Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information (ESI) for *Chem. Commun.*

First total synthesis of (±)-apparicine

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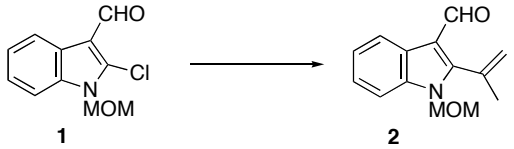
Contents

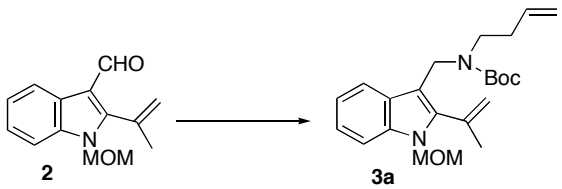
2-Isopropenyl-1-(methoxymethyl)indole-3-carbaldehyde (2).



Tetraethylammonium bromide (0.42 g, 2.01 mmol), $Bu_3Sn(CH_3)C{=}CH_2$ (1.33 g, 4.02 mmol) and $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol) were successively added to a solution of aldehyde **1**[1] (0.45 g, 2.01 mmol) in DMF (30 mL) and the mixture was stirred at 85 °C overnight. The reaction mixture was diluted with AcOEt and washed with brine. The organic solution was dried and concentrated and the resulting residue was chromatographed (SiO_2, flash, 9:1 hexanes-AcOEt) to give **2** as an oil: 0.37 g (80%); IR (film) 3057, 2934, 1663 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H), 3.31 (s, 3H), 5.35 (s, 1H), 5.44 (s, 2H), 5.76 (s, 1H), 7.33 (m, 2H), 7.49 (dm, *J* = 7.5 Hz, 1H), 8.35 (dm, *J* = 7.5 Hz, 1H), 10.0 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 25.0 (CH_3), 56.3 (CH_3), 75.2 (CH_2), 110.4 (CH), 115.2 (C), 122.1 (CH), 123.4 (CH), 123.9 (CH_2), 124.3 (CH), 125.2 (C), 133.4 (C), 136.8 (C), 153.3 (C), 186.8 (CH); ESI-HRMS $[M+H]^+$calcd for $C_{14}H_{16}NO_2$ 230.1175, found 230.1183.

[1]Hagiwara, H.; Choshi, T.; Nobuhiro, J.; Fujimoto, H.; Hibino, S. *Chem. Pharm. Bull*. **2001**, *49*, 881-886.

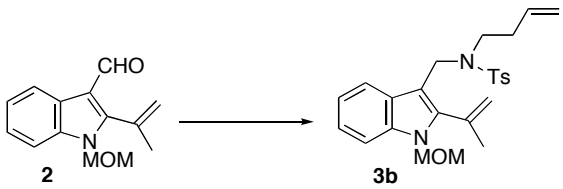
3-[*N*-(3-Butenyl)-*N*-(*tert*-butoxycarbonyl)aminomethyl]-2-isopropenyl-1-(methoxymethyl)indole (3a).



3-Butenylamine (0.24 mL, 2.60 mmol), $NaBH(OAc)_3$ (0.82 g, 3.90 mmol) and AcOH (0.08 mL, 1.36 mmol) were successively added to aldehyde **1** (0.30 g, 1.30 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred at rt overnight. The reaction mixture was partitioned between CH_2Cl_2 and 10% aqueous Na_2CO_3 and extracted with CH_2Cl_2. The organic extracts were dried and concentrated to give the crude secondary amine (0.30 g). This compound was dissolved in MeOH (10 mL) and treated with $(t\text{-}BuOCO)_2O$ (0.45 g, 2.06 mmol) and Et_3N (0.58 mL, 4.12 mmol). After the mixture was heated at reflux for 4 h, the solvent was removed and the residue was diluted with CH_2Cl_2 and washed with HCl 1N and brine. The organic solution was dried and concentrated and the residue was chromatographed (SiO_2, flash, 8:2 hexanes-AcOEt) to give carbamate **3a** as a pale yellow oil: 0.33 g (65%); IR (film) 1689, 1462, 1415 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.53 (br s, 9H), 2.12 (s, 3H), 2.13 (m, 2H), 3.10 (m, 2H) 3.26 (s, 3H), 4.66 (s, 2H), 4.96 (m, 2H), 5.15 (s, 1H), 5.38 (s, 2H), 5.60 (s, 1H), 5.65 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 24.5 (CH_3), 28.5 ($3CH_3$), 32.6 (CH_2), 39.7 (CH_2), 44.2 (CH_2), 55.7 (CH_3), 74.7 (CH_2), 79.2 (C), 109.8 (CH), 116.1 (CH_2), 120.1 (C), 120.4 (CH), 121.5 (CH_2), 122.4 (CH), 122.5 (CH), 127.9 (C), 135.5 (CH), 135.6 (C),

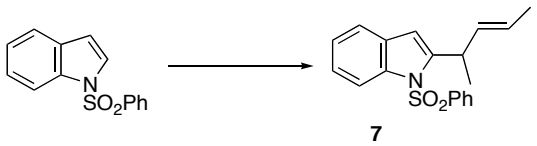
136.9 (C), 141.3 (C), 155.7 (C); ESI-HRMS $[M+H]^+$ calcd for $C_{23}H_{33}N_2O_3$ 385.2485, found 385.2477.

3-[*N*-(3-Butenyl)-*N*-(tosyl)aminomethyl]-2-isopropenyl-1-(methoxymethyl)indole (3b).



Aldehyde **2** (0.25 g, 1.09 mmol) was allowed to react as above with 3-butenylamine and $NaBH(OAc)_3$. The resulting secondary amine (0.25 g) was dissolved in CH_2Cl_2 (12 mL) and treated with TsCl (0.20 g, 1.05 mmol) and Et_3N (0.15 mL, 1.05 mmol) at rt overnight. The reaction mixture was diluted with CH_2Cl_2 and washed with 1N HCl and brine. The organic solution was dried and concentrated and the resulting residue was chromatographed (SiO_2, flash, 9:1 hexanes-AcOEt) to give sulfonamide **3b** as a pale yellow solid: 0.29 g (60%); mp 88 °C (Et_2O); IR (KBr) 1463, 1332, 1158 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.92 (m, 2H), 2.06 (s, 3H), 2.44 (s, 3H), 3.04 (m, 2H), 3.28 (s, 3H), 4.48 (s, 2H), 4.70 (dm, J = 17 Hz, 1H), 4.78 (dm, J = 10 Hz, 1H), 5.09 (s, 1H), 5.36 (s, 2H), 5.40 (m, 1H), 5.53 (br s, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.33 (m, 2H), 7.43 (d, J = 8 Hz, 1H), 7.78 (m, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.5 (CH_3), 24.5 (CH_3), 32.9 (CH_2), 43.4 (CH_2), 46.7 (CH_2), 55.7 (CH_3), 74.7 (CH_2), 107.1 (C), 109.8 (CH), 116.3 (CH_2), 120.1 (CH), 120.7 (CH), 121.9 (CH_2), 122.7 (CH), 127.3 (2 CH), 127.7 (C), 129.2 (2 CH), 134.8 (CH), 135.2 (C), 136.9 (2C), 141.4 (C), 143.0 (C); ESI-HRMS $[M+H]^+$ calcd for $C_{25}H_{31}N_2O_3S$ 439.2049, found 439.2039; $[M+Na]^+$ calcd for $C_{25}H_{30}NaN_2O_3S$ 461.1869, found 461.1866. Anal. calcd for $C_{25}H_{30}N_2O_3S$: C, 68.46%; H, 6.88%; N, 6.38%. Found: C, 68.22%; H, 6.43%; N, 6.25%.

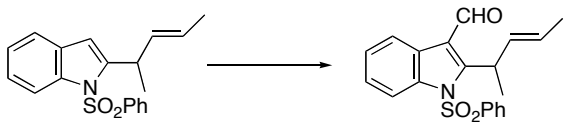
2-(1-Methyl-2-(*E*)-butenyl)-1-(phenylsulfonyl)indole (7).



n-BuLi (1.6 M in hexane, 5.83 mL, 9.33 mmol) was slowly added to a cooled (0 °C) solution of 1-(phenylsulfonyl)indole (2 g, 7.78 mmol) in THF (20 mL) and the solution was stirred at 0 °C for 2 h and then cooled to –78 °C. CuCN (0.84 g, 9.38 mmol) was added and the reaction mixture was allowed to warm to rt (2-3 h) and then cooled again to –78 °C. (*E*)-4-chloro-2-pentene (0.98 g, 9.38 mmol) was added and the stirring was continued at rt for 12 h. The reaction mixture was diluted with 20% NH_4OH and extracted with CH_2Cl_2. The organic extracts were dried and concentrated and the resulting residue was chromatographed (SiO_2, flash, hexanes and 95:5 hexanes-AcOEt) to give indole **7** as an oil: 2.15 g (85%); IR (neat) 1448, 1367, 1173 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, signals due to a minor isomer are omitted) δ 1.45 (d, J = 6.8 Hz, 3H), 1.67 (d, J = 6.0 Hz, 3H), 4.34 (m, 1H), 5.52 (m, 1H), 5.66 (m, 1H), 6.49 (s, 1H), 7.24-7.50 (m, 6H), 7.72 (m, 2H), 8.23 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6

MHz) δ 17.9 (CH_3), 21.7 (CH_3), 35.0 (CH), 108.6 (CH), 115.3 (CH), 120.3 (CH), 123.7 (CH), 124.0 (CH), 124.9 (CH), 126.2 (2CH), 129.0 (2CH), 129.9 (C), 133.5 (CH), 134.0 (CH), 137.5 (C), 139.0 (C), 147.1 (C); ESI-HRMS $[M+H]^+$ calcd for $C_{19}H_{20}NO_2S$ 326.1209, found 326.1212.

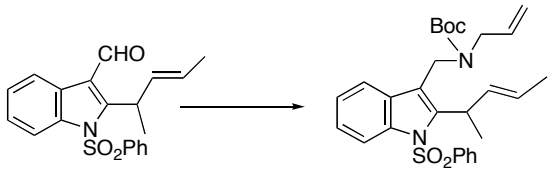
2-(1-Methyl-2-(*E*)-butenyl) 1-(phenylsulfonyl)indole-3-carbaldehyde (8).



7 **8**

Indole **7** (1 g, 3.07 mmol) in CH_2Cl_2 (20 mL) was added to a cooled (– 78 °C) solution of $TiCl_4$ (1 M in CH_2Cl_2, 6.15 mL, 6.15 mmol) and Cl_2CHOCH_3 (0.55 mL, 6.15 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred at –78 °C for 4 h. The reaction mixture was diluted with H_2O, basified with a saturated aqueous Na_2CO_3 solution and extracted with CH_2Cl_2. The organic extracts were dried and concentrated and the residue was chromatographed (SiO_2, flash, hexanes and 95:5 hexanes-AcOEt) to give aldehyde **8** as an amorphous solid: 0.83 g (76%); IR (film) 1666, 1449, 1382, 1174 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.47 (d, *J* = 6.8 Hz, 3H), 1.61 (dm, *J* = 6.4 Hz, 3H), 4.76 (m, 1H), 5.40 (m, 1H), 5.61 (dm, *J* = 15 Hz, 1H), 7.37 (m, 2H), 7.49 (m, 2H), 7.62 (m, 1H), 7.82 (d, *J* = 7.8 Hz, 2H), 8.32 (m, 2H), 10.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 17.7 (CH_3), 22.5 (CH_3), 33.8 (CH), 114.7 (CH), 119.3 (C), 122.1 (CH), 125.2 (CH), 125.7 (CH), 125.9 (CH), 126.3 (C), 126.5 (2CH), 129.6 (2CH), 133.1 (CH), 134.4 (CH), 136.4 (C), 139.4 (C), 155.3 (C), 187.5 (CH); ESI-HRMS $[M+H]^+$ calcd for $C_{20}H_{20}NO_3S$ 354.1158, found 354.1165.

3-[*N*-Allyl-*N*-(*tert*-butoxycarbonyl)aminomethyl]-2-(1-methyl-2-(*E*)-butenyl)-1-(phenylsulfonyl)indole (9).

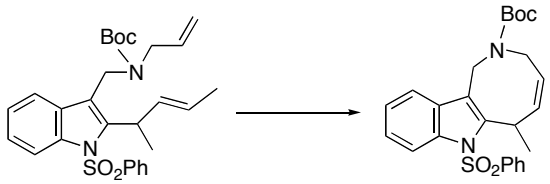


8 **9**

Allylamine (0.21 mL, 2.83 mmol), $NaBH(OAc)_3$ (0.90 g, 4.25 mmol) and AcOH (0.08 mL, 1.41 mmol) were successively added to aldehyde **8** (0.50 g, 1.41 mmol) in CH_2Cl_2 (17 mL) and the resulting mixture was stirred at rt overnight. The reaction mixture was partitioned between CH_2Cl_2 and 10% aqueous Na_2CO_3 and extracted with CH_2Cl_2. The organic extracts were dried and concentrated to give the crude secondary amine (540 mg). This compound was dissolved in MeOH (5 mL) and treated with $(t\text{-BuOCO})_2O$ (0.54 g, 2.47 mmol) and Et_3N (0.70 mL, 4.94 mmol). After the mixture was heated at reflux for 5 h, the solvent was removed and the residue was diluted with CH_2Cl_2 and washed with 2N HCl and brine. The organic extracts were dried and concentrated to give the crude product. Flash chromatography (SiO_2, hexanes and 95:5 hexanes-AcOEt) gave diene **9** as a pale yellow oil: 0.63 g (90%); IR (film) 1690, 1450, 1368, 1173 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.21 (d, *J* = 7.2 Hz, 3H), 1.42 (s, 9H), 1.52 (d, *J* = 6.4 Hz, 3H), 3.38 (br s, 2H), 4.44 (m, 1H), 4.57 (m, 2H), 4.83 (dd, *J* = 17.2 and 1.5

Hz, 1H), 4.92 (dd, *J* = 10.4 and 1.5 Hz, 1H), 5.28 (m, 1H), 5.44 (dm, *J* = 15.2 Hz, 1H), 5.50 (m, 1H), 7.20 (m, 2H), 7.32 (m, *J* = 2H), 7.43 (m, 2H), 7.60 (dm, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 18.1 (CH_3), 20.1 (CH_3), 28.6 ($3CH_3$), 33.5 (CH), 40.0 (CH_2), 46.8 (CH_2), 80.1 (C), 115.4 (CH_2), 115.6 (CH), 117.2 (C), 119.7 (CH), 123.9 (CH), 124.7 (CH), 125.2 (CH), 126.5 (2CH), 129.2 (C), 129.3 (2CH), 132.8 (CH), 133.8 (CH), 133.9 (CH), 137.1 (C), 139.7 (C), 142.9 (C), 156.1 (CO); ESI-HRMS $[M+Na]^+$ calcd for $C_{28}H_{34}N_2O_4NaS$ 517.2131, found 517.2144.

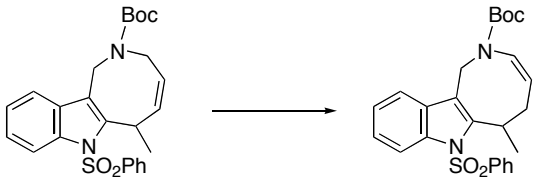
2-(*tert*-Butoxycarbonyl)-6-methyl-7-(phenylsulfonyl)-1,2,3,6-tetrahydroazocino[4,3-*b*]indole (10).



9 **10**

The second-generation Grubbs' catalyst (24 mg, 7 mol%) was added under Ar to a solution of diene **9** (200 mg, 0.40 mmol) in CH_2Cl_2 (5.7 mL) and the resulting mixture was heated at reflux for 4.5 h. The reaction mixture was concentrated and the residue was chromatographed (SiO_2, flash, 9:1 hexanes-AcOEt) to give azocinoindole **10** as a white foam: 146 mg (80%); IR (KBr) 1689, 1450, 1370, 1172 cm^{-1} ^{1}H NMR ($CDCl_3$, 400 MHz, assignments aided by gHSQC and ^{1}H gCOSY, mixture of rotamers) δ 1.42 (br s, 9H, Boc), 1.47 (br s, 3H, CH_3), 2.85 (m, 1H, 3-H), 3.81 and 4.03 (2m, 1H, 3-H), 4.37 (br s, 1H, 1-H), 4.65 (m, 1H, 6-H), 4.89 and 5.01 (2m, 1H, 1-H), 5.44 (br s, 1H, 4-H), 5.80 (br d, *J* = 11 Hz, 1H, 5-H), 7.29 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 8.28 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz, assignments aided by gHSQC) δ 24.3 (CH_3), 28.4 ($3CH_3$), 32.5 (CH, C-6), 37.0 (CH_2, C-1), 38.0 (CH_2, C-3), 79.90 (C), 115.6 (CH, C-8), 118.7 (CH, C-11), 118.9 (C), 121.0 (CH, C-4), 123.8 (CH, C-10), 124.8 (CH, C-9), 126.0 (2CH, Ph), 129.2 (2CH, Ph), 130.8 (C), 133.8 (CH, Ph), 136.9 (C), 137.6 (CH, C-5), 138.8 (C), 142.2 (C), 155.0 (CO); ESI-HRMS $[M+H]^+$ calcd for $C_{25}H_{29}N_2O_4S$ 453.1842, found 453.1851; $[M+Na]^+$calcd for $C_{25}H_{28}N_2O_4NaS$ 475.1662, found 475.1670.

2-(*tert*-Butoxycarbonyl)-6-methyl-7-(phenylsulfonyl)-1,2,5,6-tetrahydroazocino[4,3-*b*]indole (11).

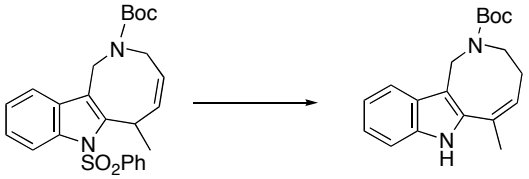


10 **11**

The second-generation Grubbs' catalyst (4.5 mg, 10 mol %) was added under Ar to a solution of azocinoindole **10** (23 mg, 0.05 mmol) in toluene (5.5 mL) and the resulting mixture was heated at reflux for 18 h. The reaction mixture was concentrated and the residue was chromatographed (SiO_2, flash, 5% hexanes-AcOEt) to give enamide **11**: 12 mg (50%); IR (film) 1700, 1650, 1450, 1363, 1173 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz,

assignments aided by gHSQC and gCOSY, mixture of rotamers) δ 1.44 and 1.46 (2s, 9H, Boc), 1.58 (s, 3H, CH_3), 2.16 (m, 1H, 5-H), 3.03 (m, 1H, 5-H), 3.82 (m, 1H, 6-H), 4.45 (m, 1H, 4-H), 4.75 and 4.90 (2d, J = 15.0 Hz, 1H, 1-H), 5.30 and 5.52 (2d, J = 15.0 Hz, 1H, 1-H), 6.10 and 6.26 (2d, J = 9.0 Hz, 1H, 3-H), 7.26 (m, 2H), 7.32 (m, 2H), 7.50 (m, 1H), 7.60 (m, 3H), 8.22 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz, gHSQC, only CH_3, CH_2 and CH signals are listed) δ 24.0 (CH_3), 28.3 ($3CH_3$), 32.8 (CH_2, C-5), 34.3 (CH, C-6), 38.7 (CH_2, C-1), 107.8 (CH, C-4), 115.4 (CH, C-8), 118.4 (CH, C-11), 124.1 (2CH, C-9, C-10), 126.8 (2CH, Ph), 127.4 (CH, C-3), 129.1 (2CH, Ph), 133.6 (CH, Ph). Anal. Calcd for $C_{24}H_{28}N_2O_4S$: C, 65.43%; H, 6.40%; N, 6.36%. Found: C, 65.58%; H, 6.24%; N, 5.94%.

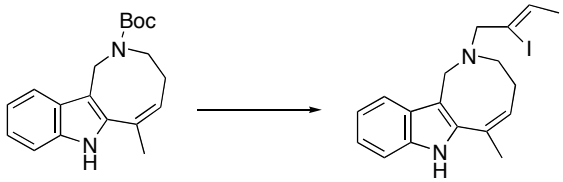
2-(*tert*-Butoxycarbonyl)-6-methyl-1,2,3,4-tetrahydroazocino[4,3-*b*]indole (12).



12

t-BuOK (0.55 g, 4.90 mmol) was added to a solution of azocinoindole **10** (0.22 g, 0.49 mmol) in THF (14 mL) and the resulting solution was heated at reflux for 48 h. The reaction mixture was partitioned between a saturated aqueous NH_4Cl solution and Et_2O and extracted with Et_2O. The organic extracts were dried and concentrated to give azocinoindole **12** as a yellow foam: 138 mg (90%). An analytical sample was obtained by flash chromatography (SiO_2, hexanes and 8:2 hexanes-AcOEt); IR (film) 3321, 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, assignments aided by gHSQC, mixture of rotamers) δ 1.35 and 1.45 (2s, 9H, Boc), 2.13 (s, 3H, CH_3), 2.37 (m, 2H, 4-H), 3.60 (m, 2H, 3-H), 4.64 (br s, 2H, 1-H), 5.69 and 5.75 (2t, J = 8 Hz, 1H, 5-H), 7.15 (m, 2H, 9-H, 10-H), 7.28 and 7.31 (2 d, J = 8 Hz, 1H, 8-H), 7.56 and 7.62 (2d, J = 8 Hz, 1H, 11-H), 7.85 and 7.89 (2 br s, 1H, NH); ^{13}C NMR ($CDCl_3$, 100.6 MHz, assignments aided by gHSQC,) δ 22.7 and 22.8 (CH_3), 28.4 and 28.5 ($3CH_3$, Boc), 28.7 (CH_2, C-4), 43.4 and 43.5 (CH_2, C-1), 46.0 and 46.7 (CH_2, C-3), 79.1 and 79.3 (C), 110.3 and 110.4 (CH, C-8), 110.8 and 111.0 (C), 118.5 and 119.0 (CH, C-11), 119.3 and 119.4 (CH, C-10), 122.1 and 122.2 (CH, C-9), 126.5 and 127.1 (CH, C-5), 127.2 and 127.3 (C), 128.9 and 129.5 (C), 132.8 and 133.4 (C), 135.7 and 135.9 (C), 156.1 and 156.5 (C); ESI-HRMS calcd for $C_{19}H_{24}N_2O_2$ 312.1837, found 312.1837.

2-(2-Iodo-2-*(Z)*-butenyl)-6-methyl-1,2,3,4-tetrahydroazocino[4,3-*b*]indole (13).



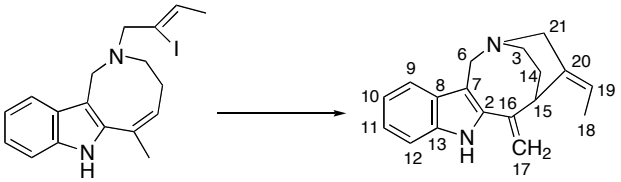
12 **13**

A solution of carbamate **12** (224 mg, 0.72 mmol) in 1.2 M HCl in MeOH (3.2 mL) was stirred at rt for 4.5 h. 20% NH_4OH was added and the organic solvent was removed. The residue was partitioned between CH_2Cl_2 and H_2O and extracted with CH_2Cl_2. The

organic extracts were dried and concentrated to give the secondary amine (127 mg), which was directly used in the next step. Diisopropylethylamine (0.15 mL, 0.89 mmol) and (*Z*)-2-iodo-2-butenyl tosylate[2] (230 mg, 0.65 mmol) were added to a solution of the above amine (127 mg, 0.59 mmol) in 1:1 CH_2Cl_2-acetonitrile (21 mL). After the reaction mixture was stirred at rt for 2 h, $MeNH_2$ (2 M in MeOH, 1.5 mL, 3 mmol) was added and the stirring was continued for 1 h. The reaction mixture was diluted with CH_2Cl_2 and washed with a saturated aqueous $NaHCO_3$ solution. The organic solution was dried and concentrated and the residue was chromatographed (hexanes and 9:1 hexanes-EtOAc) to give pure tertiary amine **13** (yellow oil): 70 mg (30%); IR (film) 3408, 2923, 1612, 1460, 742 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.79 (dd, *J* = 6.2 and 1.2 Hz, 3H), 2.11 (s, 3H), 2.14 (br s, 2H), 2.77 (br s, 2H), 3.35 (br s, 2H), 3.99 (br s, 2H), 5.81 (q, *J* = 6.2 Hz, 1H), 5.85 (t, *J* = 7.8 Hz, 1H), 7.15 (m, 2H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.95 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.7 (CH_3), 22.5 (CH_3), 26.0 (CH_2), 48.0 (CH_2), 50.6 (CH_2), 65.3 (CH_2), 110.1 (C), 110.5 (CH), 110.6 (C), 118.9 (CH), 119.5 (CH), 121.9 (CH), 126.9 (C), 128.8 (C), 130.0 (CH), 131.3 (CH), 135.8 (C), 136.1 (C); ESI-HRMS $[M+H]^+$ calcd for $C_{18}H_{22}IN_2$ 393.0822, found 393.0831.

[2](a) Rawal, V. H.; Michoud, C. *Tetrahedron Lett*. **1991**, *32*, 1695-1698. (b) Eichberg, M. J.; Dorta, R. L.; Grotjahn, D. B.; Lamottke, K.; Schmidt, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc*. **2001**, *123*, 9324-9337.

(±)-Apparicine

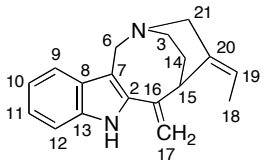


13 Apparicine (biogenetic numbering)

$Pd(OAc)_2$ (7.6 mg, 0.034 mmol), PPh_3 (26 mg, 0.10 mmol) and Ag_2CO_3 (93 mg, 0.34 mmol) were added under Ar to a solution of amine **13** (65 mg, 0.17 mmol) in 1:1 toluene-Et_3N (17 mL) and the mixture was heated at 80 ºC for 1.5 h. The solvent was removed and the residue was partitioned between CH_2Cl_2 and a saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The organic extracts were dried and concentrated and the resulting residue was chromatographed (SiO_2, flash, CH_2Cl_2 to 9:1 CH_2Cl_2-MeOH). An additional chromatography (SiO_2, 0.5% Et_2O-diethylamine) gave pure (±)-apparicine as an amorphous solid: 6.6 mg (15%); ^1H NMR ($CDCl_3$, 400 MHz, assignments aided by gHSQC) δ 1.46 (dd, *J* = 6.8 and 2.4 Hz, 3H, 18-H), 1.89 (ddt, *J* = 13.6, 6.8 and 2.4 Hz, 1H, 14-H), 2.16 (dddd, *J* = 13.6, 11.2, 8 and 5.6 Hz, 1H, 14-H), 3.07 (dddd, *J* = 13.2, 11.2, 6.8 and 1.2 Hz, 1H, 3-H), 3.20 (d, *J* = 16 Hz, 1H, 21-H), 3.42 (ddd, *J* = 13.2, 8 and 2 Hz, 1H, 3-H), 3.82 (dt, *J* = 16 and 2 Hz, 1H, 21-H), 3.92 (broad s, 1H, 15-H), 4.28 (d, *J* = 17.8 Hz, 1H, 6-H), 4.51 (d, *J* = 17.8 Hz, 1H, 6-H), 5.25 (q, *J* = 6.8 Hz, 1H, 19-H), 5.26 (s, 1H, 17-H), 5.39 (s, 1H, 17-H), 7.06 (ddd, *J* = 7.6, 7.2 and 1.2 Hz, 1H, 10-H), 7.18 (ddd, *J* = 8, 7.2 and 1.2 Hz, 1H, 11-H), 7.28 (d, *J* = 8 Hz, 1H, 12-H), 7.42 (d, *J* = 7.6 Hz, 1H, 9-H), 7.84 (broad s, 1H, NH); ^{13}C NMR ($CDCl_3$, 100.6 MHz, assignment aided by gHSQC) δ 12.6 (CH_3, C-18), 29.6 (CH_2, C-14), 41.2 (CH, C-15), 45.3 (CH_2, C-3), 54.2 (CH_2, C-6), 54.3 (CH_2, C-21), 110.2 (CH, C-12), 111.5 (C,

C-7), 112.2 (CH_2, C-17), 118.6 (CH, C-9), 119.3 (CH, C-10), 120.1 (CH, C-19), 123.0 (CH, C-11), 129.0 (C, C-8), 131.3 (C, C-20), 135.6 (C, C-16), 137.4 (C, C-13), 145.2 (C, C-2); ESI-HRMS $[M+H]^+$ calcd for $C_{18}H_{21}N_2$ 265.1699, found 265.1705.

Comparison of the NMR data of synthetic apparicine with those reported for the natural product



Apparicine
(biogenetic numbering)

^{1}H NMR data:

H	synthetic apparicine	natural product[3]
NH	7.84 (br s)	7.88 (br s)
3-H	3.07 (dddd, *J* = 13.2, 11.2, 6.8, 1.2 Hz) 3.42 (ddd, *J* = 13.2, 8, 2 Hz)	3.06 (dddd, *J* = 13.2, 11.4, 7.0, 1.2 Hz) 3.40 (ddd, *J* = 13.3, 8, 2.2 Hz)
6-H	4.28 (d, *J* = 17.8 Hz) 4.51 (d, *J* = 17.8 Hz)	4.26 (d, *J* = 17.7 Hz) 4.49 (d, *J* = 17.7 Hz)
9-H	7.42 (d, *J* = 7.6 Hz)	7.42 (dd, *J* = 7.7, 1.2 Hz)
10-H	7.06 (ddd, *J* = 7.6, 7.2, 1.2 Hz)	7.05 (ddd, *J* = 7.7, 7.3, 1.2 Hz)
11-H	7.18 (ddd, *J* = 8, 7.2, 1.2 Hz)	7.17 (ddd, *J* = 8.1, 7.3, 1.2 Hz)
12-H	7.28 (d, *J* = 8 Hz)	7.28 (dd, *J* = 8.1, 1.2 Hz)
14-H	1.89 (ddt, *J* = 13.6, 6.8, 2.4 Hz); 2.16 (dddd, *J* = 13.6, 11.2, 8, 5.6 Hz)	1.88 (dddd, *J* = 13.6, 7, 2.6, 2.2 Hz) 2.15 (dddd, *J* = 13.6, 11.4, 8, 5.4 Hz)
15-H	3.92 (br s)	3.91 (dd, *J* = 5.4, 2.6 Hz)
17-H	5.26 (s) 5.39 (s)	5.25 (s) 5.38 (s)
18-H	1.46 (dd, *J* = 6.8, 2.4 Hz)	1.45 (dd, *J* = 7, 2.3 Hz)
19-H	5.25 (q, *J* = 6.8 Hz)	5.23 (q, *J* = 7 Hz)
21-H	3.20 (d, *J* = 16 Hz) 3.82 (dt, *J* = 16, 2 Hz)	3.18 (dd, *J* = 16, 1.2 Hz) 3.80 (dd, *J* = 16, 2.3 Hz)

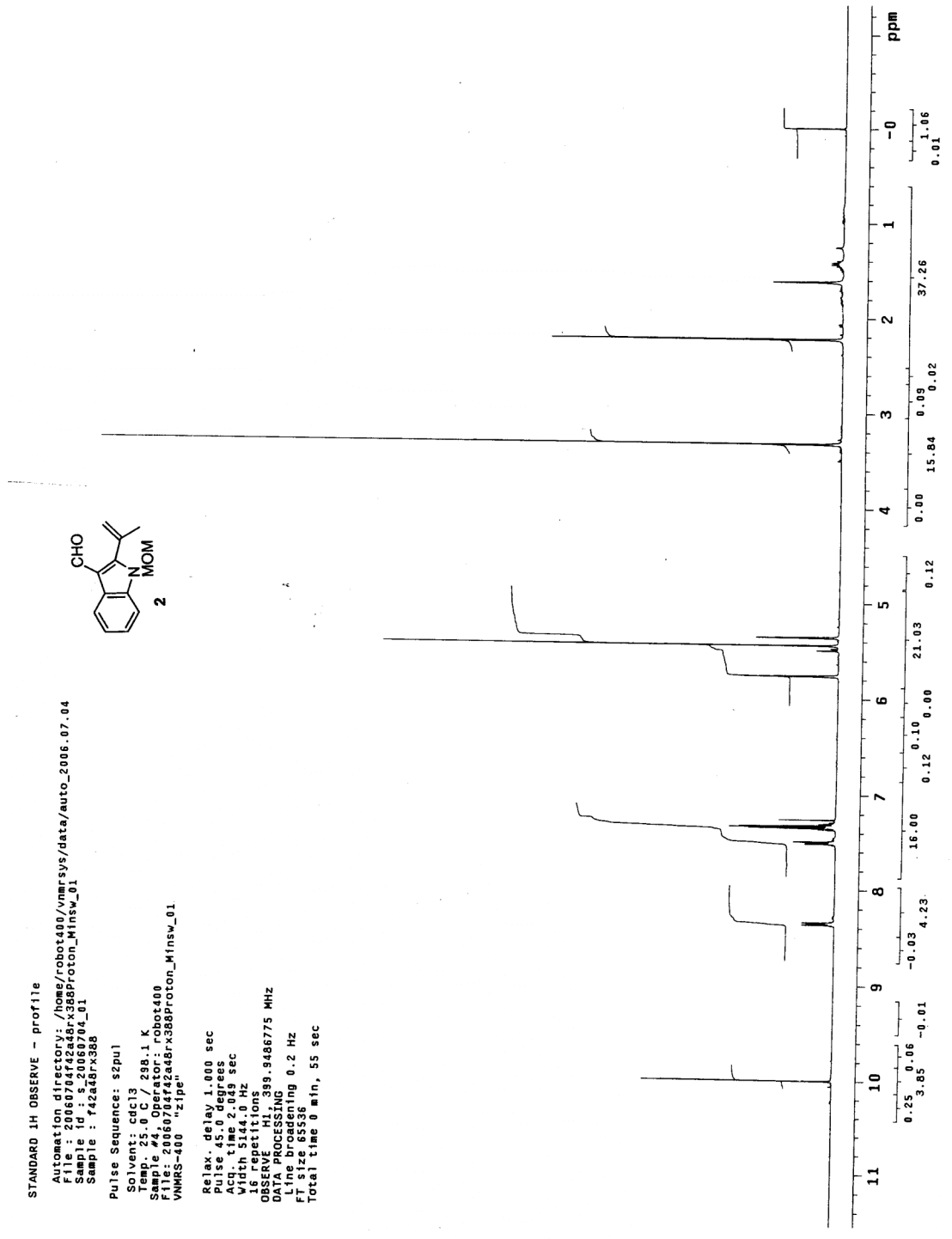
[3] van Beek, T. A.; Verpoorte, R.; Kinh, P. Q. *Planta Med*. **1985**, *51*, 277-279.

^{13}C NMR data:

C	synthetic apparicine	natural product[4,5]	
		reference 4	reference 5
C-2	145.2	142.6	144.7
C-3	45.3	45.3	45.2
C-6	54.2	54.3	53.8
C-7	111.5	111.1	109.9[b]
C-8	129.0	129.0	129.0
C-9	118.6	118.6	118.6
C-10	119.3	119.3[a]	119.6
C-11	123.0	123.0[a]	123.2[c]
C-12	110.2	110.2	110.4[d]
C-13	137.4	137.8	136.6
C-14	29.6	29.6	29.1
C-15	41.2	41.3	41.1
C-16	135.6	135.7	135.8
C-17	112.2	112.2	112.6[b]
C-18	12.6	12.5	12.6
C-19	120.1	120.3	121.4[e]
C-20	131.3	131.3	131.6
C-21	54.3	54.3	54.2

[a] Exchanged assignments in ref. 4
[b] Exchanged assignments in ref. 5
[c] Signal assigned as C-12 in ref. 5
[d] Signal assigned as C-19 in ref. 5
[e] Signal assigned as C-11 in ref. 5

[4] Massiot, G.; Zèches, M.; Thépenier, P.; Jacquier, M.-J.; Le Men-Olivier, L.; Delaude, C. *J. Chem. Soc., Chem. Commun*. **1982**, 768-769.
[5] Atta-ur-Rahman; Fatima, T.; Mehrun-Nisa; Ijaz, S.; Crank, G.; Wasti, S. *Planta Med*. **1987**, *53*, 57-59.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Sample : f42a48rx388
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Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample 44.4 Operator: robot400
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Width 5144.0 Hz
16 repetitions
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Total time 0 min, 55 sec
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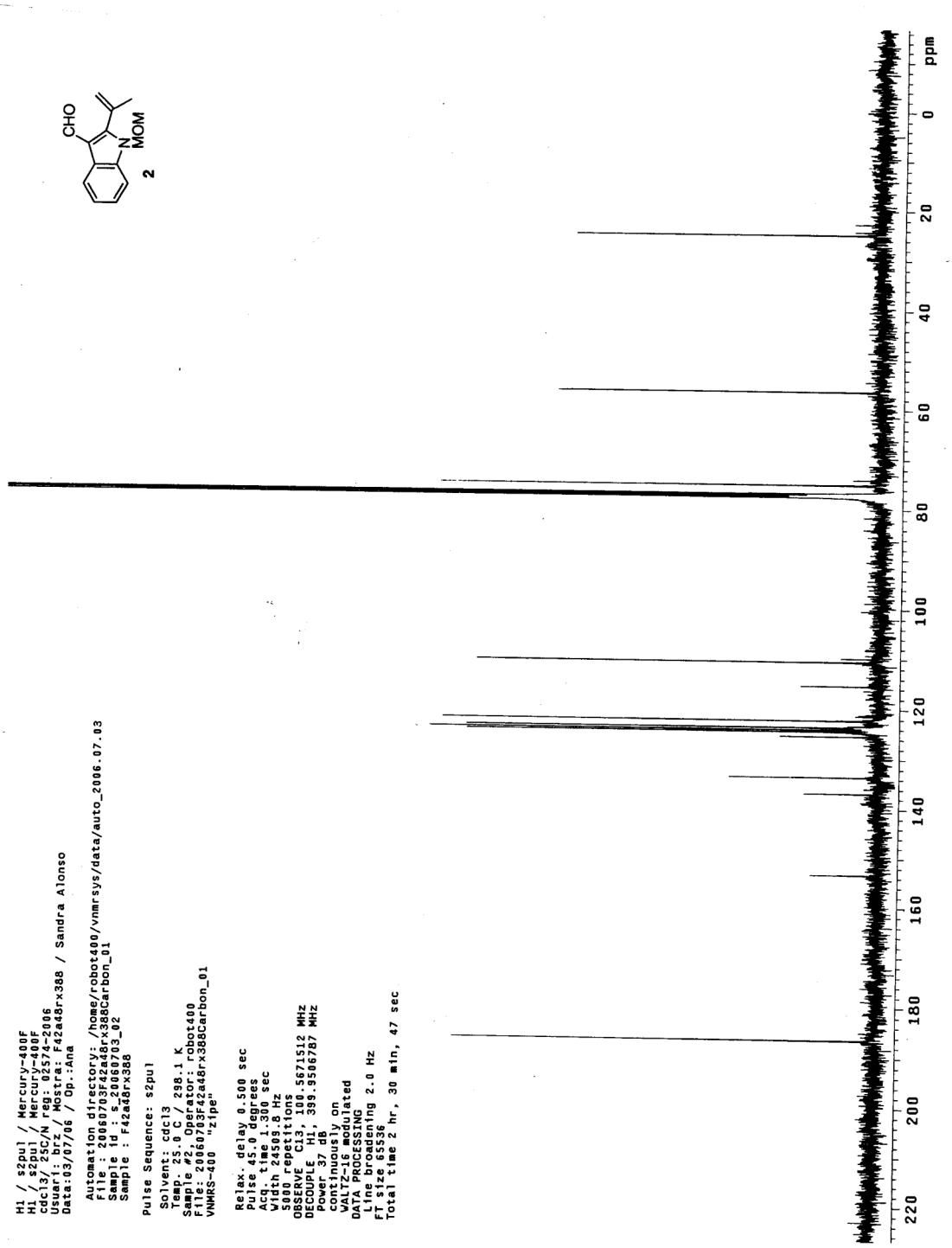
MOM
2
ppm

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H1 / s2pul / Mercury-400F
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Usuari: brz / Mostra: F42a48rx388 / Sandra Alonso
Data:03/07/06 / Op.:Ana

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    Sample : F42a48rx388

Pulse Sequence: s2pul

  Solvent: cdcl3
    Temp. 25.0 C / 298.1 K
Sample #2, Operator: robot400
File: 20060703F42a48rx388Carbon_01
VNMRS-400  "zipe"

  Relax. delay 0.500 sec
  Pulse 45.0 degrees
  Acq. time 1.380 sec
  Width 24509.8 Hz
   5000 repetitions
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DECOUPLE  H1, 399.9506787 MHz
  Power 37 dB
  continuously on
  WALTZ-16 modulated
DATA PROCESSING
  Line broadening 2.0 Hz
FT size 65536
Total time 2 hr, 30 min, 47 sec
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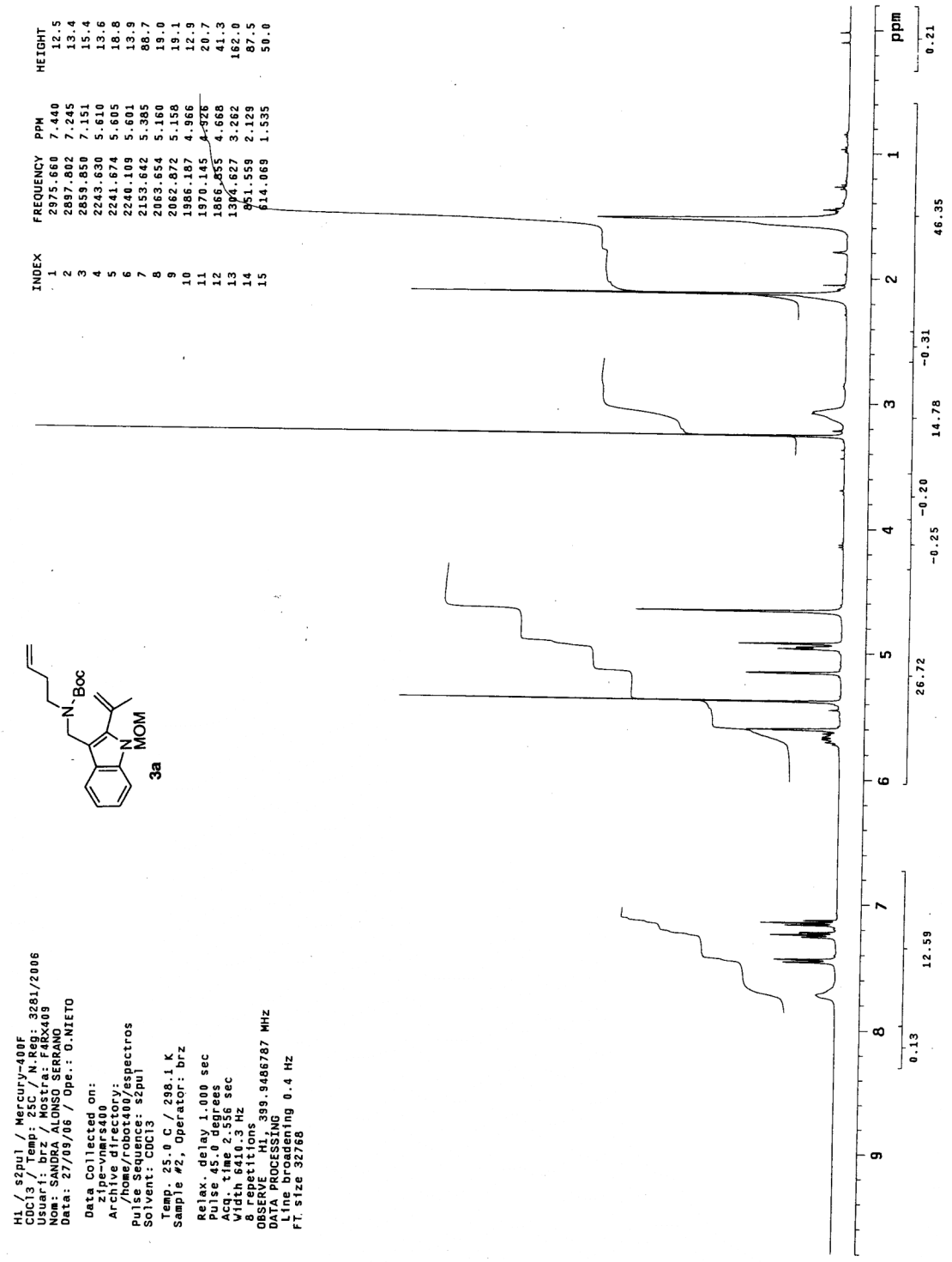
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Data: 27/09/06 / Ope.: O.NIETO
Data Collected on:
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Sample #2, Operator: brz
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.9486787 MHz
DATA PROCESSING
Line broadening 0.4 Hz
FT size 32768
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2 2897.802 7.245 13.4
3 2859.850 7.151 15.4
4 2243.630 5.610 13.6
5 2241.674 5.605 18.8
6 2240.109 5.601 13.9
7 2153.642 5.385 88.7
8 2063.654 5.160 19.0
9 2062.872 5.158 19.1
10 1986.187 4.966 12.9
11 1970.145 4.926 20.7
12 1866.855 4.668 41.3
13 1304.627 3.262 162.0
14 851.559 2.129 87.5
15 614.069 1.535 50.0
N
Boc
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MOM
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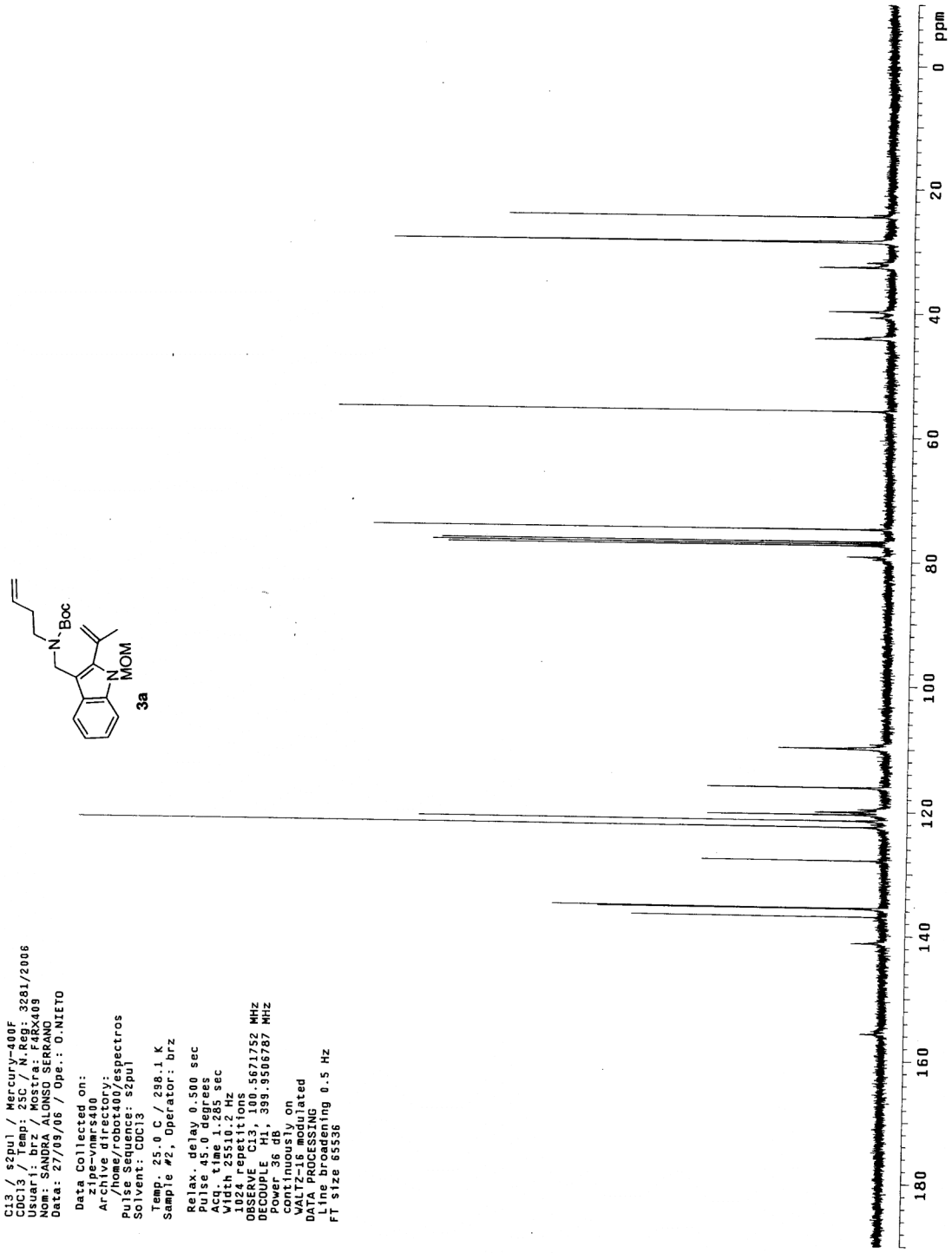
0.21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Data: 27/09/06 / Ope.: O.NIETO
Data Collected on:
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Archive directory:
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Solvent: CDCl3
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Sample #2, Operator: brz
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
1024 repetitions
OBSERVE C13, 100.5671752 MHz
DECOUPLE H1, 399.9506787 MHz
Power 36 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
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Boc
N
MOM
3a
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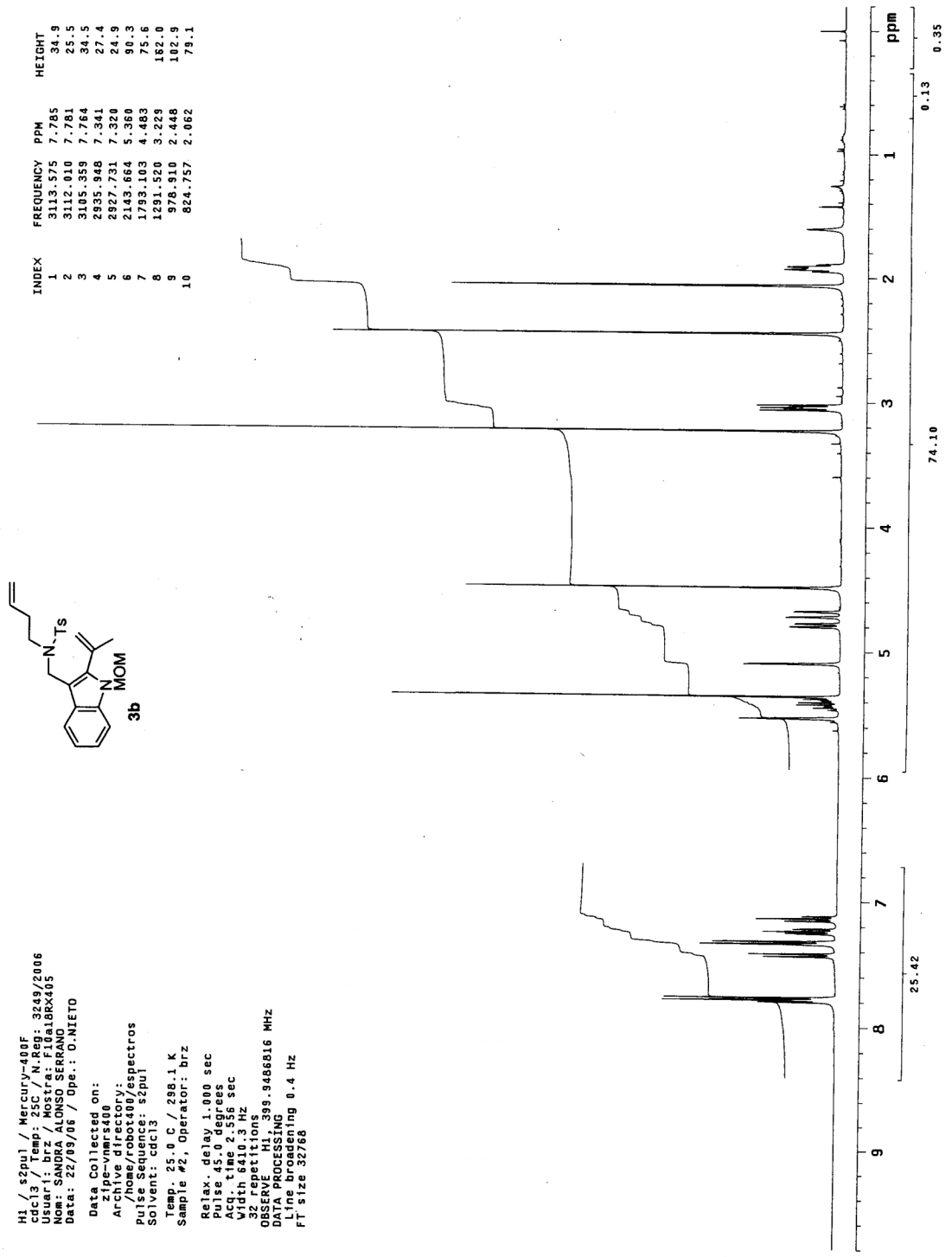
160
140
120
100
80
60
40
20
0
ppm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Nom: SANDRA ALONSO SERRANO18RX405
Data: 22/09/06 / Ope.: O.NIETO
Data Collected on:
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Archive directory:
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Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #2, Operator: brz
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
32 repetitions
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DATA PROCESSING
Line broadening 0.4 Hz
FT size 32768
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3 3105.359 7.764 34.5
4 2935.948 7.341 27.4
5 2927.731 7.320 24.9
6 2143.664 5.360 90.3
7 1793.103 4.483 75.6
8 1291.520 3.229 182.0
9 978.910 2.448 102.9
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MOM
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ppm
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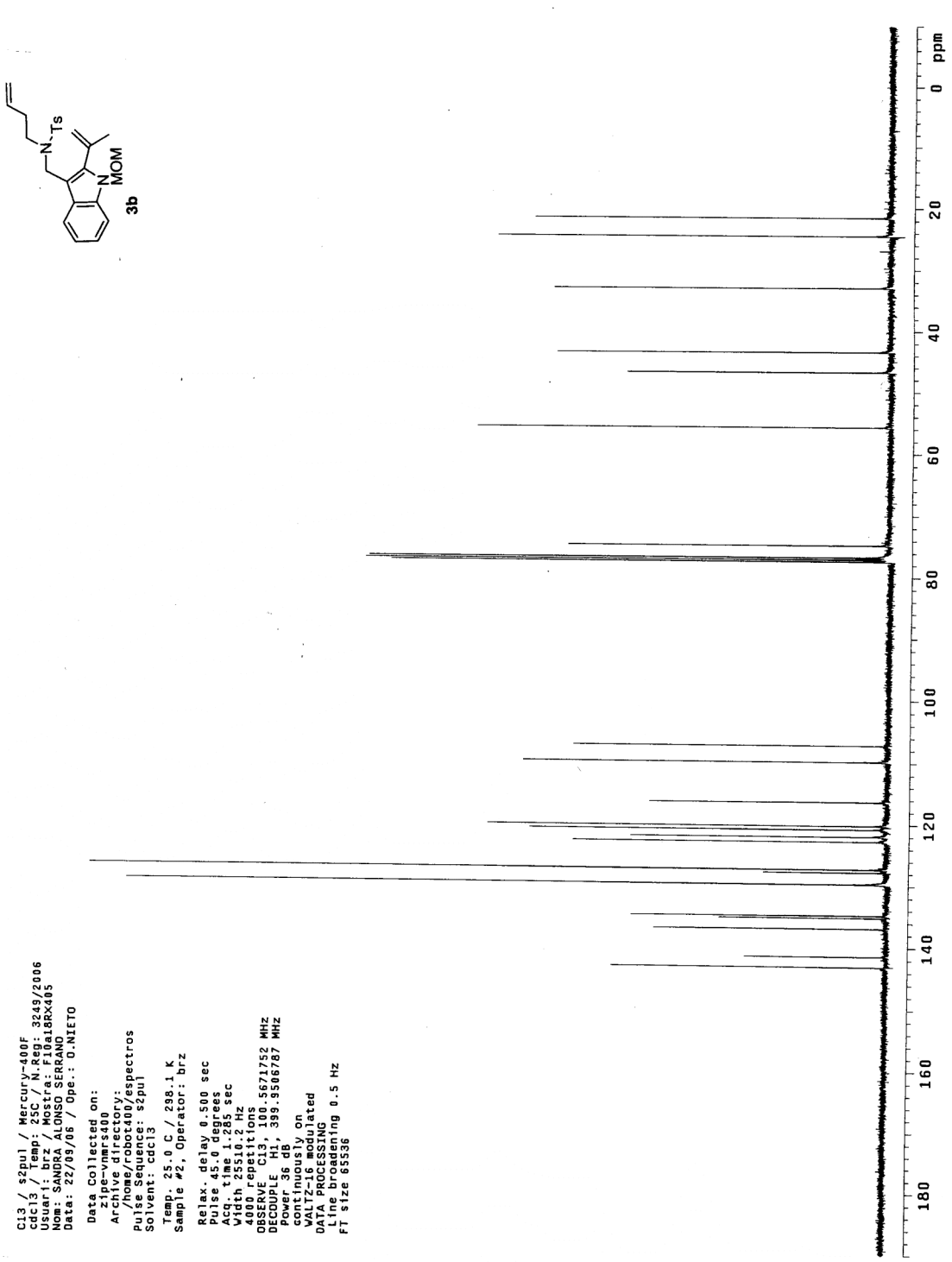
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Data: 22/09/06 / Ope.: O.NIETO
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4000 repetitions
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DECOUPLE H1, 399.9506787 MHz
Power 36 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
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MOM
3b
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140
120
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80
60
40
20
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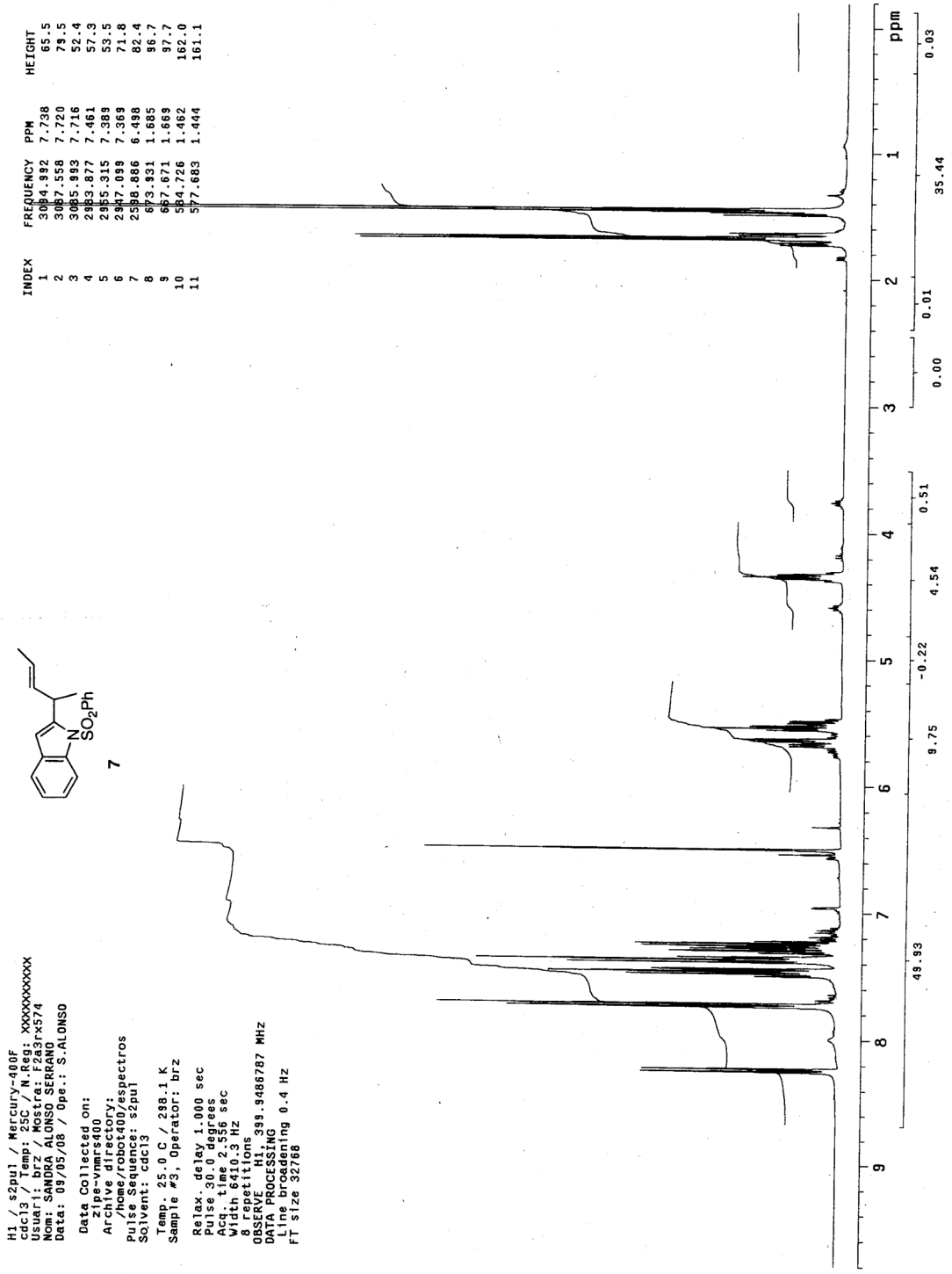
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Solvent: cdcl3
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Sample #3, Operator: brz
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.9486787 MHz
DATA PROCESSING
Line broadening 0.4 Hz
FT size 32768
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1 3094.992 7.738 65.5
2 3087.558 7.720 79.5
3 3085.993 7.716 52.4
4 2983.877 7.461 57.3
5 2955.315 7.389 53.5
6 2947.099 7.369 71.8
7 2598.886 6.498 82.4
8 673.931 1.685 96.7
9 667.671 1.669 97.7
10 584.726 1.462 162.0
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N
SO2Ph
7
ppm
9
8
7
6
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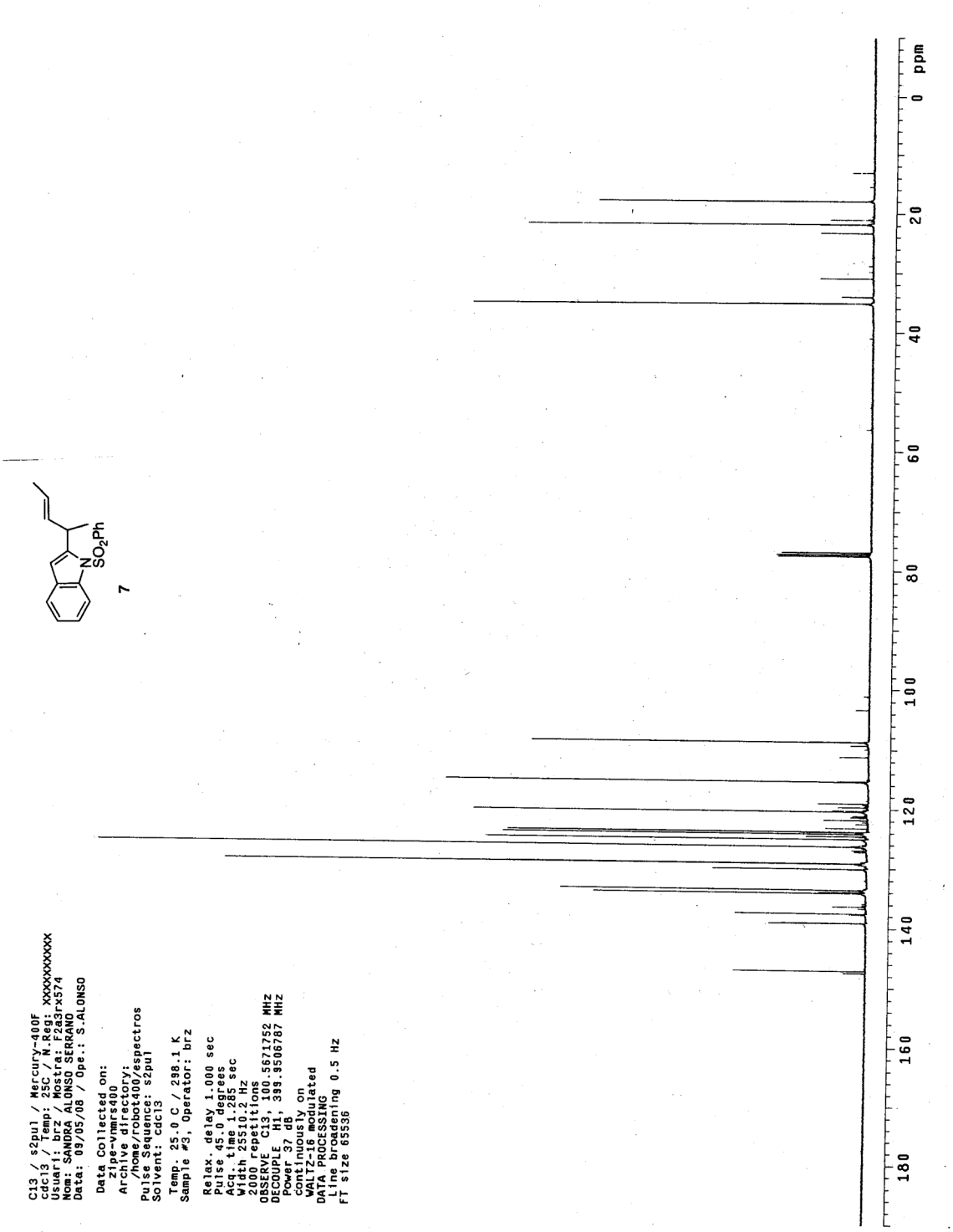
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Archive directory:
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Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
2000 repetitions
OBSERVE C13, 100.5671752 MHz
DECOUPLE H1, 399.9506787 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
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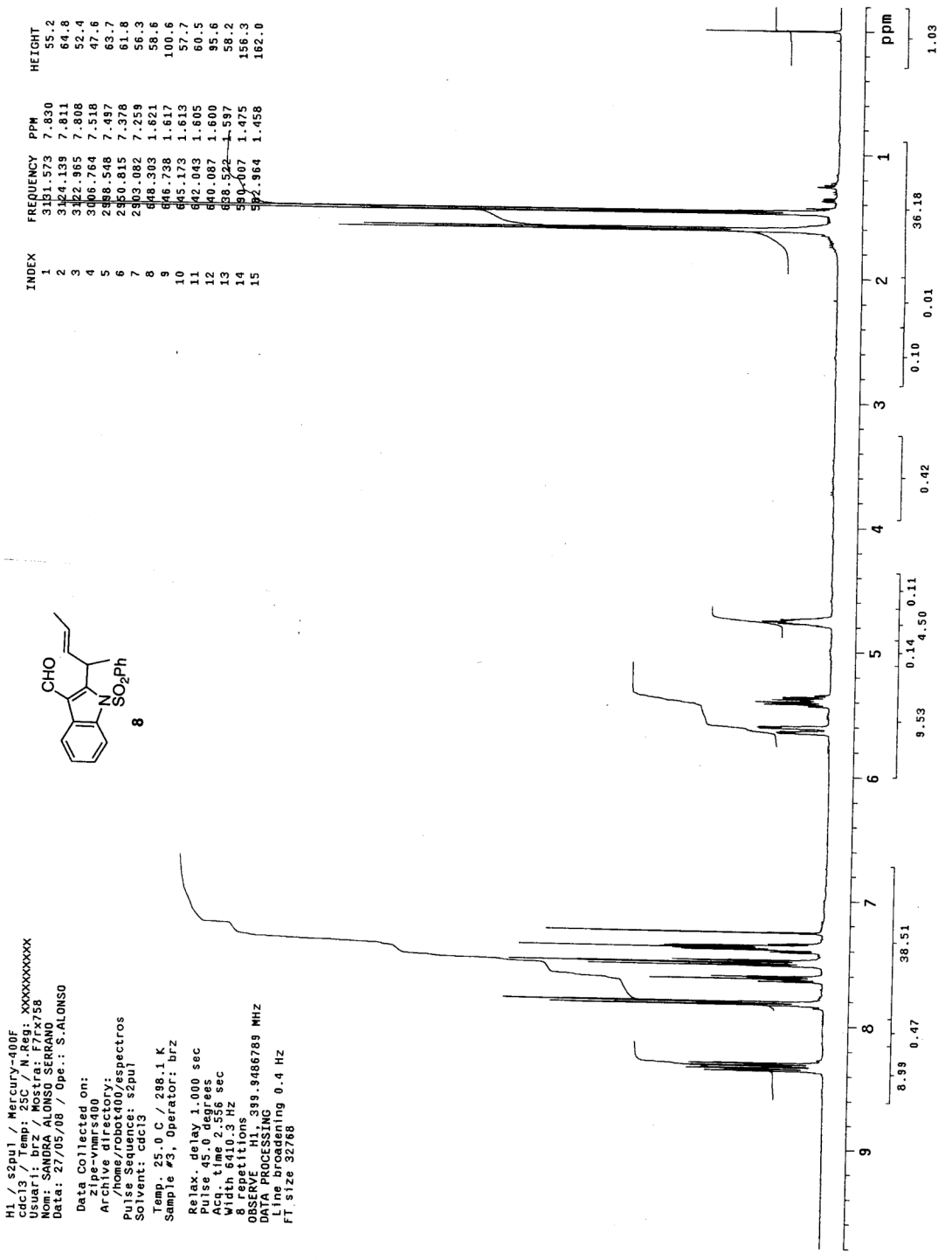
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Data: 27/05/08 / Ope.: S.ALONSO
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Temp. 25.0 C / 298.1 K
Sample #3, Operator: brz
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
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DATA PROCESSING
Line broadening 0.4 Hz
FT size 32768
CHO
N
SO2Ph
8
INDEX FREQUENCY PPM HEIGHT
1 3131.573 7.830 55.2
2 3124.139 7.811 64.8
3 3122.985 7.808 52.4
4 3006.764 7.518 47.6
5 2998.548 7.497 63.7
6 2950.815 7.378 61.8
7 2903.082 7.259 56.3
8 6648.303 1.621 58.6
9 6646.738 1.617 100.6
10 6645.173 1.613 57.7
11 6642.043 1.605 60.5
12 6640.087 1.600 95.6
13 6638.522 1.597 58.2
14 6590.007 1.475 156.3
15 6582.964 1.458 162.0
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8.99
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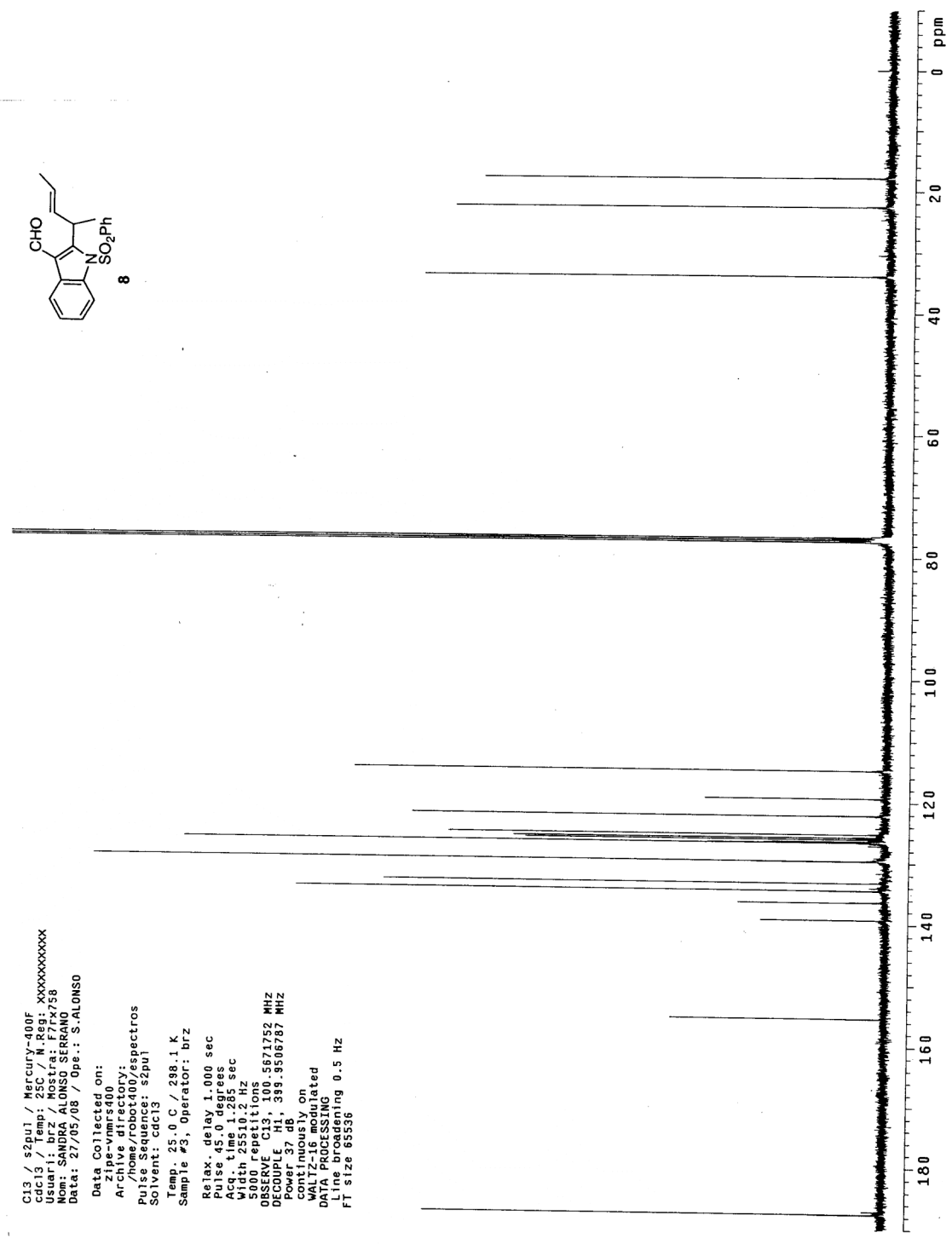
38.51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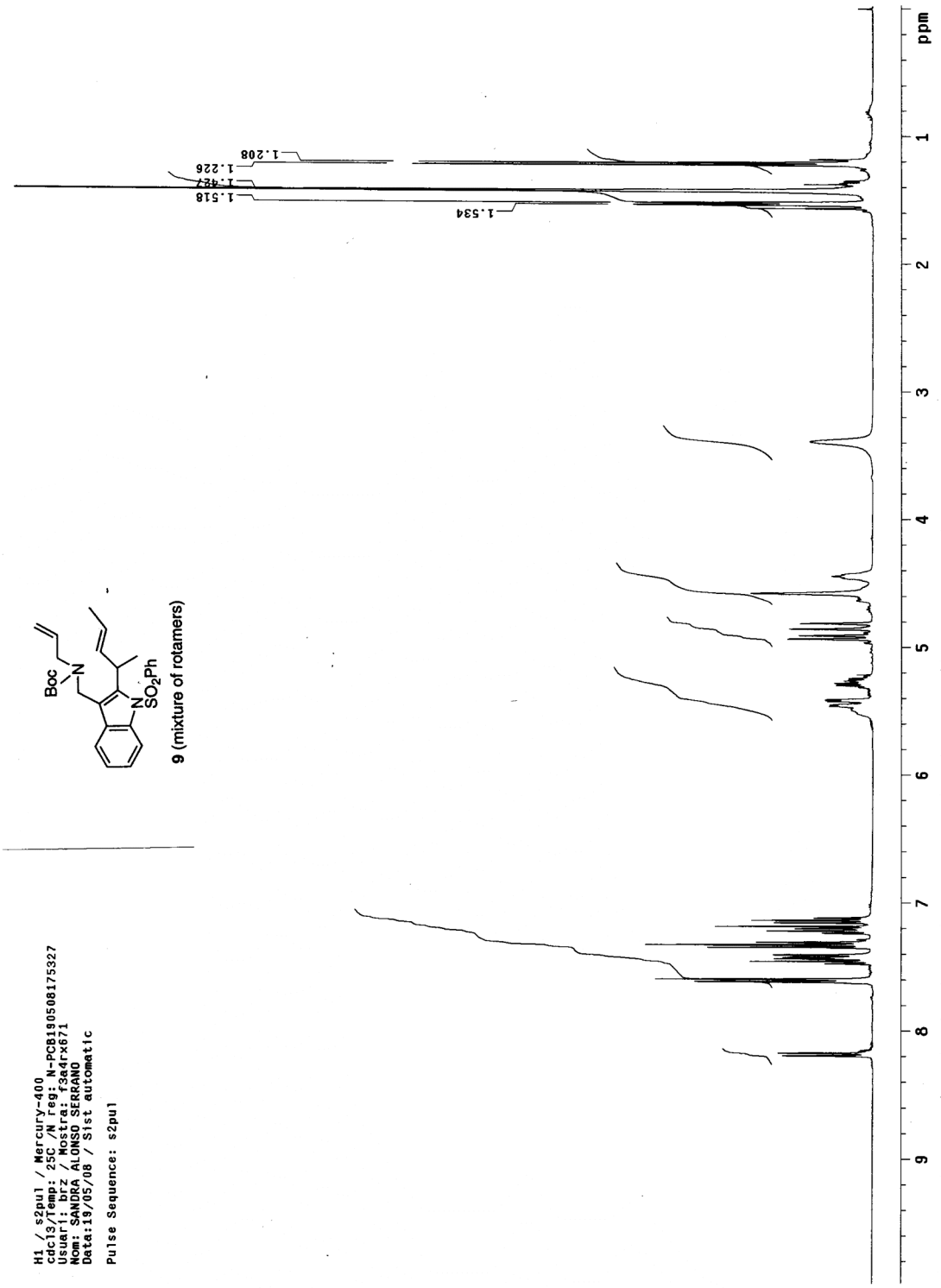
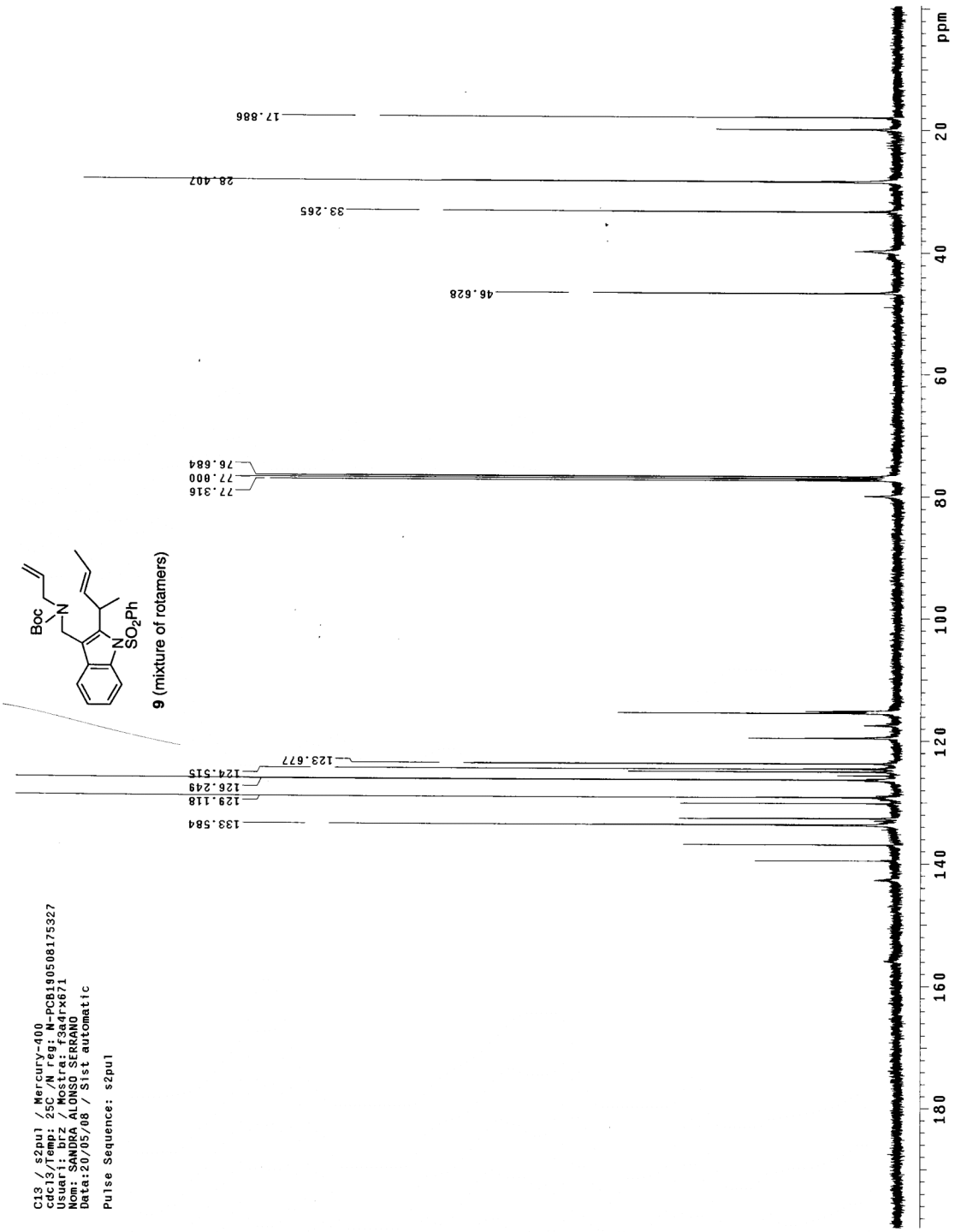
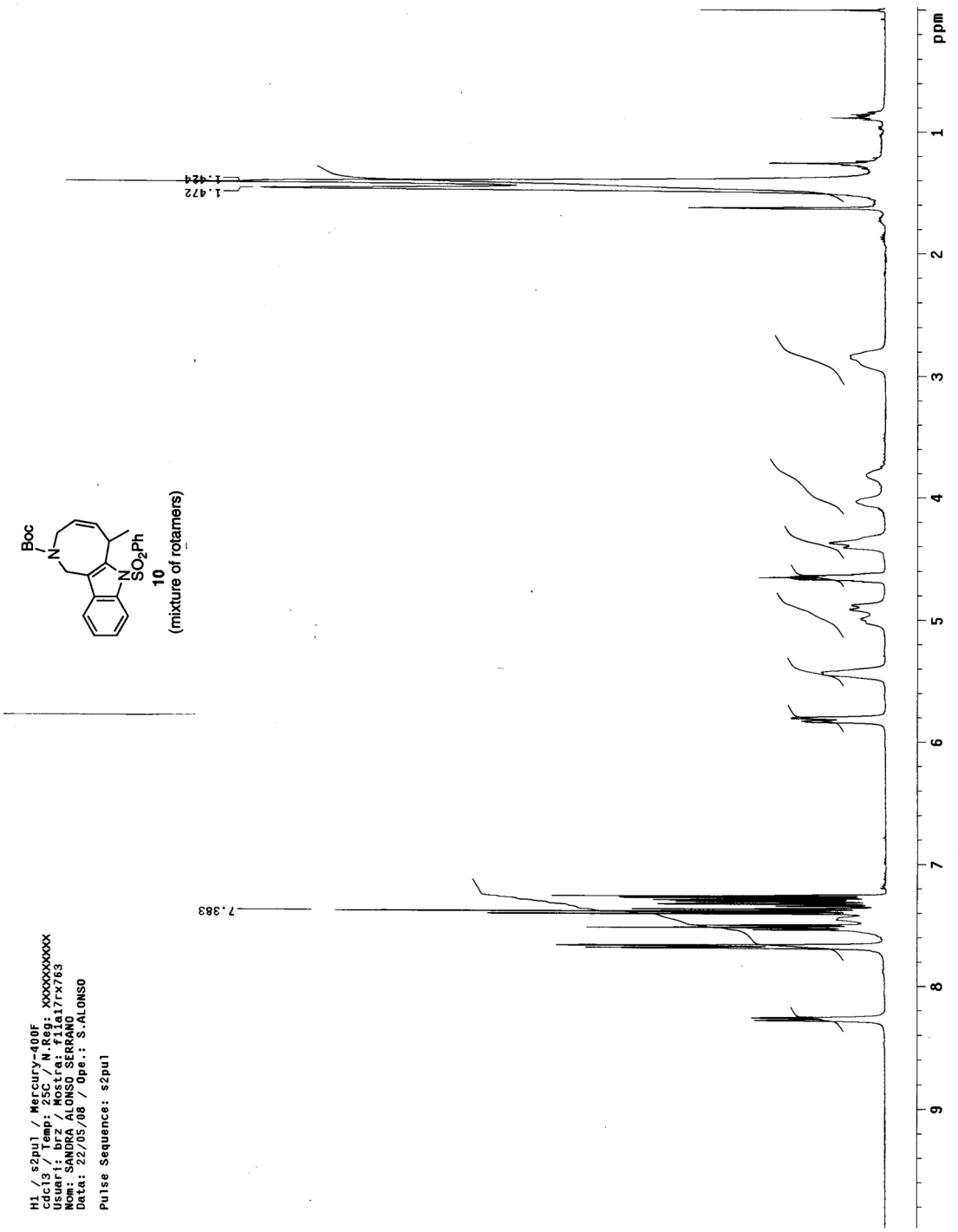
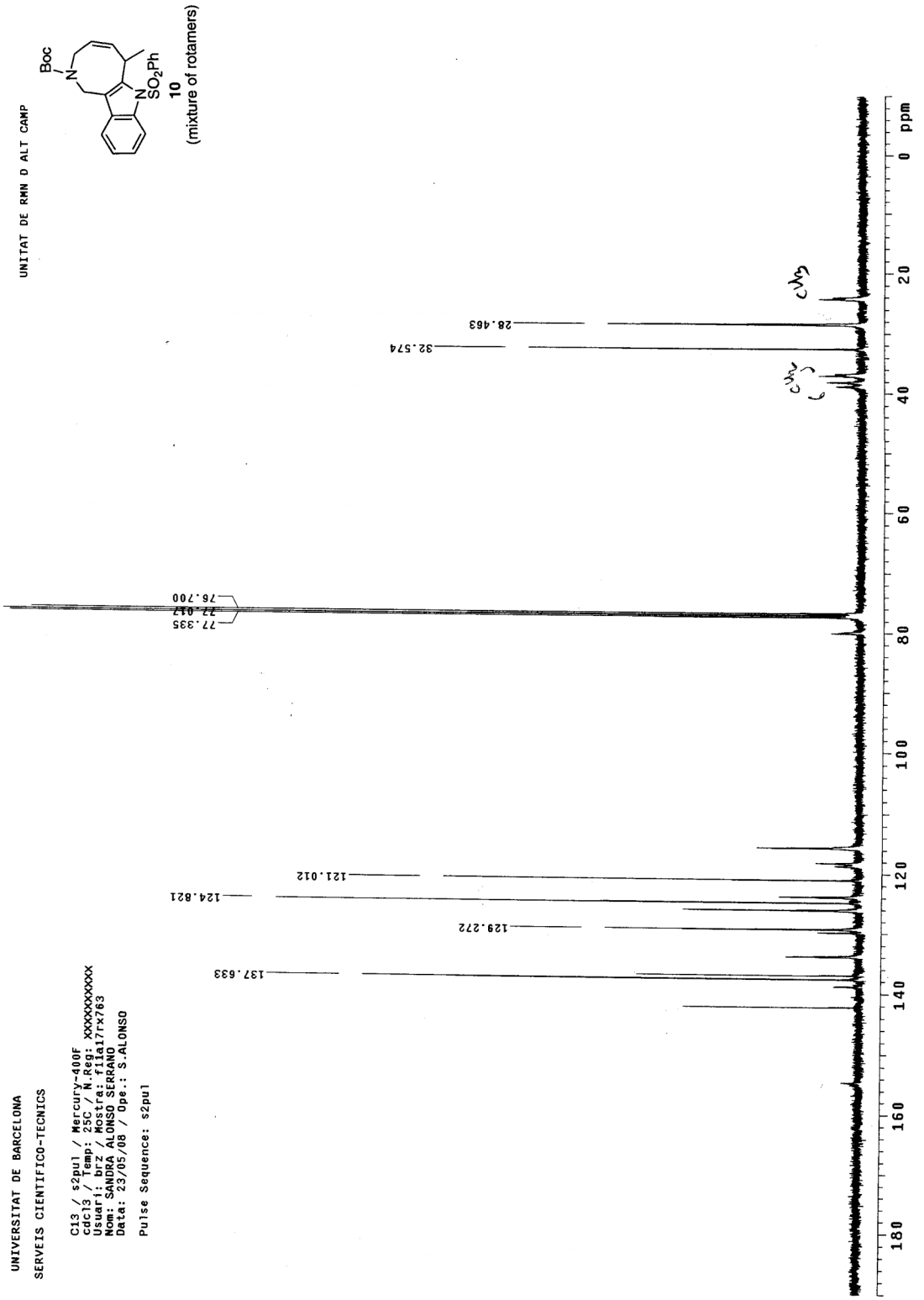
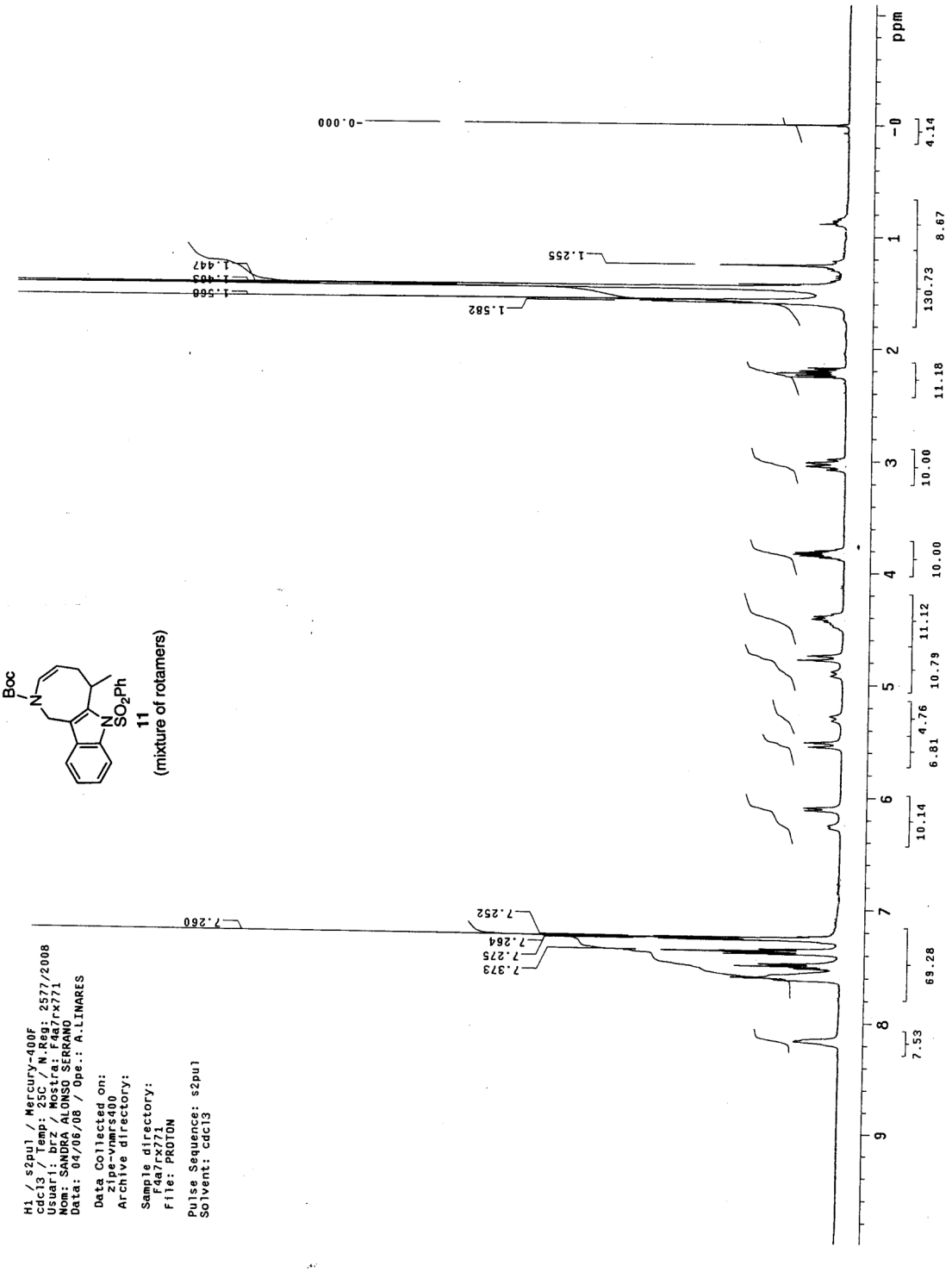
Usuari: brz / Mostra: F7FX758
Nom: SANDRA ALONSO SERRANO
Data: 27/05/08 / Ope.: S.ALONSO
Data Collected on:
zipe-vnmrs400
Archive directory:
/home/robot400/espectros
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Sample #3, Operator: brz
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
5000 repetitions
OBSERVE C13, 100.5671752 MHz
DECOUPLE H1, 399.9506787 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
CHO
N
SO2Ph
8
180
160
140
120
100
80
60
40
20
0
ppm

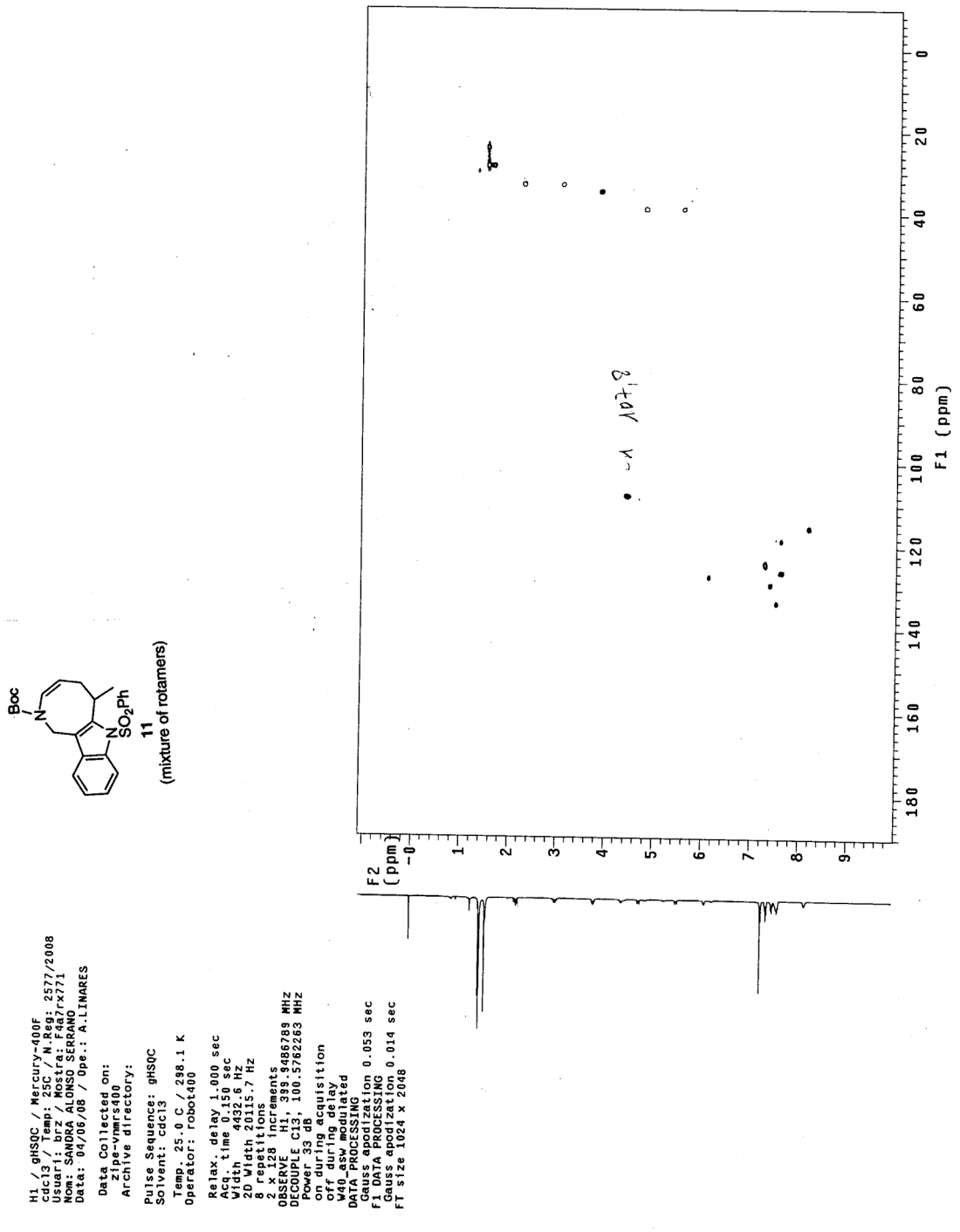

1.208
1.226
1.427
1.518
1.534
ppm
1
2
3
4
5
6
7
8
9
Boc
N
N
SO2Ph
9 (mixture of rotamers)
H1 / s2pul / Mercury-400
cdcl3/Temp: 25C /N reg: N-PCB19050817532?
Usuari: brz / Mostra: f3a4rx671
Nom: SANDRA ALONSO SERRANO
Data:19/05/08 / Sist automatic
Pulse Sequence: s2pul

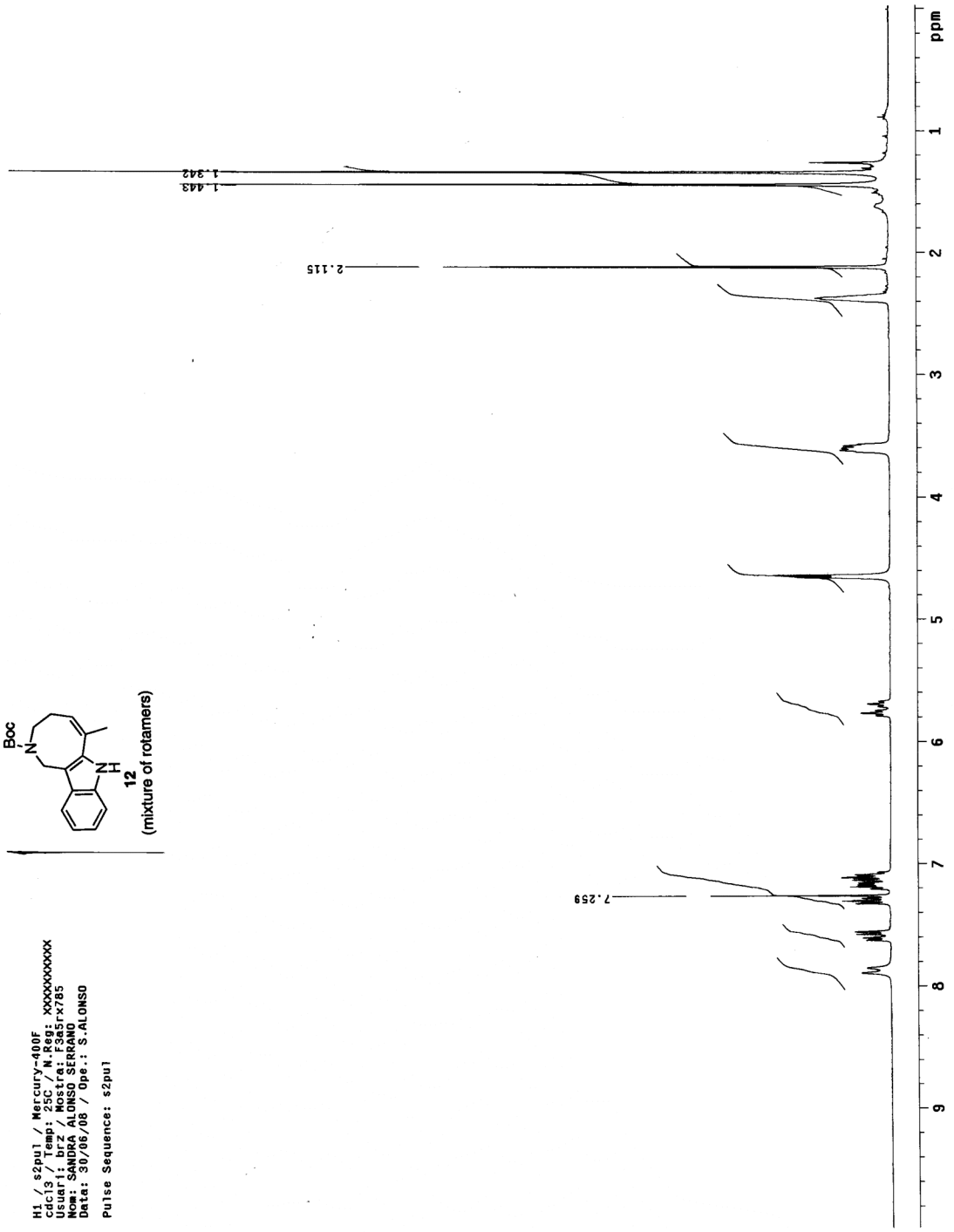

17.886
28.407
33.265
46.628
76.684
77.000
77.316
123.677
124.515
126.249
129.118
133.584
ppm
20
40
60
80
100
120
140
160
180
Boc
N
N
SO2Ph
9 (mixture of rotamers)
C13 / s2pul / Mercury-400
cdcl3/Temp: 25C /N reg: N-PCB190508175327
Usuari: brz / Mostra: f3a4rx671
Nom: SANDRA ALONSO SERRANO
Data:20/05/08 / Sist automatic
Pulse Sequence: s2pul

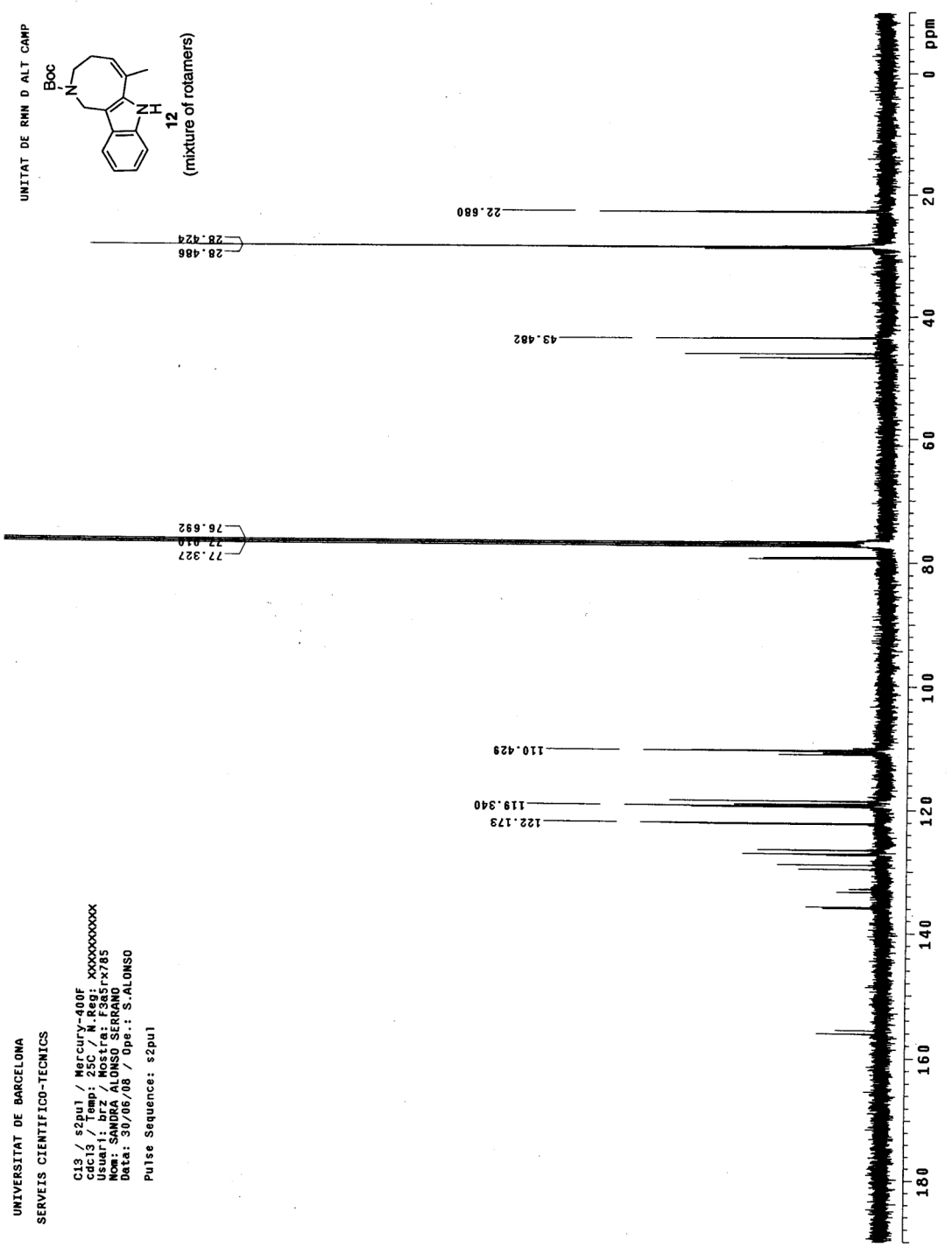

H1 /s2pul / Mercury-400F
cdcl3 / Temp: 25C / N.Reg: XXXXXXXXXX
Usuari: brZ / Mostra: fila17rx763
Nom: SANDRA ALONSO SERRANO
Data: 22/05/08 / Ope.: S.ALONSO
Pulse Sequence: s2pul
Boc
N
N
SO2Ph
10
(mixture of rotamers)
7.383
1.472
1.424
ppm
1
2
3
4
5
6
7
8
9

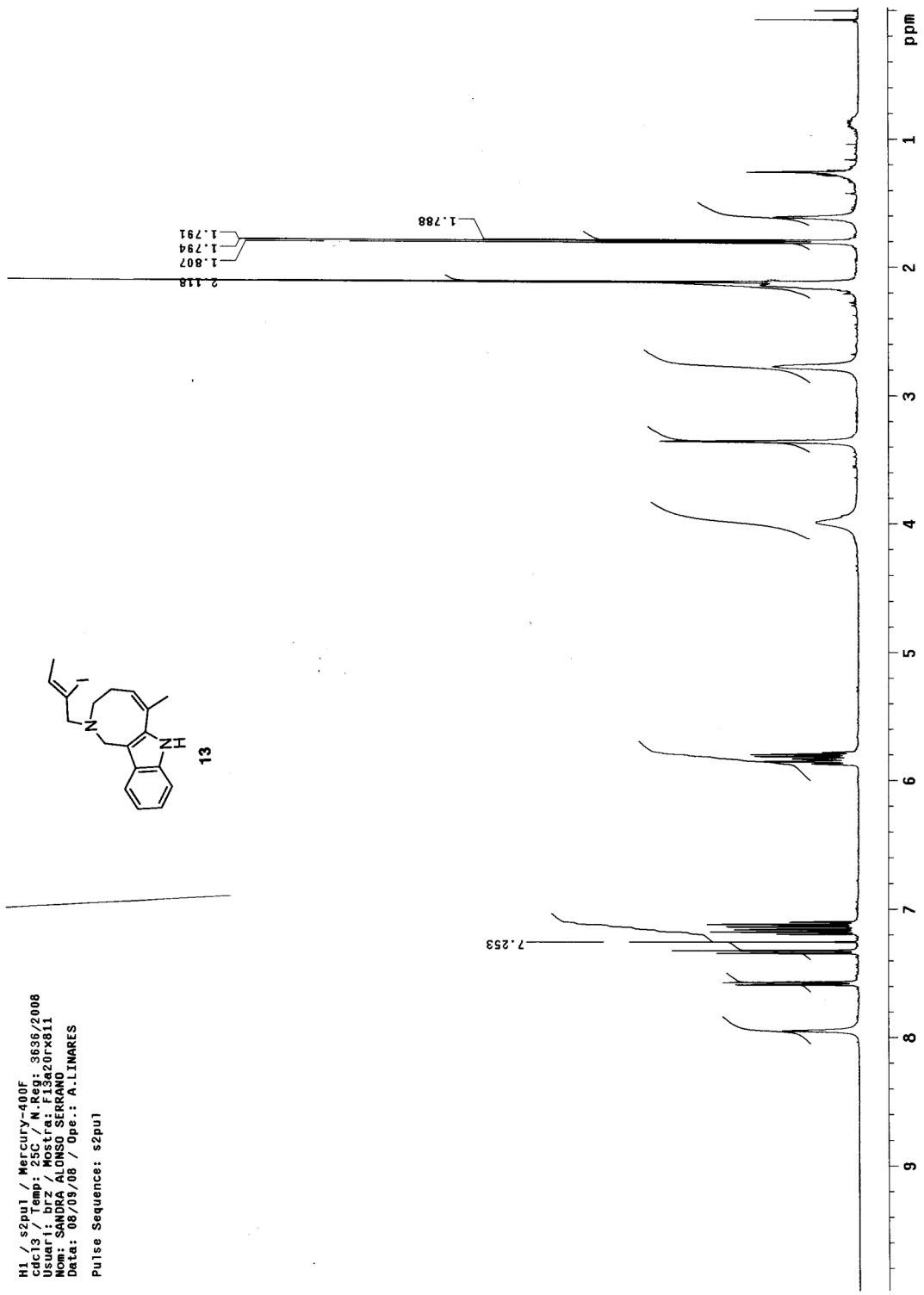

UNIVERSITAT DE BARCELONA
SERVEIS CIENTIFICO-TECNICS
C13 / s2pul / Mercury-400F
Cdcl3 / Temp: 25C / N.Reg: XXXXXXXXXX
Usuari: brz / Mostra: fila17rx763
Nom: SANDRA ALONSO SERRANO
Data: 23/05/08 / Ope.: S.ALONSO
Pulse Sequence: s2pul
UNITAT DE RMN D ALT CAMP
Boc
N
N
SO2Ph
10
(mixture of rotamers)
137.633
129.272
124.821
121.012
77.335
77.017
76.700
32.574
28.463
ppm

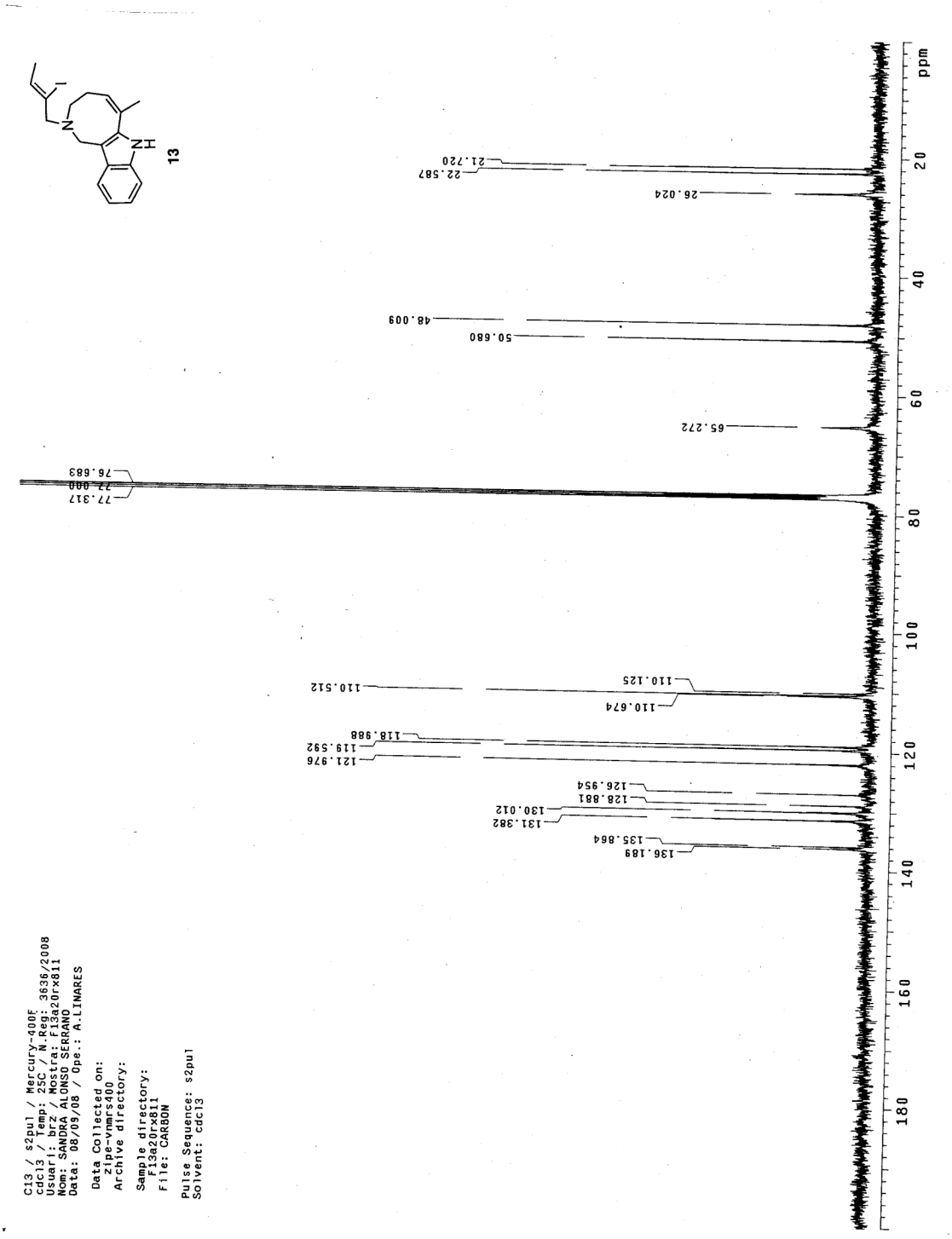

H1 / s2pul / Mercury-400F
cdcl3 / Temp: 25C / N.Reg: 2577/2008
Usuari: brz / Mostra: F4a7rx771
Nom: SANDRA ALONSO SERRANO
Data: 04/06/08 / Ope.: A.LINARES
Data Collected on:
zipe-vnmrs400
Archive directory:
Sample directory:
F4a7rx771
File: PROTON
Pulse Sequence: s2pul
Solvent: cdcl3
Boc
N
N
SO2Ph
11
(mixture of rotamers)
7.260
7.373
7.275
7.264
7.252
1.582
1.560
1.463
1.447
1.255
0.000
ppm

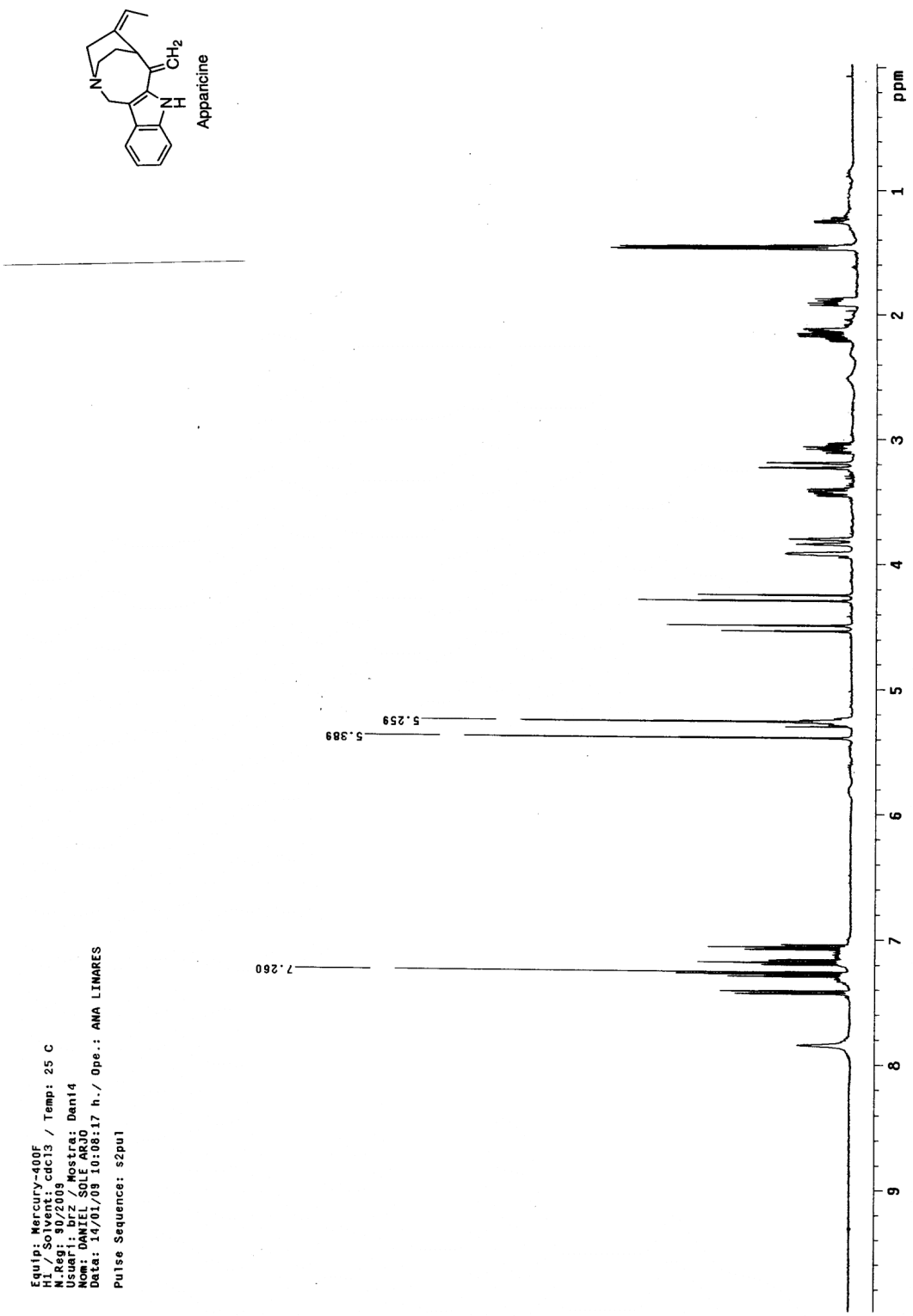

H1 / gHSQC / Mercury-400F
Cdcl3 / Temp: 25C / N.Reg: 2577/2008
Usuari: brZ / Mostra: FA7-x771
Nom: SANDRA ALONSO SERRANO
Data: 04/06/08 / Ope.: A.LINARES
Data Collected on:
zipe-vnmrs400
Archive directory:
Pulse Sequence: gHSQC
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: robot400
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4432.6 Hz
2D Width 20115.7 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 399.9486789 MHz
DECOUPLE C13, 100.5762263 MHz
Power 33 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Gauss apodization 0.053 sec
F1 DATA PROCESSING
Gauss apodization 0.014 sec
FT size 1024 x 2048
Boc
N
N
SO2Ph
11
(mixture of rotamers)
F2 (ppm)
F1 (ppm)

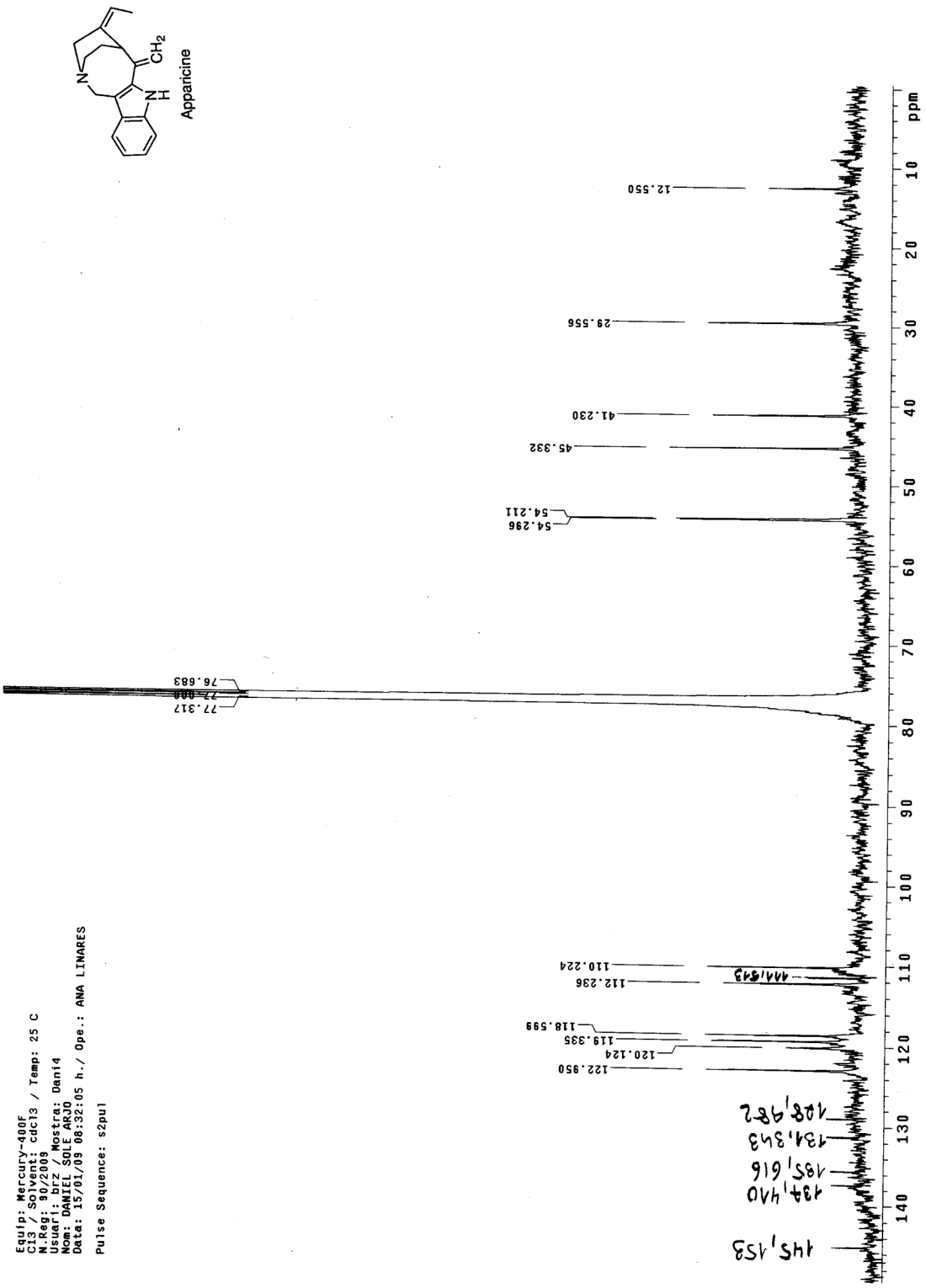

H1 / s2pul / Mercury-400F
cdcl3 / Temp: 25C / N.Reg: XXXXXXXXX
Usuari: brZ / Mostra: F3a5rx785
Nom: SANDRA ALONSO SERRANO
Data: 30/06/08 / Ope.: S.ALONSO
Pulse Sequence: s2pul
Boc
N
N
H
12
(mixture of rotamers)
1.342
1.443
2.115
7.259
ppm


UNIVERSITAT DE BARCELONA
SERVEIS CIENTIFICO-TECNICS
UNITAT DE RMN D ALT CAMP
C13 / s2pul / Mercury-400F XXXXXXXXXX
cdcl3 / Temp: 25C / N.Reg: XXXXXXXXXX
Usuari: brz / Mostra: F3a5rx785
Nom: SANDRA ALONSO SERRANO
Data: 30/06/08 / Ope.: S.ALONSO
Pulse Sequence: s2pul
Boc
N
NH
12
(mixture of rotamers)
22.680
28.486
28.424
43.482
76.692
77.010
77.327
110.429
119.340
122.173
0 ppm
20
40
60
80
100
120
140
160
180


H1 / s2pul / Mercury-400F
cdcl3 / Temp: 25C / N.Reg: 3636/2008
Usuari: brz / Mostra: Fisa20rx811
Nom: SANDRA ALONSO SERRANO
Data: 08/09/08 / Ope.: A.LINARES
Pulse Sequence: s2pul
7.253
2.118
1.807
1.794
1.781
1.788
13
ppm


13
21.720
22.587
26.024
48.009
50.680
65.272
76.683
77.000
77.317
110.125
110.512
110.674
118.988
119.592
121.976
126.954
128.881
130.012
131.382
135.864
136.189
ppm
20
40
60
80
100
120
140
160
180
C13 / s2pul / Mercury-400F
CDCl3 / Temp: 25C / N.Reg: 3636/2008
Usuario: hr2 / Mostra: f13a20rx811
Nom: SANDRA ALONSO SERRANO
Data: 08/09/08 / Ope.: A.LINARES
Data Collected on:
Zipe-vnmrs400
Archive directory:
Sample directory:
f13a20rx811
File: CARBON
Pulse Sequence: s2pul
Solvent: cdcl3


Apparicine
7.260
5.389
5.259
ppm
Equip: Mercury-400F
H1 / Solvent: cdcl3 / Temp: 25 C
N.Reg: 90/2009
Usuari: brz / Mostra: Dan14
Nom: DANIEL SOLE ARJO
Data: 14/01/09 10:08:17 h./ Ope.: ANA LINARES
Pulse Sequence: s2pul


Apparicine
Equip: Mercury-400F
C13 / Solvent: cdcl3 / Temp: 25 C
N.Reg: 30/2009
Usuario: brz / Mostra: Dan14
Nome: DANIEL SOLE ARJO
Data: 15/01/09 08:32:05 h./ Ope.: ANA LINARES
Pulse Sequence: s2pul
12.550
29.556
41.230
45.332
54.296
54.211
77.317
76.683
110.224
112.236
118.599
119.335
120.124
122.950
ppm