Supporting Information for

Allenyl Azide Cycloaddition Chemistry. 2,3-Cyclopentennelated Indole Synthesis through Indolidene Intermediates.

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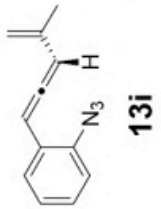
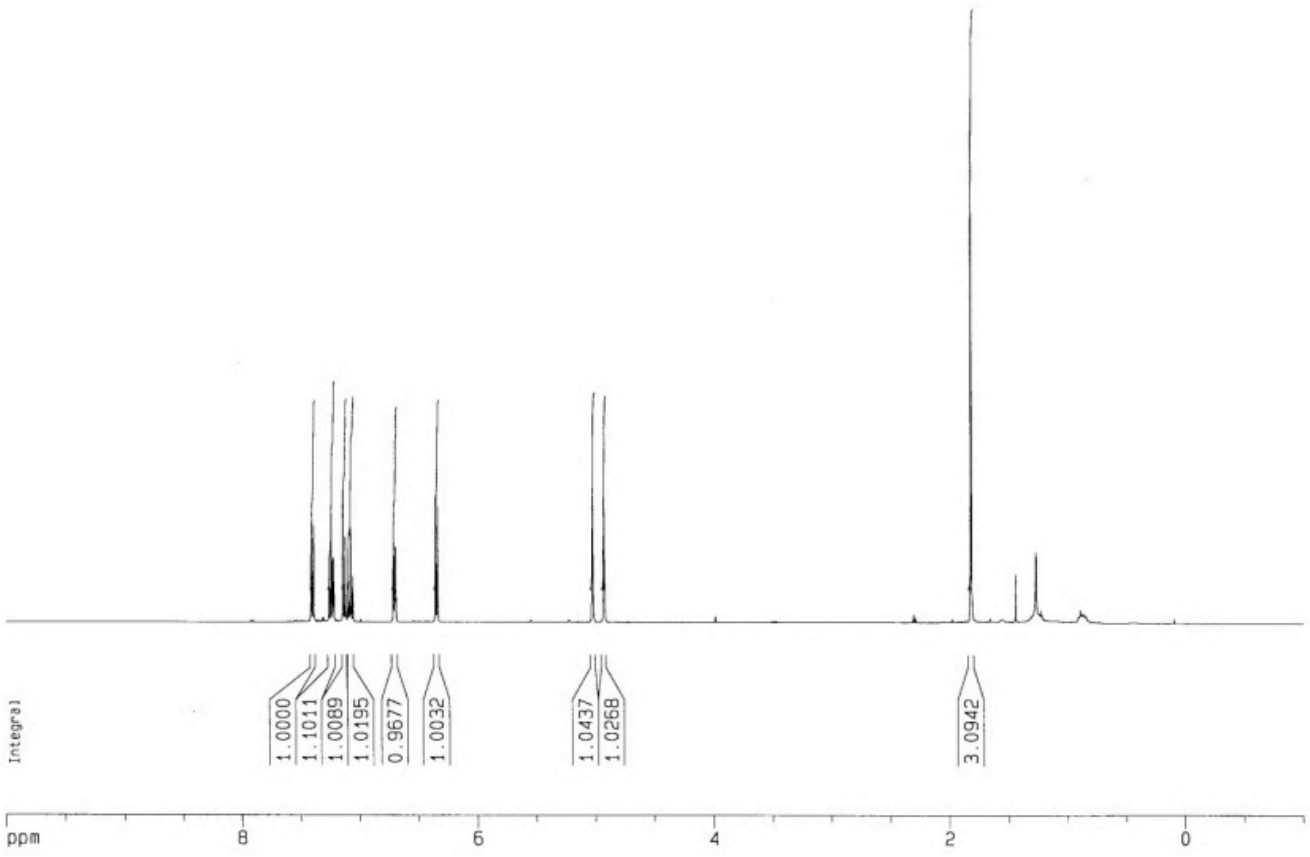
General Experimental

Moisture and oxygen sensitive reactions were carried out in flame-dried glassware under a nitrogen atmosphere. Photolysis was carried out using a Rayonet reactor with cooling fan. Solvents were dried by passage through an activated alumina column under nitrogen. All organic reagents were used as purchased unless otherwise noted. Flash chromatography was performed using 32 – 63 μm silica gel (unless otherwise noted) with the indicated solvent systems. Melting points are uncorrected.

DKH4-260 Product pale yellow oil



13i

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Current Data Parameters
NAME            DKH4-260P
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070528
Time                10.51
INSTRUM             spect
PROBHD     5 mm BBI 1H-B
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     12
DS                      2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                  71.8
DW                60.400 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec

========== CHANNEL f1 =======
NUC1                   1H
P1                  6.45 usec
PL1                 0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300174 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               10.000 ppm
F1               4001.30 Hz
F2P               -1.000 ppm
F2               -400.13 Hz
PPMCM             0.55000 ppm/cm
HZCM            220.07150 Hz/cm
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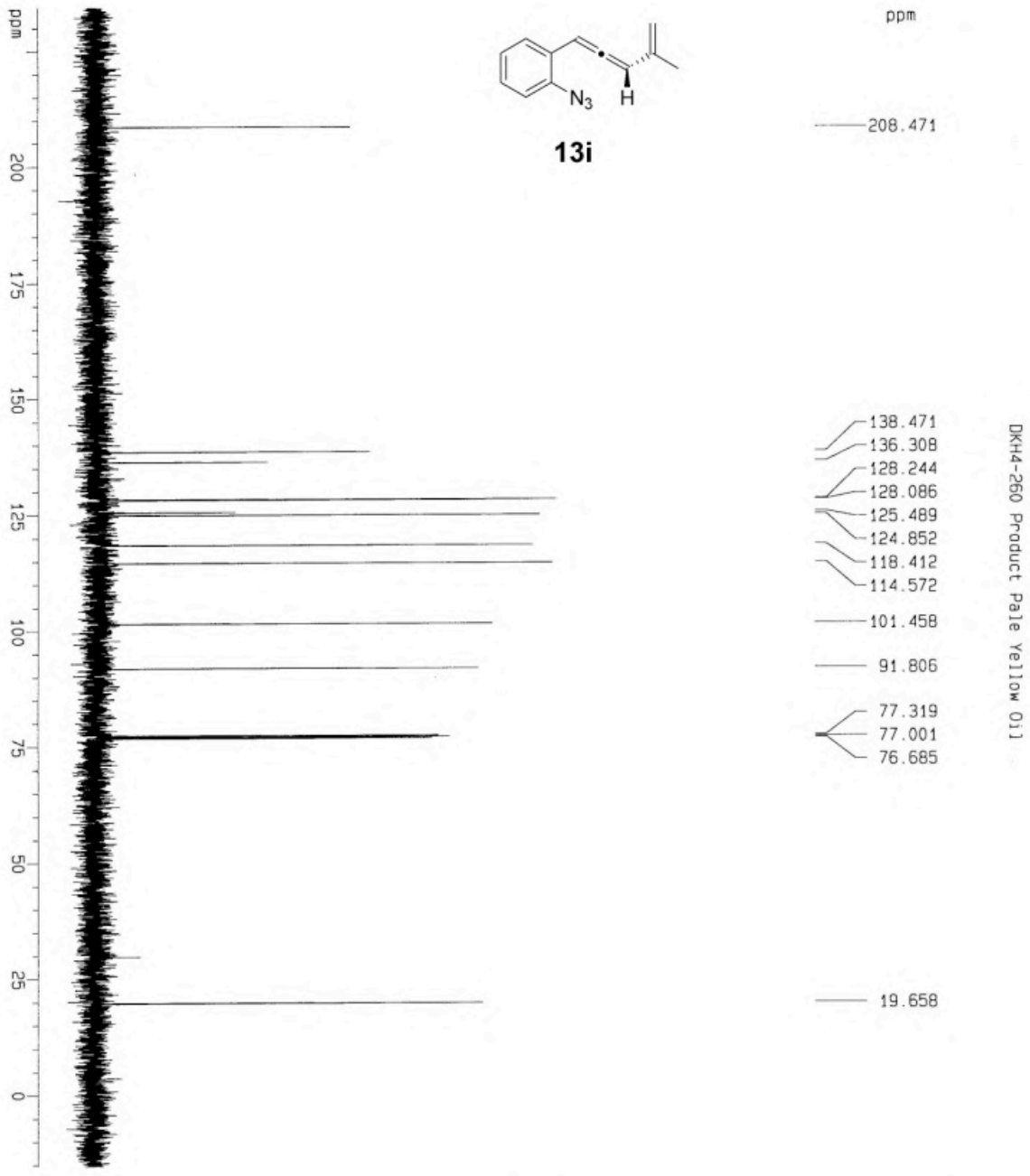


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EXPNO                         2
PROCNO                        1

F2 - Acquisition Parameters
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Time                      10.57
INSTRUM                   spect
PROBHD     5 mm BBI 1H-B
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                           75
DS                            4
SWH                  25125.629 Hz
FIDRES                0.383387 Hz
AQ                    1.3042154 sec
RG                        16384
DW                     19.900 usec
DE                         6.00 usec
TE                        300.0 K
D1                    2.00000000 sec
D11                   0.03000000 sec
D12                   0.00002000 sec

======== CHANNEL f1 ========
NUC1                        13C
P1                        16.35 usec
PL1                       -6.00 dB
SFO1                100.6237959 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                  114.00 usec
PL2                        0.00 dB
PL12                      24.00 dB
PL13                      24.00 dB
SFO2                400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127754 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40

1D NMR plot parameters
CX                        20.00 cm
F1P                      234.397 ppm
F1                     23583.35 Hz
F2P                     -15.329 ppm
F2                     -1542.28 Hz
PPMCM                  12.48630 ppm/cm
HZCM                1256.28149 Hz/cm
```

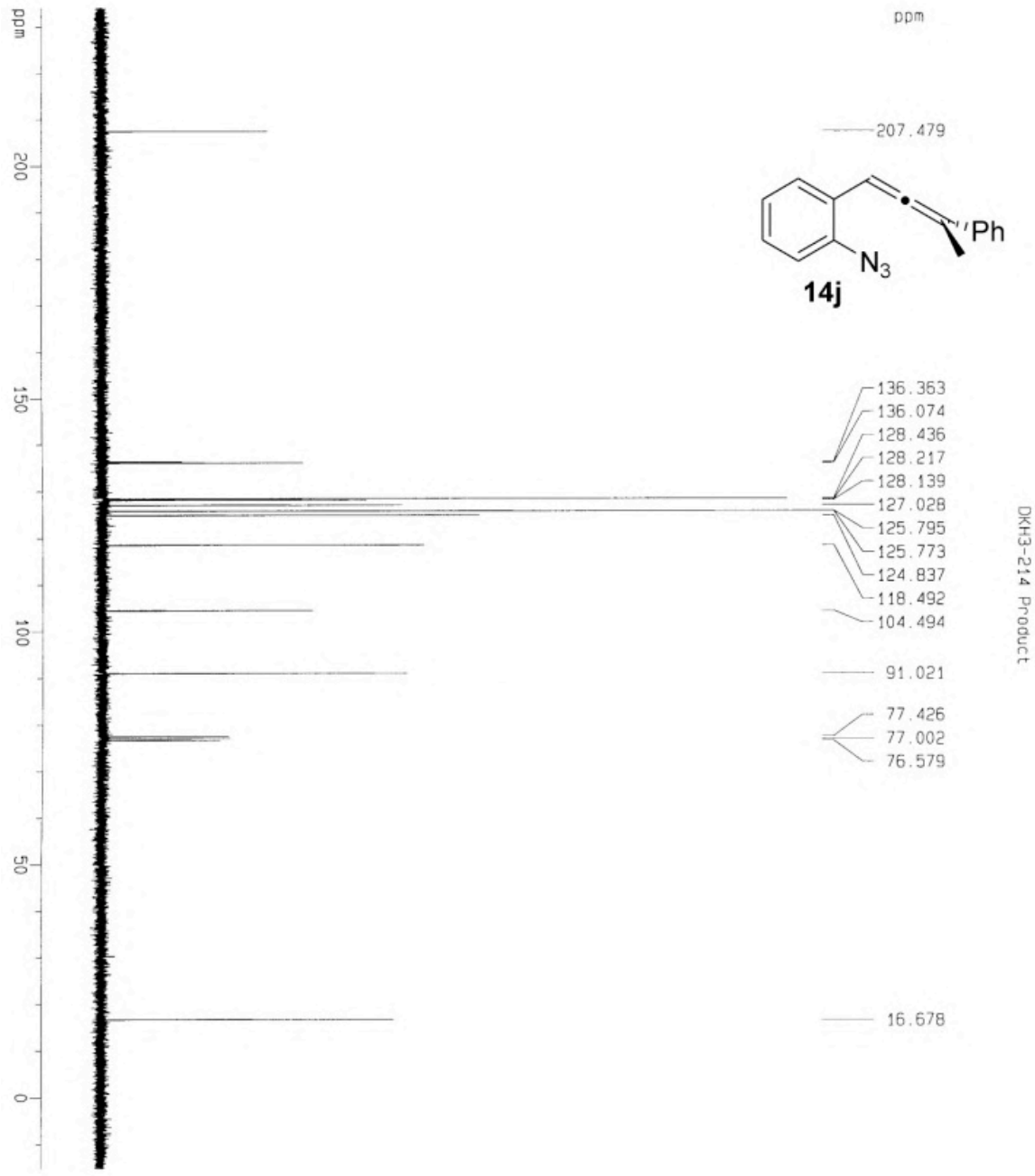
```
Current Data Parameters
NAME                  DKH3-214P
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20060927
Time               13.06
INSTRUM            spect
PROBHD     5 mm QNP 1H/1
PULPROG            zg30
TD                 65536
SOLVENT            CDCl3
NS                 16
DS                 2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                 101.6
DW                 81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1                 1.00000000 sec

======== CHANNEL f1 ========
NUC1               1H
P1                 11.70 usec
PL1                0.00 dB
SFO1               299.8718518 MHz

F2 - Processing parameters
SI                 32768
SF                 299.8700586 MHz
WDW                no
SSB                0
LB                 0.00 Hz
GB                 0
PC                 1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                10.000 ppm
F1                 2998.70 Hz
F2P                -1.000 ppm
F2                 -299.87 Hz
PPMCM              0.55000 ppm/cm
HZCM               164.92853 Hz/cm
```



Current Data Parameters
NAME DKH3-214P
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060927
Time 13.11
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 142
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433076 sec
RG 3251
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec

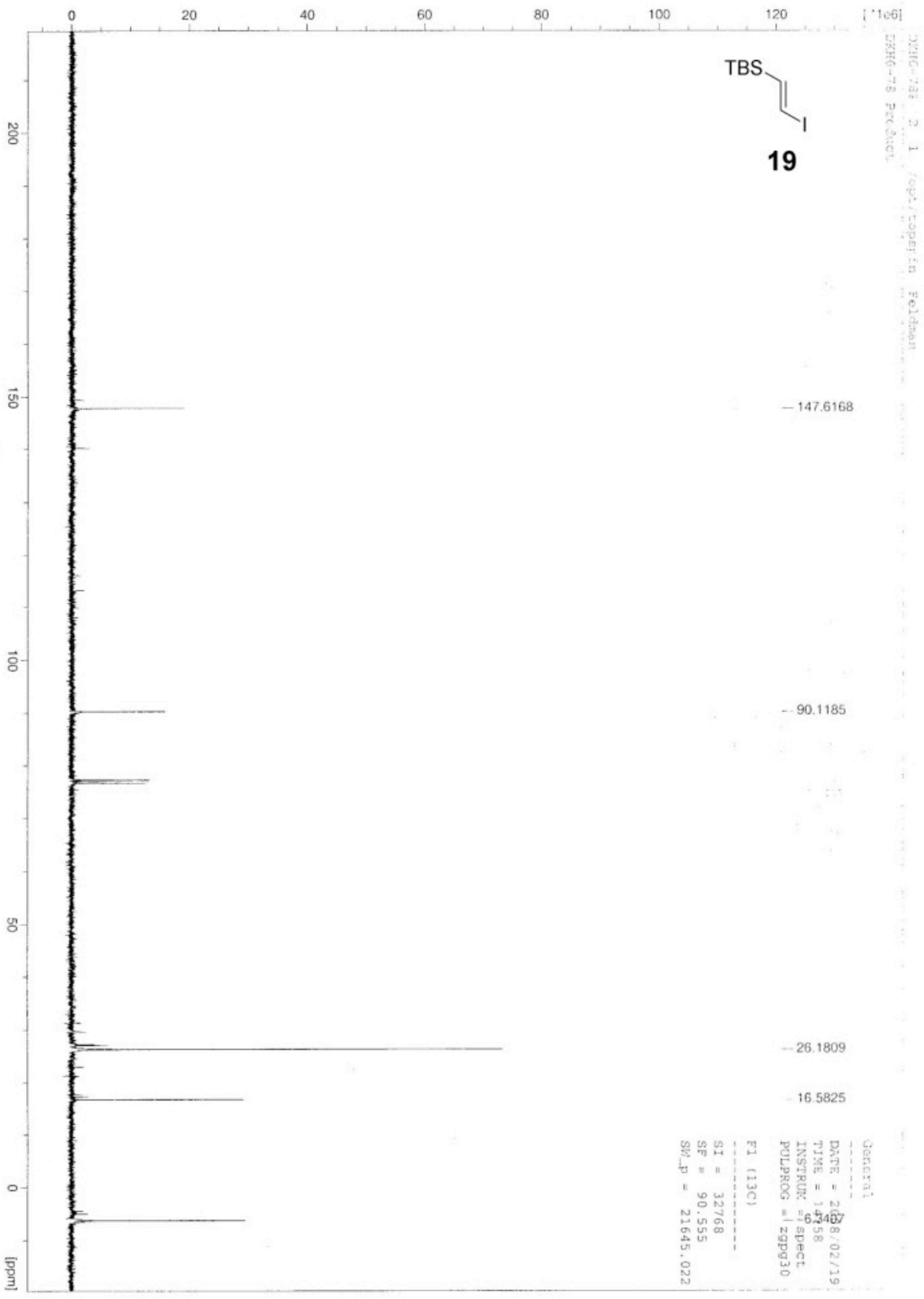
======== CHANNEL f1 ========
NUC1 13C
P1 5.40 usec
PL1 -6.00 dB
SFO1 75.4106357 MHz

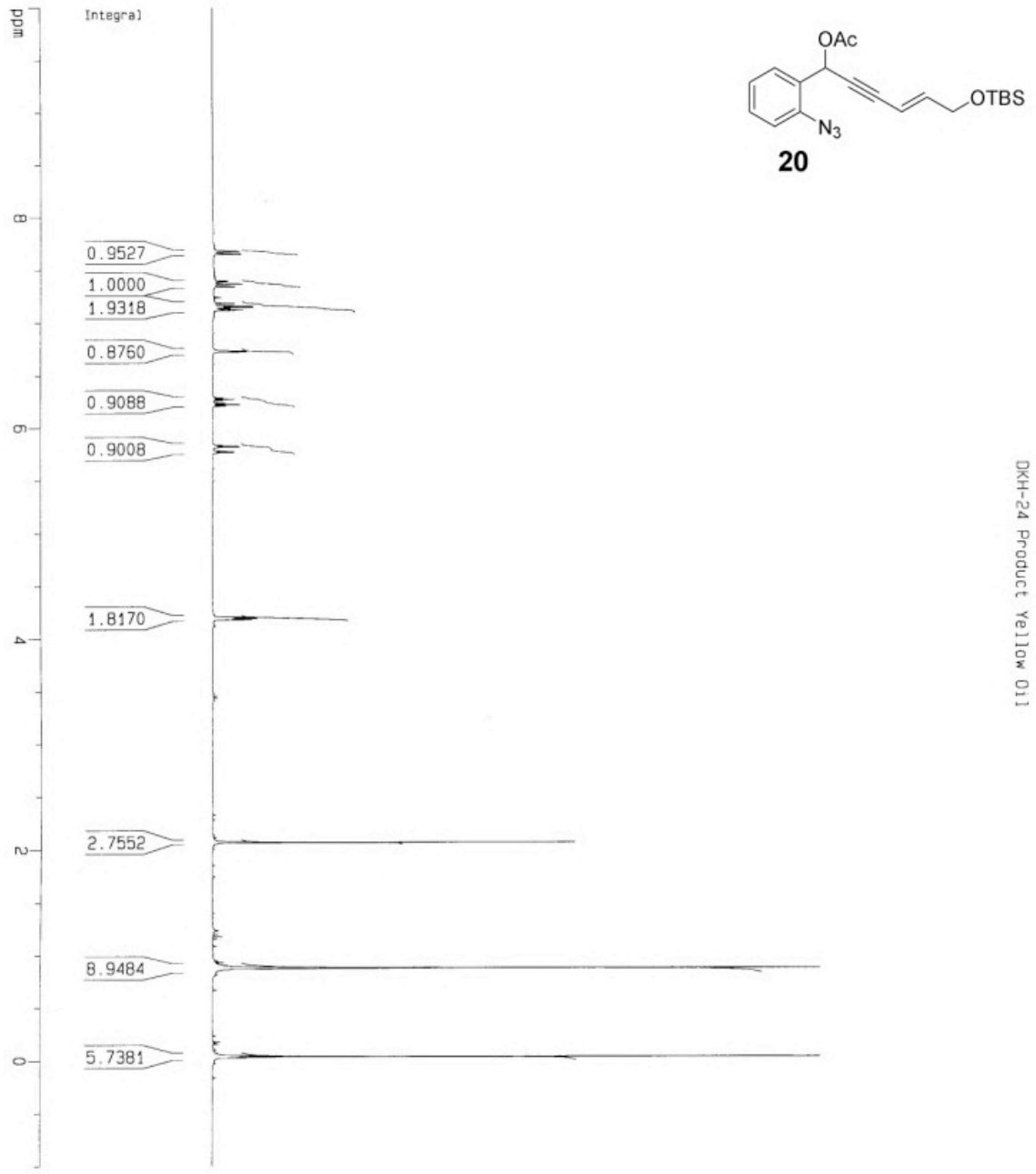
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 299.8711995 MHz

F2 - Processing parameters
SI 32768
SF 75.4023815 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 234.114 ppm
F1 17652.77 Hz
F2P -15.175 ppm
F2 -1144.22 Hz
PPMCM 12.46446 ppm/cm
HZCM 939.84961 Hz/cm

DKH6-78 Product
TBS
19
7.061
7.016
6.684
6.639
0.97
1.00
9.75
6.12
0.864
0.022
ppm
Current Data Parameters
NAME DKH6-78P
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080219
Time_ 14.55
INSTRUM spect
PROBHD 5 mm QNP 1H/15
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 13
DS 2
SWH 7440.476 Hz
FIDRES 0.113533 Hz
AQ 4.4040694 sec
RG 35.9
DW 67.200 usec
DE 6.00 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.93 usec
PL1 -3.00 dB
SFO1 360.1322240 MHz
F2 - Processing parameters
SI 32768
SF 360.1300213 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


TBS
I
19
147.6168
90.1185
26.1809
16.5825
[ppm]

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Current Data Parameters
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EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20070710
Time               16.34
INSTRUM            spect
PROBHD     5 mm QNP 1H/1
PULPROG            zg30
TD                 65536
SOLVENT            CDCl3
NS                 16
DS                 2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                 50.8
DW                 81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1                 1.00000000 sec

======== CHANNEL f1 ========
NUC1               1H
P1                 11.70 usec
PL1                0.00 dB
SFO1               299.8718518 MHz

F2 - Processing parameters
SI                 32768
SF                 299.8700159 MHz
WDW                no
SSB                0
LB                 0.00 Hz
GB                 0
PC                 1.00

1D NMR plot parameters
CX                 20.00 cm
F1P                10.000 ppm
F1                 2998.70 Hz
F2P                -1.000 ppm
F2                 -299.87 Hz
PPMCM              0.55600 ppm/cm
HZCM               164.92851 Hz/cm
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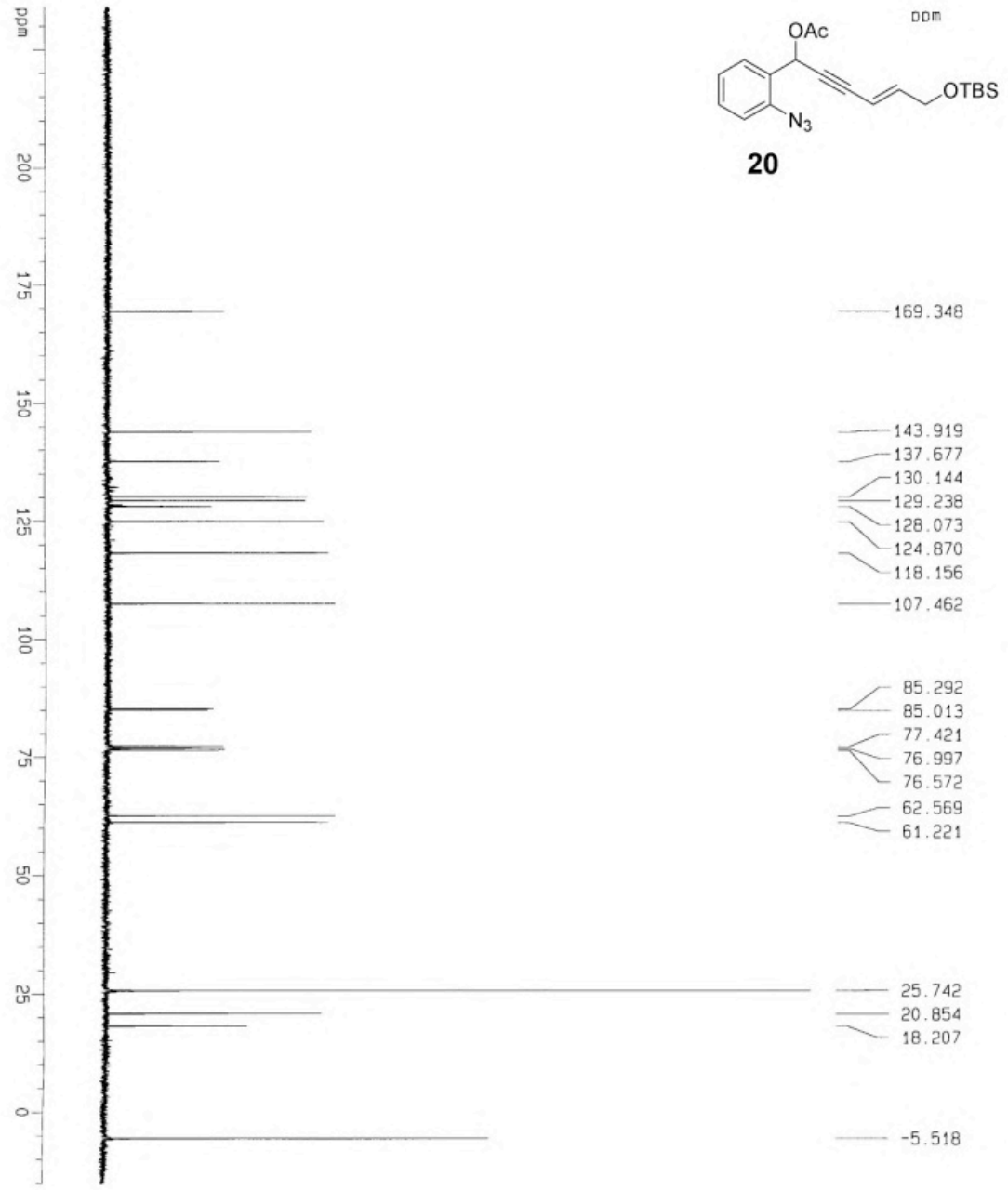


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Current Data Parameters
NAME                  DKH5-24P
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_              20070710
Time                   16.40
INSTRUM                spect
PROBHD     5 mm QNP 1H/1
PULPROG                zgpg30
TD                     65536
SOLVENT                CDCl3
NS                        76
DS                         4
SWH               18796.992 Hz
FIDRES             0.286819 Hz
AQ                 1.7433076 sec
RG                      4096
DW                    26.600 usec
DE                     6.00 usec
TE                    300.0 K
D1                 2.00000000 sec
D11                0.03000000 sec
D12                0.00002000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                       5.40 usec
PL1                     -6.00 dB
SFO1              75.4106357 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 115.00 usec
PL2                     0.00 dB
PL12                   20.00 dB
PL13                   20.00 dB
SFO2              299.8711995 MHz

F2 - Processing parameters
SI                        32768
SF                75.4023820 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40

1D NMR plot parameters
CX                        20.00 cm
F1P                      234.107 ppm
F1                     17652.20 Hz
F2P                     -15.182 ppm
F2                   -1144.79 Hz
PPMCM                  12.46445 ppm/cm
HZCM                 939.84949 Hz/cm
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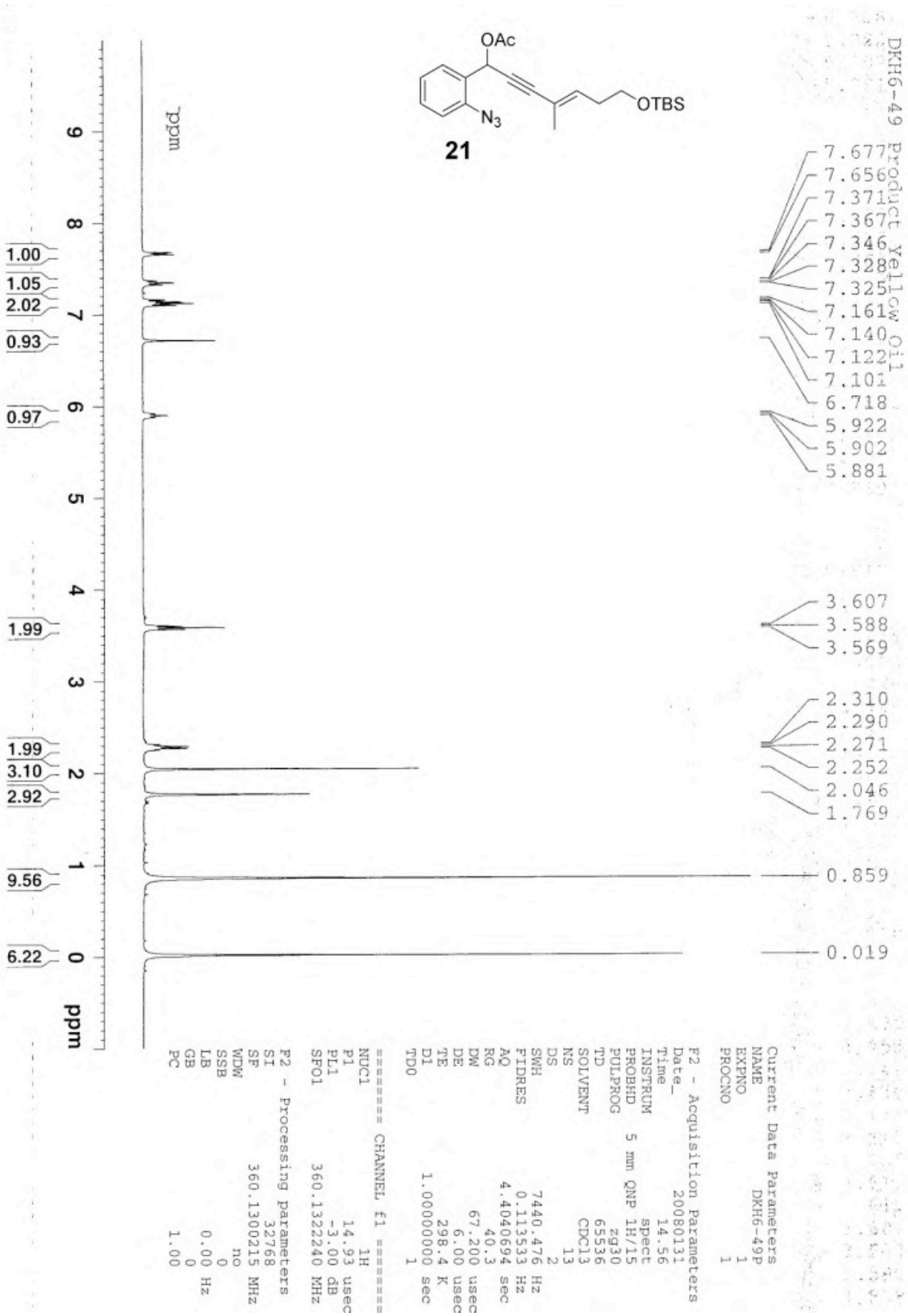
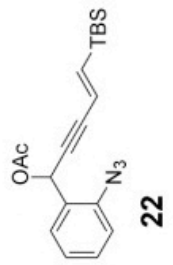
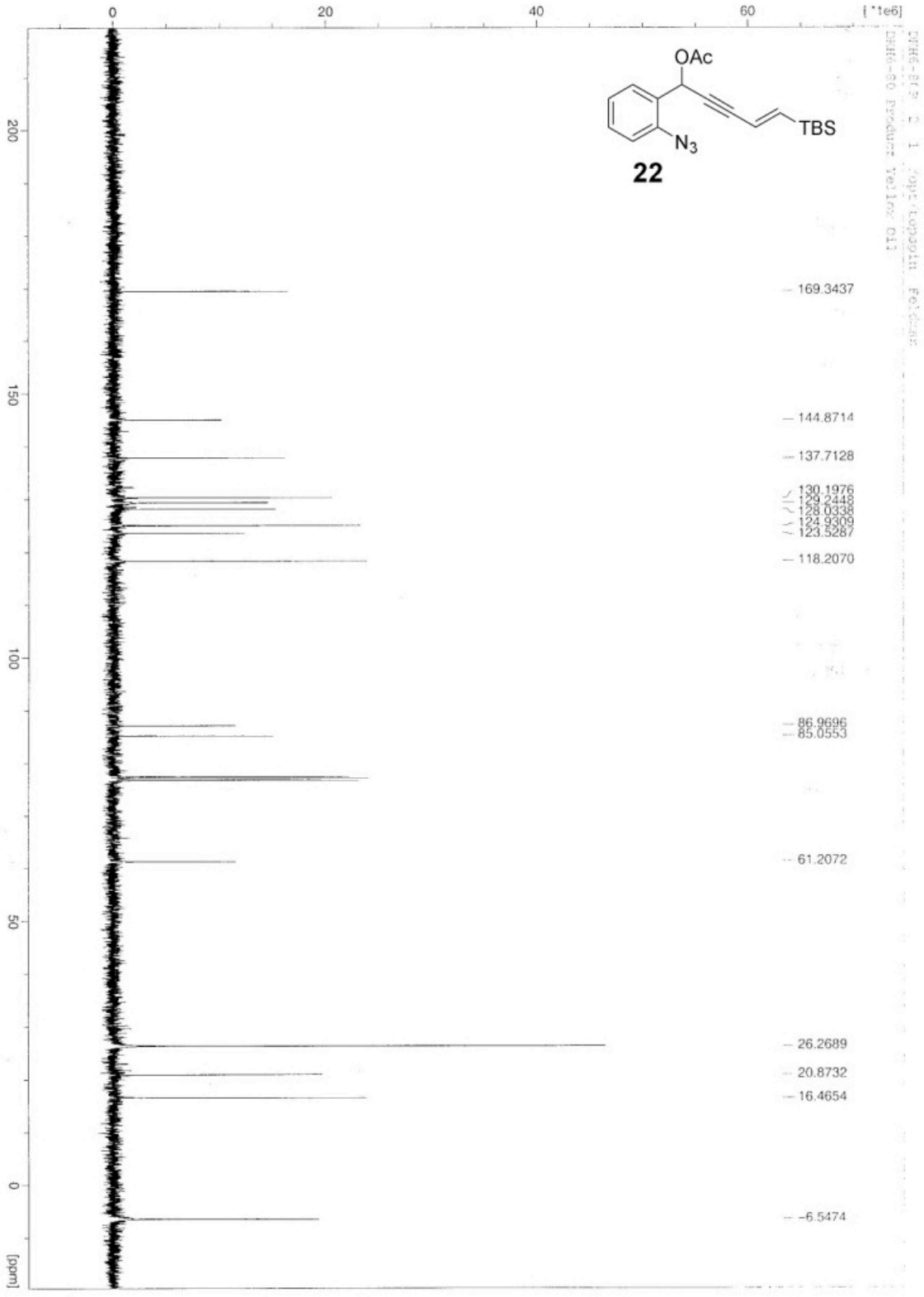

DKH6-49 Product Yellow Oil
OAc
OTBS
N3
21
7.677
7.656
7.371
7.367
7.346
7.328
7.325
7.161
7.140
7.122
7.101
6.718
5.922
5.902
5.881
3.607
3.588
3.569
2.310
2.290
2.271
2.252
2.046
1.769
0.859
0.019
1.00
1.05
2.02
0.93
0.97
1.99
1.99
3.10
2.92
9.56
6.22
ppm
Current Data Parameters
NAME DKH6-49p
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080131
Time 14.56
INSTRUM spect
PROBHD 5 mm QNP 1H/15
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 13
DS 2
SWH 7440.476 Hz
FIDRES 0.113533 Hz
AQ 4.4040694 sec
RG 40.3
DW 67.200 usec
DE 6.00 usec
TE 298.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.93 usec
PL1 -3.00 dB
SFO1 360.1322240 MHz
F2 - Processing parameters
SI 32768
SF 360.1300215 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

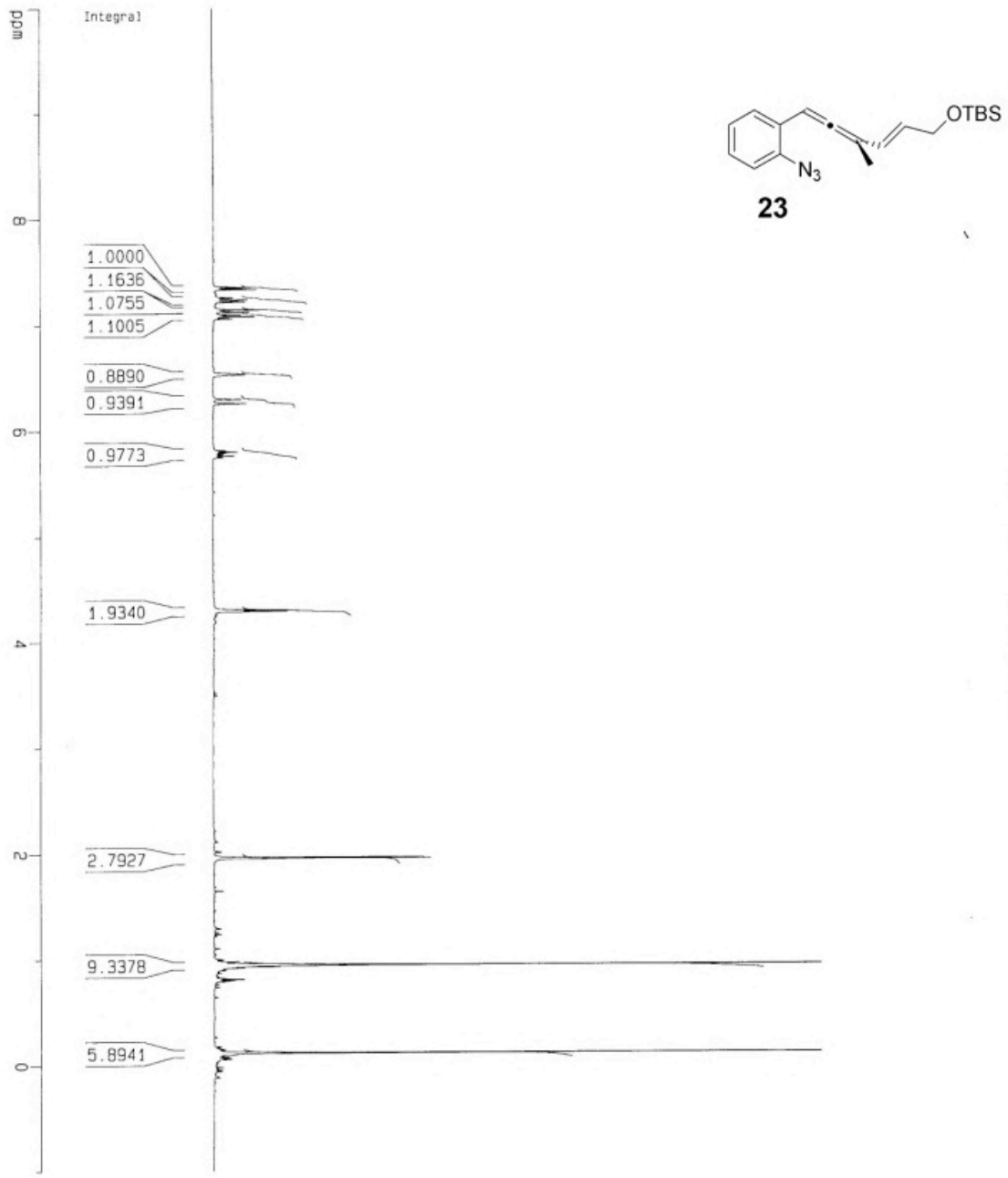
DKH6-49 Product Yellow Oil
OAc
OTBS
N3
21
BRUKER
Current Data Parameters
NAME DKH6-49P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080131
Time 15.02
INSTRUM spect
PROBHD 5 mm QNP 1H/15
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 89
DS 4
SWH 21645.021 Hz
FIDRES 0.330277 Hz
AQ 1.5139316 sec
RG 14596.5
DW 23.100 usec
DE 6.00 usec
TE 298.9 K
D1 2.00000000 sec
D11 0.03000000 sec
DELTA 1.69999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.68 usec
PL1 -3.00 dB
SFO1 90.5638160 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 -1.00 dB
PL12 20.74 dB
PL13 20.10 dB
SFO2 360.1314403 MHz
F2 - Processing parameters
SI 32768
SF 90.5647757 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200 180 160 140 120 100 80 60 40 20 0 ppm

DKH6-80 Product Yellow Oil



22


OAc
TBS
N3
22
169.3437
144.8714
137.7128
130.1976
129.2448
128.0338
124.9309
123.5287
118.2070
86.9696
85.0553
61.2072
26.2689
20.8732
16.4654
-6.5474
[ppm]

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Current Data Parameters
NAME                  DKH5-28P
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_              20070713
Time                    15.00
INSTRUM                 spect
PROBHD   5 mm BBI 1H-B
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                 8278.146 Hz
FIDRES              0.126314 Hz
AQ                  3.958243 sec
RG                        45.3
DW                      60.400 usec
DE                       6.00 usec
TE                     300.0 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       6.45 usec
PL1                      0.00 dB
SF01           400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                400.1300075 MHz
WDW                          no
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
F1P                     10.000 ppm
F1                    4001.30 Hz
F2P                     -1.000 ppm
F2                     -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 220.07150 Hz/cm
```
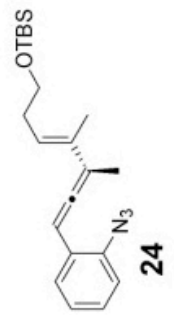
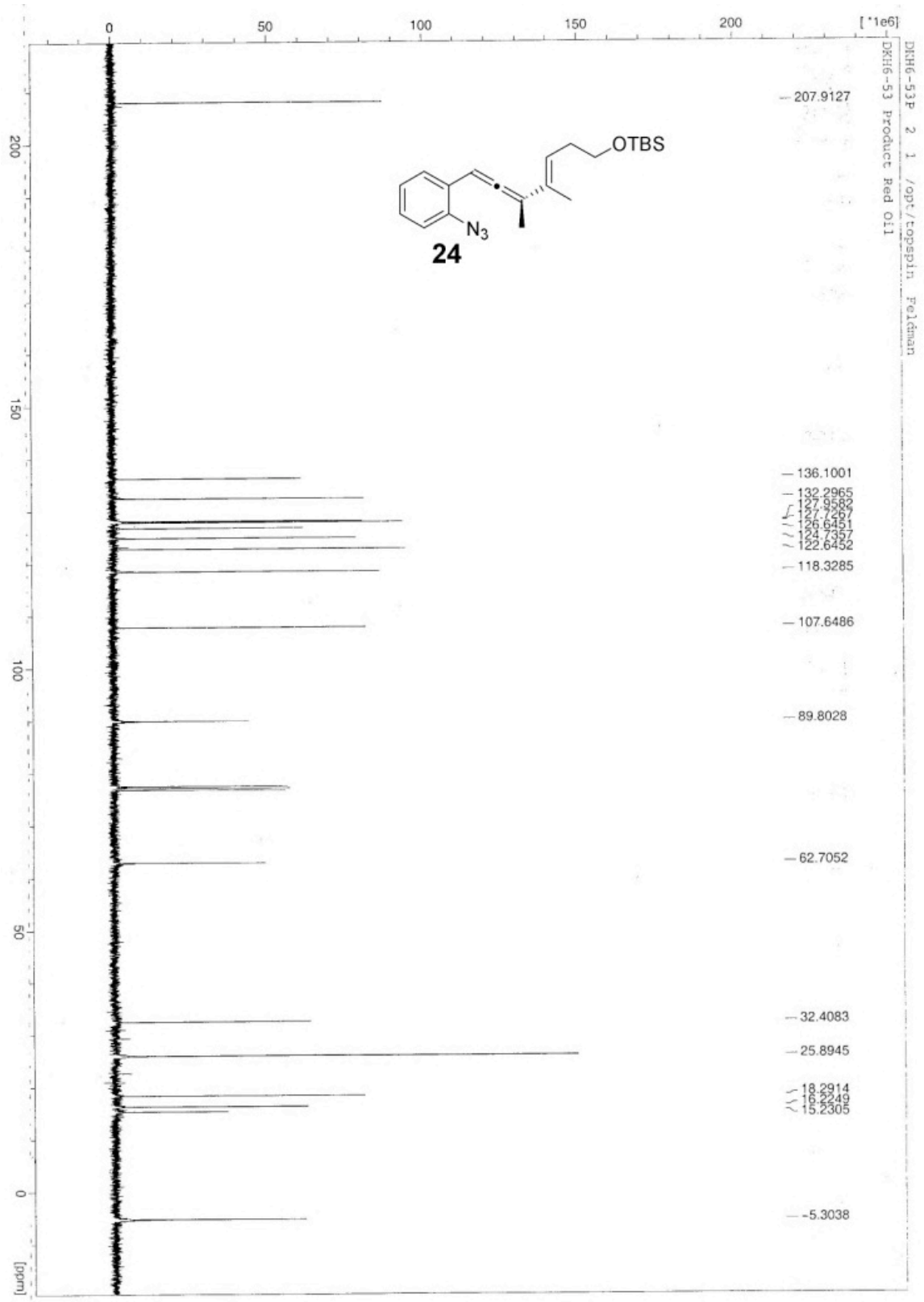

OTBS
N3
23
ppm
209.720
136.291
128.932
128.396
127.959
127.339
126.041
124.752
118.351
103.324
88.570
77.316
77.000
76.681
63.880
25.949
18.409
15.286
-5.193
DKH5-28 Product
Current Data Parameters
NAME DKH5-28P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070713
Time 15.06
INSTRUM spect
PROBHD 5 mm BBI 1H-B
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 92
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 8192
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 16.35 usec
PL1 -6.00 dB
SF01 100.6237959 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 114.00 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SF02 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127769 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 234.382 ppm
F1 23581.82 Hz
F2P -15.344 ppm
F2 -1543.80 Hz
PPMCM 12.48630 ppm/cm
HZCM 1256.28137 Hz/cm

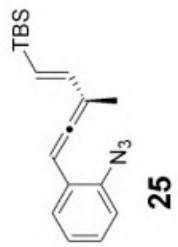
DKH6-53 Product Red Oil



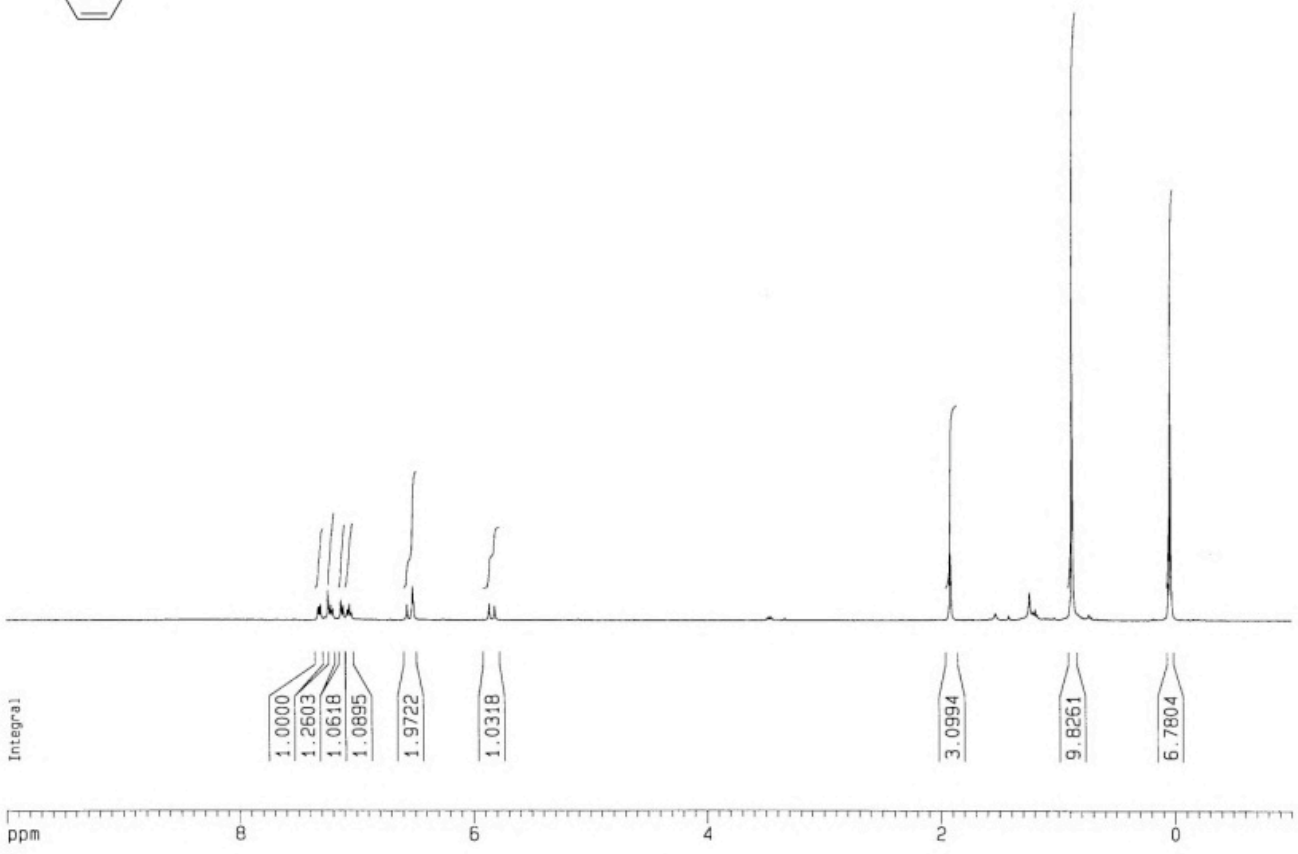
24


OTBS
N3
24
207.9127
136.1001
132.2965
127.9582
127.7225
127.2267
126.6451
124.7357
122.6452
118.3285
107.6486
89.8028
62.7052
32.4083
25.8945
18.2914
16.2249
15.2305
-5.3038
DKH6-53P 2 1 /opt/topspin Feldman
DKH6-53 Product Red Oil
[*1e6]
[ppm]

DKH6-82 Product colorless oil



25

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Current Data Parameters
NAME                  DKH6-82P
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20080221
Time                     10.31
INSTRUM                  spect
PROBHD     5 mm BBI 1H-B
PULPROG                  zg30
TD                      65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                 8278.146 Hz
FIDRES              0.126314 Hz
AQ                  3.9584243 sec
RG                     1149.4
DW                     60.400 usec
DE                      6.00 usec
TE                     300.0 K
D1                  1.00000000 sec

========== CHANNEL f1 =========
NUC1                         1H
P1                      6.45 usec
PL1                      0.00 dB
SFO1               400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF                 400.1300169 MHz
WDW                         no
SSB                          0
LB                      0.00 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                      20.00 cm
F1P                    10.000 ppm
F1                     4001.30 Hz
F2P                    -1.000 ppm
F2                     -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                220.07150 Hz/cm
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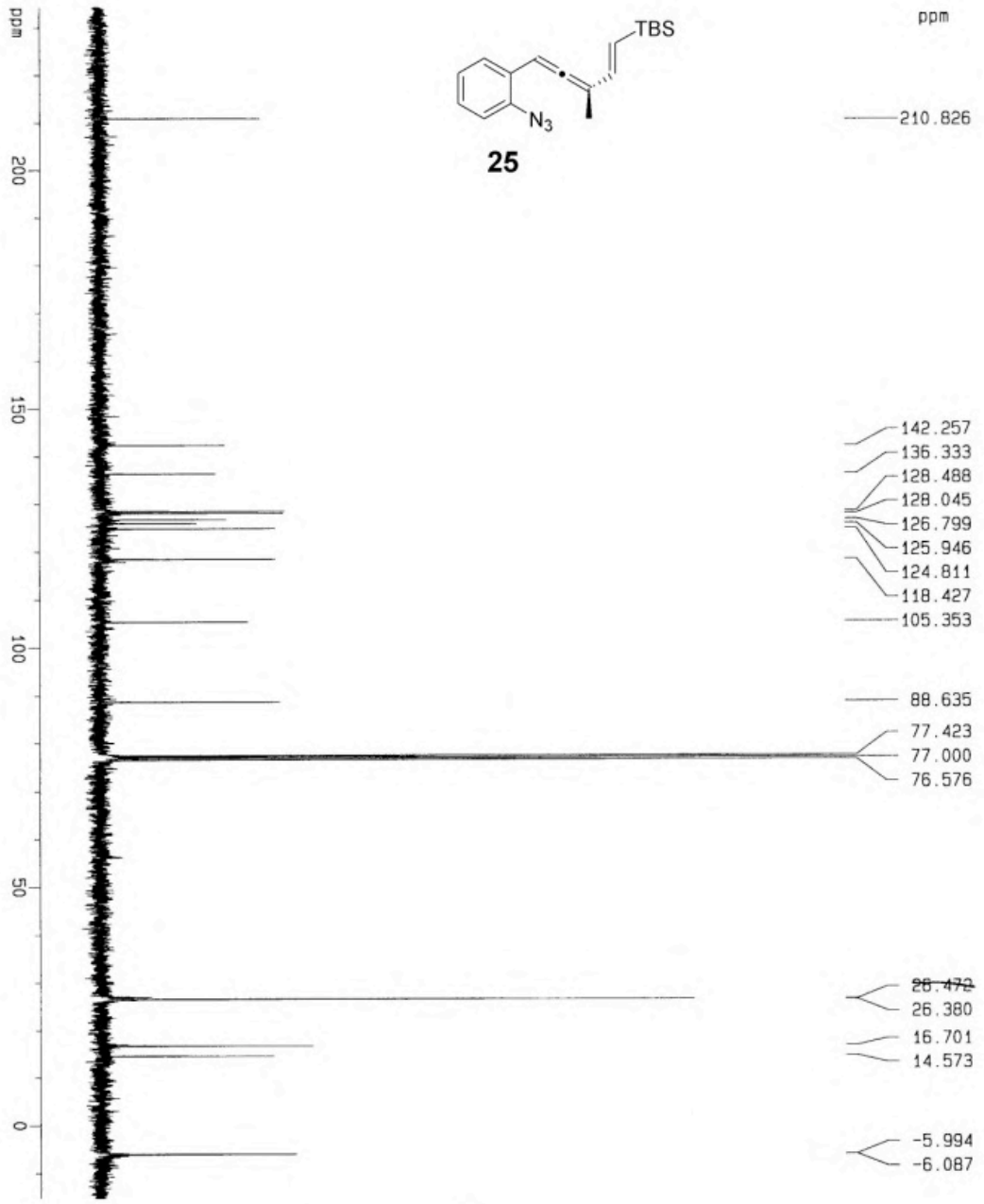


DKH6-85 Product Yellow Oil

Current Data Parameters
NAME DKH6-85P
EXPNO 2
PROCNO 1

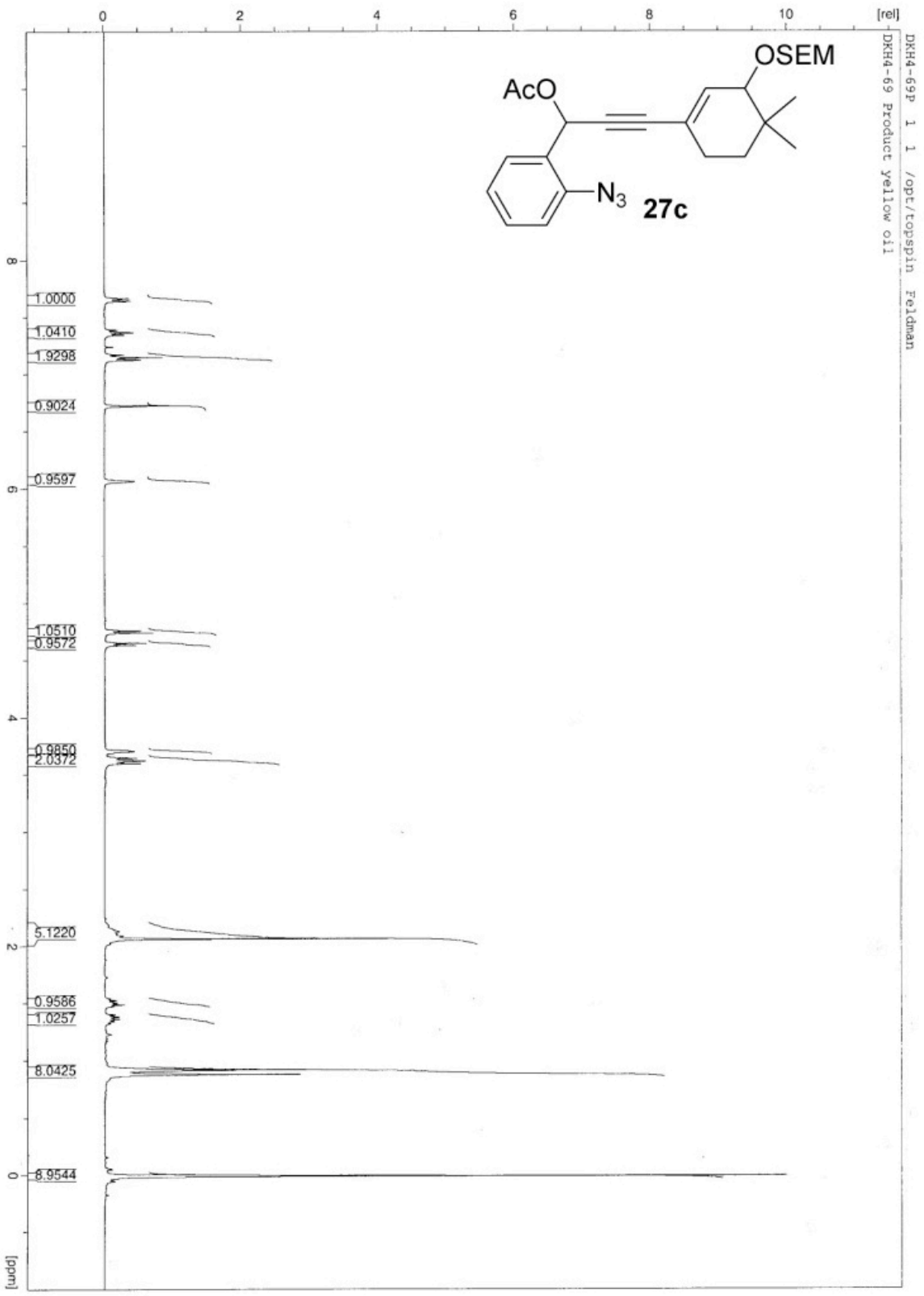
F2 - Acquisition Parameters
Date_ 20080223
Time 12.08
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 747
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 16384
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec

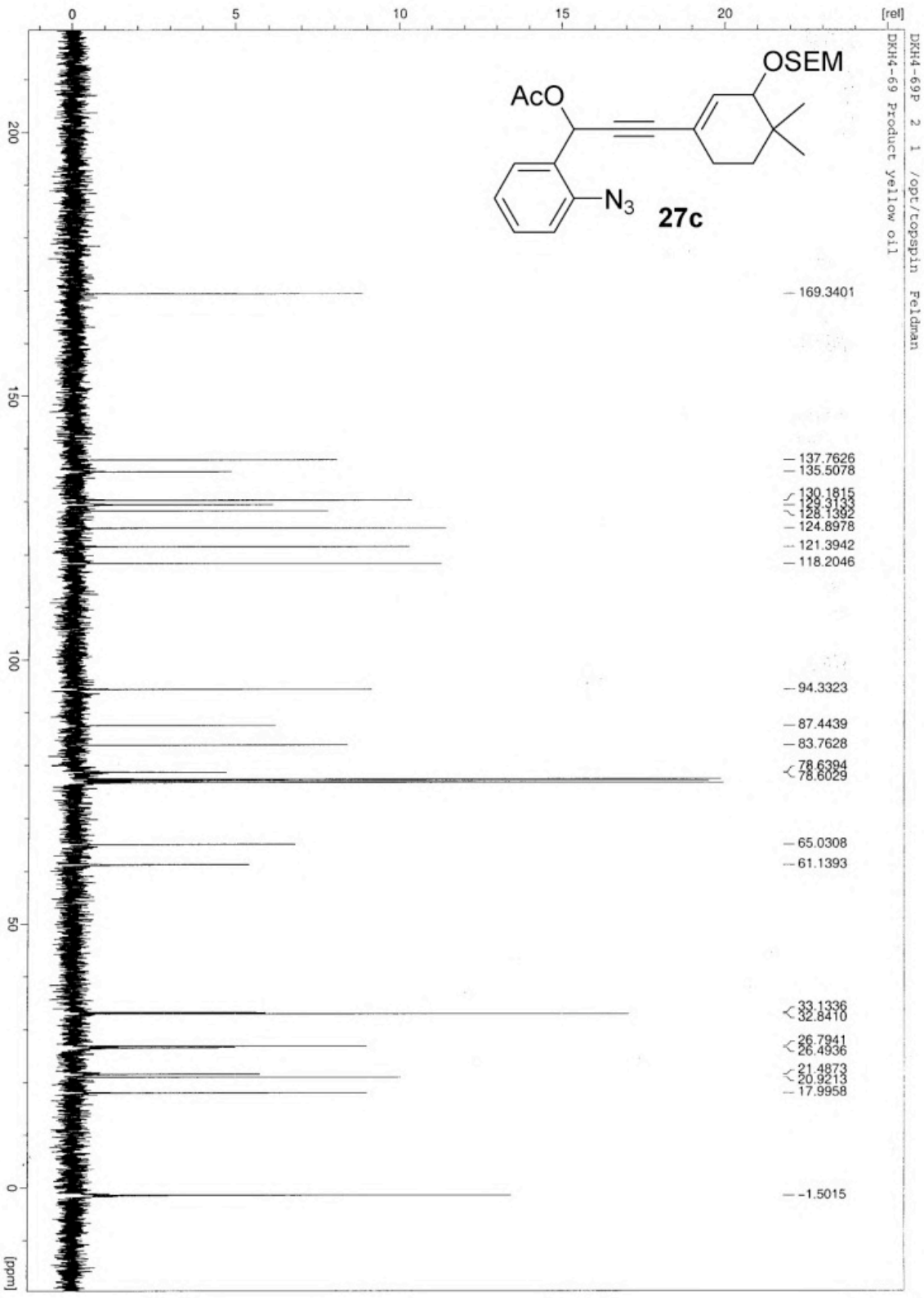
======== CHANNEL f1 ========
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz

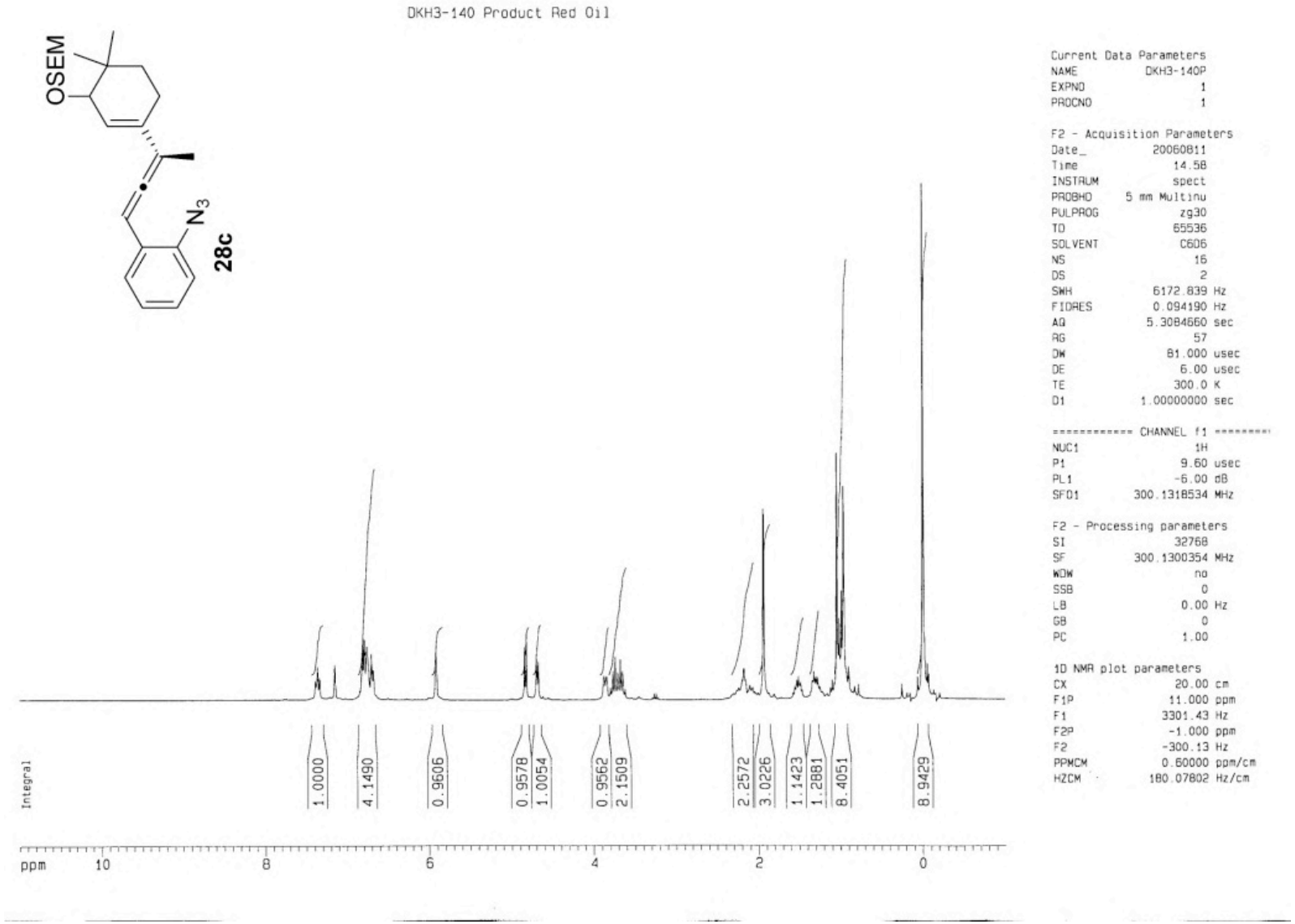
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz

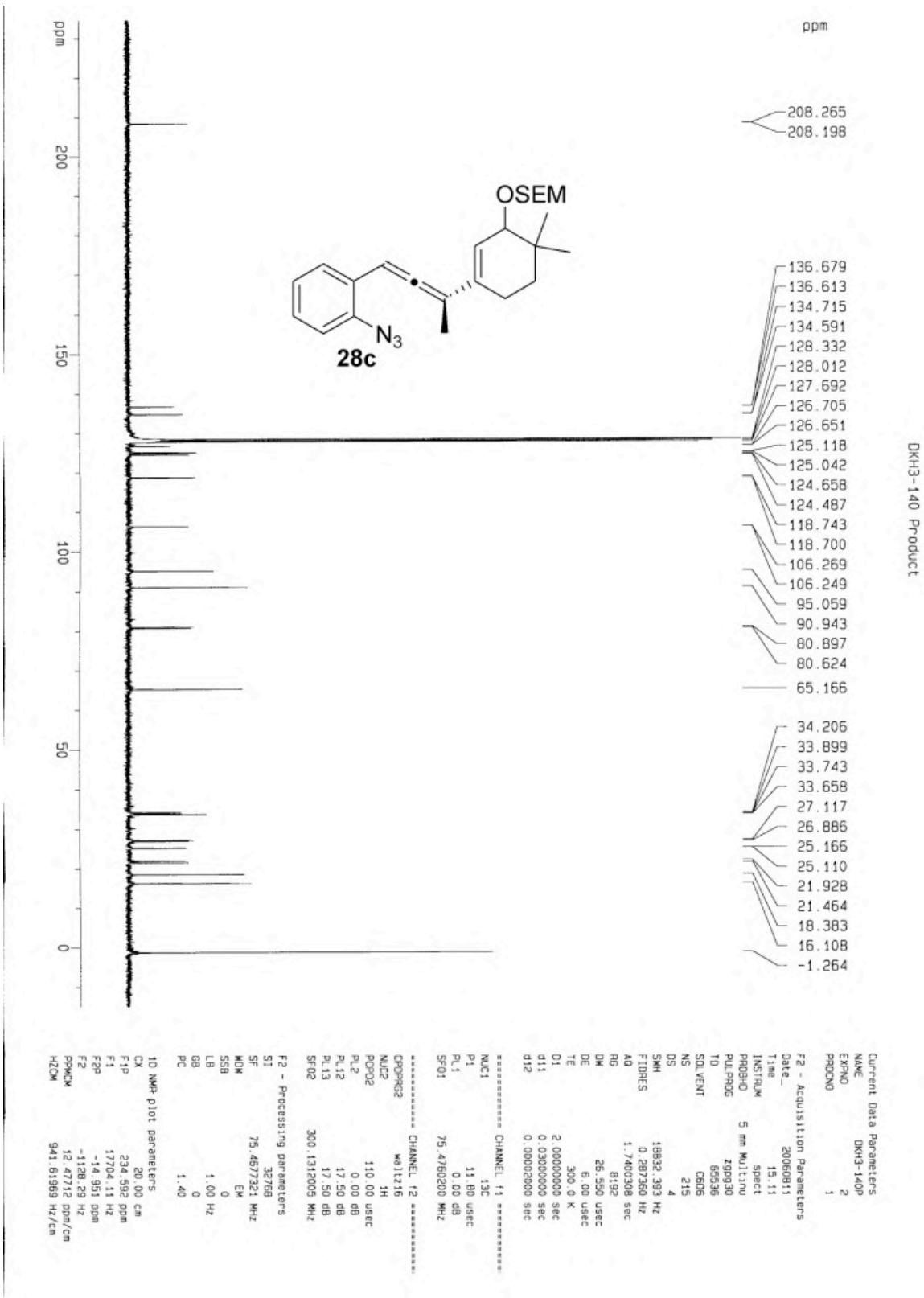
F2 - Processing parameters
SI 32768
SF 75.4677514 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

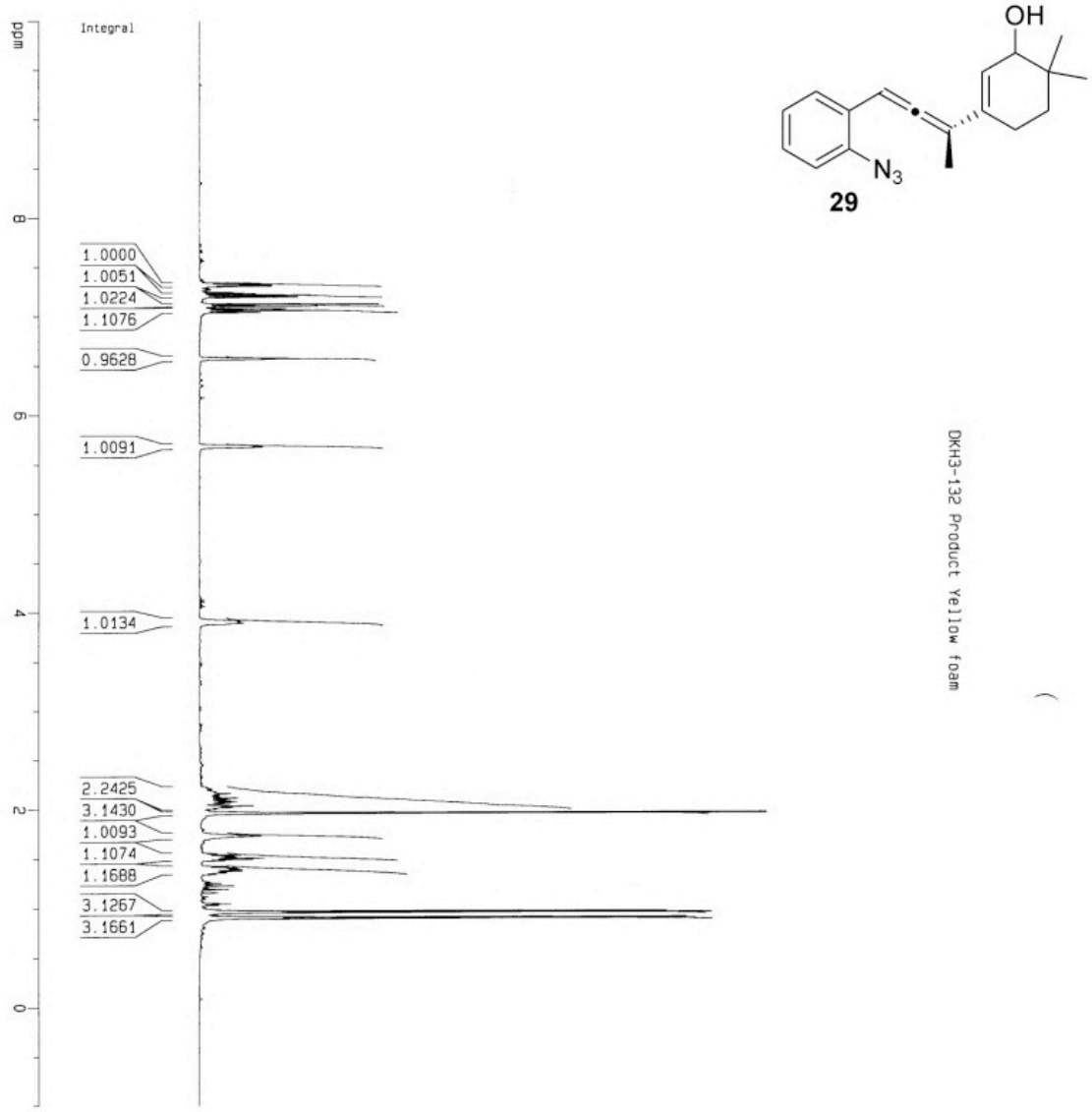
1D NMR plot parameters
CX 20.00 cm
F1P 234.335 ppm
F1 17684.71 Hz
F2P -15.208 ppm
F2 -1147.68 Hz
PPMCM 12.47711 ppm/cm
HZCM 941.61969 Hz/cm


OSEM
AcO
N3
27c
DKH4-69P 1 1 /opt/topspin Feldman
DKH4-69 Product yellow oil
1.0000
1.0410
1.9298
0.9024
0.9597
1.0510
0.9572
0.9850
2.0372
5.1220
0.9586
1.0257
8.0425
8.9544
[rel]
[ppm]

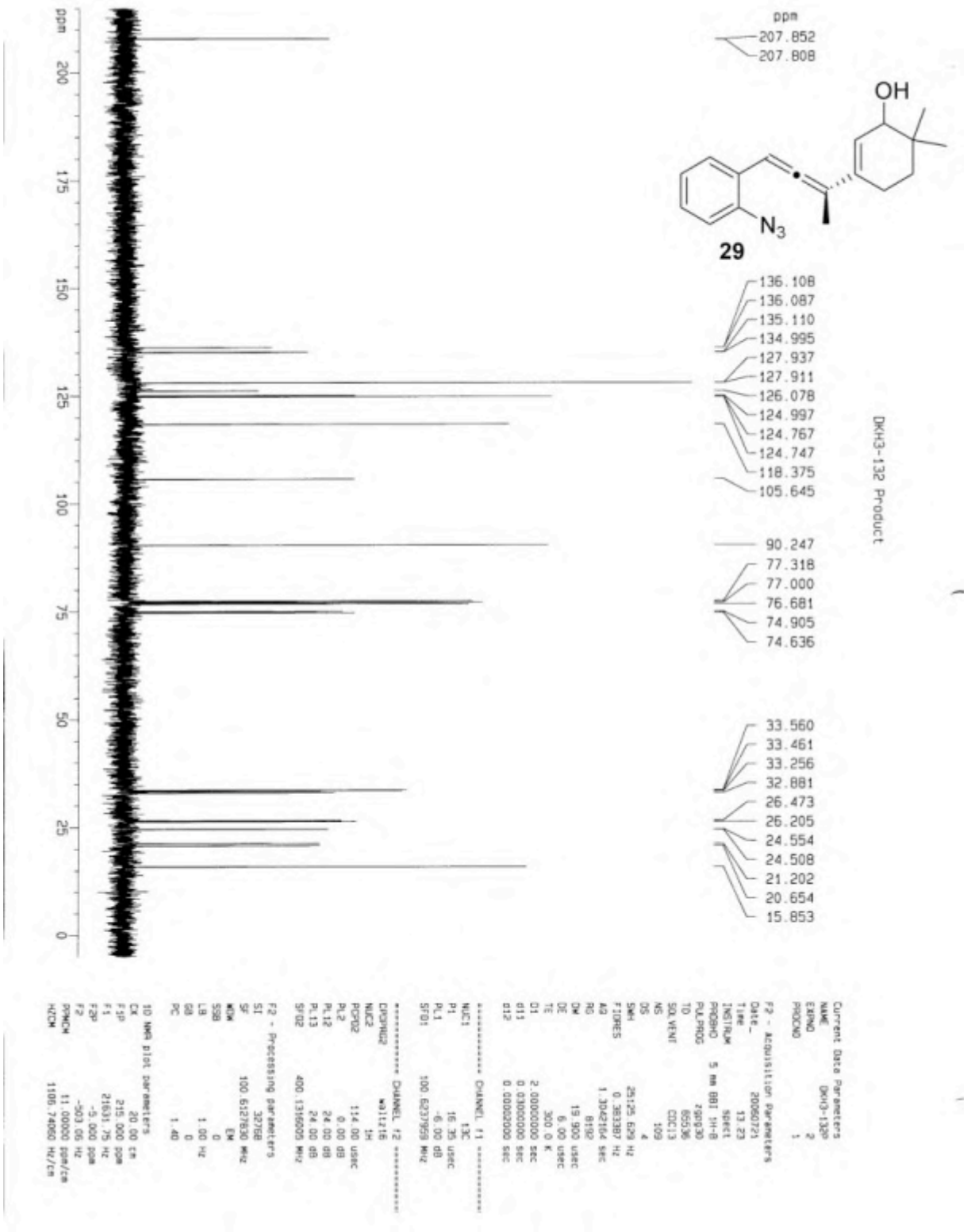

OSEM
AcO
N3
27c
169.3401
137.7626
135.5078
130.1815
129.3133
128.1392
124.8978
121.3942
118.2046
94.3323
87.4439
83.7628
78.6394
78.6029
65.0308
61.1393
33.1336
32.8410
26.7941
26.4936
21.4873
20.9213
17.9958
-1.5015
DKH4-69P 2 1 /opt/topspin Feldman
DKH4-69 Product yellow oil
[rel]
[ppm]

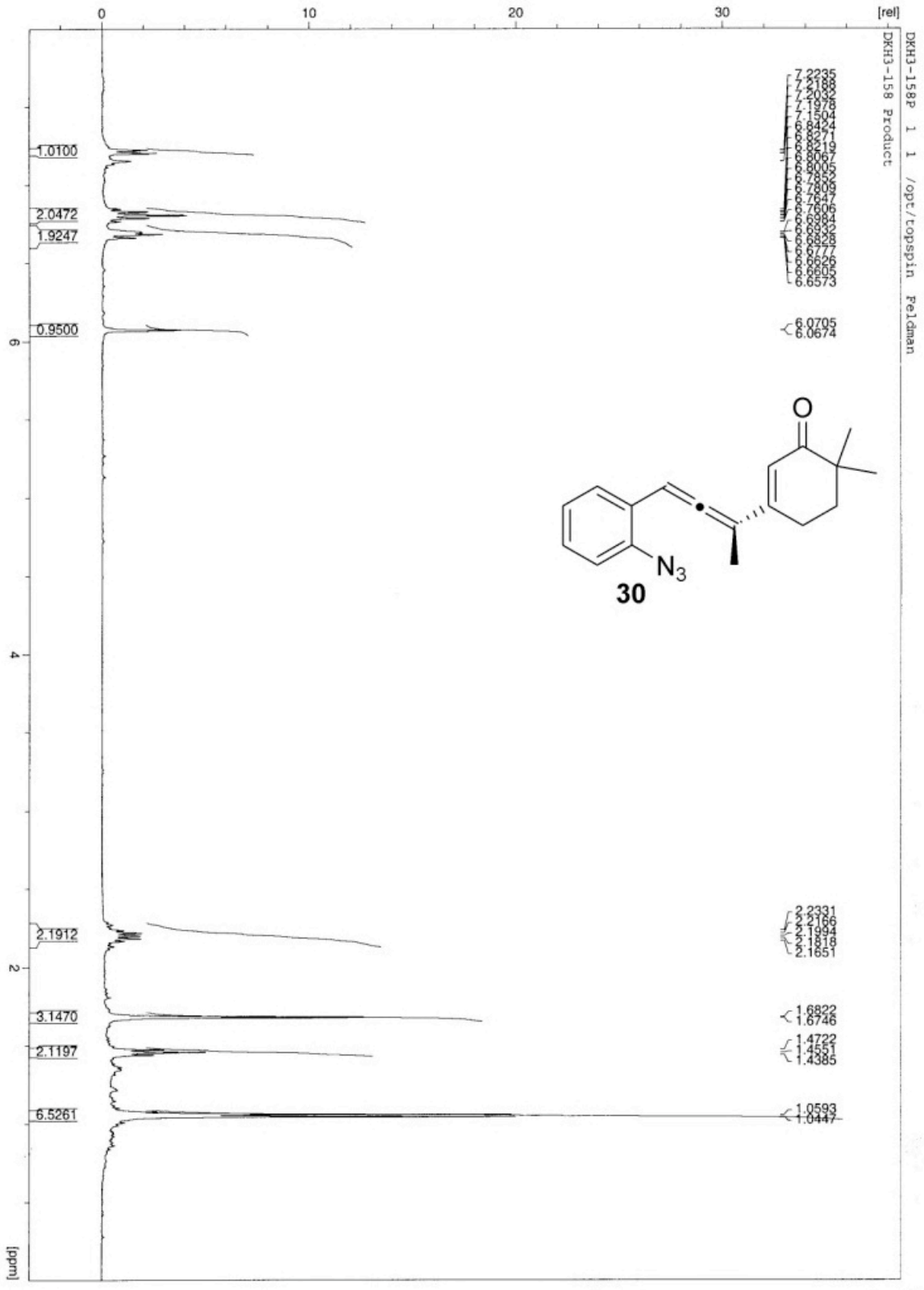

DKH3-140 Product Red Oil
OSEM
N3
28c
Integral
1.0000
4.1490
0.9606
0.9578
1.0054
0.9562
2.1509
2.2572
3.0226
1.1423
1.2881
8.4051
8.9429
ppm
10
8
6
4
2
0
Current Data Parameters
NAME DKH3-140P
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060811
Time 14.58
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg30
TD 65536
SOLVENT C606
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 57
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
========== CHANNEL f1 ========
NUC1 1H
P1 9.60 usec
PL1 -6.00 dB
SFO1 300.1318534 MHz
F2 - Processing parameters
SI 32768
SF 300.1300354 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 3301.43 Hz
F2P -1.000 ppm
F2 -300.13 Hz
PPMCM 0.60000 ppm/cm
HZCM 180.07802 Hz/cm

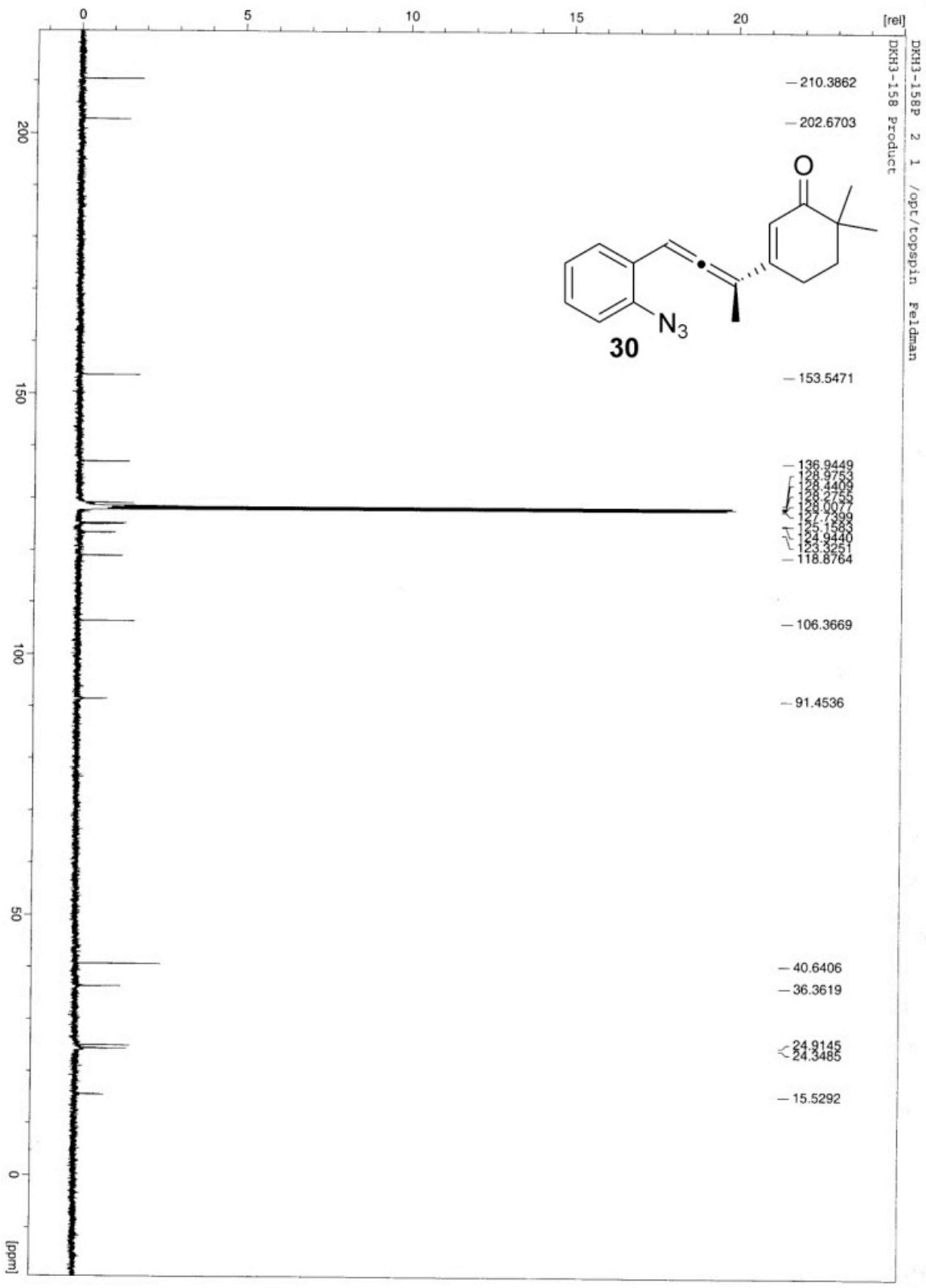

ppm
208.265
208.198
OSEM
136.679
136.613
134.715
134.591
128.332
128.012
127.692
126.705
126.651
125.118
125.042
124.658
124.487
118.743
118.700
106.269
106.249
95.059
90.943
80.897
80.624
65.166
34.206
33.899
33.743
33.658
27.117
26.886
25.166
25.110
21.928
21.464
18.383
16.108
-1.264
N3
28c
ppm
200
150
100
50
0
DKH3-140 Product
Current Data Parameters
NAME DKH3-140P
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060811
Time 15.11
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 215
DS 4
SWH 18832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7400308 sec
RG 8192
DW 26.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 11.80 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677321 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 234.592 ppm
F1 17704.11 Hz
F2P -14.951 ppm
F2 -1128.29 Hz
PPMCM 12.47712 ppm/cm
HZCM 941.61969 Hz/cm

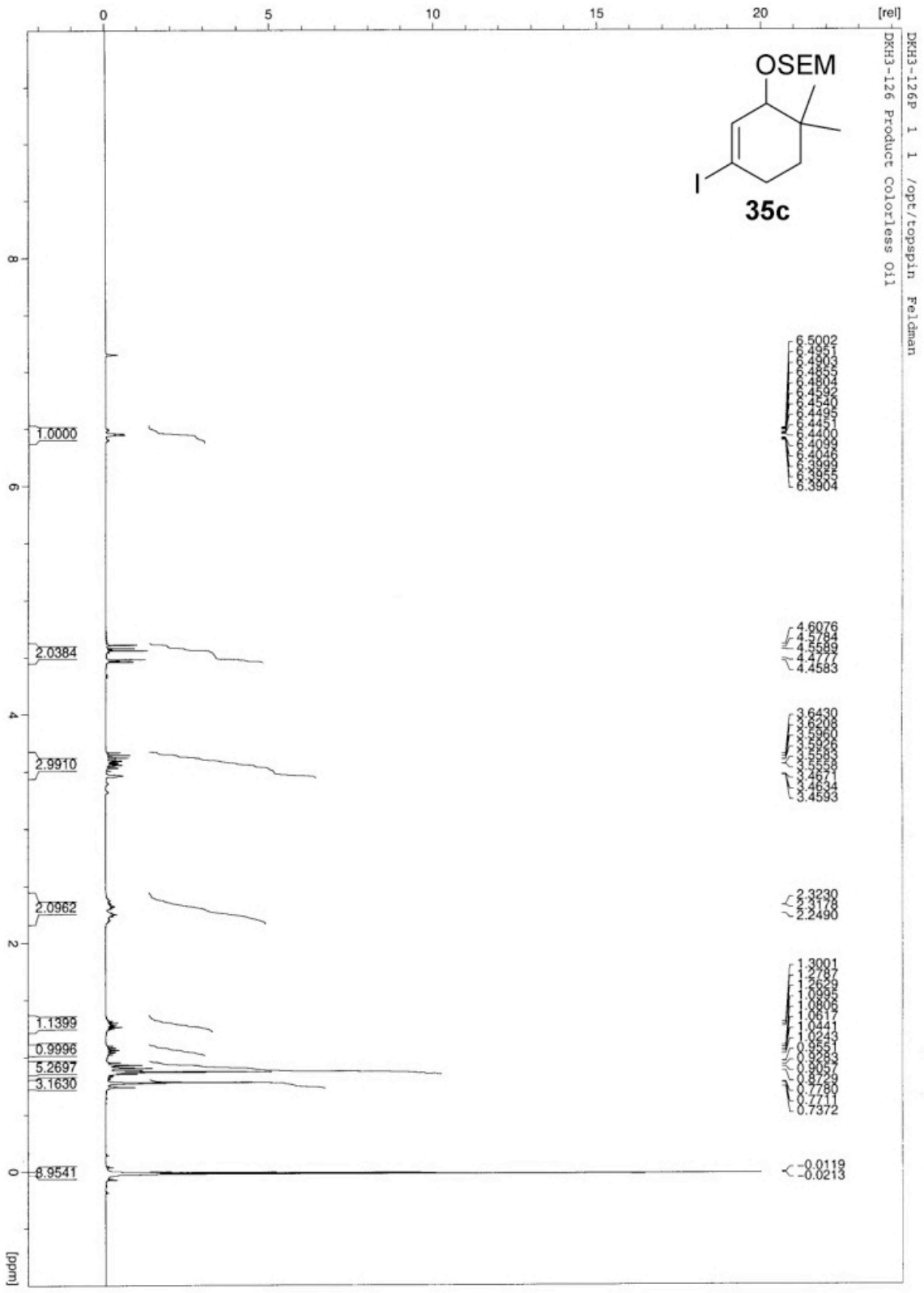


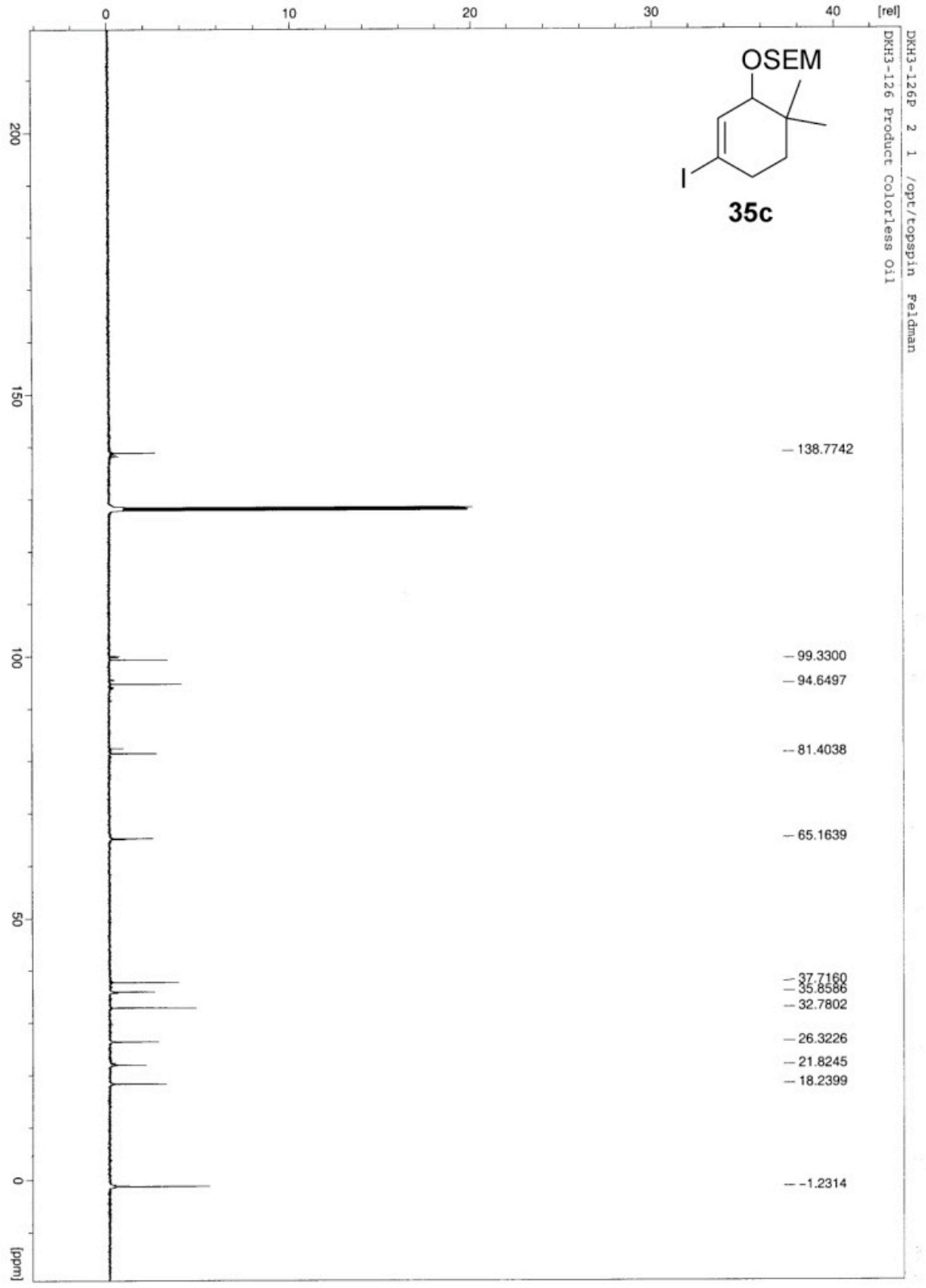

```
Current Data Parameters
NAME                  DKH3-132P
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20060721
Time                   13.15
INSTRUM                spect
PROBHD     5 mm BBI 1H-B
PULPROG                zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                827B.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                        32
DW                 60.400 usec
DE                  6.00 usec
TE                  300.0 K
D1                 1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                       6.45 usec
PL1                      0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF             400.1300169 MHz
WDW                          no
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                     10.000 ppm
F1                    4001.30 Hz
F2P                    -1.000 ppm
F2                    -400.13 Hz
PPMCM                  0.55000 ppm/cm
HZCM                220.07150 Hz/cm
```


ppm
207.852
207.808
OH
N3
29
136.108
136.087
135.110
134.995
127.937
127.911
126.078
124.997
124.767
124.747
118.375
105.645
90.247
77.318
77.000
76.681
74.905
74.636
33.560
33.461
33.256
32.881
26.473
26.205
24.554
24.508
21.202
20.654
15.853
DKH3-132 Product
ppm
200
175
150
125
100
75
50
25
0

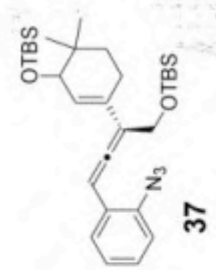

DKH3-158P 1 1 /opt/topspin Feldman
DKH3-158 Product
[rel]
[ppm]
1.0100
2.0472
1.9247
0.9500
2.1912
3.1470
2.1197
6.5261
7.2235
7.2188
7.2032
7.1978
7.1504
6.8424
6.8271
6.8219
6.8067
6.8005
6.7852
6.7809
6.7647
6.7606
6.6984
6.6932
6.6828
6.6777
6.6626
6.6605
6.6573
6.0705
6.0674
2.2331
2.2166
2.1994
2.1818
2.1651
1.6822
1.6746
1.4722
1.4551
1.4385
1.0593
1.0447
O
N3
30


DKH3-158P 2 1 /opt/topspin Feldman
DKH3-158 Product
[rel]
[ppm]
210.3862
202.6703
153.5471
136.9449
128.9753
128.4409
128.2755
128.0077
127.7399
125.1583
124.9440
123.3251
118.8764
106.3669
91.4536
40.6406
36.3619
24.9145
24.3485
15.5292
30


OSEM
I
35c
DKH3-126P 1 1 /opt/topspin Feldman
DKH3-126 Product Colorless Oil
[rel]
[ppm]
1.0000
2.0384
2.9910
2.0962
1.1399
0.9996
5.2697
3.1630
8.9541
6.5002
6.4951
6.4903
6.4855
6.4804
6.4592
6.4540
6.4495
6.4451
6.4400
6.4099
6.4046
6.3999
6.3955
6.3904
4.6076
4.5784
4.5589
4.4777
4.4583
3.6430
3.6208
3.5960
3.5926
3.5583
3.5558
3.4671
3.4634
3.4593
2.3230
2.3178
2.2490
1.3001
1.2787
1.2629
1.0955
1.0809
1.0617
1.0441
1.0243
0.9551
0.9283
0.9057
0.8729
0.7780
0.7711
0.7372
-0.0119
-0.0213

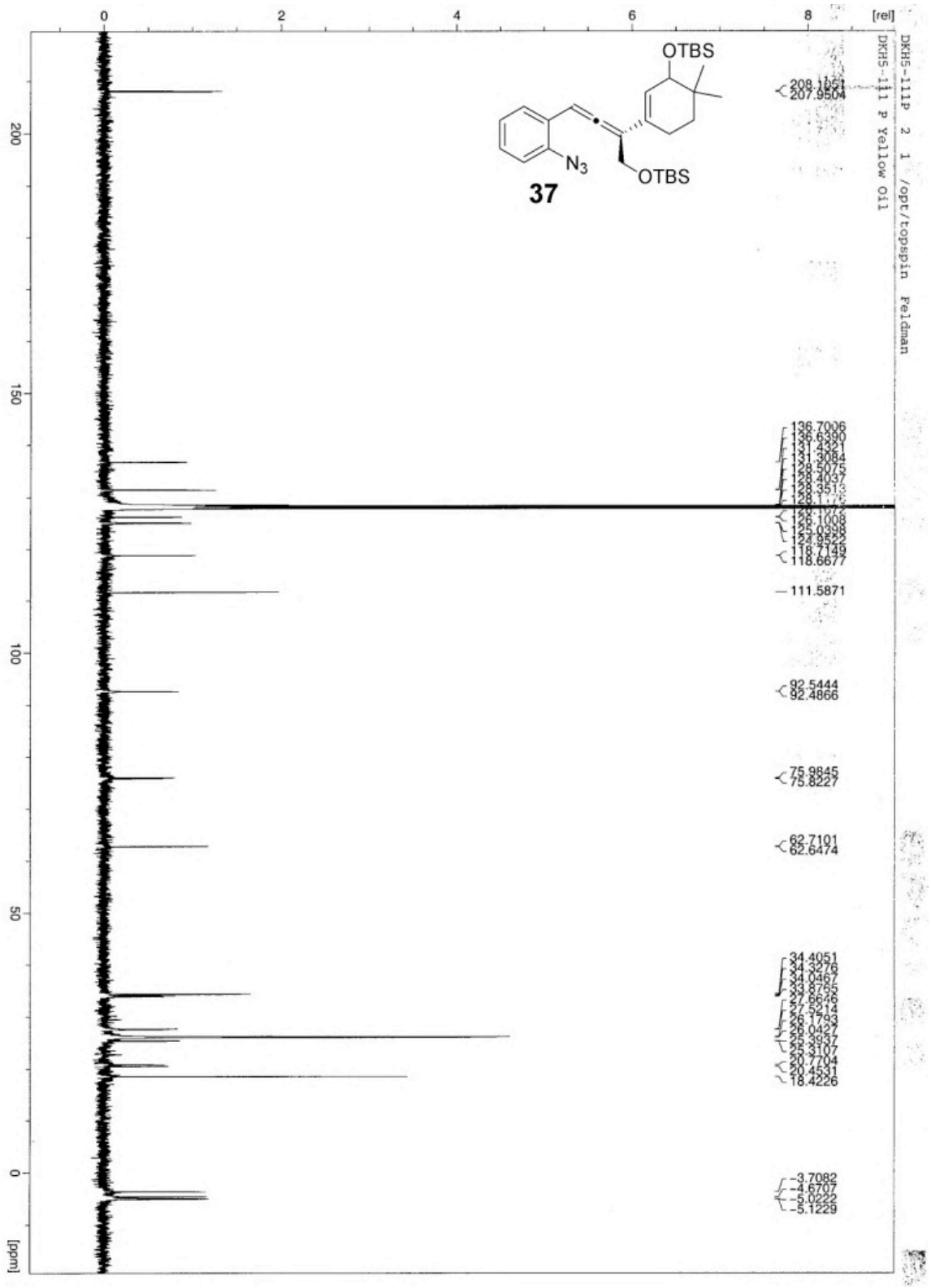

0
10
20
30
40
[rel]
200
150
100
50
0
[ppm]
DKH3-126P 2 1 /opt/topspin Feldman
DKH3-126 Product Colorless Oil
OSEM
I
35c
138.7742
99.3300
94.6497
81.4038
65.1639
37.7160
35.8586
32.7802
26.3226
21.8245
18.2399
-1.2314

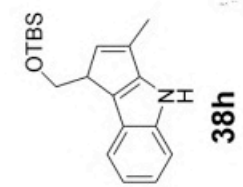
DKH5-111 P Yellow Oil



37

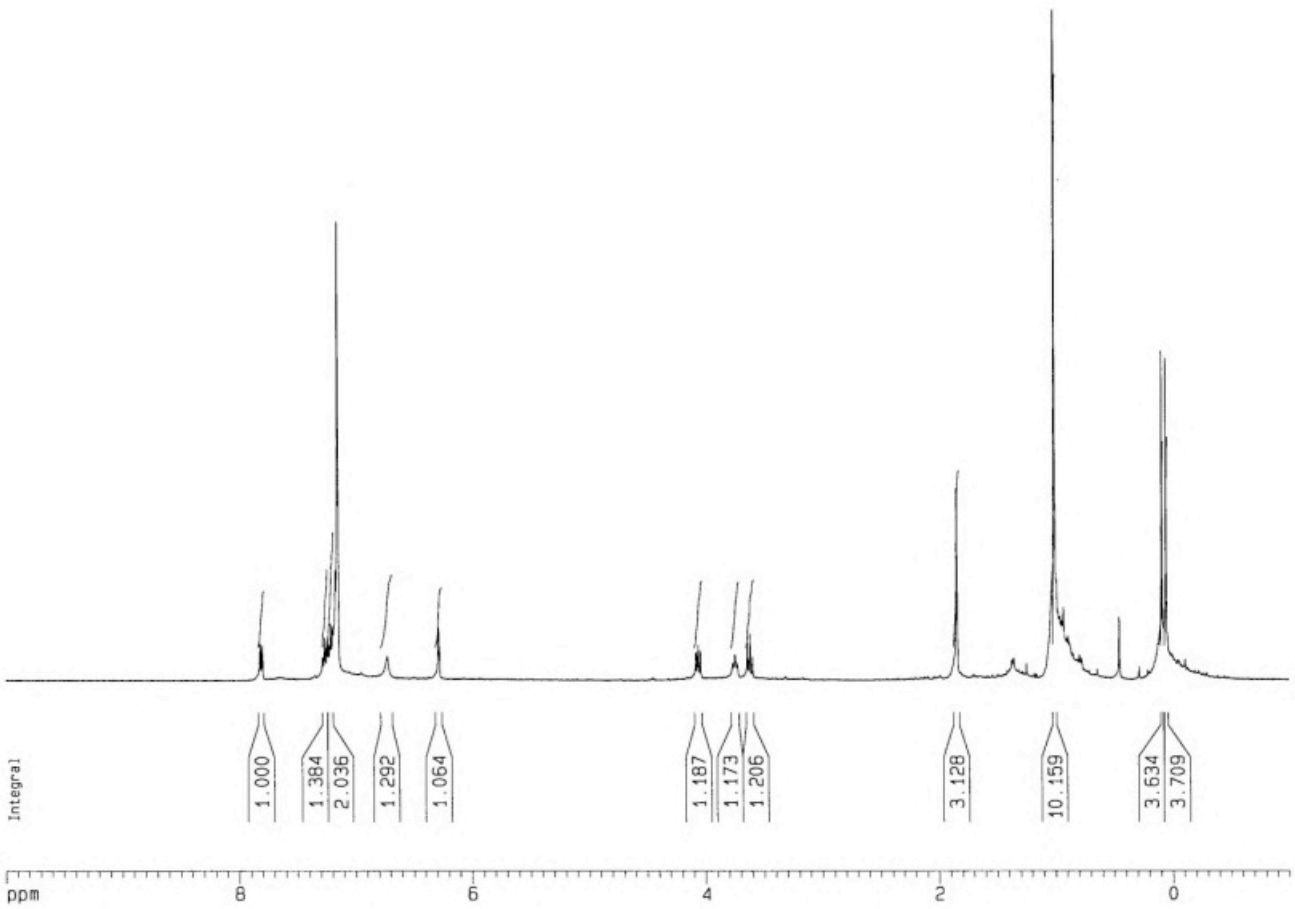

```
Current Data Parameters
NAME                  DKH5-111P
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20070905
Time                      13.57
INSTRUM                   spect
PROBHD    5 mm QNP 1H/15
PULPROG                    zg30
TD                        65536
SOLVENT                    C6D6
NS                           16
DS                            2
SWH                    7440.476 Hz
FIDRES                 0.113533 Hz
AQ                     4.4040694 sec
RG                         50.8
DW                       67.200 usec
DE                        6.00 usec
TE                       295.1 K
D1                  1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        14.93 usec
PL1                       -3.00 dB
SFO1               360.1322240 MHz

F2 - Processing parameters
SI                        32768
SF                 360.1300484 MHz
WDW                          no
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.00
```


OTBS
N3
OTBS
37
DKHS-111P 2 1 /opt/topspin Feldman
DKHS-111 P Yellow Oil
208.1151
207.9504
136.7006
136.6390
131.4321
131.3084
128.5075
128.4037
128.3513
128.1173
122.1008
122.0398
121.8552
118.7149
118.6677
111.5871
92.5444
92.4866
75.9845
75.8227
62.7101
62.6474
34.4051
34.3276
34.0467
33.8755
27.6646
27.5514
26.1793
26.0427
25.3937
25.3107
20.7704
20.4531
18.4226
-3.7082
-4.6707
-5.0222
-5.1229
[rel]
[ppm]

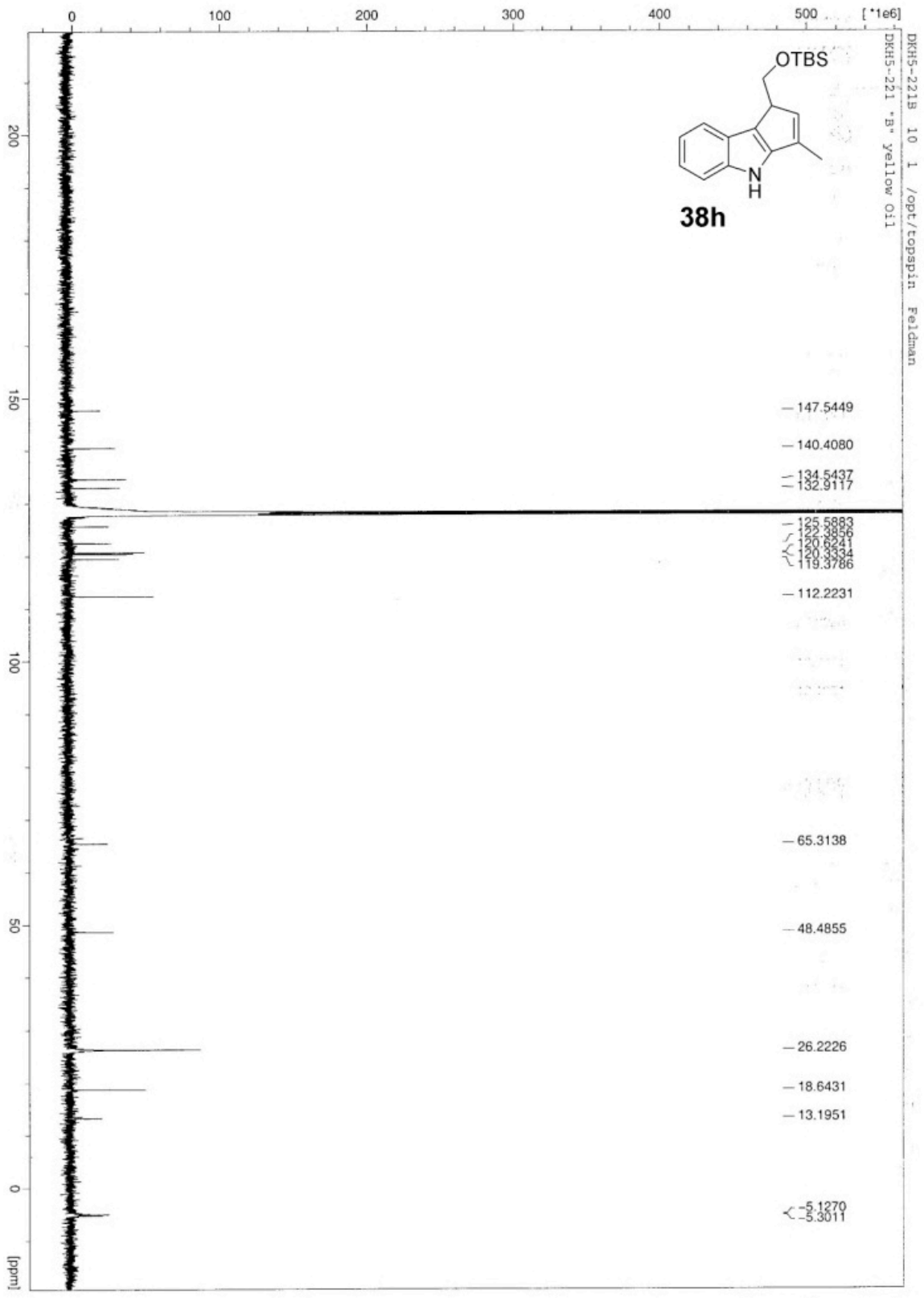


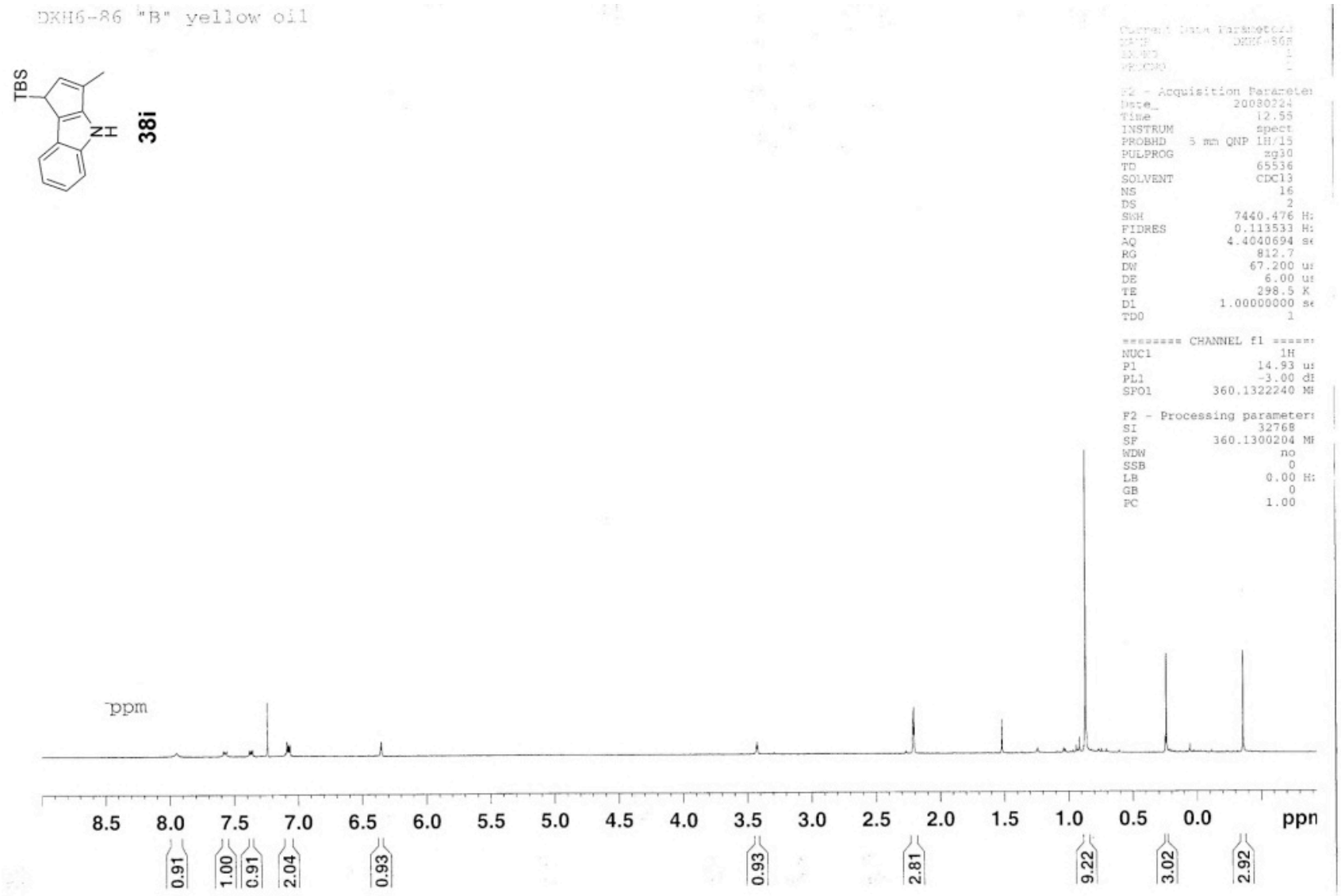
38h

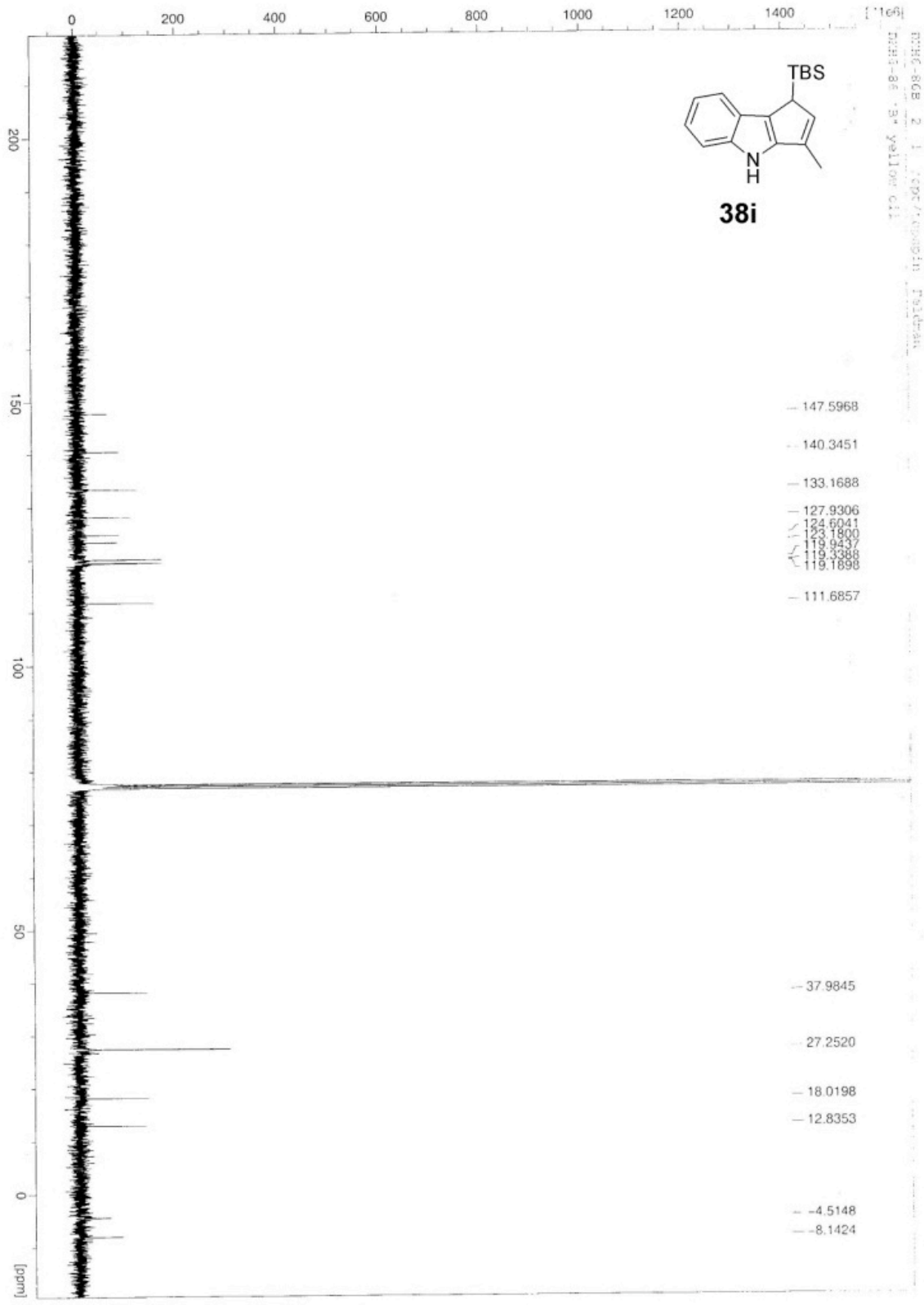
DKH5-221 "B" yellow oil



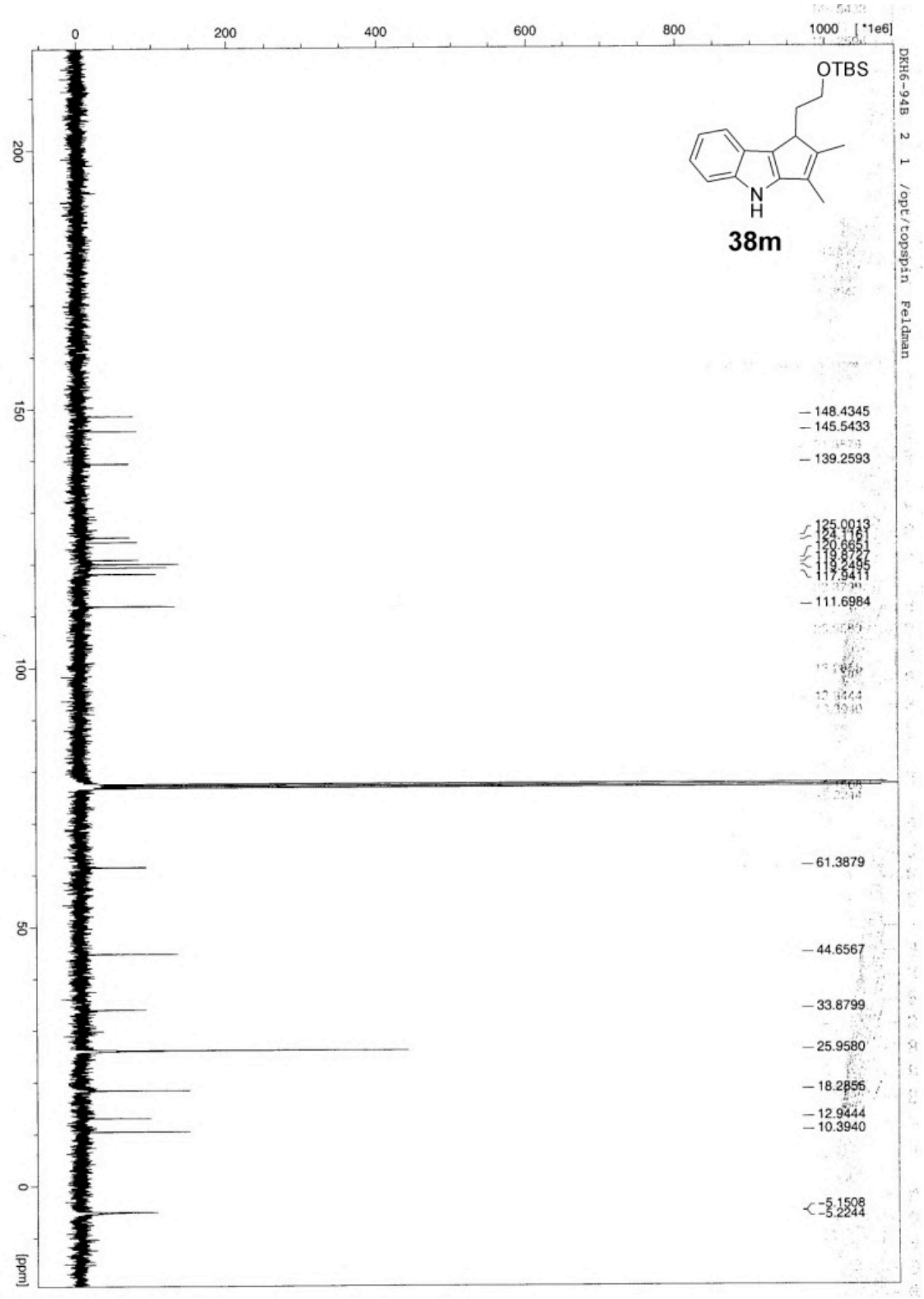

```
Current Data Parameters
NAME            DKH5-221B
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20071120
Time                14.01
INSTRUM             spect
PROBHD     5 mm BBI 1H-B
PULPROG             zg30
TD                 65536
SOLVENT             C6D6
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ              3.9584243 sec
RG                 322.5
DW                60.400 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ========
NUC1                   1H
P1                  6.45 usec
PL1                 0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300471 MHz
WDW                    no
SSB                     0
LB                 0.00 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 20.00 cm
F1P               10.000 ppm
F1                4001.30 Hz
F2P               -1.000 ppm
F2                -400.13 Hz
PPMCM             0.55000 ppm/cm
HZCM           220.07152 Hz/cm
```


0
100
200
300
400
500
[*1e6]
DKH5-221B 10 1 /opt/topspin Feldman
DKH5-221 "B" yellow Oil
OTBS
N
H
38h
147.5449
140.4080
134.5437
132.9117
125.5883
122.3856
120.6241
120.3334
119.3786
112.2231
65.3138
48.4855
26.2226
18.6431
13.1951
-5.1270
-5.3011
200
150
100
50
0
[ppm]


DKH6-86 "B" yellow oil
TBS
NH
38i
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
0.5
0.0
ppm
0.91
1.00
0.91
2.04
0.93
0.93
2.81
9.22
3.02
2.92

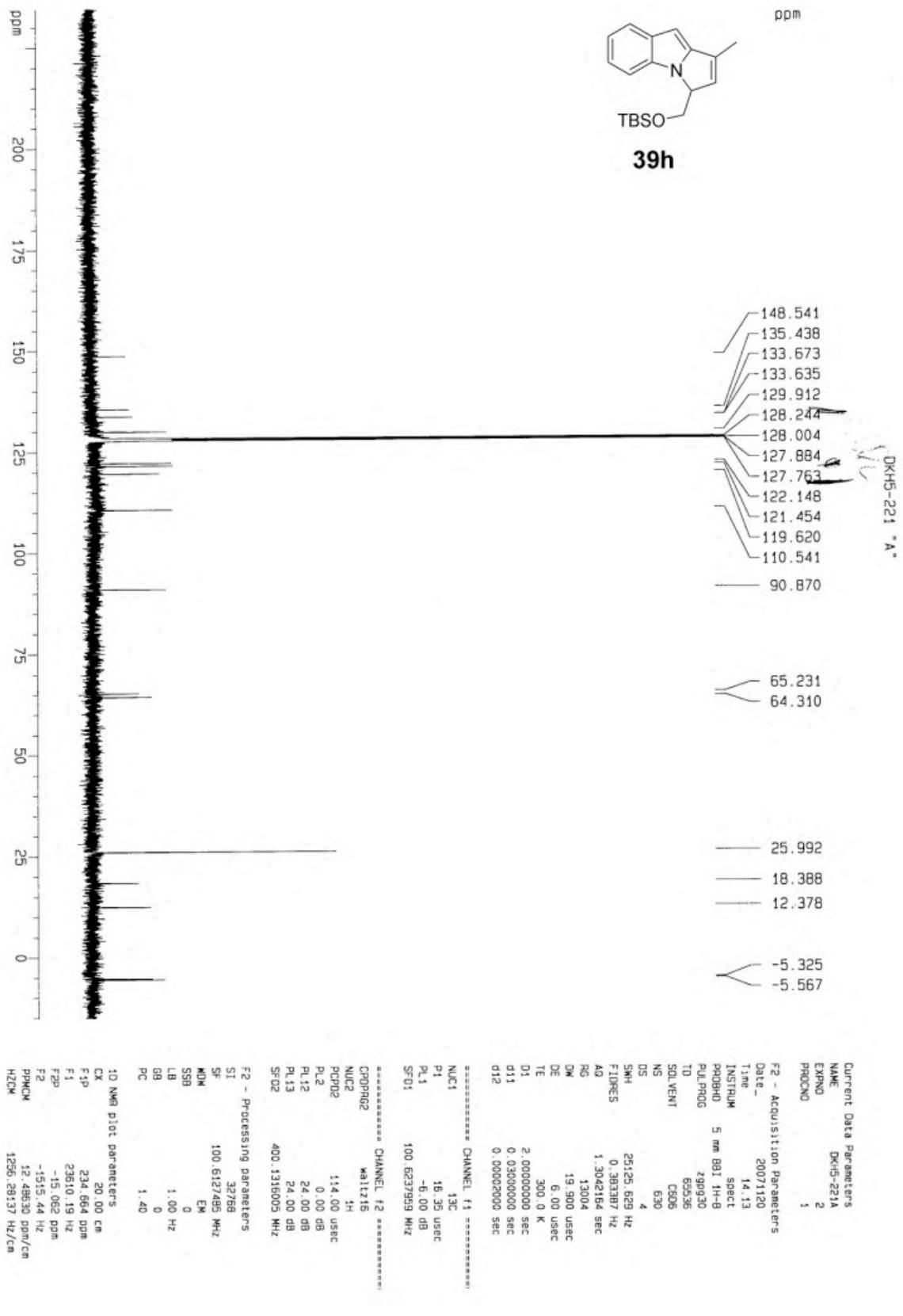

TBS
N
H
38i
147.5968
140.3451
133.1688
127.9306
124.6041
123.1800
119.9437
119.3388
119.1898
111.6857
37.9845
27.2520
18.0198
12.8353
-4.5148
-8.1424
[ppm]

```
Current Data Parameters
NAME                  DKH6-94B
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20080304
Time                   10.06
INSTRUM                spect
PROBHD     5 mm Multinu
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                6172.839 Hz
FIDRES             0.094190 Hz
AQ                 5.3084660 sec
RG                      256
DW                 81.000 usec
DE                  6.00 usec
TE                  300.0 K
D1                 1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      9.60 usec
PL1                    -6.00 dB
SFO1           300.1318534 MHz

F2 - Processing parameters
SI                       32768
SF             300.1300120 MHz
WDW                         no
SSB                          0
LB                    0.00 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 10.000 ppm
F1                 3001.30 Hz
F2P                 -1.000 ppm
F2                 -300.13 Hz
PPMCM              0.55000 ppm/cm
HZCM               165.07150 Hz/cm
```


0
200
400
600
800
1000 [*1e6]
OTBS
N
H
38m
DKH6-94B 2 1 /opt/topspin Feldman
148.4345
145.5433
139.2593
125.0013
124.1161
120.6651
119.8727
119.2495
117.9411
111.6984
61.3879
44.6567
33.8799
25.9580
18.2856
12.9444
10.3940
5.1508
5.2244
200
150
100
50
0
[ppm]

DKH5-221 "A" yellow oil


```
Current Data Parameters
NAME                  DKH5-221A
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20071120
Time                  13.55
INSTRUM                spect
PROBHD    5 mm BBI 1H-B
PULPROG                zg30
TD                    65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH               8278.146 Hz
FIDRES               0.126314 Hz
AQ                3.9584243 sec
RG                       181
DW                    60.400 usec
DE                     6.00 usec
TE                    300.0 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     6.45 usec
PL1                    0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                400.1300473 MHz
WDW                          no
SSB                           0
LB                     0.00 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                       20.00 cm
F1P                     10.000 ppm
F1                    4001.30 Hz
F2P                    -1.000 ppm
F2                     -400.13 Hz
PPMCM                 0.55000 ppm/
HZCM                220.07152 Hz/c
```



Current Data Parameters
NAME DKH5-221A
EXPNO 2
PROCNO 1

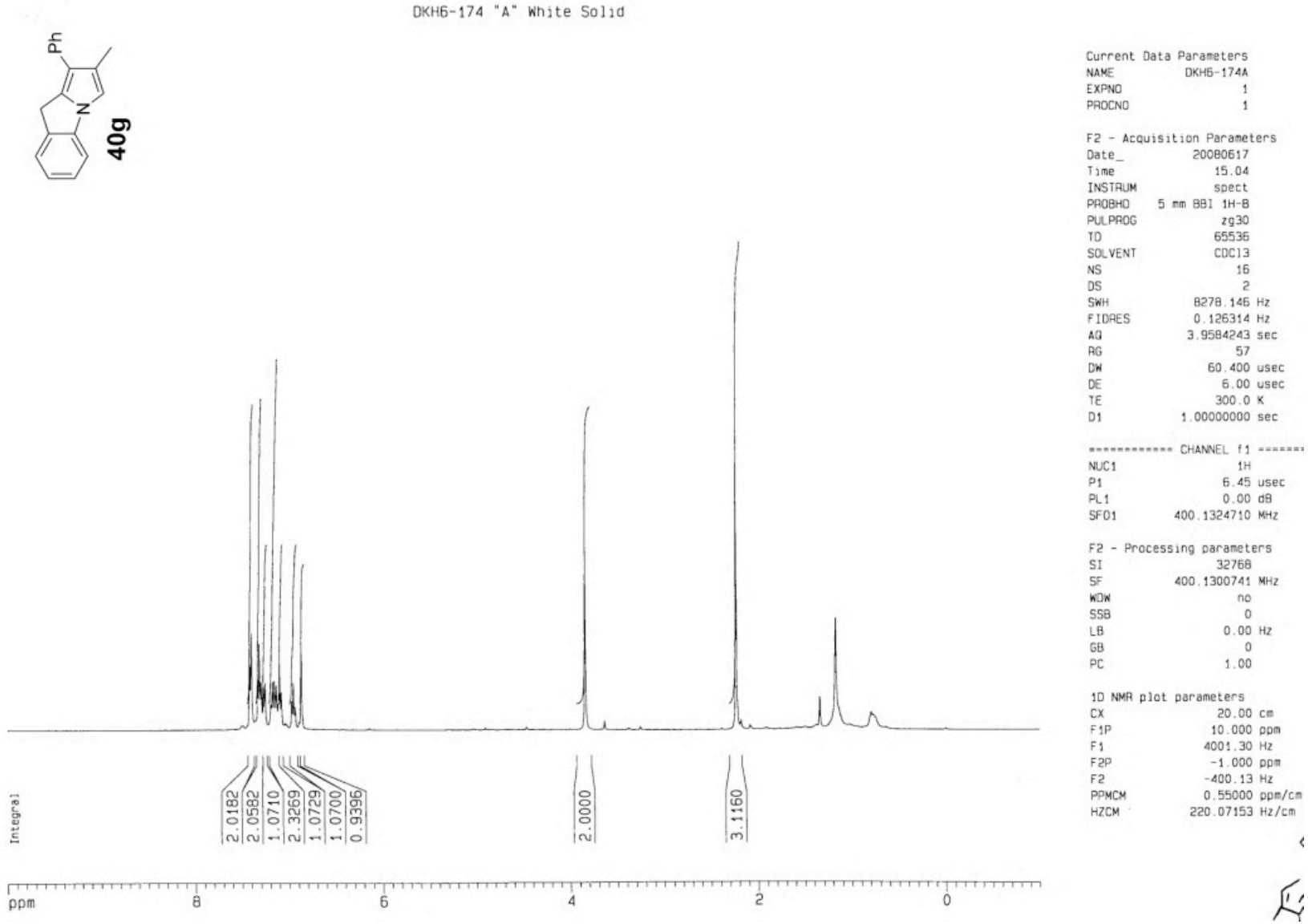
F2 - Acquisition Parameters
Date_ 20071120
Time 14.13
INSTRUM spect
PROBHD 5 mm BBI 1H-B
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 630
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042154 sec
RG 13004
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 16.35 usec
PL1 -6.00 dB
SFO1 100.6237959 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 114.00 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127485 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 234.664 ppm
F1 23610.19 Hz
F2P -15.062 ppm
F2 -1515.44 Hz
PPMCM 12.48630 ppm/cm
HZCM 1256.28137 Hz/cm



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EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time 15.04
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 57
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

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P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
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SF 400.1300741 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

1D NMR plot parameters
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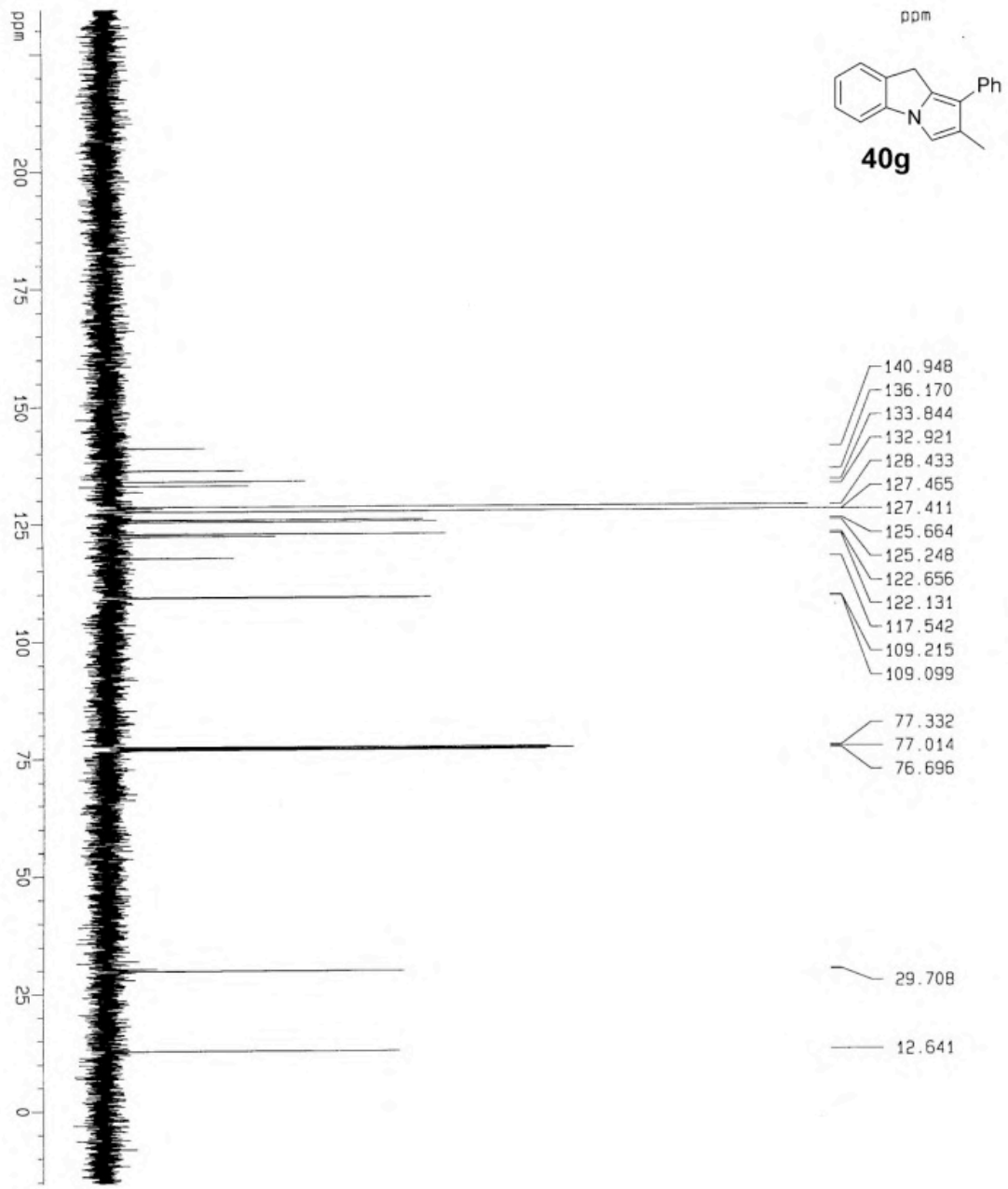
HZCM 220.07153 Hz/cm

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PROCNO                        1

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TD                     65536
SOLVENT                CDCl3
NS                       122
DS                         4
SWH              25125.629 Hz
FIDRES               0.383387 Hz
AQ                 1.3042164 sec
RG                     16384
DW                    19.900 usec
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TE                    300.0 K
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======== CHANNEL f1 ========
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PL1                    -6.00 dB
SF01           100.6237959 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 114.00 usec
PL2                    0.00 dB
PL12                  24.00 dB
PL13                  24.00 dB
SFO2           400.1316005 MHz

F2 - Processing parameters
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SF             100.6127786 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40

1D NMR plot parameters
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F1                  23580.13 Hz
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F2                  -1545.49 Hz
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HZCM              1256.28137 Hz/cm
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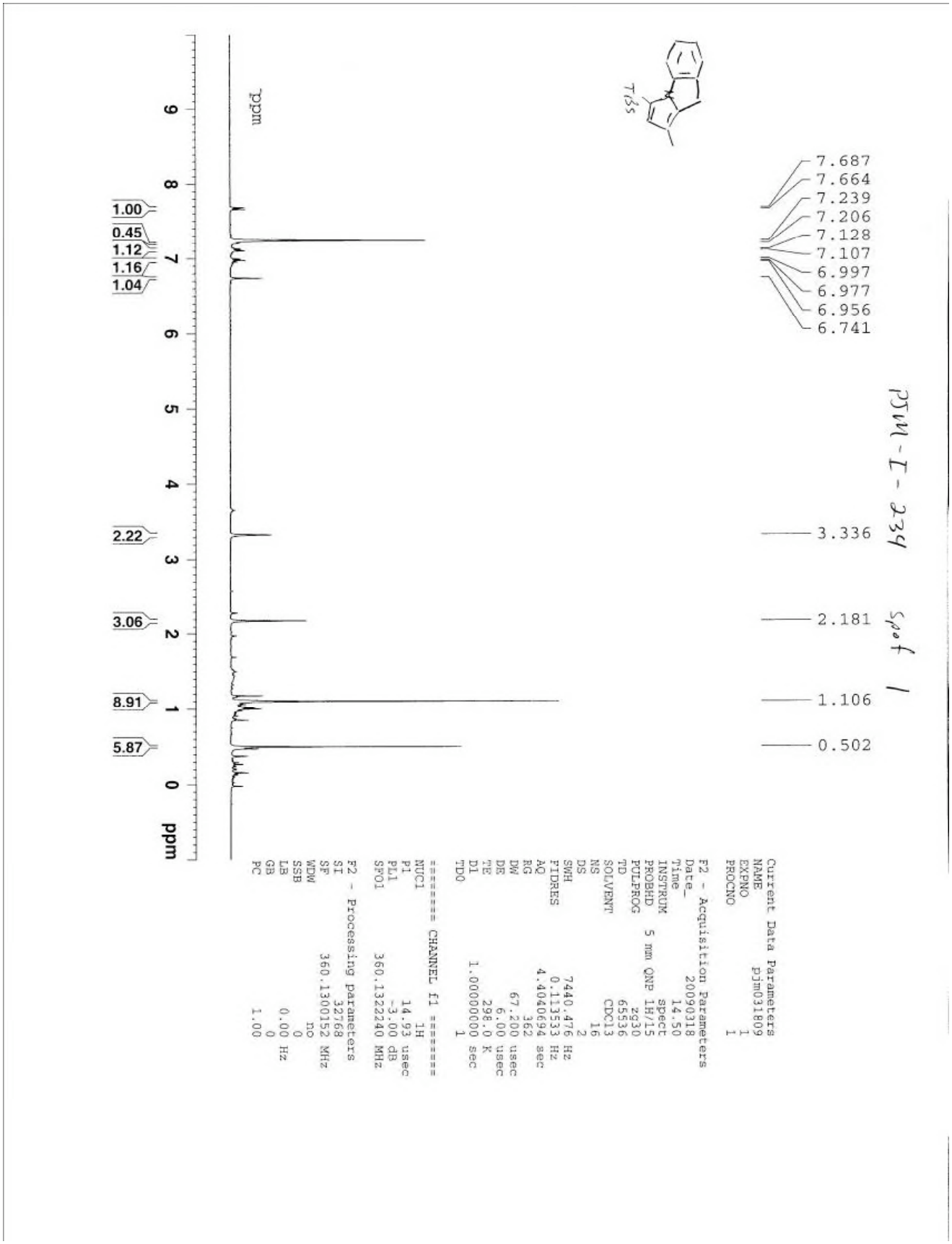
40i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7.664
7.239
7.206
7.128
7.107
6.997
6.977
6.956
6.741
3.336
2.181
1.106
0.502
Tiss
1.00
0.45
1.12
1.16
1.04
2.22
3.06
8.91
5.87
ppm
Current Data Parameters
NAME pjm031809
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
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Time 14.50
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DS 2
SWH 7440.476 Hz
FIDRES 0.113533 Hz
AQ 4.4040694 sec
RG 362
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DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
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P1 14.93 usec
PL1 -3.00 dB
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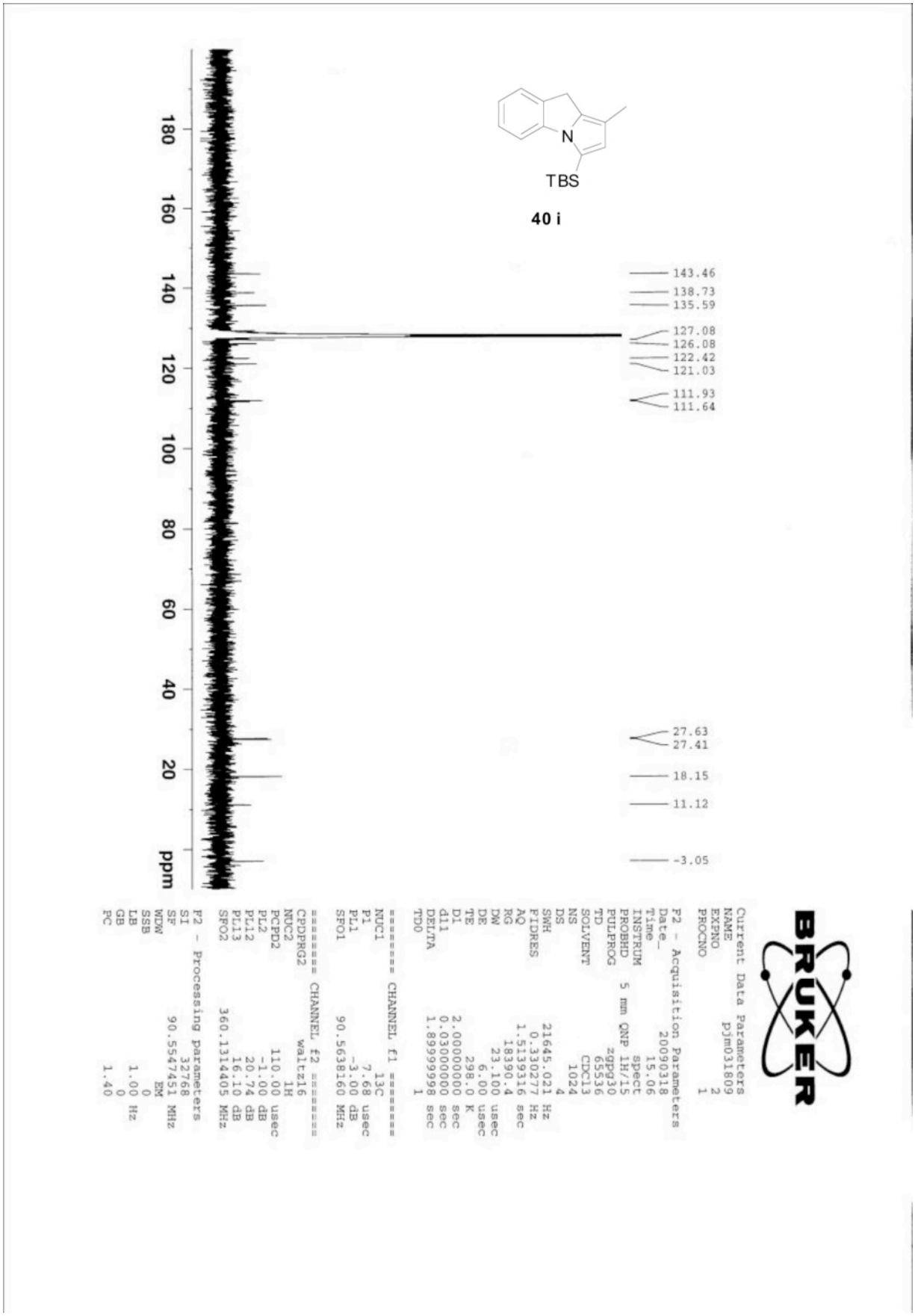
PC 1.00


N
TBS
40 i
143.46
138.73
135.59
127.08
126.08
122.42
121.03
111.93
111.64
27.63
27.41
18.15
11.12
-3.05
180
160
140
120
100
80
60
40
20
ppm
BRUKER
Current Data Parameters
NAME pjm031809
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090318
Time 15.06
INSTRUM spect
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TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 21645.021 Hz
FIDRES 0.330277 Hz
AQ 1.5139316 sec
RG 18390.4
DW 23.100 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 7.68 usec
PL1 -3.00 dB
SFO1 90.5638160 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 -1.00 dB
PL12 20.74 dB
PL13 16.10 dB
SFO2 360.1314405 MHz
F2 - Processing parameters
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SSB 0
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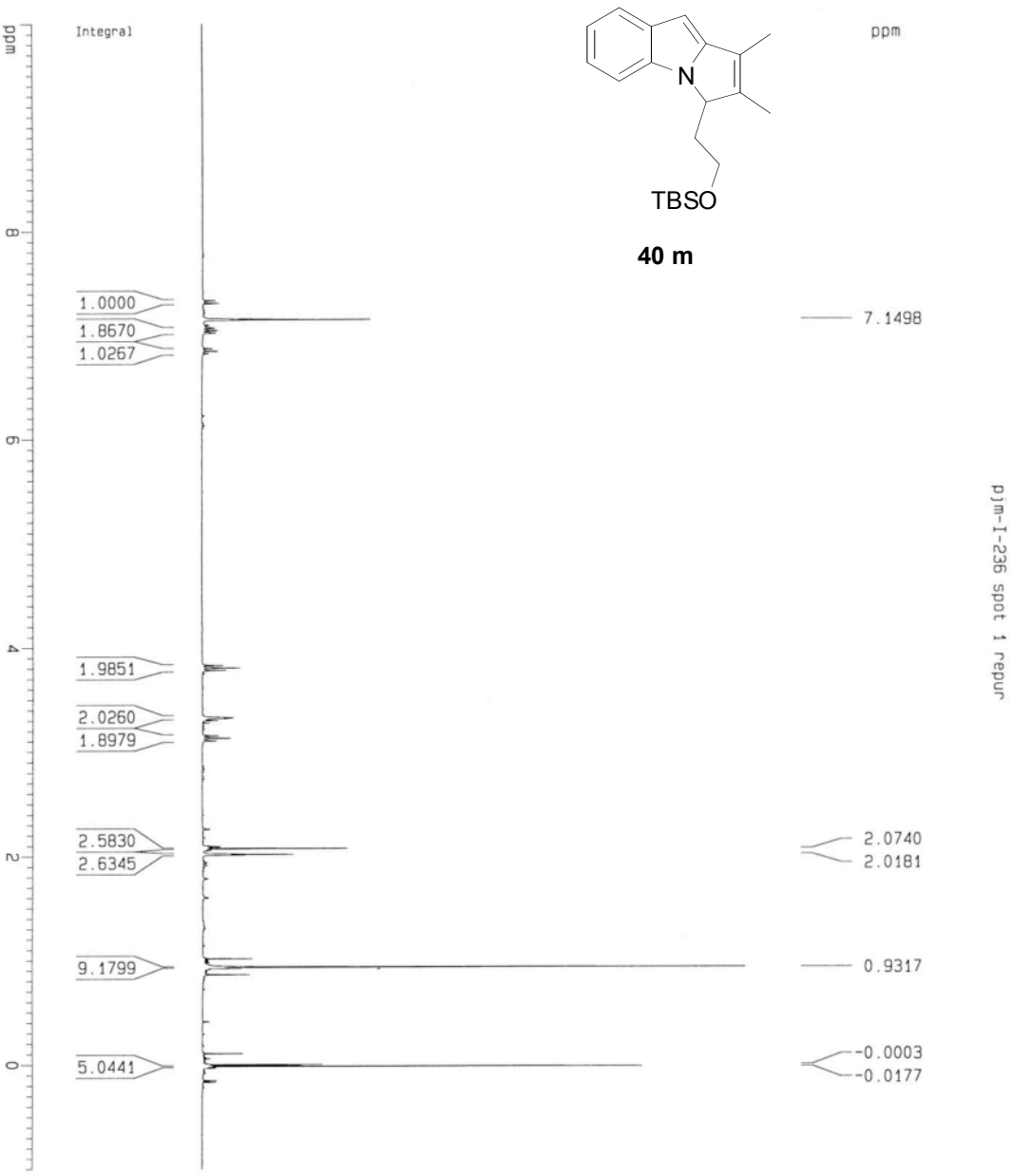
GB 0
PC 1.40


ppm
Integral
N
TBSO
40 m
1.0000
1.8670
1.0267
1.9851
2.0260
1.8979
2.5830
2.6345
9.1799
5.0441
7.1498
2.0740
2.0181
0.9317
-0.0003
-0.0177
pjm-I-236 spot 1 repur
Current Data Parameters
NAME pjm032009
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20090320
Time 12.07
INSTRUM spect
PROBHD 5 mm QNP 1H/1
PULPROG zg30
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DS 2
SWH 6172.839 Hz
FIDRES 0.094190 Hz
AQ 5.3084660 sec
RG 203.2
DW 81.000 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
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SFO1 299.8718518 MHz
F2 - Processing parameters
SI 32768
SF 299.8700382 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
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F2P -1.000 ppm
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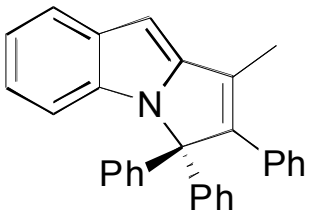
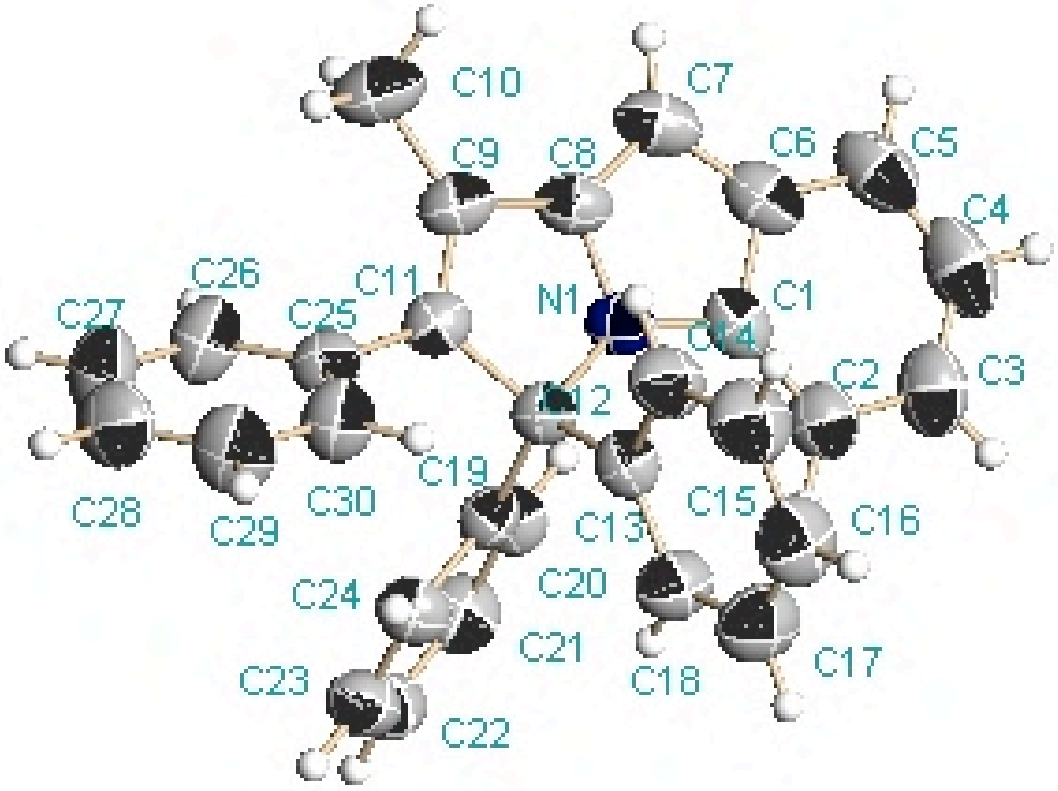
HZCM 164.92851 Hz/cm



A colorless rod shaped crystal of **39n** ($2(C_{30}H_{23}N),C_5H_{12}$) with approximate dimensions 0.13 x 0.14 x 0.29 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 298(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 20 seconds/frame. The total data collection time was about 14 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 9890 reflections to a maximum θ angle of 28.48° (0.90 Å resolution), of which 5970 were independent, completeness = 97.1%, R_{int} = 0.0364, R_{sig} = 0.0778 and 2909 were greater than 2σ(I). The final cell constants: a = 10.254(8)Å, b = 10.743(8)Å, c = 12.090(9)Å, α = 97.948(13)°, β = 106.727(13)°, γ = 102.782(13)°, volume = 1214.5(16) $Å^3$, are based upon the refinement of the XYZ-centroids of 2876 reflections above 20σ(I) with 2.310° <θ <27.366° . Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.3513.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P-1, with Z = 2 for the formula unit, C32.50 H28.5 N . The final anisotropic full-matrix least-squares refinement on F^2 with 310 variables converged at R1 = 7.21%, for the observed data and wR2 = 24.36% for all data. The goodness-of-fit was 0.958 . The largest peak on the final difference map was 0.571 $e^-/Å^3$ and the largest hole was -0.190 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.186 g/cm^3 and F(000) amounts to 462 electrons.


C10
C7
C9
C8
C6
C5
C4
C26
C11
N1
C1
C27
C25
C3
C2
C19
C28
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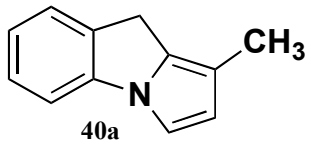
C24
C20
C21
C18
C17
C23
C22

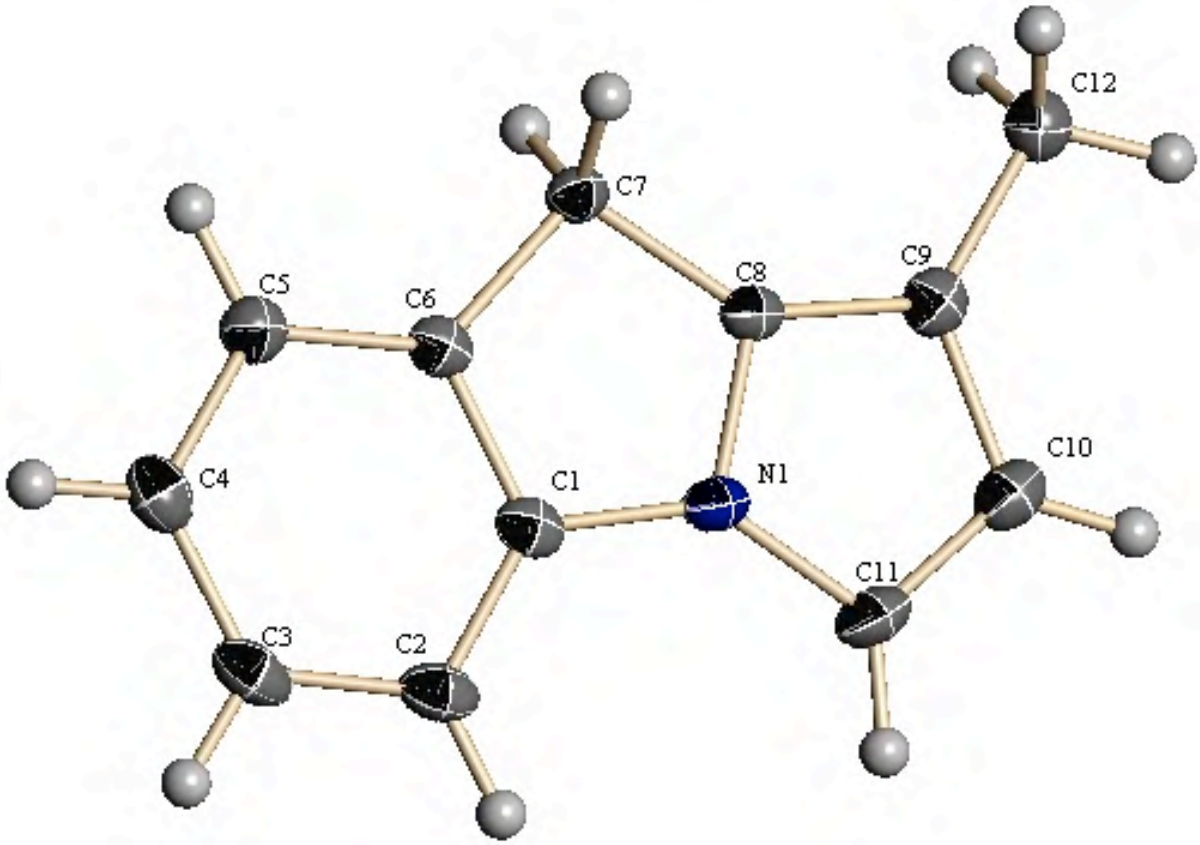


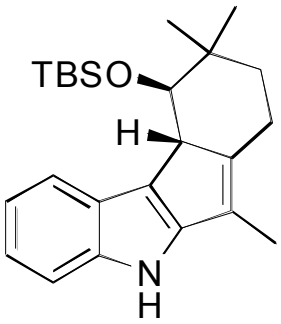
40a

A yellow plate shaped crystal of **40a** ($C_{12}H_{11}N$) with approximate dimensions 0.10 x 0.30 x 0.40 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 108(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 20 seconds/frame. The total data collection time was about 12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 5358 reflections to a maximum θ angle of 28.28° (0.90 Å resolution), of which 2066 were independent, completeness = 94.9 %, R_{int} = 0.0178, R_{sig} = 0.0245 and 1729 were greater than 2σ(I). The final cell constants: a = 11.907(4)Å, b = 5.6848(16)Å, c = 12.950(4)Å, α = 90°, β = 92.517(5)°, γ = 90°, volume = 875.7(4)$Å^3$, are based upon the refinement of the XYZ-centroids of 2113 reflections above 20σ(I) with 2.274° <θ <28.242° . Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.849448.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P2(1)/n, with Z = 4 for the formula unit, $C_{12}H_{11}N$. The final anisotropic full-matrix least-squares refinement on F^2 with 119 variables converged at R1 = 5.17 %, for the observed data and wR2 = 13.90 % for all data. The goodness-of-fit was 1.072 . The largest peak on the final difference map was 0.403 $e^-/Å^3$ and the largest hole was -0.249 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.283 g/cm^3 and F(000) amounts to 360 electrons.

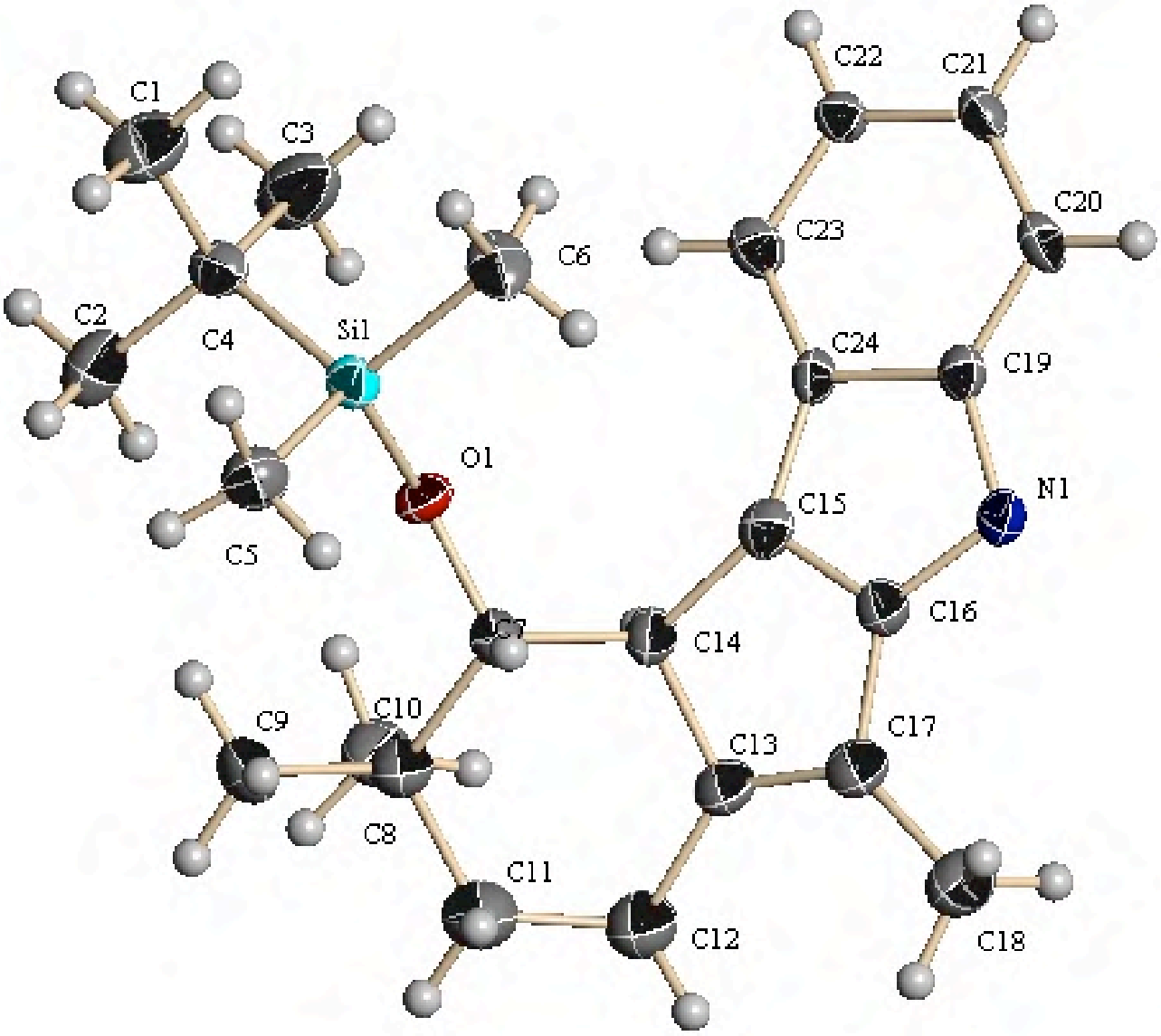

C12
C7
C5
C6
C8
C9
C10
C4
C1
N1
C11
C3
C2



A colorless block shaped crystal of **42b** ($C_{24}H_{35}NOSi$) with approximate dimensions 0.06 x 0.15 x 0.20 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 128(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 10 seconds/frame. The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 10873 reflections to a maximum θ angle of 28.34° (0.90 Å resolution), of which 11043 were independent, completeness = 94.9 %, R_{int} = 0.0536, R_{sig} = 0.1644 and 5107 were greater than 2σ(I). The final cell constants: a = 9.437(8)Å, b = 13.537(9)Å, c = 19.104(9)Å, α = 101.43(4)°, β = 97.13(4)°, γ = 99.38(4)°, volume = 2328.0(26)$Å^3$, are based upon the refinement of the XYZ-centroids of 1755 reflections above 20σ(I) with 2.230° <θ <28.348° . Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.069.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P-1, with Z = 2 for the formula unit, C48 H70 N2 O2 Si2 . The final anisotropic full-matrix least-squares refinement on F^2 with 503 variables converged at R1 = 10.20%, for the observed data and wR2 = 30.66% for all data. The goodness-of-fit was 0.984 . The largest peak on the final difference map was 0.388 $e^-/Å^3$ and the largest hole was -0.724 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.088 g/cm^3 and F(000) amounts to 832 electrons.


C1
C3
C6
C2
C4
Si1
O1
C5
C22
C21
C20
C23
C24
C19
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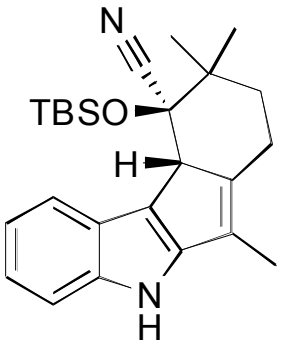
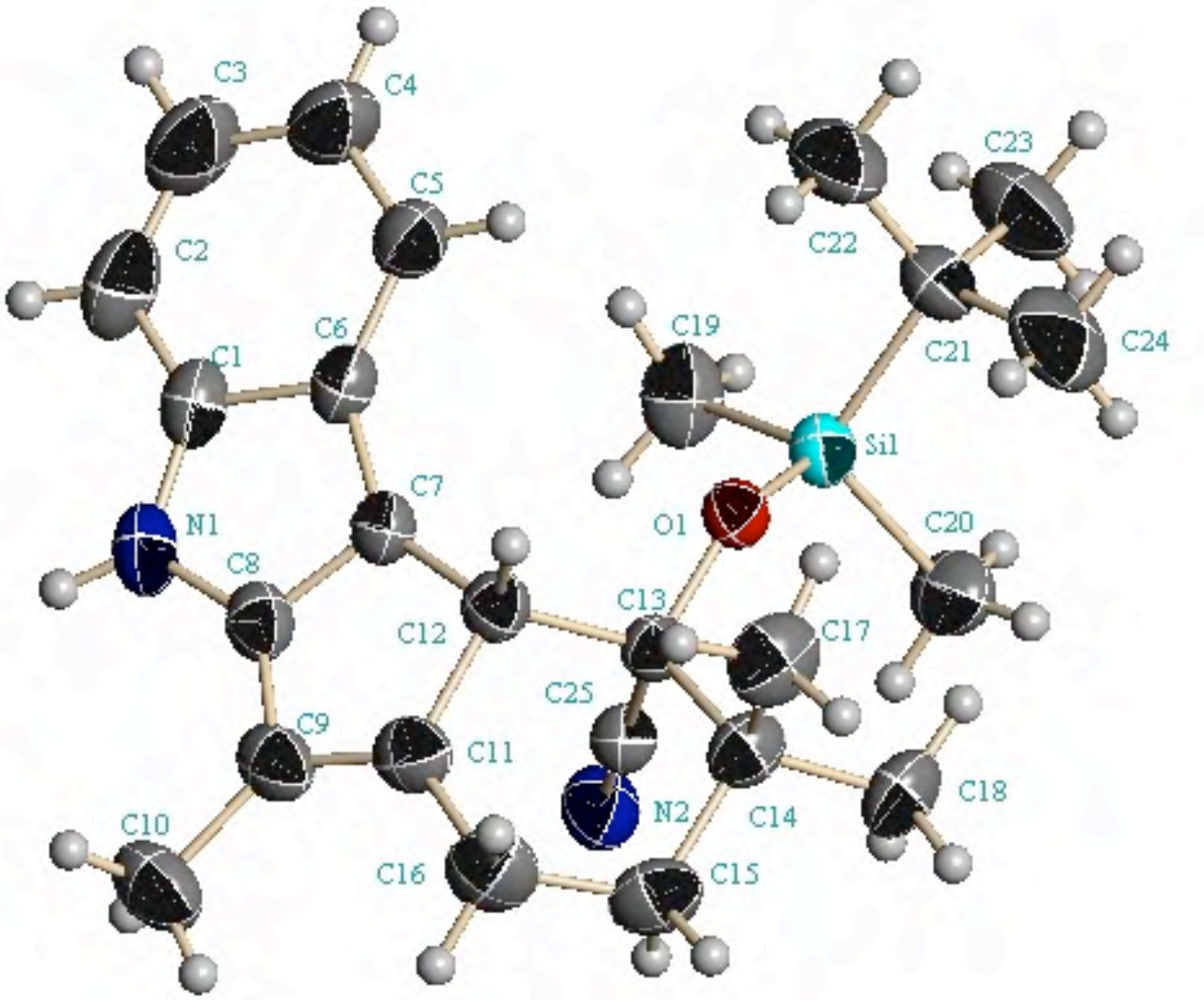
C9
C10
C17
C13
C8
C11
C12
C18



A colorless block shaped crystal of **42d** ($C_{25}H_{34}N_2OSi$) with approximate dimensions 0.20 x 0.30 x 0.40 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 129(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 5 seconds/frame. The total data collection time was about 6 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 11778 reflections to a maximum θ angle of 28.34° (0.90 Å resolution), of which 5913 were independent, completeness = 97.7%, R_{int} = 0.0152, R_{sig} = 0.0250 and 4820 were greater than 2σ(I). The final cell constants: a = 9.779(3)Å, b = 10.939(3)Å, c = 11.635(4)Å, α = 89.483(6)°, β = 77.658(5)°, γ = 85.916(5)°, volume = 1212.8(7)$Å^3$, are based upon the refinement of the XYZ-centroids of 4583 reflections above 20σ(I) with 2.137° <θ < 27.994° . Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.8805.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P-1, with Z = 2 for the formula unit, $C_{25}H_{34}N_2OSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 270 variables converged at R1 = 4.77%, for the observed data and wR2 = 14.44% for all data. The goodness-of-fit was 1.037. The largest peak on the final difference map was 0.384 $e^-/Å^3$ and the largest hole was -0.174 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.113 g/cm^3 and F(000) amounts to 440 electrons.


C3
C4
C5
C2
C6
C1
C7
N1
C8
C12
C9
C11
C10
C16
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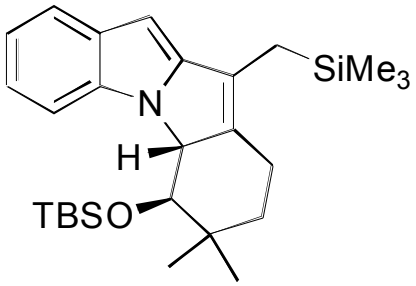
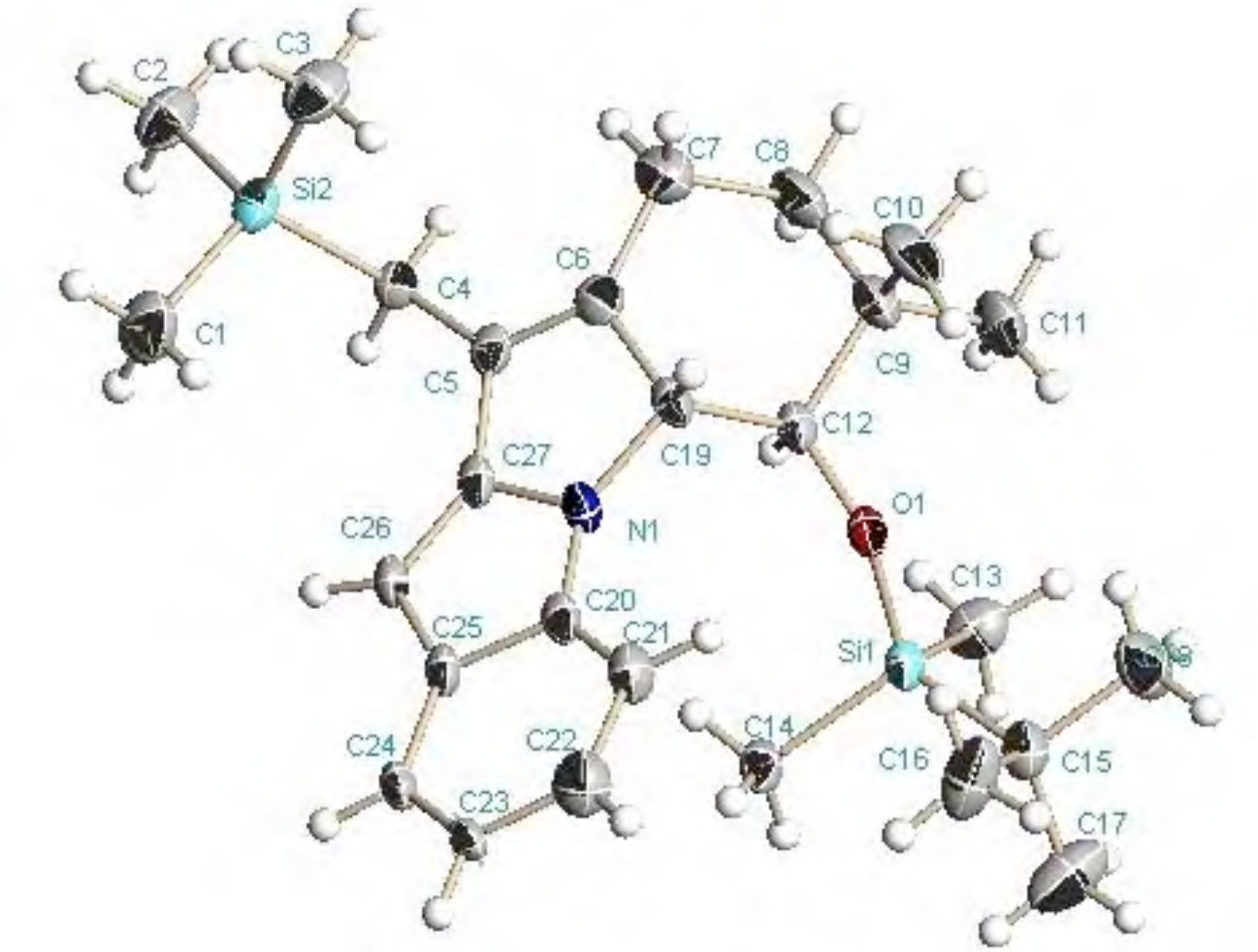
Si1
C22
C23
C21
C24
C20
C17
C18



A colorless block shaped crystal of **43e** ($C_{27}H_{43}NOSi_2$) with approximate dimensions 0.13 x 0.18 x 0.25 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 123(2)K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 10 seconds/frame. The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 24148 reflections to a maximum θ angle of 29.13° (0.90 Å resolution), of which 7027 were independent, completeness = 94.3%, R_{int} = 0.0910, R_{sig} = 0.0928 and 4448 were greater than 2σ(I). The final cell constants: *a* = 11.869(2)Å, *b* = 10.874(2)Å, *c* = 22.010(4)Å, α = 90°, β = 93.52(3)°, γ = 90°, volume = 2835.2(10)Å^3, are based upon the refinement of the XYZ-centroids of 9371 reflections above 20σ(I) with 2.534° <θ <28.570° . Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.4338. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P2(1)/c, with Z = 4 for the formula unit, $C_{27}H_{43}NOSi_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 290 variables converged at R1 = 7.38%, for the observed data and wR2 = 19.39% for all data. The goodness-of-fit was 1.022. The largest peak on the final difference map was 0.681 e^-/Å^3 and the largest hole was -0.620 e^-/Å^3. Based on the final model, the calculated density of the crystal is 1.063 g/cm^3 and F(000) amounts to 992 electrons.


C2
C3
Si2
C1
C4
C5
C6
C7
C8
C10
C11
C9
C12
C27
C19
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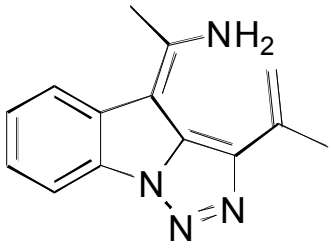
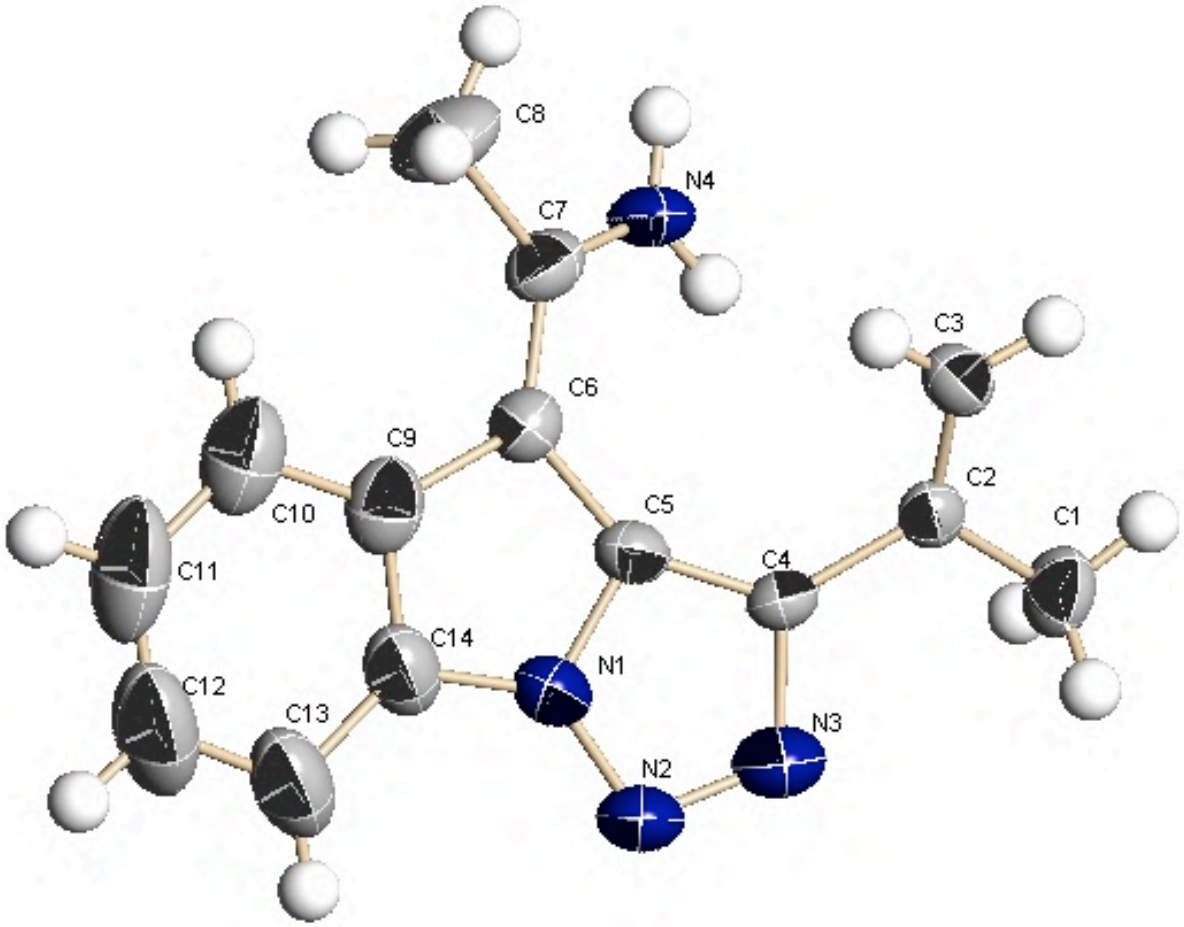
Si1
C14
C24
C22
C16
C15
C23
C17



A colorless plate shaped crystal of **54** ($C_{14}H_{14}N_4$) with approximate dimensions 0.09 x 0.20 x 0.28 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 123(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 10 seconds/frame. The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 20935 reflections to a maximum θ angle of 28.33° (0.90 Å resolution), of which 6098 were independent, completeness = 98.6%, R_{int} = 0.0440, R_{sig} = 0.0492 and 3664 were greater than 2σ(I). The final cell constants: a = 9.8894(16) Å, b = 21.213(3)Å, c = 11.8512(19) Å, α = 90°, β = 93.758(3)°, γ = 90°, volume = 2480.9(7) Å^3, are based upon the refinement of the XYZ-centroids of 5397 reflections above 20σ(I) with 2.275° <θ <28.319° . Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.8135.

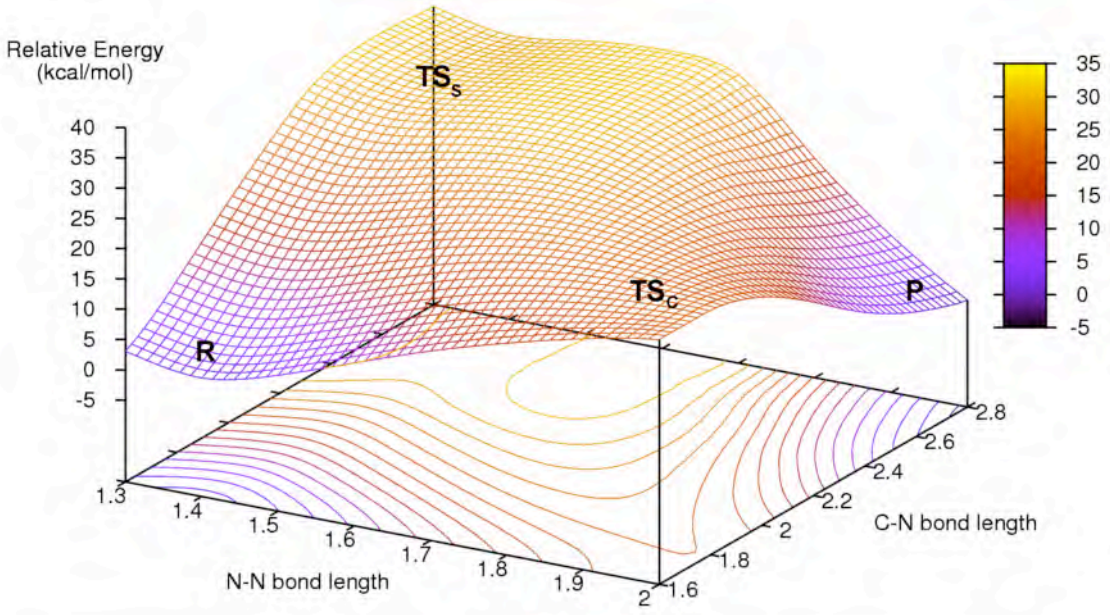
The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P2(1)/c, with Z = 8 for the formula unit, $C_{14}H_{14}N_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 329 variables converged at R1 = 6.79%, for the observed data and wR2 = 19.85% for all data. The goodness-of-fit was 0.963. The largest peak on the final difference map was 0.201 e$^-$/Å^3 and the largest hole was -0.213 e$^-$/Å^3. Based on the final model, the calculated density of the crystal is 1.276 g/cm^3 and F(000) amounts to 1008 electrons.

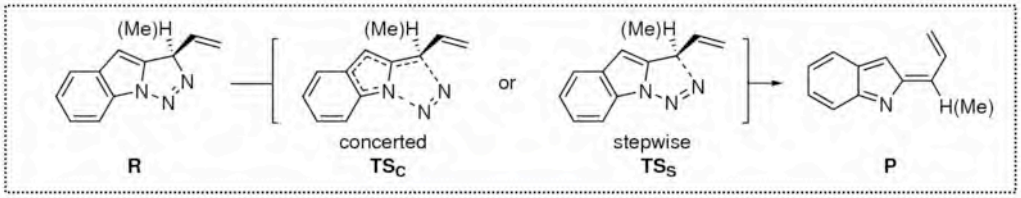

C8
N4
C7
C3
C6
C9
C2
C10
C5
C1
C11
C4
C14
N1
C12
C13
N3
N2

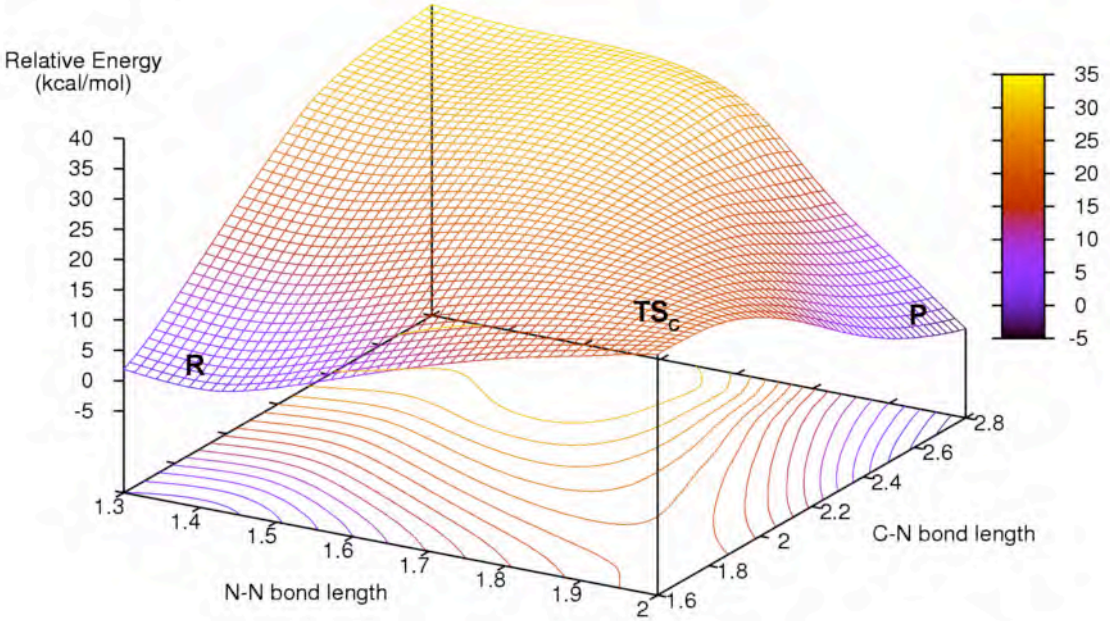
Despite having located a transition state for the **64** → **67**-type transformation in the non-methylated allenyl azide substrate in previous work (see upper diagram of the following Figure),[1] numerous attempts performed to locate the transition state associated to the stepwise N_2 extrusion (**64** → **67**) employing different optimization algorithms failed. Since the introduction of a methyl substituent at the allene terminus did not seem to justify the disappearance of the diradical pathway, we decided to carry out a thorough scan of the potential energy surface. The bond breaking C-N and N-N distances were selected as logical reaction coordinates and multiple constrained geometry optimizations were run in the ranges 1.6 to 2.8 Å for the C-N bond length and 1.3 to 2.0 Å for the N-N bond length, respectively. More than 100 geometry optimization jobs were completed to construct each surface (see Figure below). Due to near degeneracy problems raised in the diradical region associated to the stepwise extrusion, the unrestricted version of the B3LYP functional was employed, and the stability of the final wavefunctions[2] checked for the structures lying in this area (see computational methods for more details). These calculations revealed that the region around the diradical transition state in the des-methyl substrate is almost flat and the channel funneling the stepwise process is remarkably shallow, featuring a very smooth and low hillock separating the higher energy diradical transition state from the much more favorable concerted alternative (see upper diagram of Figure below). The introduction of the methyl substituent further flattens out the diradical area, transforming the hillock into a downhill shoulder and erasing the diradical transition state from the potential energy surface landscape (see lower diagram of the Figure below). Despite the differences exhibited between these surfaces, the same chemistry is expected for both methylated and des-methylated substrates, since the lowest energy pathway to N_2 loss, the concerted mechanism stays unaltered upon methylation.

(1) López, C. S.; Faza, O. N., Feldman, K. S.; Iyer, M. R.; Hester, II, D. K. *J. Am. Chem. Soc.* **2007**, *129*, 7638-7646.

(2) Bauernschmitt, R.; Ahlrichs, R. *J. Chem. Phys.* **1996**, *22*, 9047-9052.


Relative Energy
(kcal/mol)
TS$_S$
TS$_C$
R
P
N-N bond length
C-N bond length


(Me)H
or
concerted
TS$_C$
stepwise
TS$_S$
R
P
H(Me)


Relative Energy
(kcal/mol)
TS$_C$
R
P
N-N bond length
C-N bond length