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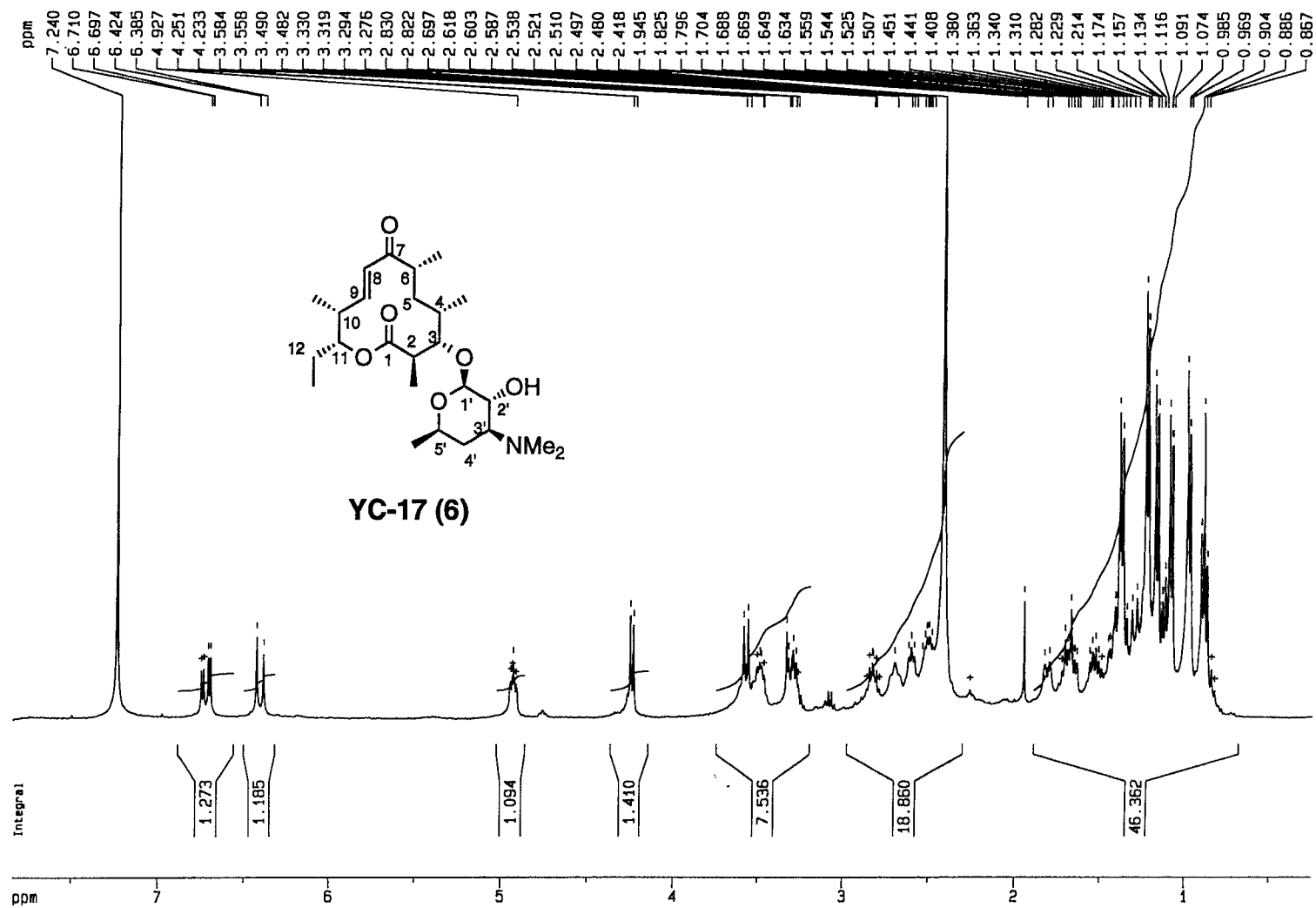


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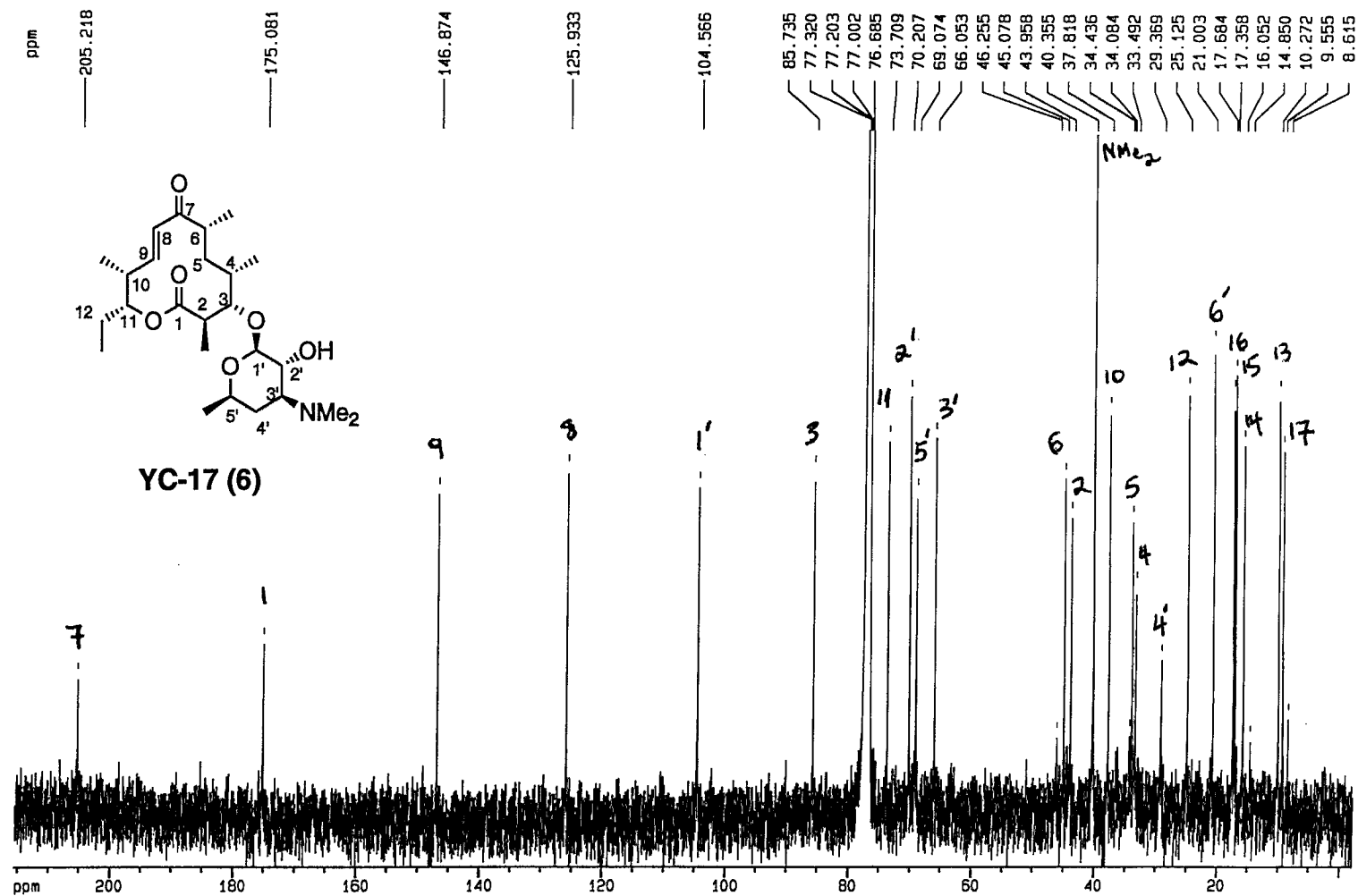
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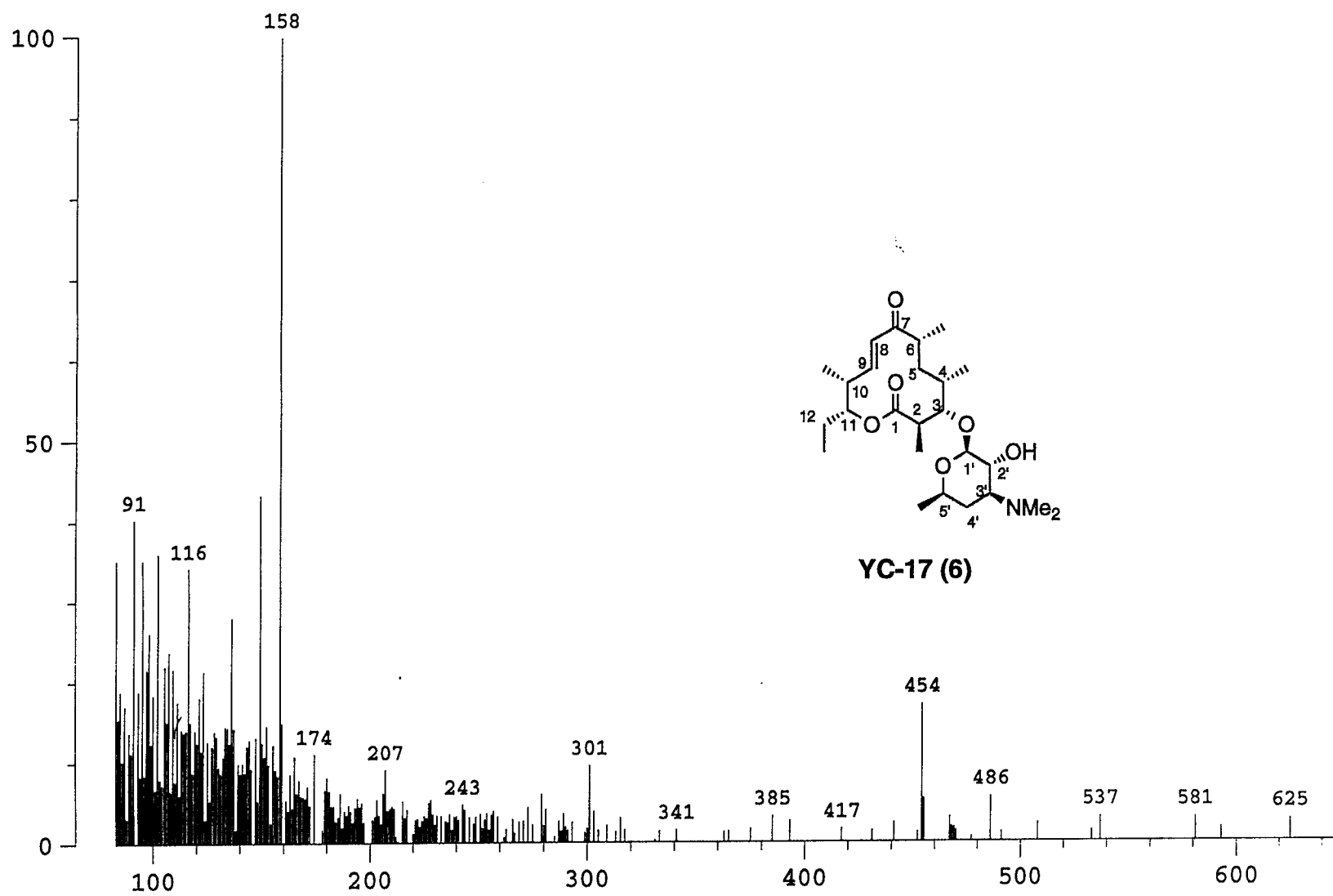
eg99a #1/1 YC-17 CDCl3 400MHz 8/18/97



I. <sup>1</sup>H NMR spectrum of YC-17 (6) [400 MHz, CDCl<sub>3</sub>]

II.  $^{13}\text{C}$  NMR spectrum of YC-17 (6) [100 MHz,  $\text{CDCl}_3$ ]

III. Low resolution FAB mass spectrum of YC-17 (6)



## IV. Experimental Section

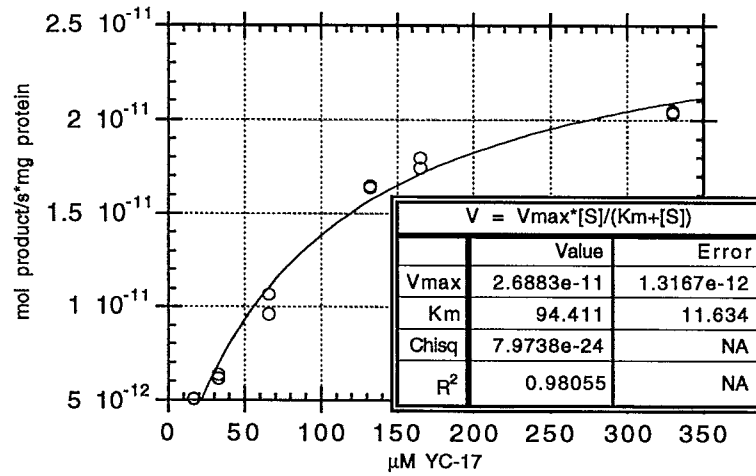
All reactions were run under nitrogen atmosphere using oven-dried glassware and syringes (250 °C, overnight) when appropriate. Dichloromethane was distilled from CaH<sub>2</sub>. <sup>1</sup>H (250 MHz and 400 MHz) and <sup>13</sup>C (100 MHz) NMR spectra were recorded on Bruker WM-250 and Avance-400 spectrometers. All chemical shifts are reported in ppm, referenced to the residual CHCl<sub>3</sub> solvent peak (<sup>1</sup>H: 87.24; <sup>13</sup>C: 877.0). Mass spectra were obtained on a Kratos MS80RFA spectrometer with fast atom bombardment (FAB) ionization (matrix: nitrobenzyl alcohol/ NaI). Unless otherwise stated, all solvents were reagent grade and used without further purification.

**Preparation of YC-17 (6).** To a dry 50 mL round-bottomed flask containing 10-deoxymethynolide (**5**) (23.3 mg, 78.7 μmol) was added 1-fluoro-2-O-methoxycarbonyl-desosamine (**7**) (35 mg, 142 μmol, 1.8 eq.), bis(cyclopentadienyl)hafnium dichloride (150 mg, 393.5 μmol, 5 eq., Aldrich), 4 Å molecular sieves (50 mg, oven-dried, powdered, Fisher) and AgClO<sub>4</sub> (81.6 mg, 393.5 μmol, 5 eq., Aldrich). A dry nitrogen atmosphere was secured and the reaction flask was cooled to -30 °C in a dry-ice/acetone bath. Reaction was initiated by the addition of freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The reaction was allowed to stir under nitrogen for 30 min. at -30 °C, at -10 °C for 30 min., and then at 0-5 °C for an additional hour. Finally, the reaction was allowed to equilibrate to room temperature and left to stir overnight. Upon completion, saturated NaHCO<sub>3</sub> (10 mL) was added and the resulting solution was filtered through Celite. The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 5mL). All organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and reduced *in vacuo* to yield a yellow oil. The crude product was chromatographed on SiO<sub>2</sub> gel (230 -400 μ mesh, Aldrich) using 1% MeOH/CHCl<sub>3</sub> as the mobile phase to afford protected YC-17 (24.3 mg, 47.3 μmol, 60 % yield).

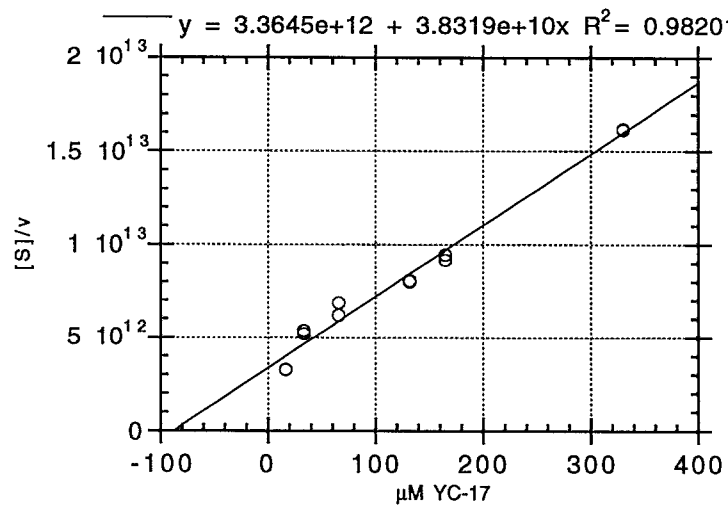
The 2'-O-methoxycarbonyl protected YC-17 thus prepared was deprotected by the addition of MeOH (5 mL), Et<sub>3</sub>N (1 mL), and H<sub>2</sub>O (1 mL). This mixture was stirred at 70 °C for 4 hours. Upon completion, the solvents were removed under high vacuum, and the crude reaction mixture was chromatographed on SiO<sub>2</sub> gel (230 -400 μ mesh, Aldrich) using 8.5% MeOH/CHCl<sub>3</sub> as the mobile phase to afford pure YC-17 **6** (15.5 mg, 33.0 μmol, 75 % yield). <sup>1</sup>H NMR, <sup>13</sup>C NMR, and FABMS spectral data were in agreement with literature values.

## V. Kinetic Data for methymycin production

**v vs. [S] methymycin production**

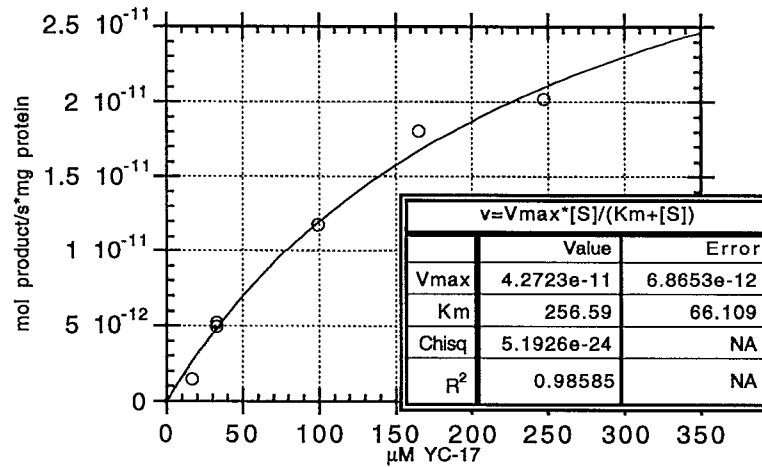


**[S]/v vs. [S] methymycin production**



## VI. Kinetic Data for neomethymycin production

**v vs. [S] neomethymycin production**



**[S]/v vs. [S] neometyhymycin production**

