An efficient and recyclable dendritic catalyst able to dramatically reduce palladium leaching in Suzuki couplings

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Supporting Information

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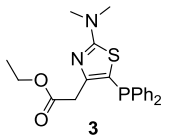
1. Complete characterisation of the ligands with attribution of NMR signals

The preparation and characterization of compounds **1**, **2**, **3**, **4** have been previously described. The latter were identified in each case by ^{1}H NMR and ^{31}P NMR (if applicable) spectroscopies and the data obtained matched literature values. Remarkably, in the case of **3**, a slightly modified procedure was used and crystals were grown from this compound thus allowing to obtain its structure by X-ray crystallography. For the preparation of compounds **3**, **4**, **5-OH**, **5-OMe**, **5-G$_1$**, **5-G$_3$**, **6-G$_1$**, **6-G$_3$**, all solvents were degassed before using.

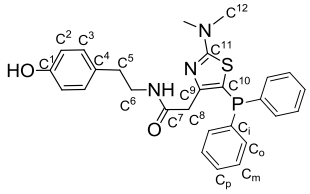
Compound 3:[1]



3

Triethylamine (3.3 mL, 23.6 mmol) was added to a solution of compound **2**[1] (2.81 g, 13.11 mmol) in anhydrous pyridine (12 mL). The mixture was cooled to -25°C and chlorodiphenylphosphine was added dropwise (15 min). The mixture was warmed up to room temperature overnight and heated to 40°C for 13 days (monitoring by ^{31}P NMR). At the end of the reaction, 70 mL of toluene were added to the mixture. The salts were eliminated by filtration under argon and the brownish solution was evaporated to dryness. Column chromatography (CH_2Cl_2/AcOEt (90:10) as eluent) of the crude oil gave 2.45 g of the expected compound as a yellow oil (47% yield).
^{31}P{^{1}H} NMR ($CDCl_3$, 121.50 MHz): δ = -28.89 ppm.
^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 1.18 (t, $^{3}J_{H-H}$ = 7.2 Hz, 3H, CH_3), 3.07 (s, 6H, $(CH_3)_2N$), 3.98 (s, 2H, CH_2-thiazolyl), 4.11 (q, $^{3}J_{H-H}$ = 7.2 Hz, 2H, CH_2O), 7.30-7.65 (m, 10H, H_{arom}).
This compound was crystallized from $CHCl_3$ by slow evaporation and the structure determined by X-ray crystallography (see section 3).

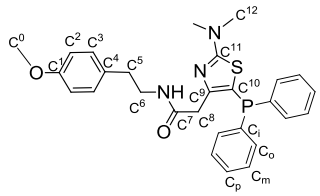
Compound 5-OH:



To a solution of **4** (315 mg, $8.05.10^{-1}$ mmol) in *N,N*-dimethylformamide [DMF] (6.5 mL) were added at 0°C hydroxybenzotriazole [HoBt] (0.156 g, 1.02 mmol) and *N,N'*-dicyclohexylcarbodiimide [DCC] (0.211 g, 1.02 mmol). After one hour at 0°C, a solution of tyramine (0.233 g, 1.7 mmol) in DMF (3 mL) was added over 5 minutes. After 2 hours at 0°C, the mixture was warmed up to room temperature and stirred for 7 days (monitoring by ^{31}P NMR). The mixture was filtered and the filtrate was freeze-dried. A first column chromatography (CH_2Cl_2/EtOH = 93/7 as eluent) of the crude product permitted to eliminate the excess of tyramine, DCU and a large part of the oxidized compound. A second column chromatography (CH_2Cl_2/AcOEt (80:20) as eluent) gave 196 mg of the expected product as a white powder (47% yield).
^{31}P{^{1}H} NMR (CD_2Cl_2, 121.50 MHz): δ = -29.79 ppm. (impurity : minus 2%; δ = 21.9 ppm : oxide).
^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ = 2.62 (t, $^{3}J_{H-H}$ = 6.8 Hz, 2H, C^5-H), 2.98 (s, 6H, C^{12}-H), 3.42 (m, 2H, C^6-H), 3.84 (d, $^{4}J_{H-P}$ = 1.2 Hz, 2H, C^8-H), 6.47 (s, 1H, OH), 6.70 (m, 2H, C^2-H), 6.90 (m, 2H, C^3-H), 7.06 (br t, $^{3}J_{H-H}$ = 5.7 Hz, 1H, NH), 7.25-7.50 (m, 10H, H_{Pph2}).
^{13}C{^{1}H} NMR (CD_2Cl_2, 75.47 MHz): δ = 34.56 (C^5), 38.27 (d, $^{3}J_{C-P}$ = 16.2 Hz, C^8), 39.93 (C^{12}), 40.79 (C^6), 113.64 (d, C^{10}, $^{1}J_{C-P}$ = 33.2 Hz), 115.36 (C^2), 128.45 (d, $^{3}J_{C-P}$= 6.8 Hz, C_m), 128.64 (C_p), 129.63 (C^3) 130.06 (C^4), 132.68 (d, $^{2}J_{C-P}$ = 19.6 Hz, C_o), 138.04 (d, $^{1}J_{C-P}$ = 6.8 Hz, C_i), 155.19 (C^1), 156.09 (d, $^{2}J_{C-P}$ = 31.7 Hz, C^9), 169, 56 (C^7), 174.47 (C^{11}).

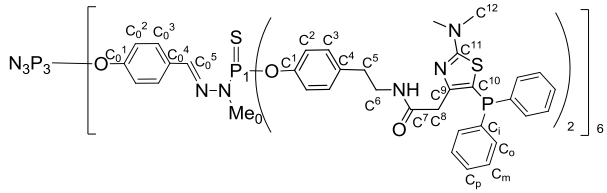
DCI-MS (NH_3) m/z: 490.2 $[M+H]^+$. This compound was crystallized from CH_2Cl_2 by slow evaporation and the structure determined by X-ray crystallography (see section 3).

Compound 5-OMe :



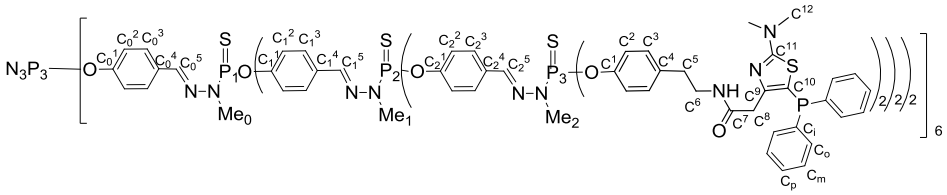
To a solution of **4**[1] (200 mg, $5.39.10^{-1}$ mmol) in DMF (5 mL) was added at 0°C 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride [EDC] (0.127 g, $6.28.10^{-1}$ mmol) and HoBt (0.088 g, $6.28.10^{-1}$ mmol). After two hours at 0°C, 2-*p*-methoxy-ethylamine (160 µL, 1.07 mmol) was added dropwise and after 1.5 hours at 0°C, the mixture was warmed up to room temperature and stirred during 3 days (monitoring by ^{31}P NMR). The mixture was filtered and the filtrate was freeze-dried. The crude oil was dissolved in dichloromethane (25 mL) and washed twice with 15 mL of water. The organic phase was dried over $MgSO_4$, filtered, and evaporated to dryness. Column chromatography (CH_2Cl_2/Acetone (80:20) as eluent, R*f* = 0.6) of the crude product gave 225 mg of the expected compound as a white powder (83% yield).
M. p. = 113.6 °C.
$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.50 MHz): δ = -29.65 ppm.
^1H NMR (CD_2Cl_2, 300.13 MHz): δ = 2.65 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, C^5-H), 2.98 (s, 6H, C^{12}-H), 3.41 (m, 2H, C^6-H), 3.77 (s, 3H, C^0-H), 3.79 (d, $^4J_{H-P}$ = 1.2 Hz, 2H, C^8-H), 6.75 (m, 2H, C^2-H), 6.86 (br s, 1H, NH), 7.00 (m, 2H, C^3-H),7.30-7.50 (m, 10H, H_{PPh_2}).
$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ = 34.58 (C^5), 38.52 (d, $^3J_{C-P}$ = 15.9 Hz, C^8), 39.86 (C^{12}), 40.52 (C^6), 55.08 (C^0), 113.17 (d, C^{10}, $^1J_{C-P}$ = 35.2 Hz), 113.68 (C^2), 128.41 (d, $^3J_{C-P}$ = 6.8 Hz, C_m), 128.60 (C_p), 129.59 (C^3), 131.24 (C^4), 132.67 (d, $^2J_{C-P}$ = 19.4 Hz, C_o), 138.14 (d, $^1J_{C-P}$ = 6.6 Hz, C_i), 156.60 (d, $^2J_{C-P}$ = 31.0 Hz, C^9), 158.06 (C^1), 168.63 (C^7), 174.32 (C^{11}).
DCI-MS (CH_4) m/z: 504.2 $[M+H]^+$.
113.6 °C.
This compound was crystallized from CH_2Cl_2 by slow evaporation and the structure determined by X-ray crystallography (see section 3).

Compound 5-G_1 :



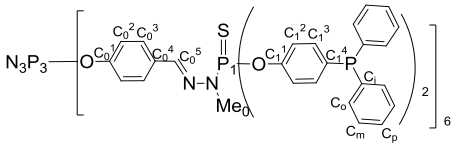
Cesium carbonate (349 mg, $1.07.10^{-3}$ mol) was added at 0°C to a solution of $\mathbf{G_1}$ (89 mg, $4.87.10^{-2}$ mmol) and **5-OH** (310 mg, $6.33.10^{-1}$ mmol) in THF (10 mL). The mixture was stirred two hours at 0°C and warmed up to room temperature. The progress of the reaction was monitored by ^{31}P NMR. After complete conversion (36 hrs) the crude mixture was centrifuged and the supernatant collected. The solvent was removed in *vacuum* and the crude product purified by column chromatography (first with dichloromethane/acetone (70:30) as eluent to eliminate the excess of free phenol, R_f = 0.6 and then with dichloromethane/ethanol (93:7) as eluent, R_f = 0.2) to give 278 mg of the desired compound as a white powder (80% yield).
$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.50 MHz): δ = -29.68 (PPh_2), 8.12 (N_3P_3), 62.78 (P_1) (impurity : minus 3%; δ = 21.2 ppm: oxide).
^1H NMR (CD_2Cl_2, 300.13 MHz): δ = 2.62 (t, $^3J_{H-H}$ = 6.6 Hz, 24H, C^5-H), 2.92 (s, 72H, C^{12}-H), 3.23 (d, $^2J_{H-P}$ = 10.2 Hz, 18H, Me_0), 3.34 (m, 24H, C^6-H), 3.77 (br s, 24H, C^8-H), 6.82 (br t, 12NH), 6.90-7.12 (m, 60H, 12 $C_0{}^2$-H, 24 C^2-H, 24 C^3-H) , 7.19-7.49 (m, 120H, H_{PPh_2}), 7.58-7.70 (m, 18H, 6 C^5-H, 12 $C_0{}^3$-H).
$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.47 MHz): δ = 33.07 (d, $^2J_{C-P}$ = 11.9 Hz, Me_0), 34.98 (C^5), 38.48 (d, $^3J_{C-P}$ = 15.8 Hz, C^8), 40.12 (C^{12}), 40.49 (C^6), 114.00 (d, C^{10}, $^1J_{C-P}$ = 33.2 Hz), 121.12 (d, $^3J_{C-P}$ = 4.5 Hz, C^2), 121.33 ($C_0{}^2$), 128.28 ($C_0{}^3$), 128.48 (d, $^3J_{C-P}$ = 6.8 Hz, C_m),128.84 (C_p), 129.80 (C^3), 132.26 ($C_0{}^4$), 132.72 (d, $^2J_{C-P}$ = 18.9 Hz, C_o), 136.45 (C^4), 137.96 (d, $^1J_{C-P}$ = 6.6 Hz, C_i), 138.69 (d, $^3J_{C-P}$ = 14.3 Hz, $C_0{}^5$), 148.99 (d, $^2J_{C-P}$ = 7.5 Hz, C^1), 151.23 (m, $C_0{}^1$), 156.08 (d, $^2J_{C-P}$ = 31.7 Hz, C^9), 169.22 (C^7), 174.32 (C^{11}).

Compound 5-G_3 :



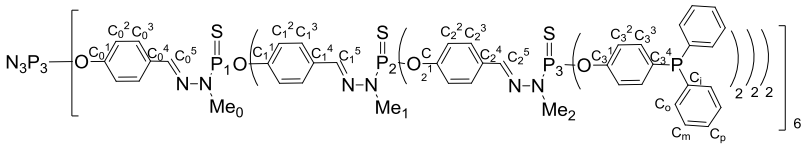
Cesium carbonate (348 mg, 1.07 mmol) was added at 0°C to a solution of **G_3** (130 mg, $1.21.10^{-2}$ mmol) and **5-OH** (310 mg, $6.33.10^{-1}$ mmol) in THF (10 mL). The mixture was stirred two hours at 0°C and warmed up to room temperature. The progress of the reaction was monitored by ^{31}P NMR. After complete conversion (72 hrs), the mixture was centrifuged and the supernatant collected. The solvent was removed in *vacuum* and the crude product purified by size exclusion chromatography (THF as eluent) to eliminate the excess of phenol and to give 420 mg of the desired compound as white powder (75% yield).
^{31}P{^{1}H} NMR (CD_2Cl_2, 121.50 MHz): δ = -29.67 (PPh_2), 7.65 (N_3P_3), 62.77 (P_2+ P_3), 62.90 (P_1) (impurity : minus 5%; δ = 19.9 ppm: oxide).
^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ = 2.61 (m, 96H, C^5-H), 2.88 (s, 288H, C^{12}-H), 3.10-3.50 (m, 222H: 126 [Me_0 + Me_1 + Me_2] + 96 C^6-H), 3.62-4.02 (br s, 96H, C^8-H), 6.75-7.12 (m, 252H: 48NH + 12 C_0^2-H + 96 C^2-H + 96 C^3-H), 7.13-7.52 (m, 552H : 24 C_1^2-H + 48 C_2^2-H + 480 H $_{PPh2}$), 7.53-7.90 (m, 126H : 12 C_0^3-H + 24 C_1^3-H + 48 C_2^3-H + 6 C_0^5-H + 12 C_1^5-H + 24 C_2^5-H).
^{13}C{^{1}H} NMR (CD_2Cl_2, 75.47 MHz): δ = 32.53 (m, Me_0, Me_1), 32.99 (d, $^2J_{C\text{-}P}$ = 12.5 Hz, Me_1), 34.90 (C^5), 38.57 (d, $^3J_{C\text{-}P}$ = 15.8 Hz, C^8), 39.91 (C^{12}), 40.40 (C^6), 113.35 (d, C^{10}, $^1J_{C\text{-}P}$ = 32.5 Hz), 121.18 (d, $^3J_{C\text{-}P}$ = 4.4 Hz, C^2), 121.83 (m, C_0^2, C_1^2 C_2^2), 128.33 (m, C_0^3, C_1^3 C_2^3), 128.47 (d, $^3J_{C\text{-}P}$ = 6.8 Hz, C_m), 128.65 (C_p), 129.81 (C^3), 132.44 (C_0^4, C_1^4 C_2^4), 132.65 (d, $^2J_{C\text{-}P}$ = 19.3 Hz, C_o), 136.63 (C^4), 138.07 (d, $^1J_{C\text{-}P}$ = 6.5 Hz, C_i), 138.95 (d, $^3J_{C\text{-}P}$ = 14.4 Hz, C_2^5), 139.54 (m, C_0^5, C_1^5), 149.02 (d, $^2J_{C\text{-}P}$ = 7.1 Hz, C^1), 151.38 (m, C_0^1, C_1^1, C_2^1), 156.60 (d, $^2J_{C\text{-}P}$ = 31.5 Hz, C^9), 168.73 (C^7), 174.28 (C^{11}).

Compound 6-G_1 :



Cesium carbonate (356.5 mg, 1.09 mmol) was added to a solution of 4-(diphenylphosphino)phenol **6^2** (198 mg, 0.71 mmol) and **G_1** (100 mg, 0.053 mmol) in THF (10 mL). The mixture was stirred overnight at room temperature, then filtered under argon and the filtrate was evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 (1 mL) and this solution was added to a mixture of 50 mL *n*-pentane/Et_2O (10:1) to allow dendrimer **6-G_1** to precipitate. **6-G_1** was obtained as a white powder in 71 % yield (186 mg, 0.039 mmol).
^{1}H NMR (300 MHz, CD_2Cl_2, 25°C) δ (ppm): 3.27 (d, $^3J_{H\text{-}P}$ = 10.5 Hz, 18H, Me_0), 6.96-6.98 (m, 12H, C_0^2-H), 7.14-7.30 (m, 168H, C_1^2-H, C_1^3-H, P<u>Ph</u>$_2$), 7.49-7.52 (m, 18H, C_0^3-H, C_0^5H);
^{31}P-{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25°C) δ (ppm): -6.67 (s, PPh_2), 8.12 (s, N_3P_3), 61.67 (s, P_1);
^{13}C-{^{1}H} NMR (75 MHz, CD_2Cl_2, 25°C) δ (ppm): 32.83 (d, $^2J_{C\text{-}P}$ = 12.5 Hz, Me_0), 121.12 (s, C_0^2), 121.35 (dd, $^3J_{C\text{-}P}$ = 7.1 Hz, $^3J_{C\text{-}P}$ = 5.0 Hz, C_1^2), 128.15 (s, C_0^3), 128.54 (d, $^3J_{C\text{-}P}$ = 7.1 Hz, C_m), 128.82 (s, C_p), 132.01 (s, C_0^4), 133.56 (d, $^2J_{C\text{-}P}$ = 19.7 Hz, C_o), 134.46 (dd, $^1J_{C\text{-}P}$ = 12.3 Hz, $^5J_{C\text{-}P}$ = 1.7 Hz, C_1^4), 135.49 (d, $^2J_{C\text{-}P}$ = 20.8 Hz, C_1^3), 136.99 (d, $^1J_{C\text{-}P}$ = 11.3 Hz, C_i), 138.94 (d, $^3J_{C\text{-}P}$ = 15.0 Hz, C_0^5), 151.11-151.21 (m, C_0^1, C_1^1).

Compound 6-G_3 :

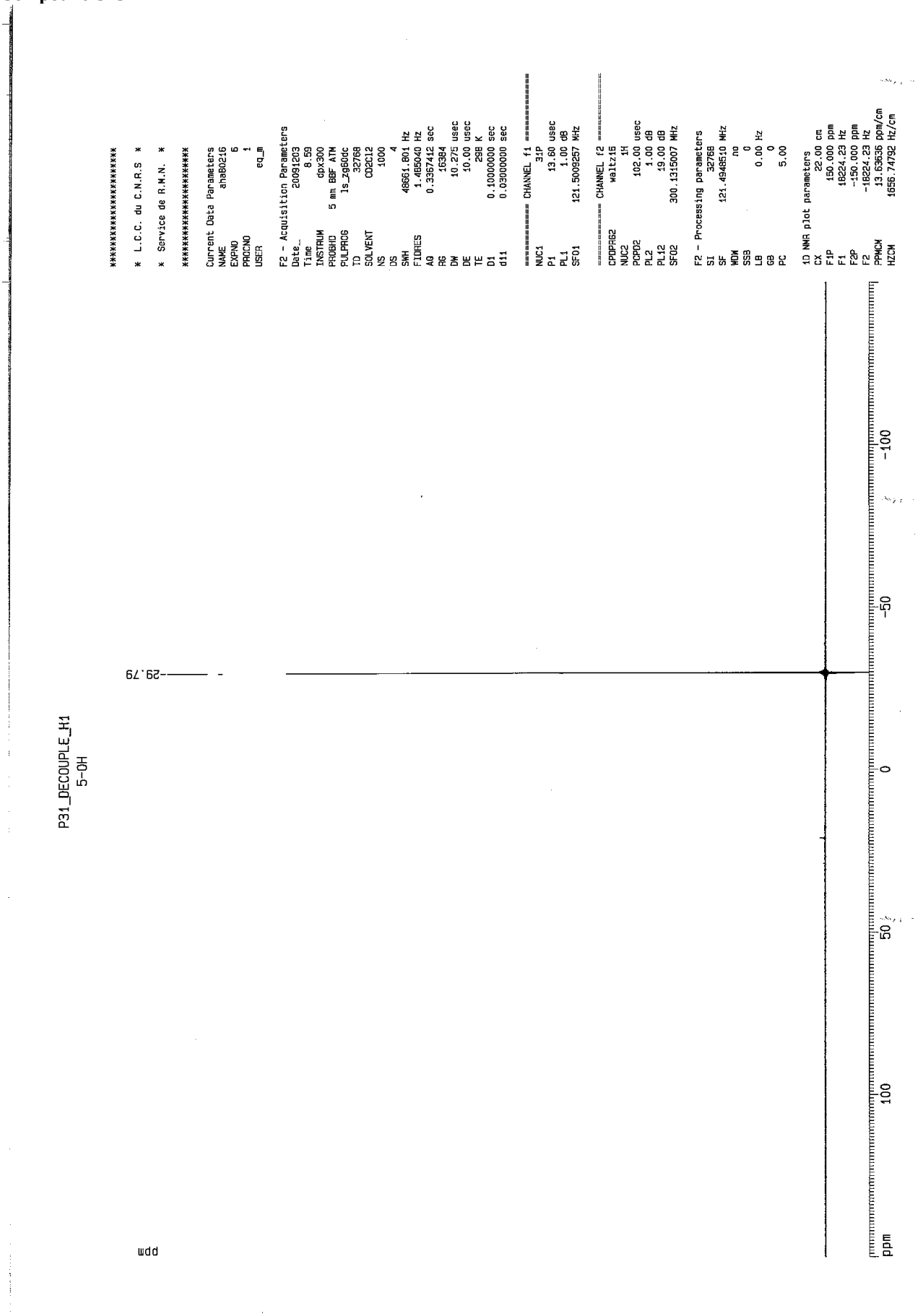


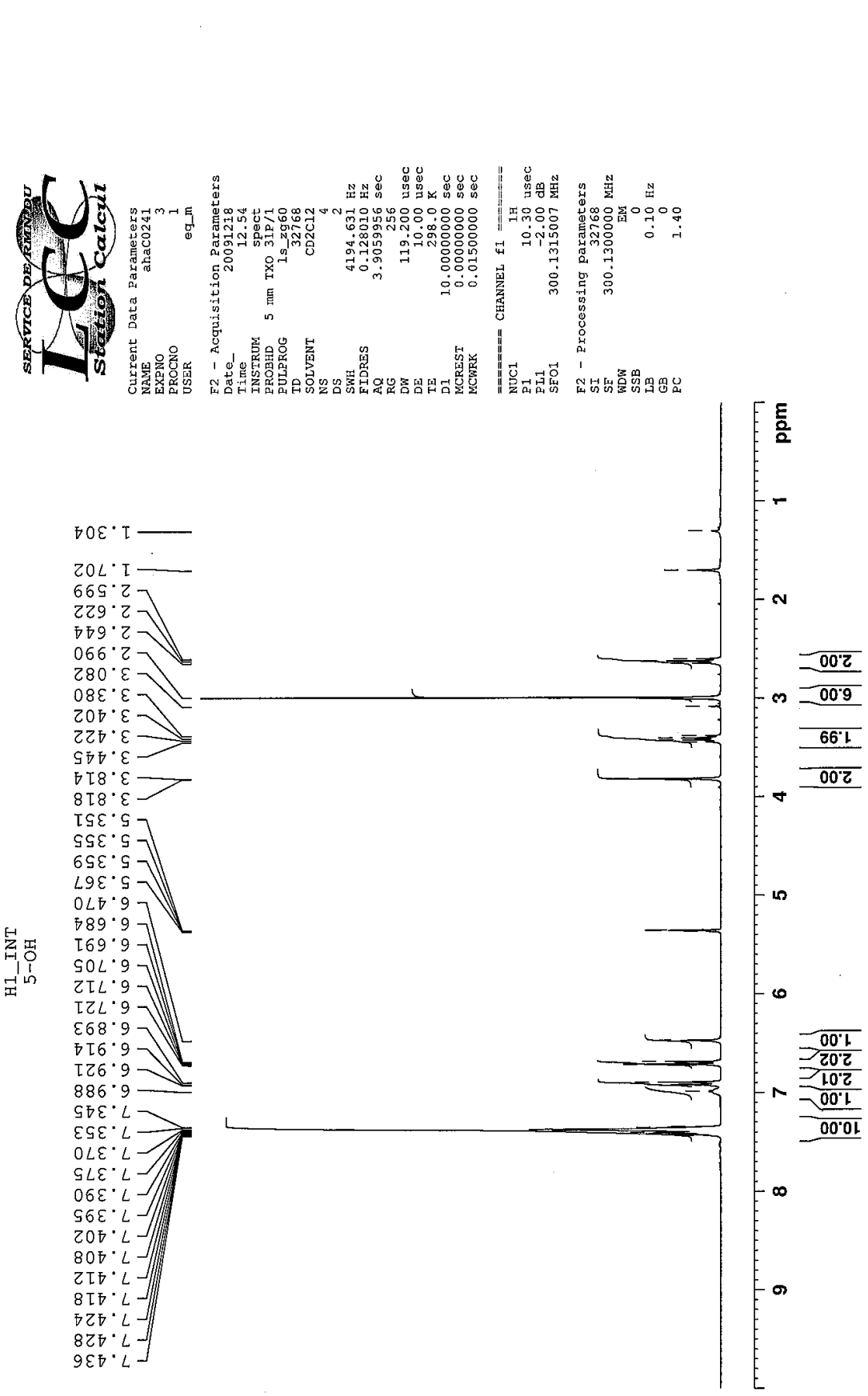
Cesium carbonate (365 mg, 1.12 mmol) was added to a solution of 4-(diphenylphosphino)phenol **6^2** (203 mg, 0.73 mmol) and **G_3** (150 mg, 0.014 mmol) in THF (10 mL). The mixture was stirred overnight at room temperature, then filtered under argon and the filtrate was evaporated to dryness. The resulting oil was dissolved in CH_2Cl_2 (2 mL) and this solution was added to a mixture of 50 mL *n*-pentane /Et_2O (10:1 then 5:5 then 5:15) to allow dendrimer **6-G_3** to precipitate. **6-G_3** was obtained as a white powder in 65 % yield (184 mg, 0.005 mmol).
^{31}P-{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25°C) δ (ppm): -6.73 (s, PPh_2), 7.92 (s, N_3P_3), 61.59 (s, P_3), 62.36 (s, P_2), 62.65(s, P_1);
^{1}H NMR (300 MHz, CD_2Cl_2, 25°C) δ (ppm): 3.23-3.26 (m, 126H, Me_0, Me_1, Me_2), 7.02-7.05 (m, 12H, C_0^2-H), 7.12-7.23 (m, 744H, C_1^2-H, C_2^2-H, C_3^2-H, C_3^3-H, P<u>Ph</u>$_2$), 7.53-7.62 (m, 126H, C_0^3-H, C_1^3-H, C_2^3-H, C_0^5H, C_1^5H, C_2^5H);
^{13}C-{^{1}H} NMR (75 MHz, CD_2Cl_2, 25°C) δ (ppm): 32.85 (d, $^2J_{C\text{-}P}$ = 13 Hz, Me_0, Me_1, Me_2), 121.39-121.73 (m, C_0^2, C_1^2, C_2^2, C_3^2,), 128.18 (s, C_2^3), 128.28 (s, C_0^3, C_1^3), 128.54 (d, $^3J_{C\text{-}P}$ = 7.1 Hz, C_m), 128.81 (s, C_p), 132.14-132.37 (m, C_0^4, C_1^4, C_2^4),

133.54 (d, $^{2}J_{C\text{-}P}$ = 19.9 Hz, C_o), 134.33 (d, $^{1}J_{C\text{-}P}$ = 12 Hz, C_3^4), 134.98 (d, $^{2}J_{C\text{-}P}$ = 21.3 Hz, C_3^3), 137.02 (d, $^{1}J_{C\text{-}P}$ = 11.6 Hz, C_i), 139.02 (s br, C_0^5, C_1^5, C_2^5), 151.18-151.29 (m, C_0^1, C_1^1, C_2^1, C_3^1).
Note: Coupling constants $J_{C\text{-}P}$ were calculated according to the ^{13}C Jmod spectrum (see section 2).

2. ^{1}H, ^{13}C and ^{31}P NMR spectra of ligands 5-OH, 5-OMe, 5-G_1, 5-G_3, 6-G_1 and 6-G_3 and of isolated coupling products (some selected examples).

Compound 5-OH

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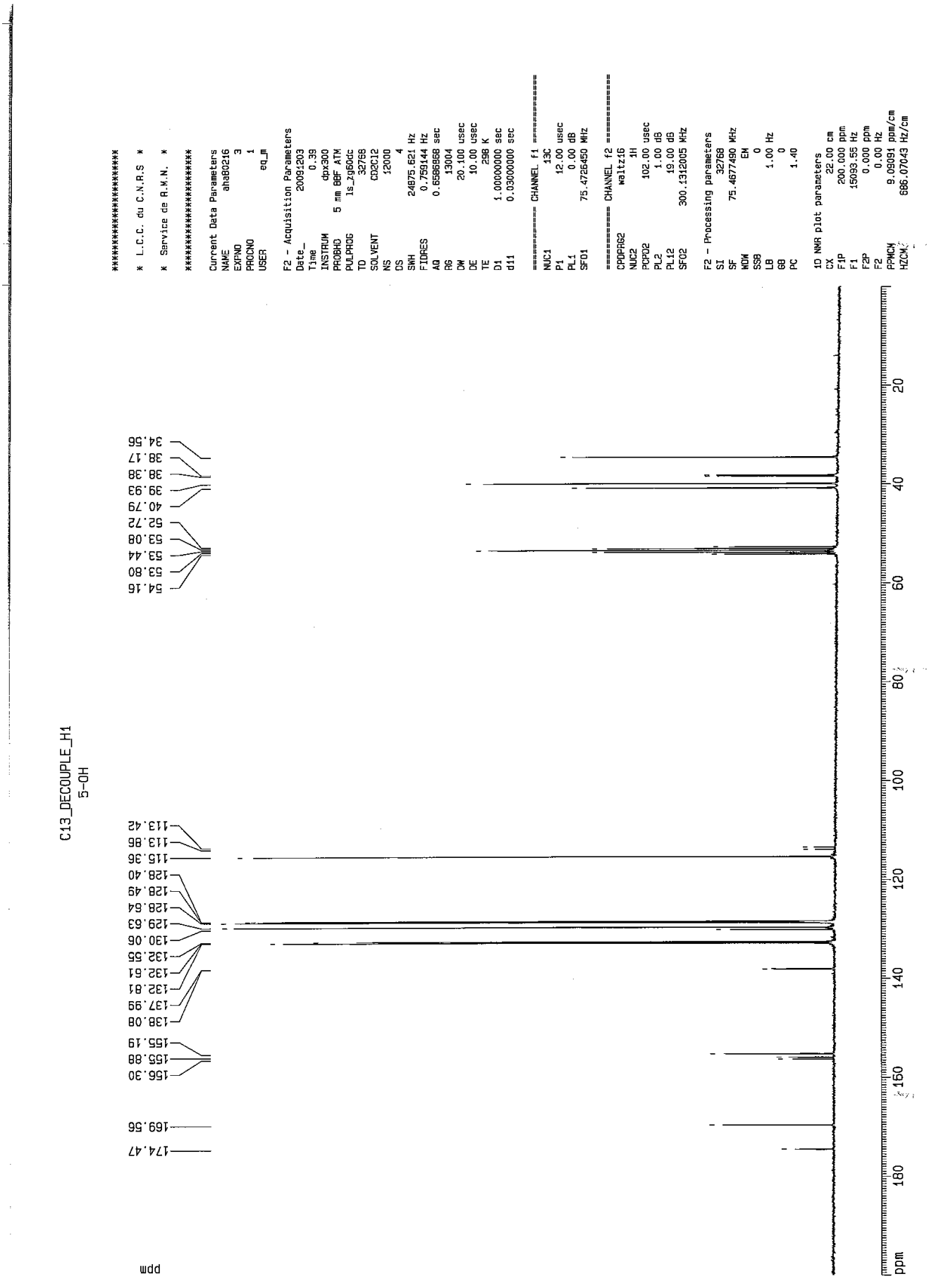
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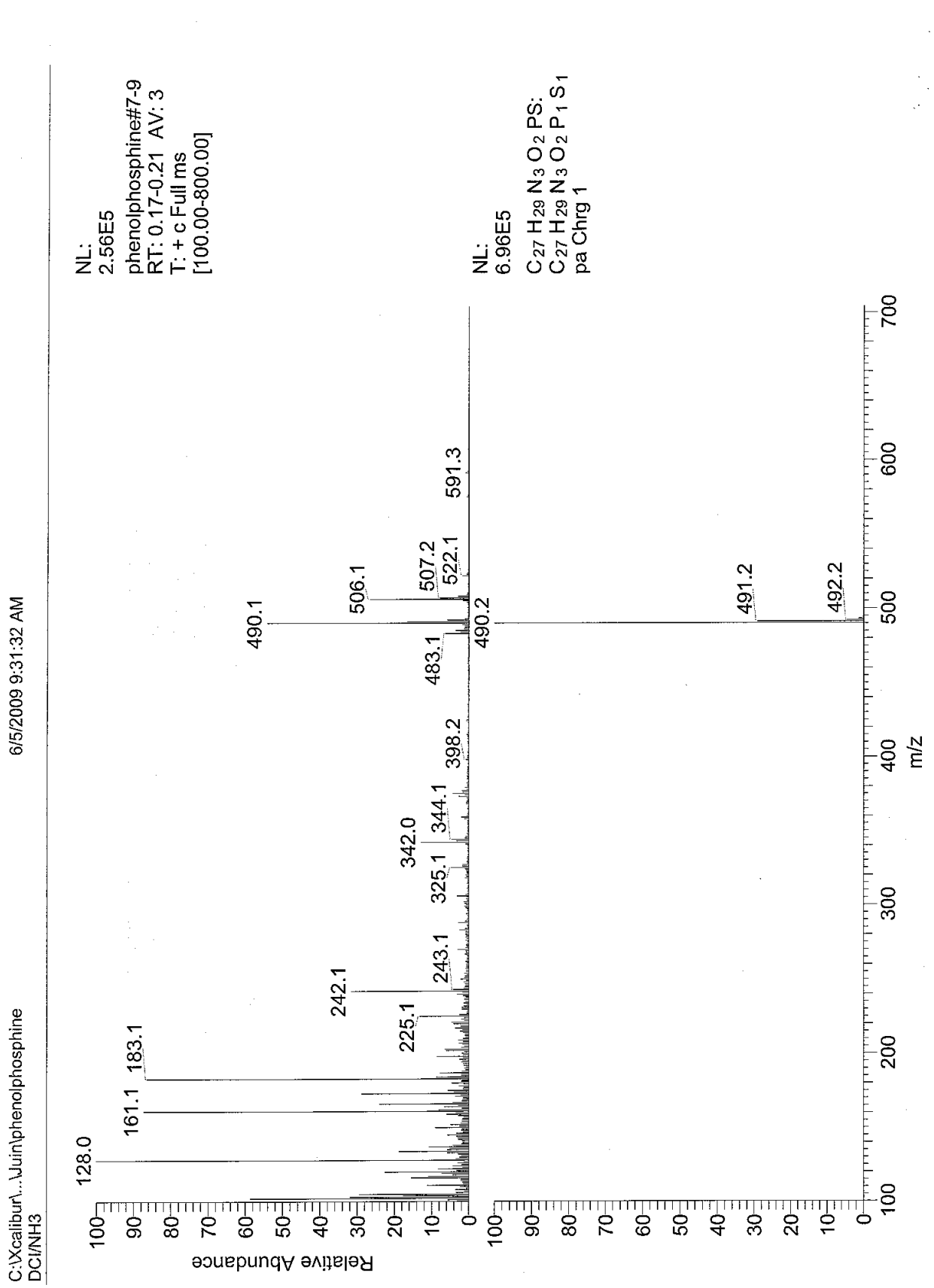
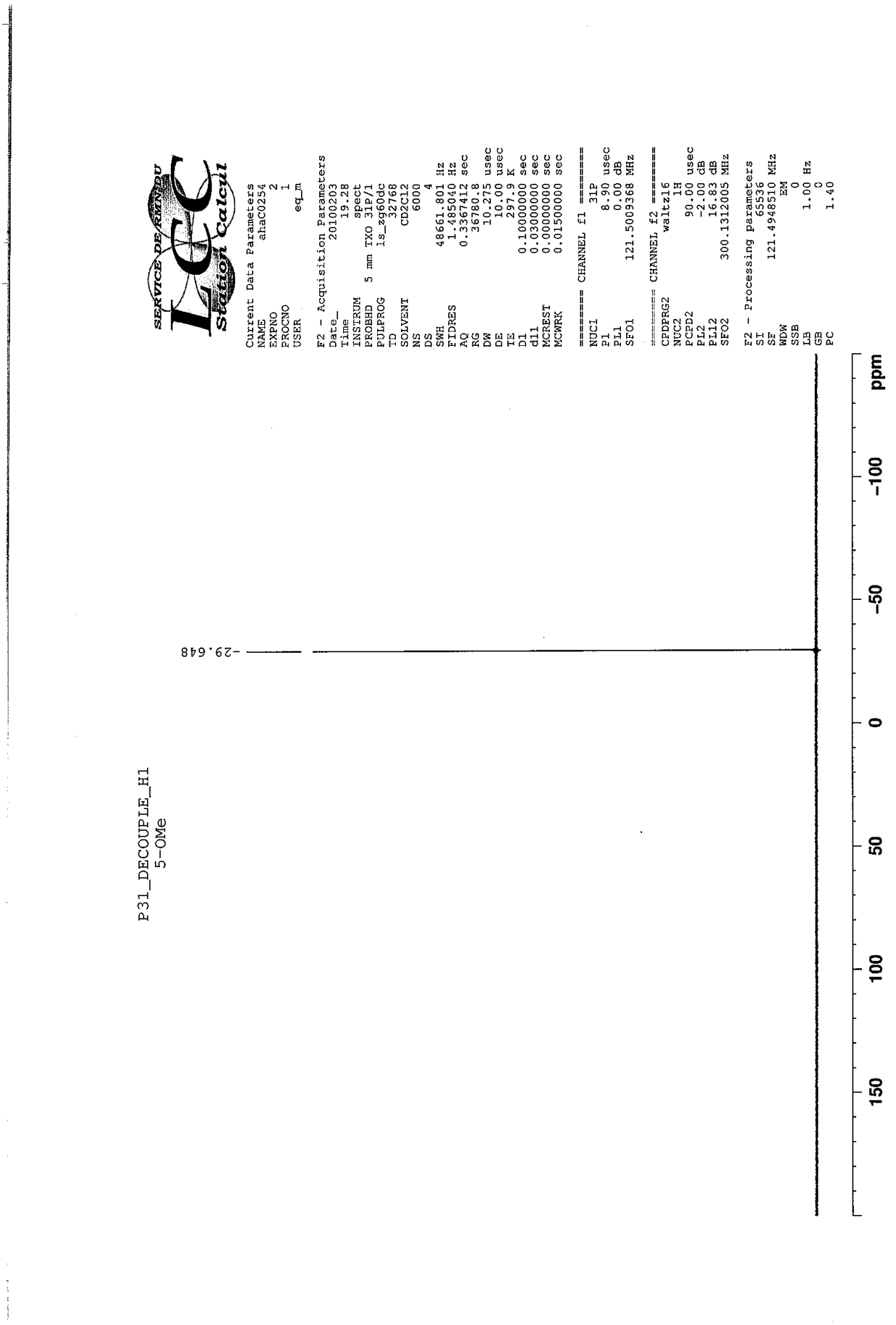
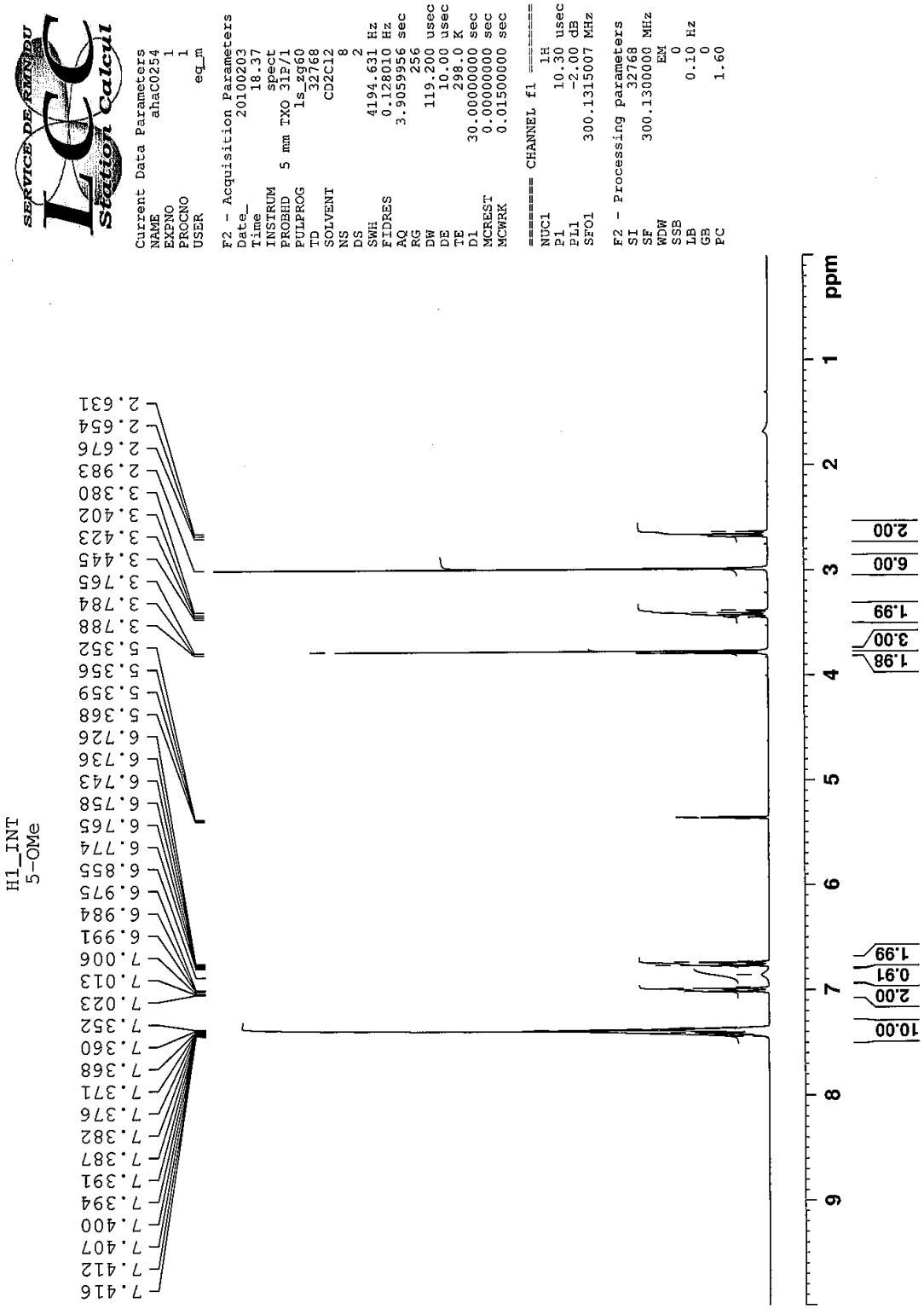
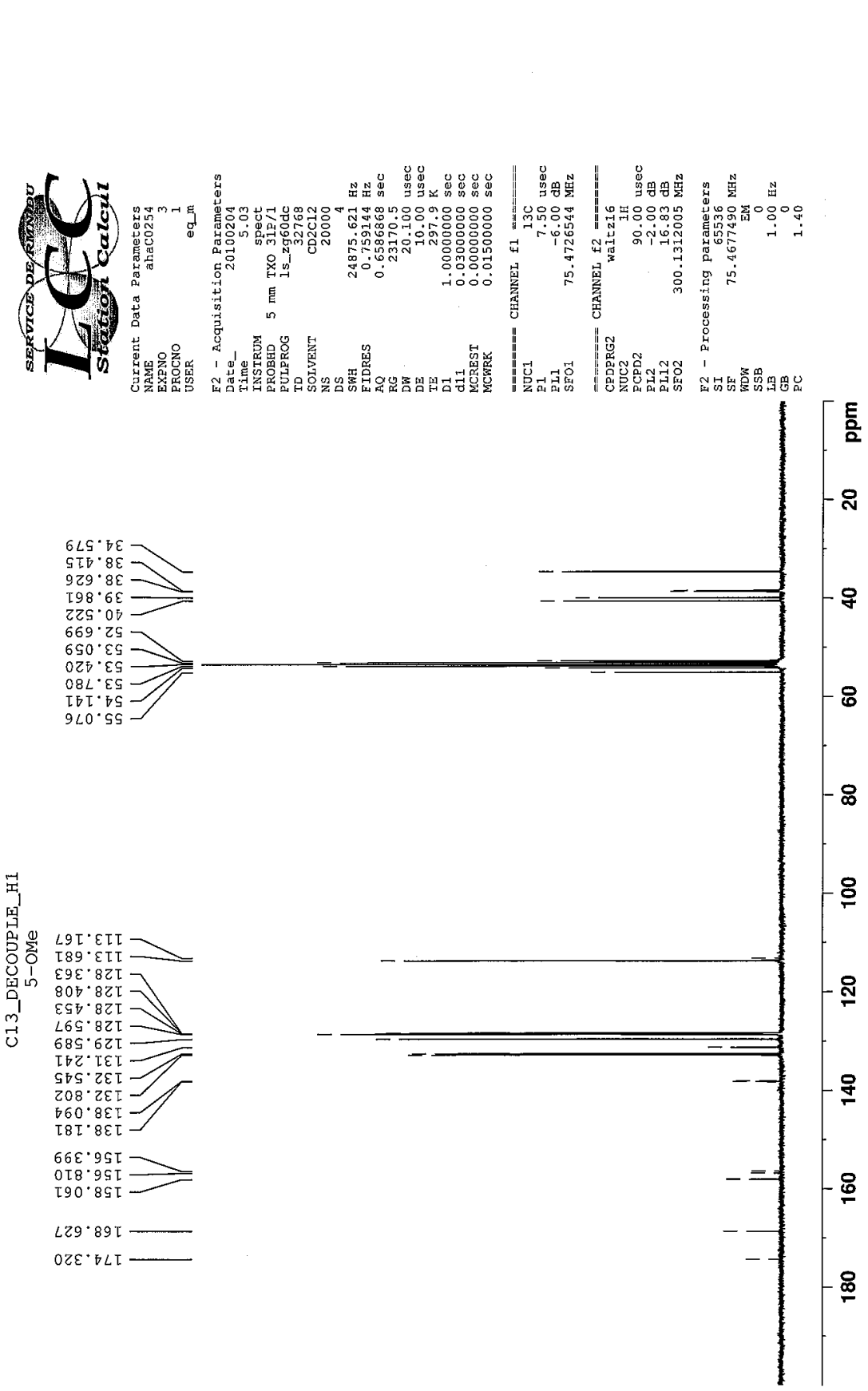
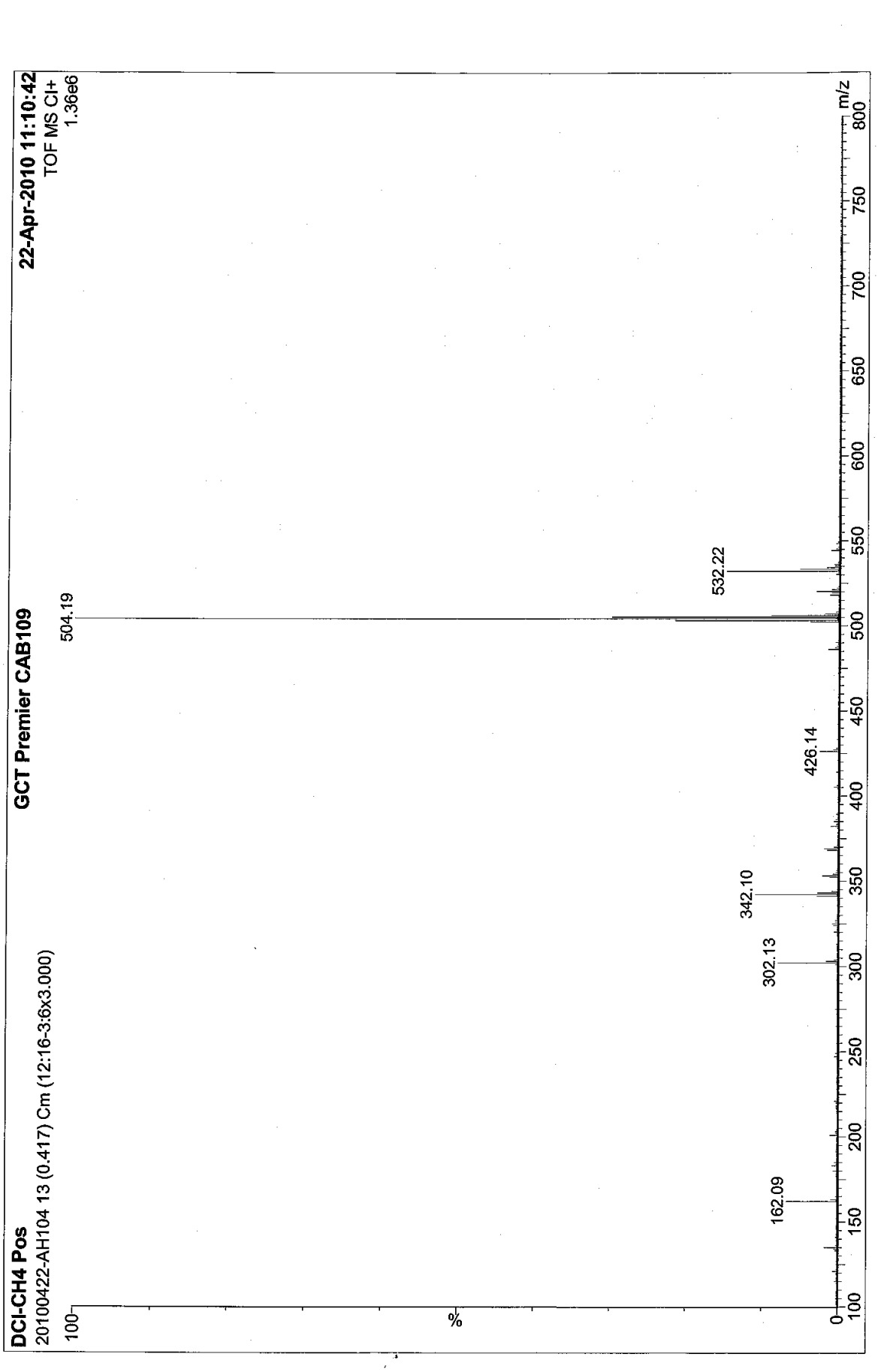

C:\Xcalibur\...\Juin\phenolphosphine
DCI/NH3
6/5/2009 9:31:32 AM
NL:
2.56E5
phenolphosphine#7-9
RT: 0.17-0.21 AV: 3
T: + c Full ms
[100.00-800.00]
NL:
6.96E5
C27 H29 N3 O2 PS:
C27 H29 N3 O2 P1 S1
pa Chrg 1
Relative Abundance
m/z
128.0
161.1
183.1
225.1
242.1
243.1
325.1
342.0
344.1
398.2
483.1
490.1
490.2
491.2
492.2
506.1
507.2
522.1
591.3

Compound 5-OMe

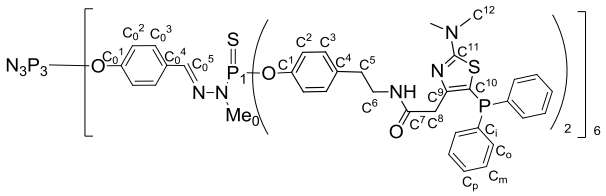


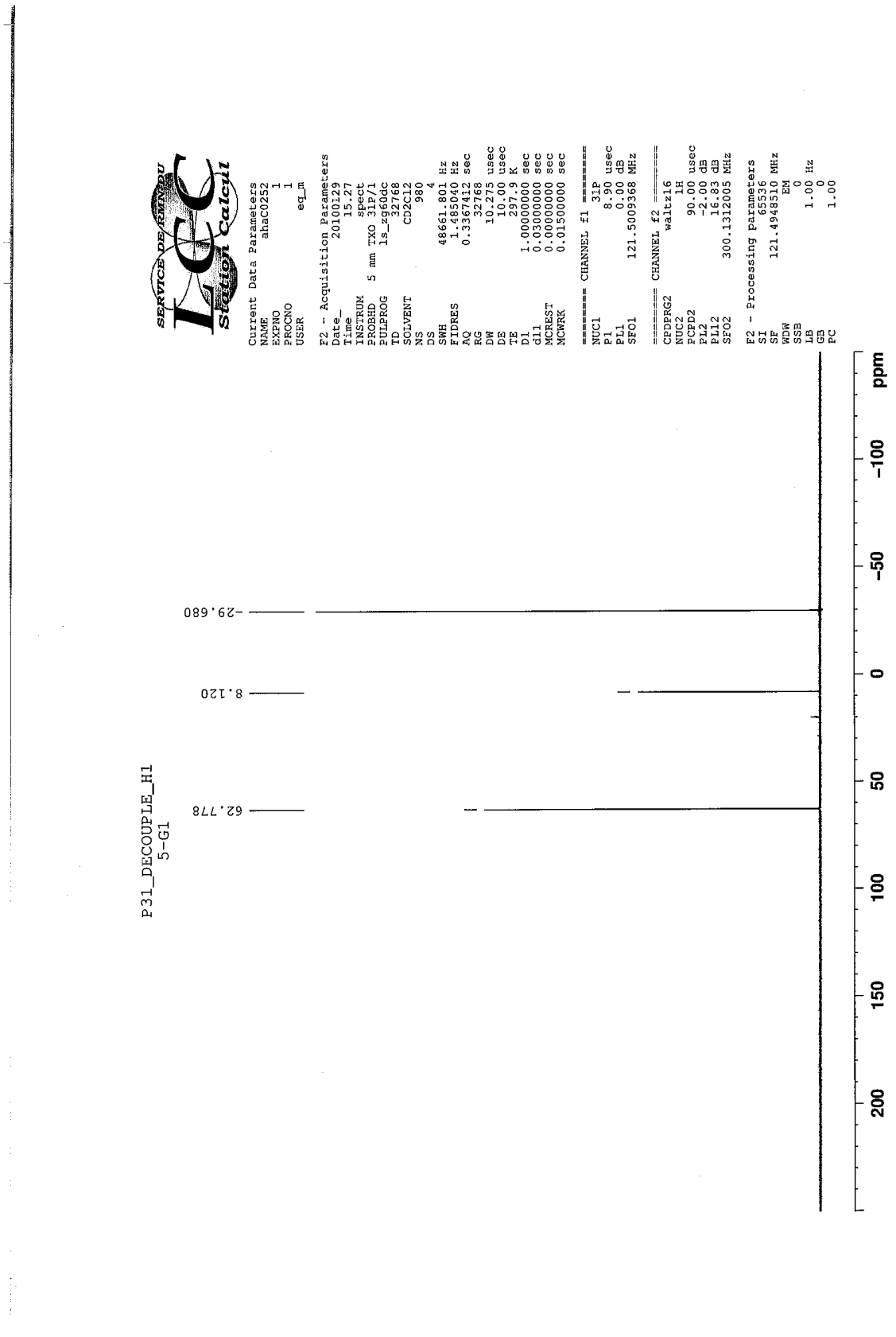

H1_INT
5-OMe
Current Data Parameters
NAME ahaC0254
EXPNO 1
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20100203
Time 18.37
INSTRUM spect
PROBHD 5 mm TXO 31P/1
PULPROG ls_zg60
TD 32768
SOLVENT CD2Cl2
NS 8
DS 2
SWH 4194.631 Hz
FIDRES 0.128010 Hz
AQ 3.90599956 sec
RG 256
DW 119.200 usec
DE 10.00 usec
TE 298.0 K
D1 30.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 -2.00 dB
SFO1 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.60
ppm
1.98
3.00
1.99
6.00
2.00
10.00
2.00
0.91
1.99

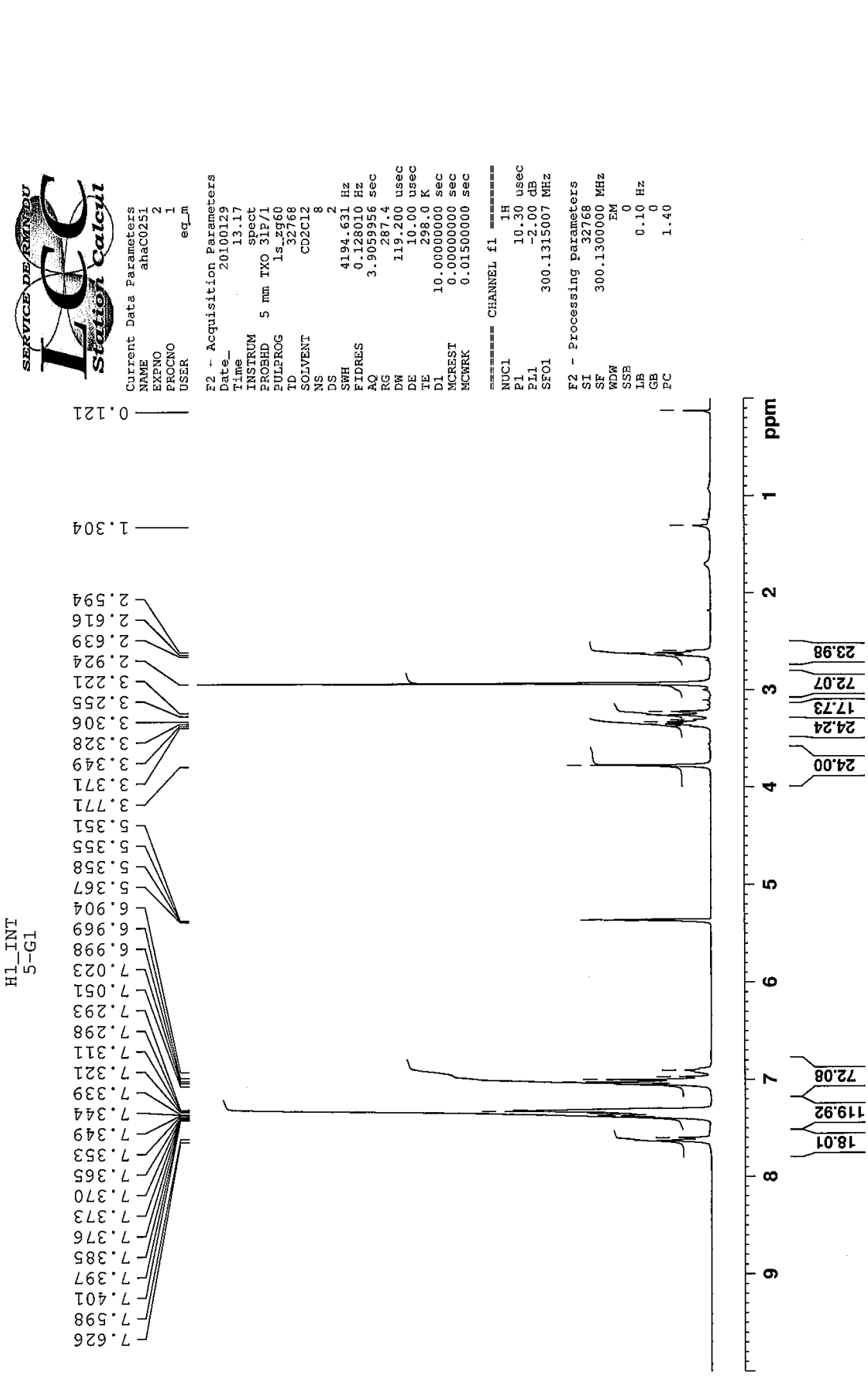

SERVICE DE RMN DU
Section Calcul
Current Data Parameters
NAME ahaC0254
EXPNO 3
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20100204
Time 5.03
INSTRUM spect
PROBHD 5 mm TXO 31P/1
PULPROG ls_zg60dc
TD 32768
SOLVENT CD2Cl2
NS 20000
DS 4
SWH 24875.621 Hz
FIDRES 0.759144 Hz
AQ 0.6586868 sec
RG 23170.5
DW 20.100 usec
DE 10.00 usec
TE 297.9 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
PL1 -6.00 dB
SFO1 75.4726544 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 16.83 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
C13_DECOUPLE_H1
5-OMe
34.579
38.415
38.626
39.861
40.522
52.699
53.059
53.420
53.780
54.141
55.076
113.167
113.681
128.363
128.408
128.453
128.597
129.589
131.241
132.545
132.802
138.094
138.181
156.399
156.810
158.061
168.627
174.320
ppm
180
160
140
120
100
80
60
40
20

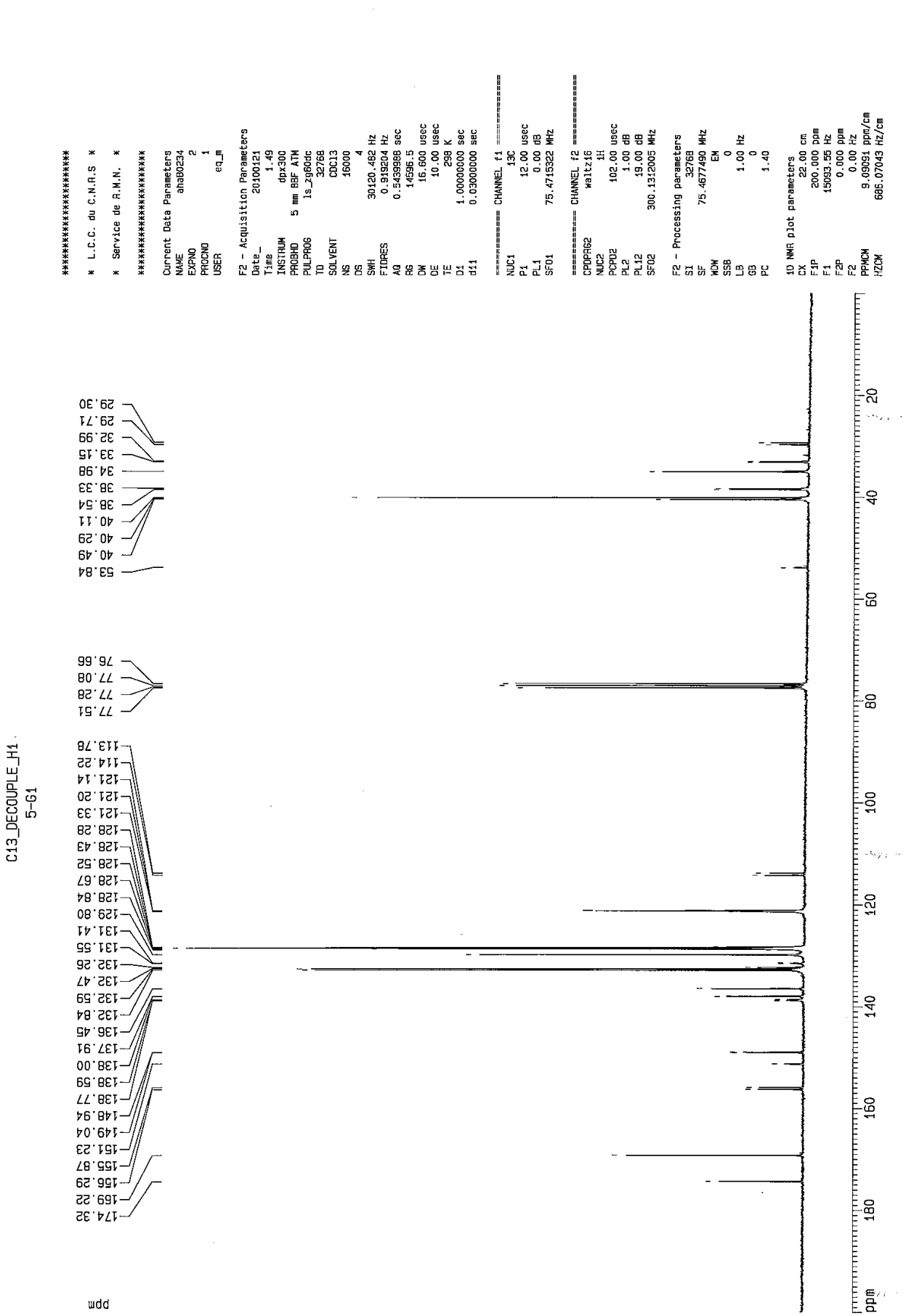


Compound 5-G$_1$:

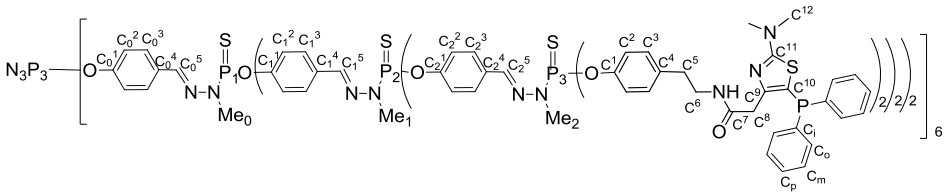


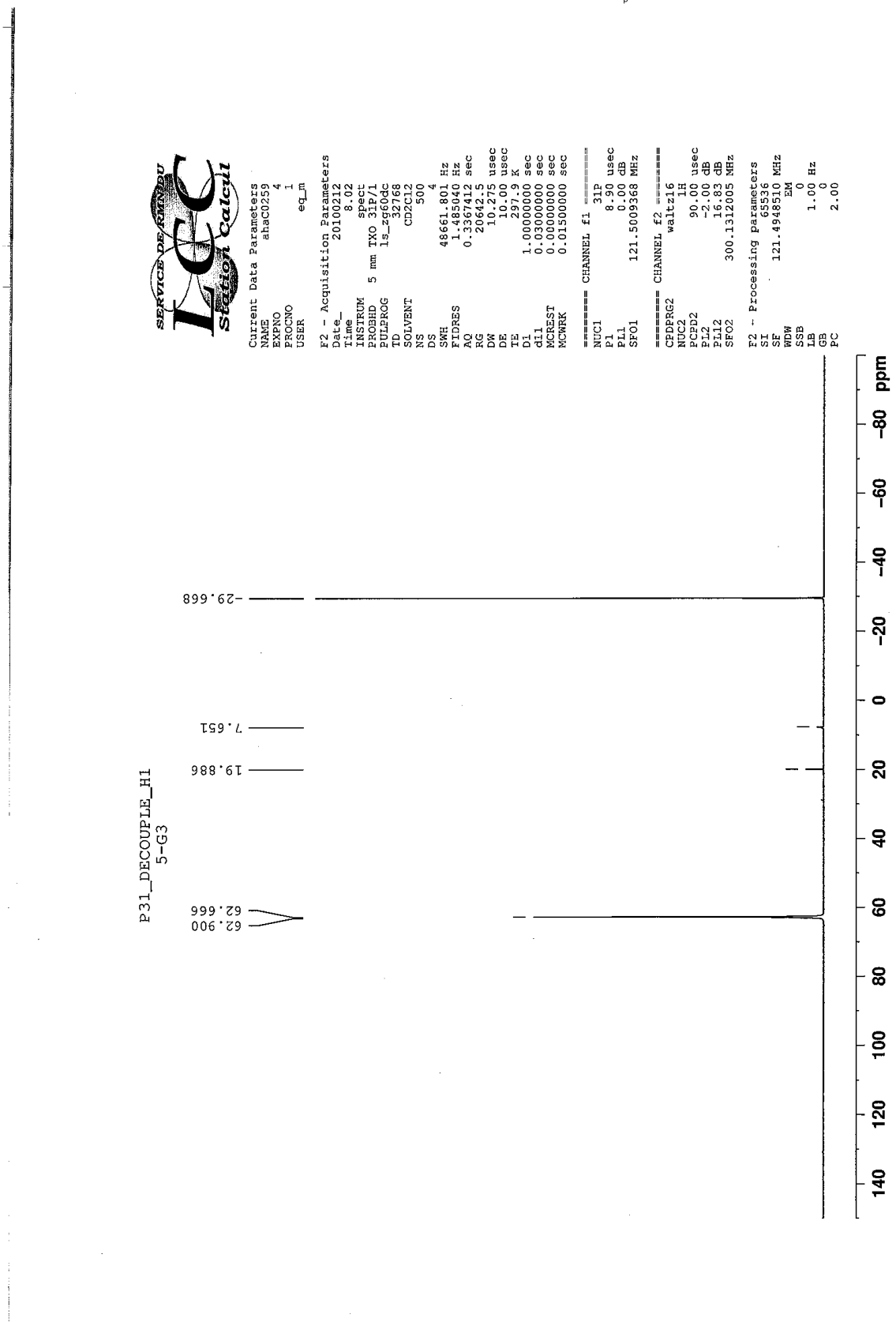


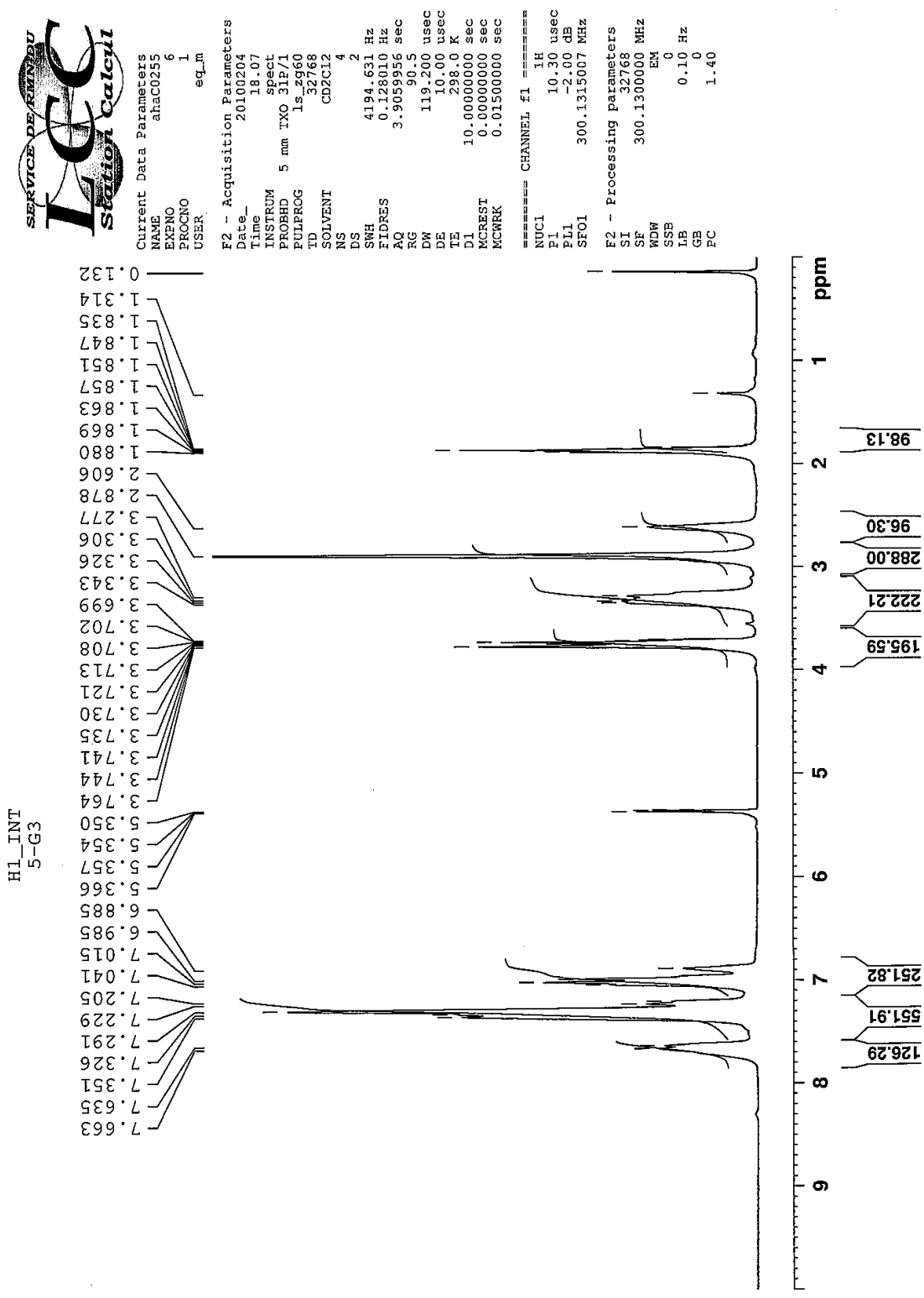

SERVICE DE RMN CEC
Station Calcul
Current Data Parameters
NAME ahac0251
EXPNO 2
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20100129
Time 13.17
INSTRUM spect
PROBHD 5 mm TXO 31P/1
PULPROG 1s_zg60
TD 32768
SOLVENT CD2Cl2
NS 8
DS 2
SWH 4194.631 Hz
FIDRES 0.128010 Hz
AQ 3.9059956 sec
RG 287.4
DW 119.200 usec
DE 10.00 usec
TE 298.0 K
D1 10.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 -2.00 dB
SFO1 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.40
H1_INT
5-G1
0.121
1.304
2.594
2.616
2.639
2.924
3.221
3.255
3.306
3.328
3.349
3.371
3.771
5.351
5.355
5.358
5.367
6.904
6.969
6.998
7.023
7.051
7.293
7.298
7.311
7.321
7.339
7.344
7.349
7.353
7.365
7.370
7.373
7.376
7.385
7.397
7.401
7.598
7.626
ppm
1
2
3
4
5
6
7
8
9
23.98
72.07
17.73
24.24
24.00
72.08
119.92
18.01

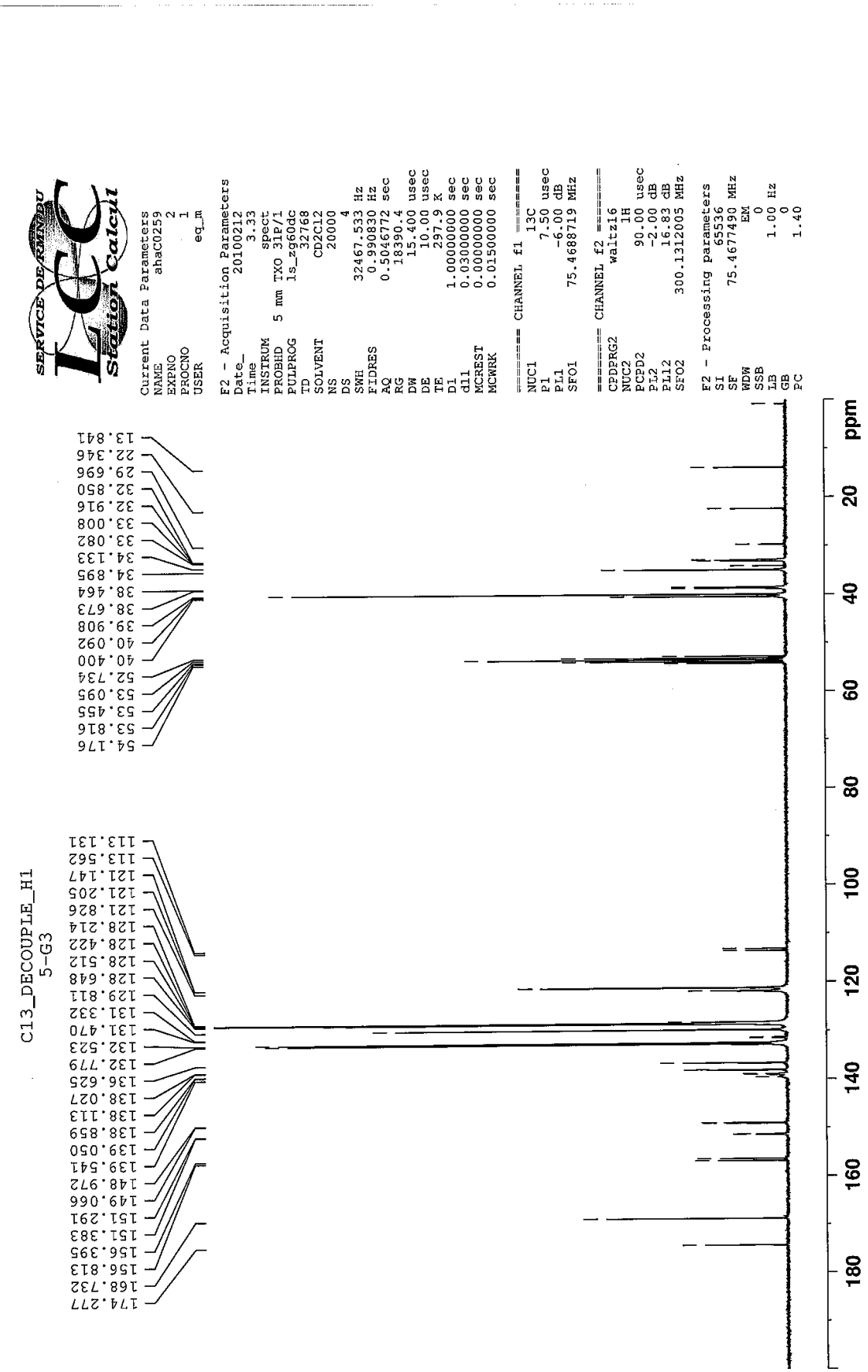

C13_DECOUPLE_H1
5-61
ppm
29.30
29.71
32.99
33.15
34.98
38.33
38.54
40.11
40.29
40.49
53.84
76.66
77.08
77.28
77.51
113.78
114.22
121.14
121.20
121.33
128.28
128.43
128.52
128.67
128.84
129.80
131.41
131.55
132.26
132.47
132.59
132.84
136.45
137.91
138.00
138.59
138.77
148.94
149.04
151.23
155.87
156.29
159.22
174.32
****
* L.C.C. du C.N.R.S *
* Service de R.M.N. *
****
Current Data Parameters
NAME ahab0234
EXPNO 2
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20100121
Time 1.49
INSTRUM dpx300
PROBHD 5 mm BBF ATM
PULPROG is_zg60dc
TD 32768
SOLVENT CDCl3
NS 16000
DS 4
SWH 30120.482 Hz
FIDRES 0.919204 Hz
AQ 0.5439988 sec
RG 14596.5
DW 16.600 usec
DE 10.00 usec
TE 298 K
D1 1.00000000 sec
d11 0.03000000 sec
========== CHANNEL f1 ==========
NUC1 13C
P1 12.00 usec
PL1 0.00 dB
SFO1 75.4715322 MHz
========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 102.00 usec
PL2 1.00 dB
PL12 19.00 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 22.00 cm
F1P 200.000 ppm
F1 15093.55 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 9.09091 ppm/cm
HZCM 686.07043 Hz/cm

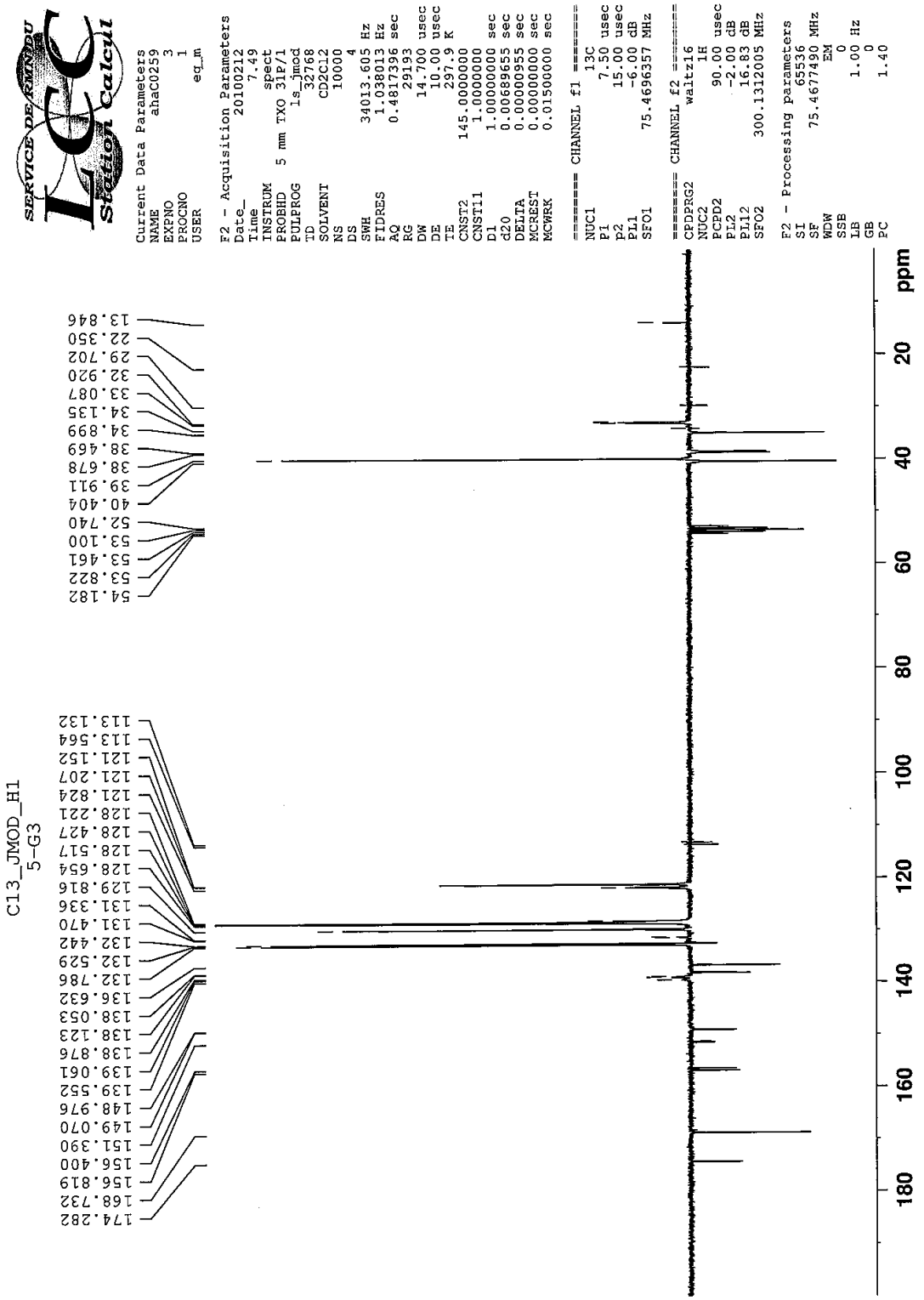
Compound 5-G_3 :



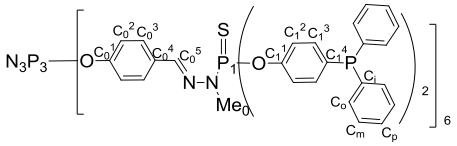


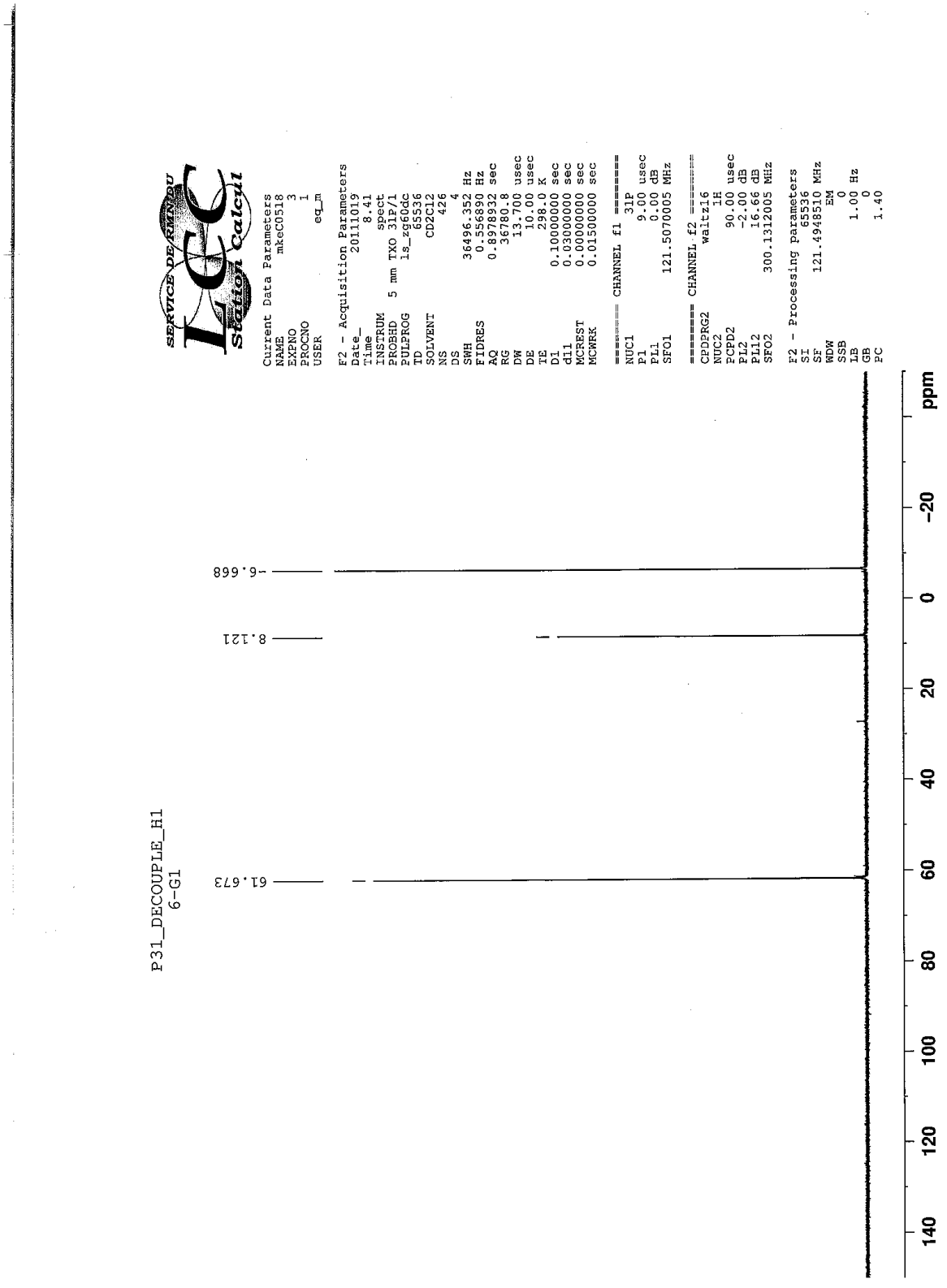

SERVICE DE RMN DU
Station Calcul
Current Data Parameters
NAME ahaC0255
EXPNO 6
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20100204
Time 18.07
INSTRUM spect
PROBHD 5 mm TXO 31P/1
PULPROG ls_zg60
TD 32768
SOLVENT CD2C12
NS 4
DS 2
SWH 4194.631 Hz
FIDRES 0.128010 Hz
AQ 3.9059956 sec
RG 90.5
DW 119.200 usec
DE 10.00 usec
TE 298.0 K
D1 10.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.30 usec
PL1 -2.00 dB
SFO1 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.40
H1_INT
5-G3
0.132
1.314
1.835
1.847
1.851
1.857
1.863
1.869
1.880
2.606
2.878
3.277
3.306
3.326
3.343
3.699
3.702
3.708
3.713
3.721
3.730
3.735
3.741
3.744
3.764
5.350
5.354
5.357
5.366
6.885
6.985
7.015
7.041
7.205
7.229
7.291
7.326
7.351
7.635
7.663
98.13
96.30
288.00
222.21
195.59
251.82
551.91
126.29
ppm
1
2
3
4
5
6
7
8
9

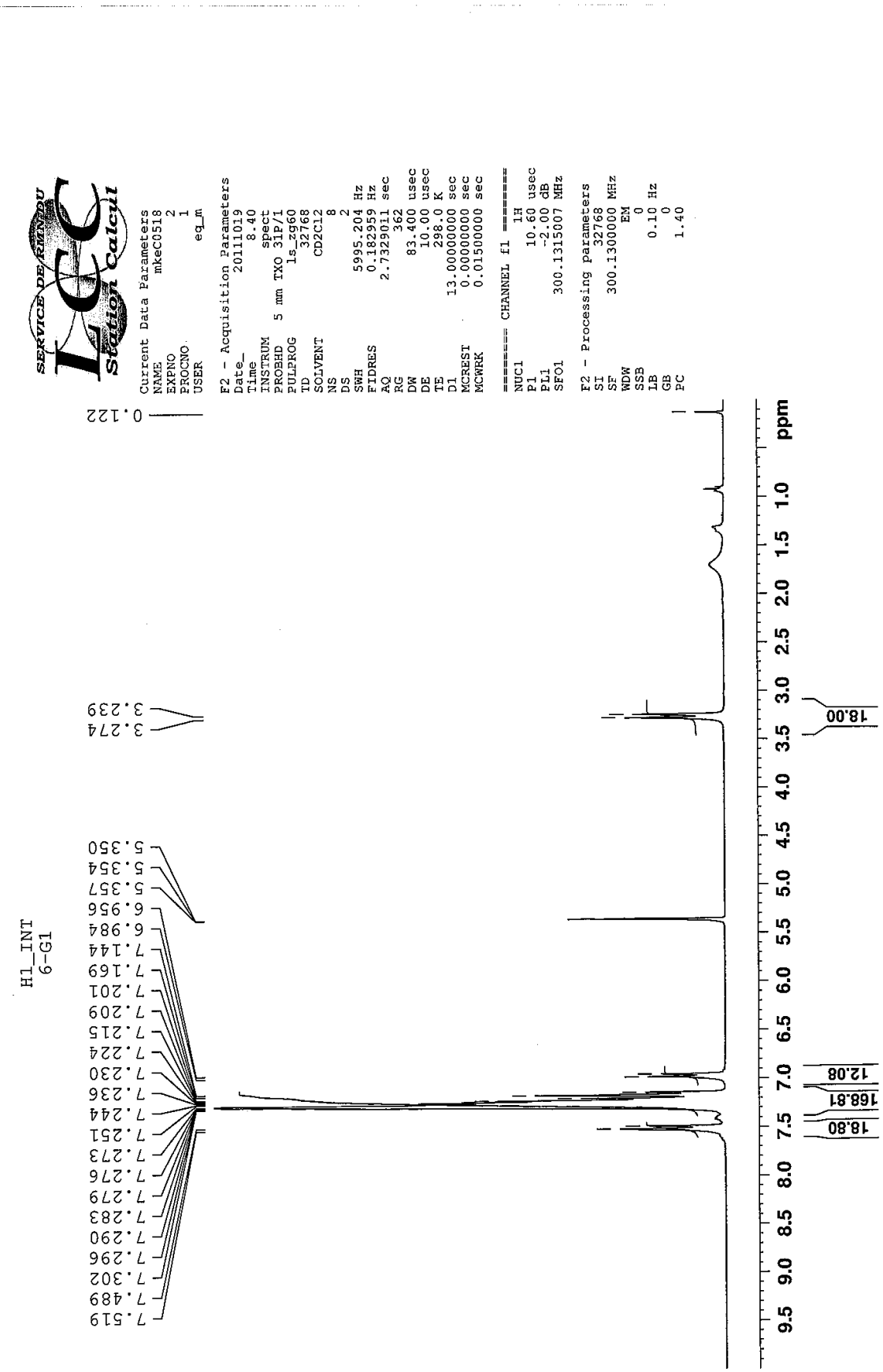


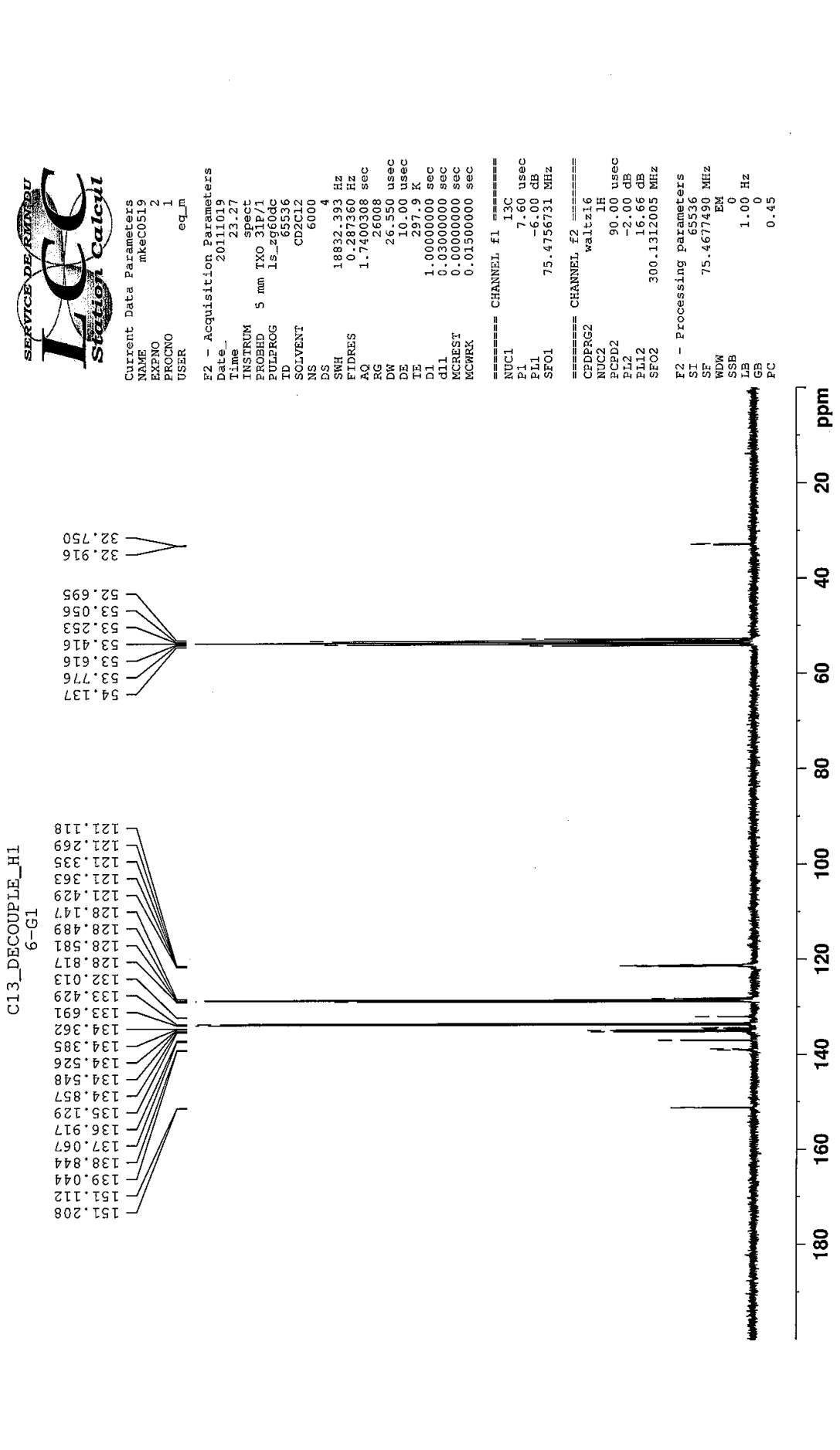

SERVICE DE RMN DU
Station Calcul
Current Data Parameters
NAME ahaC0259
EXPNO 3
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20100212
Time 7.49
INSTRUM spect
PROBHD 5 mm TXO 31P/1
PULPROG 1s_jmod
TD 32768
SOLVENT CD2Cl2
NS 10000
DS 4
SWH 34013.605 Hz
FIDRES 1.038013 Hz
AQ 0.48177396 sec
RG 29193
DW 14.700 usec
DE 10.00 usec
TE 297.9 K
CNST2 145.0000000
CNST11 1.0000000
D1 1.00000000 sec
d20 0.00689655 sec
DELTA 0.00000955 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.50 usec
P2 15.00 usec
PL1 -6.00 dB
SFO1 75.4696357 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 16.83 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
C13_JMOD_H1
5-G3
13.846
22.350
29.702
32.920
33.087
34.135
34.899
38.469
38.678
39.911
40.404
52.740
53.100
53.461
53.822
54.182
113.132
113.564
121.152
121.207
121.824
128.221
128.427
128.517
128.654
129.816
131.336
131.470
132.442
132.529
132.786
136.632
138.053
138.123
138.876
139.061
139.552
148.976
149.070
151.390
156.400
156.819
168.732
174.282
ppm
20
40
60
80
100
120
140
160
180

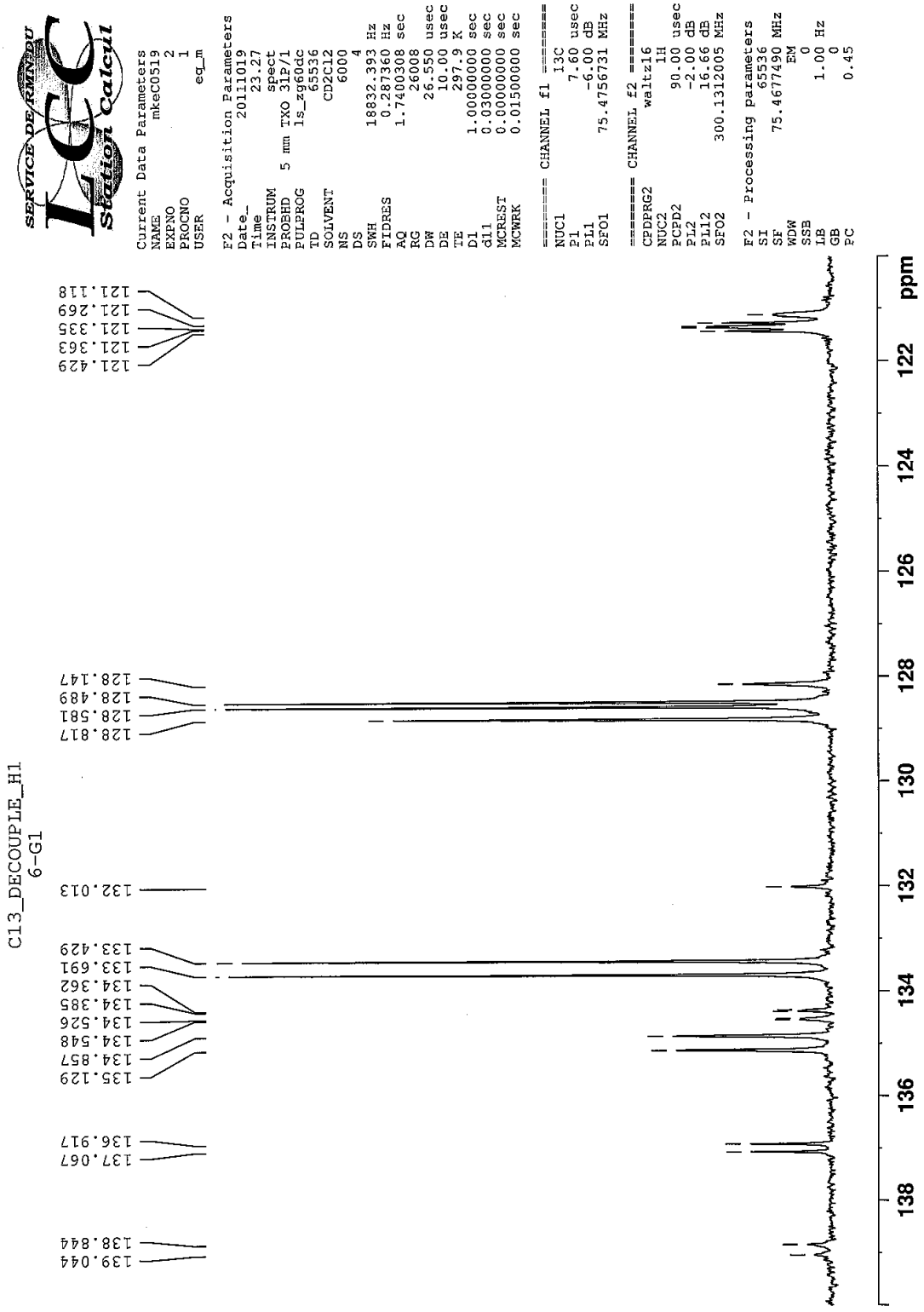
Compound 6-G_1 :



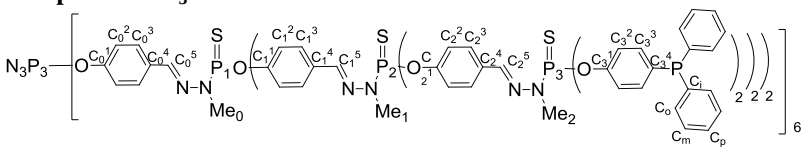


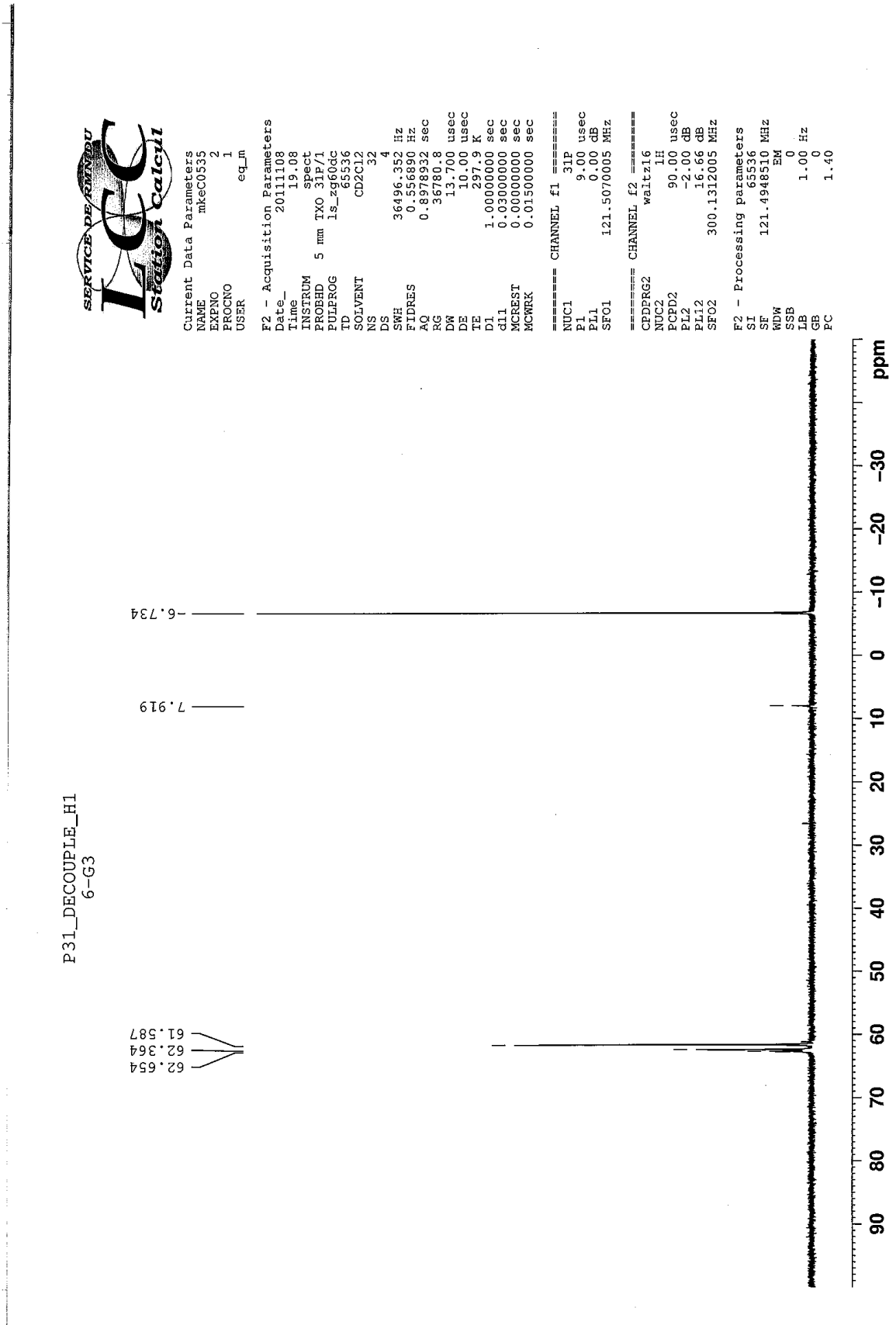

SERVICE DE RMN DU
Station Calcul
Current Data Parameters
NAME mkeC0518
EXPNO 2
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20111019
Time 8.40
INSTRUM spect
PROBHD 5 mm TXO 31P/1
PULPROG ls_zg60
TD 32768
SOLVENT CD2Cl2
NS 8
DS 2
SWH 5995.204 Hz
FIDRES 0.1829959 Hz
AQ 2.7329011 sec
RG 362
DW 83.400 usec
DE 10.00 usec
TE 298.0 K
D1 13.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 10.60 usec
PL1 -2.00 dB
SFO1 300.1315007 MHz
F2 - Processing parameters
SI 32768
SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.40
H1_INT
6-G1
0.122
3.239
3.274
5.350
5.354
5.357
6.956
6.984
7.144
7.169
7.201
7.209
7.215
7.224
7.230
7.236
7.244
7.251
7.273
7.276
7.279
7.283
7.290
7.296
7.302
7.489
7.519
18.00
12.08
168.81
18.80
ppm

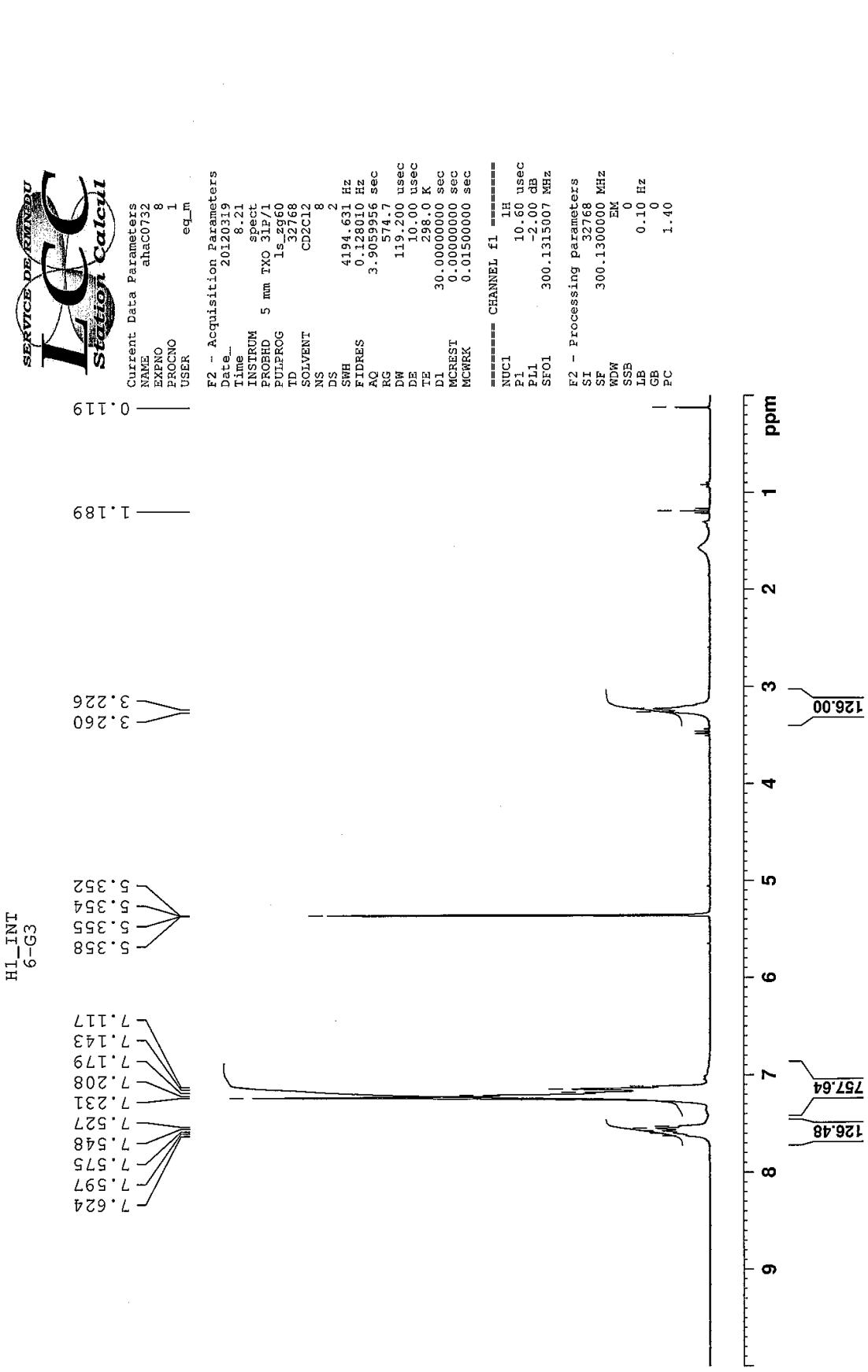

SERVICE DE RMN du
Station Calcul
Current Data Parameters
NAME mkeC0519
EXPNO 2
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20111019
Time 23.27
INSTRUM spect
PROBHD 5 mm TXO 31P/1
PULPROG ls_zg60dc
TD 65536
SOLVENT CD2Cl2
NS 6000
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.74400308 sec
RG 26008
DW 26.550 usec
DE 10.00 usec
TE 297.9 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.60 usec
PL1 -6.00 dB
SFO1 75.4756731 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 16.66 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.45
C13_DECOUPLE_H1
6-G1
32.750
32.916
52.695
53.056
53.253
53.416
53.616
53.776
54.137
121.118
121.269
121.335
121.363
121.429
128.147
128.489
128.581
128.817
132.013
133.429
133.691
134.362
134.385
134.526
134.548
134.857
135.129
136.917
137.067
138.844
139.044
151.112
151.208
180
160
140
120
100
80
60
40
20
ppm


SERVICE DE RMN DU
Station Calcul
Current Data Parameters
NAME mkeC0519
EXPNO 2
PROCNO 1
USER eq_m
F2 - Acquisition Parameters
Date_ 20111019
Time_ 23.27
INSTRUM spect
PROBHD 5 mm TXO 31P/1
PULPROG ls_zg60dc
TD 65536
SOLVENT CD2C12
NS 6000
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.74000308 sec
RG 26008
DW 26.550 usec
DE 10.00 usec
TE 297.9 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 7.60 usec
PL1 -6.00 dB
SFO1 75.4756731 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 16.66 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 65536
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 0.45
C13_DECOUPLE_H1
6-G1
121.118
121.269
121.335
121.363
121.429
128.147
128.489
128.581
128.817
132.013
133.429
133.691
134.362
134.385
134.526
134.548
134.857
135.129
136.917
137.067
138.844
139.044
ppm
122
124
126
128
130
132
134
136
138

Compound 6-G_3 :






SERVICE DE RMN DU
Station Calcul
Current Data Parameters
NAME ahac0732
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PROCNO 1
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FIDRES 0.128010 Hz
AQ 3.9059956 sec
RG 574.7
DW 119.200 usec
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D1 30.00000000 sec
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MCWRK 0.01500000 sec
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PL1 -2.00 dB
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SF 300.1300000 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.40
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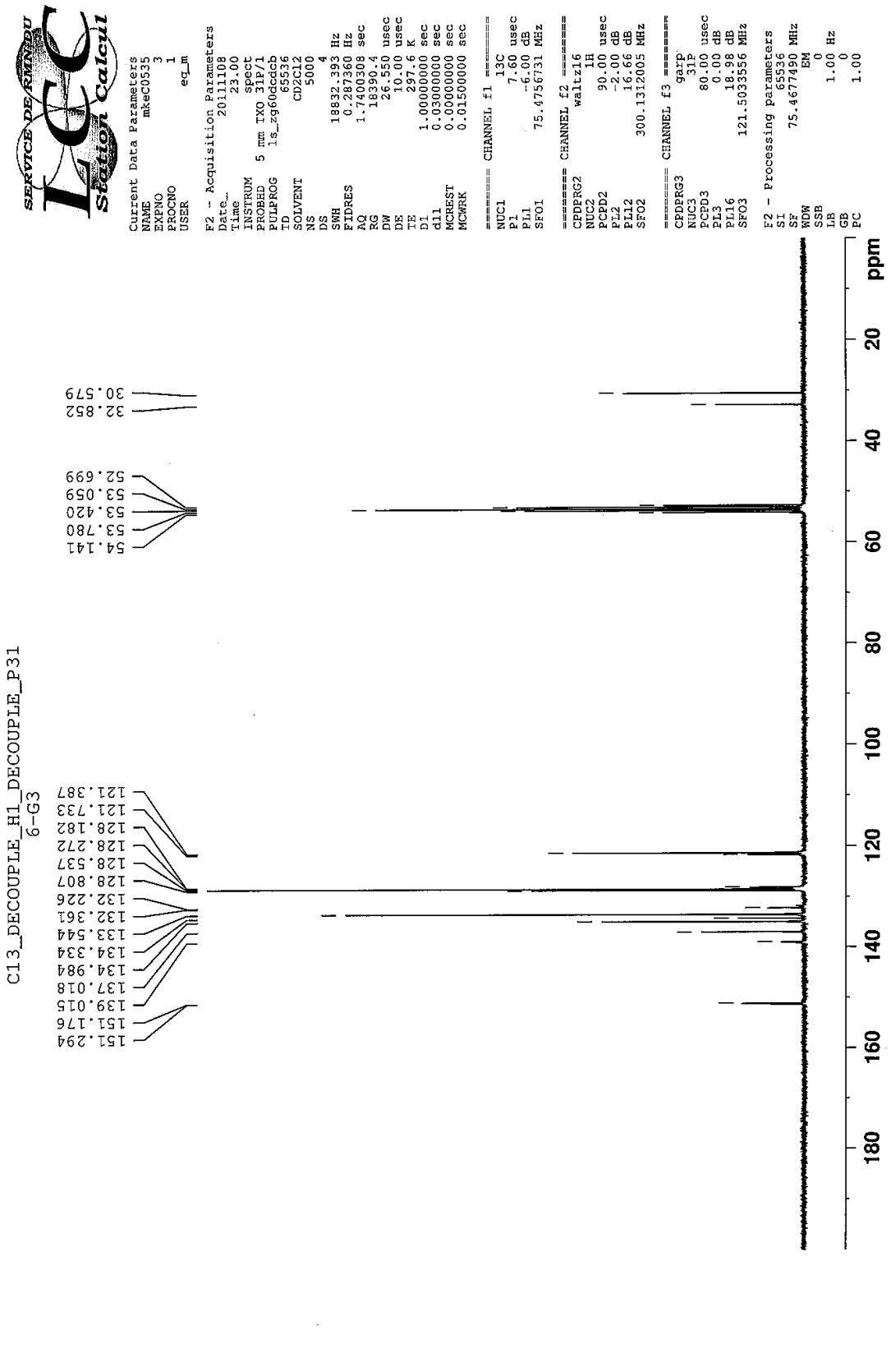
1.189
3.226
3.260
5.352
5.354
5.355
5.358
7.117
7.143
7.179
7.208
7.231
7.527
7.548
7.575
7.597
7.624
126.00
757.64
126.48
ppm
1
2
3
4
5
6
7
8
9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SWH 18832.393 Hz
FIDRES 0.2873560 Hz
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DE 10.00 usec
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D1 1.00000000 sec
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MCWRK 0.01500000 sec
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PL1 -6.00 dB
SFO1 75.4756731 MHz
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NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 16.66 dB
SFO2 300.1312005 MHz
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NUC3 31P
PCPD3 80.00 usec
PL3 0.00 dB
PL16 18.98 dB
SFO3 121.5033556 MHz
F2 - Processing parameters
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SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
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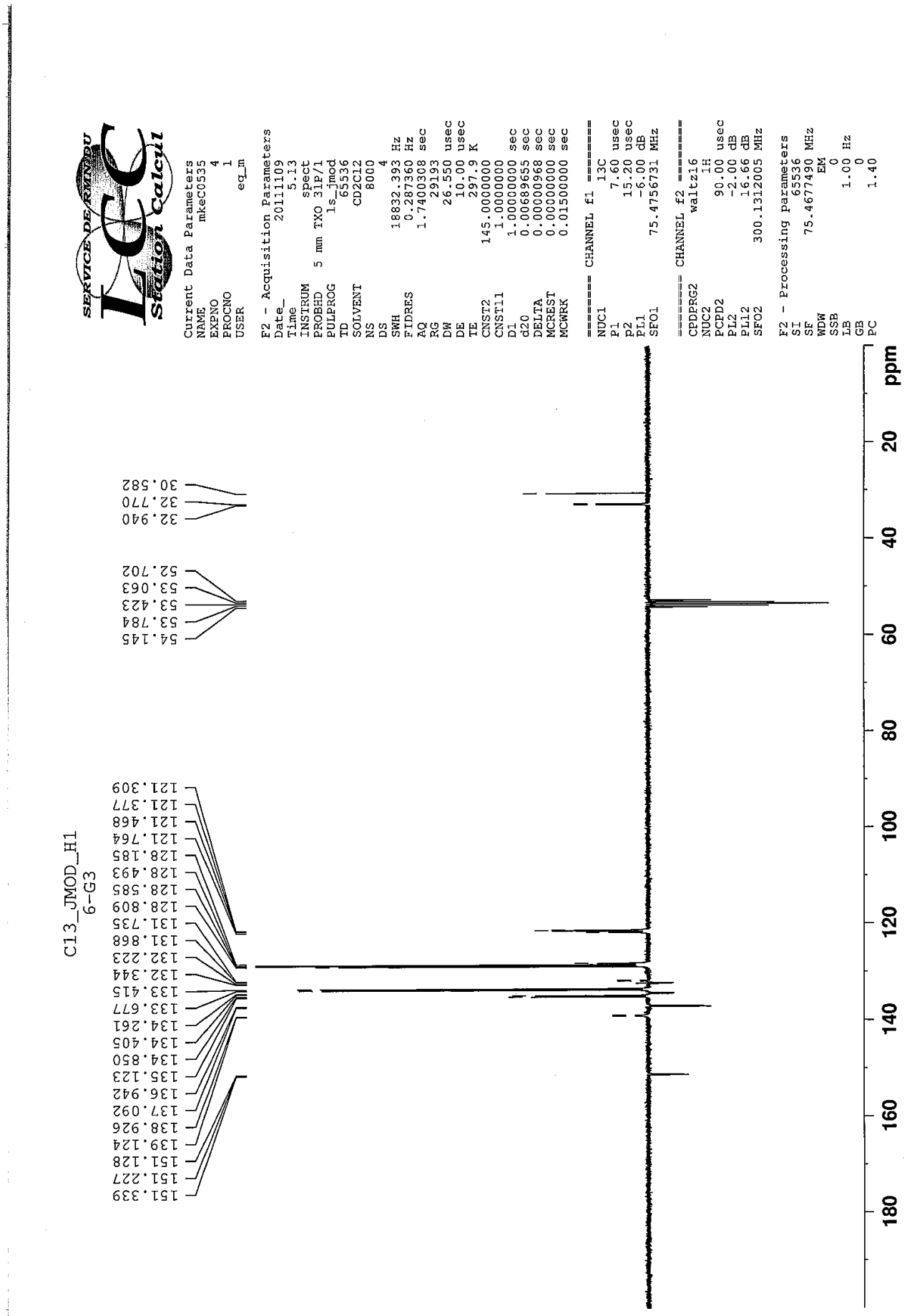
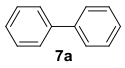
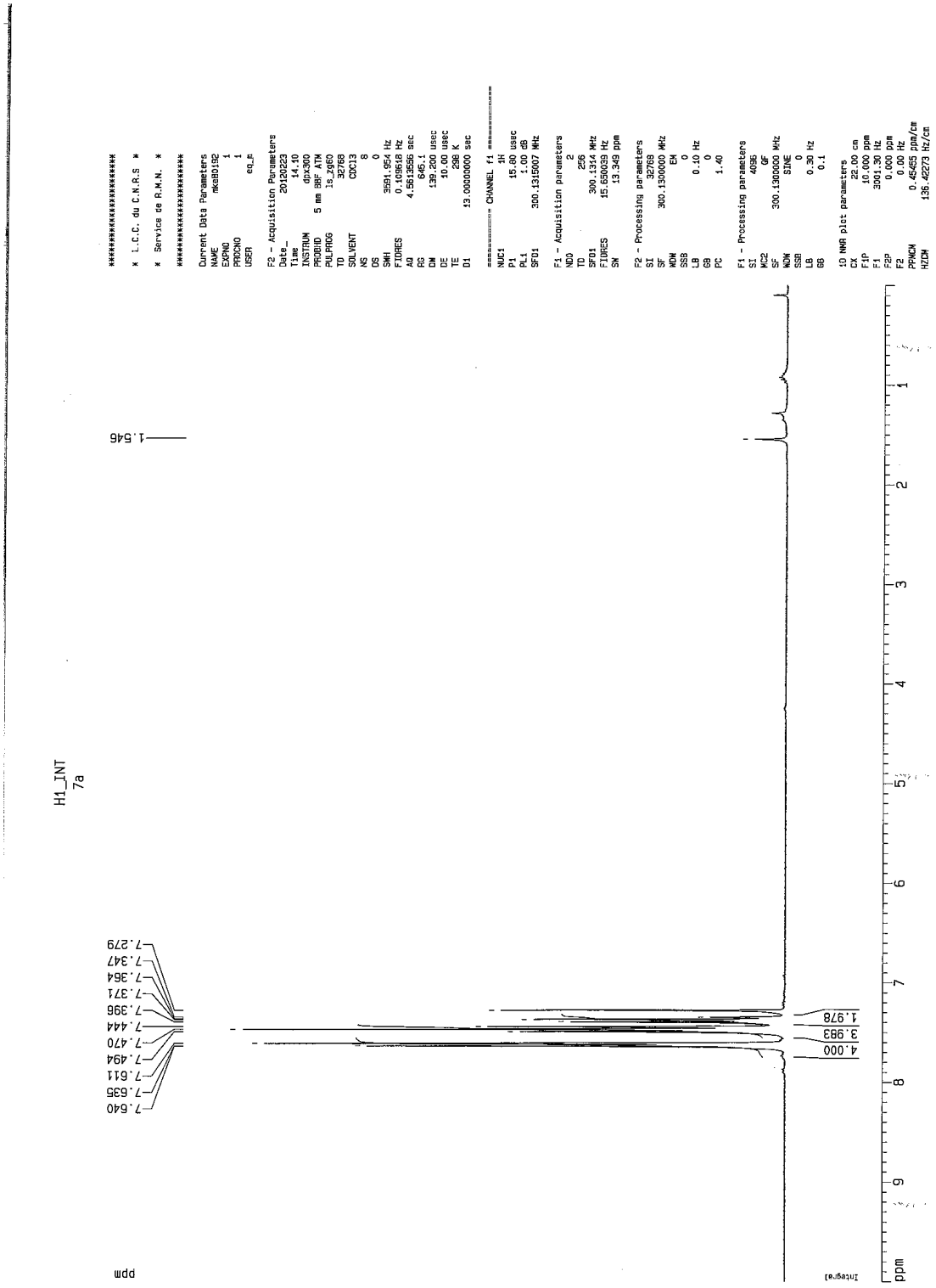
32.852
52.699
53.059
53.420
53.780
54.141
121.387
121.733
128.182
128.272
128.537
128.807
132.226
132.361
133.544
134.334
134.984
137.018
139.015
151.176
151.294
ppm
180
160
140
120
100
80
60
40
20



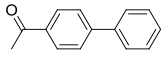
Compound 7a prepared by using **6-G_1** as the ligand**:**



The standard procedure described above was applied by using Pd(OAc) (1,12 mg, 0.005 mmol), **6-G_1** (2.0 mg, 0.00042 mmol), THF (5 mL), water (2 mL), bromobenzene (105 µL, 1 mmol), phenyl boronic acid (139 mg, 1.14 mmol) and Na_2CO_3 (318 mg, 3 mmol). The filtrate obtained was purified by silica flash chromatography (Pentane) and biphenyl **7a** was obtained as a white powder in 82 % yield (127 mg). For purity: see spectra above.
^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ (ppm): 7.35-7.40 (m, 2H), 7.44-7.49 (m, 4H), 7.61-7.64 (m, 4H).
GC**:** rt = 15.82 min.



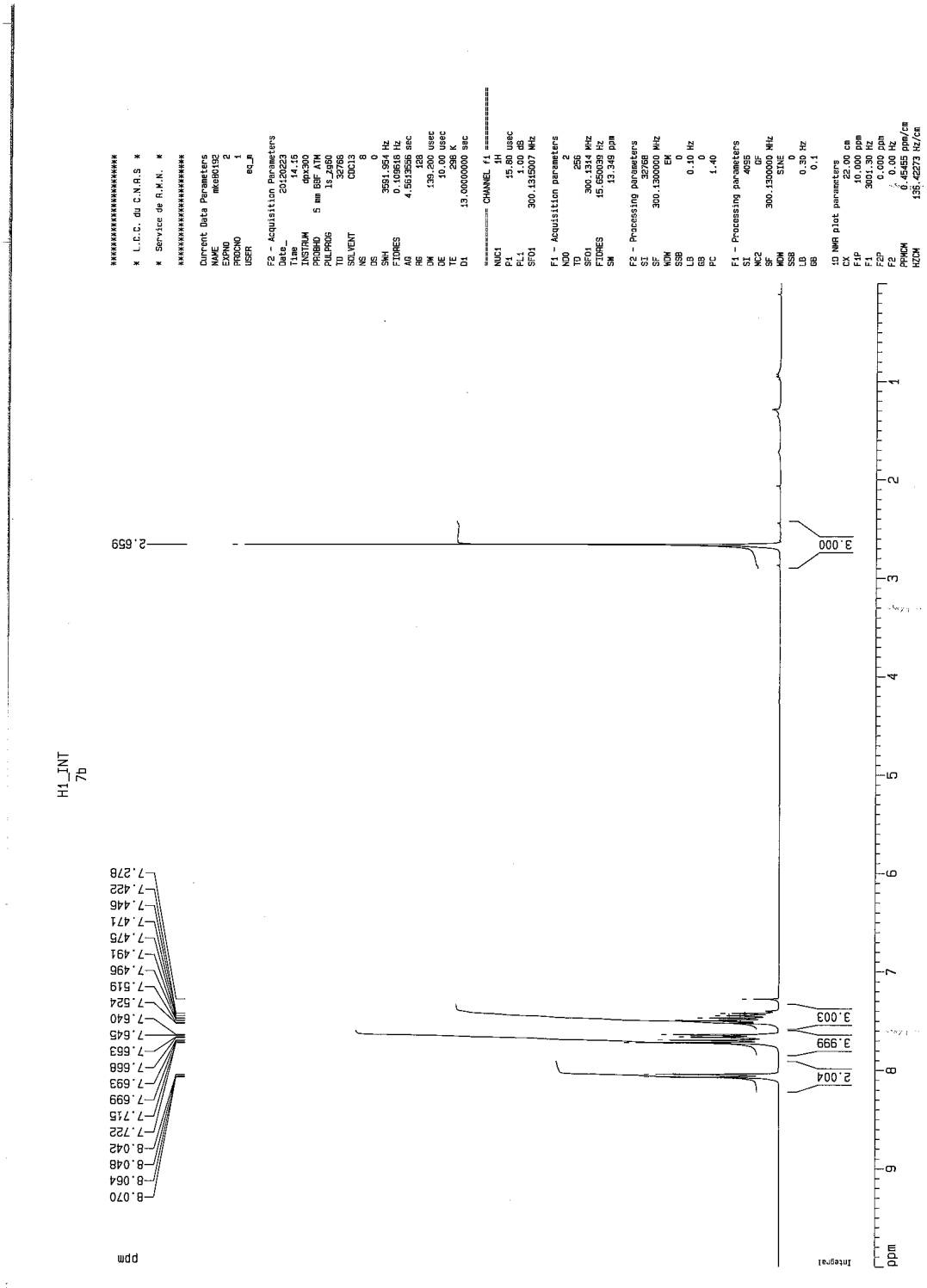
Compound 7b prepared by using **5-OMe** as the ligand**:**



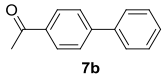
7b

The standard procedure described above was applied by using Pd(OAc) (1,12 mg, 0.005 mmol), **5-OMe** (2.5 mg, 0.005 mmol), THF (5 mL), water (2 mL), 4-bromoacetophenone (199 mg, 1 mmol), phenyl boronic acid (139 mg, 1.14 mmol) and Na_2CO_3 (318 mg, 3 mmol). The filtrate obtained was purified by silica flash chromatography (Pentane/AcOEt) and **7b** was obtained as a white powder in 92 % yield (181 mg). For purity: see spectra above.

^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ (ppm): 2.66 (s, 3H, Me), 7.42-7.52 (m, 3H), 7.64-7.72 (m, 4H), 8.04-8.07 (m, 2H).
GC**:** rt = 21.50 min.

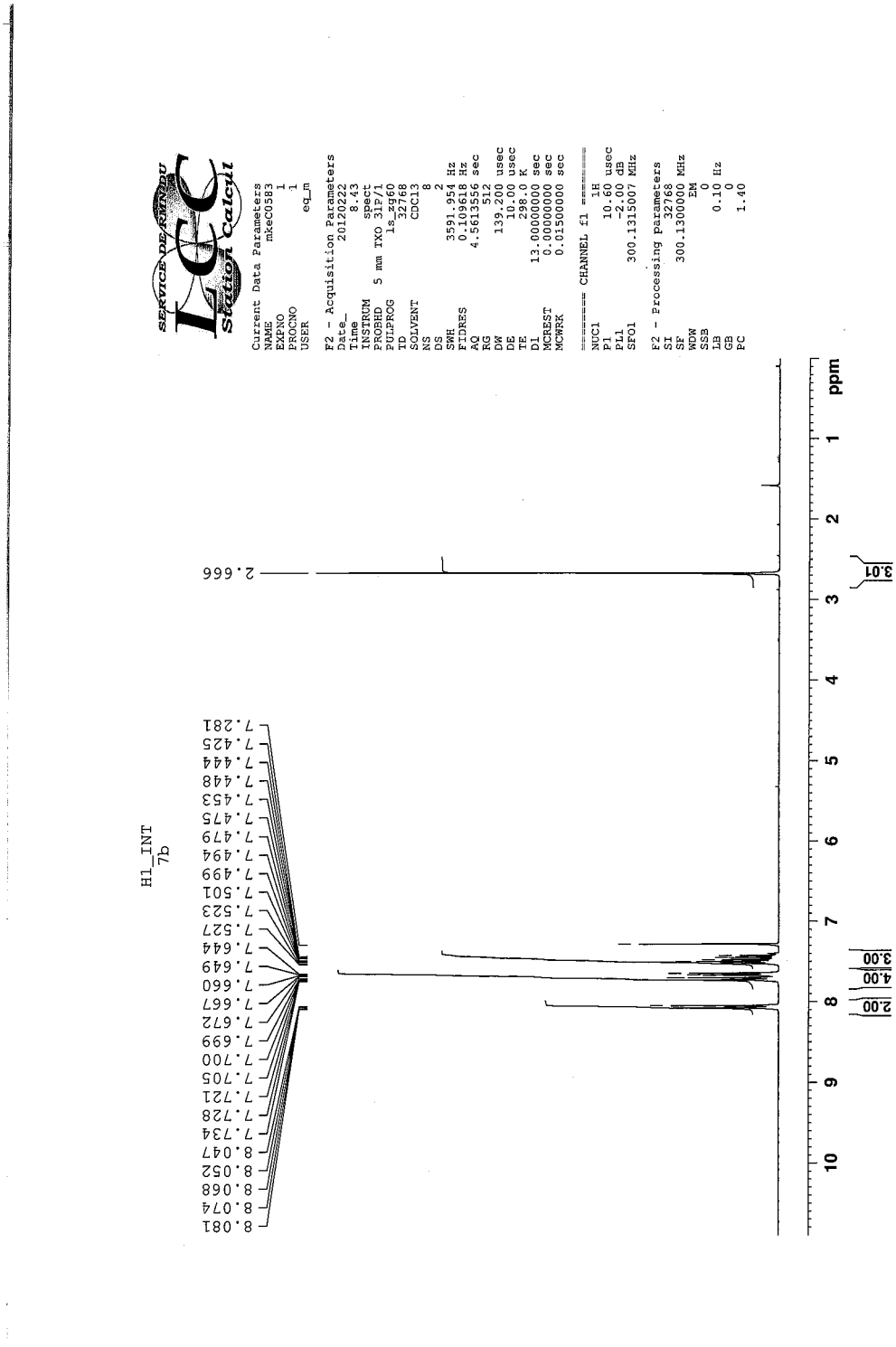


Compound 7b prepared by using **5-G_1** as the ligand**:**



The standard procedure described above was applied by using Pd(OAc) (1,12 mg, 0.005 mmol), **5-G_1** (3.0 mg, 0.00042 mmol), THF (5 mL), water (2 mL), 4-bromoacetophenone (199 mg, 1 mmol), phenyl boronic acid (139 mg, 1.14 mmol) and Na_2CO_3 (318 mg, 3 mmol). The filtrate obtained was purified by silica flash chromatography (Pentane/AcOEt) and **7b** was obtained as a white powder in 93 % yield (183 mg). For purity: see spectra above.

^{1}H NMR (300 MHz, CD_2Cl_2, 25°C) δ (ppm): 2.67 (s, 3H, Me), 7.43-7.53 (m, 3H), 7.64-7.73 (m, 4H), 8.05-8.08 (m, 2H).
GC**:** rt = 21.50 min.



3. RX data

Crystallographic data Diffraction data were collected at low temperature (180 K) on an Gemini Oxford Diffraction diffractometer for **5-OMe** and on a Bruker Kappa Apex II for **5-OH** and **3**, using a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Both diffractometers are equipped with an Oxford Cryosystems Cryostream cooler device. The structures were solved by direct methods with SIR92[3] and all non-hydrogen atoms were refined anisotropically by means of least-squares procedures on F^2 with the aid of the program SHELXL-97.[4]

Compound 3

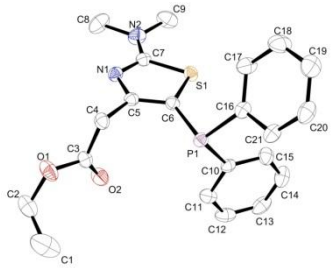


Table 1. Crystal data and structure refinement for **3**.

Identification code	**3**
Empirical formula	C21 H23 N2 O2 P S
Formula weight	398.44
Temperature	180 K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 8.7642(9) A alpha = 94.396(5) deg. b = 10.8437(11) A beta = 106.808(5) deg. c = 12.1558(12) A gamma = 109.396(5) deg.
Volume	1023.87(19) A^3
Z, Calculated density	2, 1.292 Mg/m^3
Absorption coefficient	0.254 mm^-1
F(000)	420
Crystal size	0.45 x 0.3 x 0.125 mm
Theta range for data collection	2.03 to 25.35 deg.
Limiting indices	-10<=h<=10, -13<=k<=13, -14<=l<=14
Reflections collected / unique	20382 / 3739 [R(int) = 0.0186]
Completeness to theta = 25.35	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3739 / 0 / 247
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0324, wR2 = 0.0815
R indices (all data)	R1 = 0.0346, wR2 = 0.0834
Largest diff. peak and hole	0.714 and -0.305 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	4481(1)	463(1)	1953(1)	26(1)
P(1)	5221(1)	3227(1)	3499(1)	23(1)
O(2)	8684(2)	4544(1)	2010(1)	38(1)
O(1)	11211(2)	5231(1)	3487(1)	41(1)
N(1)	7743(2)	1206(1)	2322(1)	26(1)
N(2)	6109(2)	-857(1)	1046(1)	35(1)
C(10)	3564(2)	3335(2)	2221(1)	24(1)
C(5)	7482(2)	2187(2)	2939(1)	23(1)
C(4)	9030(2)	3385(2)	3634(1)	27(1)

C(16)	3983(2)	2404(2)	4396(1)	26(1)
C(11)	4133(2)	4201(2)	1506(2)	31(1)
C(7)	6272(2)	233(2)	1751(1)	25(1)
C(15)	1815(2)	2638(2)	1936(1)	32(1)
C(6)	5841(2)	1993(1)	2877(1)	22(1)
C(3)	9566(2)	4430(2)	2928(1)	28(1)
C(21)	3366(2)	3181(2)	4986(1)	31(1)
C(9)	4479(3)	-1957(2)	548(2)	46(1)
C(20)	2517(2)	2680(2)	5749(2)	38(1)
C(12)	2975(3)	4350(2)	522(2)	38(1)
C(13)	1247(3)	3661(2)	256(2)	41(1)
C(19)	2266(3)	1398(2)	5939(2)	43(1)
C(18)	2901(3)	633(2)	5378(2)	45(1)
C(17)	3755(2)	1129(2)	4613(2)	36(1)
C(14)	665(2)	2805(2)	960(2)	41(1)
C(8)	7637(3)	-1063(2)	972(2)	47(1)
C(2)	11970(2)	6288(2)	2907(2)	45(1)
C(1)	11502(4)	7428(2)	3142(2)	74(1)

Table 3. Bond lengths [A] and angles [deg] for **3**.

S(1)-C(7)	1.7488(16)
S(1)-C(6)	1.7503(15)
P(1)-C(6)	1.7943(15)
P(1)-C(16)	1.8308(16)
P(1)-C(10)	1.8362(16)
O(2)-C(3)	1.201(2)
O(1)-C(3)	1.3441(19)
O(1)-C(2)	1.464(2)
N(1)-C(7)	1.313(2)
N(1)-C(5)	1.3738(19)
N(2)-C(7)	1.347(2)
N(2)-C(9)	1.445(2)
N(2)-C(8)	1.455(2)
C(10)-C(15)	1.387(2)
C(10)-C(11)	1.396(2)
C(5)-C(6)	1.361(2)
C(5)-C(4)	1.497(2)
C(4)-C(3)	1.507(2)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(16)-C(17)	1.387(2)
C(16)-C(21)	1.397(2)
C(11)-C(12)	1.387(3)
C(11)-H(11)	0.9300
C(15)-C(14)	1.385(2)
C(15)-H(15)	0.9300
C(21)-C(20)	1.384(2)
C(21)-H(21)	0.9300
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(20)-C(19)	1.382(3)
C(20)-H(20)	0.9300
C(12)-C(13)	1.373(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.383(3)
C(13)-H(13)	0.9300
C(19)-C(18)	1.378(3)
C(19)-H(19)	0.9300
C(18)-C(17)	1.388(3)
C(18)-H(18)	0.9300
C(17)-H(17)	0.9300
C(14)-H(14)	0.9300
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600

C(2)-C(1)	1.460(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600

C(7)-S(1)-C(6)	89.19(7)
C(6)-P(1)-C(16)	105.74(7)
C(6)-P(1)-C(10)	101.62(7)
C(16)-P(1)-C(10)	103.00(7)
C(3)-O(1)-C(2)	116.76(13)
C(7)-N(1)-C(5)	110.12(13)
C(7)-N(2)-C(9)	121.04(15)
C(7)-N(2)-C(8)	119.69(15)
C(9)-N(2)-C(8)	118.06(15)
C(15)-C(10)-C(11)	118.70(15)
C(15)-C(10)-P(1)	124.68(12)
C(11)-C(10)-P(1)	116.62(12)
C(6)-C(5)-N(1)	117.63(13)
C(6)-C(5)-C(4)	125.08(14)
N(1)-C(5)-C(4)	117.29(13)
C(5)-C(4)-C(3)	113.67(13)
C(5)-C(4)-H(4A)	108.8
C(3)-C(4)-H(4A)	108.8
C(5)-C(4)-H(4B)	108.8
C(3)-C(4)-H(4B)	108.8
H(4A)-C(4)-H(4B)	107.7
C(17)-C(16)-C(21)	118.26(15)
C(17)-C(16)-P(1)	125.08(12)
C(21)-C(16)-P(1)	116.37(12)
C(12)-C(11)-C(10)	120.74(16)
C(12)-C(11)-H(11)	119.6
C(10)-C(11)-H(11)	119.6
N(1)-C(7)-N(2)	123.99(15)
N(1)-C(7)-S(1)	114.68(11)
N(2)-C(7)-S(1)	121.33(13)
C(14)-C(15)-C(10)	120.24(16)
C(14)-C(15)-H(15)	119.9
C(10)-C(15)-H(15)	119.9
C(5)-C(6)-S(1)	108.38(11)
C(5)-C(6)-P(1)	124.03(11)
S(1)-C(6)-P(1)	127.13(9)
O(2)-C(3)-O(1)	124.54(15)
O(2)-C(3)-C(4)	126.29(14)
O(1)-C(3)-C(4)	109.16(13)
C(20)-C(21)-C(16)	120.83(16)
C(20)-C(21)-H(21)	119.6
C(16)-C(21)-H(21)	119.6
N(2)-C(9)-H(9A)	109.5
N(2)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(2)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(19)-C(20)-C(21)	120.33(16)
C(19)-C(20)-H(20)	119.8
C(21)-C(20)-H(20)	119.8
C(13)-C(12)-C(11)	119.87(16)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(12)-C(13)-C(14)	120.01(16)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
C(18)-C(19)-C(20)	119.28(17)
C(18)-C(19)-H(19)	120.4
C(20)-C(19)-H(19)	120.4
C(19)-C(18)-C(17)	120.70(18)
C(19)-C(18)-H(18)	119.6

C(17)-C(18)-H(18)	119.6
C(16)-C(17)-C(18)	120.58(16)
C(16)-C(17)-H(17)	119.7
C(18)-C(17)-H(17)	119.7
C(13)-C(14)-C(15)	120.44(17)
C(13)-C(14)-H(14)	119.8
C(15)-C(14)-H(14)	119.8
N(2)-C(8)-H(8A)	109.5
N(2)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(1)-C(2)-O(1)	109.92(18)
C(1)-C(2)-H(2A)	109.7
O(1)-C(2)-H(2A)	109.7
C(1)-C(2)-H(2B)	109.7
O(1)-C(2)-H(2B)	109.7
H(2A)-C(2)-H(2B)	108.2
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **3**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	25(1)	22(1)	28(1)	1(1)	11(1)	5(1)
P(1)	25(1)	22(1)	24(1)	2(1)	8(1)	10(1)
O(2)	30(1)	39(1)	34(1)	15(1)	3(1)	6(1)
O(1)	29(1)	40(1)	34(1)	9(1)	2(1)	-3(1)
N(1)	28(1)	29(1)	26(1)	7(1)	12(1)	14(1)
N(2)	45(1)	30(1)	34(1)	-1(1)	16(1)	18(1)
C(10)	30(1)	23(1)	24(1)	4(1)	12(1)	14(1)
C(5)	26(1)	23(1)	21(1)	7(1)	9(1)	10(1)
C(4)	23(1)	30(1)	25(1)	5(1)	5(1)	7(1)
C(16)	27(1)	32(1)	19(1)	4(1)	6(1)	14(1)
C(11)	40(1)	25(1)	31(1)	7(1)	15(1)	11(1)
C(7)	33(1)	26(1)	23(1)	8(1)	14(1)	14(1)
C(15)	31(1)	40(1)	28(1)	10(1)	14(1)	14(1)
C(6)	24(1)	21(1)	22(1)	4(1)	8(1)	8(1)
C(3)	24(1)	28(1)	27(1)	2(1)	7(1)	6(1)
C(21)	33(1)	37(1)	28(1)	5(1)	10(1)	19(1)
C(9)	62(1)	28(1)	43(1)	-2(1)	21(1)	10(1)
C(20)	41(1)	56(1)	29(1)	9(1)	16(1)	29(1)
C(12)	62(1)	31(1)	31(1)	12(1)	21(1)	23(1)
C(13)	53(1)	55(1)	26(1)	10(1)	10(1)	38(1)
C(19)	51(1)	62(1)	31(1)	20(1)	24(1)	28(1)
C(18)	67(1)	44(1)	40(1)	22(1)	30(1)	27(1)
C(17)	54(1)	37(1)	31(1)	12(1)	22(1)	25(1)
C(14)	31(1)	63(1)	33(1)	8(1)	10(1)	22(1)
C(8)	62(1)	58(1)	38(1)	2(1)	19(1)	41(1)
C(2)	36(1)	46(1)	40(1)	7(1)	10(1)	0(1)
C(1)	100(2)	47(1)	74(2)	7(1)	48(2)	9(1)

Compound 5-OH

Table 1. Crystal data and structure refinement for **5-OH**.

Identification code	**5-OH**
Empirical formula	C27 H28 N3 O2 P S
Formula weight	489.55
Temperature	180 K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P 21/c
Unit cell dimensions	a = 9.7499(4) A alpha = 90 deg. b = 30.5632(13) A beta = 101.967(2) deg. c = 8.5329(3) A gamma = 90 deg.
Volume	2487.44(17) A^3
Z, Calculated density	4, 1.307 Mg/m^3
Absorption coefficient	0.224 mm^-1
F(000)	1032
Crystal size	0.375 x 0.05 x 0.05 mm
Theta range for data collection	1.33 to 28.80 deg.
Limiting indices	-12<=h<=13, -41<=k<=38, -11<=l<=11
Reflections collected / unique	33236 / 6476 [R(int) = 0.0421]
Completeness to theta = 28.80	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6476 / 0 / 313
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.0927
R indices (all data)	R1 = 0.0649, wR2 = 0.1032
Largest diff. peak and hole	0.341 and -0.231 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **5-OH**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	10709(1)	822(1)	6131(1)	26(1)
P(1)	7587(1)	741(1)	6532(1)	21(1)
O(1)	15915(1)	2888(1)	8562(2)	44(1)
O(2)	7371(1)	2127(1)	9066(2)	37(1)
N(2)	11121(1)	1442(1)	8259(2)	23(1)
N(3)	13095(2)	1271(1)	7178(2)	31(1)
N(1)	9481(2)	2245(1)	8416(2)	25(1)
C(12)	9320(2)	970(1)	7034(2)	22(1)
C(9)	8506(2)	1992(1)	8845(2)	23(1)
C(22)	7347(2)	697(1)	4351(2)	23(1)
C(8)	9310(2)	2712(1)	8095(2)	29(1)
C(11)	9757(2)	1301(1)	8098(2)	21(1)
C(13)	11755(2)	1216(1)	7293(2)	23(1)
C(7)	10277(2)	2992(1)	9337(2)	32(1)
C(3)	12311(2)	3240(1)	8169(2)	32(1)
C(2)	13682(2)	3213(1)	7975(2)	35(1)
C(16)	7764(2)	173(1)	7223(2)	23(1)
C(5)	12719(2)	2661(1)	10061(2)	33(1)
C(1)	14579(2)	2903(1)	8822(2)	31(1)
C(23)	7055(2)	1087(1)	3491(2)	27(1)
C(10)	8859(2)	1510(1)	9124(2)	25(1)
C(27)	7415(2)	309(1)	3516(2)	29(1)

C(19)	7790(2)	-663(1)	8558(2)	33(1)
C(14)	13984(2)	1575(1)	8240(3)	42(1)
C(25)	6903(2)	700(1)	1017(2)	35(1)
C(4)	11796(2)	2963(1)	9208(2)	26(1)
C(6)	14098(2)	2630(1)	9885(2)	34(1)
C(17)	9011(2)	-31(1)	7891(3)	43(1)
C(18)	9018(2)	-448(1)	8551(3)	49(1)
C(26)	7189(2)	312(1)	1855(2)	35(1)
C(24)	6849(2)	1088(1)	1837(2)	32(1)
C(21)	6526(2)	-53(1)	7213(2)	33(1)
C(15)	13721(2)	986(1)	6165(3)	42(1)
C(20)	6538(2)	-469(1)	7866(2)	37(1)

Table 3. Bond lengths [A] and angles [deg] for **5-OH**.

S(1)-C(13)	1.7470(16)
S(1)-C(12)	1.7497(16)
P(1)-C(12)	1.7962(16)
P(1)-C(16)	1.8308(16)
P(1)-C(22)	1.8326(16)
O(1)-C(1)	1.368(2)
O(1)-H(1)	0.8400
O(2)-C(9)	1.231(2)
N(2)-C(13)	1.324(2)
N(2)-C(11)	1.378(2)
N(3)-C(13)	1.341(2)
N(3)-C(15)	1.447(2)
N(3)-C(14)	1.452(2)
N(1)-C(9)	1.334(2)
N(1)-C(8)	1.457(2)
N(1)-H(100)	0.82(2)
C(12)-C(11)	1.367(2)
C(9)-C(10)	1.522(2)
C(22)-C(27)	1.391(2)
C(22)-C(23)	1.398(2)
C(8)-C(7)	1.527(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(11)-C(10)	1.503(2)
C(7)-C(4)	1.509(2)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(3)-C(2)	1.383(3)
C(3)-C(4)	1.393(2)
C(3)-H(3)	0.9500
C(2)-C(1)	1.387(3)
C(2)-H(2)	0.9500
C(16)-C(17)	1.380(2)
C(16)-C(21)	1.390(2)
C(5)-C(4)	1.386(2)
C(5)-C(6)	1.387(3)
C(5)-H(5)	0.9500
C(1)-C(6)	1.384(3)
C(23)-C(24)	1.384(2)
C(23)-H(23)	0.9500
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(27)-C(26)	1.389(2)
C(27)-H(27)	0.9500
C(19)-C(18)	1.367(3)

C(19)-C(20)	1.376(3)
C(19)-H(19)	0.9500
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(25)-C(24)	1.383(3)
C(25)-C(26)	1.384(3)
C(25)-H(25)	0.9500
C(6)-H(6)	0.9500
C(17)-C(18)	1.393(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(26)-H(26)	0.9500
C(24)-H(24)	0.9500
C(21)-C(20)	1.387(2)
C(21)-H(21)	0.9500
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(20)-H(20)	0.9500

C(13)-S(1)-C(12)	89.29(8)
C(12)-P(1)-C(16)	105.69(7)
C(12)-P(1)-C(22)	100.74(7)
C(16)-P(1)-C(22)	103.91(7)
C(1)-O(1)-H(1)	109.5
C(13)-N(2)-C(11)	109.84(13)
C(13)-N(3)-C(15)	120.45(15)
C(13)-N(3)-C(14)	119.93(15)
C(15)-N(3)-C(14)	119.05(15)
C(9)-N(1)-C(8)	124.02(15)
C(9)-N(1)-H(100)	115.7(13)
C(8)-N(1)-H(100)	120.2(13)
C(11)-C(12)-S(1)	108.60(12)
C(11)-C(12)-P(1)	126.49(12)
S(1)-C(12)-P(1)	124.81(9)
O(2)-C(9)-N(1)	124.22(15)
O(2)-C(9)-C(10)	118.82(14)
N(1)-C(9)-C(10)	116.93(14)
C(27)-C(22)-C(23)	118.96(15)
C(27)-C(22)-P(1)	125.01(12)
C(23)-C(22)-P(1)	116.02(12)
N(1)-C(8)-C(7)	112.85(14)
N(1)-C(8)-H(8A)	109.0
C(7)-C(8)-H(8A)	109.0
N(1)-C(8)-H(8B)	109.0
C(7)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8
C(12)-C(11)-N(2)	117.46(14)
C(12)-C(11)-C(10)	124.20(14)
N(2)-C(11)-C(10)	118.32(14)
N(2)-C(13)-N(3)	124.67(15)
N(2)-C(13)-S(1)	114.80(12)
N(3)-C(13)-S(1)	120.53(12)
C(4)-C(7)-C(8)	113.00(14)
C(4)-C(7)-H(7A)	109.0
C(8)-C(7)-H(7A)	109.0
C(4)-C(7)-H(7B)	109.0
C(8)-C(7)-H(7B)	109.0
H(7A)-C(7)-H(7B)	107.8
C(2)-C(3)-C(4)	121.70(17)
C(2)-C(3)-H(3)	119.1

C(4)-C(3)-H(3)	119.1
C(3)-C(2)-C(1)	119.90(16)
C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(17)-C(16)-C(21)	117.89(15)
C(17)-C(16)-P(1)	125.31(13)
C(21)-C(16)-P(1)	116.48(12)
C(4)-C(5)-C(6)	121.81(16)
C(4)-C(5)-H(5)	119.1
C(6)-C(5)-H(5)	119.1
O(1)-C(1)-C(6)	123.29(16)
O(1)-C(1)-C(2)	117.26(16)
C(6)-C(1)-C(2)	119.44(17)
C(24)-C(23)-C(22)	120.55(16)
C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7
C(11)-C(10)-C(9)	117.49(13)
C(11)-C(10)-H(10A)	107.9
C(9)-C(10)-H(10A)	107.9
C(11)-C(10)-H(10B)	107.9
C(9)-C(10)-H(10B)	107.9
H(10A)-C(10)-H(10B)	107.2
C(26)-C(27)-C(22)	120.20(16)
C(26)-C(27)-H(27)	119.9
C(22)-C(27)-H(27)	119.9
C(18)-C(19)-C(20)	119.43(16)
C(18)-C(19)-H(19)	120.3
C(20)-C(19)-H(19)	120.3
N(3)-C(14)-H(14A)	109.5
N(3)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
N(3)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(24)-C(25)-C(26)	119.87(17)
C(24)-C(25)-H(25)	120.1
C(26)-C(25)-H(25)	120.1
C(5)-C(4)-C(3)	117.29(16)
C(5)-C(4)-C(7)	122.75(16)
C(3)-C(4)-C(7)	119.94(16)
C(1)-C(6)-C(5)	119.82(17)
C(1)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(16)-C(17)-C(18)	120.72(18)
C(16)-C(17)-H(17)	119.6
C(18)-C(17)-H(17)	119.6
C(19)-C(18)-C(17)	120.68(18)
C(19)-C(18)-H(18)	119.7
C(17)-C(18)-H(18)	119.7
C(25)-C(26)-C(27)	120.35(17)
C(25)-C(26)-H(26)	119.8
C(27)-C(26)-H(26)	119.8
C(25)-C(24)-C(23)	120.05(16)
C(25)-C(24)-H(24)	120.0
C(23)-C(24)-H(24)	120.0
C(20)-C(21)-C(16)	121.22(17)
C(20)-C(21)-H(21)	119.4
C(16)-C(21)-H(21)	119.4
N(3)-C(15)-H(15A)	109.5
N(3)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
N(3)-C(15)-H(15C)	109.5

H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(19)-C(20)-C(21)	120.03(17)
C(19)-C(20)-H(20)	120.0
C(21)-C(20)-H(20)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **5-OH**
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	21(1)	20(1)	38(1)	-6(1)	9(1)	0(1)
P(1)	19(1)	17(1)	29(1)	0(1)	5(1)	0(1)
O(1)	29(1)	26(1)	80(1)	2(1)	18(1)	0(1)
O(2)	28(1)	28(1)	60(1)	-2(1)	21(1)	1(1)
N(2)	21(1)	20(1)	28(1)	1(1)	4(1)	-2(1)
N(3)	18(1)	26(1)	47(1)	-2(1)	6(1)	-2(1)
N(1)	20(1)	19(1)	39(1)	2(1)	10(1)	1(1)
C(12)	19(1)	18(1)	29(1)	0(1)	7(1)	1(1)
C(9)	23(1)	22(1)	24(1)	-4(1)	6(1)	-2(1)
C(22)	16(1)	22(1)	29(1)	1(1)	5(1)	0(1)
C(8)	25(1)	20(1)	43(1)	5(1)	11(1)	2(1)
C(11)	23(1)	16(1)	25(1)	3(1)	6(1)	0(1)
C(13)	20(1)	18(1)	32(1)	4(1)	3(1)	1(1)
C(7)	36(1)	20(1)	44(1)	-5(1)	19(1)	-1(1)
C(3)	30(1)	22(1)	44(1)	6(1)	9(1)	1(1)
C(2)	34(1)	24(1)	49(1)	7(1)	16(1)	-3(1)
C(16)	24(1)	19(1)	25(1)	-1(1)	5(1)	-2(1)
C(5)	39(1)	26(1)	35(1)	3(1)	9(1)	-3(1)
C(1)	24(1)	19(1)	49(1)	-5(1)	10(1)	-2(1)
C(23)	23(1)	21(1)	36(1)	2(1)	6(1)	0(1)
C(10)	30(1)	19(1)	29(1)	-2(1)	11(1)	-4(1)
C(27)	29(1)	23(1)	35(1)	0(1)	8(1)	3(1)
C(19)	45(1)	20(1)	32(1)	3(1)	9(1)	-3(1)
C(14)	26(1)	46(1)	52(1)	0(1)	1(1)	-12(1)
C(25)	34(1)	45(1)	29(1)	3(1)	12(1)	-2(1)
C(4)	30(1)	17(1)	33(1)	-6(1)	9(1)	-4(1)
C(6)	33(1)	23(1)	43(1)	2(1)	3(1)	1(1)
C(17)	26(1)	30(1)	69(1)	17(1)	1(1)	-3(1)
C(18)	36(1)	32(1)	72(2)	20(1)	-5(1)	3(1)
C(26)	38(1)	32(1)	38(1)	-9(1)	14(1)	0(1)
C(24)	27(1)	32(1)	37(1)	10(1)	9(1)	-1(1)
C(21)	23(1)	24(1)	53(1)	5(1)	8(1)	0(1)
C(15)	26(1)	37(1)	68(1)	-1(1)	20(1)	5(1)
C(20)	32(1)	25(1)	56(1)	2(1)	16(1)	-6(1)

Compound 5-OMe

Table 1. Crystal data and structure refinement for **5-OMe**.

Identification code	**5-OMe**
Empirical formula	C28 H30 N3 O2 P S
Formula weight	503.59
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P 21/c
Unit cell dimensions	a = 16.0609(10) A alpha = 90 deg.
	b = 18.7305(13) A beta = 98.481(6) deg.
	c = 8.9676(6) A gamma = 90 deg.
Volume	2668.2(3) A^3
Z, Calculated density	4, 1.254 Mg/m^3
Absorption coefficient	0.211 mm^-1
F(000)	1064
Crystal size	0.18 x 0.12 x 0.04 mm
Theta range for data collection	3.36 to 25.35 deg.
Limiting indices	-19<=h<=19, -22<=k<=22, -10<=l<=10
Reflections collected / unique	26130 / 4883 [R(int) = 0.1133]
Completeness to theta = 25.35	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4883 / 1 / 322
Goodness-of-fit on F^2	0.664
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0432
R indices (all data)	R1 = 0.1210, wR2 = 0.0497
Largest diff. peak and hole	0.220 and -0.199 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **5-OMe**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	-5795(2)	2206(2)	6983(3)	61(1)
C(2)	-4401(2)	1753(2)	7673(3)	36(1)
C(3)	-3796(2)	1262(1)	7415(2)	40(1)
C(4)	-2982(2)	1327(1)	8103(3)	39(1)
C(5)	-2729(2)	1877(2)	9109(3)	38(1)
C(6)	-3345(2)	2348(2)	9393(3)	50(1)
C(7)	-4173(2)	2301(2)	8682(3)	49(1)
C(8)	-1833(2)	1945(2)	9847(3)	46(1)
C(9)	-1398(2)	2594(2)	9363(3)	57(1)
C(10)	95(2)	2357(1)	9307(3)	37(1)
C(11)	966(2)	2315(1)	10244(3)	36(1)
C(12)	1101(2)	1550(1)	10717(2)	29(1)
C(13)	644(1)	600(1)	11800(2)	28(1)
C(14)	259(2)	-581(1)	12579(2)	39(1)
C(15)	-549(2)	507(1)	13111(2)	40(1)
C(16)	1678(2)	1087(1)	10309(2)	29(1)
C(17)	3458(2)	1050(1)	10766(3)	31(1)
C(18)	3421(2)	1061(1)	12314(3)	42(1)
C(19)	4132(2)	908(2)	13355(3)	54(1)
C(20)	4885(2)	753(1)	12860(3)	58(1)
C(21)	4937(2)	754(1)	11345(3)	51(1)

C(22)	4234(2)	901(1)	10318(3)	39(1)
C(23)	2569(2)	586(2)	7990(3)	32(1)
C(24)	2806(1)	-113(2)	8371(3)	34(1)
C(25)	2808(1)	-640(2)	7283(3)	44(1)
C(26)	2585(2)	-464(2)	5787(4)	57(1)
C(27)	2342(2)	219(2)	5375(3)	56(1)
C(28)	2336(2)	753(2)	6470(3)	47(1)
N(1)	-513(1)	2640(1)	9994(2)	35(1)
N(2)	518(1)	1280(1)	11554(2)	30(1)
N(3)	194(1)	190(1)	12622(2)	32(1)
O(1)	-5191(1)	1648(1)	6911(2)	50(1)
O(2)	-34(1)	2114(1)	8026(2)	62(1)
P(1)	2562(1)	1310(1)	9364(1)	35(1)
S(1)	1485(1)	239(1)	10992(1)	31(1)

Table 3. Bond lengths [A] and angles [deg] for **5-OMe**.

C(1)-O(1)	1.434(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-O(1)	1.364(3)
C(2)-C(3)	1.381(3)
C(2)-C(7)	1.382(3)
C(3)-C(4)	1.367(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.390(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.376(3)
C(5)-C(8)	1.498(3)
C(6)-C(7)	1.391(3)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-C(9)	1.499(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-N(1)	1.452(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-O(2)	1.224(2)
C(10)-N(1)	1.340(3)
C(10)-C(11)	1.524(3)
C(11)-C(12)	1.502(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(16)	1.358(3)
C(12)-N(2)	1.379(3)
C(13)-N(2)	1.304(3)
C(13)-N(3)	1.346(3)
C(13)-S(1)	1.759(2)
C(14)-N(3)	1.450(2)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-N(3)	1.457(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-S(1)	1.748(2)
C(16)-P(1)	1.806(2)
C(17)-C(22)	1.392(3)
C(17)-C(18)	1.398(3)

C(17)-P(1)	1.833(2)
C(18)-C(19)	1.394(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.378(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.373(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.375(3)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-C(24)	1.391(3)
C(23)-C(28)	1.396(3)
C(23)-P(1)	1.834(3)
C(24)-C(25)	1.390(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.377(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.372(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.403(3)
C(27)-H(27)	0.9500
C(28)-H(28)	0.9500
N(1)-H(101)	0.863(9)

O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(1)-C(2)-C(3)	116.5(2)
O(1)-C(2)-C(7)	124.9(3)
C(3)-C(2)-C(7)	118.7(2)
C(4)-C(3)-C(2)	121.0(2)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	121.8(2)
C(3)-C(4)-H(4)	119.1
C(5)-C(4)-H(4)	119.1
C(6)-C(5)-C(4)	116.5(2)
C(6)-C(5)-C(8)	122.3(3)
C(4)-C(5)-C(8)	121.2(3)
C(5)-C(6)-C(7)	122.6(2)
C(5)-C(6)-H(6)	118.7
C(7)-C(6)-H(6)	118.7
C(2)-C(7)-C(6)	119.3(2)
C(2)-C(7)-H(7)	120.3
C(6)-C(7)-H(7)	120.3
C(5)-C(8)-C(9)	113.5(2)
C(5)-C(8)-H(8A)	108.9
C(9)-C(8)-H(8A)	108.9
C(5)-C(8)-H(8B)	108.9
C(9)-C(8)-H(8B)	108.9
H(8A)-C(8)-H(8B)	107.7
N(1)-C(9)-C(8)	114.0(2)
N(1)-C(9)-H(9A)	108.7
C(8)-C(9)-H(9A)	108.7
N(1)-C(9)-H(9B)	108.7
C(8)-C(9)-H(9B)	108.7
H(9A)-C(9)-H(9B)	107.6
O(2)-C(10)-N(1)	123.0(3)
O(2)-C(10)-C(11)	120.9(3)

N(1)-C(10)-C(11)	116.0(2)
C(12)-C(11)-C(10)	106.7(2)
C(12)-C(11)-H(11A)	110.4
C(10)-C(11)-H(11A)	110.4
C(12)-C(11)-H(11B)	110.4
C(10)-C(11)-H(11B)	110.4
H(11A)-C(11)-H(11B)	108.6
C(16)-C(12)-N(2)	117.3(2)
C(16)-C(12)-C(11)	127.5(2)
N(2)-C(12)-C(11)	114.9(2)
N(2)-C(13)-N(3)	124.5(2)
N(2)-C(13)-S(1)	114.60(18)
N(3)-C(13)-S(1)	120.86(19)
N(3)-C(14)-H(14A)	109.5
N(3)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
N(3)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
N(3)-C(15)-H(15A)	109.5
N(3)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
N(3)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(12)-C(16)-S(1)	108.81(17)
C(12)-C(16)-P(1)	126.45(18)
S(1)-C(16)-P(1)	124.54(14)
C(22)-C(17)-C(18)	117.4(2)
C(22)-C(17)-P(1)	120.09(19)
C(18)-C(17)-P(1)	122.16(19)
C(19)-C(18)-C(17)	120.7(2)
C(19)-C(18)-H(18)	119.6
C(17)-C(18)-H(18)	119.6
C(20)-C(19)-C(18)	119.9(3)
C(20)-C(19)-H(19)	120.1
C(18)-C(19)-H(19)	120.1
C(21)-C(20)-C(19)	120.2(3)
C(21)-C(20)-H(20)	119.9
C(19)-C(20)-H(20)	119.9
C(20)-C(21)-C(22)	120.0(3)
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-H(21)	120.0
C(21)-C(22)-C(17)	121.8(2)
C(21)-C(22)-H(22)	119.1
C(17)-C(22)-H(22)	119.1
C(24)-C(23)-C(28)	118.4(2)
C(24)-C(23)-P(1)	124.04(19)
C(28)-C(23)-P(1)	117.6(2)
C(25)-C(24)-C(23)	121.7(2)
C(25)-C(24)-H(24)	119.1
C(23)-C(24)-H(24)	119.1
C(26)-C(25)-C(24)	119.1(3)
C(26)-C(25)-H(25)	120.5
C(24)-C(25)-H(25)	120.5
C(27)-C(26)-C(25)	120.6(3)
C(27)-C(26)-H(26)	119.7
C(25)-C(26)-H(26)	119.7
C(26)-C(27)-C(28)	120.5(3)
C(26)-C(27)-H(27)	119.7
C(28)-C(27)-H(27)	119.7
C(23)-C(28)-C(27)	119.7(3)

C(23)-C(28)-H(28)	120.2
C(27)-C(28)-H(28)	120.2
C(10)-N(1)-C(9)	122.3(2)
C(10)-N(1)-H(101)	117.2(15)
C(9)-N(1)-H(101)	117.3(15)
C(13)-N(2)-C(12)	110.4(2)
C(13)-N(3)-C(14)	120.5(2)
C(13)-N(3)-C(15)	117.5(2)
C(14)-N(3)-C(15)	118.6(2)
C(2)-O(1)-C(1)	117.2(2)
C(16)-P(1)-C(17)	102.08(11)
C(16)-P(1)-C(23)	103.14(11)
C(17)-P(1)-C(23)	100.44(12)
C(16)-S(1)-C(13)	88.90(12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **5-OMe**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	35(2)	59(2)	88(2)	12(2)	1(2)	3(2)
C(2)	35(2)	40(2)	32(2)	6(2)	2(2)	1(2)
C(3)	50(2)	30(2)	37(2)	-4(1)	-1(2)	7(2)
C(4)	42(2)	39(2)	37(2)	1(2)	4(1)	16(2)
C(5)	40(2)	46(2)	26(2)	5(1)	2(1)	5(2)
C(6)	49(2)	55(2)	45(2)	-22(2)	5(2)	-2(2)
C(7)	39(2)	52(2)	57(2)	-15(2)	14(2)	9(2)
C(8)	44(2)	53(2)	36(2)	6(1)	-5(1)	4(2)
C(9)	45(2)	56(2)	60(2)	8(2)	-23(2)	-1(2)
C(10)	68(2)	13(2)	30(2)	7(1)	10(2)	0(2)
C(11)	42(2)	27(2)	44(2)	-2(1)	23(2)	-6(2)
C(12)	26(2)	25(2)	36(2)	2(1)	7(1)	-6(1)
C(13)	26(2)	26(2)	32(2)	4(1)	6(1)	-3(1)
C(14)	49(2)	30(2)	39(2)	6(1)	10(1)	-4(2)
C(15)	43(2)	37(2)	45(2)	4(1)	20(1)	2(2)
C(16)	29(2)	25(2)	36(2)	-1(1)	12(1)	-4(1)
C(17)	27(2)	30(2)	37(2)	-7(1)	6(1)	-7(1)
C(18)	32(2)	54(2)	42(2)	-8(1)	9(2)	-9(2)
C(19)	55(2)	69(2)	37(2)	-8(2)	3(2)	-19(2)
C(20)	42(2)	62(2)	62(2)	-7(2)	-17(2)	-4(2)
C(21)	27(2)	64(2)	59(2)	-19(2)	0(2)	-2(2)
C(22)	34(2)	44(2)	39(2)	-12(1)	5(2)	-4(2)
C(23)	26(2)	44(2)	27(2)	2(1)	9(1)	-6(2)
C(24)	24(2)	48(2)	31(2)	-6(2)	6(1)	1(2)
C(25)	32(2)	52(2)	49(2)	-13(2)	8(2)	-1(2)
C(26)	43(2)	82(3)	51(2)	-29(2)	23(2)	-23(2)
C(27)	49(2)	94(3)	25(2)	0(2)	5(1)	-32(2)
C(28)	36(2)	62(2)	41(2)	9(2)	5(2)	-13(2)
N(1)	41(2)	36(2)	26(1)	-2(1)	-7(1)	5(1)
N(2)	29(1)	23(1)	41(1)	6(1)	14(1)	0(1)
N(3)	32(1)	25(1)	43(1)	3(1)	15(1)	0(1)
O(1)	35(1)	52(1)	59(1)	1(1)	-1(1)	3(1)
O(2)	134(2)	31(1)	20(1)	-6(1)	11(1)	1(1)
P(1)	31(1)	35(1)	42(1)	2(1)	14(1)	-2(1)
S(1)	28(1)	27(1)	40(1)	3(1)	10(1)	5(1)

4. ICP-MS measurements

4.1 - Preparations of the samples:

A mixture of 1.5 mL HNO_3 (67-69%) and 0.5 mL of HCL (36%-37%) was added to the sample and the mixture was stirred at 90°C for 24 h then diluted.

4.2 - Conditions of ICP-MS:

Instrument:	Serie X 2 from Thermo Electron.
Nebuliser type:	Meinhard nebuliser.
Plasma power:	1400 W
Coolant gaz flow:	13 l/min
Auxiliary gaz flow:	0.7 l/min
Nebuliser flow:	0.88 l/min

Data acquisition:	
Detector:	ETP simulscan
Scan mode:	Peak hopping
Points per peak:	1
Dwell time per peak:	10 ms
Sweeps:	50
Isotopes used for metal determination:	105Pd, 106Pd, 108Pd

Isotopes used for internal standardisation: 115In, 185Re.

Please find above the corresponding reports.

Report R1204-271-V2

- Sample 893av corresponds to the crude product **7b** when using dendrimer **5-G_1** as the ligand (< 0.55 ppm Pd).
- Sample 915av corresponds to the crude product **7b** when using monomer **5-OMe** as the ligand (~ 1400 ppm Pd).
- Sample 915ap corresponds to the product **7b** after two purifications by column chromatography when using **5-OMe** as the ligand. Noteworthy, even after these two purifications, the coupling product does not meet the requirements of pharmaceutical industry in terms of Pd contaminants (~ 16 ppm Pd on **7b**).

Report R1204-271-V3

- Sample 915B corresponds to the crude product **7b** when using PPh_3 as the ligand (~ 2200 ppm Pd).

Report R1205-293-V2

- Sample 952 corresponds to the crude product **7b** when using dendrimer **6-G_1** as the ligand (~ 173 ppm Pd).

Toulouse, le 22 Mai 2012

Rapport d'essai

Mme OUALI

LCC
205, route de Narbonne
31077 Toulouse Cedex 04

Rapport n° : R1204-271-V2

Madame,

Nous avons le plaisir de vous communiquer les résultats des analyses réalisées dans le cadre de la prestation décrite ci-dessous.

Afin d'améliorer continuellement nos services, nous vous invitons à nous communiquer toute remarque relative à la prestation réalisée : satisfactions, insatisfactions, services supplémentaires souhaités. Veuillez donc adresser vos commentaires par fax, courriel ou directement par téléphone. L'équipe d'Antellis est à votre écoute de 9h à 18h, du lundi au vendredi.

1. Description de la prestation :

nom du projet : Polymères
devis / bon de commande : /
date de réception des échantillons : 07/03/2012

Méthode(s) d'analyse	*préparation*	*traitement*	*technique d'analyse*
A	aucune	Digestion HNO_3	ICP-MS basé sur ISO 17294
B	aucune	Digestion HNO_3, HCl	ICP-MS basé sur ISO 17294

ANTELLIS – Parc Technologique du Canal 3 rue des satellites - 31400 Toulouse
Tél. : 05.62.20.06.72 - Fax : 05.62.20.06.77 - e-mail : antellis@antellis.com – internet : www.antellis.com

2. Résultats d'analyse :

id. échantillon : 893av; 267 mg
id. Antellis : 12C016-6

Elément	Méthode d'analyse	conc. ($mg.kg^{-1}$)	incertitude (2s)
Pd	B	< 0,55	-

id. échantillon : 915ap; 100 mg
id. Antellis : 12C016-8

Elément	Méthode d'analyse	conc. ($mg.kg^{-1}$)	incertitude (2s)
Pd	B	16,09	1,02

id. échantillon : 915av; 80 mg
id. Antellis : 12C016-10

Elément	Méthode d'analyse	conc. ($mg.kg^{-1}$)	incertitude (2s)
Pd	B	1 432,71	46,08

Sébastien Aries

Dr. Sébastien Aries
Responsable Scientifique

ANTELLIS – Parc Technologique du Canal 3 rue des satellites - 31400 Toulouse
Tél. : 05.62.20.06.72 - Fax : 05.62.20.06.77 - e-mail : antellis@antellis.com – internet : www.antellis.com

Toulouse, le 16 Juillet 2012

Rapport d'essai

Mme OUALI

LCC
205, route de Narbonne
31077 Toulouse Cedex 04

Rapport n° : R1204-271-v3

Madame,

Nous avons le plaisir de vous communiquer les résultats des analyses réalisées dans le cadre de la prestation décrite ci-dessous.

Afin d'améliorer continuellement nos services, nous vous invitons à nous communiquer toute remarque relative à la prestation réalisée : satisfactions, insatisfactions, services supplémentaires souhaités. Veuillez donc adresser vos commentaires par fax, courriel ou directement par téléphone. L'équipe d'Antellis est à votre écoute de 9h à 18h, du lundi au vendredi.

1. Description de la prestation :

nom du projet : Polymères
devis / bon de commande : /
date de réception des échantillons : 07/03/2012

Méthode(s) d'analyse	*préparation*	*traitement*	*technique d'analyse*
A	aucune	Digestion HNO_3	ICP-MS basé sur ISO 17294
B	aucune	Digestion HNO_3, HCl	ICP-MS basé sur ISO 17294

2. Résultats d'analyse :

id. échantillon : 915B; 100 mg
id. Antellis : 12C016-9

Elément	Méthode d'analyse	conc. ($mg.kg^{-1}$)	incertitude (2s)
Pd	B	2 227,82	62,73

Sébastien Aries

Dr. Sébastien Aries
Responsable Scientifique

ANTELLIS – Parc Technologique du Canal 3 rue des satellites - 31400 Toulouse
Tél. : 05.62.20.06.72 - Fax : 05.62.20.06.77 - e-mail : antellis@antellis.com – internet : www.antellis.com

Toulouse, le 12 Juillet 2012

Rapport d'essai

Mme OUALI

LCC
205, route de Narbonne
31077 Toulouse Cedex 04

Rapport n° : R1205-293-v2

Madame,

Nous avons le plaisir de vous communiquer les résultats des analyses réalisées dans le cadre de la prestation décrite ci-dessous.

Afin d'améliorer continuellement nos services, nous vous invitons à nous communiquer toute remarque relative à la prestation réalisée : satisfactions, insatisfactions, services supplémentaires souhaités. Veuillez donc adresser vos commentaires par fax, courriel ou directement par téléphone. L'équipe d'Antellis est à votre écoute de 9h à 18h, du lundi au vendredi.

1. Description de la prestation :

nom du projet : Polymères
devis / bon de commande : /
date de réception des échantillons : 24/04/2012

Méthode(s) d'analyse	*préparation*	*traitement*	*technique d'analyse*
A	aucune	Digestion HNO_3, HCl	ICP-MS basé sur ISO 17294

ANTELLIS – Parc Technologique du Canal 3 rue des satellites - 31400 Toulouse
Tél. : 05.62.20.06.72 - Fax : 05.62.20.06.77 - e-mail : antellis@antellis.com – internet : www.antellis.com

2. Résultats d'analyse :

id. échantillon : MK952, 300 mg
id. Antellis : 12D039-4

Elément	Méthode d'analyse	conc. ($mg.kg^{-1}$)	incertitude (2s)
Pd	A	173,21	3,09

Sébastien Aries

Dr. Sébastien Aries
Responsable Scientifique

ANTELLIS – Parc Technologique du Canal 3 rue des satellites - 31400 Toulouse
Tél. : 05.62.20.06.72 - Fax : 05.62.20.06.77 - e-mail : antellis@antellis.com – internet : www.antellis.com

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