Supporting Information

Construction of the Azocane (Azacyclooctane) Moiety of the *Lycopodium* Alkaloid Lycopladine H via an Intramolecular Hydroaminomethylation Strategy

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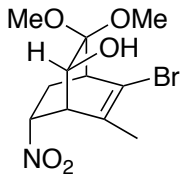
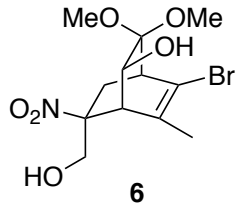
Table of Contents

General Methods. All non-aqueous reactions were carried out under an argon atmosphere in oven- or flame-dried glassware unless otherwise noted. Anhydrous tetrahydrofuran, diethyl ether, dichloromethane, and toluene were obtained from a solvent dispensing system equipped with alumina drying columns. All other solvents and reagents were used as obtained from commercial sources without further purification unless noted. Flash column chromatography was performed using silica gel 60 (230-400 mesh). Preparative thin-layer chromatography was performed using 500 or 1000 μm silica gel PF_{254} plates.



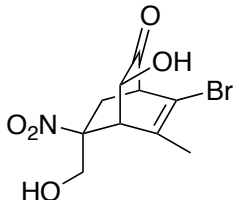
5

5-Bromo-3,3-dimethoxy-6-methyl-7-nitrobicyclo[2.2.2]oct-5-en-2-ol (5). To nitro ketone **4**[5] (3.20 g, 10.00 mmol) in MeOH (150 mL) at -78 °C was added $NaBH_4$ (415 mg, 10.97 mmol). The reaction mixture was stirred for 30 min, and then warmed to rt over 1.5 h. The solvent was partially evaporated to ~20 mL volume, and saturated aqueous NH_4Cl (100 mL) was added. The suspension was stirred for 10 min, and then extracted with EtOAc. The combined organics were dried over $MgSO_4$ and evaporated. The residue was purified by flash column chromatography (25% EtOAc in hexanes) to give nitro alcohol **5** (3.03 g, 94%) as a white solid as a single diastereomer. X-ray quality crystals were obtained by slow evaporation from hexanes: mp 107-108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (ddd, J = 9.4, 4.4, 2.6 Hz, 1H), 3.68 (dd, J = 5.9, 2.8 Hz, 1H), 3.52 (td, J = 5.3, 0.6 Hz, 1H), 3.41(s, 3H), 3.20 (s, 3H), 3.16 (d, J = 6.0 Hz, 1H), 3.15 (t, 3.0 Hz, 1H), 2.42 (ddd, J = 14.6, 9.4, 2.6 Hz, 1H), 2.23 (ddd, J = 14.6, 7.7, 0.6 Hz, 1H), 1.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.8, 115.1, 102.0, 80.9, 71.7, 51.4, 50.4, 40.0, 47.1, 27.8, 21.2; IR (thin film) 3518, 1551 cm^{-1}; HRMS (ESI) $[M+OAc]^+$ calcd for $C_{13}H_{19}BrNO_7$ 380.0345, found 380.0357.



6

5-Bromo-7-(hydroxymethyl)-3,3-dimethoxy-6-methyl-7-nitrobicyclo[2.2.2]oct-5-en-2-ol (6). To a solution of nitro alcohol **5** (15.75 g, 48.89 mmol) in MeCN (250 mL) were added aqueous formaldehyde (35%, 7.75 mL, 97.65 mmol) and triethylamine (6.80 mL, 48.79 mmol). The reaction mixture was stirred at rt for 3 d, and then evaporated. The residue was purified by flash column chromatography (2:1 hexanes/EtOAc) to give nitro diol **6** (15.32 g, 89%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (dd, *J* = 5.7, 2.7 Hz, 1H), 3.65 (m, 2H), 3.56 (d, *J* = 2.6 Hz, 1H), 3.39 (s, 3H), 3.17 (s, 3H), 3.11 (d, 5.7 Hz, 1H), 3.11 (br s, 1H), 2.91 (dd, *J* = 15.0, 2.1 Hz, 1H), 2.41 (br t, *J* = 5.9 Hz, 1H), 1.94 (s, 3H), 1.63 (dd, *J* = 15.1, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 116.0, 102.5, 94.3, 69.5, 69.0, 51.5, 50.2, 50.1, 47.9, 28.4, 21.2; HRMS (ESI) $[M+OAc]^+$ calcd for $C_{14}H_{21}BrNO_8$ 410.0451, found 410.0449.



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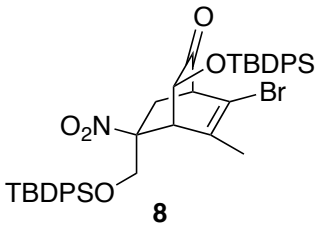
6-Bromo-3-hydroxy-8-(hydroxymethyl)-5-methyl-8-nitrobicyclo[2.2.2]oct-5-en-2-one (7). To a solution of ketal **6** (1.40 g, 3.98 mmol) in wet MeCN (2% H_2O, 35 mL) was added lithium tetrafluoroborate (1.0 M in MeCN, 4.40 mL, 4.40 mmol). The reaction mixture was heated at 85 °C for 2 h, then cooled to rt. The MeCN was evaporated, and saturated aqueous $NaHCO_3$ was added to the residue. The aqueous mixture was extracted with EtOAc, and the combined organics were dried over $MgSO_4$ and evaporated to give ketone **7** (1.21 g, 99%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.85 (s, 1H), 3.83 (d, *J* = 2.5 Hz, 1H), 3.74 (br t, 1H, CH_2**OH**), 3.40 (d, *J* = 2.6 Hz, 1H), 2.92 (dd, *J* = 15.5, 1.9 Hz, 1H), 2.79 (d, *J* = 2.3 Hz, 1H), 2.40 (t, *J* = 6.4 Hz, 1H), 2.08 (dd, *J* = 15.4, 3.4 Hz, 1H), 2.04 (s, 3H); ^{1}H NMR (300 MHz, acetone-d6) d 5.19 (d, *J* = 4.4 Hz, 1H), 4.85 (t, *J* = 5.3 Hz, 1H, CH_2**OH**), 3.94 (dd, *J* = 11.9, 5.4 Hz, 1H),

3.81 (dd, *J* = 11.9, 5.2 Hz, 1H), 3.77 (d, *J* = 4.2 Hz, 1H), 3.32 (m, 1H), 3.12 (br s, 1H, CH**OH**), 2.86 (dd, *J* = 15.5, 1.6 Hz, 1H), 2.27 (dd, *J* = 15.5, 3.4 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (75 MHz, acetone-d6) δ 204.9, 140.8, 112.5, 95.0, 69.1, 67.6, 57.4, 52.2, 29.7, 21.6; HRMS (ESI) $[M+H]^+$ calcd for $C_{10}H_{13}BrNO_5$ 305.9977, found 305.9964.



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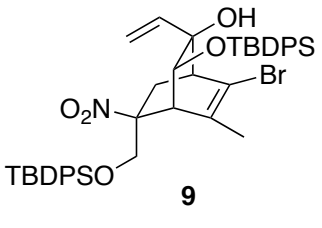
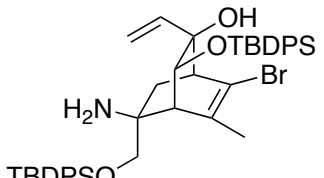
6-Bromo-3-((*tert*-butyldiphenylsilyl)oxy)-8-(((*tert*-butyldiphenylsilyl)oxy)methyl)-5-methyl-8-nitrobicyclo[2.2.2]oct-5-en-2-one (8). To a solution of diol **7** (1.30 g, 4.26 mmol) in DMF (4.25 mmol) were added *tert*-butylchlorodiphenylsilane (2.75 mL, 10.57 mmol) and imidazole (1.45 g, 21.30 mmol). The resulting solution was heated at 40 °C for 18 h, and then cooled to rt. Water was added, and the resulting heterogeneous mixture was extracted with Et_2O. The combined organics were washed with water and brine, dried over $MgSO_4$, and evaporated. The residue was purified by flash column chromatography (5% EtOAc/hexanes) to give bis-silyl ether **8** (2.38 g, 71%) as a foamy white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.46 (m, 2H), 7.40 (m, 14H), 3.84 (d, *J* = 2.4 Hz, 1H), 3.75, 3.60 (ABq, *J* = 10.9 Hz,), 3.54 (d, *J* = 2.4 Hz, 1H), 3.23 (dd, *J* = 3.1, 2.3 Hz, 1H), 2.61 (dd, *J* = 15.6, 1.8 Hz, 1H), 1.94, (dd, *J* = 15.6, 3.4 Hz, 1H), 1.86 (s, 3H), 1.07 (s, 9H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 140.3, 136.1, 136.0, 135.8, 135.7, 135.6, 133.0, 132.5, 132.2, 131.7, 131.3, 130.4, 130.3, 130.1, 128.1, 128.1, 127.8 111.5, 93.2, 69.3, 68.0, 56.4, 51.4, 29.4, 27.0, 26.8, 21.5, 19.5, 19.3; HRMS (ESI) $[M+NH_4]^+$ calcd for $C_{42}H_{52}BrN_2O_5Si_2$ 799.2598, found 799.2567.



9

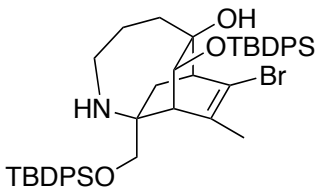
6-Bromo-3-((*tert*-butyldiphenylsilyl)oxy)-8-(((*tert*-butyldiphenylsilyl)oxy)methyl)-5-methyl-8-nitro-2-vinylbicyclo[2.2.2]oct-5-en-2-ol (9). $CeCl_3 \cdot 7H_2O$ (1.30 g, 3.50 mmol) was heated at 140 °C under high vacuum for approximately 3 h. The anhydrous $CeCl_3$ was cooled to rt under an argon atmosphere, and then suspended in THF (10 mL). The resulting suspension was stirred vigorously overnight, then cooled to -78 °C. Vinylmagnesium bromide (1 M in THF, 3.00 mL, 3.00 mmol) was added dropwise, and the resulting mixture was stirred for 30 min. A solution of ketone **8** (1.57 g, 2.00 mmol) in THF (7 mL) was added dropwise, and the reaction mixture was stirred for 5 h at -78 °C. *N*,*N*,*N*',*N*'-Tetramethylethylenediamine (0.52 mL, 3.50 mmol) was added, and the reaction mixture was warmed to rt. The mixture was poured into saturated aqueous $NaHCO_3$, and the aqueous layer was extracted with EtOAc. The combined organics were dried over $MgSO_4$ and evaporated, and the resulting residue was purified by flash column chromatography (10% EtOAc in hexanes) through a short column to afford allylic alcohol **9** (1.56 g, 96%) as a foamy white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 2H), 7.55–7.35 (m, 18H), 5.68 (dd, *J* = 17.0, 10.7 Hz, 1H), 5.31 (dd, *J* = 17.0, 1.3 Hz, 1H), 5.08 (dd, *J* = 10.7, 1.3 Hz, 1H), 3.96 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 1H, R_3C**OH**), 3.58, 3.43 (ABq, *J* = 10.7 Hz, 2H), 3.20 (d, *J* = 2.4 Hz, 1H), 2.78 (t, *J* = 2.8 Hz, 1H), 2.58 (dd, *J* = 15.7, 2.1 Hz, 1H), 1.78 (s, 3H), 1.55 (dd, *J* = 15.8, 3.5 Hz, 1H), 1.11 (s, 9H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 136.1, 135.7, 135.6, 132.8, 132.4, 132.2, 132.0, 131.5, 130.6, 130.4, 130.2, 130.2, 128.2, 128.0, 128.0, 127.9, 120.1, 115.6, 94.3, 75.6, 72.9, 69.8, 54.1, 50.5, 28.5, 27.2, 26.8, 21.3, 19.4, 19.3; HRMS (ESI) $[M+NH_4]^+$ calcd for $C_{44}H_{56}BrN_2O_5Si_2$ 827.2911, found 827.2890.



10

8-Amino-6-bromo-3-((*tert*-butyldiphenylsilyl)oxy)-8-(((*tert*-butyldiphenylsilyl)oxy)methyl)-5-methyl-2-vinylbicyclo[2.2.2]oct-5-en-2-ol (10). To nitro compound **9** (1.25 g, 1.54 mmol) partially dissolved in *i*-PrOH (30 mL) at 45 °C was added activated zinc powder[14] (1.00 g, 15.30 mmol). To the suspension was added dropwise 1 M HCl (7.60 mL, 7.60 mmol). The reaction mixture was stirred for 1 h at 45 °C, and then cooled to rt.

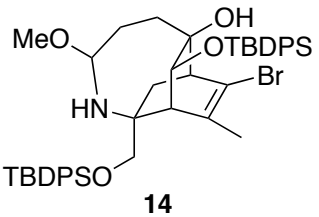
The reaction mixture was neutralized with saturated aqueous $NaHCO_3$, and filtered through a pad of Celite eluting with EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc. The combined organics were washed with water and brine, dried over $MgSO_4$, and evaporated. The residue was purified by flash column chromatography (10–20% EtOAc in hexanes) to give amine **10** (1.16 g, 96%) as a foamy white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (m, 2H), 7.61 (m, 2H), 7.51 (m, 4H), 7.44–7.33 (m, 12H), 6.08 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.50 (dd, *J* = 17.1, 1.9 Hz, 1H), 5.07 (dd, *J* = 10.8, 1.9 Hz, 1H), 4.60 (d, *J* = 2.6 Hz, 1H), 3.90 (s, 1H, R_3C**OH**), 3.04, 2.87 (ABq, 10.0 Hz, 1H), 2.65 (t, *J* = 2.8 Hz, 1H), 2.25 (d, *J* = 2.6 Hz, 1H), 1.76 (s, 3H), 1.25 (dd, *J* = 15.6, 2.2 Hz, 1H), 1.19 (dd, *J* = 15.8, 3.4 Hz, 1H), 1.10 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 136.4, 136.1, 135.8, 135.7, 133.3, 130.4, 130.1, 130.0, 128.0, 127.8, 127.7, 118.1, 114.2, 76.4, 74.1, 72.5, 56.8, 55.4, 53.4, 33.3, 27.2, 27.1, 21.3, 19.5, 19.4; HRMS (ESI) $[M+H]^+$ calcd for $C_{44}H_{55}BrNO_3Si_2$ 780.2904, found 780.2855.



13

12-Bromo-9-((*tert*-butyldiphenylsilyl)oxy)-3-(((*tert*-butyldiphenylsilyl)oxy)methyl)-11-methyl-4-azatricyclo[6.4.0.0^{3,10}]dodec-11-en-8-ol (13). To a solution of amino alkene **10** (500 mg, 0.640 mmol) in PhMe (6.4 mL) and 1,1,1,3,3,3-hexafluoroisopropanol (6.4 mL) in a pressure reactor were added di-μ-chlorido-bis[η^2,η^2-(cycloocta-1,5-diene)rhodium] (3.2 mg, 0.0065 mmol) and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos, 9.3 mg, 0.016 mmol). The reactor was sealed and pressurized with carbon monoxide (10 bar) and hydrogen (40 bar). The pressure reactor was heated at 125–135 °C for 18 h, and then cooled to rt. The gasses were vented, and the solvent was evaporated. The residue was purified by flash column chromatography (10–20% EtOAc in hexanes) to give cyclic amine **13** (384 mg, 75%) as a foamy white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.67 (m, 2H), 7.59 (m, 4H), 7.47–7.35 (m, 12H), 4.74 (d, *J* = 3.8 Hz, 1H), 3.69 (s, 1H), 3.05, 3.02 (ABq, *J* = 9.7 Hz, 1H), 2.80 (m, 2H),

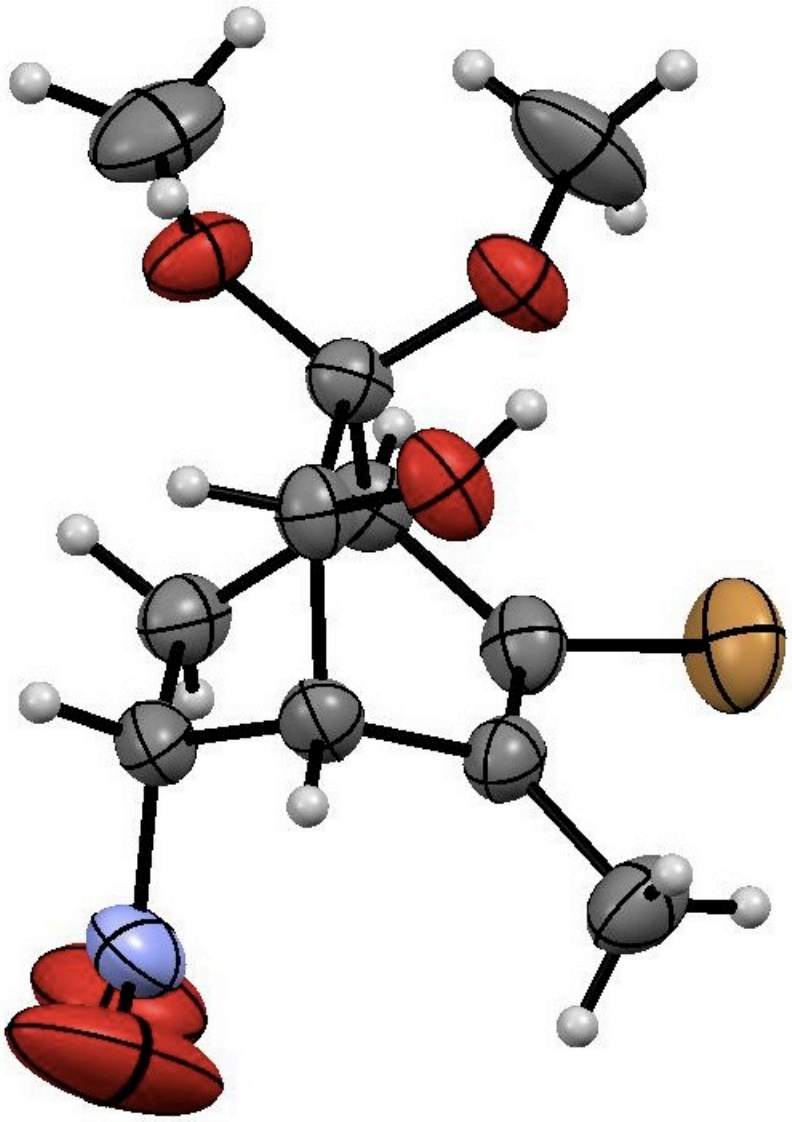
2.59 (m, 2H), 2.10 (dd, J = 14.3, 3.4 Hz, 1H), 1.74 (s, 3H), 1.65 (m, 2H), 1.27 (m, 2H), 1.14 (s, 9H), 1.06 (s, 9H), 0.72 (dd, J = 13.9, 2.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.3, 136.2, 136.1, 135.8, 135.8, 134.9, 133.5, 133.4, 133.4, 133.2, 130.2, 130.0, 129.9, 129.8, 129.7, 127.9, 127.8, 127.8, 127.7, 118.0, 75.4, 70.7, 57.8, 56.7, 55.2, 42.8, 37.4, 28.2, 27.3, 27.1, 26.2, 21.5, 19.5, 19.4; IR (thin film) 3515, 1472, 1428 cm^{-1}; HRMS (ESI) $[M+H]^+$ calcd for $C_{45}H_{57}BrNO_3Si_2$ 794.3060, found 794.3051.

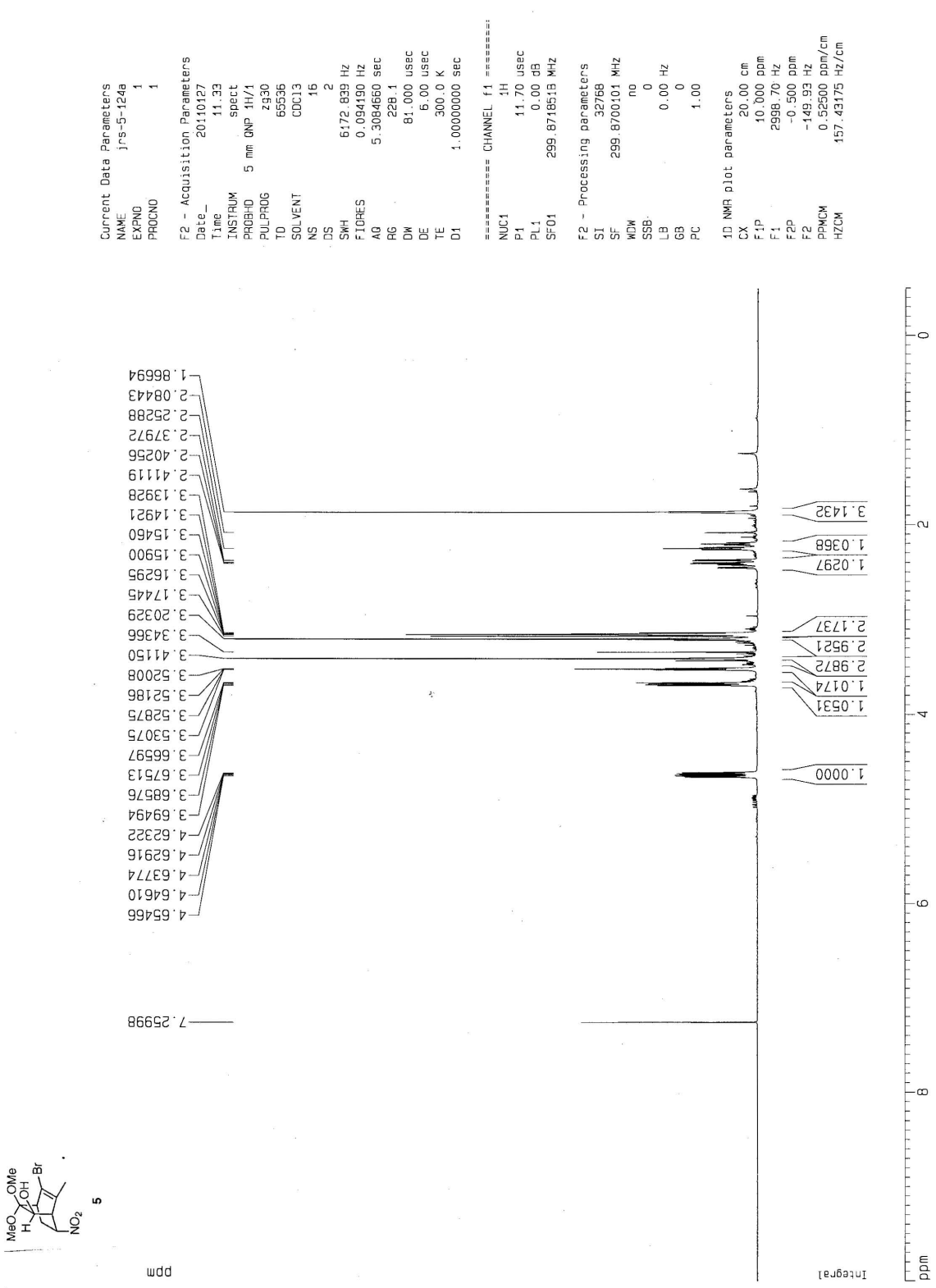


14

12-Bromo-9-((*tert*-butyldiphenylsilyl)oxy)-3-(((*tert*-butyldiphenylsilyl)oxy)methyl)-5-methoxy-11-methyl-4-azatricyclo[6.4.0.0^{3,10}]dodec-11-en-8-ol (14, R = Me**).** The reaction was run according to the above procedure for **13** in a 1:1 mixture of PhMe and MeOH using 100 mg (0.128 mmol) of amino alkene **10**. Purification of the crude product mixture by preparative TLC (15% EtOAc in hexanes) gave azocane **13** (28 mg, 28%), and *N*,*O*-acetal **14** (R = Me) (46 mg, 41%) as a foamy white solid: Data for **14**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (m, 2H), 7.70–7.50 (m, 6H), 7.44–7.33 (m, 12H), 4.53 (m, 2H), 3.29 (s, 3H), 3.27, 3.04 (ABq, J = 9.9 Hz, 2H), 2.95 (d, J = 2.9 Hz, 1H), 2.57 (t, J = 2.8 Hz, 1H), 1.90 (s, 3H), 1.84 (dd, J = 14.3, 3.4 Hz, 1H), 1.45-1.18 (m, 4H), 1.12 (s, 9H), 1.07 (s, 9H), 0.70 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 136.0, 135.8, 135.8, 135.0, 134.8, 133.5, 133.4, 130.0, 130.0, 129.7, 129.4, 127.9, 127.9, 127.8, 127.7, 127.3, 117.1, 105.5, 87.7, 77.0, 72.5, 56.2, 55.6, 54.8 (2C), 35.1, 34.8, 31.7, 27.3, 27.2, 21.6, 19.9, 19.6; LRMS (EI) $[M+H]^+$ calcd for $C_{46}H_{59}BrNO_4Si_2$ 824.3, found 824.3.

X-ray Structure of 5-Bromo-3,3-dimethoxy-6-methyl-7-nitrobicyclo[2.2.2]oct-5-en-2-ol (**5**).

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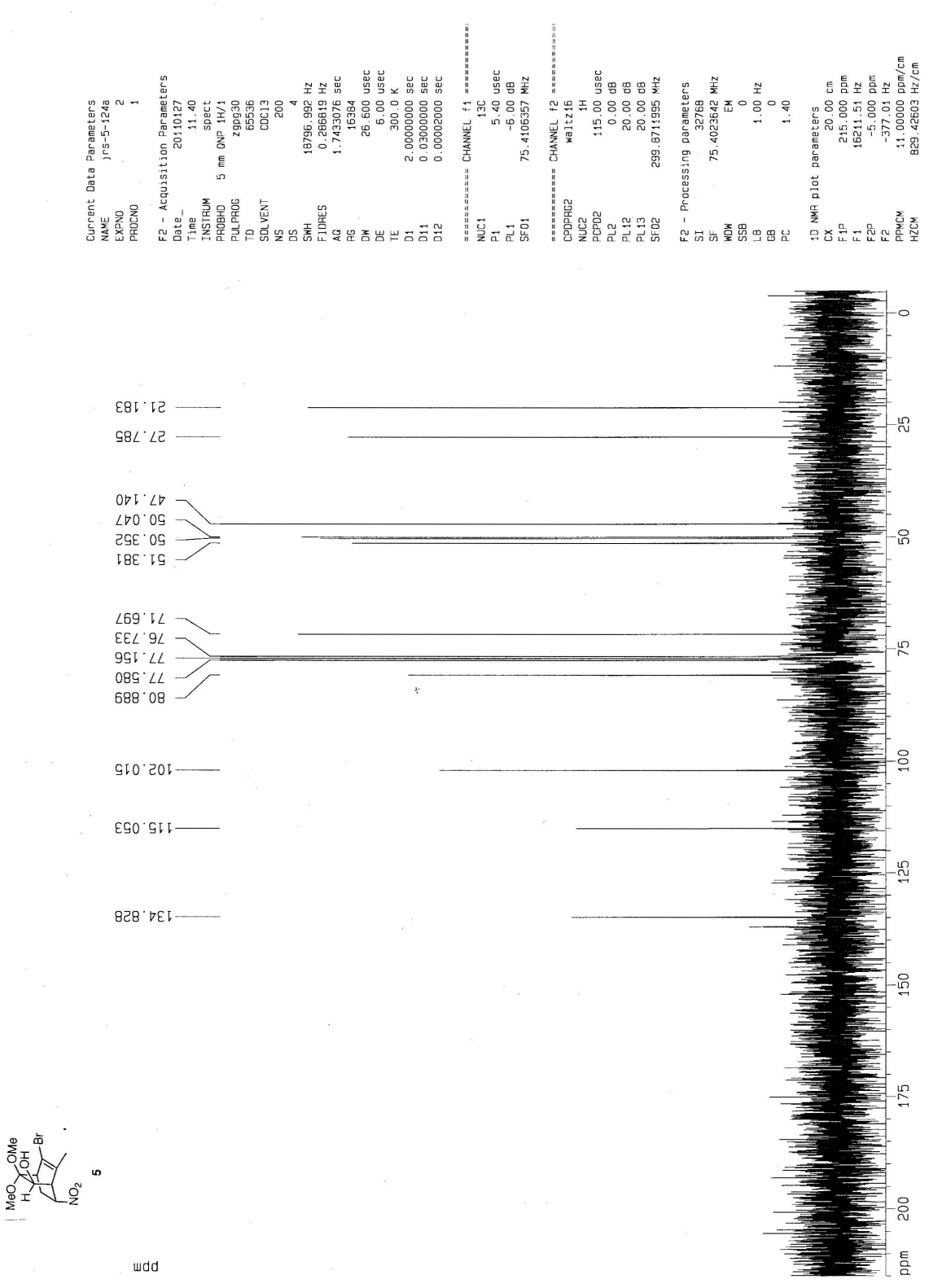
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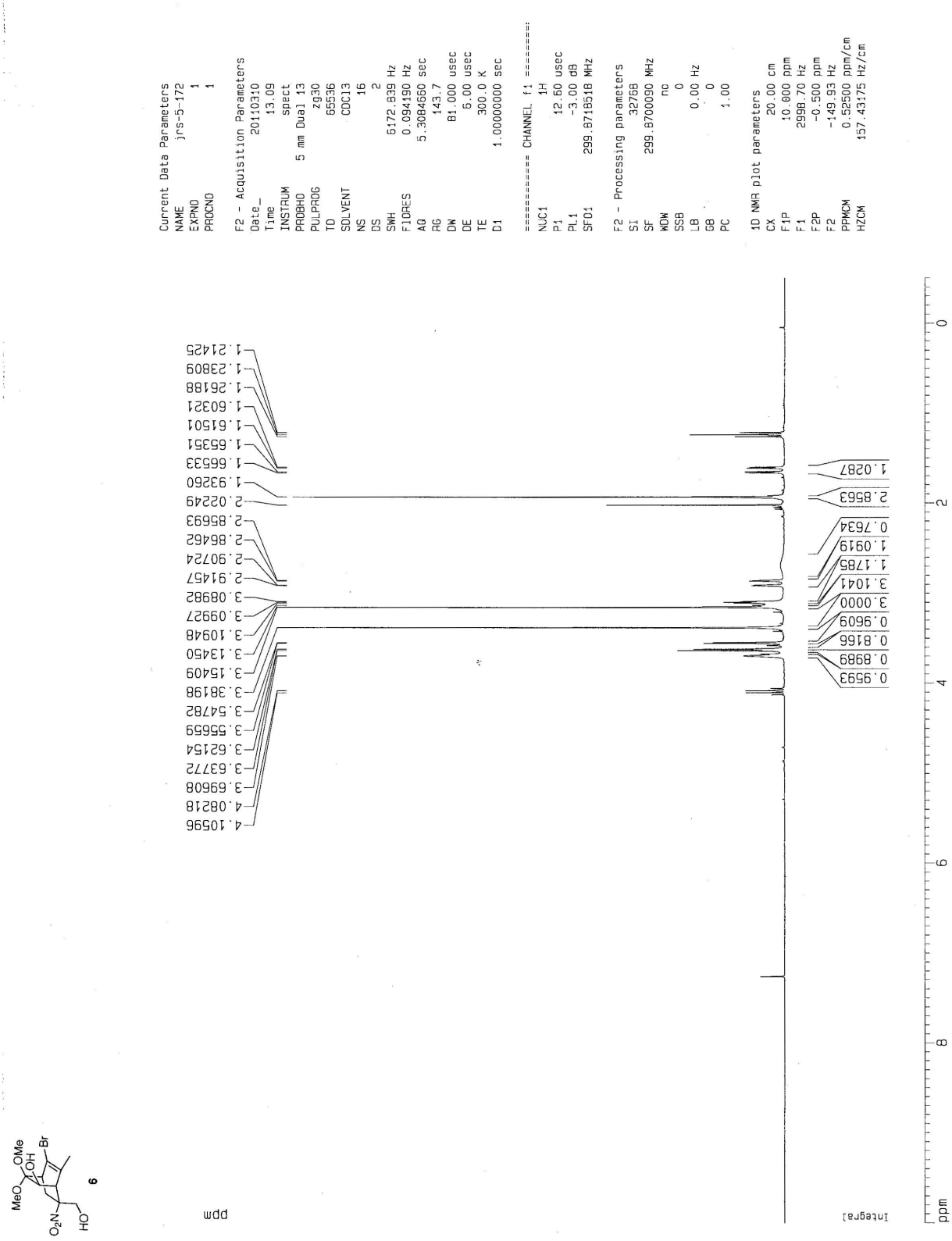
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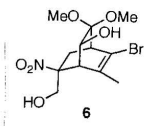
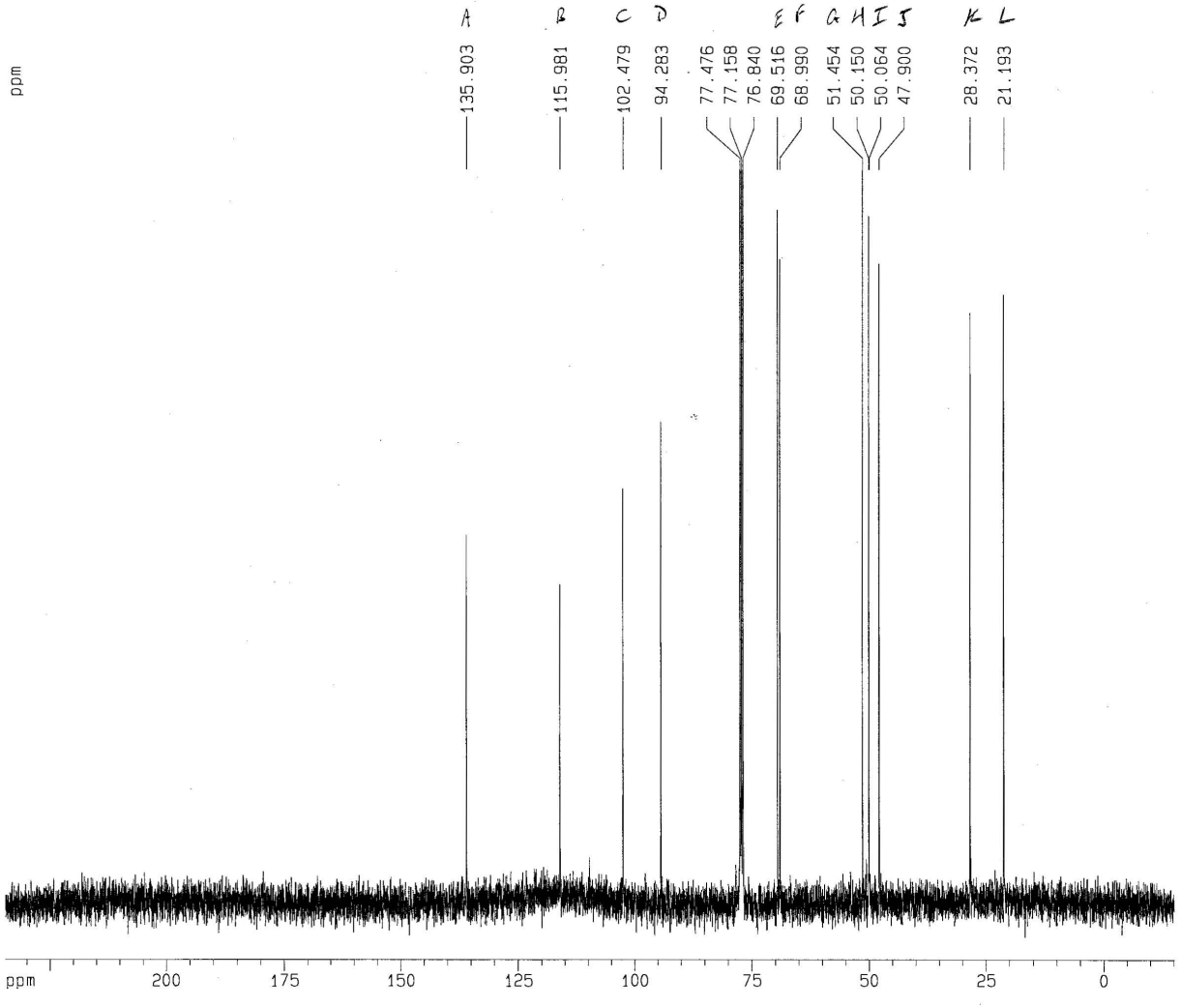
NAME jrs-5-172
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110310
Time 13.09
INSTRUM spect
PROBHD 5 mm Dual 13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 143.7
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
========== CHANNEL f1 ==========
NUC1 1H
P1 12.60 usec
PL1 -3.00 dB
SFO1 299.8718518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700090 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 2998.70 Hz
F2P -0.500 ppm
F2 -149.93 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.43175 Hz/cm
4.10596
4.08218
3.69608
3.63772
3.62154
3.55659
3.54782
3.38198
3.15409
3.13450
3.10948
3.09927
3.08982
2.91457
2.90724
2.86462
2.85693
2.02249
1.93260
1.65533
1.65351
1.61501
1.60321
1.26188
1.23809
1.21425
0.9593
0.8989
0.8166
0.9609
3.0000
3.1041
1.1785
1.0919
0.7634
2.8563
1.0287
MeO
OMe
OH
Br
O2N
HO
6
ppm
Integral
ppm



6

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Current Data Parameters
NAME                  jrs-5-178
EXPNO                         2
PROCNO                        1

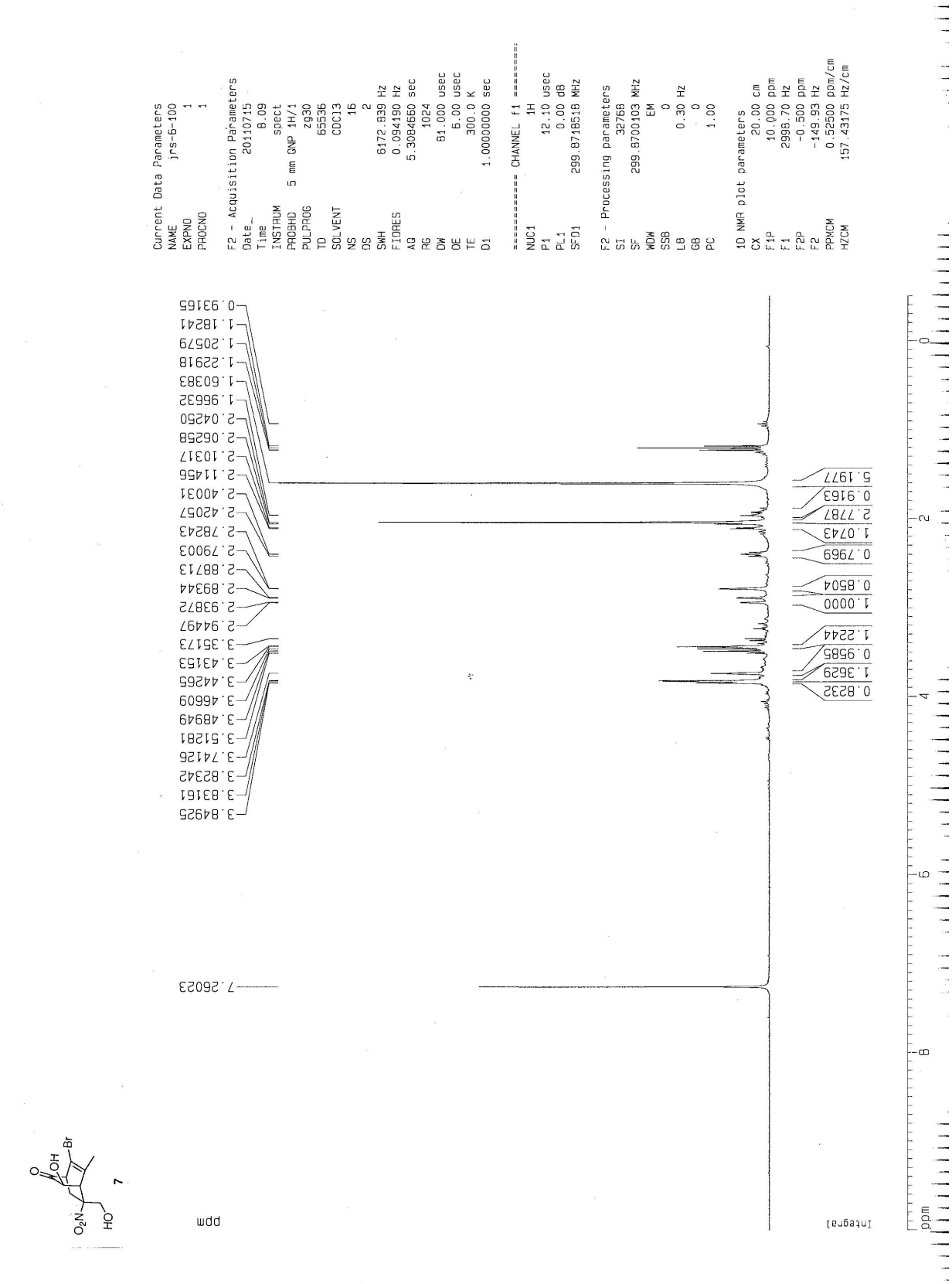
F2 - Acquisition Parameters
Date_                  20110314
Time                      16.41
INSTRUM                   spect
PROBHD     5 mm 88I 1H-B
PULPROG                 zgpg30
TD                         65536
SOLVENT                   CDCl3
NS                         1024
DS                            4
SWH                   25125.629 Hz
FIDRES                0.383387 Hz
AQ                    1.3042164 sec
RG                         8192
DW                       19.900 usec
DE                        6.00 usec
TE                       300.0 K
D1                    2.00000000 sec
d11                   0.03000000 sec
d12                   0.00002000 sec

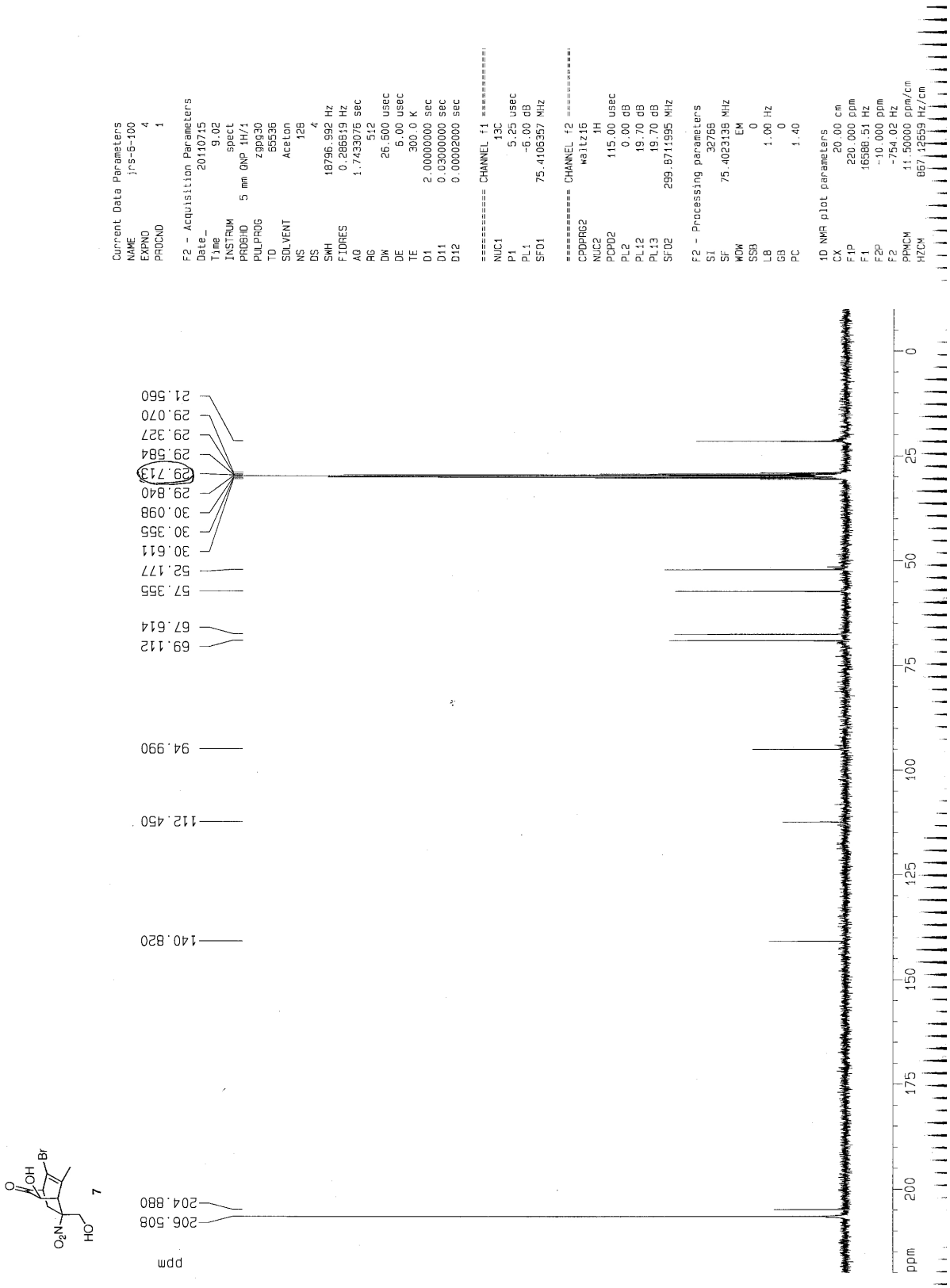
============ CHANNEL f1 ============
NUC1                        13C
P1                        16.35 usec
PL1                       -6.00 dB
SFO1                100.6237959 MHz

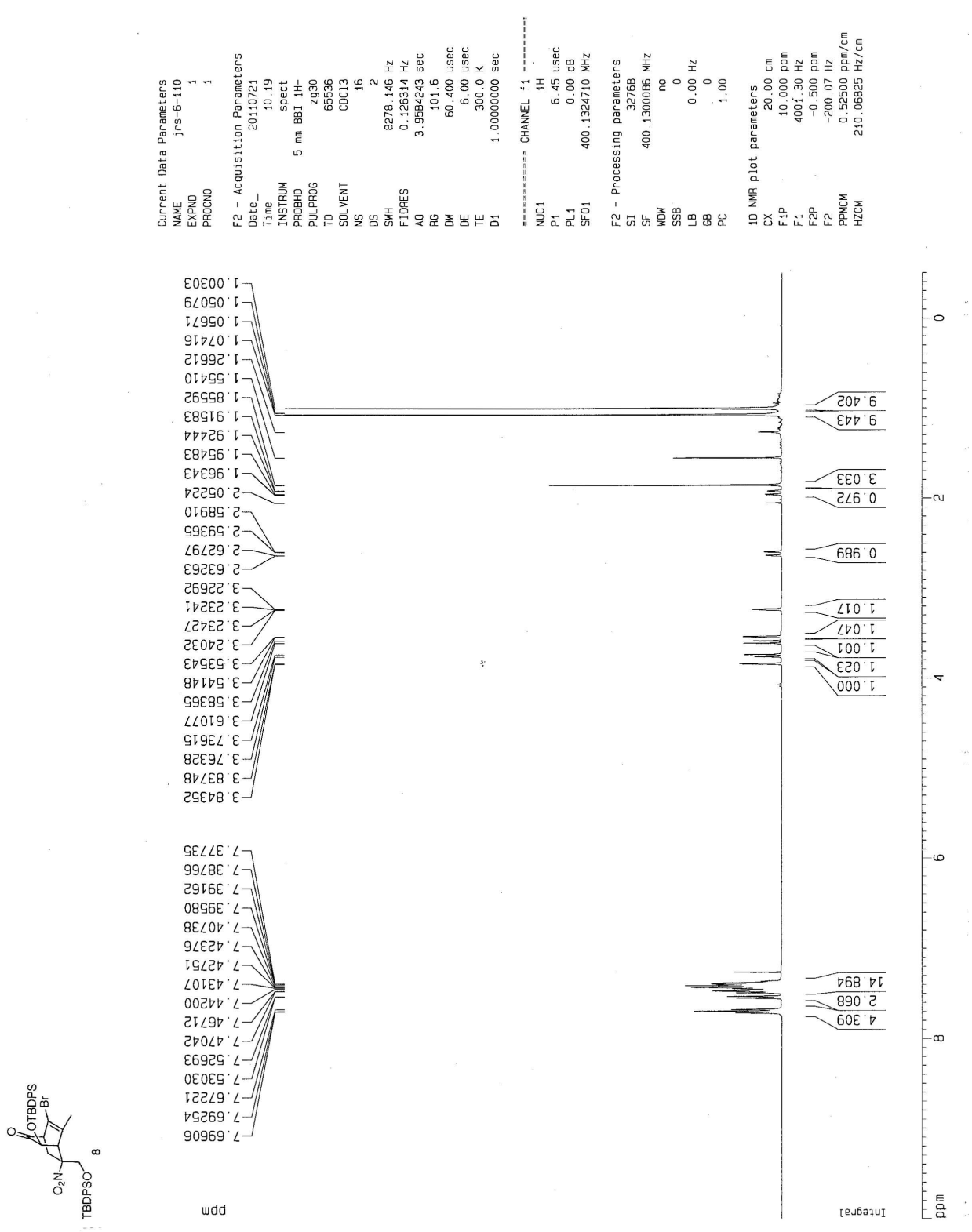
============ CHANNEL f2 ============
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    114.00 usec
PL2                       0.00 dB
PL12                     24.00 dB
PL13                     24.00 dB
SFO2                400.1316005 MHz

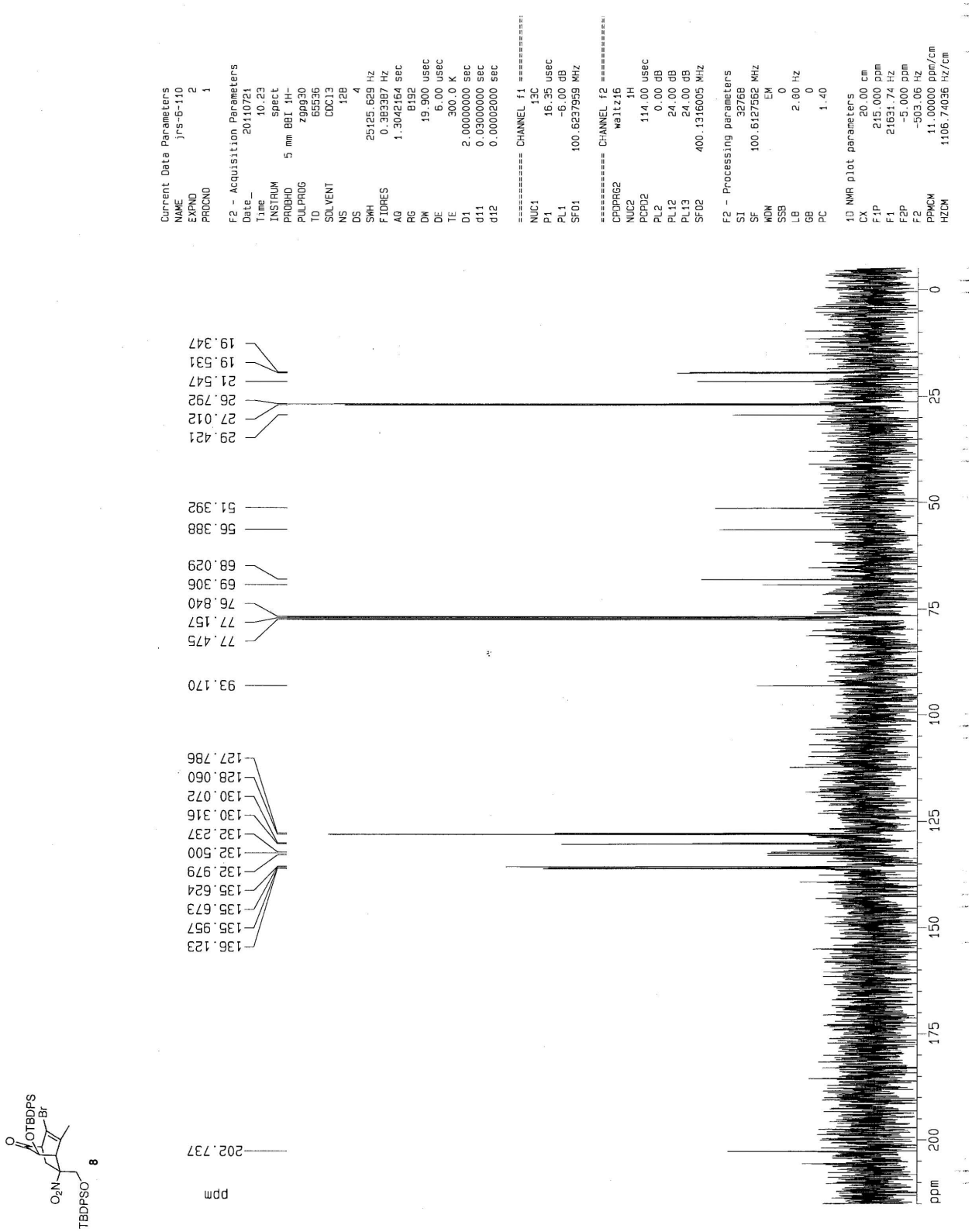
F2 - Processing parameters
SI                         32768
SF                  100.6127570 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                        1.40

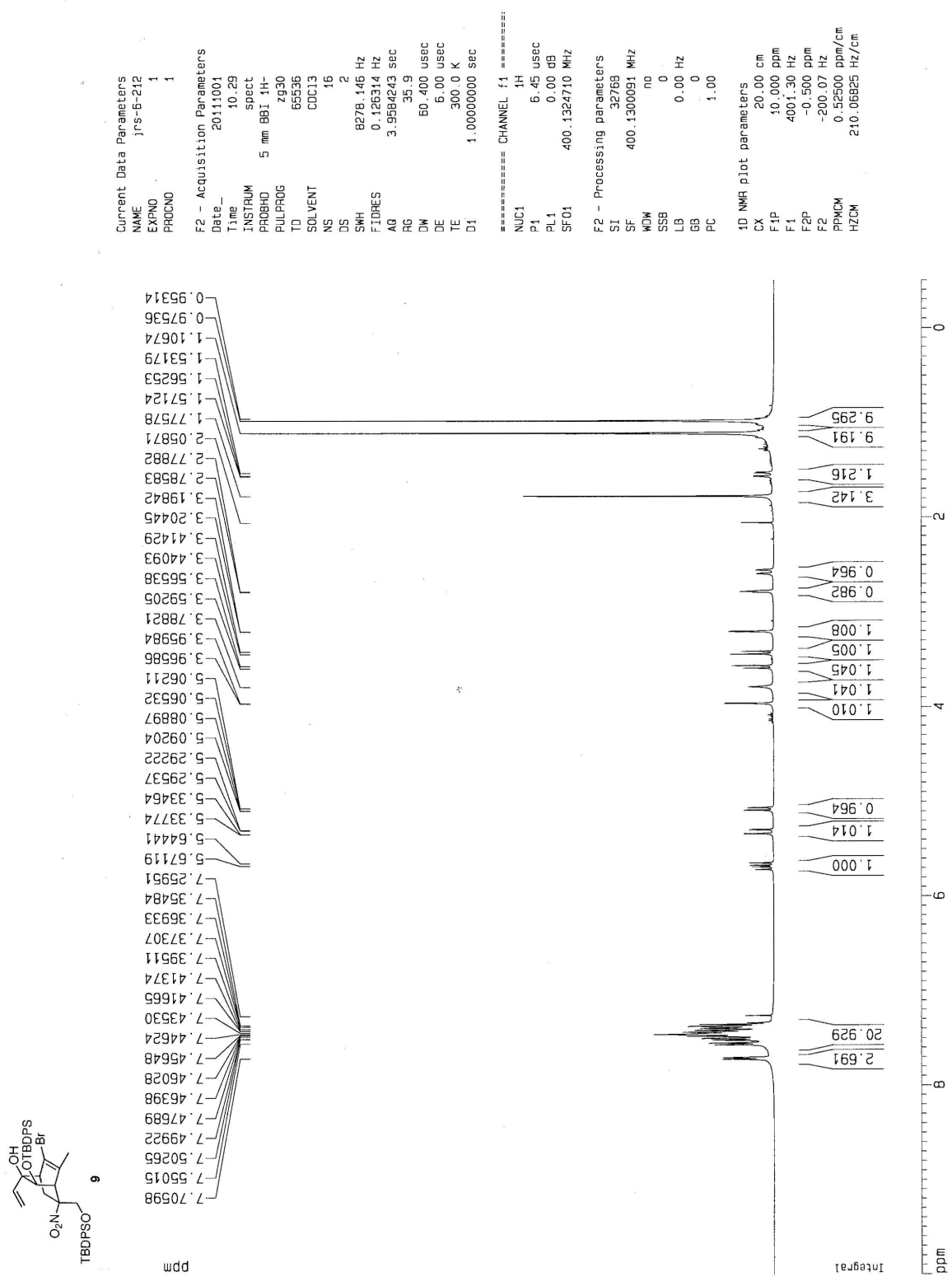
1D NMR plot parameters
CX                       20.00 cm
F1P                     234.580 ppm
F1                    23601.75 Hz
F2P                     -15.146 ppm
F2                    -1523.88 Hz
PPMCM                  12.48630 ppm/cm
HZCM                1256.28137 Hz/cm
```

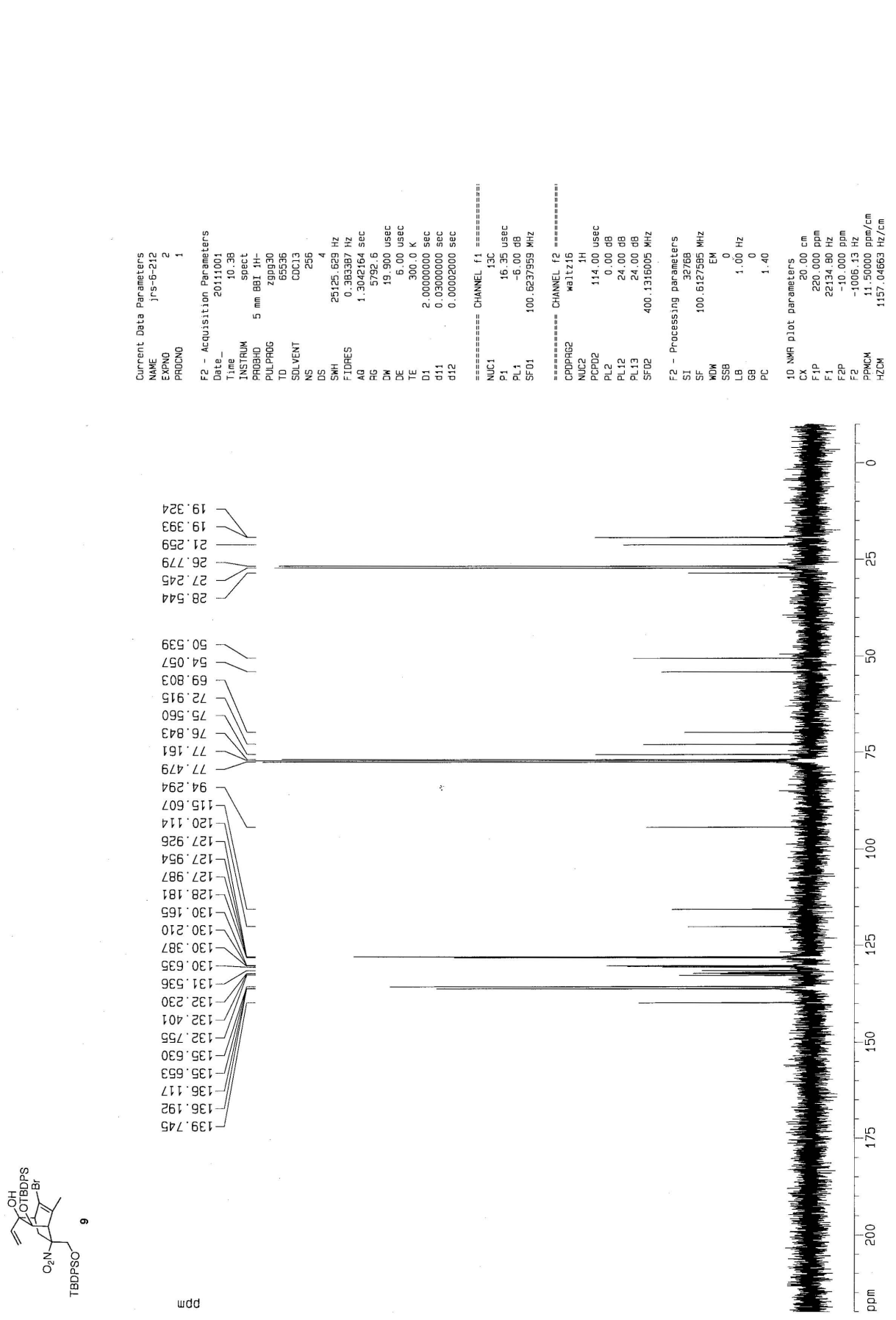

Current Data Parameters
NAME jrs-6-100
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110715
Time 8.09
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 1024
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.10 usec
PL1 0.00 dB
SFO1 299.8718518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700103 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 2998.70 Hz
F2P -0.500 ppm
F2 -149.93 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.43175 Hz/cm
7.26023
3.84925
3.83161
3.82342
3.74126
3.51281
3.48949
3.46609
3.44265
3.43153
3.35173
2.94497
2.93872
2.89344
2.88713
2.79003
2.78243
2.42057
2.40031
2.11456
2.10317
2.06258
2.04250
1.96632
1.60383
1.22918
1.20579
1.18241
0.93165
5.1977
0.9163
2.7787
1.0743
0.7969
0.8504
1.0000
1.2244
0.9585
1.3629
0.8232
ppm
Integral
Br
OH
O
O_2N
HO
7

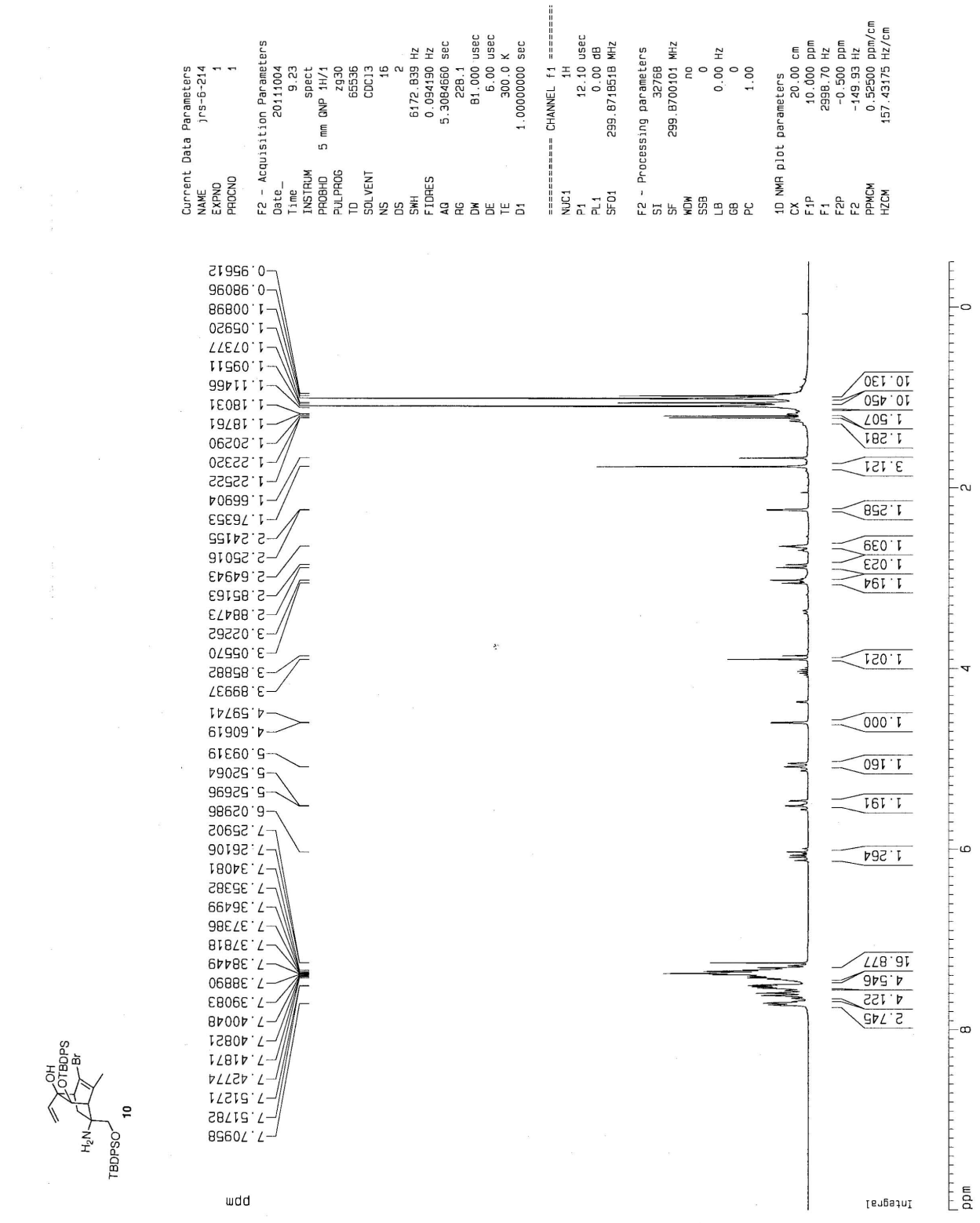

Current Data Parameters
NAME jrs-6-100
EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110715
Time 9.02
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT Aceton
NS 128
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 512
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 5.25 usec
PL1 -5.00 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 75.4023138 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 16588.51 Hz
F2P -10.000 ppm
F2 -754.02 Hz
PPMCM 11.50000 ppm/cm
HZCM 867.12659 Hz/cm
206.508
204.880
140.820
112.450
94.990
69.112
67.614
57.355
52.177
30.611
30.355
30.098
29.840
29.713
29.584
29.327
29.070
21.560
ppm
200
175
150
125
100
75
50
25
0
O
OH
Br
O2N
HO
7

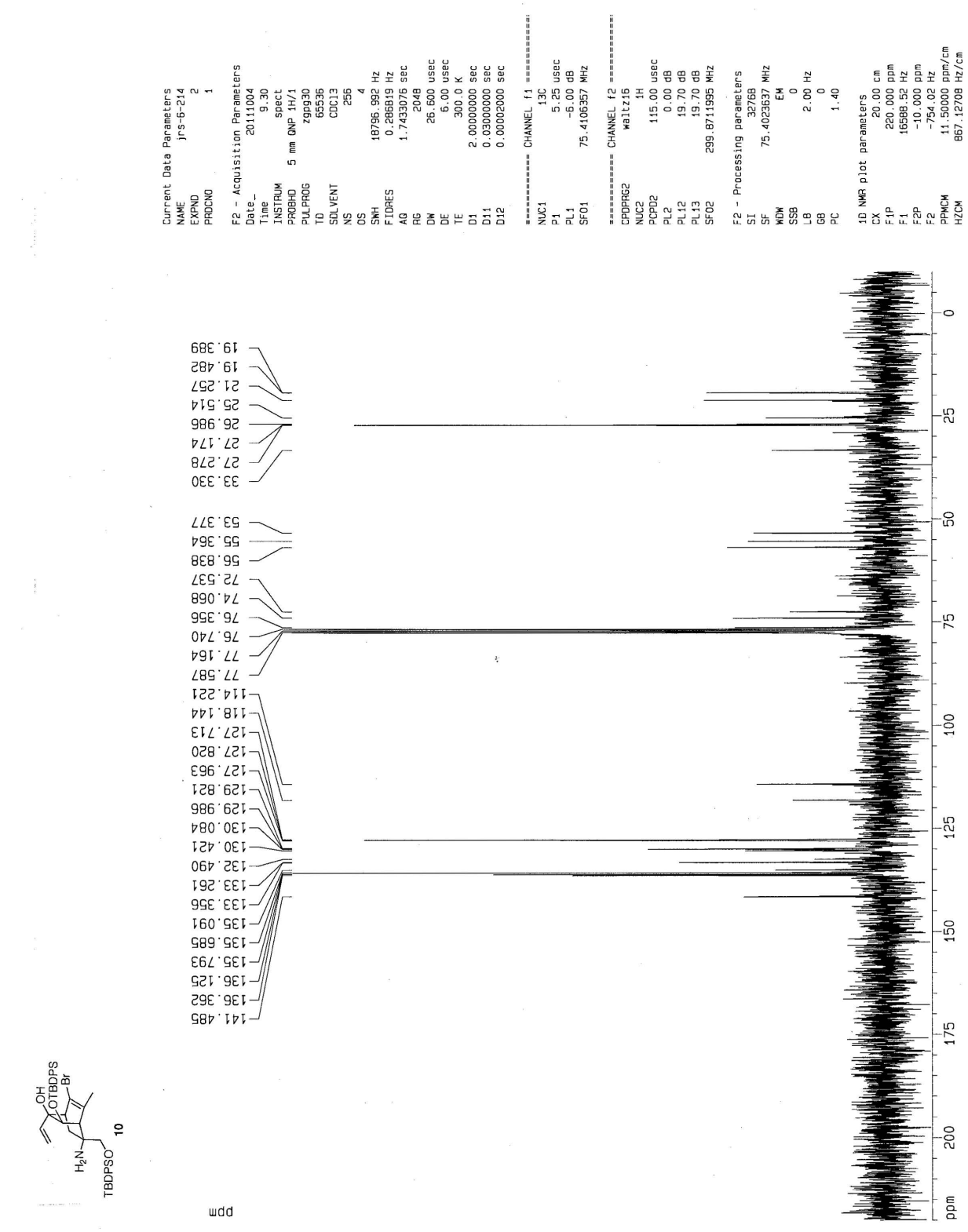

Current Data Parameters
NAME jrs-6-110
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110721
Time 10.19
INSTRUM spect
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 101.6
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300086 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 210.06825 Hz/cm
1.00303
1.05079
1.05671
1.07416
1.26612
1.55410
1.85592
1.91583
1.92444
1.95483
1.96343
2.05224
2.58910
2.59365
2.62797
2.63263
3.22692
3.23241
3.23427
3.24032
3.53543
3.54148
3.58365
3.61077
3.73615
3.76328
3.83748
3.84352
7.37735
7.38766
7.39162
7.39580
7.40738
7.42376
7.42751
7.43107
7.44200
7.46712
7.47042
7.52693
7.53030
7.67221
7.69254
7.69606
ppm
9.402
9.443
3.033
0.972
0.989
1.017
1.047
1.001
1.023
1.000
14.894
2.068
4.309
Integral
ppm
0
2
4
6
8
O
OTBDPS
Br
O2N
TBDPSO
8

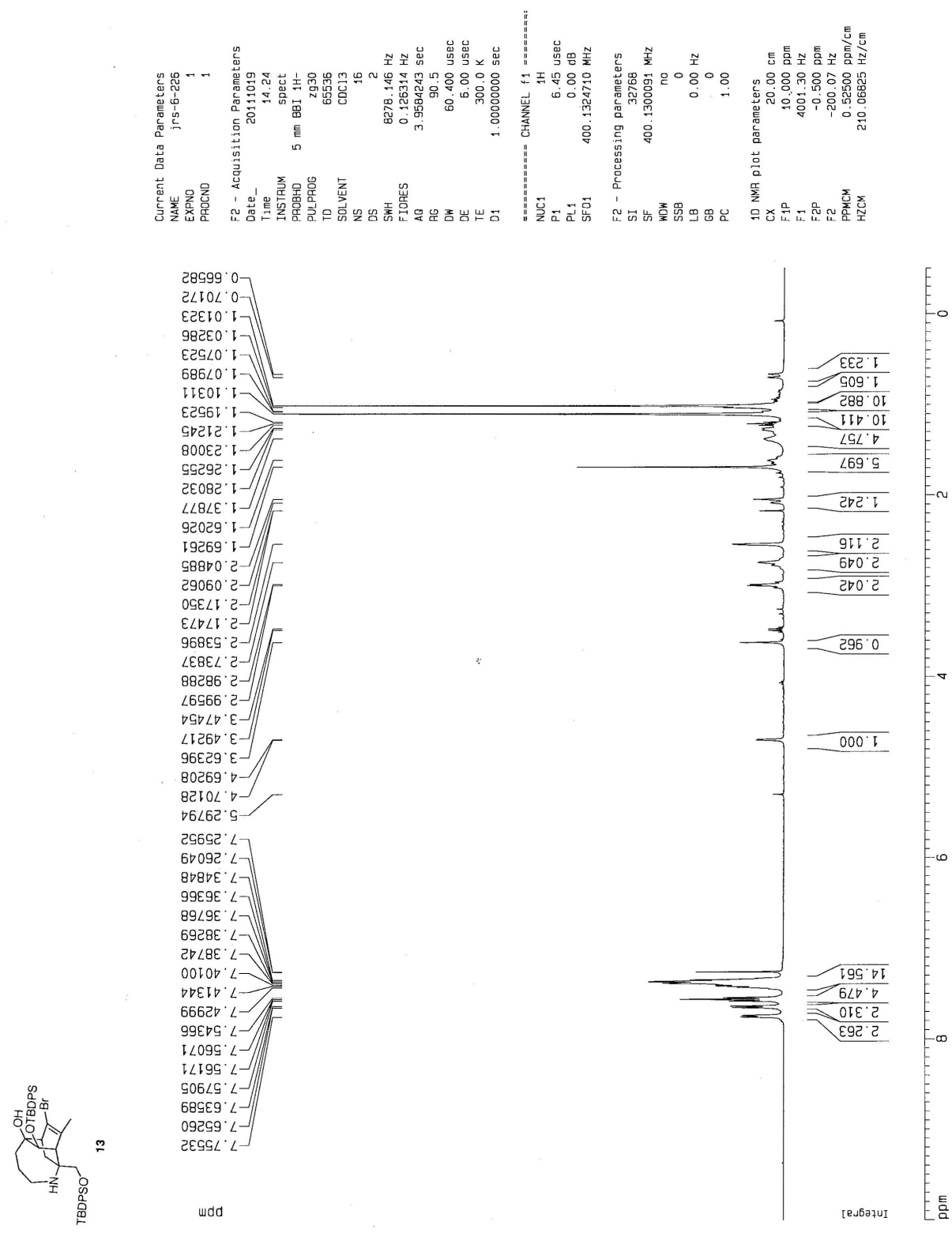

Current Data Parameters
NAME jrs-6-110
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20110721
Time 10.23
INSTRUM spect
PROBHD 5 mm BBI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 128
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 8192
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 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 100.6127562 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 215.000 ppm
F1 21631.74 Hz
F2P -5.000 ppm
F2 -503.06 Hz
PPMCM 11.00000 ppm/cm
HZCM 1106.74036 Hz/cm
202.737
136.123
135.957
135.673
135.624
132.979
132.500
132.237
130.316
130.072
128.060
127.786
93.170
77.475
77.157
76.840
69.306
68.029
56.388
51.392
29.421
27.012
26.792
21.547
19.531
19.347
ppm
ppm
0
25
50
75
100
125
150
175
200
OTBDPS
Br
O
O2N
TBDPSO
8

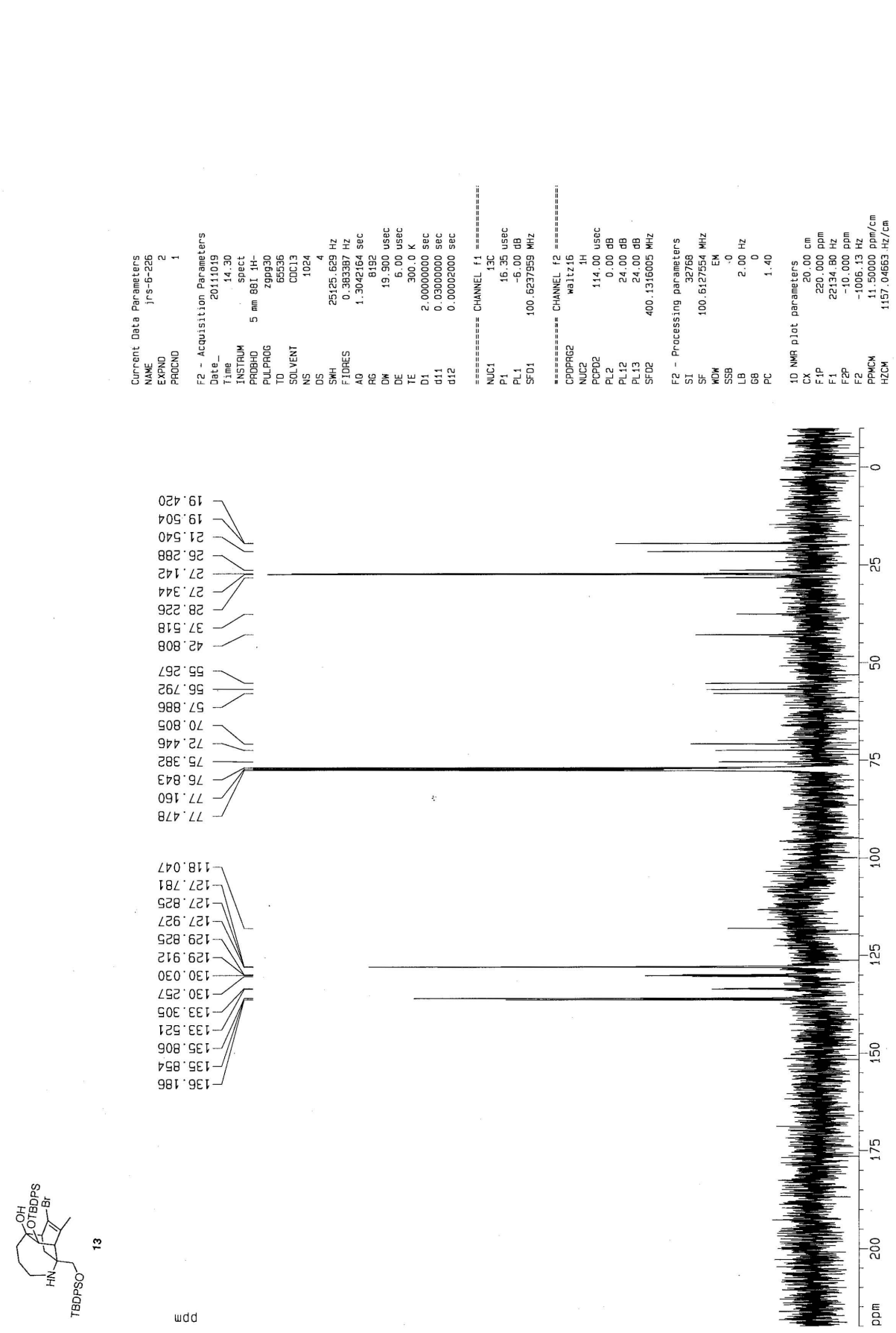

Current Data Parameters
NAME jrs-6-212
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111001
Time 10.29
INSTRUM spect
PROBHD 5 mm BBI 1H-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 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 no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 210.06825 Hz/cm
OH
OTBDPS
Br
O2N
TBDPSO
9
ppm
Integral
9.295
9.191
1.216
3.142
0.964
0.982
1.008
1.005
1.045
1.041
1.010
0.964
1.014
1.000
2.691
20.929

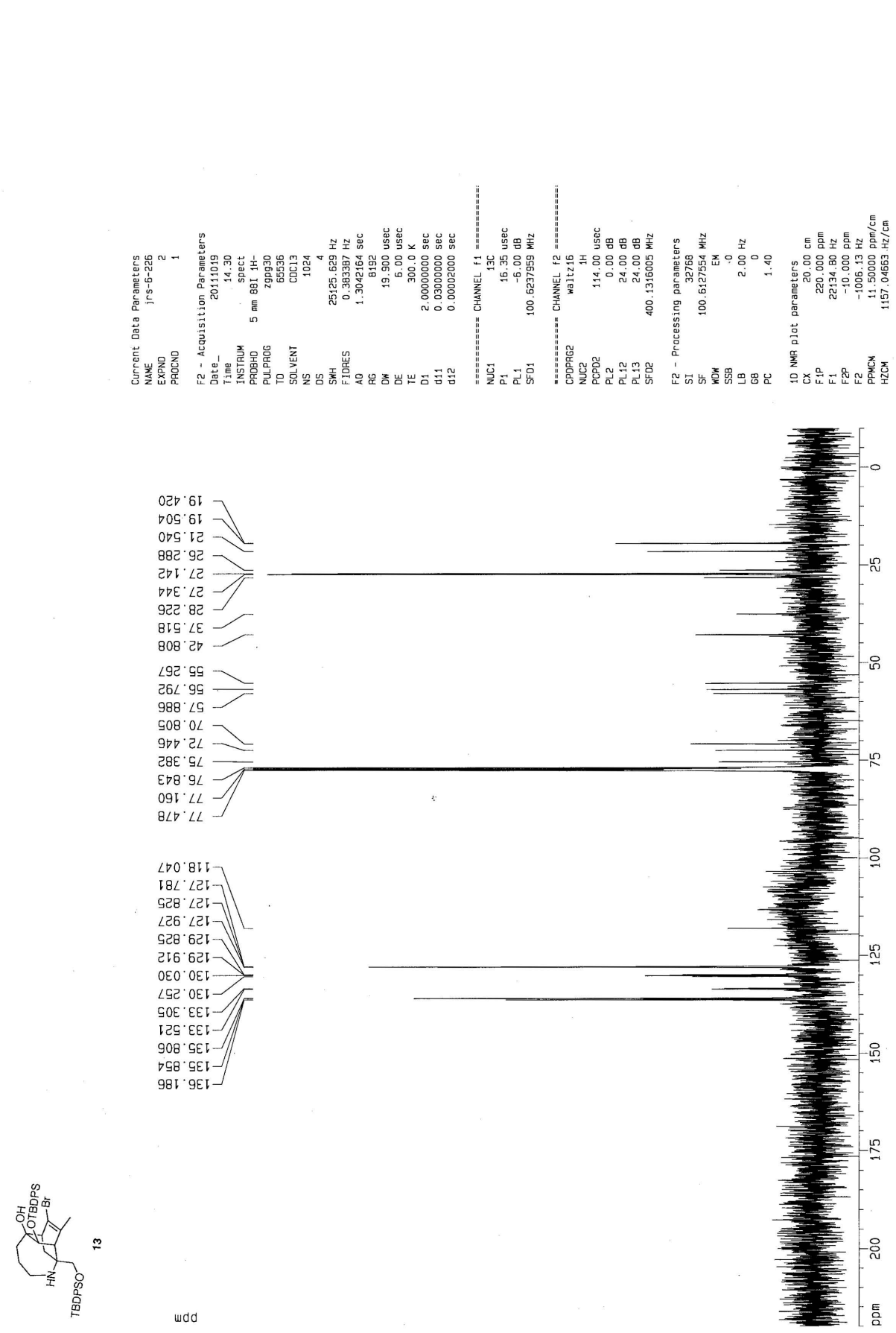

Current Data Parameters
NAME jrs-6-212
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111001
Time 10.38
INSTRUM spect
PROBHD 5 mm BBI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 5792.6
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 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 100.6127685 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 11.50000 ppm/cm
HZCM 1157.04663 Hz/cm
19.324
19.393
21.259
26.779
27.245
28.544
50.539
54.057
69.803
72.915
75.560
76.843
77.161
77.479
94.294
115.607
120.114
127.926
127.954
127.987
128.181
130.165
130.210
130.387
130.635
131.536
132.230
132.401
132.755
135.630
135.653
136.117
136.192
139.745
ppm
OH
OTBDPS
Br
O2N
TBDPSO
9


Current Data Parameters
NAME jrs-6-214
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111004
Time 9.23
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 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 12.10 usec
PL1 0.00 dB
SFO1 299.8718518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700101 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 2998.70 Hz
F2P -0.500 ppm
F2 -149.93 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.43175 Hz/cm
OH
OTBDPS
Br
H2N
TBDPSO
10
ppm
Integral


Current Data Parameters
NAME jrs-6-214
EXPND 2
PRDCNO 1
F2 - Acquisition Parameters
Date_ 20111004
Time 9.30
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
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
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 75.4023637 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 16588.52 Hz
F2P -10.000 ppm
F2 -754.02 Hz
PPMCM 11.50000 ppm/cm
HZCM 867.12708 Hz/cm
19.389
19.482
21.257
25.514
26.986
27.174
27.278
33.330
53.377
55.364
56.838
72.537
74.068
76.356
76.740
77.164
77.587
114.221
118.144
127.713
127.820
127.963
129.821
129.986
130.084
130.421
132.490
133.261
133.356
135.091
135.685
135.793
136.125
136.362
141.485
ppm
OH
OTBDPS
Br
H2N
TBDPSO
10


Current Data Parameters
NAME jrs-6-226
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111019
Time 14.24
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 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 400.1300091 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.52500 ppm/cm
HZCM 210.06825 Hz/cm
7.75532
7.65260
7.63589
7.57905
7.56171
7.56071
7.54366
7.42999
7.41344
7.40100
7.38742
7.38269
7.36768
7.36366
7.34848
7.26049
7.25952
5.29794
4.70128
4.69208
3.62396
3.49217
3.47454
2.99597
2.98288
2.73837
2.53896
2.17473
2.17350
2.09062
2.04885
1.69261
1.62026
1.37877
1.28032
1.26255
1.23008
1.21245
1.19523
1.10311
1.07989
1.07523
1.03286
1.01323
0.70172
0.65582
2.263
2.310
4.479
14.561
1.000
0.962
1.242
2.042
2.049
2.116
5.697
4.757
10.411
10.882
1.605
1.233
ppm
Integral
ppm
OH
OTBDPS
Br
HN
TBDPSO
13


Current Data Parameters
NAME jrs-6-226
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111019
Time 14.30
INSTRUM spect
PROBHD 5 mm BBI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 8192
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 100.6127554 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 11.50000 ppm/cm
HZCM 1157.04663 Hz/cm
19.420
19.504
21.540
26.288
27.142
27.344
28.226
37.518
42.808
55.267
56.792
57.886
70.805
72.446
75.382
76.843
77.160
77.478
118.047
127.781
127.825
127.927
129.825
129.912
130.030
130.257
133.305
133.521
135.806
135.854
136.186
ppm
0
25
50
75
100
125
150
175
200
ppm
OH
OTBDPS
Br
HN
TBDPSO
13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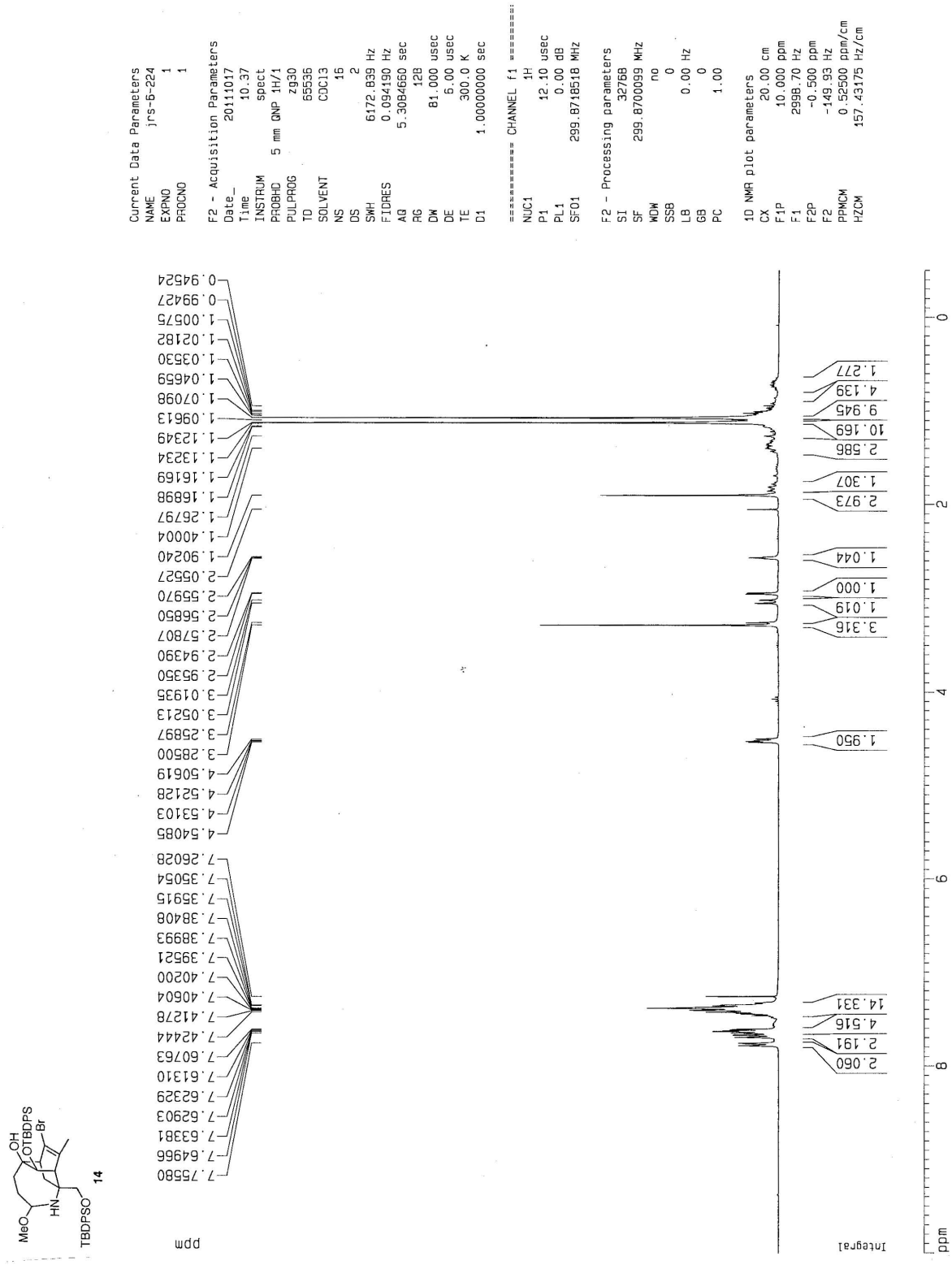
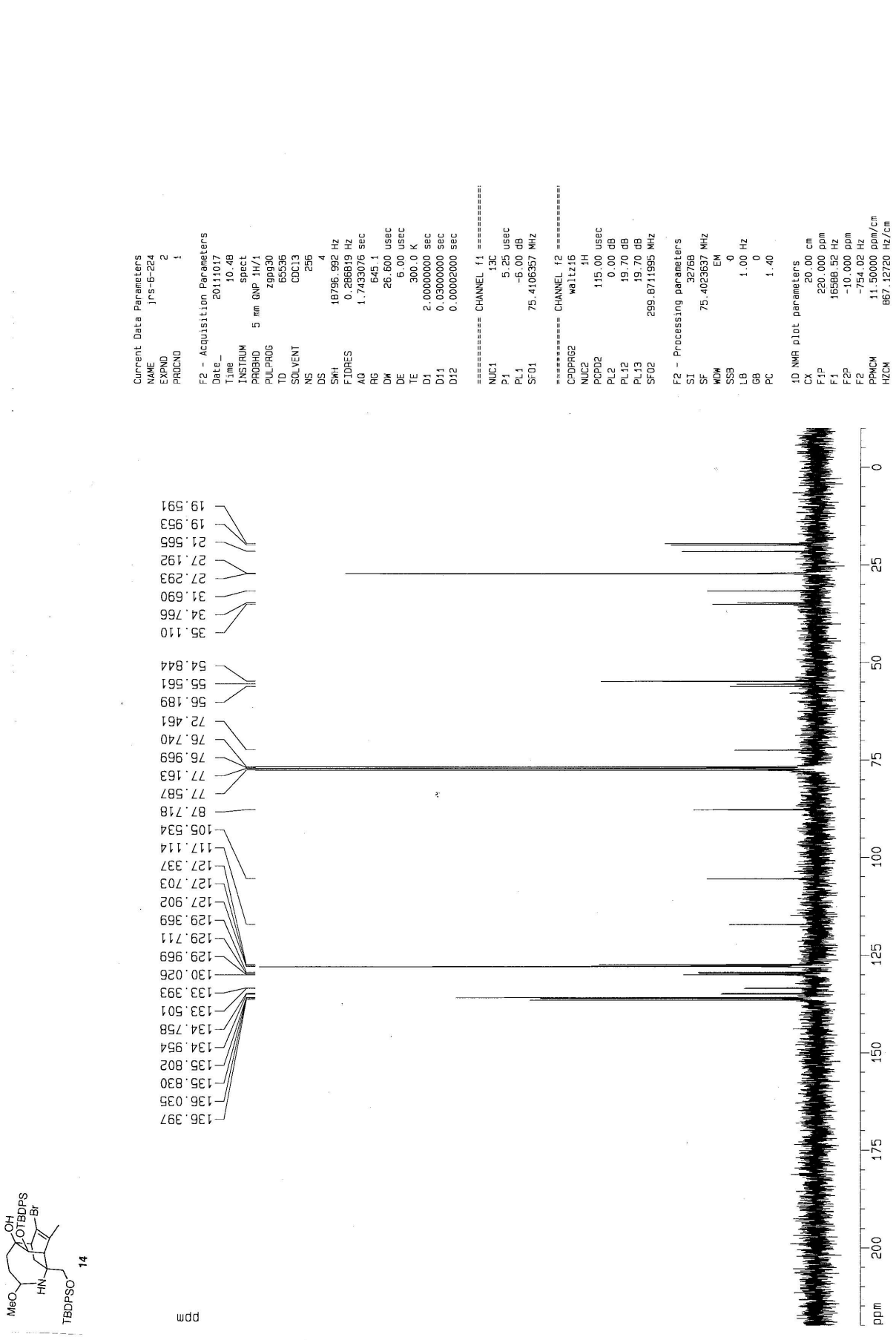
NAME jrs-6-226
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111019
Time 14.30
INSTRUM spect
PROBHD 5 mm BBI 1H-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 8192
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 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 100.6127554 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 22134.80 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PPMCM 11.50000 ppm/cm
HZCM 1157.04663 Hz/cm
OH
OTBDPS
Br
HN
TBDPSO
13
ppm
19.420
19.504
21.540
26.288
27.142
27.344
28.226
37.518
42.808
55.267
56.792
57.886
70.805
72.446
75.382
76.843
77.160
77.478
118.047
127.781
127.825
127.927
129.825
129.912
130.030
130.257
133.305
133.521
135.806
135.854
136.186
ppm


Current Data Parameters
NAME jrs-6-224
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111017
Time 10.37
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 128
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 12.10 usec
PL1 0.00 dB
SFO1 299.8718518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700099 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 2998.70 Hz
F2P -0.500 ppm
F2 -149.93 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.43175 Hz/cm
7.7580
7.6496
7.6381
7.6290
7.6232
7.6131
7.6076
7.4244
7.4127
7.4060
7.4020
7.3952
7.3899
7.3840
7.3591
7.3505
7.2602
4.5408
4.5310
4.5212
4.5061
4.2850
3.2589
3.2580
3.0521
3.0193
2.9535
2.9439
2.5780
2.5685
2.5597
2.5552
1.9024
1.4000
1.2679
1.1689
1.1616
1.1323
1.1234
1.0961
1.0709
1.0465
1.0353
1.0218
1.0057
0.9942
0.9452
ppm
1.950
3.316
1.019
1.000
1.044
2.973
1.307
2.586
10.169
9.945
4.139
1.277
2.060
2.191
4.516
14.331
Integral
ppm
0
2
4
6
8
OH
OTBDPS
Br
MeO
HN
TBDPSO
14


Current Data Parameters
NAME jrs-6-224
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20111017
Time 10.48
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 256
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 645.1
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
NUC1 13C
P1 5.25 usec
PL1 -6.00 dB
SFO1 75.4106357 MHz
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 75.4023637 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 16588.52 Hz
F2P -10.000 ppm
F2 -754.02 Hz
PPMCM 11.50000 ppm/cm
HZCM 867.12720 Hz/cm
19.591
19.953
21.565
27.192
27.293
31.690
34.766
35.110
54.844
55.561
56.189
72.461
76.740
76.969
77.163
77.587
87.718
105.534
117.114
127.337
127.703
127.902
129.369
129.711
129.969
130.026
133.393
133.501
134.758
134.954
135.802
135.830
136.035
136.397
ppm
0
25
50
75
100
125
150
175
200
ppm
OH
OTBDPS
Br
MeO
HN
TBDPSO
14