Supporting Information

Ring Expansion of Functionalized Octahydroindoles to Enantiopure *cis*-Decahydroquinolines

Marisa Mena and Josep Bonjoch,*

Laboratori de Química Orgànica, Facultat de Farmàcia, Universitat de Barcelona , Av. Joan XXIII s/n, 08028-Barcelona, Spain

Domingo Gomez Pardo and Janine Cossy

Laboratoire de Chimie Organique, associé au CNRS, ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

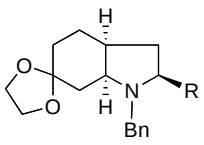
josep.bonjoch@ub.edu

Contents

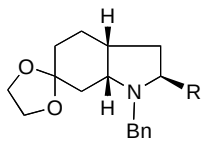
Table 1. ^{13}C NMR Chemical shifts of octahydroindoles 3-12[a]

	3	4	5	6	7	8	9a	10a	11a
C2	66.2	62.9	66.2	61.7	74.9	70.8	71.0	72.5	66.1
C3	33.6	31.7	32.1	30.5	33.3	30.6	30.6	32.2	25.4
C3a	35.7	35.2	35.0	35.6	35.6	35.6	34.6	34.8	35.6
C4	24.0	23.3	24.3	22.8	24.2	22.8	23.9	22.7	22.9
C5	31.0	29.9	31.0	28.9	31.0	29.2	27.5	29.3	28.9
C6	109.1	109.3	108.9	109.4	108.8	109.2	108.9	109.0	109.4
C7	37.5	31.9	37.8	30.6	38.2	30.9	38.2	38.8	30.4
C7a	62.5	59.5	63.0	59.3	63.0	59.4	62.9	63.3	58.9
NCH_2	58.8	53.4	58.8	51.7	60.0	53.4	58.9	63.2	51.4
***ips*-Ar**	139.1	139.0	139.2	139.3	139.2	138.5	140.0	140.0	139.4
***o*-Ar**	129.1	128.8	128.9	128.4	129.4	128.7	129.1	128.3	128.4
***m*-Ar**	127.9	128.1	128.3	128.3	128.1	128.2	128.4	128.3	128.2
***p*-Ar**	126.8	126.9	127.2	127.0	127.1	127.1	127.2	127.0	127.0
C-1'	175.0	174.2	61.2	62.4	213.2	216.4	63.5	71.9	64.7
Me	51.6	51.6	---	---	24.9	24.9	18.2	20.8	18.2
OCH_2	64.3	64.3	64.1	64.3	64.0	64.3	64.0	64.1	64.1
	64.0	64.0	63.9	63.9	64.0	63.9	64.0	63.9	63.8

[a] Values for compounds **3**, **5**, **9a, 10a** and **11a** were assigned on the basis of gHSQC spectra.



3 R = CO_2Me
5 R = CH_2OH
7 R = $COCH_3$
9a R = (*R*)-$CHOHCH_3$
10a R = (*S*)-$CHOHCH_3$

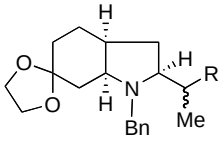


4 R = CO_2Me
6 R = CH_2OH
8 R = $COCH_3$
11a R = (*S*)-$CHOHCH_3$

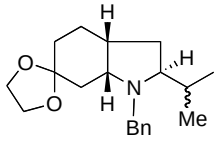
Table 1 (continued). ^{13}**C NMR Chemical shifts of octahydroindoles 3-12**[b]

	12a	**9b**	**10b**	**11b**	**12b**	**9c**[c]	**10c**[c]	**11c**[c]	**12c**[c]
C2	66.5	72.1	71.6	66.7	66.4	69.1	68.8	64.4	62.9
C3	30.3	29.7	30.4	28.2	27.1	30.1	31.0	27.7	27.4
C3a	35.3	34.5	34.5	34.6	35.0	34.4	34.6	34.8	35.2
C4	22.7	23.0	23.3	22.8	22.8	23.3	23.2	22.9	22.8
C5	29.0	29.5	29.9	29.7	29.0	29.8	29.7	29.1	29.0
C6	109.4	109.2	109.1	109.5	109.4	109.2	109.1	109.5	109.5
C7	31.2	39.2	39.1	31.0	30.9	39.1	39.3	30.2	30.6
C7a	58.8	62.5	63.7	58.9	58.3	62.2	63.8	58.2	58.4
NCH_2	53.9	61.4	61.3	52.2	52.7	60.4	61.8	52.0	52.5
***ips*-Ar**	139.5	140.6	140.7	139.9	139.8	139.2	141.2	139.8	140.0
***o*-Ar**	128.2	128.3	128.6	128.2	128.2	129.4	128.2	128.1	128.1
***m*-Ar**	127.8	128.1	128.2	128.2	128.1	128.1	128.0	128.0	128.0
***p*-Ar**	126.7	126.6	126.8	126.7	126.8	127.1	126.5	126.6	126.6
C-1'	71.1	63.4	60.6	60.9	59.8	71.1	75.2	70.7	72.3
Me	20.6	22.9	19.8	22.3	17.7	17.1	16.5	16.7	14.5
OCH_2	64.2	64.1	64.0	64.2	64.3	63.9	64.0	64.1	64.2
	63.8	63.8	63.9	63.9	63.9	63.8	63.8	63.8	63.9

[b] Values for compounds **12a**, **10b**, **11b**, **9c, 11c,** and **12c** were assigned on the basis of gHSQC spectra. [c] OAc: 170.6 / 170.7 and 21.3 /21.5.



9b R = Cl (1'*R*)
10b R = Cl (1'*S*)
9c R = OAc (1'*R*)
10c R = OAc (1'*S*)

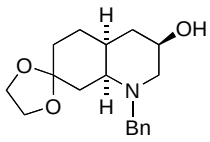


12a R = OH (1'*R*)
11b R = Cl (1'*S*)
12b R = Cl (1'*R*)
11c R = OAc (1'*S*)
12c R = OAc (1'*R*)

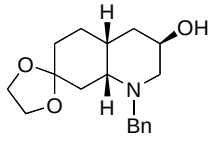
Table 2. ^{13}C NMR Chemical shifts of decahydroquinolines 13-21[a]

	13	14	15	16[b]	17	18	19[c]	21
C2	52.0	50.6	57.1	56.0	53.0	51.9	53.2	55.7
C3	68.1	65.4	69.7	61.4	75.5	73.2	73.1	73.6
C4	33.1	30.5	26.8	33.1	29.6	27.0	24.2	33.3
C4a	32.8	28.8	28.3	35.5	31.4	33.6	28.4	32.0
C5	26.9	26.6	26.4	26.7	26.6	25.0	26.8	26.9
C6	29.9	29.8	30.2	32.4	29.7	30.2	30.0	29.9
C7	109.9	109.8	109.3	109.6	109.8	109.4	109.3	109.9
C8	27.0	25.6	33.5	28.9	28.1	34.1	34.7	27.6
C8a	57.0	57.7	56.6	56.2	55.8	56.1	56.9	56.5
Me	---	---	14.9	18.4	16.8	11.5	15.7	16.9
NCH_2	58.3	58.5	55.3	52.7	52.6	55.7	55.9	52.8
Ar	126.8	127.2	127.1	126.5	126.5	126.9	140.2	126.5
	128.1	128.4	128.3	127.6	127.7	128.2	128.3	127.9
	129.5	128.7	128.5	128.1	128.2	128.2	127.9	128.1
	139.3	139.0	n.o.	141.1	141.2	139.8	126.6	140.6
OCH_2	64.2	64.3	63.9	64.0	64.1	64.2	64.2	64.1
	64.1	64.1	64.2	63.7	64.0	63.9	63.9	64.0
Other					170.6	170.4	170.7	
					21.3	21.3	21.4	

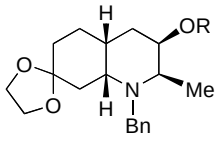
[a] Values for compounds **13**, **17**, **18**, **19** and **21** were assigned on the basis of gHSQC spectra [b] Values taken from an NMR spectrum of a mixture of **9b** and **16**. [c] Values taken from an NMR spectrum of a mixture of **11c** and **19**.



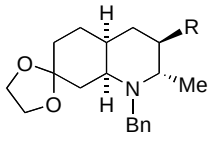
13



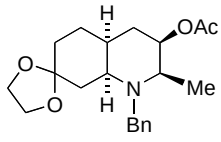
14



15 R = H
19 R = Ac



16 R = Cl
17 R = OAc
21 R = OH



18

Experimental Section

General: All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions. Analytical thin-layer chromatography was performed on SiO_2 (silica gel 60 F_{254}) or Al_2O_3 (ALOX N/UV_{254}), and the products were located with iodoplatinate spray. Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, 230-240 mesh ASTM) or Al_2O_3 (aluminium oxide 90). Drying of organic extracts was performed over anhydrous Na_2SO_4. Evaporation of solvent was accomplished with a rotatory evaporator. Chemical shifts of ^1H and ^{13}C NMR spectra are reported in ppm downfield (δ) from Me_4Si. Only noteworthy IR absorptions (cm^{-1}) are listed.

Methyl (2*S*,3a*S*,7a*S*)-1-Benzyl-6-oxooctahydroindole-2-carboxylate ethylene acetal (3). To a solution of ketone **1** (3.28 g, 11 mmol) in toluene (350 mL) were added a catalytic amount of TsOH and ethyleneglycol (1.84 mL, 33 mmol), and the reaction mixture was heated at reflux temperature for 4 h in a flask incorporating a Dean-Stark apparatus. The cooled solution was diluted with CH_2Cl_2 and washed with aqueous saturated $NaHCO_3$ (100 mL). The organic phase was dried and concentrated to give 3.64 g of **3** as a yellowish oil, which was used in the next step without further purification. An analytical sample was obtained by chromatography (SiO_2, 1% MeOH in CH_2Cl_2). R_f = 0.37 (SiO_2, hexane/EtOAc 3:2); $[\alpha]_D^{20}$ -41 (*c* = 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, gCOSY) 1.46-1.58 (m, 1H), 1.64-1.85 (m, 5H), 1.87-1.95 (m, 1H), 2.02-2.11 (m, 1H), 2.13 -2.26 (m, 1H), 2.99 (q, *J* = 7.5 Hz, 1H, H-7a), 3.41 (dd, *J* = 9.1, 7.7 Hz, 1H, H-2), 3.54 (s, 3H, OCH_3), 3.74-3.92 (m, 6H), 7.18-7.40 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT, gHSQC), see Table 1. Anal. Calcd for $C_{19}H_{25}NO_4$: C 68.86, H 7.60, N 4.22. Found: C 68.48, H 7.55, N 4.20.

Methyl (2*S*,3a*R*,7a*R*)-1-Benzyl-6-oxooctahydroindole-2-carboxylate ethylene acetal (4). Operating as above, from ketone **2** (1.03 g, 3.6 mmol), acetal **4** was obtained (1.12 g) as yellowish crystals and used in the next step without further purification. An analytical sample was obtained by chromatography (SiO_2, 1% MeOH in CH_2Cl_2): R_f = 0.24 (SiO_2, hexane/EtOAc 3:2); mp 64-66 °C; $[\alpha]_D^{20}$ -53 (*c* 0.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) 1.44-1.72 (m, 4H), 1.79-1.94 (m, 3H), 2.12

(dt, *J* = 12.9, 10.7 Hz, 1H), 2.46 -2.58 (m, 1H), 3.37 (dt, *J* = 10.5, 5.3 Hz, 1H, H-7a), 3.50 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2), 3.55 (s, 3H, OCH_3), 3.74 (d, *J* = 13.2 Hz, 1H), 3.81 (d, *J* = 13.2 Hz, 1H), 3.83 -3.96 (m, 4H), 7.18-7.40 (m, 5H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, DEPT), see Table 1. Anal. calcd for $C_{19}H_{25}NO_4$: C 68.86, H 7.60, N 4.22. Found: C 68.56, H 7.85, N 4.24.

(2*S*,3a*S*,7a*S*)-1-Benzyl-2-hydroxymethyl-6-oxooctahydroindole ethylene acetal (5). Ester **3** (603 mg, 1.82 mmol) was dissolved in THF (9 mL) and then cooled to 0 ºC. $LiBH_4$ (2 M in THF, 2.8 mL, 5.46 mmol, 3 equiv) was slowly added, and the reaction mixture was stirred at rt for 24 h. The reaction was quenched by adding H_2O (5 mL) and the organic layer was dried and concentrated to give a residue, which was purified by chromatography (SiO_2, 1% MeOH in CH_2Cl_2) to afford 441 mg (80% from **1**) of **5** as a colourless oil: R_f = 0.31 (SiO_2, CH_2Cl_2/MeOH 95:5); $[\alpha]_D^{20}$ -15 (*c* 0.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, gCOSY) 1.49 (dddd, *J* = 12.0, 5.0, 5.0, 1.2 Hz, 1H, H-5eq), 1.65 (m, 3H, H-5 and H-7), 1.75 (m, 3H, H-3 and H-4), 1.85 (dd, *J* = 12.4, 7.2 Hz, 1H, H-3), 2.20 (m, 1H, H-3a), 2.40 (brs, 1H, OH), 2.98 (dddd, *J* = 8.0, 7.5, 5.4, 1.8 Hz, 1H, H-2), 3.02 (q, *J* = 7.2 Hz, 1H, H-7a), 3.33 (dd, *J* = 11.0, 1.2 Hz, 1H, CH_2OH), 3.42 (dd, *J* = 11.0, 3.6 Hz, 1H, CH_2OH), 3.69-3.88 (m, 6H, OCH_2 and NCH_2), 7.26-7.32 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, gHSQC), see Table 1. HRFABMS calcd for $C_{18}H_{26}NO_3$ 304.1906 (MH^+), found 304.1913.

(2*S*,3a*R*,7a*R*)-1-Benzyl-2-hydroxymethyl-6-oxooctahydroindole ethylene acetal (6). Operating as above from ester **4** (627 mg, 1.89 mmol), alcohol **6** (464 mg, 81% from **2**) was obtained after chromatography (SiO_2, 1% MeOH in CH_2Cl_2), as white crystals: R_f = 0.40 (SiO_2, CH_2Cl_2/MeOH 95:5); mp 72-74 °C; $[\alpha]_D^{20}$ -72 (*c* 0.25, $CHCl_3$); ^1H NMR (400 MHz, COSY, $CDCl_3$) 1.46 (t, *J* = 12.0 Hz, 1H, H-7ax), 1.52 (dq, *J* = 12.5, 2.5 Hz, 1H, H-4eq), 1.63 (dm, *J* = 12.0 Hz, 1H, H-5eq), 1.64 (td, *J* = 10.0, 3.2 Hz, 1H, H-5ax), 1.78 (m, 1H, H-4ax), 1.80 (m, 1H, H-3β), 1.83 (dd, *J* = 12.0, 5.5 Hz, 1H, H-7eq), 2.05 (q, *J* = 12.0 Hz, 1H, H-3α), 2.30 (m, 1H, H-3a), 2.99 (dt, *J* = 10.0, 3.2 Hz, 1H, H-2), 3.24 (ddd, *J* = 12.0, 5.5, 5.5 Hz, 1H, H-7a), 3.38 (dm *J* = 10.8 Hz, 1H, CH_2OH), 3.55 (dd, *J* = 10.8, 3.2 Hz, 1H, CH_2OH), 3.64 and 3.71 (2d, *J* = 13.6 Hz, 1H each,

NCH_2), 3.77-3.93 (m, 4H, OCH_2), 7.26-7.32 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT), see Table 1. Anal. Calcd for $C_{18}H_{25}NO_3$: C 71.26, H 8.31, N 4.62. Found: C 71.05, H 8.20, N 4.57.

(2*S*,3a*S*,7a*S*)-2-Acetyl-1-benzyloctahydroindol-6-one ethylene acetal (7). To a solution of ester **3** (2.45 g, 7.4 mmol) in THF (140 mL) cooled to -20 ºC was added Me(MeO)NH.HCl (1.82 g, 18.5 mmol, 2.5 eq) and then over 30 min was added a solution of *i*-PrMgCl in THF (18.5 mL, 2.0 M, 5 equiv) maintaining the temperature at -10 °C. The mixture was stirred for 40 min and quenched with saturated aqueous NH_4Cl solution (50 mL). The organic layer was dried and concentrated to afford 2.65 g of the corresponding Weinreb amide as a yellow oil, which was used without purification: R_f = 0.21 (SiO_2, CH_2Cl_2/MeOH 96:4). To a solution of the aforementioned Weinreb amide (2.65 g, 7.4 mmol) in THF (95 mL) cooled to 0 ºC was added dropwise MeMgBr in Et_2O (6.4 mL, 3 M, 19.24 mmol, 2.6 eq). The reaction mixture was stirred at 0 ºC for 1 h and quenched with saturated aqueous NH_4Cl solution (50 mL). The organic layer was dried and concentrated to give ketone **7** (2.32 g) as an oil, which was used without further purification. R_f = 0.52 (SiO_2, CH_2Cl_2/MeOH 95:5); ^1H NMR (300 MHz, $CDCl_3$) 1.53 (m, 1H), 1.61-1.85 (m, 6H), 2.02 (dt, J = 12.3, 7.2 Hz, 1H), 2.04 (s, 3H, CH_3), 2.25 (m, 1H, H-3a), 3.02 (q, J = 6.9 Hz, 1H, H-7a), 3.29 (dd, J = 9.3, 7.8 Hz, 1H, H-2), 3.63 and 3.83 (2d, J = 13.5 Hz, 1H each, NCH_2Ar), 3.75-3.95 (m, 4H, OCH_2), 7.20- 7.35 (m, 5H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$, DEPT), see Table 1.

(2*S*,3a*R*,7a*R*)-2-Acetyl-1-benzyloctahydroindol-6-one ethylene acetal (8). The above procedure was applied to ester **4** (1.12 g) to afford the corresponding Weinreb amide (1.30 g): R_f = 0.16 (SiO_2, CH_2Cl_2/MeOH 95:5). The Weinreb amide was treated with MeMgBr in Et_2O (3.12 mL, 3 M, 9.36 mmol, 2.6 eq) and operating as in the formation of ketone **7**, 1.21 g of ketone **8** was isolated, which was used without further purification. R_f = 0.49 (SiO_2, CH_2Cl_2/MeOH 95:5); ^1H NMR (300 MHz, $CDCl_3$) 1.40 (t, J = 12.0 Hz, 1H, H-5ax), 1.50-1.70 (m, 3H), 1.75-1.90 (m, 3H), 2.07 (s, 3H, CH_3), 2.16 (dt, J = 13.5, 11.4 Hz, 1H), 2.50 (m, 1H, H-3a), 3.36 (ddd, J = 11.4, 5.7, 5.7 Hz, 1H, H-7a), 3.35 (dd, J = 11.0, 1.5 Hz, 1H, H-2), 3.57 and 3.71 (2d, J = 13.2 Hz, 1H each, CH_2Ar), 3.75-3.94 (m, 4H, OCH_2), 7.20- 7.35 (m, 5H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$, DEPT), see Table 1.

Reduction of ketone 7. To a solution of amino ketone **7** (2.29 g, 7.25 mmol) in MeOH (85 mL) at -20 °C was added $NaBH_4$ (571 mg, 14.5 mmol) in small portions. The resulting mixture was maintained at this temperature for 6 h. Then, water (25 mL) was added and the mixture was extracted with Et_2O (3x50 mL). The organic extracts were washed with brine, dried, and concentrated. Purification of the residue by chromatography (SiO_2, hexane to hexane/EtOAc 1:1) provided 1.05 g (46%) of alcohol **9a** as a colourless oil and 862 mg (37%) of alcohol **10a** as a colorless oil, after two succesive purifications. Overall yield for three steps (**3** → **9a** + **10a**): 83%; 1.2:1 ratio of alcohols **9a**:**10a**.

(2*S*,3a*S*,7a*S*)-1-Benzyl-2-[(1'*R*)-(1-hydroxyethyl)]octahydroindol-6-one ethylene acetal (9a): R_f = 0.30 (SiO_2, CH_2Cl_2/MeOH 95:5); $[\alpha]_D^{20}$ - 41 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, *g*COSY) 1.09 (d, *J* = 6.6 Hz, 3H, CH_3), 1.43-1.81 (m, 8H, H-3, H-4, H-5, and H-7), 2.20 (m, 1H, H-3a), 2.80 (ddd, *J* = 9.3, 6.9, 3.3 Hz, 1H, H-2), 3.02 (q, *J* = 7.2 Hz, 1H, H-7a), 3.66-3.85 (m, 7H, H-1', NCH_2Ar, and OCH_2), 7.26-7.32 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, gHSQC), see Table 1. HRFABMS: calcd for $C_{19}H_{28}NO_3$ 318.2069 (MH^+), found 318.2070.

(2*S*,3a*S*,7a*S*)-1-Benzyl-2-[(1'*S*)-(1-hydroxyethyl)]octahydroindol-6-one ethylene acetal (10a): R_f = 0.30 (SiO_2, CH_2Cl_2/MeOH 95:5); $[\alpha]_D^{20}$ - 32 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, gCOSY) 1.16 (d, *J* = 6.4 Hz, 3H, CH_3), 1.50 (m, 2H, H-5 and H-7), 1.60 (m, 2H, H-3 and H-5), 1.63 (t, *J* = 12.0 Hz, 1H, H-7ax), 1.77 (m, 2H, H-4), 1.88 (ddd, *J* = 12.0, 8.0, 7.0 Hz, 1H, H-3), 2.34 (m, 1H, H-3a), 2.82 (q, *J* = 7.5 Hz, 1H, H-2), 2.97 (dt, *J* = 12.0, 6.0 Hz, 1H, H-7a), 3.54 (quint, *J* = 6.2 Hz, 1H, H-1'), 3.74-3.86 (m, 6H, OCH_2, NCH_2Ar), 7.20-7.40 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, gHSQC), see Table 1. HRFABMS: calcd for $C_{19}H_{28}NO_3$ 318.2069 (MH^+), found 318.2074.

Reduction of ketone 8. The above procedure was followed using ketone **8** (1.06 g, 3.36 mmol). Purification by chromatography (SiO_2, hexane to hexane-EtOAc 1:1) afforded 622 mg (54%) of alcohol **11a** as a white solid and then 365 mg (32%) of alcohol **12a** as a white solid. Overall yield for three steps (**4** → **11a** + **12a**): 86%; 1.7:1 ratio of alcohols **11a** and **12a**.

(2*S*,3a*R*,7a*R*)-1-Benzyl-2-[(1'*S*)-(1-hydroxyethyl)]octahydroindol-6-one ethylene acetal (11a): R_f = 0.22 (SiO_2, CH_2Cl_2/MeOH 98:2); mp 73-75 °C; $[\alpha]_D^{20}$ -100 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, gCOSY) 1.13 (d, *J* = 6.4 Hz, 3H, CH_3), 1.41 (t, *J* = 12.0 Hz, 1H, H-7ax), 1.50 (dm, *J* = 12.0 Hz, 1H), 1.60-1.68 (m, 2H), 1.73-1.90 (m, 4H), 2.21 (m, 1H, H-3a), 2.76 (dq, *J* = 10.0, 2.4 Hz, 1H, H-2), 3.21 (ddd, *J* = 12.0, 5.5, 5.5 Hz, 1H, H-7a), 3.61 and 3.77 (2d, *J* = 14.0 Hz, 1H each, NCH_2Ar), 3.78-3.93 (m, 5H, OCH_2 and H-1'), 7.20-7.40 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, gHSQC), see Table 1. HRFABMS: calcd for $C_{19}H_{28}NO_3$ 318.2069 (MH^+), found 318.2074.

(2*S*,3a*R*,7a*R*)-1-Benzyl-2-[(1'*R*)-(1-hydroxyethyl)]octahydroindol-6-one ethylene acetal (12a): R_f = 0.11 (SiO_2, CH_2Cl_2/MeOH 98:2); mp 91-93 °C; $[\alpha]_D^{20}$ - 36 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$, *g*COSY) 1.22 (d, *J* = 6.6 Hz, 3H, CH_3), 1.43 (t, *J* = 12.0 Hz, 1H, H-7ax), 1.50-1.75 (m, 4H, H-3, H-4, H-5, H-7), 1.80 (m, 2H, H-4 and H-5), 2.15 (m, 1H, H-3), 2.32 (m, 1H, H-3a), 2.88 (ddd, *J* = 9.8, 4.8, 2.2 Hz, 1H, H-2), 3.22 (ddd, *J* = 11.0, 5.4, 5.4 Hz, 1H, H-7a), 3.69 (m, 1H, H-1'), 3.73-3.92 (m, 6H, NCH_2 and OCH_2), 3.96 (br s, 1H, OH), 7.20-7.40 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, gHSQC), see Table 1. HRFABMS: calcd for $C_{19}H_{28}NO_3$ 318.2069 (MH^+), found 318.2063.

Conversion of alcohols 9a-12a to their corresponding chlorides 9b-12b.

Compounds **9b-12b** were prepared according to the following procedure: to a solution of alcohol (**9a-12a**, 50 mg, 0.16 mmol) in THF (1 mL) at 0 ºC was added MsCl (0.014 mL, 0.18 mmol, 1.1 equiv), followed by Et_3N (0.09 mL, 0.64 mmol, 4.0 equiv). After 4 h at reflux, the reaction mixture was poured into an aqueous 2.5 M NaOH solution (1 mL). After extraction with CH_2Cl_2 (3 x 2 mL), the organic phase was dried and concentrated to afford compounds **9b-12b**, which were used without further purification.

(2*S*,3a*S*,7a*S*)-1-Benzyl-2-[(1'*R*)-(1-chloroethyl)]octahydroindol-6-one ethylene acetal (9b). This compound was obtained together with the expanded chloride **16**; ^{1}H NMR (300 MHz, $CDCl_3$) 1.53 (d, *J* = 6.6 Hz, 3H, CH_3), 1.40-2.10 (m, 8H), 2.25 (m, 1H), 2.85-3.00 (m, 2H), 3.80-4.00 (m,

7H), 7.20-7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$), see Table 1. HRFABMS calcd for $C_{19}H_{27}{}^{35}ClNO_3$ 336.1730 (MH^+), found 336.1731.

(2*S*,3a*S*,7a*S*)-1-Benzyl-2-[(1'*S*)-(1-chloroethyl)]octahydroindol-6-one ethylene acetal (10b): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$, gCOSY) 1.49 (d, J = 6.8 Hz, 3H, CH_3), 1.55-1.65 (m, 4H, H-5 and H-7), 1.70-1.80 (m, 3H, H-3, H-4), 1.88 (ddd, J = 12.0, 8.0, 7.0 Hz, 1H, H-3), 2.25 (m, 1H, H-3a), 2.94 (dt, J = 10.5, 6.8 Hz, 1H, H-7a), 3.15 (dt, J = 9.2, 6.4 Hz, 1H, H-2), 3.73 and 3.87 (2d, J = 13.5 Hz, 1H each, NCH_2Ar), 3.70-3.84 (m, 4H, OCH_2), 3.95 (dq, J = 11.5, 6.4 Hz, 1H, H-1'), 7.20-7.38 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, gHSQC), see Table 1) . HRFABMS calcd for $C_{19}H_{27}{}^{35}ClNO_3$ 336.1730 (MH^+), found 336.1727.

(2*S*,3a*R*,7a*R*)-1-Benzyl-2-[(1'*S*)-(1-chloroethyl)]octahydroindol-6-one ethylene acetal (11b): white solid; ^{1}H NMR (400 MHz, $CDCl_3$, *g*COSY) 1.39 (t, J = 12.0 Hz, 1H, H-7ax), 1.44 (d, J = 6.8 Hz, 3H, CH_3) 1.50-1.65 (m, 4H, H-3 and H-4), 1.75-1.95 (m, 3H, H-7eq and H-5), 2.42 (m, 1H, H-3a), 2.96 (dt, J = 10.0, 3.0 Hz, 1H, H-2), 3.23 (ddd, J = 11.6, 5.6, 5.6 Hz, 1H, H-7a), 3.72 and 3.84 (2d, J =14 Hz, 1H each, NCH_2), 3.78-3.90 (m, 4H, OCH_2), 4.05 (qd, J = 6.8, 3.2 Hz, 1H, H-1'), 7.20-7.40 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, *g*HSQC), see Table 1. HRFABMS calcd for $C_{19}H_{27}{}^{35}ClNO_3$ 336.1730 (MH^+), found 336.1741.

(2*S*,3a*R*,7a*R*)-1-Benzyl-2-[(1'*R*)-(1-chloroethyl)]octahydroindol-6-one ethylene acetal (12b): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 1.48 (d, J = 6.6 Hz, CH_3), 1.40-2.05 (m, 8H), 2.25 (m, 1H), 3.20 (m, 2H), 3.6-4.0 (m, 7H), 7.20-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$), see Table 1.

Ring expansion of chlorides 9b-12b

Method A. A solution of the appropriate chloride derivative **9b-12b** (0.16 mmol) in THF (1 mL) was treated with AgOAc (0.48 mmol, 3 equiv) at reflux for 4 h. The reaction mixture was filtered through a bed of Celite and diluted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ (10 mL), dried and concentrated to afford the corresponding mixture of acetates **9c-12c** and **17-20**. (See Table 1 in the main paper for results in each series and below for the NMR data of formed acetates).

- From **9b**, a mixture of acetates **9c** and **17** was obtained (80% overall yield) in a 1:1.3 ratio according to the NMR spectrum. Purification and separation of the compounds was performed by chromatography (SiO_2, CH_2Cl_2/EtOAc; 9:1).
- From **10b**, a mixture of acetates **10c** and **18** was obtained (70 % overall yield) in a 2.9:1 ratio according to the NMR spectrum. Purification and separation of the compounds was performed by chromatography (SiO_2, CH_2Cl_2/EtOAc; 9:1).
- From **11b**, a non-separable mixture of acetates **11c** and **19** was obtained (80 % overall yield) in a 5.7:1 ratio according to the NMR spectrum and GC-MS analysis. Purification of the mixture of compounds was performed by chromatography (SiO_2, CH_2Cl_2/EtOAc 9:1).
- From **12b**, a non-separable mixture of acetates **12c** and **20** was formed (60 % overall yield) in a 13:1 ratio according to the NMR spectrum. Purification of the mixture of compounds was performed by chromatography (SiO_2, CH_2Cl_2/EtOAc 9:1).

Ring expansion of alcohols 9a-12a

***Method B*.** A solution of the appropriate alcohol derivative **9a** – **12a** (0.16 mmol) in THF (1 mL) was treated with MsCl (0.19 mmol, 1.2 equiv) and Et_3N (0.64 mmol, 4 equiv) under an argon atmosphere at – 20 ºC for 1 h. AgOAc (0.48 mmol, 3 equiv) was added and the resulting mixture was warmed to rt over a period of 1 h. The reaction mixture was filtered through a bed of Celite and diluted with CH_2Cl_2. The organic layer was washed with a saturated aqueous $NaHCO_3$ solution (10 mL), dried and concentrated to afford the corresponding mixture of acetates.

From 9a. A mixture of acetates **9c** and **17** was obtained in a 1:2.2 ratio according the NMR spectrum in 78 % yield. Purification and separation of the compounds was performed by chromatography (SiO_2, CH_2Cl_2/EtOAc 9:1). For analytical data of **9c** and **17**, see the main text and Tables 1 and 2.

From 10a. A mixture of acetates **10c** and **18** was obtained in a 1.1:1 ratio according the NMR spectrum in 66 % yield. Purification and separation of the compounds was performed by chromatography (SiO_2, CH_2Cl_2/EtOAc 9:1).

(2*S*,3a*S*,7a*S*)-1-Benzyl-2-[(1'*S*)-(1-acetoxyethyl)]octahydroindol-6-one ethylene acetal (10c): Colourless oil. R_f = 0.26 (SiO_2, CH_2Cl_2/EtOAc 9:1). $[\alpha]_D^{20}$ - 57 (*c* 0.2, $CHCl_3$); IR 1732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, gCOSY) 1.21 (d, *J* = 6.0 Hz, 3H, CH_3), 1.50 (t, *J* = 11.0 Hz, 1H, H-5), 1.50-1.80 (m, 7H), 1.90 (s, 3H, OAc), 2.25 (m, 1H, H-3a), 2.85 (dt, *J* = 11.0, 6.4 Hz, 1H, H-7a), 3.00 (dt, *J* = 10.0, 7.0 Hz, 1H, H-2), 3.70 and 3.94 (2d , *J* = 14.0 Hz, 1H each, NCH_2Ar), 3.74-3.86 (m, 4H, OCH_2), 4.91 (quint, *J* = 6.2 Hz, 1H, H-1'), 7.20-7.35 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$), see Table 1. HRFABMS: calcd for $C_{21}H_{30}NO_4$ 360.2175 (MH^+), found 360.2163.

(2*R*,3*R*,4a*S*,8a*S*)-3-Acetoxy-1-benzyl-2-methyl-7-oxodecahydroquinoline ethylene acetal (18): Colourless oil. R_f = 0.58 (SiO_2, CH_2Cl_2/EtOAc 9:1). $[\alpha]_D^{20}$ - 24 (*c* 1.0, $CHCl_3$); IR 1733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, gCOSY) 1.10 (d, *J* = 7.0 Hz, 3H, CH_3), 1.48 (m, 1H, H-5), 1.52 (m, 1H, H-4), 1.59 (m, 2H, H-6), 1.72 (t, *J* = 12.4 Hz, 1H, H-8ax), 1. 80 (m, 1H, H-5), 1.87 (brt, *J* = 13.0 Hz, 1H, H-4ax), 1.94 (dm, *J* = 12.4 Hz, 1H, H-8eq), 2.00 (s, 3H, OAc), 2.08 (m, 1H, H-4a), 3.00 (dt, *J* = 12.8, 4.4 Hz, 1H, H-8a), 3.20 (q, *J* = 6.5 Hz, 1H, H-2); 3.78 and 3.84 (2d, *J* = 14.4 Hz, 1H each, NCH_2Ar), 3.86-3.95 (m, 4H, OCH_2), 4.99 (ddd, *J* = 12.0, 5.6, 4.4 Hz, 1H, H-3), 7.20-7.35 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, gHSQC), see Table 2 HRFABMS: calcd for $C_{21}H_{30}NO_4$ 360.2175 (MH^+), found 360.2171.

From 11a. **11c** and **19** were obtained in a 2.2:1 ratio according the NMR spectrum in 76 % yield as a unseparable mixture. Purification of the mixture of compounds was performed by chromatography (SiO_2, CH_2Cl_2/EtOAc 9:1).

(2*S*,3a*R*,7a*R*)-1-Benzyl-2-[(1'*S*)-(1-acetoxyethyl)]octahydroindol-6-one ethylene acetal (11c): Colourless oil. R_f = 0.31 (SiO_2, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, gCOSY) 1.23 (d, *J* = 6.4 Hz, 3H, CH_3), 1.35 (t, *J* = 12.4 Hz, 1H, H-7ax), 1.45-2.05 (m, 7H), 2.07 (s, 3H, OAc), 2.25 (m, 1H, H-3a), 2.89 (dt, *J* = 10.0, 2.8 Hz, 1H, H-2), 3.08 (dt, *J* = 12.0, 6.0 Hz, 1H, H-7a), 3.52 and 3.88 (2d, *J* = 13.6 Hz, 1H each, NCH_2), 3.80-4.00 (m, 4H, OCH_2), 5.14 (qd, *J* = 6.4, 2.4 Hz, 1H, H-1'), 7.15-7.35 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$, gHSQC), see Table 1. HRFABMS: calcd for $C_{21}H_{30}NO_4$ 360.2175 (MH^+), found 360.2158.

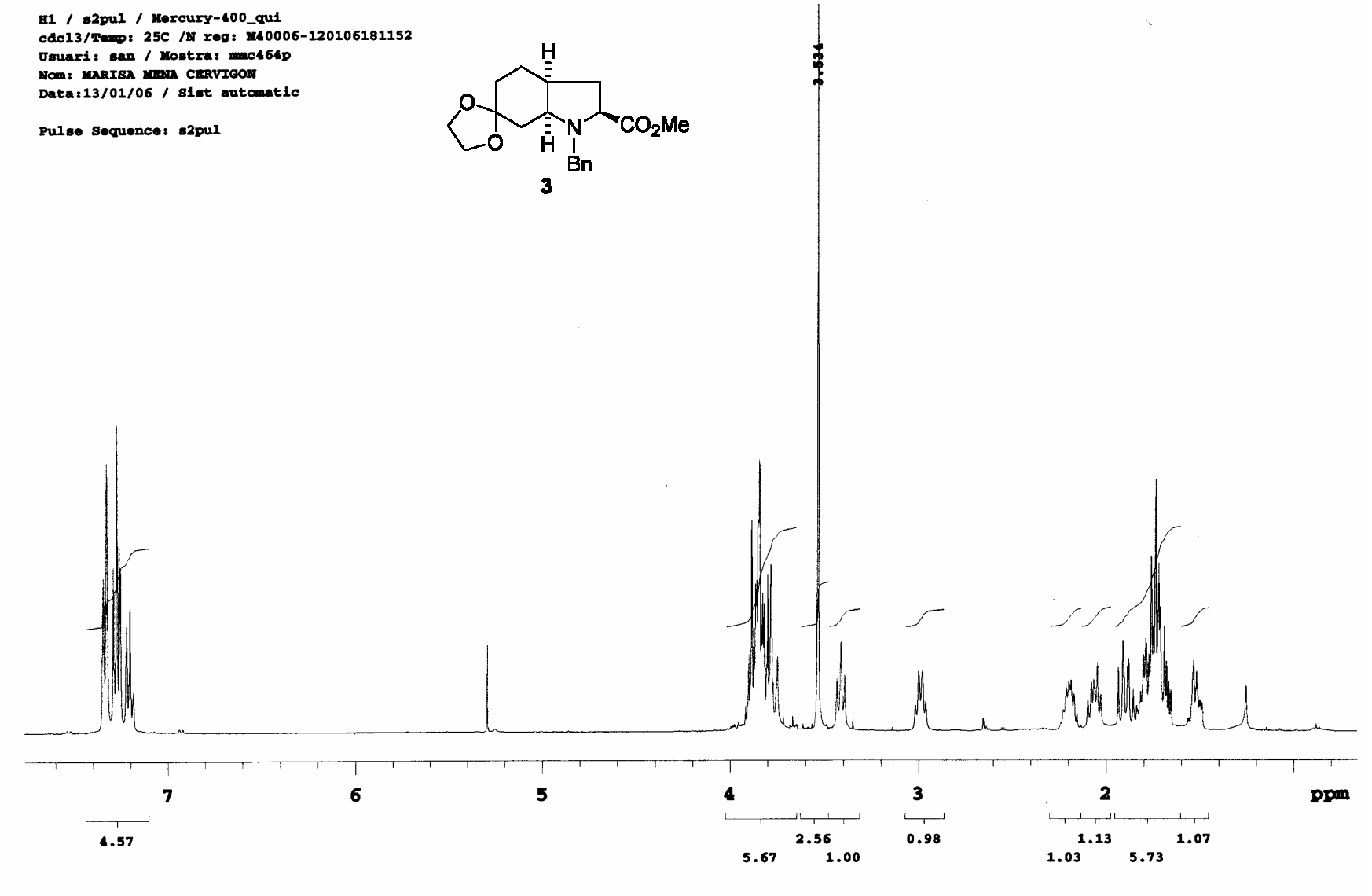
(2*R*,3*R*,4a*R*,8a*R*)-3-Acetoxy-1-benzyl-2-methyl-7-oxodecahydroquinoline ethylene acetal (19): Colourless oil. R_f = 0.31 (SiO_2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) 1.04 (d, *J* = 7.2 Hz, 3H, CH_3), 1.45-2.05 (m, 8H), 2.07 (s, 3H, OAc), 2.34 (m, 1H, H-4a), 2.89 (qd, *J* = 7.2, 1.2 Hz, 1H, H-2ax), 3.09 (dt, *J* = 11.5, 4.4 Hz, 1H, H-8a), 3.68-3.80 (m, 6H, NCH_2Ar and OCH_2), 4.82 (q, *J* = 2.8 Hz, 1H, H-3eq), 7.15-7.30 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$), see Table 2. HRFABMS: calcd for $C_{21}H_{30}NO_4$ 360.2175 (MH^+), found 360.2158.

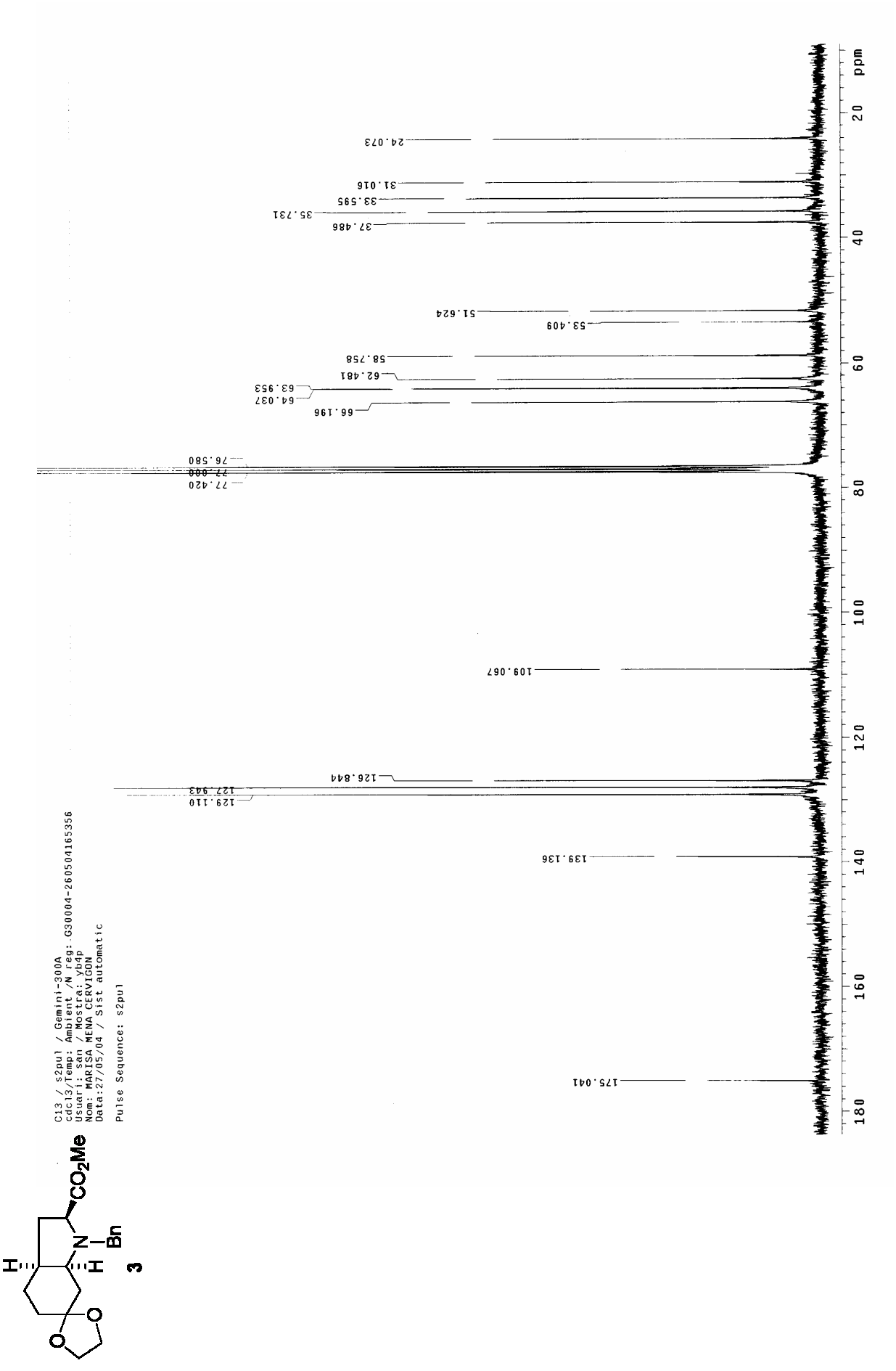
From 12a. Acetate **12c** and traces of **20** were formed in a 13:1 ratio, according the NMR spectrum and GC-MS analysis, in 40% yield as a unseparable mixture. Purification of the mixture of compounds was performed by chromatography (SiO_2, CH_2Cl_2/EtOAc 9:1).

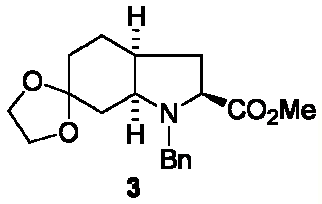
(2*S*,3a*R*,7a*R*)-1-Benzyl-2-[(1'*R*)-(1-acetoxyethyl)]octahydroindol-6-one ethylene acetal (12c): White Solid. R_f = 0.31 (SiO_2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, gCOSY) 1.24 (d, *J* = 6.4 Hz, 3H, CH_3), 1.37 (t, *J* = 12.0 Hz, 1H, H-7ax), 1.49 (dm, *J* = 12.0 Hz, 1H, H-5eq), 1.60-1.70 (m, 3H, H-5 and H-4), 1.75 (m, 1H, H-3),1.80-1.90 (m, 2H, H-3 and H-7eq), 1.96 (s, 3H, OAc), 2.28 (m, 1H, H-3a), 3.05 (ddd, *J* = 8.8, 6.4, 2.8 Hz, 1H, H-2), 3.15 (ddd, *J* = 11.2, 5.6, 5.6 Hz, 1H, H-7a), 3.69 and 3.88 (2d, *J* = 14.4 Hz, 1H each, NCH_2Ar), 3.73-3.90 (m, 4H, OCH_2), 4.95 (quint, *J* = 6.4 Hz, 1H, H-1'), 7.20-7.35 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$), see Table 1. HRFABMS: calcd for $C_{21}H_{30}NO_4$ 360.2175 (MH^+), found 360.2163.

Ring expansion of octahydroindole 9a using silver trifluoroacetate. A solution of alcohol **9a** (62 mg, 0.2 mmol) in THF (1.4 mL) was treated with MsCl (0.019 mL, 0.24 mmol, 1.2 equiv) and Et_3N (0.11 mL, 0.8 mmol, 4 equiv) under argon atmosphere at – 20 ºC for 1 h. CF_3CO_2Ag was added (221 mg, 1 mmol, 5 equiv) and the resulting mixture was warmed to room temperature over a period of 1 h. The mixture was treated with 2.5 N NaOH (1 mL) and stirred for 3 h. The reaction mixture was filtered through a bed of Celite and diluted with CH_2Cl_2. The organic layer was dried and concentrated to afford a mixture of **9a** and **21**, which was purified by chromatography (Al_2O_3, hexane/EtOAc 9:1) to give 16 mg (26%) of **9a** and 36 mg (58%) of (2*S*,3*R*,4a*S*,8a*S*)-1-Benzyl-3-hydroxy-2-methyl-7-oxodecahydroquinoline ethylene acetal (**21**): Colourless oil. R_f = 0.10 (Al_2O_3, Hexane/EtOAc 8:2). $[\alpha]_D^{20}$ +1.5 (*c* 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, COSY) 1.17 (d, *J* =

6.0 Hz, 3H, CH_3), 1.43-1.49 (m, 2H, H-5 and H-6), 1.55-1.74 (m, 5H, H-4, H-5, H-6, and H-8eq), 1.88 (t, *J* = 12.6 Hz, 1H, H-8ax), 2.04 (m, 1H, H-4a), 2.57 (dq, *J* = 9.0, 6.0 Hz, 1H, H-2ax), 2.93 (dt, *J* = 12.6, 4.5 Hz, 1H, H-8a), 3.36 (td, *J* = 9.0, 7.2 Hz, 1H, H-3ax), 3.57 and 3.90 (2d, *J* = 14.4 Hz each, NCH_2Ar), 3.79-3.94 (m, 4H, OCH_2), 7.18-7.35 (m, 5H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$, gHSQC), see Table 2. HRFABMS: calcd for $C_{19}H_{28}NO_3$ 318.2069 (MH^+), found 318.2064.


H1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40006-120106181152
Usuari: san / Mostra: mmc464p
Nom: MARISA MENA CERVIGON
Data:13/01/06 / Sist automatic
Pulse Sequence: s2pul
3.534
CO2Me
Bn
3
7
6
5
4
3
2
ppm
4.57
5.67
2.56
1.00
0.98
1.03
1.13
5.73
1.07


C13 / s2pul / Gemini-300A
cdcl3/Temp: Ambient /N reg: G30004-260504165356
Usuari: san /Mostra: yd4p
Nom: MARISA MENA CERVIGON
Data:27/05/04 / Sist automatic
Pulse Sequence: s2pul
24.073
31.016
33.595
35.731
37.486
51.624
53.409
58.758
62.481
63.953
64.037
66.196
76.580
77.000
77.420
109.067
126.844
127.943
129.110
139.136
175.041
ppm
20
40
60
80
100
120
140
160
180
CO2Me
N
Bn
H
H
O
O
3

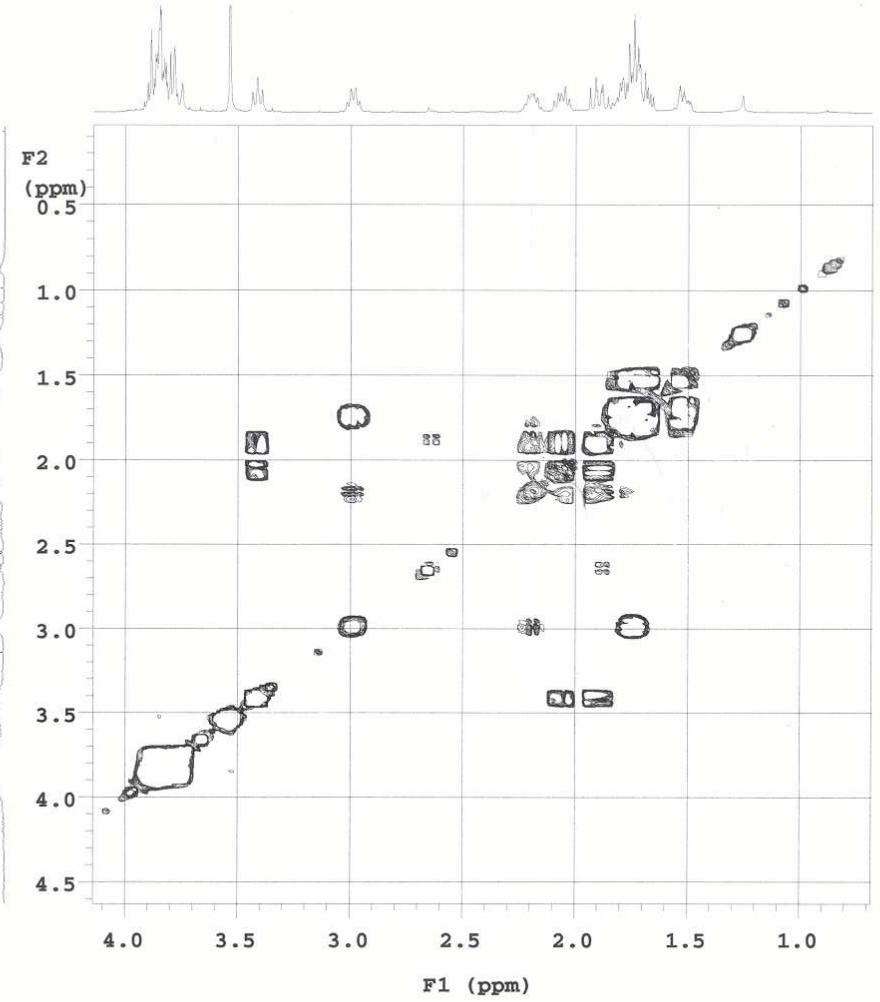


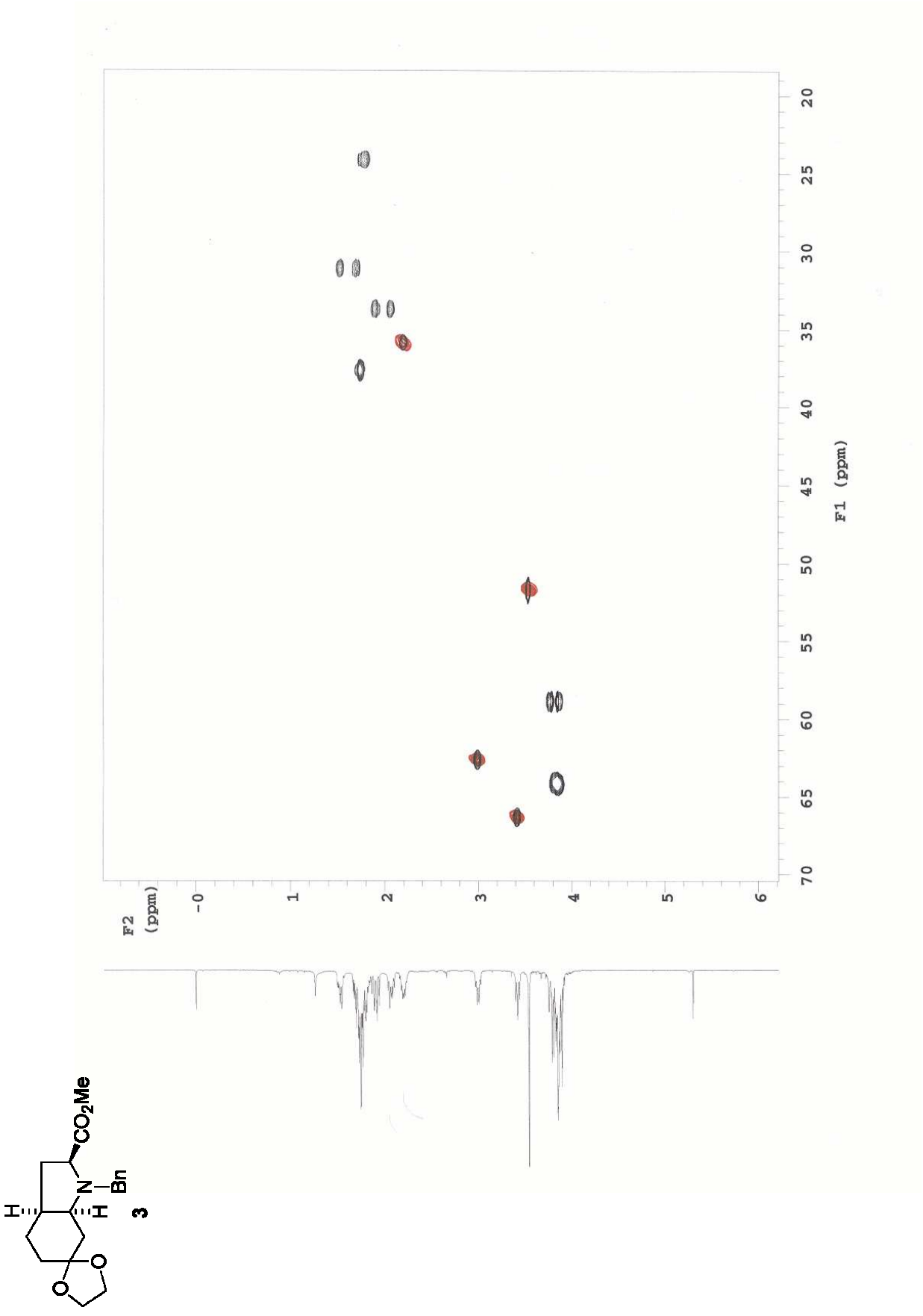
3

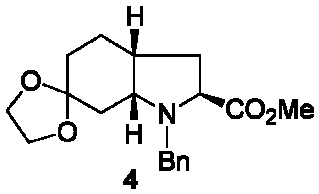
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40006-120106181
152
Usuari: san / Mostra: mmc464p
Nom: MARISA MENA CERVIGON
Data:13/01/06 / Sist automatic

exp2 gCOSY

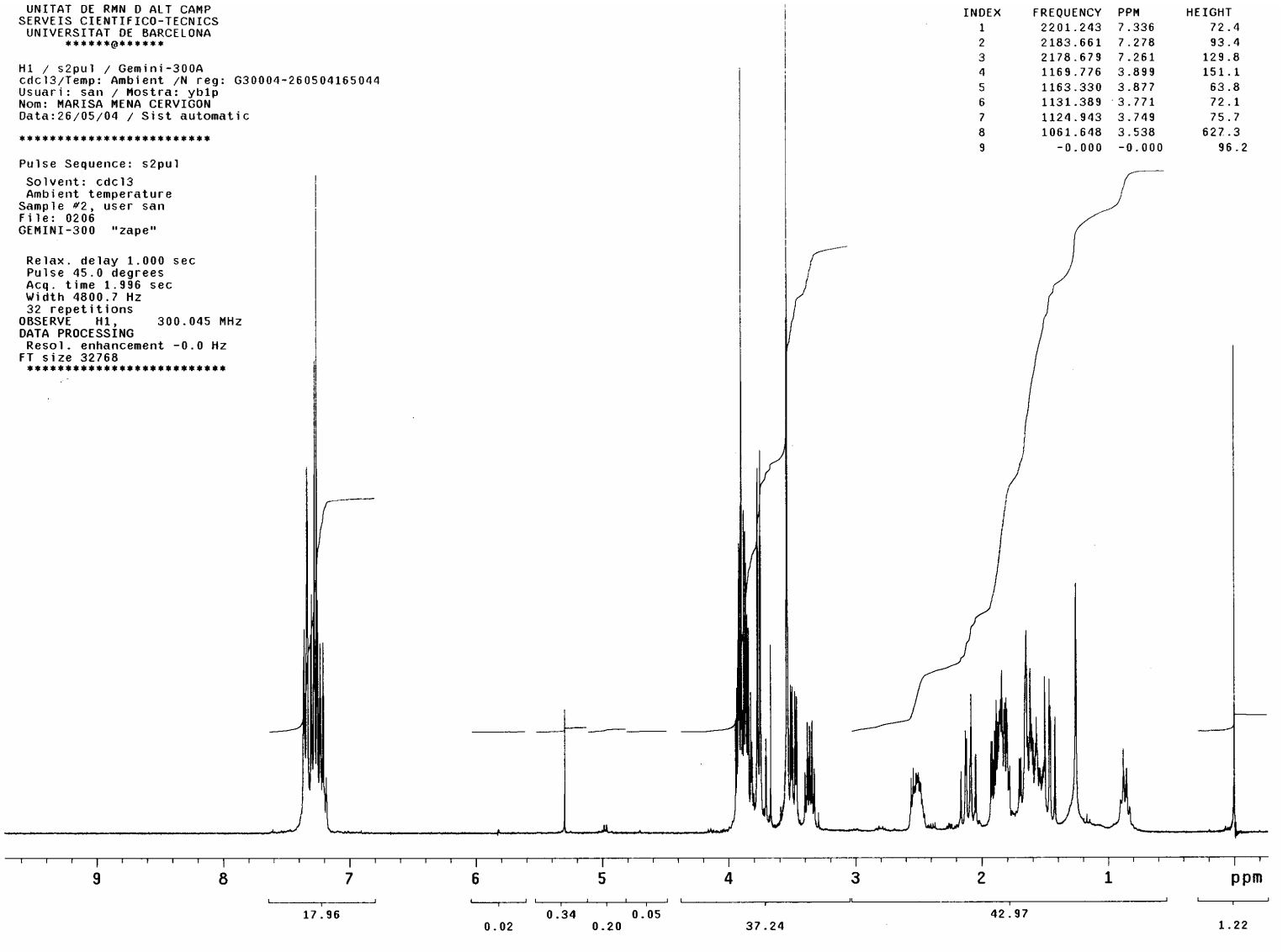
SAMPLE		FLAGS	
date	Jan 13 2006	hs	nn
solvent	cdcl3	sspul	n
sample	auto_Custom~	hsglvl	1004
	Q_13Jan2006	SPECIAL	
ACQUISITION		temp	25.0
sw	6410.3	gain	22
at	0.150	spin	0
np	1924	F2 PROCESSING	
fb	not used	sb	-0.075
ss	16	sbs	not used
d1	1.000	fn	2048
nt	2	F1 PROCESSING	
2D ACQUISITION		sb1	-0.040
sw1	6410.3	sbs1	not used
ni	256	proc1	lp
PRESATURATION		fn1	2048
satmode	n	DISPLAY	
satfrq	0	sp	15.7
satdly	0	wp	1836.0
satpwr	0	sp1	272.6
TRANSMITTER		wp1	1384.8
tn	H1	rf1	798.9
sfrq	400.114	rfp	0
tof	381.9	rfl1	798.9
tpwr	58	rfp1	0
pw	12.200	PLOT	
GRADIENTS		wc	131.8
gzlvl1	1004	sc	6.2
gt1	0.001000	wc2	131.8
gstab	0.000500	sc2	0
DECOUPLER		vs	474
dn	C13	th	5
dm	nnn	ai cdc av	

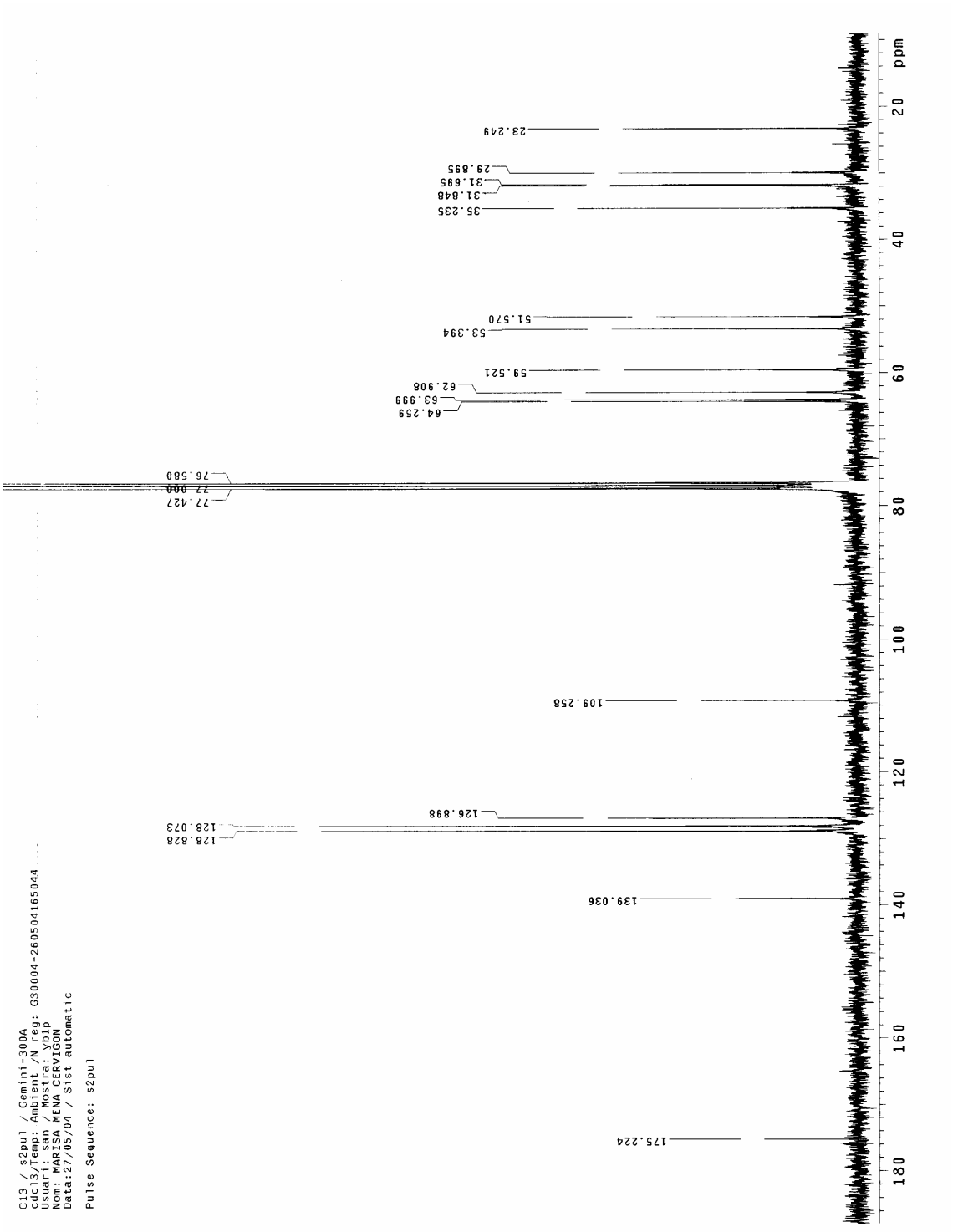


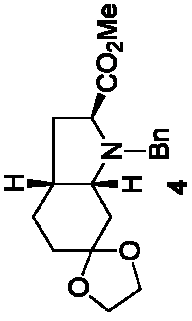

F2 (ppm)
F1 (ppm)
CO2Me
N
Bn
H
H
O
O
3

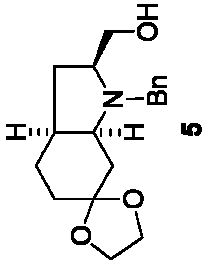

H
O
O
H
N
Bn
CO2Me

4

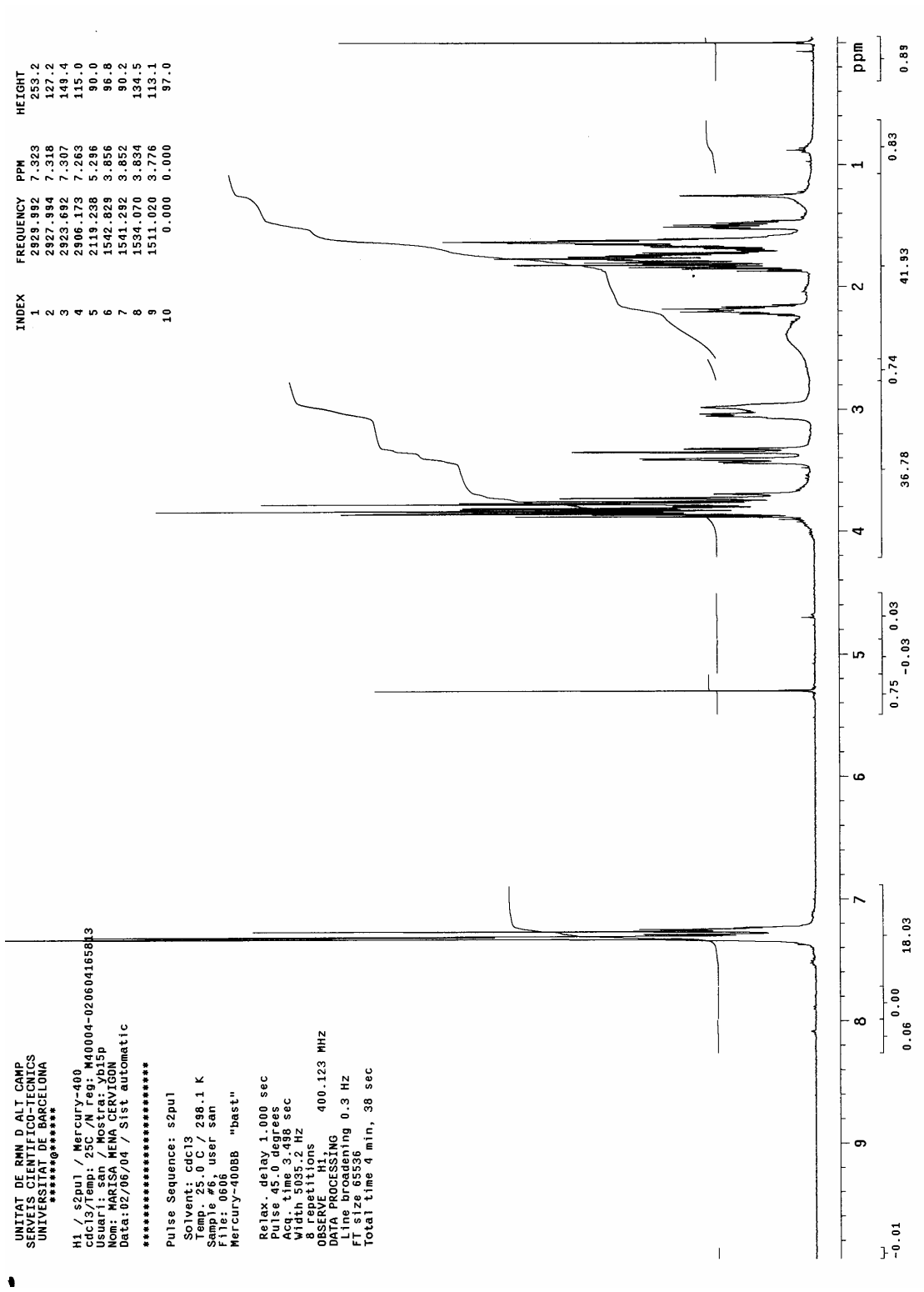

UNITAT DE RMN D ALT CAMP
SERVEIS CIENTIFICO-TECNICS
UNIVERSITAT DE BARCELONA
******@******
H1 / s2pul / Gemini-300A
cdcl3/Temp: Ambient /N reg: G30004-260504165044
Usuari: san / Mostra: yb1p
Nom: MARISA MENA CERVIGON
Data:26/05/04 / Sist automatic
****
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Sample #2, user san
File: 0206
GEMINI-300 "zape"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.996 sec
Width 4800.7 Hz
32 repetitions
OBSERVE H1, 300.045 MHz
DATA PROCESSING
Resol. enhancement -0.0 Hz
FT size 32768
****
INDEX FREQUENCY PPM HEIGHT
1 2201.243 7.336 72.4
2 2183.661 7.278 93.4
3 2178.679 7.261 129.8
4 1169.776 3.899 151.1
5 1163.330 3.877 63.8
6 1131.389 3.771 72.1
7 1124.943 3.749 75.7
8 1061.648 3.538 627.3
9 -0.000 -0.000 96.2
9
8
7
6
5
4
3
2
1
ppm
17.96
0.02
0.34
0.20
0.05
37.24
42.97
1.22

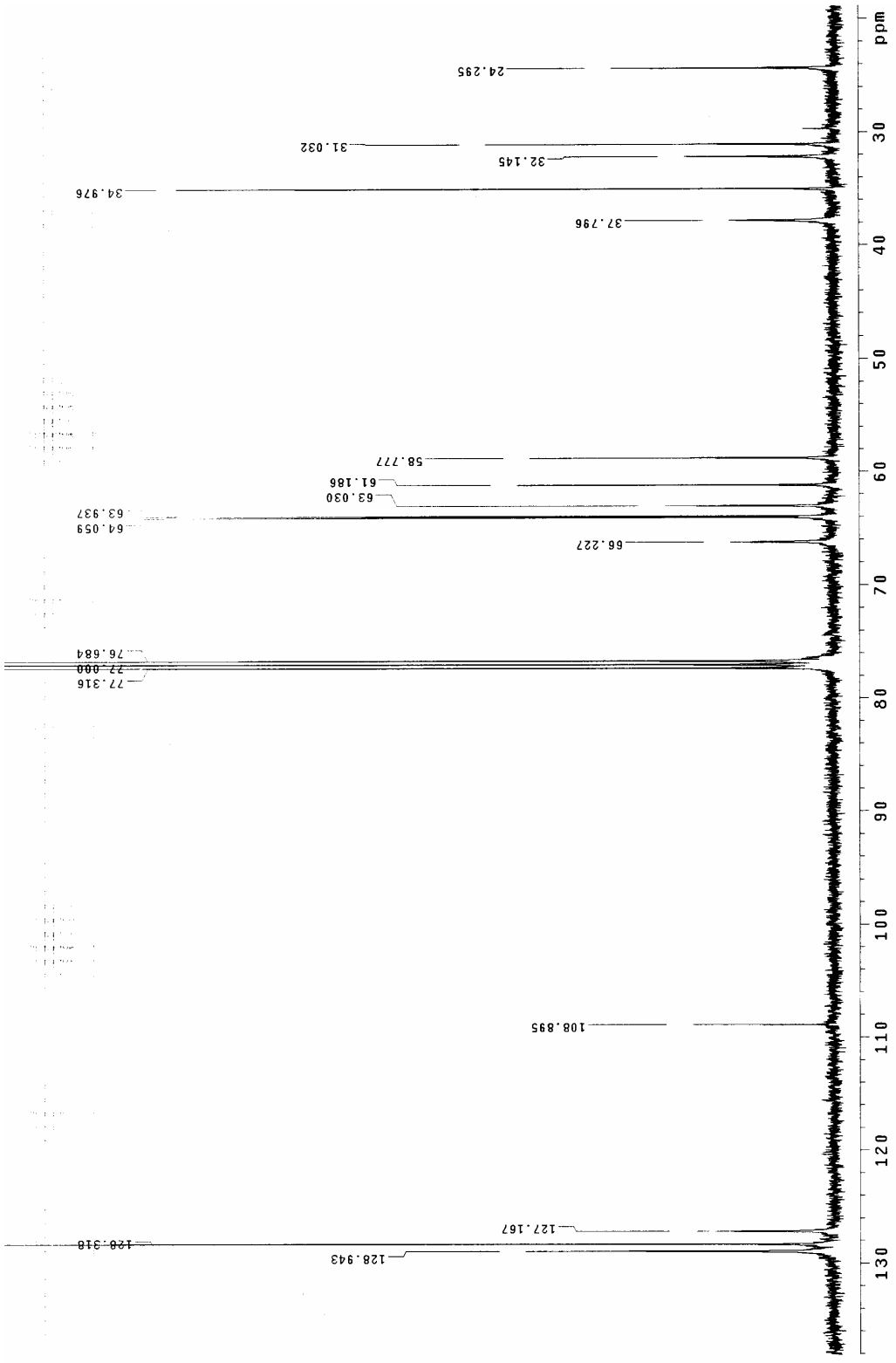

C13 / s2pul / Gemini-300A
cdcl3/Temp: Ambient /N reg: G30004-260504165044
Usuari: san /Mostra: ybip
Nom: MARISA MENA CERVIGON
Data:27/05/04 / Sist automatic
Pulse Sequence: s2pul
175.224
139.036
128.828
128.073
126.898
109.258
77.427
77.000
76.580
64.259
63.999
62.908
59.521
53.394
51.570
35.235
31.848
31.695
29.895
23.249
ppm

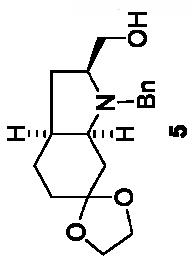

CO2Me
N
Bn
H
H
O
O
4

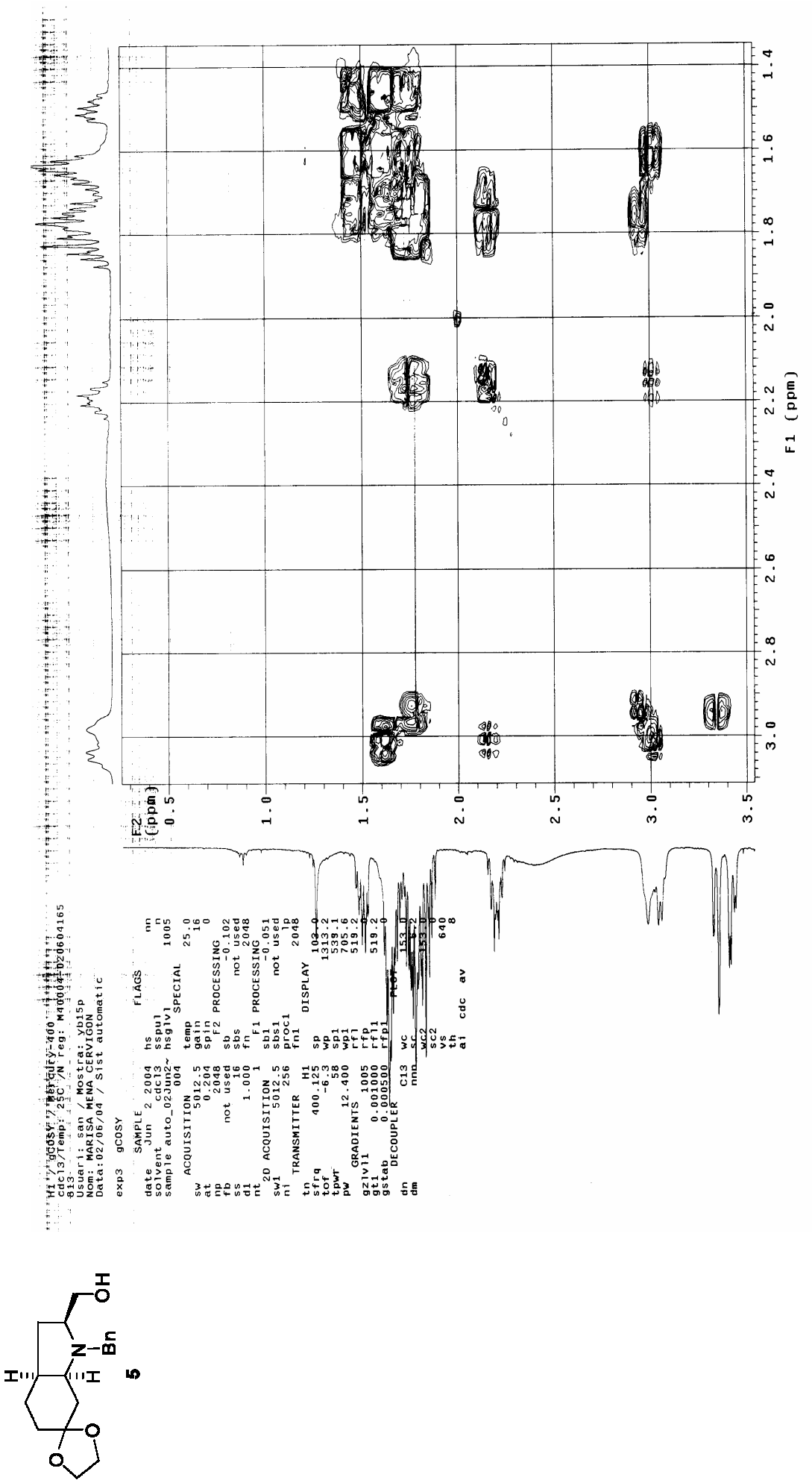

H
OH
N
Bn
H
O
O

5


UNITAT DE RMN D ALT CAMP
SERVEIS CIENTIFICO-TECNICS
UNIVERSITAT DE BARCELONA
H1 / s2pul / Mercury-400
cdcl3/Temp: 25C /N reg: M40004-020604165813
Usuari:san /Mostra:yo15p
Nom: MARISA MENA CERVIGON
Data:02/06/04 / Sist automatic
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #6, user san
File: 0606
Mercury-400BB "bast"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.438 sec
width 5035.2 Hz
repetitions
OBSERVE H1 400.123 MHz
DATA PROCESSING
line broadening 0.3 Hz
FT size 65536
Total time 4 min, 38 sec
INDEX FREQUENCY PPM HEIGHT
1 2929.992 7.323 253.2
2 2927.994 7.318 127.2
3 2923.692 7.307 149.4
4 2906.173 7.263 115.0
5 2119.238 5.296 90.0
6 1542.829 3.856 96.8
7 1541.292 3.852 90.2
8 1534.070 3.834 134.5
9 1511.020 3.776 113.1
10 0.000 0.000 97.0
ppm
-0.01
0.06
0.00
18.03
0.75
-0.03
0.03
36.78
0.74
41.93
0.83
0.89

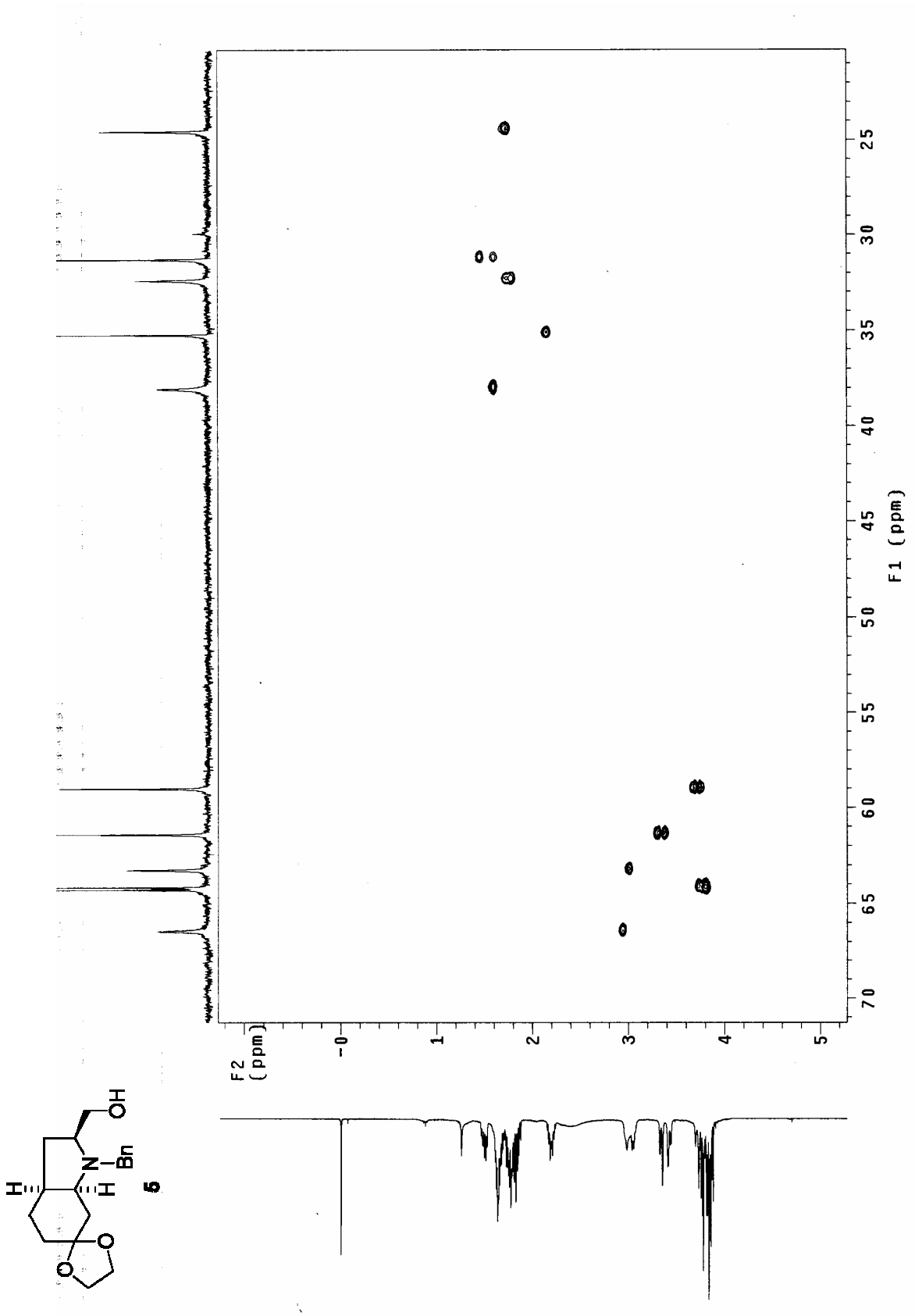

24.295
31.032
32.145
34.976
37.796
58.777
61.186
63.030
63.937
64.059
66.227
76.684
77.000
77.316
108.895
127.167
128.318
128.943
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130

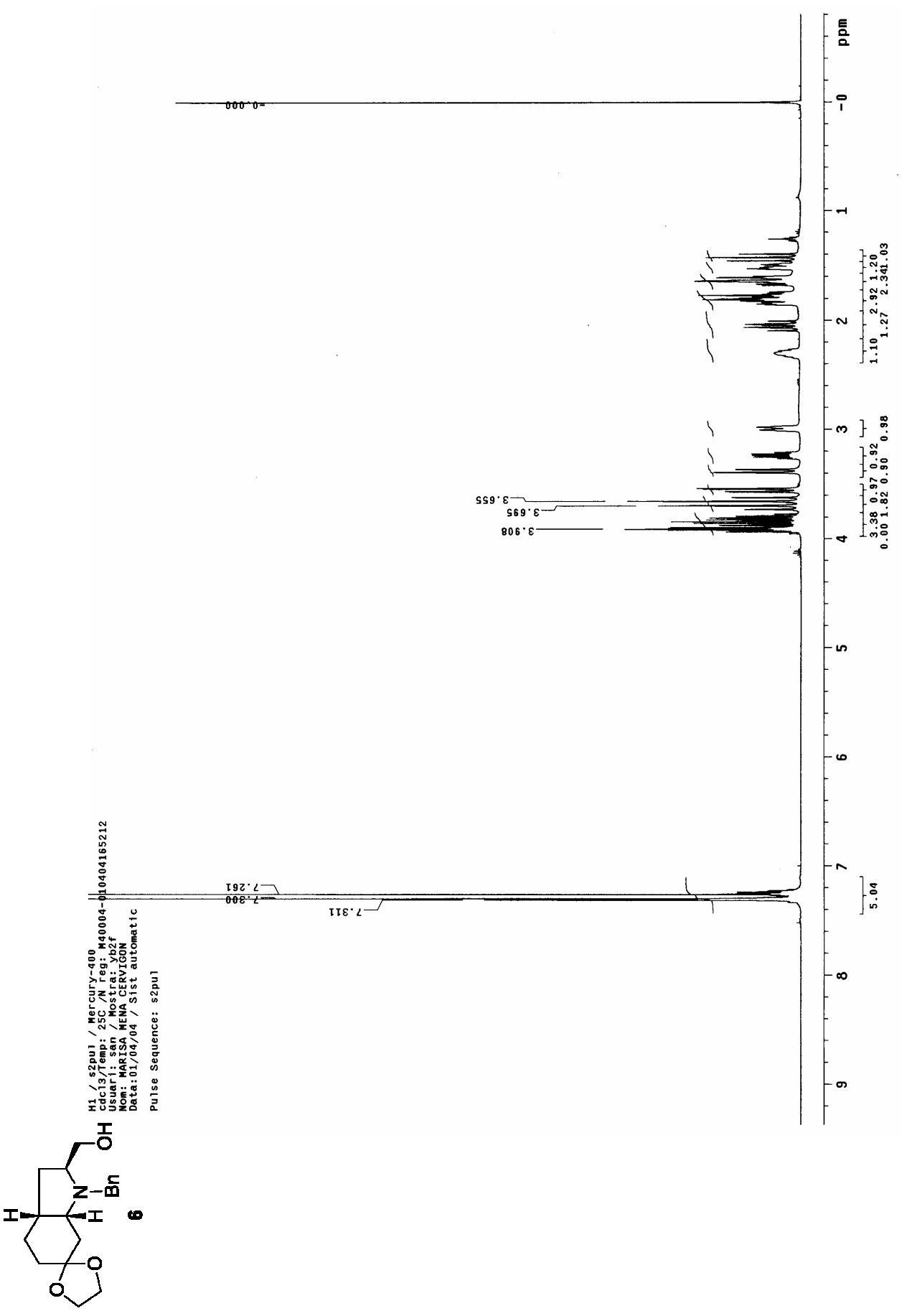

OH
N
Bn
H
H
O
O
5

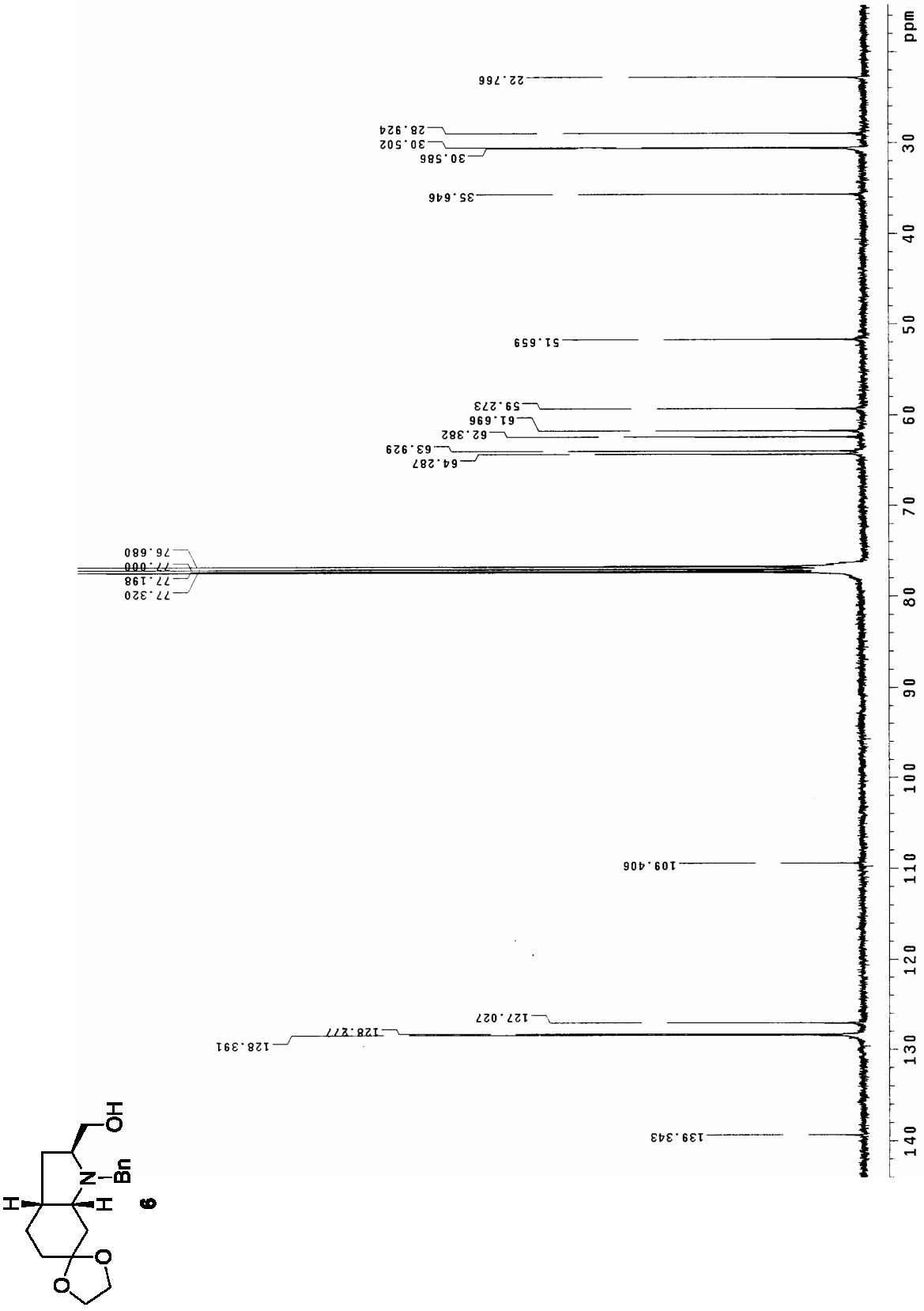

F2 (ppm)
F1 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0

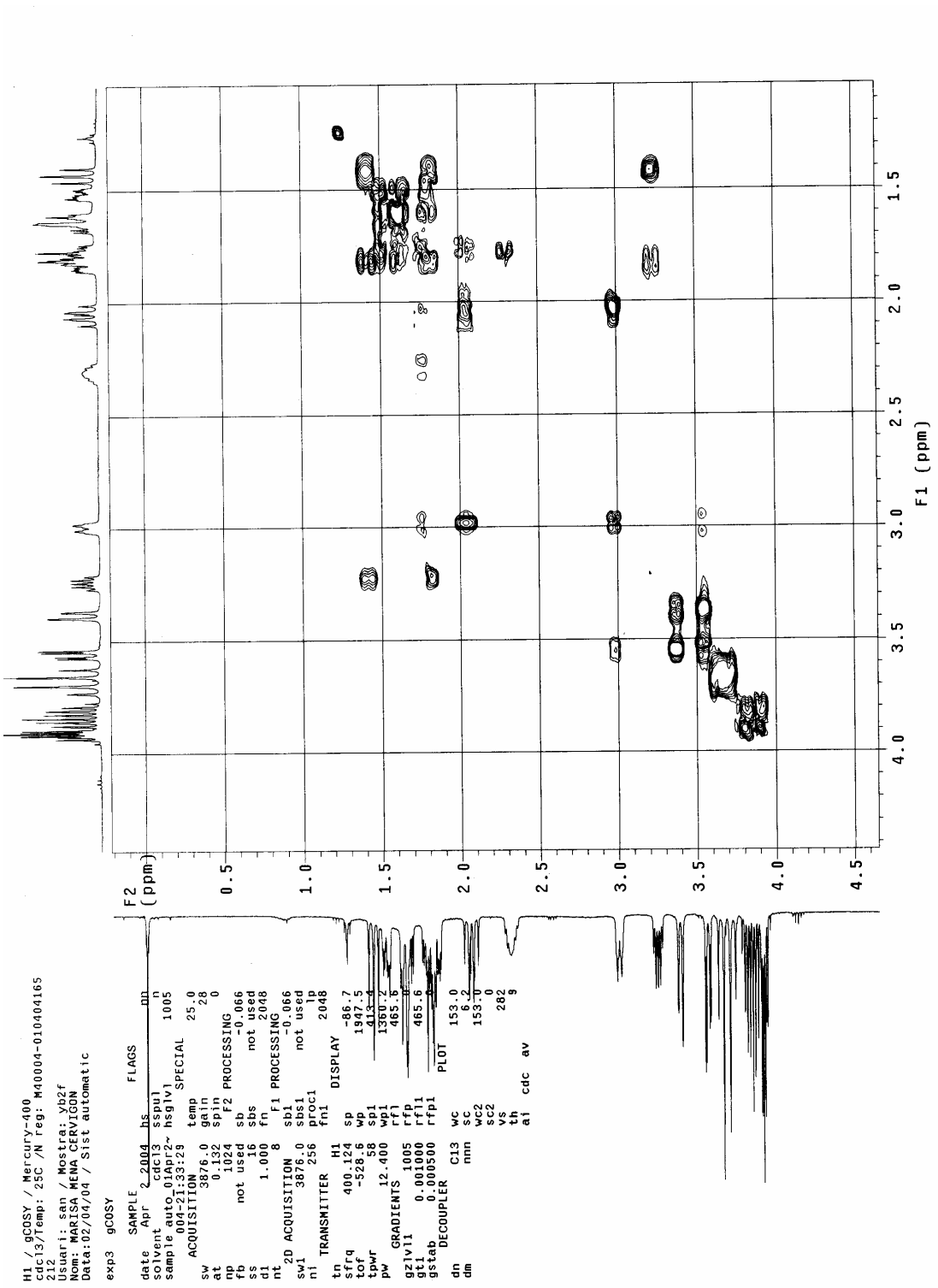
OH
N
Bn
H
H
O
O

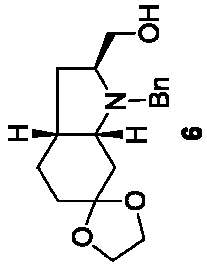
5


OH
N
Bn
H
H
O
O
O
5
F2 (ppm)
F1 (ppm)

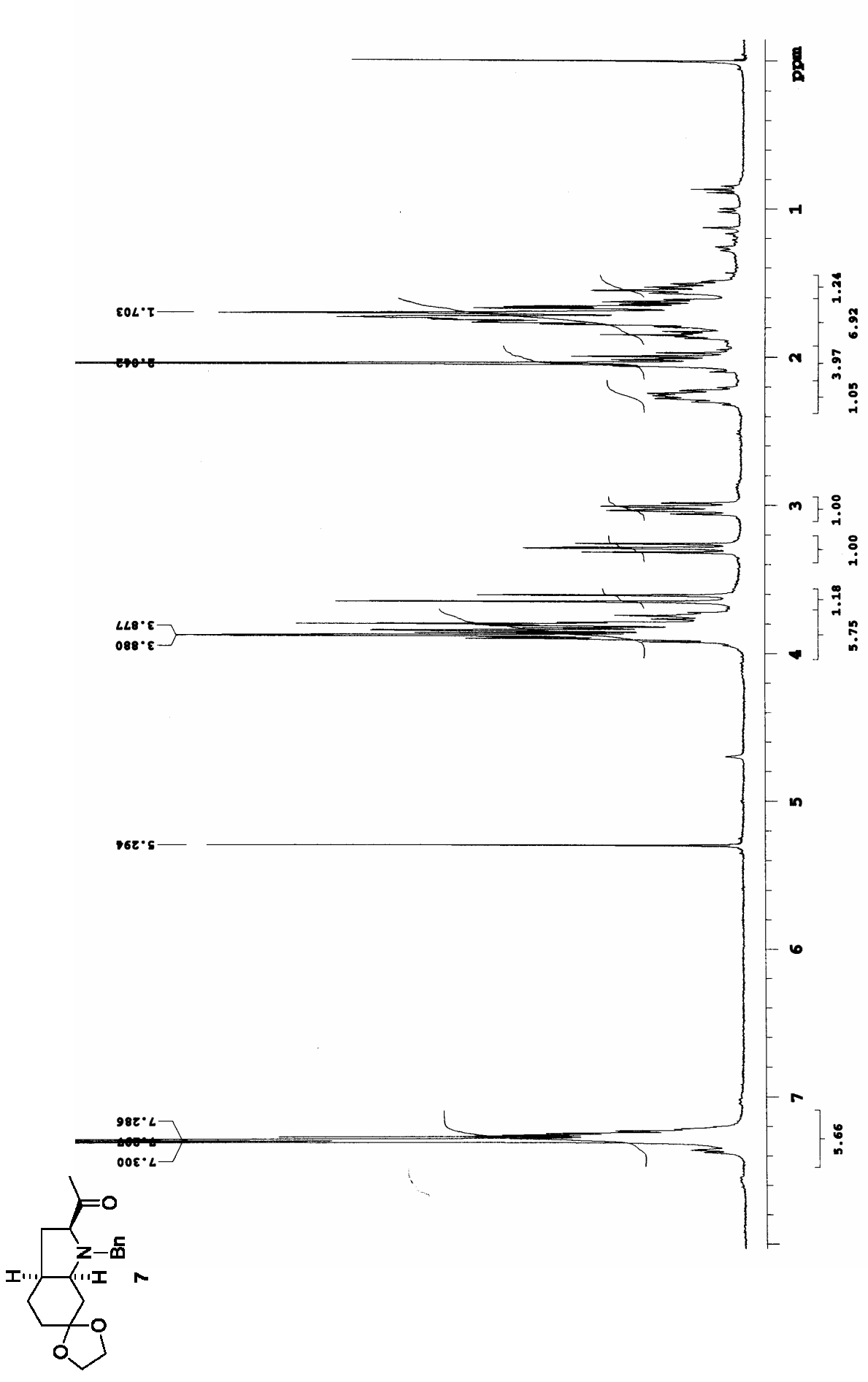

H1 / s2pul / Mercury-400
cdcl3/Temp: 25C /N reg: M40004-p10404165212
Usuari: san / Master: jb2f
Nom: MARISA MENA CERVIGON
Data:01/04/04 / Sist automatic
Pulse Sequence: s2pul
7.311
7.300
7.261
3.908
3.695
3.655
0.000
ppm
5.04
3.38 0.97 0.92
0.00 1.82 0.90 0.98
1.10 2.92 1.20
1.27 2.34 1.03
OH
N
Bn
H
H
O
O
6

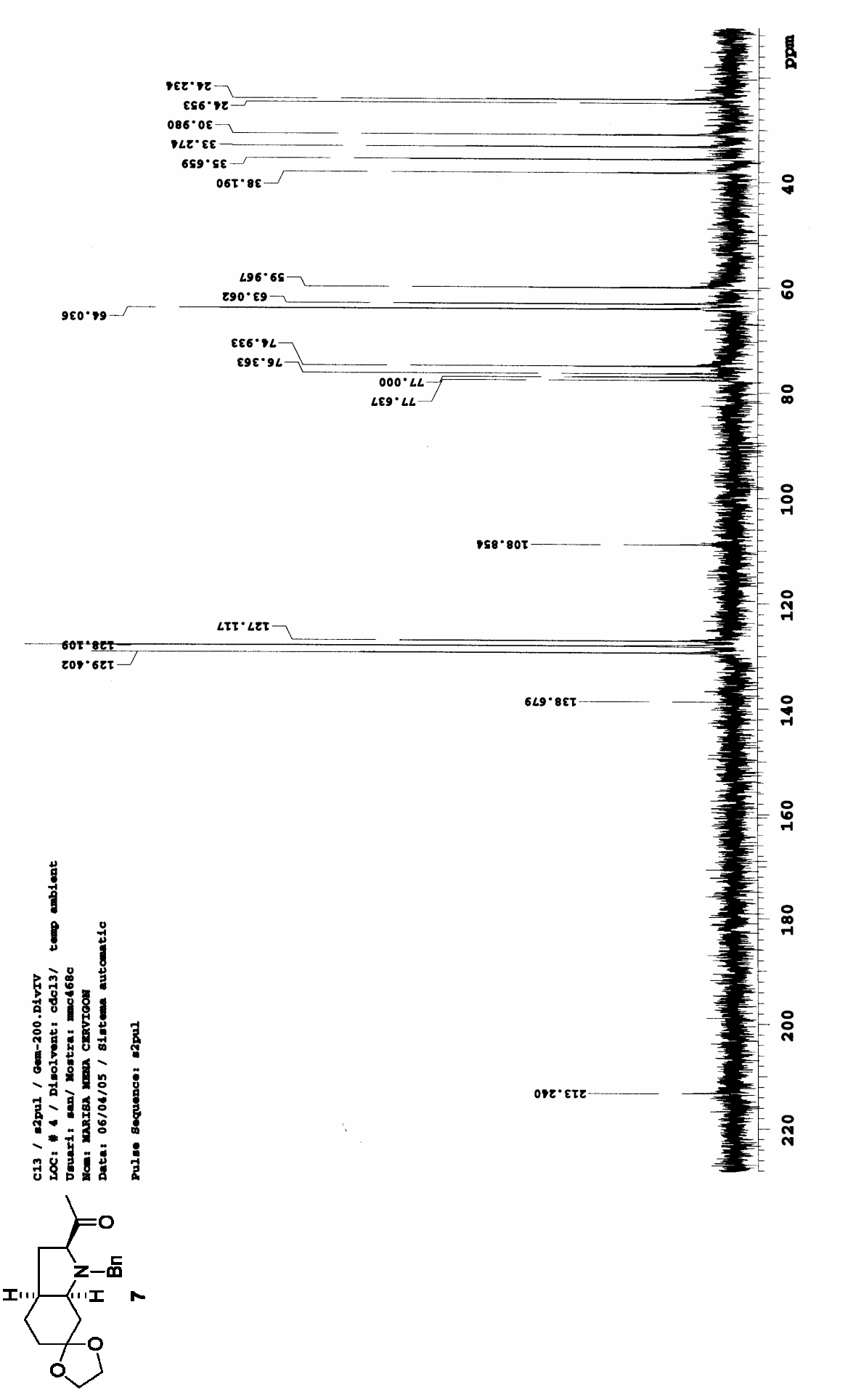

22.766
28.924
30.502
30.586
35.646
51.659
59.273
61.696
62.382
63.929
64.287
76.680
77.000
77.198
77.320
109.406
127.027
128.277
128.391
139.343
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
OH
N
Bn
H
H
O
O
6

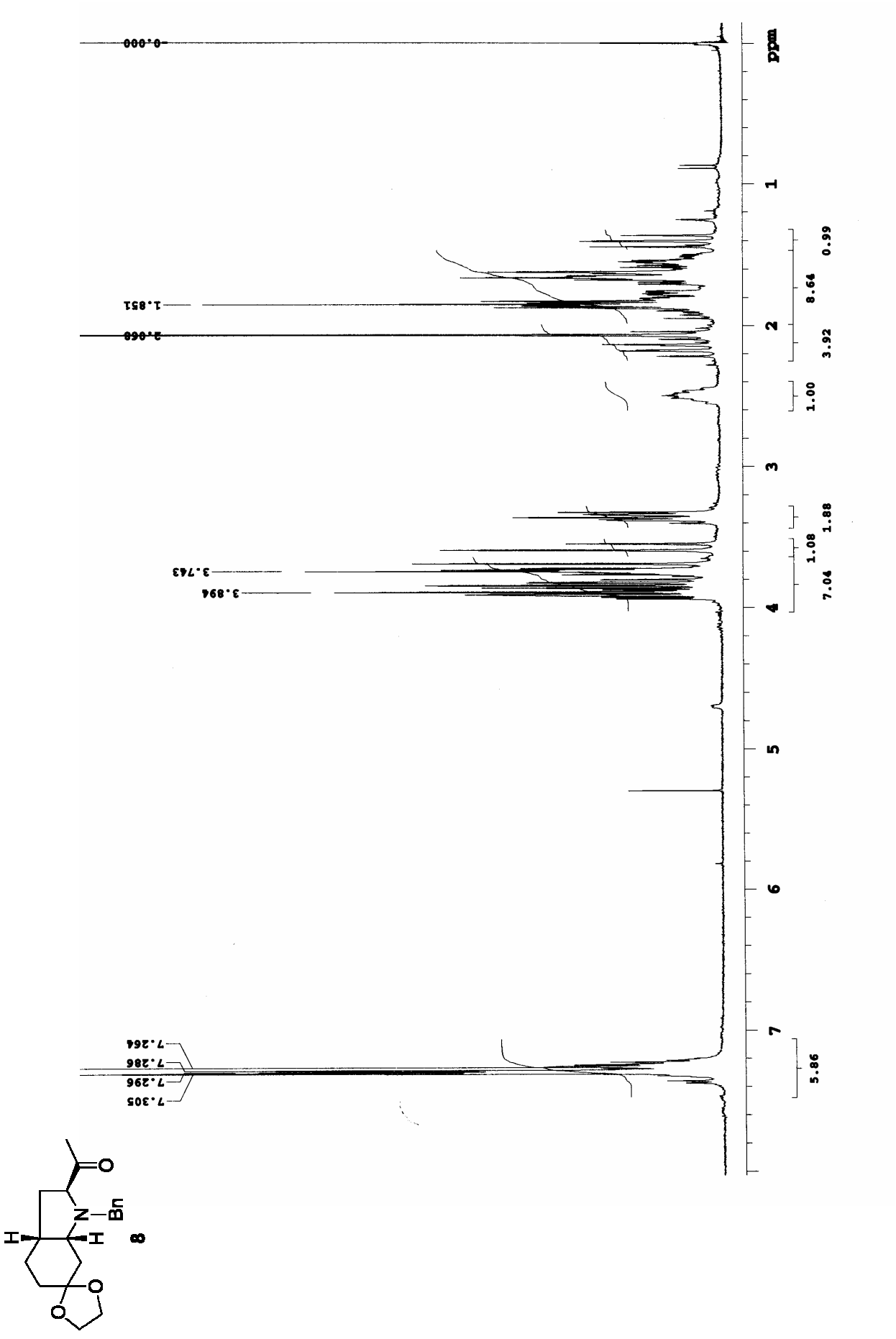

H1 / gCOSY / Mercury-400
cdcl3/Temp: 25C /N reg: M40004-010404165
212
Usuari: san / Mostra: yb2f
Nom: MARISA MENA CERVIGON
Data:02/04/04 / Sist automatic
exp3 gCOSY
SAMPLE FLAGS nn
date Apr 2 2004 hs nn
solvent cdcl3 sspul n
sample auto_01Apr2~ hsglvj 1005
004-21:33:29 SPECIAL
ACQUISITION temp 25.0
sw 3876.0 gain 28
at 0.132 spin 0
np 1024 F2 PROCESSING
fb not used sb -0.066
ss 16 sbs not used
d1 1.000 fn 2048
nt 8 f1 PROCESSING
2D ACQUISITION sb1 -0.066
sw1 3876.0 sbs1 not used
ni 256 proc1 lp
TRANSMITTER H1 fn1 2048
tn DISPLAY
sfrq 400.124 sp -86.7
tof -528.6 wp 1947.5
tpwr 58 sp1 413.4
pw 12.400 wp1 1360.2
GRADIENTS rf1 465.6
gzlvl1 1005 rfp 465.6
gt1 0.001000 rfl1
gstab 0.000500 rfp1
DECOUPLER PLOT 153.0
dn C13 wc 6.2
dm nnn sc 153.0
wc2 0
sc2 282
vs 9
th
al cdc av
F2 (ppm)
F1 (ppm)

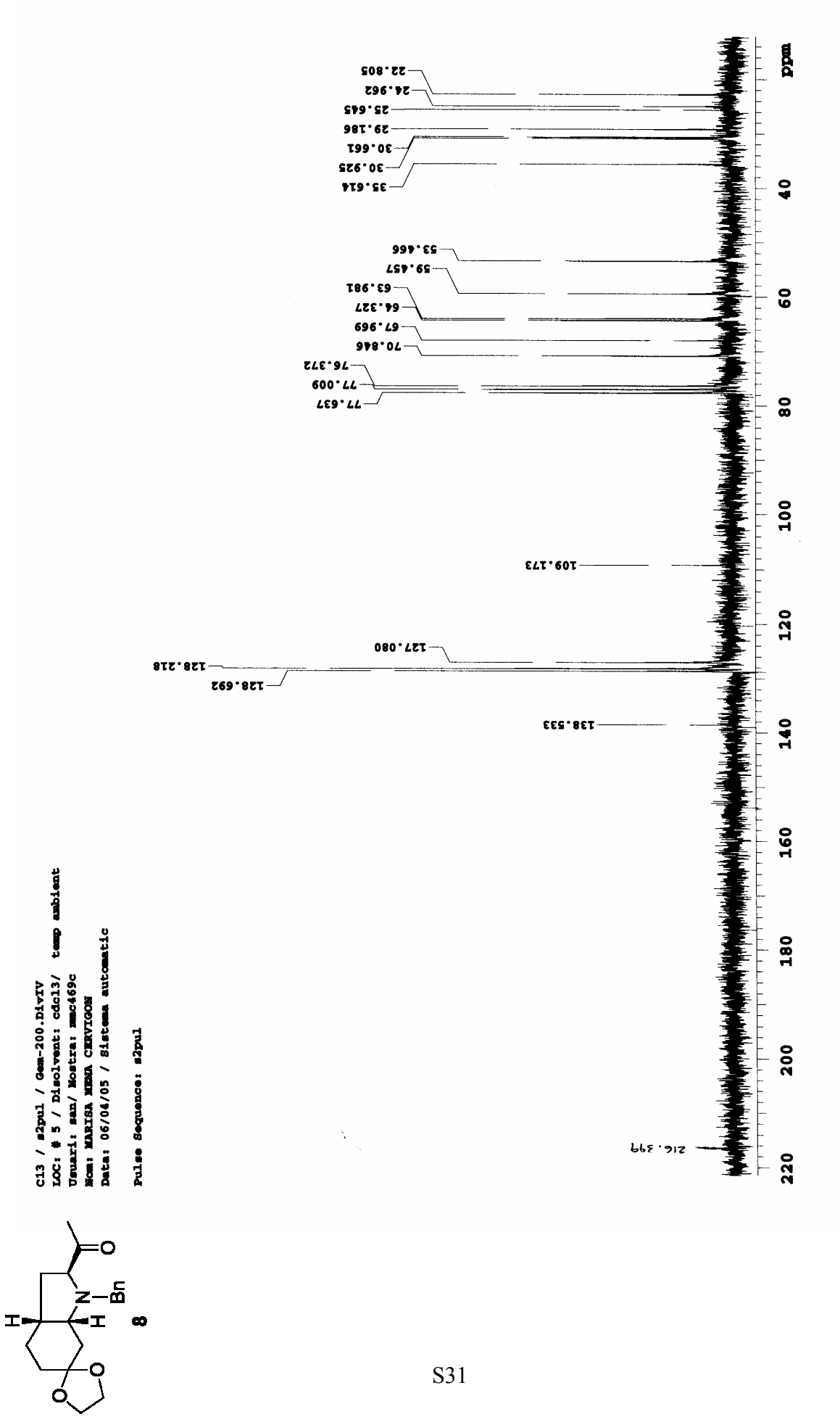

H
N
Bn
H
OH
O
O

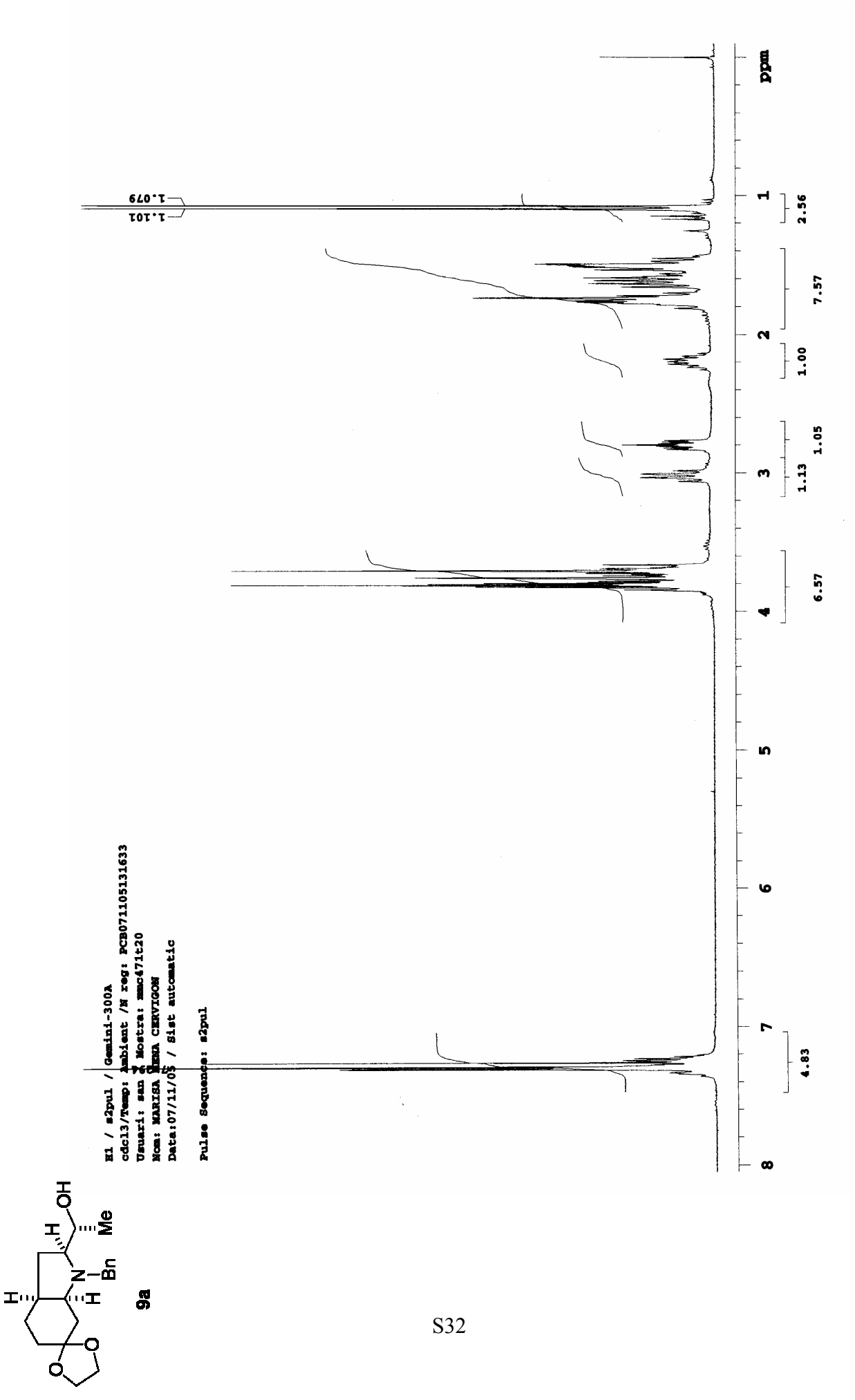
6

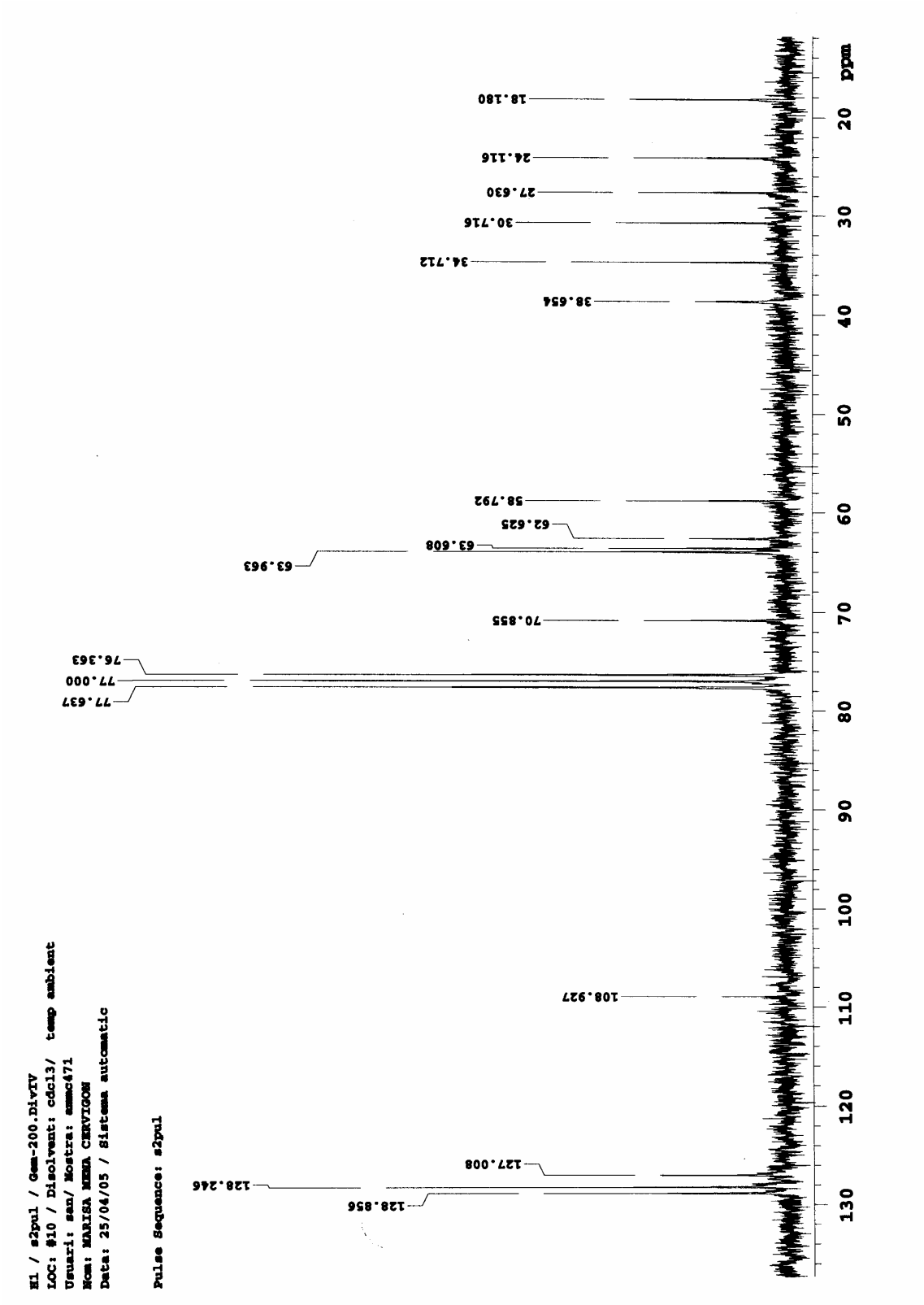

7.300
7.286
5.294
3.880
3.877
3.043
1.703
ppm
1
2
3
4
5
6
7
5.66
1.18
5.75
1.00
1.00
3.97
1.05
1.24
6.92
O
N
Bn
H
H
O
O
7

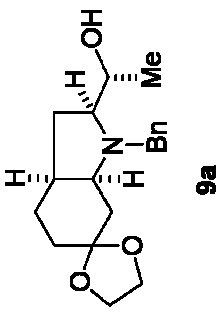

C13 / s2pul / Gem-200.DivIV
LOC: # 4 / Disolvent: cdcl3/ temp ambient
Usuari: san/ Mostra: mmc468c
Mem: MARISA MEMA CERVIGON
Data: 06/04/05 / Sistema automatic
Pulse Sequence: s2pul
213.240
138.679
129.402
128.109
127.117
108.854
77.637
77.000
76.363
74.933
64.036
63.062
59.967
38.190
35.659
33.274
30.980
24.953
24.234
ppm
220
200
180
160
140
120
100
80
60
40
N
Bn
H
H
O
O
O
7


0.000
1.851
2.060
3.743
3.894
7.264
7.286
7.296
7.305
ppm
1
2
3
4
5
6
7
0.99
8.64
3.92
1.00
1.88
1.08
7.04
5.86
O
N
Bn
H
H
O
O
8

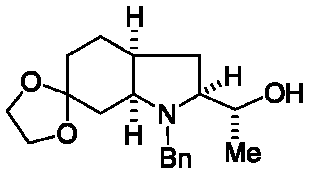

C13 / s2pul / Gem-200.DivIV
LOC: # 5 / Disolvent: cdcl3/ temp ambient
Usuari: san/ Mostra: mmc469c
Mem: MARISA MEMA CERVIGON
Data: 06/04/05 / Sistema automatic
Pulse Sequence: s2pul
ppm
216.399
138.533
128.692
128.218
127.080
109.173
77.637
77.009
76.372
70.846
67.969
64.327
63.981
59.457
53.466
35.614
30.925
30.661
29.186
25.645
24.962
22.805
N
Bn
H
H
O
O
O
8


9a
H1 / s2pul / Gemini-300A
cdcl3/Temp: Ambient /N reg: PCB071105131633
Usuari: san Mostra: smc471t20
Nom: MARISA MERA CERVIGON
Data:07/11/05 / Sist automatic
Pulse Sequence: s2pul
1.101
1.079
ppm
2.56
7.57
1.00
1.05
1.13
6.57
4.83


H1 / s2pul / Gem-200.DivTV
LOC: #10 / Disolvent: cdcl3/ temp ambient
Usuari: san/ Mostra: smmc471
Mem: MARISA MEMA CERVIGOM
Data: 25/04/05 / Sistema automatic
Pulse Sequence: s2pul
18.180
24.116
27.630
30.716
34.712
38.654
58.792
62.625
63.608
63.963
70.855
76.363
77.000
77.637
108.927
127.008
128.246
128.856
ppm

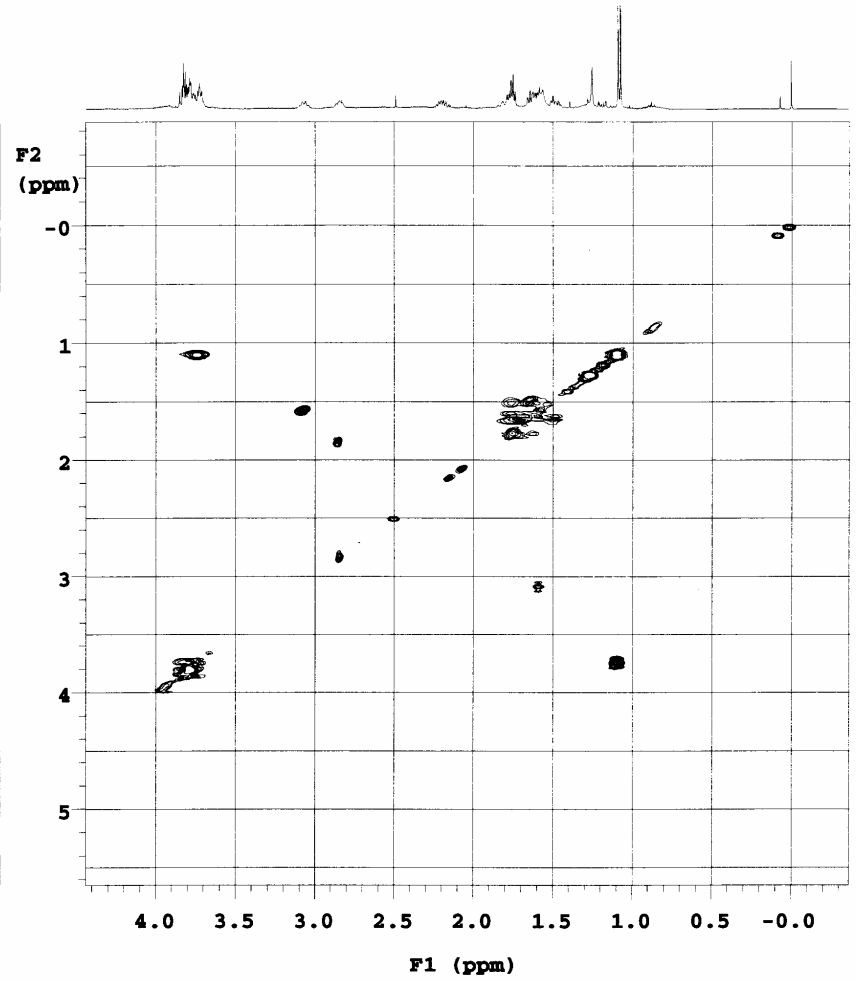

OH
H
Me
N
Bn
H
H
O
O

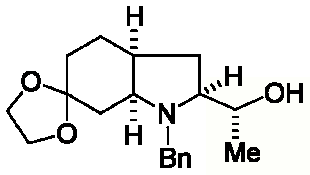
9a



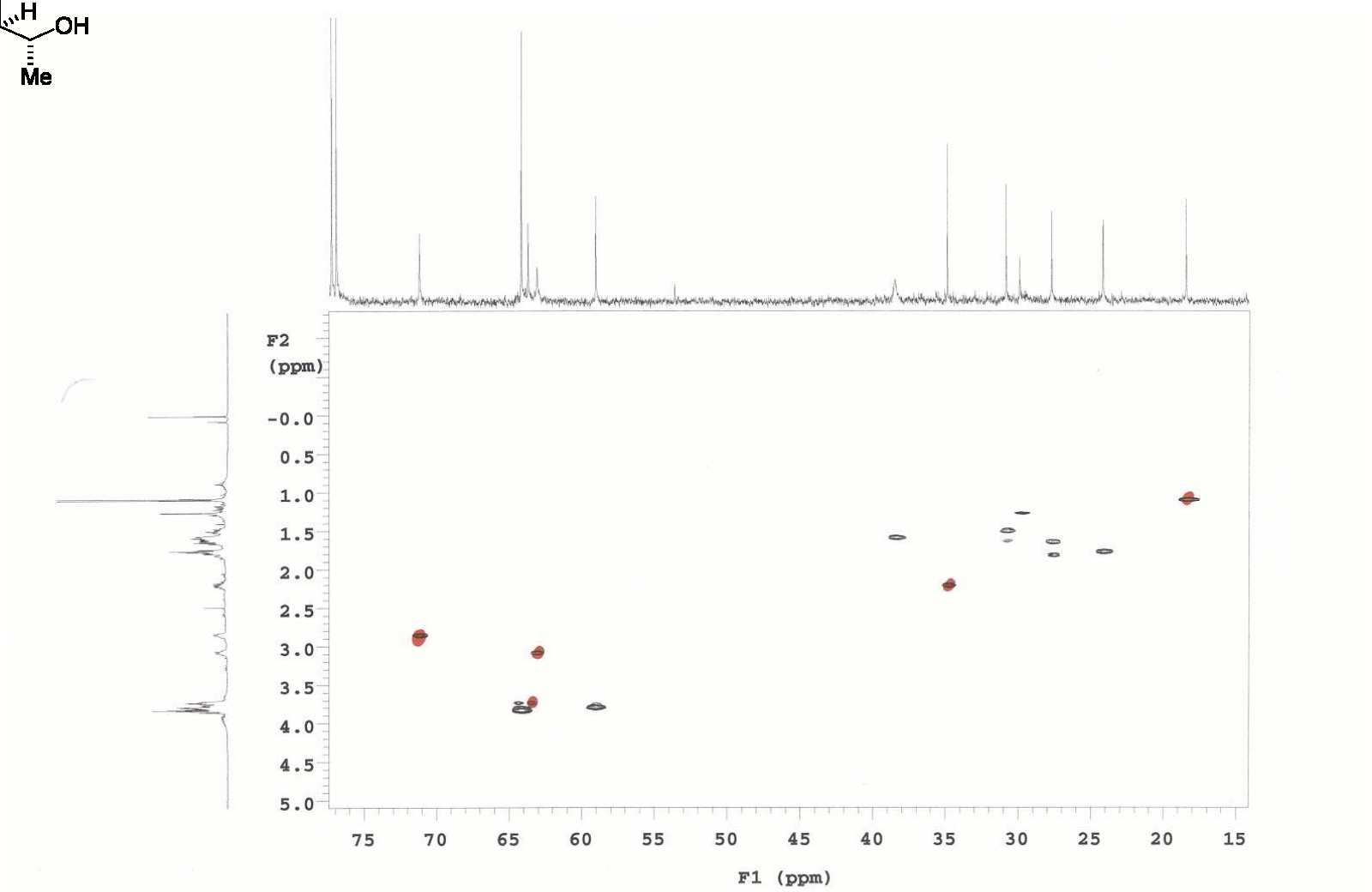
9a

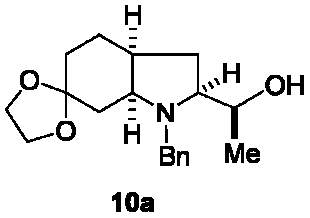
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-3560
Usuari: san / Mostra: mmc472t19a60
Nom: MARISA MENA CERVIGON
Data:23/09/05 / Sist automatic

exp5  gCOSY

      SAMPLE                FLAGS
date    Sep 23 2005   hs                 nn
solvent       cdcl3   sspul               n
sample auto_Custom~   hsglvl          1002
       Q_23Sep2005          SPECIAL
   ACQUISITION        temp             25.0
sw          5211.0    gain               26
at           0.150    spin                0
np            1564      F2 PROCESSING
fb        not used    sb             -0.075
ss              16    sbs          not used
d1           1.000    fn               2048
nt               2      F1 PROCESSING
  2D ACQUISITION      sb1            -0.049
sw1         5211.0    sbs1         not used
ni             256    proc1              lp
  PRESATURATION       fn1              2048
satmode          n          DISPLAY
satfrq           0    sp             -348.3
satdly           0    wp             2608.1
satpwr           0    sp1            -144.5
   TRANSMITTER        wp1            1920.4
tn              H1    rf1             592.8
sfrq       400.114    rfp                0
tof          -17.4    rf11            592.8
tpwr            58    rfp1               0
pw          12.200            PLOT
    GRADIENTS         wc             131.8
gzlvl1          1002  sc               6.2
gt1       0.001000    wc2            131.8
gstab     0.000500    sc2                0
    DECOUPLER         vs               243
dn              C13   th                14
dm              nnn   ai  cdc  av
```



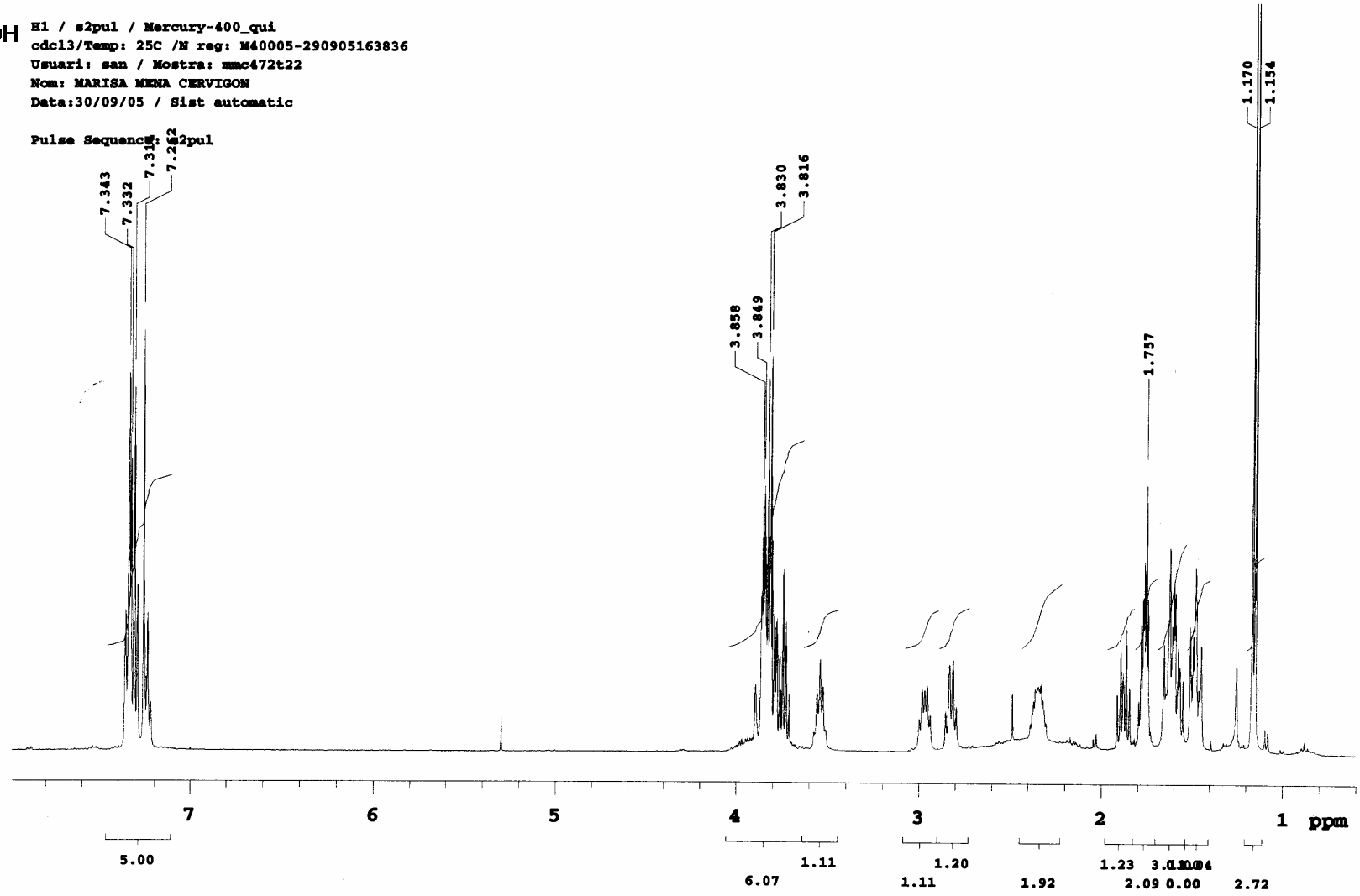

H
O
H
OH
N
O
H
Bn
Me

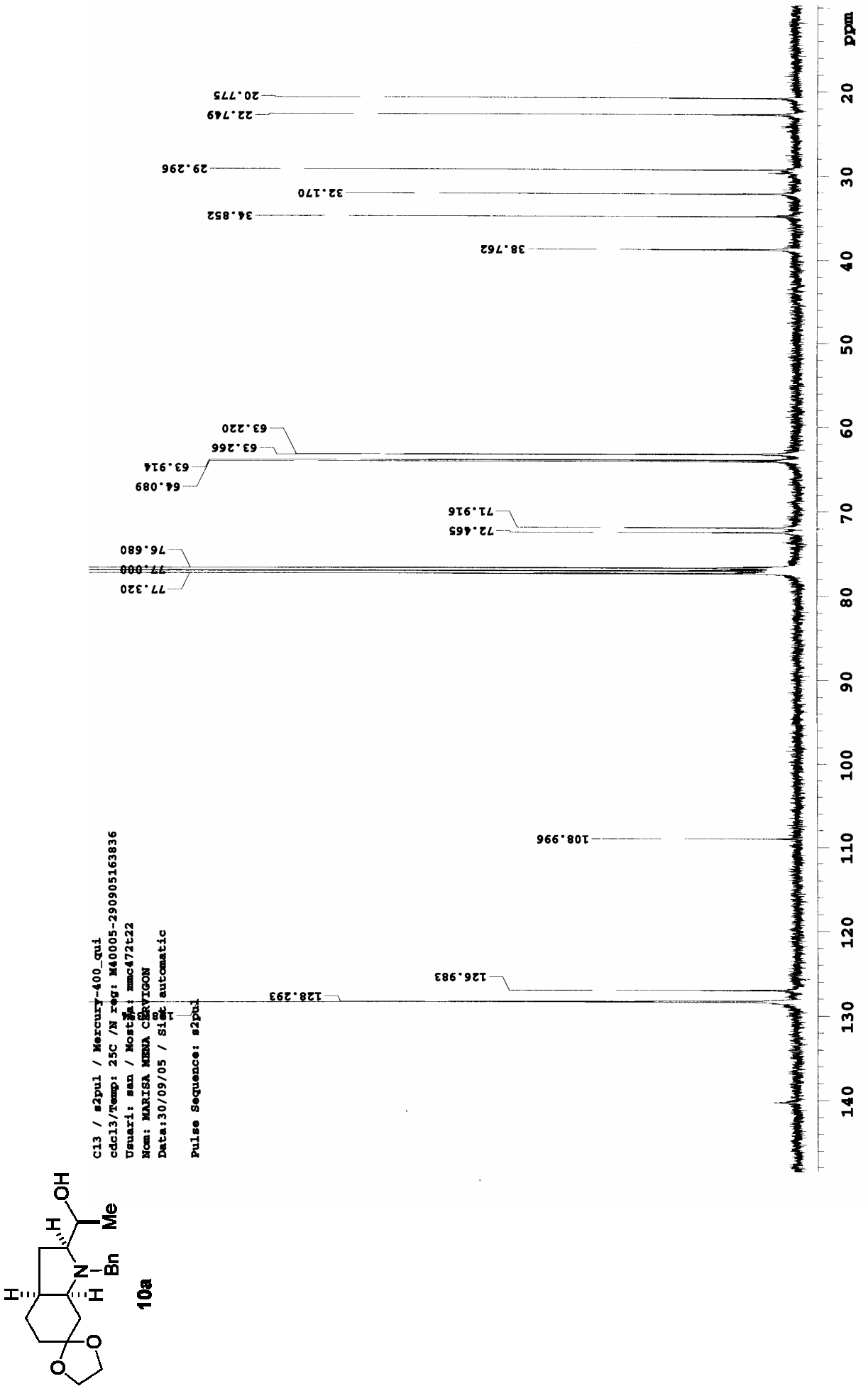
9a

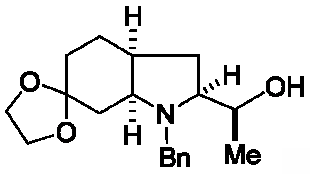

F2
(ppm)
-0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
75
70
65
60
55
50
45
40
35
30
25
20
15
F1 (ppm)


H
O
O
H
N
Bn
H
OH
Me

10a

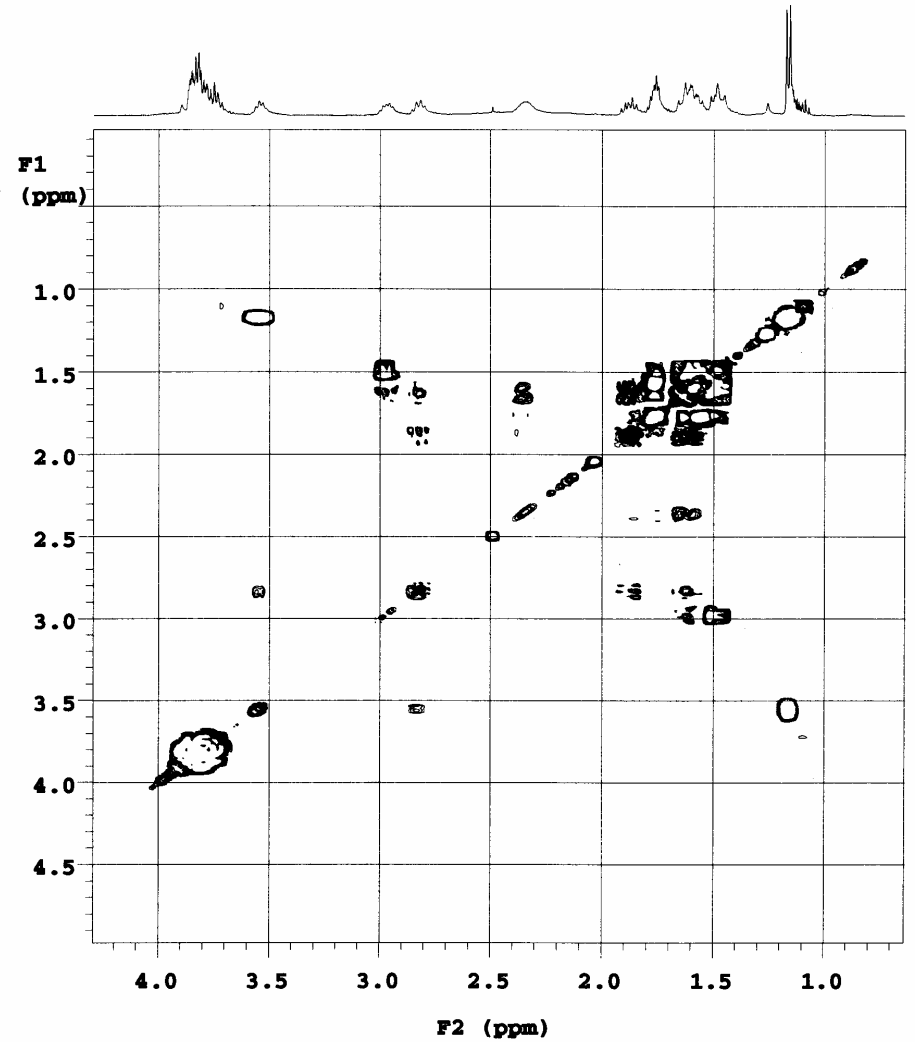

H1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-290905163836
Usuari: san / Mostra: mmc472t22
Nom: MARISA MENA CERVIGON
Data:30/09/05 / Sist automatic
Pulse Sequence: s2pul
7.343
7.332
7.316
7.262
3.858
3.849
3.830
3.816
1.757
1.170
1.154
7
6
5
4
3
2
1
ppm
5.00
6.07
1.11
1.11
1.20
1.92
1.23
2.09
0.00
2.72

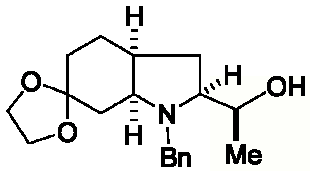

C13 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-29090516383
Usuari: sam / Mostra: mmc472t22
Nom: MARISA MIRA CERVIGON
Data:30/09/05 / Slot automatic
Pulse Sequence: s2pul
77.320
77.008
76.680
64.089
63.914
63.266
63.220
72.465
71.916
38.762
34.852
32.170
29.296
22.749
20.775
128.293
126.983
108.996
ppm
10a



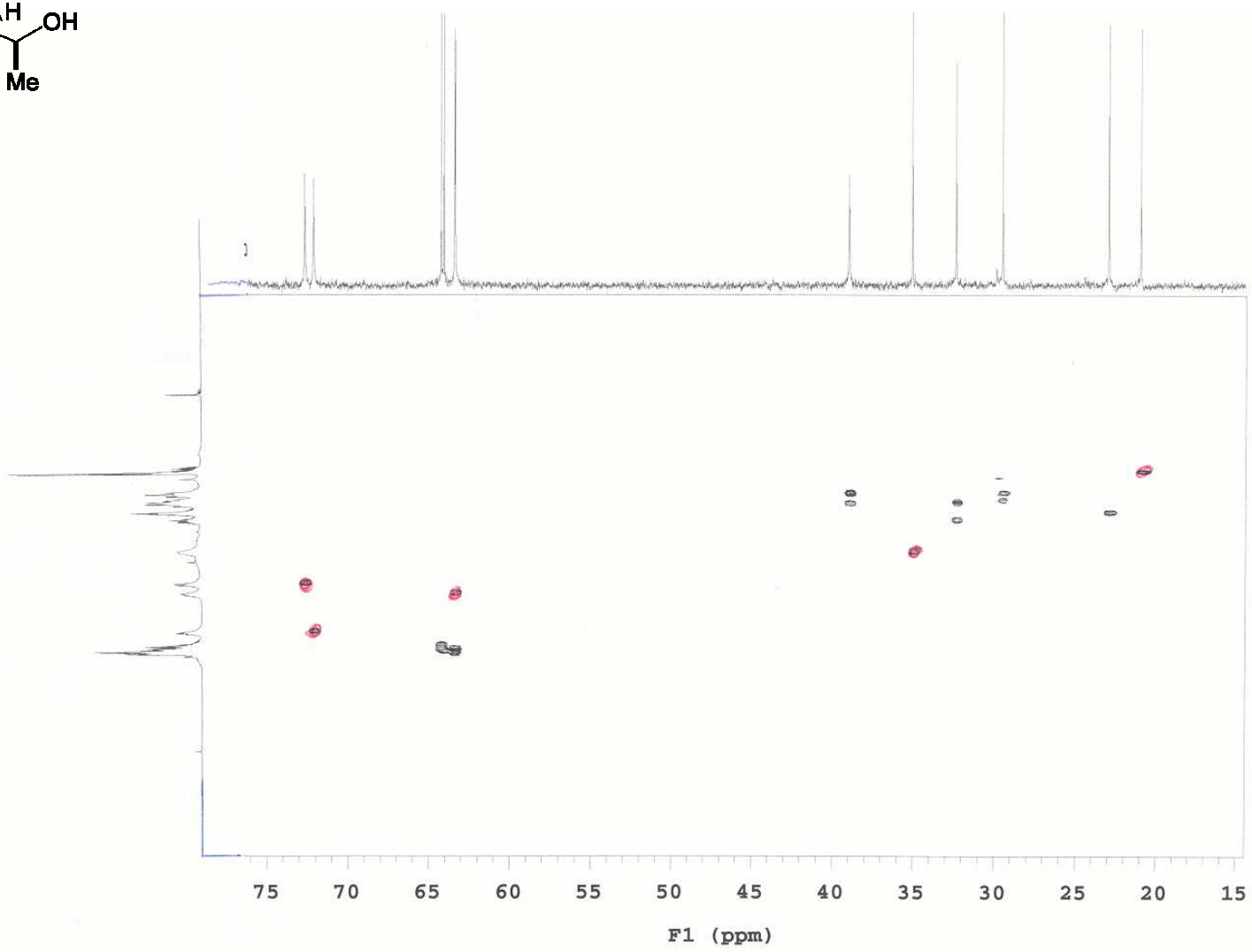
10a

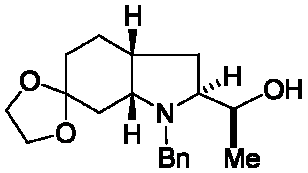
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-290905163
836
Usuari: san / Mostra: mmc472t22
Nom: MARISA MENA CERVIGON
Data:30/09/05 / Sist automatic

exp22  gCOSY

      SAMPLE                FLAGS
date    Sep 30 2005  hs                nn
solvent       cdcl3  sspul            n
sample auto_Custom~  hsglvl         1002
       Q_30Sep2005=========SPECIAL
   ACQUISITION       temp          25.0
sw          5211.0   gain            28
at             0.150 spin             0
np              1564    F2 PROCESSING
fb         not used  sb           -0.075
ss                16  sbs        not used
d1             1.000 fn             2048
nt                 4    F1 PROCESSING
  2D ACQUISITION     sb1          -0.049
sw1         5211.0   sbs1       not used
ni              256  proc1           lp
  PRESATURATION     fn1            2048
satmode           n       DISPLAY
satfrq            0  sp            254.8
satdly            0  wp           1461.9
satpwr            0  sp1            18.1
   TRANSMITTER       wp1          1971.3
tn                H1  rf1           595.9
sfrq       400.114   rfp              0
tof          -17.1   rf11          593.2
tpwr              58  rfp1             0
pw            12.200          PLOT
    GRADIENTS        wc            131.8
gslvl1          1002  sc              6.2
gt1        0.001000  wc2           131.8
gstab      0.000500  sc2              0
    DECOUPLER        vs              493
dn                C13  th               8
dm                nnn  ai  cdc  av
```



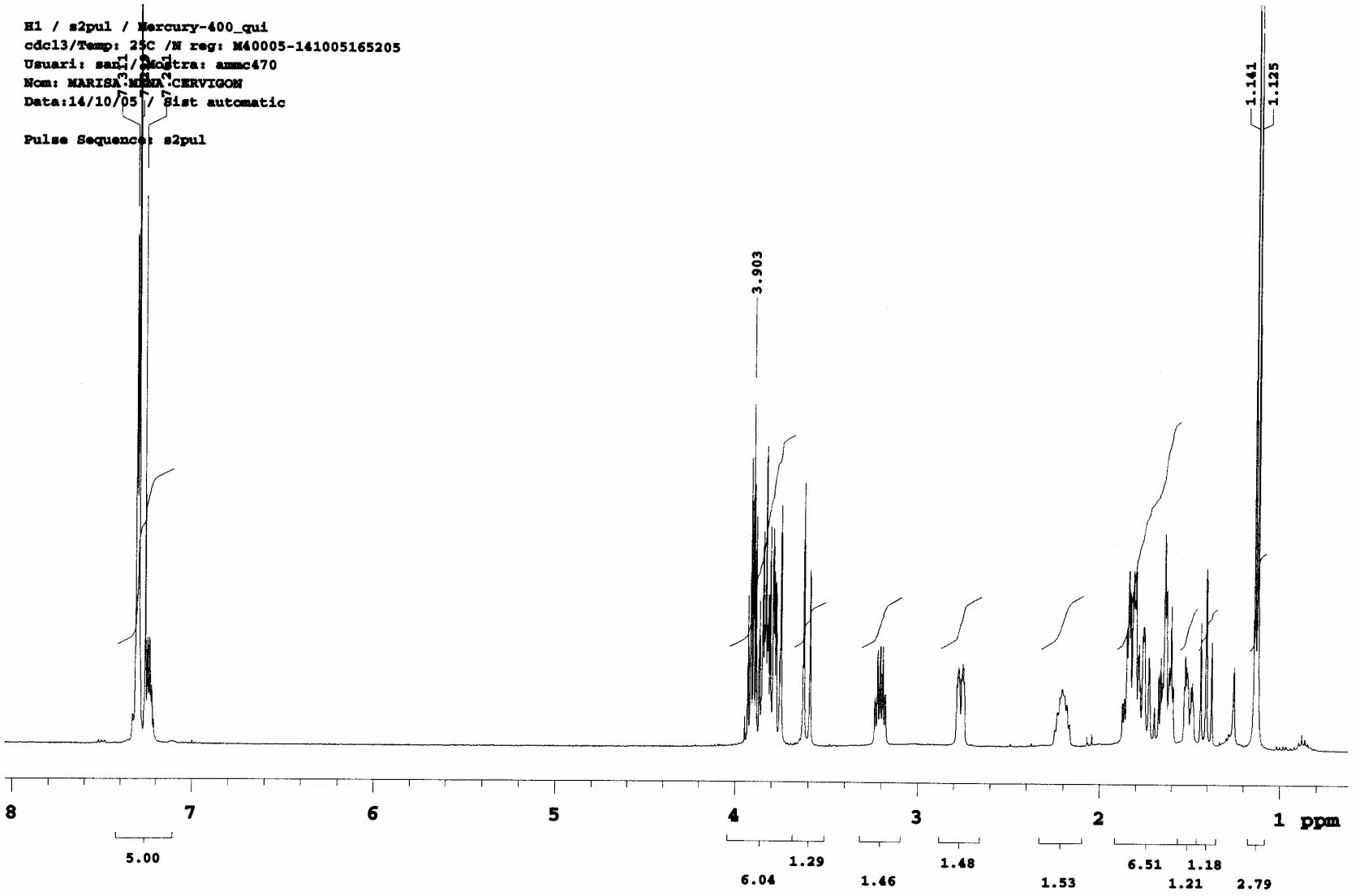


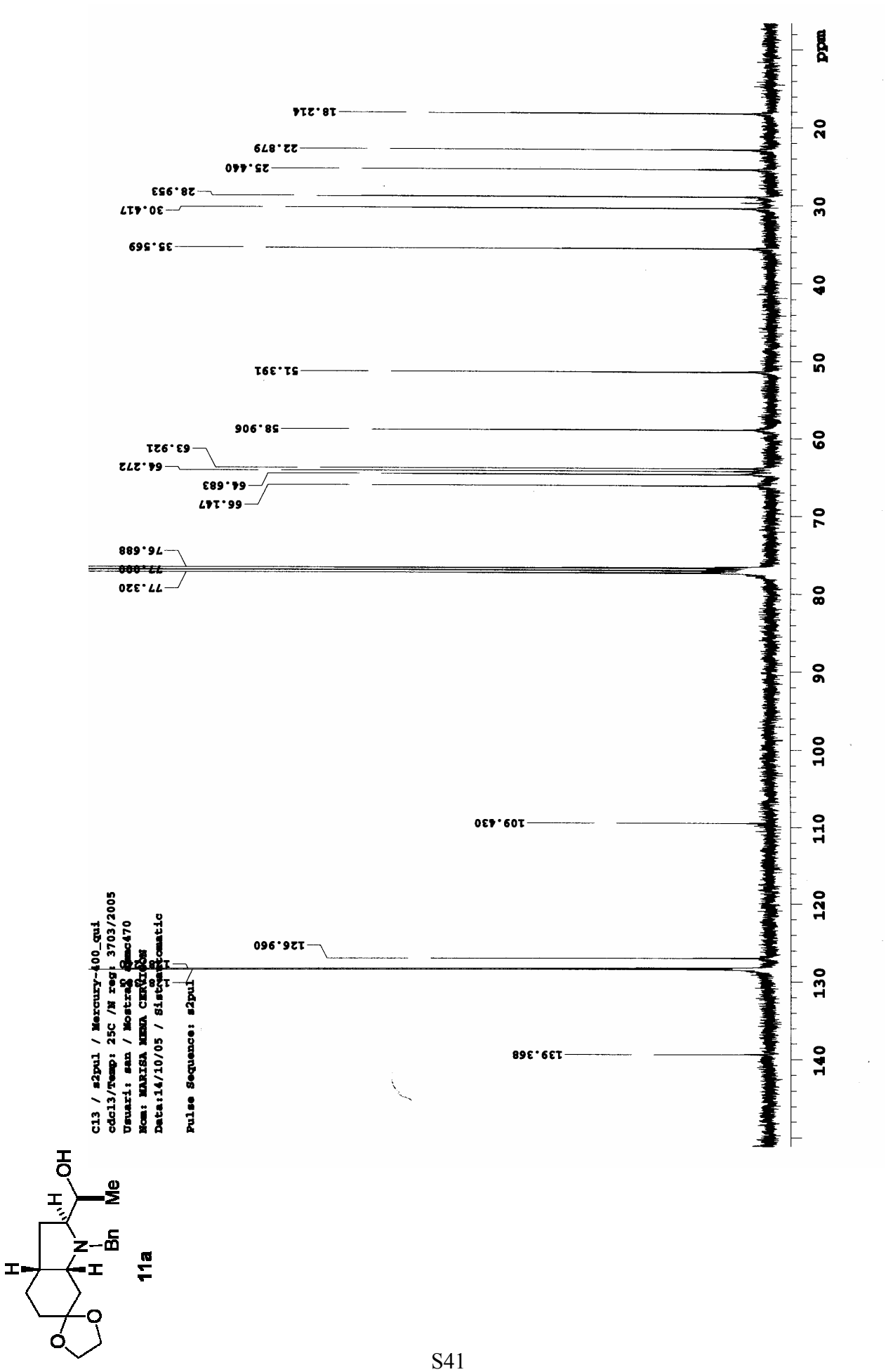
10a

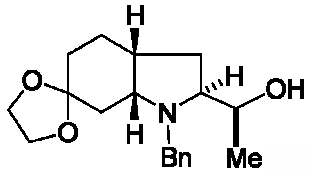



H
O
O
H
N
H
Bn
Me
OH

11a

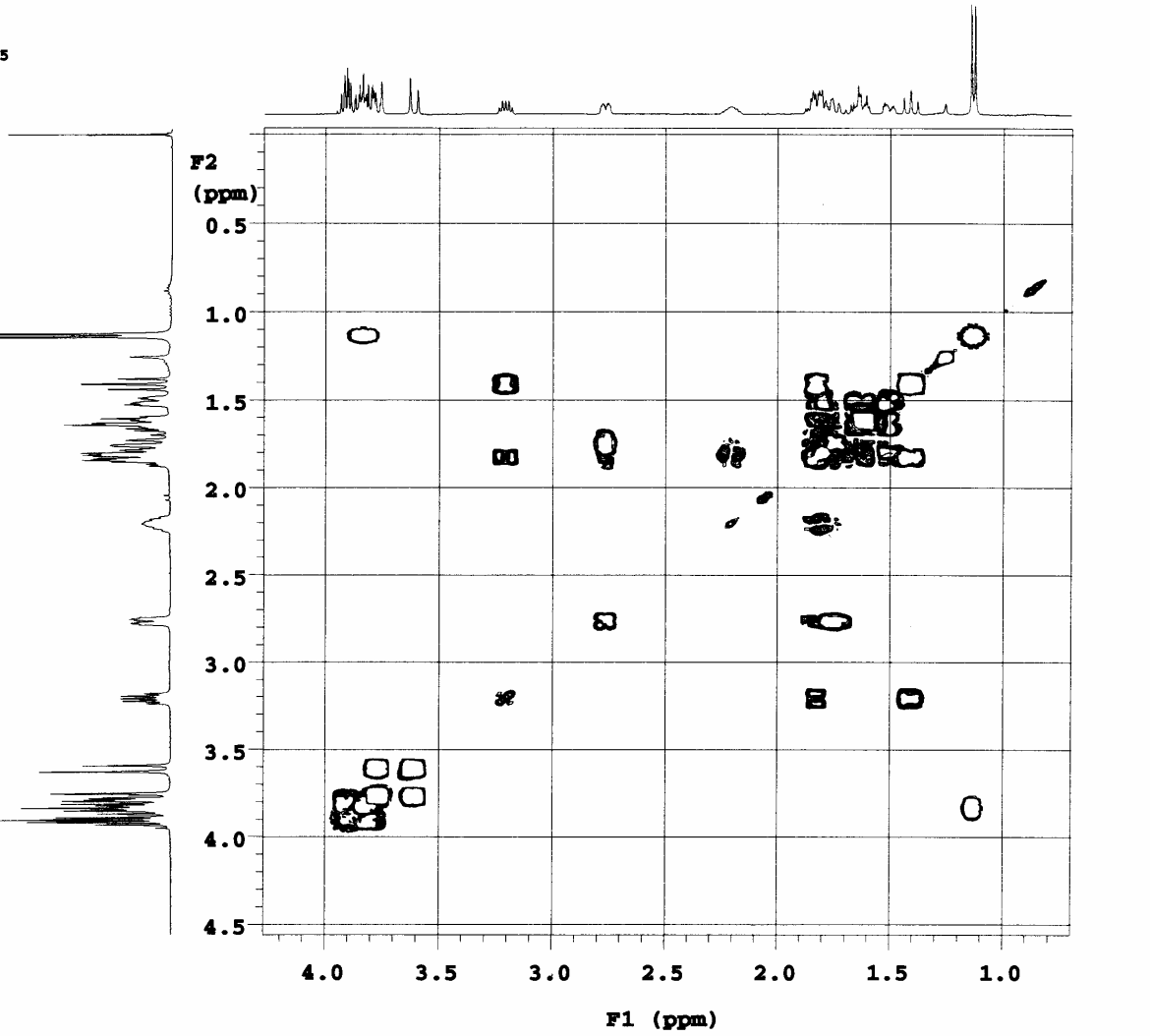

H1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-141005165205
Usuari: sant/Mostra: ammc470
Nom: MARISA MEMA CERVIGON
Data:14/10/05 / Sist automatic
Pulse Sequence: s2pul
3.903
1.141
1.125
8
7
6
5
4
3
2
1 ppm
5.00
6.04
1.29
1.46
1.48
1.53
6.51
1.21
1.18
2.79

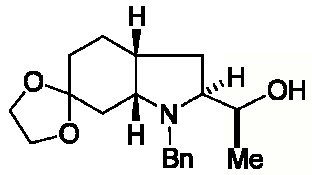

C13 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: 3703/2005
Usuari: sam / Mostra: Qmc470
Nom: MARISA MEMA CEF Carbon
Data:14/10/05 / Sistema:automatic
Pulse Sequence: s2pul
18.214
22.879
25.440
28.953
30.417
35.569
51.391
58.906
63.921
64.272
64.683
66.147
76.688
77.320
109.430
126.960
139.368
ppm
11a



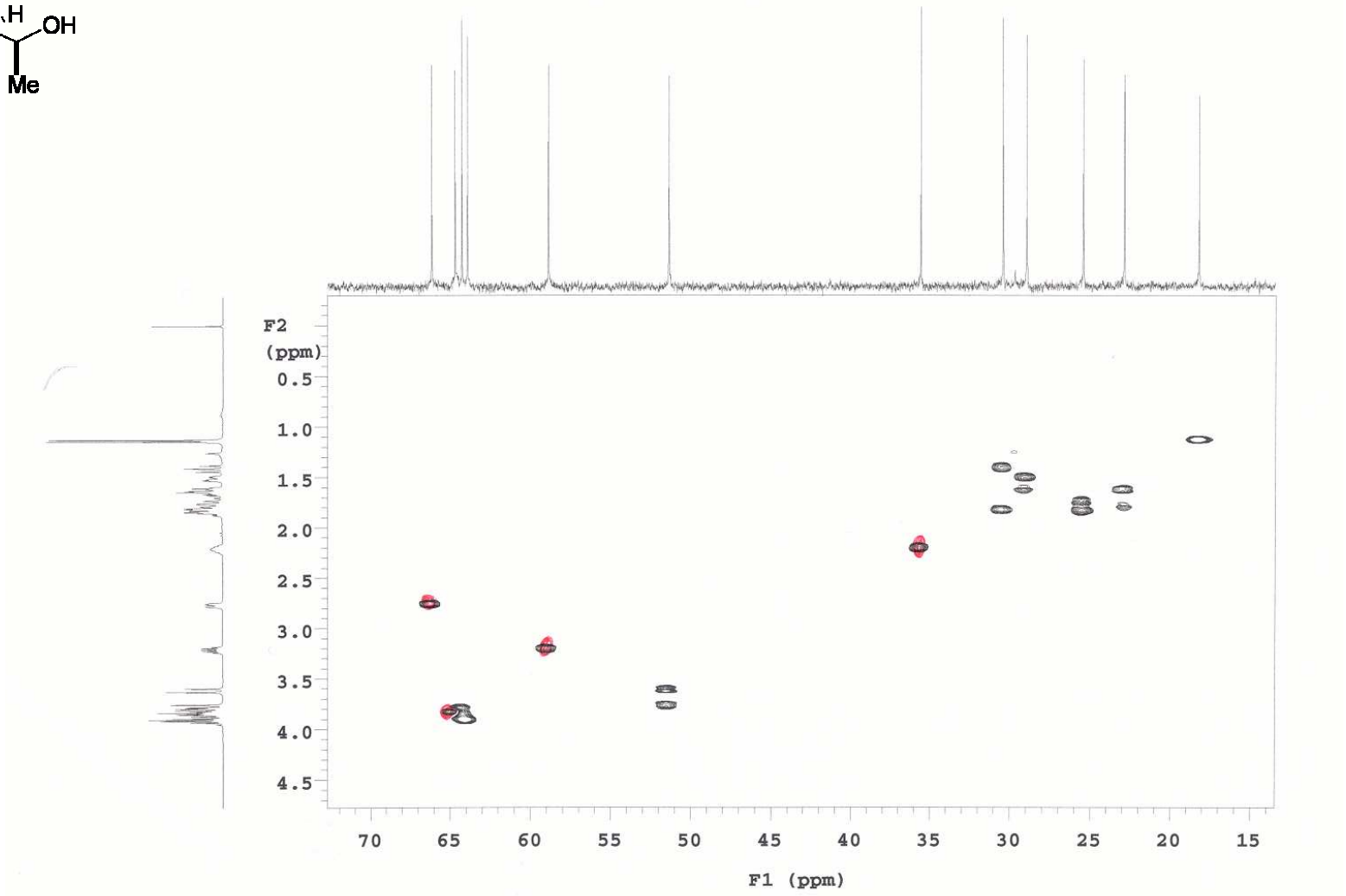
11a

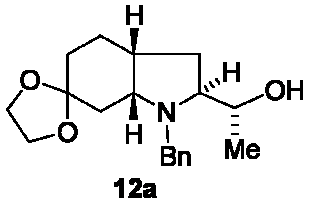
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-141005165
205
Usuari: san / Mostra: amnc470
Nom: MARISA MENA CERVIGON
Data:14/10/05 / Sist automatic

exp5  gCOSY

      SAMPLE                FLAGS
date    Oct 14 2005   hs                nn
solvent       cdcl3   sspul              n
sample auto_Custom~   hsglvl          1002
Q_14Oct2005-17:48:~       SPECIAL
                 15   temp            25.0
   ACQUISITION        gain              28
sw           3906.2   spin               0
at            0.150     F2 PROCESSING
np             1172   sb             -0.075
fb         not used   sbs         not used
ss               16   fn               2048
d1            1.000     F1 PROCESSING
nt                4   sb1            -0.066
  2D ACQUISITION      sbs1        not used
sw1          3906.2   proc1              lp
ni              256   fn1              2048
  PRESATURATION            DISPLAY
satmode           n   sp               -13.6
satfrq            0   wp              1836.7
satdly            0   sp1              280.5
satpwr            0   wp1             1428.1
   TRANSMITTER        rf1              483.2
tn                H1   rfp                0
sfrq         400.113   rf11             483.2
tof           -553.6   rfp1               0
tpwr              58          PLOT
pw            12.200   wc               131.8
    GRADIENTS          sc                 6.2
gzlvl1          1002   wc2              131.8
gt1         0.001000   sc2                0
gstab       0.000500   vs                 361
    DECOUPLER          th                 8
dn                C13   ai  cdc  av
dm                nnn
```



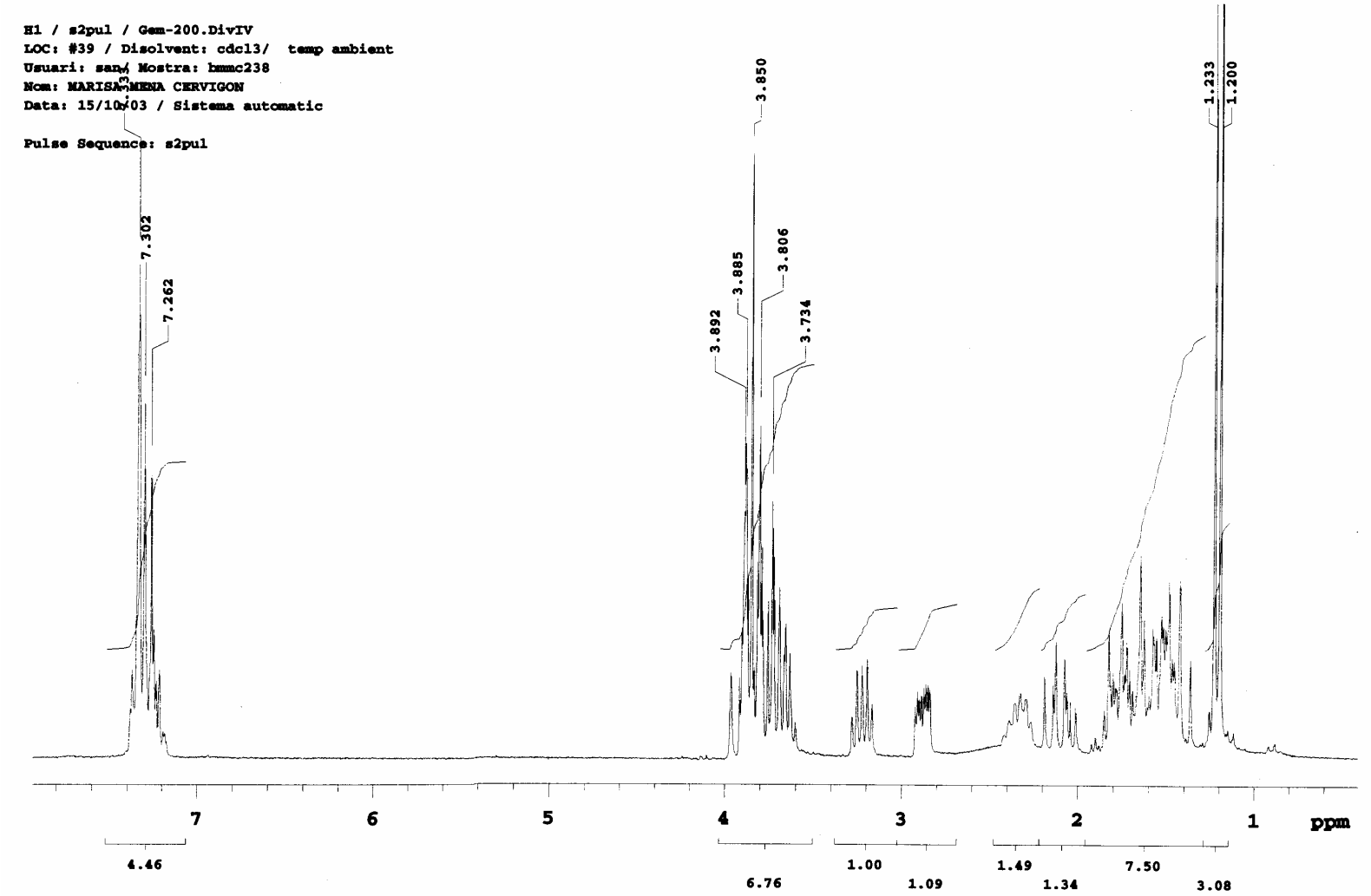

H
O
H
OH
N
O
H
Bn
Me

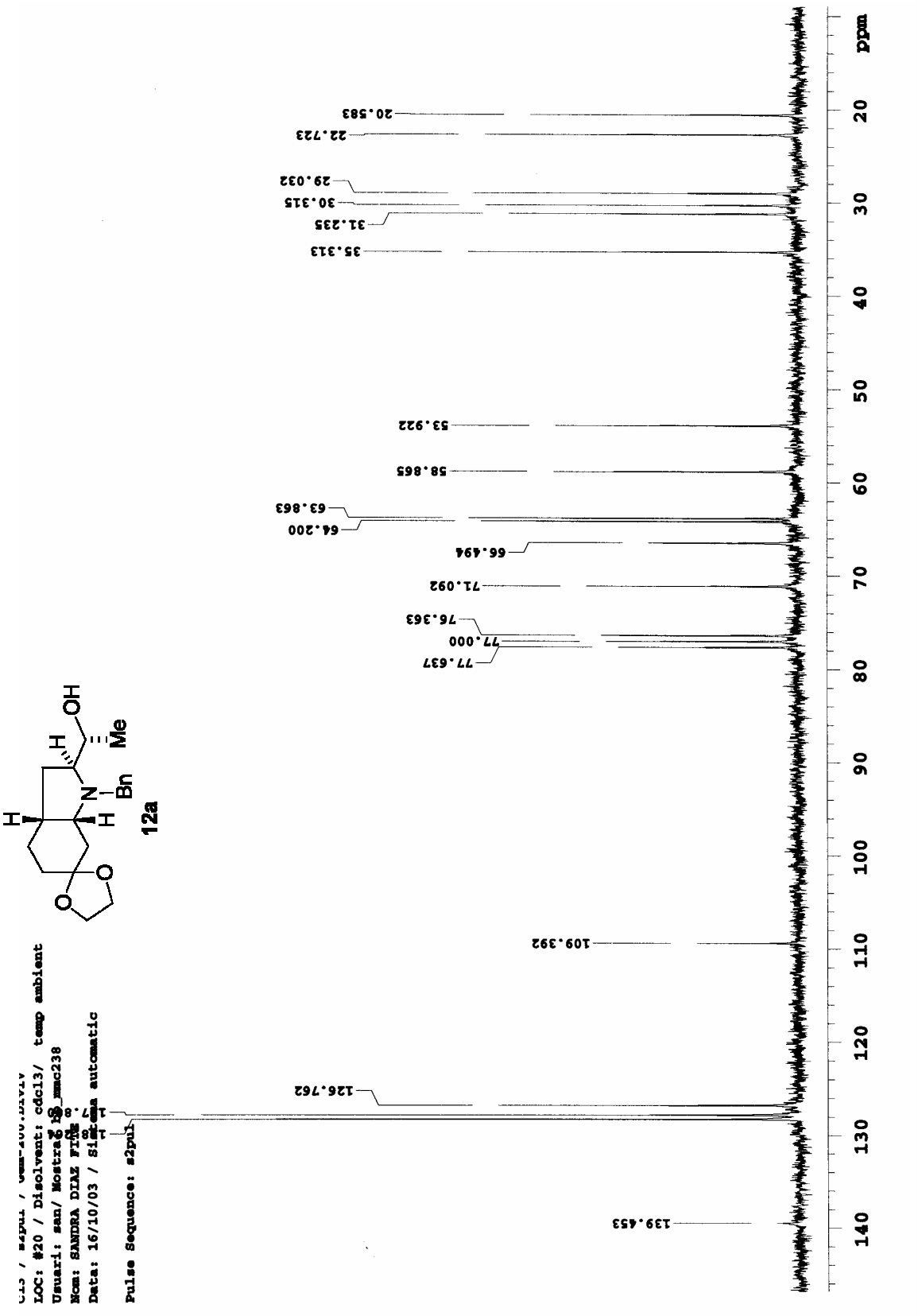
11a

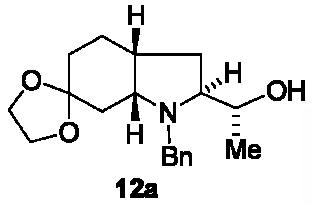

F2
(ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
70
65
60
55
50
45
40
35
30
25
20
15
F1 (ppm)


H
O
H
OH
N
O
H
Bn
Me

12a

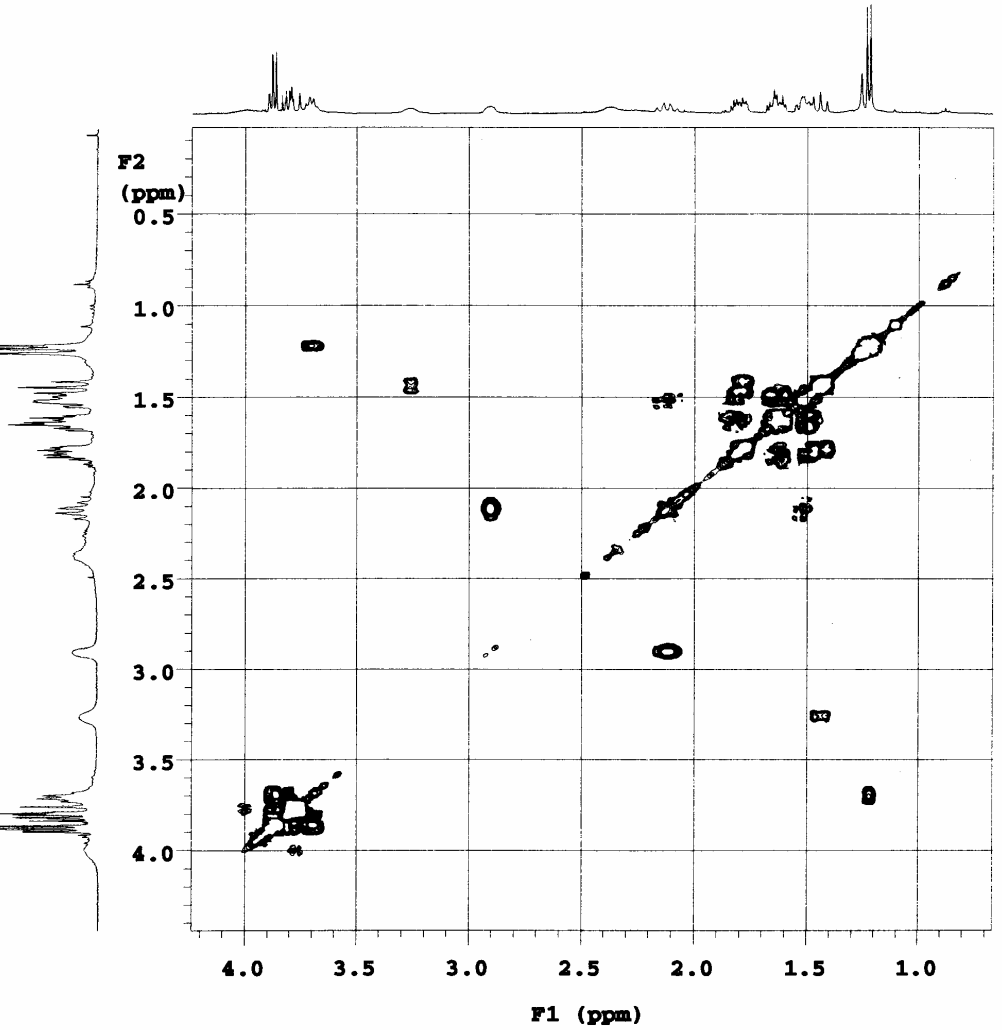

H1 / s2pul / Gem-200.DivIV
LOC: #39 / Disolvent: cdcl3/ temp ambient
Usuari: sam/ Mostra: bmmc238
Nom: MARISA MENA CERVIGON
Data: 15/10/03 / Sistema automatic
Pulse Sequence: s2pul
7.302
7.262
3.892
3.885
3.850
3.806
3.734
1.233
1.200
7
6
5
4
3
2
1
ppm
4.46
6.76
1.00
1.09
1.49
1.34
7.50
3.08

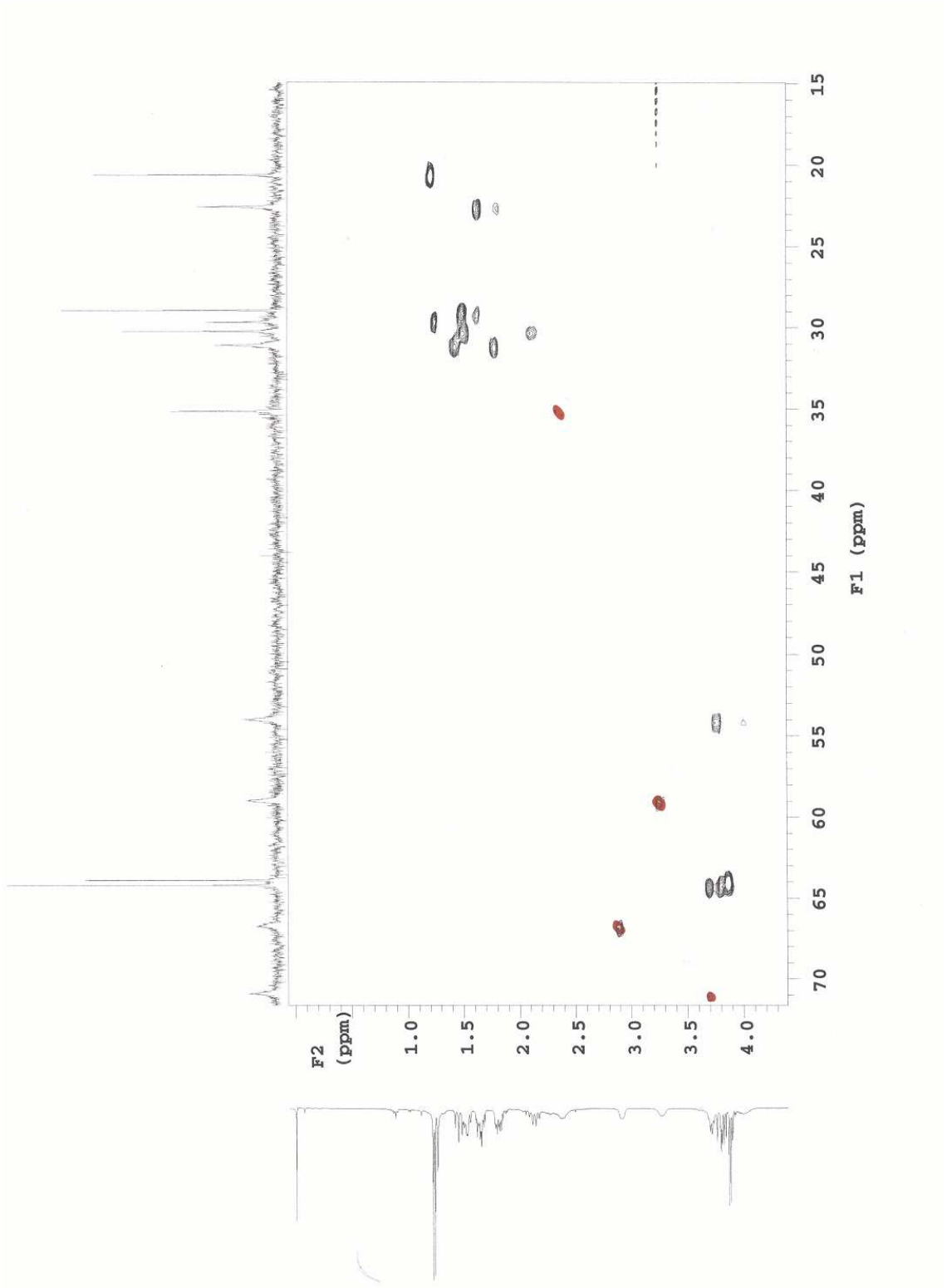

20.583
22.723
29.032
30.315
31.235
35.313
53.922
58.865
63.863
64.200
66.494
71.092
76.363
77.000
77.637
109.392
126.762
139.453
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
OH
Me
Bn
N
H
H
O
O
12a
LOC: #20 / Disolvent: cdcl3/ temp ambient
Usuari: san/ Mostra: sb_mmc238
Nom: SANDRA DIAZ FIDA
Data: 16/10/03 / Sistema automatic
Pulse Sequence: s2pul

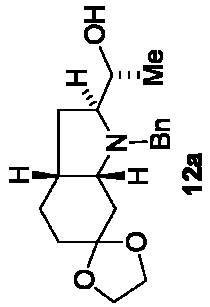


12a

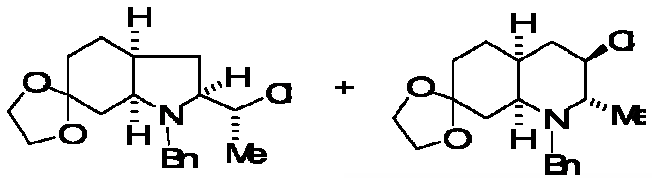
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-211005163
841
Usuari: san / Mostra: bexooh
Nom: MARISA MENA CERVIGON
Data:21/10/05 / Sist automatic

exp6  gCOSY

      SAMPLE                FLAGS
date   Oct 21 2005  hs                nn
solvent       cdcl3  sspul             n
sample auto_Custom~  hsglvl          1002
Q_21Oct2005-18:41:~       SPECIAL
                55  temp           25.0
   ACQUISITION      gain             32
sw          3937.0  spin              0
at           0.150    F2 PROCESSING
np            1182  sb            -0.075
fb        not used  sbs        not used
ss              16  fn              2048
d1           1.000    F1 PROCESSING
nt               8  sb1           -0.065
  2D ACQUISITION    sbs1       not used
sw1         3937.0  proc1             lp
ni             256  fn1             2048
  PRESATURATION           DISPLAY
satmode          n  sp              13.2
satfrq           0  wp            1762.6
satdly           0  sp1            267.2
satpwr           0  wp1           1427.8
   TRANSMITTER      rf1            487.1
tn              H1  rfp               0
sfrq       400.113  rf11           487.1
tof         -538.3  rfp1              0
tpwr            58          PLOT
pw          12.200  wc             131.8
    GRADIENTS       sc               6.2
gzlv11       1002  wc2            131.8
gt1      0.001000  sc2               0
gstab    0.000500  vs              369
    DECOUPLER       th                8
dn             C13  ai  cdc  av
dm             nnn
```



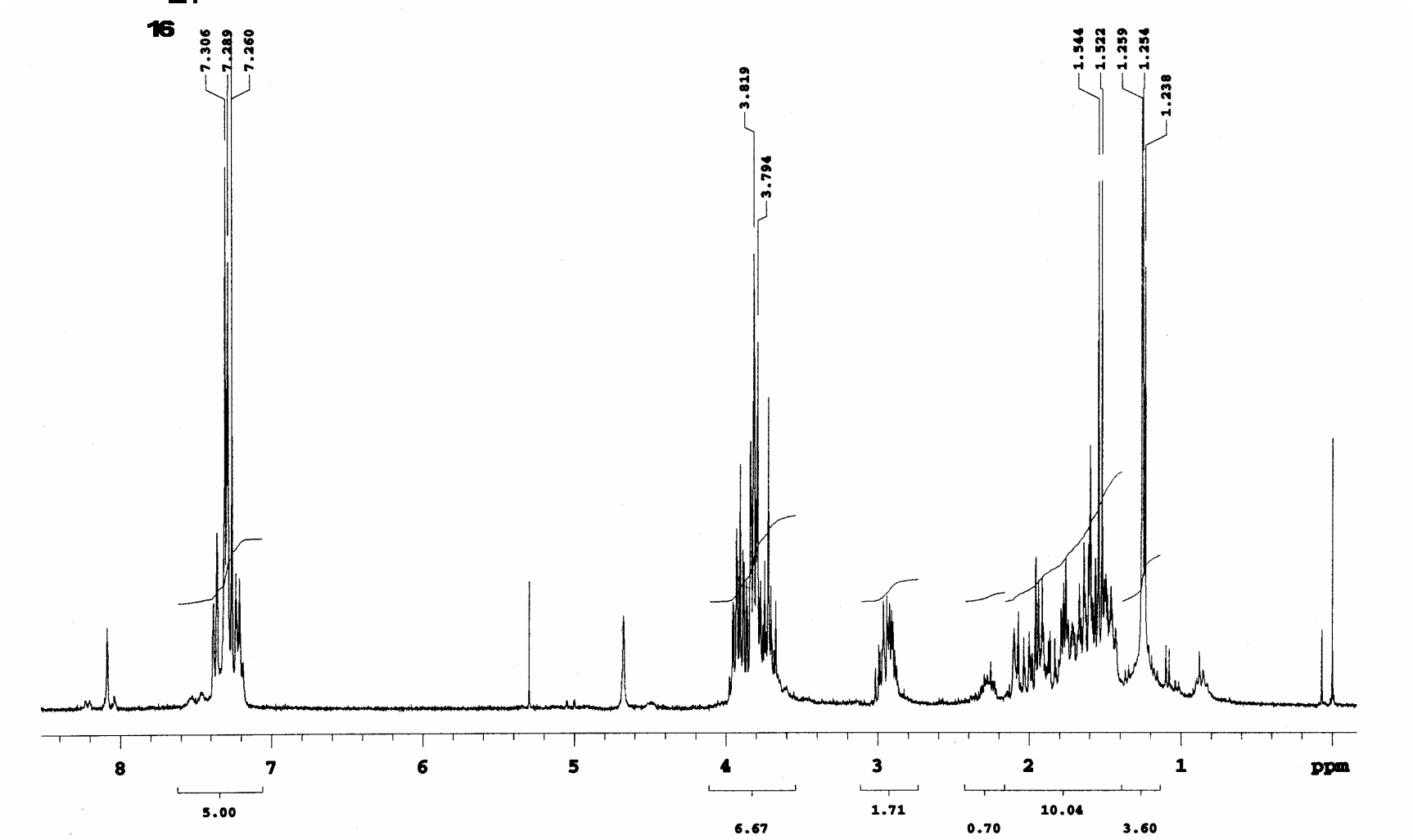

F2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
F1 (ppm)
15
20
25
30
35
40
45
50
55
60
65
70


OH
H
Me
N
Bn
H
H
O
O
O

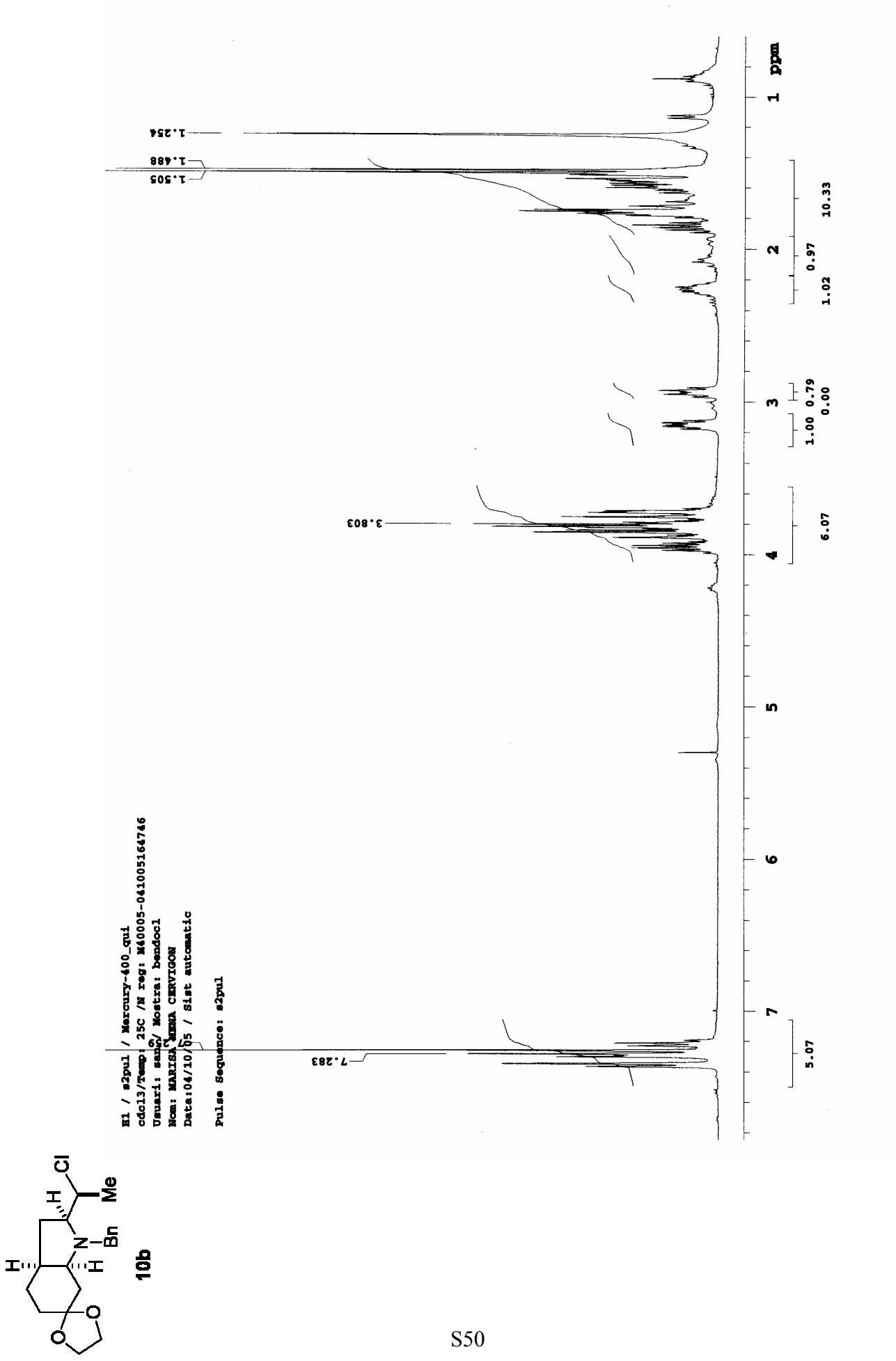
12a

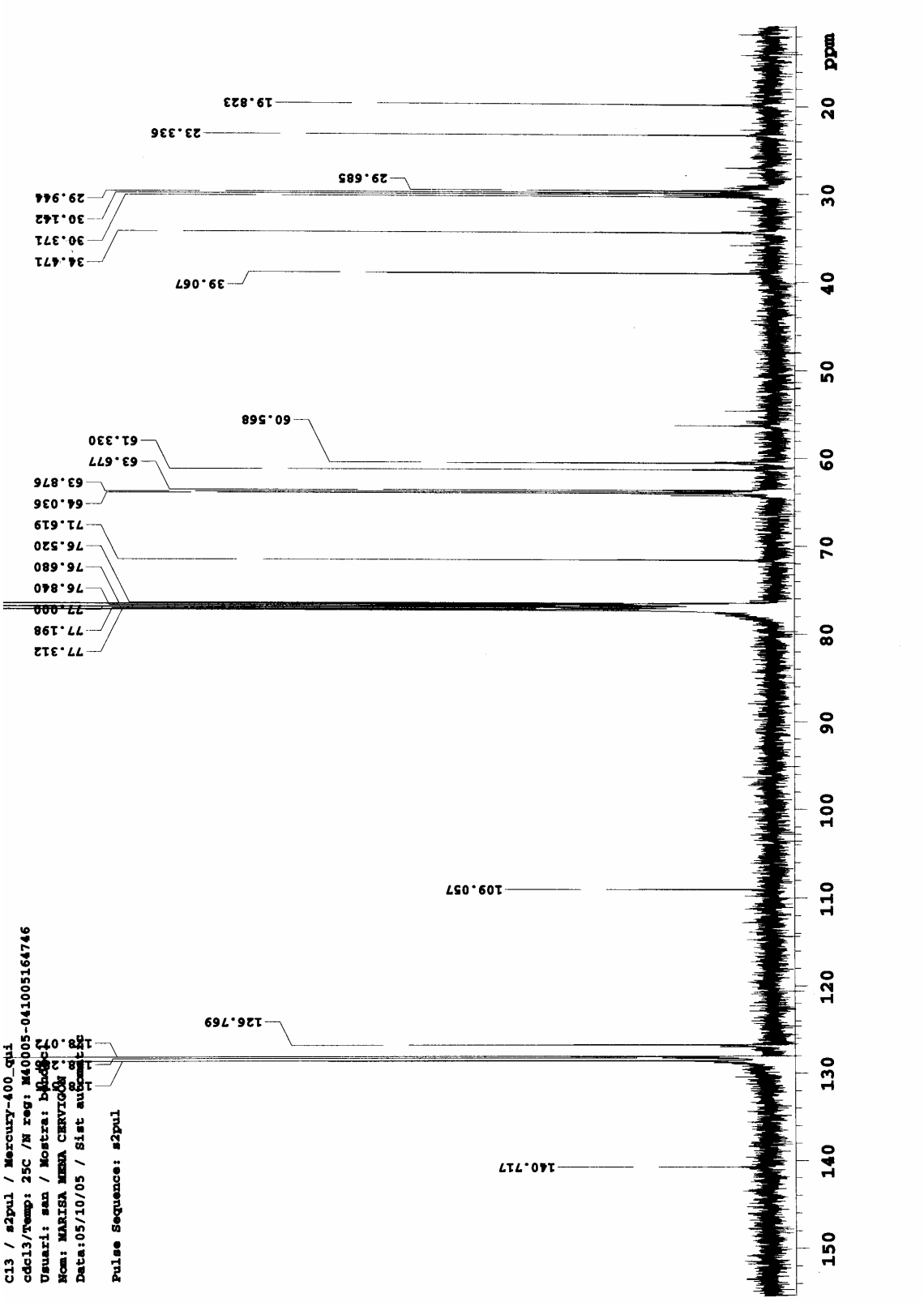


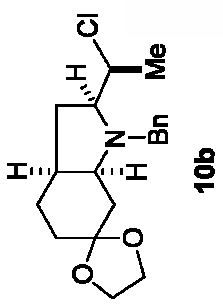
9b + 16


7.306
7.289
7.260
3.819
3.794
1.544
1.522
1.259
1.254
1.238
8
7
6
5
4
3
2
1
ppm
5.00
6.67
1.71
0.70
10.04
3.60

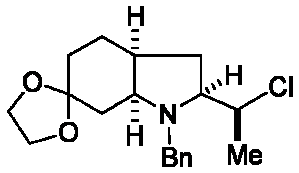
128.233
128.149
128.073
127.600
77.420
77.000
76.573
72.071
64.030
63.831
63.404
56.217
56.026
29.696
ppm
Me
Bn
N
H
O
+
Me
Bn
N
H
O


10b
Cl
H
Me
N
Bn
H
H
O
O
E1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-041005164746
Usuari: sara/ Mostra: bendocl
Ncm: MARISA MEMA CERVIGON
Data:04/10/05 / Slat automatic
Pulse Sequence: s2pul
7.283
3.803
1.505
1.488
1.254
1 ppm
2
3
4
5
6
7
10.33
0.97
1.02
1.00
0.79
0.00
6.07
5.07


C13 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-041005164746
Usuari: san / Mostra: b
Nom: MARISA MENA CERVIGON
Data:05/10/05 / Sist autom
Pulse Sequence: s2pul
19.823
23.336
29.685
29.944
30.142
30.371
34.471
39.067
60.568
61.330
63.677
63.876
64.036
71.619
76.520
76.680
76.840
77.000
77.198
77.312
109.057
126.769
140.717
ppm

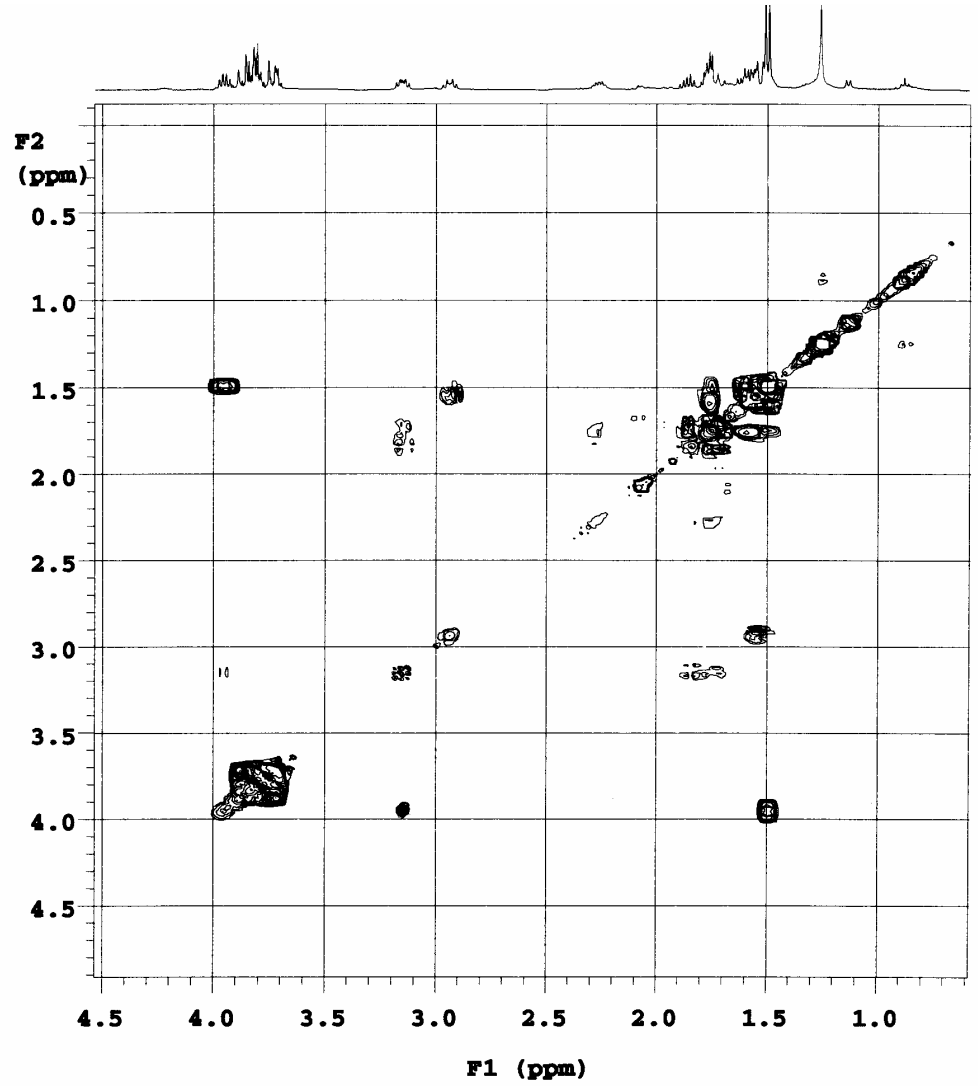

Cl
H
Me
N
Bn
H
H
O
O

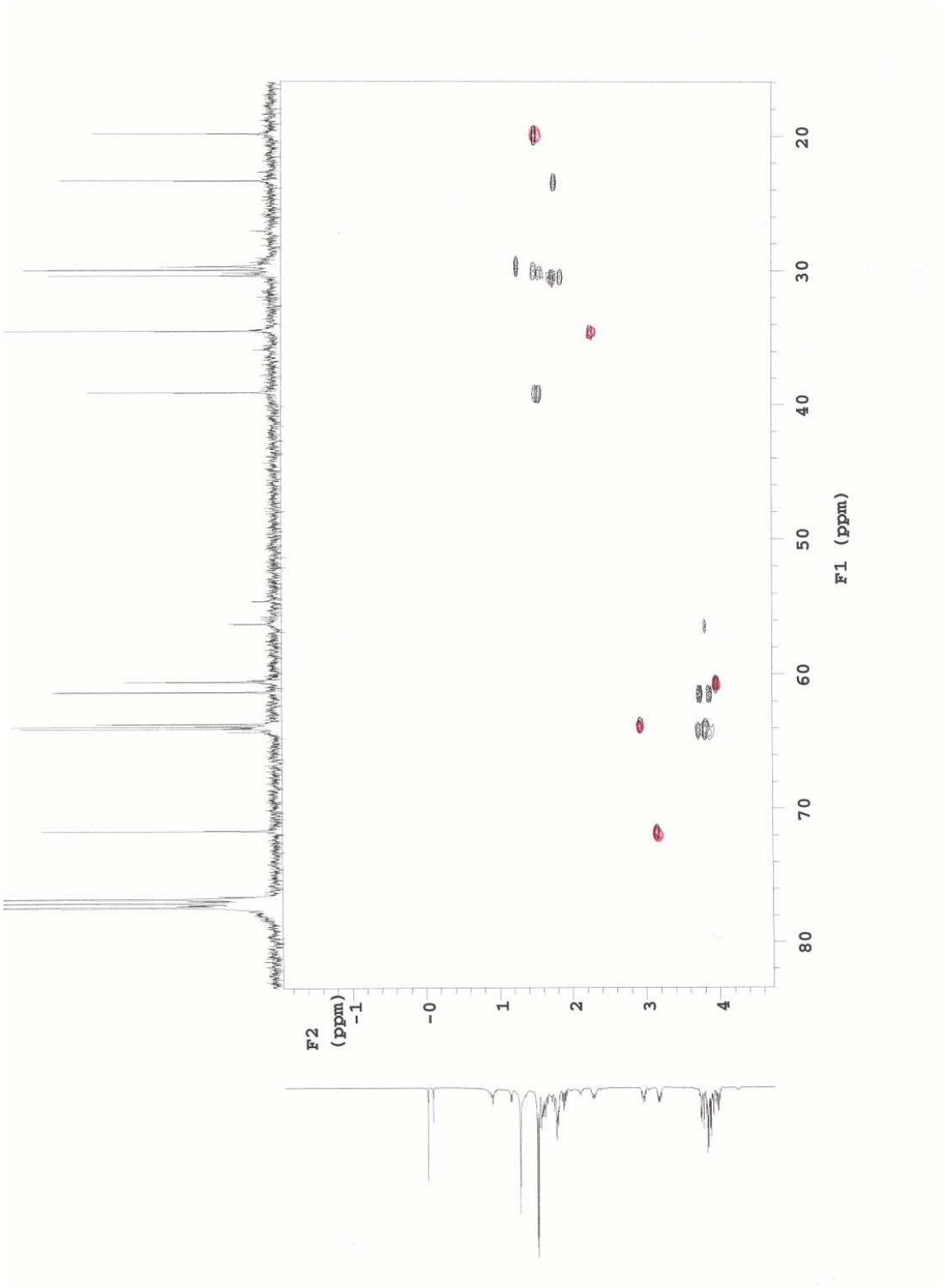
10b

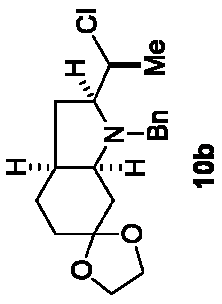


10b

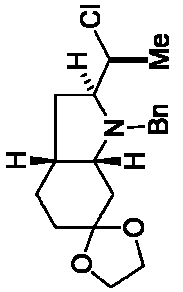
```
cdcl3/Temp: 25C /N reg: M40005-041005164
746
Usuari: san / Mostra: bendocl
Nom: MARISA MENA CERVIGON
Data:05/10/05 / Sist automatic

exp22  gCOSY

      SAMPLE                FLAGS
date    Oct  5 2005  hs                nn
solvent       cdcl3  sspul              n
sample auto_Custom~  hsglvl          1002
       Q_04Oct2005        SPECIAL
   ACQUISITION        temp           25.0
sw          6410.3  gain               32
at           0.150  spin                0
np            1924    F2 PROCESSING
fb         not used  sb            -0.075
ss               16  sbs         not used
d1            1.000  fn               2048
nt                4    F1 PROCESSING
  2D ACQUISITION     sb1           -0.040
sw1         6410.3  sbs1        not used
ni              256  proc1             lp
  PRESATURATION      fn1              2048
satmode           n         DISPLAY
satfrq            0  sp             -47.3
satdly            0  wp            2011.4
satpwr            0  sp1            234.6
   TRANSMITTER       wp1           1579.1
tn               H1  rf1            799.3
sfrq        400.114  rfp                0
tof           381.9  rfl1           799.3
tpwr             58  rfp1               0
pw           12.200          PLOT
    GRADIENTS        wc             131.8
gzlvl1         1002  sc                 6.2
gt1       0.001000  wc2            131.8
gstab     0.000500  sc2                0
    DECOUPLER        vs               252
dn               C13  th                 7
dm               nnn  ai  cdc  av
```



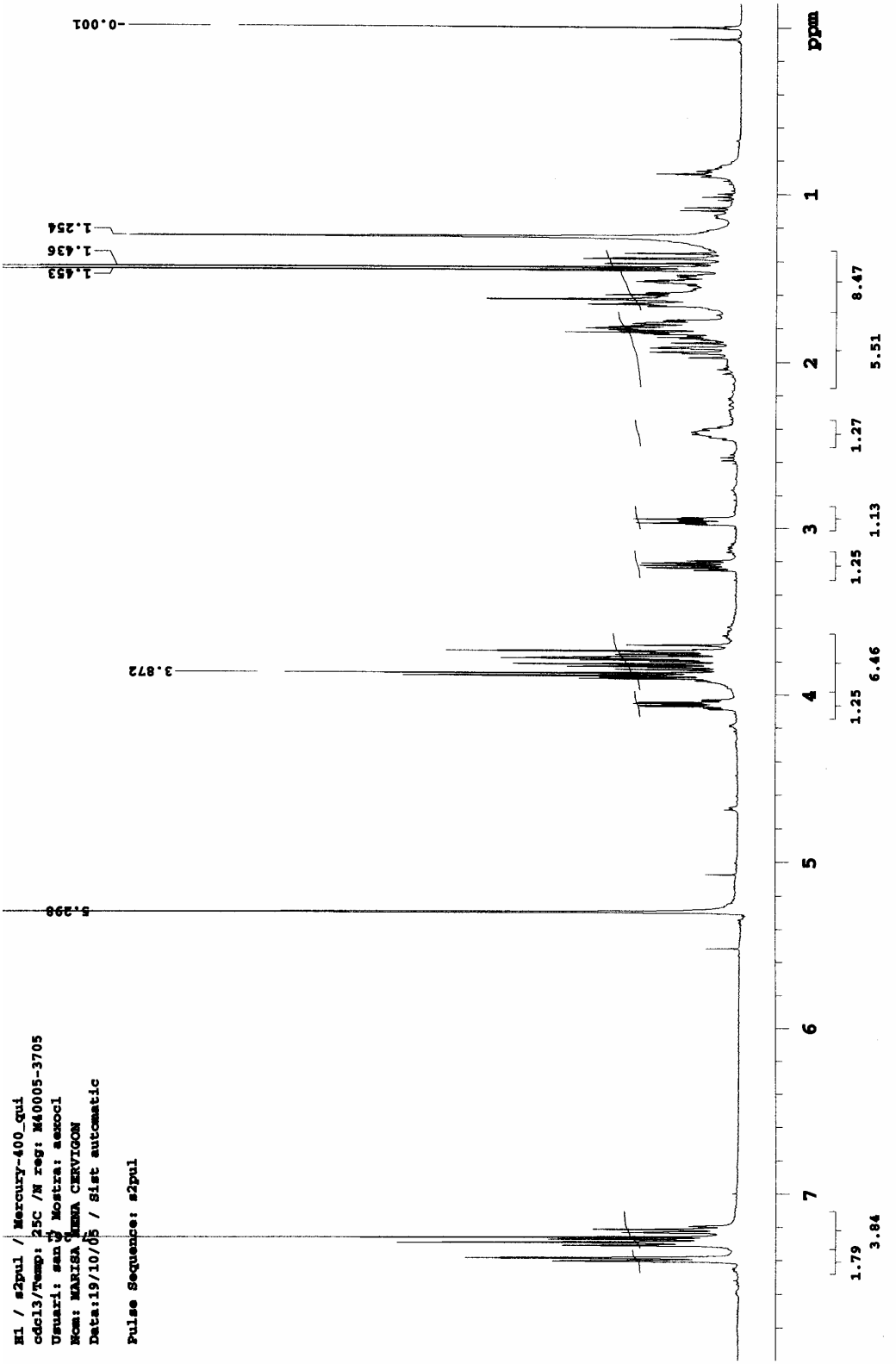


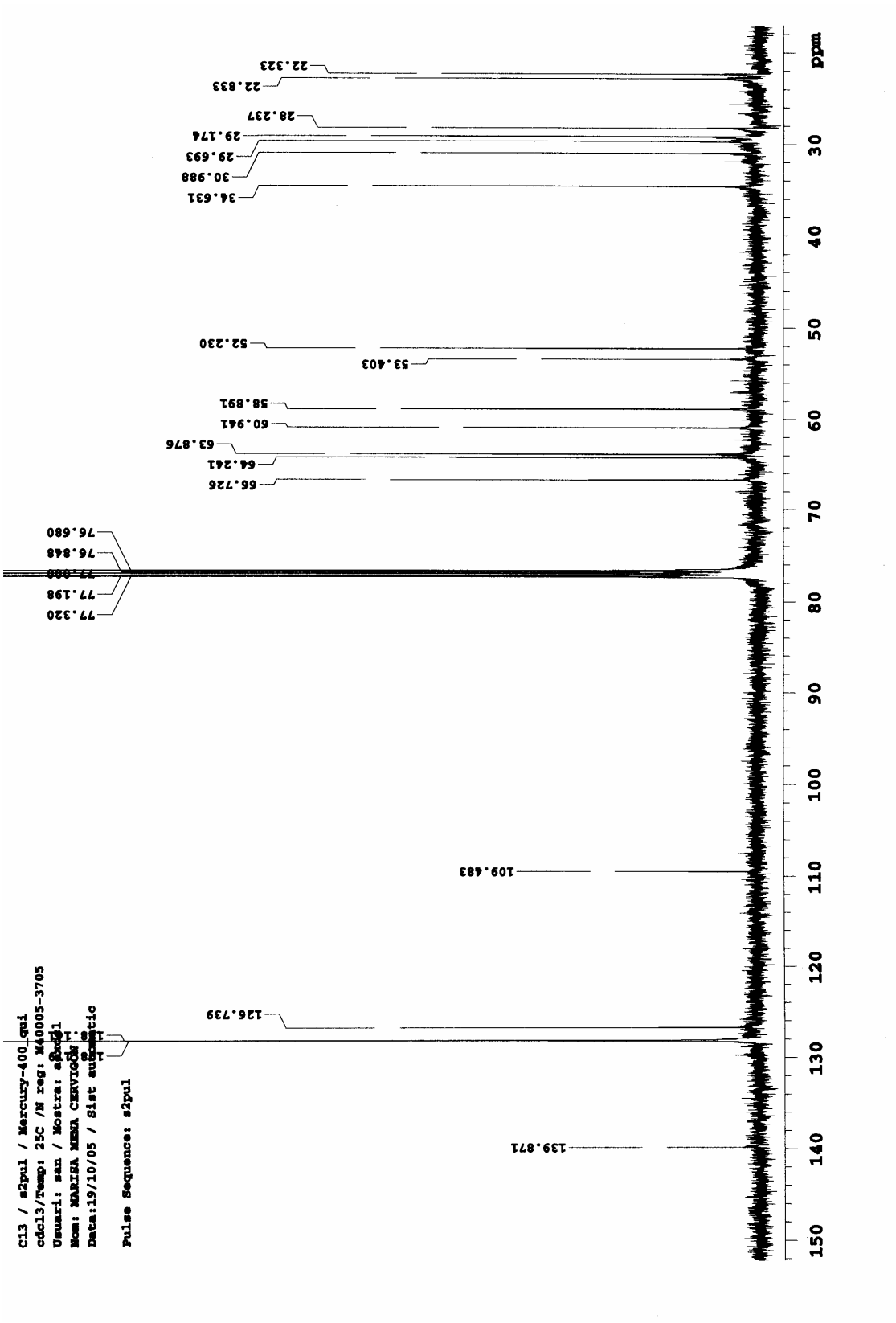


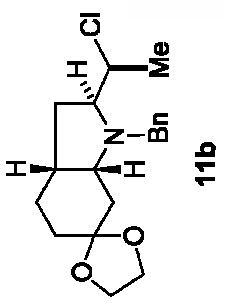
10b


H
Cl
Me
N
Bn
H
O
O

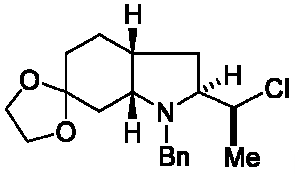
11b


-0.001
1.254
1.436
1.453
3.872
5.290
ppm
1 2 3 4 5 6 7
8.47
5.51
1.27
1.13
1.25
6.46
1.25
1.79
3.84
El / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-3705
Usuari: sanz Mostra: aexocl
Nom: MARISA MEMA CERVIGON
Data:19/10/05 / Sist automatic
Pulse Sequence: s2pul


C13 / s2pul / Mercury-400_gui
cdcl3/Temp: 25C /N reg: M40005-3705
Usuari: sam / Mostra: s2pul
Nom: MARINA MENA CERVIGON
Data:19/10/05 / Slst auto
Pulse Sequence: s2pul
22.323
22.833
28.237
29.174
29.693
30.988
34.631
52.230
53.403
58.891
60.941
63.876
64.241
66.726
76.680
76.848
77.320
77.198
109.483
126.739
139.871
ppm

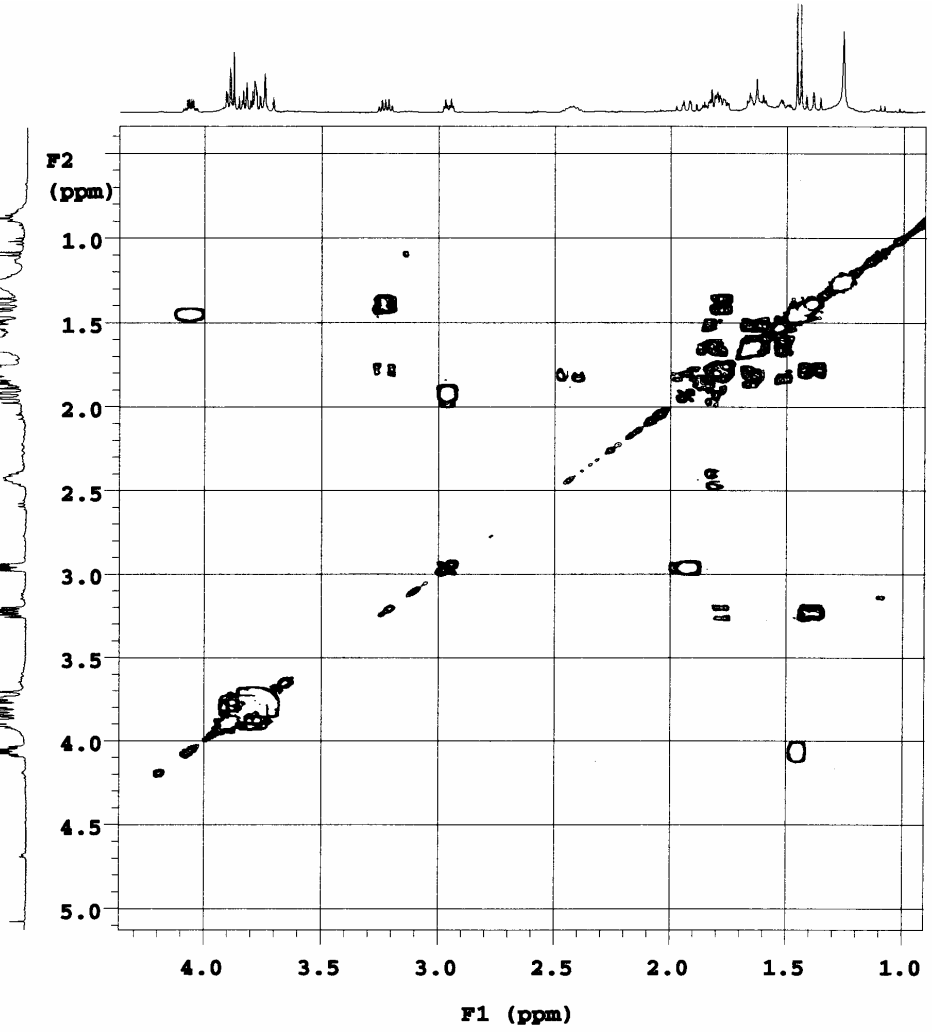

Cl
H
Me
N
Bn
H
H
O
O

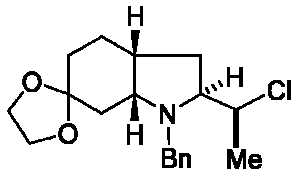
11b



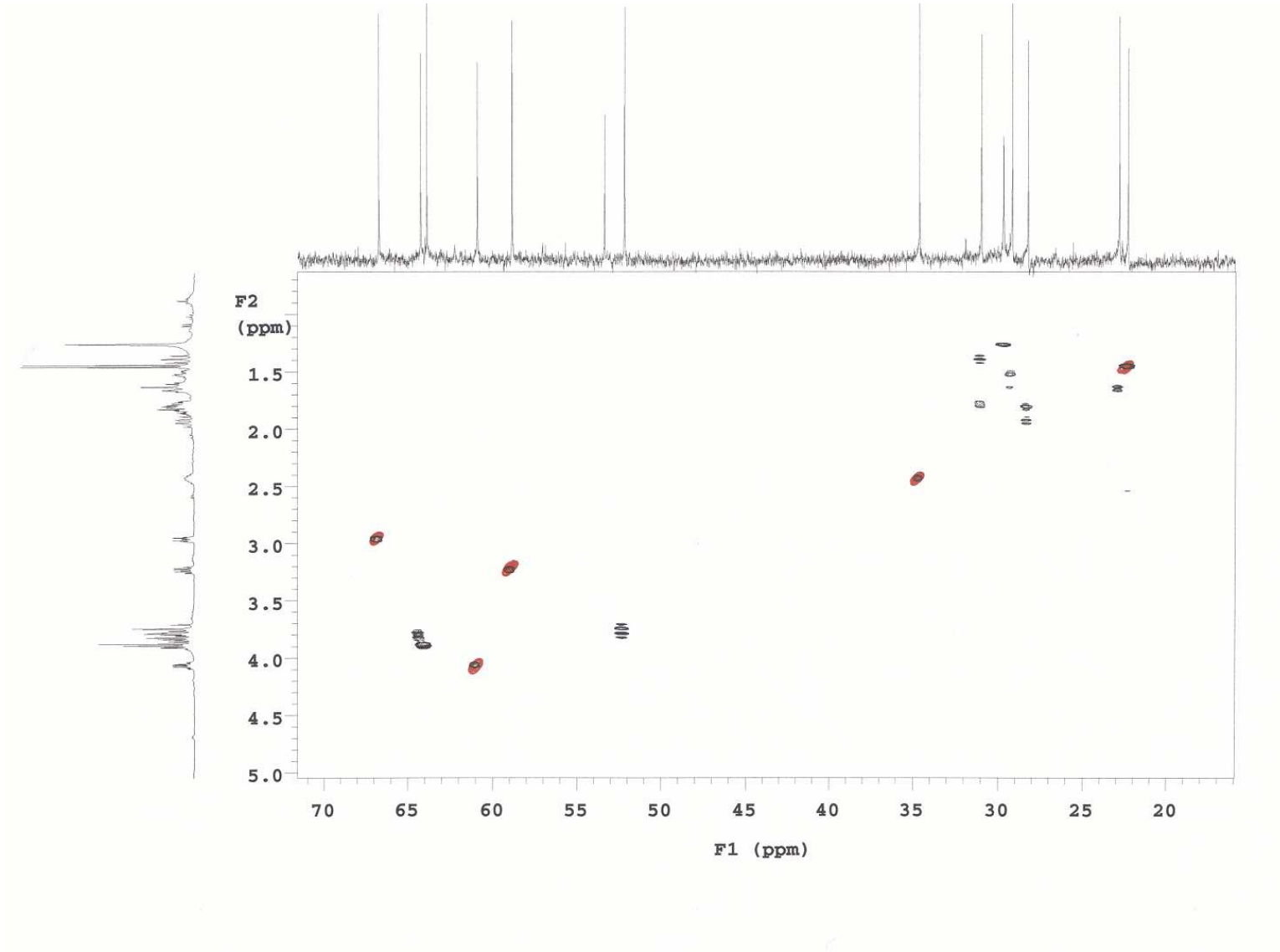
11b

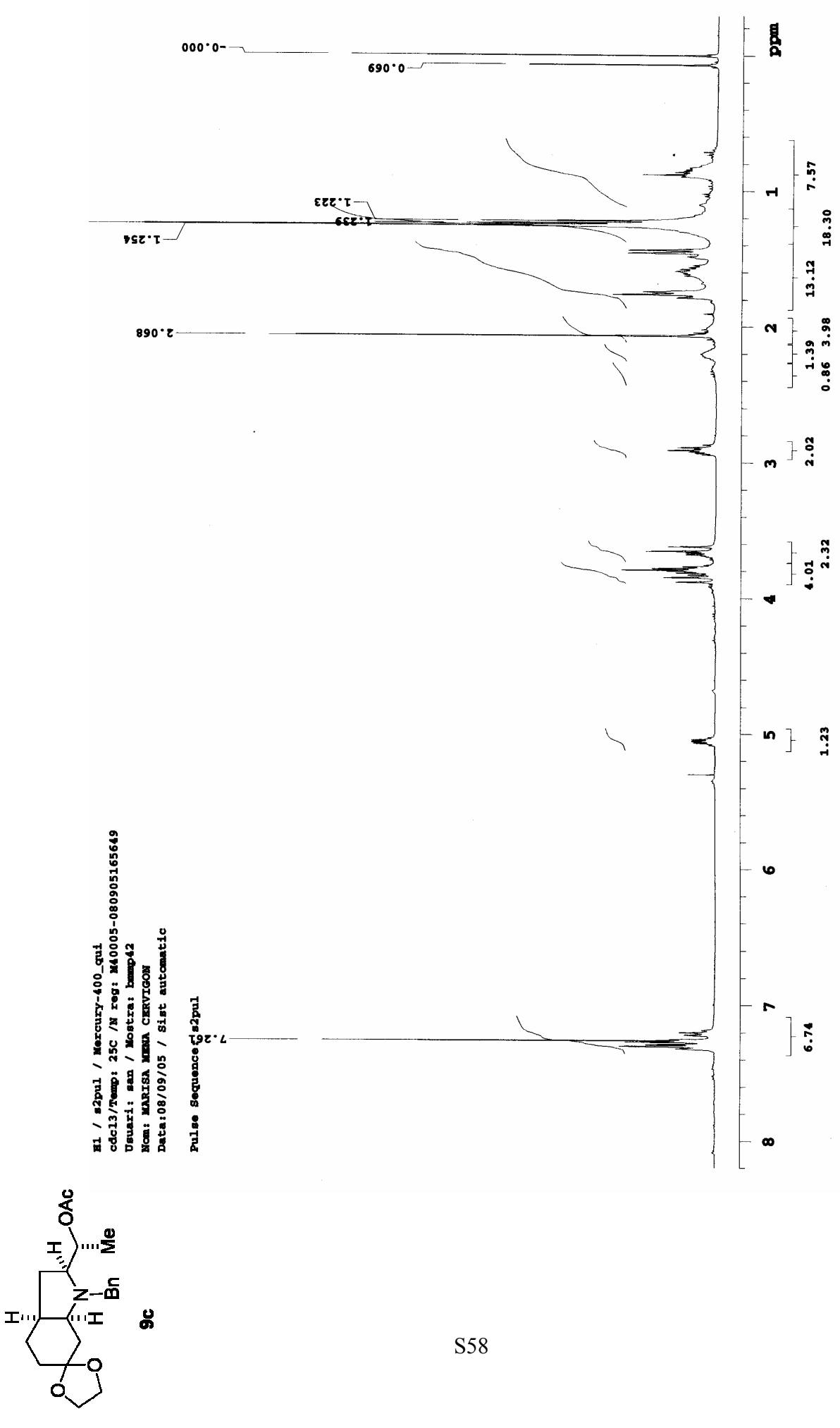
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-3705
Usuari: san / Mostra: aexocl
Nom: MARISA MENA CERVIGON
Data:19/10/05 / Sist automatic

exp4  gCOSY

      SAMPLE              FLAGS
date   Oct 19 2005  hs              nn
solvent      cdcl3  sspul            n
sample auto_Custom~ hsglvl        1002
       Q_19Oct2005       SPECIAL
   ACQUISITION      temp          25.0
sw          4273.5  gain            26
at           0.150  spin             0
np            1282    F2 PROCESSING
fb        not used  sb           -0.075
ss              16  sbs       not used
d1           1.000  fn            2048
nt               4    F1 PROCESSING
  2D ACQUISITION    sb1          -0.060
sw1         4273.5  sbs1      not used
ni             256  proc1           lp
  PRESATURATION     fn1           2048
satmode          n       DISPLAY
satfrq           0  sp           137.7
satdly           0  wp          1913.3
satpwr           0  sp1          363.3
   TRANSMITTER      wp1         1382.7
tn              H1  rf1           514.0
sfrq       400.113  rfp             0
tof         -400.6  rf11          514.0
tpwr            58  rfp1            0
pw          12.200          PLOT
    GRADIENTS       wc          131.8
gzlvl1        1002  sc            6.2
gt1       0.001000  wc2         131.8
gstab     0.000500  sc2             0
    DECOUPLER       vs            590
dn              C13 th              7
dm              nnn ai  cdc  av
```

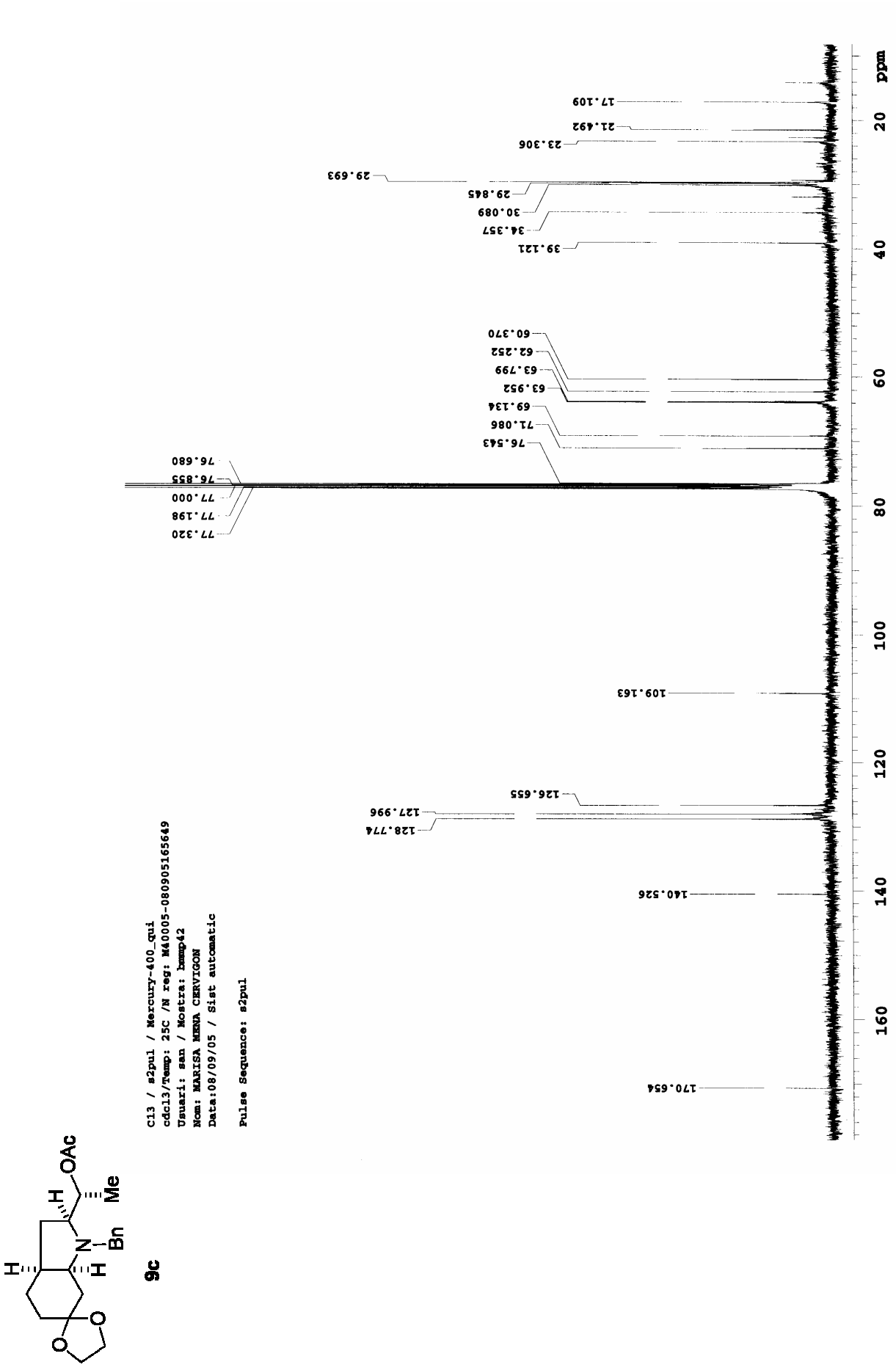


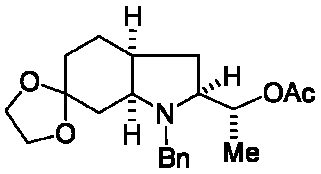

H
O
H
Cl
N
O
H
Bn
Me

11b


F2
(ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
70
65
60
55
50
45
40
35
30
25
20
F1 (ppm)

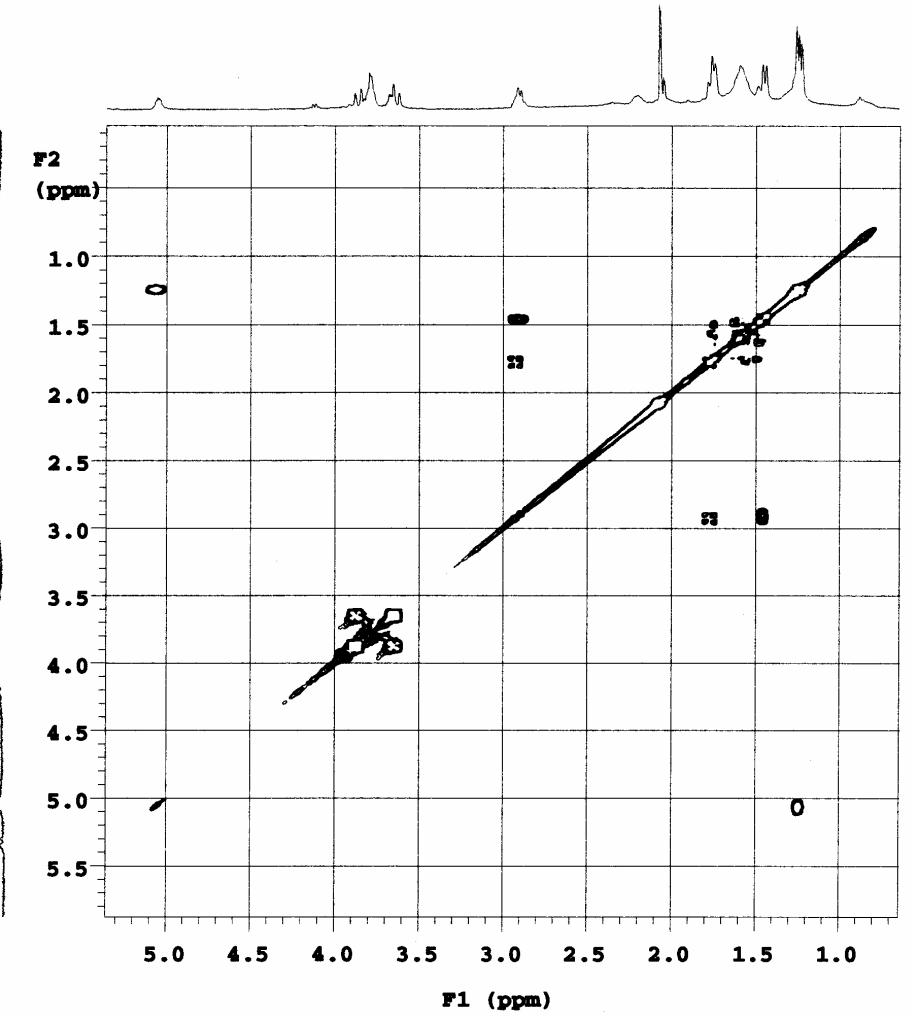

9c
H1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-080905165649
Usuari: san / Mostra: bmmp42
Nom: MARISA MENA CERVIGON
Data:08/09/05 / Sist automatic
Pulse Sequence: s2pul
7.274
2.068
1.254
1.239
1.223
0.069
-0.000
ppm
6.74
1.23
4.01
2.32
2.02
1.39
0.86
3.98
13.12
18.30
7.57

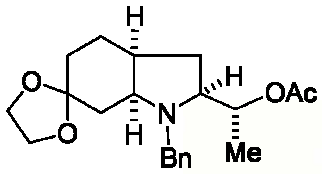

9c
C13 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-080905165649
Usuari: san / Mostra: bmmp42
Nom: MARISA MENA CERVIGON
Data:08/09/05 / Sist automatic
Pulse Sequence: s2pul
170.654
140.526
128.774
127.996
126.655
109.163
77.320
77.198
77.000
76.855
76.680
76.543
71.086
69.134
63.952
63.799
62.252
60.370
39.121
34.357
30.089
29.845
29.693
23.306
21.492
17.109
ppm



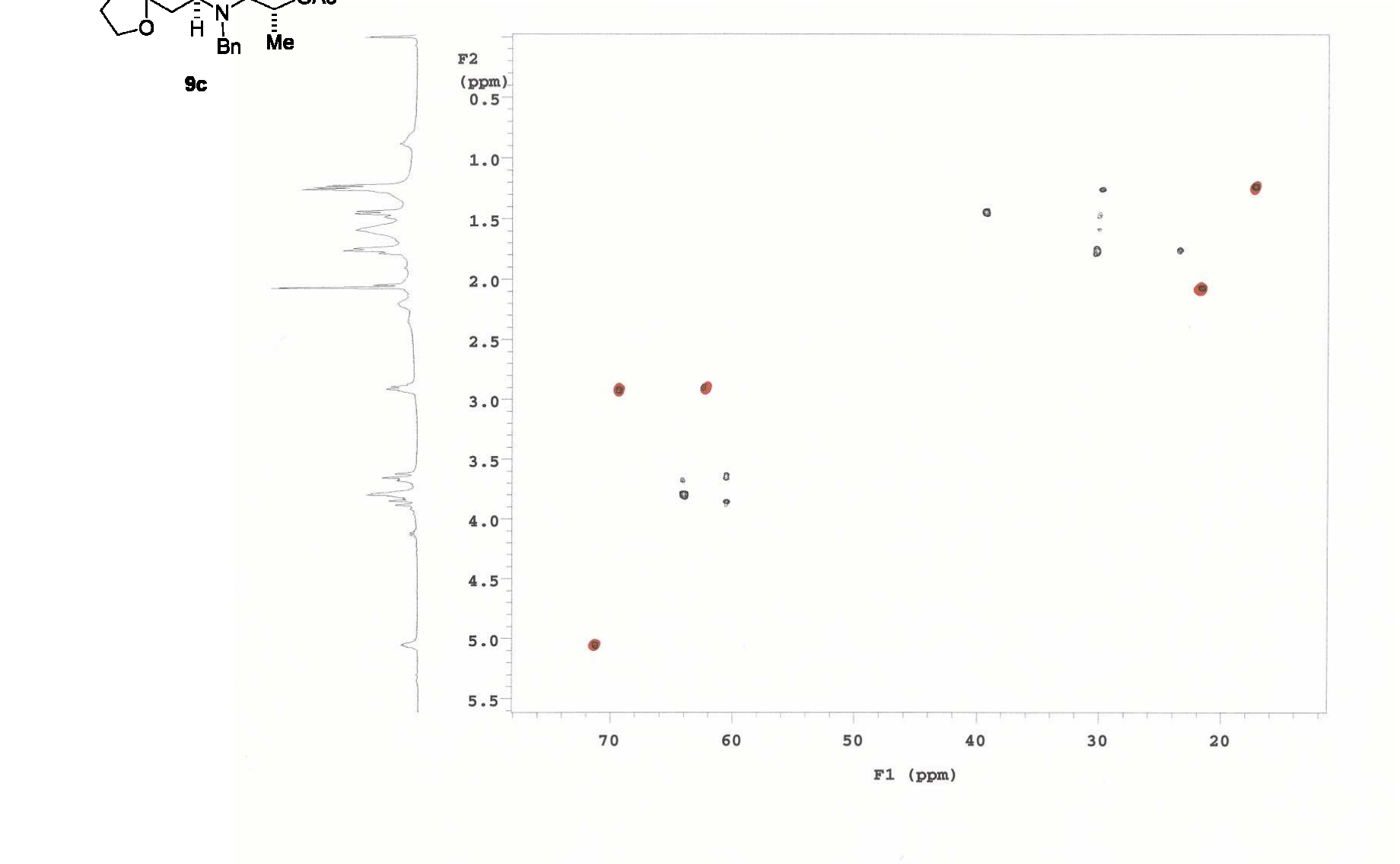
9c

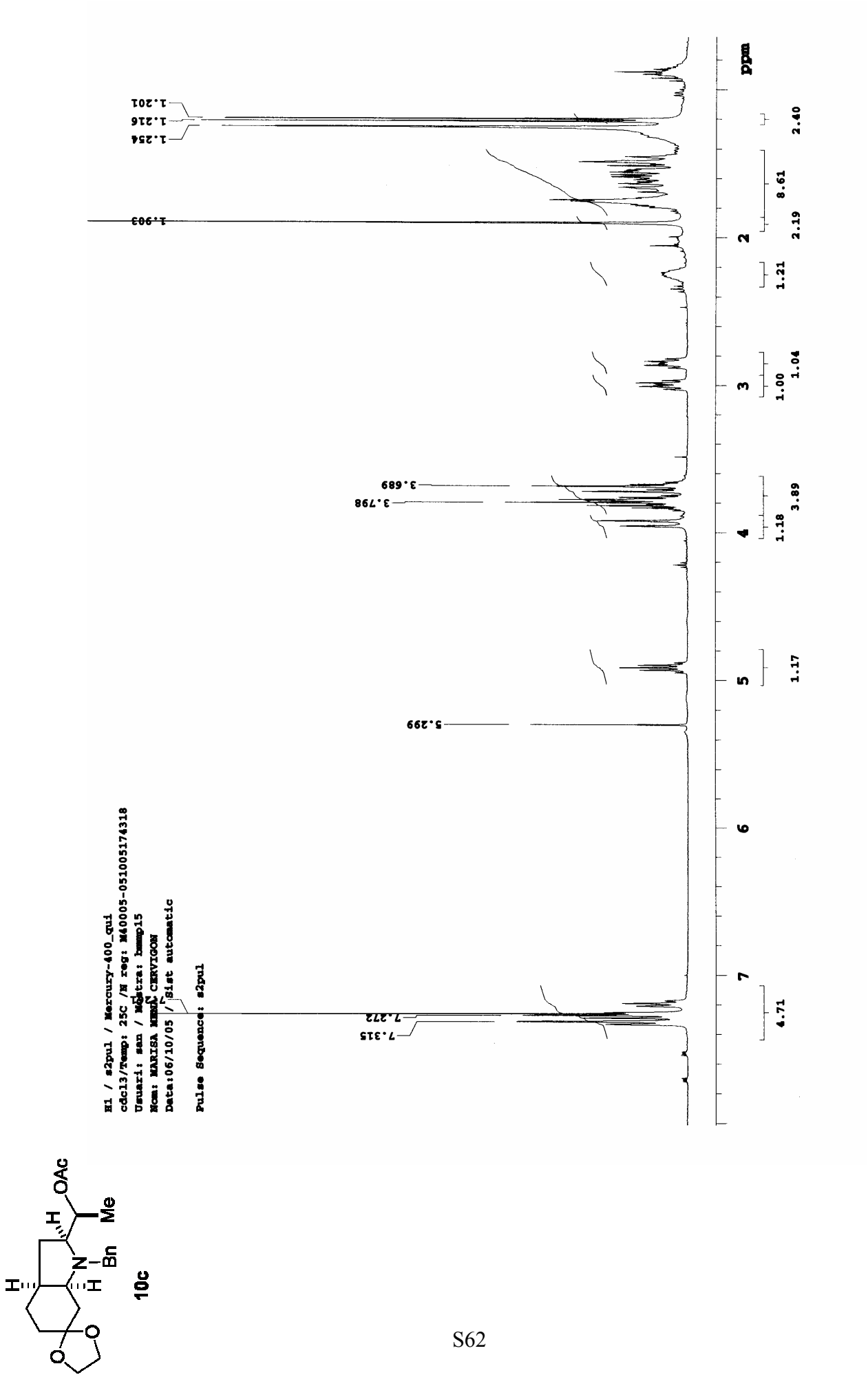
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-290905163
622
Usuari: san / Mostra: bmmp42
Nom: MARISA MENA CERVIGON
Data:29/09/05 / Sist automatic

exp6  gCOSY

      SAMPLE                FLAGS
date    Sep 29 2005  hs                 nn
solvent       cdcl3  sspul              n
sample auto_Custom~  hsglvl          1002
       Q_29Sep2005        SPECIAL
   ACQUISITION       temp           25.0
sw          3906.2   gain             36
at           0.150   spin              0
np            1172     F2 PROCESSING
fb        not used   sb             -0.075
ss              16   sbs         not used
d1           1.000   fn               2048
nt               4     F1 PROCESSING
  2D ACQUISITION     sb1            -0.066
sw1         3906.2   sbs1        not used
ni             256   proc1             lp
  PRESATURATION      fn1              2048
satmode          n        DISPLAY
satfrq           0   sp              21.1
satdly           0   wp            2329.2
satpwr           0   sp1            257.8
   TRANSMITTER       wp1           1886.3
tn              H1   rf1            483.0
sfrq       400.113   rfp                0
tof         -556.0   rf11           483.0
tpwr            58   rfp1               0
pw          12.200          PLOT
    GRADIENTS        wc             131.8
gslvl1        1002   sc               6.2
gt1       0.001000   wc2            131.8
gstab     0.000500   sc2                0
   DECOUPLER         vs              1677
dn              C13  th                 8
dm              nnn  ai  cdc  av
```




H
O
H
OAc
O
N
H
Bn
Me

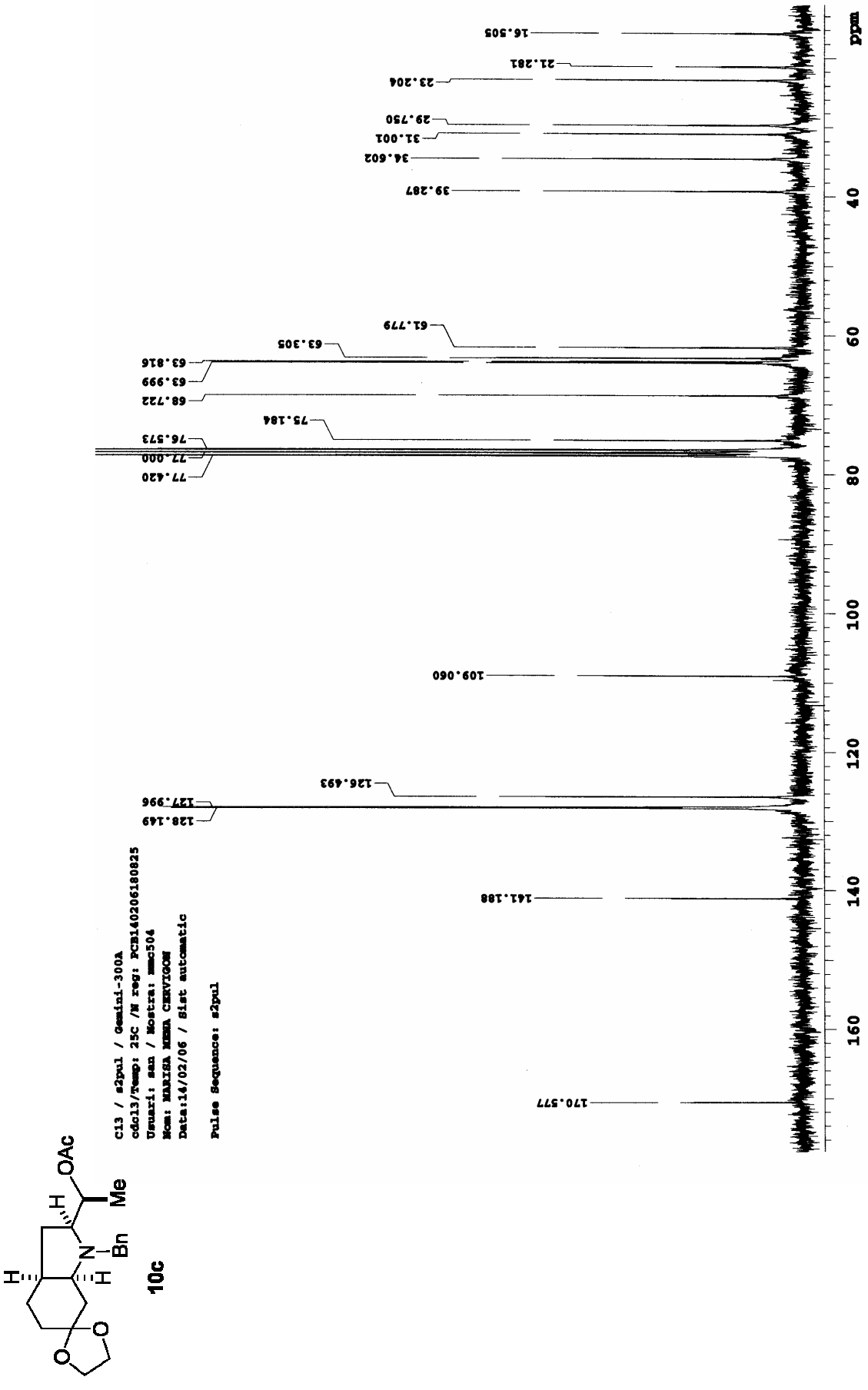
9c

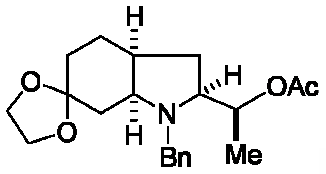

F2
(ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
70
60
50
40
30
20
F1 (ppm)


E1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /H reg: M40005-051005174318
Usuari: san / Matra: hmmp15
Nom: MARISA MESA CERVIGON
Data:06/10/05 / 8ist automatic
Pulse Sequence: s2pul
1.254
1.216
1.201
1.903
3.689
3.798
5.299
7.272
7.315
ppm
1
2
3
4
5
6
7
8.61
2.40
2.19
1.21
1.00
1.04
1.18
3.89
1.17
4.71

OAc
H
Me
N
Bn
H
H
O
O

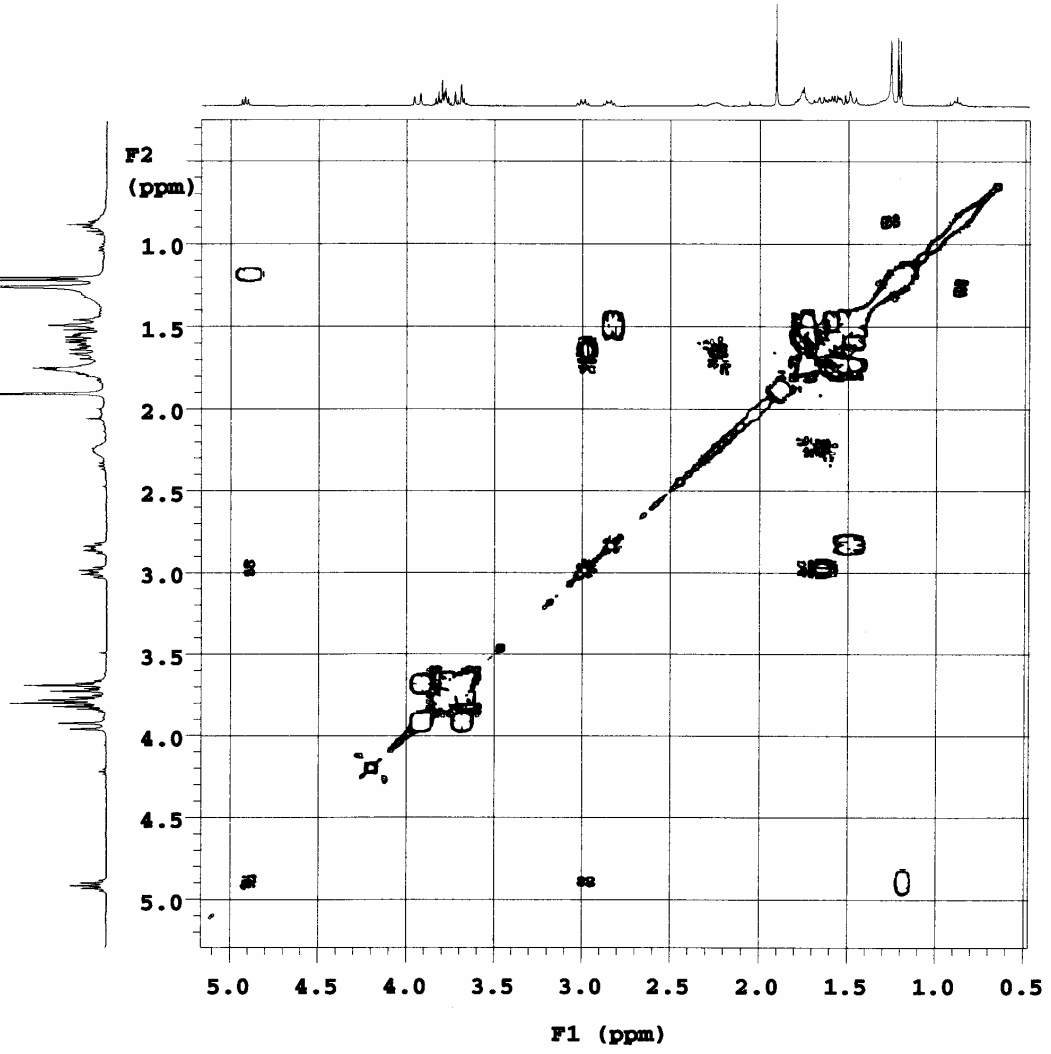
10c

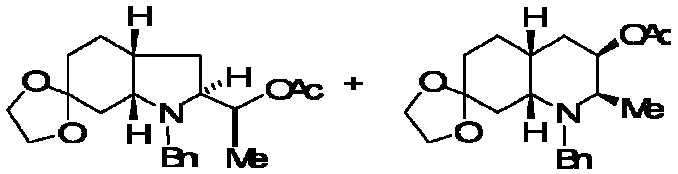

10c
C13 / s2pul / Gemini-300A
cdcl3/Temp: 25C /N reg: PCB140206180825
Usuari: san / Mostra: mmo504
Mem: MARISA MEMA CERVIGOM
Data:14/02/06 / Slst automatic
Pulse Sequence: s2pul
16.505
21.281
23.204
29.750
31.001
34.602
39.287
61.779
63.305
63.816
63.999
68.722
75.184
76.573
77.000
77.420
109.060
126.493
127.996
128.149
141.188
170.577
ppm
40
60
80
100
120
140
160



10c

```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-051005174
318
Usuari: san / Mostra: bmmp15
Nom: MARISA MENA CERVIGON
Data:06/10/05 / Sist automatic

exp22  gCOSY

      SAMPLE                FLAGS
date    Oct  6 2005  hs                nn
solvent       cdcl3  sspul              n
sample auto_Custom~  hsglvl          1002
       Q_06Oct2005        SPECIAL
   ACQUISITION       temp           25.0
sw          4065.0  gain             26
at           0.150  spin              0
np            1220     F2 PROCESSING
fb         not used  sb            -0.075
ss              16  sbs         not used
d1           1.000  fn               2048
nt               8    F1 PROCESSING
  2D ACQUISITION    sb1           -0.063
sw1         4065.0  sbs1        not used
ni             256  proc1             lp
  PRESATURATION     fn1              2048
satmode          n        DISPLAY
satfrq           0  sp             102.2
satdly           0  wp            2014.6
satpwr           0  sp1            189.6
   TRANSMITTER      wp1           1875.6
tn              H1  rf1            497.8
sfrq       400.113  rfp                0
tof         -479.0  rf11           497.8
tpwr            58  rfp1               0
pw          12.200          PLOT
    GRADIENTS       wc             131.8
gzlvl1        1002  sc               6.2
gt1       0.001000  wc2            131.8
gstab     0.000500  sc2                0
    DECOUPLER       vs               365
dn              C13  th                 5
dm              nnn  ai  cdc  av
```

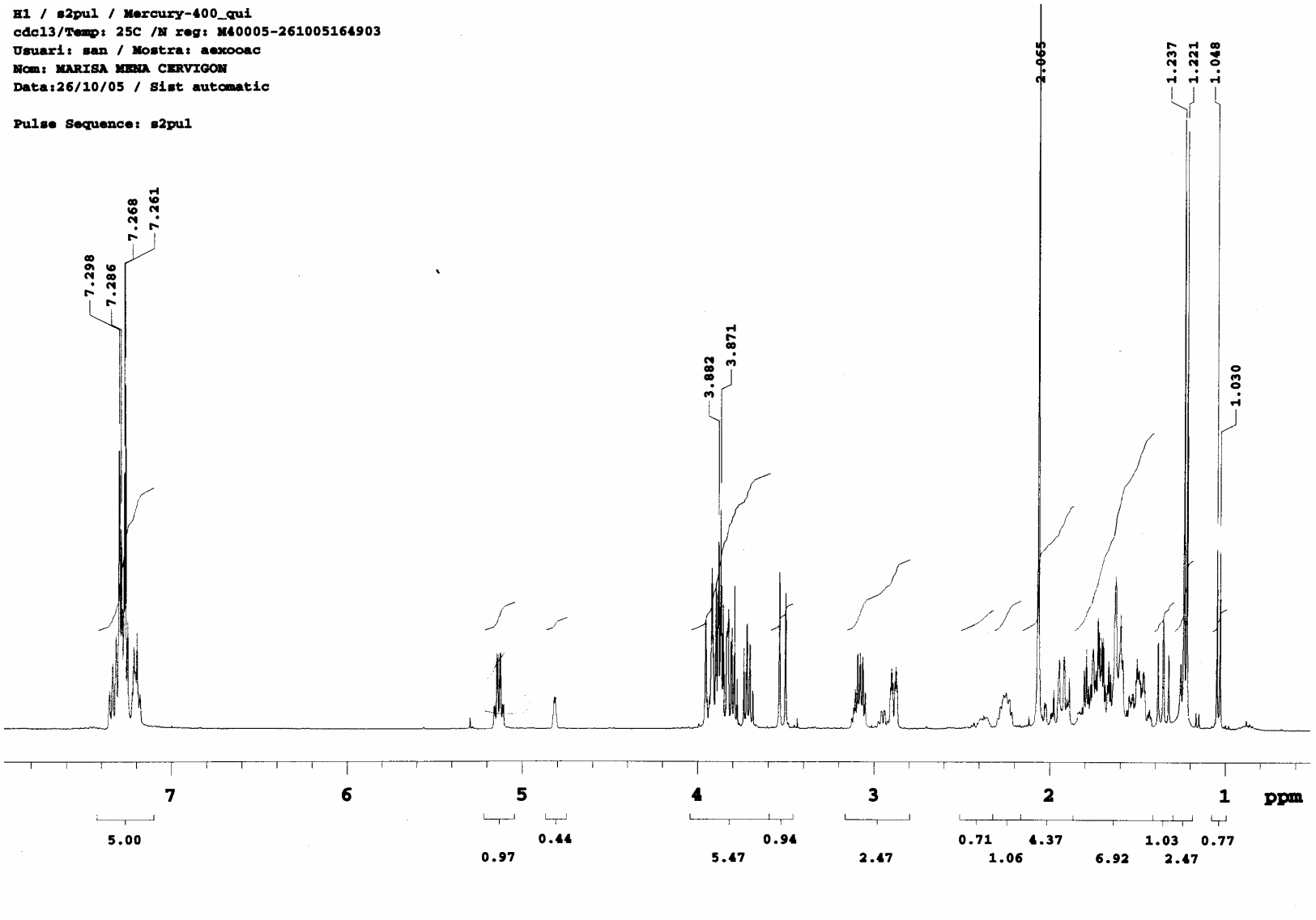


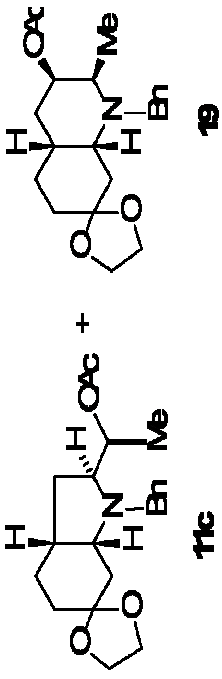


11c + **19**

H1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-261005164903
Usuari: san / Mostra: aexooac
Nom: MARISA MENA CERVIGON
Data:26/10/05 / Sist automatic

Pulse Sequence: s2pul

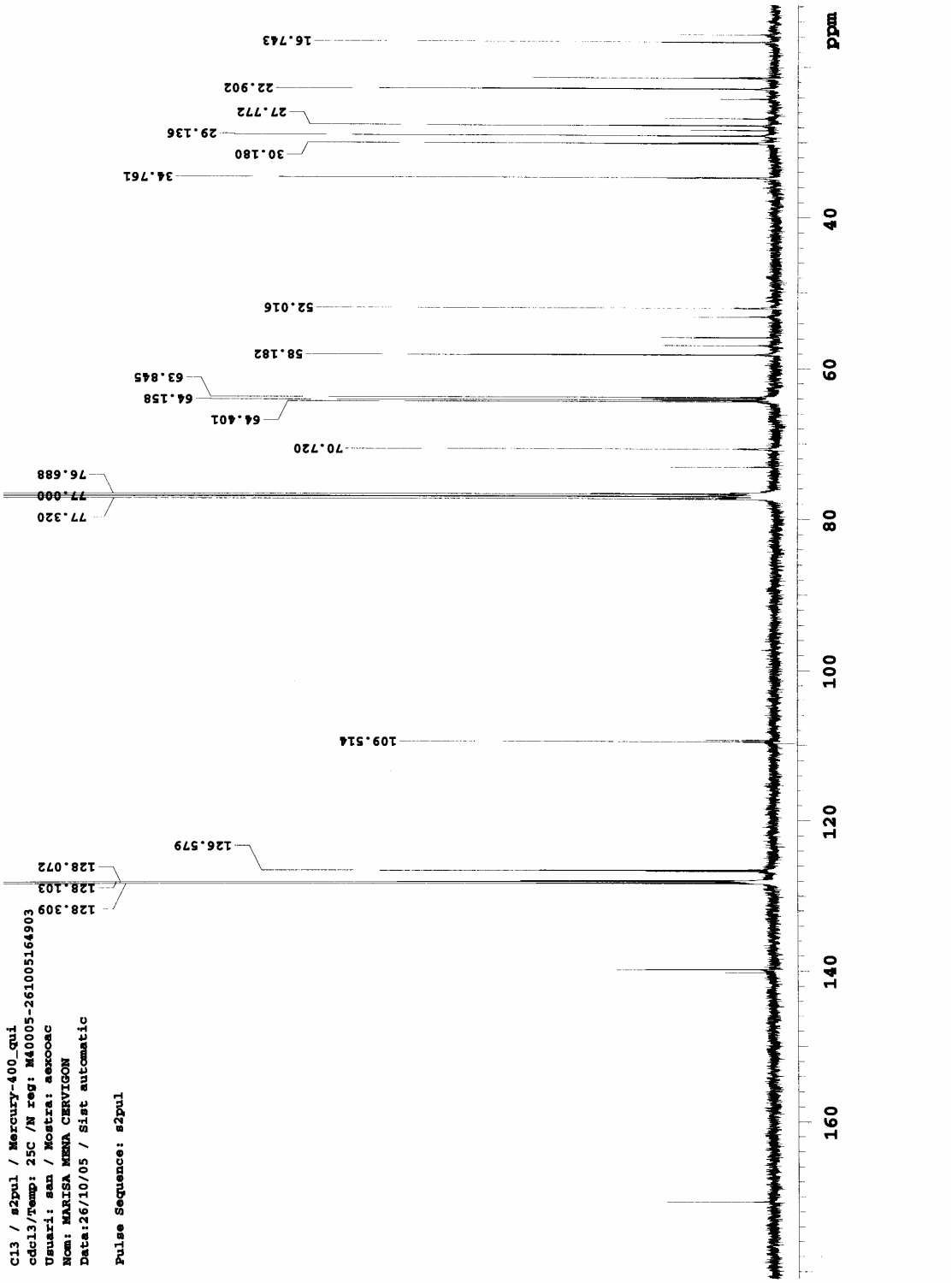


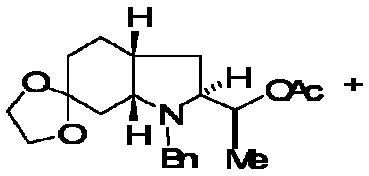

OAc
Me
Bn
H
N
H
O
O

11c +

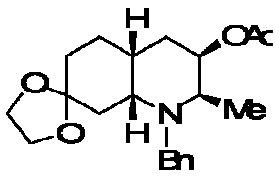
OAc
H
Me
Bn
N
H
H
O
O

11d


C13 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-261005164903
Usuari: san / Mostra: aexooac
Nom: MARISA MENA CERVIGON
Data:26/10/05 / Sist automatic
Pulse Sequence: s2pul
16.743
22.902
27.772
29.136
30.180
34.761
52.016
58.182
63.845
64.158
64.401
70.720
76.688
77.000
77.320
109.514
126.579
128.072
128.103
128.309
ppm
40
60
80
100
120
140
160

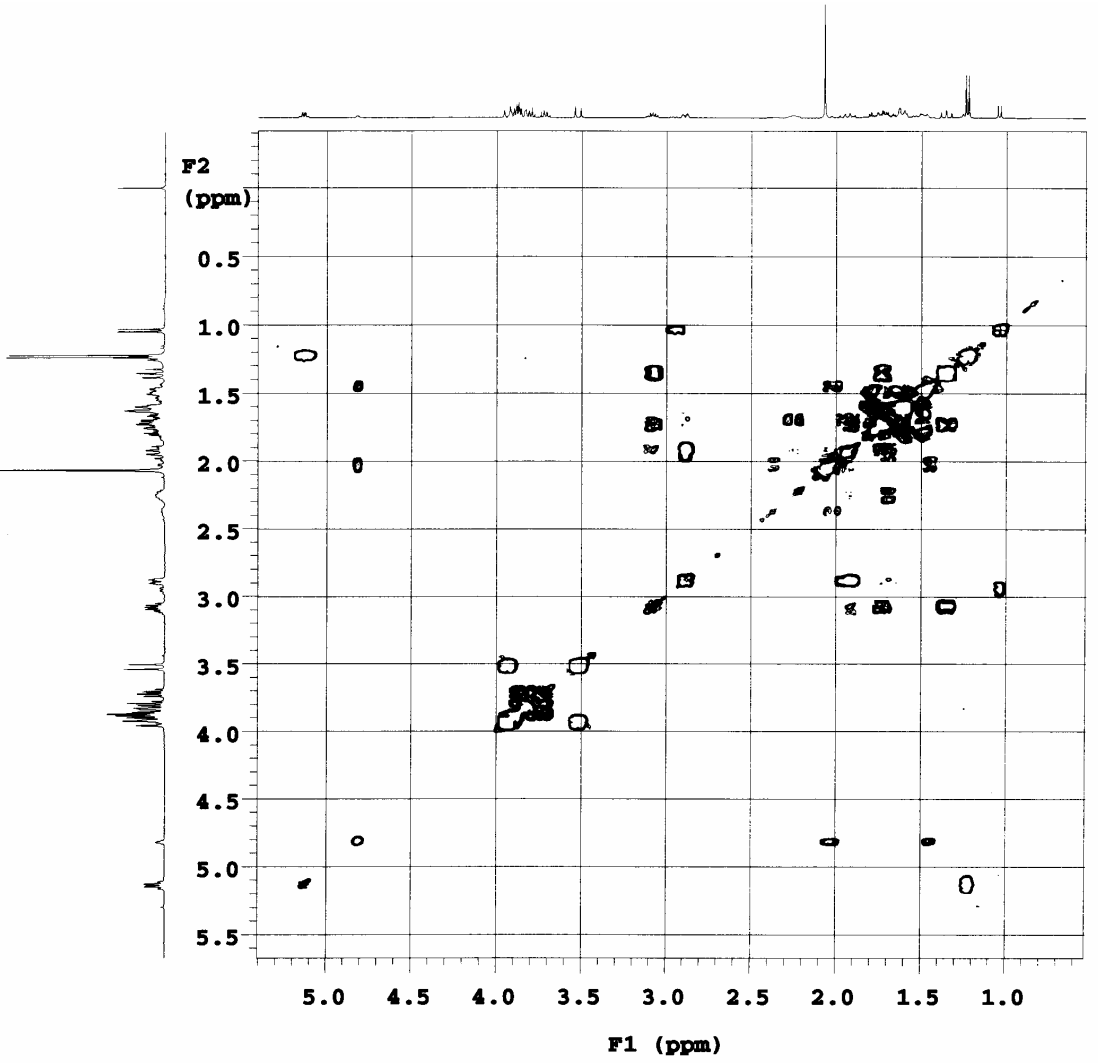


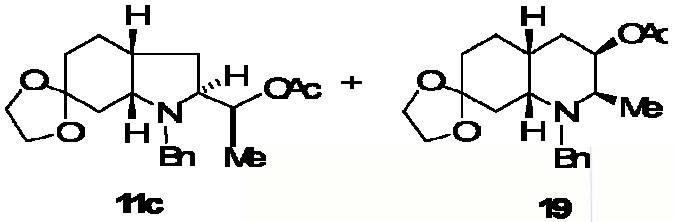
11c



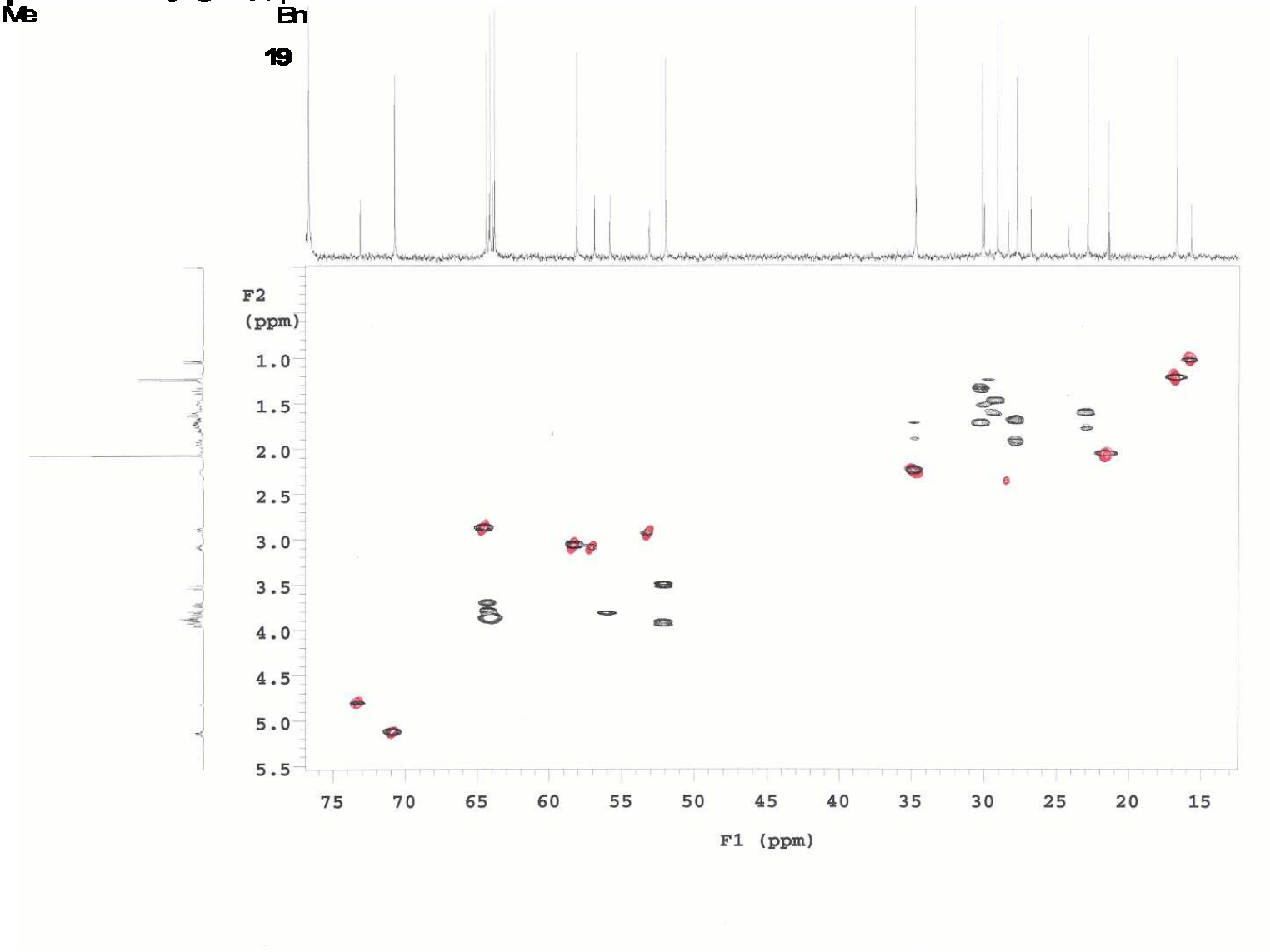
19

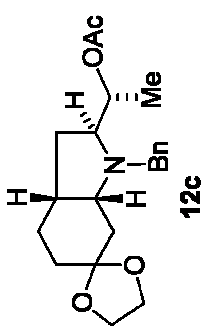
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-261005164
903
Usuari: san / Mostra: aexooac
Nom: MARISA MENA CERVIGON
Data:26/10/05 / Sist automatic

exp3  gCOSY

      SAMPLE                FLAGS
date    Oct 26 2005  hs                nn
solvent       cdcl3  sspul              n
sample auto_Custom~  hsglvl          1000
       Q_26Oct2005        SPECIAL
   ACQUISITION       temp            25.0
sw          3906.2  gain              22
at           0.150  spin               0
np            1172    F2 PROCESSING
fb         not used  sb            -0.075
ss              16  sbs         not used
d1           1.000  fn                2048
nt               4    F1 PROCESSING
  2D ACQUISITION    sb1           -0.066
sw1         3906.2  sbs1        not used
ni             256  proc1             lp
  PRESATURATION     fn1               2048
satmode          n        DISPLAY
satfrq           0  sp             -164.0
satdly           0  wp             2432.3
satpwr           0  sp1             214.0
   TRANSMITTER      wp1            1947.4
tn              H1  rf1             484.7
sfrq       400.113  rfp                0
tof         -547.3  rf11            484.7
tpwr            58  rfp1               0
pw          12.300         PLOT
    GRADIENTS       wc              131.8
gzlvl1        1000  sc                6.2
gt1       0.001000  wc2             131.8
gstab     0.000500  sc2                0
    DECOUPLER       vs                200
dn              C13  th                 6
dm              nnn  ai  cdc  av
```



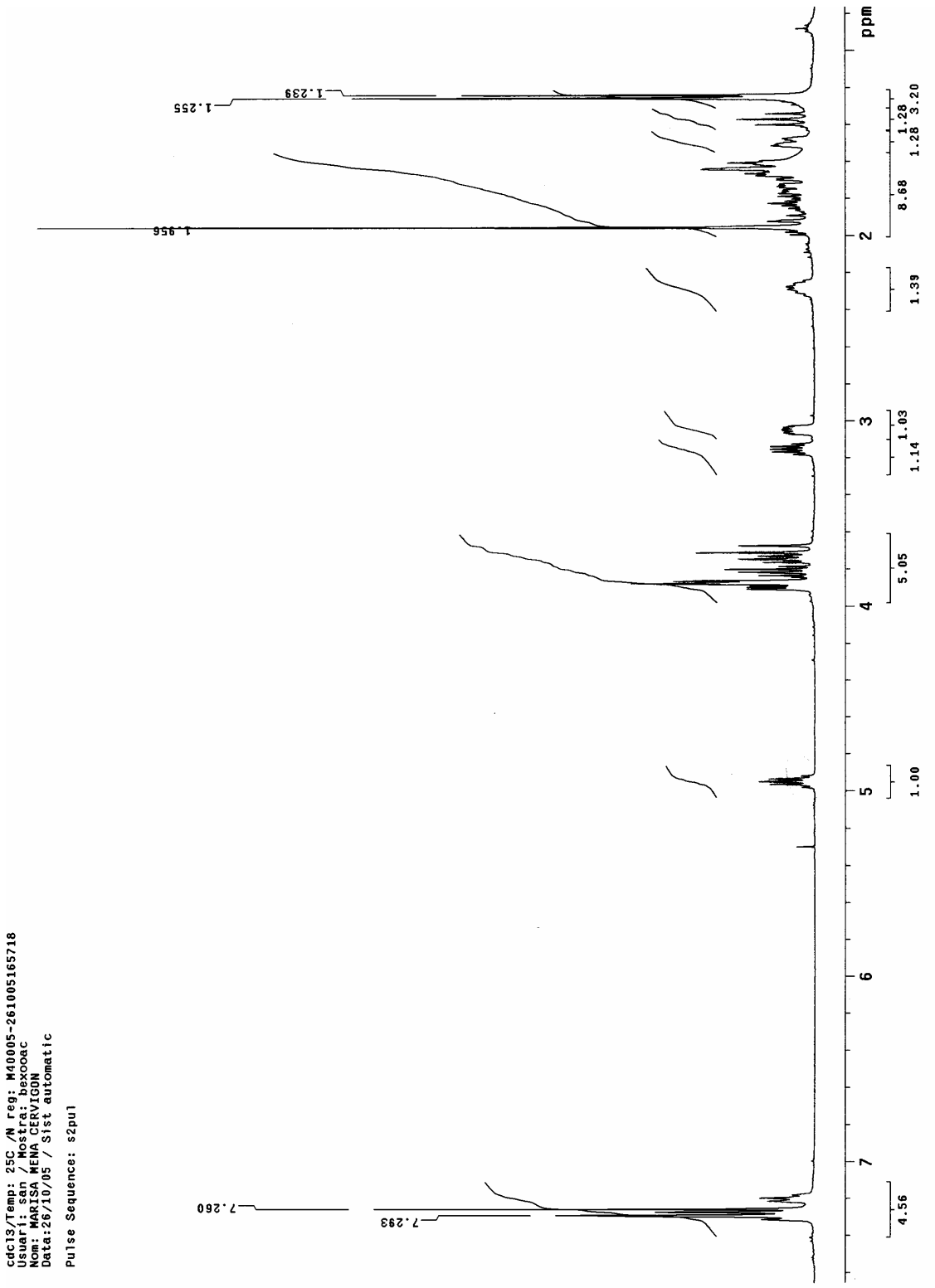

H
O
H
OAc
+
O
N
H
Bn
Me

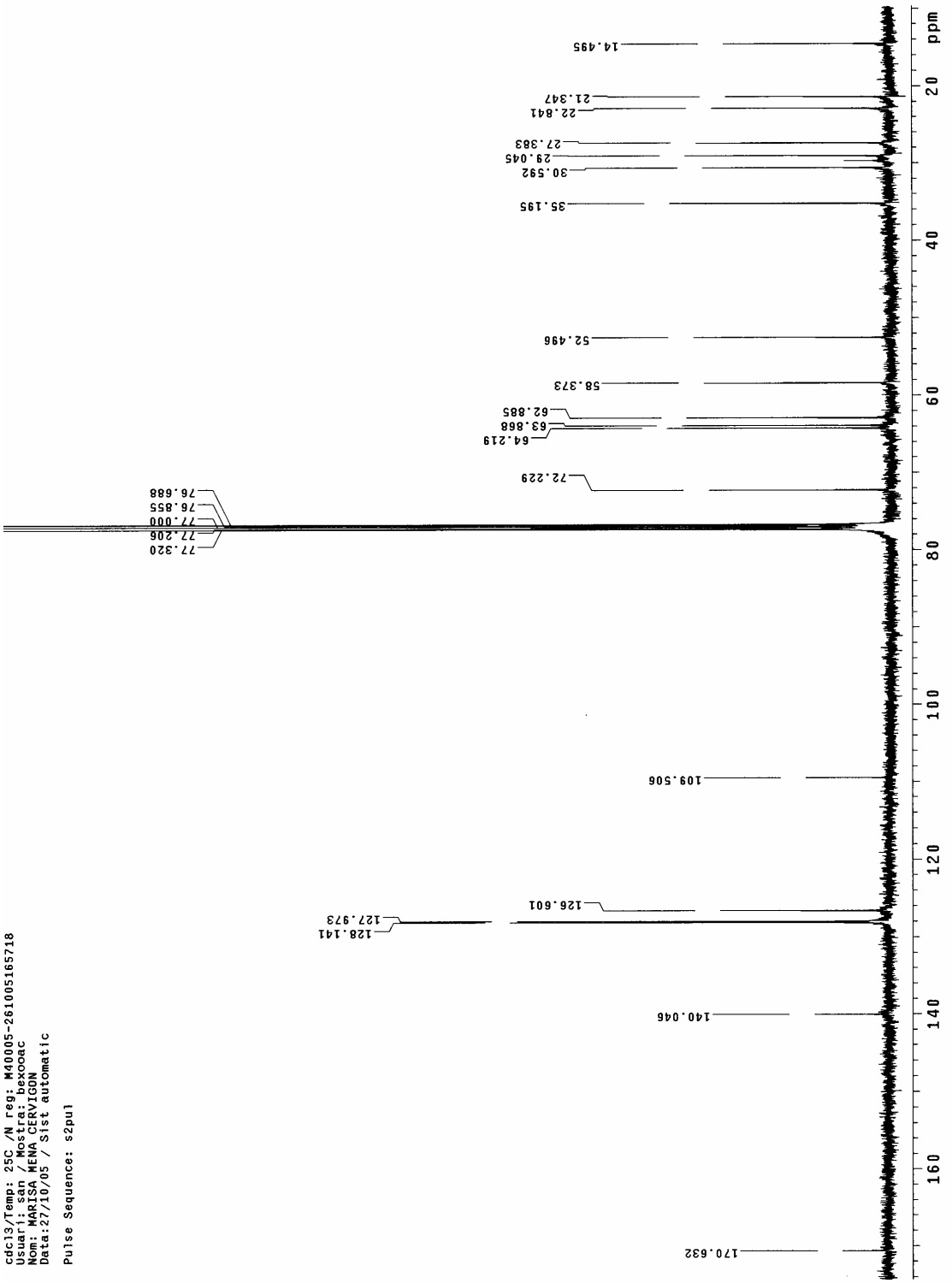
11c **19**

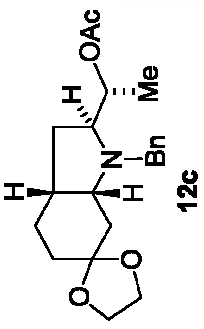

F2
(ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
75
70
65
60
55
50
45
40
35
30
25
20
15
F1 (ppm)

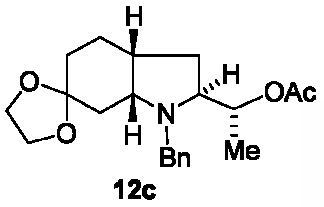

OAc
H
Me
N
Bn
H
H
O
O

12c


cdcl3/Temp: 25C /N reg: M40005-26100516571 8
Usuari: san / Mostra: bexooac
Nom: MARISA MENA CERVIGON
Data:26/10/05 / Sist automatic
Pulse Sequence: s2pul
7.260
7.293
1.255
1.239
1.956
ppm
4.56
1.00
5.05
1.14
1.03
1.39
8.68
1.28
1.28
3.20

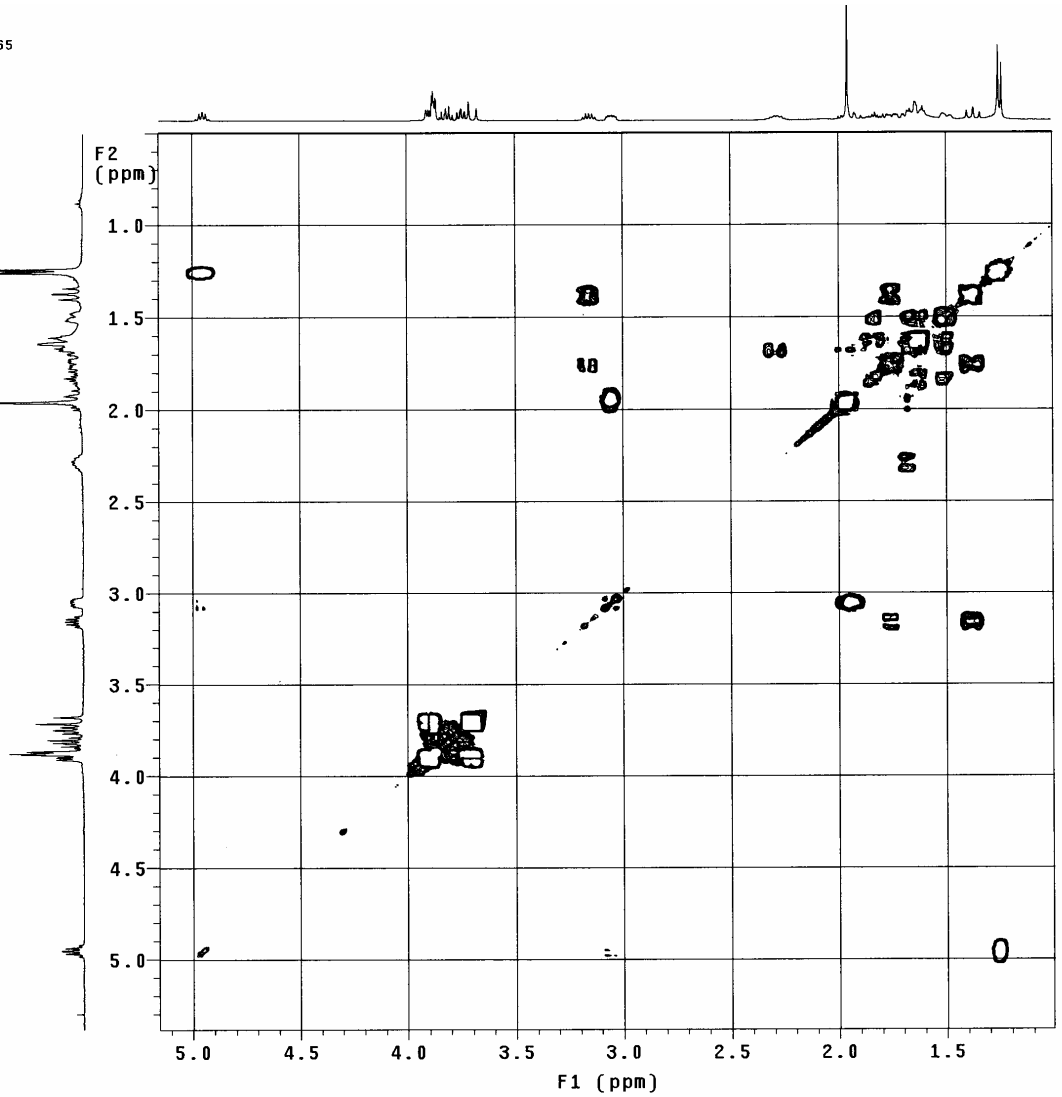

cdcl3/Temp: 25C /N reg: M40005-261005165718
Usuari: san / Mostra: bexooac
Nom: MARISA MENA CERVIGON
Data:27/10/05 / Sist automatic
Pulse Sequence: s2pul
14.495
21.347
22.841
27.383
29.045
30.592
35.195
52.496
58.373
62.885
63.868
64.219
72.229
76.688
76.855
77.000
77.206
77.320
109.506
126.601
127.973
128.141
140.046
170.632
ppm
20
40
60
80
100
120
140
160

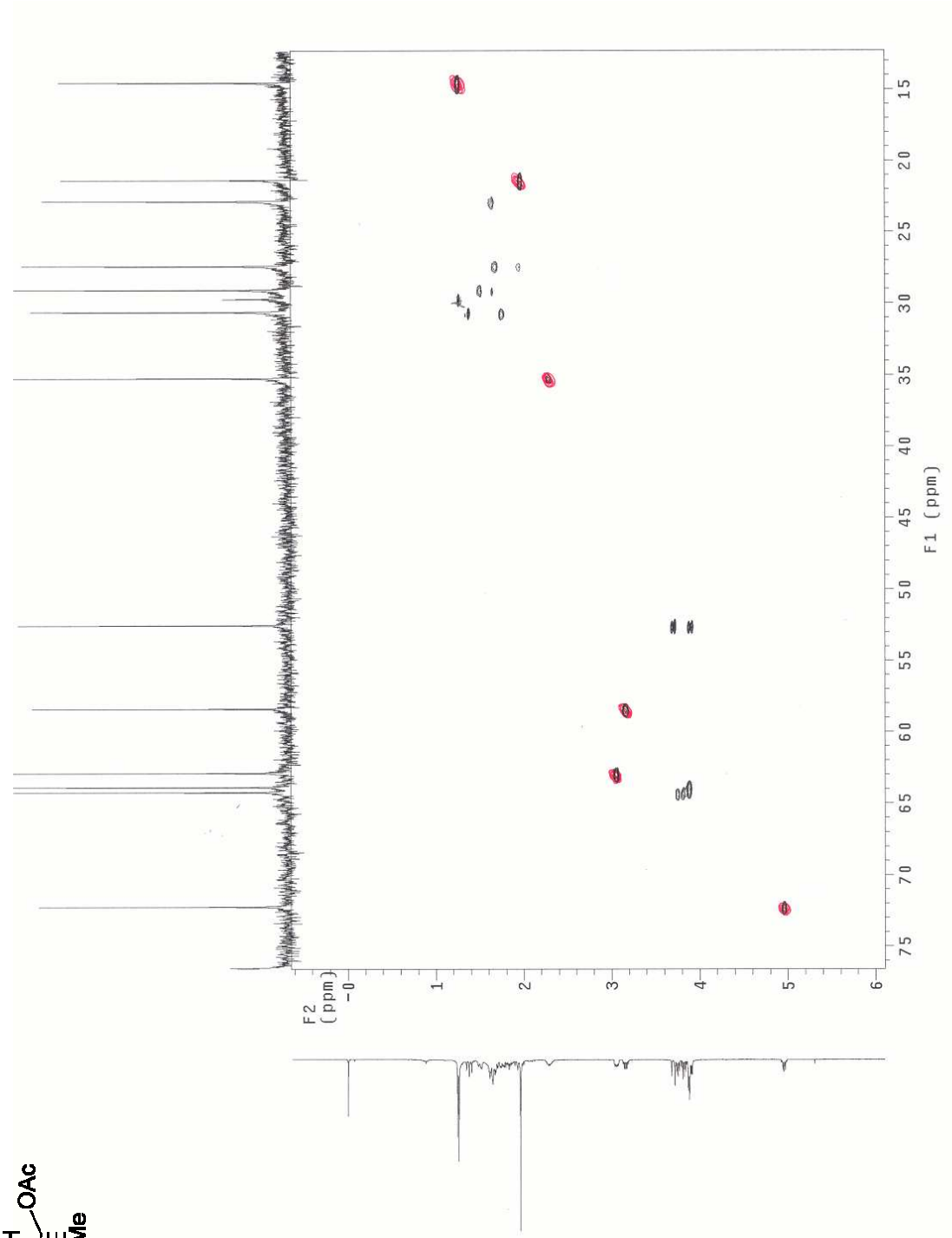

OAc
H
Me
N
Bn
H
H
O
O
12c

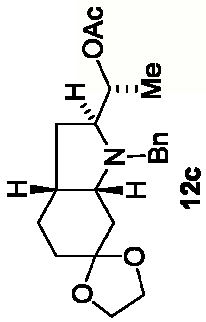


12c

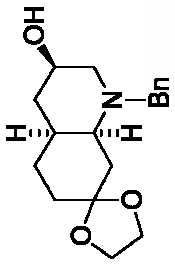
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-261005165
718
Usuari: san / Mostra: bexooac
Nom: MARISA MENA CERVIGON
Data:27/10/05 / Sist automatic

exp4  gCOSY

      SAMPLE              FLAGS
date    Oct 27 2005  hs                nn
solvent      cdcl3   sspul              n
sample auto_Custom~  hsglvl          1000
      Q_26Oct2005        SPECIAL
   ACQUISITION       temp             25.0
sw          3937.0   gain               28
at           0.150   spin                0
np            1182     F2 PROCESSING
fb        not used   sb              -0.075
ss              16   sbs         not used
di           1.000   fn                2048
nt               4     F1 PROCESSING
  2D ACQUISITION     sb1             -0.065
sw1         3937.0   sbs1        not used
ni             256   proc1              lp
  PRESATURATION      fn1               2048
satmode          n          DISPLAY
satfrq           0   sp              139.0
satdly           0   wp             1955.0
satpwr           0   sp1             402.9
   TRANSMITTER       wp1            1658.7
tn              H1   rf1             486.1
sfrq       400.113   rfp                0
tof         -539.5   rfl1            486.1
tpwr            58   rfp1               0
pw          12.300          PLOT
   GRADIENTS         wc             153.0
gzlvl1         1000   sc                6.2
gt1       0.001000   wc2            153.0
gstab     0.000500   sc2                0
   DECOUPLER         vs               334
dn              C13   th                 7
dm              nnn   ai  cdc  av
```



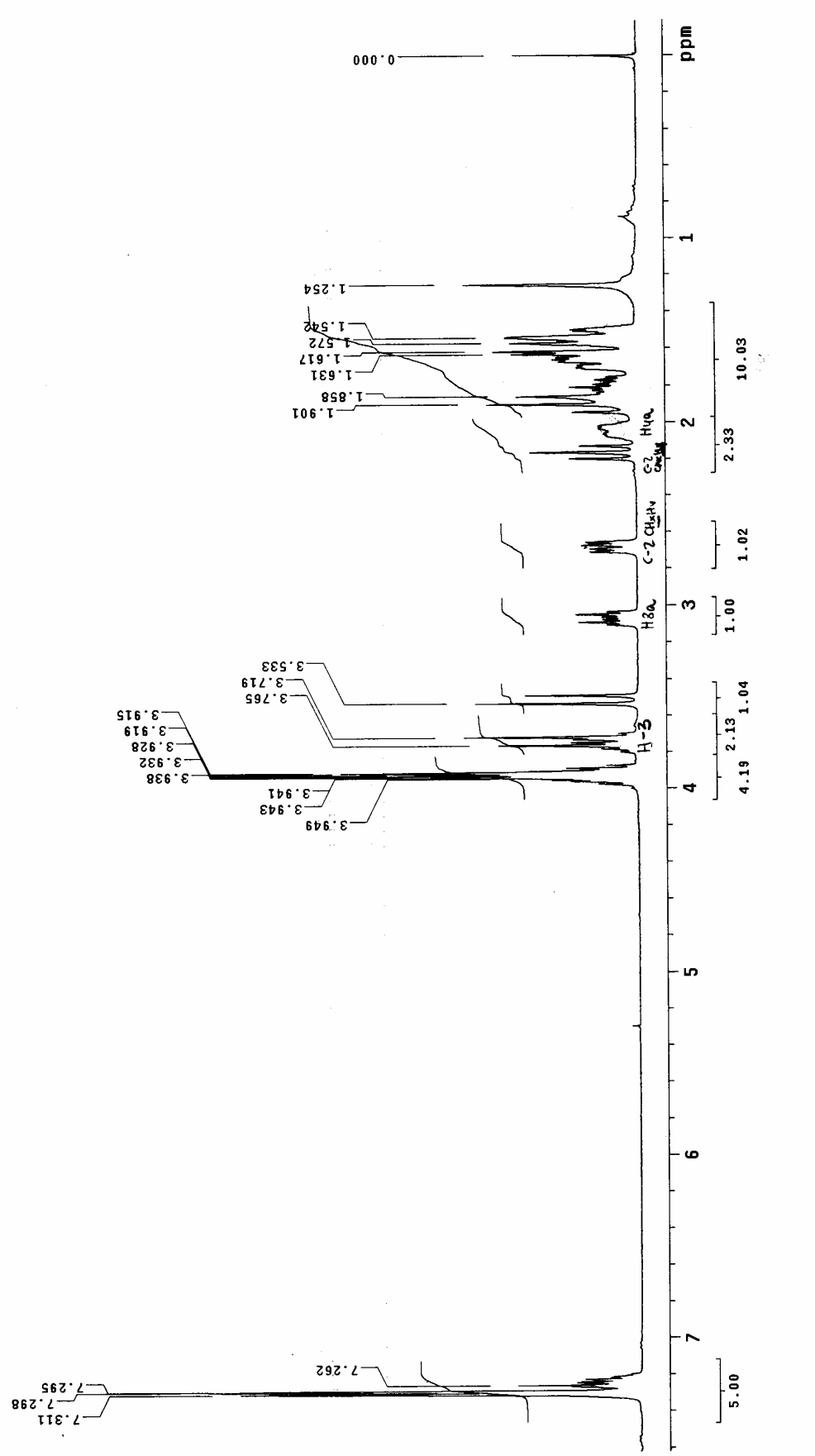


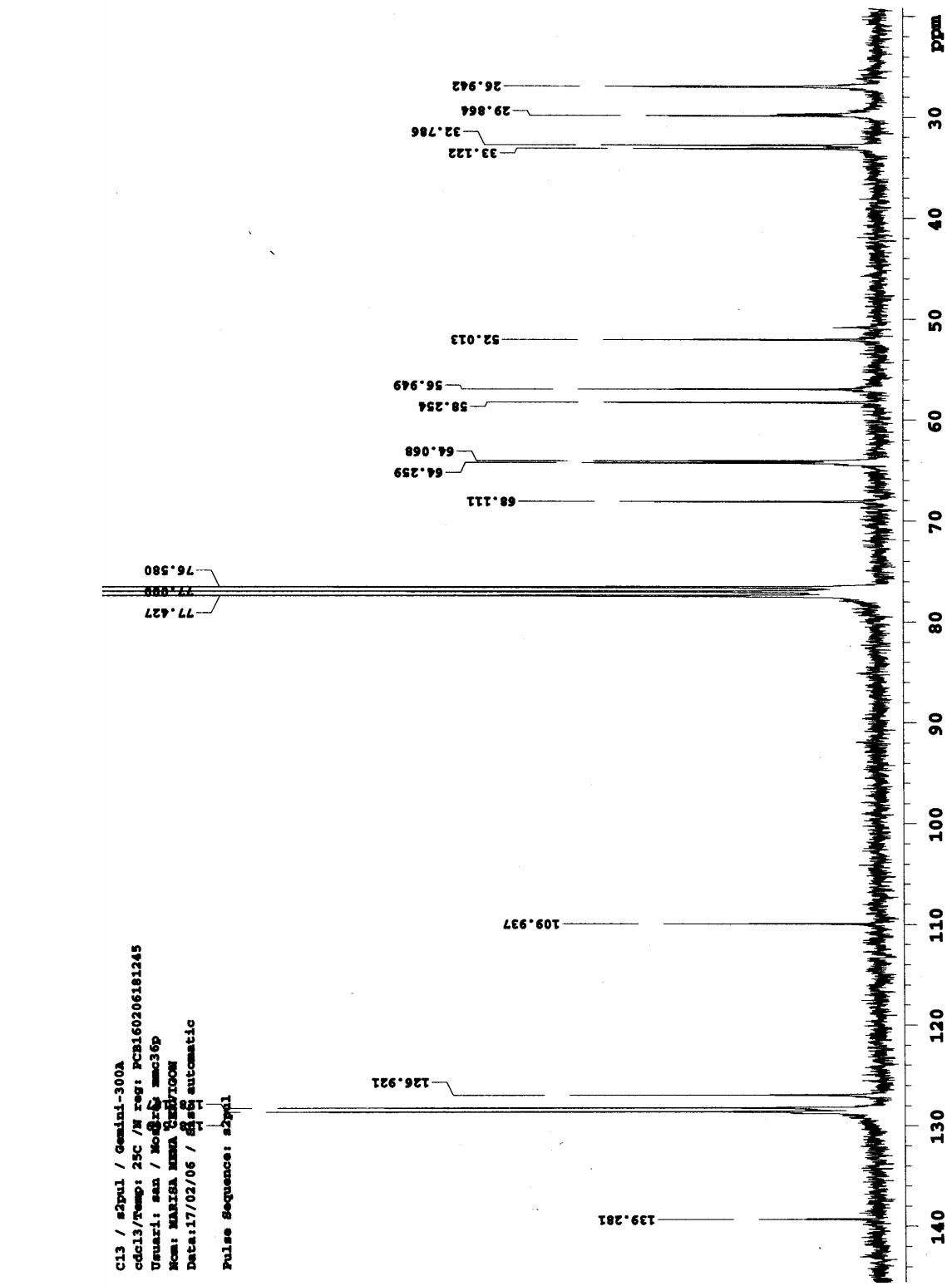


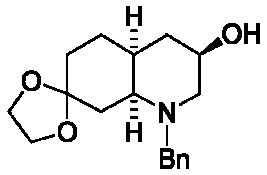
12c


OH
N
Bn
H
H
O
O

13


ppm
0.000
1.254
1.542
1.572
1.617
1.631
1.858
1.901
3.533
3.719
3.765
3.915
3.919
3.928
3.932
3.938
3.941
3.943
3.949
7.262
7.295
7.298
7.311
H-5
H8a
C-2 CH2Ph
C-2
H4a
5.00
4.19
2.13
1.04
1.00
1.02
2.33
10.03


C13 / s2pul / Gemini-300A
cdcl3/Temp: 25C /N reg: PCB160206181245
Usuari: san / Mod
Mem: MARSA MEM
Data:17/02/06 /
Pulse Sequence: s2pul
139.281
136.921
109.937
77.427
77.088
76.580
68.111
64.259
64.068
58.254
56.949
52.013
33.122
32.786
29.864
26.942
ppm
OH
N
Bn
H
H
O
O
13



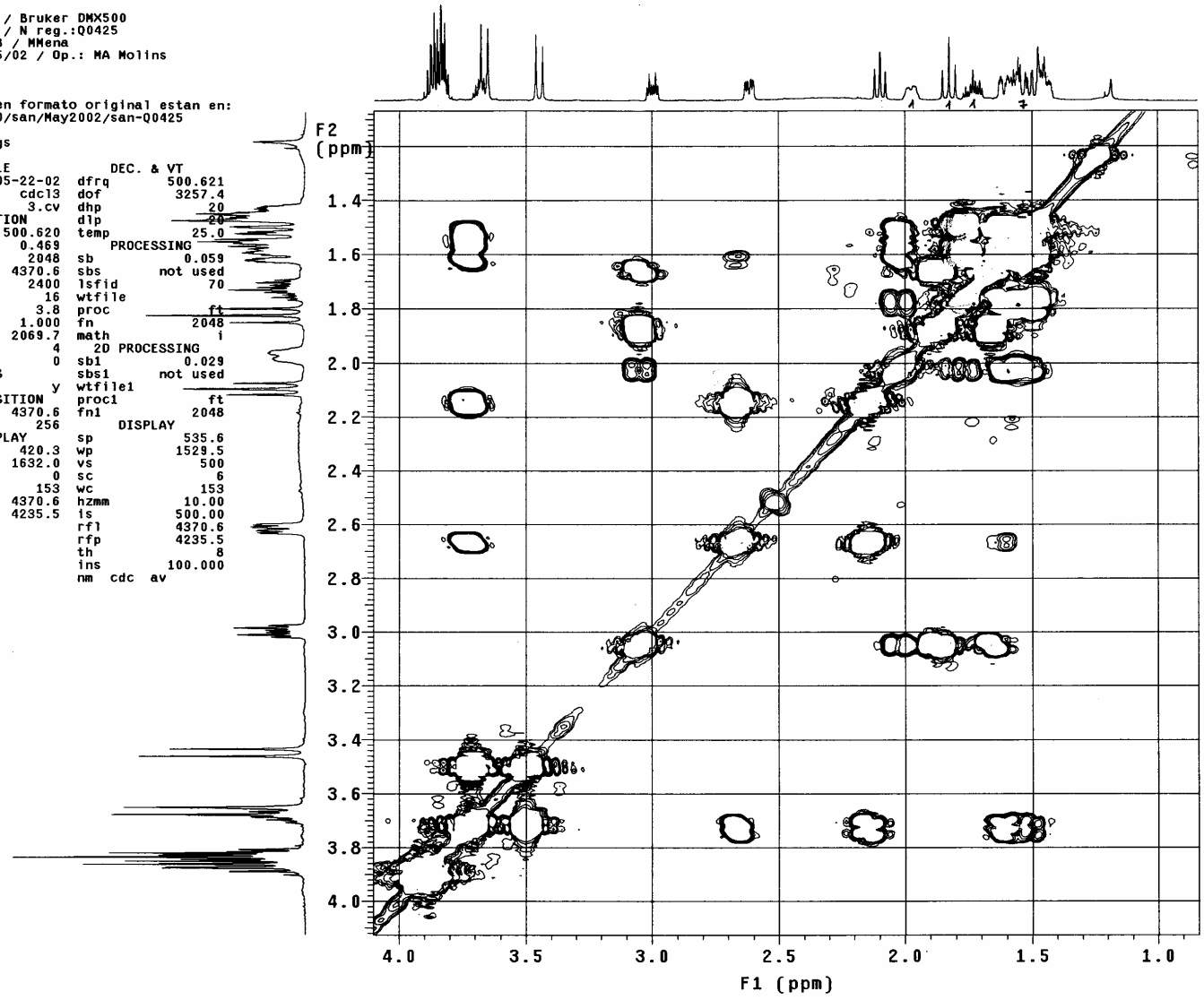
13

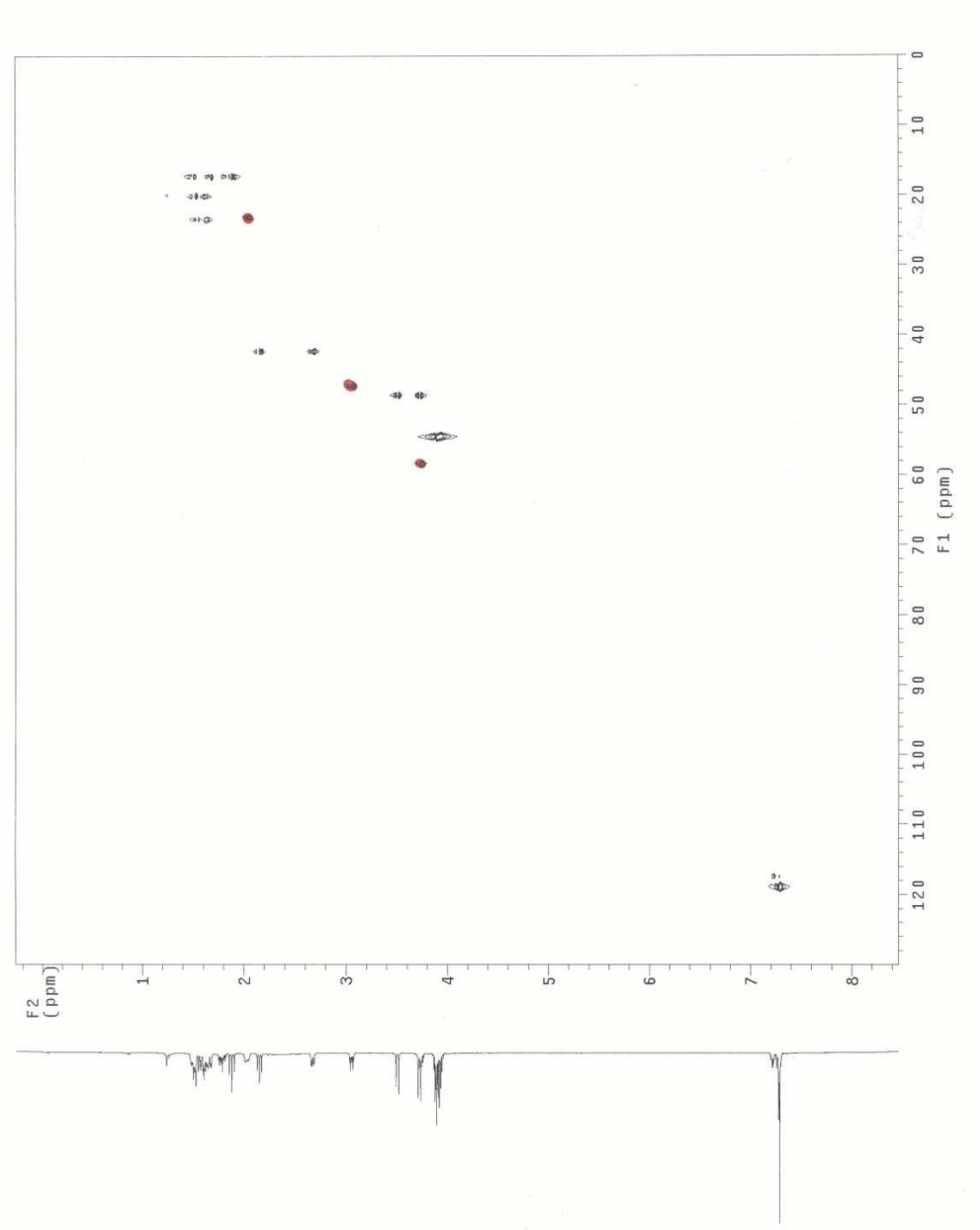
H1 / gcosy / Bruker DMX500
cdcl3/ 25C / N reg.:Q0425
san/ mmc038 / MMena
Data: 22/05/02 / Op.: MA Molins

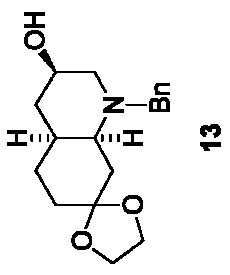
los datos en formato original estan en:
/data3/B500/san/May2002/san-Q0425

exp1 cosygs

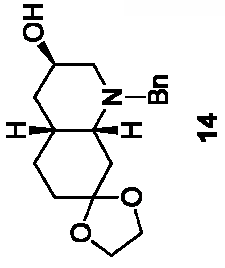
SAMPLE		DEC. & VT	
date	05-22-02	dfrq	500.621
solvent	cdcl3	dof	3257.4
file	3.cv	dhp	20
ACQUISITION		dlp	20
sfrq	500.620	temp	25.0
at	0.469	PROCESSING	
np	2048	sb	0.059
sw	4370.6	sbs	not used
fb	2400	lsfid	70
ss	16	wtfile	
pw	3.8	proc	ft
rd	1.000	fn	2048
tof	2069.7	math	i
nt	4	2D PROCESSING	
ct	0	sb1	0.029
FLAGS		sbs1	not used
dp	y	wtfile1	
2D ACQUISITION		proc1	ft
sw1	4370.6	fn1	2048
ni	256	DISPLAY	
2D DISPLAY		sp	535.6
sp1	420.3	wp	1529.5
wp1	1632.0	vs	500
sc2	0	sc	6
wc2	153	wc	153
rfl1	4370.6	hzmm	10.00
rfp1	4235.5	is	500.00
		rfl	4370.6
		rfp	4235.5
		th	8
		ins	100.000
		nm cdc av	



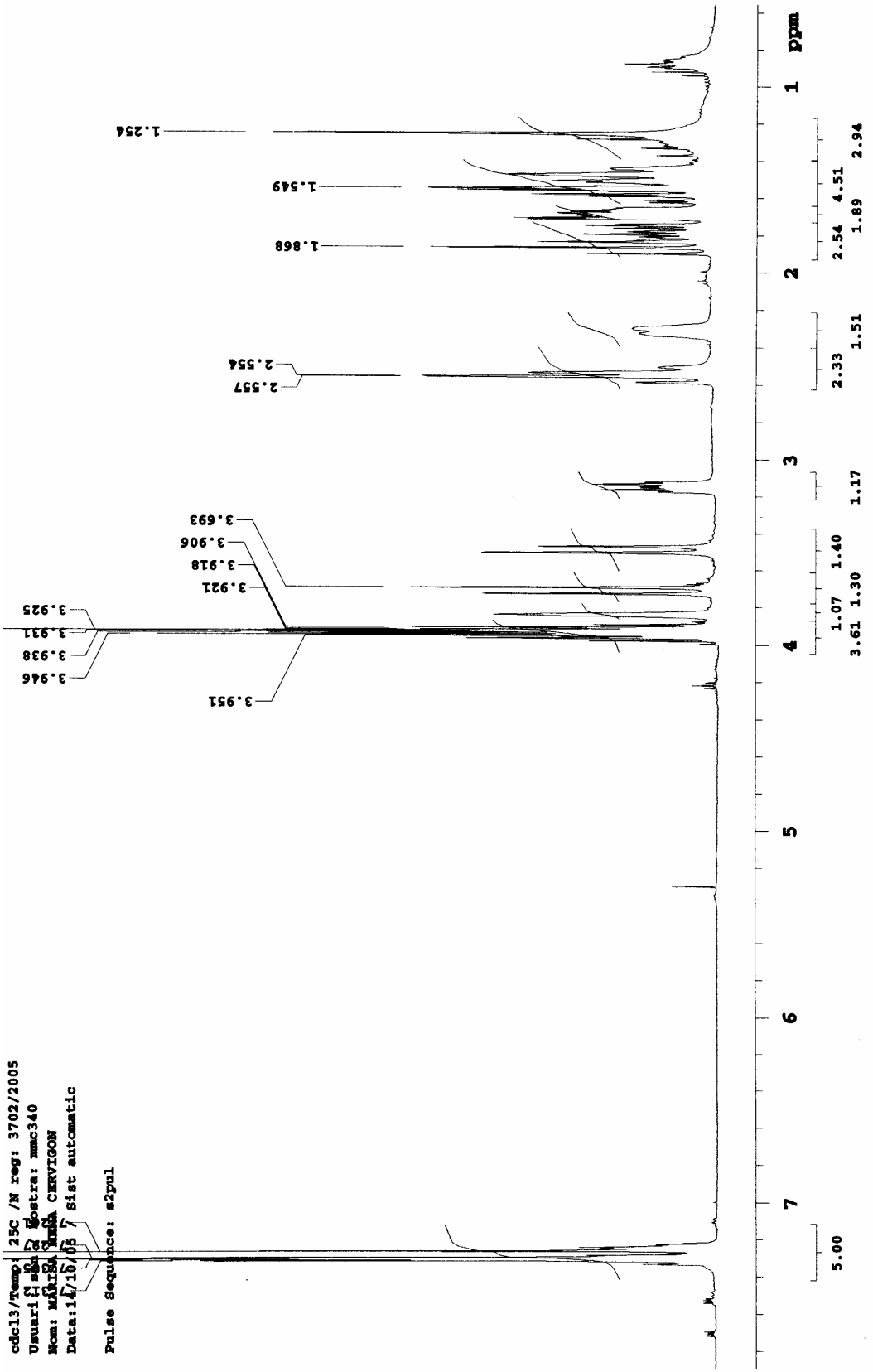


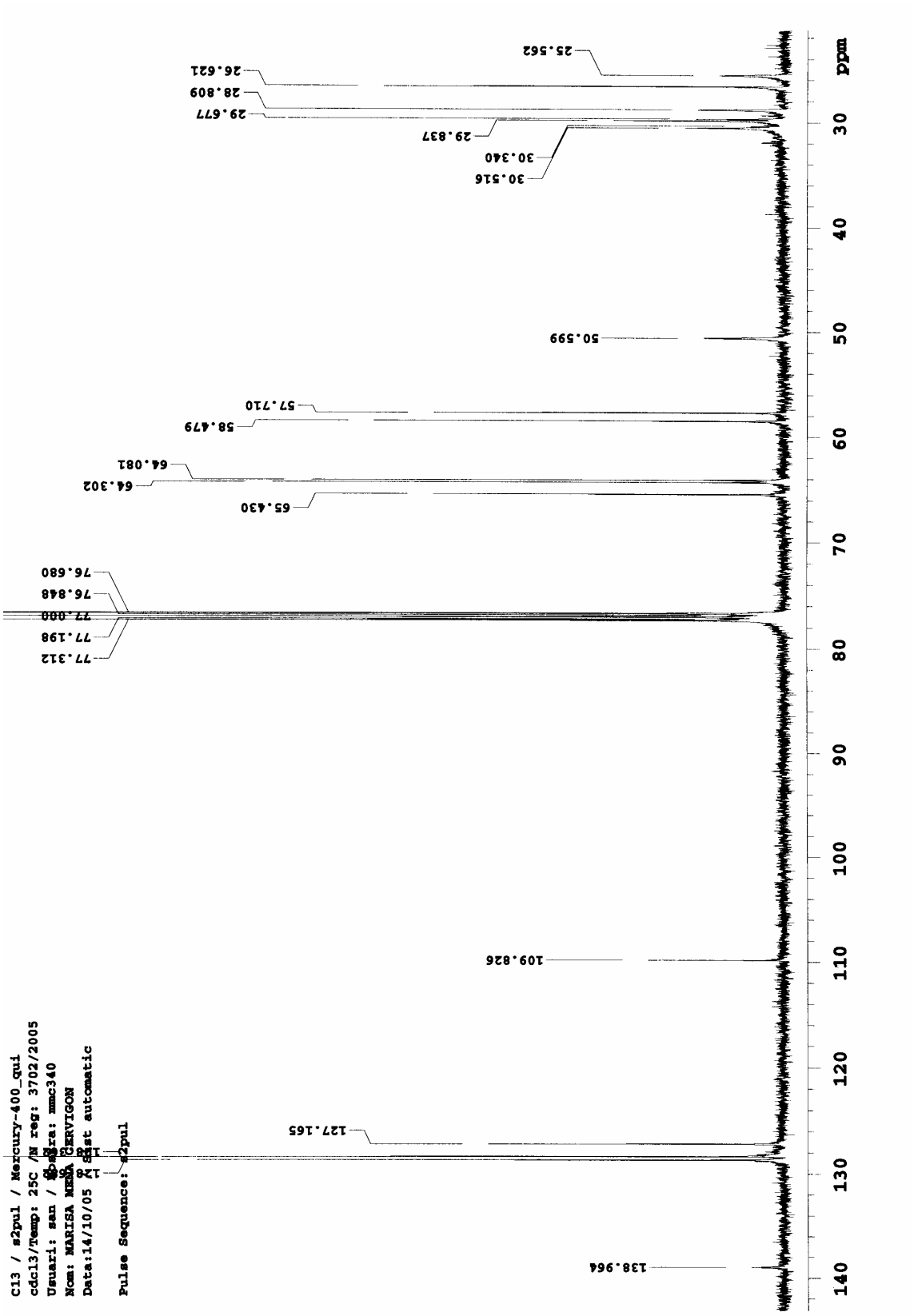


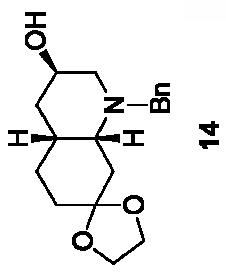
13


OH
N
Bn
H
H
O
O

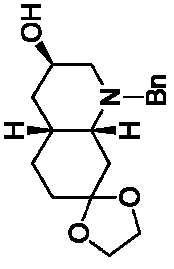
14


cdcl3/Temp: 25C /N reg: 3702/2005
Pulse Sequence: s2pul
1.254
1.549
1.868
2.554
2.557
3.693
3.906
3.918
3.921
3.925
3.931
3.938
3.946
3.951
ppm
5.00
1.07
1.40
3.61
1.30
1.17
2.33
1.51
2.54
4.51
1.89
2.94

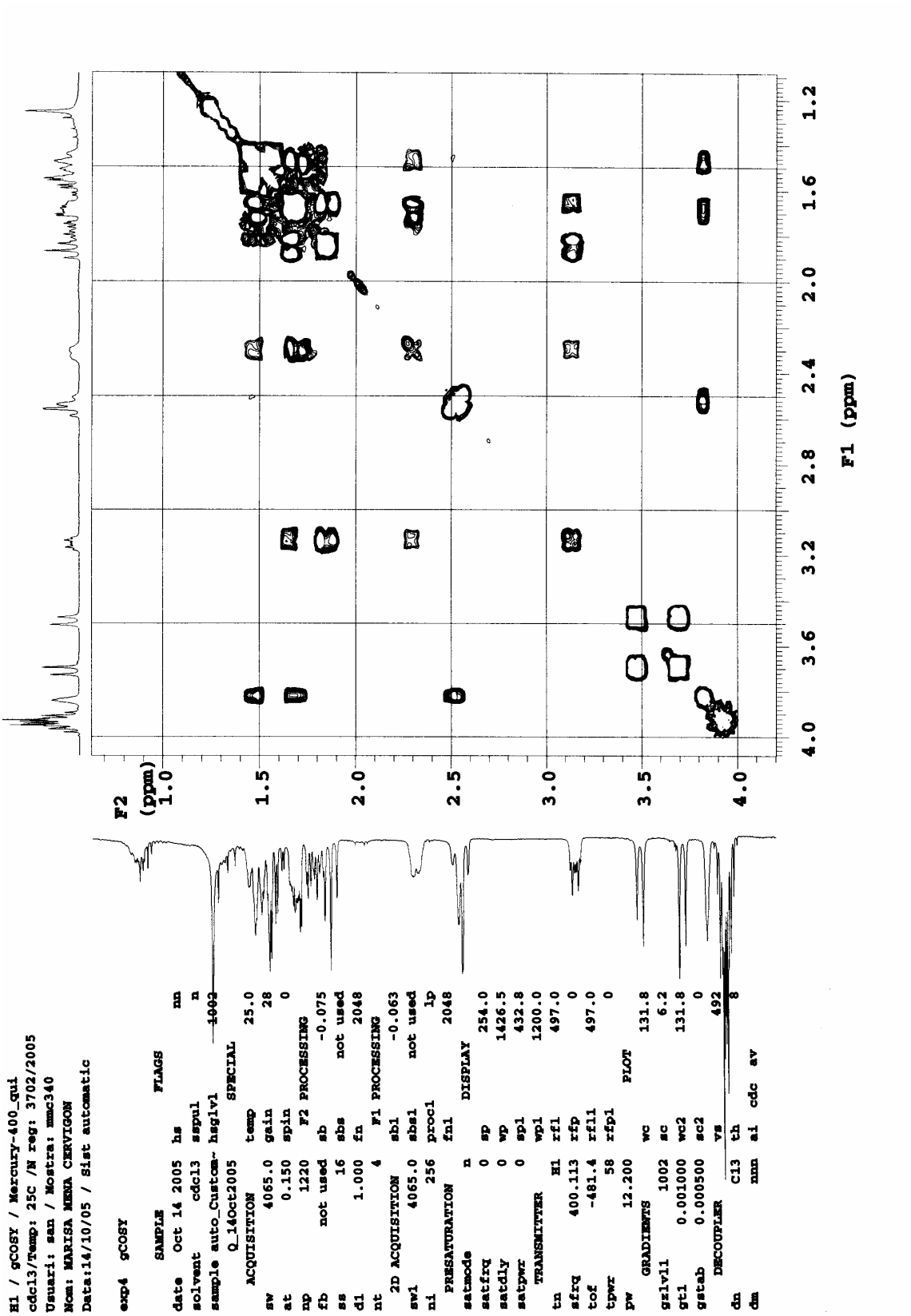

C13 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: 3702/2005
Data:14/10/05 Pulse Sequence: s2pul
138.964
127.165
109.826
77.312
77.198
77.000
76.848
76.680
65.430
64.302
64.081
58.479
57.710
50.599
30.516
30.340
29.837
29.677
28.809
26.621
25.562
ppm


OH
N
Bn
H
H
O
O

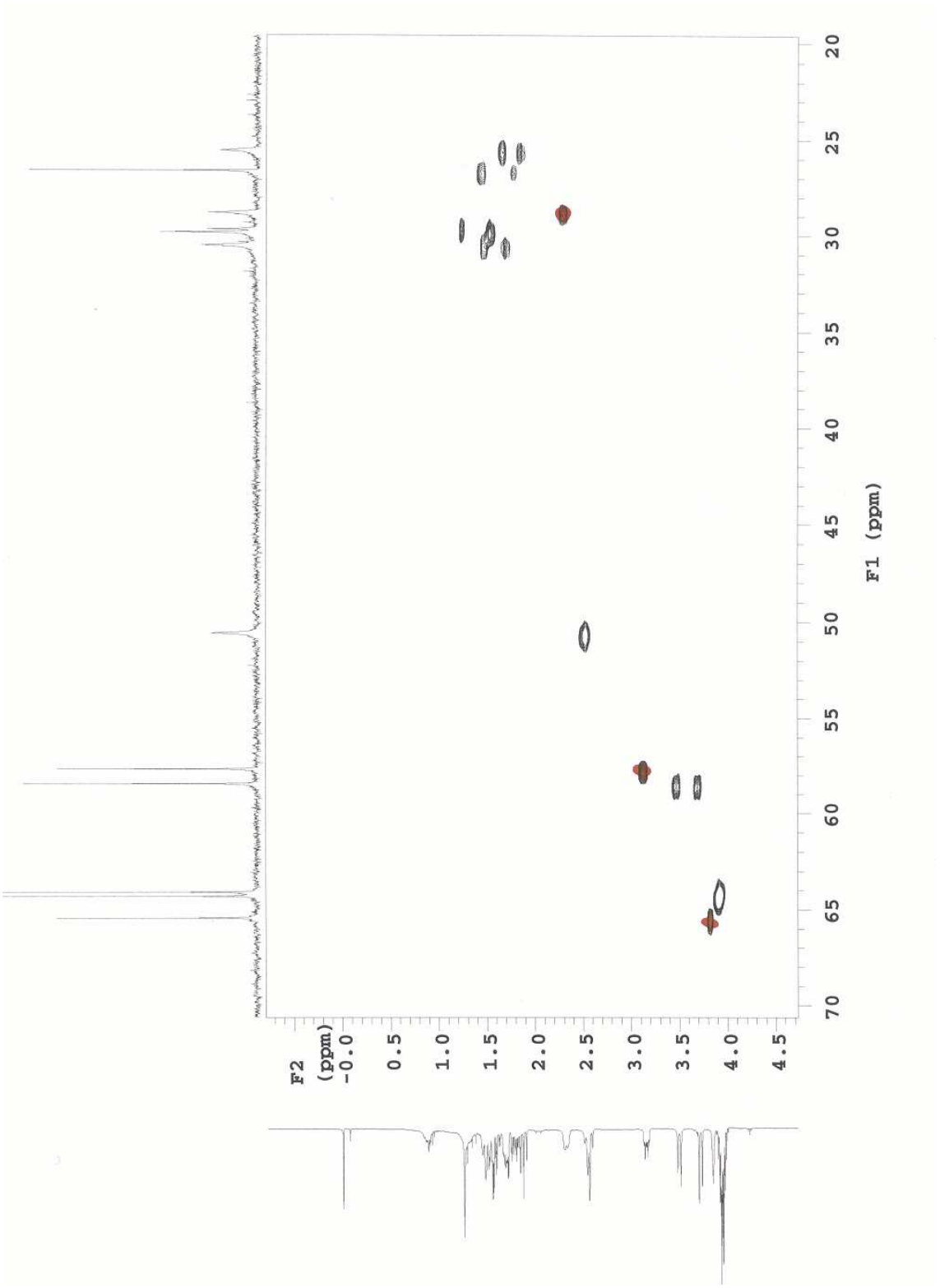
14

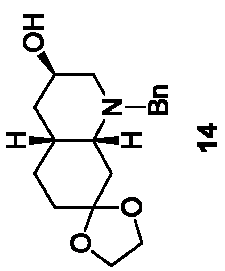


14

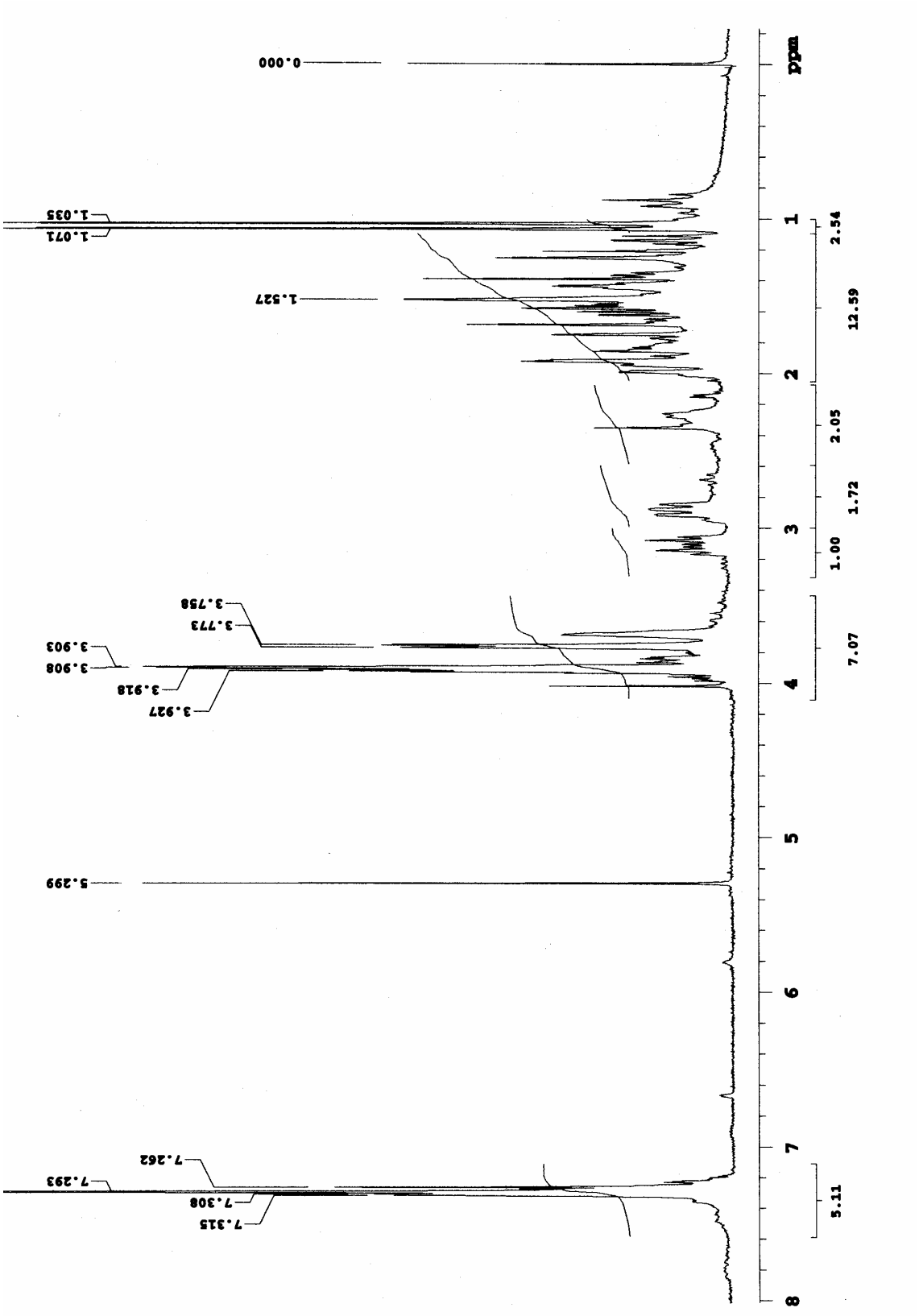


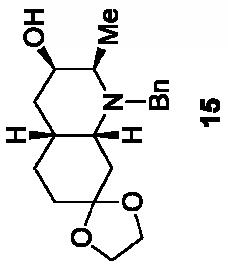

```
H1 / gCOSY / Mercury-400_gui
cdcl3/Temp: 25C /N reg: 3702/2005
Usuari: san / Mostra: mmc340
Nom: MARISA MENA CERVIGON
Data:14/10/05 / Sist automatic

exp4  gCOSY

      SAMPLE                FLAGS                  nn
date   Oct 14 2005  hs                             n
solvent     cdcl3   sspul                          n
sample auto_Custom~ hsglvl          1002
      0_14Oct2005       SPECIAL
   ACQUISITION          temp          25.0
sw         4065.0      gain            28
at            0.150    spin             0
np             1220     F2 PROCESSING
fb        not used     sb          -0.075
ss               16    sbs        not used
d1            1.000    fn            2048
nt                4     F1 PROCESSING
  2D ACQUISITION       sb1         -0.063
sw1        4065.0      sbs1       not used
ni              256    procs            1p
  PRESATURATION        fn1           2048
satmode          n     DISPLAY
satfrq           0     sp             254.0
satdly           0     wp            1426.5
satpwr           0     sp1            432.8
  TRANSMITTER          wp1           1200.0
tn                H1   rf1            497.0
sfrq         400.113   rfp                0
tof         -481.4     rfl1           497.0
tpwr             58    rfp1               0
pw           12.200          PLOT
   GRADIENTS           wc             131.8
gzlvl1           1002  sc               6.2
gt1         0.001000   wc2            131.8
gstab       0.000500   sc2                0
   DECOUPLER           vs               492
dn                C13  th                 8
dm                nnn  ai   cdc   av
```

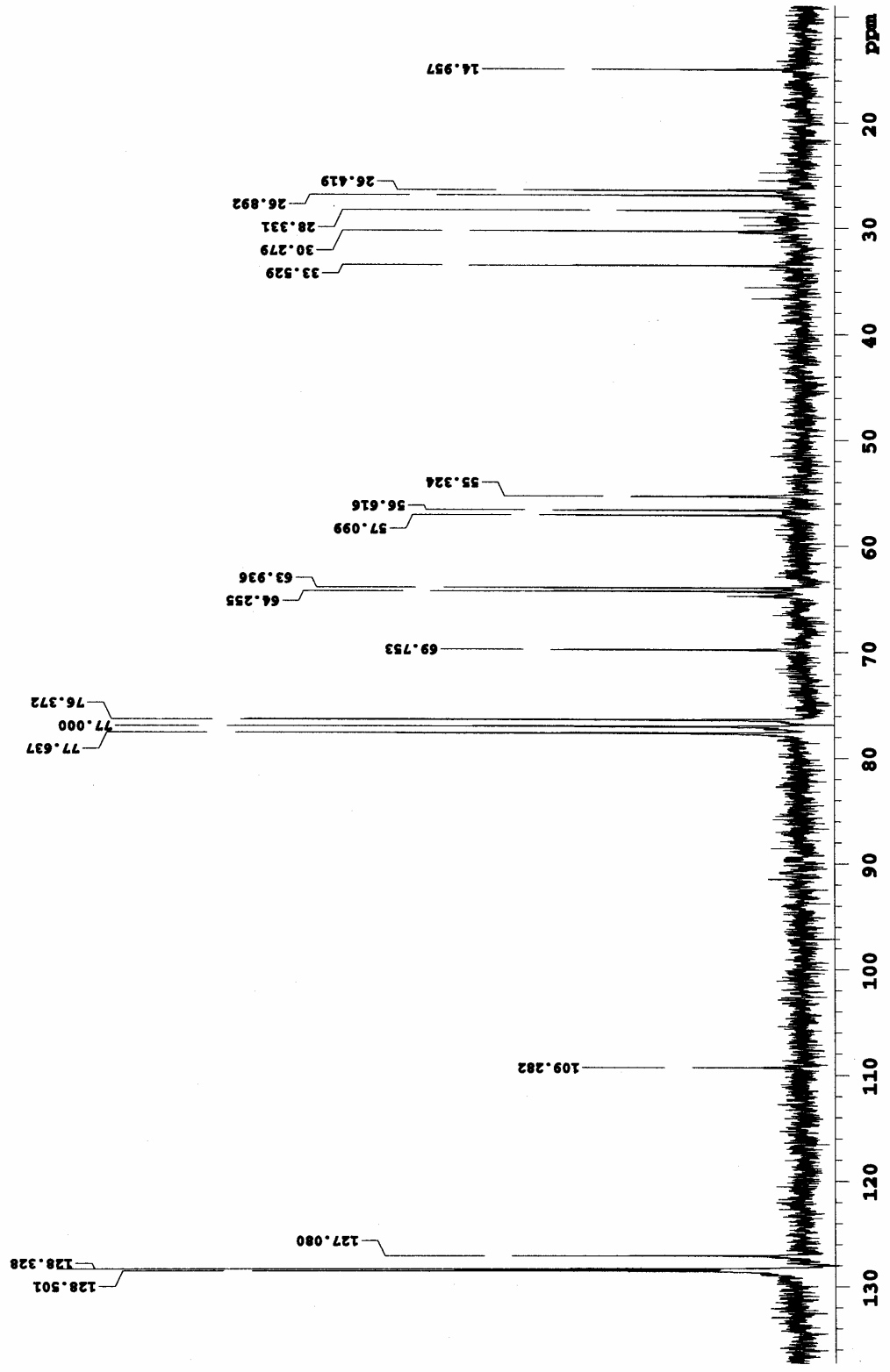


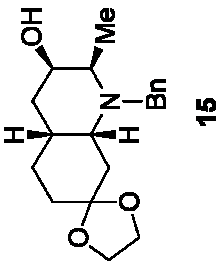


14

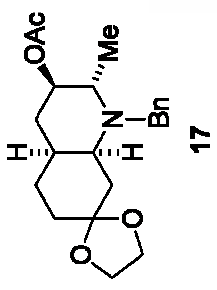

0.000
1.035
1.071
1.527
3.758
3.773
3.903
3.908
3.918
3.927
5.299
7.262
7.293
7.308
7.315
ppm
1
2
3
4
5
6
7
8
2.54
12.59
2.05
1.72
1.00
7.07
5.11

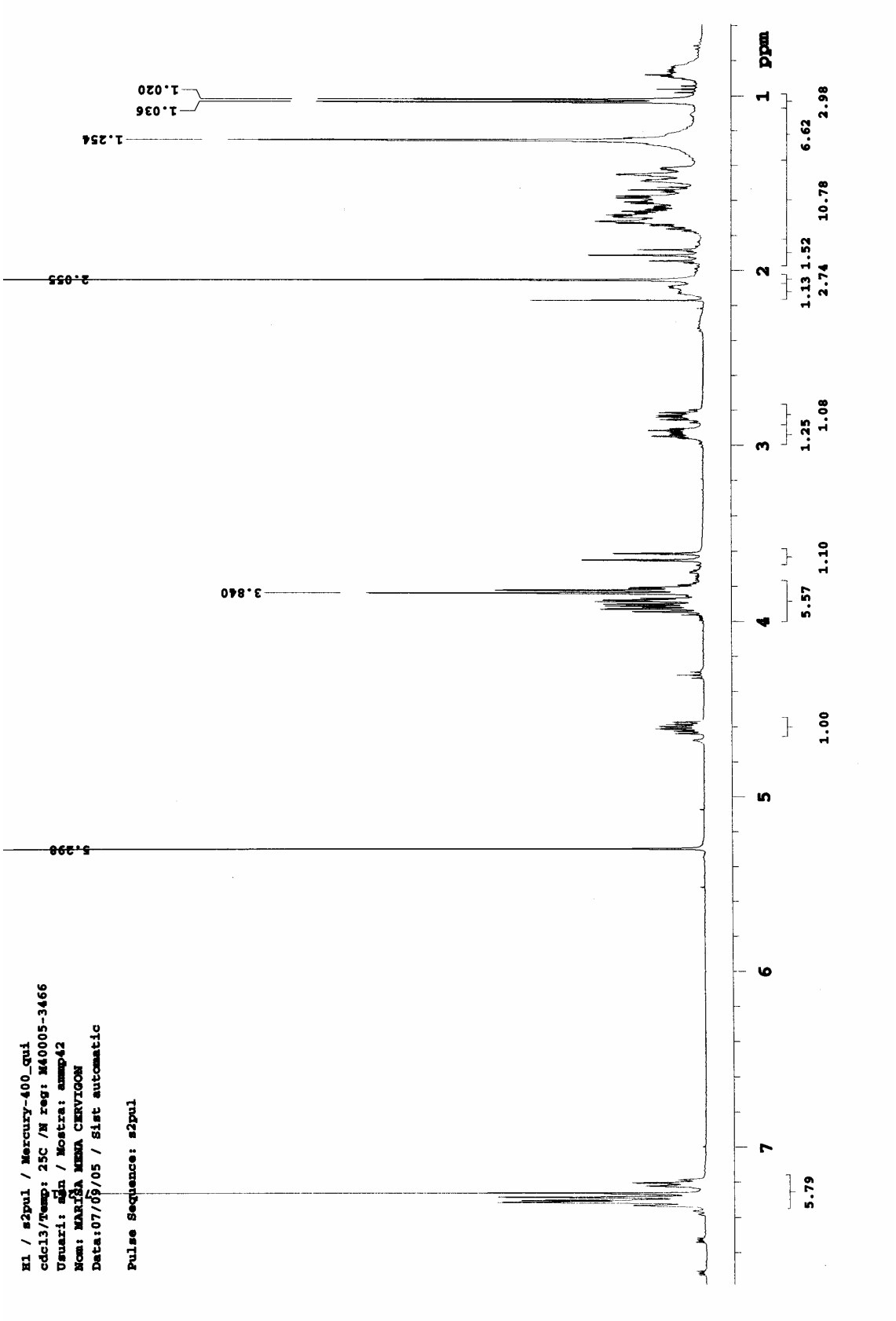

OH
Me
N
Bn
H
H
O
O
15

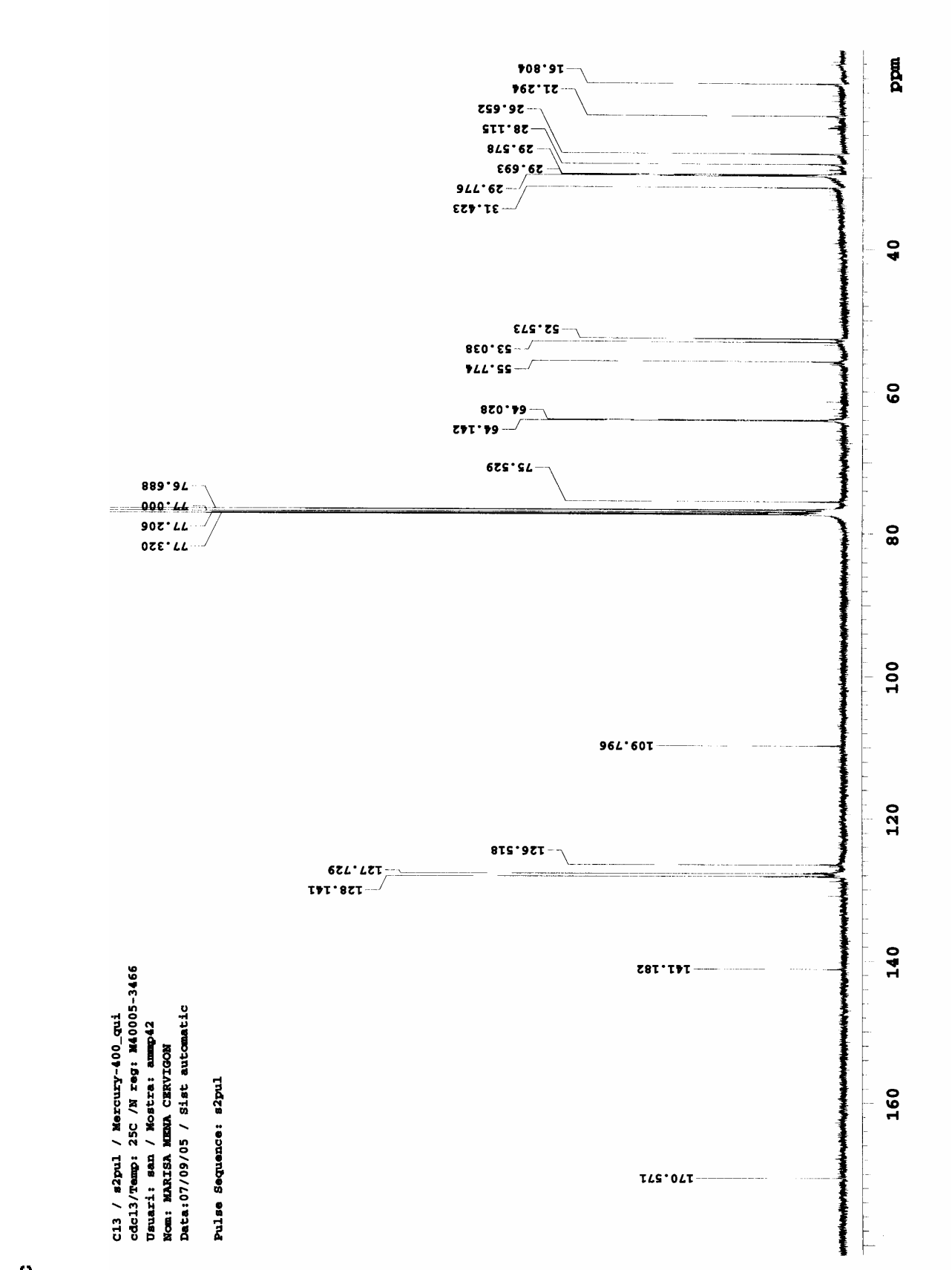

14.957
26.419
26.892
28.331
30.279
33.529
55.324
56.616
57.099
63.936
64.255
69.753
76.372
77.000
77.637
109.282
127.080
128.328
128.501
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130

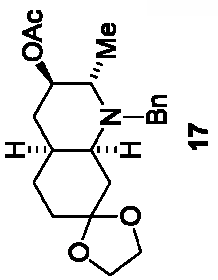

OH
Me
N
Bn
H
H
O
O

15

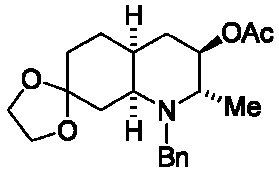

OAc
Me
N
Bn
H
H
O
O
17


H1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-3466
Usuari: adm / Mostra: ammp42
Nom: MARIA MENA CERVIGON
Data:07/09/05 / Sist automatic
Pulse Sequence: s2pul
5.298
3.840
2.055
1.254
1.036
1.020
ppm
1.00
5.57
1.10
1.25
1.08
1.13
1.52
2.74
10.78
6.62
2.98
5.79


C13 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-3466
Usuari: san / Mostra: ammp42
Nom: MARISA MENA CERVIGON
Data:07/09/05 / Sist automatic
Pulse Sequence: s2pul
170.571
141.182
128.141
127.729
126.518
109.796
77.320
77.206
77.000
76.688
75.529
64.142
64.028
55.774
53.038
52.573
31.423
29.776
29.693
29.578
28.115
26.652
21.294
16.804
ppm
160
140
120
100
80
60
40

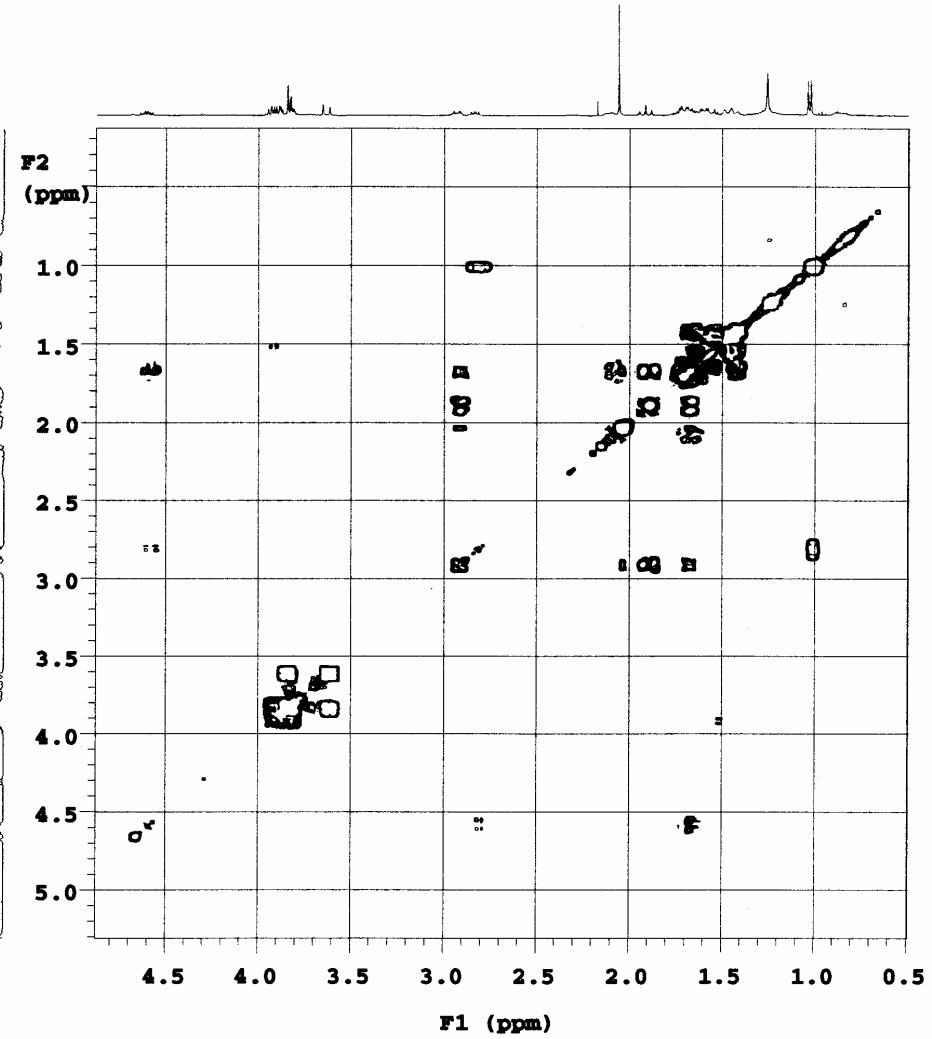

OAc
Me
N
Bn
H
H
O
O
O

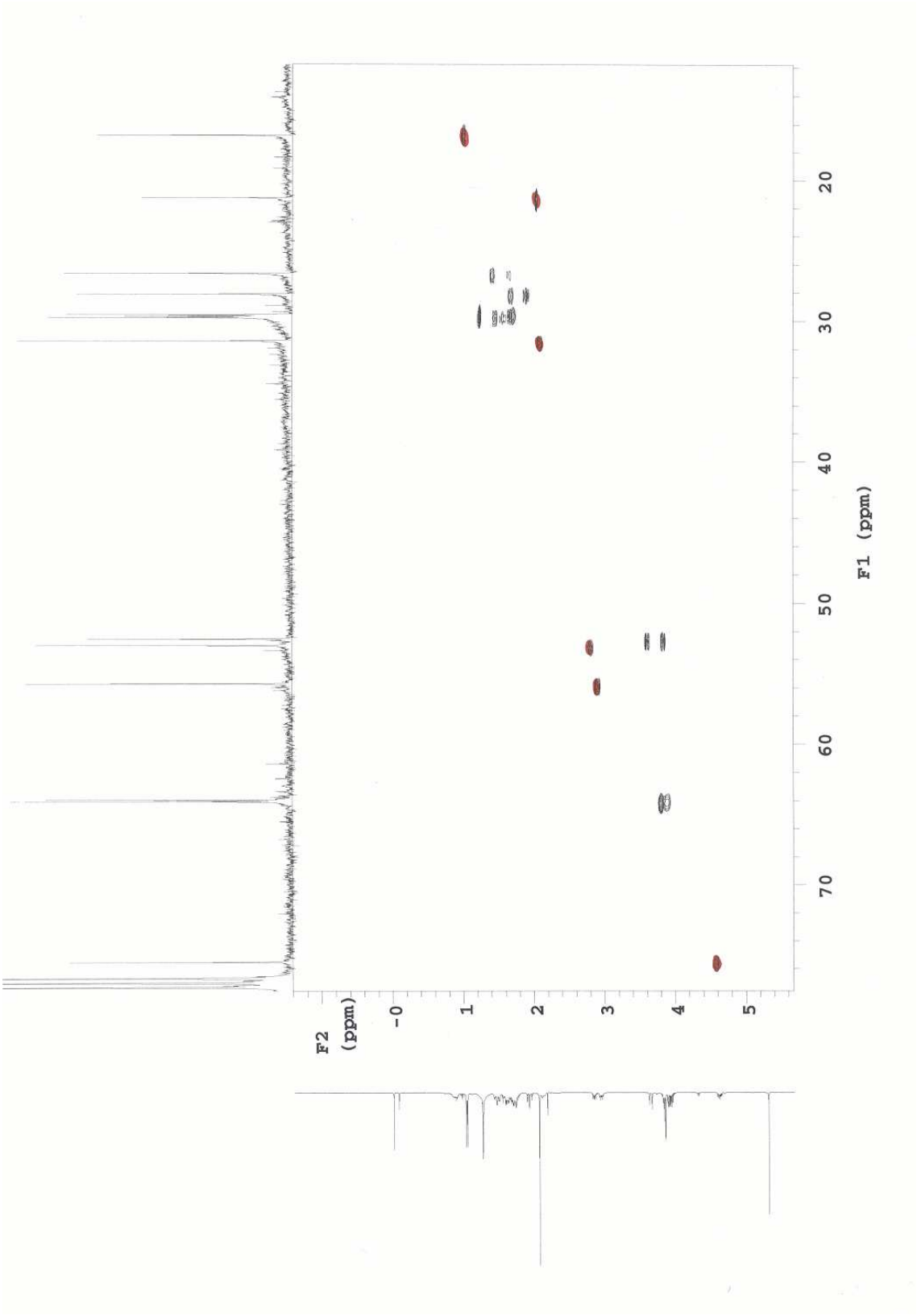
17

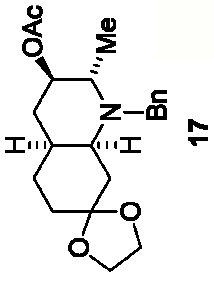


17

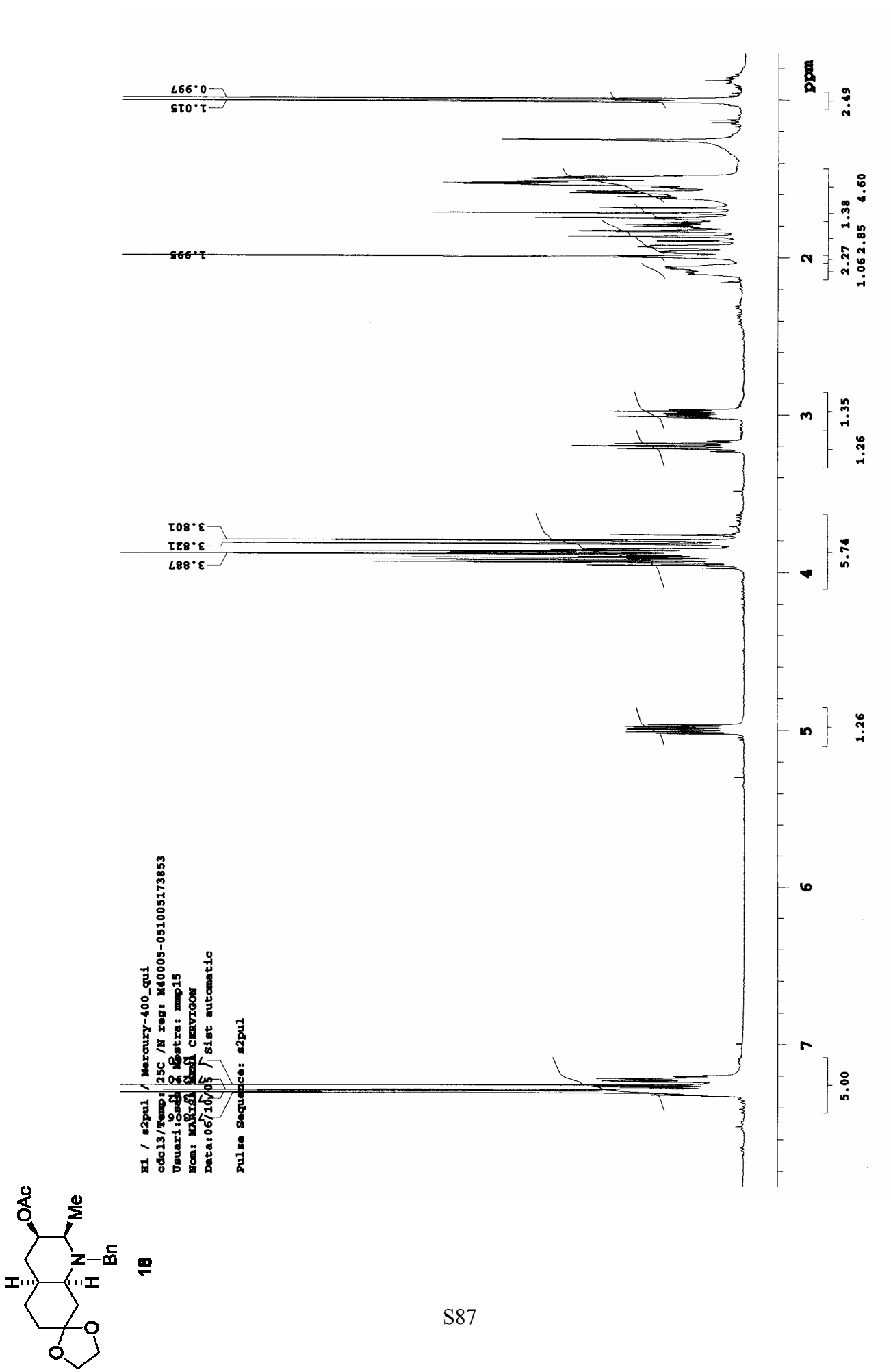
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-3466
Usuari: san / Mostra: ammp42
Nom: MARISA MENA CERVIGON
Data:07/09/05 / Sist automatic

exp3  gCOSY

      SAMPLE                FLAGS
date    Sep  7 2005   hs                nn
solvent       cdcl3   sspul              n
sample auto_Customm~  hsglvl          1002
       Q_07Sep2005        SPECIAL
   ACQUISITION        temp            25.0
sw           4310.3   gain              28
at            0.150   spin               0
np             1294     F2 PROCESSING
fb         not used   sb             -0.075
ss               16   sbs         not used
d1            1.000   fn                2048
nt                4     F1 PROCESSING
  2D ACQUISITION     sb1            -0.059
sw1          4310.3   sbs1        not used
ni              256   proc1              lp
  PRESATURATION      fn1               2048
satmode           n         DISPLAY
satfrq            0   sp                54.4
satdly            0   wp              2068.8
satpwr            0   sp1              197.7
   TRANSMITTER        wp1             1752.8
tn               H1   rf1              573.4
sfrq        400.113   rfp                 0
tof          -430.2   rf11             573.4
tpwr             58   rfp1                0
pw           12.200          PLOT
    GRADIENTS         wc              131.8
gzlvl1         1002   sc                6.2
gt1        0.001000   wc2             131.8
gstab      0.000500   sc2                 0
    DECOUPLER         vs                171
dn               C13   th                  7
dm               nnn   ai  cdc  av
```

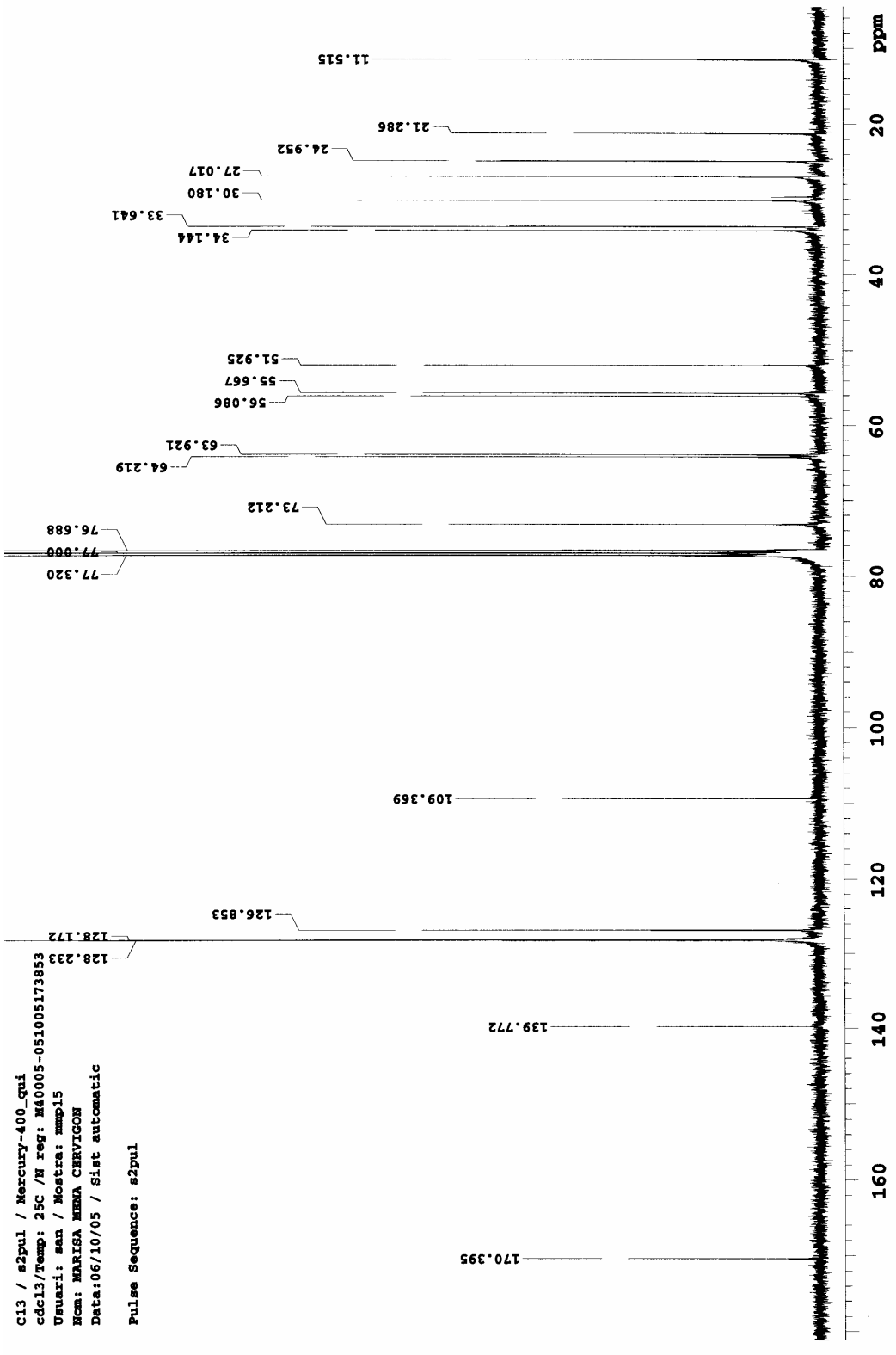


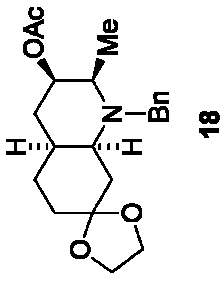




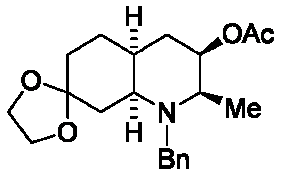
17


OAc
Me
N
Bn
H
H
O
O
18
E1 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-051005173853
Pulse Sequence: s2pul
0.997
1.015
1.995
3.801
3.821
3.887
ppm
2.49
4.60
1.38
2.85
2.27
1.06
1.35
1.26
5.74
1.26
5.00


C13 / s2pul / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-051005173853
Usuari: san / Mostra: mmp15
Ncm: MARISA MENA CERVIGON
Data:06/10/05 / Sist automatic
Pulse Sequence: s2pul
170.395
139.772
128.233
128.172
126.853
109.369
77.320
77.000
76.688
73.212
64.219
63.921
56.086
55.667
51.925
34.144
33.641
30.180
27.017
24.952
21.286
11.515
ppm

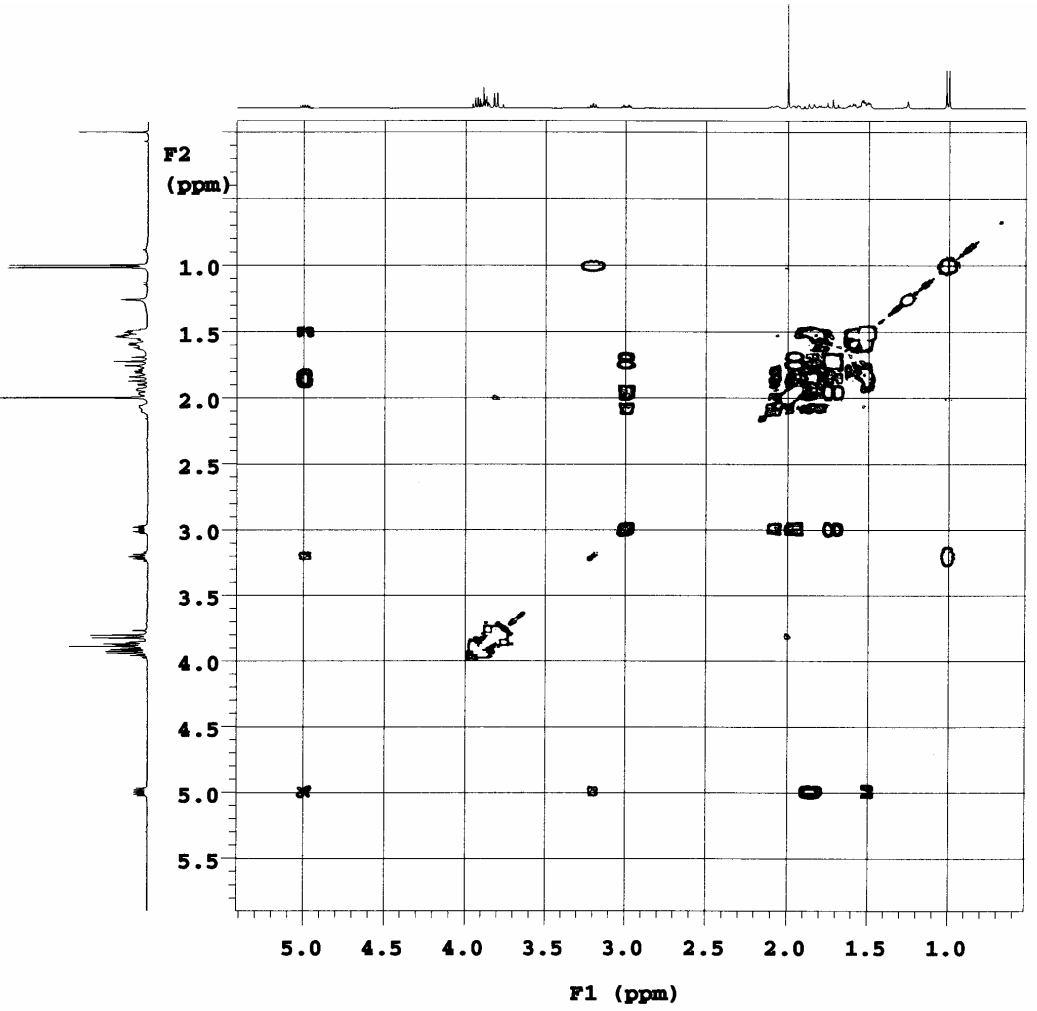

OAc
Me
N
Bn
H
H
O
O

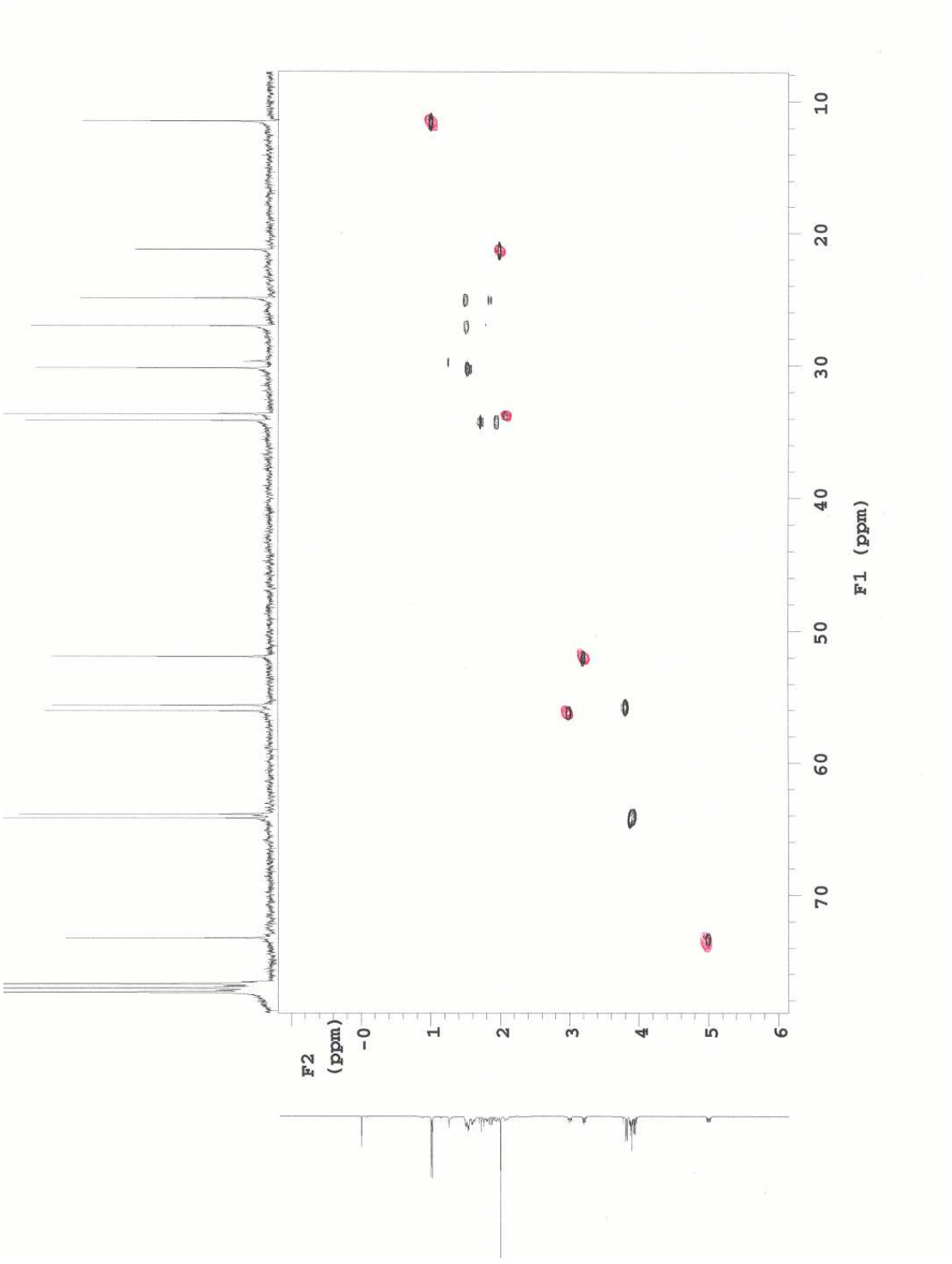
18

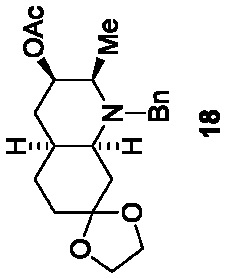


18

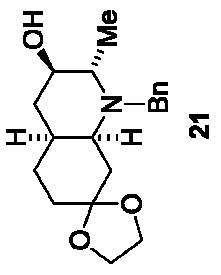
```
H1 / gCOSY / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-051005173
853
Usuari: san / Mostra: mmp15
Nom: MARISA MENA CERVIGON
Data:06/10/05 / Sist automatic

exp22  gCOSY

      SAMPLE                FLAGS
date    Oct  6 2005  hs                nn
solvent       cdcl3  sspul             n
sample auto_Custom~  hsglvl          1002
       Q_06Oct2005        SPECIAL
   ACQUISITION        temp           25.0
sw          3937.0  gain              26
at           0.150  spin               0
np            1182    F2 PROCESSING
fb        not used  sb             -0.075
ss              16  sbs         not used
d1           1.000  fn              2048
nt               4    F1 PROCESSING
  2D ACQUISITION    sb1            -0.065
sw1         3937.0  sbs1        not used
ni             256  proc1             lp
  PRESATURATION     fn1             2048
satmode          n       DISPLAY
satfrq           0  sp              -31.7
satdly           0  wp             2389.9
satpwr           0  sp1             210.7
   TRANSMITTER      wp1            1955.0
tn              H1  rf1             485.8
sfrq       400.113  rfp                0
tof         -540.4  rf11            485.8
tpwr            58  rfp1               0
pw          12.200          PLOT
    GRADIENTS       wc             131.8
gzlvl1         1002  sc               6.2
gt1       0.001000  wc2            131.8
gstab     0.000500  sc2                0
    DECOUPLER       vs               139
dn              C13  th                 6
dm              nnn  ai  cdc  av
```





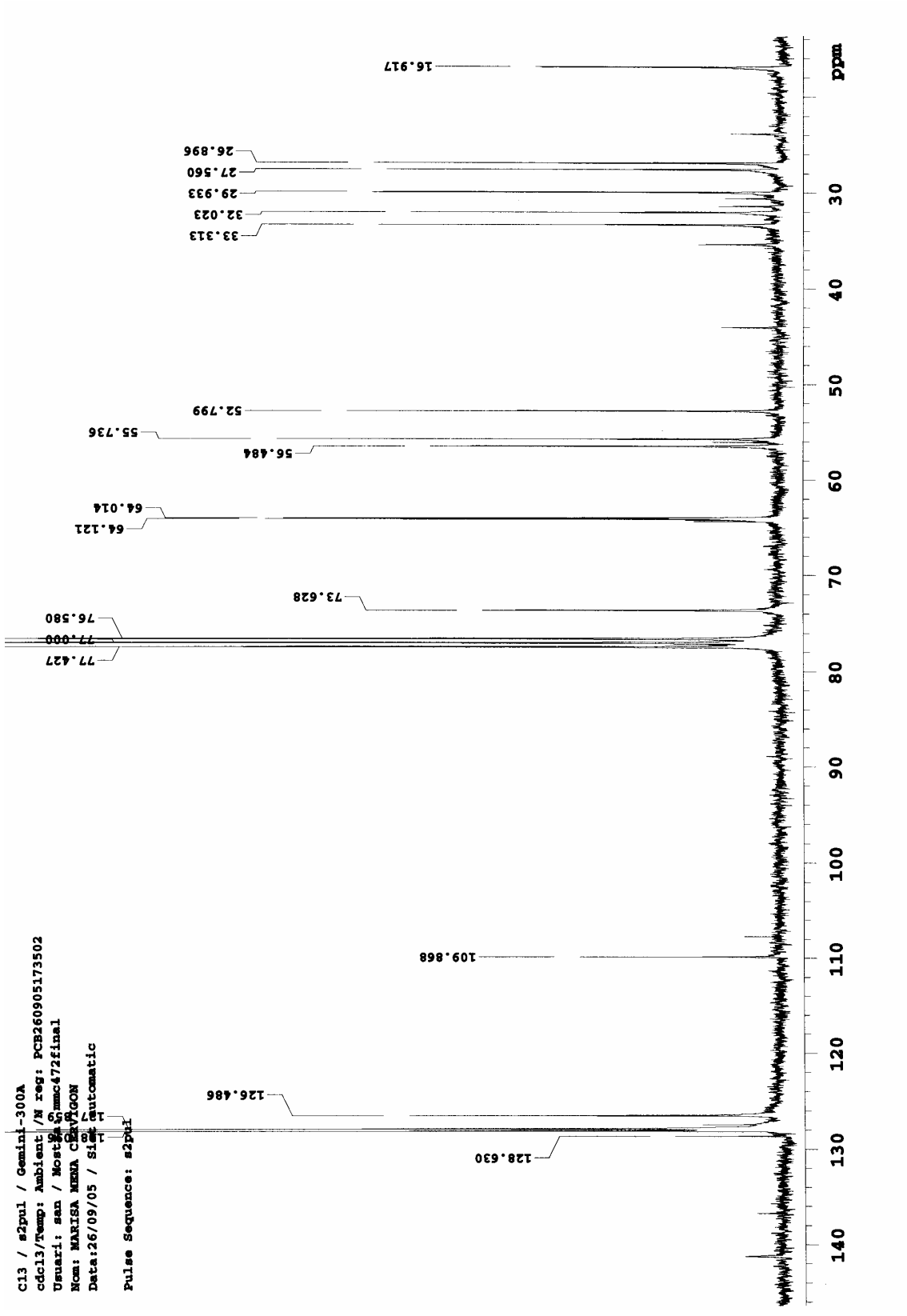


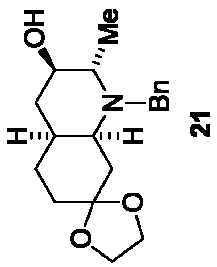
18


OH
Me
Bn
N
H
H
O
O

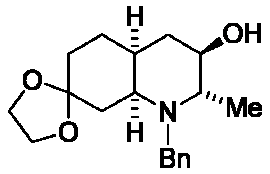
21


H1 / s2pul / Gemini-300A
cdcl3/Temp: Ambient /N reg: G30005-260905145523
Usuari: sac / Mostra: mmc472final
Nom: MARISA MENA CERVIGON
Data:26/09/05 / Slst automatic
Pulse Sequence: s2pul
7.283
3.908
3.838
1.672
1.180
1.160
ppm


C13 / s2pul / Gemini-300A
cdcl3/Temp: Ambient /N reg: PCB260905173502
Usuari: san / Most
Mem: MARISA MENA
Data:26/09/05 / Sis
Pulse Sequence: s2pul
16.917
26.896
27.560
29.933
32.023
33.313
52.799
55.736
56.484
64.014
64.121
73.628
76.580
77.000
77.427
109.868
126.486
128.630
ppm

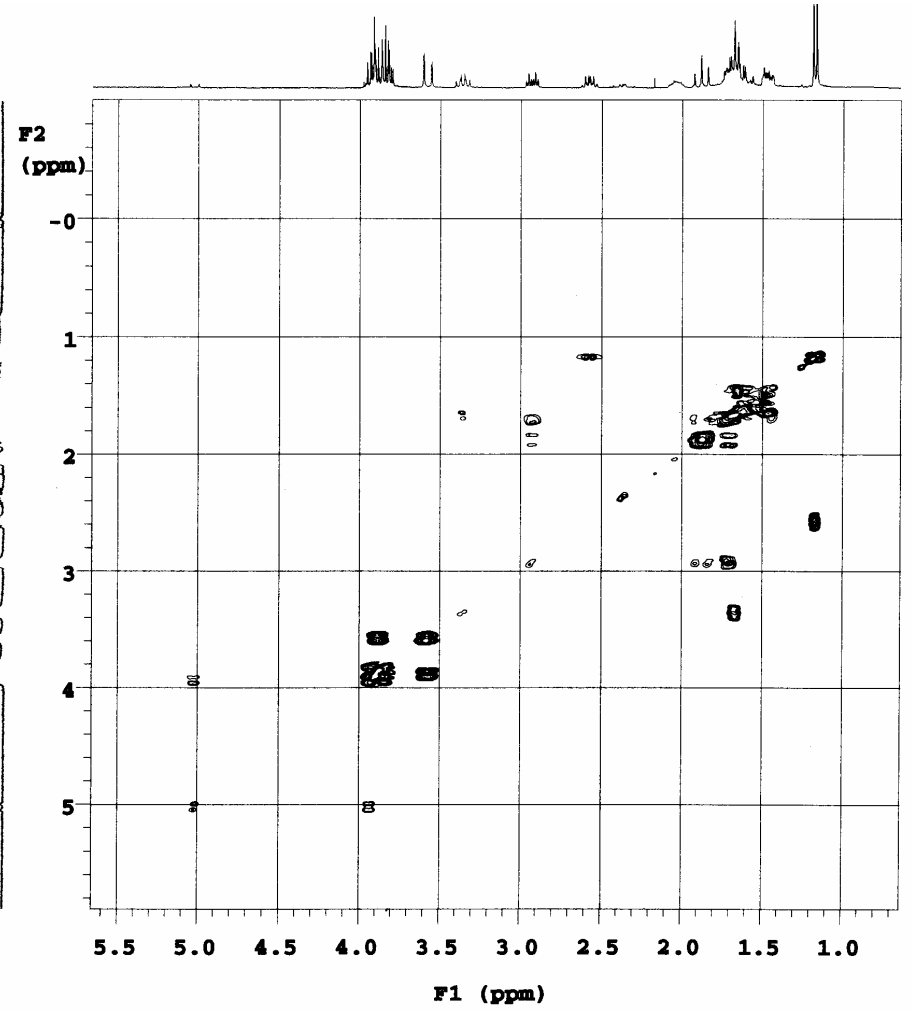

OH
Me
N
Bn
H
H
O
O

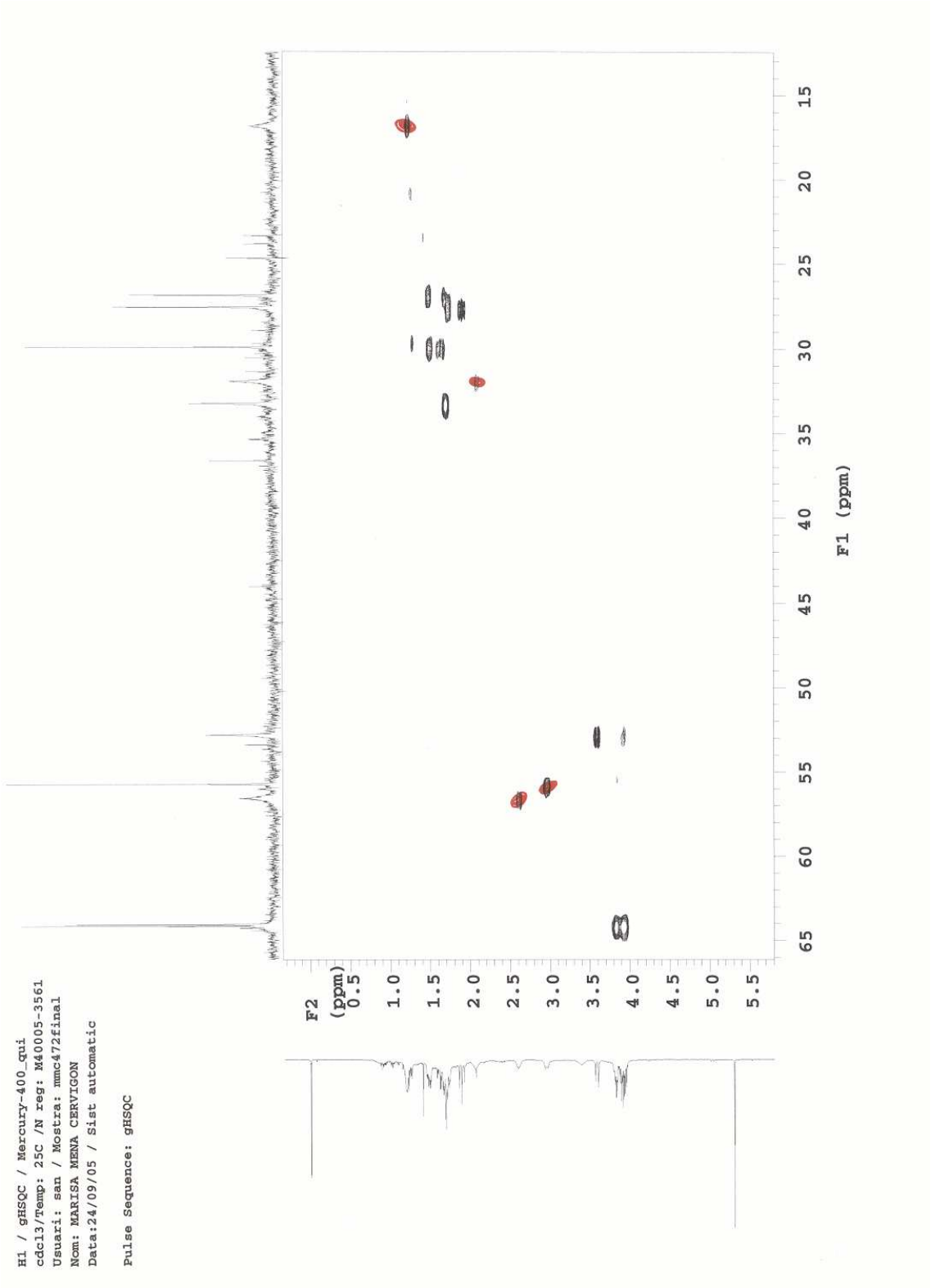
21

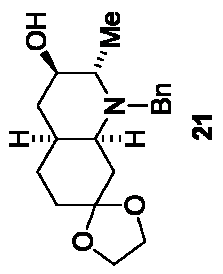


21


```
H1 / COSY / Gemini-300A
cdcl3/Temp: Ambient /N reg: G30005-26090
5145523
Usuari: san / Mostra: mmc472final
Nom: MARISA MENA CERVIGON
Data:26/09/05 / Sist automatic

exp7  COSY

      SAMPLE              SPECIAL
date    Sep 26 2005  temp       not used
solvent       cdcl3  gain             22
sample auto_26Sep2~  spin              0
                005       GRADIENTS
   ACQUISITION       PFGflg            n
sw           2837.4  hsglvl         2000
at            0.180  hsgt       0.005000
np             1024    F2 PROCESSING
fb             2250  sb           -0.090
ss                2  sbs        not used
d1            1.000  fn             2048
nt                4    F1 PROCESSING
  2D ACQUISITION     sb1          -0.090
sw1          2837.4  sbs1       not used
ni              256  proc1            lp
   TRANSMITTER       fn1            2048
tn               H1       DISPLAY
sfrq        300.046  sp           -299.4
tof          -397.5  wp           2066.3
tpwr      not used   sp1           191.5
pw           14.800  wp1          1506.0
  PRESATURATION      rf1            316.1
satmode           n  rfp               0
satpwr            0  rf11           316.1
satdly            0  rfp1              0
satfrq            0          PLOT
    DECOUPLER        wc           131.8
dn               H1  sc             6.2
dm              nnn  wc2          131.8
      FLAGS          sc2               0
hs               nn  vs             4771
sspul             n  th               11
                     ai  cdc  av
```




H1 / gHSQC / Mercury-400_qui
cdcl3/Temp: 25C /N reg: M40005-3561
Usuari: san / Mostra: mmc472final
Nom: MARISA MENA CERVIGON
Data:24/09/05 / Sist automatic
Pulse Sequence: gHSQC
F2 (ppm)
F1 (ppm)


OH
Me
N
Bn
H
H
O
O

21