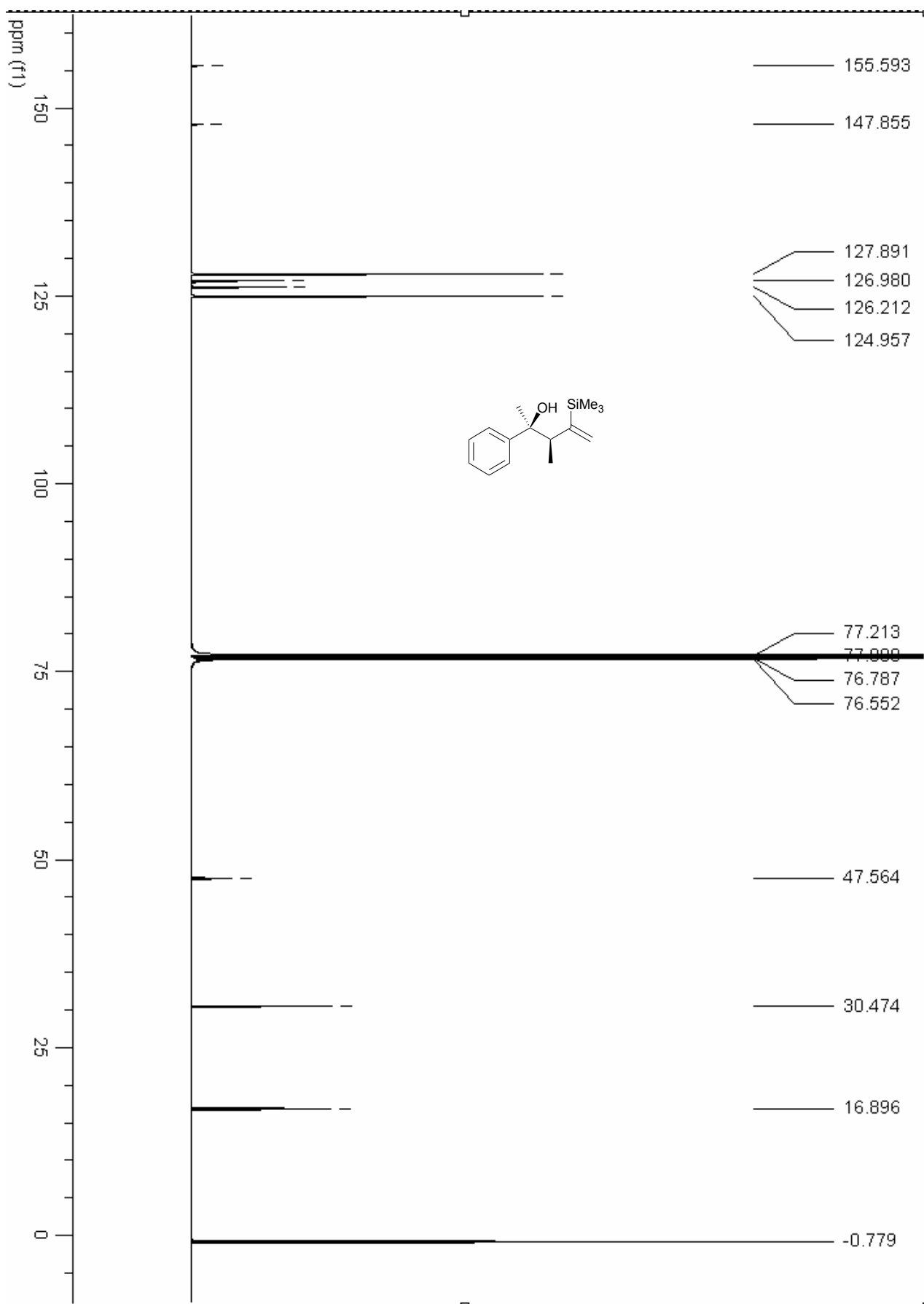
2-methyl-1-(6-nitro-benzo[1,3]dioxol-5-yl)-3-trimethylsilanyl-but-3-en-1-ol **9**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



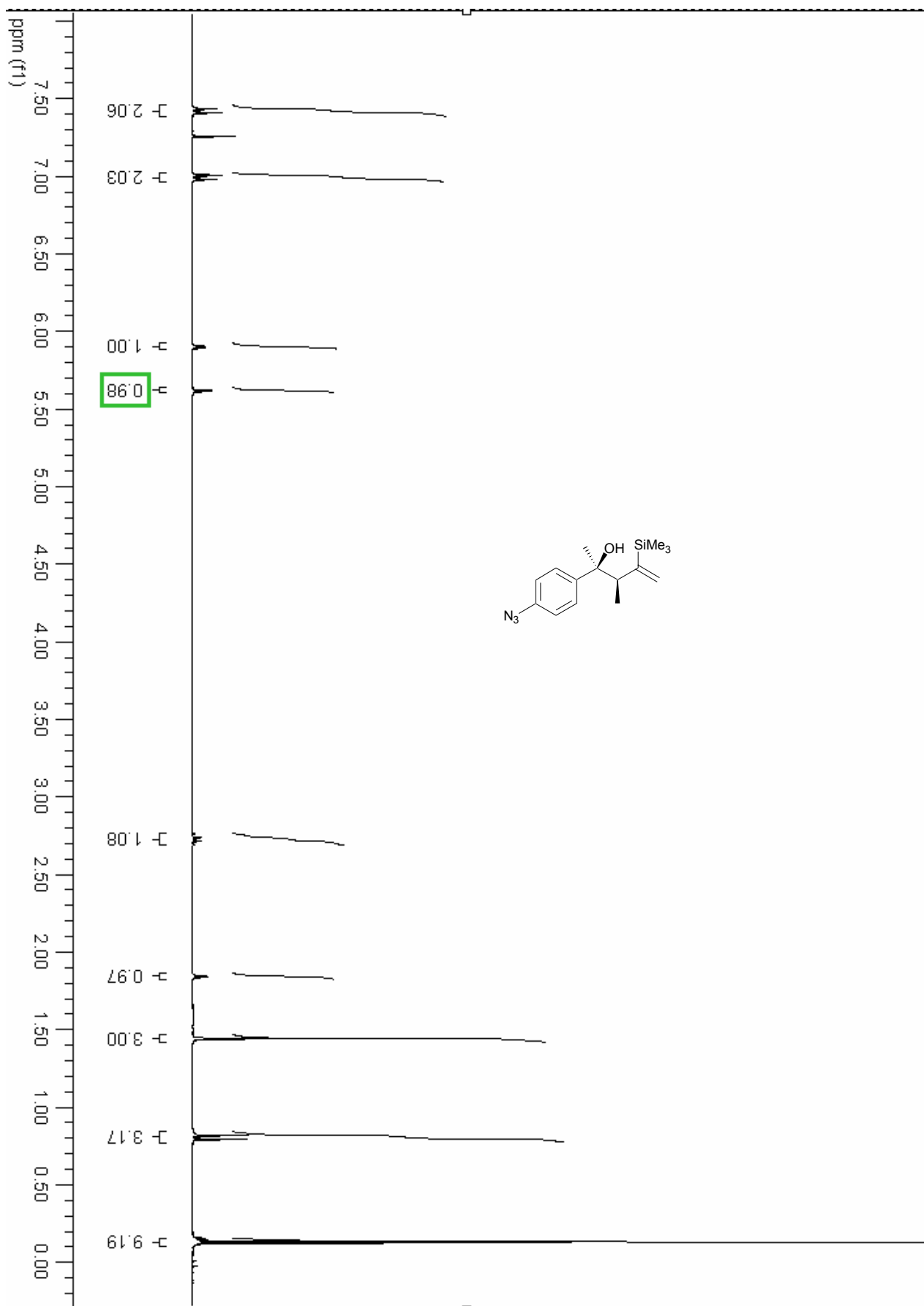
3-methyl-2-phenyl-4-trimethylsilyl-pent-4-en-2-ol **10**,  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):



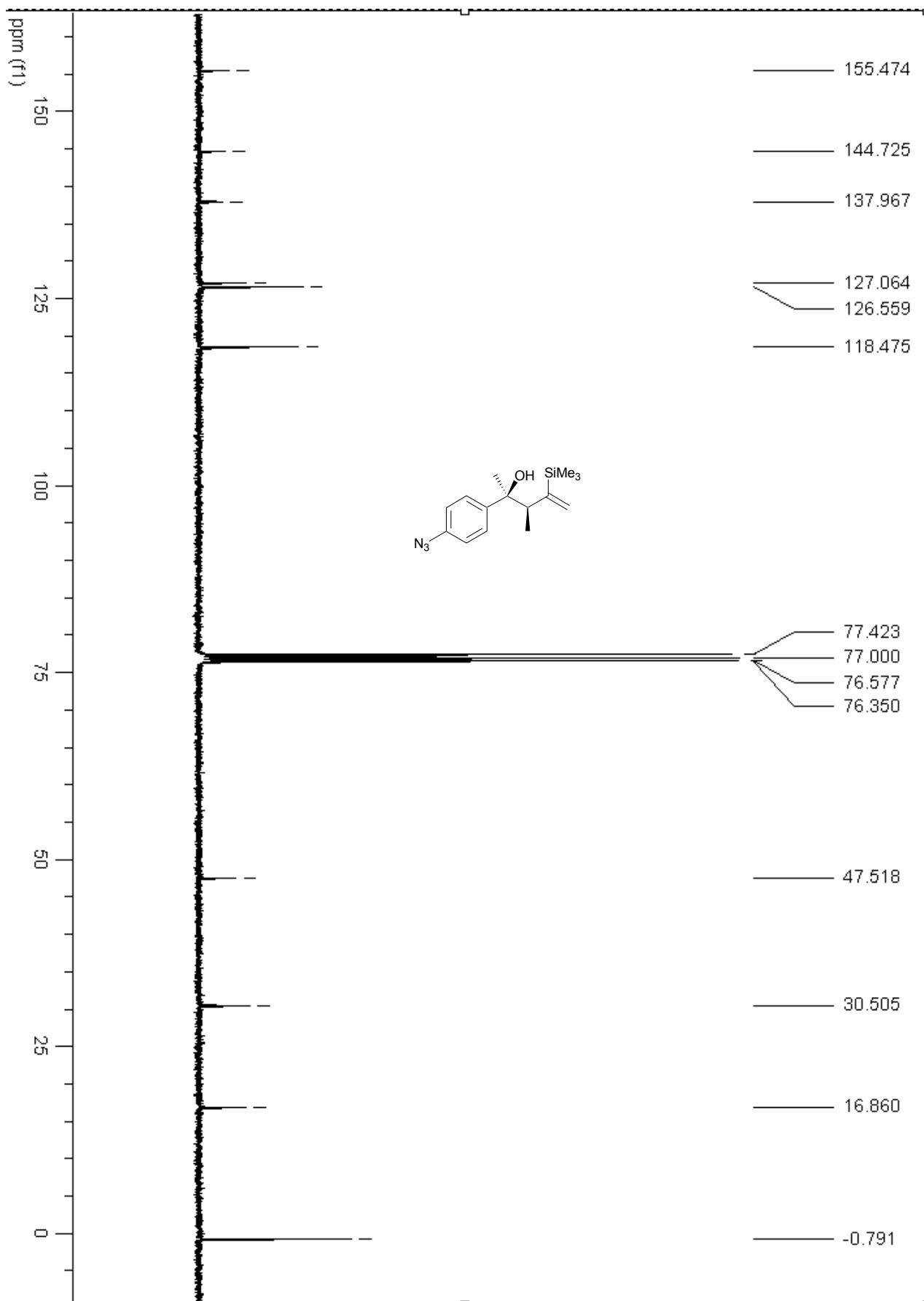
3-methyl-2-phenyl-4-trimethylsilyl-pent-4-en-2-ol **10**,  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ):



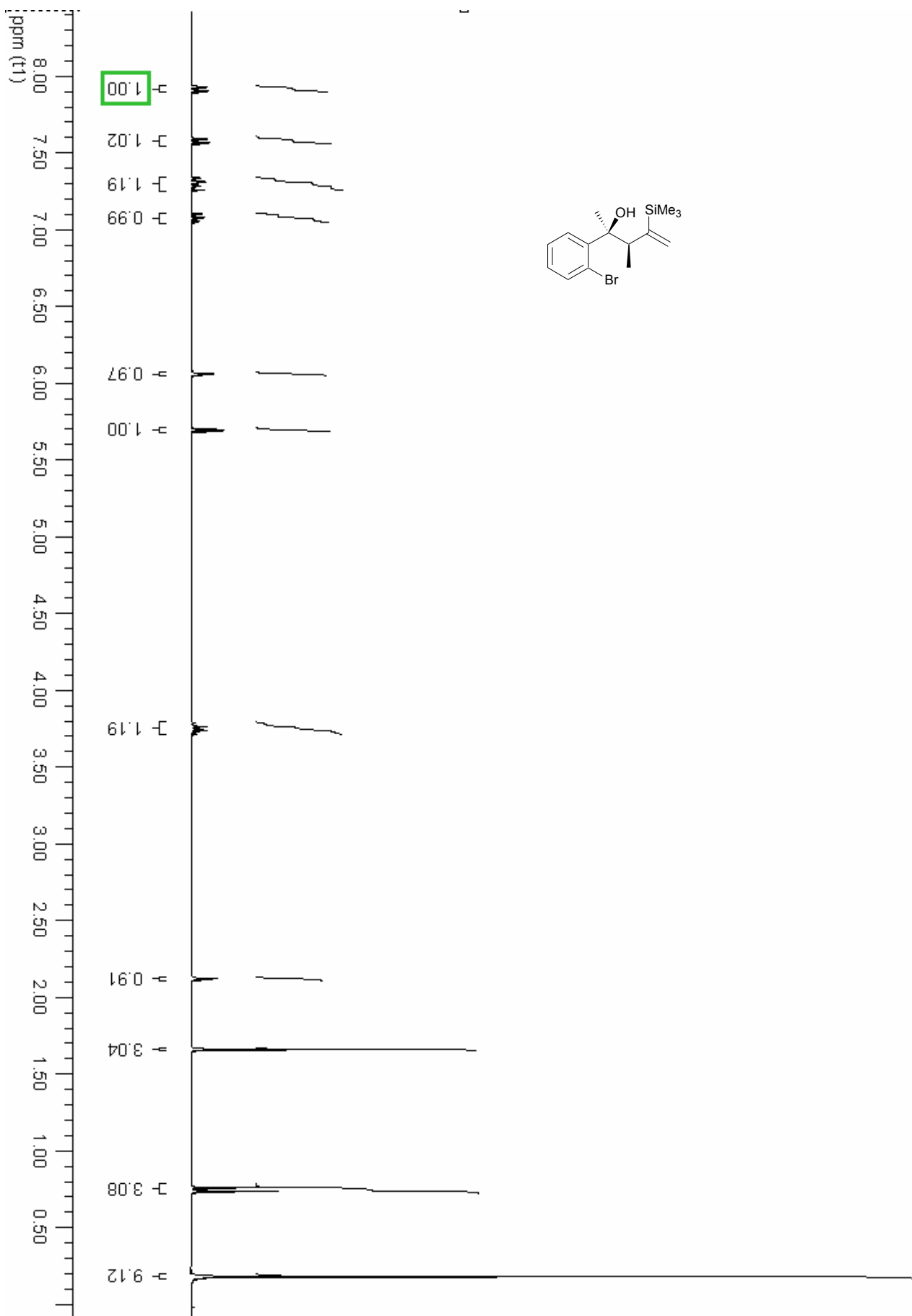
2-(4-azido-phenyl)-3-methyl-4-trimethylsilyl-pent-4-en-2-ol **11**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):



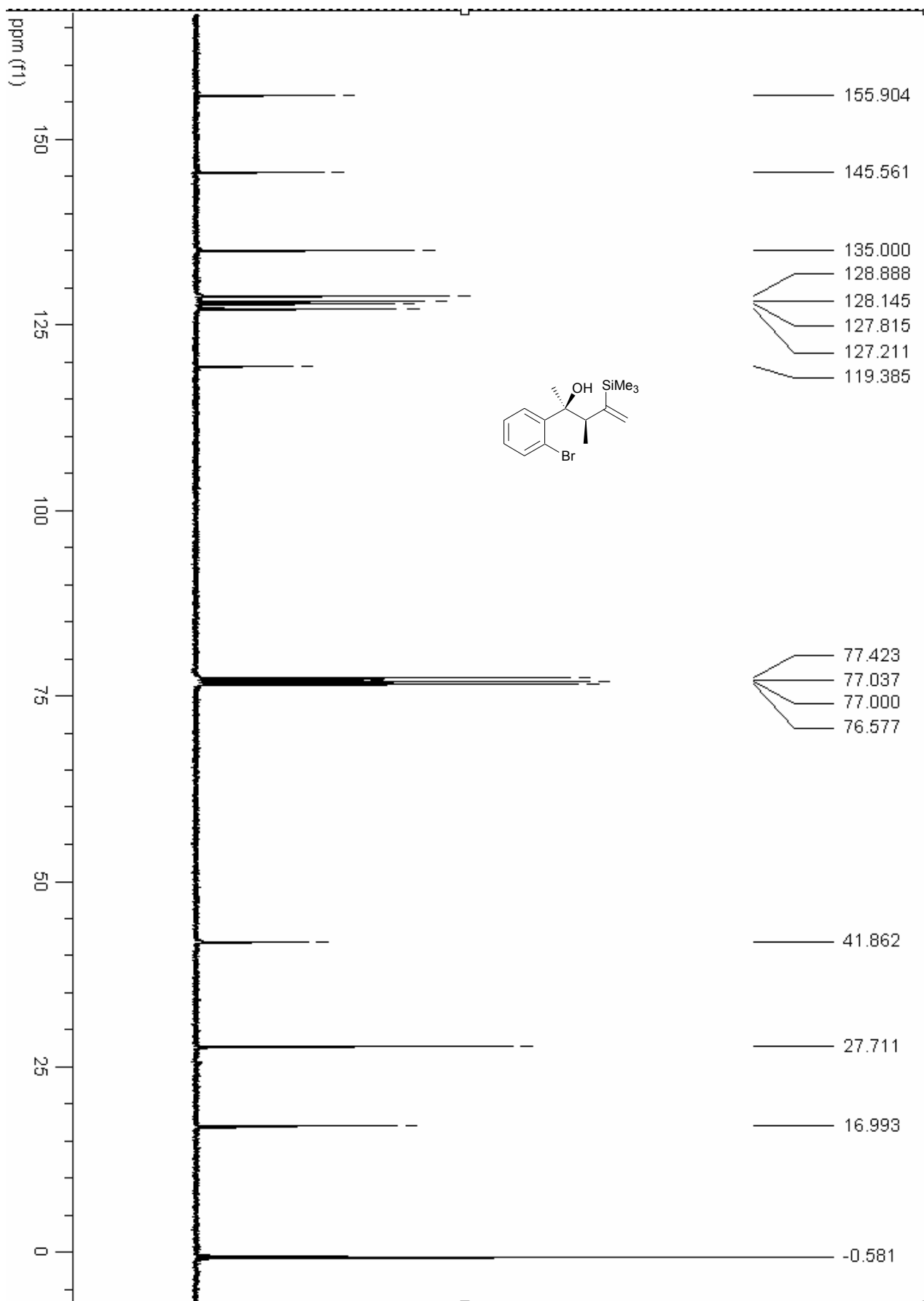
2-(4-azido-phenyl)-3-methyl-4-trimethylsilyl-pent-4-en-2-ol **11**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



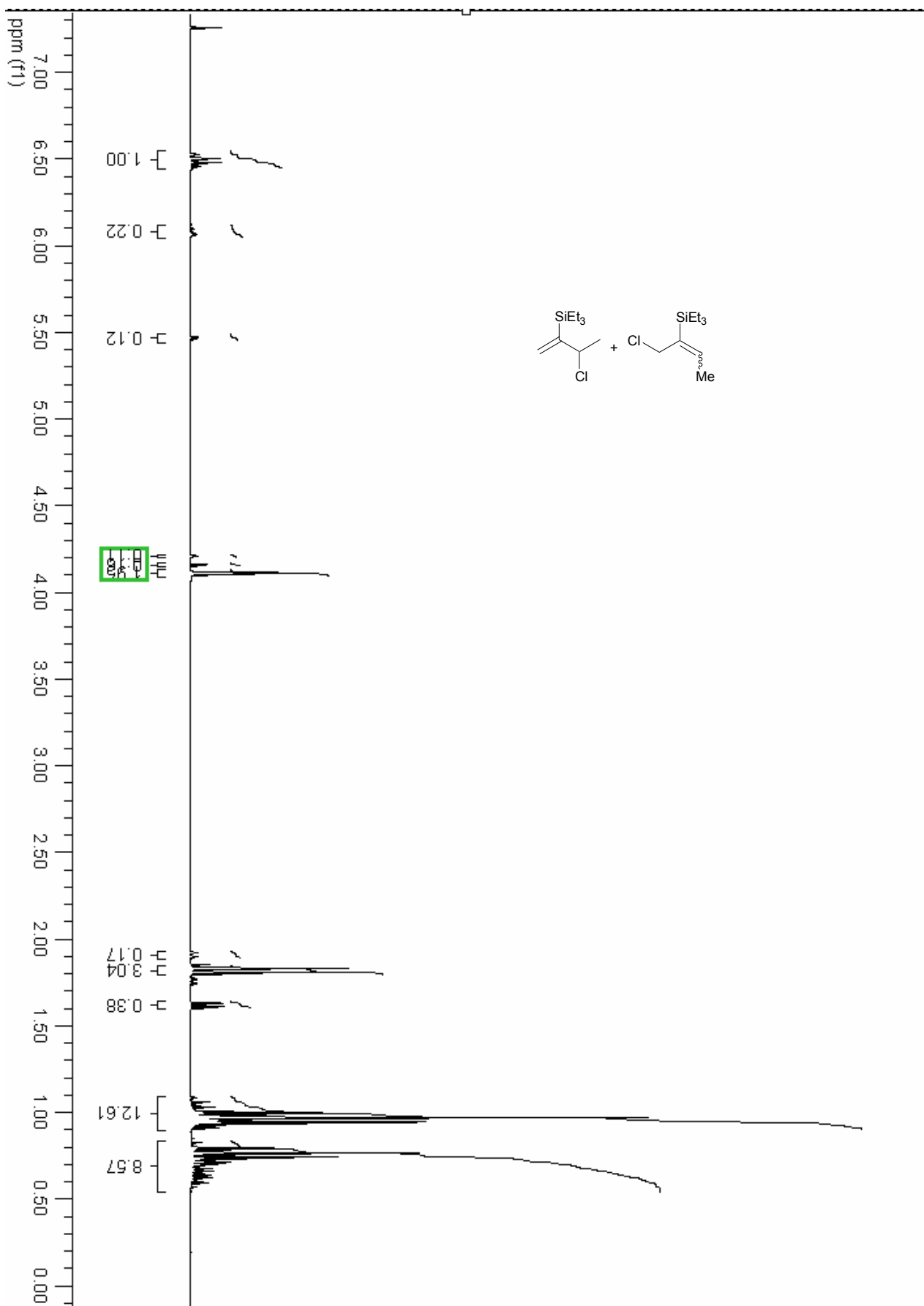
2-(2-bromo-phenyl)-3-methyl-4-trimethylsilyl-pent-4-en-2-ol **12**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):



2-(2-bromo-phenyl)-3-methyl-4-trimethylsilyl-pent-4-en-2-ol **12**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):

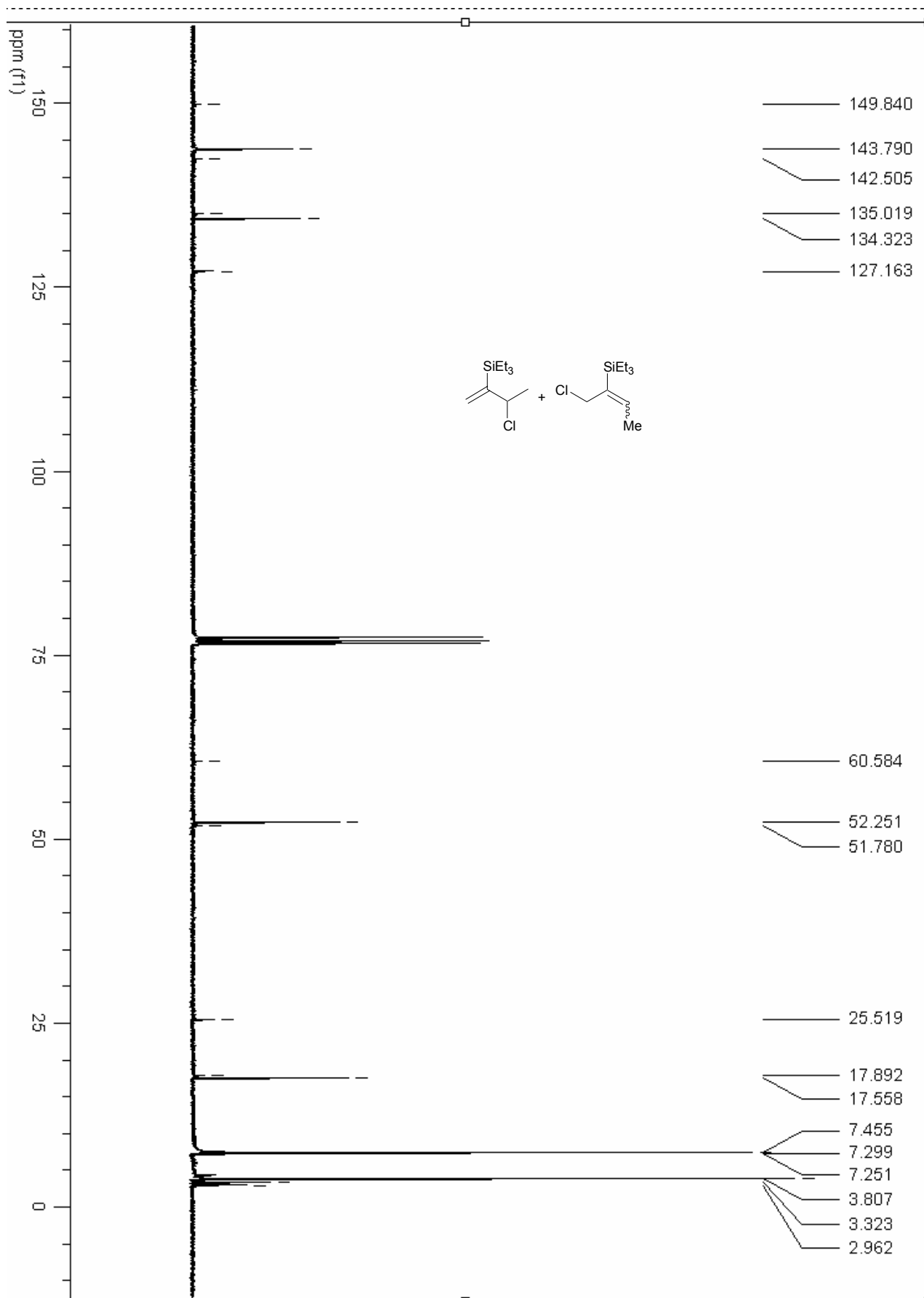


[1-(1-chloro-ethyl)-vinyl]-triethyl-silane **13a** and (1-chloromethyl-propenyl)-triethyl-silane **13b**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):

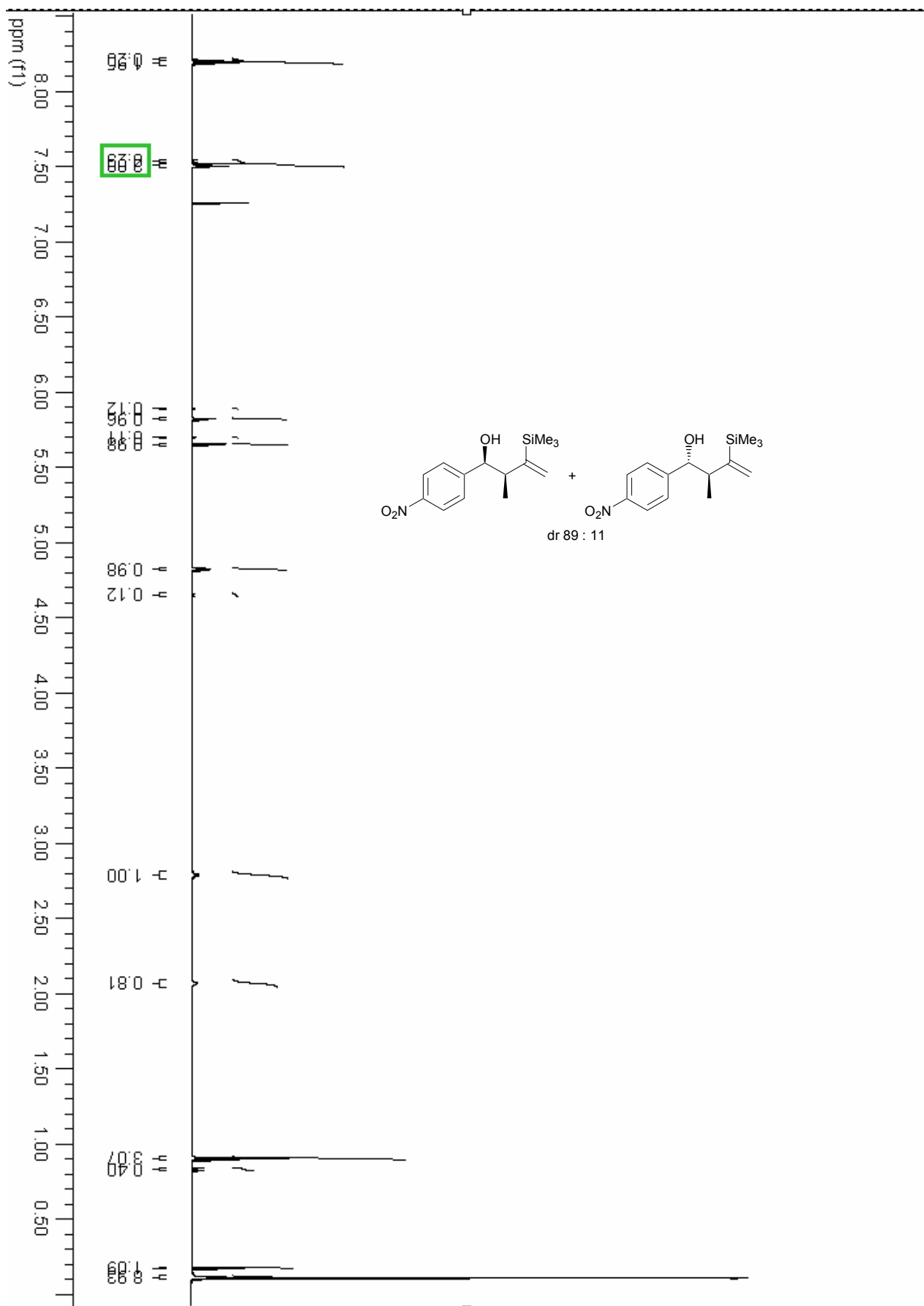




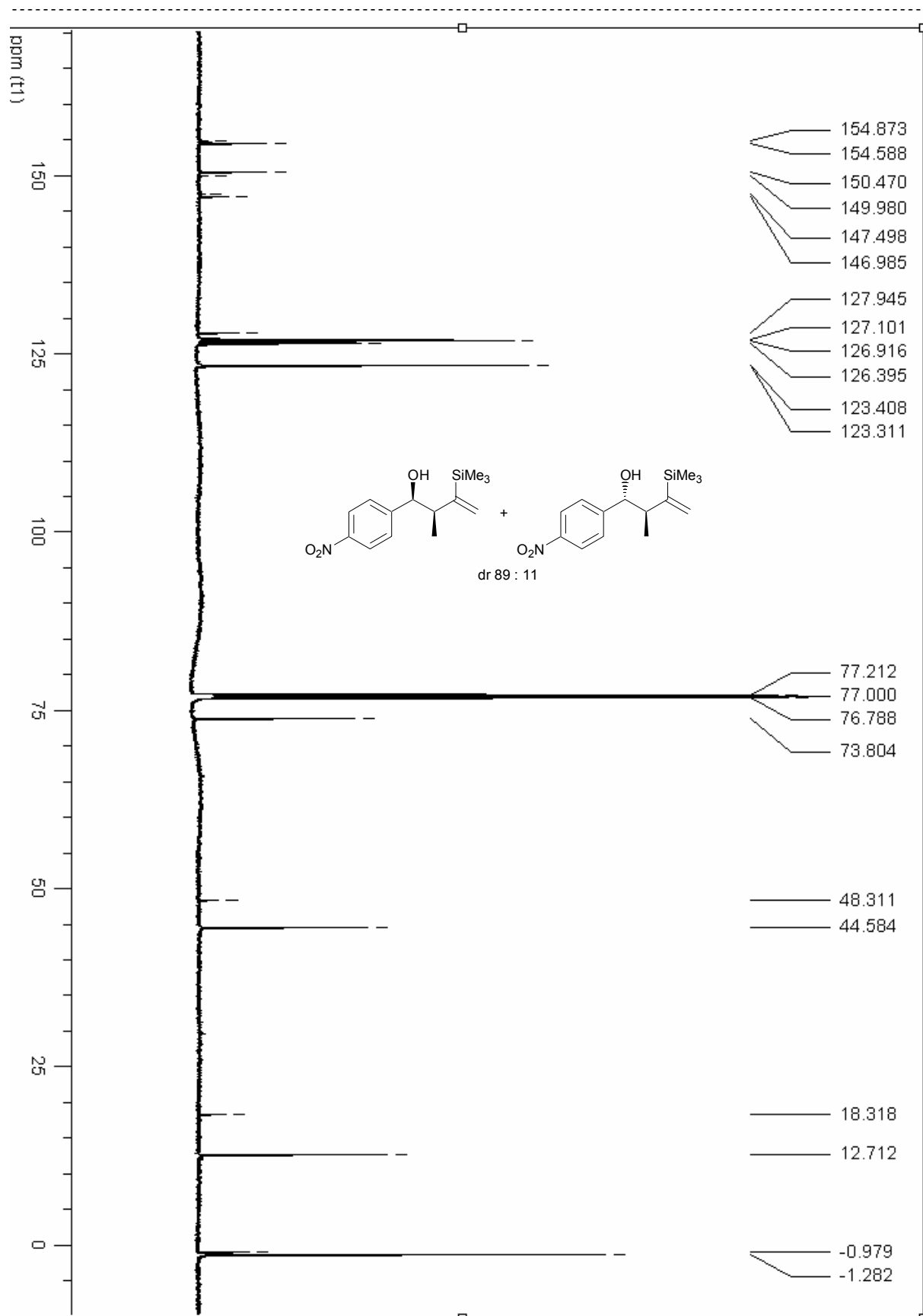
[1-(1-chloro-ethyl)-vinyl]-triethyl-silane **13a** and (1-chloromethyl-propenyl)-triethyl-silane **13b**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):



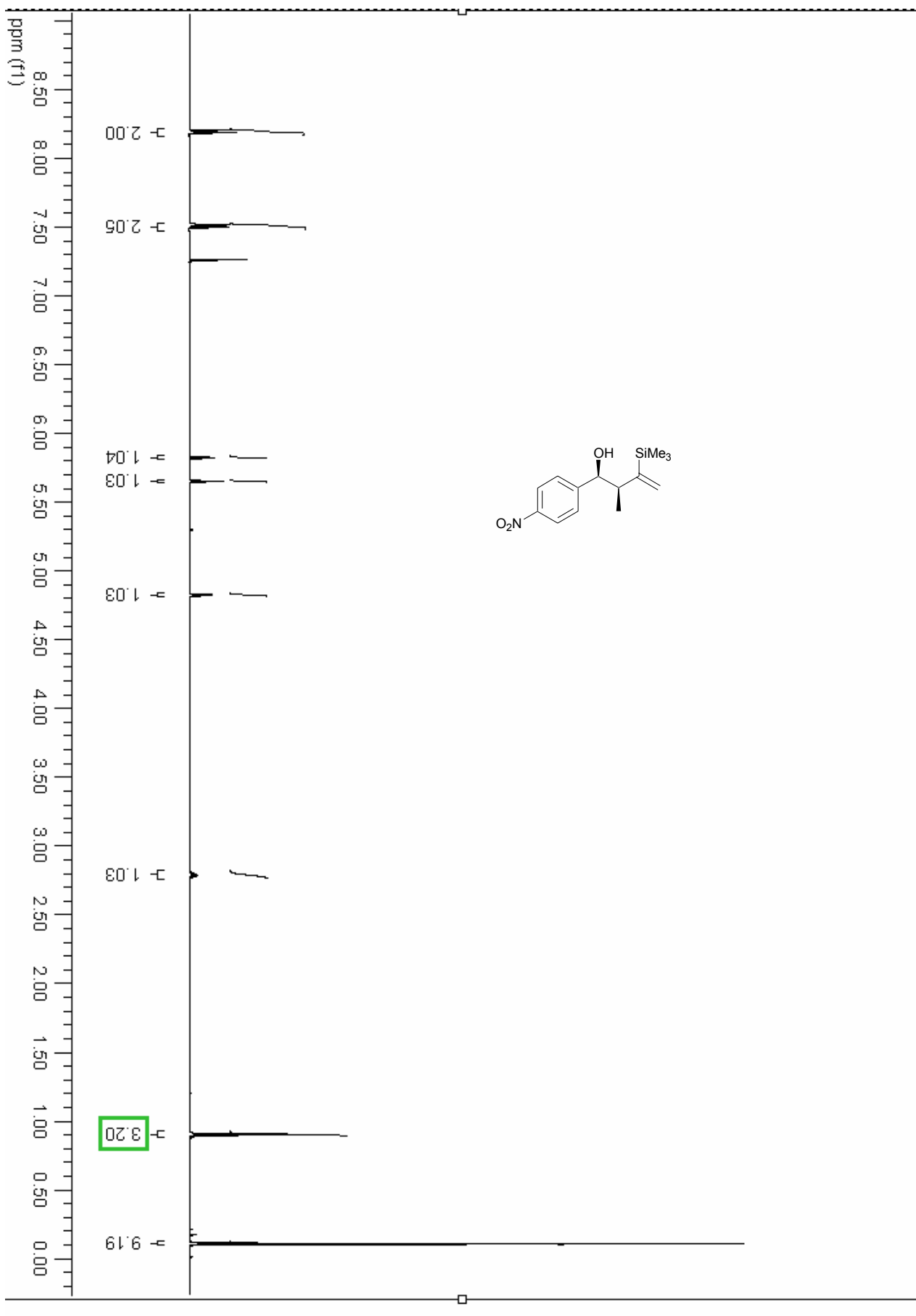
2-methyl-1-(4-nitro-phenyl)-3-trimethylsilyl-but-3-en-1-ol **15**,  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):



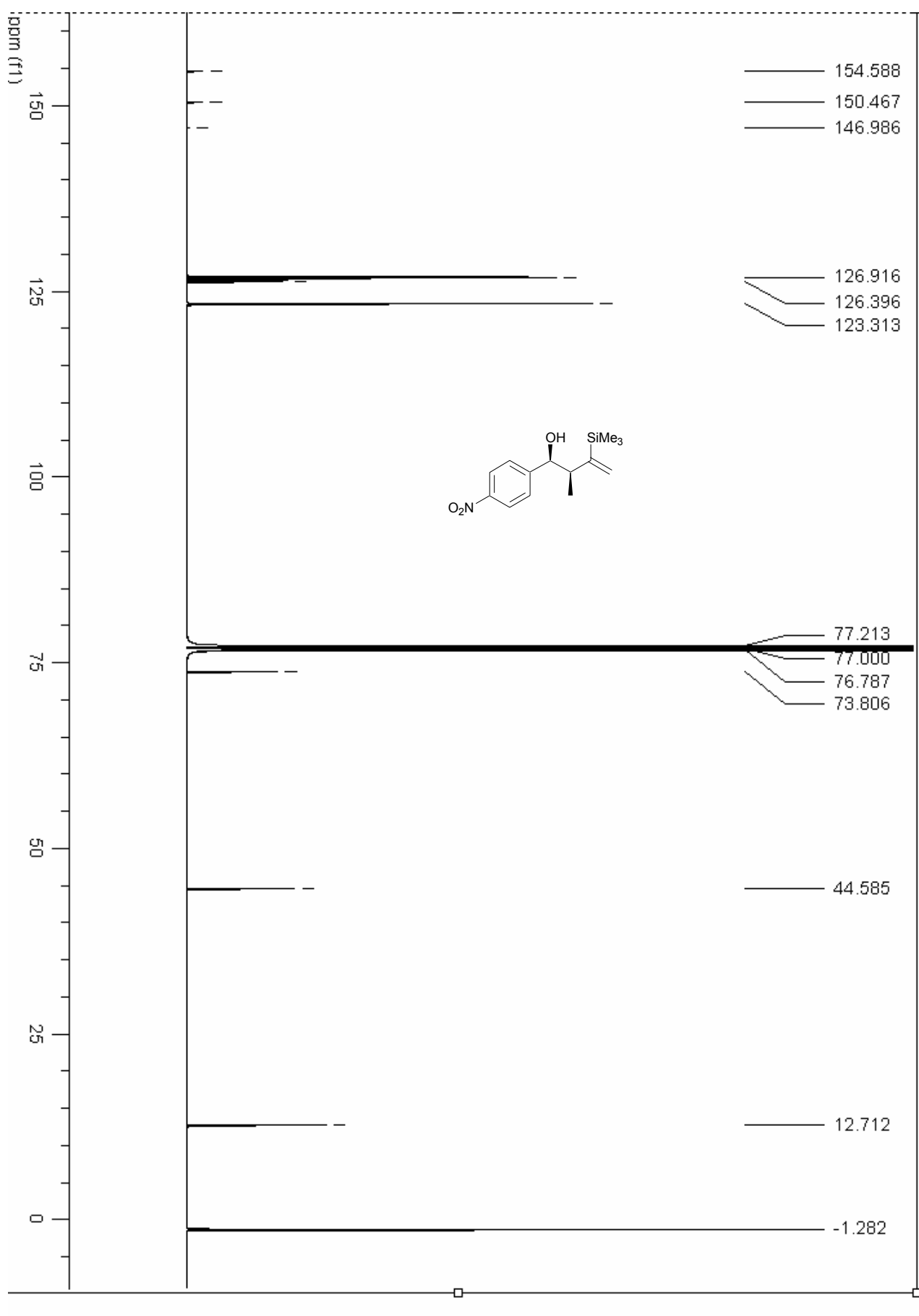
2-methyl-1-(4-nitro-phenyl)-3-trimethylsilanyl-but-3-en-1-ol **15**,  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ):



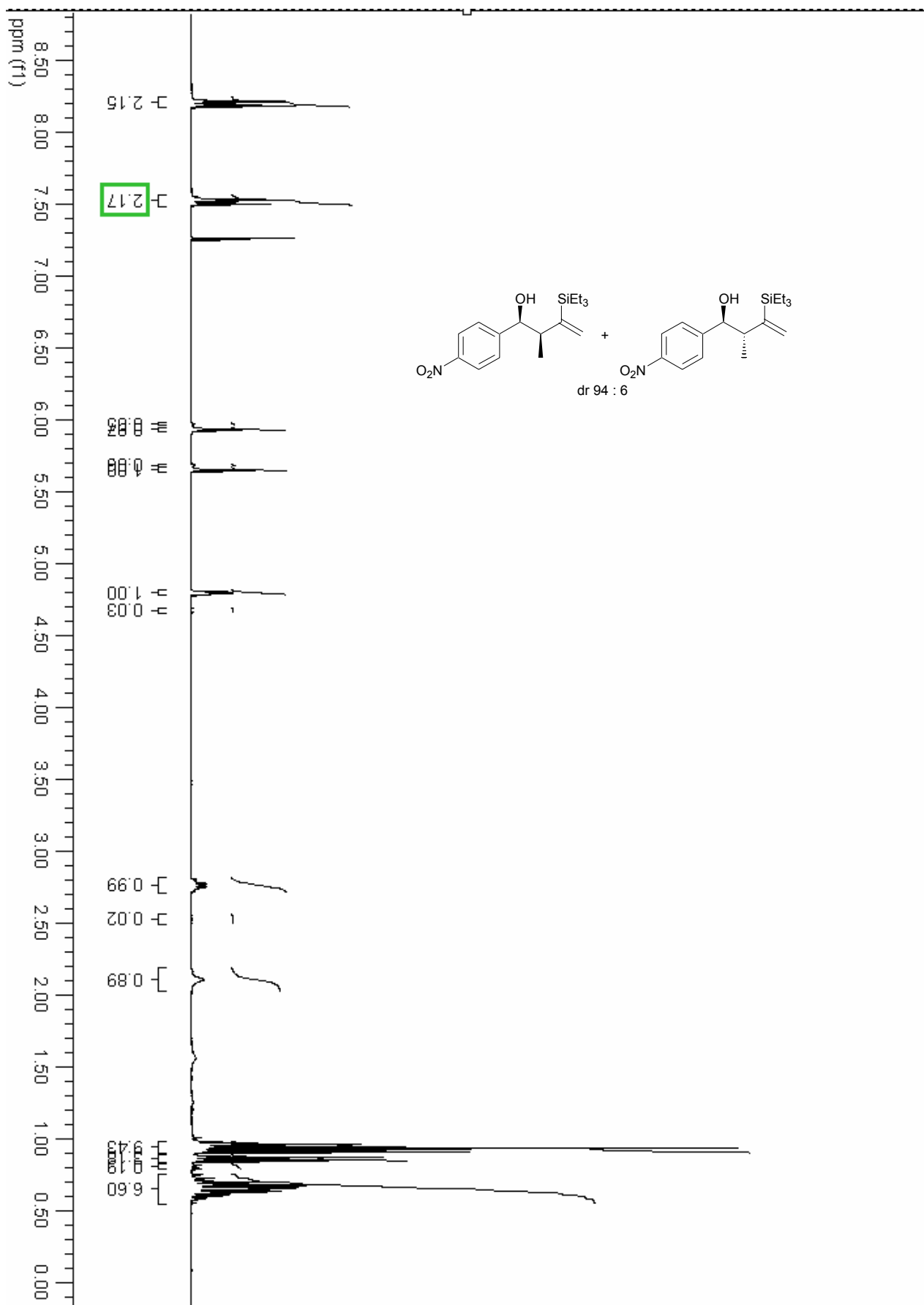
15 (recrystallised from ethyl acetate/hexane),  $^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):



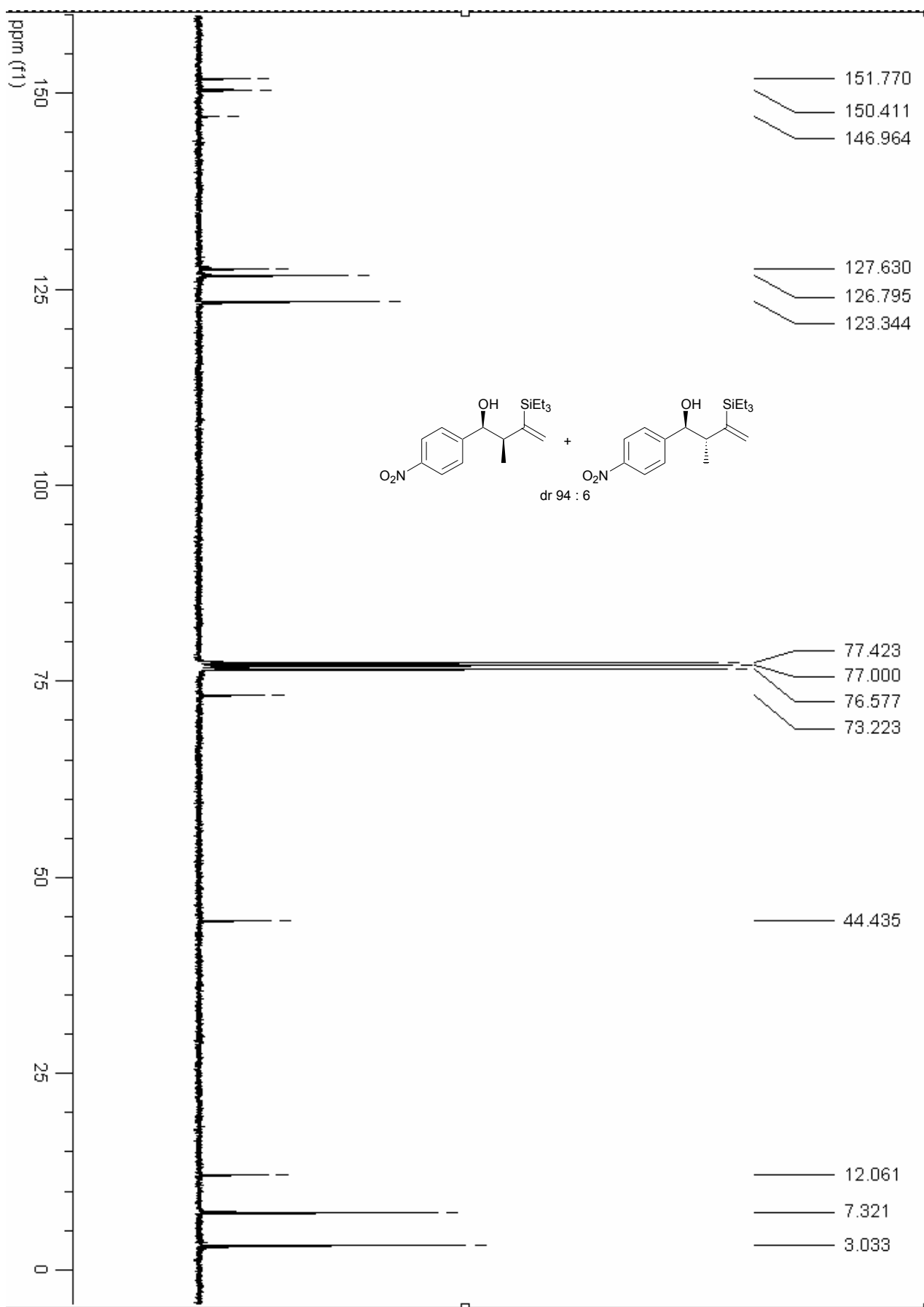
15 (recrystallised from ethyl acetate/hexane),  $^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ ):



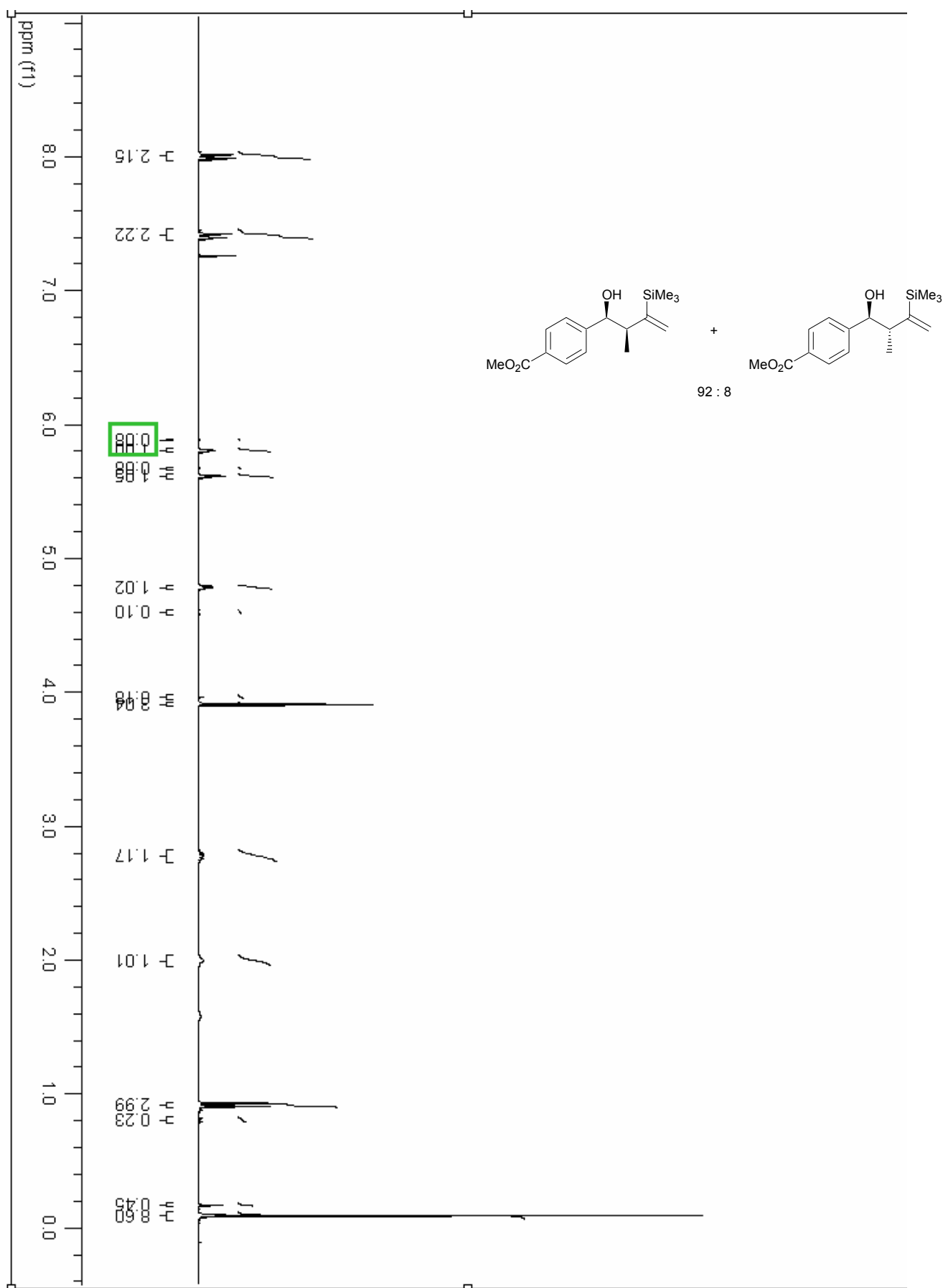
2-methyl-1-(4-nitro-phenyl)-3-triethylsilyl-but-3-en-1-ol **16**,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):



2-methyl-1-(4-nitro-phenyl)-3-triethylsilyl-but-3-en-1-ol **16**,  $^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ):

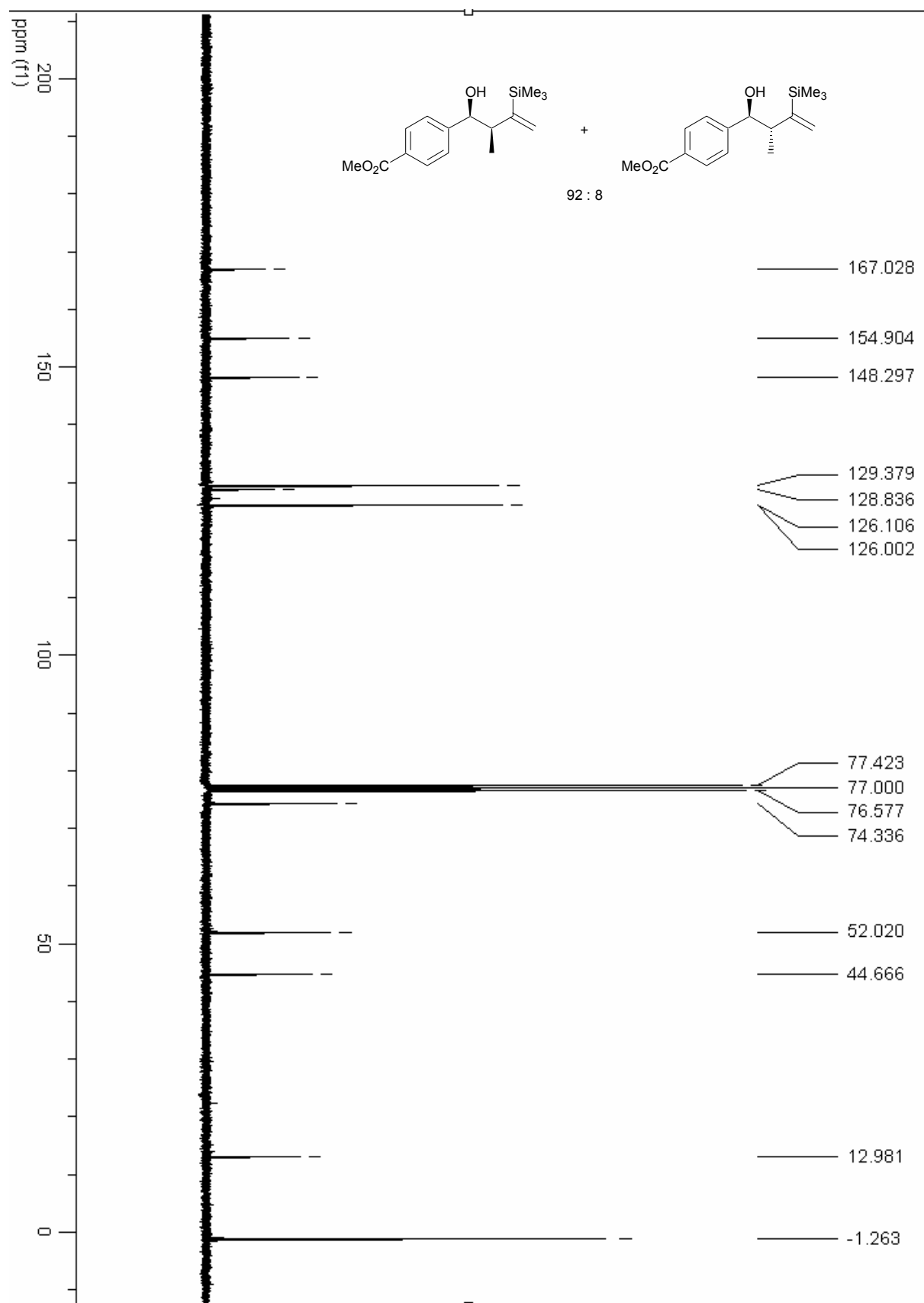


4-(1-hydroxy-2-methyl-3-trimethylsilyl-but-3-enyl)-benzoic acid methyl ester,  $^1\text{H-NMR}$   
(300 MHz,  $\text{CDCl}_3$ ):

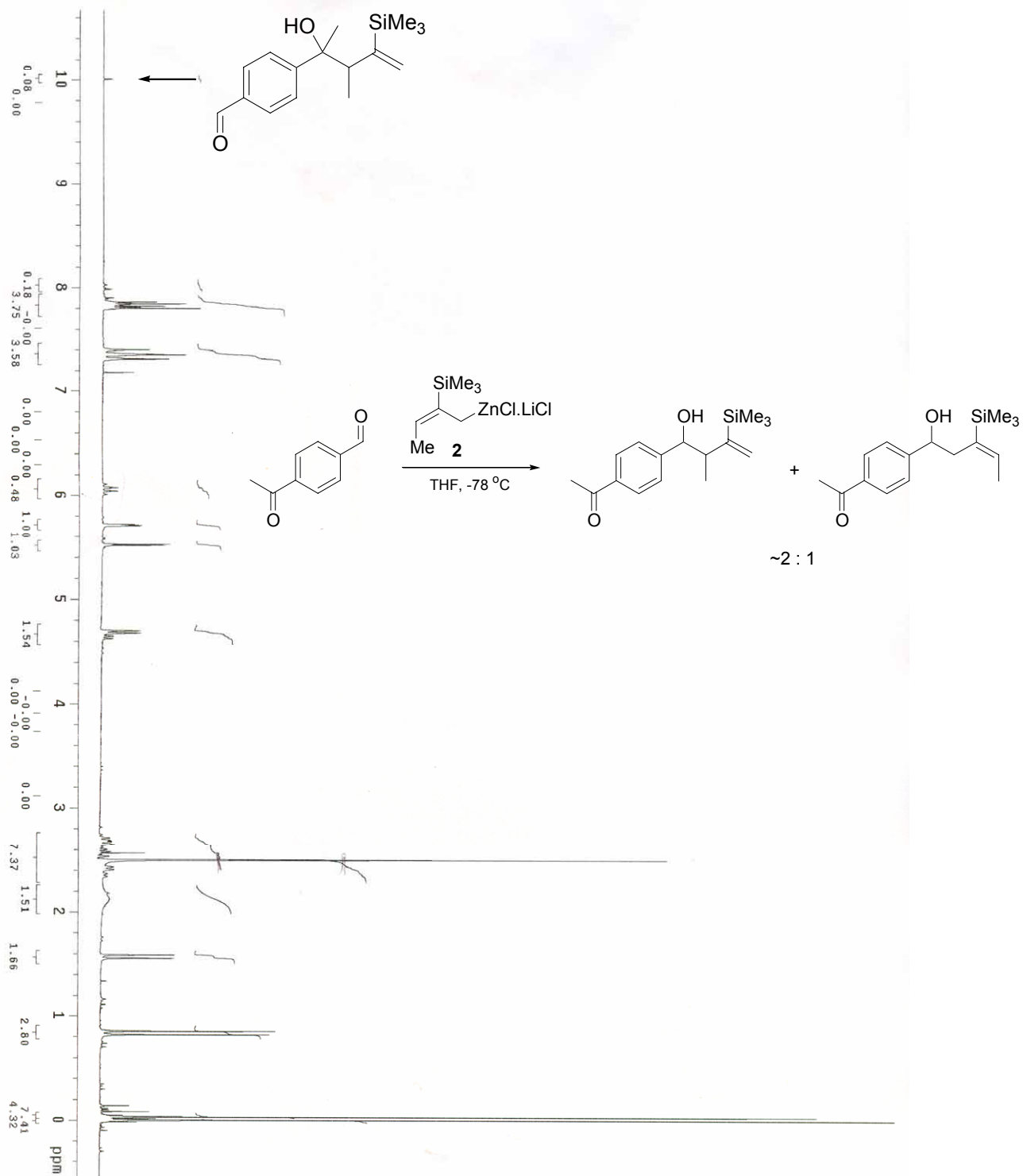




4-(1-hydroxy-2-methyl-3-trimethylsilyl-but-3-enyl)-benzoic acid methyl ester,  $^{13}\text{C}$ -NMR  
(75 MHz,  $\text{CDCl}_3$ ):



Reaction of **2** with 4-Acetyl-benzaldehyde,  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):

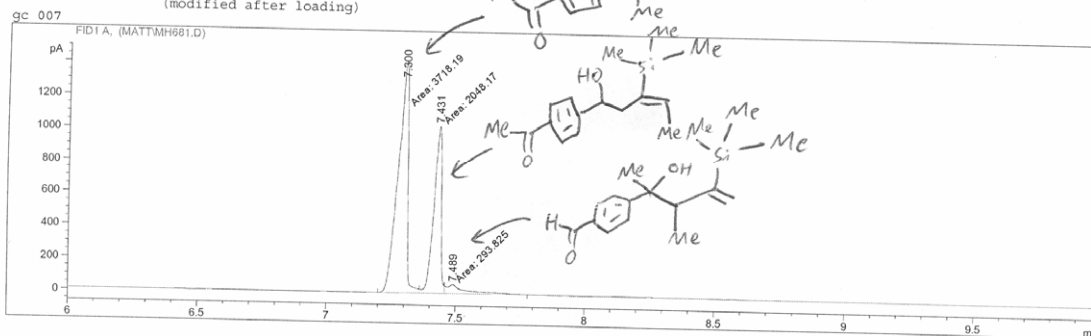


**Reaction of 2 with 4-Acetyl-benzaldehyde, GC**

Data File C:\HPCHEM\2\DATA\MATT\MH681.D

Sample Name: t

-----  
 Injection Date : 2/29/08 10:48:10 AM  
 Sample Name : t  
 Acq. Operator : matt  
 Location : Vial 1  
 Inj : 1  
 Inj Volume : Manually  
 Acq. Method : C:\HPCHEM\2\METHODS\KOLJA.M  
 Last changed : 2/28/08 8:29:11 PM by matt  
 (modified after loading)  
 Analysis Method : C:\HPCHEM\2\METHODS\KOLJA.M  
 Last changed : 2/29/08 12:15:49 PM by matt  
 (modified after loading)



-----  
 Area Percent Report  
 -----

Sorted By : Signal  
 Multiplier : 1.0000  
 Dilution : 1.0000  
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

GC 007 2/29/08 12:16:05 PM matt

Page 1 of 2

Data File C:\HPCHEM\2\DATA\MATT\MH681.D

Sample Name: t

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.300	MM	0.0435	3718.19019	1424.06152	61.35444
2	7.431	MM	0.0332	2048.16528	1027.07397	33.79710
3	7.489	MM	0.0887	293.82541	55.20864	4.84846

Totals : 6060.18088 2506.34414

Results obtained with enhanced integrator:

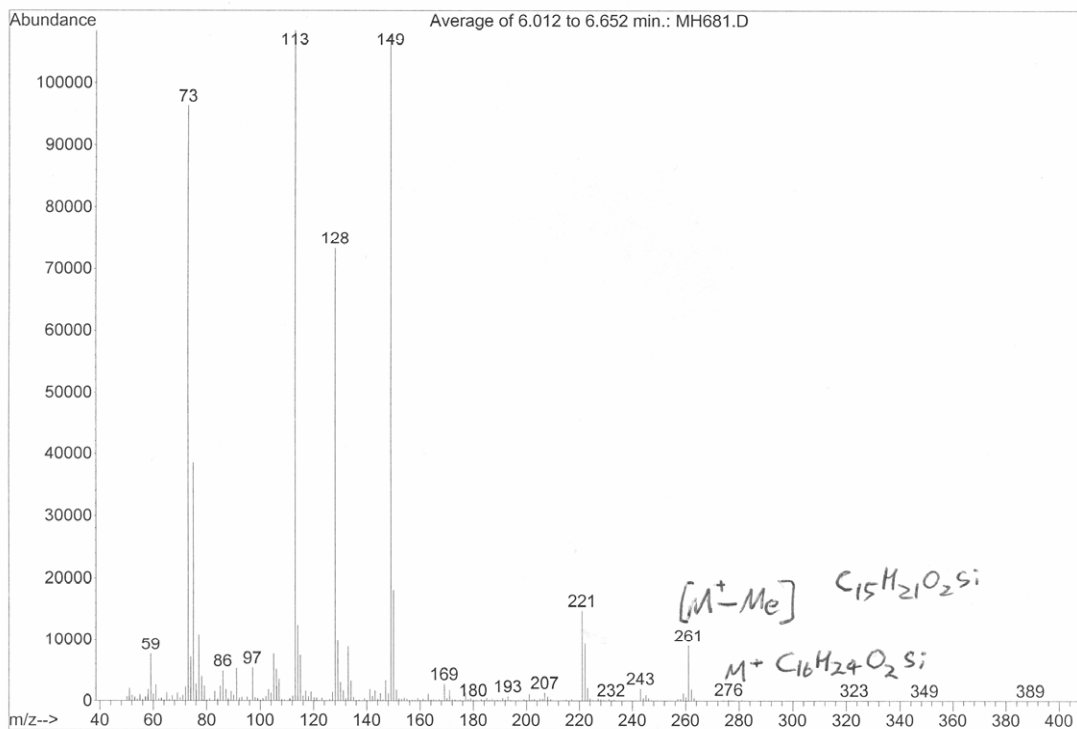
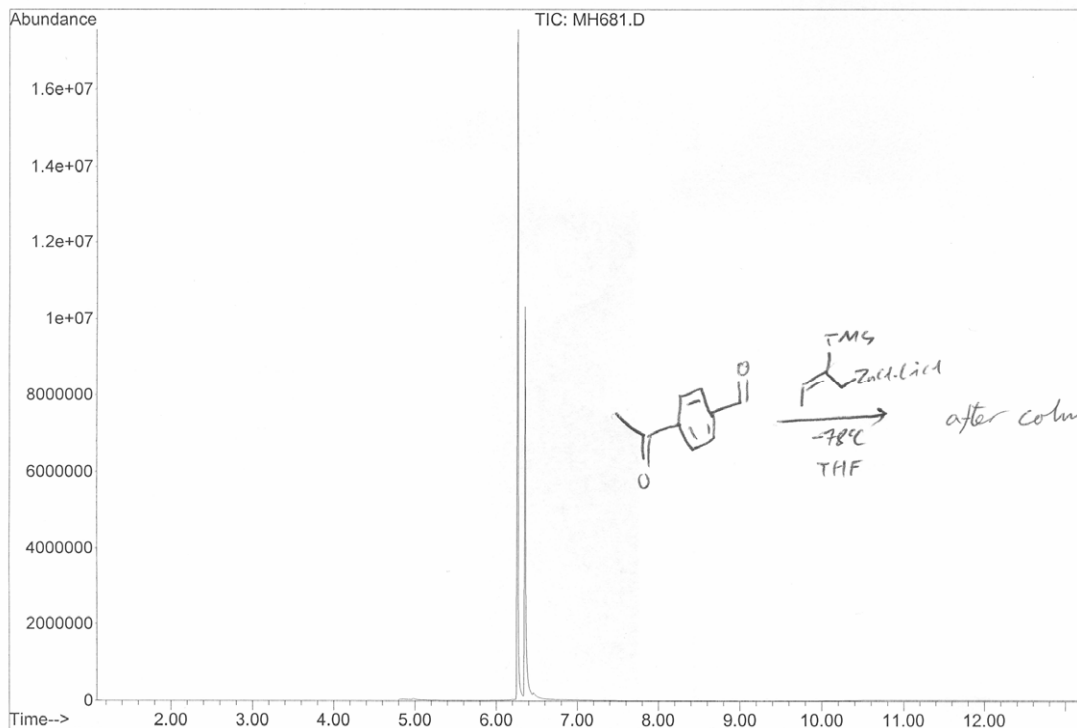
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 \*\*\* End of Report \*\*\*

GC 007 2/29/08 12:16:05 PM matt

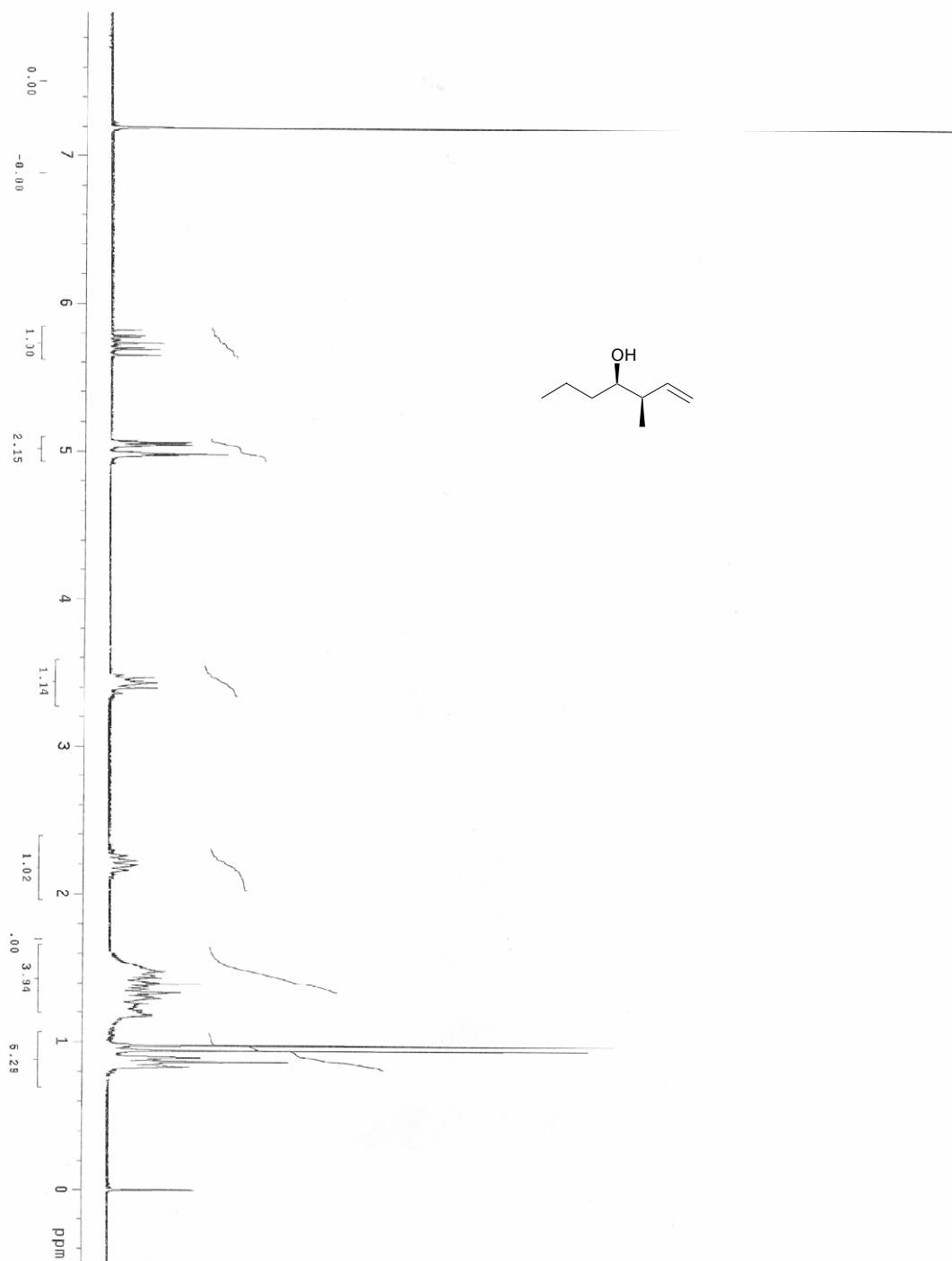
Page 2 of 2

### Reaction of 2 with 4-Acetyl-benzaldehyde, GC-MS

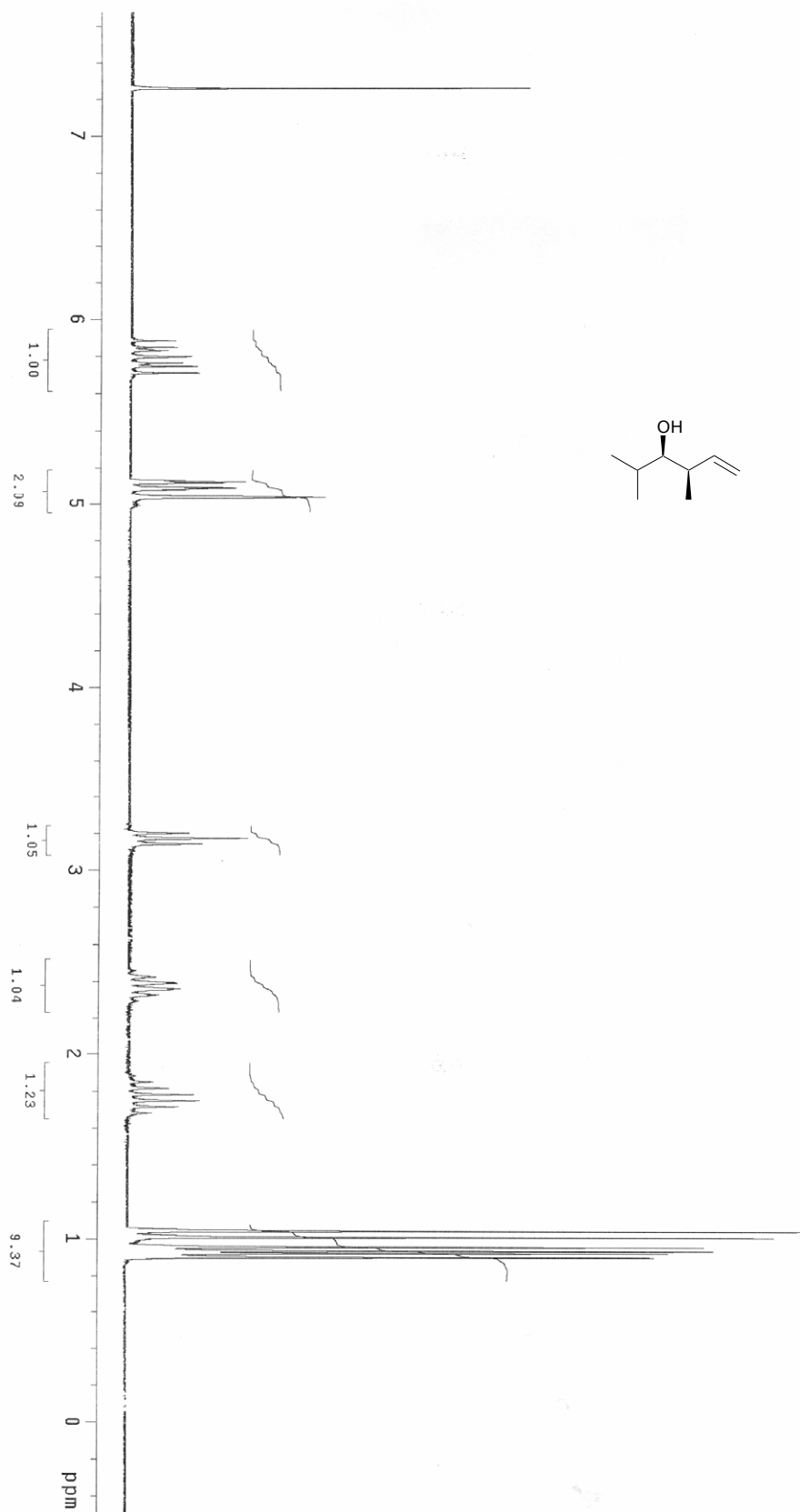
File : C:\MSDCHEM\1\DATA\MH681.D  
Operator :  
Acquired : 29 Feb 2008 12:12 using AcqMethod 70-1  
Instrument : GC-MS2  
Sample Name :  
Misc Info :  
Vial Number: 25



**3-methyl-hept-1-en-4-ol,  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):**



2,4-dimethyl-hex-5-en-3-ol,  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):



**1-cyclohexyl-2-methyl-but-3-en-1-ol,  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ ):**

