Room-Temperature Highly Efficient Suzuki-Miyaura Reactions in Water in the Presence of Stilbazo

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Supporting Information

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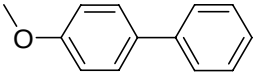
1. Typical experimental procedure for the palladium-catalyzed Suzuki-Miyaura cross-coupling reaction in H_2O.

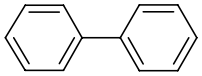
Stilbazo (5 mol %) was added to a mixture of ArX (0.2 mmol) and arylboronic acid (0.22 mmol), K_2CO_3 (0.4 mmol) and H_2O (1 mL) in a 5-mL round-bottom flask filled with N_2. The reaction mixture was stirred at room temperature for an appropriate time until complete conversion of aryl halide took place (monitored by TLC). After

completion, the mixture was extracted with CH_2Cl_2 (3×3 mL) and the combined organic extracts were dried over anhydrous sodium sulfate and evaporated under vacuum, leaving the crude product, which was purified by column chromatography to afford the corresponding products.

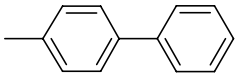
2. Analytical data for 3a-3k and 4a-4j

4-Methoxy-biphenyl (**3a**) [1] 

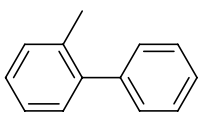
White solid; mp 88–90°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 4H), 7.41 (t, J = 7.2 Hz, 2H), 7.30 (t, J = 7.2, 1H), 6.99 (d, J = 8.4Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 140.8, 133.8, 128.7, 128.2, 126.8, 126.7, 114.2, 55.4.

Biphenyl (**3b**) [1] 

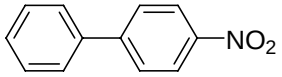
White solid; mp 68–70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 4H), 7.46 (t, J = 7.6 Hz, 4H), 7.37 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 128.7, 127.2, 127.1.

4-Methyl-biphenyl (**3c**) [1] 

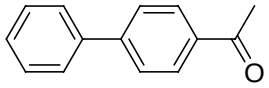
White solid; mp 44– 46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (t, J = 7.6 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.43-7.39 (m, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 8.0 Hz, 2H), 2.38 (s, 3H).

2-Methyl-biphenyl (**3d**) [1] 

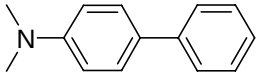
Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 7.24-7.26 (m, 4H), 7.31-7.36 (m, 3H), 7.39-7.46 (m, 2H).

4-Nitro-biphenyl (**3e**) [1] 

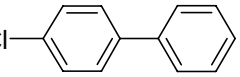
Yellow solid; mp 112–114°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J= 8.8 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.64 (t, J = 8.8 Hz, 2H), 7.52-7.43 (m, 3H).

4-Acetyl-biphenyl (**3f**) [1] 

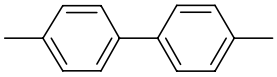
White solid; mp 116–118°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.49-7.38 (m, 3H), 2.64 (s, 3H).

4- (N, N-dimethylamino) biphenyl (3g) [2] 

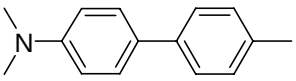
White solid; mp 121-123°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.49 (m, 4H), 7.41 (t, J = 7.6Hz, 2H), 7.27 (m, 1H), 6.82 (d, J = 8.8Hz, 2H), 2.99 (s, 6H).

4-Chloro-biphenyl (3h) [1] 

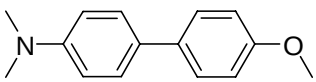
White solid; mp 77-79°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.48 (m, 4H), 7.46-7.34 (m, 5H).

4, 4'-Dimethyl-biphenyl (**3i**) [3] 

White solid; mp 118-120°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 4H), 7.24 (d, J = 8.0 Hz, 4H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 136.7, 129.4, 129.1, 126.8, 21.1.

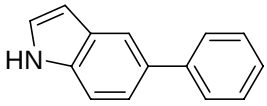
4-Methyl -4'-(N, N-Dimethylamino) biphenyl (**3j**) [4] 

Gray solid; mp 132-133°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 2.98 (s, 6H), 2.36 (s, 3H).

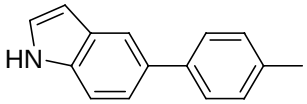
4-Methoxy-4'- (*N, N*-dimethylamino) biphenyl (**3k**) [5] 

Gray solid; mp 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.8 Hz,

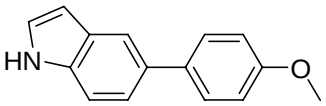
2H), 7.46 (d, *J* = 9.2 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.09 (s, 3H), 2.98 (s, 6H).

5-phenyl-1H-indole (**4a**) [6] 

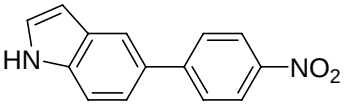
White solid; mp 68-70°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.86 (s, 1H), 7.66 (d, *J* = 8.0Hz, 2H), 7.45-7.41(m, 4H), 7.31 (t, *J* = 6.8 Hz, 1H), 7.24-7.23(m, 1H), 6.61 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 135.3, 133.4, 128.7, 128.4, 127.3, 124.9, 122.0, 120.8, 119.3, 111.3, 103.1.

5-*p*-tolyl-1H-indole (**4b**) [7] 

White solid; mp: 78-79°C ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (br s, 1H), 7.83 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 2H), 7.25-6.99 (m, 3H), 6.60 (s, 1H), 2.39 (s, 3H).

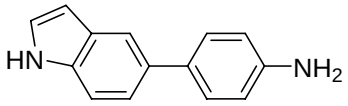
5-(4-methoxyphenyl)-1H-indole (**4c**) [7] 

White solid; mp 109-110°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.80 (s, 1H), 7.58-7.56 (m, 2H), 7.46-7.38 (m, 2H), 7.22 (t, *J* = 2.4 Hz, 1H), 6.99-6.96 (m, 2H), 6.59 (t, *J* = 2.4 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 135.2, 135.0, 133.1, 128.4, 128.2, 124.6, 121.8, 118.8, 118.7, 111.2, 103.0, 55.9.

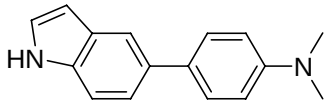
5-(4-nitrophenyl)-1H-indole (**4d**) [8] 

Yellow solid; mp 132-133°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.28 (m, 3H), 7.92 (d, *J* = 0.8 Hz, 1H), 7.80-7.78 (m, 2H), 7.52-7.46 (m, 2H), 7.30-7.23 (m, 1H),

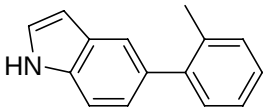
6.65 (t, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDC_{l3}) δ 149.1, 146.3, 136.1, 130.8, 128.5, 127.6, 125.6, 124.1, 120.0, 111.8, 103.4.

5-(4-aminophenyl)-1H-indole (**4e**) [8] 

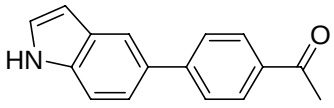
Gray solid; mp: 126-127°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.98 (br s, 1H), 7.64 (s, 1H), 7.39-25 (m, 5H), 6.64 (d, J = 8.4 Hz, 2H), 6.42 (t, J= 2.0 Hz, 1H), 5.04 (br s 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 134.6, 132.0, 129.6, 128.1, 127.2, 126.9, 125.6, 125.4, 119.8, 116.6, 114.6, 111.5, 101.2.

5-(4-*N, N*-dimethylaminophenyl)-1H-indole (**4f**) [8] 

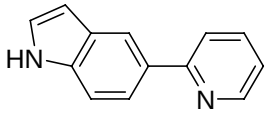
White solid; mp 138-140°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.80 (s, 1H), 7.57 (d, J = 8.8 Hz, 2H), 7.42 (s, 2H), 7.22 (t, J = 2.4 Hz, 1H), 6.89 (d, J = 6.8 Hz, 2H), 6.58 (s, 1H), 2.99 (s, 6H).

5-(2-Methylphenyl) -1H-indole (**4g**) [7] 

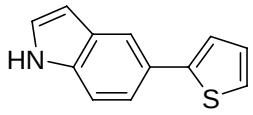
White solid; mp: 65-66°C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.64 (m, 1H), 7.41-7.37 (m, 1H), 7.31-7.10 (m, 6H), 6.55 (s, 1H), 2.30 (s, 1H).

5-(4-Acetylphenyl)-1H-indole (**4h**) [8] 

White solid; mp 135-137°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (br s, 1H), 8.04 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.51-7.46 (m, 2H), 7.25 (t, J = 8.4 Hz, 1H), 6.63 (t, J = 2.4 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 147.3, 135.8, 135.0, 131.9, 128.9, 128.4, 127.2, 125.3, 121.8, 119.7, 111.4, 103.1, 26.6.

5-(pyridin-2-yl)-1H-indole (**4i**) [8] 

White solid; mp: 122-124°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.8 Hz, 1H), 8.34 (br s, 1H), 8.27 (s, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.79-7.71 (m, 2H), 7.48 (d, J = 8.4 Hz, 1H), 7.25 (t, J = 3.2 Hz, 1H), 7.23-7.16 (m, 1H), 6.63 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 149.44, 136.67, 136.4, 131.5, 128.3, 124.9, 121.4, 121.1, 120.4, 119.6, 111.2, 103.4.

5-(thiophen-2-yl)-1H-indole (**4j**) [9] 

White solid; mp 118-120°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.48-7.36 (m, 4H), 7.27-7.21 (m, 2H), 6.57(s, 1H).

3. References

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2. A. G. Molander and B. Biolatto, *J. Org. Chem.* 2003**, 68***,* 4302.
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8. PCT *Int. Appl.* 2006, 292.

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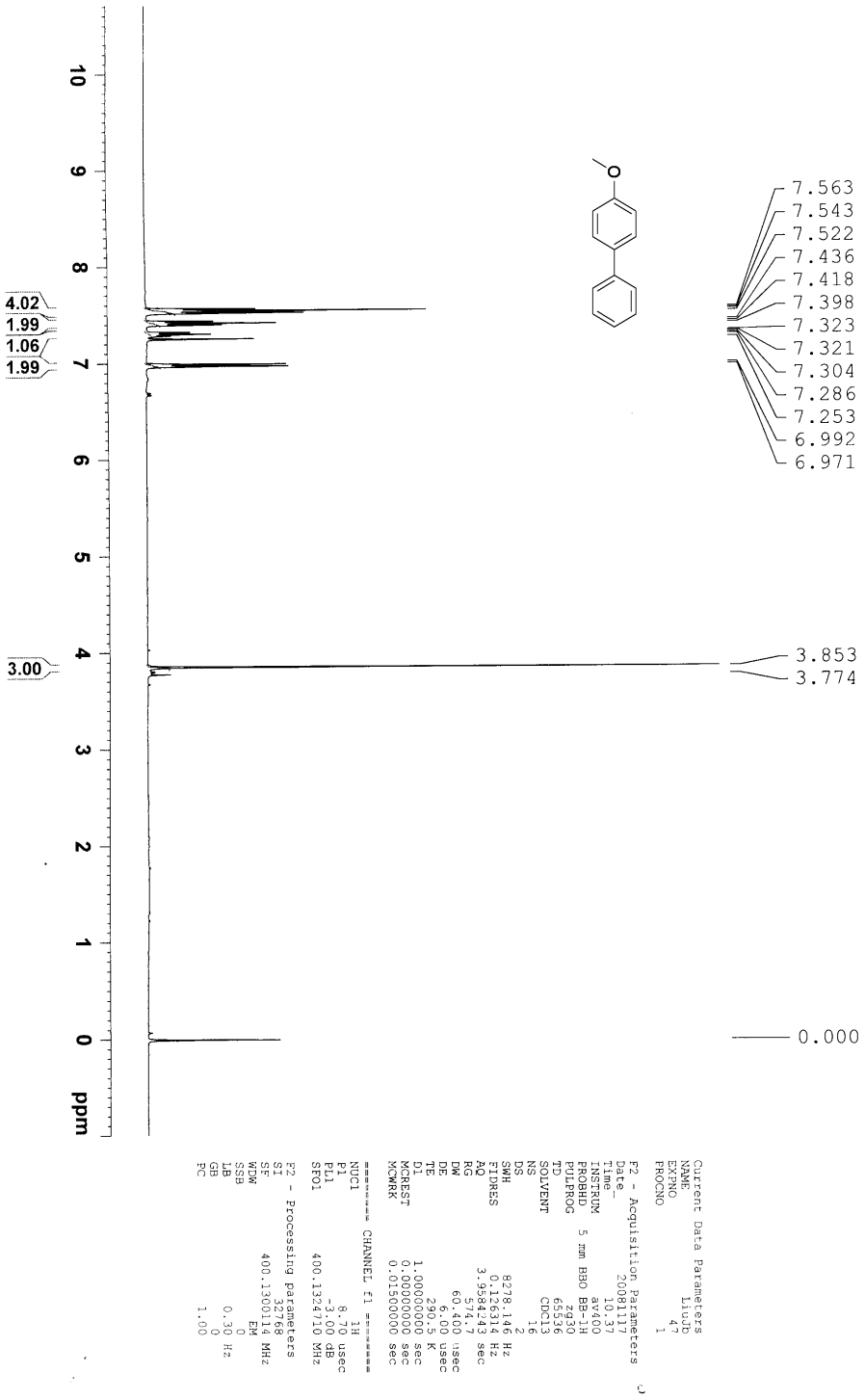
4. NMR spectra

4-Methoxy-biphenyl (3a)



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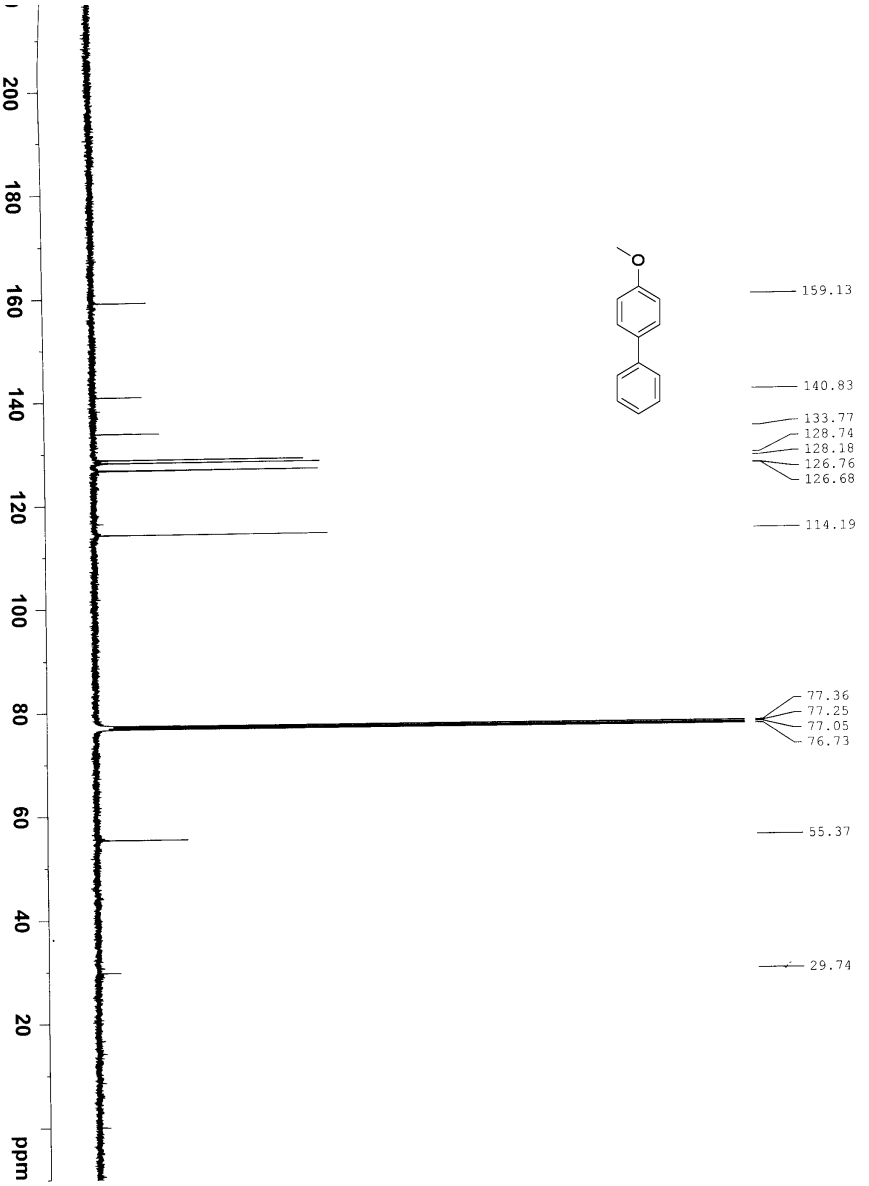

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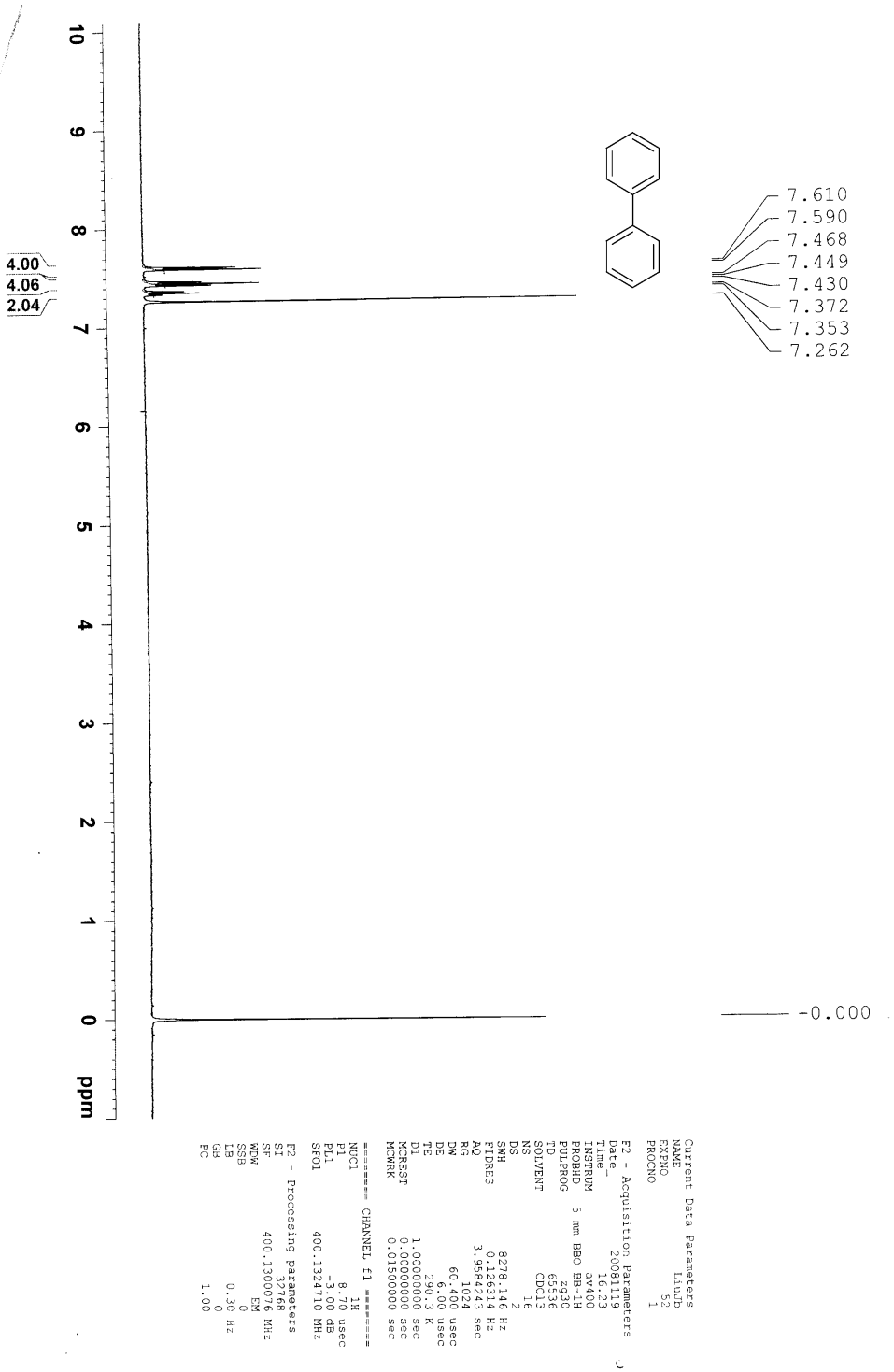
Biphenyl (**3b**)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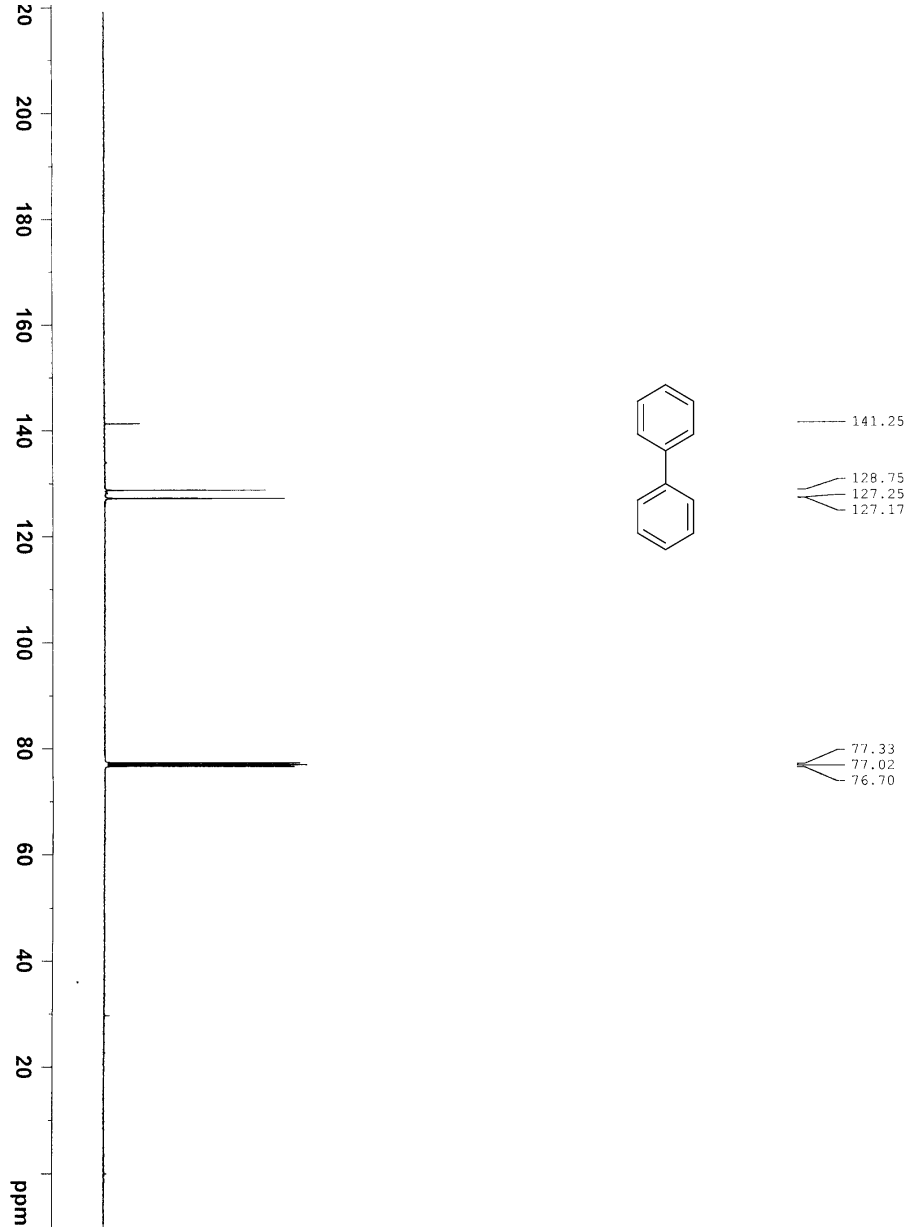
Biphenyl (3b)

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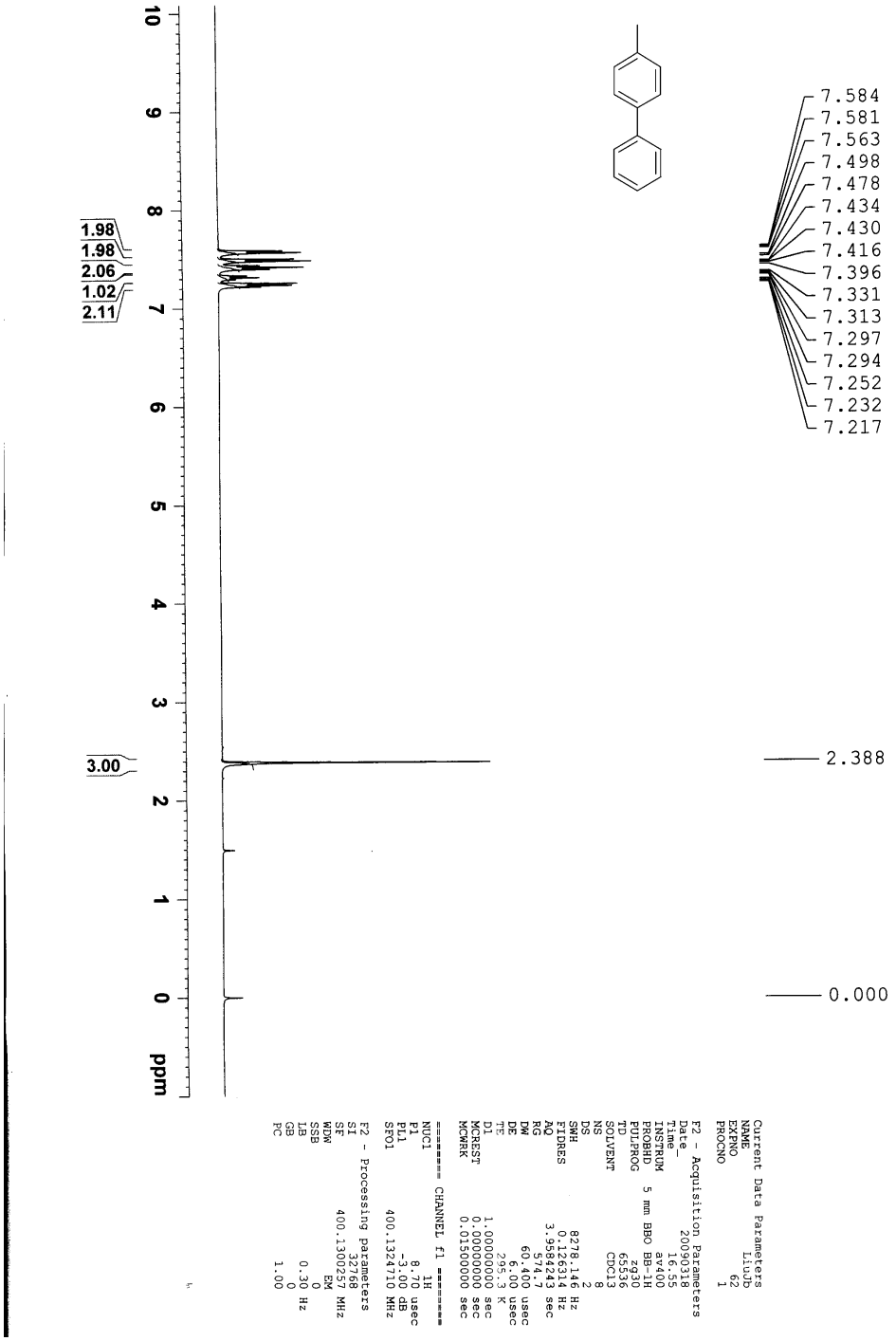
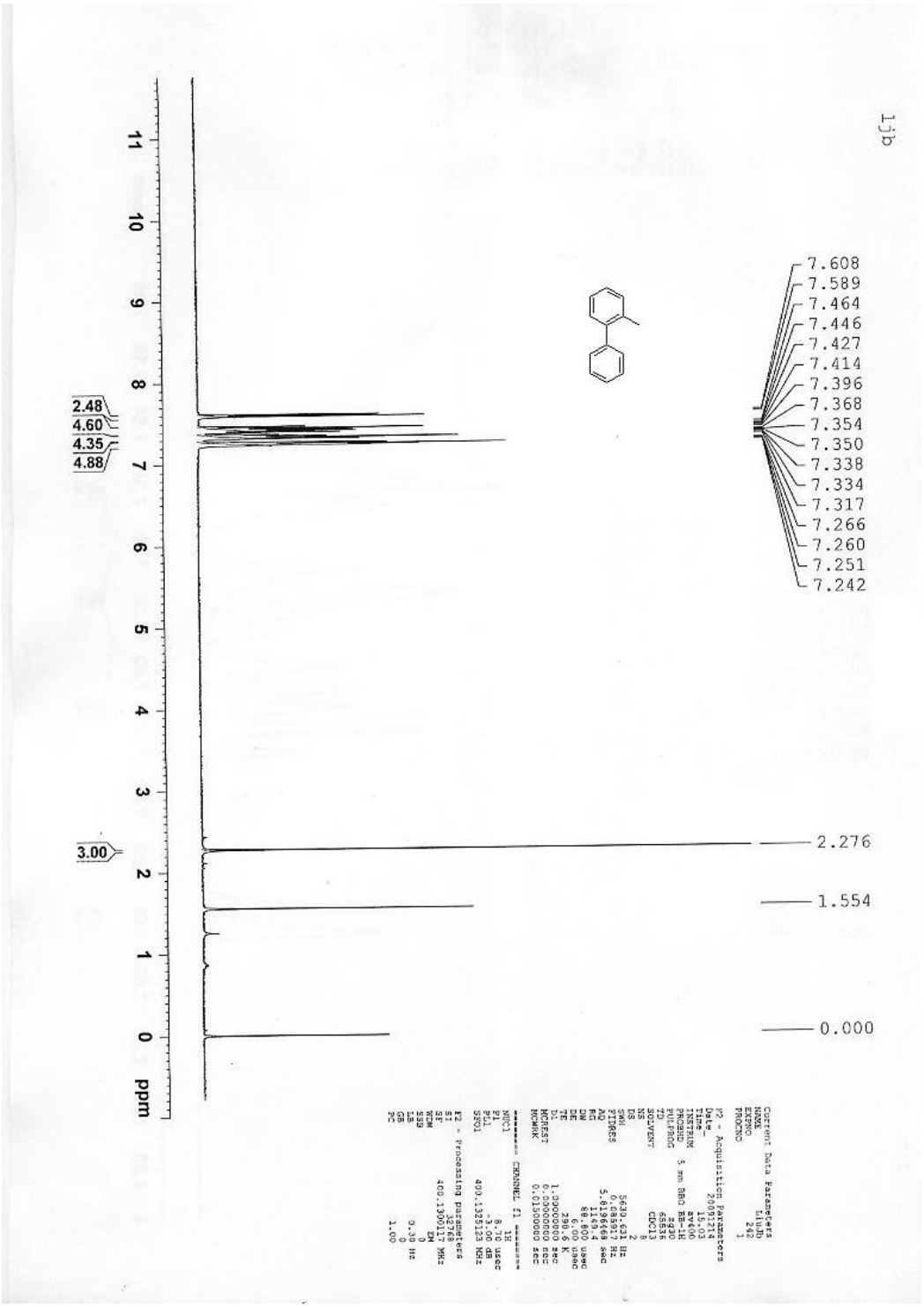
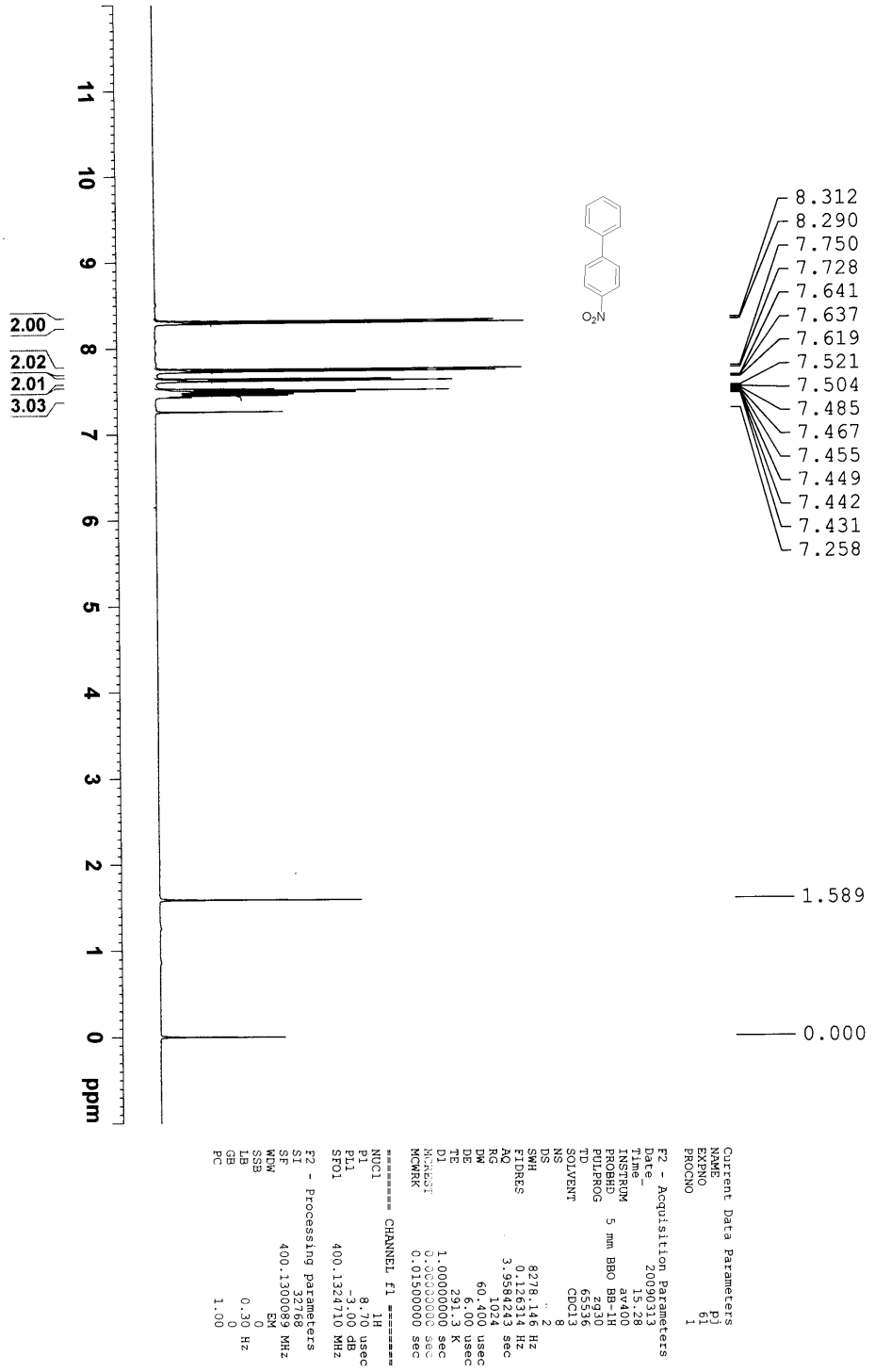
4-Methyl-biphenyl (3c)



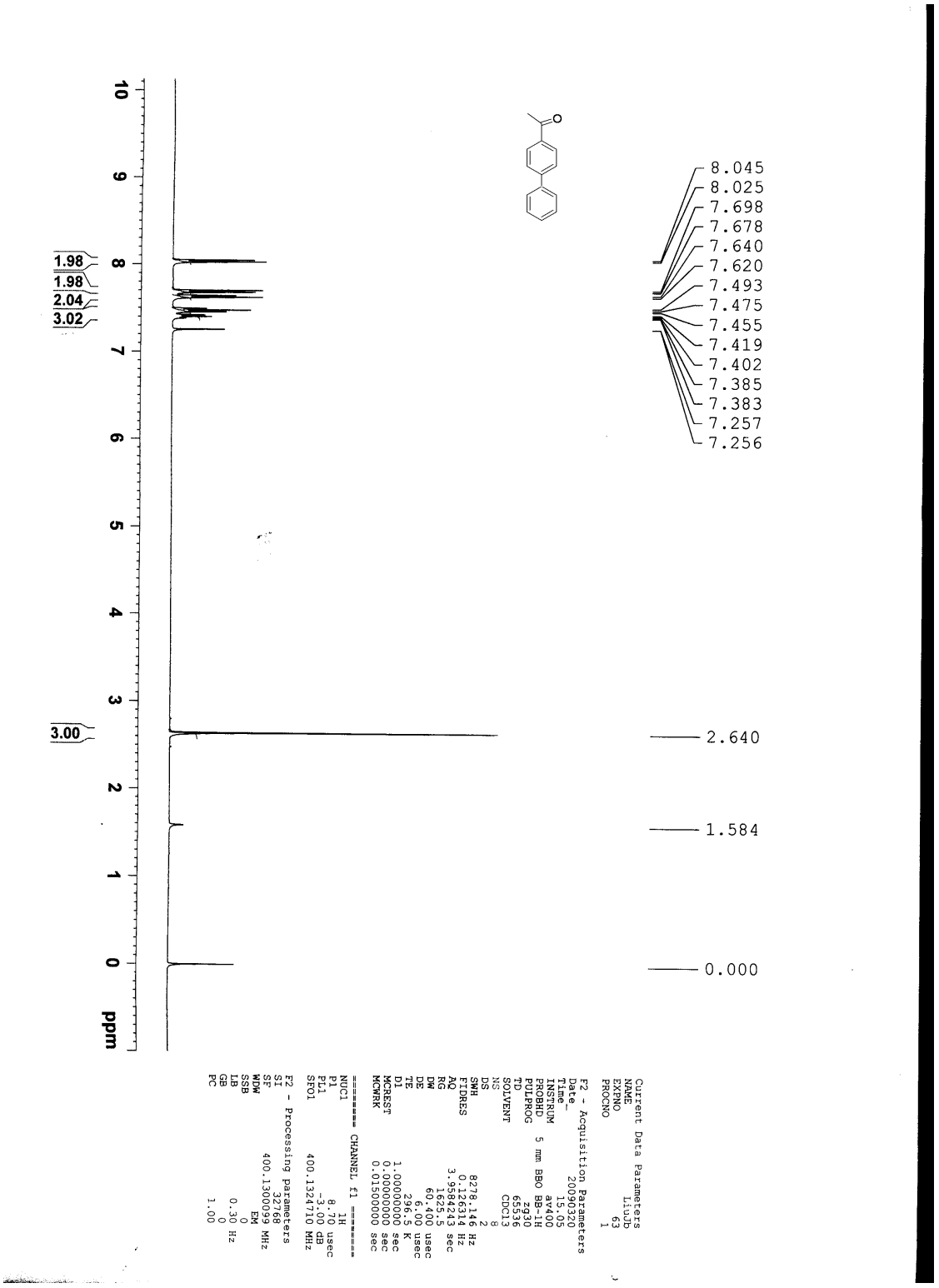
2-Methyl-biphenyl (**3d**)



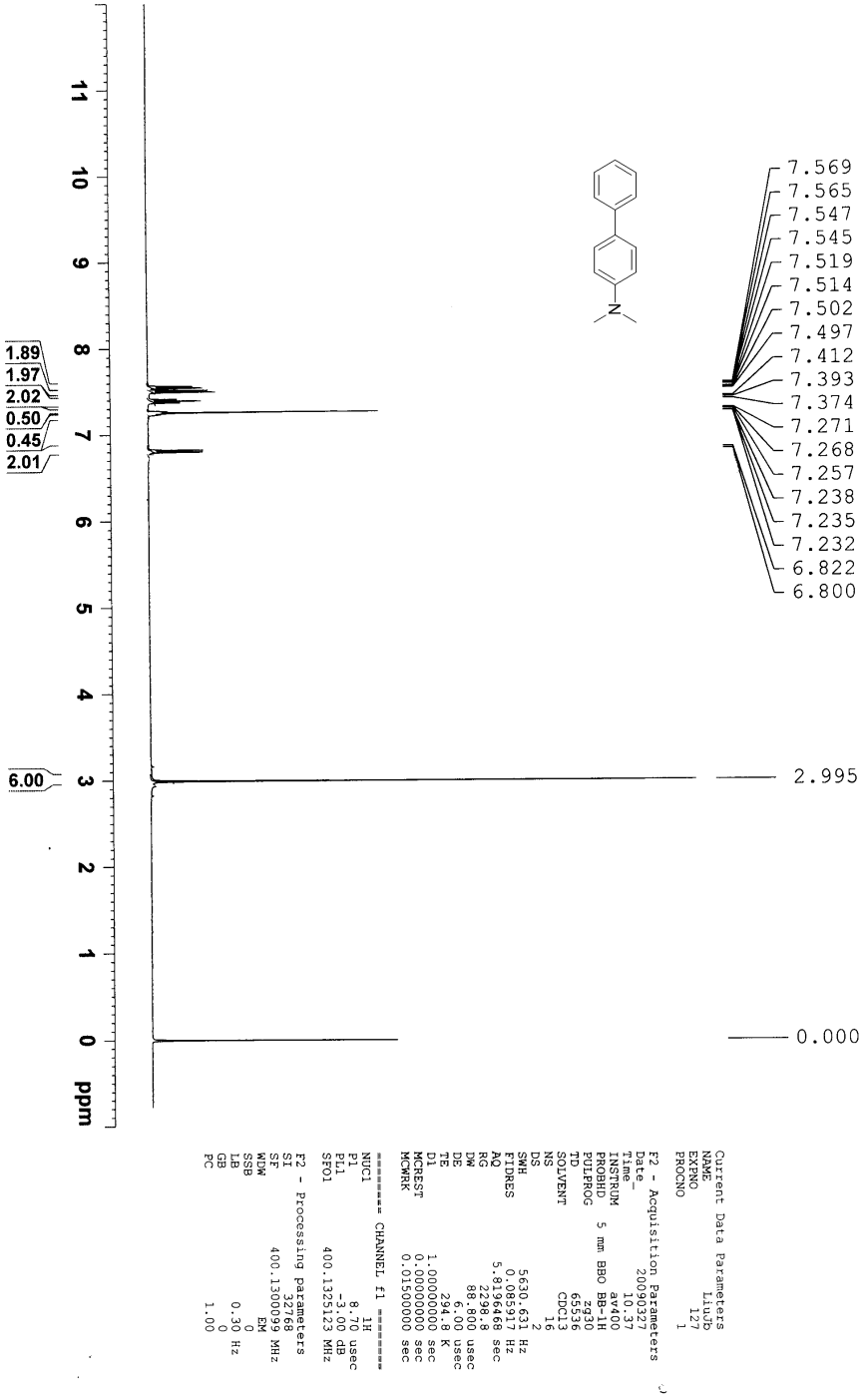
4-Nitro-biphenyl (3e)



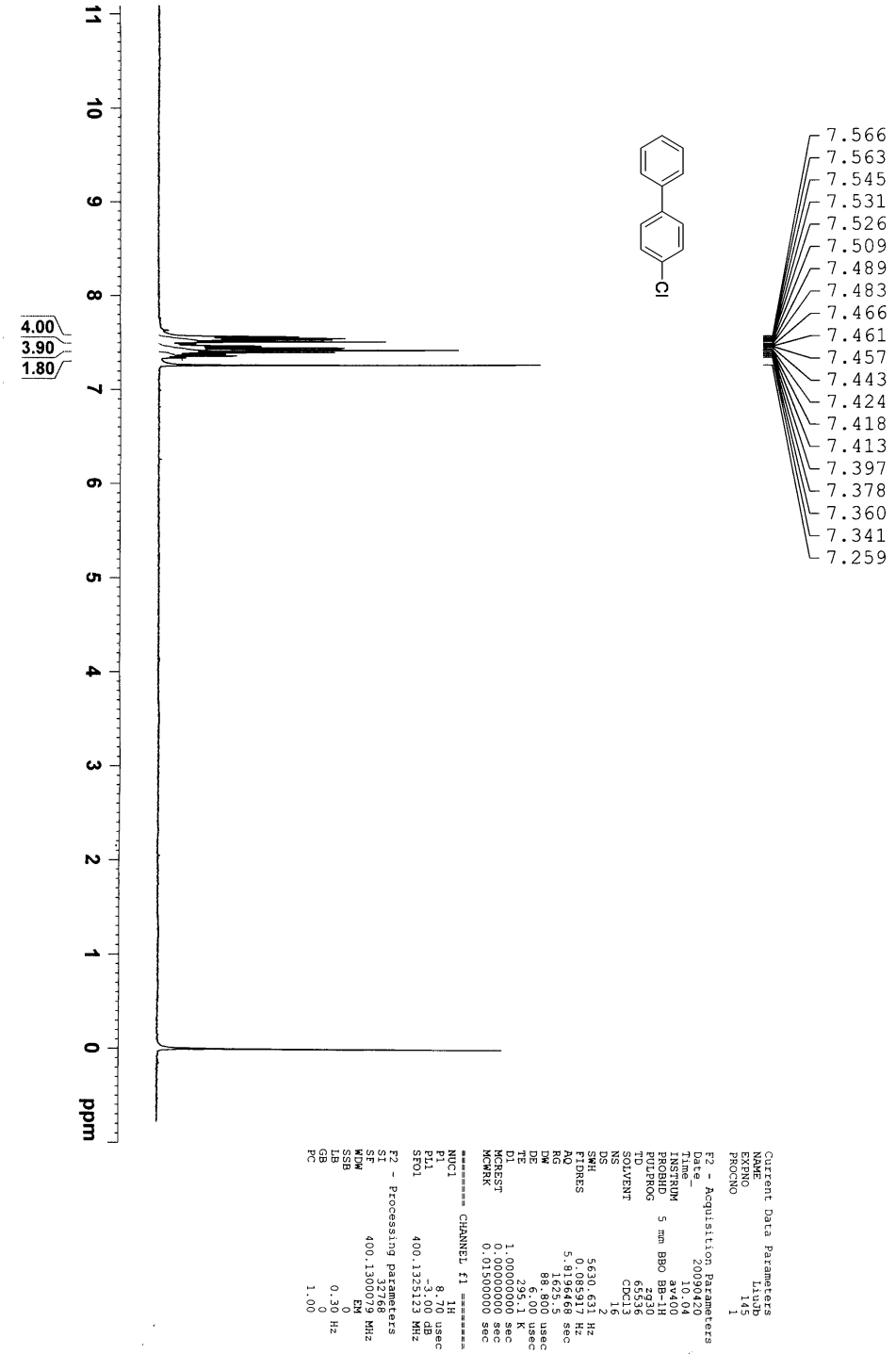
4-Acetyl-biphenyl (3f)



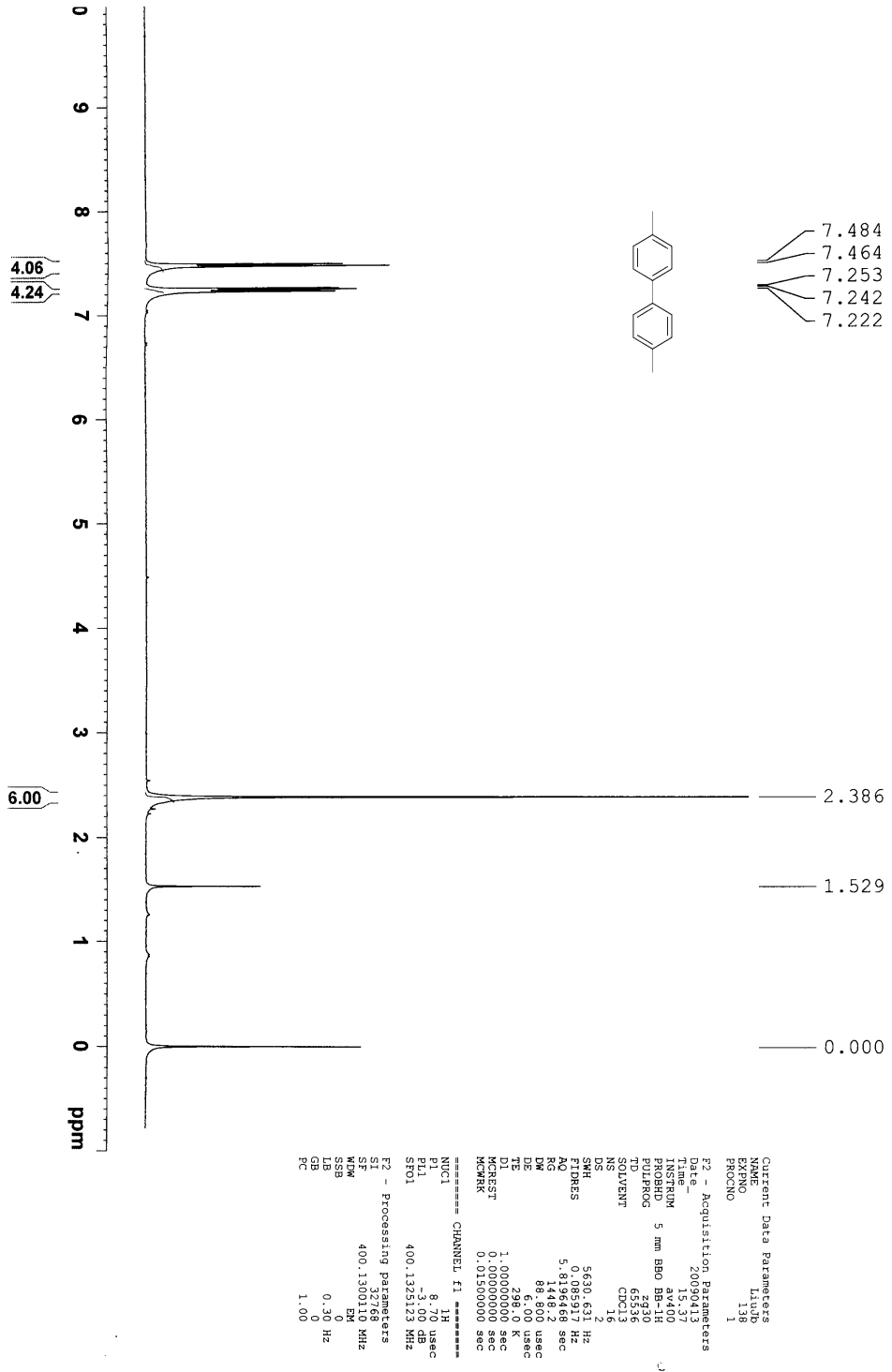
4- (N, N-dimethylamino) biphenyl (3g)



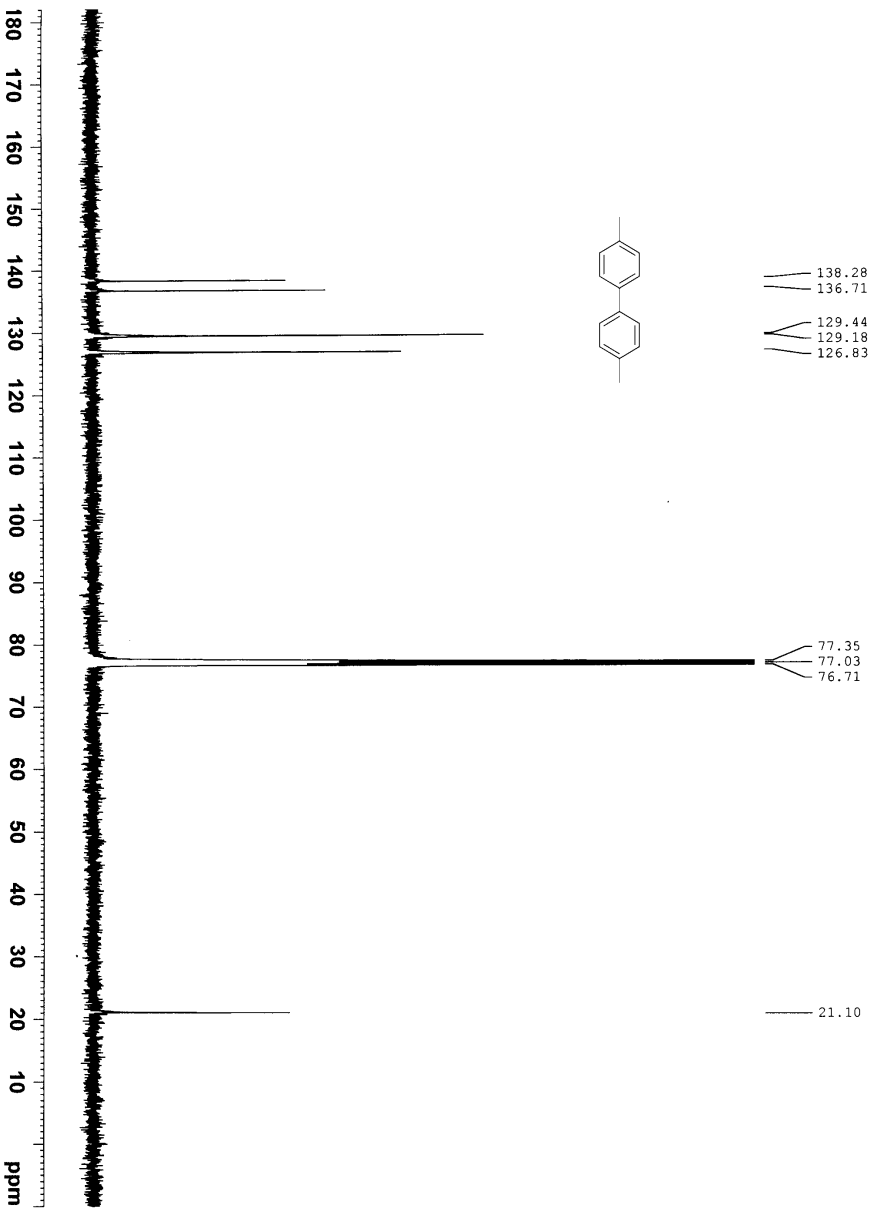
4-Chloro-biphenyl (3h)



4, 4’-Dimethyl-biphenyl (3i)



4, 4’-Dimethyl-biphenyl (3i)

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Current Data Parameters
NAME                  Liu3b
EXPNO                    144
PROCNO                     1

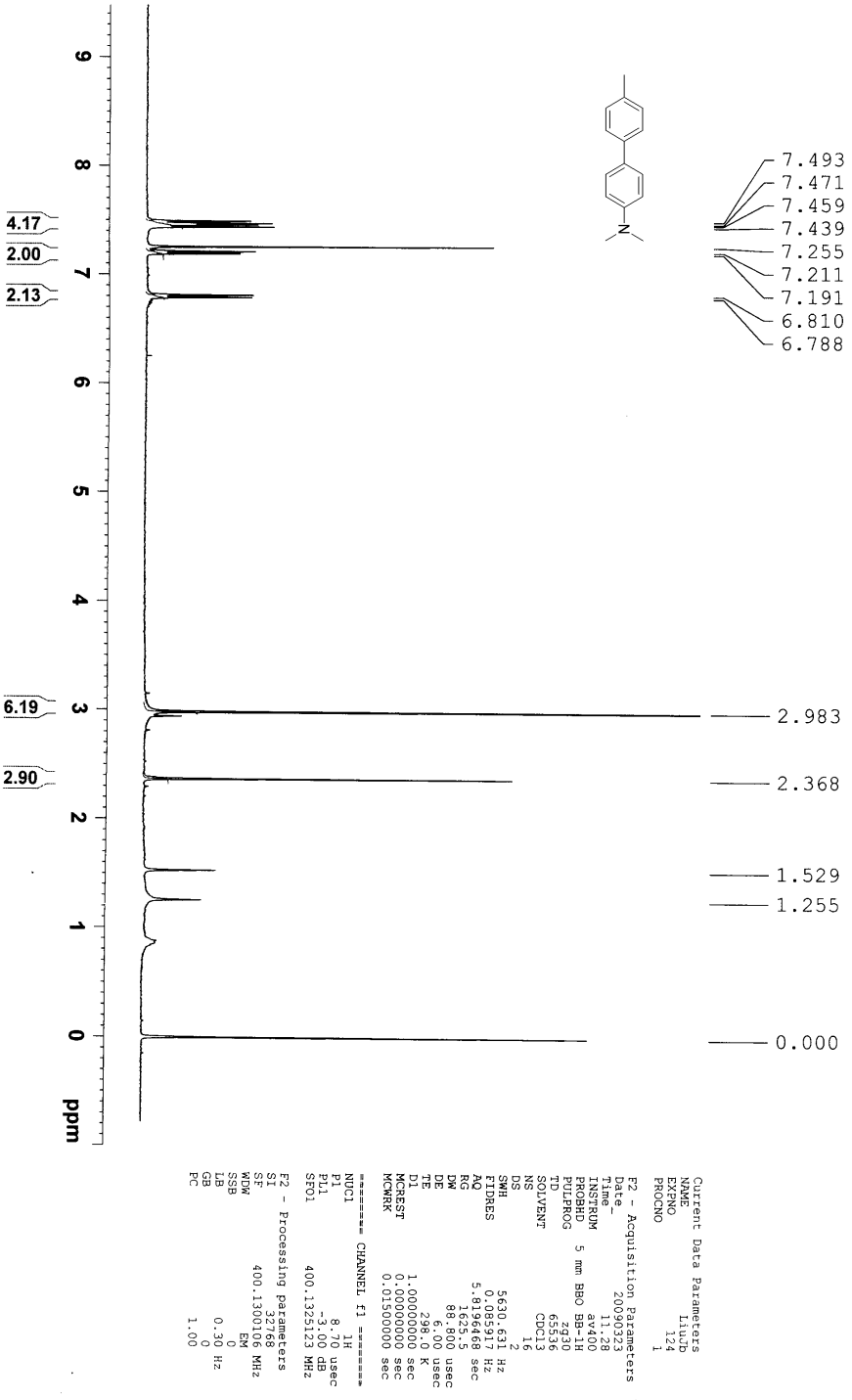
F2 - Acquisition Parameters
Date_              20090415
Time                   23.17
INSTRUM                av400
PROBHD   5 mm BBO BB-1H
PULPROG                zgpg30
TD                     65536
SOLVENT                CDCl3
NS                     6144
DS                        4
SWH              23980.814 Hz
FIDRES               0.365918 Hz
AQ                1.3664756 sec
RG                     9195.2
DW                    20.850 usec
DE                     6.00 usec
TE                     294.8 K
D1                2.00000000 sec
D11               0.03000000 sec
MCREST            0.00000000 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                     8.50 usec
PL1                   -2.00 dB
SFO1          100.6228298 MHz

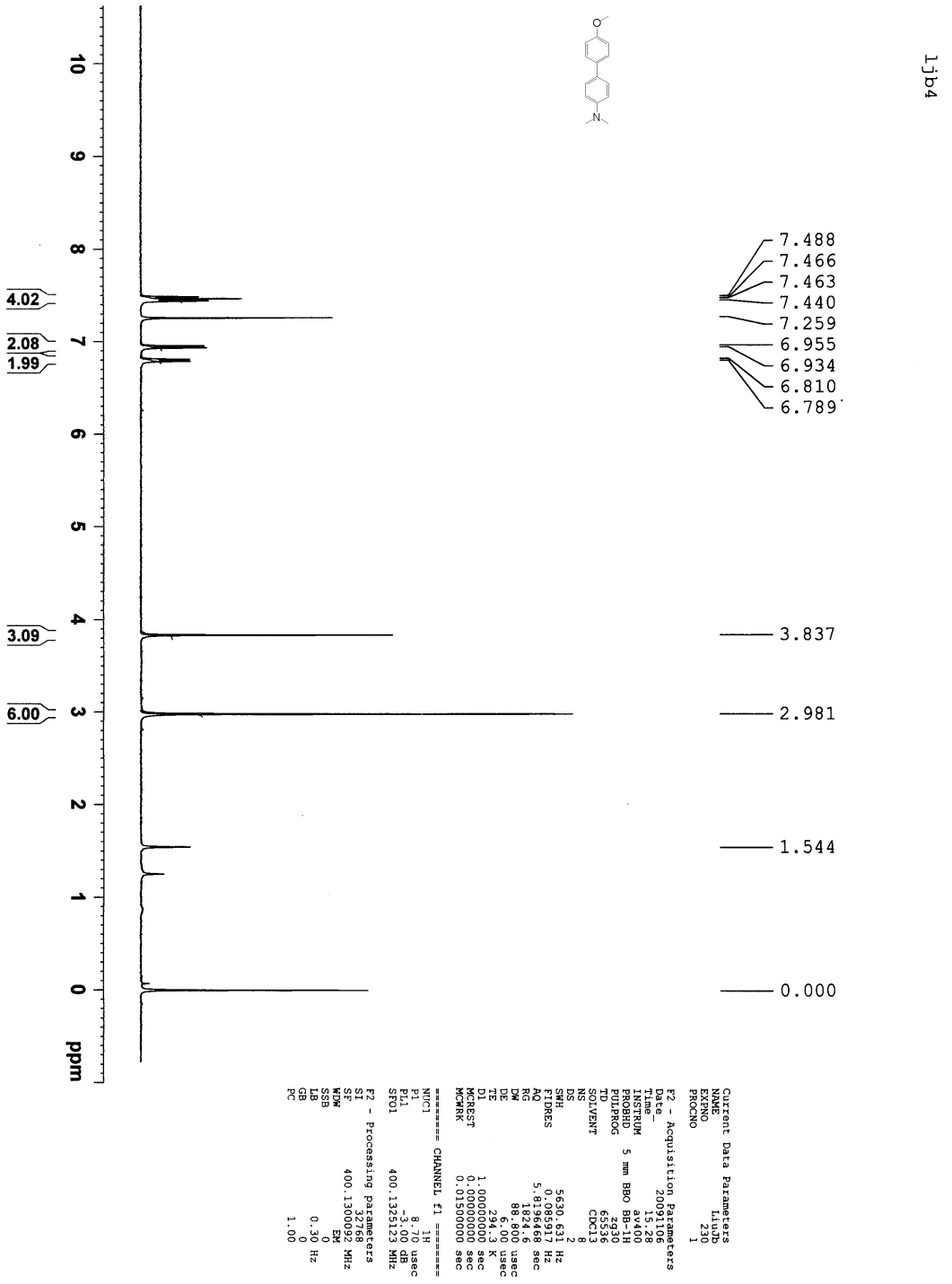
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                   13.00 dB
PL12                  16.27 dB
PL13                  20.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF            100.6127690 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

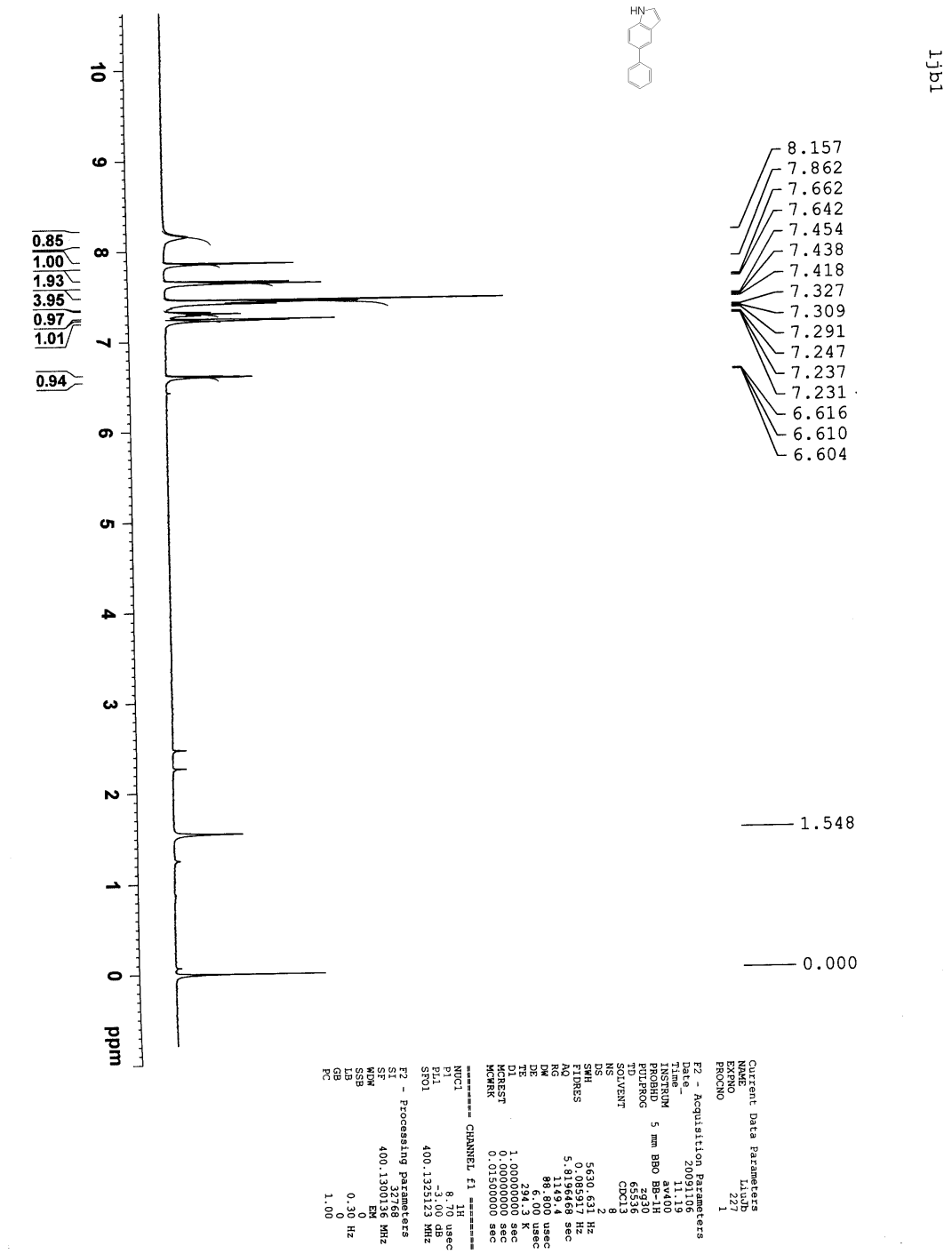
4-Methyl -4'-(N, N-Dimethylamino) biphenyl (3j)



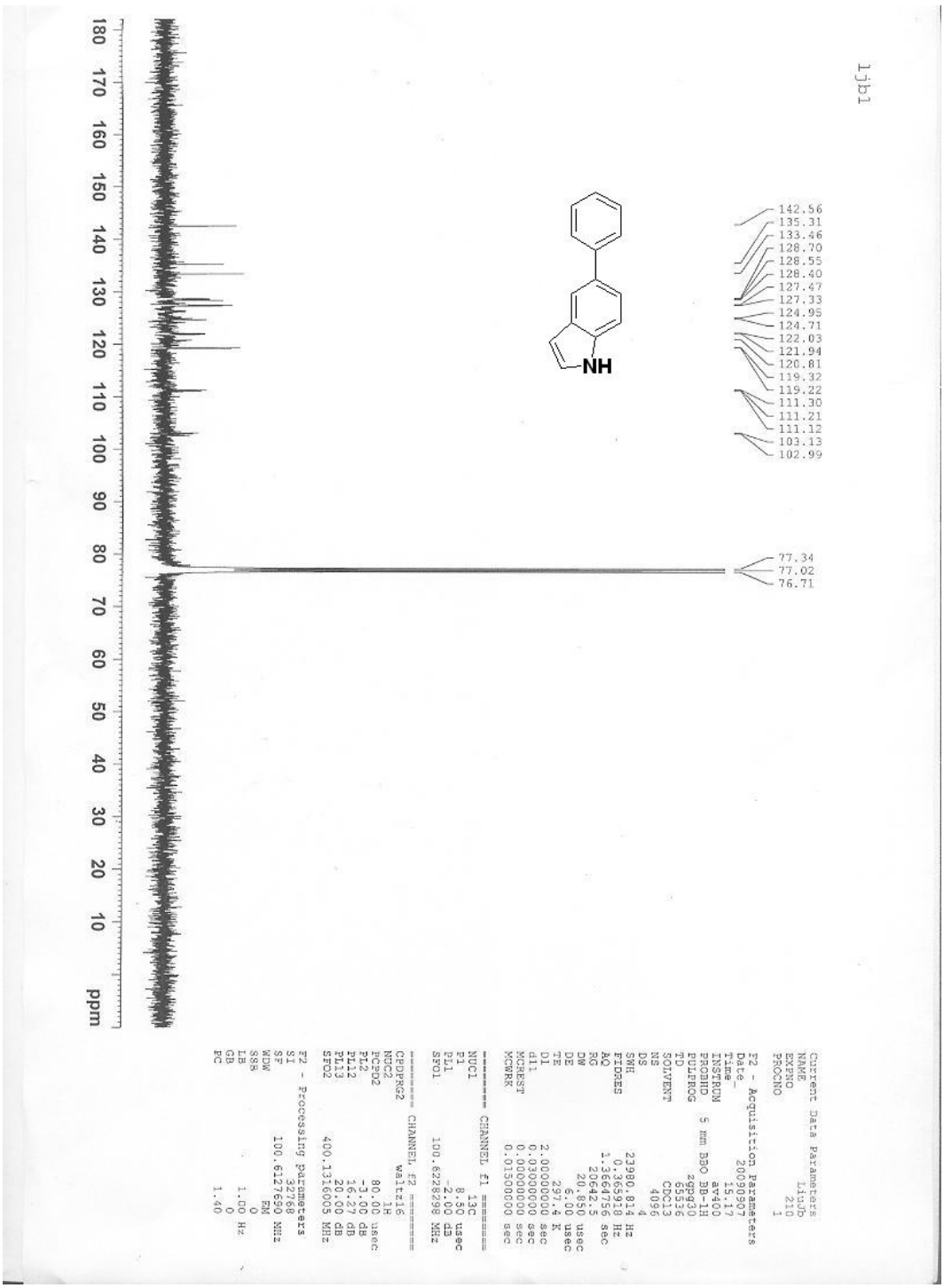
4-Methoxy-4'- (*N*, *N*-dimethylamino) biphenyl (3k)



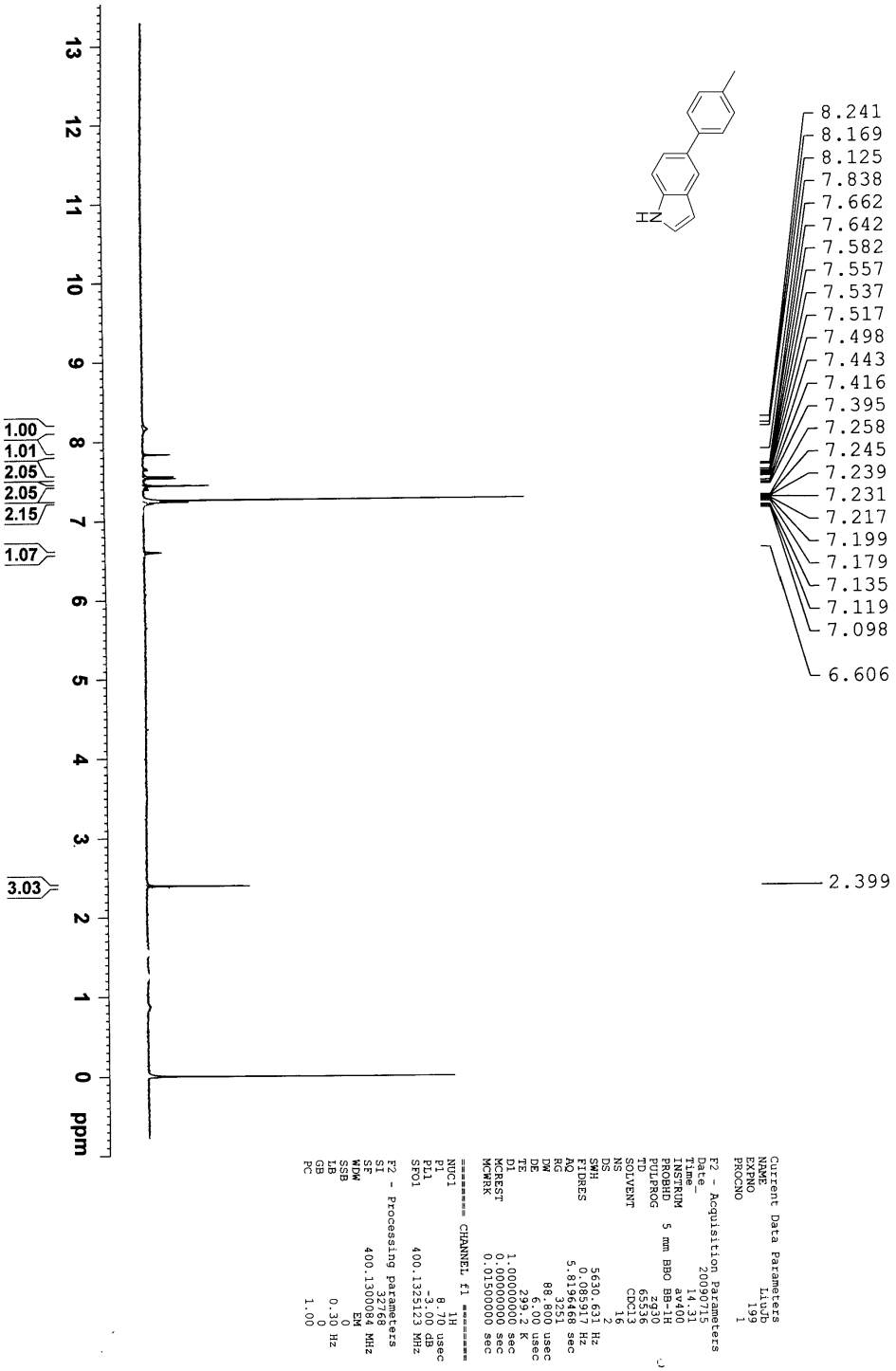
5-phenyl-1H-indole (4a)



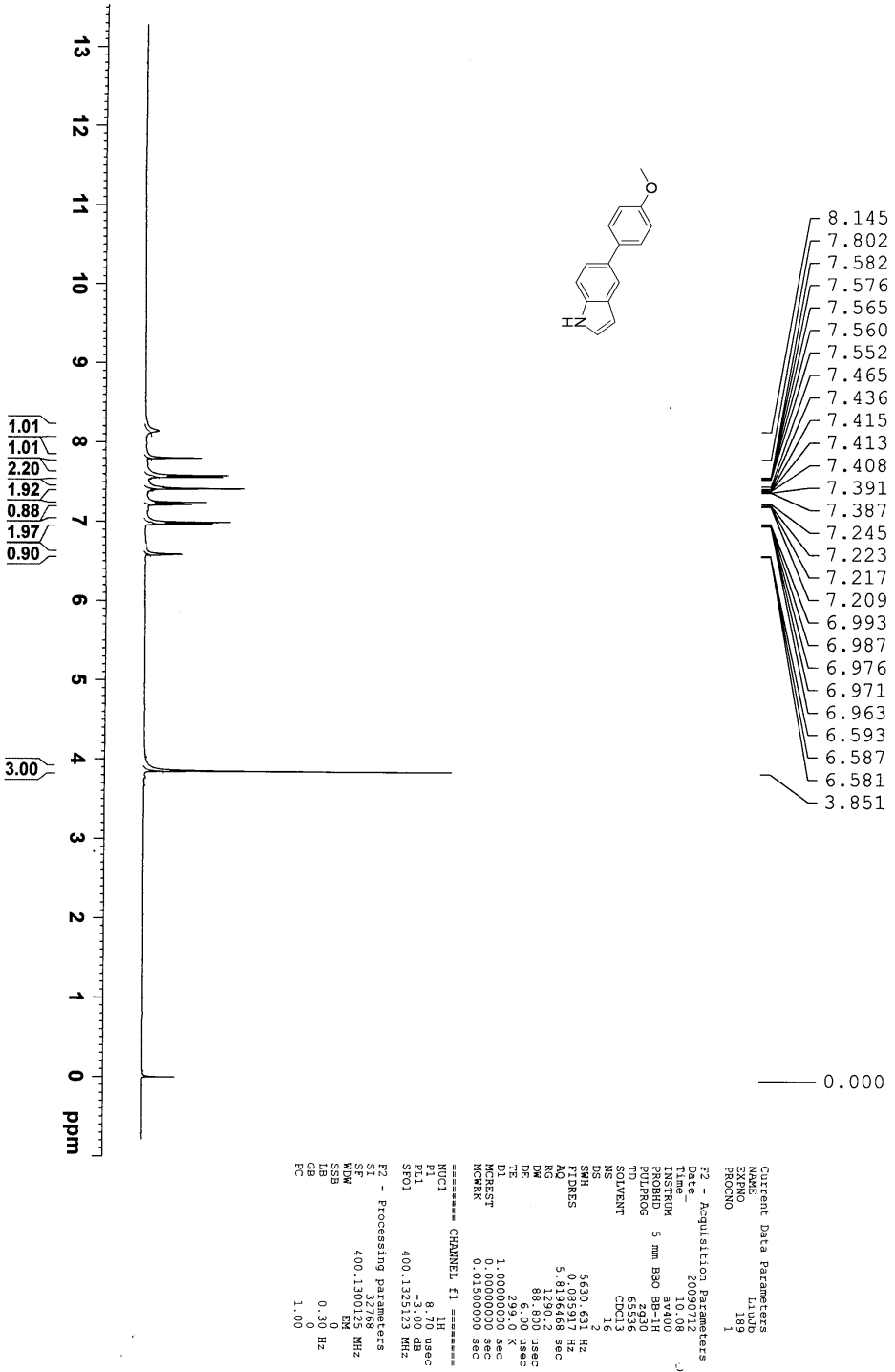
5-phenyl-1H-indole (4a)



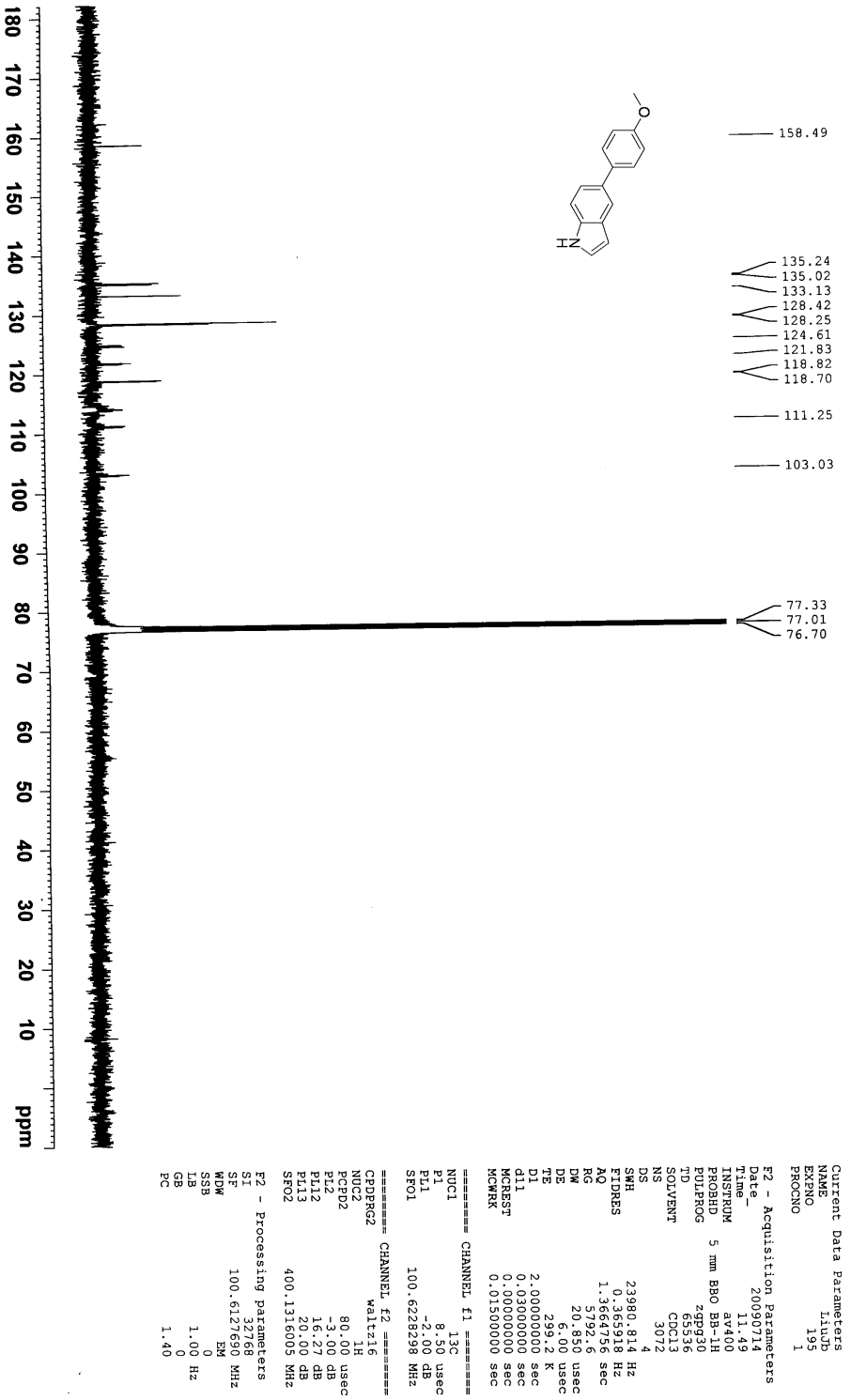
5-*p*-tolyl-1H-indole (4b)



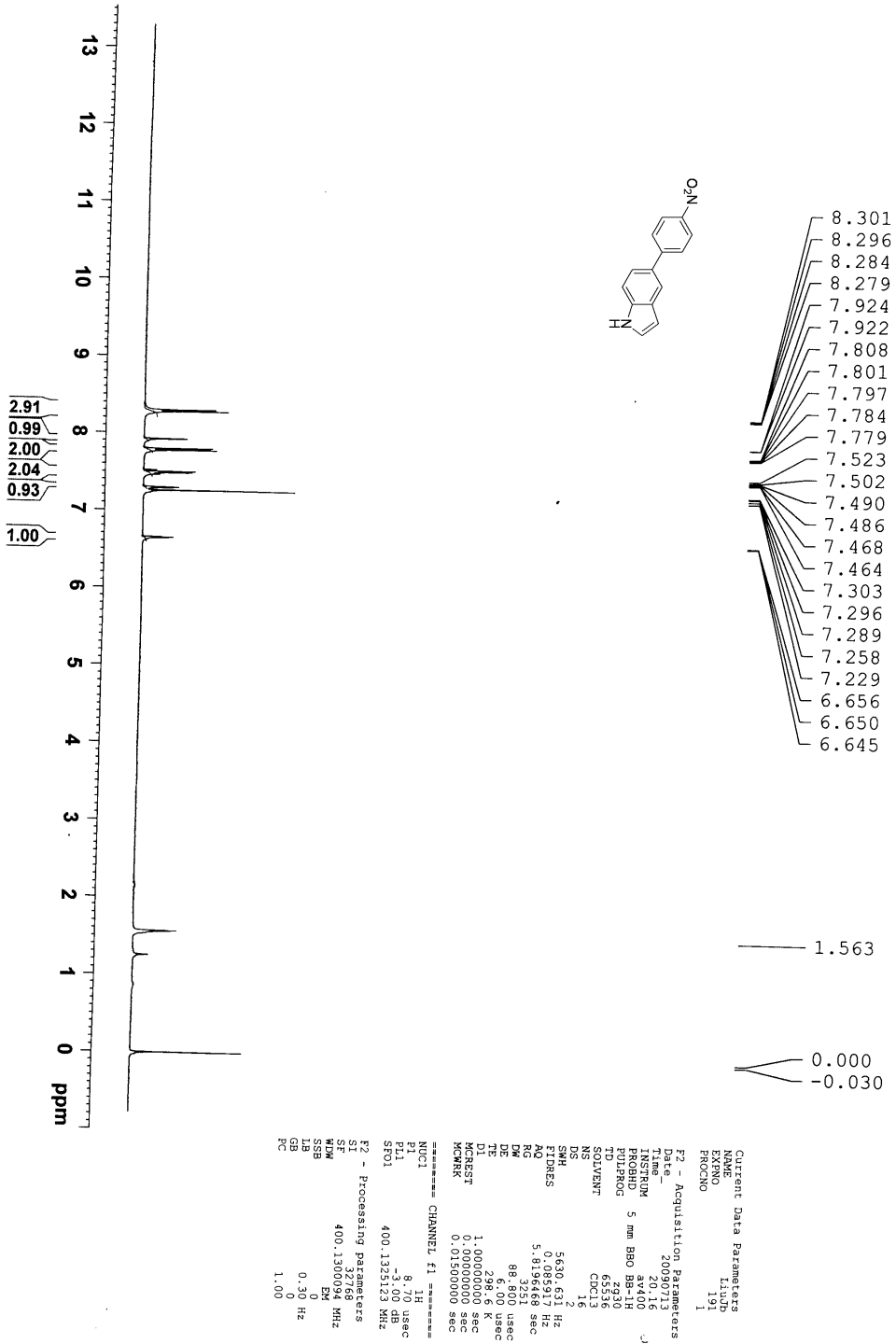
5-(4-methoxyphenyl)-1H-indole (4c)



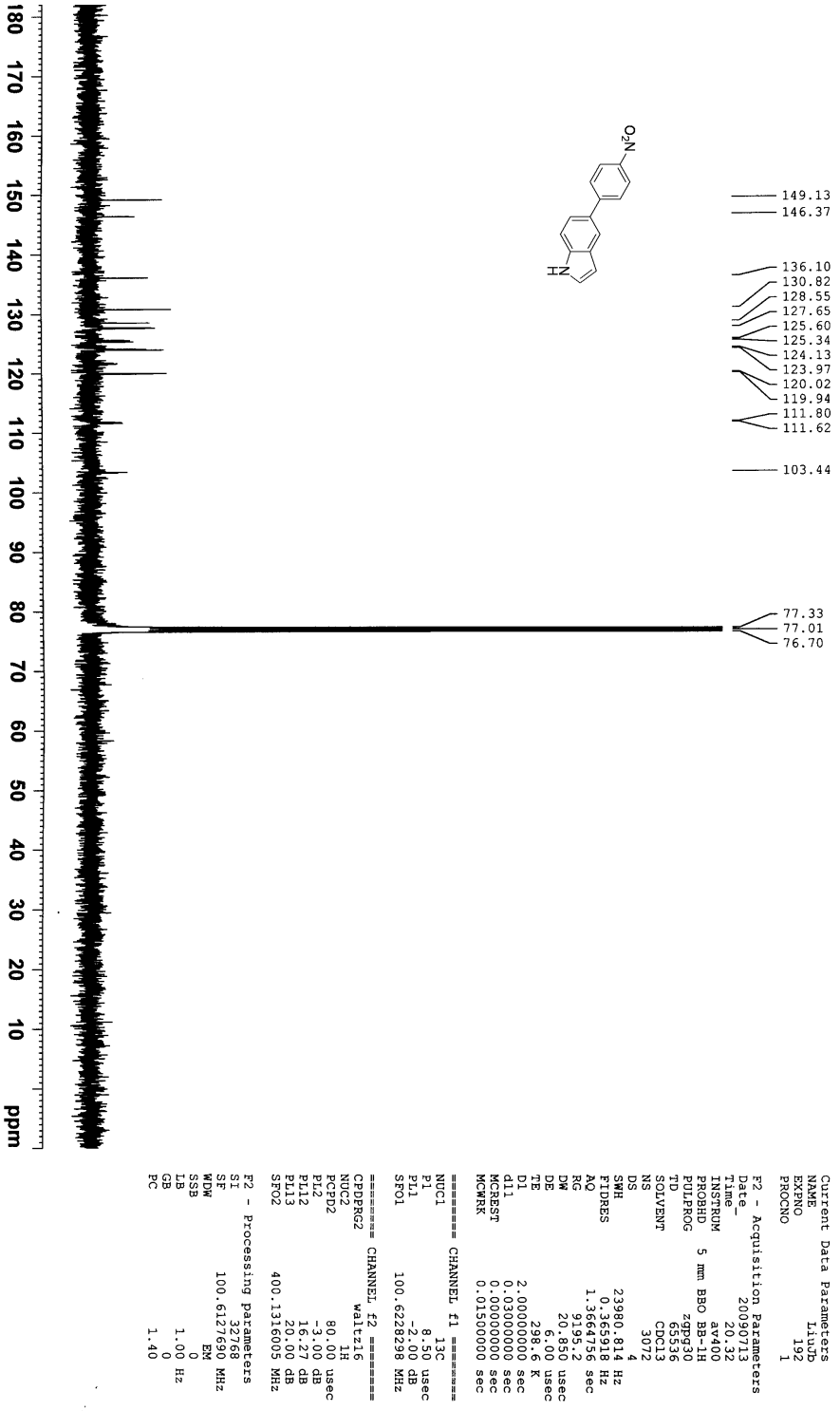
5-(4-methoxyphenyl)-1H-indole (4c)



5-(4-nitrophenyl)-1H-indole (4d)



5-(4-nitrophenyl)-1H-indole (4d)



Current Data Parameters
NAME LiuJb
EXPNO 192
PROCNO 1

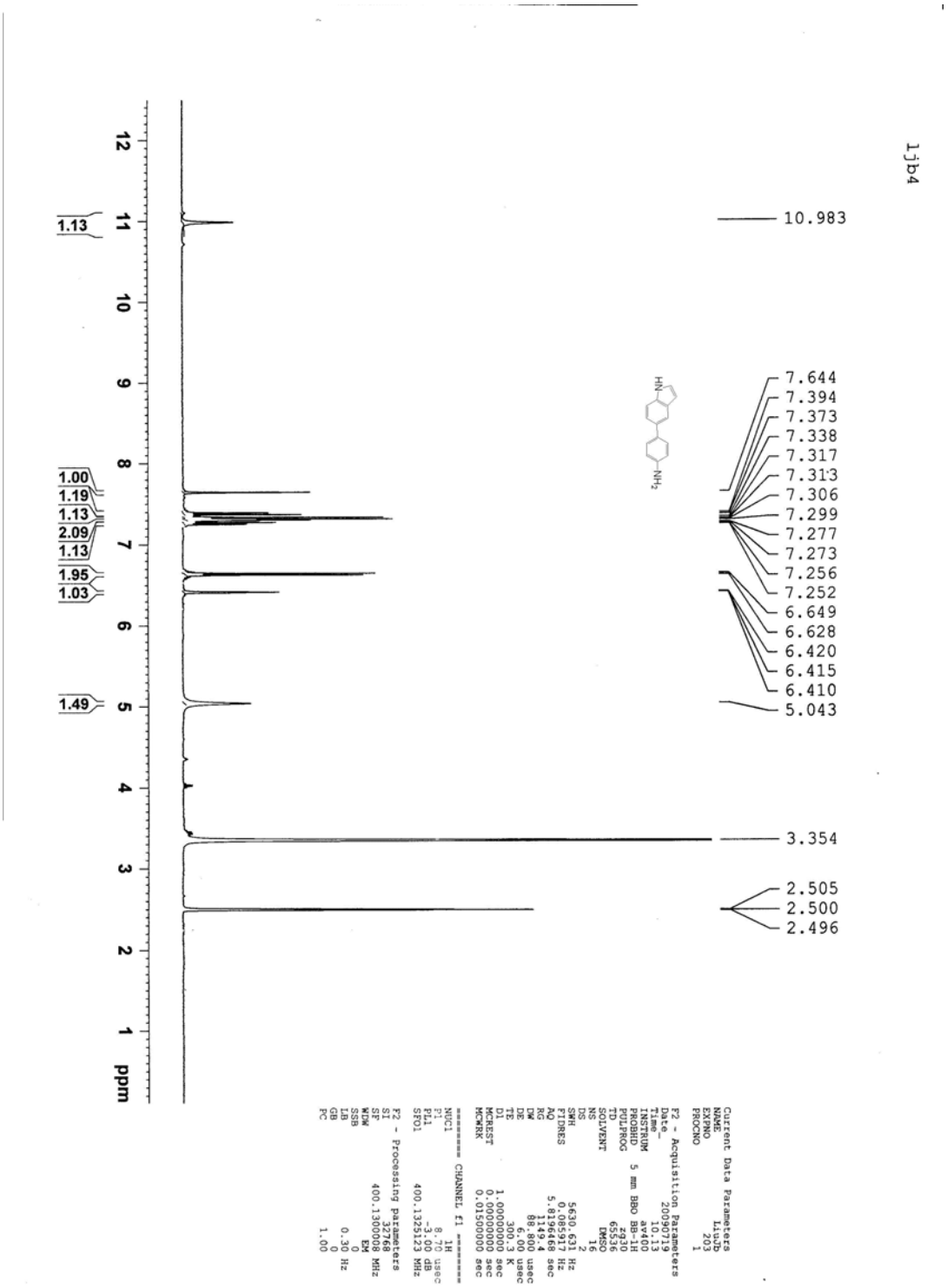
F2 - Acquisition Parameters
Date_ 20090713
Time_ 20.32
INSTRUM av400
PROBHD BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 3072
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 9195.2
DW 20.850 usec
DE 6.00 usec
TE 298.6 K
D1 2.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
SFO1 100.6228298 MHz

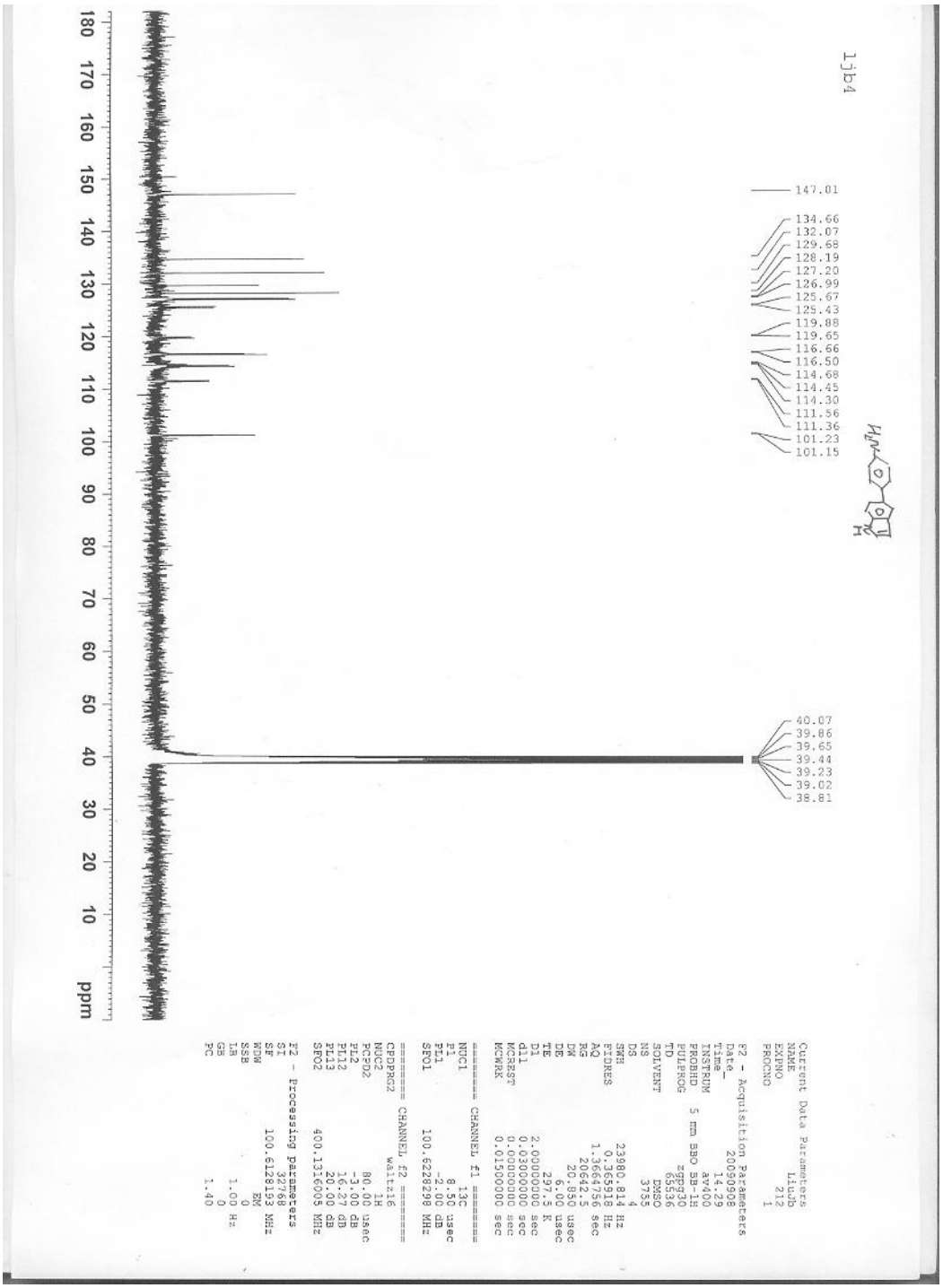
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.00 dB
PL12 16.27 dB
PL13 20.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

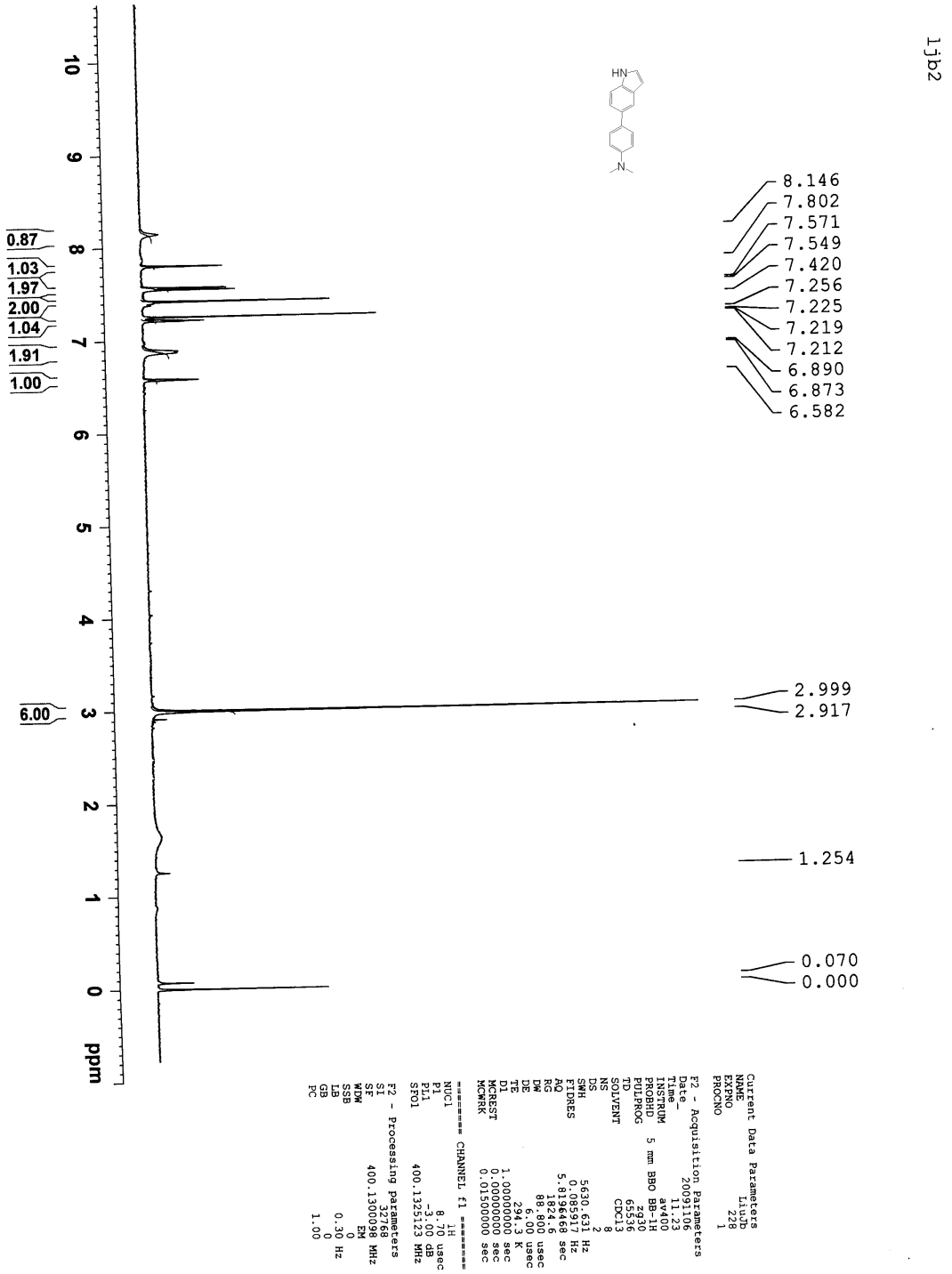
5-(4-aminophenyl)-1H-indole (4e)



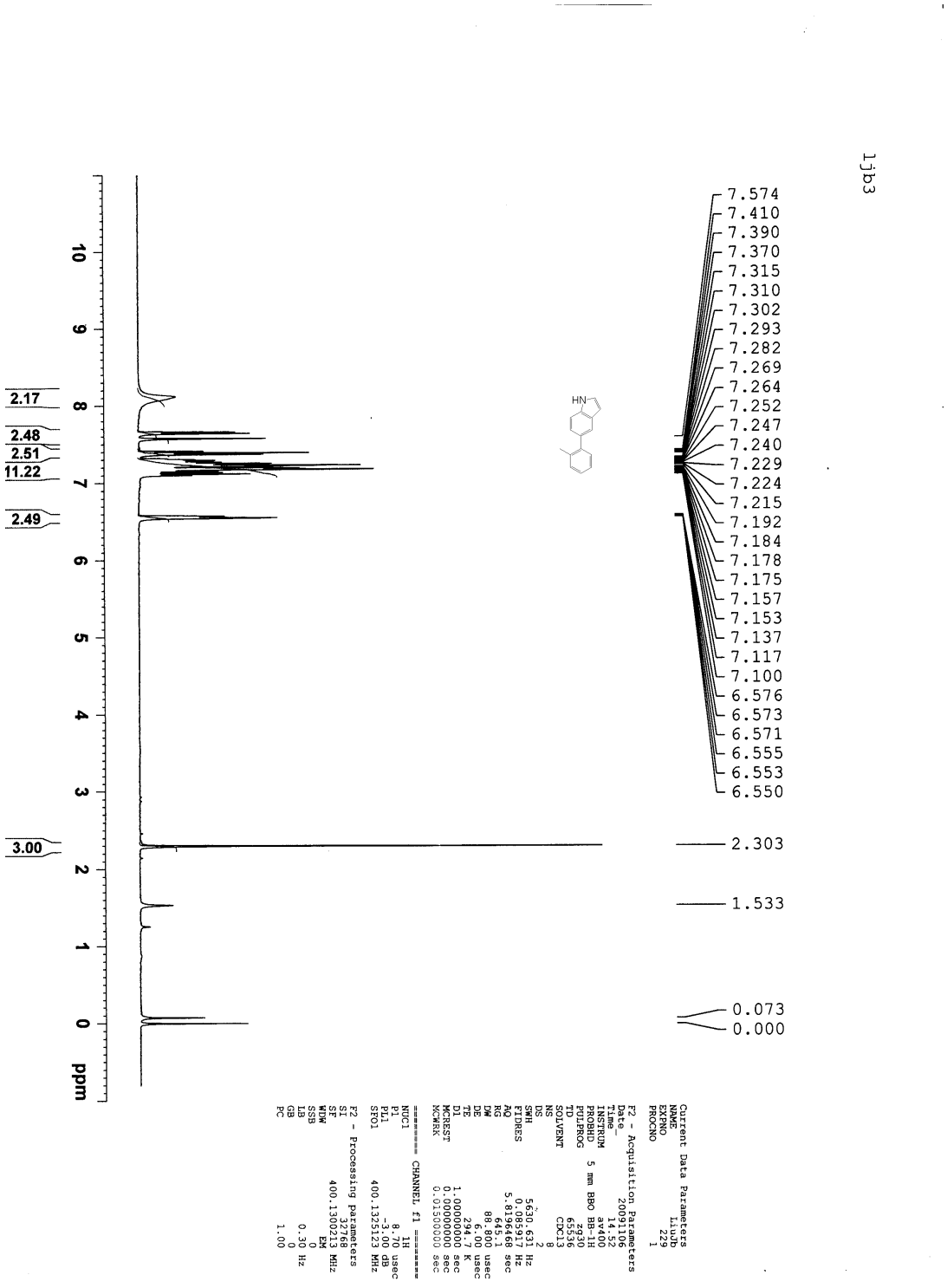
5-(4-aminophenyl)-1H-indole (4e)



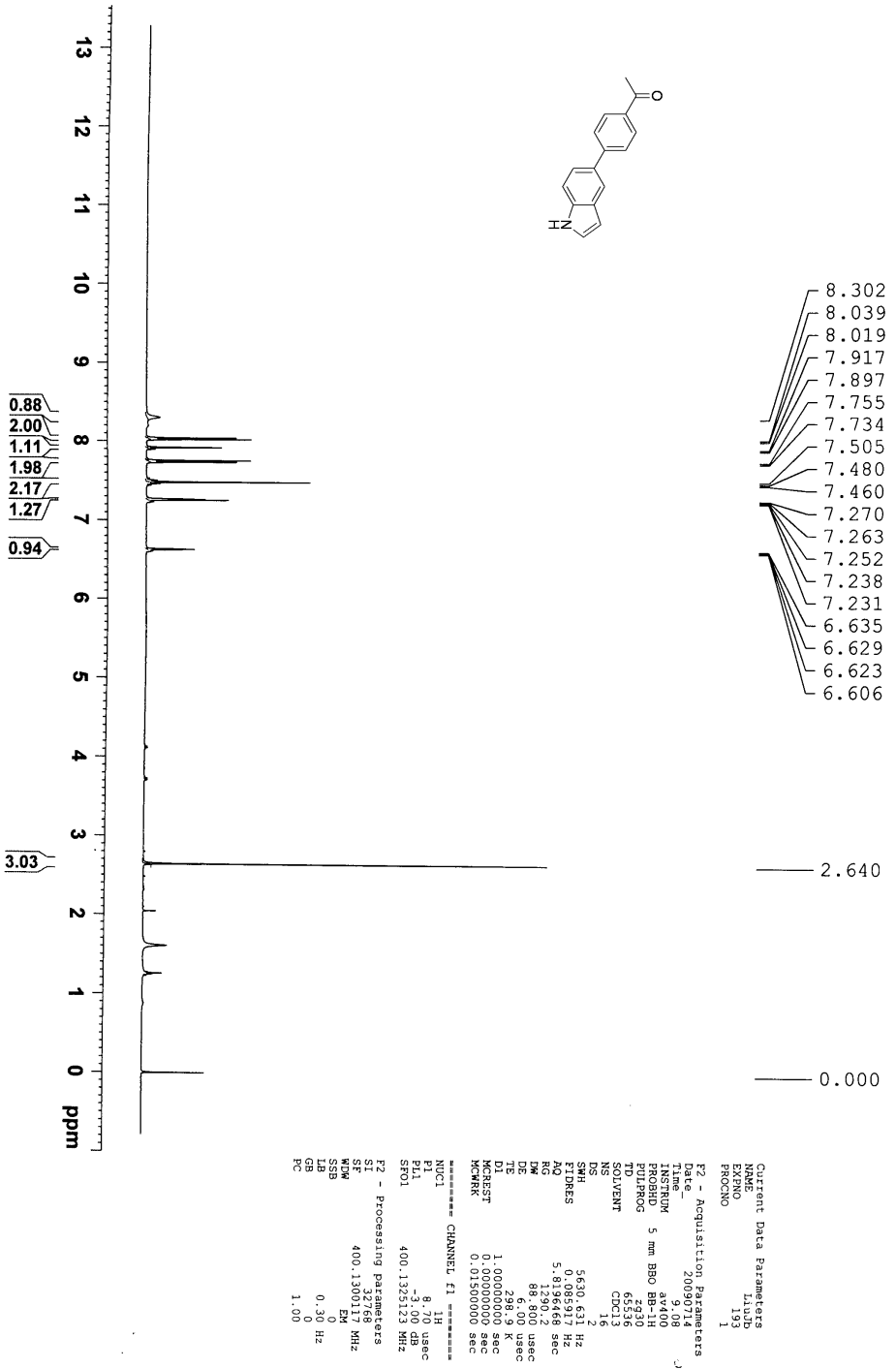
5-(4-*N*, *N*-dimethylaminophenyl)-1H-indole (4f)



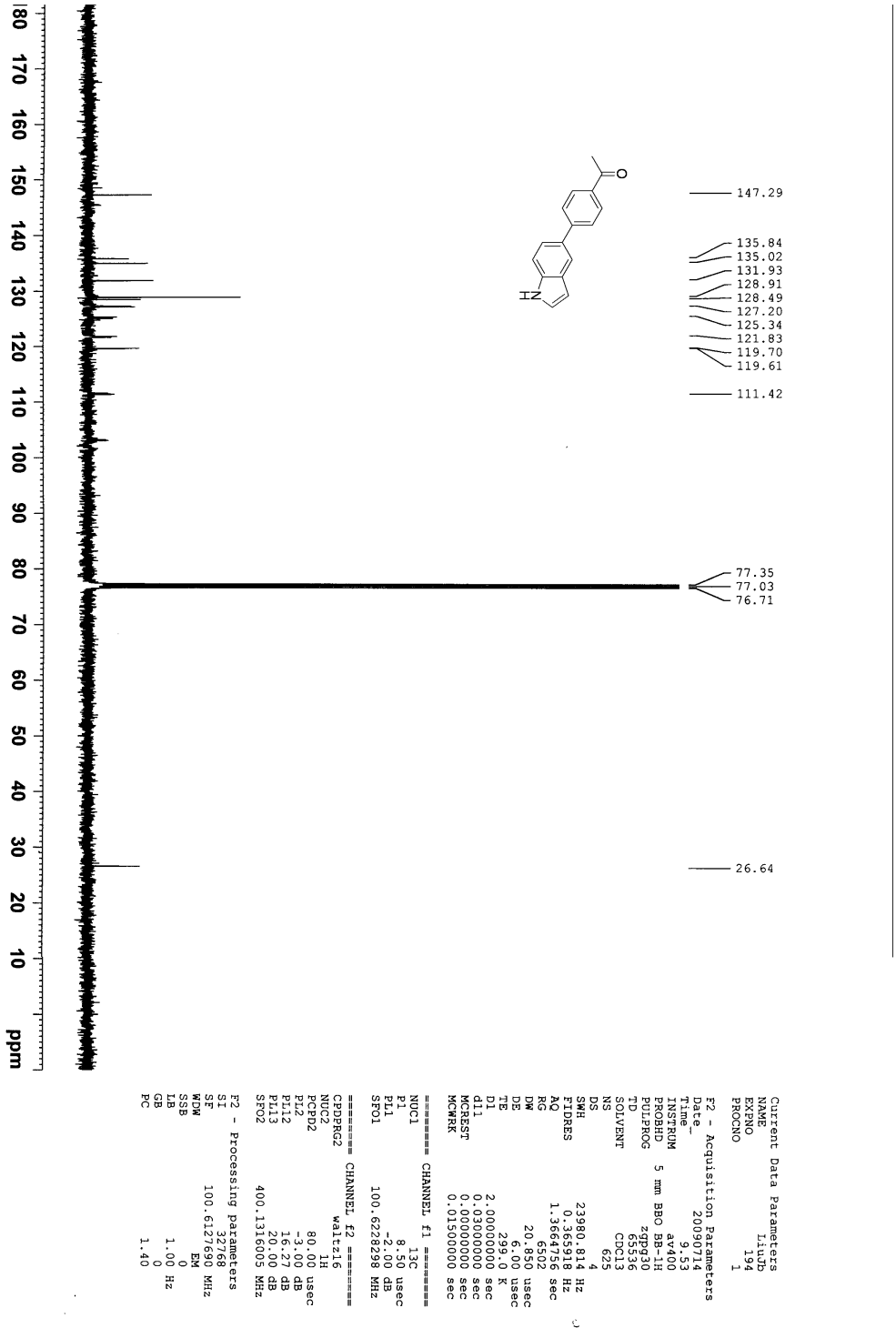
5-(2-Methylphenyl) -1H-indole (4g) [7]



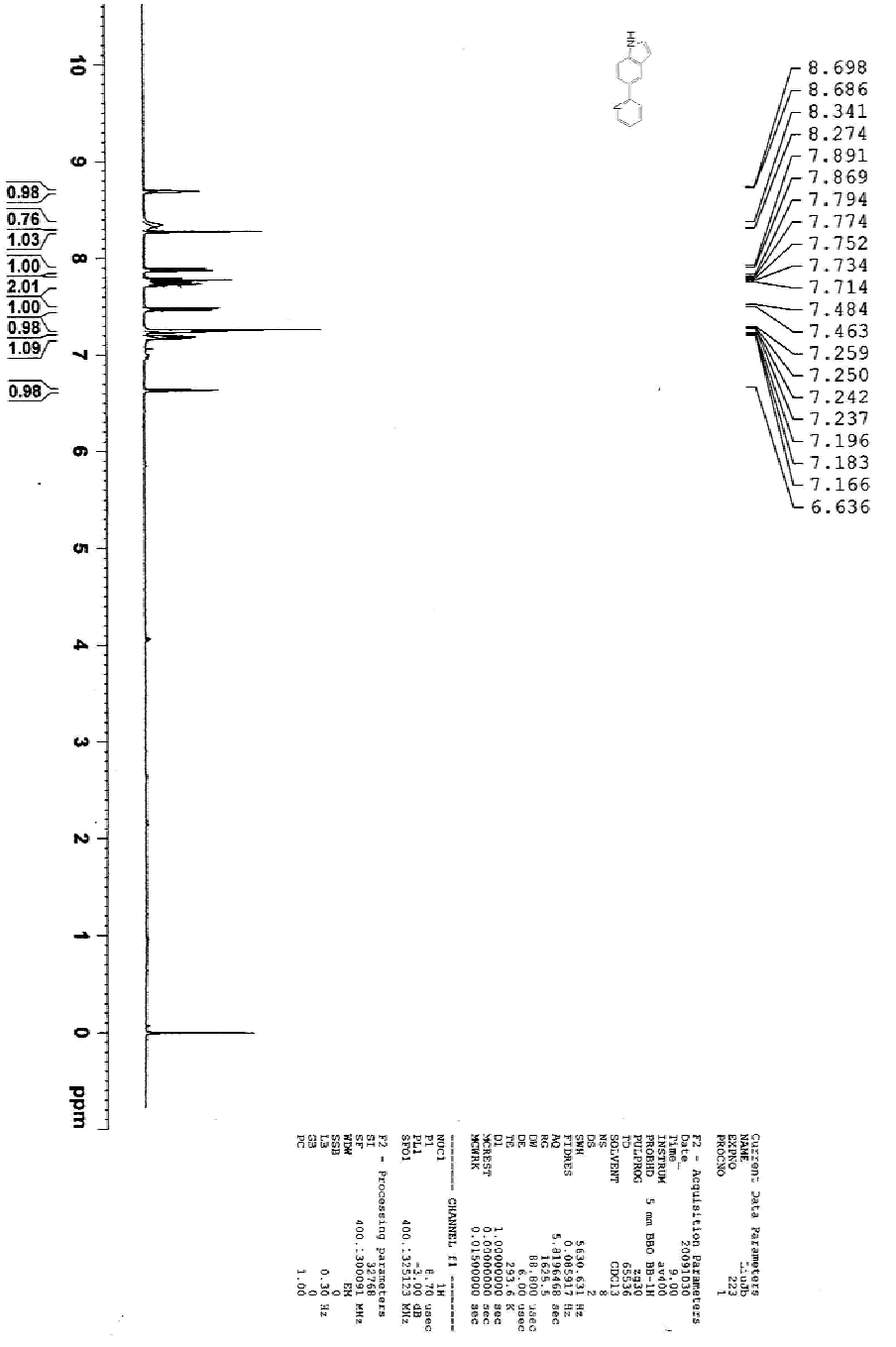
5-(4-Acetylphenyl)-1H-indole (4h)



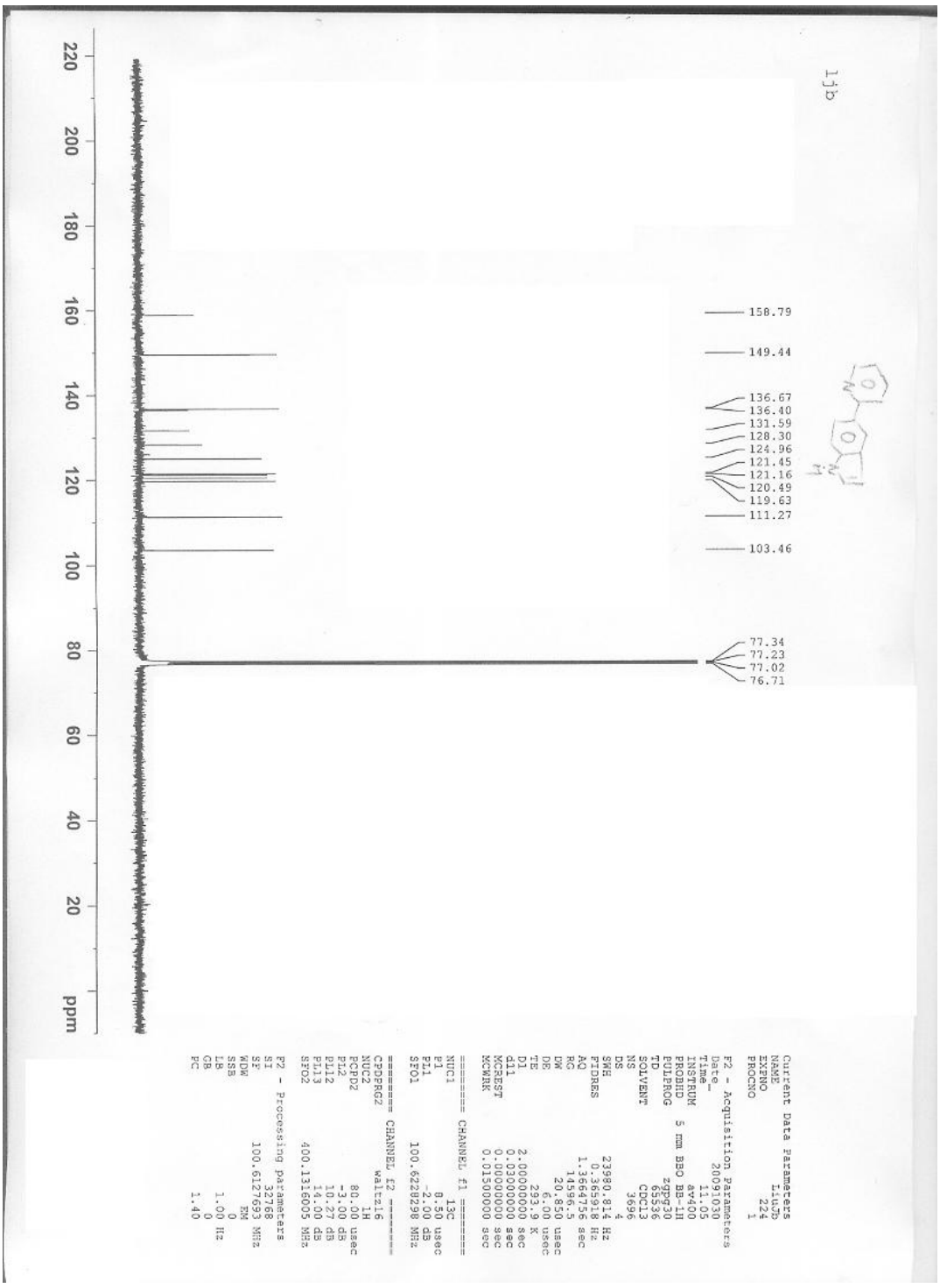
5-(4-Acetylphenyl)-1H-indole (4h)



5-(pyridin-2-yl)-1H-indole (4i)



5-(pyridin-2-yl)-1H-indole (4i)



5-(thiophen-2-yl)-1H-indole (4j)