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Supporting Information

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Total Synthesis of Paliurine F

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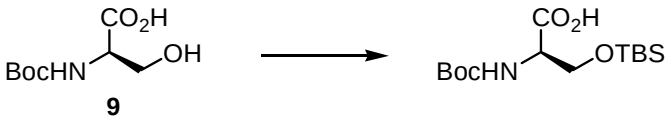
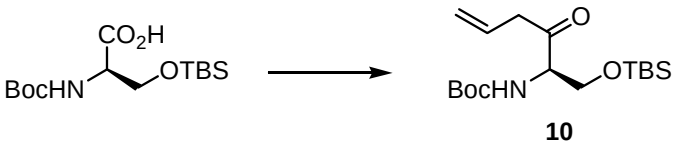
General Information. All reactions were carried out in oven or flame-dried glassware under an argon atmosphere employing standard techniques in handling air-sensitive materials. All solvents were reagent grade. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under argon immediately prior to use. Dichloromethane, toluene and acetonitrile were freshly distilled from calcium hydride. Triethylamine, diisopropylethylamine, *N*-methylmorpholine, *N*,*N*'-dimethylethylenediamine, diethylamine and 2,6-lutidine were distilled over calcium hydride. *N*,*N*-Dimethylformamide, HMPA, NMP and dimethylsulfoxide were distilled over calcium hydride. *n*-Butyllithium was purchased from Aldrich and standardized by titration with menthol/1,10-phenanthroline. Copper(I) iodide (99,999 % purity) was purchased from Aldrich and used as supplied. All other reagents were used as supplied. Unless otherwise noted, reactions were magnetically stirred and monitored by thin layer chromatography using Merck-Kiesegel $60F_{254}$ plates. Flash chromatographies were performed with silica gel 60 (particle size 35-70 μm) supplied by SDS. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise noted. Proton NMR spectra were recorded using an internal deuterium lock at ambient temperature on a Bruker 300 MHz spectrometer. Internal references of δ_H 7.26 and δ_H 2.50 were respectively used for $CDCl_3$ and DMSO-*d*$_6$. Data are presented as follows: chemical shift (in ppm on the δ scale relative to δ_{TMS} = 0), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, m = multiplet, br = broad), coupling constant (*J*/Hz) and integration. Resonances that are either partially or fully obscured are denoted obscured (obs.). Carbon-13 NMR spectra were recorded on a Varian 75 MHz spectrometer. Internal references of δ_C 77.16 and δ_C 39.52 were respectively used for $CDCl_3$ and DMSO-*d*$_6$. Infrared spectra were recorded on a Nicolet OPUS IR (impact 400D) spectrophotometer. Optical rotations were recorded on an Perkin Elmer 341 polarimeter at 589 nm and reported as follows: $[\alpha]_D^{20}$, concentration (*c* in g/100 mL) and solvent. Melting points were recorded on an Buchi B-545. UV spectra were recorded in methanol on a Shimadzu UV-160A. Mass spectra were obtained on a GCMS HP MS 5989B spectrometer.

Due to the presence of the *N*-Boc-pyrrolidine moeity, it was necessary to record ^1H and ^{13}C NMR spectra of most intermediates in DMSO-*d6* at temperatures ranging from 333 to 345K (see details below; the use of higher temperatures resulted in degradation of intermediates). Even at those temperatures, some ^{13}C peaks were poorly resolved and are denoted "broad" (br.).

Experimental Procedures



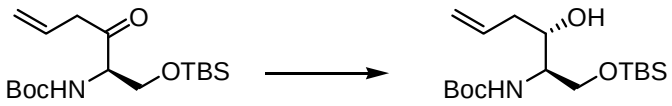
***N*-(*tert*-Butoxycarbonyl)-*O*-(*tert*-butyldimethylsilyl)-D-serine.**[S1] To a solution of commercially available *N*-Boc-D-serine **9** (17.6 g, 86 mmol) in DMF (170 mL) were added at 0 °C imidazole (17.5 g, 258 mmol) and TBSCl (16.9 g, 112 mmol). The resulting mixture was slowly warmed to rt, stirred overnight, and poured into a mixture of 1M HCl (300 mL) and ether (600 mL) to hydrolyze the silyl ester. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, and extracted with 1M NaOH (120 mL). The aqueous layer was next acidified by slow addition of 1M HCl (200 mL) and extracted with ether. Combined organic layers were finally dried over $MgSO_4$, filtered and concentrated under vacuum to yield the desired product as a pale yellow and sticky oil (21.3 g, 67 mmol, 78 %). $[\alpha]_D^{20}$ -15 (*c* 8.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.43 (br. s, 1H), 5.38 (d, *J* = 8.5 Hz, 1H), 4.35 (br. d, *J* = 8.5 Hz, 1H), 4.05 (A of ABX syst., *J* = 1.9, 10.1 Hz, 1H), 3.82 (B of ABX syst., *J* = 2.8, 10.1 Hz, 1H), 1.41 (s, 9H), 0.83 (s, 9H), 0.01, 0.00 (s, s, 3H, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.4, 155.7, 80.2, 63.6, 55.5, 28.3, 25.8, 18.3, -5.5, -5.6; IR (neat) ν_{max} 3447, 2950, 2576, 1685, 1506 cm^{-1}; ESIMS (positive mode): 319.4, 262.3; HRMS (CI, NH_3) *m/z* calcd for $C_{14}H_{30}NO_5Si$ $[M+H]^+$ 320.1893, found 320.1889.



(*R*)-*N*-*tert*-Butoxycarbonyl-[1-(tert-butyl-dimethyl-silyloxymethyl)-2-oxo-pent-4-enyl]-amine 10. To a solution of *N*-(*tert*-Butoxycarbonyl)-*O*-(*tert*-butyldimethylsilyl)-D-serine (5.0 g, 15.7 mmol) in THF (70 mL) was added dropwise at -10 °C a solution of *n*BuLi (1.6 M solution

[S1] W. R. Ewing, M. M. Joullié, *Heterocycles* **1988**, *27*, 2843-2850.

in hexanes, 9.8 mL, 15.7 mmol). The resulting thick gelatinous suspension was stirred at -10 °C for 30 minutes, cooled to -78 °C and treated with a solution of allylmagnesium bromide (0.8 M solution in ether, 45.0 mL, 36.0 mmol).[S2] The obtained light grey slurry was stirred for 1 hour at 78 °C, warmed to rt over 1 hour, stirred at this temperature for 30 minutes and poured into a mixture of saturated NH_4Cl solution, ice and ether. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum to yield the desired product **10** as a colorless oil (5.3 g, 15.4 mmol, 98 %). This unstable product was immediately used without further purification in the next step. $[\alpha]_D^{20}$ -55 (*c* 2.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.82-5.98 (m, 1H), 5.45 (d, *J* = 6.9 Hz, 1H), 5.07-5.18 (m, 2H), 4.30 (app. quint., *J* = 3.6 Hz, 1H), 4.04 (A of ABX syst., *J* = 2.8, 10.4 Hz, 1H), 3.79 (B of ABX syst., *J* = 4.0, 10.4 Hz, 1H), 3.34 (A' of A'B'X' syst., *J* = 6.8, 17.6 Hz, 1H), 3.25 (B' of A'B'X' syst., *J* = 6.8, 17.6 Hz, 1H), 1.42 (s, 9H), 0.82 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.9, 155.4, 130.0, 119.2, 79.9, 63.4, 61.0, 45.0, 28.4, 25.8, 18.2, -5.5; IR (neat) ν_{max} 3441, 2955, 1705, 1639, 1485, 1250, 1163, 840 cm^{-1}; ESIMS (positive mode): 366.3, 329.4, 310.3, 268.3; HRMS (CI, NH_3) *m/z* calcd for $C_{17}H_{34}NO_4Si$ $[M+H]^+$ 344.2257, found 344.2259.

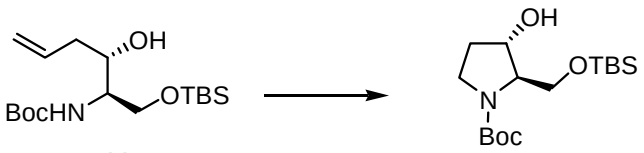


10 **11**

(1*R*,2*S*)-*N*-*tert*-Butoxycarbonyl-[1-(tert-butyl-dimethyl-silyloxymethyl)-2-hydroxy-pent-4-enyl]-amine 11.[S3] A solution of **10** (5.3 g, 15.4 mmol) in absolute ethanol (160 mL) was treated with sodium borohydride (1.15 g, 30.4 mmol) at -78 °C. The resulting mixture was stirred for 80 minutes, carefully quenched by addition of a saturated aqueous solution of NH_4Cl, warmed to rt, concentrated under vacuum and diluted with 1M NaOH solution and ether. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum to yield the

[S2] P. Mazerolles, P. Boussaguet, V. Huc, *Organic Syntheses* **1999**, *76*, 221-224.
[S3] For assignment of relative stereochemisty, see p. S17.

desired product **11** as a colorless oil (5.2 g, 15.0 mmol, 98 %). Diastereoisomeric excess was determined by analysis of crude ^{1}H NMR spectra and was found to be higher than 95%. $[\alpha]_D^{20}$ -30 (*c* 2.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.69-5.85 (m, 1H), 5.19 (d, *J* = 8.3 Hz, 1H), 5.02-5.11 (m, 2H), 3.89 (A of ABX syst., *J* = 2.6, 10.5 Hz, 1H), 3.72 (B of ABX syst., *J* = 2.4, 10.5 Hz, 1H), 3.64 (app. quint., *J* = 6.2 Hz, 1H), 3.44-3.53 (br. m, 1H), 3.10 (d, *J* = 7.2 Hz, 1H), 2.27 (app. t, *J* = 6.7 Hz, 2H), 1.36 (s, 9H), 0.82 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.7, 134.6, 117.7, 79.3, 72.6, 63.1, 53.9, 39.3, 28.4, 25.8, 18.1, -5.6; IR (neat) ν_{max} 3375, 2971, 2879, 1716, 1491, 1173, 840 cm^{-1}; ESIMS (positive mode): 713.6, 384.4, 368.4, 329.4, 268.3, 246.3; HRMS (CI, NH_3) *m/z* calcd for $C_{17}H_{36}NO_4Si$ $[M+H]^+$ 346.2414, found 346.2407.

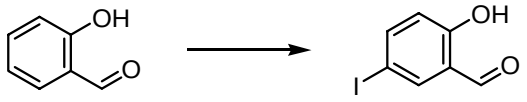


11 **7**

(1*R*,2*S*)-1-*tert*-Butoxycarbonyl-2-(*tert*-butyl-dimethyl-silyloxymethyl)-3-hydroxy-pyrrolidine 7. To a solution of **10** (3.5 g, 10.1 mmol) in THF (150 mL) and water (10 mL) was added osmium tetroxide (4% wt solution in water, 3.2 mL, 0.5 mmol) and sodium periodate (8.65 g, 40.4 mmol). The resulting white slurry was vigorously stirred at rt for 90 minutes and quenched by addition of a 10% wt aqueous solution of sodium thiosulfate. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were successively washed with 10% wt aqueous sodium thiosulfate solution and brine, dried over $MgSO_4$, filtered and concentrated under vacuum to yield the intermediate *N*-Boc-aminal as a complex mixture of rotamers and diastereoisomers.

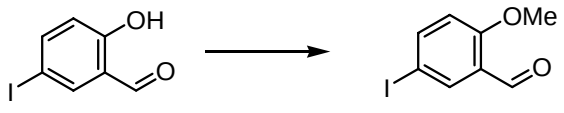
The resulting brownish oil was dissolved in dry dichloromethane, treated with triethylsilane (1.9 mL, 12.0 mmol) and $BF_3{\cdot}OEt_2$ (1.3 mL, 12.0 mmol) dropwise at -78 °C, and stirred for 3h30 while carefully keeping the temperature below -75 °C. The reaction mixture was finally quenched by addition of a saturated aqueous solution of $NaHCO_3$ (20 mL), warmed to rt and diluted with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed brine, dried over $MgSO_4$, filtered

and concentrated. The crude residue was purified by flash chromatography over silica gel (petroleum ether/AcOEt: 8/2) to yield the cyclized product **7** as a white solid (2.4 g, 7.2 mmol, 72 %). Mp: 110 °C; $[\alpha]_D^{20}$ -38 (*c* 2.3, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6, 343 K): δ 4.66 (s, 1H), 4.18 (br. s, 1H), 3.67 (app. q, *J* = 6.8 Hz, 1H), 3.53 (br. s, 2H), 3.39 (td, *J* = 9.8, 7.3 Hz, 1H), 3.23 (td, *J* = 9.8, 2.6 Hz, 1H), 1.92-20.4 (m, 1H), 1.62-1.73 (m, 1H), 1.42 (s, 9H), 0.88 (s, 9H), 0.05, 0.03 (s, s, 3H, 3H); ^{13}C NMR (75 MHz, DMSO-d_6, 343 K): δ 153.4, 77.7, 71.7 (br.), 66.6, 61.8 (br.), 44.4, 31.4 (br.), 27.8, 25.3, 17.4, -5.9, -6.0; IR (KBr) ν_{max} 3375, 2925, 2756, 2592, 1675, 1424, 1096, 835 cm^{-1}; ESIMS (positive mode): 354.3, 298.3, 254.2; HRMS (CI, NH_3) *m/z* calcd for $C_{16}H_{34}NO_4Si$ $[M+H]^+$ 332.2257, found 332.2252.



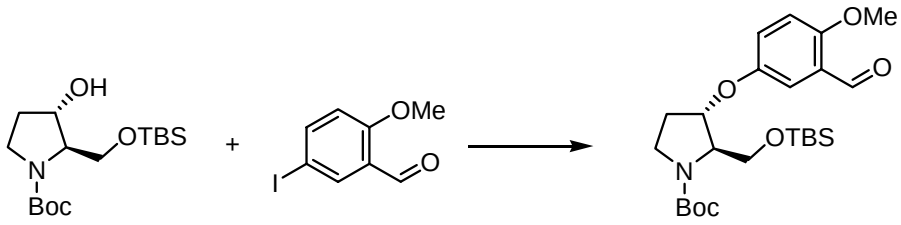
2-Hydroxy-5-iodo-benzaldehyde.[S4] To a solution of salicylaldehyde (20.0 g, 164 mmol) in glacial acetic acid (200 mL) was added iodine monochloride (9.2 mL, 181 mmol). The resulting brown mixture was stirred at rt for 2 days and at 40 °C for a day, concentrated under vacuum, and the residue was diluted with water and dichloromethane. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were successively washed with 10% wt aqueous sodium thiosulfate solution and brine, dried over $MgSO_4$, filtered and concentrated under vacuum to yield a yellow-brown solid which was stored in the dark (38.0 g, 153 mmol, 93%). Mp: 83 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.98 (s, 1H), 9.87 (d, *J* = 0.3 Hz, 1H), 7.88 (d, *J* = 2.2 Hz, 1H), 7.80 (dd, *J* = 2.2, 8.7 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.5, 161.3, 145.4, 141.9, 122.6, 120.3, 80.5; IR (KBr) ν_{max} 3216, 1670, 1460, 1270, 1265, 1142 cm^{-1}; ESIMS (positive mode): 248.3, 219.3, 127.5; HRMS (CI, NH_3) *m/z* calcd for $C_7H_5IO_2$ $[M]^+$ 247.9334, found 247.9329.

[S4] procedure adapted from: Y. J. Cho, K. Y. Rho, S. R. Keum, S. H. Kim, C. M. Yoon, *Synth. Commun.* **1999**, *29*, 2061-2068.



8

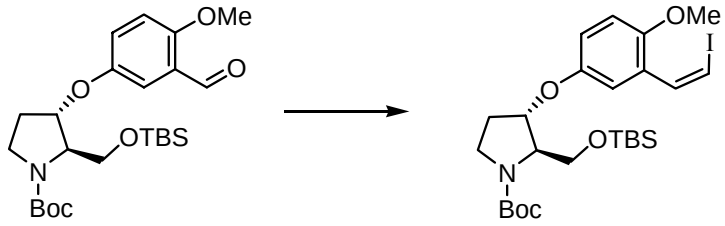
5-Iodo-2-methoxy-benzaldehyde 8. To a solution of 2-hydroxy-5-iodo-benzaldehyde (29.6 g, 119 mmol) in dry acetone (700 mL) was added potassium carbonate (24.9 g, 180 mmol) and dimethylsulfate (12.5 mL, 132 mmol). The resulting orange mixture was refluxed for 2 hours, cooled to rt, concentrated in vacuo and diluted with water and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2, combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude residue was finally washed with pentane to give the desired ether as a brown solid which was stored in the dark (31.2 g, 180 mmol, quant.). Mp: 145 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.25 (s, 1H), 7.98 (d, J = 2.3 Hz, 1H), 7.71 (dd, J = 2.3, 8.8 Hz, 1H), 6.70 (d, J = 8.8 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.3, 161.5, 144.1, 136.9, 126.5, 114.3, 83.0, 55.9; IR (KBr) ν_{max} 2960, 2865, 1689, 1474 cm^{-1}; ESIMS (positive mode): 262.5, 244.3, 202.7; HRMS (CI, NH_3) *m/z* calcd for $C_8H_7IO_2$ $[M+H]^+$ 261.9491, found 261.9490.



7 **8** **12**

(2*R*,3*S*)-1-(*tert*-Butoxycarbonyl)-2-(*tert*-butyldimethylsilyloxy)methyl-3-(3-formyl-4-methoxy-phenoxy)-pyrrolidine 12. A 15 mL pressure tube was charged with 5-iodo-2-methoxy-benzaldehyde **8** (1.3 g, 5.0 mmol), alcohol **7** (1.8 g, 5.4 mmol), cesium carbonate (3.25 g, 10.0 mmol), 1,10-phenanthroline (180 mg, 1.0 mmol) and copper(I) iodide (95 mg, 0.5 mmol). Toluene (3 mL) was added, the pressure tube was closed and the brownish suspension was heated to 125°C for 24 hours. Another portion of 5-iodo-2-methoxy-benzaldehyde **8** (650 mg, 2.5 mmol) was then added and the reaction mixture was heated for an additional 24 hours and cooled to rt. Crude reaction mixture was finally filtrated over a plug of silica gel (washed with

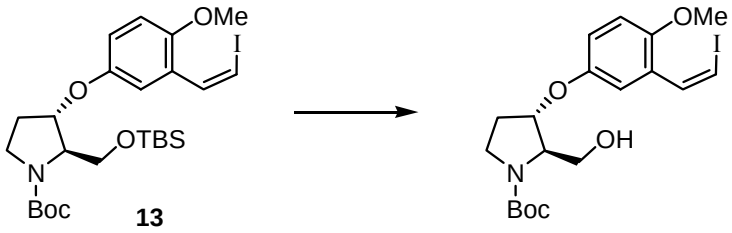
AcOEt), concentrated and purified by flash chromatography over silica gel (gradient from CH_2Cl_2 to CH_2Cl_2/EtOH: 95/5) to yield the aryl ether as a pale yellow sticky oil (1.9 g, 4.1 mmol, 75 %); $[\alpha]_D^{20}$ -5 (*c* 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6, 345 K): δ 10.33 (s, 1H), 7.27 (d, *J* = 3.1 Hz, 1H), 7.22-7.25 (m, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 4.82 (d, *J* = 4.1 Hz, 1H), 3.78-3.93 (m, 2H), 3.88 (s, 3H), 3.58-3.63 (m, 1H), 3.34-3.51 (m, 2H), 2.23 (app. qt, *J* = 9.8, 4.7 Hz, 1H), 2.10 (app. dd, *J* = 13.4, 6.2 Hz, 1H), 1.42 (s, 9H), 0.88 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6, 345 K): δ 186.9, 155.2, 152.2, 149.4, 123.8, 123.0, 113.0, 112.5, 78.8 (br.), 77.2, 62.6, 60.7 (br.), 55.0, 43.3, 27.0 (br.), 26.7, 24.2, 16.4, -7.1; IR (neat) ν_{max} 2883, 2755, 1694, 1490, 1398 cm^{-1}; ESIMS (positive mode): 970.0, 953.7, 599.5, 583.5, 488.4; HRMS (CI, NH_3) *m/z* calcd for $C_{24}H_{39}NO_6Si$ $[M]^+$ 465.2547, found 465.2552.



[2*R*,3*S*,3(3*Z*)]-1-(*tert*-Butoxycarbonyl)-2-(*tert*-butyldimethylsilyloxy)methyl-3-[3-(2-iodovinyl)-4-methoxy-phenoxy]-pyrrolidine 13. To a suspension of methyltriphenyl-phosphonium iodide[S5] (1.05 g, 1.98 mmol) in THF (11 mL) was added dropwise at rt a solution of NaHMDS (2.0 M solution in THF, 990 μL, 1.98 mmol). The resulting red-orange solution was stirred at rt for 20 min and cooled to -78 °C before adding HMPA (1.3 mL) and a solution of **12** (700 mg, 1.5 mmol) in THF (7 mL). The reaction mixture was stirred at -78 °C for two hours and quenched at -78 °C by addition of a saturated aqueous solution of $NaHCO_3$. The mixture was warmed to rt, diluted with Et_2O and filtered through a plug of Celite® which was thoroughly washed with ether. The biphasic filtrate was separated and the organic layer was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel (AcOEt/petroleum ether: 1/9) to give the desired vinyl iodide **13** as a yellow oil (860 mg, 1.46 mmol, 97 %). Diastereoisomeric excess was determined by analysis of crude ^{1}H NMR

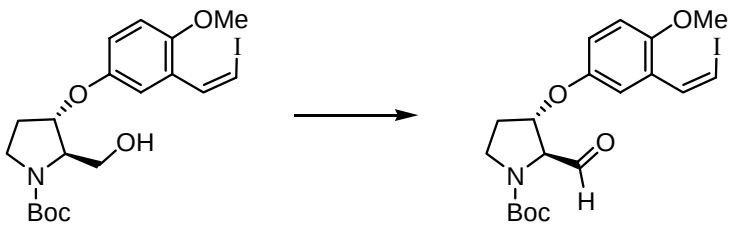
[S5] M. C. Hillier, A. T. Price, A. I. Meyers, *J. Org. Chem.* **2001**, *66*, 6037-6045.

spectra and was found to be higher than 95%. $[\alpha]_D^{20}$ -4 (*c* 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6, 333 K): δ 7.27 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 2.5 Hz, 1H), 6.86-6.87 (m, 2H), 6.66 (d, *J* = 8.5 Hz, 1H), 4.68 (d, *J* = 4.1 Hz, 1H), 3.74 (A of ABX syst., *J* = 3.2, 10.8 Hz, 1H), 3.68-3.73 (m, 1H), 3.66 (s, 3H), 3.45-3.55 (m, 1H), 3.25-3.37 (m, 2H), 2.07-2.20 (m, 1H), 1.92-1.98 (m, 1H), 1.32 (s, 9H), 0.77 (s, 3H), 0.79 (s, 6H), 0.03 (s, 3H), -0.12 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6, 333 K): δ 153.3, 151.1, 149.6, 134.2, 126.3, 117.0, 115.9, 112.4, 82.5, 80.3, 78.4, 63.6, 61.7 (br.), 55.8, 44.4, 28.5 (br.), 27.8, 25.4, 17.4, -3.6, -5.9; IR (neat) ν_{max} 2960; 1685; 1486; 1394; 1235; 1117; 830 cm^{-1}; CIMS (NH_3 gas): 590; 534; 476; HRMS (CI, NH_3) *m/z* calcd for $C_{25}H_{40}INO_5Si$ $[M]^+$ 589.1720, found: 589.1724.

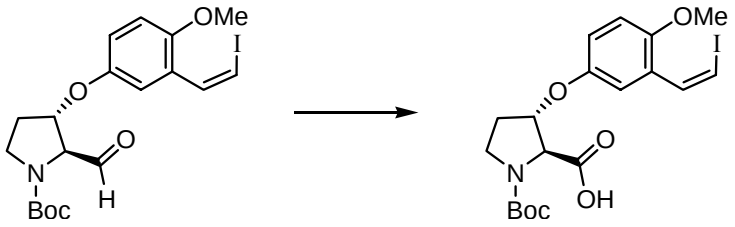


[2*R*,3*S*,3(3*Z*)]-1-(*tert*-Butoxycarbonyl)-2-hydroxymethyl-3-[3-(2-iodovinyl)-4-methoxy-phenoxy]-pyrrolidine. A solution of **13** (860 mg, 1.46 mmol) in THF (18 mL) was treated with a solution of TBAF (1M solution in THF, 2.2 mL, 2.2 mmol) at -10 °C. The resulting light yellow mixture was warmed to rt over 50 minutes and quenched with water. The aqueous layer was extracted with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated to give the crude unprotected alcohol (contaminated with *tert*-butyldimethyl-silanol) as an orange oil (694 mg, 1.46 mmol, quant.) which was used without further purification in the next step. An analytical sample was purified by flash chromatography over silica gel (EtOH/DCM: 3/97). $[\alpha]_D^{20}$ -7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6, 333 K): δ 7.37 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 2.3 Hz, 1H), 6.98-6.99 (m, 2H), 6.76 (d, *J* = 8.5 Hz, 1H), 4.78-4.90 (m, 2H), 3.82-3.86 (app. dd, *J* = 3.7, 7.6 Hz, 1H), 3.76 (s, 3H), 3.59-3.71 (m, 1H), 3.31-3.43 (m, 3H), 2.14-2.28 (m, 1H), 1.99-2.09 (m, 1H), 1.41 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6, 333 K): δ 153.5, 150.9, 149.7, 134.2, 126.3, 116.7, 115.7, 112.4, 82.5, 79.4 (br.), 78.2, 64.1, 60.3 (br.), 55.8, 44.2, 28.5 (br.), 27.9; IR (neat) ν_{max} 3406, 2950, 1675, 1491, 1414,

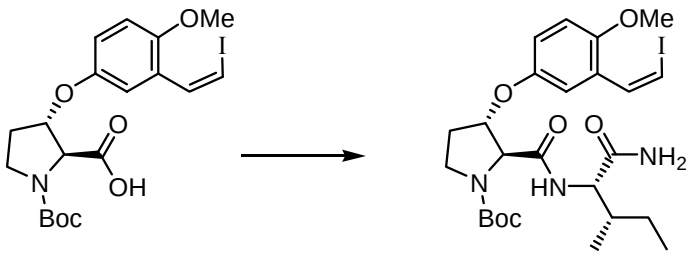
1214, 1035, 866, 764 cm^{-1}; ESIMS (positive mode): 514.3, 498.2; HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{27}INO_5$ $[M+H]^+$ 476.0934, found: 476.0921.



[2*R*,3*S*,3(3*Z*)]-1-(*tert*-Butoxycarbonyl)-2-formyl-3-[3-(2-iodovinyl)-4-methoxy-phenoxy]-pyrrolidine. DMSO (265 µL, 3.7 mmol) was added to a solution of oxalyl chloride (270 µL, 3.1 mmol) in dichloromethane (10 mL) at -78 °C. The resulting solution was stirred at -78 °C for 30 minutes and a solution of [2*R*,3*S*,3(3*Z*)]-1-(*tert*-butoxycarbonyl)-2-hydroxymethyl-3-[3-(2-iodovinyl)-4-methoxy-phenoxy]-pyrrolidine (694 mg, 1.46 mmol) in dichloromethane (15 mL) was added dropwise *via* cannula. The reaction mixture was stirred for 40 minutes at -78 °C before adding triethylamine dropwise (880 µL, 6.3 mmol), and the mixture was warmed to -10 °C over 2 hours. The reaction was next quenched at -10 °C with water and diluted with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated to give the desired aldehyde as an orange oil (691 mg, 1.46 mmol, quant.) which was used without purification in the next step. An analytical sample was purified by flash chromatography over silica gel (AcOEt/petroleum ether: 35/65) to give a colorless oil. $[\alpha]_D^{20}$ -27 (*c* 1.3, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6, 335 K): δ 9.60 (s, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.00-7.01 (m, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 5.00 (br. s, 1H), 4.35 (app. s, 1H), 3.77 (s, 3H), 3.50-3.57 (m, 2H), 2.03-2.12 (m, 2H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6, 333 K): δ 198.7, 151.4, 150.8 and 149.9 (rotamers), 149.7, 134.1, 126.4, 117.1, 116.3, 112.3, 82.9, 79.2, 78.1 (br.), 70.1, 55.8, 44.3, 29.6 (br.), 27.7; IR (neat) ν_{max} 2971, 1726, 1675, 1482, 1388, 1276, 1045, 748 cm^{-1}; ESIMS (positive mode): 512.1, 496.1, 440.0, 312.8, 311.2; HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{25}INO_5$ $[M+H]^+$ 474.0777, found: 474.0773.



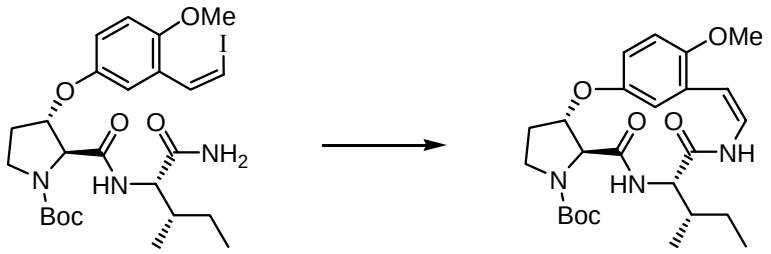
[2*R*,3*S*,3(3*Z*)]-1-(*tert*-Butoxycarbonyl)-3-[3-(2-iodovinyl)-4-methoxy-phenoxy]-proline. To a solution of [2*R*,3*S*,3(3*Z*)]-1-(*tert*-butoxycarbonyl)-2-formyl-3-[3-(2-iodovinyl)-4-methoxy-phenoxy]-pyrrolidine (691 mg, 1.46 mmol) in a mixture of THF (5 mL) and *tert*-butanol (14 mL) was added 2-methylprop-2-ene (90 %, 1.6 mL, 13.2 mmol), followed by a solution of sodium chlorite (80 %, 400 mg, 3.5 mmol) and sodium dihydrogen phosphate dihydrate (485 mg, 3.1 mmol) in water (10 mL). The yellow reaction mixture was then stirred for 1 hour, carefully quenched with a 1M HCl solution and diluted with ether. The aqueous layer was extracted with ether, combined organic layers were dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel (EtOH/DCM: 6/94) to give the free carboxylic acid as a yellow oily solid (486 mg, 0.99 mmol, 68 % over three steps). $[\alpha]_D^{20}$ -24 (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6, 345 K): δ 7.38 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 2.3 Hz, 1H), 7.01-7.02 (m, 2H), 6.77 (d, J = 8.5 Hz, 1H), 4.90 (br. s, 1H), 4.28 (app. s, 1H), 3.77 (s, 3H), 3.44-3.60 (m, 2H), 2.09-2.19 (m, 2H), 1.39 (br. s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6, 345 K): δ 170.7, 153.0, 151.3, 149.2, 134.2, 126.5, 116.7, 116.2, 112.5, 82.7, 80.1 (br.), 78.8, 64.5 (br.), 55.8, 44.0, 28.9 (br.), 27.7; IR (neat) ν_{max} 3441, 2919, 1731, 1680, 1419, 1214 cm^{-1}; HRMS (CI, NH_3) *m/z* calcd for $C_{19}H_{25}INO_6$ $[M+H]^+$ 490.0727, found: 490.0733.



6

[2*R*,3*S*,3(3*Z*)]-{1-(*tert*-Butoxycarbonyl)-3-[3-(2-iodovinyl)-4-methoxy-phenoxy]-prolyl}-isoleucinamide 6. To a solution of [2*R*,3*S*,3(3*Z*)]-1-(*tert*-butoxycarbonyl)-3-[3-(2-iodovinyl)-4-methoxy-phenoxy]-proline (1.09 g, 2.23 mmol) and isoleucinamide acetate[S6] (424 mg, 2.23 mmol) in DMF (20 mL) was added 1-hydroxybenzotriazole (HOBt, 316 mg, 2.34 mmol). 1-(3-Dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (EDC, 470 mg, 2.45 mmol) and *N*-methylmorpholine (620 µL, 5.60 mmol) were next added at 0 °C and the solution was stirred for 16 hours while progressively warmed to rt. The yellow reaction mixture was quenched with water and diluted with ether. The aqueous layer was extracted with ether and the combined organic layers were successively washed with a 1M HCl aqueous solution, saturated aqueous solution of $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel (AcOEt/petroleum ether: 9/1) to give the desired peptide **6** (992 mg, 1.65 mmol, 75 %) as a pale yellow solid. Mp: 87 °C; $[\alpha]_D^{20}$ -31 (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6, 343 K): δ 7.65 (d, J = 8.5 Hz, 1H), 7.38 (d, J = 8.5 Hz, 1H), 7.28 (d, J = 2.3 Hz, 1H), 7.00-7.06 (m, 2H), 6.80-7.20 (br. s, 2H), 6.77 (d, J = 8.5 Hz, 1H), 4.83 (br. s, 1H), 4.36, 4.43 (rotamers, s, s, 1H), 4.19 (dd, J = 6.7, 8.4 Hz 1H), 3.80, 3.77 (rotamers, s, s, 3H), 3.46-3.56 (m, 2H), 2.05-2.10 (m, 2H), 1.72-1.84 (m, 1H), 1.47-1.50 (m, 1H), 1.41 (s, 9H), 1.05-1.20 (m, 1H), 0.87 (t, J = 6.4 Hz, 3H), 0.84 (d, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6, 343 K): δ 172.1, 168.6, 153.5, 151.2, 149.3, 134.1, 126.3, 116.8, 116.0, 112.5, 83.7, 79.5 (br.), 79.0, 65.7 (br.), 56.6, 55.9, 44.3, 36.4, 28.8 (br.), 27.7, 23.9, 15.1, 10.6; IR (KBr) ν_{max} 3314, 2960, 2720, 1680, 1486, 1394, 1214, 1168, 1025 cm^{-1}; ESIMS (positive mode): 624.2, 640.2; HRMS (CI, NH_3) *m/z* calcd for $C_{25}H_{37}IN_3O_6$ $[M+H]^+$ 602.1727, found: 602.1741.

[S6] T. Moriguchi, T. Yanagi, M. Kunimori, T. Wada, M. Sekine, *J. Org. Chem.* **2000,** *65,* 8229-8238.



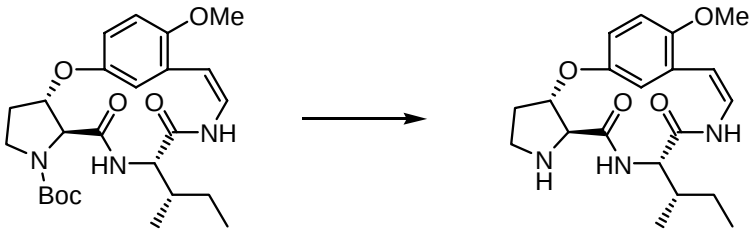
6 **5**

cyclopeptide core 5. A 100 mL flask was charged with iodo-amide **6** (350 mg, 0.59 mmol), copper(I) iodide (23 mg, 0.12 mmol) and cesium carbonate (285 mg, 0.88 mmol). The flask was evacuated under high vacuum, backfilled with argon and closed with a rubber septa. Dry and degassed THF (78 mL) and *N*,*N*'-dimethylethylene-1,2-diamine (26 μL, 0.24 mmol) were next added, the rubber septa was replaced by a glass stopper and the light blue suspension was heated to 60°C for 20 hours. The reaction mixture was cooled to rt and filtrated over a plug of silica gel (washed with AcOEt) and concentrated. The crude residue was purified by flash chromatography over silica gel (gradient from Et_2O/EtOH: 99/1 to Et_2O/EtOH: 95/5) to give the recovered starting peptide **6** (70 mg, 0.12 mmol, 20 %) and the desired cyclized product **5** (193 mg, 0.41 mmol, 70 %, 89 % based on recovered starting material) as a white solid. Mp: 188 °C; $[\alpha]_D^{20}$ -436 (*c* 0.54, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (d, *J* = 11.2 Hz, 1H), 7.22 (d, *J* = 5.0 Hz, 1H), 6.87 (dd, *J* = 6.9, 11.2 Hz, 1H), 6.83 (d, *J* = 9.2 Hz, 1H), 6.74 (dd, *J* = 2.9, 8.9 Hz, 1H), 6.65 (d, *J* = 2.9 Hz, 1H), 5.85 (d, *J* = 9.1 Hz, 1H), 5.43 (dt, *J* = 2.7, 8.1 Hz, 1H), 4.25 (app. t, *J* = 4.6 Hz, 1H), 4.15 (d, *J* = 2.6 Hz, 1H), 3.70-3.78 (m, 1H), 3.73 (s, 3H), 3.30-3.39 (m, 1H), 2.39-2.50 (m, 1H), 2.14-2.24 (m, 1H), 2.00-2.10 (m, 1H), 1.38 (s, 9H), 1.05-1.32 (m, 2H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.81 (t, *J* = 9.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.4, 167.6, 155.3, 151.6, 151.4, 124.5, 121.7, 117.8, 113.9, 111.5, 106.7, 81.2, 78.0, 64.9, 60.4, 56.2, 46.0, 35.3, 32.2, 28.4, 24.6, 16.2, 11.9; IR (KBr) ν_{max} 3319, 2919, 1706, 1650, 1506, 1404, 1214, 1163, 1122, 1030, 764 cm^{-1}; CIMS (NH_3 gas): 491.0, 473.0, 418.0 ; HRMS (CI, NH_3) *m/z* calcd for $C_{25}H_{36}N_3O_6$ $[M+H]^+$ 474.2604, found: 474.2607.

Alternate procedure for macrocyclization using CuTc. A 15 mL pressure tube was charged with iodo-amide **6** (50 mg, 0.083 mmol), copper(I) thiophenecarboxylate[S7] (CuTc, 5.0 mg, 0.025

[S7] prepared according to G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* **1996**, *118*, 2748-2749.

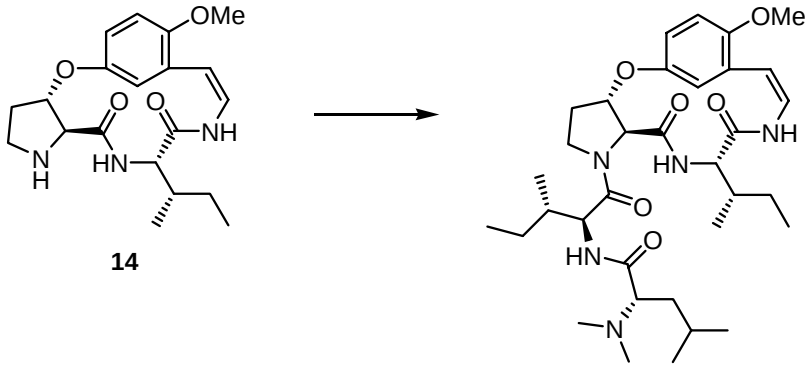
mmol) and cesium carbonate (40.7 mg, 0.125 mmol). The pressure was evacuated under high vacuum, backfilled with argon and closed with a rubber septa. Dry and degassed NMP (11.5 mL) was next added and the tube was sealed and the yellow suspension was heated to 90°C for 20 hours. The reaction mixture was cooled to rt, and diluted with ether and water. The aqueous layer was extracted with ether and the combined organic layers were washed brine, dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel (gradient from Et_2O/EtOH: 99/1 to Et_2O/EtOH: 95/5) to give the desired cyclized product **5** (23.5 mg, 0.050 mmol, 60 %) as a white solid.



5 **14**

deprotected cyclopeptide core 14. To a solution of **5** (100 mg, 0.21 mmol) in dichloromethane (4.7 mL) were added at -10 °C 2,6-lutidine (25 μL, 21.1 mmol) and a solution of trimethylsilyl trifluoromethanesulfonate (1.4 M solution in dichloromethane, 600 μL, 84.0 mmol). The resulting light pink solution was stirred for 1 hour while progressively warmed to 0 °C. The mixture was next hydrolyzed at 0 °C by addition of a saturated aqueous solution of $NaHCO_3$ and diluted with dichloromethane. The aqueous layer was extracted with dichloromethane and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel (AcOEt/EtOH/Et_3N: 85/14/1) to give the desired *N*-deprotected macrocycle **14** (63 mg, 0.17 mmol, 80 %) as a white solid. Mp: 218 °C; $[\alpha]_D^{20}$ -452 (*c* 0.49, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (br. s, 1H), 6.91 (dd, *J* = 9.2, 11.3 Hz, 1H), 6.92 (d, *J* = 9.1 Hz, 1H), 6.82 (dd, *J* = 2.9, 9.0 Hz, 1H), 6.65 (br. s, 1H), 5.95 (d, *J* = 8.9 Hz, 1H), 5.09-5.11 (m, 1H), 4.32 (br. s, 1H,), 3.79 (s, 3H), 3.43 (br. s, 1H), 3.13-3.20 (m, 1H), 2.90-2.95 (m, 1H), 2.16-2.26 (m, 3H), 1.95-2.03 (br. m, 1H), 1.37-1.47 (m, 1H), 1.02-1.14 (m, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.0, 167.0 (br.), 151.2, 151.1, 124.1, 121.5, 117.5, 113.8, 111.1, 107.2, 80.9,

69.6, 60.1 (br.), 56.1, 47.5 (br.), 35.6 (br.), 32.0, 25.3, 16.0, 11.7; ESIMS (positive mode): 412.3, 396.4, 374.4, 359.4, 346.4 ; HRMS (CI, NH_3) *m/z* calcd for $C_{20}H_{28}N_3O_4$ $[M+H]^+$ 374.2080, found: 374.2069.



Paliurine F **4**

Paliurine F 4. To a cooled solution of *N*-Fmoc-L-isoleucine (90 mg, 0.25 mmol) and 1-hydroxyazabenzotriazole (HOAt, 42 mg, 0.31 mmol) in DMF (2 mL) were added *O*-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*′,*N*′-tetramethyluronium hexafluorophosphate (HATU, 90 mg, 0.24 mmol) and diisopropylamine (125 μL, 0.72 mmol) at 0 °C. The resulting yellow solution was stirred at 0 °C for 20 minutes and added dropwise *via* cannula to a cooled solution of **14** (63 mg, 0.17 mmol) in DMF (2 mL) at 0 °C. The flask containing the activated acid was rinced with an additional portion of DMF (2 mL) which was cannulated into the solution of the amine. The resulting yellow solution was warmed to rt and stirred overnight. The mixture was quenched at 0 °C with a saturated aqueous solution of NH_4Cl and diluted with ether. The aqueous layer was extracted with ether and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated to give an orange oil which was used in the next step without further purification.

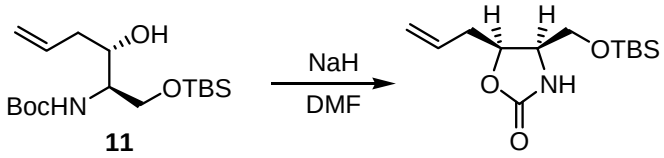
This oil was dissolved in CH_3CN (2.5 mL) and diethylamine was added (630 μL, 6.1 mmol) at rt. After 40 minutes, the crude yellow mixture was concentrated under vacuum and residue was immediately engaged in the next step without further purification.

To a cooled solution of *N*,*N*-dimethyl-L-leucine (50 mg, 0.25 mmol) and 1-hydroxyazabenzotriazole (HOAt, 44 mg, 0.32 mmol) in DMF (2 mL) were added

O-(7-azabenzotriazol-1-yl)-*N*,*N*,*N'*,*N'*-tetramethyluronium hexafluorophosphate (HATU, 90 mg, 0.24 mmol) and diisopropylethylamine (125 μL, 0.72 mmol) at 0 °C. The resulting yellow solution was stirred at 0 °C for 20 minutes and added dropwise *via* cannula to a solution of the previously deprotected amine in DMF (2 mL) at 0 °C. The flask containing the activated acid was rinced with an additional portion of DMF (2 mL) which was cannulated into the solution of the amine. The yellow solution was warmed to rt and stirred overnight. The mixture was hydrolyzed at 0 °C with a saturated aqueous solution of NH_4Cl and diluted with ether. The aqueous layer was extracted with ether and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography over silica gel (AcOEt/EtOH: 99.5/0.5) to give the desired synthetic paliurine F **4** (61 mg , 97 μmol, 57 % over three steps) as a white solid. R_f: 0.26 (Merck-Kiesegel $60F_{254}$ TLC plates, AcOEt/EtOH: 99/1); Mp: 192 °C {Lit.: unreported}; $[\alpha]_D^{20}$ -468 (*c* 1.1, CH_3CN) {Lit.: natural paliurine F: $[\alpha]_D^{20}$: -323 (*c* 1.0, CH_3CN)}[S8]; ^{1}H NMR (300 MHz, $CDCl_3$):[S9] δ 8.46 (d, *J* = 11.4 Hz, 1H), 7.41 (d, *J* = 9.0 Hz, 1H), 7.20 (d, *J* = 5.0 Hz, 1H), 6.93 (dd, *J* = 9.2, 11.3 Hz, 1H), 6.88 (d, *J* = 9.2 Hz, 1H), 6.80 (dd, *J* = 2.9, 9.0 Hz, 1H), 6.69 (d, *J* = 2.9 Hz, 1H), 5.92 (d, *J* = 9.0 Hz, 1H), 5.53 (dt, *J* = 3.2, 7.3 Hz, 1H), 4.56 (app. t, *J* = 8.5 Hz, 1H), 4.49 (d, *J* = 3.2 Hz, 1H), 4.38 (dt, *J* = 2.2, 8.5 Hz, 1H), 4.27 (app. t, *J* = 4.4 Hz, 1H), 3.78 (s, 3H), 3.55 (app. dt, *J* = 6.6, 10.8 Hz, 1H), 2.89 (dd, *J* = 5.3, 8.6 Hz, 1H), 2.59 (ddt, *J* = 13.1, 2.3, 7.1 Hz, 1H), 2.24-2.38 (m, 1H), 2.25 (s, 6H), 2.02-2.15 (m, 1H), 1.65-1.83 (m, 1H), 1.47-1.60 (m, 1H), 1.40-1.49 (m, 1H), 1.36-1.46 (m, 1H), 1.31-1.39 (m, 1H), 1.03-1.18 (m, 2H), 1.06-1.10 (m, 1H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.3 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$):[S9] δ 174.0, 172.0, 170.4, 167.2, 151.6, 151.2, 124.4, 121.6, 117.8, 113.9, 111.3, 106.8, 76.9, 67.4, 64.5, 60.4, 56.1, 53.8, 46.9, 42.4, 37.5, 37.1, 35.2, 32.7, 26.0, 24.8, 24.6, 23.4, 22.2, 16.3, 15.4, 11.8, 10.8; UV λ_{max} (log ε): 220 (4.62), 296 (4.09), 320 (4.39); IR (KBr) ν_{max} 3406, 3324, 2955, 2883, 1690, 1640, 1506, 1429, 1261, 1225, 1178, 1035, 820, 764 cm^{-1} CIMS (NH_3 gas): 628, 487, 416, 402, 374, 324, 227; HRMS (FAB) *m/z* calcd for $C_{34}H_{54}N_5O_6$ $[M+H]^+$ 628.4074, found: 628.4061.

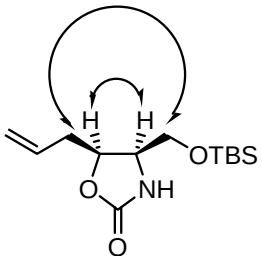
[S8] H. Y. Lin, C. H Chen, B. J. You, K. C. S. C. Liu, S. S. Lee, *J. Nat. Prod.* **2000**, *63*, 1338-1343.
[S9] See Paliurine F Spectral Data Compared to Reported Data page S18.

Assignment of stereochemistry for Alcohol 11.



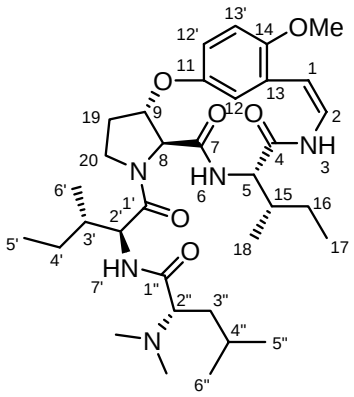
(4*R*,5*S*)-5-Allyl-4-(tert-butyl-dimethyl-silanyloxymethyl)-oxazolidin-2-one. A solution of **11** (200 mg, 0.58 mmol) in DMF (6 mL) was treated with sodium hydride (60% wt in mineral oil, 25.5 mg, 0.64 mmol) at 0°C. The resulting mixture was slowly warmed to rt over 1 hour and quenched by addition of a saturated aqueous solution of NH_4Cl. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude residue was purified by flash chromatography over silica gel (AcOEt/petroleum ether: 35/65) to give the corresponding oxazolidinone (69 mg , 0.25 mmol, 43 %) as a colorless oil. $[\alpha]_D^{20}$ 19 (*c* 0.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 6.05 (s, 1H), 5.69-5.90 (m, 1H), 5.07-5.19 (m, 2H), 4.66 (td, *J* = 7.9, 5.6 Hz, 1H), 3.76-3.86 (m, 1H), 3.60-3.70 (m, 2H), 2.53-2.63 (m, 1H), 2.41-2.50 (m, 1H), 0.87 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.6, 133.1, 118.3, 78.4, 61.7, 56.6, 33.5, 25.8, 18.2, -5.4; IR (neat) ν_{max} 3375, 2963, 1716 1164 cm^{-1}; HRMS (CI, NH_3) *m/z* calcd for $C_{13}H_{26}NO_3Si$ $[M+H]^+$ 272.1682, found 272.1671.

Selected nuclear Overhauser effects:



Paliurine F Spectral Data Compared to Reported Data

^{1}H NMR (Synthetic at 300 MHz; Natural at 400 MHz)

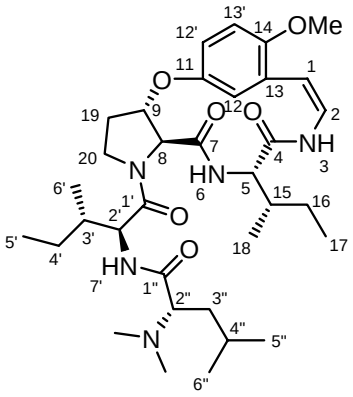


Paliurine F

	Synthetic		**Natural**		
Position	δ	multiplicity	δ	multiplicity	Δδ
1 (1H)	5.91	d, *J* = 9.0 Hz	5.91	d, *J* = 9.0 Hz	0.00
2 (1H)	6.92	dd, *J* = 11.3, 9.2 Hz	6.92	dd, *J* = 11.3, 9.0 Hz	0.00
3 (1H)	8.45	d, *J* = 11.4 Hz	8.44	d, *J* = 11.3 Hz	0.01
5 (1H)	4.26	app. t, *J* = 4.4 Hz	4.26	dd, *J* = 4.4, 4.8 Hz	0.00
6 (1H)	7.19	d, *J* = 5.0 Hz	7.19	d, *J* = 4.8 Hz	0.00
8 (1H)	4.48	d, *J* = 3.2 Hz	4.48	d, *J* = 3.2 Hz	0.00
9 (1H)	5.52	dt, *J* = 3.2, 7.3 Hz	5.52	dt, *J* = 3.2, 7.2 Hz	0.00
12 (1H)	6.68	d, *J* = 2.9 Hz	6.68	d, *J* = 2.9 Hz	0.00
12' (1H)	6.79	dd, *J* = 9.0, 2.9 Hz	6.79	dd, *J* = 9.0, 2.9 Hz	0.00
13' (1H)	6.87	d, *J* = 9.2 Hz	6.87	d, *J* = 9.0 Hz	0.00
15 (1H)	2.01-2.14	m	2.08	m	0.00
16 (1H)	1.02-1.17	m	1.09	m	0.01
16 (1H)	1.30-1.38	m	1.34	m	0.00
17 (3H)	0.86	t, *J* = 7.5 Hz	0.86	t, *J* = 7.4 Hz	0.00
18 (3H)	0.95	d, *J* = 7.0 Hz	0.95	d, *J* = 7.0 Hz	0.00
19α (1H)	2.23-2.37	m	2.32	m	-0.02
19β (1H)	2.58	ddt, *J* = 13.1, 2.3, 7.1 Hz	2.58	ddt, *J* = 12.9, 2.3, 6.8 Hz	0.00

20α (1H)	4.37	dt, *J* = 2.2, 8.5 Hz	4.37	dt, *J* = 2.1, 8.4 Hz	0.00
20β (1H)	3.54	app. dt, *J* = 6.6, 10.8 Hz	3.54	m	0.00
OMe (3H)	3.77	s	3.78	s	-0.01
2' (1H)	4.55	app. t, *J* = 8.5 Hz	4.55	dd, *J* = 8.9, 8.5 Hz	0.00
3' (1H)	1.65-1.83	m	1.77	m	-0.03
4' (1H)	1.05-1.09	m	1.06	m	-0.01
4' (1H)	1.39-1.48	m	1.44	m	0.00
5' (3H)	0.84	t, *J* = 7.5 Hz	0.84	t, *J* = 7.5 Hz	0.00
6' (3H)	0.81	d, *J* = 6.6 Hz	0.81	d, *J* = 6.8 Hz	0.00
7' (1H)	7.40	d, *J* = 9.0 Hz	7.41	d, *J* = 8.9 Hz	-0.01
2" (1H)	2.88	dd, *J* = 8.6, 5.3 Hz	2.89	dd, *J* = 8.4, 5.0 Hz	-0.01
3" (1H)	1.35-1.45	m	1.40	m	0.00
3" (1H)	1.47-1.59	m	1.53	m	0.00
4" (1H)	1.02-1.17	m	1.10	m	0.00
5" (3H)	0.90	d, *J* = 6.3 Hz	0.90	d, *J* = 6.4 Hz	0.00
6" (3H)	0.92	d, *J* = 6.4 Hz	0.92	d, *J* = 6.5 Hz	0.00
NMe_2 (6H)	2.24	s	2.24	s	0.00

^{13}C NMR (Synthetic at 75 MHz; Natural at 100 MHz)



Paliurine F

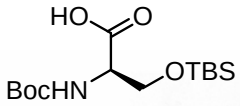
	Synthetic	**Natural**	
Position	δ	δ	Δδ
1	106.6	106.8	-0.2
2	121.6	121.6	0.0
4	167.0	167.2	-0.2
5	60.3	60.4	-0.1
7	170.5	170.4	0.1
8	64.7	64.5	0.2
9	76.9	76.9	0.0
11	151.4	151.2	0.2
12	111.5	111.3	0.2
12'	117.8	117.8	0.0
13	124.8	124.4	0.4
13'	114.3	113.9	0.4
14	151.8	151.6	0.2
15	35.4	35.2	0.2
16	24.8	24.8	0.0
17	11.7	11.8	-0.1
18	16.2	16.3	-0.1
19	32.7	32.7	0.0
20	46.8	46.9	-0.1

OMe	56.2	56.1	-0.1
1'	172.0	172.0	0.0
2'	53.9	53.8	0.1
3'	37.6	37.5	0.1
4'	24.7	24.6	0.1
5'	10.8	10.8	0.0
6'	15.4	15.4	0.0
1"	173.7	174.0	-0.3
2"	67.7	67.4	0.3
3"	37.2	37.1	0.1
4"	26.0	26.0	0.0
5"	23.3[a]	23.4	-0.1
6"	22.2[a]	22.2	0.0
NMe_2	42.3	42.4	-0.1

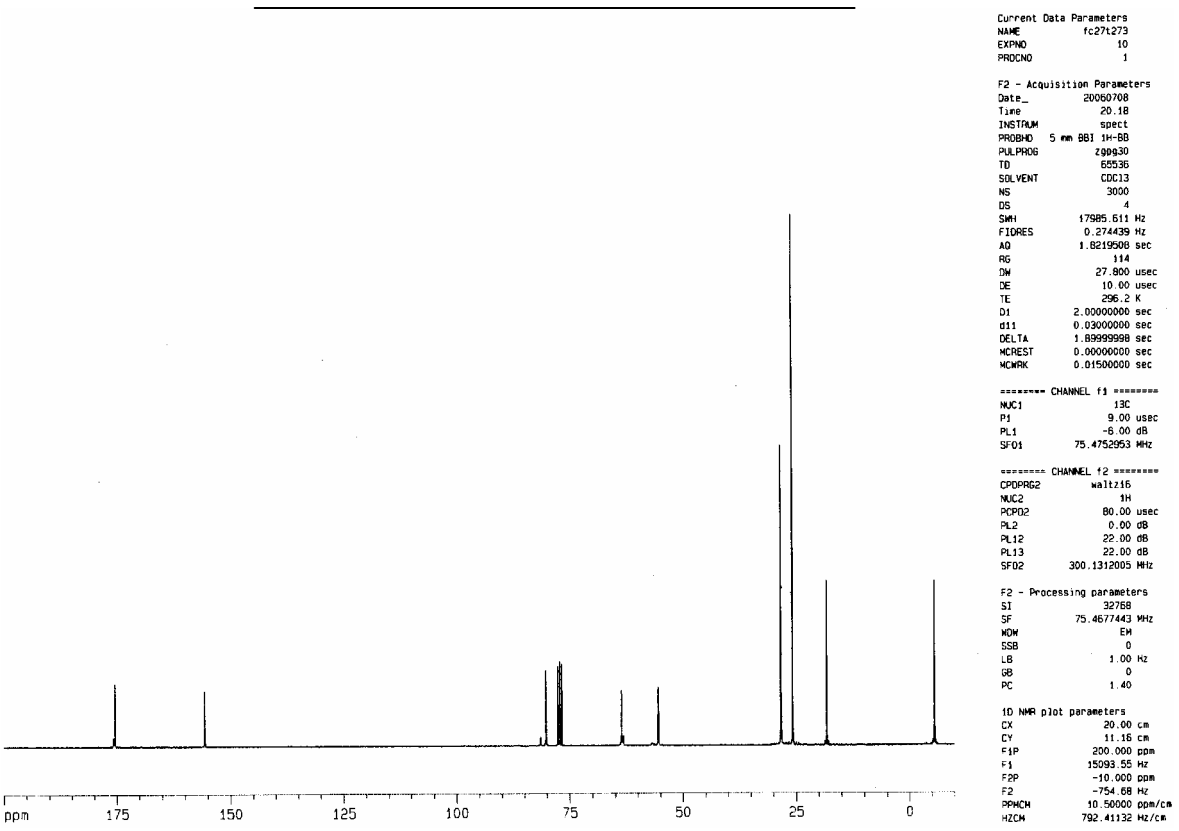
[a] both assignments can be interchanged

Supporting Information

^{1}H and ^{13}C NMR spectra of intermediates and synthetic paliurine F


HO
O
BocHN
OTBS

Integral
1.2351
1.0063
1.0164
1.0633
1.0700
9.0000
9.4715
6.4581
ppm
10
8
6
4
2
0
Current Data Parameters
NAME fc27t273
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060708
Time 20.37
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6313.131 Hz
FIDRES 0.192661 Hz
AQ 2.5952756 sec
RG 32
DW 79.200 usec
DE 6.50 usec
TE 296.1 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.20 usec
PL1 0.00 dB
SFO1 300.1328512 MHz
F2 - Processing parameters
SI 32768
SF 300.1300110 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 11.67 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.62500 ppm/cm
HZCM 187.58125 Hz/cm


ppm
175
150
125
100
75
50
25
0
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PROCNO 1
F2 - Acquisition Parameters
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Time 20.18
INSTRUM spect
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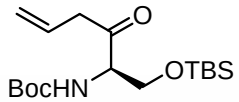
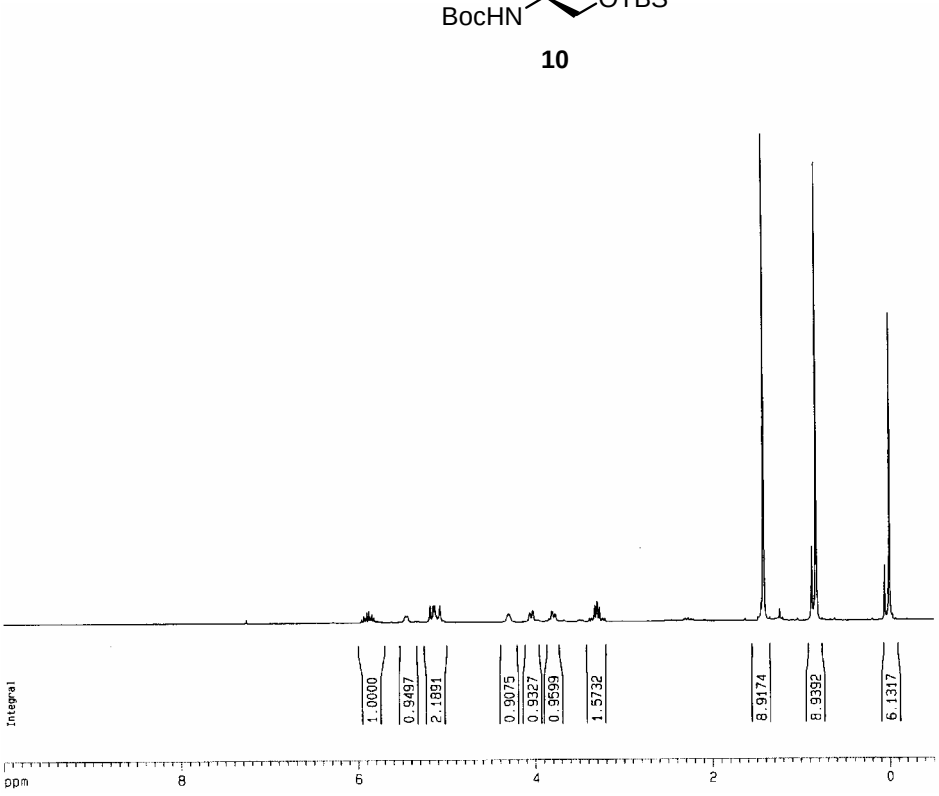
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 114
DW 27.800 usec
DE 10.00 usec
TE 296.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -6.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 22.00 dB
PL13 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677443 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 11.16 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 10.50000 ppm/cm
HZCM 792.41132 Hz/cm



10

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EXPNO                       14
PROCNO                       1

F2 - Acquisition Parameters
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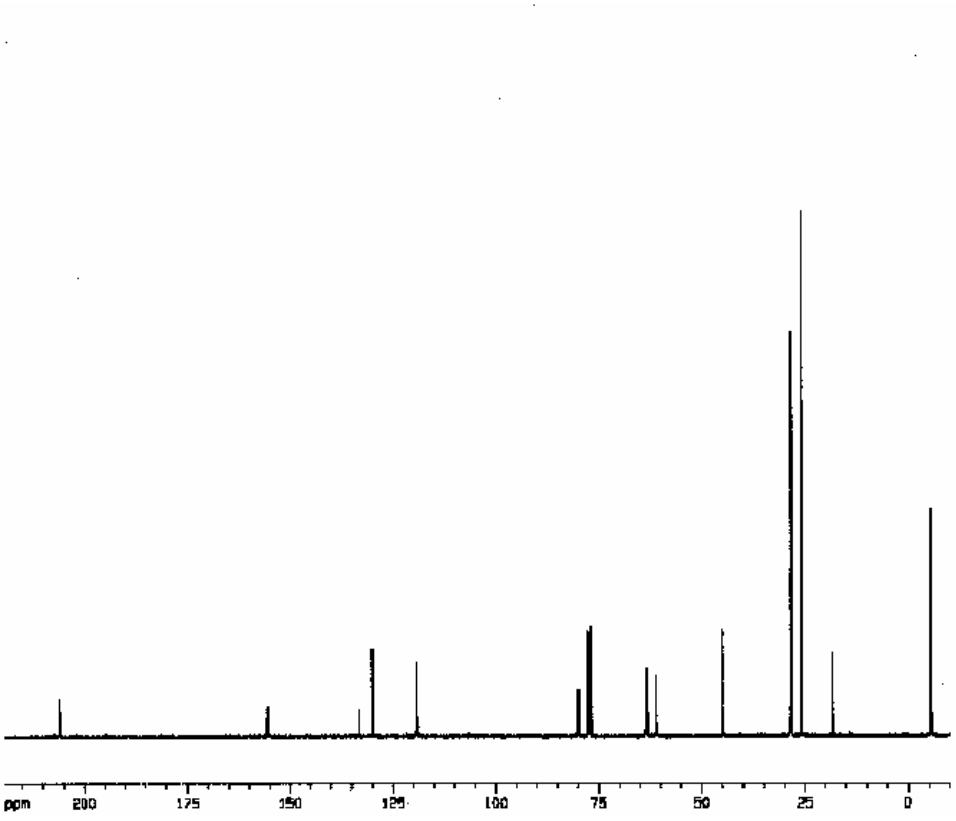
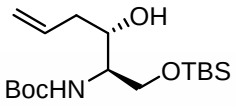
Time                      0.47
INSTRUM                   spect
PROBHD    5 mm BBI 1H-BB
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                  6172.839 Hz
FIDRES               0.094190 Hz
AQ                   5.3084660 sec
RG                          64
DW                     81.000 usec
DE                     10.00 usec
TE                     296.1 K
D1                   1.00000000 sec
MCREST               0.00000000 sec
MCWRK                0.01500000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       6.20 usec
PL1                      0.00 dB
SFO1                300.1318534 MHz

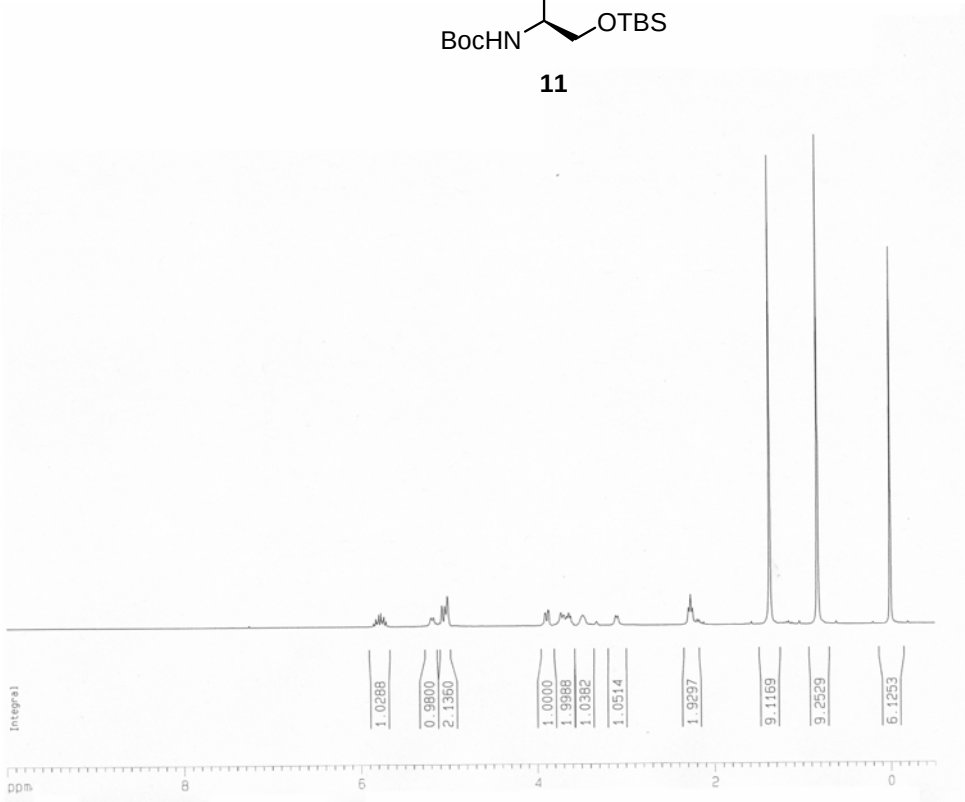
F2 - Processing parameters
SI                       32768
SF                  300.1300149 MHz
WDW                         EM
SSB                          0
LB                       0.30 Hz
GB                           0
PC                       1.00

1D NMR plot parameters
CX                      20.00 cm
CY                      11.71 cm
F1P                     10.000 ppm
F1                      3001.30 Hz
F2P                     -0.500 ppm
F2                      -150.06 Hz
PPMCM                   0.52500 ppm/cm
HZCM                    157.56825 Hz/cm
```





11

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Current Data Parameters
NAME                 fc27g485
EXPNO                      14
PROCNO                      1

F2 - Acquisition Parameters
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Time                    4.49
INSTRUM                spect
PROBHD   5 mm BBI 1H-BB
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         16
DS                          2
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                  5.3084660 sec
RG                       28.5
DW                     81.000 usec
DE                     10.00 usec
TE                     296.0 K
D1                  1.00000000 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      6.20 usec
PL1                     0.00 dB
SF01             300.1318534 MHz

F2 - Processing parameters
SI                         32768
SF                  300.1300154 MHz
WDW                           EM
SSB                            0
LB                      0.30 Hz
GB                             0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                     10.78 cm
F1P                   10.000 ppm
F1                  3001.30 Hz
F2P                   -0.500 ppm
F2                  -150.06 Hz
PPMCM                0.52500 ppm/cm
HZCM                157.56825 Hz/cm
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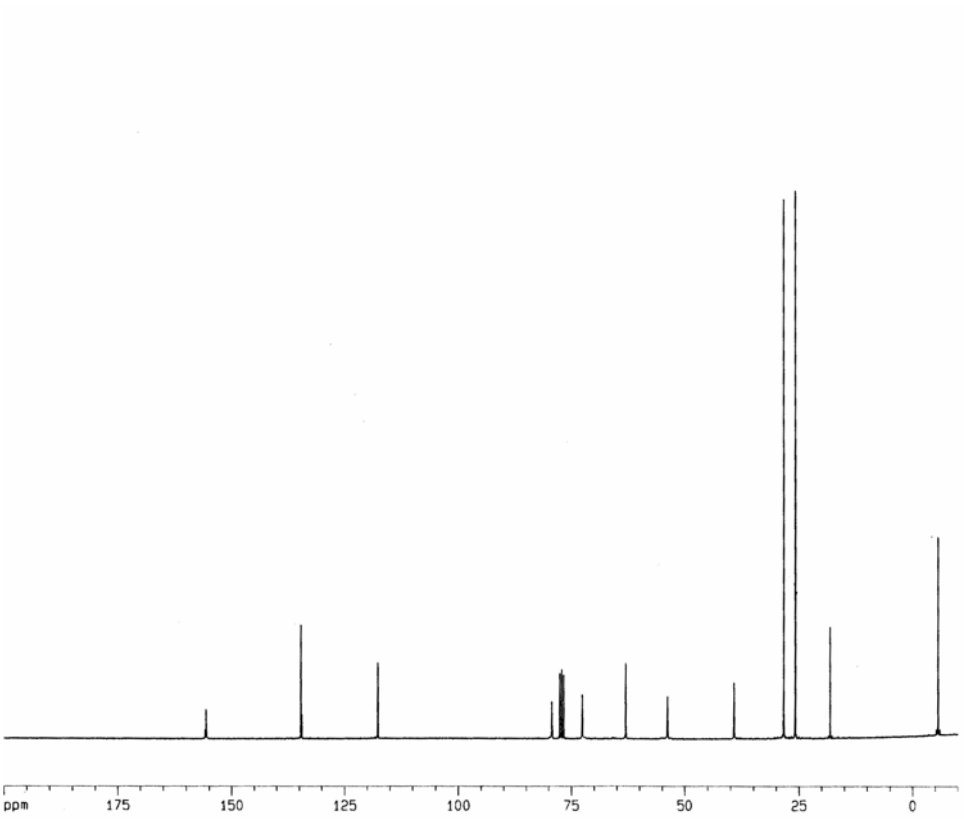


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Current Data Parameters
NAME                 fc27g485
EXPNO                      10
PROCNO                      1

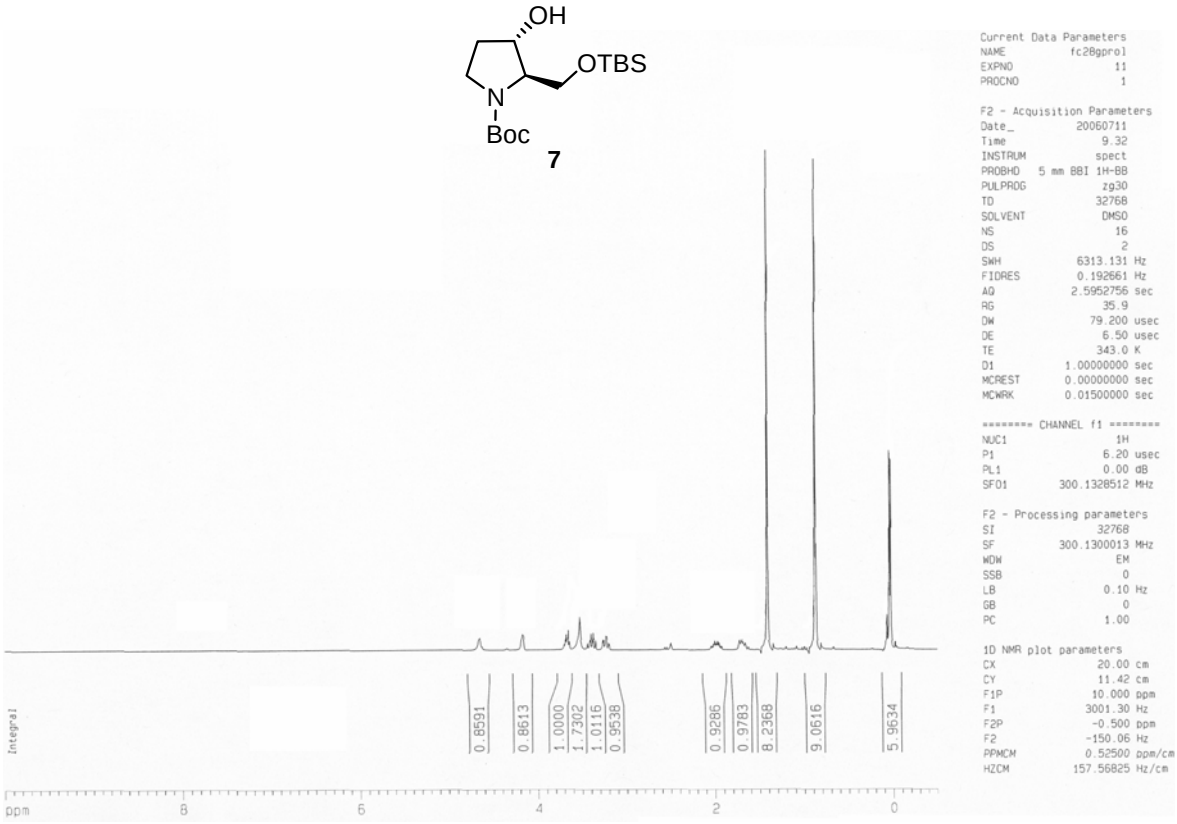
F2 - Acquisition Parameters
Date_               20060709
Time                    4.22
INSTRUM                spect
PROBHD   5 mm BBI 1H-BB
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       3000
DS                          4
SWH                17985.611 Hz
FIDRES              0.274439 Hz
AQ                  1.8219508 sec
RG                        128
DW                     27.800 usec
DE                     10.00 usec
TE                     296.1 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                      9.00 usec
PL1                    -6.00 dB
SF01             75.4752953 MHz

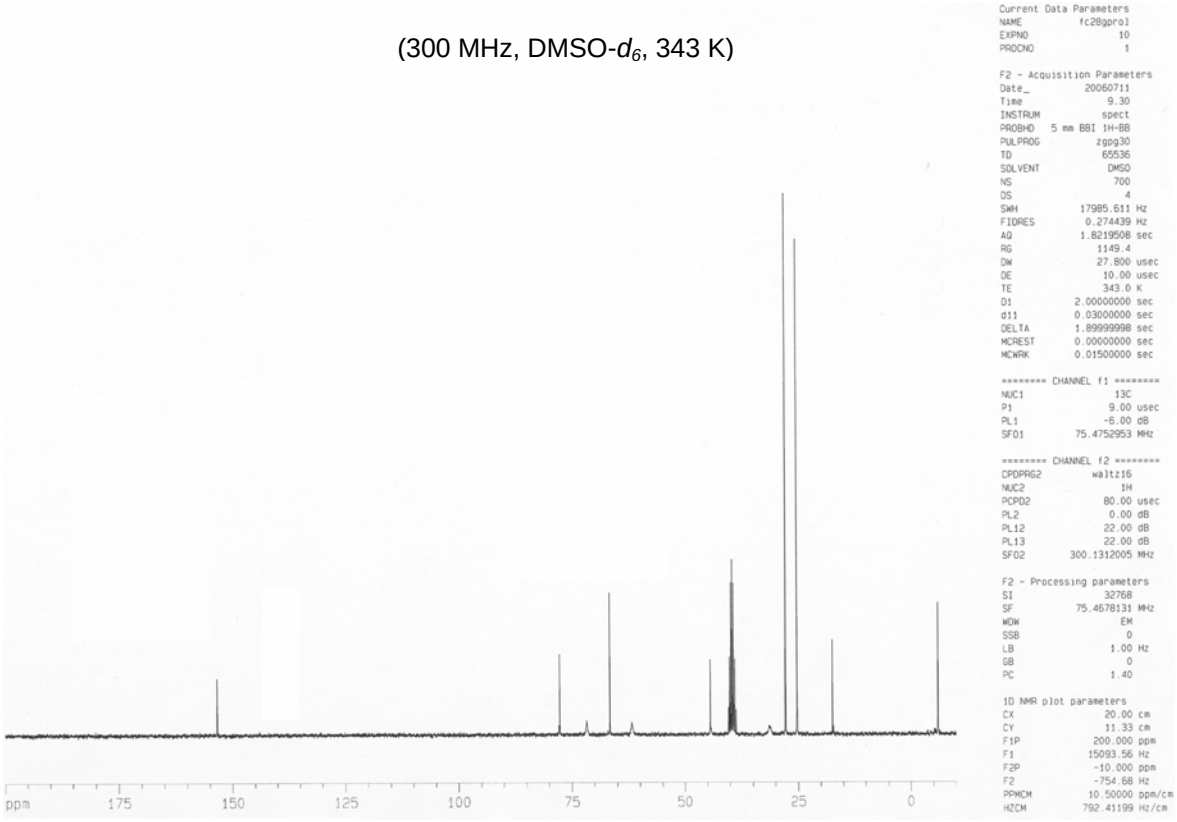
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   22.00 dB
PL13                   22.00 dB
SF02             300.1312005 MHz

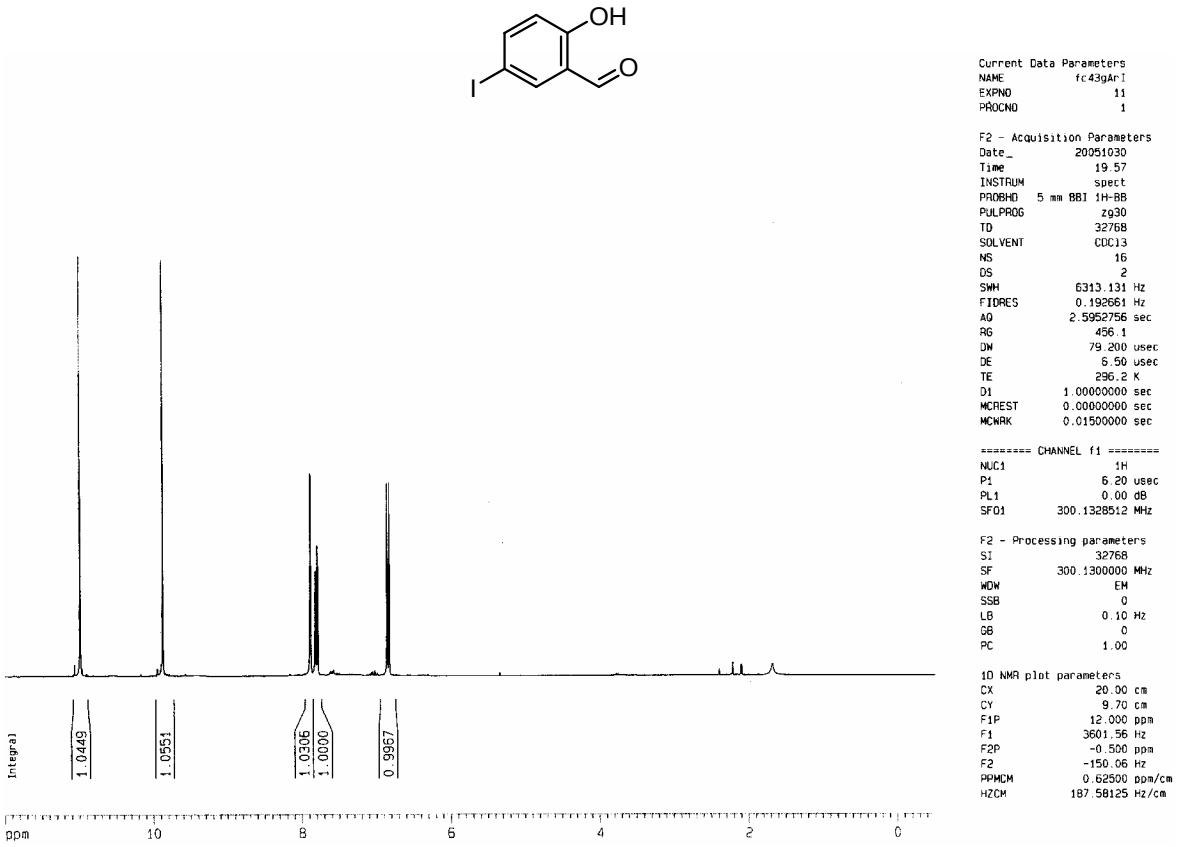
F2 - Processing parameters
SI                         32768
SF                  75.4677471 MHz
WDW                           EM
SSB                            0
LB                      1.00 Hz
GB                             0
PC                      1.40

1D NMR plot parameters
CX                     20.00 cm
CY                     11.51 cm
F1P                   200.000 ppm
F1                  15093.55 Hz
F2P                   -10.000 ppm
F2                  -754.68 Hz
PPMCM               10.50000 ppm/cm
HZCM               792.41138 Hz/cm
```



(300 MHz, DMSO-d_6, 343 K)



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EXPNO                      11
PROCNO                      1

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Time                   19.57
INSTRUM                spect
PROBHD   5 mm BBI 1H-BB
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 6313.131 Hz
FIDRES                0.192661 Hz
AQ                 2.5952756 sec
RG                     456.1
DW                    79.200 usec
DE                     6.50 usec
TE                     296.2 K
D1                 1.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       6.20 usec
PL1                      0.00 dB
SFO1              300.1328512 MHz

F2 - Processing parameters
SI                        32768
SF                300.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.10 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                       20.00 cm
CY                        9.70 cm
F1P                     12.000 ppm
F1                     3601.56 Hz
F2P                     -0.500 ppm
F2                     -150.06 Hz
PPMCM                  0.62500 ppm/cm
HZCM                 187.58125 Hz/cm
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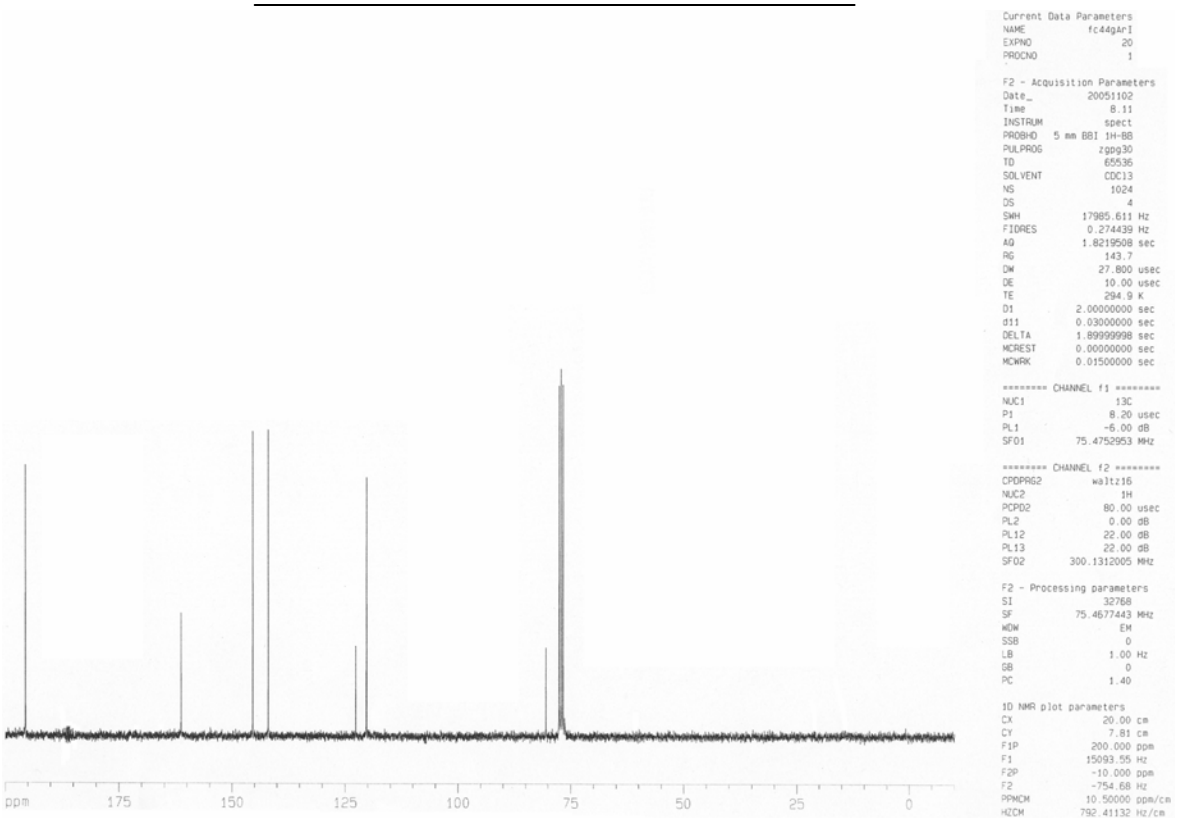


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Current Data Parameters
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EXPNO                      20
PROCNO                      1

F2 - Acquisition Parameters
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Time                    8.11
INSTRUM                spect
PROBHD   5 mm BBI 1H-BB
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH                17985.611 Hz
FIDRES                0.274439 Hz
AQ                 1.8219508 sec
RG                     143.7
DW                    27.800 usec
DE                     10.00 usec
TE                     294.9 K
D1                 2.00000000 sec
d11                0.03000000 sec
DELTA              1.89999998 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                       8.20 usec
PL1                     -6.00 dB
SFO1              75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    22.00 dB
PL13                    22.00 dB
SFO2              300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF                75.4677443 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40

1D NMR plot parameters
CX                       20.00 cm
CY                        7.81 cm
F1P                    200.000 ppm
F1                    15093.55 Hz
F2P                    -10.000 ppm
F2                     -754.68 Hz
PPMCM                 10.50000 ppm/cm
HZCM                 792.41132 Hz/cm
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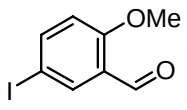
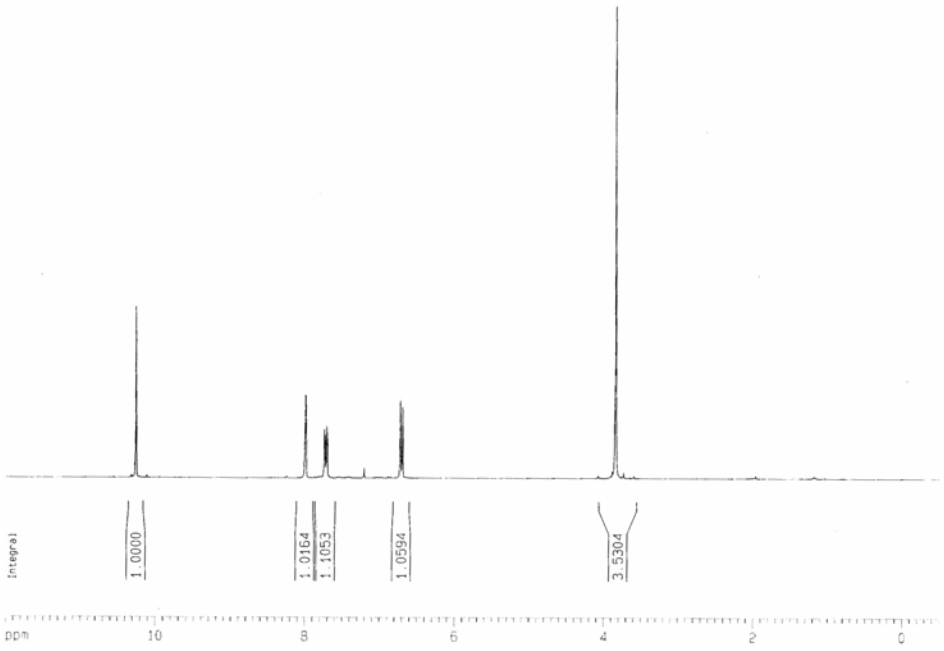


8

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Current Data Parameters
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EXPNO                      12
PROCNO                      1

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Time                    2.39
INSTRUM                spect
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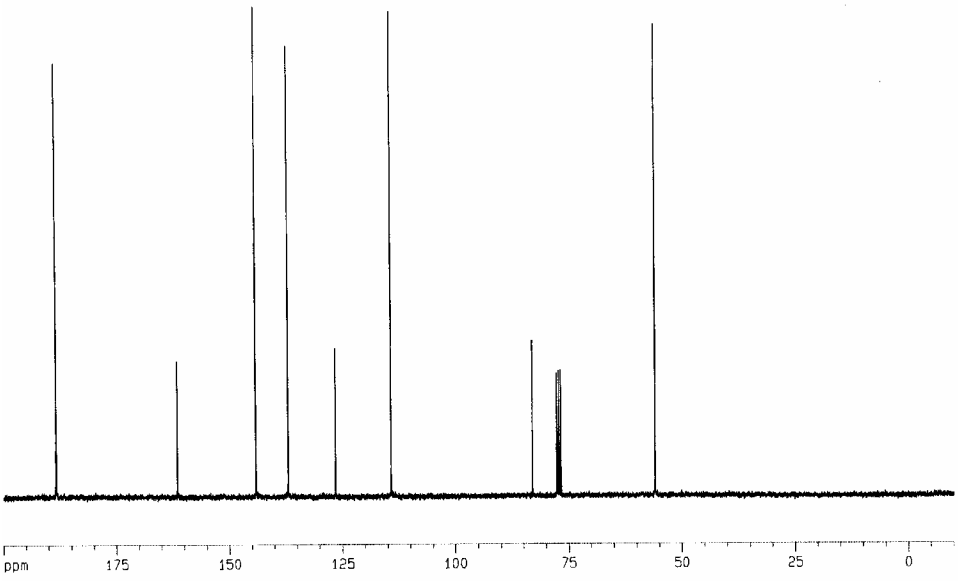
PULPROG                zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 6313.131 Hz
FIDRES              0.192661 Hz
AQ                  2.5952756 sec
RG                      228.1
DW                     79.200 usec
DE                      6.50 usec
TE                     297.4 K
D1                  1.00000000 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       6.20 usec
PL1                      0.00 dB
SFO1              300.1328512 MHz

F2 - Processing parameters
SI                         32768
SF                300.1300332 MHz
WDW                           EM
SSB                            0
LB                          0.10 Hz
GB                             0
PC                          1.00

1D NMR plot parameters
CX                         20.00 cm
CY                         10.10 cm
F1P                       12.000 ppm
F1                       3601.56 Hz
F2P                       -0.500 ppm
F2                       -150.07 Hz
PPMCM                    0.62500 ppm/cm
HZCM                   187.58128 Hz/cm
```




```
Current Data Parameters
NAME                 fc24vb09
EXPNO                      10
PROCNO                      1

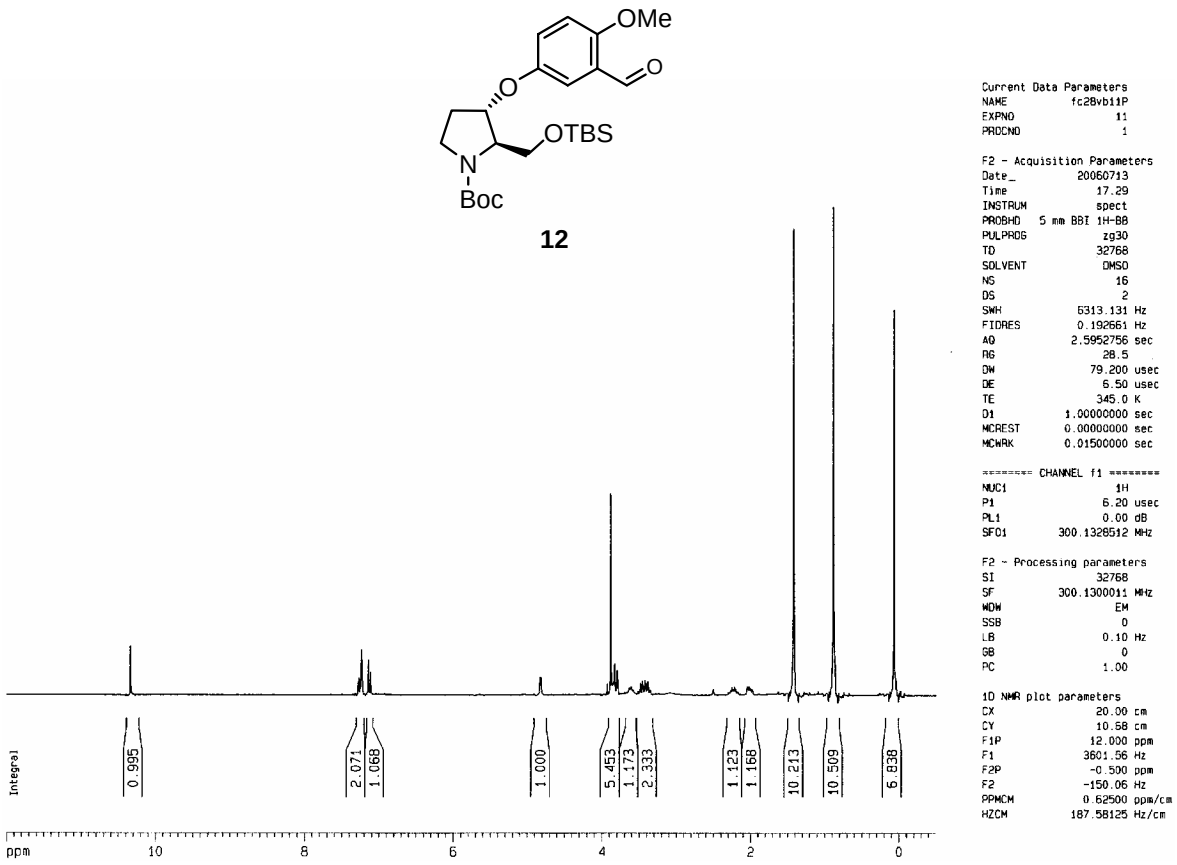
F2 - Acquisition Parameters
Date_               20060515
Time                   10.15
INSTRUM                spect
PROBHD   5 mm BBI 1H-BB
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                      1024
DS                         4
SWH                17985.611 Hz
FIDRES              0.274439 Hz
AQ                  1.8219508 sec
RG                       128
DW                     27.800 usec
DE                     10.00 usec
TE                     297.1 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.00 usec
PL1                      -6.00 dB
SFO1              75.4752953 MHz

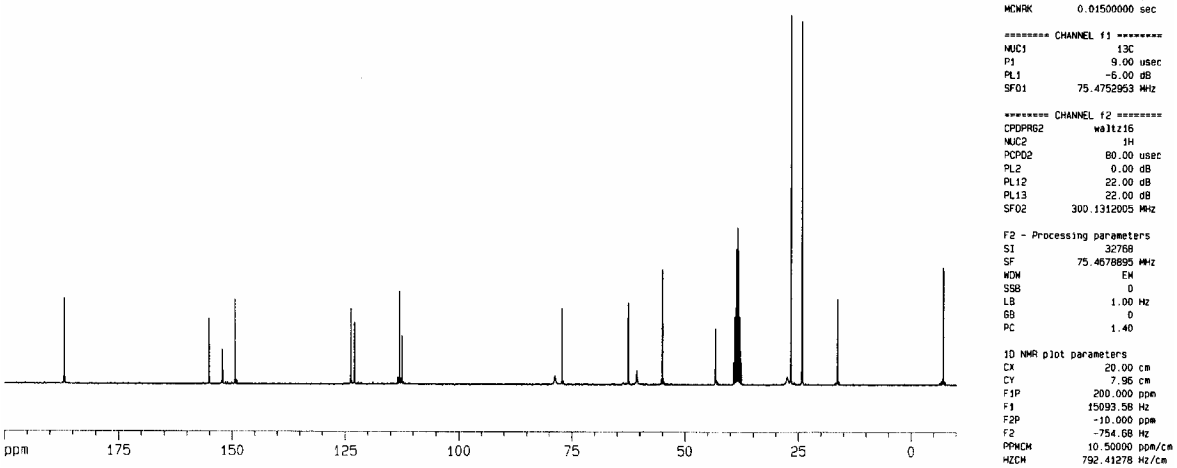
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    22.00 dB
PL13                    22.00 dB
SFO2              300.1312005 MHz

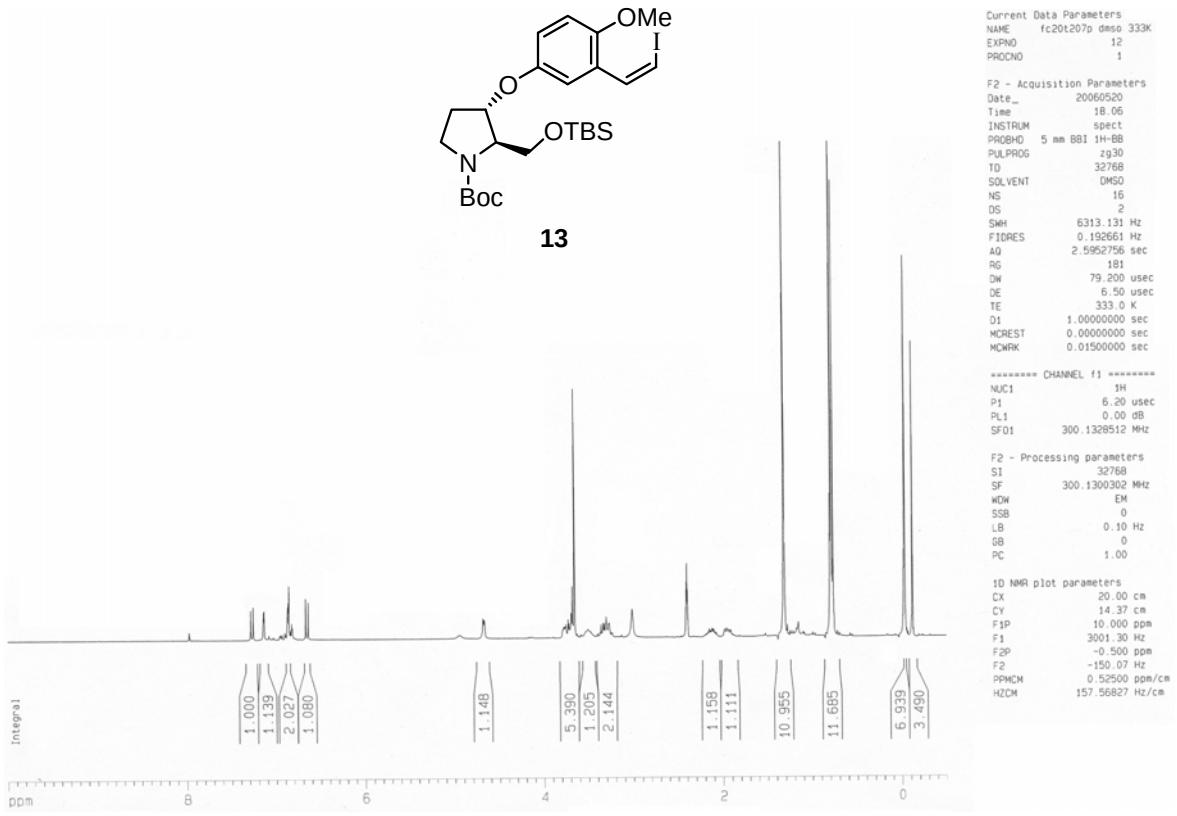
F2 - Processing parameters
SI                         32768
SF                75.4677487 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                         20.00 cm
CY                         10.26 cm
F1P                      200.000 ppm
F1                     15093.55 Hz
F2P                      -10.000 ppm
F2                      -754.68 Hz
PPMCM                   10.50000 ppm/cm
HZCM                   792.41138 Hz/cm
```



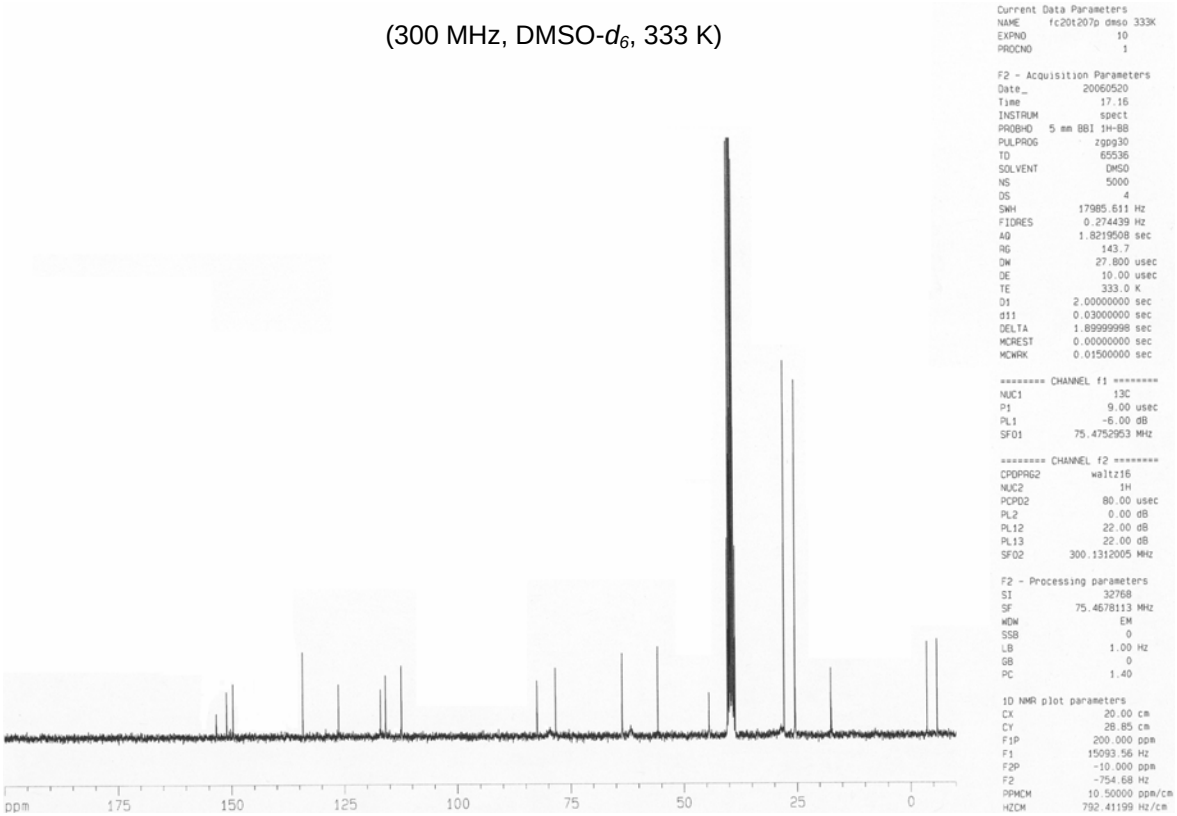
(300 MHz, DMSO-d_6, 345 K)

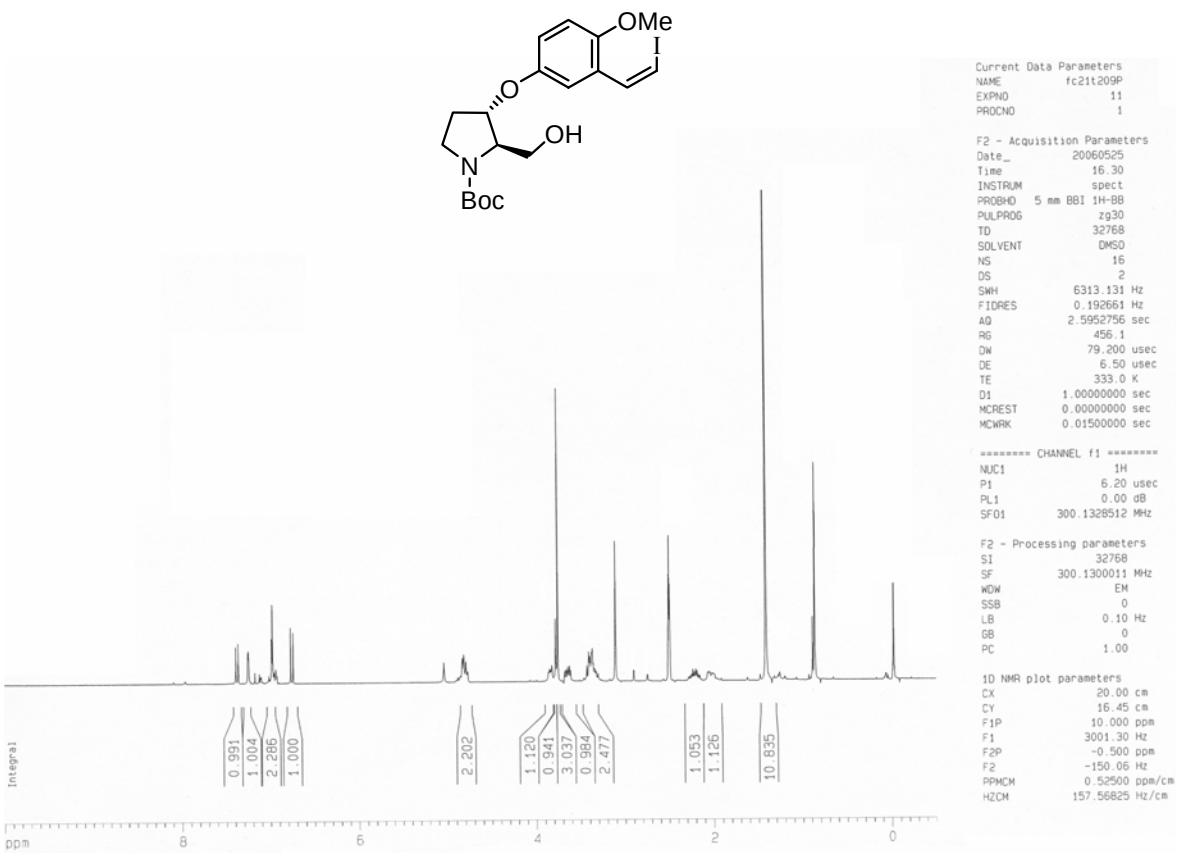




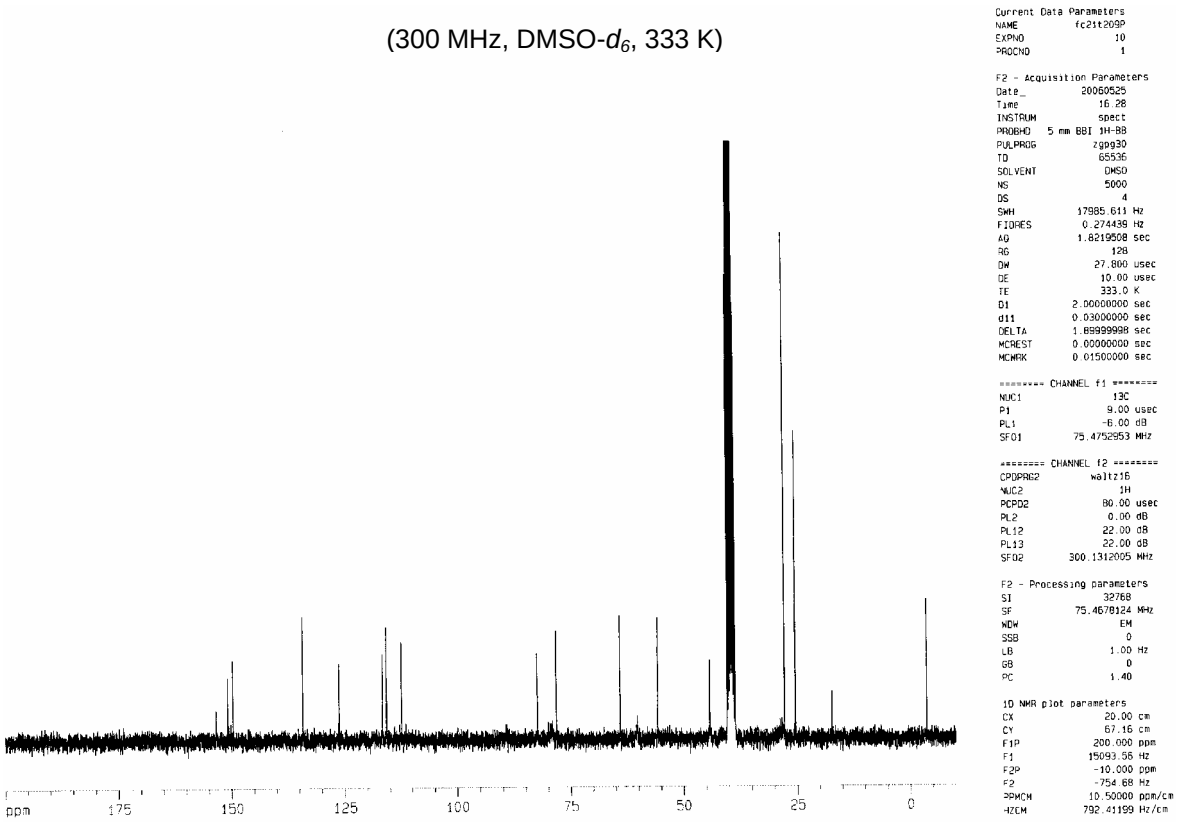
13

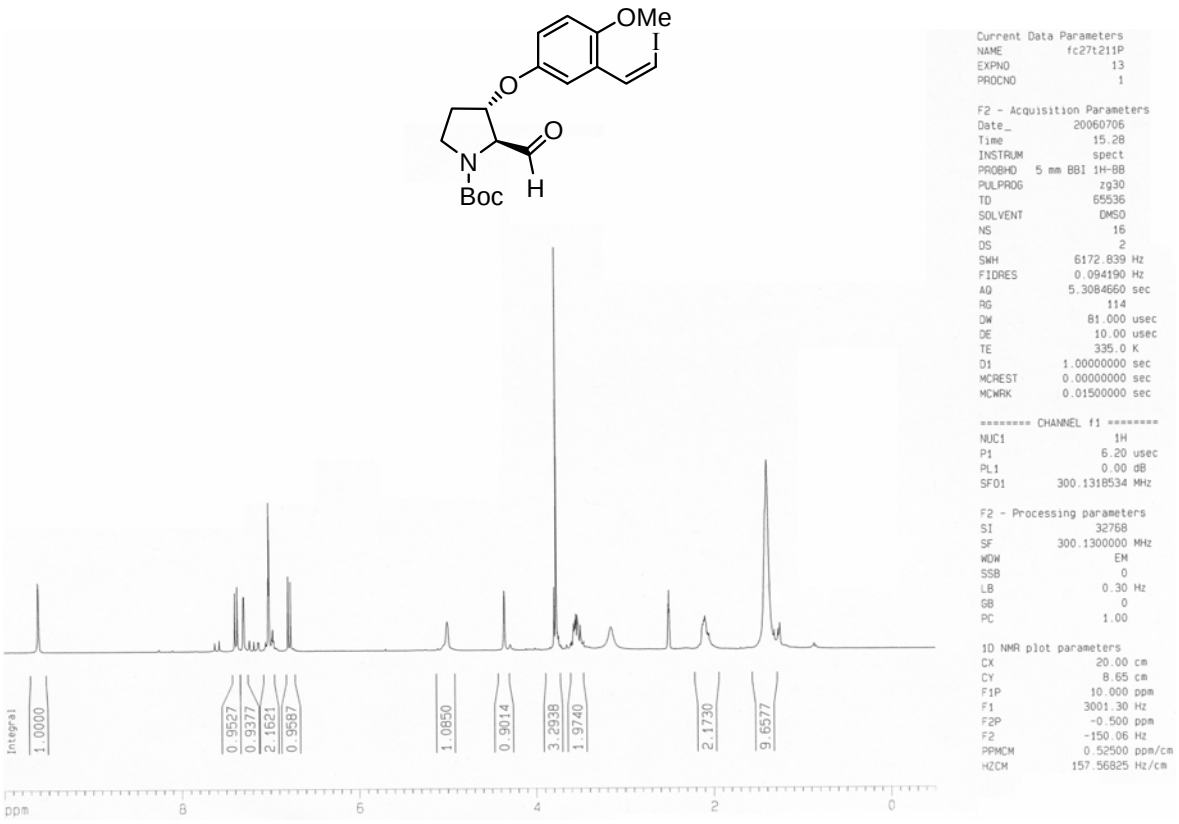
(300 MHz, DMSO-d_6, 333 K)



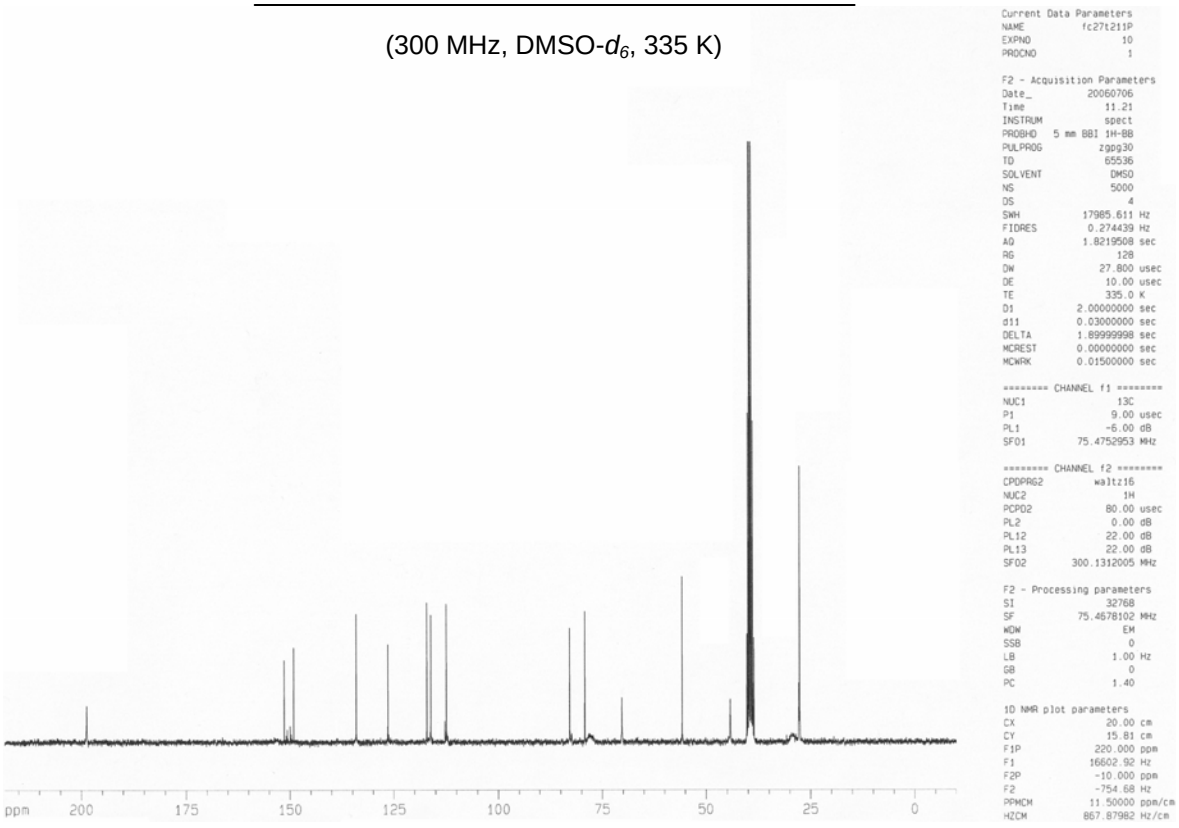


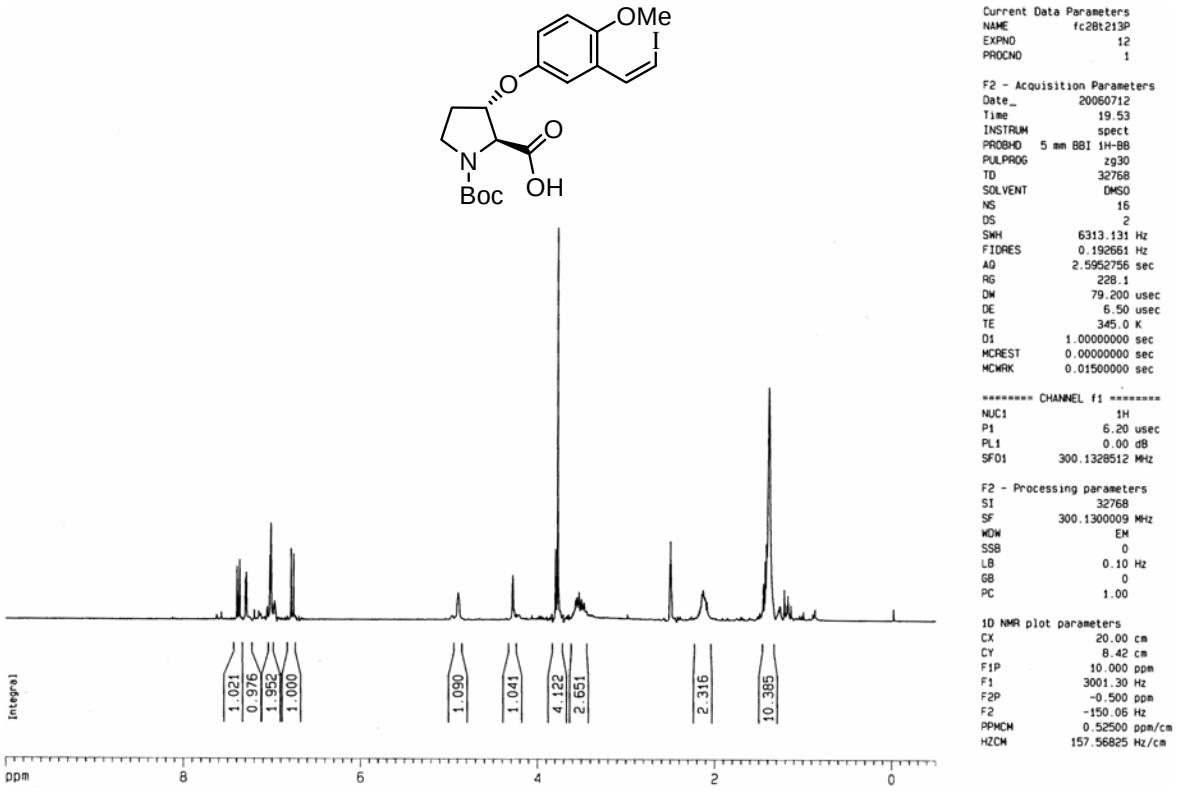
(300 MHz, DMSO-d_6, 333 K)





(300 MHz, DMSO-d_6, 335 K)






```
Current Data Parameters
NAME            fc28t213P
EXPNO                  12
PROCNO                  1

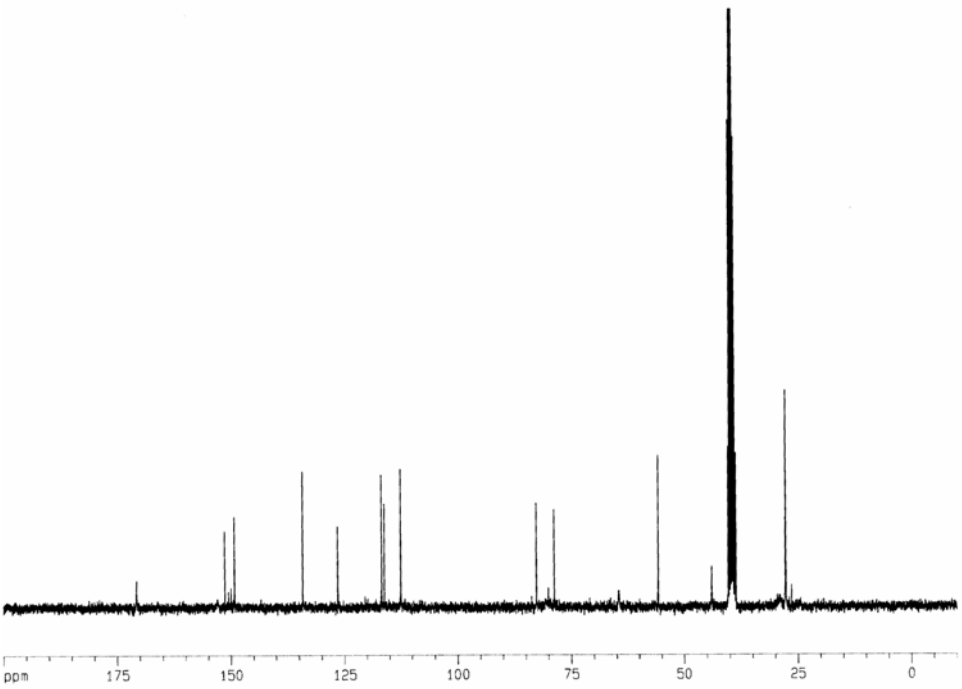
F2 - Acquisition Parameters
Date_            20060712
Time                19.53
INSTRUM             spect
PROBHD   5 mm BBI 1H-BB
PULPROG             zg30
TD                 32768
SOLVENT             DMSO
NS                     16
DS                      2
SWH             6313.131 Hz
FIDRES          0.192661 Hz
AQ              2.5952756 sec
RG                  228.1
DW                 79.200 usec
DE                  6.50 usec
TE                 345.0 K
D1              1.00000000 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   6.20 usec
PL1                  0.00 dB
SFO1          300.1328512 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300009 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                  8.42 cm
F1P               10.000 ppm
F1              3001.30 Hz
F2P               -0.500 ppm
F2              -150.06 Hz
PPMCM           0.52500 ppm/cm
HZCM          157.56825 Hz/cm
```

(300 MHz, DMSO-d_6, 345 K)




```
Current Data Parameters
NAME            fc28t213P
EXPNO                  10
PROCNO                  1

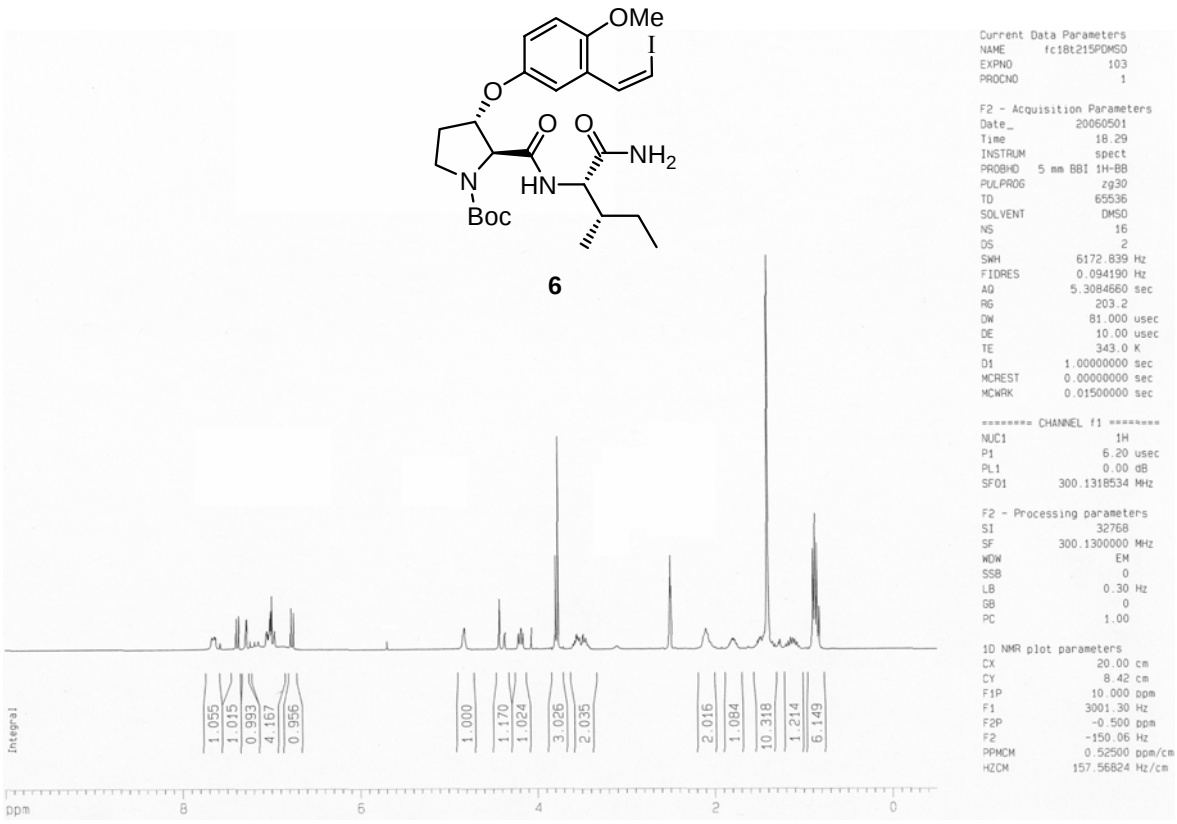
F2 - Acquisition Parameters
Date_            20060712
Time                16.18
INSTRUM             spect
PROBHD   5 mm BBI 1H-BB
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                   5000
DS                      4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                   128
DW                 27.800 usec
DE                 10.00 usec
TE                 345.0 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   9.00 usec
PL1                 -6.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                22.00 dB
PL13                22.00 dB
SFO2          300.1312005 MHz

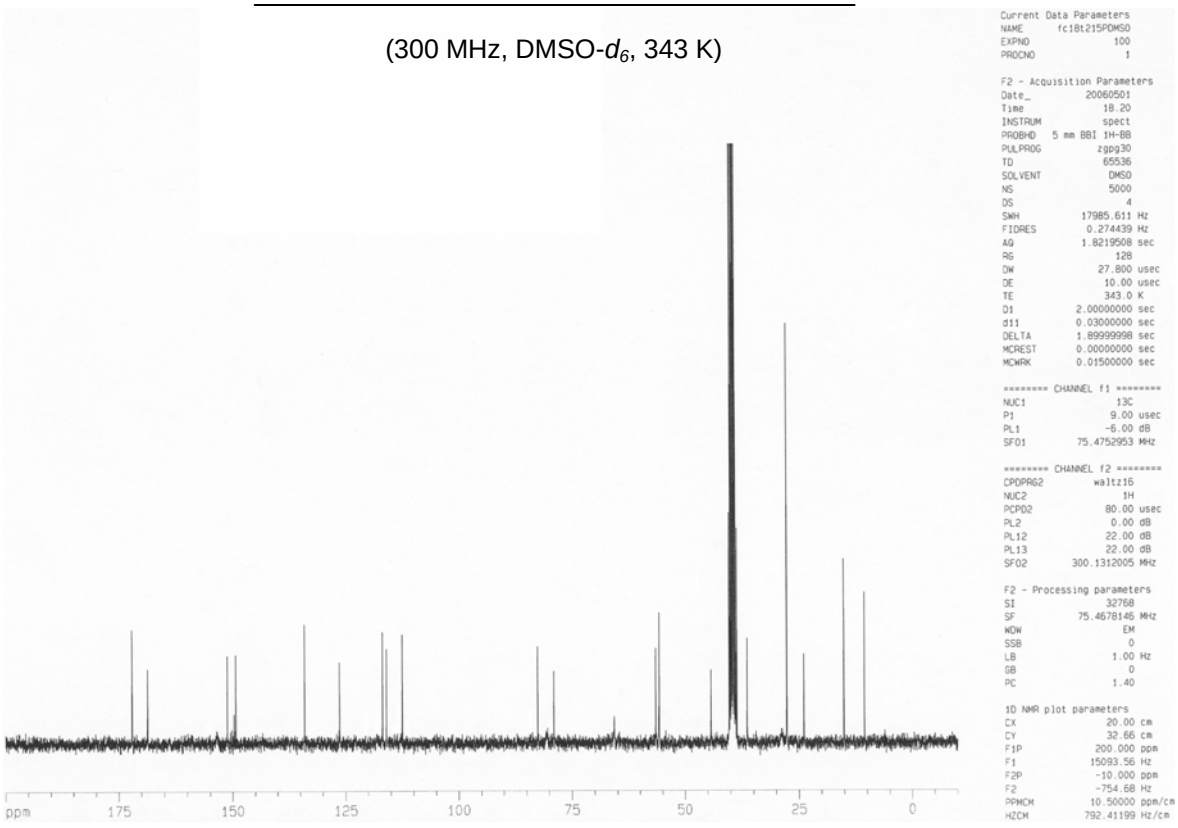
F2 - Processing parameters
SI                 32768
SF          75.4678141 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

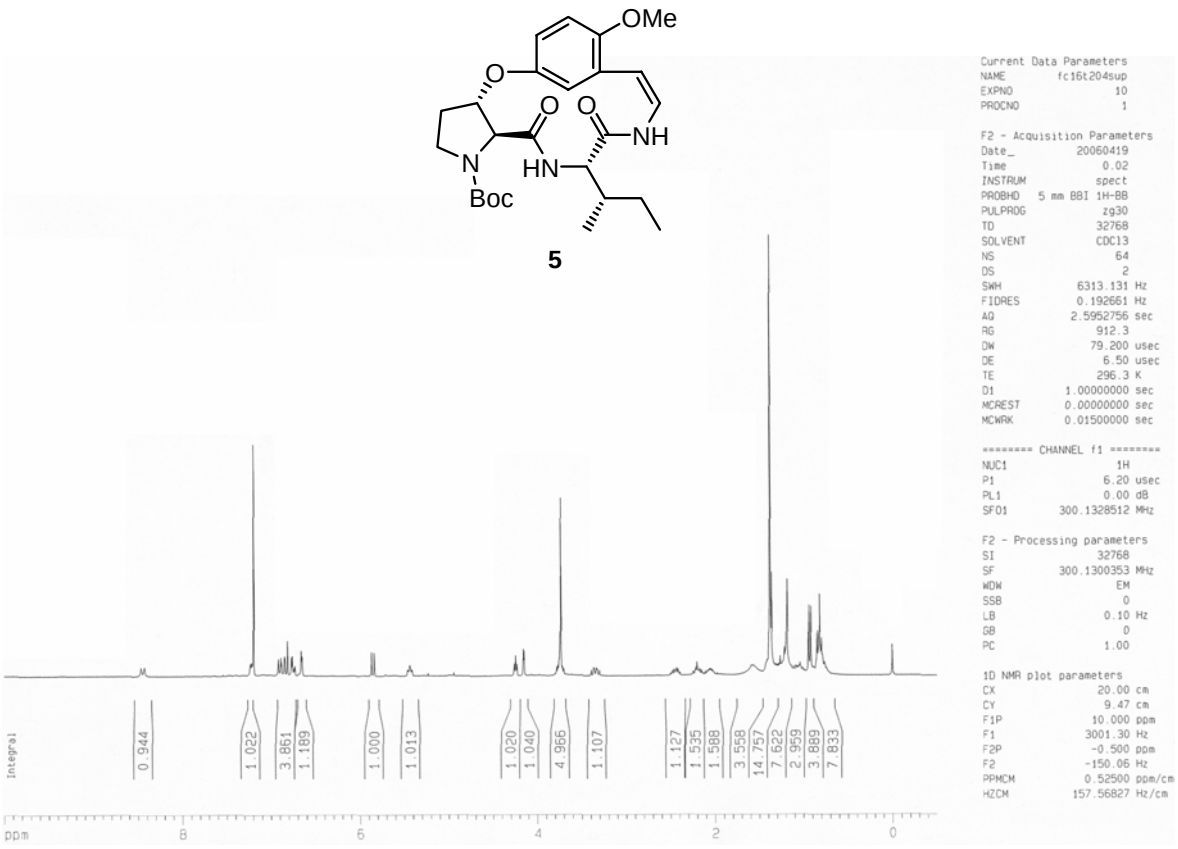
1D NMR plot parameters
CX                 20.00 cm
CY                 23.56 cm
F1P              200.000 ppm
F1              15093.56 Hz
F2P              -10.000 ppm
F2              -754.68 Hz
PPMCM           10.50000 ppm/cm
HZCM          792.41199 Hz/cm
```

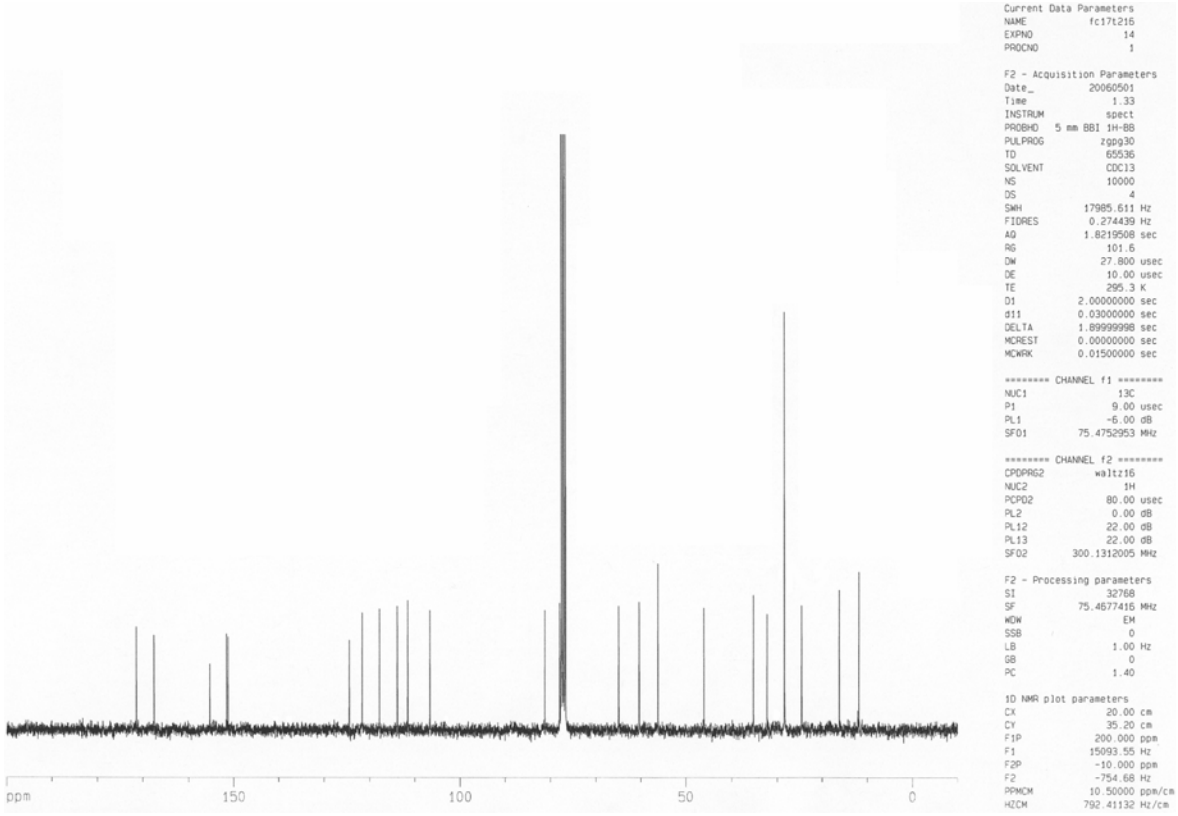


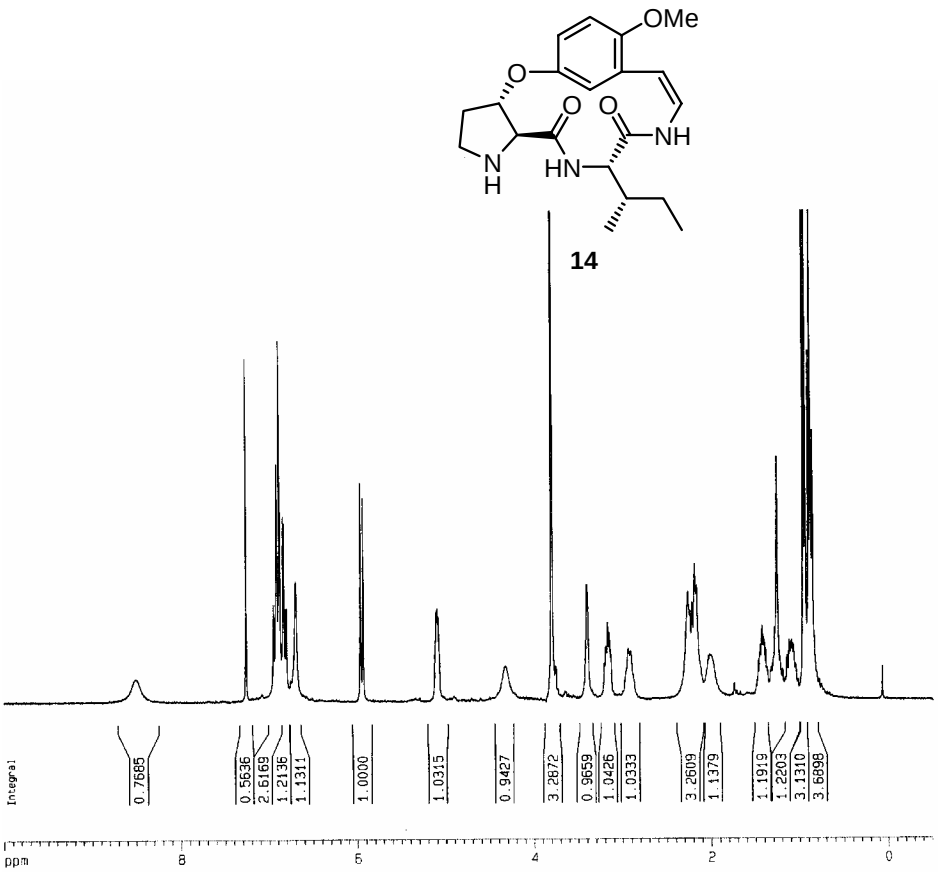
6

(300 MHz, DMSO-d_6, 343 K)




OMe
O
O
O
NH
N
HN
Boc
5
Integral
0.944
1.022
3.861
1.189
1.000
1.013
1.020
1.040
4.966
1.107
1.127
1.535
1.588
3.558
14.757
7.622
2.959
3.889
7.833
ppm
8
6
4
2
0
Current Data Parameters
NAME fc16t204sup
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060419
Time 0.02
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 64
DS 2
SWH 6313.131 Hz
FIDRES 0.192661 Hz
AQ 2.5952756 sec
RG 912.3
DW 79.200 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.20 usec
PL1 0.00 dB
SFO1 300.1328512 MHz
F2 - Processing parameters
SI 32768
SF 300.1300353 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 9.47 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56827 Hz/cm


ppm
150
100
50
0
Current Data Parameters
NAME fc17t216
EXPNO 14
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060501
Time 1.33
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 101.6
DW 27.800 usec
DE 10.00 usec
TE 295.3 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -6.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 22.00 dB
PL13 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677416 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 35.20 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 10.50000 ppm/cm
HZCM 792.41132 Hz/cm



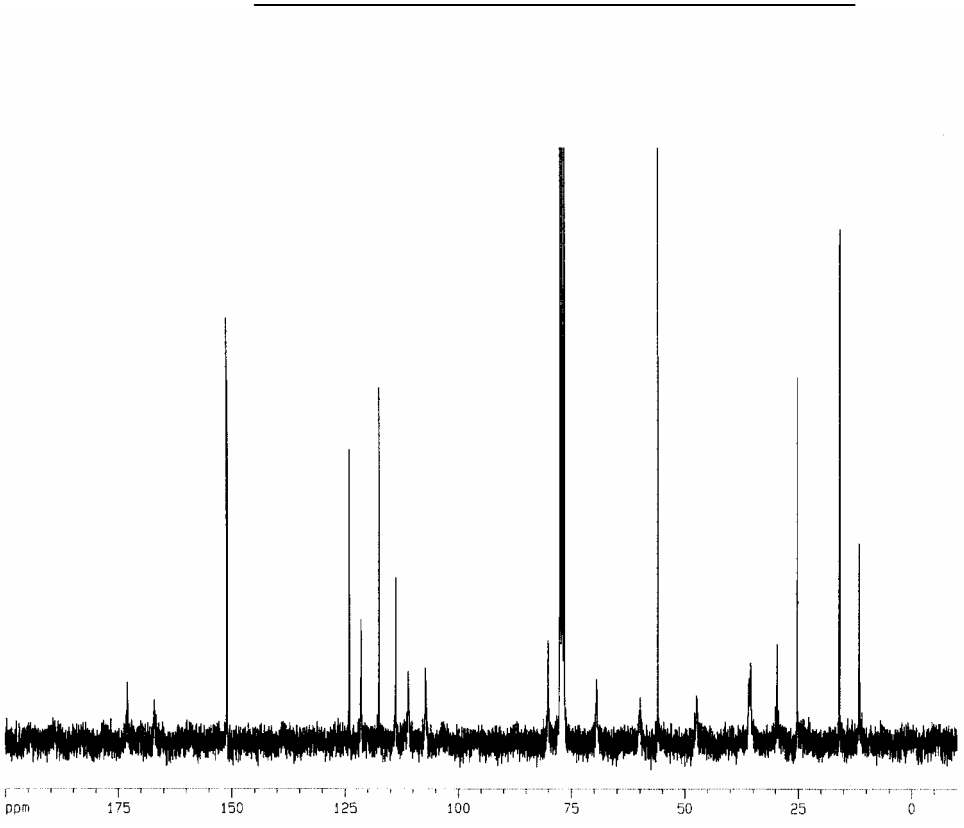

```
Current Data Parameters
NAME          fc24t249P
EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
Date_          20060618
Time              20.50
INSTRUM           spect
PROBHD  5 mm BBI 1H-BB
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                   16
DS                    2
SWH           6313.131 Hz
FIDRES        0.192661 Hz
AQ            2.5952756 sec
RG                456.1
DW               79.200 usec
DE                6.50 usec
TE               296.2 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                 6.20 usec
PL1                0.00 dB
SF01         300.1328512 MHz

F2 - Processing parameters
SI                32768
SF          300.1300149 MHz
WDW                  EM
SSB                   0
LB                 0.10 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                30.85 cm
F1P               10.000 ppm
F1              3001.30 Hz
F2P               -0.500 ppm
F2              -150.07 Hz
PPMCM             0.52500 ppm/cm
HZCM            157.56825 Hz/cm
```




```
Current Data Parameters
NAME          fc24t249P
EXPNO                10
PROCNO                1

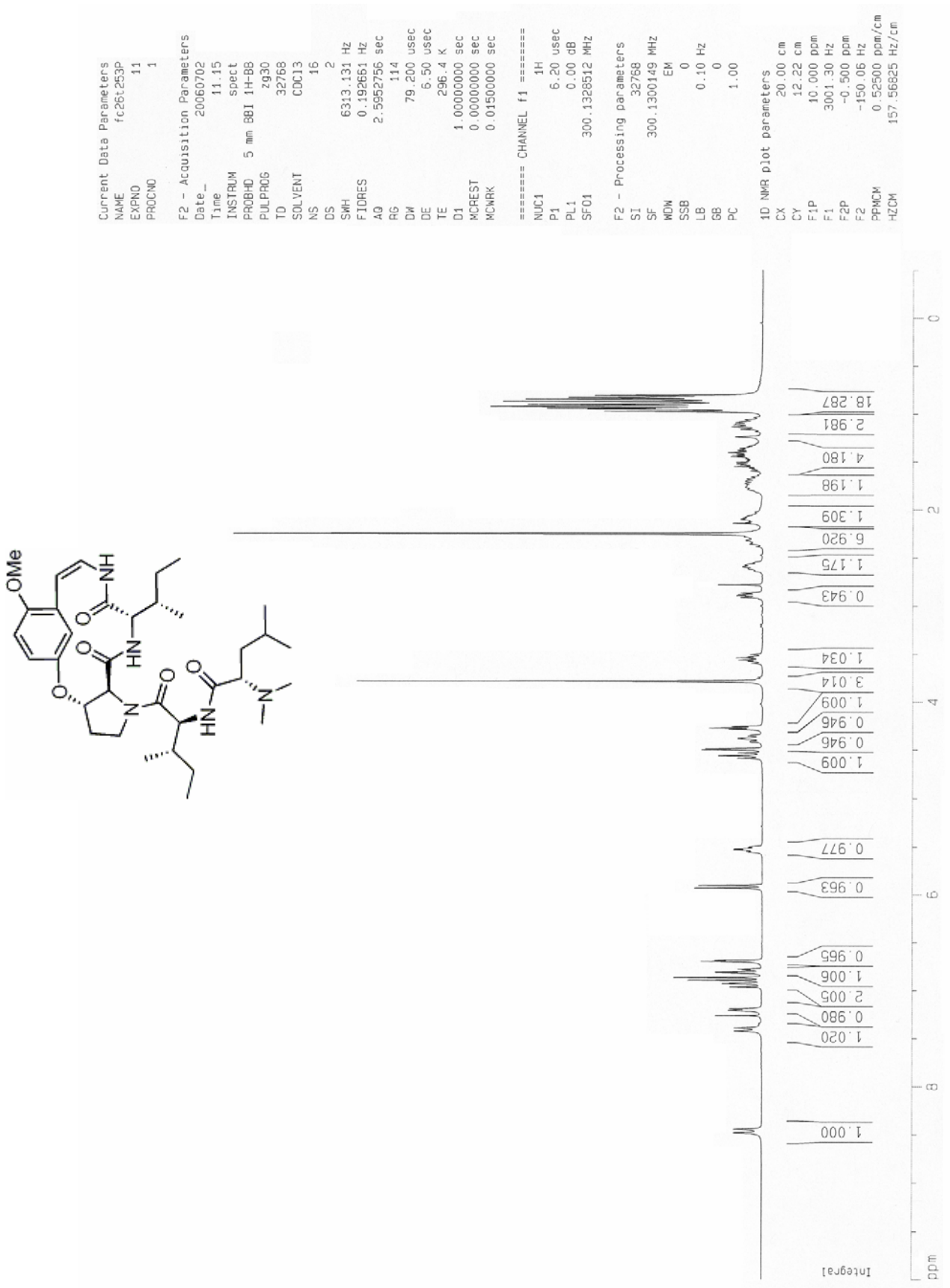
F2 - Acquisition Parameters
Date_          20060618
Time              15.26
INSTRUM           spect
PROBHD  5 mm BBI 1H-BB
PULPROG          zgpg30
TD               65536
SOLVENT          CDCl3
NS               20000
DS                    4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                101.6
DW               27.800 usec
DE               10.00 usec
TE               296.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

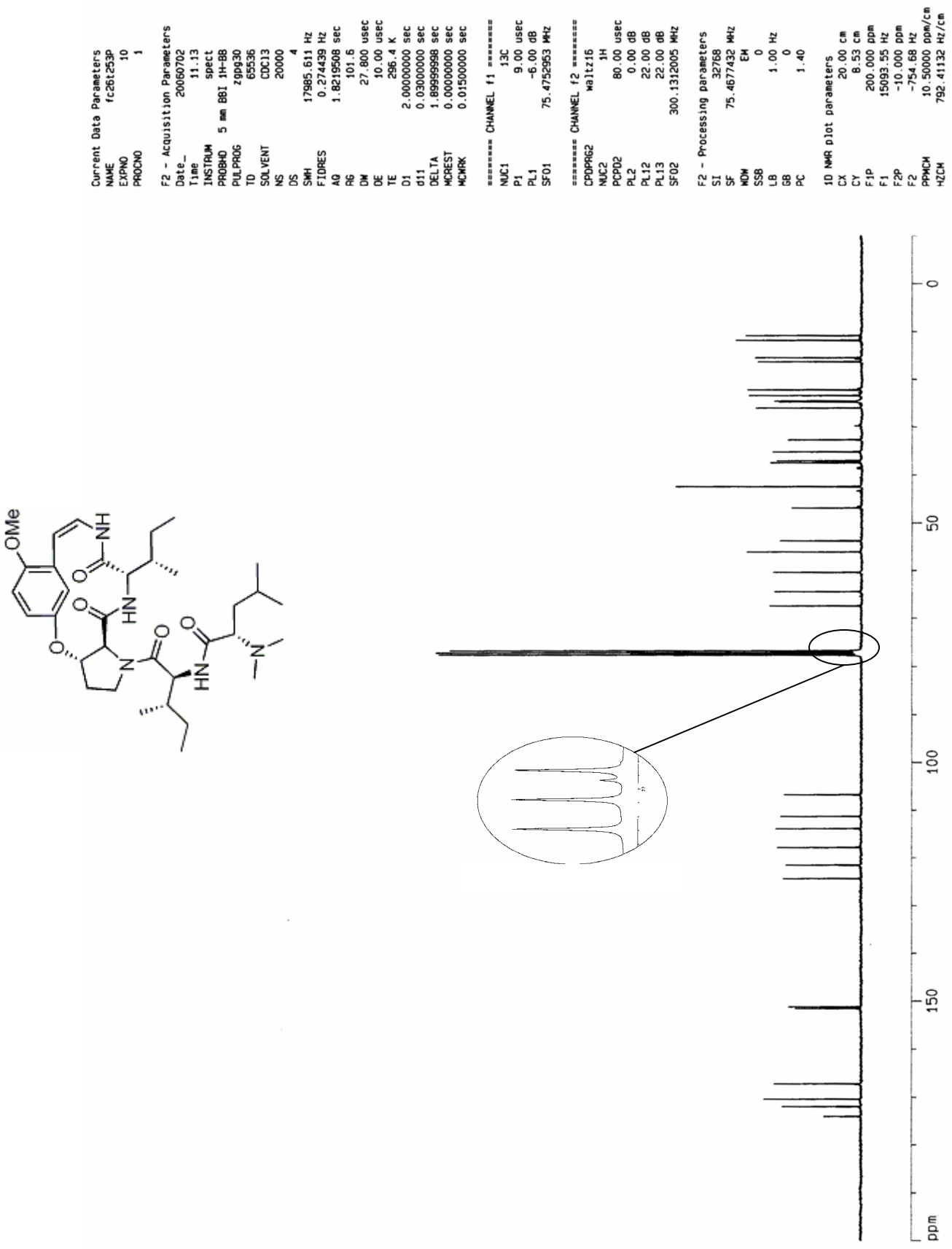
======== CHANNEL f1 ========
NUC1                13C
P1                 9.00 usec
PL1               -6.00 dB
SF01         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                0.00 dB
PL12              22.00 dB
PL13              22.00 dB
SF02         300.1312005 MHz

F2 - Processing parameters
SI                32768
SF          75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY               118.20 cm
F1P              200.000 ppm
F1             15093.55 Hz
F2P             -10.000 ppm
F2             -754.68 Hz
PPMCM            10.50000 ppm/cm
HZCM           792.41138 Hz/cm
```


Current Data Parameters
NAME fc26t253P
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060702
Time 11.15
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6313.131 Hz
FIDRES 0.192661 Hz
AQ 2.5952756 sec
RG 114
DW 79.200 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.20 usec
PL1 0.00 dB
SFO1 300.1328512 MHz
F2 - Processing parameters
SI 32768
SF 300.1300149 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
CY 12.22 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm
OMe
NH
HN
HN
N
O
Integral
1.000
1.020
0.980
2.005
1.006
0.965
0.963
0.977
1.009
0.946
0.946
1.009
3.014
1.034
0.943
1.175
6.920
1.309
1.198
4.180
2.981
18.287
ppm


Current Data Parameters
NAME fc26t253P
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060702
Time 11.13
INSTRUM spect
PROBHD 5 mm BBI 1H-BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 20000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 101.6
DW 27.800 usec
DE 10.00 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 usec
PL1 -6.00 dB
SF01 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 22.00 dB
PL13 22.00 dB
SF02 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677432 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
CY 8.53 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 10.50000 ppm/cm
HZCM 792.41132 Hz/cm
OMe
NH
HN
HN
N
N
O
ppm
0
50
100
150