Two-Step Total Syntheses of Canthin-6-one Alkaloids: New One-Pot Sequential Pd-Catalyzed Suzuki-Miyaura Coupling and Cu-Catalyzed Amidation Reaction

Supporting Information

Andreas Gollner[†,‡] and Panayiotis A. Koutentis*[,†]

[†]*Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus*

[‡]*Cyano Research Corporation Ltd, P.O. Box 28670, 2081 Nicosia, Cyprus*

E-mail: koutenti@ucy.ac.cy, andreas.gollner@univie.ac.at

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General

Anhydrous Na_2SO_4 was used for drying organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography[1] was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm). Melting points were determined using a PolyTherm-A, Wagner & Munz, Koefler-Hotstage Microscope apparatus or where noted using a TA Instruments DSC Q1000 with samples hermetically sealed in aluminium pans under an argon atmosphere; using heating rates of 5 °C/min. Solvents used for recrystallization are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda-25 UV/*vis* spectrophotometer and inflections are identified by the abbreviation "inf". IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with a Pike *Miracle* Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 machine (at 300 and 75 MHz, respectively) and coupling constants *J* are given in Hz. Deuterated solvents were used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Low resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GCMS with direct inlet probe.

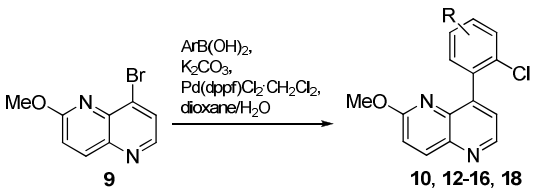
1 Harwood, L. M. *Aldrichimica Acta* **1985**, *18*, 25.

2. Experimental part

2.1. Stepwise synthesis of canthin-6-ones

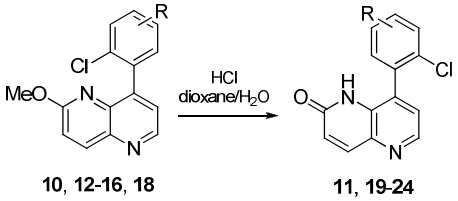
2.1.1. General reaction procedures

Procedure 1: General procedure for the Suzuki-Miyaura coupling of 8-bromo-2-methoxy-1,5-naphthyridine (9):



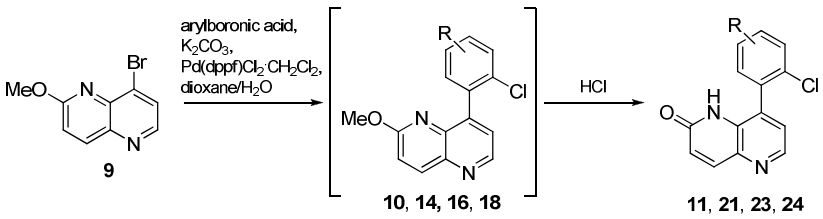
8-Bromo-2-methoxy-1,5-naphthyridine **9** (50 – 300 mg, 0.21 – 1.26 mmol), K_2CO_3 (2 equiv), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (0.02 – 0.04 equiv) and the corresponding 2-chlorophenylboronic acid (1.2 – 1.5 equiv) were dissolved in dioxane/H_2O (3:1) (2 mL/mmol). The stirred mixture was heated to reflux (preheated oil bath) and refluxed for 1 – 2 h until the reaction was finished (TLC), before it was allowed to cool to rt. It was diluted with CH_2Cl_2, dried (Na_2SO_4), filtrated and adsorbed onto silica gel. Dry flash chromatography (hexane/t-BuOMe, 3:1) gave **10**, **12-16**, **18** (85 – 98%) as colorless solids or viscous oils. The solids could be recrystallized (pentane) to give colorless needles.

Procedure 2: General procedure for demethylation of 2-methoxy-1,5-naphthyridines using aqueous HCl:



To a stirred solution of the 2-methoxy-1,5-naphthyridine **10**, **12-16**, **18** (0.25 to 1.50 mmol) in dioxane (5 mL/mmol) was added a mixture of conc HCl and water (1:1) (7 mL/mmol). The mixture was refluxed for 2 – 3 h until the reaction was finished (TLC), diluted with H_2O and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried (Na_2SO_4), filtrated and adsorbed onto silica gel. Dry flash chromatography (t-BuOMe) gave **11**, **19-24** (84 – 90% yield) which could be recrystallized (t-BuOMe) to give colorless needles. The material could also be used crude for the next step without chromatography or recrystallization.

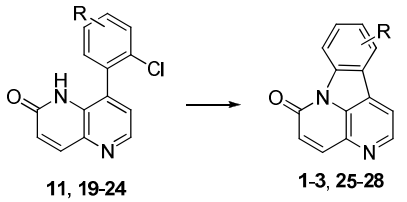
Procedure 3: General procedure for the one-pot Suzuki-Miyaura coupling and demethylation:



8-Bromo-2-methoxy-1,5-naphthyridine **9** (100 – 300 mg, 0.42 – 1.26 mmol), K_2CO_3 (2 equiv), $Pd(dppf)Cl_2.CH_2Cl_2$ (0.02 – 0.04 equiv) and the corresponding 2-chlorophenylboronic acid (1.2 – 1.5

equiv) were dissolved in dioxane/H_2O (3:1) (2 mL/mmol). The stirred mixture was heated to reflux (preheated oil bath) until completion (TLC) of the coupling, *ca.* 1 – 2 h. A mixture of conc HCl and H_2O (2:1) (4 mL/mmol) was added to the refluxing mixture and heating was continued for 1 – 2 h until the demethylation was complete (TLC). The reaction was allowed to cool rt, diluted with water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried (Na_2SO_4), filtrated and adsorbed onto silica gel. Dry flash chromatography (t-BuOMe) gave **11**, **21**, **23**, **24** (80 – 90%) which could be recrystallized (t-BuOMe) to give colorless needles.
The material could also be used crude for the next step without the use of chromatography or recrystallization after a filtration of the dried (Na_2SO_4) solution through a short pad of silica.

Procedure 4: General procedure for the final amidation (1-3, 25-28):



11, 19-24 **1-3, 25-28**

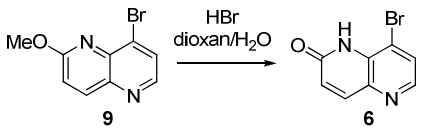
The starting material (**11**, **19-24**, 0.2 to 1 mmol), Cs_2CO_3 (2 equiv) and CuI (0.05 to 0.10 equiv) were dissolved in dioxane (4 mL/mmol) and then DMEDA (0.1 to 0.2 equiv) and H_2O (2 equiv) were added. The stirred reaction mixture was refluxed (preheated oil bath) until the reaction was complete (TLC, 15 – 60 min) and then allowed to cool to rt. The mixture was diluted (CH_2Cl_2), dried (Na_2SO_4), filtered and adsorbed onto silica gel. Dry flash chromatography (EtOAc) followed by recrystallization (acetone) gave the canthin-6-ones **1**-**3**, **25**-**28** (91–99%) as lightly colored to colorless needles.
The compounds could be obtained microanalytically pure without the use of chromatography, by simply filtering the dried (Na_2SO_4) solution through a short pad of silica, evaporation and recrystallization.

2.1.2. Preparation and characterization of compounds 1-3, 6, 10-28

Preparation of 6-methoxy-1,5-naphthyridin-4(1*H*)-one (**8**): Morgentin, R.; Pasquet, G.; Boutron, P.; Jung, F.; Lamorlette, M.; Maudet, M.; Ple, P. *Tetrahedron*, **2008**, *64*, 2772.

Preparation of 8-bromo-2-methoxy-1,5-naphthyridine (**9**): Alemparte-Gallardo, C.; Ballell-Pages, L.; Barros-Aguirre, D.; Cacho-Izquierdo, M.; Castro-Pichel, J.; Fiandor-Roman, J. M.; Hennessy, A. J.; Pearson, N. D.; Remuinan-Blanco, M. J. WO2009090222, **2009**.

8-Bromo-1,5-naphthyrid-2(1*H*)-one (6)



9 **6**

8-Bromo-2-methoxy-1,5-naphthyridine (**9**) (5 g, 21 mmol) was dissolved in dioxane (10 mL) and a mixture of HBr and water [20 mL, HBr (48%)/H_2O (3:2)] was added. The mixture was refluxed for 90 min, diluted with water and extracted with CH_2Cl_2 (2 × 100 mL). The aqueous phase was neutralized and again extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried (Na_2SO_4), filtrated and evaporated. The resulting colorless solid was recrystallized (t-BuOMe) to give 8-bromo-1,5-naphthyrid-2(1*H*)-one (**6**) as colorless needles (4.25 g, 18.9 mmol, 90%).

mp 204 – 206 °C (t-BuOMe).

Elemental Analysis: Found: C, 42.70; H, 2.16; N, 12.39. $C_8H_5BrN_2O$ requires C, 42.70; H, 2.24; N, 12.45%.

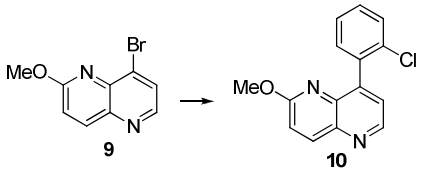
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 9.26 (br s, 1H, NH), 8.33 (d, *J* 5.1, 1H), 7.93 (d, *J* 9.8, 1H), 7.64 (d, *J* 5.1, 1H), 6.89 (d, *J* 9.8, 1H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 161.6 (C_q), 145.6 (CH), 142.0 (CH), 138.5 (C_q), 133.1 (C_q), 127.9 (CH), 127.1 (CH), 119.2 (C_q).

ν_{max}/cm^{-1} 1672m, 1655s, 1603m, 1572m, 1547m, 1450w, 1379m, 1321m, 1267w, 1192m, 1126m, 1074w, 860m, 849s, 824m, 808s, 781w, 752m.

m/*z* (EI) 226 (M^++2, 78%), 224 (M^+, 77), 198 (31), 196 (34), 183 (7), 169 (5), 129 (4), 119 (7), 118 (12), 117 (84), 116 (11).

8-(2-Chlorophenyl)-2-methoxy-1,5-naphthyridine (10):



Procedure 1: Bromo-2-methoxy-1,5-naphthyridine **9** (300 mg, 1.26 mmol), K_2CO_3 (347 mg, 2.51 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (20.5 mg, 0.03 mmol), 2-chlorophenylboronic acid (294 mg, 1.88 mmol). Product: 8-(2-Chlorophenyl)-2-methoxy-1,5-naphthyridine (**10**) as colorless solid (333 mg, 1.23 mmol, 98%).

mp 79 – 80 °C (pentane).

Elemental Analysis: (Found: C, 66.63; H, 4.3; N, 10.31. $C_{15}H_{11}ClN_2O$ requires C, 66.55; H, 4.10; N, 10.35%).

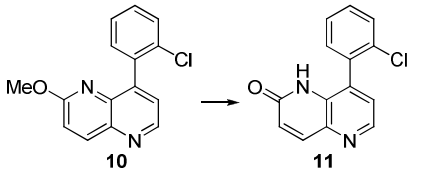
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.84 (d, *J* 4.5, 1H), 8.26 (d, *J* 9.0, 1H), 7.55-7.50 (m, 2H), 7.44-7.34 (m, 3H), 7.12 (d, *J* 9.0, 1H), 3.81 (s, 3H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 161.9 (C_q), 147.4 (CH), 144.8 (C_q), 142.2 (C_q), 140.1 (CH), 140.0 (C_q), 136.5 (C_q) 133.6 (C_q), 131.8 (CH), 129.54 (CH), 129.45 (CH), 126.3 (CH), 125.0 (CH), 116.8 (CH), 53.7 (CH_3).

ν_{max}/cm^{-1} 1667m, 1613m, 1599m, 1582m, 1491s, 1468w, 1456w, 1435m, 1398s, 1360w, 1337s, 1283m, 1265s, 1254s, 1111w, 1070w, 1055m, 1035w, 1020m, 858s, 835s, 808m, 754s, 740m, 727m.

m/*z* (EI) 235 (M^+-Cl, 100), 220 (21), 205 (8), 192 (20), 164 (5), 139 (4), 126 (2), 117 (2), 103 (3).

8-(2-Chlorophenyl)-1,5-naphthyrid-2(1*H*)-one (11):



Procedure 2: 8-(2-Chlorophenyl)-2-methoxy-1,5-naphthyridine (**10**) (200 mg, 0.739 mmol), conc HCl/H_2O (1:1) (4 mL).

Product: 8-(2-Chlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**11**) as colorless needles (171 mg, 0.67 mmol, 90%).

mp 196 – 198 °C (t-BuOMe).

Elemental Analysis: Found: C, 65.54; H, 3.42; N, 10.86. $C_{14}H_9ClN_2O$ requires C, 65.51; H, 3.53; N, 10.91%).

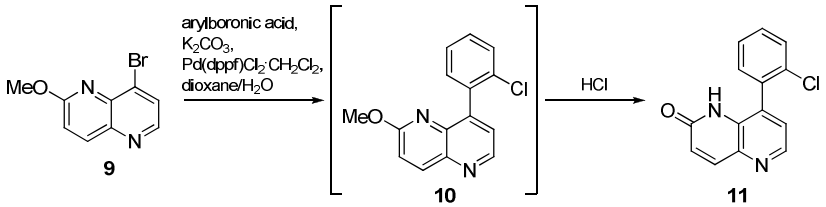
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.60 (d, *J* 4.7, 1H), 8.59 (br s, 1H, NH), 8.03 (d, *J* 9.8, 1H), 7.58 (dd, *J* 7.6, 1.6, 1H), 7.52-7.41 (m, 2H), 7.33-7.28 (m, 2H), 6.83 (d, *J* 9.8, 1H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 161.8 (C_q), 144.9 (CH), 142.3 (CH), 137.8 (C_q), 133.7 (C_q), 133.5 (C_q), 132.4 (C_q), 132.2 (C_q), 131.4 (CH), 131.2 (CH), 130.8 (CH), 128. 0 (CH), 126.1 (CH), 125.5 (CH).

ν_{max}/cm^{-1} 1651s, 1605s, 1593m, 1568w, 1554w, 1473w, 1454m, 1433m, 1417w, 1381m, 1327m, 1304w, 1153w, 1113m, 1080w, 1051m, 1032w, 959w, 833w, 855m, 818m, 792w, 766s, 735m, 710m.

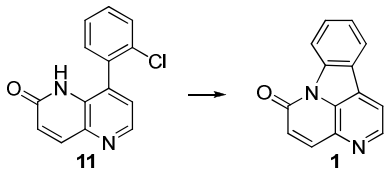
m/*z* (EI) 258 (M^++2, 19%), 256 (M^+, 56), 221 (100), 193 (25), 167 (6), 140 (13), 113 (6), 100 (2), 96 (10).

8-(2-Chlorophenyl)-1,5-naphthyrid-2(1*H*)-one (11), *via* one-pot procedure 3:



Procedure 3: 8-Bromo-2-methoxy-1,5-naphthyridine **9** (200 mg, 0.84 mmol), K_2CO_3 (231 mg, 1.67 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (14 mg, 0.02 mmol), 2-chlorophenylboronic acid (157 mg, 1 mmol), aq HCl (3.4 mL).
Product: 8-(2-Chlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**11**) (193 mg, 0.75 mmol, 90%) as colorless needles, identical to that described above.

Canthin-6-one (1):



Procedure 4: 8-(2-Chlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**11**) (150 mg, 0.58 mmol), Cs_2CO_3 (381 mg, 1.17 mmol), CuI (5.6 mg, 0.03 mmol), dioxane (3 mL), DMEDA (5.1 mg, 0.06 mmol) and H_2O (21 mg).
Product: Canthin-6-one (**1**) as light yellow needles (127 mg, 0.58 mmol, 99%).

mp (DSC) onset: 157.2 °C; peak max: 159.7 °C (acetone) Lit.: 162.5-163.5 °C (Haynes, H. F.; Nelson, E. R.; Price, J. R. *Aust. J. Res., Ser. A* **1952**, *5*, 387.).

Elemental Analysis: Found: C, 76.32; H, 3.63; N, 12.78. $C_{14}H_8N_2O$ requires C, 76.35; H, 3.66; N, 12.72%.

^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 8.77 (d, *J* 5.0, 1H), 8.58 (d, *J* 8.0, 1H), 8.11 (d, *J* 7.7, 1H), 7.98 (d, *J* 9.8, 1H), 7.94 (d, *J* 5.0, 1H), 7.68 (ddd, *J* 7.9, 7.9, 1.1, 1H), 7.52 (ddd, *J* 7.6, 7.6, 0.9, 1H), 6.91 (d, *J* 9.8, 1H).

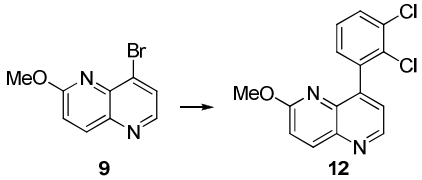
^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 159.1 (C_q), 145.5 (CH), 139.4 (CH), 139.1 (C_q), 136.0 (C_q), 131.7 (C_q), 130.3 (CH), 129.6 (C_q), 128.4 (CH), 125.2 (CH), 124.1 (C_q), 122.4 (CH), 116.6 (CH), 116.0 (CH).

ν_{max}/cm^{-1} 1668s, 1634m, 1602m, 1464m, 1435m, 1396w, 1333m, 1306m, 1285w, 1246w, 1192w, 1140m, 1055m, 1017w, 999w, 885w, 864w, 841s, 795m, 758s.

λ_{max}(DCM)/nm 232 (log ε 4.36), 252 (4.26), 261 (4.22) 269 (4.18), inf 293 (4.03), 300 (4.04), inf 346 (4.07), 362 (4.30); 381 (4.28).

m/*z* (EI) 221 (M^++1, 17%), 220 (M^+, 100), 192 (74), 165 (11), 164 (11), 140 (6), 139 (13), 110 (8), 96 (13), 83 (12), 69 (12).

8-(2,3-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (12):



Procedure 1: Bromo-2-methoxy-1,5-naphthyridine **9** (150 mg, 0.63 mmol), K_2CO_3 (172 mg, 1.25 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (20.5 mg, 0.03 mmol), 2,3-dichlorophenylboronic acid (180 mg, 0.94 mmol).
Product: 8-(2,3-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (**12**) as colorless needles (178 mg, 0.58 mmol, 93%).

mp 101 – 103 °C (pentane).

Elemental Analysis: Found: C, 59.06; H, 3.32; N, 9.10. $C_{15}H_{10}Cl_2N_2O$ requires C, 59.04; H, 3.30; N, 9.18%.

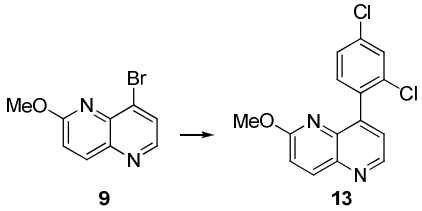
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.84 (d, *J* 4.5, 1H), 8.26 (d, *J* 9.0, 1H), 7.59-7.52 (m, 1H), 7.49 (d, *J* 4.5, 1H), 7.32-7.28 (m, 2H), 7.13 (d, *J* 9.0, 1H), 3.79 (s, 3H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 162.1 (C_q), 147.3 (CH), 144.6 (C_q), 142.2 (C_q), 140.1 (CH), 139.8 (C_q), 138.8 (C_q), 133.3 (C_q), 132.1 (C_q), 130.2 (CH), 129.9 (CH), 126.9 (CH), 124.7 (CH), 117.0 (CH), 53.8 (CH_3).

ν_{max}/cm^{-1} 1660m, 1651m, 1613s, 1587m, 1482s, 1470w, 1456w, 1435m, 1398s, 1379w, 1363w, 1337s, 1283m, 1258s, 1105m, 1068w, 1055w, 1018m, 858s, 847m, 833m, 806s, 781m, 762m, 735m.

m/*z* (EI) 271 (MH^+-Cl, 73%), 269 (M^+-Cl, 100), 256 (12), 254 (14), 241 (3), 239 (6), 228 (7), 226 (12), 203 (9), 191 (6),176 (5), 164 (8), 138 (3), 113 (4), 102 (4).

8-(2,4-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (13)



Procedure 1: Bromo-2-methoxy-1,5-naphthyridine **9** (157 mg, 0.66 mmol), K_2CO_3 (182 mg, 1.31 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (21.2 mg, 0.03 mmol), 2,4-dichlorophenylboronic acid (188 mg, 0.99 mmol).
Product: 8-(2,4-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (**13**) as colorless needles (186 mg, 0.61 mmol, 93%)

mp 116 – 118 °C (pentane)

Elemental Analysis: Found: C, 59.03; H, 3.20; N, 9.07. $C_{15}H_{10}Cl_2N_2O$ requires C, 59.04; H, 3.30; N, 9.18%.

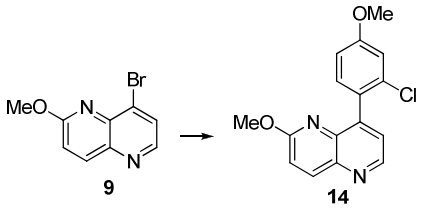
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.83 (d, *J* 4.5, 1H), 8.26 (d, *J* 9.0, 1H), 7.56-7.54 (m, 1H), 7.47 (d, *J* 4.5, 1H), 7.37 (br s, 2H), 7.13 (d, *J* 9.0, 1H), 3.82 (s, 3H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 162.0 (C_q), 147.3 (CH), 143.6 (C_q), 142.2 (C_q), 140.2 (CH), 139.8 (C_q), 135.1 (C_q), 134.7 (C_q), 134.4 (C_q), 132.7 (CH), 129.5 (CH), 126.7 (CH), 124.9 (CH), 117.0 (CH), 53.8 (CH_3).

ν_{max}/cm^{-1} 1613m, 1587m, 1491s, 1470m, 1429m, 1398m, 1360w, 1339s, 1285m, 1256m, 1148w, 1103w, 1074w, 1055w, 1015m, 870w, 858s, 845m, 831w, 808s, 783m, 754w, 735m.

m/*z* (EI) 271 (MH^+-Cl, 40%), 269 (M^+-Cl, 100), 256 (9), 254 (25), 241 (3), 239 (5), 228 (5), 226 (14), 191 (4), 164 (12).

8-(2-Chloro-4-methoxyphenyl)-2-methoxy-1,5-naphthyridine (14):



Procedure 1: Bromo-2-methoxy-1,5-naphthyridine **9** (150 mg, 0.62 mmol), K_2CO_3 (173 mg, 1.26 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (20.4 mg, 0.03 mmol), 2-chloro-4-methoxyphenylboronic acid (174 mg, 0.94 mmol).
Product: 8-(2-Chloro-4-methoxyphenyl)-2-methoxy-1,5-naphthyridine (**14**) as colorless needles (165 mg, 0.549 mmol, 88%).

mp 114 – 116 °C (pentane)

Elemental Analysis: Found: C, 63.92; H, 4.37; N, 9.29. $C_{16}H_{13}ClN_2O_2$ requires C, 63.90; H, 4.36; N, 9.31%.

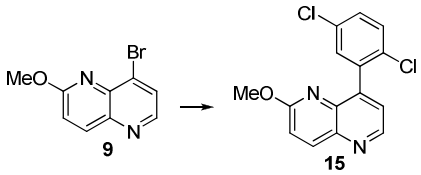
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.81 (d, *J* 4.3, 1H), 8.25 (d, *J* 9.0, 1H), 7.52 (d, *J* 4.3, 1H), 7.36 (d, *J* 8.5, 1H), 7.11 (d, *J* 9.0, 1H), 7.08 (d, *J* 2.4, 1H), 6.92 (dd, *J* 8.5, 2.4, 1H), 3.88 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 161.9 (C_q), 160.1 (C_q), 147.3 (CH), 144.7 (C_q), 142.1 (C_q), 140.3 (C_q), 140.1 (CH), 134.2 (C_q), 132.7 (CH), 128.6 (C_q), 125.4 (CH), 116.7 (CH), 114.9 (CH), 112.5 (CH), 55.7 (CH_3), 53.8 (CH_3).

ν_{max}/cm^{-1} 1602m, 1584m, 1493s, 1477m, 1462m, 1452w, 1433w, 1398m, 1338m, 1290s, 1265m, 1219m, 1114w, 1066w, 1142s, 1036m, 1020m, 860s, 843m, 812m, 735w.

m/*z* (EI) 266 (MH^+-Cl, 41%), 265 (M^+-Cl, 100), 250 (59), 235 (11), 221 (16), 207 (23), 192 (13), 179 (14), 164 (4), 153 (5), 133 (13), 126 (4).

8-(2,5-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (15)



Procedure 1: Bromo-2-methoxy-1,5-naphthyridine **9** (154 mg, 0.64 mmol), K_2CO_3 (178 mg, 1.29 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (21 mg, 0.03 mmol), 2,5-dichlorophenylboronic acid (184 mg, 0.97 mmol).
Product: 8-(2,5-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (**15**) as colorless needles (173 mg, 0.57 mmol, 88%).

mp 106 – 108 °C (pentane).

Elemental Analysis: Found: C, 58.85; H, 3.18; N, 9.08. $C_{15}H_{10}Cl_2N_2O$ requires C, 59.04; H, 3.30; N, 9.18%.

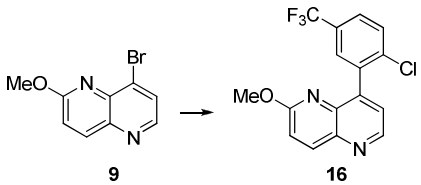
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.84 (d, *J* 4.5, 1H), 8.25 (d, *J* 9.0, 1H), 7.51 (d, *J* 4.5, 1H), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 1H), 7.13 (d, *J* 9.0, 1H), 3.83 (s, 3H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 162.1 (C_q), 147.4 (CH), 143.2 (C_q), 142.4 (C_q), 140.2 (CH), 139.6 (C_q), 137.9 (C_q), 132.1 (C_q), 132.0 (CH), 130.7 (CH), 129.4 (CH), 124.8 (CH), 53.8 (CH_3).

ν_{max}/cm^{-1} 1614m, 1580w, 1551w, 1491s, 1458w, 1435m, 1400m, 1386w, 1358w, 1337m, 1283m, 1259m, 1132w, 1118w, 1103w, 1080w, 1051m, 1028m, 988m, 925w, 856s, 837w, 804s, 729m.

m/*z* (EI) 271 (M^+-Cl, 64%), 269 (M^+-Cl, 100), 256 (17), 254 (50), 241 (5), 239 (8), 228 (11), 226 (34), 203 (5), 191 (9), 164 (9), 138 (4), 120 (5), 113 (5), 102 (6).

8-[2-Chloro-5-(trifluoromethyl)phenyl]-2-methoxy-1,5-naphthyridine (16):



Procedure 1: Bromo-2-methoxy-1,5-naphthyridine (**9**) (200 mg, 0.84 mmol), K_2CO_3 (231 mg, 1.67 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (27 mg, 0.03 mmol), 2-chloro-5-(trifluoromethyl)phenylboronic acid (282 mg, 1.26 mmol). The reaction was stopped after 45 min.

Product: 8-[2-Chloro-5-(trifluoromethyl)phenyl]-2-methoxy-1,5-naphthyridine (**16**) as colorless needles (255 mg, 0.75 mmol, 90%).

mp 107 – 108 °C (pentane).

Elemental Analysis: (Found: C, 56.58; H, 2.85; N, 8.10. $C_{16}H_{10}ClF_3N_2O$ requires C, 56.74; H, 2.98; N, 8.27%).

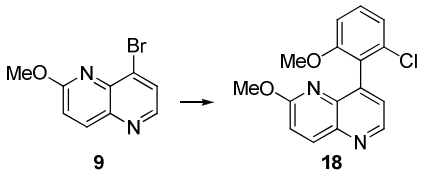
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.85 (d, *J* 4.5, 1H), 8.27 (d, *J* 9.0, 1H), 7.79 (br s, 1H), 7.72-7.64 (m, 2H), 7.58 (d, *J* 4.5, 1H), 7.14 (d, *J* 9.0, 1H), 3.79 (s, 3H).

^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 162.0 (C_q), 147.3 (CH), 142.4 (C_q), 142.3 (C_q), 140.3 (CH), 139.7 (C_q), 137.3 C_q), 137.0 (C_q), 130.1 (CH), 129.2 ($CF_3C\underline{CH}$, q, J_{CF} 3.8), 128.4 ($CF_3\underline{C_q}$, q, J_{CF} 32.9), 125.9 ($CF_3C\underline{CH}$, q, J_{CF} 3.7), 124.8 (CH), 124.0 (C_qF_3, q, J_{CF} 271.7), 116.6 (CH), 53.5 (CH_3).

ν_{max}/cm^{-1} 1609m, 1586w, 1506w, 1491s, 1472w, 1454w, 1439w, 1400m, 1363w, 1340s, 1327m, 1287s, 1273m, 1256w, 1175s, 1142m, 1115s, 1076s, 1053w, 1022m, 987m, 927w, 901m, 868m, 843w, 808m, 731m.

m/*z* (EI) 340 (M^++2, 1%), 338 (M^+, 4), 319 (3), 303 (M^+-Cl, 100), 288 (26), 273 (6), 260 (20), 254 (4), 226 (2).

8-(2-Chloro-6-methoxyphenyl)-2-methoxy-1,5-naphthyridine (18):



Procedure 1: Bromo-2-methoxy-1,5-naphthyridine **9** (200 mg, 0.84 mmol), K_2CO_3 (231 mg, 1.67 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (27 mg, 0.03 mmol), 2-chloro-6-methoxyphenylboronic acid (234 mg, 1.26 mmol).
Product: 8-(2-Chloro-6-methoxyphenyl)-2-methoxy-1,5-naphthyridine (**18**) as a viscous oil (214 mg, 0.71 mmol, 85%).

Elemental Analysis: Found: C, 64.02; H, 4.26; N, 9.29. $C_{16}H_{13}ClN_2O_2$ requires C, 63.90; H, 4.36; N, 9.31%.

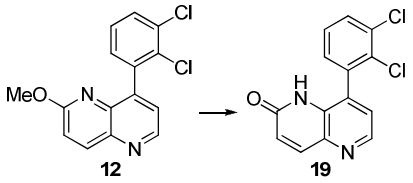
^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 8.81 (d, *J* 4.5, 1H), 8.23 (d, *J* 9.0, 1H), 7.46 (d, *J* 4.3, 1H), 7.37 (dd, *J* 8.2, 8.2, 1H), 7.15 (d, *J* 8.1, 1H), 7.10 (d, *J* 9.0, 1H), 6.69 (d, *J* 8.2, 1H), 3.74 (s, 3H), 3.67 (s, 3H).

^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 161.7 (C_q), 158.2 (C_q), 147.4 (CH), 142.1 (C_q), 141.5 (C_q), 140.3 (C_q), 140.1 (CH), 134.0 (C_q), 129.6 (CH), 129.2 (C_q), 125.8 (CH), 121.3 (CH), 116.2 (CH), 109.2 (CH), 55.9 (CH_3), 53.2 (CH_3).

ν_{max}/cm^{-1} 1612m, 1597m, 1573m, 1489s, 1462m, 1431m, 1398m, 1364w, 1335m, 1256s, 1186w, 1109w, 1078w, 1042s, 1018m, 924w, 849m, 806m, 777m, 746m, 733w.

m/*z* (EI) 271 (MH^+-OMe, 39), 269 (M^+-OMe, 93), 265 (M^+-Cl, 99), 254 (16), 250 (38), 235 (15), 221 (9), 207 (28), 192 (8), 179 (16), 169 (11), 133 (12), 125 (9), 111 (15), 97 (21).

8-(2,3-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (19):



Procedure 2: 8-(2,3-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (**12**) (120 mg, 0.40 mmol), conc HCl/H_2O (1:1) (3 mL).
Product: 8-(2,3-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**19**) as colorless needles (97 mg, 0.33 mmol, 84%).

mp 224 – 226 °C (t-BuOMe).

Elemental Analysis: Found: C, 57.65; H, 2.73; N, 9.55. $C_{14}H_8Cl_2N_2O$ requires C, 57.76; H, 2.77; N, 9.62%.

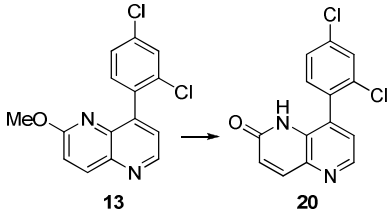
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 9.34 (br s, 1H, NH), 8.60 (d, *J* 4.7, 1H), 8.02 (d, *J* 9.8, 1H), 7.65 (dd, *J* 8.0, 1.5, 1H), 7.38 (dd, *J* 7.8, 7.8, 1H), 7.27 (d, *J* 4.7, 1H), 7.22 (dd, *J* 7.7, 1.5, 1H), 6.77 (d, *J* 9.8, 1H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 162.2 (C_q), 144.9 (CH), 142.3 (CH), 137.9 (C_q), 134.8 (C_q), 134.6 (C_q), 133.6 (C_q), 132.33 (C_q), 132.29 (C_q), 131.9 (CH), 129.4 (CH), 128.4 (CH), 126.2 (CH), 125.2 (CH).

ν_{max}/cm^{-1} 1658s, 1607m, 1581w, 1452w, 1425w, 1410m, 1383m, 1327w, 1300m, 1153w, 1122w, 1097w, 1074w, 1045m, 980m, 898w, 854m, 837w, 781m, 763m, 744w, 723m.

m/*z* (EI) 294 (M^++4, 5%), 292 (M^++2, 30), 290 (M^+, 45), 257 (32), 255 (100), 227 (16), 220 (11), 192 (19), 174 (5), 164 (12), 148 (3), 138 (6), 127 (9), 113 (15), 96 (9).

8-(2,4-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (20)



Procedure 2: 8-(2,4-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (**13**) (120 mg, 0.40 mmol), conc HCl/H_2O (1:1) (3 mL).
Product: 8-(2,4-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**20**) as colorless needles (102 mg, 0.35 mmol, 89%).

mp 172 – 175 °C (t-BuOMe).

Elemental Analysis: Found: C, 57.81; H, 2.75; N, 9.61. $C_{14}H_8Cl_2N_2O$ requires C, 57.76; H, 2.77; N, 9.62%.

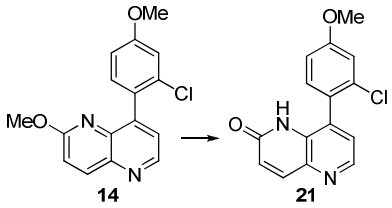
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 9.16 (br s, 1H, NH), 8.62 (d, *J* 4.5, 1H), 8.05 (d, *J* 9.8, 1H), 7.61 (d, *J* 1.9, 1H), 7.45 (dd, *J* 8.3, 1.9, 1H), 7.30-7.26 (m, 2H), 6.80 (d, *J* 9.8, 1H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 162.2 (C_q), 144.9 (CH), 142.3 (CH), 137.9 (C_q), 136.8 (C_q), 134.5 (C_q), 132.9 (C_q), 132.5 (C_q), 132.1 (CH), 131.0 (C_q), 130.6 (CH), 128.3 (CH), 126.2 (CH), 125.5 (CH).

ν_{max}/cm^{-1} 1613s, 1587m, 1491s, 1470m, 1429m, 1398m, 1360w, 1339s, 1285m, 1253m, 1103m, 1074w, 1055w, 1014m, 872w, 858s, 844m, 831w, 808s, 783m, 735m.

m/*z* (EI) 294 (M^++4, 4%), 292 (M^++2, 36), 290 (M^+, 51), 257 (32), 255 (100), 227 (21), 220 (4), 192 (23), 174 (7), 164 (11), 148 (4), 138 (10), 127 (11), 113 (16), 96 (9).

8-(2-Chloro-4-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (21):



Procedure 2: 8-(2-Chloro-4-methoxyphenyl)-2-methoxy-1,5-naphthyridine (**14**) (135 mg, 0.45 mmol), conc HCl/H_2O (1:1) (3 mL).
Product: 8-(2-Chloro-4-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (**21**) as light orange plates (109 mg, 0.38 mmol, 85%).

mp 191 – 192 °C (t-BuOMe).

Elemental Analysis: Found: C, 62.87; H, 3.77; N, 9.86. $C_{15}H_{11}ClN_2O_2$ requires C, 62.84; H, 3.87; N, 9.77%.

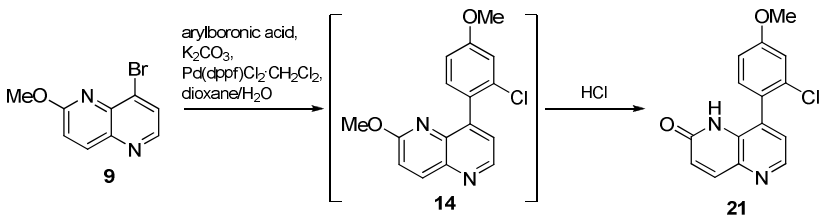
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.59 (d, *J* 4.7, 1H), 8.50 (br s, 1H, NH), 8.03 (d, *J* 9.8, 1H), 7.29 (d, *J* 4.7, 1H), 7.22 (d, *J* 8.5, 1H), 7.11 (br s, 1H), 6.97 (d, *J* 8.5, 1H), 6.84 (d, *J* 9.8, 1H), 3.89 (s, 3H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 161.8 (C_q), 161.5 (C_q), 11.9 (CH), 142.4 (CH), 137.8 (C_q), 134.3 (C_q), 133.6 (C_q), 132.7 (C_q), 131.8 (CH), 126.0 (CH), 125.9 (CH), 123.9 (C_q), 116.0 (CH), 114.3 (CH), 56.0 (CH_3).

ν_{max}/cm^{-1} 1654s, 1609m, 1568w, 1555w, 1499m, 1464w, 1452m, 1423w, 1381m, 1325w, 1290m, 1281w, 1223m, 1157w, 1115w, 1074w, 1043m, 1046m, 966w, 854s, 812m, 793w, 754m.

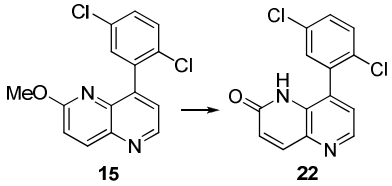
m/*z* (EI) 288 (M^++2, 20%), 286 (M^+, 55), 251 (M^+-Cl, 100), 236 (32), 221 (3), 208 (27), 180 (15), 179 (14), 153 (4), 126 (6), 104 (4), 97 (3), 90 (6).

8-(2-Chloro-4-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (21), *via* one-pot procedure 3:



Procedure 3: 8-Bromo-2-methoxy-1,5-naphthyridine **9** (100 mg, 0.42 mmol), K_2CO_3 (116 mg, 0.84 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (14 mg, 0.02 mmol), 2-chloro-4-methoxyphenylboronic acid (117 mg, 0.63 mmol), aq HCl (1.8 mL).
Product: 8-(2-Chloro-4-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (**21**) (96 mg, 0.34 mmol, 80%) as colorless needles, identical to that described above.

8-(2,5-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (22)



Procedure 2: 8-(2,5-Dichlorophenyl)-2-methoxy-1,5-naphthyridine (**15**) (120 mg, 0.40 mmol), conc HCl/H_2O (1:1) (3 mL).
Product: 8-(2,5-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**22**) as colorless needles (97 mg, 0.33 mmol, 85%).

mp 202 – 203 °C (t-BuOMe).

Elemental Analysis: Found: C, 57.80; H, 2.86; N, 9.71. $C_{14}H_8Cl_2N_2O$ requires C, 57.76; H, 2.77; N, 9.62%.

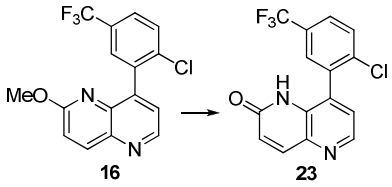
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.74 (br s, 1H, NH), 8.62 (d, *J* 4.7, 1H), 8.07 (d, *J* 10.0, 1H), 7.54 (d, *J* 8.7, 1H), 7.48 (dd, *J* 8.7, 2.5, 1H), 7.33 (d, *J* 2.5, 1H), 7.30 (d, *J* 4.7, 1H), 6.84 (d, *J* 10.0, 1H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 161.8 (C_q), 144.8 (CH), 142.2 (CH), 137.8 (C_q) 134.0 (C_q), 133.7 (C_q), 132.6 (C_q), 132.3 (C_q), 131.9 (CH), 131.5 (CH), 131.1 (CH), 126.4 (CH), 125.3 (CH).

ν_{max}/cm^{-1} 1651s, 1605s, 1581w, 1560w, 1470m, 1452m, 1416w, 1395w, 1375m, 1325m, 1141w, 1117m, 1099m, 1082w, 1049m, 976m, 918w, 851s, 826s, 793w, 772m, 727w, 706m.

m/*z* (EI) 294 (M^++4, 4%), 292 (M^++2, 27), 290 (M^+, 41), 257 (34), 255 (100), 227 (16), 220 (11), 201 (3), 192 (26), 164 (10), 138 (8), 113 (13), 96 (7).

8-[2-Chloro-5-(trifluoromethyl)phenyl]-1,5-naphthyrid-2(1*H*)-one (23):



Procedure 2: 8-[2-Chloro-5-(trifluoromethyl)phenyl]-2-methoxy-1,5-naphthyridine (**16**) (150 mg, 0.44 mmol), conc HCl/H_2O (1:1) (4 mL).
Product: 8-[2-Chloro-5-(trifluoromethyl)phenyl]-1,5-naphthyrid-2(1*H*)-one (**23**) as colorless needles (135 mg, 0.42 mmol, 94%).

mp 252 – 255 °C (t-BuOMe).

Elemental Analysis: (Found: C, 55.52; H, 2.52; N, 8.70. $C_{15}H_8ClF_3N_2O$ requires C, 55.49; H, 2.48; N, 8.63%).

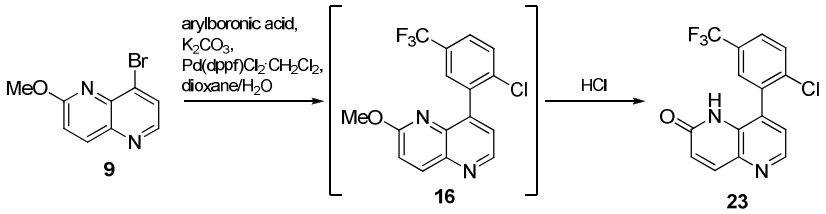
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 10.02 (br s, 1H, NH), 8.60 (d, *J* 4.7, 1H), 8.00 (d, *J* 9.8, 1H), 7.75 (dd, *J* 8.5, 2.1, 1H), 7.70 (d, *J* 8.5, 1H), 7.58 (d, *J* 2.1, 1H), 7.27 (d, *J* 4.7, 1H), 6.62 (d, *J* 9.8, 1H).

^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 162.1 (CH), 144.7 (CH), 142.2 (CH), 138.0 (C_q), 137.6 (C_q), 133.8 (C_q), 132.4 (C_q), 132.2 (C_q), 131.1 (CH), 129.9 ($CF_3\underline{C}_q$, q, J_{CF} 33.1), 128.4 ($CF_3C\underline{CH}$, q, J_{CF} 3.8), 127.6 ($CF_3C\underline{CH}$, q, J_{CF} 3.8), 125.7 (CH), 125.2 (CH), 123.5 (C_qF_3, q, J_{CF} 272.4).

ν_{max}/cm^{-1} 1657s, 1605m, 1583w, 1557w, 1398w, 1379m, 1339s, 1294m, 1263w, 1173m, 1150m, 1117s, 1084s, 1051m, 978w, 901m, 854m, 831m, 785m, 708m.

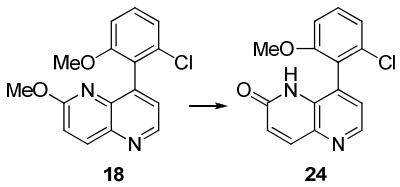
m/*z* (EI) 326 (M^++2, 5%), 324 (M^+, 17), 289 (M^+-Cl, 37), 269 (2), 261 (7), 241 (3), 215 (3), 192 (4), 169 (3).

8-[2-Chloro-5-(trifluoromethyl)phenyl]-1,5-naphthyrid-2(1*H*)-one (23), *via* one-pot procedure 3:



Procedure 3: 8-Bromo-2-methoxy-1,5-naphthyridine **9** (100 mg, 0.42 mmol), K_2CO_3 (116 mg, 0.84 mmol), Pd(dppf)Cl_2·CH_2Cl_2 (14 mg, 0.02 mmol), 2-chloro-5-(trifluoromethyl)phenylboronic acid (141 mg, 0.63 mmol), aq HCl (1.8 mL).
Product: 8-[2-Chloro-5-(trifluoromethyl)phenyl]-1,5-naphthyrid-2(1*H*)-one (**23**) (121 mg, 0.37 mmol, 89%) as colorless needles, identical to that described above.

8-(2-Chloro-4-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (24):



Procedure 2: 8-(2-Chloro-6-methoxyphenyl)-2-methoxy-1,5-naphthyridine (**18**) (200 mg, 0.67 mmol), conc HCl/H_2O (1:1) (4 mL).
Product: 8-(2-Chloro-6-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (**24**) as colorless needles (179 mg, 0.62 mmol, 94%).

mp 168 – 170 °C (t-BuOMe).

Elemental Analysis: Found: C, 62.90; H, 3.95; N, 9.66. $C_{15}H_{11}ClN_2O_2$ requires C, 62.84; H, 3.87; N, 9.77%.

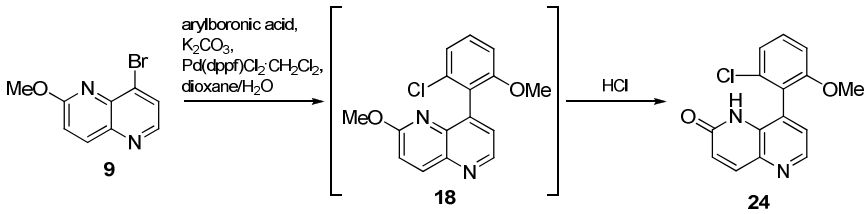
^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.60 (br d, *J* 4.2, 1H), 8.44 (br s, 1H, NH), 8.05 (d, *J* 9.8, 1H), 7.43 (dd, *J* 8.3, 8.3 1H), 7.27 (d, *J* 4.2, 1H), 7.18 (d, *J* 8.3, 1H), 6.96 (d, *J* 8.4, 1H), 6.83 (d, *J* 9.8, 1H), 3.72 (s, 3H).

^{13}C NMR (75 MHz; $CDCl_3$) δ_C 161.9 (C_q), 158.1 (C_q), 144.9 (CH), 142.4 (CH), 137.7 (C_q), 134.9 (C_q), 132.9 (C_q), 131.9 (CH), 130.7 (C_q), 126.6 (CH), 126.0 (CH), 122.6 (CH), 120.5 (C_q), 110.0 (CH), 56.3 (CH_3).

ν_{max}/cm^{-1} 1718w, 1674s, 1643w, 1614w, 1597w, 1572w, 1470w, 1446w, 1435m, 1382m, 1242w, 1213w, 1143m, 1114w, 1036m, 962w, 885w, 845m, 783m, 758m, 743w, 708w.

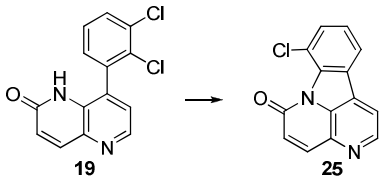
m/*z* (EI) 288 (M^++2, 31%), 286 (M^+, 100), 267 (9), 257 (31), 255 (84), 251 (56), 236 (53), 227 (11), 221 (34), 208 (24), 192 (21), 179 (179), 164 (6), 153 (9), 146 (12), 140 (6), 126 (17), 114 (13), 111 (6), 104 (9), 100 (7), 96 (10).

8-(2-Chloro-4-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (24), *via* one-pot procedure 3:



Procedure 3: 8-Bromo-2-methoxy-1,5-naphthyridine **9** (200 mg, 0.84 mmol), K_2CO_3 (231 mg, 1.67), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (28 mg, 0.03 mmol), 2-chloro-6-methoxyphenylboronic acid (234 mg, 1.26 mmol), aq HCl (3.6 mL).
Product: 8-(2-Chloro-6-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (**24**) (197 mg, 0.69 mmol, 82%) as colorless needles, identical to that described above.

8-Chlorocanthin-6-one (25):



Procedure 4: 8-(2,3-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**19**) (80 mg, 0.28 mmol), Cs_2CO_3 (179 mg, 0.55 mmol), CuI (5.3 mg, 0.03 mmol), dioxane (2 mL), DMEDA (4.8 mg, 0.06 mmol) and H_2O (10 mg).
Product: 8-Chlorocanthin-6-one (**25**) as tan colored needles (66 mg, 0.26 mmol, 94%).

mp (DSC) onset: 226.3 °C, peak max: 227.9 °C (acetone).

Elemental Analysis: Found: C, 66.12; H, 2.83; N 10.92. $C_{14}H_7ClN_2O$ requires C, 66.03; H, 2.77; N, 11.00%.

^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.76 (br d, *J* 4.9, 1H), .8.04-7.86 (m, 3H), 7.68 (d, *J* 7.9, 1H), 7.42 (dd, *J* 7.7, 7.7, 1H, H-10), 6.95 (d, *J* 9.7, 1H).

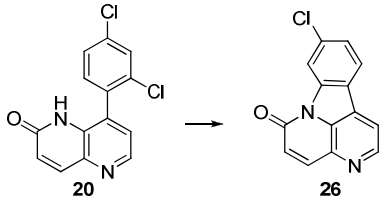
^{13}C NMR (75 MHz; $CDCl_3$) δ_C 158.1 (C_q), 145.4 (CH), 139.0 (CH), 137.3 (C_q), 137.1 (C_q), 133.6 (CH), 133.0 (C_q), 130.2 (CH), 129.7 (C_q), 128.2 (C_q), 126.7 (CH), 122.8 (C_q), 120.8 (CH), 155.6 (CH).

ν_{max}/cm^{-1} 1687s, 1647w, 1634m, 1597m, 1435s, 1395m, 1334m, 1281s, 1263w, 1242w, 1172m, 1059w, 1016m, 849m, 831m, 795s, 777m, 771w, 735m.

λ_{max}(DCM)/nm 230 (log ε 4.38), inf 247 (4.20), inf 256 (4.19), 267 (4.10), inf 275 (4.10), 301 (4.05), 365 (4.15), 382 (4.08).

m/*z* (EI) 256 (M^++2, 36%), 254 (M^+, 100), 228 (26), 226 (71), 201 (5), 191 (20), 190 (5), 164 (20), 148 (6), 138 (11), 113 (15), 100 (8).

9-Chlorocanthin-6-one (26):



Procedure 4: 8-(2,4-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**20**) (90 mg, 0.31 mmol), Cs_2CO_3 (201 mg, 0.62 mmol), CuI (6 mg, 0.03 mmol), dioxane (2 mL), DMEDA (5.4 mg, 0.06 mmol) and H_2O (11 mg).
Product: 9-Chlorocanthin-6-one (**26**) as pink needles (77 mg, 0.30 mmol, 98%).

mp (DSC) onset: 245.3 °C, peak max: 246.2 °C (acetone).

Elemental Analysis: Found: C, 65.92; H, 2.71; N, 10.97. $C_{14}H_7ClN_2O$ requires C, 66.03; H, 2.77; N, 11.00%).

^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 8.81 (d, *J* 5.1, 1H), 8.67 (d, *J* 1.9, 1H, H-8), 8.07 (d, *J* 8.4, 1H, H-11), 8.02 (d, *J* 9.8, 1H), 7.96 (d, *J* 5.1, 1H), 7.52 (dd, *J* 8.4, 1.9, 1H, H-10), 6.94 (d, *J* 9.8, 1H).

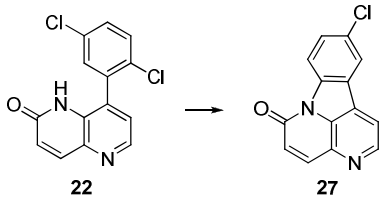
^{13}C NMR (75 MHz; $CDCl_3$) δ_C 159.7 (C_q), 146.4 (CH), 140.3 (CH), 140.2 (C_q), 137.3 (C_q), 136.7 (C_q), 132.7 (C_q), 129.9 (C_q), 129.2 (CH), 126.6 (CH), 123.8 (CH), 123.3 (C_q), 118.1 (CH), 116.8 (CH).

ν_{max}/cm^{-1} 1672s, 1655m, 1635m, 1441m, 1415m, 1389w, 1329m, 1312m, 1256w, 1190w, 1063m, 854s, 818s, 800s.

λ_{max}(DCM)/nm 230 (log ε 4.38), 262 (4.30), inf 294(3.98), 303 (4.01), inf 347 (3.98), 363 (4.18), inf 371 (3.91), 381 (4.15).

m/*z* (EI) 256 (M^++2, 31%), 254 (M^+, 100), 228 (15), 226 (42), 191 (14), 164 (13), 138 (7), 127 (5), 113 (12), 100 (7).

10-Chlorocanthin-6-one (27):



Procedure 4: 8-(2,5-Dichlorophenyl)-1,5-naphthyrid-2(1*H*)-one (**22**) (90 mg, 0.31 mmol), Cs_2CO_3 (201 mg, 0.62 mmol), CuI (6 mg, 0.03 mmol), dioxane (2 mL), DMEDA (5.4 mg, 0.06 mmol) and H_2O (11 mg).
Product: 10-Chlorocanthin-6-one (**27**) as pale pink needles (76 mg, 0.30 mmol, 96%).

mp (DSC) onset: 264.3 °C, peak max: 265.1 °C (acetone).

Elemental Analysis: Found: C, 65.99; H, 2.67; N, 10.92. $C_{14}H_7ClN_2O$ requires C, 66.03; H, 2.77; N, 11.00%.

^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.85 (br d, *J* 5.0, 1H), 8.60 (d, *J* 8.7, 1H), 8.08 (d, *J* 2.1, 1H, H-11), 8.05 (d, *J* 9.8, 1H), 7.95 (d, *J* 5.0, 1H), 7.66 (dd, *J* 8.7, 2.1, 1H, H-9), 6.99 (d, *J* 9.8, 1H).

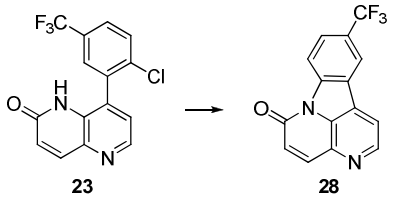
^{13}C NMR (75 MHz; $CDCl_3$) δ_C 159.4 (C_q), 145.9 (CH), 139.7 (CH), 137.9 (C_q), 136.4 (C_q), 132.5 (C_q), 131.7 (C_q), 131.2 (CH), 129.5 (C_q), 129.3 (CH), 125.9 (C_q), 122.9 (CH), 118.4 (CH), 116.8 (CH).

ν_{max}/cm^{-1} 1667s, 1634m, 1619w, 1591w, 1462m, 1441m, 1412w, 1392m, 1331s, 1292m, 1119w, 1070w, 1055s, 1005w, 966m, 897w, 849s, 828m, 814s.

λ_{max}(DCM)/nm 230 (log ε 4.45), 265 (4.30), 272 (4.33), inf 290 (4.04), 299 (3.99), inf 349 (4.03), 365 (4.29), 383 (4.30).

m/*z* (EI) 256 (M^++2, 17%), 254 (M^+, 47), 228 (12), 226 (38), 200 (3), 191 (9), 164 (10), 138 (4), 127 (4), 113 (11), 99 (4).

10-(Trifluoromethyl)canthin-6-one (28):



23 **28**

Procedure 4: 8-[2-Chloro-5-(trifluoromethyl)phenyl]-1,5-naphthyrid-2(1*H*)-one (**23**) (120 mg, 0.37 mmol), Cs_2CO_3 (241 mg, 0.74 mmol), CuI (7.1 mg, 0.04 mmol), dioxane (2.5 mL), DMEDA (6.5 mg, 0.07 mmol) and H_2O (13 mg).
Product 10-(Trifluoromethyl)canthin-6-one (**28**) as colorless needles (109 mg, 0.36 mmol, 98%).

mp (DSC) onset: 209.4 °C, peak max: 209.8 °C (acetone)

Elemental Analysis: (Found: C, 62.61; H, 2.40; N, 9.67. $C_{15}H_7F_3N_2O$ requires C, 62.51; H, 2.45; N, 9.72%)

^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.89 (br d, *J* 4.8, 1H, H-9), 8.79 (d, *J* 8.7, 1H), 8.40 (br s, 1H, H-11), 8.08 (d, *J* 10.0, 1H), 8.03 (d, *J* 4.9, 1H), 7.97 (dd, *J* 8.7, 1.2, 1H, H-8), 7.01 (d, *J* 10.0, 1H).

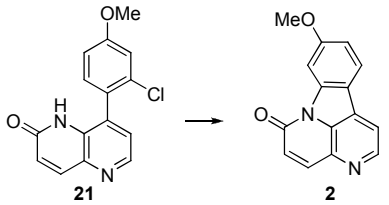
^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 159.2 (C_q), 146.2 (CH), 140.9 (C_q), 140.1 (CH), 136.7 (C_q), 132.5 (C_q), 128.7 (CH), 127.5 ($CF_3C\underline{C}H$, q, J_{CF} 3.7), 127.5 ($CF_3\underline{C}_q$, q, J_{CF} 32.9), 124.7 (C_q), 124.2 (C_qF_3, q, J_{CF} 272.2), 120.1 ($CF_3C\underline{C}H$, q, J_{CF} 3.8), 117.2 (CH), 116.6 (CH).

ν_{max}/cm^{-1} 1684m, 1641w, 1418s, 1329m, 1288m, 1271m, 1236s, 1153m, 1142w, 1109s, 1047m, 1003w, 964m, 931m, 901s, 853m, 833m.

λ_{max}(DCM)/nm 230 (log ε 4.34), 257 (4.19), inf 267 (4.07), 287 (4.01), inf 296 (4.01), 346 (4.01), 361 (4.27), 371 (4.02), 379 (4.28)

m/*z* (EI) 289 (M^++1, 18%), 288 (M^+, 100), 269 (9), 260 (94), 241 (14), 233 (5), 210 (13), 191 (8), 165 (13), 164 (12), 119 (13), 105 (24).

9-Methoxycanthin-6-one (2):



Procedure 4: 8-(2-Chloro-4-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (**21**) (100 mg, 0.35 mmol), Cs_2CO_3 (227 mg, 0.70 mmol), CuI (7 mg, 0.04 mmol), dioxane (2.2 mL), DMEDA (6 mg, 0.07 mmol) and H_2O (13 mg).
Product: 9-Methoxycanthin-6-one (**2**) as light yellow needles (85 mg, 0.34 mmol, 97%).

mp (DSC) onset: 180.1 °C, peak max: 181.6 °C (acetone) Lit.: 181 – 183 °C (Kardono, L. B. S.; Angerhofer, C. K.; Tsauri, S.; Padmawinata, K.; Pezzuto, J. M.; Kinghorn, D. *J. Nat. Prod.* **1991**, *54*, 1360.), 178 – 180 °C (Giesbrecht, A. M.; Gottlieb, H. E.; Gottlieb, O. R.; Goulart, M. O. F.; De Lama, R. A.; Santana, A. E. G. *Phytochemistry*, **1980**, *19*, 313.).

Elemental Analysis: Found: C, 72.03; H, 3.92; N, 11.08. $C_{15}H_{10}N_2O_2$ requires C, 71.99; H, 4.03; N, 11.19%.

^{1}H NMR (300 MHz; $CDCl_3$) δ_H 8.74 (d, *J* 5.1, 1H), 8.16 (d, *J* 2.4, 1H, H-8), 8.01 (d, *J* 9.8, 1H), 7.92 (d, *J* 8.7, 1H), 7.82 (d, *J* 5.1, 1H), 7.05 (dd, *J* 8.7, 2.4, 1H, H-10), 6.94 (d, *J* 9.8, 1H), 3.98 (s, 3H).

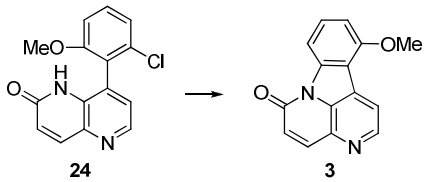
^{13}C NMR (75 MHz; $CDCl_3$) δ_C 162.7 (C_q), 159.8 (C_q), 145.8 (CH), 141.5 (C_q), 139.8 (CH), 135.6 (C_q), 132.4 (C_q), 130.7 (C_q), 128.8 (CH), 123.6 (CH), 117.3 (C_q), 115.7 (CH), 114.4 (CH), 101.4 (CH), 56.1 (CH_3).

ν_{max}/cm^{-1} 1667s, 1632s, 1609m, 1493m, 1452m, 1437m, 1422m, 1391w, 1331m, 1310w, 1275s, 1223m, 1152m, 1059w, 1030m, 916w, 840m, 831m, 814s, 750w.

λ_{max}(DCM)/nm 230 (log ε 4.24), 263 (4.30), 272 (4.47), inf 309 (4.05), 349 (4.11), 363 (4.10).

m/*z* (EI) 251 (M^++1, 24%), 250 (M^+, 100), 235 (10), 221 (35), 207 (39), 192 (16), 179 (41), 169 (38), 153 (19), 149 (16), 147 (23), 125 (14), 119 (13), 100 (12).

Amaroridine (3):



Procedure 4: 8-(2-Chloro-6-methoxyphenyl)-1,5-naphthyrid-2(1*H*)-one (**24**) (150 mg, 0.52 mmol), Cs_2CO_3 (341 mg, 1.05 mmol), CuI (10 mg, 0.05 mmol), dioxane (3 mL), DMEDA (9.3 mg, 0.11 mmol) and H_2O (19 mg).
Product: Amaroridine (**3**) as light yellow needles (119 mg, 0.48 mmol, 91%).

mp (DSC) onset: 229.6 °C, peak max: 230.5 °C (acetone) Lit.: 237 – 238 °C (Clarke, P. J.; Jewers, K.; Jones, H. F. *J. Chem. Soc.*, *Perkin Trans. 1*, **1980**, 1614.).

Elemental Analysis: Found: C, 71.92; H, 4.00; N, 11.15. $C_{15}H_{10}N_2O_2$ requires C, 71.99; H, 4.03; N, 11.19%.

^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 8.75 (d, *J* 4.9, 1H), 8.17 (d, *J* 8.1, 1H), 8.05 (d, *J* 4.9, 1H), 7.99 (d, *J* 9.8, 1H), 7.64 (dd, *J* 8.2, 8.2, 1H, H-9), 7.01 (d, *J* 9.8, 1H), 6.90 (d, *J* 9.8, 1H), 4.10 (s, 3H).

^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 159.2 (C_q), 156.7 (C_q), 145.7 (CH), 140.1 (C_q), 139.5 (CH), 135.3 (C_q), 131.8 (CH), 131.3 (C_q), 128.7 (C_q), 127.9 (CH), 118.0 (CH), 113.1 (C_q), 109.0 (CH), 106.8 (CH), 55.5 (CH_3).

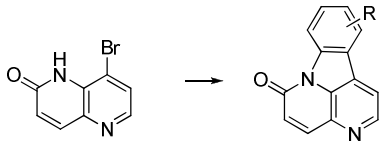
ν_{max}/cm^{-1} 1692s, 1632m, 1609m, 1589w, 1503m, 1462w, 1445m, 1431m, 1398w, 1352m, 1331m, 1271s, 1140s, 1130m, 1121w, 1072m, 1007w, 866w, 849m, 783s, 739m.

λ_{max}(DCM)/nm 235 (log ε 4.22), 246 (4.22), inf 252 (4.21), 316 (4.01), inf 326 (4.01), 375 (4.10), 398 (4.01).

m/*z* (EI) 251 (M^++1, 17%), 250 (M^+, 100), 235 (11), 222 (13), 207 (32), 192 (3), 179 (24), 164 (2), 153 (7), 125 (10), 110 (5), 96 (6).

2.2. Second generation approach: One-pot Suzuki-Miyaura coupling and amidation reaction

2.2.1. General procedures

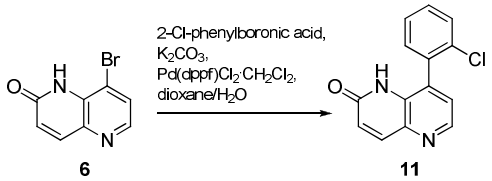


Procedure 5: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), K_2CO_3 (184 mg, 1.33 mmol), arylboronic acid (1.1 equiv) and Pd(dppf)Cl_2·CH_2Cl_2 (7.4 mg, 0.01 mmol) were dissolved in a mixture of dioxane and water (3:1) (0.7 mL). The mixture was immediately heated to reflux (preheated oil bath) and stirred for 30 min before a preformed deep blue complex of CuI (4.2 mg, 0.02 mmol) and DMEDA (4 mg, 0.04 mmol) in dioxane/water (3:1) (0.4 mL) was added to the refluxing mixture. The mixture was refluxed another 15 min before it was allowed to cool to rt. The reaction mixture was diluted with EtOAc and dried (Na_2SO_4). Dry flash chromatography of the solution (EtOAc) gave the canthin-6-ones as colorless to slightly yellow solids (92 – 95% yield), which could be recrystallized (acetone) to give colorless needles.

Procedure 6: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), K_2CO_3 (184 mg, 1.33 mmol), arylboronic acid (2 equiv) and Pd(dppf)Cl_2·CH_2Cl_2 (18 mg, 0.02 mmol) were dissolved in a mixture of dioxane and water (3:1) (0.7 mL). The mixture was immediately heated to reflux (preheated oil bath) and stirred for 80 min before a preformed deep blue complex of CuI (8.4 mg, 0.04 mmol) and DMEDA (8 mg, 0.09 mmol) in dioxane/water (3:1) (0.6 mL) was added to the refluxing mixture. The mixture was refluxed another 40 min before it was allowed to cool to rt. The reaction mixture was diluted with EtOAc and dried (Na_2SO_4). Dry flash chromatography of the solution (EtOAc) gave the canthin-6-ones as colorless to slightly yellow solids (70 – 92% yield), which could be recrystallized (acetone) to give colorless needles.

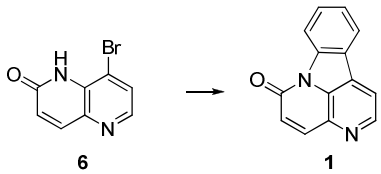
2.2.2. Preparation and characterization of compounds **1**, **2**, **11**, **25-31**

8-(2-Chlorophenyl)-1,5-naphthyrid-2(1*H*)-one (11):



8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (50 mg, 0.22 mmol), K_2CO_3 (92 mg, 0.67 mmol), 2-chlorophenylboronic acid (82 mg, 0.27 mmol) and $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (4 mg, 0.01 mmol) were dissolved in a mixture of dioxane and water (3:1) (0.5 mL). The mixture was immediately heated to reflux (preheated oil bath) and stirred for 30 min before it was allowed to cool to rt. It was diluted (CH_2Cl_2), dried (Na_2SO_4), filtered and adsorbed onto silica gel. Dry flash chromatography (t-BuOMe) gave **11** (55 mg, 0.21 mmol, 96%) as colorless needles, identical to that described above.

Canthin-6-one (1):

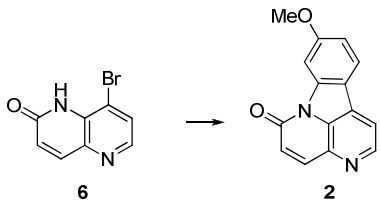


Procedure 5: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2-chlorophenylboronic acid (83 mg, 0.53 mmol).
Product: Canthin-6-one (**1**) as light yellow needles (93 mg, 0.42 mmol, 95%), identical to that described above.

Variations of Procedure 1:

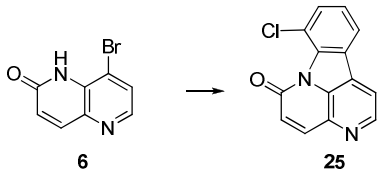
-Addition of all reagents at the beginning of the reaction gave no product and 8-bromo-1,5-naphthyrid-2(1*H*)-one (**6**) was recovered.
-Addition of CuI at the beginning of the reaction with the Suzuki-Miyaura reagents followed after 30 min by the addition of DMEDA gave after a further 30 min canthin-6-one (**1**) in comparable high yields.
-Without the addition of DMEDA only a trace of canthinone **1** was observed after refluxing the reaction for 15 h.

9-Methoxycanthin-6-one (2):



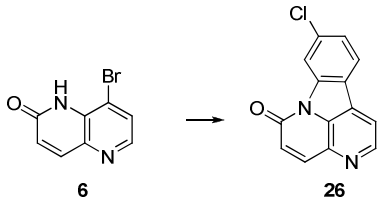
Procedure 6: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2-chloro-4-methoxyphenylboronic acid (166 mg, 0.89 mmol).
Product: 9-Methoxycanthin-6-one (**2**) as light yellow needles (103 mg, 0.41 mmol, 92%), identical to that described above.

8-Chlorocanthin-6-one (25):



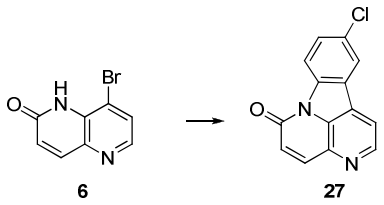
Procedure 6: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2,3-dichlorophenylboronic acid (169 mg, 0.89 mmol).
Product: 8-Chlorocanthin-6-one (**25**) as tan colored needles (92 mg, 0.36 mmol, 82%), identical to that described above.

9-Chlorocanthin-6-one (26):



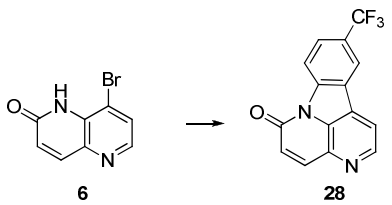
Procedure 6: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2,4-dichlorophenylboronic acid (169 mg, 0.89 mmol).
Product: 9-Chlorocanthin-6-one (**26**) as pink needles (93 mg, 0.36 mmol, 82%), identical to that described above.

10-Chlorocanthin-6-one (27):



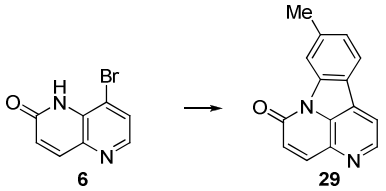
Procedure 6: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2,5-dichlorophenylboronic acid (169 mg, 0.89 mmol).
Product: 10-Chlorocanthin-6-one (**27**) as pale pink needles (87 mg, 0.34 mmol, 77%), identical to that described above.

10-(Trifluoromethyl)canthin-6-one (28):



Procedure 6: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2-chloro-5-(trifluromethyl)phenylboronic acid (199 mg, 0.89 mmol).
Products: 10-(Trifluoromethyl)canthin-6-one (**28**) as colorless needles (89 mg, 0.31 mmol, 71%) and unreacted **6** (12 mg, 0.05 mmol, 12%), identical to that described above.

9-Methylcanthin-6-one (29):



Procedure 5: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2-chloro-4-methylphenylboronic acid (91 mg, 0.53 mmol).
Product: 4-Methylcanthin-6-one (**29**) as light tan needles (94 mg, 0.40 mmol, 92%).

mp (DSC) onset: 158.8 °C, peak max: 159.5 °C (acetone).

Elemental Analysis: Found: C, 77.03; H, 4.36; N, 11.89. $C_{15}H_{10}N_2O$ requires C, 76.91; H, 4.30; N, 11.96%.

^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 8.76 (d, *J* 5.1, 1H), 8.44 (br s, 1H, H-8), 7.98 (d, *J* 7.8, 1H), 7.97 (d, *J* 9.8, 1H), 7.90 (d, *J* 5.1, 1H), 7.34 (dd, *J* 7.9, 0.8, 1H), 6.90 (d, *J* 9.8, 1H), 2.57 (s, 3H).

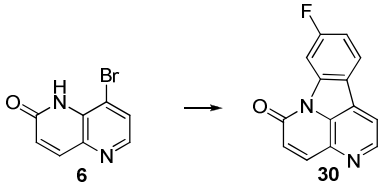
^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 159.2 (C_q), 145.5 (CH), 141.6 (C_q), 139.6 (C_q), 139.4 (C_q), 135.9 (C_q), 131.9 (C_q), 129.8 (C_q), 128.3 (CH), 126.4 (CH), 122.0 (CH), 121.7 (C_q), 116.9 (CH), 115.7 (CH), 21.7 (CH_3).

ν_{max}/cm^{-1} 1684s, 1668m, 1636m, 11450m, 1418w, 1392w, 1335m, 1312m, 1246w, 1150m, 1059m, 997w, 912w, 874m, 853m, 837s, 810s, 787m, 720m.

λ_{max}(DCM)/nm 232 (log ε 4.42), 261 (342), 270 (4.39), inf 295 (4.10), 307 (4.15), inf 347 (4.17), 363 (4.34), 3.82 (4.27).

m/*z* (EI) 235 (M^++1, 19%), 234 (M^+, 100), 206 (49), 179 (9), 151 (6), 117 (6), 103 (8).

9-Fluorocanthin-6-one (30):



Procedure 6: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2-chloro-4-fluorophenylboronic acid (155 mg, 0.89 mmol).
Product: 9-Fluorocanthin-6-one (**30**) as colorless needles (93 mg, 0.39 mmol, 88%).

mp (DSC) onset: 193.3 °C, peak max: 194.8 °C (acetone) Lit.: 155 – 158 °C (Soriano-Agaton, F.; Lagoutte, D.; Poupon, E.; Roblot, F.; Fournet A.; Gantier, J.-C.; Hocquemiller, R. *J. Nat. Prod.* **2005**, *68*, 1581.).

Elemental Analysis: (Found: C, 70.65; H, 2.83; N, 11.70. $C_{14}H_7FN_2O$ requires C, 70.59; H, 2.96; N, 11.76%).

^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 8.76 (d, *J* 5.1, 1H), 8.29 (dd, $^3J_{HF}$ 9.3, $^4J_{HH}$ 2.1, 1H, H-8), 8.05 (dd, $^3J_{HH}$ 8.6, $^4J_{HF}$ 5.3, 1H, H-11), 7.98 (d, *J* 9.8, 1H), 7.89 (d, *J* 5.1, 1H), 7.24 (dd, $^3J_{HF}$ 8.9, $^3J_{HH}$ 8.9, $^4J_{HH}$ 2.3, 1H, H-10), 6.89 (d, *J* 9.8, 1H).

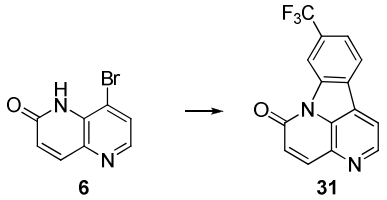
^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 165.5 (C_q), 160.6 (C_qF, d, J_{CF} 241.4), 145.8 (CH), 139.9 (C_q), 139.8 (CH), 135.9 (C_q), 132.3 (C_q), 129.03 (C_q), 128.2 (CH), 123.7 (CFCHCH, J_{CF} 10.4), 120.5 (CFCHC$_q$, J_{CF} 2.2), 115.9 (CH), 113.1 (CFCH, J_{CF} 24.7), 104.5 (CFCH, J_{CF} 28.5).

ν_{max}/cm^{-1} 1676s, 1635m, 1557w, 1539w, 1489m, 1462m, 1447s, 1419w, 1390w, 1339m, 1307m, 1296w, 1261m, 1244m, 1204w, 1188w, 1157w, 1138s, 1078w, 1051w, 991m, 958w, 941w, 854s, 831s, 754w, 731w, 702m.

λ_{max}(DCM)/nm 230 (log ε 4.30), 260 (4.39), inf 292 (4.03), 300 (4.06), inf 343 (4.12), 360 (4.30), 369 (4.05), 378 (4.23).

m/*z* (EI) 239 (M^++1, 14%), 238 (M^+, 100), 210 (65), 182 (14), 157 (9), 132 (6), 131 (6), 119 (7), 105 (9), 91 (9).

9-(Trifluoromethyl)canthin-6-one (31):



6 31

Procedure 6: 8-Bromo-1,5-naphthyrid-2(1*H*)-one (**6**) (100 mg, 0.44 mmol), 2-chloro-4-(trifluoromethyl)phenylboronic acid (199 mg, 0.89 mmol).
Product: 9-(Trifluoromethyl)canthin-6-one (**31**) as colorless needles (100 mg, 0.35 mmol, 78%).

mp (DSC) onset: 208.7 °C, peak max: 209.1 °C (acetone).

Elemental Analysis: (Found: C, 62.66; H, 2.40; N, 9.74. $C_{15}H_7F_3N_2O$ requires C, 62.51; H, 2.45; N, 9.72%).

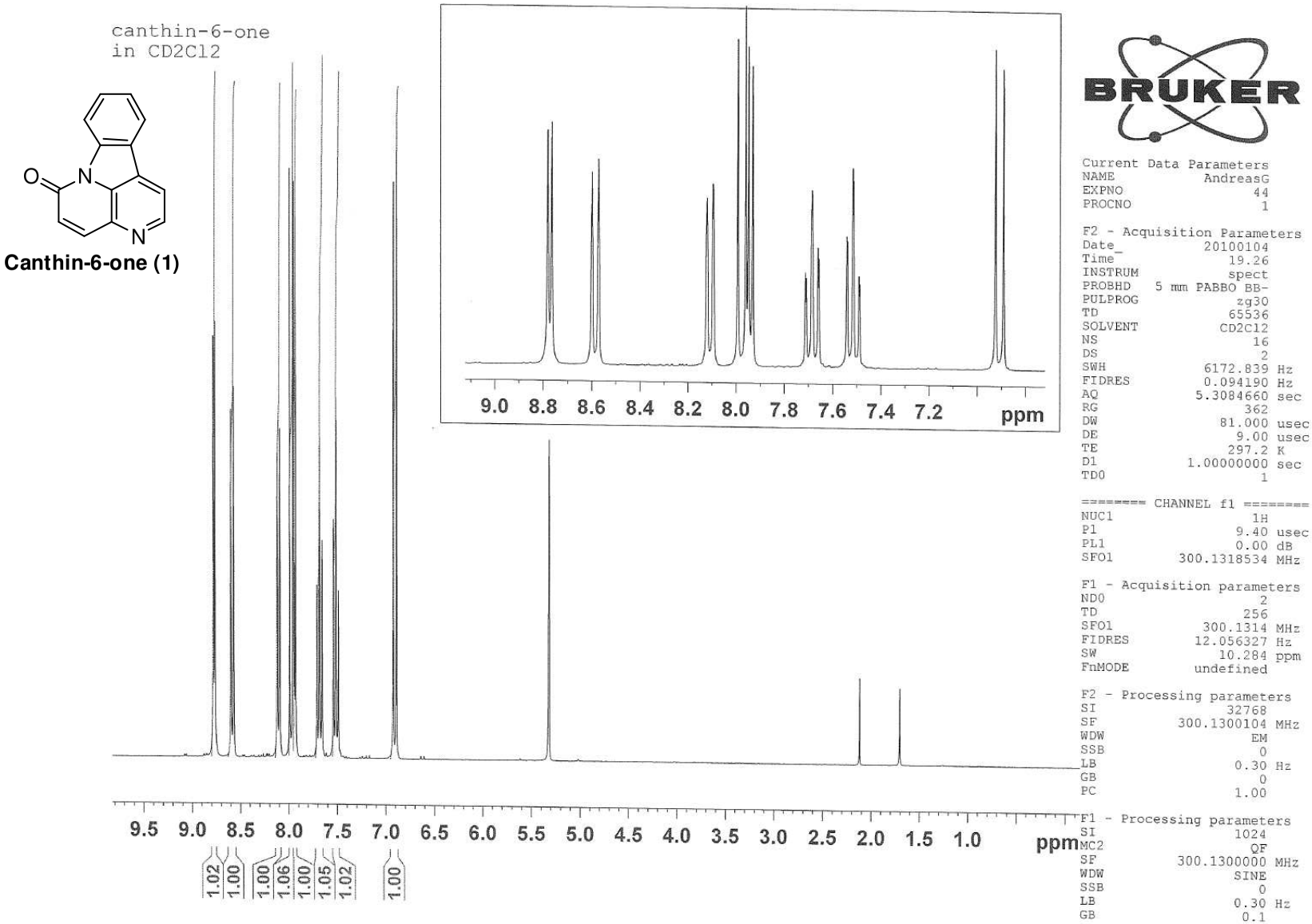
^{1}H NMR (300 MHz; CD_2Cl_2) δ_H 8.93 (s, 1H, H-8), 8.86 (d, *J* 5.1, 1H), 8.28 (d, *J* 8.1, 1H), 8.05 (d, *J* 9.9, 1H), 8.04 (d, *J* 5.1, 1H), 7.81 (d, *J* 8.1, 1H), 6.97 (d, *J* 9.9, 1H).

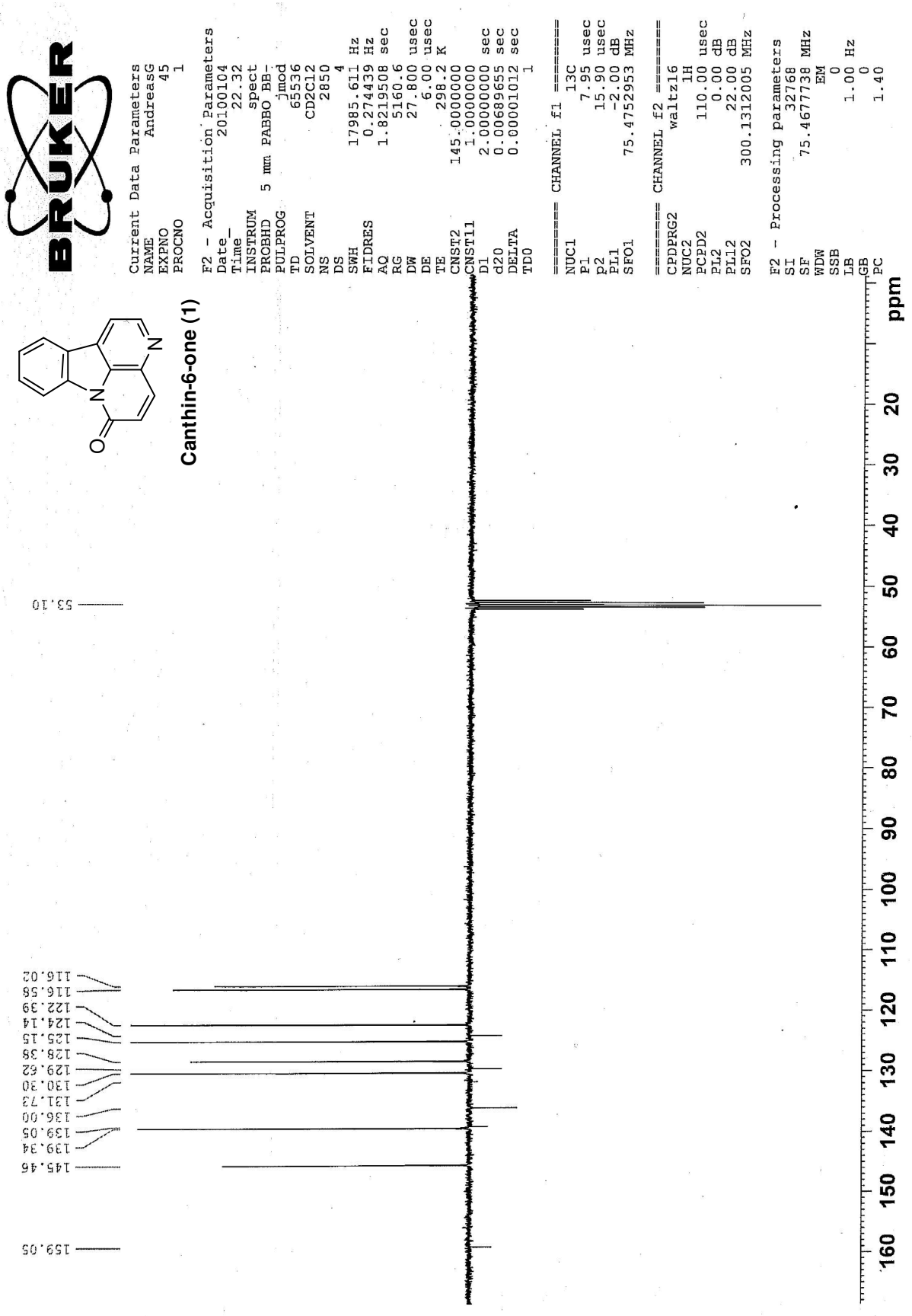
^{13}C NMR (75 MHz; CD_2Cl_2) δ_C 159.2 (C_q), 146.1 (CH), 140.0 (CH), 138.7 (C_q), 136.7 (C_q), 132.6 (C_q), 132.0 (CF_3C_q, q, J_{CF} 32.7), 128.8 (CH), 128.6 (C_q), 127.4 (C_q), 124.0 (C_qF_3, q, J_{CF} 272.7), 123.2 (CH), 122.3 (CF_3CCH, q, J_{CF} 4.0), 116.9 (CH), 114.2 (CF_3CCH, q, J_{CF} 4.1).

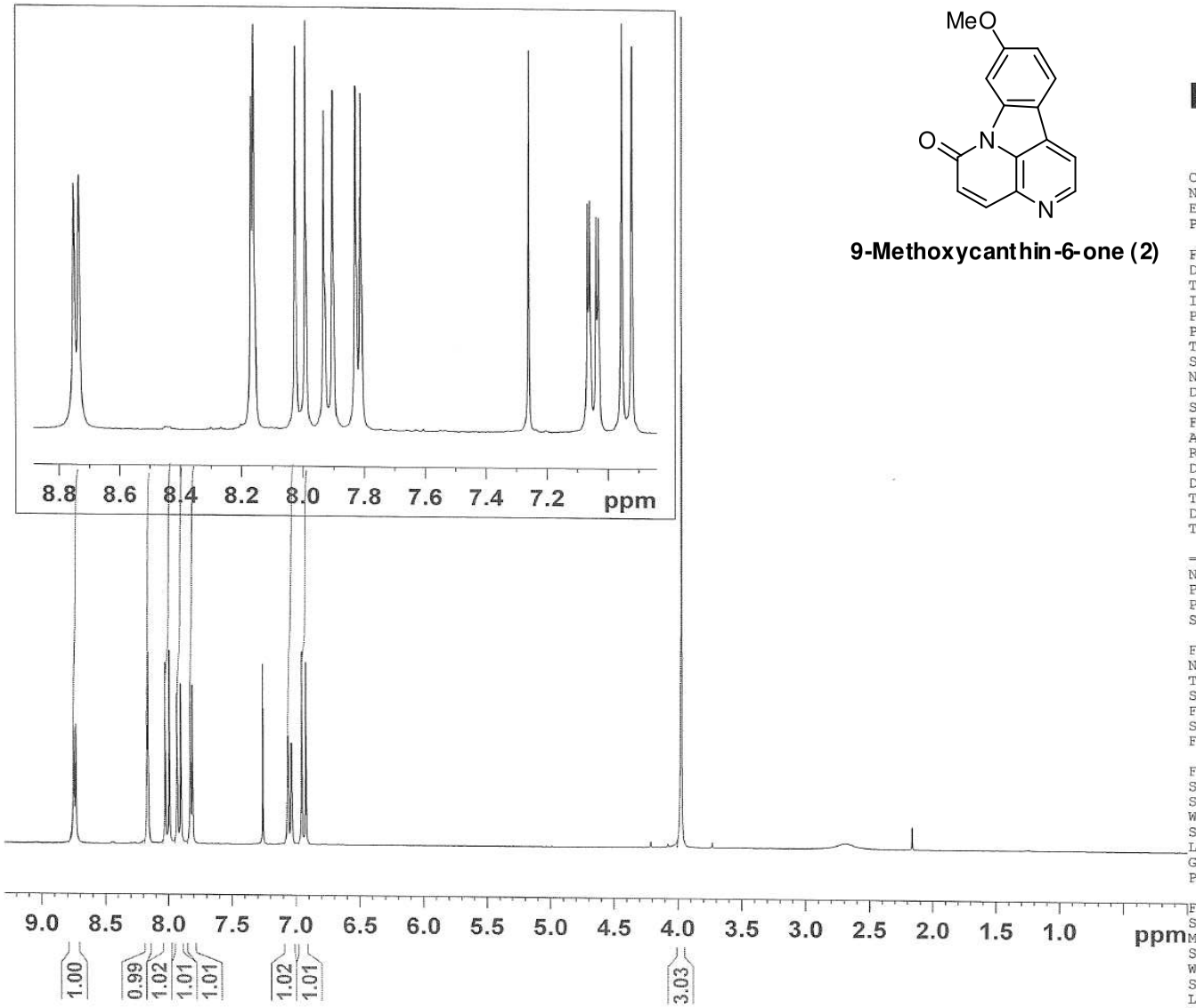
ν_{max}/cm^{-1} 1678s, 1641w, 1608w, 1466w, 1449w, 1425m, 1398m, 1339m, 1306m, 1263w, 1240m, 1175m, 1152s, 1126m, 1111s, 1055m, 906w, 891m, 849m, 835m, 817m, 727m.

λ_{max}(DCM)/nm 231 (log ε 4.39), inf 262 (4.13), 269 (4.15), 286 (4.06), inf 295 (4.04), inf 347 (4.05), 363 (4.33), inf 373 (4.10), 381 (4.36).

m/*z* (EI) 289 (M^++1, 18%), 288 (M^+, 100), 269 (5), 260 (72), 241 (4), 226 (17), 224 (17), 210 (5), 207 (4), 196 (7), 191 (6), 165 (7), 144 (8), 130 (9), 117 (18).


canthin-6-one
in CD2Cl2
Canthin-6-one (1)
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.02 1.00 1.00 1.06 1.00 1.05 1.02 1.00
BRUKER
Current Data Parameters
NAME AndreasG
EXPNO 44
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100104
Time 19.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 362
DW 81.000 usec
DE 9.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300104 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1


Canthin-6-one (1)
Current Data Parameters
NAME Andreasg
EXPNO 45
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100104
Time 22.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2C12
NS 2850
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 5160.6
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677738 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
159.05
145.46
139.34
139.05
136.00
131.73
130.30
129.62
128.38
125.15
124.14
122.39
116.56
116.02
53.10
ppm



9-Methoxycanthin-6-one (2)

BRUKER

```
Current Data Parameters
NAME                 Andreas G
EXPNO                      165
PROCNO                       1

F2 - Acquisition Parameters
Date_               20091117
Time                    0.20
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                  5.3084660 sec
RG                      456.1
DW                     81.000 usec
DE                      9.00 usec
TE                     296.2 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                      9.40 usec
PL1                     0.00 dB
SFO1           300.1318534 MHz

F1 - Acquisition parameters
ND0                          2
TD                         256
SFO1                300.1314 MHz
FIDRES             12.056327 Hz
SW                     10.284 ppm
FnMODE               undefined

F2 - Processing parameters
SI                       32768
SF             300.1300062 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

F1 - Processing parameters
SI                        1024
MC2                         QF
SF             300.1300000 MHz
WDW                       SINE
SSB                          0
LB                        0.30 Hz
GB                         0.1
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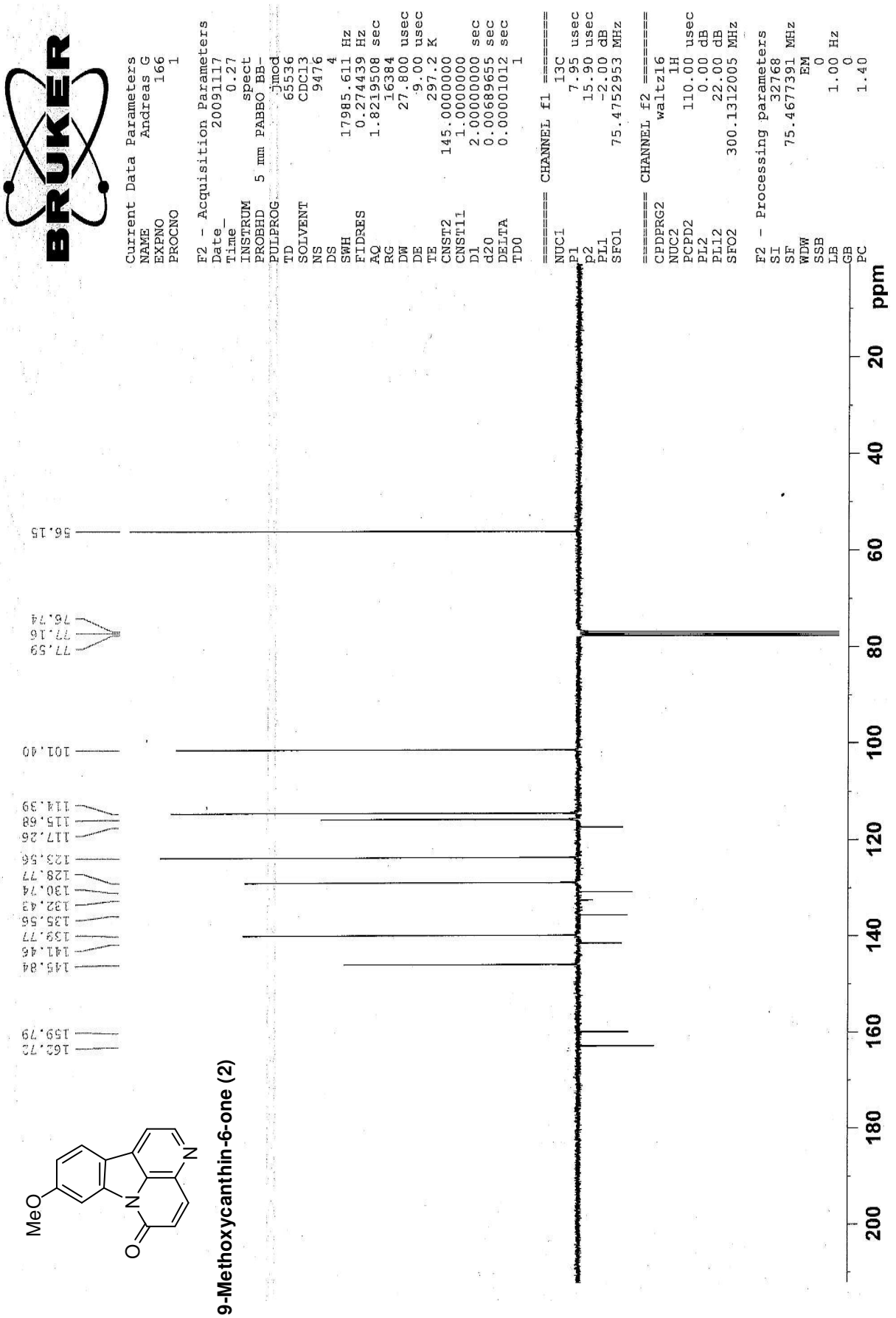
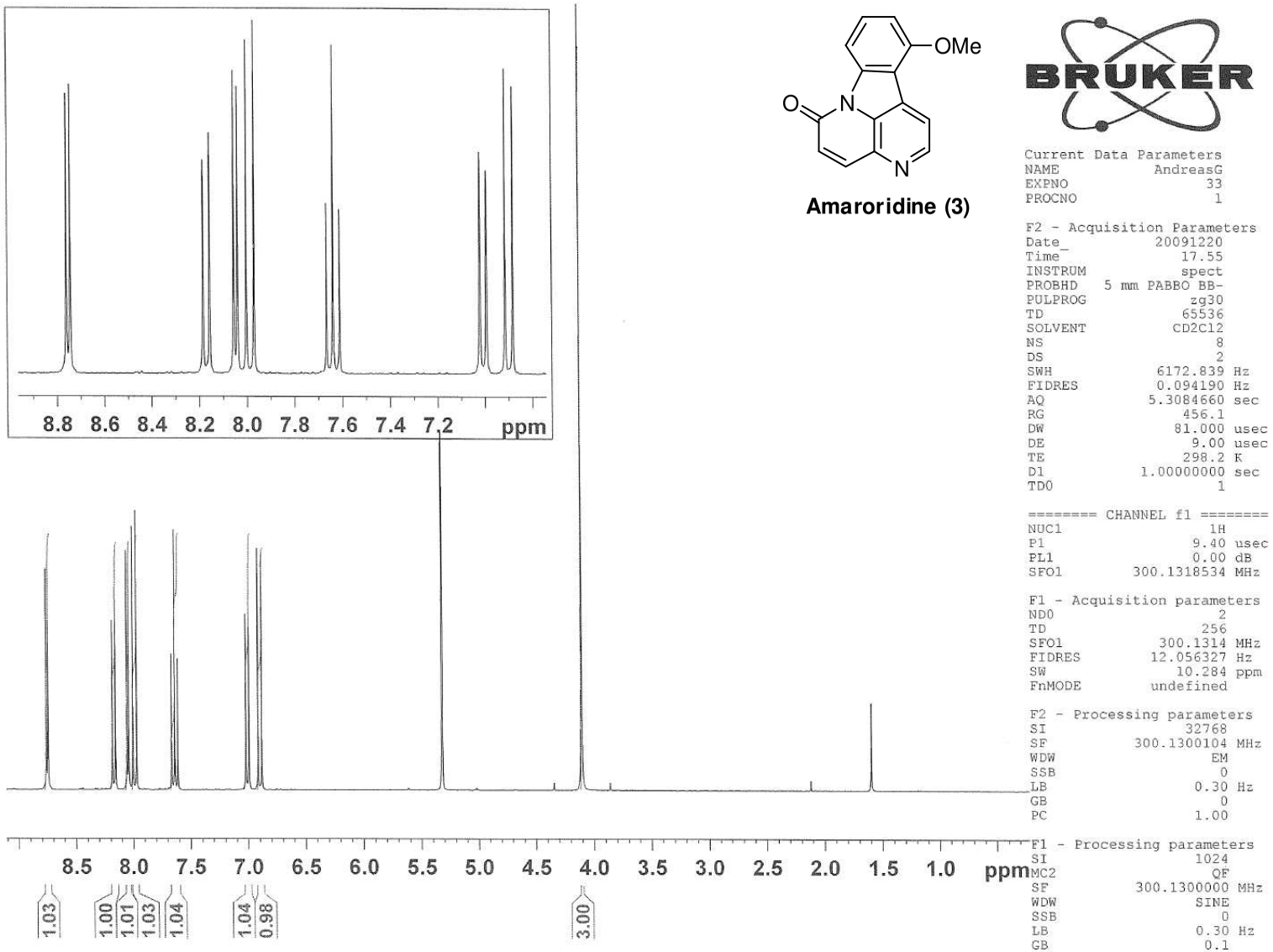


9-Methoxycanthin-6-one (2)



Amaroridine (3)

BRUKER

```
Current Data Parameters
NAME                 AndreasG
EXPNO                      33
PROCNO                      1

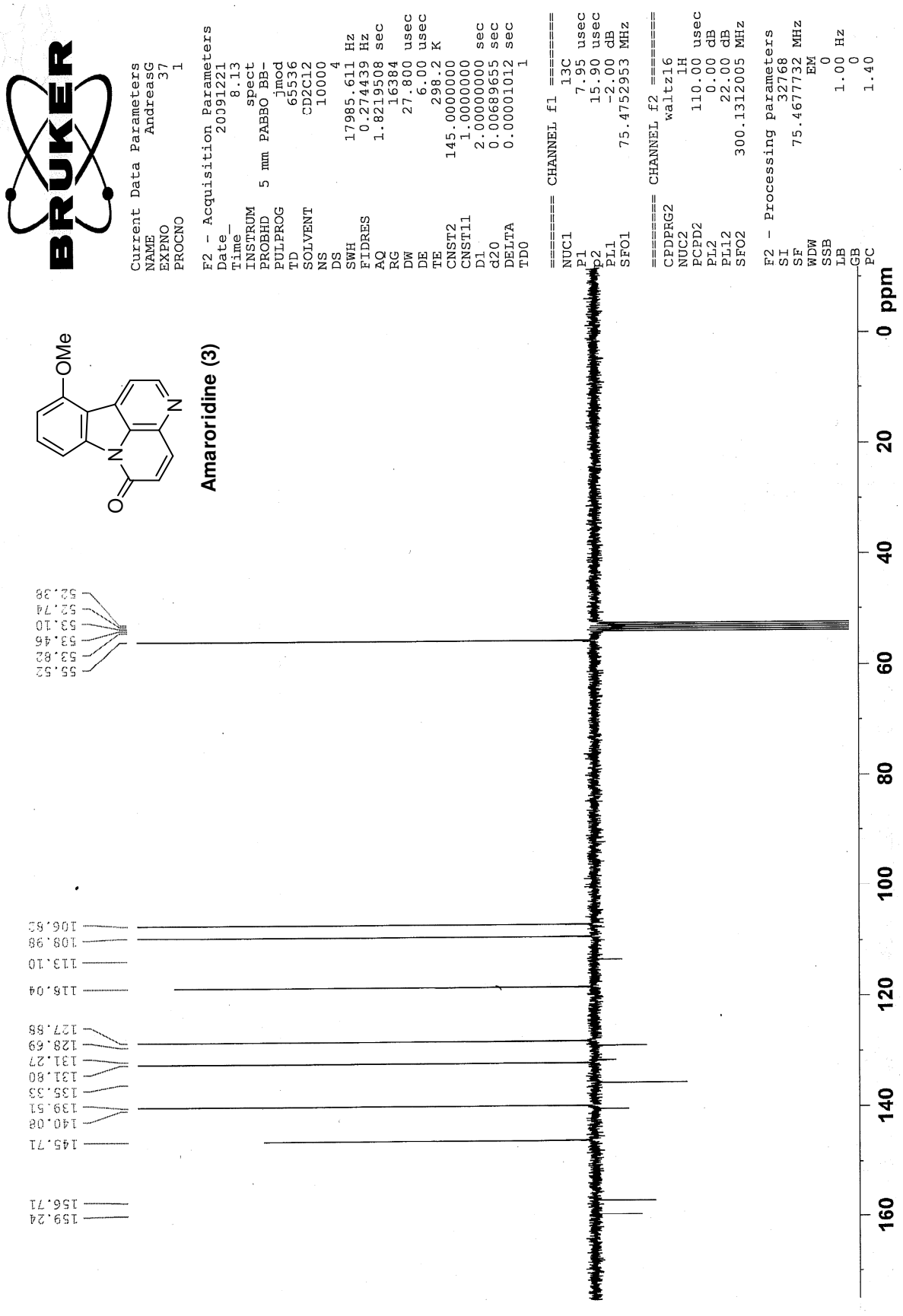
F2 - Acquisition Parameters
Date_               20091220
Time                   17.55
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT              CD2Cl2
NS                          8
DS                          2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                     456.1
DW                    81.000 usec
DE                     9.00 usec
TE                    298.2 K
D1                 1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      9.40 usec
PL1                     0.00 dB
SFO1           300.1318534 MHz

F1 - Acquisition parameters
ND0                         2
TD                        256
SFO1             300.1314 MHz
FIDRES           12.056327 Hz
SW                   10.284 ppm
FnMODE           undefined

F2 - Processing parameters
SI                      32768
SF             300.1300104 MHz
WDW                        EM
SSB                         0
LB                      0.30 Hz
GB                          0
PC                       1.00

F1 - Processing parameters
SI                       1024
MC2                        QF
SF             300.1300000 MHz
WDW                      SINE
SSB                         0
LB                      0.30 Hz
GB                       0.1
```


BRUKER
Current Data Parameters
NAME AndreasG
EXPNO 37
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091221
Time_ 8.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2Cl2
NS 10000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
P2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677732 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMe
N
N
O
Amaroridine (3)
52.38
52.74
53.10
53.46
53.82
55.52
106.85
109.98
113.10
118.04
127.88
128.69
131.27
131.80
135.33
139.51
140.08
145.71
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140
120
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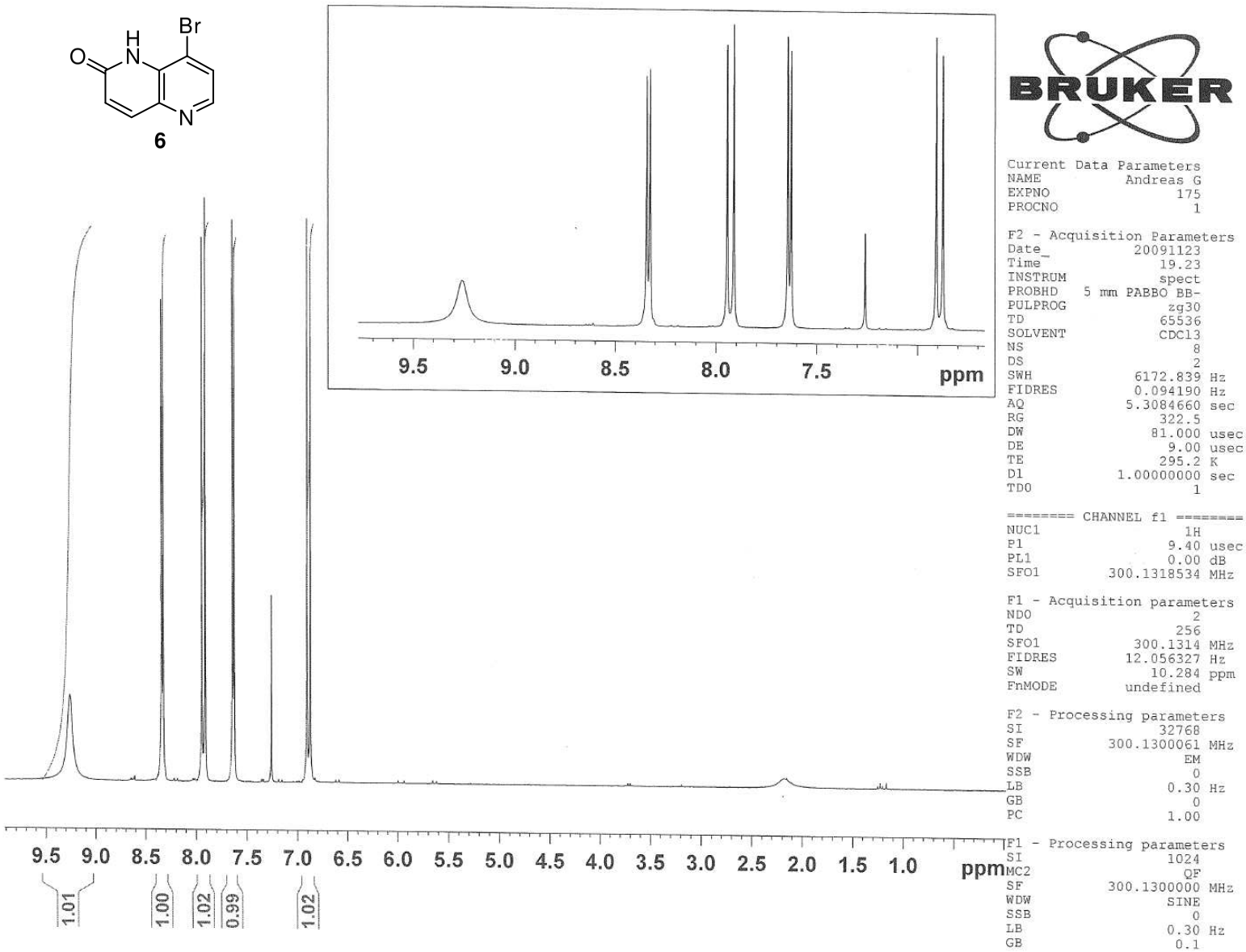
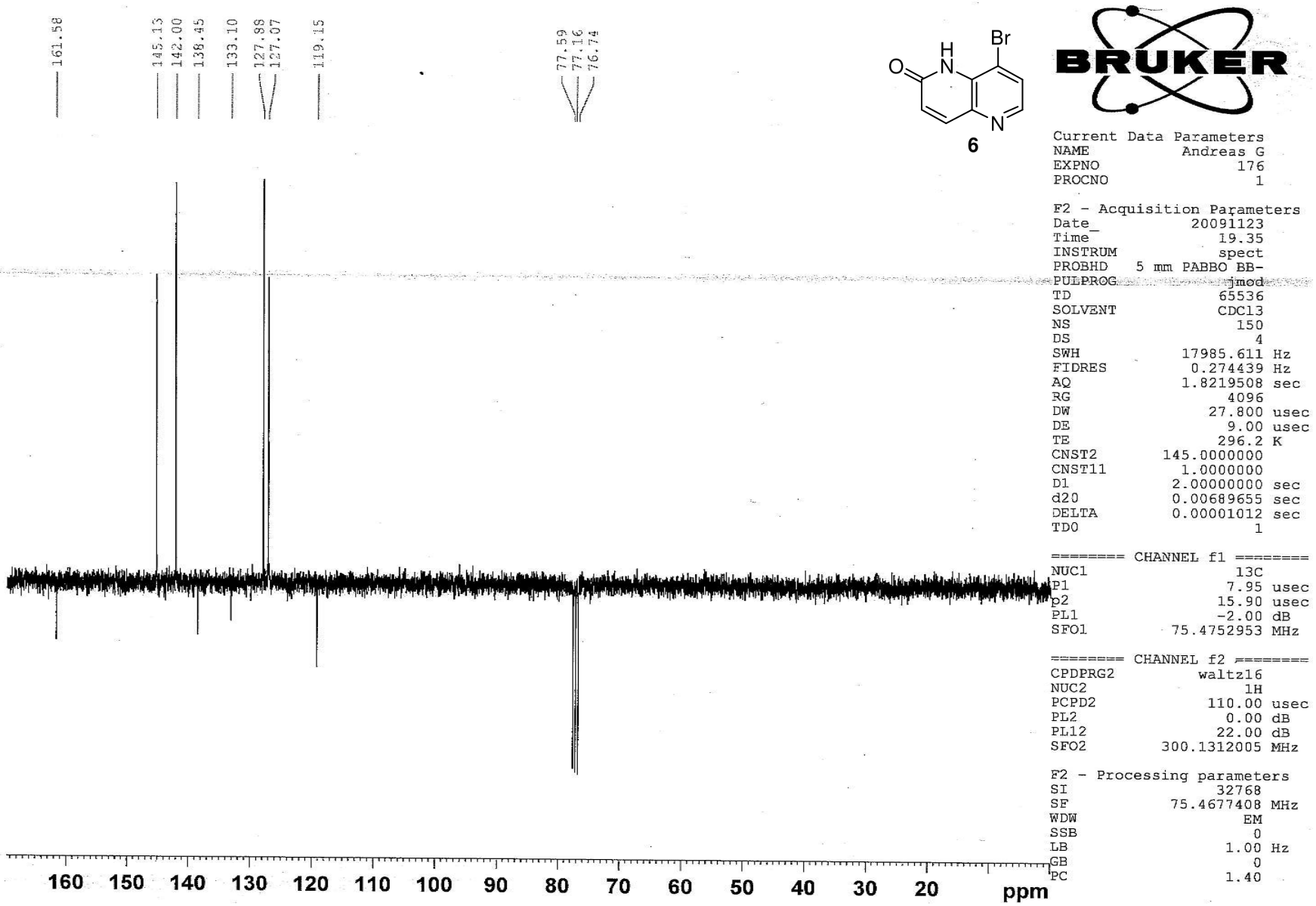
80
60
40
20
0 ppm


Br
H
N
O
N
6
9.5
9.0
8.5
8.0
7.5
ppm
BRUKER
Current Data Parameters
NAME Andreas G
EXPNO 175
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091123
Time 19.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 322.5
DW 81.000 usec
DE 9.00 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
1.01
1.00
1.02
0.99
1.02



BRUKER

Current Data Parameters
NAME Andreas G
EXPNO 176
PROCNO 1

F2 - Acquisition Parameters
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Time 19.35
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 150
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4096
DW 27.800 usec
DE 9.00 usec
TE 296.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
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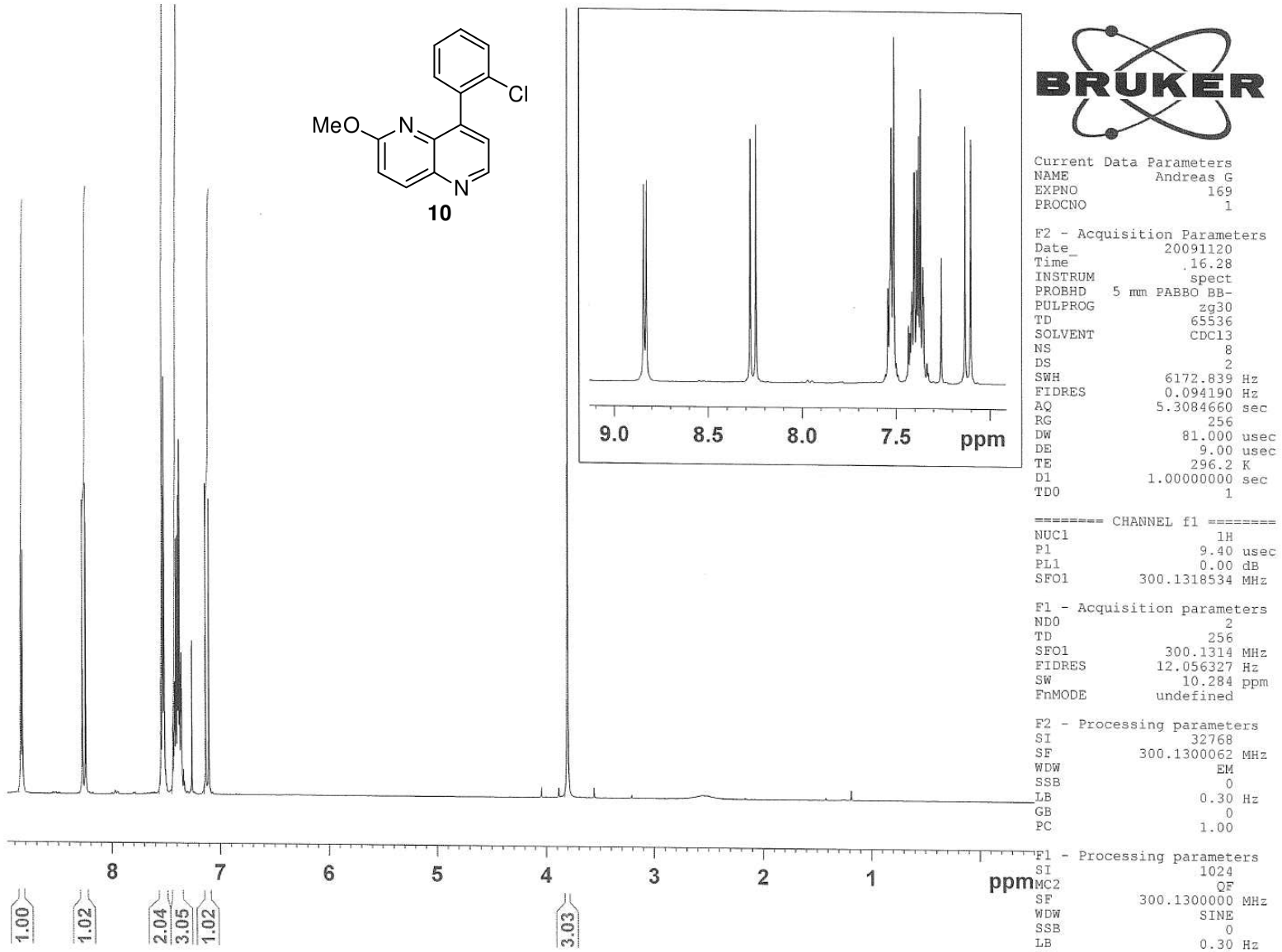
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



BRUKER

```
Current Data Parameters
NAME                 Andreas G
EXPNO                      169
PROCNO                       1

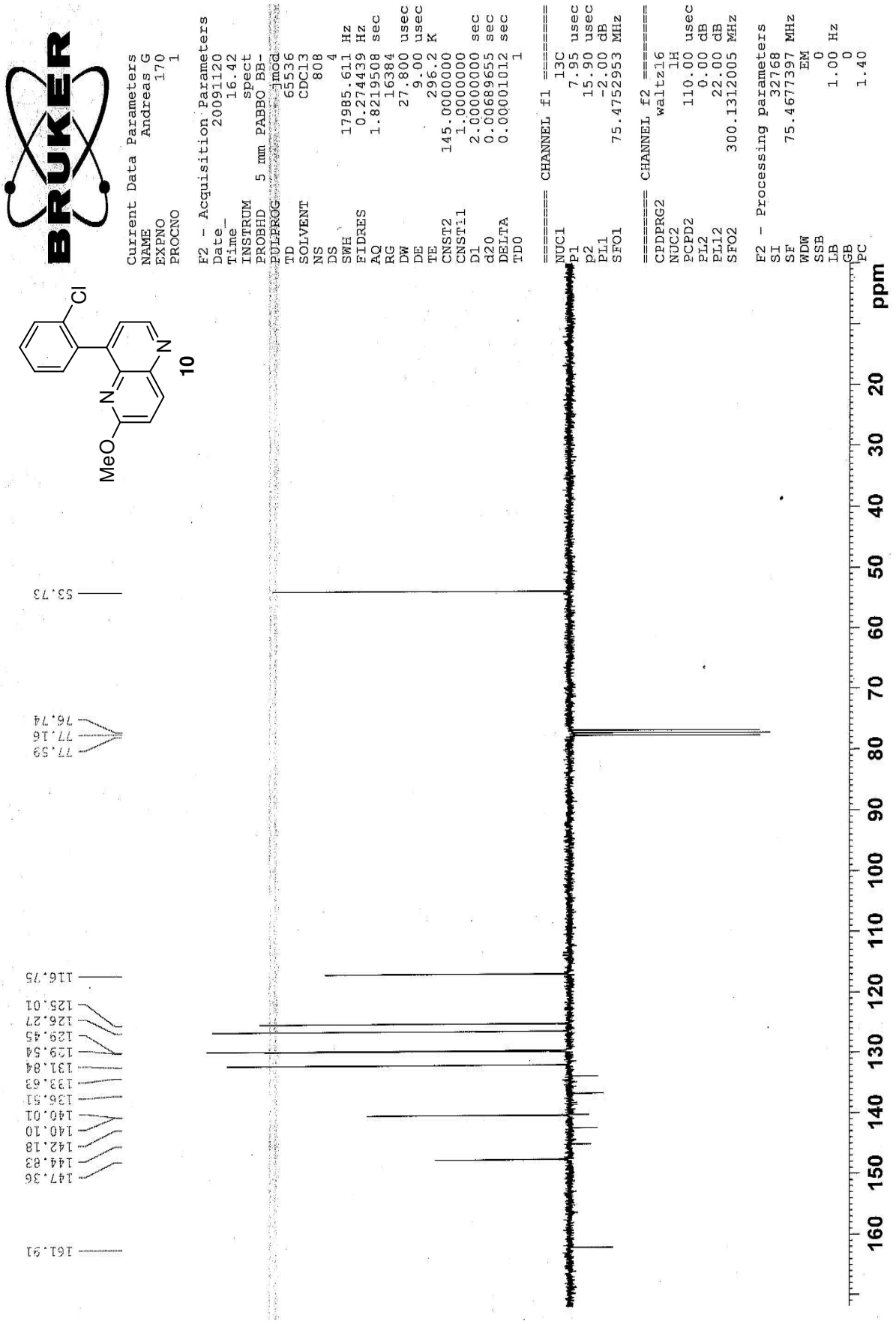
F2 - Acquisition Parameters
Date_               20091120
Time                    16.28
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                        256
DW                   81.000 usec
DE                    9.00 usec
TE                   296.2 K
D1                 1.00000000 sec
TD0                         1

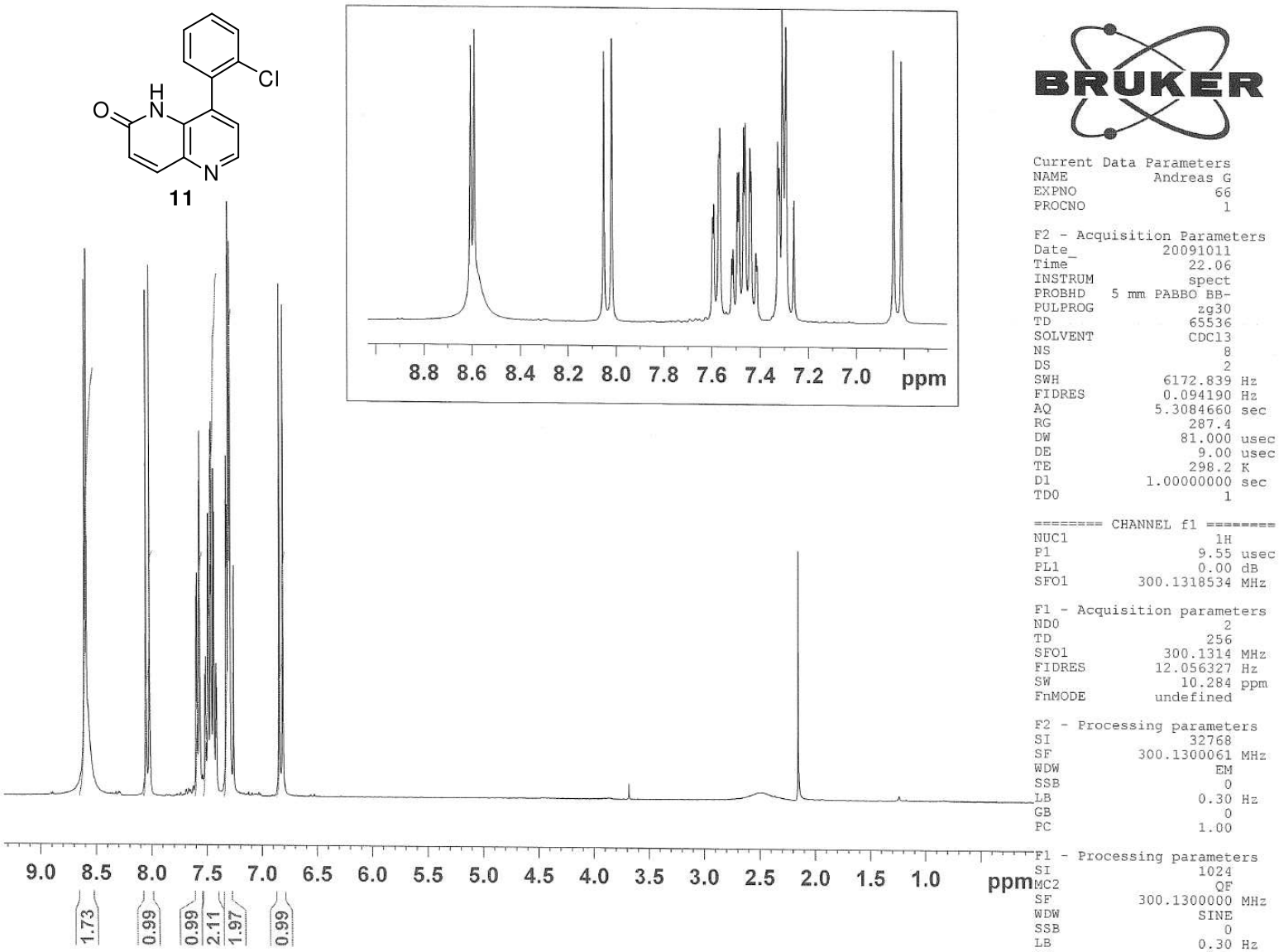
======== CHANNEL f1 ========
NUC1                       1H
P1                    9.40 usec
PL1                   0.00 dB
SFO1           300.1318534 MHz

F1 - Acquisition parameters
ND0                         2
TD                        256
SFO1               300.1314 MHz
FIDRES            12.056327 Hz
SW                   10.284 ppm
FnMODE           undefined

F2 - Processing parameters
SI                      32768
SF             300.1300062 MHz
WDW                        EM
SSB                         0
LB                    0.30 Hz
GB                          0
PC                       1.00

F1 - Processing parameters
SI                       1024
MC2                        QF
SF             300.1300000 MHz
WDW                      SINE
SSB                         0
LB                    0.30 Hz
GB                       0.1
```


Current Data Parameters
NAME Andreas G
EXPNO 170
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091120
Time 16.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 808
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 296.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677397 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
N
N
MeO
10
53.73
76.74
77.16
77.59
116.75
125.01
126.27
129.45
129.54
131.84
133.63
136.51
140.01
140.10
142.18
144.83
147.36
161.91
ppm



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```
Current Data Parameters
NAME                 Andreas G
EXPNO                       66
PROCNO                       1

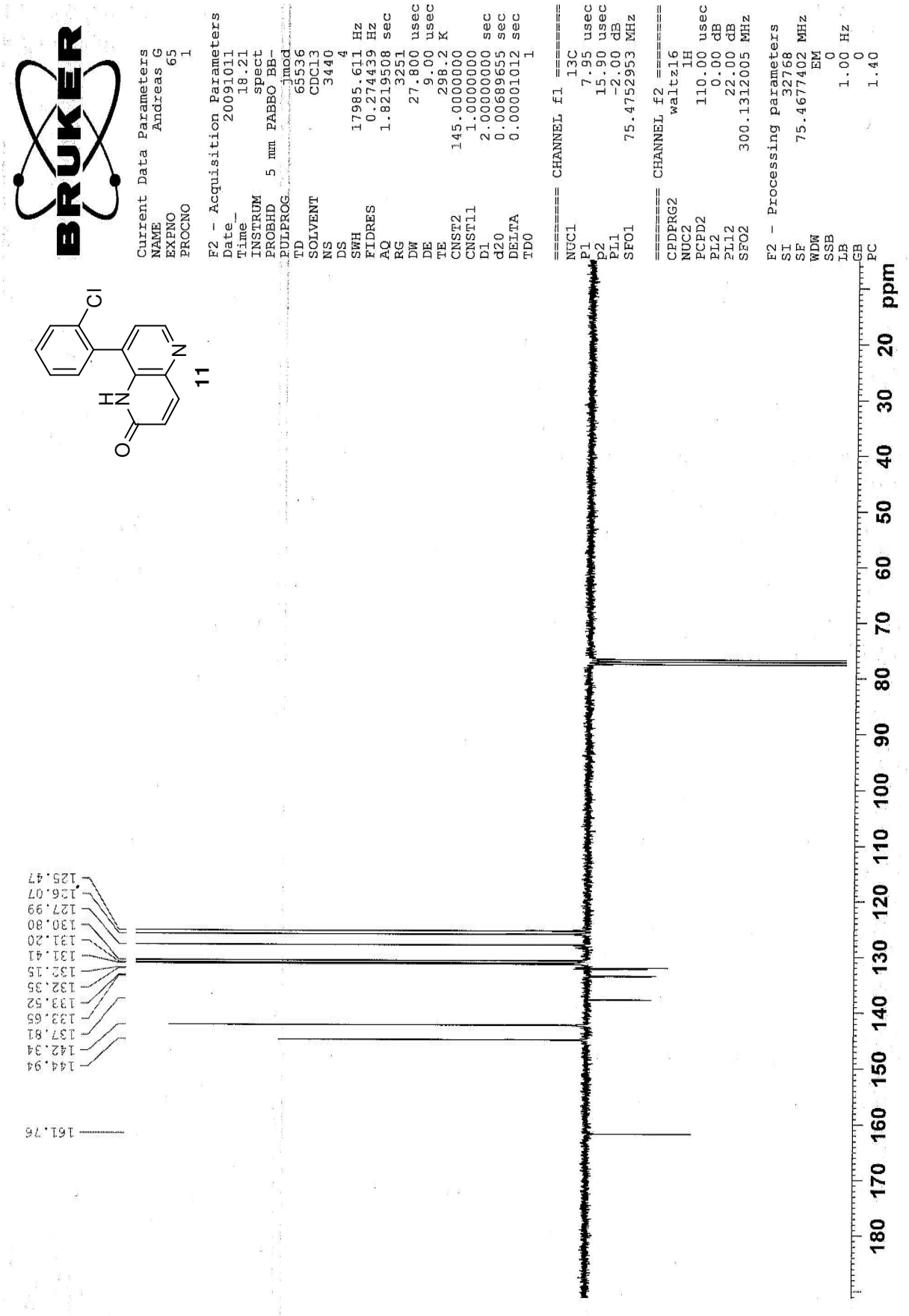
F2 - Acquisition Parameters
Date_                 20091011
Time                     22.06
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          2
SWH                  6172.839 Hz
FIDRES               0.094190 Hz
AQ                   5.3084660 sec
RG                       287.4
DW                      81.000 usec
DE                       9.00 usec
TE                      298.2 K
D1                1.00000000 sec
TD0                         1

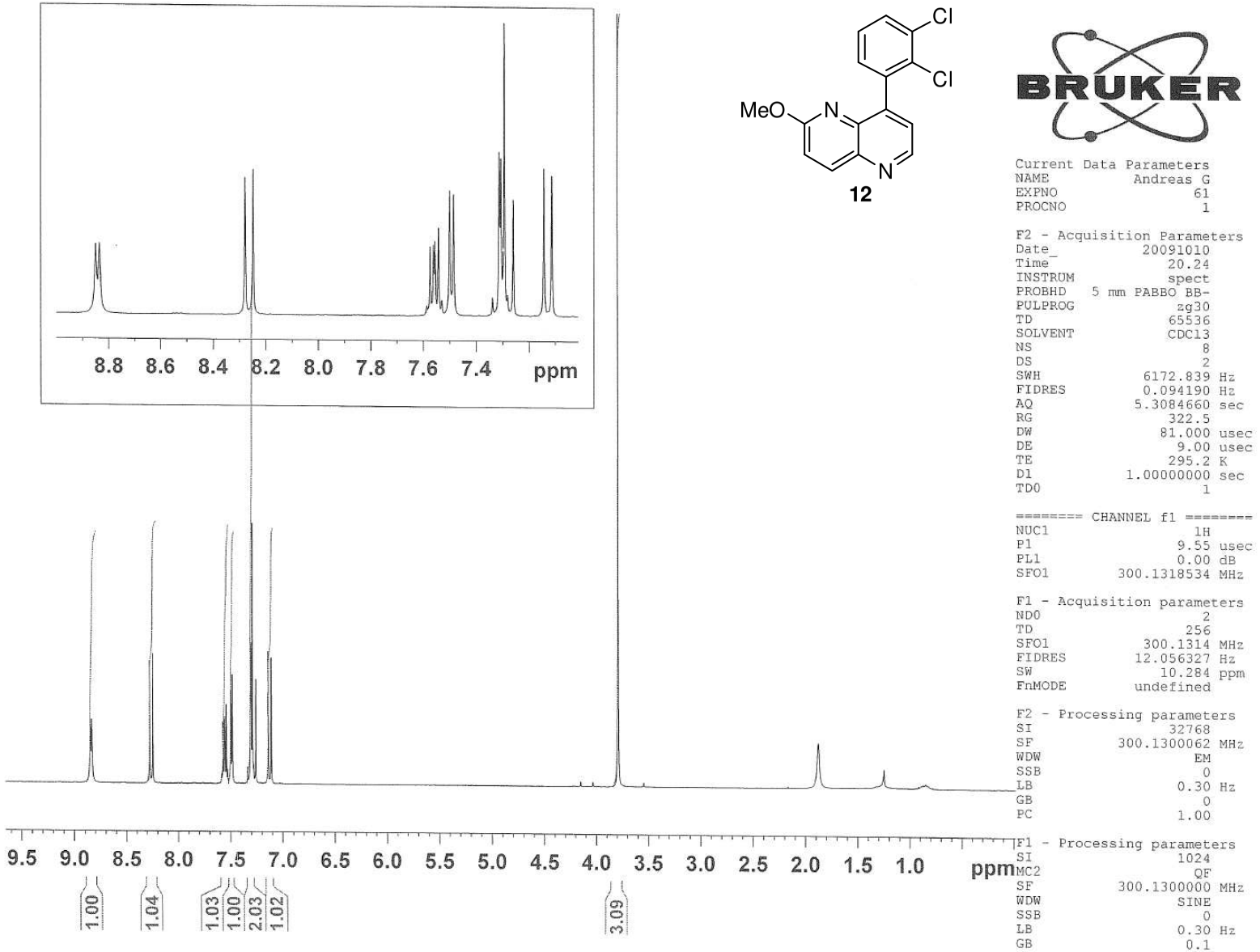
======== CHANNEL f1 ========
NUC1                        1H
P1                       9.55 usec
PL1                      0.00 dB
SFO1              300.1318534 MHz

F1 - Acquisition parameters
ND0                         2
TD                        256
SFO1                300.1314 MHz
FIDRES             12.056327 Hz
SW                     10.284 ppm
FnMODE               undefined

F2 - Processing parameters
SI                      32768
SF                300.1300061 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

F1 - Processing parameters
SI                       1024
MC2                        QF
SF                300.1300000 MHz
WDW                      SINE
SSB                         0
LB                       0.30 Hz
GB                        0.1
```


Current Data Parameters
NAME Andreas G
EXPNO 65
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091011
Time 18.21
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 3440
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.82195508 sec
RG 3251
DW 27.800 usec
DE 9.00 usec
TE 298.2 K
CNST2 145.00000000
CNST11 1.00000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
P2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677402 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
11
161.76
144.94
142.34
137.81
133.65
133.52
132.35
132.15
131.41
131.20
130.80
127.99
126.07
125.47
ppm



BRUKER

```
Current Data Parameters
NAME                 Andreas G
EXPNO                       61
PROCNO                       1

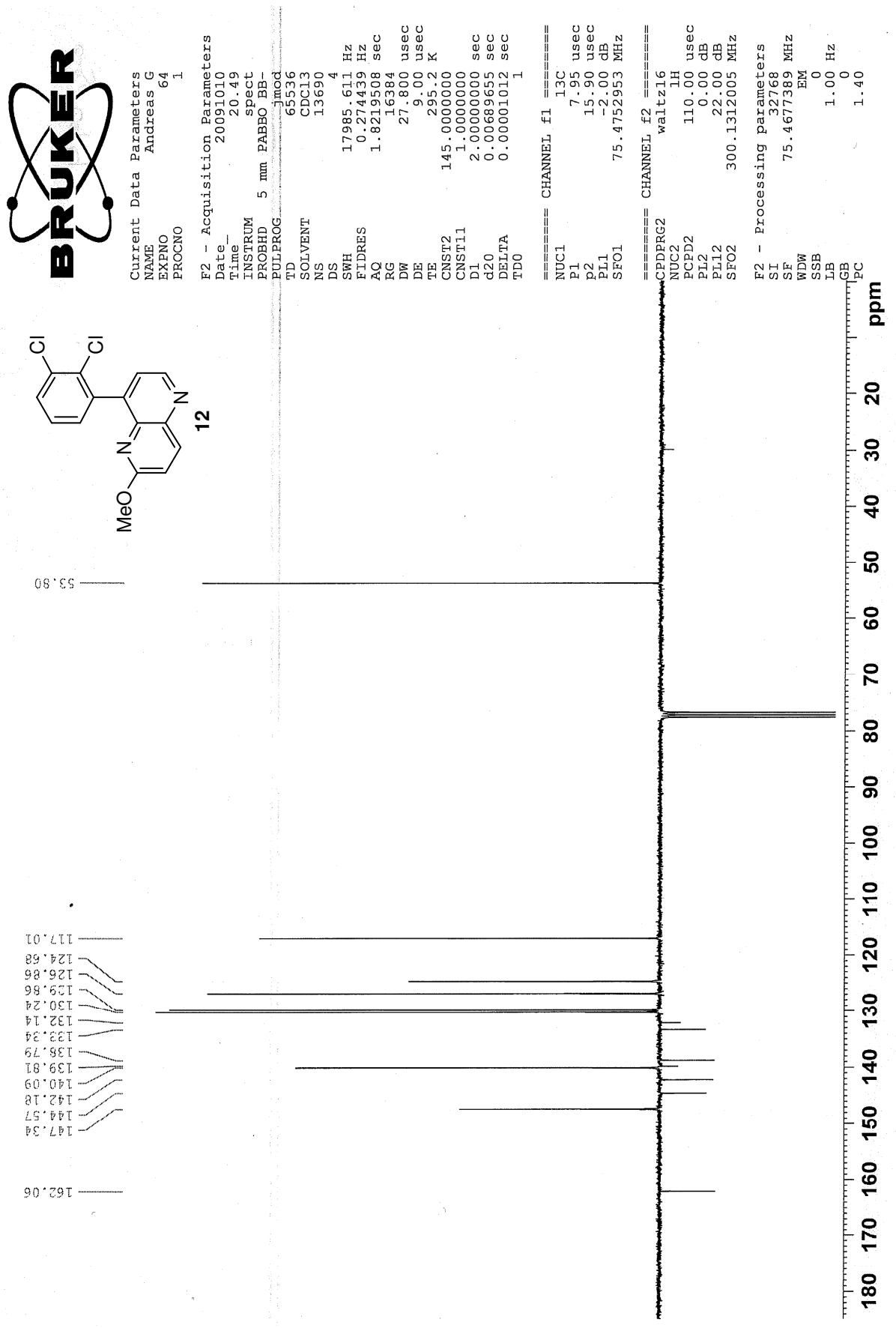
F2 - Acquisition Parameters
Date_               20091010
Time                   20.24
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        2
SWH                6172.839 Hz
FIDRES            0.094190 Hz
AQ                5.3084660 sec
RG                    322.5
DW                   81.000 usec
DE                    9.00 usec
TE                   295.2 K
D1                1.00000000 sec
TD0                       1

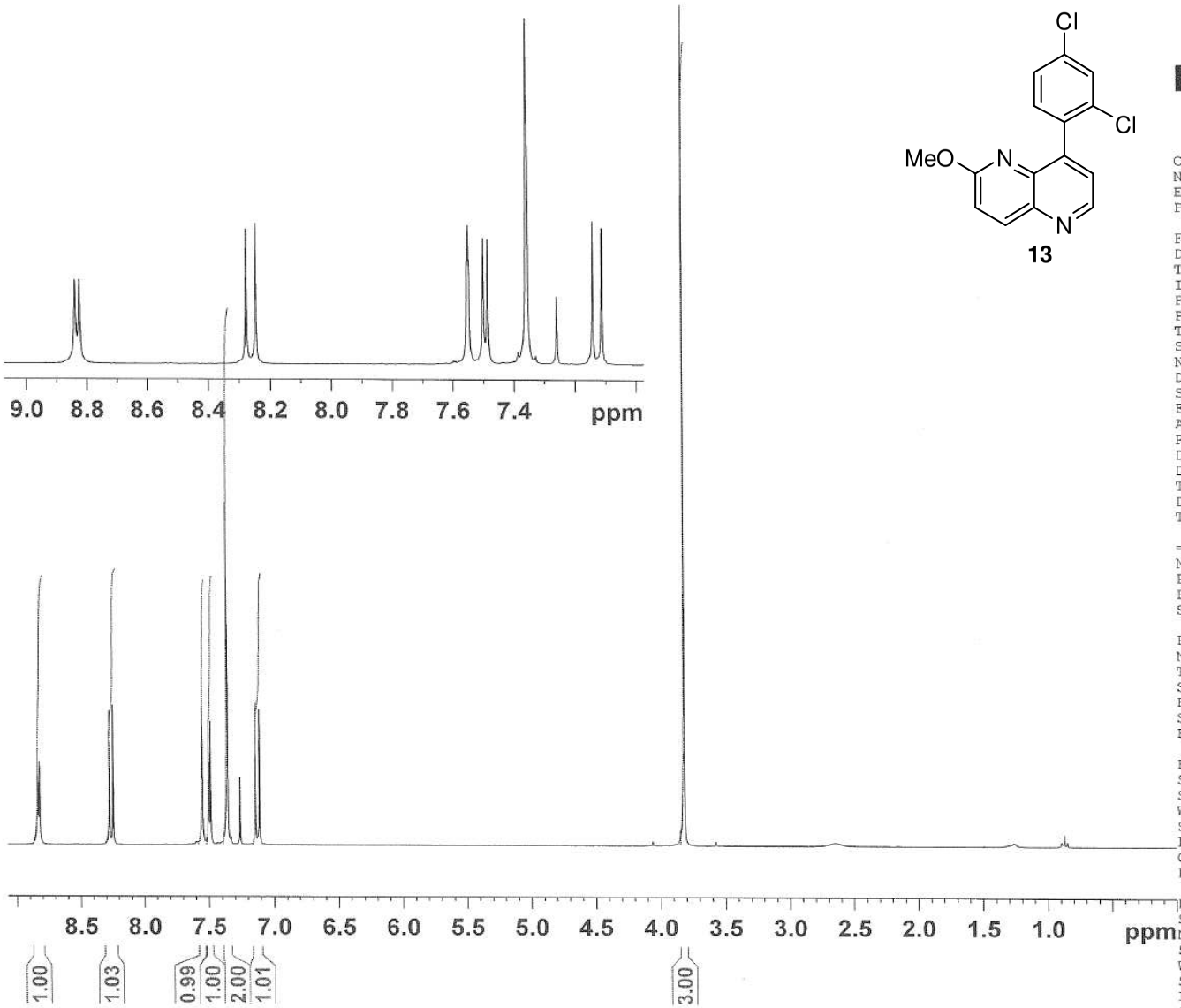
======== CHANNEL f1 ========
NUC1                     1H
P1                    9.55 usec
PL1                   0.00 dB
SFO1           300.1318534 MHz

F1 - Acquisition parameters
ND0                       2
TD                      256
SFO1             300.1314 MHz
FIDRES          12.056327 Hz
SW                 10.284 ppm
FnMODE           undefined

F2 - Processing parameters
SI                    32768
SF             300.1300062 MHz
WDW                      EM
SSB                       0
LB                    0.30 Hz
GB                        0
PC                     1.00

F1 - Processing parameters
SI                     1024
MC2                      QF
SF             300.1300000 MHz
WDW                    SINE
SSB                       0
LB                    0.30 Hz
GB                     0.1
```


Current Data Parameters
NAME Andreas G
EXPNO 64
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091010
Time 20.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 13690
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 295.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677389 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
Cl
N
N
MeO
12
53.80
117.01
124.68
126.86
129.86
130.24
132.14
133.34
136.79
139.81
140.09
142.18
144.57
147.34
162.06
ppm



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BRUKER

```
Current Data Parameters
NAME                 Andreas G
EXPNO                      145
PROCNO                       1

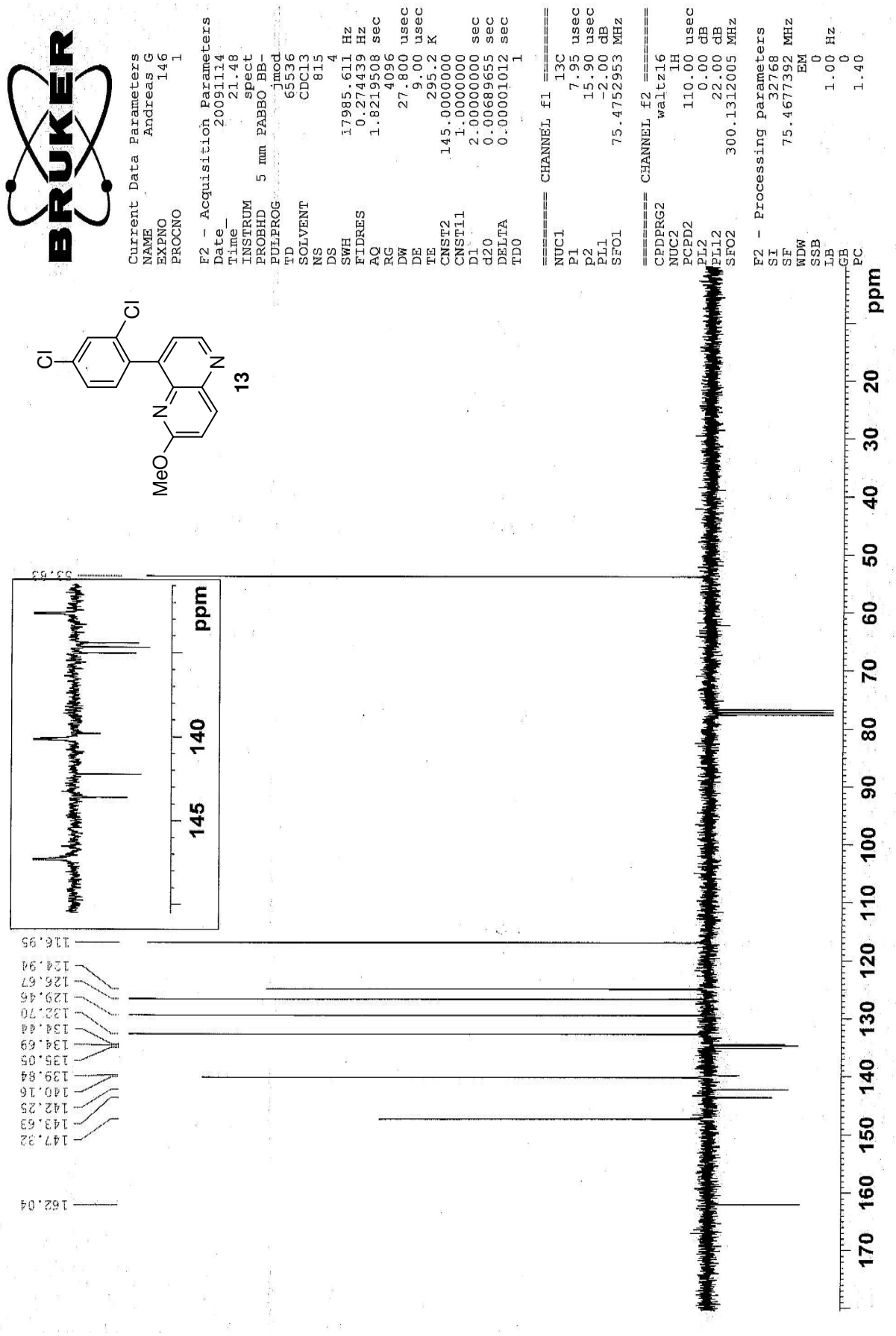
F2 - Acquisition Parameters
Date_               20091114
Time                   21.33
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                  5.3084660 sec
RG                       362
DW                    81.000 usec
DE                     9.00 usec
TE                    295.2 K
D1                  1.00000000 sec
TD0                          1

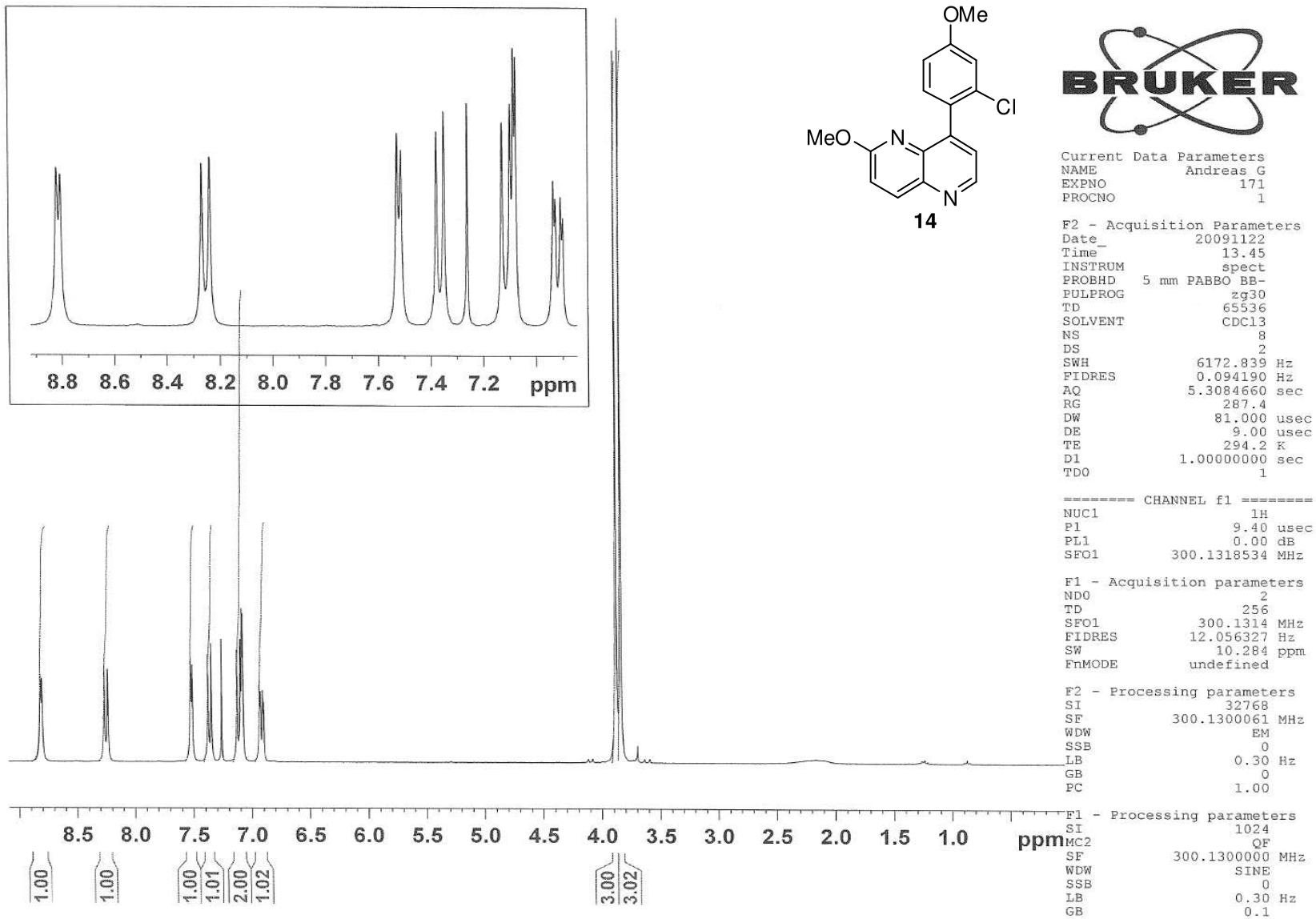
======== CHANNEL f1 ========
NUC1                       1H
P1                     9.40 usec
PL1                    0.00 dB
SFO1           300.1318534 MHz

F1 - Acquisition parameters
ND0                          2
TD                         256
SFO1                300.1314 MHz
FIDRES             12.056327 Hz
SW                    10.284 ppm
FnMODE             undefined

F2 - Processing parameters
SI                       32768
SF                 300.1300062 MHz
WDW                         EM
SSB                          0
LB                     0.30 Hz
GB                           0
PC                        1.00

F1 - Processing parameters
SI                        1024
MC2                         QF
SF                 300.1300000 MHz
WDW                       SINE
SSB                          0
LB                     0.30 Hz
GB                        0.1
```


Current Data Parameters
NAME Andreas G
EXPNO 146
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091114
Time 21.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 815
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4096
DW 27.800 usec
DE 9.00 usec
TE 295.2 K
CNST2 145.0000000
CNST11 1.00000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677392 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
Cl
N
N
MeO
13
ppm
145
140
53.63
116.95
124.94
126.67
129.46
133.70
134.44
134.69
135.05
139.84
140.16
142.25
143.63
147.32
162.04



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BRUKER

```
Current Data Parameters
NAME                 Andreas G
EXPNO                      171
PROCNO                       1

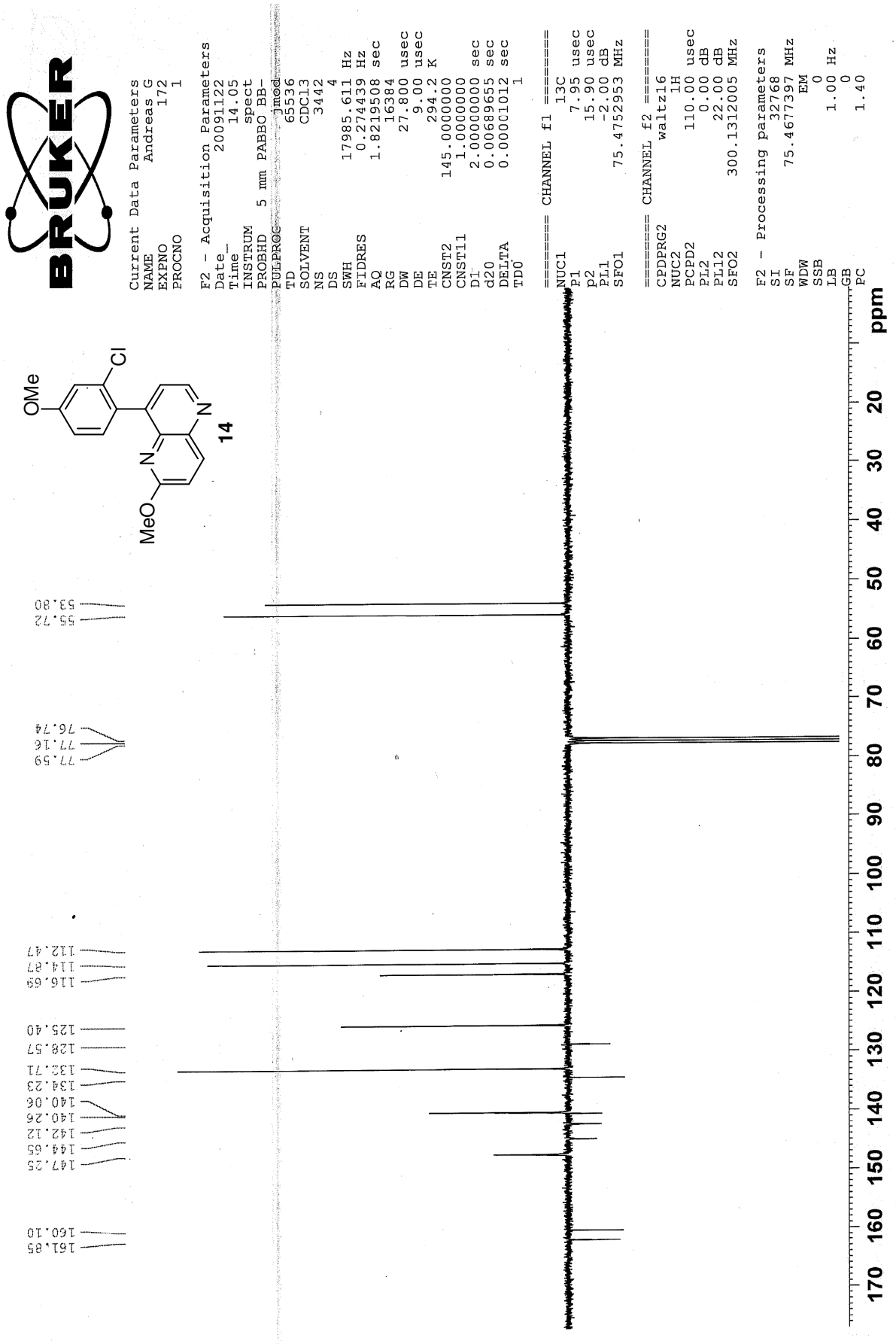
F2 - Acquisition Parameters
Date_                 20091122
Time                     13.45
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          2
SWH                  6172.839 Hz
FIDRES               0.094190 Hz
AQ                   5.3084660 sec
RG                       287.4
DW                      81.000 usec
DE                       9.00 usec
TE                      294.2 K
D1                   1.00000000 sec
TD0                          1

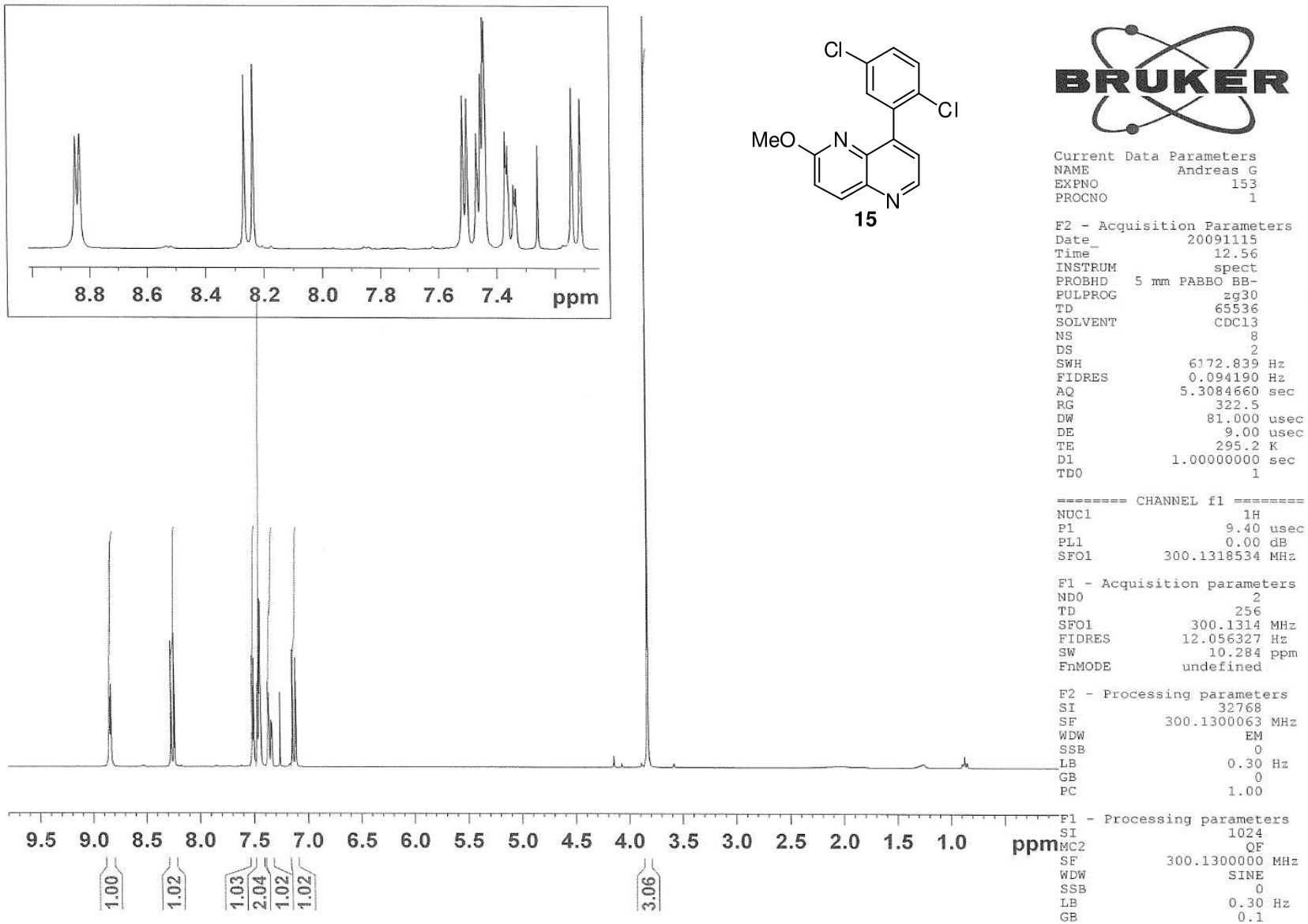
======== CHANNEL f1 ========
NUC1                        1H
P1                       9.40 usec
PL1                      0.00 dB
SFO1           300.1318534 MHz

F1 - Acquisition parameters
ND0                          2
TD                         256
SFO1                300.1314 MHz
FIDRES             12.056327 Hz
SW                     10.284 ppm
FnMODE             undefined

F2 - Processing parameters
SI                       32768
SF                 300.1300061 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

F1 - Processing parameters
SI                        1024
MC2                         QF
SF                 300.1300000 MHz
WDW                       SINE
SSB                          0
LB                        0.30 Hz
GB                         0.1
```


BRUKER
Current Data Parameters
NAME Andreas G
EXPNO 172
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091122
Time_ 14.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 3442
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 294.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.0000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
p1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677397 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
OMe
Cl
N
N
MeO
14
53.80
55.72
76.74
77.16
77.59
112.47
114.87
116.69
125.40
128.57
132.71
134.23
140.06
140.26
142.12
144.65
147.25
160.10
161.85
ppm



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```
Current Data Parameters
NAME                 Andreas G
EXPNO                      153
PROCNO                       1

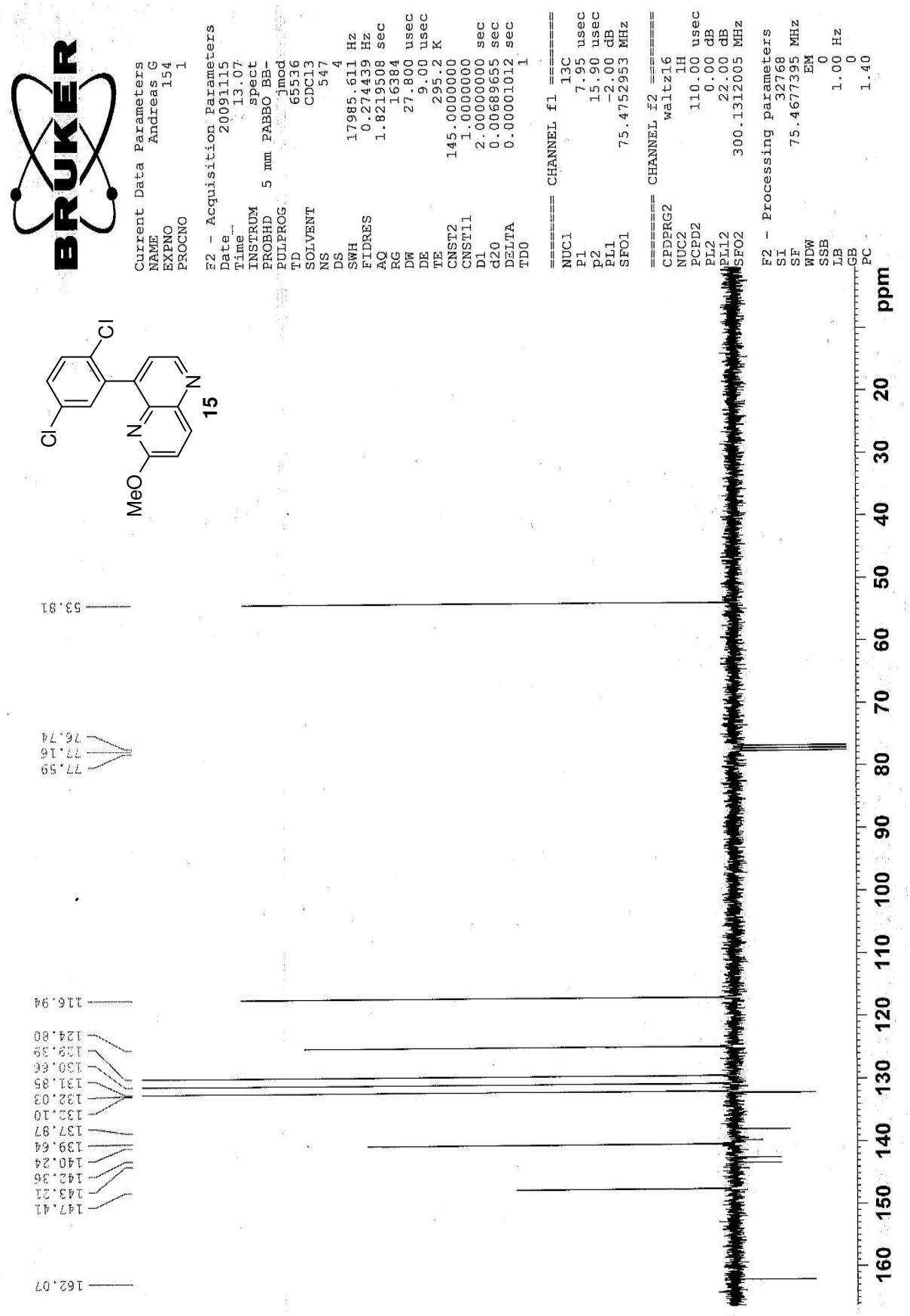
F2 - Acquisition Parameters
Date_               20091115
Time                    12.56
INSTRUM                 spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                  5.3084660 sec
RG                      322.5
DW                     81.000 usec
DE                      9.00 usec
TE                      295.2 K
D1                  1.00000000 sec
TD0                        1

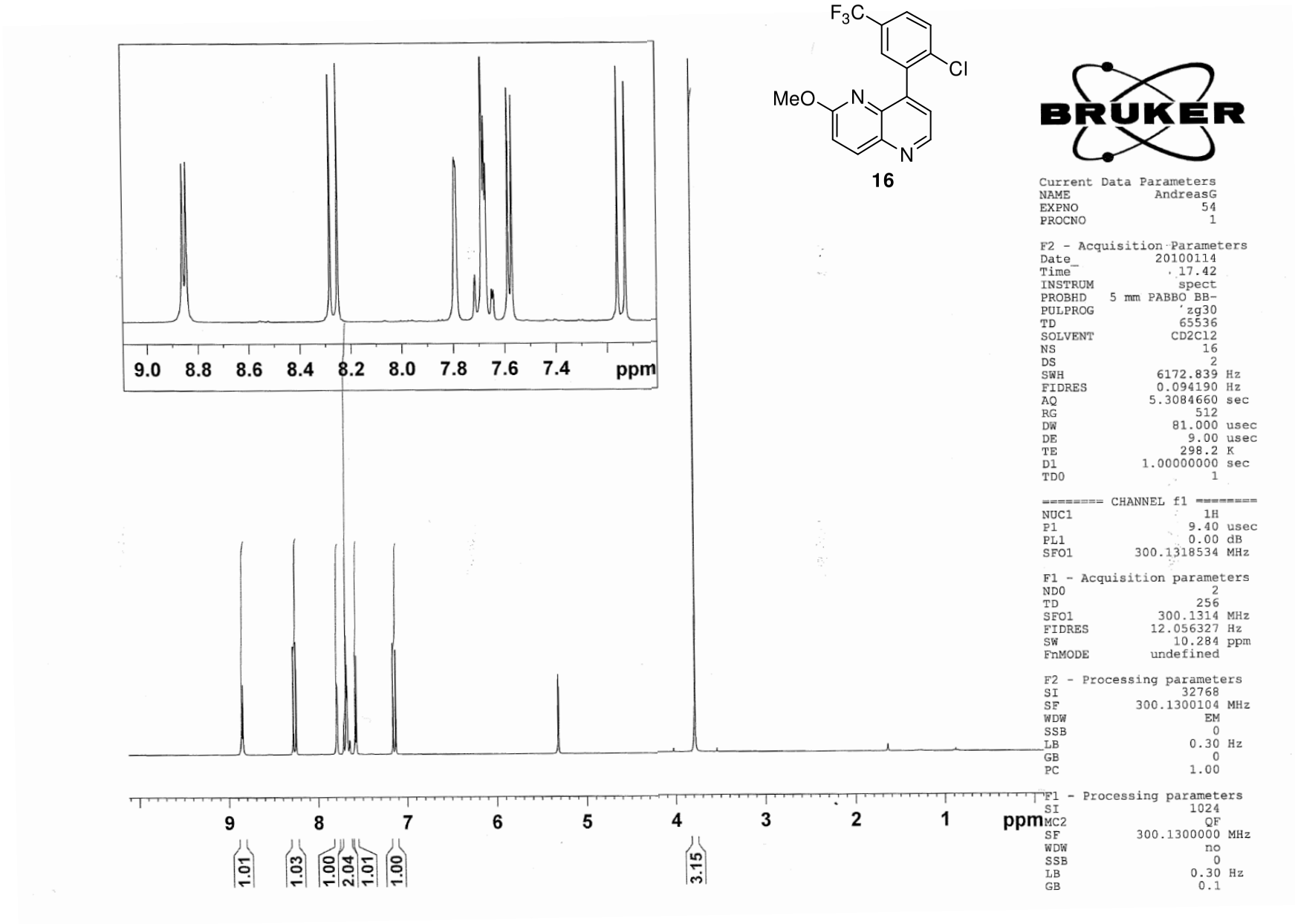
======== CHANNEL f1 ========
NUC1                       1H
P1                      9.40 usec
PL1                     0.00 dB
SFO1             300.1318534 MHz

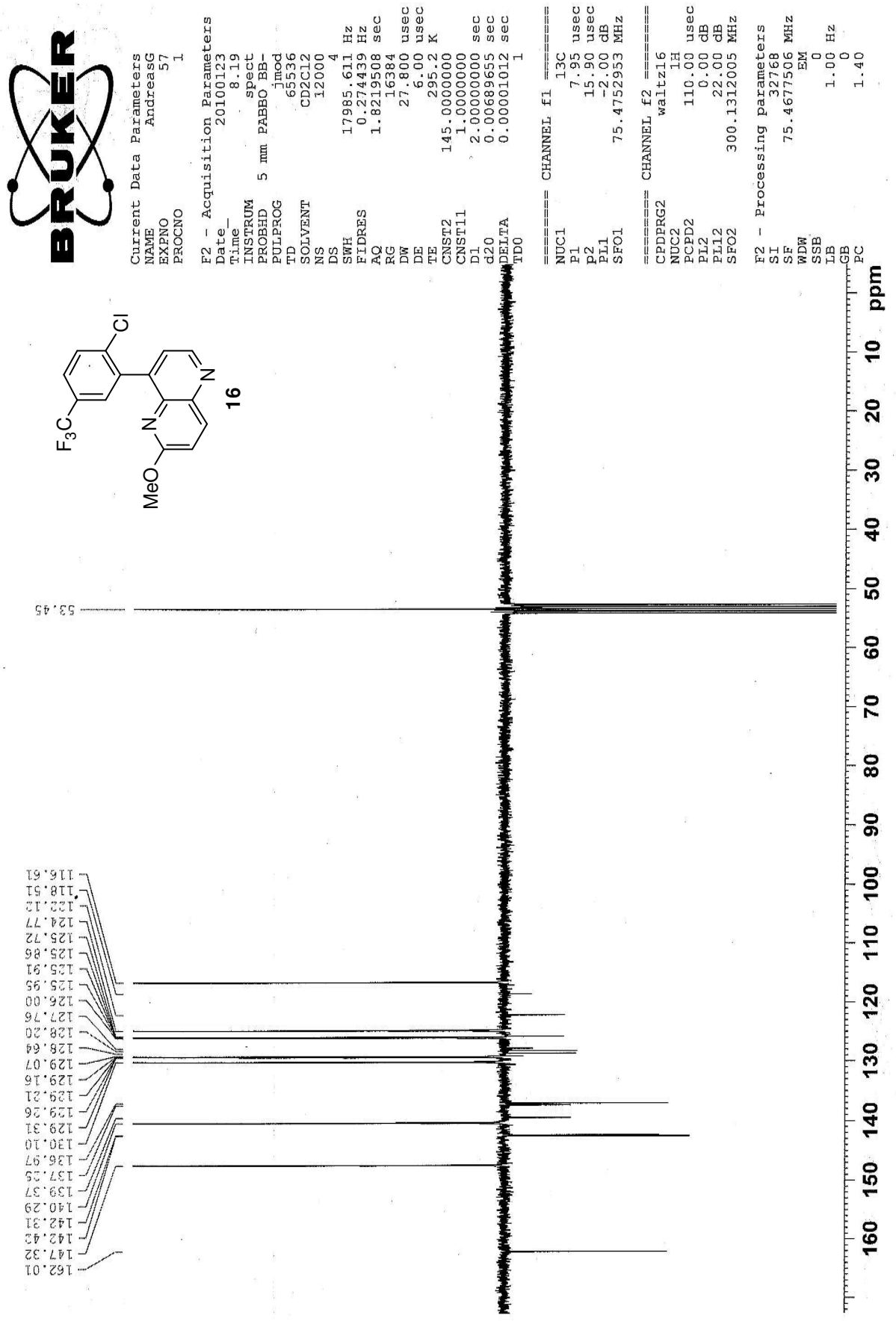
F1 - Acquisition parameters
ND0                        2
TD                       256
SFO1                300.1314 MHz
FIDRES             12.056327 Hz
SW                     10.284 ppm
FnMODE               undefined

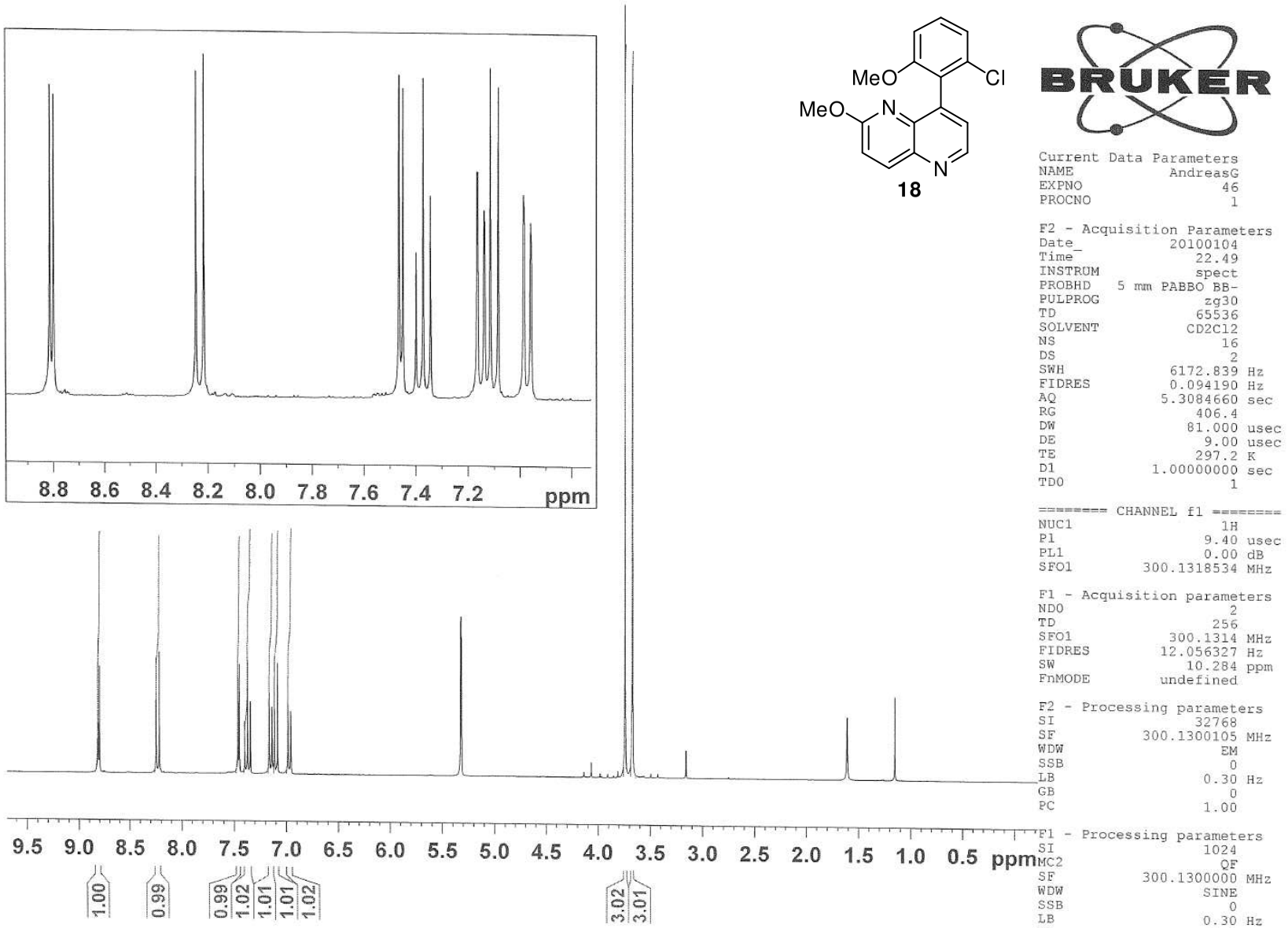
F2 - Processing parameters
SI                       32768
SF                300.1300063 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

F1 - Processing parameters
SI                        1024
MC2                         QF
SF                300.1300000 MHz
WDW                      SINE
SSB                         0
LB                       0.30 Hz
GB                        0.1
```


Current Data Parameters
NAME Andreas G
EXPNO 154
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091115
Time 13.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 547
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 295.2 K
CNST2 145.0000000
CNST11 1.00000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
P2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677395 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
Cl
N
N
MeO
15
53.81
76.74
77.16
77.59
116.94
124.80
129.39
130.66
131.85
132.03
133.10
137.87
139.64
140.24
142.36
143.21
147.41
162.07
ppm


F3C
Cl
MeO
N
N
16
BRUKER
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 ppm
9 8 7 6 5 4 3 2 1 ppm
1.01
1.03
1.00
2.04
1.01
1.00
3.15
Current Data Parameters
NAME AndreasG
EXPNO 54
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100114
Time 17.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 512
DW 81.000 usec
DE 9.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300104 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW no
SSB 0
LB 0.30 Hz
GB 0.1


Current Data Parameters
NAME AndreasG
EXPNO 57
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100123
Time_ 8.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2Cl2
NS 12000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 6.00 usec
TE 295.2 K
CNST2 145.0000000
CNST11 1.00000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677506 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
F3C
N
N
MeO
16
53.45
162.01
147.32
142.42
142.31
140.29
139.37
137.25
136.97
130.10
129.31
129.26
129.21
129.16
129.07
128.64
128.20
127.76
126.00
125.95
125.91
125.86
125.72
124.77
122.12
118.51
116.61
ppm



BRUKER

```
Current Data Parameters
NAME                 AndreasG
EXPNO                      46
PROCNO                      1

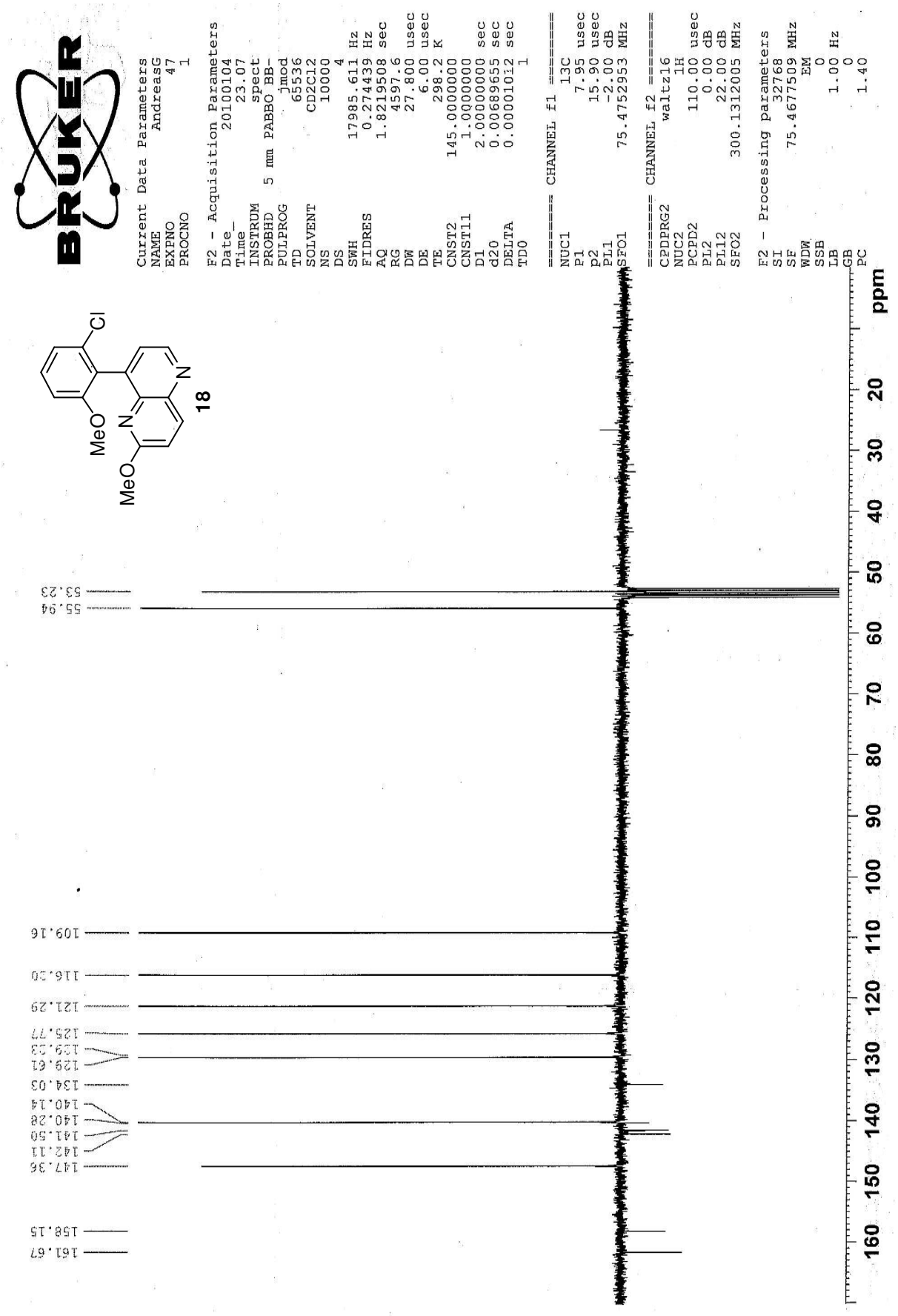
F2 - Acquisition Parameters
Date_               20100104
Time                   22.49
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT             CD2Cl2
NS                         16
DS                          2
SWH                6172.839 Hz
FIDRES                0.094190 Hz
AQ                 5.3084660 sec
RG                     406.4
DW                    81.000 usec
DE                     9.00 usec
TE                    297.2 K
D1                 1.00000000 sec
TD0                         1

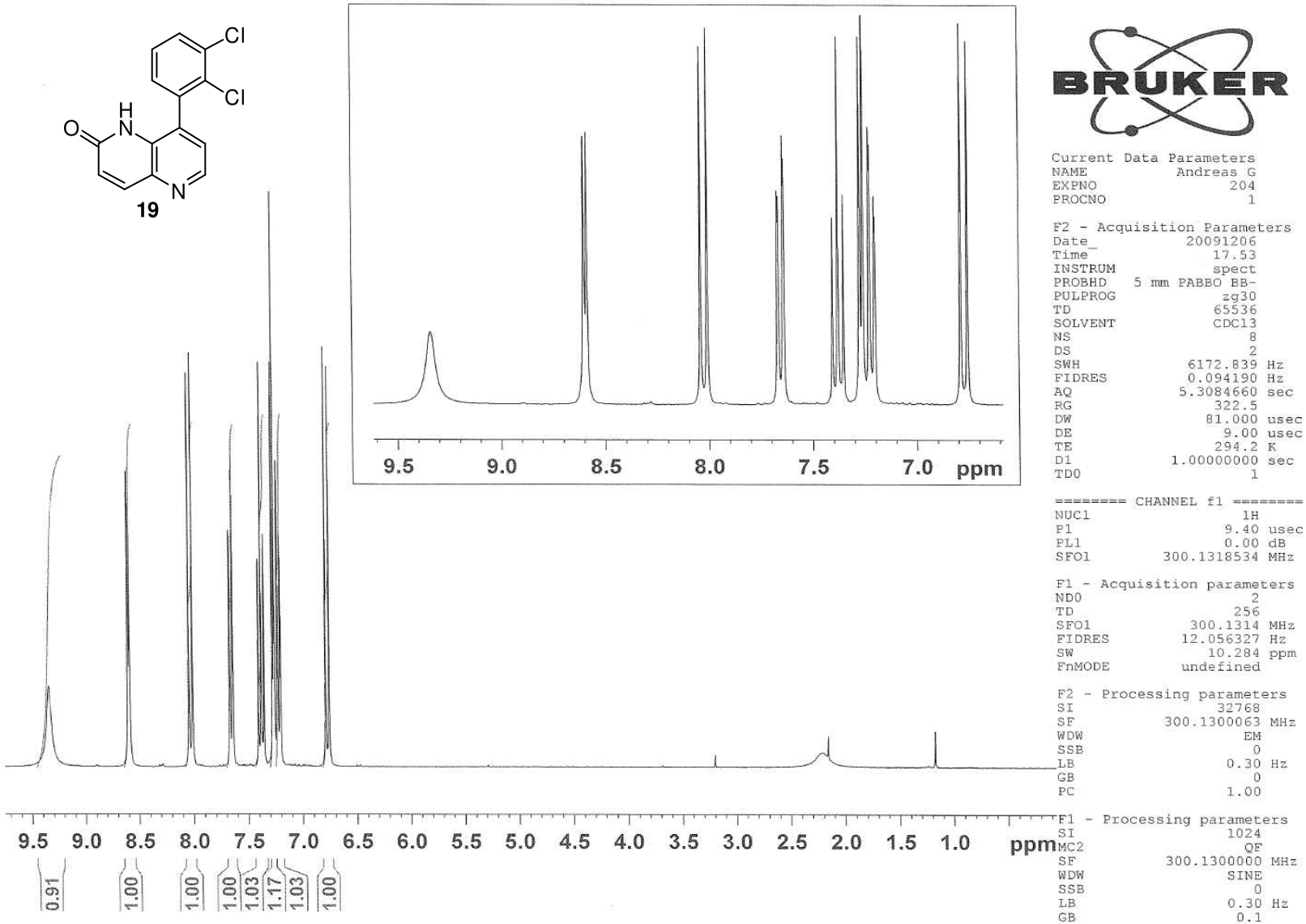
======== CHANNEL f1 ========
NUC1                       1H
P1                      9.40 usec
PL1                     0.00 dB
SFO1           300.1318534 MHz

F1 - Acquisition parameters
ND0                         2
TD                        256
SFO1               300.1314 MHz
FIDRES            12.056327 Hz
SW                    10.284 ppm
FnMODE            undefined

F2 - Processing parameters
SI                      32768
SF             300.1300105 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

F1 - Processing parameters
SI                       1024
MC2                        QF
SF             300.1300000 MHz
WDW                      SINE
SSB                         0
LB                       0.30 Hz
GB                        0.1
```


Current Data Parameters
NAME AndreasG
EXPNO 47
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100104
Time 23.07
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2Cl2
NS 10000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4597.6
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677509 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
MeO
N
N
MeO
18
53.23
55.94
109.16
116.30
121.29
125.77
129.33
129.61
134.03
140.14
140.28
141.50
142.11
147.36
158.15
161.67
ppm



BRUKER

Current Data Parameters
NAME Andreas G
EXPNO 204
PROCNO 1

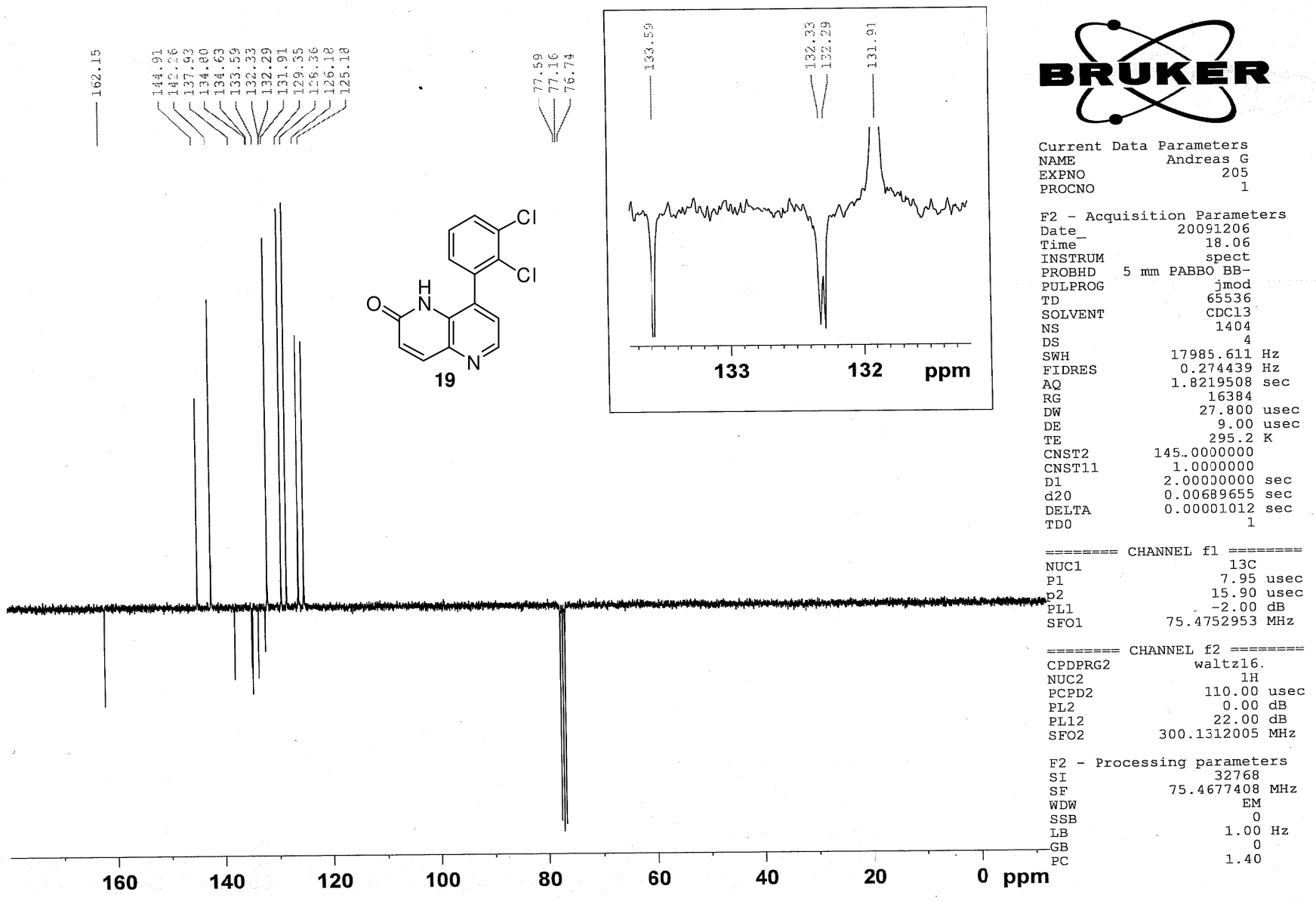
F2 - Acquisition Parameters
Date_ 20091206
Time 17.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 322.5
DW 81.000 usec
DE 9.00 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1

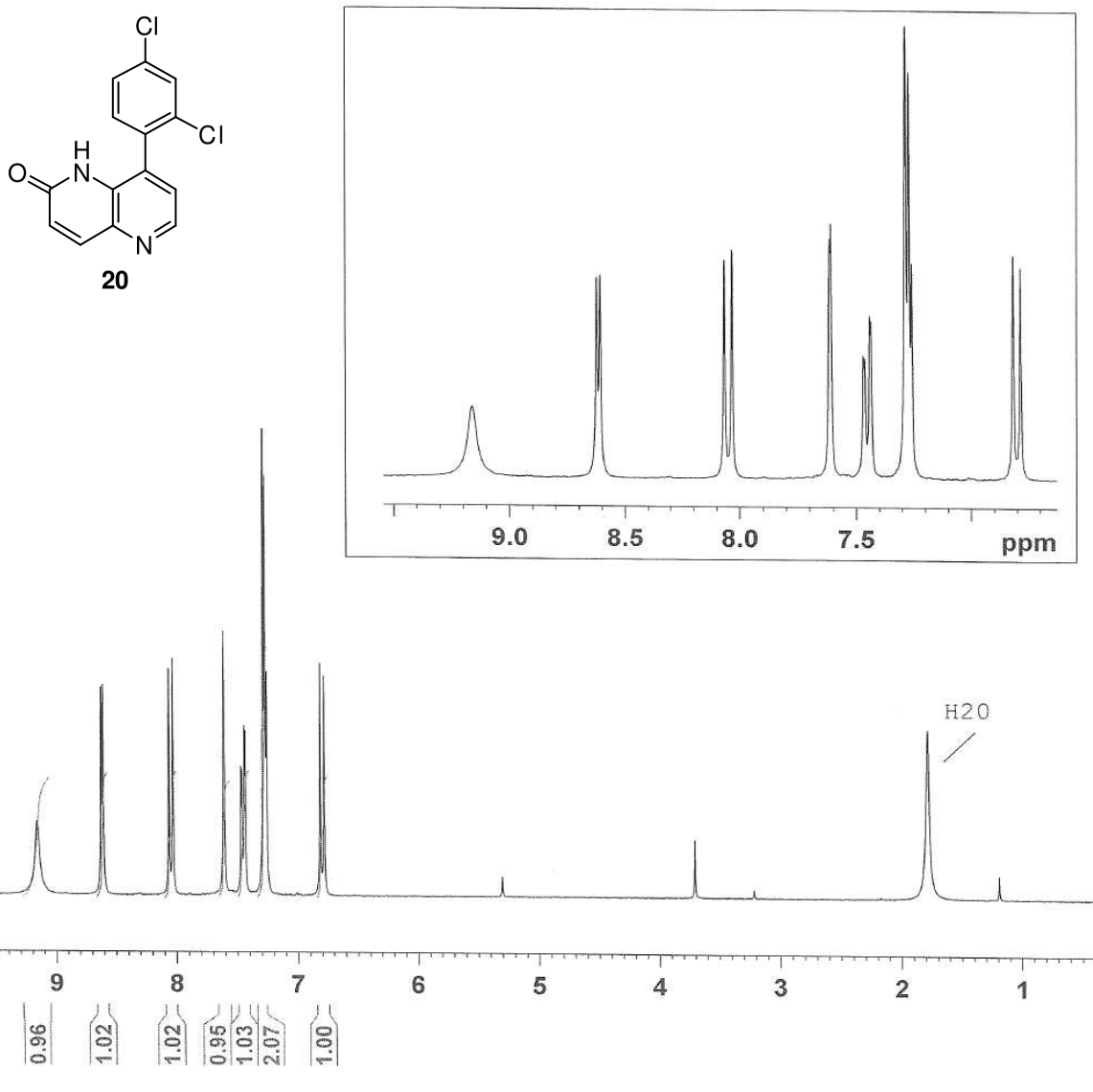
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined

F2 - Processing parameters
SI 32768
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1


162.15
144.91
142.56
137.93
134.80
134.63
133.59
132.33
132.29
131.91
129.35
126.36
126.18
125.18
77.59
77.16
76.74
133.59
132.33
132.29
131.91
133
132
ppm
Cl
Cl
H
N
O
N
19
160
140
120
100
80
60
40
20
0 ppm
BRUKER
Current Data Parameters
NAME Andreas G
EXPNO 205
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091206
Time 18.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 1404
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 295.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16.
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677408 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



BRUKER

```
Current Data Parameters
NAME                  Andreas G
EXPNO                       198
PROCNO                        1

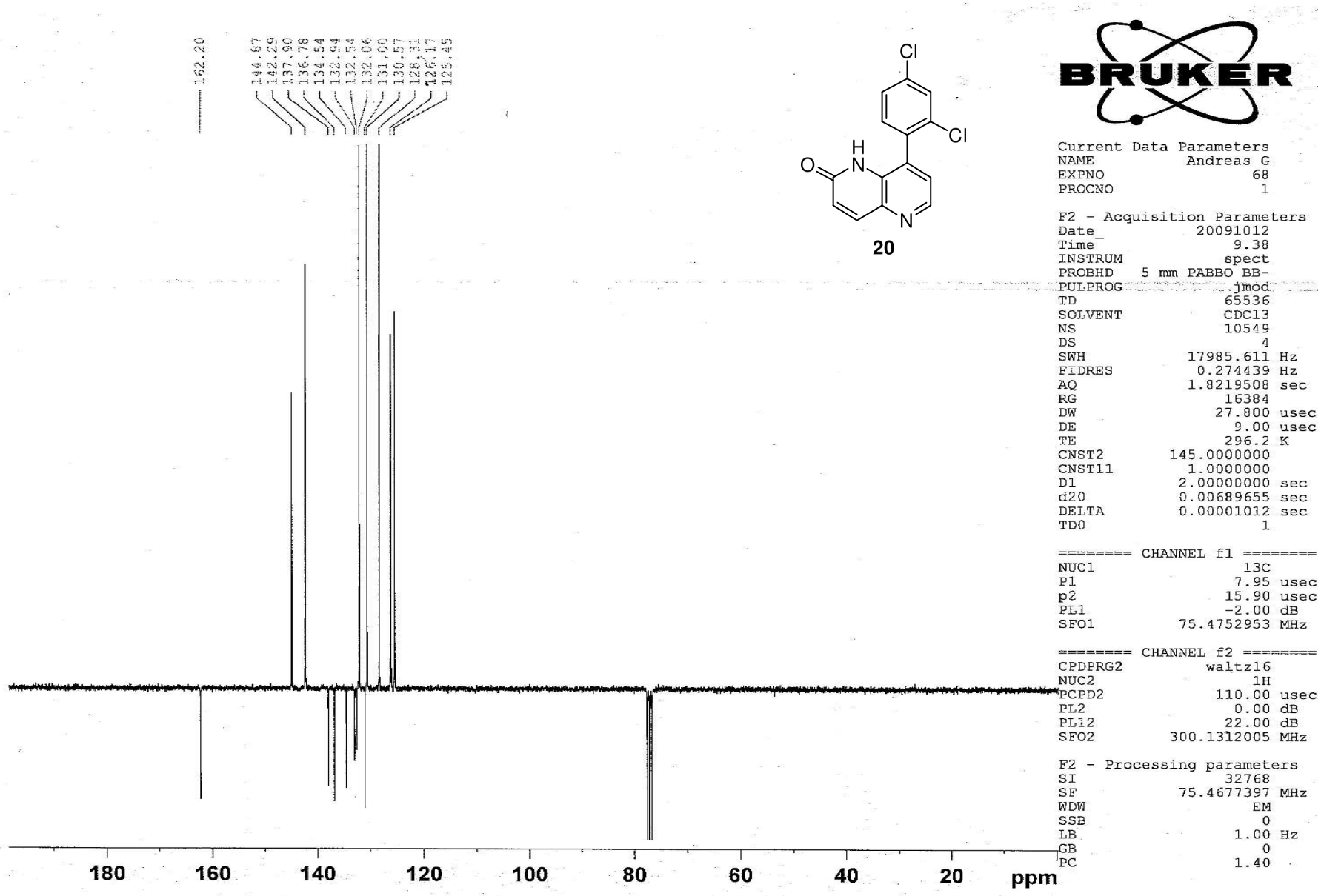
F2 - Acquisition Parameters
Date_                  20091206
Time                      15.20
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                            8
DS                            2
SWH                    6172.839 Hz
FIDRES                 0.094190 Hz
AQ                     5.3084660 sec
RG                        406.4
DW                       81.000 usec
DE                        9.00 usec
TE                       294.2 K
D1                     1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        9.40 usec
PL1                       0.00 dB
SFO1                300.1318534 MHz

F1 - Acquisition parameters
ND0                           2
TD                          256
SFO1                 300.1314 MHz
FIDRES              12.056327 Hz
SW                     10.284 ppm
FnMODE               undefined

F2 - Processing parameters
SI                        32768
SF                  300.1300026 MHz
WDW                          EM
SSB                           0
LB                        0.30 Hz
GB                            0
PC                         1.00

F1 - Processing parameters
SI                         1024
MC2                          QF
SF                  300.1300000 MHz
WDW                        SINE
SSB                           0
LB                        0.30 Hz
GB                         0.1
```



BRUKER

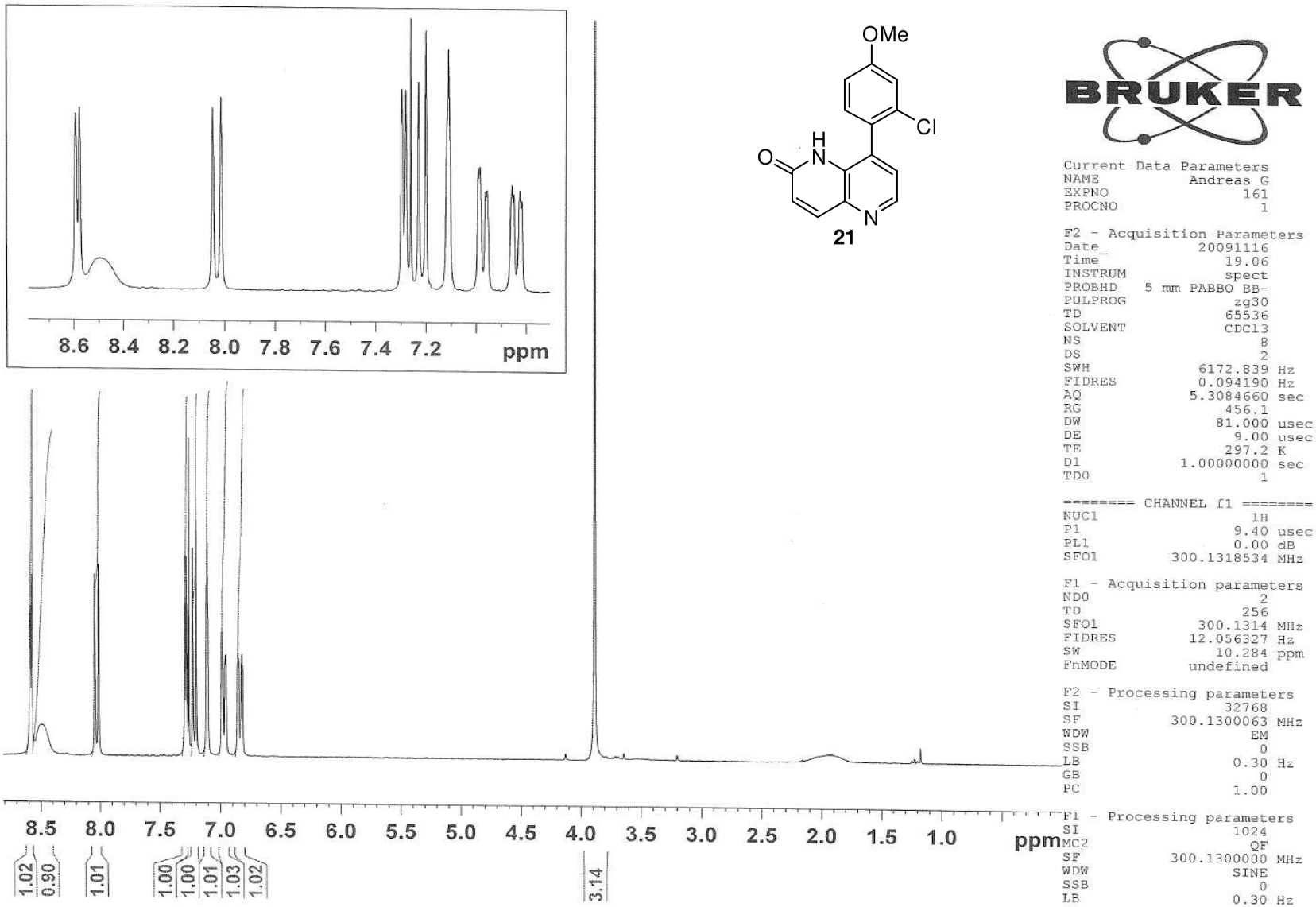
Current Data Parameters
NAME Andreas G
EXPNO 68
PROCNO 1

F2 - Acquisition Parameters
Date_ 20091012
Time 9.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG .jmod
TD 65536
SOLVENT CDCl3
NS 10549
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 296.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677397 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



BRUKER

Current Data Parameters
NAME Andreas G
EXPNO 161
PROCNO 1

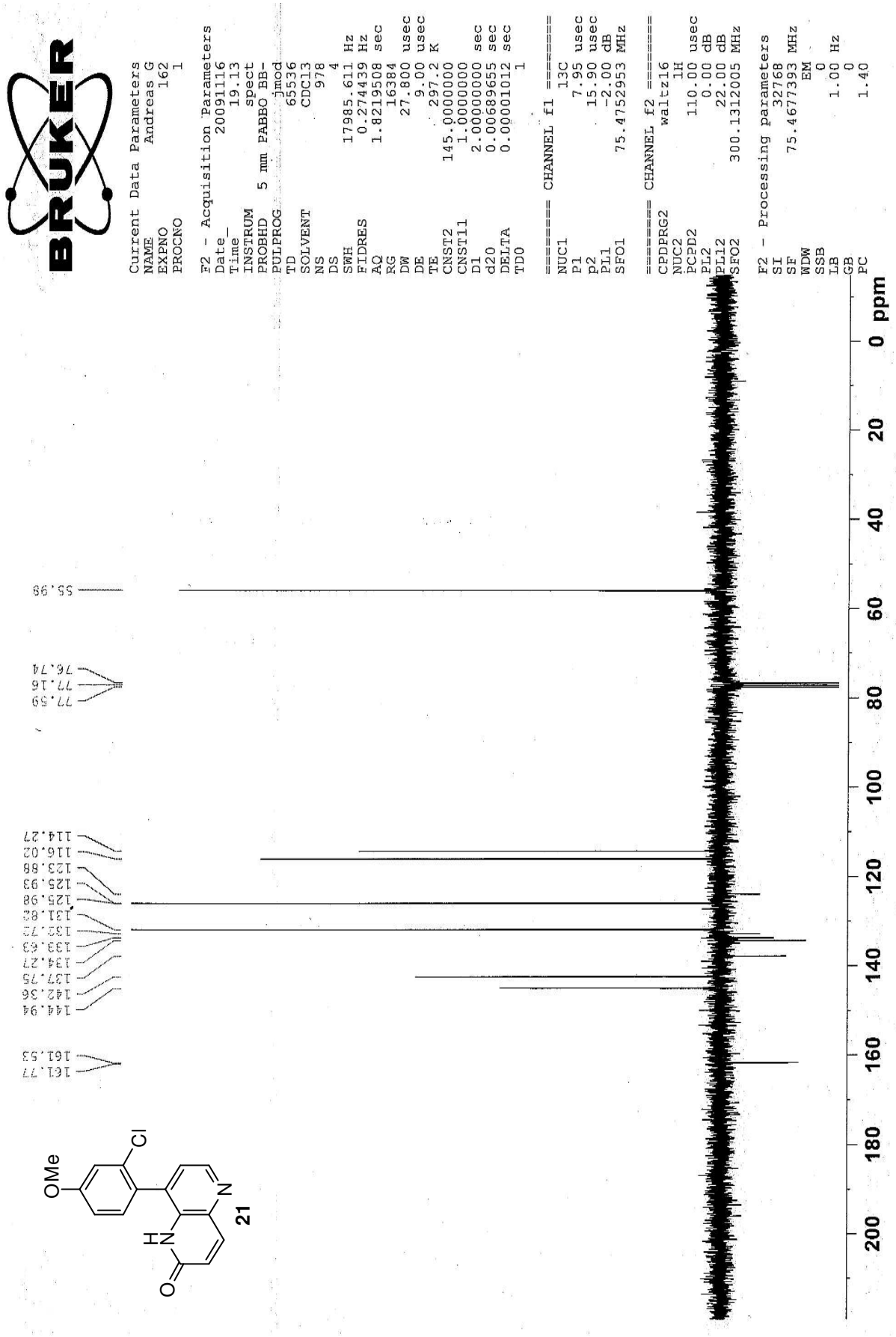
F2 - Acquisition Parameters
Date_ 20091116
Time 19.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 9.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1

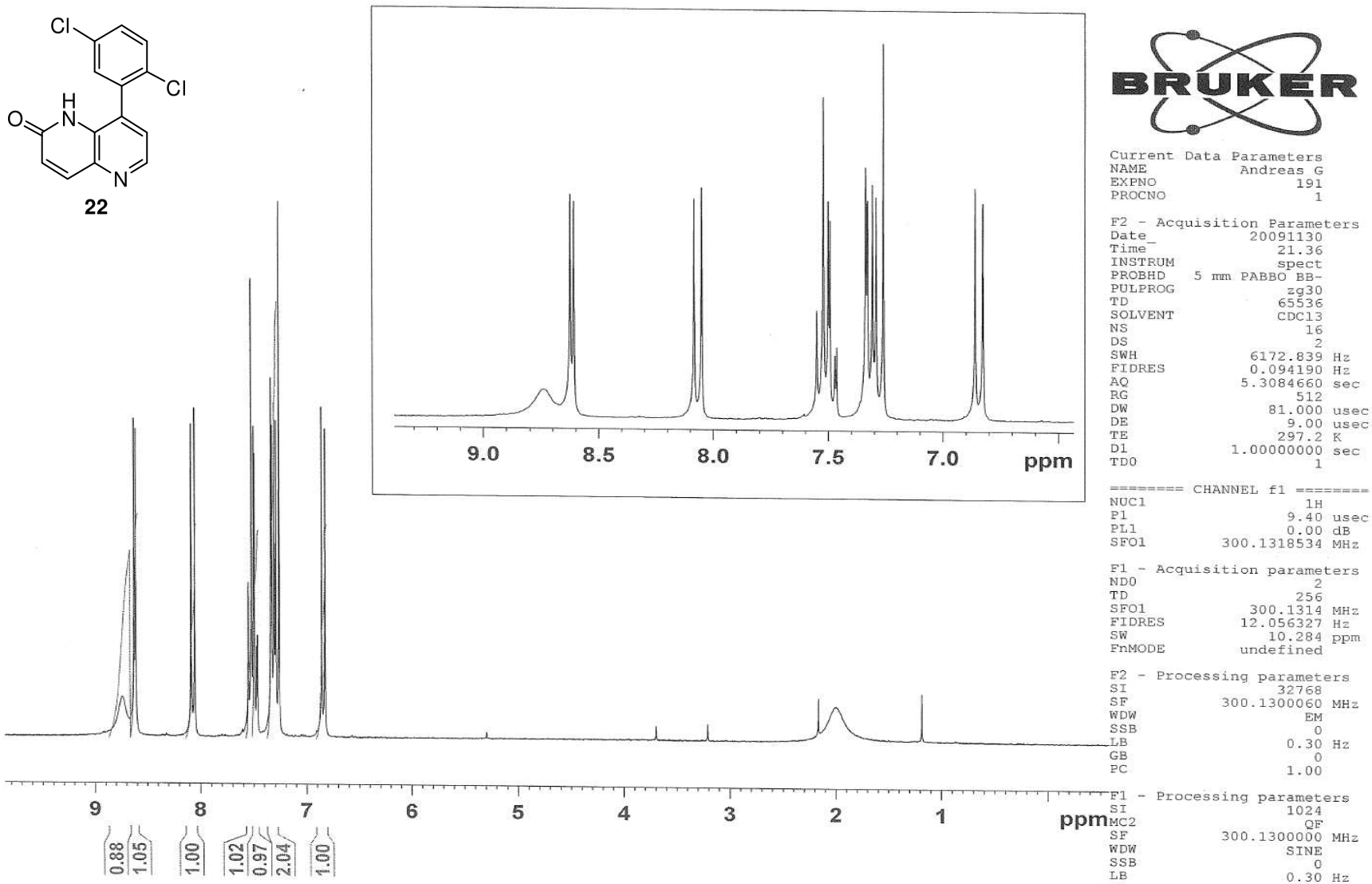
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz

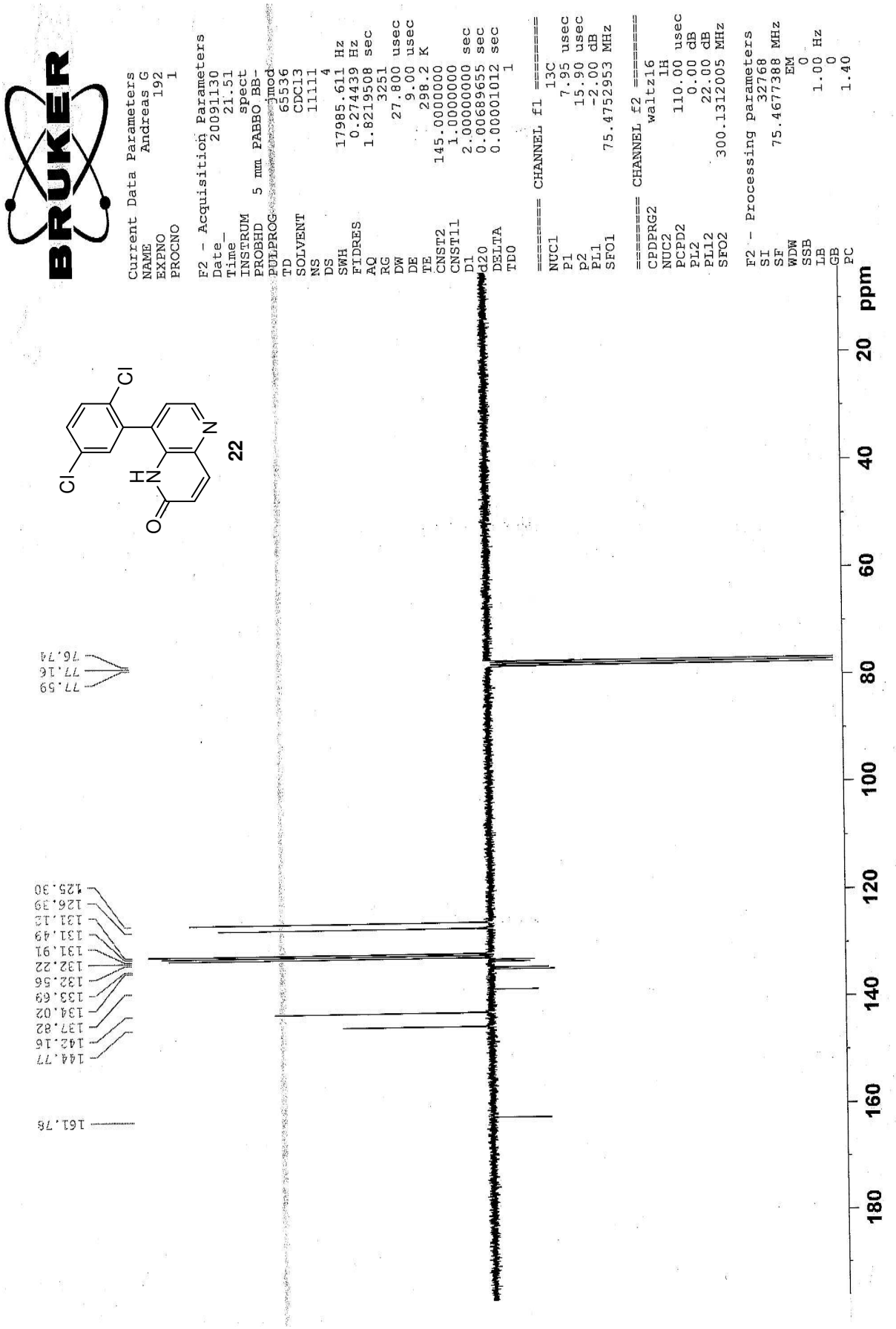
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined

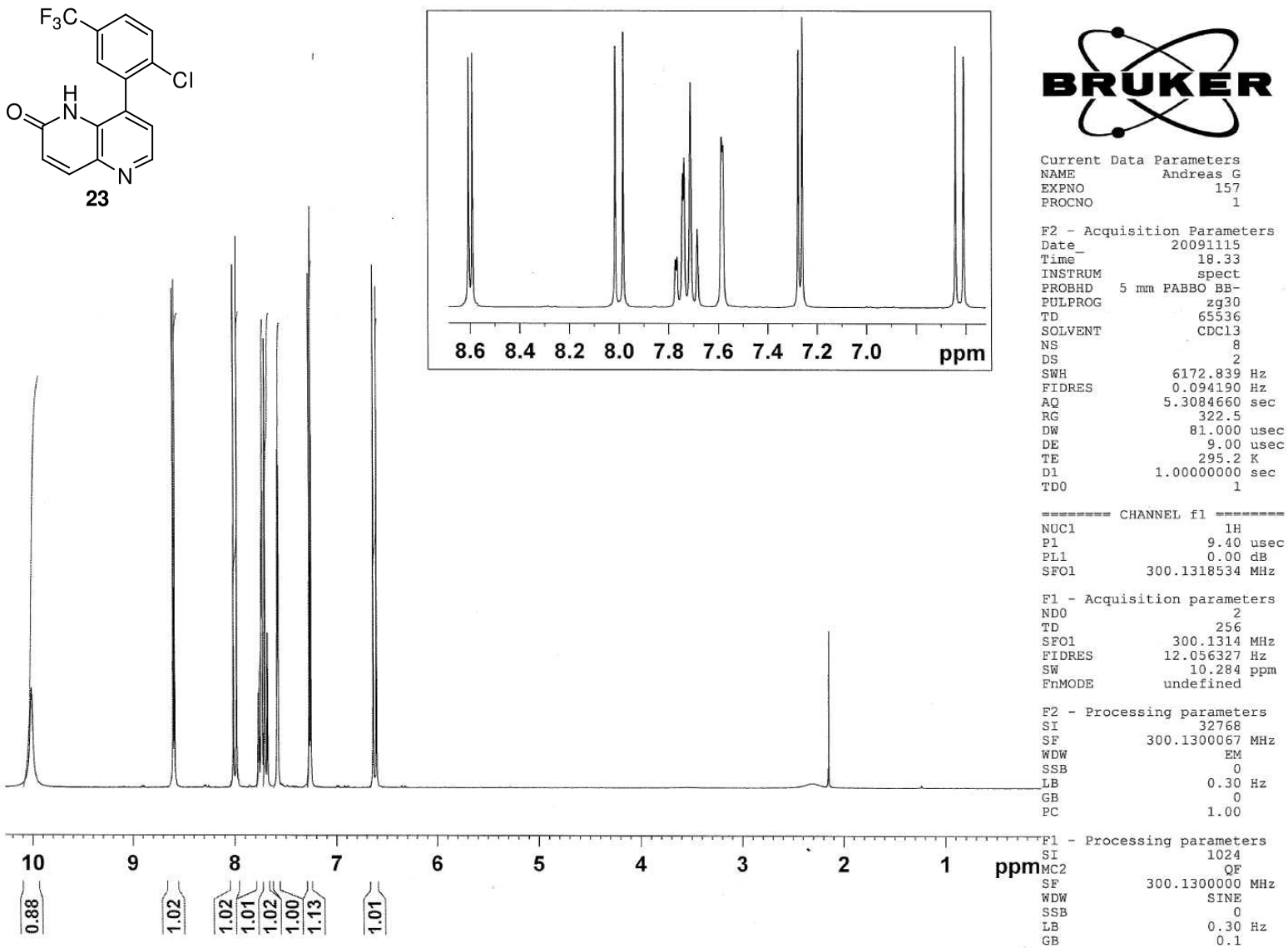
F2 - Processing parameters
SI 32768
SF 300.1300063 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1


Current Data Parameters
NAME Andreas G
EXPNO 162
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091116
Time 19.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 978
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 297.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677393 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
55.98
76.74
77.16
77.59
114.27
116.02
123.88
125.93
125.98
131.82
132.73
133.63
134.27
137.75
142.56
144.94
161.53
161.77
OMe
Cl
N
H
N
O
21
200
180
160
140
120
100
80
60
40
20
0 ppm


Cl
Cl
H
N
O
N
22
9.0
8.5
8.0
7.5
7.0
ppm
9
8
7
6
5
4
3
2
1
ppm
0.88
1.05
1.00
1.02
0.97
2.04
1.00
BRUKER
Current Data Parameters
NAME Andreas G
EXPNO 191
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091130
Time 21.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 512
DW 81.000 usec
DE 9.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300060 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1


Current Data Parameters
NAME Andreas G
EXPNO 192
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091130
Time 21.51
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 11111
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 3251
DW 27.800 usec
DE 9.00 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677388 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
22
ppm
20
40
60
80
100
120
140
160
180
77.59
77.16
76.74
161.76
144.77
142.16
137.82
134.02
133.69
132.56
132.22
131.91
131.49
131.12
126.39
125.30



BRUKER

```
Current Data Parameters
NAME                 Andreas G
EXPNO                      157
PROCNO                       1

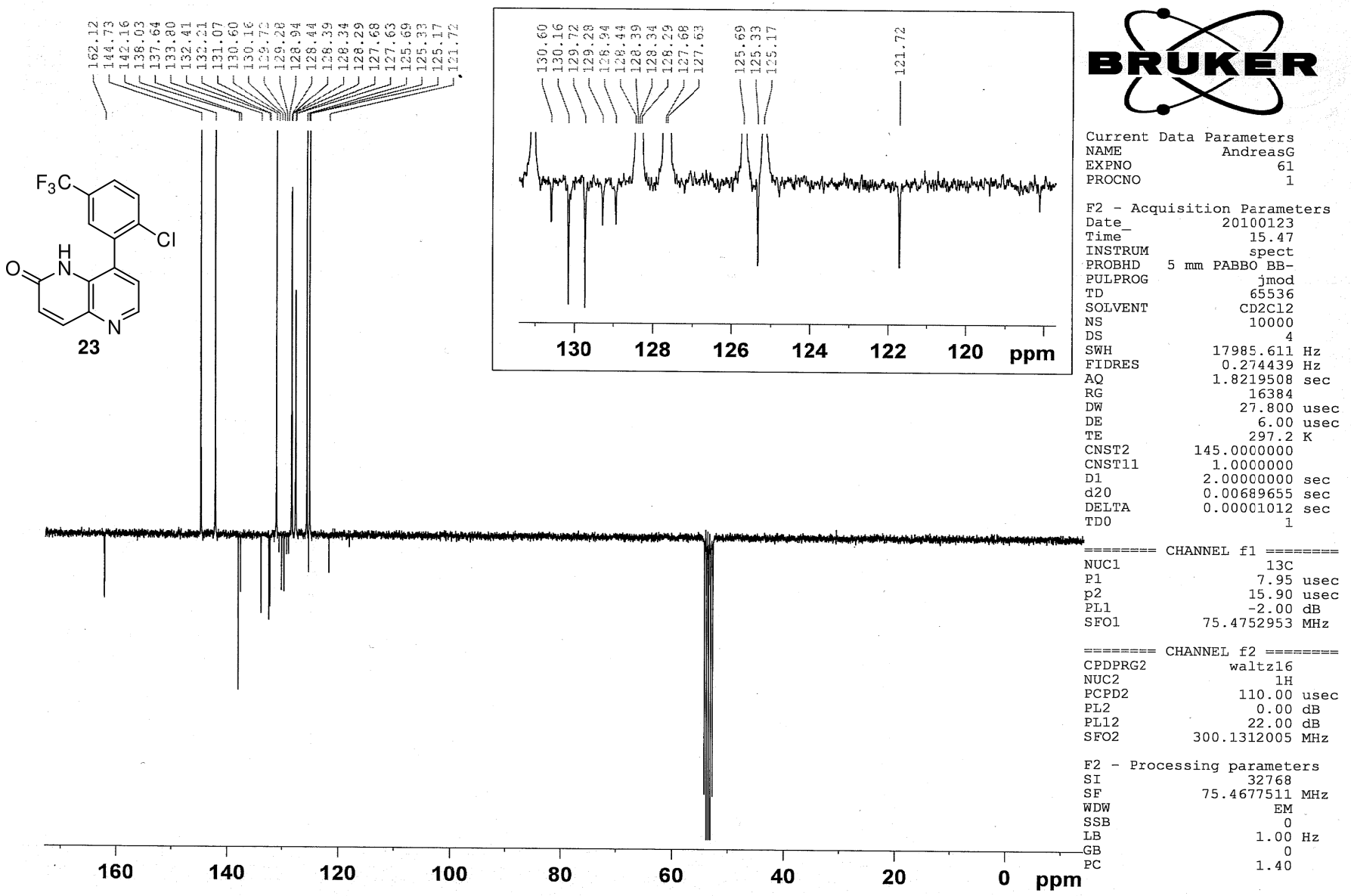
F2 - Acquisition Parameters
Date_               20091115
Time                   18.33
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         2
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                  5.3084660 sec
RG                      322.5
DW                     81.000 usec
DE                      9.00 usec
TE                     295.2 K
D1                  1.00000000 sec
TD0                        1

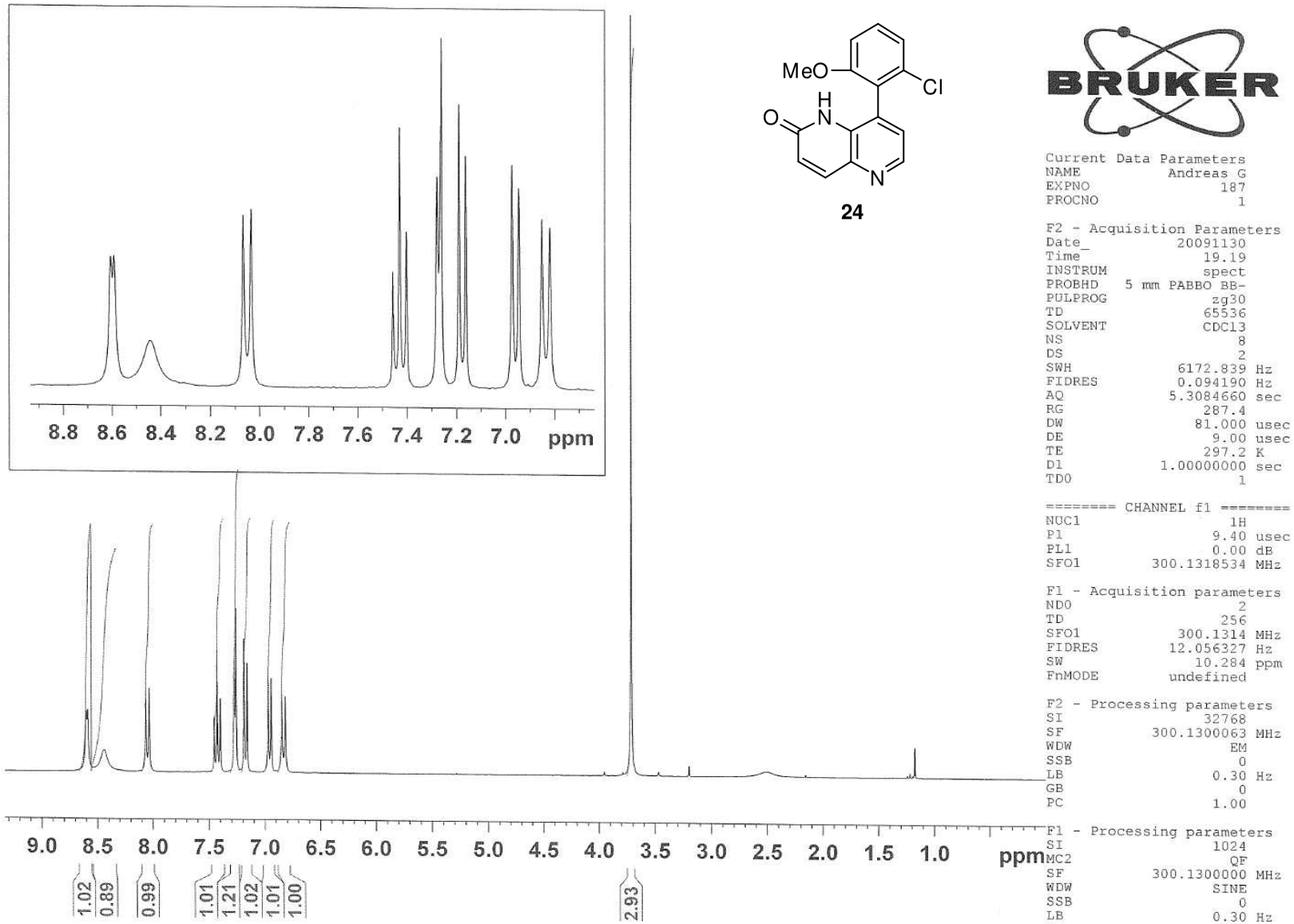
======== CHANNEL f1 ========
NUC1                       1H
P1                      9.40 usec
PL1                     0.00 dB
SFO1             300.1318534 MHz

F1 - Acquisition parameters
ND0                        2
TD                       256
SFO1                300.1314 MHz
FIDRES              12.056327 Hz
SW                     10.284 ppm
FnMODE               undefined

F2 - Processing parameters
SI                       32768
SF               300.1300067 MHz
WDW                         EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

F1 - Processing parameters
SI                        1024
MC2                         QF
SF               300.1300000 MHz
WDW                       SINE
SSB                         0
LB                       0.30 Hz
GB                        0.1
```


162.12
144.73
142.16
136.03
137.64
133.80
132.41
132.21
131.07
130.60
130.16
129.72
129.28
128.94
128.44
128.39
128.34
128.29
127.68
127.63
125.69
125.33
125.17
121.72
F3C
Cl
H
N
O
N
23
130.60
130.16
129.72
129.28
128.94
128.44
128.39
128.34
128.29
127.68
127.63
125.69
125.33
125.17
121.72
130
128
126
124
122
120
ppm
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME AndreasG
EXPNO 61
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100123
Time 15.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2Cl2
NS 10000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 6.00 usec
TE 297.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677511 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



BRUKER

```
Current Data Parameters
NAME                 Andreas G
EXPNO                      187
PROCNO                       1

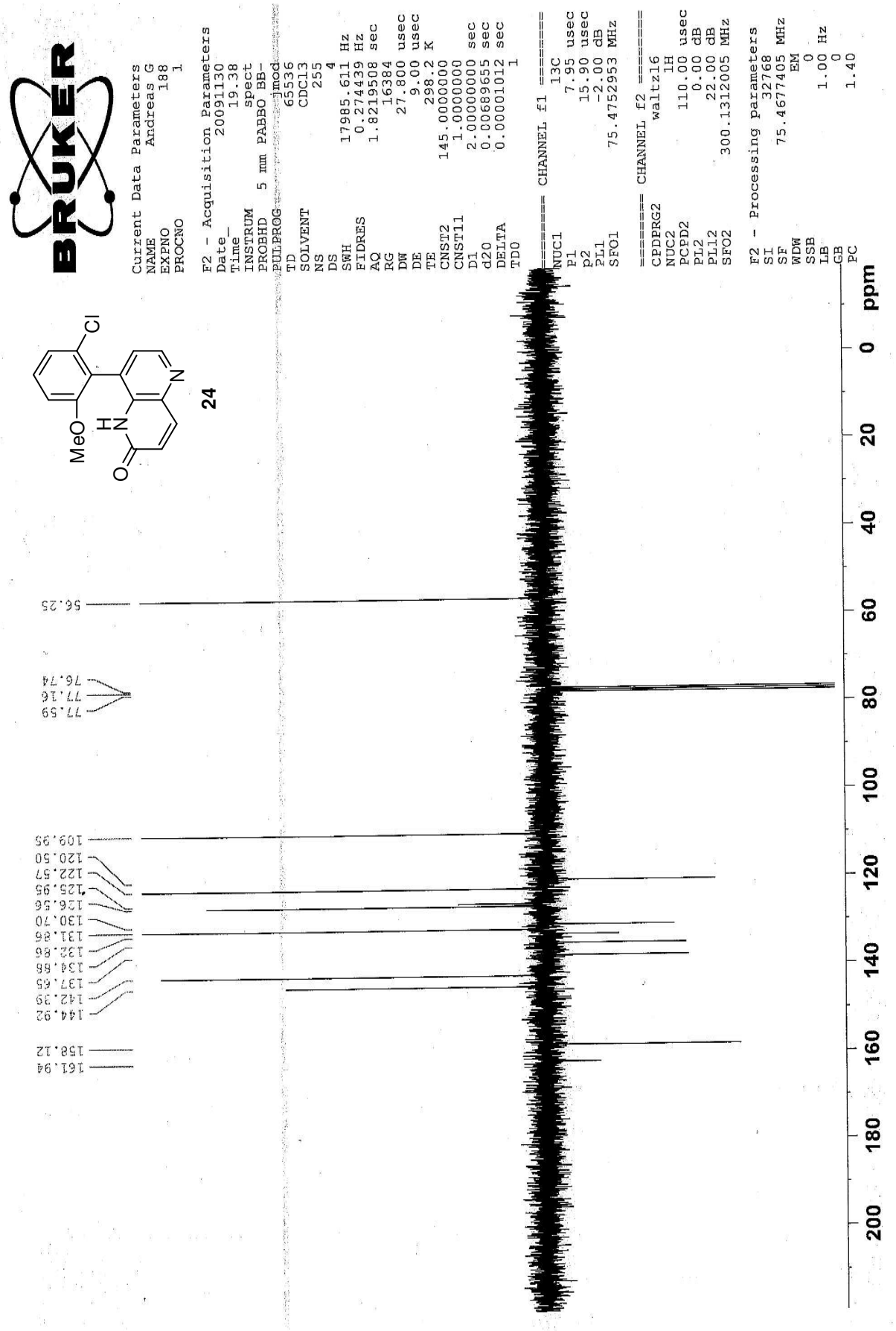
F2 - Acquisition Parameters
Date_               20091130
Time                     19.19
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          8
DS                          2
SWH                  6172.839 Hz
FIDRES               0.094190 Hz
AQ                   5.3084660 sec
RG                       287.4
DW                      81.000 usec
DE                       9.00 usec
TE                      297.2 K
D1                   1.00000000 sec
TD0                          1

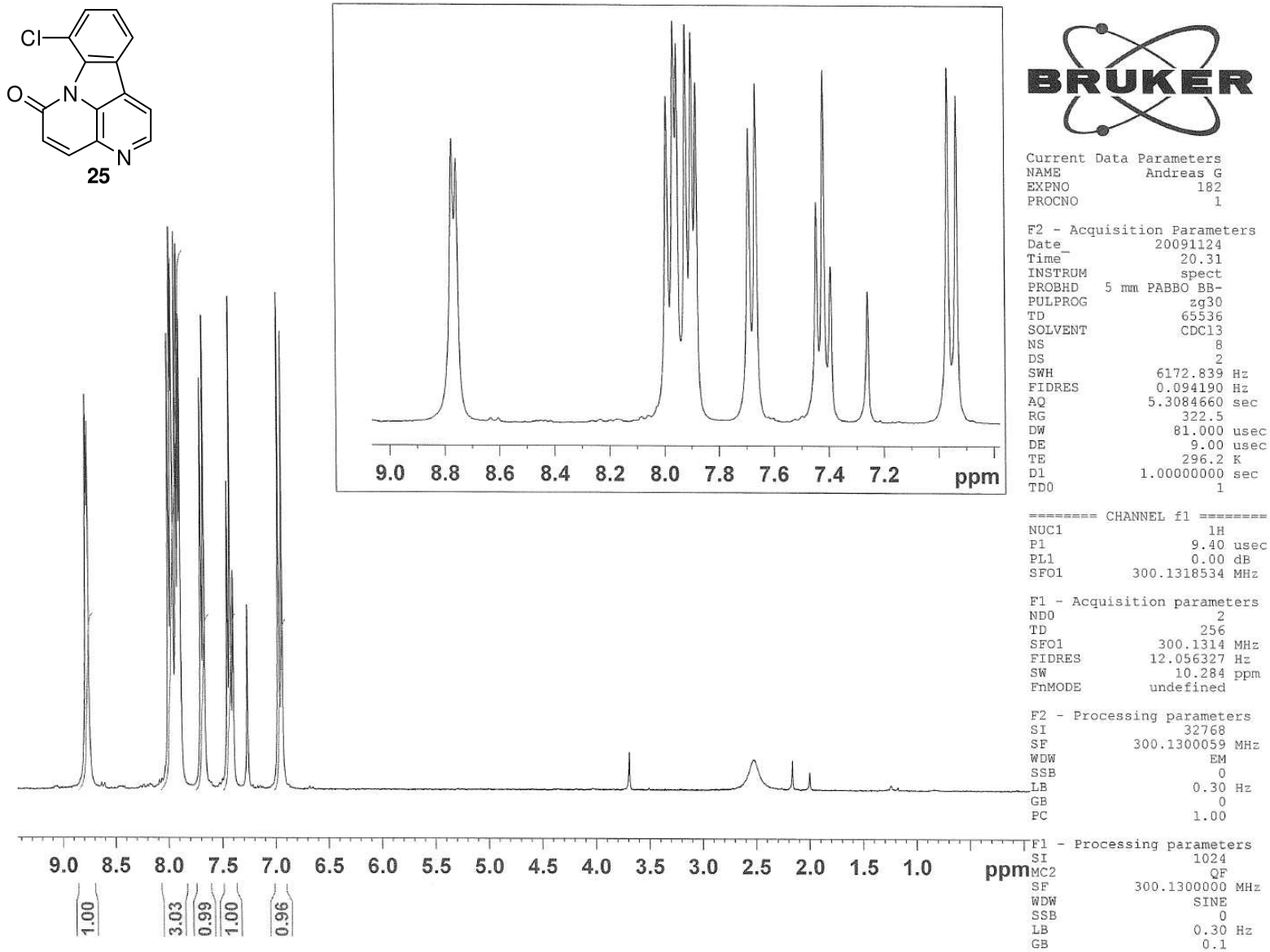
======== CHANNEL f1 ========
NUC1                        1H
P1                       9.40 usec
PL1                      0.00 dB
SFO1                300.1318534 MHz

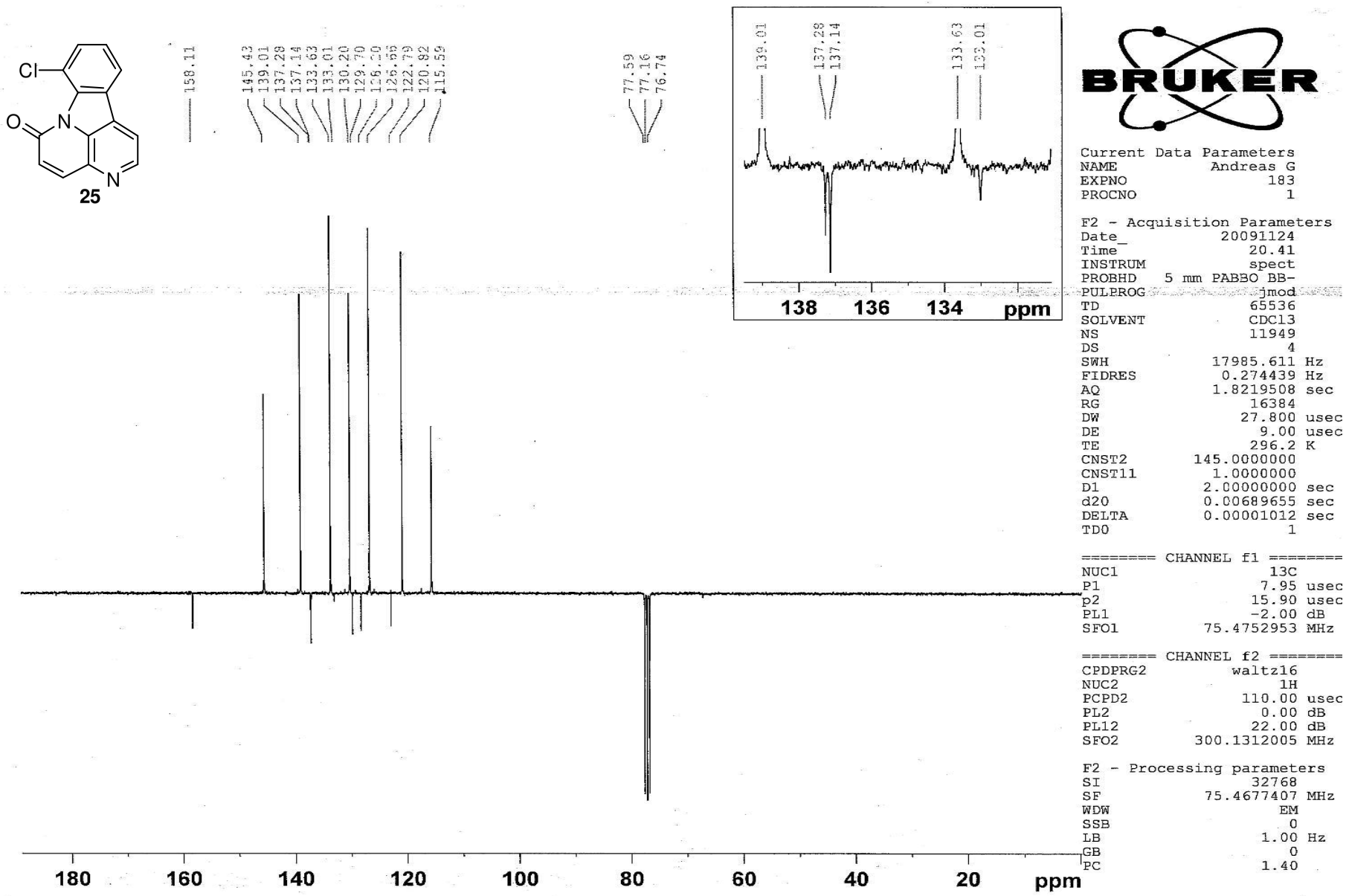
F1 - Acquisition parameters
ND0                          2
TD                         256
SFO1                300.1314 MHz
FIDRES               12.056327 Hz
SW                       10.284 ppm
FnMODE                 undefined

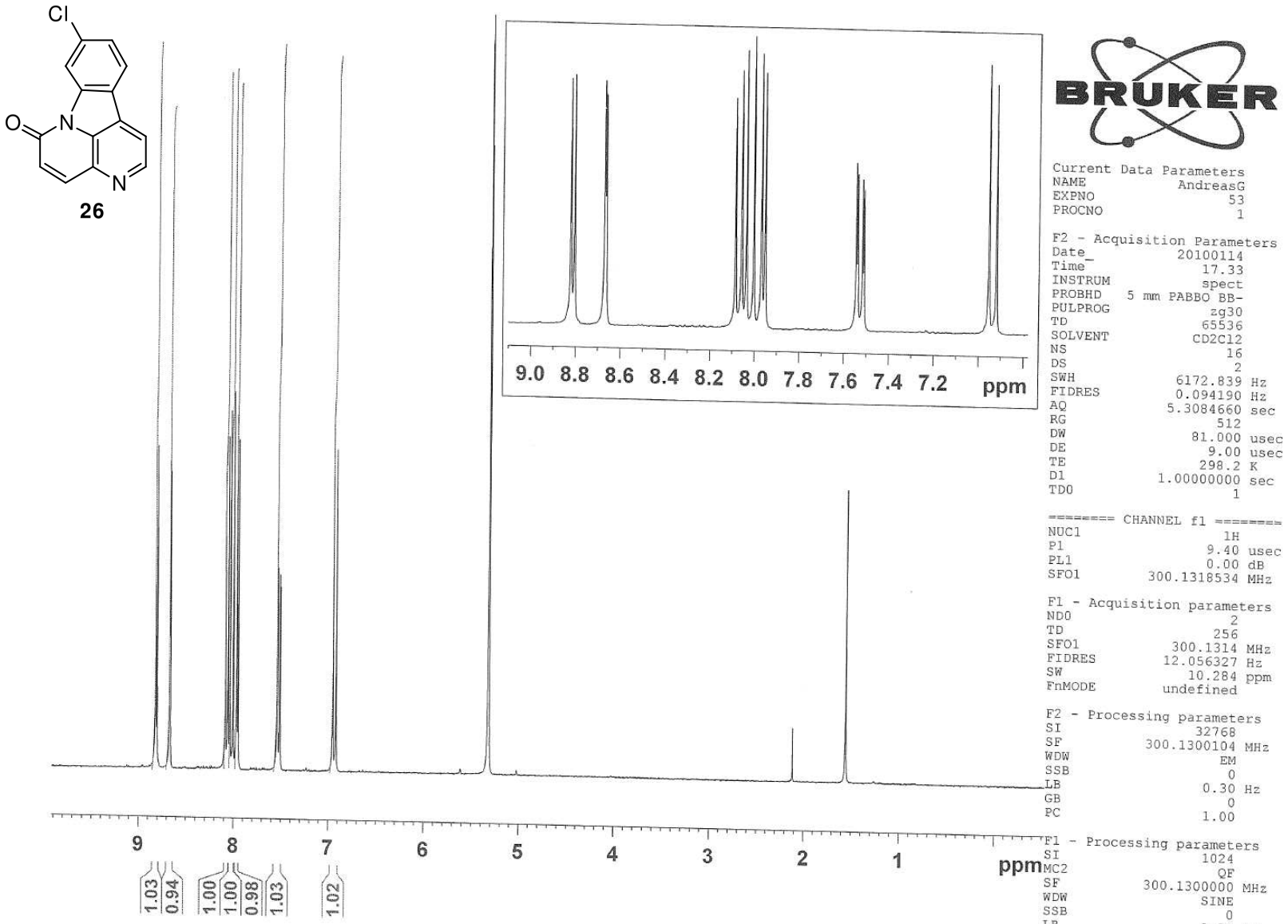
F2 - Processing parameters
SI                       32768
SF                  300.1300063 MHz
WDW                         EM
SSB                          0
LB                       0.30 Hz
GB                           0
PC                       1.00

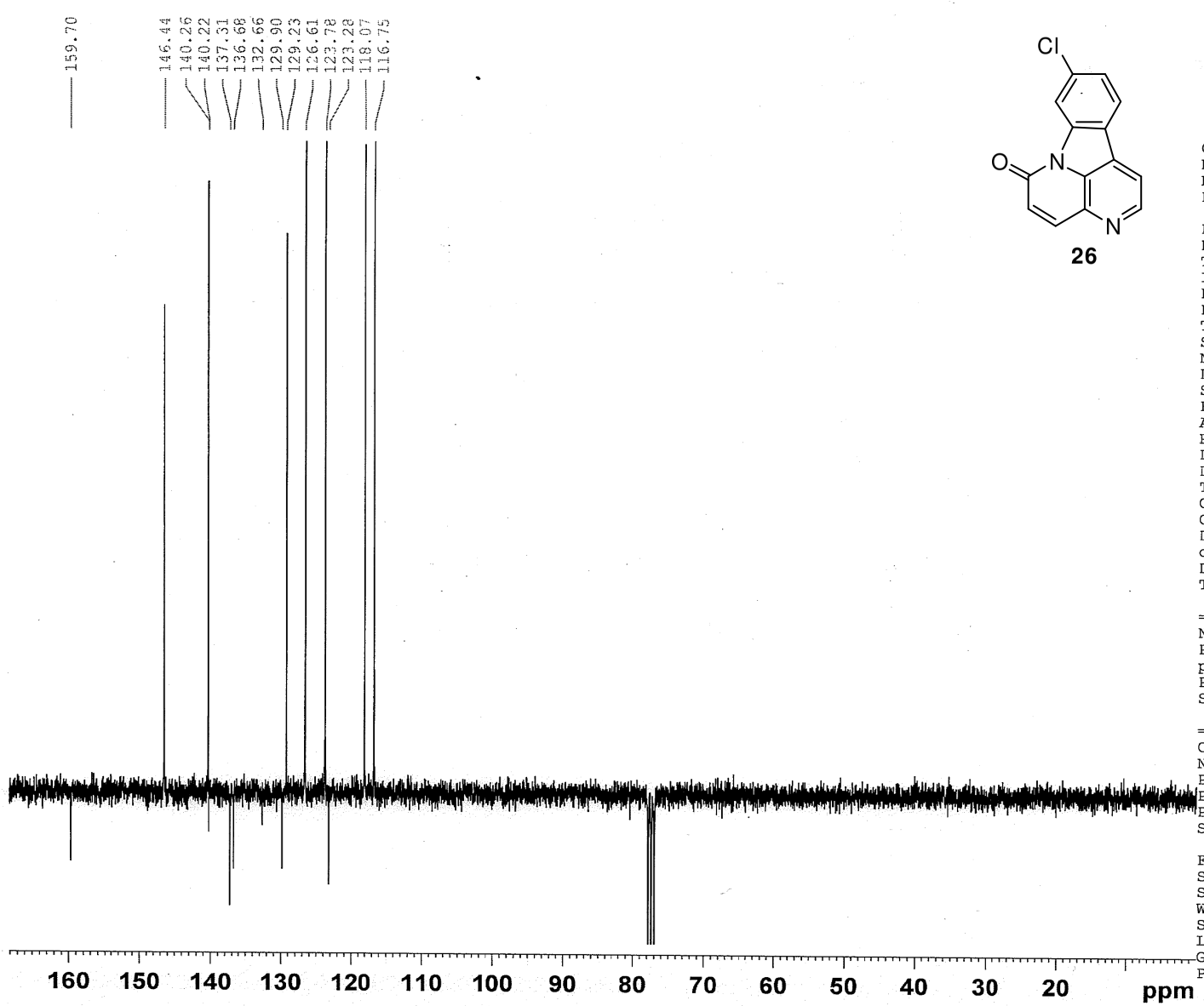
F1 - Processing parameters
SI                        1024
MC2                         QF
SF                  300.1300000 MHz
WDW                       SINE
SSB                          0
LB                       0.30 Hz
GB                        0.1
```


BRUKER
Current Data Parameters
NAME Andreas G
EXPNO 188
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091130
Time_ 19.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 255
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.82195508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.00000000
D1 2.000000000 sec
d20 0.00689655 sec
DELTA 0.000001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677405 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
24
Cl
MeO
N
H
O
56.25
76.74
77.16
77.59
109.95
120.50
122.57
125.95
126.56
130.70
131.86
132.86
134.86
137.65
142.39
144.92
158.12
161.94
ppm
0
20
40
60
80
100
120
140
160
180
200


Cl
O
N
N
25
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
3.03
0.99
1.00
0.96
BRUKER
Current Data Parameters
NAME Andreas G
EXPNO 182
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091124
Time 20.31
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 322.5
DW 81.000 usec
DE 9.00 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1


Cl
O
N
N
25
158.11
145.43
139.01
137.28
137.14
133.63
133.01
130.20
129.70
126.50
126.05
122.79
120.82
115.59
77.59
77.16
76.74
139.01
137.28
137.14
133.63
133.01
138
136
134
ppm
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME Andreas G
EXPNO 183
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091124
Time 20.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 11949
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 296.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677407 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


Cl
O
N
N
26
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9 8 7 6 5 4 3 2 1 ppm
1.03 0.94 1.00 1.00 0.98 1.03 1.02
BRUKER
Current Data Parameters
NAME AndreasG
EXPNO 53
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100114
Time 17.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 512
DW 81.000 usec
DE 9.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300104 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1



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BRUKER

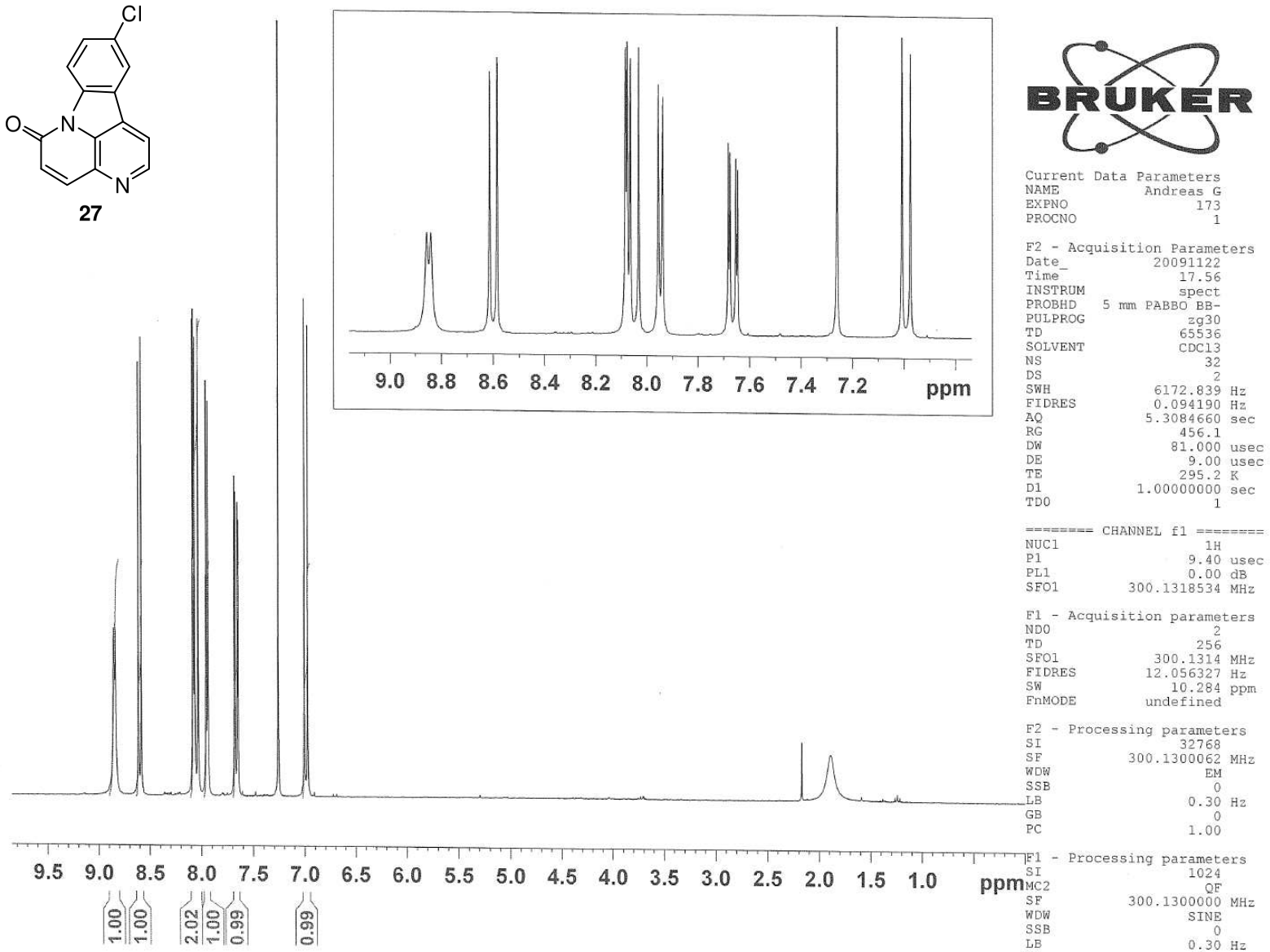
Current Data Parameters
NAME Andreas G
EXPNO 140
PROCNO 1

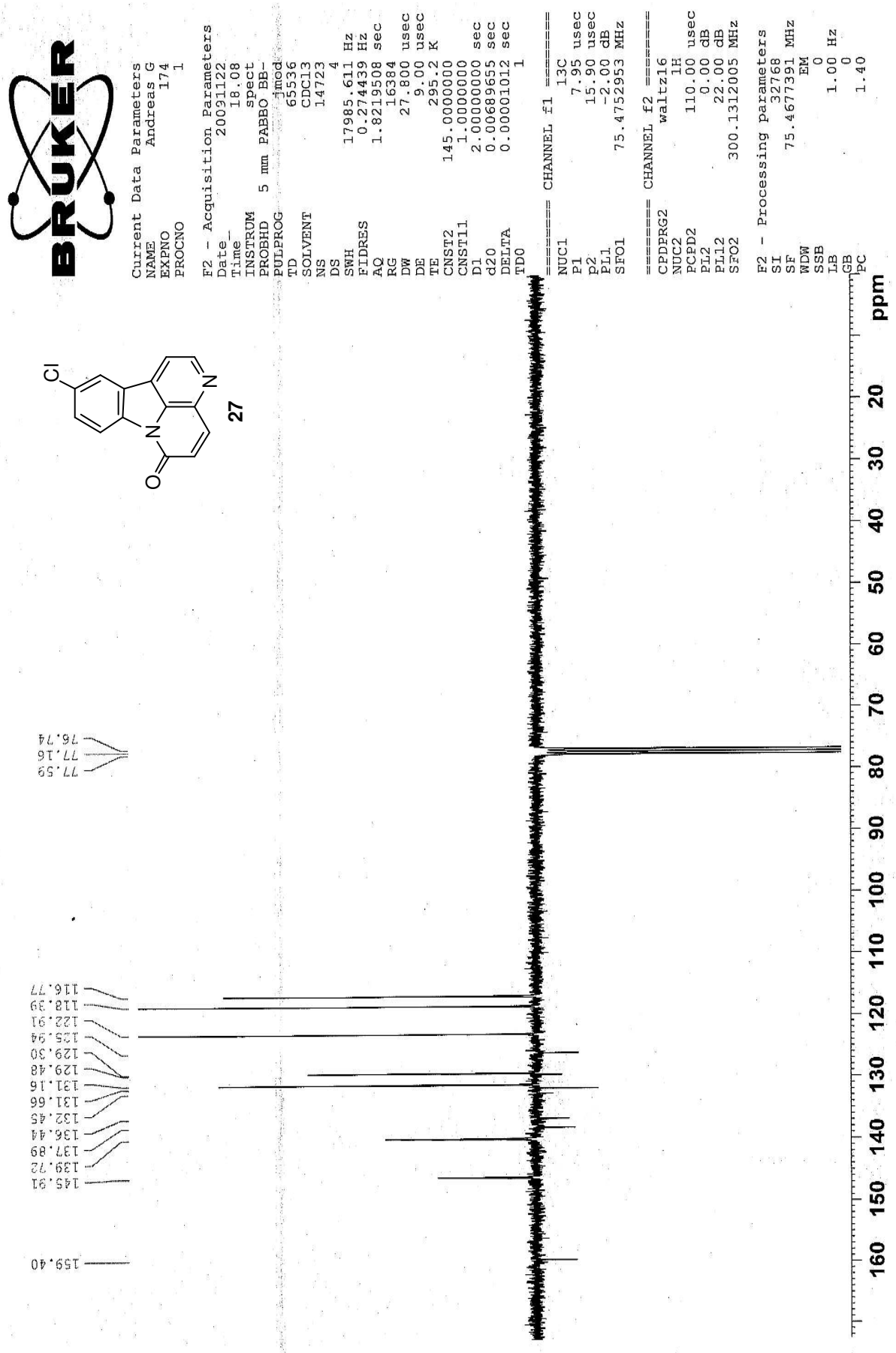
F2 - Acquisition Parameters
Date_ 20091114
Time 15.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 2437
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 4096
DW 27.800 usec
DE 9.00 usec
TE 297.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1

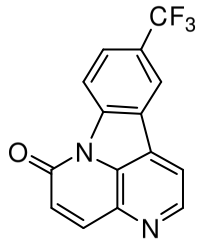
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


Cl
O
N
N
27
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00
1.00
2.02
1.00
0.99
0.99
BRUKER
Current Data Parameters
NAME Andreas G
EXPNO 173
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091122
Time 17.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 9.00 usec
TE 295.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300062 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1


Current Data Parameters
NAME Andreas G
EXPNO 174
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091122
Time 18.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 14723
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 9.00 usec
TE 295.2 K
CNST2 145.0000000
CNST11 1.00000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
P2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677391 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Cl
N
N
O
27
159.40
145.91
139.72
137.89
136.44
132.45
131.66
131.16
129.48
129.30
125.94
122.91
118.39
116.77
77.59
77.16
76.74
ppm



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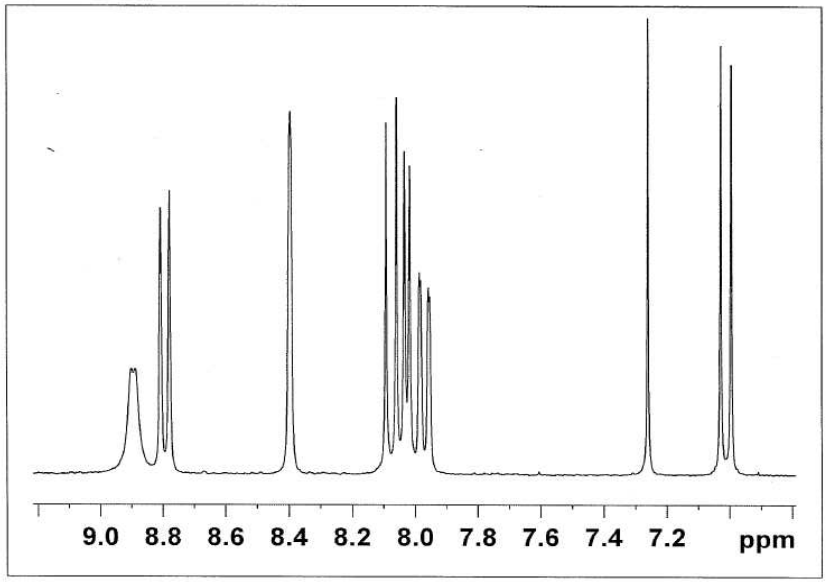
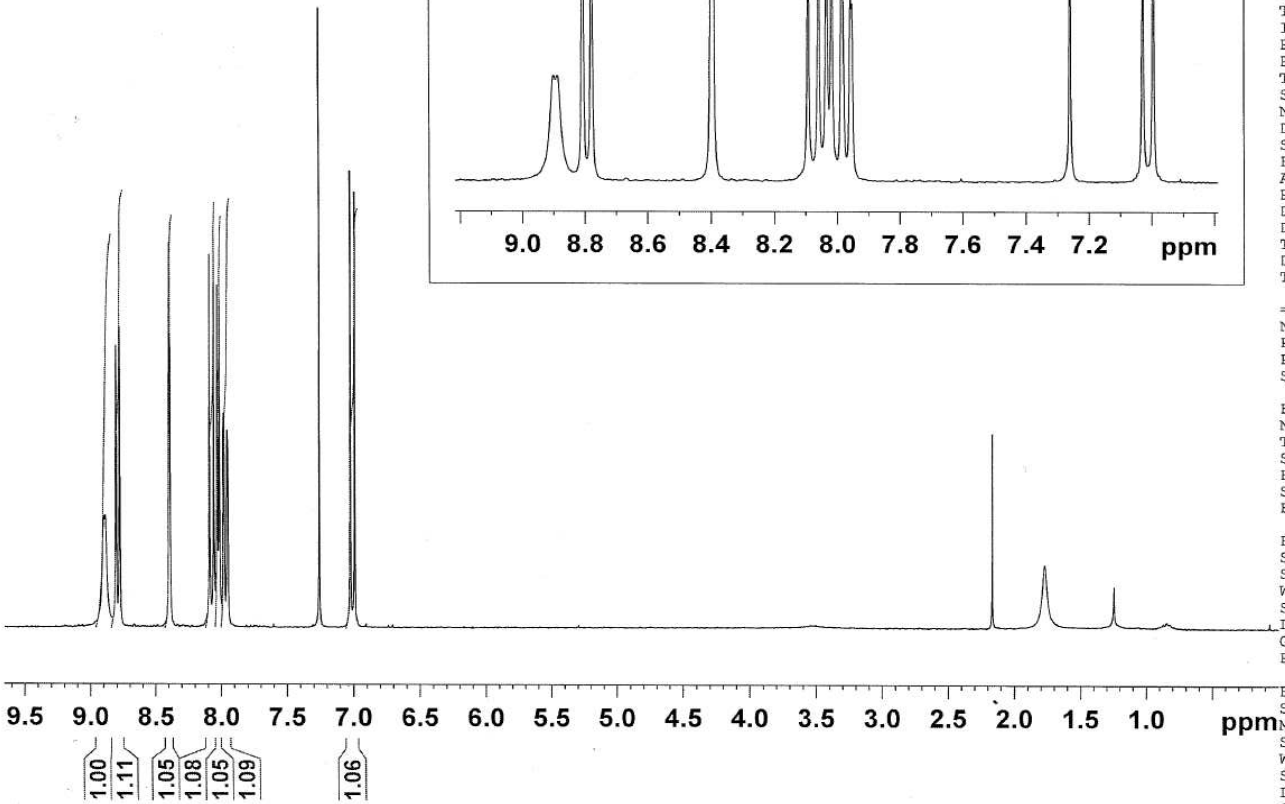




BRUKER

```
Current Data Parameters
NAME                 Andreas G
EXPNO                      163
PROCNO                       1

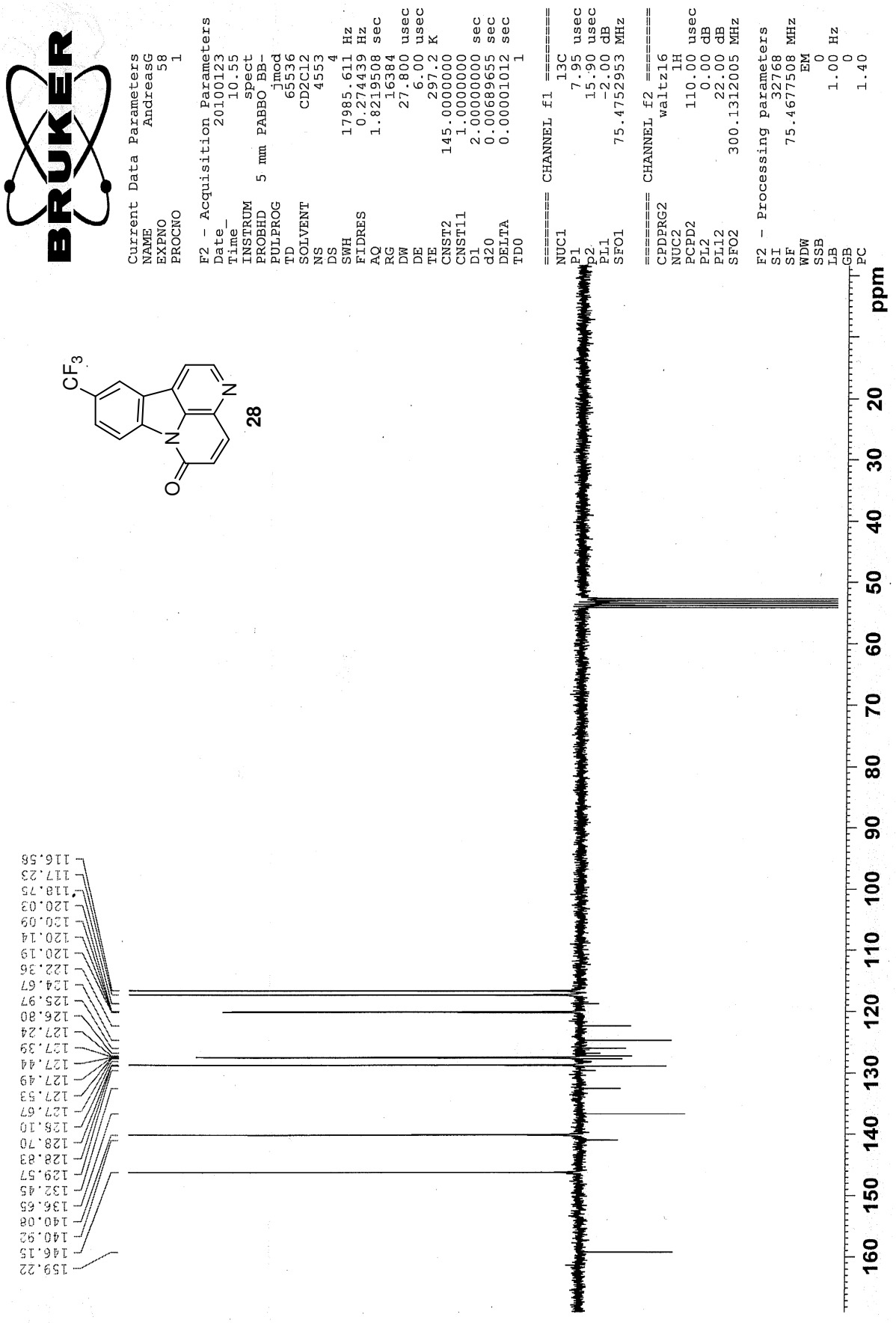
F2 - Acquisition Parameters
Date_                 20091116
Time                     20.22
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  6172.839 Hz
FIDRES               0.094190 Hz
AQ                   5.3084660 sec
RG                       574.7
DW                      81.000 usec
DE                       9.00 usec
TE                      297.2 K
D1                   1.00000000 sec
TD0                          1

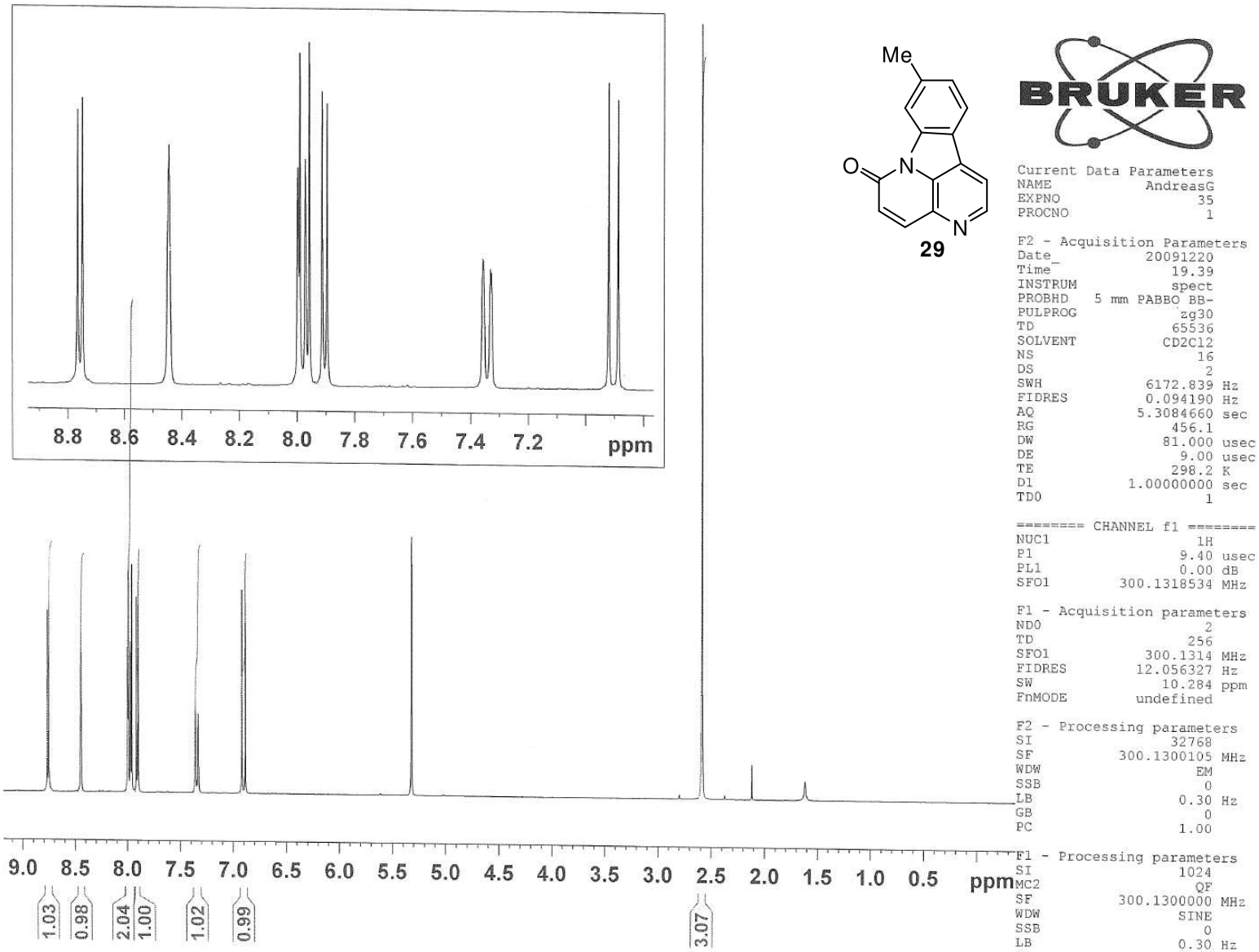
======== CHANNEL f1 ========
NUC1                        1H
P1                       9.40 usec
PL1                      0.00 dB
SFO1           300.1318534 MHz

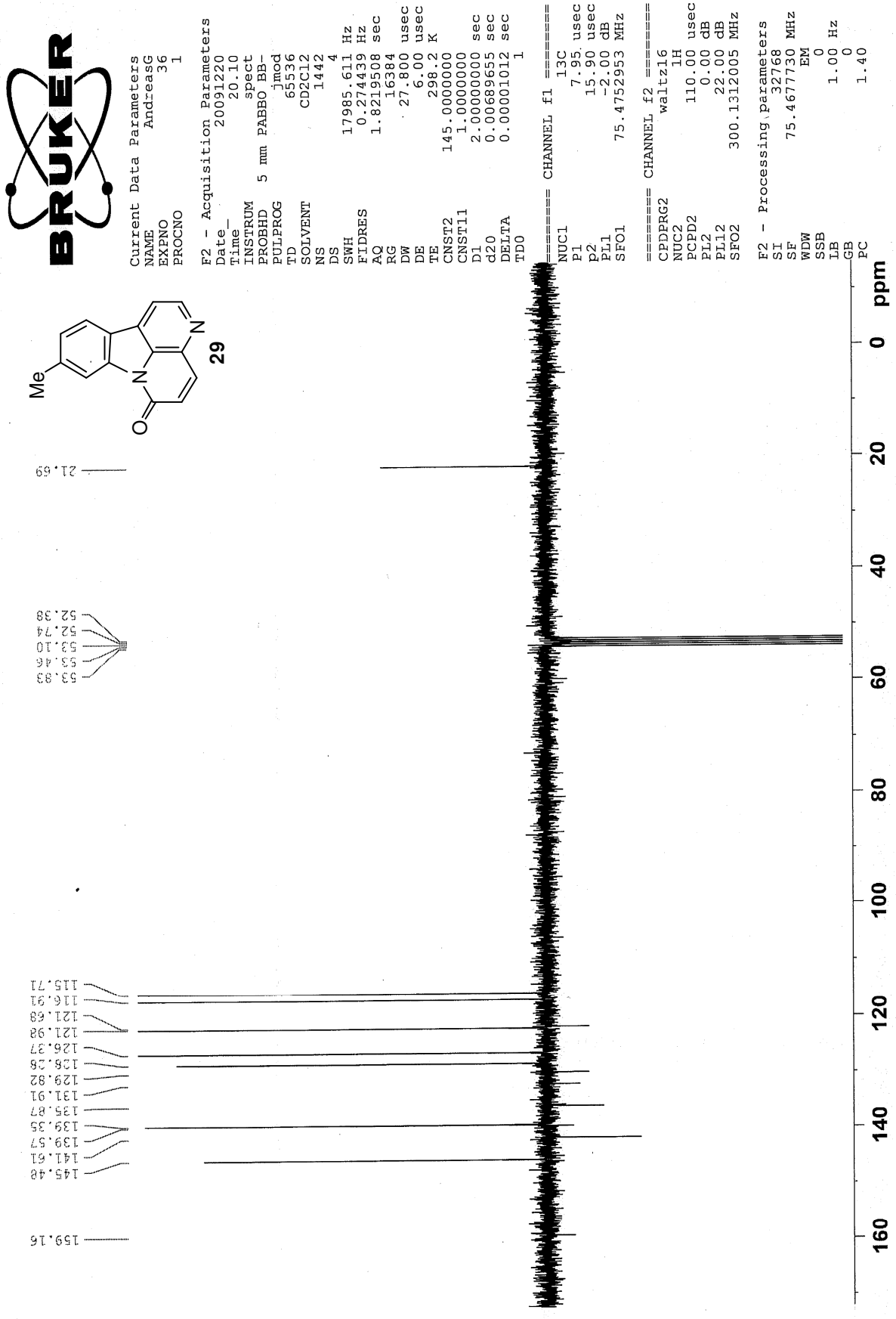
F1 - Acquisition parameters
ND0                          2
TD                         256
SFO1             300.1314 MHz
FIDRES           12.056327 Hz
SW                   10.284 ppm
FnMODE           undefined

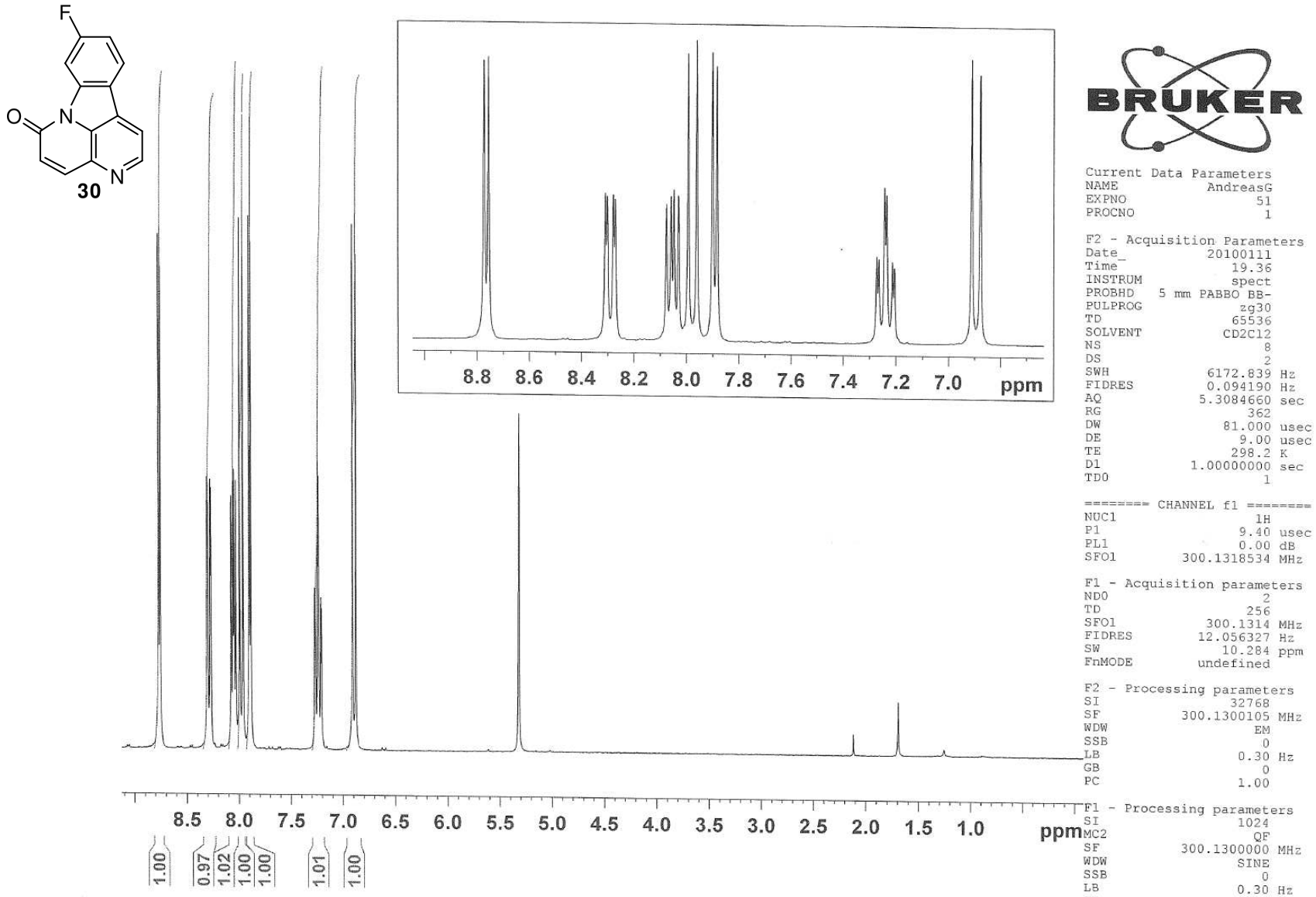
F2 - Processing parameters
SI                       32768
SF             300.1300061 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00

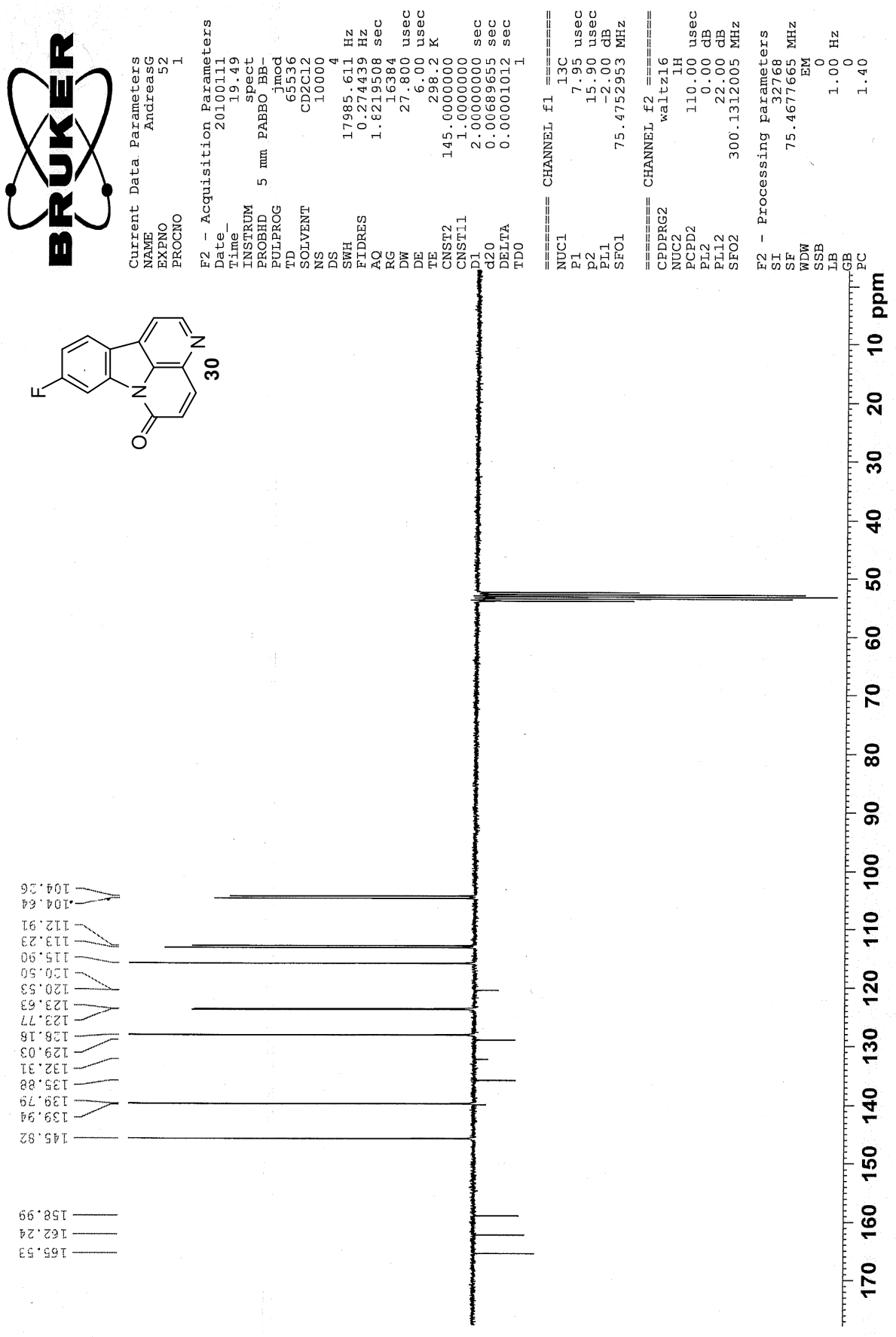
F1 - Processing parameters
SI                        1024
MC2                         QF
SF             300.1300000 MHz
WDW                       SINE
SSB                          0
LB                        0.30 Hz
GB                         0.1
```

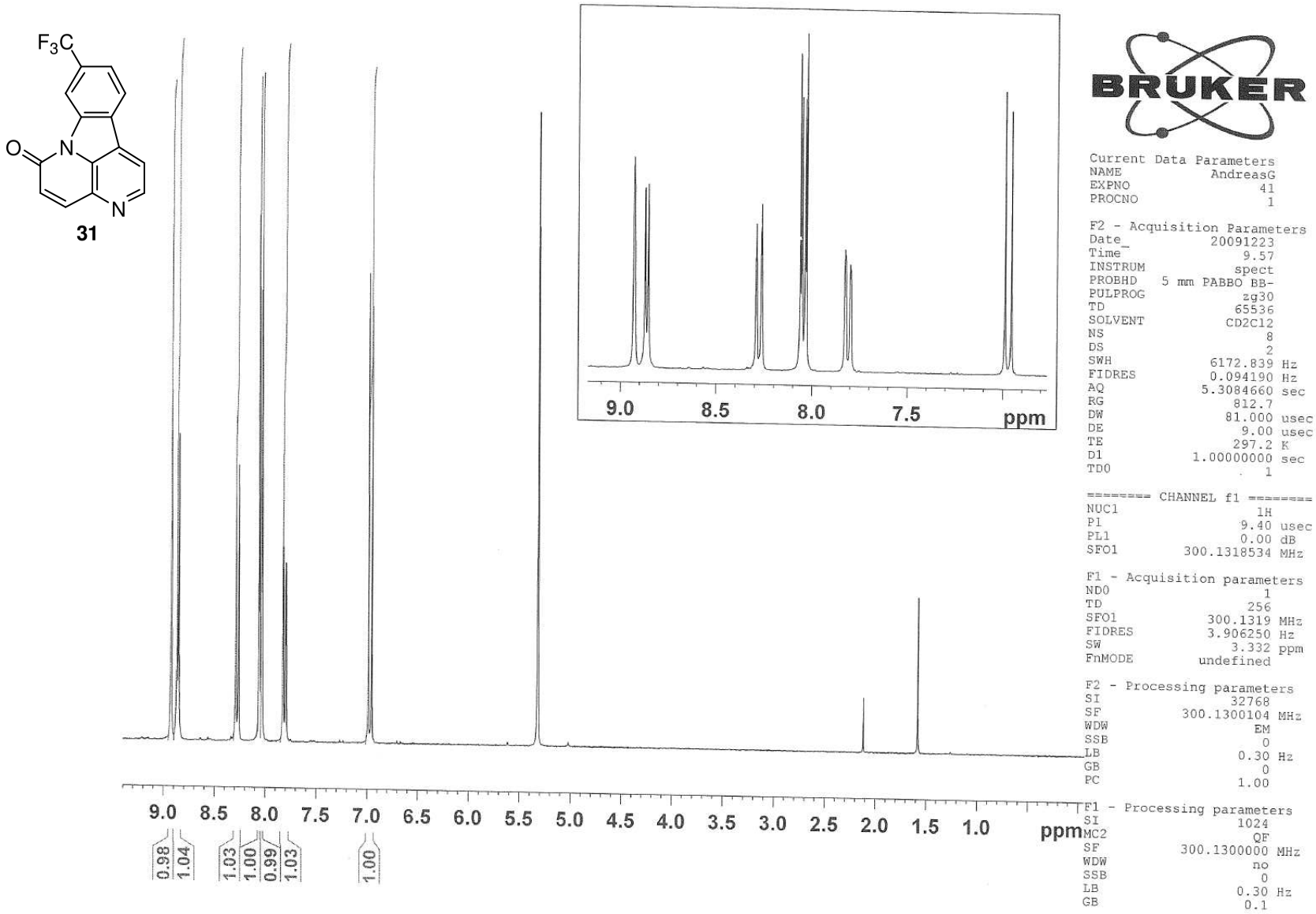

Current Data Parameters
NAME AndreasG
EXPNO 58
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100123
Time_ 10.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2Cl2
NS 4553
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 6.00 usec
TE 297.2 K
CNST2 145.0000000
CNST11 1.00000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677508 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
CF3
N
N
O
28
159.22
146.15
140.92
140.08
136.65
132.45
129.57
128.83
128.70
126.10
127.67
127.53
127.49
127.44
127.39
127.24
126.80
125.97
124.67
122.36
120.19
120.14
120.09
120.03
118.75
117.23
116.58
ppm

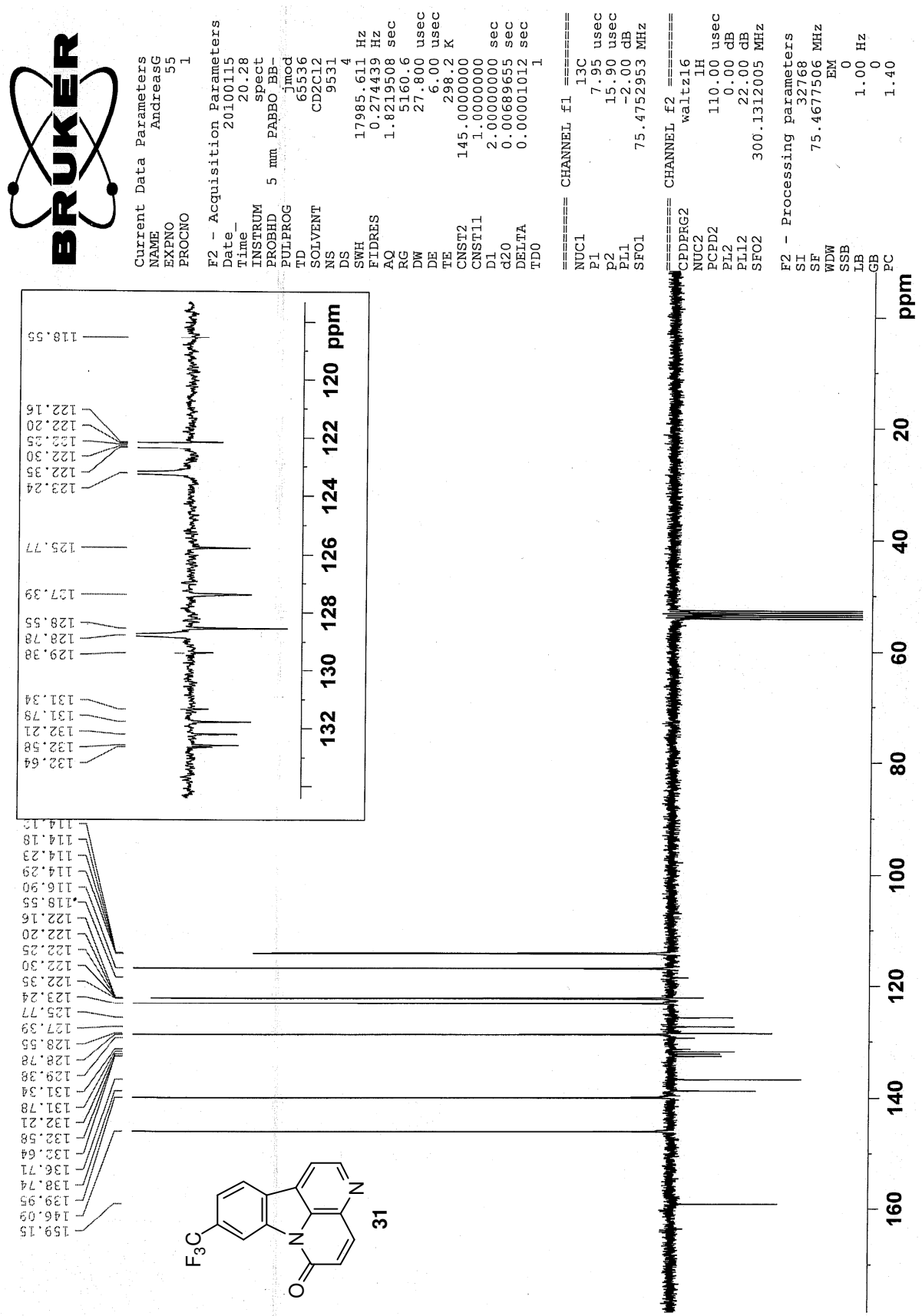

Me
O
N
N
29
BRUKER
Current Data Parameters
NAME AndreasG
EXPNO 35
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091220
Time 19.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 456.1
DW 81.000 usec
DE 9.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300105 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.03
0.98
2.04
1.00
1.02
0.99
3.07


Current Data Parameters
NAME Andreasg
EXPNO 36
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091220
Time_ 20.10
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2Cl2
NS 1442
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.82195508 sec
RG 16384
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
CNST2 145.00000000
CNST11 1.00000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677730 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
Me
N
N
O
29
21.69
52.38
52.74
53.10
53.46
53.83
115.71
116.91
121.69
121.98
126.37
128.28
129.82
131.91
135.87
139.35
139.57
141.61
145.48
159.16
160
140
120
100
80
60
40
20
0
ppm


F
O
N
N
30
8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 0.97 1.02 1.00 1.00 1.01 1.00
BRUKER
Current Data Parameters
NAME AndreasG
EXPNO 51
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100111
Time 19.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 362
DW 81.000 usec
DE 9.00 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 2
TD 256
SFO1 300.1314 MHz
FIDRES 12.056327 Hz
SW 10.284 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300105 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW SINE
SSB 0
LB 0.30 Hz
GB 0.1


Current Data Parameters
NAME AndreasG
EXPNO 52
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100111
Time_ 19.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2Cl2
NS 10000
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 16384
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677665 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
30
F
N
N
O
165.53
162.24
158.99
145.82
139.94
139.79
135.88
132.31
129.03
128.18
123.77
123.63
120.53
120.50
115.90
113.23
112.91
104.64
104.36
ppm


F3C
O
N
N
31
9.0
8.5
8.0
7.5
ppm
BRUKER
Current Data Parameters
NAME AndreasG
EXPNO 41
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091223
Time 9.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 8
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 812.7
DW 81.000 usec
DE 9.00 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 9.40 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
F1 - Acquisition parameters
ND0 1
TD 256
SFO1 300.1319 MHz
FIDRES 3.906250 Hz
SW 3.332 ppm
FnMODE undefined
F2 - Processing parameters
SI 32768
SF 300.1300104 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 QF
SF 300.1300000 MHz
WDW no
SSB 0
LB 0.30 Hz
GB 0.1
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm
0.98
1.04
1.03
1.00
0.99
1.03
1.00


Current Data Parameters
NAME AndreasG
EXPNO 55
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100115
Time 20.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG jmod
TD 65536
SOLVENT CD2Cl2
NS 9531
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 5160.6
DW 27.800 usec
DE 6.00 usec
TE 298.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001012 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
p1 7.95 usec
p2 15.90 usec
PL1 -2.00 dB
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 22.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677506 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
118.55
122.16
122.20
122.25
122.30
122.35
123.24
125.77
127.39
128.55
128.78
129.38
131.34
131.79
132.21
132.58
132.64
159.15
146.09
139.95
138.74
136.71
133.64
132.58
132.21
131.78
131.34
129.38
128.78
128.55
127.59
125.77
123.24
122.35
122.30
122.25
122.20
122.16
119.55
116.90
114.29
114.23
114.18
114.15
132 130 128 126 124 122 120 ppm
160 140 120 100 80 60 40 20 ppm
F3C
O
N
N
31