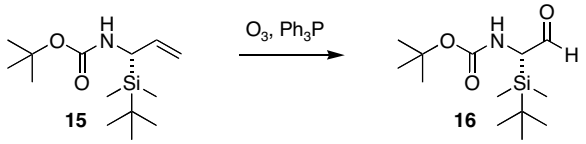
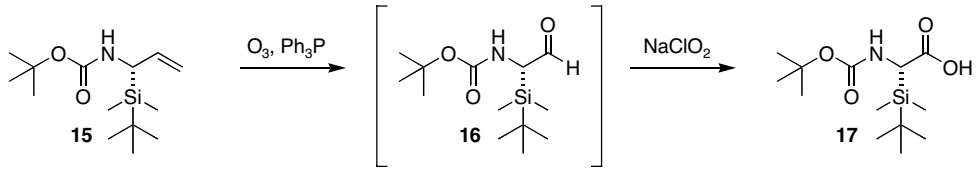


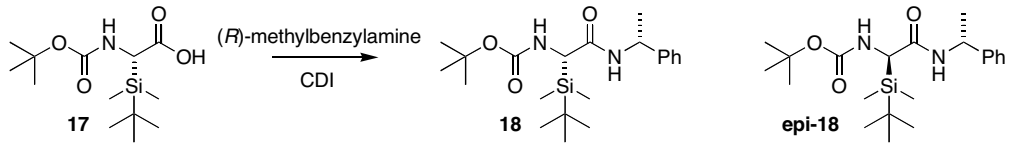
[1-(*tert*-Butyl-dimethyl-silanyl)-2-oxo-ethyl]-carbamic acid *tert*-butyl ester 16. Through a -78 °C mixture of **15** (50 mg, 0.18 mmol) in methylene chloride (4 mL) and methanol (1 mL) with sodium bicarbonate (15 mg, 0.18 mmol) was bubbled a stream of ozone, until the solution became blue. The ozone was replaced with argon until the color dissipated. Triphenylphosphine (94 mg, 0.36 mmol) was added and the mixture was warmed to room temperature, filtered and concentrated. Flash chromatography over silica gel (10:1 hexane/ethyl acetate) gave **16** (39 mg, 80%) as a colorless oil.

Rf = 0.45 (10:1 hexane/ethyl acetate);
IR (KBr, CH_2Cl_2): 3334, 2959, 2931, 2898, 2886, 2861, 1718, 1700, 1506, 1367, 1253, 1171 cm^{-1};
^{1}H-NMR (500 MHz, $CDCl_3$): 9.60 (s, 1H), 5.12 (d, J = 7.0 Hz, 1H), 4.53 (d, J = 8.0 Hz, 1H), 1.43 (s, 9H), 0.98 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H).



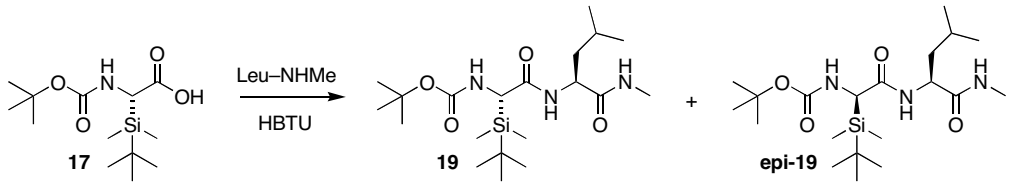
***tert*-Butoxycarbonylamino-(*tert*-butyl-dimethyl-silanyl)-acetic acid 17.** To a -78 °C mixture of **15** (100, 0.36 mmol) in methylene chloride (4 mL) and methanol (1 mL) with sodium bicarbonate (30 mg, 0.36 mmol) was bubbled a stream of ozone. After the solution had become blue, the ozone was replaced by argon until the solution was colorless. Triphenylphosphine (188 mg, 0.72 mmol) was added and the mixture was warmed to room temperature, filtered and concentrated. The residue was taken up in *tert*-butanol (4 mL) and distilled water (1 mL), to which sodium dihydrogenphosphate (87 mg, 0.72 mmol) and 2-methyl-2-butene (1.0 mL) were added. After 10 minutes, sodium chlorite (133mg, 1.44 mmol) was added and the mixture became yellow. After stirring for 2 h the yellow color faded. Following addition of saturated NH_4Cl (40 mL) solution and extraction of the aqueous phase with ethyl acetate (3x20mL), the combined organics were dried over $MgSO_4$ and concentrated. Flash chromatography (4:1:0.4 hexane/ethyl acetate/acetic acid) gave **17** as a colorless solid (76 mg, 73%).

mp 78.5-80.0 °C;
Rf = 0.30 (4:1:0.4 hexane/ethyl acetate/acetic acid);
IR (KBr, CH_2Cl_2): 3432, 3273, 2932, 2861, 1705, 1497, 1395, 1256, 1167, 847 cm^{-1}.
^{1}H-NMR (400 MHz, $CDCl_3$): 4.84 (d, J = 7.2 Hz, 1H), 4.18 (d, J = 9.2 Hz, 1H), 1.44 (s, 9H), 0.97 (s, 9H), 0.15(s, 3H), 0.12(s, 3H);
^{13}C-NMR (400 MHz, $CDCl_3$): 179.9, 156.3, 80.43, 45.4, 28.7, 28.4, 26.9, 18.0, -6.5, -7.0;
MS (FAB+/NBA/NaBr) 312 (100, MNa+), 256 (11), 234 (14), 212 (8), 198 (8), 188(13);
Exact Mass Calcd. for $C_{13}H_{27}NO_4NaSi$: (MNa^+) 312.1607; Found: 312.1608;



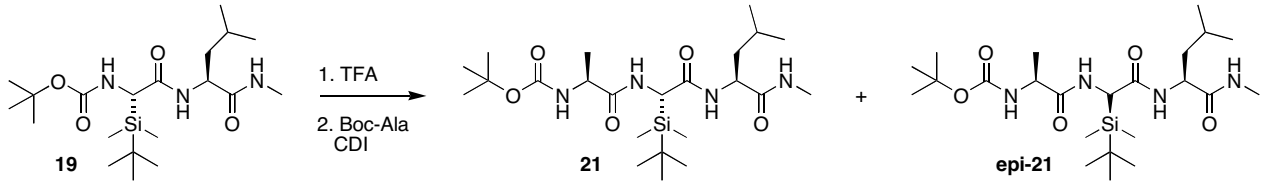
(*S*)-[(*tert*-Butyl-dimethyl-silanyl)-(1(*R*)-phenyl-ethylcarbamoyl)-methyl]-carbamic acid *tert*-butyl ester 18. To a solution of **17** (90 mg, 0.31 mmol) in methylene chloride (2 mL) and tetrahydrofuran (2 mL) was added carbonyldiimidazole (103 mg, 0.62 mmol) and, after 1h, (*R*) (+)-α-methyl benzylamine (120 μL, 0.93 mmol) was added and the resulting mixture was stirred overnight. Following addition of diethyl ether (10 mL), the mixture was filtered and concentrated. Flash chromatography (1.5:1:0.02 methylene chloride/ethyl acetate/methanol) gave an inseparable mixture of **18** and **epi-18** (4:1) as a colorless solid (66 mg, 37%).

Colorless crystal, mp 162-163°C;
Rf = 0.30 (1.5:1:0.02 methylene chloride/ethyl acetate/methanol);
IR (KBr, CH_2Cl_2): 3323, 3284, 2963, 2857, 1680, 1631, 1522, 1347, 1174, 794 cm^{-1}.
^{1}H-NMR (500 MHz, $CDCl_3$): 5.95 (m, 1H), 5.11 (m, 1H), 4.88 (m, 1H), 3.90 (m, 1H), 1.50~1.41 (m, 12H), 0.93 (m, 9H), 0.11~0.02 (m, 6H)
^{13}C-NMR (300 MHz, $CDCl_3$): ;
MS (FAB+/NBA/NaBr) 415 (100, MNa+), 393 (7, MH+), 337 (8), 315 (13), 293 (10), 279 (9), 188 (10);
Exact Mass (FAB+/NBA/NaBr) Calcd. for $C_{21}H_{36}N_2O_3NaSi$: 415.2393 (MNa+); Found 415.2398;



***N*-[(1,1-Dimethylethoxy)carbonyl]-2(*S*)-[(1,1-dimethylethyl)dimethylsilyl]glycyl-*N*-methyl-L-leucinamide 19.**
To a solution of **17** (50 mg, 0.17 mmol) in methylene chloride (2 mL) and dimethylformamide (4 mL) was added HBTU (77mg, 0.20 mmol) and the mixture was stirred for 2 h. In a separate flask, *N*-[(1,1-dimethylethoxy)carbonyl]-*N*-methyl-L-leucinamide (104mg, 0.43 mmol) in methylene chloride was treated with trifluoroacetic acid (0.1 ml, 1.23 mmol) for 2 h. This mixture was then transferred to the solution of activated **17**, followed by addition of *N,N*-diisopropylethylamine 37 μL, 0.20 mmol) and the solution was then stirred overnight. Saturated ammonium chloride (5 mL) was added and the aqueous phase was extracted with ethyl acetate (3x20 mL), the combined organics were dried over $MgSO_4$ and concentrated. Flash chromatography (6.5:1:0.01 methylene chloride/ethyl acetate/methanol) gave an inseparable mixture of **19** and **epi-19** (2:1) as a colorless solids (63 mg, 88%).

Colorless crystals, mp 162-163 °C;
Rf = 0.30 (6.5:1:0.01 methylene chloride/ethyl acetate/methanol);
IR (KBr, CH_2Cl_2): 3261, 3117, 2957, 2931, 2858, 1710, 1665, 1620, 1514, 1249, 1168, 842 cm^{-1}.
^{1}H-NMR (500 MHz, $CDCl_3$): 6.73 (m, 1H), 6.02 (m, 1H), 4.83 (m, 1H), 4.48 (m, 1H), 4.39 (m, 1H), 3.85~3.75 (m, 1H), 2.76 (d, J = 5.0 Hz, 3H), 1.84~1.49 (m, 3H), 1.46 (m, 9H), 0.96~0.89 (m, 15H), 0.15~0.07(m, 6H);
^{13}C-NMR (300 MHz, $CDCl_3$):;
MS (FAB+/NBA/NaBr) 438 (100, MNa+), 416 (5, MH+), 360 (2), 338 (13), 316 (2), 216 (5), 188 (3), 167(3);
Exact Mass (FAB+/NBA/NaBr) Calcd. for $C_{20}H_{41}N_3O_4Si$: 438.2764 (MNa+); Found 438.2764;



***N*-[(1,1-Dimethylethoxy)carbonyl]-l-alanyl-(2(*S*)-[(1,1-dimethylethyl)dimethylsilyl]glycyl-*N*-methyl-L-leucinamide 21.** Trifluoroacetic acid (32 μL, 0.4 mmol) was added to a solution of a 2:1 mixture of **19** and **epi-19** (17 mg, 0.04 mmol) in methylene chloride (2 mL). After 2 h the starting **19** had fully reacted as judged by TLC. In a separate flask, to a solution of Boc-protected-L-alanine (15 mg, 0.08 mmol) in methylene chloride was added 1,1-carbonyldiimidazole (15 mg, 0.088 mmol) and then stirred for 1 h. The solution of deprotected **19** was then transferred to the solution of activated alanine and stirred overnight. After addition of water (2 mL) and extraction with methylene chloride (3x20mL), the combined organics were dried over $MgSO_4$ and concentrated. Flash chromatography (2.5:1:0.1 hexane/ethyl acetate/methanol) gave **21** and **ept-21** (2:1) as colorless solids (10 mg, 50%).

mp 144.0°C;

Rf = 0.30 (4:1:0.4 hexane/ethyl acetate/acetic acid);

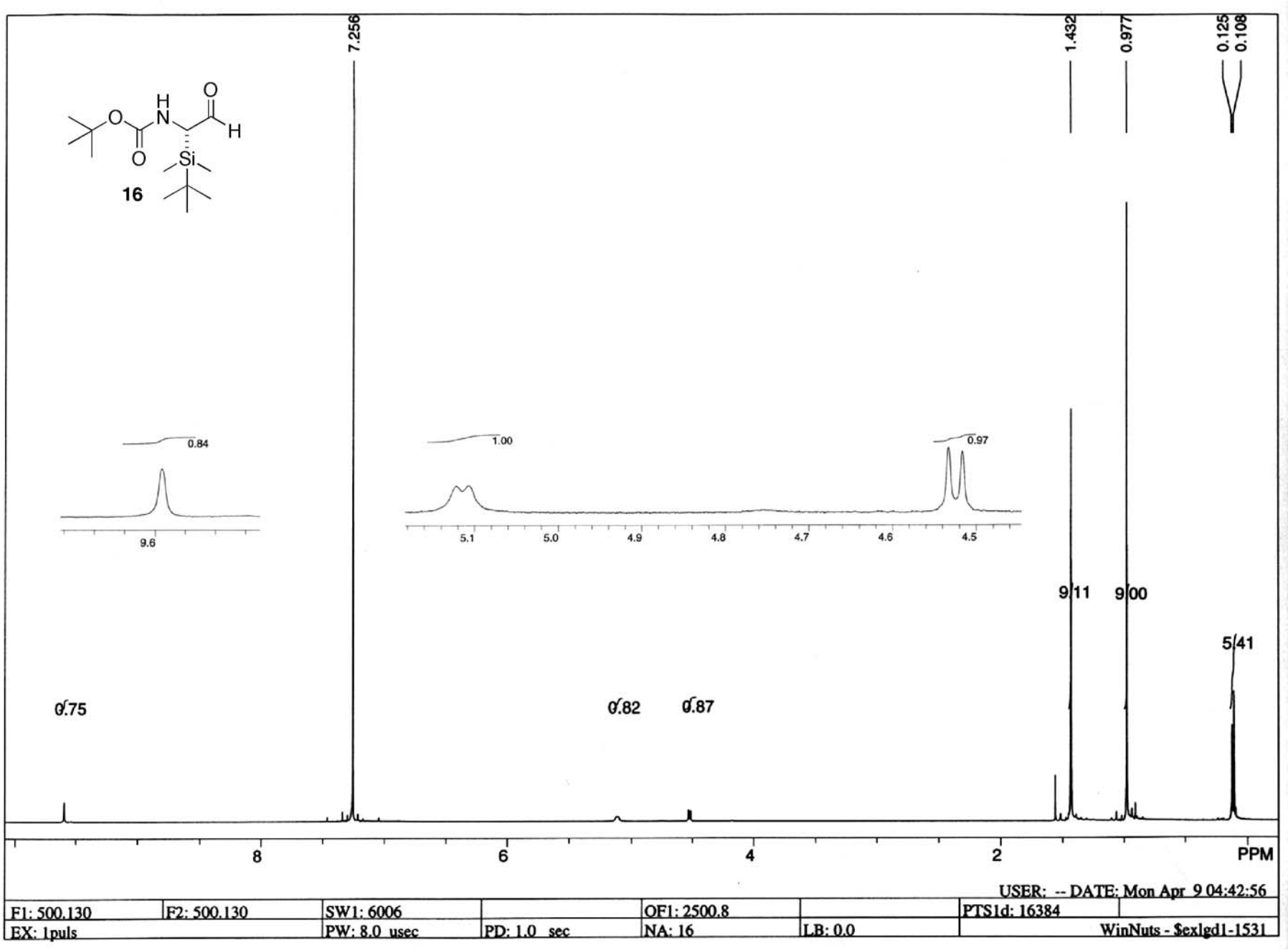
IR (KBr, CH_2Cl_2): 3306, 2957, 2860, 1666, 1631, 1532, 1367, 1252, 1170, 824 cm^{-1}.

^{1}H-NMR (500 MHz, $CDCl_3$): 6.87 (m, 2H), 6.69 (m, 1H), 4.87 (s, 1H), 4.47 (m, 1H), 4.00 (m, 2H), 2.77 (d, J = 4.0 Hz, 3H), 1.91~1.57 (m, 3H), 1.45 (s, 9H), 1.37 (d, J = 7.5 Hz, 3H), 0.96~0.88 (m, 15H), 0.16(s, 3H), 0.12(s, 3H);

^{13}C-NMR (300 MHz, $CDCl_3$): 174.2, 173.2, 171.6, 156.9, 81.9, 52.8, 52.2, 45.7, 40.1, 28.5, 26.9, 26.6, 25.1, 23.7, 20.9, 18.0, 17.6, -6.6, -7.1;

MS (FAB+/NBA/NaBr) 509 (100, MNa+), 487 (1, MH+), 409 (9), 395 (8), 287 (3), 167(6);

Exact Mass Calcd. for $C_{23}H_{46}N_4O_5NaSi$: (MNa^+) 509.3135; Found: 509.3139;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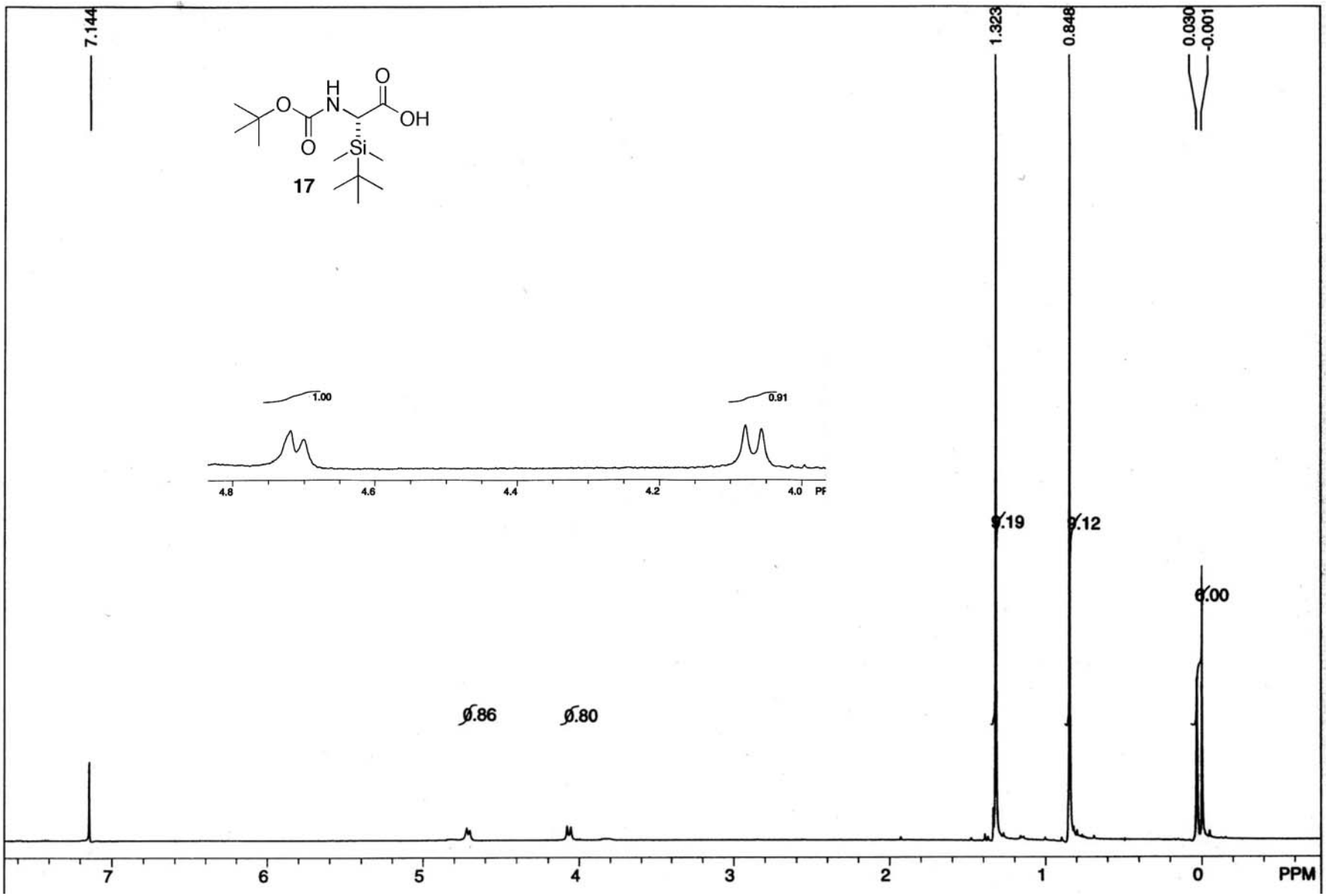
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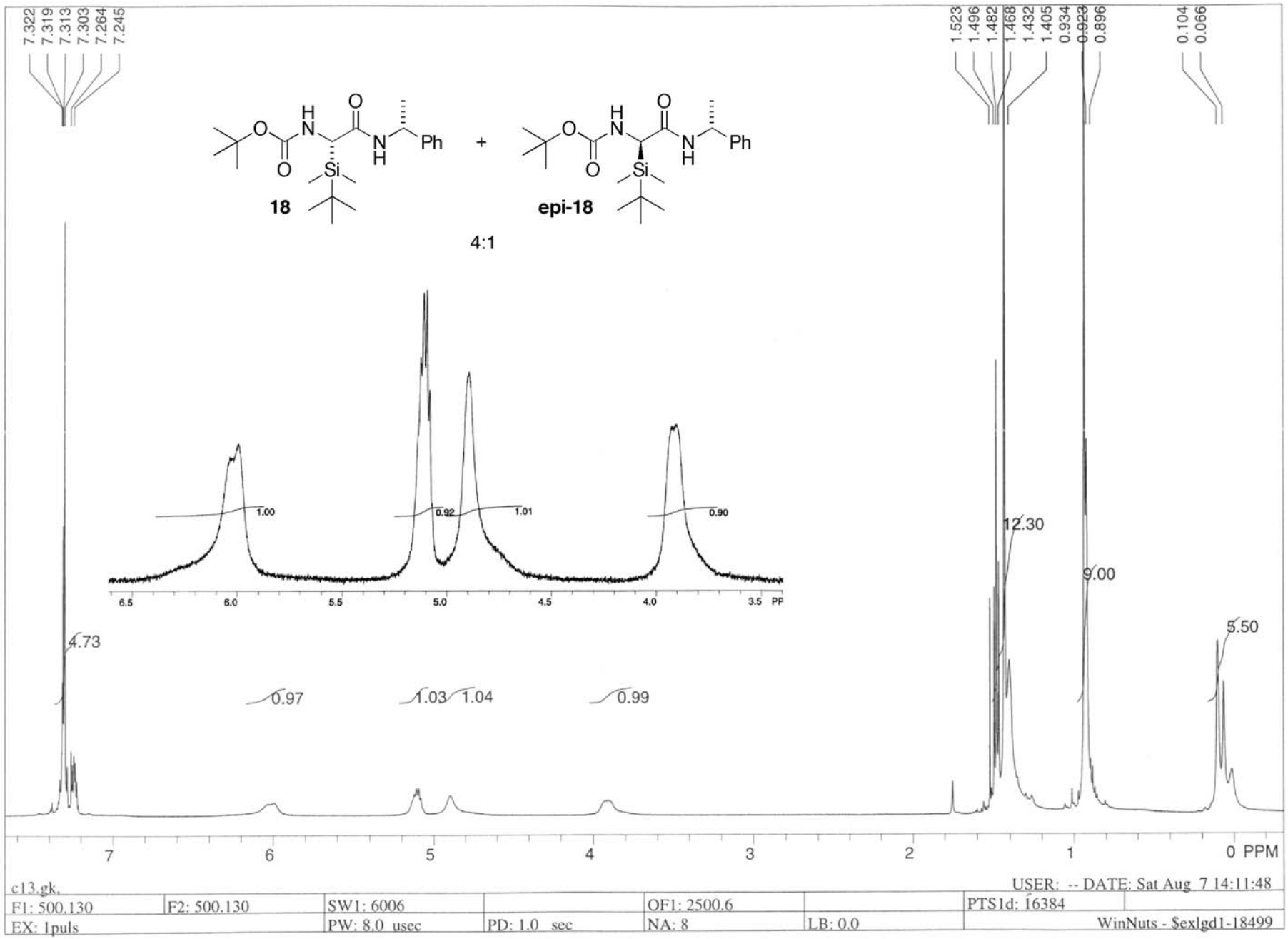
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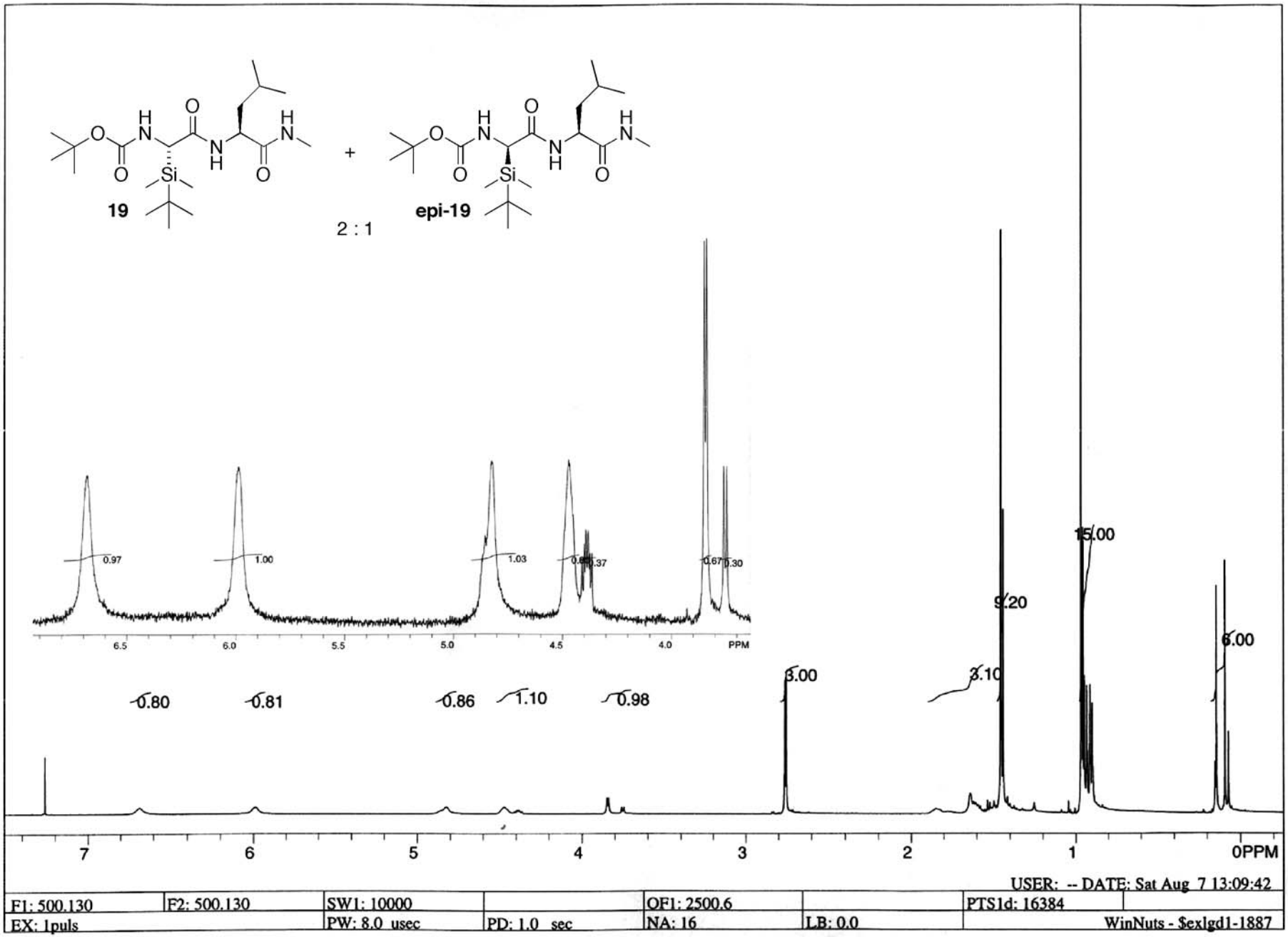
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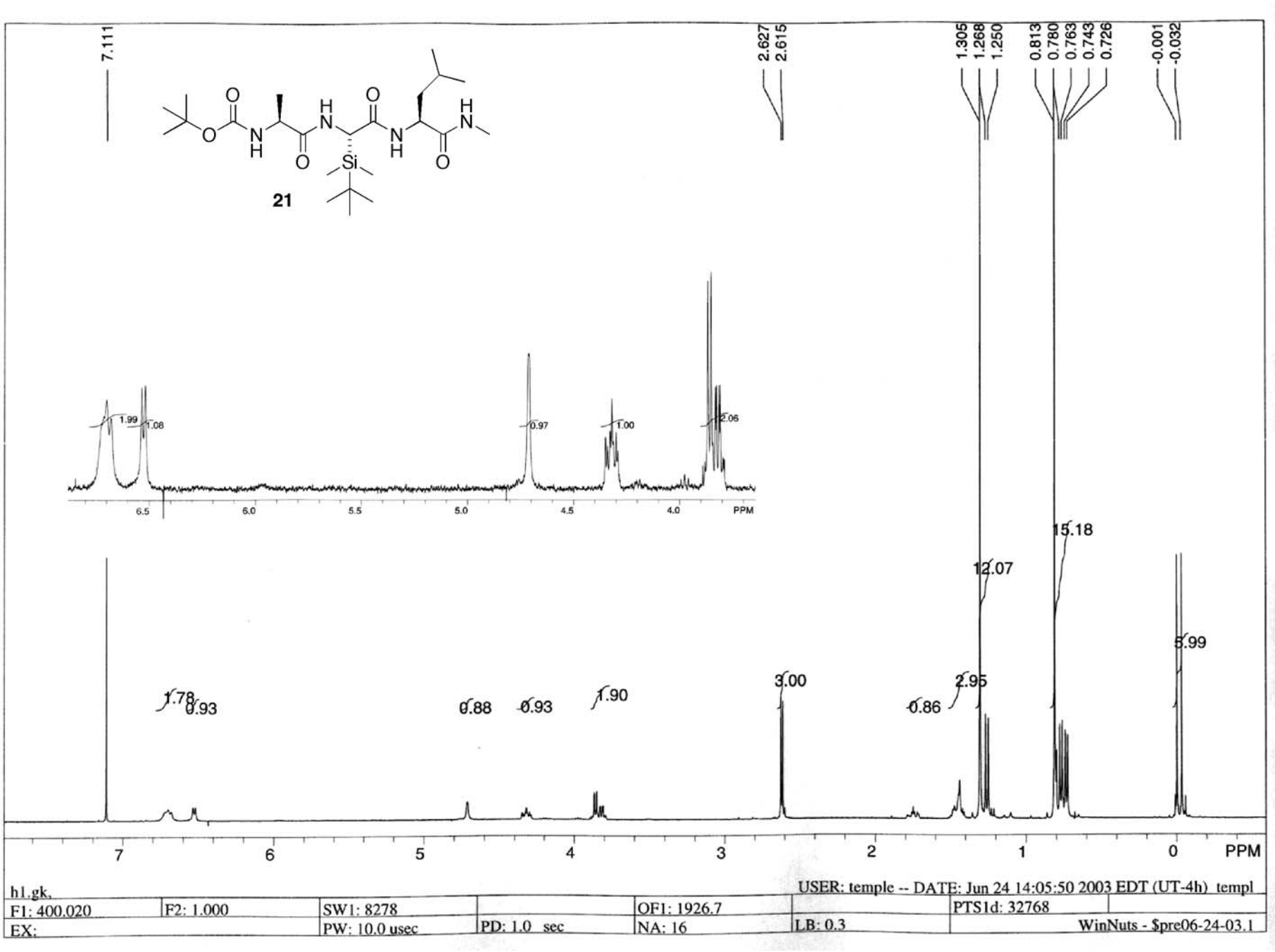
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