

SUPPORTING INFORMATION

Unexpected Regio- and Chemoselectivity of Cationic Gold-Catalyzed Cycloisomerizations of Propargylureas: Access to Tetrasubstituted 3,4- Dihydropyrimidin-2(1*H*)-ones

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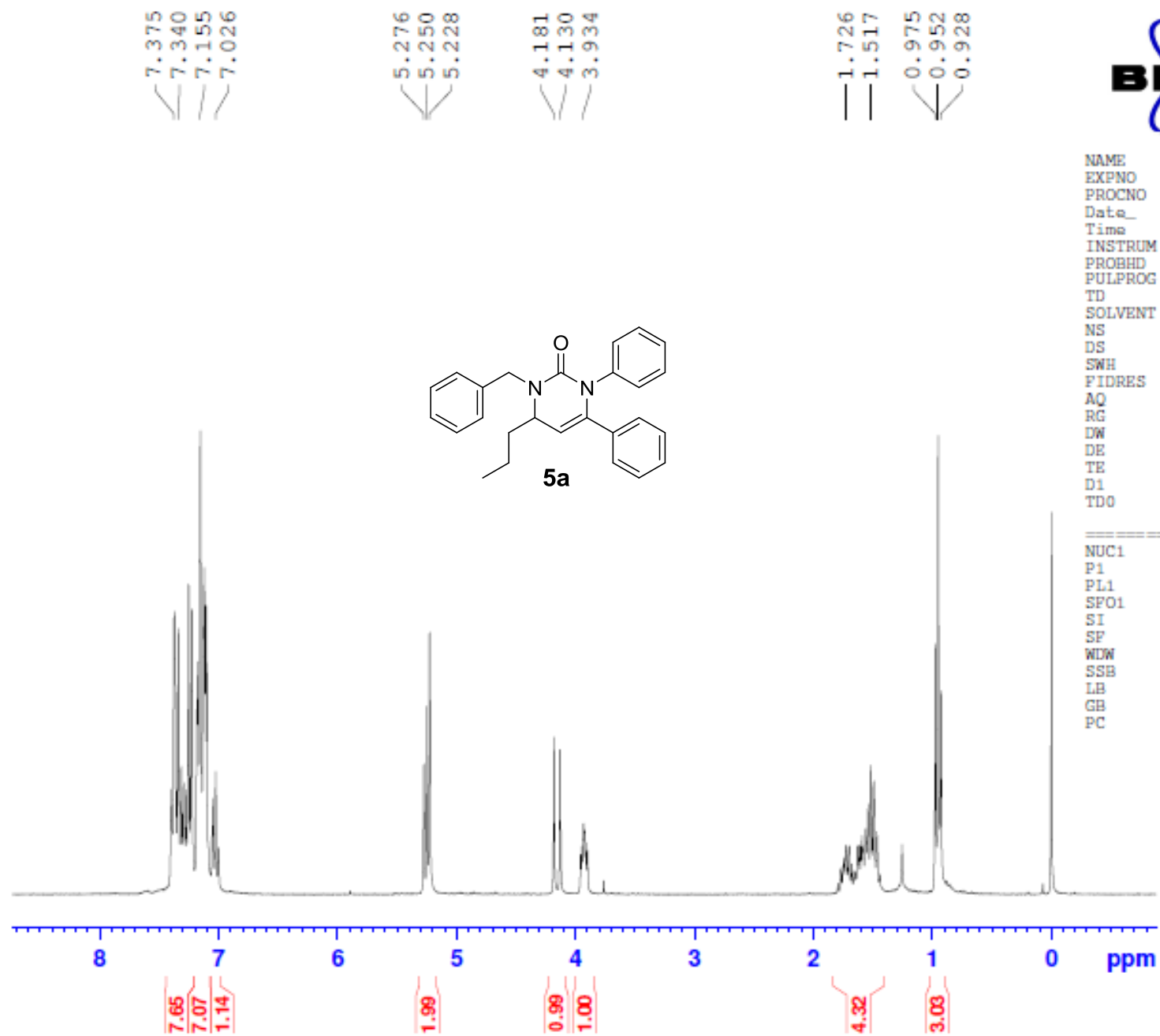
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† Present address: Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260, United States

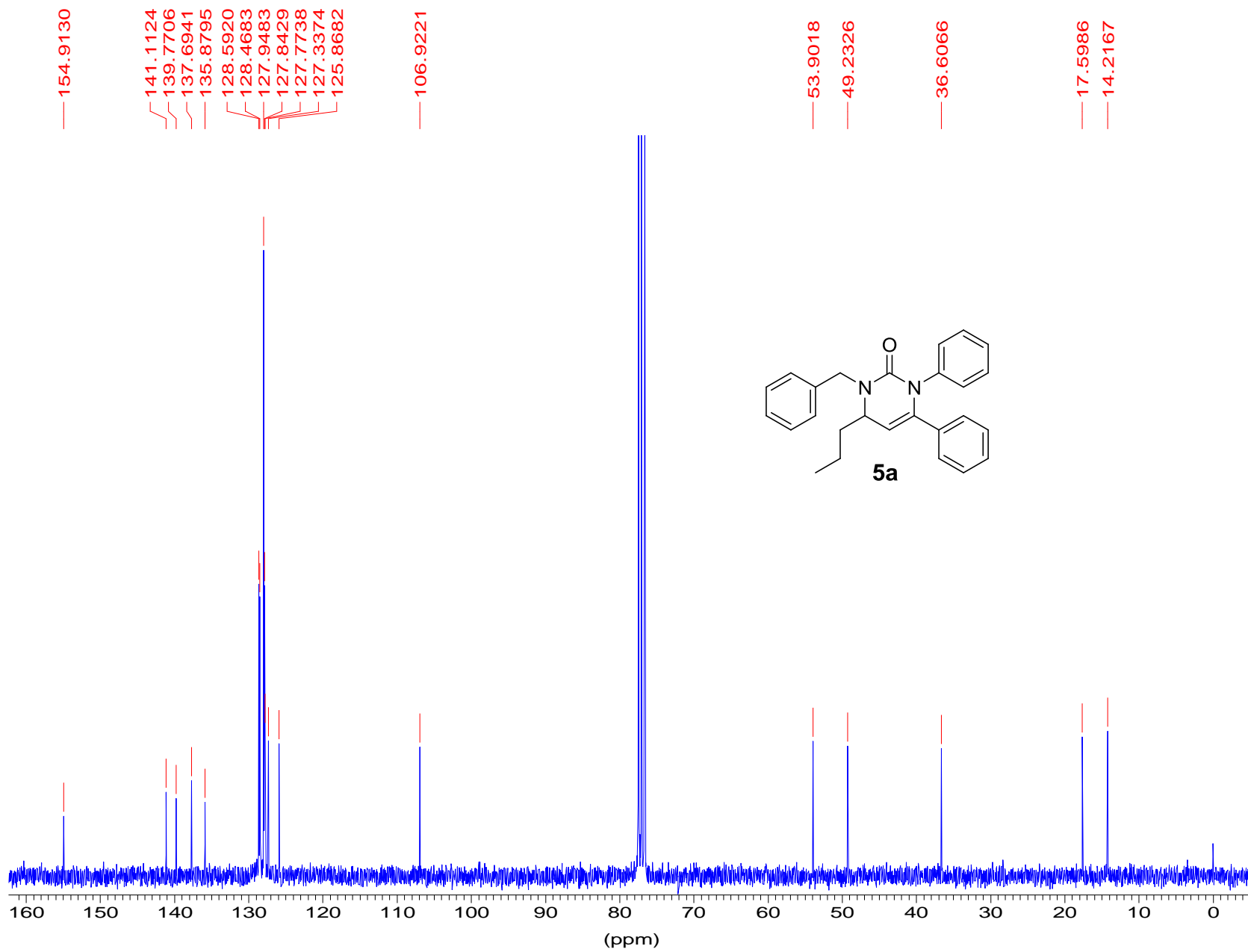
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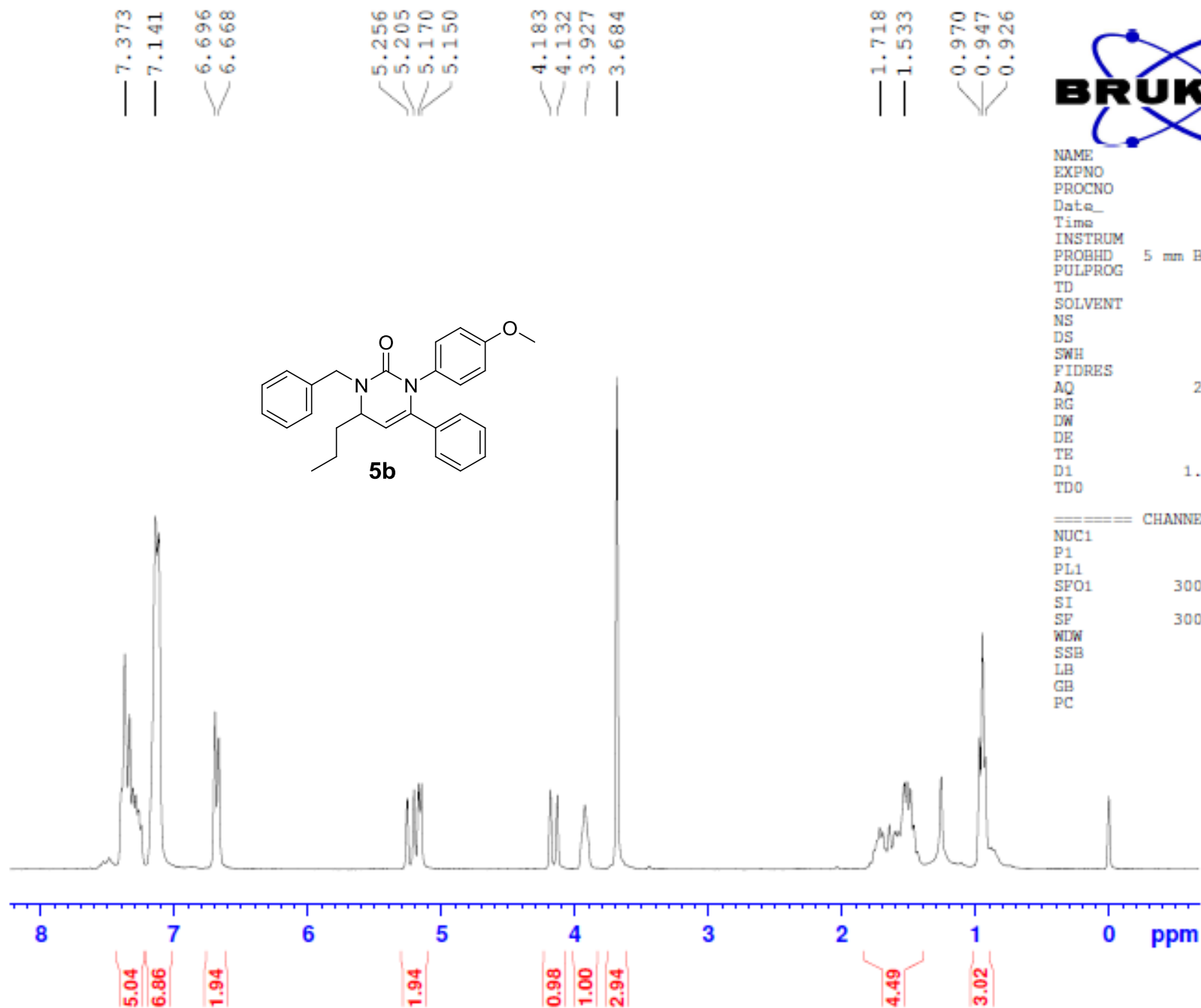
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```
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PROCNO        1
Date_         20130301
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PULPROG       zg30
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SOLVENT       CDCl3
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FIDRES        0.188380 Hz
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TD0           1
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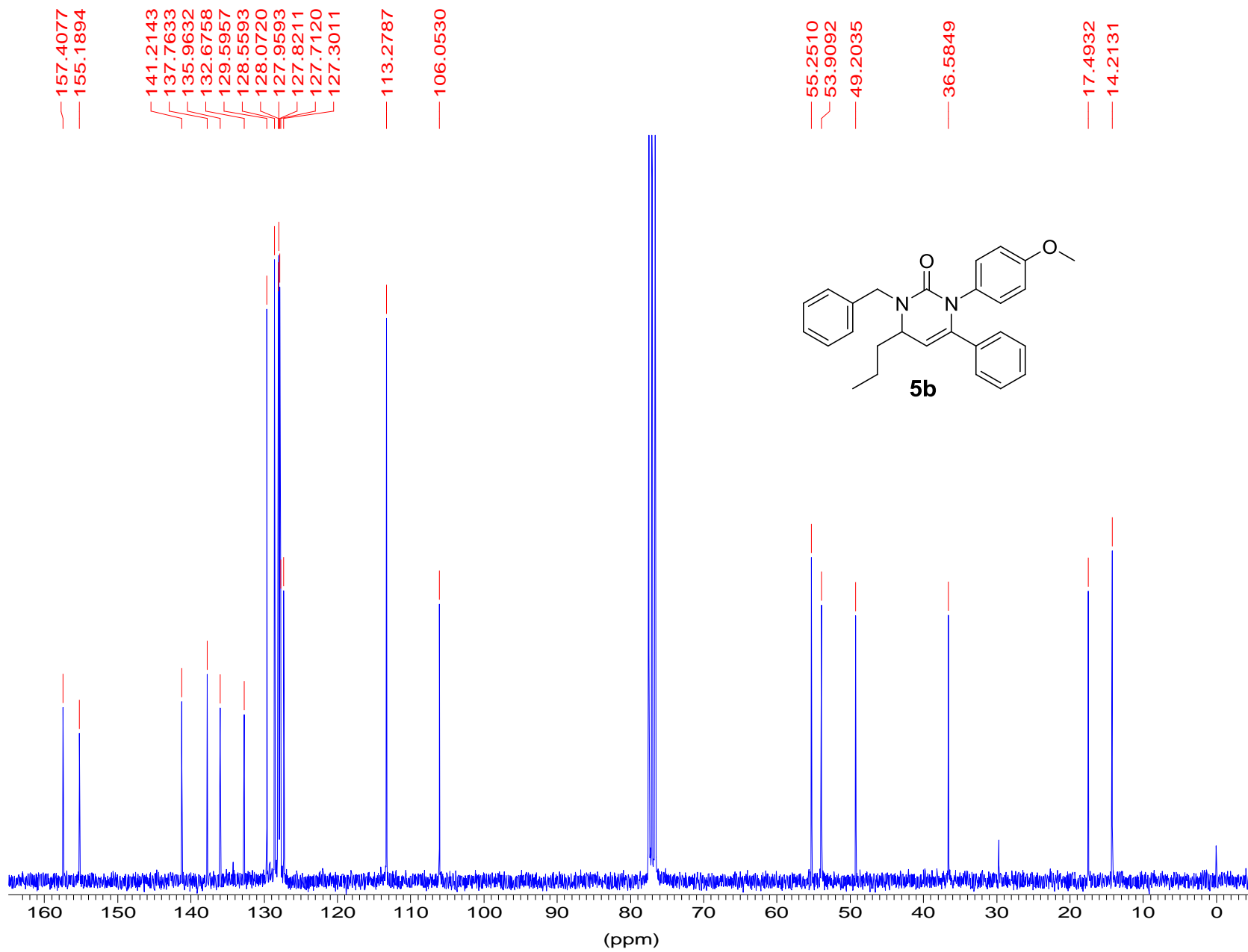
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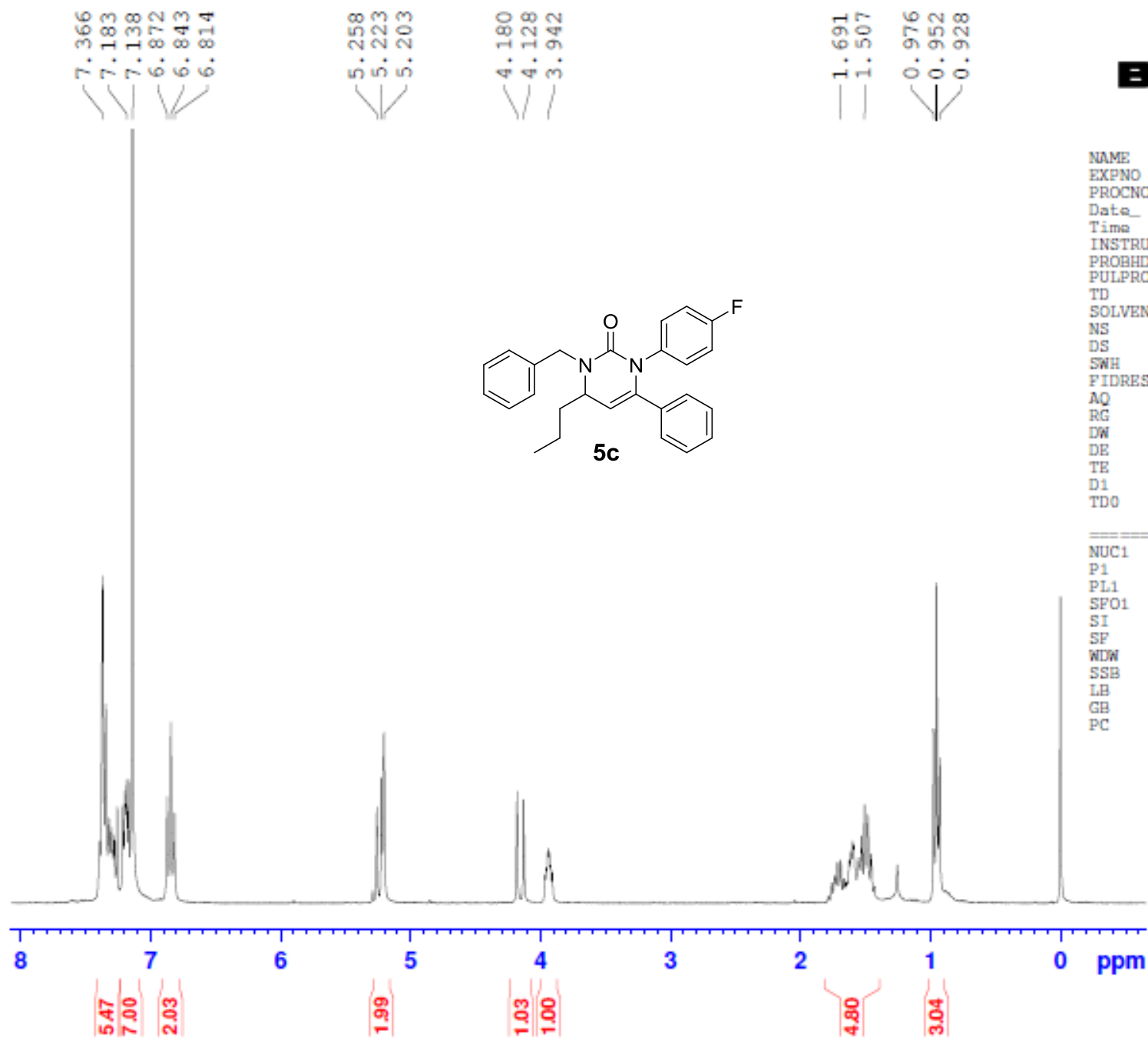




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TD            32768
SOLVENT       CDC13
NS            16
DS            2
SWH           6172.839 Hz
FIDRES        0.188380 Hz
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DE            6.50 usec
TE            296.5 K
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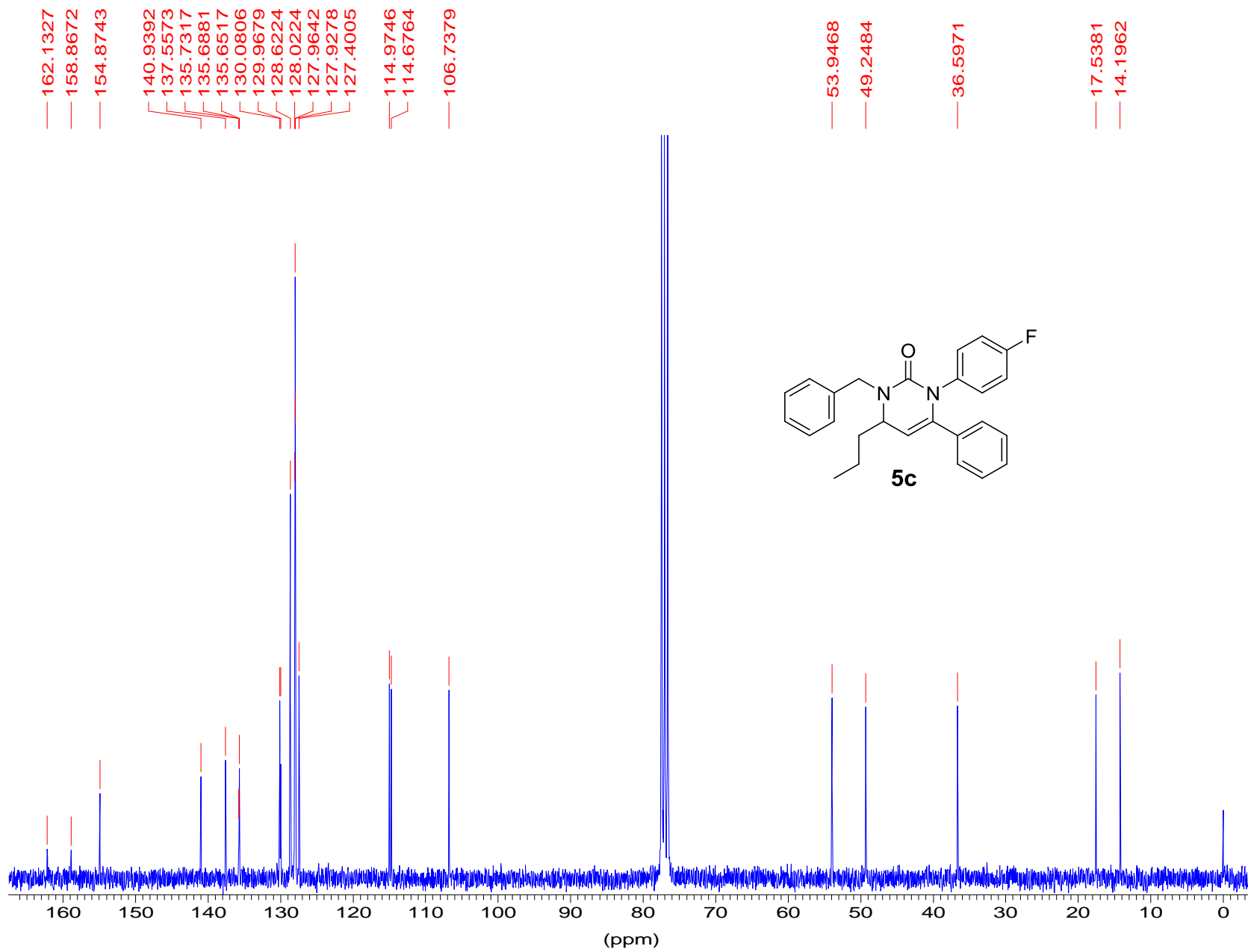
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P1            9.50 usec
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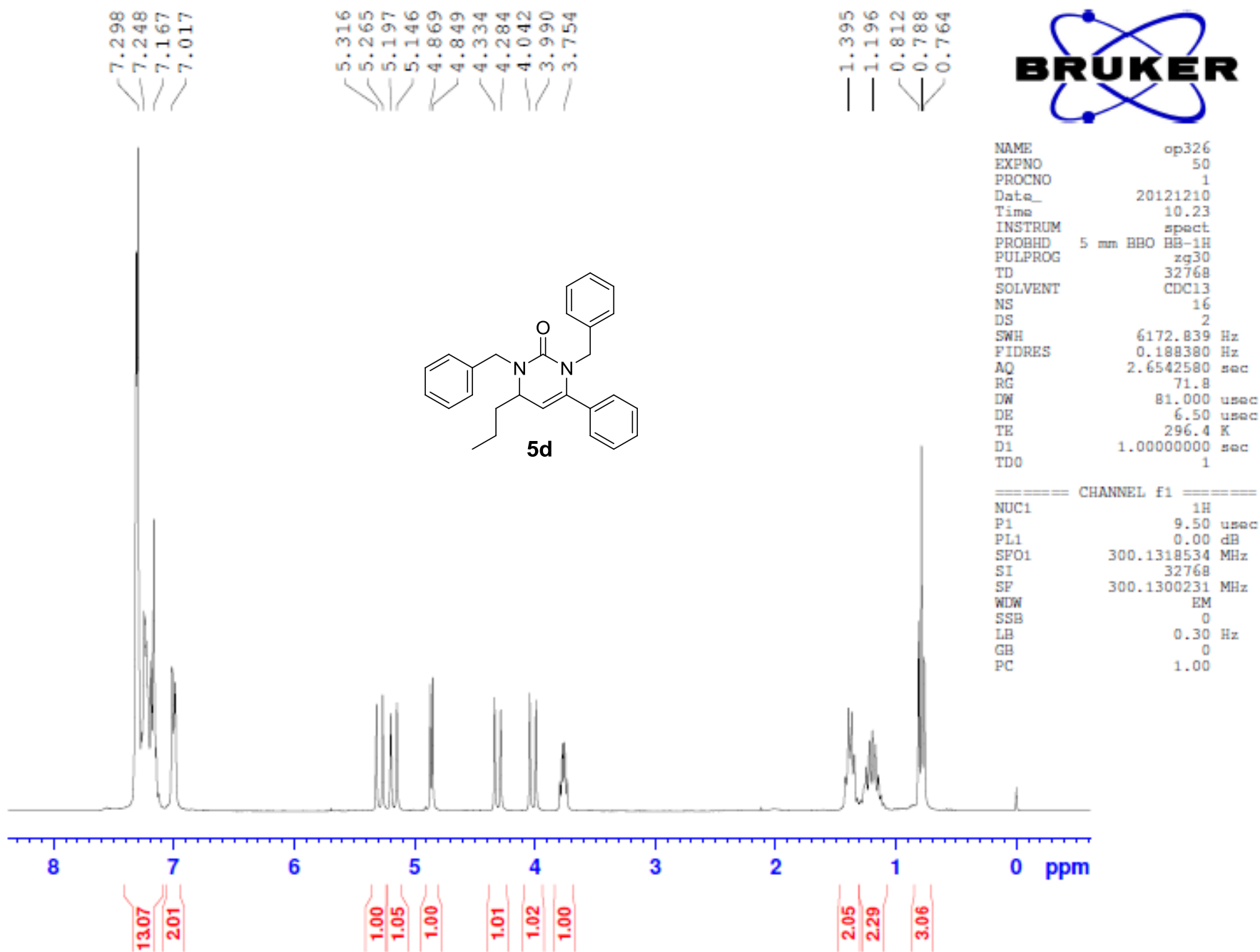


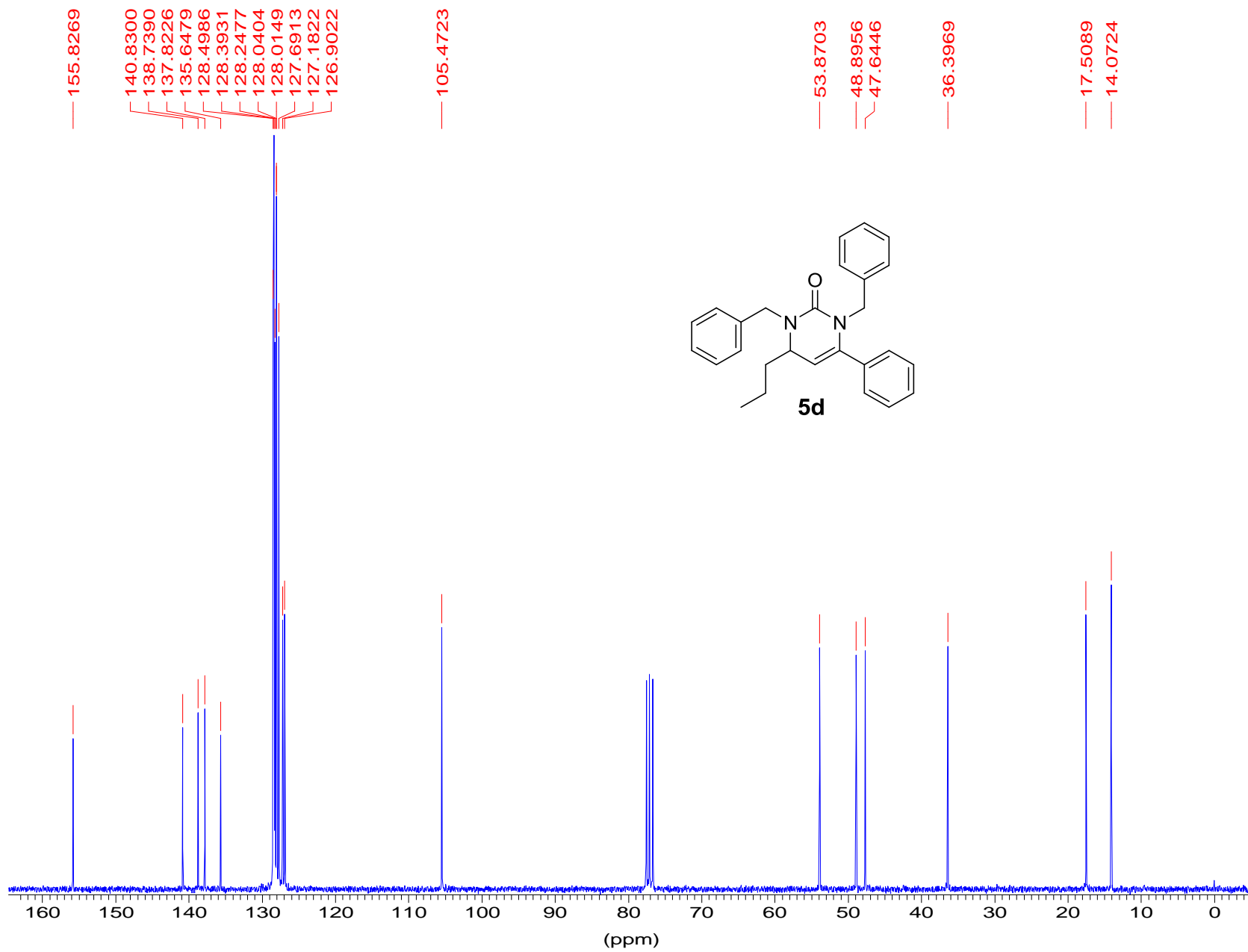


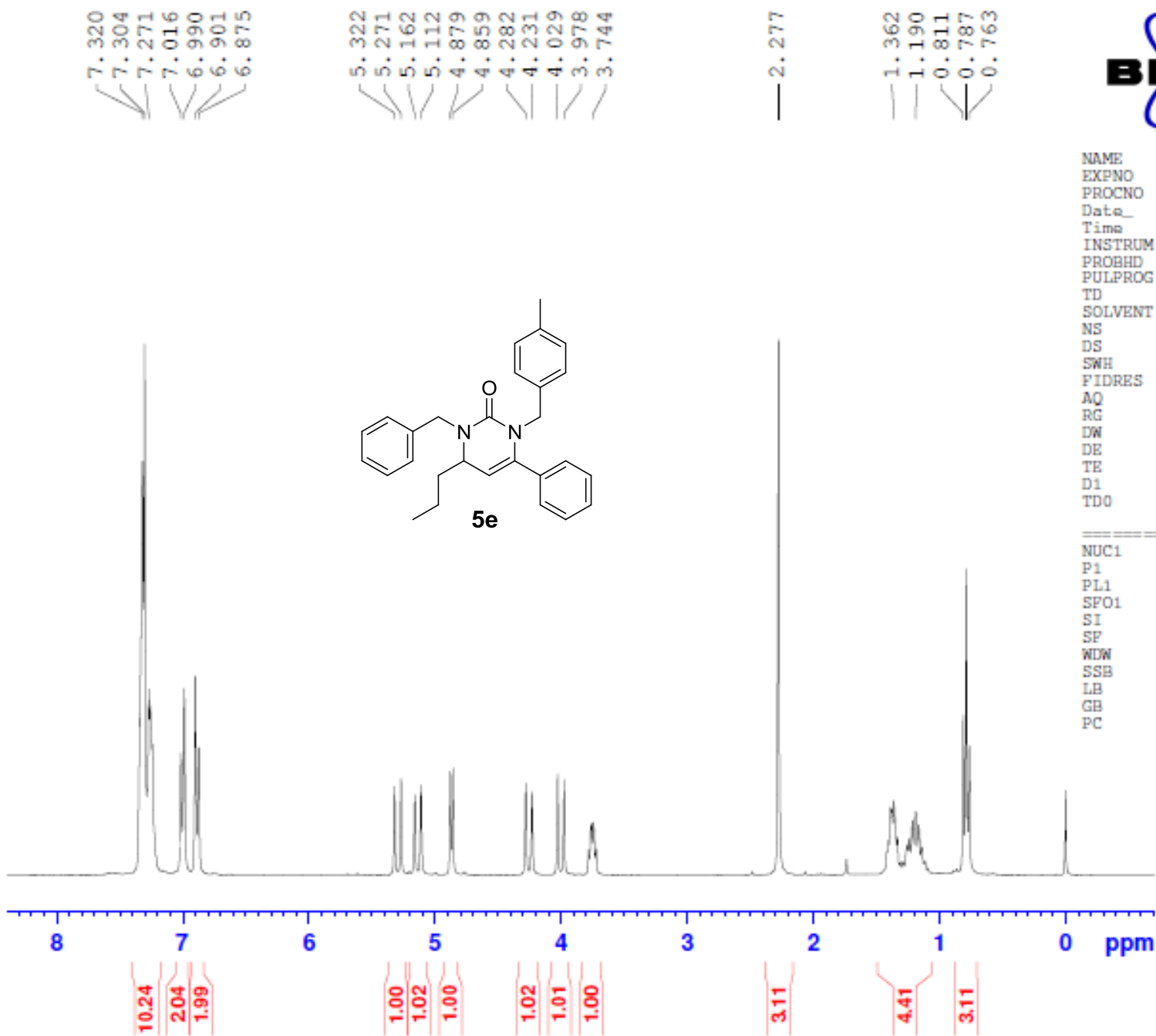
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PROCNO 1
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Time 10.04
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TD 32768
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 362
DW 81.000 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1

==== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
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SSB 0
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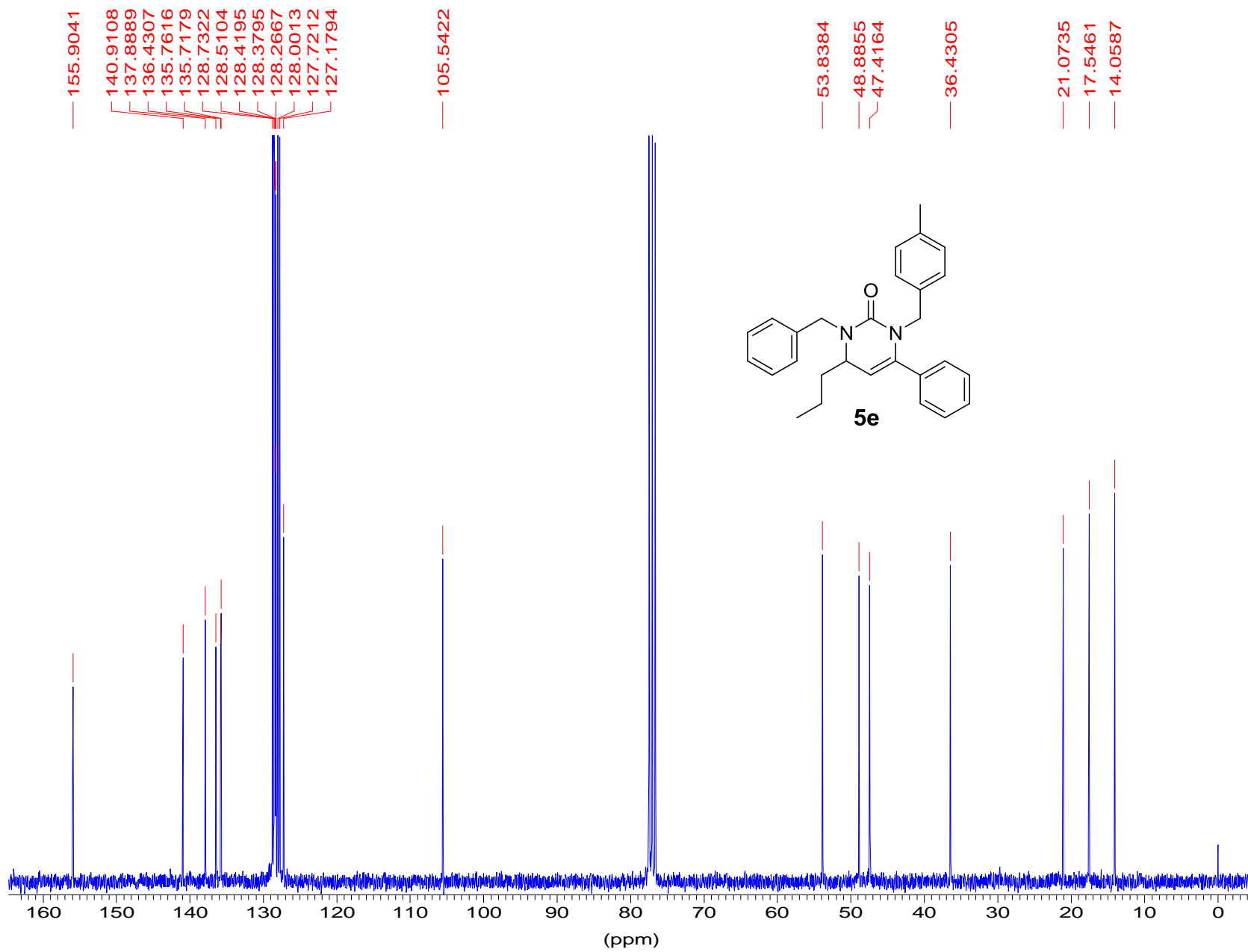


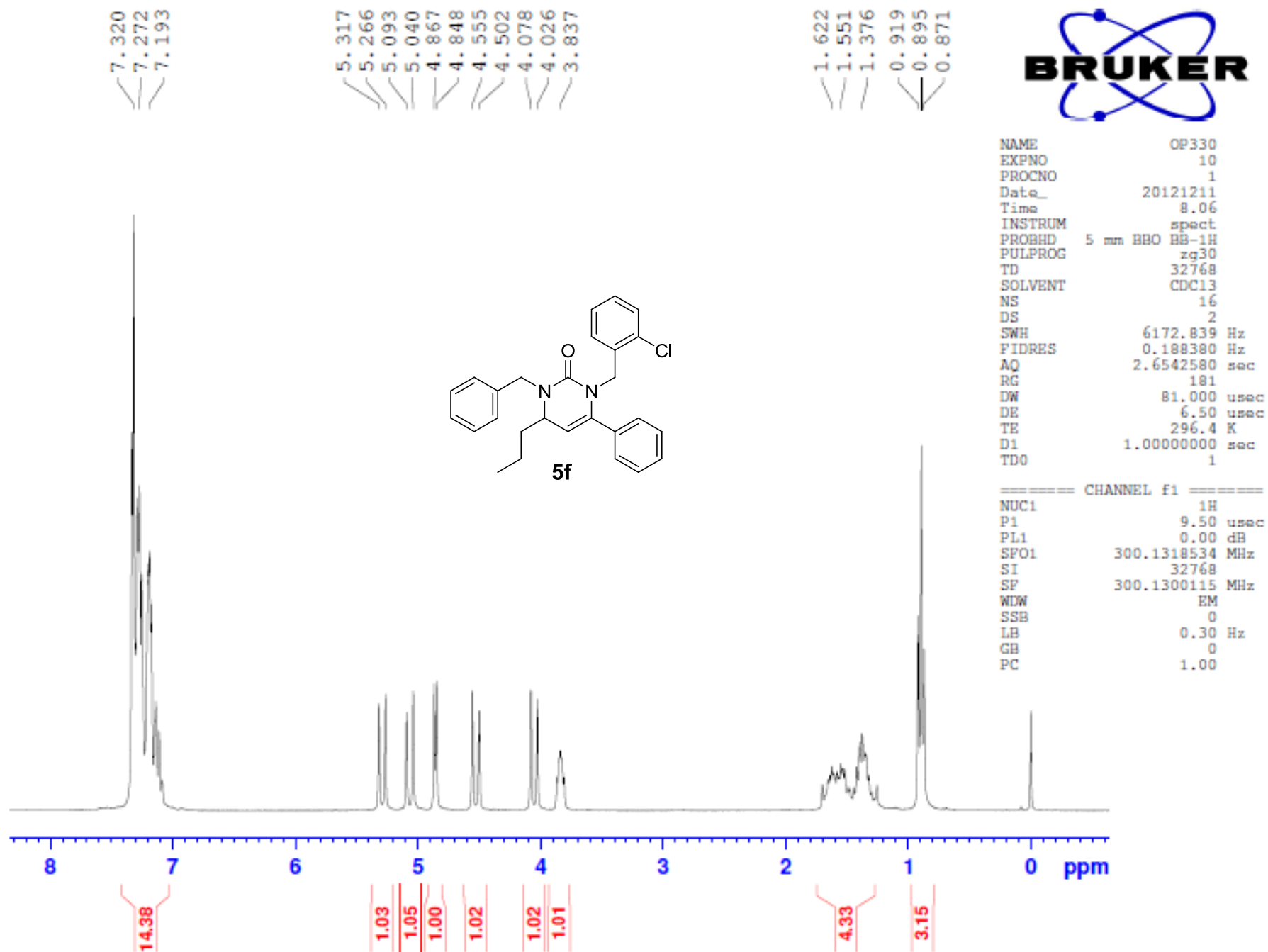


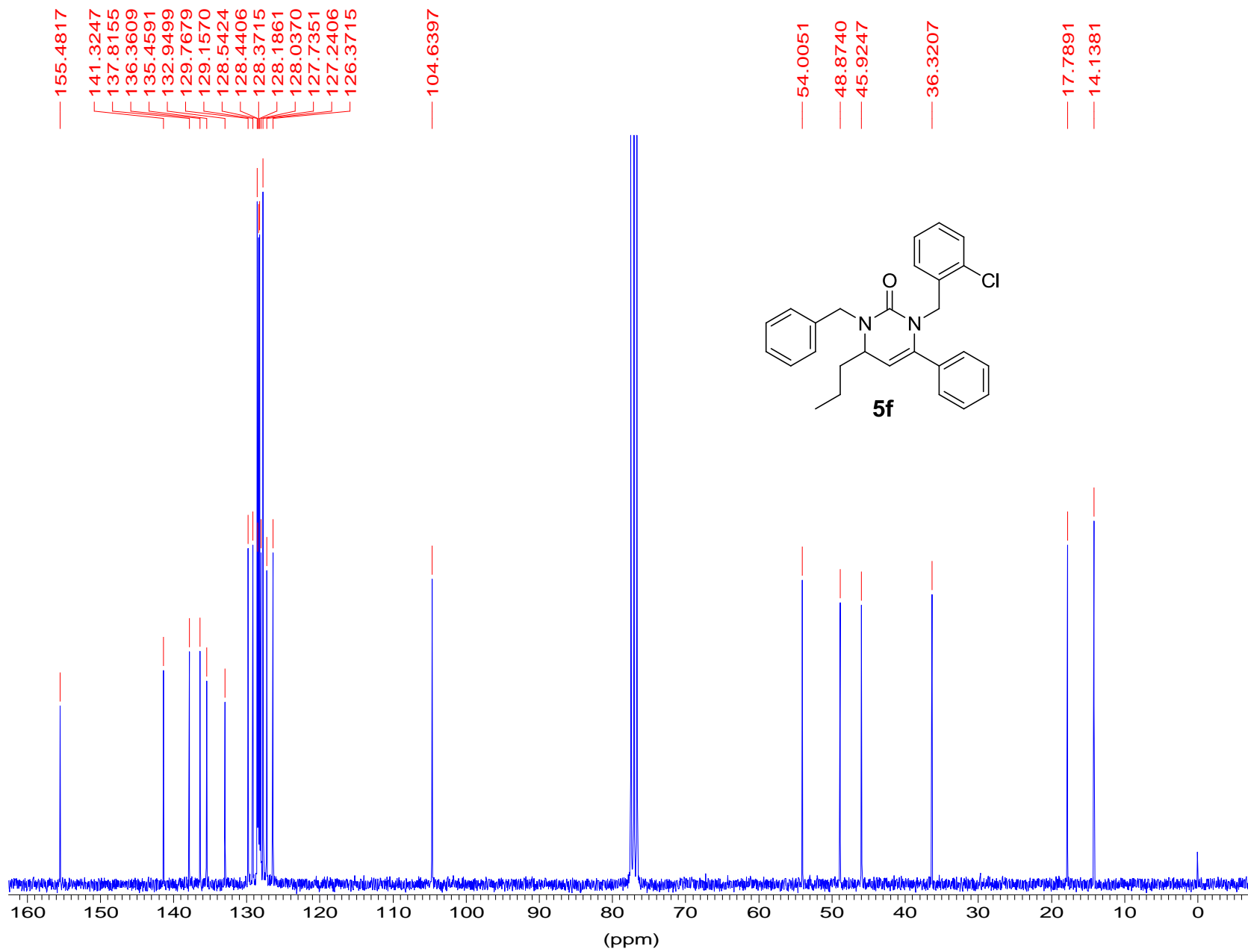


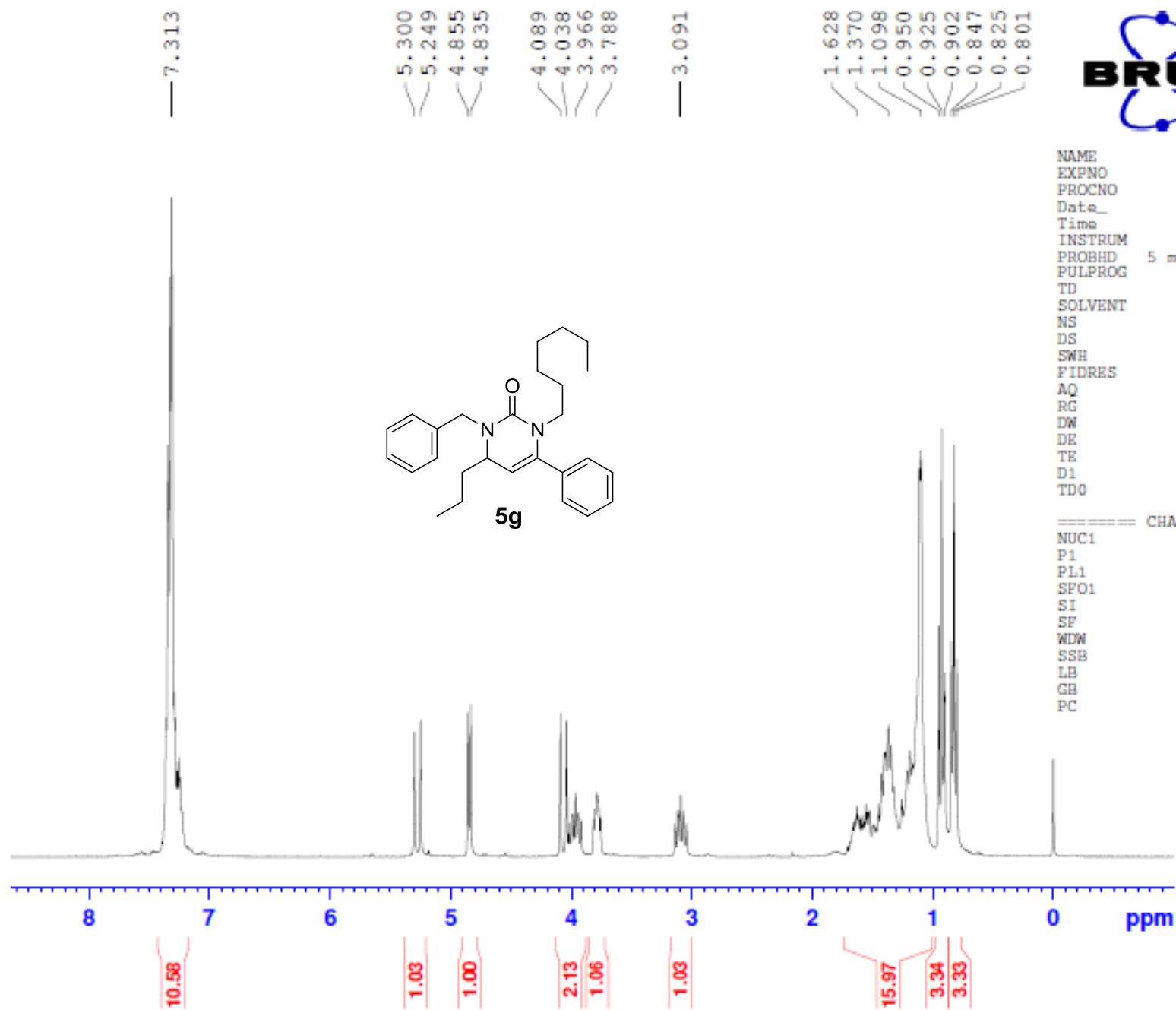
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SOLVENT CDCl3
NS 16
DS 2
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FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 181
DW 81.000 usec
DE 6.50 usec
TE 296.7 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
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SSB 0
LB 0.30 Hz
GB 0
PC 1.00



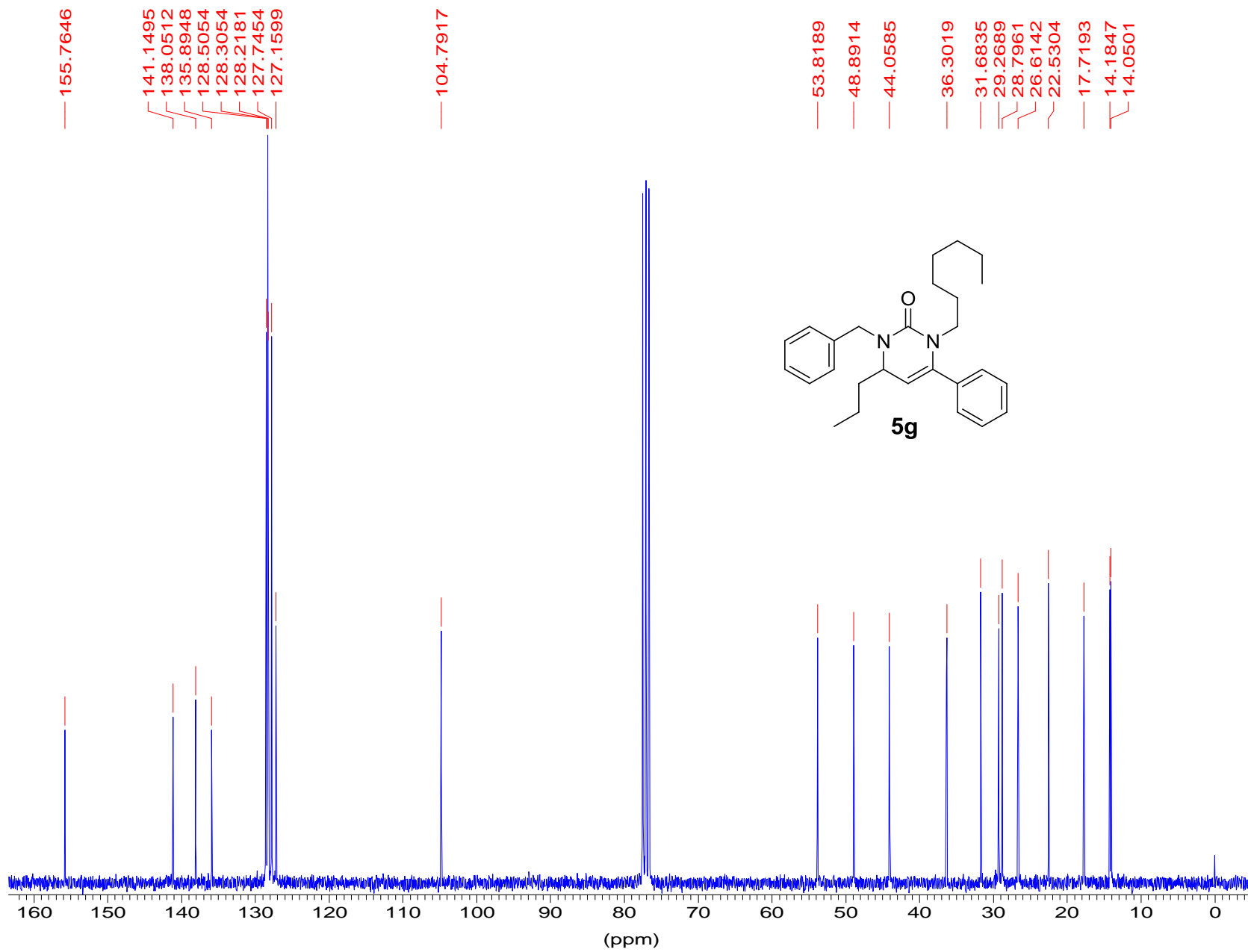






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PROCNO 1
Date_ 20121210
Time 10.10
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 128
DW 81.000 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300079 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





```
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EXPNO         10
PROCNO        1
Date_         20130130
Time          8.40
INSTRUM       spect
PROBHD        5 mm BBO HB-1H
PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            16
DS            2
SWH           6172.839 Hz
FIDRES        0.188380 Hz
AQ            2.6542580 sec
RG            512
DW            81.000 usec
DE            6.50 usec
TE            296.4 K
D1            1.00000000 sec
TD0           1
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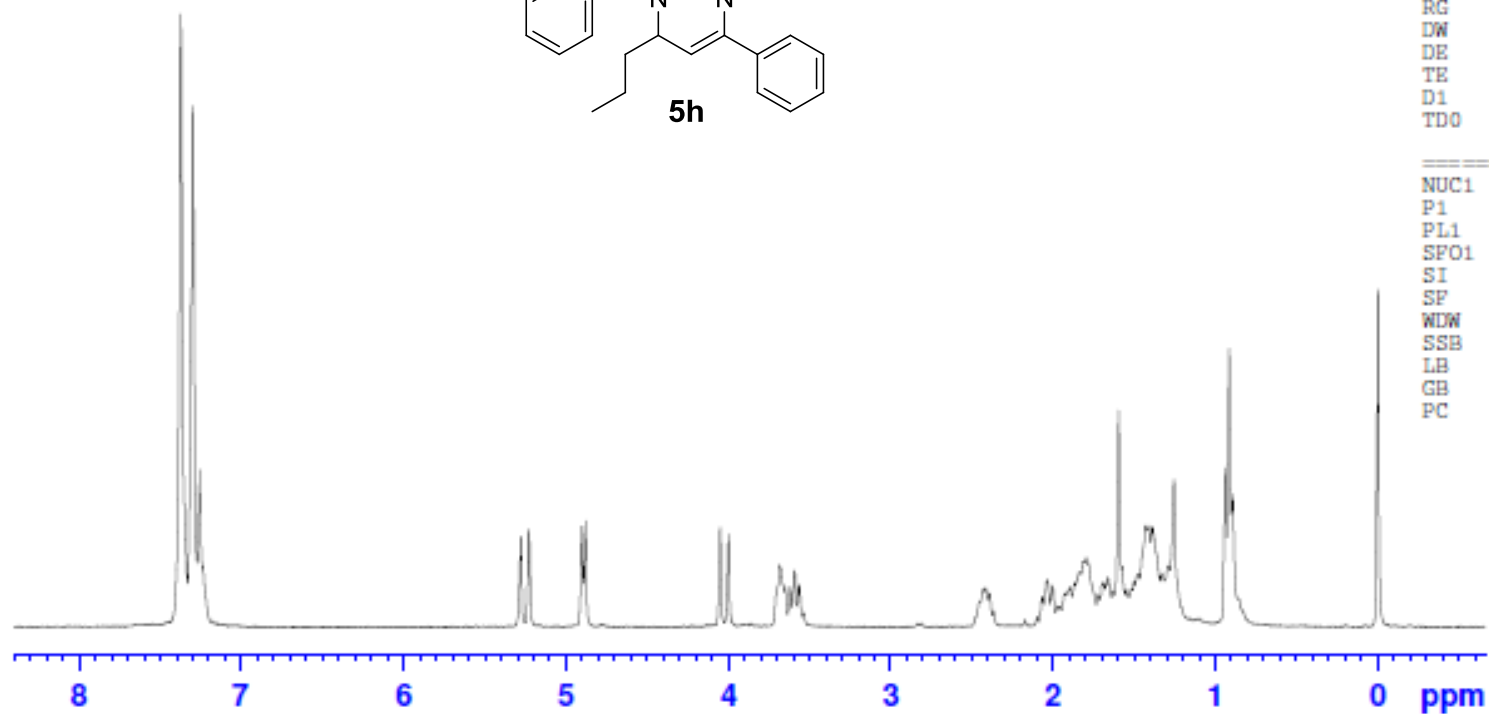
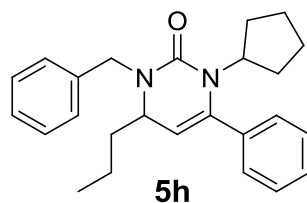
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SI            32768
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WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
```

7.374
7.298
7.259

5.280
5.229
4.903
4.881

4.052
4.000
3.684
3.593

2.417
2.039
1.795
1.410
0.939
0.915
0.893



10.77

1.05

1.00

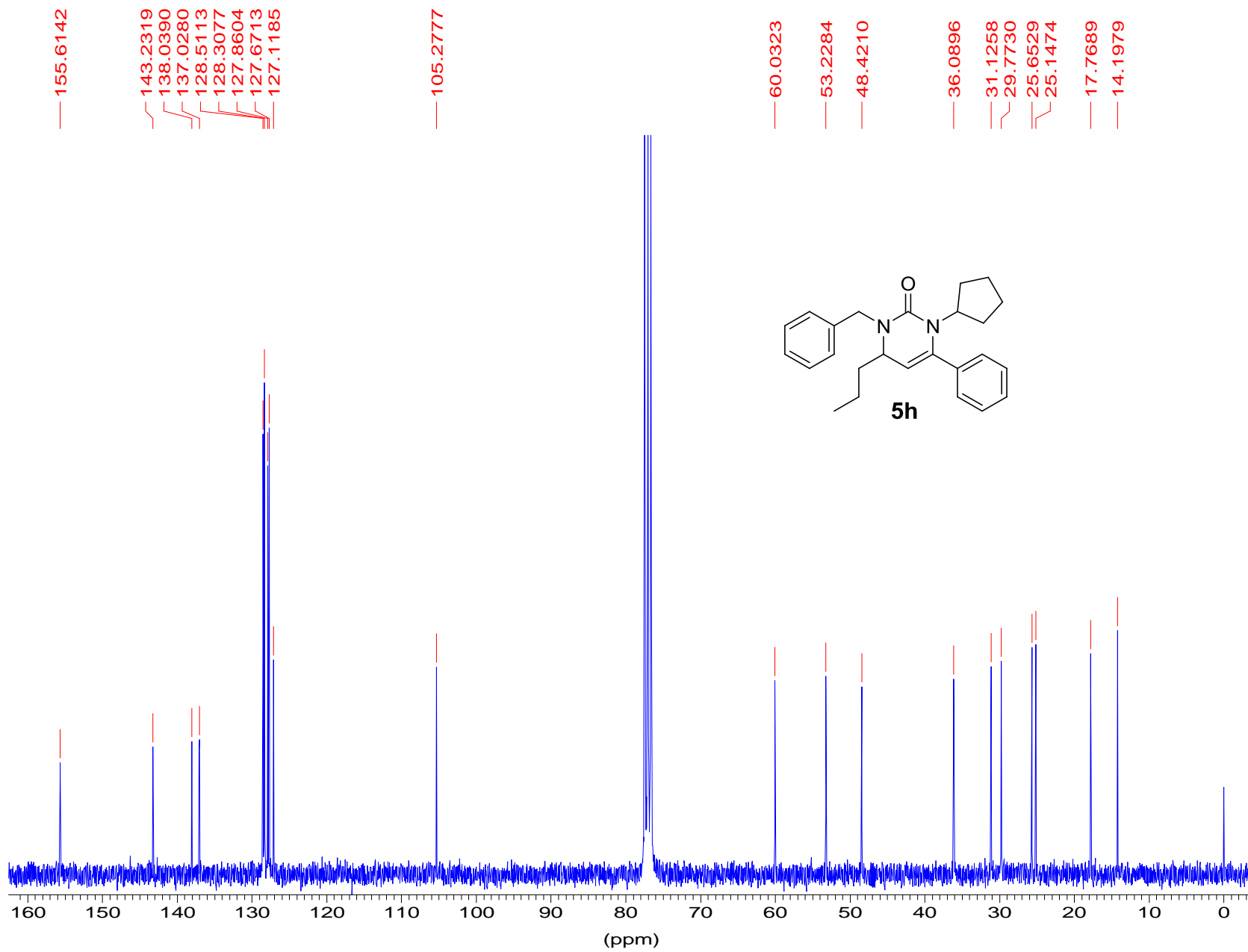
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2.05

1.04

14.64

3.36

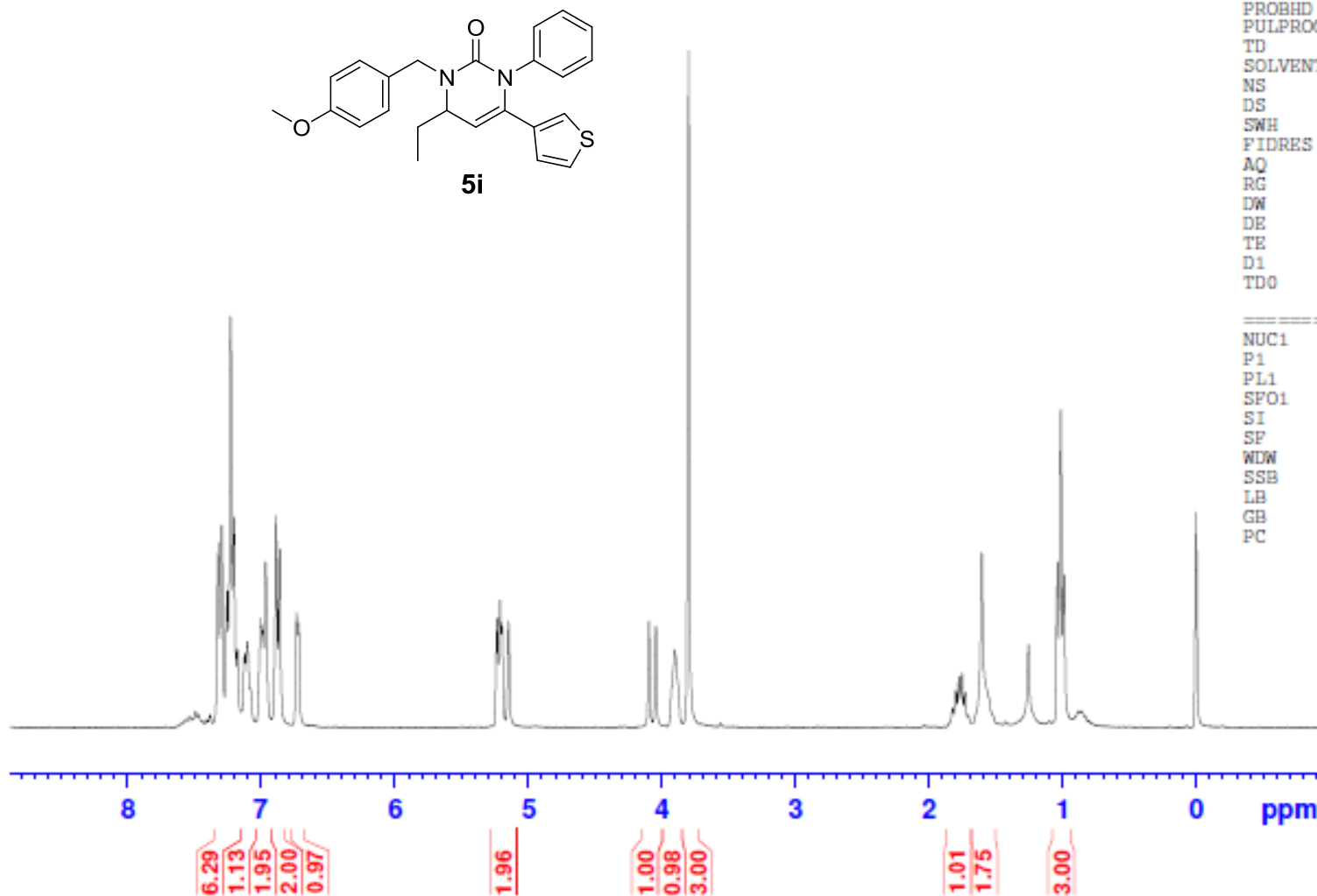
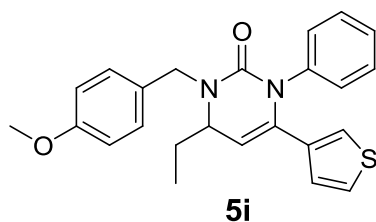


7.324
7.297
7.232
7.105
6.970
6.890
6.863
6.737

5.235
5.214
5.200
5.149

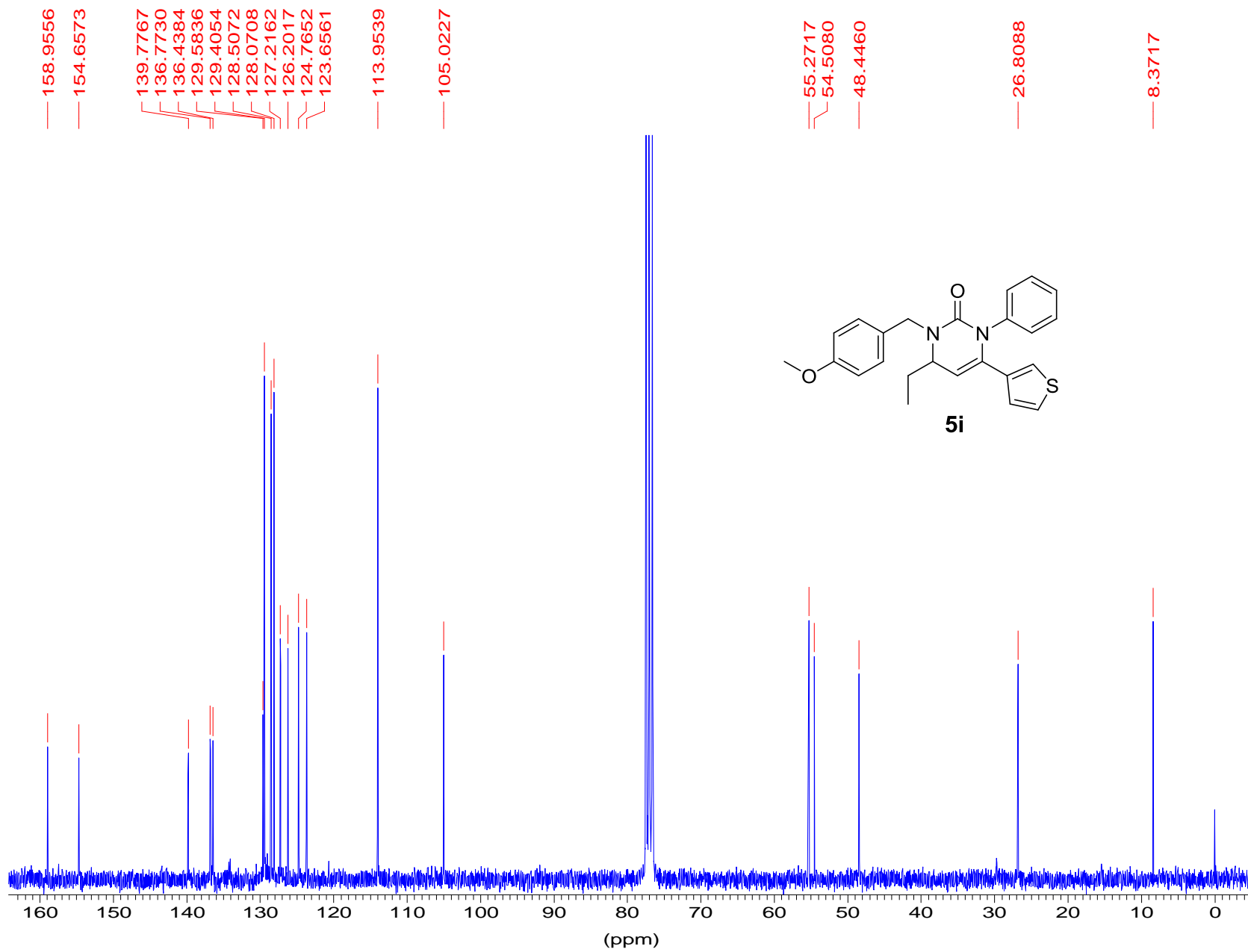
4.098
4.047
3.906
3.801

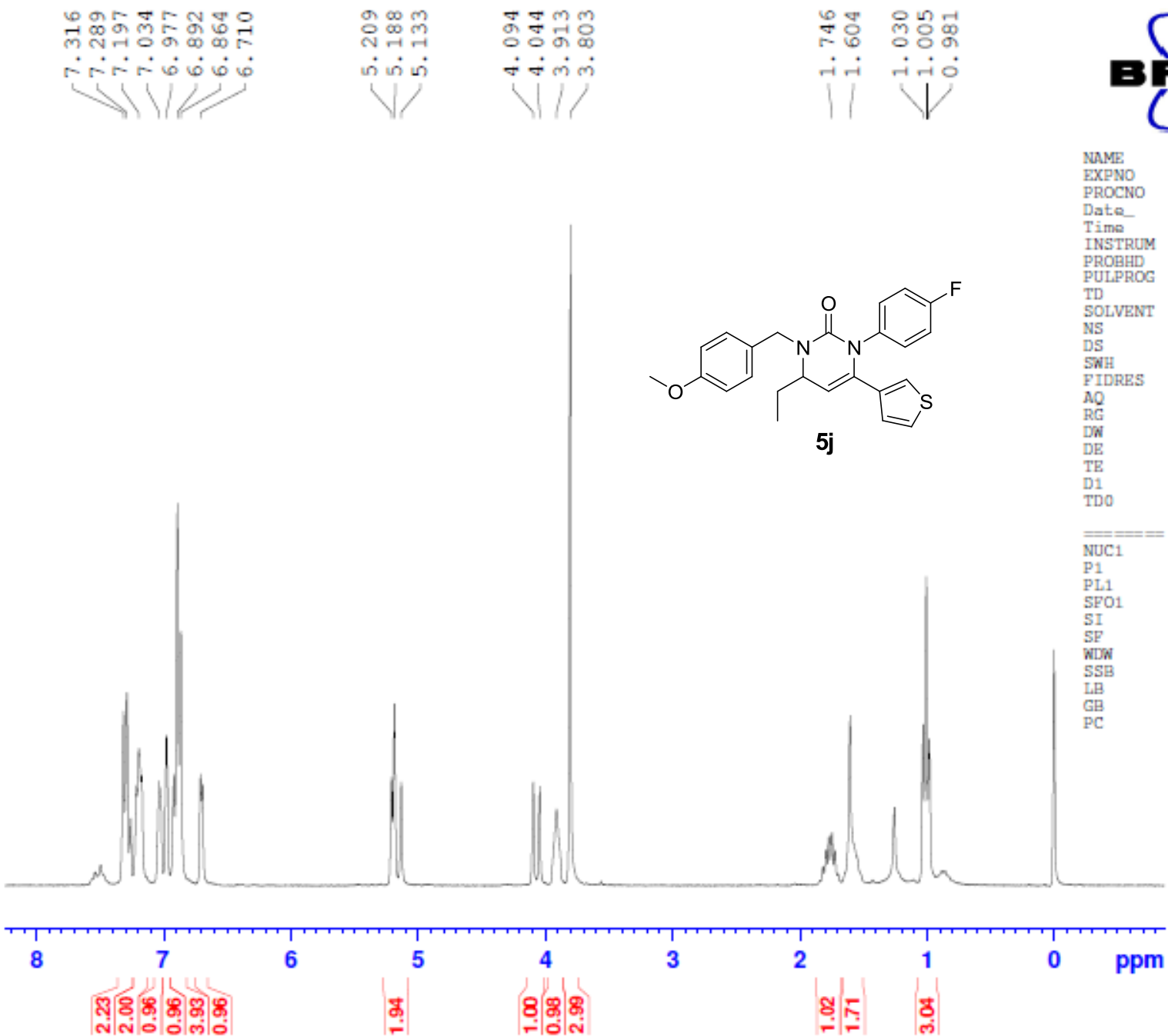
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1.606
1.038
1.014
0.990



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INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            16
DS            2
SWH           6172.839 Hz
FIDRES        0.188380 Hz
AQ            2.6542580 sec
RG            456.1
DW            81.000 usec
DE            6.50 usec
TE            296.2 K
D1            1.00000000 sec
TD0           1
```

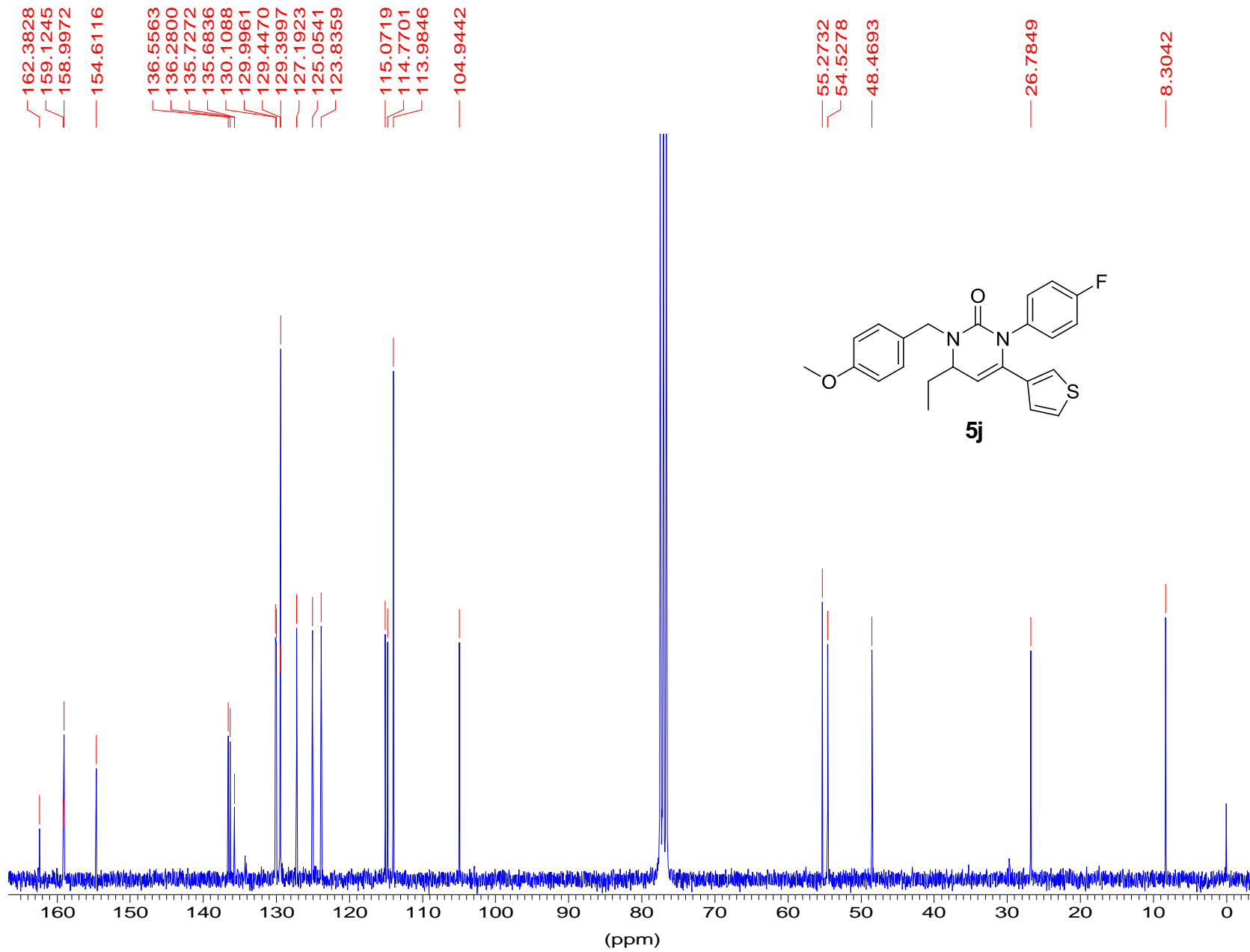
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PL1           0.00 dB
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SI            32768
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WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
```

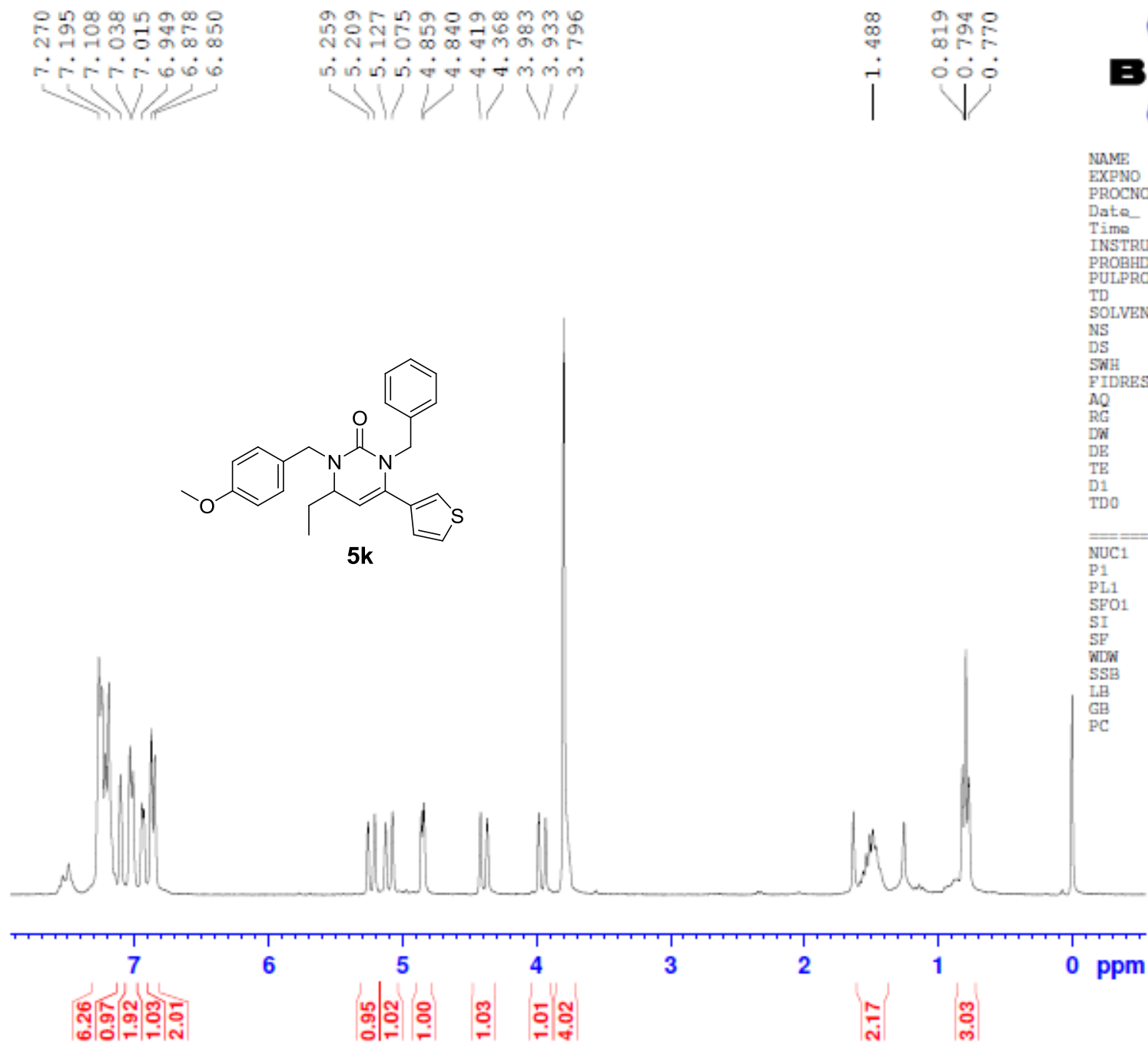




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NAME          OP313
EXPNO         10
PROCNO        1
Date_         20121120
Time          8.34
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            16
DS            2
SWH           6172.839 Hz
FIDRES        0.188380 Hz
AQ            2.6542580 sec
RG            456.1
DW            81.000 usec
DE            6.50 usec
TE            296.2 K
D1            1.00000000 sec
TD0           1
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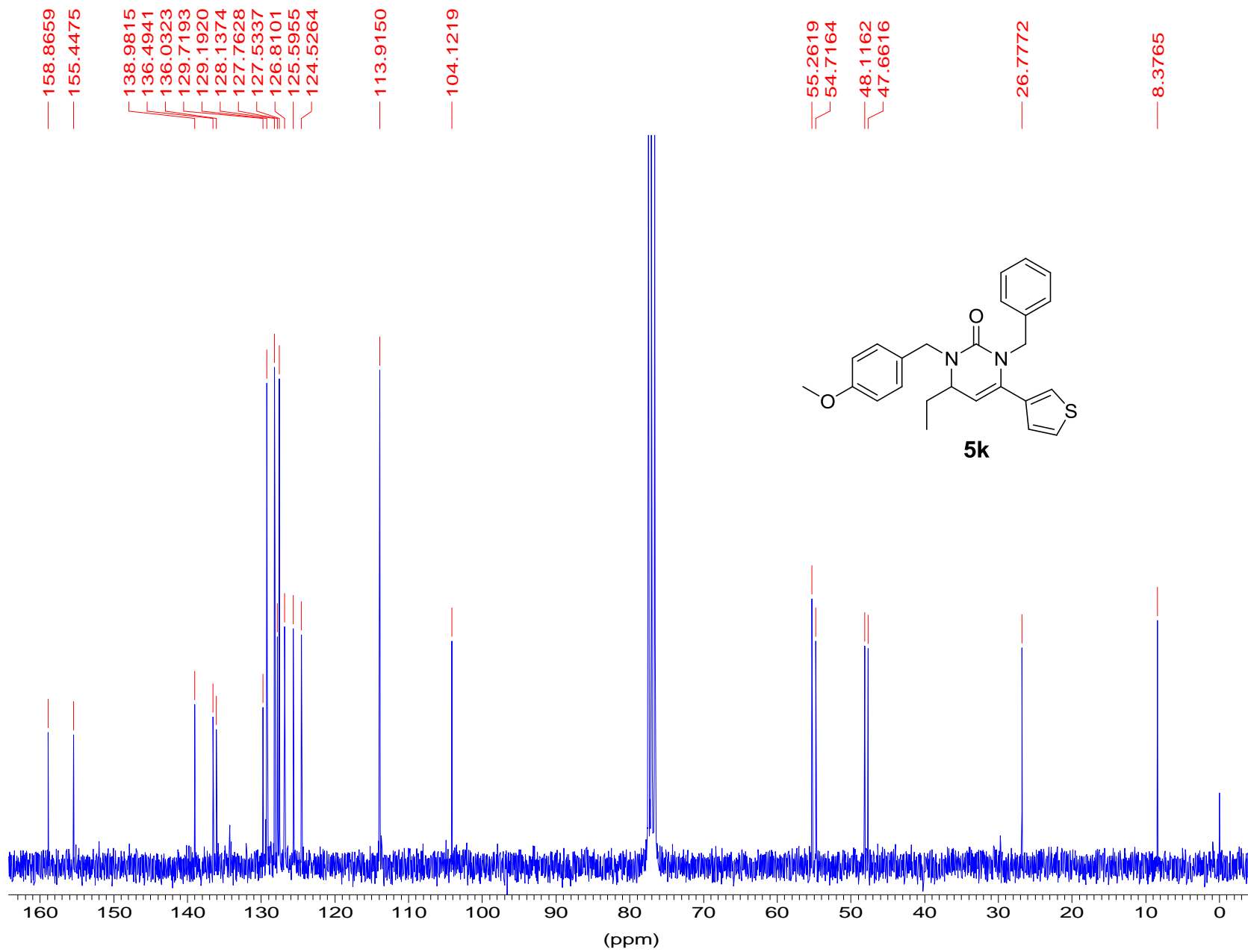
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WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
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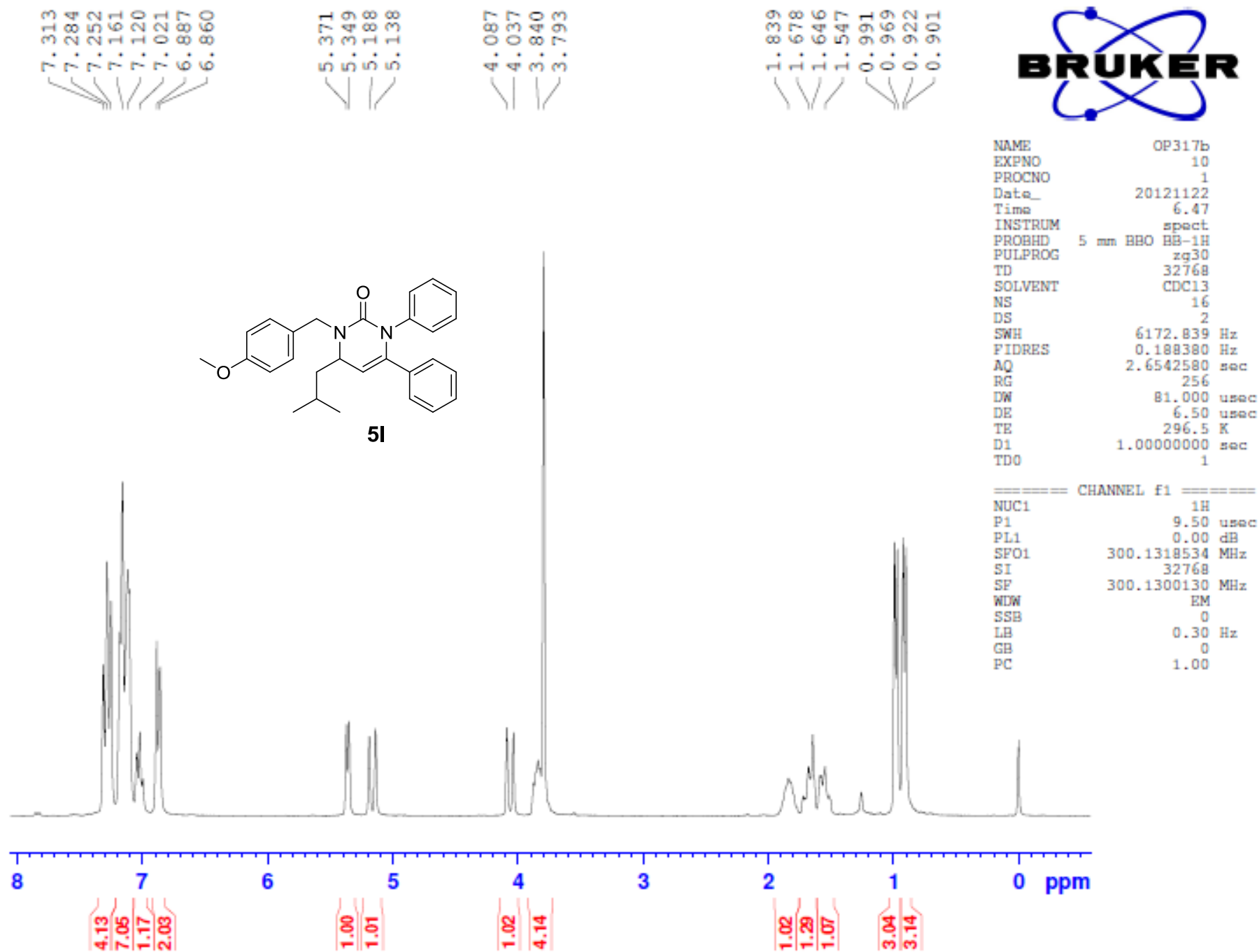


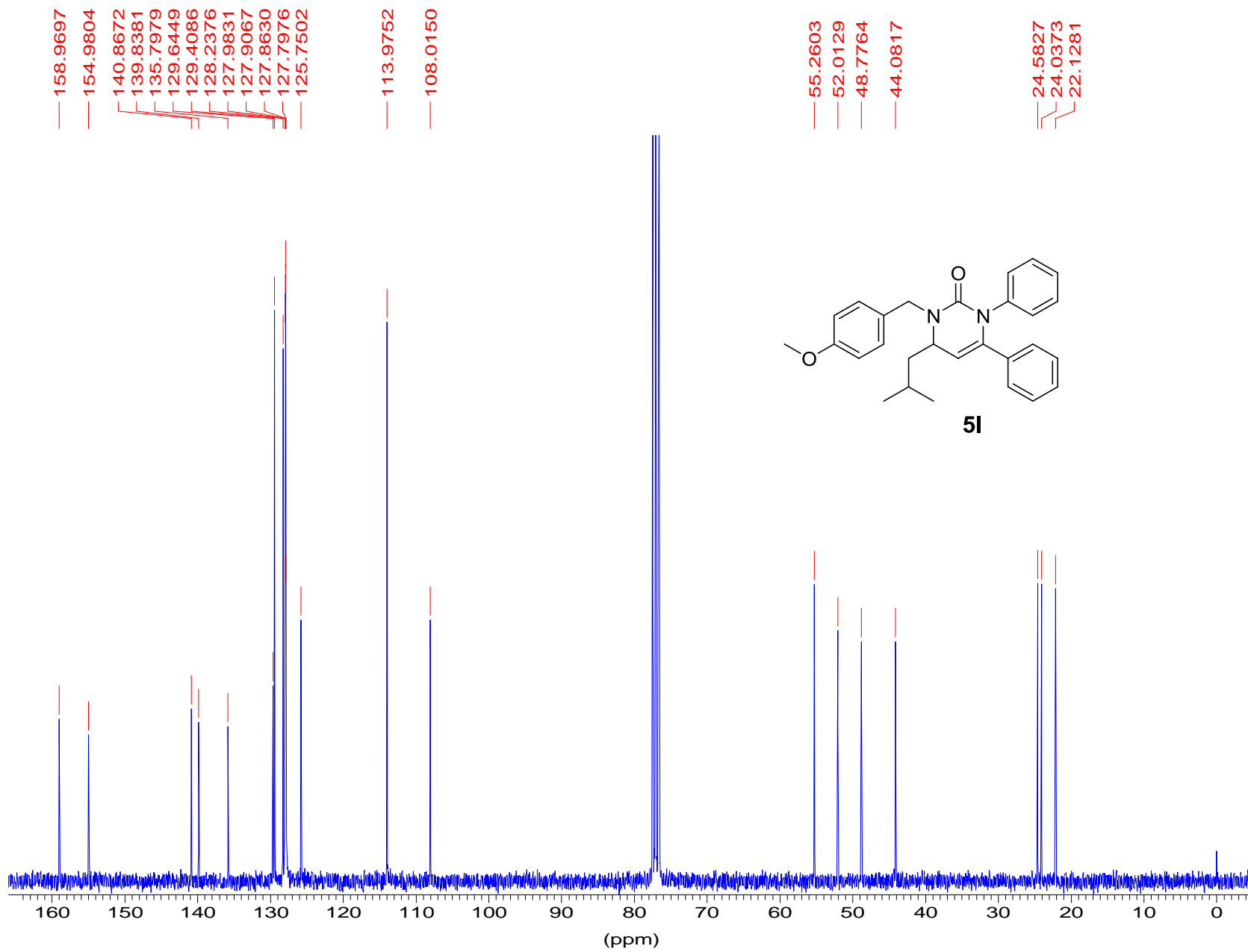


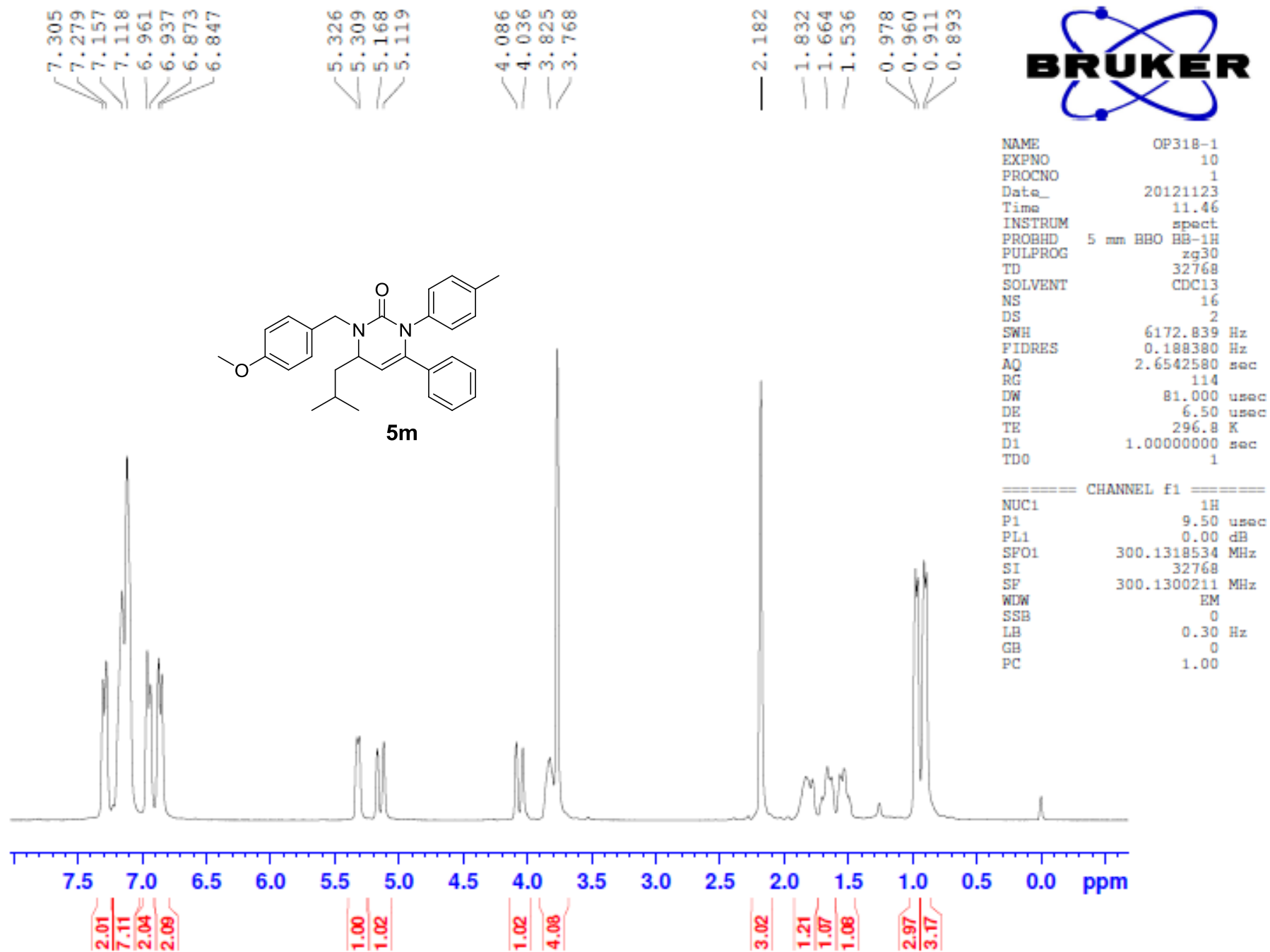
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PROCNO 1
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 362
DW 81.000 usec
DE 6.50 usec
TE 296.2 K
D1 1.00000000 sec
TD0 1

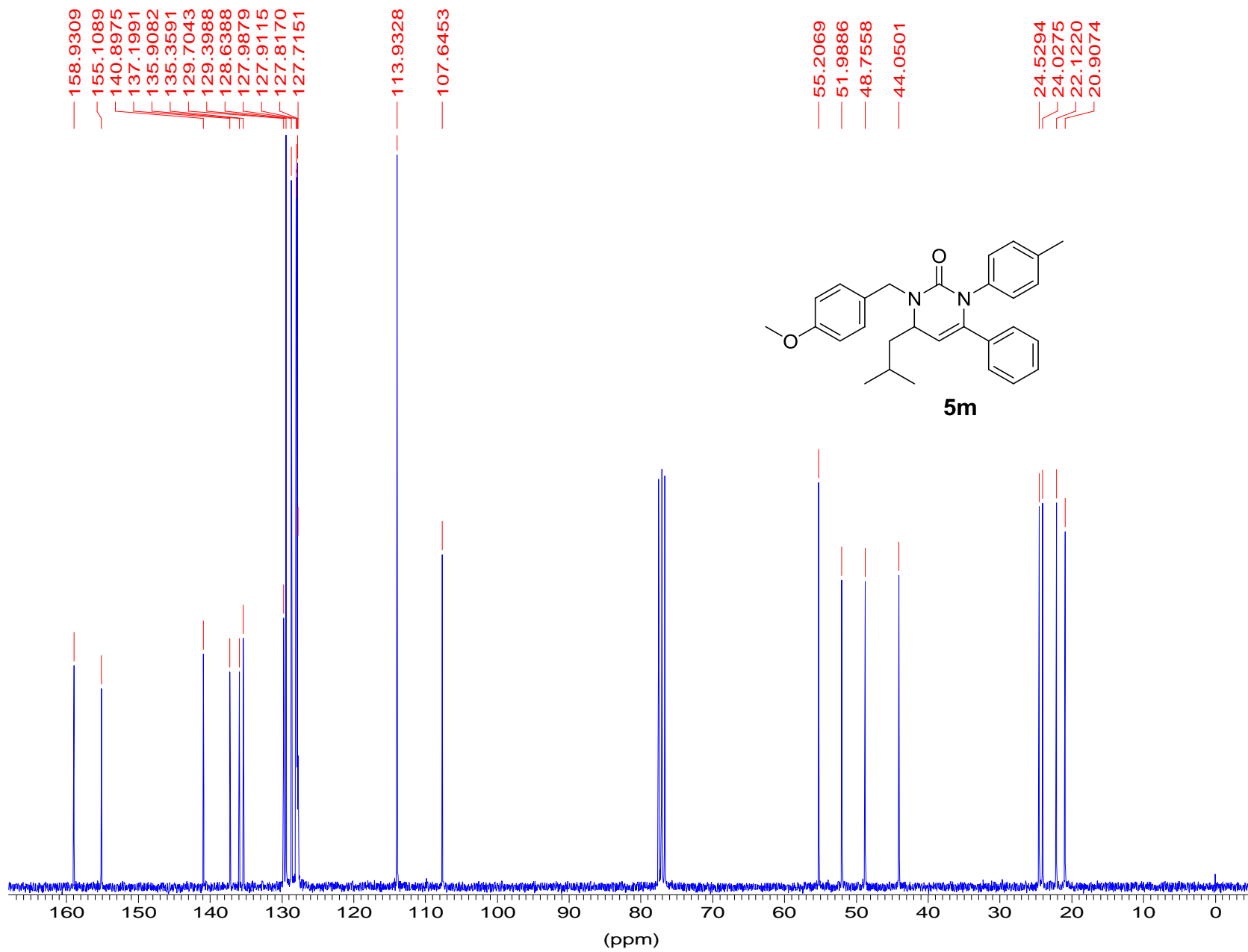
===== CHANNEL f1 =====
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PL1 0.00 dB
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SI 32768
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SSB 0
LB 0.30 Hz
GB 0
PC 1.00

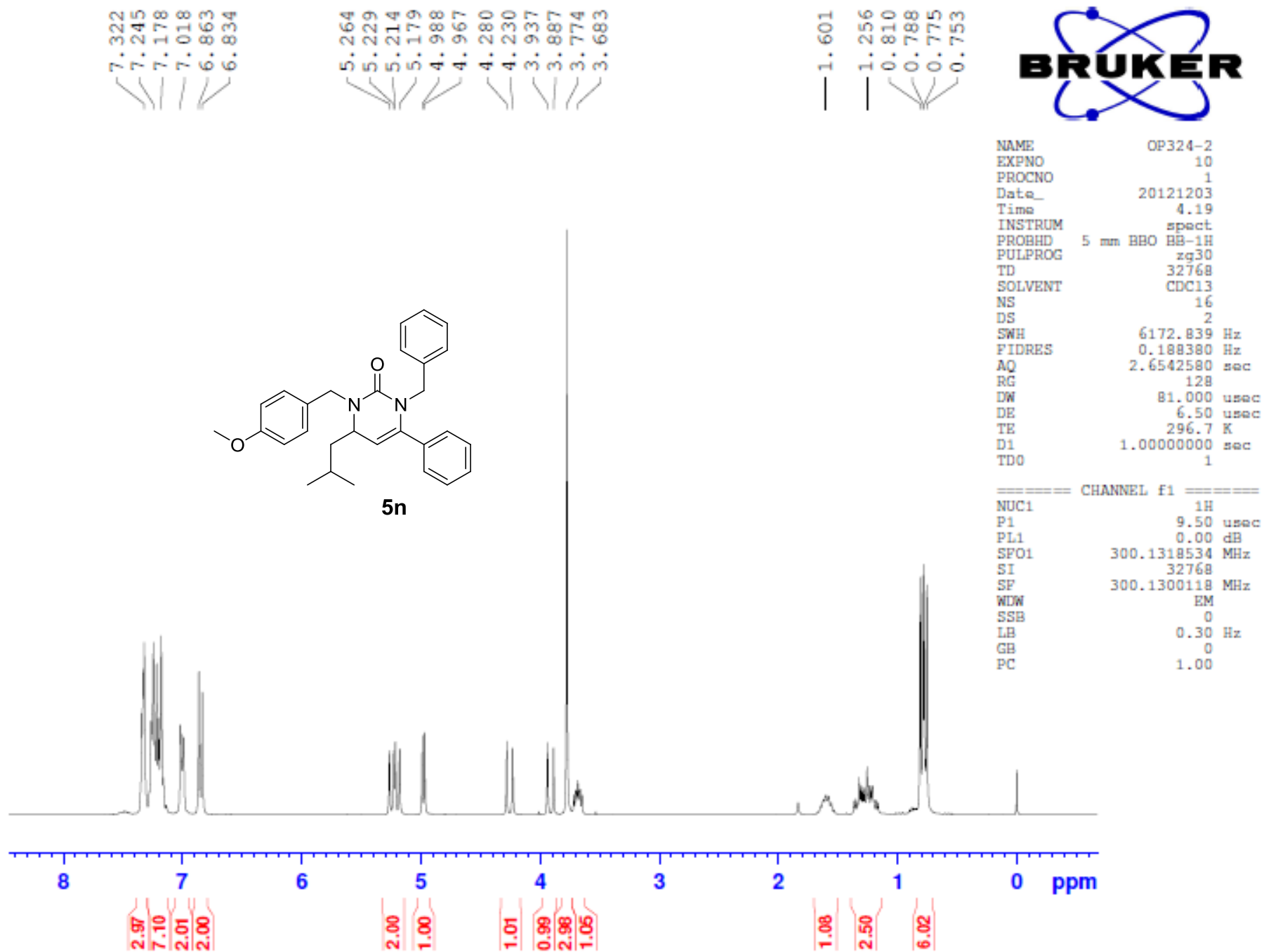


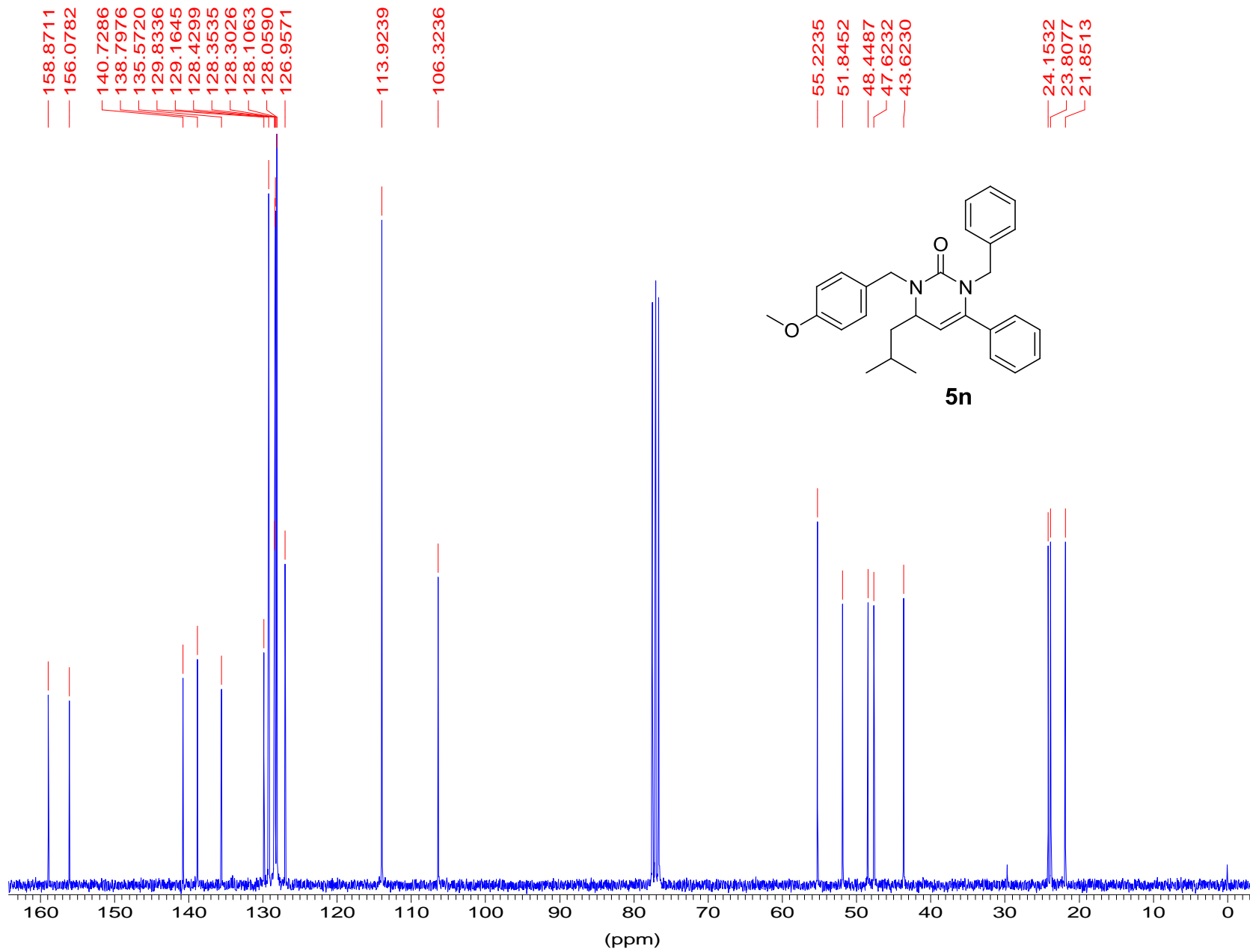


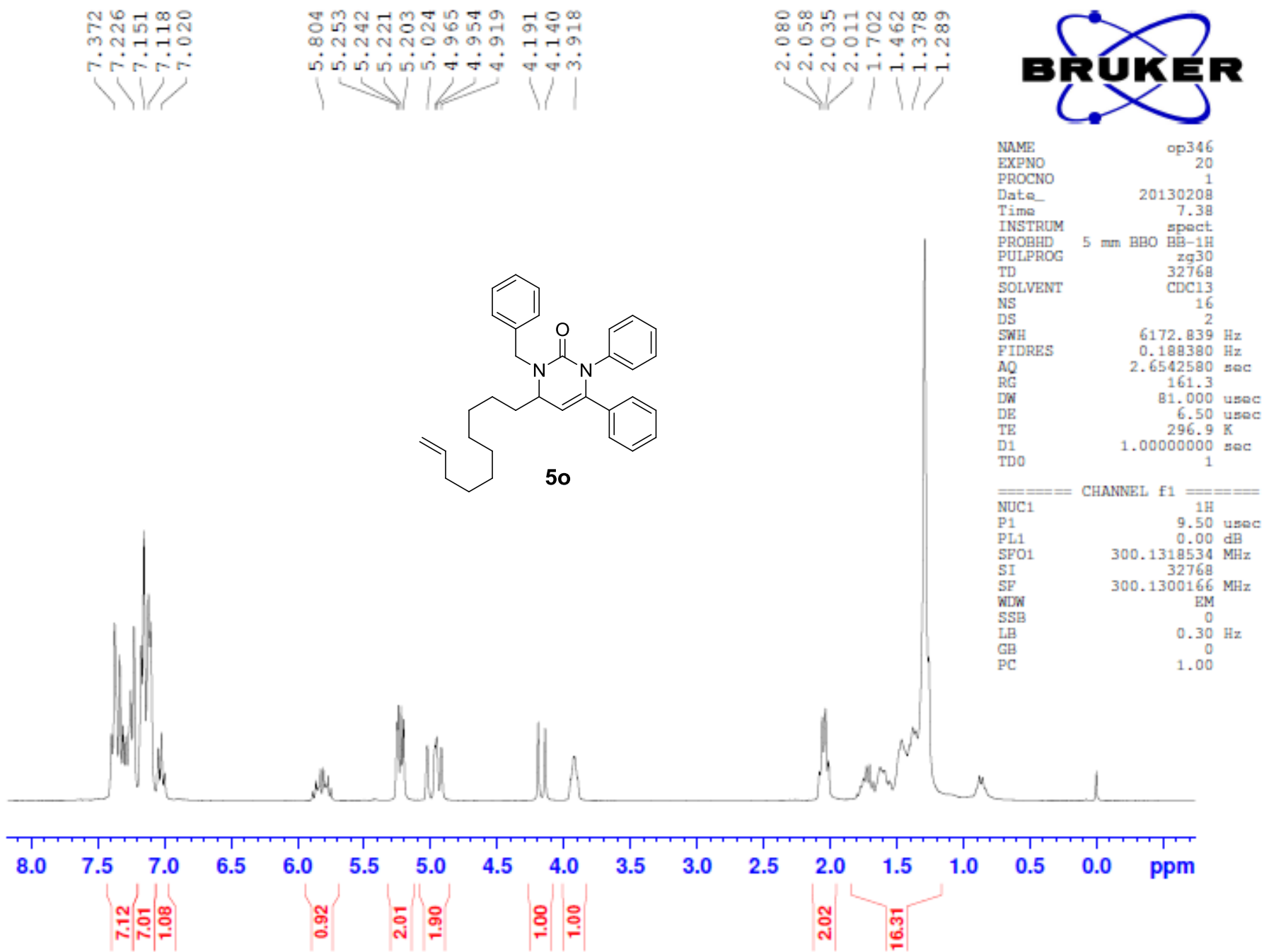


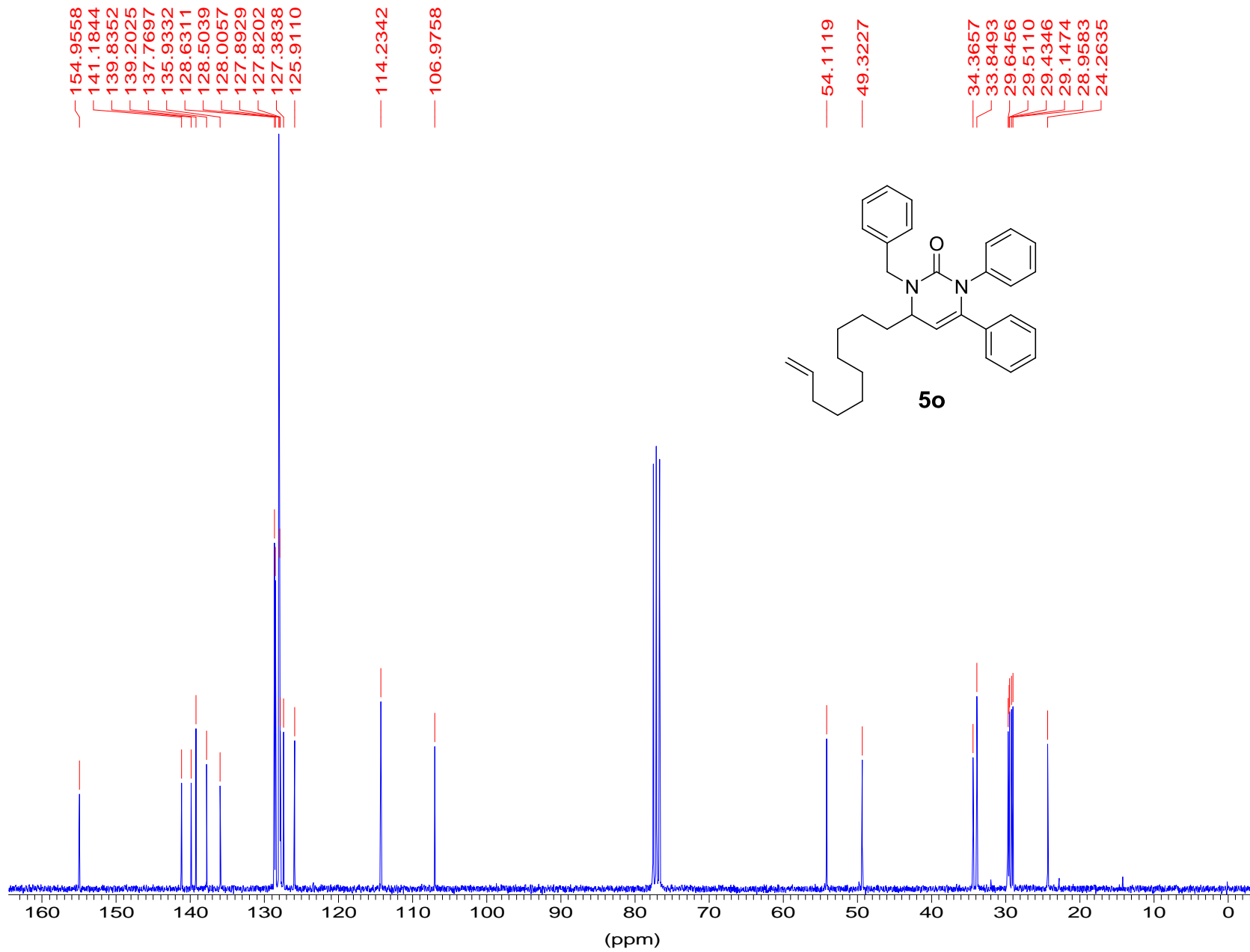














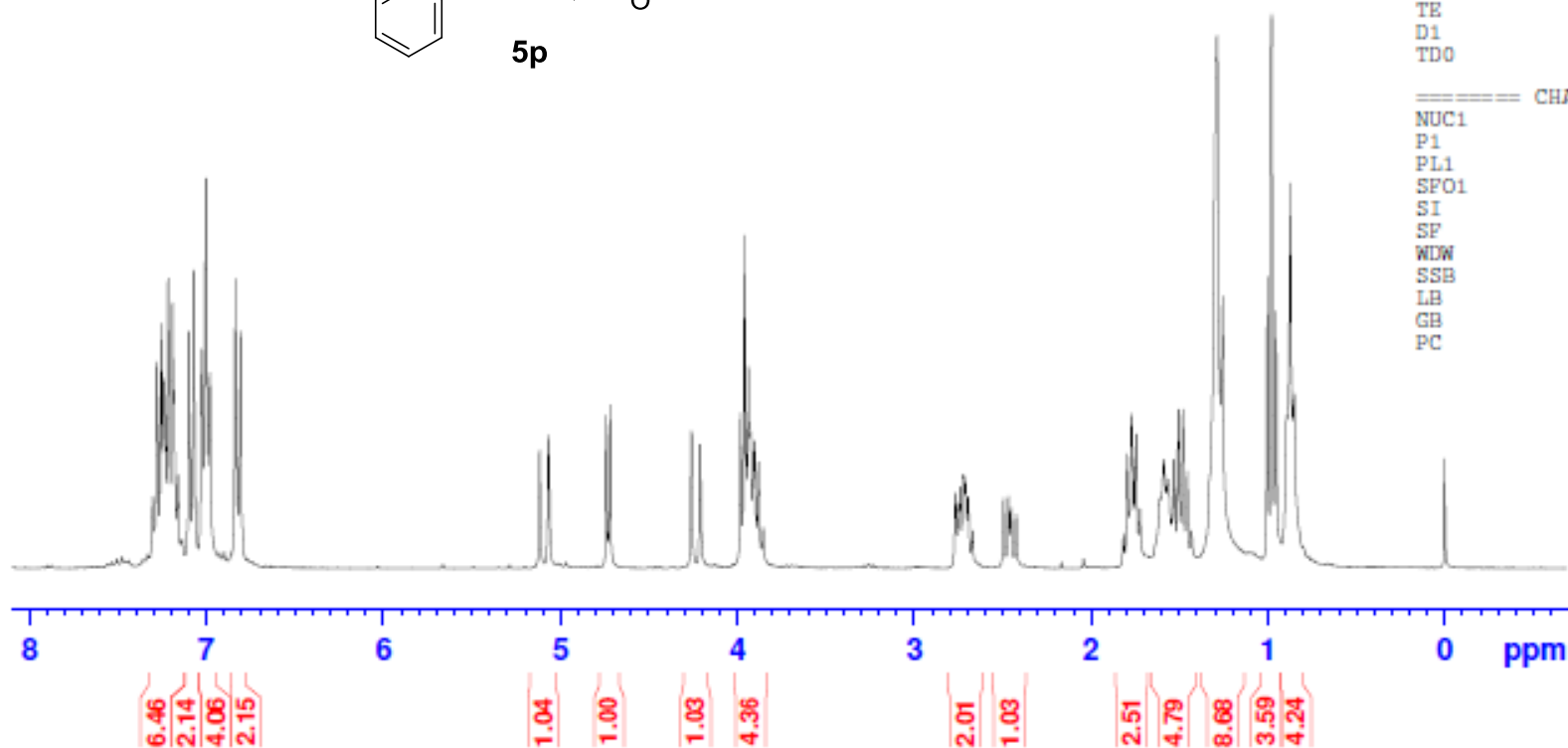
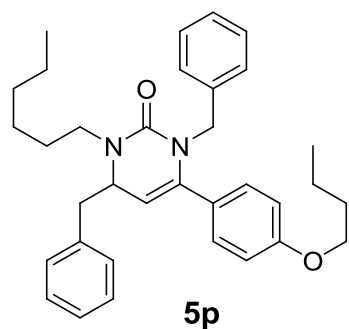
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
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TE 296.6 K
D1 1.00000000 sec
TD0 1

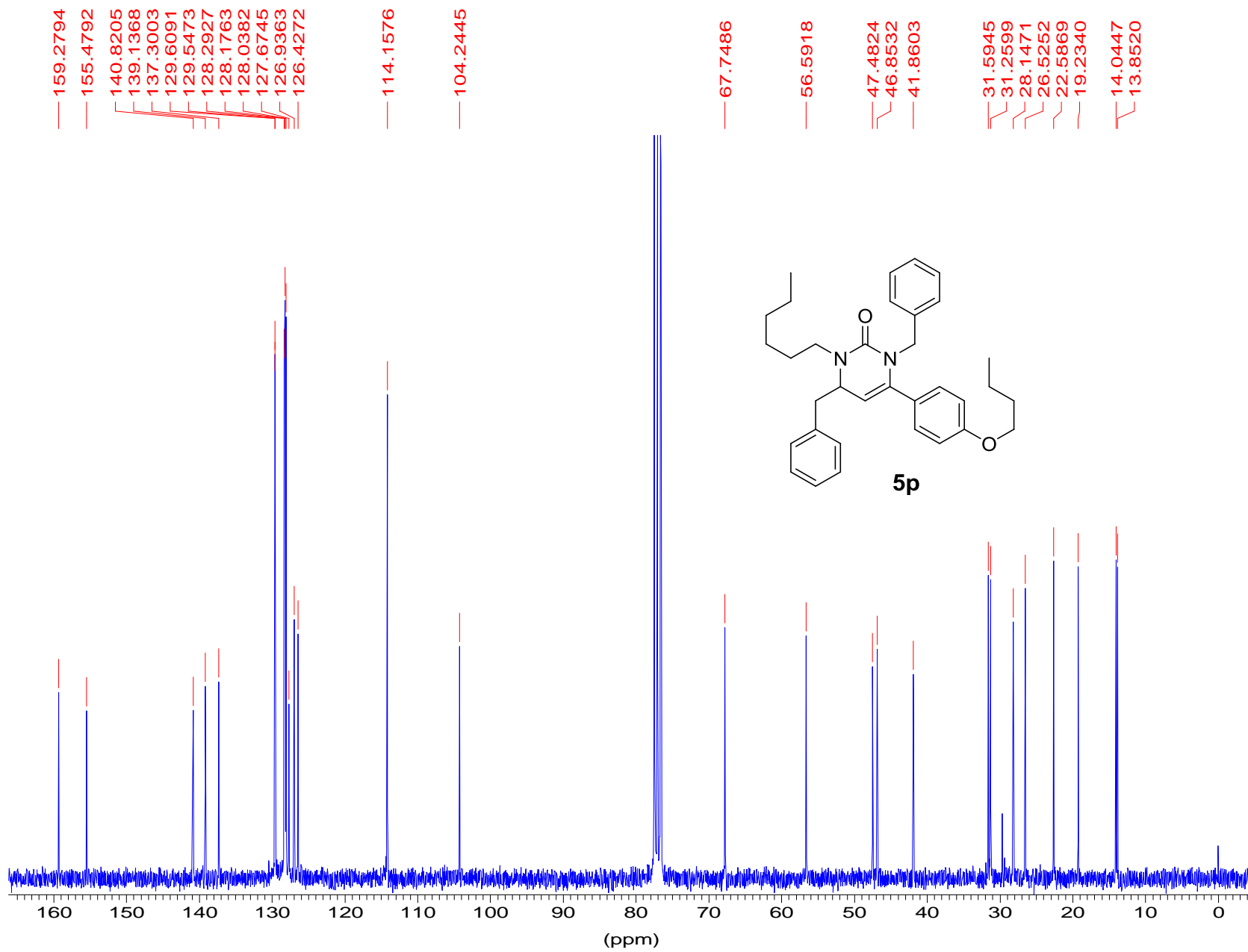
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SSB 0
LB 0.30 Hz
GB 0
PC 1.00

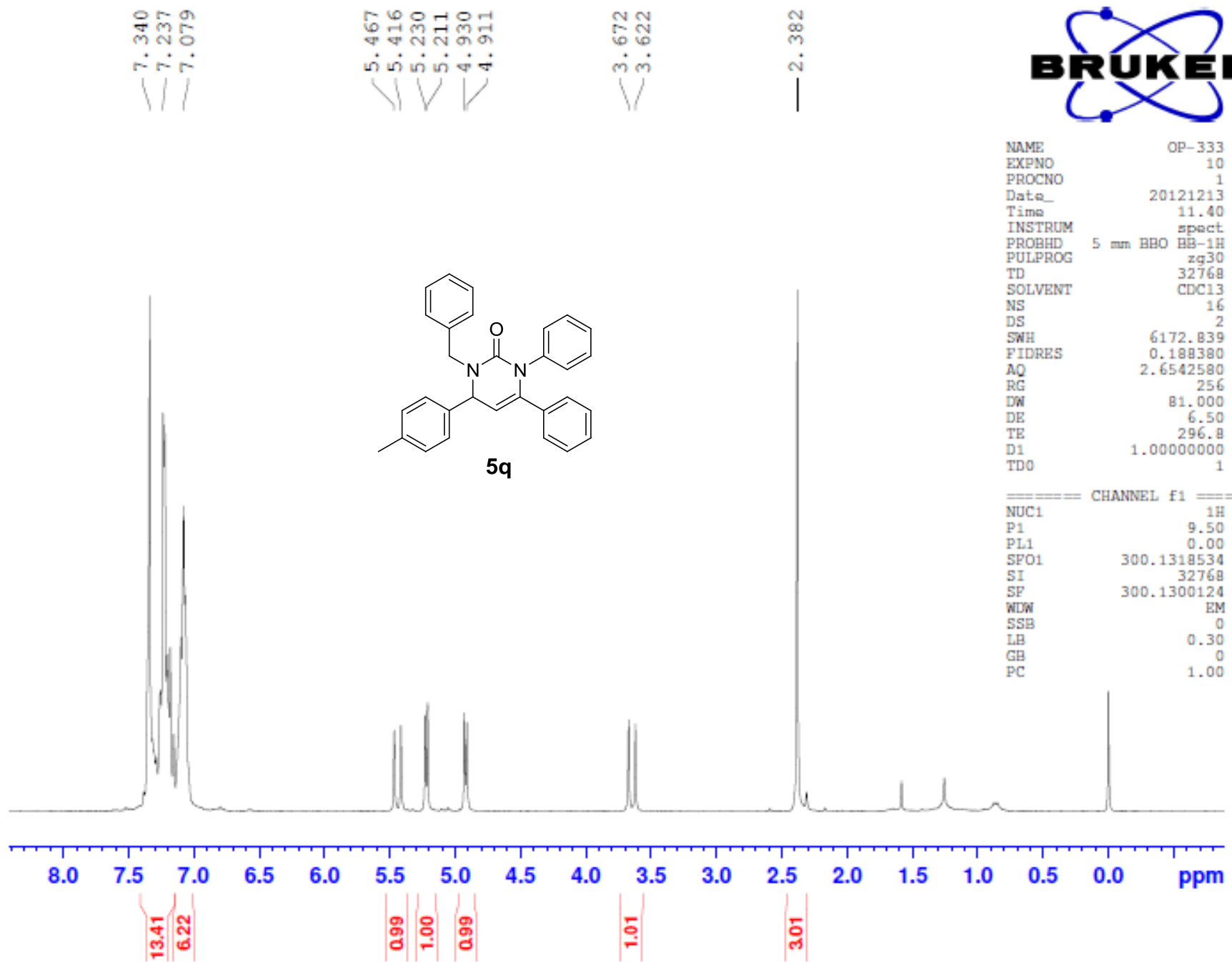
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7.002
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6.836
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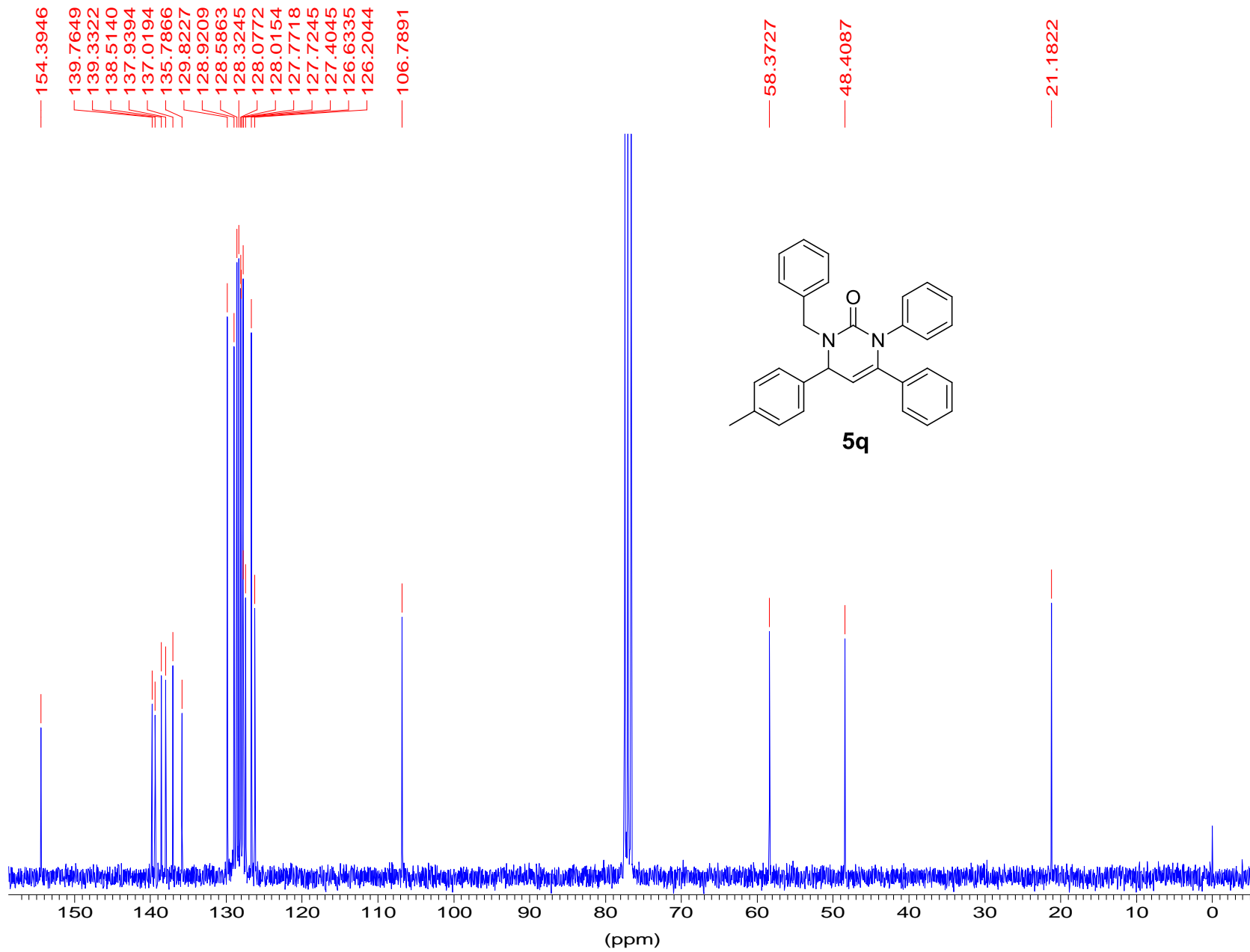
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4.718
4.258
4.208
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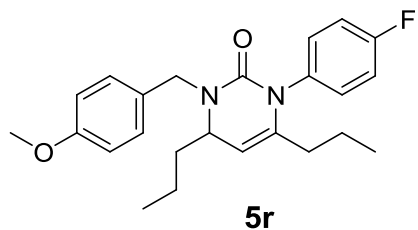
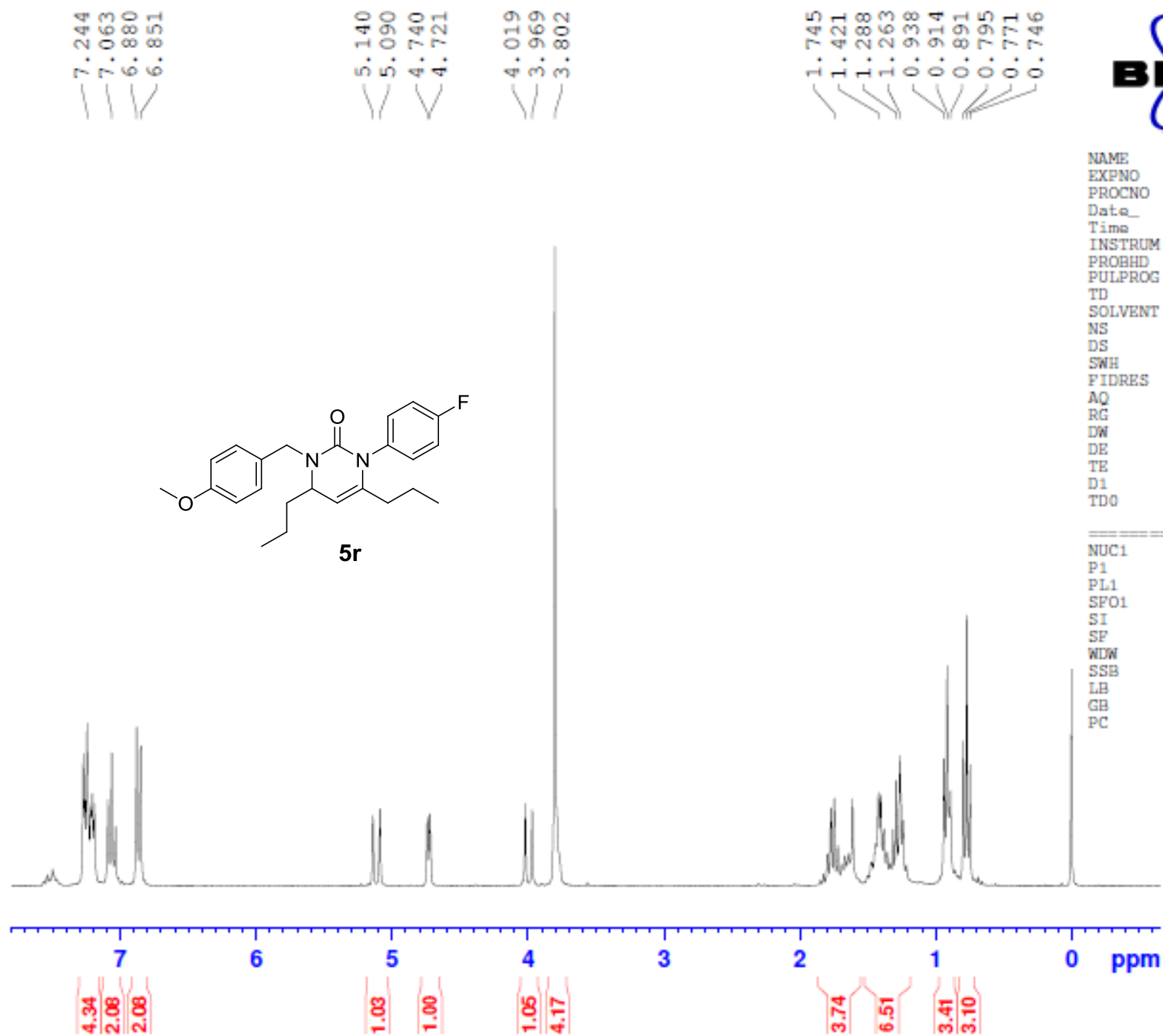
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1.587
1.505
1.288
1.002
0.978
0.954
0.873





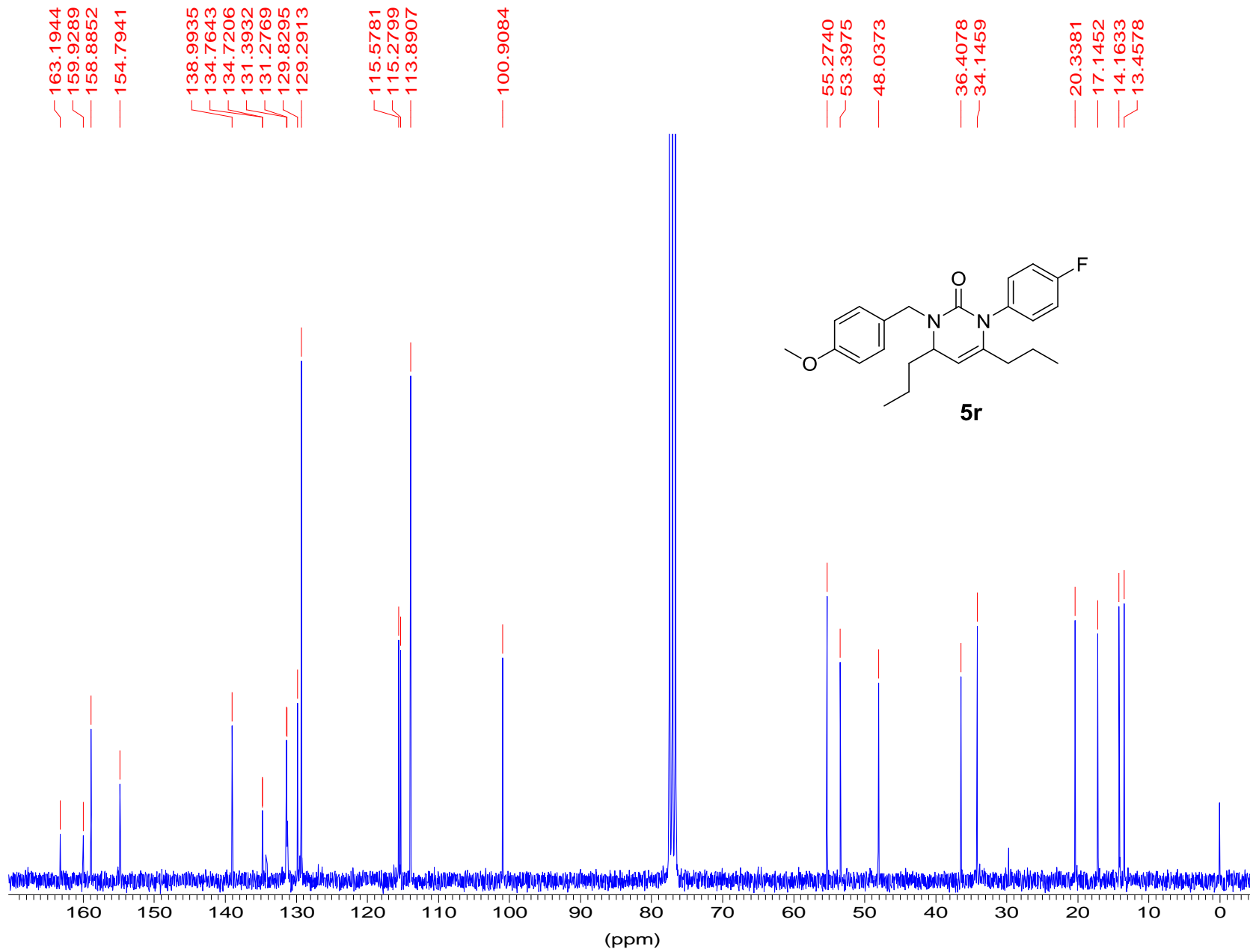


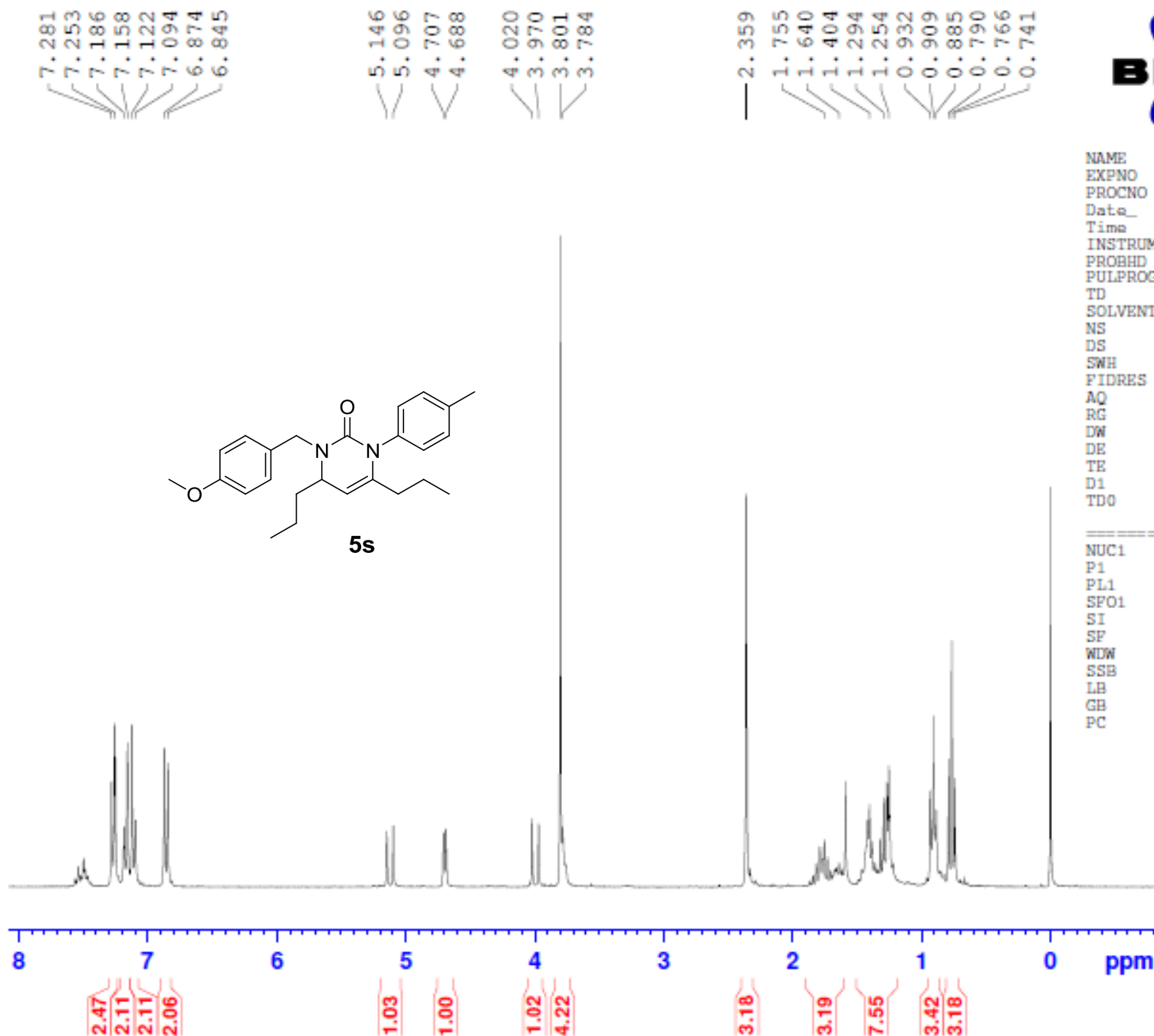


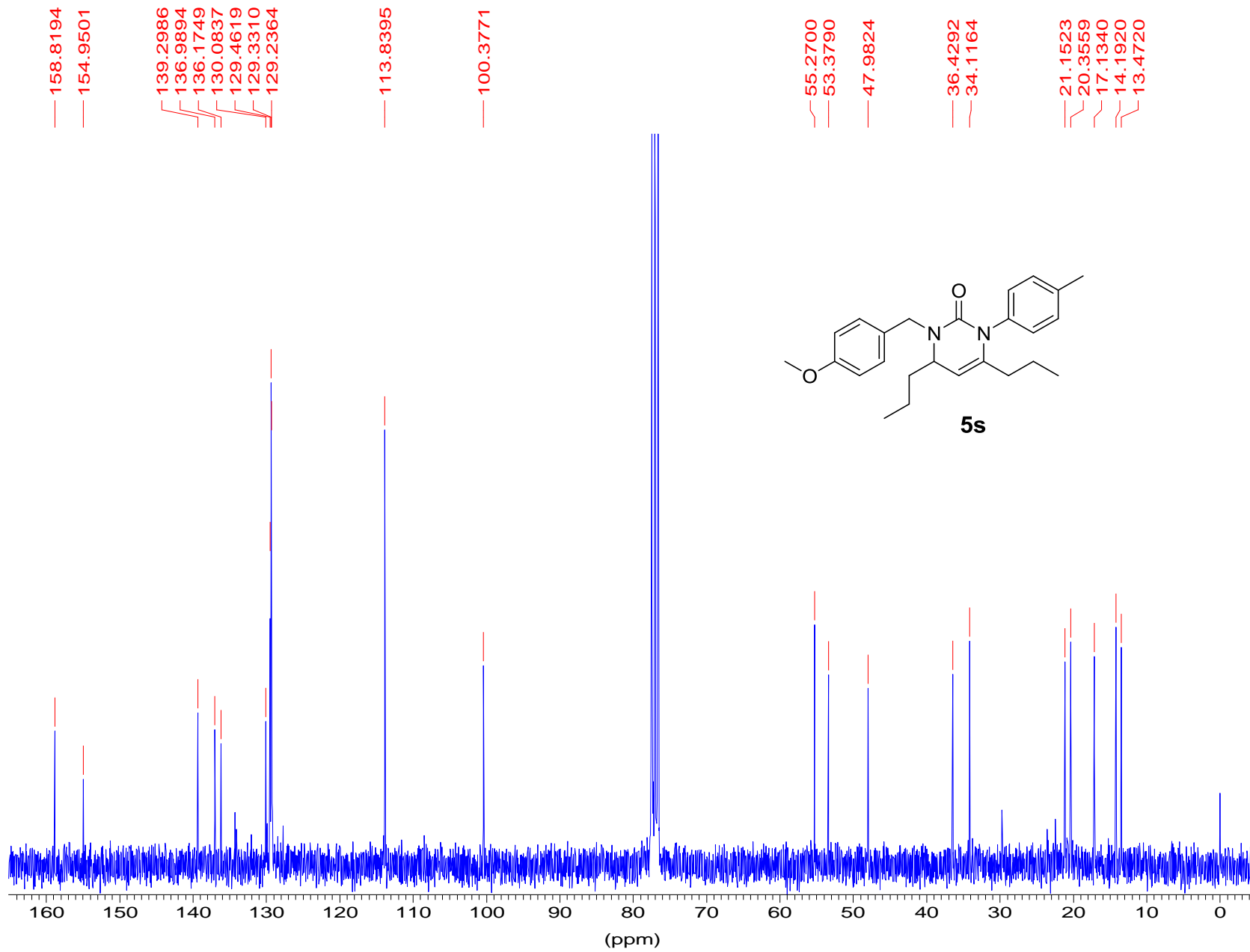


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PROCNO 1
Date_ 20121214
Time 10.37
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 362
DW 81.000 usec
DE 6.50 usec
TE 296.9 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00









NAME OP317b2
EXPNO 30
PROCNO 1
Date_ 20121127
Time 9.13
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 456.1
DW 81.000 usec
DE 6.50 usec
TE 296.7 K
D1 1.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300072 MHz
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SSB 0
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GB 0
PC 1.00

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7.107
6.892
6.863
6.836

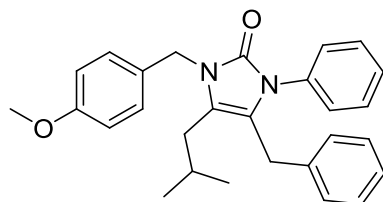
4.897

3.810
3.677

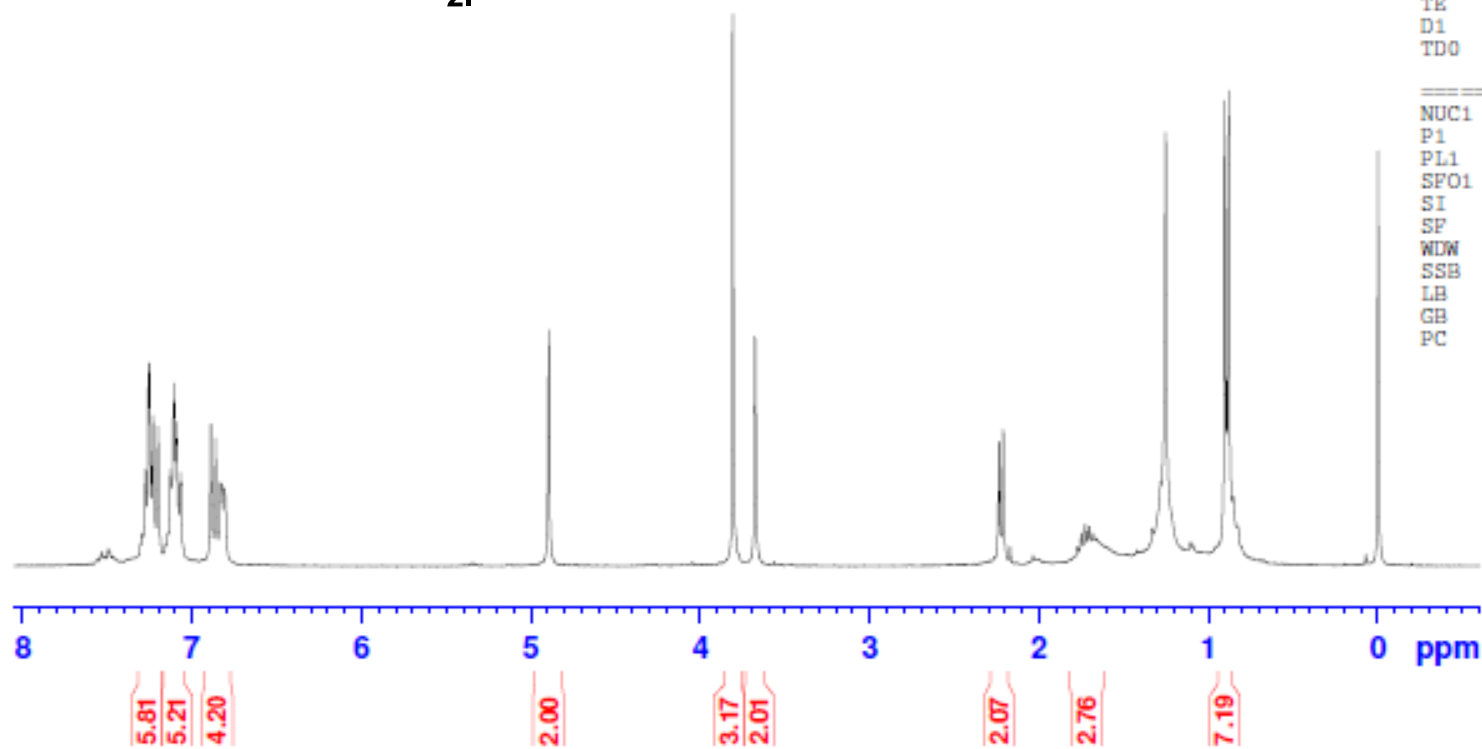
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2.213

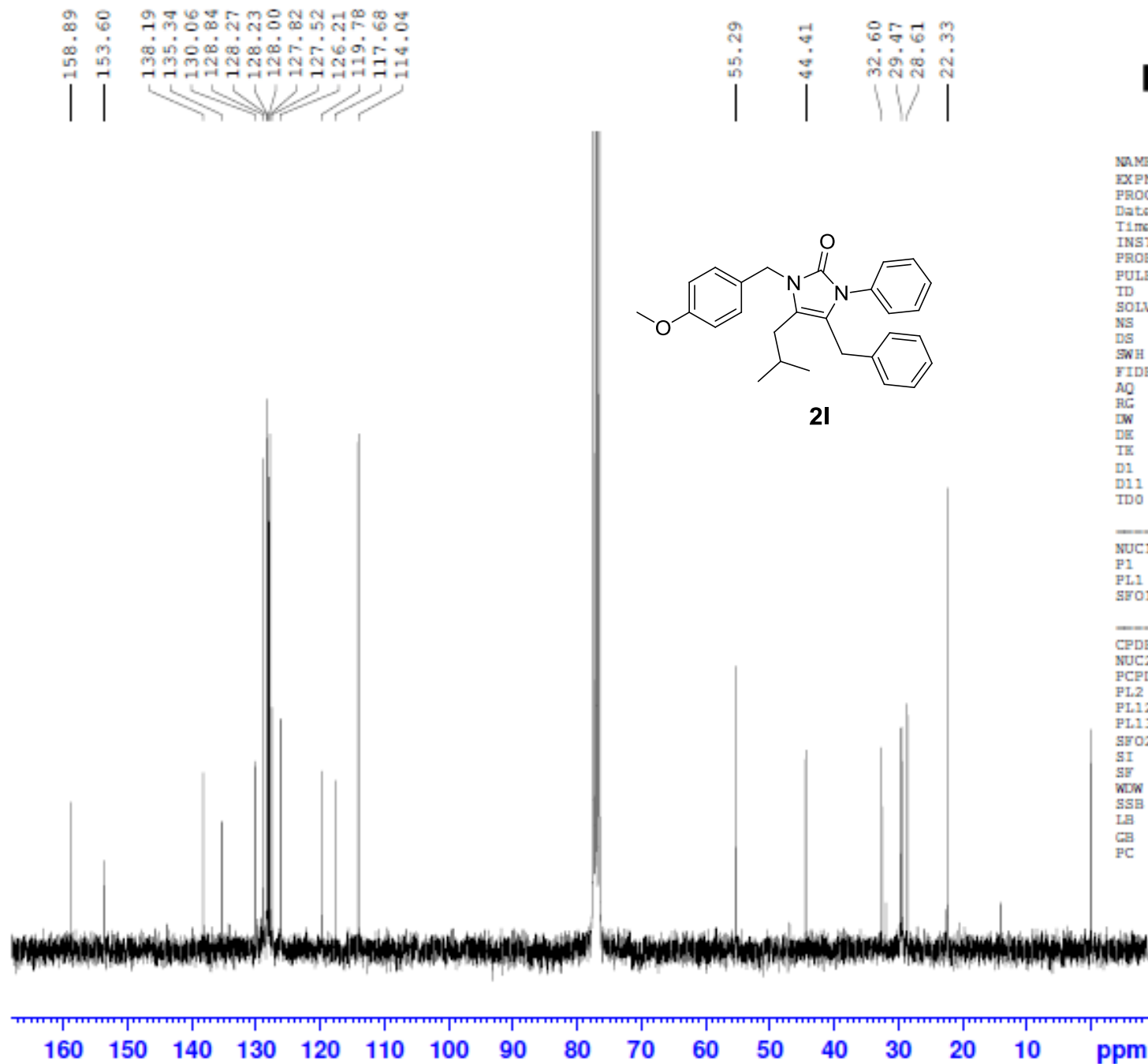
1.729

0.904
0.882



21

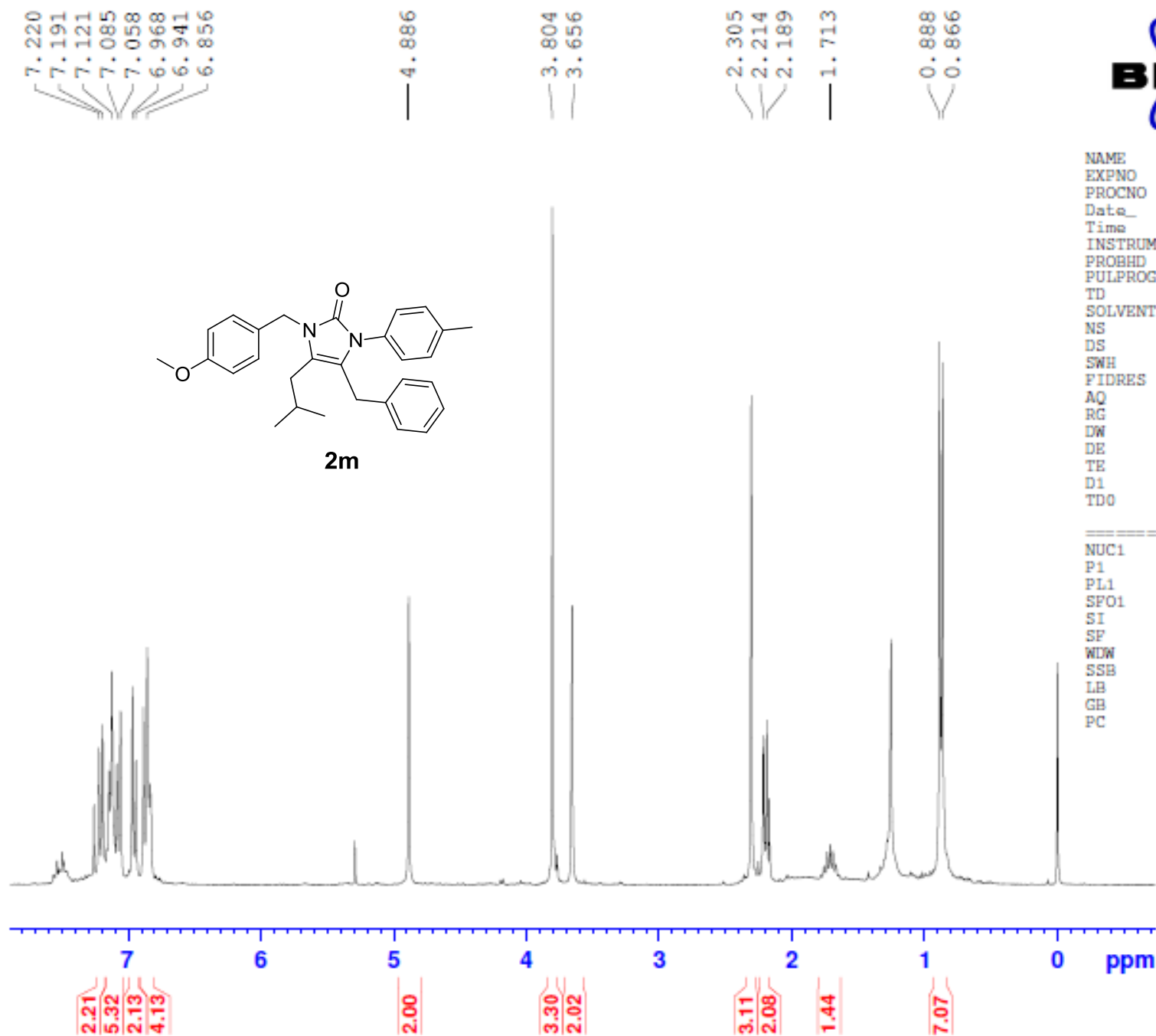




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EXPNO         31
PROCNO        1
Data_         20121130
Time          16.03
INSTRUM       spect
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PULPROG       zgpg30
TD            65536
SOLVENT       CDC13
NS            4096
DS            4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
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DW            27.800 usec
DE            6.50 usec
TE            298.4 K
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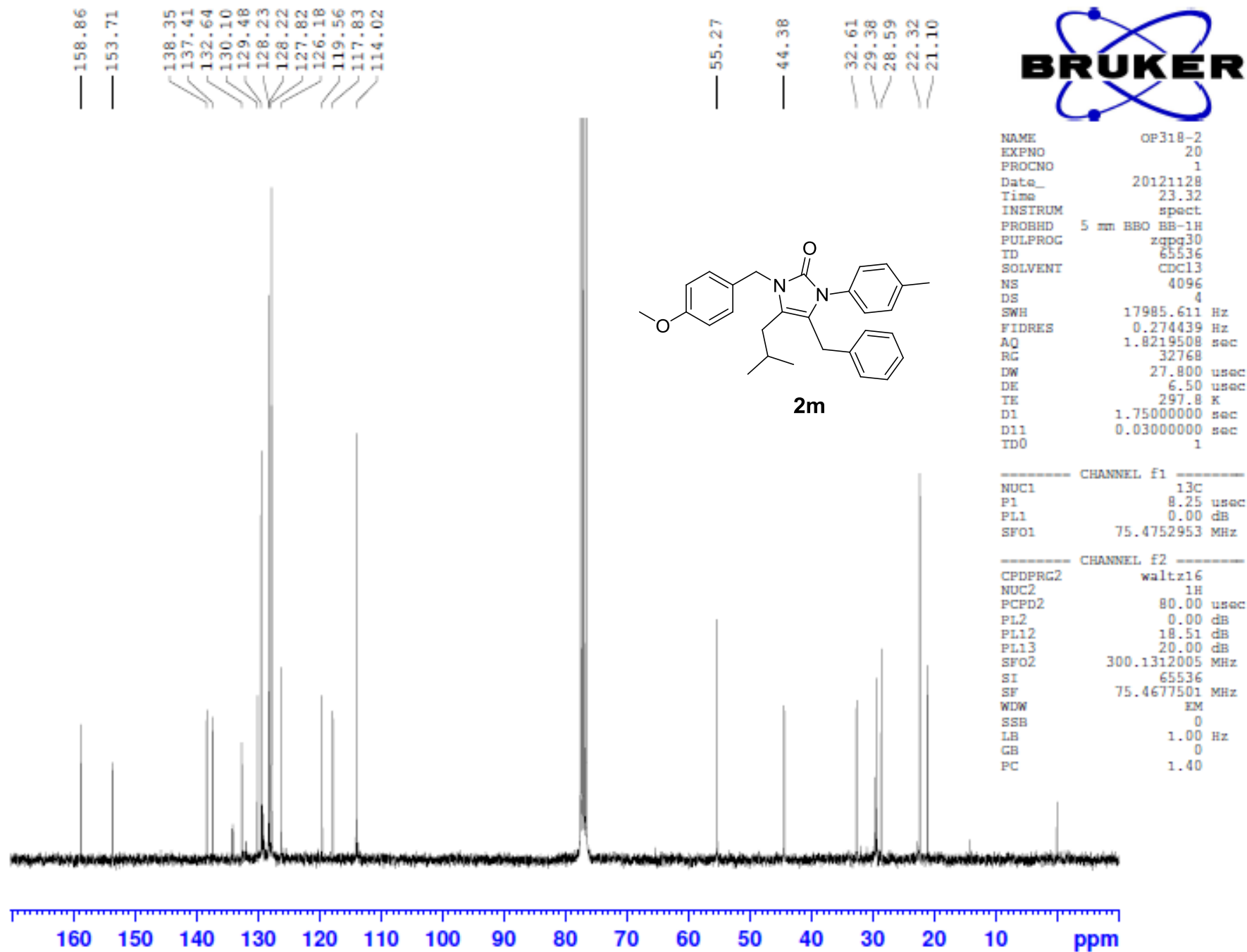
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PL1           0.00 dB
SFO1          75.4752953 MHz
```

```
----- CHANNEL f2 -----
CPDPRG2      waltz16
NUC2          1H
PCPD2        80.00 usec
PL2           0.00 dB
PL12         18.51 dB
PL13         20.00 dB
SFO2         300.1312005 MHz
SI           65536
SF           75.4677495 MHz
WDW          EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
```



NAME OP318-2
EXPNO 30
PROCNO 1
Date_ 20121130
Time 4.58
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 322.5
DW 81.000 usec
DE 6.50 usec
TE 296.8 K
D1 1.00000000 sec
TDO 1

==== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00





NAME op333r2-5
EXPNO 23
PROCNO 1
Date_ 20130206
Time 11.41
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDC13
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 574.7
DW 81.000 usec
DE 6.50 usec
TE 296.8 K
D1 1.00000000 sec
TD0 1

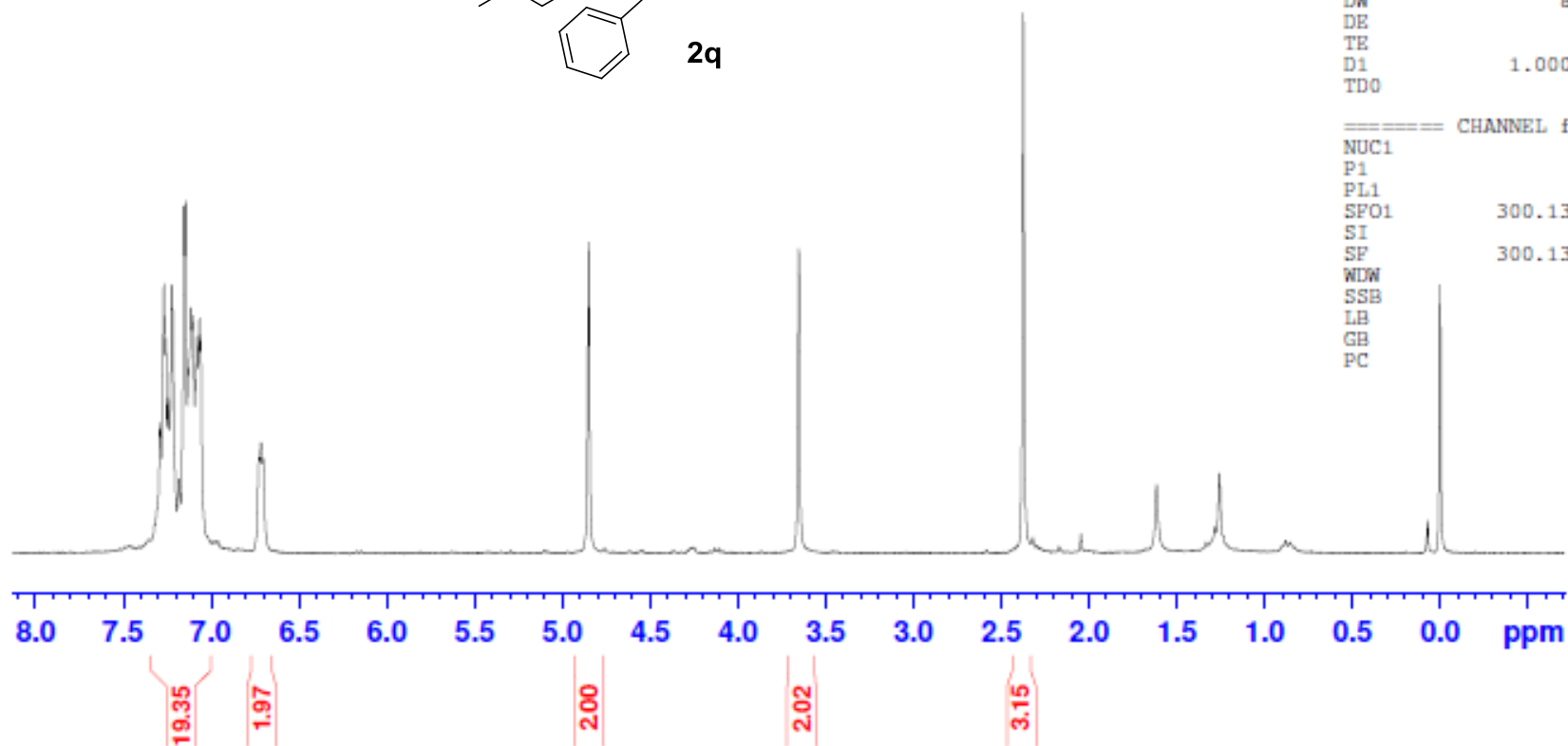
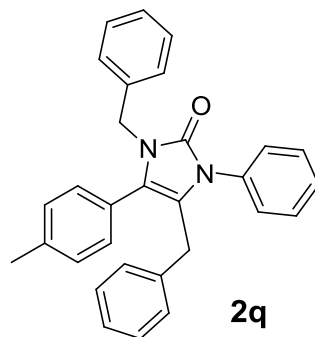
===== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

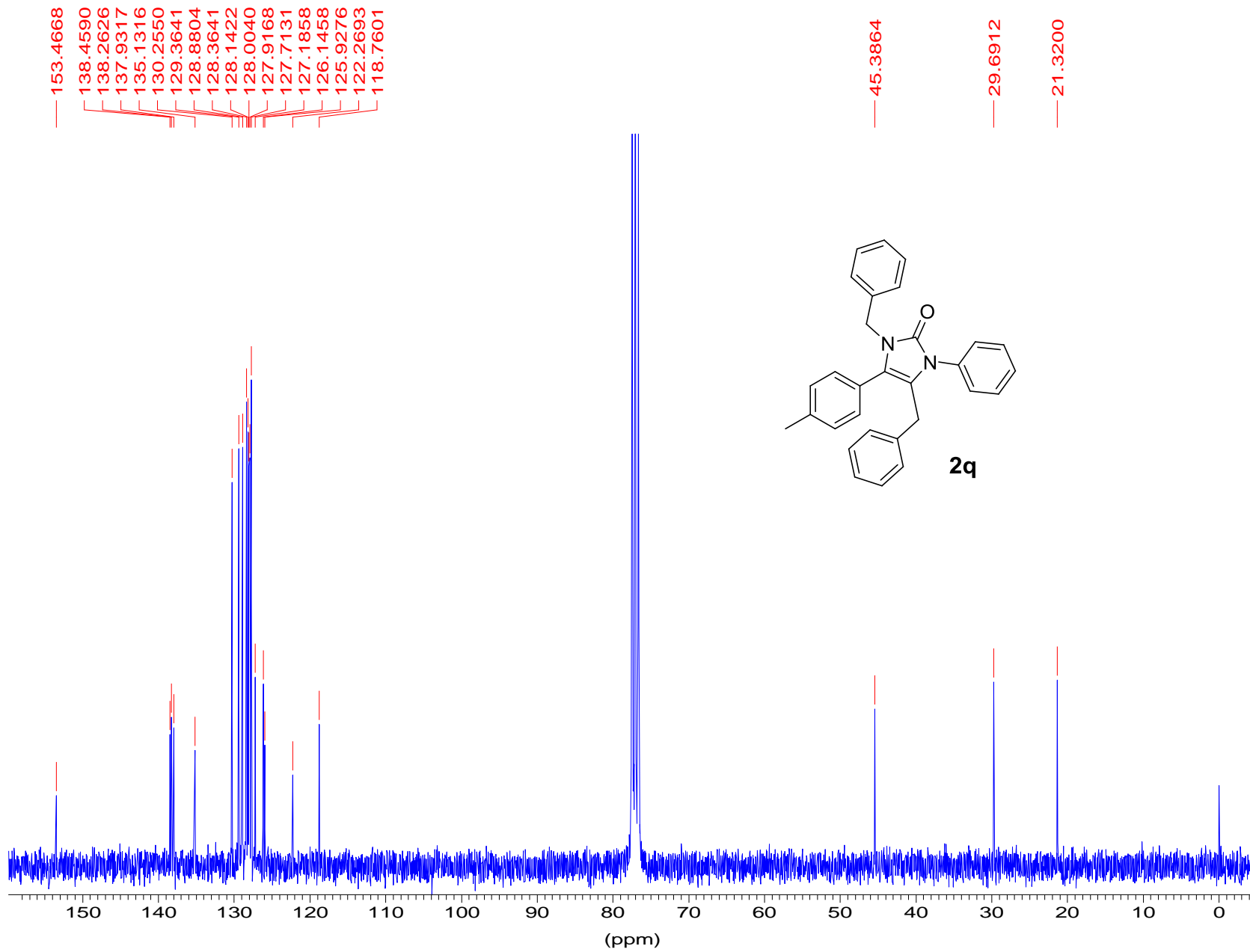
7.268
7.221
7.145
7.066
6.716

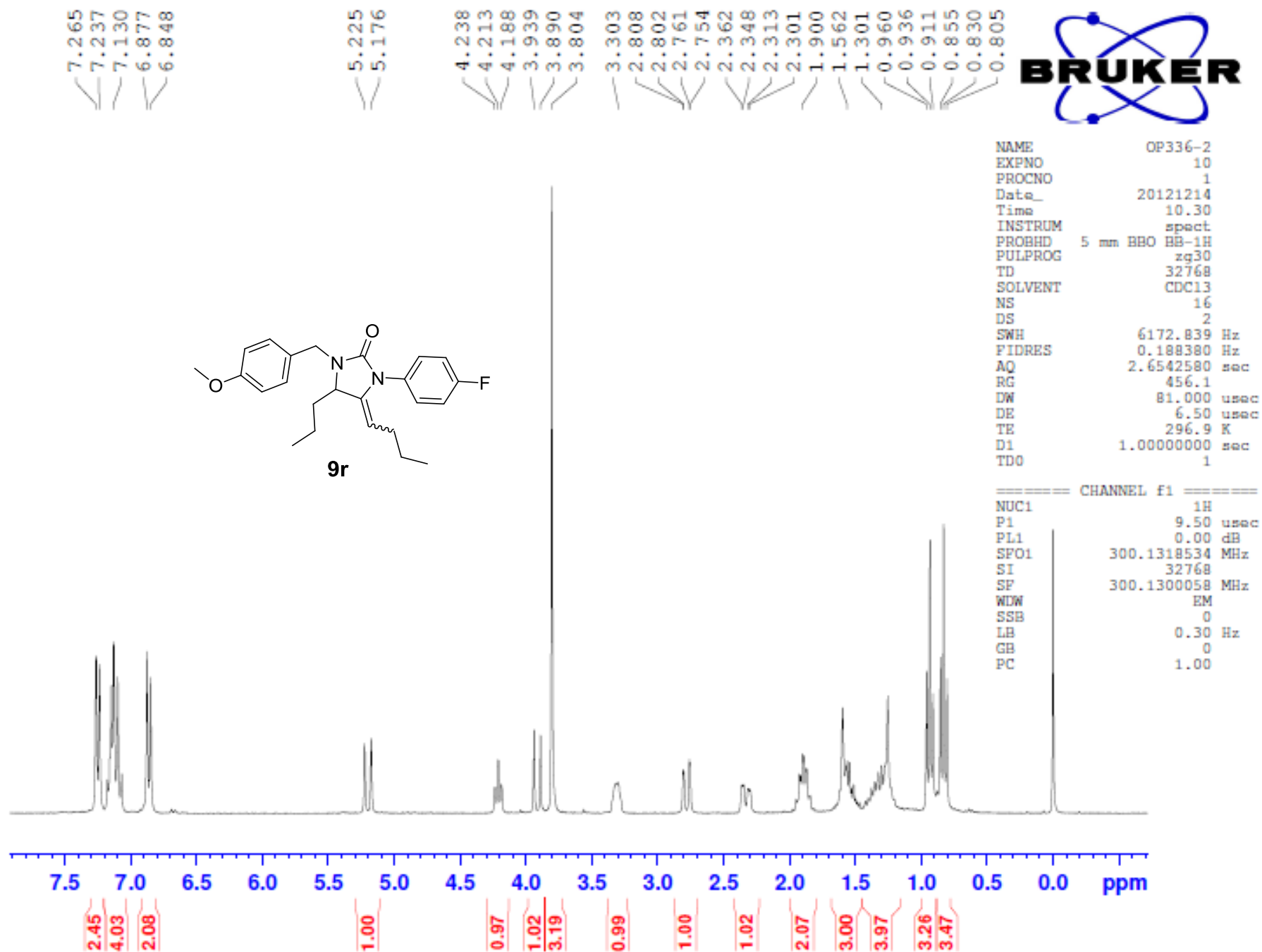
4.849

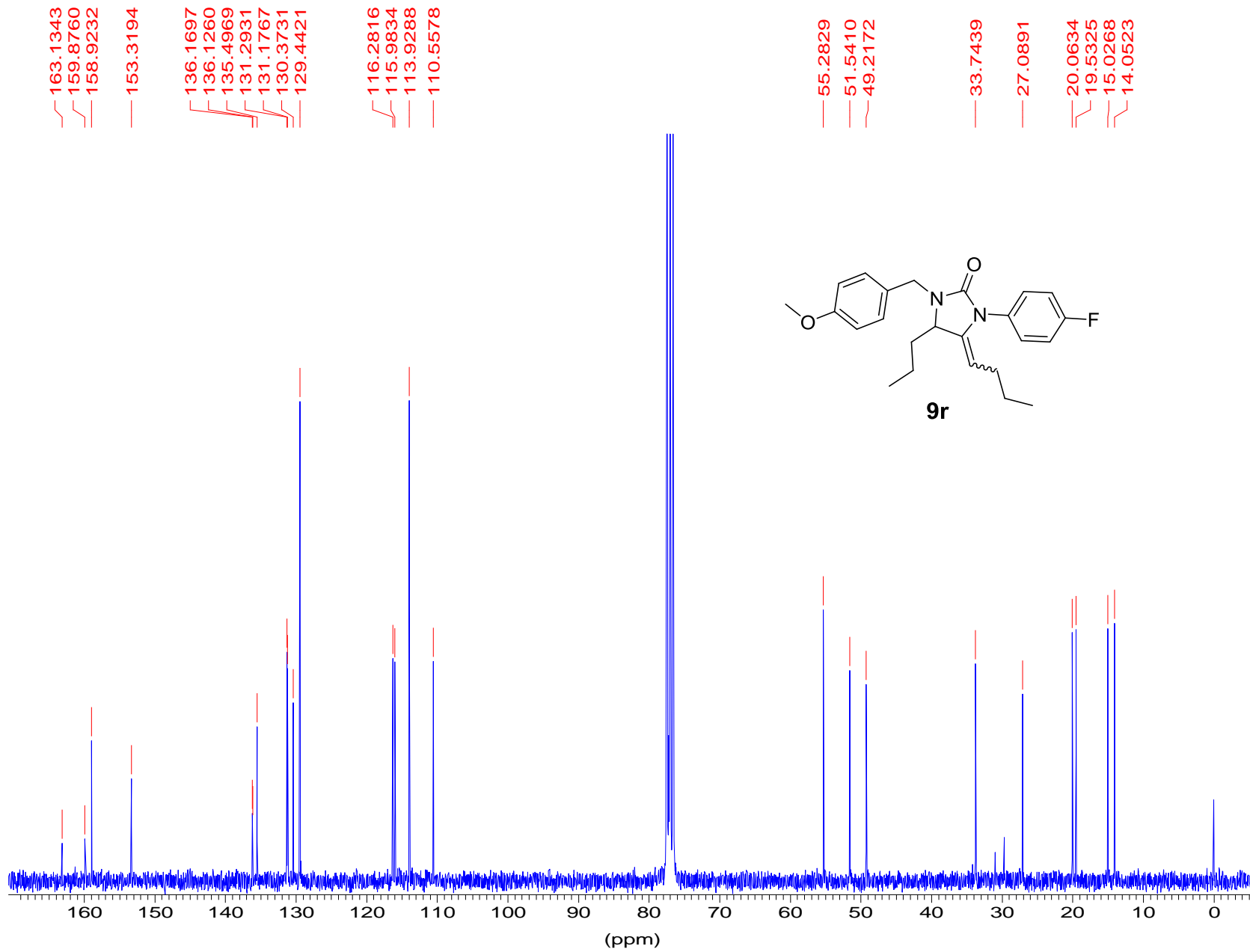
3.652

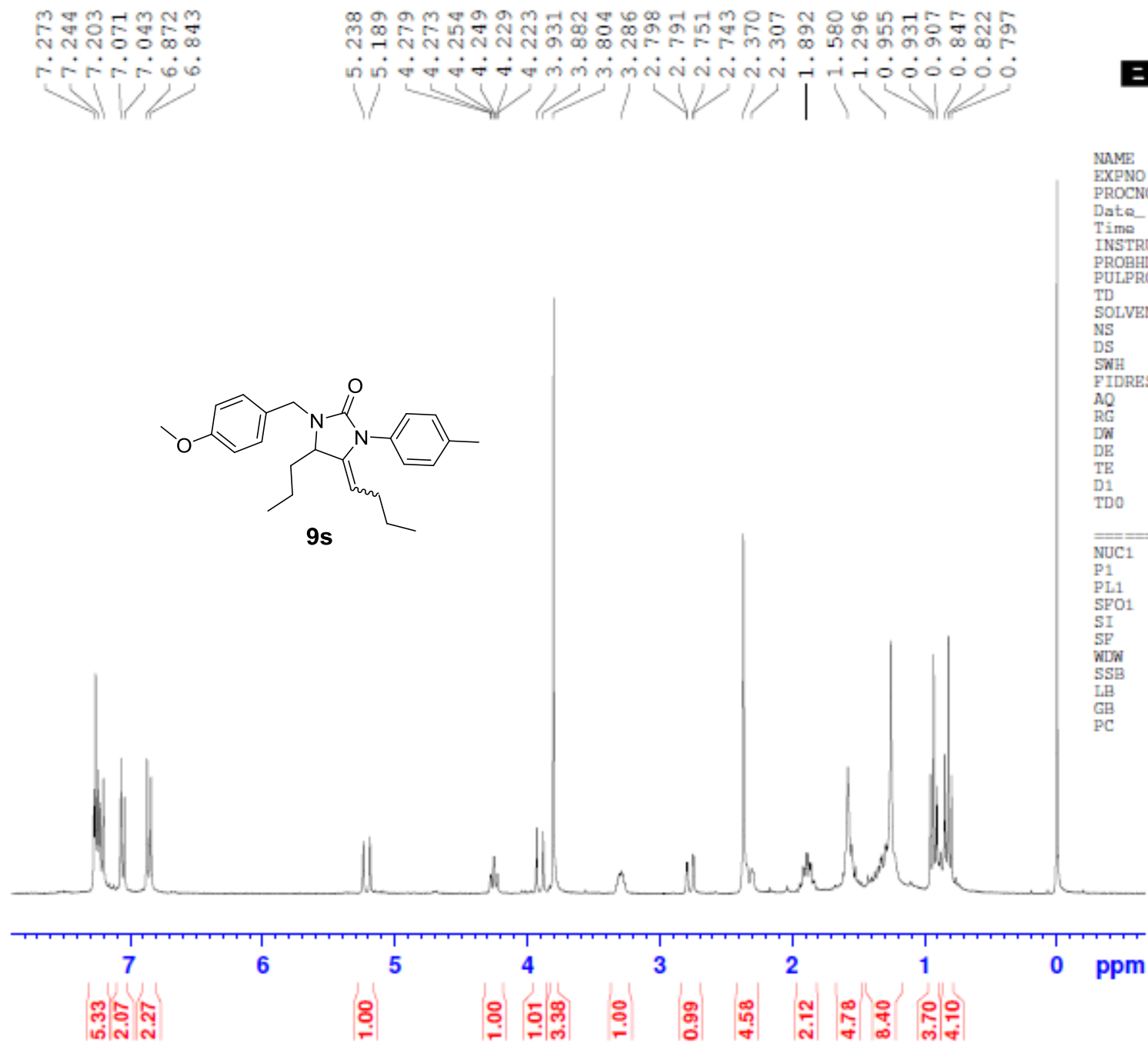
2.373





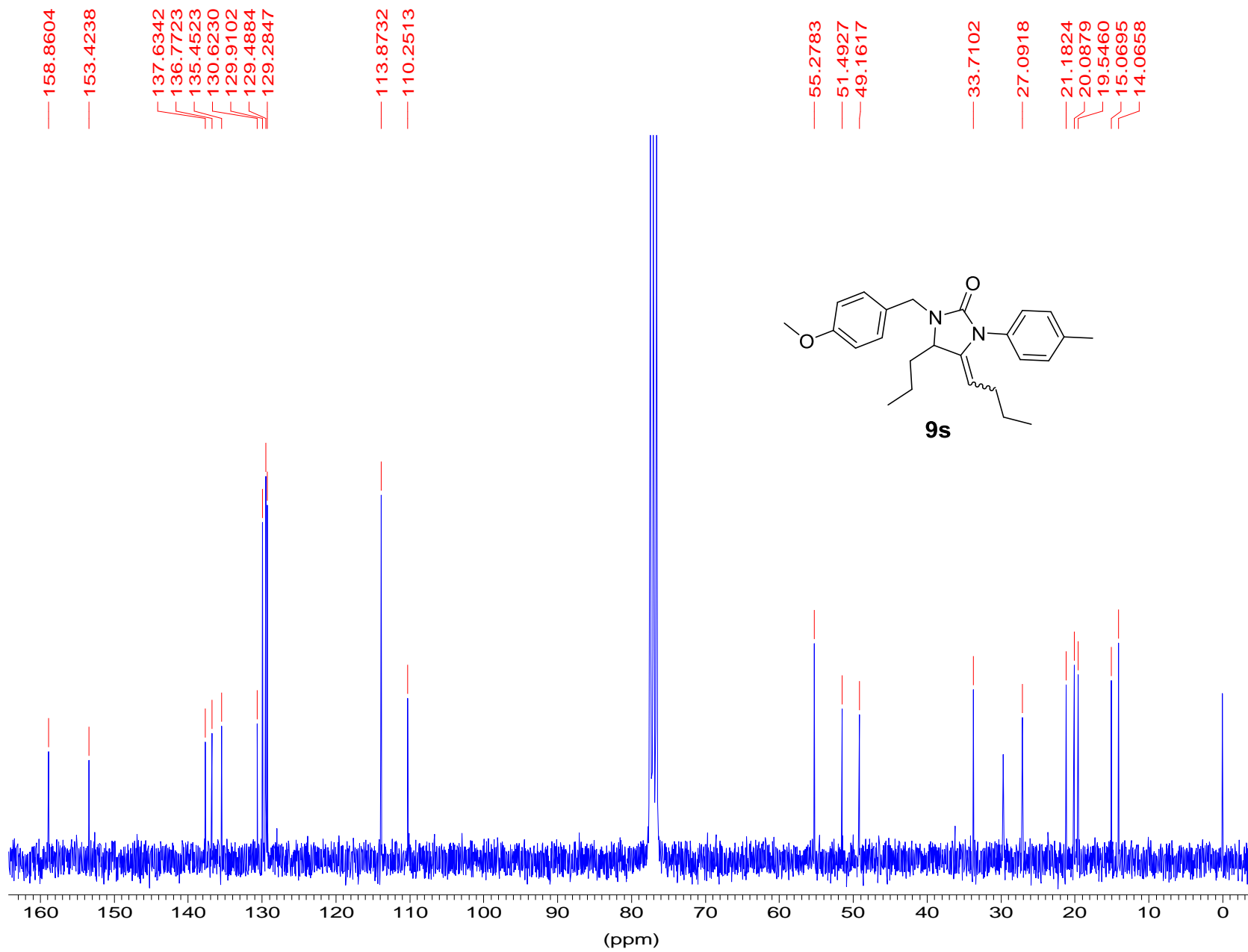


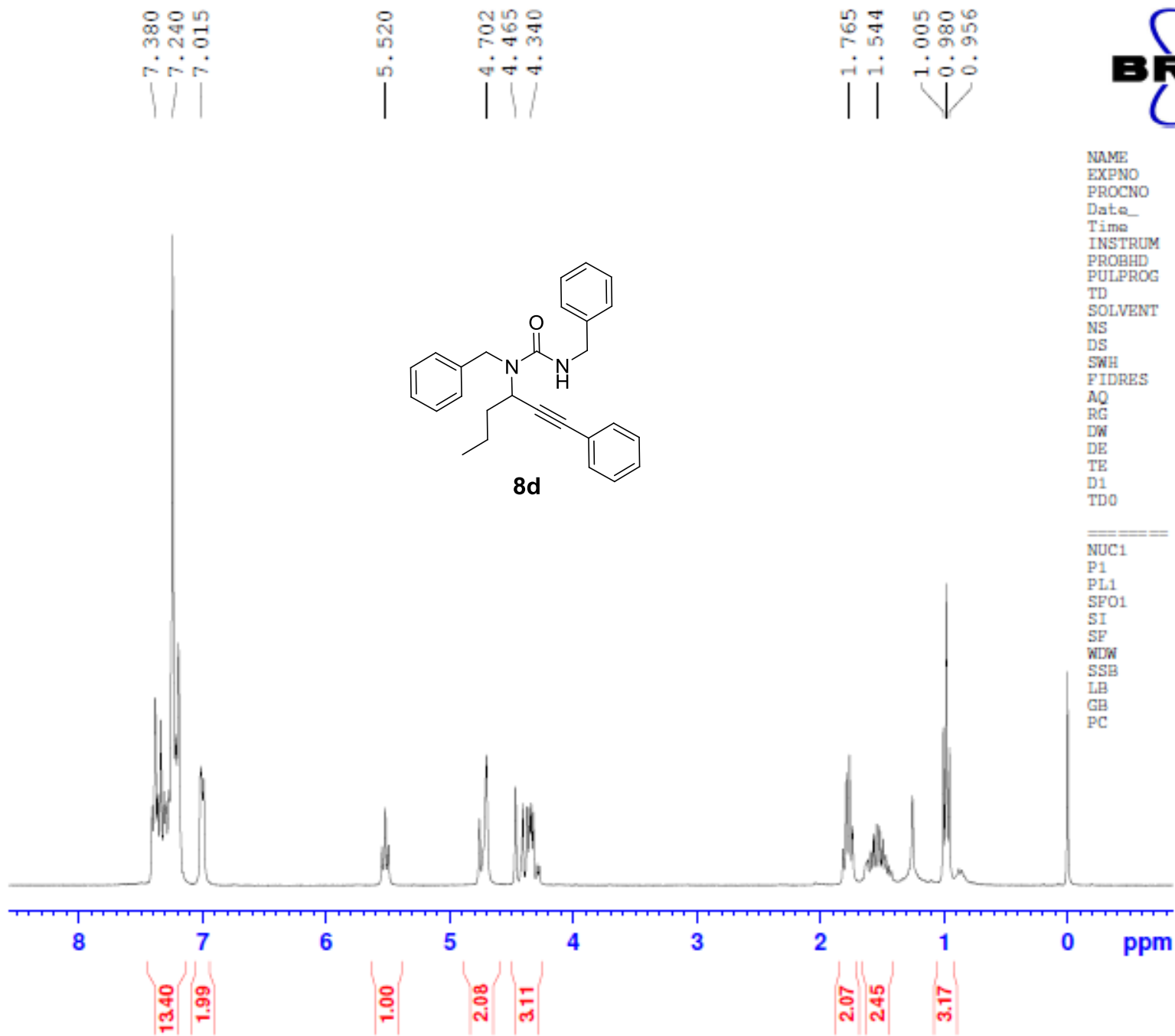




NAME OP335-2
EXPNO 20
PROCNO 1
Date_ 20121219
Time 5.20
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 574.7
DW 81.000 usec
DE 6.50 usec
TE 296.7 K
D1 1.00000000 sec
TD0 1

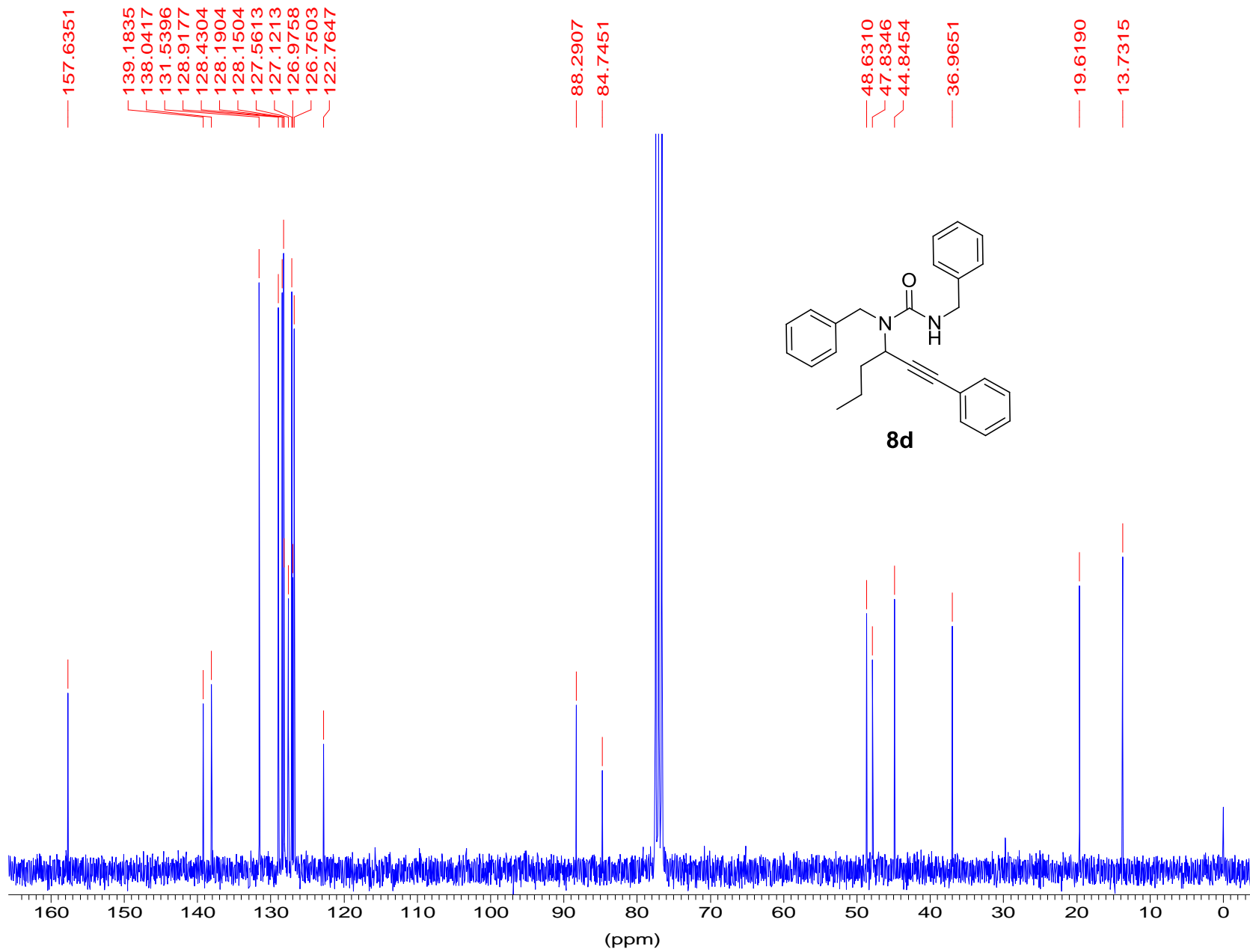
==== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300061 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

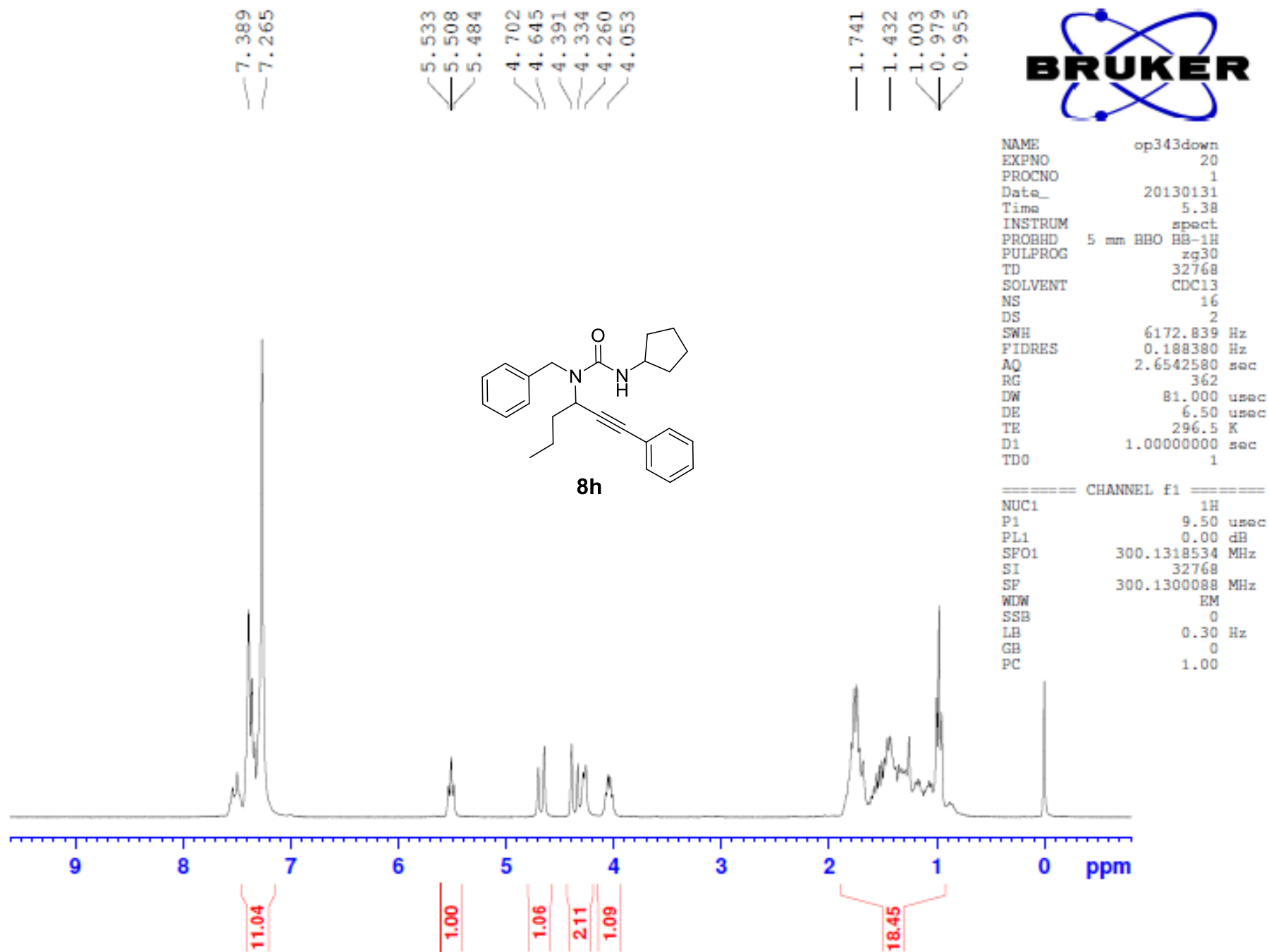


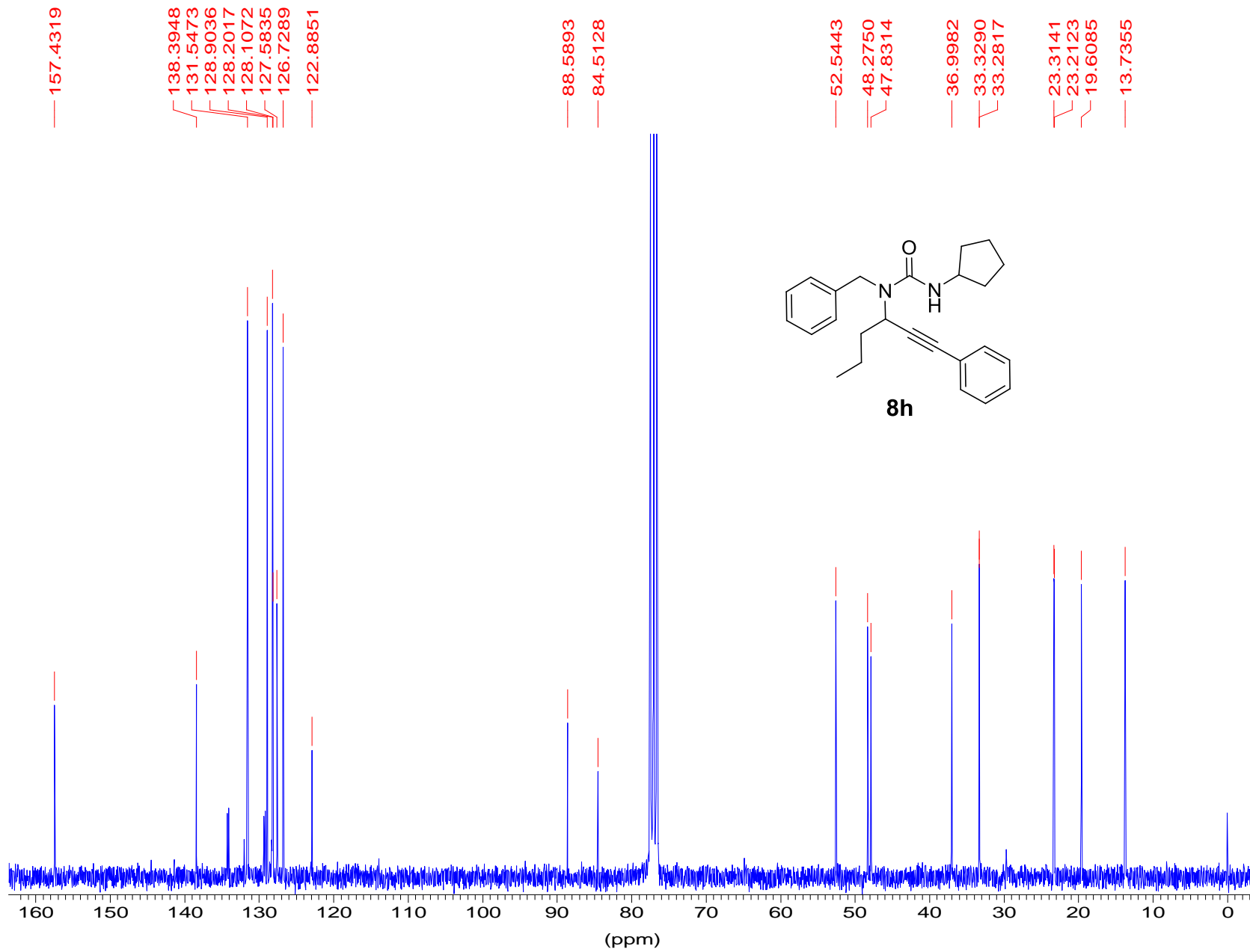


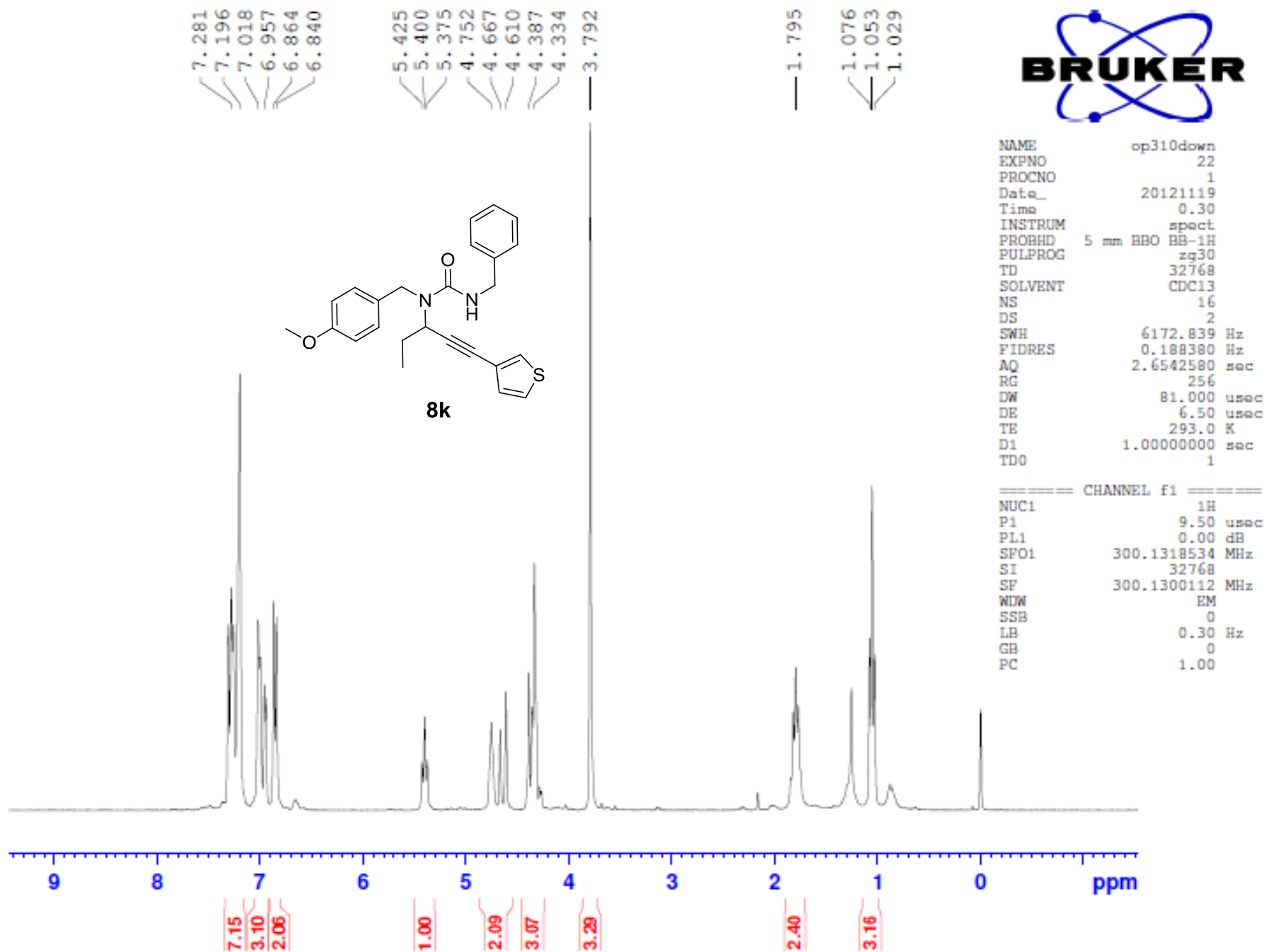
NAME PVureal
EXPNO 20
PROCNO 1
Date_ 20130125
Time 10.26
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 362
DW 81.000 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TDO 1

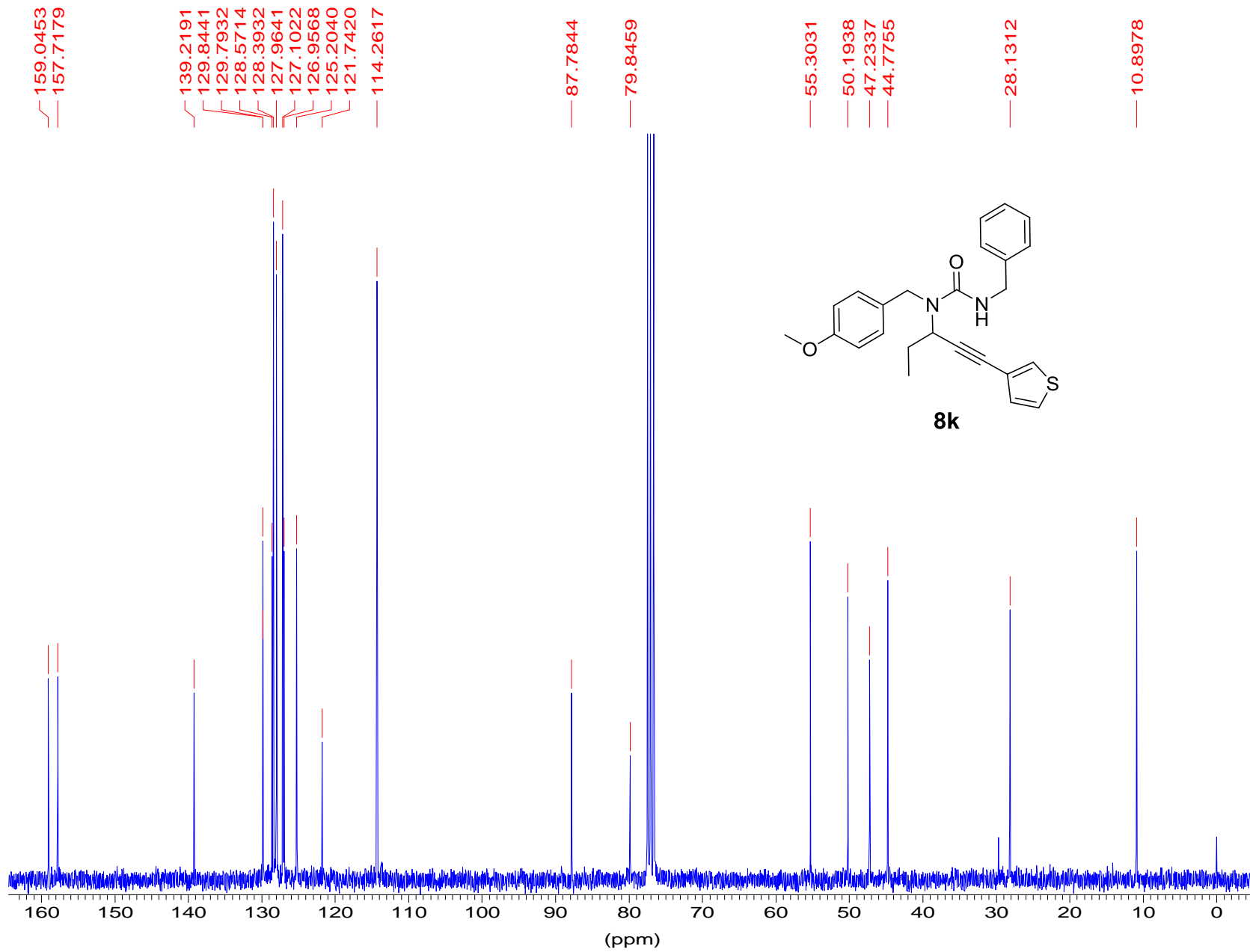
==== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300106 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00













NAME op333r22HPLC
EXPNO 20
PROCNO 1
Date_ 20130215
Time 7.53
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 6172.839 Hz
FIDRES 0.188380 Hz
AQ 2.6542580 sec
RG 574.7
DW 81.000 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TDO 1

==== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SFO1 300.1318534 MHz
SI 32768
SF 300.1300075 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

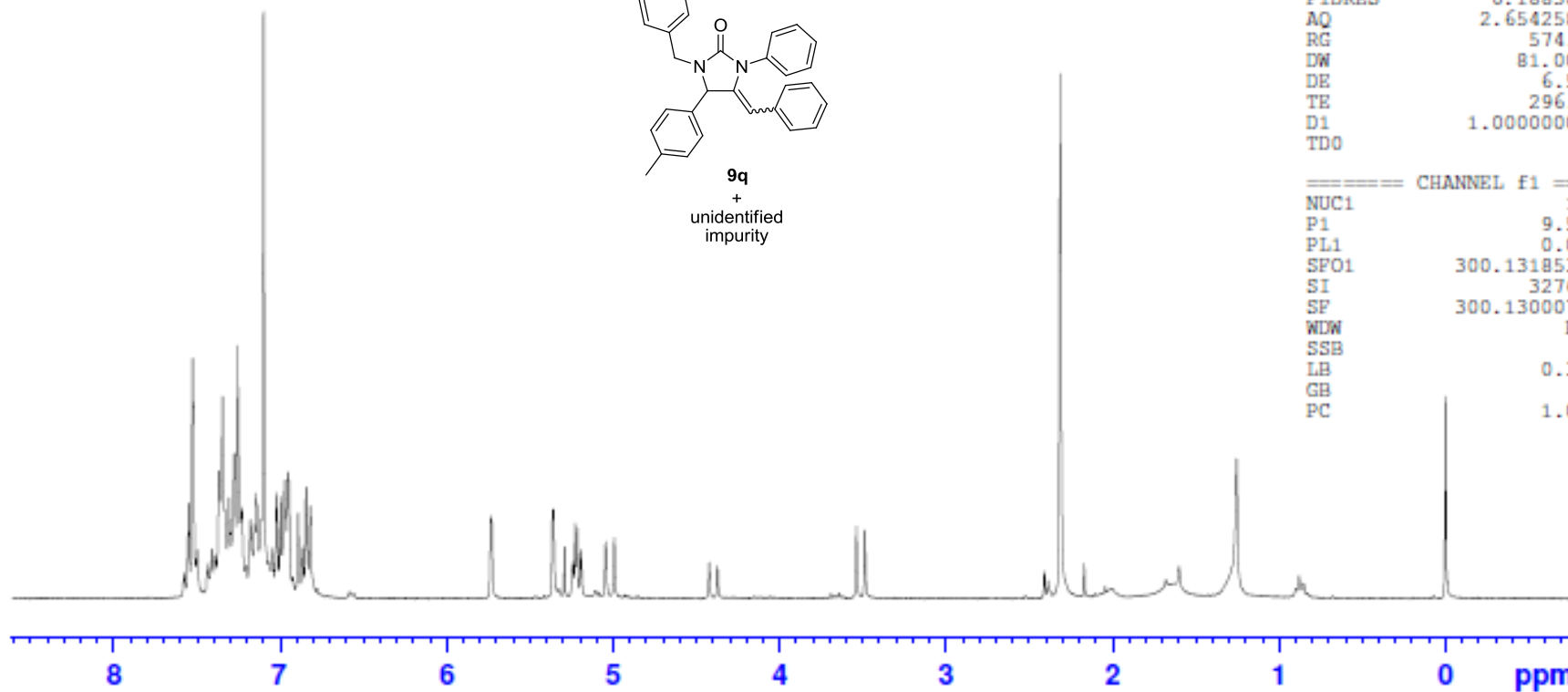
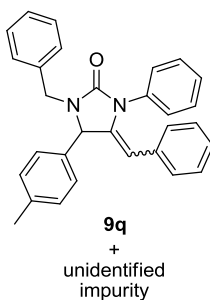
7.527
7.347
7.255
7.101
6.951
6.844

5.736
5.730
5.364
5.358
5.045
4.994

4.423
4.373

3.539
3.488

2.316



34.63

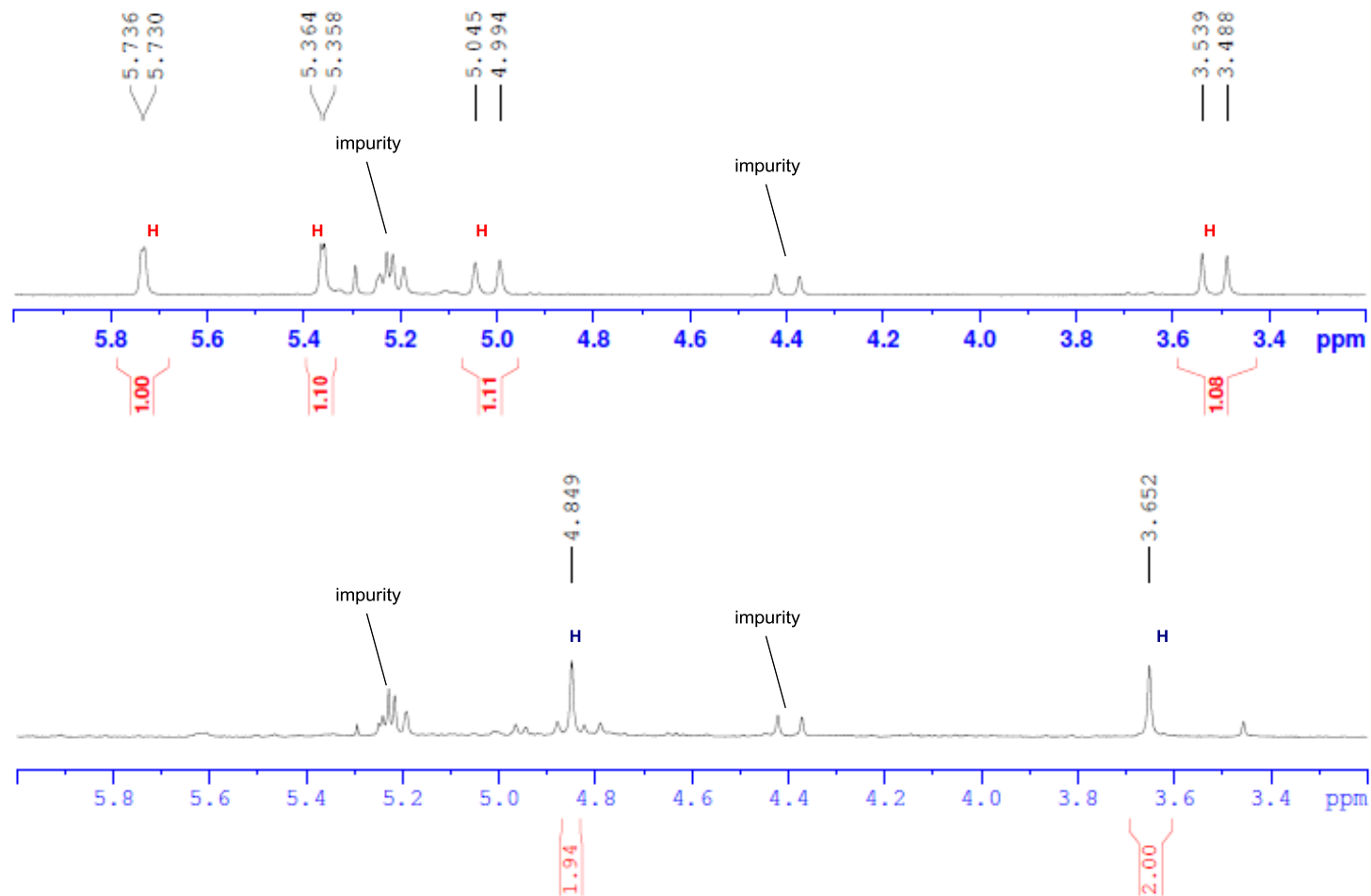
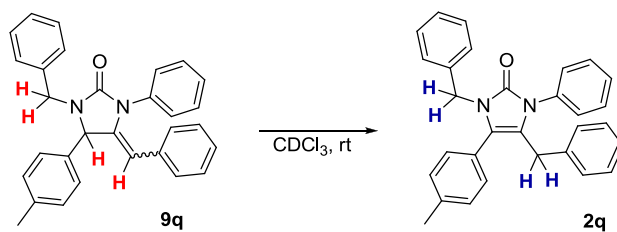
1.00

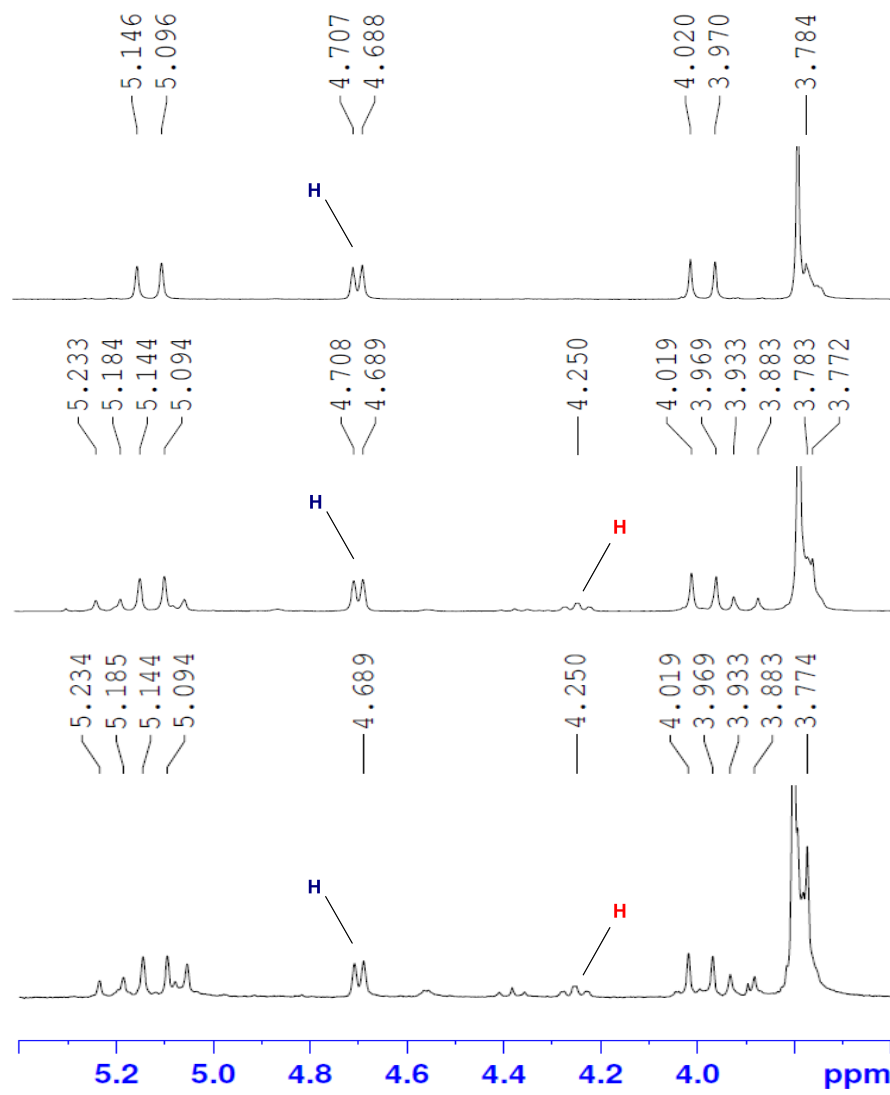
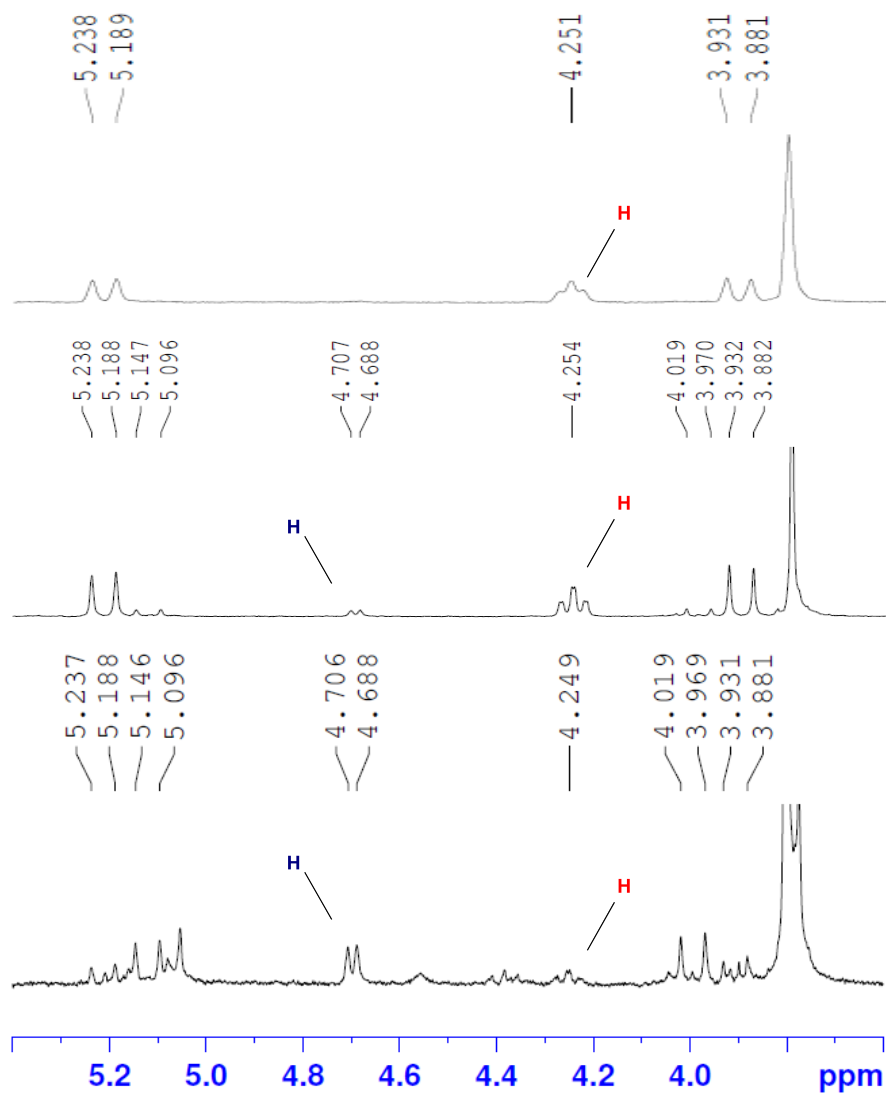
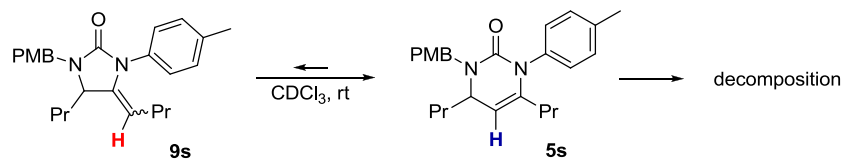
1.10

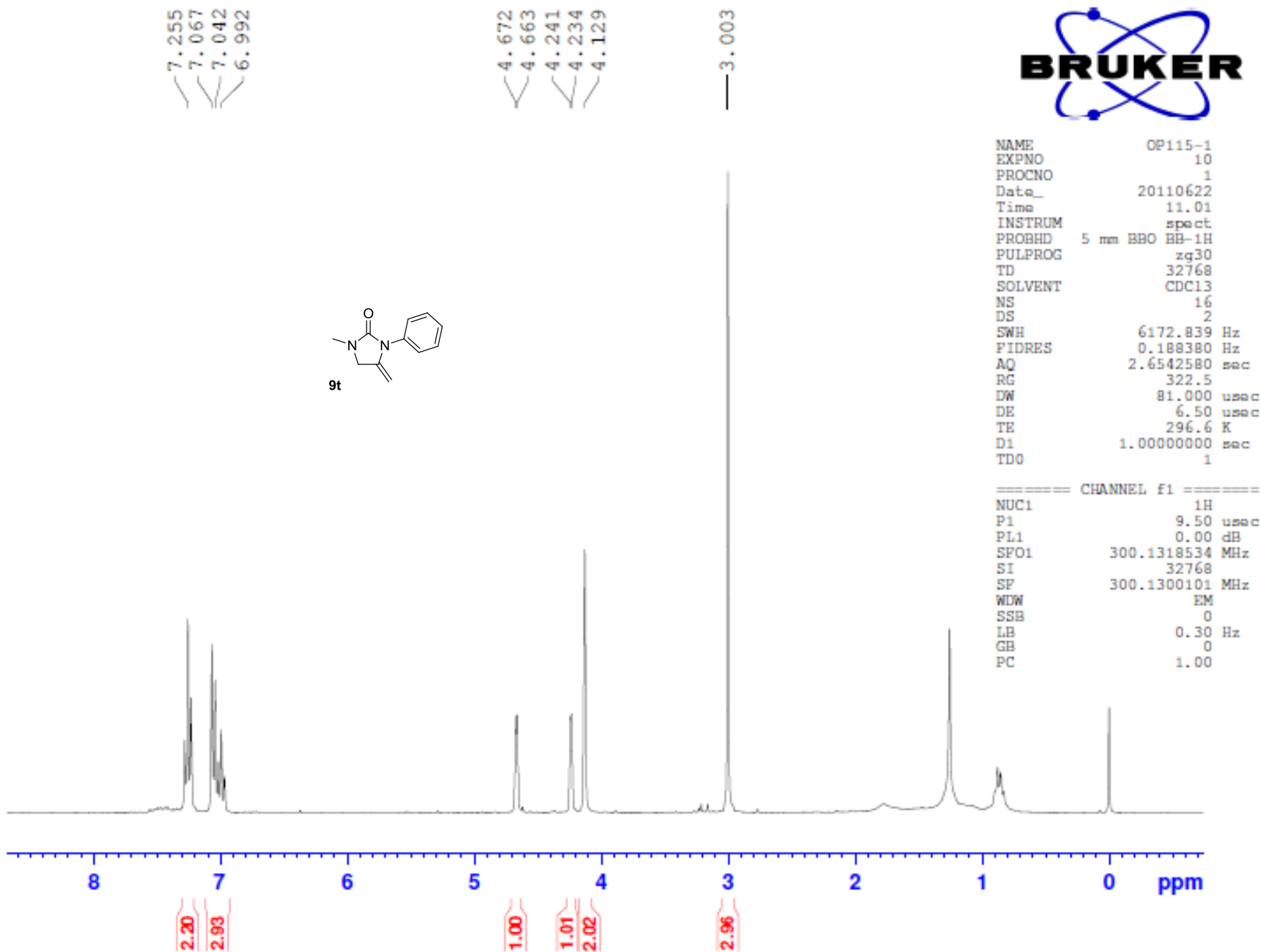
1.11

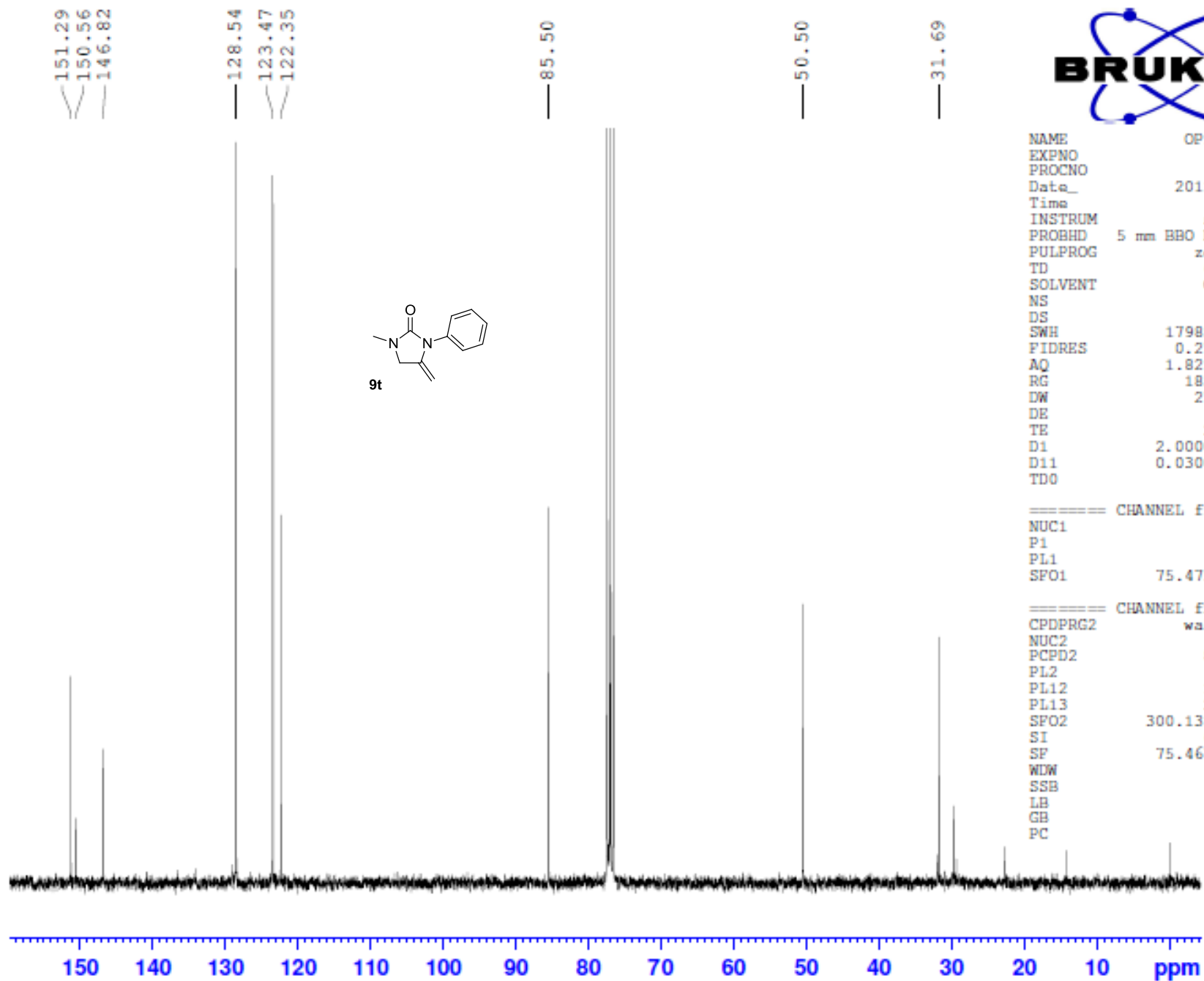
1.06

4.93









NAME OP115-1
EXPNO 11
PROCNO 1
Date_ 20110623
Time 0.19
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDC13
NS 1024
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 18390.4
DW 27.800 usec
DE 6.50 usec
TE 297.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1

==== CHANNEL f1 =====
NUC1 13C
P1 8.25 usec
PL1 0.00 dB
SFO1 75.4752953 MHz

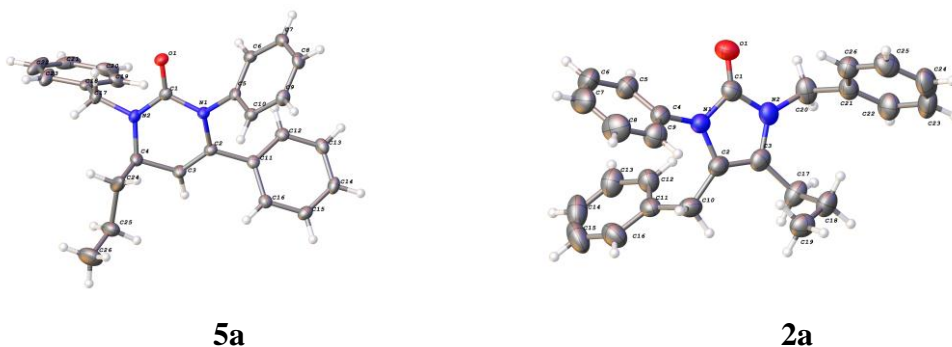
==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 18.51 dB
PL13 20.00 dB
SFO2 300.1312005 MHz
SI 65536
SF 75.4677507 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Crystallographic data

X-ray intensity data for **5a** and **2a** were collected at respectively 100K and room temperature on an Agilent Supernova diffractometer, equipped with an Atlas CCD detector, using Mo K α radiation ($\lambda = 0.7107 \text{ \AA}$). The images were interpreted and integrated with the CrysAlisPro software from Agilent Technologies.¹ Using Olex2,² the structure was solved with the ShelxS³ structure solution program using Direct Methods and refined with the ShelxL³ refinement package using full-matrix least squares minimization on F^2 . In structure **5a**, C25 and C26 are modeled in two positions with occupancies of 0.5. Non hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors were fixed at 1.2 times U_{eq} of the parent atoms (1.5 for methyl groups). CCDC-966797 and CCDC-966798 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5a C₂₆H₂₆N₂O, $M = 382.49 \text{ g mol}^{-1}$, monoclinic, P2₁/n (no. 14), $a = 9.9630(9) \text{ \AA}$, $b = 10.2126(5) \text{ \AA}$, $c = 21.0844(18) \text{ \AA}$, $\beta = 97.452(10)$, $V = 2127.2(3) \text{ \AA}^3$, $T = 100.5(9) \text{ K}$, $Z = 4$, $\rho_{\text{calcd}} = 1.194 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.073 \text{ mm}^{-1}$, $F(000) = 816.0$, crystal size $0.2 \times 0.2 \times 0.2 \text{ mm}^3$, 9185 reflections measured, 4353 unique ($R_{\text{int}} = 0.0253$) which were used in all calculations. The final wR_2 was 0.1122 (all data) and R_1 was 0.0458 ($>2\sigma(I)$).

2a C₂₆H₂₆N₂O, $M = 382.49 \text{ g mol}^{-1}$, triclinic, P-1 (no. 2), $a = 7.8694(12) \text{ \AA}$, $b = 10.0748(12) \text{ \AA}$, $c = 13.8855(9) \text{ \AA}$, $\alpha = 101.946(8) \text{ \AA}$, $\beta = 92.094(8)$, $\gamma = 105.143(12) \text{ \AA}$, $V = 1034.8(2) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 2$, $\rho_{\text{calcd}} = 1.228 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.075 \text{ mm}^{-1}$, $F(000) = 408.0$, crystal size $0.6 \times 0.4 \times 0.2 \text{ mm}^3$, 21448 reflections measured, 4251 unique ($R_{\text{int}} = 0.0164$) which were used in all calculations. The final wR_2 was 0.1156 (all data) and R_1 was 0.0427 ($>2\sigma(I)$).



¹ CrysAlis PRO. Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England, 2012.

² O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

³ G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.