

## Supporting Information

### *Total and Syntheses of Fostriecin*

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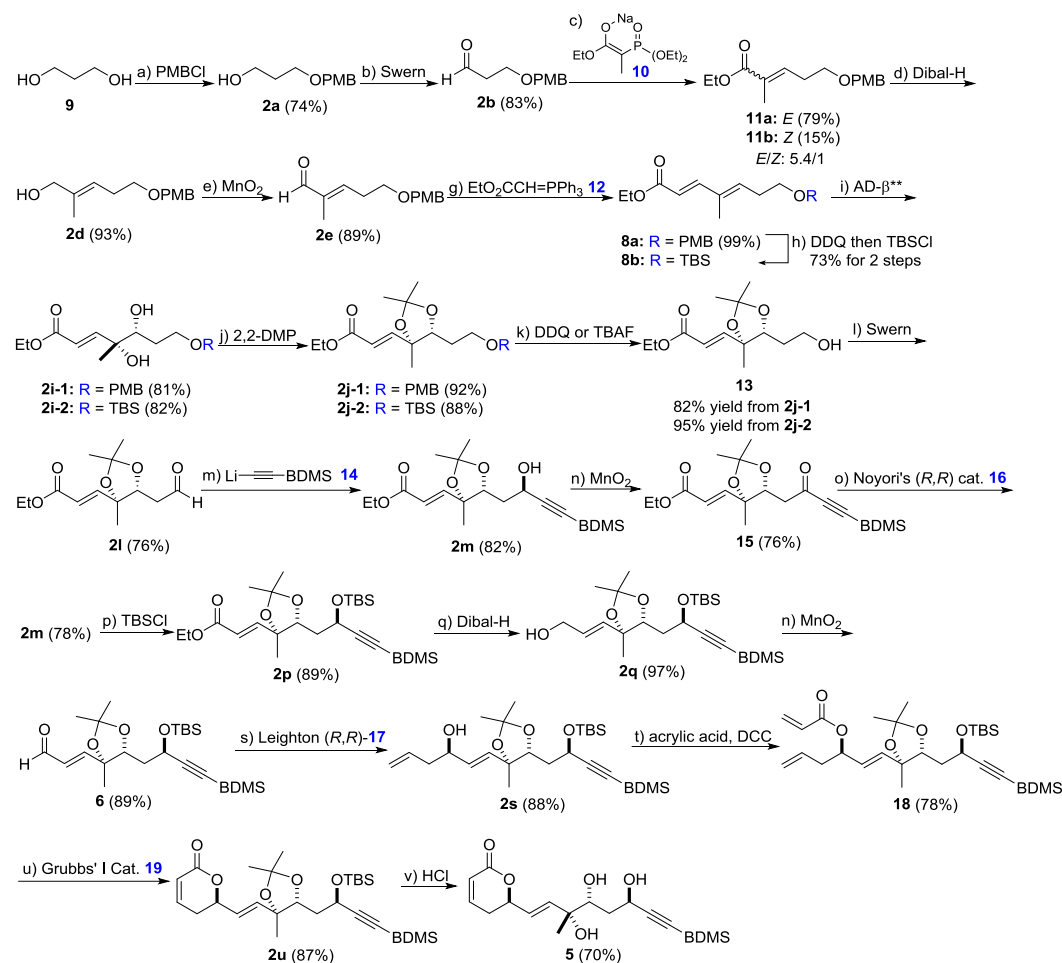
## **General Methods**

All reagents were purchased from commercial sources and used without further purification. Dichloromethane, DMF and THF used in reactions were taken from a solvent purification system in which the solvents are purified by successive passage through columns of alumina and copper under argon. Methanol used in reactions was dried in a sealed bottle over activated 3 Å molecular sieves. Air and/or moisture-sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven/flamed-dried glassware and standard syringe/septa techniques. Unless stated otherwise, all reactions were monitored by thin layer chromatography on silica gel 60 F254 (0.25 mm, Merck) glass plates and visualized by quenching of fluorescence and by charring after treatment with *p*-anisaldehyde or phosphomolybdic acid or potassium permanganate stain.  $R_f$  values were obtained by elution in the stated solvent ratios (v/v). In the reaction work-up involving extractions, solutions of organic solvents were washed with equal amounts of aqueous solutions, unless otherwise noted. All column chromatography was performed on silica gel 60 (40–60  $\mu\text{m}$ ). Melting points were measured on an Electrothermal Mel-Temp apparatus and were not corrected. Optical rotations were measured on a Jasco DIP-370 digital polarimeter in the solvent specified. FTIR spectra were run on Thermo Nicolet (Madison Wisconsin, USA) 8700 main bench with a Continuum FTIR microscope attached, and samples cast from a chloroform solution onto an IR-transparent silicon wafer.  $^1\text{H}$  NMR spectra were recorded at 270, 500 and 600 MHz, while  $^{13}\text{C}$  NMR spectra were recorded at 67.5, 150 and 500 MHz correspondingly. Chemical shifts of both  $^1\text{H}$  and  $^{13}\text{C}$  NMR were referenced to internal tetramethylsilane (0.00 ppm) or  $\text{CHCl}_3$  (7.26 ppm,  $\text{CDCl}_3$ ). High resolution electrospray mass spectra were recorded on an Agilent Technologies 6220 Accurate-Mass TOF spectrometer with samples dissolved in a suitable solvent.

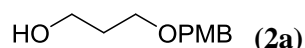
The following experimental section outlines the synthetic and spectroscopic details for the all the synthetic pathways explored in the manuscript. Of the experimental

detailed, the one for the following compounds are being disclosed for the first time: **24, 27-37, 39, 43-51** and accordingly the procedures include,  $R_f$ ,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, HRMS, melting points, and optical rotation when relevant.

## Intermediates related to Scheme 2:



### 3-((4-methoxybenzyl)oxy)propan-1-ol (**2a**)<sup>1</sup>

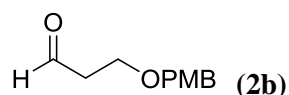


Propane-1,3-diol **9** (2 g, 26.28 mmol) was taken in 100 mL of anhydrous THF and NaH (60% dispersion in mineral oil, 1.16 g, 28.91 mmol) was added to it portion wise at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. Tetrabutylammonium iodide (TBAI, 1.07 g, 2.89 mmol) was added to it followed by the addition of 4-methoxybenzylchloride (PMBCl) (4.12 g, 26.28 mmol) in THF (10 mL). The reaction mixture was stirred for a further 8 h at room temperature. H<sub>2</sub>O was added carefully to the reaction mixture to quench any excess of NaH. The reaction mixture was then extracted with EtOAc. The organic solution was washed with water, brine,

<sup>1</sup> Spectral data matched which was previously reported, see: (a) Shibahara, S.; Fujino, M.; Tashiro, Y.; Okamoto, N.; Esumi, T.; Takahashi, K.; Ishihara, J.; Hatakeyama S. Total Synthesis of (+)-Fostriecin and (+)-Phoslactomycin B. *Synthesis*, **2009**, *17*, 293. (b) Kretschmer, M.; Menche, D. Stereocontrolled Synthesis of the C8-C22 Fragment of Rhizopodin. *Org. Lett.* **2012**, *14*, 382.

dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 3:2 (v/v) hexane/EtOAc) to afford the PMB mono-protecting compound **2a** (3.80 g, 74% yield) as a yellow liquid. *R<sub>f</sub>* = 0.214 (6:4 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3521, 2905, 2856, 1650, 1463, 1366, 1172, 1086, 1033, 819; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 3.74 (t, *J* = 5.8 Hz, 2H), 3.62 (t, *J* = 5.9 Hz, 2H), 2.71 (s, 1H), 1.84 (p, *J* = 5.8 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz): δ 158.8, 130.0, 128.9 (2C), 113.4 (2C), 72.4, 67.8, 60.1, 54.5, 32.3; HRMS (ESI<sup>+</sup>) calculated for [C<sub>11</sub>H<sub>16</sub>O<sub>3</sub> + H]<sup>+</sup>: 197.1172, Found: 197.1176.

### 3-((4-methoxybenzyl)oxy)propanal (**2b**)<sup>2</sup>

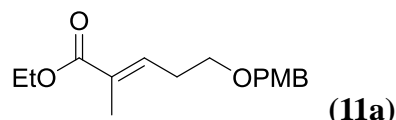


To a 5 mL anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution, DMSO (0.24 g, 3.06 mmol) was added, and the mixture was cooled to -78 °C under argon, followed by the dropwise addition of oxalylchloride (0.26 g, 2.04 mmol). After 30 min, PMB-propanol **2a** (200 mg, 1.02 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added and the reaction was stirred at -78 °C for additional 1.5 h under argon. Et<sub>3</sub>N (0.52 g, 5.10 mmol) was then added and the reaction mixture was allowed to react 6 h under room temperature. 1 M NaHSO<sub>4</sub> (10 mL) was added carefully to the reaction mixture to quench the excessive Et<sub>3</sub>N and oxalylchloride, and the reaction mixture was then extracted with Et<sub>2</sub>O. The combined organic phases were washed with saturated aqueous solution of NaHCO<sub>3</sub>, brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 8:1 (v/v) hexane/EtOAc) to afford the PMB-propanal **2b** (165.0 mg, 83% yield) as a yellow liquid. *R<sub>f</sub>* = 0.237 (4:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2980, 2905, 2856, 1706, 1463, 1366, 1172, 1086, 1033, 819; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 9.78 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.88

<sup>2</sup> Spectral data matched which was previously reported, see: (a) Hayashi, Y.; Yamaguchi, H.; Toyoshima, M.; Okado, K.; Toyo, T.; Shoji, M. Formal Total Synthesis of Fostriecin via 1,4-Asymmetric Induction Using Alkyne-Cobalt Complex. *Chem. Eur. J.* **2010**, *16*, 10150. (b) Hernandez, D.; Lindsay, K.B.; Nielsen, L.; Mittag, T.; Bjerglund, K.; Friis, S.; Mose, R.; Skrydstrup, T. Further Studies toward the Stereocontrolled Synthesis of Silicon-Containing Peptide Mimics. *J. Org. Chem.* **2010**, *75*, 3283.

(d,  $J = 8.5$  Hz, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 3.78 (t,  $J = 6.2$  Hz, 2H), 2.68 (td,  $J = 6.1, 1.7$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  201.3, 159.4, 130.0, 129.4 (2C), 113.9 (2C), 73.0, 63.6, 55.3, 43.9. HRMS (ESI+) calculated for  $[\text{C}_{11}\text{H}_{14}\text{O}_3 + \text{Na}]^+$ : 217.0841, Found: 217.0842.

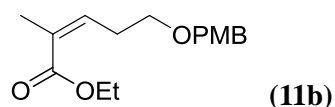
### Ethyl (*E*)-5-((4-methoxybenzyl)oxy)-2-methylpent-2-enoate (**11a**)<sup>3</sup>



Triethyl 2-phosphonopropionate **10** (220.77 mg, 0.93 mmol) was added dropwise to a suspension of NaH 60% weight in mineral oil (37.07 mg, 0.93 mmol) in anhydrous THF (7 mL) at 0 °C under an argon atmosphere. After 1 h stirring, PMB-propanal **2b** (150 mg, 0.77 mmol) was added, and the reaction was stirred at room temperature for another 2 h. The reaction mixture was quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$ , and was then extracted with  $\text{Et}_2\text{O}$ . The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 20:1 (v/v) hexane/ $\text{EtOAc}$ ) to afford the PMB-enoate **11a** in (142.4 mg, 79% yield) as a colorless oil.  $R_f = 0.216$  (10:1 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 2931, 2905, 2856, 1706, 1612, 1512, 1366, 1244, 1086, 1033, 819;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  7.25 (d,  $J = 8.5$  Hz, 2H), 6.87 (d,  $J = 8.5$  Hz, 2H), 6.77 (t,  $J = 7.2$  Hz, 1H), 4.45 (s, 2H), 4.18 (q,  $J = 7.1$  Hz, 2H), 3.80 (s, 3H), 3.53 (t,  $J = 6.8$  Hz, 2H), 2.47 (q,  $J = 6.9$  Hz, 2H), 1.84 (s, 3H), 1.29 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  168.1, 159.3, 138.4, 130.4, 129.5, 129.4 (2C), 113.9 (2C), 72.8, 68.4, 60.6, 55.4, 29.5, 14.4, 12.7. HRMS (MALDI-TOF/CCA) calculated for  $[\text{C}_{16}\text{H}_{22}\text{O}_4 + \text{H}]^+$ : 279.1591, Found: 279.1593.

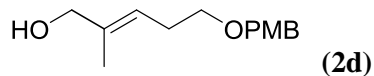
### Ethyl (*Z*)-5-((4-methoxybenzyl)oxy)-2-methylpent-2-enoate (**11b**)

<sup>3</sup> Spectral data matched which was previously reported, see: Hayashi, Y.; Yamaguchi, H.; Toyoshima, M.; Okado, K.; Toyo, T.; Shoji, M. Formal Total Synthesis of Fostriecin via 1,4-Asymmetric Induction Using Cobalt-Alkyne Complex. *Org. Lett.* **2008**, *10*, 1405.



Triethyl 2-phosphonopropionate **10** (220.77 mg, 0.93 mmol) was added dropwise to a suspension of NaH 60% weight in mineral oil (37.07 mg, 0.93 mmol) in anhydrous THF (7 mL) at 0 °C under an argon atmosphere. After 1 h stirring, PMB-propanal **2b** (150 mg, 0.77 mmol) was added, then stirred at room temperature for another 2 h. The reaction mixture was quenched by saturated aqueous solution of NH<sub>4</sub>Cl, and was then extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 20:1 (v/v) hexane/EtOAc) to afford the PMB-enoate **11b** in (26.4 mg, 15% yield) as a colorless oil.  $R_f = 0.378$  (10:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2931, 2905, 2856, 1706, 1612, 1512, 1463, 1366, 1244, 1086, 1033, 819; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.26 (d,  $J = 8.6$  Hz, 2H), 6.87 (d,  $J = 8.6$  Hz, 2H), 6.06 – 5.97 (m, 1H), 4.45 (s, 2H), 4.18 (q,  $J = 7.1$  Hz, 2H), 3.80 (s, 3H), 3.51 (t,  $J = 6.5$  Hz, 2H), 2.77 (q,  $J = 6.5$  Hz, 2H), 1.91 – 1.89 (m, 3H), 1.29 (t,  $J = 7.1$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz): δ 168.0, 159.3, 139.5, 130.6, 129.4, 128.7 (2C), 113.9 (2C), 72.6, 69.3, 60.2, 55.4, 30.3, 20.8, 14.4. HRMS (MALDI-TOF/CCA) calculated for [C<sub>16</sub>H<sub>22</sub>O<sub>4</sub> + H]<sup>+</sup>: 279.1591, Found: 279.1593.

**(E)-5-((4-methoxybenzyl)oxy)-2-methylpent-2-en-1-ol (2d)**<sup>4</sup>

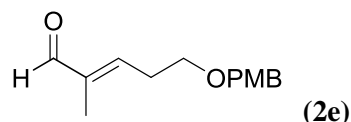


To a solution of enoate **11a** (350 mg, 1.26 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) was dropwise added diisobutylaluminum hydride (*i*-Bu)<sub>2</sub>AlH (1.0 M in CH<sub>2</sub>Cl<sub>2</sub>, 8.80 mL, 8.80 mmol) at -78 °C under an argon atmosphere. After stirring for 2 h at -78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 1 h. Then the reaction mixture was diluted with Et<sub>2</sub>O and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 15 mL). The biphasic mixture

<sup>4</sup> Spectral data matched which was previously reported, see: Chakraborty, T. K.; Purkait, S.; Das, S. Synthesis of chiral 4-hydroxy-2,3-unsaturated carbonyl compounds from 3,4-epoxy alcohols by oxidation: application in the formal synthesis of macrophelide A. *Tetrahedron* **2003**, 59, 9127.

was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with Et<sub>2</sub>O. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 3:1 (v/v) hexane/EtOAc) to afford the primary alcohol **2d** (277.30 mg, 93% yield) as a colorless oil.  $R_f = 0.219$  (6:4 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3523, 2903, 2857, 1649, 1461, 1367, 1175, 1085, 819; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.26 (d,  $J = 8.5$  Hz, 2H), 6.88 (d,  $J = 8.5$  Hz, 2H), 5.43 (t,  $J = 7.0$  Hz, 1H), 4.45 (s, 2H), 3.99 (s, 2H), 3.80 (s, 3H), 3.46 (t,  $J = 7.0$  Hz, 2H), 2.36 (q,  $J = 7.0$  Hz, 2H), 1.67 (s, 3H), 1.65 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  159.2, 136.8, 130.5, 129.4 (2C), 122.0, 113.8 (2C), 72.6, 69.5, 68.6, 55.3, 28.4, 13.9. HRMS (MALDI-TOF/CCA) calculated for [C<sub>14</sub>H<sub>20</sub>O<sub>3</sub> + H]<sup>+</sup>: 237.1485, Found: 237.1482.

#### 5-((4-methoxybenzyl)oxy)-2-methylpent-2-enal (**2e**)<sup>4</sup>

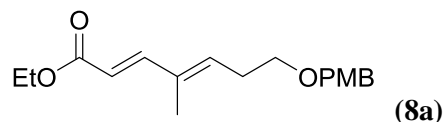


To a solution of the Dibal-H reduction product alcohol **2d** (100 mg, 0.423 mmol) in 5.0 mL of anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added activated MnO<sub>2</sub> (551.8 mg, 6.348 mmol), and the mixture stirred vigorously for 24 h at room temperature, the reaction mixture was filtered through celite, and the celite was washed with CH<sub>2</sub>Cl<sub>2</sub> and ethyl acetate. The filtrate was then dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 12:1 (v/v) hexane/EtOAc) to afford the enal **2e** (88.2 mg, 89% yield) as a colorless oil. Fortunately, at this point we were able to convert the undesired *Z*-isomer to the desired *E*-isomer **2e** by treating the crude mixture with 10 mol % trifluoroacetic acid (TFA) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, which gave an 81% yield.  $R_f = 0.284$  (6:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2931, 2857, 1706, 1649, 1612, 1461, 1367, 1175, 1085, 819; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  9.41 (s, 1H), 7.26 (d,  $J = 8.4$  Hz, 2H), 6.89 (d,  $J = 8.5$  Hz, 2H), 6.55 (t,  $J = 6.9$  Hz, 1H), 4.47 (s, 2H), 3.81 (s, 3H), 3.60 (t,  $J = 6.4$  Hz, 2H), 2.64 (q,  $J = 6.6$  Hz, 2H), 1.75 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  195.3, 159.4, 151.2, 140.7, 130.2, 129.5 (2C),



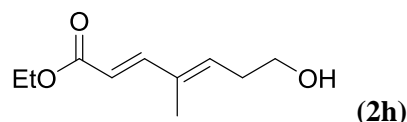
114.0 (2C), 72.9, 68.0, 55.4, 29.8, 9.5. HRMS (MALDI-TOF/CCA) calculated for  $[C_{14}H_{18}O_3 + H]^+$ : 235.1392, Found: 235.1394.

**Ethyl (2E,4E)-7-((4-methoxybenzyl)oxy)-4-methylhepta-2,4-dienoate (8a)**



To a solution of  $MnO_2$  oxidative enal **2e** (100 mg, 0.427 mmol) in 2.0 mL of anhydrous THF was added (Carboethoxymethylene)-triphenylphosphorane **12** (297.4 mg, 0.854 mmol), the reaction was stirred for 48 h at room temperature. The crude was concentrated in vacuo, then purified by column chromatography (silica gel, 50:1 (v/v) hexane/EtOAc) to afford dienoate **8a** (129.5 mg, 99% yield) as a colorless oil.  $R_f$  = 0.289 (15:1 (v/v) hexane/EtOAc); IR (neat,  $cm^{-1}$ ): 3413, 2935, 1714, 1612, 1512, 1444, 1244, 1085, 1033;  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  7.32 (d,  $J$  = 15.7 Hz, 1H), 7.25 (d,  $J$  = 8.4 Hz, 2H), 6.88 (d,  $J$  = 8.5 Hz, 2H), 5.91 (t,  $J$  = 7.3 Hz, 1H), 5.80 (d,  $J$  = 15.7 Hz, 1H), 4.44 (s, 2H), 4.20 (q,  $J$  = 7.1 Hz, 2H), 3.80 (s, 3H), 3.50 (t,  $J$  = 6.8 Hz, 2H), 2.50 (q,  $J$  = 6.9 Hz, 2H), 1.78 (d,  $J$  = 1.6 Hz, 3H), 1.29 (t,  $J$  = 7.1 Hz, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 500 MHz):  $\delta$  167.5, 159.2, 149.2, 137.8, 134.2, 130.3, 129.3 (2C), 116.0, 113.8 (2C), 72.7, 68.7, 60.2, 55.3, 29.5, 14.3, 12.3. HRMS (MALDI-TOF/CCA) calculated for  $[C_{18}H_{24}O_4 + H]^+$ : 305.1747, Found: 305.1744.

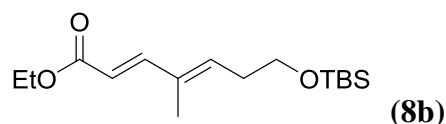
**(2E,4E)-ethyl 7-hydroxy)-4-methylhepta-2,4-dienoate (2h)**



To 0.55 ml of  $CH_2Cl_2$ - $H_2O$  (10:1 (v/v)) solution, dienoate **8a** (25.0 mg, 0.082 mmol) was added and stirred at room temperature for 10 min, then 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (28.0 mg, 0.123 mmol) was added and the resulting solution was allowed to stir for 3 h at room temperature, during which time it turned dark green, brown, dark pink and ultimately, pink. The reaction mixture was extracted with  $Et_2O$ , and was then washed with saturated aqueous

solution of NaHCO<sub>3</sub>, brine. The combined organic fraction was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to afford crude product. The crude was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the deprotected dienoate **2h** (13.3 mg, 88% yield) as a colorless liquid. *R*<sub>f</sub> = 0.282 (2:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3546, 3454, 3372, 2922, 2909, 1733, 1168; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.32 (d, *J* = 15.7 Hz, 1H), 5.91 (t, *J* = 7.4 Hz, 1H), 5.81 (d, *J* = 15.7 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.72 (t, *J* = 6.5 Hz, 2H), 2.48 (q, *J* = 6.8 Hz, 2H), 1.87 (s, 1H), 1.80 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz): δ 167.6, 149.2, 137.3, 135.2, 116.4, 61.9, 60.4, 32.4, 14.4, 12.5. HRMS (MALDI-TOF/CCA) calculated for [C<sub>10</sub>H<sub>16</sub>O<sub>3</sub> + H]<sup>+</sup>: 185.1172, Found: 185.1171.

**(2*E*,4*E*)-ethyl 7-(*tert*-butyldimethylsilyloxy)-4-methylhepta-2,4-dienoate (8b)<sup>5</sup>**

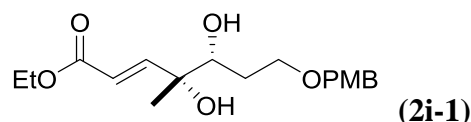


To a solution of previous deprotected dienoate **2h** (30.0 mg, 0.16 mmol) in dry DMF (1.0 mL), imidazole (33.3 mg, 0.48 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 30 min. Then *tert*-Butyldimethylsilyl chloride (49.1 mg, 0.32 mmol) was added into the above solution and stirred for 10 h at room temperature. The reaction mixture was quenched by H<sub>2</sub>O, extracted by Et<sub>2</sub>O, and was then washed with brine. The combined organic fraction was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to afford the yellow liquid crude product. The crude was purified by column chromatography (silica gel, 249:1 (v/v) hexane/EtOAc) to afford the TBS-protected dienoate **8b** (40.3 mg, 83% yield) as a colorless liquid. *R*<sub>f</sub> = 0.430 (40:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2928, 2857, 1698; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 7.31 (d, *J* = 15.7 Hz, 1H), 5.91 (t, *J* = 7.3 Hz, 1H), 5.80 (d, *J* = 15.7 Hz, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.67 (t, *J* = 6.7 Hz, 2H), 2.42 (q, *J* = 6.8 Hz, 2H), 1.78 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.04

<sup>5</sup> Spectral data matched which was previously reported, see: Clarke, P. A.; Davie, R. L.; Peace, S. Synthesis of the B-ring of FR182877. Investigation of the reactions of 6-fumaryl 1,3,8-nonatrienes. *Tetrahedron*, **2005**, *61*, 2335.

(s, 6H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  167.7, 149.5, 138.2, 134.4, 116.0, 62.2, 60.3, 32.7, 26.0 (3C), 18.4, 14.5, 12.5, -5.2 (2C). HRMS (MALDI-TOF/CCA) calculated for  $[\text{C}_{16}\text{H}_{30}\text{O}_3\text{Si} + \text{H}]^+$ : 299.2037, Found: 299.2035.

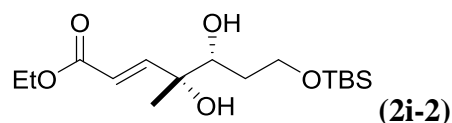
**(*E*,4*R*,5*R*)-ethyl-7-(4-methoxybenzyloxy)-4,5-dihydroxy-4-methylhept-2-enoate**  
**(2i-1)**



To a 250 mL round bottom flask was added 1:1 *t*-butyl alcohol (30 mL)/ $\text{H}_2\text{O}$  (30 mL),  $\text{K}_3\text{Fe}(\text{CN})_6$  (9.81 g, 30.0 mmol),  $\text{K}_2\text{CO}_3$  (4.14 g, 30.0 mmol),  $\text{KHCO}_3$  (3.01 g, 30.0 mmol),  $\text{CH}_3\text{SO}_2\text{NH}_2$  (0.95 g, 10.0 mmol),  $(\text{DHQD})_2\text{-PHAL}$  (401 mg, 0.5 mmol, 2 mol %) and  $\text{OsO}_4$  (51 mg, 0.2 mmol, 1 mol %). The mixture was stirred at room temperature for 15 min and then cooled to 0 °C. To this solution was added solution of dienoate **8a** (3.00 g, 16.8 mmol) in 2 mL of  $\text{CH}_2\text{Cl}_2$  dropwise and the reaction was stirred vigorously at 0 °C overnight. Saturated aqueous solution of  $\text{Na}_2\text{SO}_3$  was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **2i-1** (2.74 g, 81% yield).  $R_f = 0.20$  (7:3 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 3510, 2989, 1736;  $[\alpha]_D^{25} -6^\circ$  ( $c$  2.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.22 (d,  $J = 8.4$  Hz, 2H), 6.98 (d,  $J = 15.8$  Hz, 1H), 6.86 (d,  $J = 8.4$  Hz, 2H), 6.10 (d,  $J = 15.6$  Hz, 1H), 4.43 (s, 2H), 4.17 (q,  $J = 7.2$  Hz, 2H), 3.78 (s, 3H), 3.74-3.59 (m, 3H), 1.81-1.75 (m, 2H), 1.27 (t,  $J = 7.2$  Hz, 3H), 1.25 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.6, 159.3, 152.1, 129.4 (2C), 120.2, 113.8 (2C), 76.6, 74.7, 73.0, 68.7, 60.4, 55.2, 30.2, 22.8, 14.2; HRMS (CI) calcd for  $[\text{C}_{18}\text{H}_{26}\text{O}_6 + \text{Na}]^+$ : 361.1627, Found: 361.1621.

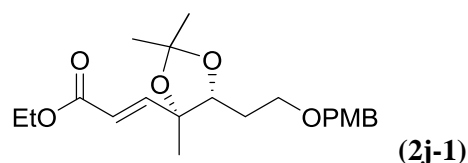
**(*E*,4*R*,5*R*)-ethyl-4,5-dihydroxy-7-*tert*-butyldimethylsilyl-4-methylhept-2-enoate**

**(2i-2)**



To a 250 mL round bottom flask was added 1:1 *t*-butyl alcohol (50 mL)/H<sub>2</sub>O (50 mL), K<sub>3</sub>Fe(CN)<sub>6</sub> (16.5 g, 50.3 mmol), K<sub>2</sub>CO<sub>3</sub> (6.94 g, 50.3 mmol), KHCO<sub>3</sub> (5.08 g, 50.3 mmol), CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (1.59 g, 16.8 mmol), (DHQD)<sub>2</sub>-PHAL (270 mg, 0.34 mmol, 2 mol %) and OsO<sub>4</sub> (43 mg, 0.17 mmol, 1 mol %). The mixture was stirred at room temperature for 15 min and then cooled to 0 °C. To this solution was added enoate **8b** (5.01 g, 16.8 mmol) dropwise and the reaction was stirred vigorously at 0 °C overnight. Saturated aqueous solution of Na<sub>2</sub>SO<sub>3</sub> was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **2i-2** (4.57 g, 82% yield). *R*<sub>f</sub> = 0.25 (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3430, 2980, 1758; [α]<sub>D</sub><sup>25</sup> -11° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 6.99 (d, *J* = 15.6 Hz, 1H), 6.11 (d, *J* = 15.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.95-3.72 (m, 4H), 2.94 (bs, 1H), 1.74-1.67 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 3H), 0.87 (s, 9H), 0.06 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 166.6, 152.3, 120.2, 77.2, 74.6, 62.6, 60.3, 32.1, 25.8 (3C), 26.8, 18.0, 14.2, -5.64 (2C); HRMS (CI) calcd for [C<sub>16</sub>H<sub>32</sub>O<sub>6</sub>Si + Na]<sup>+</sup>: 371.1806, Found: 371.1861.

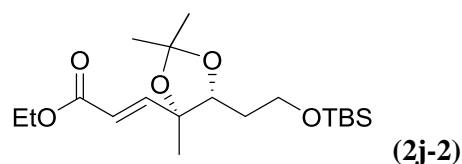
**(*E*)-ethyl-3-((4*R*,5*R*)-5-(2-(4-methoxybenzyloxy)ethyl-2,2,4-trimethyl-1,3-dioxolane-4-yl)acrylate (2j-1)**



To a solution of diol **2i-1** (3.38 g, 10.0 mmol) in 30 mL acetone was added

2,2-dimethoxypropane (10.42 g, 100.0 mmol) and CSA (223 mg, 1.0 mmol) at room temperature. In an hour, the reaction was quenched by adding saturated solution of NaHCO<sub>3</sub> and the mixture was filtered through a pad of celite. The aqueous layer was separated and extracted with Et<sub>2</sub>O. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, (9:1 (v/v) hexane/EtOAc) to afford compound **2j-1** (3.48 g, 92% yield) as a colorless oil. *R<sub>f</sub>* = 0.25 (9:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2990, 1728; [α]<sup>25</sup><sub>D</sub> -15° (*c* 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 15.8 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.44 (s, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.95 (dd, *J* = 8.9, 3.9 Hz, 1H), 3.80 (s, 3H), 3.64-3.49 (m, 2H), 1.93-1.72 (m, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 166.4, 159.1, 149.4, 130.2, 129.2 (2C), 120.3, 113.7 (2C), 108.0, 81.6, 78.8, 72.7, 67.0, 60.5, 55.2, 29.5, 28.3, 26.3, 20.8, 14.2; HRMS (CI) calcd for [C<sub>21</sub>H<sub>30</sub>O<sub>6</sub> + Na]<sup>+</sup>: 401.1934, Found: 401.1940.

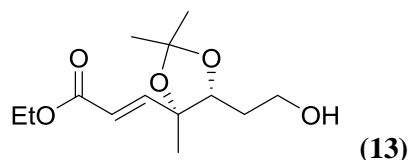
**(*E*)-ethyl-3-((4*R*,5*R*)-5-(2-*tert*-butyldimethylsilylethyl-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (**2j-2**)**



To a solution of diol **2i-2** (2.20 g, 6.62 mmol) in 25 mL acetone was added 2,2-dimethoxypropane (13.80 g, 132.5 mmol) and CSA (0.15 g, 0.66 mmol) at room temperature. In an hour, the reaction was quenched by adding saturated aqueous solution of NaHCO<sub>3</sub> and the mixture was filtered through a pad of celite. The aqueous layer was separated and extracted with Et<sub>2</sub>O. The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford compound **2j-2** (2.17 g, 88% yield) as a colorless oil. *R<sub>f</sub>* = 0.60 (4:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2980, 1710; [α]<sup>25</sup><sub>D</sub> -14° (*c* 1.0,

CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 6.89 (d, *J* = 15.8 Hz, 1H), 6.04 (d, *J* = 15.8 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.96 (dd, *J* = 8.9, 3.7 Hz, 1H), 3.81-3.65 (m, 2H), 1.83-1.68 (m, 2H), 1.46 (s, 3H), 1.36 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 166.4, 149.5, 120.3, 107.9, 81.5, 78.3, 60.5, 60.1, 32.2, 28.3, 26.3, 25.9 (3C), 20.9, 18.3, 14.2, -5.4, -5.4; HRMS (CI) calcd for [C<sub>19</sub>H<sub>36</sub>O<sub>5</sub>Si + Na]<sup>+</sup>: 395.2224, Found: 395.2229.

**(*E*)-ethyl-3-((4*R*,5*R*)-5-(2-hydroxyethyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate**  
**(13)**

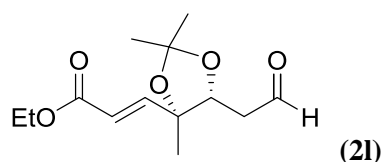


To a 10 mL round bottom flask was added 2.75 ml of 10:1 CH<sub>2</sub>Cl<sub>2</sub> (2.50 mL)/H<sub>2</sub>O (0.25 mL) and ether **2j-1** (155.2 mg, 0.41 mmol) at room temperature and stirred for 10 min, then 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (140.3 mg, 0.62 mmol) was added and the resulting solution was stirred at room temperature for 3 h. The reaction mixture was extracted by Et<sub>2</sub>O. The combined organic phases were washed with saturated aqueous solution of NaHCO<sub>3</sub>, brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford crude product. The crude was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford compound **13** (93.2 mg, 88% yield) as a colorless liquid. Similarly, to a solution of silyl ether **2j-2** (2.45 g, 6.58 mmol) in 20 mL THF was added TBAF (9.87 mL, 9.87 mmol) at 0 °C. In two hour, the reaction was quenched by adding saturated aqueous solution of NH<sub>4</sub>Cl. The aqueous layer was separated, extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **13** (1.61 g, 95% yield) as a colorless oil. *R<sub>f</sub>* = 0.30 (4:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3498, 2980, 1720; [α]<sub>D</sub><sup>25</sup> -25° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 6.89 (d, *J* = 15.6 Hz, 1H), 6.10 (d, *J* = 15.6 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.95 (dd, *J* = 10.1, 2.7 Hz, 1H),

3.79 (dd,  $J = 6.4, 5.2$  Hz, 2H), 2.22 (bs, 1H), 1.91-1.65 (m, 2H), 1.46 (s, 3H), 1.37 (s, 3H), 1.28 (t,  $J = 7.2$  Hz, 3H), 1.22 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.7, 149.1, 120.5, 108.5, 81.8, 80.5, 60.9, 60.6, 31.4, 28.3, 26.4, 20.9, 14.2; HRMS (CI) calcd for  $[\text{C}_{13}\text{H}_{22}\text{O}_5 + \text{Na}]^+$ : 281.1359, Found: 281.1368.

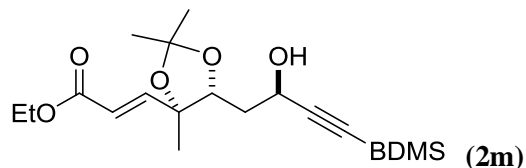
**(E)-ethyl-3-((4R,5R)-5-(formylethyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate**

**(2l)**



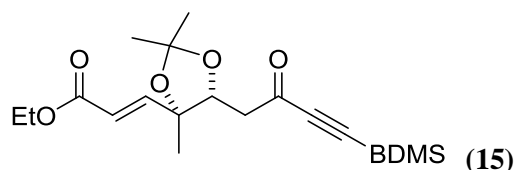
To a solution of oxalyl chloride (0.98 g, 7.7 mmol) in 30 mL of  $\text{CH}_2\text{Cl}_2$  was added DMSO (0.69 g, 8.85 mmol) at  $-78$  °C. After stirring for 30 min, alcohol **13** (1.52 g, 5.9 mmol) in 5 mL of  $\text{CH}_2\text{Cl}_2$  was added dropwise. The mixture was stirred for another 90 min, and then  $\text{Et}_3\text{N}$  (1.98 g, 19.5 mmol) was added. In 2 h, the reaction was quenched with saturated aqueous solution of  $\text{NaHCO}_3$ , and the reaction mixture was extracted with  $\text{EtOAc}$ . The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 4:1 (v/v) hexane/ $\text{EtOAc}$ ) to afford compound **2l** (1.14 g, 76% yield) as a colorless oil.  $R_f = 0.51$  (1:1 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 2986, 1720;  $[\alpha]_D^{25} -26^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  9.78 (t,  $J = 2.0$  Hz, 1H), 6.87 (d,  $J = 15.6$  Hz, 1H), 6.11 (d,  $J = 15.6$  Hz, 1H), 4.31 (dd,  $J = 9.4, 3.5$  Hz, 1H), 4.19 (q,  $J = 7.2$  Hz, 2H), 2.74 (ddd,  $J = 16.8, 9.4, 2.2$  Hz, 1H), 2.52 (ddd,  $J = 16.6, 3.5, 1.5$  Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H), 1.29 (t,  $J = 7.2$  Hz, 3H), 1.21 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  198.9, 166.2, 148.4, 121.0, 108.9, 81.3, 76.2, 60.6, 43.2, 28.1, 26.3, 21.0, 14.2; HRMS (CI) calcd for  $[\text{C}_{13}\text{H}_{20}\text{O}_5\text{Si} + \text{Na}]^+$ : 279.1203, Found: 279.1205.

**(E)-ethyl-3-((4R,5R)-5-((R)-4-(benzyltrimethylsilyl)-2-hydroxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (2m)**



To a solution of benzyldimethylsilane **14** (0.13 g, 0.75 mmol) in 4 mL of THF was added *n*-BuLi (0.31 mL, 0.75 mmol) at  $-78\text{ }^{\circ}\text{C}$ , and the reaction was stirred for 0.5 h. Then a solution of aldehyde **2l** (0.18 g, 0.68 mmol) in 1 mL THF was added into the above mixture at  $-78\text{ }^{\circ}\text{C}$ . After stirring for 2 h, the reaction was quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . The aqueous layer was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated to afford the crude product. The crude product was purified by column chromatography (silica gel, 7:3 (v/v) hexane/EtOAc) to afford compound **2m** and its enantiomer (0.14 g, 82% yield) as a yellow oil.  $R_f = 0.35$  (7:3 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 3432, 2986, 1718;  $[\alpha]_D^{25} -15^{\circ}$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.23-7.17 (m, 2H), 7.10-7.03 (m, 3H), 6.88 (d,  $J = 15.8$  Hz, 1H), 6.10 (d,  $J = 15.6$  Hz, 1H), 4.56 (bs, 1H), 4.19 (q,  $J = 7.2$  Hz, 2H), 2.74 (d,  $J = 7.2$  Hz, 1H), 2.15 (s, 2H), 1.95 (ddd,  $J = 17.3, 10.6, 3.2$  Hz, 1H), 1.77 (ddd,  $J = 14.1, 7.4, 2.2$  Hz, 1H), 1.46 (s, 3H), 1.36 (s, 3H), 1.27 (t,  $J = 7.2$  Hz, 3H), 1.23 (s, 3H), 0.11 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.3, 148.8, 138.7, 128.3 (2C), 128.1 (2C), 124.4, 120.6, 108.6, 107.0, 88.1, 81.5, 78.1, 60.5, 60.3, 36.0, 28.2, 26.3, 26.0, 21.1, 14.2,  $-2.3$  (2C); HRMS (CI) calcd for  $[\text{C}_{24}\text{H}_{34}\text{O}_5\text{Si} + \text{Na}]^+$ : 453.2073, Found: 453.2067.

**(E)-ethyl-3-((4R,5R)-5-(4-(benzyltrimethylsilyl)-2-oxobut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (15)**

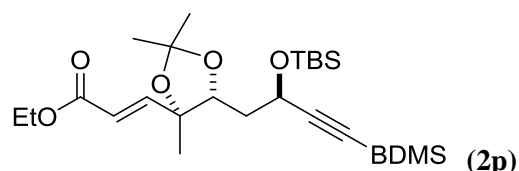


To a mixture alcohol **2m** and its enantiomer (105 mg, 0.25 mmol) in 2 mL of  $\text{CH}_2\text{Cl}_2$  was added  $\text{MnO}_2$  (213 mg, 2.45 mmol) at room temperature. In 24 h, the reaction



mixture was filtered through a pad of celite and washed with EtOAc. The organic phases were washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford ketone **15** (80 mg, 76% yield) as a colorless oil.  $R_f = 0.45$  (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2989, 1680;  $[\alpha]_D^{25} -15^\circ$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  7.24-7.21 (m, 2H), 7.14-7.04 (m, 3H), 6.89 (d, *J* = 15.6 Hz, 1H), 6.12 (d, *J* = 15.6 Hz, 1H), 4.38 (dd, *J* = 9.2, 3.7 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.87 (dd, *J* = 16.6, 9.2 Hz, 1H), 2.64 (dd, *J* = 16.8, 4.0 Hz, 1H), 2.26 (s, 2H), 1.46 (s, 3H), 1.38 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 3H), 0.21 (s, 3H), 0.20 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):  $\delta$  183.1, 166.2, 148.6, 137.7, 128.4 (2C), 128.3 (2C), 124.8, 120.9, 102.4, 98.1, 81.2, 76.8, 60.6, 44.7, 28.2, 26.2, 25.2, 21.1, 14.2, -2.8, -2.9; HRMS (CI) calcd for [C<sub>24</sub>H<sub>32</sub>O<sub>5</sub>Si + Na]<sup>+</sup>: 451.1911, Found: 451.1928.

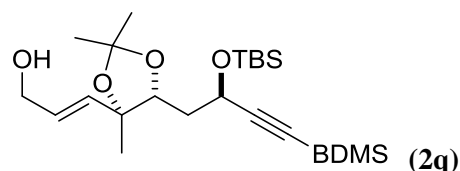
**(E)-ethyl-3-((4*R*,5*R*)-5-((*R*)-4-(benzyltrimethylsilyl)-2-*tert*-butyldimethylsilyloxy-but-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (**2p**)**



To a solution of **2m** (220 mg, 0.51 mmol) in dry DMF (5.0 mL), imidazole (104.2 mg, 1.53 mmol) was added in one portion, and the reaction mixture was allowed to stir at room temperature for 30 min. Then *tert*-butyldimethylsilyl chloride (153.7 mg, 1.02 mmol) was added into the above solution and stirred for 3 h at room temperature. The reaction mixture was quenched by H<sub>2</sub>O, extracted by Et<sub>2</sub>O, and was then washed with brine. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to afford the crude product. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **2p** (213 mg, 89% yield) as a colorless oil.  $R_f = 0.32$  (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2986, 1752;  $[\alpha]_D^{25} +62^\circ$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 270 MHz):  $\delta$  7.26-7.19 (m, 2H), 7.11-7.05 (m, 3H), 6.90 (d,  $J = 15.6$  Hz, 1H), 6.08 (d,  $J = 15.6$  Hz, 1H), 4.54-4.49 (m, 1H), 4.20 (q,  $J = 7.2$  Hz, 2H), 4.04-3.99 (m, 1H), 2.19 (s, 2H), 1.83 (ddd,  $J = 7.9, 4.5, 4.5$  Hz, 2H), 1.46 (s, 3H), 1.34 (s, 3H), 1.29 (t,  $J = 7.2$  Hz, 3H), 1.22 (s, 3H), 0.89 (s, 9H) 0.11 (s, 6H), 0.09 (s, 3H), 0.06 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):  $\delta$  166.3, 149.1, 138.1, 128.3 (2C), 128.1 (2C), 124.3, 120.4, 108.5, 108.2, 81.3, 77.2, 60.5, 60.1, 38.2, 28.3, 26.4, 26.0, 25.7 (3C), 21.1, 18.2, 14.2, -2.3 (2C), -4.6, -5.1; HRMS (CI) calcd for [C<sub>30</sub>H<sub>48</sub>O<sub>5</sub>Si<sub>2</sub> + Na]<sup>+</sup>: 567.2932, Found: 567.2934.

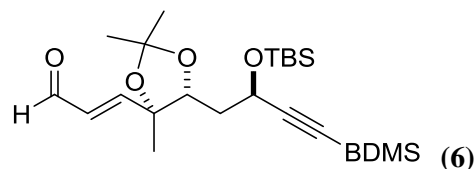
**(*R*)-4-(benzyltrimethylsilyl)-1-((4*R*,5*R*)-5-((*E*)-3-tert-butyltrimethylsilyloxyprop-1-en-2-yl)-2,2,5-trimethyl-1,3-dioxolan-4-yl)but-3-yn-2-ol (2q)**



To a solution of ester **2p** (380 mg, 0.70 mmol) in 3 mL of THF was added DIBAL-H (1.61 mL, 1.0 M in hexanes, 1.61 mmol) dropwise at  $-78$  °C. In 1 h, the reaction was quenched by adding 1 mL of acetone and saturated aqueous solution of sodium potassium tartrate solution (Rochelle's salt, 10 mL), warmed to room temperature, diluted with ether and stirred for 1 h. The aqueous layer was extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 7:3 (v/v) hexane/EtOAc) to afford the allylic alcohol **2q** (341 mg, 97% yield) as a colorless oil.  $R_f = 0.24$  (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3402, 2989;  $[\alpha]_D^{25} +76^\circ$  ( $c$  1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): 7.24-7.19 (m, 2H), 7.11-7.04 (m, 3H), 5.93 (ddd,  $J = 15.6, 5.2, 5.2$  Hz, 1H), 5.71 (d,  $J = 15.8$  Hz, 1H), 4.54-4.49 (m, 1H), 4.15 (d,  $J = 4.5$  Hz, 2H), 4.01-3.96 (m, 1H), 2.18 (s, 2H), 1.83 (ddd,  $J = 7.9, 3.5, 3.5$  Hz, 2H), 1.45 (s, 3H), 1.34 (s, 3H), 1.21 (s, 3H), 0.90 (s, 9H) 0.13 (s, 3H), 0.11 (s, 6H), 0.10 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):  $\delta$  138.8, 133.7, 129.7, 128.3 (2C), 128.1 (2C), 124.3, 108.7, 107.6, 81.3, 77.9, 63.1,

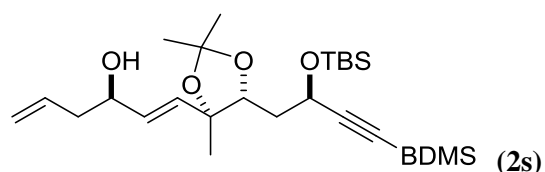
60.2, 38.0, 28.4, 26.7, 26.0, 25.8 (3C), 20.9, 18.2, -2.3 (2C), -4.6, -5.1; HRMS (CI) calcd for [C<sub>28</sub>H<sub>46</sub>O<sub>4</sub>Si<sub>2</sub> + Na]<sup>+</sup>: 525.2827, Found: 525.2835.

**(E)-3-((4R,5R)-5-((R)-4-(benzyltrimethylsilyl)-2-*tert*-butyldimethylsilyloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylaldehyde (6)**



To a solution of alcohol **2q** (336 mg, 0.69 mmol) in 3 mL of CH<sub>2</sub>Cl<sub>2</sub> was added MnO<sub>2</sub> (0.6 g, 6.9 mmol) at room temperature. In 8 h, the reaction mixture was filtered through a pad of celite. The filtrate was concentrated to afford the crude product. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford compound **6** (307 mg, 89% yield) as a colorless oil. R<sub>f</sub> = 0.58 (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2986, 1758; [α]<sup>25</sup><sub>D</sub> +84° (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 9.56 (d, *J* = 7.7 Hz, 1H), 7.24-7.19 (m, 2H), 7.11-7.05 (m, 3H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.35 (dd, *J* = 15.6, 7.9 Hz, 1H), 4.52 (dd, *J* = 10.1, 3.0 Hz, 1H), 4.05 (dd, *J* = 9.9, 2.5 Hz, 1H), 2.19 (s, 2H), 1.85-1.75 (m, 2H), 1.48 (s, 3H), 1.35 (s, 3H), 1.27 (s, 3H), 0.89 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 193.2, 157.7, 138.7, 130.7, 128.3 (2C), 128.1 (2C), 124.3, 108.4, 108.2, 87.3, 81.3, 77.1, 60.0, 38.2, 28.2, 26.2, 25.9, 25.6 (3C), 20.8, 18.1, -2.3, -2.3, -4.6, -5.1; HRMS (CI) calcd for [C<sub>28</sub>H<sub>44</sub>O<sub>4</sub>Si<sub>2</sub> + Na]<sup>+</sup>: 523.2670, Found: 523.2665.

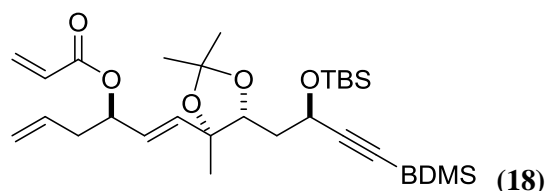
**(R,E)-1-((4R,5R)-5-((R)-4-(benzyltrimethylsilyl)-2-*tert*-butyldimethylsilyloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)hexa-1,5-dien-3-ol (2s)**



To a solution of (*R,R*)-**17** (983 mg, 1.78 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added a

solution of aldehyde **6** (297 mg, 0.60 mmol) in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> dropwise at -10 °C. The reaction flask was stirred at -10 °C for 48 h, was then diluted with EtOAc and quenched by adding 1 M NaHSO<sub>4</sub>. The mixture was vigorously stirred at room temperature for 30 min, and filtered through a pad of celite. The filtrate was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford compound **2s** (283 mg, 88% yield) as a light yellow oil. R<sub>f</sub> = 0.32 (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3630, 2932; [α]<sup>25</sup><sub>D</sub> +55° (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.22-7.20 (m, 2H), 7.10-7.06 (m, 3H), 5.81 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.82-5.76 (m, 1H), 5.70 (d, *J* = 15.6 Hz, 1H), 5.15 (d, *J* = 6.0 Hz, 1H), 5.12 (s, 1H), 4.52 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.19 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.97 (dd, *J* = 9.6, 2.4 Hz, 1H), 2.33 (ddd, *J* = 13.2, 6.6, 6.6 Hz, 1H), 2.28 (ddd, *J* = 13.8, 7.2, 6.6 Hz, 1H), 2.19 (s, 2H), 1.83-1.74 (m, 2H), 1.45 (s, 3H), 1.34 (s, 3H), 1.20 (s, 3H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 138.9, 134.0, 133.4, 132.3, 128.4 (2C), 128.2 (2C), 124.3, 118.3, 108.8, 107.6, 87.1, 81.3, 78.0, 71.1, 60.2, 41.8, 38.1, 28.4, 26.6, 26.1, 25.8 (3C), 21.1, 18.2, -2.3, -2.3, -4.6, -5.1; HRMS (CI) calcd for [C<sub>31</sub>H<sub>50</sub>O<sub>4</sub>Si<sub>2</sub> + Na]<sup>+</sup>: 565.3140, Found: 565.3132.

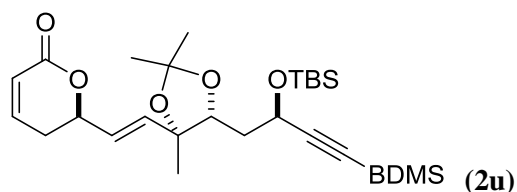
**(*R,E*)-1-((4*R*,5*R*)-5-((*R*)-4-(benzyltrimethylsilyl)-2-*tert*-butyldimethylsilyloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)hexa-1,5-dien-3-ylacrylate (**18**)**



To a solution of alcohol **2s** (317 mg, 0.59 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added acrylic acid (127 mg, 1.76 mmol), DCC (362 mg, 1.76 mmol) and catalytic amount of DMAP (5 mg, 7 mmol %). In 5 h, the reaction mixture was diluted with Et<sub>2</sub>O and filtered through a pad of celite and washed with Et<sub>2</sub>O. The organic phase was washed with saturated aqueous solution of NaHSO<sub>4</sub>, saturated aqueous solution of NaHCO<sub>3</sub>, brine

and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic phase was then concentrated under reduced pressure to afford the crude product. The crude was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to provide the ester **18** (274 mg, 78% yield) as a colorless oil. R<sub>f</sub> = 0.71 (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2987, 1727; [α]<sub>D</sub><sup>25</sup> +50° (c 0.7, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.22-7.20 (m, 2H), 7.10-7.06 (m, 3H), 6.39 (dd, *J* = 17.4, 1.2 Hz, 1H), 6.10 (dd, *J* = 17.4, 10.2 Hz, 1H), 5.81 (dd, *J* = 10.2, 1.2 Hz, 1H), 5.79 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.76-5.69 (m, 1H), 5.75 (s, 1H), 5.41 (dd, *J* = 6.6, 6.0 Hz, 1H), 5.10 (dd, *J* = 3.0, 1.2 Hz, 1H), 5.08-5.06 (m, 1H), 5.51 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.96 (dd, *J* = 10.2, 2.4 Hz, 1H), 2.42 (ddd, *J* = 6.9, 6.9, 1.2 Hz, 1H), 2.19 (s, 2H), 1.82-1.72 (m, 2H), 1.45 (s, 3H), 1.33 (s, 3H), 1.17 (s, 3H), 0.90 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H), 0.10 (s, 3H), 0.10 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 165.2, 138.9, 135.7, 132.9, 130.6, 128.7, 128.4 (2C), 128.2 (2C), 127.4, 124.4, 118.1, 108.7, 107.6, 87.0, 81.3, 78.0, 73.1, 60.2, 39.1, 38.3, 34.9, 28.4, 26.5, 26.1, 25.8 (3C), 21.4, 18.2, -2.2, -2.3, -4.6, -5.1; HRMS (CI) calcd for [C<sub>34</sub>H<sub>52</sub>O<sub>5</sub>Si<sub>2</sub>+ Na]<sup>+</sup>: 619.3245, Found: 619.3234.

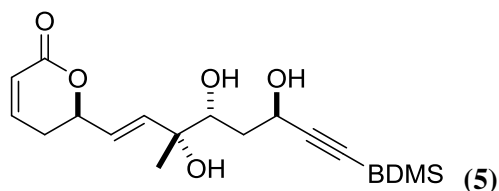
**(*R*)-6-((*E*)-2-((4*R*,5*R*)-5-((*R*)-4-(benzyltrimethylsilyl)-2-*tert*-butyldimethylsilyloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)vinyl-5,6-dihydropyran-2-one (**2u**)**



To a solution of triene **18** (177 mg, 0.30 mmol) in 15 mL CH<sub>2</sub>Cl<sub>2</sub> was added Grubbs catalyst **19** (25 mg, 10 mmol %) in 15 mL CH<sub>2</sub>Cl<sub>2</sub>. The reaction was refluxed for 2 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 7:3 (v/v) hexane/EtOAc) to afford the lactone **2u** (142 mg, 87% yield) as a colorless oil. R<sub>f</sub> = 0.16 (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2930, 1731; [α]<sub>D</sub><sup>25</sup> +137° (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.22-7.20 (m, 2H), 7.10-7.06 (m, 3H), 6.88-6.85 (m, 1H), 6.05 (d, *J* = 9.6 Hz, 1H), 5.91 (dd, *J* = 15.6, 5.4 Hz, 1H), 5.84 (dd, *J* = 15.6 Hz, 1H), 4.94 (ddd, *J* = 10.2, 5.4, 4.8 Hz, 1H),

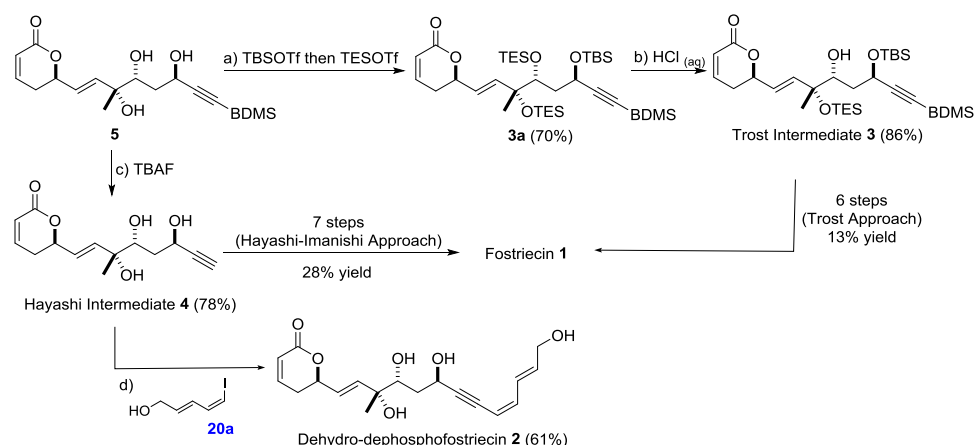
4.51 (dd,  $J = 9.0, 2.4$  Hz, 1H), 3.97 (dd,  $J = 9.6, 2.4$  Hz, 1H), 2.44-2.41 (m, 2H), 2.19 (s, 2H), 1.82-1.75 (m, 2H), 1.45 (s, 3H), 1.33 (s, 3H), 1.20 (s, 3H), 0.90 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  163.7, 144.4, 138.9, 130.6, 128.7, 128.4 (2C), 128.2 (2C), 126.8, 124.4, 121.7, 109.8, 107.8, 81.2, 77.9, 77.1, 60.1, 38.1, 29.8, 28.4, 26.6, 26.1, 25.8 (3C), 21.0, 18.2, -2.2, -2.3, -4.5, -5.1; HRMS (CI) calcd for  $[\text{C}_{32}\text{H}_{48}\text{O}_5\text{Si}_2 + \text{Na}]^+$ : 591.2932, Found: 591.2930.

**(*R*)-6-((*E*,3*R*,4*R*,5*R*)-8-(benzyltrimethylsilyl)-3,4,6-trihydroxy-3-methyloct-1-en-7-ynyl)-5,6-dihydropyran-2-one (5)**

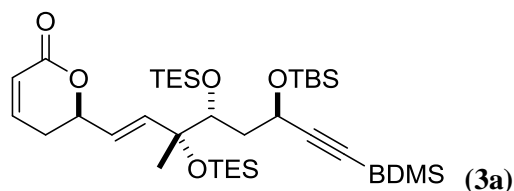


To a 10 mL round bottom flask was added acetonide **2u** (53 mg, 0.093 mmol) and 10 mol % aqueous solution of 1:1 HCl (0.7 mL)/THF (0.7 mL). The mixture was stirred at 65 °C for 0.5 h, then cooled down to room temperature and quenched by saturated aqueous solution of  $\text{NaHCO}_3$ . The solution was extracted with  $\text{Et}_2\text{O}$ , and combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:4 (v/v) hexane/ $\text{EtOAc}$ ) to provide the pyranone **5** (27 mg, 70% yield) as a colorless oil.  $R_f = 0.31$  (2:8 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 3407, 2981, 1742;  $[\alpha]_D^{25} +66^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.24-7.21 (m, 2H), 7.11-7.06 (m, 3H), 6.88 (ddd,  $J = 9.0, 6.0, 3.0$  Hz, 1H), 6.05 (dd,  $J = 9.6, 2.4$  Hz, 1H), 5.97-5.94 (m, 2H), 4.97 (ddd,  $J = 10.2, 4.8, 4.2$  Hz, 1H), 4.60 (dd,  $J = 4.8, 4.2$  Hz, 1H), 3.69 (d,  $J = 9.6$  Hz, 1H), 3.13 (d,  $J = 2.4$  Hz, 1H), 2.76 (s, 1H), 2.46 (dddd,  $J = 18.6, 14.4, 5.4, 4.8$  Hz, 2H), 2.21 (s, 2H), 1.93-1.80 (m, 2H), 1.28 (s, 3H), 0.14 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  164.1, 145.0, 138.8, 137.9, 128.3 (2C), 128.2 (2C), 126.6, 124.4, 121.4, 107.5, 88.3, 77.3, 74.5, 74.0, 60.8, 37.1, 29.8, 26.0, 22.4, -2.2 (2C); HRMS (CI) calcd for  $[\text{C}_{23}\text{H}_{30}\text{O}_5\text{Si} + \text{Na}]^+$ : 437.1755, Found: 437.1756.

### Intermediates related to Scheme 3:



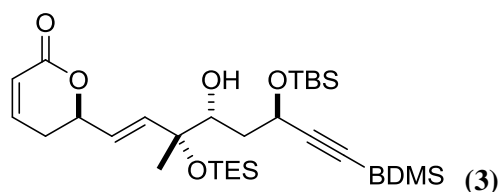
### (*R*)-6-((*E*,3*R*,4*R*,5*R*)-8-(benzyltrimethylsilyloxy)-3,4-bis(trimethylsilyloxy)-6-*tert*-butyl dimethylsilyloxybut-3-methyloct-1-en-7-ynyl)-5,6-dihydropyran-2-one (**3a**)



To a solution of lactone **5** (22 mg, 0.053 mmol) in 1.0 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 2,6-lutidine (62 μl, 0.53 mmol) at -78 °C and stirred for 10 min. TBSOTf (34.4 mg, 0.13 mmol) was added to the reaction mixture, and monitored by the TLC. After the spot representing for the starting material disappeared, TESOTf (113.7 mg, 0.43 mmol) was added into the reaction. The reaction was stirred at -78 °C for 1 h, was then diluted with CH<sub>2</sub>Cl<sub>2</sub> and quenched by saturated aqueous solution of NaHCO<sub>3</sub>. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:4 (v/v) hexane/EtOAc) to provide compound **3a** (28 mg, 70% yield) as a colorless oil. *R*<sub>f</sub> = 0.88 (3:7 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2956, 1736; [α]<sup>25</sup><sub>D</sub> +38° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 7.22-7.19 (m, 2H), 7.09-7.06 (m, 3H), 6.86 (ddd, *J* = 8.4, 4.8, 3.0 Hz, 1H), 6.05 (ddd, *J* = 10.2, 1.8, 1.8 Hz, 1H), 5.91 (dd, *J* = 16.2, 1.2 Hz, 1H), 5.79 (dd, *J* = 15.6, 6.0 Hz, 1H), 4.97 (ddd, *J* = 9.6, 6.0, 1.2 Hz, 1H), 4.50 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.68 (dd, *J* = 6.0, 5.4 Hz, 1H), 2.47-2.42 (m, 2H), 2.19 (s, 2H), 1.97 (ddd, *J* = 13.2, 7.8, 2.4 Hz, 2H), 1.37 (s, 3H), 0.97 (t, *J* = 8.4 Hz, 18H),

0.89 (s, 9H), 0.67-0.63 (m, 12H), 0.13 (s, 3H), 0.11 (s, 3H), 0.10 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  164.0, 144.4, 138.9, 138.2, 128.3 (2C), 128.2 (2C), 125.9, 124.3, 121.7, 109.5, 87.6, 78.1, 77.9, 76.0, 61.0, 43.6, 30.0, 26.1, 25.9 (3C), 25.7, 18.2, 7.3 (3C), 7.1 (3C), 7.0 (3C), 5.4 (3C), -2.3 (2C), -3.9, -4.4; HRMS (CI) calcd for  $[\text{C}_{41}\text{H}_{72}\text{O}_5\text{Si}_4 + \text{Na}]^+$ : 779.4349, Found: 779.4354.

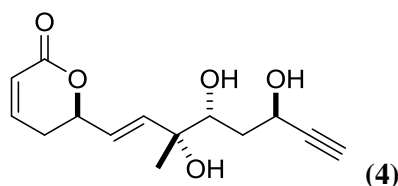
**(R)-6-((E,3R,4R,5R)-8-(benzyltrimethylsilyloxy)-3-trimethylsilyloxy-4-hydroxy-6-tert-butyltrimethylsilyloxybut-3-methyloct-1-en-7-ynyl)-5,6-dihydropyran-2-one (3)**



A solution of silyl ether **3a** (23 mg, 0.03 mmol) in a mixture of 1M HCl/THF/ $\text{CH}_3\text{CN}$  : 1/3/6 was stirred at  $-10\text{ }^\circ\text{C}$ . In 1.5 h, the reaction was then diluted with EtOAc and quenched by saturated aqueous solution of  $\text{NaHCO}_3$ . The reaction mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:9 (v/v) hexane/EtOAc) to provide compound **3** (17 mg, 86% yield) as a colorless oil.  $R_f = 0.51$  (3:7 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 3511, 2957, 1726;  $[\alpha]_D^{25} +54^\circ$  ( $c$  0.8,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.22-7.20 (m, 2H), 7.10-7.05 (m, 3H), 6.88 (ddd,  $J = 9.8, 4.8, 3.0$  Hz, 1H), 6.06 (ddd,  $J = 9.6, 1.8, 1.8$  Hz, 1H), 5.91 (dd,  $J = 16.2, 1.2$  Hz, 1H), 5.82 (dd,  $J = 16.2, 6.0$  Hz, 1H), 4.97 (dddd,  $J = 9.6, 6.0, 6.0, 1.2$  Hz, 1H), 4.66 (dd,  $J = 7.2, 3.0$  Hz, 1H), 3.75 (dd,  $J = 10.8, 1.2$  Hz, 1H), 2.95 (d,  $J = 2.4$  Hz, 1H), 2.46-2.43 (m, 2H), 2.19 (s, 2H), 1.84 (ddd,  $J = 14.4, 7.8, 1.2$  Hz, 1H), 1.51 (ddd,  $J = 14.4, 10.8, 3.6$  Hz, 1H), 1.37 (s, 3H), 0.95 (t,  $J = 8.4$  Hz, 9H), 0.90 (s, 9H), 0.60 (q,  $J = 8.4$  Hz, 6H), 0.13 (s, 3H), 0.12 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  163.9, 144.4, 138.9, 137.7, 128.3 (2C), 128.2 (2C), 126.7, 124.3, 121.7, 108.2, 87.8, 77.5, 76.9, 75.1, 61.7, 38.9, 29.6, 26.1, 25.8 (3C), 22.6, 18.1, 7.1 (3C), 6.75 (3C), -2.3, -2.4, -4.6, -5.2; HRMS (CI) calcd for  $[\text{C}_{35}\text{H}_{58}\text{O}_5\text{Si}_3 + \text{Na}]^+$ : 665.3484, Found: 665.3469.

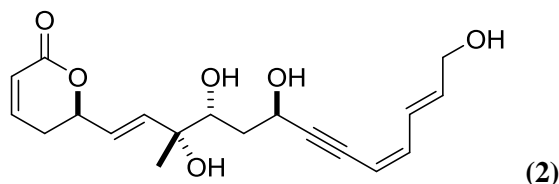


**(R)-5,6-dihydro-6-((E,3R,4R,6R)-3,4,6-trihydroxy-3-methyloct-1-en-7-ynyl)pyran-2-one (4)**



To a solution of lactone **5** (37 mg, 0.089 mmol) in 0.5 mL of THF was added TBAF (0.13 mL, 1.0 M in THF) at 0 °C. After stirring at 0 °C for 2 h, the reaction was quenched by saturated aqueous solution of NaHCO<sub>3</sub>. The reaction mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:9 (v/v) hexane/EtOAc) to provide compound **4** (18 mg, 78% yield) as a colorless oil.  $R_f = 0.21$  (1:9 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3406, 2907, 1739;  $[\alpha]_D^{25} +33^\circ$  (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  6.88 (ddd,  $J = 8.4, 6.0, 3.0$  Hz, 1H), 6.04 (dd,  $J = 9.6, 1.2$  Hz, 1H), 5.96 (d,  $J = 15.6$  Hz, 1H), 5.93 (ddd,  $J = 15.6, 4.8, 4.8$  Hz, 1H), 4.97 (ddd,  $J = 9.6, 4.8, 4.8$  Hz, 1H), 4.68 (bs, 1H), 4.00 (d,  $J = 9.0$  Hz, 1H), 3.4 (d,  $J = 9.6$  Hz, 1H), 2.53-2.41 (m, 3H), 1.91-1.82 (m, 2H), 1.27 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):  $\delta$  164.1, 145.1, 138.6, 126.8, 121.4, 84.4, 77.2, 74.6, 74.2, 73.4, 60.4, 36.8, 29.8, 22.5; HRMS (CI) calcd for [C<sub>14</sub>H<sub>18</sub>O<sub>5</sub> + Na]<sup>+</sup>: 289.1046, Found: 289.1045.

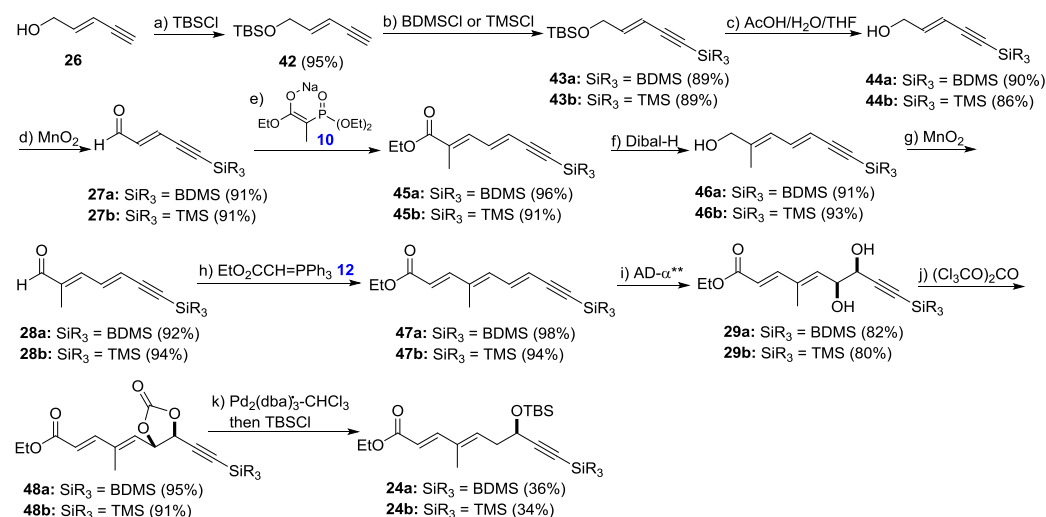
**(R)-5,6-dihydro-6-((1E,3R,4R,6R,9Z,11E)-3,4,6,13-tetrahydroxy-3-methyltrideca-1,9,11-trien-7-ynyl)-pyran-2-one (2)**



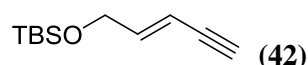
To a solution of vinyl iodide **20a** (27 mg, 0.13 mmol) in 0.5 mL of Et<sub>3</sub>N was added Pd<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (9 mg, 0.013 mmol) and CuI (7 mg, 0.026 mmol) at room temperature. After 10 min, alkyne **4** (17 mg, 0.064 mmol) in 0.5 mL of Et<sub>3</sub>N was added into the reaction and kept stirring at room temperature for 2 h. Then the reaction was diluted

with EtOAc and quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . The reaction mixture was extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated to afford the crude product. The crude was purified by column chromatography (silica gel, 1:9 (v/v) hexane/EtOAc) to provide compound **2** (13 mg, 61% yield) as a colorless oil.  $R_f = 0.35$  (9:1 (v/v)  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ); IR (neat,  $\text{cm}^{-1}$ ): 3486, 2942, 1712;  $[\alpha]_D^{25} +52^\circ$  ( $c$  0.8,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  6.90-6.84 (m, 2H), 6.40 (dd,  $J = 10.8, 10.8$  Hz, 1H), 6.01-5.92 (m, 3H), 5.89 (ddd,  $J = 15.6, 6.0, 6.0$  Hz, 1H), 5.40 (d,  $J = 10.2$  Hz, 1H), 4.97 (dddd,  $J = 9.6, 6.0, 6.0, 1.2$  Hz, 1H), 4.95 (ddd,  $J = 15.6, 10.2, 4.8$  Hz, 1H), 4.80 (d,  $J = 2.4$  Hz, 1H), 4.26 (d,  $J = 2.4$  Hz, 1H), 4.09 (ddd,  $J = 7.2, 3.0, 3.0$  Hz, 1H), 3.53 (ddd,  $J = 7.2, 7.2, 7.2$  Hz, 1H),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  164.4, 145.3, 140.1, 139.6, 137.9, 136.0, 134.3, 126.3, 121.3, 108.3, 95.6, 82.5, 74.8, 62.2, 61.6, 36.2, 29.9, 29.7, 22.4; HRMS (CI) calcd for  $[\text{C}_{19}\text{H}_{24}\text{O}_6 + \text{Na}]^+$ : 371.1465, Found: 371.1458.

### Intermediates related to Scheme 5:



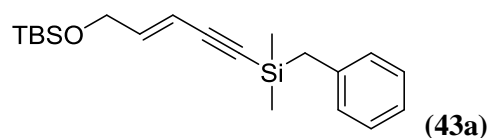
### *(E)*-pent-2-en-4-ynyloxy(*tert*-butyl)dimethylsiane (**42**)



To the solution of 2-penten-4-yn-1-ol **26** (10.0 g, 121.8 mmol) in 100 mL of  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_3\text{N}$  (30.8 g, 304.5 mmol), TBSCl (23.8 g, 158.4 mmol) and DMAP (0.73 g, 6.1 mmol)

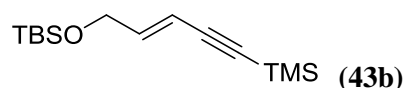
were added at room temperature. The reaction mixture was stirred at room temperature for 15 h, and quenched with saturated aqueous solution of NaHCO<sub>3</sub>. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the combined organic solution was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the TBS protecting alkyne **42** (22.7g, 95% yield) as a viscous oil. R<sub>f</sub> = 0.59 (9:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2955, 1740, 1463; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 6.30 (ddd, *J* = 15.8, 4.0, 4.0 Hz, 1H), 5.75 (dddd, *J* = 15.8, 2.2, 2.2, 2.2 Hz, 1H), 4.23 (dd, *J* = 3.7, 2.5 Hz, 2H), 2.87 (d, *J* = 1.7 Hz, 1H), 0.91 (s, 9H), 0.69 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 144.3, 107.5, 82.1, 77.3, 62.7, 25.8 (3C), 18.3, -5.4 (2C); HRMS (CI) calcd for [C<sub>11</sub>H<sub>20</sub>OSi + Na]<sup>+</sup>: 219.1175, Found: 219.1181.

**(*E*)- 5-(benzyltrimethylsilyl)pent-2-en-4-ynoxy)(*tert*-butyl)dimethylsiane (43a)**



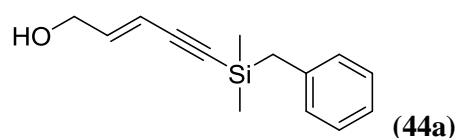
To a solution of alkyne **42** (5.0 g, 25.5 mmol) in 60 mL of THF flask was added *n*-BuLi (1.7 g, 26.8 mmol) at -78 °C. BDMSCl (5.0 g, 27.6 mmol) was dissolved in 5 mL of THF and then added dropwise into the previous solution. The reaction mixture was stirred at -78 °C for 2 h and quenched with saturated aqueous solution of NH<sub>4</sub>Cl. The aqueous layer was extracted with EtOAc, and the combined organic solution was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the silyl ether **43a** (7.81 g, 89% yield) as a viscous oil. R<sub>f</sub> = 0.56 (9:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2959, 1600, 1494; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 7.28-7.23 (m, 2H), 7.15-7.10 (m, 3H), 6.30 (ddd, *J* = 15.8, 4.2, 4.0 Hz, 1H), 5.84 (ddd, *J* = 15.8, 2.2, 2.2 Hz, 1H), 4.27 (dd, *J* = 4.0, 2.2 Hz, 2H), 2.26 (s, 2H), 0.96 (s, 9H), 0.18 (s, 6H), 0.11 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 143.9, 138.9, 128.3 (2C), 128.1 (2C), 124.3, 108.5, 104.9, 92.9, 62.7, 26.3, 25.8 (3C), 18.3, -2.2 (2C), -5.4 (2C); HRMS (CI) calcd for [C<sub>20</sub>H<sub>32</sub>OSi<sub>2</sub> + Na]<sup>+</sup>: 219.1175, Found: 219.1171.

**(E)-5-(benzyl dimethylsilyl)pent-2-en-4-yn-1-yl tert-butyl dimethylsilyl ether (43b)**



To a solution of alkyne **42** (25.1 g, 128.1 mmol) in 150 mL of THF flask was added *n*-BuLi (9.8 g, 153.0 mmol) at  $-78$  °C. TMSCl (18.1 g, 166.4 mmol) was dissolved in 30 mL of THF and then added dropwise into the previous solution. The reaction mixture was stirred at  $-78$  °C for 2 h and quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$ . The aqueous layer was extracted with EtOAc, and the combined organic solution was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the silyl ether **43b** (30.6 g, 89% yield) as a viscous oil.  $R_f = 0.58$  (9:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2980;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  6.25 (ddd,  $J = 15.8, 4.2, 4.0$  Hz, 1H), 5.79 (ddd,  $J = 15.8, 2.2, 2.0$  Hz, 1H), 4.21 (dd,  $J = 4.2, 2.2$  Hz, 2H), 0.90 (s, 9H), 0.18 (s, 9H), 0.05 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  143.6, 108.6, 103.6, 94.4, 62.7, 25.8 (3C), 18.3,  $-0.07$  (3C),  $-5.4$  (2C); HRMS (CI) calcd for  $[\text{C}_{14}\text{H}_{20}\text{OSi}_2 + \text{Na}]^+$ : 291.1571, Found: 291.1577.

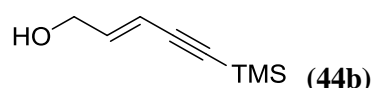
**(E)-5-(benzyl dimethylsilyl)pent-2-en-4-yn-1-ol (44a)**



A mixture of 50 mL AcOH/ $\text{H}_2\text{O}$ /THF: 3/1/1 was added to silyl ether **43a** (2.98 g, 8.65 mmol) at room temperature. The reaction was stirred at room temperature for 12 h and quenched with saturated aqueous solution of  $\text{K}_2\text{CO}_3$ . The aqueous layer was extracted with  $\text{Et}_2\text{O}$  and the combined organic solution was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **44a** (1.79 g, 90% yield) as a colorless oil.  $R_f = 0.16$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 3363, 2959, 1600, 1494;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):

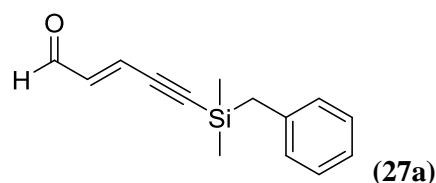
$\delta$  7.27-7.21 (m, 2H), 7.13-7.07 (m, 3H), 6.30 (ddd,  $J = 16.1, 5.0, 4.9$  Hz, 1H), 5.77 (ddd,  $J = 16.1, 2.0, 1.7$  Hz, 1H), 4.20 (dd,  $J = 4.9, 2.0$  Hz, 2H), 2.23 (s, 2H), 0.16 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  143.0, 138.8, 128.3 (2C), 128.1 (2C), 124.3, 110.0, 104.2, 93.5, 62.5, 26.1, 20.7,  $-2.3$  (2C); HRMS (CI) calcd for  $[\text{C}_{14}\text{H}_{18}\text{OSi} + \text{Na}]^+$ : 253.1019, Found: 253.1022.

**(E)-5-(trimethylsilyl)pent-2-en-4-yn-1-ol (44b)**



A mixture of 150 mL AcOH/H<sub>2</sub>O/THF: 3/1/1 was added to silyl ether **43b** (26.8 g, 100 mmol) at room temperature. The reaction was stirred at room temperature for 12 h and quenched with saturated aqueous solution of K<sub>2</sub>CO<sub>3</sub>. The aqueous layer was extracted with Et<sub>2</sub>O and the combined organic solution was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **44b** (13.2 g, 86% yield) as a colorless oil.  $R_f = 0.25$  (7:3 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 3363, 2959, 1600, 1494;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  6.27 (ddd,  $J = 15.8, 5.2, 5.0$  Hz, 1H), 5.74 (ddd,  $J = 16.1, 2.0, 1.8$  Hz, 1H), 4.20 (dd,  $J = 4.4, 3.7$  Hz, 2H), 2.20 (bs, 1H), 0.17 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  142.9, 110.2, 103.0, 95.2, 62.6,  $-0.2$  (3C); HRMS (CI) calcd for  $[\text{C}_{14}\text{H}_{18}\text{OSi} + \text{Na}]^+$ : 176.2722, Found: 176.2727.

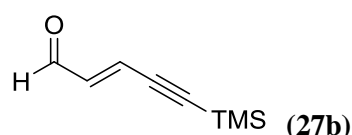
**(E)-5-(benzyltrimethylsilyl)pent-2-en-4-ynal (27a)**



To a solution of primary alcohol **44a** (1.79 g, 7.79 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was added MnO<sub>2</sub> (6.78 g, 77.85 mmol) at room temperature. The reaction mixture was stirred at room temperature for 16 h and then filtered through a pad of celite and washed

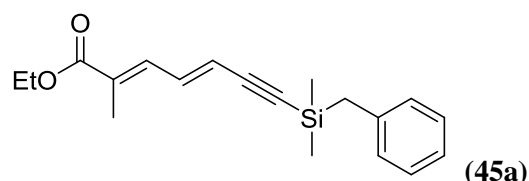
with Et<sub>2</sub>O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the aldehyde **27a** (1.62 g, 91% yield) as a colorless oil.  $R_f = 0.53$  (9:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2989, 1710, 1456; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  9.56 (d,  $J = 7.2$ , Hz, 1H), 7.28-7.22 (m, 2H), 7.15-7.06 (m, 3H), 6.57 (d,  $J = 16.1$  Hz, 1H), 6.46 (dd,  $J = 15.8, 7.2$  Hz, 1H), 2.27 (s, 2H), 0.21 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):  $\delta$  193.1, 140.2, 138.2, 131.8, 128.3 (4C), 124.6, 109.6, 101.7, 25.6, -2.6 (2C); HRMS (CI) calcd for [C<sub>14</sub>H<sub>16</sub>OSi + Na]<sup>+</sup>: 251.0862, Found: 251.0855.

**(E)-5-(trimethylsilyl)pent-2-en-4-ynal (27b)**



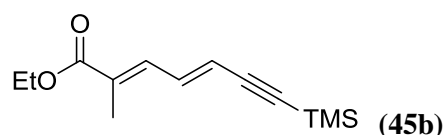
To a solution of primary alcohol **44b** (10.4 g, 67.5 mmol) in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> was added MnO<sub>2</sub> (58.0 g, 672 mmol) at room temperature. The reaction mixture was stirred at room temperature for 16 h and then filtered through a pad of celite and washed with Et<sub>2</sub>O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the aldehyde **27b** (9.3 g, 91% yield) as a colorless oil.  $R_f = 0.23$  (9:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3369, 2989, 1680; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  9.54 (d,  $J = 7.2$ , Hz, 1H), 6.57 (d,  $J = 15.8$  Hz, 1H), 6.44 (dd,  $J = 15.8, 7.4$  Hz, 1H), 0.22 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):  $\delta$  193.1, 140.1, 132.1, 111.4, 100.6, -0.6 (3C); HRMS (CI) calcd for [C<sub>8</sub>H<sub>12</sub>OSi + H]<sup>+</sup>: 153.0736, Found: 153.0730.

**(2E, 4E)-ethyl-7-(benzyltrimethylsilyl)-2-methylhepta-2,4-dien-ynoate (45a)**



Triethyl 2-phosphonopropionate **10** (2.07 g, 8.67 mmol) was added dropwise to *n*-BuLi (0.56 g, 2.3 M, 8.67 mmol) in THF (30 mL) at  $-78\text{ }^{\circ}\text{C}$  under an argon atmosphere. After 30 min stirring, aldehyde **27a** (1.52 g, 6.67 mmol) in 1 mL of THF was added dropwise, and the reaction was stirred at room temperature for another 2 h. The reaction mixture was quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$ , and was then extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the dienynoate **45a** (1.99 g, 96% yield) as a colorless oil.  $R_f = 0.63$  (9:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2982, 1705;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.26-7.18 (m, 2H), 7.13-7.07 (m, 3H), 6.90 (d,  $J = 15.3$  Hz, 1H), 6.88 (d,  $J = 15.3$  Hz, 1H), 5.91 (d,  $J = 15.3$  Hz, 1H), 4.22 (q,  $J = 7.2$  Hz, 2H), 2.25 (s, 2H), 1.99 (s, 3H), 1.31 (t,  $J = 7.2$  Hz, 3H), 0.17 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  167.8, 137.7, 136.4, 130.1, 128.3 (2C), 128.1 (2C), 124.4, 117.2, 105.3, 99.4, 82.6, 60.8, 26.1, 14.2, 13.0,  $-2.3$  (2C); HRMS (CI) calcd for  $[\text{C}_{19}\text{H}_{24}\text{O}_2\text{Si} + \text{Na}]^+$ : 335.1438, Found: 335.1433.

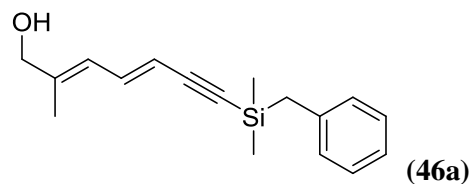
**(2E, 4E)-ethyl-2-methyl-7-(trimethylsilyl)hepta-2,4-dien-6-ynoate (45b)**



Triethyl 2-phosphonopropionate **10** (15.6 g, 65.7 mmol) was added dropwise to *n*-BuLi (3.86 g, 2.3 M, 60.2 mmol) in THF (200 mL) at  $-78\text{ }^{\circ}\text{C}$  under an argon atmosphere. After 30 min stirring, aldehyde **27b** (8.32 g, 54.8 mmol) in 10 mL of THF was added dropwise, and the reaction was stirred at room temperature for another 2 h. The reaction mixture was quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$ , and was then extracted with EtOAc. The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the dienynoate **45b** (12.2 g, 91% yield) as a colorless oil.  $R_f = 0.32$  (9:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2986, 1708;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.14 (dd,  $J$

= 11.9, 1.2 Hz, 1H), 6.90 (dd,  $J = 15.3, 11.9$  Hz, 1H), 5.90 (d,  $J = 15.3$  Hz, 1H), 4.20 (q,  $J = 7.2$ , 2H), 1.96 (d,  $J = 1.2$  Hz, 3H), 1.29 (t,  $J = 7.2$ , 3H), 0.19 (s, 9H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  167.8, 137.4, 136.5, 129.9, 117.3, 103.9, 100.8, 60.8, 14.2, 12.9, -0.3 (3C); HRMS (CI) calcd for  $[\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si} + \text{H}]^+$ : 237.1311, Found: 237.1306.

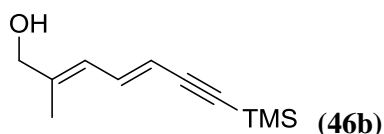
**(2E,4E)-7-(benzyl dimethylsilyl)-2-methylhepta-2,4-dien-6-yn-1-ol (46a)**



To a solution of dienynoate **45a** (1.68 g, 5.38 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was dropwise added diisobutylaluminum hydride ( $i\text{-Bu}$ ) $_2\text{AlH}$  (1.0 M in  $\text{CH}_2\text{Cl}_2$ , 16.1 mL, 16.1 mmol) at  $-78$  °C under an argon atmosphere. After stirring for 30 min at  $-78$  °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 30 min. Then the reaction mixture was diluted with  $\text{Et}_2\text{O}$  and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 15 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with  $\text{Et}_2\text{O}$ . The combined organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/ $\text{EtOAc}$ ) to afford the primary alcohol **46a** (443 mg, 91% yield) as a colorless oil.  $R_f = 0.21$  (4:1 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 3429, 2982;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.26-7.21 (m, 2H), 7.12-7.07 (m, 3H), 6.90 (dd,  $J = 15.6, 11.4$  Hz, 1H), 6.14 (d,  $J = 11.4$  Hz, 1H), 5.61 (d,  $J = 15.6$  Hz, 1H), 4.11 (s, 2H), 2.24 (s, 2H), 1.82 (s, 3H), 0.16 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  141.2, 138.7, 128.4 (2C), 128.1 (2C), 124.3, 123.5, 110.3, 106.2, 95.4, 67.8, 26.3, 14.4, 13.0, -2.1 (2C); HRMS (CI) calcd for  $[\text{C}_{17}\text{H}_{22}\text{OSi} + \text{Na}]^+$ : 293.1332, Found: 293.1327.

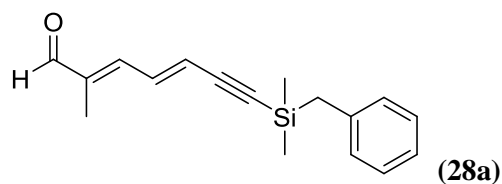
**(2E, 4E)-2-methyl-7-(trimethylsilyl)hepta-2,4-dien-6-yn-1-ol (46b)**





To a solution of dienynoate **45b** (8.69 g, 36.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was dropwise added diisobutylaluminum hydride (*i*-Bu)<sub>2</sub>AlH (1.0 M in CH<sub>2</sub>Cl<sub>2</sub>, 92.0 mL, 92.0 mmol) at -78 °C under an argon atmosphere. After stirring for 30 min at -78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 30 min. Then the reaction mixture was diluted with Et<sub>2</sub>O and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 150 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with Et<sub>2</sub>O. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **46b** (6.66 g, 93% yield) as a colorless oil. *R*<sub>f</sub> = 0.20 (4:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3429, 2982; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 6.88 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.13-6.07 (m, 1H), 5.58 (d, *J* = 15.6 Hz, 1H), 4.05 (s, 2H), 1.71 (d, *J* = 0.8 Hz, 3H), 0.80 (s, 1H), 0.19 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 141.0, 138.4, 123.4, 110.4, 104.8, 96.9, 67.7, 14.3, -0.1 (3C); HRMS (CI) calcd for [C<sub>11</sub>H<sub>18</sub>OSi + H]<sup>+</sup>: 195.1205, Found: 195.1216.

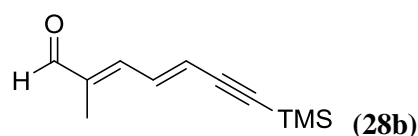
**(2E,4E)-7-(benzyltrimethylsilyl)-2-methylhepta-2,4-dien-6-ynal (28a)**



To a solution of primary alcohol **46a** (342 mg, 1.26 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added MnO<sub>2</sub> (1.10 g, 12.6 mmol) at room temperature. The reaction mixture was stirred at room temperature for 18 h and then filtered through a pad of celite and washed with Et<sub>2</sub>O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the ynal **28a** (310 mg, 92% yield) as a colorless oil. *R*<sub>f</sub> = 0.60 (4:1 (v/v) hexane/EtOAc); IR (neat,

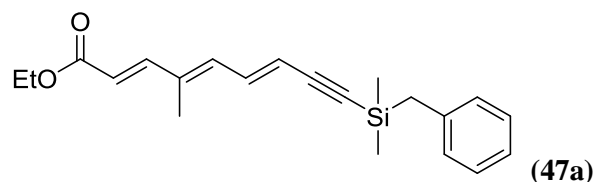
cm<sup>-1</sup>): 3370, 2990, 1456; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 9.47 (s, 1H), 7.27-7.22 (m, 2H), 7.14-7.07 (m, 3H), 7.04 (dd, *J* = 15.3, 11.6 Hz, 1H), 6.83 (d, *J* = 11.6 Hz, 1H), 6.04 (d, *J* = 15.3 Hz, 1H), 2.25 (s, 2H), 1.89 (s, 3H), 0.19 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 194.3, 146.2, 139.7, 138.6, 128.4 (2C), 128.2 (2C), 124.5, 119.3, 100.6, 100.2, 26.0, 9.8, -2.3 (2C); HRMS (CI) calcd for [C<sub>17</sub>H<sub>20</sub>OSi + Na]<sup>+</sup>: 291.1175, Found: 291.1179.

**(2*E*, 4*E*)-2-methyl-7-(trimethylsilyl)hepta-2,4-dien-6-ynal (28b)**



To a solution of primary alcohol **46b** (6.66 g, 34.3 mmol) in 80 mL of CH<sub>2</sub>Cl<sub>2</sub> was added MnO<sub>2</sub> (29.9 g, 343.3 mmol) at room temperature. The reaction mixture was stirred at room temperature for 18 h and then filtered through a pad of celite and washed with Et<sub>2</sub>O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the ynal **28b** (6.24 mg, 94% yield) as a colorless oil. *R<sub>f</sub>* = 0.64 (4:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3370, 2990, 1456; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 9.45 (s, 1H), 7.04 (dd, *J* = 15.3, 11.4 Hz, 1H), 6.82 (d, *J* = 11.4 Hz, 1H), 6.04 (d, *J* = 15.3 Hz, 1H), 1.87 (d, *J* = 1.0 Hz, 3H), 0.21 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 194.4, 146.3, 139.5, 136.7, 119.5, 103.5, 103.0, 9.7, -0.3 (3C); HRMS (CI) calcd for [C<sub>11</sub>H<sub>16</sub>OSi + Na]<sup>+</sup>: 215.0862, Found: 215.0865.

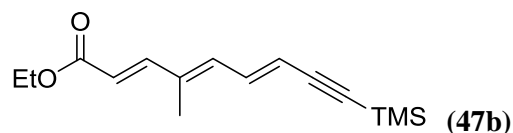
**(2*E*, 4*E*, 6*E*)-ethyl-9-(benzyltrimethylsilyl)-4-methylnona-2,4,6-trien-8-ynoate (47a)**



To a solution of MnO<sub>2</sub> oxidative ynal **28a** (1.50 g, 5.6 mmol) in 15 mL of toluene was added (Carboethoxymethylene)-triphenylphosphorane **12** (2.54 g, 7.28 mmol), the

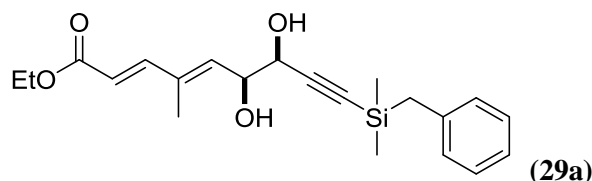
reaction was refluxed for 3 h. After cooling down to room temperature, the solvent was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the trienoate **47a** (1.78 g, 98% yield) as a colorless oil.  $R_f = 0.36$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2988, 1719;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.33 (d,  $J = 15.6$  Hz, 1H) 7.27-7.21 (m, 2H), 7.13-7.07 (m, 3H), 6.97 (dd,  $J = 15.3, 11.6$  Hz, 1H), 6.40 (d,  $J = 11.6$  Hz, 1H), 5.96 (d,  $J = 15.6$  Hz, 1H), 5.79 (d,  $J = 15.3$  Hz, 1H), 4.23 (q,  $J = 7.2$  Hz, 2H), 2.25 (s, 2H), 1.93 (s, 3H), 1.31 (t,  $J = 7.2$  Hz, 3H), 0.17 (s, 6H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  167.0, 147.9, 138.7, 138.2, 136.8, 136.2, 128.3 (2C), 128.1 (2C), 124.3, 118.6, 114.7, 105.6, 99.0, 60.3, 26.1, 14.3, 12.7,  $-2.2$  (2C); HRMS (CI) calcd for  $[\text{C}_{21}\text{H}_{26}\text{O}_2\text{Si} + \text{Na}]^+$ : 361.1594, Found: 361.1589.

**(2E,4E,6E)-ethyl-4-methyl-9-(trimethylsilyl)nona-2,4,6-trien-8-ynoate (47b)**



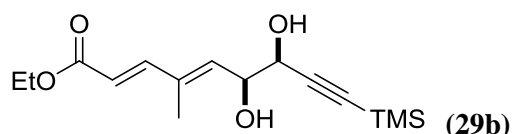
To a solution of  $\text{MnO}_2$  oxidative ynal **28b** (5.57 g, 29.0 mmol) in 70 mL of toluene was added (Carboethoxymethylene)-triphenylphosphorane **12** (13.13 g, 37.7 mmol), the reaction was refluxed for 5 h. After cooling down to room temperature, the solvent was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the trienoate **47b** (7.15 g, 94% yield) as a colorless oil.  $R_f = 0.60$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2988, 1719;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.30 (d,  $J = 15.6$  Hz, 1H), 6.96 (dd,  $J = 15.3, 11.6$  Hz, 1H), 6.38 (d,  $J = 11.6$  Hz, 1H), 5.93 (d,  $J = 15.6$  Hz, 1H), 5.78 (d,  $J = 15.3$  Hz, 1H), 4.20 (q,  $J = 7.2$  Hz, 2H), 1.93 (d,  $J = 0.73$  Hz, 3H), 1.29 (t,  $J = 7.2$  Hz, 3H), 0.19 (s, 9H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  167.0, 147.9, 137.9, 136.9, 136.1, 118.5, 114.9, 104.4, 100.1, 60.3, 14.3, 12.7,  $-0.2$  (3C); HRMS (CI) calcd for  $[\text{C}_{15}\text{H}_{22}\text{O}_2\text{Si} + \text{Na}]^+$ : 285.1281, Found: 285.1287.

**(2E,4E,6S,7S)-ethyl-9-(benzyltrimethylsilyl)-6,7-dihydroxy-4-methylnona-2,4-dien-8-ynoate (29a)**



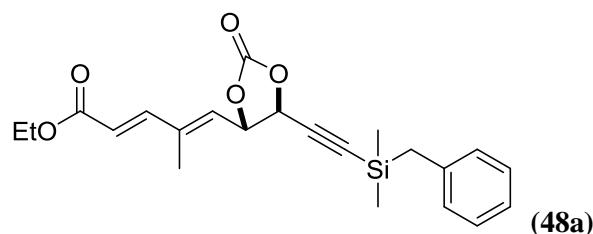
To a 50 mL round bottom flask was added 1:1 *t*-butyl alcohol (40 mL)/H<sub>2</sub>O (40 mL), K<sub>3</sub>Fe(CN)<sub>6</sub> (9.67 g, 29.5 mmol), K<sub>2</sub>CO<sub>3</sub> (4.08 g, 29.5 mmol), CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (0.94 g, 9.85 mmol), (DHQ)<sub>2</sub>-PHAL (152 mg, 0.20 mmol, 2 mol %) and OsO<sub>4</sub> (25 mg, 0.10 mmol, 1 mol %). The mixture was stirred at room temperature for 15 min and then cooled to 0 °C. To this solution was added trienoate **47a** (3.33 g, 9.85 mmol) in 2 mL CH<sub>2</sub>Cl<sub>2</sub> dropwise and the reaction was stirred vigorously at 0 °C overnight. Saturated aqueous solution of Na<sub>2</sub>SO<sub>3</sub> was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 1:1 (v/v) hexane/EtOAc) to afford the diol **29a** (3.00 g, 82% yield) as a colorless oil. *R*<sub>f</sub> = 0.15 (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>) 3446, 2983, 1762; [α]<sub>D</sub><sup>25</sup> -13.8° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 7.26-7.21 (m, 2H), 7.12-7.07 (m, 3H), 6.89 (dd, *J* = 15.6, 11.4 Hz, 1H), 6.18 (d, *J* = 11.4 Hz, 1H), 5.63 (d, *J* = 15.3 Hz, 1H), 4.34-4.24 (m, 4H), 2.23 (s, 2H), 1.88 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.15 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 172.9, 139.5, 138.9, 138.2, 128.3 (2C), 128.1 (2C), 125.4, 124.3, 111.3, 105.9, 95.9, 76.6, 72.2, 62.2, 26.2, 14.1, 13.9, -2.2 (2C); HRMS (CI) calcd for [C<sub>21</sub>H<sub>28</sub>O<sub>4</sub>Si + Na]<sup>+</sup>: 395.1649, Found: 395.1653.

**(2E,4E,6S,7S)-ethyl-6,7-dihydroxy-4-methyl-9-(trimethylsilyl)nona-2,4-dien-8-ynoate (29b)**



To a 500 mL round bottom flask was added 1:1 *t*-butyl alcohol (100 mL)/H<sub>2</sub>O (100 mL), K<sub>3</sub>Fe(CN)<sub>6</sub> (26.8 g, 81.9 mmol), K<sub>2</sub>CO<sub>3</sub> (11.31 g, 81.9 mmol), KHCO<sub>3</sub> (8.24 g, 81.9 mmol), CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (0.85 g, 27.3 mmol), (DHQ)<sub>2</sub>-PHAL (0.42 g, 0.55 mmol, 2 mol %) and OsO<sub>4</sub> (69 mg, 0.27 mmol, 1 mol %). The mixture was stirred at room temperature for 15 min and then cooled to 0 °C. To this solution was added trienoate **47b** (7.15 g, 27.3 mmol) in 5 mL CH<sub>2</sub>Cl<sub>2</sub> dropwise and the reaction was stirred vigorously at 0 °C overnight. Saturated aqueous solution of Na<sub>2</sub>SO<sub>3</sub> was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude product. The residue was purified by column chromatography (silica gel, 1:1 (v/v) hexane/EtOAc) to afford the diol **29b** (6.47 g, 80% yield) as a colorless oil. R<sub>f</sub> = 0.19 (19:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>) 3446, 2983, 1762; [α]<sub>D</sub><sup>25</sup> +14° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 6.88 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.15 (d, *J* = 12.1 Hz, 1H), 5.62 (d, *J* = 15.6 Hz, 1H), 4.30-4.21 (m, 4H), 1.84 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 172.9, 139.3, 138.0, 125.4, 111.5, 104.5, 97.5, 76.7, 72.2, 62.2, 14.1, 13.8, -0.1 (3C); HRMS (CI) calcd for [C<sub>15</sub>H<sub>24</sub>O<sub>4</sub>Si + Na]<sup>+</sup>: 319.1336, Found: 319.1332.

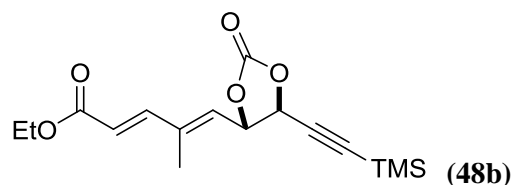
**(2E,4E)-ethyl-5-((4S,5S)-5-(2-(benzyl dimethylsilyl)ethynyl)-2-oxo-1,3-dioxolan-4-yl)-4-ethylpenta-2,4-dienoate (48a)**



To a solution of diol **29a** (506 mg, 1.36 mmol) in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> was added pyridine (0.45 mL, 5.44 mmol) and (Cl<sub>3</sub>CO)<sub>2</sub>CO (484 mg, 1.63 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. After stirring for 2 h at 0 °C, the reaction mixture was quenched by saturated aqueous

solution of NH<sub>4</sub>Cl and extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the carbonate **48a** (440 mg, 95% yield) as a colorless oil. *R<sub>f</sub>* = 0.57 (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2989, 1714; [α]<sub>D</sub><sup>25</sup> -101° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 7.23-7.21 (m, 2H), 7.13-7.06 (m, 3H), 6.81 (dd, *J* = 15.3, 11.1 Hz, 1H), 6.22 (d, *J* = 11.1 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 5.04 (d, *J* = 5.2 Hz, 1H), 4.71 (d, *J* = 5.5 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.23 (s, 2H), 1.86 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.16 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 167.0, 153.0, 138.7, 136.4, 132.6, 128.8, 128.3 (2C), 128.2 (2C), 124.4, 114.9, 104.9, 98.1, 82.6, 76.0, 63.0, 26.1, 14.0, 11.7, -2.3 (2C); HRMS (CI) calcd for [C<sub>22</sub>H<sub>26</sub>O<sub>5</sub>Si + Na]<sup>+</sup>: 421.1442, Found: 421.1439.

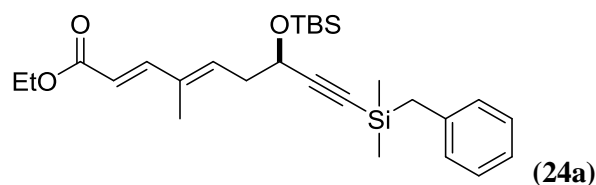
**(2*E*,4*E*)-ethyl-4-methyl-((4*S*,5*S*)-5-(2-(trimethylsilyl)ethynyl)-2-oxo-1,3-dioxolan-4-yl)penta-2,4-dienoate (**48b**)**



To a solution of diol **29b** (4.81 g, 16.2 mmol) in 60 mL of CH<sub>2</sub>Cl<sub>2</sub> was added pyridine (4.68 mL, 56.9 mmol) and (Cl<sub>3</sub>CO)<sub>2</sub>CO (5.78 g, 19.5 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C. After stirring for 3 h at 0 °C, the reaction mixture was quenched by saturated aqueous solution of NH<sub>4</sub>Cl and extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 19:1 (v/v) hexane/EtOAc) to afford the carbonate **48b** (4.76 g, 91% yield) as a colorless oil. *R<sub>f</sub>* = 0.61 (19:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2989, 1714; [α]<sub>D</sub><sup>25</sup> -80° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 6.81 (dd, *J* = 15.6, 11.4 Hz, 1H), 6.21 (d, *J* = 11.4 Hz, 1H), 5.74 (d, *J* = 15.6 Hz, 1H), 5.02 (d, *J* = 5.2 Hz, 1H), 4.70 (d, *J* = 5.4 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.84 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.19 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz):

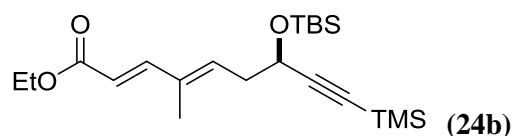
$\delta$  166.9, 153.1, 136.2, 132.4, 128.9, 115.0, 103.7, 99.7, 82.7, 75.9, 62.9, 14.0, 11.6, -0.2 (3C); HRMS (CI) calcd for  $[\text{C}_{16}\text{H}_{22}\text{O}_5\text{Si} + \text{H}]^+$ : 323.1310, Found: 322.1306.

**(*R,2E,4E*)-ethyl-9-(benzyl dimethylsilyl)-7-hydroxy-4-methylnona-2,4-dien-8-ynoate (24a)**



To a solution of carbonate **48a** (193 mg, 0.48 mmol) in 4 mL of  $\text{CH}_2\text{Cl}_2$  was added  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  (25 mg, 0.024 mmol),  $\text{PPh}_3$  (12 mg, 0.048 mmol),  $\text{Et}_3\text{N}$  (245 mg, 2.24 mmol) and  $\text{HCO}_2\text{H}$  (111 mg, 2.42 mmol) at room temperature. After stirring at room temperature for 4 h, the reaction mixture was quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and extracted with  $\text{EtOAc}$ . The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated to afford the crude alcohol. To a solution of the above crude alcohol in 0.5 mL of DMF was added imidazole (104 mg, 1.52 mmol) and  $\text{TBSCl}$  (114 mg, 0.76 mmol) at room temperature. In 0.5 h, the reaction mixture was purified by chromatography (silica gel, 19:1 (v/v) hexane/ $\text{EtOAc}$ ) without work up to provide the ester **24a** (82 mg, 36% yield for two steps) as a colorless oil with 32% of the recovered starting material.  $R_f = 0.35$  (7:3 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 3410, 2968, 1690;  $[\alpha]_D^{25} +36^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.23-7.21 (m, 2H), 7.10-7.08 (m, 3H), 6.84 (dd,  $J = 15.6, 11.4$  Hz, 1H), 5.94 (d,  $J = 11.4$  Hz, 1H), 5.51 (d,  $J = 15.6$  Hz, 1H), 4.29 (dd,  $J = 8.4, 4.8$  Hz, 1H), 4.16 (q,  $J = 7.2$  Hz, 2H), 2.48 (dd,  $J = 13.2, 4.2$  Hz, 1H), 2.43 (dd,  $J = 13.8, 8.4$  Hz, 1H), 2.23 (s, 2H), 1.85 (s, 3H), 1.27 (t,  $J = 6.6$  Hz, 3H), 0.89 (s, 9H) 0.15 (s, 6H), 0.05 (s, 3H), 0.01 (s, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  173.2, 139.1, 138.2, 128.4 (2C), 128.1 (2C), 127.9, 124.3, 109.3, 94.9, 71.4, 60.8, 45.6, 26.3, 25.7, 25.6 (3C), 21.0, 18.2, 17.5, 14.2, -2.1 (2C), -5.1, -5.3; HRMS (CI) calcd for  $[\text{C}_{27}\text{H}_{42}\text{O}_3\text{Si}_2 + \text{Na}]^+$ : 493.2564, Found: 493.2559.

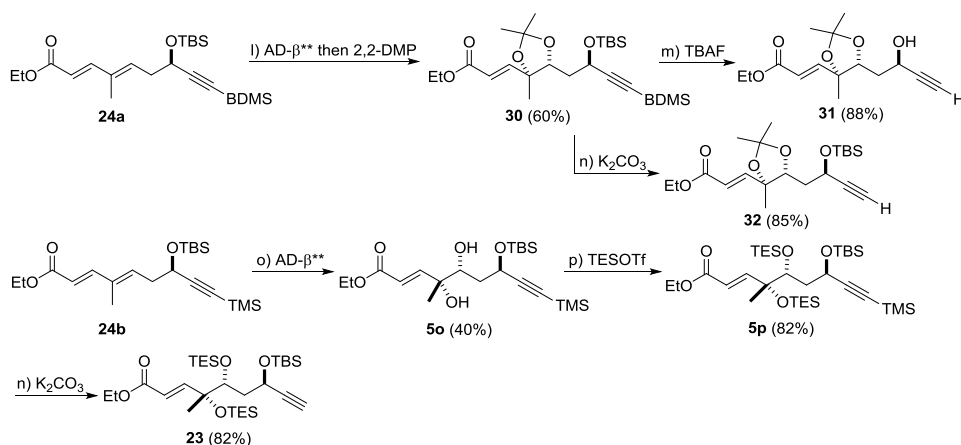
**(*R,2E,4E*)-ethyl-7-*tert*-butyldimethylsiloxy-4-methyl-9-(trimethylsilyl)nona-2,4-dien-8-ynoate (**24b**)**



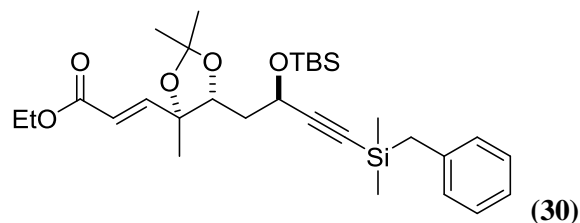
To a solution of carbonate **48b** (103 mg, 0.32 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (7 mg, 0.007 mmol), PPh<sub>3</sub> (4 mg, 0.13 mmol), Et<sub>3</sub>N (98 mg, 0.97 mmol) and HCO<sub>2</sub>H (46 mg, 0.97 mmol) at room temperature. After stirring at room temperature for 4 h, the reaction mixture was quenched with saturated aqueous solution of NH<sub>4</sub>Cl and extracted with EtOAc. The organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude alcohol. To a solution of the above crude alcohol in 0.5 mL of DMF was added imidazole (66 mg, 0.97 mmol) and TBSCl (72 mg, 0.48 mmol) at room temperature. In 0.5 h, the reaction mixture was purified by chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) without work up to provide the ester **24b** (43 mg, 34% yield for two steps) as a colorless oil with 30% of the recovered starting material. *R<sub>f</sub>* = 0.36 (7:3 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 2968, 1690; [α]<sub>D</sub><sup>25</sup> -20° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 6.84 (dd, *J* = 15.3, 11.4 Hz, 1H), 5.92 (d, *J* = 11.4 Hz, 1H), 5.51 (d, *J* = 15.3 Hz, 1H), 4.27 (dd, *J* = 7.7, 4.7 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 2.49-2.41 (m, 2H), 1.83 (s, 3H), 1.27 (t, *J* = 6.6 Hz, 3H), 0.89 (s, 9H), 0.19 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 173.2, 138.8, 138.0, 128.0, 109.4, 105.0, 96.3, 71.4, 60.8, 45.6, 25.7 (3C), 18.2, 17.5, 14.2, -0.03 (3C), -5.1, -5.3; HRMS (CI) calcd for [C<sub>21</sub>H<sub>38</sub>O<sub>3</sub>Si<sub>2</sub> + Na]<sup>+</sup>: 417.2251, Found: 417.2247.



## Intermediates related to Scheme 5:



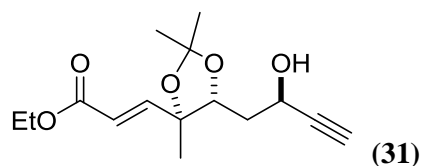
**(*E*)-ethyl-3-((4*R*,5*R*)-5-((*R*)-4-(benzyltrimethylsilyl)-2-*tert*-butyldimethylsiloxy-but-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)acrylate (**30**)**



To a 50 mL round bottom flask was added 1:1 *t*-butyl alcohol (10 mL)/H<sub>2</sub>O (10 mL), K<sub>3</sub>Fe(CN)<sub>6</sub> (4.35 g, 13.2 mmol), K<sub>2</sub>CO<sub>3</sub> (1.82 g, 13.2 mmol), CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (0.42 g, 4.4 mmol), (DHQD)<sub>2</sub>-PHAL (137 mg, 0.18 mmol, 4 mol %) and OsO<sub>4</sub> (22 mg, 0.09 mmol, 2 mol %). The mixture was stirred at room temperature for 30 min and then cooled to 0 °C. To this solution was added compound **24a** (2.07 g, 4.4 mmol) in 1 mL CH<sub>2</sub>Cl<sub>2</sub> dropwise and the reaction was stirred vigorously at 0 °C overnight. Saturated aqueous solution of Na<sub>2</sub>SO<sub>3</sub> was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude diol. To a solution of the above crude diol in 5 mL of acetone was added 2,2-dimethoxypropane (9.17 g, 88 mmol) and CSA (0.10 g, 10 mol %) at room temperature. After stirring at room temperature for 3 h, the reaction was quenched with saturated aqueous solution of NaHCO<sub>3</sub> and extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>,

and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the acetonide **30** (1.440 g, 60% yield for two steps) as a colorless oil.  $R_f = 0.32$  (7:3 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2986, 1752;  $[\alpha]_D^{25} +62^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.26-7.19 (m, 2H), 7.11-7.05 (m, 3H), 6.90 (d,  $J = 15.6$  Hz, 1H), 6.08 (d,  $J = 15.6$  Hz, 1H), 4.54-4.49 (m, 1H), 4.20 (q,  $J = 7.2$  Hz, 2H), 4.04-3.99 (m, 1H), 2.19 (s, 2H), 1.83 (ddd,  $J = 7.9, 4.5, 4.5$  Hz, 2H), 1.46 (s, 3H), 1.34 (s, 3H), 1.29 (t,  $J = 7.2$  Hz, 3H), 1.22 (s, 3H), 0.89 (s, 9H) 0.11 (s, 6H), 0.09 (s, 3H), 0.06 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.3, 149.1, 138.1, 128.3 (2C), 128.1 (2C), 124.3, 120.4, 108.5, 108.2, 81.3, 77.2, 60.5, 60.1, 38.2, 28.3, 26.4, 26.0, 25.7 (3C), 21.1, 18.2, 14.2, -2.3 (2C), -4.6, -5.1; HRMS (CI) calcd for  $[\text{C}_{30}\text{H}_{48}\text{O}_5\text{Si}_2 + \text{Na}]^+$ : 567.2932, Found: 567.2934.

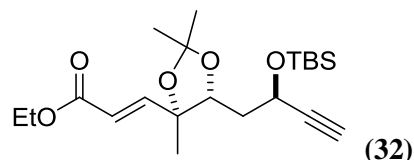
**(E)-ethyl-3-((4R,5R)-5-((R)-2-hydroxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)-acrylate (31)**



To a solution of compound **30** (665 mg, 1.55 mmol) in 5 mL of THF was added TBAF (607 mg, 2.32 mL, 2.32 mmol) at 0 °C. After stirring at 0 °C for 4 h, the reaction was quenched with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and extracted with  $\text{Et}_2\text{O}$ . The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the allylic alcohol **31** (385 mg, 88% yield) as a colorless oil.  $R_f = 0.33$  (7:3 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 3489, 2989, 1752;  $[\alpha]_D^{25} -3^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  6.87 (d,  $J = 15.6$  Hz, 1H), 6.11 (d,  $J = 15.6$  Hz, 1H), 4.65-4.58 (m, 1H), 4.26 (dd,  $J = 10.9, 2.5$  Hz, 1H), 4.20 (q,  $J = 7.2$  Hz, 2H), 2.89 (d,  $J = 8.2$  Hz, 1H), 2.49 (d,  $J = 2.0$  Hz, 1H), 2.00 (ddd,  $J = 14.1, 10.6, 3.5$  Hz, 1H), 1.80 (ddd,  $J = 14.3, 6.9, 2.5$  Hz, 1H), 1.47 (s, 3H), 1.39 (s, 3H), 1.29 (t,  $J = 7.2$  Hz, 3H), 1.23 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.4, 148.7, 120.6,

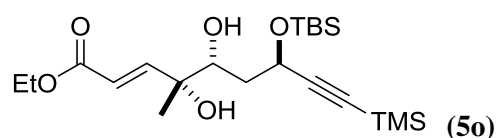
108.7, 83.8, 81.5, 78.0, 73.3, 60.6, 59.8, 35.8, 28.2, 26.3, 21.0, 14.1; HRMS (CI) calcd for  $[C_{15}H_{22}O_5 + Na]^+$ : 305.1359, Found: 305.1385.

**(E)-ethyl-3-((4R,5R)-5-((R)-2-tert-butyltrimethylsilyloxybut-3-ynyl)-2,2,4-trimethyl-1,3-dioxolan-4-yl)-acrylate (32)**



To a solution of compound **30** (330 mg, 0.61 mmol) in 5 mL of EtOH was added  $K_2CO_3$  (251 mg, 1.82 mmol) at room temperature. The reaction was stirred at room temperature for 24 h, then diluted with EtOAc and quenched by 1 M  $NaHSO_4$ . The reaction mixture was extracted with  $Et_2O$ , and the combined organic phases were washed with brine, dried over anhydrous  $Na_2SO_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the silyl ether **32** (204 mg, 85% yield) as a colorless oil.  $R_f = 0.66$  (7:3 (v/v) hexane/EtOAc); IR (neat,  $cm^{-1}$ ): 2989, 1752;  $[\alpha]_D^{25} +33^\circ$  ( $c$  1.0,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , 270 MHz):  $\delta$  6.84 (d,  $J = 15.6$  Hz, 1H), 6.05 (d,  $J = 15.6$  Hz, 1H), 4.52-4.46 (m, 1H), 4.17 (q,  $J = 7.2$  Hz, 2H), 4.01-3.96 (m, 1H), 2.39 (d,  $J = 8.2$  Hz, 1H), 1.85-1.80 (m, 2H), 1.43 (s, 3H), 1.31 (s, 3H), 1.26 (t,  $J = 7.2$  Hz, 3H), 1.17 (s, 3H), 0.86 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H);  $^{13}C$  NMR ( $CDCl_3$ , 67.5 MHz):  $\delta$  166.3, 149.0, 120.3, 108.1, 85.2, 81.2, 77.1, 72.2, 60.4, 59.4, 38.3, 28.3, 26.3, 25.6 (3C), 21.0, 18.1, 14.1, -4.7, -5.3; HRMS (CI) calcd for  $[C_{21}H_{36}O_5Si + Na]^+$ : 419.2224, Found: 419.2197.

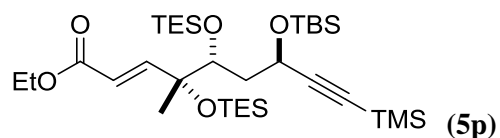
**(E,4R,5R,7R)-ethyl-4,5-dihydroxy-7-tert-butyltrimethylsilyloxy-4-methyl-9-(trimethylsilyl)non-2-en-8-ynoate (5o)**



To a 100 mL round bottom flask was added 1:1 *t*-butyl alcohol (20 mL)/ $H_2O$  (20 mL),  $K_3Fe(CN)_6$  (3.03 g, 9.22 mmol),  $K_2CO_3$  (1.27 g, 9.22 mmol),  $KHCO_3$  (0.93 g, 9.22

mmol), CH<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub> (0.29 g, 3.07 mmol), (DHQD)<sub>2</sub>-PHAL (99 mg, 0.13 mmol, 4 mol %) and OsO<sub>4</sub> (16 mg, 0.062 mmol, 2 mol %). The mixture was stirred at room temperature for 30 min and then cooled to 0 °C. To this solution was added dienoate **24b** (1.18 g, 3.07 mmol) in 2 mL CH<sub>2</sub>Cl<sub>2</sub> dropwise and the reaction was stirred vigorously at 0 °C for 8 h. Saturated aqueous solution of Na<sub>2</sub>SO<sub>3</sub> was added to quench the reaction while stirring vigorously. EtOAc was added to the reaction mixture, and after separation of the layers, the aqueous layer was further extracted with EtOAc. The combined organic phases were washed with 2 M KOH and brine to remove the methanesulfonamide, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to afford the crude diol. The crude product was purified by column chromatography (silica gel, 1:1 (v/v) hexane/EtOAc) to afford the diol **5o** (0.53 g, 40% yield) as a colorless oil. *R*<sub>f</sub> = 0.46 (1:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3446, 2983, 1762; [α]<sub>D</sub><sup>25</sup> +52° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 7.01 (d, *J* = 15.8 Hz, 1H), 6.13 (d, *J* = 15.6 Hz, 1H), 4.73 (dd, *J* = 4.7, 4.5 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.06-4.02 (m, 1H), 3.64 (bs, 1H), 2.58 (s, 1H), 1.84-1.80 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.26 (s, 3H), 0.88 (s, 9H), 0.16 (s, 12H), 0.15 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 166.6, 152.3, 120.3, 105.5, 90.7, 74.7, 74.0, 62.5, 60.4, 37.6, 25.7 (3C), 22.6, 18.0, 14.2, -0.3 (3C), -4.6, -5.3; HRMS (CI) calcd for [C<sub>21</sub>H<sub>40</sub>O<sub>5</sub>Si<sub>2</sub> + Na]<sup>+</sup>: 451.2306, Found: 451.2307.

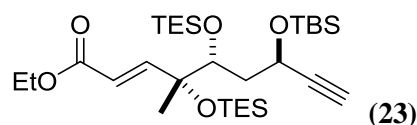
**(*E*,4*R*,5*R*,7*R*)-ethyl-4,5-bistriethylsilyl-7-*tert*-butyldimethylsilyl-4-methyl-9-(trimethylsilyl)non-2-en-8-ynoate (**5p**)**



To a solution of diol **5o** (43 mg, 0.10 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was added 2,6-lutidine (0.12 mL, 1.0 mmol) and TESOTf (159 mg, 0.6 mmol) at -78 °C. The reaction mixture was warmed up to -10 °C and stirred for 2 h. Then the reaction was quenched with saturated aqueous solution of NH<sub>4</sub>Cl and extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v)

hexane/EtOAc) to afford compound **5p** (54 mg, 82% yield) as a colorless oil.  $R_f = 0.52$  (9:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2986, 1752;  $[\alpha]_D^{25} +14^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.00 (d,  $J = 15.8$  Hz, 1H), 5.97 (d,  $J = 15.6$  Hz, 1H), 4.47 (dd,  $J = 7.7, 7.2$  Hz, 1H), 4.20 (q,  $J = 7.2$  Hz, 2H), 3.73 (dd,  $J = 5.9, 5.9$  Hz, 1H), 1.98-1.88 (m, 1H), 1.59-1.49 (m, 1H), 1.49 (s, 3H), 1.28 (t,  $J = 7.2$  Hz, 3H), 0.97 (t,  $J = 7.9$  Hz, 9H), 0.93 (t,  $J = 7.9$  Hz, 9H), 0.88 (s, 9H), 0.65 (q,  $J = 7.9$  Hz, 6H), 0.52 (q,  $J = 7.9$  Hz, 6H), 0.15 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.7, 152.1, 120.0, 108.2, 89.1, 78.7, 76.0, 60.8, 60.2, 43.6, 25.9 (3C), 25.3, 18.2, 14.2, 7.2 (3C), 7.0 (3C), 6.9 (3C), 5.4 (3C),  $-0.3$  (3C),  $-4.1$ ,  $-4.4$ ; HRMS (CI) calcd for  $[\text{C}_{33}\text{H}_{68}\text{O}_5\text{Si}_4 + \text{Na}]^+$ : 679.4036, Found: 679.4037.

**(*E,4R,5R,7R*)-ethyl-4,5-bistriethylsilyl-7-tert-butyltrimethylsilyl-4-methyl-9-non-2-en-8-ynoate (**23**)**

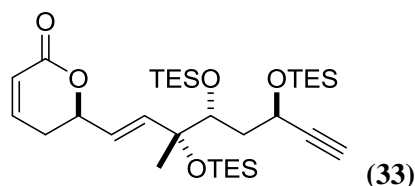


To a solution of compound **5p** (315 mg, 0.48 mmol) in 5 mL of EtOH was added  $\text{K}_2\text{CO}_3$  (199 mg, 1.48 mmol) at room temperature. The reaction was stirred at room temperature for 24 h, then diluted with EtOAc and quenched by 1 M  $\text{NaHSO}_4$ . The reaction mixture was extracted with  $\text{Et}_2\text{O}$ , and the combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the silyl ether **23** (258 mg, 92% yield) as a colorless oil.  $R_f = 0.44$  (9:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2989, 1752;  $[\alpha]_D^{25} +17^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.01 (d,  $J = 15.8$  Hz, 1H), 5.96 (d,  $J = 15.8$  Hz, 1H), 4.48 (ddd,  $J = 8.2, 6.2, 2.0$  Hz, 1H), 4.20 (q,  $J = 7.2$  Hz, 2H), 3.74 (dd,  $J = 6.4, 5.7$  Hz, 1H), 2.39 (d,  $J = 2.2$  Hz, 1H), 1.99 (ddd,  $J = 13.9, 8.2, 5.4$  Hz, 1H), 1.60-1.51 (m, 1H), 1.39 (s, 3H), 1.29 (t,  $J = 7.2$  Hz, 3H), 0.97 (t,  $J = 7.9$  Hz, 18H), 0.89 (s, 9H), 0.64 (q,  $J = 7.9$  Hz, 12H), 0.14 (s, 3H), 0.11 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.6, 152.0, 120.1, 86.1, 78.5, 76.0, 72.8, 60.3, 60.1, 43.6, 25.8 (3C), 25.3, 18.2, 14.3, 7.2 (3C), 7.0 (3C), 6.9

(3C), 5.4 (3C), -4.10, -4.48; HRMS (CI) calcd for  $[C_{30}H_{60}O_5Si_3 + Na]^+$ : 607.3641, Found: 607.3643.

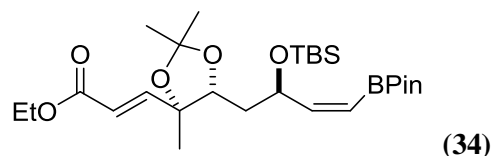
### Compounds in Scheme 6:

#### **(R)-5,6-dihydro-6-((E, 3R, 4R, 6R)-3,4,6-tritriethylsilyl-3-methyloct-1-en-7-ynyl)pyran-2-one (33)**



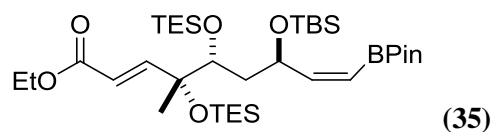
To a solution of triol **4** (79 mg, 0.30 mmol) in 3.0 mL of  $CH_2Cl_2$  was added 2,6-lutidine (317 mg, 2.96 mmol) at  $-78\text{ }^\circ C$ . After stirring for 10 min at  $-78\text{ }^\circ C$ , TESOTf (309 mg, 1.17 mmol) was added to the reaction mixture and kept stirring for 30 min. The reaction mixture was diluted with  $CH_2Cl_2$ , quenched by saturated aqueous solution of  $NaHCO_3$ , and extracted with  $CH_2Cl_2$ . The combined organic phases were washed with brine, dried over anhydrous  $Na_2SO_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 1:4 (v/v) hexane/EtOAc) to afford the TES protected compound **33** (143 mg, 78% yield) as a colorless oil.  $R_f = 0.35$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $cm^{-1}$ ): 2956, 1736;  $[\alpha]_D^{25} +51^\circ$  ( $c$  1.0,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , 600 MHz):  $\delta$  6.86 (ddd,  $J = 8.4, 5.4, 3.0$  Hz, 1H), 6.04 (ddd,  $J = 10.2, 1.8, 1.8$  Hz, 1H), 5.91 (dd,  $J = 16.2, 1.2$  Hz, 1H), 5.79 (dd,  $J = 15.6, 6.6$  Hz, 1H), 4.97 (ddd,  $J = 9.6, 6.6, 1.2$  Hz, 1H), 4.50 (ddd,  $J = 7.8, 6.0, 1.8$  Hz, 1H), 3.68 (dd,  $J = 6.6, 5.4$  Hz, 1H), 2.47-2.42 (m, 2H), 2.39 (d,  $J = 1.8$  Hz, 1H), 2.05-1.97 (m, 1H), 1.46-1.51 (m, 1H), 0.97 (t,  $J = 7.8$  Hz, 27H), 0.71-0.59 (m, 18H);  $^{13}C$  NMR ( $CDCl_3$ , 150 MHz):  $\delta$  164.1, 144.5, 138.1, 125.7, 86.0, 78.0, 77.9, 75.9, 72.7, 59.8, 43.3, 30.0, 26.0, 7.2 (3C), 7.0 (3C), 6.9 (3C), 6.8 (3C), 5.4 (3C), 5.2 (3C). HRMS (CI) calcd for  $[C_{32}H_{60}O_5Si_3 + Na]^+$ : 631.3592, Found: 631.3565.

#### **(2E,4S,5R,7R,8Z)-ethyl-7-tert-butyl dimethylsiloxy-4-methyl-2,2,4-trimethyl-1,3-dioxolan-4-yl)-9-(3,3,4,4-tetramethylborolan-1-yl)nona-2,8-dienoate (34)**



To a solution of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (8 mg, 0.017 mmol, 1.5 mol %) in 1 mL of cyclohexane was added  $\text{Pi-Pr}_3$  (11 mg, 0.068 mmol, 6.0 mol %),  $\text{Et}_3\text{N}$  (38 mg, 0.37 mmol) and catecholborane (39 mg, 0.32 mmol) at room temperature. After stirring at room temperature for 30 minutes, alkyne **32** (132 mg, 0.034 mmol) in 1 mL of cyclohexane was added, and the reaction was stirred for 6 h. Then pinacol (60 mg, 0.51 mmol) in 1 mL of cyclohexane was added dropwise and the reaction mixture was stirred for another 12 h at room temperature. The reaction was quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and extracted with  $\text{Et}_2\text{O}$ . The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/ $\text{EtOAc}$ ) to afford compound **34** (119 mg, 70% yield) as a colorless oil.  $R_f = 0.24$  (9:1 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 2986, 1758;  $[\alpha]_D^{25} -0.03^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  6.86 (d,  $J = 15.6$  Hz, 1H), 6.30 (dd,  $J = 13.6, 8.4$  Hz, 1H), 6.05 (d,  $J = 15.6$  Hz, 1H), 5.32 (dd,  $J = 13.6, 0.75$  Hz, 1H), 5.02 (ddd,  $J = 8.6, 8.6, 3.9$  Hz, 1H), 4.18 (q,  $J = 7.2$  Hz, 2H), 4.00 (dd,  $J = 8.9, 3.2$  Hz, 1H), 1.52 (ddd,  $J = 8.4, 4.2, 4.2$  Hz, 2H), 1.43 (s, 3H), 1.33 (s, 3H), 1.27 (t,  $J = 7.2$  Hz, 3H), 1.25 (s, 12H), 1.15 (s, 3H), 0.83 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.4, 157.2, 149.7, 120.0, 107.8, 83.1, 81.4, 77.7, 69.3, 60.4, 37.7, 28.4, 26.4, 25.8 (3C), 24.8 (2C), 24.7 (2C), 21.1, 20.0, 18.1, 14.2,  $-4.4, -5.0$ ; HRMS (CI) calcd for  $[\text{C}_{27}\text{H}_{49}\text{BO}_7\text{Si} + \text{Na}]^+$ : 547.3233, Found: 547.3234.

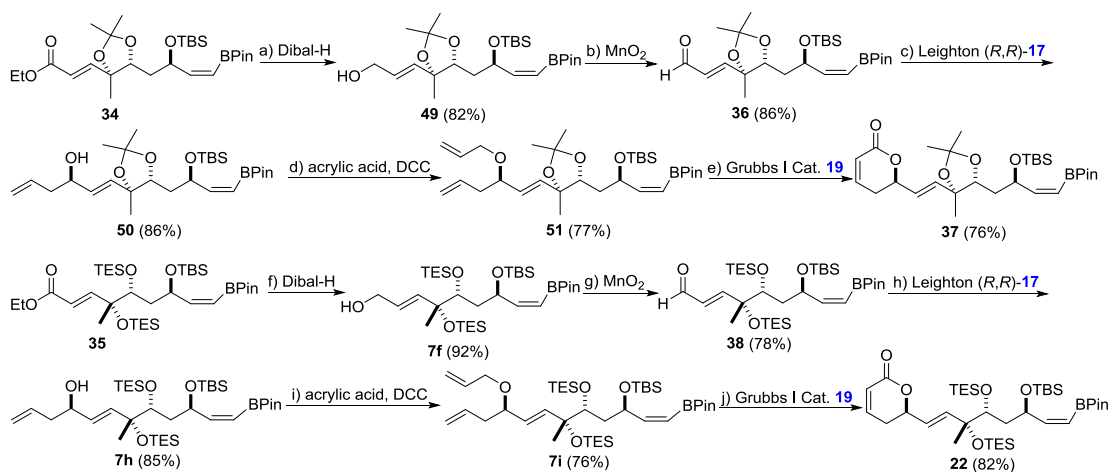
**(2E,4S,5R,7R,8Z)-ethyl-4,5-bistriethylsilyl-7-tert-butyl dimethylsilyl-4-methyl-9-(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl)nona-2,8-dienoate (35)**



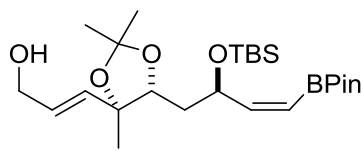
To a solution of  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (20 mg, 0.04 mmol, 1.5 mol %) in 3 mL of cyclohexane was added  $\text{Pi-Pr}_3$  (26 mg, 0.16 mmol, 6.0 mol %),  $\text{Et}_3\text{N}$  (84 mg, 0.83 mmol) and catecholborane (86 mg, 0.71 mmol) at room temperature. After stirring at room temperature for 30 minutes, alkyne **23** (438 mg, 0.72 mmol) in 1 mL of cyclohexane was added, and the reaction was stirred for 6 h. Then pinacol (133 mg, 1.13 mmol) in 1 mL of cyclohexane was added dropwise and the reaction mixture was stirred for another 12 h at room temperature. The reaction was quenched by saturated aqueous solution of  $\text{NH}_4\text{Cl}$  and extracted with  $\text{Et}_2\text{O}$ . The combined organic phases were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/ $\text{EtOAc}$ ) to afford compound **35** (407 mg, 79% yield) as a colorless oil.  $R_f = 0.35$  (9:1 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 2986, 1758;  $[\alpha]_D^{25} +24^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  7.03 (d,  $J = 15.8$  Hz, 1H), 6.19 (dd,  $J = 13.9, 8.9$  Hz, 1H), 5.91 (d,  $J = 15.6$  Hz, 1H), 5.30 (d,  $J = 13.6$  Hz, 1H), 4.78 (td,  $J = 9.4, 3.7$  Hz, 1H), 4.21-4.14 (m, 2H), 3.76 (dd,  $J = 8.1, 1.7$  Hz, 1H), 2.14-2.05 (m, 1H), 1.87-1.79 (m, 1H), 1.36 (s, 3H), 1.26 (s, 12 H), 1.28 (t,  $J = 7.2$  Hz, 3H), 0.96 (dt,  $J = 8.2, 7.7$  Hz, 18H), 0.86 (s, 9H), 0.73-0.56 (m, 12H), 0.06 (s, 3H), 0.00 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  166.9, 157.7, 153.0, 119.7, 83.2, 78.2, 75.4, 69.0, 60.2, 42.0, 26.9 (3C), 25.9 (2C), 24.9 (2C), 24.6, 24.2, 21.2, 17.9, 14.2, 7.2 (3C), 7.1 (3C), 6.74 (3C), 5.60 (3C), -3.0, -4.0; HRMS (CI) calcd for  $[\text{C}_{36}\text{H}_{73}\text{BO}_7\text{Si}_3 + \text{Na}]^+$ : 735.4649, Found: 735.4648.

#### Intermediates related to Scheme 7:





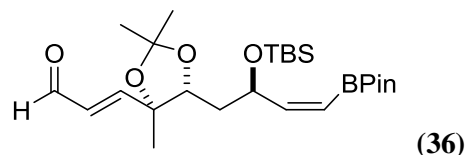
**(2*E*,4*S*,5*R*,7*R*,8*Z*)-4-methyl-9-(3,3,4,4-tetramethylborolan-1-yl)nona-2,8-diene-1,3-dioxolan-7-*tert*-butyldimethylsiloxyol (49)**



To a solution of ester **34** (65 mg, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was dropwise added diisobutylaluminum hydride (*i*-Bu)<sub>2</sub>AlH (1.0 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.31 mL, 0.31 mmol) at –78 °C under an argon atmosphere. After stirring for 30 min at –78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 30 min. Then the reaction mixture was diluted with Et<sub>2</sub>O and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 5 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with Et<sub>2</sub>O. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the primary alcohol **49** (49 mg, 82% yield) as a colorless oil. *R*<sub>f</sub> = 0.32 (4:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3427, 2982; [α]<sub>D</sub><sup>25</sup> –7° (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 6.30 (dd, *J* = 13.2, 7.8 Hz, 1H), 5.9 (ddd, *J* = 15.6, 5.4, 5.4 Hz, 1H), 5.71 (ddd, *J* = 16.2, 1.8, 1.2 Hz, 1H), 5.32 (dd, *J* = 13.8, 0.6 Hz, 1H), 5.21–5.02 (m, 2H), 4.14 (dd, *J* = 5.4, 4.8 Hz, 1H), 3.98 (dd, *J* = 10.2, 2.4 Hz, 1H), 1.56–1.44 (m, 2H), 1.42 (s, 3H), 1.34 (s, 3H), 1.26 (s, 12H), 1.41 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), 0.01 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz): δ 157.3, 134.4, 129.2, 107.2, 83.2, 81.4, 78.5, 69.5, 63.3, 37.7, 28.5, 26.8, 25.9 (3C), 24.9 (2C), 24.8 (2C), 21.0,

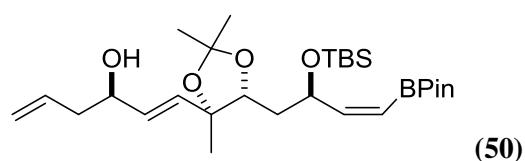
18.2, -4.3, -4.9; HRMS (CI) calcd for  $[C_{25}H_{47}BO_6Si + Na]^+$ : 505.3127, Found: 505.2984.

**(2E,4S,5R,7R,8Z)-1,3-dioxolan-7-tert-butyldimethylsiloxy-4-methyl-9-(3,3,4,4-tetramethylborolan-1-yl)nona-2,8-dienal (36)**



To a solution of primary alcohol **49** (28 mg, 0.058 mmol) in 1 mL of  $CH_2Cl_2$  was added  $MnO_2$  (51 mg, 0.58 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4 h and then filtered through a pad of celite and washed with  $Et_2O$ . The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/ $EtOAc$ ) to afford the enal **36** (24 mg, 86% yield) as a colorless oil.  $R_f = 0.60$  (7:3 (v/v) hexane/ $EtOAc$ ); IR (neat,  $cm^{-1}$ ): 3427, 2982, 1680;  $[\alpha]_D^{25} -15^\circ$  (c 1.0,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , 270 MHz):  $\delta$  9.57 (d,  $J = 7.7$  Hz, 1H), 6.74 (d,  $J = 15.6$  Hz, 1H), 6.36 (dd,  $J = 15.8, 7.4$  Hz, 1H), 6.30 (dd,  $J = 13.8, 5.9$  Hz, 1H), 5.36 (d,  $J = 13.8$  Hz, 1H), 5.04 (td,  $J = 9.2, 3.0$  Hz, 1H), 4.06 (dd,  $J = 10.2, 2.0$  Hz, 1H), 1.61-1.54 (m, 2H), 1.46 (s, 3H), 1.36 (s, 12H), 1.26 (s, 12H), 1.22 (s, 3H), 0.85 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H);  $^{13}C$  NMR ( $CDCl_3$ , 67.5 MHz):  $\delta$  194.3, 158.6, 157.2, 130.7, 108.2, 83.2, 81.7, 69.3, 37.9, 28.6, 26.4, 25.8 (3C), 24.9 (2C), 24.8 (2C), 21.1, 20.7, -4.3, -4.9; HRMS (CI) calcd for  $[C_{25}H_{45}BO_6Si + Na]^+$ : 503.2970, Found: 503.2972.

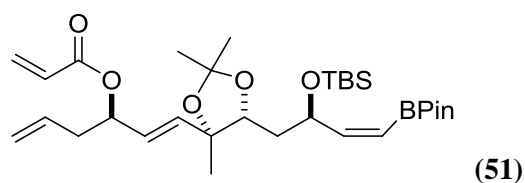
**(1Z,3R,5R,6S,7E,9R)-6-methyl-1-(3,3,4,4-tetramethylborolan-1-yl)dodeca-1,7,11-triene-3-tert-butyldimethylsiloxy-1,3-dioxolan-9-ol (50)**



To a solution of Leighton allylsilane reagent (*R,R*)-**17** (72 mg, 0.13 mmol) in 0.3 mL of  $CH_2Cl_2$  was dropwise added enal **36** (21 mg, 0.044 mmol) in 0.4 mL of  $CH_2Cl_2$  at  $-10$

°C. The reaction was stirred  $-10\text{ }^{\circ}\text{C}$  at for 36 h, then diluted with EtOAc and quenched by adding 1 N NaHSO<sub>4</sub>. The reaction mixture was vigorously stirred at room temperature for 1 h, then filtered through a pad of celite, and the filtrate was extracted with EtOAc. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the allylic alcohol **50** (38 mg, 86% yield) as a light yellow oil.  $R_f = 0.30$  (9:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 3450, 2981, 1755;  $[\alpha]_D^{25} +9^{\circ}$  ( $c$  1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  6.19 (dd,  $J = 13.2, 8.4$  Hz, 1H), 5.83-5.76 (m, 2H), 5.70 (dd,  $J = 15.6$  Hz, 1H), 5.33 (d,  $J = 13.8$  Hz, 1H), 5.14 (d,  $J = 8.4$  Hz, 1H), 5.11 (s, 1H), 5.03 (td,  $J = 10.2, 2.4$  Hz, 1H), 4.18 (d,  $J = 5.4$  Hz, 1H), 3.98 (d,  $J = 9.6$  Hz, 1H), 2.34 (ddd,  $J = 13.8, 6.6, 6.0$  Hz, 1H), 2.27 (ddd,  $J = 14.4, 7.8, 7.2$  Hz, 1H), 1.53-1.46 (m, 1H), 1.43 (s, 3H), 1.35 (s, 3H), 1.27 (s, 12H), 1.13 (s, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta$  157.3, 134.1, 133.9, 131.9, 118.2, 107.2, 83.1, 81.4, 78.5, 71.2, 69.5, 41.9, 37.8, 28.5, 26.7, 25.9 (3C), 24.9 (2C), 24.7 (2C), 21.2, 18.2,  $-4.3, -4.9$ ; HRMS (CI) calcd for [C<sub>28</sub>H<sub>51</sub>BO<sub>6</sub>Si + Na]<sup>+</sup>: 545.3440, Found: 545.3443.

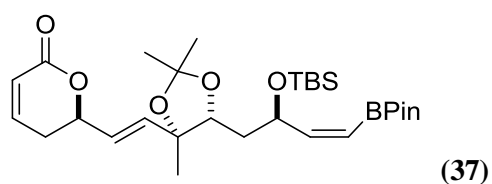
**(4R,5E,7S,8R,10R,11Z)-1,3-dioxolan-10-tert-butyl dimethylsiloxy-7-methyl-12-(3,3,4,4-tetramethyl-borolan-1-yl)dodeca-1,5,11-trien-4-yl acrylate (51)**



To a solution of allylic alcohol **50** (30 mg, 0.043 mmol) in 1.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added acrylic acid (15 mg, 0.21 mmol), DCC (43 mg, 0.21 mmol) and catalytic amount of DMAP (2 mg, 0.016 mmol). The reaction was stirred at room temperature for 3 h, then diluted with Et<sub>2</sub>O and filtered through a pad of celite. The filtrate was extracted with Et<sub>2</sub>O, and the combined organic phases were washed with saturated aqueous solution of NaHSO<sub>4</sub>, saturated aqueous solution of NaHCO<sub>3</sub>, brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by column chromatography

(silica gel, 9:1 (v/v) hexane/EtOAc) to afford the ester **51** (25 mg, 77% yield) as a colorless oil.  $R_f = 0.50$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2987, 1736;  $[\alpha]_D^{25} +12^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  6.38 (dd,  $J = 17.4, 1.2$  Hz, 1H), 6.32 (dd,  $J = 13.8, 8.4$  Hz, 1H), 6.10 (dd,  $J = 16.8, 10.2$  Hz, 1H), 5.80 (dd,  $J = 10.2, 1.2$  Hz, 1H), 5.76-5.70 (m, 3H), 5.40 (dd,  $J = 6.0, 6.0$  Hz, 1H), 5.33 (d,  $J = 13.8$  Hz, 1H), 5.10-5.03 (m, 3H), 3.97 (dd,  $J = 10.8, 2.4$  Hz, 1H), 2.41 (dd,  $J = 6.6, 6.6$  Hz, 2H), 1.49 (ddd,  $J = 21.6, 10.2, 3.0$  Hz, 2H), 1.43 (s, 3H), 1.34 (s, 3H), 1.27 (s, 12H), 1.12 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  187.4, 136.3, 133.0, 130.5, 128.8, 127.0, 118.1, 107.3, 83.2, 81.4, 78.4, 73.2, 69.4, 39.1, 37.9, 29.7, 28.5, 26.5, 25.9 (3C), 24.9 (2C), 24.8 (2C), 21.4, 18.1, -4.3, -4.9; HRMS (CI) calcd for  $[\text{C}_{31}\text{H}_{53}\text{BO}_7\text{Si} + \text{Na}]^+$ : 599.3546, Found: 599.3573.

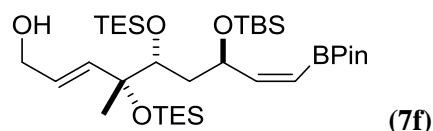
**(R)-5,6-dihydro-6-((1E,3S,4R,6R,7Z)-1,3-dioxolan-6-tert-butyldimethylsiloxy-3-methyl-8-(3,3,4,4-tetramethylborolan-1-yl)octa-1,7-dienyl)pyran-2-one (37)**



To a solution of ester **51** (14 mg, 0.024 mmol) in 2.5 mL of  $\text{CH}_2\text{Cl}_2$  was added Grubbs catalyst **29** (4 mg, 0.005 mmol, 20 mol %). The reaction was refluxed for 3 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the lactone **37** (10 mg, 76% yield) as a colorless oil.  $R_f = 0.25$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2930, 1731;  $[\alpha]_D^{25} +32^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  6.86 (ddd,  $J = 9.0, 5.4, 3.0$  Hz, 1 H), 6.32 (dd,  $J = 13.8, 8.4$  Hz, 1H), 6.05 (ddd,  $J = 9.6, 1.2, 1.2$  Hz, 1H), 5.88 (dd,  $J = 15.6, 4.8$  Hz, 1H), 5.84 (d,  $J = 16.2$  Hz, 1H), 5.34 (d,  $J = 13.8$  Hz, 1H), 5.03 (ddd,  $J = 9.6, 3.6, 3.0$  Hz, 1H), 4.94 (ddd,  $J = 9.6, 4.8, 4.8$  Hz, 1H), 3.98 (dd,  $J = 10.2, 2.4$  Hz, 1H), 2.45-2.41 (m, 2H), 1.52-1.46 (m, 2H), 1.44 (s, 3H), 1.35 (s, 3H), 1.28 (s, 12H), 1.15 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  163.8, 157.3, 144.4, 136.5, 126.4, 121.7, 107.3, 83.2, 81.3, 78.4, 77.3, 69.4, 39.1, 37.7,

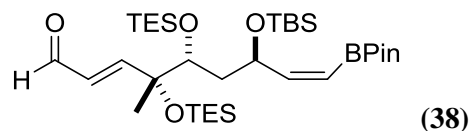
29.8, 28.5, 26.6, 25.9 (3C), 24.9 (2C), 24.8 (2C), 21.1, 18.1, -4.3, -5.0; HRMS (CI) calcd for  $[C_{29}H_{49}BO_7Si + Na]^+$ : 571.3233, Found: 571.3205.

**(2E,4R,5R,7R,8Z)-4,5-bistriethylsilyl-7-tert-butyldimethylsilyl-4-methyl-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-2,8-dien-1-ol (7f)**



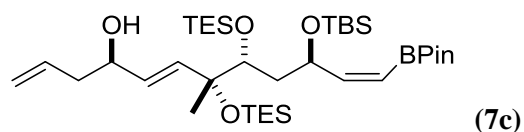
To a solution of ester **35** (140 mg, 0.20 mmol) in  $CH_2Cl_2$  (2 mL) was dropwise added diisobutylaluminum hydride (*i*-Bu) $_2$ AlH (1.0 M in  $CH_2Cl_2$ , 0.45 mL, 0.45 mmol) at -78 °C under an argon atmosphere. After stirring for 30 min at -78 °C, the reaction mixture was allowed warming up to 0 °C and kept stirring for 30 min. Then the reaction mixture was diluted with  $Et_2O$  and was quenched with saturated aqueous solution of potassium sodium tartrate (Rochelle's salt, 10 mL). The biphasic mixture was stirred until two layers separated once stopped stirring. The aqueous layer was extracted with  $Et_2O$ . The combined organic phases were washed with brine, dried over  $Na_2SO_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 4:1 (v/v) hexane/ $EtOAc$ ) to afford the primary alcohol **7f** (123 mg, 92% yield) as a colorless oil.  $R_f$  = 0.33 (4:1 (v/v) hexane/ $EtOAc$ ); IR (neat,  $cm^{-1}$ ): 3427, 2982;  $[\alpha]_D^{25} +4^\circ$  (*c* 1.0,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , 270 MHz):  $\delta$  6.19 (dd,  $J = 13.9, 8.9$  Hz, 1H), 5.77-5.74 (m, 2H), 5.31 (d,  $J = 13.9$  Hz, 1H), 4.76 (td,  $J = 9.4, 4.2$  Hz, 1H), 4.15 (bs, 2H), 3.76 (dd,  $J = 7.4, 2.0$  Hz, 1H), 1.82 (ddd,  $J = 14.1, 9.4, 2.2$  Hz, 1H), 1.30 (s, 3H), 1.27 (s, 6 H), 1.26 (s, 6 H), 0.96 (dt,  $J = 8.2, 7.7$  Hz, 18H), 0.86 (s, 9H), 0.72-0.53 (m, 12H), 0.07 (s, 3H), 0.01 (s, 3H);  $^{13}C$  NMR ( $CDCl_3$ , 67.5 MHz):  $\delta$  157.8, 137.1, 128.1, 83.3 (3C), 77.9, 75.8, 69.4, 63.8, 42.4, 26.1 (3C), 25.0 (2C), 24.7 (2C), 23.4, 18.3, 7.3 (3C), 7.2 (3C), 6.9 (3C), 5.7 (3C), -2.9, -3.9; HRMS (CI) calcd for  $[C_{34}H_{71}BO_6Si_3 + Na]^+$ : 693.4544, Found: 693.4549.

**(2E,4R,5R,7R,8Z)-4,5-bistriethylsilyl-7-tert-butyldimethylsilyl-4-methyl-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-2,8-dienal (38)**



To a solution of primary alcohol **7f** (30 mg, 0.045 mmol) in 1 mL of CH<sub>2</sub>Cl<sub>2</sub> was added MnO<sub>2</sub> (39 mg, 0.45 mmol) at room temperature. The reaction mixture was stirred at room temperature for 4 h and then filtered through a pad of celite and washed with Et<sub>2</sub>O. The filtrate was concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the enal **38** (25 mg, 78% yield) as a colorless oil.  $R_f = 0.45$  (9:1 (v/v) hexane/EtOAc); IR (neat, cm<sup>-1</sup>): 3427, 2982, 1680;  $[\alpha]_D^{25} +43^\circ$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 9.56 (d, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 6.25 (dd, *J* = 15.6, 7.9 Hz, 1H), 6.18 (dd, *J* = 13.9, 9.2 Hz, 1H), 5.31 (d, *J* = 13.9 Hz, 1H), 4.76 (td, *J* = 9.6, 3.7 Hz, 1H), 3.83 (dd, *J* = 8.4, 1.5 Hz, 1H), 1.88 (ddd, *J* = 14.3, 10.2, 2.4 Hz, 1H), 1.42 (s, 3H), 1.26 (s, 12H), 0.98 (t, *J* = 8.2 Hz, 9H), 0.95 (t, *J* = 7.4 Hz, 9H), 0.87 (s, 9H), 0.76-0.56 (m, 12H), 0.07 (s, 3H), 0.02 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 67.5 MHz): δ 194.0, 162.7, 157.5, 130.7, 83.2, 78.3, 75.5, 68.8, 41.8, 26.1 (3C), 24.9, 24.6, 18.2, 7.2 (3C), 7.1 (3C), 6.8 (3C), 5.6 (3C), -2.9, -3.9; HRMS (CI) calcd for [C<sub>34</sub>H<sub>69</sub>BO<sub>6</sub>Si<sub>3</sub> + Na]<sup>+</sup>: 691.4387, Found: 691.4393.

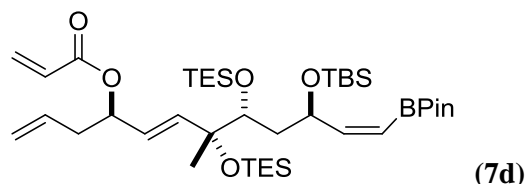
**(1Z,3R,5R,6R,7E,9R)-4,5-bistriethylsilyl-7-tert-butyltrimethylsilyl-6-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodeca-1,7,11-trien-1-ol (7h)**



To a solution of Leighton allylsilane reagent (*R,R*)-**17** (102 mg, 0.19 mmol) in 0.3 mL of CH<sub>2</sub>Cl<sub>2</sub> was dropwise added enal **38** (42 mg, 0.063 mmol) in 0.4 mL of CH<sub>2</sub>Cl<sub>2</sub> at -10 °C. The reaction was stirred -10 °C at for 36 h, then diluted with EtOAc and quenched by adding 1 N NaHSO<sub>4</sub>. The reaction mixture was vigorously stirred at room temperature for 1 h, then filtered through a pad of celite, and the filtrate was extracted with EtOAc. The combined organic phases were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was purified by

column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the allylic alcohol **7h** (38 mg, 85% yield) as a light yellow oil.  $R_f = 0.30$  (9:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 3450, 2981, 1755;  $[\alpha]_D^{25} +9^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz):  $\delta$  6.19 (dd,  $J = 13.8, 9.2$  Hz, 1H), 5.87-5.73 (m, 2H), 5.60 (dd,  $J = 15.8, 6.2$  Hz, 1H), 5.30 (d,  $J = 13.9$  Hz, 1H), 5.16-5.09 (m, 2H), 4.76 (td,  $J = 9.4, 3.7$  Hz, 1H), 4.18 (dd,  $J = 6.2, 5.9$  Hz, 1H), 3.71 (dd,  $J = 7.7, 1.5$  Hz, 1H), 2.37-2.25 (m, 2H), 1.83 (ddd,  $J = 14.1, 9.6, 1.7$  Hz, 1H), 1.10-1.21 (m, 1H), 1.30 (s, 3H), 1.26 (s, 6H), 1.25 (s, 6H), 0.97 (t,  $J = 8.2$  Hz, 9H), 0.95 (t,  $J = 7.4$  Hz, 9H), 0.87 (s, 9H), 0.69 (q,  $J = 8.2$  Hz, 6H), 0.58 (q,  $J = 7.9$  Hz, 6H), 0.08 (s, 3H), 0.01 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 67.5 MHz):  $\delta$  157.8, 135.9, 134.3, 131.1, 118.0, 83.1, 77.8, 75.7, 71.6, 69.3, 42.3, 41.7 (3C), 26.0 (3C), 24.9 (2C), 24.6 (2C), 23.5, 18.2, 7.3 (3C), 7.2 (3C), 6.8 (3C), 5.6 (3C), -2.9, -4.1; HRMS (CI) calcd for  $[\text{C}_{37}\text{H}_{75}\text{BO}_6\text{Si}_3 + \text{Na}]^+$ : 733.4857, Found: 733.4855.

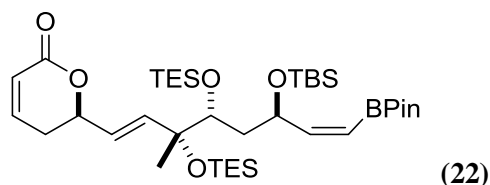
**(4R,5E,7R,8R,10R,11Z)-7,8-bistriethylsilyl-10-tert-butyl dimethylsilyl-7-methyl-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodeca-1,5,11-trien-4-ylacrylate**  
(**7i**)



To a solution of allylic alcohol **7h** (30 mg, 0.043 mmol) in 1.5 mL of  $\text{CH}_2\text{Cl}_2$  was added acrylic acid (15 mg, 0.21 mmol), DCC (43 mg, 0.21 mmol) and catalytic amount of DMAP (2 mg, 0.016 mmol). The reaction was stirred at room temperature for 3 h, then diluted with  $\text{Et}_2\text{O}$  and filtered through a pad of celite. The filtrate was extracted with  $\text{Et}_2\text{O}$ , and the combined organic phases were washed with saturated aqueous solution of  $\text{NaHSO}_4$ , saturated aqueous solution of  $\text{NaHCO}_3$ , brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) to afford the ester **7i** (25 mg, 76% yield) as a colorless oil.  $R_f = 0.50$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2987, 1736;  $[\alpha]_D^{25} +10^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  6.37 (dd,  $J = 17.4, 1.2$  Hz, 1H),

6.18 (dd,  $J = 13.8, 9.0$  Hz, 1H), 6.09 (dd,  $J = 17.4, 10.2$  Hz, 1H), 5.80 (dd,  $J = 15.6, 10.8$  Hz, 2H), 5.76-5.70 (m, 1H), 5.59 (dd,  $J = 15.6, 6.6$  Hz, 1H), 5.41 (dd,  $J = 6.6, 6.0$  Hz, 1H), 5.29 (d,  $J = 13.8$  Hz, 1H), 5.08-5.03 (m, 2H), 3.96 (dt,  $J = 9.6, 3.6$  Hz, 1H), 3.70 (dd,  $J = 7.8, 1.2$  Hz, 1H), 3.21-3.17 (m, 1H), 2.42 (dd,  $J = 6.6, 6.6$  Hz, 1H), 1.92-1.90 (m, 1H), 1.75-1.73 (m, 1H), 1.29 (s, 3H), 1.26 (s, 6H), 1.25 (s, 6H), 0.96 (t,  $J = 7.8$  Hz, 9H), 0.92 (t,  $J = 8.4$  Hz, 9H), 0.87 (s, 9H), 0.67 (qd,  $J = 7.8, 2.4$  Hz, 24 6H), 0.56 (q,  $J = 7.8$  Hz, 6H), 0.07 (s, 3H), 0.01 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  165.2, 157.9, 137.8, 133.2, 130.2, 128.8, 126.6, 117.9, 83.1, 77.8, 75.7, 73.4, 69.1, 55.7, 42.2, 39.1, 34.9 (3C), 26.1, 25.5 (3C), 24.9 (2C), 24.7 (2C), 24.6, 18.2, 7.2 (3C), 7.1 (3C), 6.8 (3C), 5.7 (3C), -2.9, -4.1; HRMS (CI) calcd for  $[\text{C}_{40}\text{H}_{77}\text{BO}_7\text{Si}_3 + \text{Na}]^+$ : 787.4962, Found: 787.4961.

**(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*)-3,4-bistriethylsilyl-6-*tert*-butyldimethylsilyl-3-methyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octa-1,7-dienyl)pyran-2-one (22)**



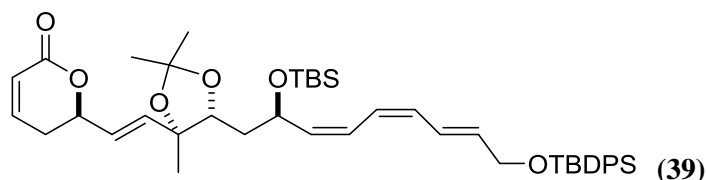
To a solution of ester **7d** (25 mg, 0.032 mmol) in 3.5 mL of  $\text{CH}_2\text{Cl}_2$  was added Grubbs catalyst **29** (6 mg, 0.007 mmol, 20 mol %). The reaction was refluxed for 3 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 4:1 (v/v) hexane/EtOAc) to afford the lactone **22** (20 mg, 82% yield) as a colorless oil.  $R_f = 0.35$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $\text{cm}^{-1}$ ): 2930, 1731;  $[\alpha]_D^{25} +32^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  6.86 (ddd,  $J = 8.4, 3.6, 1.2$  Hz, 1 H), 6.20 (dd,  $J = 13.8, 9.6$  Hz, 1H), 6.04 (ddd,  $J = 9.6, 1.8, 1.8$  Hz, 1H), 5.91 (dd,  $J = 15.6, 1.2$  Hz, 1H), 5.72 (dd,  $J = 15.6, 6.0$  Hz, 1H), 5.30 (dd,  $J = 13.8, 1.2$  Hz, 1H), 4.92 (ddd,  $J = 6.6, 6.0, 1.2$  Hz, 1H), 4.79 (dd,  $J = 9.6, 3.6$  Hz, 1H), 3.72 (dd,  $J = 9.6, 1.8$  Hz, 1H), 2.43-2.41 (m, 2H), 1.84 (ddd,  $J = 14.4, 10.2, 1.8$  Hz, 1H), 1.33 (s, 3H), 1.27 (s, 6H), 1.26 (s, 6H), 1.05 (m, 1H), 0.97 (dd,  $J = 8.4, 7.8$  Hz, 9H), 0.92 (dd,  $J = 8.4,$



7.8 Hz, 9H), 0.87 (s, 9H), 0.67 (qd,  $J = 8.4, 4.2$  Hz, 6H), 0.59 (q,  $J = 7.8$  Hz, 6H), 0.08 (s, 3H), 0.02 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  164.0, 157.8, 144.4, 138.9, 125.5, 121.7, 83.2, 77.9, 77.7, 75.6, 69.1, 42.1, 29.8 (3C), 26.1 (3C), 24.9 (2C), 24.6 (2C), 24.4, 18.2, 7.3 (3C), 7.2 (3C), 6.9 (3C), 5.7 (3C), -2.9, -4.0; HRMS (CI) calcd for  $[\text{C}_{38}\text{H}_{73}\text{BO}_7\text{Si}_3 + \text{Na}]^+$ : 759.4649, Found: 759.4648.

### Compounds in Scheme 8:

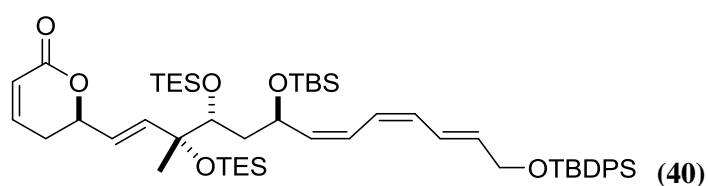
**(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*,9*Z*,11*E*)-1,3-dioxolan-6-*tert*-butyldimethylsiloxy-13-*tert*-butyldiphenylsiloxy-3-methyltrideca-1,7,9,11-tetraenyl)pyran-2-one (39)**



To a suspension of  $\text{Ag}_2\text{O}$  aqueous (8 mg, 0.030 mmol) in 1 mL of THF was added *Z*-vinylboronate **37** (8 mg, 0.015 mmol) in 0.5 mL of THF at room temperature. In 2 min, a solution of iodide **20b** (20 mg, 0.045 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (4 mg, 0.003 mmol) in 0.5 mL of THF was added. The mixture was stirred at 65 °C for 1.5 h, then cooled down to room temperature, diluted with  $\text{Et}_2\text{O}$ , and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 1:4 (v/v) hexane/ $\text{EtOAc}$ ) to afford the triene **39** (8 mg, 77% yield) as a colorless oil.  $R_f = 0.30$  (1:4 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 3407, 2981, 1742;  $[\alpha]_D^{25} +19^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  7.69-7.68 (m, 4H), 7.44-7.36 (m, 6H), 6.87 (ddd,  $J = 9.0, 8.4, 3.0$  Hz, 1H), 6.77 (dd,  $J = 13.8, 12.0$  Hz, 1H), 6.35 (dd,  $J = 12.0, 11.4$  Hz, 1H), 6.24 (dd,  $J = 10.8, 12.0$  Hz, 1H), 6.09 (d,  $J = 10.8$  Hz, 1H), 6.06-6.04 (m, 1H), 5.88 (dd,  $J = 15.6, 5.4$  Hz, 1H), 5.86-5.82 (m, 2H), 5.45 (dd,  $J = 10.2, 9.6$  Hz, 1H), 4.95 (ddd,  $J = 10.2, 4.8, 4.8$  Hz, 1H), 4.78 (td,  $J = 9.0, 4.8$  Hz, 1H), 4.30 (d,  $J = 3.6$  Hz, 1H), 4.03 (dd,  $J = 9.0, 3.0$  Hz, 1H), 2.46-2.36 (m, 4H), 1.54-1.51 (m, 1H), 1.47 (s, 3H), 1.36 (s, 3H), 1.15 (s, 3H), 1.08 (s, 9H), 0.88 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  163.0, 144.4, 136.3, 135.9, 135.5 (2C), 134.3,

133.6, 130.1, 129.7 (2C), 128.3, 127.7 (2C), 126.6, 124.5, 123.4, 122.4, 121.7, 107.7, 81.2, 78.4, 77.3, 65.7, 64.2, 60.4, 37.7, 31.6, 29.8, 28.5, 26.8 (3C), 26.7, 25.9, 22.6, 21.0, 20.9, 19.3, 18.1, 14.2, 14.1, -4.2, -5.0; HRMS (CI) calcd for  $[C_{44}H_{62}O_6Si_2 + Na]^+$ : 765.3977, Found: 765.3981.

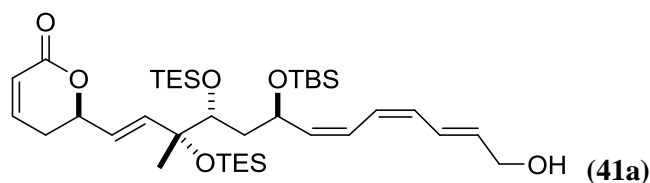
**(R)-5,6-dihydro-6-((1E,3R,4R,6R,7Z,9Z,11E)-3,4-bistriethylsilyl-6-tert-butyl dimethylsilyl-13-tert-butyl diphenylsilyl-3-methyltrideca-1,7,9-11-tetraenyl)pyran-2-one (40)**



To a solution of  $Pd_2(dba)_3 \cdot CHCl_3$  (2 mg, 0.0019 mmol) in 0.5 mL of THF was added  $PPh_3$  (4mg, 0.015 mmol) at room temperature. The color changed from dark red to light yellow, then the solution was added to a flask containing iodide **20b** (13 mg, 0.029 mmol). After stirring for 2 min, the solution was added into the mixture of Z-vinylboronate **22** (7 mg, 0.0092 mmol) and  $Ag_2O$  (7 mg, 0.029 mmol) in 0.5 mL THF at room temperature. The reaction mixture was heated at 65 °C for 1.5 h, then cooled down to room temperature, diluted with  $Et_2O$ , and filtered through a pad of Celite. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, 9:1 (v/v) hexane/ $EtOAc$ ) to afford the triene **40** (8 mg, 80% yield) as a colorless oil.  $R_f = 0.15$  (9:1 (v/v) hexane/ $EtOAc$ ); IR (neat,  $cm^{-1}$ ): 2981, 1703;  $[\alpha]_D^{25} +22^\circ$  (c 0.6,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , 600 MHz):  $\delta$  7.69-7.60 (m, 4H), 7.44-7.36 (m, 6H), 6.85 (ddd,  $J = 9.6, 4.8, 3.6$  Hz, 1H), 6.75 (dd,  $J = 15.6, 11.4$  Hz, 1H), 6.30 (dd,  $J = 11.4, 11.4$  Hz, 1H), 6.20 (dd,  $J = 11.4, 11.4$  Hz, 1H), 6.06 (d,  $J = 11.4$  Hz, 1H), 6.04 (ddd,  $J = 9.6, 1.8, 1.8$  Hz, 1H), 5.87 (dd,  $J = 15.6, 1.2$  Hz, 1H), 5.83 (ddd,  $J = 15.0, 5.4, 5.4$  Hz, 1H), 5.75 (dd,  $J = 15.6, 6.6$  Hz, 1H), 5.42 (dd,  $J = 11.4, 9.0$  Hz, 1H), 4.93 (ddd,  $J = 15.6, 6.6, 1.2$  Hz, 1H), 4.69 (td,  $J = 9.0, 9.0, 3.0$  Hz, 1H), 4.29 (d,  $J = 3.6$  Hz, 1H), 3.70 (dd,  $J = 8.4, 1.8$  Hz, 1H), 2.43-2.41 (m, 3H), 1.90 (ddd,  $J = 14.4, 9.6, 1.8$  Hz, 2H), 1.33 (s, 3H), 1.08 (s, 9H), 1.00 (t,  $J = 8.4$  Hz, 9H),

0.96 (t,  $J = 8.4$  Hz, 9H), 0.88 (s, 9H), 0.68 (qd,  $J = 7.8, 2.4$  Hz, 6H), 0.68 (qd,  $J = 7.8, 1.2$  Hz, 6H), 0.05 (s, 3H), 0.04 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  164.1, 144.5, 138.5, 136.6, 135.5 (4C), 134.8, 134.1, 133.6, 129.7, 129.6, 128.4, 127.7 (4C), 125.9, 124.6, 123.6, 122.4, 121.7, 78.0, 77.6, 76.2, 66.0, 64.2, 42.5, 29.8, 26.8 (3C), 26.0 (3C), 24.7, 19.3, 18.1, 7.2 (3C), 7.2 (3C), 6.9 (3C), 5.8 (3C),  $-3.1, -4.1$ ; HRMS (CI) calcd for  $[\text{C}_{53}\text{H}_{86}\text{O}_6\text{Si}_4 + \text{Na}]^+$ : 953.5392, Found: 953.5395.

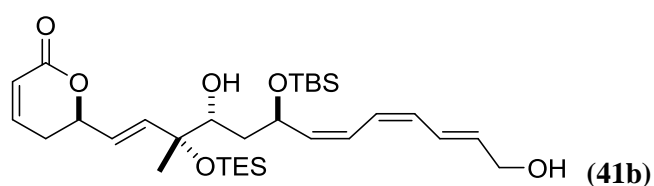
**(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*,9*Z*,11*E*)-3,4-bis(triethylsilyl)-6-*tert*-butyldimethylsilyl-13-hydroxy-3-methyltrideca-1,7,9-11-tetraenyl)pyran-2-one (41a)**



To a 5 mL solution of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{Pyridine}$ : 9/1/2, silyl ether **40** (10 mg, 0.011 mmol) was added, then dropwise addition of  $\text{HF}\cdot\text{pyridine}$  complex (15  $\mu\text{L}$ ) at room temperature. After stirring for 48 h, the reaction was diluted with  $\text{Et}_2\text{O}$  and quenched by saturated aqueous solution of  $\text{NaHCO}_3$ . The aqueous solution was extracted with  $\text{Et}_2\text{O}$ , and the combined organic phases were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 7:3 (v/v) hexane/ $\text{EtOAc}$ ) to afford the alcohol **41a** (3 mg, 40% yield) and the diol **41b** (3 mg, 45% yield). Both of these two compounds appeared as colorless oil.  $R_f = 0.52$  (1:1 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 3425, 2987, 1720;  $[\alpha]_D^{25} +45^\circ$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  6.86 (ddd,  $J = 9.0, 4.8, 3.6$  Hz, 1H), 6.73 (ddd,  $J = 15.0, 11.4, 1.2$  Hz, 1H), 6.37 (dd,  $J = 11.4, 11.4$  Hz, 1H), 6.24 (dd,  $J = 11.4, 11.4$  Hz, 1H), 6.06 (d,  $J = 11.4$  Hz, 1H), 6.04 (ddd,  $J = 9.6, 1.8, 1.8$  Hz, 1H), 5.91 (dd,  $J = 15.6, 6.0, 5.4$  Hz, 1H), 5.86 (dd,  $J = 15.6, 1.2$  Hz, 1H), 5.74 (dd,  $J = 15.6, 6.6$  Hz, 1H), 5.45 (dd,  $J = 10.2, 9.6$  Hz, 1H), 4.93 (ddd,  $J = 15.6, 6.0, 1.2$  Hz, 1H), 4.68 (td,  $J = 9.6, 9.6, 2.4$  Hz, 1H), 4.25 (d,  $J = 4.8$  Hz, 1H), 3.70 (dd,  $J = 8.4, 1.8$  Hz, 1H), 2.43-2.41 (m, 2H), 1.89 (ddd,  $J = 14.4, 10.2, 1.8$  Hz, 2H), 1.33 (s, 3H), 1.08 (ddd,  $J = 11.4, 8.4, 3.0$  Hz, 2H), 0.98 (t,  $J = 8.4$  Hz, 9H), 0.95 (t,  $J = 8.4$  Hz, 9H), 0.87 (s, 9H), 0.67 (qd,  $J = 7.8, 2.4$  Hz,

6H), 0.61 (qd,  $J = 7.8, 1.2$  Hz, 6H), 0.04 (s, 3H), 0.02 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  164.0, 144.5, 138.4, 137.1, 133.8, 129.4, 126.0, 125.9, 124.5, 122.2, 121.7, 77.9, 77.6, 76.2, 66.0, 63.4, 42.5, 29.7 (3C), 26.0 (3C), 24.7, 18.1, 13.3, 7.2 (3C), 7.2 (3C), 6.9 (3C), 5.8 (3C),  $-3.05, -4.10$ ; HRMS (CI) calcd for  $[\text{C}_{37}\text{H}_{68}\text{O}_6\text{Si}_3 + \text{Na}]^+$ : 715.4192, Found: 715.4215.

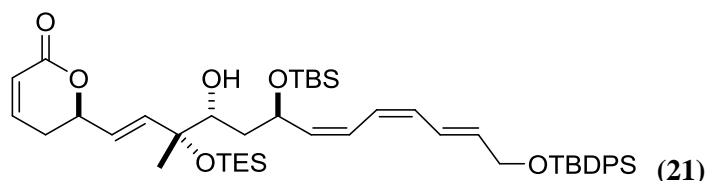
**(*R*)-5,6-dihydro-6-((1*E*,3*R*,4*R*,6*R*,7*Z*,9*Z*,11*E*)-3-triethylsilyl-6-*tert*-butyldimethylsilyl-4,13-hydroxy-3-methyltrideca-1,7,9-11-tetraenyl)pyran-2-one (**41b**)**



To a 0.6 mL solution of  $\text{CH}_3\text{CN}/\text{H}_2\text{O}/\text{Pyridine}$ : 9/1/2, silyl ether **41a** (6 mg, 0.008 mmol) was added, then dropwise addition of  $\text{HF}\cdot\text{pyridine}$  complex (12  $\mu\text{L}$ ) at room temperature. After stirring for 24 h, the reaction was diluted with  $\text{Et}_2\text{O}$  and quenched by saturated aqueous solution of  $\text{NaHCO}_3$ . The aqueous solution was extracted with  $\text{Et}_2\text{O}$ , and the combined organic phases were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, 7:3 (v/v) hexane/ $\text{EtOAc}$ ) to afford the diol **41b** (4 mg, 82% yield) as a colorless oil.  $R_f = 0.24$  (1:1 (v/v) hexane/ $\text{EtOAc}$ ); IR (neat,  $\text{cm}^{-1}$ ): 3420, 2980, 1715;  $[\alpha]_D^{25} -11^\circ$  ( $c$  0.4,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz):  $\delta$  6.88 (ddd,  $J = 9.0, 5.4, 3.6$  Hz, 1H), 6.73 (ddd,  $J = 15.0, 11.4, 1.2$  Hz, 1H), 6.38 (dd,  $J = 11.4, 11.4$  Hz, 1H), 6.20 (dd,  $J = 11.4, 11.4$  Hz, 1H), 6.06 (d,  $J = 10.8$  Hz, 1H), 6.04 (ddd,  $J = 9.6, 1.8, 1.8$  Hz, 1H), 5.91 (dd,  $J = 15.0, 6.0, 5.4$  Hz, 1H), 5.88 (dd,  $J = 16.2, 1.2$  Hz, 1H), 5.79 (dd,  $J = 15.6, 6.0$  Hz, 1H), 5.55 (dd,  $J = 10.2, 9.6$  Hz, 1H), 4.96 (ddd,  $J = 10.2, 6.0, 1.2$  Hz, 1H), 4.91 (td,  $J = 7.8, 7.8, 2.4$  Hz, 1H), 4.24 (dd,  $J = 4.8, 4.8$  Hz, 1H), 3.67 (dd,  $J = 11.4, 2.4$  Hz, 1H), 2.95 (d,  $J = 2.4$  Hz, 1H), 2.46-2.42 (m, 2H), 1.64 (dd,  $J = 13.8, 7.8$  Hz, 2H), 1.31 (s, 3H), 0.92 (t,  $J = 8.4$  Hz, 9H), 0.87 (s, 9H), 0.77 (q,  $J = 7.8$  Hz, 6H), 0.06 (s, 3H), 0.02 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  164.1, 144.6, 138.1, 136.3, 134.1, 129.8, 127.1, 126.2, 124.3, 122.3, 122.0, 77.8, 77.1, 75.1, 67.1, 63.6, 39.2, 29.8, 26.0 (3C),

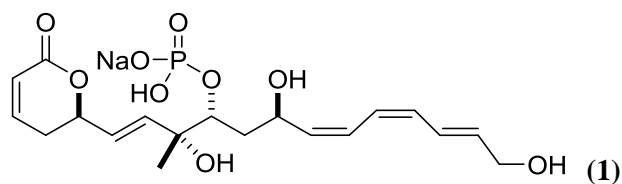
22.3, 18.3, 7.3 (3C), 6.9 (3C), -4.1, -4.9; HRMS (CI) calcd for  $[C_{31}H_{54}O_6Si_2 + Na]^+$ : 601.3392, Found: 601.3350.

**(R)-5,6-dihydro-6-((1E,3R,4R,6R,7Z,9Z,11E)-3-bistriethylsilyl-4-hydroxy-6-tert-butyl-13-tert-butyl-11-tetraenyl)pyran-2-one (21)**



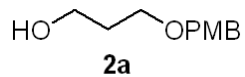
To a solution of diol **41b** (5 mg, 0.0083 mmol) in 0.2 mL of  $CH_2Cl_2$  was added imidazole (2 mg, 0.027 mmol) and TBDPSCl (3 mg, 0.012 mmol) at 0 °C. After stirring for 15 min at 0 °C, the reaction mixture was purified by chromatography (silica gel, 9:1 (v/v) hexane/EtOAc) without workup provided compound **21** (5 mg, 78% yield) as a yellow oil.  $R_f = 0.46$  (4:1 (v/v) hexane/EtOAc); IR (neat,  $cm^{-1}$ ): 3412, 2981, 1728;  $[\alpha]_D^{25} -18^\circ$  ( $c$  0.4,  $CHCl_3$ );  $^1H$  NMR ( $CDCl_3$ , 600 MHz):  $\delta$  7.69-7.67 (m, 4H), 7.44-7.33 (m, 6H), 6.88 (ddd,  $J = 8.4, 5.4, 3.6$  Hz, 1H), 6.75 (dd,  $J = 15.6, 11.4$  Hz, 1H), 6.33 (dd,  $J = 11.4, 11.4$  Hz, 1H), 6.15 (dd,  $J = 11.4, 11.4$  Hz, 1H), 6.07-6.03 (m, 2H), 5.89 (dd,  $J = 15.6, 1.2$  Hz, 1H), 5.83 (ddd,  $J = 15.6, 5.4, 5.4$  Hz, 1H), 5.80 (dd,  $J = 15.6, 6.0$  Hz, 1H), 5.53 (dd,  $J = 10.2, 9.6$  Hz, 1H), 4.98-4.91 (m, 2H), 4.29 (d,  $J = 4.2$  Hz, 2H), 3.68 (d,  $J = 10.8$  Hz, 1H), 2.99 (d,  $J = 2.4$  Hz, 1H), 2.46-2.43 (m, 2H), 1.64 (dd,  $J = 13.8, 7.8$  Hz, 1H), 1.33-1.37 (m, 1H), 1.32 (s, 3H), 1.08 (s, 9H), 0.93 (t,  $J = 7.8$  Hz, 9H), 0.88 (s, 9H), 0.57 (q,  $J = 7.8$  Hz, 6H), 0.07 (s, 3H), 0.04 (s, 3H);  $^{13}C$  NMR ( $CDCl_3$ , 150 MHz):  $\delta$  163.9, 144.3, 137.9, 135.5 (4C), 134.3, 133.6, 133.6, 130.1, 129.7 (2C), 127.7 (4C), 126.8, 124.5, 123.2, 122.3, 121.8, 77.6, 75.0, 67.0, 64.2, 39.0, 29.6 (3C), 26.8 (3C), 25.8 (3C), 22.2, 19.3, 18.1, 7.1 (3C), 6.7 (3C), -4.33, -5.07; HRMS (CI) calcd for  $[C_{47}H_{72}O_6Si_3 + Na]^+$ : 839.4492, Found: 839.4528.

**Fosriecin (1)**



To a solution of alcohol **21** (5 mg, 0.006 mmol) in 0.4 mL of pyridine was added  $\text{PCl}_3$  (4.1 mg, 0.03 mmol) at 0 °C and stirred for 15 min. 4-Methoxybenzyl alcohol (20.7 mg, 0.15 mmol) was added into the reaction mixture, and the reaction was gradually warmed to room temperature. After stirring at room temperature for 1 h, the reaction was diluted with 1.2 mL of  $\text{CH}_2\text{Cl}_2$ , then *tert*-Butyl hydroperoxide (5.5 M in decane, 55  $\mu\text{L}$ , 0.35 mmol) was added and stirred at room temperature for 1.5 h. The reaction was quenched by saturated aqueous solution of  $\text{NaHCO}_3$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic phases were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was treated with 48% HF-acetonitrile (1: 19, 0.3 mL) at room temperature for 15 min. After ice cooling, pyridine (95  $\mu\text{L}$ ) was added to the reaction mixture, and the mixture was stirred at room temperature for another 23 h. The reaction mixture was basified with saturated aqueous solution of  $\text{NaHCO}_3$ , extracted with  $\text{Et}_2\text{O}$ , and the combined organic solution was concentrated under reduced pressure. The residue was purified by 18-reversed phase column chromatography (silica gel, 9:1 (v/v)  $\text{H}_2\text{O}$ /acetonitrile) to afford the fostriecin **1** (0.5 mg, 31% yield) as a white solid.  $[\alpha]_D^{25} -325^\circ$  ( $c$  0.1,  $\text{D}_2\text{O}$ );  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ , 600 MHz):  $\delta$  7.03 (ddd,  $J = 10, 6, 3$  Hz, 1H), 6.70 (dd,  $J = 15, 12$  Hz, 1H), 6.49 (t,  $J = 11$  Hz, 1H), 6.29 (t,  $J = 12$  Hz, 1H), 6.09 (t,  $J = 11$  Hz, 1H), 5.96 (dd,  $J = 10, 2$  Hz, 1H), 5.92-5.84 (m, 3H), 5.50 (t,  $J = 10$  Hz, 1H), 5.06 (m, 1H), 4.88 (t,  $J = 9$  Hz, 1H), 4.12 (d,  $J = 6$  Hz, 2H), 4.10-4.06 (m, 1H), 2.56 (td,  $J = 19, 6$  Hz, 1H), 2.44-2.50 (m, 1H), 1.58 (t,  $J = 12$  Hz, 1H), 1.46 (m, 1H), 1.24 (s, 3H);  $^{13}\text{C NMR}$ : Data was not available due to lack of sample; HRMS (CI) calcd for  $[\text{C}_{19}\text{H}_{26}\text{NaO}_9\text{P} + \text{Na}]^+$ : 475.1104, Found: 475.1114.

**<sup>1</sup>H and <sup>13</sup>C NMR Spectra**



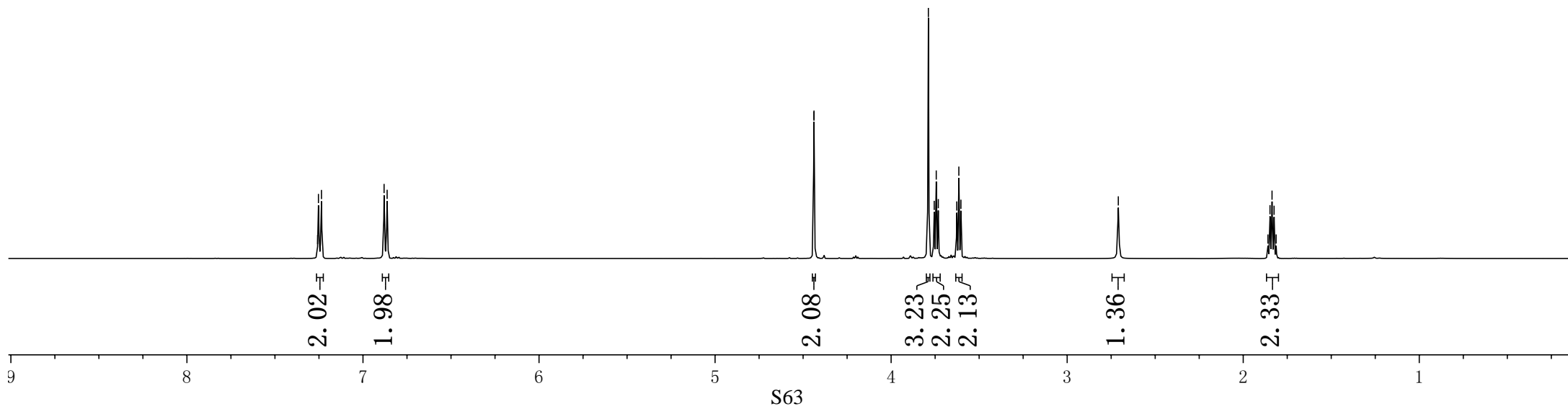
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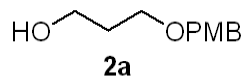
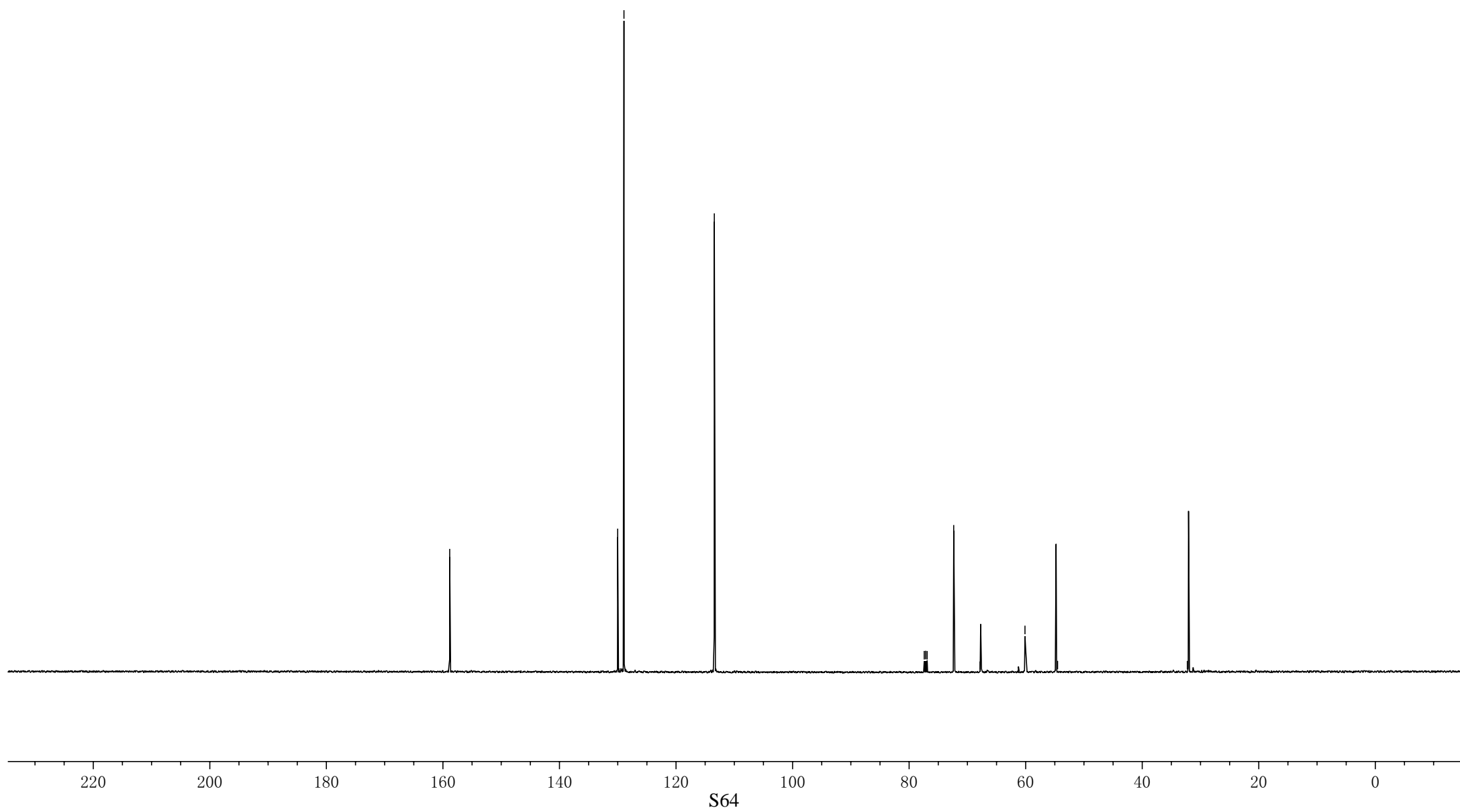
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2.7095

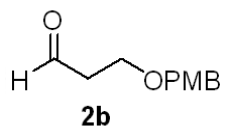
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<sup>1</sup>H NMR spectrum of **2a** (CDCl<sub>3</sub>, 500 Hz)



 $^{13}\text{C}$  NMR spectrum of **2a** ( $\text{CDCl}_3$ , 500 Hz)



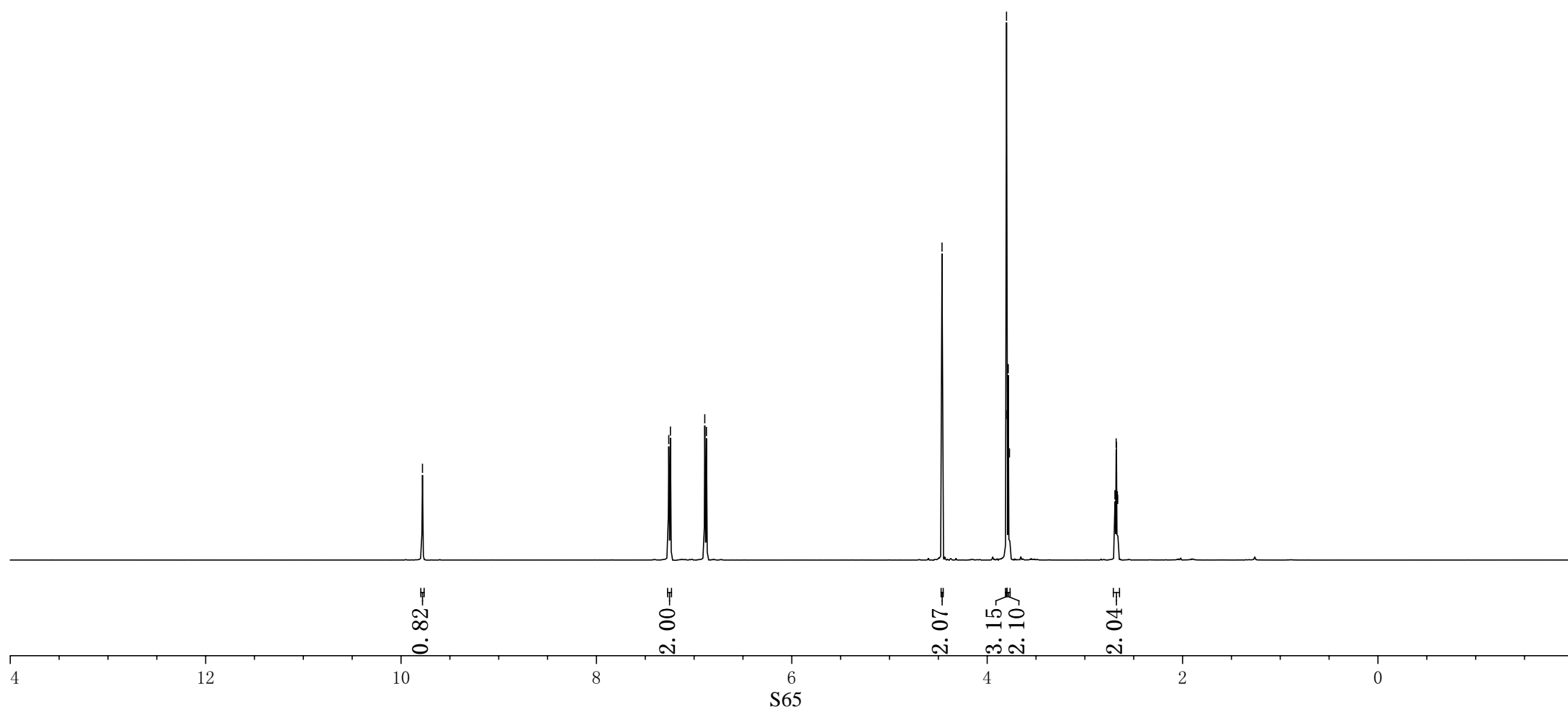


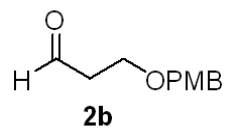
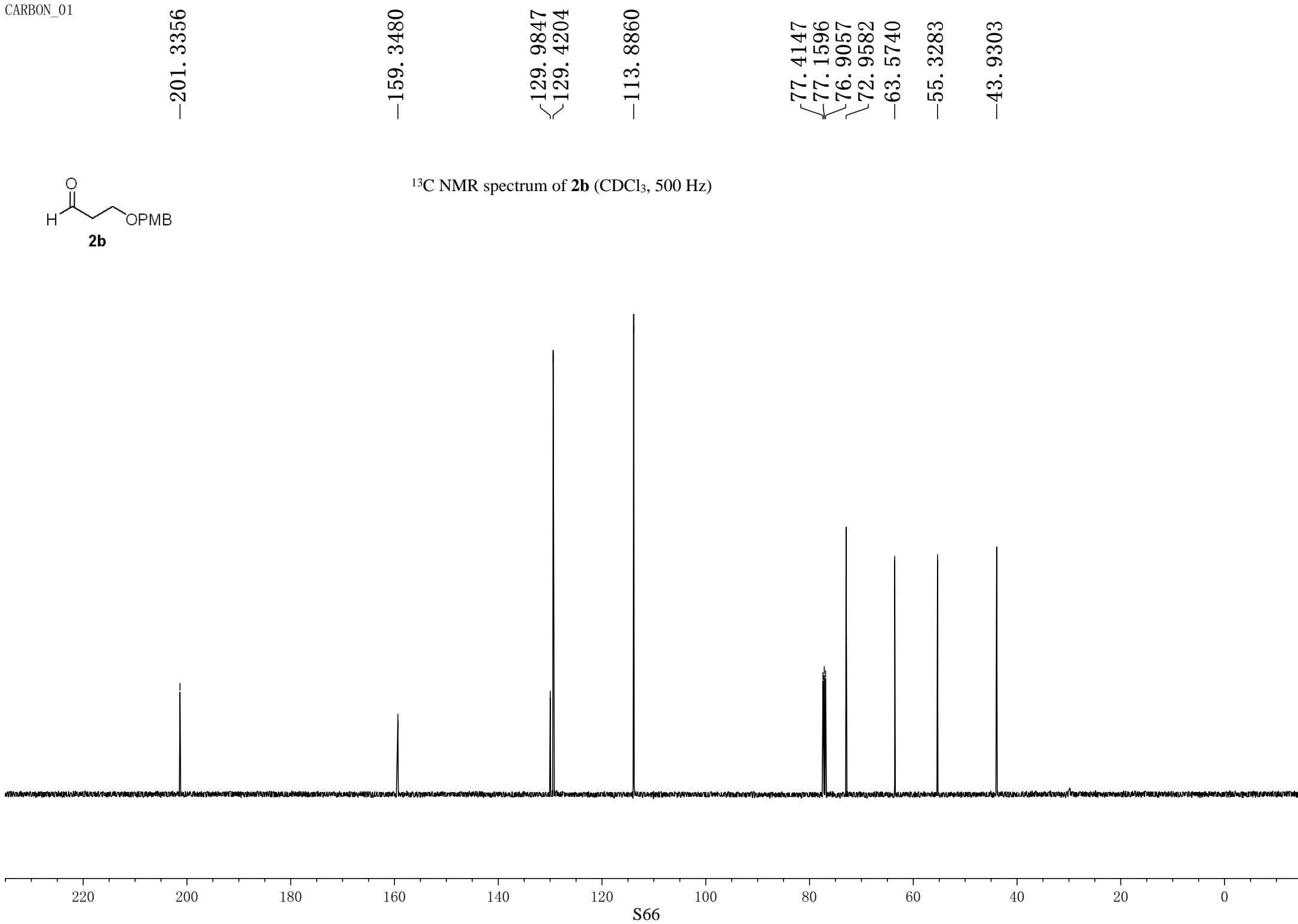
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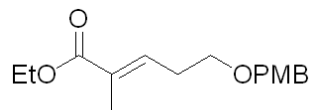
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<sup>1</sup>H NMR spectrum of **2b** (CDCl<sub>3</sub>, 500 Hz)

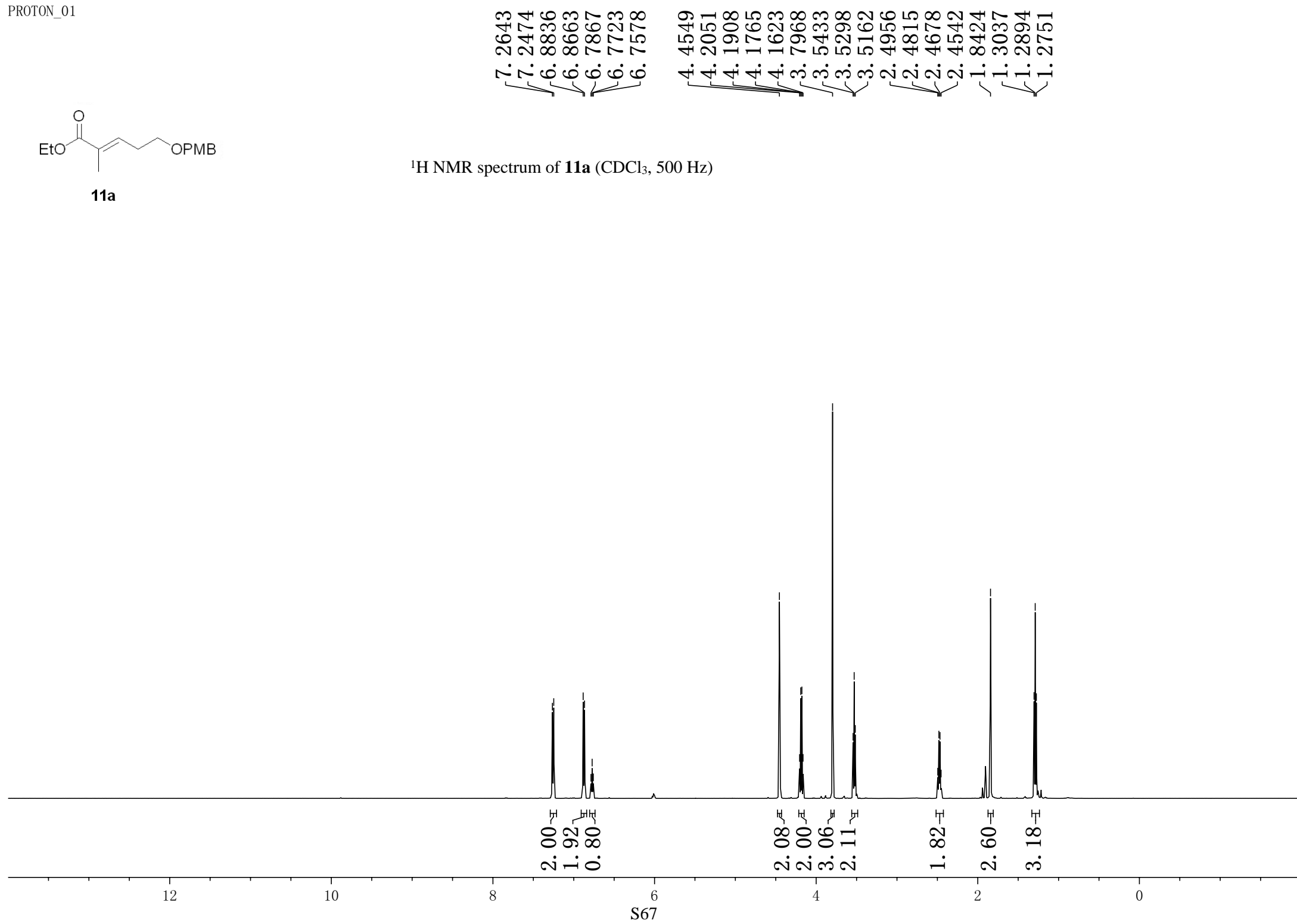


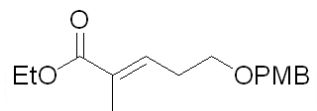
<sup>13</sup>C NMR spectrum of **2b** (CDCl<sub>3</sub>, 500 Hz)



**11a**

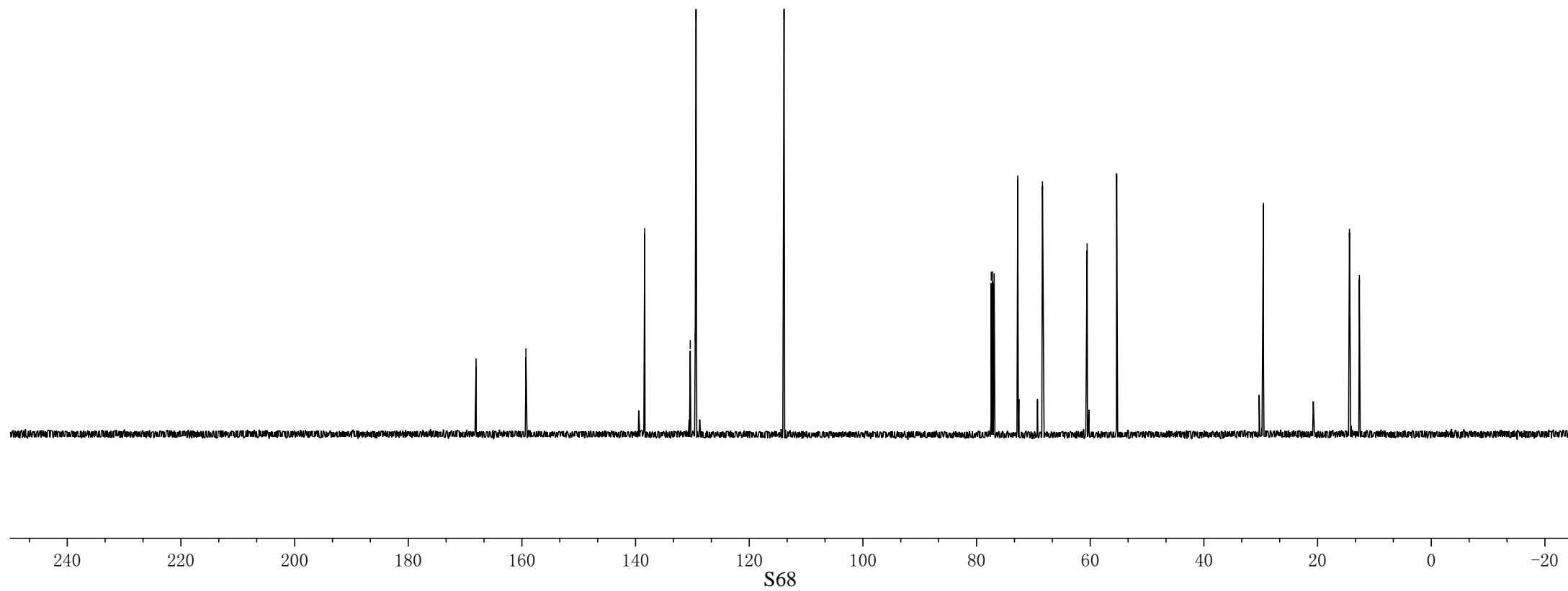
<sup>1</sup>H NMR spectrum of **11a** (CDCl<sub>3</sub>, 500 Hz)

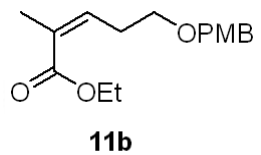


**11a**<sup>13</sup>C NMR spectrum of **11a** (CDCl<sub>3</sub>, 500 Hz)

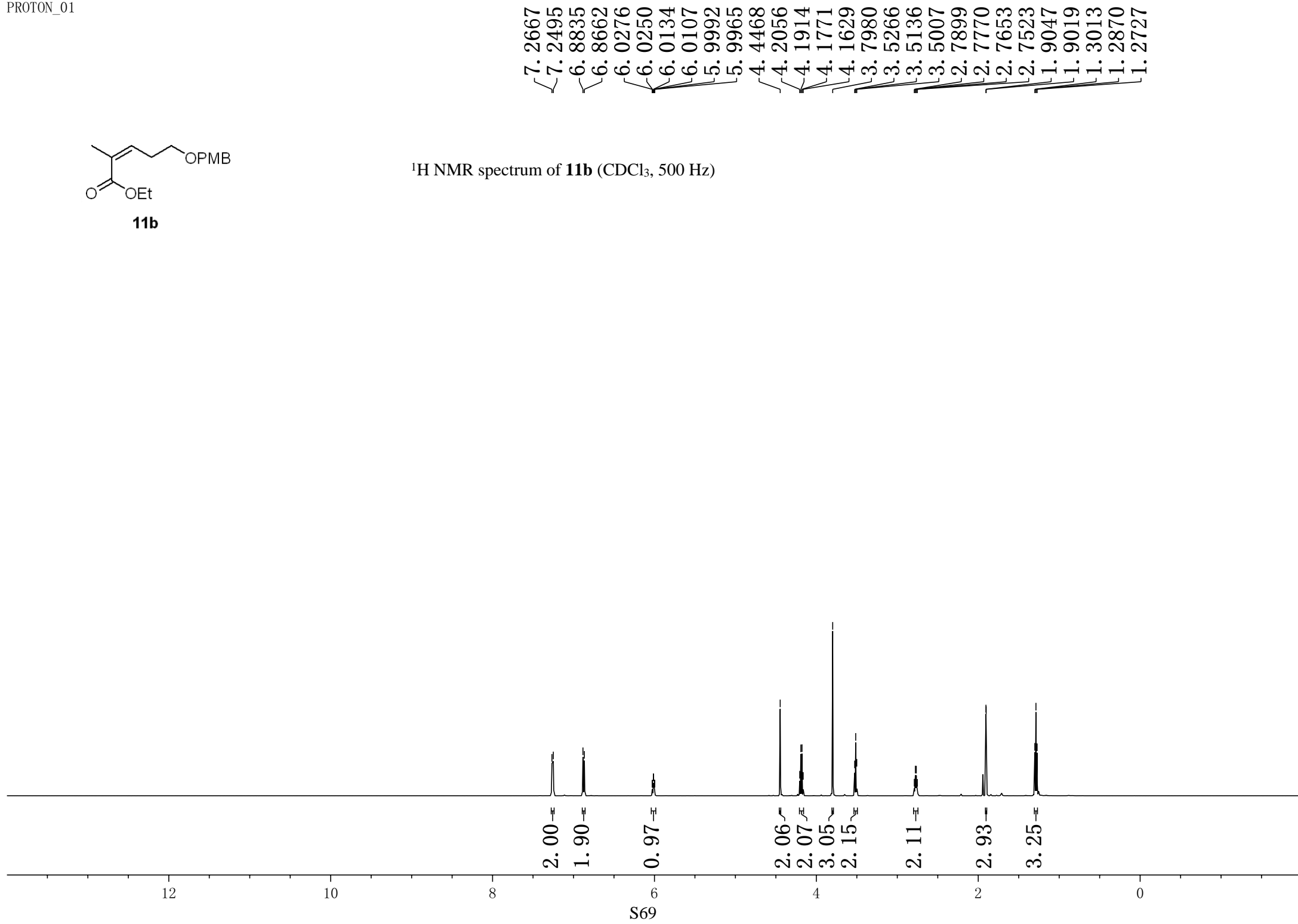
Chemical shift values (ppm) for the <sup>13</sup>C NMR spectrum of **11a** (CDCl<sub>3</sub>, 500 Hz):

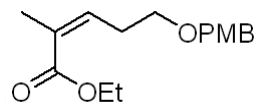
- 168.0654
- 159.2914
- 138.3912
- 130.3789
- 129.5045
- 129.3565
- 113.8782
- 77.4142
- 77.1596
- 76.9053
- 72.7524
- 68.4049
- 60.5485
- 55.3534
- 29.5280
- 14.3896
- 12.6466





<sup>1</sup>H NMR spectrum of **11b** (CDCl<sub>3</sub>, 500 Hz)

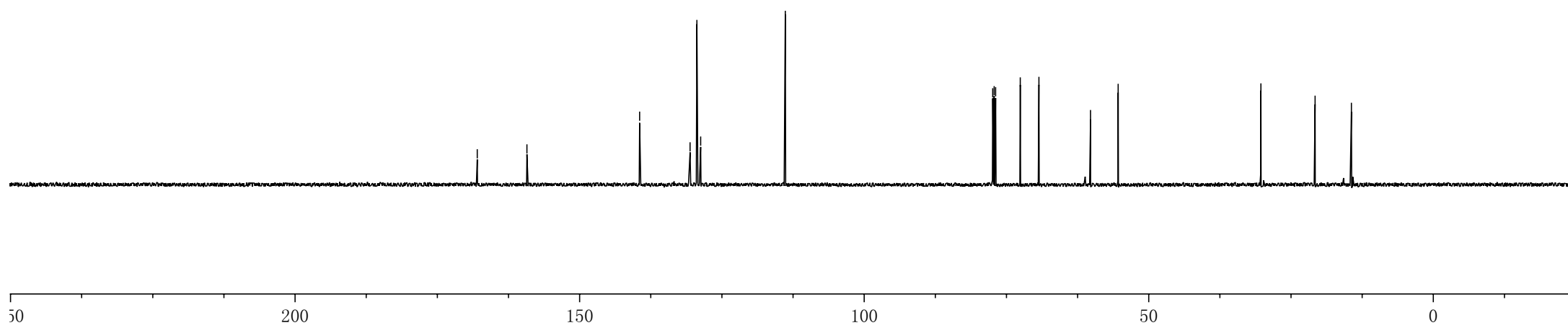


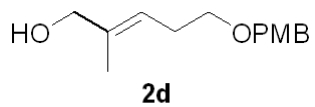
**11b**

$^{13}\text{C}$  NMR chemical shifts (ppm):

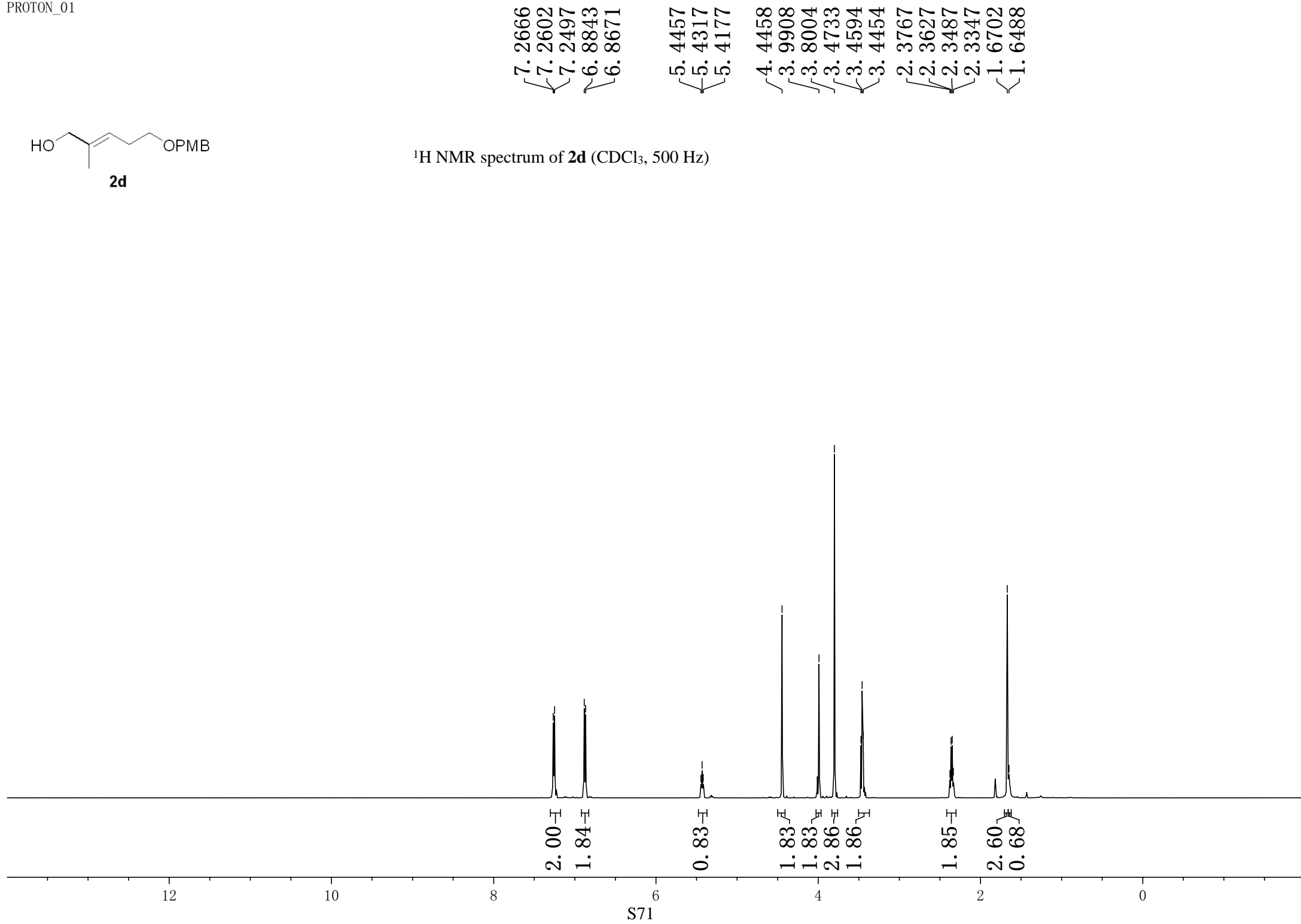
- 167.9889
- 159.2603
- 139.4569
- 130.5950
- 129.3948
- 128.7327
- 113.8618
- 77.4147
- 77.1604
- 76.9059
- 72.5754
- 69.2980
- 60.2305
- 55.3738
- 30.2914
- 20.7702
- 14.3896

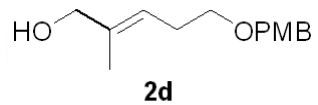
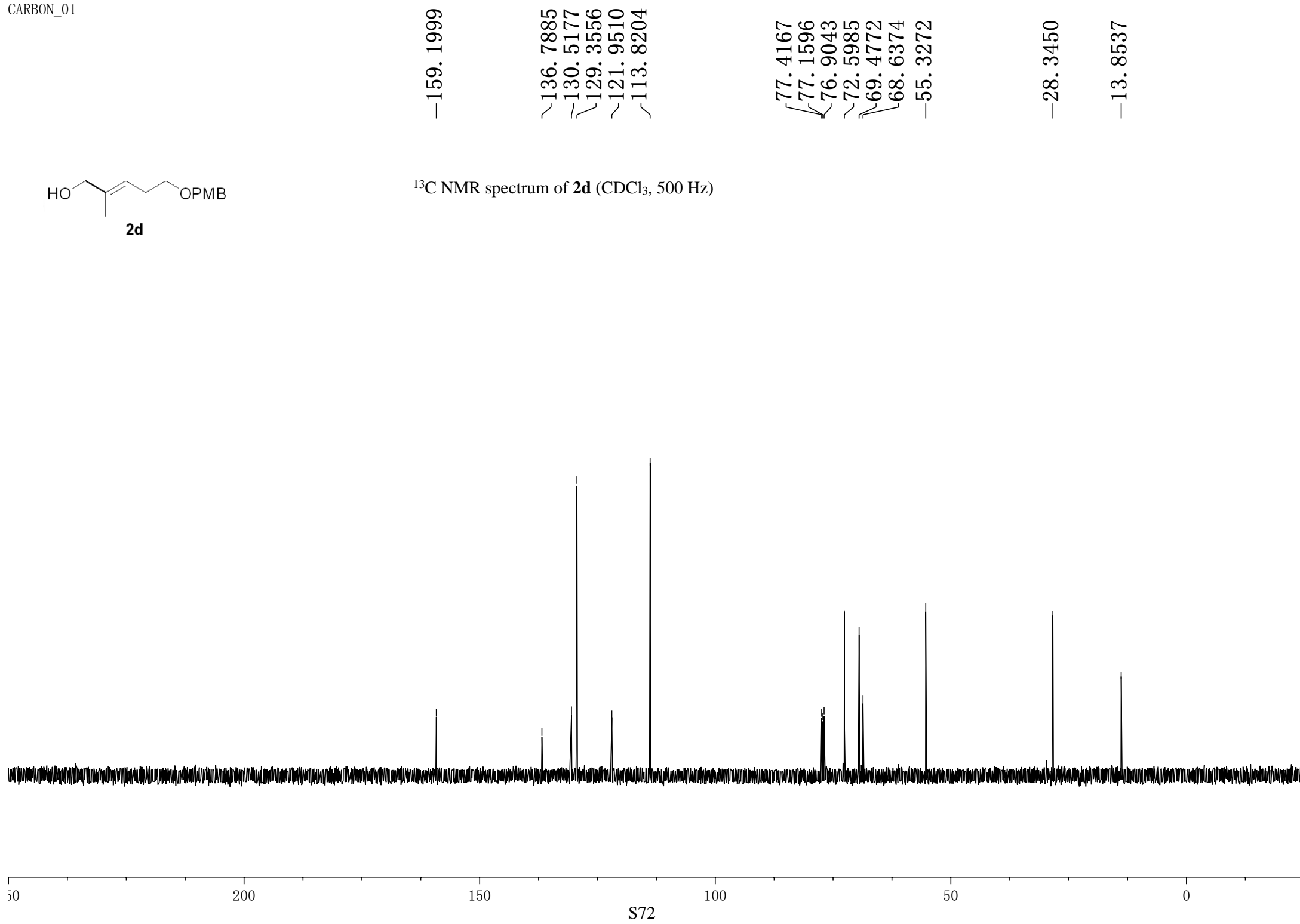
$^{13}\text{C}$  NMR spectrum of **11b** ( $\text{CDCl}_3$ , 500 Hz)



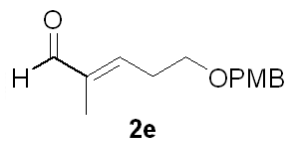


<sup>1</sup>H NMR spectrum of **2d** (CDCl<sub>3</sub>, 500 Hz)



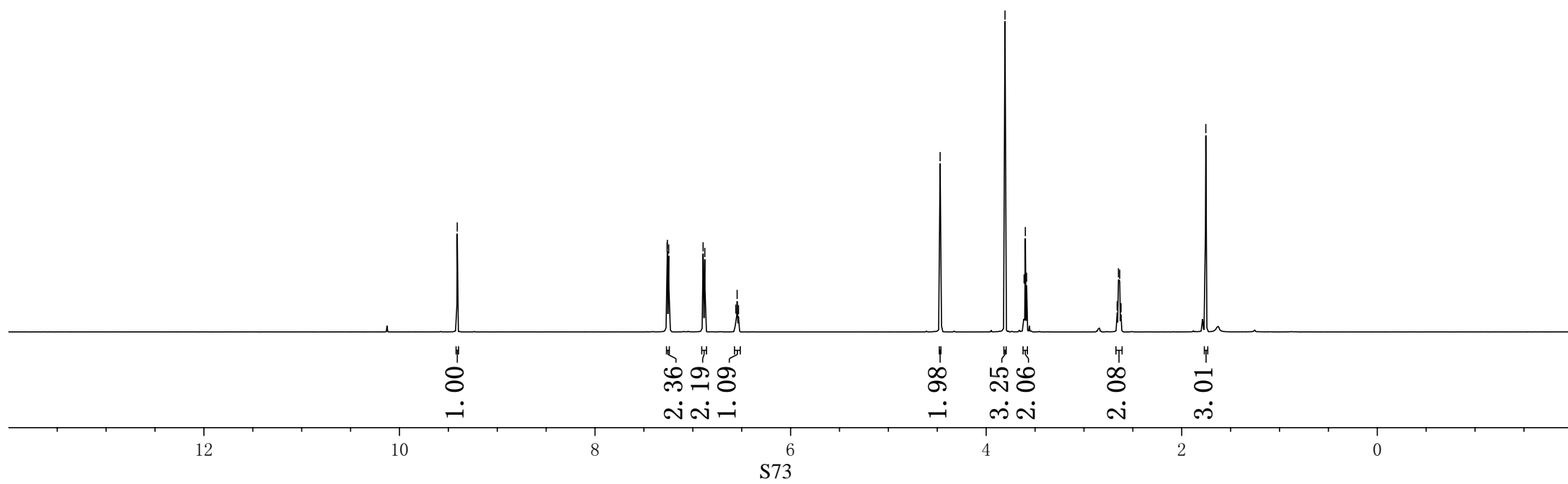
<sup>13</sup>C NMR spectrum of **2d** (CDCl<sub>3</sub>, 500 Hz)

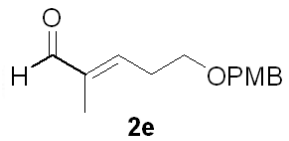




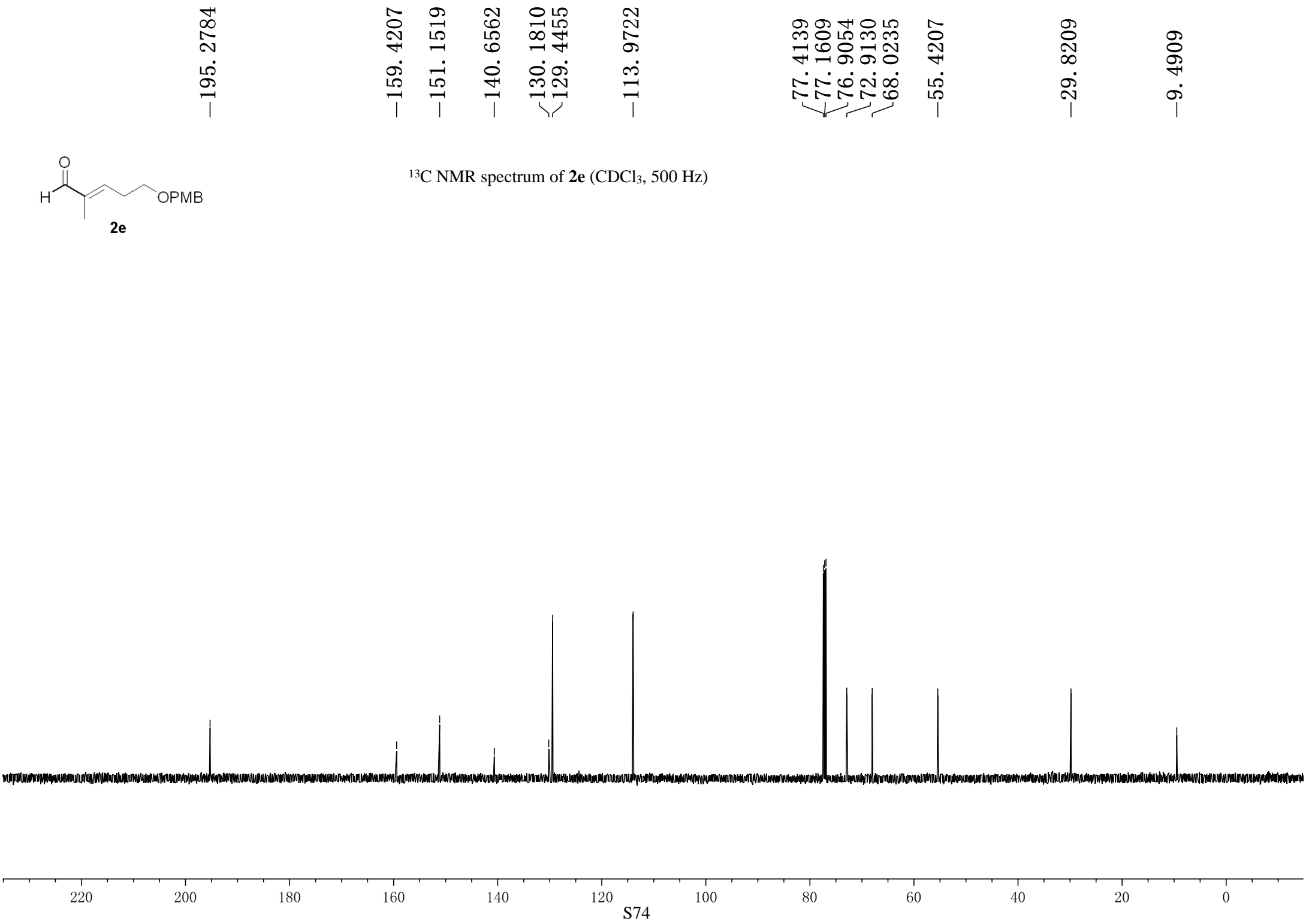
—9.4092  
 7.2627  
 7.2603  
 7.2465  
 6.8946  
 6.8775  
 6.5604  
 6.5467  
 6.5327  
 —4.4707  
 3.8074  
 3.6121  
 3.5993  
 3.5865  
 2.6603  
 2.6472  
 2.6341  
 2.6209  
 —1.7536

<sup>1</sup>H NMR spectrum of **2e** (CDCl<sub>3</sub>, 500 Hz)

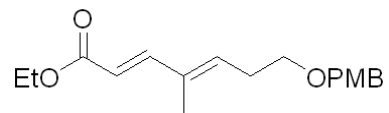




<sup>13</sup>C NMR spectrum of **2e** (CDCl<sub>3</sub>, 500 Hz)

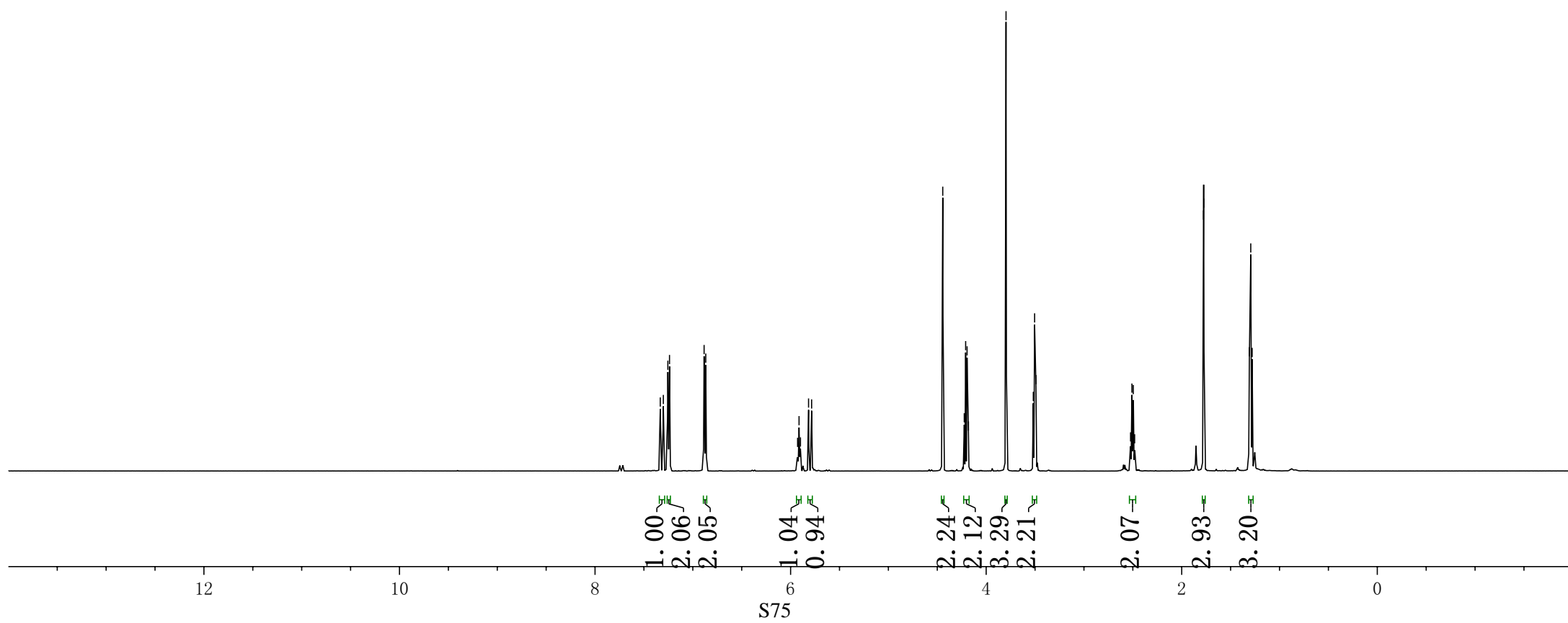


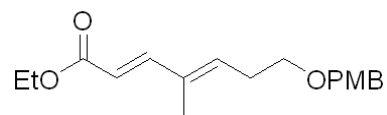
7.3329  
 7.3015  
 7.2553  
 7.2385  
 6.8847  
 6.8676  
 5.9284  
 5.9136  
 5.8993  
 5.8164  
 5.7850  
 4.4440  
 4.2240  
 4.2098  
 4.1954  
 4.1812  
 3.7968  
 3.5179  
 3.5045  
 3.4909  
 2.5232  
 2.5094  
 2.4955  
 2.4816  
 1.7776  
 1.7745  
 1.3083  
 1.2940  
 1.2797



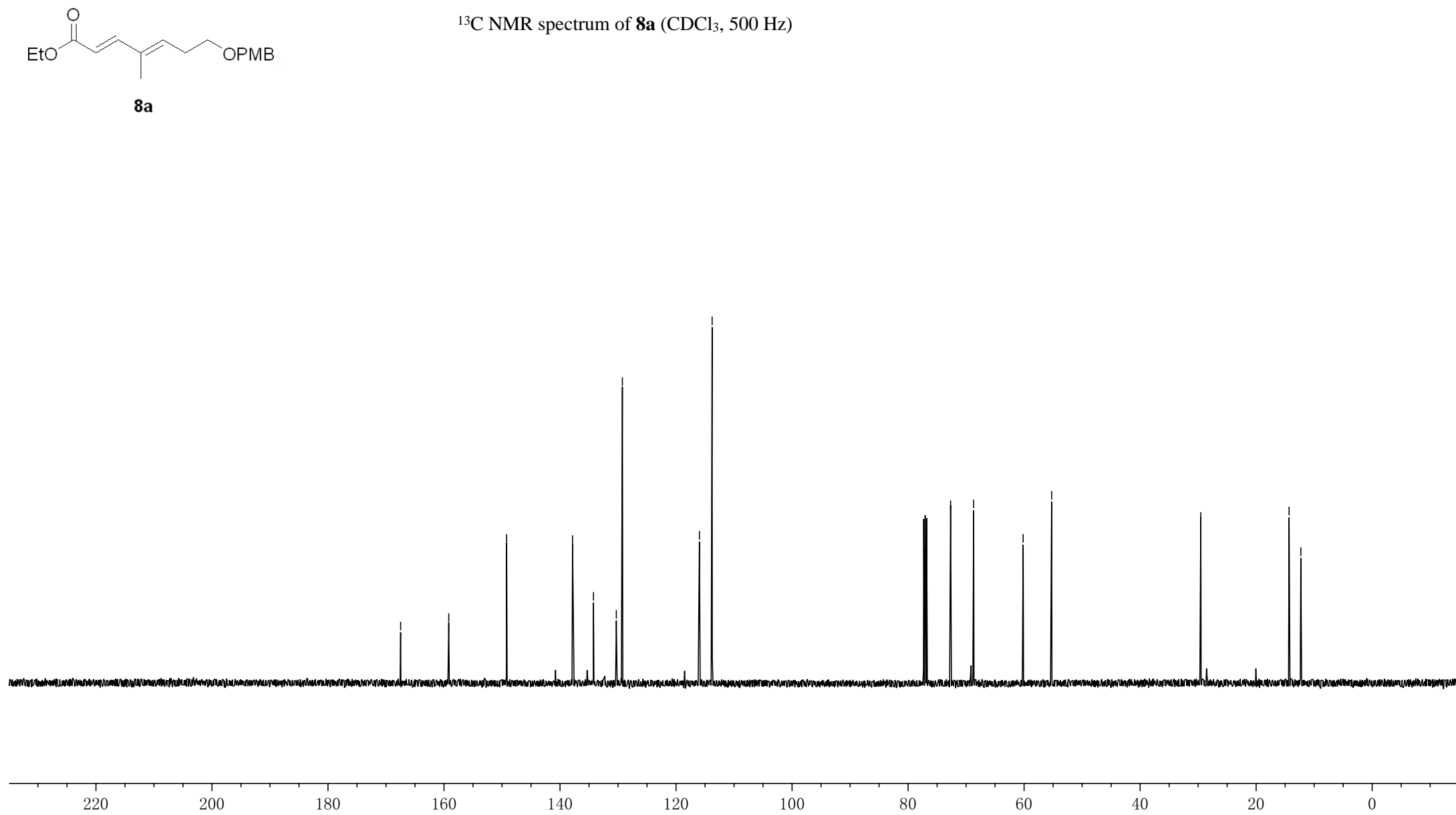
**8a**

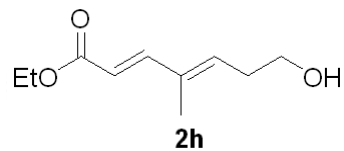
<sup>1</sup>H NMR spectrum of **8a** (CDCl<sub>3</sub>, 500 Hz)



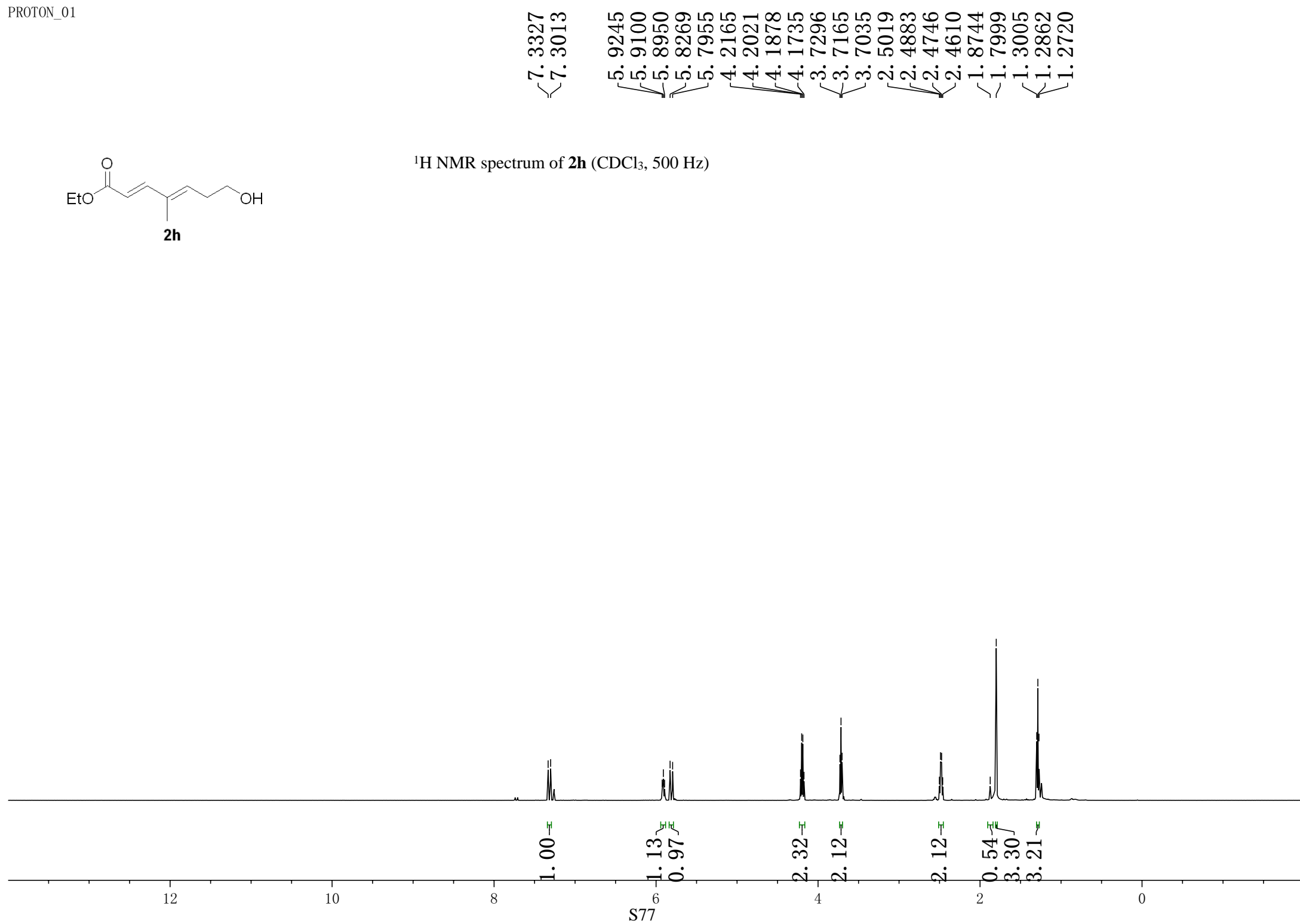
**8a**

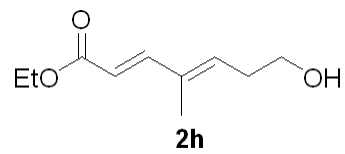
$^{13}\text{C}$  NMR spectrum of **8a** ( $\text{CDCl}_3$ , 500 Hz)





<sup>1</sup>H NMR spectrum of **2h** (CDCl<sub>3</sub>, 500 Hz)





-167.6166

-149.1603

-137.3139

-135.1822

-116.4242

-61.8889

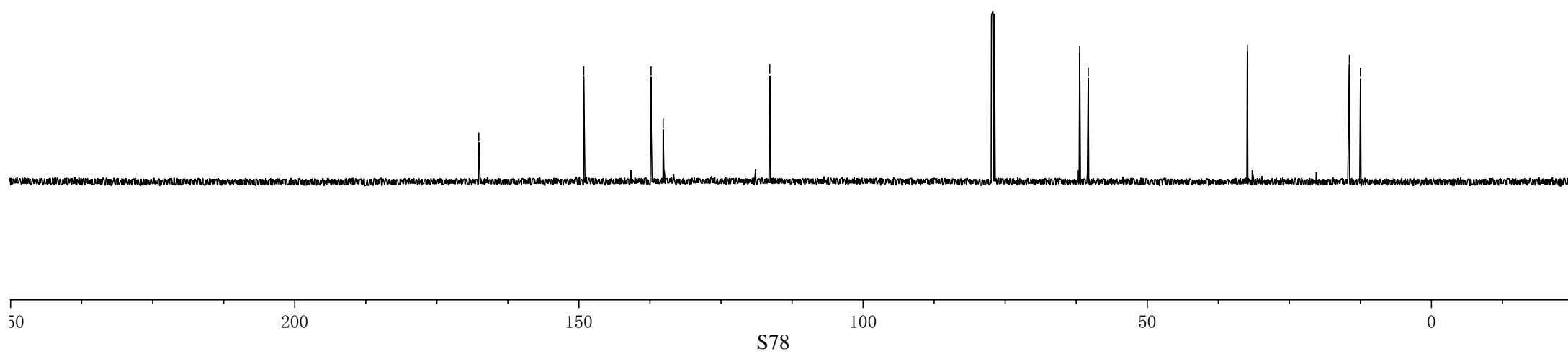
-60.3855

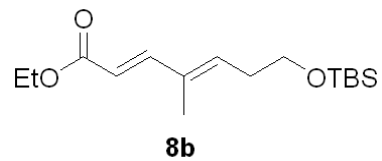
-32.3964

-14.4350

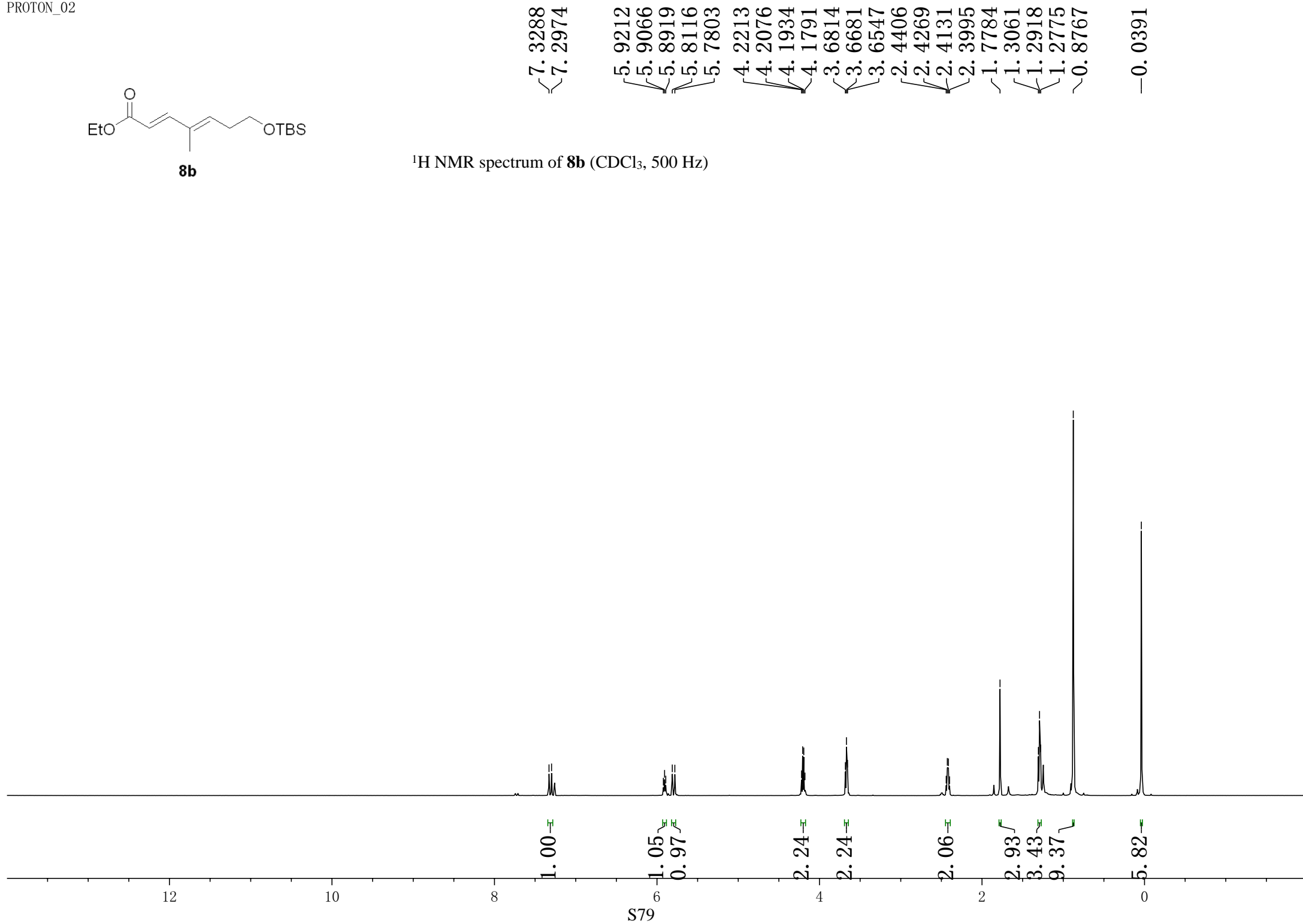
-12.4842

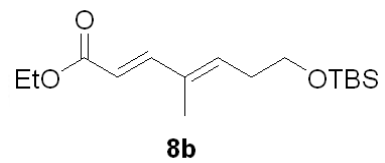
<sup>13</sup>C NMR spectrum of **2h** (CDCl<sub>3</sub>, 500 Hz)





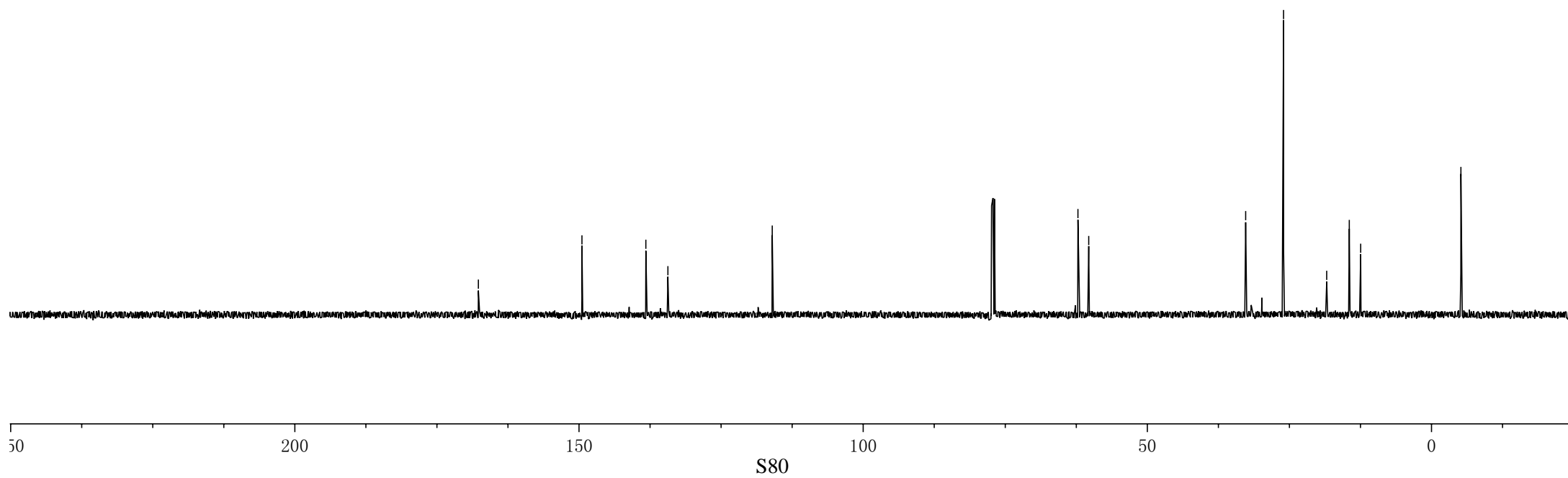
<sup>1</sup>H NMR spectrum of **8b** (CDCl<sub>3</sub>, 500 Hz)





$^{13}\text{C}$  NMR spectrum of **8b** ( $\text{CDCl}_3$ , 500 Hz)

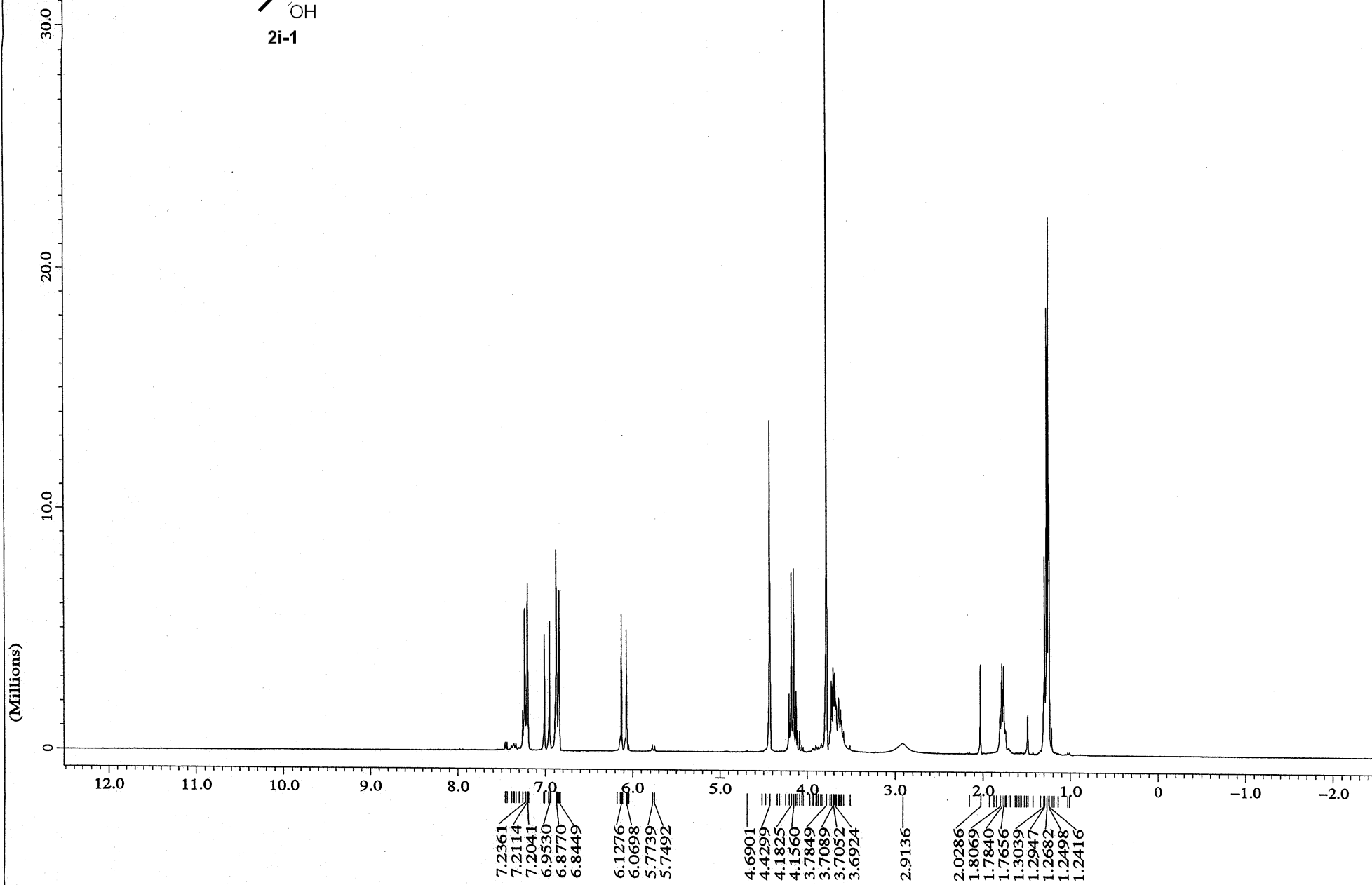
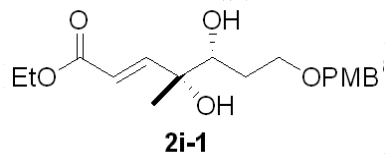
—167.7071  
—149.4831  
—138.2393  
—134.3592  
—116.0009  
/62.2125  
/60.3146  
/32.6995  
/26.0334  
/18.4418  
/14.4673  
/12.4629  
--5.1724





dg486.3

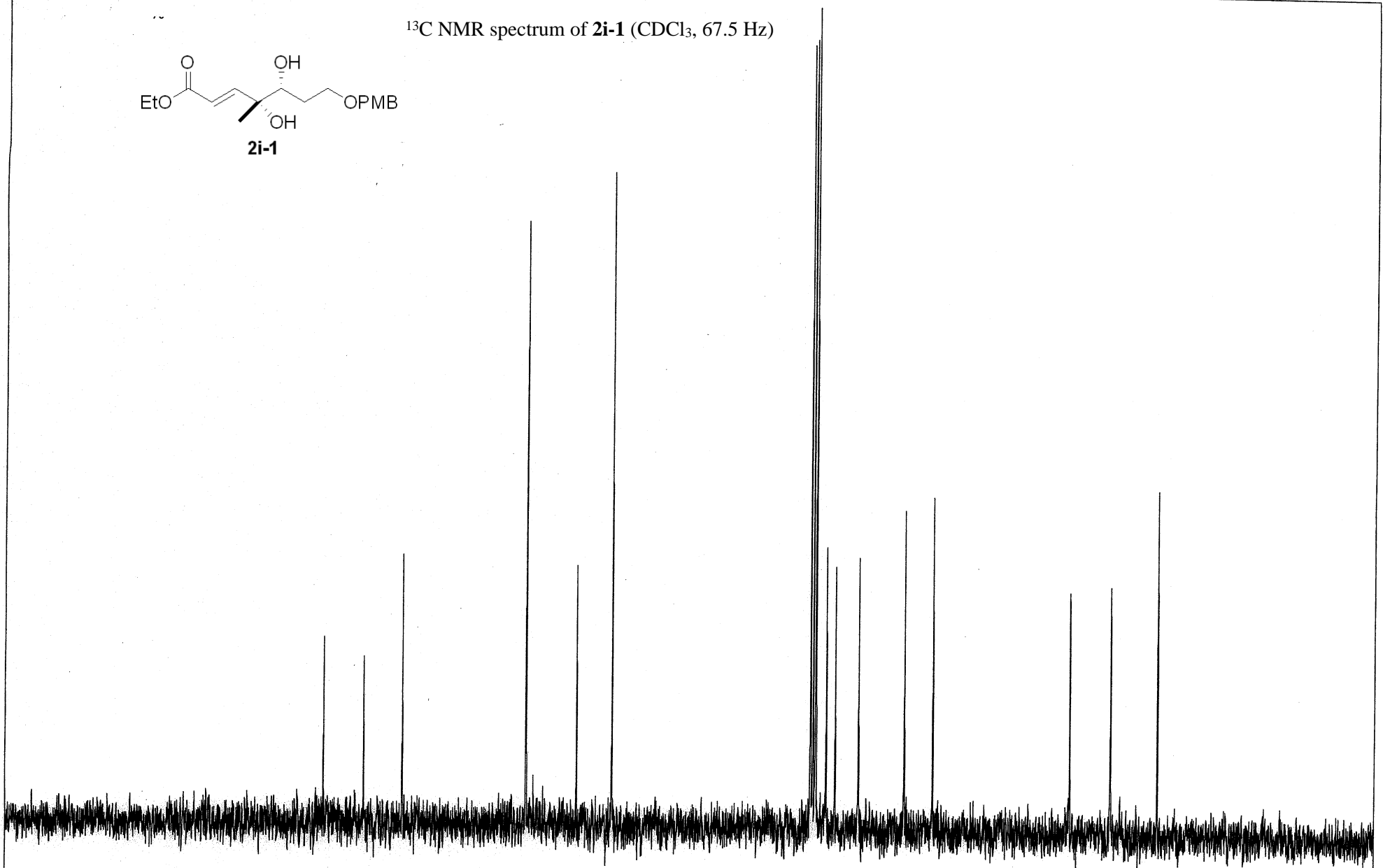
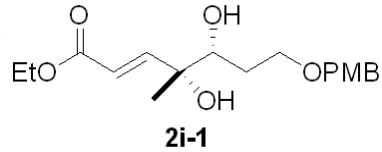
<sup>1</sup>H NMR spectrum of **2i-1** (CDCl<sub>3</sub>, 270 Hz)



X : parts per Million : 1H

S81

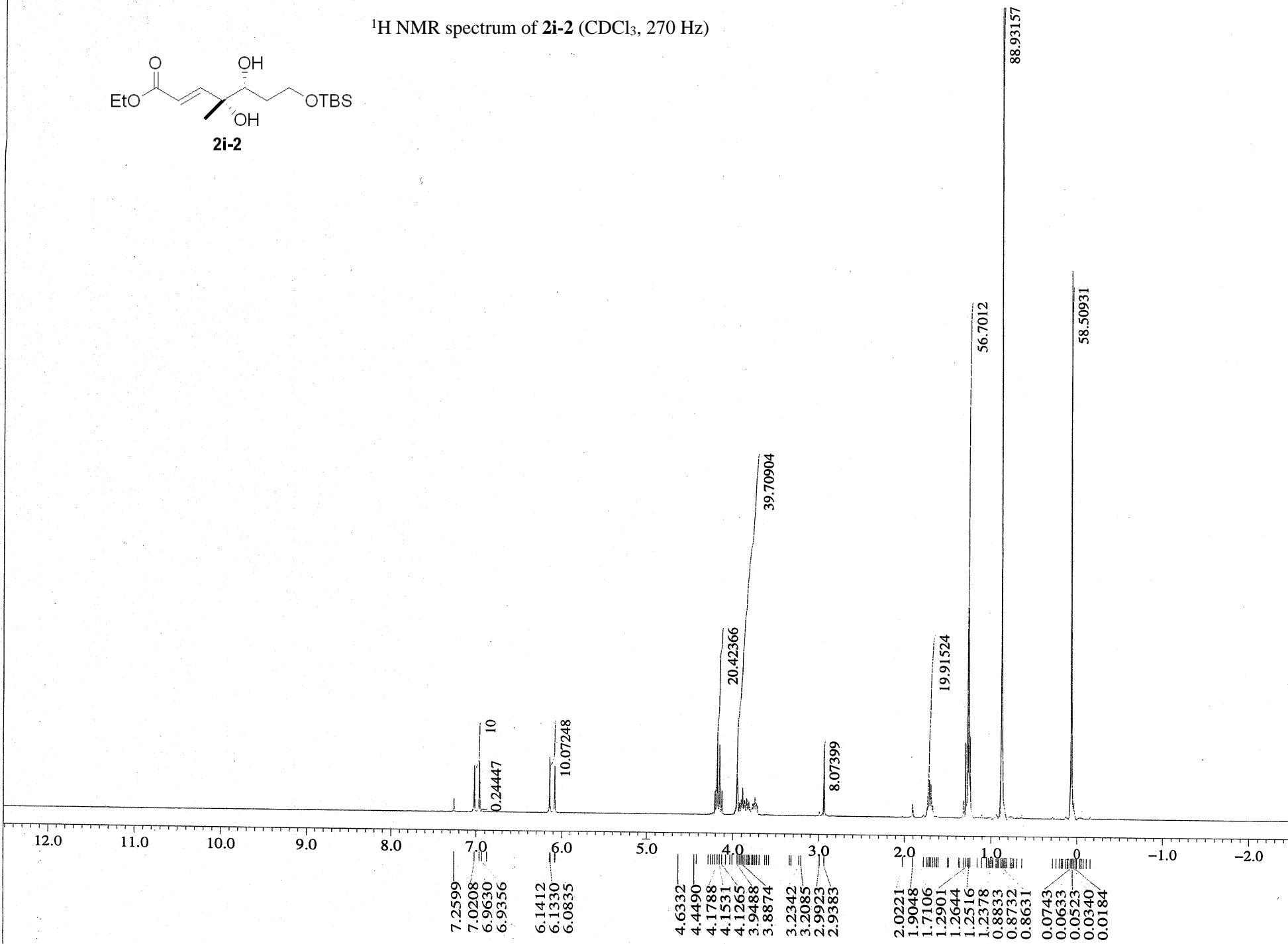
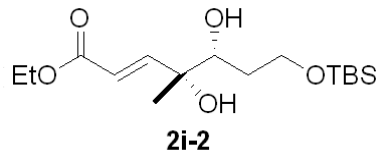
<sup>13</sup>C NMR spectrum of **2i-1** (CDCl<sub>3</sub>, 67.5 Hz)



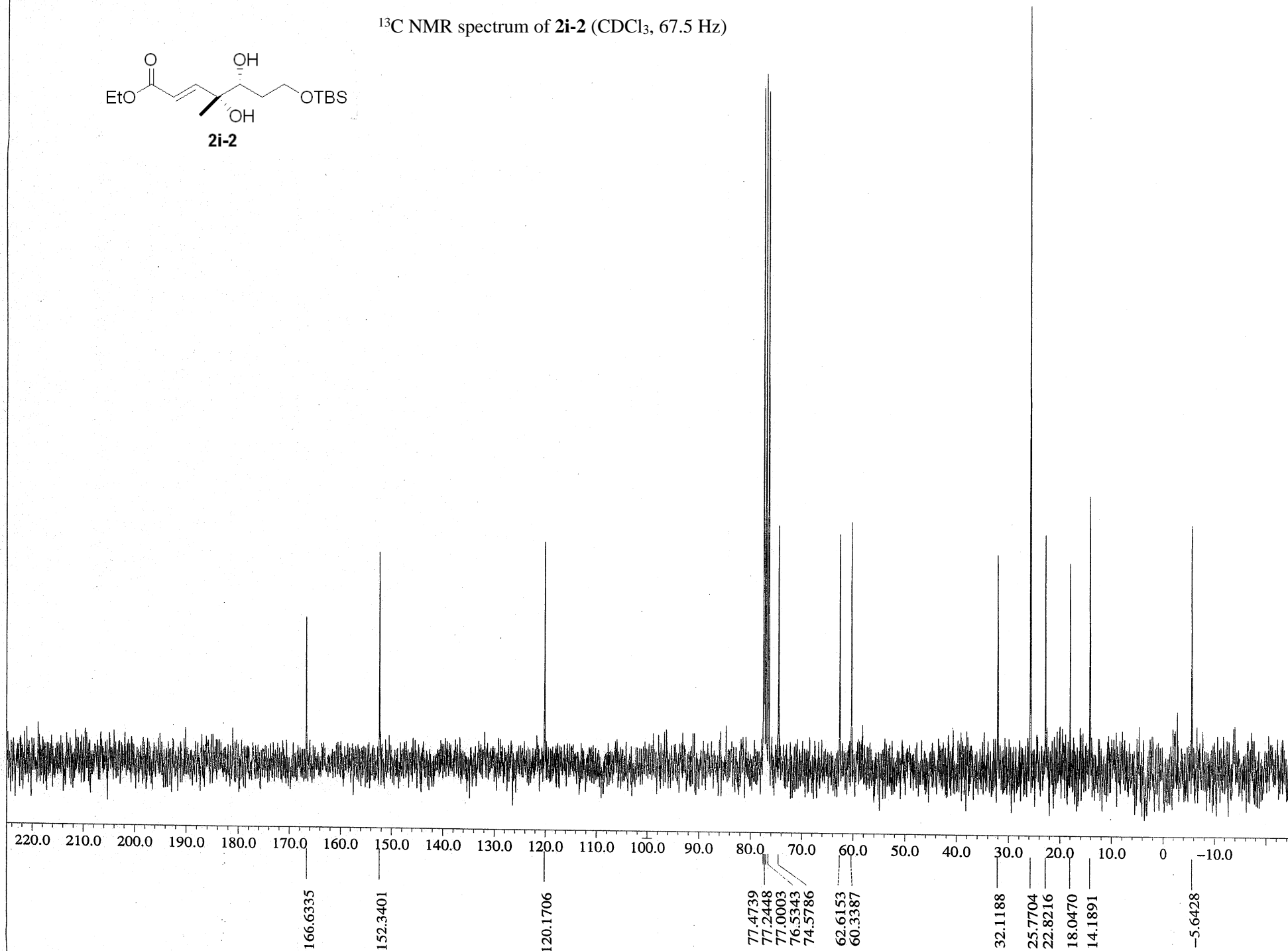
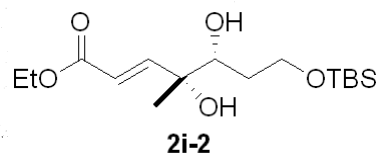
| Chemical Shift (ppm) |
|----------------------|
| 166.6009             |
| 159.2747             |
| 152.1472             |
| 129.4505             |
| 129.3588             |
| 120.1992             |
| 113.8126             |
| 77.4719              |
| 76.9983              |
| 76.5323              |
| 74.6530              |
| 73.0258              |
| 68.7477              |
| 60.3673              |
| 55.1878              |
| 30.2146              |
| 22.7585              |
| 14.1565              |

X : parts per Million : <sup>13</sup>C

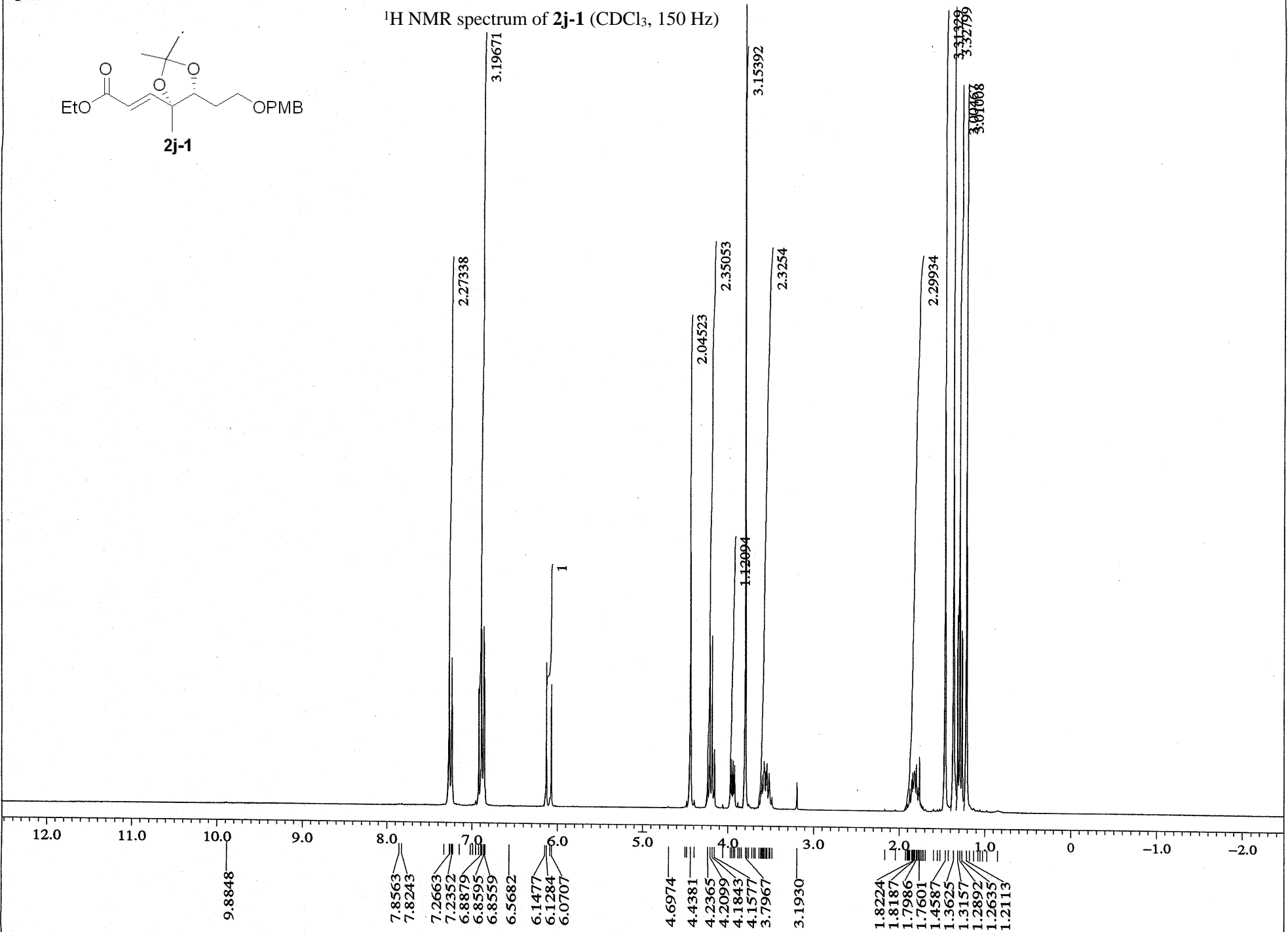
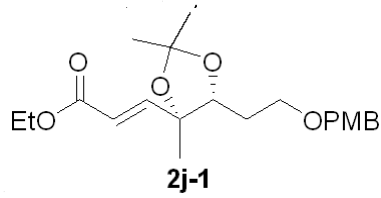
<sup>1</sup>H NMR spectrum of **2i-2** (CDCl<sub>3</sub>, 270 Hz)



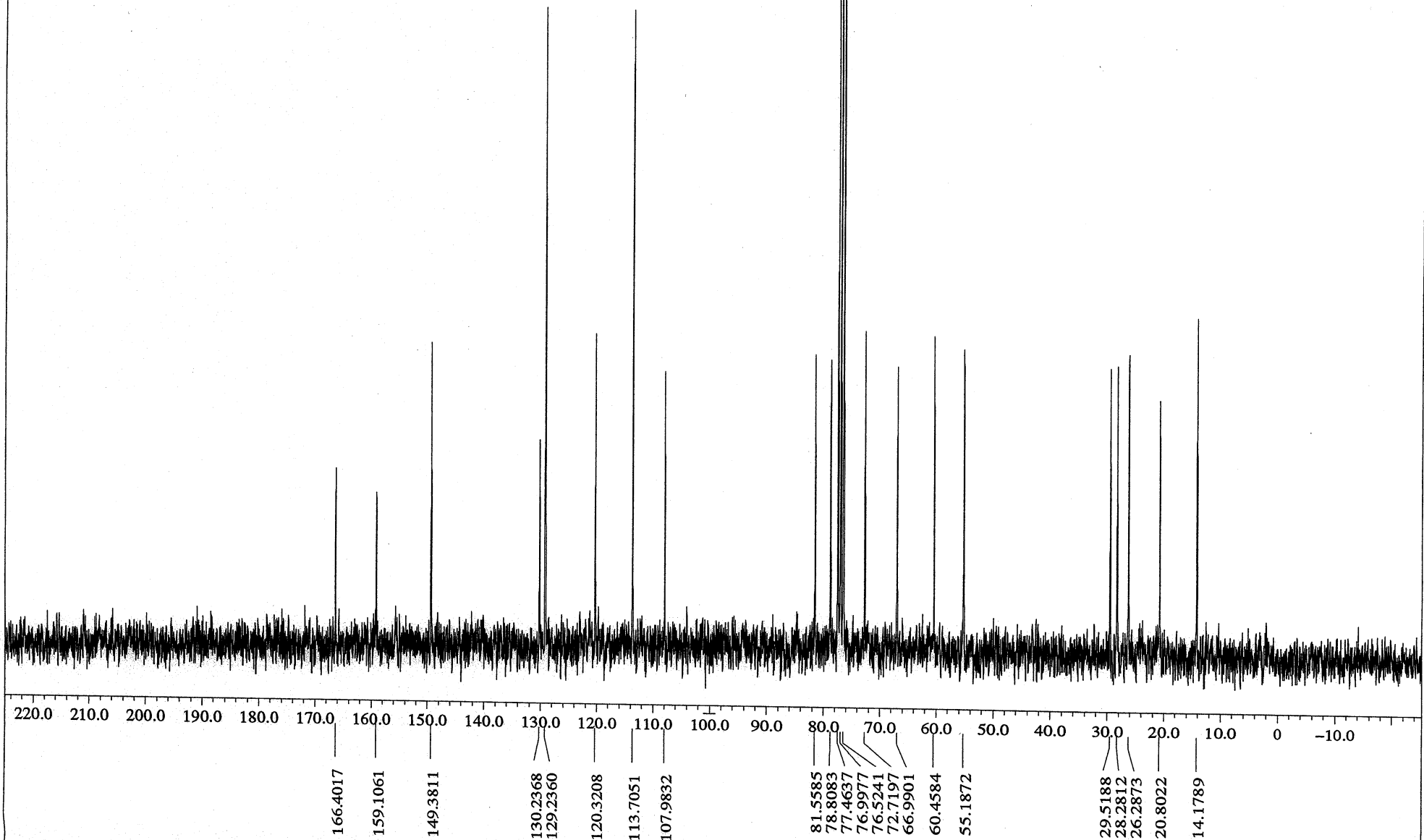
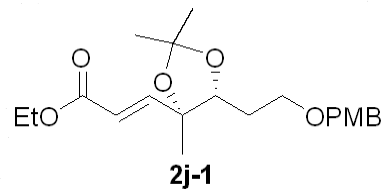
X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **2i-2** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

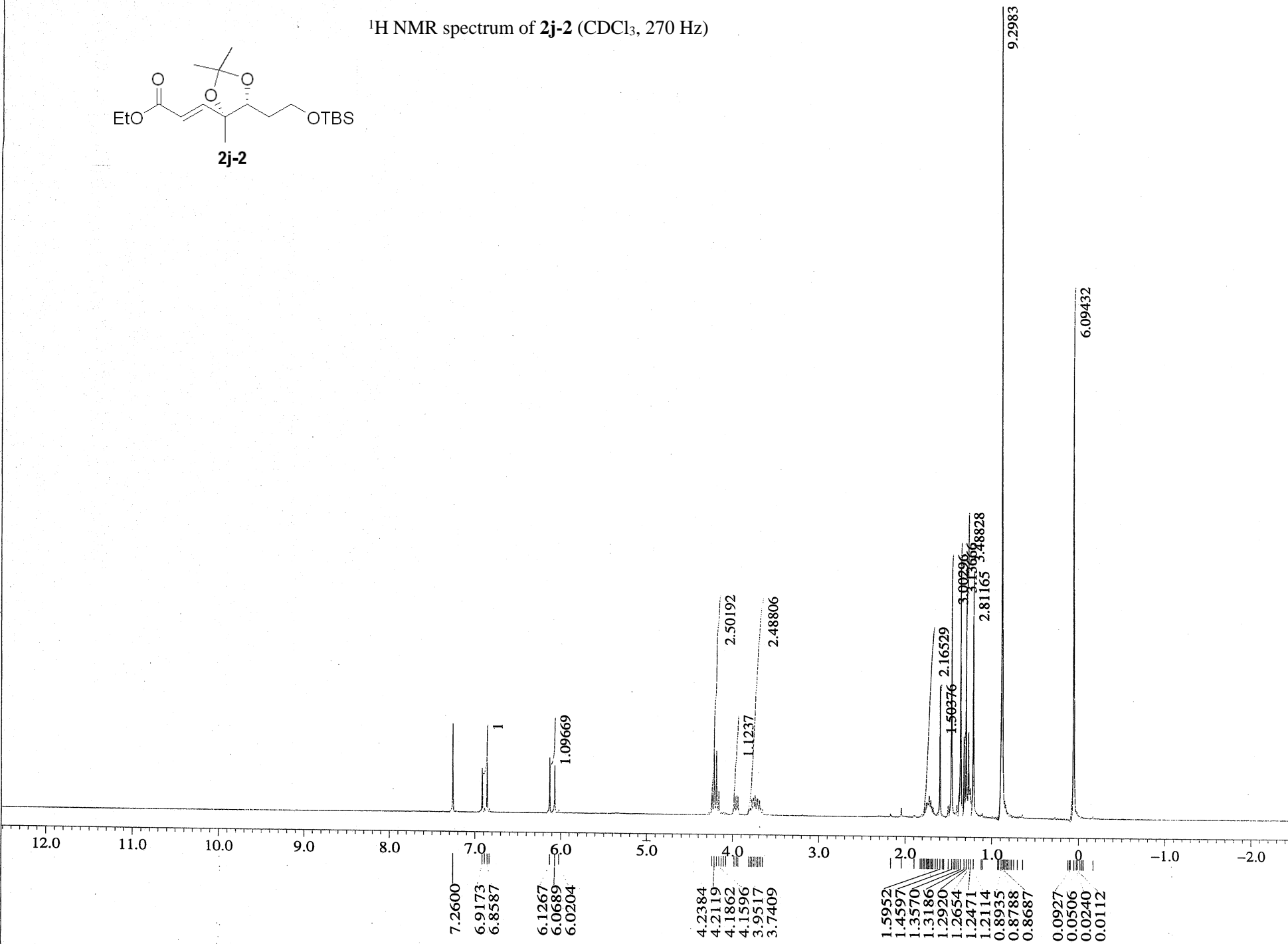
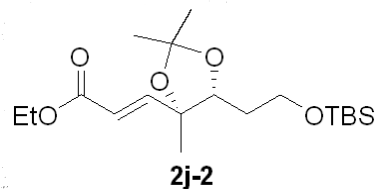
<sup>1</sup>H NMR spectrum of **2j-1** (CDCl<sub>3</sub>, 150 Hz)

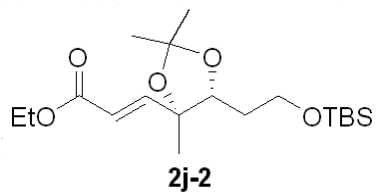
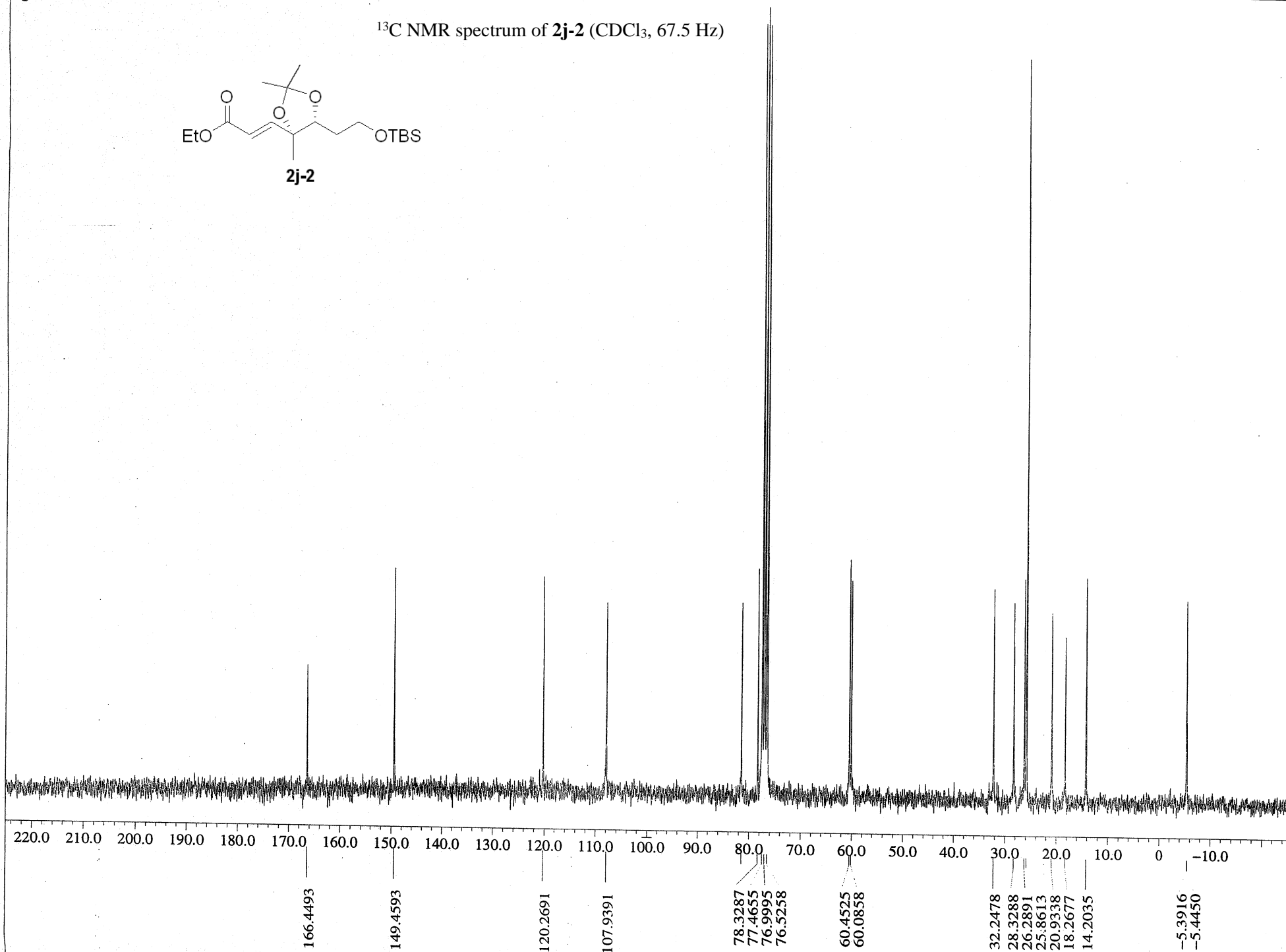


X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **2j-1** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

<sup>1</sup>H NMR spectrum of **2j-2** (CDCl<sub>3</sub>, 270 Hz)

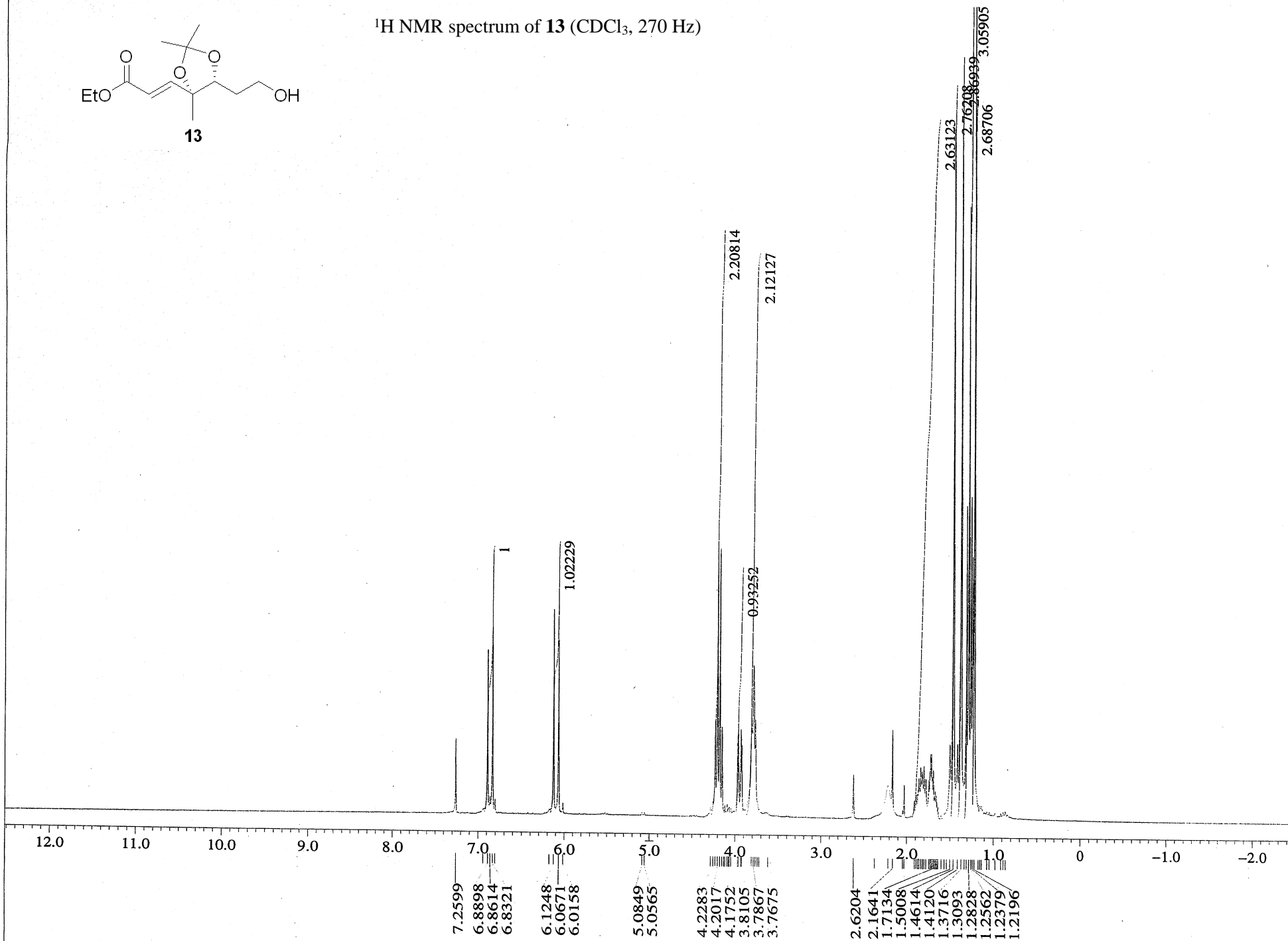
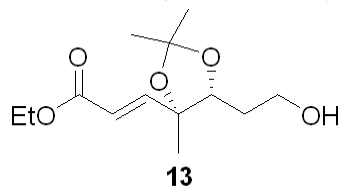


$^{13}\text{C}$  NMR spectrum of **2j-2** ( $\text{CDCl}_3$ , 67.5 Hz)**2j-2**X : parts per Million :  $^{13}\text{C}$ 

S88

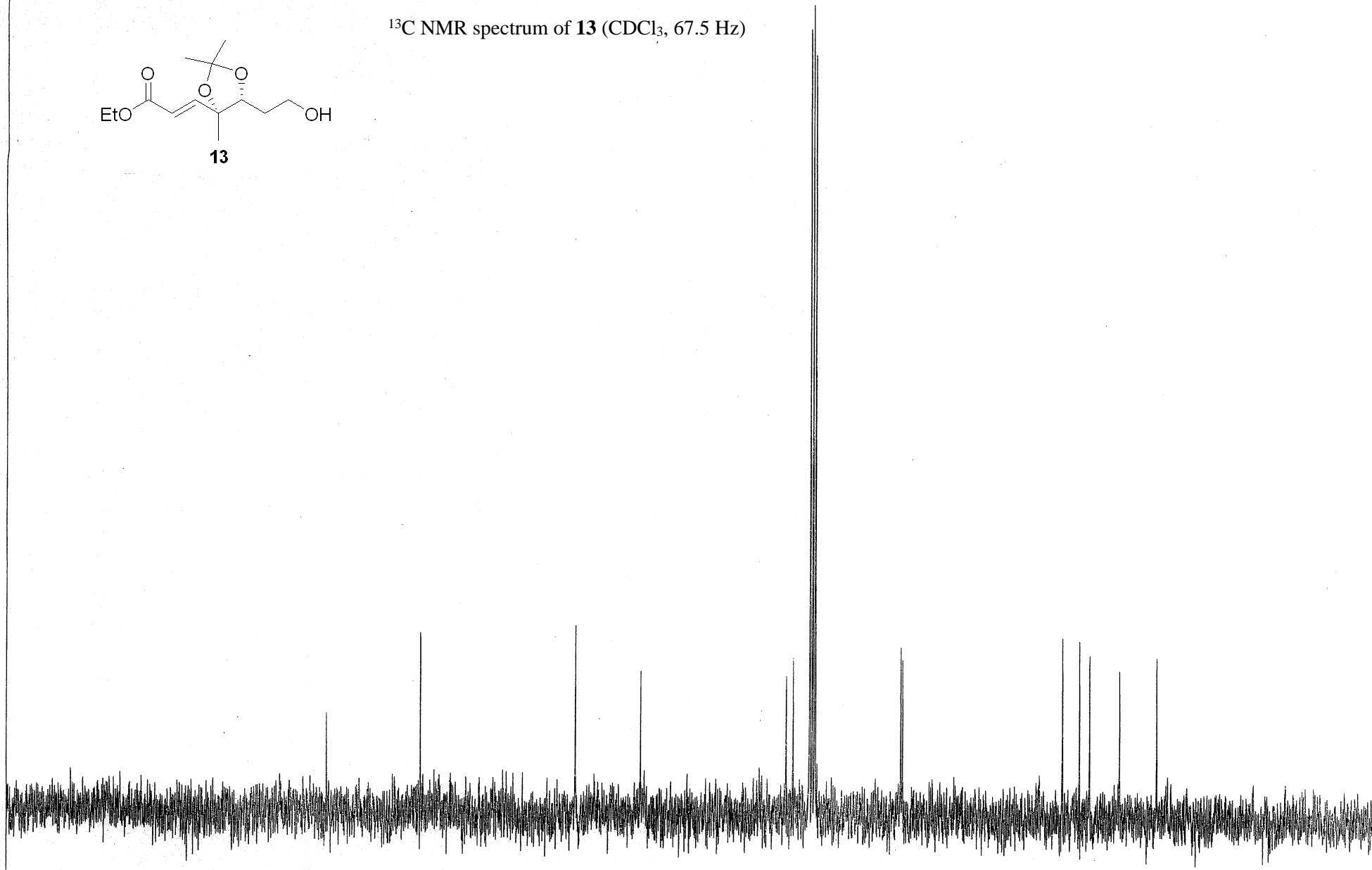
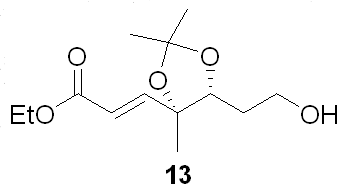


<sup>1</sup>H NMR spectrum of **13** (CDCl<sub>3</sub>, 270 Hz)



X : parts per Million : 1H

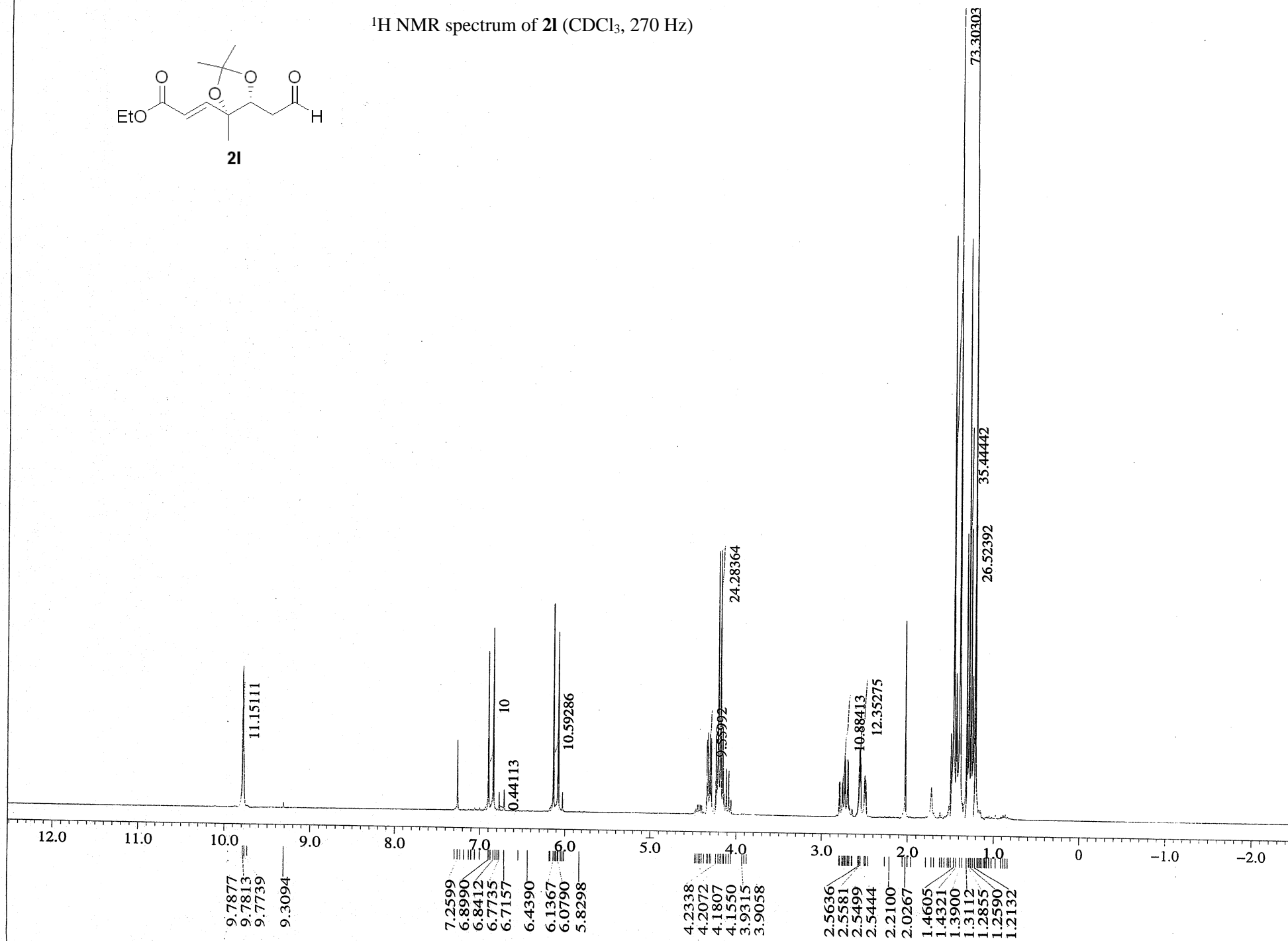
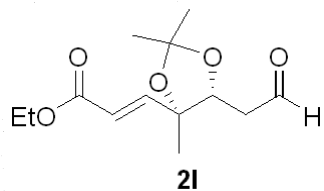
<sup>13</sup>C NMR spectrum of **13** (CDCl<sub>3</sub>, 67.5 Hz)



| Chemical Shift (ppm) |
|----------------------|
| 166.6693             |
| 149.0528             |
| 120.5120             |
| 108.5181             |
| 80.5350              |
| 77.4716              |
| 76.9979              |
| 76.5319              |
| 60.9170              |
| 60.5808              |
| 31.3906              |
| 28.2814              |
| 26.4098              |
| 20.9247              |
| 14.1791              |

X : parts per Million : <sup>13</sup>C

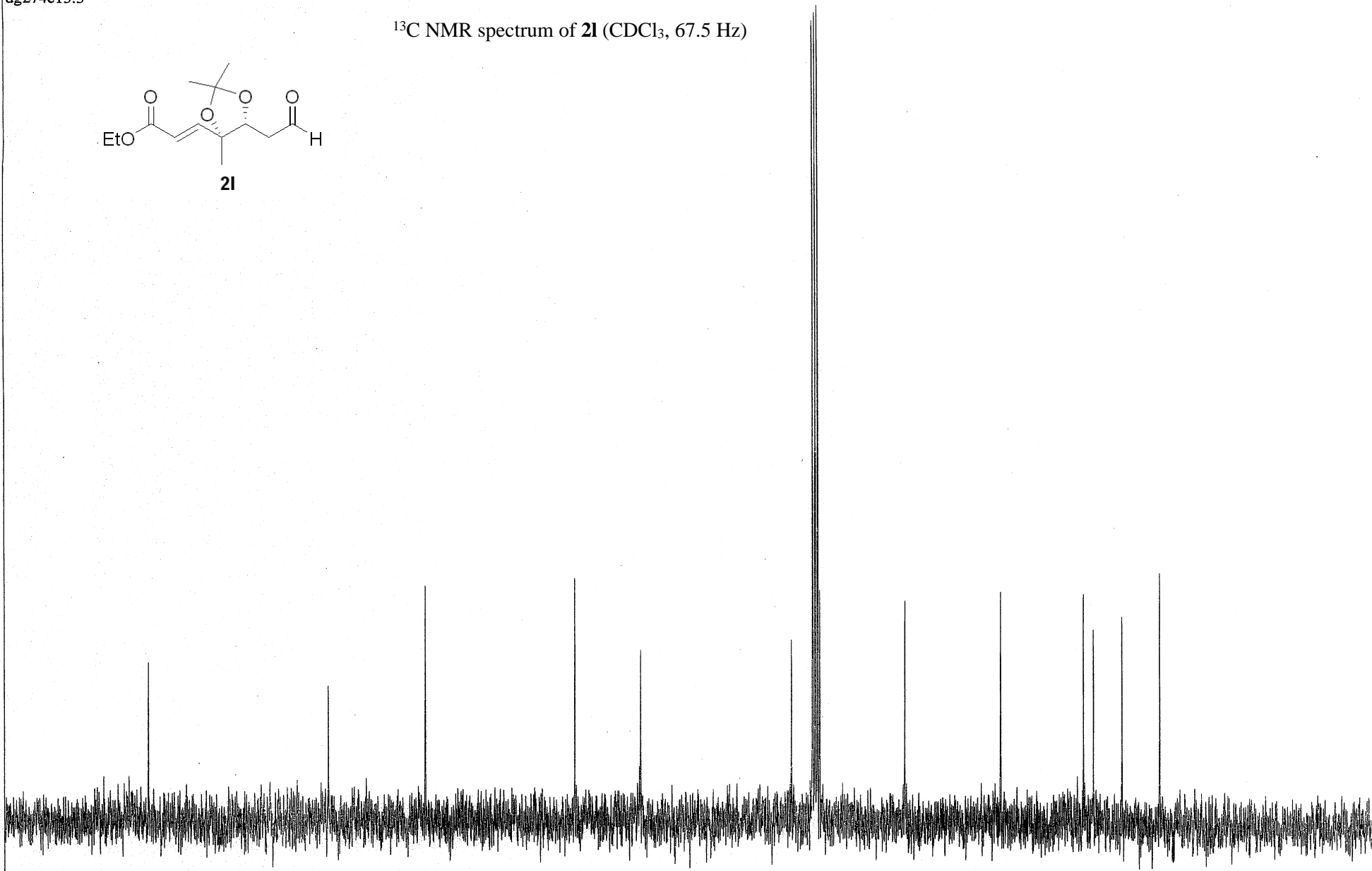
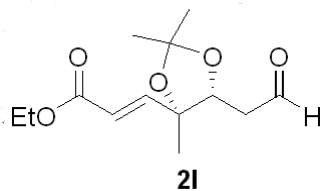
<sup>1</sup>H NMR spectrum of **21** (CDCl<sub>3</sub>, 270 Hz)



X : parts per Million : 1H

dg274c13.3

<sup>13</sup>C NMR spectrum of **21** (CDCl<sub>3</sub>, 67.5 Hz)



220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

198.9082

166.2115

148.3811

120.9557

108.8930

77.4722

76.9985

76.5325

76.1887

60.6349

43.1865

28.1368

26.2958

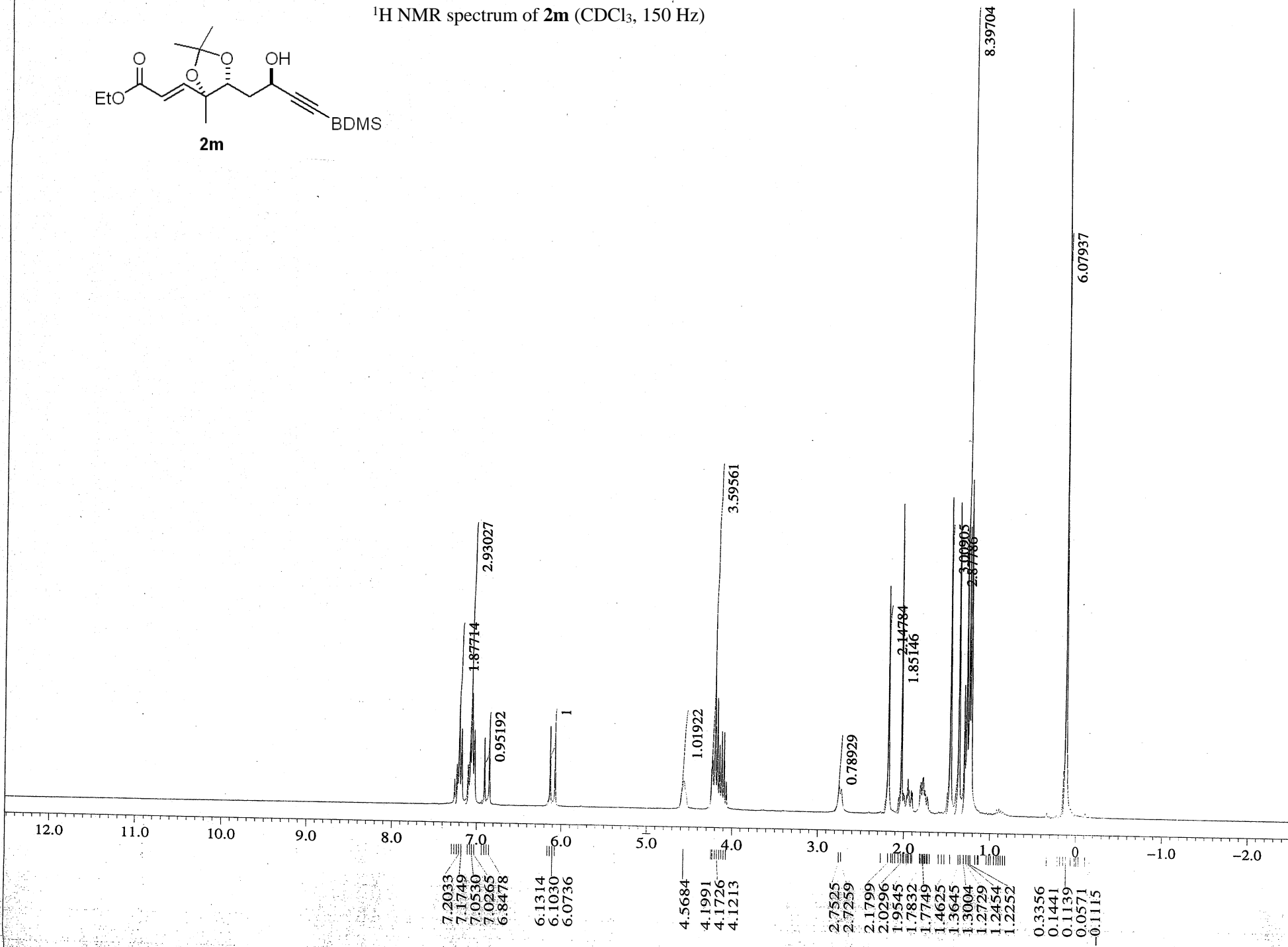
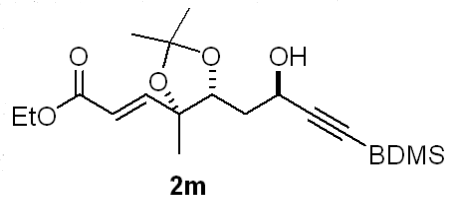
21.0398

14.1796

X : parts per Million : <sup>13</sup>C

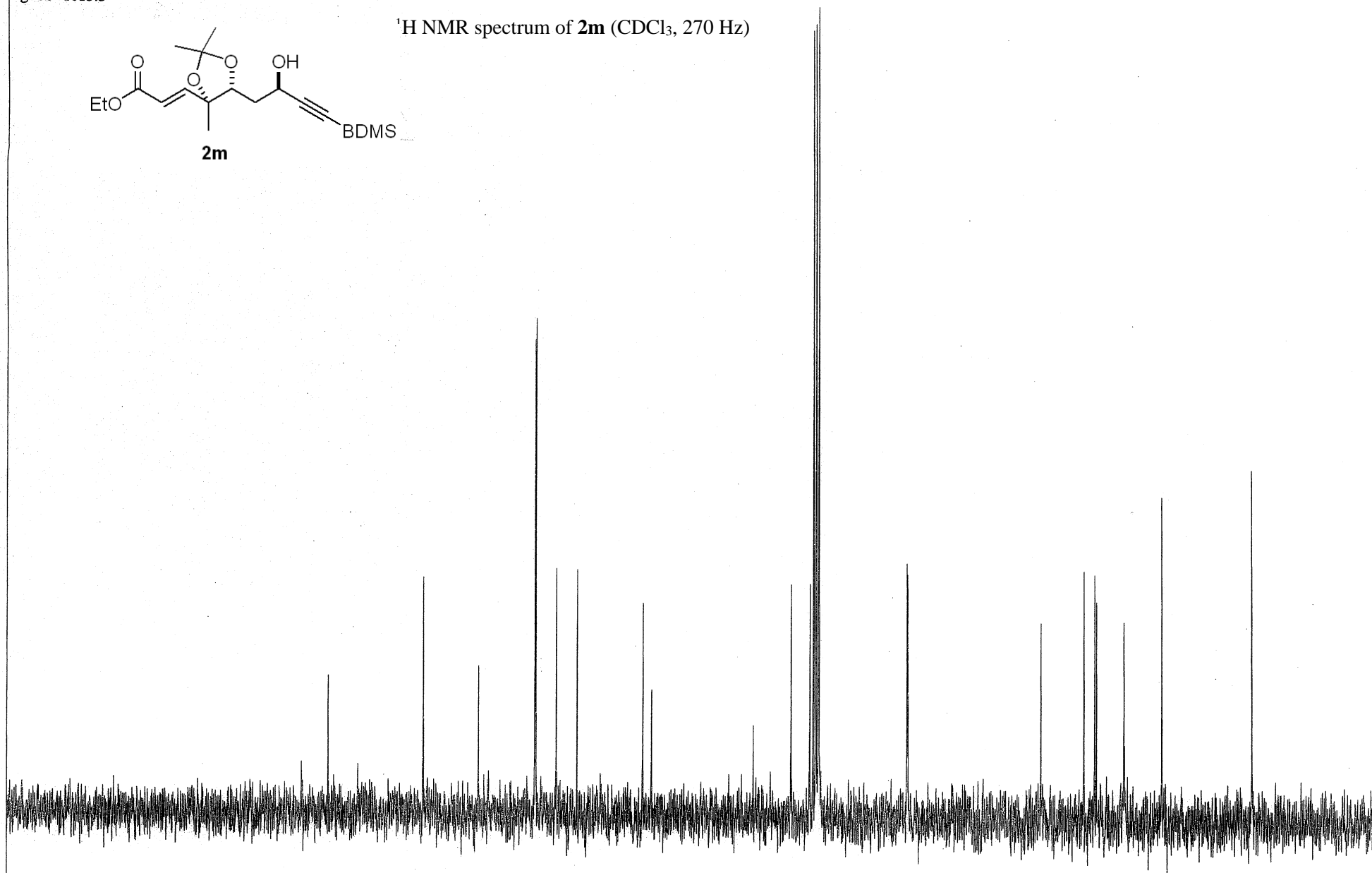
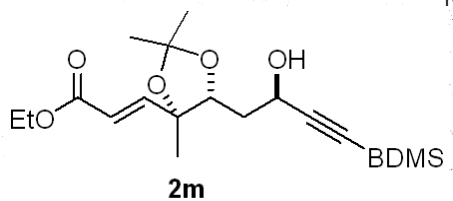
S92

<sup>1</sup>H NMR spectrum of **2m** (CDCl<sub>3</sub>, 150 Hz)



X : parts per Million : 1H

<sup>1</sup>H NMR spectrum of **2m** (CDCl<sub>3</sub>, 270 Hz)



220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

166.2818

148.8258

138.6883

128.2681

128.1153

124.3720

120.5981

108.6043

78.1154

77.4660

77.0000

76.5264

60.5295

60.4149

36.0452

28.2453

26.3126

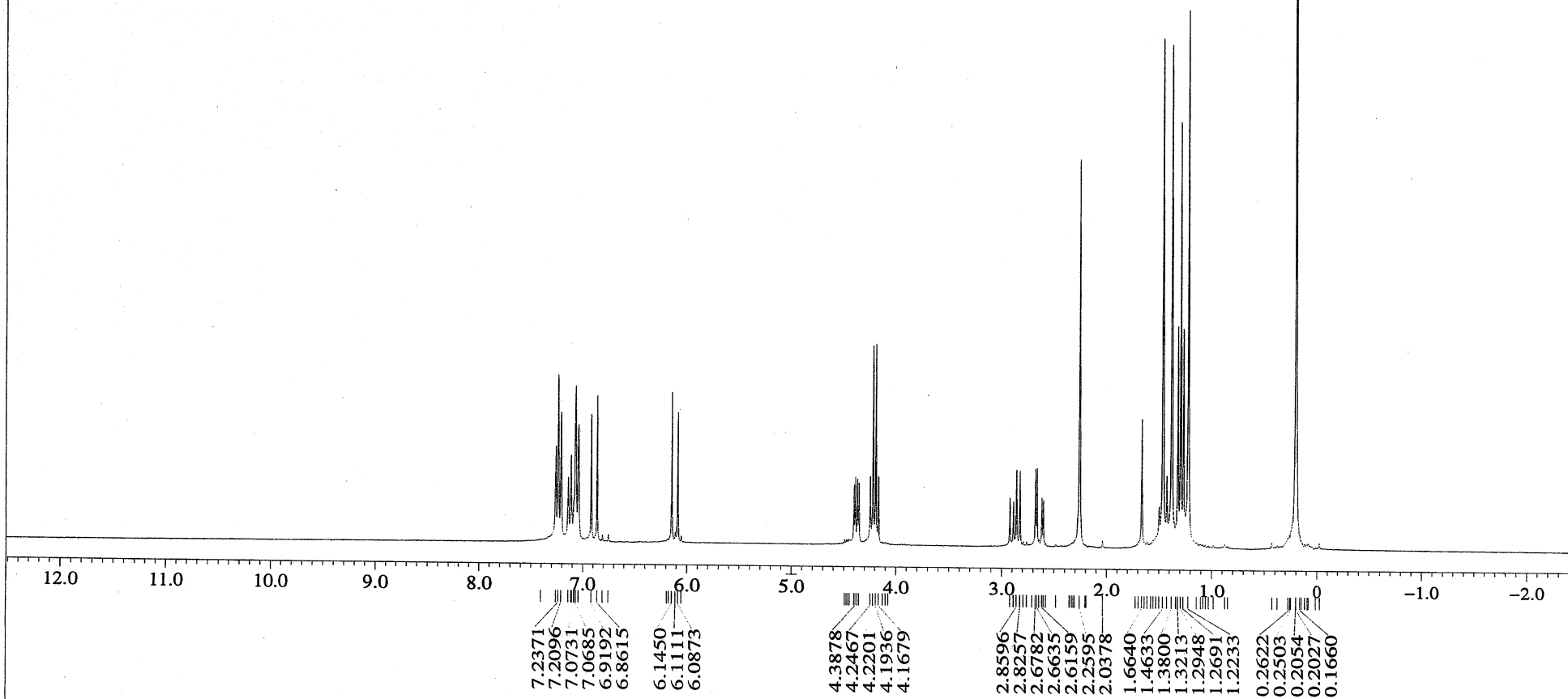
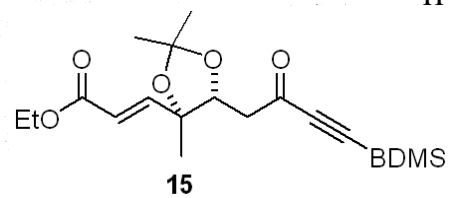
25.9841

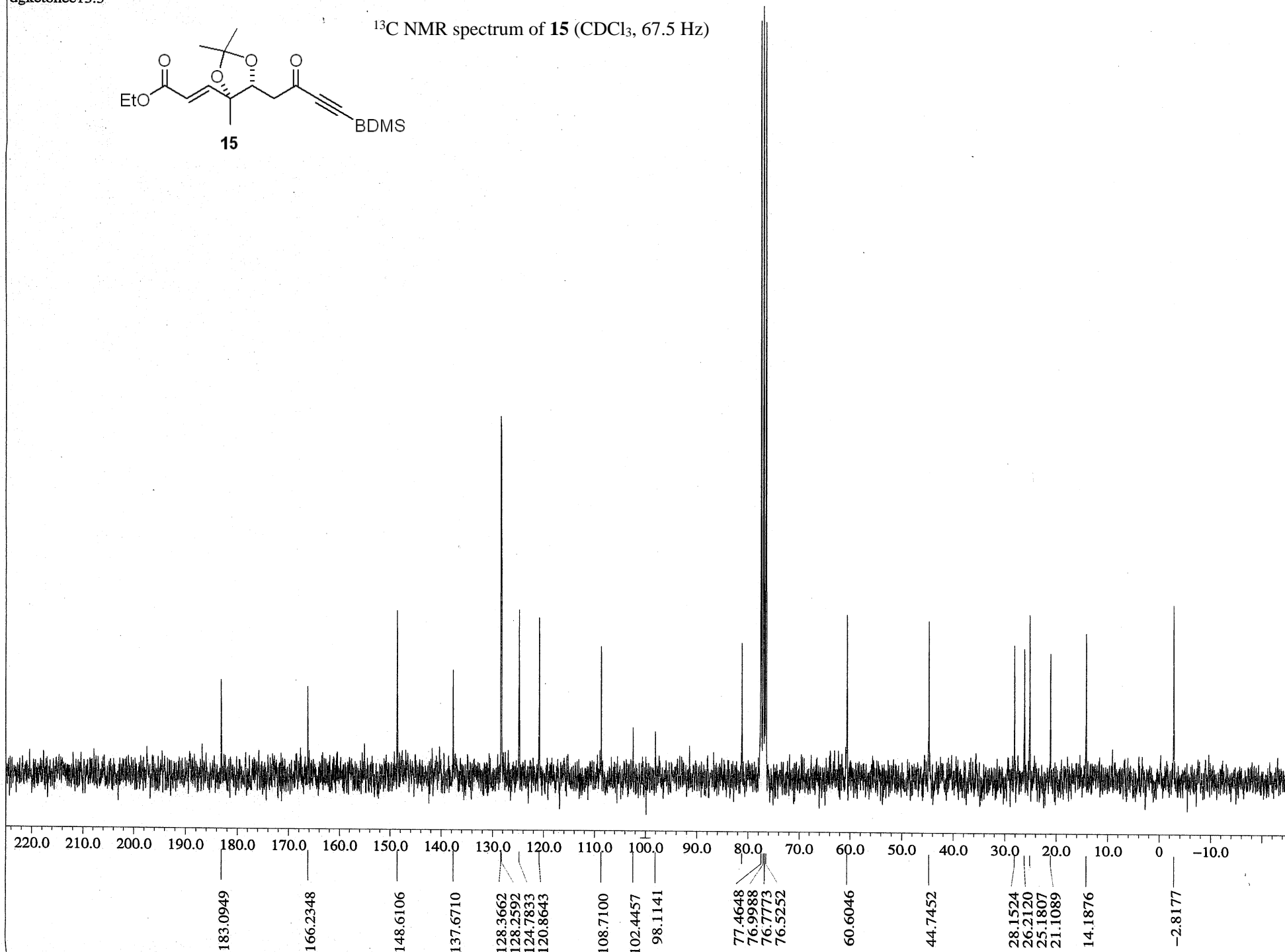
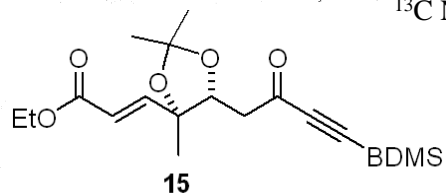
21.0566

14.1506

-2.2588

X : parts per Million : 13C

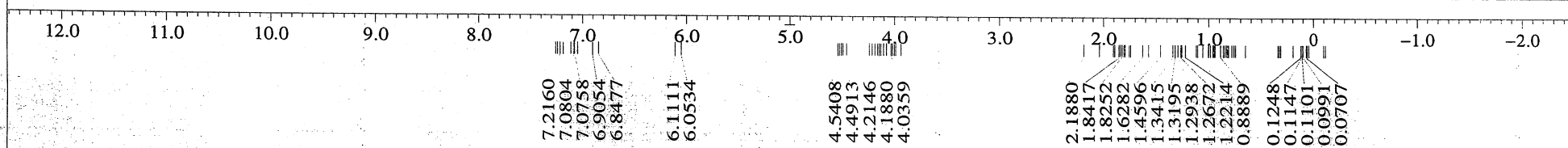
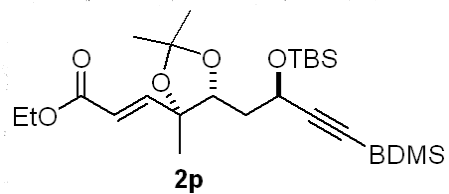
$^1\text{H}$  NMR spectrum of **15** ( $\text{CDCl}_3$ , 270 Hz)

$^{13}\text{C}$  NMR spectrum of **15** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$



dg291.3

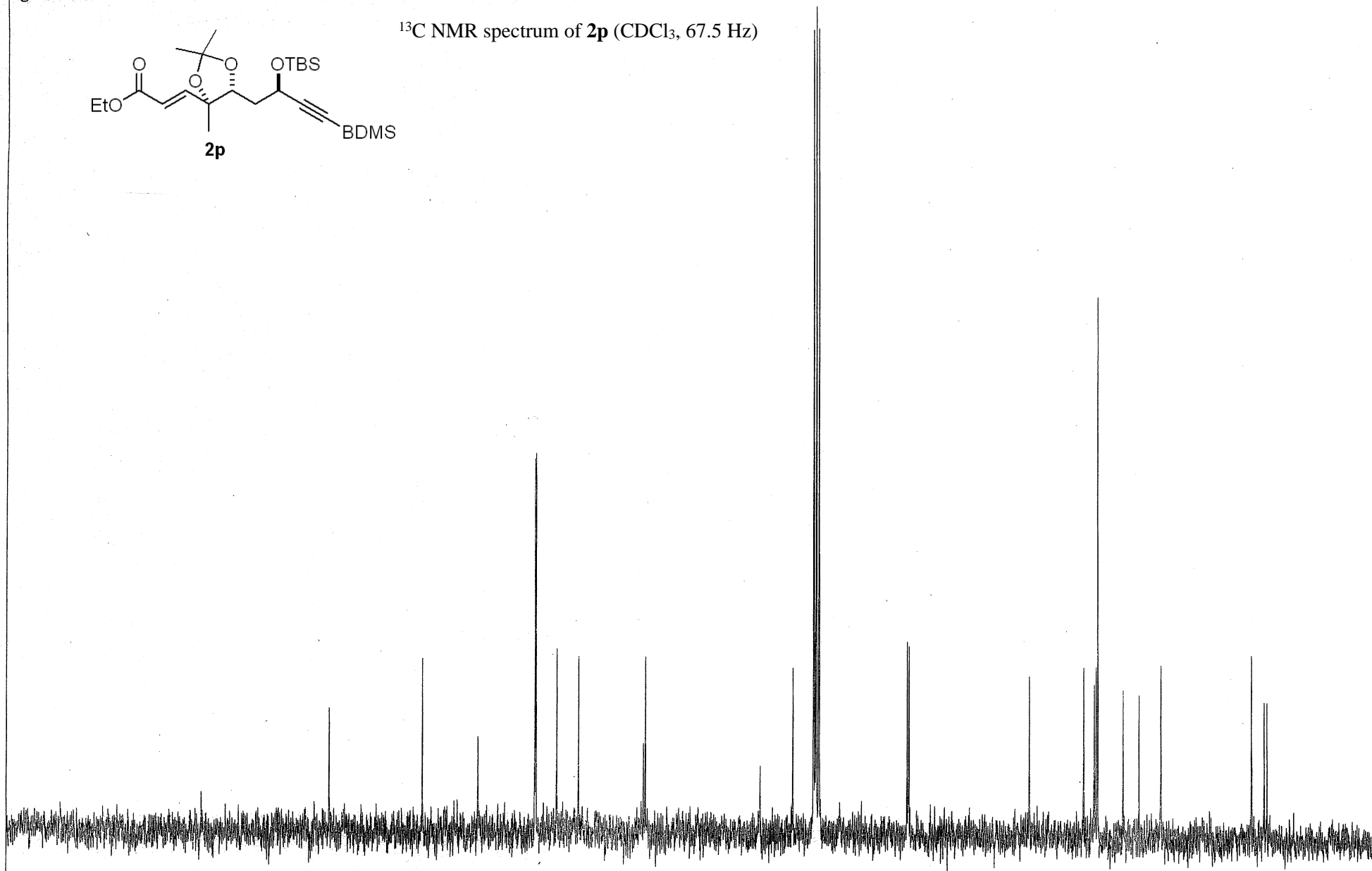
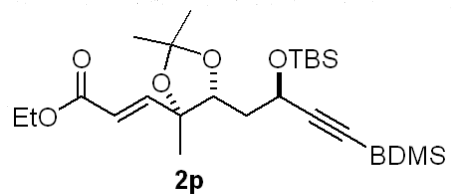
<sup>1</sup>H NMR spectrum of **2p** (CDCl<sub>3</sub>, 270 Hz)



X : parts per Million : 1H

dg291c13.3

<sup>13</sup>C NMR spectrum of **2p** (CDCl<sub>3</sub>, 67.5 Hz)

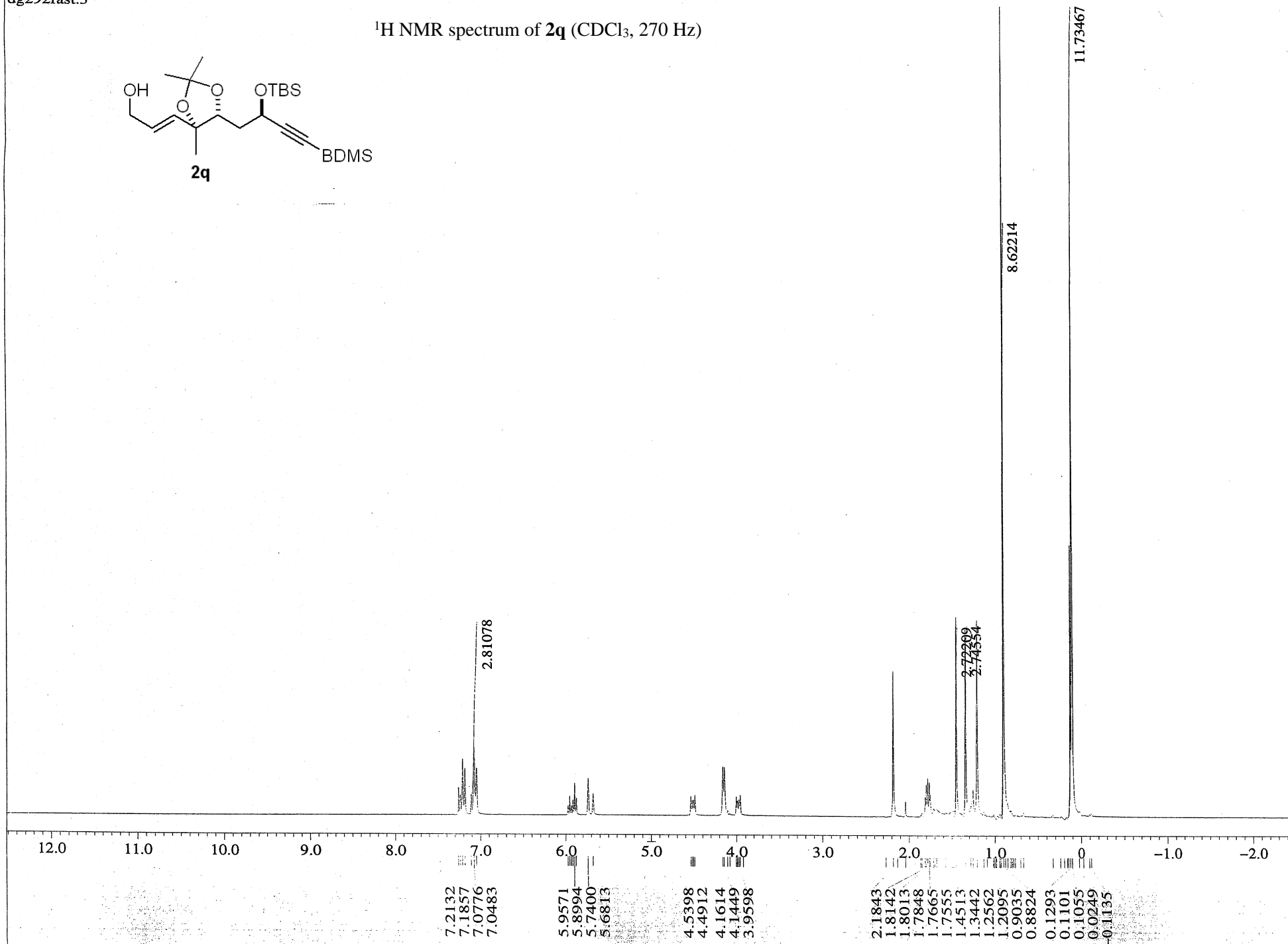
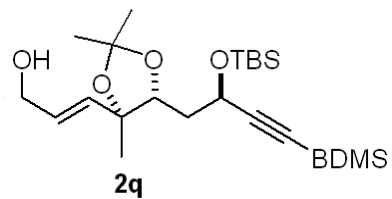


220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

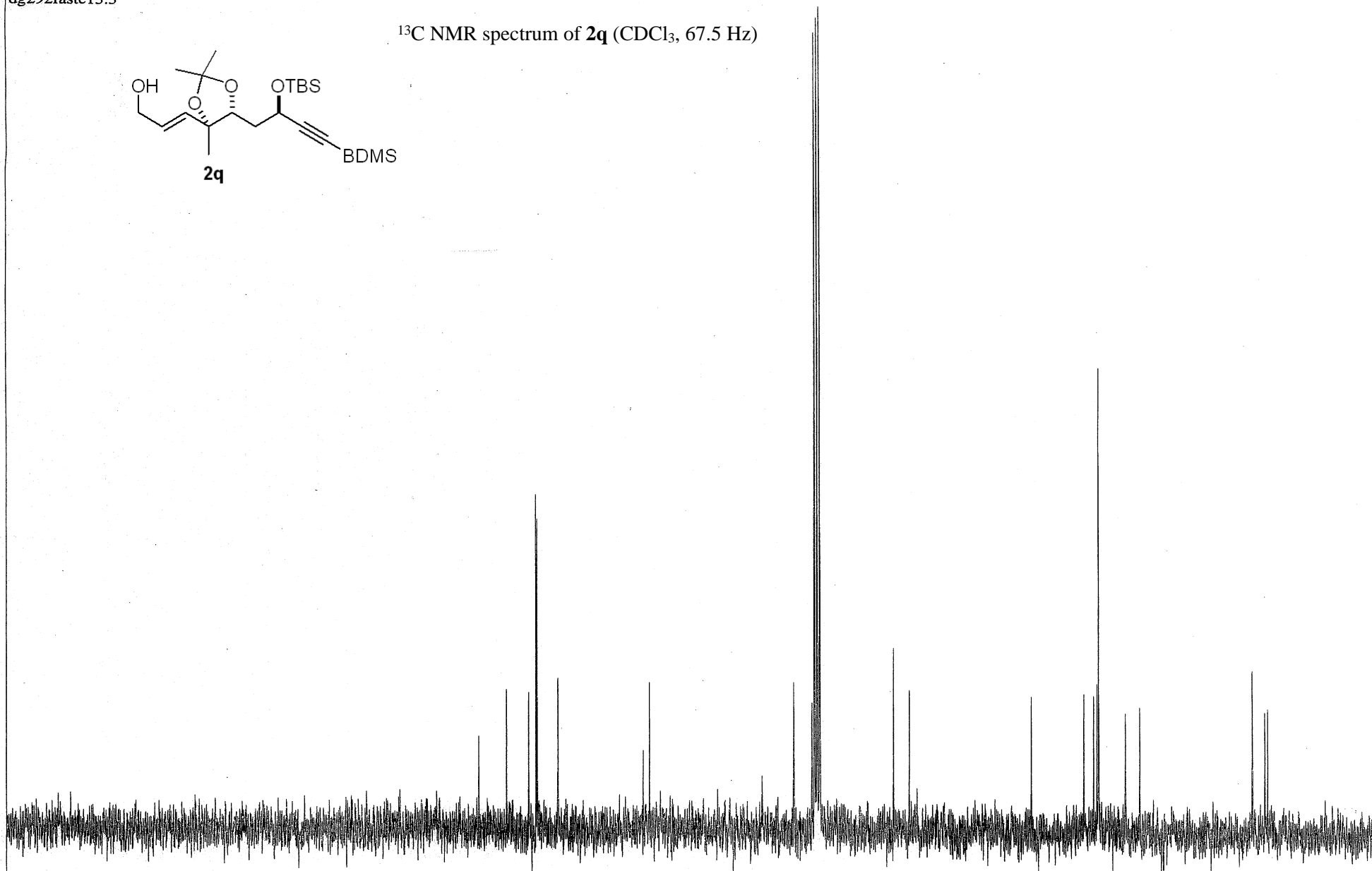
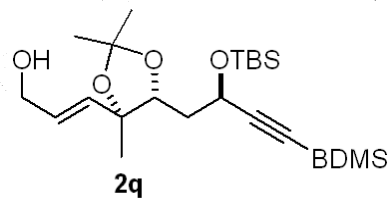
166.3185 149.1298 138.8166 128.3277 128.1443 124.3399 120.3827 108.4881 108.1520 77.4721 77.2353 76.9985 76.5248 60.4592 60.1230 38.1826 28.3202 26.3721 26.0283 25.7304 21.0856 18.1750 14.2025 -2.2680 -4.5904 -5.1099

X : parts per Million : <sup>13</sup>C

<sup>1</sup>H NMR spectrum of **2q** (CDCl<sub>3</sub>, 270 Hz)



<sup>13</sup>C NMR spectrum of **2q** (CDCl<sub>3</sub>, 67.5 Hz)

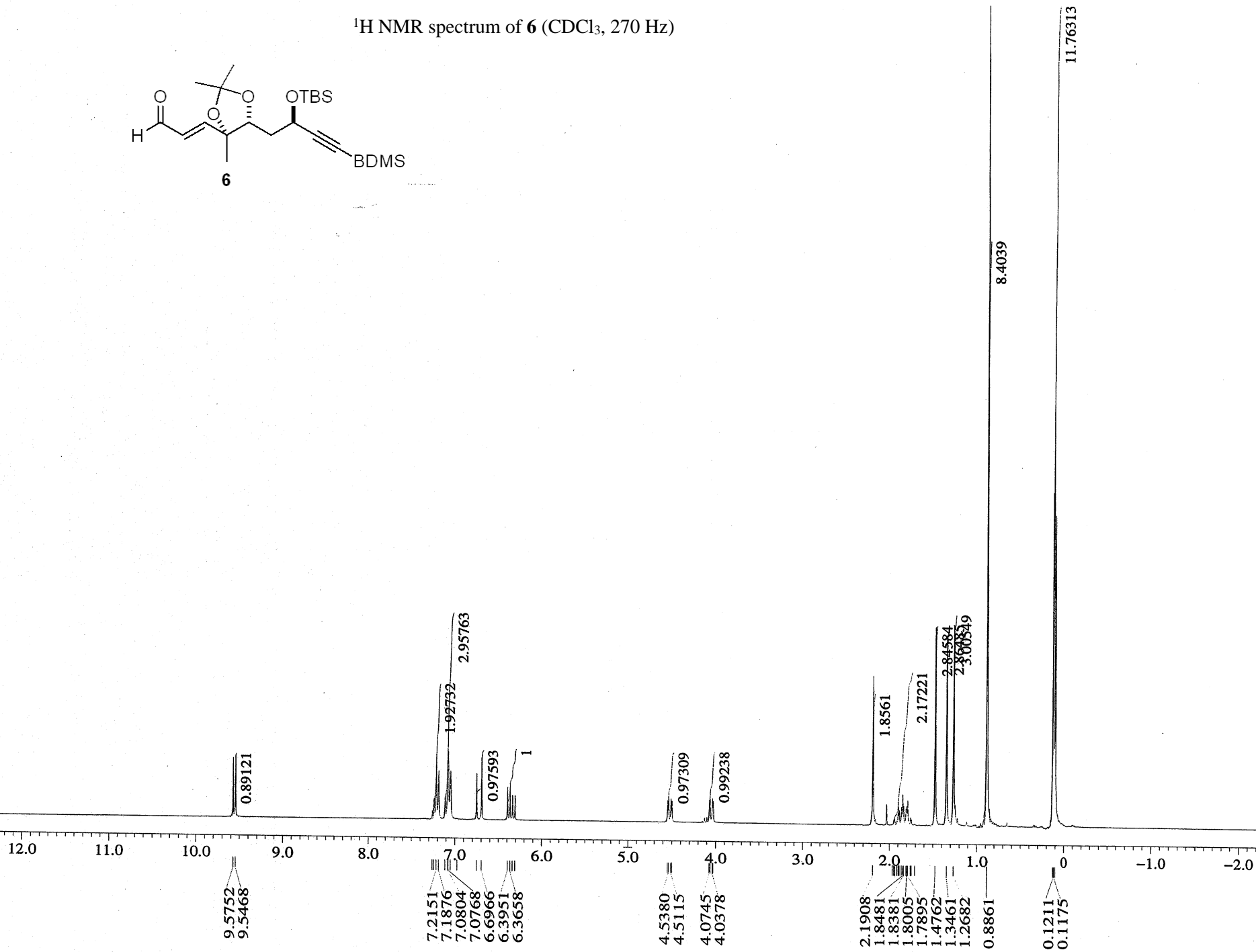
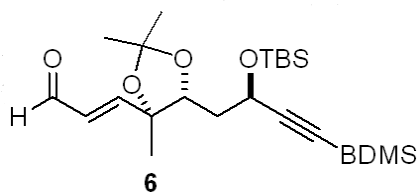


| Chemical Shift (ppm) |
|----------------------|
| 138.8402             |
| 133.7447             |
| 129.6576             |
| 128.3284             |
| 128.1374             |
| 124.3253             |
| 108.7027             |
| 107.5368             |
| 81.2543              |
| 77.4652              |
| 76.9992              |
| 76.5256              |
| 63.0802              |
| 60.2154              |
| 38.0076              |
| 28.4355              |
| 26.6708              |
| 26.0443              |
| 25.7540              |
| 20.8648              |
| 18.2063              |
| -2.2826              |
| -2.2826              |
| -2.2826              |

X : parts per Million : <sup>13</sup>C

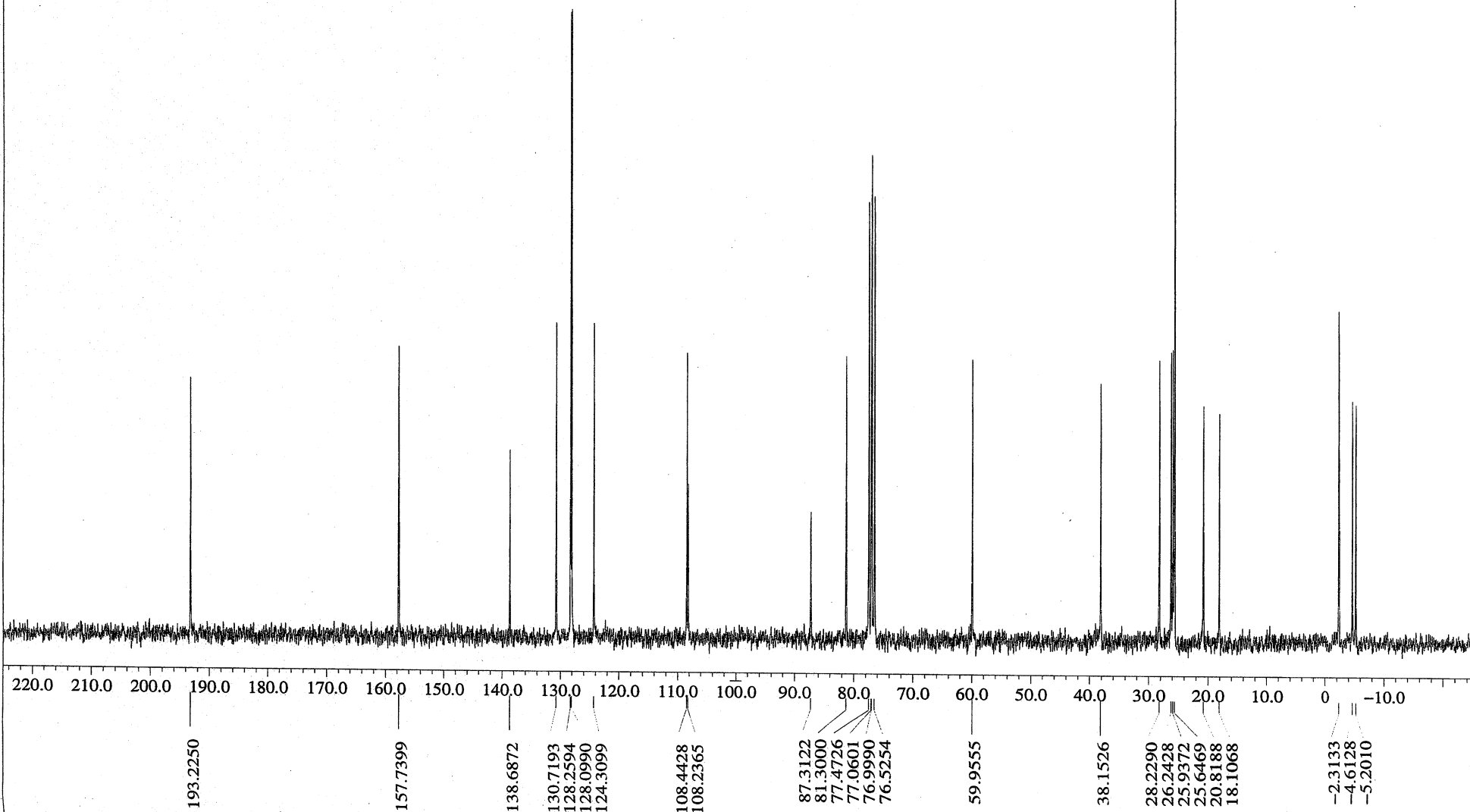
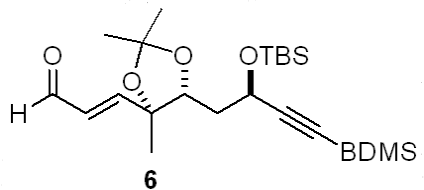
dg305.3

<sup>1</sup>H NMR spectrum of **6** (CDCl<sub>3</sub>, 270 Hz)



X : parts per Million : 1H

S101

$^{13}\text{C}$  NMR spectrum of **6** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

## STANDARD PROTON PARAMETERS

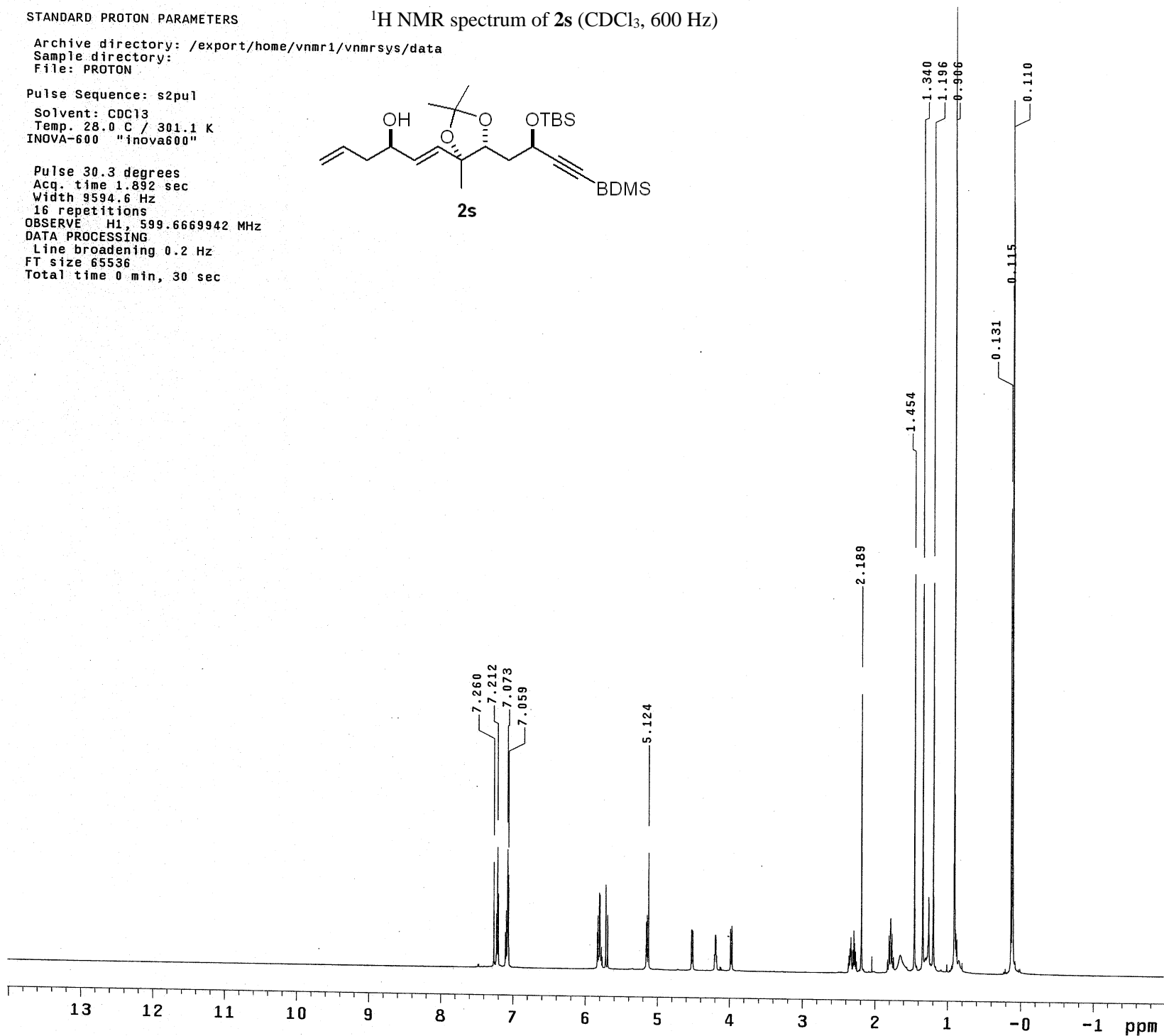
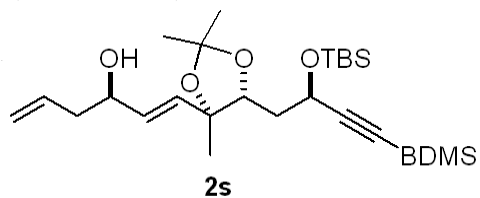
 $^1\text{H}$  NMR spectrum of **2s** ( $\text{CDCl}_3$ , 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1

Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Pulse 30.3 degrees  
Acq. time 1.892 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6669942 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 65536  
Total time 0 min, 30 sec



dg294\_13Jun2005

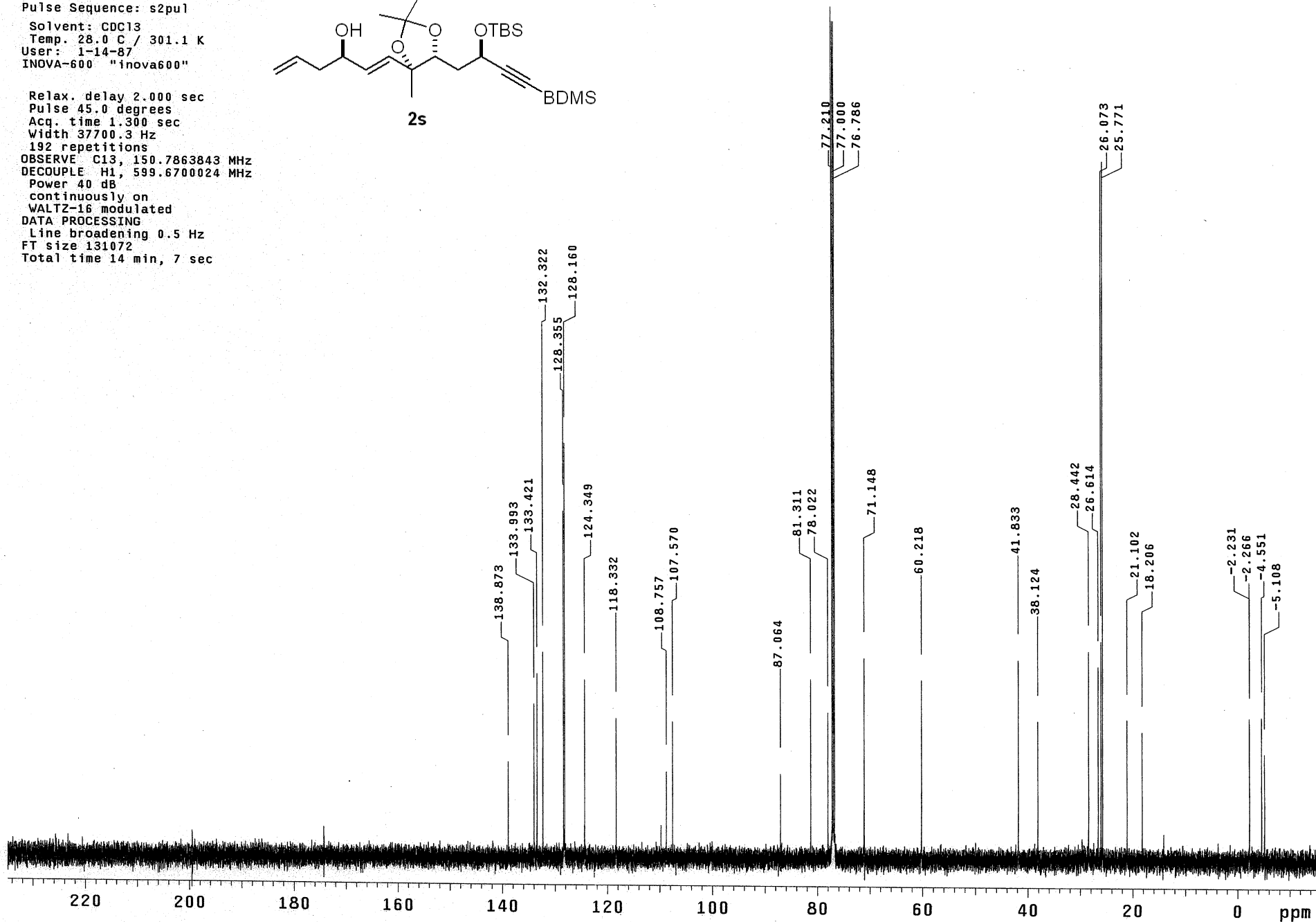
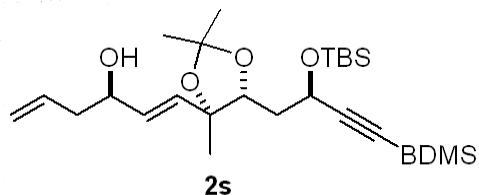
<sup>13</sup>C NMR spectrum of 2s (CDCl<sub>3</sub>, 150 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg294\_13Jun2005  
File: CARBON

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 37700.3 Hz  
192 repetitions  
OBSERVE C13, 150.7863843 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 14 min, 7 sec





dg296\_15Jun2005

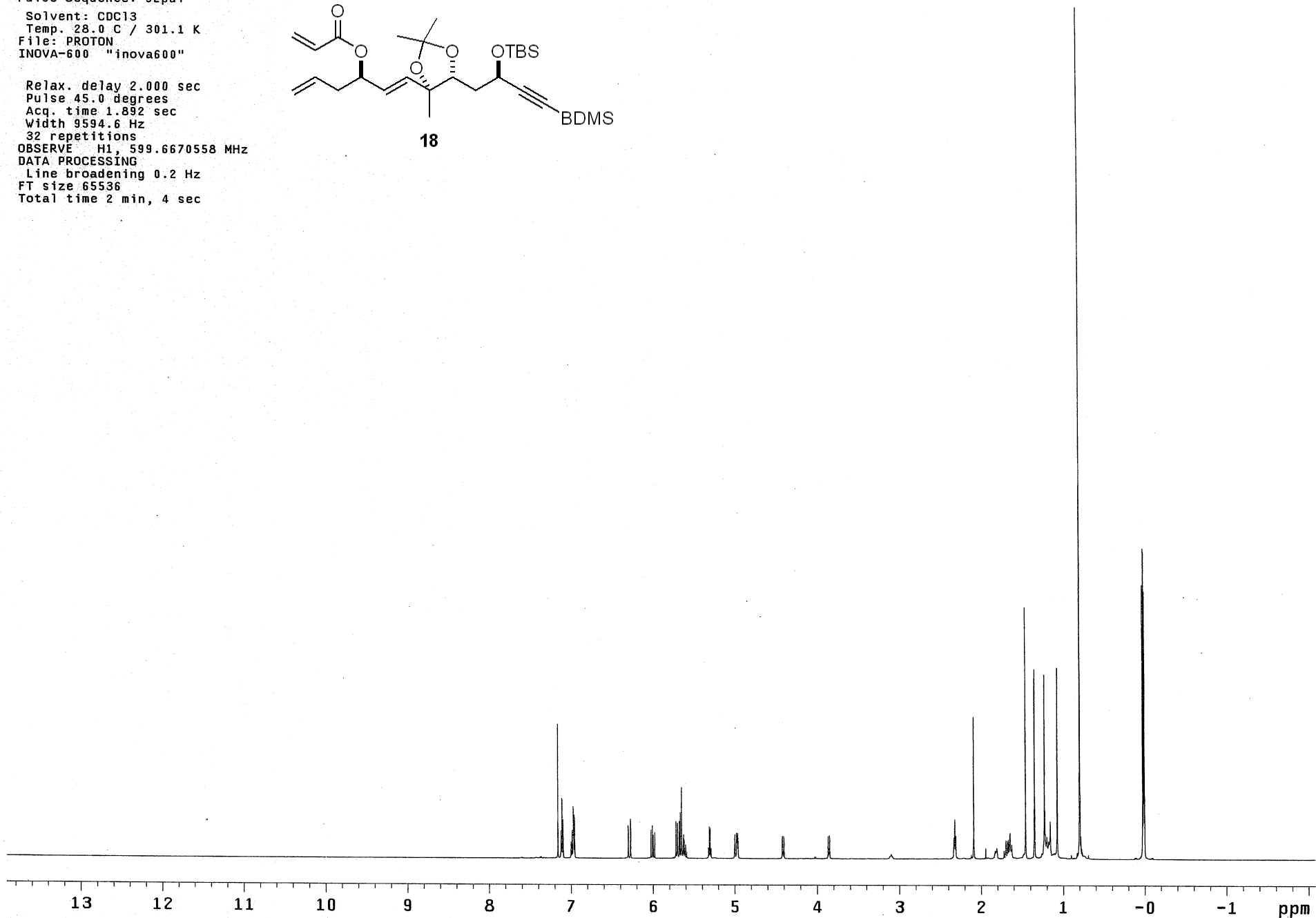
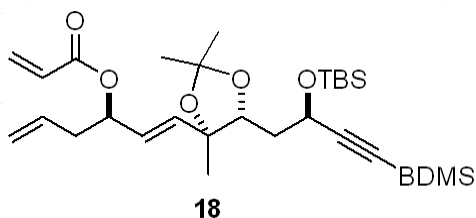
<sup>1</sup>H NMR spectrum of **18** (CDCl<sub>3</sub>, 600 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg296\_15Jun2005

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
File: PROTON  
INOVA-600 "inova600"

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 9594.6 Hz  
32 repetitions  
OBSERVE H1, 599.6670558 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 65536  
Total time 2 min, 4 sec



S105

dg296\_15Jun2005

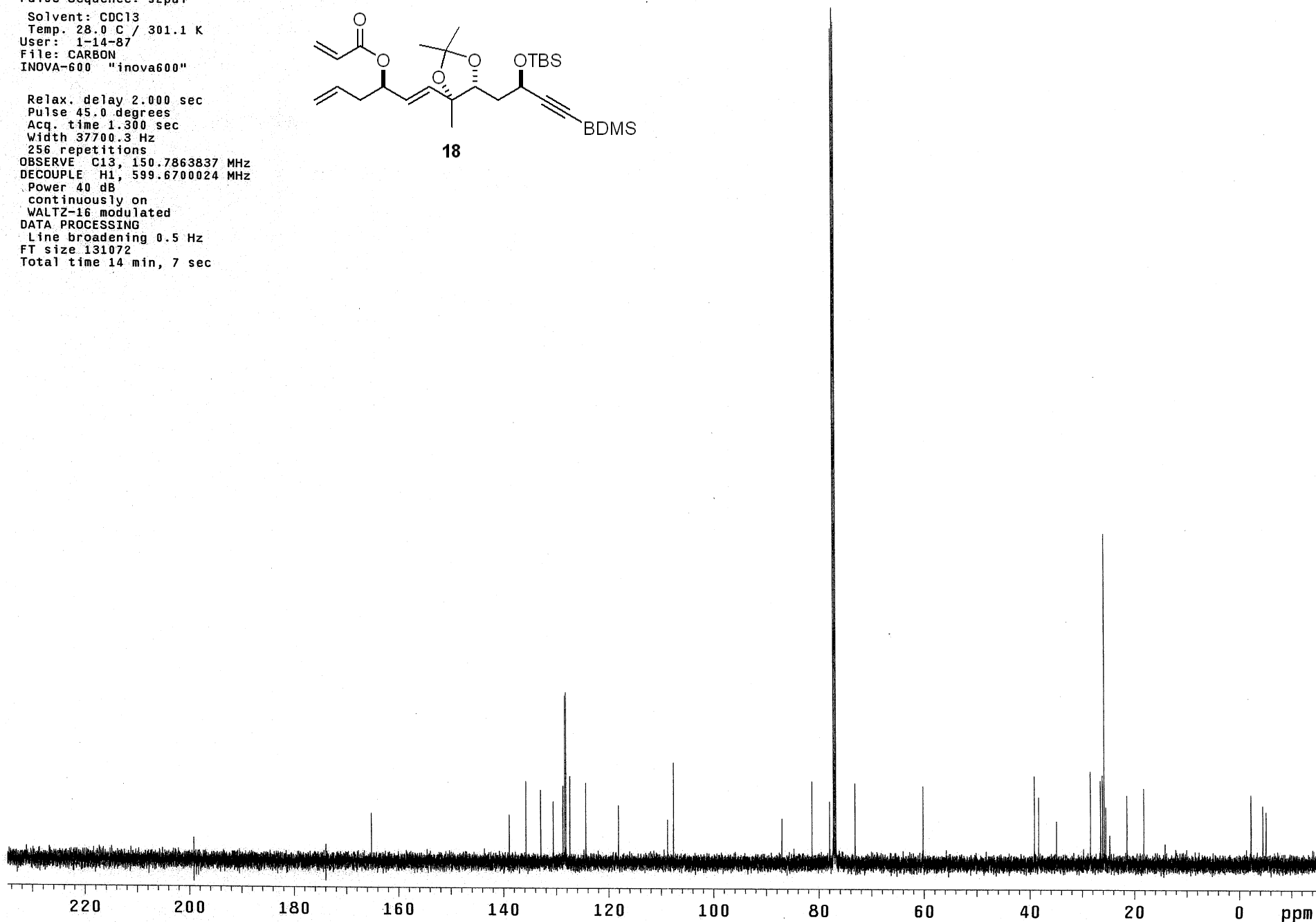
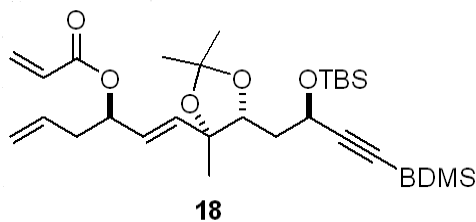
<sup>13</sup>C NMR spectrum of **18** (CDCl<sub>3</sub>, 150 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg296\_15Jun2005

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
File: CARBON  
INNOVA-600 "inova600"

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 37700.3 Hz  
256 repetitions  
OBSERVE C13, 150.7863837 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 14 min, 7 sec



dg299\_18Jun2005

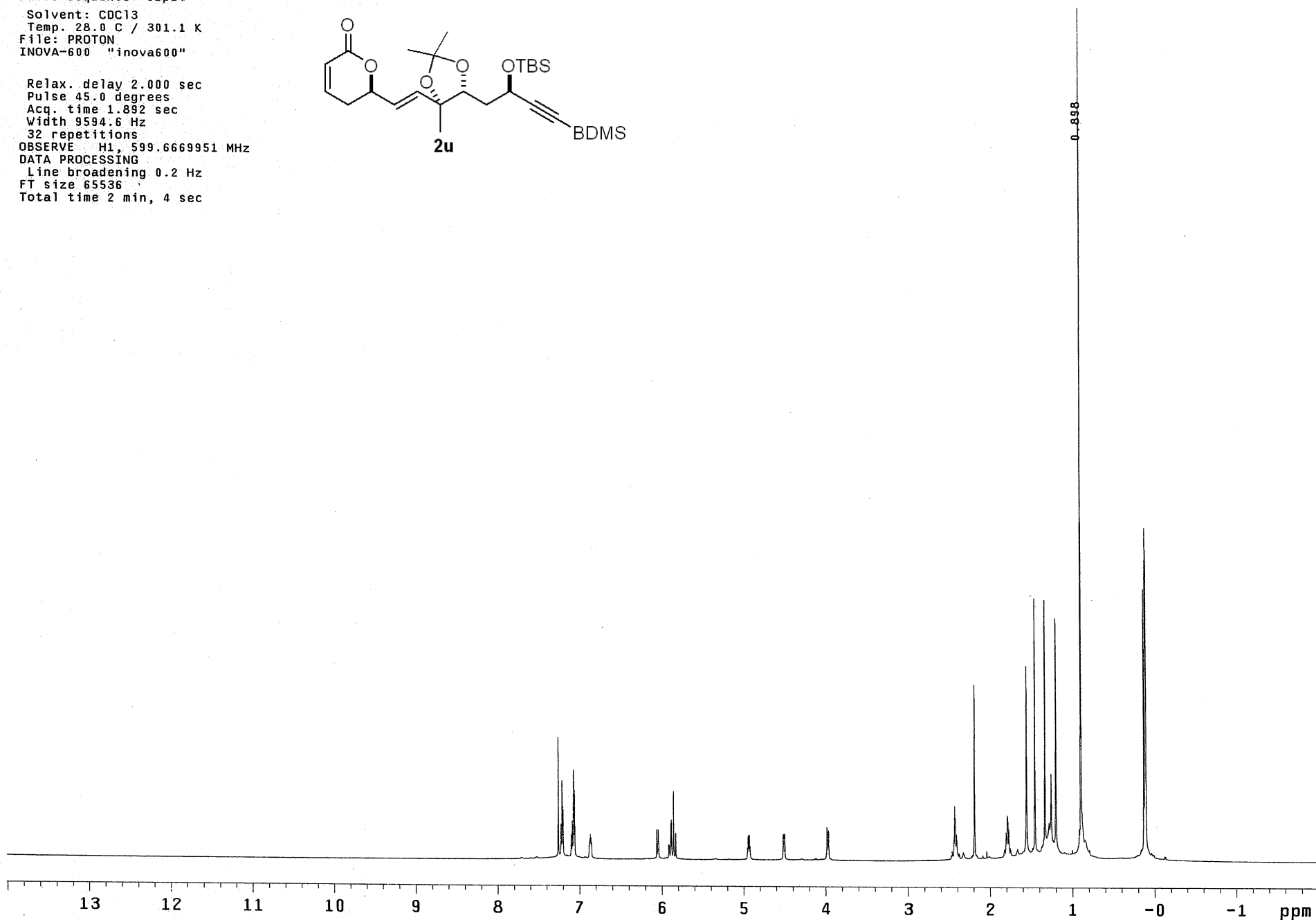
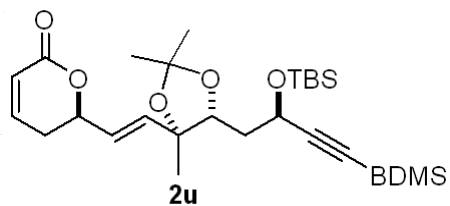
<sup>1</sup>H NMR spectrum of **2u** (CDCl<sub>3</sub>, 600 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg299\_18Jun2005

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
File: PROTON  
INOVA-600 "inova600"

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 9594.6 Hz  
32 repetitions  
OBSERVE H1, 599.6669951 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 65536  
Total time 2 min, 4 sec



S107

dg299\_18Jun2005

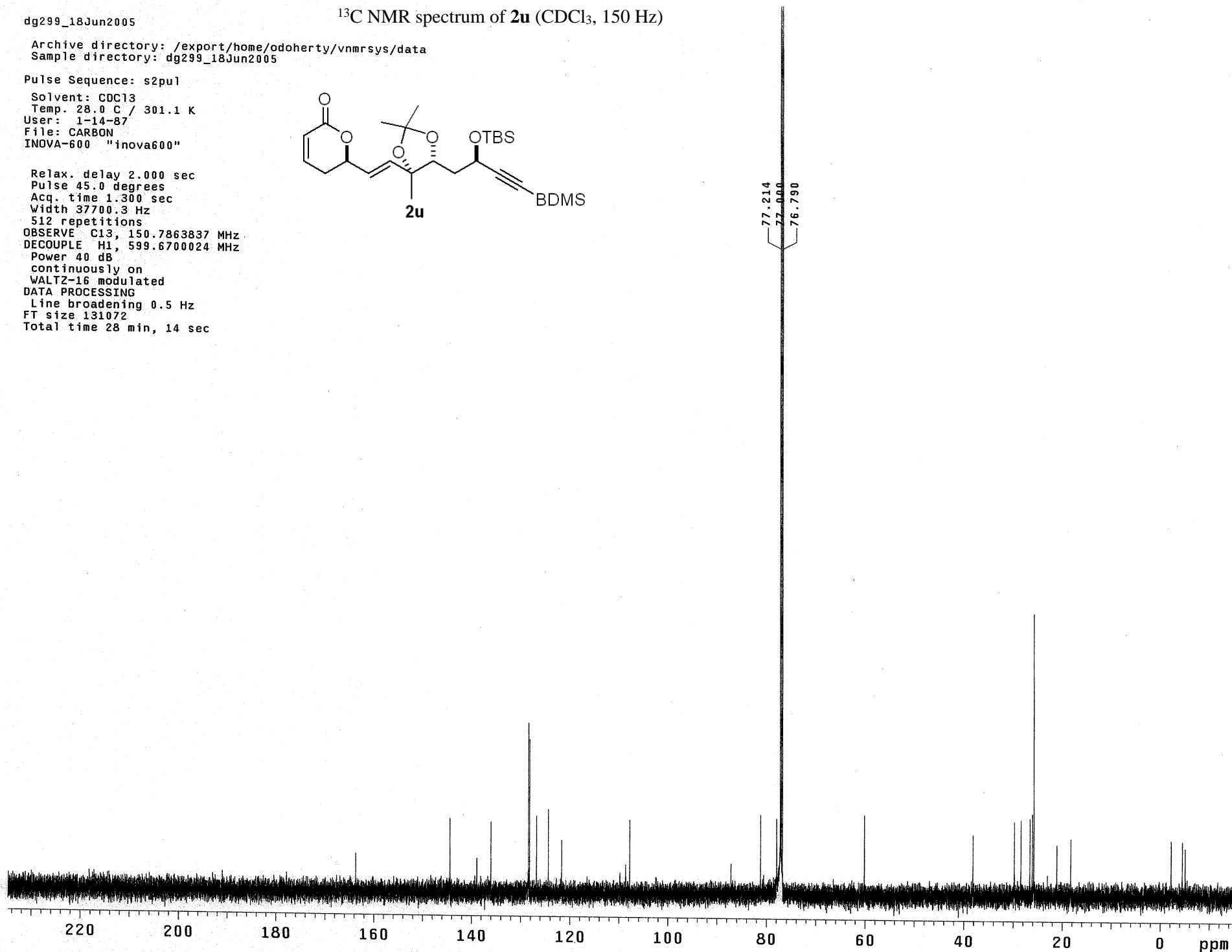
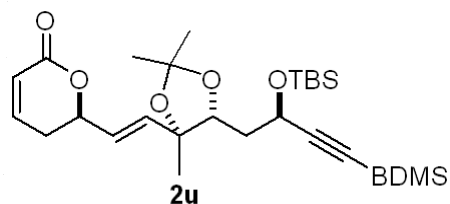
<sup>13</sup>C NMR spectrum of **2u** (CDCl<sub>3</sub>, 150 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg299\_18Jun2005

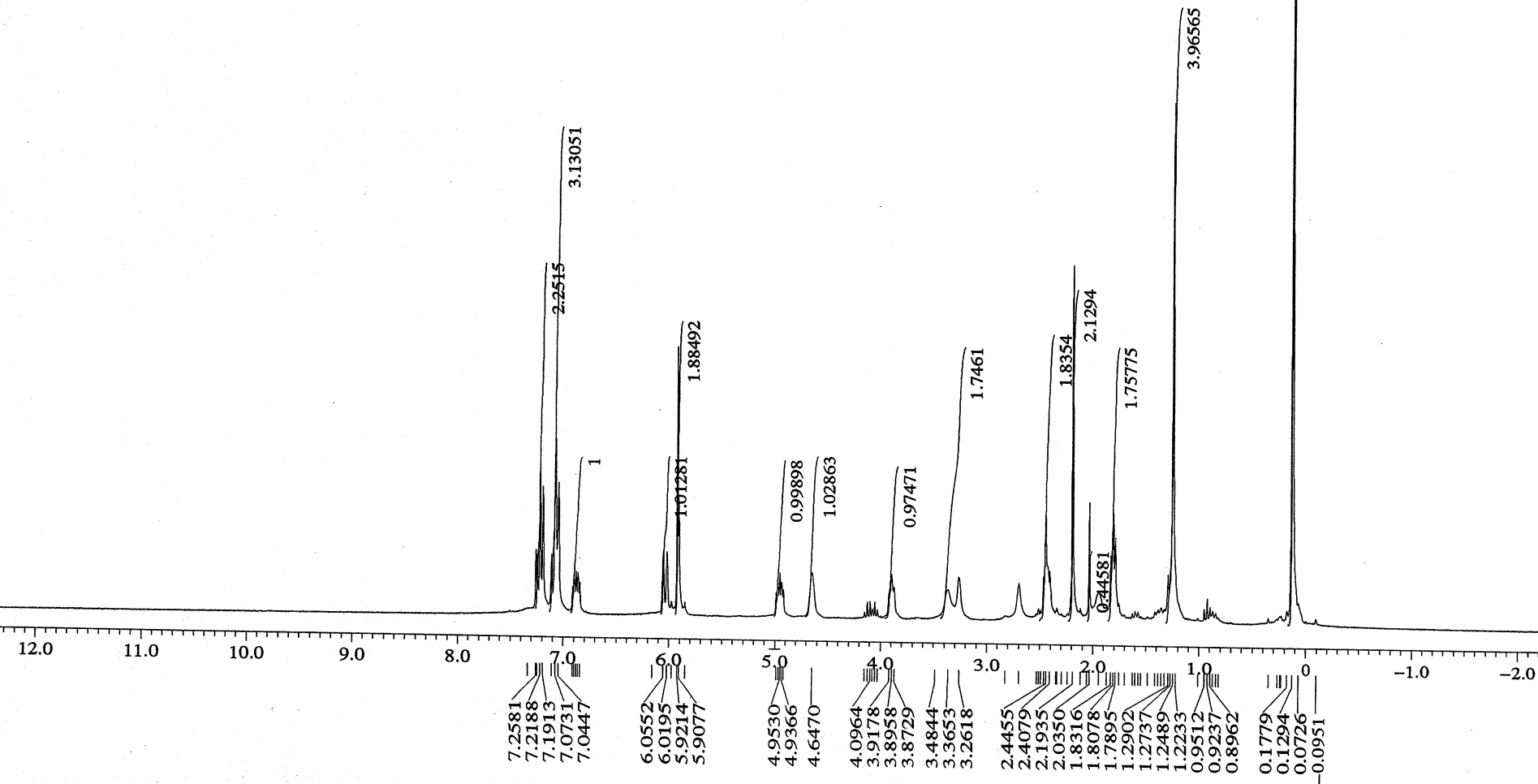
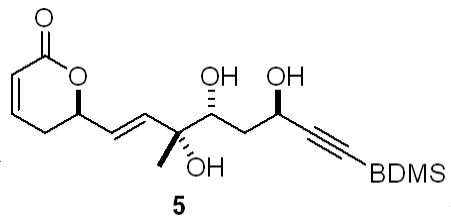
Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
File: CARBON  
INOVA-600 "inova600"

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 37700.3 Hz  
512 repetitions  
OBSERVE C13, 150.7863837 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 28 min, 14 sec

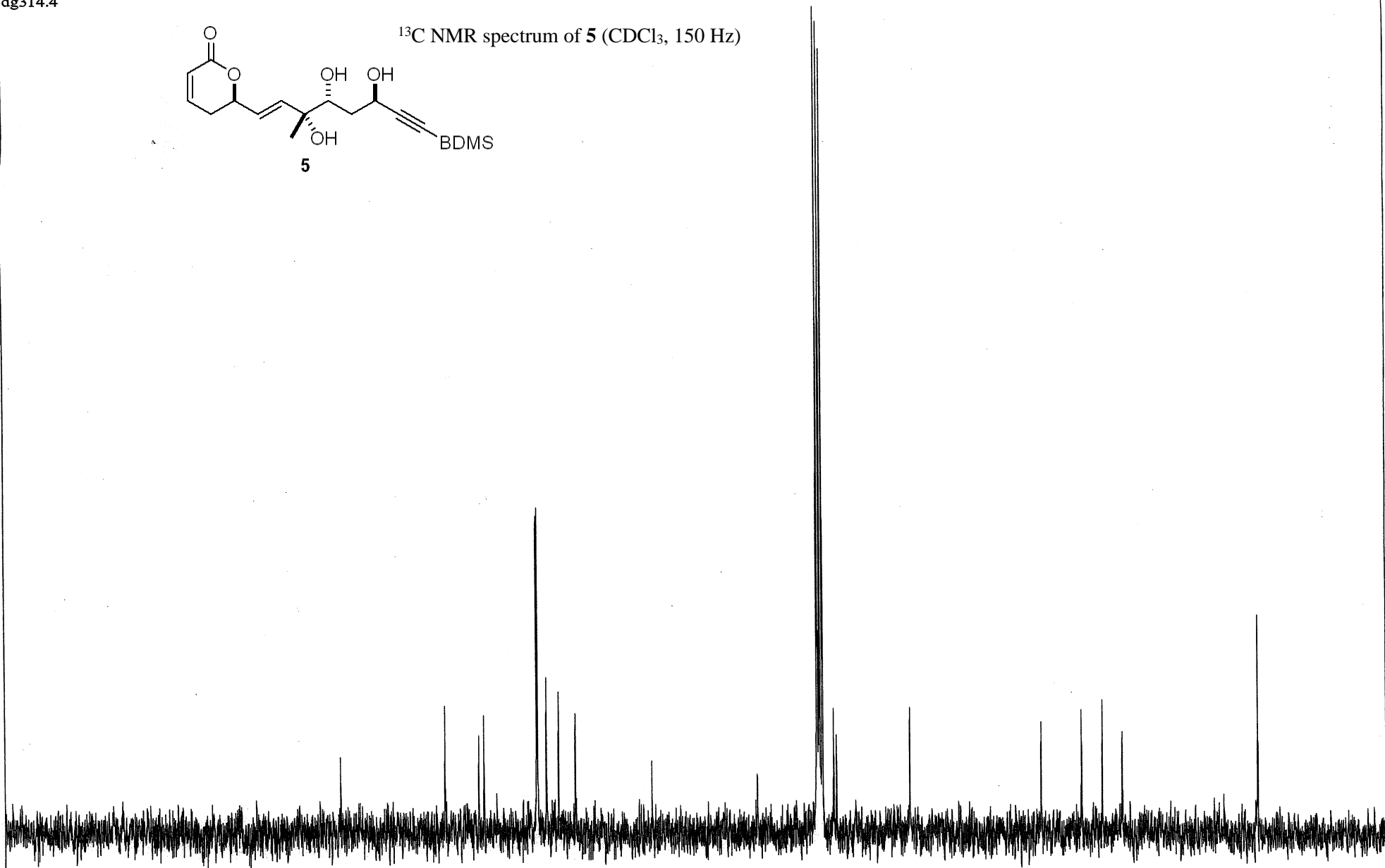
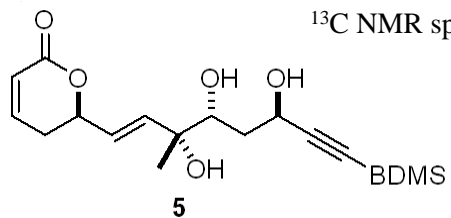


<sup>1</sup>H NMR spectrum of **5** (CDCl<sub>3</sub>, 600 Hz)



X : parts per Million : 1H

dg314.4



220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

164.1354

144.9758

137.9170

128.3448

128.1614

126.6030

124.3876

121.3624

107.4816

88.2608

77.4740

77.2677

77.0003

76.5343

74.5175

74.0209

60.7818

37.0538

29.7811

26.0455

22.4473

-2.1440

X : parts per Million : <sup>13</sup>C

S110

## STANDARD PROTON PARAMETERS

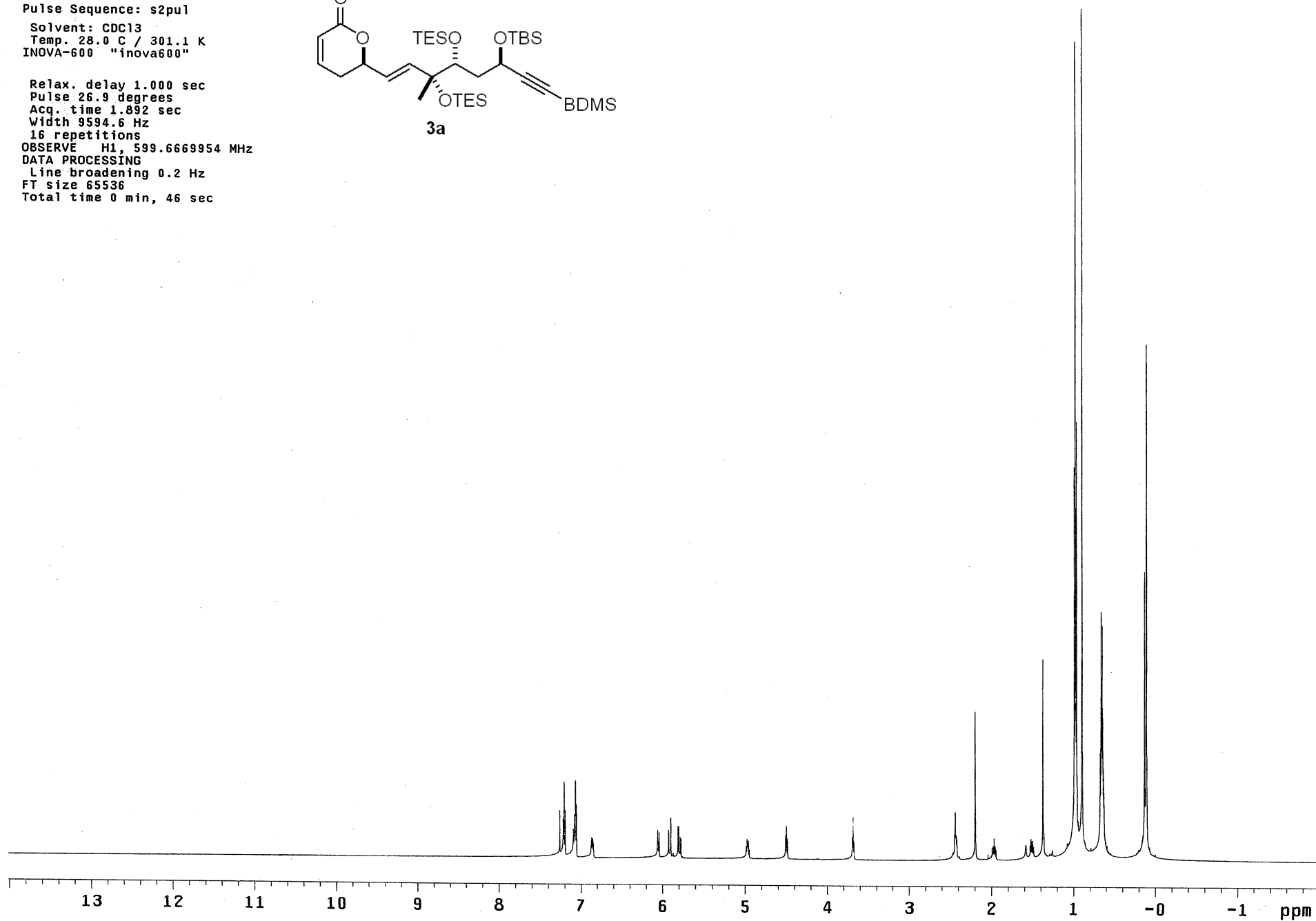
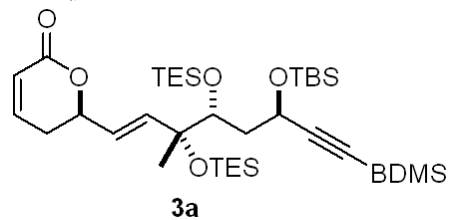
 $^1\text{H}$  NMR spectrum of **3a** ( $\text{CDCl}_3$ , 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1

Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 26.9 degrees  
Acq. time 1.892 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6669954 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 65536  
Total time 0 min, 46 sec



S111

dg366-1\_03Nov2005

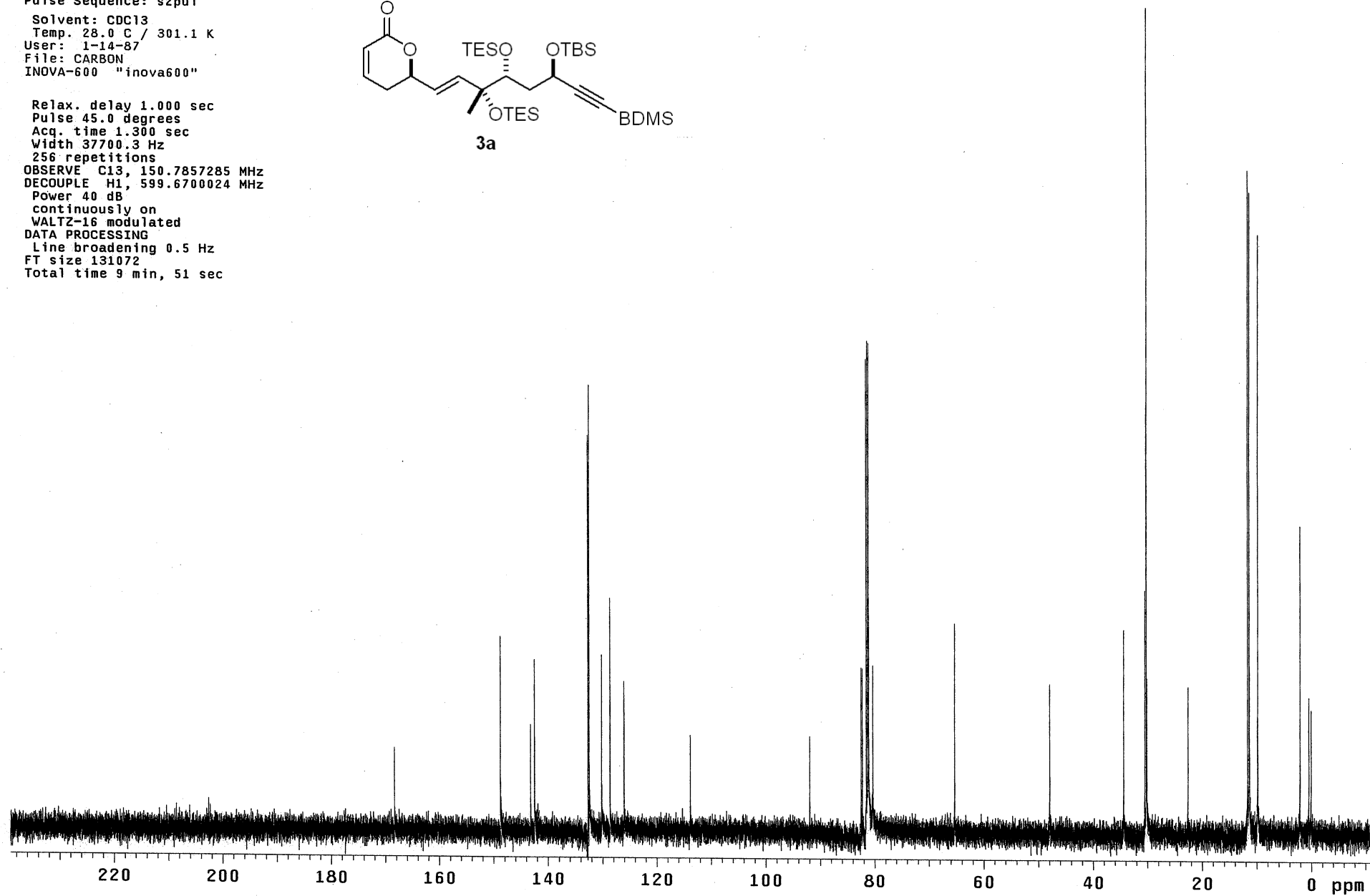
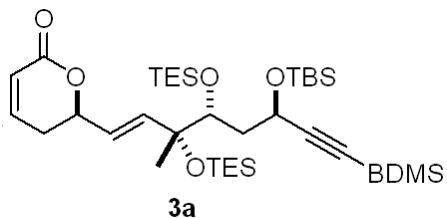
$^{13}\text{C}$  NMR spectrum of **3a** ( $\text{CDCl}_3$ , 150 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg366-1\_03Nov2005

Pulse Sequence: s2pu1

Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
File: CARBON  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 37700.3 Hz  
256 repetitions  
OBSERVE C13, 150.7857285 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 9 min, 51 sec





dg367\_04Nov2005

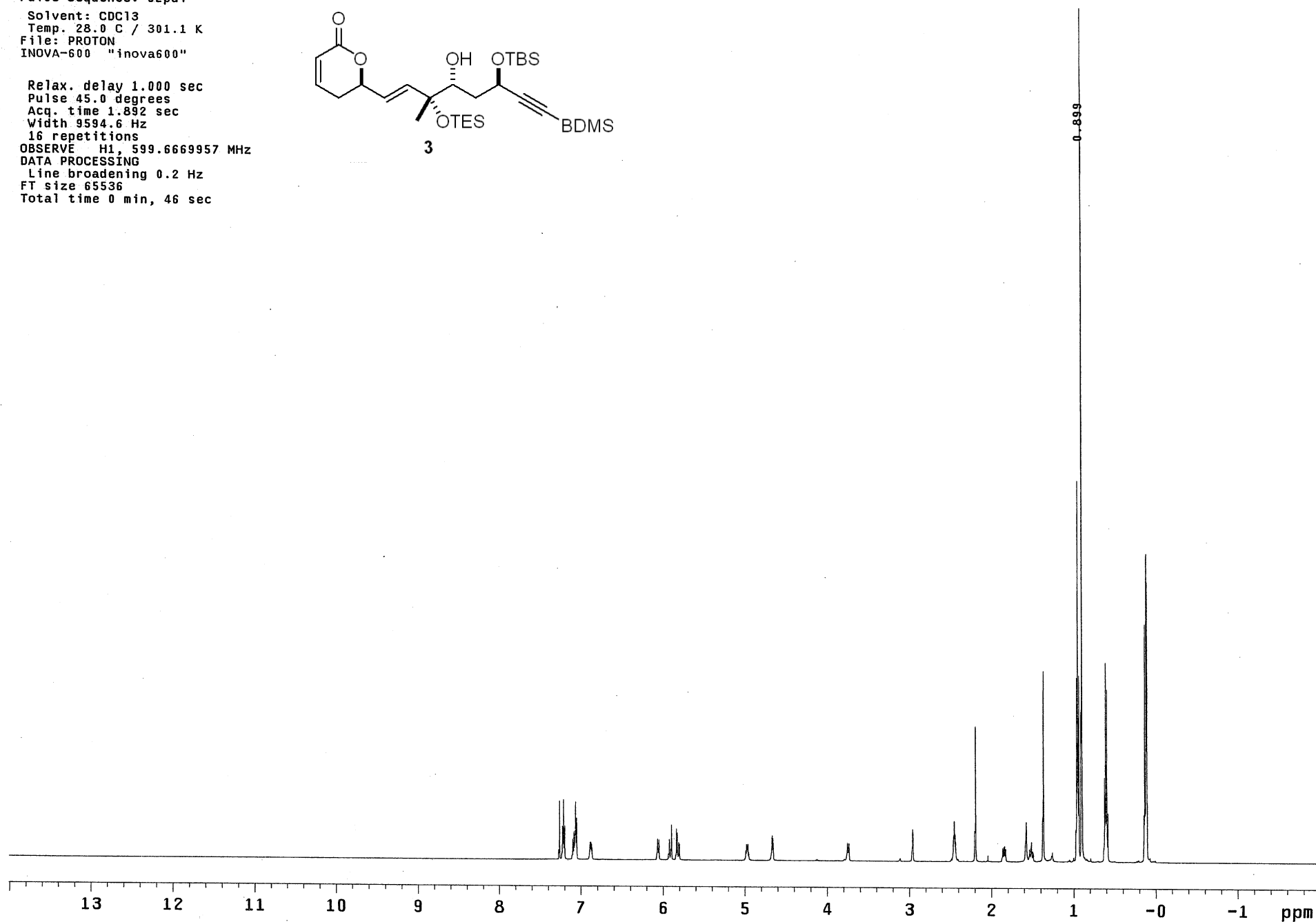
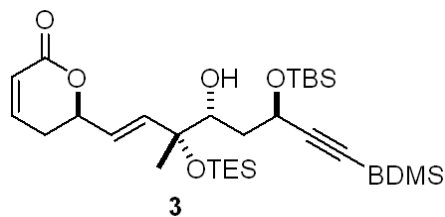
<sup>1</sup>H NMR spectrum of **3** (CDCl<sub>3</sub>, 600 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg367\_04Nov2005

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
File: PROTON  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6669957 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 65536  
Total time 0 min, 46 sec



S113

dg367\_04Nov2005

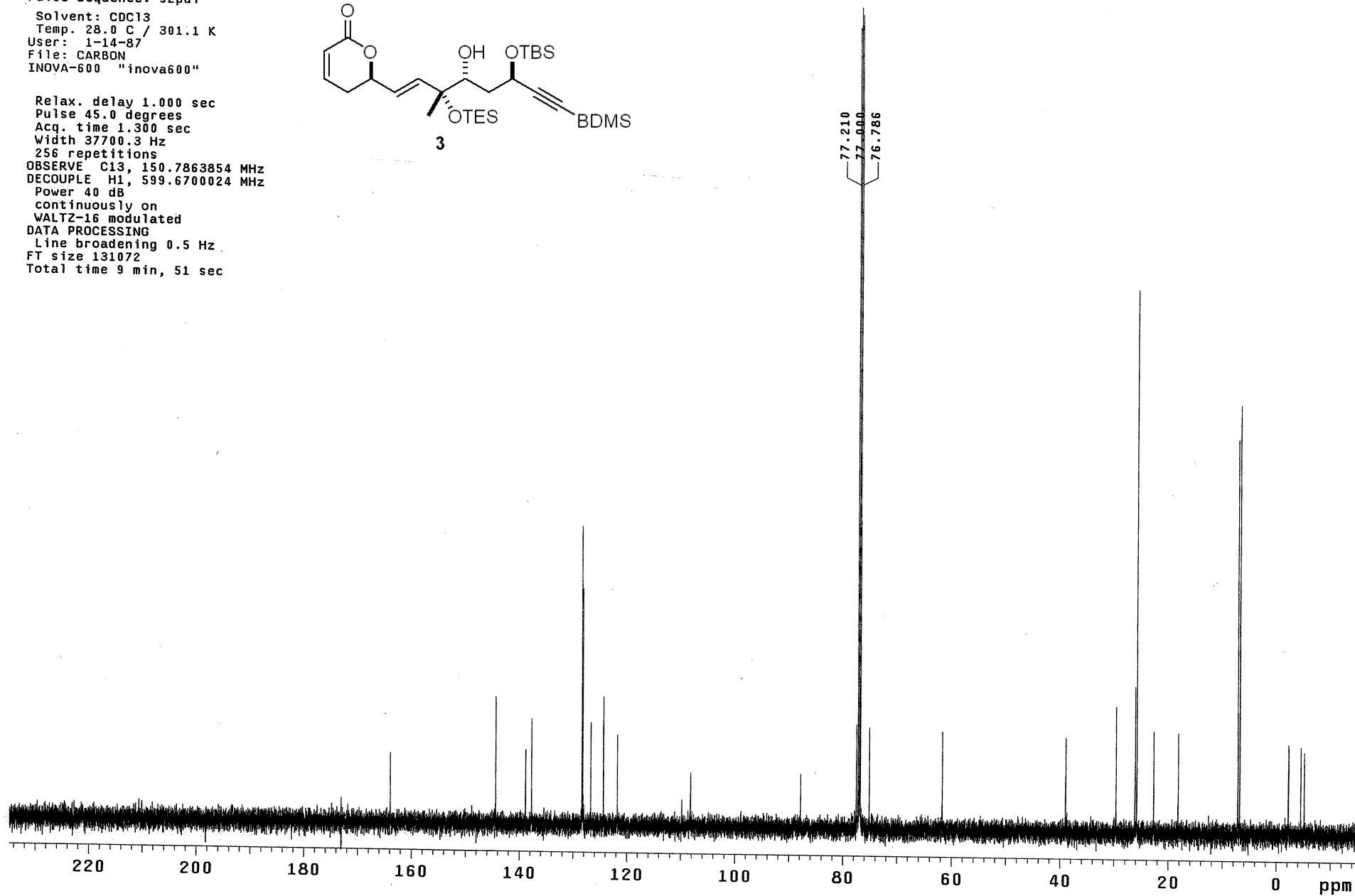
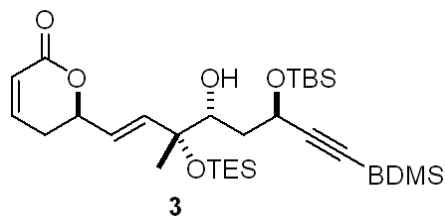
$^{13}\text{C}$  NMR spectrum of **3** ( $\text{CDCl}_3$ , 150 Hz)

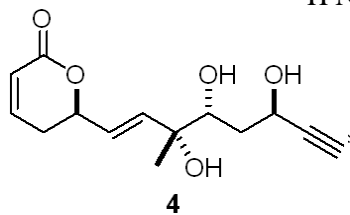
Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg367\_04Nov2005

Pulse Sequence: s2pu1

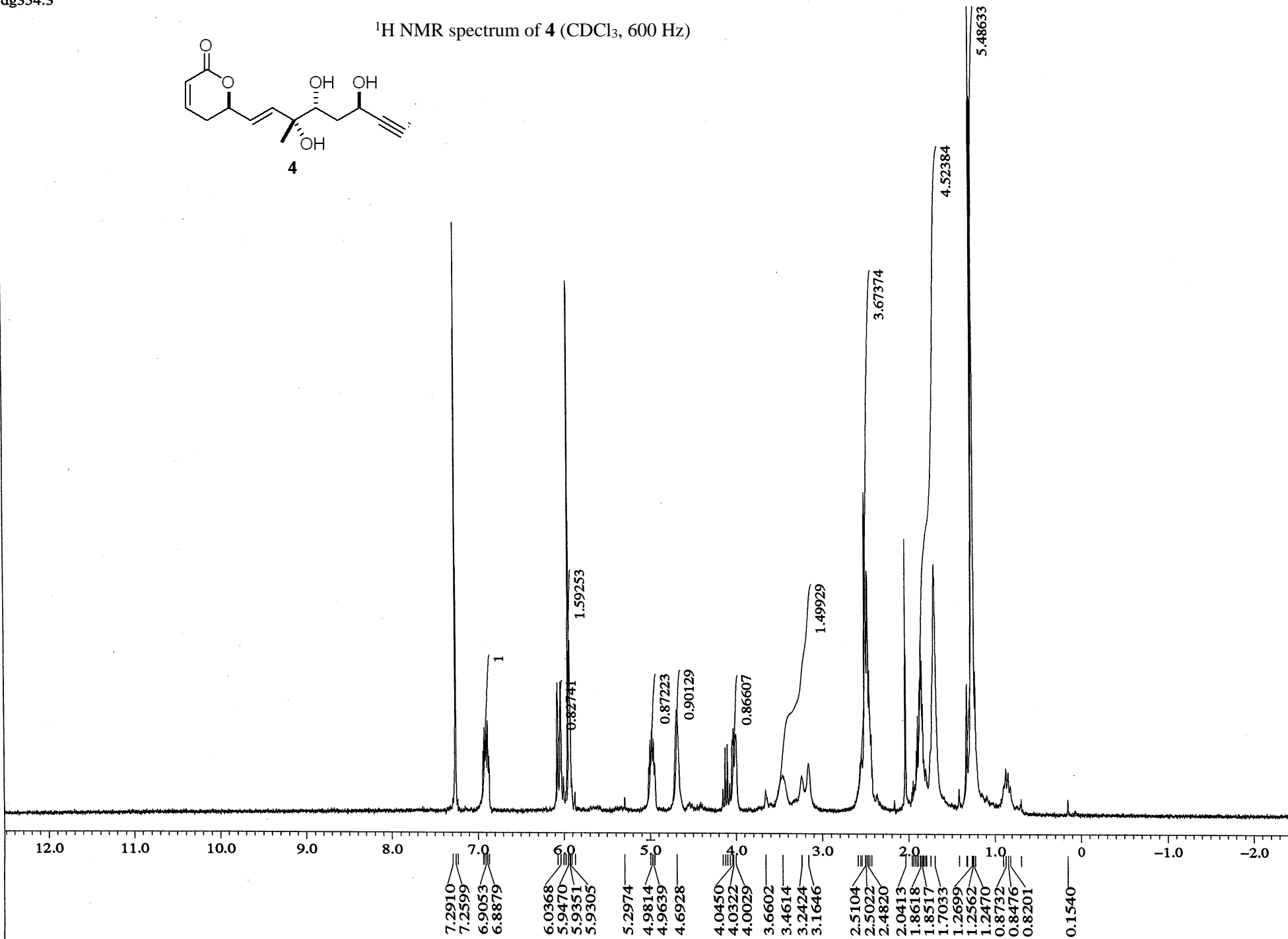
Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
File: CARBON  
INNOVA-600 "inova600"

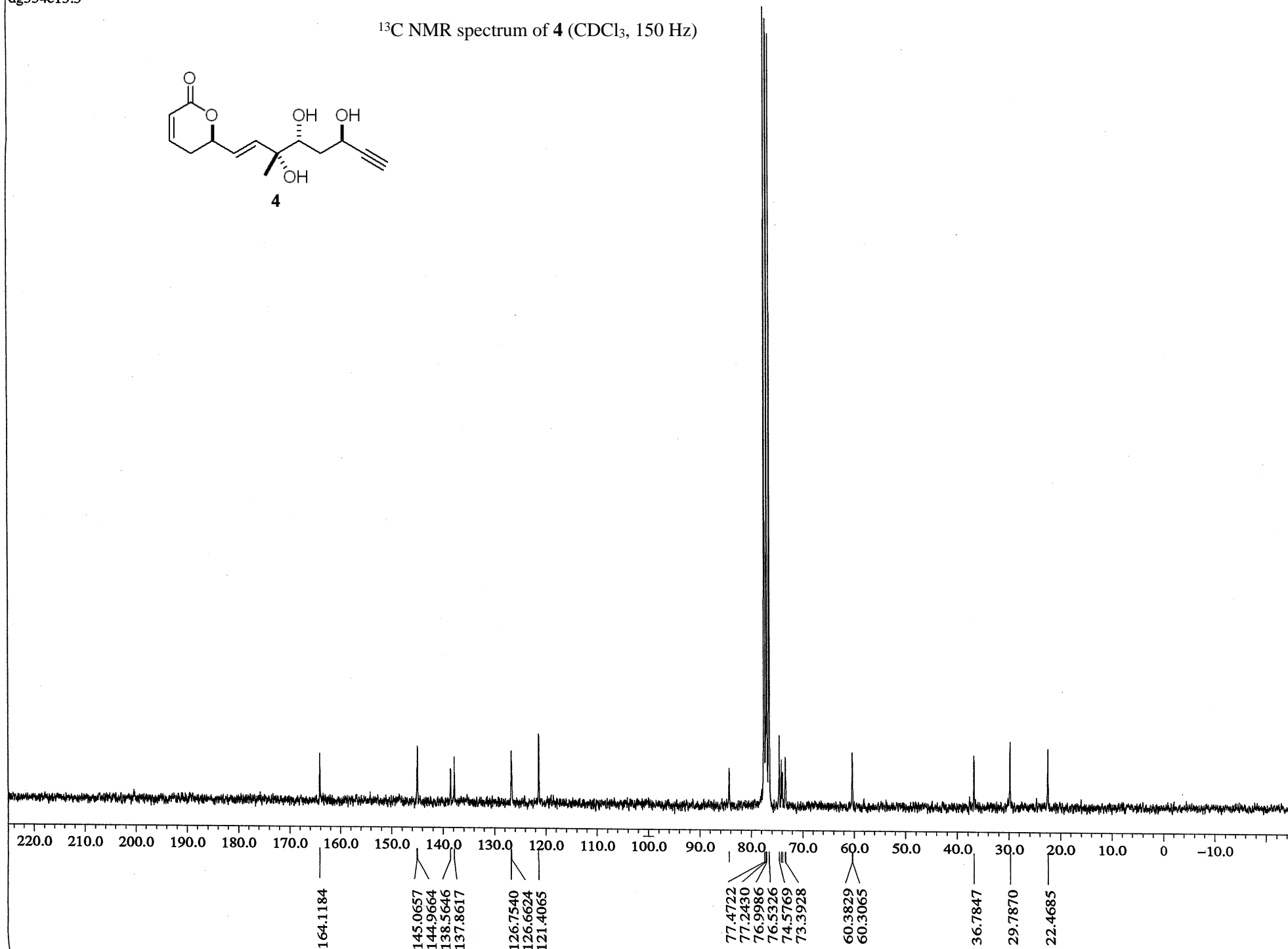
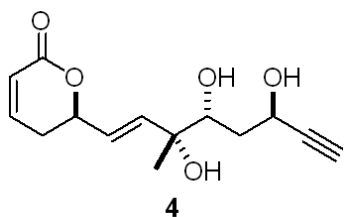
Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 37700.3 Hz  
256 repetitions  
OBSERVE  $\text{C}13$ , 150.7863854 MHz  
DECOUPLE  $\text{H}1$ , 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 9 min, 51 sec



<sup>1</sup>H NMR spectrum of 4 (CDCl<sub>3</sub>, 600 Hz)

4



$^{13}\text{C}$  NMR spectrum of **4** ( $\text{CDCl}_3$ , 150 Hz)X : parts per Million :  $^{13}\text{C}$

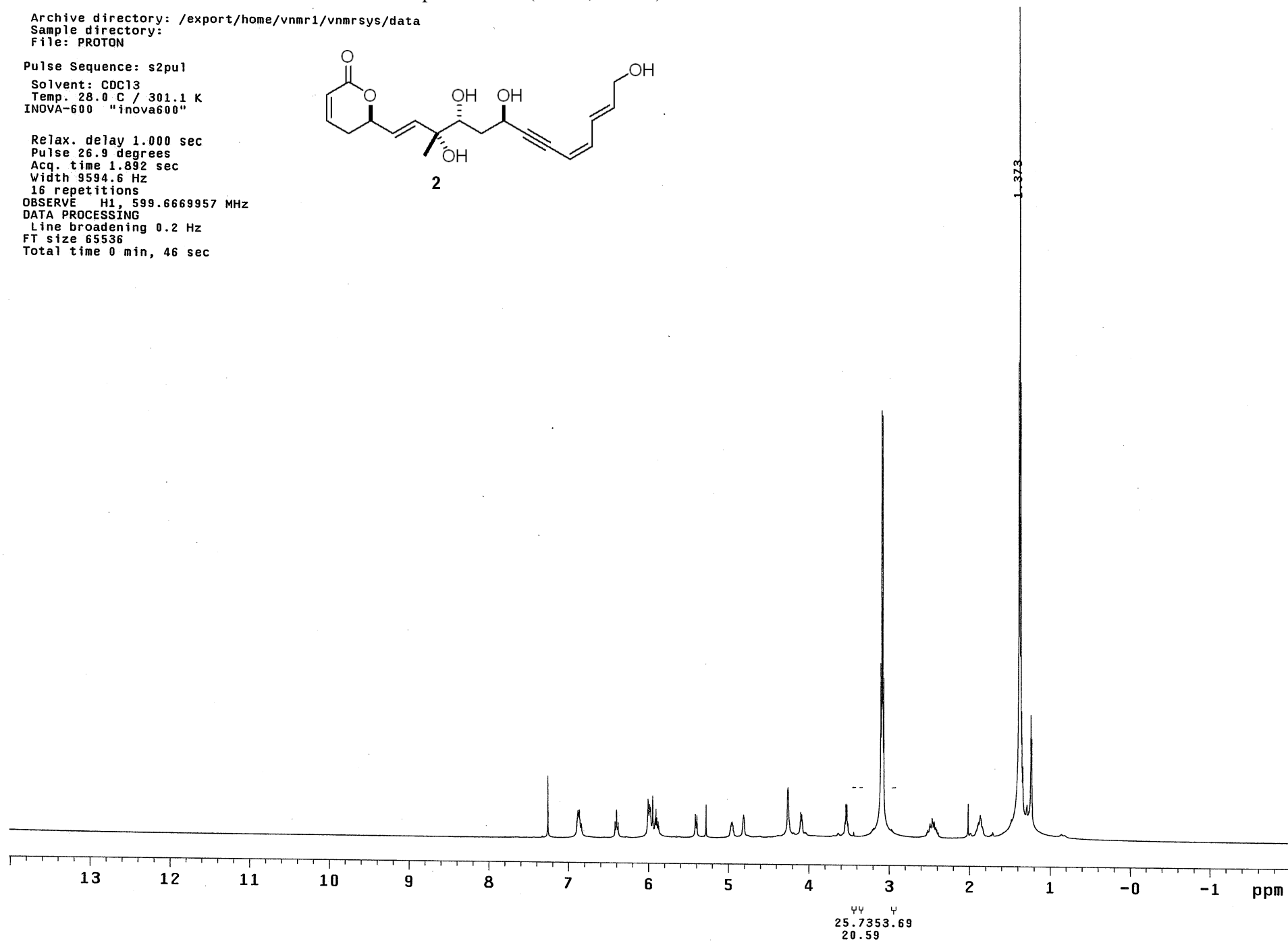
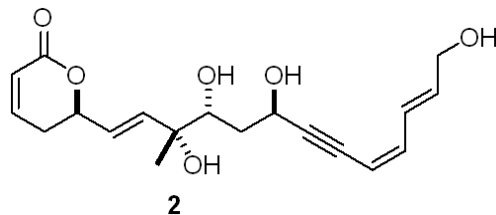
## STANDARD PROTON PARAMETERS

<sup>1</sup>H NMR spectrum of 2 (CDCl<sub>3</sub>, 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1  
Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 26.9 degrees  
Acq. time 1.892 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6669957 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 65536  
Total time 0 min, 46 sec

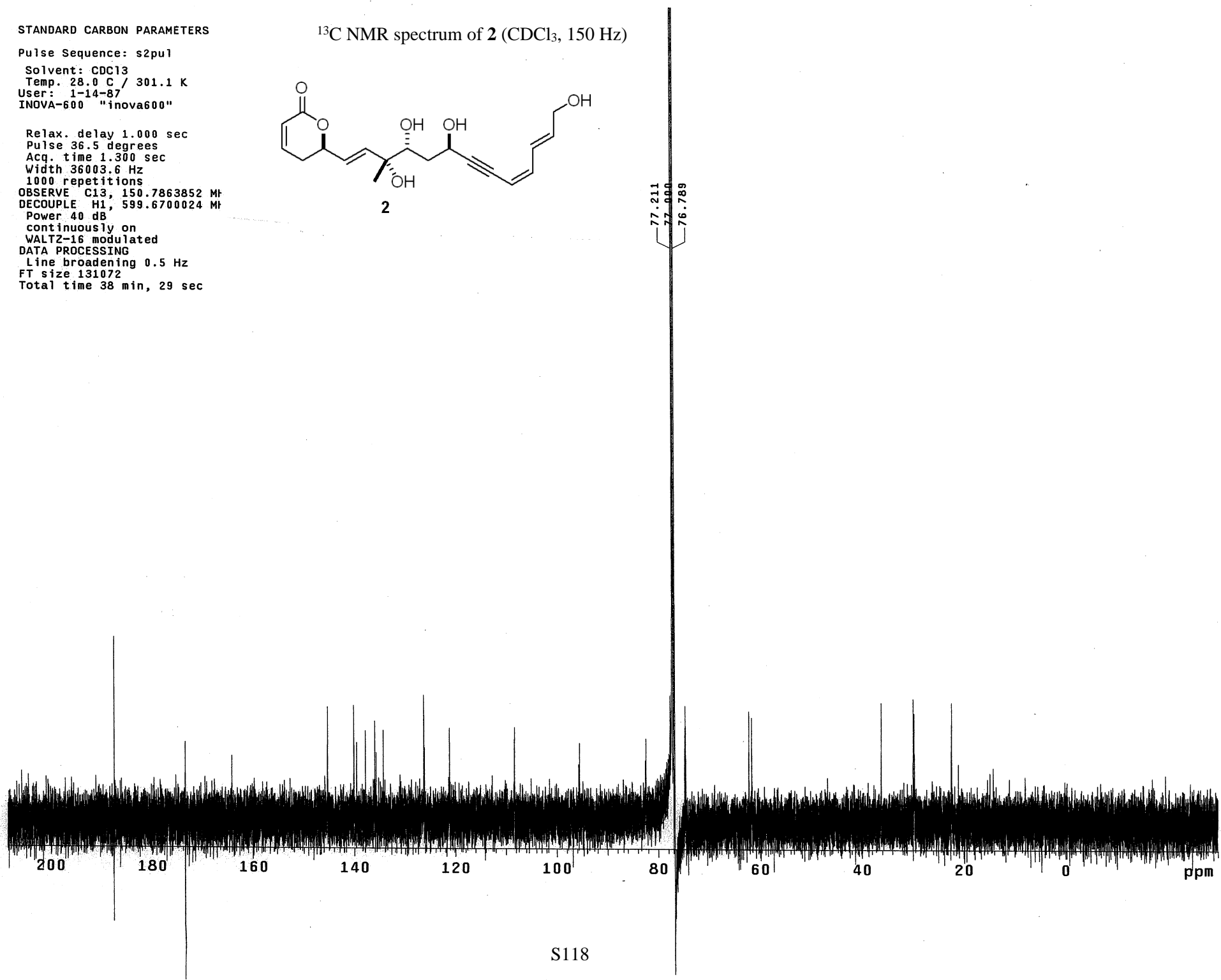
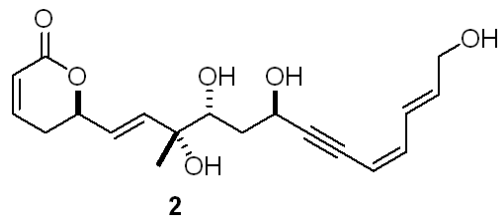


STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1  
Solvent: CDCl3  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"

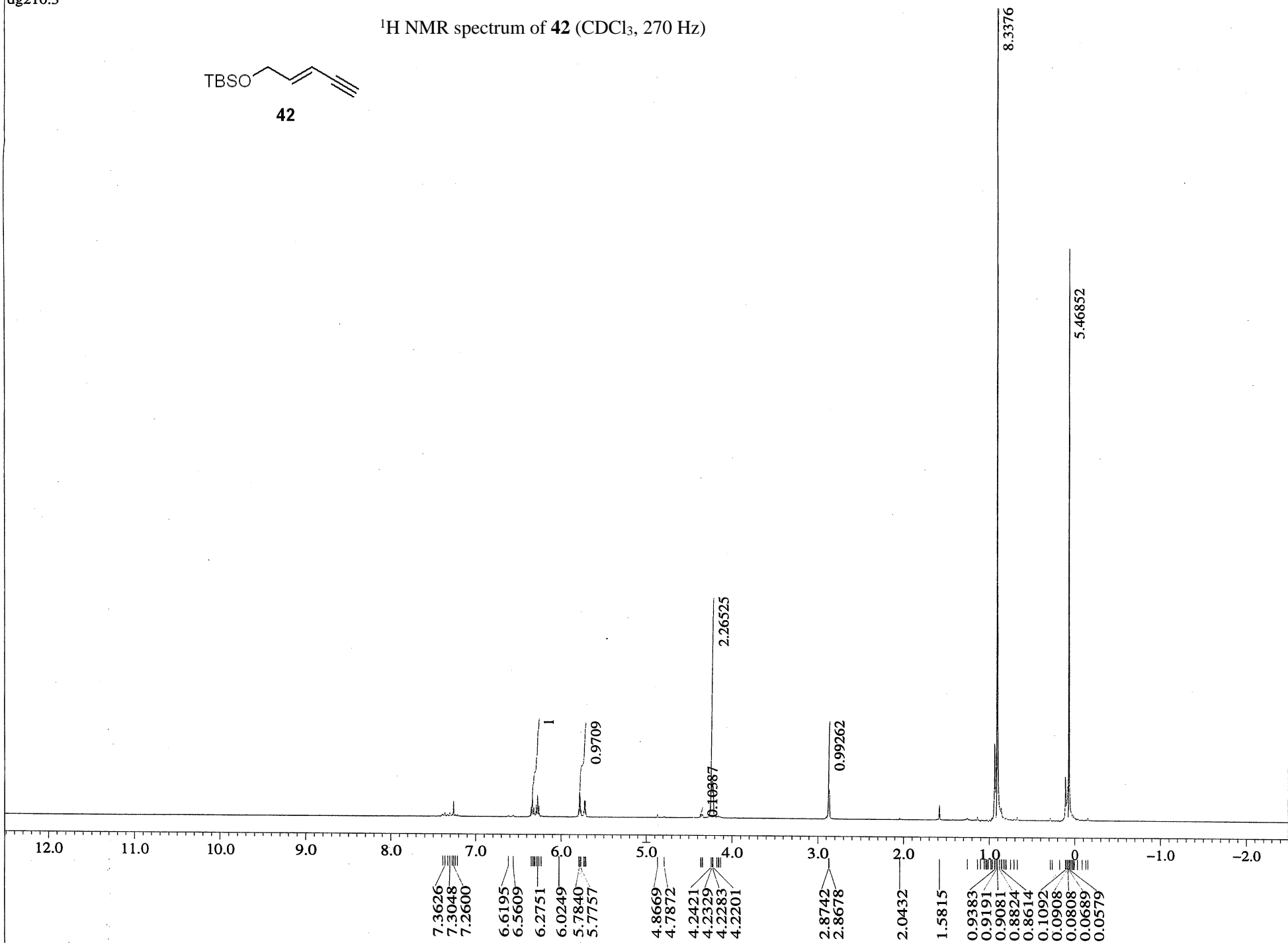
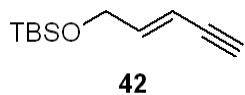
Relax. delay 1.000 sec  
Pulse 36.5 degrees  
Acq. time 1.300 sec  
Width 36003.6 Hz  
1000 repetitions  
OBSERVE C13, 150.7863852 MF  
DECOUPLE H1, 599.6700024 MF  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 38 min, 29 sec

<sup>13</sup>C NMR spectrum of 2 (CDCl<sub>3</sub>, 150 Hz)



dg210.3

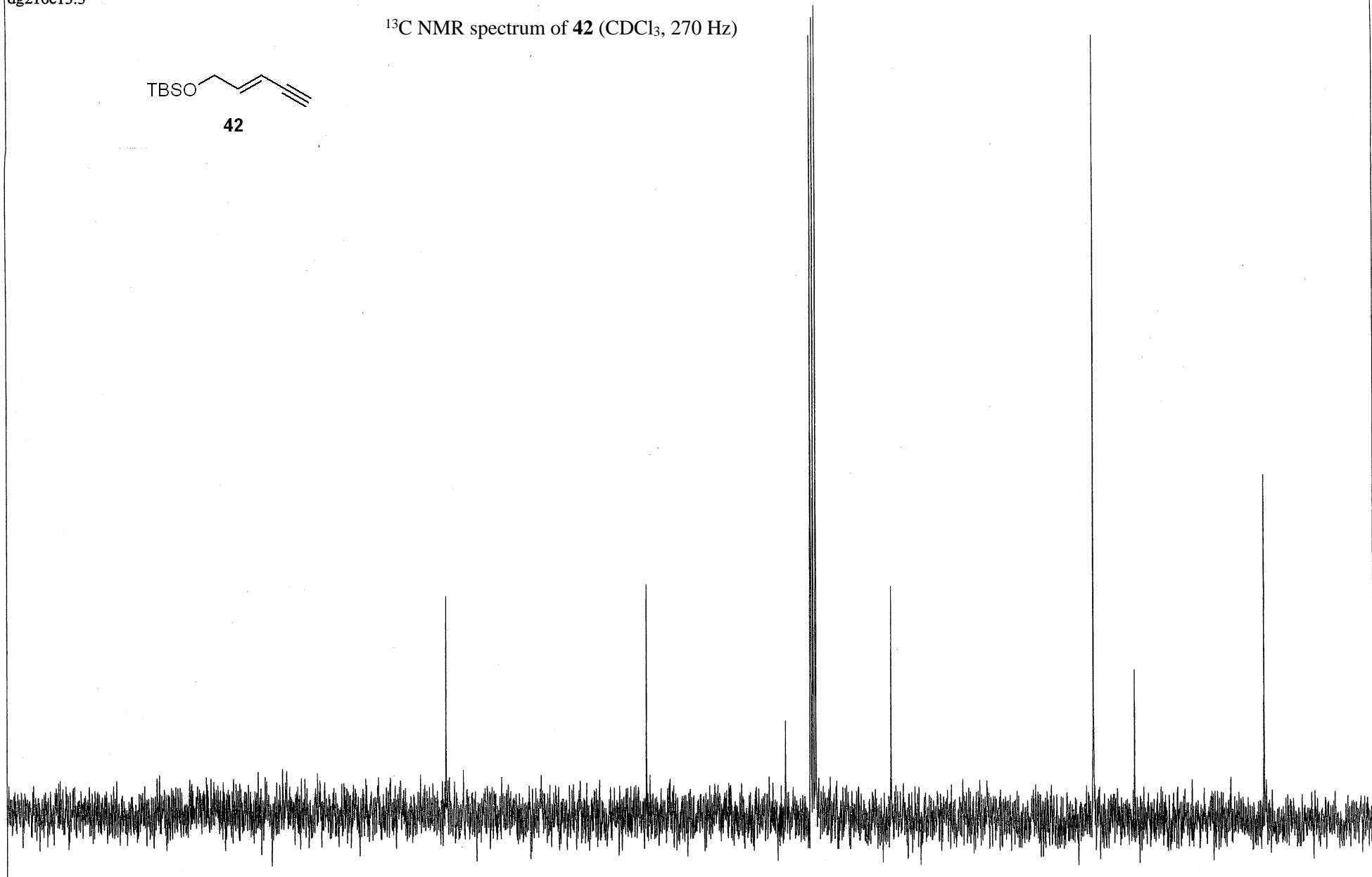
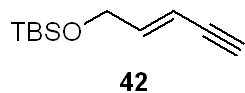
<sup>1</sup>H NMR spectrum of **42** (CDCl<sub>3</sub>, 270 Hz)



X : parts per Million : 1H

dg210c13.3

<sup>13</sup>C NMR spectrum of **42** (CDCl<sub>3</sub>, 270 Hz)



220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

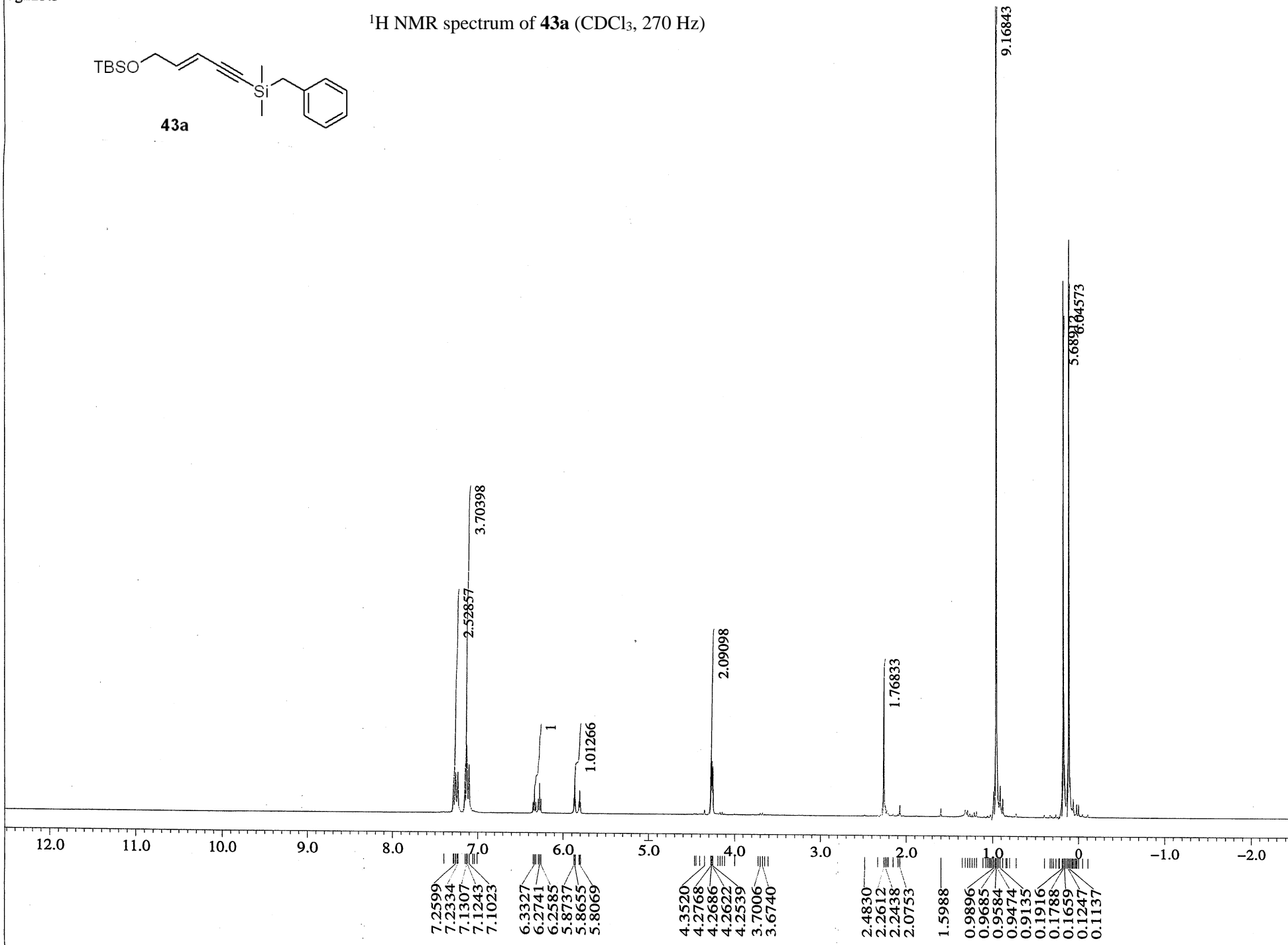
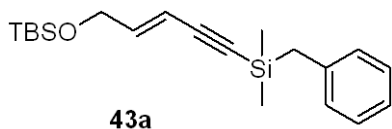
144.3029  
107.5344  
82.0723  
77.4657  
77.3358  
76.9997  
76.5261  
62.6682  
25.8386  
18.3290  
-5.4066

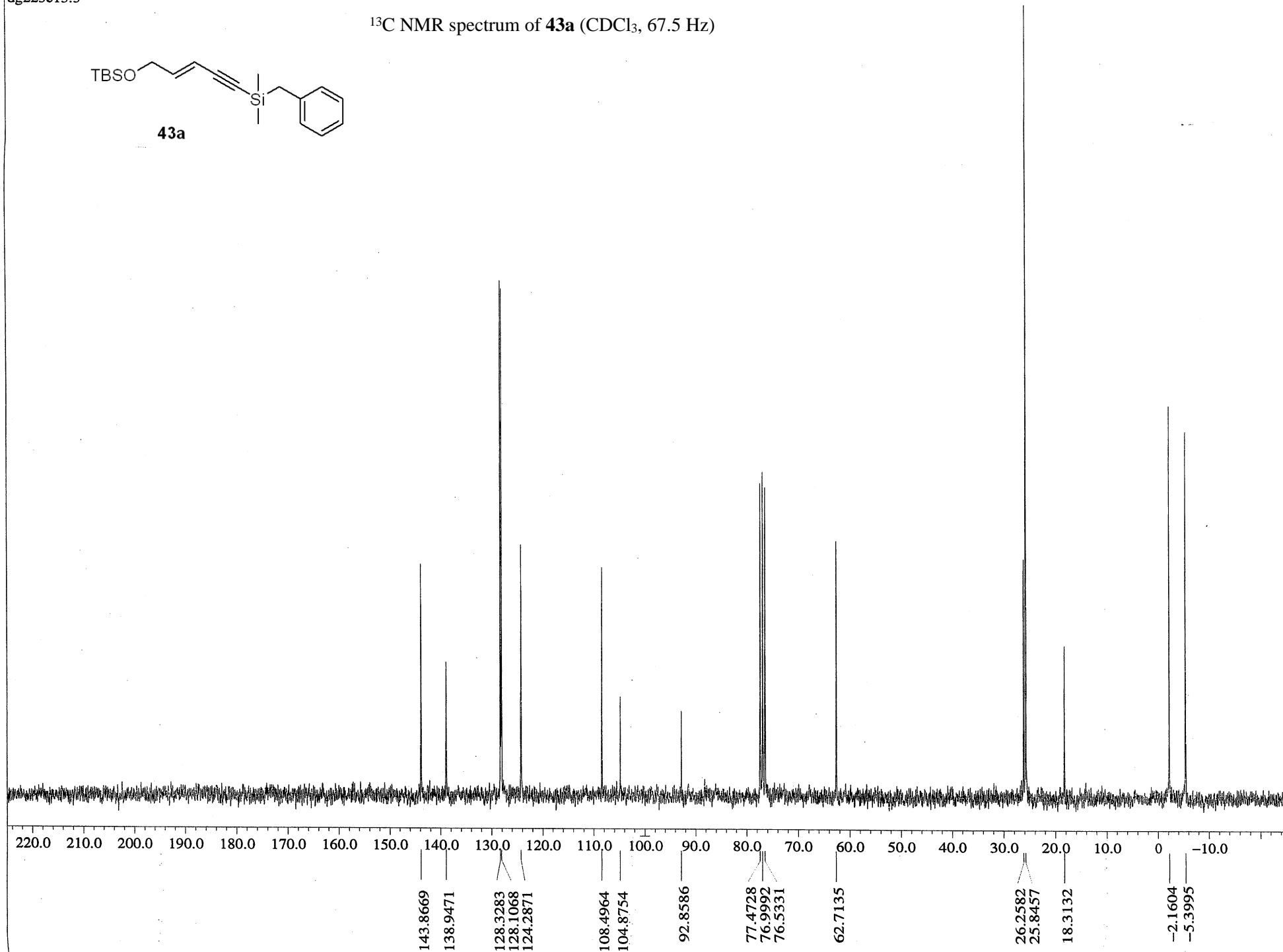
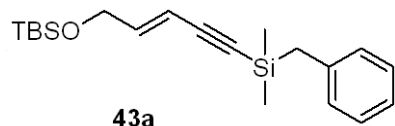
X : parts per Million : 13C

S120



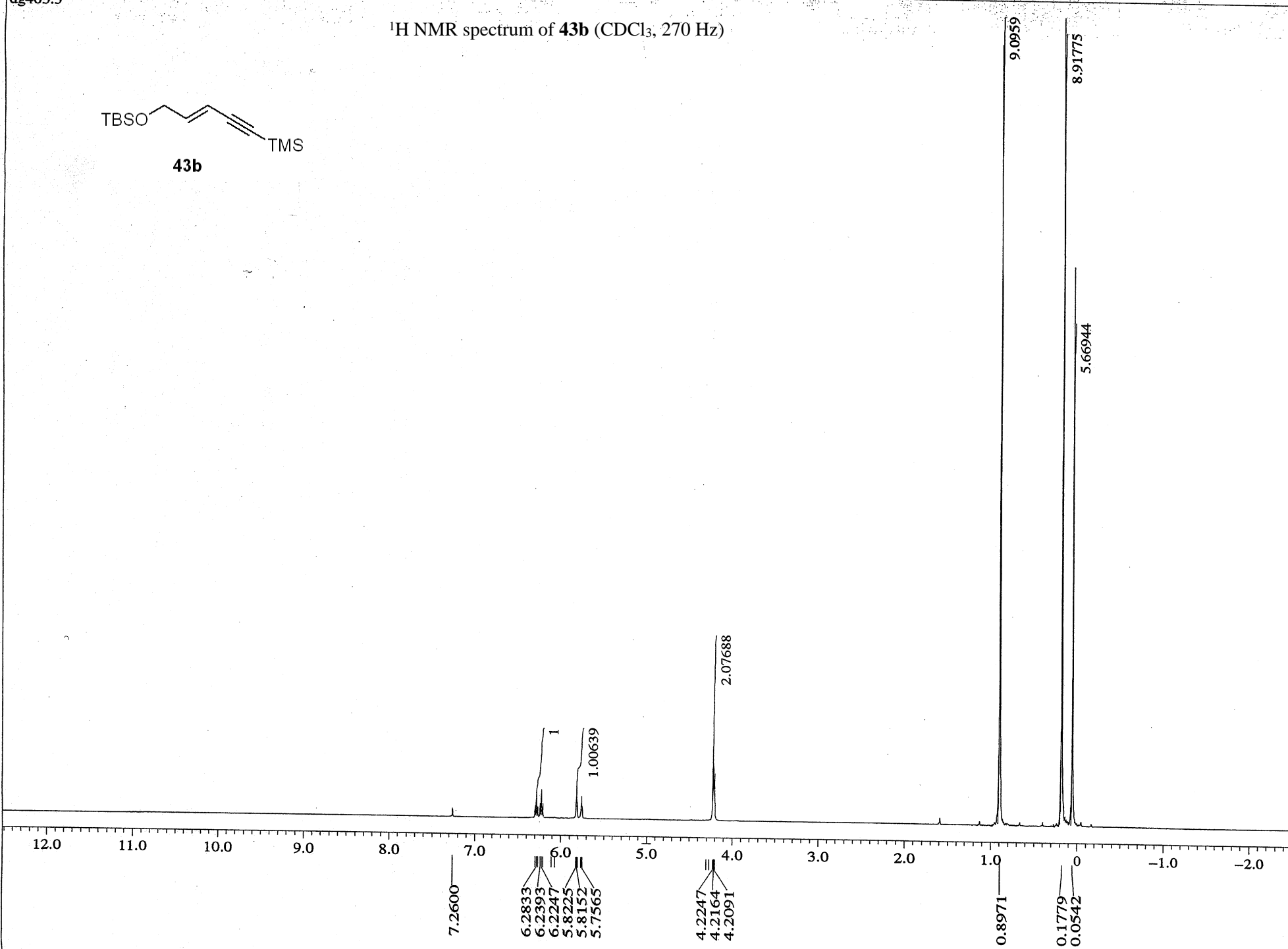
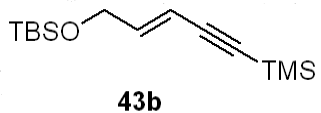
<sup>1</sup>H NMR spectrum of **43a** (CDCl<sub>3</sub>, 270 Hz)



$^{13}\text{C}$  NMR spectrum of **43a** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

dg405.3

$^1\text{H}$  NMR spectrum of **43b** ( $\text{CDCl}_3$ , 270 Hz)



7.2600

6.2833  
6.2393  
6.2247  
5.8225  
5.8152  
5.7565

1

1.00639

4.2247  
4.2164  
4.2091

2.07688

0.8971

0.1779  
0.0542

9.0959

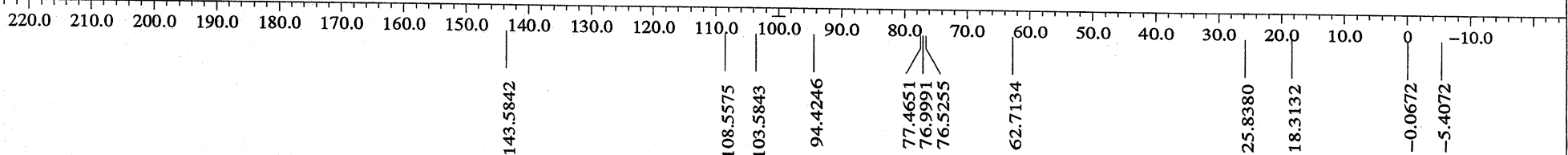
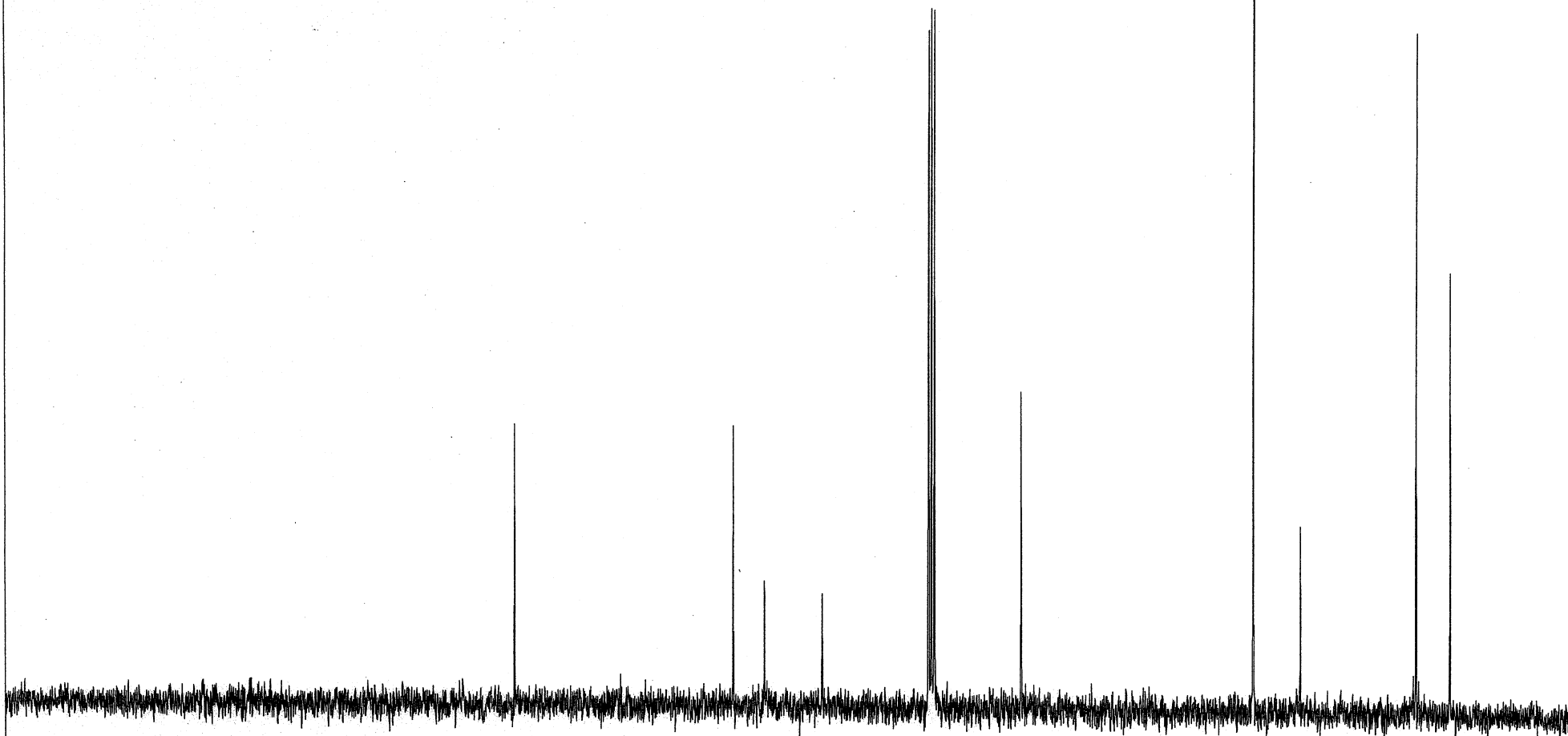
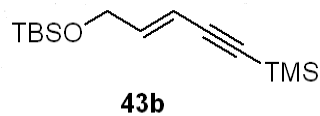
8.91775

5.66944

X : parts per Million : 1H

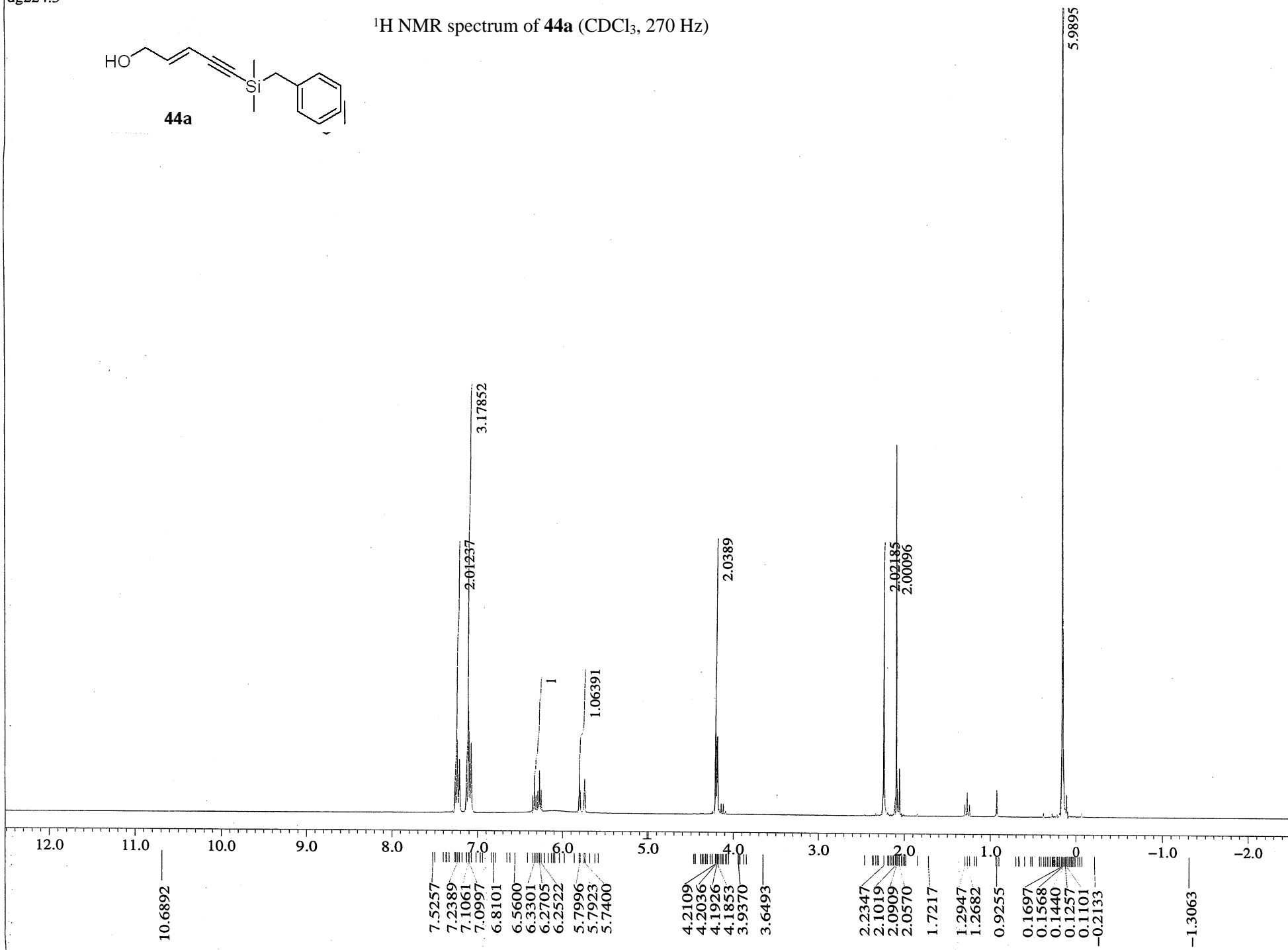
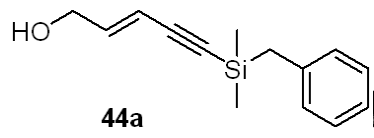
S123

<sup>13</sup>C NMR spectrum of **43b** (CDCl<sub>3</sub>, 67.5 Hz)

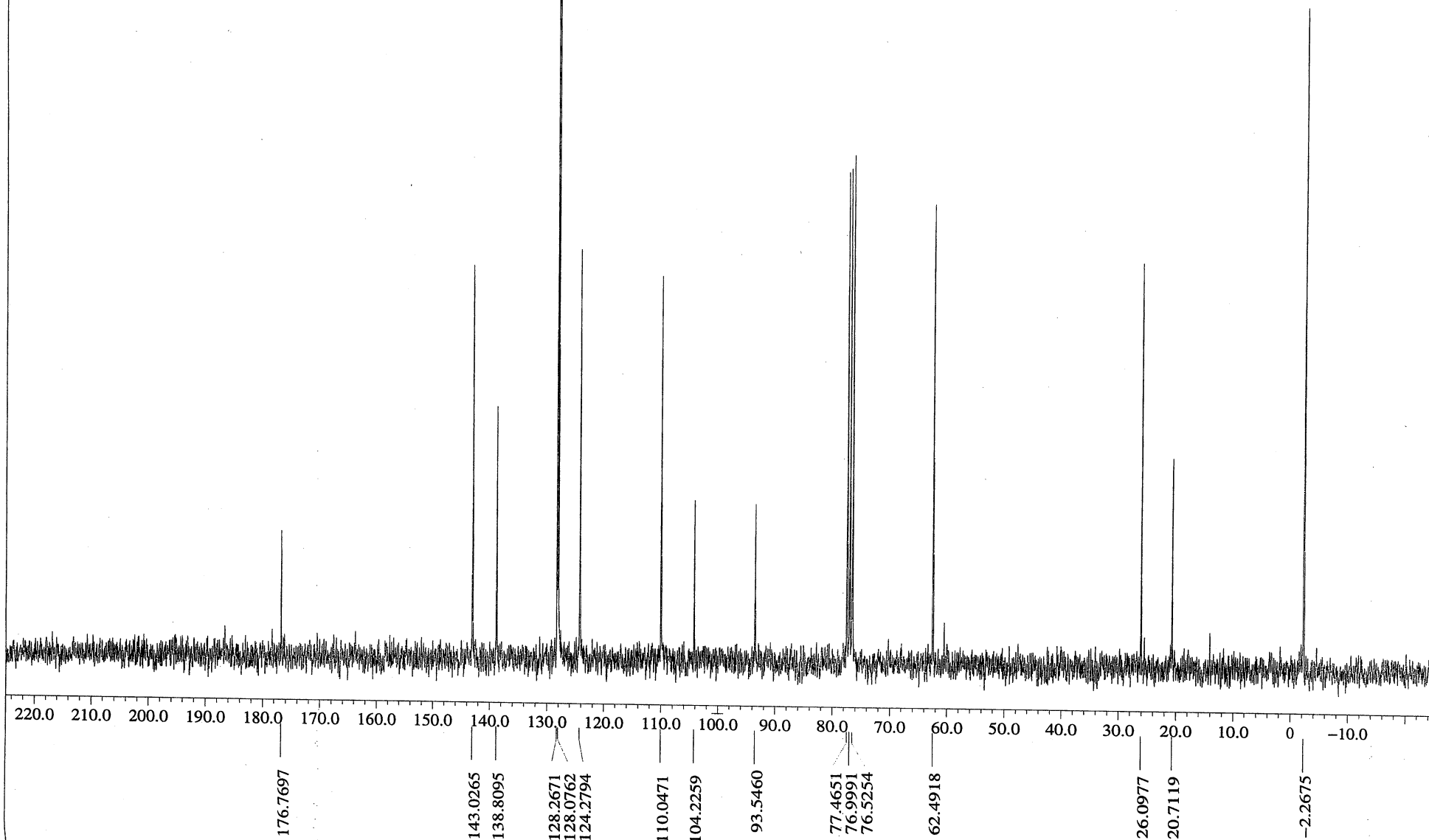
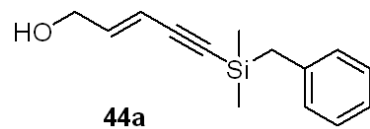


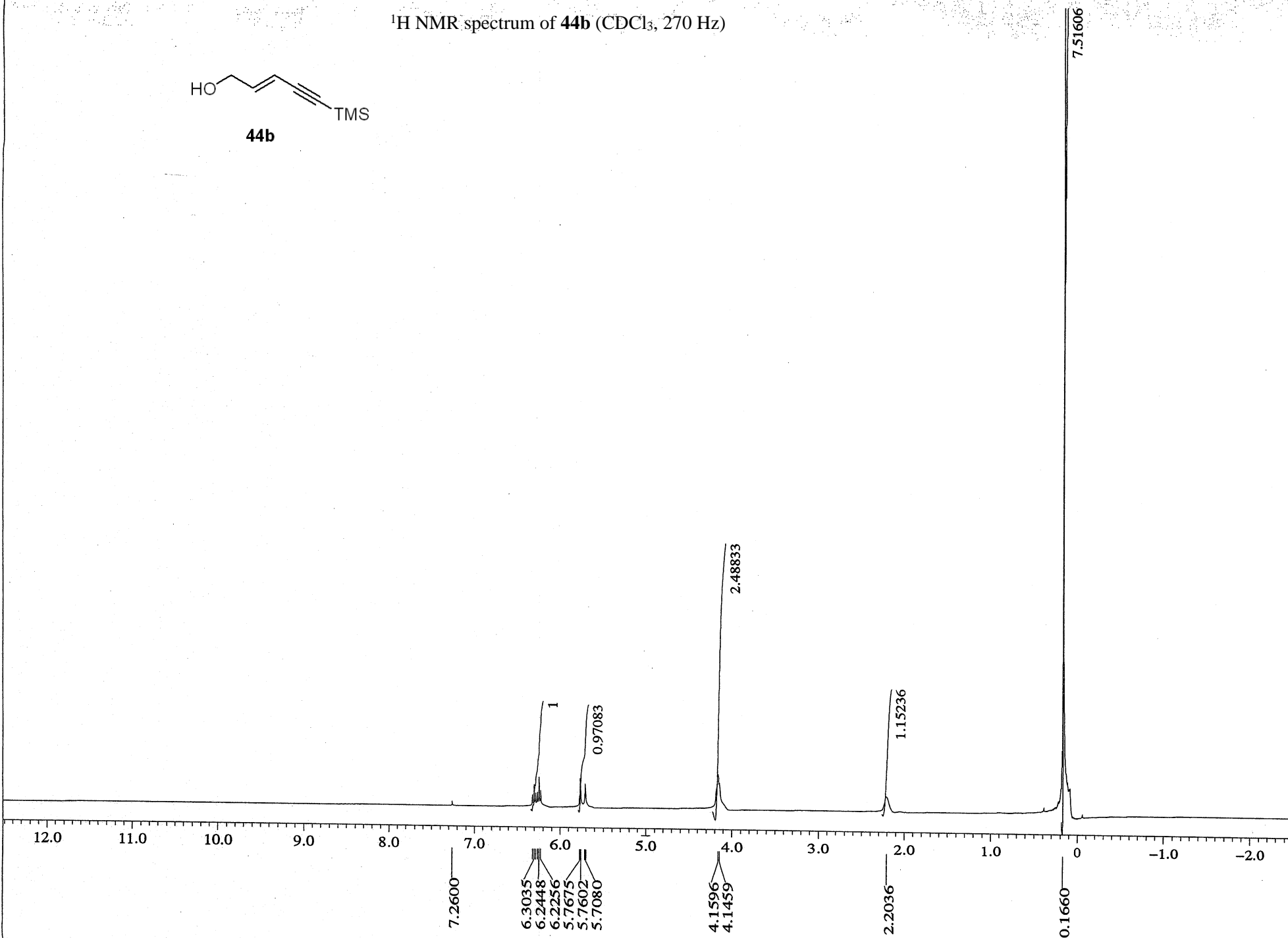
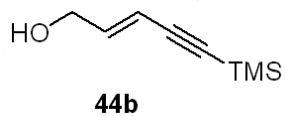
X : parts per Million : <sup>13</sup>C

<sup>1</sup>H NMR spectrum of **44a** (CDCl<sub>3</sub>, 270 Hz)



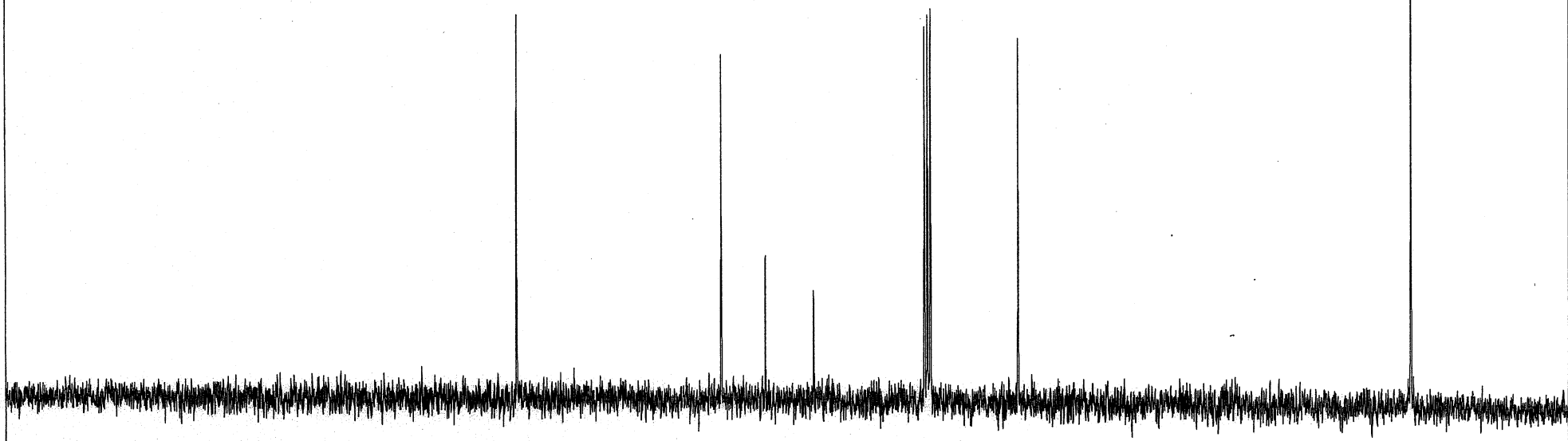
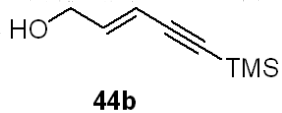
X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **44a** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

$^1\text{H}$  NMR spectrum of **44b** ( $\text{CDCl}_3$ , 270 Hz)X : parts per Million :  $^1\text{H}$

dg406.4

<sup>13</sup>C NMR spectrum of **44b** (CDCl<sub>3</sub>, 67.5 Hz)



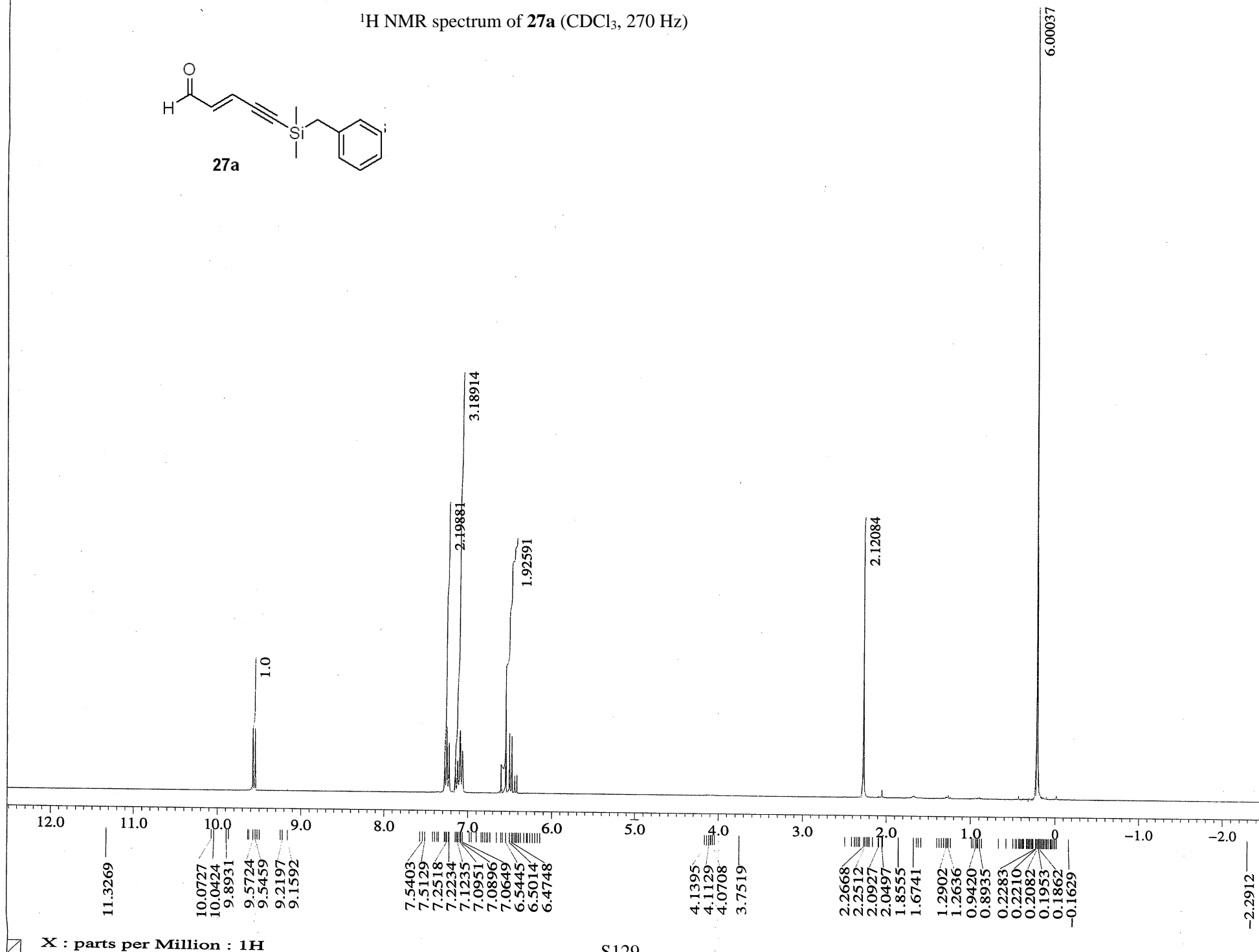
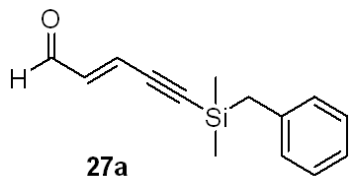
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

142.9350  
110.1619  
102.9733  
95.1811  
77.4729  
76.9993  
76.5333  
62.6372  
-0.1741

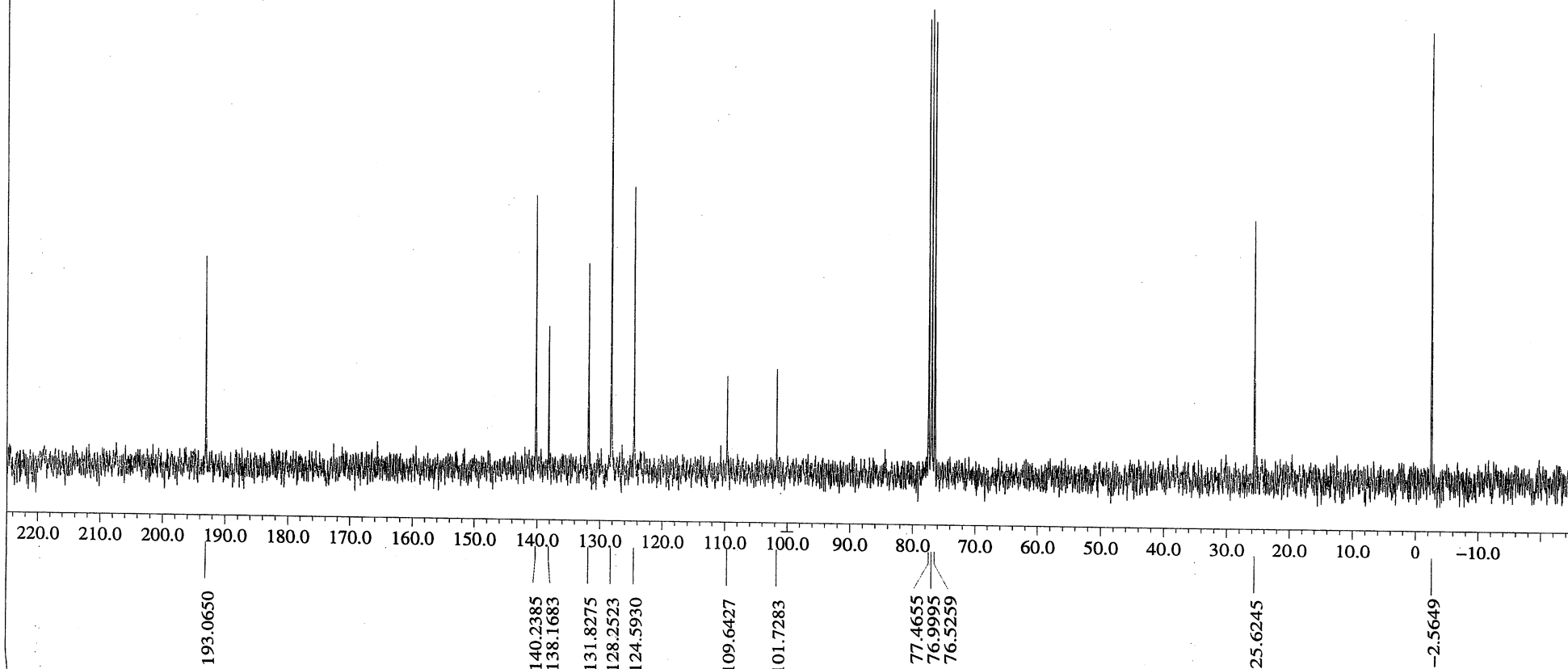
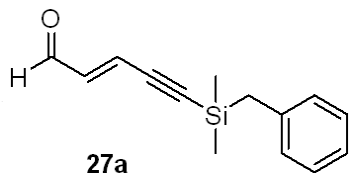
X : parts per Million : <sup>13</sup>C

S128

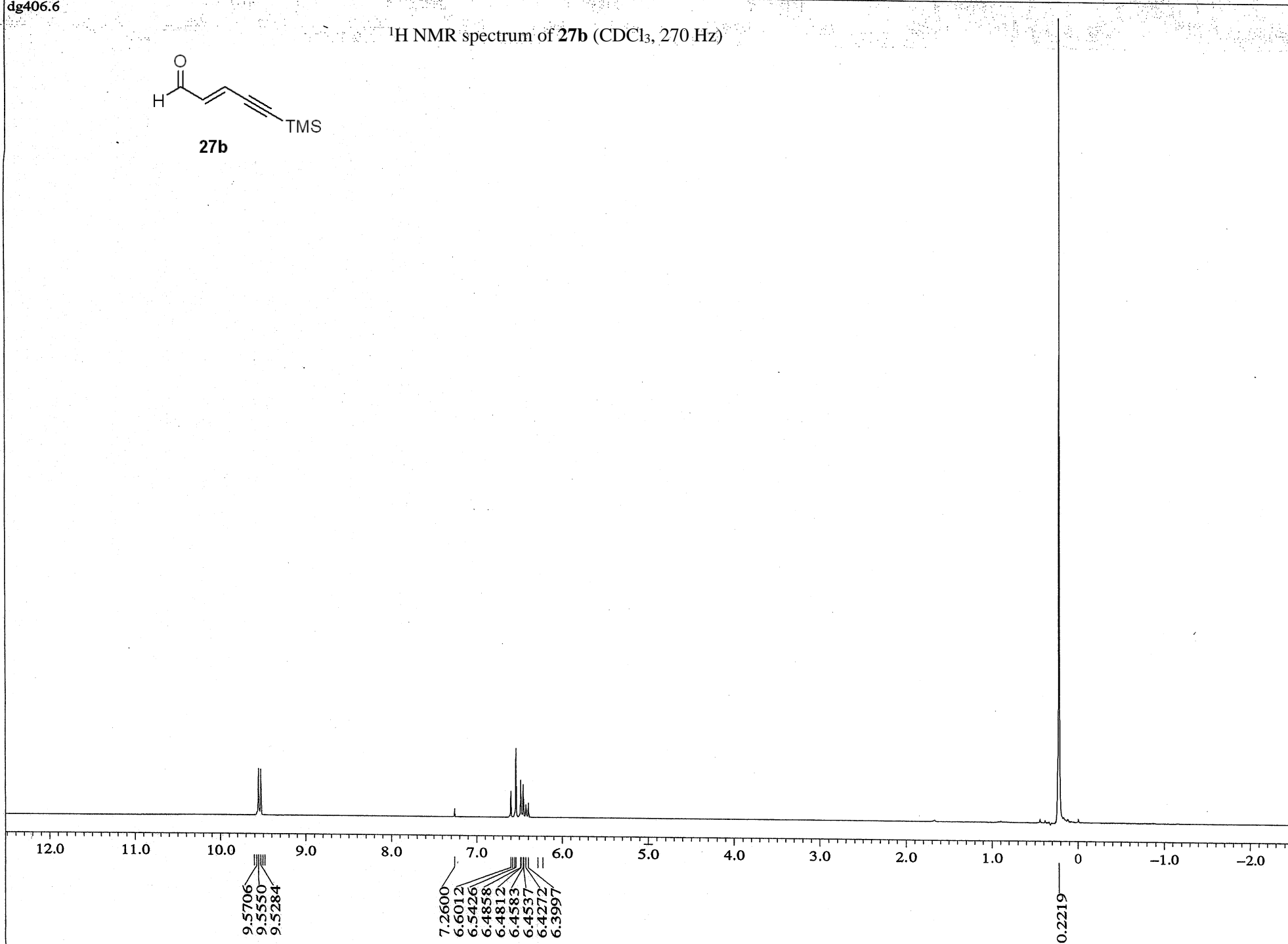
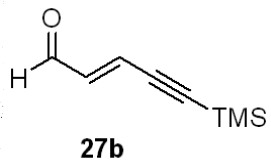


$^1\text{H}$  NMR spectrum of **27a** ( $\text{CDCl}_3$ , 270 Hz)X : parts per Million :  $^1\text{H}$

<sup>13</sup>C NMR spectrum of **27a** (CDCl<sub>3</sub>, 67.5 Hz)



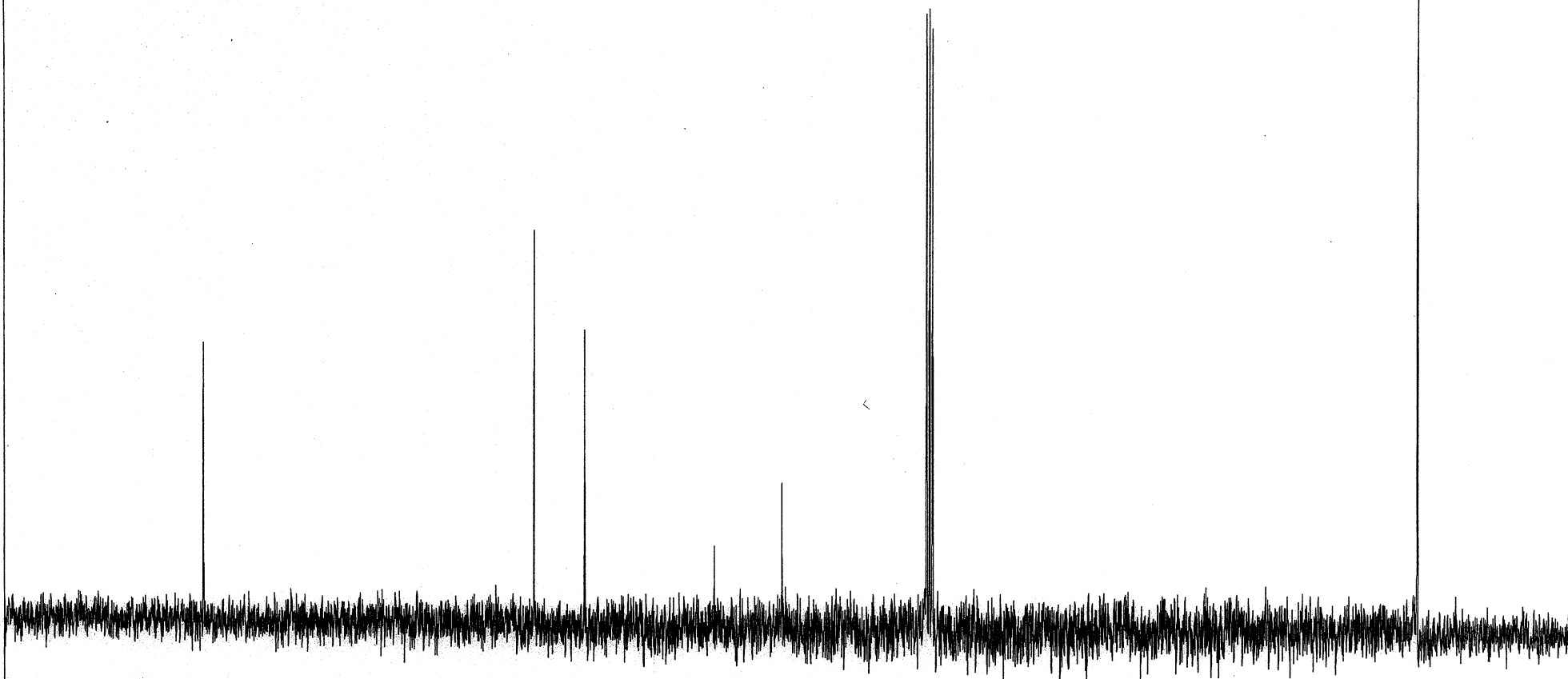
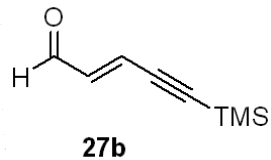
X : parts per Million : <sup>13</sup>C

<sup>1</sup>H NMR spectrum of **27b** (CDCl<sub>3</sub>, 270 Hz)

X : parts per Million : 1H

dg406.7

<sup>13</sup>C NMR spectrum of **27b** (CDCl<sub>3</sub>, 67.5 Hz)



220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

193.1098

140.0694

132.0862

111.3528

100.5660

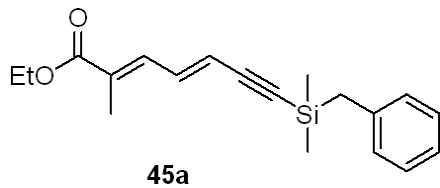
77.4720  
76.9984  
76.5324

-0.5569

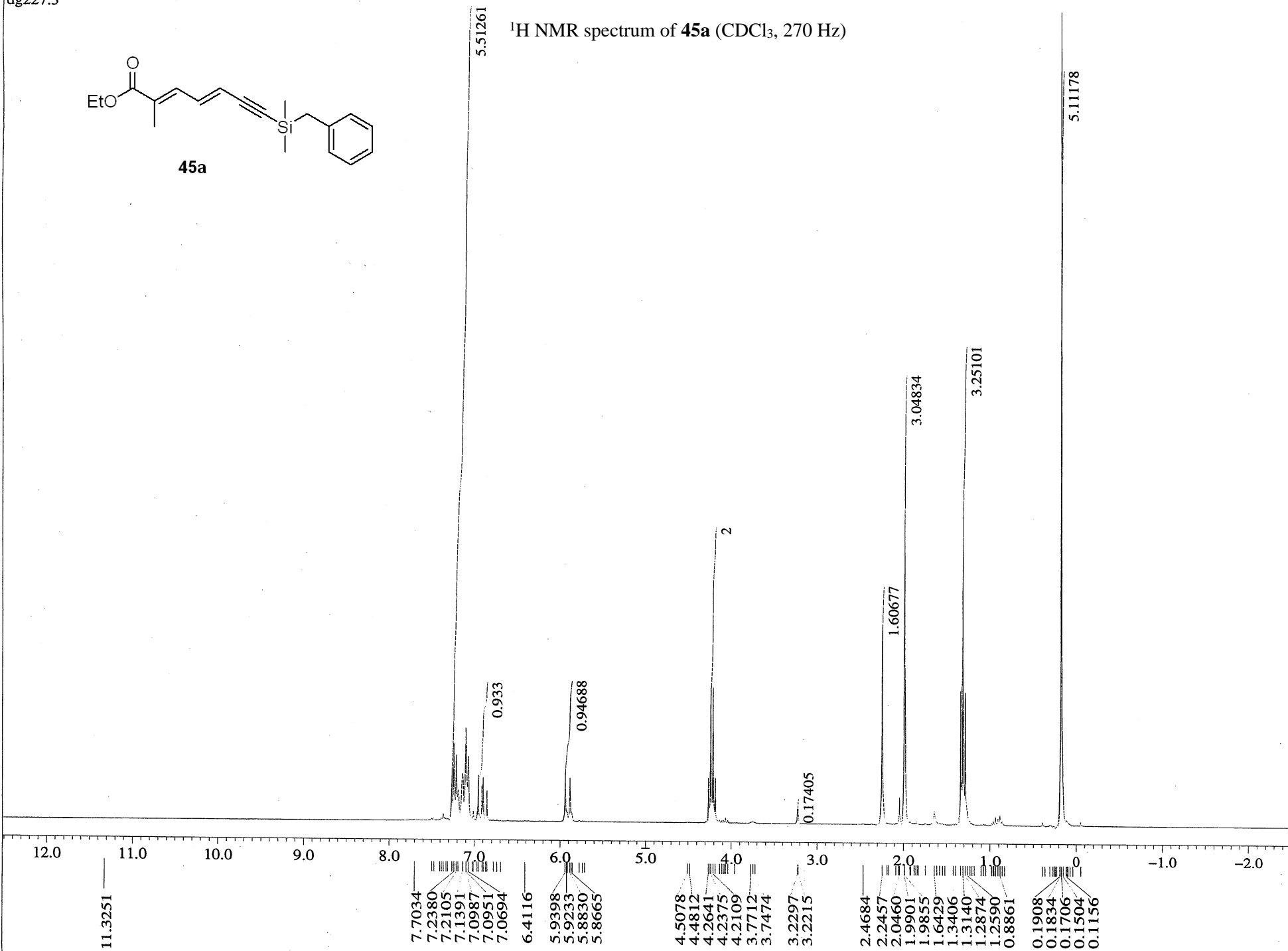
X : parts per Million : <sup>13</sup>C

S132

dg227.3

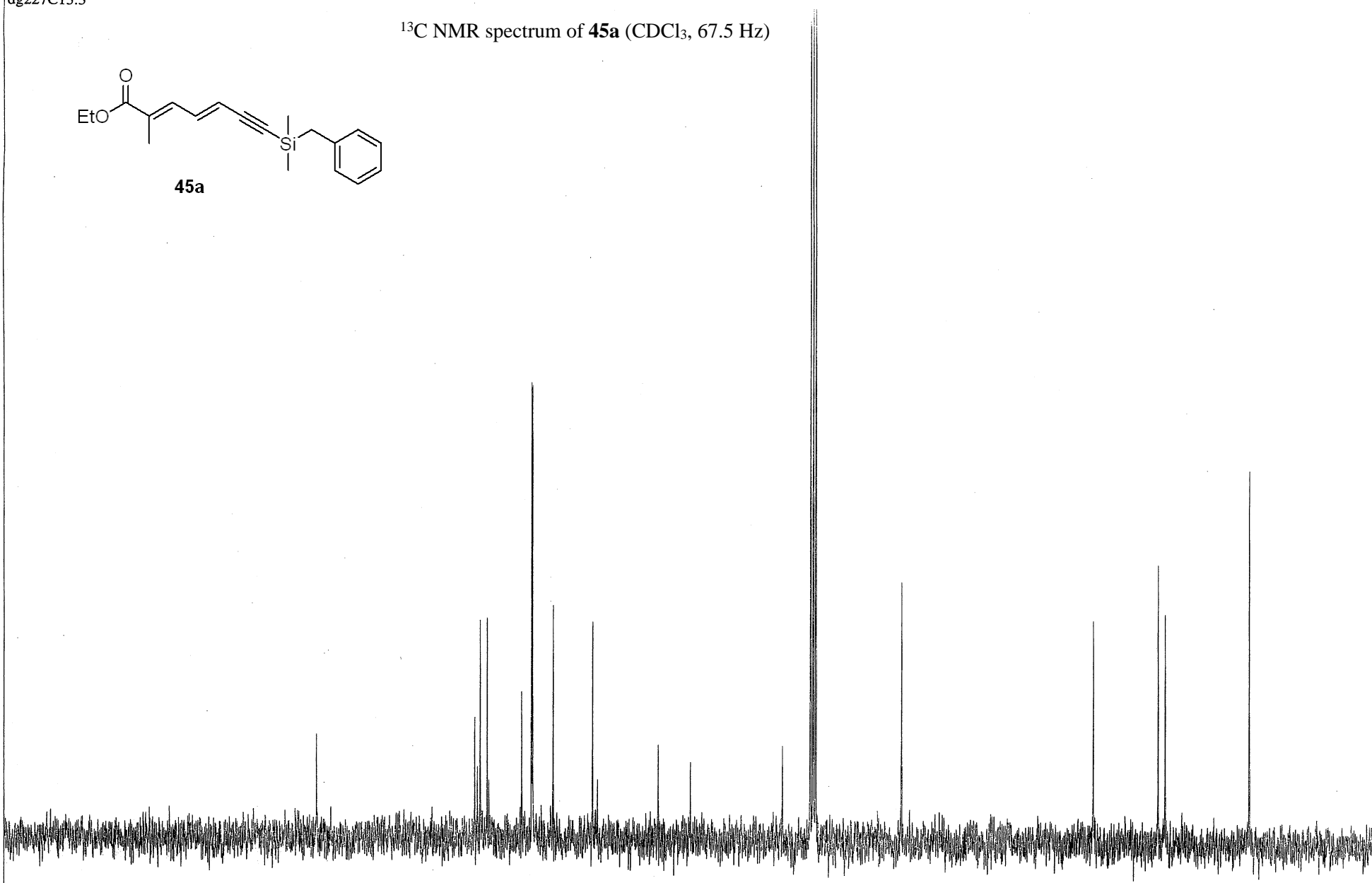
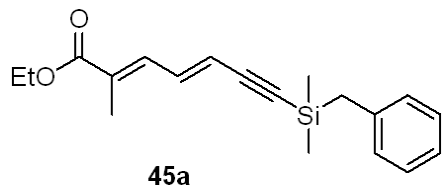


<sup>1</sup>H NMR spectrum of **45a** (CDCl<sub>3</sub>, 270 Hz)



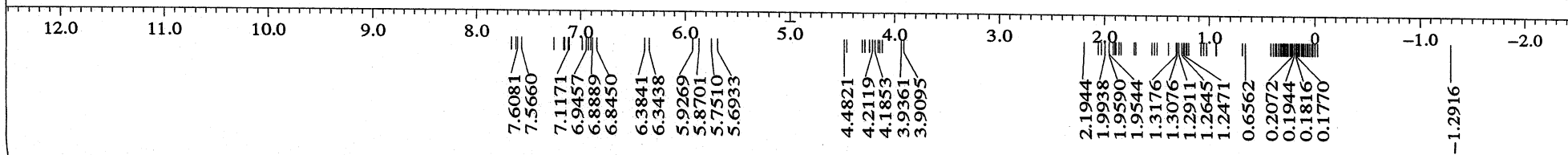
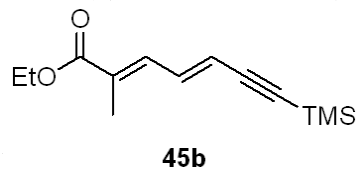
X : parts per Million : 1H

<sup>13</sup>C NMR spectrum of **45a** (CDCl<sub>3</sub>, 67.5 Hz)



| Chemical Shift (ppm) |
|----------------------|
| 167.8324             |
| 138.6957             |
| 137.6950             |
| 136.4039             |
| 130.1396             |
| 128.3214             |
| 128.1610             |
| 124.4024             |
| 117.1526             |
| 105.3192             |
| 99.3833              |
| 82.5614              |
| 77.4659              |
| 76.9999              |
| 76.5262              |
| 60.8196              |
| 26.0527              |
| 14.2421              |
| 12.9663              |
| -2.2896              |

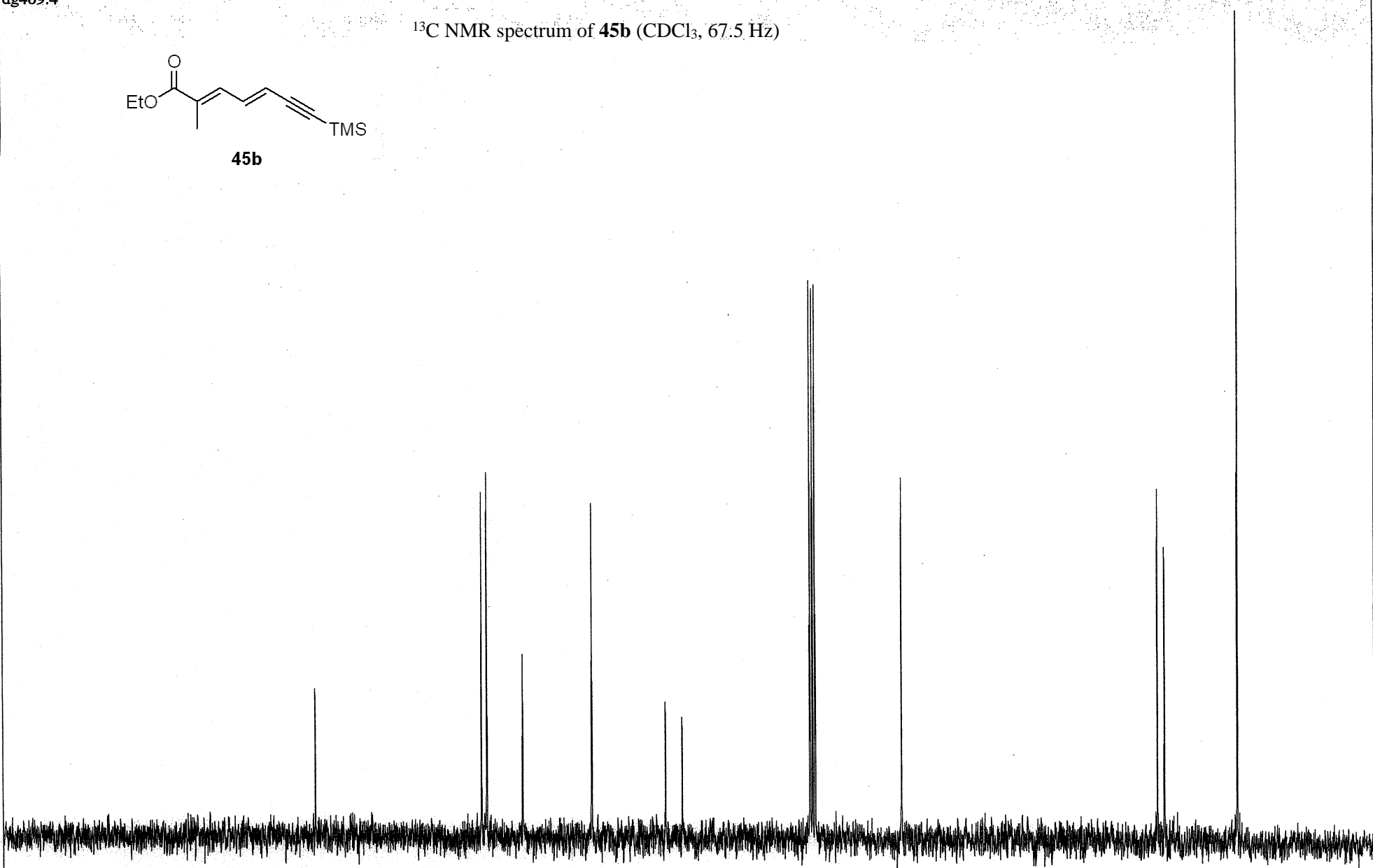
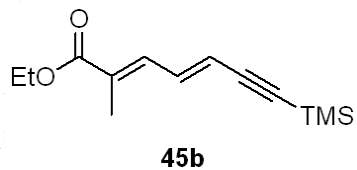
X : parts per Million : 13C

$^1\text{H}$  NMR spectrum of **45b** ( $\text{CDCl}_3$ , 270 Hz)

X : parts per Million : 1H

dg409.4

$^{13}\text{C}$  NMR spectrum of **45b** ( $\text{CDCl}_3$ , 67.5 Hz)



220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

167.8322

137.4274  
136.4648

129.9407

117.3204

103.8904  
100.8499

77.4733  
76.9996  
76.5336

60.7812

14.2342  
12.9355

-0.2501

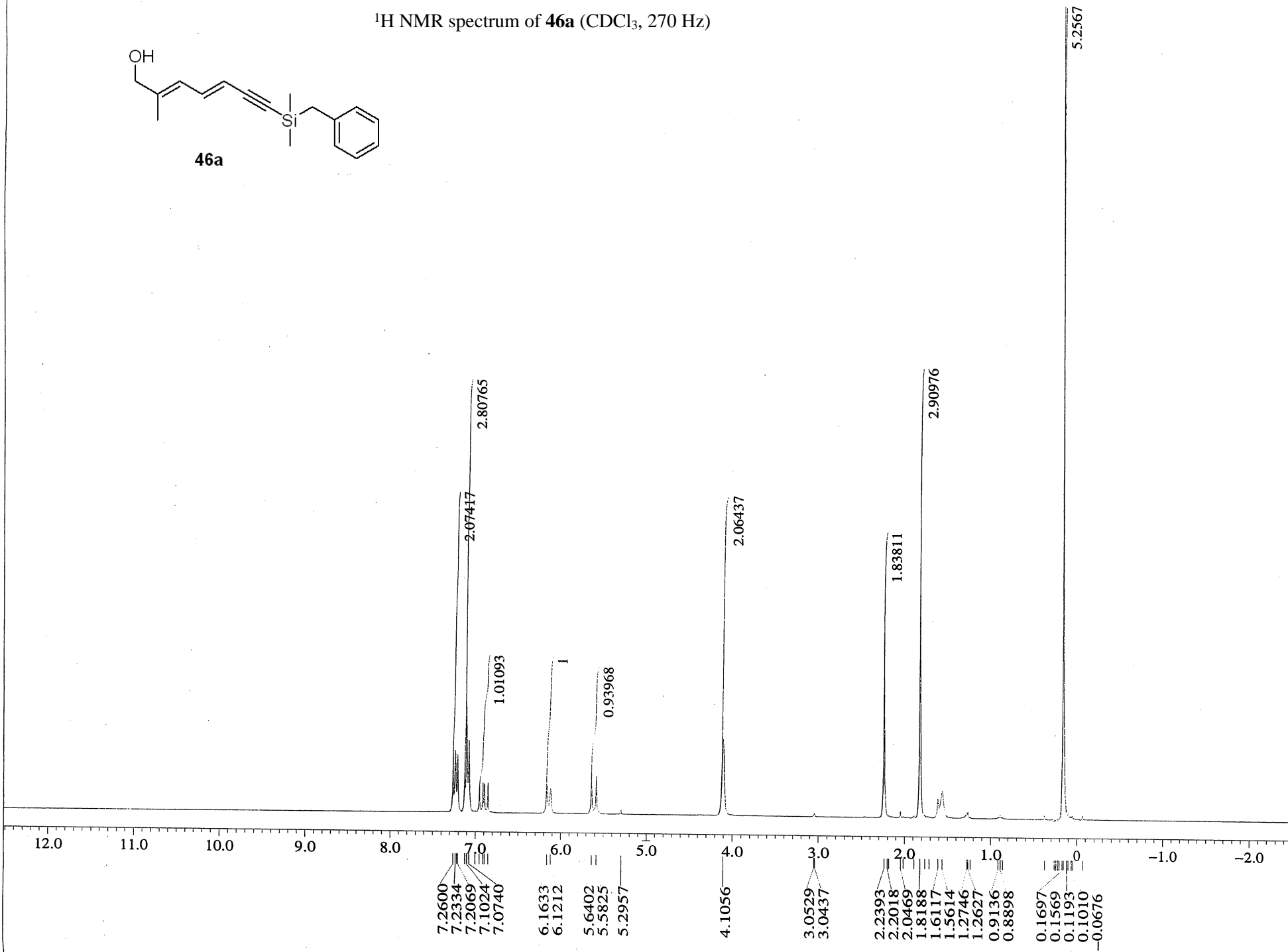
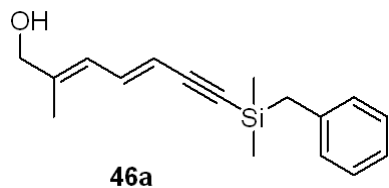
X : parts per Million :  $^{13}\text{C}$

S136

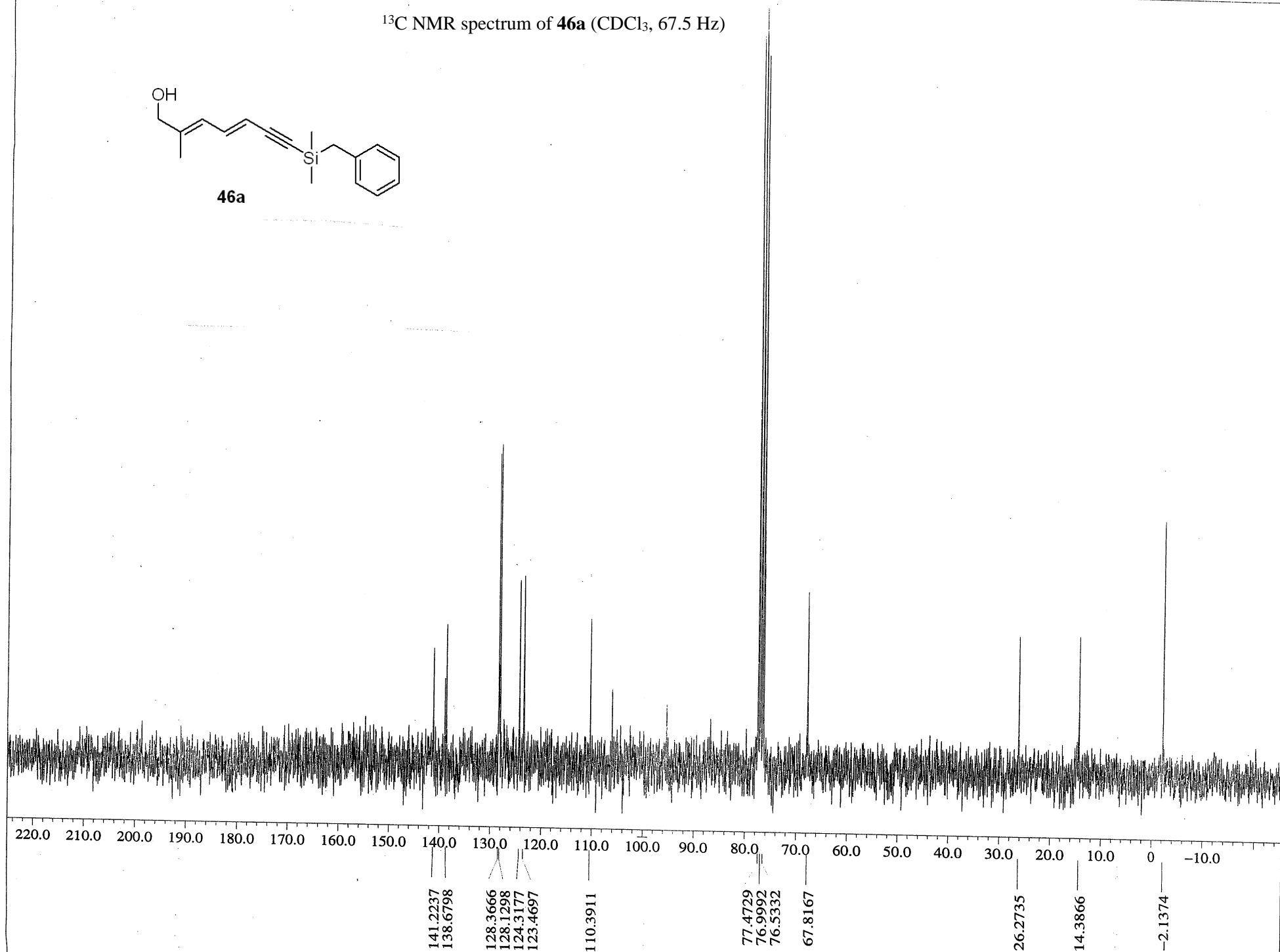
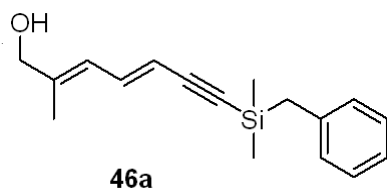


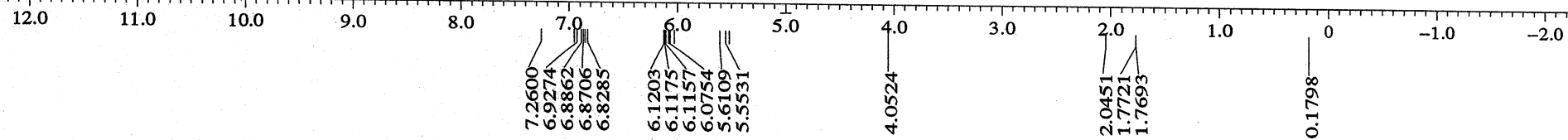
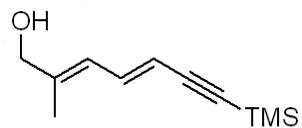
dg330.3

<sup>1</sup>H NMR spectrum of **46a** (CDCl<sub>3</sub>, 270 Hz)



X : parts per Million : 1H

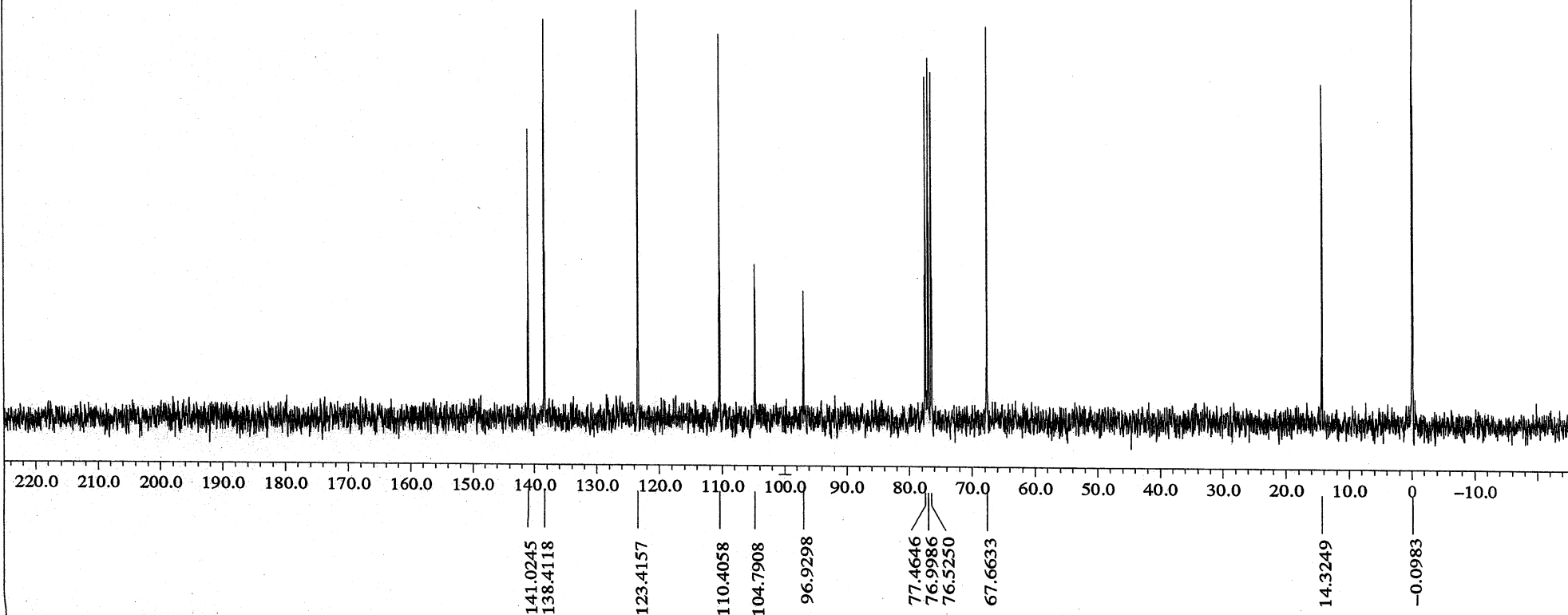
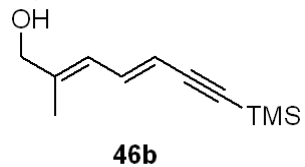
$^{13}\text{C}$  NMR spectrum of **46a** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

<sup>1</sup>H NMR spectrum of **46b** (CDCl<sub>3</sub>, 270 Hz)

X : parts per Million : 1H

dg410C13.3

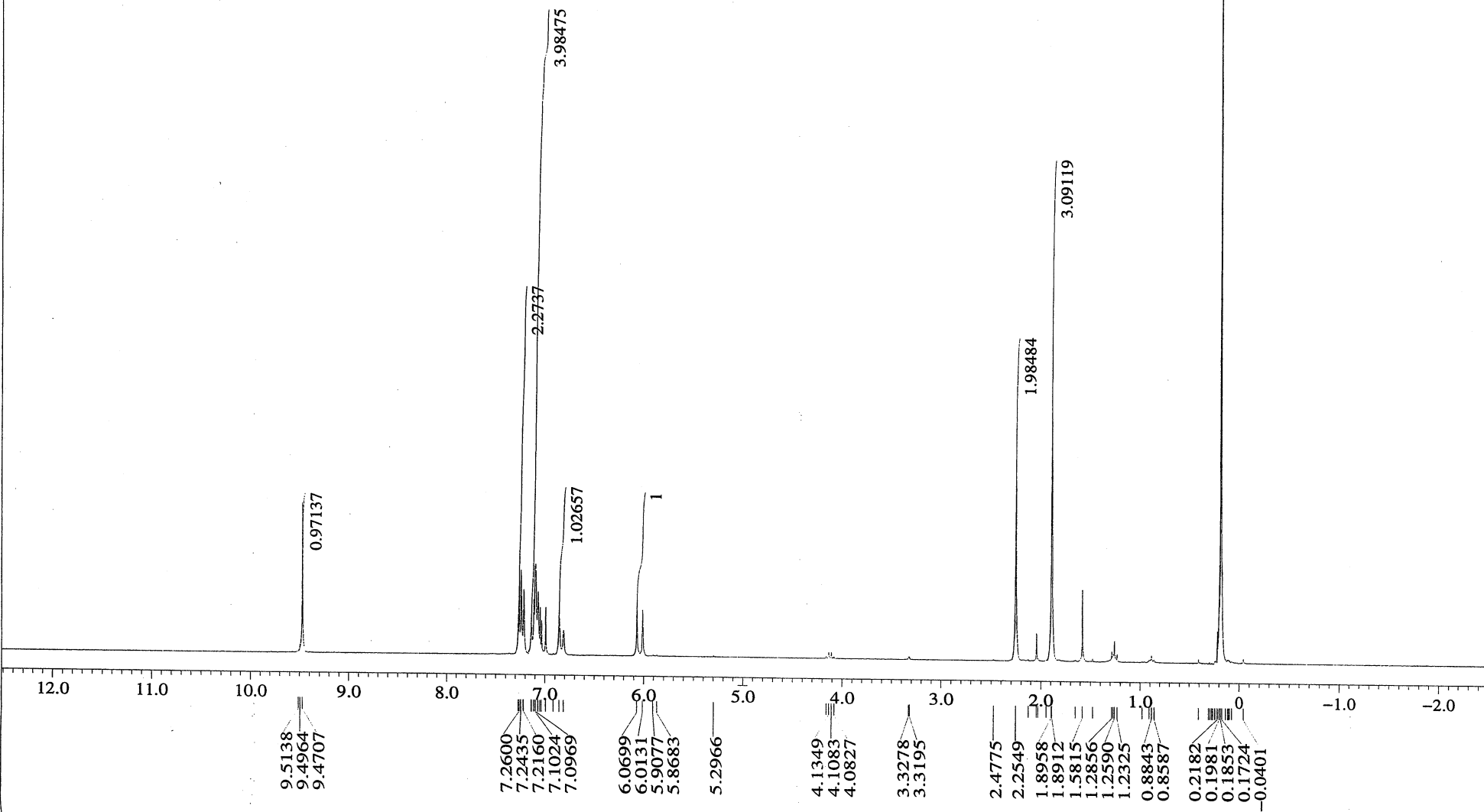
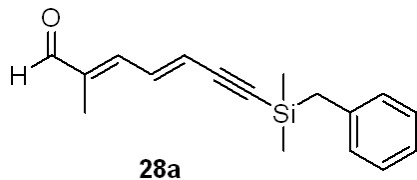
$^{13}\text{C}$  NMR spectrum of **46b** ( $\text{CDCl}_3$ , 67.5 Hz)



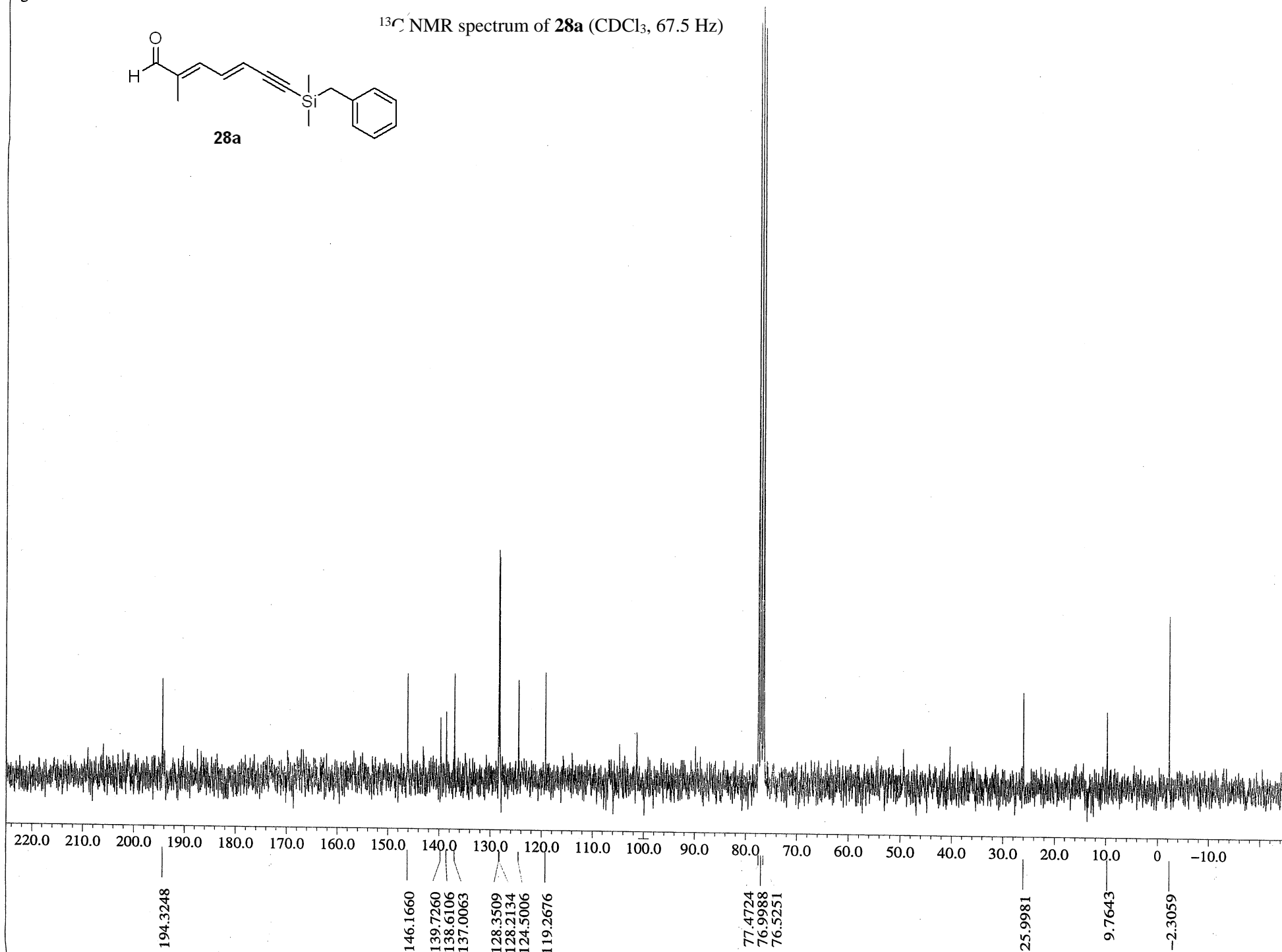
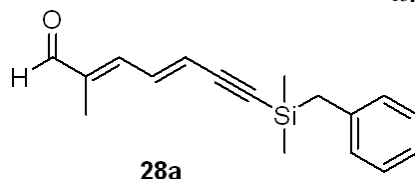
X : parts per Million :  $^{13}\text{C}$

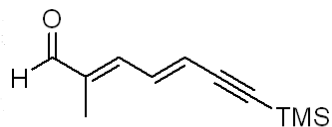
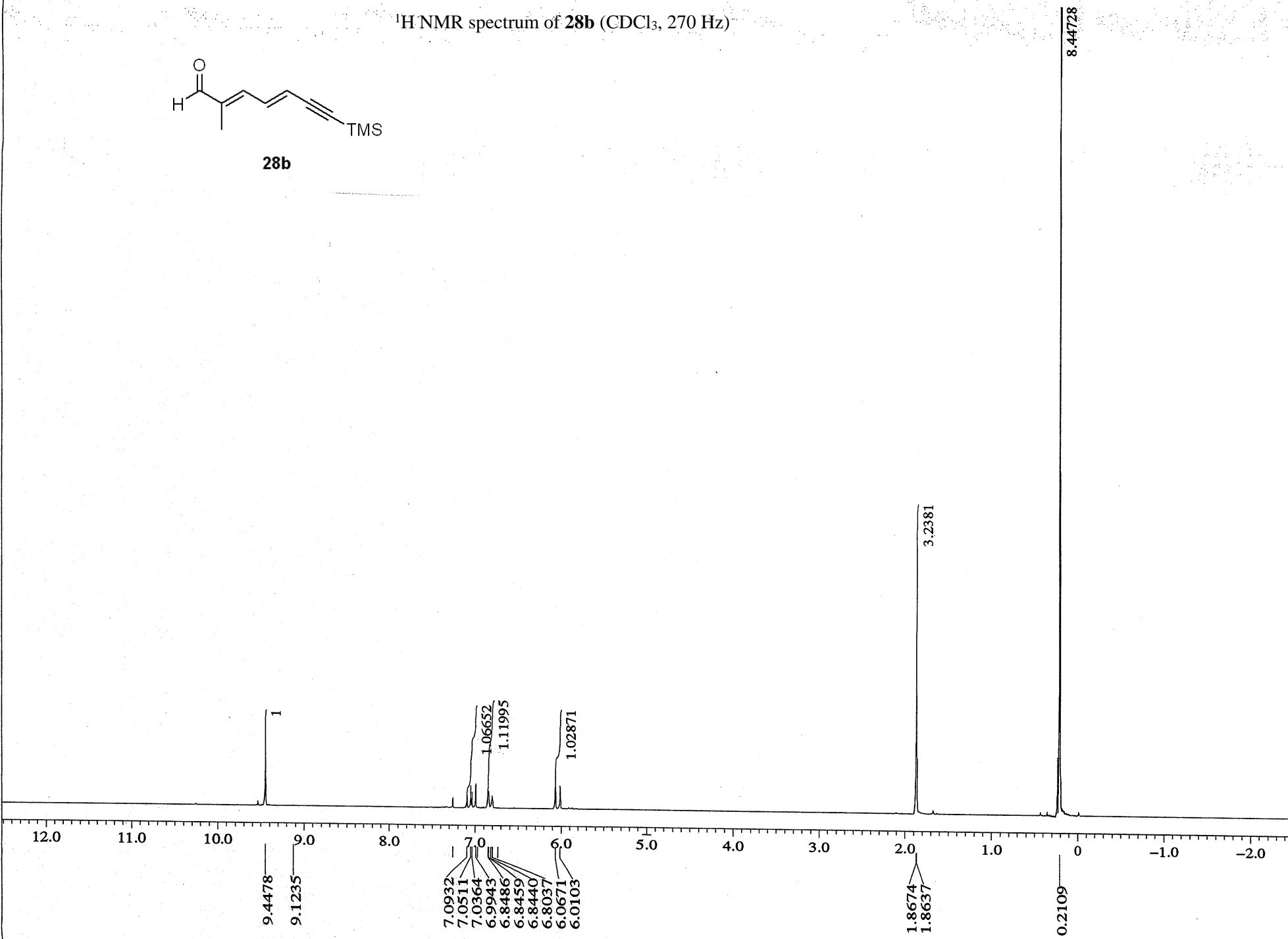
S140

<sup>1</sup>H NMR spectrum of **28a** (CDCl<sub>3</sub>, 270 Hz)



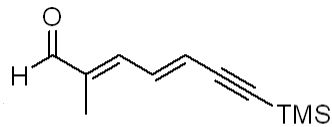
X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **28a** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

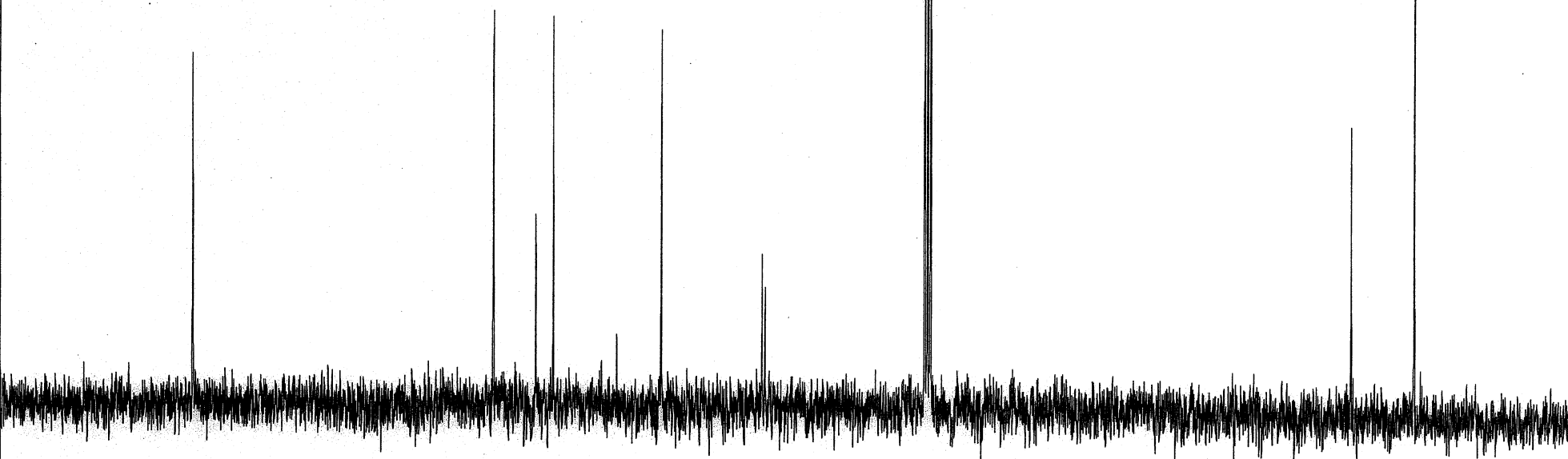
$^1\text{H}$  NMR spectrum of **28b** ( $\text{CDCl}_3$ , 270 Hz)**28b**

dg411.3

<sup>13</sup>C NMR spectrum of **28b** (CDCl<sub>3</sub>, 67.5 Hz)



**28b**



194.3623

146.3257

139.5266

136.7458

119.4578

103.4609

102.9720

77.4717

76.9980

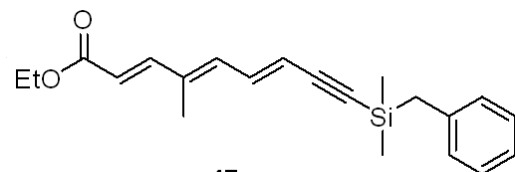
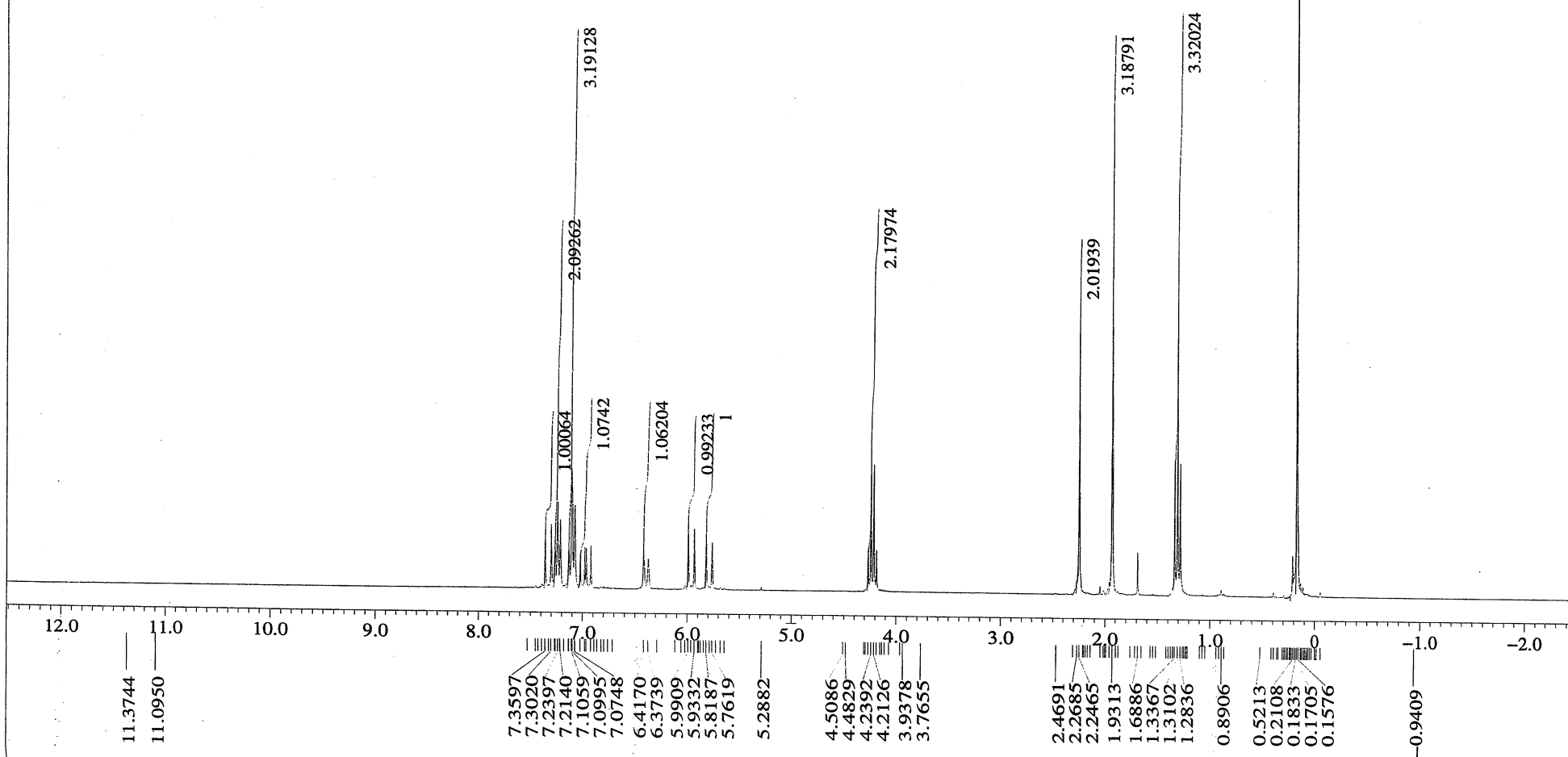
76.5320

9.7025

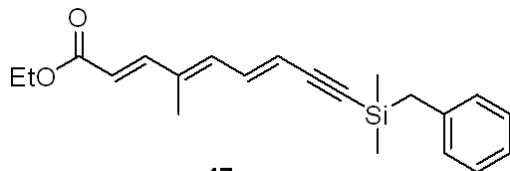
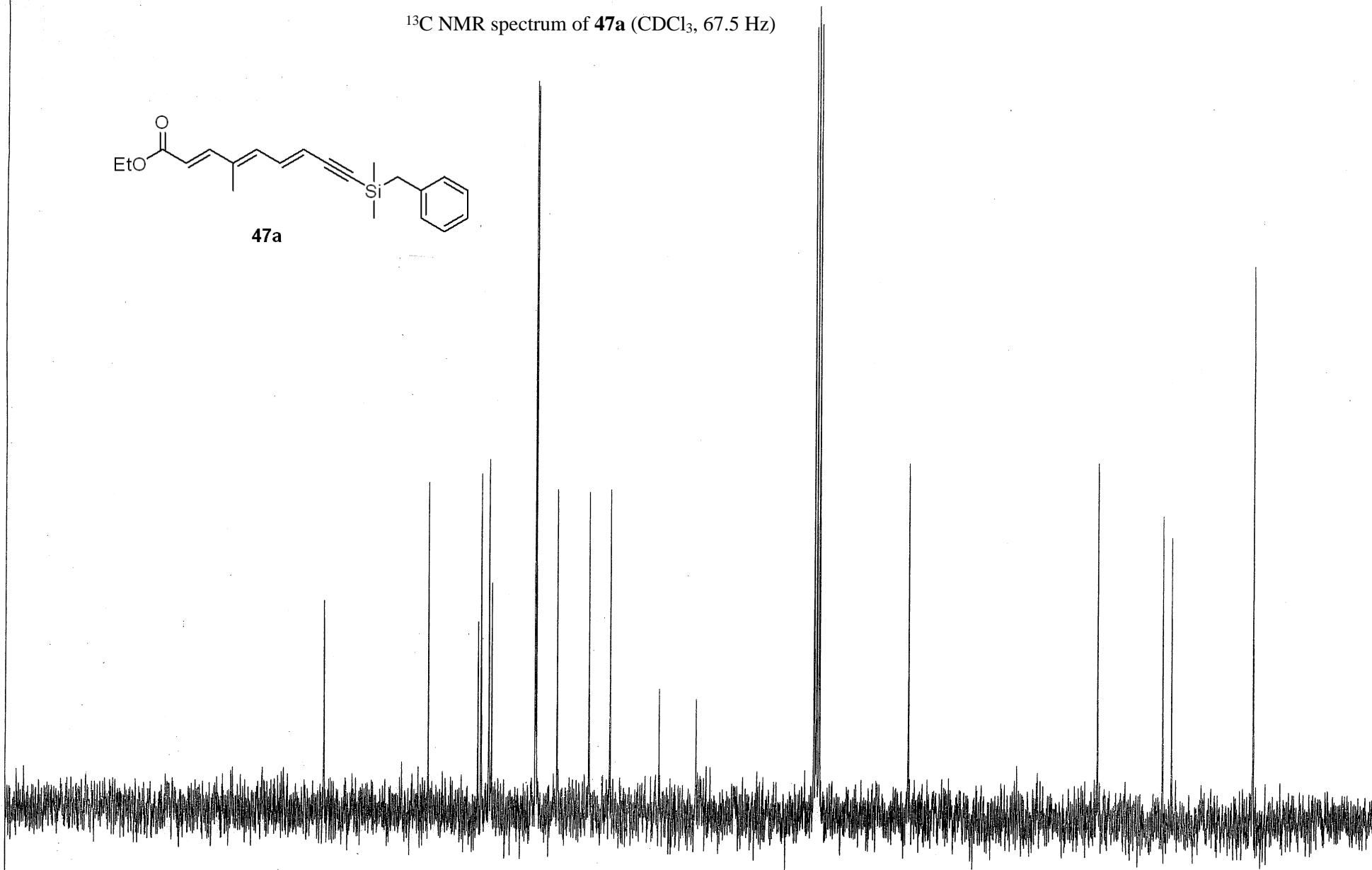
-0.3128

X : parts per Million : 13C



$^1\text{H}$  NMR spectrum of **47a** ( $\text{CDCl}_3$ , 270 Hz)**47a**

X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **47a** ( $\text{CDCl}_3$ , 67.5 Hz)**47a**

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

167.0145

147.8625

138.7487

138.1834

136.7548

136.2430

128.3132

128.1375

124.3637

118.5806

114.6845

77.4730

76.9993

76.5333

60.3378

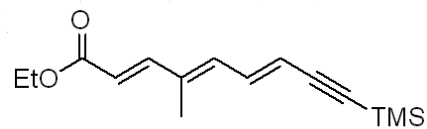
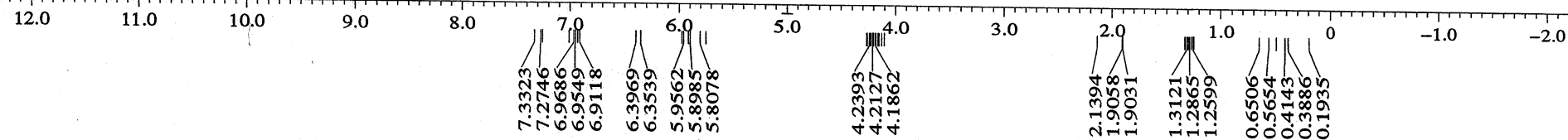
26.1056

14.2721

12.6679

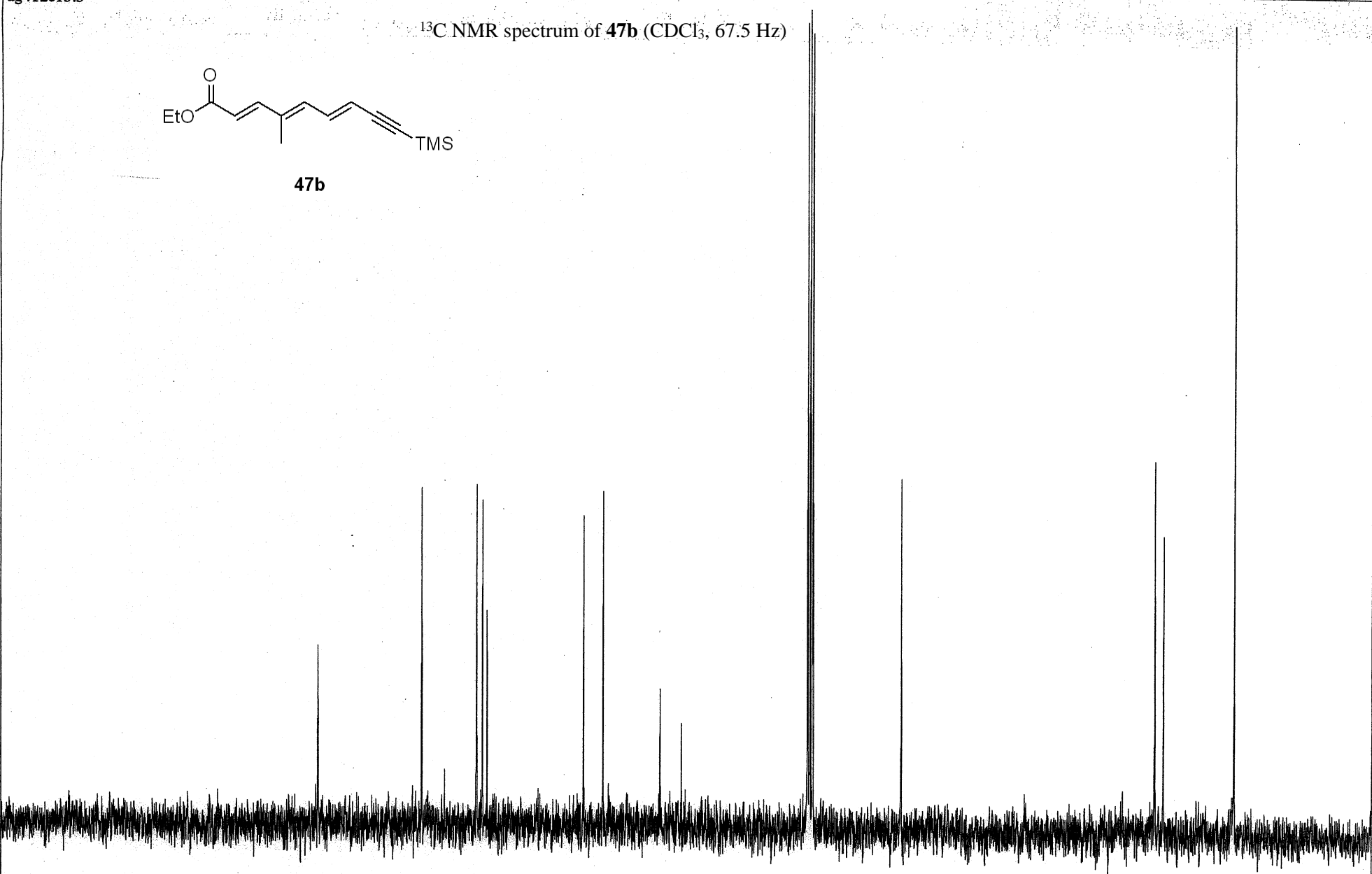
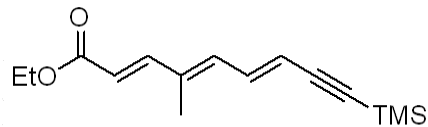
-2.2443

X : parts per Million :  $^{13}\text{C}$

$^1\text{H}$  NMR spectrum of **47b** ( $\text{CDCl}_3$ , 270 Hz)**47b**

X : parts per Million : 1H

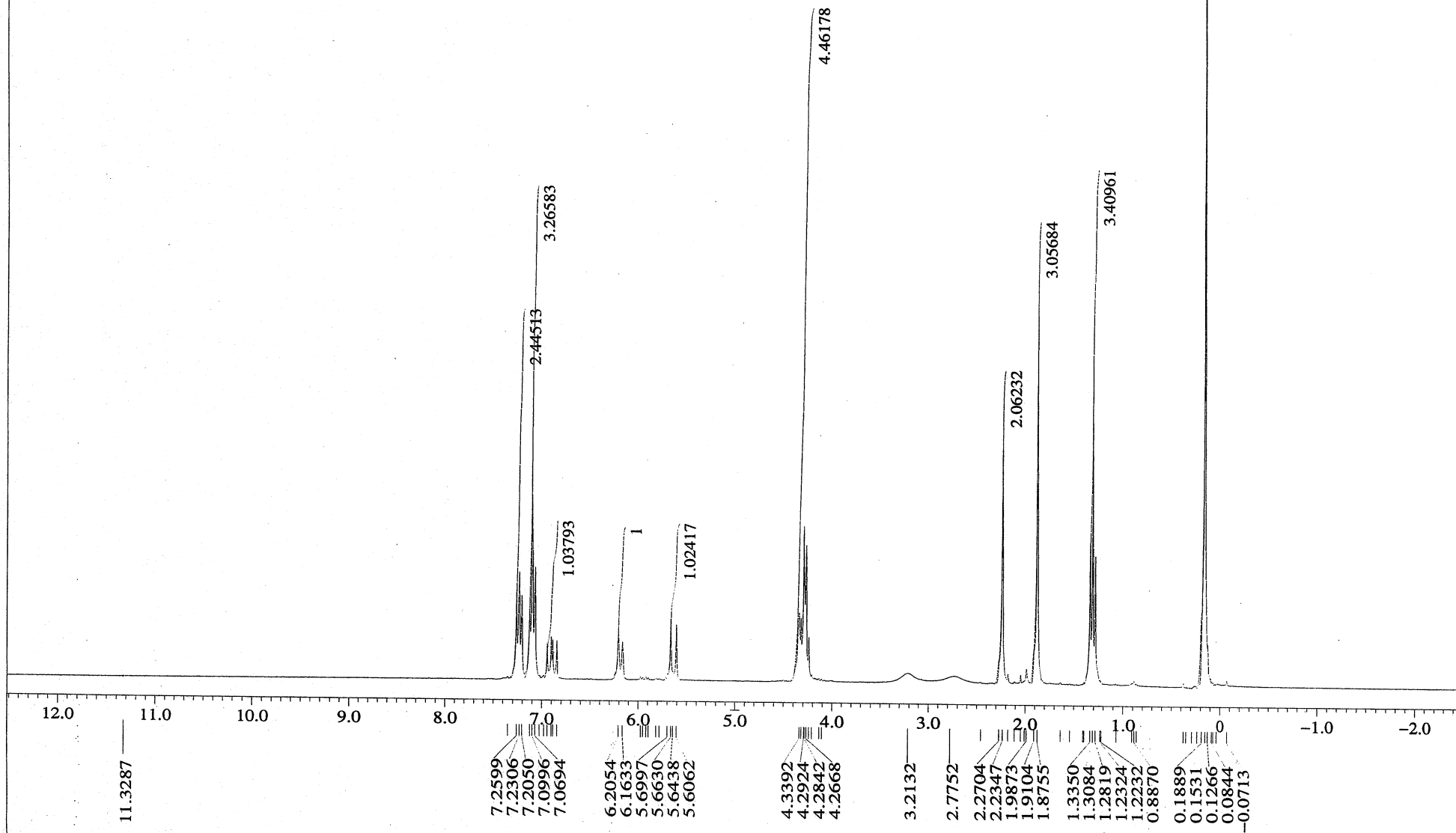
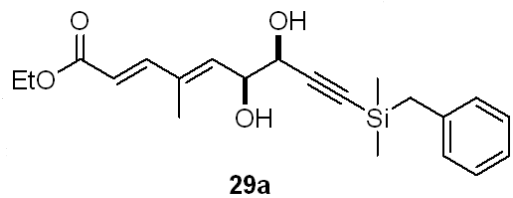
<sup>13</sup>C NMR spectrum of **47b** (CDCl<sub>3</sub>, 67.5 Hz)



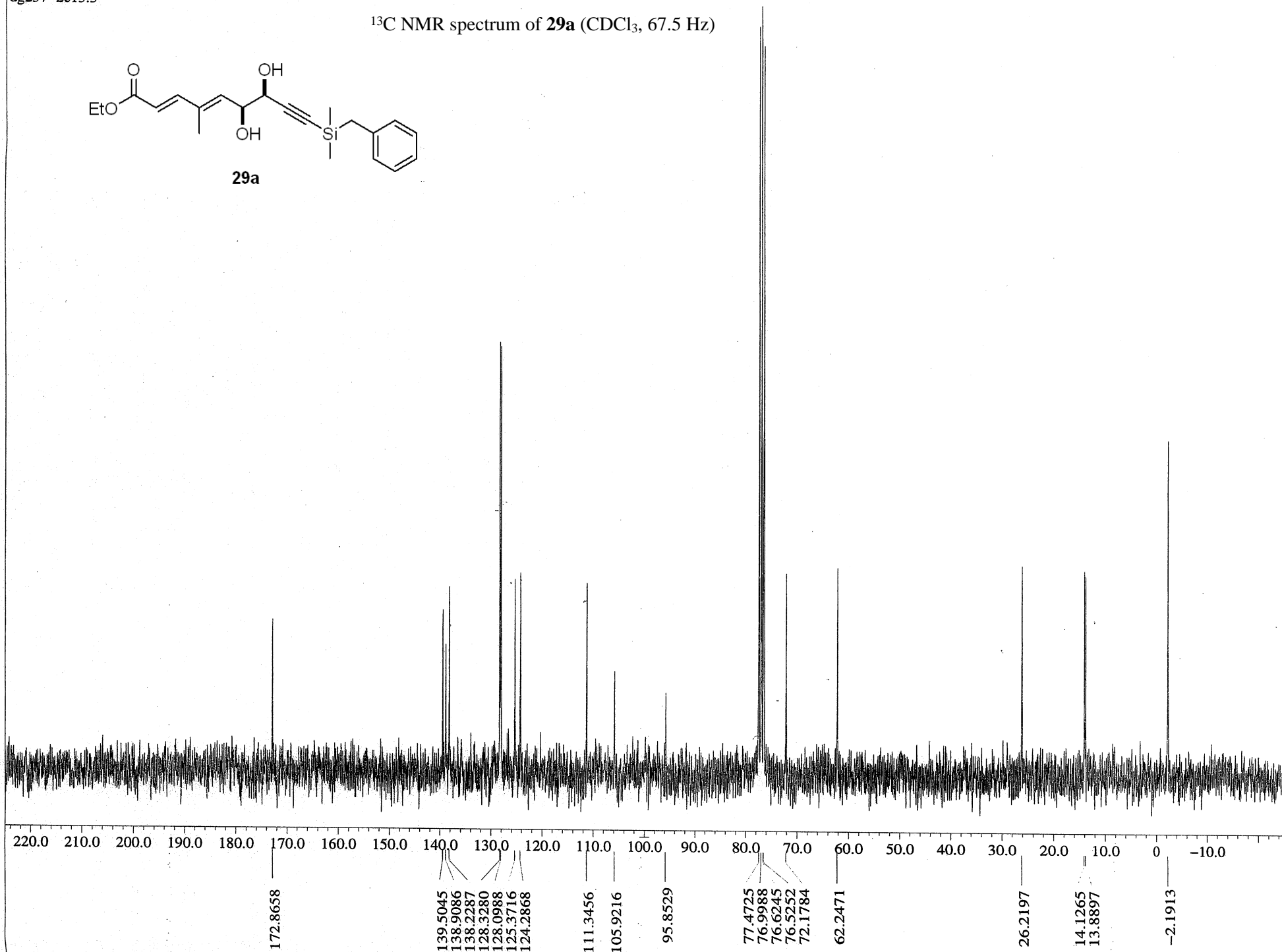
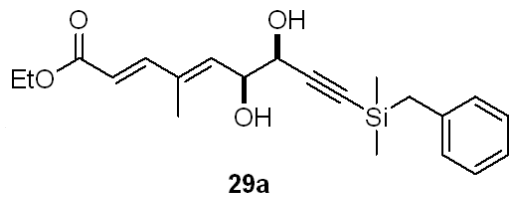
| Chemical Shift (ppm) |
|----------------------|
| 167.0290             |
| 147.9076             |
| 137.9305             |
| 136.8533             |
| 136.0665             |
| 118.4653             |
| 114.8519             |
| 104.4317             |
| 77.4646              |
| 76.9986              |
| 76.5249              |
| 60.3218              |
| 14.2638              |
| 12.6518              |
| -0.1976              |

X : parts per Million : <sup>13</sup>C

<sup>1</sup>H NMR spectrum of **29a** (CDCl<sub>3</sub>, 270 Hz)

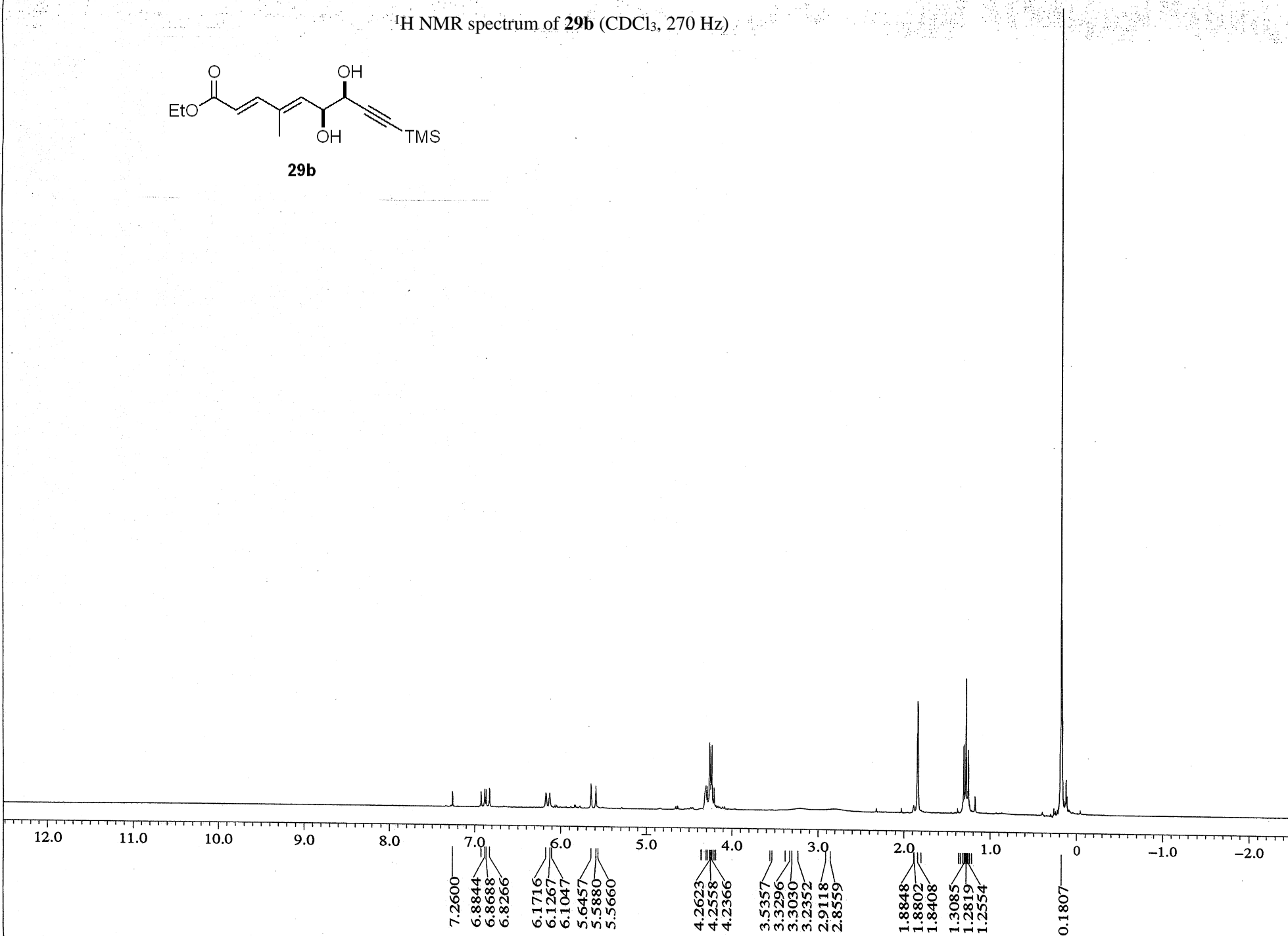
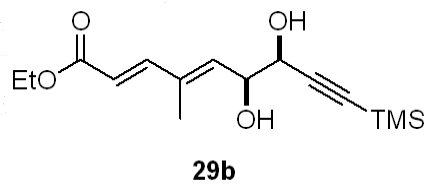


X : parts per Million : 1H

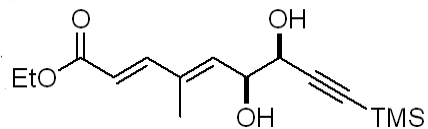
$^{13}\text{C}$  NMR spectrum of **29a** ( $\text{CDCl}_3$ , 67.5 Hz)

X : parts per Million : 13C

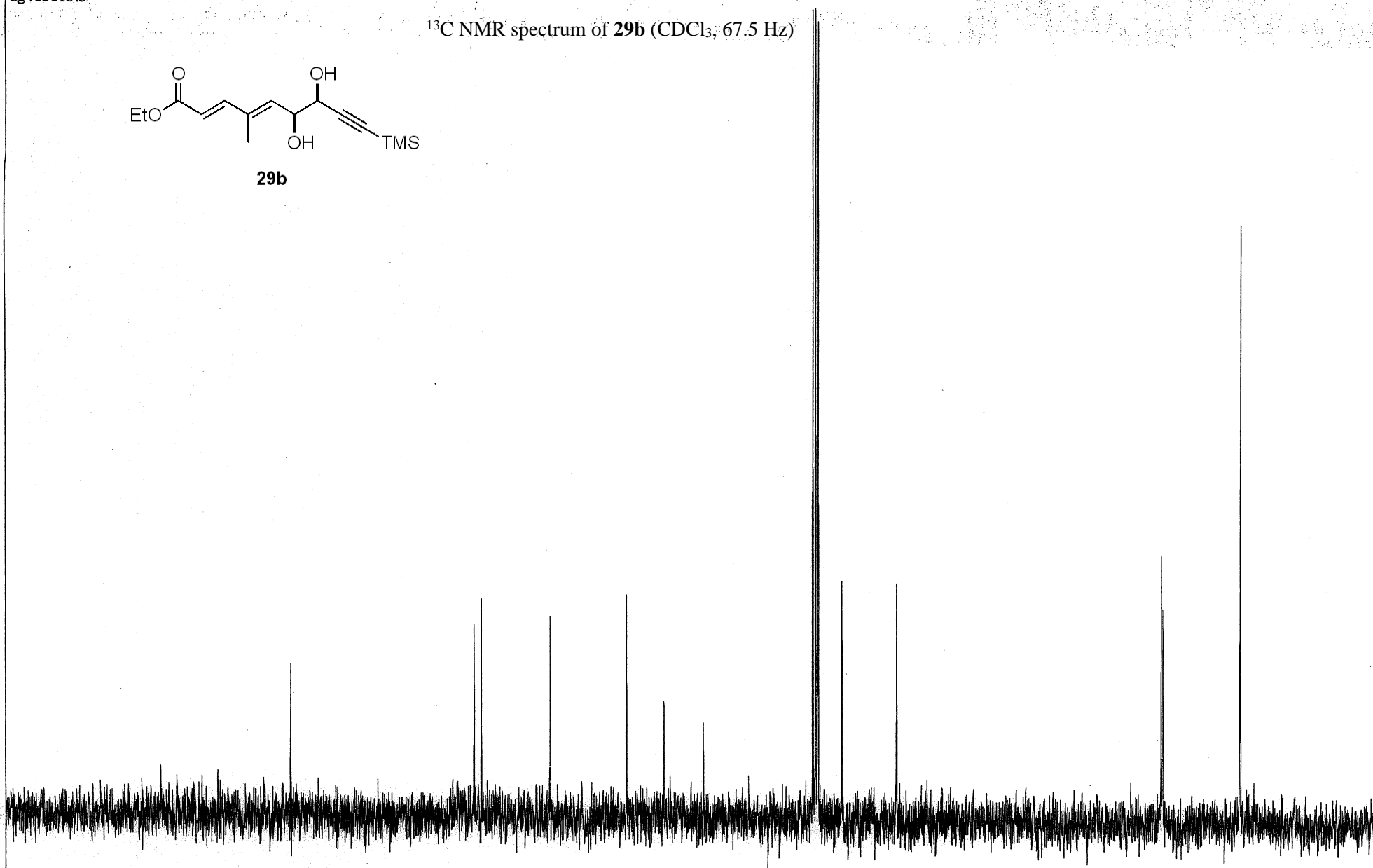
S150

$^1\text{H}$  NMR spectrum of **29b** ( $\text{CDCl}_3$ , 270 Hz)

<sup>13</sup>C NMR spectrum of **29b** (CDCl<sub>3</sub>, 67.5 Hz)



**29b**



220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

172.8794

139.2736  
137.9673

125.4234

111.4662

77.4708  
76.9971  
76.6839  
76.5311  
72.1996

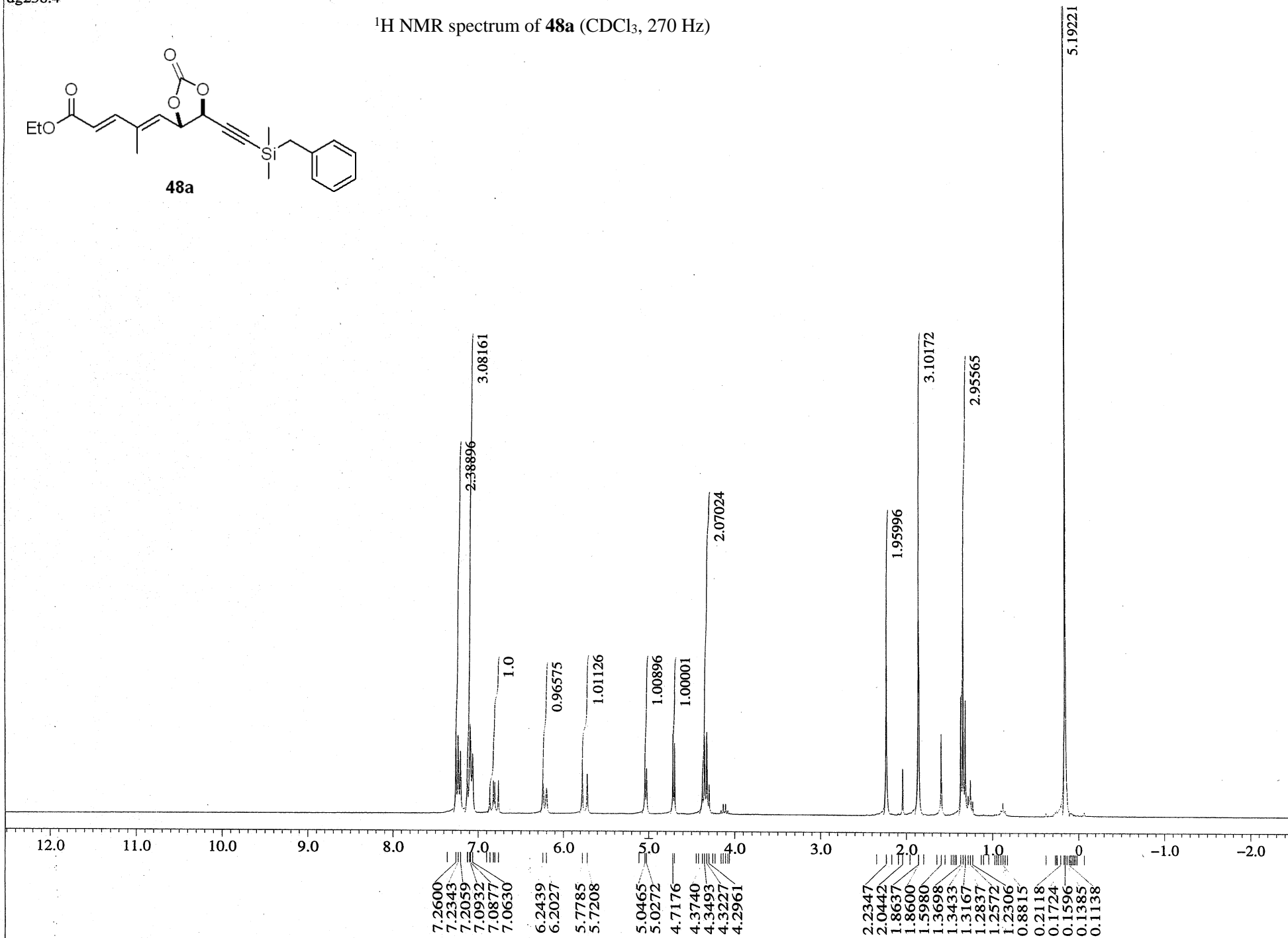
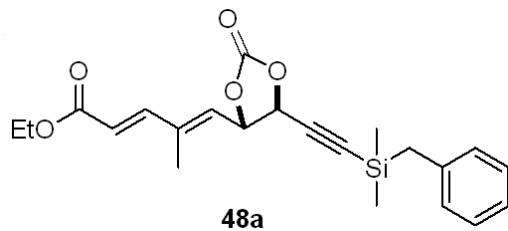
62.2149

14.1172  
13.8345

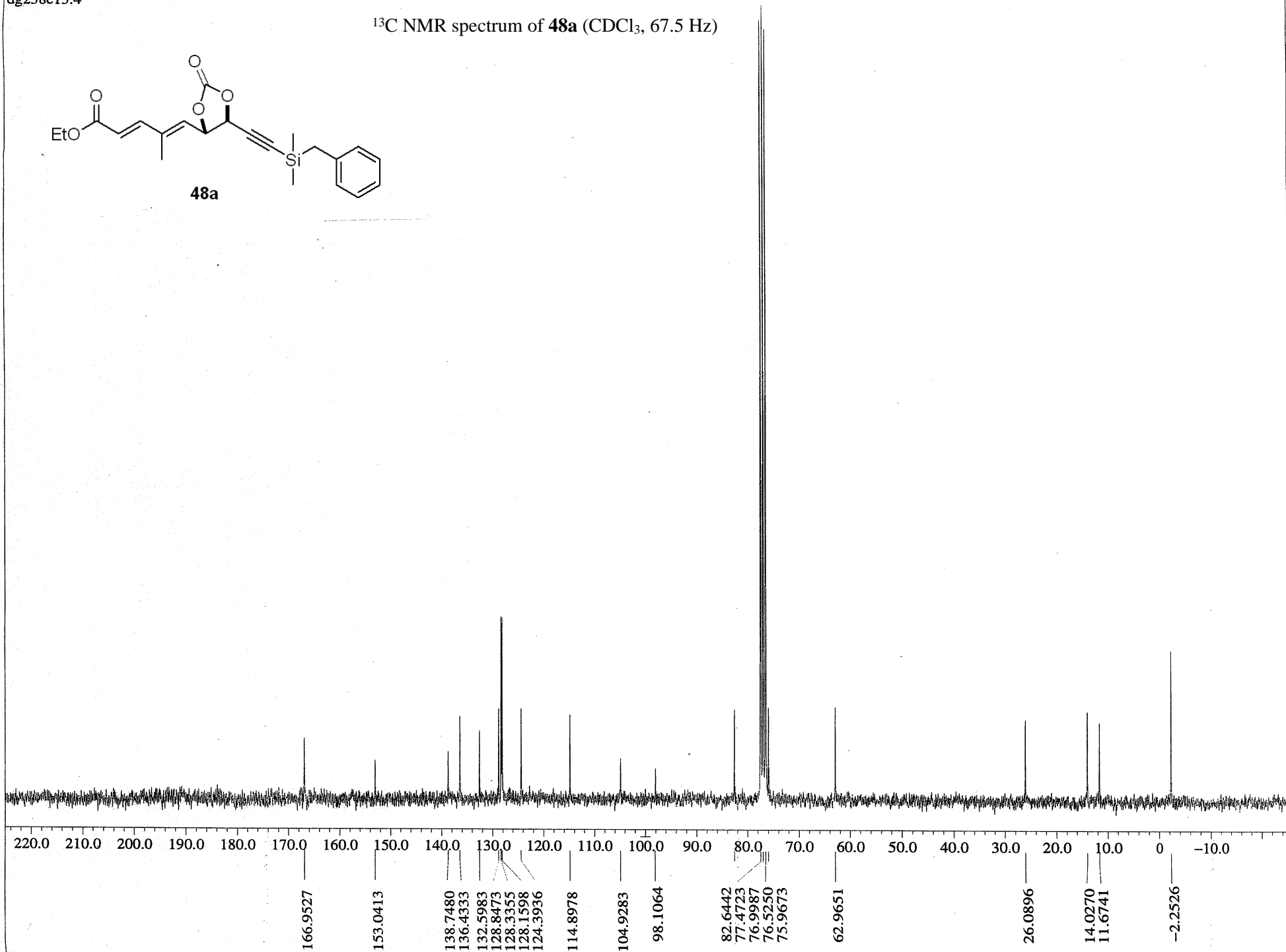
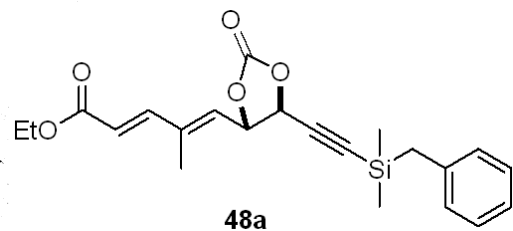
-0.1151

X : parts per Million : <sup>13</sup>C

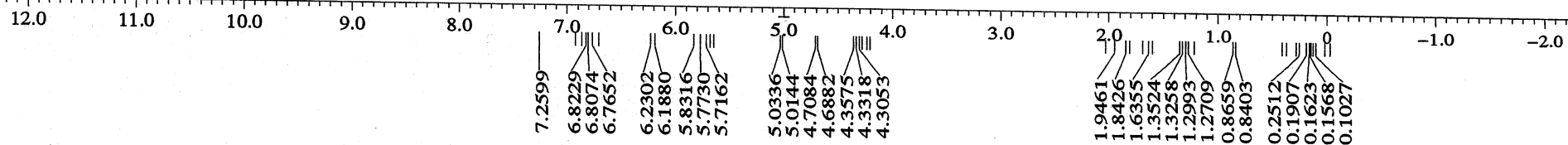
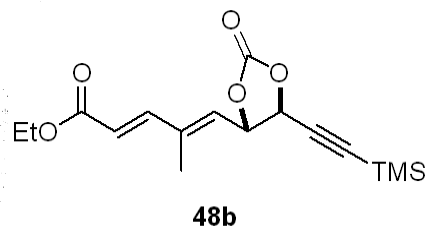


<sup>1</sup>H NMR spectrum of **48a** (CDCl<sub>3</sub>, 270 Hz)

X : parts per Million : 1H

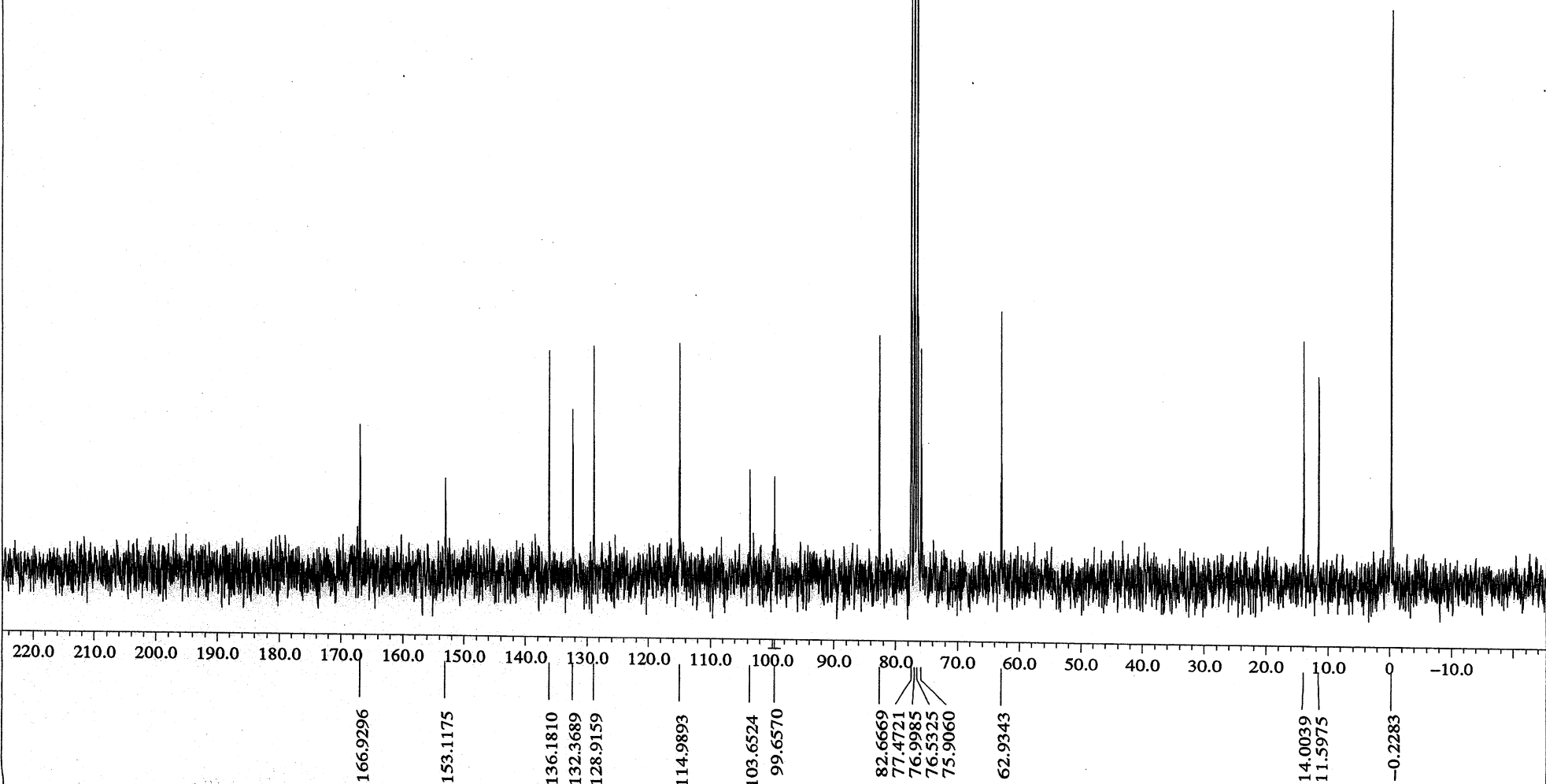
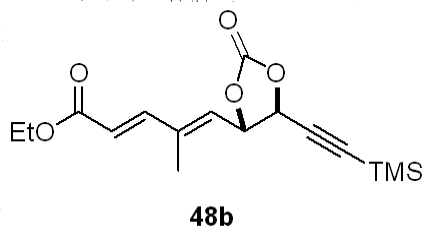
$^{13}\text{C}$  NMR spectrum of **48a** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$ 

S154

$^1\text{H}$  NMR spectrum of **48b** ( $\text{CDCl}_3$ , 270 Hz)

X : parts per Million : 1H

<sup>13</sup>C NMR spectrum of **48b** (CDCl<sub>3</sub>, 67.5 Hz)



X : parts per Million : <sup>13</sup>C

dg244-11\_27Apr2005

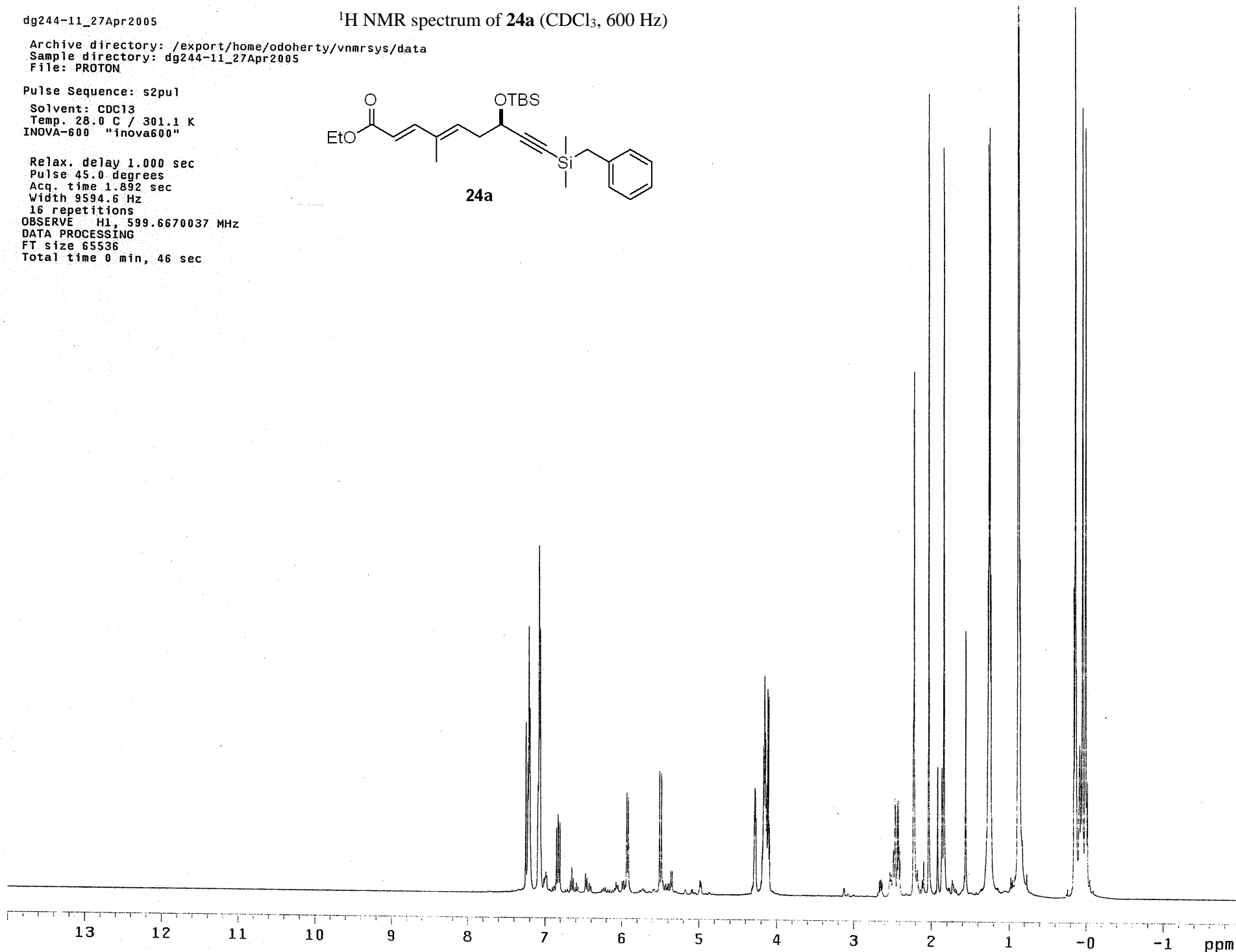
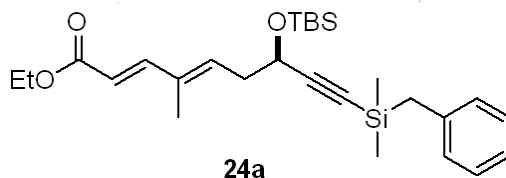
<sup>1</sup>H NMR spectrum of **24a** (CDCl<sub>3</sub>, 600 Hz)

Archive directory: /export/home/odoherly/vnmrsys/data  
Sample directory: dg244-11\_27Apr2005  
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6670037 MHz  
DATA PROCESSING  
FT size 65536  
Total time 0 min, 46 sec



S157

dg244-11\_27Apr2005

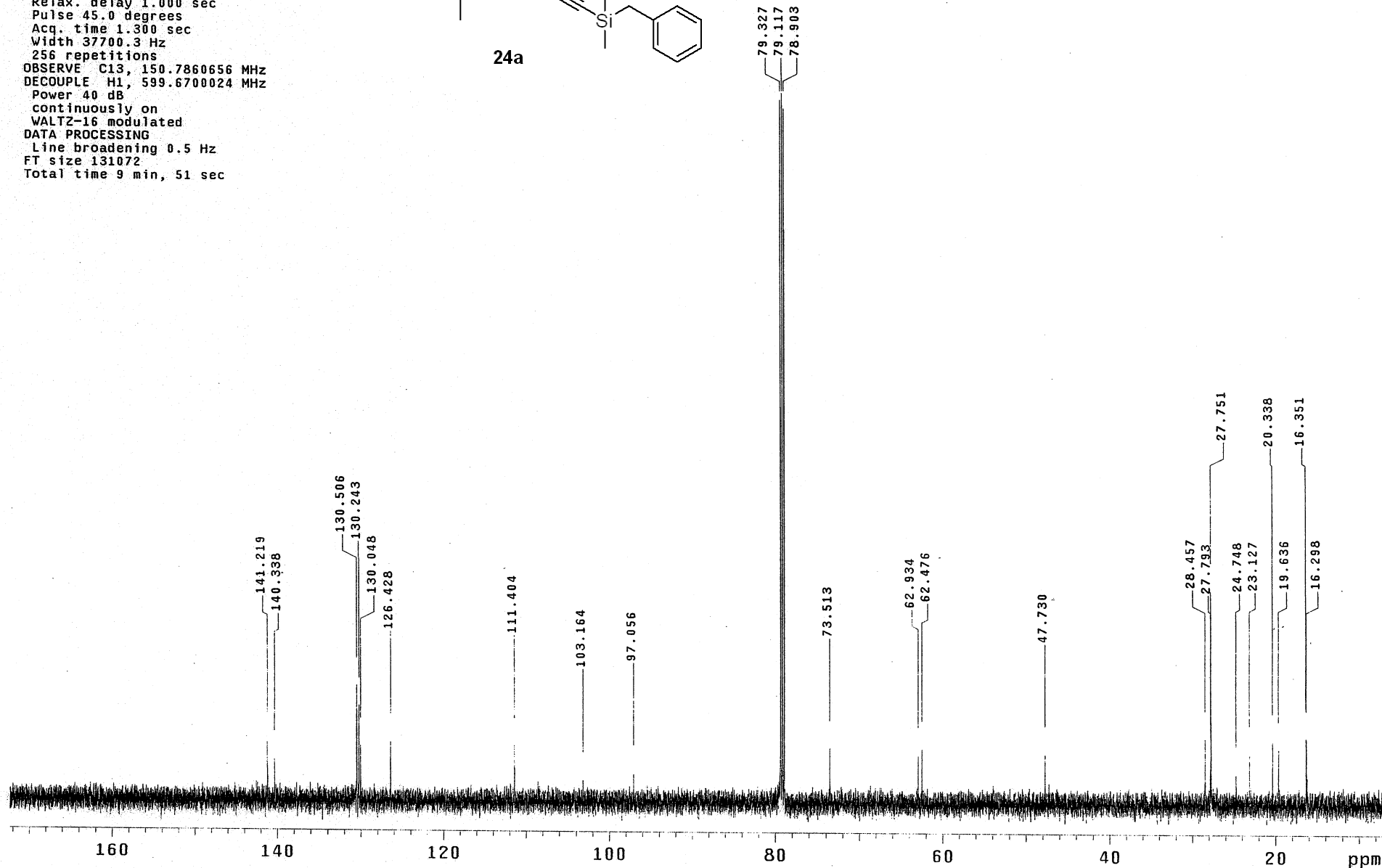
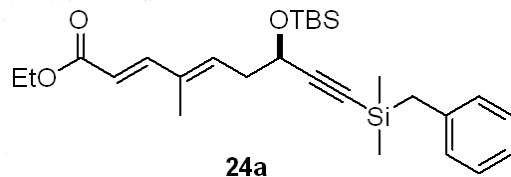
<sup>13</sup>C NMR spectrum of **24a** (CDCl<sub>3</sub>, 150 Hz)

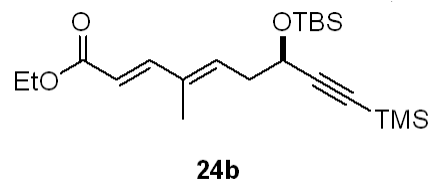
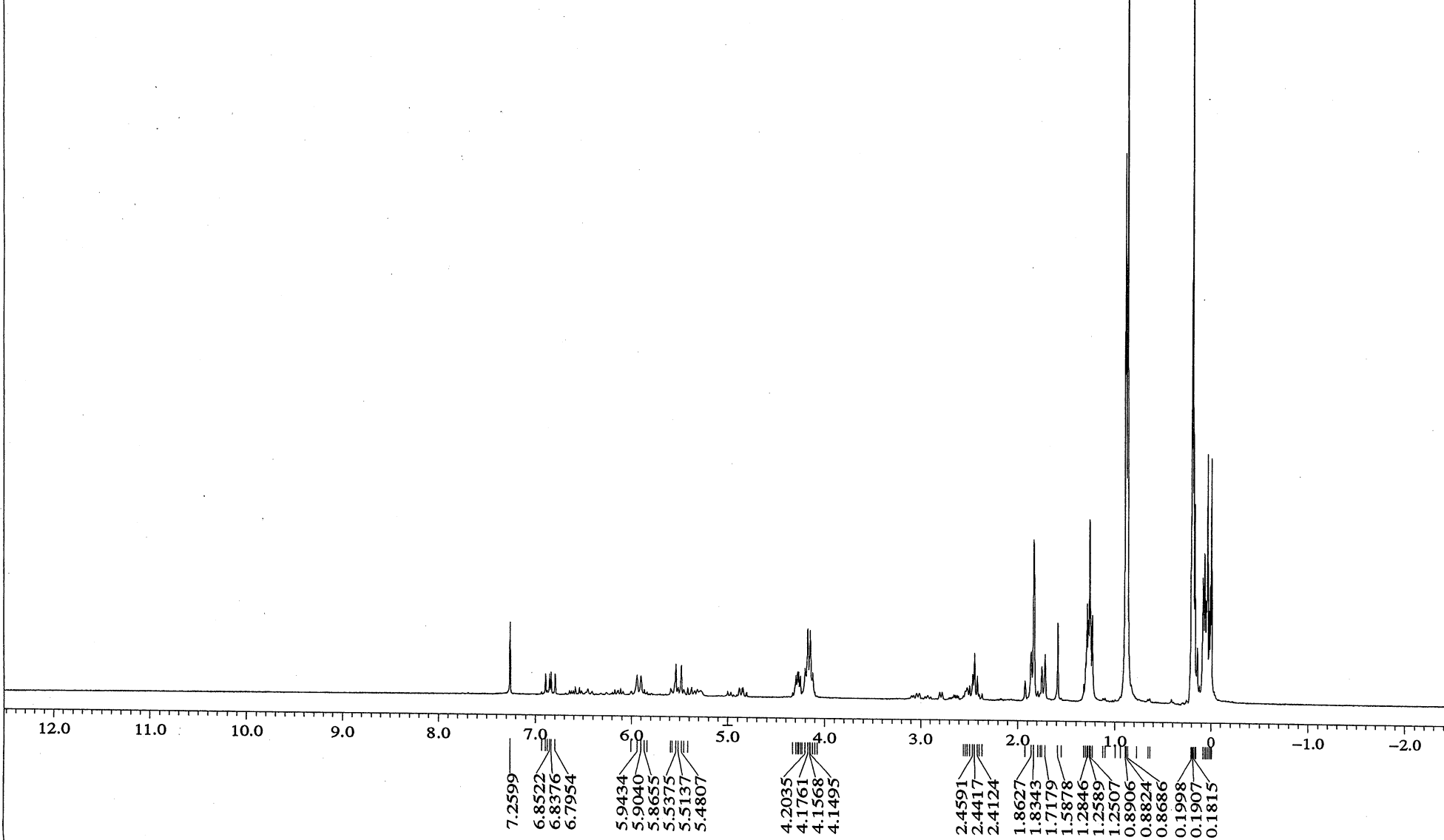
Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg244-11\_27Apr2005  
File: CARBON

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 37700.3 Hz  
256 repetitions  
OBSERVE C13, 150.7860656 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 9 min, 51 sec

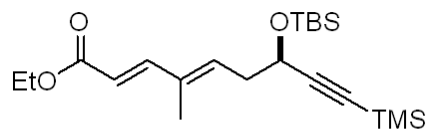


$^1\text{H}$  NMR spectrum of **24b** ( $\text{CDCl}_3$ , 270 Hz)**24b**

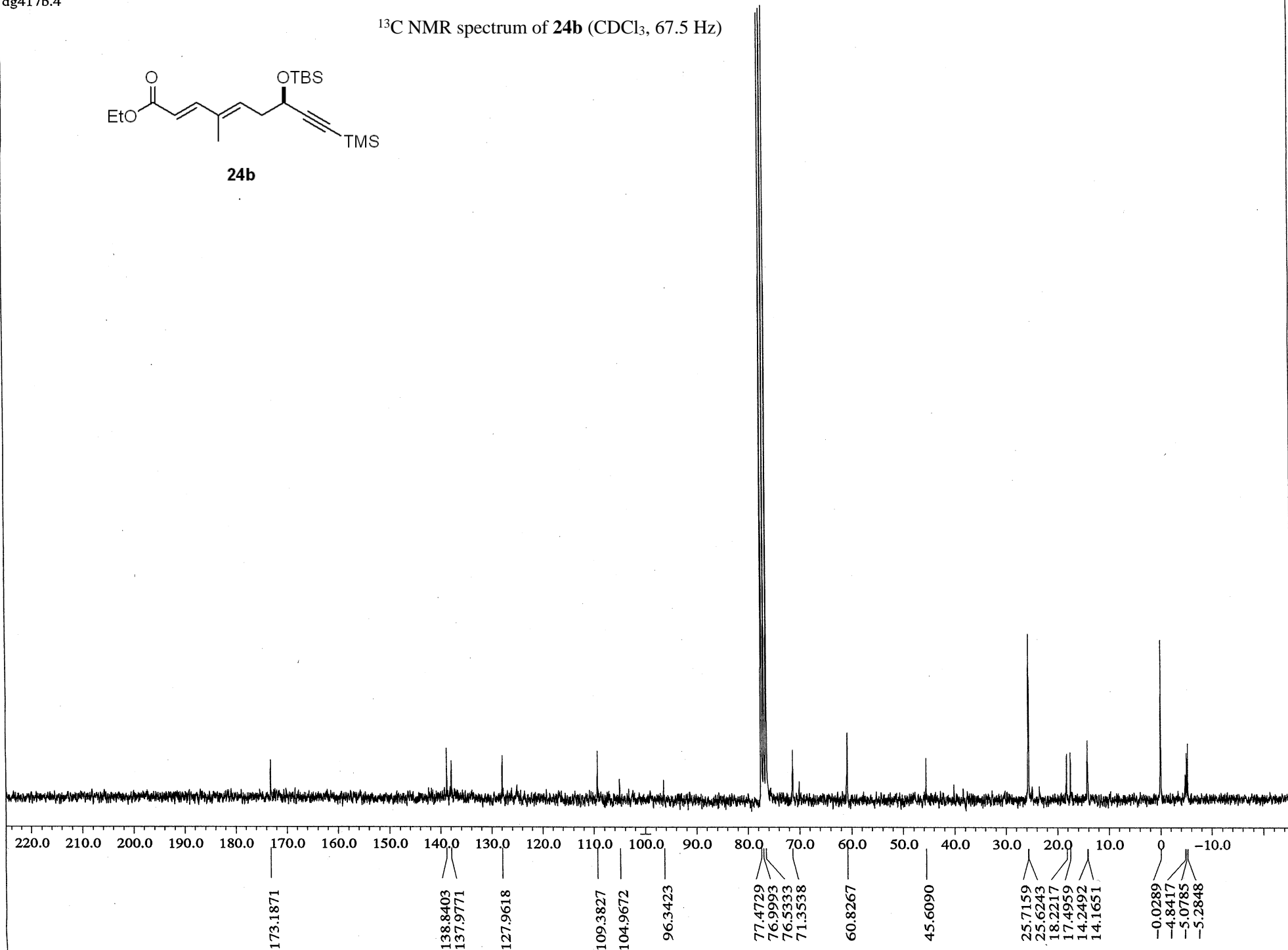
X : parts per Million : 1H

dg417b.4

$^{13}\text{C}$  NMR spectrum of **24b** ( $\text{CDCl}_3$ , 67.5 Hz)



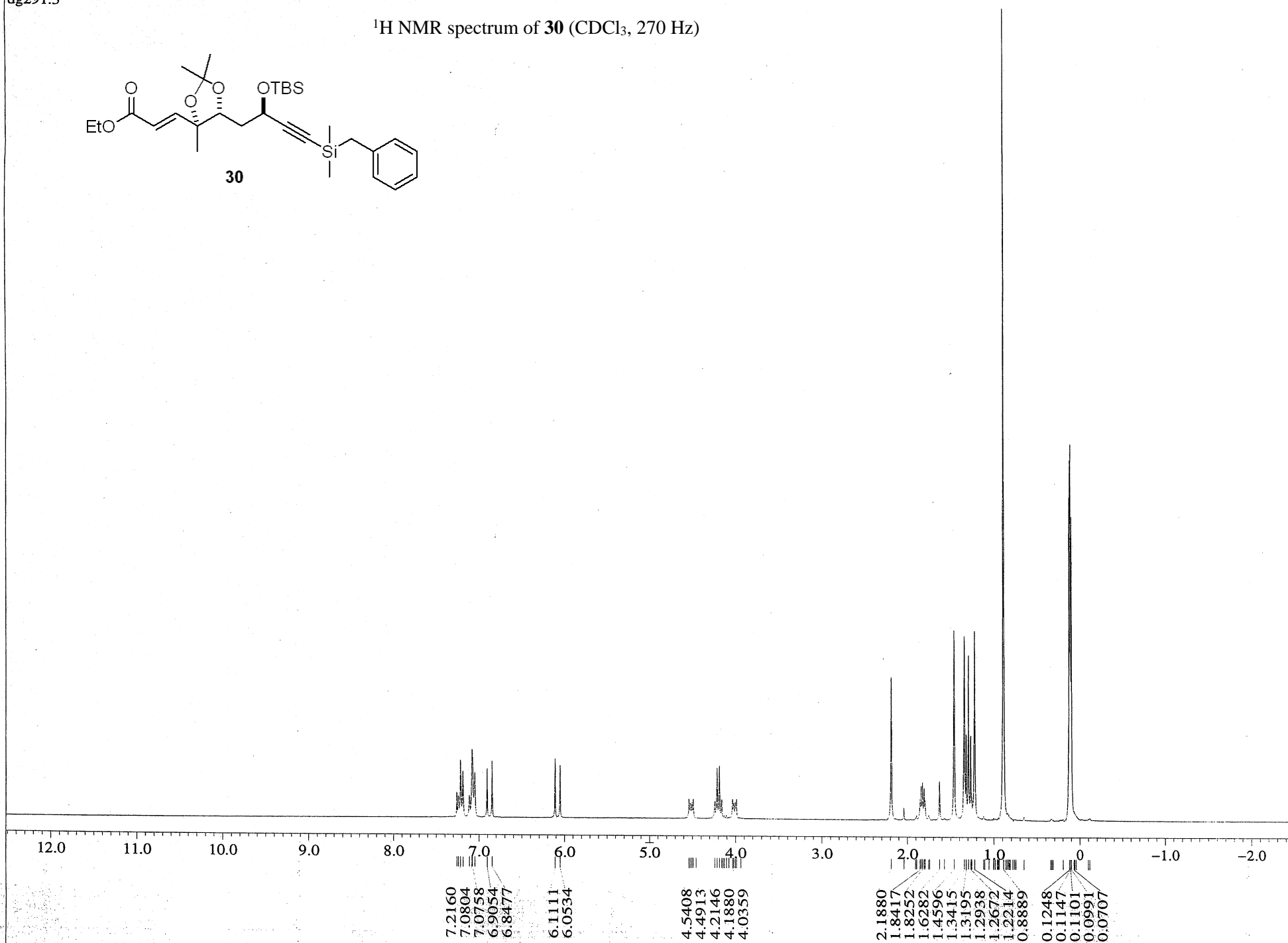
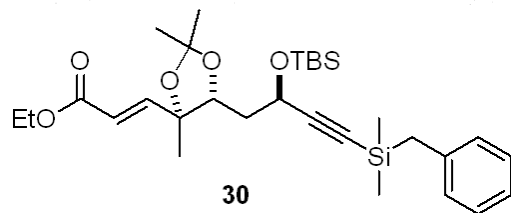
**24b**



X : parts per Million :  $^{13}\text{C}$

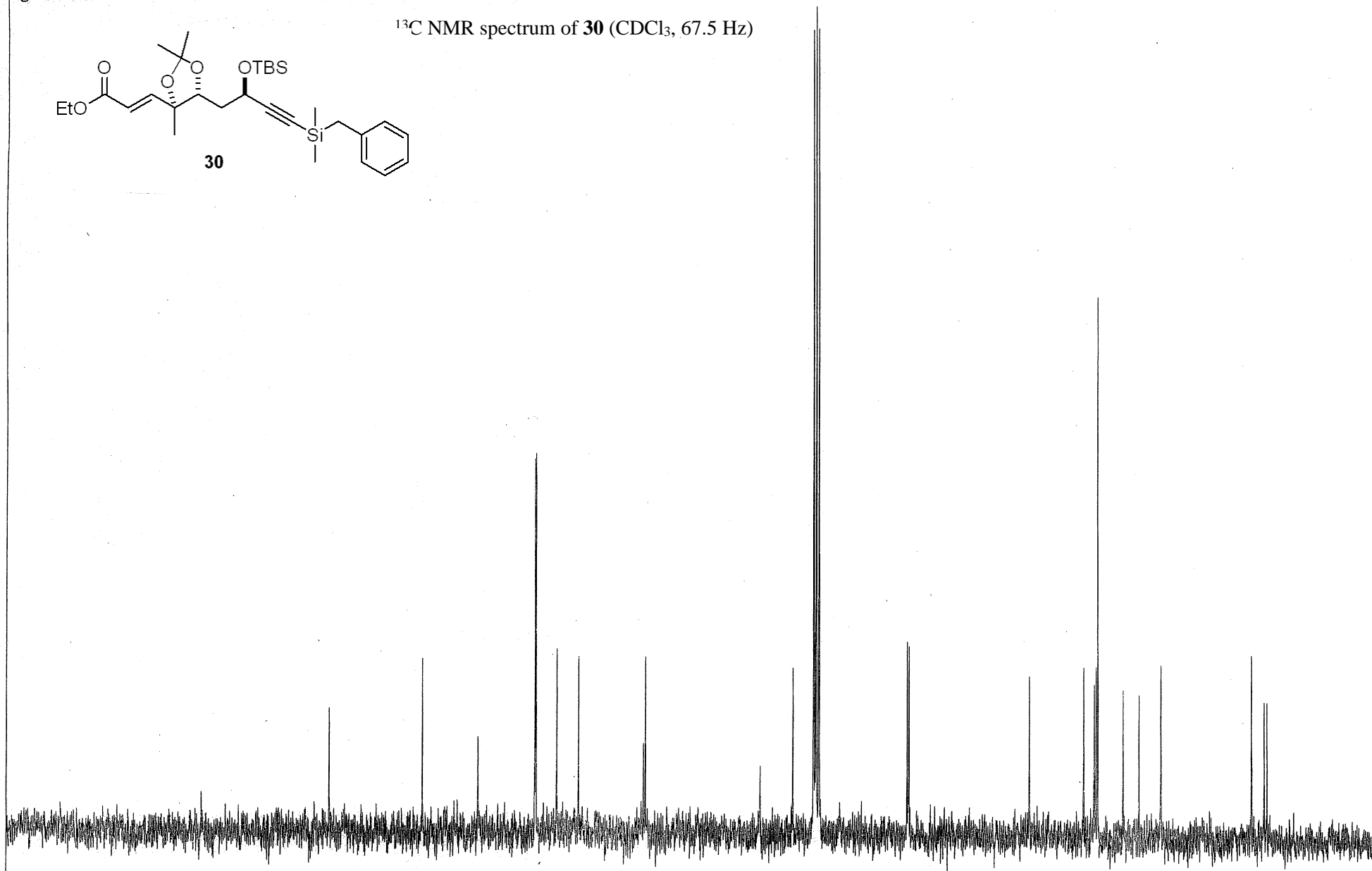
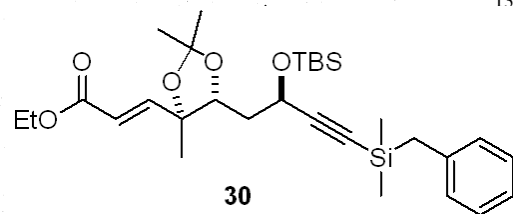
S160



$^1\text{H}$  NMR spectrum of **30** ( $\text{CDCl}_3$ , 270 Hz)

dg291c13.3

<sup>13</sup>C NMR spectrum of **30** (CDCl<sub>3</sub>, 67.5 Hz)

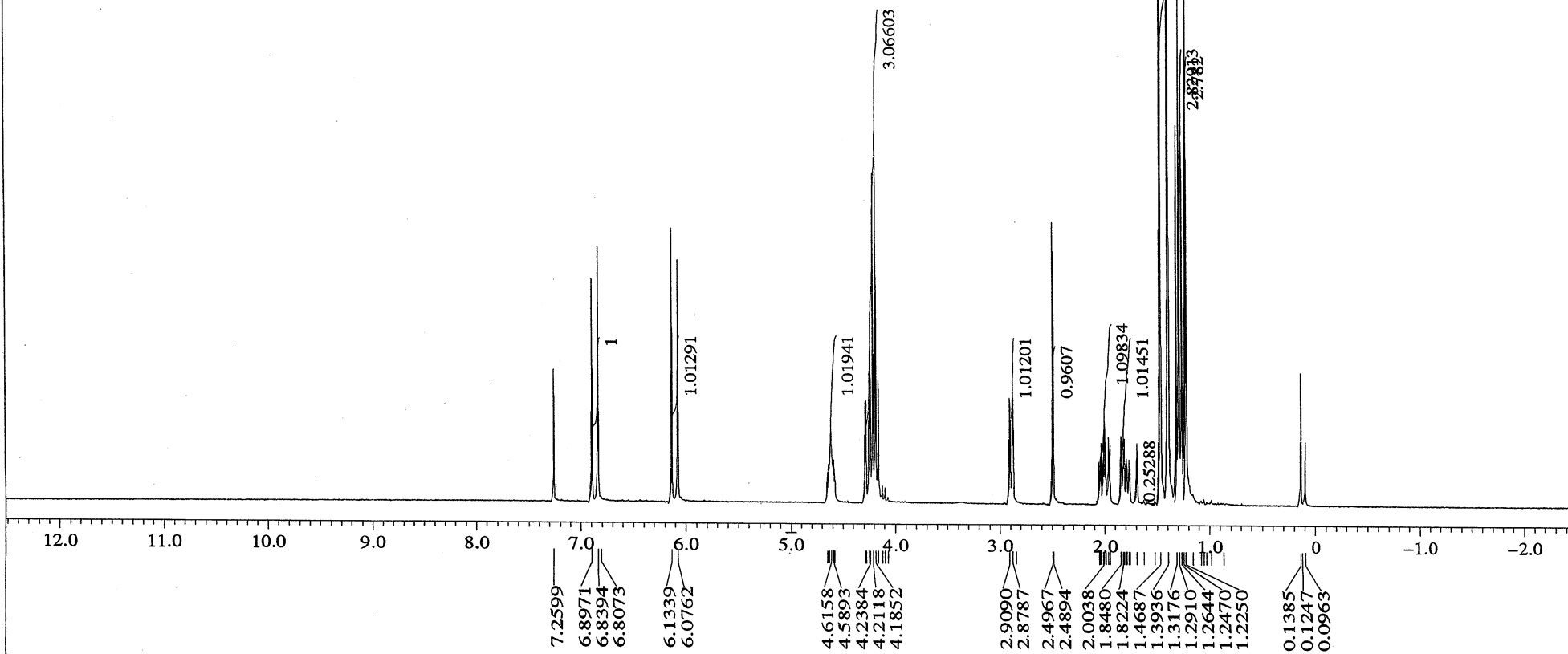
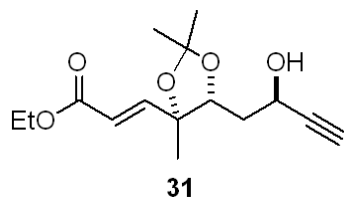


220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0

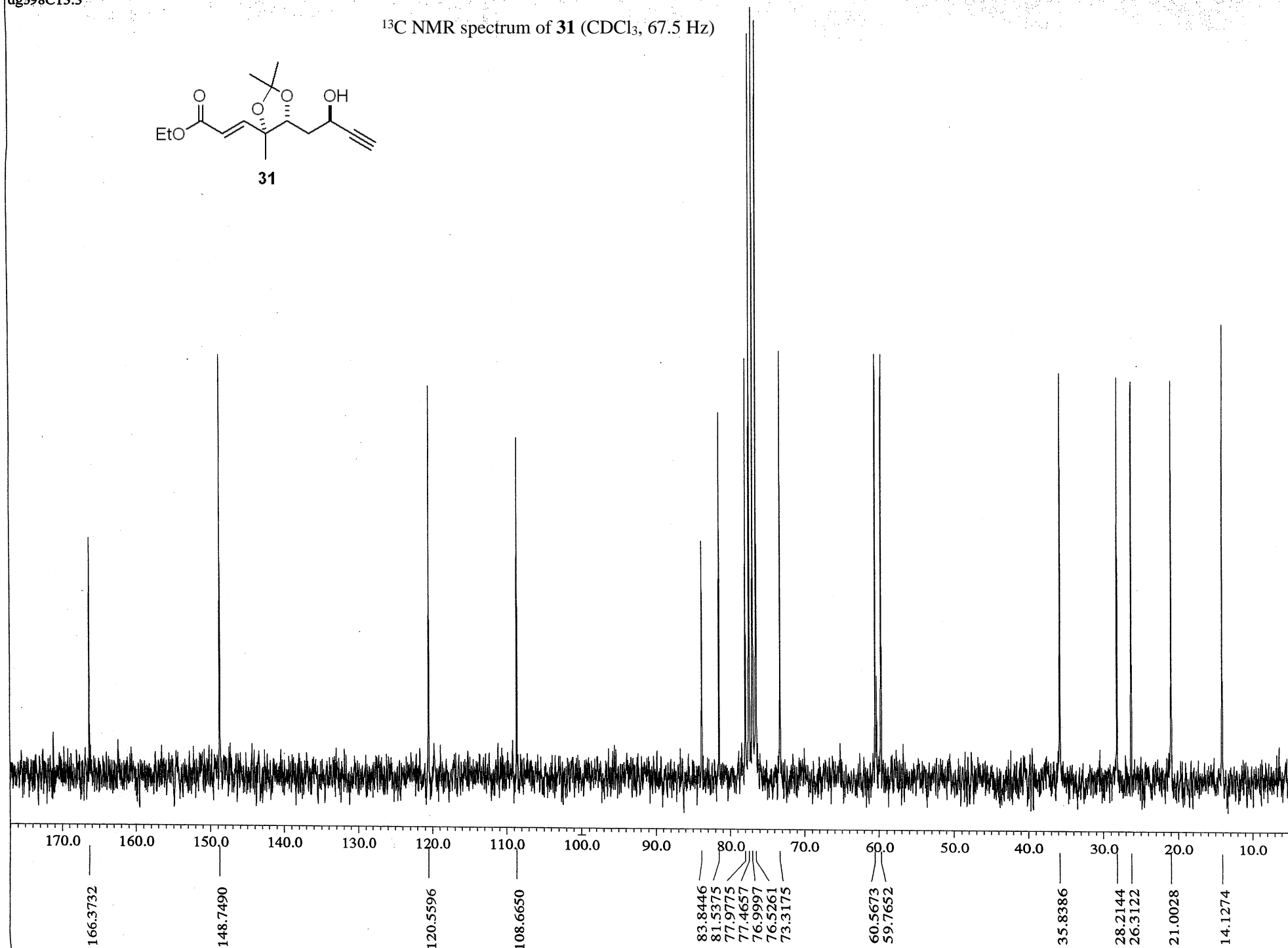
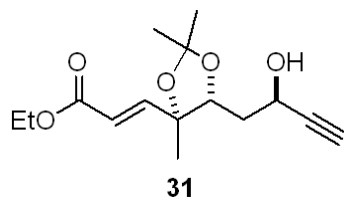
166.3185 149.1298 138.8166 128.3277 128.1443 124.3399 120.3827 108.4881 108.1520 77.4721 77.2353 76.9985 76.5248 60.4592 60.1230 38.1826 28.3202 26.3721 26.0283 25.7304 21.0856 18.1750 14.2025 -2.2680 -4.5904 -5.1099

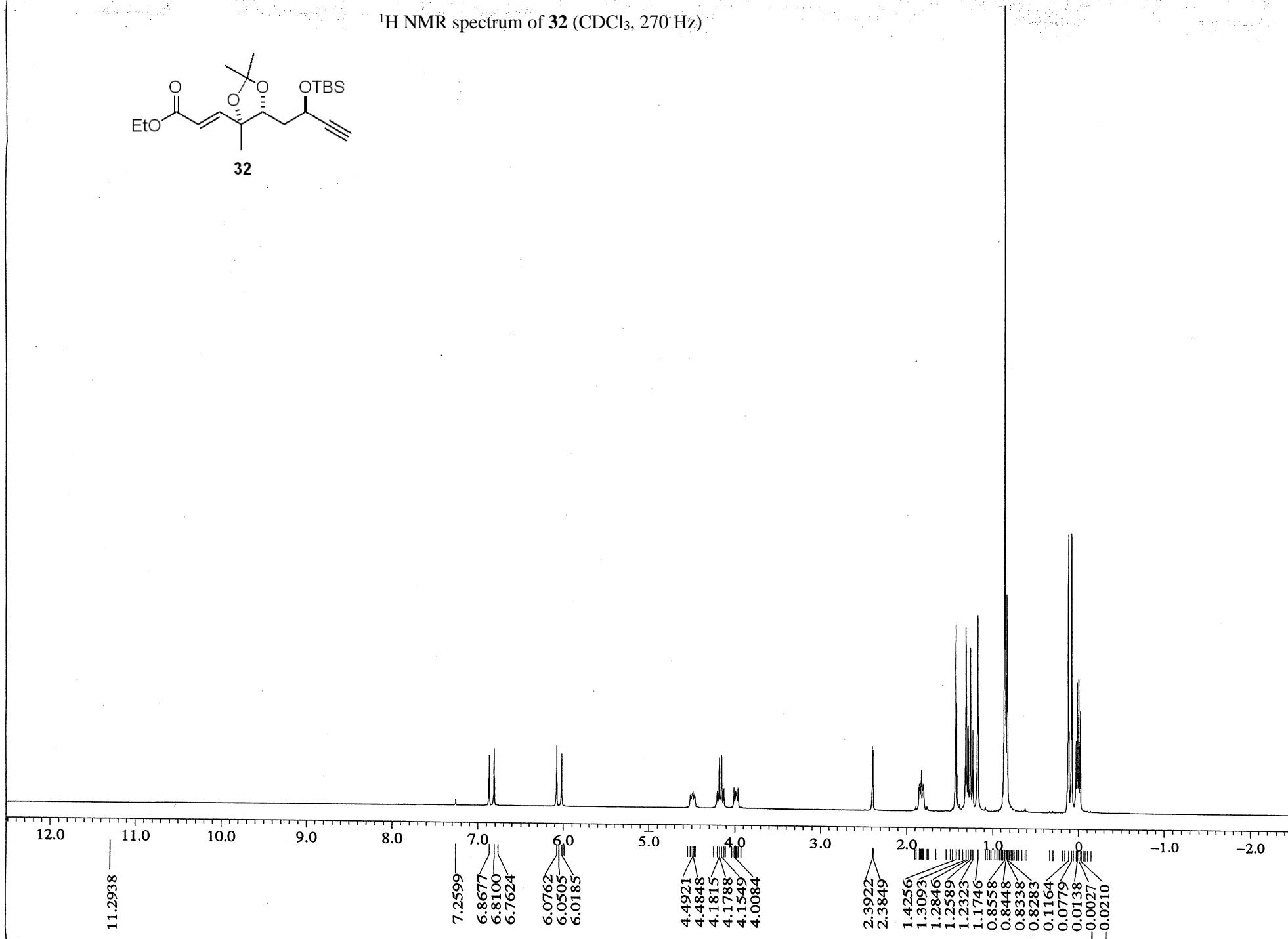
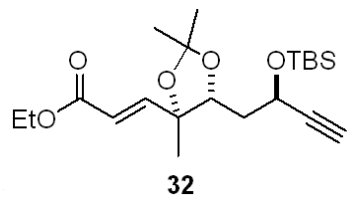
X : parts per Million : <sup>13</sup>C

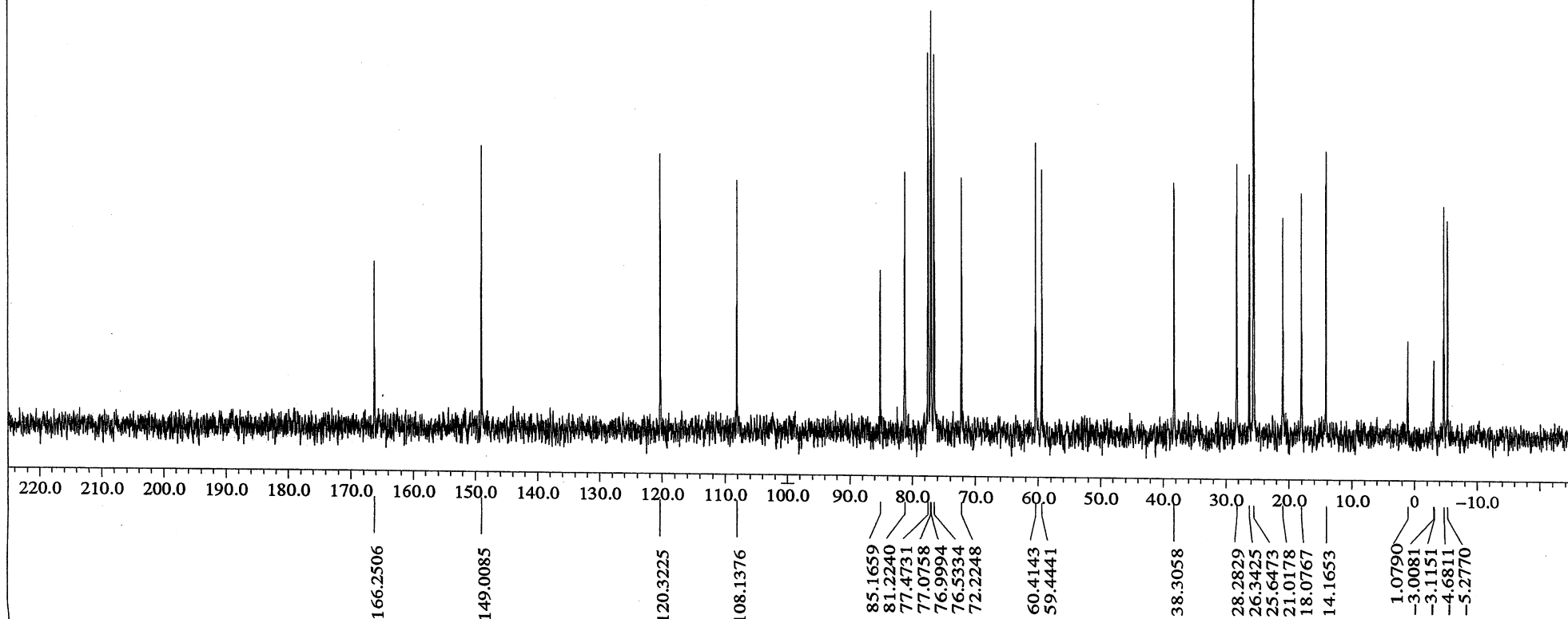
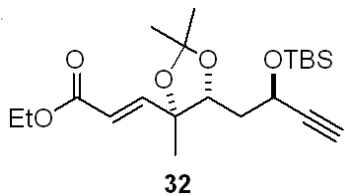
<sup>1</sup>H NMR spectrum of **31** (CDCl<sub>3</sub>, 270 Hz)

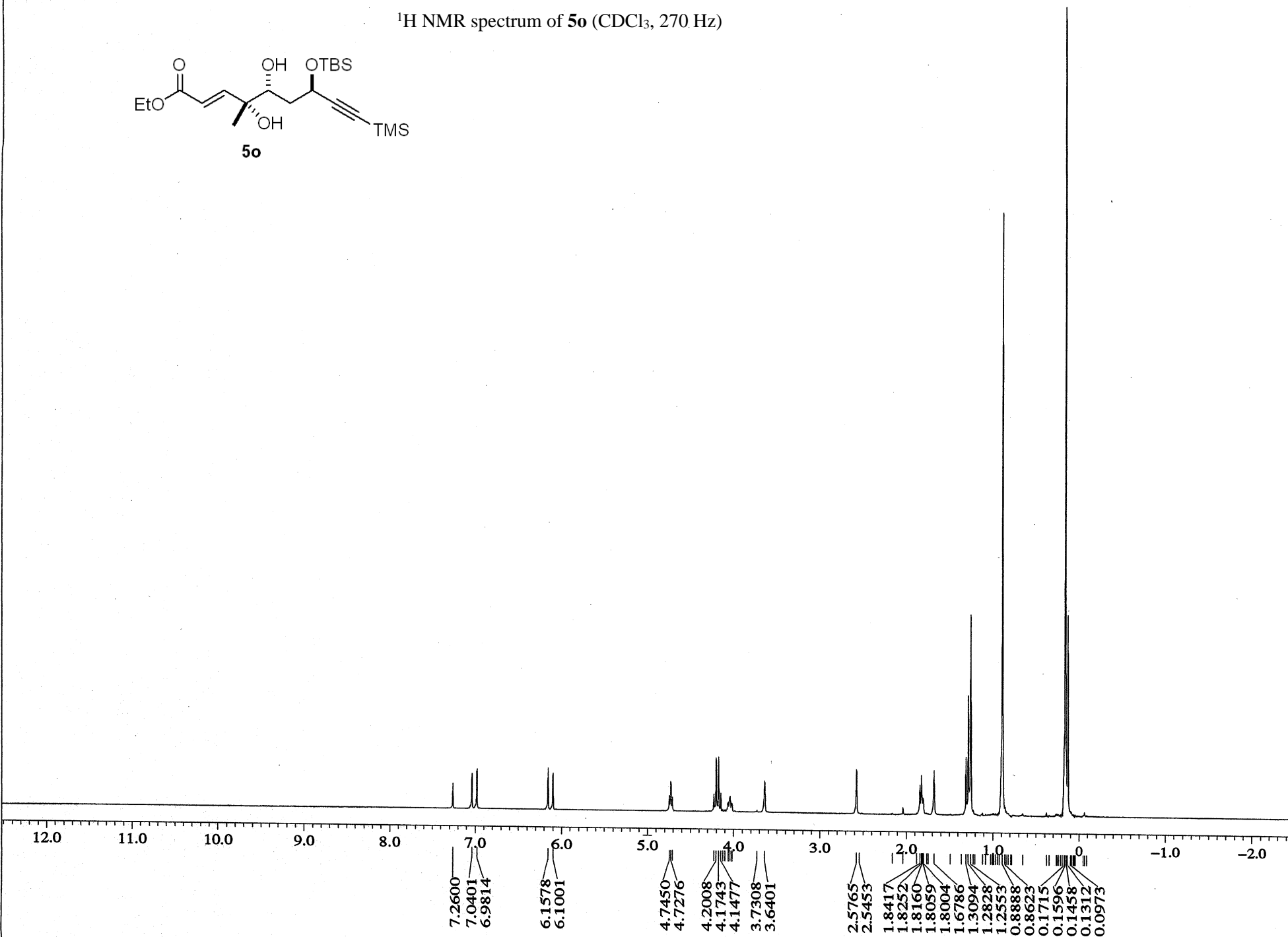
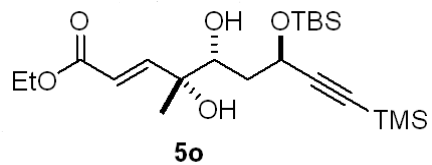


X : parts per Million : 1H

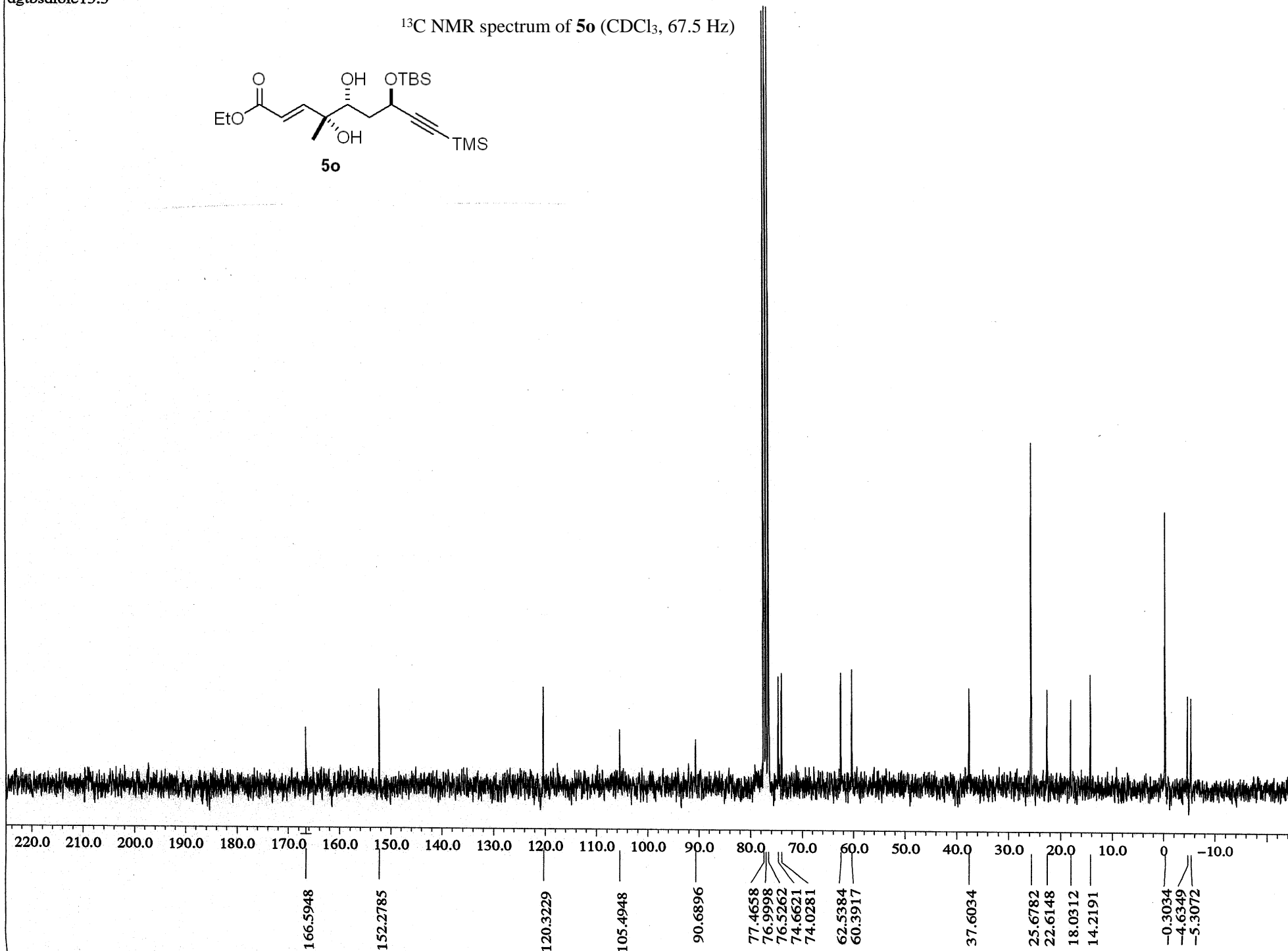
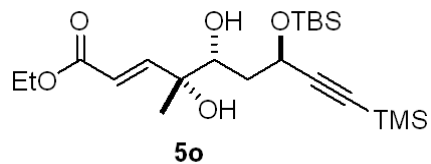
$^{13}\text{C}$  NMR spectrum of **31** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

$^1\text{H}$  NMR spectrum of **32** ( $\text{CDCl}_3$ , 270 Hz)X : parts per Million :  $^1\text{H}$

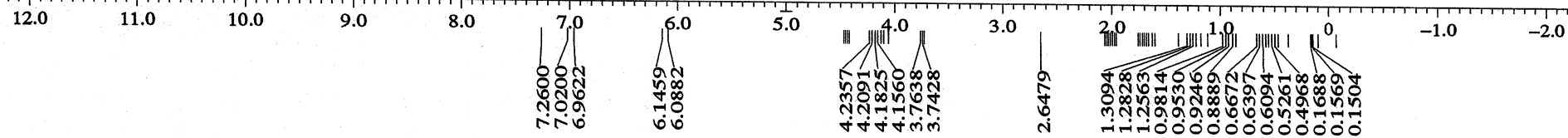
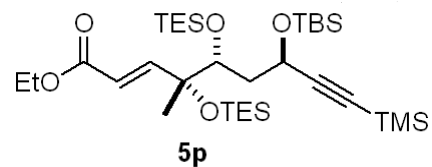
$^{13}\text{C}$  NMR spectrum of **32** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

$^1\text{H}$  NMR spectrum of **5o** ( $\text{CDCl}_3$ , 270 Hz)

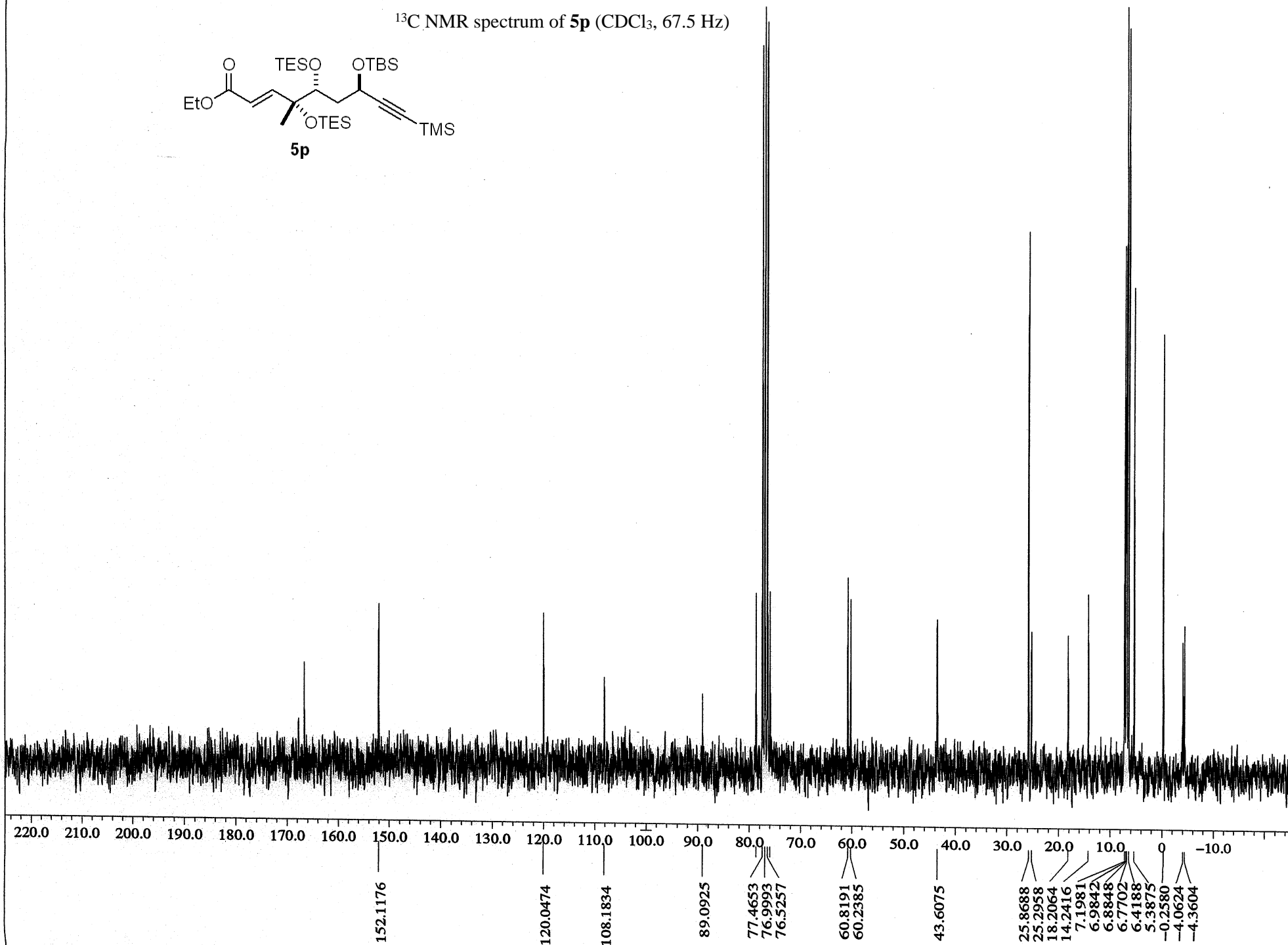
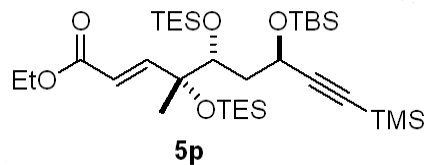
X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **5o** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$



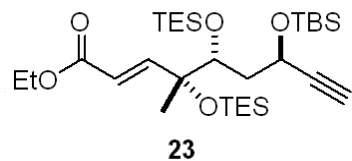
$^1\text{H}$  NMR spectrum of **5p** ( $\text{CDCl}_3$ , 270 Hz)

X : parts per Million : 1H

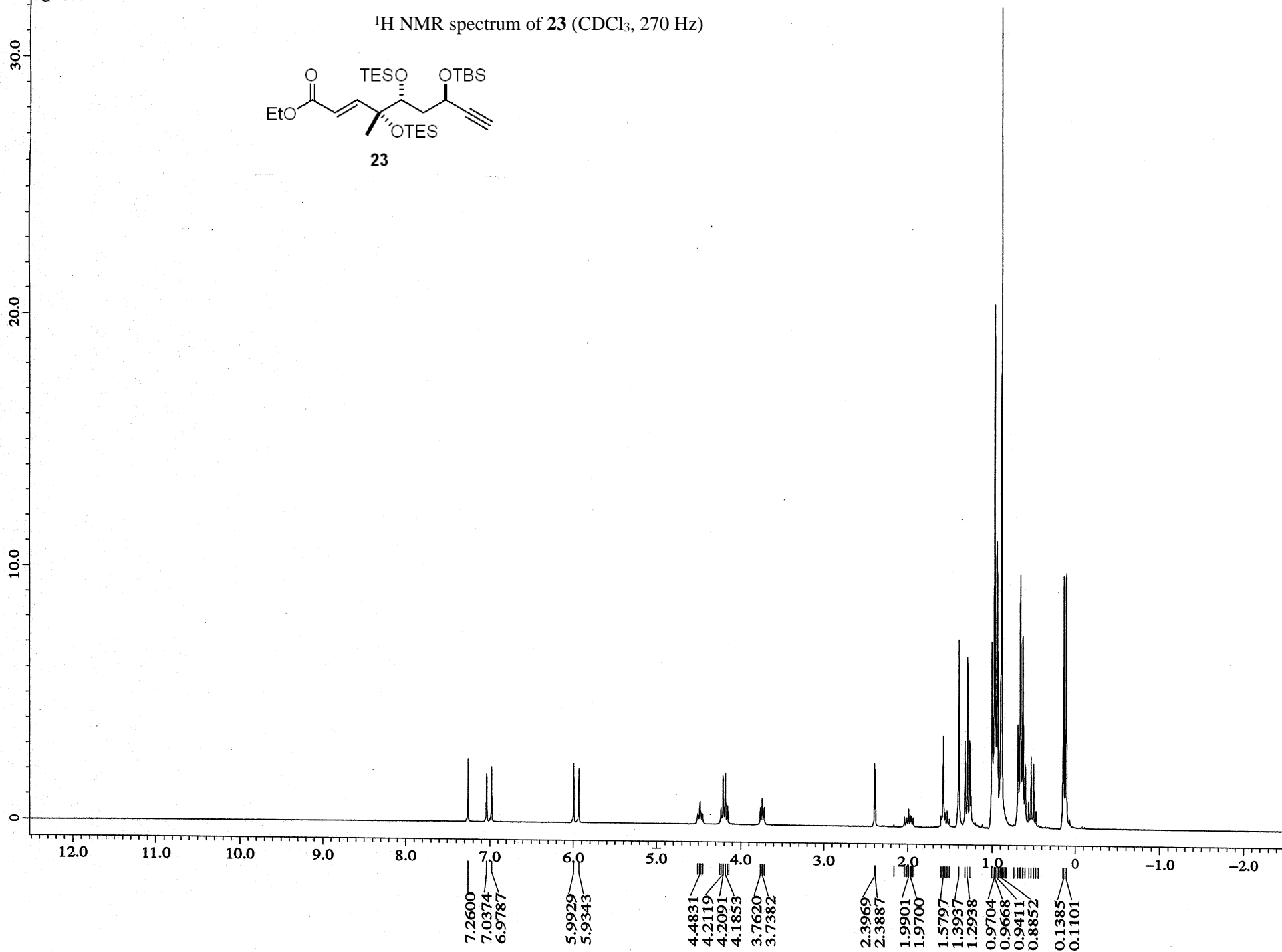
$^{13}\text{C}$  NMR spectrum of **5p** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

dg460.3

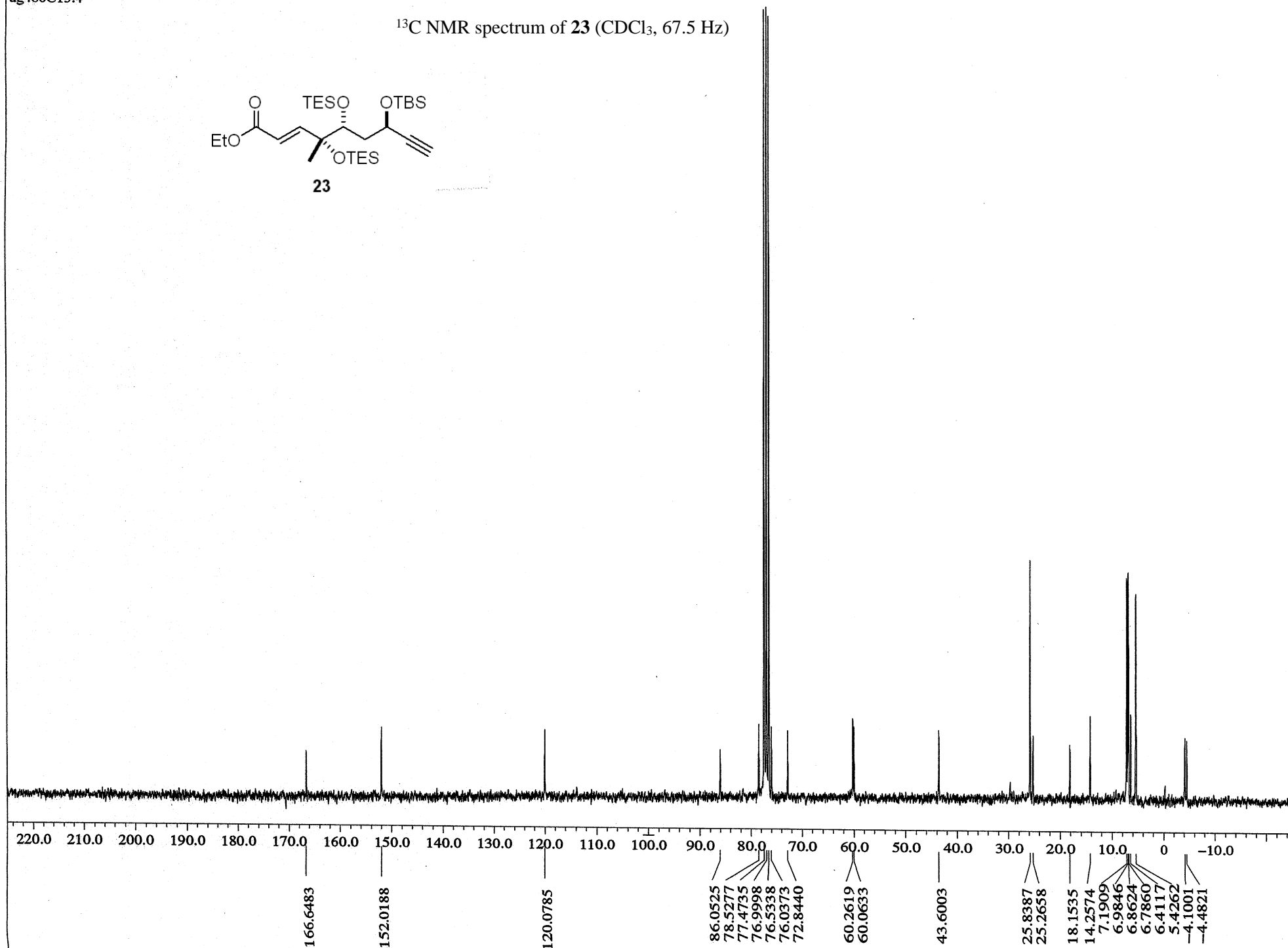
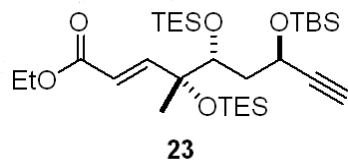
<sup>1</sup>H NMR spectrum of **23** (CDCl<sub>3</sub>, 270 Hz)



(Millions)



X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **23** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

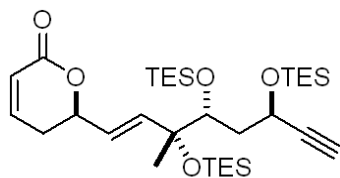
dg376\_21Nov2005

<sup>1</sup>H NMR spectrum of **33** (CDCl<sub>3</sub>, 600 Hz)

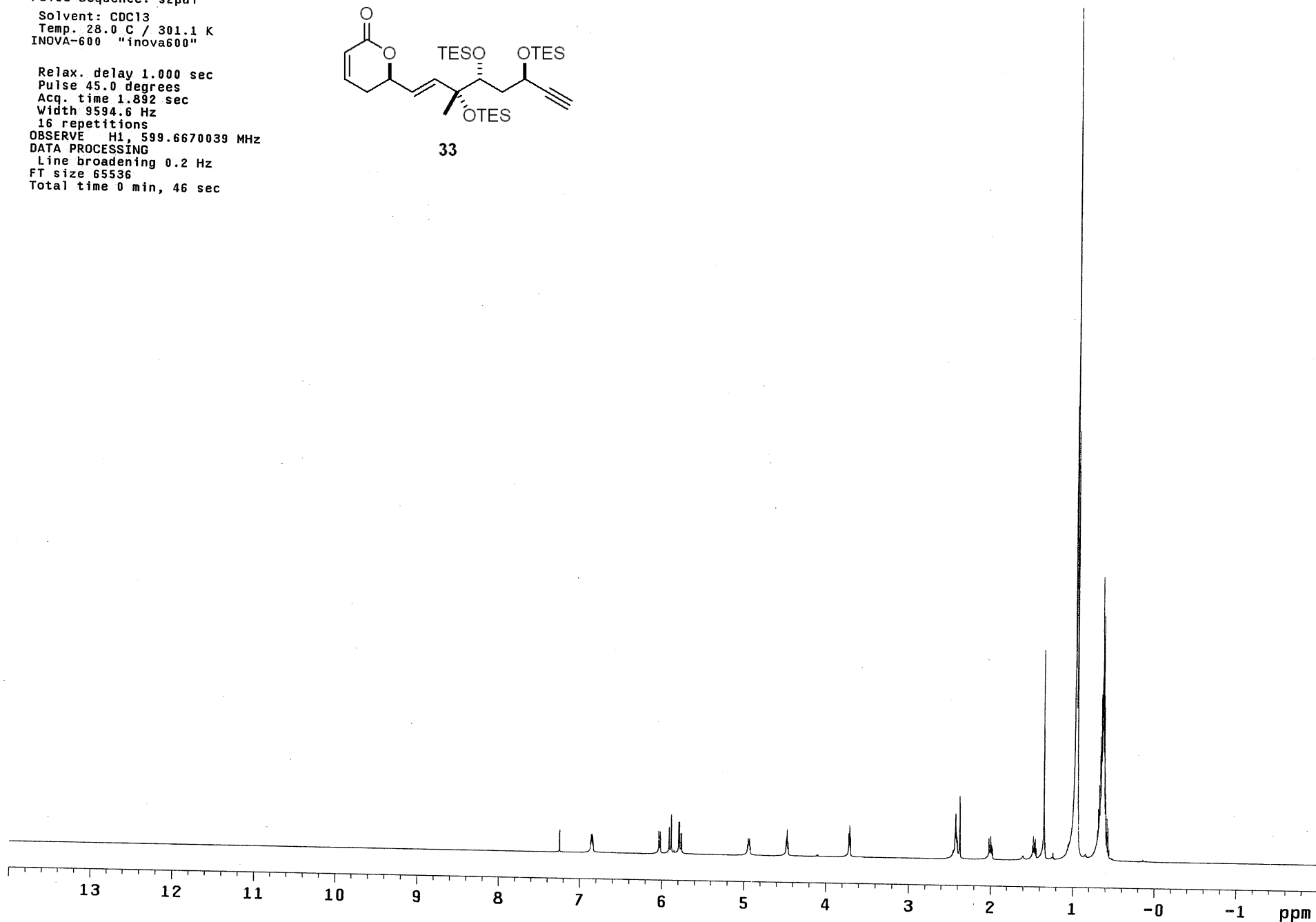
Archive directory: /export/home/odoherty/vnmrsys/data  
Sample directory: dg376\_21Nov2005  
File: PROTON

Pulse Sequence: s2pul  
Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6670039 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 65536  
Total time 0 min, 46 sec



**33**



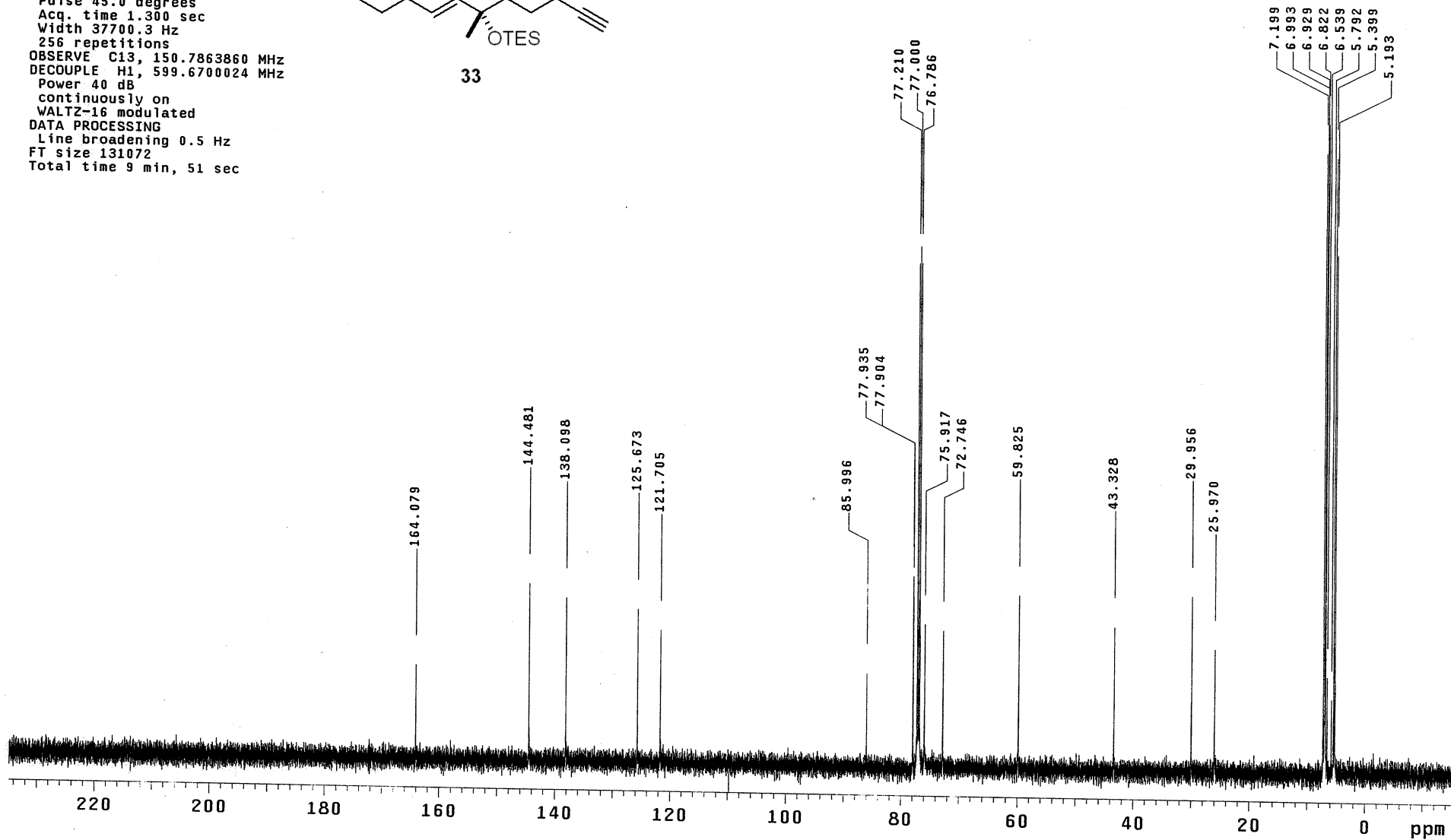
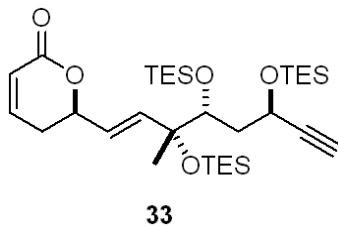
dg376\_21Nov2005

$^{13}\text{C}$  NMR spectrum of **33** ( $\text{CDCl}_3$ , 150 Hz)

Archive directory: /export/home/odoherty/vnmrsys/data,  
Sample directory: dg376\_21Nov2005

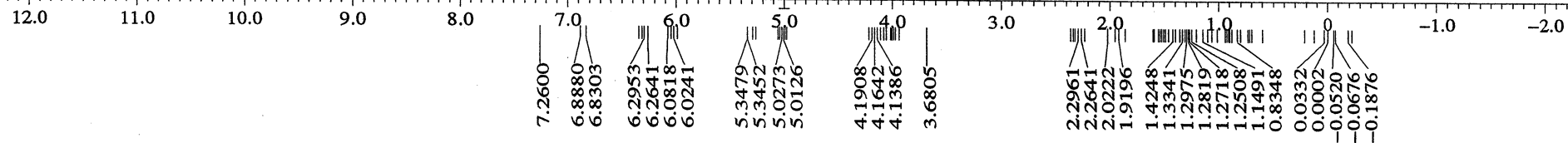
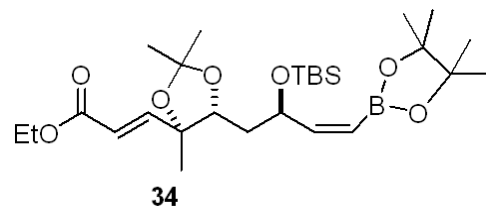
Pulse Sequence: s2pul  
Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
File: CARBON  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.300 sec  
Width 37700.3 Hz  
256 repetitions  
OBSERVE  $\text{C}13$ , 150.7863860 MHz  
DECOUPLE  $\text{H}1$ , 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 131072  
Total time 9 min, 51 sec

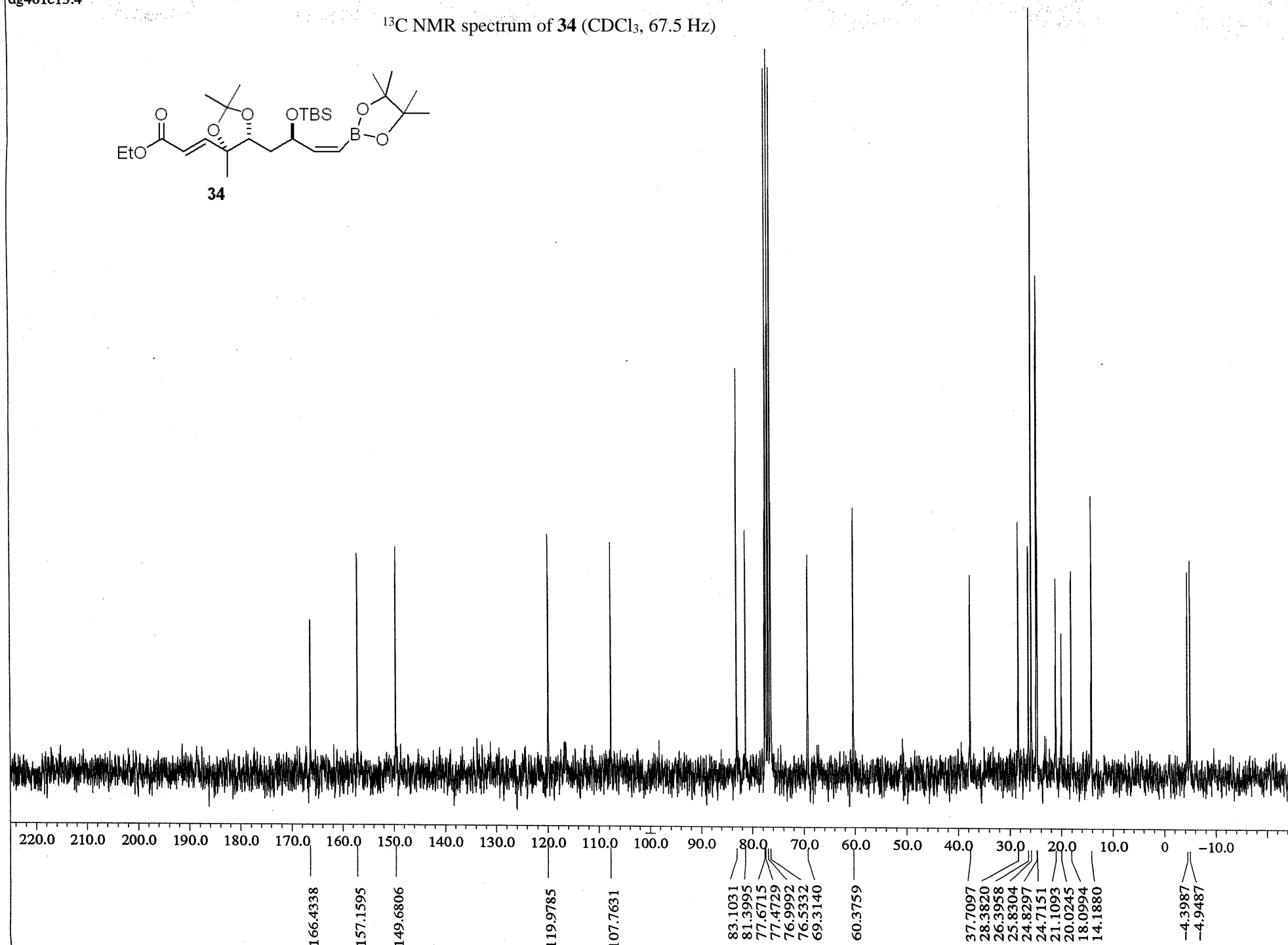
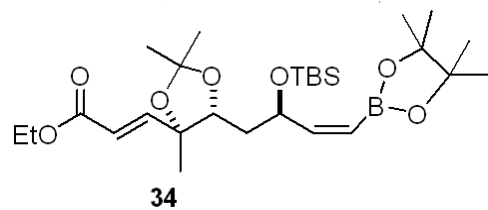


dg401.5

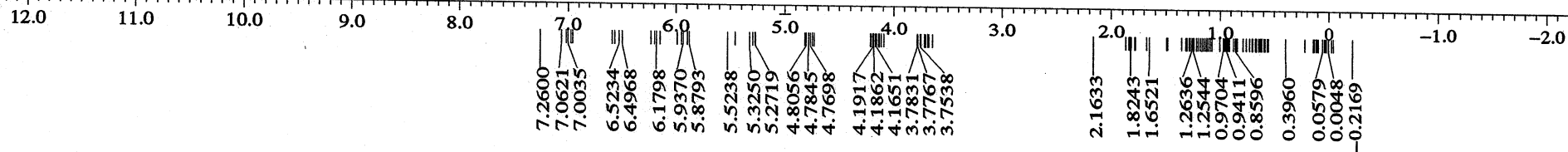
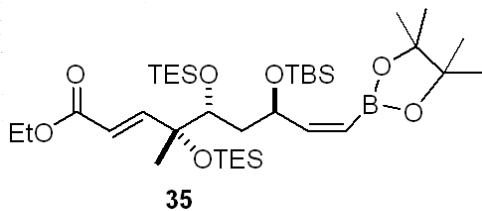
<sup>1</sup>H NMR spectrum of **34** (CDCl<sub>3</sub>, 270 Hz)



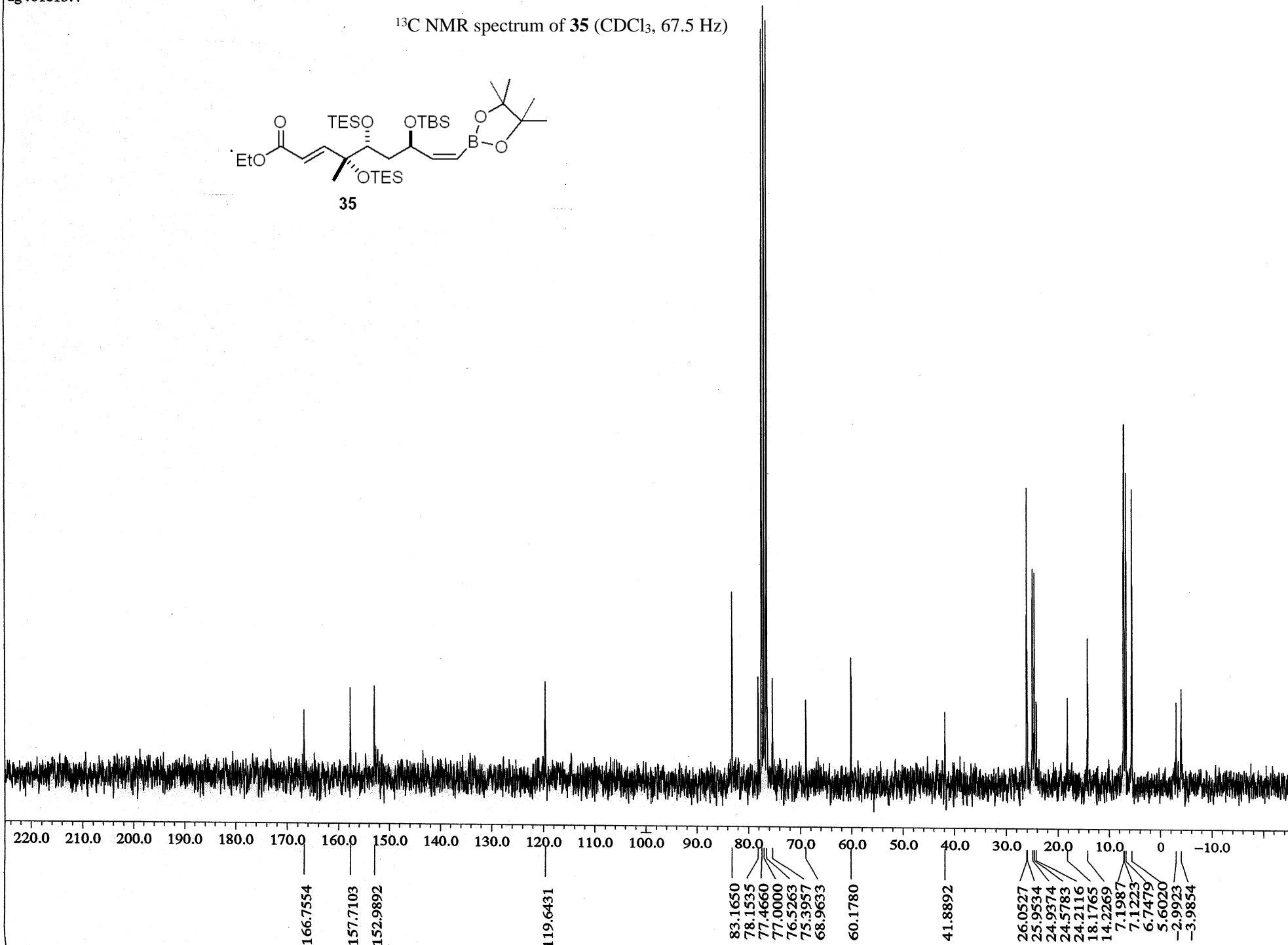
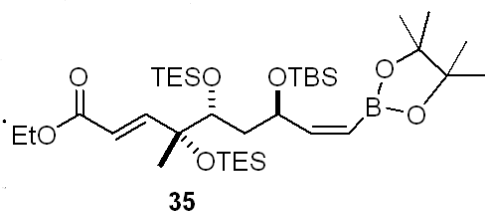
X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **34** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

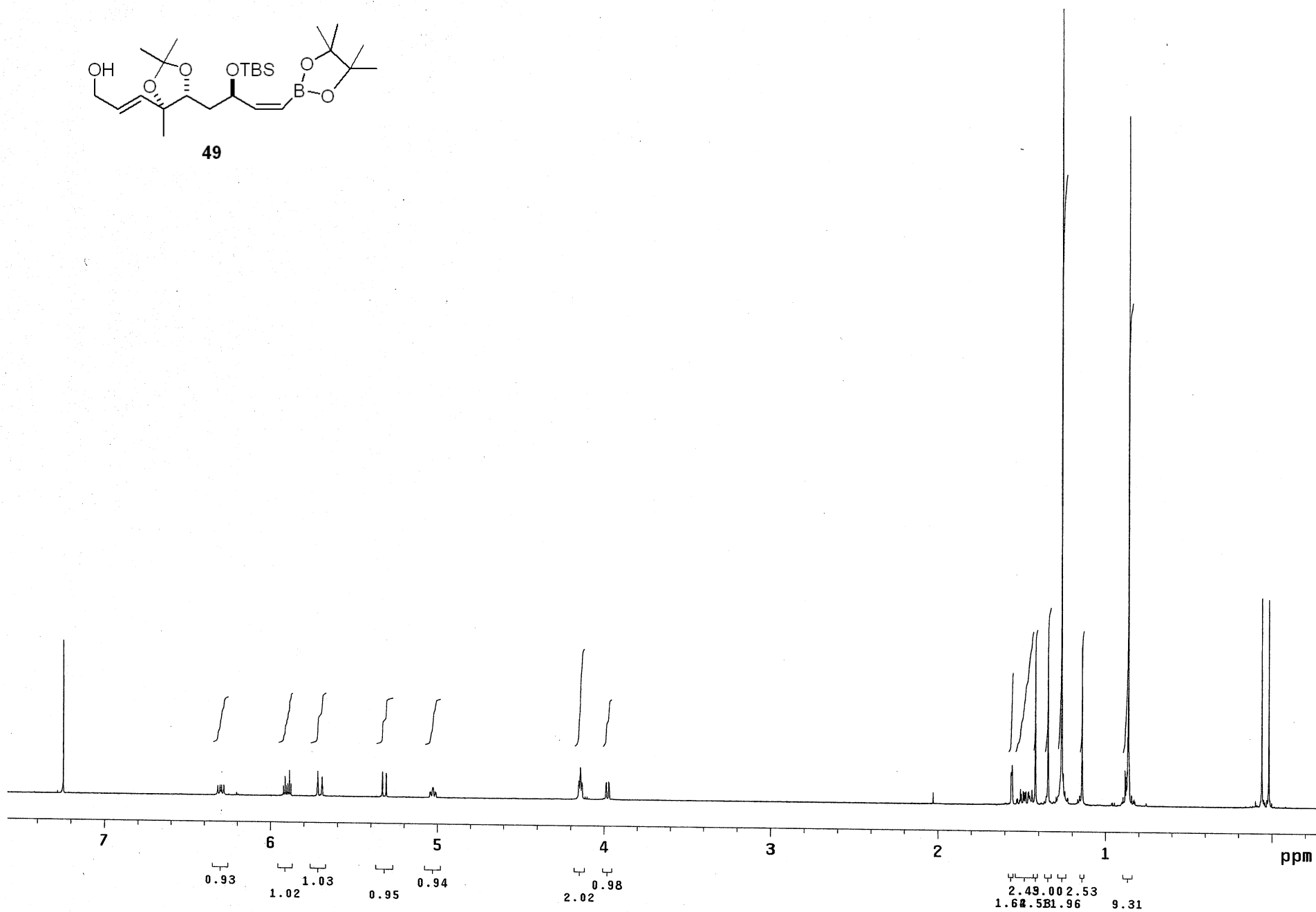
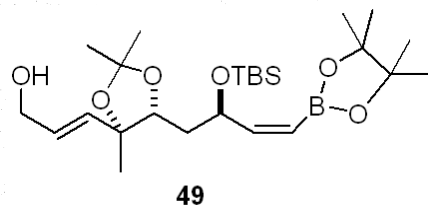


$^1\text{H}$  NMR spectrum of **35** ( $\text{CDCl}_3$ , 270 Hz)

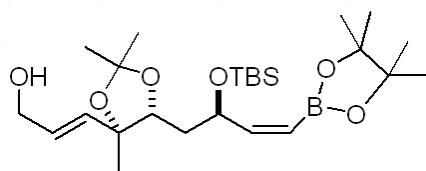
X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **35** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

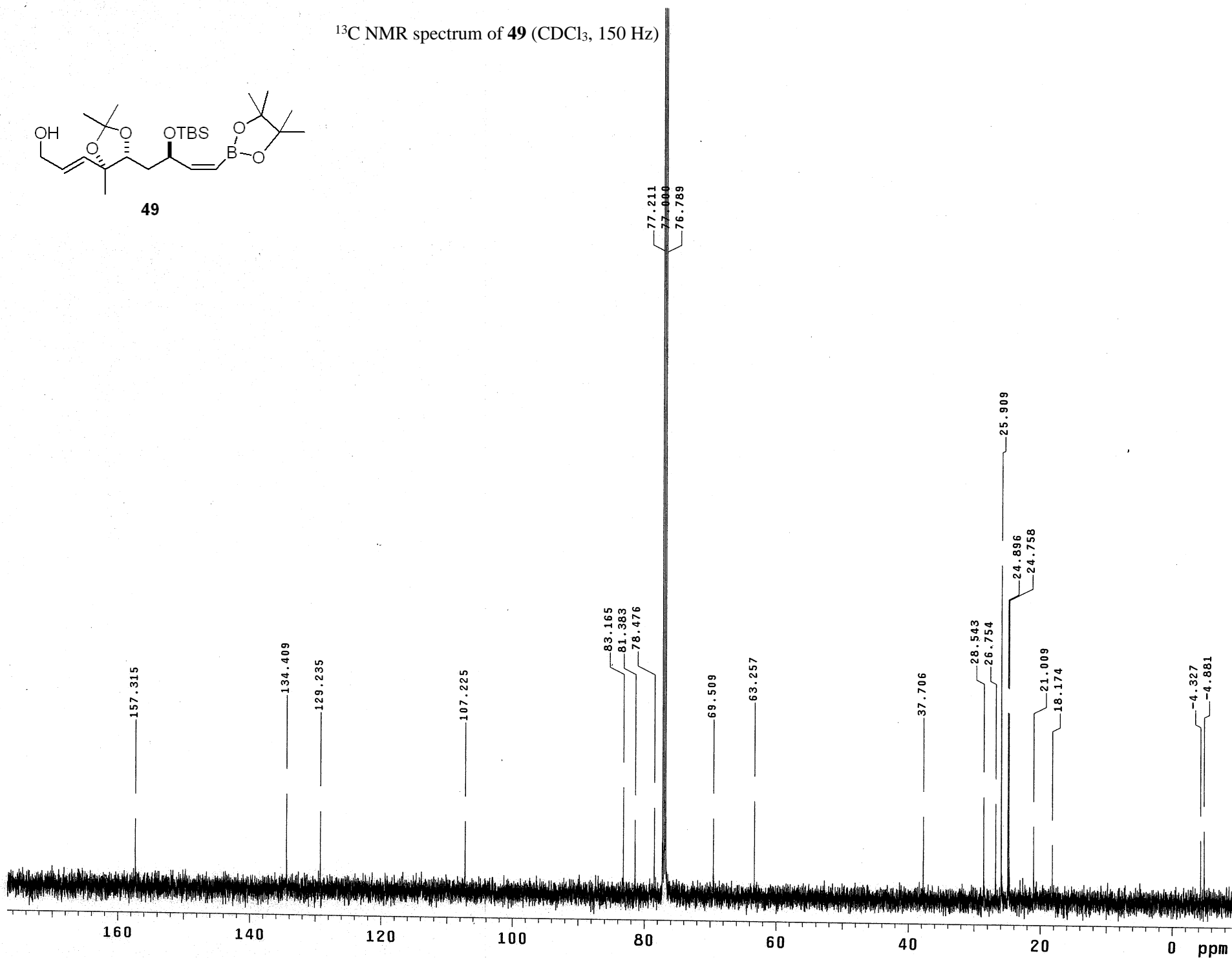
$^1\text{H}$  NMR spectrum of **49** ( $\text{CDCl}_3$ , 600 Hz)

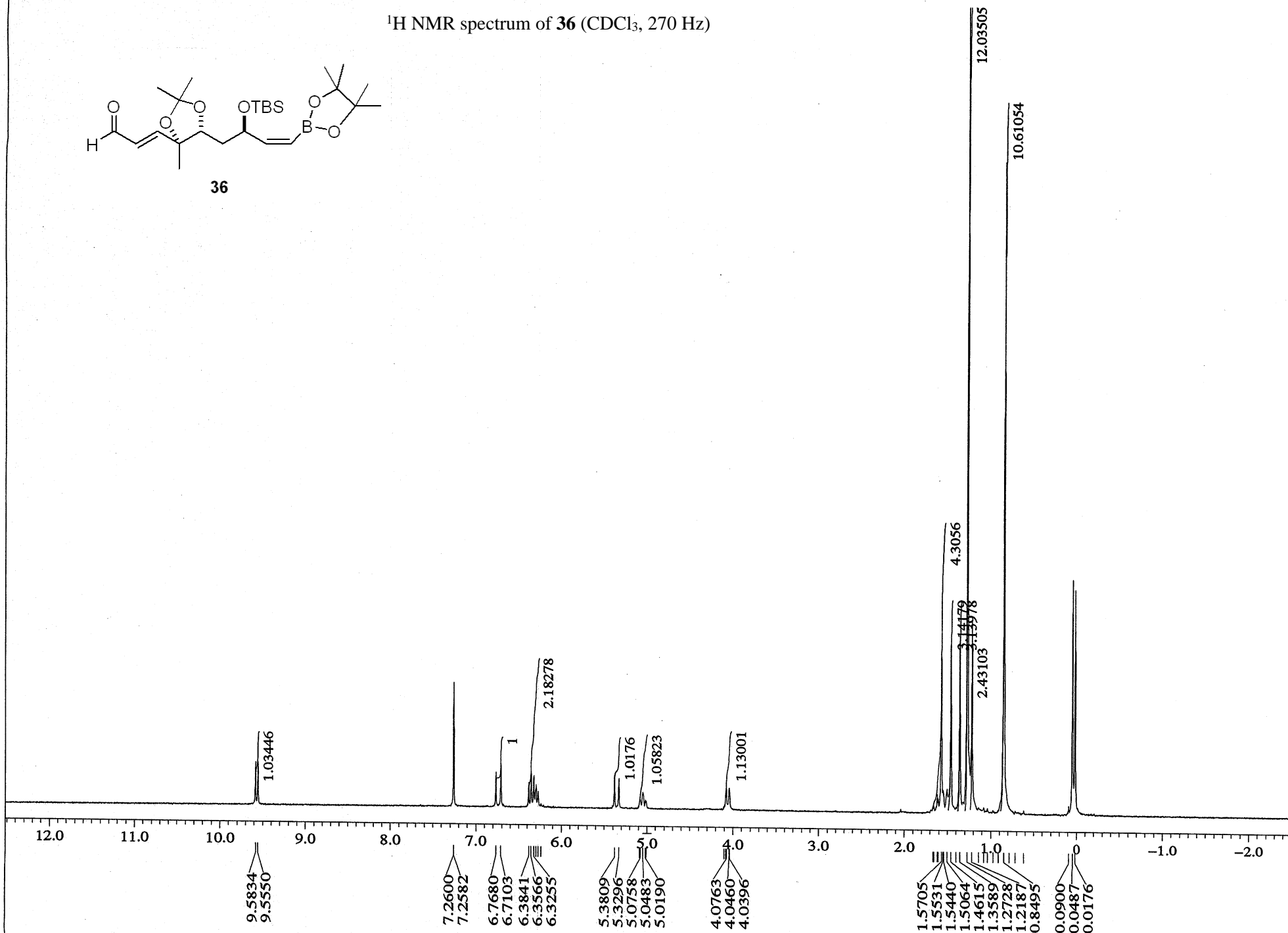
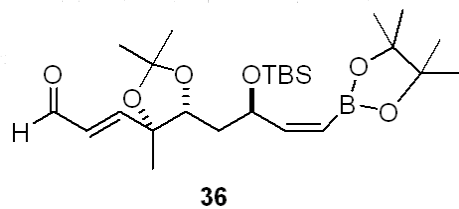


$^{13}\text{C}$  NMR spectrum of **49** ( $\text{CDCl}_3$ , 150 Hz)

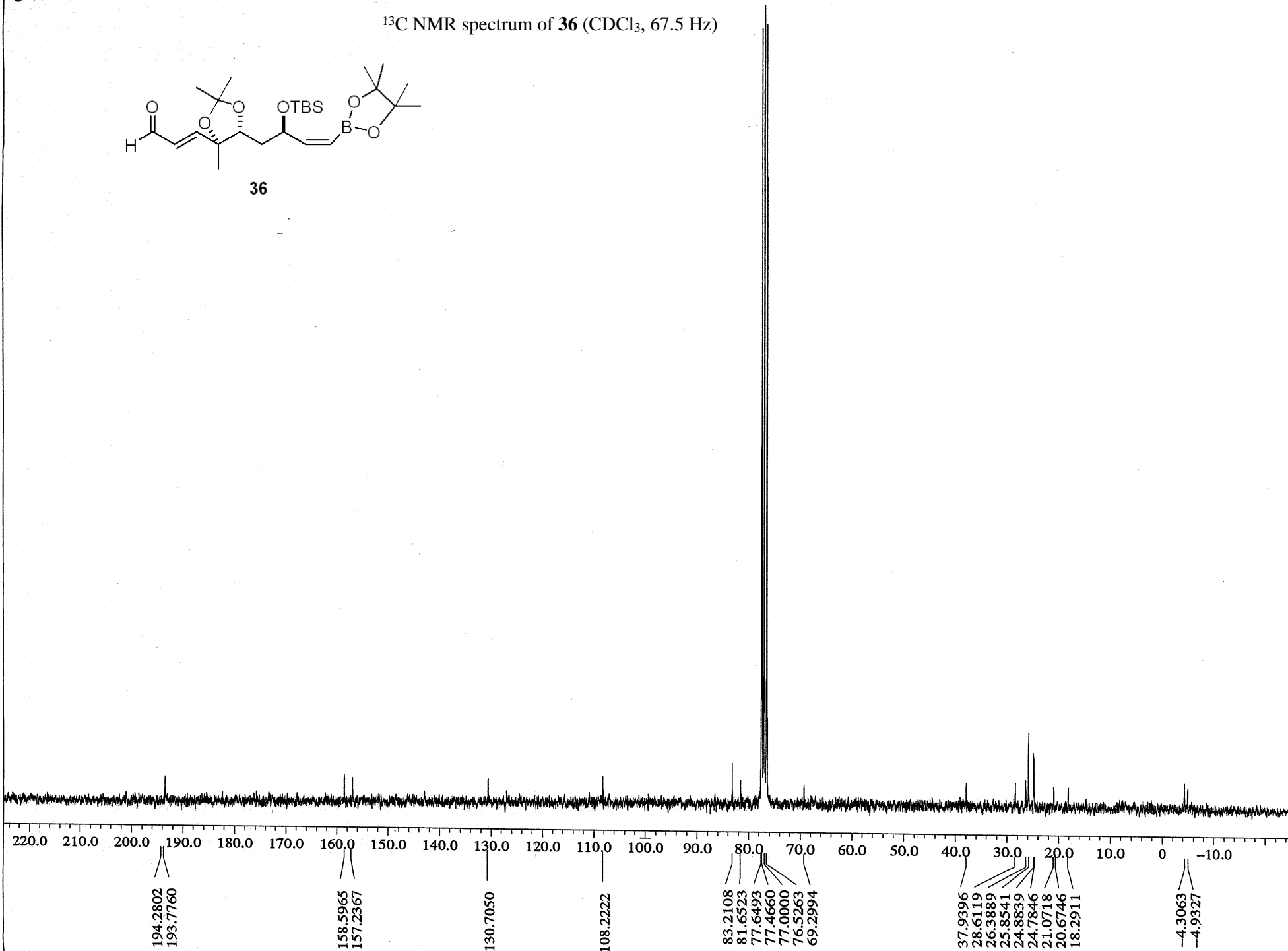
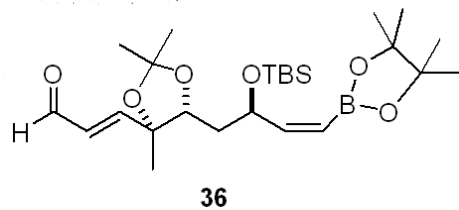


**49**



$^1\text{H}$  NMR spectrum of **36** ( $\text{CDCl}_3$ , 270 Hz)

X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **36** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

## STANDARD PROTON PARAMETERS

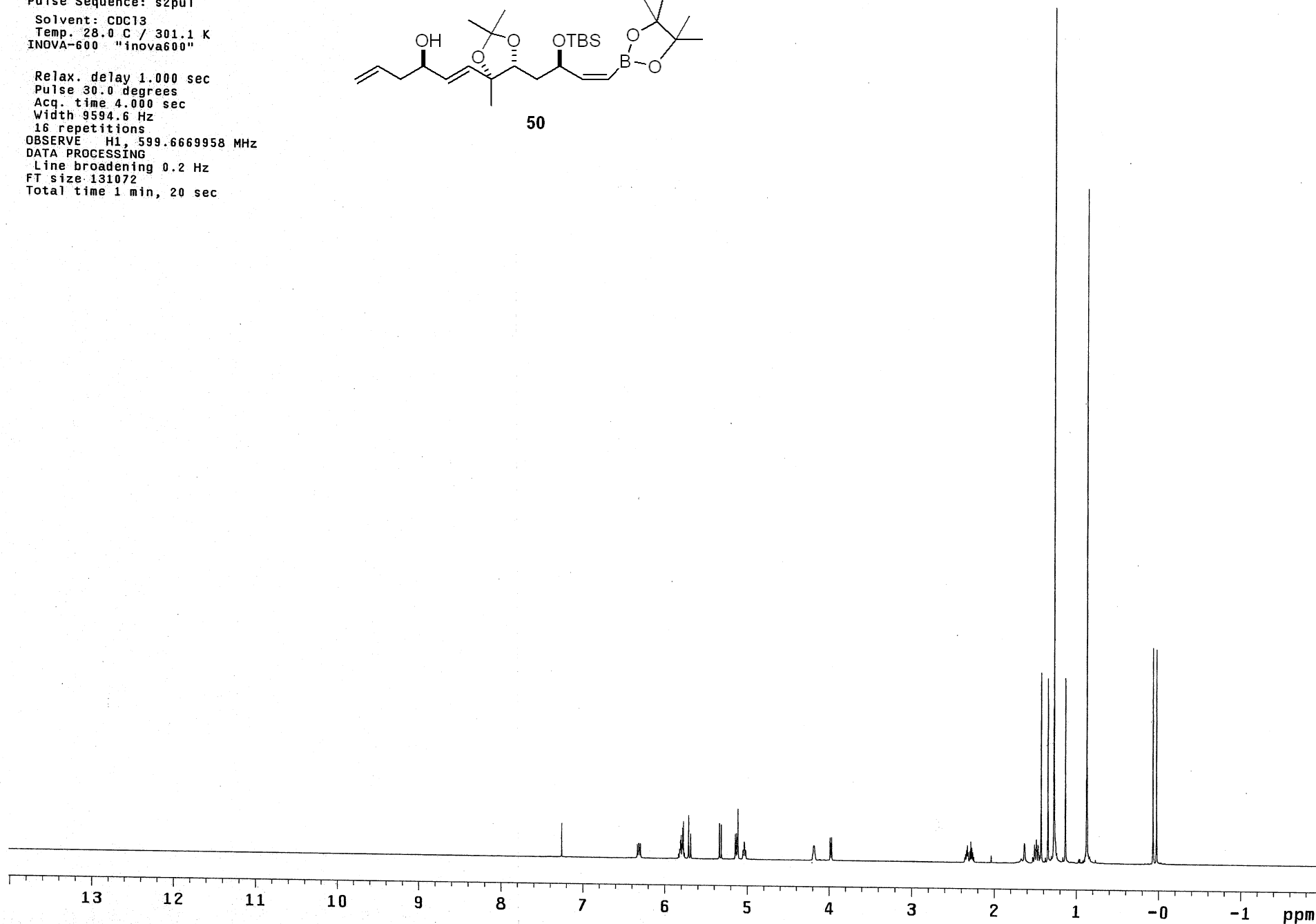
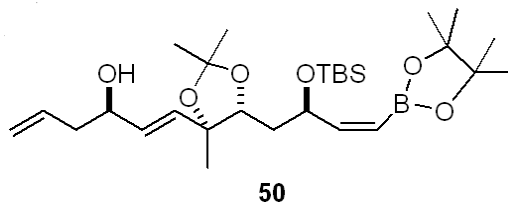
<sup>1</sup>H NMR spectrum of **50** (CDCl<sub>3</sub>, 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6669958 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 131072  
Total time 1 min, 20 sec

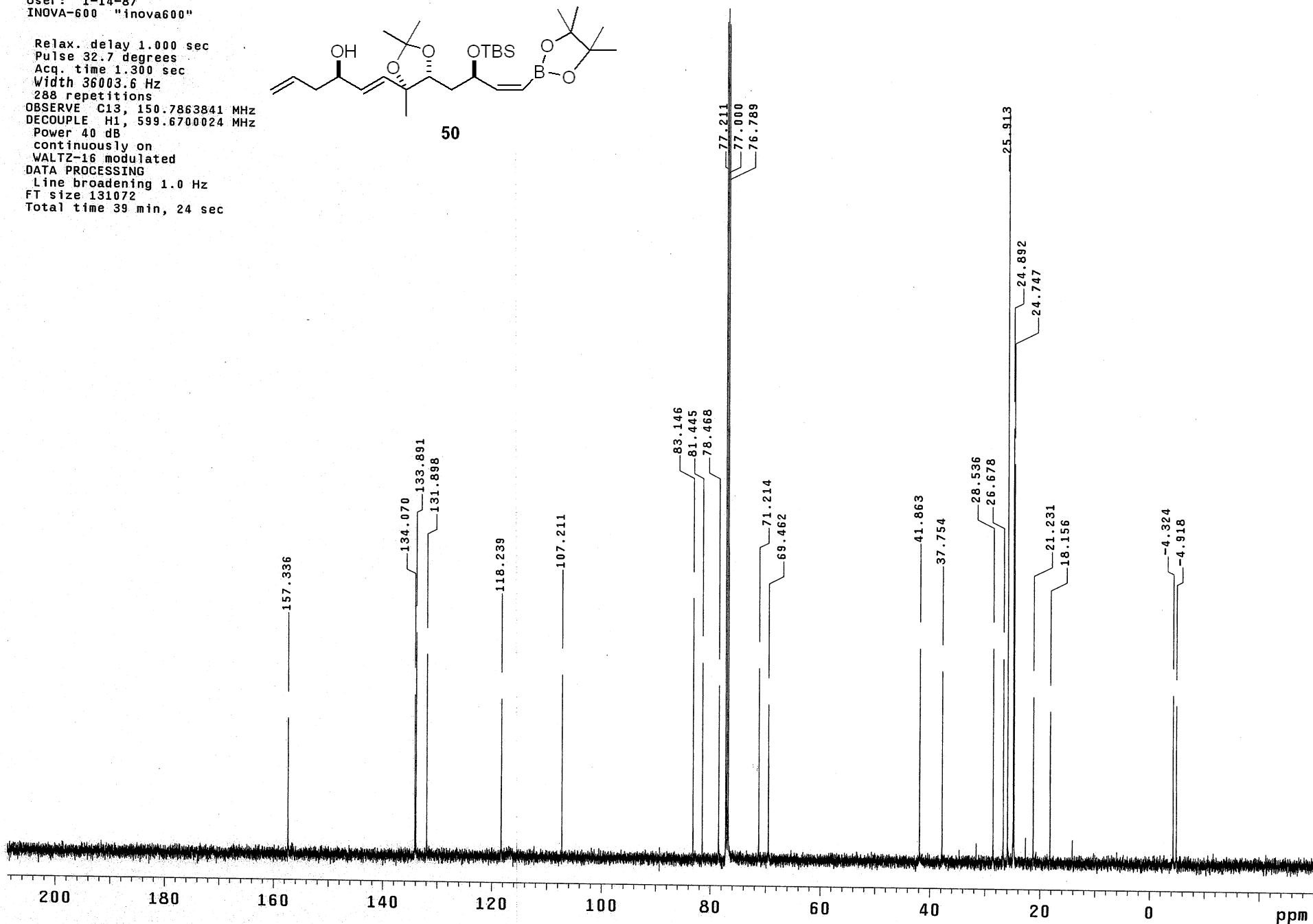
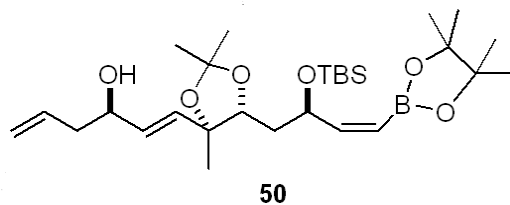


S183

## STANDARD CARBON PARAMETERS

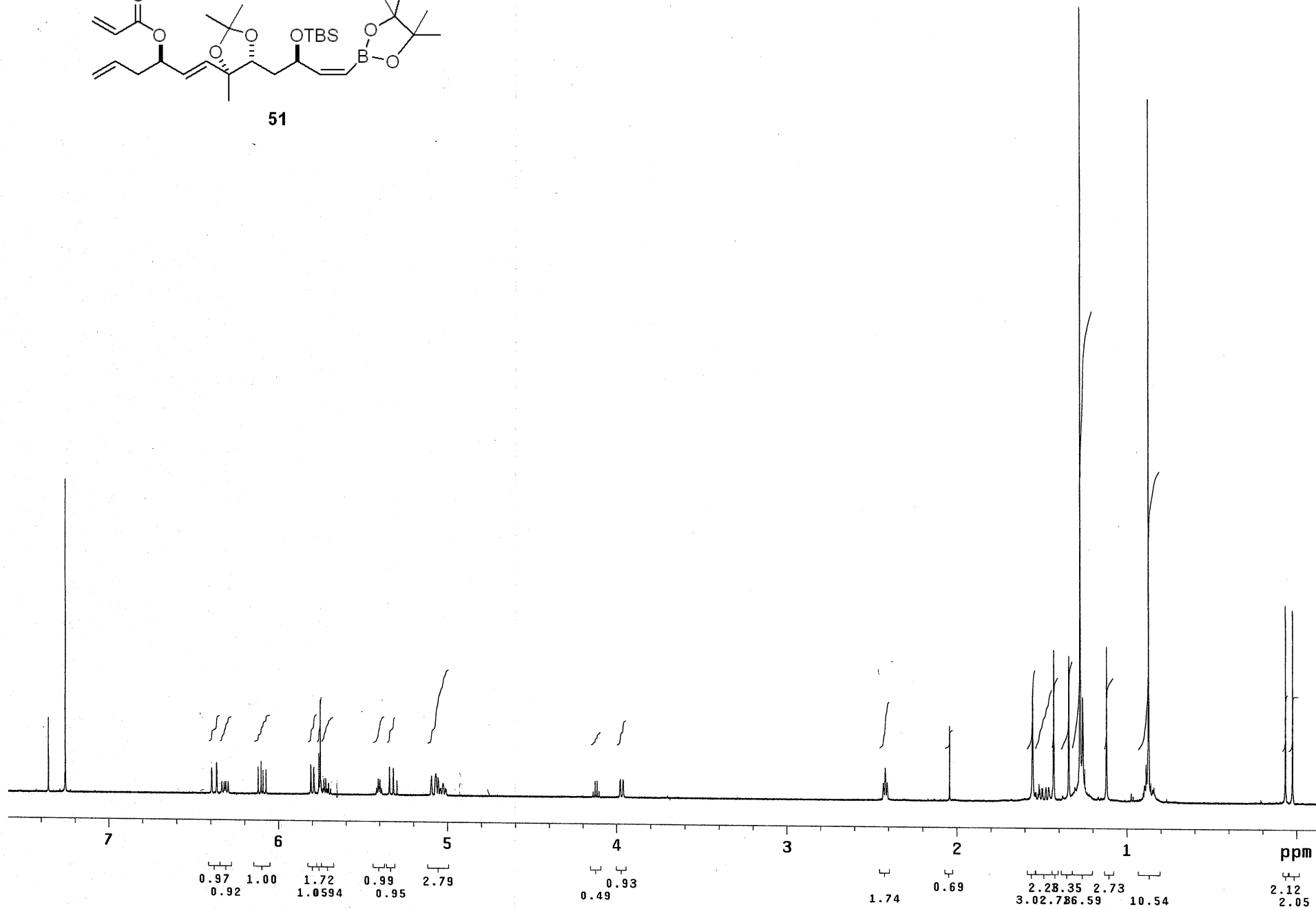
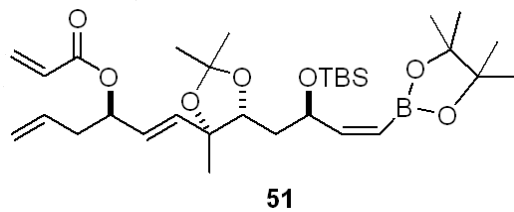
 $^{13}\text{C}$  NMR spectrum of **50** ( $\text{CDCl}_3$ , 150 Hz)

Pulse Sequence: s2pu1

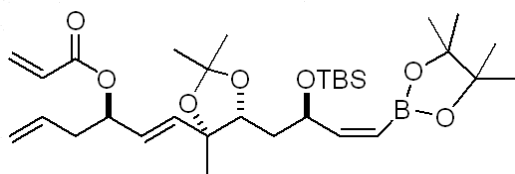
Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"Relax. delay 1.000 sec  
Pulse 32.7 degrees  
Acq. time 1.300 sec  
Width 36003.6 Hz  
288 repetitions  
OBSERVE C13, 150.7863841 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 39 min, 24 sec



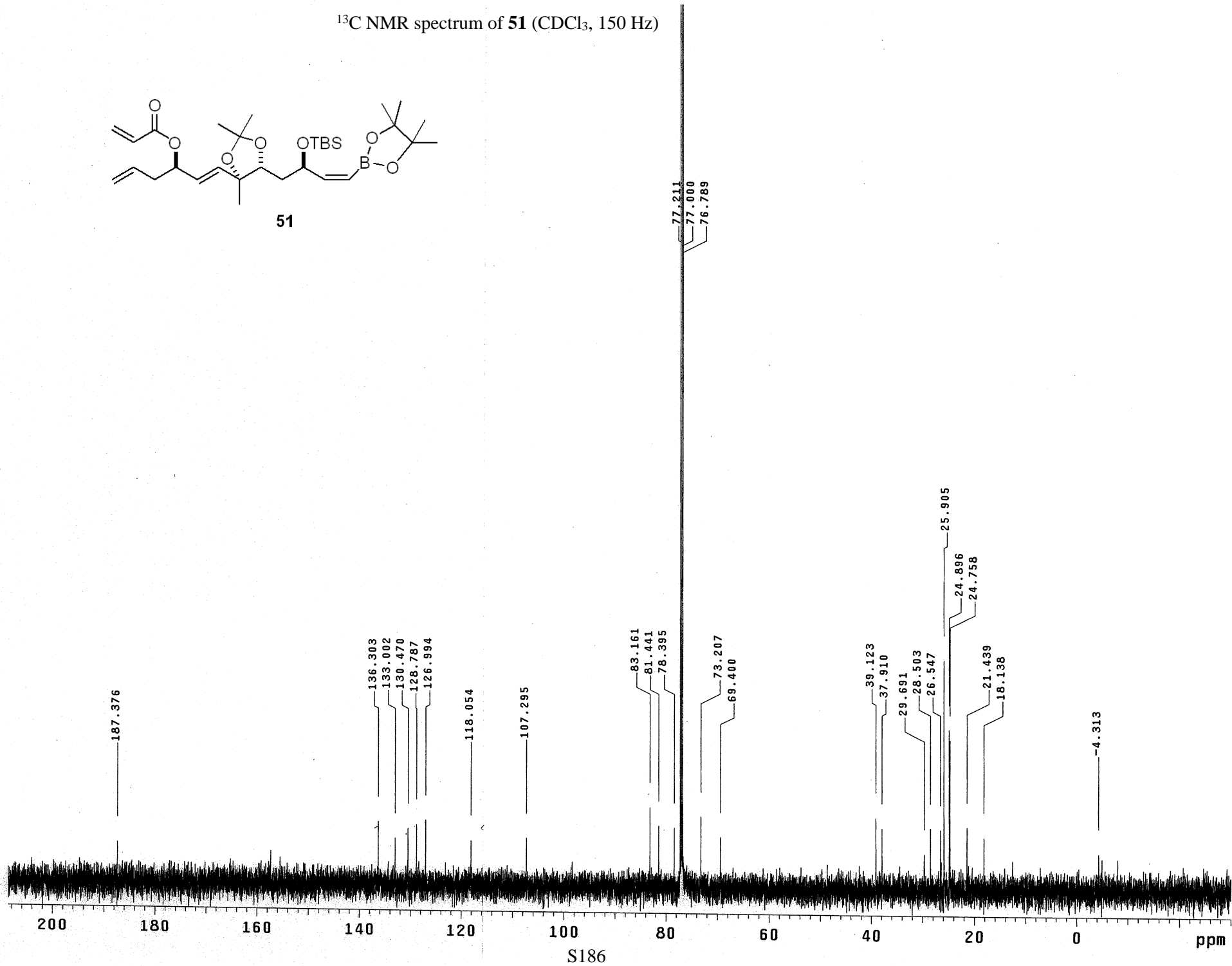
$^1\text{H}$  NMR spectrum of **51** ( $\text{CDCl}_3$ , 600 Hz)



<sup>13</sup>C NMR spectrum of **51** (CDCl<sub>3</sub>, 150 Hz)



**51**



## STANDARD PROTON PARAMETERS

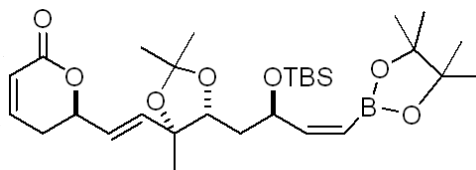
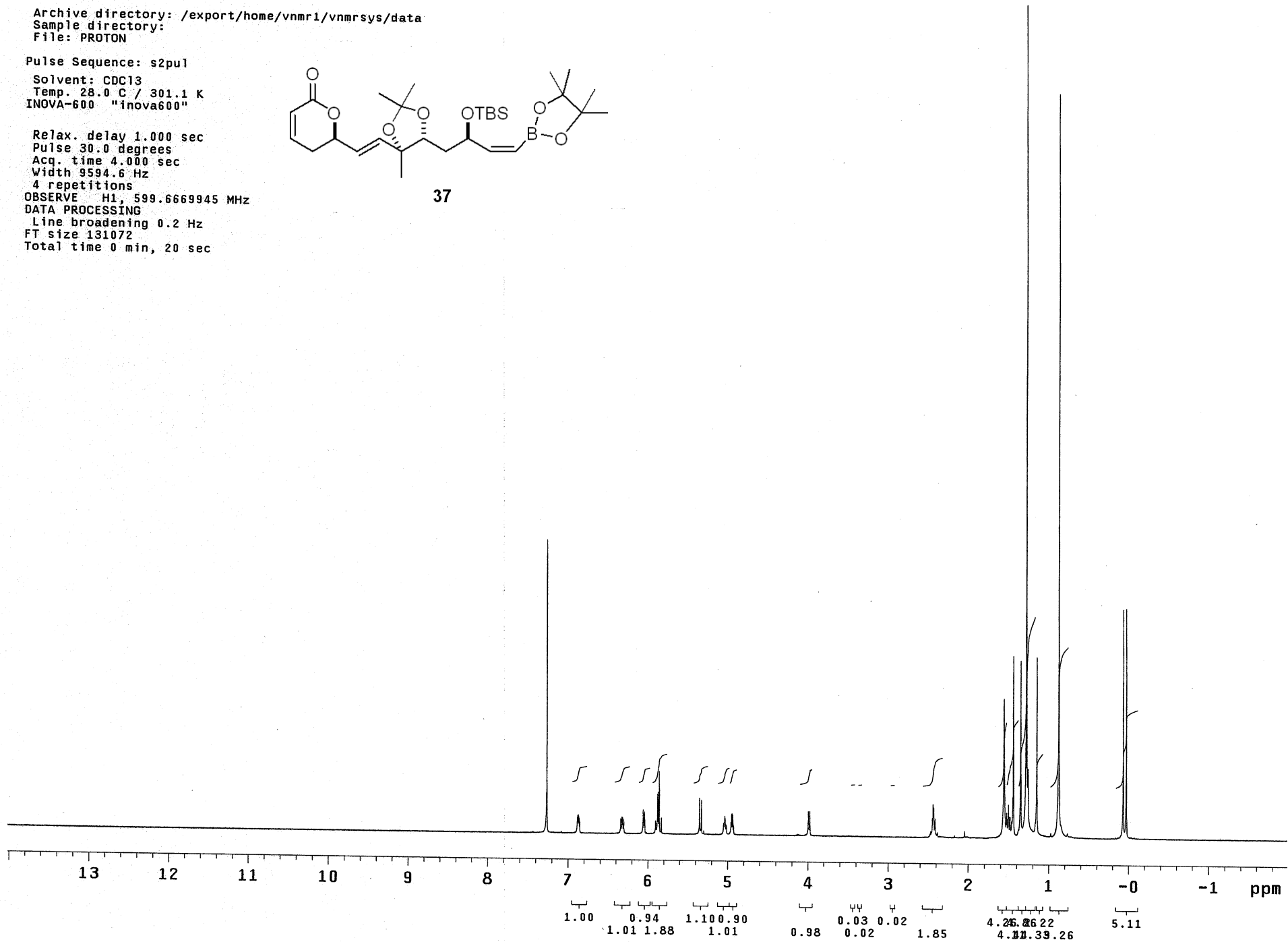
<sup>1</sup>H NMR spectrum of **36** (CDCl<sub>3</sub>, 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
4 repetitions  
OBSERVE H1, 599.6669945 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 131072  
Total time 0 min, 20 sec

**37**

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>

Temp. 28.0 C / 301.1 K

User: 1-14-87

INOVA-600 "inova600"

Relax. delay 1.000 sec

Pulse 29.9 degrees

Acq. time 1.300 sec

Width 36003.6 Hz

1688 repetitions

OBSERVE C13, 150.7863835 MHz

DECOUPLE H1, 599.6700024 MHz

Power 40 dB

continuously on

WALTZ-16 modulated

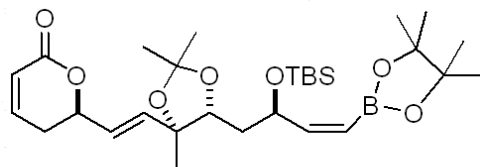
DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

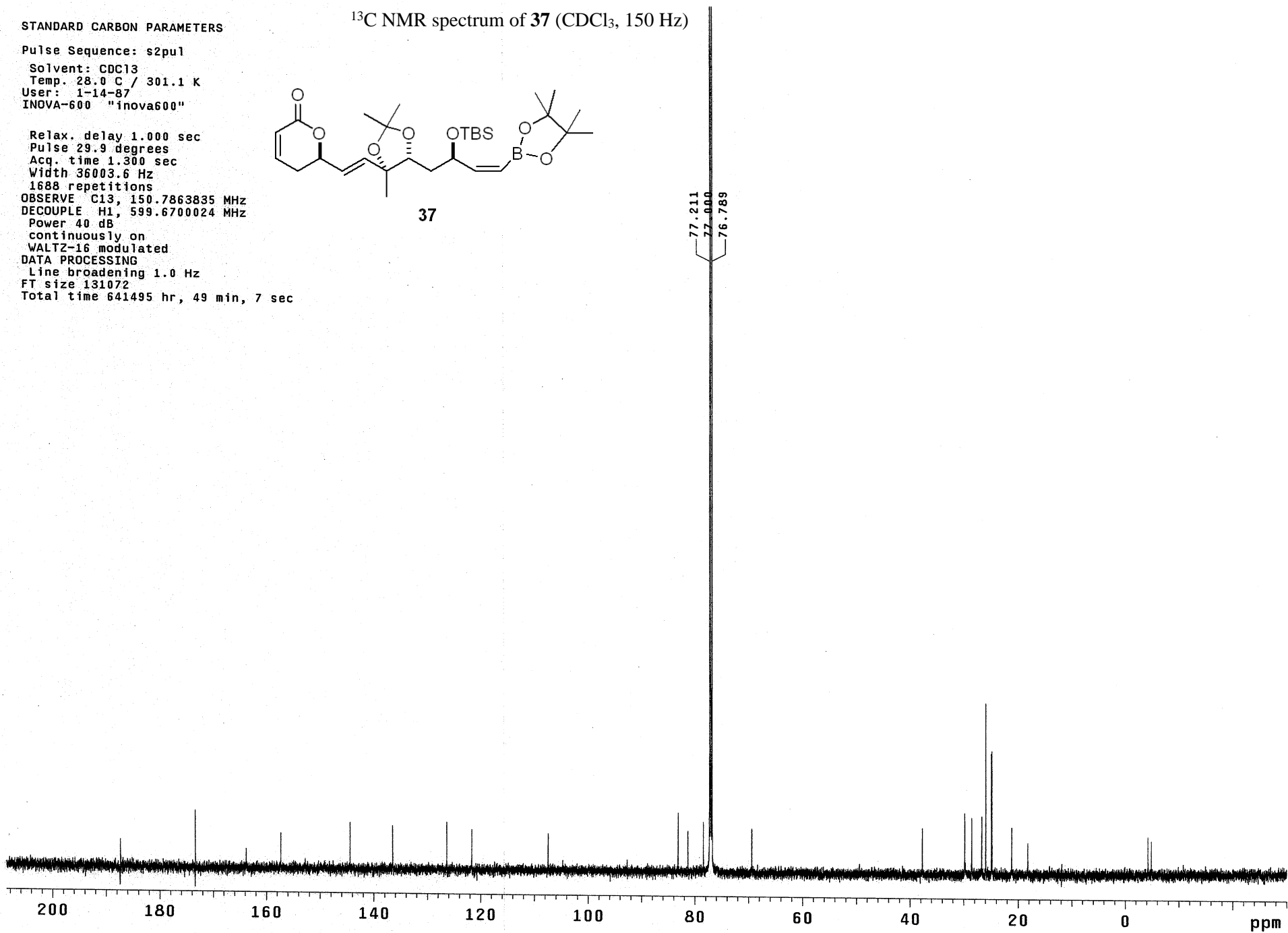
Total time 641495 hr, 49 min, 7 sec

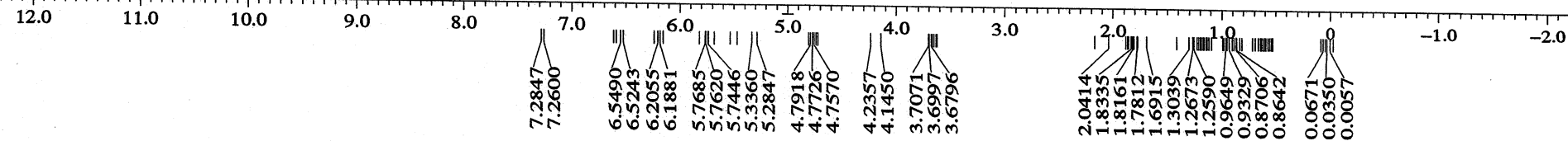
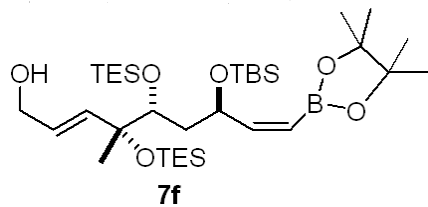
<sup>13</sup>C NMR spectrum of **37** (CDCl<sub>3</sub>, 150 Hz)



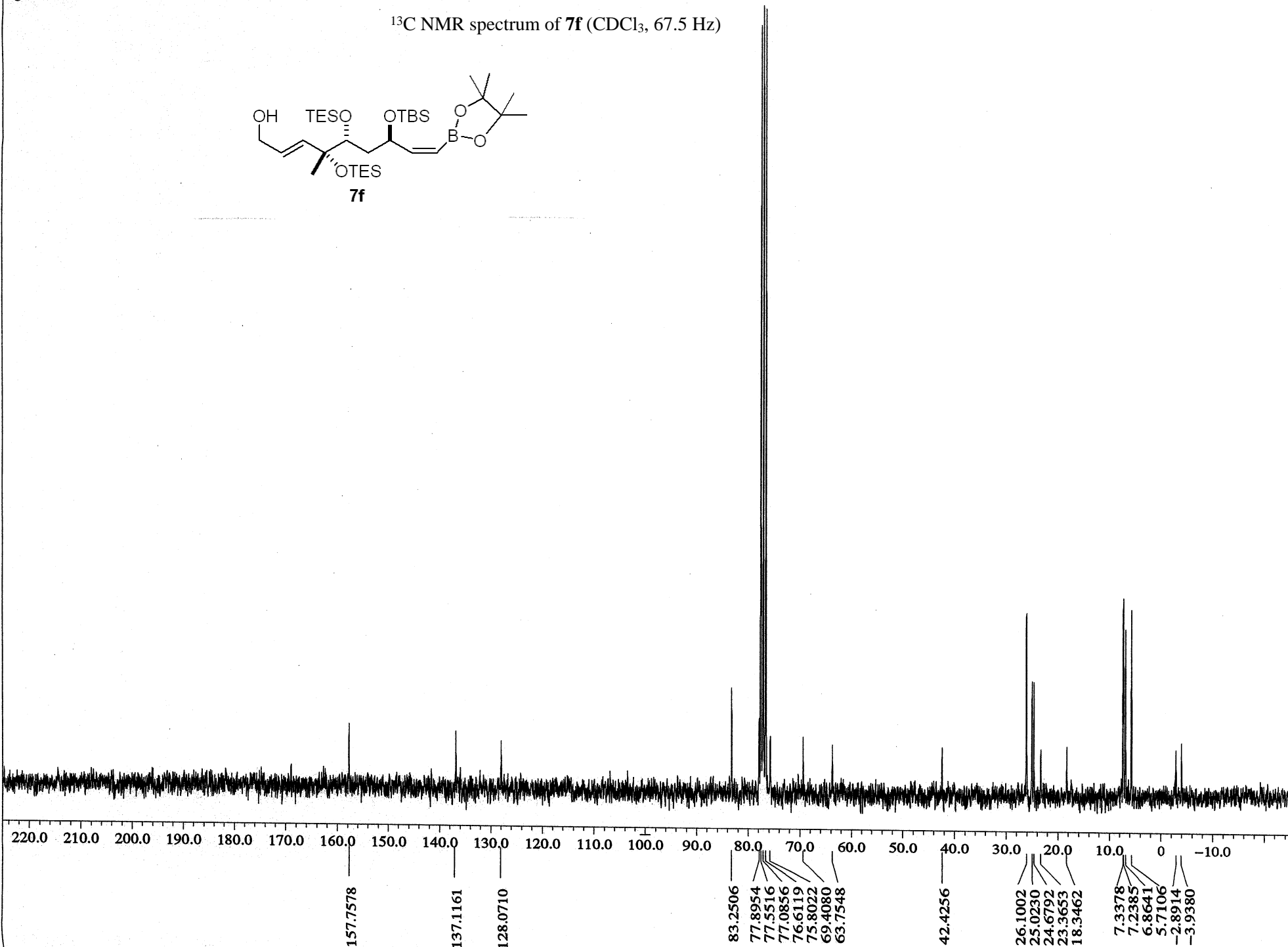
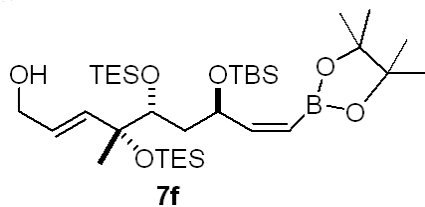
**37**

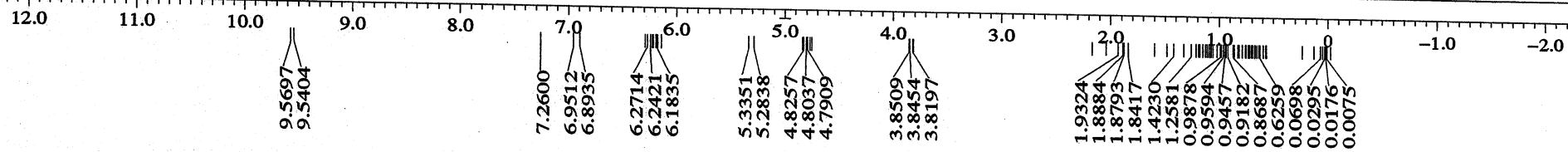
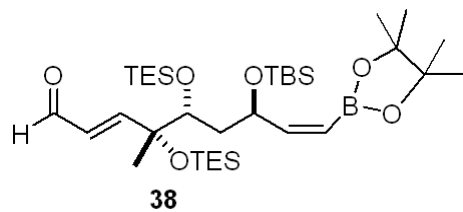
77.211  
77.000  
76.789

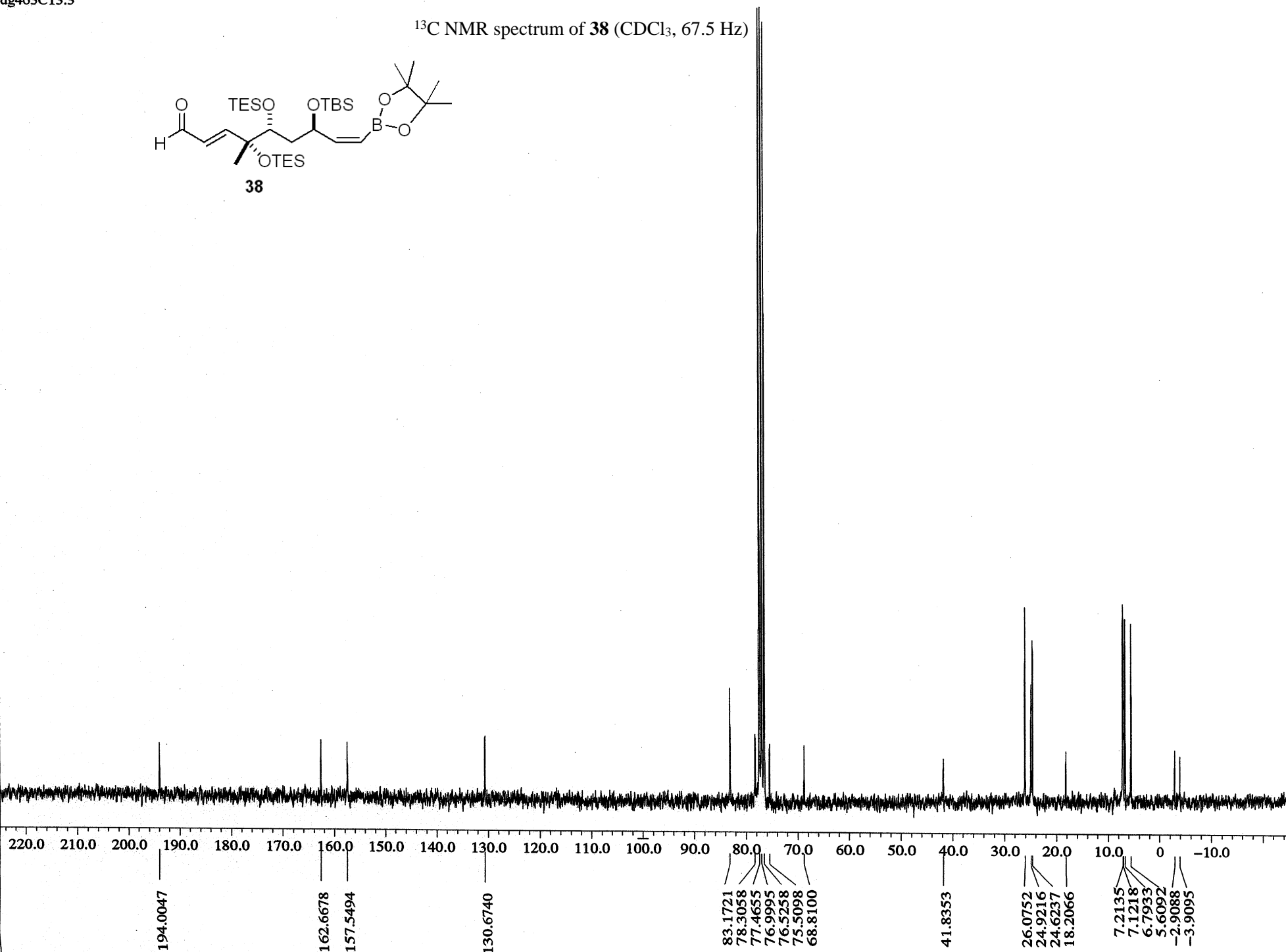
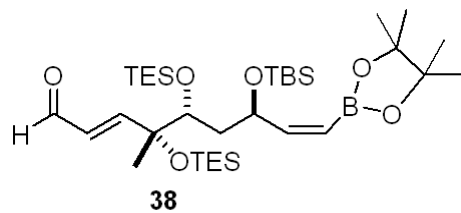


$^1\text{H}$  NMR spectrum of **7f** ( $\text{CDCl}_3$ , 270 Hz)

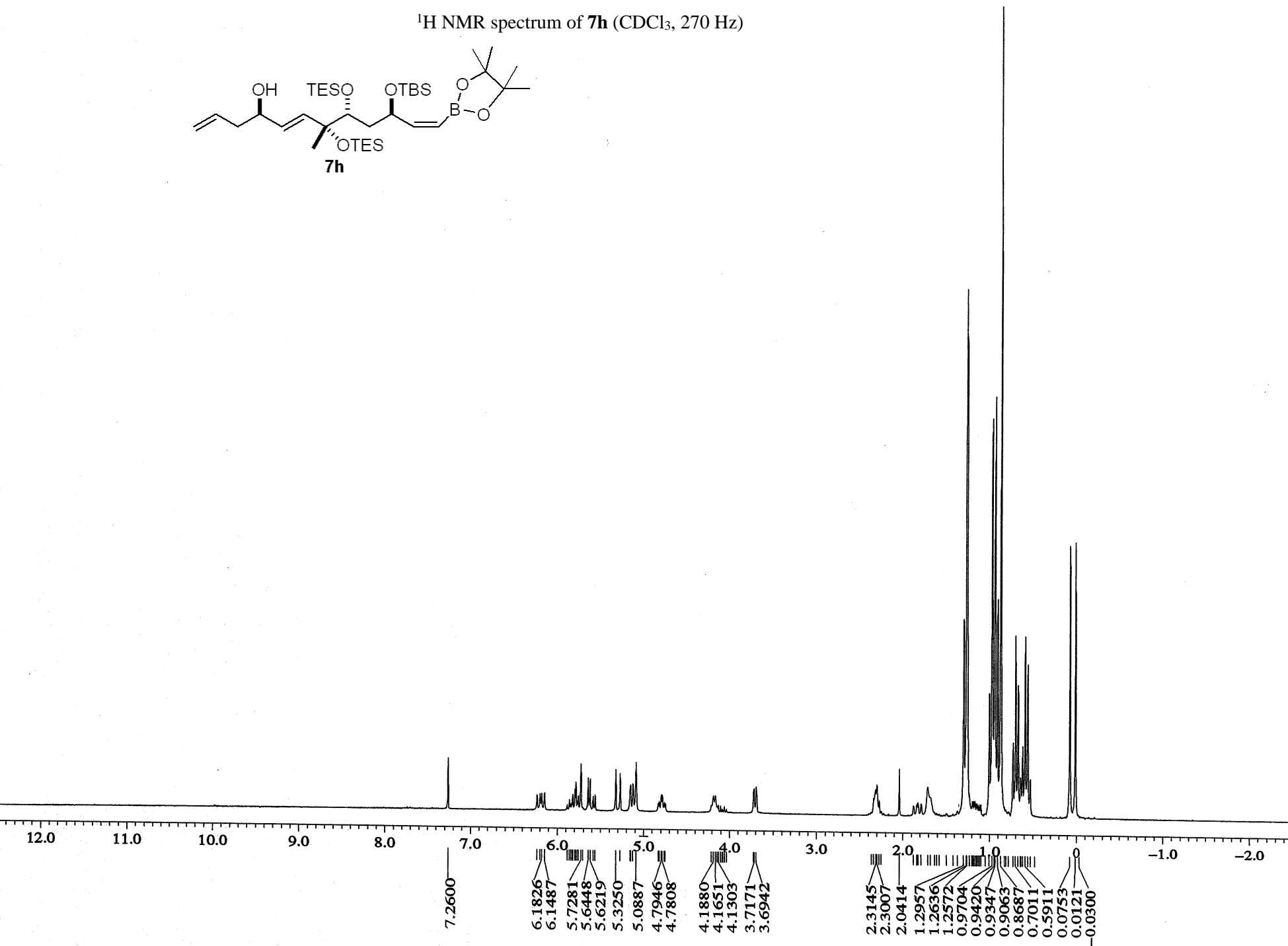
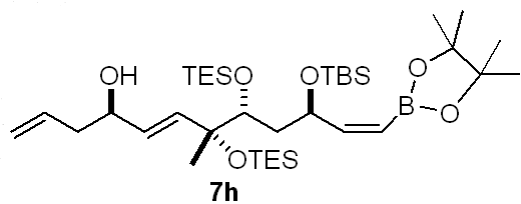
X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **7f** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

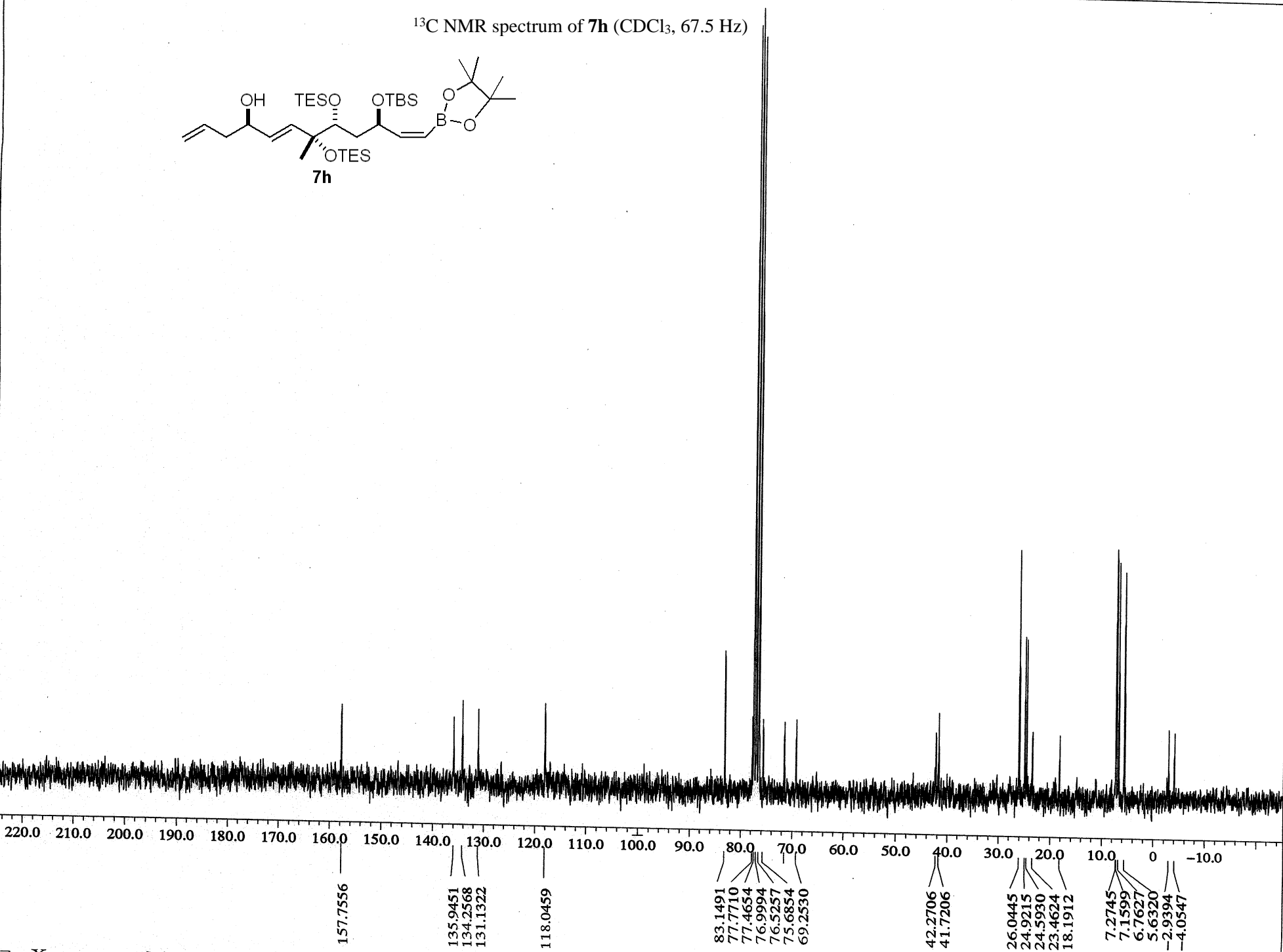
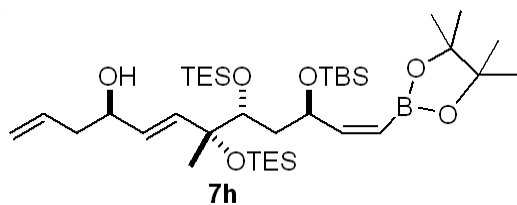
$^1\text{H}$  NMR spectrum of **38** ( $\text{CDCl}_3$ , 270 Hz)X : parts per Million :  $^1\text{H}$

$^{13}\text{C}$  NMR spectrum of **38** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$



$^1\text{H}$  NMR spectrum of **7h** ( $\text{CDCl}_3$ , 270 Hz)

X : parts per Million : 1H

$^{13}\text{C}$  NMR spectrum of **7h** ( $\text{CDCl}_3$ , 67.5 Hz)X : parts per Million :  $^{13}\text{C}$

## STANDARD PROTON PARAMETERS

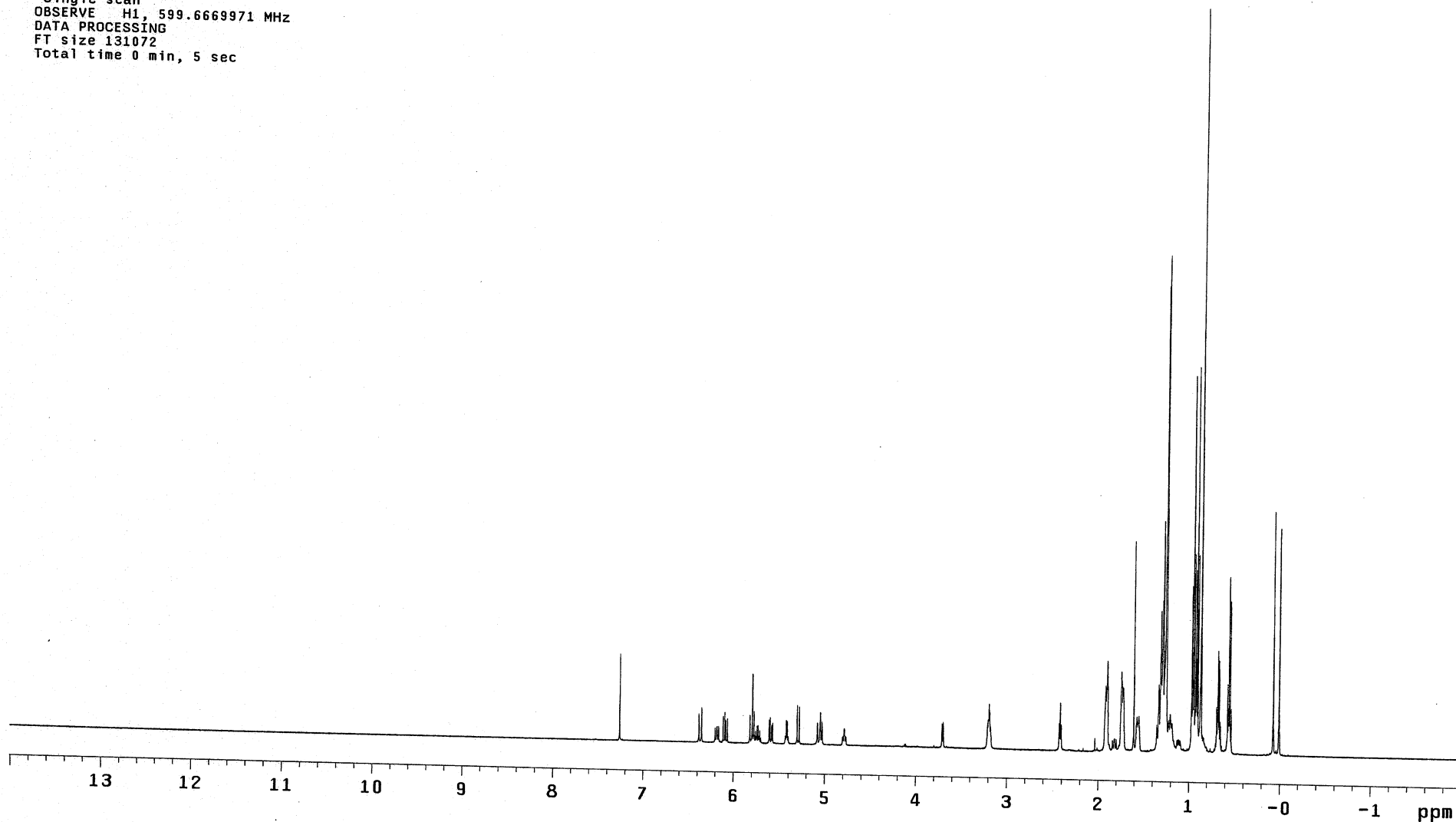
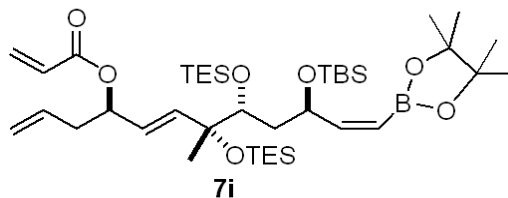
 $^1\text{H}$  NMR spectrum of **7i** ( $\text{CDCl}_3$ , 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1

Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

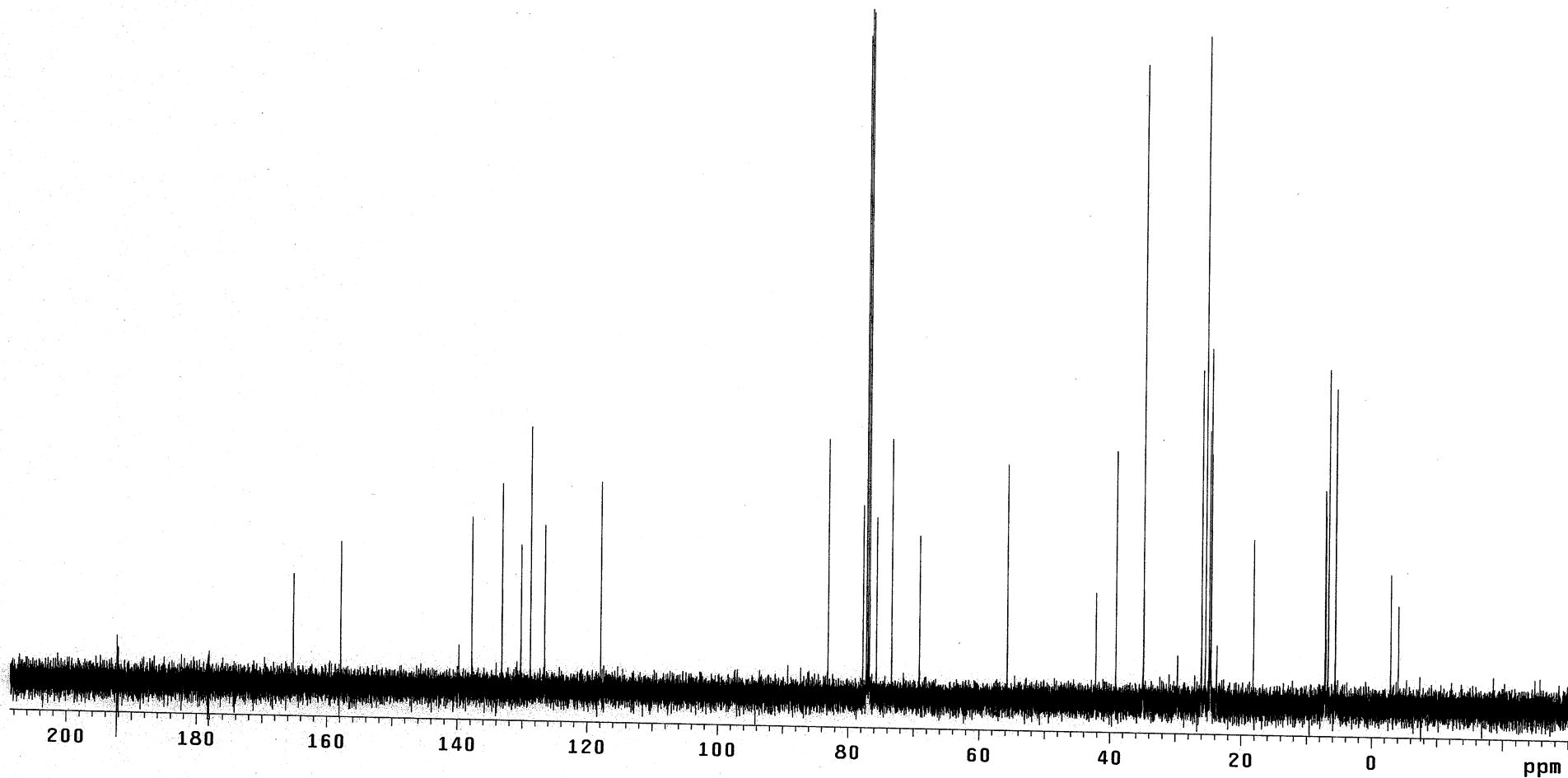
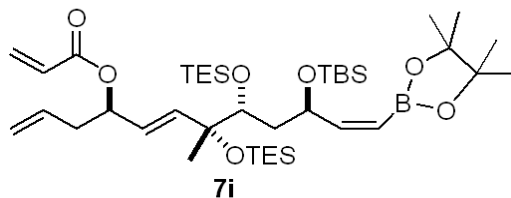
Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
Single scan  
OBSERVE H1, 599.6669971 MHz  
DATA PROCESSING  
FT size 131072  
Total time 0 min, 5 sec



## STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1  
Solvent: CDCl3  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"

Relax. delay 0.500 sec  
Pulse 29.9 degrees  
Acq. time 1.400 sec  
Width 36003.6 Hz  
416 repetitions  
OBSERVE C13, 150.7863846 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
FT size 131072  
Total time 32 min, 34 sec

 $^{13}\text{C}$  NMR spectrum of **7i** (CDCl<sub>3</sub>, 150 Hz)

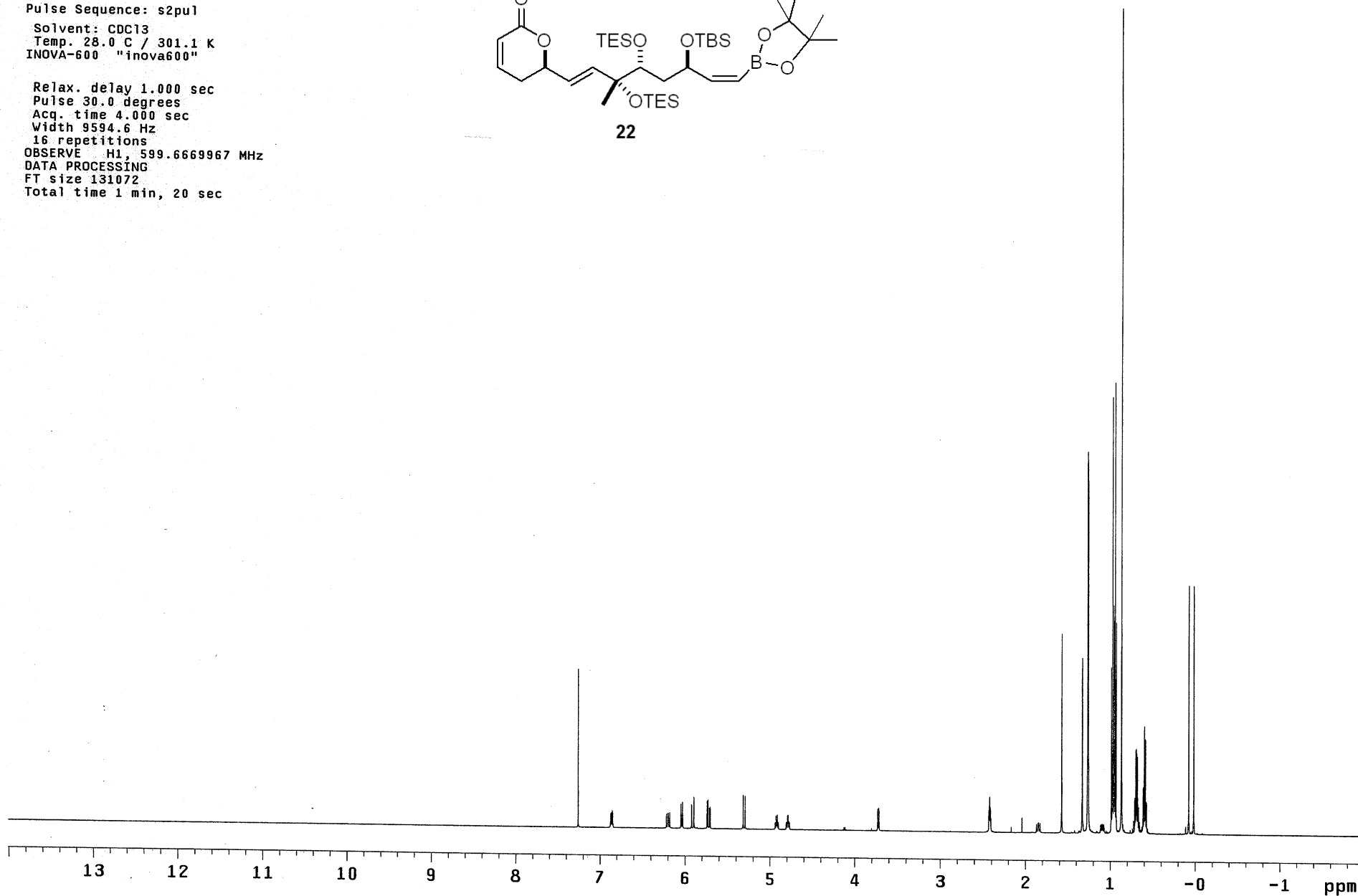
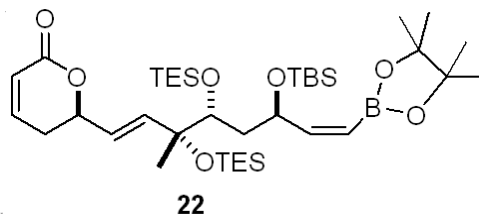
## STANDARD PROTON PARAMETERS

 $^1\text{H}$  NMR spectrum of **22** ( $\text{CDCl}_3$ , 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1  
Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6669967 MHz  
DATA PROCESSING  
FT size 131072  
Total time 1 min, 20 sec



## STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>

Temp. 28.0 C / 301.1 K

User: 1-14-87

INOVA-600 "inova600"

Relax. delay 0.500 sec

Pulse 29.9 degrees

Acq. time 1.400 sec

Width 36003.6 Hz

704 repetitions

OBSERVE C13, 150.7863841 MHz

DECOUPLE H1, 599.6700024 MHz

Power 40 dB

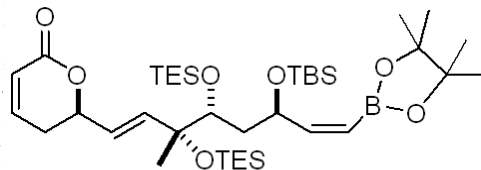
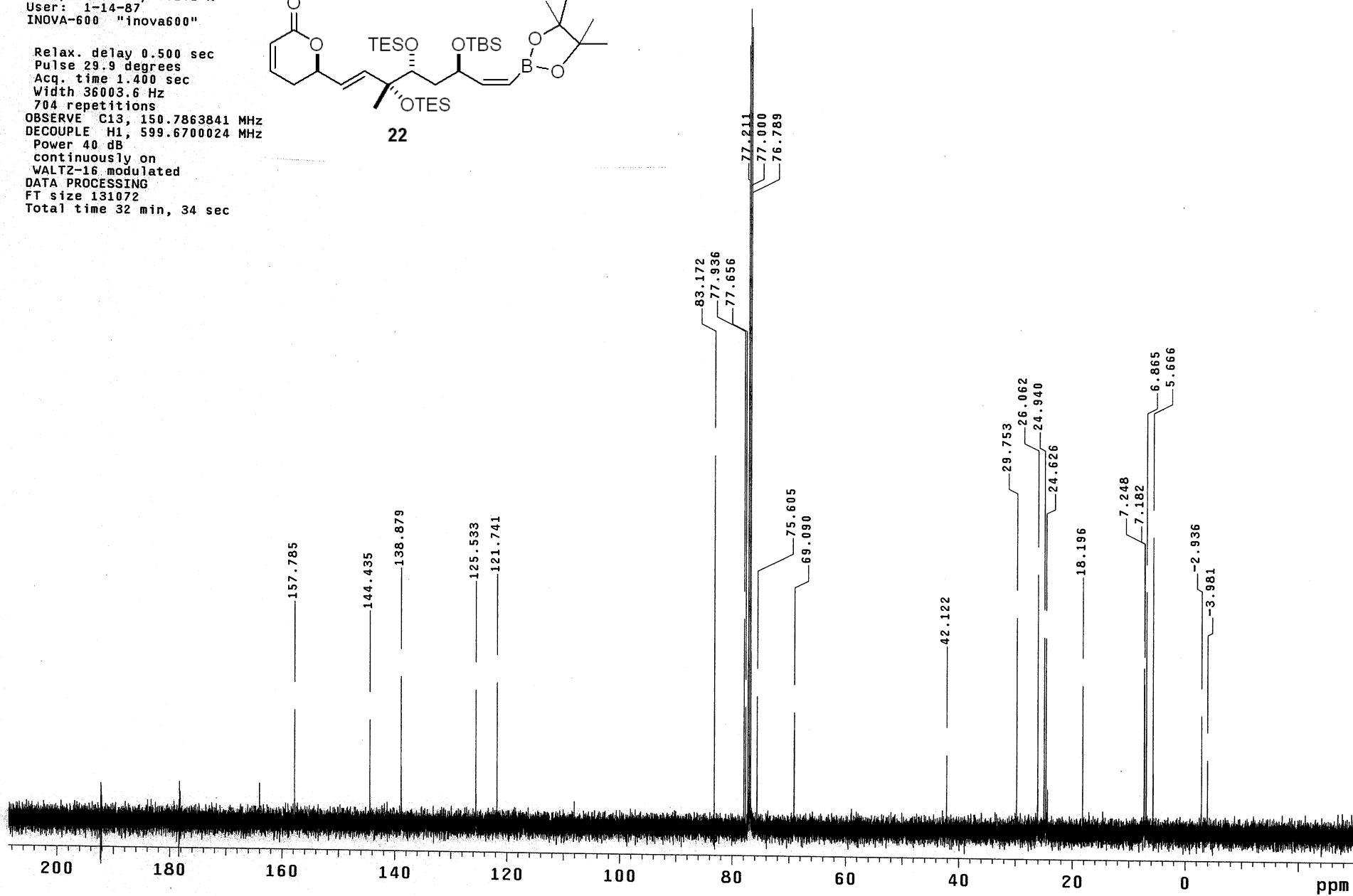
continuously on

WALTZ-16 modulated

DATA PROCESSING

FT size 131072

Total time 32 min, 34 sec

<sup>13</sup>C NMR spectrum of **22** (CDCl<sub>3</sub>, 150 Hz)**22**

## STANDARD PROTON PARAMETERS

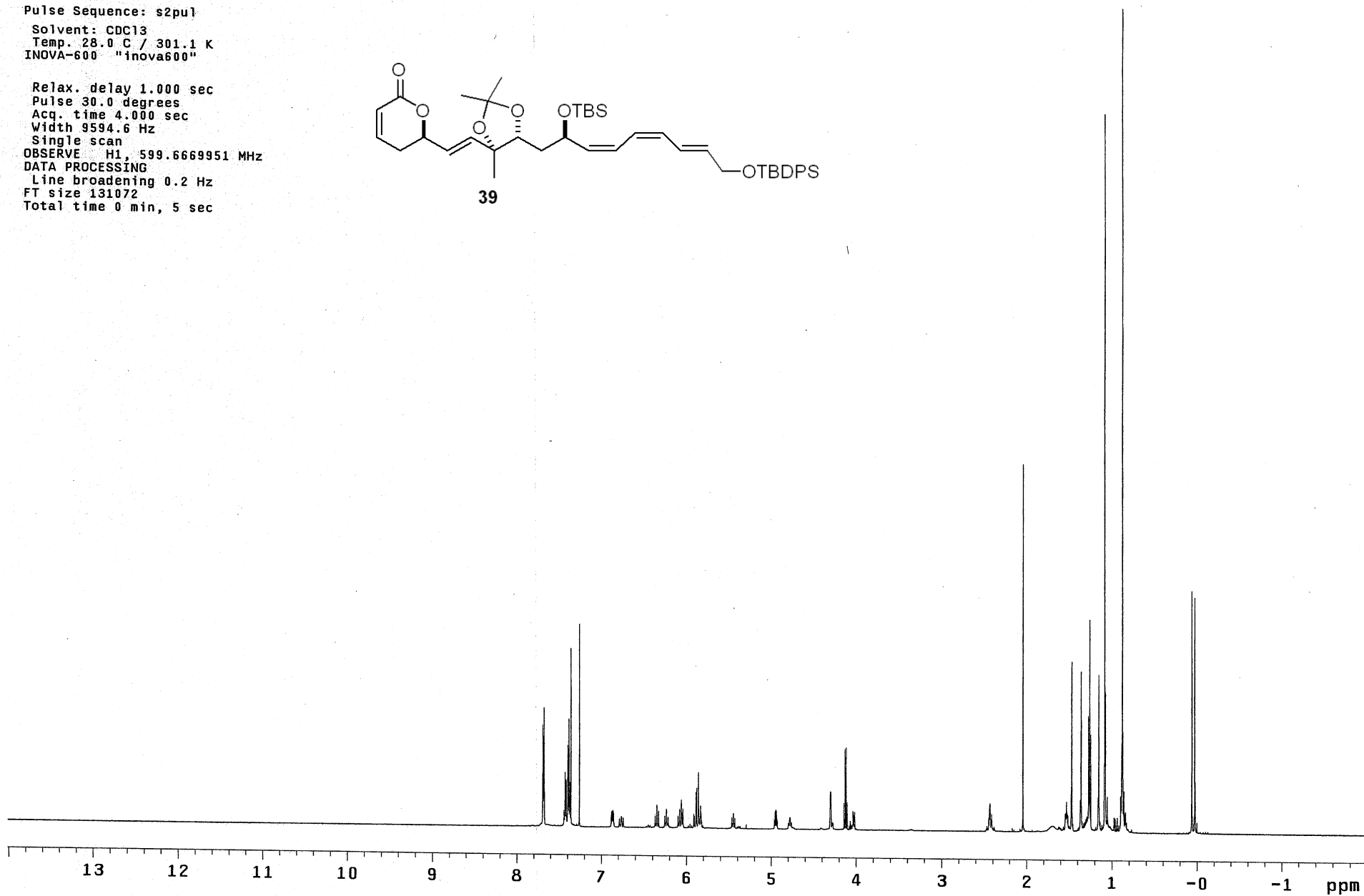
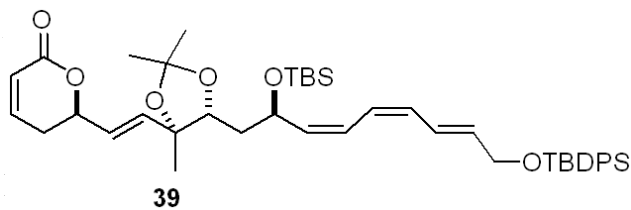
 $^1\text{H}$  NMR spectrum of **39** ( $\text{CDCl}_3$ , 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pul

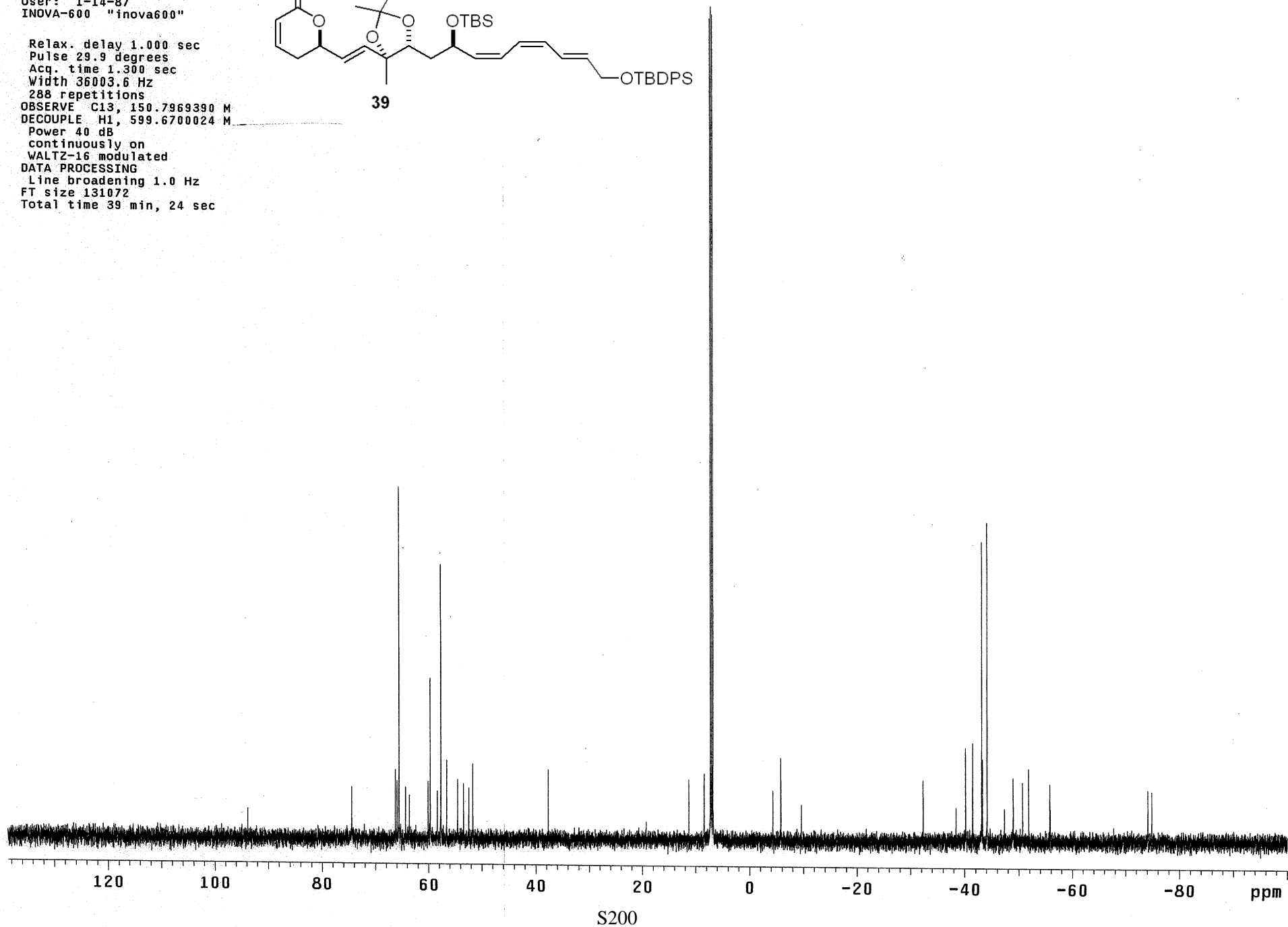
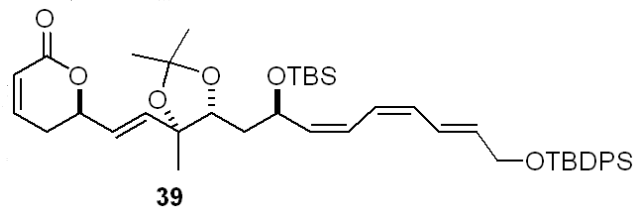
Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
Single scan  
OBSERVE H1, 599.6669951 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 131072  
Total time 0 min, 5 sec



## STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"Relax. delay 1.000 sec  
Pulse 29.9 degrees  
Acq. time 1.300 sec  
Width 36003.6 Hz  
288 repetitions  
OBSERVE C13, 150.7969390 M  
DECOUPLE H1, 599.6700024 M  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 39 min, 24 sec<sup>13</sup>C NMR spectrum of **39** (CDCl<sub>3</sub>, 150 Hz)



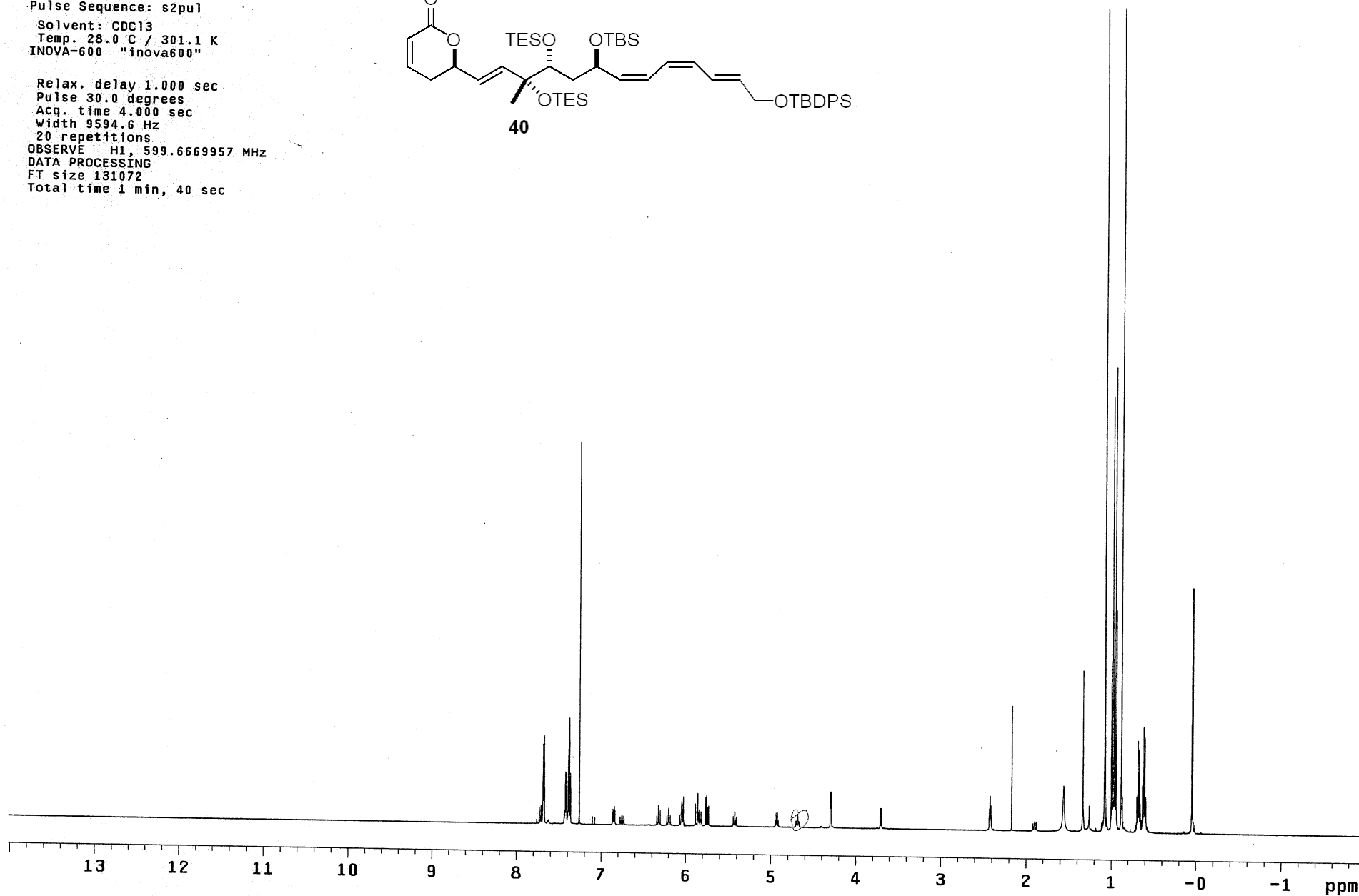
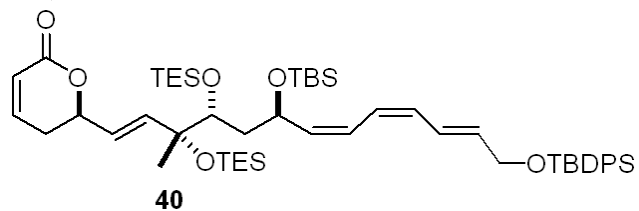
## STANDARD PROTON PARAMETERS

Archive directory: /export/home/vnmr1/  
Sample directory:  
File: PROTON

Pulse Sequence: s2pul

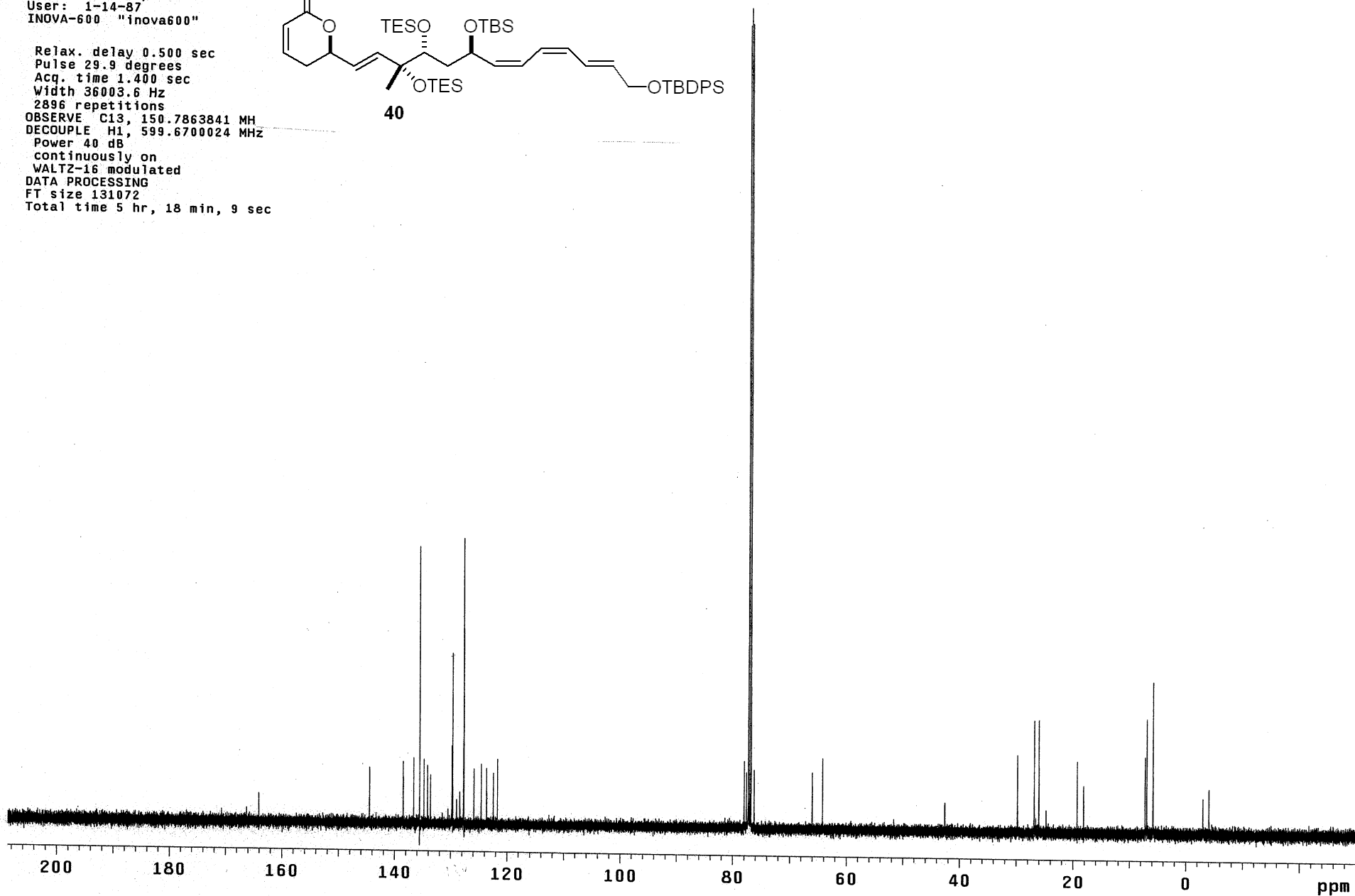
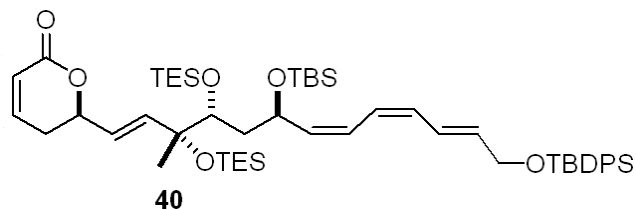
Solvent: CDCl3  
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
20 repetitions  
OBSERVE H1, 599.6669957 MHz  
DATA PROCESSING  
FT size 131072  
Total time 1 min, 40 sec

 $^1\text{H}$  NMR spectrum of **40** (CDCl<sub>3</sub>, 600 Hz)

## STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"Relax. delay 0.500 sec  
Pulse 29.9 degrees  
Acq. time 1.400 sec  
Width 36003.6 Hz  
2896 repetitions  
OBSERVE C13, 150.7863841 MH  
DECOUPLE H1, 599.6700024 MHZ  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
FT size 131072  
Total time 5 hr, 18 min, 9 sec<sup>13</sup>C NMR spectrum of **40** (CDCl<sub>3</sub>, 150 Hz)

## STANDARD PROTON PARAMETERS

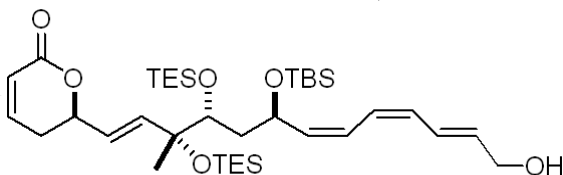
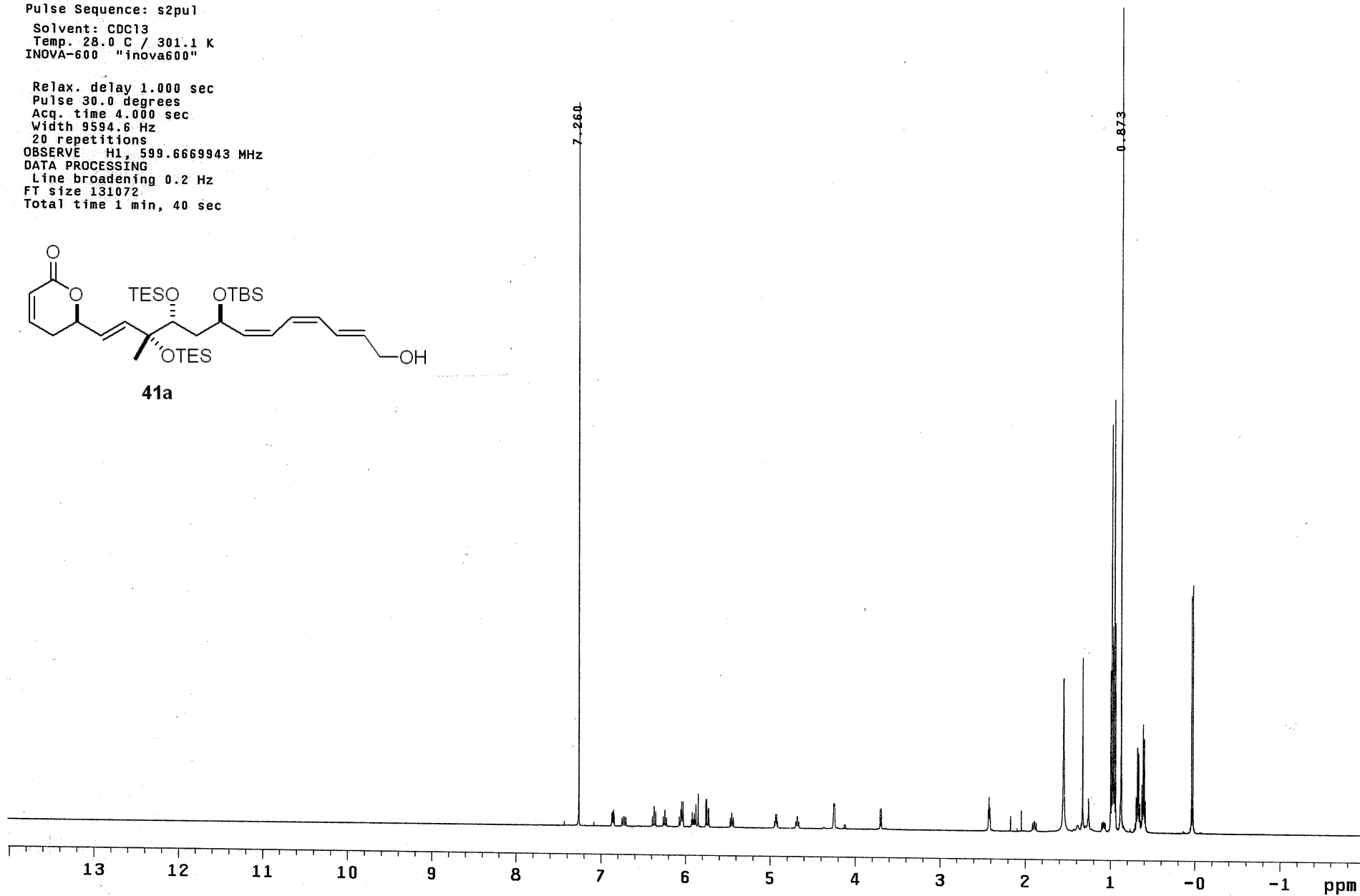
 $^1\text{H}$  NMR spectrum of **41a** ( $\text{CDCl}_3$ , 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1

Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
20 repetitions  
OBSERVE H1, 599.6669943 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 131072  
Total time 1 min, 40 sec

**41a**

<sup>13</sup>C NMR spectrum of **41a** (CDCl<sub>3</sub>, 150 Hz)

STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1

Solvent: CDCl<sub>3</sub>  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"

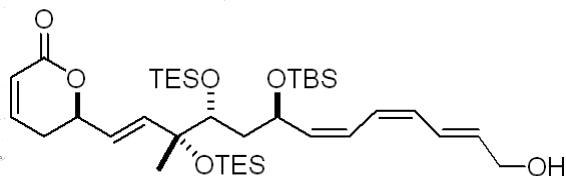
Relax. delay 0.500 sec  
Pulse 29.9 degrees  
Acq. time 1.400 sec  
Width 36003.6 Hz  
736 repetitions

OBSERVE C13, 150.7863830 MHz  
DECOUPLE H1, 599.6700024 MHz

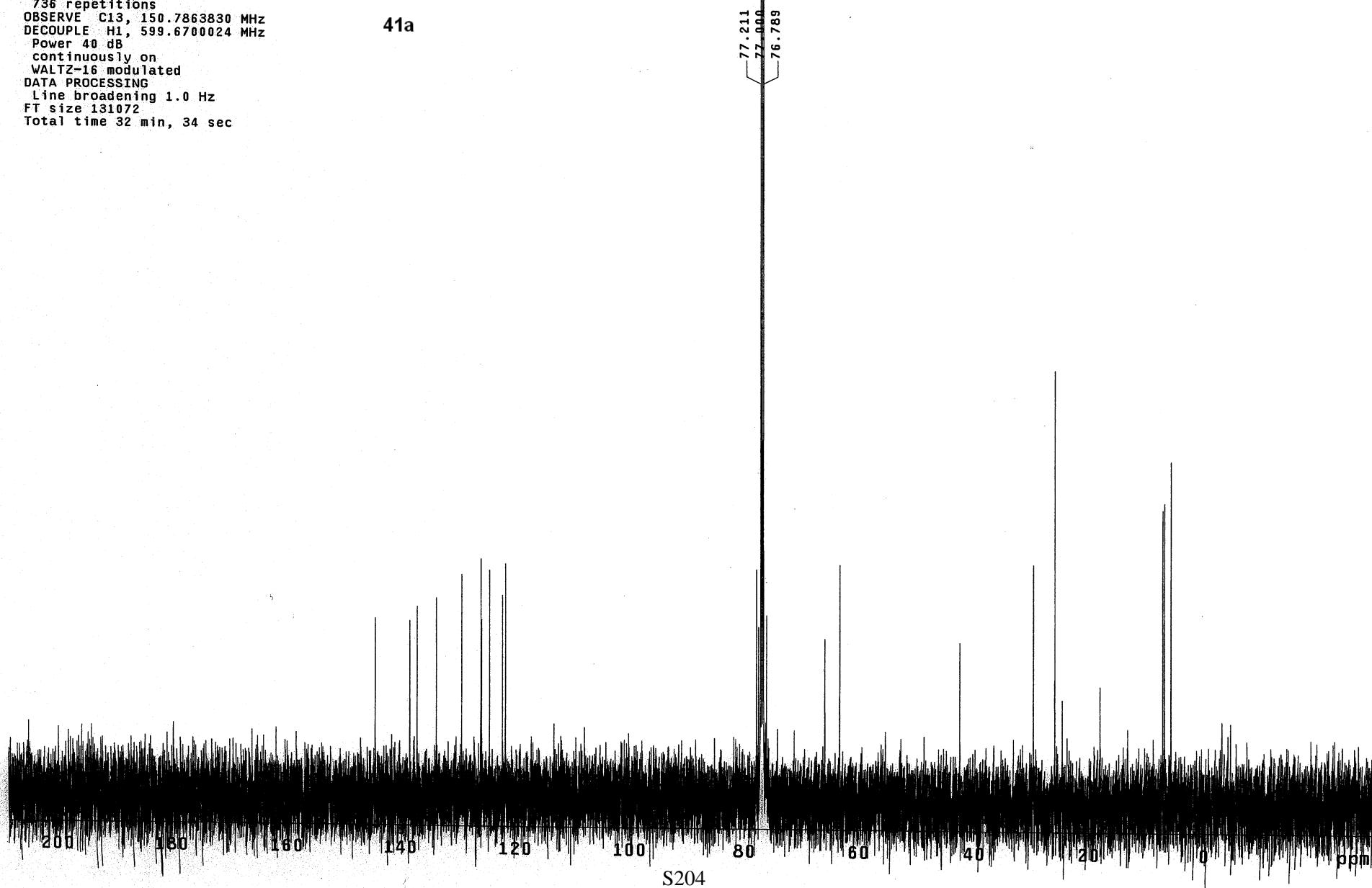
Power 40 dB  
continuously on  
WALTZ-16 modulated

DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072

Total time 32 min, 34 sec



**41a**



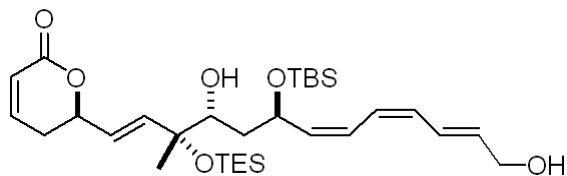
STANDARD PROTON PARAMETERS

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

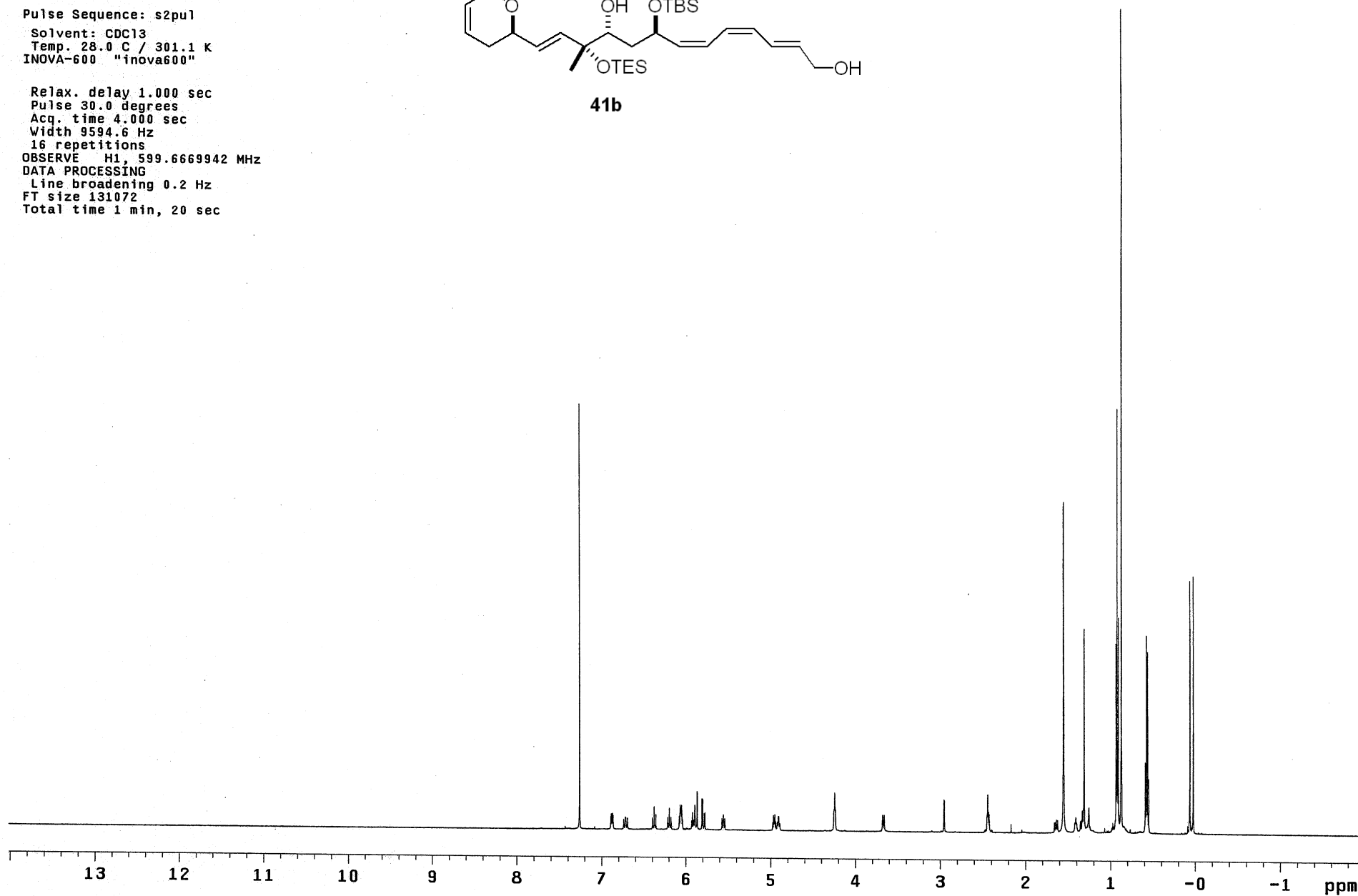
Pulse Sequence: s2pu1  
Solvent: CDCl3  
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
16 repetitions  
OBSERVE H1, 599.6669942 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 131072  
Total time 1 min, 20 sec

<sup>1</sup>H NMR spectrum of **41b** (CDCl<sub>3</sub>, 600 Hz)



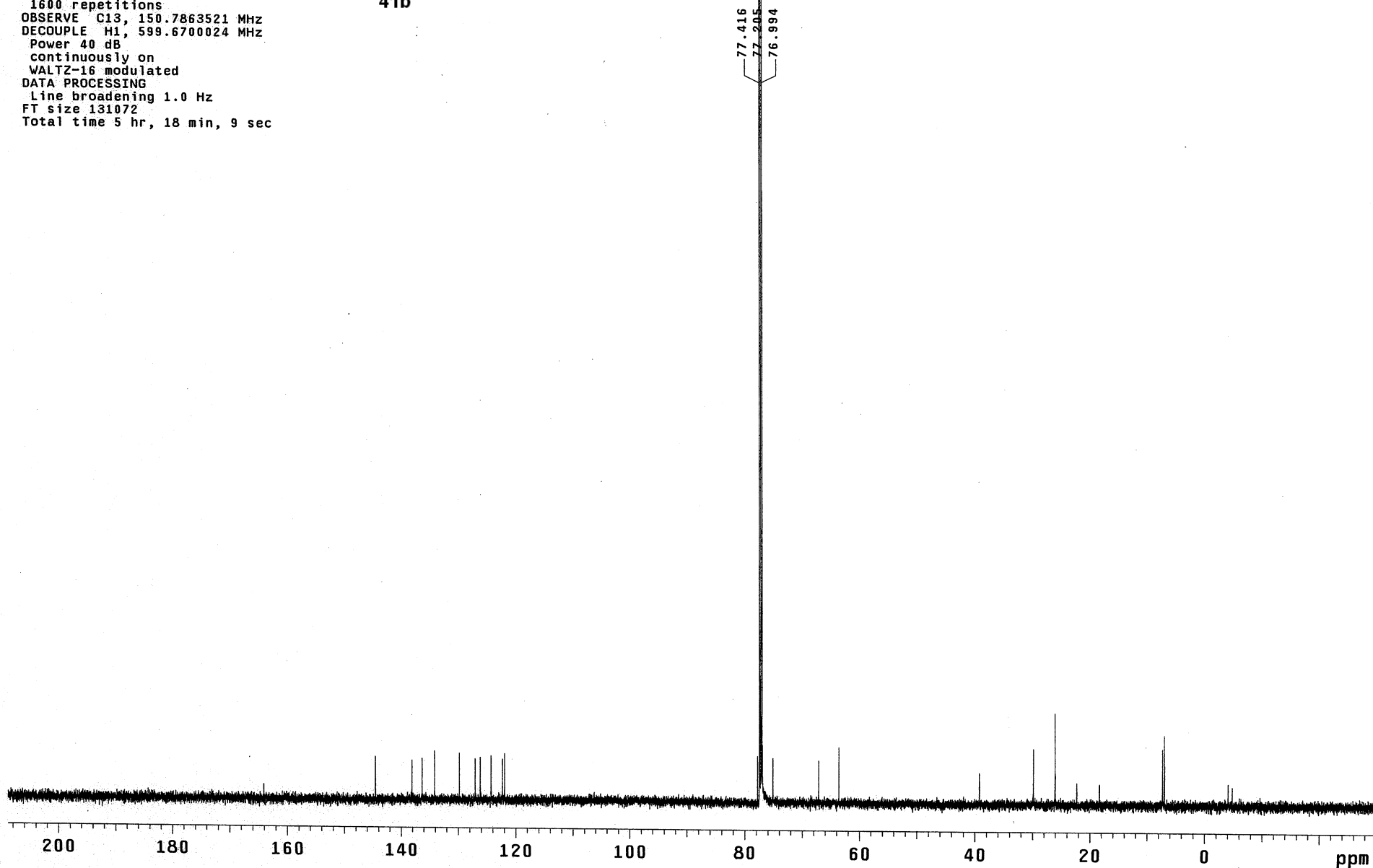
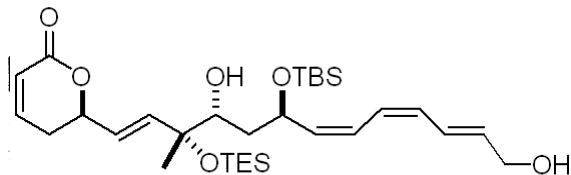
**41b**



## STANDARD CARBON PARAMETERS.

Pulse Sequence: s2pu1  
Solvent: CDCl3  
Temp. 28.0 C / 301.1 K  
User: 1-14-87  
INOVA-600 "inova600"

Relax. delay 0.500 sec  
Pulse 29.9 degrees  
Acq. time 1.400 sec  
Width 36003.6 Hz  
1600 repetitions  
OBSERVE C13, 150.7863521 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 5 hr, 18 min, 9 sec

 $^{13}\text{C}$  NMR spectrum of **41b** (CDCl<sub>3</sub>, 150 Hz)

## STANDARD PROTON PARAMETERS

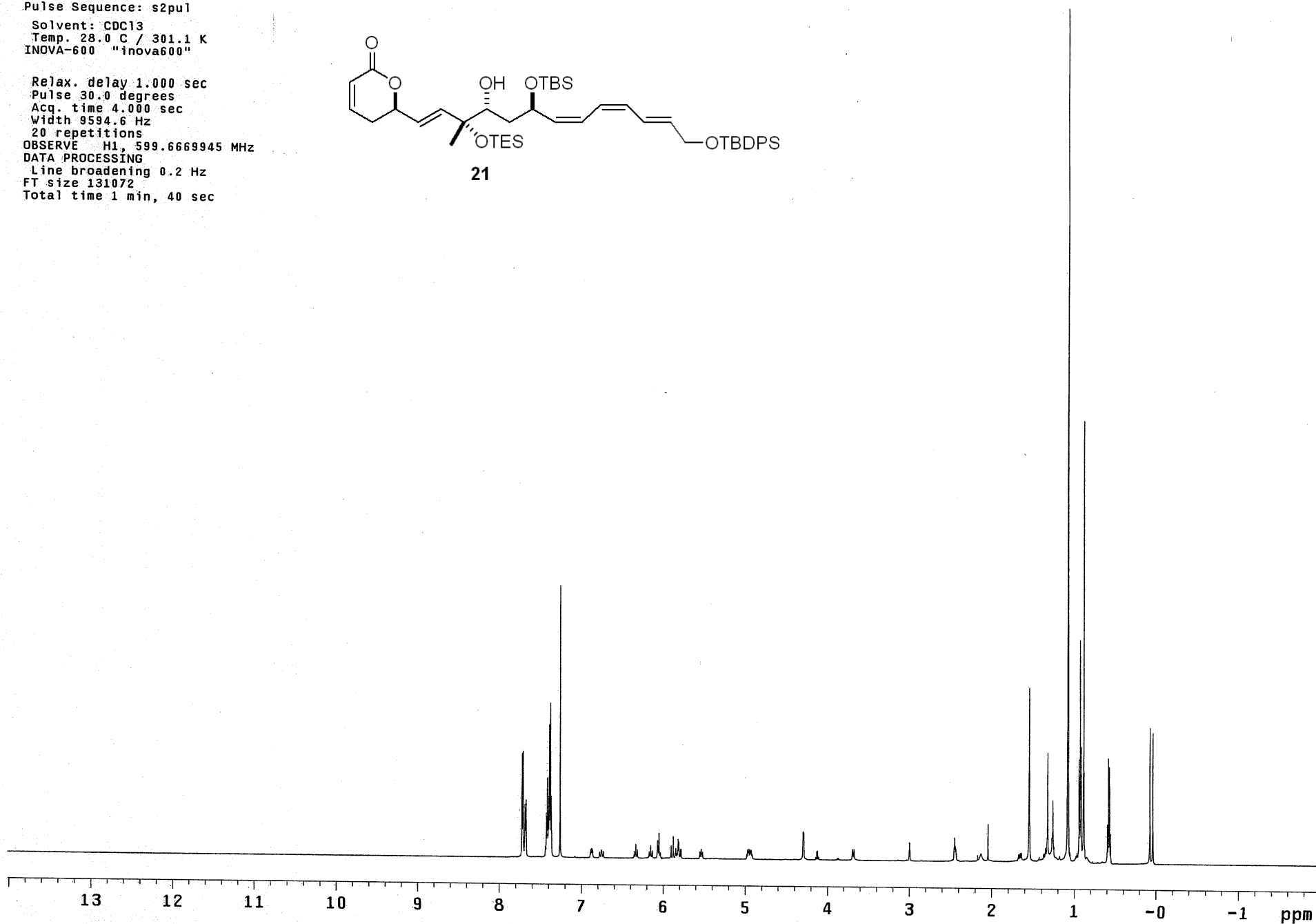
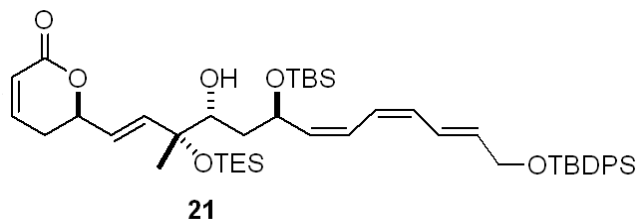
 $^1\text{H}$  NMR spectrum of **21** ( $\text{CDCl}_3$ , 600 Hz)

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1

Solvent:  $\text{CDCl}_3$   
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
20 repetitions  
OBSERVE H1, 599.6669945 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 131072  
Total time 1 min, 40 sec

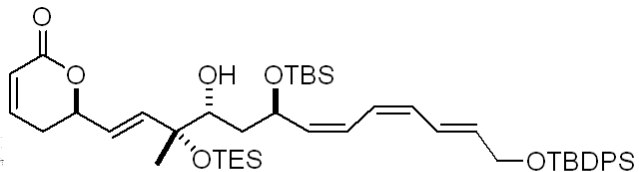
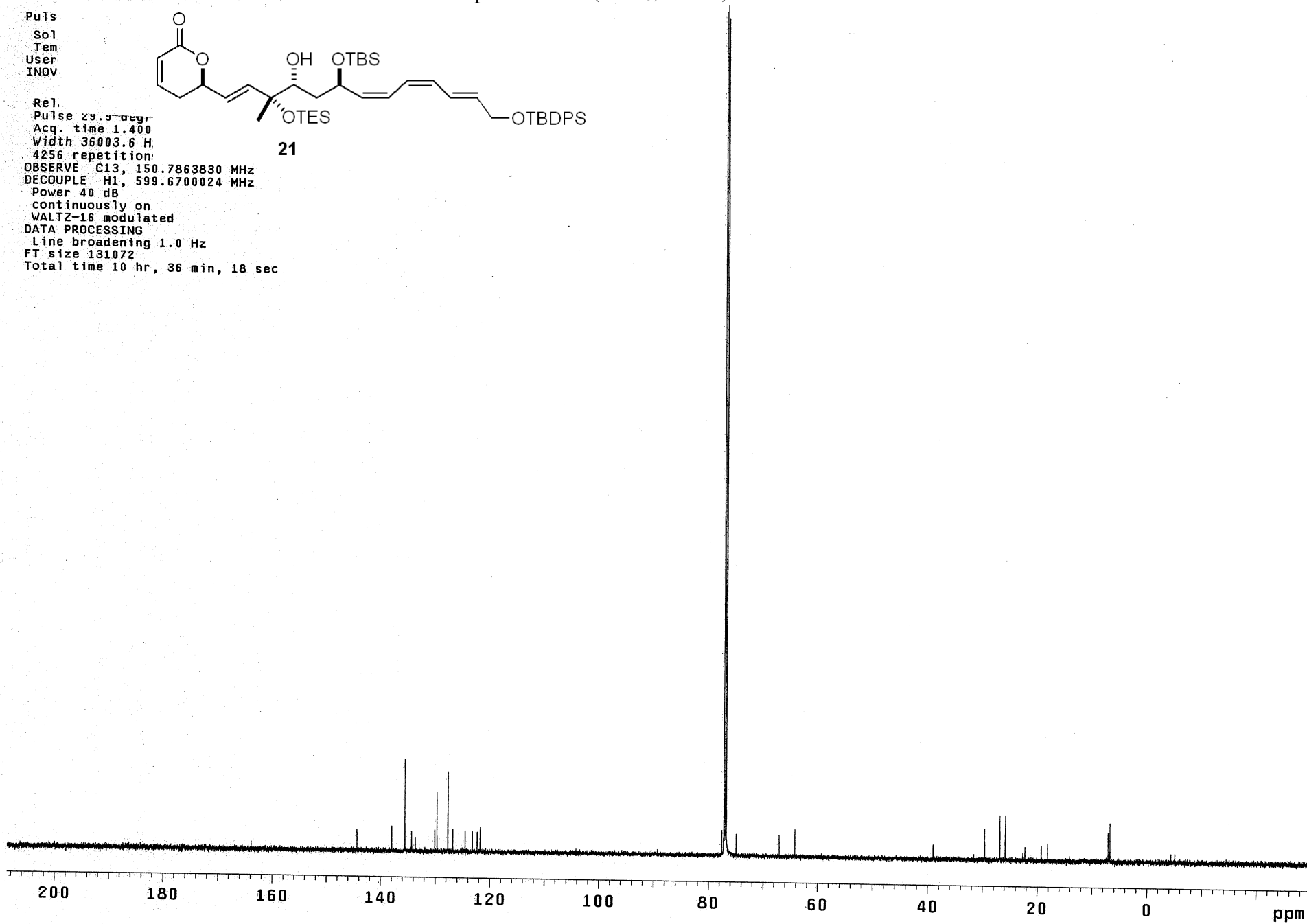


## STANDARD CARBON PARAMETERS

 $^{13}\text{C}$  NMR spectrum of **21** ( $\text{CDCl}_3$ , 150 Hz)

Puls  
Sol  
Tem  
User  
INOV

Rel.  
Pulse 29.9 deg  
Acq. time 1.400  
Width 36003.6 Hz  
4256 repetition  
OBSERVE C13, 150.7863830 MHz  
DECOUPLE H1, 599.6700024 MHz  
Power 40 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 10 hr, 36 min, 18 sec

**21**



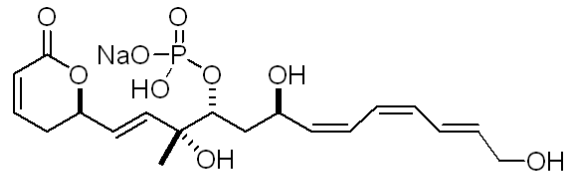
<sup>1</sup>H NMR spectrum of Fostriecin 1 (CDCl<sub>3</sub>, 600 Hz)

mingdeH1-2-28-07

Archive directory: /export/home/vnmr1/vnmrsys/data  
Sample directory:  
File: PROTON

Pulse Sequence: s2pu1  
Solvent: D2O  
Temp. 28.0 C / 301.1 K  
INOVA-600 "inova600"

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 4.000 sec  
Width 9594.6 Hz  
256 repetitions  
OBSERVE H1, 599.6684447 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 131072  
Total time 21 min, 22 sec



Fostriecin 1

