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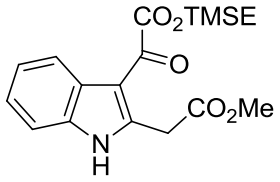
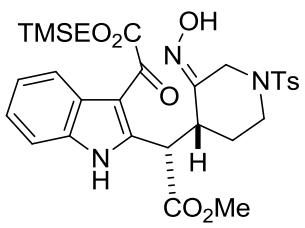
General Methods. All non-aqueous reactions were carried out in oven- or flame-dried glassware under an argon atmosphere. All chemicals were purchased from commercial vendors and used as is, unless otherwise specified. Anhydrous tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were obtained from a solvent purification system (Glass Contour). Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 250 μm EMD 60 F_{254} precoated silica gel plates. Flash column chromatography was performed using Silicycle silica gel P60 (230-400 mesh). Sonication reactions were performed in a Branson 1510 sonicator. FT-IR spectral data were recorded on a Thermo Nicolet FT-IR spectrometer equipped with a Diamond ATR accessory. ^{1}H and ^{13}C NMR spectral data were recorded on Bruker DPX-300, AMX-360 or DRX 400 MHz spectrometers. Chemical shifts are reported relative to chloroform (δ 7.26), methanol (δ 3.31), or DMSO (δ 2.50) for ^{1}H NMR and chloroform (δ 77.2), methanol (δ 49.0), or DMSO (δ 39.5) for ^{13}C NMR. Nominal mass spectra were recorded on Applied Biosystems 150EX. High resolution mass spectra were recorded on a Waters LCT Premier time-of-flight (TOF) mass spectrometer. X-Ray data was collected on a Bruker SMART APEX CCD area dector system.

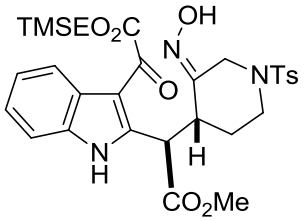


5

Synthesis of Keto Diester 5. To a stirred solution of the readily prepared indole ester **4**[7] (3.50 g, 18.5 mmol) in Et_2O (310 mL) at 0 ℃ was added oxalyl chloride (1.84 mL, 21.4 mmol). The resultant orange solution was stirred at rt for 16 h and then cooled to 0 ℃. 2-Trimethylsilylethanol (8.0 mL, 55.9 mmol) was added, followed by slow addition of triethylamine (6.4 mL, 47 mmol) over 5 min. The resulting red suspension was stirred at 0 ℃ for 1.5 h and then diluted with water. The organic layer was separated and the aqueous layer extracted with Et_2O. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a viscous red oil which was purified by flash chromatography on silica gel (gradient 20% to 40% EtOAc/hexanes) to yield indole-3-oxoacetate **5** (6.03 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) 10.50 (s, 1H), 7.83-7.78 (m, 1H), 7.45-7.40 (m, 1H), 7.30-7.23 (m, 2H), 4.56-4.50 (m, 2H), 4.32 (s, 2H), 3.82 (s, 3H), 1.22-1.16 (m, 2H), 0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) 182.5; 171.3, 166.5, 142.3, 135.4, 126.1, 124.0, 123.4, 120.3, 112.3, 110.5, 65.2, 53.1, 32.9, 17.8, -1.1; LRMS-ES+ *m/z* (relative intensity) 362 (MH^+, 80); HRMS-ES+ ($C_{18}H_{24}NO_5Si$) calcd 362.1424 (MH^+), found 362.1416.



11a

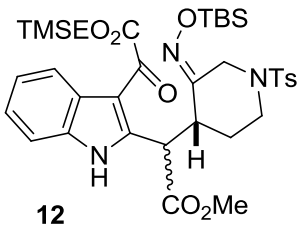


11b

Synthesis of Nitrosoalkene Michael Adducts 11a/b. To a -78 ℃ solution of indole **5** (8.18 g, 22.6 mmol) was added LiHMDS (47.5 mL, 47.5 mmol, 1.0 M in THF) and the resulting solution was stirred for 30 min. A solution of α-chlorooxime **7** (9.6 g, 31.7 mmol) in THF (69 mL) was added via cannula over 10 min. The reaction mixture was stirred at -78 ℃ for 2 h and then diluted with $NH_4Cl_{(aq)}$. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to give a residue which was purified by flash chromatography on silica gel (gradient 20% to 50% EtOAc/hexanes) to yield diastereomeric Michael adducts **11a** and **11b** (14.01 g, 99%, ~1.2 : 1 by ^{1}H NMR) which were carried on to the next step without separation. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.31 (s, 0.5H), 10.23 (s, 0.5H), 8.90 (s, 0.5H), 8.66 (s, 0.5H), 7.79-7.58 (m, 3H), 7.39-7.17 (m, 5H), 5.59 (d, *J* = 5.9 Hz, 0.5H), 5.13 (d, *J* = 8.6 Hz, 0.5H), 4.93 (d, *J* = 14.5 Hz, 0.5H), 4.60-4.50 (m, 2H), 3.69-4.47 (m, 4H) 3.37 (p, *J* = 5.7 Hz, 0.5H), 3.20 (d, *J* = 14.6 Hz, 0.5 H); 3.10 (q, *J* = 7.3 Hz, 0.5H), 2.97-2.85 (m, 1H), 2.44-2.28 (m, 3H), 2.08-2.03 (m, 0.5H), 1.78-1.76 (m, 0.5H), 1.41-1.31 (m, 0.5H), 0.11-0.07 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.6, 183.0, 172.6, 171.9, 166.5, 166.5, 152.8, 152.7, 144.61, 144.57, 143.5, 143.4, 135.83, 135.80, 130.4, 130.3, 128.06, 127.96, 125.8, 125.6, 124.4, 124.2, 123.4, 123.2, 120.0, 119.6, 112.9, 112.7, 111.2, 111.1, 65.33, 65.29, 53.3, 53.2, 45.4, 44.9, 44.2, 43.4, 42.9, 42.7,

42.3, 41.9, 27.9, 27.8, 22.0, 21.9, 17.8, 14.6, 14.2, -1.1; LRMS-ES+ *m/z* (relative intensity) 666 ($M+K^+$, 100); HRMS-ES+ ($C_{30}H_{41}N_4O_8SSi$) calcd 645.2414 ($M+NH_4^+$), found 645.2445.

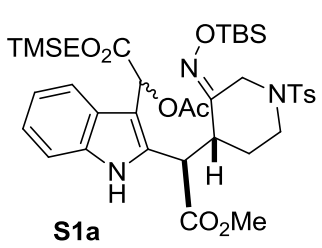
For characterization of the isomers, a small amount of the mixture was separated by flash chromatography on silica gel (gradient 2 to 10% Et_2O/CH_2Cl_2) to afford **11a** (less polar) as an orange foamy solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H, NH), 7.91 (s, 1H), 7.62(d, *J* = 8.0 Hz, 3H), 7.38 (m, 1H), 7.26-7.19 (m, 4H), 5.52 (d, *J* = 6.1.1 Hz, 1H), 4.87 (d, *J* = 14.6 Hz, 1H), 4.50 (t, *J* = 8.2 Hz, 2H), 3.64 (s, 3H), 3.30 (m, 1H), 3.18 (d, *J* = 14.7 Hz, 1H), 2.82 (m, 1H), 2.43 (m, 1H), 2.34 (s, 3H), 2.02 (dd, *J* = 3.4, 12.8 Hz, 1H), 1.38 (m, 1H), 1.15 (t, *J* = 8.7 Hz, 2H), 0.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.2, 171.5, 166.0, 153.1, 144.2, 135.3, 133.0, 130.0, 127.7, 125.3, 123.9, 122.9, 119.6, 112.4, 111.1, 64.9, 52.9, 45.0, 43.0, 42.6, 42.0, 27.5, 21.6, 17.5, -1.4. **11b** (more polar, brown foamy solid), ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.97 (s, 1H), 7.61-7.57 (m, 3H), 7.29-7.23 (m, 2H), 1.17-7.14 (m, 3H), 5.00 (d, *J* = 8.4 Hz, 1H), 4.50-4.39 (m, 3H), 3.67 (s, 3H), 3.45-3.38 (m, 3H), 2.94 (m, 1H), 2.82 (m, 1H), 2.34 (s, 3H), 1.69 (m, 2H), 1.09-1.05 (m, 2H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 182.9, 172.8, 166.2, 152.9, 144.5, 143.5, 135.7, 133.3, 130.3, 128.1, 125.8, 124.4, 123.4, 120.2, 122.6, 111.2, 65.3, 53.3, 45.0, 44.1, 43.3, 42.0, 28.0, 22.0, 17.8, -1.1.



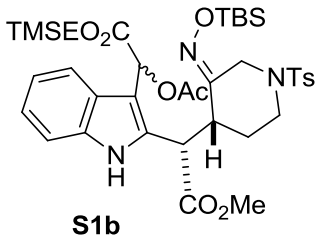
12

Synthesis of α-Ketoester 12. To a solution of ester oxime mixture **11a/b** (5.66 g, 9.01 mmol) and imidazole (2.47 g, 36.3 mmol) in CH_2Cl_2 (240 mL) was added TBSCl (4.10 g, 27.2 mmol). The resulting suspension was stirred for 12 h at rt and then diluted with 1 M HCl. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to give a residue which was purified by flash chromatography on silica gel (30% EtOAc/hexanes) yielding *O*-TBS-oximes **12** (5.98 g, 89%) as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 0.5H), 9.79 (s, 0.5H), 7.77-7.61 (m, 3H), 7.41-7.21 (m, 5H) 5.56 (d, *J* = 5.7, 0.5H), 5.06-4.97 (m, 1H), 4.84 (d, *J* = 15.0, 0.5H), 4.54-4.45 (m, 2H), 3.69-3.60 (m, 4H), 3.41 (dt, *J* = 7.1, 12.6 Hz, 0.5H), 3.30 (d, *J* = 15.0, 0.5H), 3.18 (d, *J* = 14.9, 0.5H), 3.00-2.92 (m, 1H), 2.85-2.70 (m, 0.5H), 2.42 (s, 1.5H) 2.32 (s, 1.5H), 2.06-1.98 (m, 0.5H), 1.85-1.70 (m, 0.5H), 1.65-1.55 (m, 0.5H), 1.40-1.35 (m, 1H), 1.20-1.13 (m, 2H), 0.99 (m, 9H), 0.31-0.20 (m, 6H), 0.10-0.07 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.4, 182.8, 172.6, 171.0, 166.3, 166.1, 157.9, 156.8, 144.40, 144.37, 143.6, 143.4, 135.5, 135.4, 133.9, 133.6, 130.20, 130.15, 128.0, 127.9, 126.0, 125.7, 124.4, 124.2, 123.5, 123.2, 120.6, 120.0, 112.4, 112.2, 111.3, 65.1, 53.2, 53.0, 45.2, 44.1, 43.5, 43.3, 42.9, 28.1, 27.7, 26.34, 26.28, 21.93, 21.85, 18.3, 18.2, 17.79, 17.76, -1.1, -4.2, -4.6, -4.8; LRMS-ES+ *m/z* (relative intensity) 780 ($M+K^+$, 100); HRMS-ES+ ($C_{36}H_{52}N_3O_8SSi_2$) calcd 742.3014

(MH^+), found 742.3005.



S1a

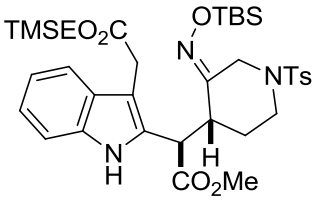


S1b

Synthesis of Acetates S1a/b. To a stirred solution of α-ketoesters **12** (21.5 g, 29 mmol) in MeOH (55 mL) and THF (425 mL) cooled to 0 ℃ was added $NaBH_4$ (1.32 g, 34.7 mmol). The resulting solution was stirred for 1 h at 0 ℃, and then diluted with $NH_4Cl_{(aq)}$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine and then dried over $MgSO_4$. Removal of the solvent *in vacuo* provided the indole-3-hydroxyl acetate products as a white powder.

Without further purification, this mixture was dissolved in a 1:1 (v/v) mixture of Ac_2O:pyridine (292 mL) and the solution was stirred at rt for 12 h. After removing the volatiles *in vacuo*, **S1a** and **S1b** were separated by flash chromatography on silica gel (gradient 15% to 40% EtOAc/hexanes). **S1a** (more polar isomer, orange foamy solid, 12.60 g, 55%, ~3:1 mixture of acetoxy diastereomers): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 0.75H), 9.03 (s, 0.25H), 7.75-7.71 (m, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.32-7.13 (m, 5H), 6.21 (s, 0.25H), 6.18 (s, 0.75H), 4.97-4.88 (m, 1H), 4.52 (d, *J* = 5.9 Hz, 0.25H), 4.48 (d, *J* = 5.5 Hz, 0.75H), 4.28-4.20 (m, 1H), 4.09-4.02 (m, 1H), 3.67-3.55 (m, 4H), 3.41-3.31 (m, 2H), 3.00-2.93 (m, 1H), 2.39-2.36 (m, 3H), 2.14 (s, 3H), 1.95-1.70 (m, 3H), 1.60-1.40 (m, 2H), 0.98 (s, 9H), 0.29-0.18 (m, 6H), 0.00-0.02

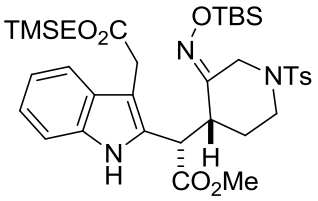
(m, 9H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 171.0, 170.8, 170.6, 170.5, 169.1, 157.3, 144.0, 135.3, 135.2, 133.7, 133.5, 132.2, 131.7, 129.8, 127.6, 126.2, 126.1, 122.7, 120.3, 119.3, 111.2, 108.0, 107.8, 67.7, 64.2, 53.4, 52.5, 44.8, 43.2, 42.9, 42.7, 42.4, 42.1, 28.0, 26.0, 25.9, 21.5, 20.9, 20.7, 17.9, 17.3, -1.56, -1.59, -4.8, -5.1; **S1b** (less polar isomer, orange foamy solid, 8.29 g, 36%, ~2:1 mixture of acetoxy diastereomers): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73-8.71 (m, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.35-7.14 (m, 5H), 6.24-6.22 (m, 1H), 5.02 (t, *J* = 7.1 Hz, 1H), 4.34-4.07 (m, 3H), 3.66-3.53 (m, 4H), 3.15-3.07 (m, 2H), 2.72 (d, *J* = 11.3, 3.2 Hz, 1H), 2.45 (s, 3H), 2.20-2.18 (m, 3H), 1.58-1.39 (m, 2H), 1.00-0.89 (m, 12H), 0.26 (s, 3H), 0.20 (s, 3H), 0.02-0.04 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 173.0, 170.9, 170.8, 169.3, 169.2, 156.7, 144.4, 136.1, 136.0, 133.8, 133.6, 132.4, 132.2, 130.2, 128.1, 126.7, 123.5, 123.4, 121.1, 120.2, 111.5, 108.54, 108.50, 68.4, 68.0, 64.7, 64.5, 53.9, 53.0, 52.9, 45.4, 44.4, 44.1, 42.8, 42.6, 42.5, 28.5, 28.0, 26.4, 22.0, 21.2, 21.1, 18.4, 17.7, 17.6, -1.2, -4.8, -4.9 (2C); LRMS-ES+ (mixture of diastereomers **S1a/b)** *m/z* (relative intensity) 824 ($M+K^+$, 25); HRMS-ES+ ($C_{38}H_{56}N_3O_9SSi_2$) calcd 786.3276 (MH^+), found 786.3286.



13

Synthesis of Indole Diester 13. To a solution of acetate **S1a** (2.94 g, 3.75 mmol) in *t*-BuOH (80 mL) was added 10% Pd/C (1.20 g). The resulting mixture was

evacuated and backfilled with H_2 from a balloon and TEA (10.0 mL) was then added. The resulting mixture was warmed to 30 ℃ and stirred for 4 days until all the starting material was consumed as judged by TLC. The reaction mixture was then diluted with EtOAc, filtered through a pad of Celite and concentrated *in vacuo* to give a residue which was purified by flash chromatography on silica gel (gradient 10% to 25% EtOAc/hexanes) to afford indole **13** (2.47 g, 91%) as an off-white foam. ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.74 (br s, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.28-7.24 (m, 3H), 7.17 (dd, *J* = 7.1, 7.5 Hz, 1H), 7.09 (dd, *J* = 7.3, 7.4 Hz, 1H), 4.82 (d, *J* = 15.1 Hz, 1H), 4.33 (d, *J* = 6 Hz, 1H), 4.11-4.07 (m, 2H), 3.64 (s, 3H), 3.60 (d, *J* = 4.4 Hz, 2H), 3.58-3.55 (m, 1H), 3.36 (d, *J* = 15.2 Hz, 1H), 3.30-3.25 (m, 1H), 2.90 (td, *J* = 4.0, 11.9 Hz, 1H), 2.36 (s, 3H), 1.89-1.84 (m, 1H), 1.59-1.54 (m, 1H), 0.94(s, 9H), 0.21(s, 3H), 0.15(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 171.6, 157.2, 144.0, 135.4, 133.7, 130.0, 129.9, 129.5, 128.9, 127.7 (2C), 122.3, 119.7, 118.9, 111.0, 107.6, 63.2, 52.5, 44.7, 43.0, 42.7, 42.3, 30.8, 27.6, 26.0, 21.6, 18.0, 17.4, -1.4, -4.8, -5.0; LRMS-ES+ *m/z* (relative intensity) 766 ($M+K^+$, 75); HRMS-ES+ ($C_{36}H_{57}N_4O_7SSi_2$) calcd 745.3487 ($M+NH_4^+$), found 745.3478.

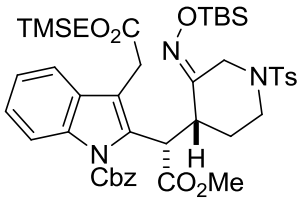


14

Synthesis of Indole Diester 14. Following a similar procedure described for preparation of **13**, acetate **S1b** (3.95 g, 5.03 mmol) was reduced by catalytic

hydrogenation to afford indole diester **14** as an off white foamy solid (3.16 g, 86%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 7.0, 7.1 Hz, 1H), 7.11 (dd, *J* = 7.1, 7.2 Hz, 1H), 5.03 (d, *J* = 14.4 Hz, 1H), 4.17-4.13 (m, 2H), 4.06 (d, *J* = 10.7 Hz, 1H), 3.64 (app. s, 2H), 3.62 (s, 3H), 3.57 (m, 1H), 3.06-3.00 (m, 2H), 2.66 (td, *J* = 3.8, 11.5 Hz, 1H), 2.44 (s, 3H), 1.46 (m, 1H), 1.39 (m, 1H), 0.97 (s, 9H), 0.23 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 171.4, 156.5, 144.0, 135.7, 133.4, 129.8, 128.0 (2C), 127.8, 122.7, 120.1, 119.2, 111.0, 108.3, 63.3, 52.5, 45.2, 43.8, 42.5, 42.0, 30.6, 27.8, 26.1, 25.9, 21.7, 18.1, 17.5, -1.4, -5.1, -5.2; HRMS-ES+ ($C_{36}H_{54}N_3O_7SSi_2$) calcd 728.3221 (MH^+), found 728.3224.

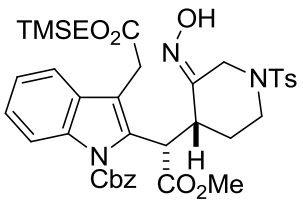
Epimerization of Ester 13 to Ester 14. To a solution of diester **13** (4.45 g, 6.12 mmol) in THF (81 mL) cooled to -78 ^{o}C was added dropwise KHMDS solution (0.5 M in toluene, 13.5 mL, 6.73 mmol, 1.1 equiv.). After the addition was complete, the cooling bath was removed and the reaction mixture was stirred at rt for 30 min. To the resultant olive green solution was added glacial acetic acid (0.40 mL) followed by saturated $NH_4Cl_{(aq).}$ The mixture was extracted with EtOAc. The organic phase washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel (30% EtOAc/hexanes) to afford diester **14** as a slightly yellow foam (3.23 g, 73%), which was identical to ester **14** prepared from hydrogenation of **S1b**.



15

Synthesis of *N*-Cbz Derivative 15. A stirred solution of indole **14** (1.05 g, 1.45 mmol) in acetonitrile (40 mL) was heated to 90 ^{o}C. Dibenzyl dicarbonate (2.07 g, 7.24 mmmol) was added, followed immediately by DMAP (0.53 g, 4.33 mmol). After gas evolvution stopped (~1 min), the reaction mixture was heated at 90 ^{o}C for another 2 min, and cooled to rt. The solvent was removed *in vacuo* to give a pale brown residue, which was purified by flash chromatography on silica gel (5 to 20 % EtOAc/hexanes) to afford **15** as a white foam (1.23 g, 99%, ~2:1 Cbz rotamers). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 0.7H), 8.00 (m, 0.3H), 7.64 (d, *J* = 6.9 Hz, 2H), 7.57 (d, *J* = 6.4 Hz, 0.7H), 7.46-7.26 (m, 9H), 5.68 (d, *J* = 10.1 Hz, 0.3H), 5.17 (d, *J* = 11.7 Hz, 0.7H), 5.52-5.46 (m, 0.7H), 5.29 (d, *J* = 13.1 Hz, 0.7H), 5.16 (d, *J* = 9.3 Hz, 1.7H), 4.14-4.10 (m, 2H), 3.90 (d, *J* = 15.9 Hz, 0.3H), 3.65-3.53 (m, 2.7H), 3.48 (s, 3H), 3.11 (m, 1H), 2.90 (d, *J* = 13.2 Hz, 0.3H), 2.68 (d, *J* = 13.2 Hz, 0.7H), 2.60 (m, 0.3H), 2.49-2.44 (m, 3H), 2.17 (m, 0.7H), 1.40 (m, 0.3H), 1.12 (m, 1.7H), 0.98 (m, 9H), 0.22 (s, 2H), 0.19-0.17 (m, 4H),0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 171.1, 170.8, 170.1, 155.8, 155.6, 151.8, 151.3, 143.8, 135.9, 135.6, 134.8, 133.4, 132.5, 132.2, 129.8, 129.4, 129.2, 129.0, 128.8, 127.9, 125.3, 123.5, 119.3, 118.9, 118.6, 117.2, 115.8, 69.3, 68.6, 63.6, 63.4, 52.1, 45.7, 42.8, 42.4, 42.0, 41.3, 40.7, 30.9, 30.2, 28.6, 27.5, 26.2, 25.6, 21.7, 18.3, 17.5, -1.5, -5.1; LRMS-ES+ *m/z* (relative intensity) 862 (MH^+, 90); HRMS-ES$^+$ ($C_{44}H_{60}N_3O_9SSi_2$) calcd 862.3589 (MH^+), found

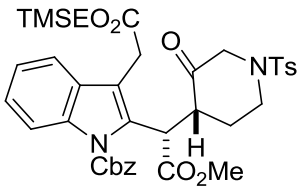
862.3585.



16

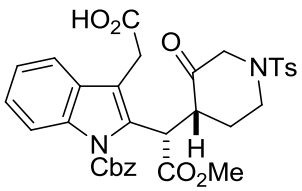
Synthesis of Oxime 16. To a stirred solution of *O*-TBS-oxime **15** (12.9 g, 14.9 mmol) in THF (600 mL) was added AcOH (6.6 mL) followed by TBAF (22.1 mL, 22.1 mmol, 1.0 M in THF). The resulting solution was stirred at rt overnight and then diluted with $NH_4Cl_{(aq)}$. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* to give a residue which was purified by flash column chromatography on silica gel (30% EtOAc/hexanes) to yield free oxime **16** as a pale foam (11.1 g, 100%, ~2:1 Cbz rotamers). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (m, 0.7H), 8.0-7.8 (m, 1.3H), 7.65 (d, *J* = 7.1 Hz, 2H), 7.54 (m, 0.7H), 7.45 (m, 3.5H), 7.35-7.26 (m, 6H), 5.68 (m, 0.3H), 5.57 (d, *J* = 11.5 Hz, 0.7H), 5.47 (s, 0.7H), 5.18 (m, 1.4H), 5.07 (m, 1H), 4.13 (m, 2H), 3.87 (m, 0.3H), 3.65-3.59 (m, 3H), 3.48 (s, 3H), 3.09 (m, 1H), 2.91 (0.3H), 2.68 (d, *J* = 13.1 Hz, 0.7H), 2.60 (m, 0.3H), 2.48-2.44 (m, 3H), 2.19 (m, 0.7H),, 1.64 (m, 0.4H), 1.40 (m, 0.3H), 1.17 (1.60H), 0.94 (t, *J* = 8.8 Hz, 2H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 171.5, 170.8, 170.5, 152.9, 151.8, 151.4, 143.9, 135.8, 135.5, 134.7, 133.0, 132.3, 132.0, 129.8, 129.4, 129.2, 129.1, 129.0, 128.8, 128.6, 127.9, 127.8, 127.1, 125.3, 124.9, 123.5, 123.2, 119.3, 118.6, 117.2, 116.1, 115.9, 69.5, 68.7, 65.4, 64.5, 63.8, 63.4, 52.6, 52.3, 45.7, 42.4, 41.8, 41.0, 40.7, 40.5, 31.0, 30.7, 30.3, 28.5, 27.6, 21.6, 21.1, 19.2, 17.3, 13.8,

-1.5; LRMS-ES+ *m/z* (relative intensity) 748 (MH^+, 75); HRMS-ES+ ($C_{38}H_{46}N_3O_8SSi_2$) calcd 748.2724 (MH^+), found 748.2690.



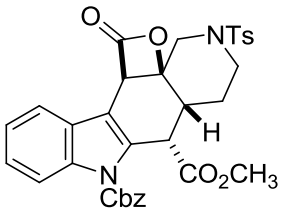
17

Synthesis of Ketone 17. Oxime **16** (11.14 g, 14.9 mmol) was added to a mixture of levulinic acid and 1 M HCl (334 g, 9:1 v/v) and the mixture was stirred at 30 °C for 4.5 h. The reaction mixture was diluted with water (1 L), and was extracted with dichloromethane. The organic layer was washed with sat. $NaHCO_3$, water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography on silica gel (gradient, 20 to 30% EtOAc/hexanes) to afford ketone **17** as a slightly pink foam (10.04 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.55-7.26 (m, 10H), 5.54 (d, *J* = 11.8 Hz, 1H), 5.20 (d, *J* = 11.6 Hz, 1H), 4.91 (d, *J* = 6.6 Hz, 1H), 4.18-4.07 (m, 2H), 4.21 (d, *J* = 13.6 Hz, 1H), 3.62 (s, 2H), 3.48 (s, 3H), 3.32 (q, *J* = 9.3 Hz, 1H), 3.20 (d, *J* = 13.6 Hz, 1H), 2.48 (s, 3H), 2.46 (m, 1H), 1.46-1.42 (m, 2H), 0.95 (t, *J* = 8.6 Hz, 2H), 0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 171.2, 170.2, 151.5, 144.3, 135.4, 134.7, 132.2, 131.7, 130.0, 129.3, 129.1, 128.9, 128.0, 125.4, 123.7, 119.3, 117.4, 115.9, 68.9, 63.8, 56.1, 52.4, 48.8, 45.3, 40.0, 30.8, 27.5, 21.7, 17.4, -1.5; LRMS-ES+ m/z (relative intensity) 750 ($M+NH_4^+$, 75); HRMS-ES+ ($C_{38}H_{48}N_3O_9SSi$) calcd 750.2881 ($M+NH_4^+$), found 750.2878.



18

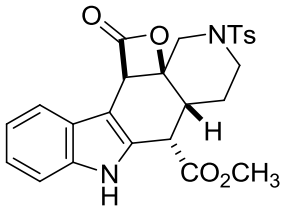
Synthesis of Keto Acid 18. To a stirred solution of TMSE-ester **17** (3.95 g, 5.38 mmol) in CH_2Cl_2 (138 mL) was added TFA (34 mL). The resulting solution was stirred at rt for 9 h and the solvent was removed *in vacuo* to give a residue which was purified by flash column chromatography on silica gel (40% EtOAc/hexanes + 1% AcOH) to give keto acid **18** (3.39 g, 100%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.9 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.50-7.16 (m, 10H), 5.54 (d, *J* = 11.8 Hz, 1H), 5.21 (d, *J* = 11.1 Hz, 1H), 4.87 (d, *J* = 6.2 Hz, 1H), 4.00 (13.4 Hz, 1H), 3.68 (s, 2H), 3.46 (s, 3H), 3.36-3.29 (m, 1H), 3.18 (d, *J* = 13.9 Hz, 1H), 2.48 (s, 3H), 1.41 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 175.3, 171.1, 151.4, 144.3, 137.9, 135.4, 134.5, 132.2, 131.9, 129.9, 129.3, 129.1, 128.8, 128.2, 127.9, 125.5, 125.3, 123.7, 119.1, 116.6, 115.9, 68.9, 56.0, 52.4, 48.7, 45.2, 40.0, 30.0, 27.5, 21.6; LRMS-ES+ m/z (relative intensity) 633 (MH^+, 100); HRMS-ES+ ($C_{33}H_{36}N_3O_9S$) calcd 650.2172 ($M+NH_4^+$), found 650.2142.



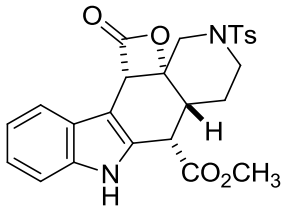
19

Synthesis of β-Lactone 19. To a stirred suspension of 4-PPY (1.09 g, 7.35 mmol), 2-bromo-*N*-propylpyridinium triflate (2.57 g, 7.35 mmol) and DIPEA (1.7 mL,

9.8 mmol) in CH_2Cl_2 (79 mL) at rt was added a solution of keto acid **18** (3.00 g, 4.90 mmol) and glacial acetic acid (0.35 mL, 6.1 mmol) in CH_2Cl_2 over 1 h *via* a syringe pump. The resultant orange solution was stirred for another 3 h at rt. Solvent was then removed *in vacuo* to give a residue which was purified by flash chromatography on silica gel (gradient, 30-40% EtOAc/hexanes) affording β-lactone **19** as an off white solid (2.71 g, 93%). FTIR (film) 1835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ~97:3 mixture of diastereomers determined by ^1H NMR, only the major diastereomer peaks are reported) δ 8.02 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.4 Hz,, 1H), 7.45 (m, 2H), 7.42-7.31 (m, 7H), 5.46 (d, *J* = 10.8 Hz, 1H), 5.32 (d, *J* = 12.0 Hz, 1H), 4.76 (s, 1H), 4.41 (d, *J* = 5.7 Hz, 1H), 3.88 (d, *J* = 12.0 Hz, 1H), 3.50 (m, 1H), 3.50 (s, 3H), 2.95 (d, *J* = 11.8 Hz, 1H), 2.55 (dd, *J* = 7.3, 14.5 Hz, 1H), 1.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 165.4, 151.8, 144.5, 136.6, 134.5, 132.3, 130.1, 129.9, 129.0, 128.9, 128.8, 127.8, 126.9, 125.8, 123.8, 118.8, 115.6, 110.6, 75.6, 69.4, 53.0, 52.2, 50.9, 44.8, 43.3, 38.5, 25.1, 21.7; LRMS-ES+ m/z (relative intensity) 615 (MH+, 100). HRMS-ES+ ($C_{33}H_{34}N_3O_8S$) calcd 632.2067 ($M+NH_4^+$), found 632.2053.



20

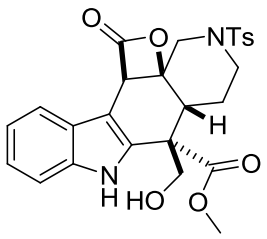


21

Synthesis of NH-Indole Esters 20 and 21. 10% Pd/C (0.54 g) was suspended in a solution of *N*-Cbz β-lactone **19** (2.71 g, 4.41 mmol) in EtOAc (280 mL). One drop

of glacial acetic acid was added to the mixture, followed by three evacuation-backfill cycles with hydrogen gas from a balloon. The reaction mixture was stirred under a balloon of H_2 for 1.5 h at rt. The mixture was filtered through a pad of Celite, concentrated and the residue was purified by flash chromatography on silica gel (gradient, 2 to 5% Et_2O/CH_2Cl_2) to afford indole **20** (1.99 g, 94%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (br s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.25-7.18 (m, 2H), 4.86 (s, 1H), 4.21 (d, *J* = 4.5 Hz, 1H), 4.09 (d, *J* = 11.6 Hz, 1H), 3.86 (s,3H), 3.72 (dd, *J* = 2.0, 9.6 Hz, 1H), 2.78 (d, *J* = 11.6 Hz, 1H), 2.71 (ddd, *J* = 4.5, 12.6 Hz, 1H), 2.46 (s, 3H), 2.30 (td, *J* = 2.5, 12.0 Hz, 1H), 1.58 (m, 1H), 1.40 (qd, *J* = 4.5, 13.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 166.1, 144.5, 136.1, 132.6, 130.1, 129.1, 127.9, 125.7, 122.8, 120.7, 118.3, 111.7, 101.4, 53.6, 53.0, 51.7, 45.4, 39.5, 39.1, 24.5, 21.7; HRMS (*m/z*): $[M + NH_4]^+$ calcd for $C_{25}H_{28}N_3O_6S$, 498.1693; found, 498.1663.

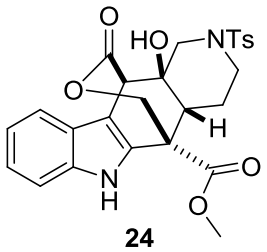
Indole **21** (65 mg,3 %) was obtained as a white solid. ^{1}H NMR (300 MHz, DMSO-*d6*) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.15 (dd, *J* = 7.1, 7.4 Hz, 1H), 7.08 (dd, *J* = 7.4, 7.5 Hz, 1H), 4.84 (s, 1H), 4.03-4.00 (m, 2H), 3.51 (br s, 4H), 2.94 (dd, *J* = 3.6, 12.6 Hz, 1H), 2.88 (d, *J* = 11.6 Hz, 1H), 2.46-2.43 (m, 1H), 2.41 (s, 3H), 1.95 (br d, *J* = 10.1 Hz, 1H), 1.08 (qd, *J* = 4.3, 12.9 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-*d6*) δ 170.9, 166.9, 143.9, 136.2, 132.6, 130.0, 127.5, 125.4, 121.6, 119.3, 117.9, 111.5, 100.2, 76.8, 52.4, 52.1, 50.7, 44.8, 42.8, 38.8, 30.7, 28.7, 21.0; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{25}N_2O_6S$, 481.1428; found 481.1395.



23

Synthesis of α-Hydroxymethyl Ester 23. To a solution of indole β-lactone **20** (255 mg, 0.531 mmol) in THF (25 mL) cooled to -78 °C was added a solution of LiHMDS (1.0 M in THF, 1.60 mL, 1.60 mmol) dropwise with stirring. The resulting orange red solution was stirred at -78 °C for another 30 min. A solution of freshly distilled monomeric formaldehyde[15] in THF (~0.5 M, 10.6 mL, 5.3 mmol) was added dropwise. The resulting brownish red solution was stirred at -78 °C for 5 min, then warmed to -40 °C and stirred for another 15 min. The reaction mixture was then quenched at -40 °C by addition of glacial acetic acid (0.10 mL, 1.6 mmol). The bright yellow solution was diluted with dichloromethane, quickly washed with ice cold water and dried over Na_2SO_4. After concentration of the solution, the residue was purified by column chromatography on silica gel (5% Et_2O/CH_2Cl_2, then 50% EtOAc/hexanes) to afford α-hydroxymethyl ester **23** as an off-white solid (160 mg, 59%). FT-IR (ATR) 3403, 1824 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H, NH), 7.62-7.66 (m, 4H), 7.34-7.42 (m, 4H), 7.16-7.25 (m, 2H), 4.86 (s, 1H), 3.97-4.02 (m, 3H), 3.83 (s, 3H), 3.68 (app. d, *J* = 15.6Hz , 1H), 2.74 (d, *J* = 15.7 Hz, 1H), 2.57 (dd, *J* = 6.4, 15.9 Hz, 1H), 2.46 (s, 3H), 2.26 (td, *J* = 4.2, 15.7 Hz, 1H), 2.13 (t, *J* = 8.2 Hz, 1H), 1.43-1.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 167.1, 144.7, 136.6, 132.9, 131.6, 130.2, 128.0, 125.7, 123.2, 120.8, 118.6, 111.8, 101.0, 69.5, 55.4, 54.1, 53.1, 51.7, 45.3, 40.7, 26.8, 21.8. ESI MS (*m/z*): $[M + H]^+$ 511.3; HRMS-ES (*m/z*):

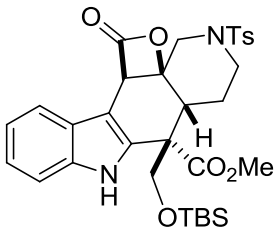
$[M + H]^+$ calcd for $C_{26}H_{27}N_2O_7S$, 511.1539; found, 511.1538.



24

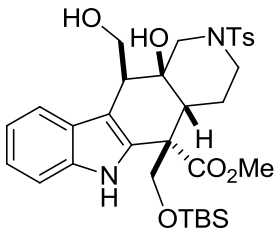
Synthesis of ε-Lactone 24. To a solution of β-lactone **23** (200 mg, 0.39 mmol) in dichloromethane (2.6 mL) at rt was added triethylamine (10.6 mL, excess). The resulting slightly yellow solution was stirred at rt for 2 h, evaporated to dryness and the residue was purified by flash column chromatography on silica gel (5% Et_2O/CH_2Cl_2, then 50% EtOAc/hexanes) to afford ε-lactone **24** as an off white solid (65 mg, 33%). The recovered β-lactone **23** was subjected to another translactonization under the same conditions. After 2 runs, 40 mg of β-lactone **23** was recovered and ε-lactone **24** was isolated as an off white foam (92 mg, BRSM, 58%). FT-IR (ATR) 3407, 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H, NH), 7.61 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.27 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.5 Hz), 4.90 (d, *J* = 11.7 Hz, 1H), 4.37 (d, *J* = 11.7 Hz, 1H), 4.16 (s, 1H), 3.93 (s, 3H), 3.65 (br s, 1H), 3.58 (d, *J* = 13.5 Hz, 1H), 3.52-3.58 (m, 1H), 3.01 (m, 1H), 2.81 (dd, *J* = 3.8, 13.6 Hz, 1H), 2.59 (d, *J* = 13.6 Hz, 1H), 2.37 (s, 3H),1.40 (m, 1H), 0.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 167.8, 144.2, 135.9, 134.4, 132.0, 130.2, 127.4, 124.9, 122.8, 120.9, 118.0, 113.7, 112.1, 107.0, 76.0, 73.6, 53.7, 53.0, 52.8, 52.2, 50.6, 42.4, 23.8, 21.7; ESI MS (*m/z*): $[M + H]^+$ 511.3; HRMS (*m/z*): $[M + NH_4]^+$ calcd for $C_{26}H_{30}N_3O_7S$, 528.1799; found,

528.1797.



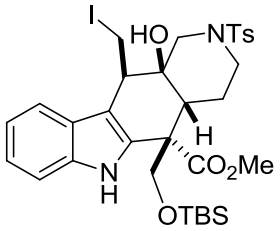
25

Synthesis of *O*-TBS β-Lactone 25. To a solution of hydroxymethyl compound **23** (100 mg, 0.196 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added 2,6-lutidine (226 μL, 1.95 mmol) and freshly distilled TBSOTf (225 μL, 0.98 mmol) with stirring. The colorless reaction mixture was stirred at 0 °C and monitored by TLC. Once the reaction was complete (~40 min), the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (gradient, 5% to 30% EtOAc/hexanes) to afford *O*-TBS ether **25** as a white foam (105 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (br s, 1H, NH), 7.66-7.63 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.23 (m, 1H), 7.19 (dd, *J* = 7.5, 7.6 Hz, 1H), 4.84 (s, 1H), 4.03 (d, *J* = 10.1 Hz, 1H), 4.00 (d, *J* = 12.4 Hz, 1H), 3.88 (d, *J* = 9.2 Hz, 1H), 3.81 (s, 3H), 3.70 (m, 1H), 2.74 (d, *J* = 11.6 Hz, 1H), 2.55 (dd, *J* = 4.7, 12.1 Hz, 1H), 2.46 (s, 3H), 2.27 (td, *J* = 3.0, 11.8 Hz,, 1H), 1.55-1.47 (m, 2H), 0.80 (s, 9H), -0.17 (s, 3H), -0.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 167.4, 144.8, 136.4, 132.7, 132.4, 130.4, 128.2, 125.7, 123.1, 120.7, 118.7, 111.7, 100.4, 70.3, 55.8, 54.4, 53.0, 51.9, 45.5, 41.3, 27.1, 26.1, 25.9, 22.0, 18.4, -5.6; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{32}H_{41}N_2O_7SSi$, 625.2404; found 625.2390.



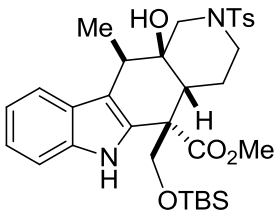
26

Synthesis of Indole Diol Ester 26. To a solution of *O*-TBS β-lactone **25** (120 mg, 0.193 mmol) in THF at rt was added $LiBH_4$ (22 mg, 1.0 mmol). The reaction mixture was stirred at rt for 12 h, diluted with $NH_4Cl_{(aq)}$ and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4 and the solvent was removed *in vacuo* to give a residue which was purified by flash chromatography on silica gel (2% to 5% Et_2O/ CH_2Cl_2) affording diol **26** as a white solid (90 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (br s, 1H), 7.69-7.66 (m, 3H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.22 (dd, *J* = 7.6, 7.8 Hz, 1H), 7.14 (dd, *J* = 7.1, 7.4 Hz, 1H), 4.87 (d, *J* = 12.2 Hz, 1H), 4.44 (d, *J* = 12.9 Hz, 1H), 4.23 (d, *J* = 8.7 Hz, 1H), 4.08 (d, *J* = 9.5 Hz, 2H), 3.71 (s, 3H), 3.67 (m, 1H), 2.45 (s, 3H), 2.25 (dd, *J* = 10.5, 10.8 Hz, 1H), 2.17 (d, *J* = 11.8 Hz, 1H), 1.92 (d, *J* = 12.2 Hz, 1H), 1.59 (m, 1H), 1.40 (m, 1H), 0.87 (s, 9H), -0.05 (s, 3H), -0.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 144.3, 137.0, 135.0, 133.2, 130.2, 128.1, 125.8, 122.3, 120.2, 119.2, 111.9, 103.8, 74.5, 71.8, 61.0, 55.8, 54.9, 52.5, 47.6, 46.1, 37.4, 26.4, 26.2, 22.0, 18.5, -5.2, -5.5; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{32}H_{45}N_2O_7SSi$, 629.2717; found 629.2717.



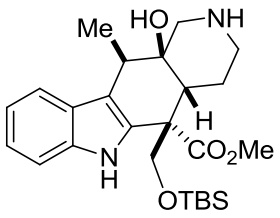
27

Synthesis of Iodo Alcohol 27. To a solution of PPh_3 (229 mg, 0.87 mmol) and I_2 (222 mg, 0.87 mmol) in CH_2Cl_2 (9 mL) at rt was added imidazole (99 mg, 1.48 mmol). The resulting yellow suspension was stirred at rt for 10 min. A solution of diol **26** (122 mg, 0.195 mmol) in CH_2Cl_2 (15 mL) was added dropwise, and the bright yellow suspension was stirred at rt for 5 h. The mixture was diluted with CH_2Cl_2 and washed with 5% $Na_2S_2O_3$. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography on silica gel (2% Et_2O/ CH_2Cl_2) to afford iodo alcohol **27** as a white foamy solid (133 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (br s, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.37-7.33 (m, 3H), 7.20 (dd, *J* = 7.1, 7.5 Hz, 1H), 7.14 (dd, *J* = 7.4, 7.4 Hz, 1H), 4.17-4.09 (m, 2H), 4.00-3.96 (m, 1H), 3.90-3.88 (m, 2H), 3.68 (s, 3H), 3.30 (s, 1H), 2.44 (s, 3H), 2.30 (m, 1H), 2.18 (m, 1H), 2.08 (dd, *J* = 3.1, 11.5 Hz, 1H), 1.63 (m, 1H), 1.43 (m, 1H), 0.84 (s, 9H), -0.08 (s, 3H), -0.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 144.0, 136.5, 132.7, 132.3, 132.1, 129.9, 128.7, 127.9, 126.0, 122.0, 119.6, 111.4, 108.9, 72.9, 71.0, 54.8, 54.3, 52.3, 45.6, 36.4, 25.8, 21.6, 18.2, 4.8, 1.1, -5.6, -5.7; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{32}H_{44}IN_2O_6SSi$, 739.1734; found, 739.1764.



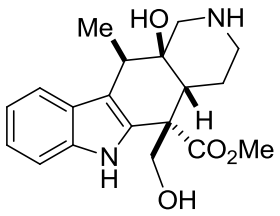
28

Synthesis of Methyl Compound 28. 10% Pd/C (158 mg) was suspended in a stirred solution of iodide **27** (29 mg, 0.039 mmol) in *t*-BuOH/EtOAc (1:1 v/v, 30 mL). The reaction mixture was evacuated and backfilled with H_2 three times from a balloon and stirred under a H_2 atmosphere at rt. After 3.5 h, the reaction was evacuated and back filled with argon, and another portion of 10% Pd/C (32 mg) was added and the reaction mixture was stirred under H_2 at rt for another 12 h. The Pd/C was filtered off through a pad of Celite, and the solvent was removed *in vacuo* to afford a yellow foamy solid. This material was purified by flash column chromatography on silica gel (CH_2Cl_2, then 2% Et_2O/CH_2Cl_2) to afford methyl compound **28** as a white solid (23 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (br s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.34-7.32 (m, 3H), 7.17 (dd, *J* = 7.1, 7.6 Hz, 1H), 7.08 (dd, *J*= 7.2, 7.4 Hz, 1H), 4.13 (d, *J* = 9.4 Hz, 1H), 4.00 (d, *J* = 9.4 Hz, 1H), 3.96 (d, *J* = 11.8 Hz, 1H), 3.72 (s, 3H), 3.66 (q, *J* = 7.0 Hz, 1H), 3.09 (s, 1H), 2.45 (s, 3H), 2.26 (t, *J* = 10.4 Hz, 1H), 2.04 (d, *J* = 13.0 Hz, 1H), 2.00 (dd, *J* = 3.7, 12.6 Hz, ,1H), 1.63 (qd, *J* = 4.4, 12.9 Hz, 1H), 1.57 (d, *J* = 6.9 Hz, 3H), 0.80 (s, 3H), -0.07 (s, 3H), -0.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 143.9, 137.1, 133.0, 130.0, 129.9, 129.8, 127.9, 126.7, 121.7, 120.5, 119.1, 111.4, 111.2, 72.5, 70.7, 55.1, 53.4, 52.3, 48.2, 46.0, 30.5, 26.5, 25.8, 25.7, 21.7, 18.1, 12.8, -5.7, -5.8; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{32}H_{45}N_2O_6SSi$, 613.2768; found, 613.2772.



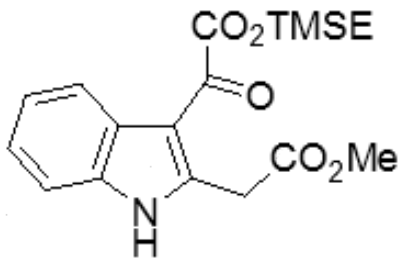
29

Synthesis of Piperidine 29. Magnesium turnings (399 mg, excess) were added to a solution of compound **28** (21.6 mg, 0.035 mmol) in anhydrous methanol, and the mixture was sonicated at rt until all the magnesium turnings dissolved (~45 min). The reaction mixture was then poured into $NH_4Cl_{(aq)}$ at 0 ^oC, and extracted with $CHCl_3$. The organic extract was dried over Na_2SO_4, and evaporated to dryness *in vacuo* to give a white foamy solid. This material was purified by flash chromatography on silica gel (2% to 5% MeOH/$CHCl_3$, then 1% NEt_3 in 5% MeOH/$CHCl_3$) to afford piperidine **29** as a white solid (15.6 mg, 96%). ^1H NMR (400 MHz, CD_3OD) δ 7.90 (br s, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 7.2, 7.4 Hz, 1H), 6.98 (dd, *J* = 7.2, 7.3 Hz, 1H), 4.34 (d, *J* = 9.3 Hz, 1H), 4.20 (d, *J* = 9.4 Hz, 1H), 3.77 (s, 3H), 3.42 (q, *J* = 6.7 Hz, 1H), 3.28 (m, 1H), 3.03 (q, *J* = 7.2 Hz, 1H), 2.94 (br d, *J* = 12.6 Hz, 1H), 2.69 (m, 1H), 2.50 (d, *J* = 12.7 Hz, 1H), 2.29 (m, 1H), 1.49 (d, *J* = 6.7 Hz, 3H), 0.83 (s, 9H), -0.02 (s, 3H), -0.10 (s, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 175.1, 138.6, 131.7, 127.9, 122.2, 120.8, 119.4, 112.7, 112.0, 79.6, 72.4, 71.6, 56.9, 54.0, 52.7, 47.8, 45.4, 32.1, 26.4, 19.2, 14.5, -5.4, -5.5; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{39}N_2O_4Si$, 459.2674; found, 459.2676.



(±)-3

Synthesis of (±)-Alstilobanine A (3). A solution of *O*-TBS indole **29** (16.5 mg, 0.036 mmol) in $CHCl_3$ (3.3 mL) at 0 ^oC was treated with a solution of hydrogen chloride in MeOH (1.25 M, 3.3 mL). The resultant colorless solution was stirred at rt for 2 h, and the volatiles were removed under high vacuum to afford (±)-alstilobanine A (**3**) hydrochloride salt as a white solid (12.2 mg, 100%). ^1H NMR (400 MHz, CD_3OD) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 7.4, 7.5 Hz, 1H), 6.98 (dd, *J* = 7.4, 7.5 Hz, 1H), 4.14 (d, *J* = 10.9 Hz, 1H), 4.04 (d, *J* = 10.8 H, 1H), 3.78 (s, 3H), 3.54 (d, *J* = 12.5 Hz, 1H), 3.26 (q, *J* = 7.1 Hz, 1H), 3.09 (m, 1H), 2.93 (m, 1H), 2.87 (d, *J* = 12.6 Hz, 1H), 2.52 (m, 1H), 2.06 (m, 1H), 1.87 (m, 1H), 1.43 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, CD_3OD) δ 174.9, 138.9, 130.9, 127.2, 122.5, 119.6, 119.5, 113.3, 112.2, 71.0, 68.7, 55.2, 53.0, 50.5, 42.4 (2C), 34.4, 22.6, 15.7; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{19}H_{25}N_2O_4$, 345.1809; found,345.1809.



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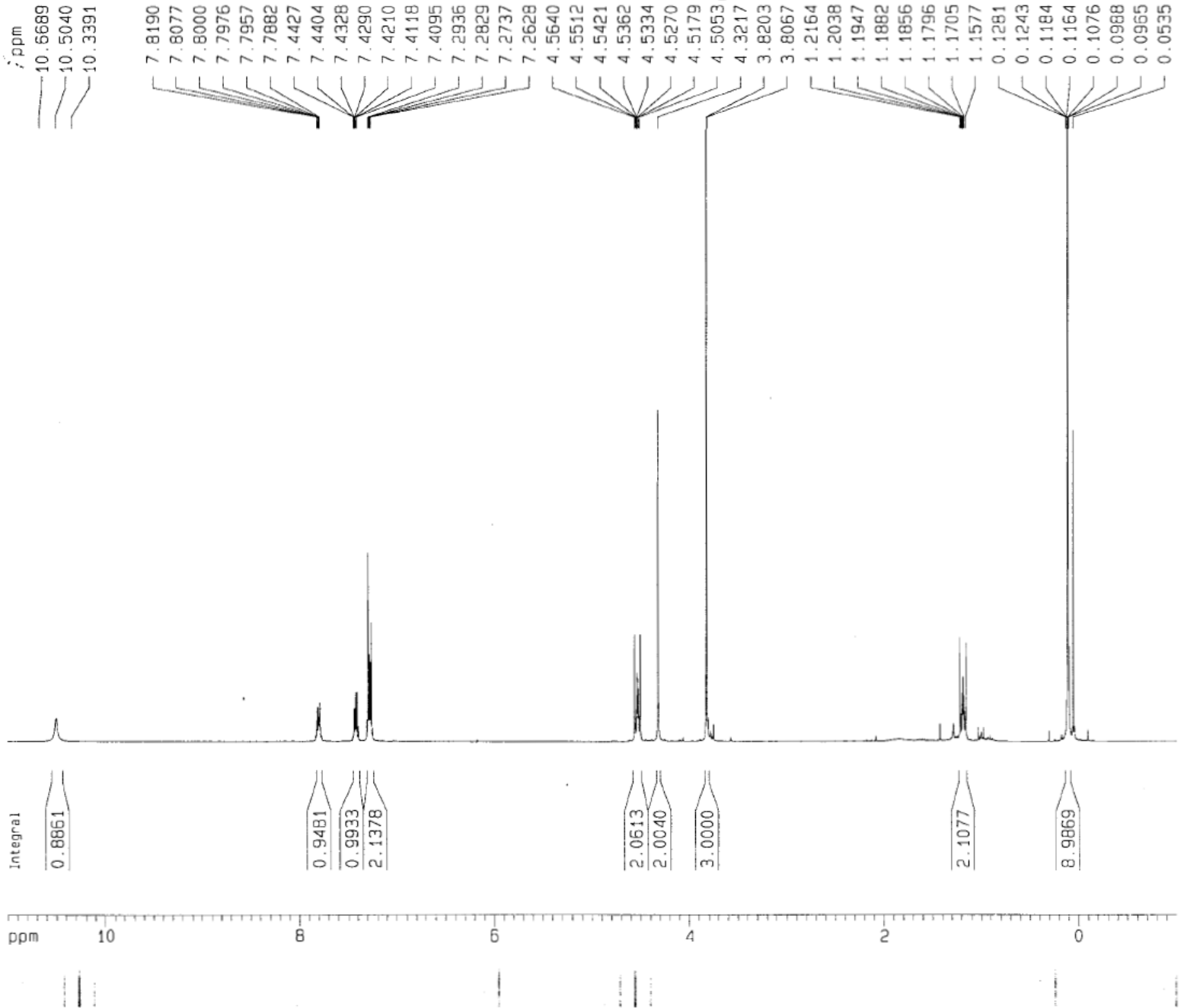


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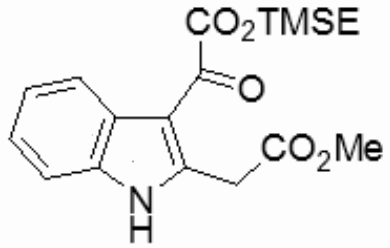

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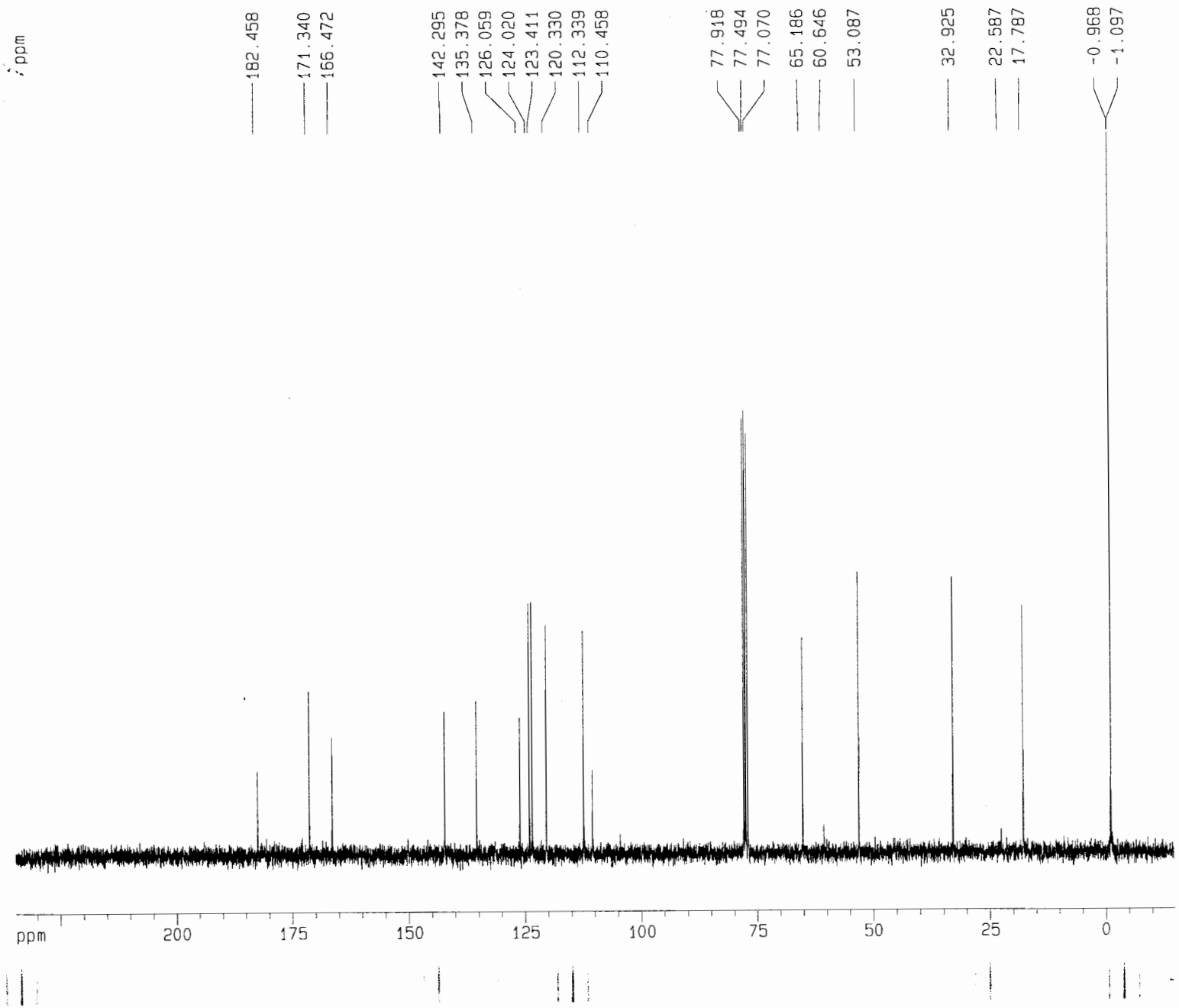


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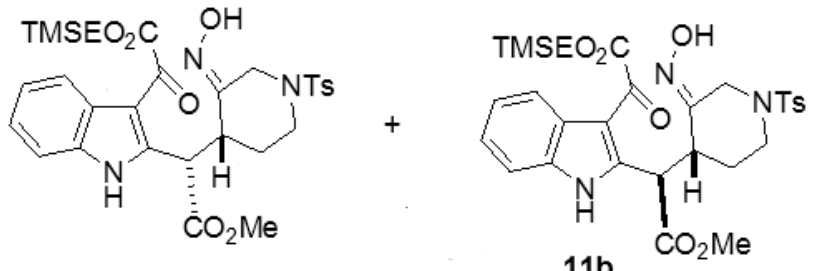
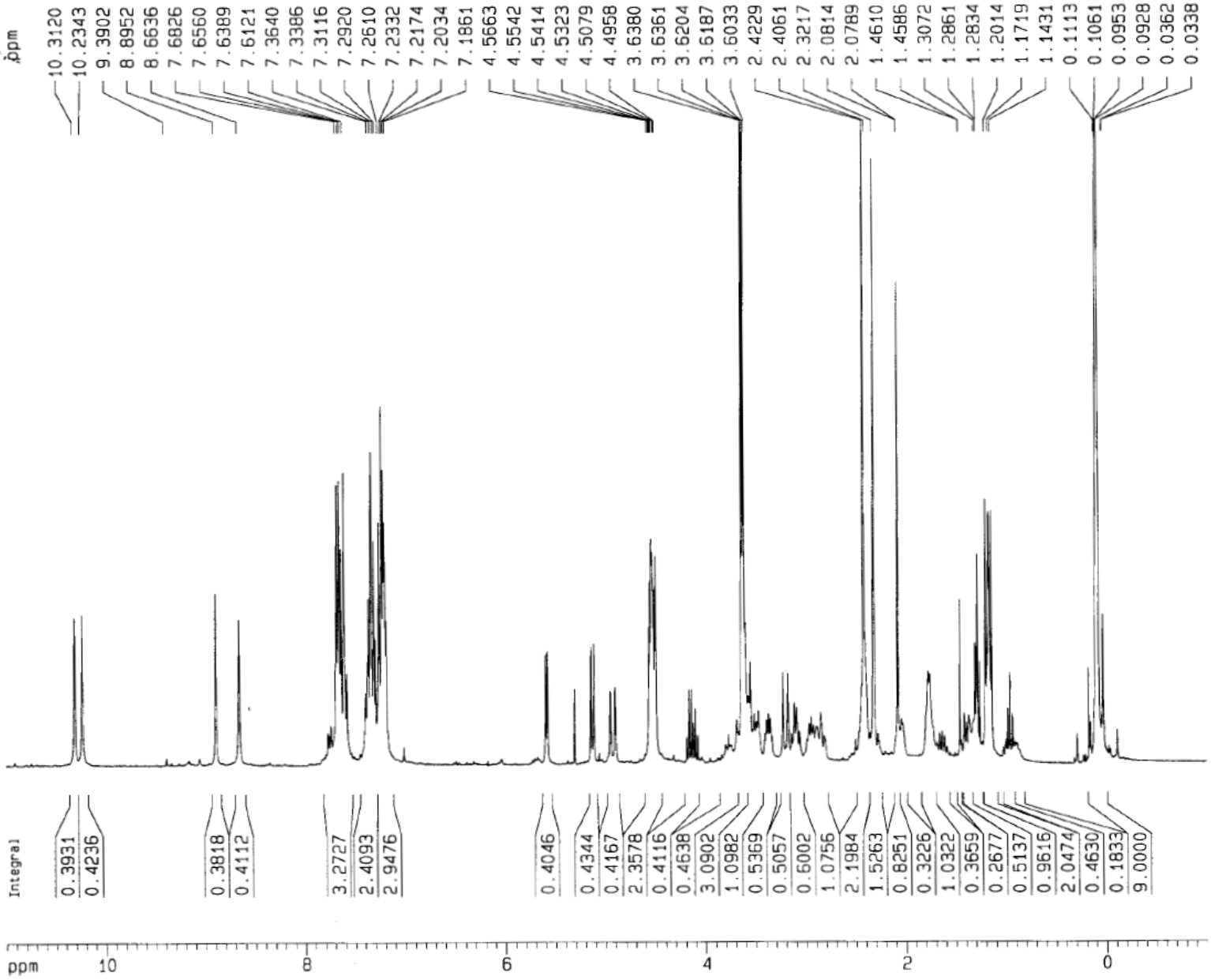
Diastereomeric products mixture of the Nitrosoalkene Michael addition



11a 11b

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1D NMR plot parameters
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F2P                -1.000 ppm
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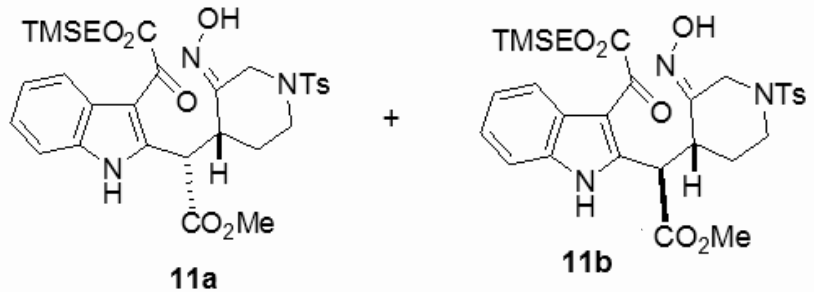
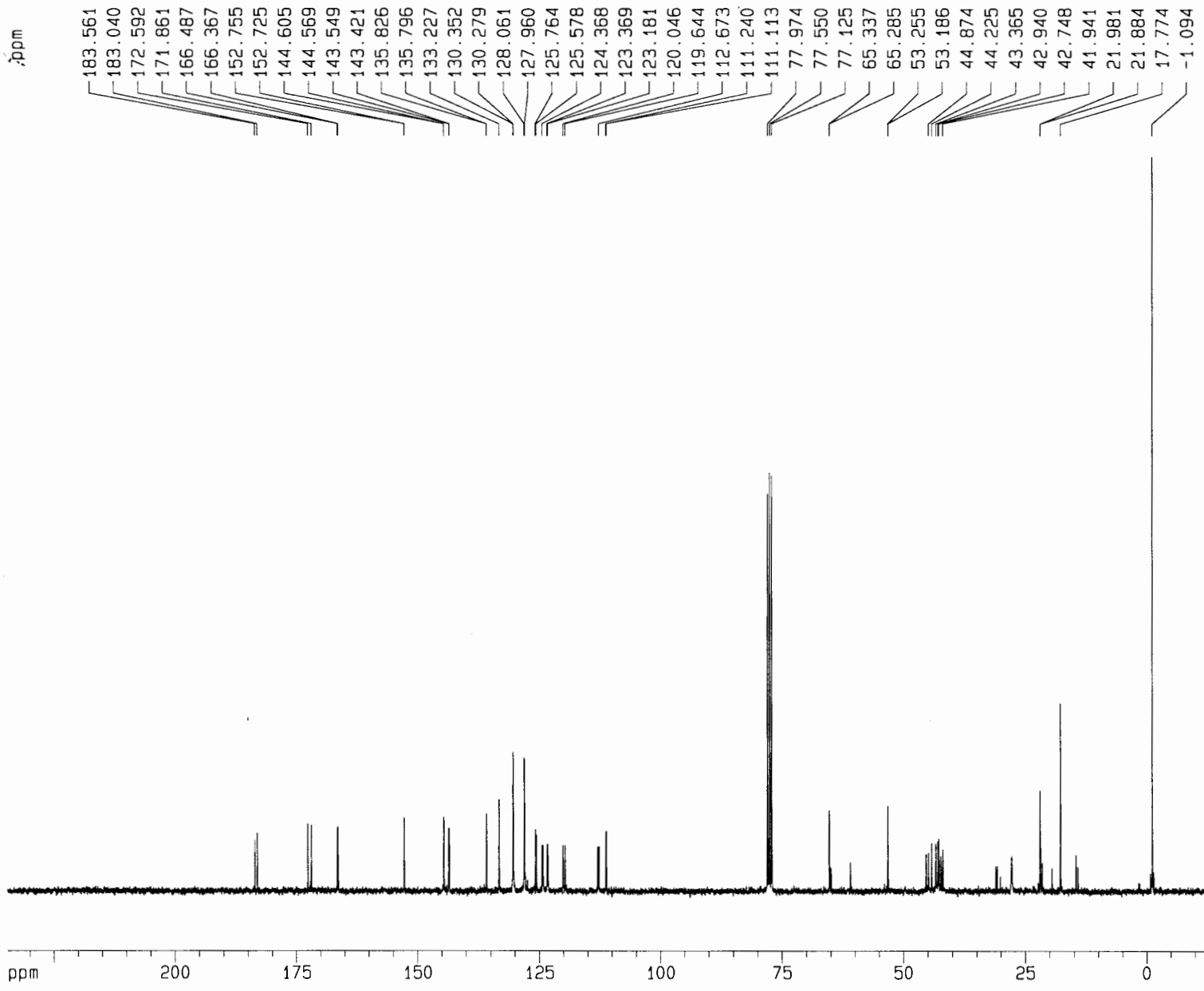
Diastereomeric products mixture of the Nitrosoalkene Michael addition



11a **11b**

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F2 - Processing parameters
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1D NMR plot parameters
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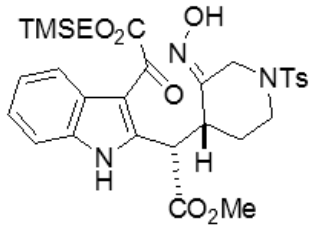

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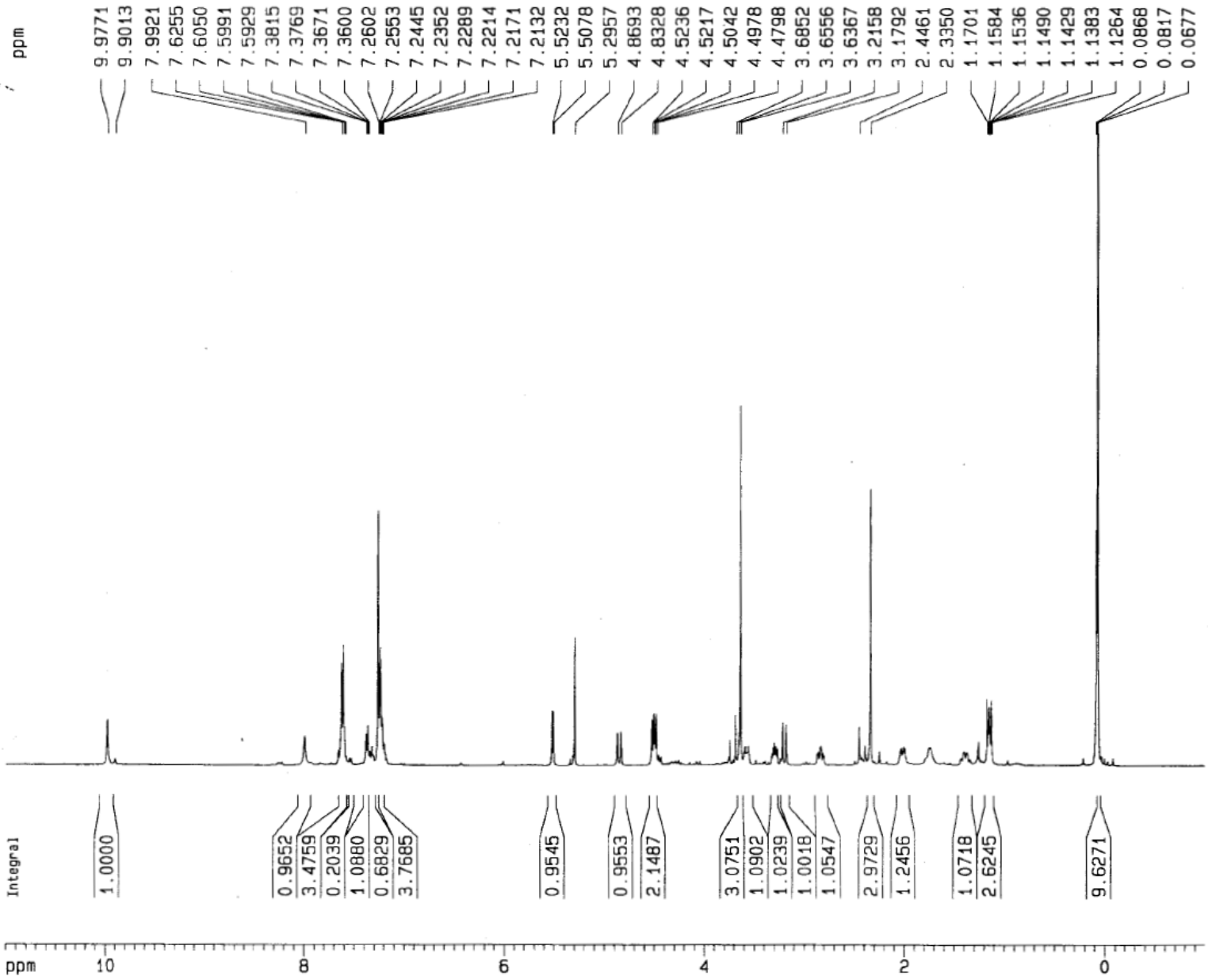

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F2 - Processing parameters

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1D NMR plot parameters

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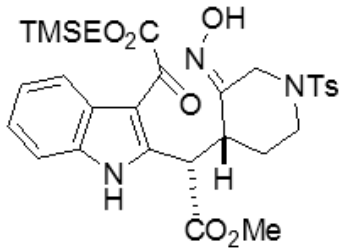
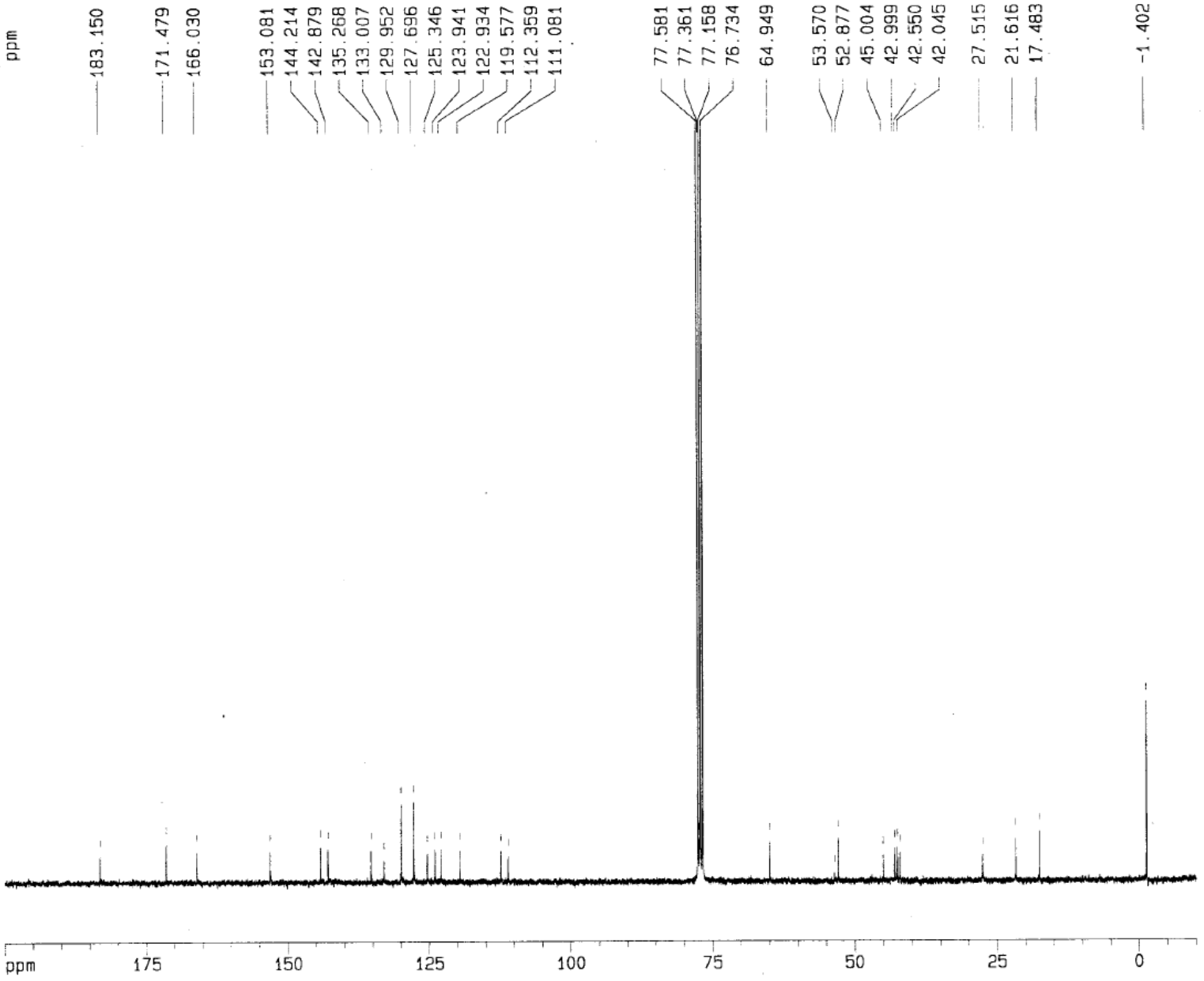


11a

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HZCM        792.41132 Hz/cm
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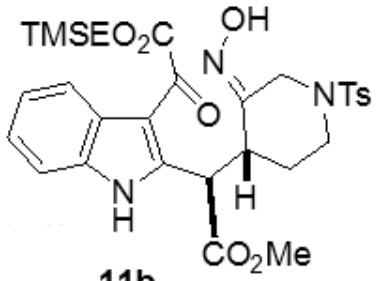
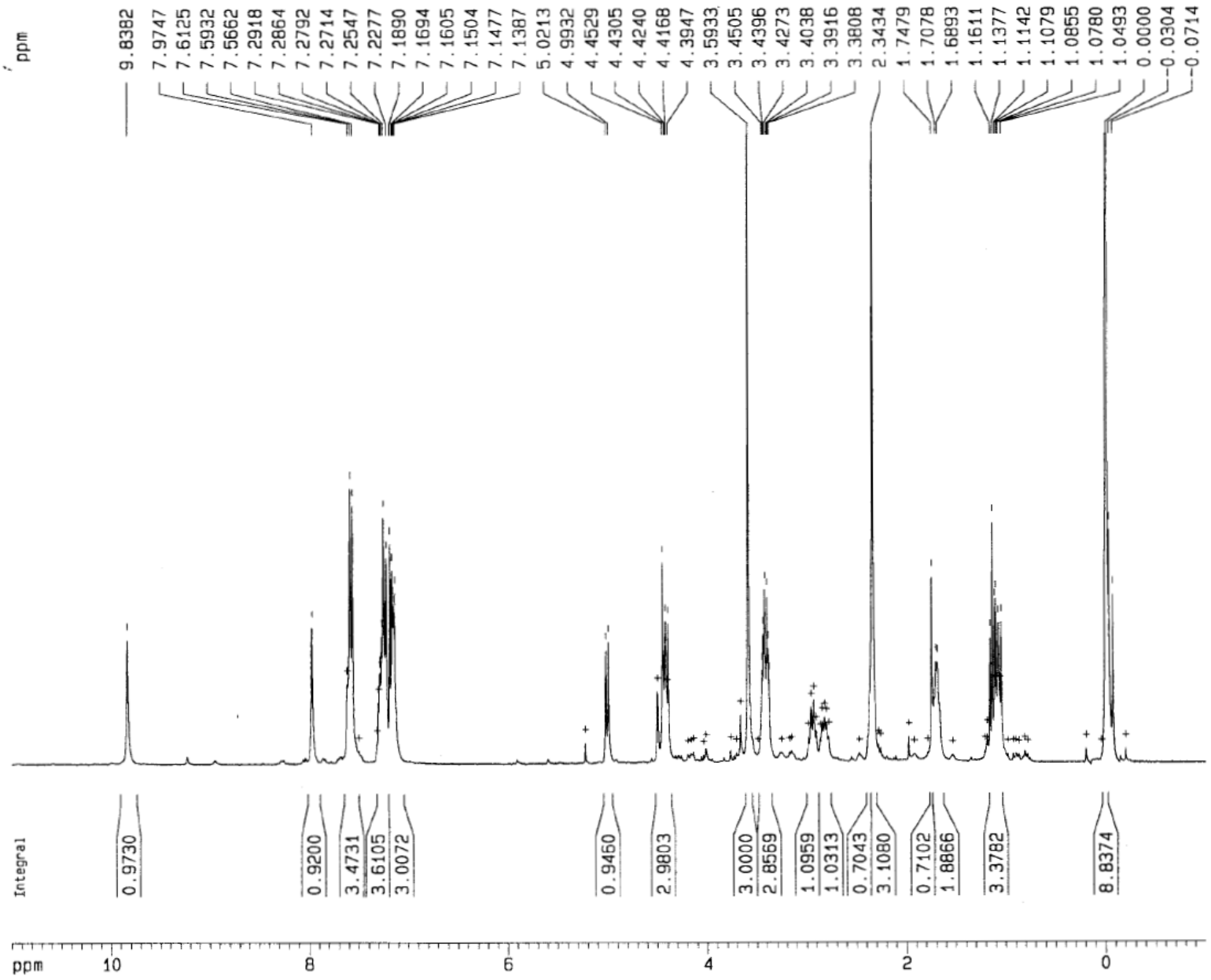


11b

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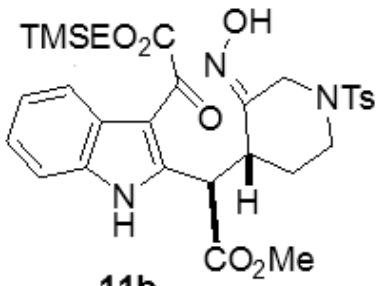
Current Data Parameters
NAME      033111FYQI-NAM
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110331
Time               15.24
INSTRUM            spect
PROBHD     5 mm Multinu
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           6172.839 Hz
FIDRES        0.094190 Hz
AQ            5.3084660 sec
RG                322.5
DW               81.000 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

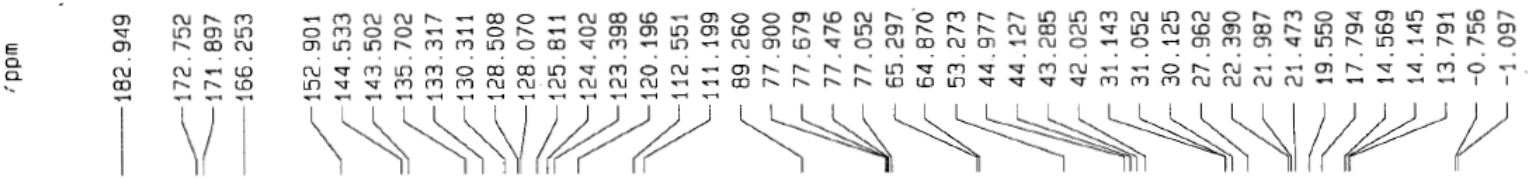
============ CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1        300.1318534 MHz

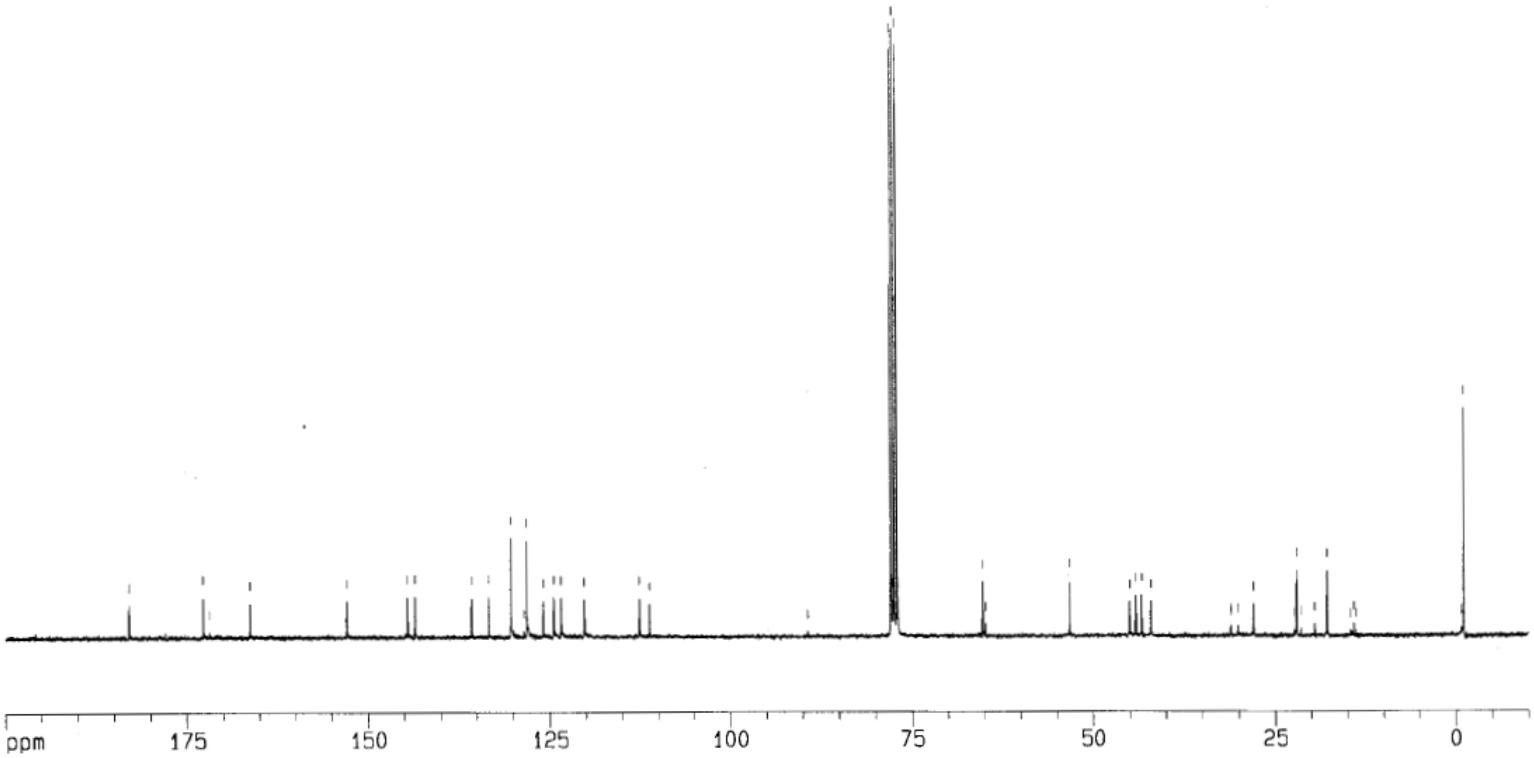
F2 - Processing parameters
SI                32768
SF          300.1300277 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
F1P               11.000 ppm
F1              3301.43 Hz
F2P               -1.000 ppm
F2              -300.13 Hz
PPMCM          0.60000 ppm/cm
HZCM          180.07802 Hz/cm
```



11b






```
Current Data Parameters
NAME        092412FYQ-11b
EXPNO                   2
PROCNO                  1

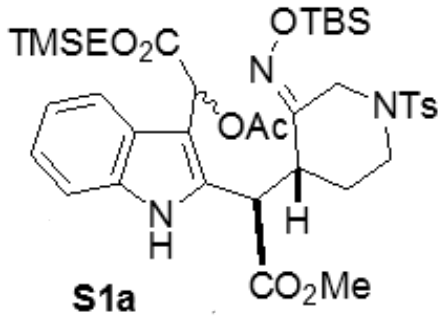
F2 - Acquisition Parameters
Date_            20120924
Time                23.14
INSTRUM             spect
PROBHD    5 mm QNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  3584
DS                     4
SWH          18796.992 Hz
FIDRES       0.286819 Hz
AQ           1.7433076 sec
RG                  2048
DW              26.600 usec
DE               6.00 usec
TE              300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1               5.25 usec
PL1             -6.00 dB
SF01        75.4106357 MHz

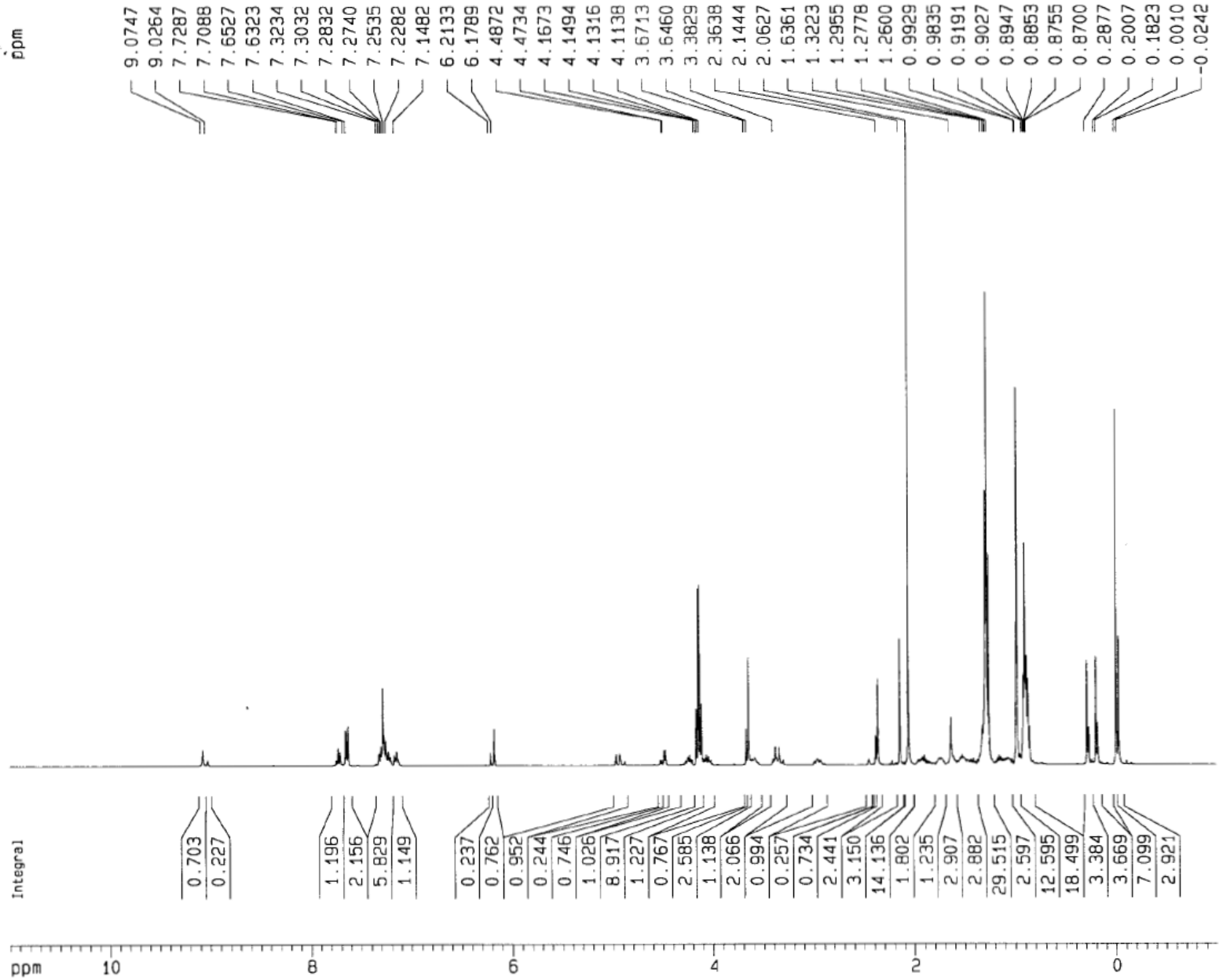
============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2          115.00 usec
PL2              0.00 dB
PL12            19.70 dB
PL13            19.70 dB
SF02       299.8711995 MHz

F2 - Processing parameters
SI                 32768
SF          75.4023410 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               200.000 ppm
F1              15080.47 Hz
F2P               -10.000 ppm
F2               -754.02 Hz
PPMCM           10.50000 ppm/cm
HZCM          791.72461 Hz/cm
```



S1a



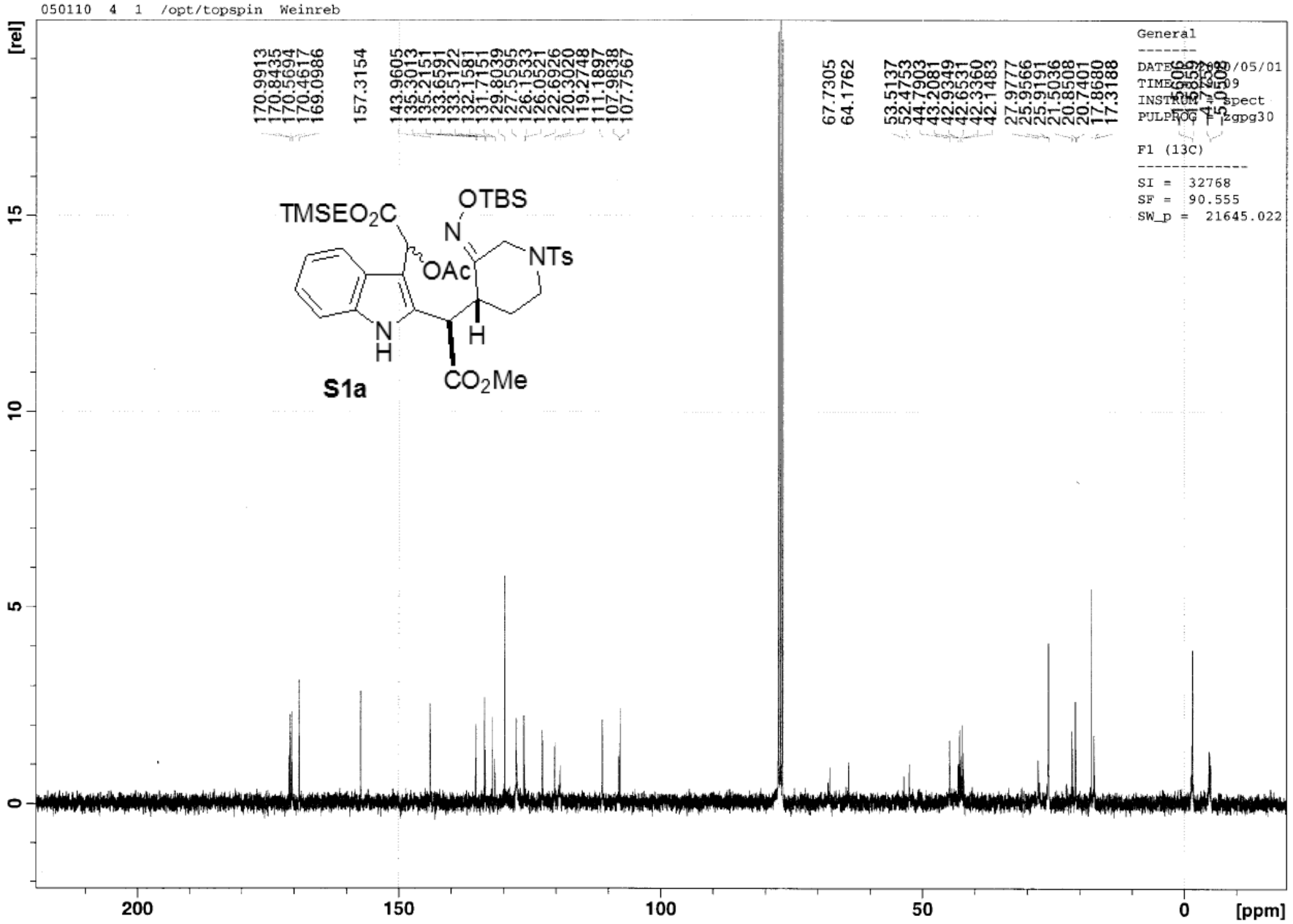

```
Current Data Parameters
NAME        012710mmm4284
EXPNO               2
PROCNO              1

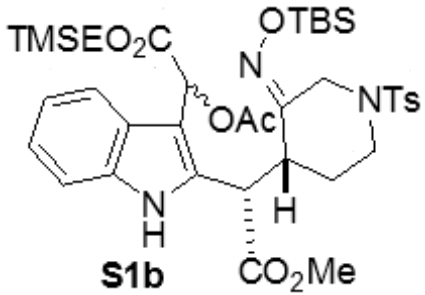
F2 - Acquisition Parameters
Date_          20100127
Time             10.11
INSTRUM          spect
PROBHD    5 mm BBI 1H-B
PULPROG          zg30
TD              33110
SOLVENT          CDCl3
NS                 16
DS                  2
SWH          8278.146 Hz
FIDRES       0.250019 Hz
AQ           1.9998940 sec
RG                 64
DW              60.400 usec
DE               6.00 usec
TE              300.0 K
D1           1.00000000 sec

============ CHANNEL f1 =========
NUC1               1H
P1              6.45 usec
PL1             0.00 dB
SFO1       400.1324710 MHz

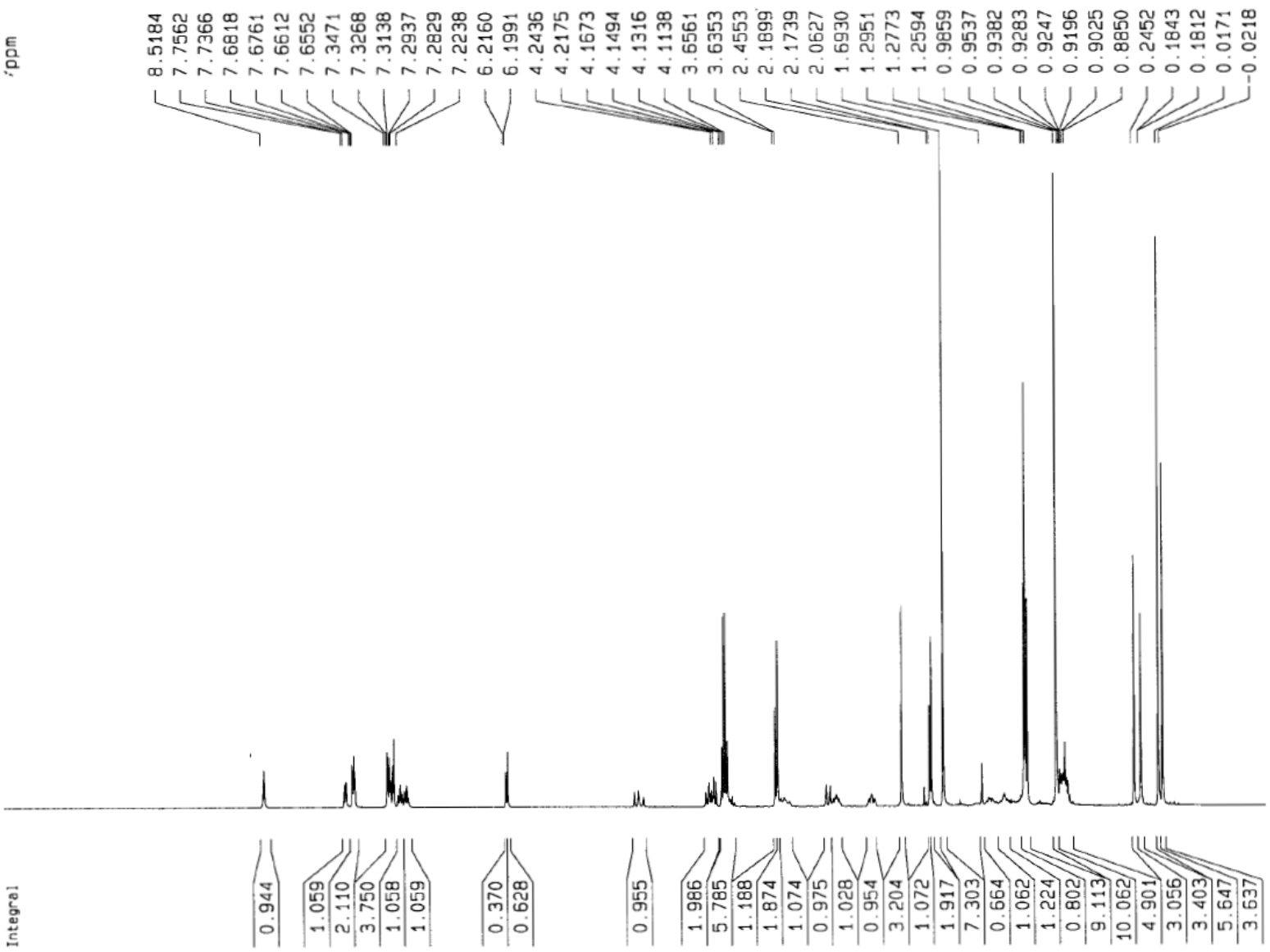
F2 - Processing parameters
SI                32768
SF         400.1300000 MHz
WDW                no
SSB                 0
LB              0.00 Hz
GB                  0
PC              1.00

1D NMR plot parameters
CX             20.00 cm
F1P            11.000 ppm
F1           4401.43 Hz
F2P            -1.000 ppm
F2           -400.13 Hz
PPMCM          0.60000 ppm/cm
HZCM         240.07800 Hz/cm
```


050110 4 1 /opt/topspin Weinreb
[rel]
170.9913
170.8435
170.5694
170.4617
169.0986
157.3154
143.9605
136.3013
135.2151
133.6591
133.5122
132.1581
131.7151
129.8039
127.5595
126.1533
126.0521
122.6926
120.3020
119.2748
111.1897
107.9838
107.7567
67.7305
64.1762
53.5137
52.4753
44.7903
43.2081
42.9349
42.6531
42.3360
42.1483
27.9777
25.9566
25.9191
21.5036
20.8508
20.7401
17.8680
17.3188
General
DATE
TIME
INSTRUM spect
PULPROG zgpg30
F1 (13C)
SI = 32768
SF = 90.555
SW_p = 21645.022
TMSEO2C
OTBS
N
OAc
NTs
N
H
H
CO2Me
S1a
15
10
5
0
200
150
100
50
0
[ppm]



S1b



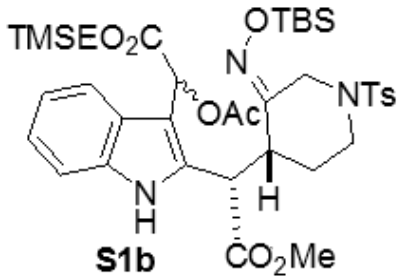

```
Current Data Parameters
NAME        012710mmm4284
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20100127
Time                10.05
INSTRUM             spect
PROBHD     5 mm BBI 1H-B
PULPROG             zg30
TD                 33110
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           8278.146 Hz
FIDRES        0.250019 Hz
AQ            1.9998940 sec
RG                    57
DW              60.400 usec
DE               6.00 usec
TE               300.0 K
D1            1.00000000 sec

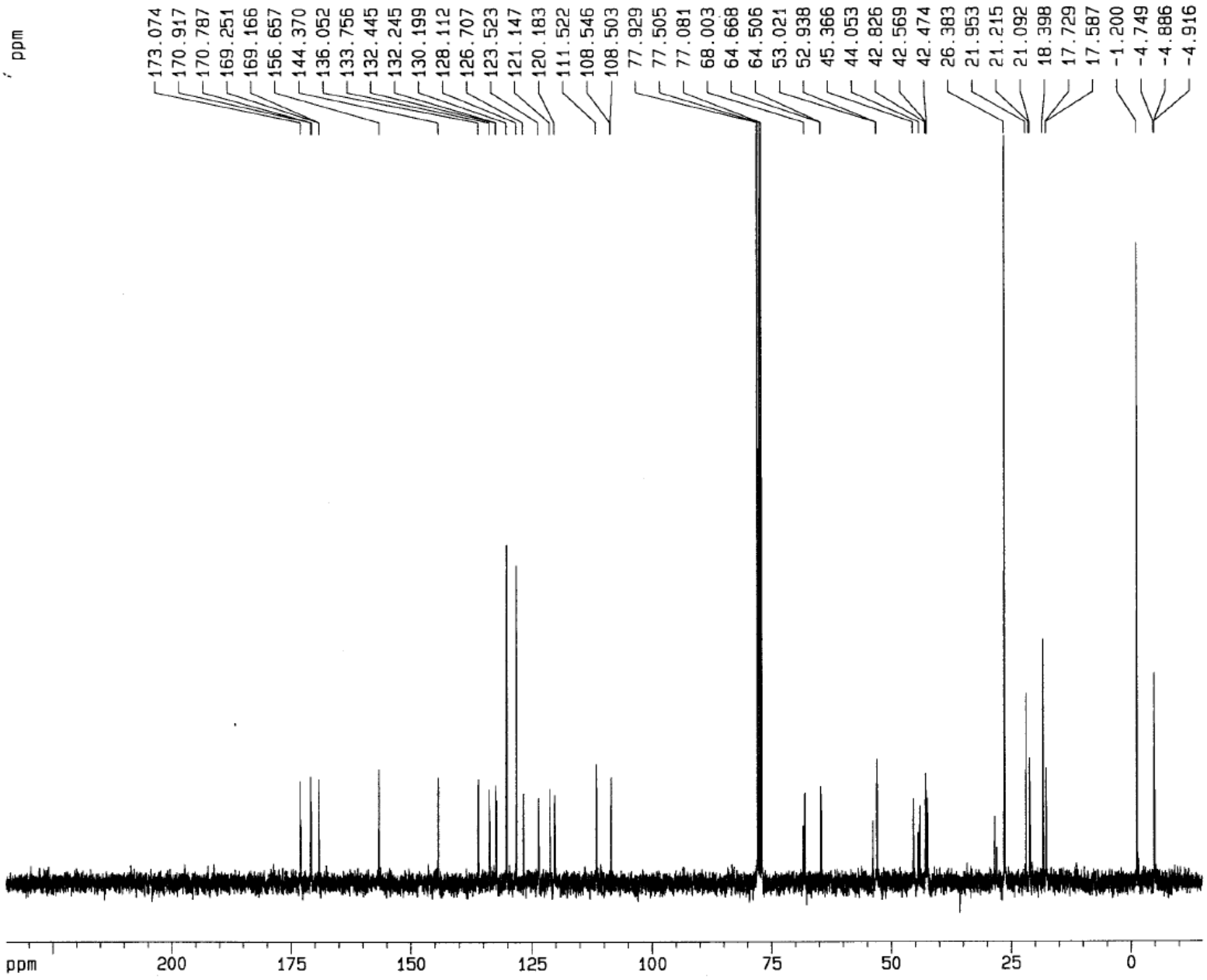
========== CHANNEL f1 =========
NUC1                   1H
P1                 6.45 usec
PL1                0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF          400.1300000 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               11.000 ppm
F1              4401.43 Hz
F2P               -1.000 ppm
F2              -400.13 Hz
PPMCM           0.60000 ppm/cm
HZCM          240.07800 Hz/cm
```



S1b



Current Data Parameters

NAME	050110
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20100501
Time	17.37
INSTRUM	spect
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	599
DS	4
SWH	18832.393 Hz
FIDRES	0.287360 Hz
AQ	1.7400308 sec
RG	16384
DW	26.550 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	11.80 usec
PL1	0.00 dB
SFO1	75.4760200 MHz

========== CHANNEL f2 ==========

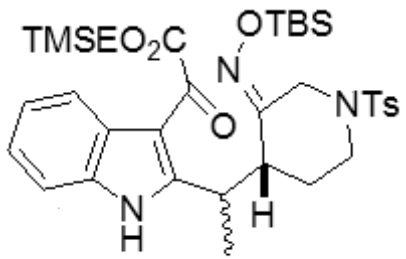
CPDPRG2	waltz16
NUC2	1H
PCPD2	110.00 usec
PL2	0.00 dB
PL12	17.50 dB
PL13	17.50 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

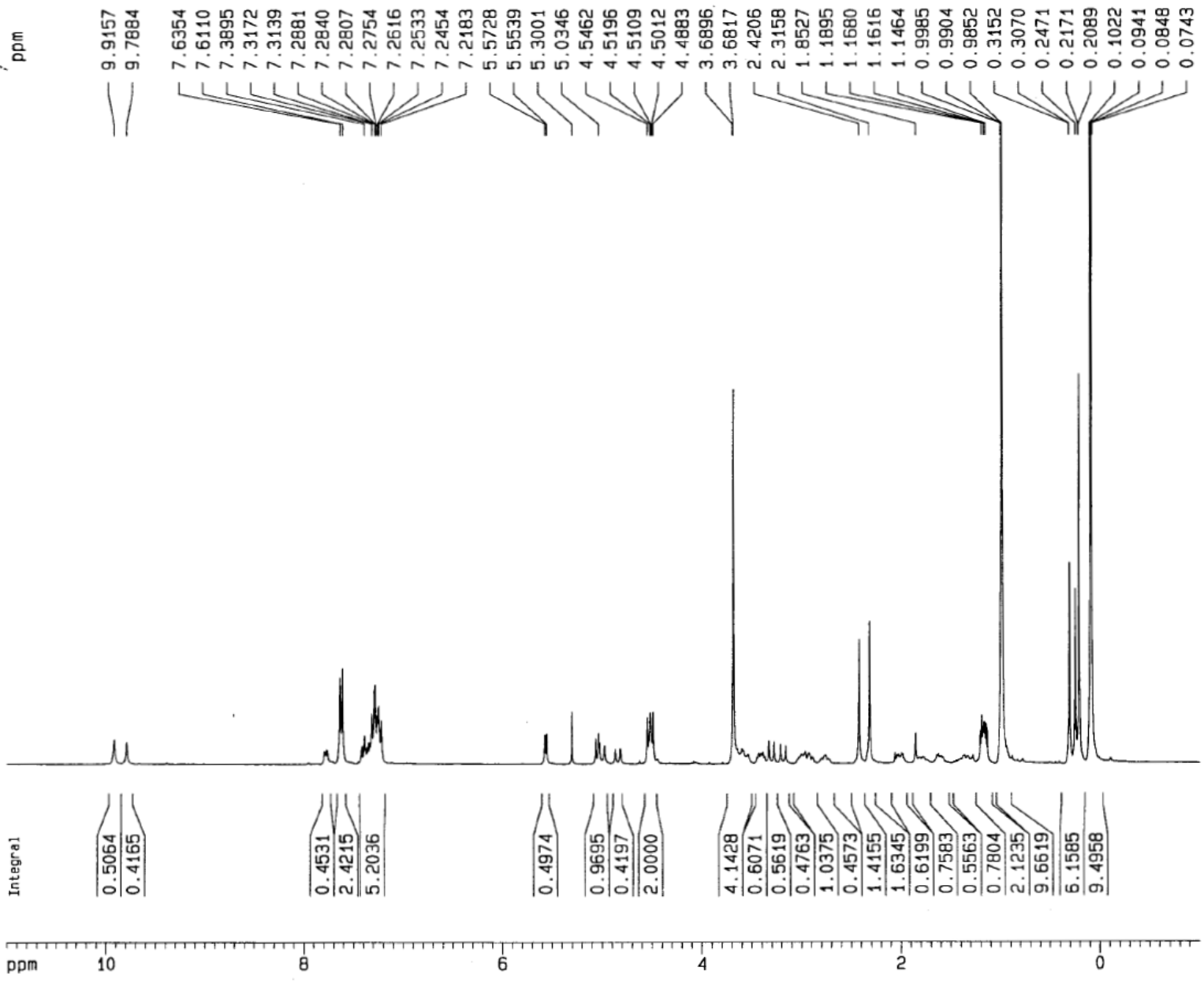
SI	32768
SF	75.4677190 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	234.765 ppm
F1	17717.16 Hz
F2P	-14.778 ppm
F2	-1115.23 Hz
PPMCM	12.47712 ppm/cm
HZCM	941.61951 Hz/cm



12



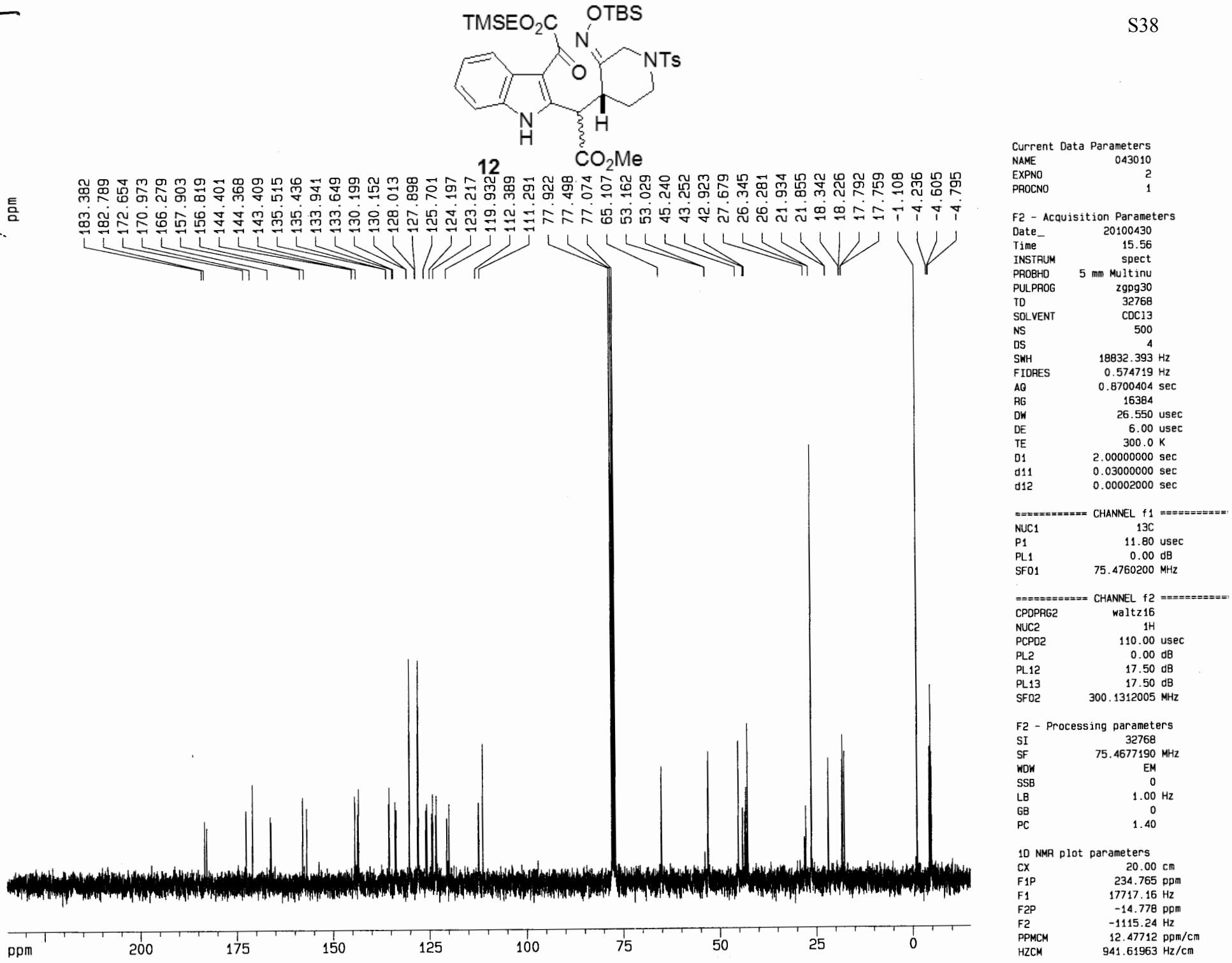

```
Current Data Parameters
NAME                  043010
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20100430
Time                  15.47
INSTRUM               spect
PROBHD      5 mm Multinu
PULPROG               zg30
TD                    24690
SOLVENT               CDCl3
NS                        8
DS                        2
SWH               6172.839 Hz
FIDRES            0.250014 Hz
AQ                1.9999400 sec
RG                      114
DW                 81.000 usec
DE                  6.00 usec
TE                  300.0 K
D1                1.00000000 sec

============ CHANNEL f1 ========
NUC1                      1H
P1                   9.60 usec
PL1                 -6.00 dB
SFO1            300.1318534 MHz

F2 - Processing parameters
SI                        32768
SF              300.1300000 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 11.000 ppm
F1                 3301.43 Hz
F2P                -1.000 ppm
F2                 -300.13 Hz
PPMCM              0.60000 ppm/cm
HZCM             180.07800 Hz/cm
```



Current Data Parameters

NAME	043010
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20100430
Time	15.56
INSTRUM	spect
PROBHD	5 mm Multinu
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	500
DS	4
SWH	18832.393 Hz
FIDRES	0.574719 Hz
AQ	0.8700404 sec
RG	16384
DW	26.550 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
d11	0.03000000 sec
d12	0.00002000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	11.80 usec
PL1	0.00 dB
SFO1	75.4760200 MHz

========== CHANNEL f2 ==========

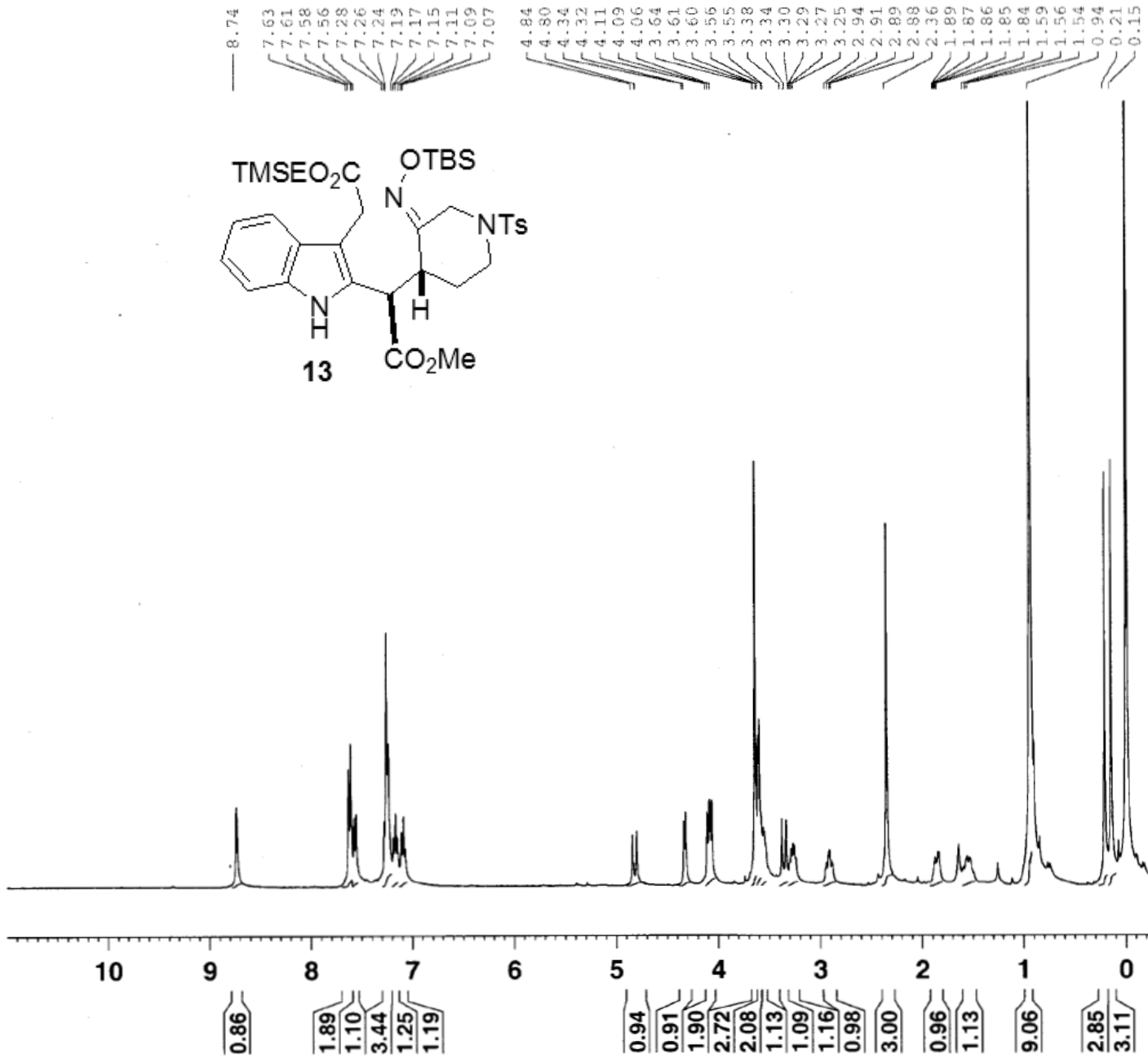
CPDPRG2	waltz16
NUC2	1H
PCPD2	110.00 usec
PL2	0.00 dB
PL12	17.50 dB
PL13	17.50 dB
SFO2	300.1312005 MHz

F2 - Processing parameters

SI	32768
SF	75.4677190 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	234.765 ppm
F1	17717.16 Hz
F2P	-14.778 ppm
F2	-1115.24 Hz
PPMCM	12.47712 ppm/cm
HZCM	941.61963 Hz/cm



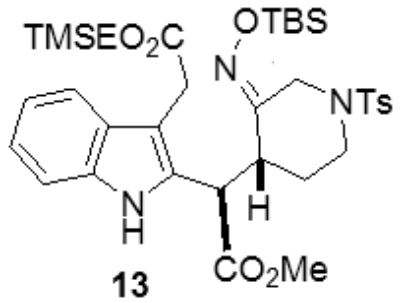
BRUKER

```
Current Data Parameters
NAME      092212FYQ-Compound13
EXPNO                        1
PROCNO                       1

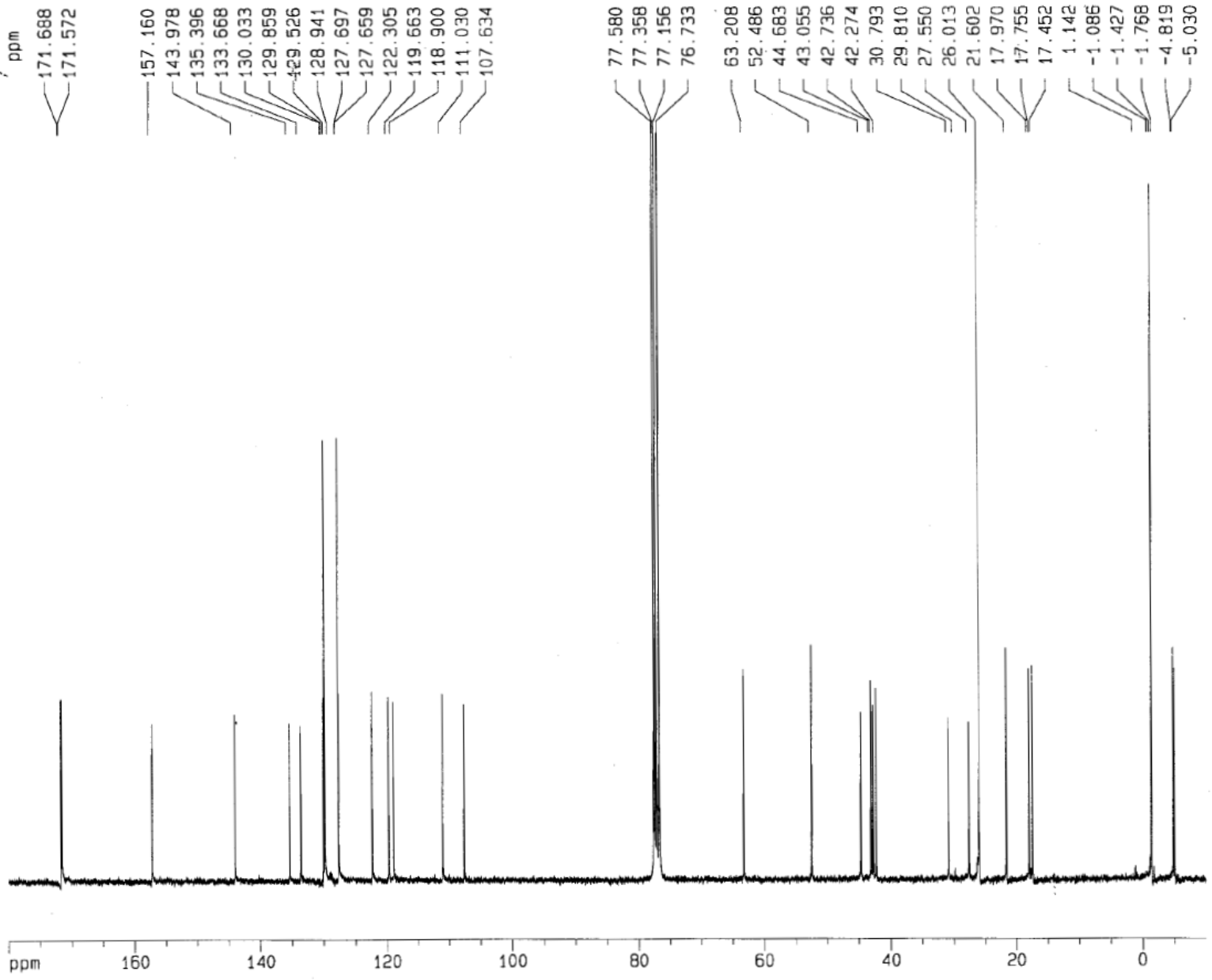
F2 - Acquisition Parameters
Date_              20120922
Time                 23.19
INSTRUM              spect
PROBHD    5 mm QNP 1H/15
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               7440.476 Hz
FIDRES            0.113533 Hz
AQ                4.4040694 sec
RG                     181
DW                  67.200 usec
DE                   6.00 usec
TE                  295.7 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  14.93 usec
PL1                 -3.00 dB
SFO1          360.1322240 MHz

F2 - Processing parameters
SI                   32768
SF            360.1300145 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```



13




```
Current Data Parameters
NAME      092212FYGcpd13
EXPNO                 2
PROCNO                1

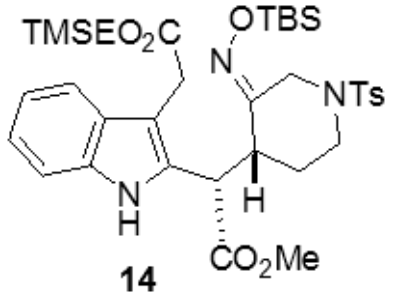
F2 - Acquisition Parameters
Date_          20120922
Time              22.08
INSTRUM           spect
PROBHD  5 mm QNP 1H/1
PULPROG        zgpg30
TD              65536
SOLVENT         CDCl3
NS               7168
DS                  4
SWH         18796.992 Hz
FIDRES      0.286819 Hz
AQ          1.7433076 sec
RG               1024
DW           26.600 usec
DE            6.00 usec
TE           300.0 K
D1          2.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec

========== CHANNEL f1 ==========
NUC1              13C
P1           5.25 usec
PL1           -6.00 dB
SFO1       75.4106357 MHz

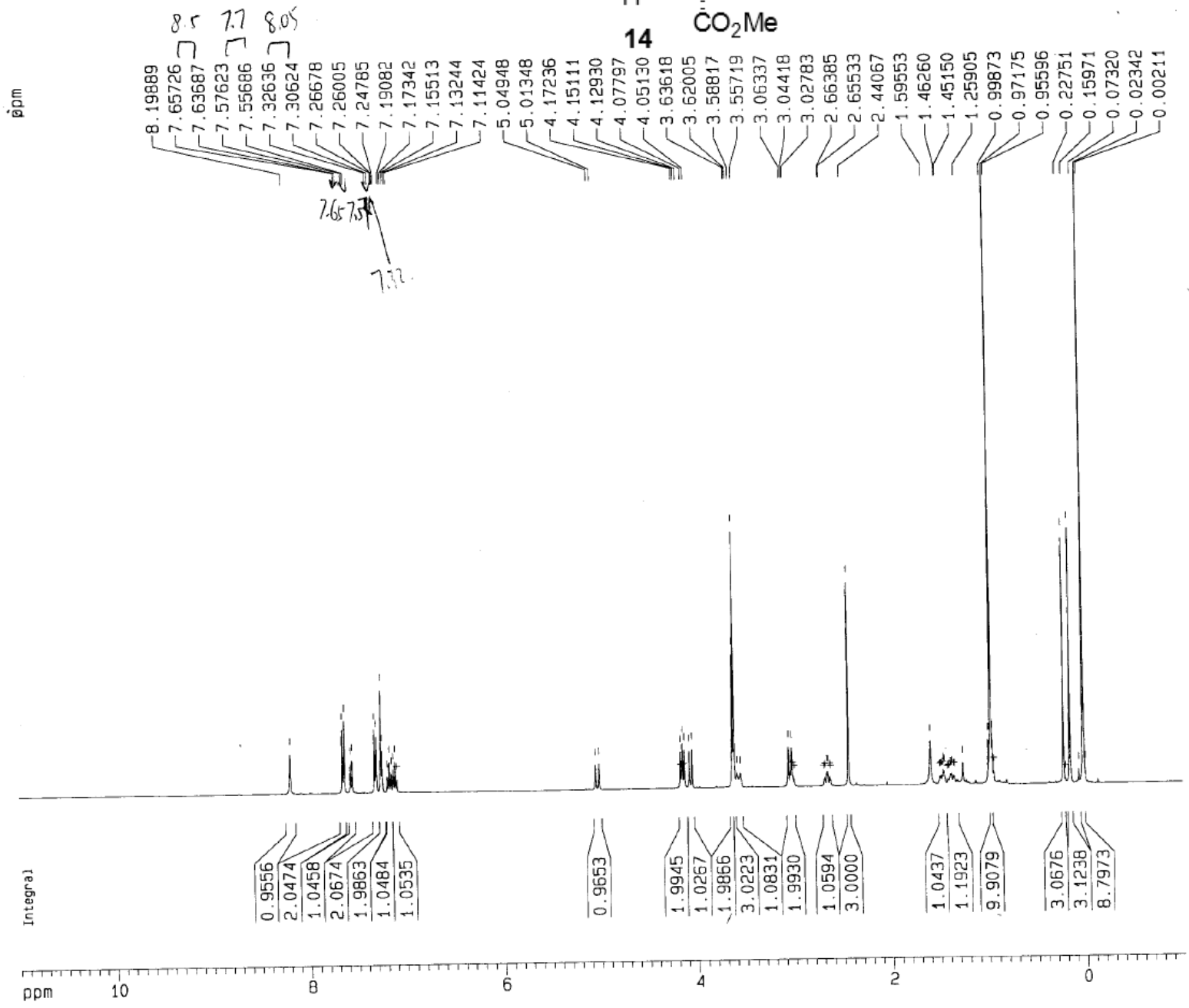
========== CHANNEL f2 ==========
CPDPRG2       waltz16
NUC2              1H
PCPD2       115.00 usec
PL2           0.00 dB
PL12          19.70 dB
PL13          19.70 dB
SFO2      299.8711995 MHz

F2 - Processing parameters
SI               32768
SF         75.4023654 MHz
WDW                EM
SSB                 0
LB             1.00 Hz
GB                  0
PC               1.40

1D NMR plot parameters
CX              20.00 cm
F1P          180.000 ppm
F1         13572.43 Hz
F2P          -10.000 ppm
F2          -754.02 Hz
PPMCM        9.50000 ppm/cm
HZCM       716.32251 Hz/cm
```



14



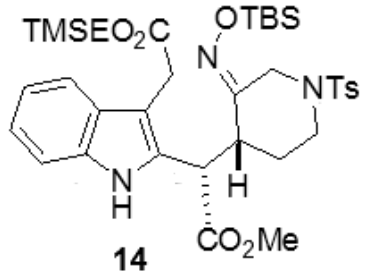

```
Current Data Parameters
NAME      071911FJII-019
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20110719
Time               9.33
INSTRUM           spect
PROBHD  5 mm BBI 1H-
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH          8278.146 Hz
FIDRES       0.126314 Hz
AQ           3.9584243 sec
RG                90.5
DW           60.400 usec
DE            6.00 usec
TE            300.0 K
D1           1.00000000 sec

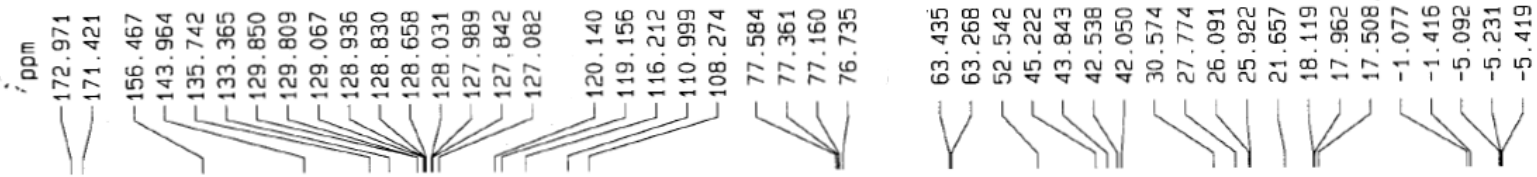
========== CHANNEL f1 ========
NUC1                 1H
P1            6.45 usec
PL1            0.00 dB
SFO1     400.1324710 MHz

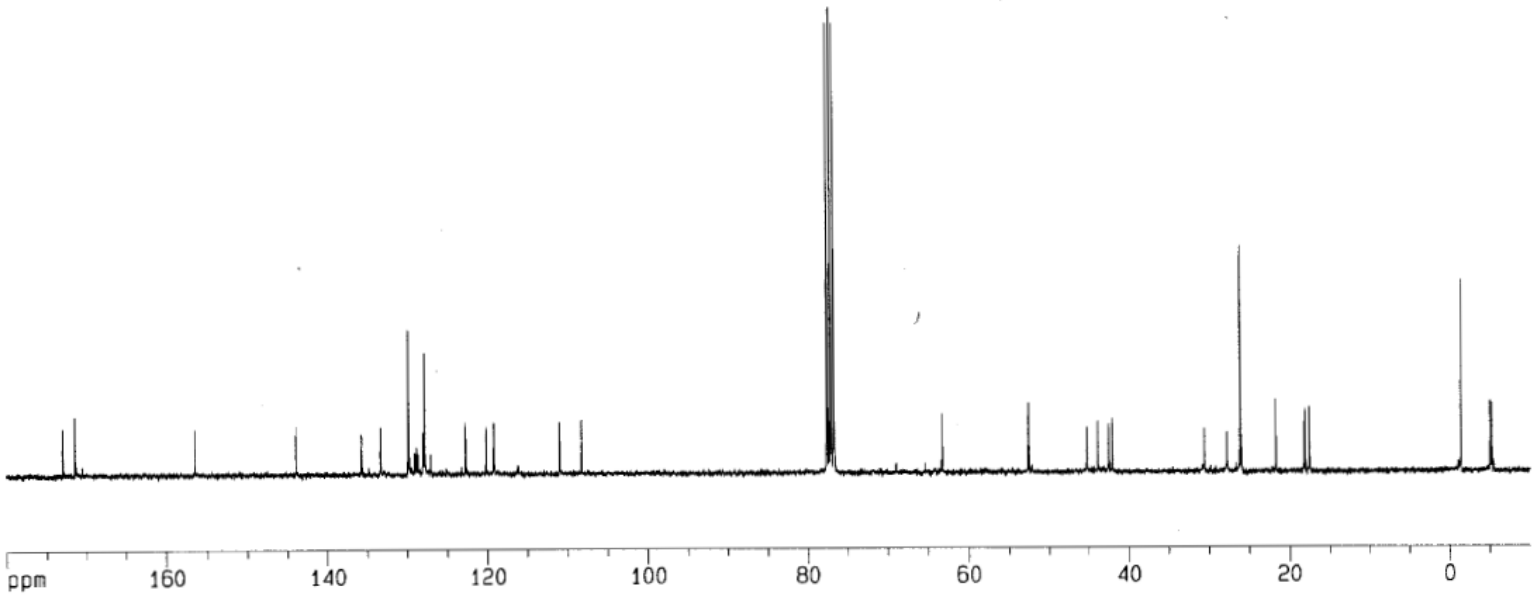
F2 - Processing parameters
SI                32768
SF     400.1300086 MHz
WDW                  EM
SSB                   0
LB             0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX            20.00 cm
F1P          11.000 ppm
F1          4401.43 Hz
F2P          -1.000 ppm
F2          -400.13 Hz
PPMCM        0.60000 ppm/cm
HZCM       240.07800 Hz/cm
```



14






```
Current Data Parameters
NAME      092212FYGcpd14
EXPNO                 2
PROCNO                1

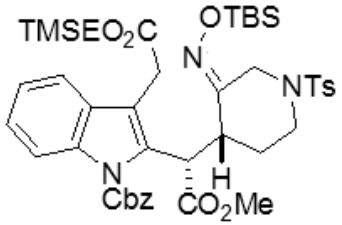
F2 - Acquisition Parameters
Date_          20120922
Time              23.19
INSTRUM           spect
PROBHD    5 mm QNP 1H/1
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                1024
DS                   4
SWH          18796.992 Hz
FIDRES       0.286819 Hz
AQ           1.7433076 sec
RG                1024
DW             26.600 usec
DE              6.00 usec
TE             300.0 K
D1          2.00000000 sec
D11         0.03000000 sec
D12         0.00002000 sec

============ CHANNEL f1 ============
NUC1               13C
P1              5.25 usec
PL1            -6.00 dB
SFO1       75.4106357 MHz

============ CHANNEL f2 ============
CPDPRG2        waltz16
NUC2               1H
PCPD2         115.00 usec
PL2             0.00 dB
PL12           19.70 dB
PL13           19.70 dB
SFO2      299.8711995 MHz

F2 - Processing parameters
SI                32768
SF         75.4023660 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              180.000 ppm
F1             13572.43 Hz
F2P              -10.000 ppm
F2              -754.02 Hz
PPMCM            9.50000 ppm/cm
HZCM           716.32251 Hz/cm
```



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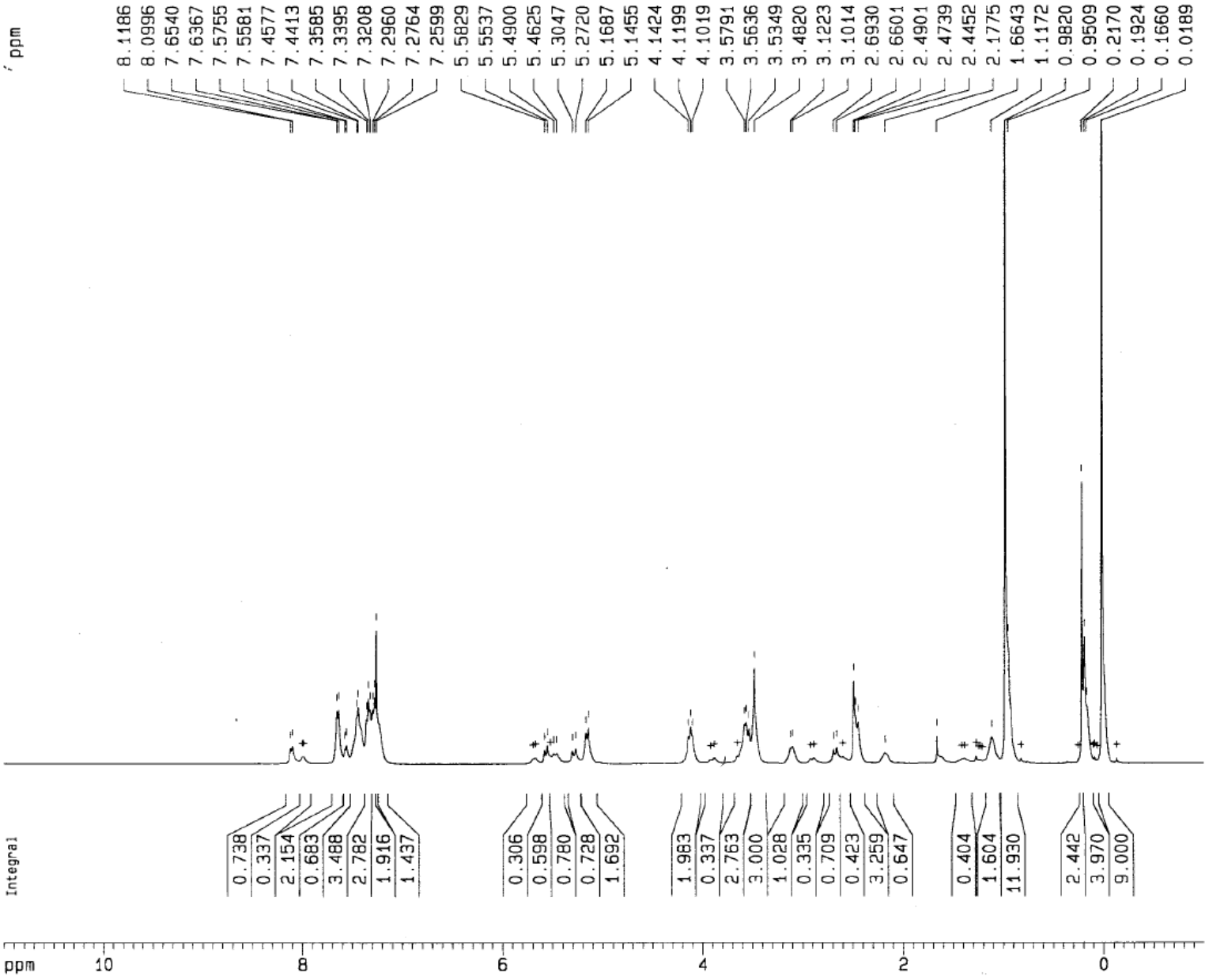


Current Data Parameters

NAME	092512FYQ-15
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120925
Time	18.02
INSTRUM	spect
PROBHD	5 mm BBI 1H-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	57
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ========

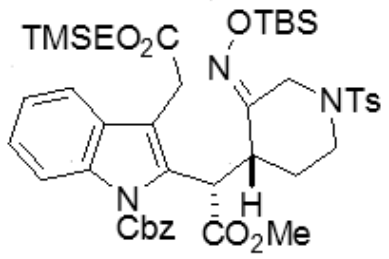
NUC1	1H
P1	6.45 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	11.000 ppm
F1	4401.43 Hz
F2P	-1.000 ppm
F2	-400.13 Hz
PPMCM	0.60000 ppm/cm
HZCM	240.07800 Hz/cm



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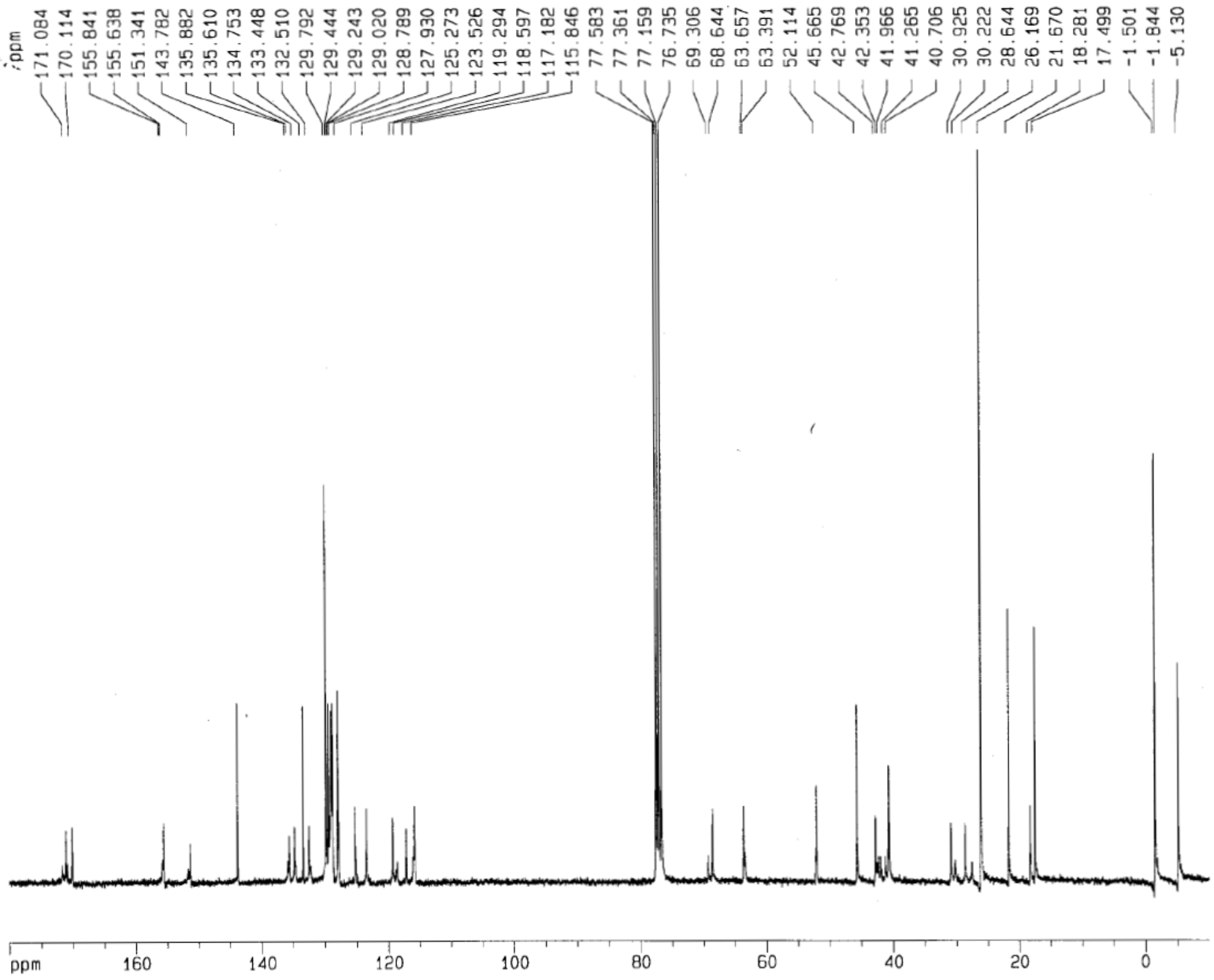


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Current Data Parameters
NAME         092412FYQ-15
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_             20120925
Time                  6.27
INSTRUM              spect
PROBHD     5 mm GNP 1H/1
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   6656
DS                      4
SWH           18796.992 Hz
FIDRES         0.286819 Hz
AQ             1.7433076 sec
RG                   1024
DW                26.600 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec

========== CHANNEL f1 ==========
NUC1                  13C
P1                   5.25 usec
PL1                 -6.00 dB
SFO1          75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              115.00 usec
PL2                 0.00 dB
PL12               19.70 dB
PL13               19.70 dB
SFO2          299.8711995 MHz

F2 - Processing parameters
SI                   32768
SF            75.4023671 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40

1D NMR plot parameters
CX                   20.00 cm
F1P                 180.000 ppm
F1                13572.43 Hz
F2P                -10.000 ppm
F2                 -754.02 Hz
PPMCM              9.50000 ppm/cm
HZCM             716.32251 Hz/cm
```

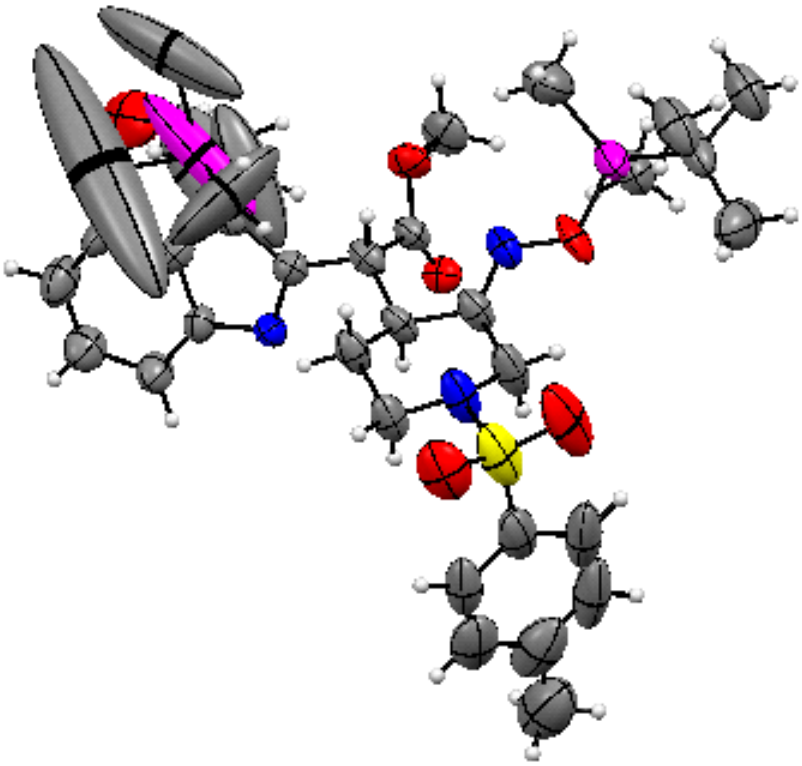
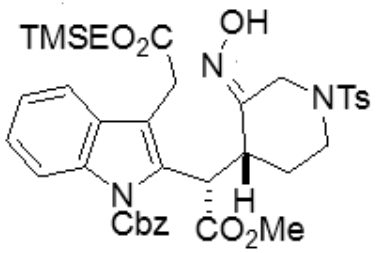


Fig. 1 ORTEP of *N*-Cbz derivative **15**



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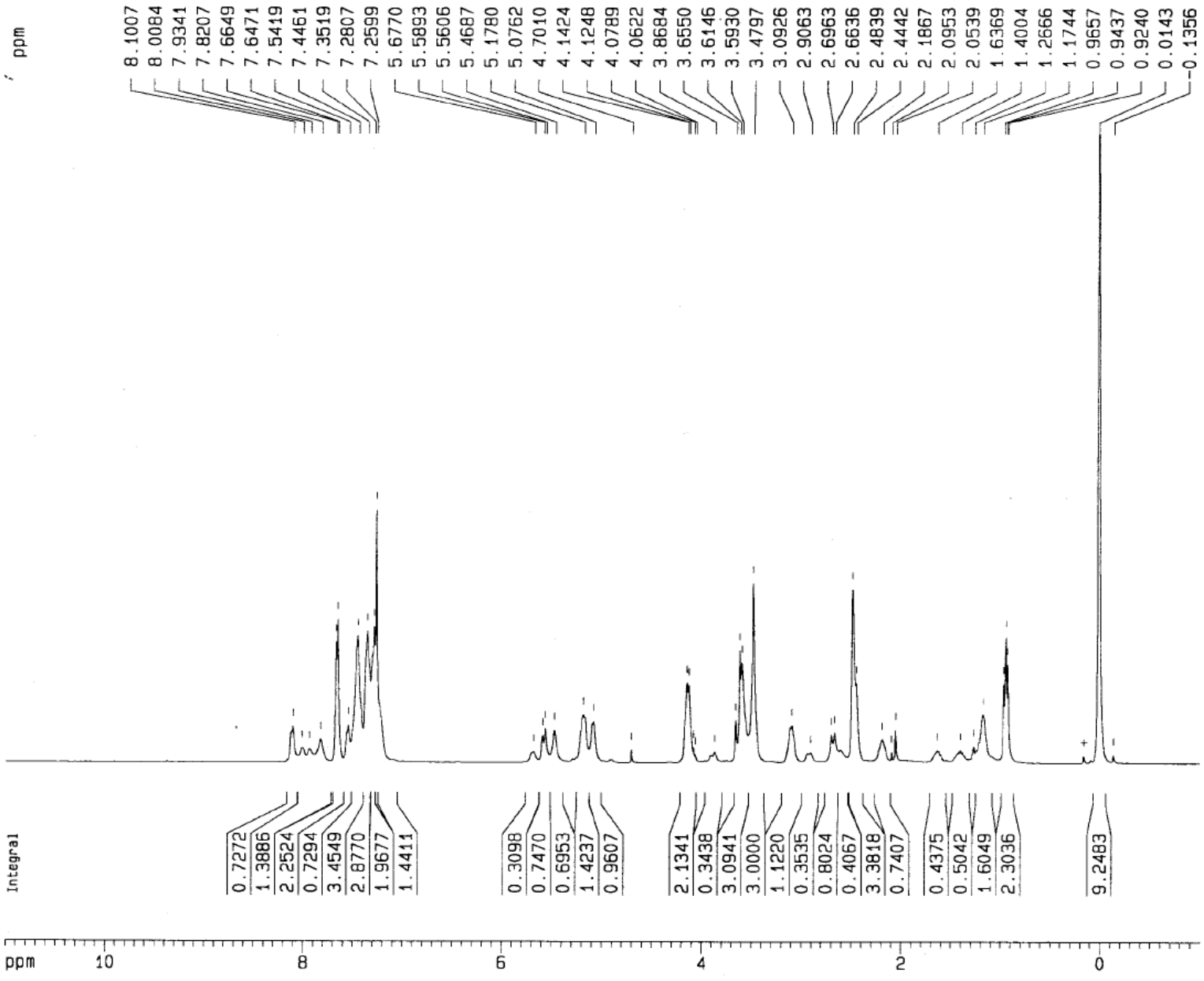


Current Data Parameters

NAME	092512FYQ-16
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120925
Time	18.29
INSTRUM	spect
PROBHD	5 mm BBI 1H-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	50.8
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ========

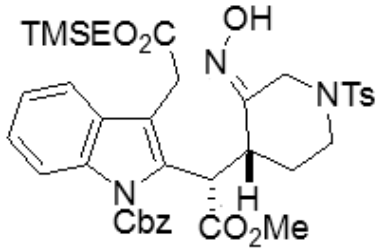
NUC1	1H
P1	6.45 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	11.000 ppm
F1	4401.43 Hz
F2P	-1.000 ppm
F2	-400.13 Hz
PPMCM	0.60000 ppm/cm
HZCM	240.07800 Hz/cm



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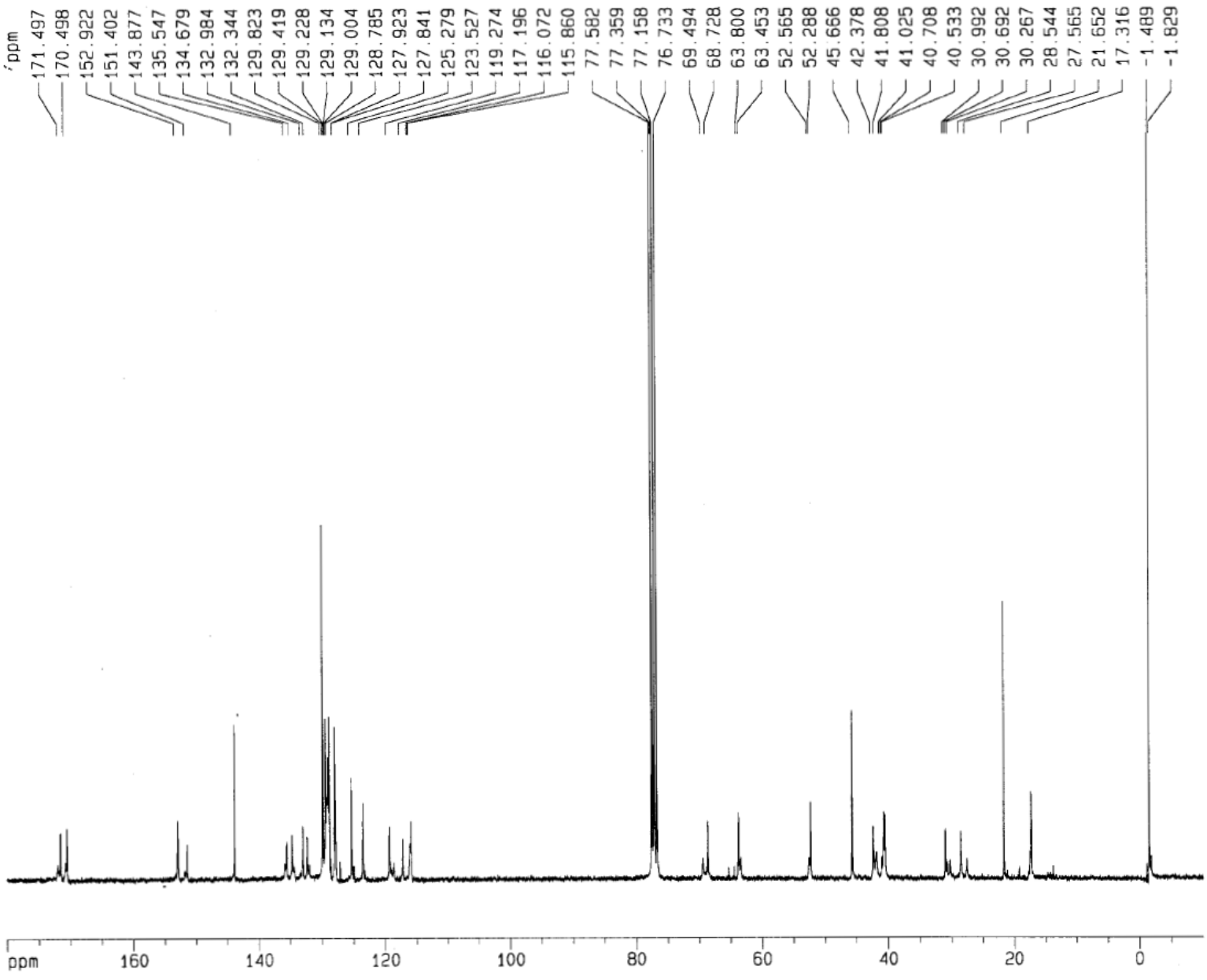


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Current Data Parameters
NAME                  092512FYG-16
EXPNO                            1
PROCNO                           1

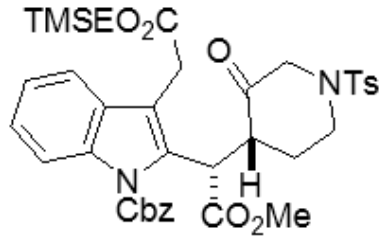
F2 - Acquisition Parameters
Date_                     20120926
Time                          7.49
INSTRUM                      spect
PROBHD     5 mm QNP 1H/1
PULPROG                    zgpg30
TD                          65536
SOLVENT                     CDCl3
NS                           8192
DS                              4
SWH                   18796.992 Hz
FIDRES                0.286819 Hz
AQ                    1.7433076 sec
RG                           4096
DW                      26.600 usec
DE                       6.00 usec
TE                       300.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec

========== CHANNEL f1 ==========
NUC1                         13C
P1                        5.25 usec
PL1                      -6.00 dB
SFO1                 75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2                  waltz16
NUC2                         1H
PCPD2                   115.00 usec
PL2                       0.00 dB
PL12                     19.70 dB
PL13                     19.70 dB
SFO2                299.8711995 MHz

F2 - Processing parameters
SI                           32768
SF                   75.4023694 MHz
WDW                             EM
SSB                              0
LB                        1.00 Hz
GB                               0
PC                            1.40

1D NMR plot parameters
CX                       20.00 cm
F1P                     180.000 ppm
F1                    13572.43 Hz
F2P                     -10.000 ppm
F2                     -754.02 Hz
PPMCM                  9.50000 ppm/cm
HZCM                 716.32251 Hz/cm
```



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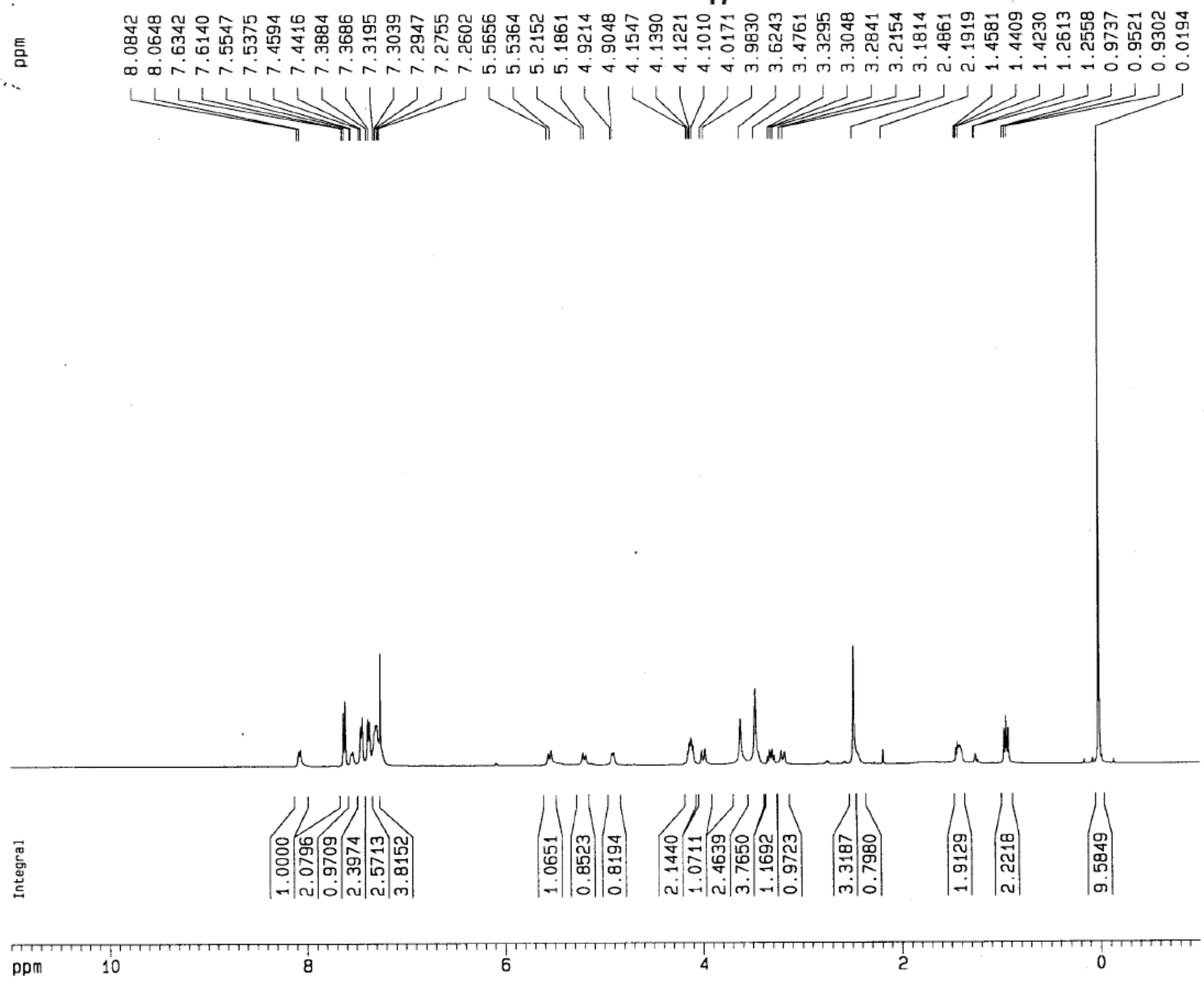


Current Data Parameters

NAME	092612FYQ-17
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120926
Time	9.06
INSTRUM	spect
PROBHD	5 mm BBI 1H-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	114
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ========

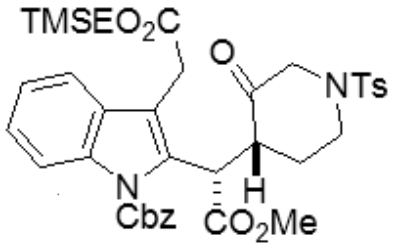
NUC1	1H
P1	6.45 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

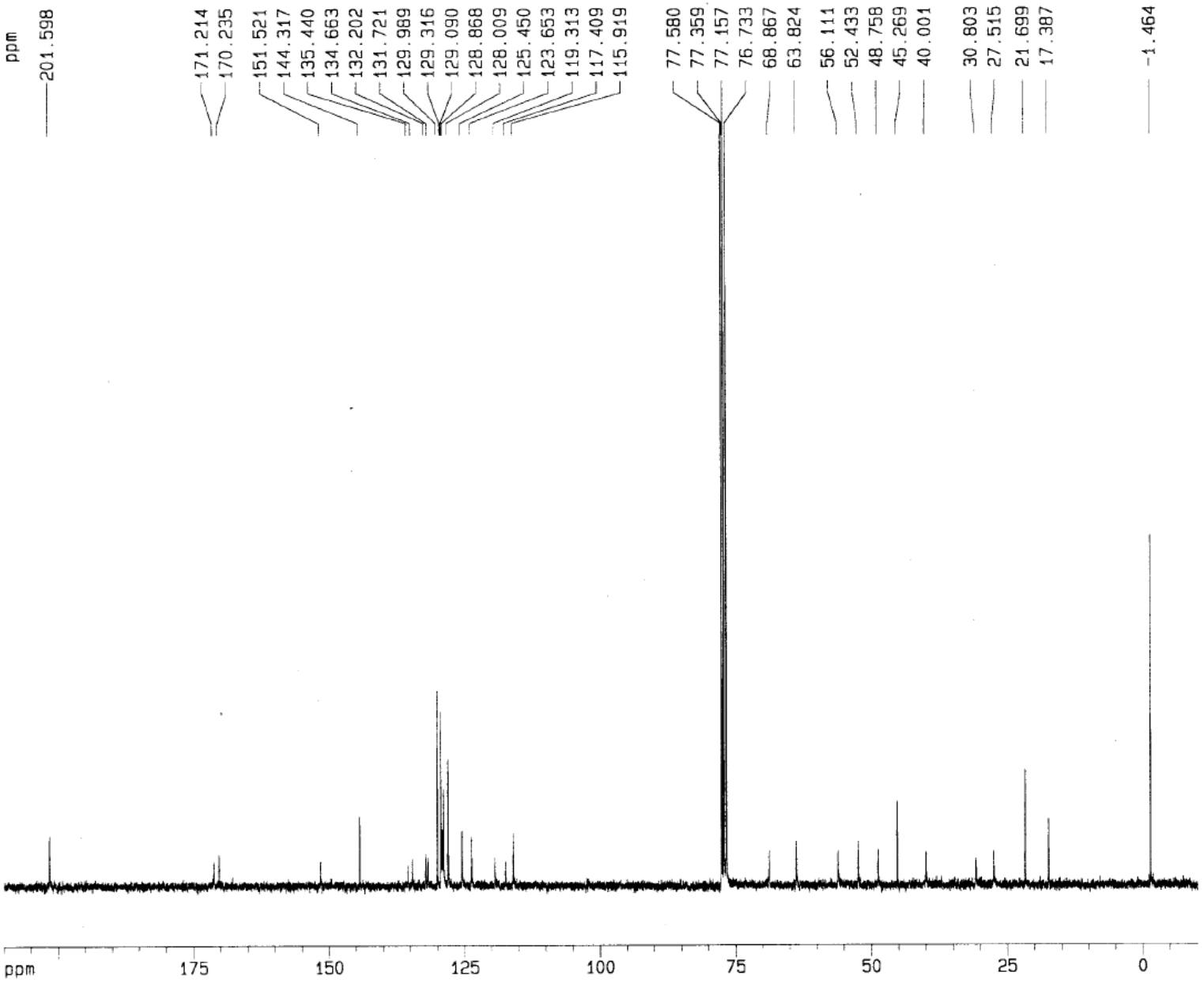
SI	32768
SF	400.1300091 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	11.000 ppm
F1	4401.43 Hz
F2P	-1.000 ppm
F2	-400.13 Hz
PPMCM	0.60000 ppm/cm
HZCM	240.07800 Hz/cm



17




```
Current Data Parameters
NAME          092512FYG-17
EXPNO                    2
PROCNO                   1

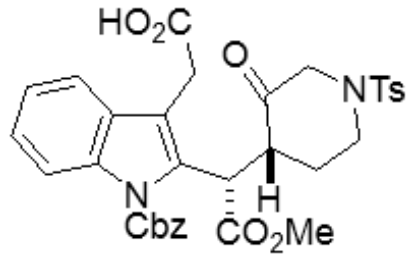
F2 - Acquisition Parameters
Date_              20120925
Time                 21.56
INSTRUM              spect
PROBHD     5 mm Multinu
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   1024
DS                      4
SWH             18832.393 Hz
FIDRES          0.287360 Hz
AQ              1.7400308 sec
RG                  13004
DW                 26.550 usec
DE                  6.00 usec
TE                 300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                  9.75 usec
PL1                 0.00 dB
SFO1          75.4760200 MHz

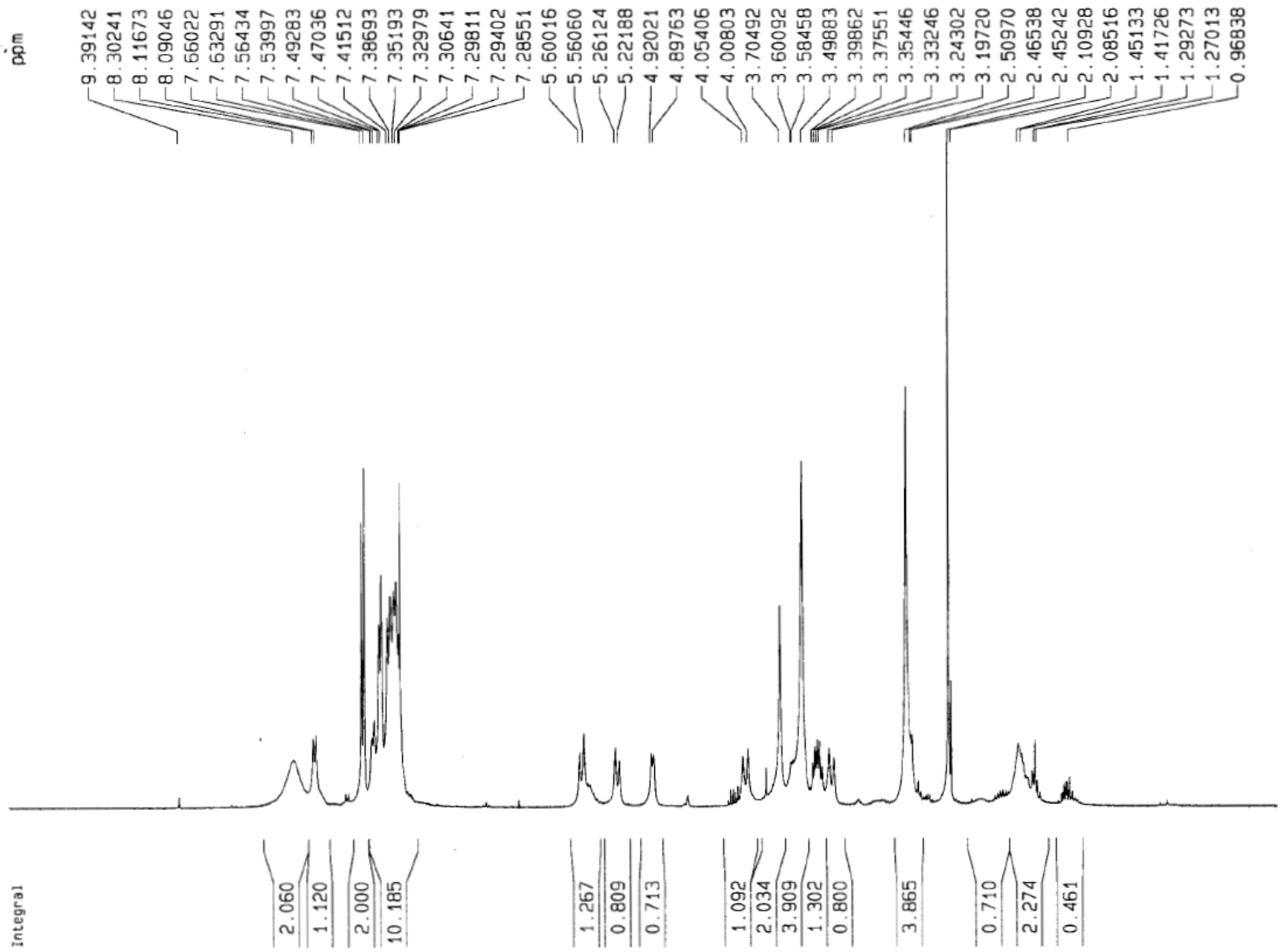
============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                 1H
PCPD2             110.00 usec
PL2                 0.00 dB
PL12                17.50 dB
PL13                17.50 dB
SFO2          300.1312005 MHz

F2 - Processing parameters
SI                  32768
SF             75.4677428 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40

1D NMR plot parameters
CX                  20.00 cm
F1P                210.000 ppm
F1                 15848.23 Hz
F2P                -10.000 ppm
F2                 -754.68 Hz
PPMCM              11.00000 ppm/cm
HZCM              830.14514 Hz/cm
```



18

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Current Data Parameters
NAME        032310mmm5085
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20100323
Time                6.57
INSTRUM            spect
PROBHD     5 mm QNP 1H/1
PULPROG             zg30
TD                 24690
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           6172.839 Hz
FIDRES        0.250014 Hz
AQ            1.9999400 sec
RG                228.1
DW               81.000 usec
DE                6.00 usec
TE                300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                 11.70 usec
PL1                 0.00 dB
SFO1         299.8718518 MHz

F2 - Processing parameters
SI                    32768
SF           299.8700000 MHz
WDW                      no
SSB                       0
LB                 0.00 Hz
GB                        0
PC                     1.00

1D NMR plot parameters
CX                20.00 cm
F1P               11.000 ppm
F1              3298.57 Hz
F2P               -1.000 ppm
F2              -299.87 Hz
PPMCM          0.60000 ppm/cm
HZCM         179.92200 Hz/cm
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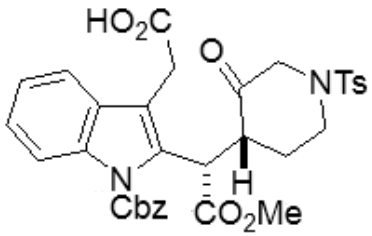

18

ppm
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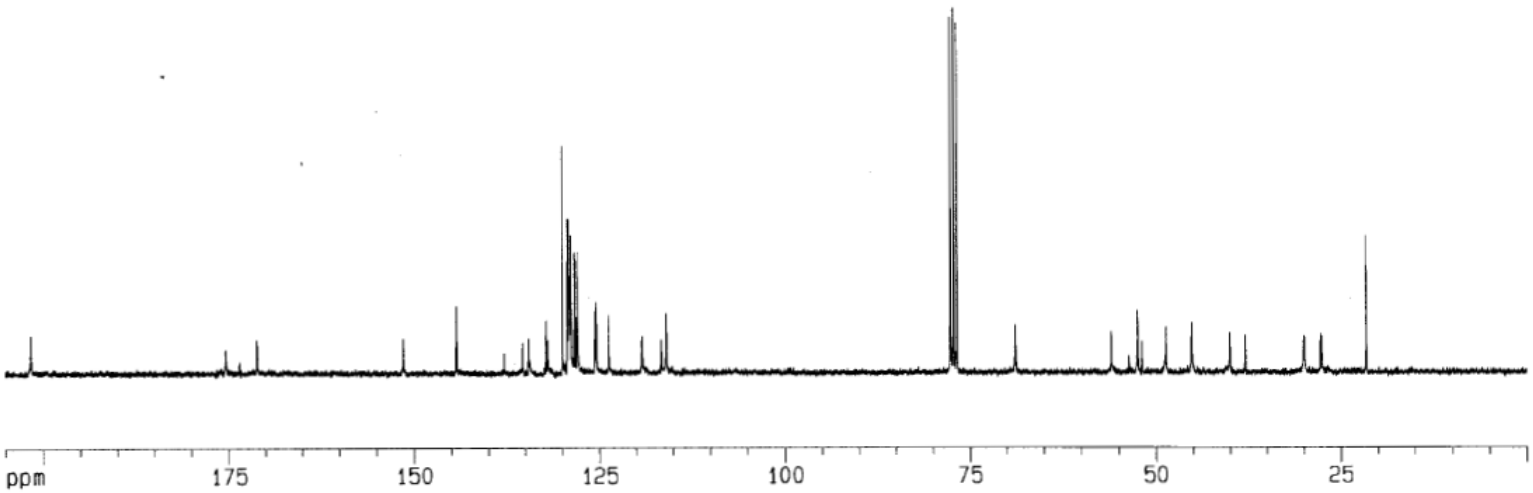
173.425
171.093
151.407
144.272
137.868
135.354
134.540
132.190
131.909
129.934
129.680
129.263
129.057
128.790
128.540
128.353
128.251
127.912
125.488
125.324
123.673
119.132
116.605
115.909
77.587
77.361
77.162
76.737
68.862
55.963
53.542
52.433
51.890
48.675
45.167
40.045
37.952
30.021
29.872
27.759
27.518
21.599
21.489

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Current Data Parameters
NAME        092512FYQ-18
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120925
Time               23.10
INSTRUM            spect
PROBHD     5 mm QNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  769
DS                    4
SWH           18796.992 Hz
FIDRES        0.286819 Hz
AQ            1.7433076 sec
RG                 4096
DW               26.600 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

========== CHANNEL f1 ==========
NUC1                13C
P1                5.25 usec
PL1              -6.00 dB
SFO1         75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2          115.00 usec
PL2              0.00 dB
PL12            19.70 dB
PL13            19.70 dB
SFO2        299.8711995 MHz

F2 - Processing parameters
SI                 32768
SF           75.4023746 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX               20.00 cm
F1P             205.000 ppm
F1             15457.49 Hz
F2P              0.000 ppm
F2               0.00 Hz
PPMCM          10.25000 ppm/cm
HZCM          772.87439 Hz/cm
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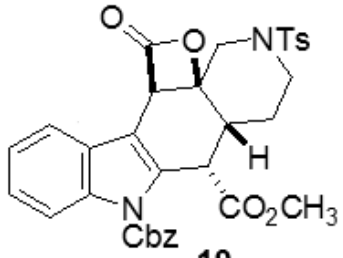
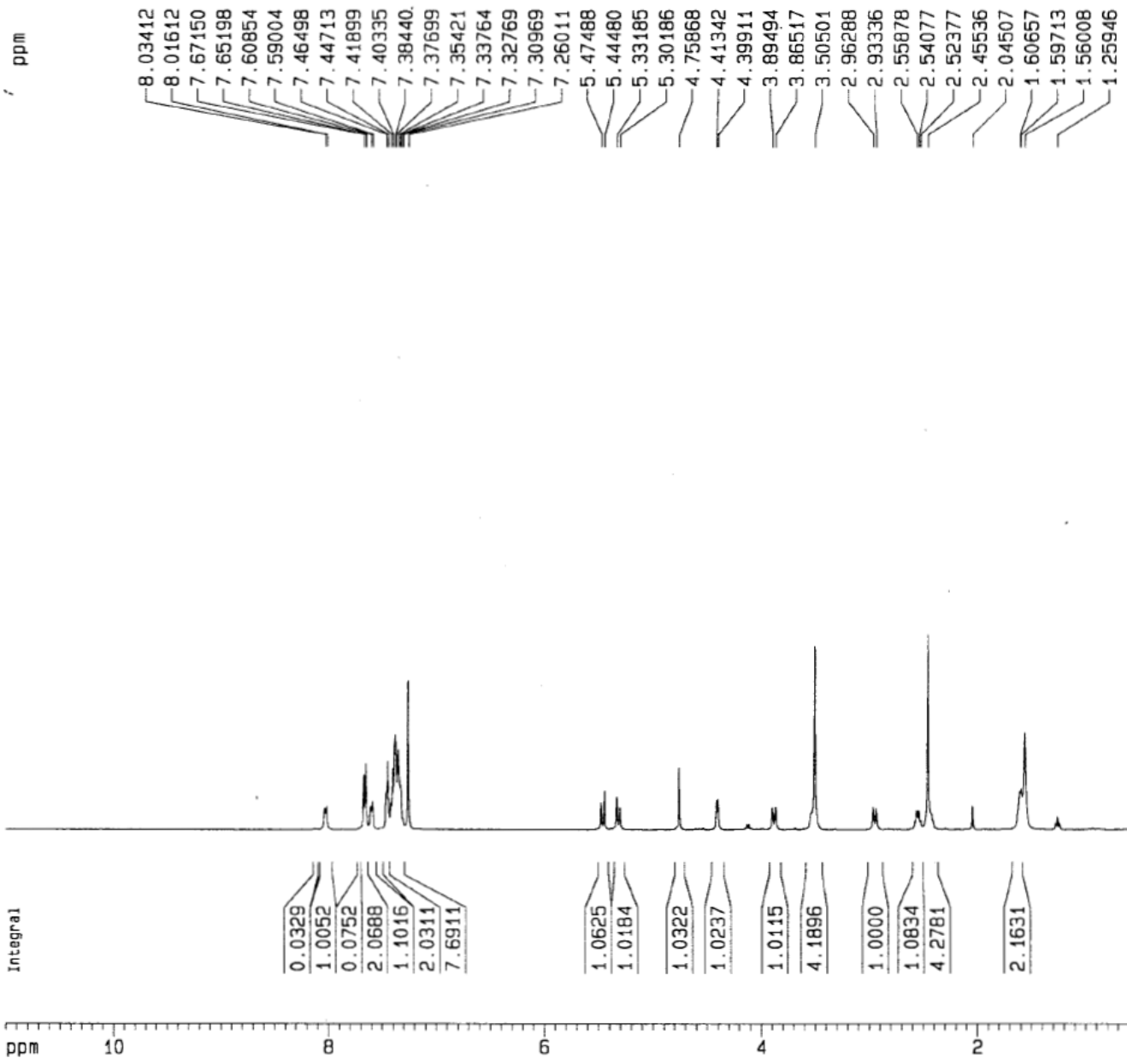


19

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Current Data Parameters
NAME      090112FJIV101
EXPNO                1
PROCNO               1

F2 - Acquisition Parameters
Date_         20120901
Time              8.24
INSTRUM          spect
PROBHD   5 mm BBI 1H-
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                 16
DS                  2
SWH          8278.146 Hz
FIDRES       0.126314 Hz
AQ           3.9584243 sec
RG               645.1
DW              60.400 usec
DE               6.00 usec
TE              300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ========
NUC1                1H
P1               6.45 usec
PL1              0.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                32768
SF         400.1300094 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00

1D NMR plot parameters
CX              20.00 cm
F1P          11.000 ppm
F1           4401.43 Hz
F2P          -1.000 ppm
F2           -400.13 Hz
PPMCM        0.60000 ppm/cm
HZCM       240.07800 Hz/cm
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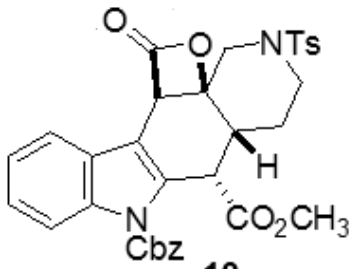

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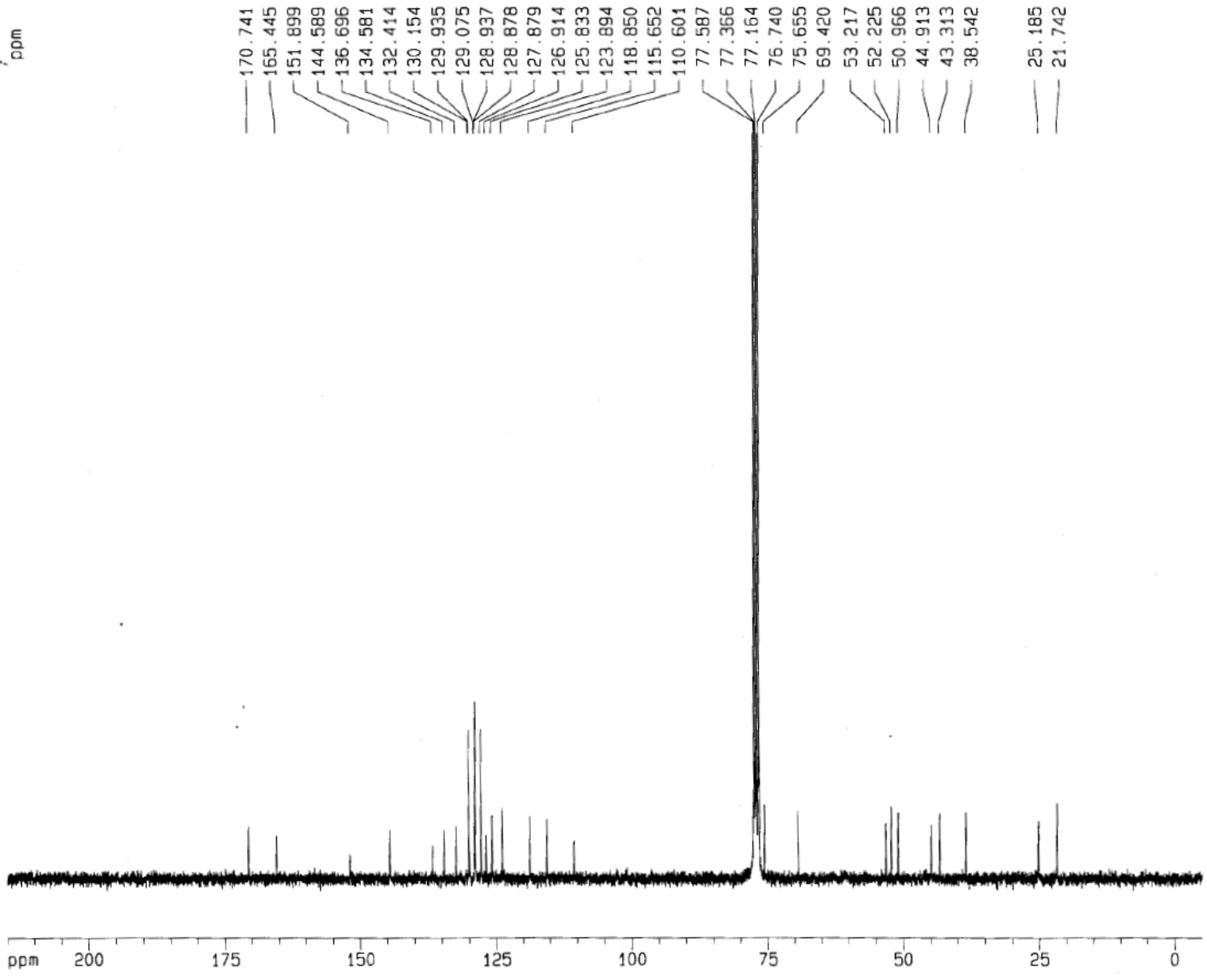


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Current Data Parameters
NAME        092612FYQ-19C
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120927
Time                6.39
INSTRUM             spect
PROBHD    5 mm QNP 1H/1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  7168
DS                     4
SWH           18796.992 Hz
FIDRES         0.286819 Hz
AQ             1.7433076 sec
RG                812.7
DW               26.600 usec
DE                6.00 usec
TE                300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

========== CHANNEL f1 ==========
NUC1                13C
P1                5.25 usec
PL1              -6.00 dB
SF01         75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2          115.00 usec
PL2               0.00 dB
PL12             19.70 dB
PL13             19.70 dB
SF02        299.8711995 MHz

F2 - Processing parameters
SI                 32768
SF          75.4023625 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                20.00 cm
F1P           215.000 ppm
F1            16211.51 Hz
F2P            -5.000 ppm
F2             -377.01 Hz
PPMCM        11.00000 ppm/cm
HZCM        829.42596 Hz/cm
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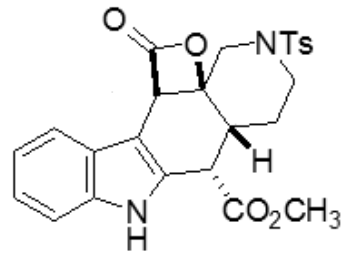

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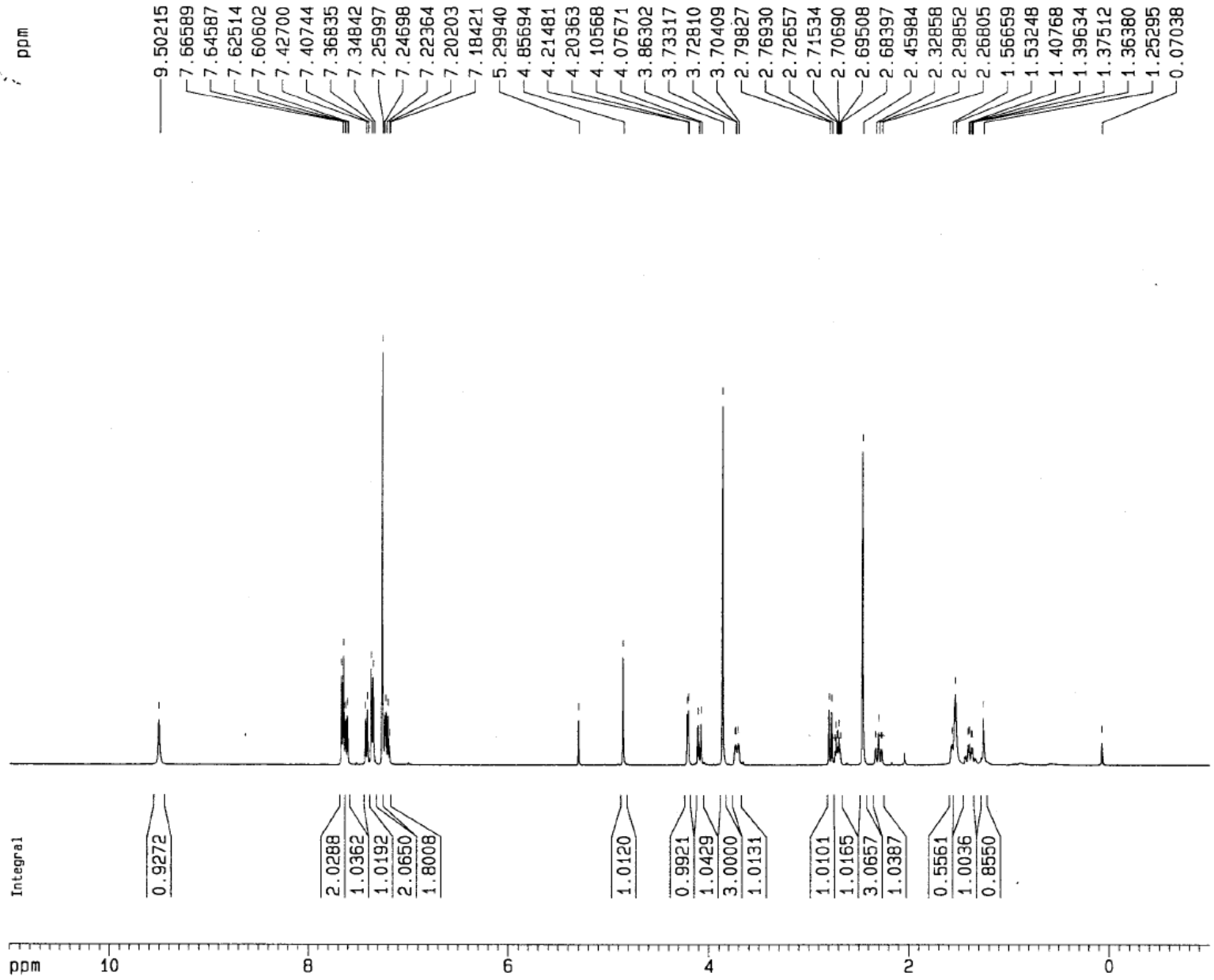


Current Data Parameters

NAME	092612FYQ-20
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20120926
Time	22.45
INSTRUM	spect
PROBHD	5 mm BBI 1H-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	574.7
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ========

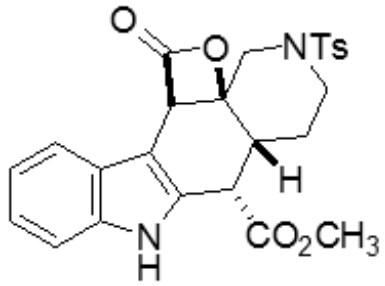
NUC1	1H
P1	6.45 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300096 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	11.000 ppm
F1	4401.43 Hz
F2P	-1.000 ppm
F2	-400.13 Hz
PPMCM	0.60000 ppm/cm
HZCM	240.07800 Hz/cm



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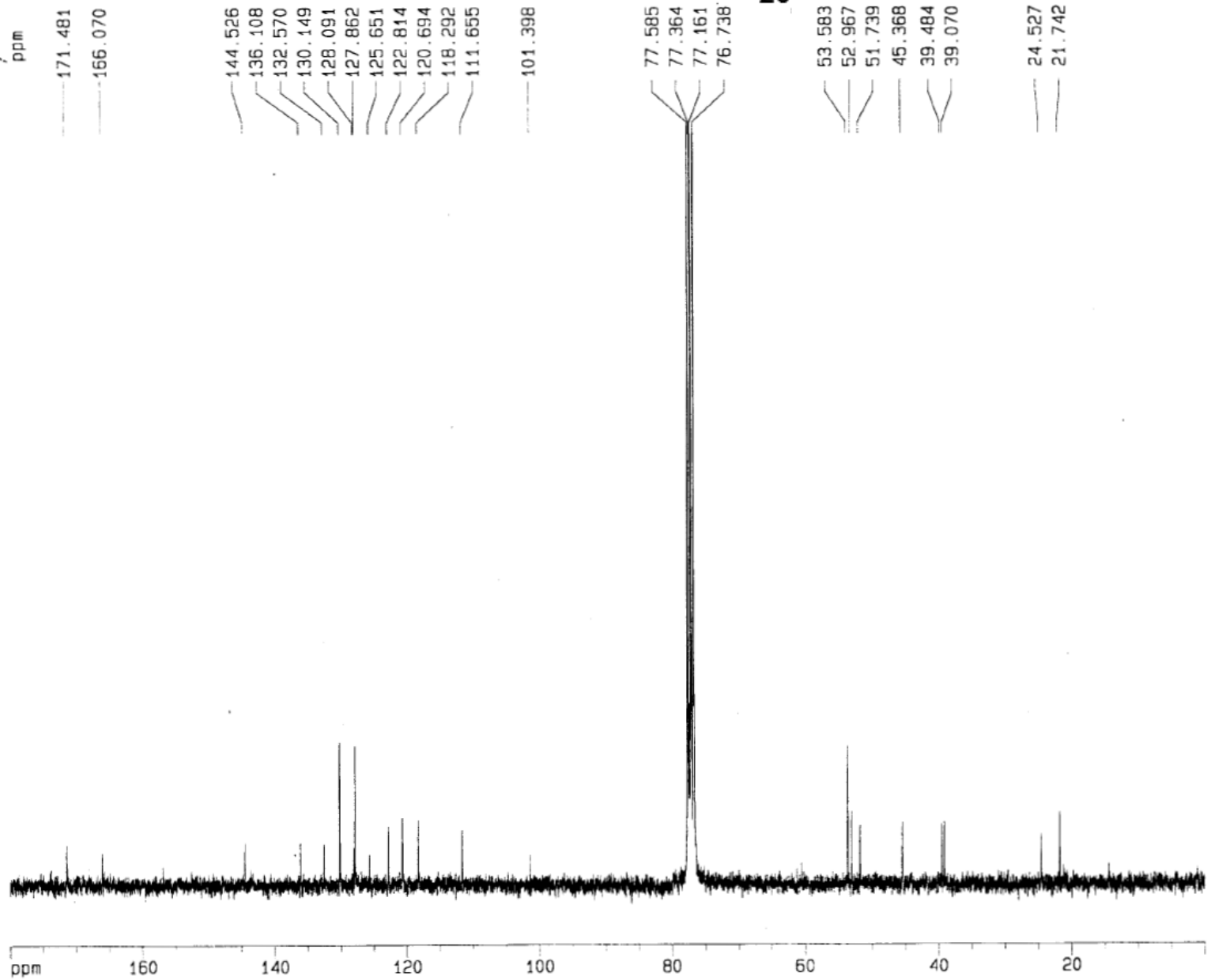


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Current Data Parameters
NAME      092312FYGcpd20
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20120924
Time               9.30
INSTRUM           spect
PROBHD     5 mm Multinu
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                19456
DS                    4
SWH           18832.393 Hz
FIDRES        0.287360 Hz
AQ            1.7400308 sec
RG               11585.2
DW               26.550 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

========== CHANNEL f1 ==========
NUC1                 13C
P1                9.75 usec
PL1               0.00 dB
SFO1         75.4760200 MHz

========== CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           110.00 usec
PL2               0.00 dB
PL12             17.50 dB
PL13             17.50 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677382 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40

1D NMR plot parameters
CX               20.00 cm
F1P             180.000 ppm
F1            13584.19 Hz
F2P             0.000 ppm
F2              0.00 Hz
PPMCM          9.00000 ppm/cm
HZCM         679.20959 Hz/cm
```
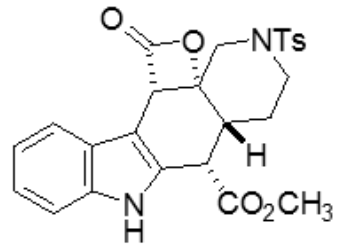
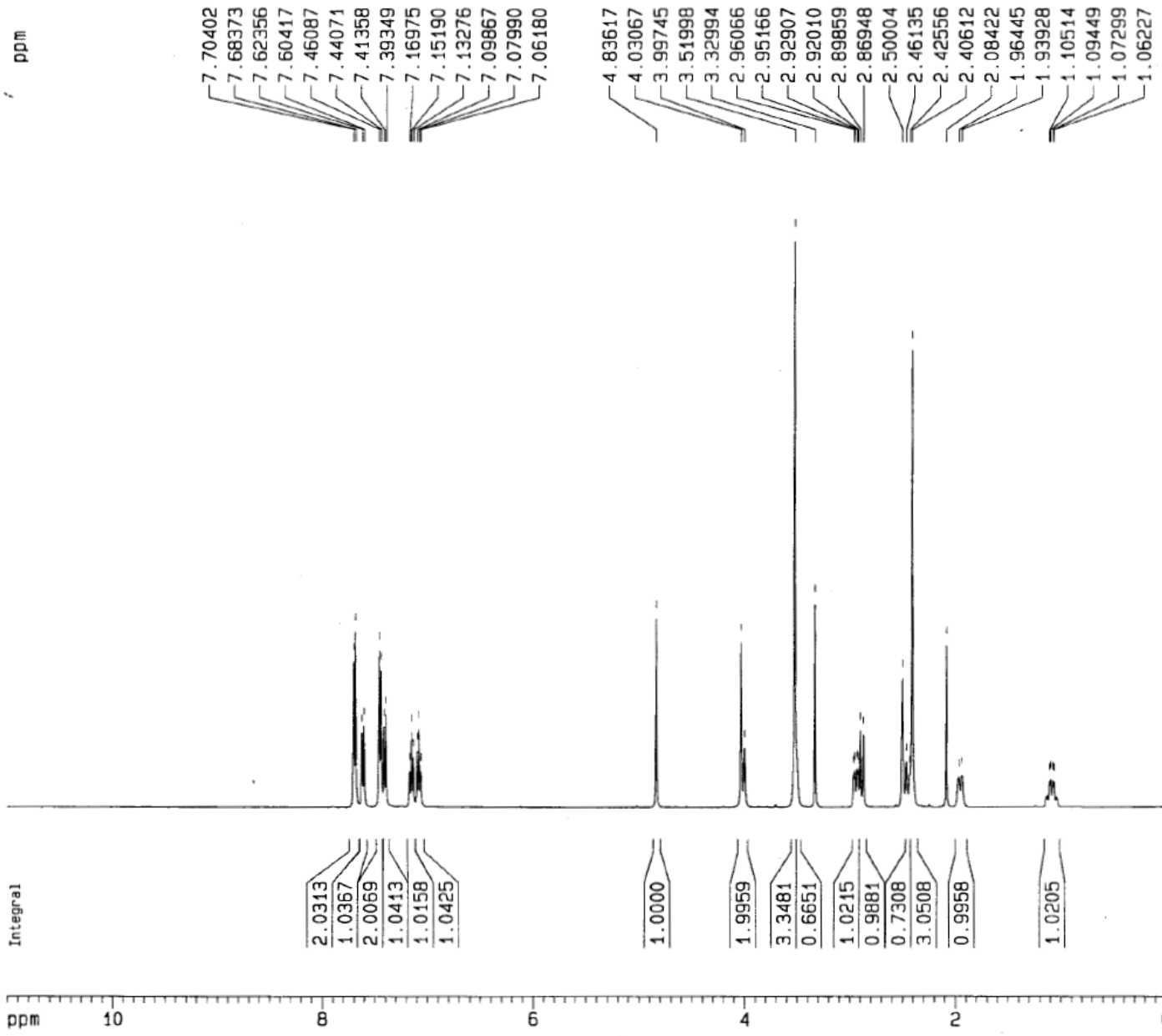



21



Current Data Parameters

NAME	092612FYQ-21
EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

Date_	20120926
Time	23.04
INSTRUM	spect
PROBHD	5 mm BBI 1H-
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	362
DW	60.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec

========== CHANNEL f1 ========

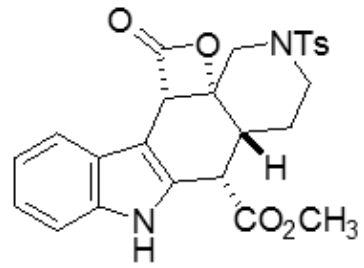
NUC1	1H
P1	6.45 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

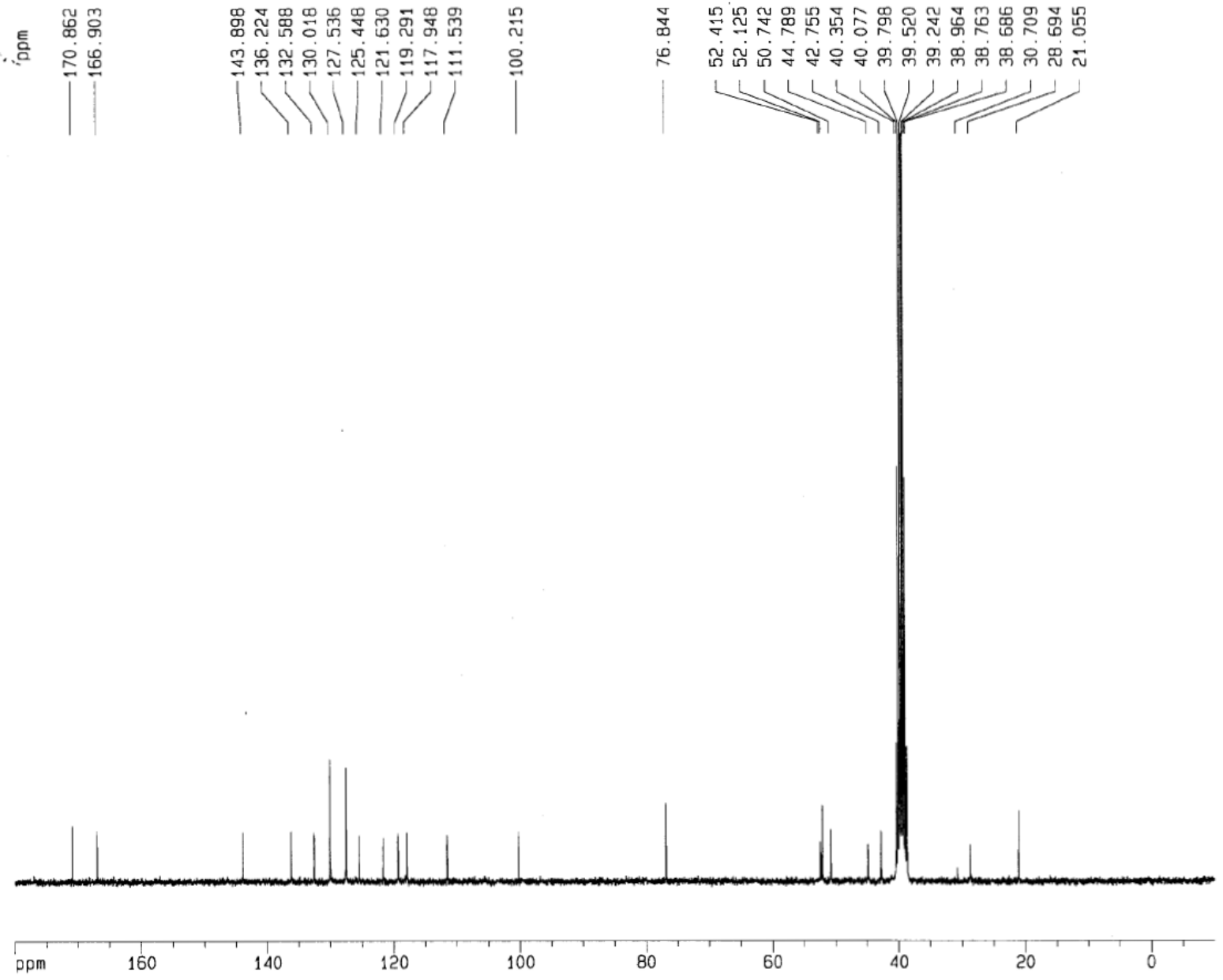
SI	32768
SF	400.1300029 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

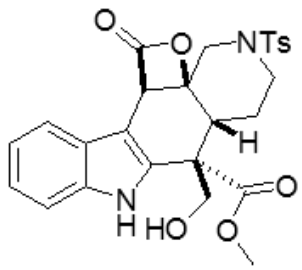
CX	20.00 cm
F1P	11.000 ppm
F1	4401.43 Hz
F2P	-1.000 ppm
F2	-400.13 Hz
PPMCM	0.60000 ppm/cm
HZCM	240.07800 Hz/cm



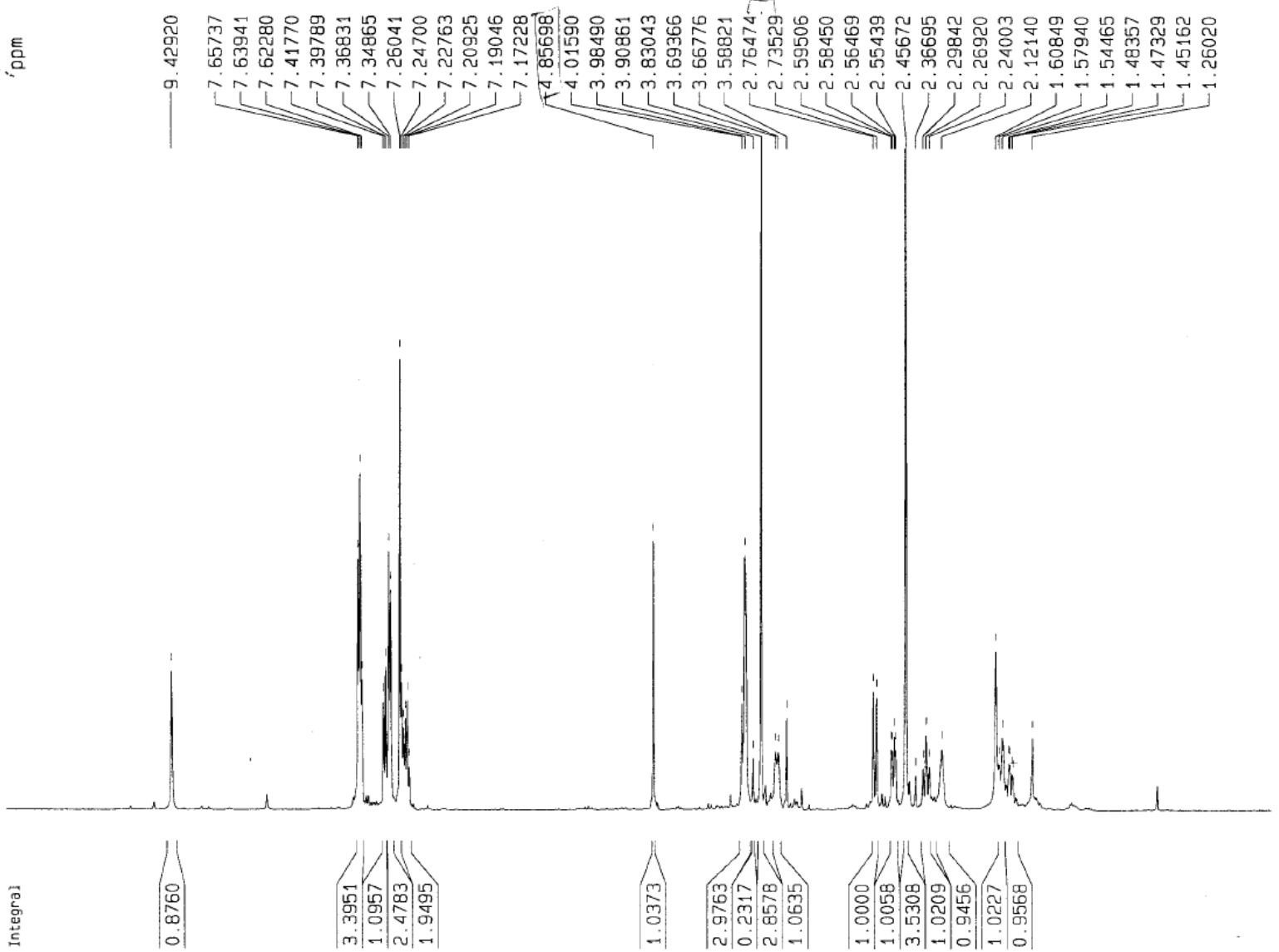
21



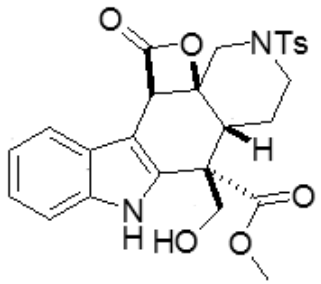

```
Current Data Parameters
NAME          092612FYQ-21
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120926
Time                 23.03
INSTRUM              spect
PROBHD     5 mm GNP 1H/1
PULPROG           zgpg30
TD                 65536
SOLVENT             DMSO
NS                  1375
DS                     4
SWH           18796.992 Hz
FIDRES        0.286819 Hz
AQ            1.7433076 sec
RG                   512
DW              26.600 usec
DE               6.00 usec
TE               300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

========== CHANNEL f1 ==========
NUC1                 13C
P1                5.25 usec
PL1               -6.00 dB
SFO1         75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           115.00 usec
PL2               0.00 dB
PL12             19.70 dB
PL13             19.70 dB
SFO2         299.8711995 MHz

F2 - Processing parameters
SI                32768
SF           75.4024070 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              180.000 ppm
F1             13572.43 Hz
F2P              -10.000 ppm
F2               -754.02 Hz
PPMCM           9.50000 ppm/cm
HZCM          716.32288 Hz/cm
```



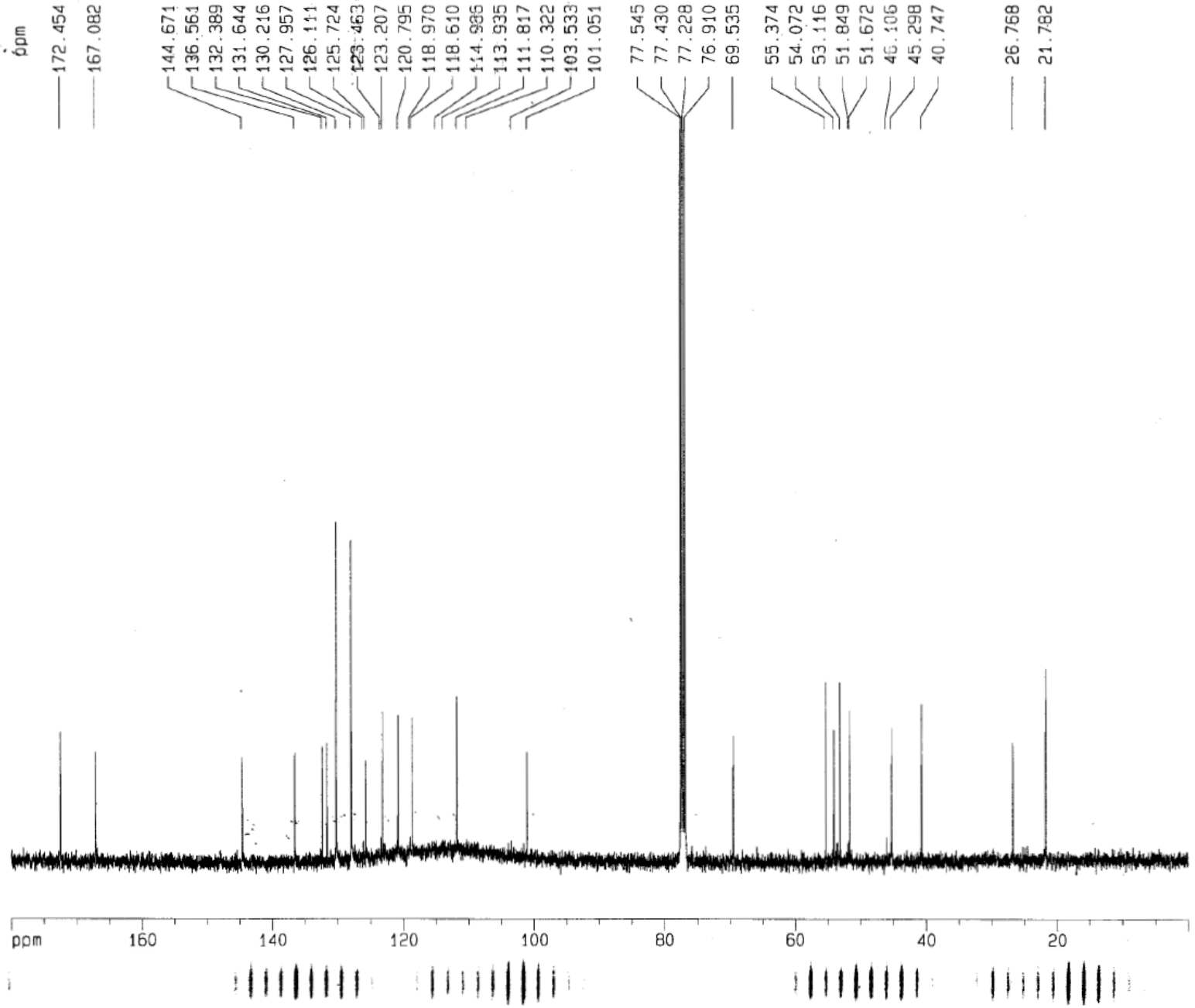
23



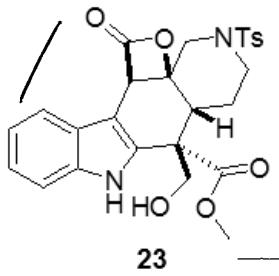

```
Current Data Parameters
NAME      080111FJII-052
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110801
Time               17.58
INSTRUM            spect
PROBHD     5 mm BBI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                 161.3
DW                60.400 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 =========
NUC1                   1H
P1                  6.45 usec
PL1                 0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF            400.1300089 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                11.000 ppm
F1                 4401.43 Hz
F2P                -1.000 ppm
F2                 -400.13 Hz
PPMCM             0.60000 ppm/cm
HZCM             240.07800 Hz/cm
```



23




```
Current Data Parameters
NAME      080111FJII-052
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110802
Time                2.55
INSTRUM            spect
PROBHD     5 mm BBI 1H-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 5120
DS                    4
SWH           25125.629 Hz
FIDRES        0.383387 Hz
AQ            1.3042164 sec
RG                16384
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

========== CHANNEL f1 ==========
NUC1                13C
P1                16.35 usec
PL1               -6.00 dB
SFO1         100.6237959 MHz

========== CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2           114.00 usec
PL2               0.00 dB
PL12             24.00 dB
PL13             24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127499 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               180.000 ppm
F1              18110.29 Hz
F2P               0.000 ppm
F2                 0.00 Hz
PPMCM           9.00000 ppm/cm
HZCM          905.51471 Hz/cm
```



23

FYQ-II-052053P HMQC

H(14)*2

(all)

TsCH2

C19 → CH2

C15(CH) → (CH)

C3 → CH2

C19 → (CH)

COMe(CH3)

C21(CH2)

QC7 → C16

CH2 – C17

C7 (QC6)

Ar-CH { Cq/12, Cq/12, C6/11, C10/11

C8 (QC9) →

TsC*4 →

C2 → QC4

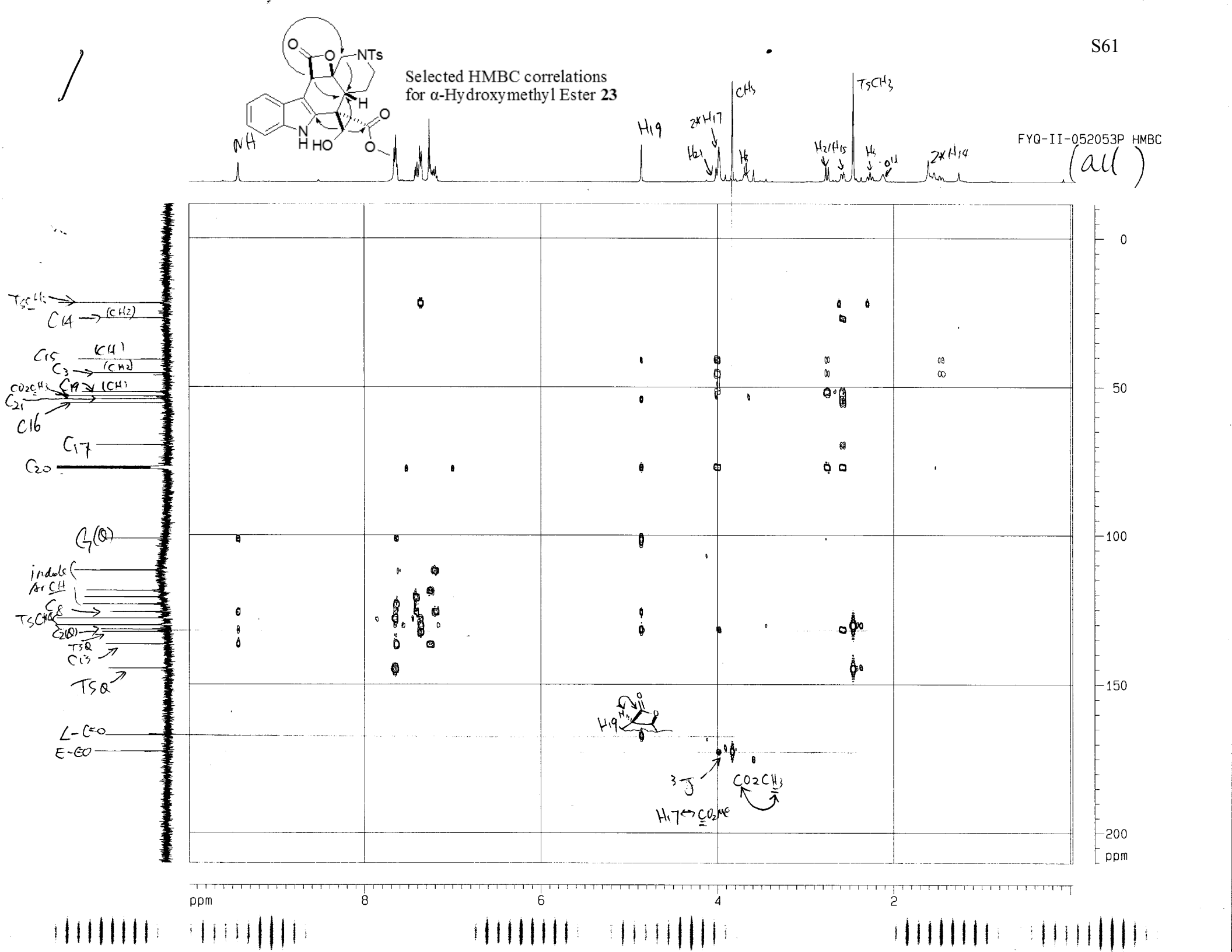
Ts (QC1) →

QC2

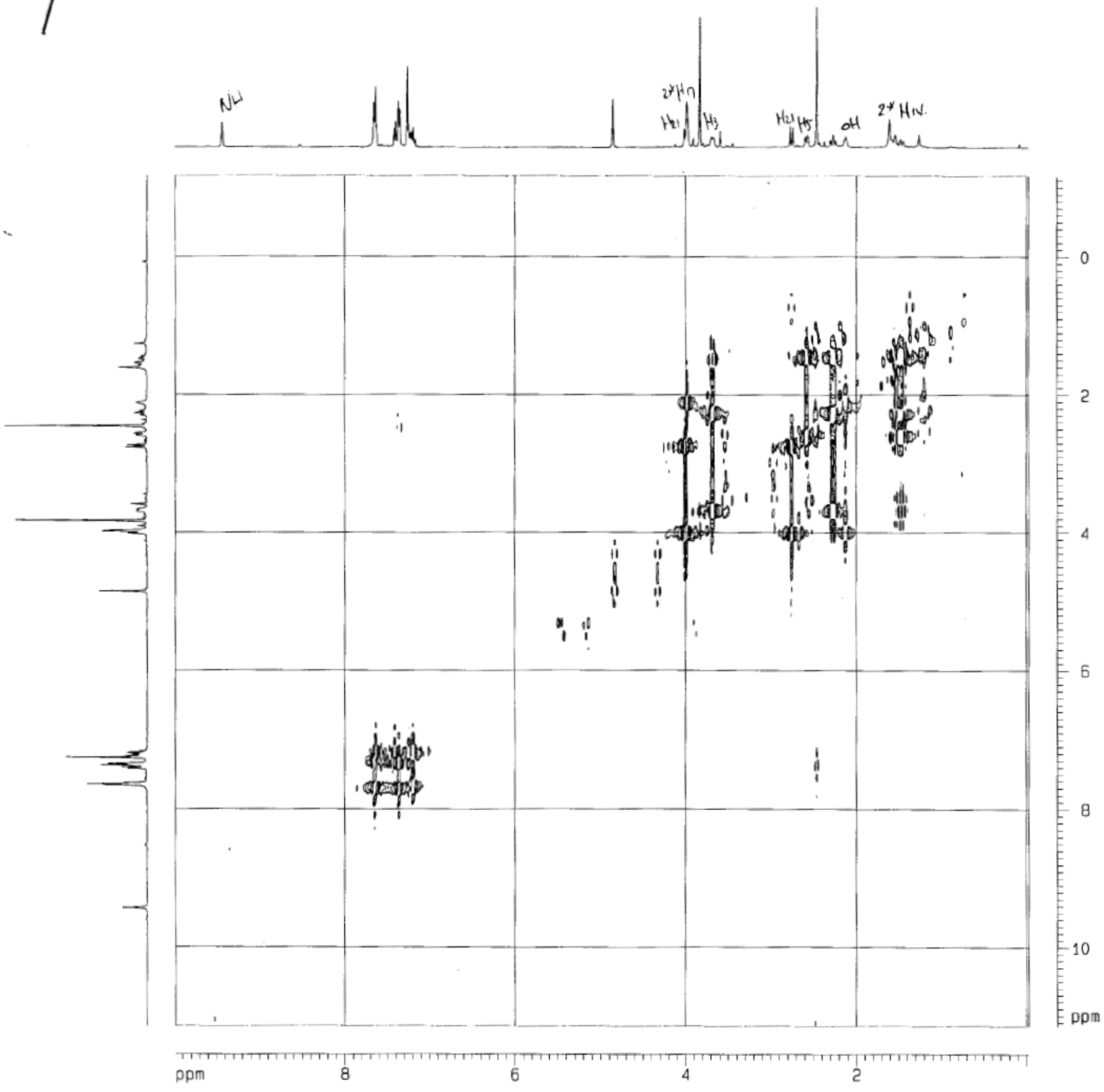
Ts(QC1) →

0
25
50
75
100
125
150
ppm

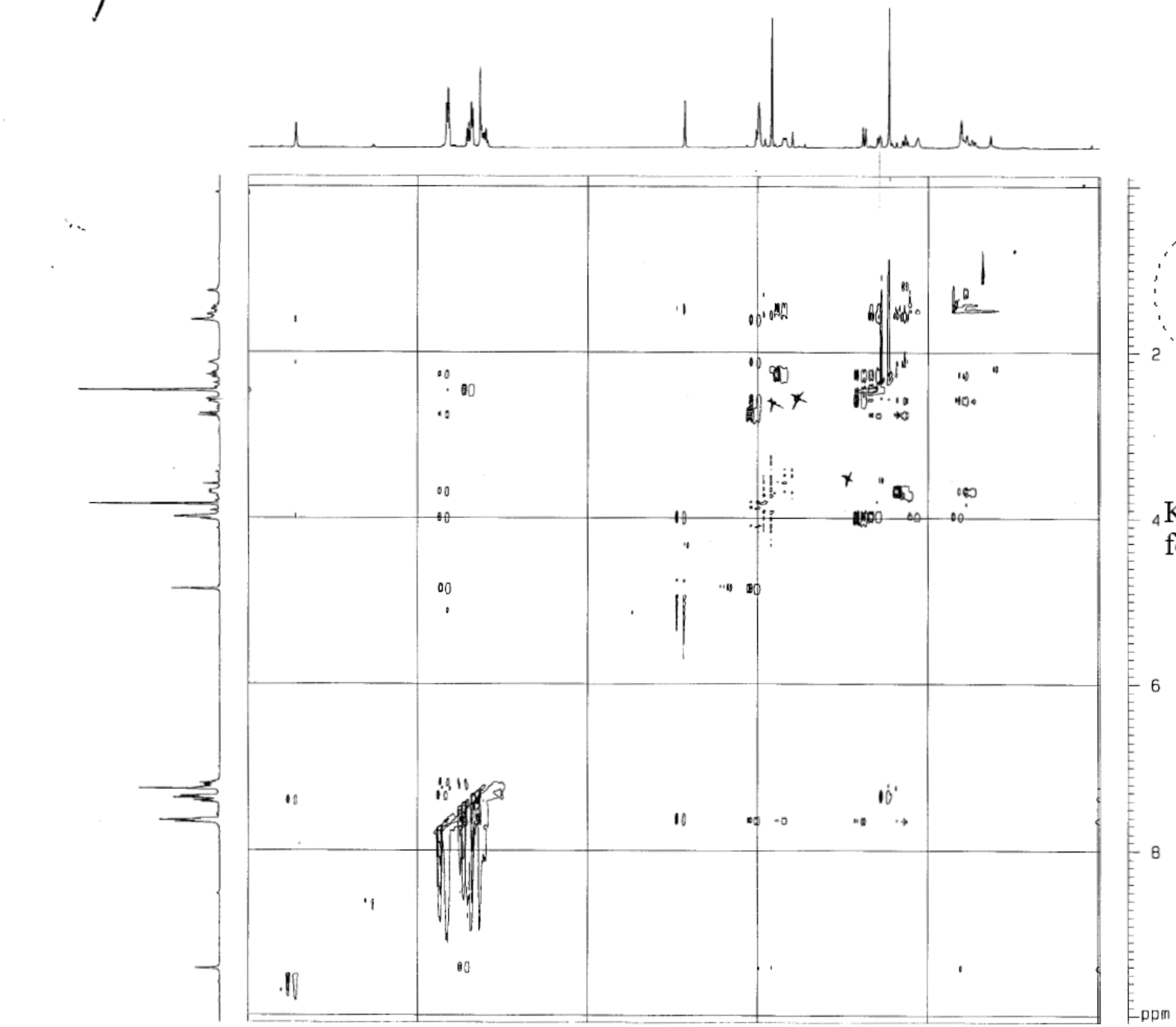
ppm 8 6 4 2

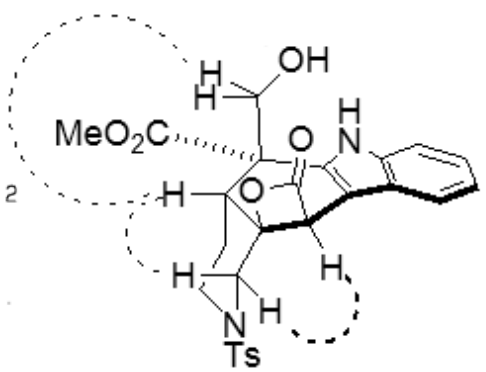

Selected HMBC correlations
for α-Hydroxymethyl Ester 23
NTs
NH
N
H
HO
O
H19
2×H17
H21
H5
CH3
TsCH3
H21/H15
H3
OH
2×H14
FYQ-II-052053P HMBC
(all)
TsCH3
C14
(CH2)
C15
CH
C3
(CH2)
CO2CH3
CH
(CH)
C21
C16
C17
C20
C(Q)
indole
Ar CH
C8
TsCH3
C2(Q)
TsQ
C13
TsQ
L-C=O
E-C=O
3J
H17↔CO2Me
CO2CH3
0
50
100
150
200
ppm
ppm
8
6
4
2

FYQ-II-052053P COSY



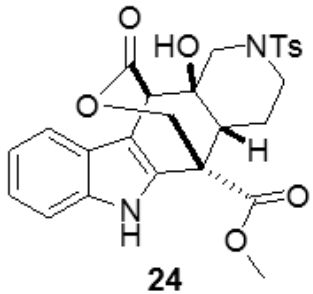
FYQ-II-052053P NOESY





Key nOe correlations for α-Hydroxymethyl Ester **23**

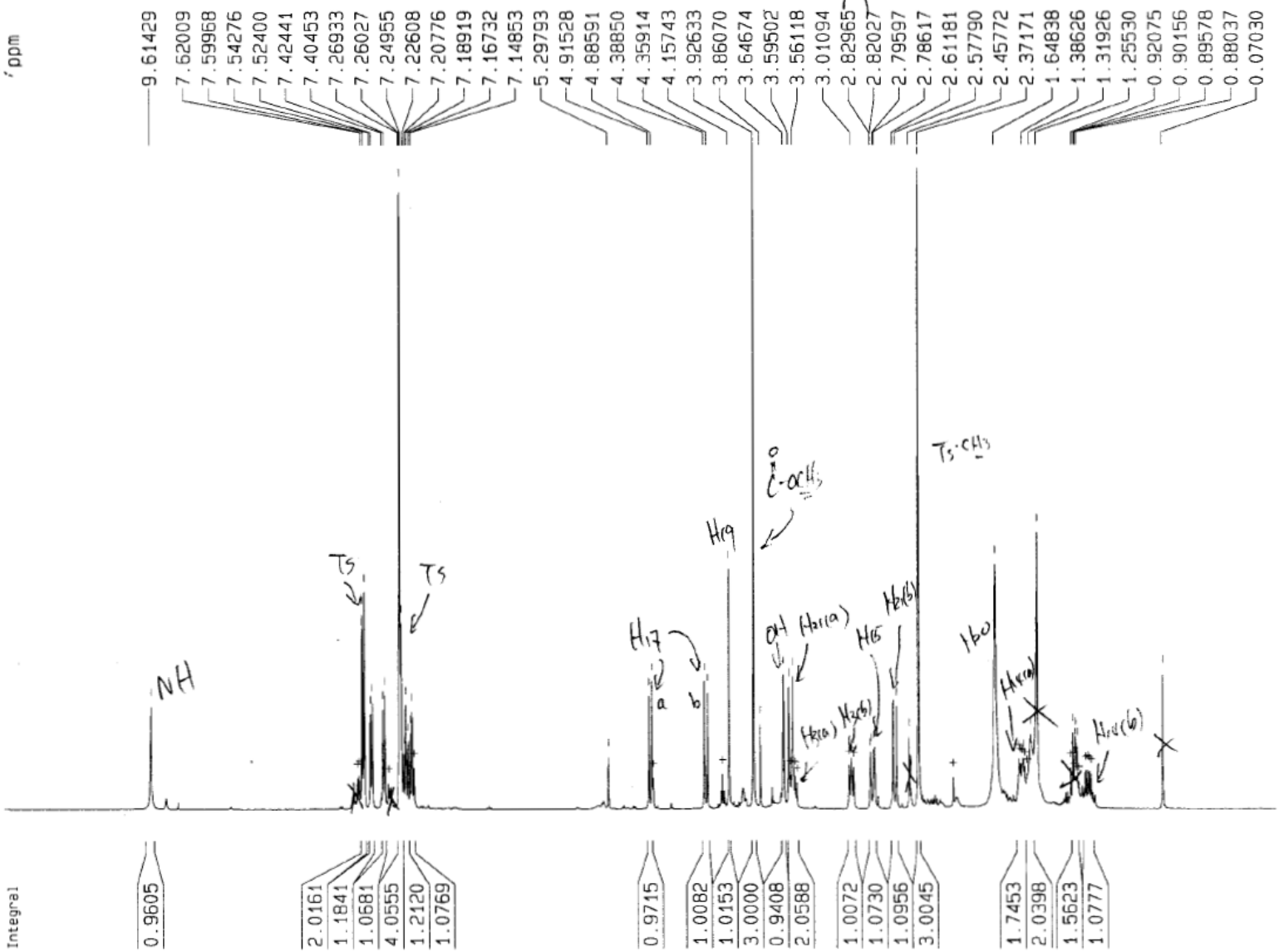
--- = nOe correlation



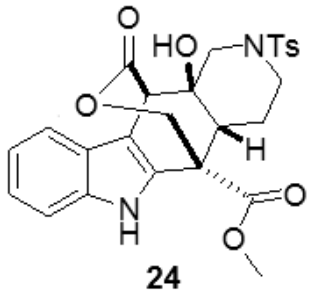
24

13.5

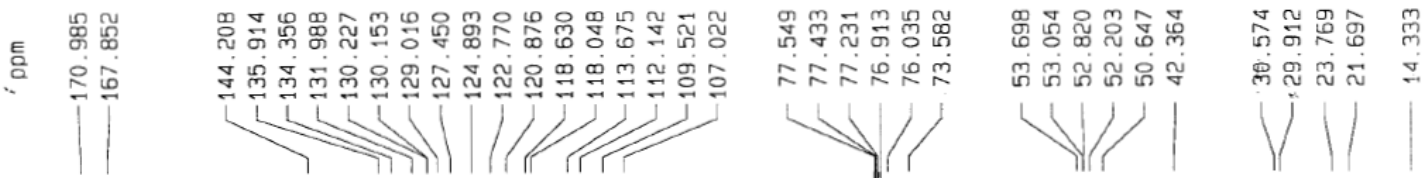
3.5

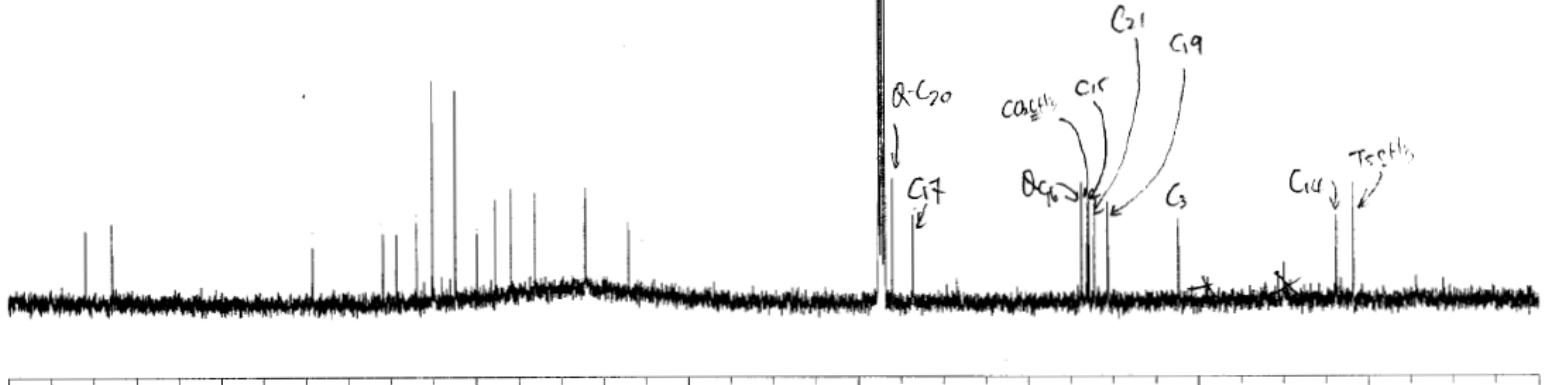



```
Current Data Parameters
NAME      080811FJII-064
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110808
Time               18.57
INSTRUM            spect
PROBHD     5 mm BBI 1H-
PULPROG             zg30
TD                 65536
SOLVENT             CDCl3
NS                    16
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                 203.2
DW              60.400 usec
DE               6.00 usec
TE              300.0 K
D1            1.00000000 sec

========== CHANNEL f1 ========
NUC1                   1H
P1                  6.45 usec
PL1                 0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF            400.1300091 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                11.000 ppm
F1                 4401.43 Hz
F2P                -1.000 ppm
F2                 -400.13 Hz
PPMCM              0.60000 ppm/cm
HZCM             240.07800 Hz/cm
```

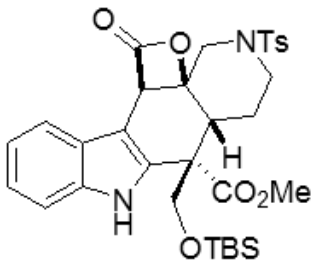


24






```
Current Data Parameters
NAME      080811FJII-064
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110809
Time                4.49
INSTRUM            spect
PROBHD     5 mm BBI 1H-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 6144
DS                    4
SWH           25125.629 Hz
FIDRES        0.383387 Hz
AQ            1.3042164 sec
RG                16384
DW               19.900 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

========== CHANNEL f1 ==========
NUC1                13C
P1                16.35 usec
PL1               -6.00 dB
SFO1         100.6237959 MHz

========== CHANNEL f2 ==========
CPDPRG2          waltz16
NUC2                1H
PCPD2            114.00 usec
PL2                0.00 dB
PL12              24.00 dB
PL13              24.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127484 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                20.00 cm
F1P              180.000 ppm
F1             18110.29 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM             9.00000 ppm/cm
HZCM          905.51471 Hz/cm
```



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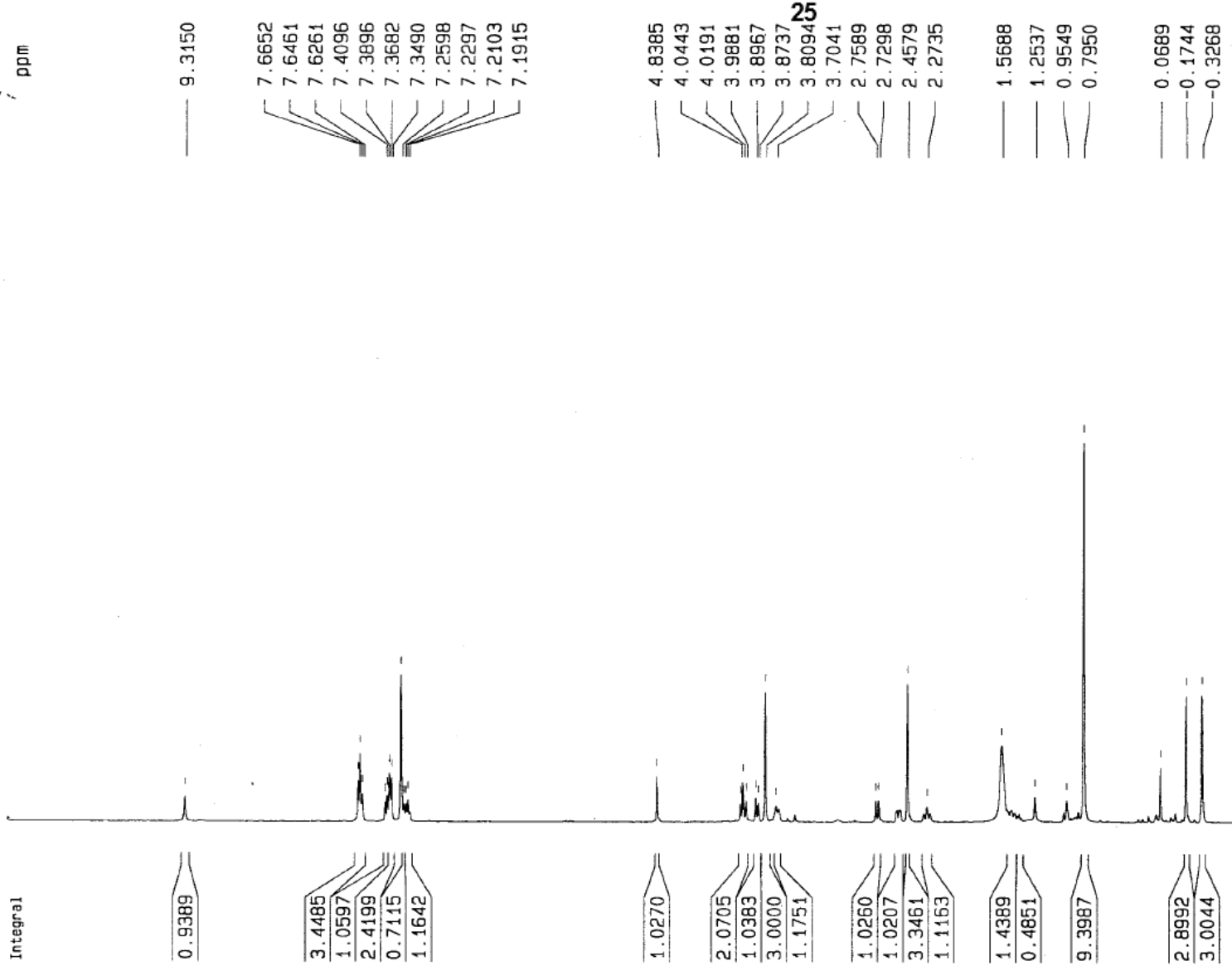


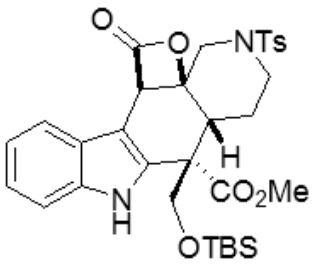

```
Current Data Parameters
NAME      090712FJIII291
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120907
Time               11.52
INSTRUM            spect
PROBHD     5 mm BBI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                 322.5
DW              60.400 usec
DE               6.00 usec
TE              300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =========
NUC1                   1H
P1                  6.45 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300096 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                11.000 ppm
F1               4401.43 Hz
F2P                -1.000 ppm
F2               -400.13 Hz
PPMCM             0.60000 ppm/cm
HZCM            240.07800 Hz/cm
```



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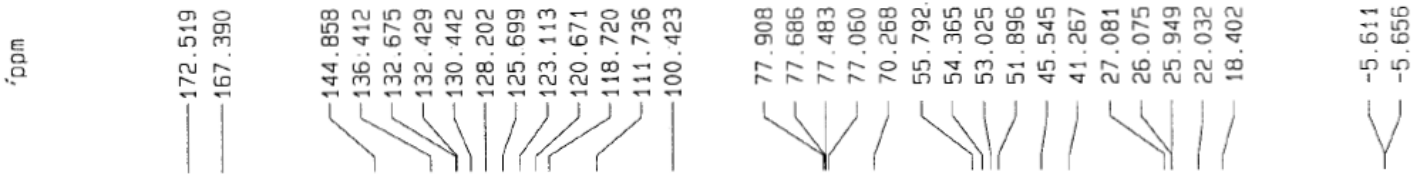
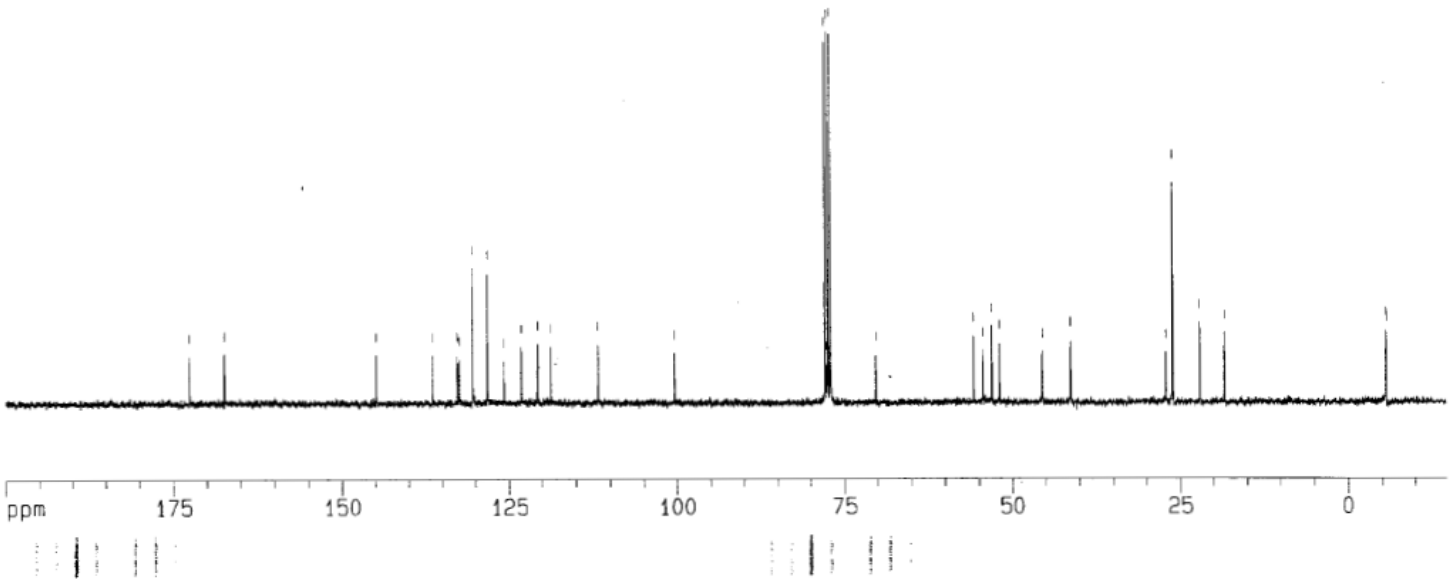
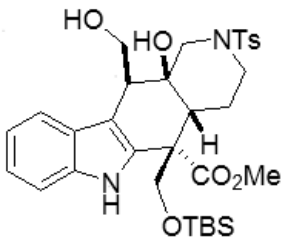





```
Current Data Parameters
NAME      090512FJIII290
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20120905
Time              17.10
INSTRUM           spect
PROBHD    5 mm QNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  830
DS                    4
SWH           18796.992 Hz
FIDRES        0.286819 Hz
AQ            1.7433076 sec
RG                  512
DW               26.600 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                5.25 usec
PL1              -6.00 dB
SFO1         75.4106357 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2          115.00 usec
PL2               0.00 dB
PL12             19.70 dB
PL13             19.70 dB
SFO2        299.8711995 MHz

F2 - Processing parameters
SI                32768
SF           75.4023410 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
F1P              200.000 ppm
F1             15080.47 Hz
F2P              -30.000 ppm
F2             -2262.07 Hz
PPMCM           11.50000 ppm/cm
HZCM          867.12695 Hz/cm
```



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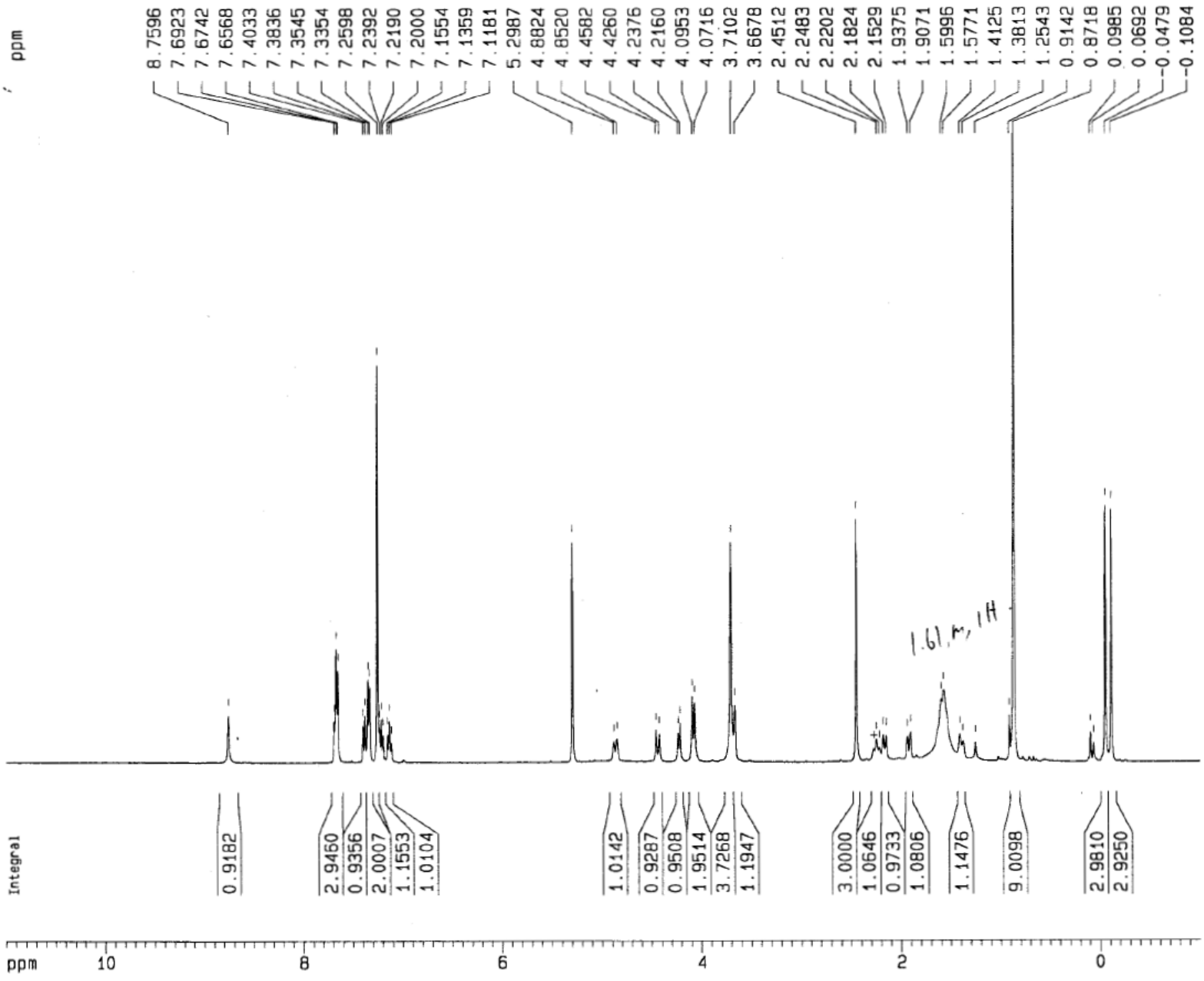
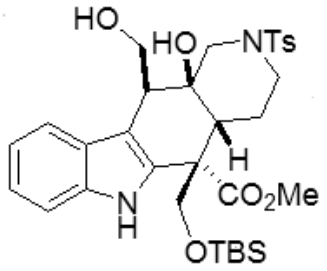


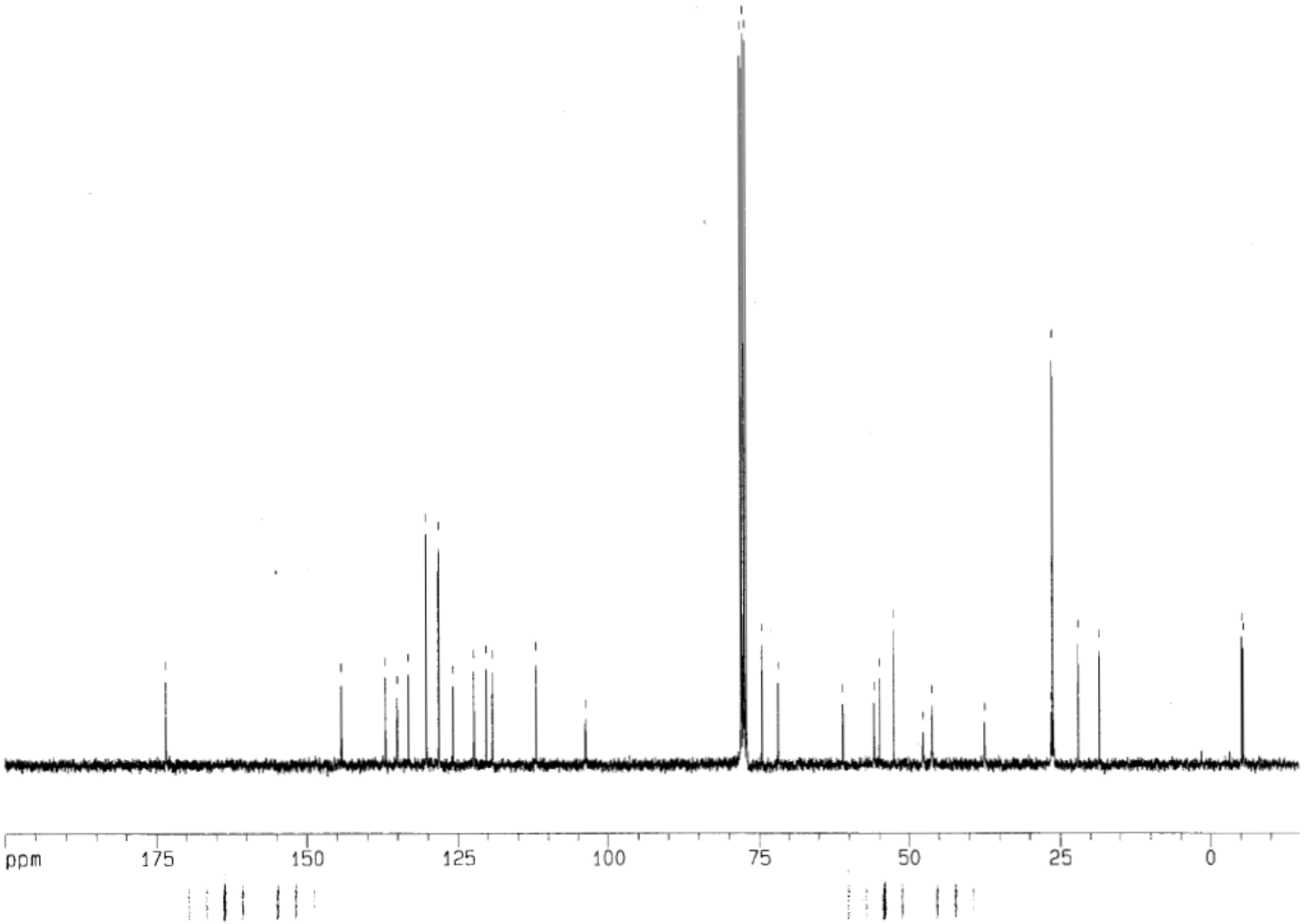

```
Current Data Parameters
NAME      090712FJIII292
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120907
Time               11.45
INSTRUM            spect
PROBHD     5 mm BBI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                456.1
DW               60.400 usec
DE                6.00 usec
TE                300.0 K
D1           1.00000000 sec

============ CHANNEL f1 ========
NUC1                  1H
P1                 6.45 usec
PL1                0.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300096 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               11.000 ppm
F1              4401.43 Hz
F2P               -1.000 ppm
F2              -400.13 Hz
PPMCM           0.60000 ppm/cm
HZCM          240.07800 Hz/cm
```



26

ppm

173.380
144.297
136.969
135.010
133.158
130.212
128.102
125.794
122.336
120.190
119.178
111.926
103.676
77.913
77.691
77.489
77.065
74.477
71.820
61.014
55.774
54.913
52.530
47.606
46.113
37.439
26.459
26.213
21.998
18.477
-5.225
-5.483

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Current Data Parameters
NAME      090612FJIII292
EXPNO                  2
PROCNO                 1

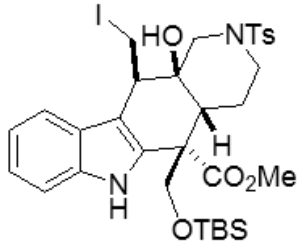
F2 - Acquisition Parameters
Date_           20120906
Time               16.43
INSTRUM            spect
PROBHD     5 mm QNP 1H/1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  567
DS                    4
SWH           18796.992 Hz
FIDRES        0.286819 Hz
AQ            1.7433076 sec
RG                 1024
DW               26.600 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                 5.25 usec
PL1               -6.00 dB
SFO1          75.4106357 MHz

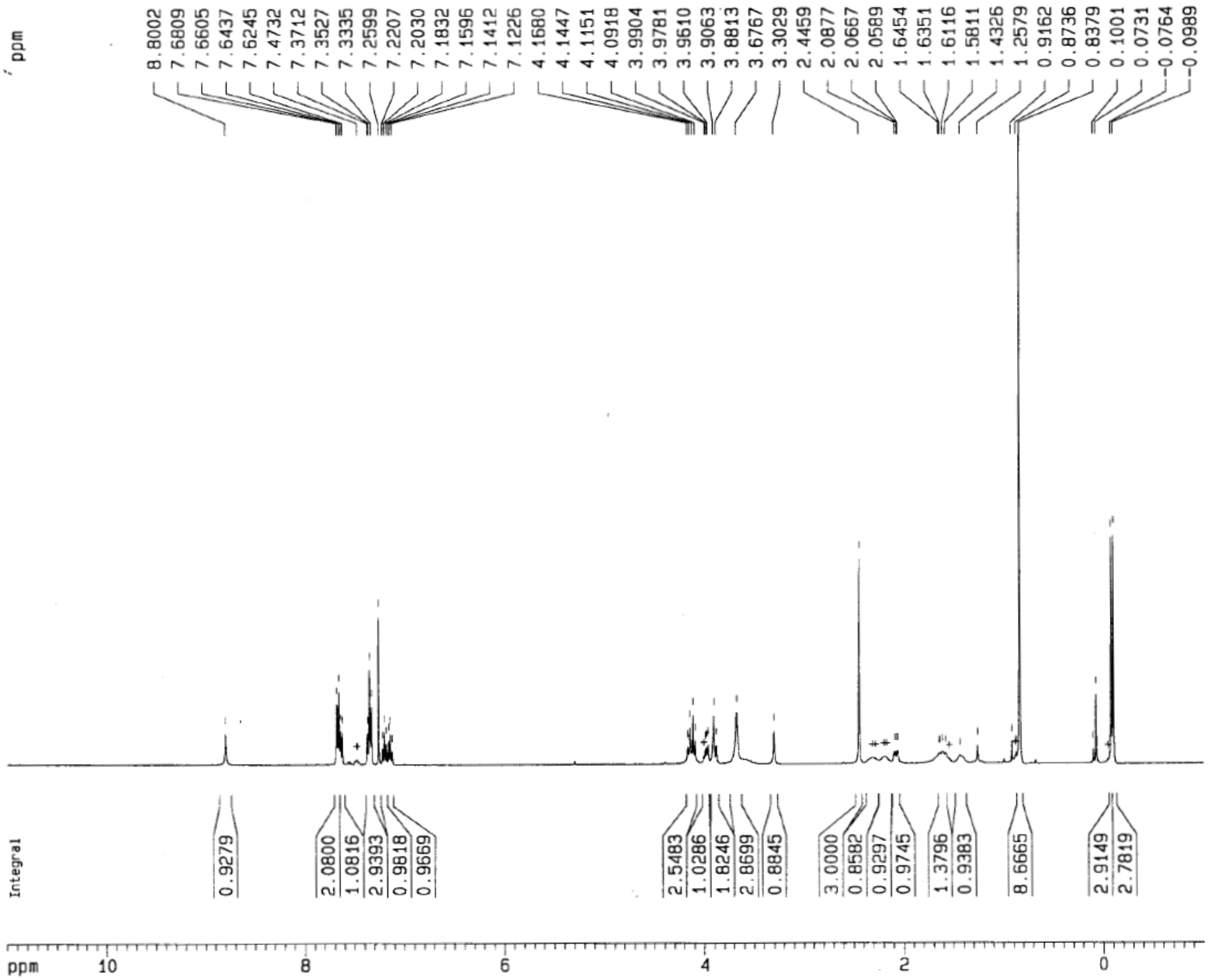
============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2          115.00 usec
PL2               0.00 dB
PL12             19.70 dB
PL13             19.70 dB
SFO2         299.8711995 MHz

F2 - Processing parameters
SI                 32768
SF            75.4023410 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 20.00 cm
F1P               200.000 ppm
F1              15080.47 Hz
F2P               -30.000 ppm
F2              -2262.07 Hz
PPMCM             11.50000 ppm/cm
HZCM            867.12695 Hz/cm
```



27



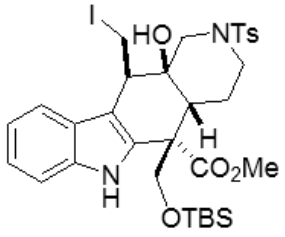
Current Data Parameters
NAME 090712FJIII294
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120907
Time 19.09
INSTRUM spect
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 574.7
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

========== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 4401.43 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.60000 ppm/cm
HZCM 240.07800 Hz/cm



27

ppm

173.302
144.361
136.878
133.140
132.517
130.223
128.223
126.294
122.353
119.992
111.738
109.185
77.879
77.656
77.455
77.031
73.339
71.459
55.212
54.630
52.636
45.911
36.622
26.155
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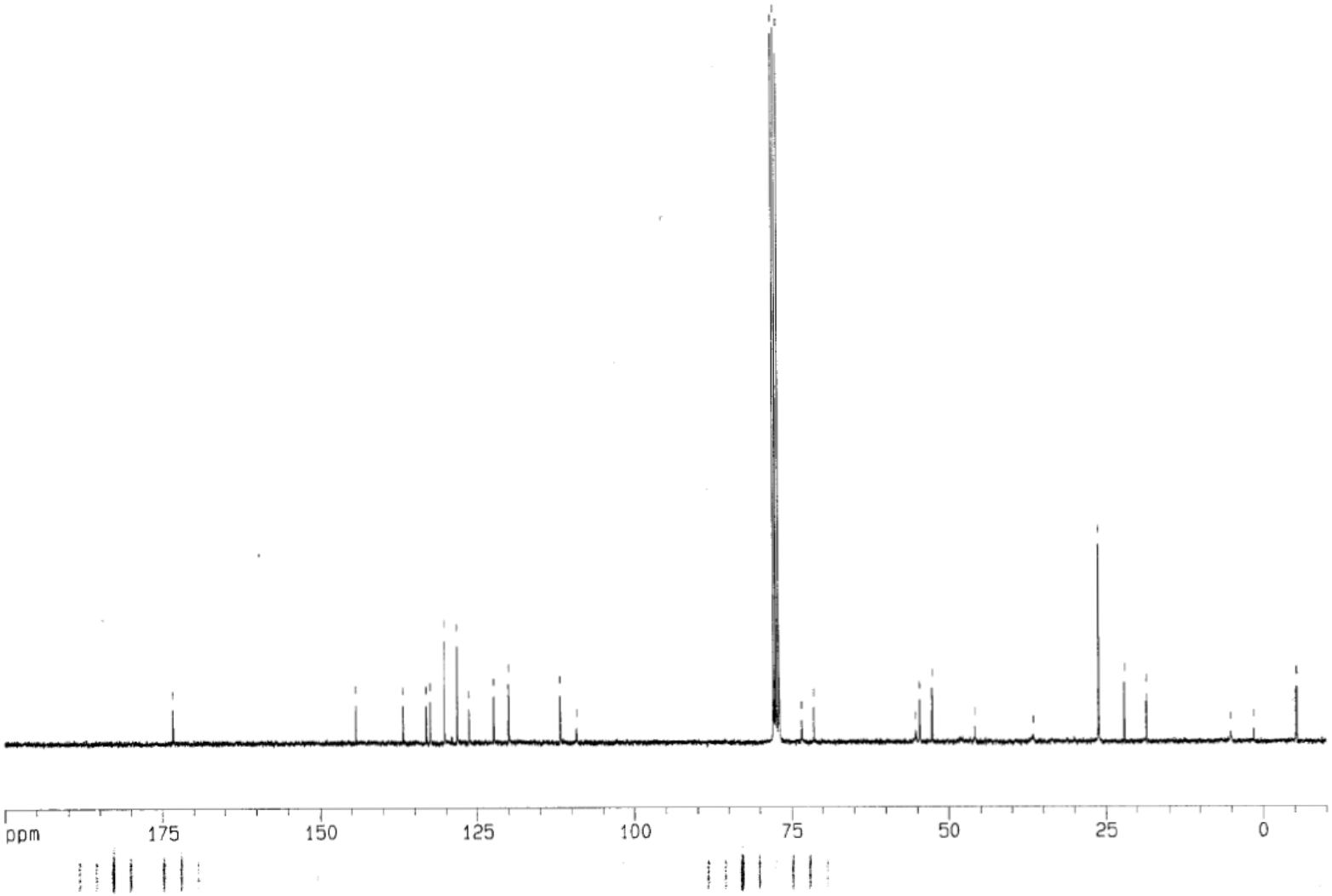
18.522
5.190
1.453
-5.223
-5.332



Current Data Parameters
NAME 090812FJIII294
EXPNO 2
PROCNO 1

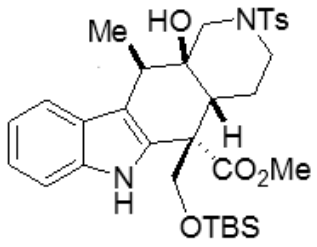
F2 - Acquisition Parameters
Date_ 20120908
Time 14.13
INSTRUM spect
PROBHD 5 mm CNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2848
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 1625.5
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 5.25 usec
PL1 -6.00 dB
SFO1 75.4106357 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 19.70 dB
PL13 19.70 dB
SFO2 299.8711995 MHz

F2 - Processing parameters
SI 32768
SF 75.4023410 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 200.000 ppm
F1 15080.47 Hz
F2P -10.000 ppm
F2 -754.02 Hz
PPMCM 10.50000 ppm/cm
HZCM 791.72461 Hz/cm



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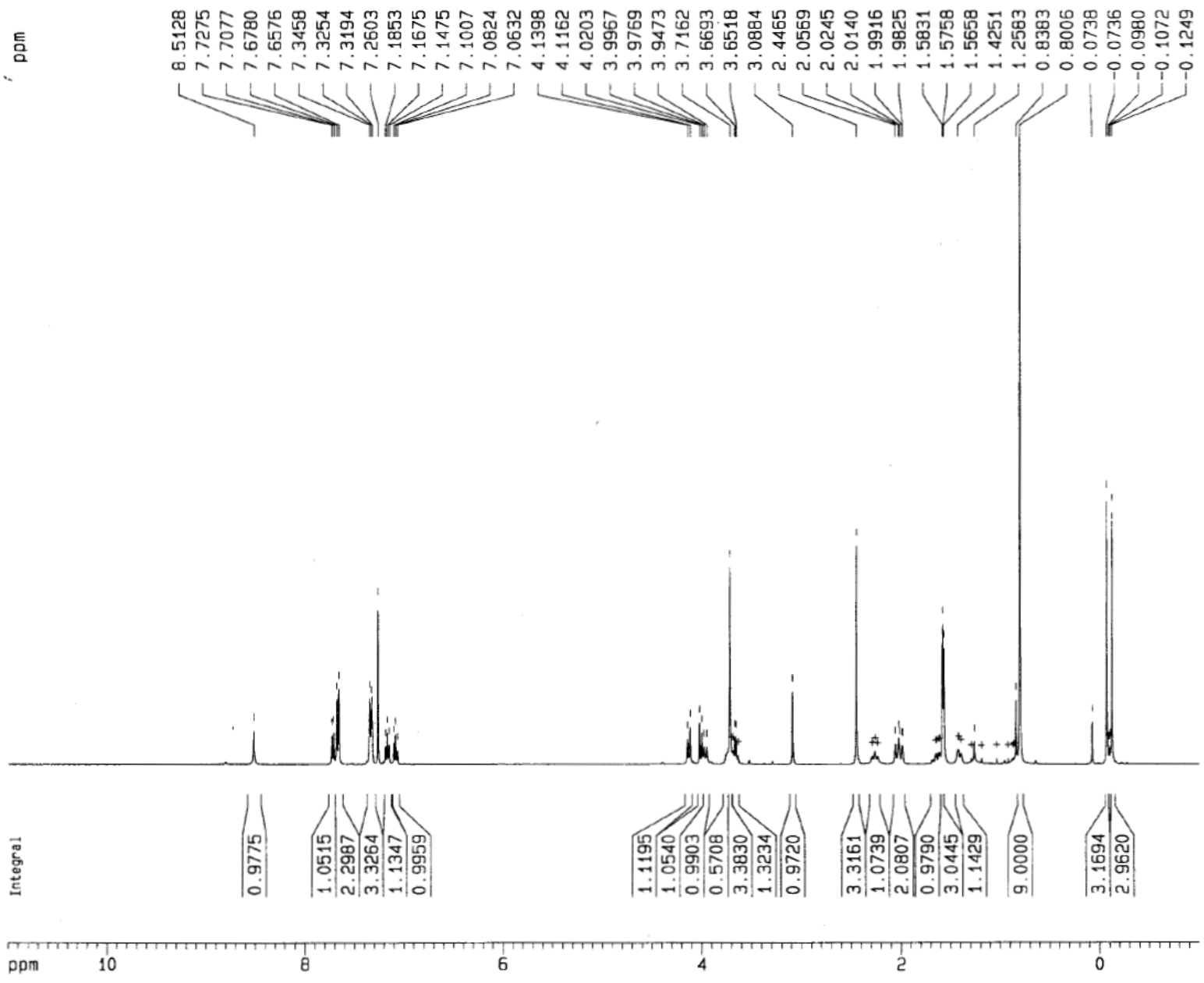


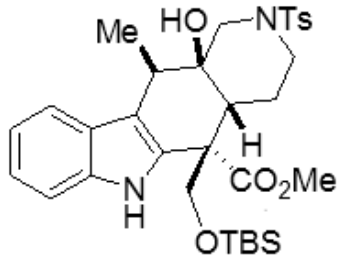

```
Current Data Parameters
NAME      090912FJIII296
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120909
Time               22.57
INSTRUM            spect
PROBHD     5 mm BBI 1H-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           8278.146 Hz
FIDRES        0.126314 Hz
AQ            3.9584243 sec
RG                724.1
DW               60.400 usec
DE                6.00 usec
TE                300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =========
NUC1                  1H
P1                 6.45 usec
PL1                0.00 dB
SF01         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300091 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                20.00 cm
F1P               11.000 ppm
F1              4401.43 Hz
F2P               -1.000 ppm
F2              -400.13 Hz
PPMCM          0.60000 ppm/cm
HZCM          240.07800 Hz/cm
```



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Current Data Parameters
NAME 090912FJIII296
EXPNO 1

ppm
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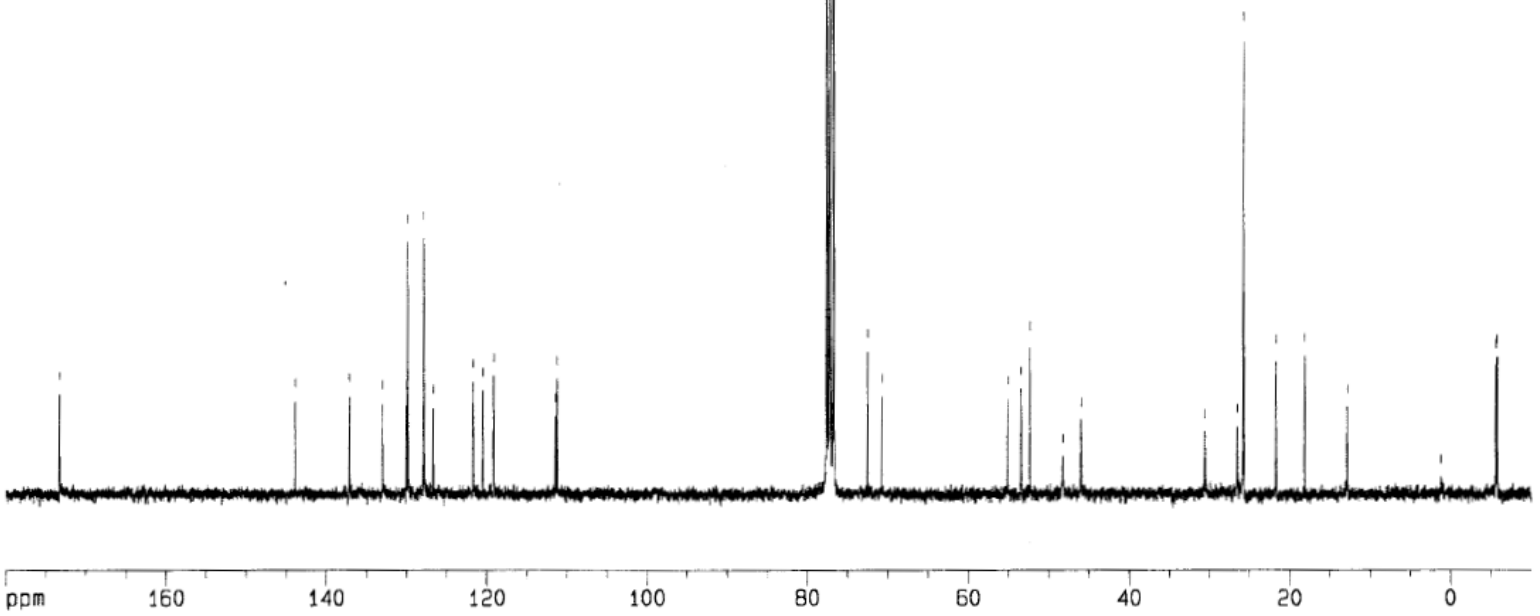
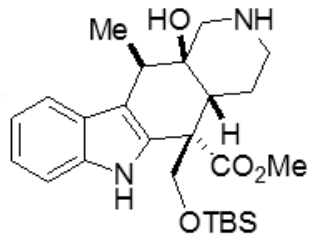
143.880
137.126
132.953
130.016
129.920
129.841
127.862
126.712
121.704
120.523
119.106
111.366
111.200
77.584
77.362
77.160
76.736
72.463
70.674
55.138
53.454
52.346
48.185
45.953
30.547
26.516
25.834
25.727
21.686
18.149
12.809
1.159
-5.683
-5.795





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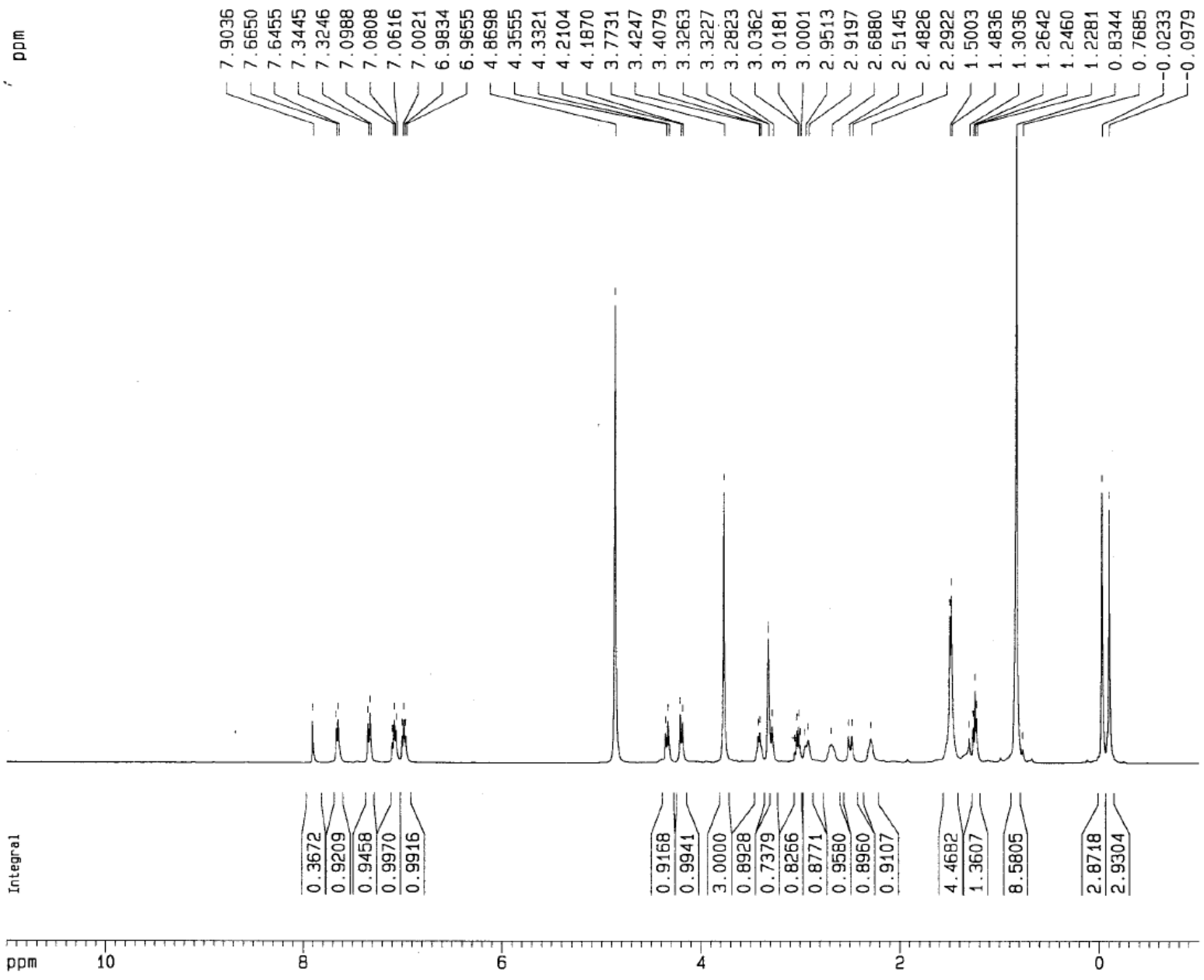


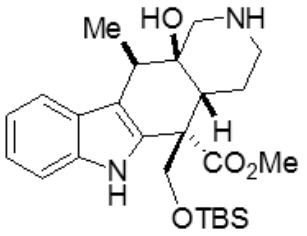
Current Data Parameters
NAME 091212FJIII299
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120912
Time 20.11
INSTRUM spect
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 65536
SOLVENT MeOH
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 101.6
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

========== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300009 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 4401.43 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.60000 ppm/cm
HZCM 240.07800 Hz/cm



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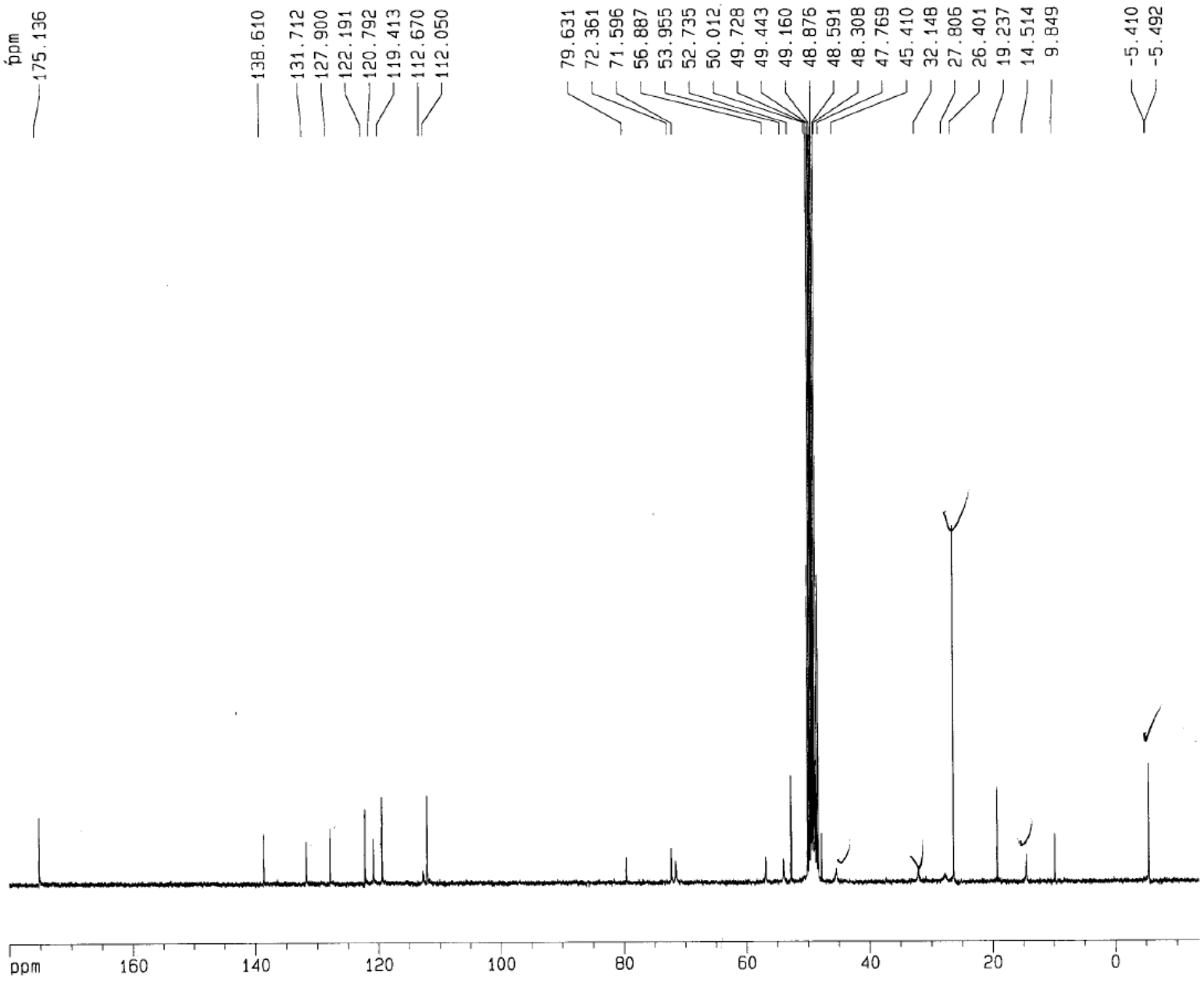



```
Current Data Parameters
NAME      091312FJIII299
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20120913
Time              20.19
INSTRUM           spect
PROBHD  5 mm QNP 1H/1
PULPROG         zgpg30
TD               65536
SOLVENT           MeOH
NS                5720
DS                   4
SWH          18796.992 Hz
FIDRES       0.286819 Hz
AQ           1.7433076 sec
RG                 512
DW              26.600 usec
DE               6.00 usec
TE              300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
D12          0.00002000 sec

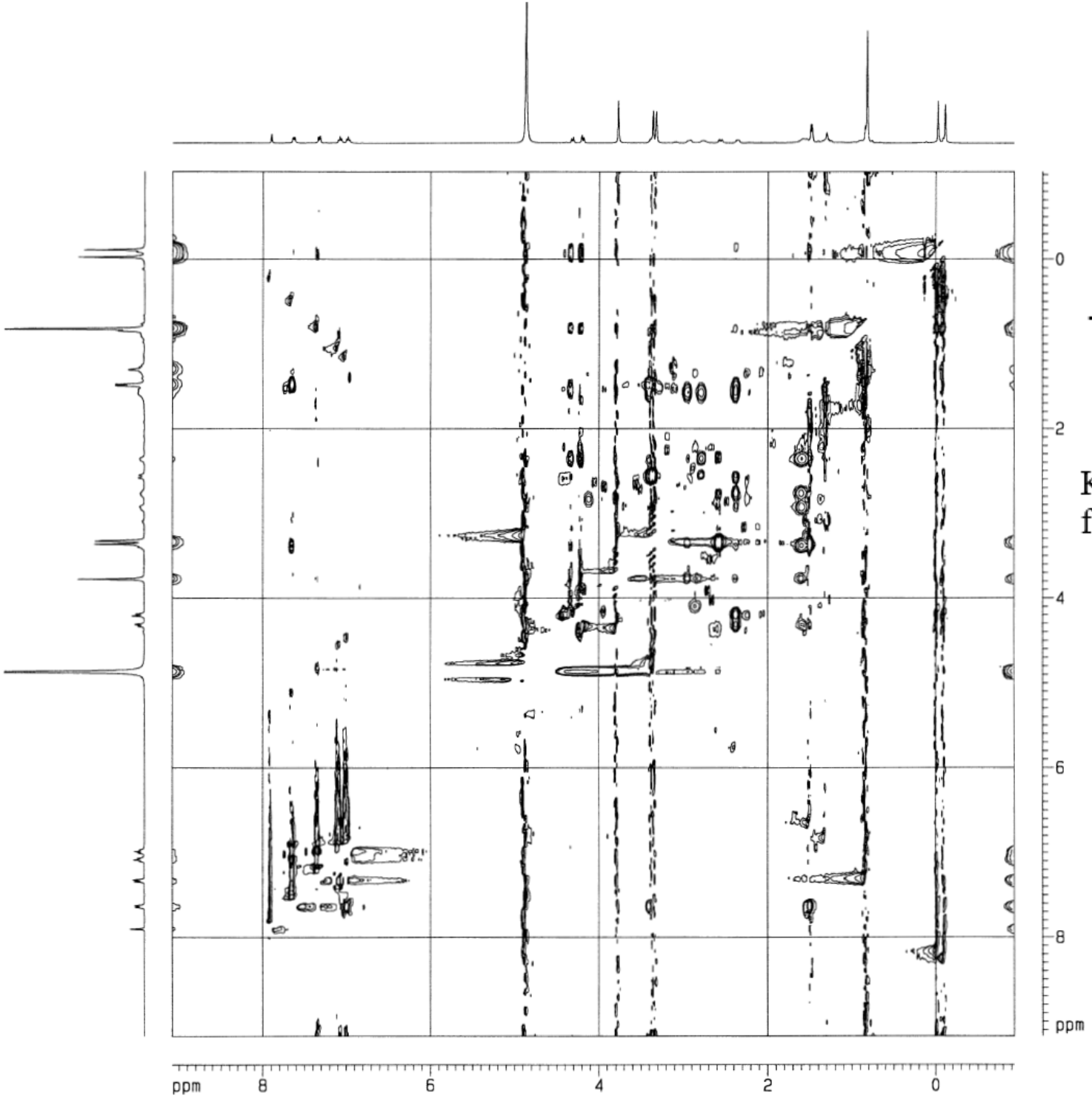
========== CHANNEL f1 ==========
NUC1               13C
P1              5.25 usec
PL1             -6.00 dB
SFO1        75.4106357 MHz

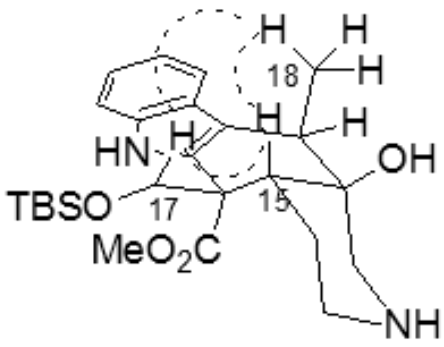
========== CHANNEL f2 ==========
CPDPRG2         waltz16
NUC2                1H
PCPD2          115.00 usec
PL2              0.00 dB
PL12            19.70 dB
PL13            19.70 dB
SFO2       299.8711995 MHz

F2 - Processing parameters
SI                 32768
SF          75.4022561 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

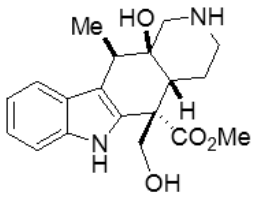
1D NMR plot parameters
CX                 20.00 cm
F1P               180.000 ppm
F1              13572.41 Hz
F2P               -15.000 ppm
F2              -1131.03 Hz
PPMCM             9.75000 ppm/cm
HZCM            735.17212 Hz/cm
```

FYQ-III-299 NOESY

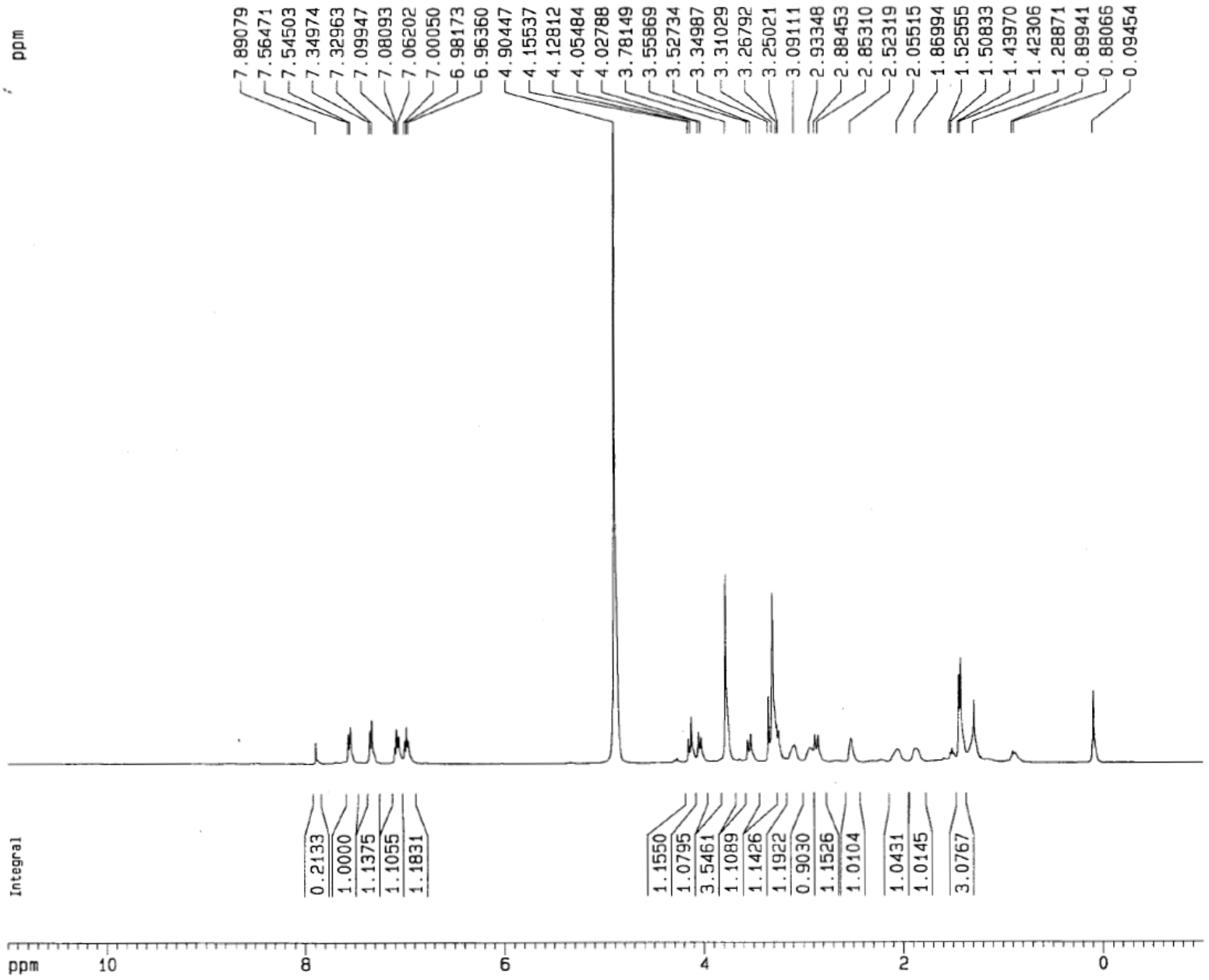




Key nOe correlations for piperidine **29**



(±)-3



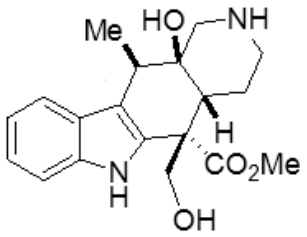

```
Current Data Parameters
NAME          092012FJV015
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20120920
Time                 20.21
INSTRUM              spect
PROBHD     5 mm BBI 1H-
PULPROG              zg30
TD                  65536
SOLVENT              MeOH
NS                     16
DS                      2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  143.7
DW                 60.400 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec

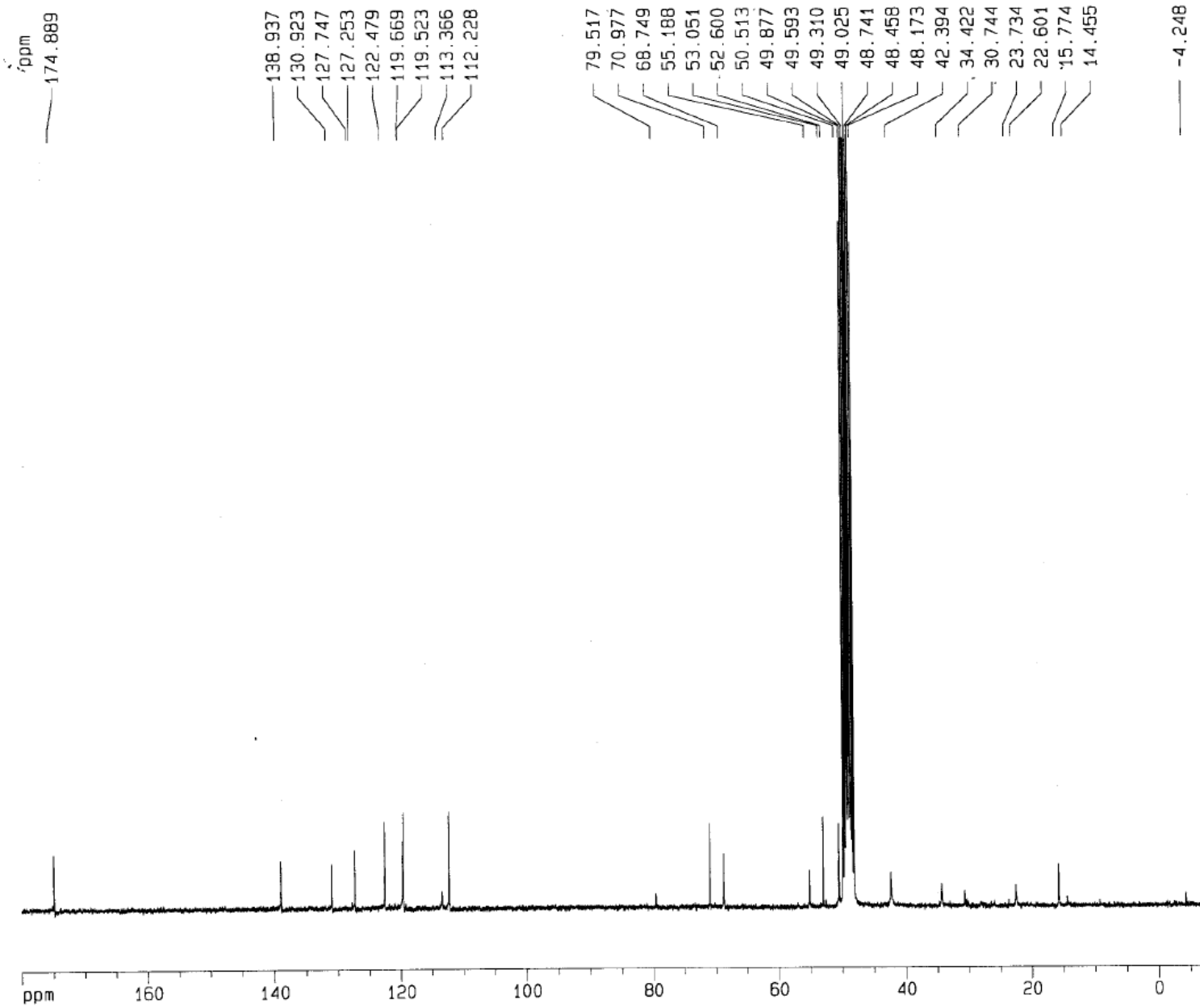
============ CHANNEL f1 ========
NUC1                    1H
P1                   6.45 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                      32768
SF            400.1300067 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 11.000 ppm
F1                 4401.43 Hz
F2P                -1.000 ppm
F2                 -400.13 Hz
PPMCM              0.60000 ppm/cm
HZCM             240.07800 Hz/cm
```



(±)-3

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Current Data Parameters
NAME          092112FJV015
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20120922
Time                   3.55
INSTRUM               spect
PROBHD     5 mm QNP 1H/1
PULPROG              zgpg30
TD                    65536
SOLVENT                MeOH
NS                    11264
DS                        4
SWH           18796.992 Hz
FIDRES         0.286819 Hz
AQ             1.7433076 sec
RG                     8192
DW               26.600 usec
DE                6.00 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec

============ CHANNEL f1 ============
NUC1                   13C
P1                5.25 usec
PL1               -6.00 dB
SFO1          75.4106357 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                   1H
PCPD2           115.00 usec
PL2               0.00 dB
PL12             19.70 dB
PL13             19.70 dB
SFO2         299.8711995 MHz

F2 - Processing parameters
SI                    32768
SF            75.4022676 MHz
WDW                      EM
SSB                       0
LB                 1.00 Hz
GB                        0
PC                     1.40

1D NMR plot parameters
CX                20.00 cm
F1P              180.000 ppm
F1               13572.41 Hz
F2P              -15.000 ppm
F2               -1131.03 Hz
PPMCM             9.75000 ppm/cm
HZCM            735.17218 Hz/cm
```
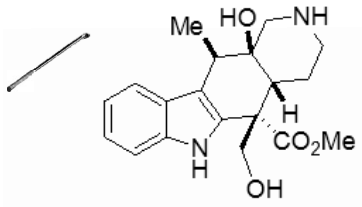
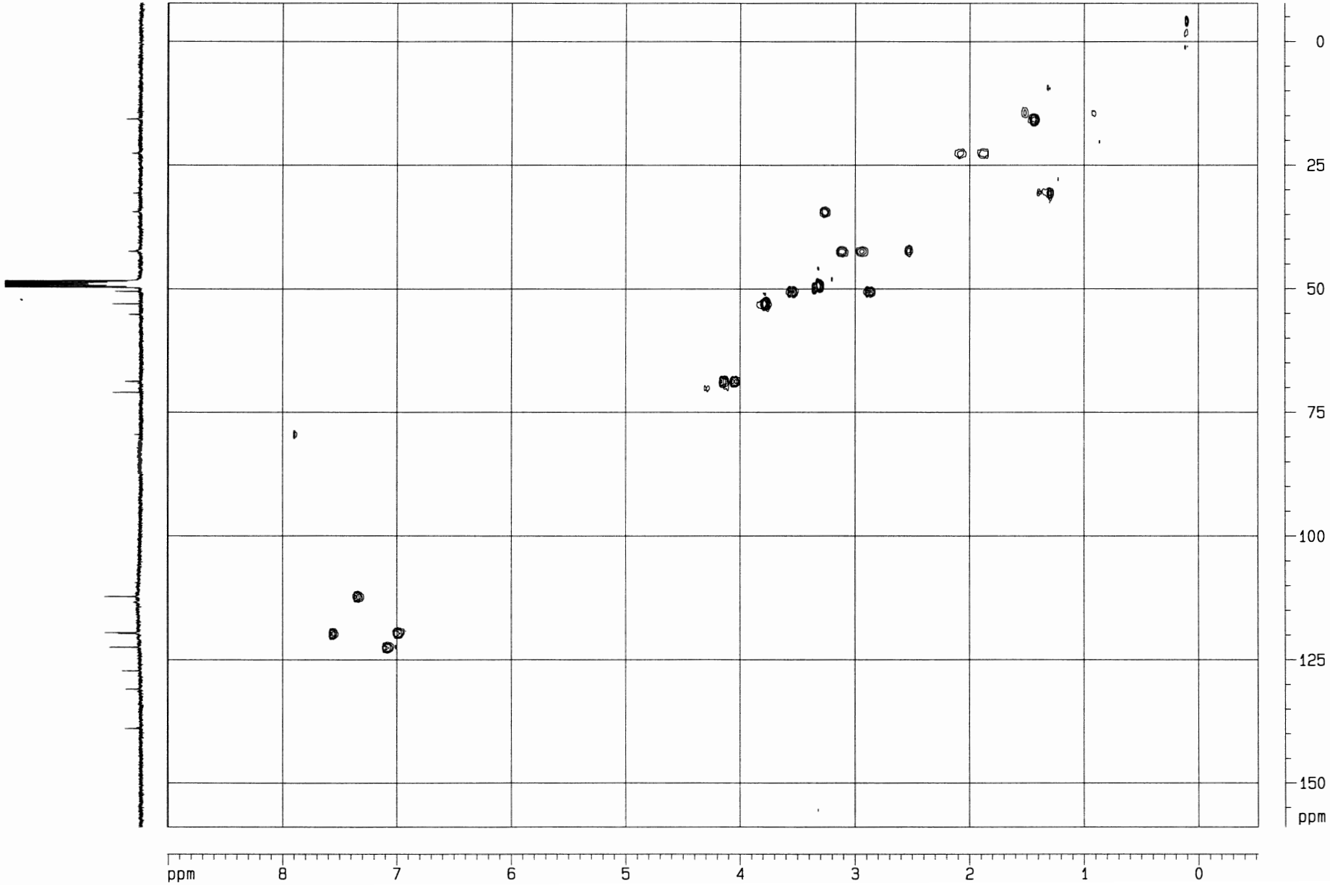
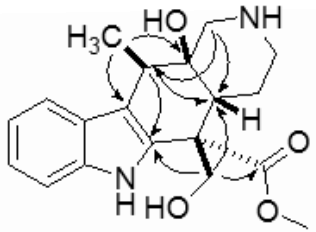



(±)-3

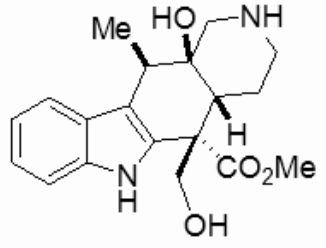
FYQ-V-015 HMQC d4-MeOD



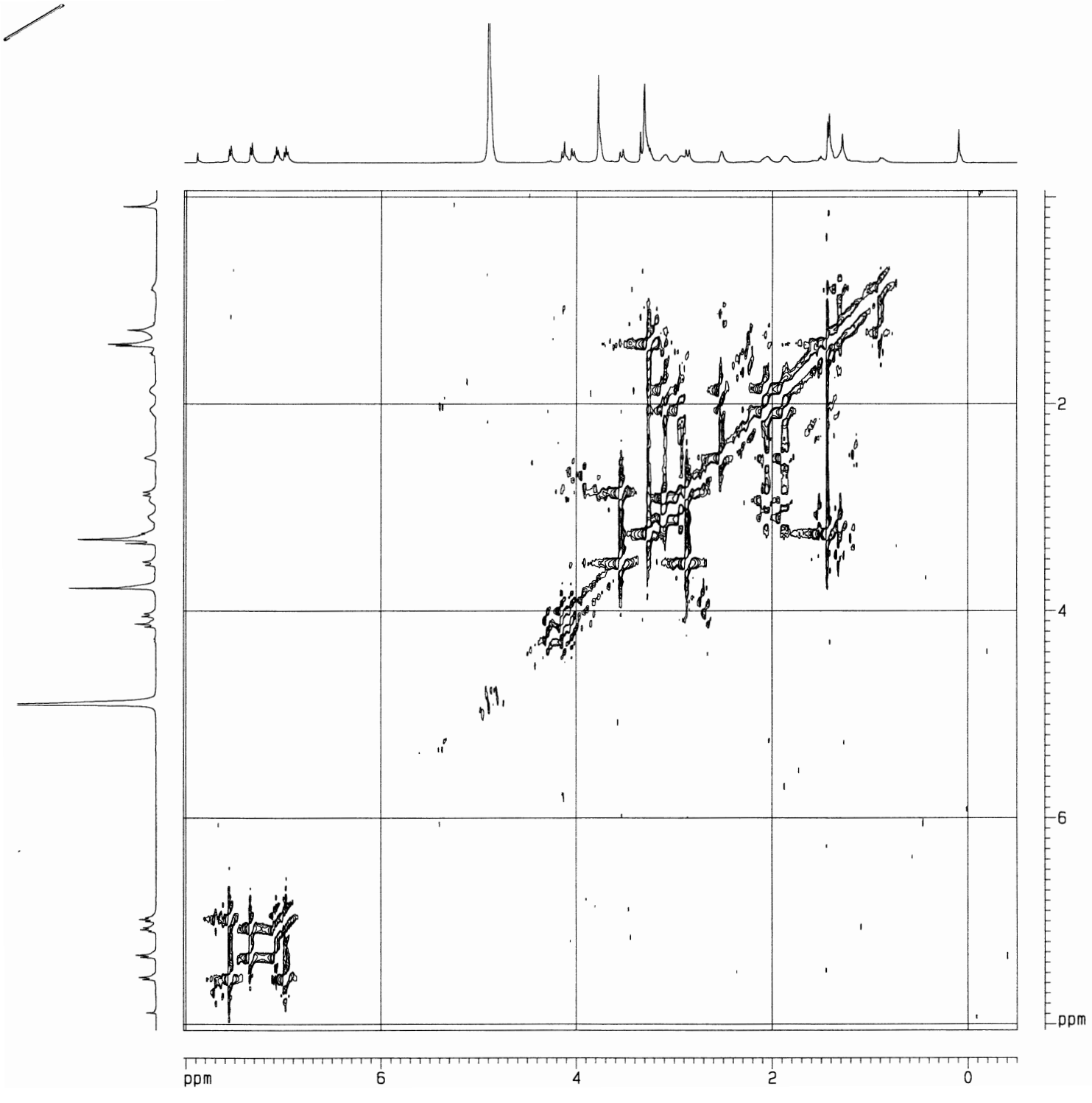


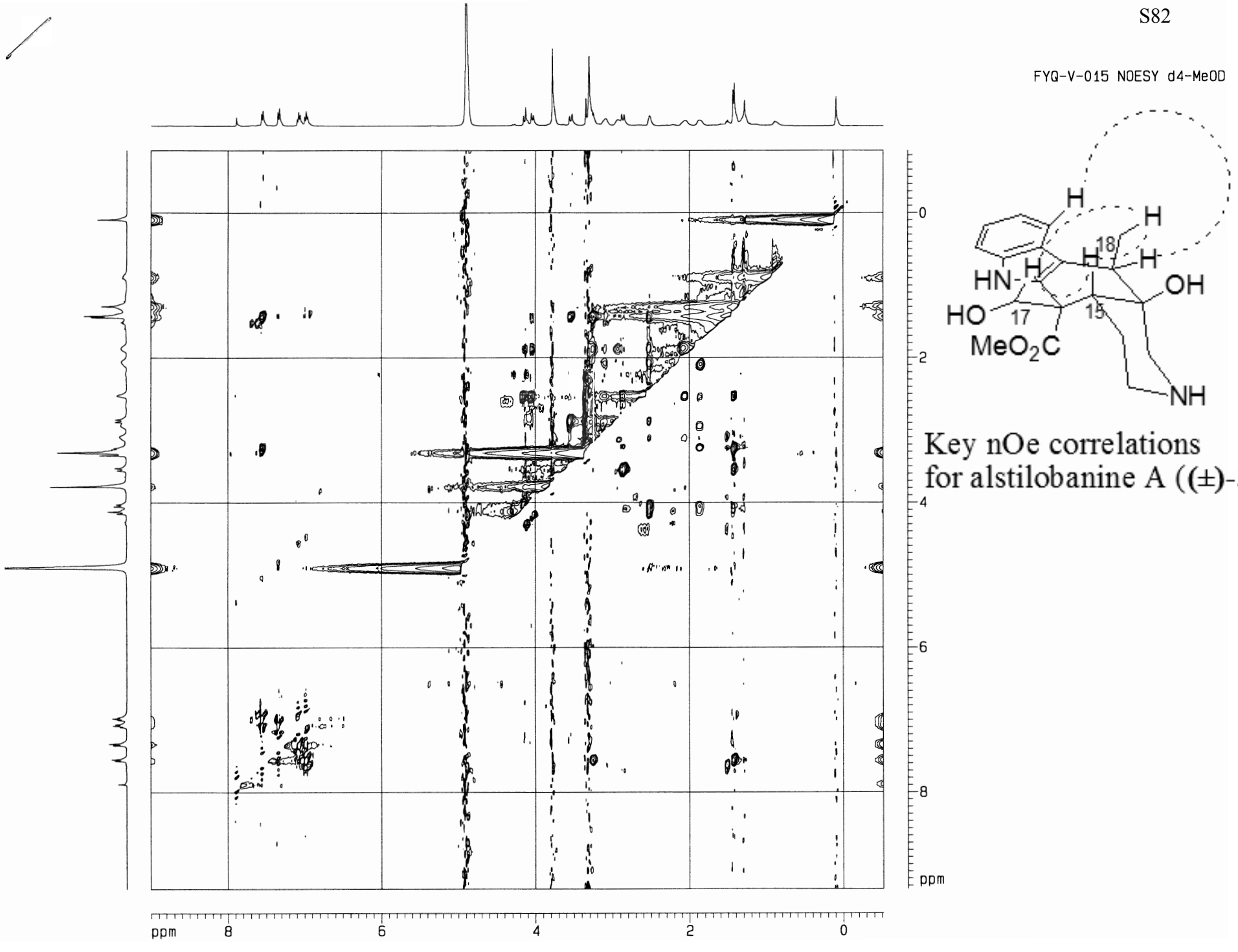
Selected HMBC correlations for alstilobanine A ((±)-**3**)

FYQ-V-015 COSY d4-MeOD



(±)-3





Key nOe correlations for alstilobanine A ((±)-**3**)