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Total Synthesis and Stereochemical Assignment of Scytonemin A

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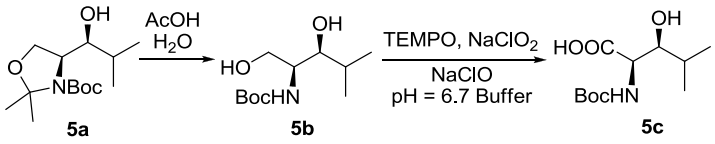
1. General Experimental

All reactions were conducted in flame-dried or oven-dried glassware under an atmosphere of dry nitrogen or argon. Oxygen and/or moisture sensitive solids and liquids were transferred appropriately. Concentration of solutions *in vacuo* was accomplished using a rotary evaporator fitted with a water aspirator. Residual solvents were removed under high vacuum (0.1-0.2 mm Hg). All reaction solvents were purified before use: Tetrahydrofuran were distilled from sodium benzophenone ketyl. Toluene was distilled over molten sodium metal. Dichloromethane, dimethylformamide, diethylamine, triethylamine and diisoproylethylamine were distilled from CaH_2. Methanol was distilled from Mg/I_2. Flash column chromatography was performed using the indicated solvents on E. Qingdao silica gel 60 (230 – 400 mesh ASTM). TLC was carried out using pre-coated sheets (Qingdao silica gel 60-F250, 0.2 mm). Compounds were visualized with UV light, iodine, *p*-anisaldehyde stain, ceric ammonium molybdate stain, or phosphomolybdic acid in EtOH. 1H NMR spectra were recorded on Bruker DPX 300 MHz, AV 500 MHz or AV 600 MHz spectrometers. Chemical shifts were reported in parts per million (ppm), relative to either a tetramethylsilane (TMS) internal standard or the signals due to the solvent. The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublets; other combinations are derived from those listed above. Coupling constants (*J*) are reported in Hertz. 13C NMR spectra were completely heterodecoupled and measured at 75, 125, or 150 MHz. High resolution mass spectra were measured on ABI Q-star Elite. Optical rotations were recorded on a Perkin-Elmer 351 polarimeter at 589 nm, 100 mm cell at 20^oC. Data were reported as follow: optical rotation (c (g/100 mL), solvent).

2. Experimental procedures

2.1. Synthesis of pentapeptide 2

2.1.1 Synthesis of Boc-*D-(2R,3S)-threo*-3-hydroxyleucine (HyLeu) and dipeptide 5



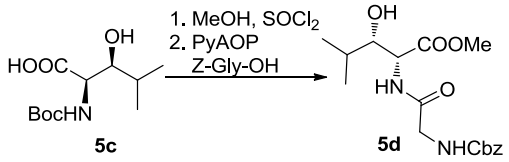
Alcohol **5a**[1] (1.50 g, 5.49 mmol) was dissolved in AcOH-H_2O (25 mL, 5/1, v/v) and stirred at room temperature for 24 h. The reaction was cooled to 0 ^oC and quenched by addition of $NaHCO_3$ (s) to adjust pH 10–11. The aqueous residue was extracted with ethyl acetate (2 x 100 mL). The combined organic phases were washed with brine (30 mL), dried over Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:2 to 1:1) to give 1,3-diol **5b** (1.15 g, 90%) as a colorless oil.

R_f 0.5 (ethyl acetate / hexane, 2:1); $[\alpha]_D^{20}$ = +16.8 (*c* 1.10, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.21 (brs, 1H), 3.89 – 3.69 (m, 3H), 3.49 (d, *J* = 8.1 Hz, 1H), 2.66 (d, *J* = 3.8 Hz, 1H), 2.47 (t, *J* = 5.1 Hz, 1H), 1.81 – 1.69 (m, 1H), 1.45 (s, 9H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H) ; **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.4, 79.6, 77.5, 64.9, 52.0, 30.9, 28.3, 18.9, 18.8; **HRMS (ESI)**: *m/z* calcd for $C_{11}H_{23}NO_4Na^+$ $[M+Na]^+$ 256.1519, found 256.1527.

1,3-Diol **5b** (1.50 g, 6.43 mmol) was dissolved in MeCN (100 mL) and aqueous solution of NaH_2PO_4-Na_2HPO_4 (60 mL, pH 6.7). To this solution, TEMPO (300.0 mg, 1.93 mmol), $NaClO_2$ (2.36 g, 19.30 mmol) and bleach solution (1.4 mL, 10% in water) were sequentially added. The reaction mixture was gently heated at 35 ℃ and stirred for 3 h (monitored by TLC). The reaction was then quenched at 0 ^oC by acidification to pH 1−2 with HCl (1M, aqueous solution). The aqueous solution was extracted with ethyl acetate (2 x 300 mL). The combined organic layers were washed with saturated aqueous solution of $Na_2S_2O_3$ (20 mL), brine (20 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure to give Boc-*D-(2R,3S)-threo*-3-hydroxyleucine (HyLeu) **5c** (1.45 g), which was used in the next

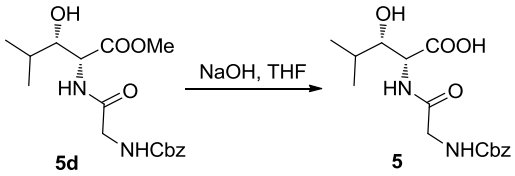
[1]Willams, L.; Zhang, Z.; Shao, F.; Carroll, P. J.; Joullit, M. M. *Tetrahedron* **1996**, *52*, 11673–11694.

step of reaction without further purification.



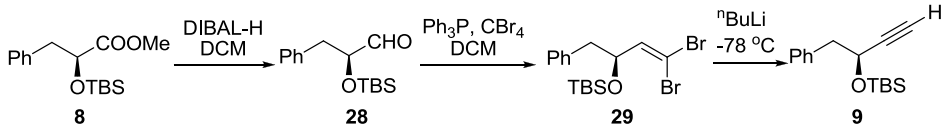
$SOCl_2$ (1.9 mL, 25.72 mmol) was added to a solution of acid **5c** (1.45 g) in MeOH (100 mL) at 0 ^oC. The reaction mixture was refluxed for 10 h before it was concentrated under reduced pressure. To a solution of the crude amine hydrochloride salt and Cbz-Gly-OH (1.70 g, 7.71 mmol) in CH_2Cl_2 (30 mL), DIPEA (4.5 mL, 25.72 mmol) and PyAOP (5.03 g, 9.65 mmol) were added sequentially at 0 ^oC. The reaction mixture was warmed to room temperature and stirred for 24 h. The reaction was quenched by addition of water (1 mL) and diluted with ethyl acetate (200 mL). The organic phase washed with saturated aqueous solution of NH_4Cl (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:1 to 2:1) to afford dipeptide **5d** (1.71 g, 73% 3 steps) as a colorless oil.

$\boldsymbol{R_f}$ 0.3 (ethyl acetate / hexane, 2:1); $[\alpha]_D^{20} = -2.0$ (*c* 0.87, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 7.03 (d, *J* = 9.1 Hz, 1H), 5.76 (brs, 1H), 5.12 (s, 2H), 4.81 (dd, *J* = 9.1, 1.9 Hz, 1H), 3.94 (brs, 2H), 3.73 (s, 4H), 3.08 (brs, 1H), 1.70 – 1.51 (m, 1H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.91 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.2, 169.6, 156.6, 136.0, 128.4, 128.1, 128.0, 77.3, 67.1, 54.3, 52.6, 44.2, 30.8, 18.8; **HRMS (ESI)** *m/z* calcd for $C_{17}H_{25}N_2O_6^+[M+H]^+$ 353.1707, found 353.1704.



To a stirred solution of **5d** (88.0 mg, 0.25 mmol) in THF (5 mL), NaOH (2.5 mL, 1 M in water) was added at room temperature. The reaction mixture was stirred at room temperature for 4 h. Then it was acidified to pH 1−2 with HCl (1.0 M in water) and extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure to afford the desired acid **5** (81.0 mg, 92%), which was used directly in the next step without further purification.

2.1.2 Synthesis of Ahda fragment and pentapeptide 2



DIBAL-H (85.0 mL, 85.00 mmol, 1.0 M in toluene) was added to a solution of ester **8** (20.00 g, 67.92 mmol) in CH_2Cl_2 (120 mL) at −78 ℃. The reaction mixture was stirred at −78 ℃ for 5 h and quenched by addition of MeOH (2 mL) with careful. The reaction solution was then treated by saturated aqueous solution of Rochelle salt (150 mL) with vigorous stirring for 2 h. Layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 300 mL). The combined organic layers were successively washed with water (30 mL), saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (20 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure to produce the corresponding crude aldehyde **28**, which was subjected to next step of reaction without further purifications.

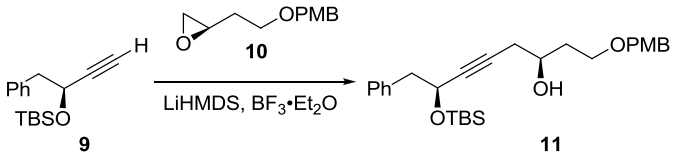
CBr_4 (39.8 g, 120.00 mmol) was slowly added to a solution of Ph_3P (62.94 g, 240.00 mmol) in CH_2Cl_2 (250 mL) at 0 ℃. The reaction mixture was then stirred at room temperature for 30 min. A solution of aldehyde **28** and DIPEA (15.7 mL, 90.00 mmol) in CH_2Cl_2 (100 mL) was added at 0 ℃. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The solution was poured into hexane (500 mL), the precipitation formed was removed by filtration. The filtrate was collected and the solid was dissolved in CH_2Cl_2 (250 mL), poured into hexanes (250 mL) and filtered again to remove the precipitation. The above procedures were repeated once with CH_2Cl_2 (125 mL)-hexane (125 mL). The combined filtrate was concentrated under reduced pressure to yield a yellow oil contaminated by solid precipitations. The residue was purified by column chromatography (silica gel, hexane) to give the dibromoalkene **29** (21.5 g, 76% in two steps) as a colorless oil.

$\boldsymbol{R_f}$ 0.6 (Hexane); $[\alpha]_D^{20}$ = +2.1 (*c* 2.05, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 5H), 6.46 (d, *J* = 7.9 Hz, 1H), 4.46 (td, J = 7.9, 4.6 Hz, 1H), 2.90 – 2.70 (m, 2H), 0.83 (s, 9H), -0.08 (s, 3H), -0.18 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.6, 137.4, 130.0, 128.1, 126.4, 88.4, 75.0, 43.1, 25.7, 18.0, -4.9, -5.4; **HRMS (ESI)** *m/z* calcd for $C_{16}H_{24}Br_2OSiNa^+$ $[M+Na]^+$ 440.9855, found 440.9837.

^{n}BuLi (44.6 mL, 111.50 mmol, 2.5 M in hexane) was added dropwise to a solution of dibromoalkene **29** (21.20 g, 50.71 mmol) in THF (250 mL) at −78 ^{o}C. 1 h later, the reaction was quenched by addition of

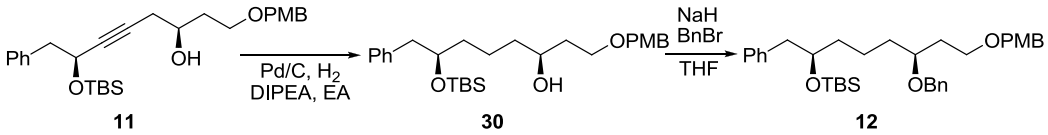
saturated aqueous solution of NH_4Cl (5 mL). Volatiles were removed under reduced pressure, the residue was dissolved in ethyl acetate (500 mL). The solution was successively washed with H_2O (25 mL) and brine (25 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:60 to 1:40) afforded **9** (11.87 g, 90%) as a colorless oil.

$\boldsymbol{R_f}$ 0.5 (hexane); $[\alpha]_D^{20}$ = −9.1 (*c* 1.61，$CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.38-7.19 (m, 5H), 4.49 (ddd, *J* = 7.7, 5.9, 2.1 Hz, 1H), 3.07 – 2.91 (m, 2H) , 2.44 (d, *J* = 2.1 Hz, 1H), 0.86 (s, 9H), -0.01 (s, 3 H), -0.06 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 137.4, 129.9, 128.1, 126.6, 85.1, 72.7, 64.1, 45.1, 25.7, 18.2, -5.1, -5.3; **HRMS (ESI)** *m/z* calcd for $C_{16}H_{24}OSiNa^+$ $[M+Na]^+$ 283.1489, found: 283.1480.



To a solution of alkyne **9** (3.12 g, 12.00 mmol) in THF (50 mL) at −78 ℃, LiHMDS (24.0 mL, 24.00 mmol, 1.0 M in THF) was added dropwise and the reaction mixture was stirred for 1 h. BF_3•Et_2O (2.2 mL, 17.50 mmol) was added and stirred for 30 min at −78 ℃. A solution of epoxide **10** (2.00 g, 9.60 mmol) in THF (20 mL) was added slowly. The reaction was stirred for further 3 h at −78 ℃ and quenched by addition of saturated aqueous solution of NH_4Cl (1 mL). Volatiles were removed under reduced pressure, the residue was diluted with water (15 mL) and extracted with ethyl acetate (3 x 100 mL). The organic layers were combined and washed with brine (15 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:10 to 1:4) to afford compound **11** (4.27 g, 95% from **10**) as a colorless oil.

$\boldsymbol{R_f}$ 0.4 (ethyl acetate / hexane, 1:4); $[\alpha]_D^{20}$ = −24.2 (*c* 1.22, $CHCl_3$);**^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.24 – 7.13 (m, 7H), 6.86 – 6.81 (m, 2H), 4.49 – 4.43 (m, 1H), 4.39 (s, 2H), 3.88 – 3.80 (m, 1H), 3.73 (s, 3H), 3.61 (ddd, *J* = 9.3, 6.3, 4.7 Hz, 1H), 3.53 (ddd, *J* = 9.4, 7.6, 4.5 Hz, 1H), 2.95 – 2.86 (m, 3H), 2.40 – 2.27 (m, 2H), 1.79 (dddd, *J* = 14.2, 6.4, 4.5, 3.2 Hz, 1H), 1.70 (dddd, *J* = 14.4, 8.5, 7.6, 4.7 Hz, 1H), 0.81 (s, 9H), -0.07 (s, 3H), -0.09 (s, 3H) ; **^{13}C NMR** ($CDCl_3$, 150 MHz) δ 159.2, 137.7, 130.0, 129.7, 129.1, 127.9, 126.3, 113.7, 83.6, 81.4, 72.8, 69.3, 68.0, 64.3, 55.1, 45.3, 35.2, 27.3, 25.6, 18.1, -5.1, -5.3; **HRMS (ESI)** *m/z* calcd for $C_{28}H_{40}O_4SiNa^+$ $[M+Na]^+$ 491.2588, found 491.2595.



11 **30** **12**

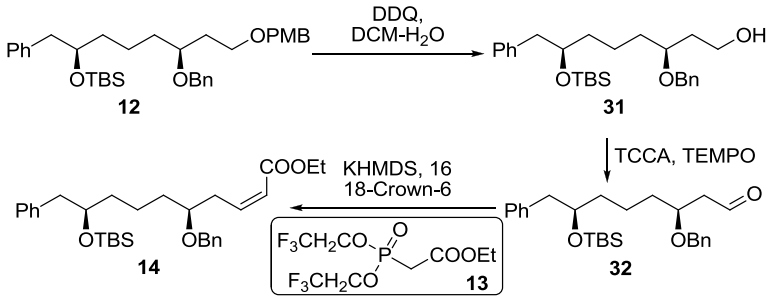
To a solution of **11** (8.99 g, 19.18 mmol) in ethyl acetate (200 mL), palladium on charcoal (1 g, 10% Pd) and *N*,*N*-diisopropylethylamine（5.0 mL, 28.70 mmol）were added. The reaction vessel was sealed and the inner atmosphere was switched to H_2 and stirred for 48 h at room temperature. The catalyst was removed by filtration through a pad of Celite and washed with ethyl acetate (3 x 50 mL). The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:4) to afford product **30** (8.88 g, 98%) as a colorless oil.

$\boldsymbol{R_f}$ 0.4 (ethyl acetate / hexane, 1:4); $[\boldsymbol{\alpha}]_D^{20}$ = −10.3 (*c* 1.54, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 4H), 7.13 – 7.07 (m, 3H), 6.83 – 6.78 (m, 2H), 4.38 (s, 2H), 3.77 (dq, *J* = 7.2, 5.6 Hz, 1H), 3.73 (s, 3H), 3.71 (dd, *J* = 4.5, 2.7 Hz, 1H), 3.62 (dt, *J* = 9.3, 5.2 Hz, 1H), 2.80 (d, *J* = 3.2, 1H), 2.71 – 2.59 (m, 2H), 1.69 – 1.62 (m, 2H), 1.52 – 1.26 (m, 6H), 0.78 (s, 9H), -0.12 (s, 3H), -0.27 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.3, 139.5, 130.1, 129.8, 129.3, 128.1, 126.0, 113.9, 73.7, 73.0, 71.4, 69.0, 55.3, 43.8, 37.6, 37.0, 36.4, 25.9, 21.2, 18.1, -4.7, -4.9; **HRMS (ESI)** *m/z* calcd for $C_{28}H_{44}NaO_4Si^+$ $[M+Na]^+$ 495.2901, found 495.2887.

Alcohol **30** (10.01 g, 21.15 mmol) in THF (50 mL) was added to NaH (2.50 g, 62.50 mmol, 60 wt% in mineral oil) suspended in THF (200 mL) at 0 ℃. 20 min later, BnBr (3.8 mL, 31.99 mmol) was added slowly. The reaction mixture was allowed to warm to 45 ^oC and stirred for 12 h. The reaction was quenched with saturated aqueous solution of NH_4Cl (1 mL) at 0 ^oC. Volatiles were removed under reduced pressure, the residue was diluted with water (20 mL) and extracted with ethyl acetate (2 x 200 mL). The combined organic phases were washed successively with water (15 mL), saturated aqueous solution of NH_4Cl (15 mL) and brine (15 mL), dried over anhydrous $NaSO_4$ (s) and concentrated reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:50 to 1:10) to give product **12** (10.71 g, 90%) as a colorless oil.

$\boldsymbol{R_f}$ 0.6 (ethyl acetate / hexane, 1:10); $[\boldsymbol{\alpha}]_D^{20}$ = +7.4 (*c* 1.62, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 9H), 7.17 – 7.08 (m, 3H), 6.91 – 6.79 (m, 2H), 4.45 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 3.82 – 3.76 (m, 1H), 3.74 (s, 3H), 3.56 – 3.45 (m, 3H), 2.67 (d, *J* = 6.3 Hz, 2H), 1.84 – 1.71 (m, 2H), 1.54 – 1.28 (m, 6H), 0.81 (s, 9H), -0.09 (s, 3H), -0.23 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 139.4, 139.0, 130.7, 129.8, 129.3, 128.3, 128.1, 127.8, 127.4, 126.0, 113.8, 76.4, 73.8, 72.7, 71.3, 66.8, 55.3, 44.0, 37.2, 34.5, 34.5, 25.9, 21.1, 18.1, -4.6, -4.8; **HRMS (ESI)** *m/z* calcd for $C_{35}H_{50}O_4SiNa^+$ $[M+Na]^+$ 585.3371, found 585.3354.



DDQ (3.16 g, 13.92 mmol) was added to a solution of compound **12** (6.02 g, 10.70 mmol) in CH_2Cl_2-H_2O (180 mL, 8/1, v/v) at 0 ℃. 10 min later, the reaction mixture was brought to ambient temperature and stirred for 3 h. The reaction mixture was diluted with CH_2Cl_2 (500 mL) and washed with a 1:1 mixture of saturated aqueous solution of $NaHCO_3$ and saturated aqueous solution of $Na_2S_2O_3$ (3 x 100 mL) and brine (20 mL), dried over anhydrous Na_2SO_4. The organic layer was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:8 to 1:4) to yield alcohol **31** (4.07 g, 86%) as a colorless oil.

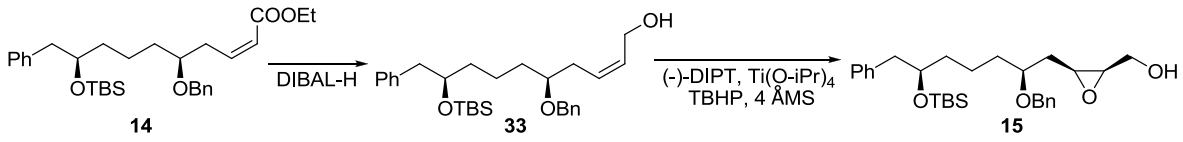
***R*$_f$** 0.4 (ethyl acetate / hexane, 1:4); $[\alpha]_D^{20}$ = +19.6 (*c* 1.51, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.30 – 7.23 (m, 3H), 7.20 – 7.13 (m, 3H), 4.56 (d, *J* = 11.4 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 3.88 – 3.74 (m, 2H), 3.75 – 3.67 (m, 1H), 3.66 – 3.57 (m, 1H), 2.78 – 2.65 (m, 2H), 2.38 (brs, 1H), 1.86 – 1.66 (m, 2H), 1.66 – 1.55 (m, 1H), 1.55 – 1.30 (m, 5H), 0.85 (s, 9H), -0.04 (s, 3H), -0.17 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.3, 138.4, 129.7, 128.5, 128.1, 127.9, 127.7, 126.0, 78.5, 73.7, 71.0, 60.7, 44.0, 37.0, 36.0, 33.7, 25.9, 20.9, 18.1, -4.6, -4.8; **HRMS (ESI)** *m/z* calcd for $C_{27}H_{42}O_3SiNa^+$ $[M+Na]^+$ 465.2795, found 465.2786.

Trichloroisocyanuric acid (2.02 g, 8.70 mmol) and TEMPO (31.0 mg, 0.20 mmol) were subsequently added to a solution of alcohol **31** (3.19 g, 7.20 mmol) in CH_2Cl_2 (70 mL) at 0^{o}C. The reaction mixture was stirred at 0 ℃ for 30 min before it was filtered through a pad of Celite and washed with CH_2Cl_2 (2 x 100 mL). The combined filtrate was washed successively with saturated aqueous solution of $NaHCO_3$ (30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure to give the

crude aldehyde **32** (*ca*. 3.06 g), which was used directly in the next step without further purification.

To a solution of phosphate **13** (3.62 g, 10.90 mmol) and 18-crown-6 (3.82 g, 14.50 mmol) in THF (100 mL) at −78 ℃, KHMDS (21.8 mL, 10.90 mmol, 0.5 M) was added. 30 min later, a solution of the above aldehyde **32** in THF (50 mL) was slowly added via a syringe. The reaction mixture was stirred for 2 h at −78 ℃, then it was carefully quenched by addition of saturated aqueous solution of NH_4Cl (2 mL) and allowed to warm to room temperature. Volatiles were removed under reduced pressure. The residue was dissolved in ethyl acetate (500 mL). The organic solution was washed successively with water (15 mL), saturated aqueous solution of NH_4Cl (15 mL) and brine (15 mL), dried over anhydrous $NaSO_4$ (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:10) to give the desired product **14** (2.68 g, 73% 2 steps) as a colorless oil and the undesired *E* configuration byproduct (ca. 0.2g).

***R*f** 0.7 (ethyl acetate / hexane, 1:10); $[\alpha]_D^{20}$= −10.7 (*c* 0.57, $CHCl_3$) ; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ7.43 – 7.26 (m, 7H), 7.26 – 7.15 (m, 3H), 6.39 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.89 (dt, *J* = 11.6, 1.7 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.92 – 3.78 (m, 1H), 3.64 – 3.49 (m, 1H), 3.11 – 2.92 (m, 2H), 2.74 (d, *J* = 6.3 Hz, 2H), 1.70 – 1.36 (m, 6H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), -0.01 (s, 3H), -0.16 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 166.3, 146.2, 139.3, 138.6, 129.7, 128.3, 128.0, 127.7, 127.5, 125.9, 121.1, 78.1, 73.7, 70.8, 59.8, 43.9, 37.0, 34.3, 32.9, 25.9, 21.3, 18.0, 14.2, -4.8, -4.9; **HRMS (ESI)** *m/z* calcd for $C_{31}H_{46}O_4SiNa^+$ $[M+Na]^+$ 533.3058, found 533.3042.



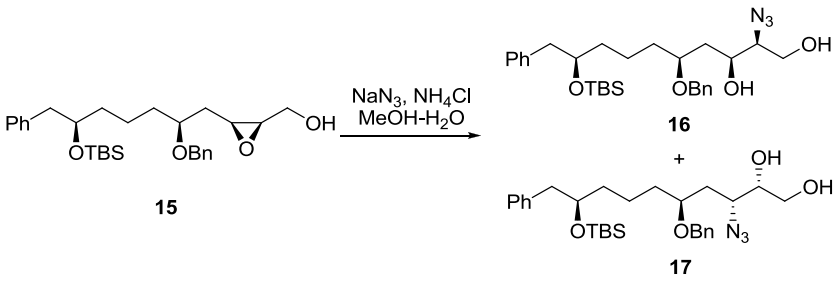
DIBAL-H (27.5 mL, 27.50 mmol, 1.0 M in toluene) was added slowly to a solution of ester **14** (4.01 g, 7.85 mmol) in THF (50 mL) at −78 ℃. The reaction mixture was then warmed to −36 ℃ and stirred for 4 h, it was quenched by careful addition of methanol (1 mL). The reaction mixture was stirred for 30 min, then it was poured into saturated aqueous solution of Rochelle salt (50 mL). The mixture was virgously stirred at room temperature for 2 h. Volatiles were removed under reduced pressure. The aqueous residue was extracted with ethyl acetate (2 x 200 mL). The combined organic extracts were washed with saturated aqueous solution of NH_4Cl (30 mL) and brine (30 mL), dried over anhydrous Na_2SO_4 (s) and concentrated

under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:10 to 1:5) gave alcohol **33** (3.38 g, 92%) as a colorless oil.

$\boldsymbol{R_f}$ 0.3 (ethyl acetate / hexanes, 1:5); $[\alpha]_D^{20}$ = −9.3 (*c* 1.00, $CHCl_3$) ; **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.31 – 7.25 (m, 4H), 7.25 – 7.17 (m, 3H), 7.16 – 7.09 (m, 3H), 5.74 – 5.70 (m, 1H), 5.58 – 5.52 (m, 1H), 4.45 (s, 2H), 4.11 – 4.01 (m, 2H), 3.78 (dddd, *J* = 5.8, 5.8, 5.8, 5.8 Hz, 1H), 3.36 (dddd, *J* = 5.4, 5.4, 5.4, 5.4 Hz, 1H), 2.70 – 2.63 (m, 2H), 2.35 – 2.30 (m, 1H), 2.26 – 2.20 (m, 1H), 1.97 (brs, 1H), 1.20 – 1.53 (m, 6H), 0.82 (s, 9H), -0.08 (s, 3H), -0.21 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 139.3, 138.4, 130.9, 129.8, 128.9, 128.4, 128.2, 127.9, 127.7, 126.1, 78.4, 73.7, 71.4, 58.2, 44.0, 37.0, 34.1, 32.0, 25.9, 21.2, 18.1, -4.6, -4.8; **HRMS (ESI)** *m/z* calcd for $C_{29}H_{44}O_3SiNa^+$ $[M+Na]^+$ 491.2952, found: 491.2941.

D-(–)-diisopropyl tartrate (1.8 mL, 8.65 mmol) was added to a solution of $Ti(O^iPr)_4$ (2.1 mL, 7.73 mmol) and 4Å molecular sieves (3.00 g) in CH_2Cl_2 (20 mL) at –20 ℃. 30 min later, *tert*-butyl hydroperoxide (3.7 mL, ~5.5 M in decane) was dropwise added at –20 ℃. After being stirred for another 20 min, a solution of allylic alcohol **33** (3.02 g, 6.44 mmol) in CH_2Cl_2 (80 mL) was dropwise added to the solution via a syringe. The reaction mixture was then stirred slowly for 24 h at –20 ℃ and maintained in a refrigerator at –20 ℃ for 6 days. The reaction was quenched by addition of an aqueous solution of 3 M NaOH (*aq.*) -brine (100 mL, 3/7, v/v). The reaction mixture was allowed to warm to room temperature, diluted with CH_2Cl_2 (500 mL) and stirred for another 1.5 h. The reaction mixture was then filtered through a pad of Celite, the filtration residue was eluted with CH_2Cl_2 (100 mL). The filtrate was partitioned and layers were seperated. The organic phase was washed with brine (30 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / CH_2Cl_2, 1:10) to afford the desired epoxide **15** (2.68 g, 86%, *dr* = 12:1) as a colorless oil.

$\boldsymbol{R_f}$ 0.6 (ethyl acetate / CH_2Cl_2, 1:10) ; $[\alpha]_D^{20}$ = +0.3 (*c* 0.63, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.35 – 7.24 (m, 7H), 7.20 – 7.14 (m, 3H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 3.82 (dddd, *J* = 6.0, 6.0, 6.0, 11.6 Hz, 1H), 3.74 – 3.69 (m, 1H), 3.64 – 3.59 (m, 1H), 3.56 (dddd, *J* = 5.5, 5.5, 5.5, 11.0 Hz, 1H), 3.25-3.09 (m, 2H), 2.76 – 2.65 (m, 2H), 2.36 (dt, *J* = 8.1, 4.4 Hz, 1H), 1.93 (ddd, *J* = 5.5, 5.5, 16.6 Hz, 1 H), 1.73 (ddd, *J* = 5.5, 7.6, 16.6 Hz, 1H), 1.69 – 1.28 (m, 6H), 0.85 (s, 9H),-0.04 (s, 3H), -0.16 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 139.2, 138.0, 129.7, 128.5, 128.2, 128.0, 127.9, 126.1, 76.8, 73.6, 71.3, 60.5, 55.9, 53.6, 44.1, 36.9, 33.5, 31.6, 25.9, 21.5, 18.1, -4.6, -4.8; **HRMS (ESI)** *m/z* calcd for$C_{29}H_{44}O_4SiNa^+$ $[M+Na]^+$ 507.2901, found 507.2899.



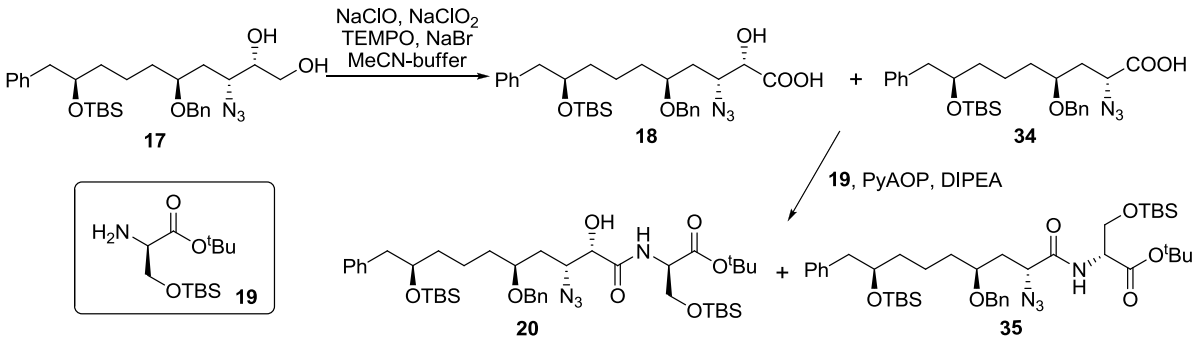
NH_4Cl (s) (1.00 g, 18.58 mmol) and NaN_3 (s) (2.01 g, 31.0 mmol) were sequentially added to a solution of **15** (1.50 g, 3.10 mmol) in MeOH-H_2O (27 mL, 8/1, v/v) at room temperature. The reaction mixture was refluxed for 24 h. After it was cooled to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethyl acetate (200 mL) and then washed with brine (20 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / CH_2Cl_2: 1:4) to give the required product **17** (1.10 g, 67%) along with its regio-isomer **16** (0.26 g, 16%) as colorless oils.

Analytical data for 1,3-diol **16**:

$\boldsymbol{R_f}$ 0.7 (ethyl acetate / CH_2Cl_2, 1:4); $[\alpha]_D^{20}$ = +16.6 (*c* 0.50, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.41 – 7.24 (m, 7H), 7.24 – 7.12 (m, 3H), 4.64 (d, J = 11.2 Hz, 1H), 4.40 (d, *J* = 11.2 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.94 – 3.79 (m, 4H), 3.76 – 3.65 (m, 1H), 3.32 – 3.24 (m, 1H), 2.80 – 2.69 (m, 2H), 2.37 (t, *J* = 5.4 Hz, 1H), 1.87 (dt, *J* = 14.6, 9.8 Hz, 1H), 1.72 – 1.53 (m, 3H), 1.53 – 1.35 (m, 4H), 0.88 (s, 9H), -0.01 (s, 3H), -0.13 (s, 3H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 139.2, 137.7, 129.7, 128.6, 128.2, 128.0, 127.9, 126.1, 79.4, 73.6, 72.8, 70.7, 66.1, 63.2, 44.1, 37.4, 37.0, 33.6, 25.9, 20.3, 18.1, -4.6, -4.7; **HRMS (ESI)**: *m/z* calcd for $C_{29}H_{46}N_3O_4Si^+$ $[M+H]^+$ 528.3252, found 528.3259.

Analytical data for 1,2-diol **17** :

$\boldsymbol{R_f}$ 0.5 (ethyl acetate / CH_2Cl_2, 1:4); $[\alpha]_D^{20}$= +36.8 (*c* 0.67, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.25-7.36 (m, 7 H), 7.15-7.25 (m, 3 H), 4.60 (d, *J* = 11.1 Hz, 1 H), 4.40 (d, *J* = 11.1 Hz, 1 H), 3.83-3.85 (m, 1 H), 3.60-3.66 (m, 4 H), 3.53-3.58 (m, 1 H), 2.68-2.76 (m, 2 H), 2.21 (brs, 2 H), 1.69-1.79 (m, 2 H), 1.66-1.68 (m, 1 H), 1.64-1.65 (m, 1 H), 1.36-1.55 (m, 4 H), 0.86 (s, 9H), -0.03 (s, 3 H), -0.16 (s, 3 H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 139.2, 138.3, 129.7, 128.5, 128.1, 127.9, 127.8, 126.0, 75.9, 74.5, 73.6, 71.2, 64.0, 61.1, 44.0, 37.0, 36.0, 33.9, 25.9, 20.5, 18.1, -4.7, -4.8; **HRMS (ESI)** *m/z* calcd for $C_{29}H_{45}N_3O_4SiNa^+$ $[M+Na]^+$ 550.3072, found 550.3061.



1,2-diol **17** (200.0 mg, 0.38 mmol) was dissolved in saturated aqueous solution of Na_2HPO_4-MeCN (7 mL, 1/1, v/v), then the solution was adjusted to pH 8–9 with NaOH (1 M aqueous solution). TEMPO (3.0 mg, 0.019 mmol), $NaClO_2$ (91.0 mg, 1.10 mmol) and NaBr (103.0 mg, 1.00 mmol) were sequentially added to the solution at room temperature. A solution of bleach (40 μL, 10% in water) was added to the reaction mixture every 3 h until all the starting material was consumed (monitored by TLC). After being acidified to pH 1–2 with HCl (1.0 M aqueous solution) at 0 ^{o}C, the reaction mixture was extracted with ethyl acetate (2 x 50 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue contained an inseparable mixture of carboxylic acids **18** and **34** (*ca.* 185.0 mg in total), which was directly subjected to next step of reaction.

To a solution of the carboxylic acids obtained above and amine **19** (135.0 mg, 0.49 mmol) in CH_2Cl_2 (5 mL), DIPEA (260 μL, 1.52 mmol) and PyAOP (297.2 mg, 0.57 mmol) were added sequentially at 0 ^{o}C. The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was then quenched with H_2O (1 mL) and diluted with ethyl acetate (100 mL). The organic solution was washed sequentially with saturated aqueous solution of NH_4Cl (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:8 to 1:4) to afford the desired dipeptide **20** (227.6 mg, 75%) and **35** **(**35.1 mg, 12%) as colorless oils.

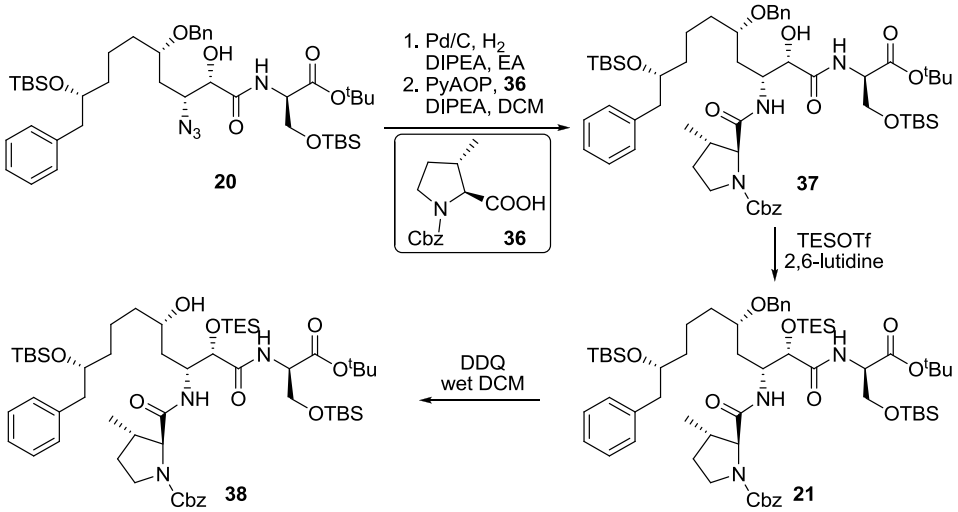
Analytical data for compound **20**:

***R*$_f$** 0.4 (ethyl acetate / hexane, 1:4); $[\alpha]_D^{20}$ = −2.3 (*c* 1.03, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 7H), 7.22 – 7.17 (m, 3H), 4.65 – 4.54 (m, 2H), 4.40 (d, *J* = 11.1 Hz, 1H), 4.14 (s, 1H), 4.12 – 4.04 (m, 2H), 3.93 – 3.79 (m, 2H), 3.60 (d, *J* = 4.3 Hz, 1H), 3.33 (brs, 1H), 2.83 – 2.68 (m, 2H), 1.95 – 1.79 (m, 2H), 1.62 – 1.63 (m, 2H), 1.49 (s, 14H), 0.88 (s, 9H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), -0.01 (s, 3H), -0.15 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.5, 168.9, 139.2, 138.0, 129.7, 128.5, 128.1, 127.9, 127.8,

126.1, 82.2, 76.0, 73.6(2), 71.0, 63.6, 61.1, 54.7, 44.0, 37.1, 35.4, 33.7, 28.0, 25.9, 25.7, 20.4, 18.1, 18.1, -4.7, -4.8, -5.6; **HRMS (ESI)** *m/z* calcd for $C_{42}H_{70}N_4O_7Si_2Na^+$ $[M+Na]^+$ 821.4675, found 821.4709.

Analytical data for compound **35**:

R_f 0.6 (ethyl acetate / hexane, 1:4); **^{1}H NMR** (300MHz, $CDCl_3$) δ 7.41 – 7.15 (m, 10H), 7.11 (d, *J* = 10.3 Hz, 1H), 4.64 (d, *J* = 11.3 Hz, 1H), 4.51 (dt, *J* = 8.1, 2.7 Hz, 1H), 4.44 (d, *J* = 11.3 Hz, 1H), 4.21 (dd, *J* = 10.8, 3.0 Hz, 1H), 4.06 (dd, *J* = 10.0, 2.5 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.81 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.73 – 3.60 (m, 1H), 2.74 (d, *J* = 6.3 Hz, 2H), 2.27 – 2.17 (m, 1H), 1.86 – 1.55 (m, 3H), 1.50 (s, 13H), 0.91 (s, 9H), 0.88 (s, 9H), 0.065 (s, 3H), 0.061 (s, 3H), -0.02 (s, 3H), -0.16 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.5, 168.8, 139.2, 138.3, 129.7, 128.3, 128.1, 127.7, 127.6, 126.0, 82.2, 75.0, 73.5, 70.7, 63.4, 61.3, 54.6, 43.8, 37.4, 37.0, 33.6, 27.9, 25.8, 25.6, 20.4, 18.1, 18.0, -4.8, -4.9, -5.6; **HRMS (ESI)** *m/z* calcd for $C_{41}H_{68}N_4O_6Si_2Na^+$ $[M+Na]^+$ 791.4570, found 791.4583.



To a solution of azide **20** (150.0 mg, 0.19 mmol) in ethyl acetate (5 mL), DIPEA (40 μL, 0.23 mmol), palladium on charcoal (20.0 mg, 10% Pd) was added at room temperature. The reaction vessel was sealed and the inner atmosphere was switched to H_2 and stirred for 24 h at room temperature. The catalyst was removed by filtration through a pad of Celite and washed with ethyl acetate (3 x 30 mL). The filtrate was concentrated under reduced pressure to produce the corresponding amine (*ca*. 137.0 mg)**,** which was used in next step of reaction without further purifications.

To a solution of amine (derived from **20** as indicated above) and carboxylic acid **36** (89.0 mg, derived from sponifiction of 100 mg correspoding methyl ester) in 5 mL CH_2Cl_2, DIPEA (130 μL, 0.76 mmol) and PyAOP (188.0 mg, 0.36 mmol) were sequentially added at 0 ^oC. The reaction mixture was warmed to room

temperature and stirred for 12 h, then it was quenched addition of water (1 mL) and diluted with ethyl acetate (100 mL). The organic solution was washed with saturated aqueous solution of NH_4Cl (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:4 to 1:2) to give dipeptide **37** (145.1 mg, 75% from **20**) as a colorless oil.

$\boldsymbol{R_f}$ 0.5 (ethyl acetate / hexane, 1:2); $[\boldsymbol{\alpha}]_D^{20}$ = −14.5 (*c* 1.00, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.66 – 7.52 (m, 1H), 7.40 – 7.12 (m, 15H), 6.88 – 6.62 (m, 1H), 5.54 – 5.41 (m, 0.6H), 5.21 – 5.01 (m, 2H), 4.97 – 4.85 (m, 0.4H), 4.59 – 4.39 (m, 2H), 4.30 – 4.11 (m, 2H), 4.09 – 3.97 (m, 1H), 3.87 – 3.72 (m, 2H), 3.70 – 3.41 (m, 4H), 2.77 – 2.62 (m, 2H), 2.47 – 2.26 (m, 1H), 2.13 – 1.92 (m, 2H), 1.84 – 1.72 (m, 1H), 1.61 – 1.31 (m, 17H), 1.08 – 0.99 (m, 3H), 0.87 (s, 9H), 0.84 (s, 9H), 0.03 (s, 6H), -0.06 (s, 3H), -0.22 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 173.2, 172.9, 172.0, 171.8, 168.6, 155.1, 154.8, 139.3, 138.4, 137.9, 136.4, 136.4, 129.7, 128.4, 128.4, 128.3, 128.0, 127.9, 127.6, 125.9, 81.8, 81.6, 76.1, 74.5, 73.6, 71.2, 67.6, 67.0, 63.5, 54.3, 54.1, 51.4, 50.9, 46.3, 45.9, 43.7, 39.6, 37.5, 37.3, 35.3, 34.6, 33.9, 33.5, 32.4, 31.6, 28.0, 25.9, 25.7, 20.3, 19.9, 18.6, 18.3, 18.1, 18.0, -4.8, -5.0, -5.7; **HRMS (ESI)** *m/z* calcd for $C_{56}H_{88}N_3O_{10}Si_2^+$ $[M+H]^+$ 1018.6003, found 1018.5999.

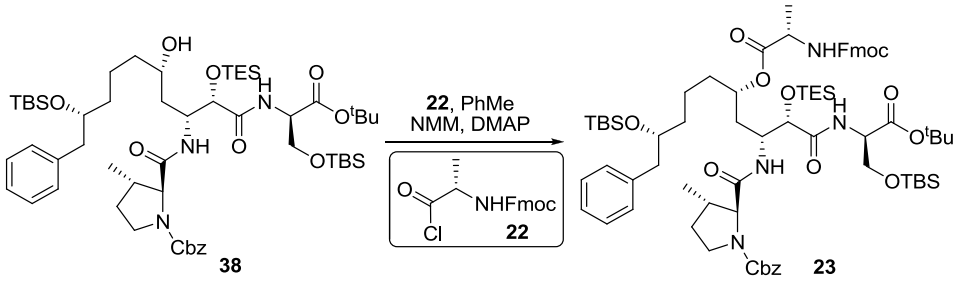
2,6-Lutidine (210.0 μL, 1.80 mmol) was added to a stirred solution of **37** (190.0 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) at −78 °C, followed by dropwise addition of TESOTf (210.0 μL, 0.94 mmol) at –78 °C. The reaction mixture was stirred at –78 °C for 4 h before it was quenched with water (0.5 mL) and diluted with ethyl acetate (150 mL). The organic solution was then washed successively with citric acid (3 x 10 mL, 10wt% in water), saturated aqueous solution of $NaHCO_3$ (2 x 10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure.The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:8 to 1:2) to obtain **21** (192.6 mg, 94%) as a colorless oil.

$\boldsymbol{R_f}$ 0.7 (ethyl acetate / hexane, 1:2); $[\boldsymbol{\alpha}]_D^{20}$ = −22.5 (*c* 1.05, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.62 – 7.51 (m, 1H), 7.44 – 7.13 (m, 15H), 7.03 – 6.96 (m, 0.5H), 6.92 – 6.85 (m, 0.5H), 5.26 (d, *J* = 12.9 Hz, 0.5H), 5.14 (d, *J* = 5.9 Hz, 1H), 4.98 (d, *J* = 13.0 Hz, 0.5H), 4.59 – 4.39 (m, 3H), 4.37 – 4.21 (m, 1.5H), 4.15 – 4.04 (m, 1.5H), 3.85 (d, *J* = 5.0 Hz, 1H), 3.82 – 3.55 (m, 4H), 3.46 – 3.25 (m, 1H), 2.77 – 2.59 (m, 2H), 2.52 – 2.42 (m, 1H), 2.16 – 2.05 (m, 1H), 1.96 – 1.83 (m, 1H), 1.59 – 1.24 (m, 17H), 1.19 – 1.09 (m, 3H), 0.98 – 0.80 (m, 27H), 0.73 – 0.55 (m, 6H), 0.04 (s, 6H), -0.09 (s, 3H),

-0.24 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 172.2, 172.0, 171.5, 171.2, 168.5, 168.4, 155.0, 139.3, 139.0, 138.8, 136.7, 136.3, 129.7, 128.3, 128.2, 128.0, 127.7, 127.5, 127.1, 125.8, 81.8, 76.1, 76.0, 73.7, 73.2, 73.0, 72.2, 72.0, 68.3, 66.9, 63.6, 54.0, 49.1, 46.4, 45.9, 43.7, 39.6, 38.1, 35.1, 34.8, 34.0, 33.6, 32.1, 31.4, 28.0, 25.8, 25.7, 21.1, 20.9, 18.8, 18.5, 18.1, 18.0, 6.6, -4.8, -5.1, -5.7; **HRMS (ESI)** *m/z* calcd for $C_{62}H_{102}N_3O_{10}Si_3^+$ $[M+H]^+$ 1132.6868, found 1132.6877.

To a solution of tripeptide **21** (192.6 mg, 0.17 mmol) in CH_2Cl_2 (7 mL, A.R. grade, H_2O < 0.5 wt%), DDQ (115.8 mg, 0.51 mmol) was added at room temperature. The reaction mixture was stirred for 10 h. Volatiles were removed under reduced pressure, the residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:4 to 1:2) to give **38** (134.7 mg, 76%) as a colorless oil.

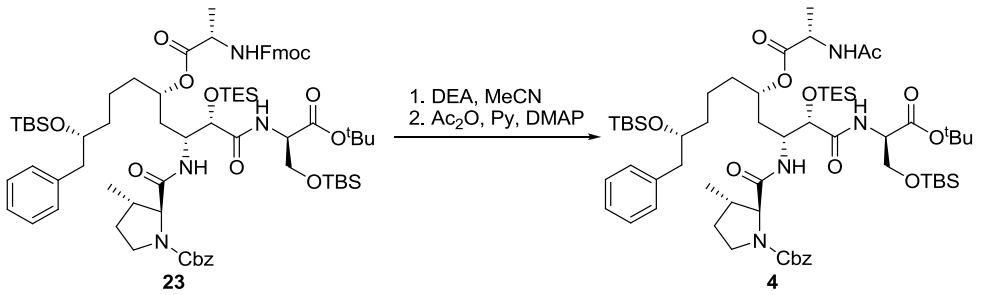
$\boldsymbol{R_f}$ 0.6 (EA / Hex, 1:2); $[\boldsymbol{\alpha}]_D^{20}$ = −6.9 (*c* 2.50, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.71 – 7.53 (m, 2H), 7.40 – 7.08 (m, 10H), 5.21 – 5.05 (m, 2H), 4.51 (d, *J* = 8.3 Hz, 1H), 4.40 – 4.02 (m, 4H), 3.87 (d, *J* = 3.1 Hz, 1H), 3.78 (dd, *J* = 10.0, 2.7 Hz, 2H), 3.68 – 3.54 (m, 2H), 3.52 – 3.22 (m, 1H), 2.80 – 2.54 (m, 2H), 2.51 – 2.39 (m, 1H), 2.12 – 1.98 (m, 1H), 1.73 – 1.31 (m, 16H), 1.21 – 1.09 (m, 4H), 1.01 – 0.94 (m, 9H), 0.89 (s, 9H), 0.81 (s, 9H), 0.67 (dq, *J* = 15.6, 7.7 Hz, 6H), 0.05 (s, 6H), -0.12 (s, 3H), -0.28 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 173.13, 172.86, 172.15, 172.08, 168.34, 168.28, 155.03, 154.83, 139.54, 136.60, 136.34, 129.75, 128.33, 127.88, 127.77, 127.67, 127.15, 125.75, 82.08, 73.78, 72.80, 72.72, 67.89, 67.81, 66.95, 66.89, 66.66, 63.54, 54.13, 49.46, 49.34, 46.32, 45.89, 43.51, 39.76, 38.36, 37.35, 37.06, 32.26, 31.49, 27.97, 25.80, 25.71, 21.93, 18.87, 18.56, 18.13, 17.95, 6.64, 4.46, -4.84, -5.18, -5.72; **HRMS (ESI)** *m/z* calcd for $C_{55}H_{96}N_3O_{10}Si_3^+$ $[M+H]^+$ 1042.6398, found 1042.6396.



To a solution of alcohol **38** (134.7 mg, 0.13 mmol) in dry toluene (10 mL) *N*-methylmorpholine (57 μL, 5.20 mmol) and DMAP (79.4 mg, 0.65 mmol) were added at 0 ^oC, followed by dropwise addition of **22** (428.7 mg, 1.3 mmol) in dry toluene (10 mL). After being stirred for 0.5 h at 0 ^oC, the reaction mixture was allowed to warm to room temperature and stirred for another 4 h. The reaction was quenched by addition of

H_2O (1 mL) and diluted with ethyl acetate (150 mL). The organic solution was washed successively with saturated aqueous solution of $NaHCO_3$ (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure.The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:4 to 1:2) to provide **23** (149.4 mg, 86%) as a colorless oil.

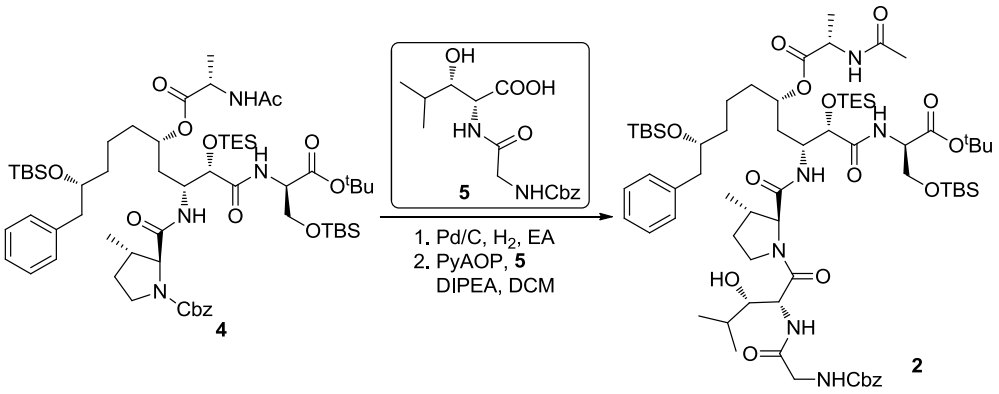
***R*f** 0.6 (ethyl acetate / hexane, 1:2); $[\alpha]_D^{20}$ = −2.2 (*c* 1.00, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.66 – 7.52 (m, 3H), 7.44 – 7.10 (m, 15H), 7.07 – 6.86 (m, 1H), 5.78 (d, *J* = 6.7 Hz, 0.5H), 5.60 (d, *J* = 7.3 Hz, 0.5H), 5.36 – 5.21 (m, 1H), 5.20 – 4.81 (m, 2H), 4.56 – 3.97 (m, 8H), 3.85 – 3.52 (m, 5H), 2.77 – 2.60 (m, 2H), 2.53 – 2.40 (m, 1H), 2.17 – 2.00 (m, 2H), 1.63 – 1.33 (m, 19H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.05 – 0.93 (m, 9H), 0.90 (s, 9H), 0.83 (s, 9H), 0.77 – 0.60 (m, 6H), 0.06 (s, 6H), -0.08 (s, 3H), -0.23 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 172.1, 171.6, 168.3, 155.7, 154.9, 144.0, 143.8, 141.2, 139.2, 136.8, 129.7, 128.3, 128.0, 127.5, 127.3, 127.0, 125.9, 125.1, 119.8, 82.0, 73.5, 73.0, 71.5, 71.3, 68.3, 68.1, 66.8, 66.7, 63.4, 54.0, 49.9, 48.5, 48.3, 47.1, 46.4, 46.1, 43.8, 39.4, 37.8, 37.0, 35.0, 32.4, 31.5, 28.0, 25.8, 25.7, 20.9, 18.8, 18.1, 17.9, 6.7, 4.4, -4.8, -5.1, -5.7, -5.7; **HRMS (ESI)** *m/z* calcd for $C_{73}H_{111}N_4O_{13}Si_3^+$ $[M+H]^+$ 1335.7450, found 1335.7440.



DEA (0.4 mL) was added to a solution of compound **23** (149.3 mg, 0.11 mmol) in MeCN (5 mL) at room temperature. The reaction mixture was stirred at room temperature for 8 h and then concentrated under reduced pressure. The residue was re-dissolved in CH_2Cl_2 (5 mL) and concentrated under reduced pressure. The crude amine was used in next step of reaction without further purification.

To a solution of above amine in CH_2Cl_2 (5 mL), pyridine (88 μL, 1.10 mmol), acetic anhydride (47 μL, 0.50 mmol) and DMAP (72.0 mg, 0.59 mmol) were sequentially added at room temperature. After being stirred for 1 h, the reaction was quenched by dilution with ethyl acetate (100 mL). The organic solution was washed with saturated aqueous solution of $NaHCO_3$ (20 mL) and brine (10 mL), dried over anhydrous

Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:2 to 1:1) to produce compound **4** (117.0 mg, 92%) as a colorless oil. $\boldsymbol{R_f}$ 0.6 (ethyl acetate / hexane, 1:1); $[\boldsymbol{\alpha}]_D^{20}$ = −4.9 (*c* 0.4, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.64 – 7.48 (m, 1H), 7.37 – 7.09 (m, 10H), 7.05 (d, *J* = 8.9 Hz, 0.5H), 6.94 (d, *J* = 9.5 Hz, 0.5H), 6.64 (d, *J* = 6.5 Hz, 0.5H), 6.50 (d, *J* = 6.5 Hz, 0.5H), 5.27 (d, *J* = 13.0 Hz, 0.5H), 5.12 (s, 1H), 5.05 (d, *J* = 13.1 Hz, 0.5H), 4.86 (brs, 1H), 4.65 – 4.54 (m, 1H), 4.49 (d, *J* = 7.0 Hz, 1H), 4.38 – 4.20 (m, 1.5H), 4.16 – 4.05 (m, 1H), 3.96 (s, 0.5H), 3.82 –3.64 (m, 5H), 2.66 (d, *J* = 6.3 Hz, 2H), 2.49 – 2.36 (m, 1H), 2.13 – 2.01 (m, 2H), 1.98 (s, 3H), 1.58 – 1.31 (m, 20H), 1.13 (d, *J* = 6.8 Hz, 3H), 0.98-0.93 (m, 9H), 0.88 (s, 9H), 0.82 (s, 9H), 0.77 – 0.56 (m, 6H), 0.05 (s, 6H), -0.08 (s, 3H), -0.23 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 172.0, 171.6, 169.4, 168.4, 168.2, 154.9, 139.2, 136.8, 129.7, 128.3, 128.0, 127.5, 127.2, 125.9, 82.0, 73.4, 73.0, 71.2, 68.2, 68.0, 66.7, 63.4, 54.0, 48.3, 46.4, 46.1, 43.9, 39.4, 37.9, 36.9, 35.0, 32.3, 31.5, 28.0, 25.8, 25.7, 23.1, 20.9, 18.7, 18.4, 18.2, 18.1, 17.9, 6.6, 4.4, -4.8, -5.1, -5.7; **HRMS (ESI)** *m/z* calcd for $C_{60}H_{103}N_4O_{12}Si_3^+$ $[M+H]^+$ 1155.6875, found 1155.6881.



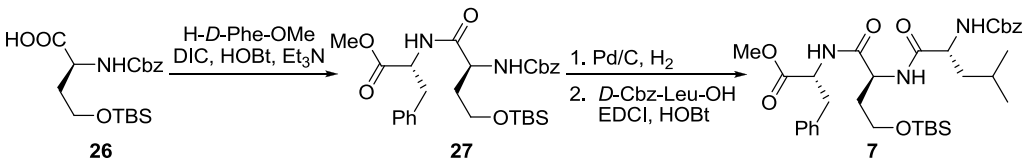
To a solution of **4** (117.0 mg, 0.10 mmol) in ethyl acetate (5 mL), palladium on charcoal (ca. 20 mg, 10% Pd) was added. The reaction vessel was sealed and the inner atmosphere was switched to H_2 and stirred for 24 h at room temperature. The catalyst was removed by filtration through a pad of Celite and washed with ethyl acetate (3 x 30 mL). The filtrate was concentrated under reduced pressure to produce the corresponding amine **4a** (98.0 mg), which was used in next step of reaction without further purifications.

To a solution of amine **4a** and carboxylic acid **5** in CH_2Cl_2 (5 mL), DIPEA (130 μL, 0.76 mmol) and PyAOP (188.0 mg, 0.36 mmol) were added at 0 ^oC. The reaction mixture was warmed to room temperature and stirred for 12 h. The reaction was quenched by addition of water (1 mL) and diluted with ethyl acetate

(100 mL). The organic solution was washed with saturated aqueous solution of NH_4Cl (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane / MeOH, 3:1:0.05) to produce the pentapeptide **2** (91.3 mg, 68% from compound **4**) as a colorless oil.

$\boldsymbol{R_f}$ 0.4 (ethyl acetate / hexane / MeOH, 3:1:0.05); $[\alpha]_D^{20}$ = −1.4 (*c* 0.53, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.86 (brs, 1H), 7.56 (brs, 1H), 7.38 – 7.23 (m, 7H), 7.22 – 7.11 (m, 3H), 6.84 (s, 1H), 6.53 (brs, 1H), 6.20 (s, 1H), 5.13 (s, 2H), 4.75 (s, 1H), 4.50 (s, 2H), 4.28 (brs, 2H), 4.16 (brs, 1H), 4.09 – 3.99 (m, 1H), 3.97 – 3.73 (m, 5H), 3.69 – 3.48 (m, 3H), 2.69 (d, *J* = 6.1 Hz, 2H), 2.30 (s, 1H), 2.12 (brs, 4H), 1.83 – 1.64 (m, 3H), 1.65 – 1.51 (m, 3H), 1.50 – 1.28 (m, 16H), 1.13 (d, *J* = 5.8 Hz, 3H), 1.06 – 0.95 (m, 12H), 0.94 – 0.82 (m, 21H), 0.82 – 0.71 (m, 6H), 0.02 (s, 6H), -0.06 (s, 3H), -0.19 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.3, 172.1, 171.2, 170.3, 169.5, 168.2, 168.2, 156.4, 139.2, 136.2, 129.7, 128.4, 128.0, 127.9, 127.8, 125.8, 82.1, 82.0, 77.4, 77.0, 76.6, 76.2, 73.4, 71.8, 67.5, 66.9, 63.4, 54.0, 51.1, 48.7, 48.3, 46.8, 44.1, 43.8, 37.0, 36.3, 35.1, 34.7, 32.5, 29.7, 27.9, 25.8, 25.7, 23.0, 20.8, 19.0, 18.9, 18.4, 18.1, 17.9, 6.7, 4.4, -4.8, -5.1, -5.7; **HRMS (ESI)** *m/z* calcd for $C_{68}H_{117}N_6O_{15}Si_3^+$ $[M+H]^+$ 1341.7879, found 1341.7872.

2.2. Synthesis of hexapeptide 24



To a solution of acid **26** (1.10 g, 3.00 mmol) and H-*D*-Phe-OMe (663.0 mg, 3.70 mmol) in CH_2Cl_2 (15 mL), DIPEA (2.1 mL, 12.00 mmol), HOBt (730.0 mg, 5.4 mmol) and DIC (0.84 mL, 5.4 mmol) were sequentially added at 0 ^oC. The reaction mixture was stirred at room temperature for 16 h. and then quenched with saturated aqueous solution of NH_4Cl (1 mL) and diluted with ethyl acetate (150 mL). The organic solution was successively washed with saturated aqueous solution of NH_4Cl (20 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 (s) and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:2 to 1:1) to give the desired dipeptide **27** (1.38 g, 87%) as a white foam.

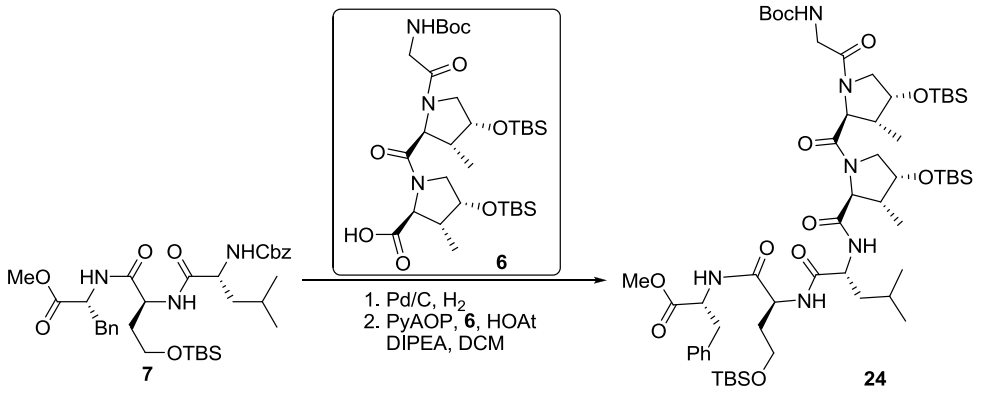
$\boldsymbol{R_f}$ 0.6 (ethyl acetate / hexane, 1:1); $[\alpha]_D^{20}$ = −35.0 (*c* 1.55, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 –

7.31 (m, 5H), 7.27 – 7.20 (m, 3H), 7.11 (d, *J* = 6.0 Hz, 2H), 6.84 (d, *J* = 5.5 Hz, 1H), 6.31 (s, 1H), 5.14 (s, 2H), 4.88 (dd, *J* = 12.3, 5.5 Hz, 1H), 4.37 (d, *J* = 4.4 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.72 (s, 3H), 3.71 – 3.66 (m, 1H), 3.12 (d, *J* = 3.9 Hz, 2H), 2.05 – 1.89 (m, 2H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.5, 171.3, 156.2, 136.3, 135.7, 129.2, 128.6, 128.5, 128.1, 127.9, 127.1, 66.9, 60.7, 54.5, 53.0, 52.1, 37.9, 33.8, 25.8, 18.0, -5.7; **HRMS (ESI)** m/z calcd for $C_{28}H_{41}N_2O_6Si^+$ [M+H$^+$] 529.2728, found 529.2735.

To a solution of dipeptide **27** (500.0 mg, 0.95 mmol) in ethyl acetate (10 mL) at room temperature, palladium on charcoal (ca. 50 mg, 10% Pd) was added. The reaction vessel was sealed and the inner atmosphere was switched to H_2 and stirred for 10 h at room temperature. The catalyst was removed by filtration through a pad of Celite and washed with ethyl acetate (3 x 30 mL). The filtrate was concentrated under reduced pressure to produce the corresponding amine(*ca.* 369.0 mg), which was used in next step of reaction without further purifications.

To a solution of above amine and *D*-Cbz-Leu-OH (604.9 mg, 2.28 mmol) in CH_2Cl_2 (10 mL), TEA (0.53 mL, 3.80 mmol), HOBt (205.4 mg, 1.52 mmol), EDCI (291.4 mg, 1.52 mmol) were sequentially added sequentially at 0 ^{o}C. The reaction mixture was stirred at room temperature for 16 h before it was quenched by addition of saturated aqueous solution of NH_4Cl (1 mL) and diluted with ethyl acetate (150 mL). The organic solution was successively washed with saturated aqueous solution of NH_4Cl (20 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 (s) and evaporated under reduced pressure. The residue was purified by column chromatography to give the corresponding product **7** (560.4 mg, 92%) as a white foam.

$\boldsymbol{R_f}$ 0.5 (ethyl acetate / hexane, 1:2); $[\alpha]_D^{20}$ = −17.6 (c 1.68, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42 – 7.17 (m, 8H), 7.13 (d, *J* = 7.5 Hz, 2H), 5.21 (d, *J* = 6.8 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.99 (d, *J* = 12.2 Hz, 1H), 4.78 (dd, *J* = 14.0, 7.0 Hz, 1H), 4.59 (dd, *J* = 11.3, 5.2 Hz, 1H), 4.06 (dd, *J* = 13.6, 7.1 Hz, 1H), 3.84 – 3.73 (m, 1H), 3.69 (s, 1H), 3.65 (s, 3H), 3.09 (qd, *J* = 13.8, 6.7 Hz, 2H), 2.07 – 1.84 (m, 3H), 1.74 – 1.45 (m, 3H), 0.92 (s, 16H), 0.09 (s, 3H), 0.08 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.2, 171.7, 170.8, 156.3, 136.2, 136.1, 129.2, 128.5, 128.3, 128.2, 128.0, 127.0, 67.1, 60.8, 54.1, 53.7, 52.1, 52.0, 41.1, 37.8, 33.6, 26.0, 24.7, 23.0, 21.9, 18.3, -5.4, -5.5; **HRMS (ESI)** m/z calcd for $C_{34}H_{52}N_3O_7Si^+$ [M+H]$^+$ 642.3569, found 642.3576.



To a solution of tripeptide **7** (352.7 mg, 0.55 mmol) in ethyl acetate (10 mL), palladium on charcoal (ca. 40 mg, 10% Pd) was added. The reaction vessel was sealed and the inner atmosphere was switched to H_2 and stirred for 24 h at room temperature. The catalyst was removed by filtration through a pad of Celite and washed with ethyl acetate (3 x 30 mL). The filtrate was concentrated under reduced pressure to produce the corresponding amine **7a** (*ca.* 253.0 mg), which was used in next step of reaction without further purifications.

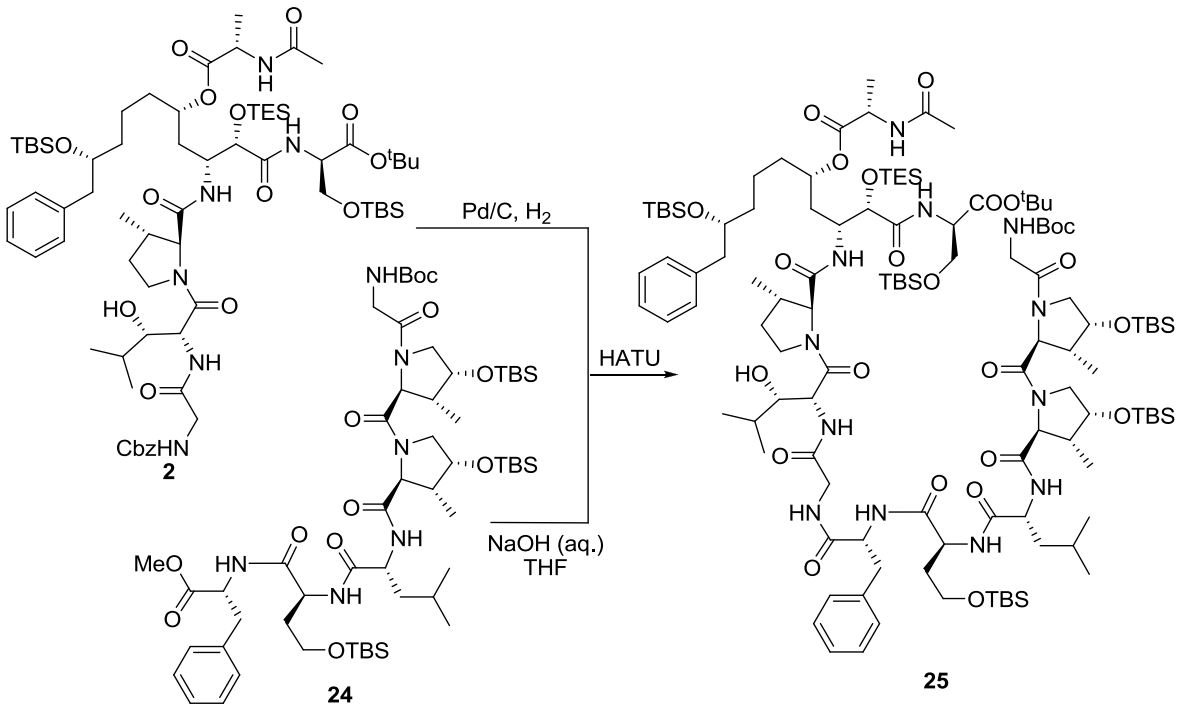
To a stirred solution of carboxylic acid **6**[2] (296.1 mg, 0.45 mmol) and the amine **7a** obtained above in MeCN (5 mL), DIPEA (0.32 mL, 1.83 mmol), HOAT (54.4 mg, 0.40 mmol) and HATU (258.6 mg, 0.68 mmol) were sequentially added at 0 ^{o}C. The reaction mixture was warmed to room temperature and stirred for 12 h and then quenched by addition of water (1 mL) and diluted with ethyl acetate (100 mL). The organic solution was washed with saturated aqueous solution of NH_4Cl (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 1:4 to 1:2) to afford hexapeptide **24** (397.7 mg, 63%, from **7**) as a colorless oil.

$\boldsymbol{R_f}$ 0.6 (ethyl acetate / hexane, 1:2); $[\boldsymbol{\alpha}]_D^{20}$ = +61.1 (*c* 0.75, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.13 (m, 6H), 5.41 (brs, 1H), 4.95 (d, *J* = 9.4 Hz, 1H), 4.77 (ddd, *J* = 11.6, 7.5, 4.3 Hz, 1H), 4.42 – 4.34 (m, 2H), 4.29 (t, *J* = 3.1 Hz, 1H), 4.21 (brs, 1H), 4.09 – 4.06 (m, 1H), 3.99 – 3.96 (m, 1H), 3.82 – 3.81 (m, 2H), 3.73 (s, 3H), 3.69 – 3.65 (m, 2H), 3.59 – 3.46 (m, 2H), 3.33 (d, *J* = 10.9 Hz, 1H), 3.13 (dd, *J* = 15.2, 4.2 Hz, 1H), 2.65 (dd, *J* = 15.2, 11.5 Hz, 1H), 2.36 – 2.27 (m, 2H), 2.00 – 1.91 (m, 1H), 1.81 – 1.70 (m, 2H), 1.41 (s, 9H), 1.31 – 1.18 (m, 3H), 1.08 – 1.02 (m, 6H), 1.00 (s, 9H), 0.93 (d, *J* = 6.6

[2] Tripeptide **6** was prepared following our previous reported procedures: Wang L.; Liu J. Y.; Zhang, Hui,; Xu, Z. X,; Ye, T. *Synlett*, **2010**, 563–566.

Hz, 3H), 0.88 (s, 9H), 0.85 (s, 9H), 0.80 (d, *J* = 6.5 Hz, 3H), 0.19 (s, 3H), 0.15 (s, 3H), 0.06 (s, 6H), -0.00 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.0, 172.5, 171.1, 171.1, 170.8, 166.8, 155.5, 137.2, 129.0, 128.4, 126.1, 79.3, 73.8, 73.5, 72.6, 66.1, 62.5, 62.3, 60.3, 60.0, 56.8, 55.2, 52.3, 51.6, 51.1, 50.3, 43.9, 42.5, 42.4, 38.3, 35.7, 34.8, 28.2, 25.8, 25.7, 24.6, 23.3, 20.5, 18.1, 18.1, 18.0, 11.1, 10.7, -4.71, -4.79, -4.94, -5.03, -5.47, -5.55; **HRMS (ESI)** *m/z* calcd for $C_{57}H_{103}N_6O_{12}Si_3^+$ $[M+H]^+$: 1147.6936; found: 1147.6939.

2.3. Total synthesis of 9-(*R*)-scytonemin A (1a)



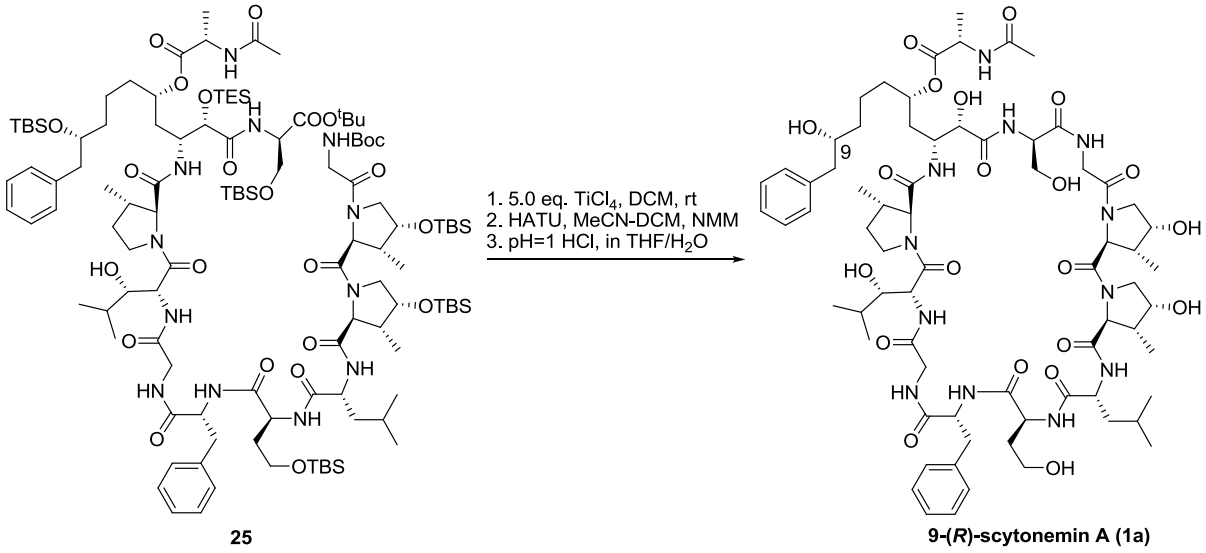
To a solution of compound **2** (50.0 mg, 0.037 mmol) in ethyl acetate (5 mL), palladium on charcoal (ca. 10 mg, 10% Pd) was added. The reaction vessel was sealed and the inner atmosphere was switched to H_2 and stirred for 24 h at room temperature. The catalyst was removed by filtration through a pad of Celite and washed with ethyl acetate (3 x 30 mL). The filtrate was concentrated under reduced pressure to produce the corresponding amine **2a** (*ca.* 33.0 mg), which was used in next step of reaction without further purifications.

A solution of NaOH (0.8 mL, 0.5 M) was added to a stirred solution of **24** (50.0 mg, 0.044 mmol) in THF (3 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h before it was acidified to pH 1−2 with HCl (1.0 M in water) and extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure to afford the desired acid **3** (*ca.* 45.0 mg), which was used directly in the next step without further purification.

To a solution of the above amine **2a** and carboxylic acid **3** in dry MeCN (5 mL), *N*-Methylmorpholine (15.0 μL, 0.14 mmol), HOAT (5.4 mg, 0.04 mmol) and HATU (34.0 mg, 0.09 mmol) were sequentially added at 0 ^oC. The reaction mixture was warmed to room temperature and stirred for 12 h and then quenched by addition of water (1 mL) and diluted with ethyl acetate (100 mL). The organic solution was washed with saturated aqueous solution of NH_4Cl (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate / hexane, 3:1) to give the linear undecapeptide **25** (40.4 mg, 47% from **2**) as a colorless oil.

$\boldsymbol{R_f}$ 0.3 (ethyl acetate / hexane / MeOH, 2:1:0.05); $[\boldsymbol{\alpha}]_D^{20}$ = +10.1 (*c* 0.44, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) exists as rotational conformers: δ 7.67 – 7.53 (m, 2H), 7.49 – 7.41 (m, 2H), 7.35 – 7.28 (m, 2H), 7.25 – 7.20 (m, 5H), 7.15 (q, *J* = 5.6 Hz, 3H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.36 (s, 1H), 5.44 (s, 1H), 4.77 (s, 1H), 4.70 (dd, *J* = 15.1, 7.4 Hz, 1H), 4.60 – 4.41 (m, 3H), 4.32 – 4.04 (m, 8H), 4.04 – 3.94 (m, 2H), 3.90 – 3.61 (m, 9H), 3.59 – 3.51 (m, 1H), 3.50 – 3.44 (m, 1H), 3.39 – 3.30 (m, 1H), 3.25 (dd, *J* = 15.0, 7.3 Hz, 1H), 3.17 – 3.08 (m, 1H), 2.90 – 2.80 (m, 1H), 2.73 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.65 (dd, *J* = 13.4, 7.1 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.37 – 2.24 (m, 3H), 2.12 – 2.08 (m, 1H), 2.05 (s, 1H), 2.03 (s, 2H), 2.01 (s, 1H), 1.98 – 1.91 (m, 1H), 1.81 – 1.69 (m, 4H), 1.68 – 1.50 (m, 7H), 1.49 – 1.36 (m, 23H), 1.23 – 1.19 (m, 2H), 1.18 – 1.13 (m, 2H), 1.12 – 1.04 (m, 8H), 1.02 – 0.93 (m, 24H), 0.92 – 0.80 (m, 40H), 0.75 – 0.67 (m, 6H), 0.18 – -0.01 (m, 24H), -0.06 – -0.09 (m, 3H), -0.22 (s, 0.8H), -0.24 (s, 2.2H); **^{13}C NMR** (125 MHz, $CDCl_3$) exists as rotational conformers: δ 174.38, 172.63, 172.52, 172.22, 171.74, 171.66, 171.63, 171.15, 170.62, 170.18, 169.99, 168.67, 167.10, 155.72, 139.35, 137.00, 129.80, 129.74, 129.20, 128.74, 128.61, 128.04, 128.00, 126.57, 125.94, 125.89, 81.92, 79.33, 75.58, 73.93, 73.63, 72.93, 68.23, 66.40, 63.68, 62.71, 59.54, 56.61, 55.23, 54.82, 54.24, 51.55, 50.54, 48.75, 48.10, 46.19, 43.91, 43.78, 43.10, 42.60, 38.43, 37.28, 36.86, 35.97, 34.63, 33.85, 31.95, 31.45, 29.66, 28.36, 28.10, 25.93, 25.86, 25.82, 25.79, 24.73, 23.37,

23.18, 23.13, 22.64, 20.99, 20.87, 20.16, 18.87, 18.21, 18.14, 18.01, 17.87, 14.02, 11.27, 11.00, 6.74, 4.60, -4.65, -4.67, -4.86, -4.94, -4.97, -5.43, -5.62, -5.65. **HRMS (ESI)**: *m/z* calcd for $C_{116}H_{209}N_{12}O_{24}Si_6^+$ $[M+H]^+$ 2322.4113, found 2322.3150.



25 **9-(*R*)-scytonemin A (1a)**

To a stirred solution of undecapeptide **25** (32.5 mg, 0.014 mmol) in CH_2Cl_2 (5.0 mL), $TiCl_4$ (70.0 μL, 1.0 M in DCM) was added at 0 ^oC. The reaction mixture was then allowed to warm to room temperature and stirred for 4 h. The reaction was quenched by addition of aqueous solution of $KHSO_4$ (5 mL, 0.1 M) and stirred for another 2h. The reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed with NaH_2PO_4-Na_2HPO_4 buffer (2 x 5 mL, 0.1 M, pH 7.1) and brine (5 mL). The organic layer was dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure.

The residue was dried under high vacuum for 2h and then dissolved in MeCN-CH_2Cl_2 (40 mL, 9/1, v/v) at 0 ^oC. To this solution, *N*-Methylmorpholine (40.0 μL, 0.36 mmol) and HATU (45.6 mg, 0.12 mmol) were added at 0 ^oC. The reaction mixture was stirred at room temperature for additional 12 h. The reaction was quenched by addition of water (1 mL) and diluted with ethyl acetate (100 mL). The organic solution was washed with saturated aqueous solution of NH_4Cl (5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4 (s) and concentrated under reduced pressure.

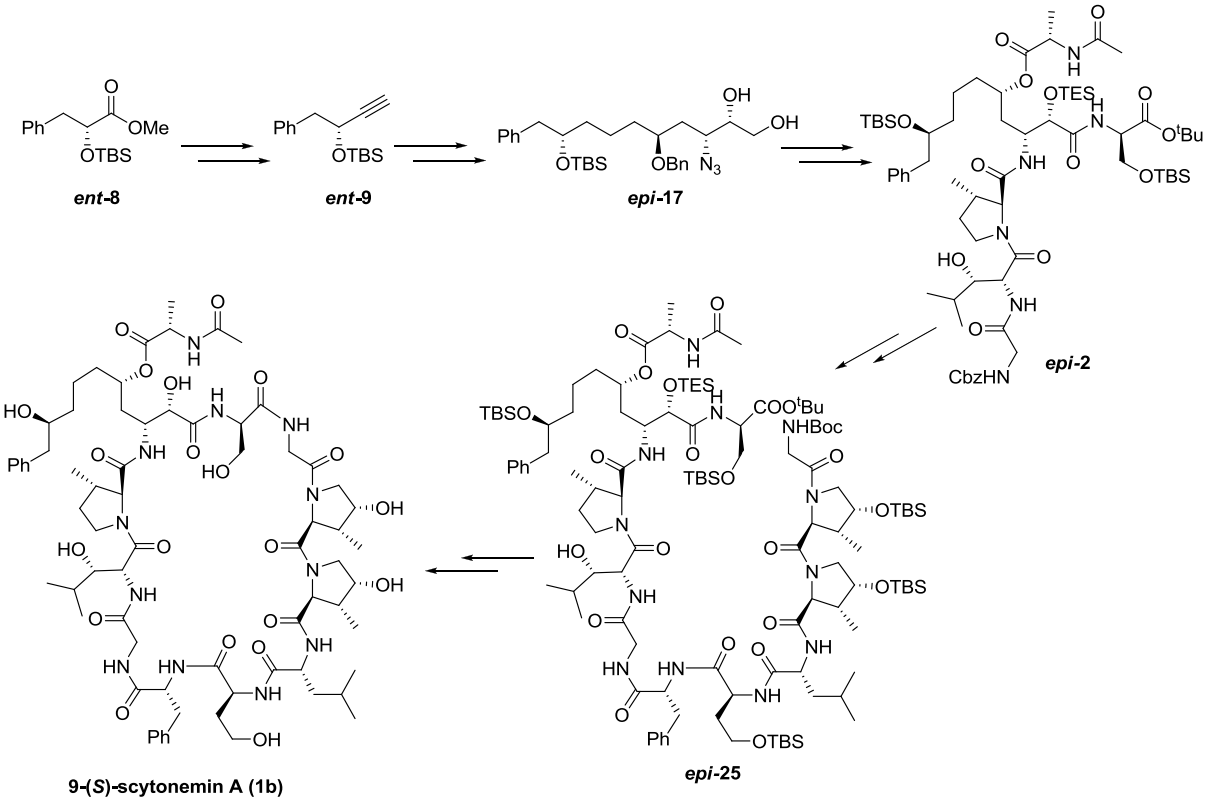
The above crude residue was dissolved in THF-HCl (0.1 M, aqueous solution) (9 mL, prepared by addition of 4.3 mL *con.* HCl to 500 mL THF) and stirred for 36 h. The reaction was monitored by HRMS until all silyl protective groups were removed. Volatiles were removed by evaporation under reduced pressure. The

residue was directly subjected to purification by HPLC (Agilent 1200 system, Agilent SB-C18 column (reverse-phase, 21.2 × 250 mm, 7 μm), linear elution gradient consisting of H_2O-MeCN (from 10% to 98% MeCN over 25 min) at a flow rate of 10 mL/min, retention time: 15.9−16.2 min) to produce 9-(*R*)-scytonemin A **1a** (5.5 mg, 27% 3 steps) as a white powder.

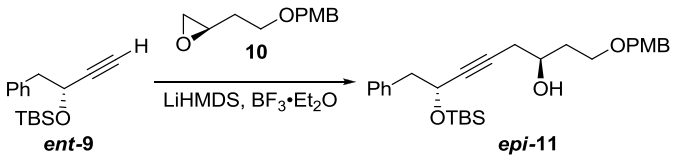
$[\alpha]_D^{20}$ = +37 (*c* 0.06, MeOH); Ref[3]:$[\alpha]_D^{20}$ = +38.8 (*c* 0.04, MeOH); **^{1}H NMR** (500 MHz, DMSO-d6) δ 8.41 (s, 1H), 8.19 (s, 1H), 8.17 (d, *J* = 6.6 Hz, 1H), 8.00 (s, 1H), 7.92 (s, 1H), 7.82 (s, 1H), 7.72 (s, 2H), 7.65 (s, 2H), 7.28 – 7.14 (m, 10H), 4.79 – 4.70 (m, 2H)，4.47 (s, 1H)，4.32 – 4.19 (m, 3H)，4.19 – 4.11 (m, 2H)，4.11 – 4.05 (m, 2H)，4.06 – 4.00 (m, 1H)，4.00 – 3.91 (m, 3H)，3.87 – 3.78 (m, 4H)，3.76 – 3.68 (m, 3H)，3.66 – 3.56 (m, 5H)，3.53 – 3.52 (m, 1H)，3.43 – 3.41 (m, 1H)，3.08 (d, *J* = 13.2 Hz, 1H)，2.89 – 2.82 (m, 1H)，2.63 (brs, 5H)，2.24 – 2.12 (m, 2H)，2.12 – 2.01 (m, 2H)，1.87 – 1.63 (m, 9H)，1.59 – 1.51 (m, 3H)，1.50 – 1.39 (m, 3H)，1.33 – 1.19 (m, 5H)， 1.08 – 1.01 (m, 6H)，0.99 (d, *J* = 6.3 Hz, 3H)，0.91 (s, 3H)，0.90 (s, 3H)，0.89 – 0.88 (m, 3H)，0.81 (d, *J* = 5.5 Hz, 3H); **^{13}C NMR** (150 MHz, DMSO-d6) δ 172.42,172.17, 172.07, 172.01, 171.43, 171.28, 171.01, 170.17, 169.95, 169.27, 169.10, 168.56, 166.68, 139.81, 138.01, 129.41, 129.05, 128.17, 128.02, 126.26, 125.72, 75.62, 72.94, 71.37, 71.19, 71.04, 70.90, 67.06, 65.58, 62.21, 61.46, 57.62, 56.36, 55.08, 54.25, 54.01, 52.38, 50.74, 50.50, 48.24, 47.88, 46.29, 43.68, 43.68, 42.33, 42.33, 41.77, 41.10, 37.09, 36.64, 36.47, 34.97, 34.29, 32.06, 30.16, 24.41, 23.47, 22.26, 20.72, 20.64, 19.58, 18.50, 18.30, 17.05, 11.38, 10.56; **HRMS (ESI)** *m/z* calcd for $C_{71}H_{107}N_{12}O_{21}^+$ $[M+H]^+$ 1463.7668, found 1463.7686.

[3]Helms, G. L.; Moore, R. E.; Niemczura, W. P.; Patterson, G. M. L.; Tomer, K. B.; Gross, M. L. *J. Org. Chem.* **1988**, *53*, 1298–1307.

2.4. Analytical data for intermediates of 9-(*S*)-scytonemin A (1b)

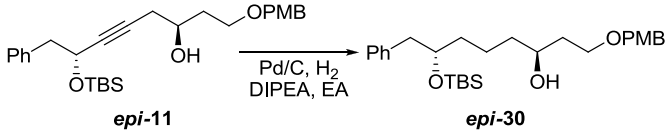


Scheme 1 Synthesis of 9-(*S*)-scytonemin A (**1b**).



epi-**11**was prepared from epoxide **10** in 95% yield. Analytical data for *epi*-**11**:

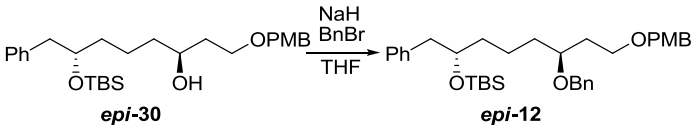
$[\alpha]_D^{20}$ = +19.9 (*c* 1.19, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27 – 7.15 (m, 7H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.51 – 4.45 (m, 1H), 4.43 (s, 2H), 3.90 – 3.83 (m, 1H), 3.79 (s, 3H), 3.65 (ddd, *J* = 9.5, 6.2, 4.7 Hz, 1H), 3.57 (ddd, *J* = 9.4, 7.9, 4.5 Hz, 1H), 2.93 – 2.90 (m, 2H), 2.84 (d, *J* = 3.8 Hz, 1H), 2.44 – 2.30 (m, 2H), 1.85 – 1.77 (m, 1H), 1.76 – 1.69 (m, 1H), 0.83 (s, 9H), -0.05 (s, 3H), -0.07 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.4, 137.9, 130.1, 129.9, 129.3, 128.0, 126.4, 113.9, 83.8, 81.5, 73.0, 69.6, 68.2, 64.4, 55.3, 45.5, 35.4, 27.4, 25.7, 18.2, -4.9, -5.2; **HRMS (ESI)**: *m/z* calcd for $C_{28}H_{40}O_4SiNa^+$ $[M+Na]^+$ 491.2588, found 491.2573.



epi-**30** was prepared from *epi*-**11** in 97% yield. Analytical data for *epi*-**30**:

$[\alpha]_D^{20}$ = +1.20 (*c* 1.09, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 4H), 7.20 – 7.13 (m, 3H), 6.90 – 6.84 (m, 2H), 4.44 (s, 2H), 3.84 (t, *J* = 5.8 Hz, 1H), 3.79 (s, 3H), 3.77 (brs, 1H), 3.72 – 3.64 (m, 1H), 3.63 – 3.57 (m, 1H), 2.84 (d, *J* = 2.2 Hz, 1H), 2.75 – 2.69 (m, 2H), 1.76 – 1.68 (m, 2H), 1.50 – 1.35 (m, 6H), 0.85 (s, 9H), -0.05 (s, 3H), -0.19 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.3, 139.4, 130.1, 129.7, 129.2, 128.0, 125.9, 113.9, 73.7, 72.9, 71.2, 68.8, 55.2, 43.9, 37.6, 37.0, 36.4, 25.9, 21.2, 18.0, -4.7, -4.9;

HRMS (ESI) *m/z* calcd for $C_{28}H_{45}O_4Si^+$ $[M+H]^+$ 473.3082, found 473.3084.

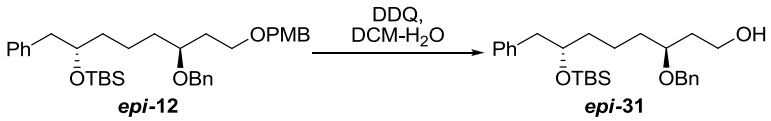


***epi*-30** ***epi*-12**

epi-**12** was prepared from *epi*-**30** in 86% yield. Analytical data for *epi*-**12**:

$[\alpha]_D^{20}$ = +3.30 (*c* 0.90, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 9H), 7.19 – 7.12 (m, 3H), 6.88 – 6.82 (m, 2H), 4.48 (d, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 3.84 – 3.79 (m, 1H), 3.78 (s, 3H), 3.59 – 3.47 (m, 3H), 2.70 (d, *J* = 6.3 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.53 – 1.38 (m, 6H), 0.85 (s, 9H), -0.04 (s, 3H), -0.19 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.2, 139.4, 139.1, 130.8, 129.7, 129.3, 128.3, 128.1, 127.7, 127.4, 126.0, 113.8, 76.3, 73.8, 72.6, 71.2, 66.8, 55.3, 44.0, 37.2, 34.6, 34.5, 25.9, 21.0, 18.1, -4.6, -4.8;

HRMS (ESI) *m/z* calcd for $C_{35}H_{51}O_4Si^+$ $[M+H]^+$ 563.3551, found 563.3541.

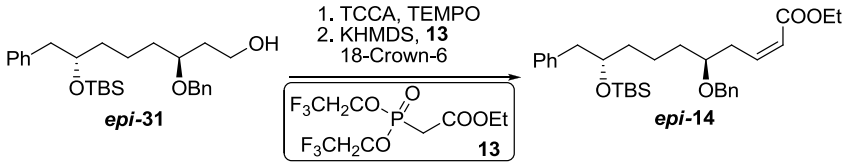


***epi*-12** ***epi*-31**

epi-**31** was prepared from *epi*-**12** in 86% yield. Analytical data for *epi*-**31**:

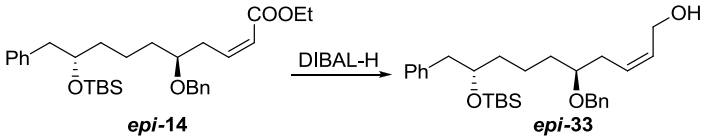
$[\alpha]_D^{20}$ = +21.4 (*c* 1.04, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.28 – 7.21 (m, 3H), 7.19 – 7.12 (m, 3H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 11.5 Hz, 1H), 3.86 – 3.79 (m, 1H), 3.78 – 3.74 (m, 1H), 3.73 – 3.67 (m, 1H), 3.64 – 3.57 (m, 1H), 2.76 – 2.64 (m, 2H), 2.31 (s, 1H), 1.83 – 1.68 (m, 2H), 1.68 – 1.56 (m, 1H), 1.53 – 1.30 (m, 5H), 0.84 (s, 9H), -0.05 (s, 3H), -0.18 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.3, 138.5, 129.7, 128.4, 128.1, 127.8, 127.7, 126.0, 78.4, 73.6, 71.0, 60.7, 44.0, 37.1, 36.0, 33.8, 25.9, 20.9, 18.1, -4.7, -4.8;

HRMS (ESI) *m/z* calcd for $C_{27}H_{43}O_3Si^+$ $[M+H]^+$, 443.2976, found 443.2983.



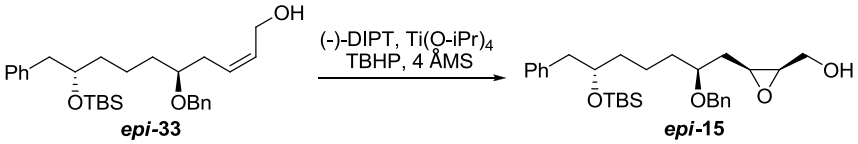
epi-**14** was prepared from *epi*-**31** in 81% yield (*Z*:*E* > 10:1). Analytical data for *epi*-**14**:

$[\alpha]_D^{20}$ = −6.5 (*c* 0.58, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 4H), 7.27 – 7.21 (m, 3H), 7.18 – 7.11 (m, 3H), 6.32 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.83 (dt, *J* = 11.6, 1.8 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.84 – 3.74 (m, 1H), 3.54 – 3.48 (m, 1H), 2.95 – 2.90 (m, 2H), 2.68 (d, *J* = 6.3 Hz, 2H), 1.61 – 1.55 (m, 1H), 1.49 – 1.37 (m, 5H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.83 (s, 9H), -0.07 (s, 3H), -0.20 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.1, 145.9, 139.2, 138.6, 129.5, 128.0, 127.8, 127.5, 127.2, 125.7, 120.9, 78.0, 73.5, 70.6, 59.5, 43.7, 36.8, 34.2, 32.9, 25.7, 21.0, 17.8, 14.0, -4.9, -5.1; **HRMS (ESI)** *m/z* calcd for $C_{31}H_{47}O_4Si^+$ $[M+H]^+$ 511.3238, found 511.3239.



epi-**33** was prepared from *epi*-**14** in 93% yield. Analytical data for *epi*-**33**:

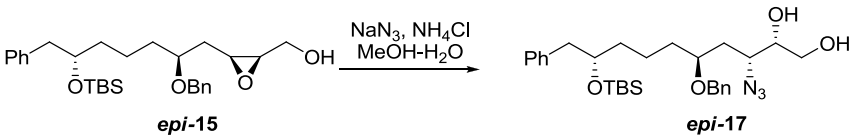
$[\alpha]_D^{20}$ = −1.0 (*c* 1.53, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.29 – 7.21 (m, 3H), 7.21 – 7.10 (m, 3H), 5.81 – 5.72 (m, 1H), 5.64 – 5.54 (m, 1H), 4.49 (s, 2H), 4.18 – 4.03 (m, 2H), 3.82 (t, *J* = 5.3 Hz, 1H), 3.43 – 3.35 (m, 1H), 2.74 – 2.66 (m, 2H), 2.36 (dt, *J* = 14.6, 7.0 Hz, 1H), 2.30 – 2.22 (m, 1H), 1.83 (s, 1H), 1.58 – 1.52 (m, 1H), 1.49 – 1.38 (m, 5H), 0.85 (s, 9H), -0.05 (s, 3H), -0.18 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.3, 138.5, 130.8, 129.7, 128.9, 128.3, 128.1, 127.8, 127.6, 126.0, 78.3, 73.7, 71.3, 58.2, 44.0, 37.0, 34.1, 32.0, 25.9, 21.2, 18.1, -4.7, -4.8; **HRMS (ESI)** *m/z* calcd for $C_{29}H_{45}O_3Si^+$ $[M+H]^+$ 469.3132, found 469.3129.



epi-**15** was prepared from *epi*-**33** in 86% yield. Analytical data for *epi*-**15**:

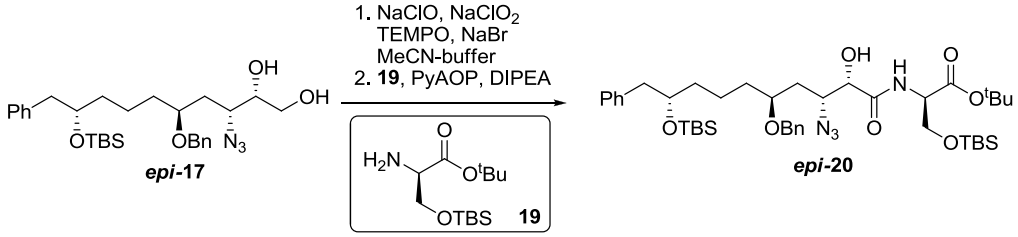
$[\alpha]_D^{20}$ = +5.6 (*c* 0.95, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 7H), 7.19 – 7.10 (m, 3H), 4.51 (d, *J* = 11.7 Hz, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 3.86 – 3.75 (m, 1H), 3.77 – 3.65 (m, 1H), 3.64 – 3.57

(m, 1H), 3.53 (dd, *J* = 10.8, 5.5 Hz, 1H), 3.14 – 3.07 (m, 2H), 2.76 – 2.62 (m, 2H), 2.21 (s, 1H), 1.91 (dt, *J* = 14.7, 5.5 Hz, 1H), 1.75 – 1.62 (m, 2H), 1.48 – 1.35 (m, 5H), 0.84 (s, 9H), -0.05 (s, 3H), -0.18 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.2, 138.2, 129.7, 128.5, 128.2, 128.0, 127.8, 126.1, 73.6, 71.3, 60.5, 55.9, 53.6, 44.1, 36.9, 33.7, 31.8, 25.9, 21.5, 18.1, -4.6, -4.8; **HRMS (ESI)** *m/z* calcd for $C_{29}H_{45}O_4Si^+$ $[M+H]^+$ 485.3082, found 485.3077.



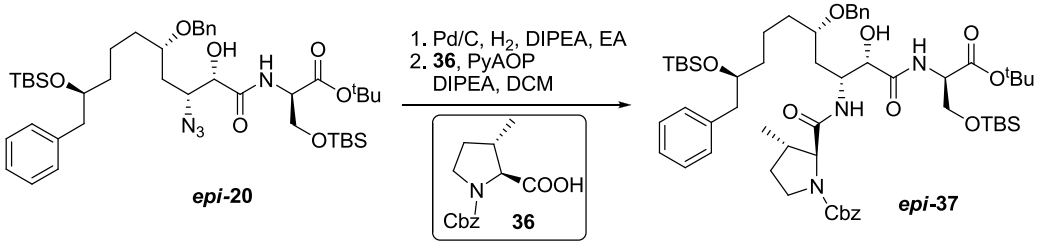
epi-**17** was prepared from *epi*-**15** in 86% yield. Analytical data for *epi*-**17**:

$[\alpha]_D^{20}$ = +38.6 (*c* 1.12, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 7H), 7.20 – 7.12 (m, 3H), 4.59 (d, *J* = 11.1 Hz, 1H), 4.39 (d, *J* = 11.1 Hz, 1H), 3.87 – 3.80 (m, 1H), 3.67 – 3.52 (m, 5H), 2.76 – 2.64 (m, 2H), 2.54 (s, 1H), 2.06 (s, 1H), 1.75 – 1.68 (m, 2H), 1.54 – 1.30 (m, 6H), 0.84 (s, 9H), -0.05 (s, 3H), -0.18 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.2, 138.2, 129.7, 128.5, 128.2, 128.0, 127.8, 126.1, 76.0, 74.5, 73.6, 71.2, 64.1, 61.2, 44.0, 37.1, 36.0, 34.0, 25.9, 20.5, 18.1, -4.7, -4.8; **HRMS** (ESI): *m/z* calcd for $C_{29}H_{46}N_3O_4Si^+$ $[M+H]^+$ 528.3252, found 528.3248.



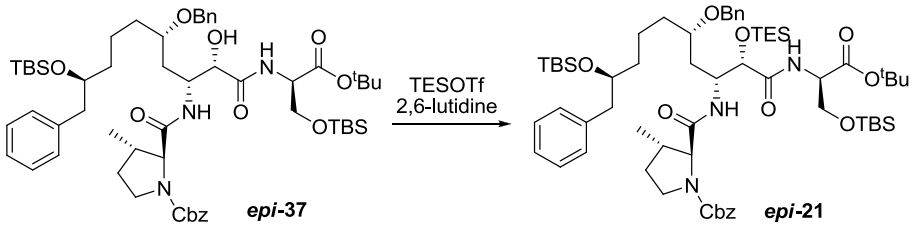
epi-**20** was prepared from *epi*-**17** in 76% yield. Analytical data for *epi*-**20**:

$[\alpha]_D^{20}$ = +1.7 (*c* 1.20, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.24 (m, 7H), 7.24 – 7.12 (m, 3H), 4.64 – 4.53 (m, 2H), 4.40 (d, *J* = 11.1 Hz, 1H), 4.15 (dd, *J* = 6.4, 2.5 Hz, 1H), 4.07 (dd, *J* = 10.0, 2.5 Hz, 2H), 3.88 – 3.80 (m, 2H), 3.65 – 3.55 (m, 1H), 3.30 (d, *J* = 6.4 Hz, 1H), 2.74 (dd, *J* = 6.3, 2.0 Hz, 2H), 1.93 – 1.80 (m, 2H), 1.70 – 1.31 (m, 16H), 0.88 (s, 9H), 0.88 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H), -0.02 (s, 3H), -0.16 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.3, 168.8, 139.1, 137.8, 129.6, 128.4, 128.1, 127.8, 127.8, 126.0, 82.1, 75.8, 73.5, 73.5, 70.9, 63.4, 60.9, 54.6, 43.9, 37.0, 35.2, 33.6, 27.9, 25.8, 25.6, 20.3, 18.0, 18.0, -4.8, -4.9, -5.7, -5.7; **HRMS (ESI)** *m/z* calcd for $C_{42}H_{71}N_4O_7Si_2^+$ $[M+H]^+$ 799.4856, found 799.4871.



epi-**37** was prepared from *epi*-**20** in 73% yield. Analytical data for *epi*-**37**:

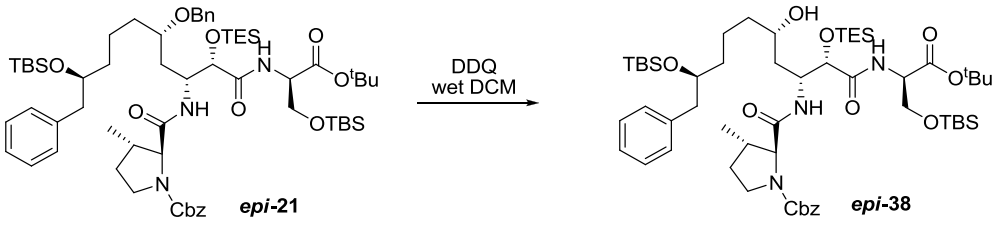
$[\alpha]_D^{20}$ = −9.6 (*c* 0.59, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.59 (dd, *J* = 22.1, 7.4 Hz, 1H), 7.42 – 7.11 (m, 15H), 6.87 (d, *J* = 6.8 Hz, 0.4H), 6.67 (d, *J* = 7.5 Hz, 0.6H), 5.52 (d, *J* = 6.5 Hz, 0.6H), 5.22 – 5.00 (m, 2H), 4.92 (s, 0.4H), 4.62 – 4.39 (m, 2H), 4.33 – 4.10 (m, 2H), 4.10 – 3.99 (m, 1H), 3.81 (s, 2H), 3.73 – 3.40 (m, 4H), 2.78 – 2.63 (m, 2H), 2.50 – 2.27 (m, 1H), 2.15 – 1.96 (m, 1H), 1.84 – 1.66 (m, 1H), 1.60 – 1.30 (m, 17H), 1.12 – 0.96 (m, 3H), 0.87 (s, 9H), 0.85 (s, 9H), 0.03 (s, 6H), -0.05 (s, 3H), -0.20 (brs, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 173.2, 172.9, 172.0, 171.7, 168.6, 167.0, 155.0, 139.3, 138.5, 136.5, 129.7, 128.4, 128.4, 128.3, 128.0, 127.9, 127.6, 125.9, 81.6, 76.1, 74.5, 73.6, 71.1, 67.6, 67.0, 63.5, 54.3, 51.3, 46.3, 45.9, 43.8, 39.6, 37.5, 37.3, 35.1, 34.5, 33.9, 33.5, 32.2, 31.5, 27.9, 25.8, 25.6, 20.5, 20.1, 18.7, 18.2, 18.1, 18.0, 17.9, -4.8, -5.0, -5.7; **HRMS (ESI)** *m/z* calcd for $C_{56}H_{88}N_3O_{10}Si_2^+$ $[M+H]^+$ 1018.6003, found 1018.6018.



epi-**21** was prepared from *epi*-**37** in 92% yield. Analytical data for *epi*-**21**:

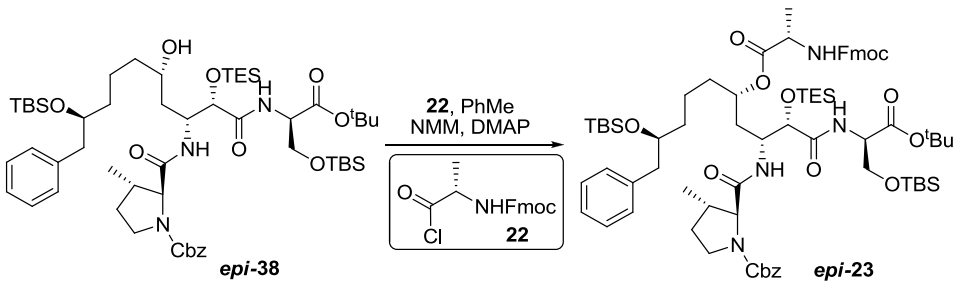
$[\alpha]_D^{20}$ = −17.4 (*c* 0.81, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.65 – 7.49 (m, 1H), 7.45 – 7.12 (m, 15H), 7.00 (d, *J* = 9.0 Hz, 0.5H), 6.90 (d, *J* = 9.6 Hz, 0.5H), 5.26 (d, *J* = 12.6 Hz, 0.5H), 5.14 (s, 1H), 4.99 (d, *J* = 13.0 Hz, 0.5H), 4.59 – 4.40 (m, 3H), 4.35 – 4.22 (m, 1.5H), 4.14 – 4.04 (m, 1.5H), 3.85 (d, *J* = 5.0 Hz, 1H), 3.82 – 3.54 (m, 4H), 3.51 – 3.25 (m, 1H), 2.77 – 2.58 (m, 2H), 2.54 – 2.40 (m, 1H), 2.18 – 2.03 (m, 1H), 1.98 – 1.86 (m, 1H), 1.60 – 1.23 (m, 17H), 1.21 – 1.09 (m, 3H), 0.98 – 0.79 (m, 27H), 0.72 – 0.56 (m, 6H), 0.04 (s, 6H), -0.07 (s, 3H), -0.23 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 172.3, 172.1, 171.5, 171.2, 168.5, 168.4, 155.0, 150.0, 139.3, 138.9, 136.3, 129.7, 128.3, 128.2, 127.9, 127.7, 127.5, 127.2, 127.1, 125.8, 81.8, 75.9, 73.7, 73.0, 72.2, 71.9, 68.3, 66.9,

63.6, 54.0, 49.1, 46.4, 45.9, 43.8, 39.7, 38.1, 37.5, 34.9, 34.6, 33.9, 33.5, 32.1, 31.4, 28.0, 25.8, 25.7, 21.1, 20.9, 18.8, 18.5, 18.1, 18.0, 6.6, 4.4, -4.8, -5.1, -5.8; **HRMS (ESI)** *m/z* calcd for $C_{62}H_{102}N_3O_{10}Si_3^+$ $[M+H]^+$ 1132.6868, found 1132.6852.



epi-**38** was prepared from *epi*-**21** in 76% yield. Analytical data for *epi*-**38**:

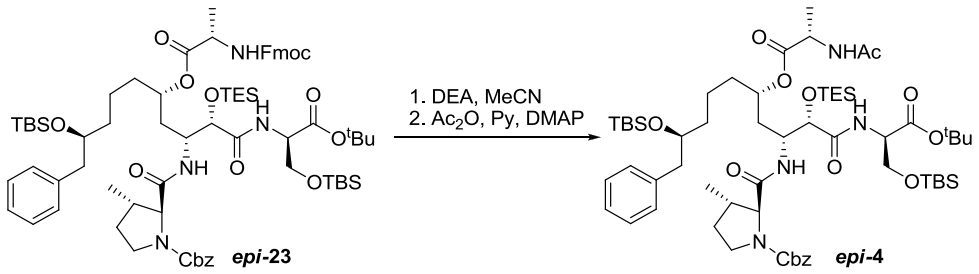
$[\alpha]_D^{20}$ = −3.5 (*c* 0.68, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.72 – 7.50 (m, 2H), 7.41 – 7.09 (m, 10H), 5.22 – 5.04 (m, 2H), 4.52 (d, *J* = 8.3 Hz, 1H), 4.41 – 3.98 (m, 4H), 3.87 (d, *J* = 5.0 Hz, 1H), 3.84 – 3.26 (m, 4H), 2.82 – 2.55 (m, 2H), 2.50 – 2.39 (m, 1H), 2.11 – 1.99 (m, 1H), 1.73 – 1.32 (m, 17H), 1.22 – 1.10 (m, 4H), 1.05 – 0.92 (m, 9H), 0.88 (s, 9H), 0.82 (s, 9H), 0.76 – 0.60 (m, 6H), 0.05 (s, 6H), -0.10 (s, 3H), -0.26 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 173.1, 172.8, 172.1, 168.3, 155.0, 154.8, 139.5, 136.6, 136.4, 129.7, 128.3, 127.9, 127.7, 127.1, 125.7, 82.1, 73.9, 72.8, 67.8, 66.9, 66.6, 63.6, 54.1, 49.5, 49.3, 46.3, 45.9, 43.6, 39.8, 38.3, 37.3, 37.0, 32.2, 31.5, 28.0, 25.8, 25.7, 22.0, 18.9, 18.6, 18.1, 18.0, 6.6, 4.5, -4.8, -5.1, -5.7; **HRMS (ESI)** *m/z* calcd for $C_{55}H_{96}N_3O_{10}Si_3^+$ $[M+H]^+$ 1042.6398, found 1042.6380.



epi-**23** was prepared from *epi*-**38** in 88% yield. Analytical data for *epi*-**23**:

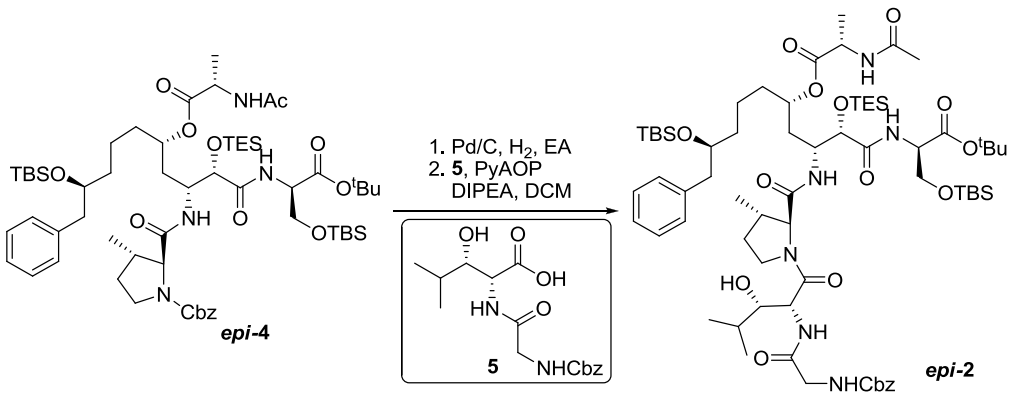
$[\alpha]_D^{20}$ = +1.0 (*c* 0.70, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.64 – 7.51 (m, 3H), 7.42 – 7.11 (m, 15H), 7.07 – 6.84 (m, 1H), 5.80 – 5.52 (m, 1H), 5.32 – 4.83 (m, 3H), 4.56 – 4.18 (m, 6H), 4.16 – 3.92 (m, 2H), 3.82 – 3.52 (m, 5H), 2.76 – 2.59 (m, 2H), 2.52 – 2.38 (m, 1H), 2.15 – 1.96 (m, 2H), 1.59 – 1.32 (m, 19H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.02 – 0.94 (m, 9H), 0.89 (s, 9H), 0.82 (s, 9H), 0.78 – 0.59 (m, 6H), 0.06 (s, 6H), -0.09 (s, 3H), -0.25 (s, 3H). **^{13}C NMR** (75

MHz, $CDCl_3$) exists as rotational conformers: δ 172.2, 172.1, 172.1, 171.6, 168.4, 168.3, 155.7, 154.9, 144.0, 143.8, 141.2, 139.2, 136.8, 129.7, 128.3, 127.9, 127.5, 127.3, 127.0, 125.8, 125.1, 119.8, 82.0, 73.4, 73.0, 71.5, 71.3, 68.3, 68.1, 66.8, 66.7, 63.5, 54.0, 49.8, 48.5, 48.3, 47.1, 46.4, 46.1, 43.8, 39.4, 37.8, 37.0, 35.0, 32.3, 31.5, 29.6, 28.0, 25.8, 25.7, 20.8, 18.8, 18.5, 18.1, 17.9, 6.7, 4.4, -4.8, -5.1, -5.7. **HRMS (ESI)** *m/z* calcd for $C_{73}H_{111}N_4O_{13}Si_3^+$ $[M+H]^+$ 1335.7450, found 1335.7458.



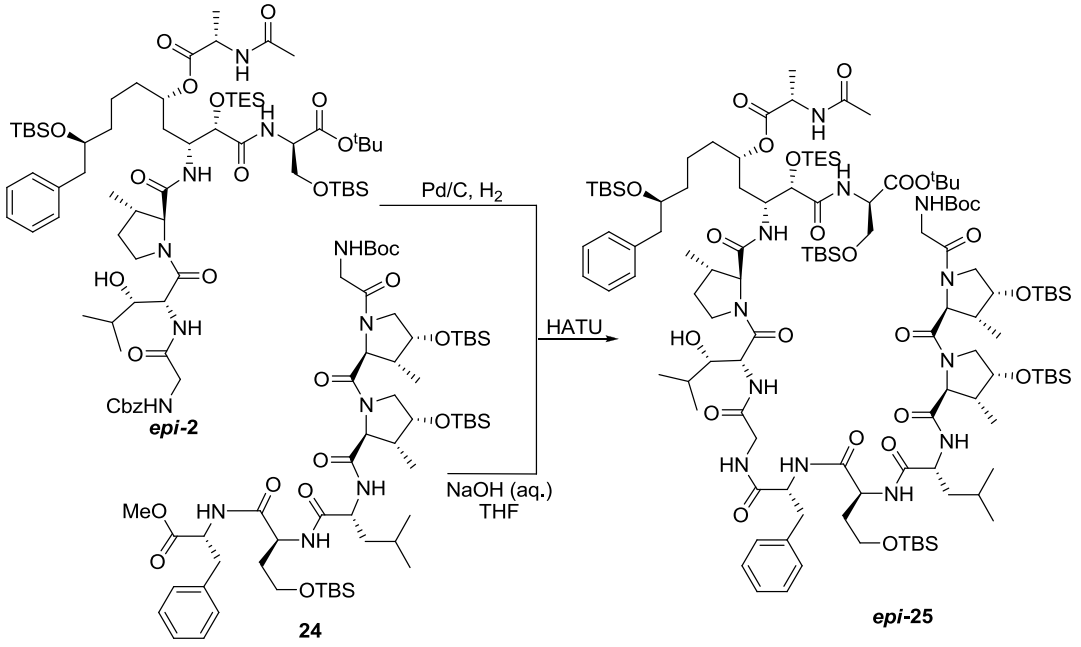
epi-**4** was prepared from *epi*-**23** in 91% yield. Analytical data for *epi*-**4**:

$[\alpha]_D^{20}$ = +0.3 (*c* 0.77, $CHCl_3$); **^{1}H NMR** (300 MHz, $CDCl_3$) exists as rotational conformers: δ 7.54 (d, *J* = 8.5 Hz, 1H), 7.40 – 7.10 (m, 10H), 7.05 (d, *J* = 9.1 Hz, 0.5H), 6.93 (d, *J* = 9.4 Hz, 0.5H), 6.61 (d, *J* = 7.3 Hz, 0.5H), 6.47 (d, *J* = 6.8 Hz, 0.5H), 5.27 (d, *J* = 12.8 Hz, 0.5H), 5.12 (s, 1H), 5.05 (d, *J* = 13.1 Hz, 0.5H), 4.86 (brs, 1H), 4.64 – 4.45 (m, 2H), 4.37 – 4.18 (m, 1.5H), 4.16 – 4.04 (m, 1H), 3.96 (s, 0.5H), 3.81 – 3.49 (m, 5H), 2.67 (d, *J* = 6.3 Hz, 2H), 2.43 (dt, *J* = 12.7, 6.5 Hz, 1H), 2.14 – 2.01 (m, 2H), 1.98 (s, 3H), 1.57 – 1.29 (m, 20H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.06 – 0.91 (m, 9H), 0.88 (s, 9H), 0.82 (s, 9H), 0.75 – 0.55 (m, 6H), 0.05 (s, 6H), -0.08 (s, 3H), -0.24 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) exists as rotational conformers: δ 172.1, 172.0, 171.6, 169.3, 168.2, 154.9, 139.2, 136.8, 129.7, 128.3, 128.0, 127.5, 127.2, 125.8, 82.0, 73.4, 73.0, 71.2, 71.2, 68.2, 68.0, 66.7, 63.4, 54.0, 48.4, 46.4, 46.0, 43.9, 39.5, 37.9, 36.9, 34.9, 32.3, 31.5, 28.0, 25.8, 25.7, 23.1, 20.7, 18.7, 18.4, 18.2, 18.1, 17.9, 6.6, 4.4, -4.8, -5.1, -5.73, -5.74; **HRMS (ESI)** *m/z* calcd for $C_{60}H_{103}N_4O_{12}Si_3^+$ $[M+H]^+$ 1155.6875, found 1155.6878.



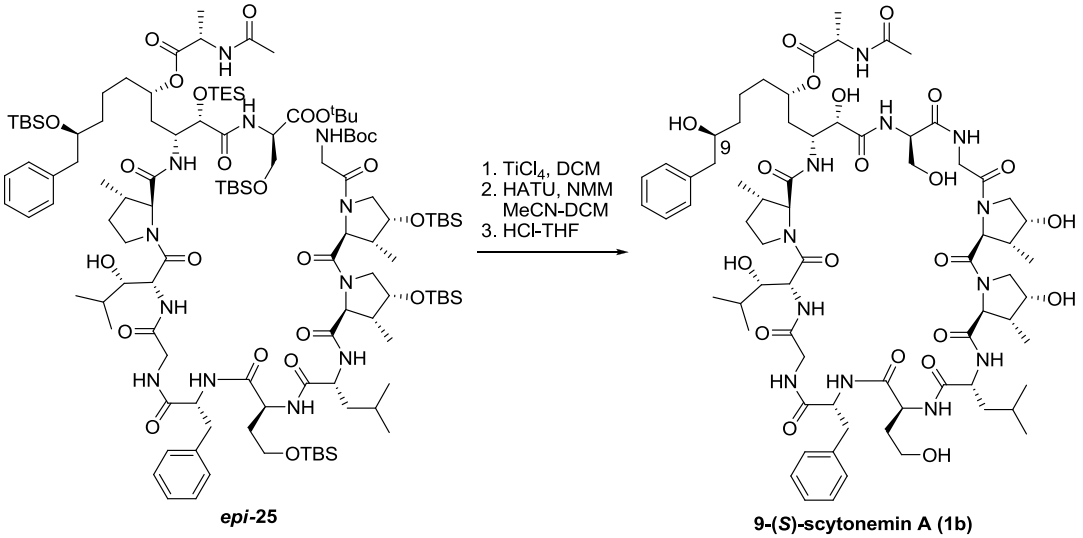
epi-**2** was prepared from *epi*-**4** in 70% yield. Analytical data for *epi*-**2**:

$[\alpha]_D^{20}$ = −5.8 (*c* 0.90, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.38 – 7.27 (m, 5H), 7.24 – 7.21 (m, 2H), 7.18 – 5.12 (m, 3H), 5.13 (d, *J* = 5.4 Hz, 2H), 4.87 (s, 1H), 4.52 – 4.38 (m, 3H), 4.34 (dd, *J* = 14.9, 7.4 Hz, 1H), 4.23 (s, 1H), 4.18 (d, *J* = 8.9 Hz, 1H), 4.00 – 3.91 (m, 3H), 3.84 (d, *J* = 7.5 Hz, 2H), 3.65 (d, *J* = 7.8 Hz, 3H), 3.29 (s, 1H), 2.71 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.64 (dd, *J* = 13.2, 7.1 Hz, 1H), 2.38 (brs, 1H), 2.25 (brs, 1H), 2.10 (s, 3H), 1.89 – 1.58 (m, 5H), 1.49 – 1.40 (m, 18H), 1.14 (d, *J* = 6.9 Hz, 1H), 1.04 (t, *J* = 8.0 Hz, 9H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.90 – 0.85 (m, 12H), 0.85 – 0.76 (m, 15H), 0.06 (s, 6H), -0.06 (s, 3H), -0.25 (s, 3H); **^{13}C NMR** (125 MHz, MeOD) δ 174.8, 173.3, 172.7, 172.6, 172.3, 171.6, 168.5, 168.2, 157.6, 139.1, 136.3, 129.4, 128.2, 127.9, 127.8, 127.6, 125.7, 82.9, 75.9, 73.9, 73.6, 70.9, 67.3, 67.0, 63.0, 55.8, 55.0, 49.5, 46.1, 44.3, 43.4, 37.1, 36.6, 35.6, 35.0, 31.7, 31.4, 27.2, 25.1, 25.1, 21.1, 20.8, 18.2, 18.1, 17.9, 17.5, 17.4, 15.8, 5.9, 4.3, -5.7, -6.0, -6.6, -6.7; **HRMS (ESI)** *m/z* calcd for $C_{68}H_{117}N_6O_{15}Si_3^+$ $[M+H]^+$ 1341.7879, found 1341.7872.



epi-**25** was prepared from *epi*-**2** in 51% yield. Analytical data for *epi*-**25**:

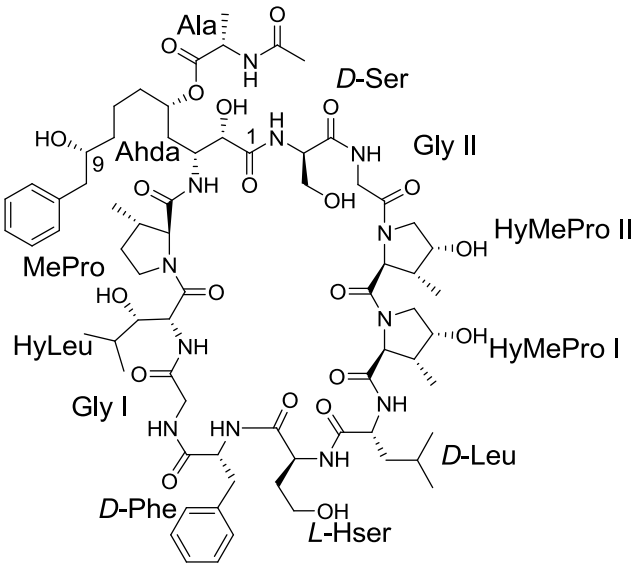
$[\alpha]_D^{20}$ = +21.2 (*c* 0.70, MeOH); **^{1}H NMR** (500 MHz, MeOD) exists as rotational conformers: δ 7.31 – 7.13 (m, 10H), 4.56 – 4.25 (m, 9H), 4.19 (d, *J* = 9.1 Hz, 1H), 4.17 – 4.12 (m, 1H), 4.10 – 4.05 (m, 1H), 4.00 (d, *J* = 10.2 Hz, 1H), 3.93 – 3.82 (m, 5H), 3.80 – 3.67 (m, 5H), 3.62 (dd, *J* = 7.0, 3.3 Hz, 1H), 3.56 – 3.45 (m, 3H), 3.27 – 3.20 (m, 1H), 2.76 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.65 (dd, *J* = 13.3, 7.2 Hz, 1H), 2.40 – 2.23 (m, 4H), 2.00 (s, 3H), 1.78 – 1.55 (m, 9H), 1.47 (s, 11H), 11.45 – 1.40 (m, 16H), 1.14 (t, *J* = 7.1 Hz, 6H), 1.10 (d, *J* = 6.6 Hz, 3H), 1.06 – 1.01 (m, 12H), 1.00 – 0.95 (m, 9H), 0.93 (s, 15H), 0.91 (s, 15H), 0.89 (s, 12H), 0.85 (s, 9H), 0.80 – 0.74 (m, 6H), 0.17 – 0.11 (m, 12H), 0.09 (s, 6H), 0.05 – 0.02 (m, 6H), -0.03 (s, 6H), -0.24 (s, 2.3H), -0.26 (s, 0.7H); **^{13}C NMR** (125 MHz, MeOD) exists as rotational conformers: δ 173.50, 172.52, 172.41, 172.28, 172.25, 172.21, 172.11, 171.71, 171.69, 171.05, 169.71, 169.68, 168.80, 156.59, 139.27, 137.17, 129.50, 128.87, 128.25, 127.75, 126.48, 125.69, 82.10, 79.18, 75.57, 73.72, 73.64, 73.58, 71.33, 67.94, 66.24, 63.33, 63.22, 63.14, 59.36, 56.37, 55.55, 54.79, 51.51, 51.14, 48.89, 48.53, 46.20, 43.51, 43.13, 42.64, 42.32, 41.84, 39.31, 39.04, 37.50, 37.20, 37.00, 36.55, 34.68, 33.78, 31.83, 31.62, 30.26, 29.29, 29.00, 27.44, 27.23, 25.23, 25.14, 25.06, 25.03, 24.94, 24.66, 22.44, 21.23, 20.20, 19.95, 18.73, 17.86, 17.80, 17.76, 17.63, 17.60, 17.53, 16.47, 12.98, 10.71, 10.34, 5.93, 4.25, -5.55, -5.84, -5.86, -5.98, -6.05, -6.22, -6.39, -6.62, -6.64; **HRMS (ESI)** *m/z* calcd for $C_{116}H_{209}N_{12}O_{24}Si_6^+[M+H]^+$ 2322.4113, found 2322.4152.



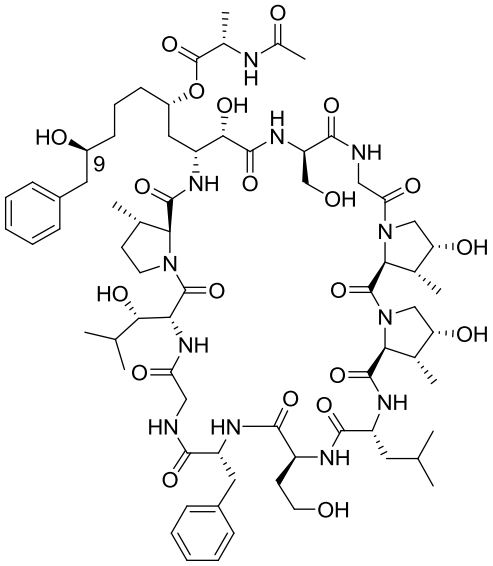
9-(*S*)-scytonemin A (**1b**) was prepared from *epi*-**25** in 30% yield (11.7 mg). Analytical data for 9-(*S*)-scytonemin A (**1b**):

$[\alpha]_D^{20}$ = +26 (*c* 0.06, MeOH); **^{1}H NMR** (500 MHz, DMSO-d6) δ 8.38 (s, 1H), 8.16 (d, *J* = 6.6 Hz, 1H), 7.96 (s, 1H), 7.92 (d, *J* = 6.7 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.74 – 7.57 (m, 3H), 7.26 – 7.13 (m, 10H), 5.29 (s, 1H), 5.19 (s, 1H), 5.12 (s, 1H), 4.81 (s, 1H), 4.74 (s, 1H), 4.66 (s, 1H), 4.43 (d, *J* = 5.3 Hz, 2H), 4.36 (s, 1H), 4.32 – 4.19 (m, 3H), 4.19 – 4.11 (m, 2H), 4.11 – 4.05 (m, 2H), 4.06 – 4.00 (m, 1H), 4.00 – 3.91 (m, 3H), 3.87 – 3.78 (m, 4H), 3.76 – 3.68 (m, 3H), 3.66 – 3.56 (m, 5H), 3.53 – 3.52 (m, 1H), 3.43 – 3.41 (m, 1H), 3.08 (d, *J* = 13.2 Hz, 1H), 2.89 – 2.82 (m, 1H), 2.63 (brs, 5H), 2.24 – 2.12 (m, 2H), 2.12 – 2.01 (m, 2H), 1.87 – 1.63 (m, 9H), 1.59 – 1.51 (m, 3H), 1.50 – 1.39 (m, 3H), 1.33 – 1.19 (m, 5H), 1.08 – 1.01 (m, 6H), 0.99 (d, *J* = 6.3 Hz, 3H), 0.91 (s, 3H), 0.90 (s, 3H), 0.89 – 0.88 (m, 3H), 0.81 (d, *J* = 5.5 Hz, 3H); **^{13}C NMR** (150 MHz, DMSO-d6) δ 172.39, 172.17, 172.05, 172.03, 171.44, 171.24, 171.00, 170.18, 169.92, 169.25, 169.07, 168.51, 166.66, 139.78, 137.98, 129.42, 129.03, 128.16, 128.01, 126.26, 125.72, 75.65, 72.97, 71.37, 71.19, 71.05, 71.05, 67.06, 65.58, 62.22, 61.44, 57.61, 56.36, 55.05, 54.22, 54.01, 52.30, 50.74, 50.49, 48.25, 47.85, 46.30, 43.69, 43.69, 42.31, 42.31, 41.75, 41.10, 37.07, 36.63, 36.63, 35.10, 34.30, 32.09, 30.16, 24.40, 23.46, 22.25, 20.86, 20.62, 19.56, 18.50, 18.28, 17.06, 11.37, 10.54; **HRMS (ESI)** *m/z* calcd for $C_{71}H_{107}N_{12}O_{21}^+$ $[M+H]^+$ 1463.7668, found 1463.7686.

2.5. ^{13}C NMR comparison of synthetic scytonemin A (1a, 1b) & natural scytonemin A (in DMSO-d6)



9-(*R*)-scytonemin A (**1a**)



9-(*S*)-scytonemin A (**1b**)

Amino unit	Assignment	δ, ppm Natural Scytonemin A (75 M)	δ_{1a}, ppm 9-(*R*)-Scytonemin A (**1a**) (150M)	$\Delta\delta_a = \delta_{1a} - \delta$ (ppm)	δ_{1b}, ppm 9-(*S*)-Scytonemin A (**1b**) (150M)	$\Delta\delta_b = \delta_{1b} - \delta$ (ppm)
Carbonyl	C=O	172.46	172.42	-0.04	172.39	-0.07
	C=O	172.27	172.17	-0.10	172.17	-0.10
	C=O	172.18	172.07	-0.11	172.05	-0.13
	C=O	172.18	172.01	-0.17	172.03	-0.15
	C=O	171.55	171.43	-0.12	171.44	-0.11
	C=O	171.39	171.28	-0.11	171.24	-0.15
	C=O	171.10	171.01	-0.09	171.00	-0.10
	C=O	170.33	170.17	-0.16	170.18	-0.15
	C=O	170.09	169.95	-0.14	169.92	-0.17
	C=O	169.39	169.27	-0.12	169.25	-0.14
	C=O	169.18	169.10	-0.08	169.07	-0.11
	C=O	168.65	168.56	-0.09	168.51	-0.14
	C=O	166.78	166.68	-0.10	166.66	-0.12
Ahda	C1'	139.74	139.81	+0.07	139.78	+0.04
	C3',5'	128.98	129.05	+0.07	129.03	+0.05
	C2',6'	128.09	128.17	+0.08	128.16	+0.07
	C4'	125.65	125.72	+0.07	125.72	+0.07
	C2	72.87	72.94	+0.07	72.97	+0.10
	C3	50.74	50.74	0	50.74	0

Amino unit	Assignment	δ, ppm Natural Scytonemin A (75 M)	δ_{1a}, ppm 9-(*R*)-Scytonemin A (**1a**) (150M)	$\Delta\delta_a = \delta_{1a} - \delta$ (ppm)	δ_{1b}, ppm 9-(*S*)-Scytonemin A (**1b**) (150M)	$\Delta\delta_b = \delta_{1b} - \delta$ (ppm)
Ahda	C4	36.45	36.47	+0.02	36.63	+0.18
	C5	71.03	71.04	+0.01	71.05	+0.02
	C6	34.24	34.29	+0.05	34.30	+0.06
	C7	20.62	20.72	+0.10	20.86	+0.24
	C8	39.79	*	-	*	-
	C9	70.86	70.90	+0.04	71.05	+0.19
	C10	43.64	43.68	+0.04	43.69	+0.05
Ala	C2	47.82	47.88	+0.06	47.85	+0.03
	C3	17.02	17.05	+0.03	17.06	+0.04
	CH3	22.21	22.26	+0.05	22.25	+0.04
MePro	C2	62.24	62.21	-0.03	62.22	-0.02
	C3	42.28	42.33	+0.05	42.31	+0.03
	C4	32.05	32.06	+0.01	32.09	+0.04
	C5	43.64	43.68	+0.04	43.69	+0.05
	CH3	18.28	18.30	+0.02	18.28	0
HyLeu	C2	52.32	52.38	+0.06	52.30	-0.02
	C3	75.58	75.62	+0.04	75.65	+0.07
	C4	30.13	30.16	+0.03	30.16	+0.03
	CH3	19.55	19.58	+0.03	19.56	+0.01
	CH3	18.44	18.50	+0.06	18.50	+0.06
Gly Ⅰ	C2	46.24	46.29	+0.05	46.30	+0.06
D-Phe	C1'	137.90	138.01	+0.11	137.98	+0.08
	C3',C5'	129.33	129.41	+0.08	129.42	+0.09
	C2',6'	127.94	128.02	+0.08	128.01	+0.07
	C4'	126.20	126.26	+0.06	126.26	+0.06
	C2	54.14	54.25	+0.11	54.22	+0.08
	C3	37.06	37.09	+0.03	37.07	+0.01
L-Hser	C2	50.49	50.50	+0.01	50.49	0
	C3	34.93	34.97	+0.04	35.10	+0.17
	C4	57.61	57.62	+0.01	57.61	0
D-Leu	C2	48.18	48.24	+0.06	48.25	+0.07
	C3	41.08	41.10	+0.02	41.10	+0.02
	C4	24.40	24.41	+0.01	24.40	0
	CH3	23.42	23.47	+0.05	23.46	+0.04
	CH3	20.62	20.64	+0.02	20.62	0

Amino unit	Assignment	δ, ppm Natural Scytonemin A (75 M)	δ_{1a}, ppm 9-(*R*)-Scytonemin A (**1a**) (150M)	$\Delta\delta_a = \delta_{1a} - \delta$ (ppm)	δ_{1b}, ppm 9-(*S*)-Scytonemin A (**1b**) (150M)	$\Delta\delta_b = \delta_{1b} - \delta$ (ppm)
HyMePro Ⅰ	C2	67.02	67.06	+0.04	67.06	+0.04
	C3	36.56	36.64	+0.08	36.63	+0.07
	C4	71.33	71.37	+0.04	71.37	+0.04
	C5	56.31	56.36	+0.05	56.36	+0.05
	CH3	11.36	11.38	+0.02	11.37	+0.01
HyMePro Ⅱ	C2	65.57	65.58	+0.01	65.58	+0.01
	C3	41.71	41.77	+0.06	41.75	+0.04
	C4	71.17	71.19	+0.02	71.19	+0.02
	C5	53.95	54.01	+0.06	54.01	+0.06
	CH3	10.52	10.56	+0.04	10.54	+0.02
D-Ser	C2	54.91	55.08	+0.17	55.05	+0.14
	C3	61.41	61.46	+0.05	61.44	+0.03
Gly Ⅱ	C2	42.28	42.33	+0.05	42.31	+0.03

Note: * stands for the peak was hidden by peaks of deuterated solvent.

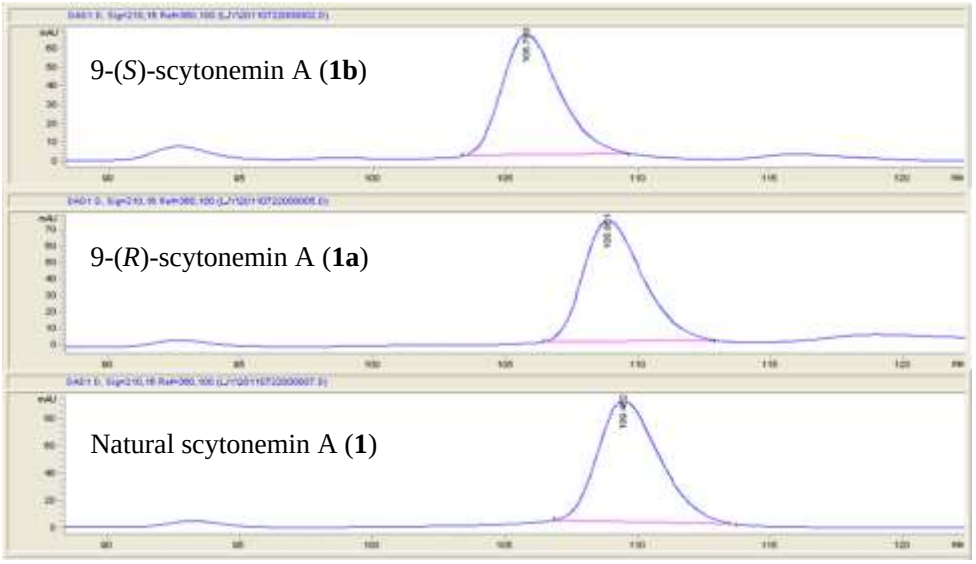
3. HPLC comparison of synthetic samples and natural scytonemin A

HPLC Analysis Conditions:

Agilent 1200 system, CHIRALPAK AS-RH column (reverse-phase, 4.6 × 150 mm, 5 μm), a constant elution consisting of H_2O-MeCN (74:26) at a flow rate of 0.1 mL/min.

HPLC Chromatogram Comparison

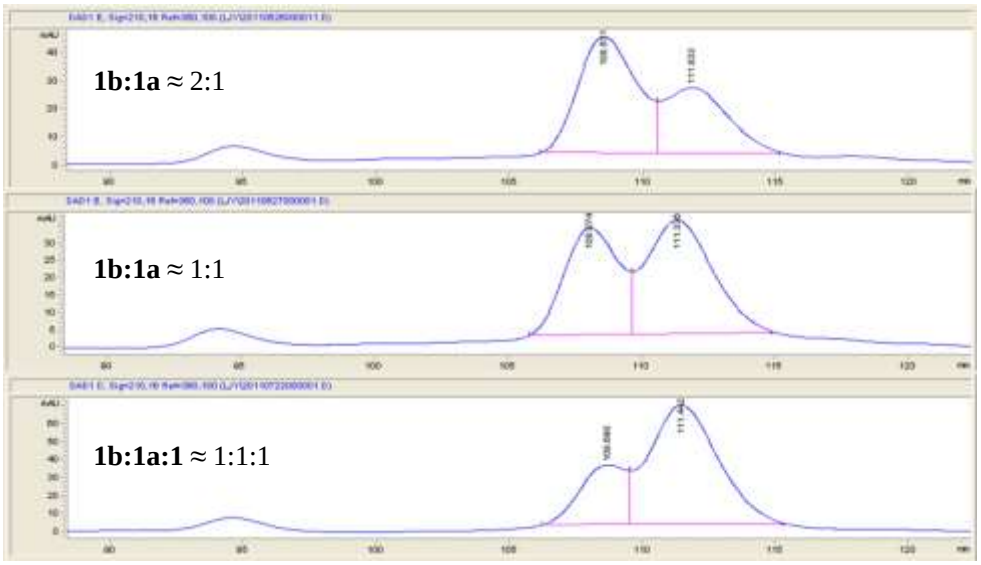
Synthetic scytonemin A (1a and 1b) and natural scytonemin A (injected separately)



HPLC Chromatogram Comparison

Co-injection of synthetic and natural scytonemin A

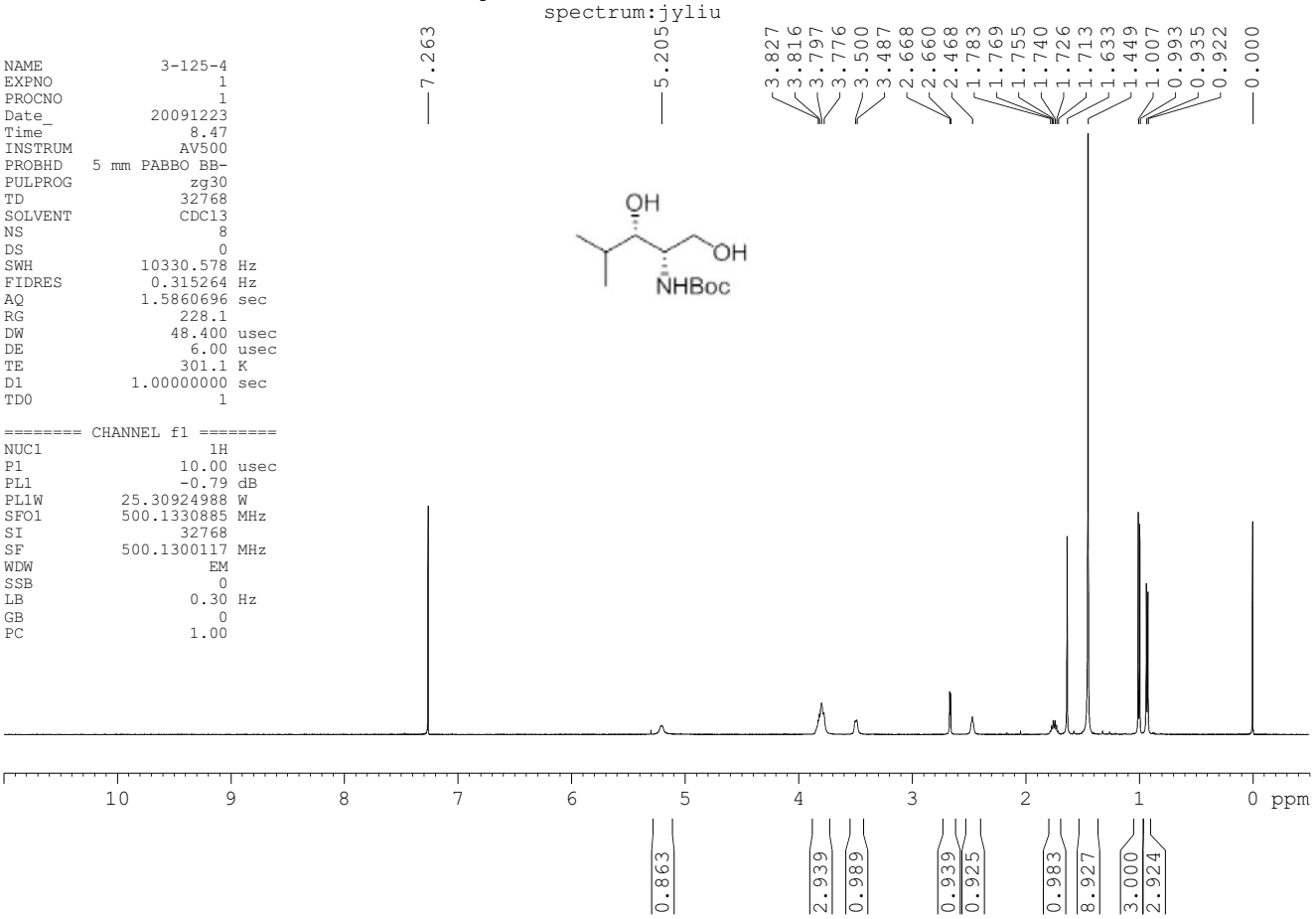
(**1** *for natural scytonemin A;* **1a** for 9-(*R*)-scytonemin A; **1b** for 9-(*S*)-scytonemin A)



4. ^{1}H & ^{13}C NMR Spectra

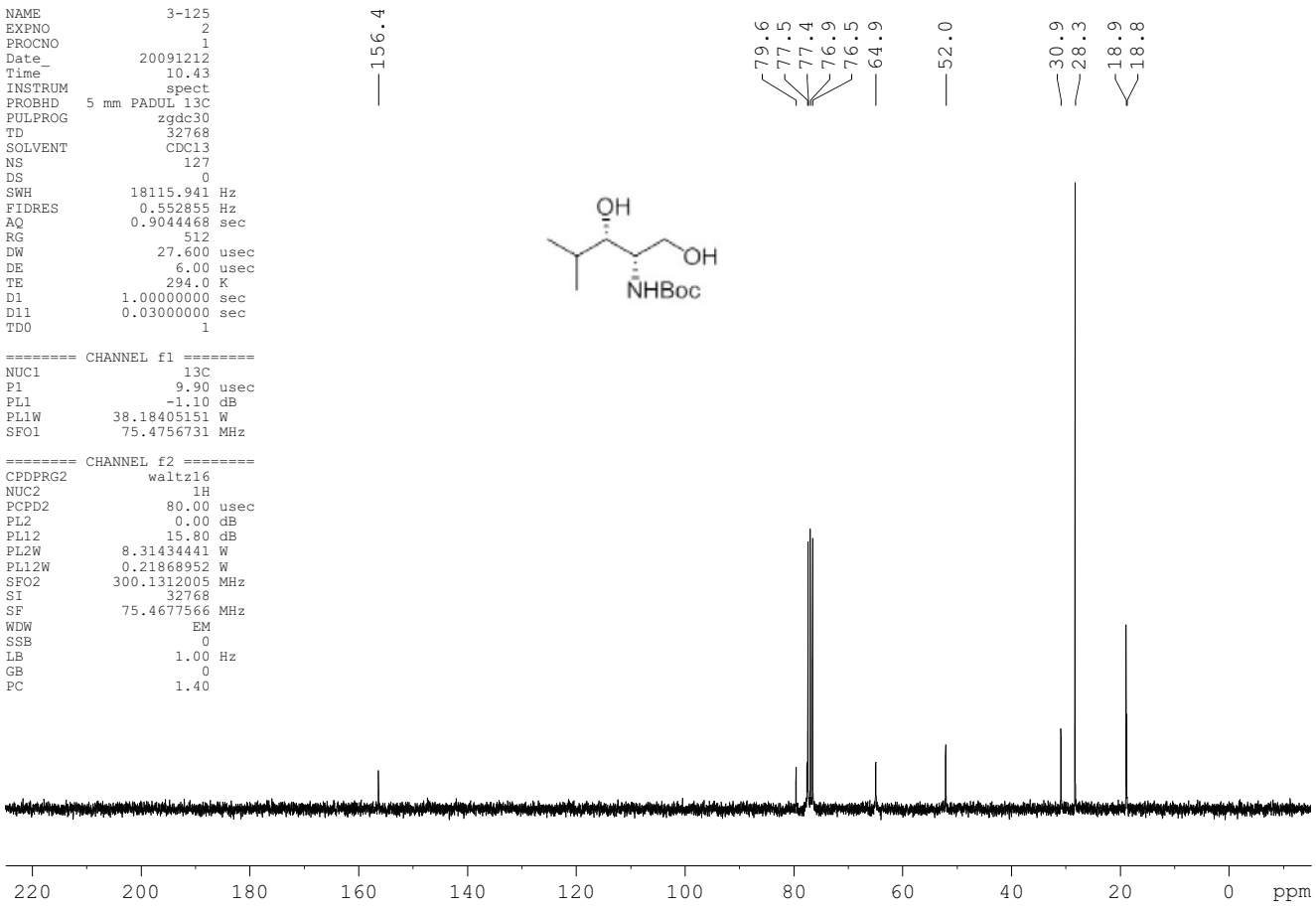
Avance 500, Bruker, SZPKU
sample:3-125-4, solvent:CDCl3
spectrum:jyliu

```
NAME            3-125-4
EXPNO                 1
PROCNO                1
Date_          20091223
Time               8.47
INSTRUM           AV500
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES         0.315264 Hz
AQ            1.5860696 sec
RG                228.1
DW               48.400 usec
DE                6.00 usec
TE               301.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -0.79 dB
PL1W        25.30924988 W
SFO1        500.1330885 MHz
SI                32768
SF          500.1300117 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

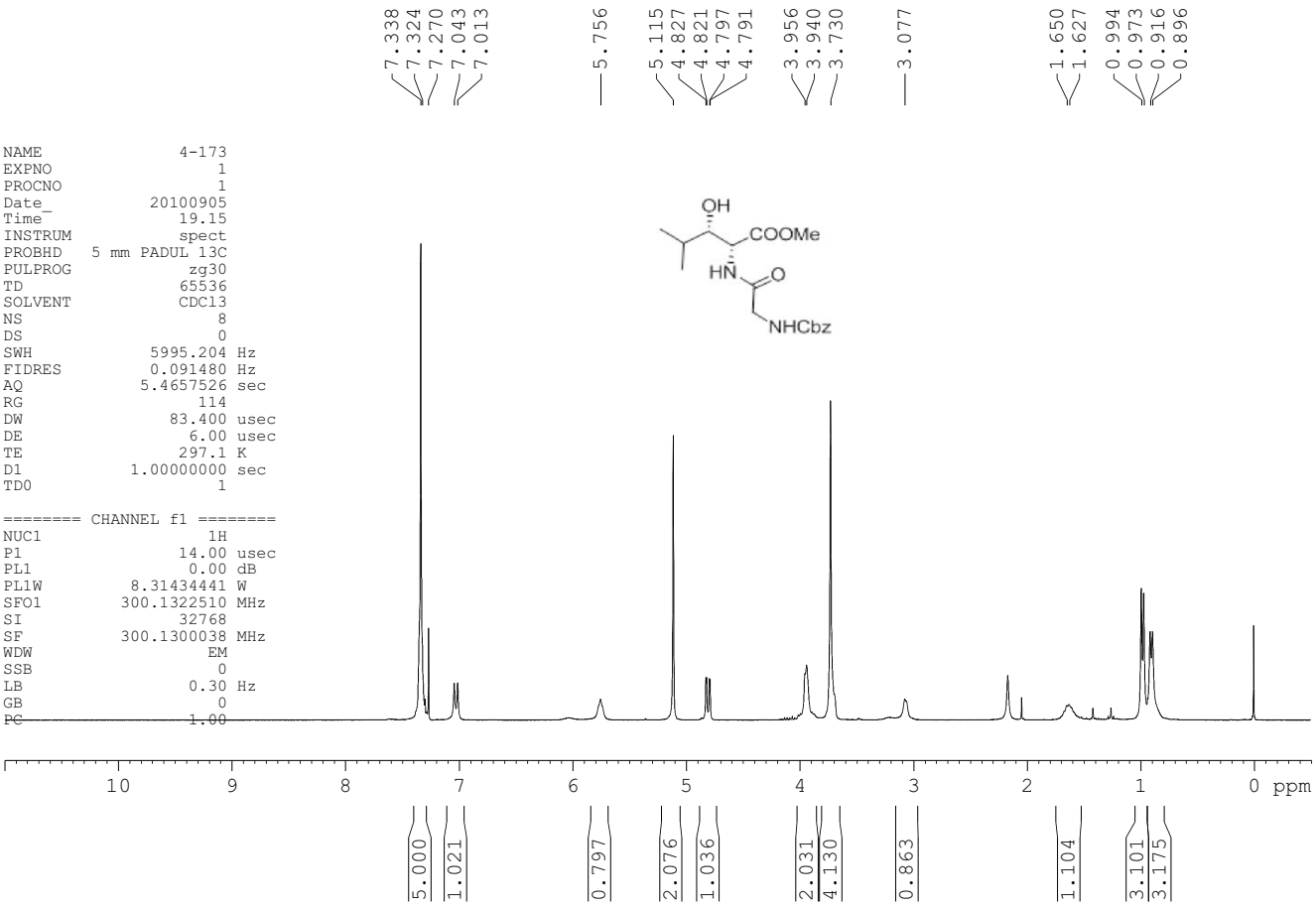


sample name: 3-125
solvent: CDCl3

```
NAME              3-125
EXPNO                 2
PROCNO                1
Date_          20091212
Time              10.43
INSTRUM           spect
PROBHD   5 mm PADUL 13C
PULPROG          zgdc30
TD                32768
SOLVENT           CDCl3
NS                  127
DS                    0
SWH           18115.941 Hz
FIDRES         0.552855 Hz
AQ            0.9044468 sec
RG                  512
DW               27.600 usec
DE                6.00 usec
TE               294.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.90 usec
PL1               -1.10 dB
PL1W        38.18405151 W
SFO1         75.4756731 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.80 dB
PL2W         8.31434441 W
PL12W        0.21868952 W
SFO2        300.1312005 MHz
SI                32768
SF           75.4677566 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



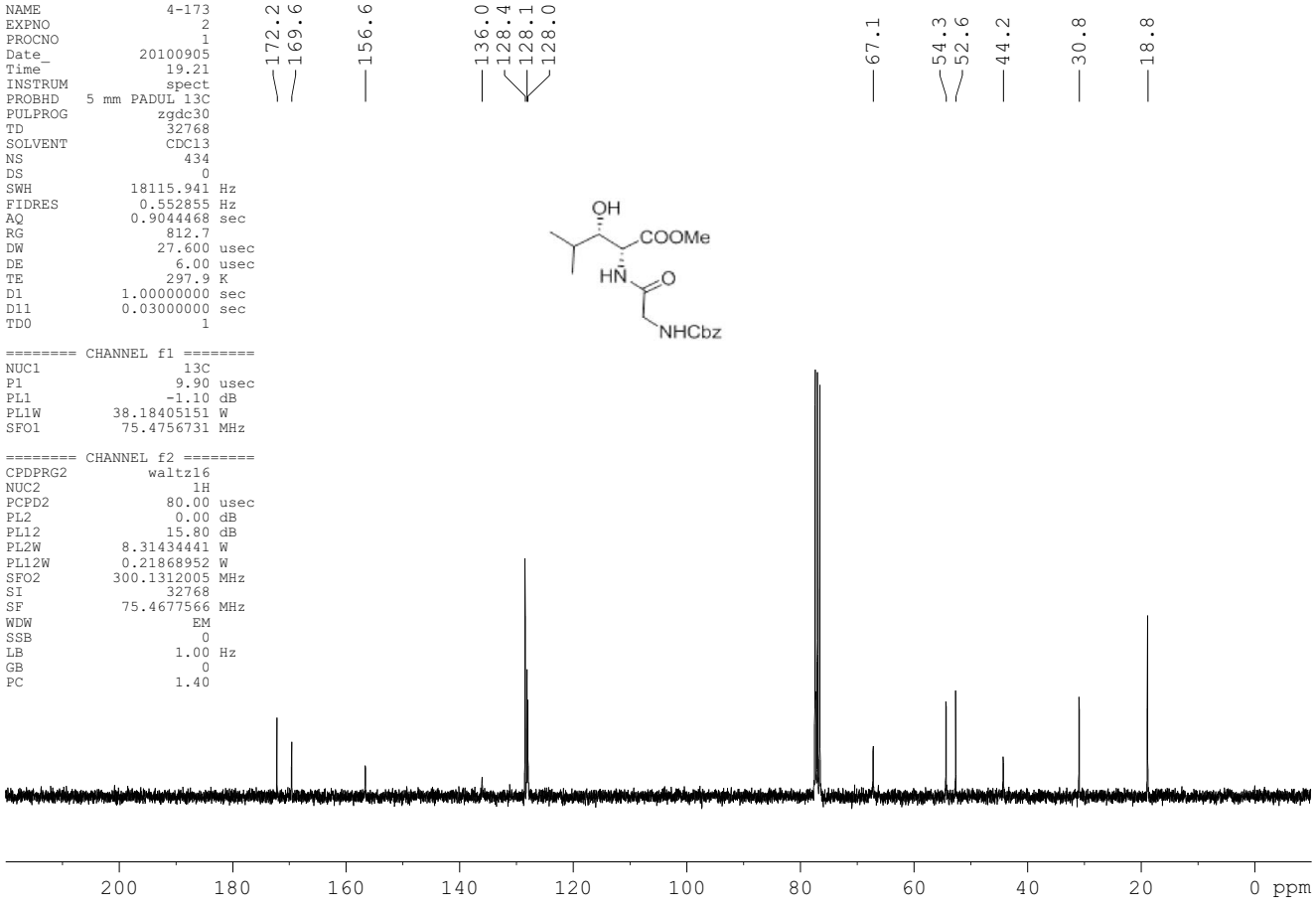
sample name:4-173
solvent:CDCl3
Bruker 300M



NAME 4-173
EXPNO 1
PROCNO 1
Date_ 20100905
Time 19.15
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.091480 Hz
AQ 5.4657526 sec
RG 114
DW 83.400 usec
DE 6.00 usec
TE 297.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 300.1322510 MHz
SI 32768
SF 300.1300038 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

sample name: 4-173
solvent: CDCl3
Bruker 300M

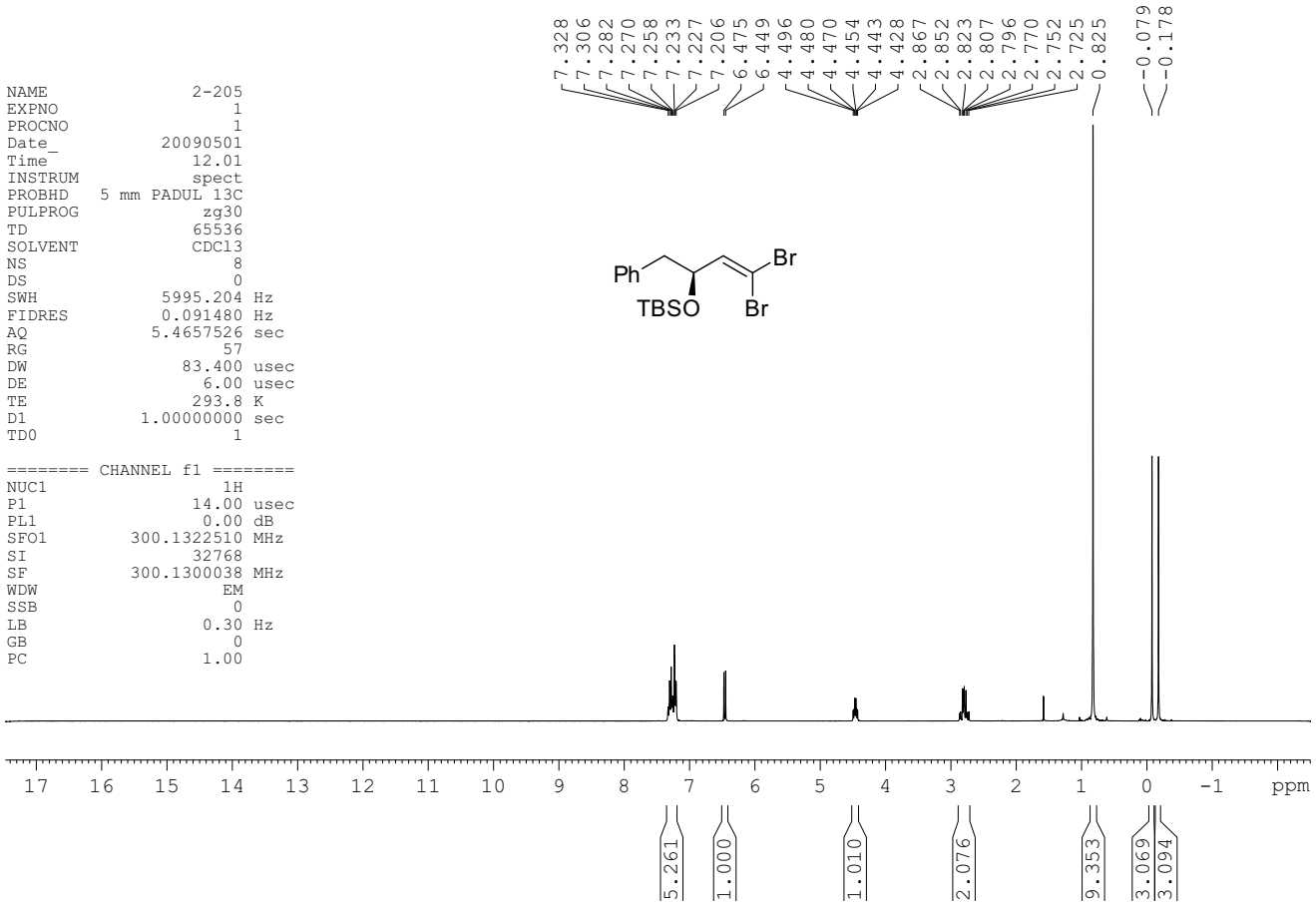


NAME 4-173
EXPNO 2
PROCNO 1
Date_ 20100905
Time 19.21
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 434
DS 0
SWH 18115.941 Hz
FIDRES 0.552855 Hz
AQ 0.9044468 sec
RG 812.7
DW 27.600 usec
DE 6.00 usec
TE 297.9 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -1.10 dB
PL1W 38.18405151 W
SFO1 75.4756731 MHz

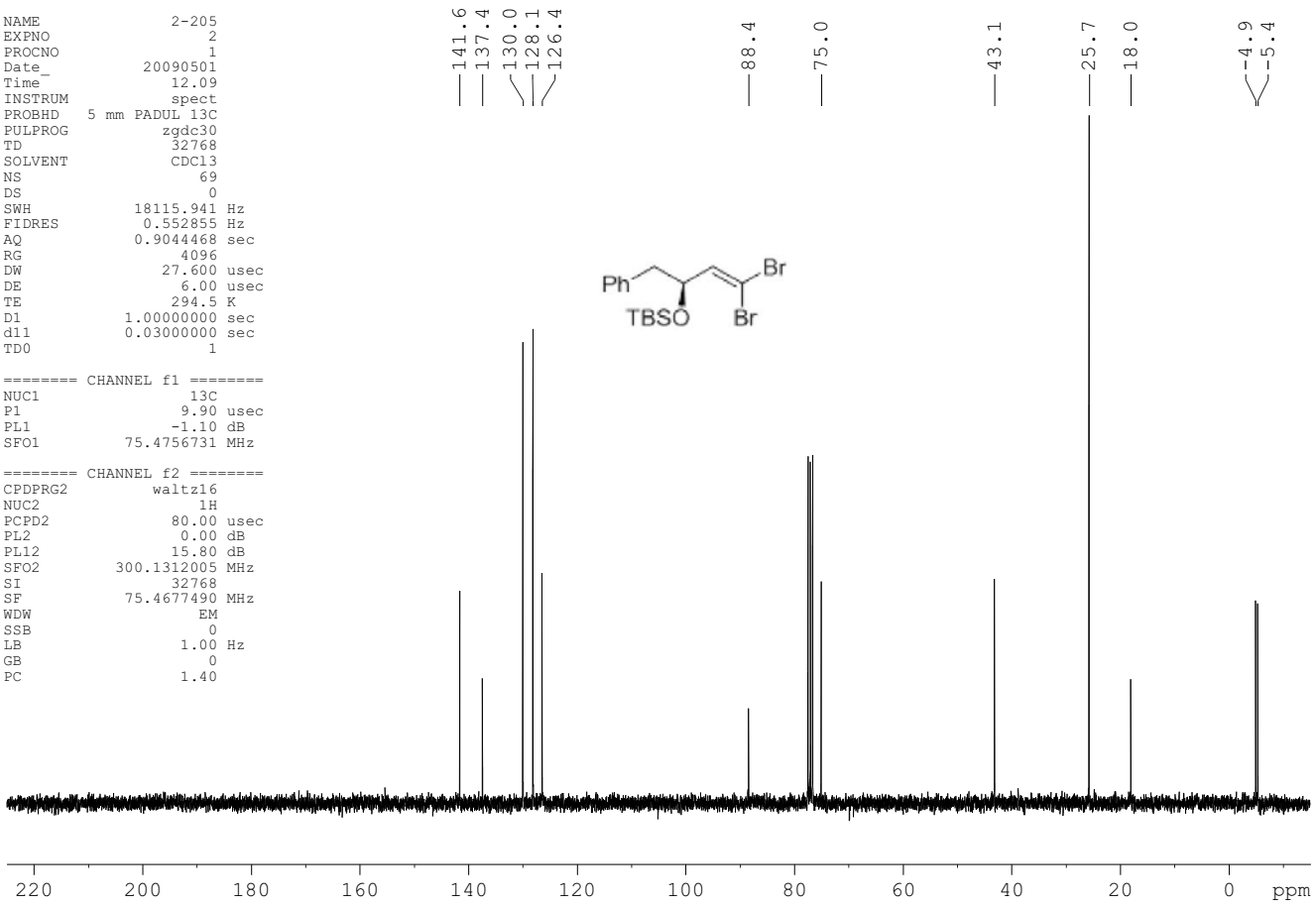
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.80 dB
PL2W 8.31434441 W
PL12W 0.21868952 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677566 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

samole name:2-205
solvent:CDCl3



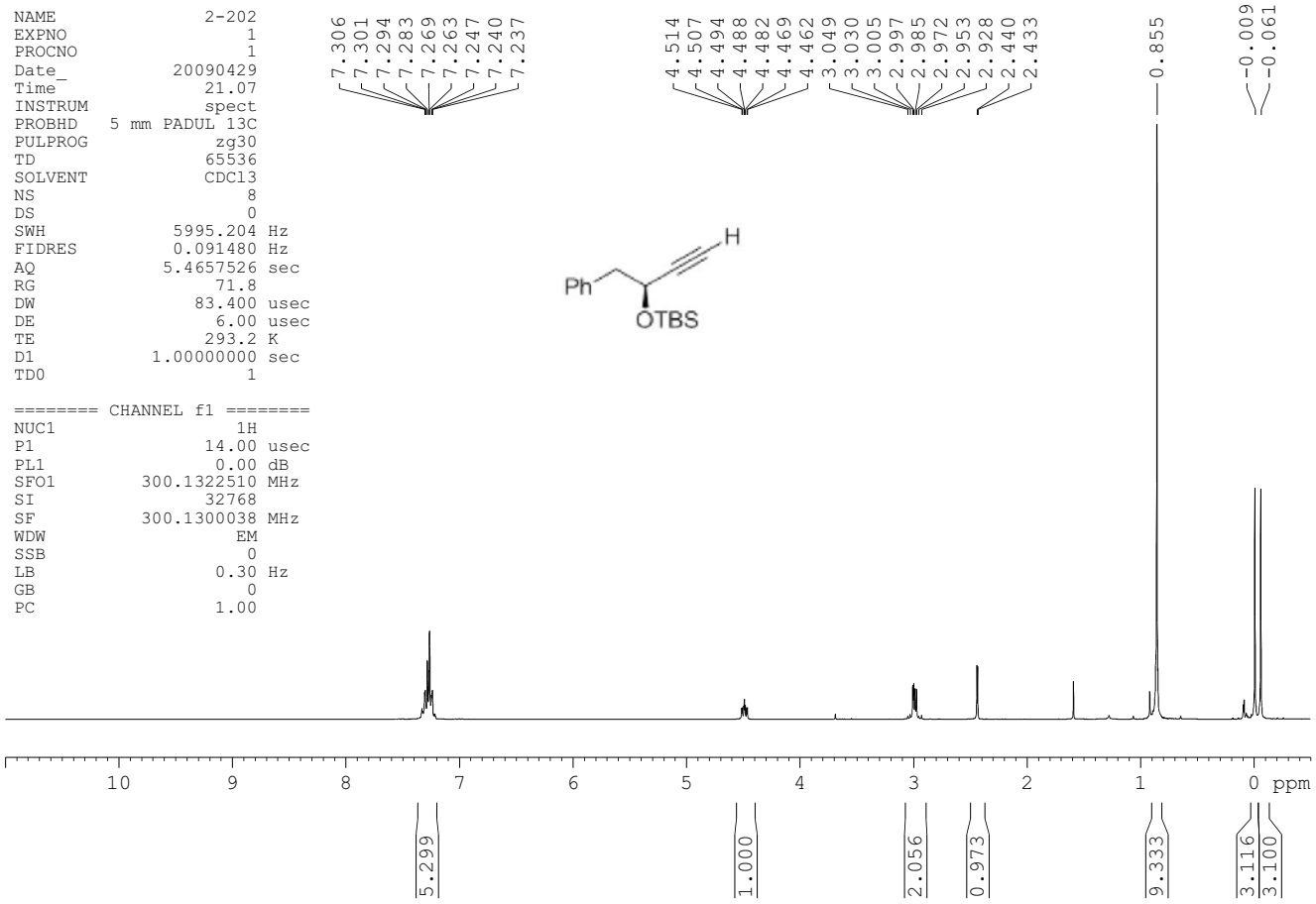

```
NAME                2-205
EXPNO                   1
PROCNO                  1
Date_            20090501
Time                12.01
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              5995.204 Hz
FIDRES           0.091480 Hz
AQ               5.4657526 sec
RG                     57
DW                 83.400 usec
DE                  6.00 usec
TE                 293.8 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.00 usec
PL1                 0.00 dB
SFO1         300.1322510 MHz
SI                  32768
SF           300.1300038 MHz
WDW                    EM
SSB                     0
LB                  0.30 Hz
GB                      0
PC                  1.00
```

sample name:2-205
solvent:CDCl3

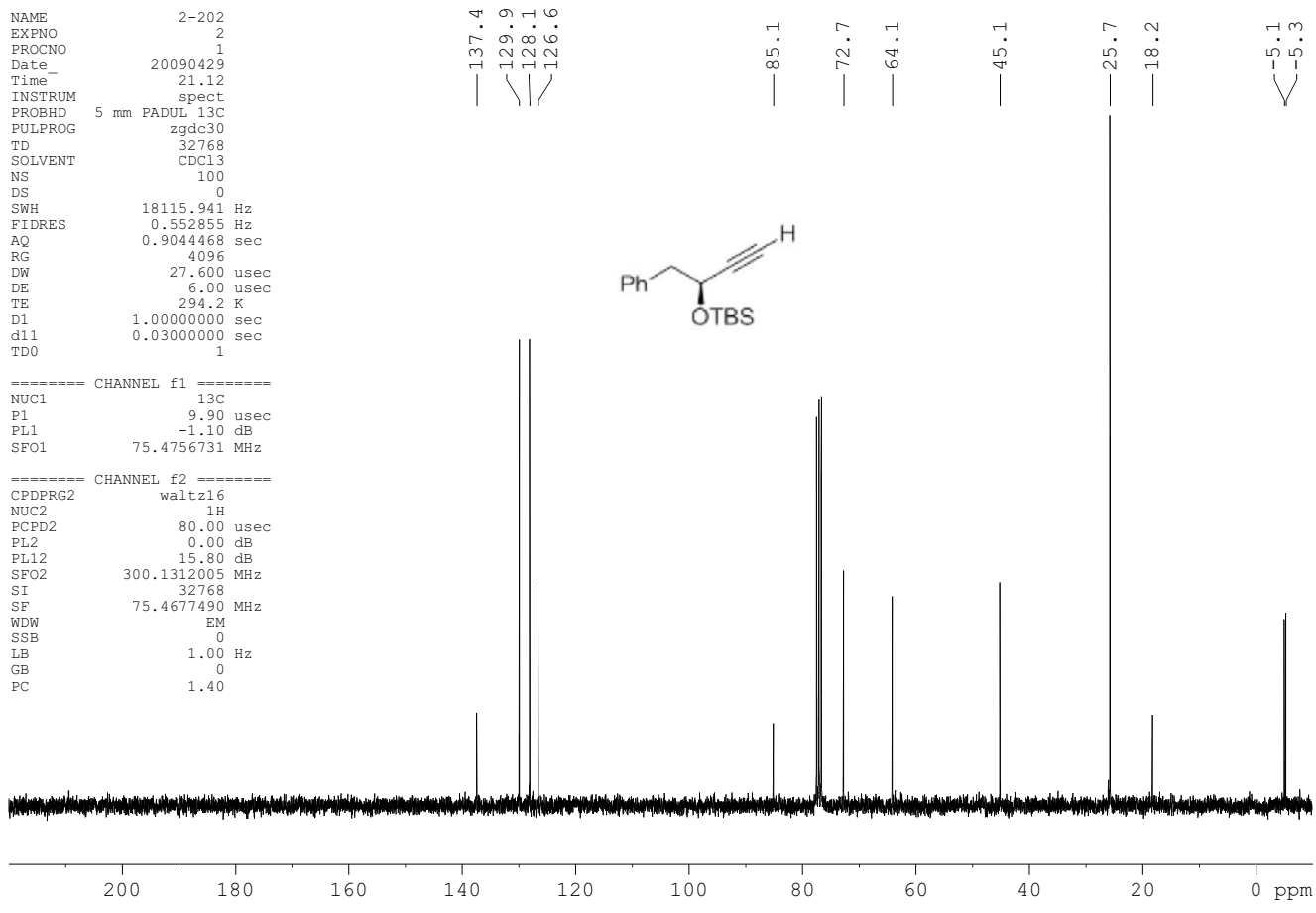


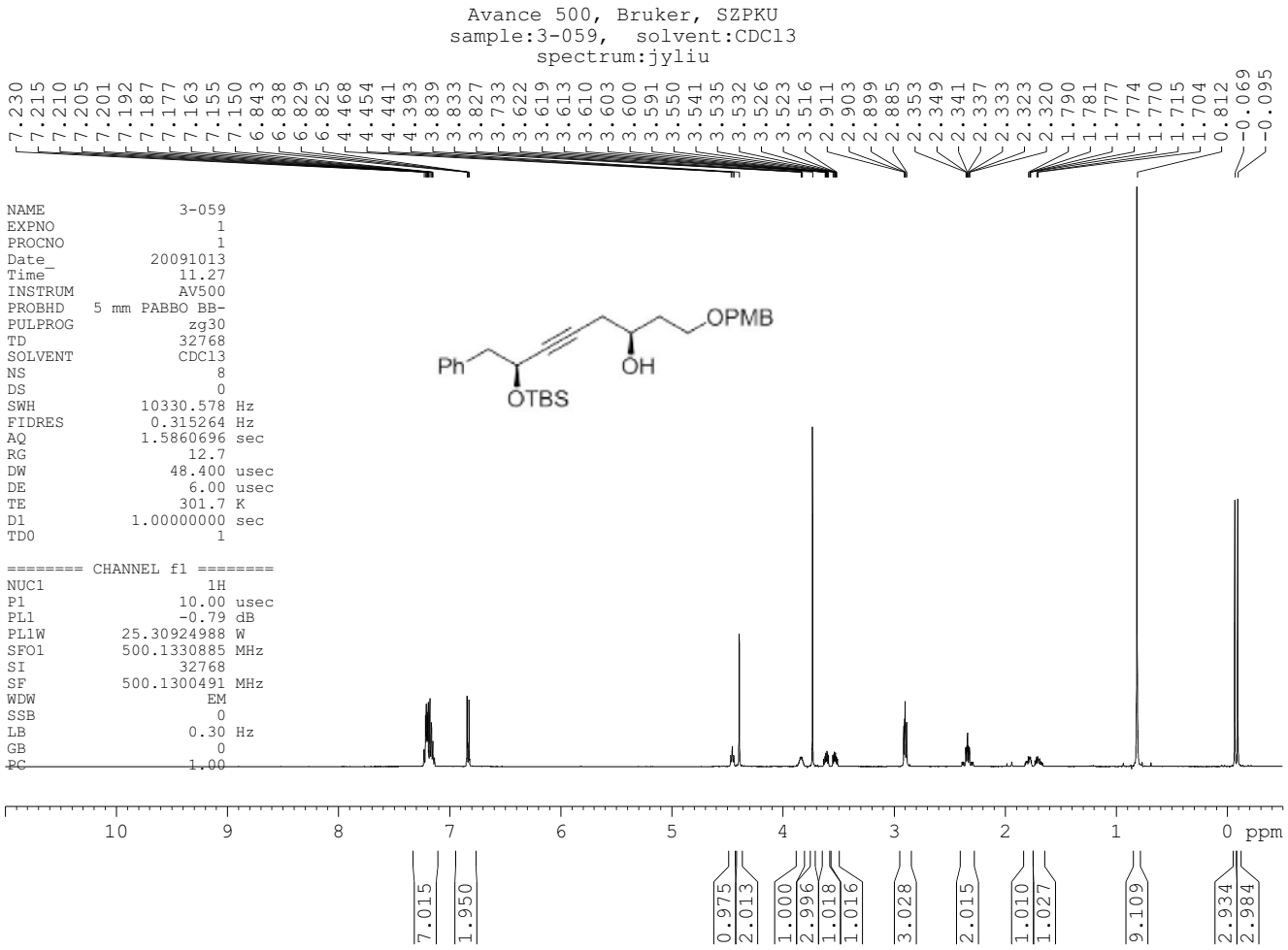

```
NAME                2-205
EXPNO                   2
PROCNO                  1
Date_            20090501
Time                12.09
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG           zgdc30
TD                  32768
SOLVENT             CDCl3
NS                     69
DS                      0
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ               0.9044468 sec
RG                   4096
DW                27.600 usec
DE                  6.00 usec
TE                 294.5 K
D1            1.00000000 sec
d11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.90 usec
PL1                -1.10 dB
SFO1         75.4756731 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.80 dB
SFO2         300.1312005 MHz
SI                  32768
SF           75.4677490 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                  1.40
```

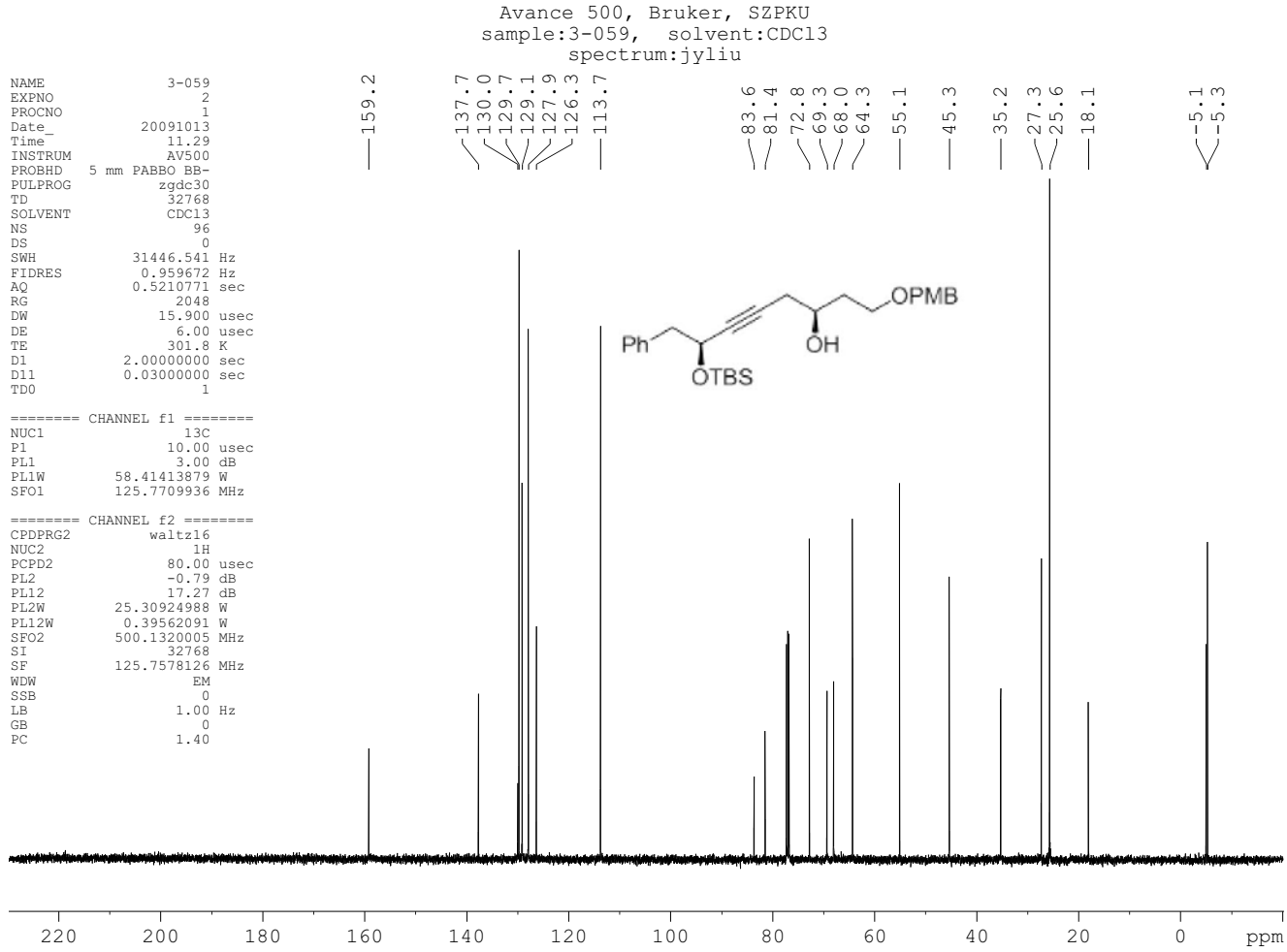
samole name:2-202
solvent:CDCl3

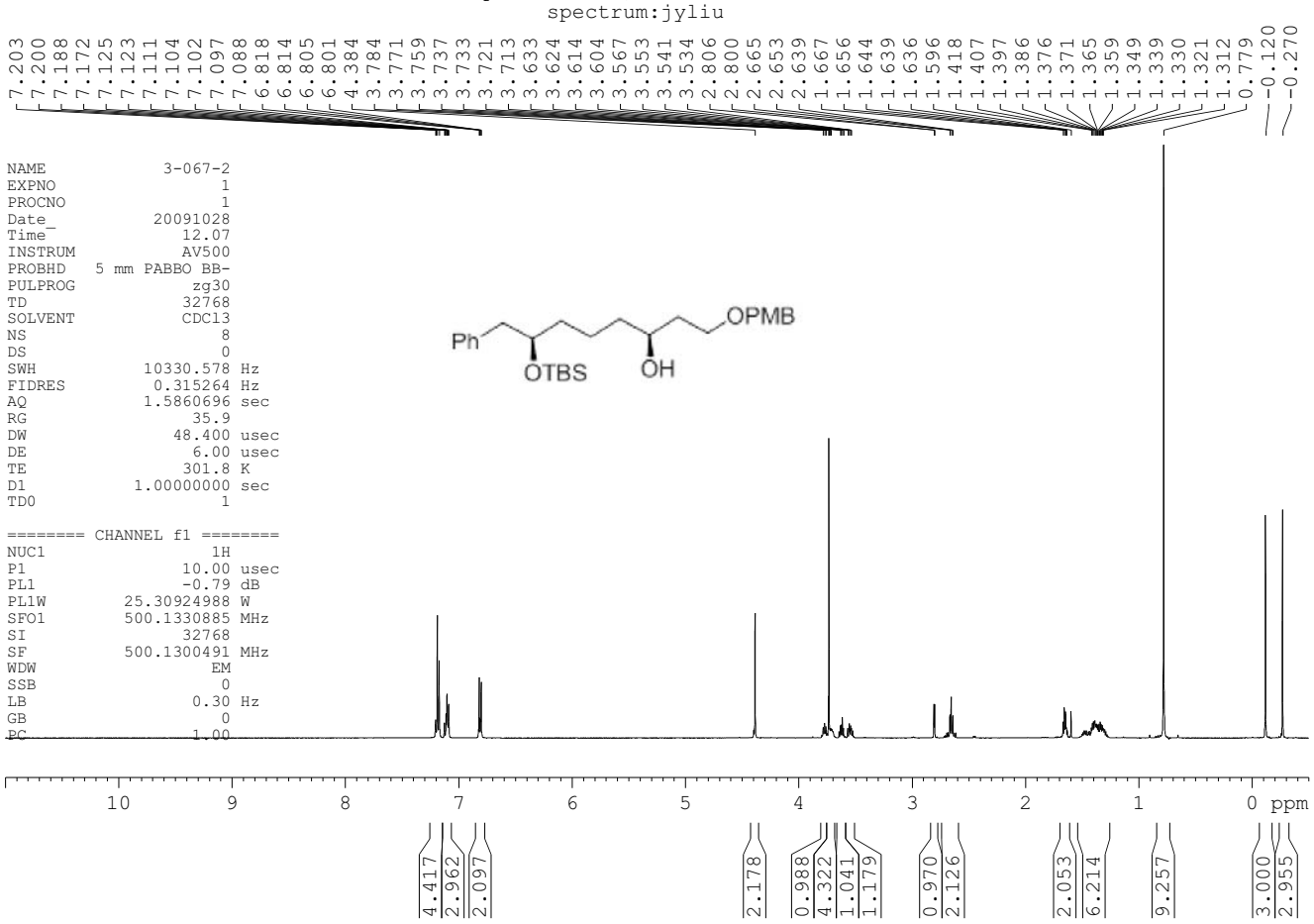


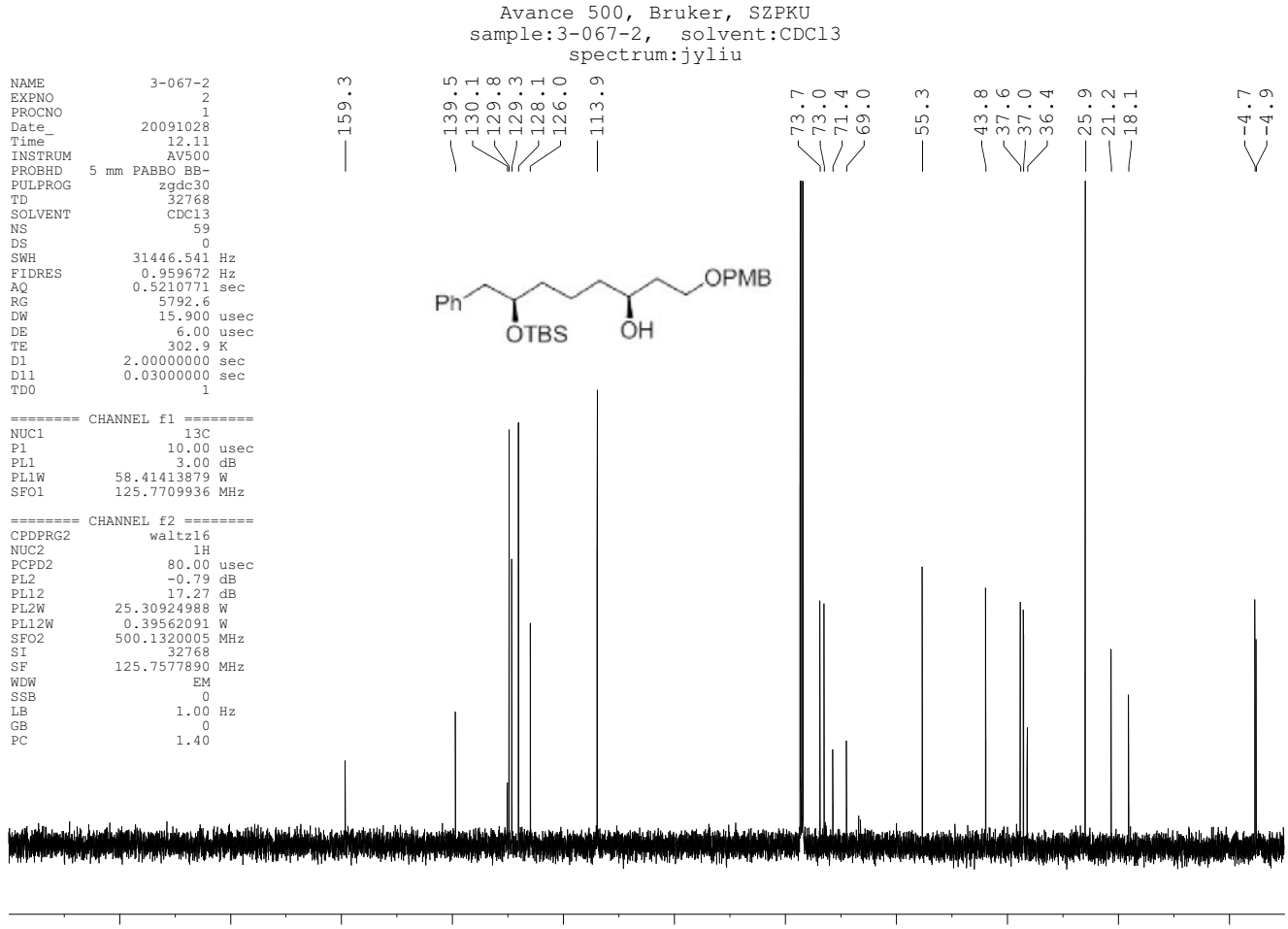
2-202
CDCl3



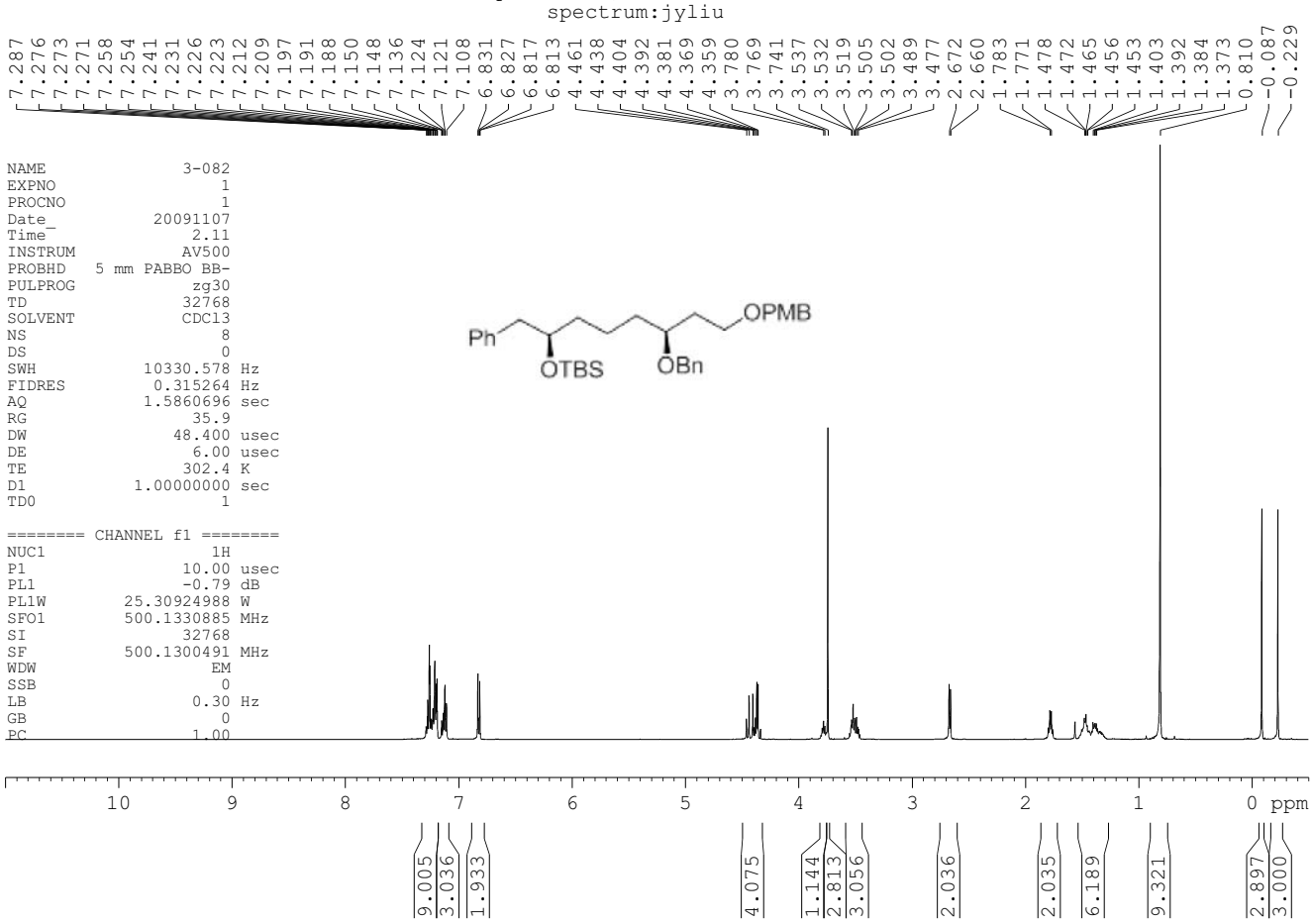

Avance 500, Bruker, SZPKU
sample:3-059, solvent:CDCl3
spectrum:jyliu
7.230 7.215 7.210 7.205 7.201 7.192 7.187 7.177 7.163 7.155 7.150 6.843 6.838 6.829 6.825 4.468 4.454 4.441 4.393 3.839 3.833 3.827 3.733 3.622 3.619 3.613 3.610 3.603 3.600 3.591 3.550 3.541 3.535 3.532 3.526 3.523 3.516 2.911 2.903 2.899 2.885 2.353 2.349 2.341 2.337 2.333 2.323 2.320 1.790 1.781 1.777 1.774 1.770 1.715 1.704 0.812 -0.069 -0.095
NAME 3-059
EXPNO 1
PROCNO 1
Date_ 20091013
Time 11.27
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 12.7
DW 48.400 usec
DE 6.00 usec
TE 301.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300491 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OPMB
Ph
OH
OTBS
10 9 8 7 6 5 4 3 2 1 0 ppm
7.015 1.950 0.975 2.013 1.000 2.996 1.018 1.016 3.028 2.015 1.010 1.027 9.109 2.934 2.984


Avance 500, Bruker, SZPKU
sample:3-059, solvent:CDCl3
spectrum:jyliu
159.2 137.7 130.0 129.7 129.1 127.9 126.3 113.7 83.6 81.4 72.8 69.3 68.0 64.3 55.1 45.3 35.2 27.3 25.6 18.1 -5.1 -5.3
NAME 3-059
EXPNO 2
PROCNO 1
Date_ 20091013
Time 11.29
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 96
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 2048
DW 15.900 usec
DE 6.00 usec
TE 301.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7578126 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OPMB
Ph
OH
OTBS
220 200 180 160 140 120 100 80 60 40 20 0 ppm

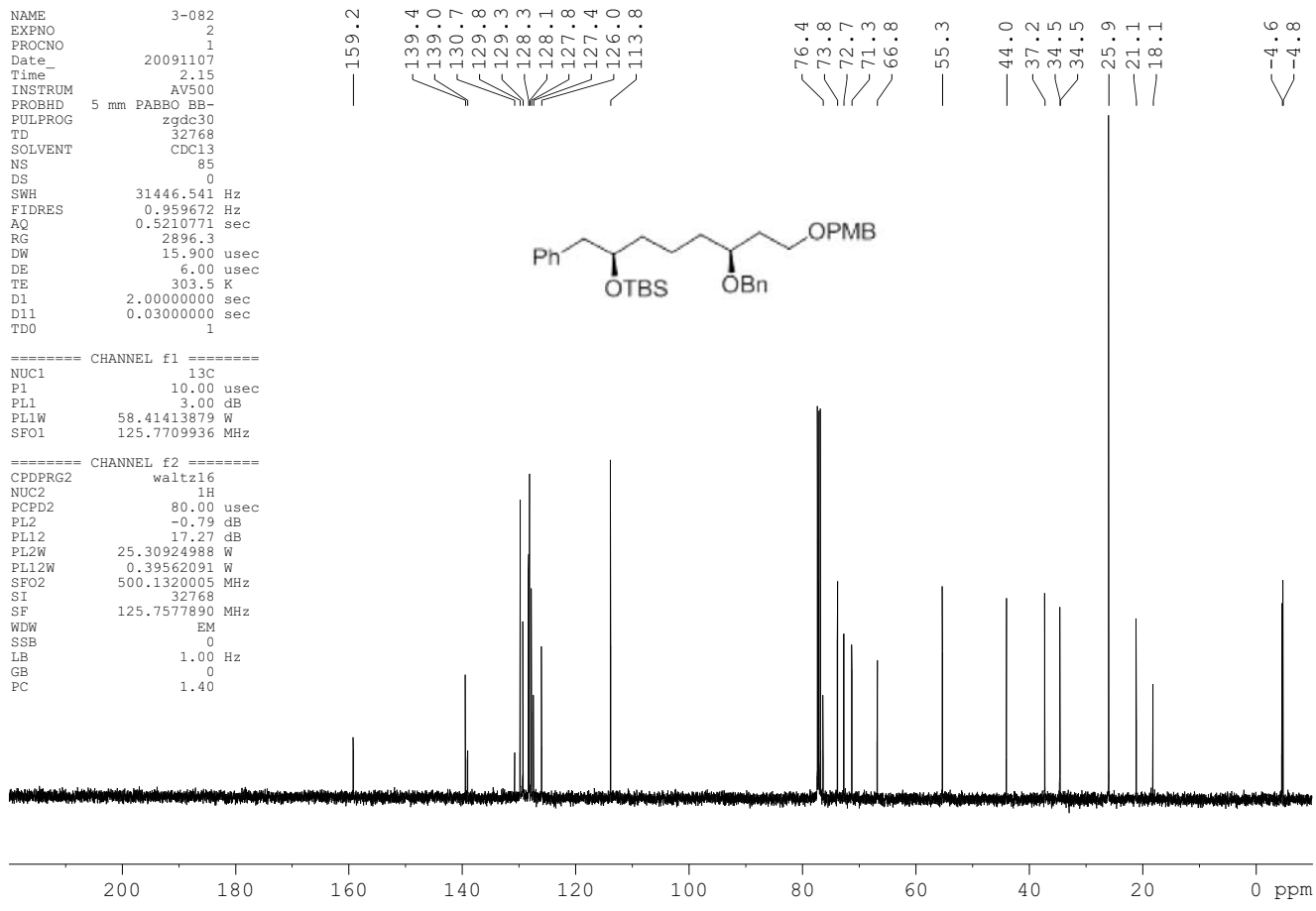

Avance 500, Bruker, SZPKU
sample:3-067-2, solvent:CDCl3
spectrum:jyliu
NAME 3-067-2
EXPNO 1
PROCNO 1
Date_ 20091028
Time 12.07
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 35.9
DW 48.400 usec
DE 6.00 usec
TE 301.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300491 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OTBS
OH
OPMB
10 9 8 7 6 5 4 3 2 1 0 ppm


Avance 500, Bruker, SZPKU
sample:3-067-2, solvent:CDCl3
spectrum:jyliu
NAME 3-067-2
EXPNO 2
PROCNO 1
Date_ 20091028
Time 12.11
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 59
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 5792.6
DW 15.900 usec
DE 6.00 usec
TE 302.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Ph
OTBS
OH
OPMB
200 180 160 140 120 100 80 60 40 20 0 ppm

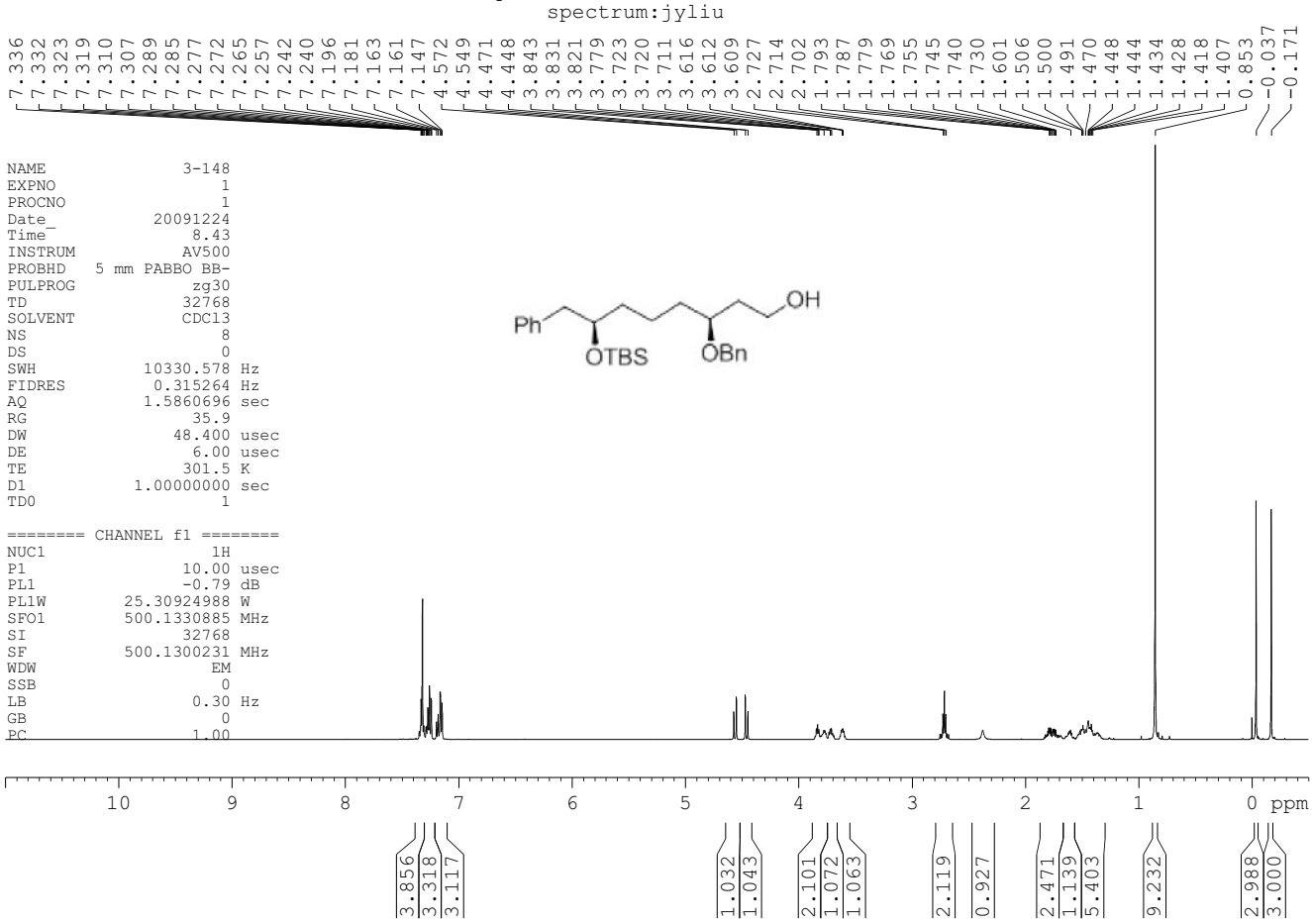
Avance 500, Bruker, SZPKU
sample:3-082, solvent:CDCl3
spectrum:jyliu



Avance 500, Bruker, SZPKU
sample:3-082, solvent:CDCl3
spectrum:jyliu

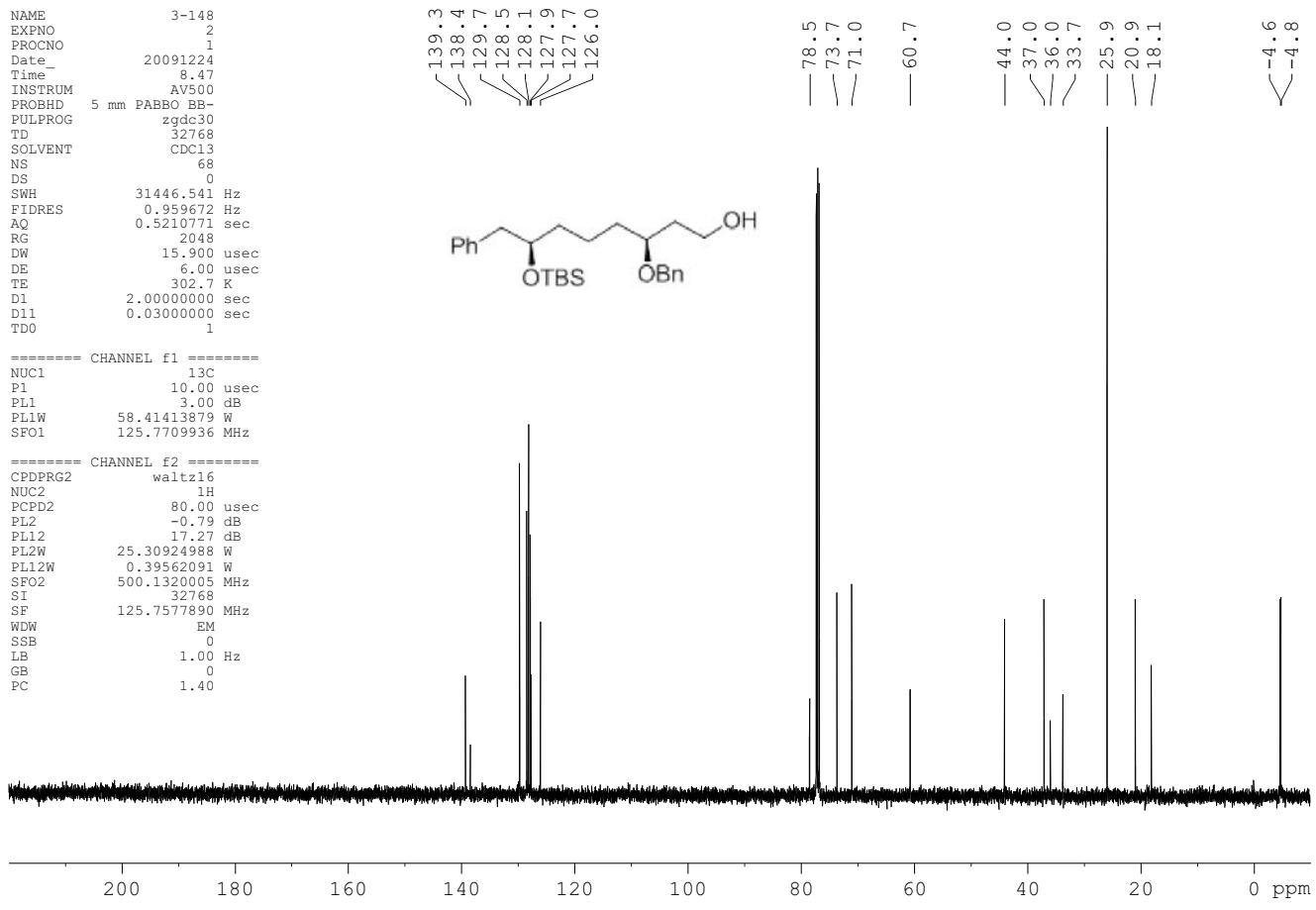


Avance 500, Bruker, SZPKU
sample:3-148, solvent:CDCl3
spectrum:jyliu



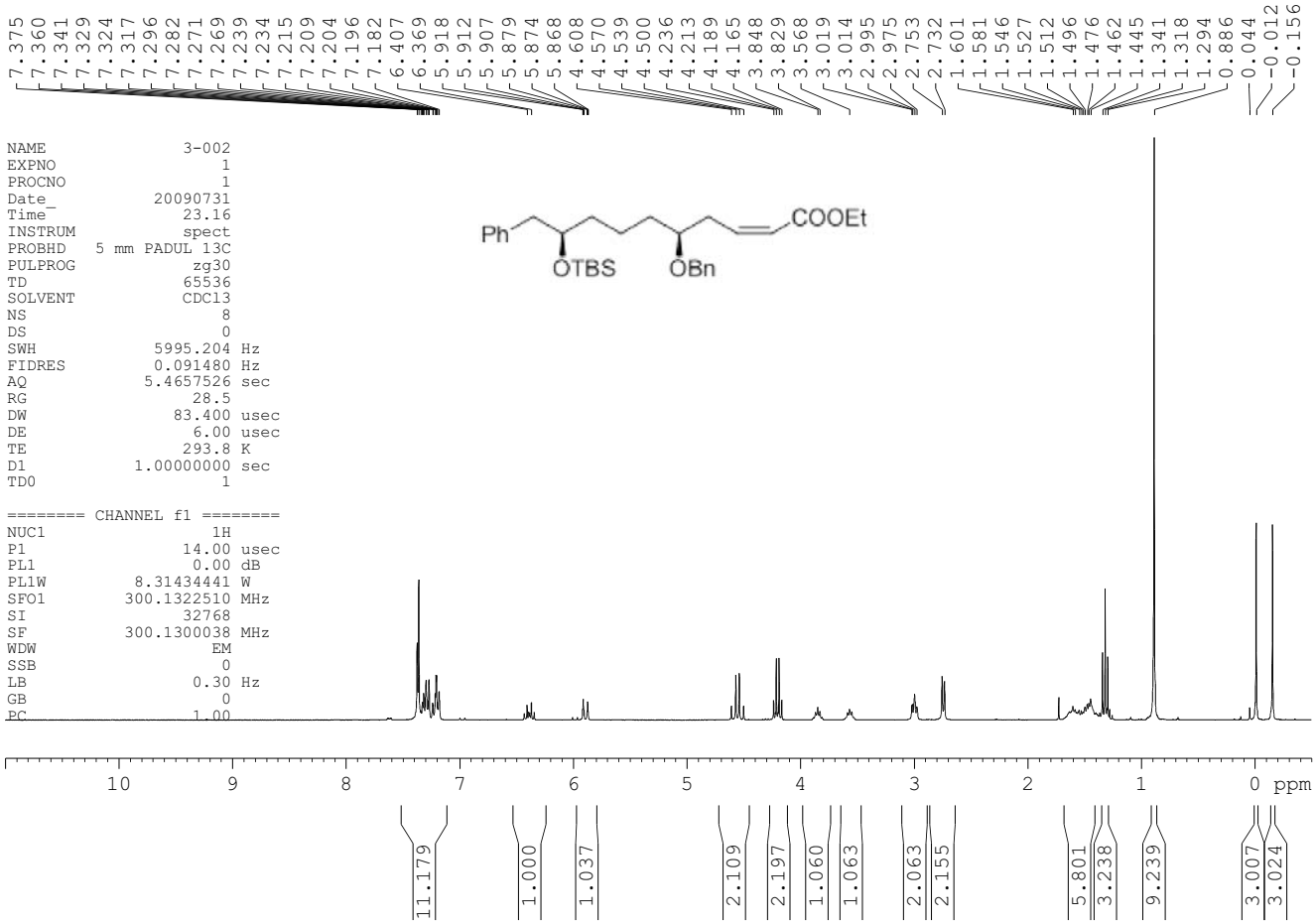

```
NAME               3-148
EXPNO                  1
PROCNO                 1
Date_           20091224
Time                8.43
INSTRUM            AV500
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES          0.315264 Hz
AQ             1.5860696 sec
RG                  35.9
DW                48.400 usec
DE                 6.00 usec
TE                301.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                1H
P1                10.00 usec
PL1               -0.79 dB
PL1W         25.30924988 W
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300231 MHz
WDW                EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

Avance 500, Bruker, SZPKU
sample:3-148, solvent:CDCl3
spectrum:jyliu

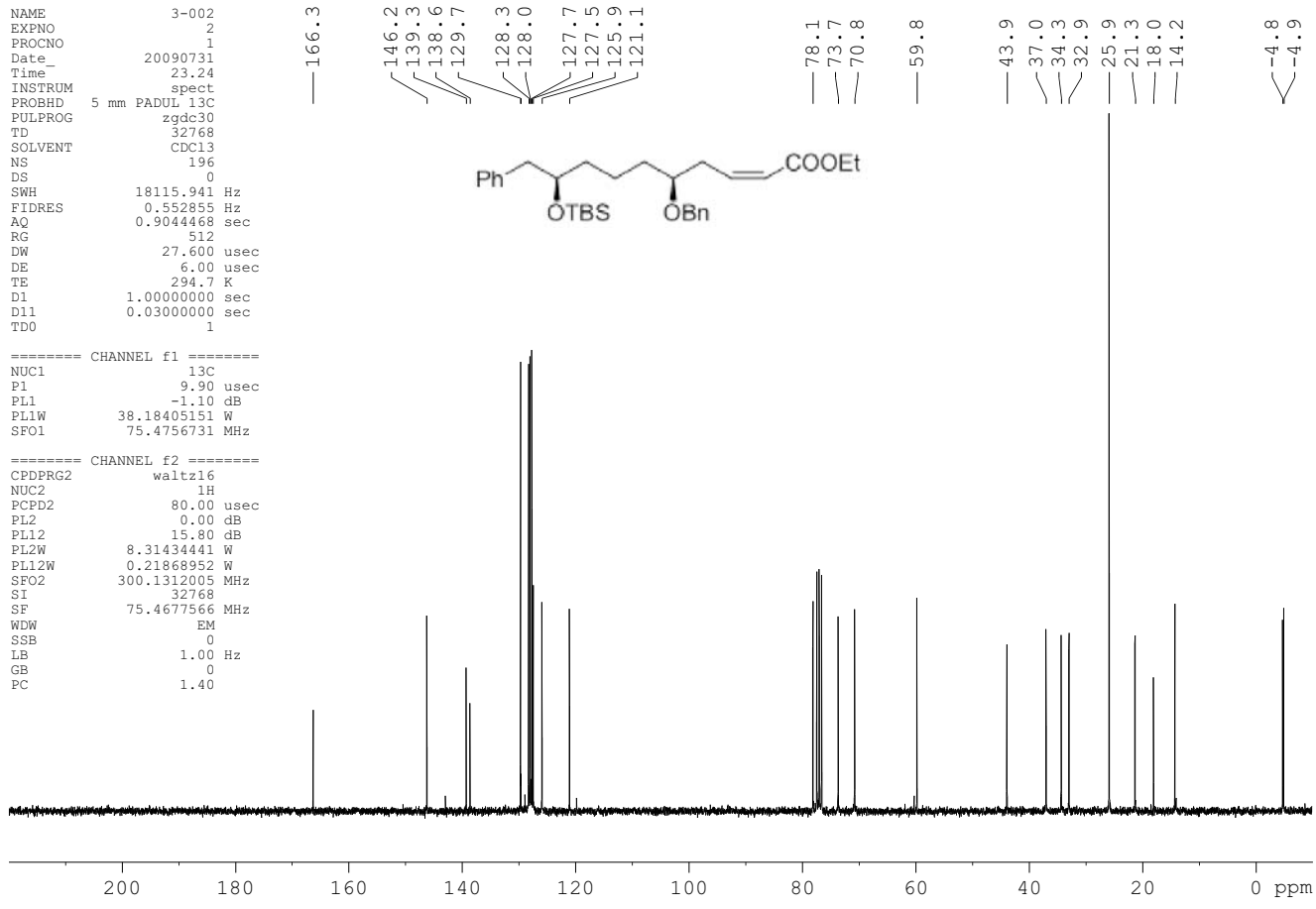


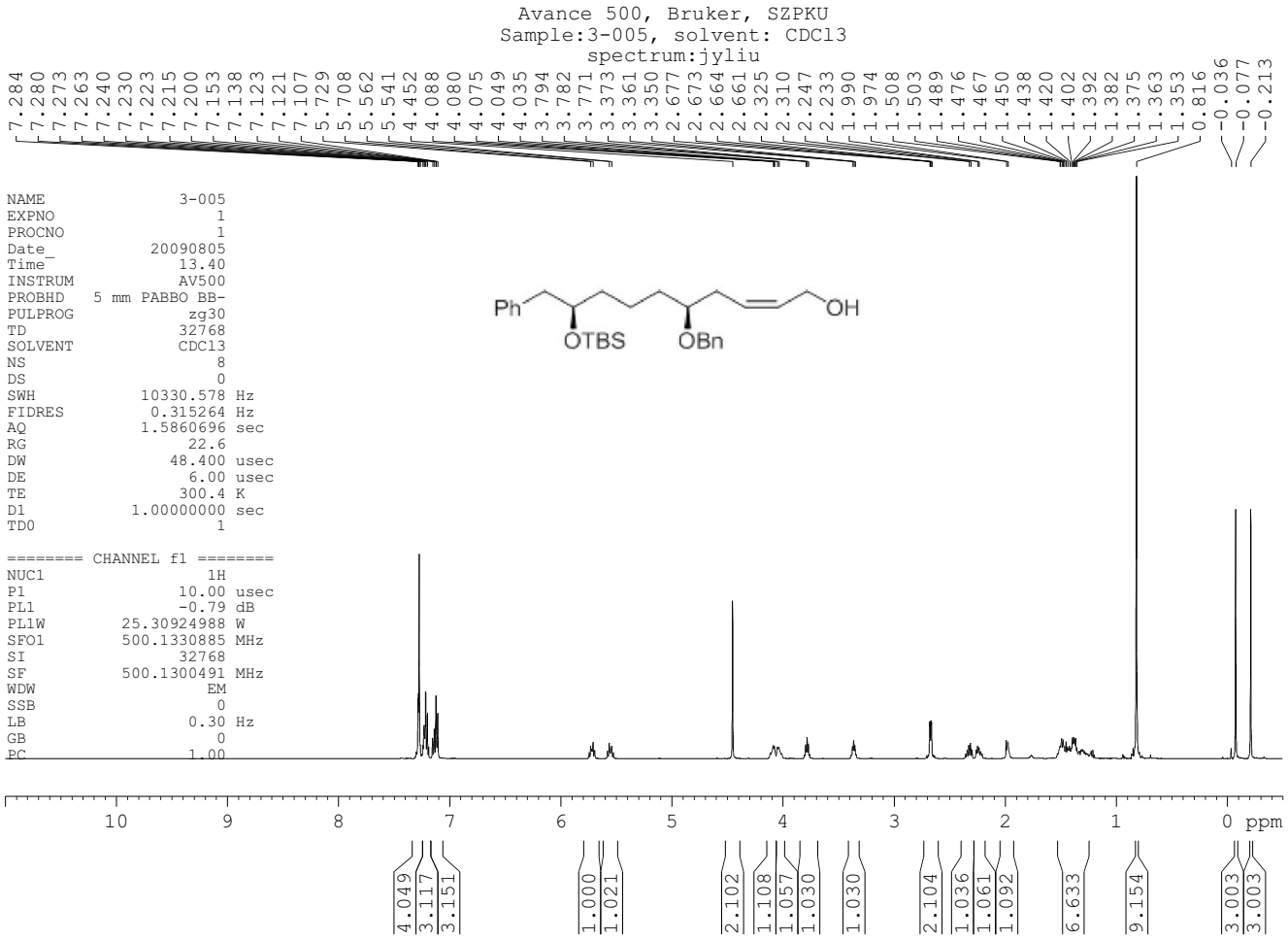

```
NAME               3-148
EXPNO                  2
PROCNO                 1
Date_           20091224
Time                8.47
INSTRUM            AV500
PROBHD   5 mm PABBO BB-
PULPROG           zgdc30
TD                 32768
SOLVENT            CDCl3
NS                    68
DS                     0
SWH            31446.541 Hz
FIDRES          0.959672 Hz
AQ             0.5210771 sec
RG                  2048
DW                15.900 usec
DE                 6.00 usec
TE                302.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PL1                3.00 dB
PL1W         58.41413879 W
SFO1         125.7709936 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             80.00 usec
PL2               -0.79 dB
PL12              17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

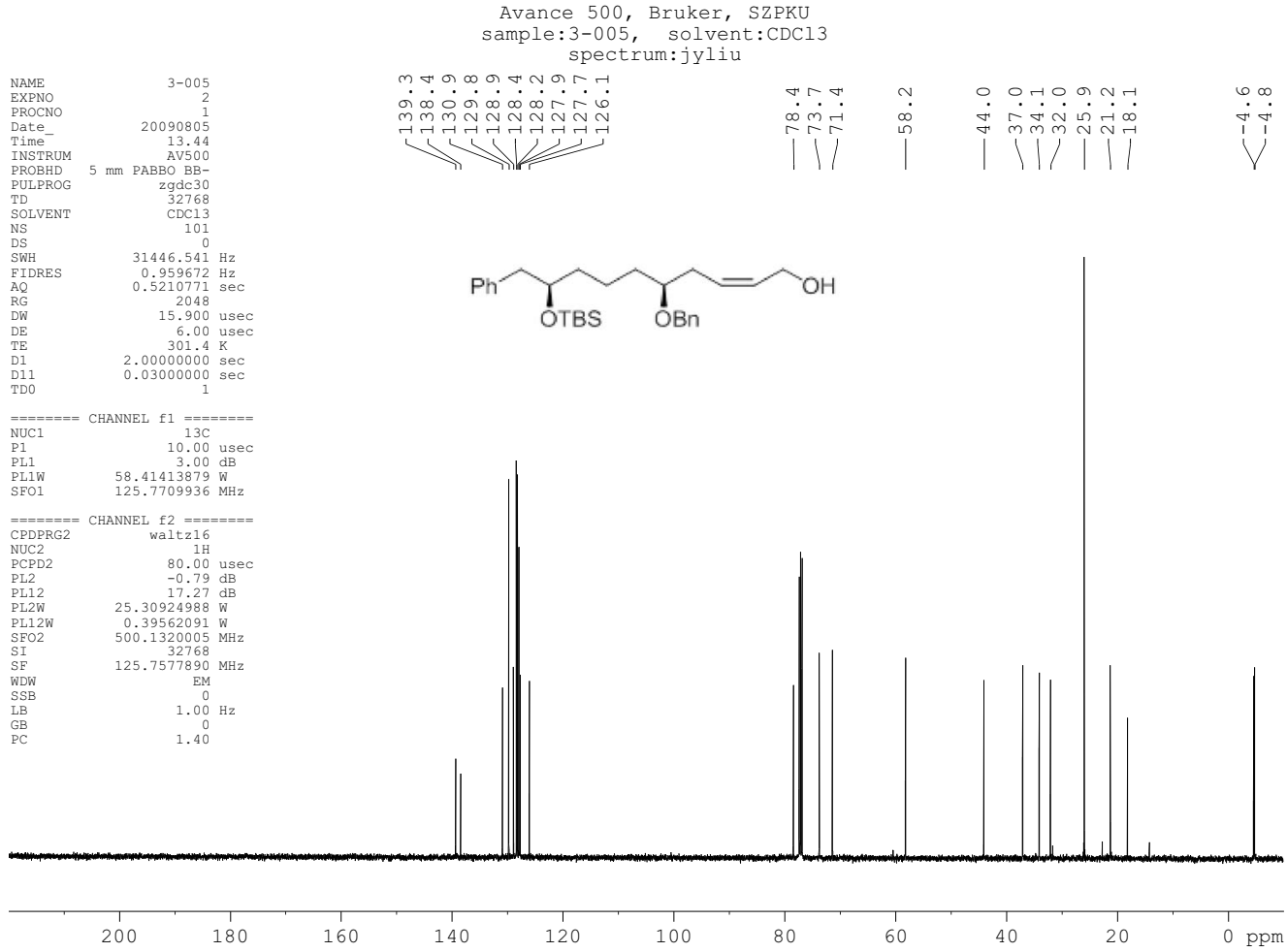
samole name:3-002
solvent:CDCl3



sample name: 3-002
solvent: CDCl3



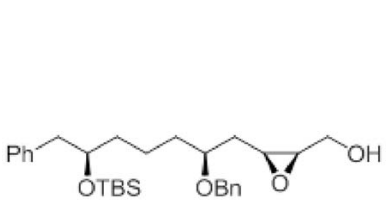

Avance 500, Bruker, SZPKU
Sample:3-005, solvent: CDCl3
spectrum:jyliu
7.284 7.280 7.273 7.263 7.240 7.230 7.223 7.215 7.200 7.153 7.138 7.123 7.121 7.107 5.729 5.708 5.562 5.541 4.452 4.088 4.080 4.075 4.049 4.035 3.794 3.782 3.771 3.373 3.361 3.350 2.677 2.673 2.664 2.661 2.325 2.310 2.247 2.233 1.990 1.974 1.508 1.503 1.489 1.476 1.467 1.450 1.438 1.420 1.402 1.392 1.382 1.375 1.363 1.353 0.816 -0.036 -0.077 -0.213
NAME 3-005
EXPNO 1
PROCNO 1
Date_ 20090805
Time 13.40
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 22.6
DW 48.400 usec
DE 6.00 usec
TE 300.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300491 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OTBS
OBn
OH
10 9 8 7 6 5 4 3 2 1 0 ppm
4.049 3.117 3.151 1.000 1.021 2.102 1.108 1.057 1.030 1.030 2.104 1.036 1.061 1.092 6.633 9.154 3.003 3.003


Avance 500, Bruker, SZPKU
sample:3-005, solvent:CDCl3
spectrum:jyliu
139.3 138.4 130.9 129.8 128.9 128.4 128.2 127.9 127.7 126.1 78.4 73.7 71.4 58.2 44.0 37.0 34.1 32.0 25.9 21.2 18.1 -4.6 -4.8
NAME 3-005
EXPNO 2
PROCNO 1
Date_ 20090805
Time 13.44
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 101
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 2048
DW 15.900 usec
DE 6.00 usec
TE 301.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Ph
OTBS
OBn
OH
200 180 160 140 120 100 80 60 40 20 0 ppm

Avance 500, Bruker, SZPKU
sample:3-012-p, solvent:CDCl3
spectrum:jyliu

7.339 7.337 7.332 7.326 7.322 7.309 7.302 7.298 7.285 7.274 7.260 7.249 7.245 7.199 7.184 7.160 7.157 7.143 4.539 4.516 4.497 4.473 3.824 3.812 3.717 3.705 3.630 3.618 3.559 3.143 3.131 3.123 3.121 3.119 3.112 3.103 3.100 2.725 2.712 2.704 2.692 1.918 1.657 1.546 1.532 1.523 1.437 1.426 1.418 1.408 1.315 1.309 1.302 1.297 0.853 -0.002 -0.036 -0.164

```
NAME            3-012-p
EXPNO                 1
PROCNO                1
Date_          20090909
Time              10.15
INSTRUM           AV500
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES        0.315264 Hz
AQ            1.5860696 sec
RG                   57
DW                48.400 usec
DE                 6.00 usec
TE                299.6 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -0.79 dB
PL1W        25.30924988 W
SFO1        500.1330885 MHz
SI                32768
SF          500.1300186 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



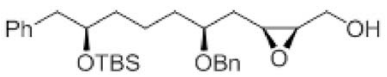
10 9 8 7 6 5 4 3 2 1 0 ppm

7.531 2.963 2.129 1.000 1.001 1.010 1.108 1.978 2.010 0.913 1.003 1.127 1.620 2.048 2.122 0.871 1.015 9.048 2.930 2.931

Avance 500, Bruker, SZPKU
sample:3-012-p, solvent:CDCl3
spectrum:jyliu

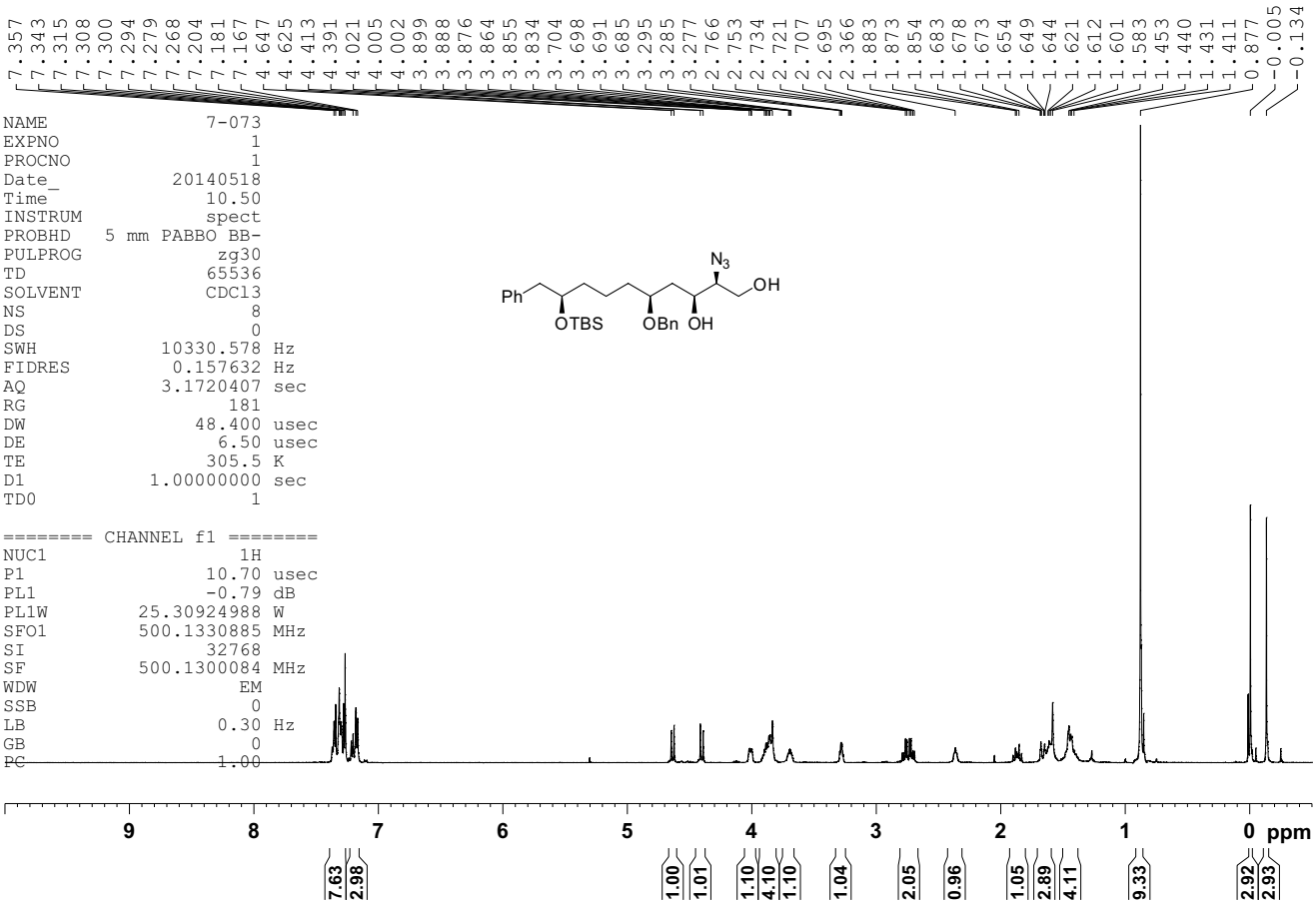
139.2 138.0 129.7 128.5 128.2 128.0 127.9 126.1 76.8 73.6 71.3 60.5 55.9 53.6 44.1 36.9 33.5 31.6 25.9 21.5 18.1 -4.6 -4.8

```
NAME            3-012-p
EXPNO                 2
PROCNO                1
Date_          20090909
Time              10.22
INSTRUM           AV500
PROBHD   5 mm PABBO BB-
PULPROG           zgdc30
TD                32768
SOLVENT           CDCl3
NS                  164
DS                    0
SWH           31446.541 Hz
FIDRES        0.959672 Hz
AQ            0.5210771 sec
RG                 4096
DW                15.900 usec
DE                 6.00 usec
TE                301.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PL1                3.00 dB
PL1W        58.41413879 W
SFO1        125.7709936 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -0.79 dB
PL12              17.27 dB
PL2W        25.30924988 W
PL12W        0.39562091 W
SFO2        500.1320005 MHz
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

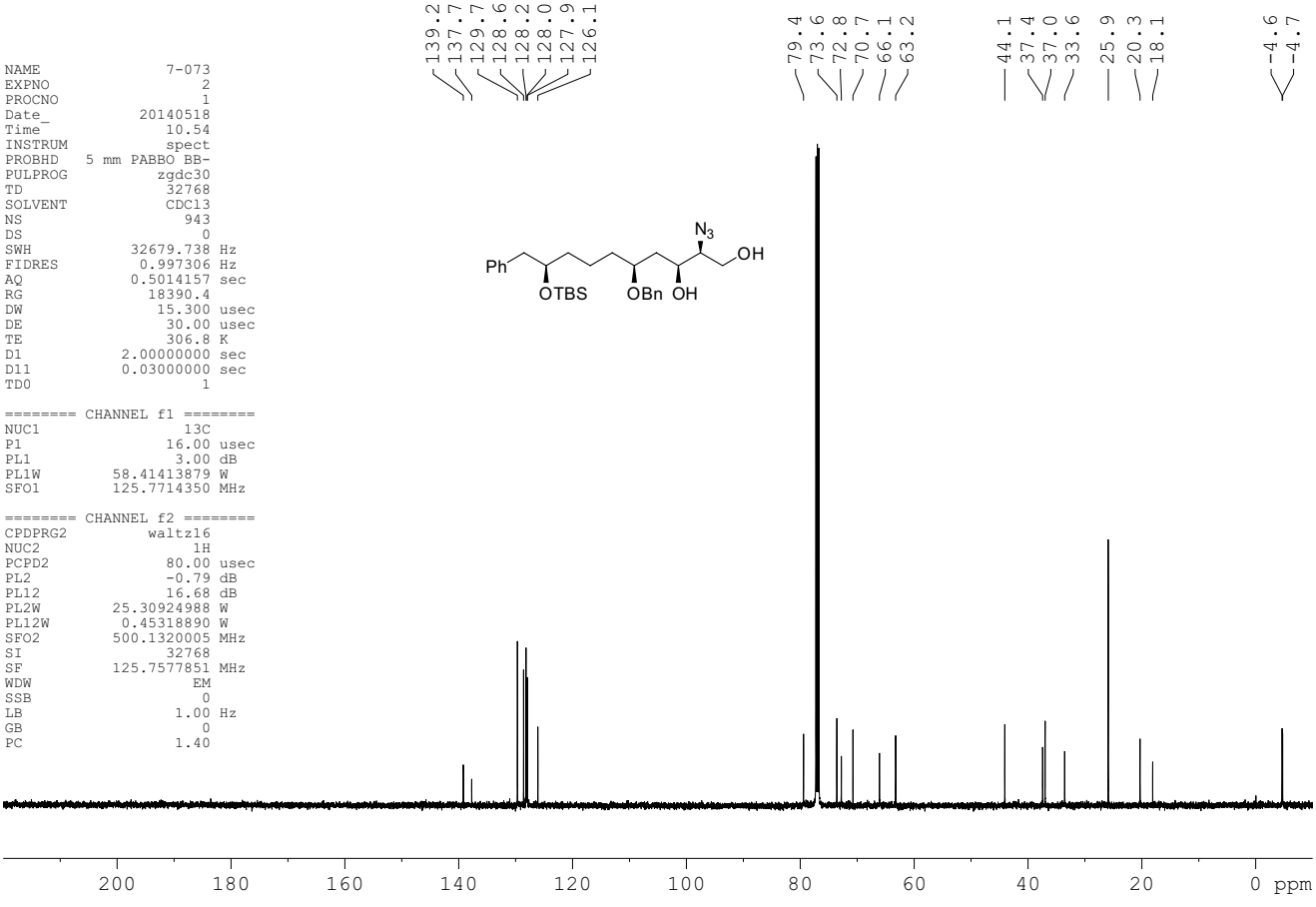


200 180 160 140 120 100 80 60 40 20 0 ppm

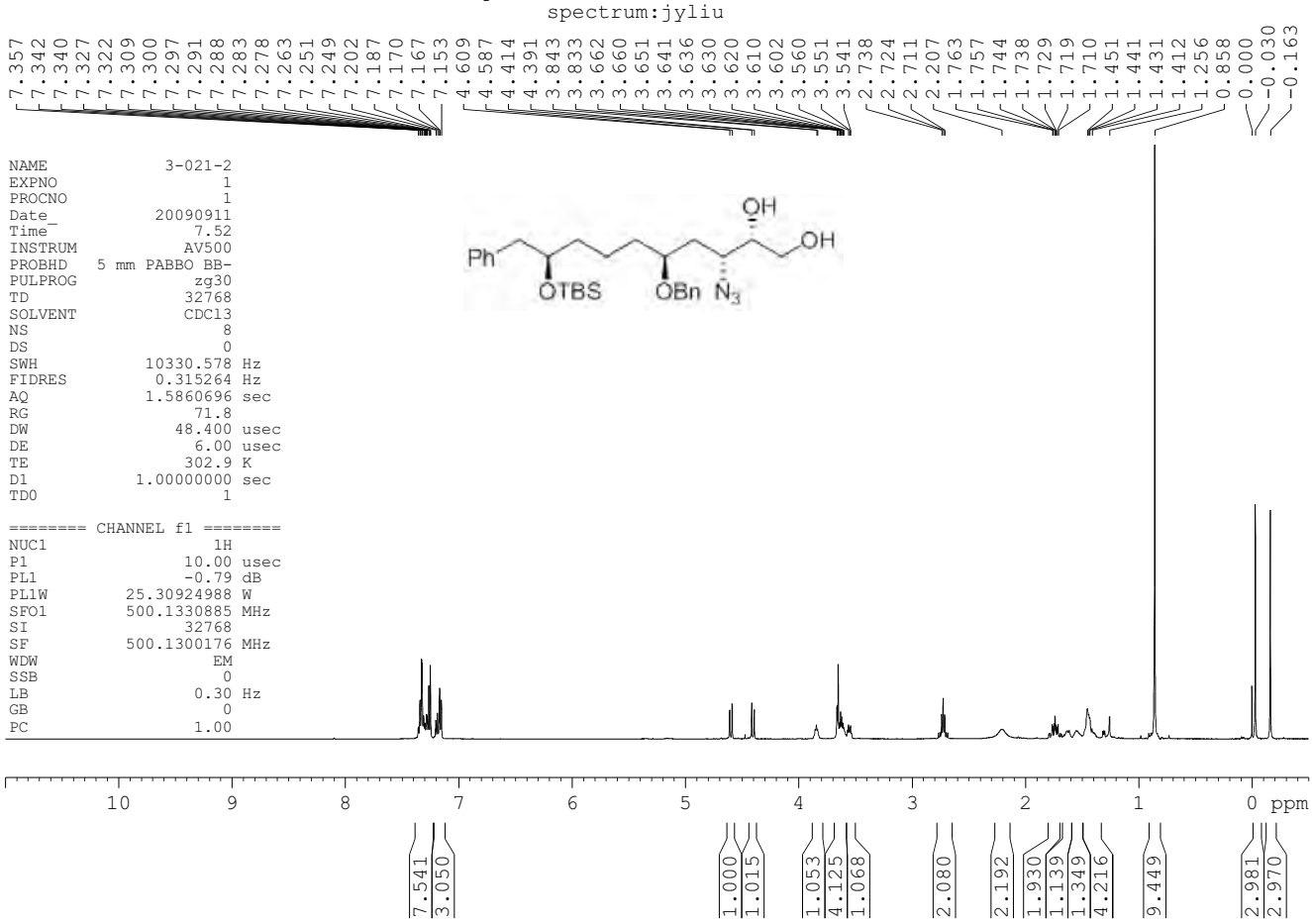
PKUSZ Avance 500 Sample name:7-073
solvent:CDCl3 spectrum: Liujy



Avance 500, Bruker, SZPKU
sample:7-073 solvent:CDCl3

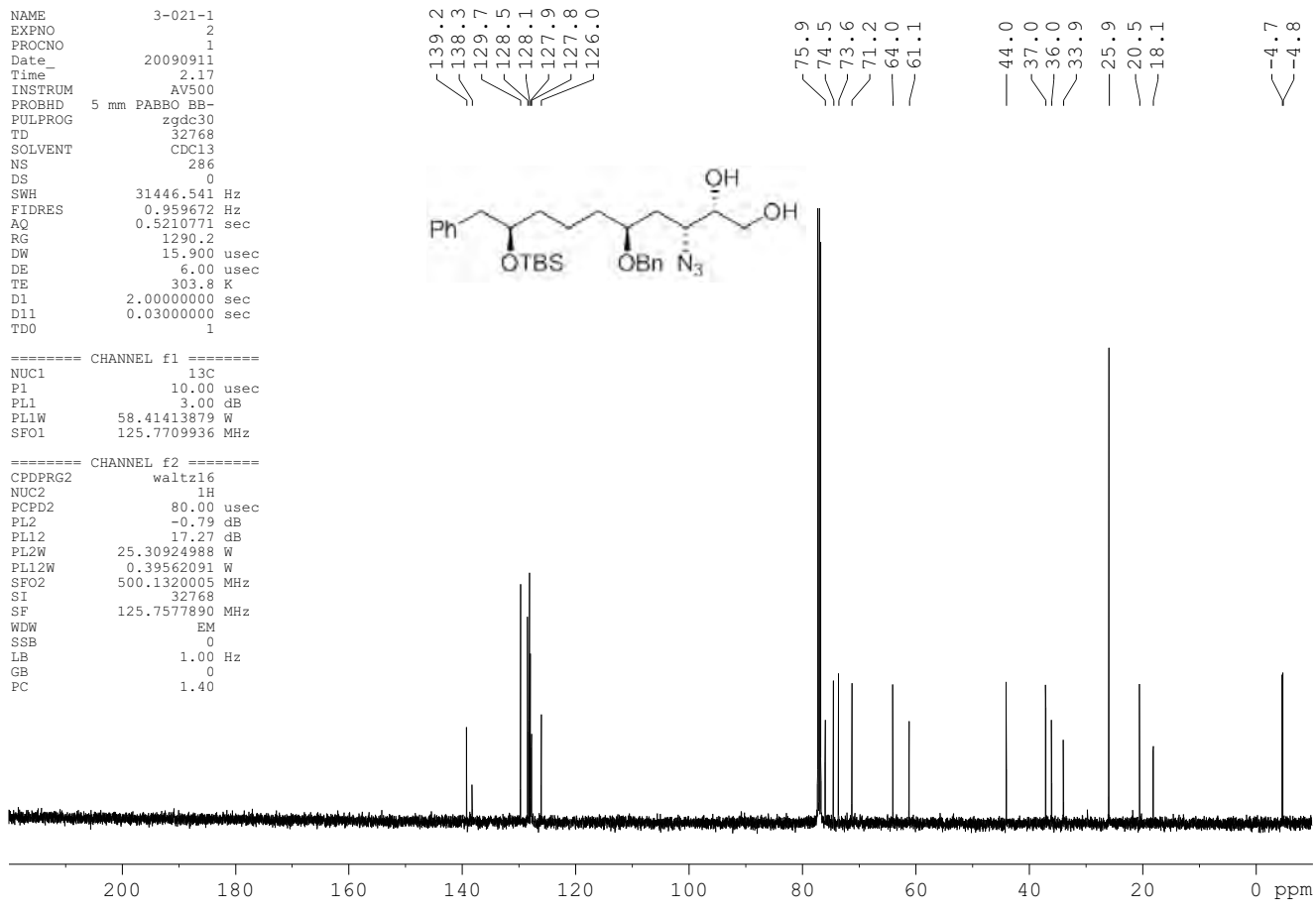


Avance 500, Bruker, SZPKU
sample:3-021-2, solvent:CDCl3
spectrum:jyliu

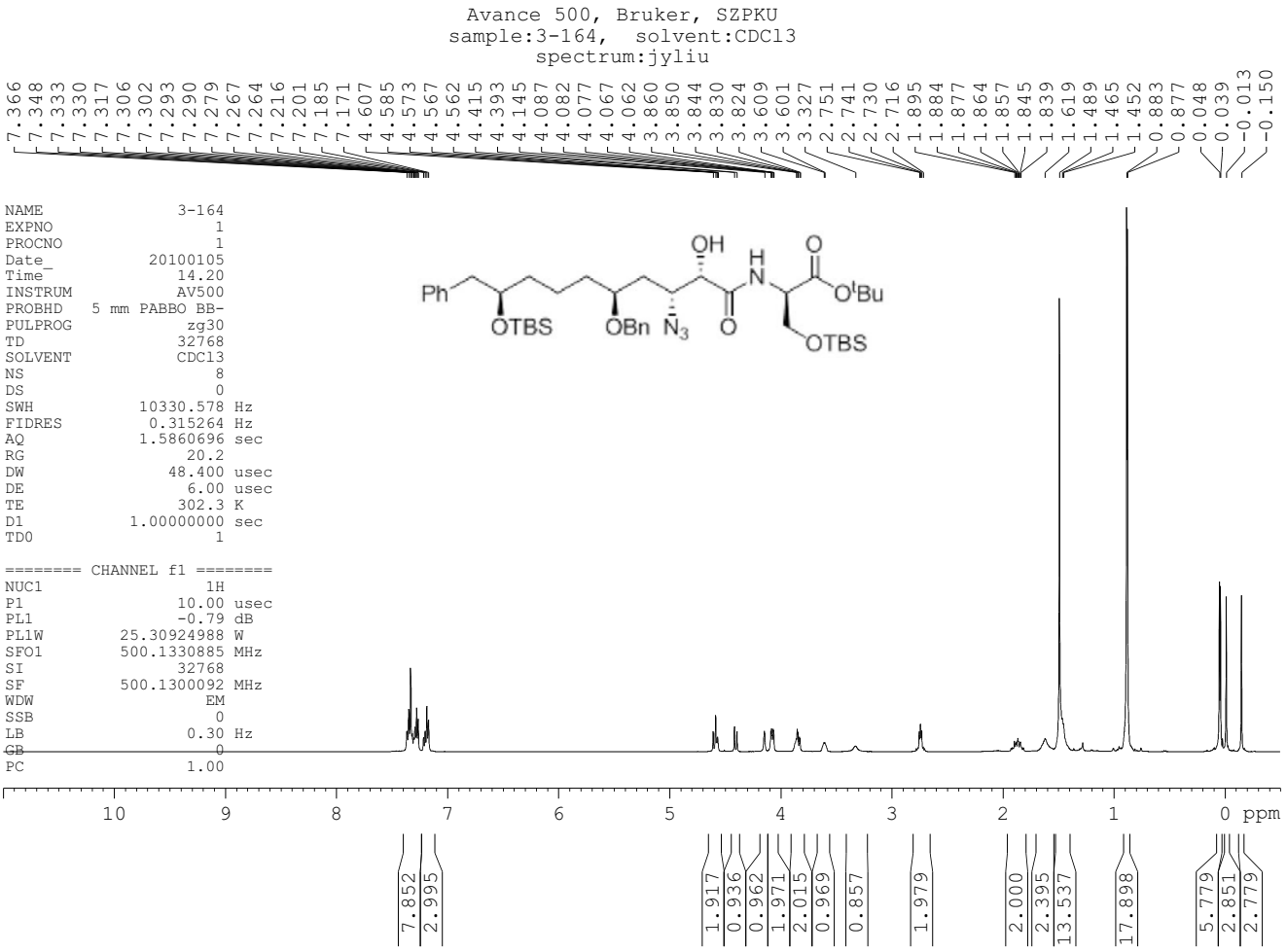


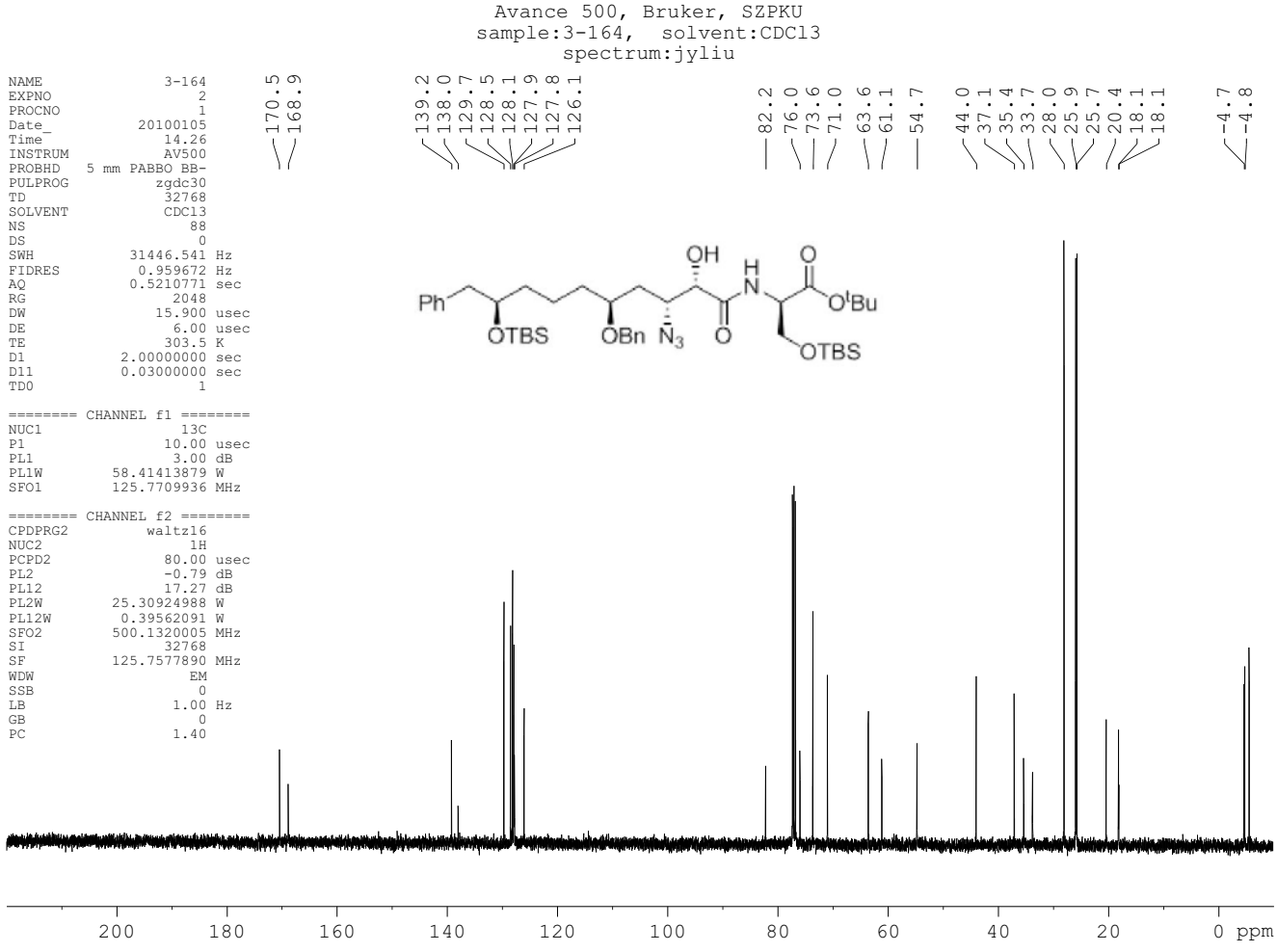

```
NAME            3-021-2
EXPNO                 1
PROCNO                1
Date_          20090911
Time               7.52
INSTRUM           AV500
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES         0.315264 Hz
AQ            1.5860696 sec
RG                 71.8
DW               48.400 usec
DE                6.00 usec
TE               302.9 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -0.79 dB
PL1W        25.30924988 W
SFO1       500.1330885 MHz
SI                32768
SF         500.1300176 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

Avance 500, Bruker, SZPKU
sample:3-021-1, solvent:CDCl3
spectrum:jyliu

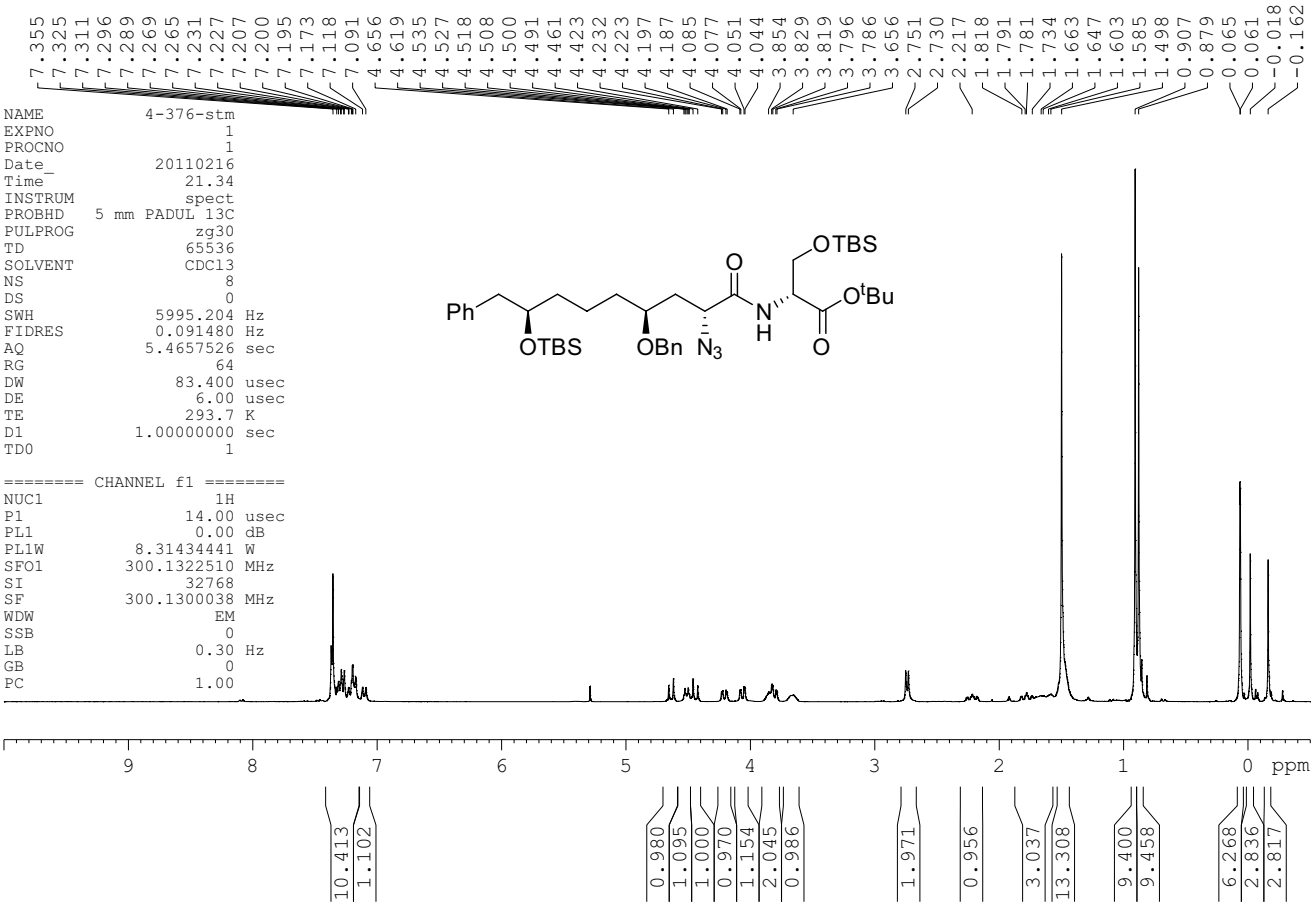



```
NAME            3-021-1
EXPNO                 2
PROCNO                1
Date_          20090911
Time               2.17
INSTRUM           AV500
PROBHD   5 mm PABBO BB-
PULPROG          zgdc30
TD                32768
SOLVENT           CDCl3
NS                  286
DS                    0
SWH           31446.541 Hz
FIDRES         0.959672 Hz
AQ            0.5210771 sec
RG                1290.2
DW               15.900 usec
DE                6.00 usec
TE               303.8 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PL1                3.00 dB
PL1W        58.41413879 W
SFO1       125.7709936 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -0.79 dB
PL12              17.27 dB
PL2W        25.30924988 W
PL12W        0.39562091 W
SFO2       500.1320005 MHz
SI                32768
SF         125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

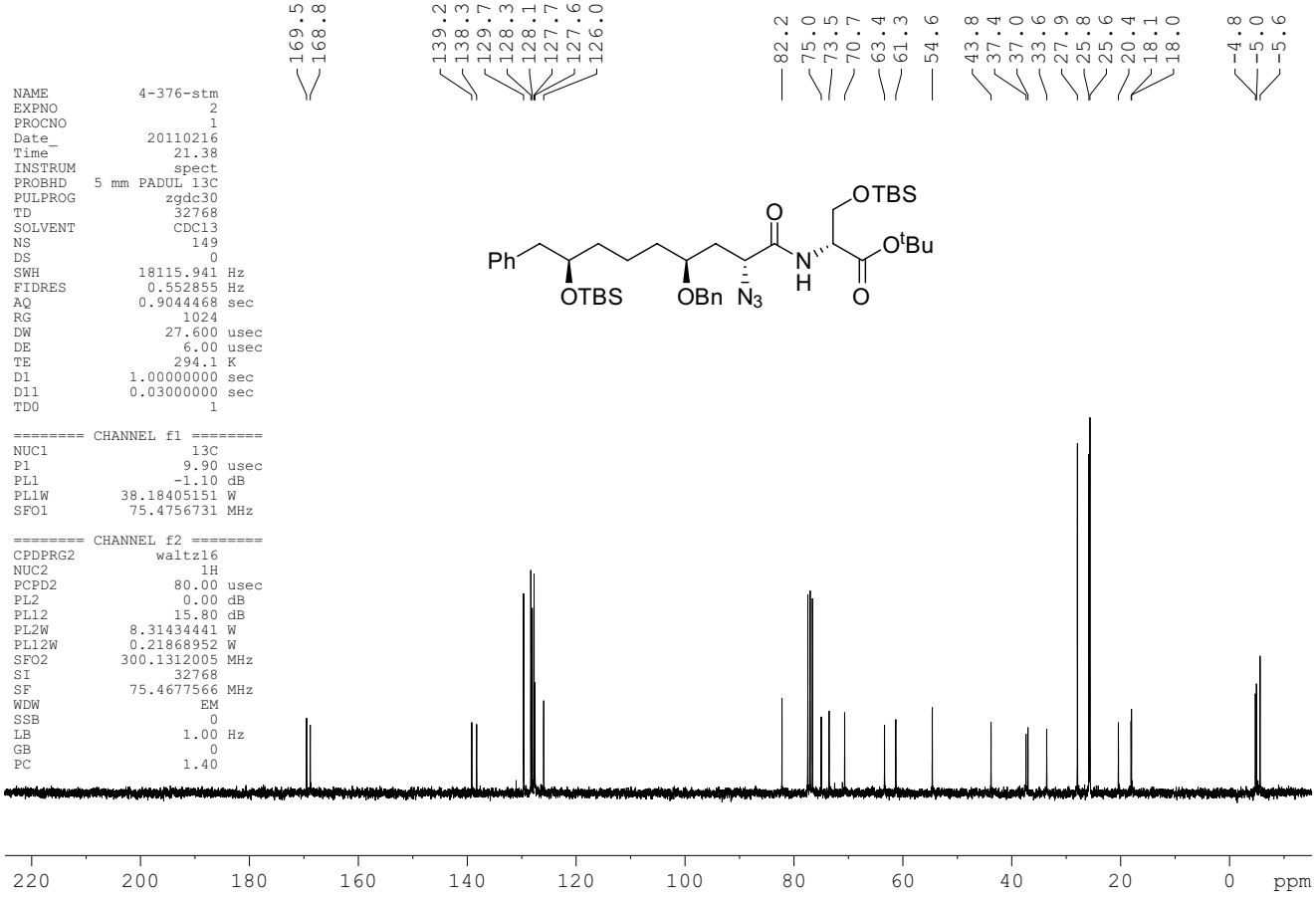

Avance 500, Bruker, SZPKU
sample:3-164, solvent:CDCl3
spectrum:jyliu
7.366 7.348 7.333 7.330 7.317 7.306 7.302 7.293 7.290 7.279 7.267 7.264 7.216 7.201 7.185 7.171 4.607 4.585 4.573 4.567 4.562 4.415 4.393 4.145 4.087 4.082 4.077 4.067 4.062 3.860 3.850 3.844 3.830 3.824 3.609 3.601 3.327 2.751 2.741 2.730 2.716 1.895 1.884 1.877 1.864 1.857 1.845 1.839 1.619 1.489 1.465 1.452 0.883 0.877 0.048 0.039 -0.013 -0.150
NAME 3-164
EXPNO 1
PROCNO 1
Date_ 20100105
Time 14.20
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 20.2
DW 48.400 usec
DE 6.00 usec
TE 302.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OTBS
OBn
N3
OH
H
N
O
O
OtBu
OTBS
10 9 8 7 6 5 4 3 2 1 0 ppm
7.852 2.995 1.917 0.936 0.962 1.971 2.015 0.969 0.857 1.979 2.000 2.395 13.537 17.898 5.779 2.851 2.779


Avance 500, Bruker, SZPKU
sample:3-164, solvent:CDCl3
spectrum:jyliu
170.5 168.9 139.2 138.0 129.7 128.5 128.1 127.9 127.8 126.1 82.2 76.0 73.6 71.0 63.6 61.1 54.7 44.0 37.1 35.4 33.7 28.0 25.9 25.7 20.4 18.1 18.1 -4.7 -4.8
NAME 3-164
EXPNO 2
PROCNO 1
Date_ 20100105
Time 14.26
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 88
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 2048
DW 15.900 usec
DE 6.00 usec
TE 303.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Ph
OTBS
OBn
N3
OH
H
N
O
O
OtBu
OTBS
200 180 160 140 120 100 80 60 40 20 0 ppm

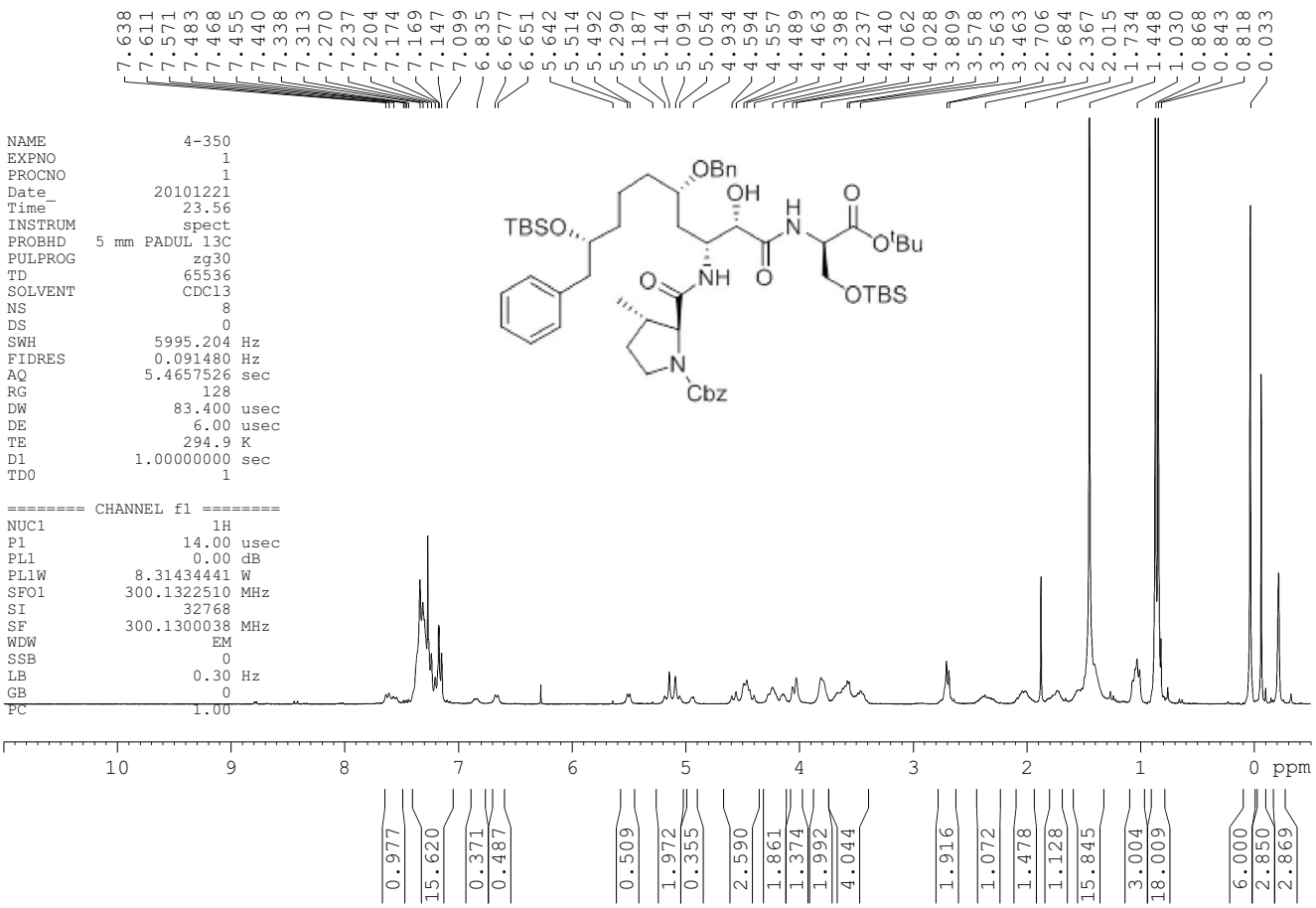
sample name:4-376-stm
solvent:CDCl3
Bruker 300M



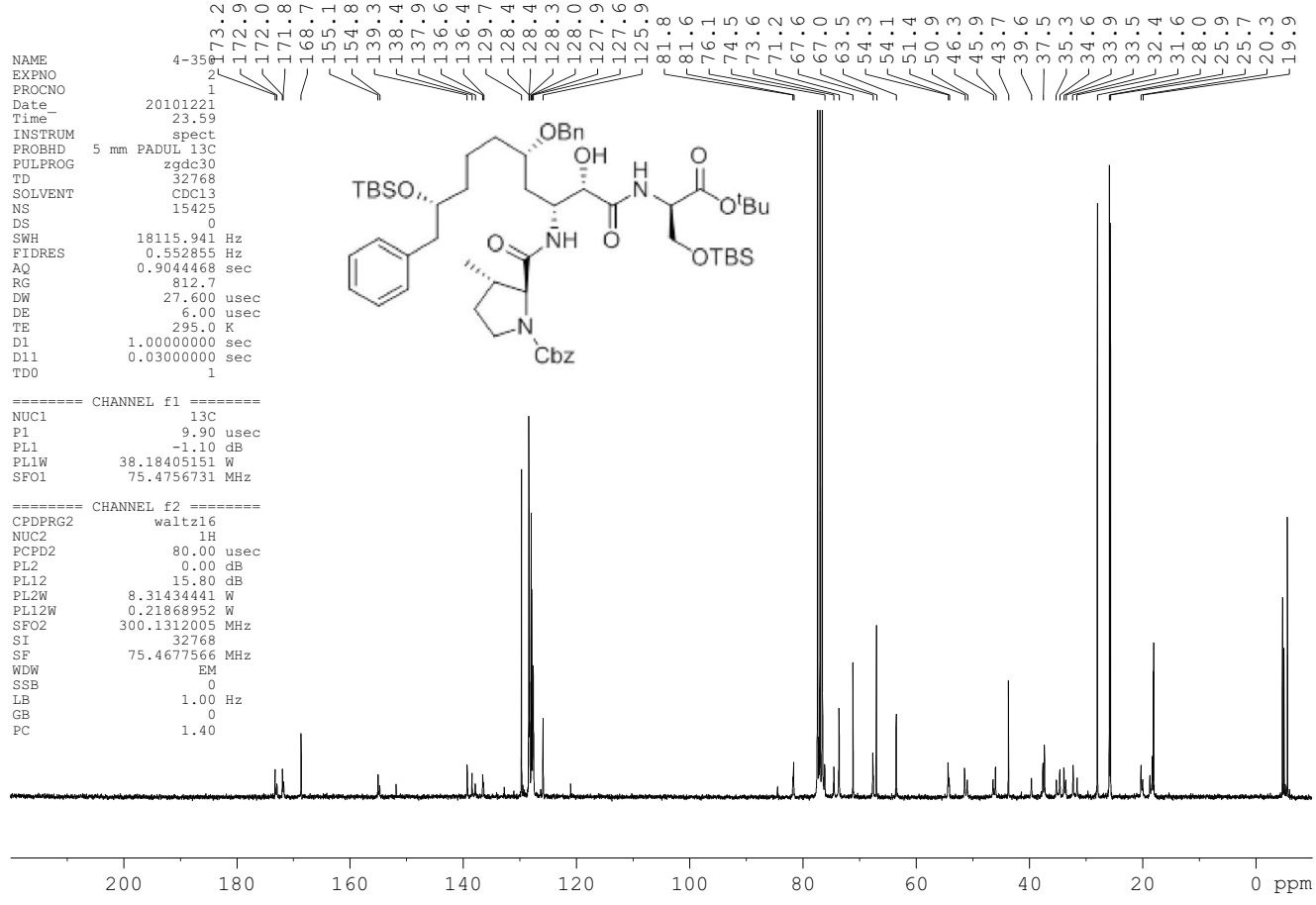
sample name: 4-376-stm
solvent: CDCl3
Bruker 300M



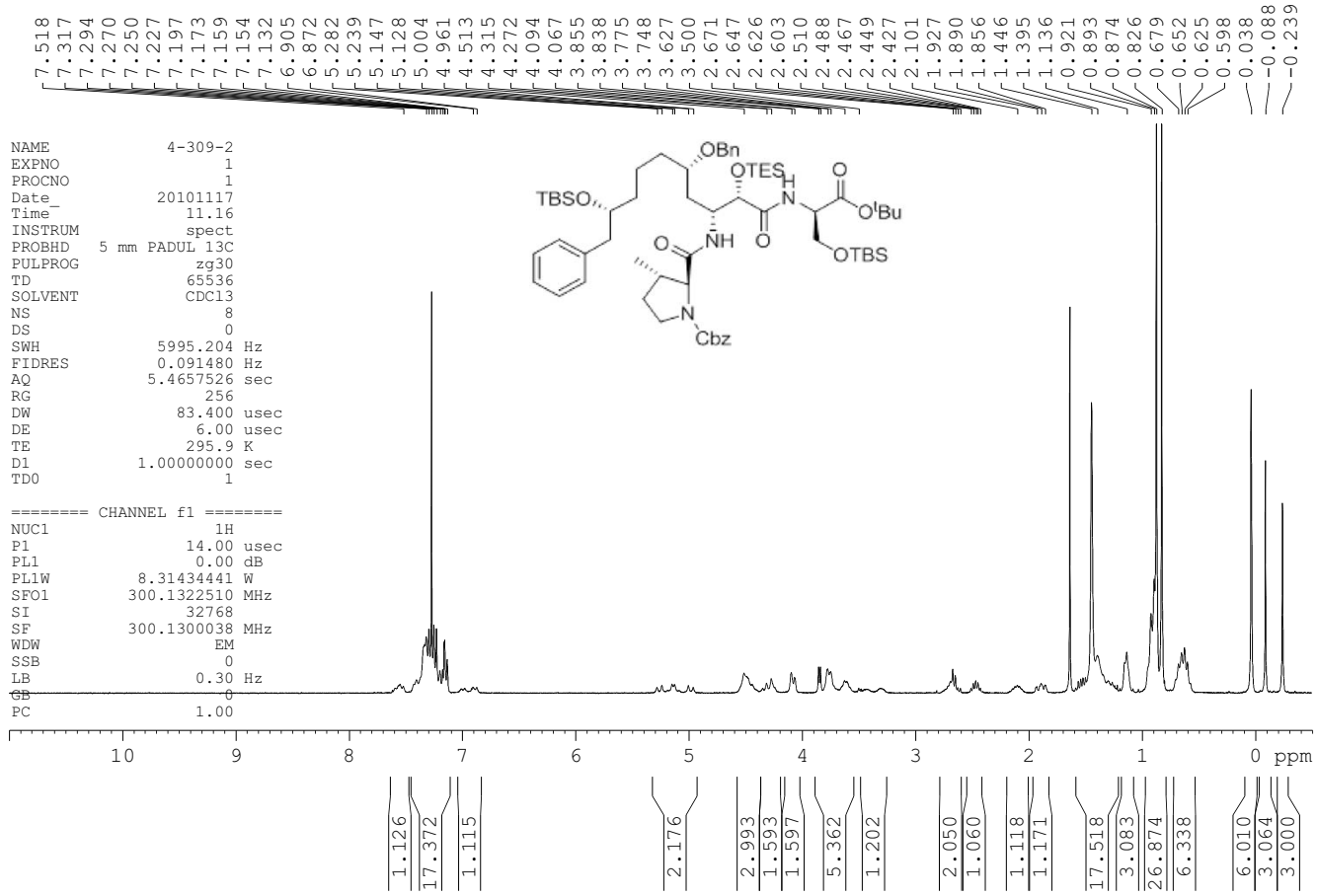
sample name:4-350
solvent:CDCl3
Bruker 300M



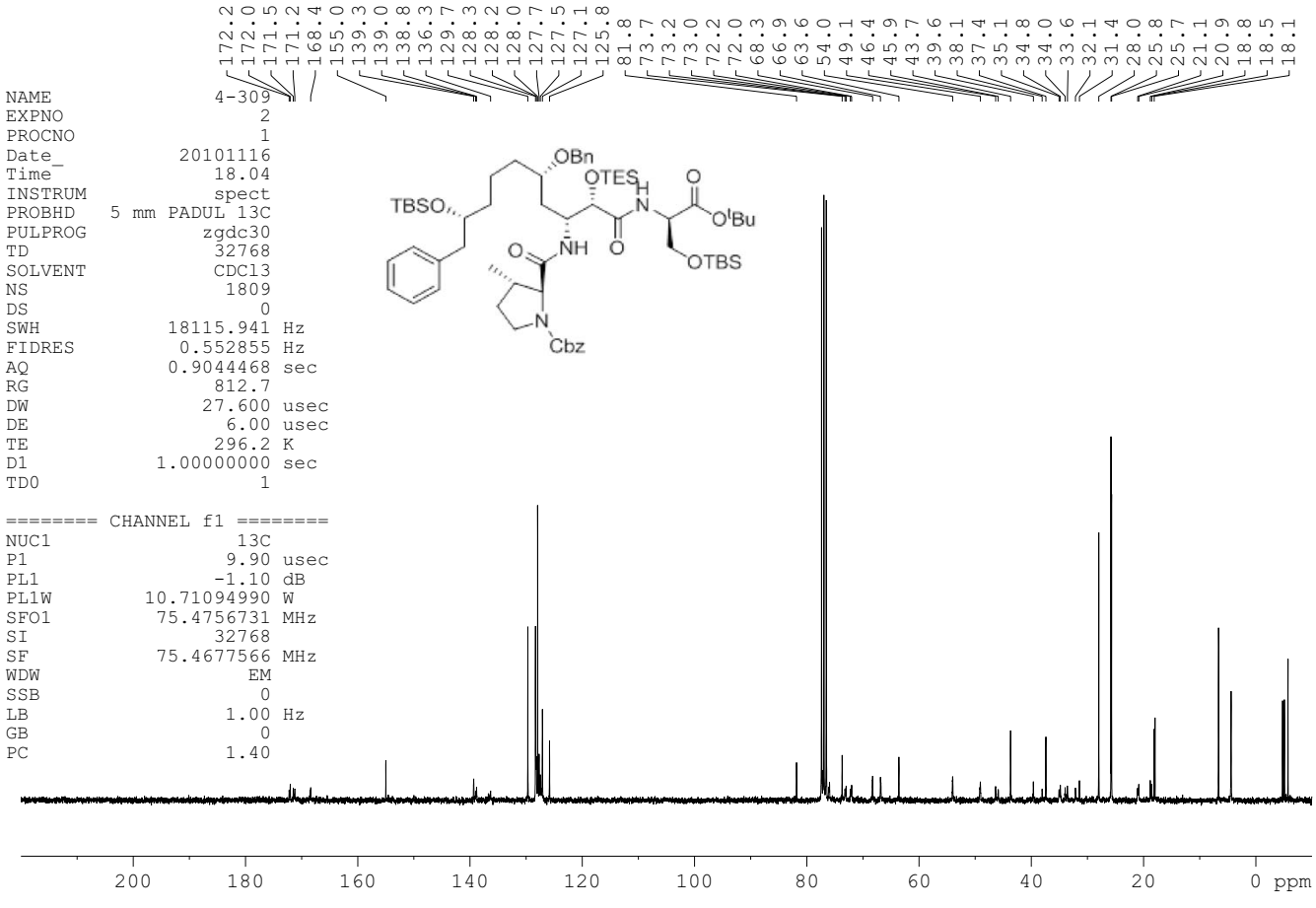
sample name: 4-350
solvent: CDCl3
Bruker 300M



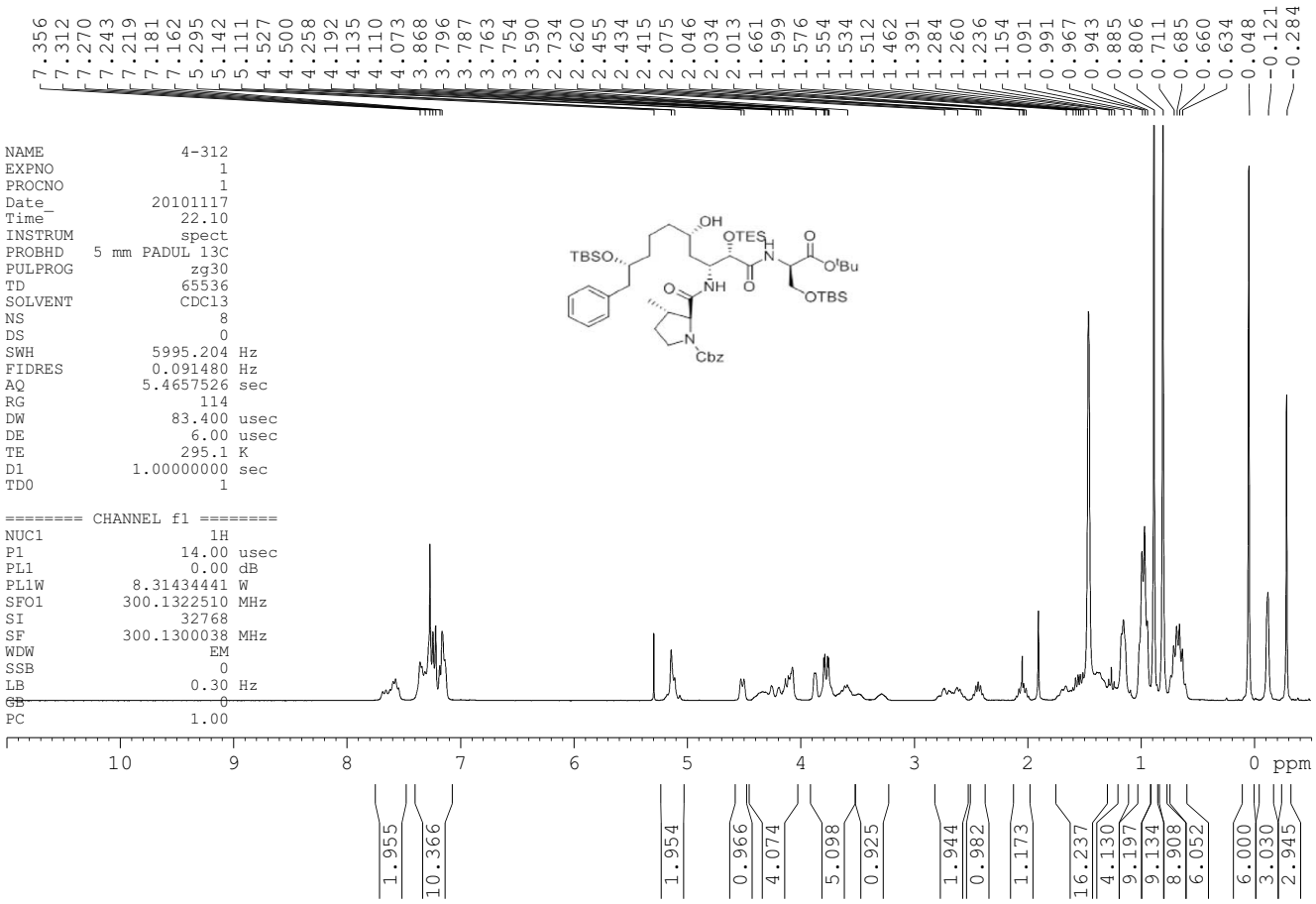
sample name:4-309-2
solvent:CDCl3
Bruker 300M



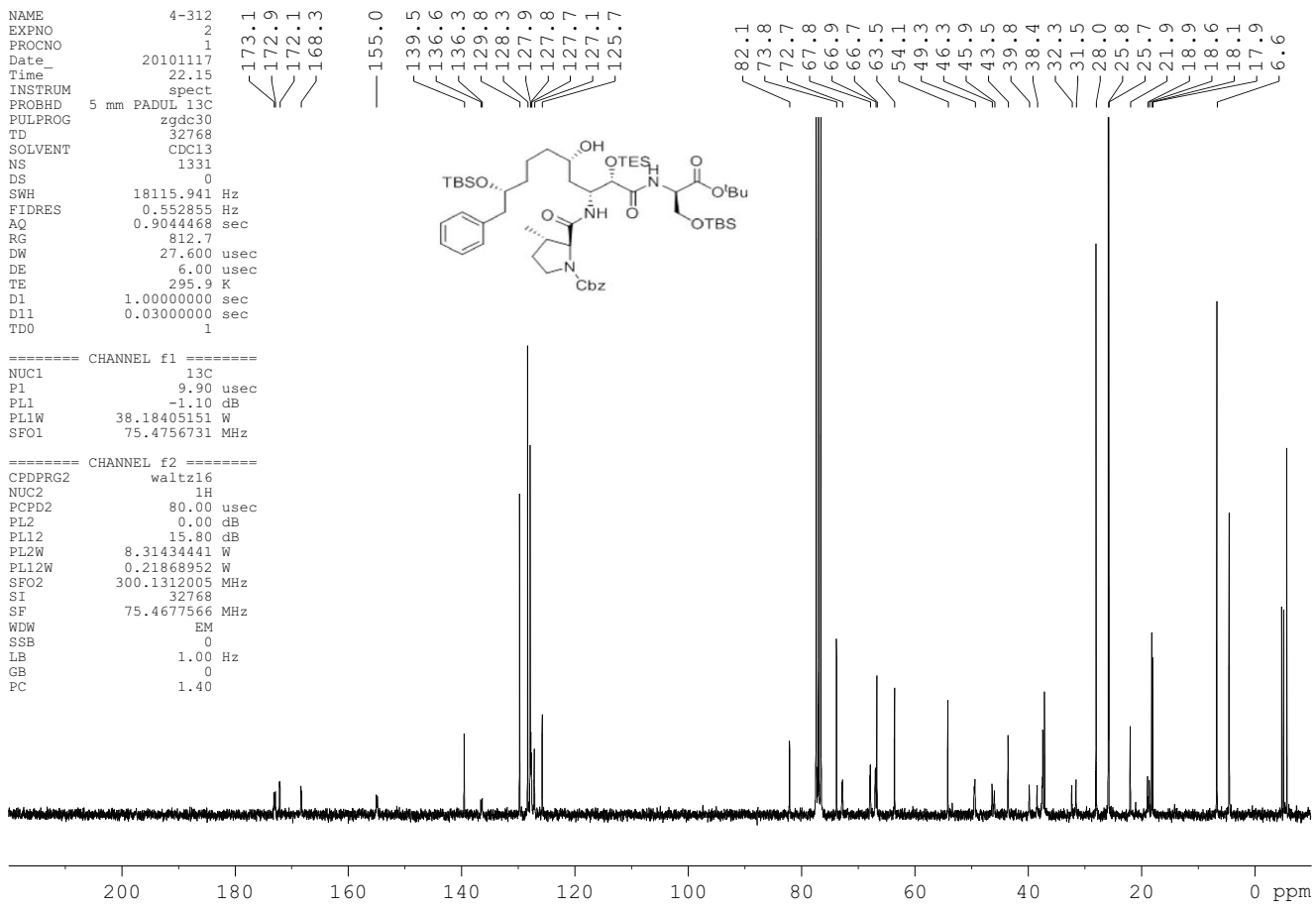
sample name: 4-309
solvent: CDCl3
Bruker 300M

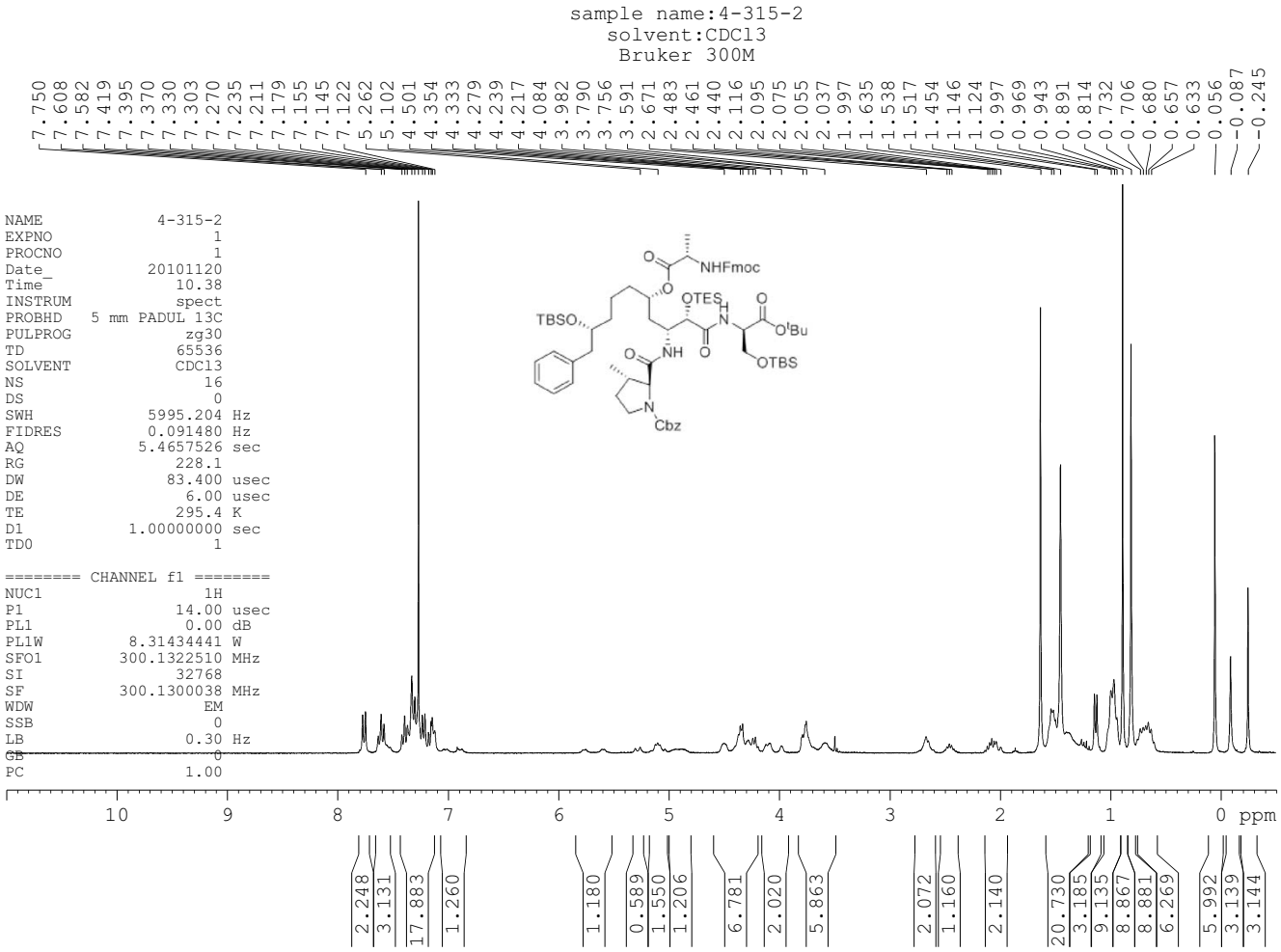


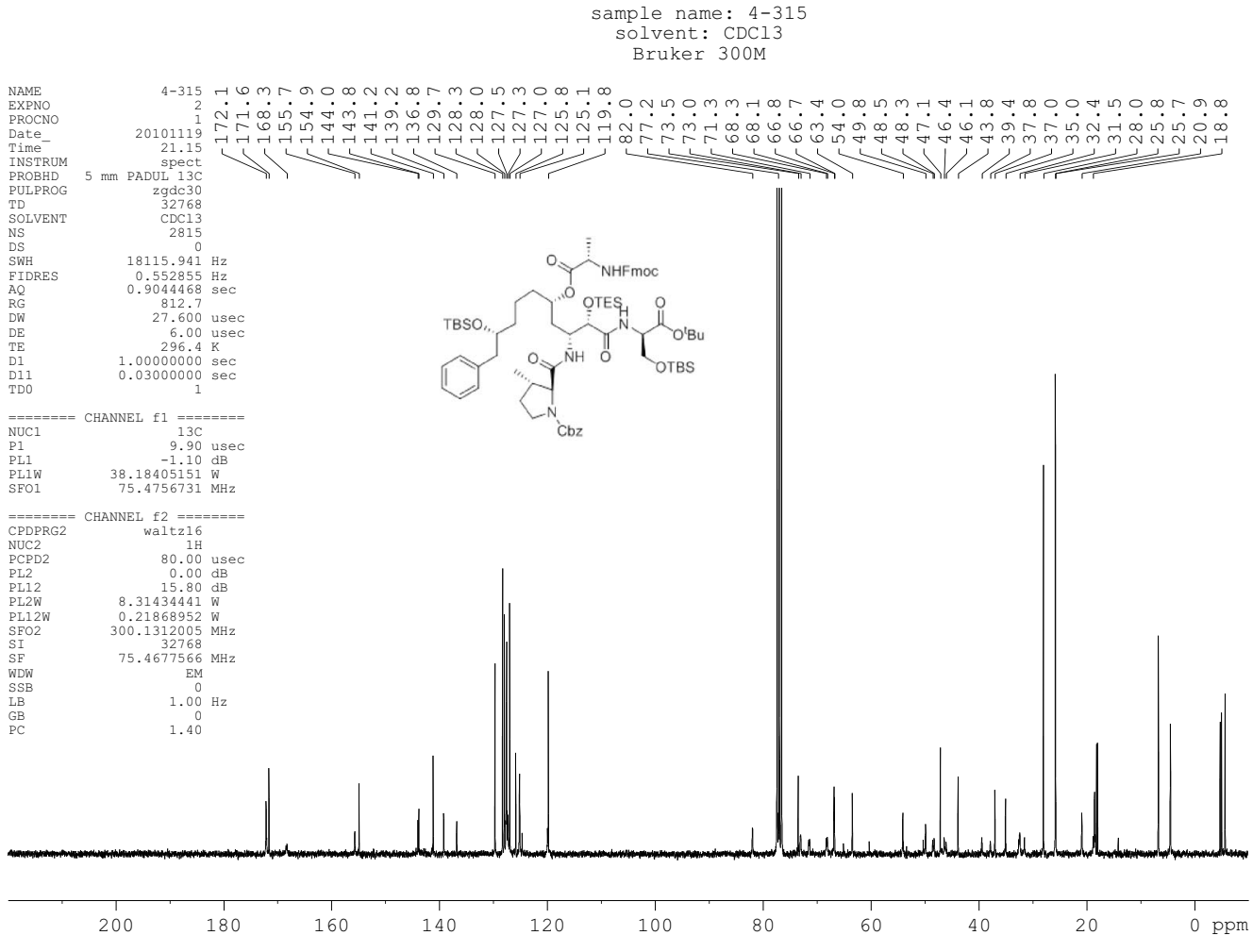
sample name:4-312
solvent:CDCl3
Bruker 300M



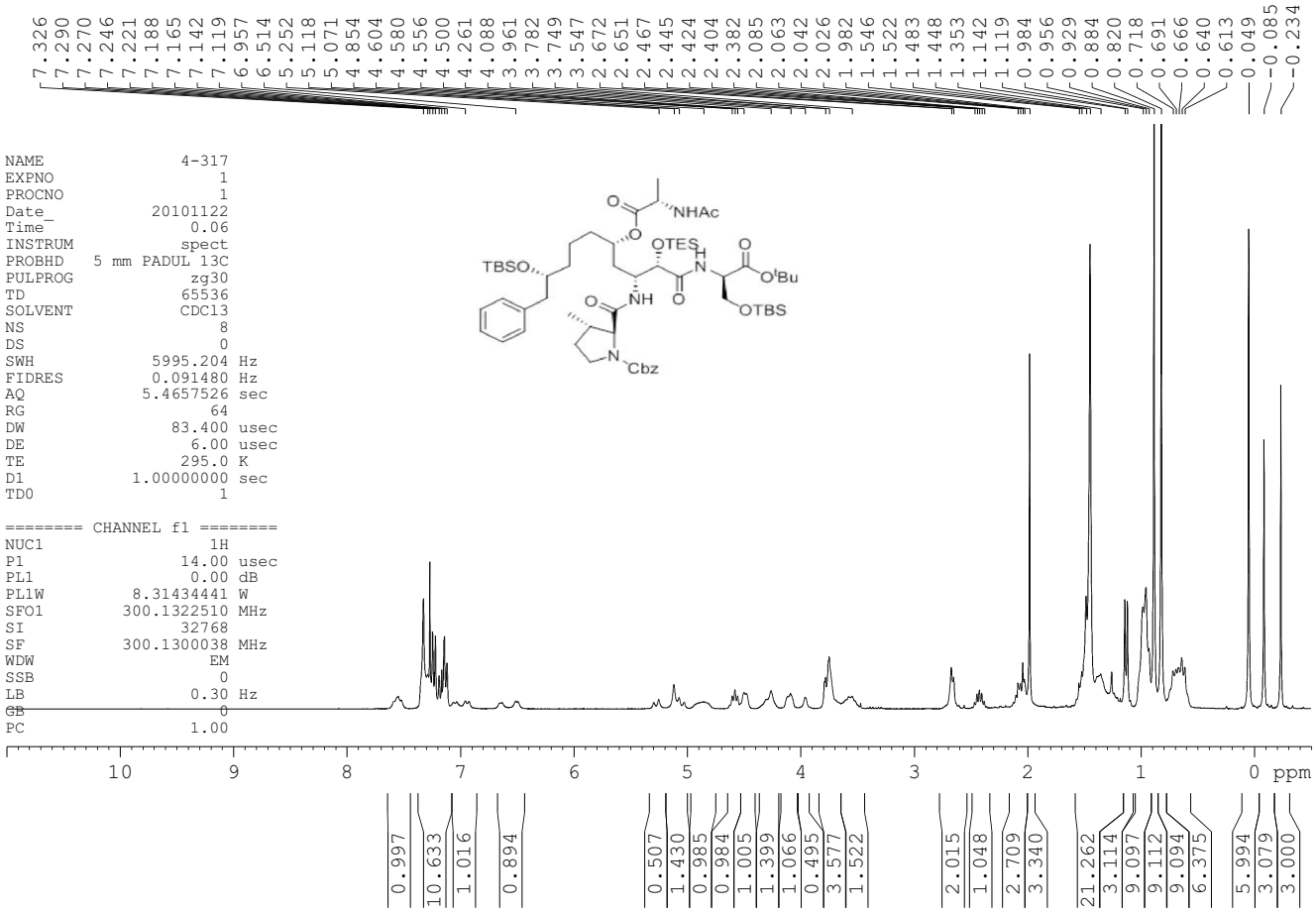
sample name: 4-312
solvent: CDCl3
Bruker 300M



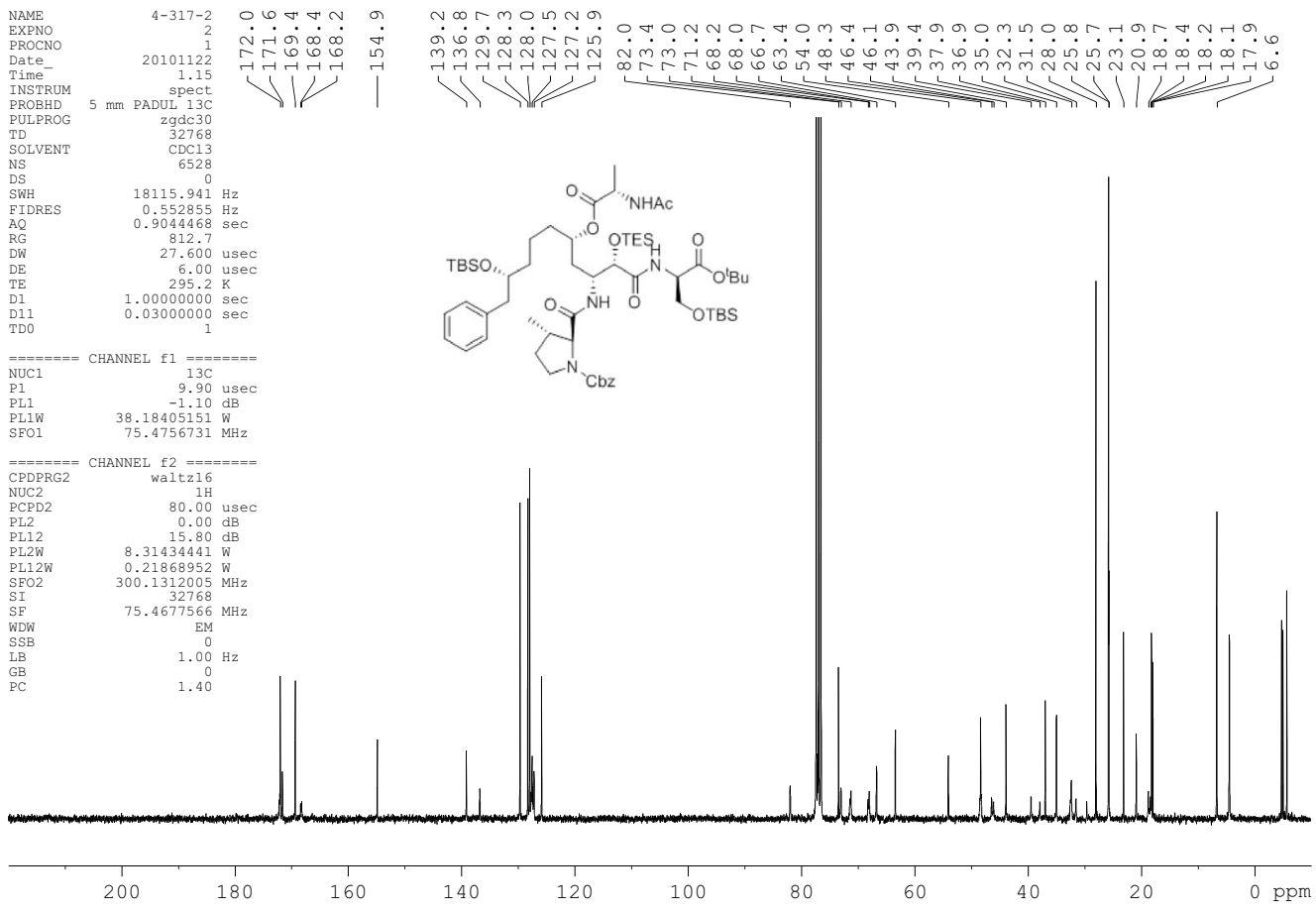

sample name:4-315-2
solvent:CDCl3
Bruker 300M
NAME 4-315-2
EXPNO 1
PROCNO 1
Date_ 20101120
Time_ 10.38
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.091480 Hz
AQ 5.4657526 sec
RG 228.1
DW 83.400 usec
DE 6.00 usec
TE 295.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 300.1322510 MHz
SI 32768
SF 300.1300038 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
NHFmoc
OTES
TBSO
O'Bu
OTBS
NH
Cbz
ppm

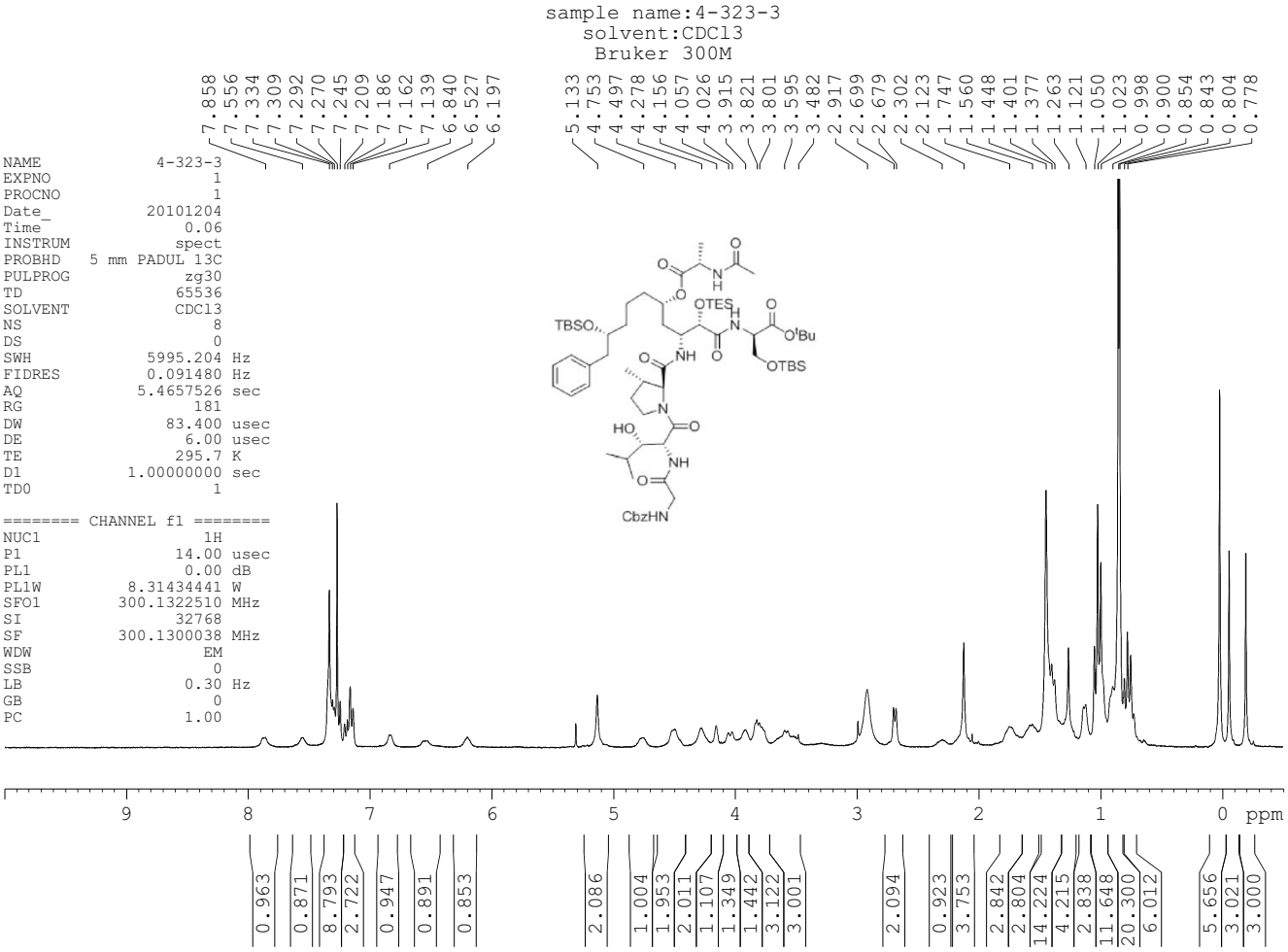

sample name: 4-315
solvent: CDCl3
Bruker 300M
NAME 4-315
EXPNO 2
PROCNO 1
Date_ 20101119
Time_ 21.15
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 2815
DS 0
SWH 18115.941 Hz
FIDRES 0.552855 Hz
AQ 0.9044468 sec
RG 812.7
DW 27.600 usec
DE 6.00 usec
TE 296.4 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -1.10 dB
PL1W 38.18405151 W
SFO1 75.4756731 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.80 dB
PL2W 8.31434441 W
PL12W 0.21868952 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677566 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
NHFmoc
OTES
TBSO
O'Bu
OTBS
NH
Cbz
ppm

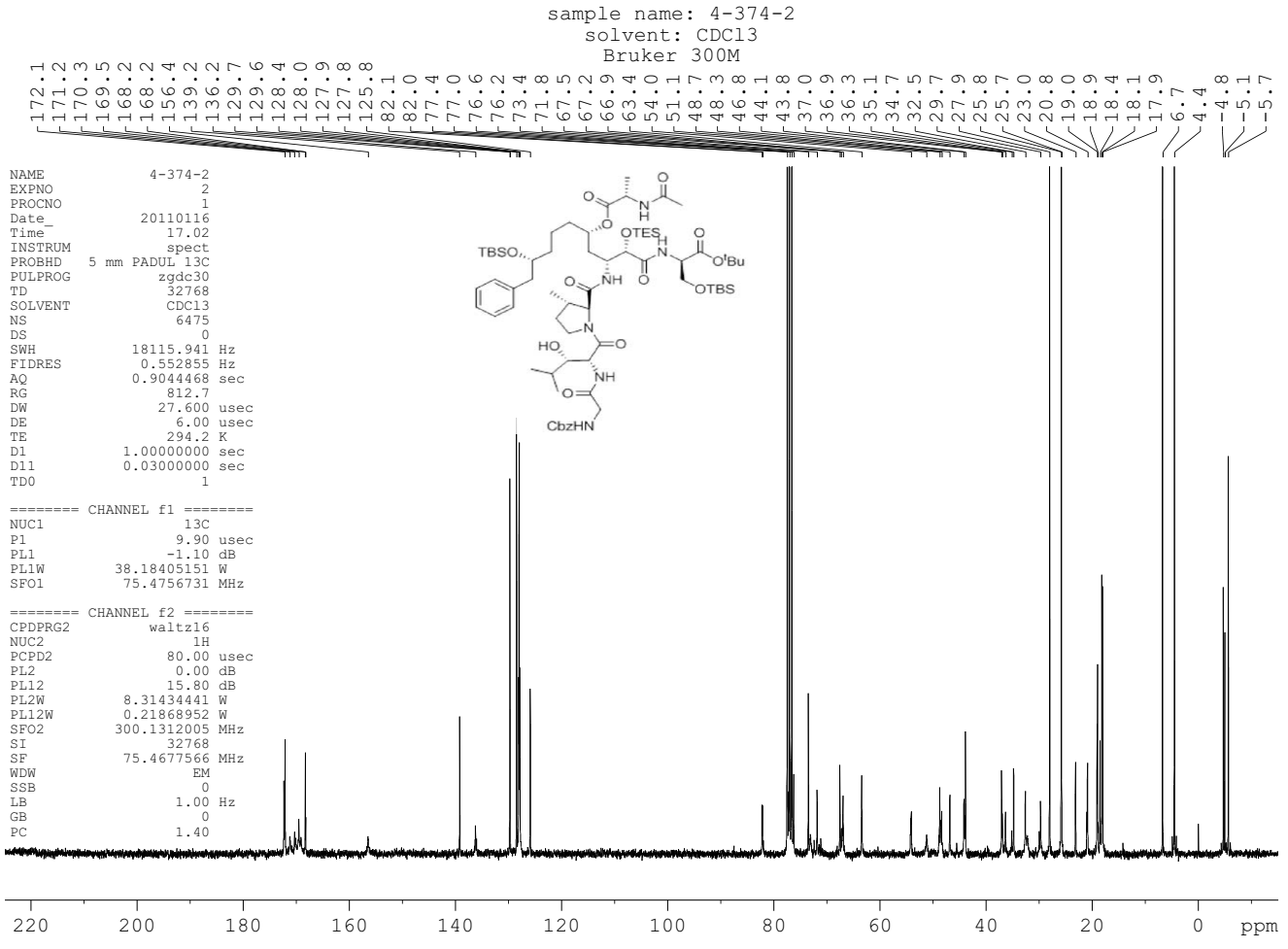
sample name:4-317
solvent:CDCl3
Bruker 300M

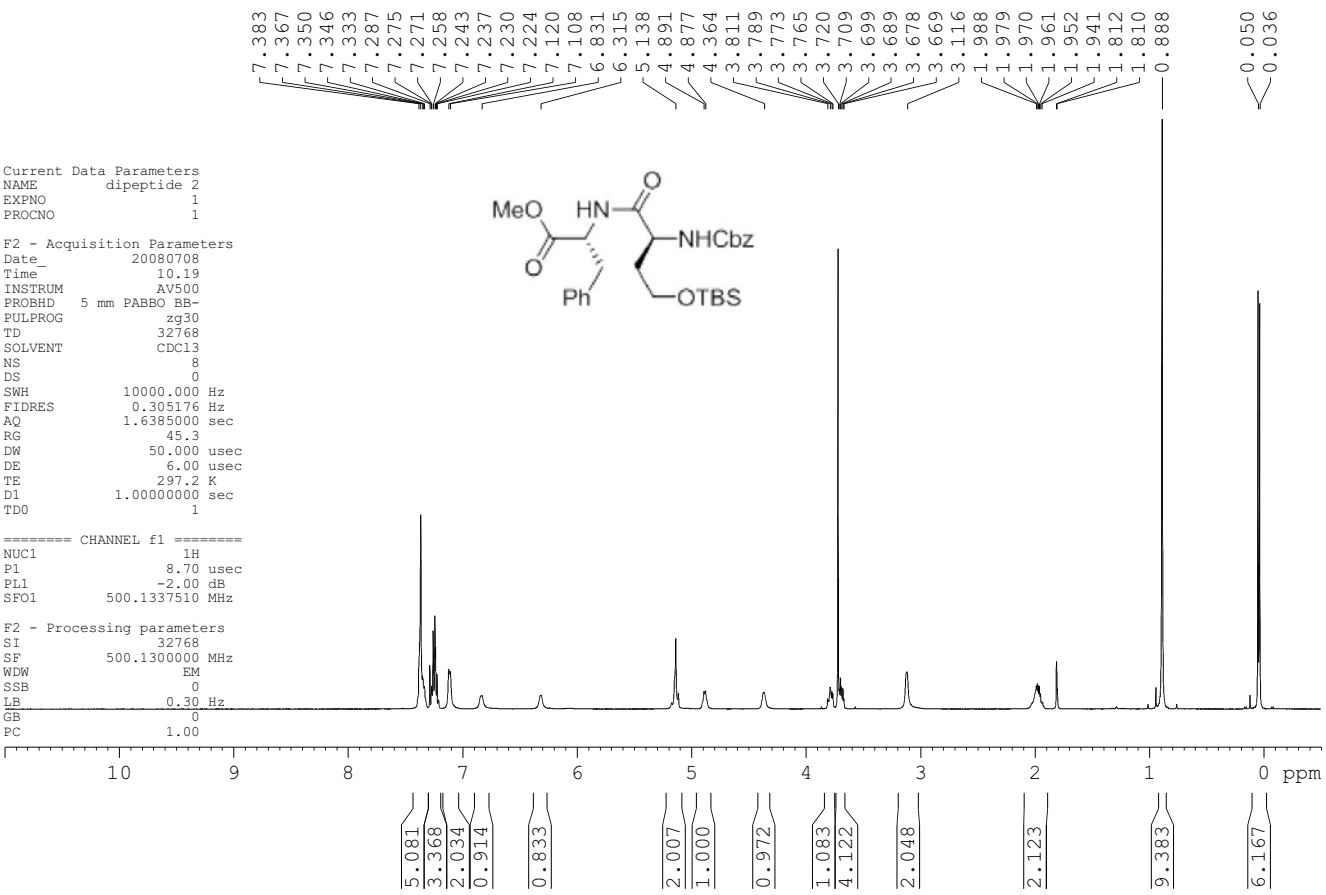


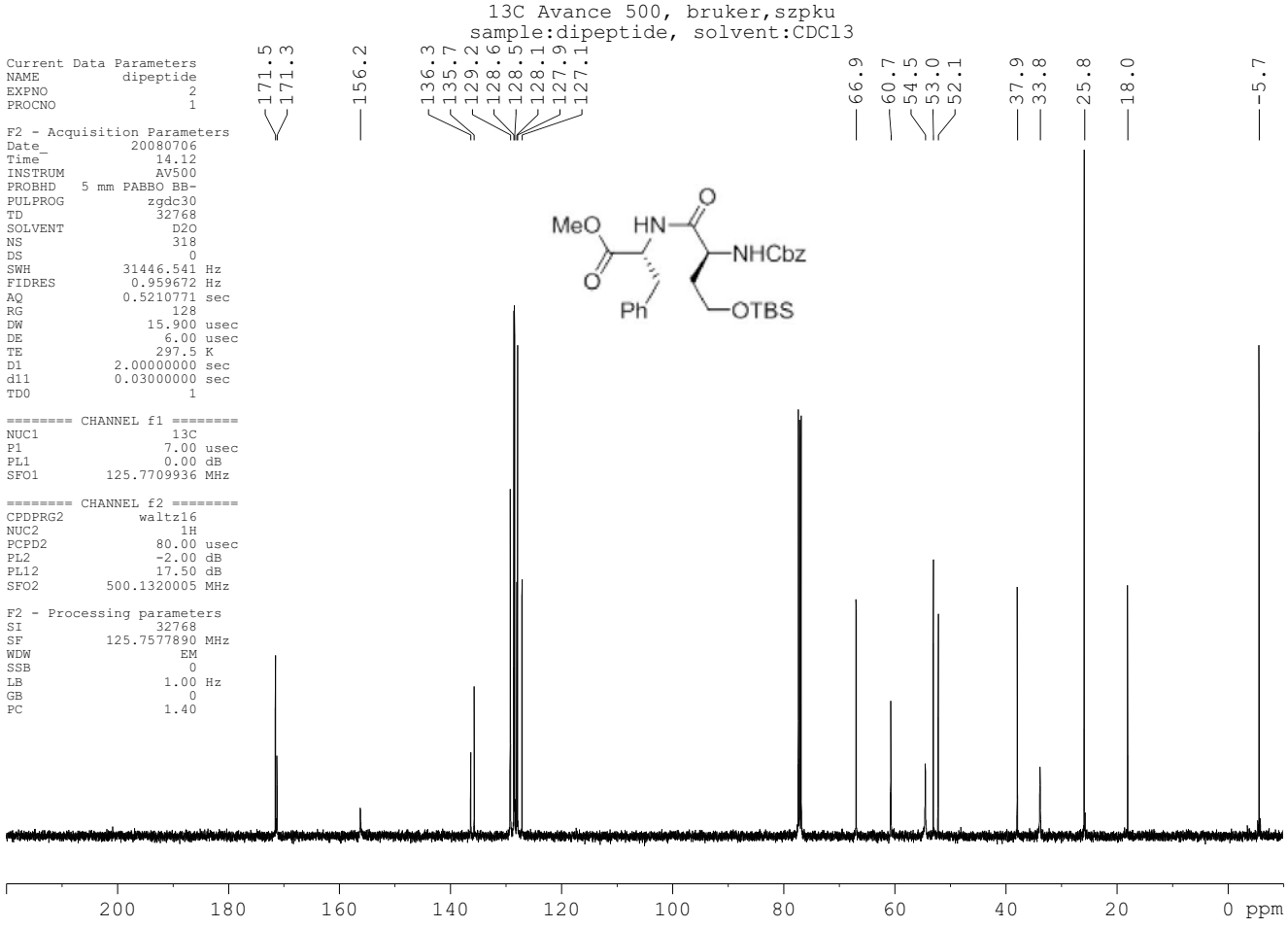
sample name: 4-317-
solvent: CDCl3
Bruker 300M



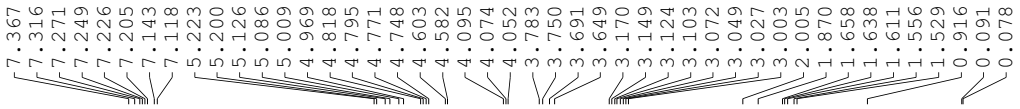

sample name:4-323-3
solvent:CDCl3
Bruker 300M
NAME 4-323-3
EXPNO 1
PROCNO 1
Date_ 20101204
Time 0.06
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 5995.204 Hz
FIDRES 0.091480 Hz
AQ 5.4657526 sec
RG 181
DW 83.400 usec
DE 6.00 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 300.1322510 MHz
SI 32768
SF 300.1300038 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.858 7.556 7.334 7.309 7.292 7.270 7.245 7.209 7.186 7.162 7.139 6.840 6.527 6.197
5.133 4.753 4.497 4.278 4.156 4.057 4.026 3.915 3.821 3.801 3.595 3.482 2.917 2.699 2.679 2.302 2.123 1.747 1.560 1.448 1.401 1.377 1.263 1.121 1.050 1.023 0.998 0.900 0.854 0.843 0.804 0.778
TBSO
OTES
O'Bu
OTBS
HO
CbzHN
9 8 7 6 5 4 3 2 1 0 ppm
0.963 0.871 8.793 2.722 0.947 0.891 0.853 2.086 1.004 1.953 2.011 1.107 1.349 1.442 3.122 3.001 2.094 0.923 3.753 2.842 2.804 14.224 4.215 2.838 11.648 20.300 6.012 5.656 3.021 3.000


sample name: 4-374-2
solvent: CDCl3
Bruker 300M
172.1 171.2 170.3 169.5 168.2 168.2 156.4 139.2 136.2 129.7 129.6 128.4 128.0 127.9 127.8 125.8 82.1 82.0 77.4 77.0 76.6 76.2 73.4 71.8 67.5 67.2 66.9 63.4 54.0 51.1 48.7 48.3 46.8 44.1 43.8 37.0 36.9 36.3 35.1 34.7 32.5 29.7 27.9 25.8 25.7 23.0 20.8 19.0 18.9 18.4 18.1 17.9 6.7 4.4 -4.8 -5.1 -5.7
NAME 4-374-2
EXPNO 2
PROCNO 1
Date_ 20110116
Time 17.02
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 6475
DS 0
SWH 18115.941 Hz
FIDRES 0.552855 Hz
AQ 0.9044468 sec
RG 812.7
DW 27.600 usec
DE 6.00 usec
TE 294.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -1.10 dB
PL1W 38.18405151 W
SFO1 75.4756731 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.80 dB
PL2W 8.31434441 W
PL12W 0.21868952 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677566 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
TBSO
OTES
O'Bu
OTBS
HO
CbzHN
220 200 180 160 140 120 100 80 60 40 20 0 ppm

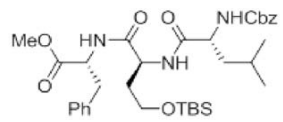

Avance 500, Bruker, A&T Center SZPKU
ample name:dipeptide 2; Solvent:CDCl
Spectrum:stanard
7.383 7.367 7.350 7.346 7.333 7.287 7.275 7.271 7.258 7.243 7.237 7.230 7.224 7.120 7.108 6.831 6.315 5.138 4.891 4.877 4.364 3.811 3.789 3.773 3.765 3.720 3.709 3.699 3.689 3.678 3.669 3.116 1.988 1.979 1.970 1.961 1.952 1.941 1.812 1.810 0.888 0.050 0.036
MeO HN NHCbz Ph OTBS
Current Data Parameters
NAME dipeptide 2
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080708
Time 10.19
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6385000 sec
RG 45.3
DW 50.000 usec
DE 6.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 8.70 usec
PL1 -2.00 dB
SFO1 500.1337510 MHz
F2 - Processing parameters
SI 32768
SF 500.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
5.081 3.368 2.034 0.914 0.833 2.007 1.000 0.972 1.083 4.122 2.048 2.123 9.383 6.167


13C Avance 500, bruker,szpku
sample:dipeptide, solvent:CDCl3
171.5 171.3 156.2 136.3 135.7 129.2 128.6 128.5 128.1 127.9 127.1 66.9 60.7 54.5 53.0 52.1 37.9 33.8 25.8 18.0 -5.7
MeO HN NHCbz Ph OTBS
Current Data Parameters
NAME dipeptide
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080706
Time 14.12
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT D2O
NS 318
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 128
DW 15.900 usec
DE 6.00 usec
TE 297.5 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 0.00 dB
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.50 dB
SFO2 500.1320005 MHz
F2 - Processing parameters
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

sample name:1-55-p
solvent:CDCl3

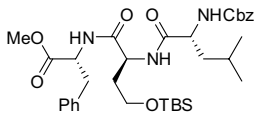



```
NAME              1-55-p
EXPNO                  1
PROCNO                 1
Date_           20080703
Time               14.54
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             5995.204 Hz
FIDRES          0.091480 Hz
AQ              5.4657526 sec
RG                 101.6
DW                83.400 usec
DE                 6.00 usec
TE                295.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.00 usec
PL1                0.00 dB
SFO1         300.1322510 MHz
SI                 32768
SF           300.1300038 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

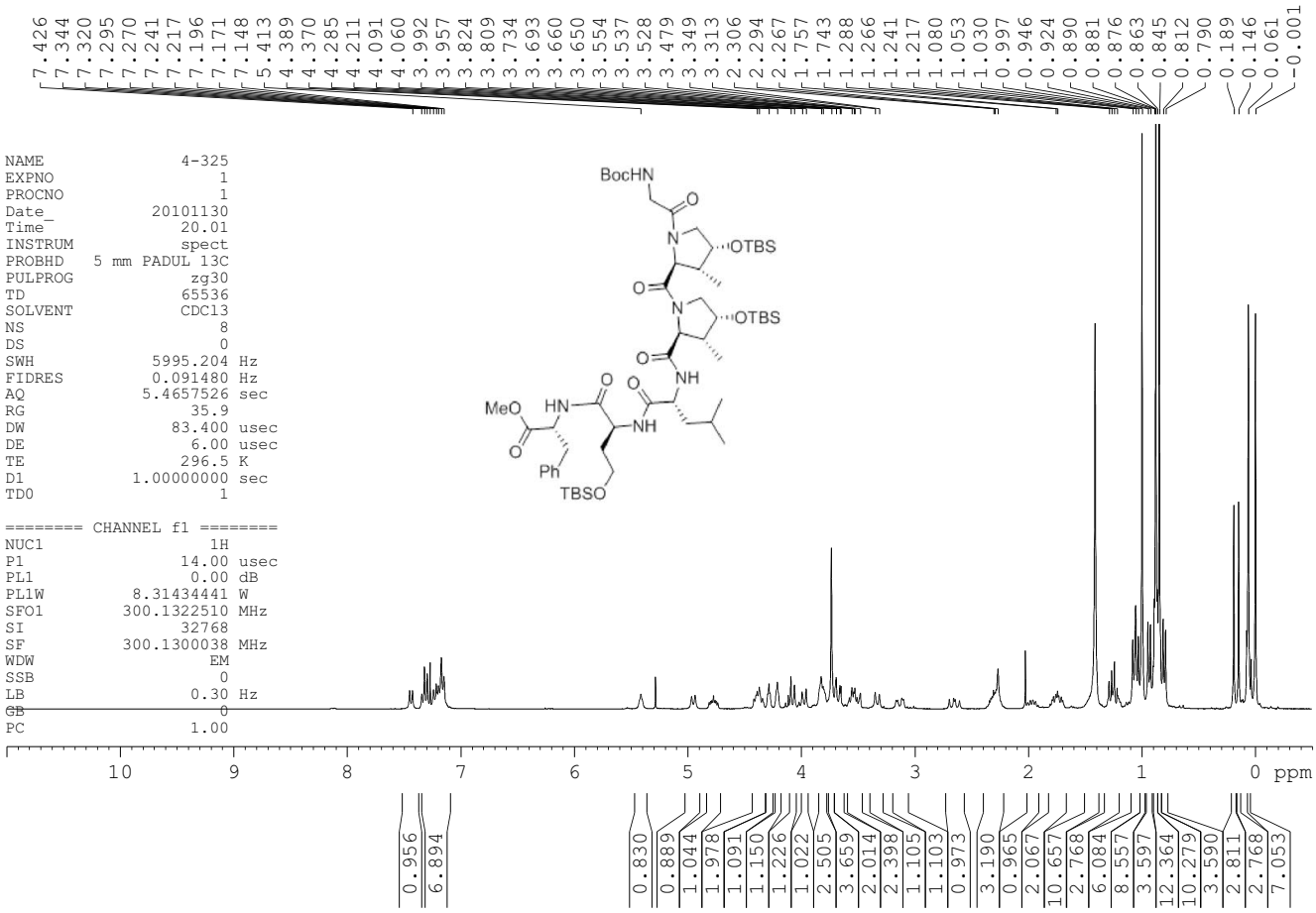


1-55-p
CDCl3

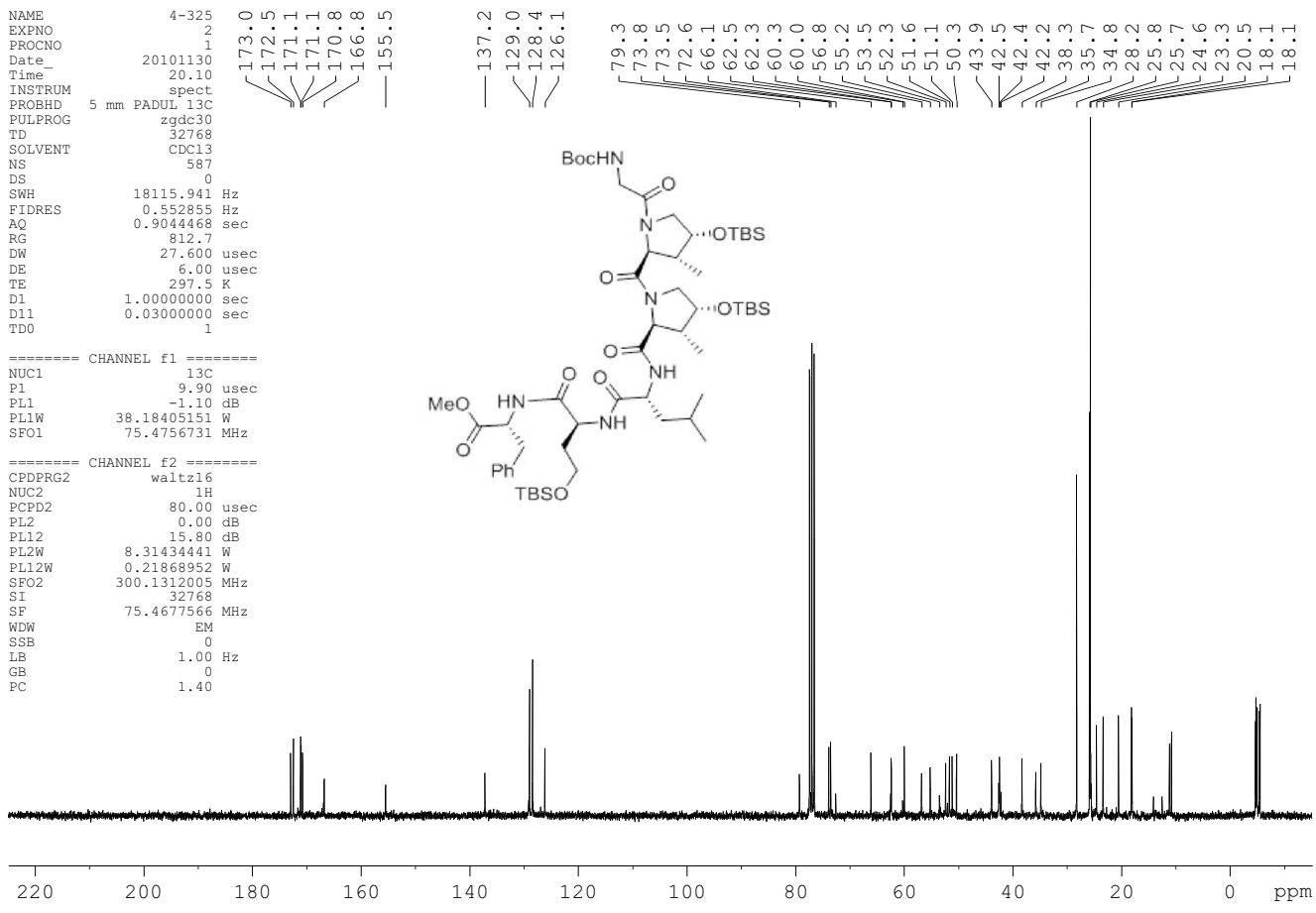

```
NAME              1-55-p
EXPNO                  2
PROCNO                 1
Date_           20080703
Time               15.03
INSTRUM            spect
PROBHD   5 mm PADUL 13C
PULPROG           zgdc30
TD                 32768
SOLVENT            CDCl3
NS                   740
DS                     0
SWH            18115.941 Hz
FIDRES          0.552855 Hz
AQ              0.9044468 sec
RG                1149.4
DW                27.600 usec
DE                 6.00 usec
TE                295.7 K
D1            1.00000000 sec
d11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.90 usec
PL1               -1.10 dB
SFO1         75.4756731 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              15.80 dB
SFO2        300.1312005 MHz
SI                 32768
SF           75.4677490 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```



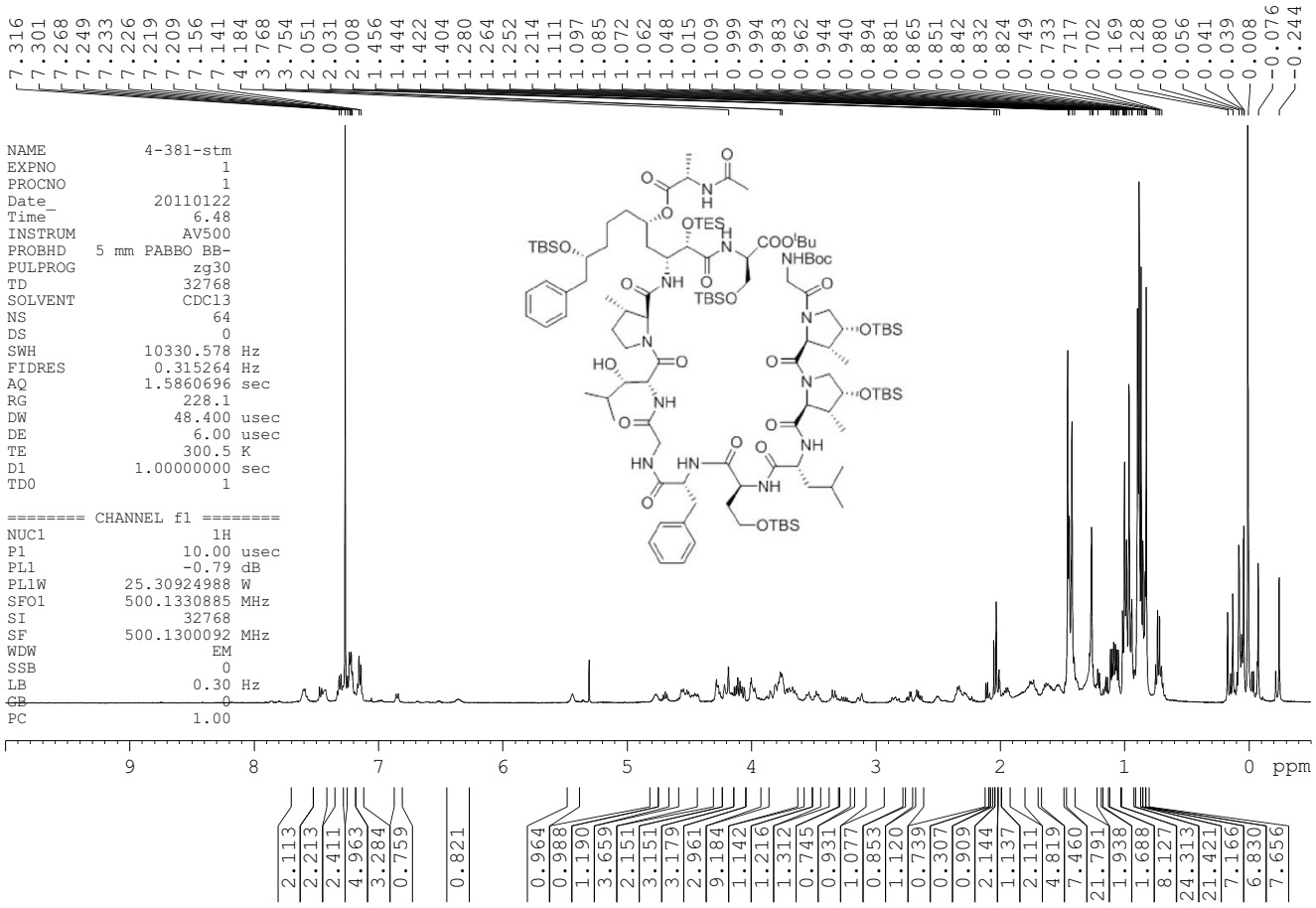
sample name:4-325
solvent:CDCl3
Bruker 300M



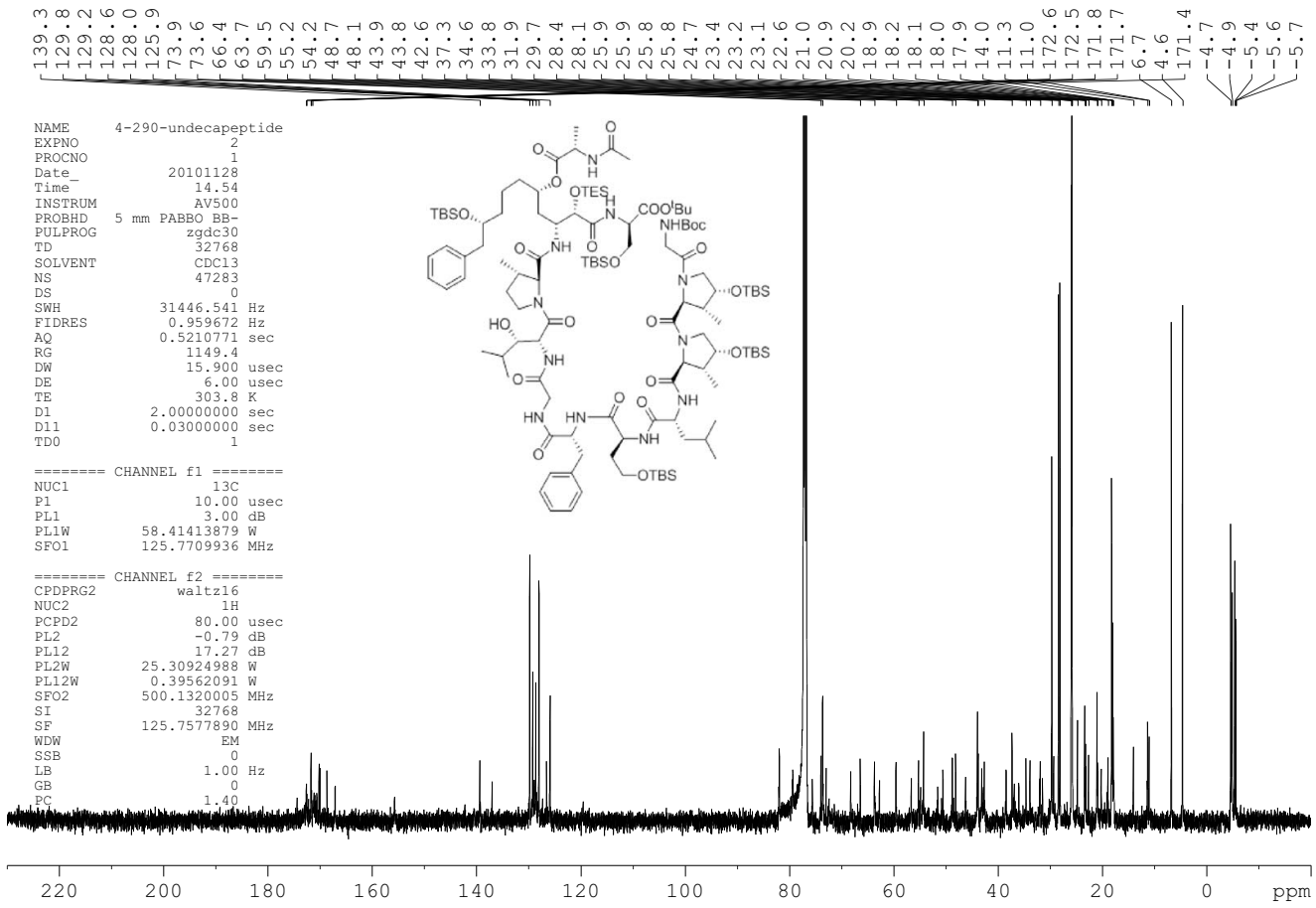
sample name: 4-325
solvent: CDCl3
Bruker 300M



Avance 500, Bruker, SZPKU
sample:4-381-stm, solvent:CDCl3
spectrum:jyliu



Avance 500, Bruker, SZPKU
sample:4-290-undecapeptide, solvent:CDCl3
spectrum:jyliu

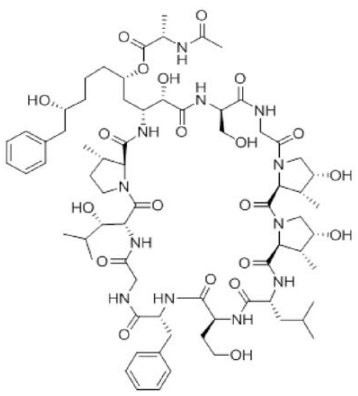


Avance 500, Bruker, SZPKU
sample:4-TM-L-5-DMSO, solvent:DMSO
spectrum:jyliu

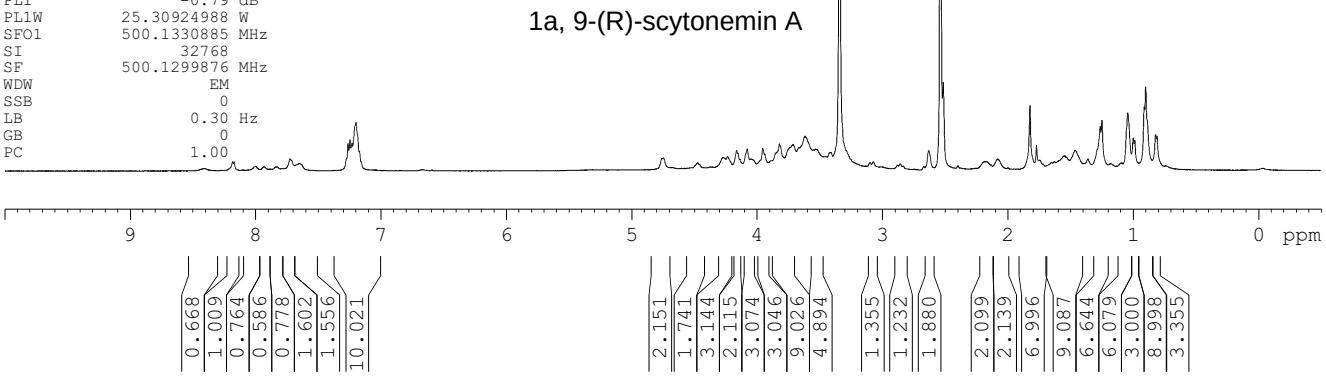
8.405 8.181 8.167 7.998 7.924 7.824 7.722 7.646 7.259 7.244 7.227 7.197 7.168

4.744 4.472 4.267 4.160 4.075 3.952 3.819 3.709 3.614 3.530 3.409 3.096 3.070 2.878 2.856 2.627 2.186 2.077 1.820 1.768 1.648 1.626 1.554 1.541 1.459 1.356 1.261 1.246 1.040 0.997 0.984 0.909 0.897 0.819

NAME	4-TM-L-5-DMSO
EXPNO	1
PROCNO	1
Date_	20110403
Time	15.58
INSTRUM	AV500
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	32768
SOLVENT	DMSO
NS	128
DS	0
SWH	10330.578 Hz
FIDRES	0.315264 Hz
AQ	1.5860696 sec
RG	256
DW	48.400 usec
DE	6.00 usec
TE	301.7 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	10.00 usec
PL1	-0.79 dB
PL1W	25.30924988 W
SFO1	500.1330885 MHz
SI	32768
SF	500.1299876 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



1a, 9-(R)-scytonemin A



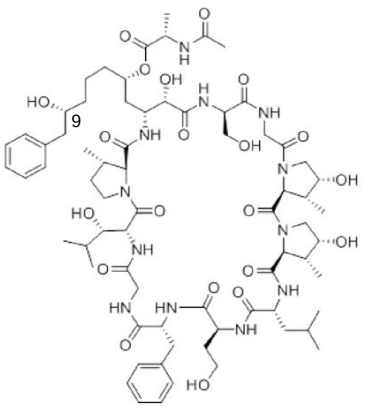
0.668 1.009 0.764 0.586 0.778 1.602 1.556 10.021

2.151 1.741 3.144 2.115 3.074 3.046 9.026 4.894 1.355 1.232 1.880 2.099 2.139 6.996 9.087 6.644 6.079 3.000 8.998 3.355

TM-L-1

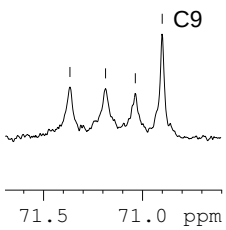
172.417 172.168 172.068 172.007 171.429 171.285 171.014 169.953 169.275 169.102 168.559 166.681 139.814 138.008 129.409 129.047 128.165 128.017 126.264 125.723 75.622 72.943 71.367 71.187 71.036 70.900 67.059 65.581 61.460 57.615 55.080 54.247 50.743 50.500 48.238 47.877 46.286 43.676 42.333 41.772 41.099 37.091 36.642 36.474 34.290 32.062 30.159 24.405 23.471 22.255 20.717 20.638 19.582 18.496 18.301 17.051 11.380 10.562

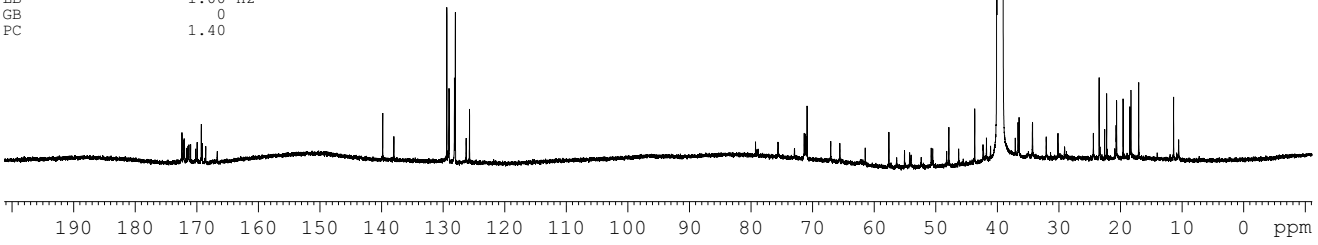
NAME	TM-L-1
EXPNO	2
PROCNO	1
Date_	20110415
Time	11.50
INSTRUM	spect
PROBHD	5 mm CP2 1H-31
PULPROG	zgpg30
TD	65536
SOLVENT	DMSO
NS	68649
DS	4
SWH	32051.281 Hz
FIDRES	0.489064 Hz
AQ	1.0224116 sec
RG	203
DW	15.600 usec
DE	18.00 usec
TE	298.0 K
D1	3.00000000 sec
D11	0.03000000 sec
======== CHANNEL f1 ========	
NUC1	13C
P1	11.40 usec
SI	65536
SF	150.9028658 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

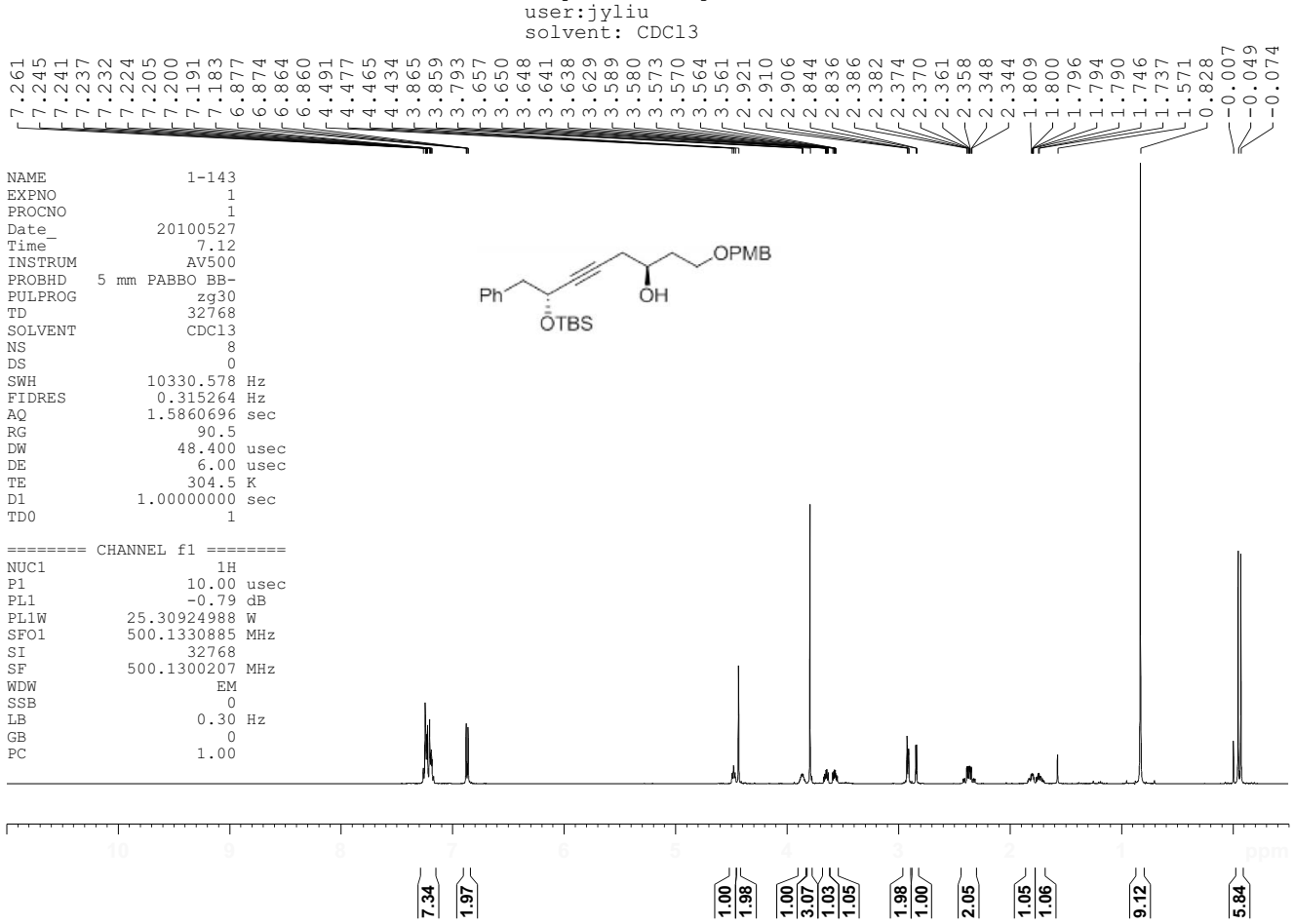


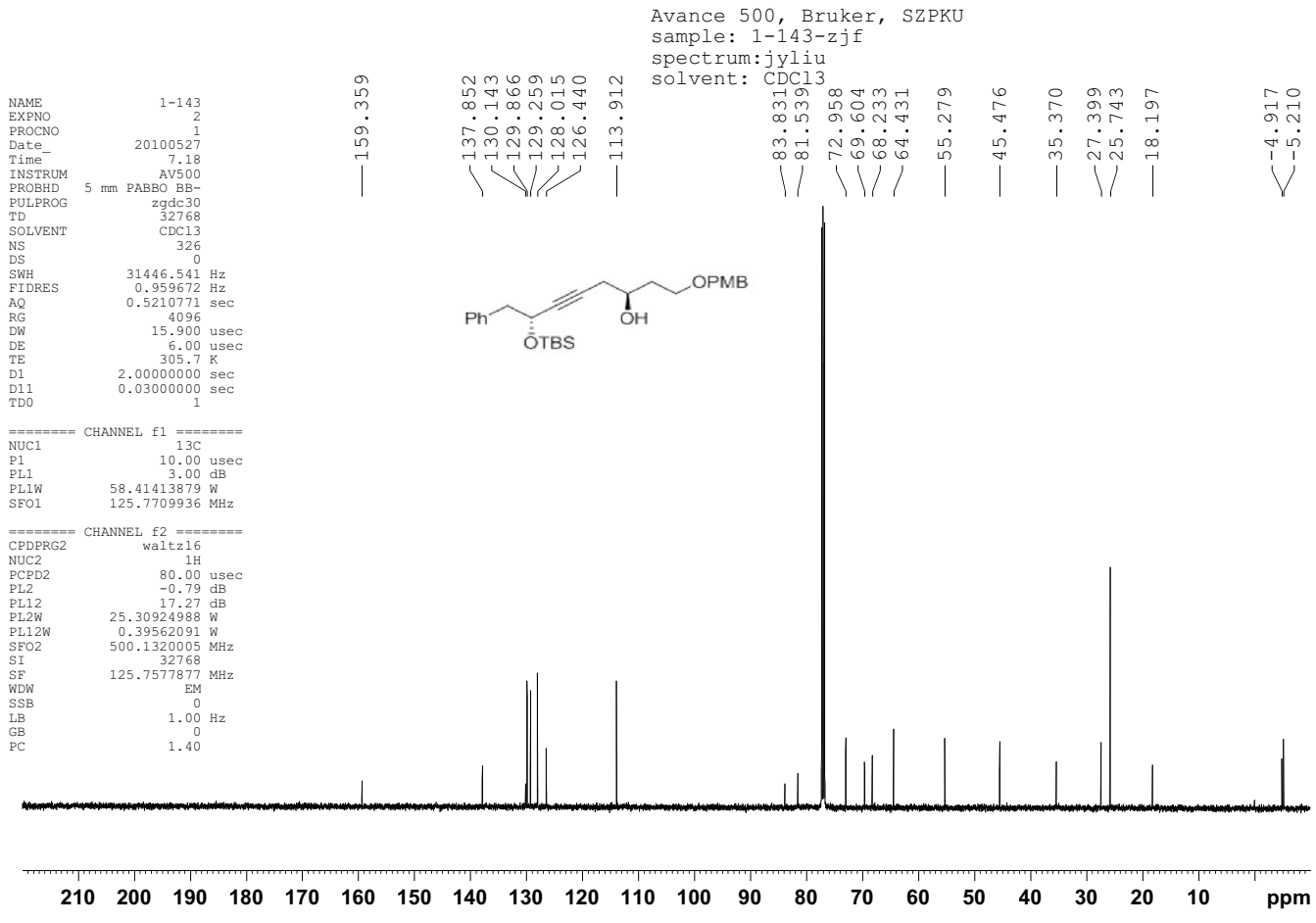
1a, 9-(R)-scytonemin A

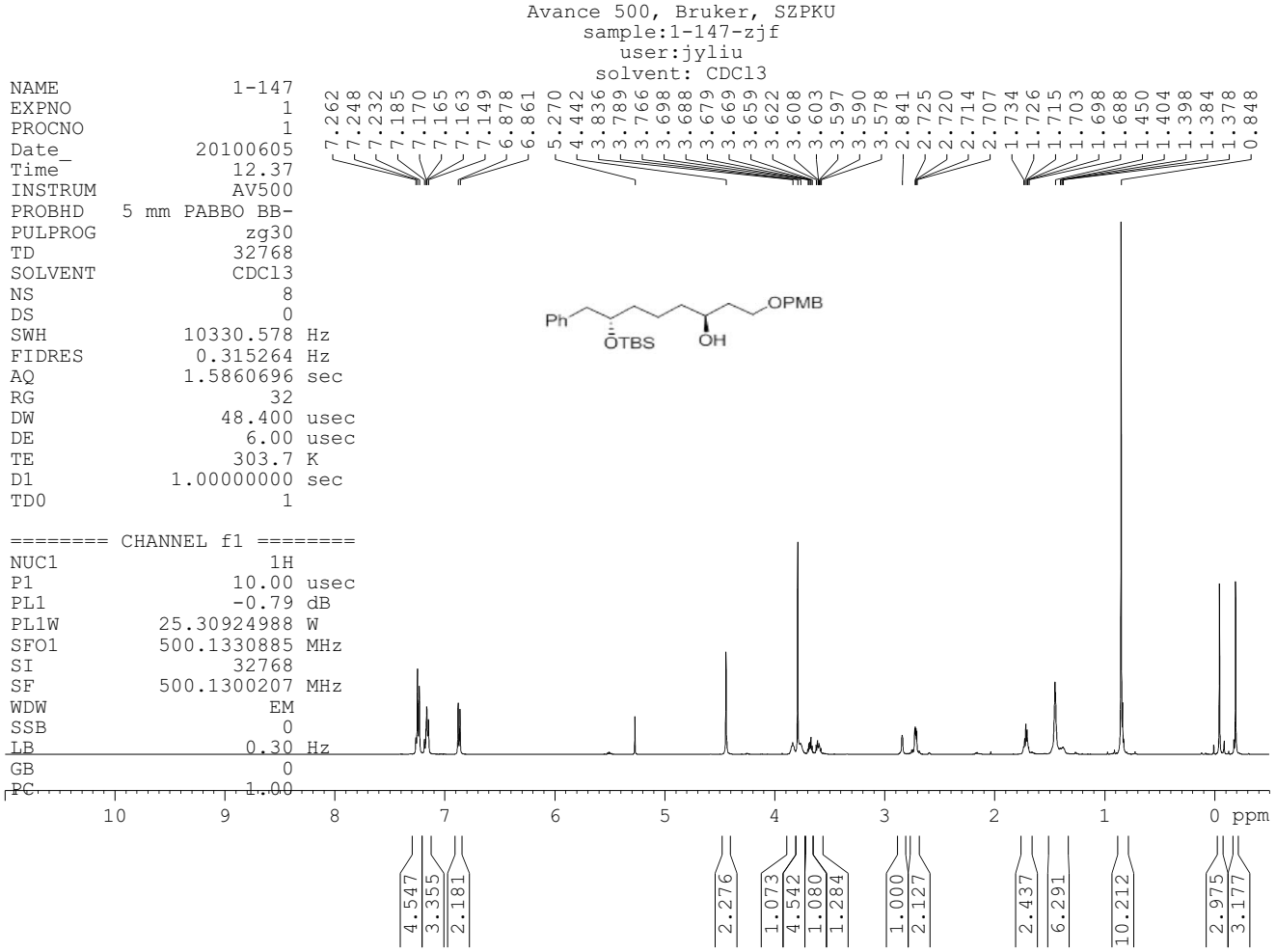
71.37 71.19 71.04 70.90

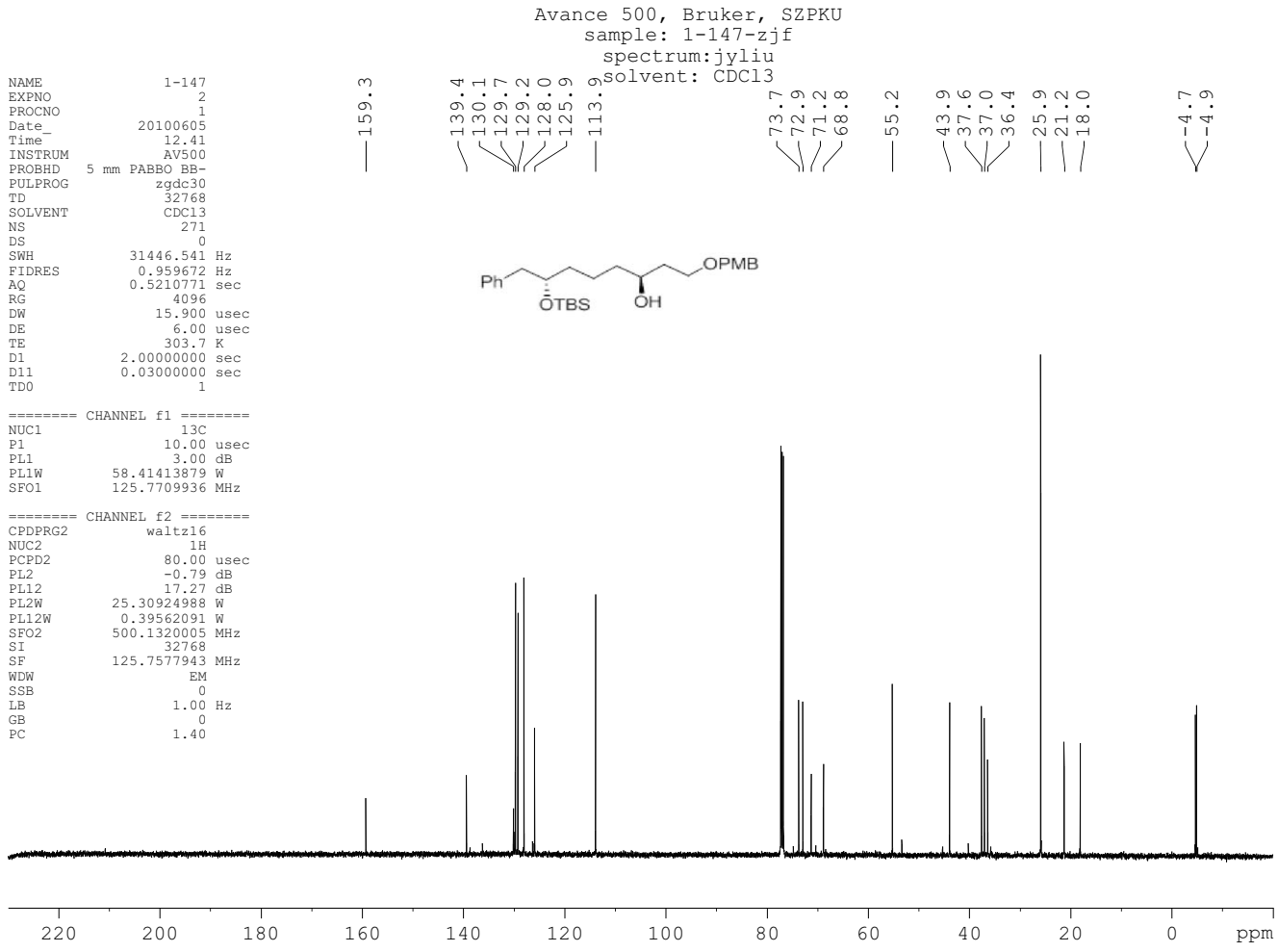


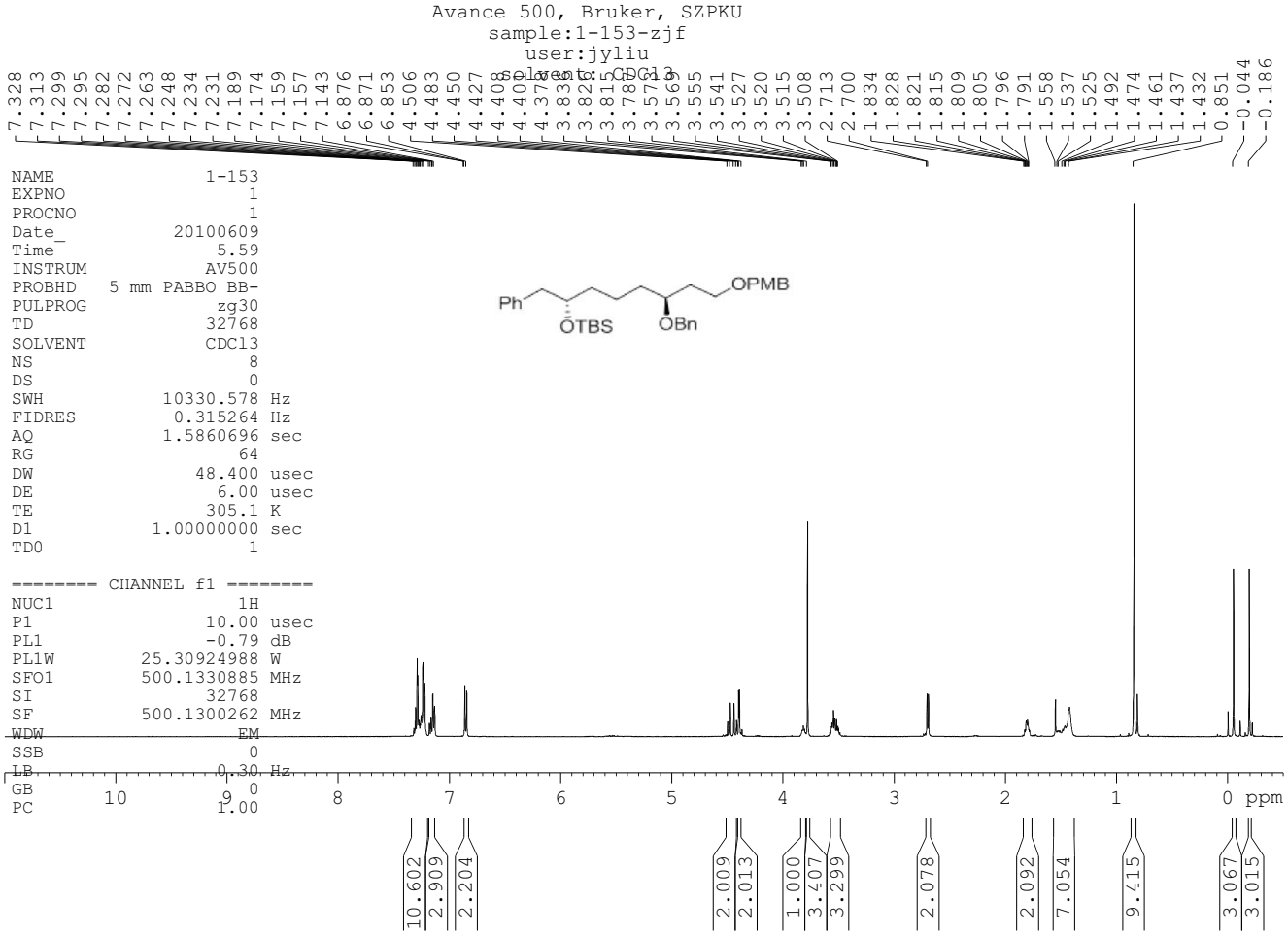


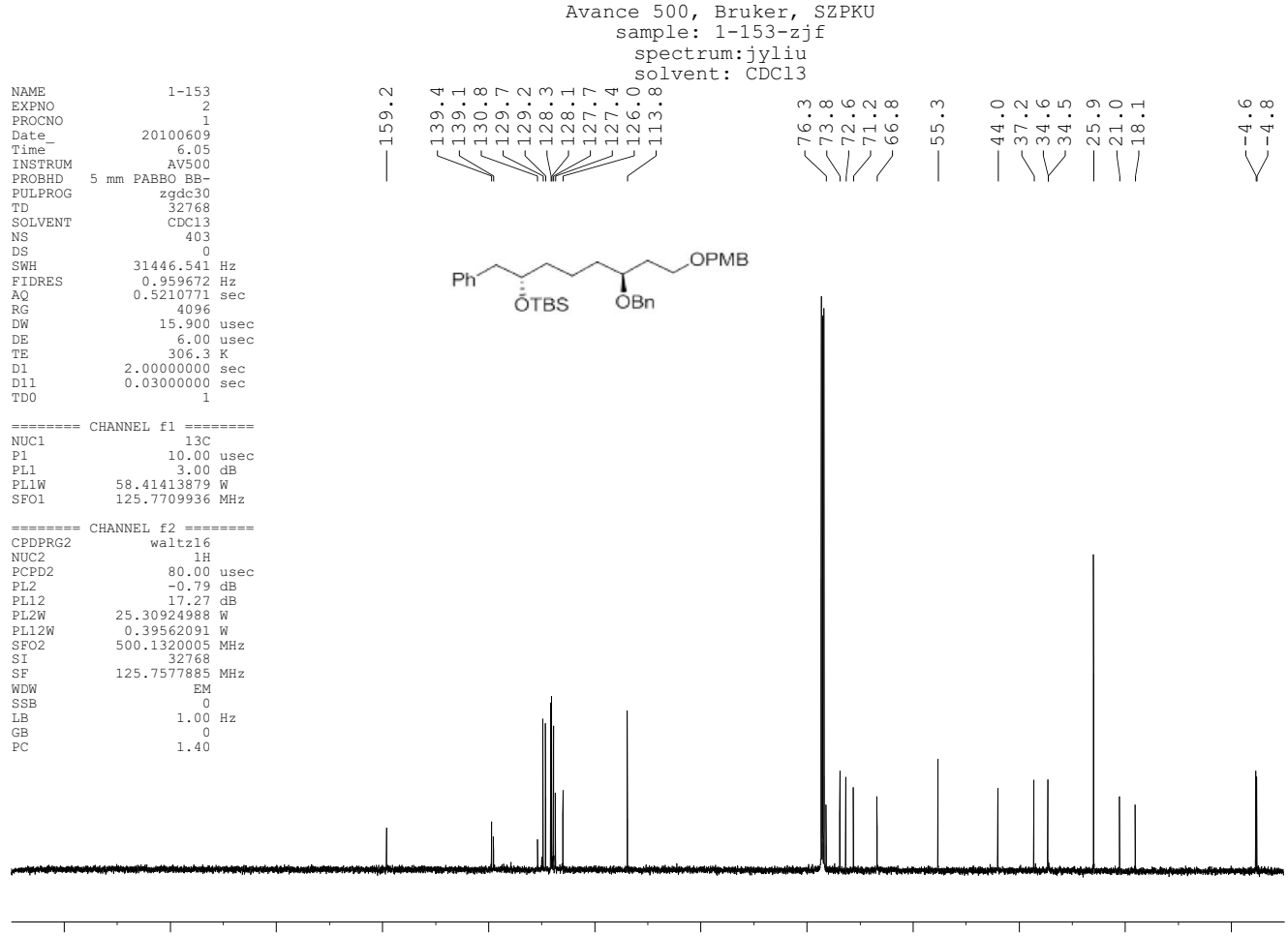

Avance 500, Bruker, SZPKU
sample:1-143-zjf
user:jyliu
solvent: CDCl3
NAME 1-143
EXPNO 1
PROCNO 1
Date_ 20100527
Time 7.12
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 90.5
DW 48.400 usec
DE 6.00 usec
TE 304.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300207 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OPMB
Ph
OH
OTBS
ppm

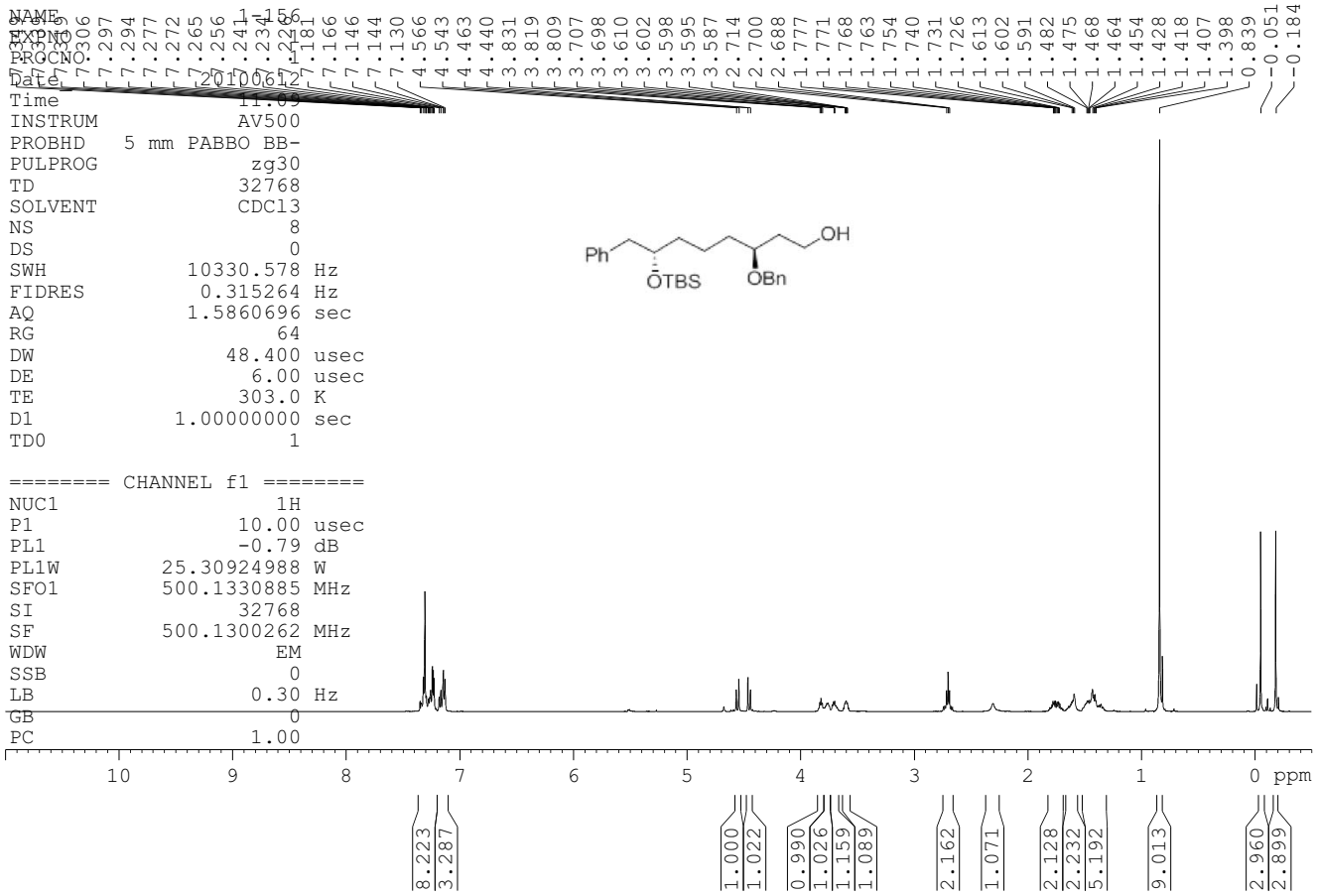

Avance 500, Bruker, SZPKU
sample: 1-143-zjf
spectrum:jyliu
solvent: CDCl3
NAME 1-143
EXPNO 2
PROCNO 1
Date_ 20100527
Time 7.18
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 326
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 4096
DW 15.900 usec
DE 6.00 usec
TE 305.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577877 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OPMB
Ph
OH
OTBS
ppm

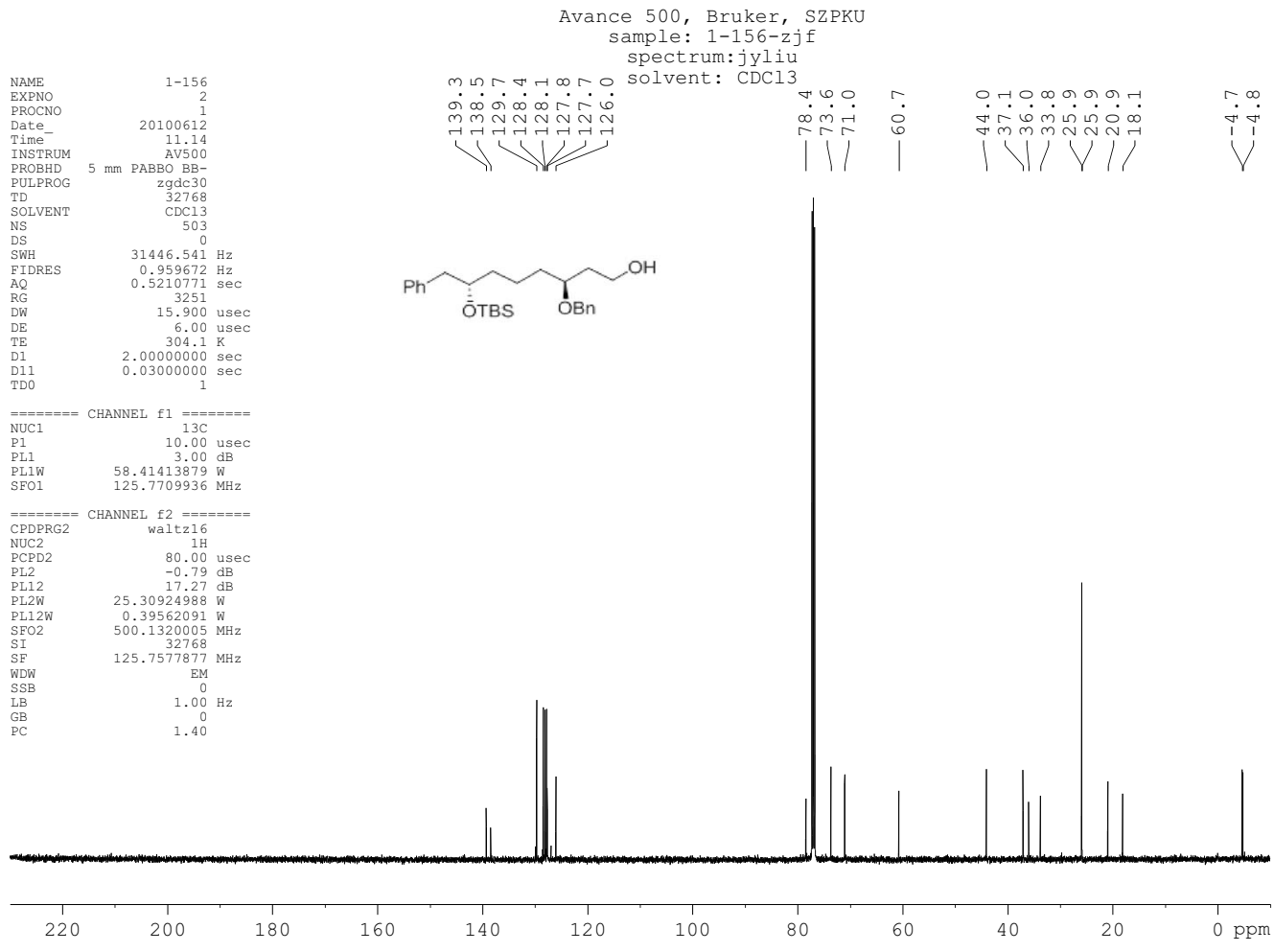

Avance 500, Bruker, SZPKU
sample:1-147-zjf
user:jyliu
solvent: CDCl3
NAME 1-147
EXPNO 1
PROCNO 1
Date_ 20100605
Time 12.37
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 32
DW 48.400 usec
DE 6.00 usec
TE 303.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300207 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
7.262 7.248 7.232 7.185 7.170 7.165 7.163 7.149 6.878 6.861 5.270 4.442 3.836 3.789 3.766 3.698 3.688 3.679 3.669 3.659 3.622 3.608 3.603 3.597 3.590 3.578 2.841 2.725 2.720 2.714 2.707 1.734 1.726 1.715 1.703 1.698 1.688 1.450 1.404 1.398 1.384 1.378 0.848
Ph
OTBS
OH
OPMB
10 9 8 7 6 5 4 3 2 1 0 ppm
4.547 3.355 2.181 2.276 1.073 4.542 1.080 1.284 1.000 2.127 2.437 6.291 10.212 2.975 3.177

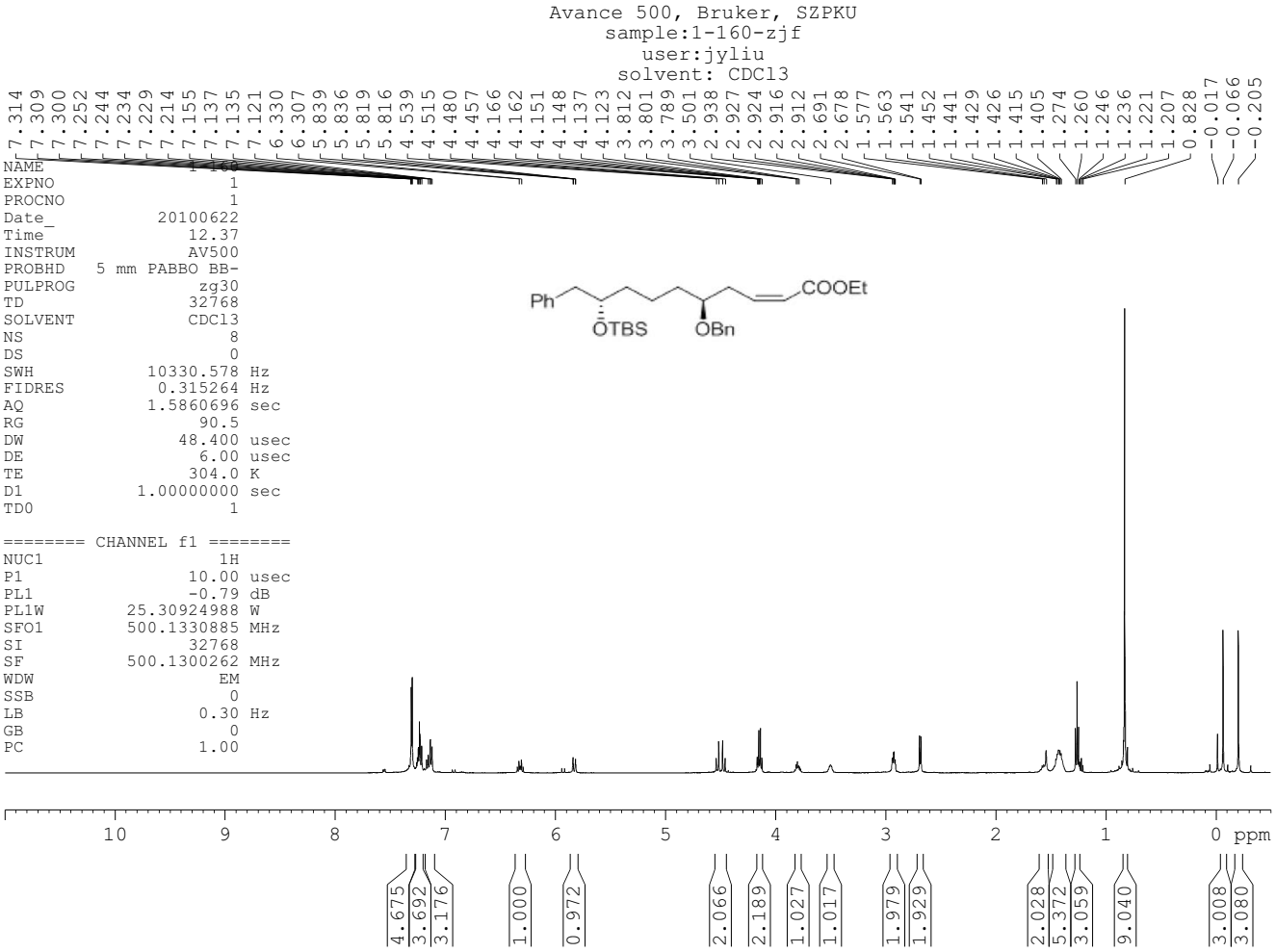

Avance 500, Bruker, SZPKU
sample: 1-147-zjf
spectrum:jyliu
solvent: CDCl3
NAME 1-147
EXPNO 2
PROCNO 1
Date_ 20100605
Time 12.41
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 271
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 4096
DW 15.900 usec
DE 6.00 usec
TE 303.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577943 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
159.3 139.4 130.1 129.7 129.2 128.0 125.9 113.9 73.7 72.9 71.2 68.8 55.2 43.9 37.6 37.0 36.4 25.9 21.2 18.0 -4.7 -4.9
Ph
OTBS
OH
OPMB
220 200 180 160 140 120 100 80 60 40 20 0 ppm

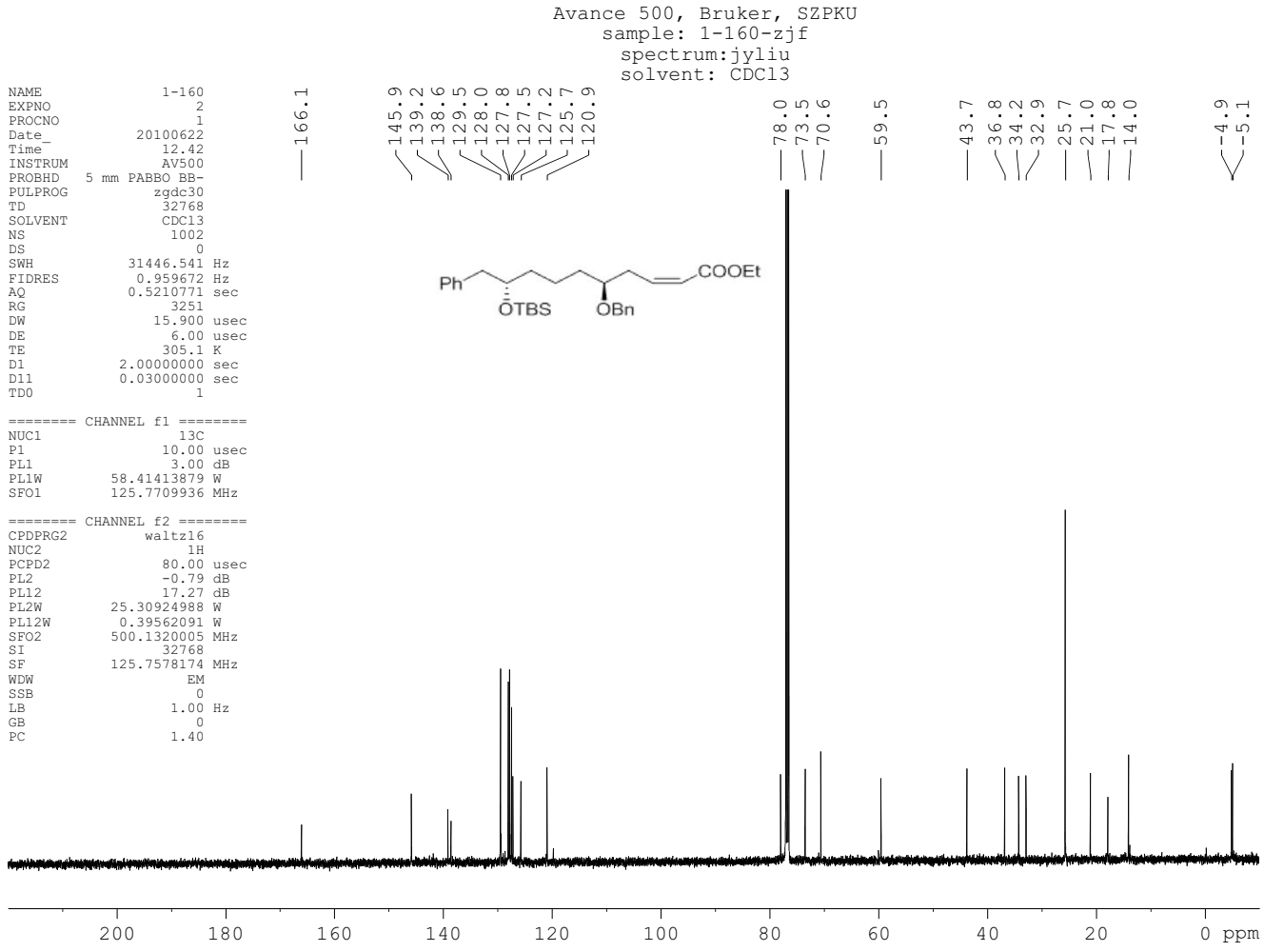

Avance 500, Bruker, SZPKU
sample:1-153-zjf
user:jyliu
solvent: CDCl3
7.328 7.313 7.299 7.295 7.282 7.272 7.263 7.248 7.234 7.231 7.189 7.174 7.159 7.157 7.143 6.876 6.871 6.853 4.506 4.483 4.450 4.427 4.408 4.407 4.378 3.838 3.826 3.817 3.780 3.578 3.569 3.555 3.541 3.527 3.520 3.515 3.508 2.713 2.700 1.834 1.828 1.821 1.815 1.809 1.805 1.796 1.791 1.558 1.537 1.525 1.492 1.474 1.461 1.437 1.432 0.851 -0.044 -0.186
NAME 1-153
EXPNO 1
PROCNO 1
Date_ 20100609
Time 5.59
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 64
DW 48.400 usec
DE 6.00 usec
TE 305.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300262 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OTBS
OBn
OPMB
10 9 8 7 6 5 4 3 2 1 0 ppm
10.602 2.909 2.204 2.009 2.013 1.000 3.407 3.299 2.078 2.092 7.054 9.415 3.067 3.015

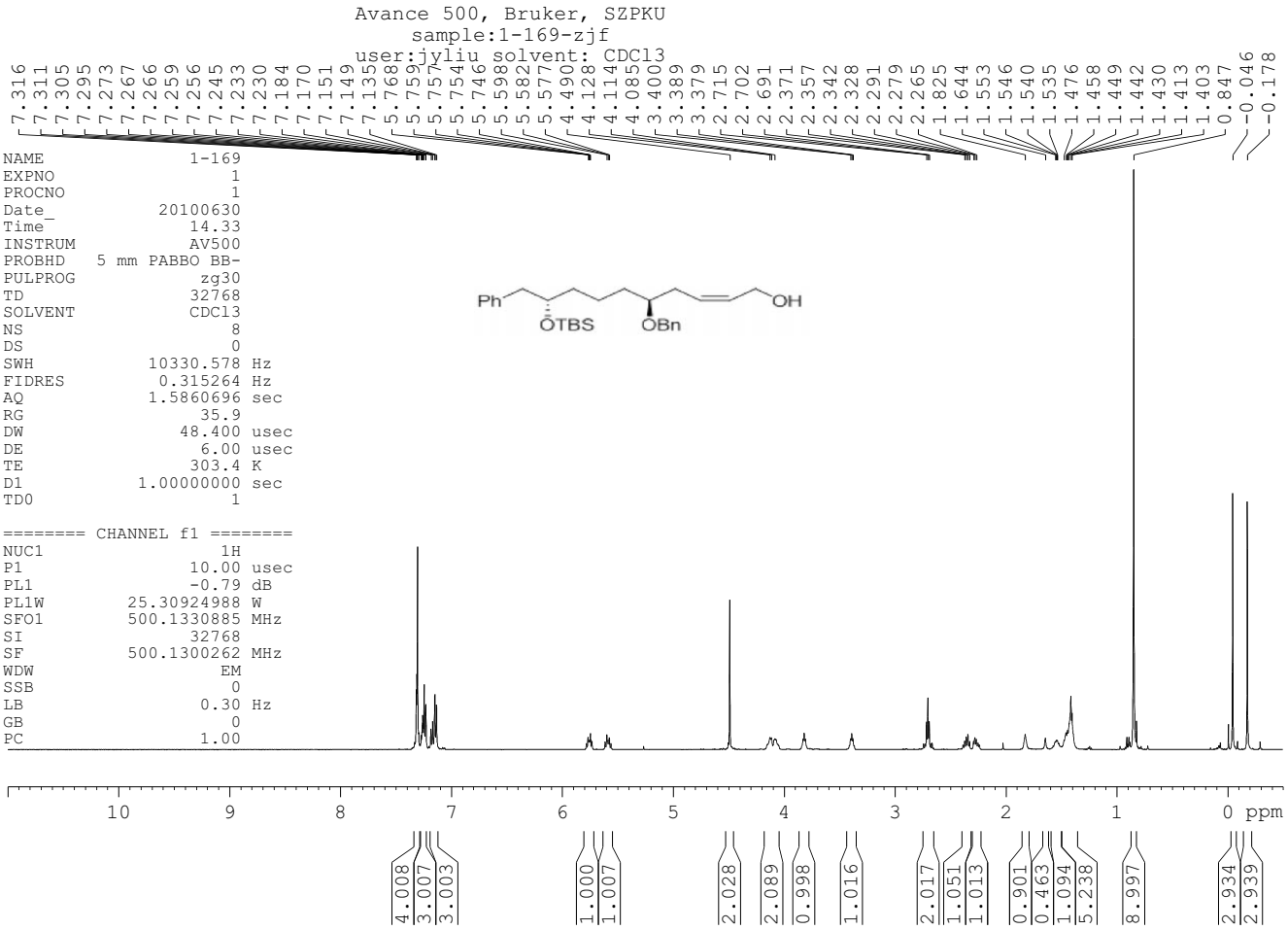

Avance 500, Bruker, SZPKU
sample: 1-153-zjf
spectrum:jyliu
solvent: CDCl3
159.2 139.4 139.1 130.8 129.7 129.2 128.3 128.1 127.7 127.4 126.0 113.8 76.3 73.8 72.6 71.2 66.8 55.3 44.0 37.2 34.6 34.5 25.9 21.0 18.1 -4.6 -4.8
NAME 1-153
EXPNO 2
PROCNO 1
Date_ 20100609
Time 6.05
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 403
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 4096
DW 15.900 usec
DE 6.00 usec
TE 306.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Ph
OTBS
OBn
OPMB
220 200 180 160 140 120 100 80 60 40 20 0 ppm

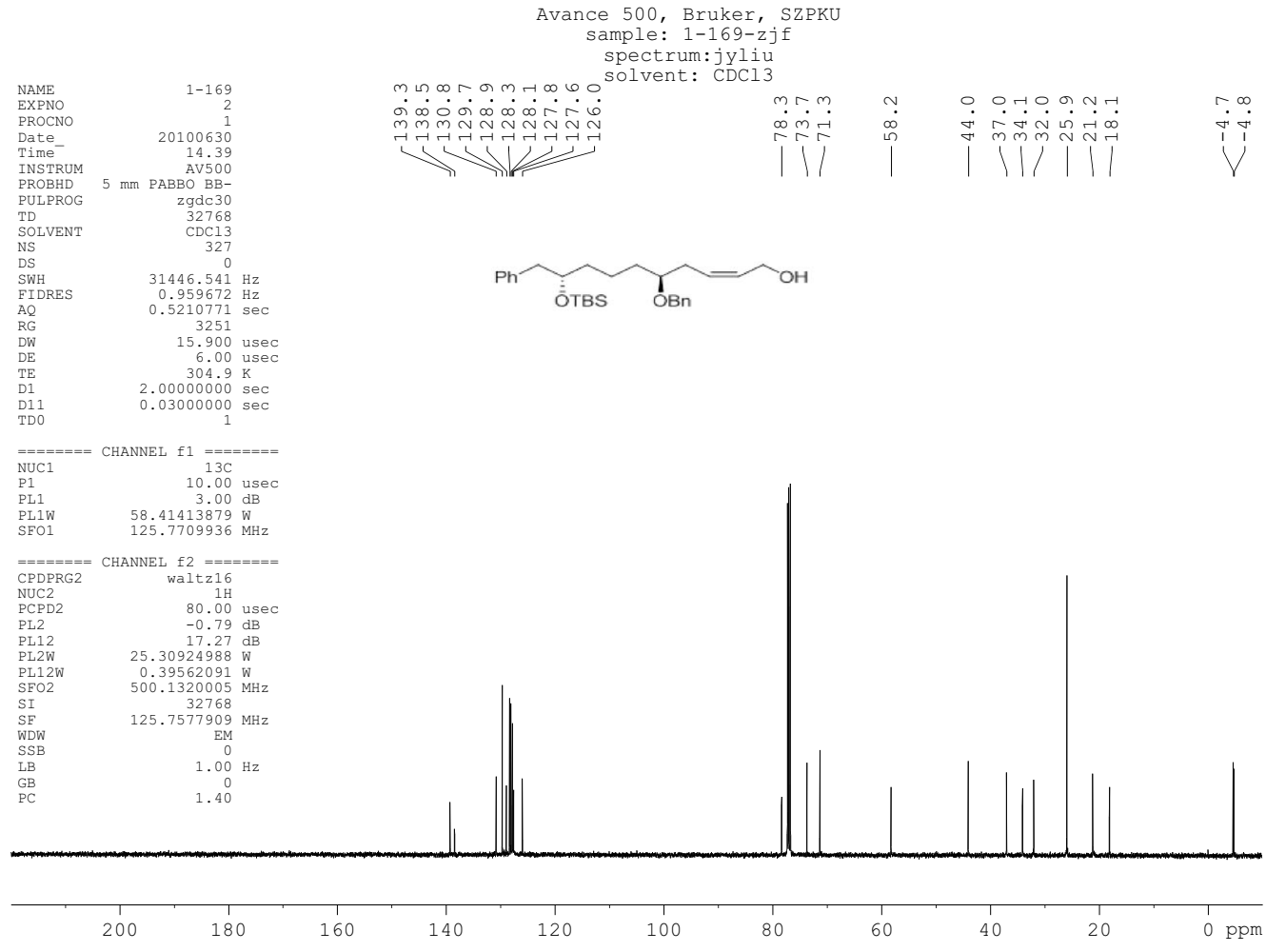

Avance 500, Bruker, SZPKU
sample:1-156-zjf
user:jyliu
solvent: CDCl3
NAME 1-156
EXPNO 1
PROCNO 1
Date_ 20100612
Time 11.09
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 64
DW 48.400 usec
DE 6.00 usec
TE 303.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300262 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OTBS
OBn
OH
ppm


Avance 500, Bruker, SZPKU
sample: 1-156-zjf
spectrum:jyliu
solvent: CDCl3
NAME 1-156
EXPNO 2
PROCNO 1
Date_ 20100612
Time 11.14
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 503
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 3251
DW 15.900 usec
DE 6.00 usec
TE 304.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577877 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Ph
OTBS
OBn
OH
ppm

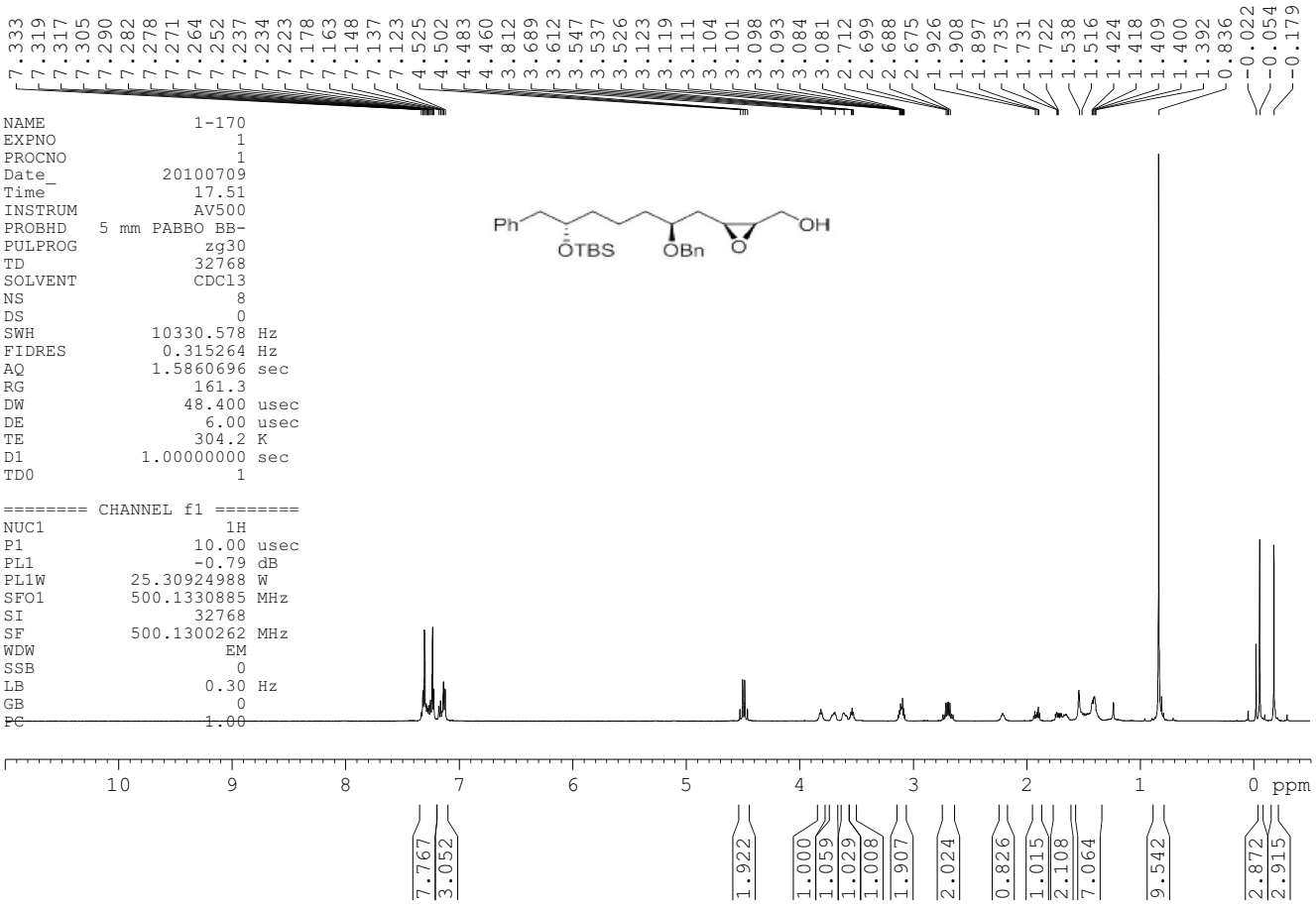

Avance 500, Bruker, SZPKU
sample:1-160-zjf
user:jyliu
solvent: CDCl3
7.314 7.309 7.300 7.252 7.244 7.234 7.229 7.214 7.155 7.137 7.135 7.121 6.330 6.307 5.839 5.836 5.819 5.816 4.539 4.515 4.480 4.457 4.166 4.162 4.151 4.148 4.137 4.123 3.812 3.801 3.789 3.501 2.938 2.927 2.924 2.916 2.912 2.691 2.678 1.577 1.563 1.541 1.452 1.441 1.429 1.426 1.415 1.405 1.274 1.260 1.246 1.236 1.221 1.207 0.828 -0.017 -0.066 -0.205
NAME 1-160
EXPNO 1
PROCNO 1
Date_ 20100622
Time 12.37
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 90.5
DW 48.400 usec
DE 6.00 usec
TE 304.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300262 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OTBS
OBn
COOEt
10 9 8 7 6 5 4 3 2 1 0 ppm
4.675 3.692 3.176 1.000 0.972 2.066 2.189 1.027 1.017 1.979 1.929 2.028 5.372 3.059 9.040 3.008 3.080


Avance 500, Bruker, SZPKU
sample: 1-160-zjf
spectrum:jyliu
solvent: CDCl3
166.1 145.9 139.2 138.6 129.5 128.0 127.8 127.5 127.2 125.7 120.9 78.0 73.5 70.6 59.5 43.7 36.8 34.2 32.9 25.7 21.0 17.8 14.0 -4.9 -5.1
NAME 1-160
EXPNO 2
PROCNO 1
Date_ 20100622
Time 12.42
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 1002
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 3251
DW 15.900 usec
DE 6.00 usec
TE 305.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7578174 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Ph
OTBS
OBn
COOEt
200 180 160 140 120 100 80 60 40 20 0 ppm

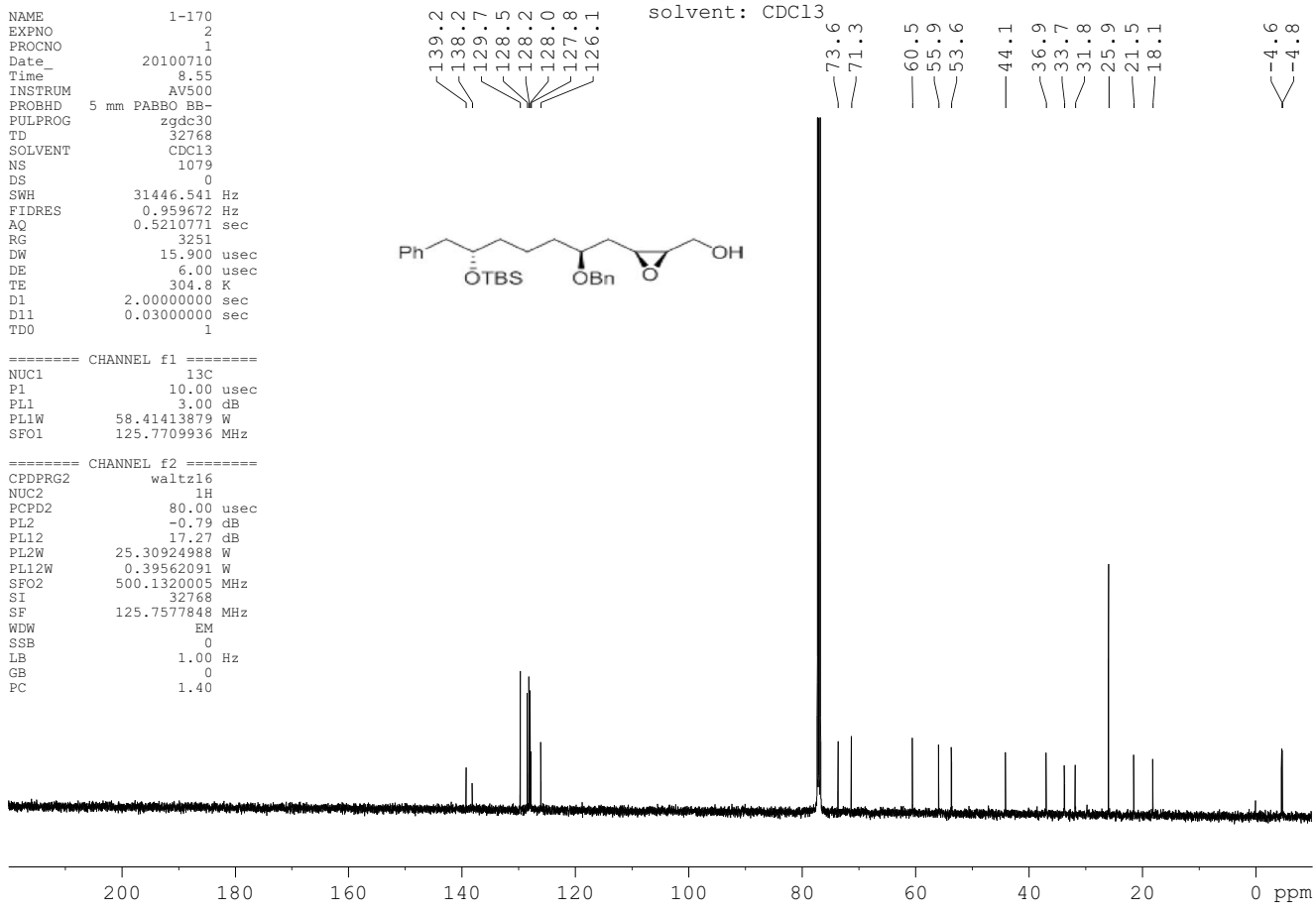

Avance 500, Bruker, SZPKU
sample:1-169-zjf
user:jyliu solvent: CDCl3
7.316 7.311 7.305 7.295 7.273 7.267 7.266 7.259 7.256 7.245 7.233 7.230 7.184 7.170 7.151 7.149 7.135 5.768 5.759 5.757 5.754 5.746 5.598 5.582 5.577 4.490 4.128 4.114 4.085 3.400 3.389 3.379 2.715 2.702 2.691 2.371 2.357 2.342 2.328 2.291 2.279 2.265 1.825 1.644 1.553 1.546 1.540 1.535 1.476 1.458 1.449 1.442 1.430 1.413 1.403 0.847 -0.046 -0.178
NAME 1-169
EXPNO 1
PROCNO 1
Date_ 20100630
Time 14.33
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 35.9
DW 48.400 usec
DE 6.00 usec
TE 303.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300262 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Ph
OTBS
OBn
OH
10 9 8 7 6 5 4 3 2 1 0 ppm
4.008 3.007 3.003 1.000 1.007 2.028 2.089 0.998 1.016 2.017 1.051 1.013 0.901 0.463 1.094 5.238 8.997 2.934 2.939

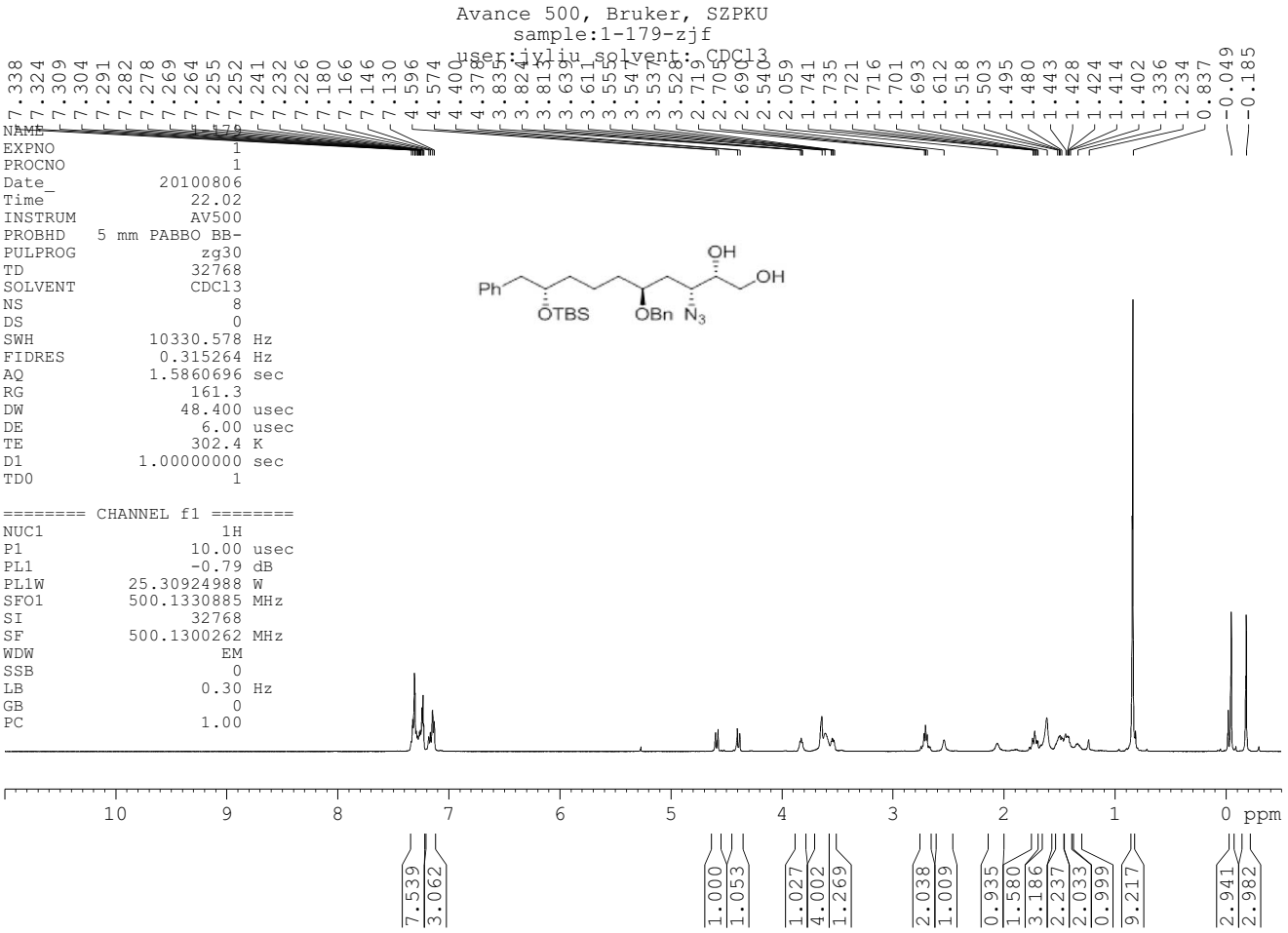

Avance 500, Bruker, SZPKU
sample: 1-169-zjf
spectrum:jyliu
solvent: CDCl3
139.3 138.5 130.8 129.7 128.9 128.3 128.1 127.8 127.6 126.0 78.3 73.7 71.3 58.2 44.0 37.0 34.1 32.0 25.9 21.2 18.1 -4.7 -4.8
NAME 1-169
EXPNO 2
PROCNO 1
Date_ 20100630
Time 14.39
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 327
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 3251
DW 15.900 usec
DE 6.00 usec
TE 304.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577909 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Ph
OTBS
OBn
OH
200 180 160 140 120 100 80 60 40 20 0 ppm

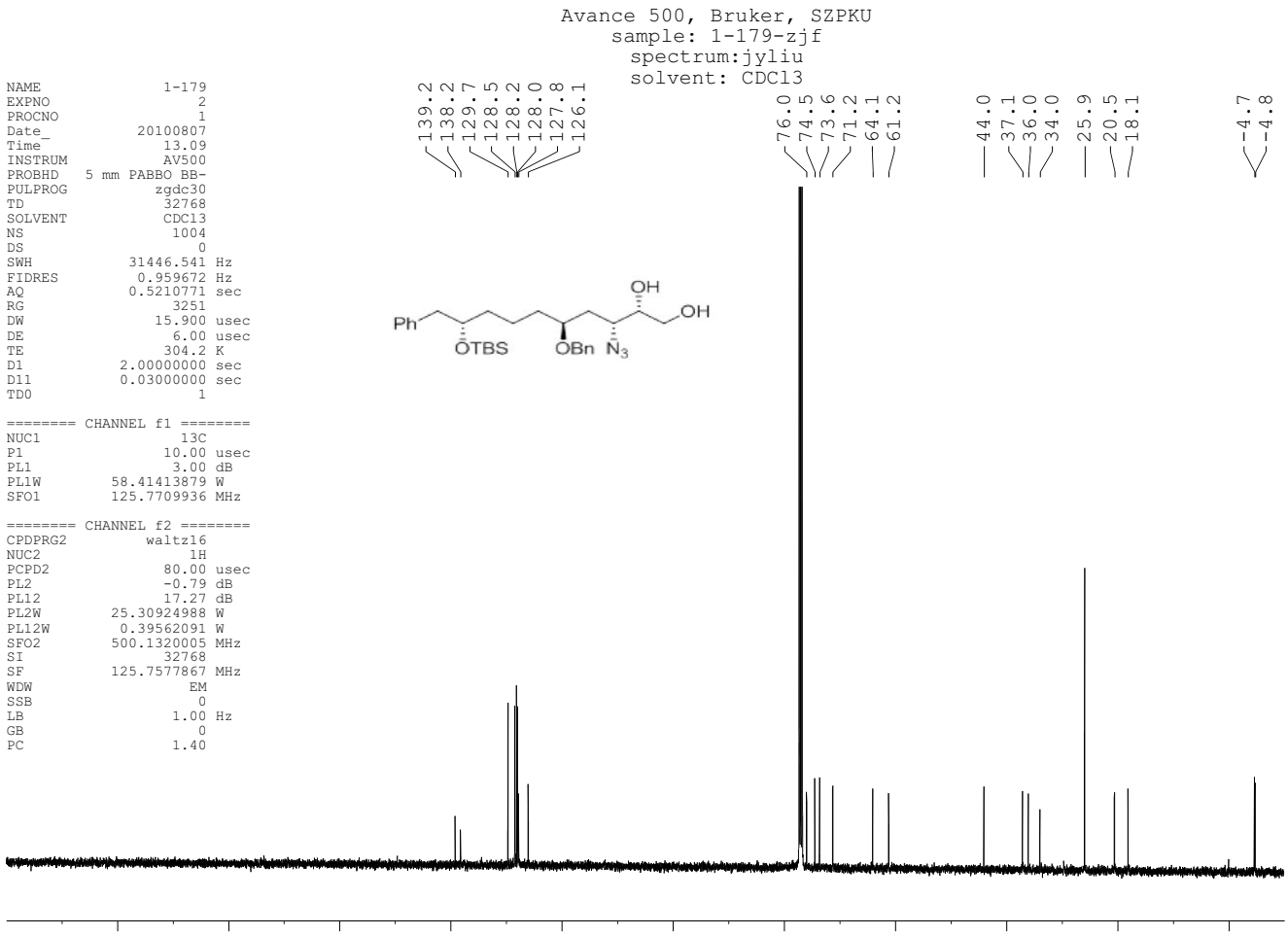
Avance 500, Bruker, SZPKU
sample:1-170-zjf
user:jyliu solvent: CDCl3



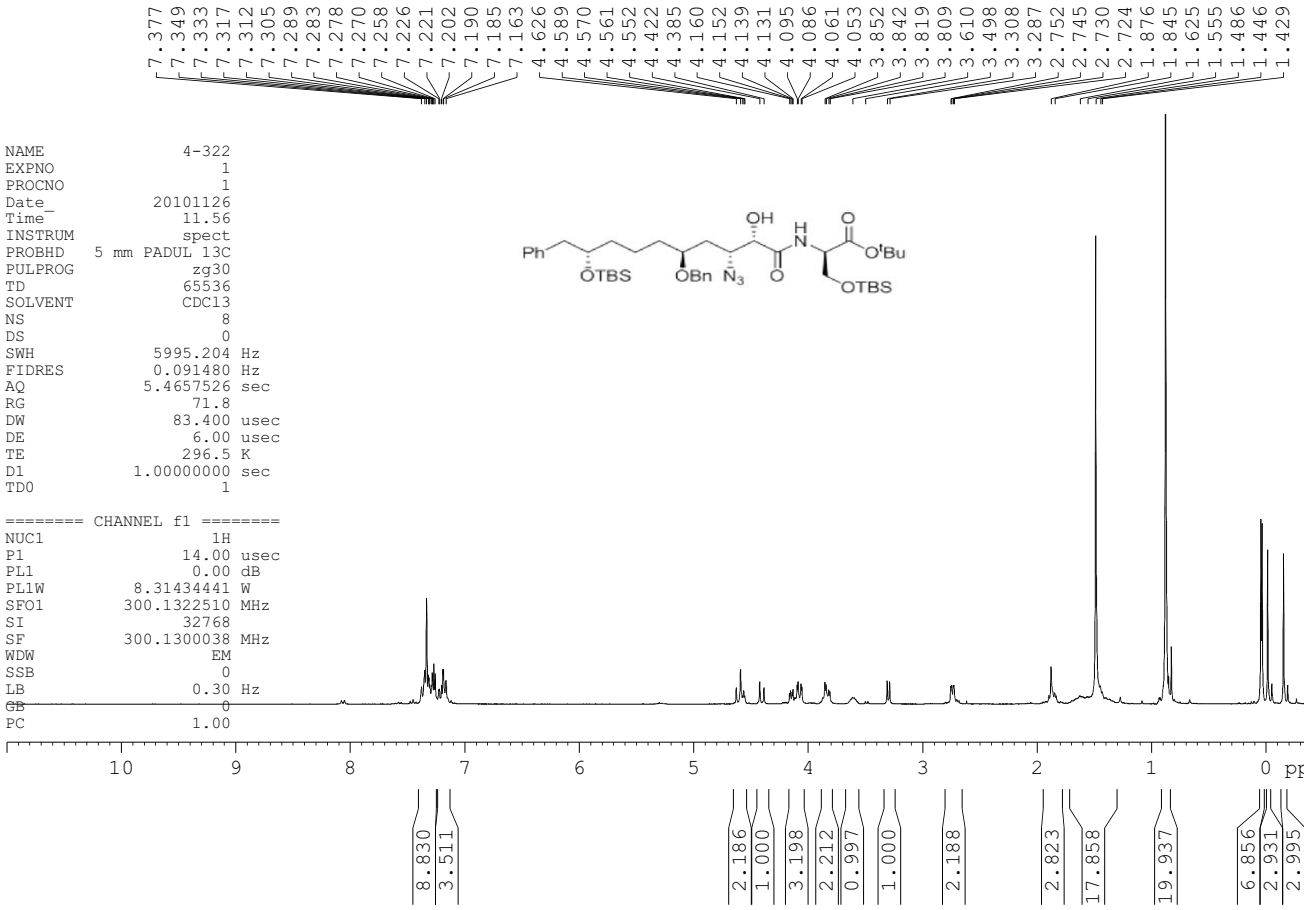
Avance 500, Bruker, SZPKU
sample: 1-170-zjf
spectrum:jyliu
solvent: CDCl3



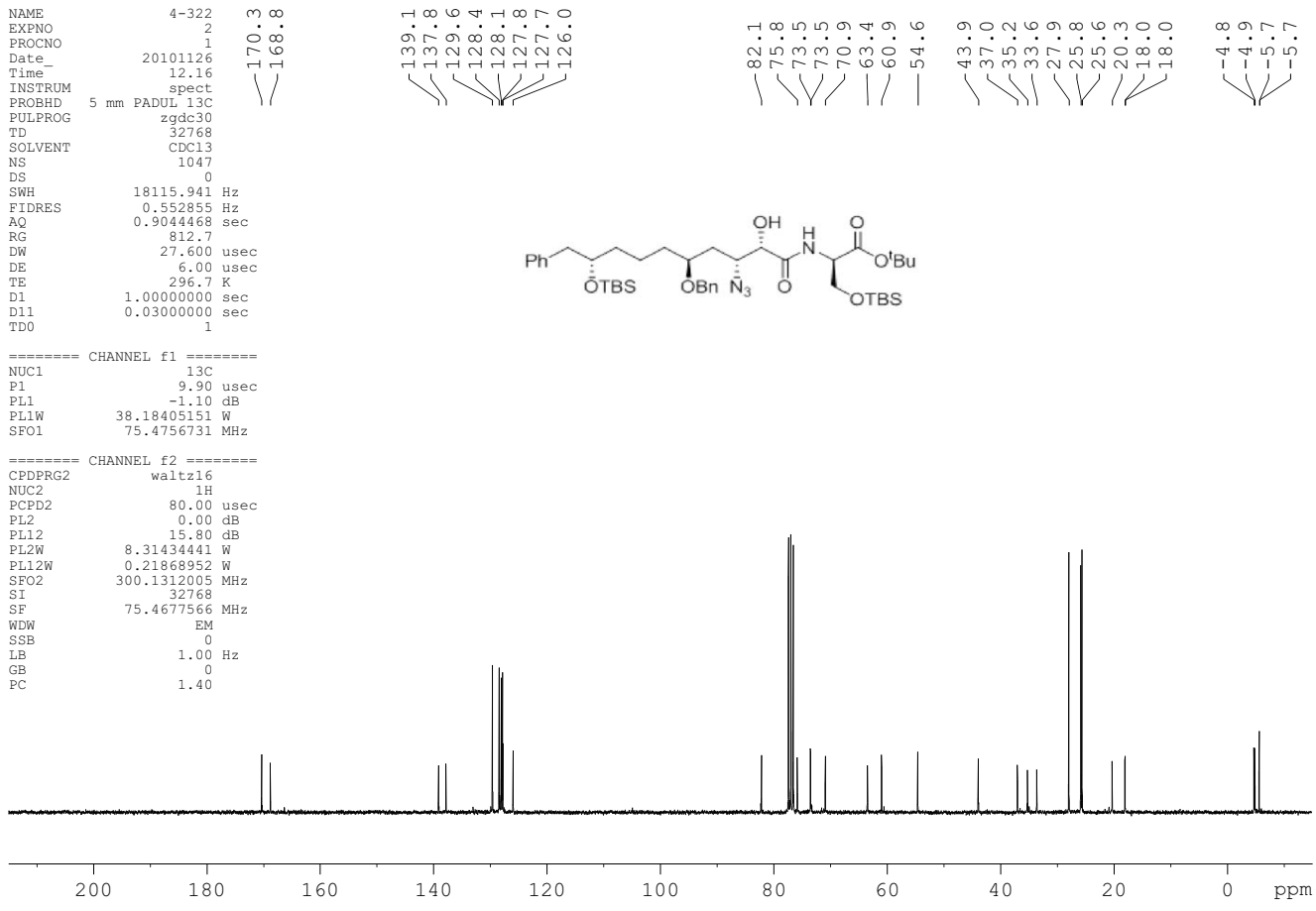

Avance 500, Bruker, SZPKU
sample:1-179-zjf
user:jyliu solvent: CDCl3
NAME 1-179
EXPNO 1
PROCNO 1
Date_ 20100806
Time 22.02
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 161.3
DW 48.400 usec
DE 6.00 usec
TE 302.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300262 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
OH
Ph
OTBS
OBn
N3
10 9 8 7 6 5 4 3 2 1 0 ppm


Avance 500, Bruker, SZPKU
sample: 1-179-zjf
spectrum:jyliu
solvent: CDCl3
NAME 1-179
EXPNO 2
PROCNO 1
Date_ 20100807
Time 13.09
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT CDCl3
NS 1004
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 3251
DW 15.900 usec
DE 6.00 usec
TE 304.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577867 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OH
OH
Ph
OTBS
OBn
N3
200 180 160 140 120 100 80 60 40 20 0 ppm

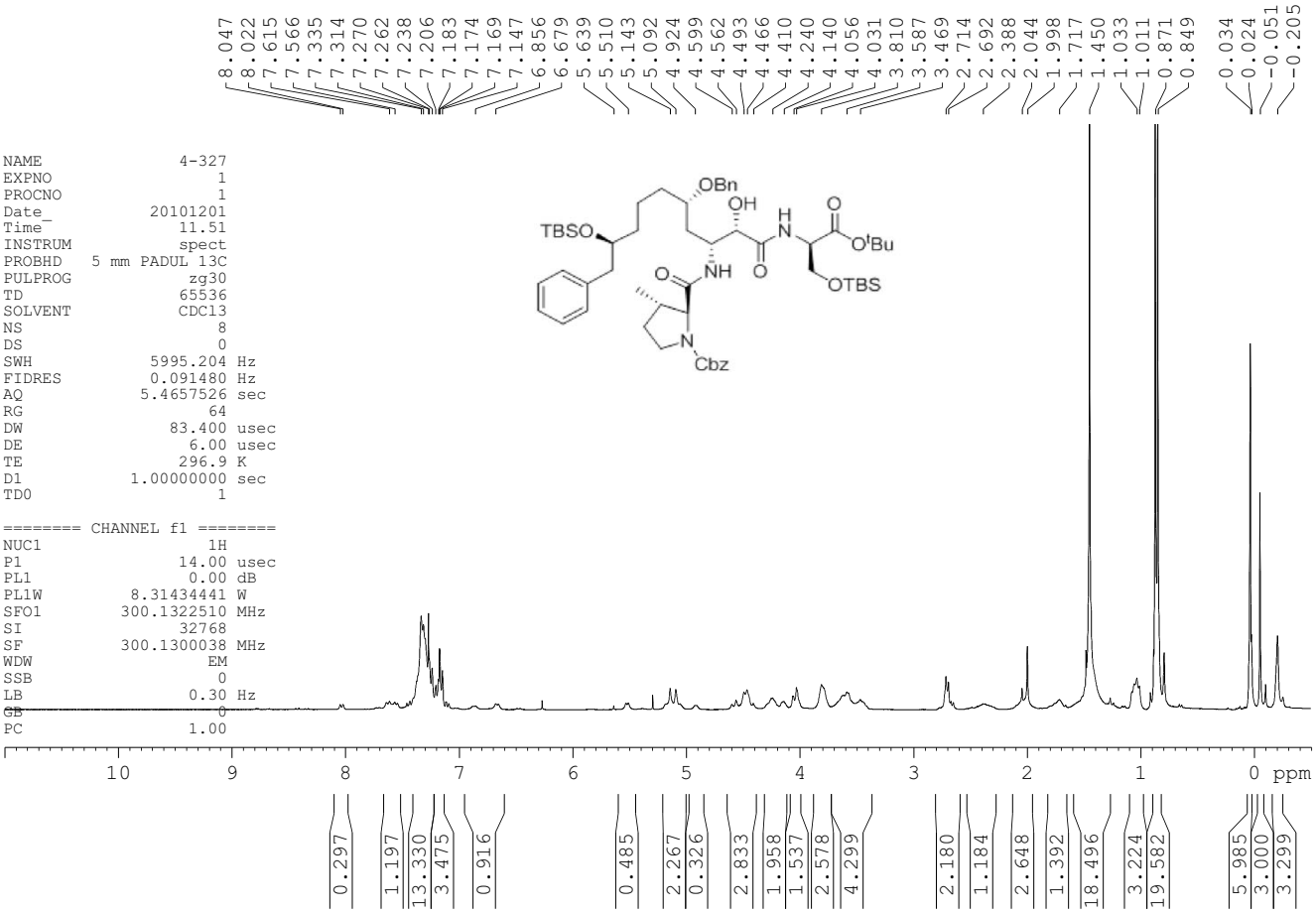
sample name:4-322
solvent:CDCl3
Bruker 300M



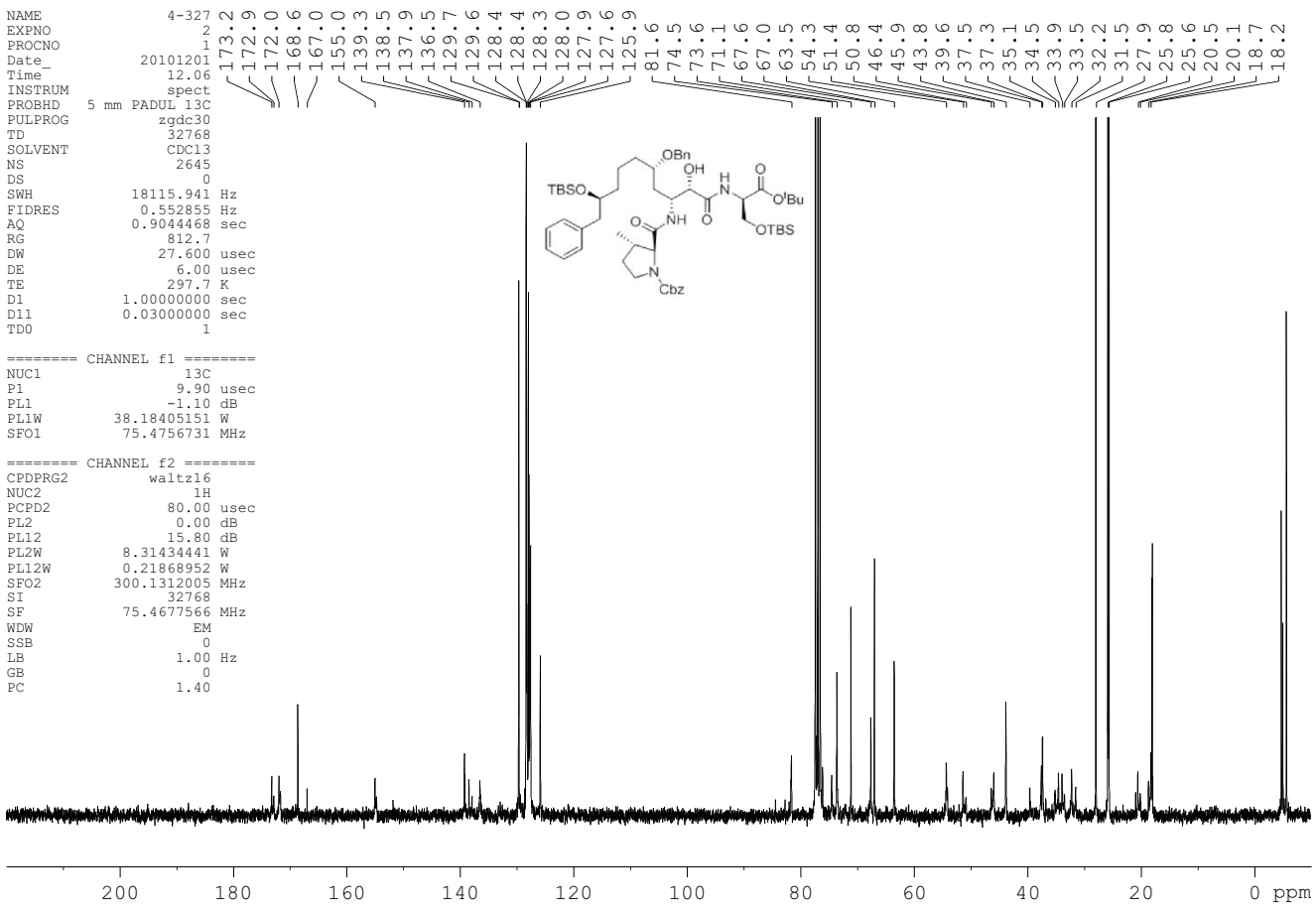
sample name: 4-322
solvent: CDCl3
Bruker 300M



sample name:4-327
solvent:CDCl3
Bruker 300M



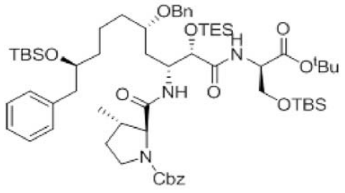
sample name: 4-327
solvent: CDCl3
Bruker 300M



sample name:4-328
solvent:CDCl3
Bruker 300M

7.528 7.409 7.345 7.318 7.295 7.270 7.251 7.228 7.199 7.175 7.162 7.157 7.135 6.911 6.880 5.299 5.277 5.235 5.144 5.012 4.513 4.312 4.293 4.099 4.075 3.862 3.845 3.777 3.745 3.633 2.684 2.661 2.640 2.616 2.496 2.474 2.456 2.434 2.105 2.054 1.936 1.898 1.839 1.445 1.398 1.141 0.922 0.893 0.875 0.835 0.682 0.654 0.627 0.602 0.040 -0.074 -0.229

```
NAME                4-328
EXPNO                   1
PROCNO                  1
Date_            20101202
Time                11.55
INSTRUM             spect
PROBHD    5 mm PADUL 13C
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              5995.204 Hz
FIDRES           0.091480 Hz
AQ              5.4657526 sec
RG                     64
DW                83.400 usec
DE                 6.00 usec
TE                296.6 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.00 usec
PL1                  0.00 dB
PL1W          8.31434441 W
SFO1         300.1322510 MHz
SI                  32768
SF           300.1300038 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



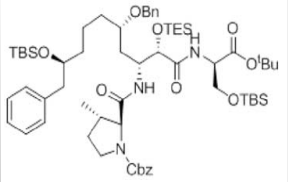
10 9 8 7 6 5 4 3 2 1 0 ppm

1.022 15.764 1.027 0.616 0.947 0.563 2.910 1.552 1.609 5.061 0.987 1.953 1.037 1.055 0.906 17.751 2.924 27.740 6.337 6.122 3.000 2.931

sample name: 4-328
solvent: CDCl3
Bruker 300M

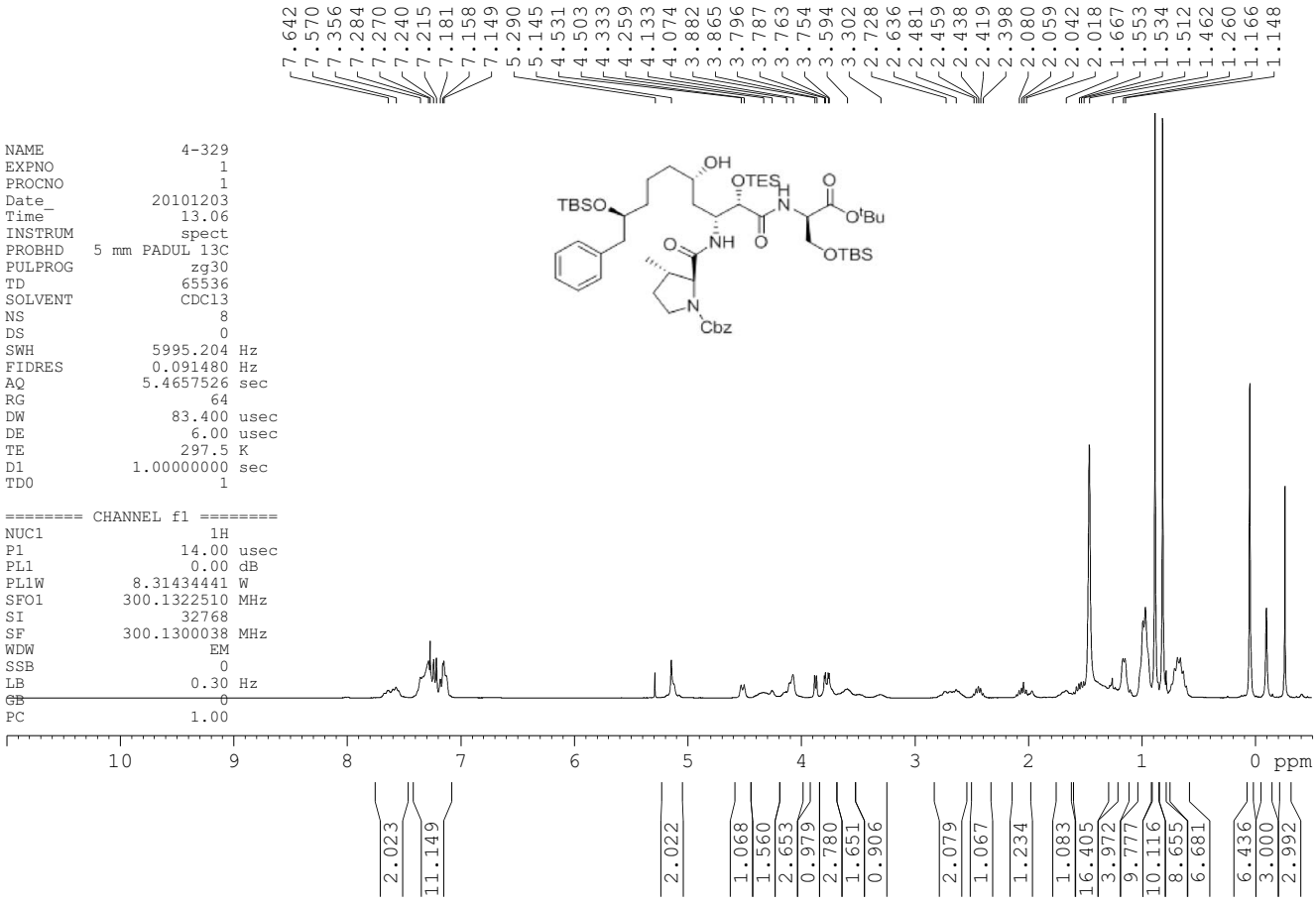
172.1 171.5 171.2 168.4 155.0 139.3 138.9 136.7 136.3 129.7 128.3 128.2 127.9 127.7 127.1 125.8 81.8 75.9 73.7 73.0 72.2 71.9 68.3 66.9 63.6 53.9 49.1 46.4 45.9 43.8 39.7 38.1 37.4 34.9 34.6 33.9 33.5 32.1 31.4 28.0 25.8 25.7 21.1 20.9 18.8 18.5 18.1

```
NAME                4-328
EXPNO                   2
PROCNO                  1
Date_            20101202
Time                12.01
INSTRUM             spect
PROBHD    5 mm PADUL 13C
PULPROG            zgdc30
TD                  32768
SOLVENT             CDCl3
NS                   2752
DS                      0
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ               0.9044468 sec
RG                  812.7
DW                27.600 usec
DE                 6.00 usec
TE                297.5 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.90 usec
PL1                 -1.10 dB
PL1W         38.18405151 W
SFO1         75.4756731 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                15.80 dB
PL2W          8.31434441 W
PL12W         0.21868952 W
SFO2         300.1312005 MHz
SI                  32768
SF           75.4677566 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

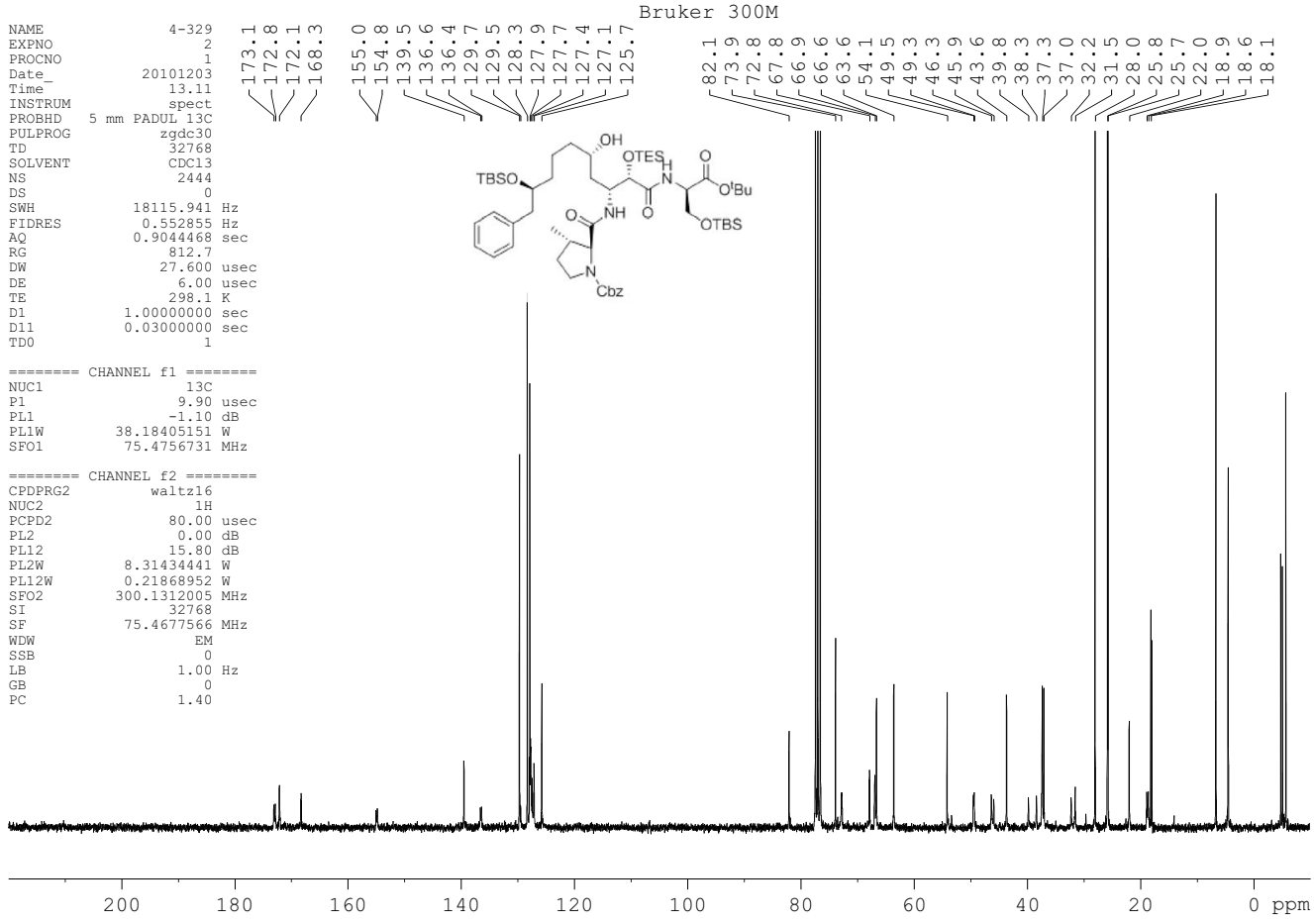


200 180 160 140 120 100 80 60 40 20 0 ppm

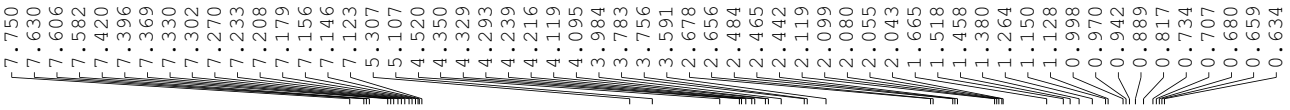
sample name:4-329
solvent:CDCl3
Bruker 300M



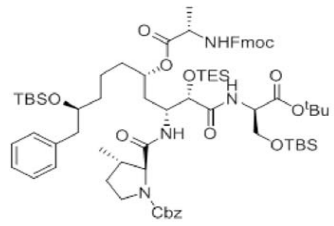
sample name: 4-329
solvent: CDCl3
Bruker 300M

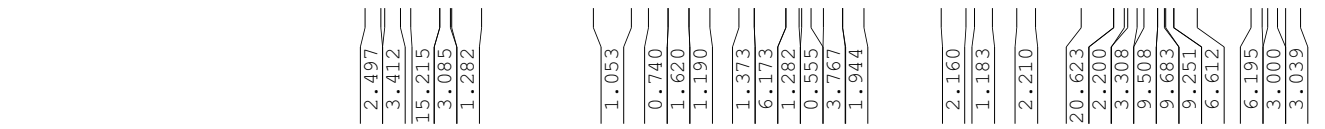


sample name:4-331-2
solvent:CDCl3
Bruker 300M

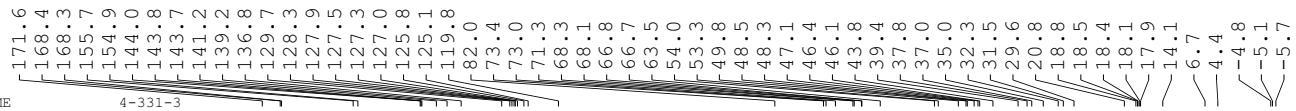



```
NAME              4-331-2
EXPNO                   1
PROCNO                  1
Date_            20101205
Time                 0.02
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              5995.204 Hz
FIDRES           0.091480 Hz
AQ               5.4657526 sec
RG                    256
DW                 83.400 usec
DE                  6.00 usec
TE                 296.0 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.00 usec
PL1                 0.00 dB
PL1W          8.31434441 W
SFO1         300.1322510 MHz
SI                  32768
SF           300.1300038 MHz
WDW                    EM
SSB                     0
LB                  0.30 Hz
GB                      0
PC                  1.00
```

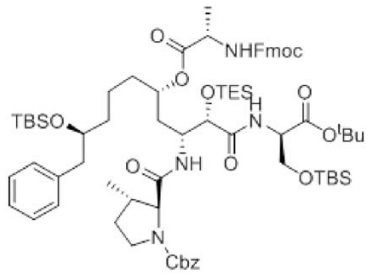




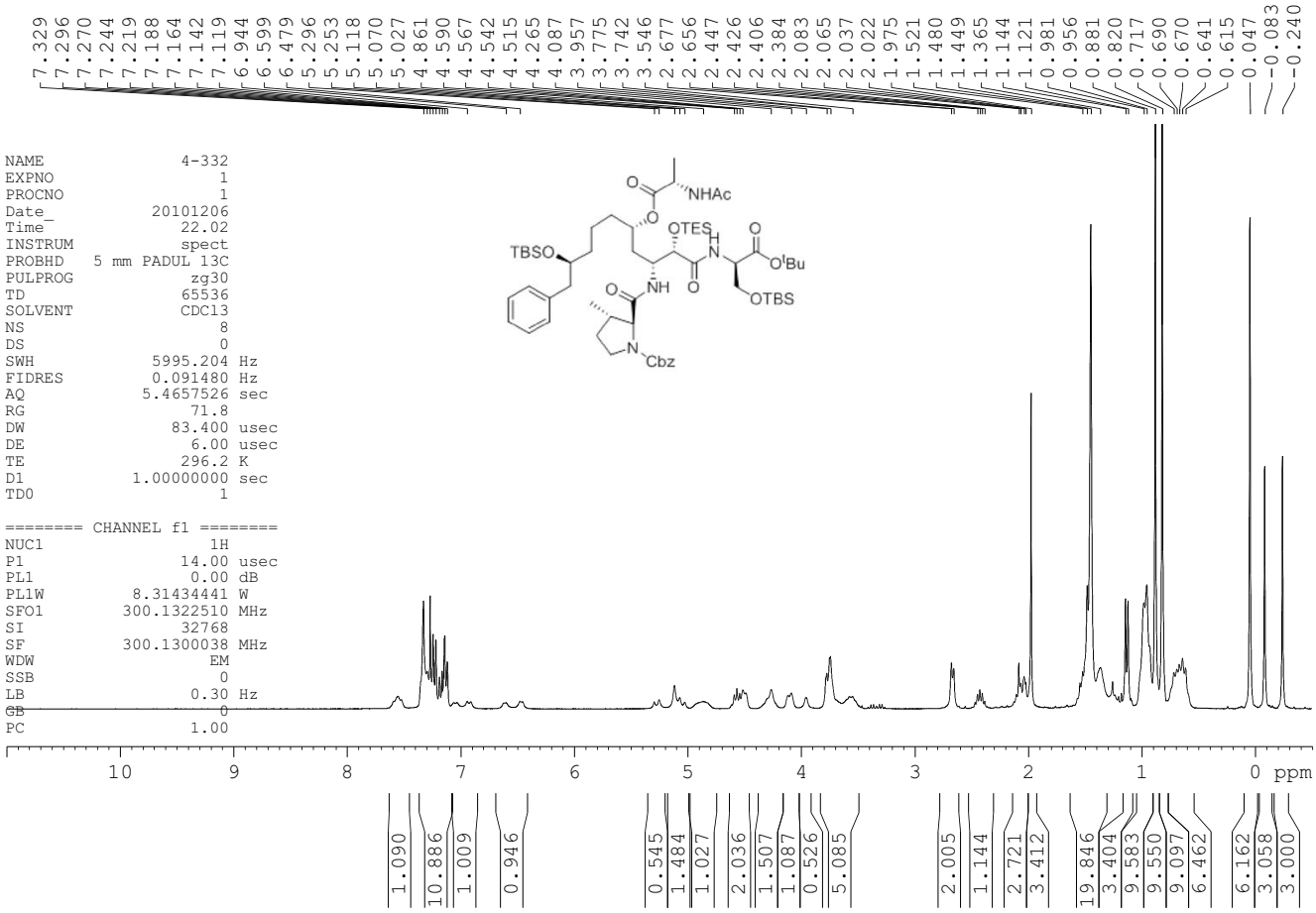
sample name:4-331-3
solvent: CDCl3
Bruker 300M



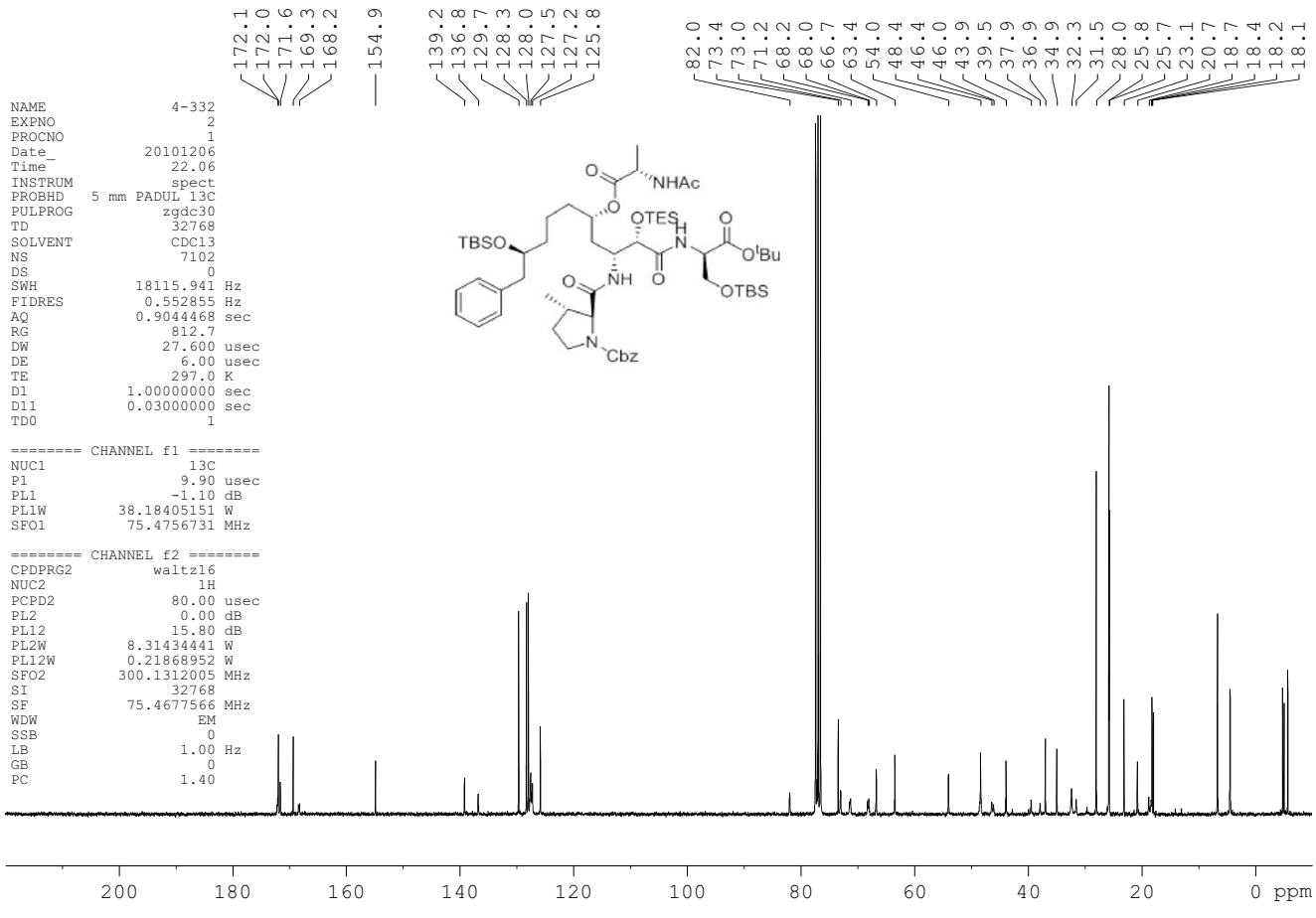

```
NAME              4-331-3
EXPNO                   2
PROCNO                  1
Date_            20101205
Time                 0.45
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG           zgdc30
TD                  32768
SOLVENT             CDCl3
NS                  14639
DS                      0
SWH             18115.941 Hz
FIDRES           0.552855 Hz
AQ               0.9044468 sec
RG                  812.7
DW                 27.600 usec
DE                  6.00 usec
TE                 296.1 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.90 usec
PL1                -1.10 dB
PL1W         38.18405151 W
SFO1          75.4756731 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               15.80 dB
PL2W          8.31434441 W
PL12W         0.21868952 W
SFO2         300.1312005 MHz
SI                  32768
SF            75.4677566 MHz
WDW                    EM
SSB                     0
LB                  1.00 Hz
GB                      0
PC                  1.40
```

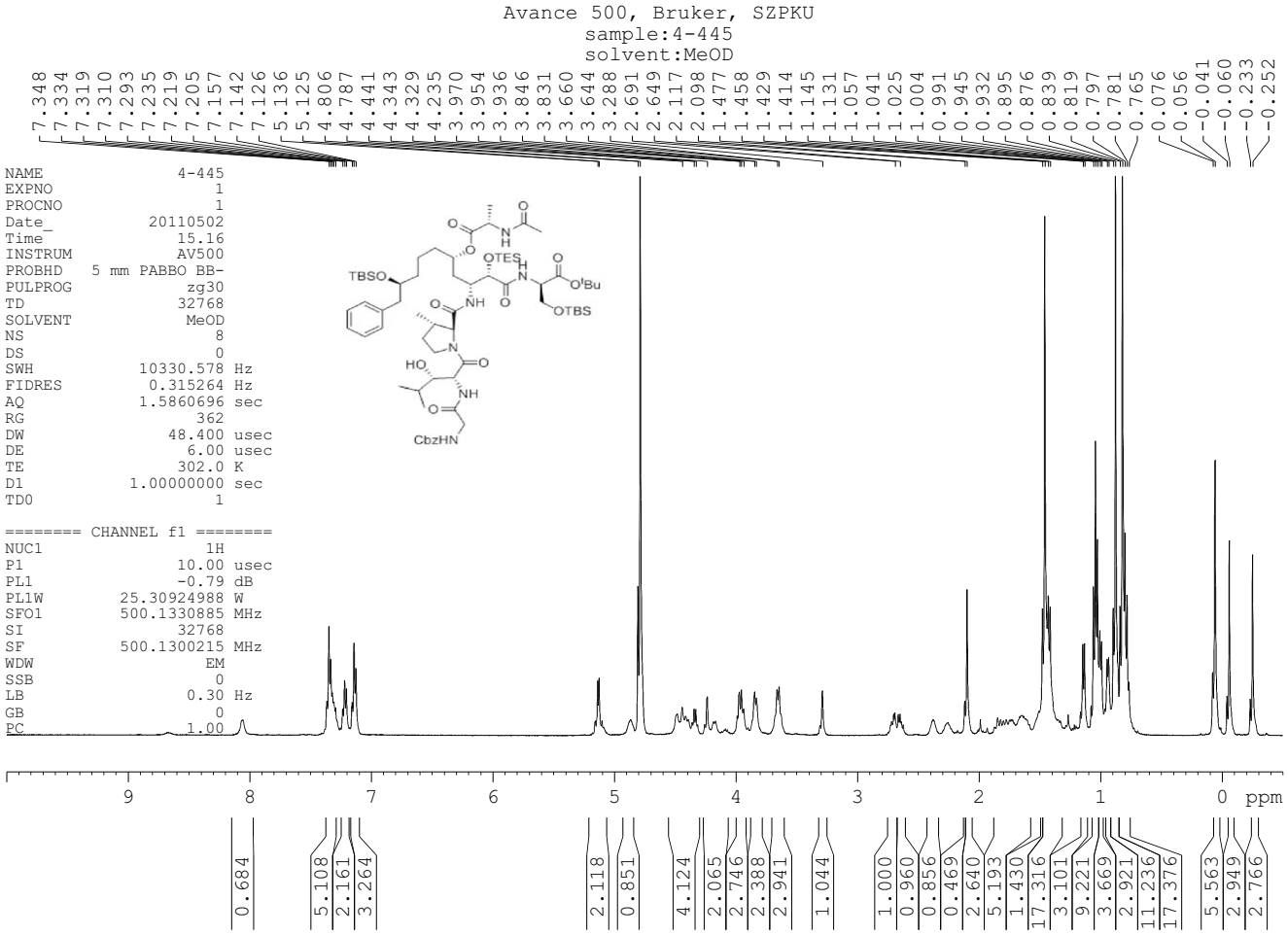


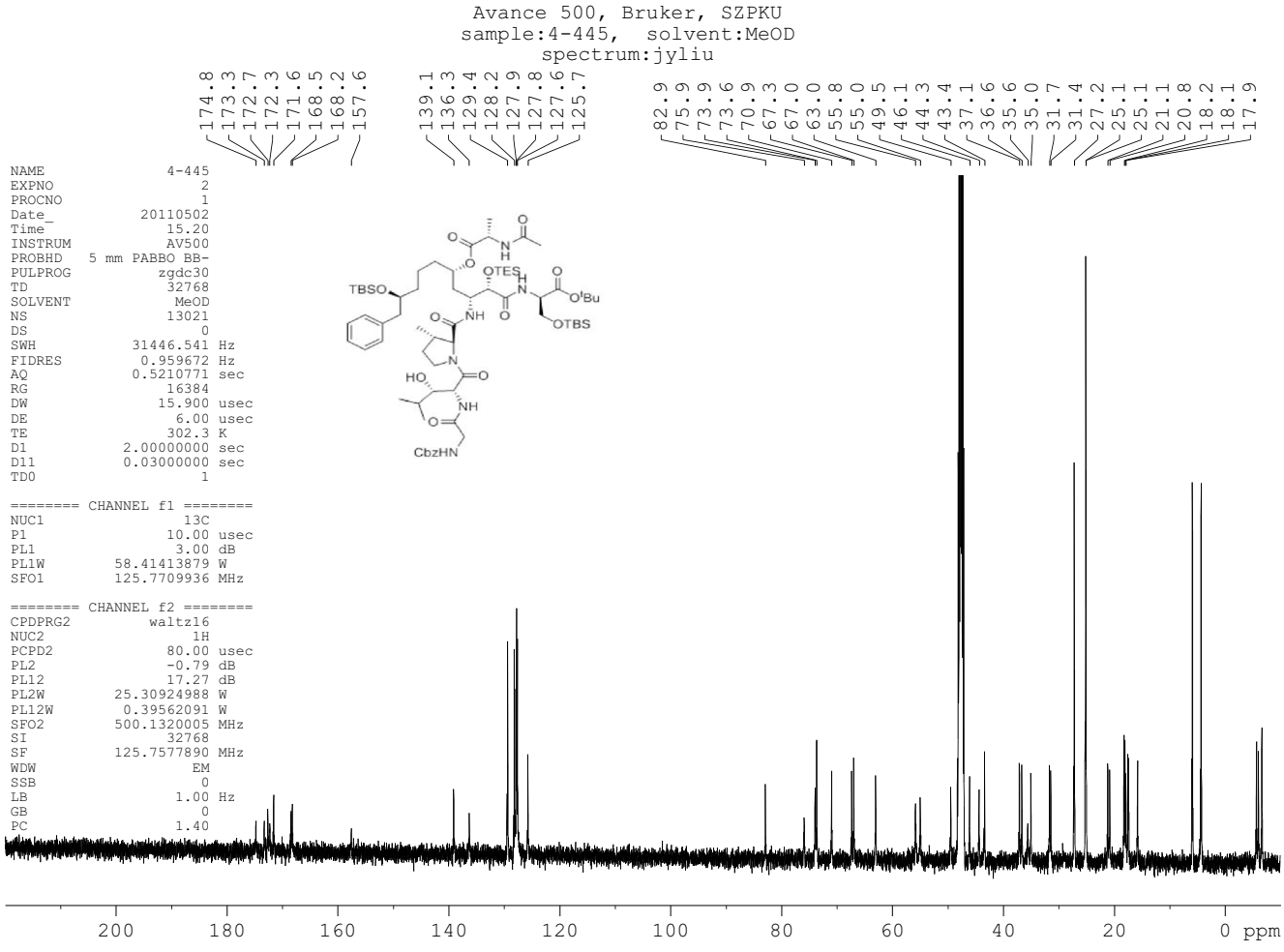
sample name:4-332
solvent:CDCl3
Bruker 300M

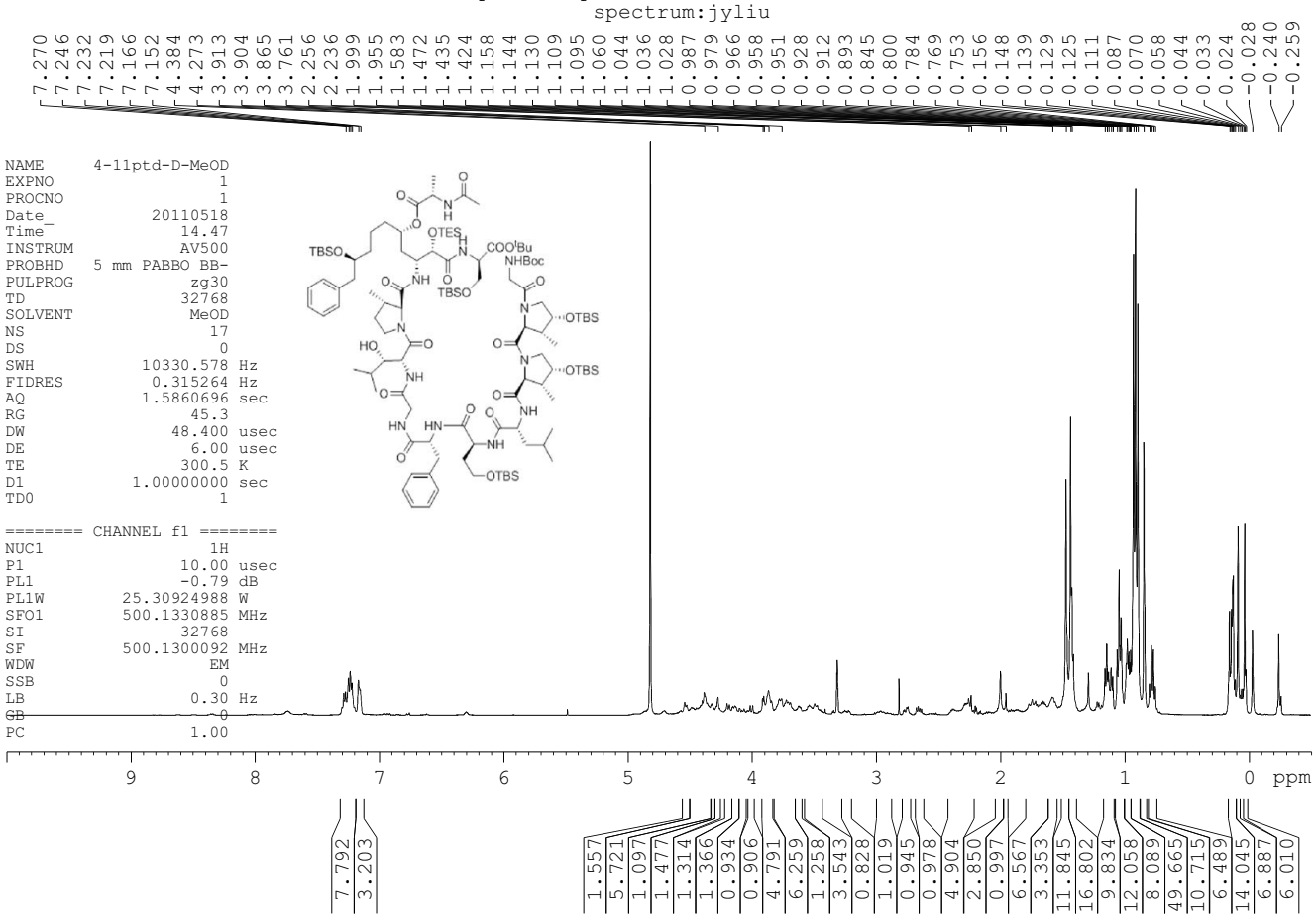


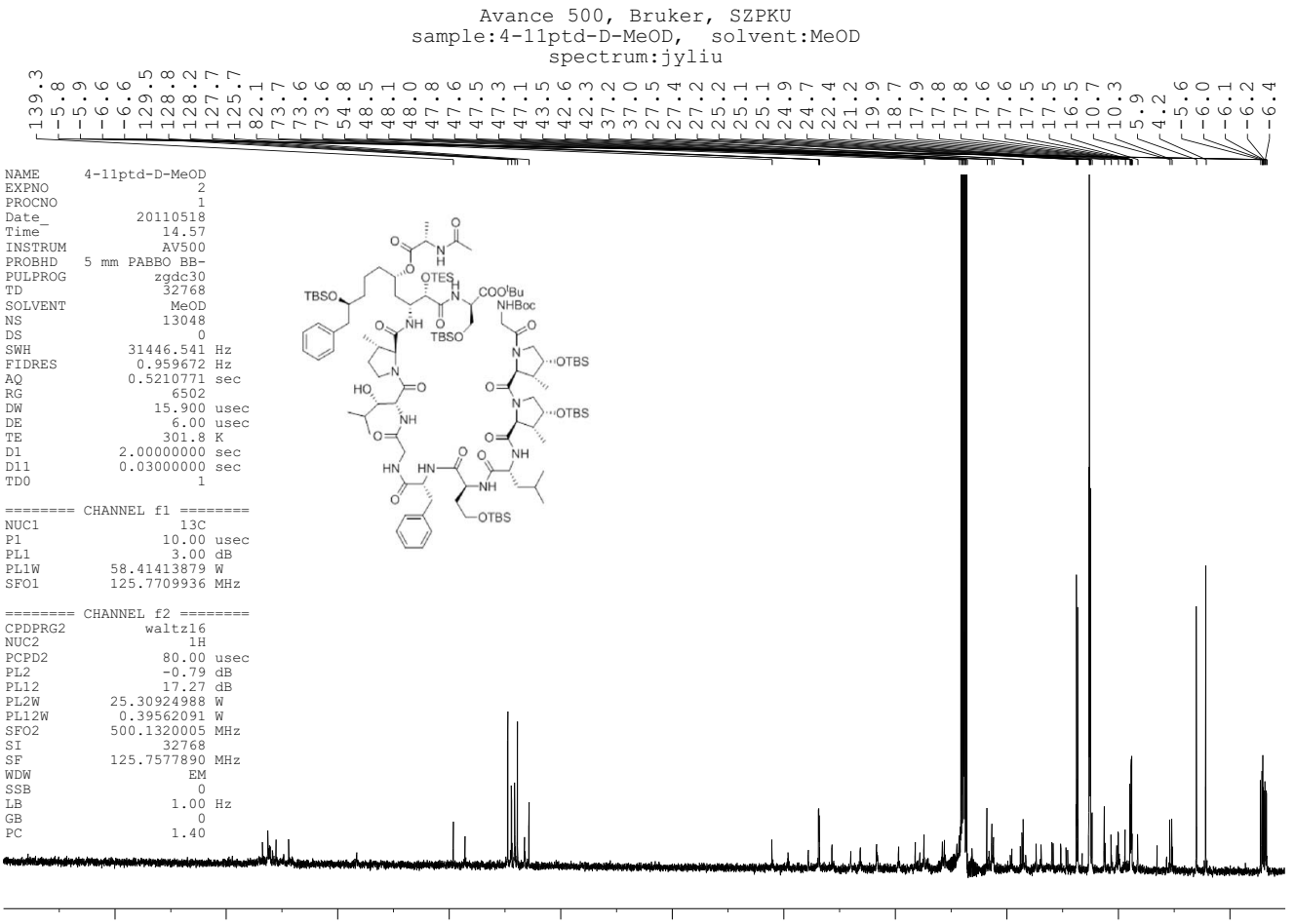
sample name:4-332
solvent: CDCl3
Bruker 300M

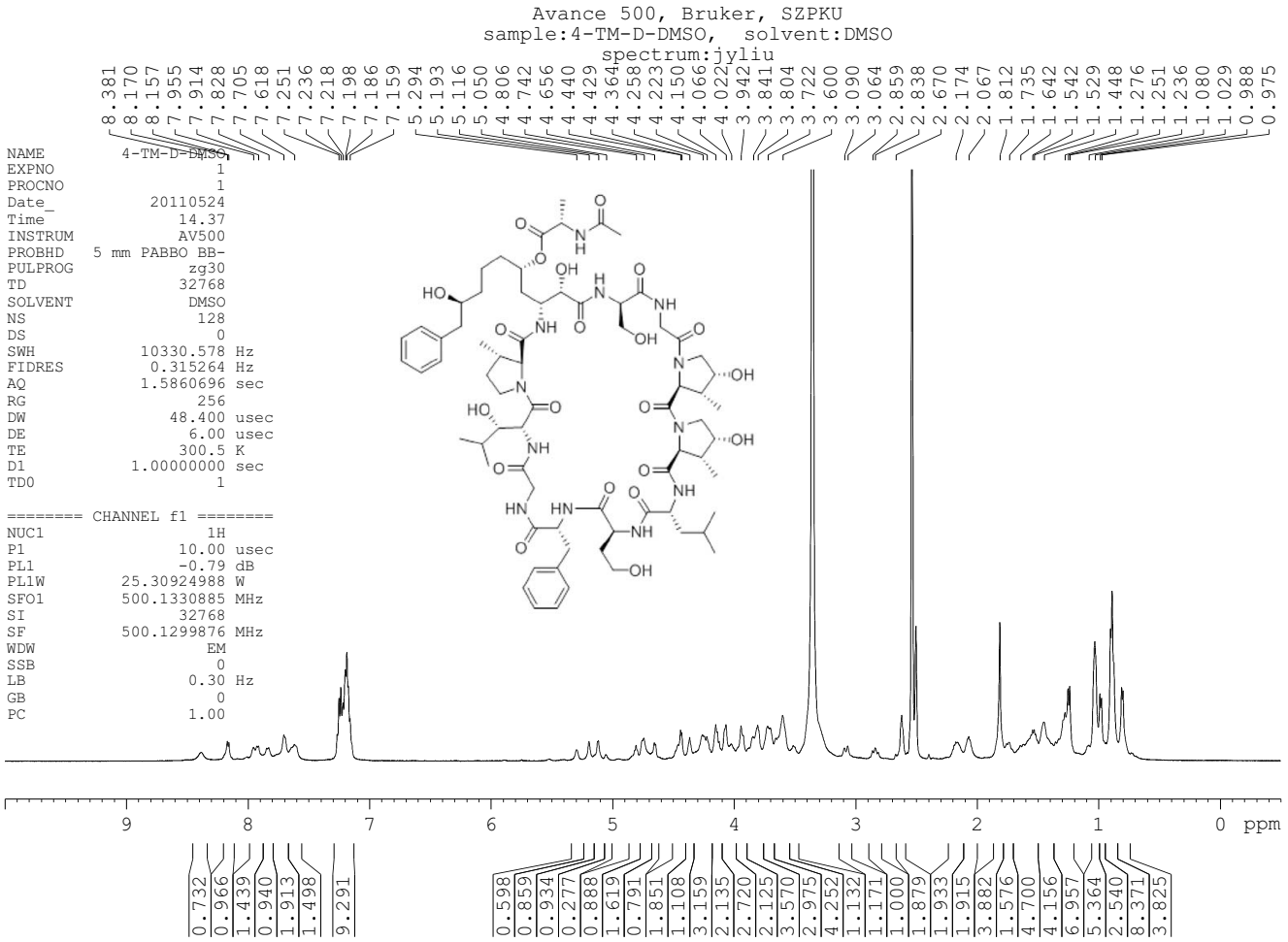


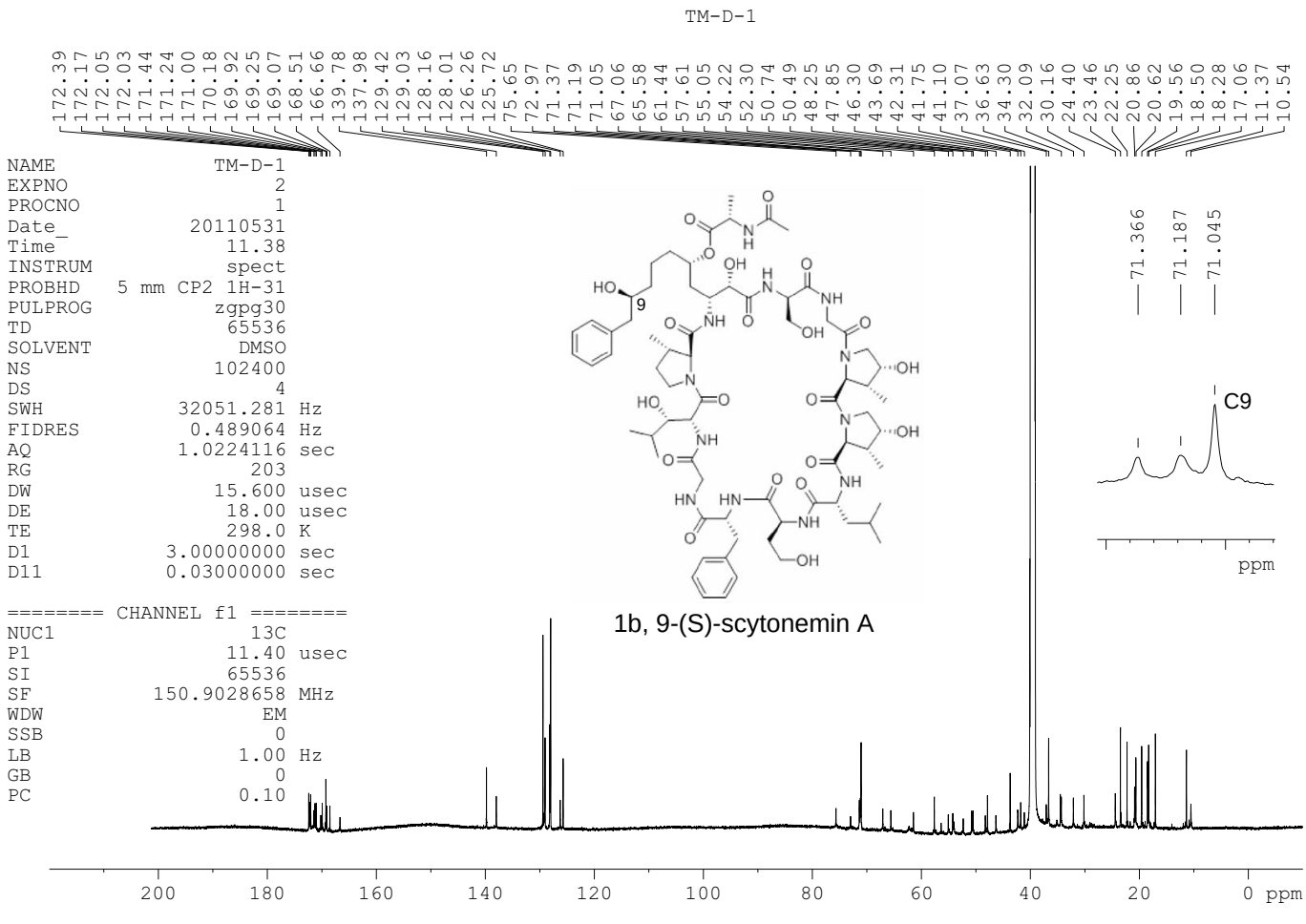

Avance 500, Bruker, SZPKU
sample:4-445
solvent:MeOD
NAME 4-445
EXPNO 1
PROCNO 1
Date_ 20110502
Time 15.16
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 362
DW 48.400 usec
DE 6.00 usec
TE 302.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300215 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

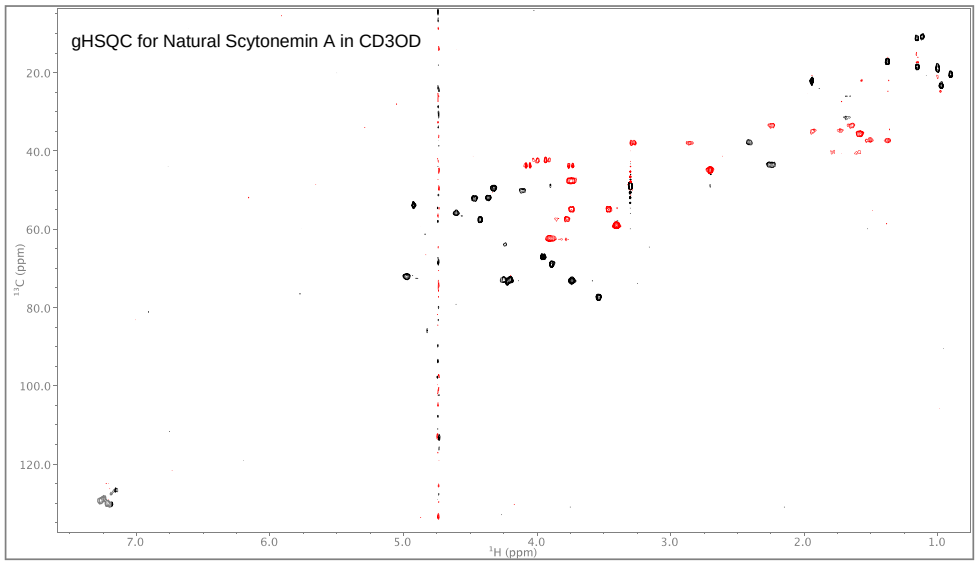

Avance 500, Bruker, SZPKU
sample:4-445, solvent:MeOD
spectrum:jyliu
NAME 4-445
EXPNO 2
PROCNO 1
Date_ 20110502
Time 15.20
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT MeOD
NS 13021
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 16384
DW 15.900 usec
DE 6.00 usec
TE 302.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
ppm

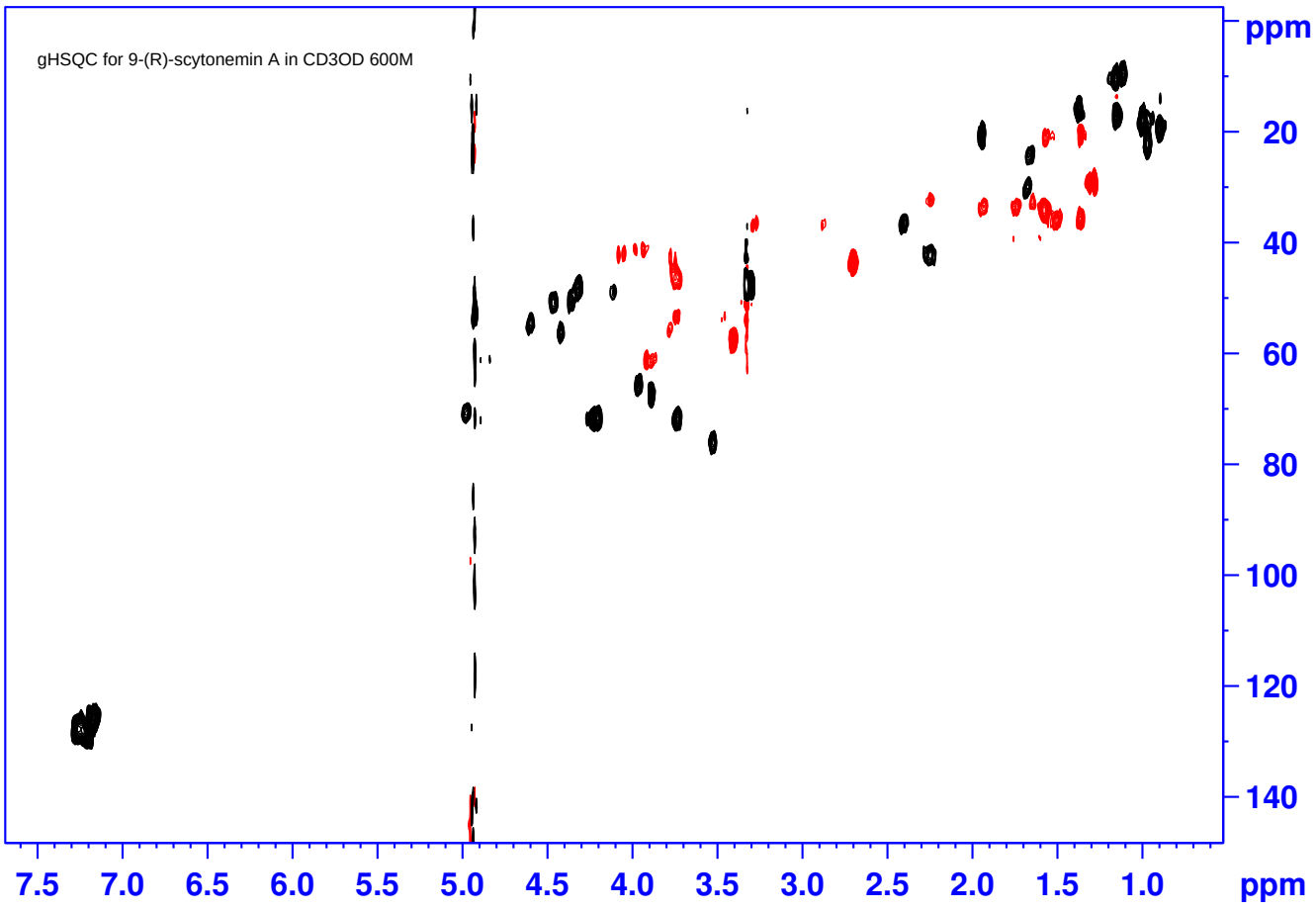

Avance 500, Bruker, SZPKU
sample:4-11ptd-D-3-MeOD, solvent:MeOD
spectrum:jyliu
NAME 4-11ptd-D-MeOD
EXPNO 1
PROCNO 1
Date_ 20110518
Time 14.47
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 17
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 45.3
DW 48.400 usec
DE 6.00 usec
TE 300.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300092 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm

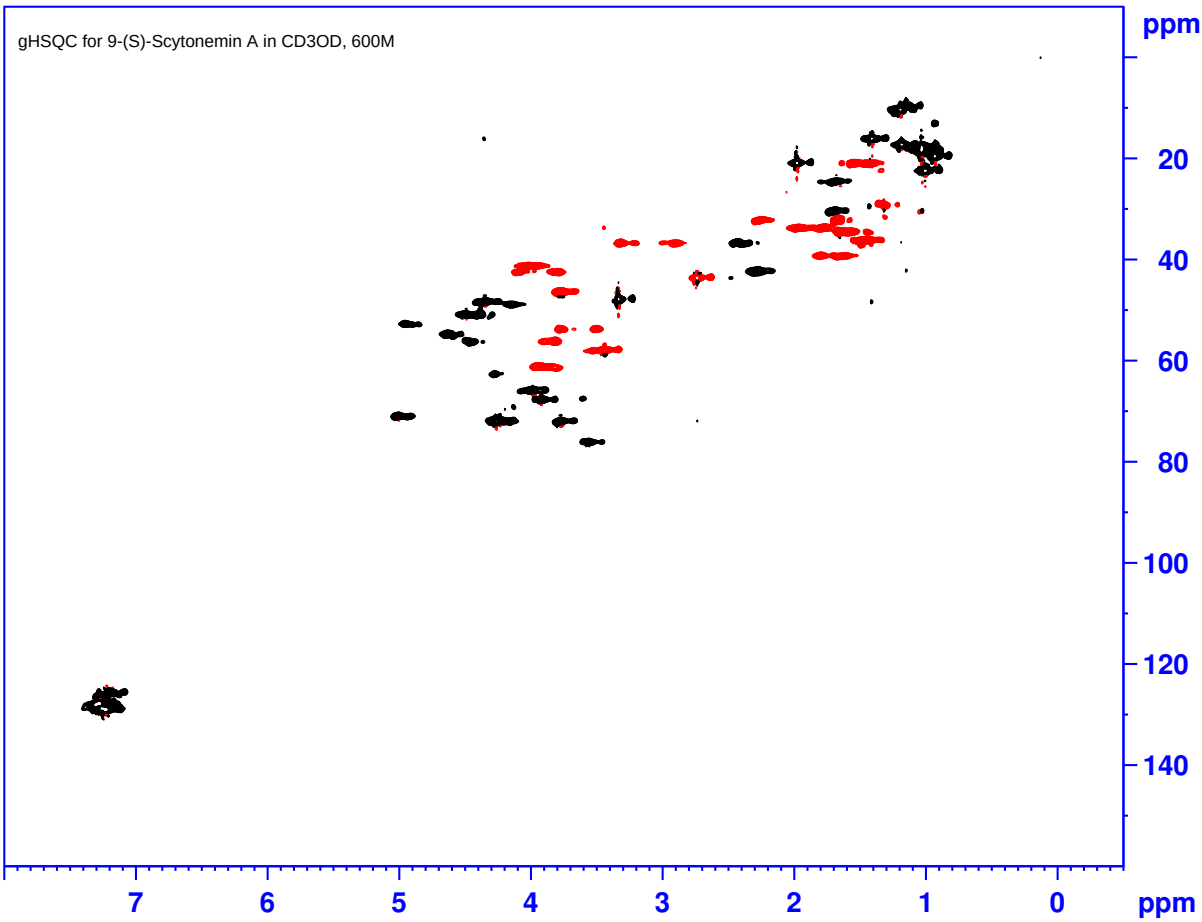

Avance 500, Bruker, SZPKU
sample:4-11ptd-D-MeOD, solvent:MeOD
spectrum:jyliu
NAME 4-11ptd-D-MeOD
EXPNO 2
PROCNO 1
Date_ 20110518
Time 14.57
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 32768
SOLVENT MeOD
NS 13048
DS 0
SWH 31446.541 Hz
FIDRES 0.959672 Hz
AQ 0.5210771 sec
RG 6502
DW 15.900 usec
DE 6.00 usec
TE 301.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PL1 3.00 dB
PL1W 58.41413879 W
SFO1 125.7709936 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -0.79 dB
PL12 17.27 dB
PL2W 25.30924988 W
PL12W 0.39562091 W
SFO2 500.1320005 MHz
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
ppm

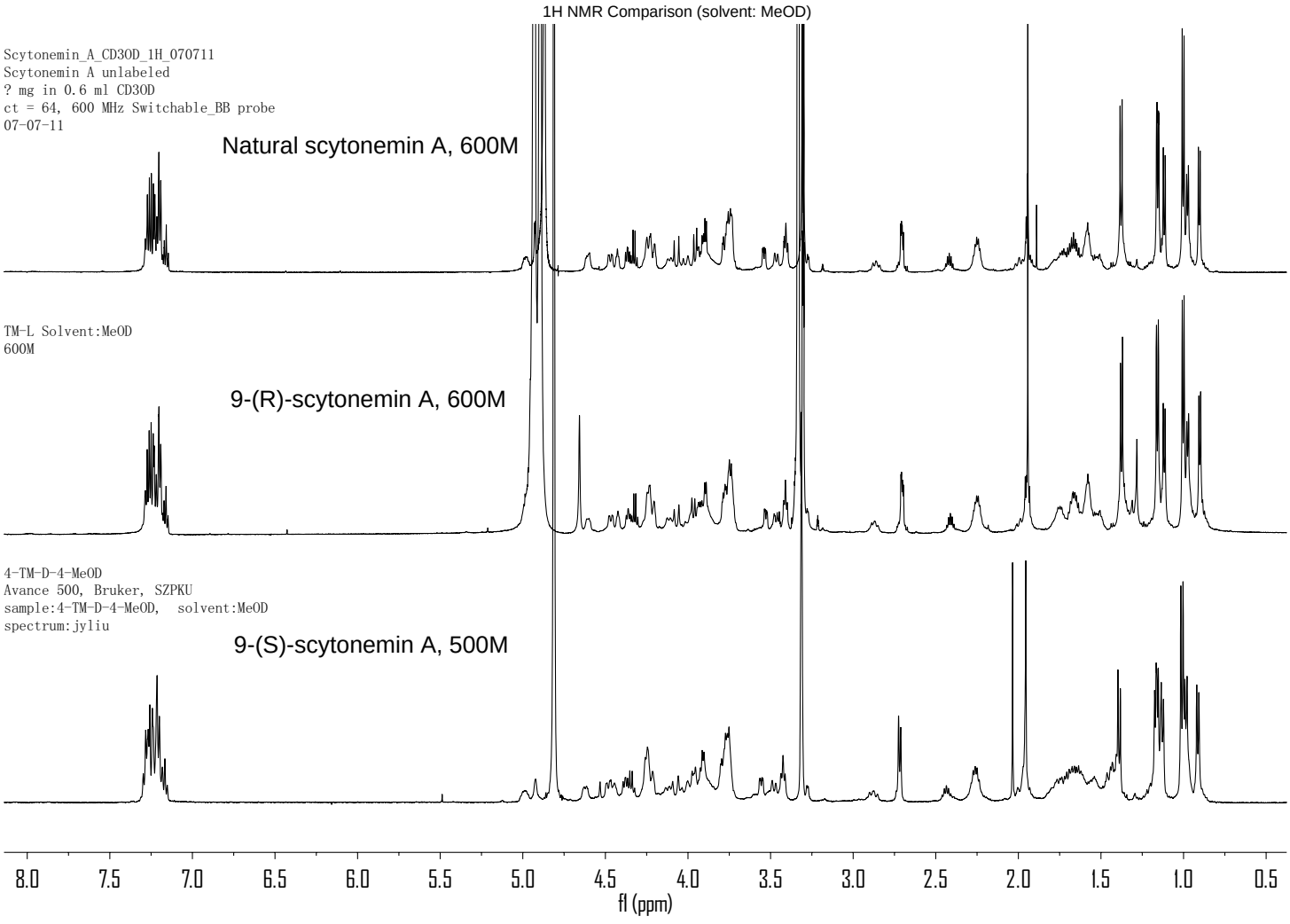

Avance 500, Bruker, SZPKU
sample:4-TM-D-DMSO, solvent:DMSO
spectrum:jyliu
NAME 4-TM-D-DMSO
EXPNO 1
PROCNO 1
Date_ 20110524
Time 14.37
INSTRUM AV500
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT DMSO
NS 128
DS 0
SWH 10330.578 Hz
FIDRES 0.315264 Hz
AQ 1.5860696 sec
RG 256
DW 48.400 usec
DE 6.00 usec
TE 300.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1299876 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
ppm


TM-D-1
NAME TM-D-1
EXPNO 2
PROCNO 1
Date_ 20110531
Time 11.38
INSTRUM spect
PROBHD 5 mm CP2 1H-31
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 102400
DS 4
SWH 32051.281 Hz
FIDRES 0.489064 Hz
AQ 1.0224116 sec
RG 203
DW 15.600 usec
DE 18.00 usec
TE 298.0 K
D1 3.00000000 sec
D11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 11.40 usec
SI 65536
SF 150.9028658 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.10
71.366
71.187
71.045
C9
ppm
1b, 9-(S)-scytonemin A
ppm


gHSQC for Natural Scytonemin A in CD3OD
20.0
40.0
60.0
80.0
100.0
120.0
^{13}C (ppm)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
^{1}H (ppm)


gHSQC for 9-(R)-scytonemin A in CD3OD 600M
ppm
20
40
60
80
100
120
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


gHSQC for 9-(S)-Scytonemin A in CD3OD, 600M
ppm
20
40
60
80
100
120
140
7
6
5
4
3
2
1
0
ppm


1H NMR Comparison (solvent: MeOD)
Scytonemin_A_CD3OD_1H_070711
Scytonemin A unlabeled
? mg in 0.6 ml CD3OD
ct = 64, 600 MHz Switchable_BB probe
07-07-11
Natural scytonemin A, 600M
TM-L Solvent:MeOD
600M
9-(R)-scytonemin A, 600M
4-TM-D-4-MeOD
Avance 500, Bruker, SZPKU
sample:4-TM-D-4-MeOD, solvent:MeOD
spectrum:jyliu
9-(S)-scytonemin A, 500M
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)