

Brønsted Acid Activation of α -Diazo Imides: A Highly *syn*-Selective Glycolate Mannich Reaction

Timothy L. Troyer, Hubert Muchalski, and Jeffrey N. Johnston*

Department of Chemistry & Vanderbilt Institute of Chemical Biology

Vanderbilt University

2301 Vanderbilt Place, Nashville, TN 37235-1822

S-II-X

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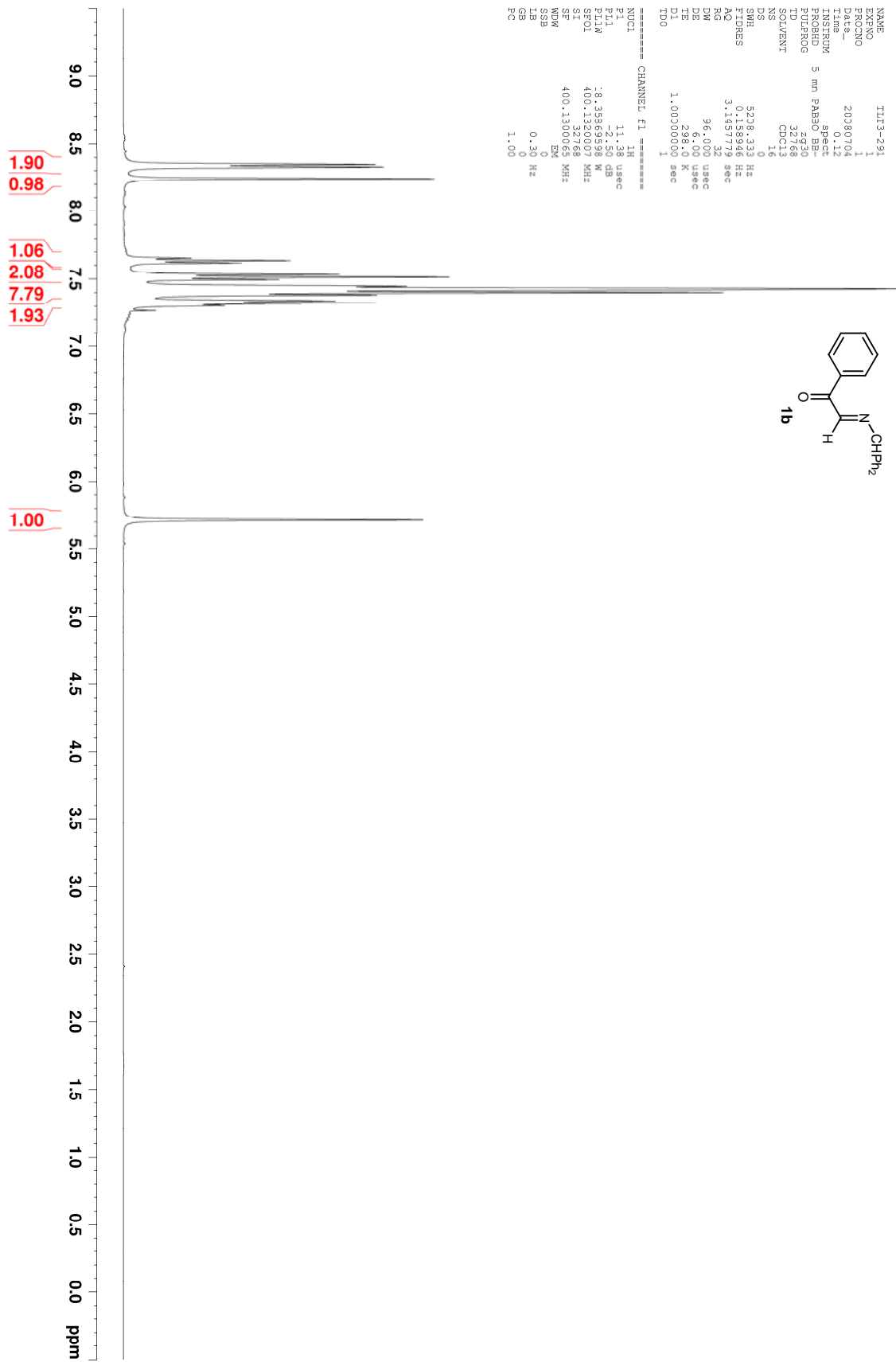
Figure 1. ¹H NMR (400 MHz, CDCl₃) of **1b**

Figure 2. ¹³C NMR (100 MHz, CDCl₃) of **1b**

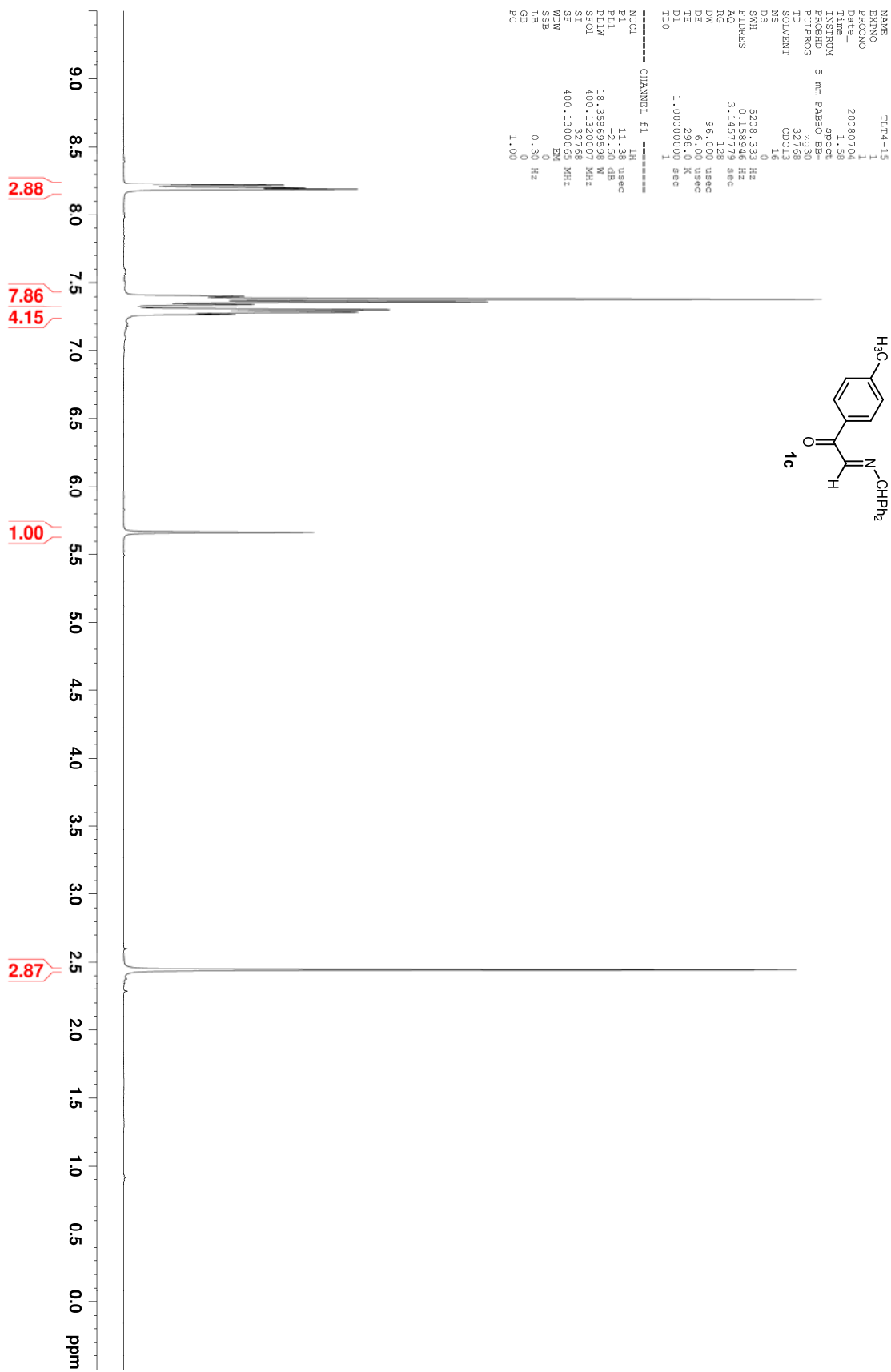
Figure 3. ¹H NMR (400 MHz, CDCl₃) of 1c

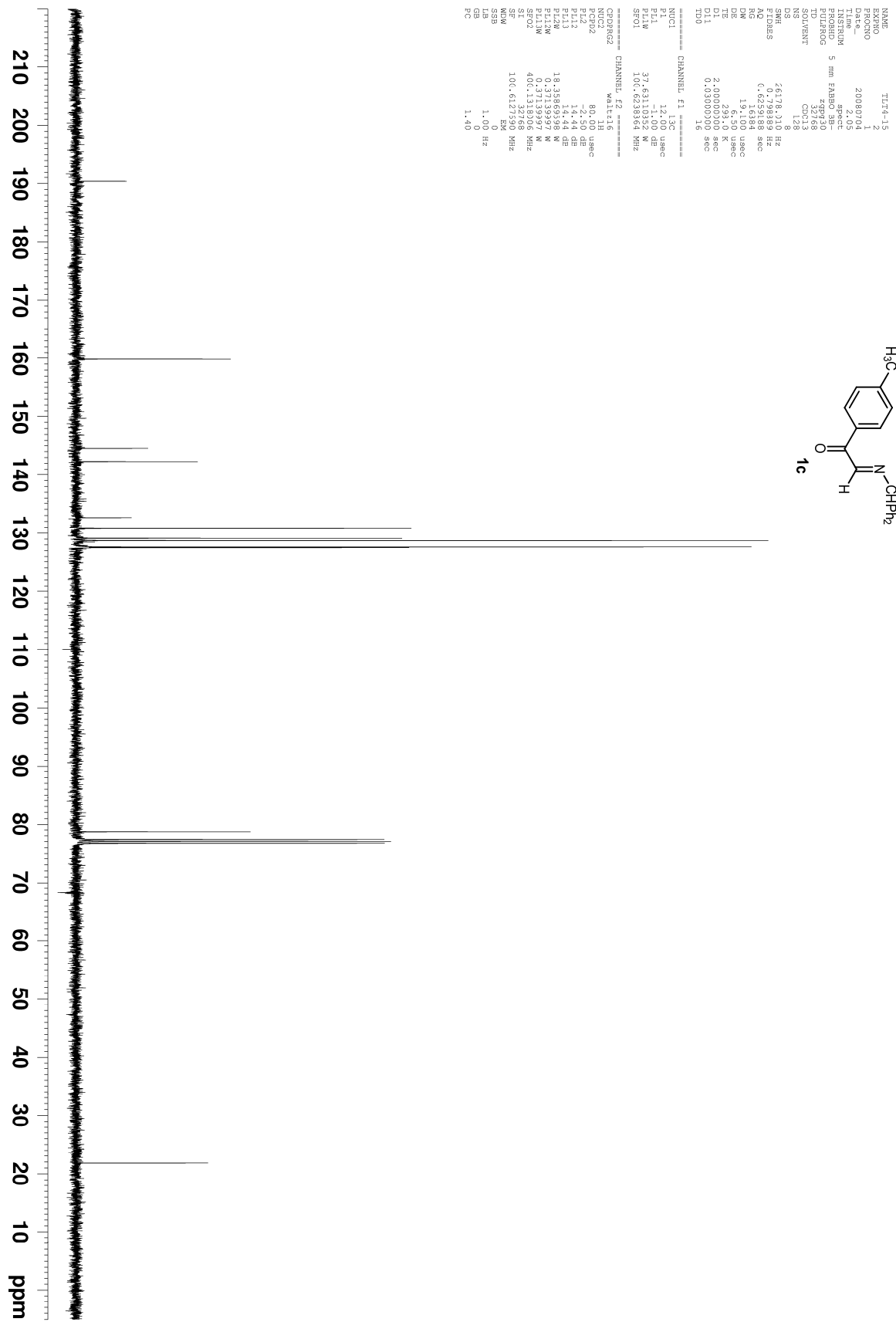
Figure 4. ¹³C NMR (100 MHz, CDCl₃) of 1c

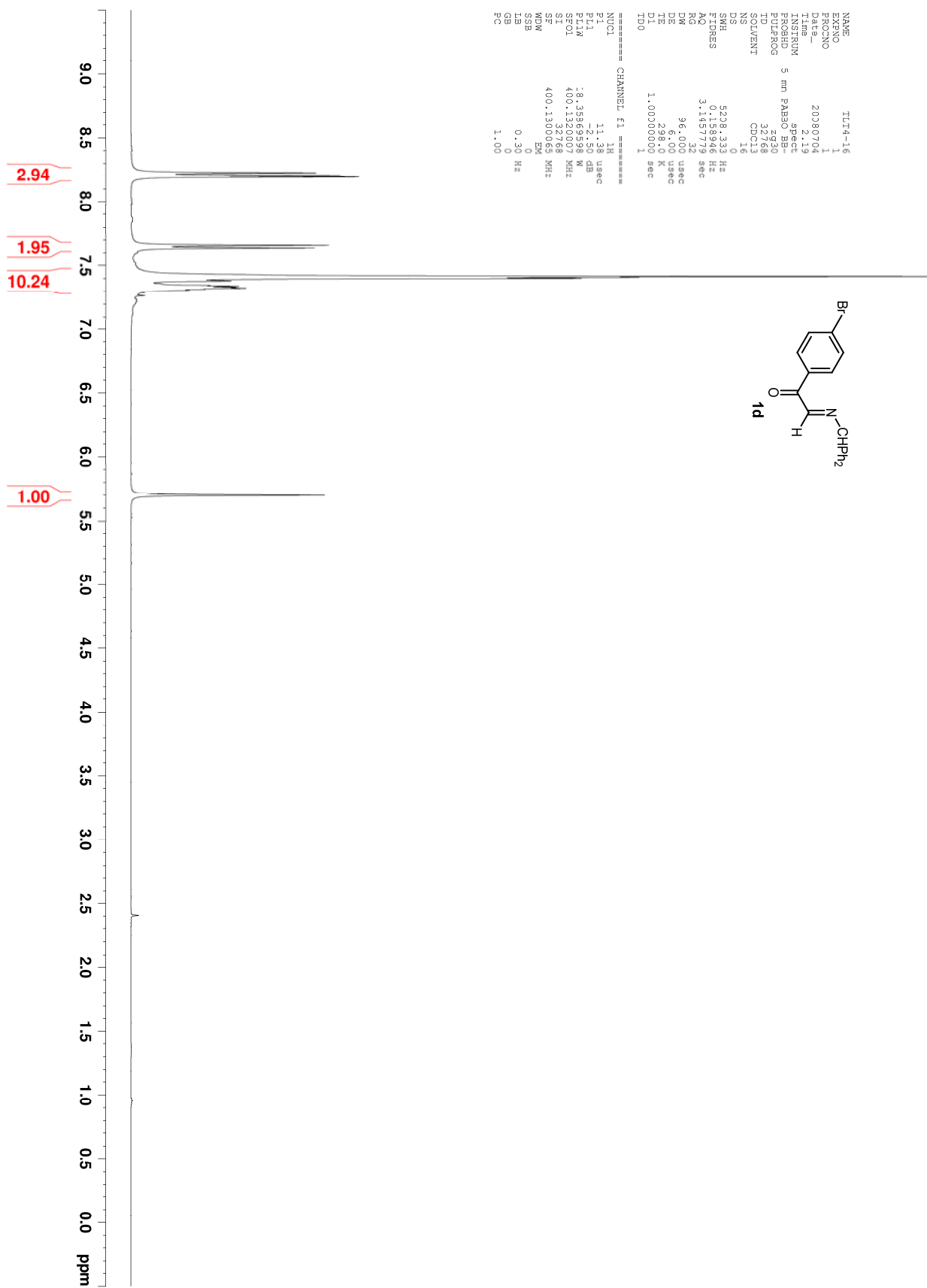
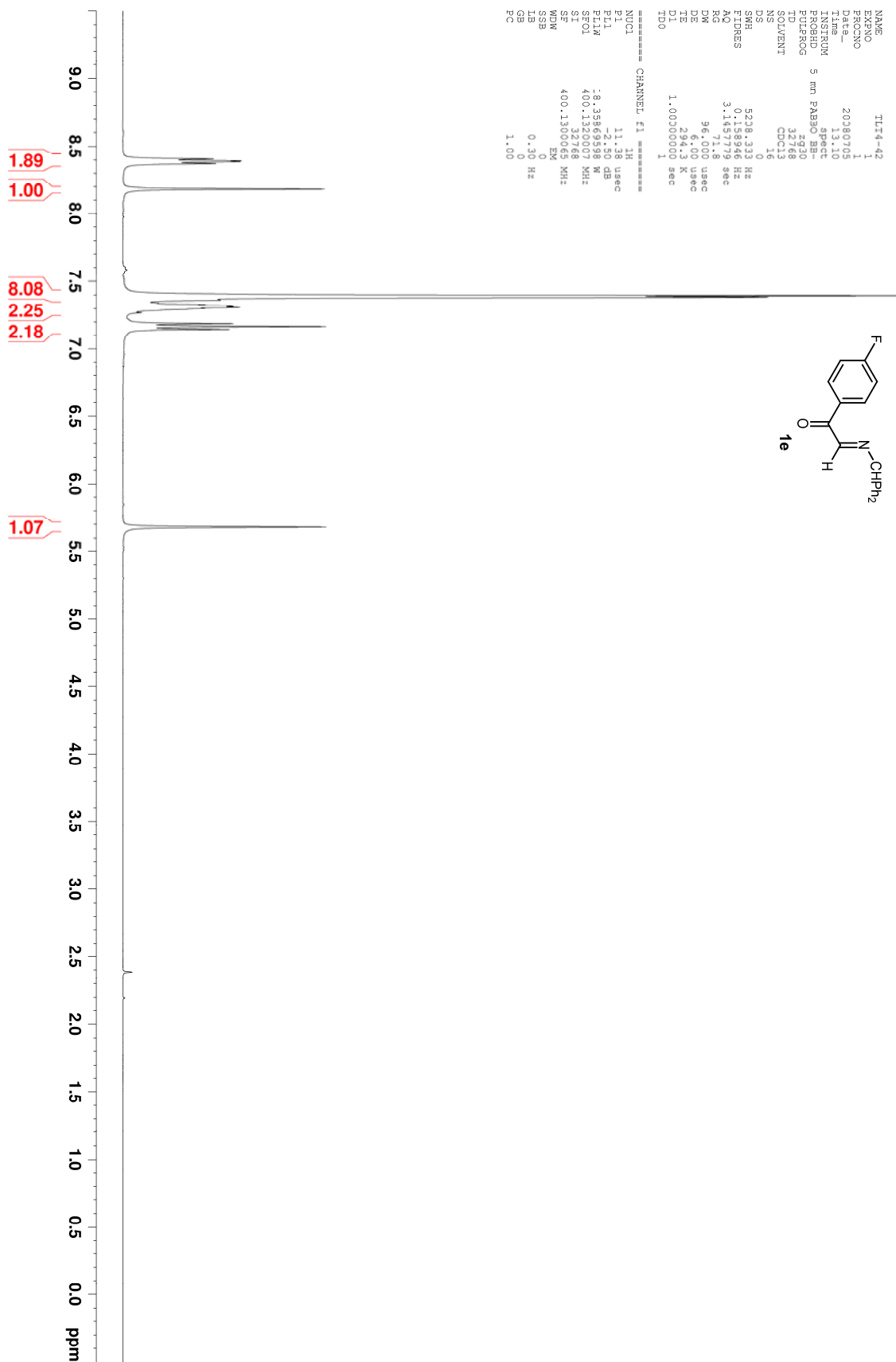
Figure 5. ¹H NMR (400 MHz, CDCl₃) of **1d**

Figure 7. ¹H NMR (400 MHz, CDCl₃) of **1e**

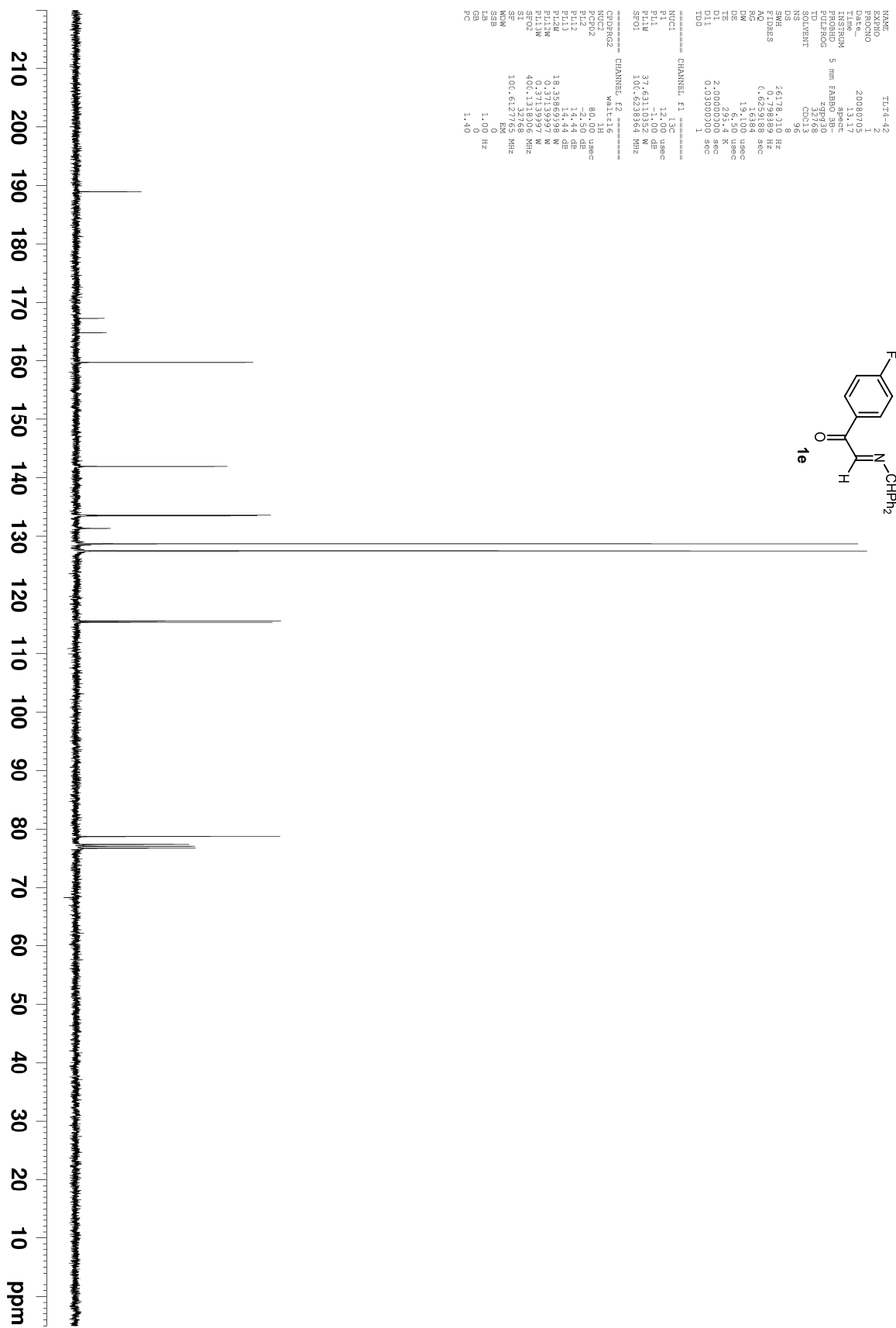
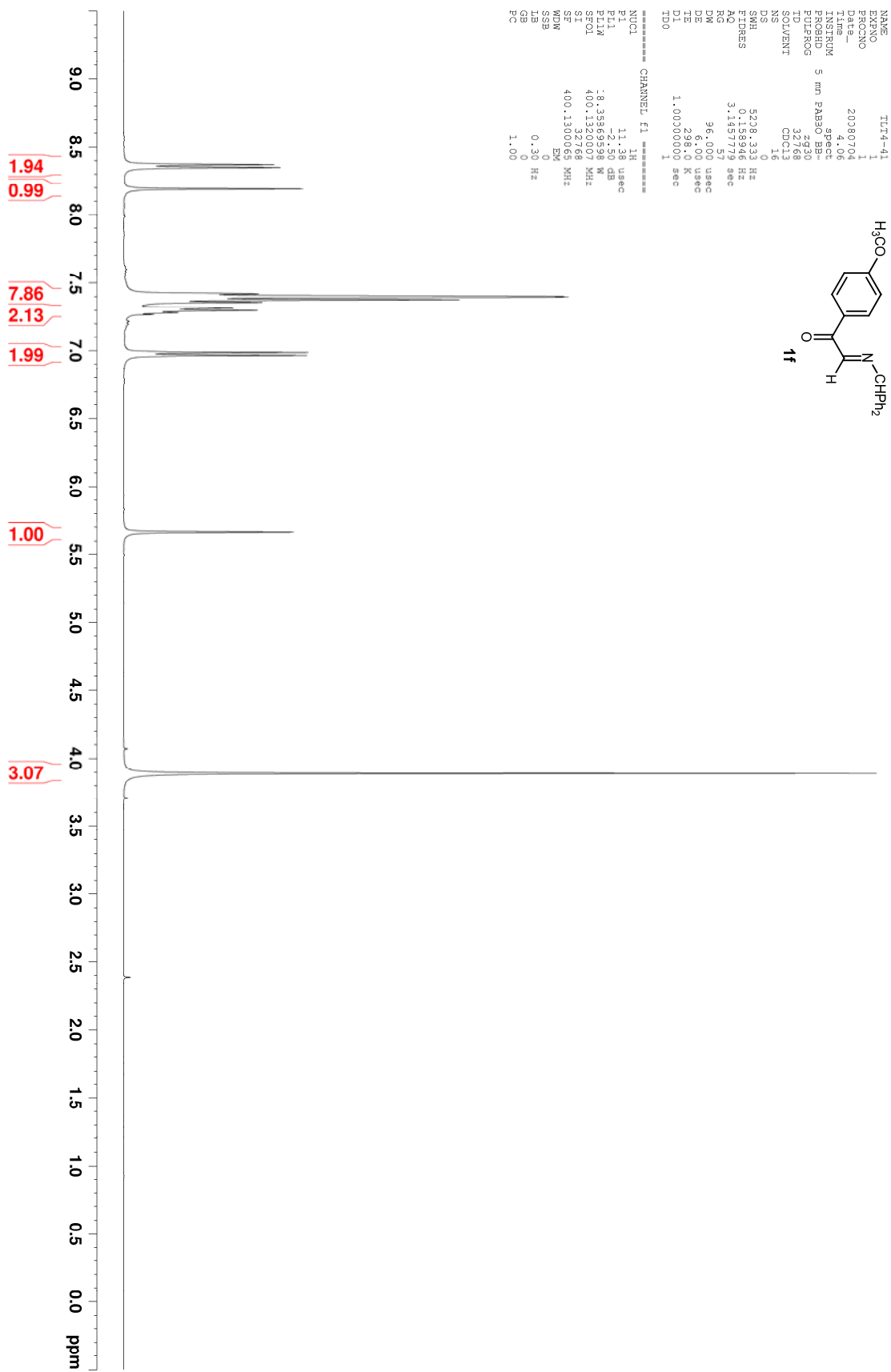


Figure 9. ¹H NMR (400 MHz, CDCl₃) of **1f**

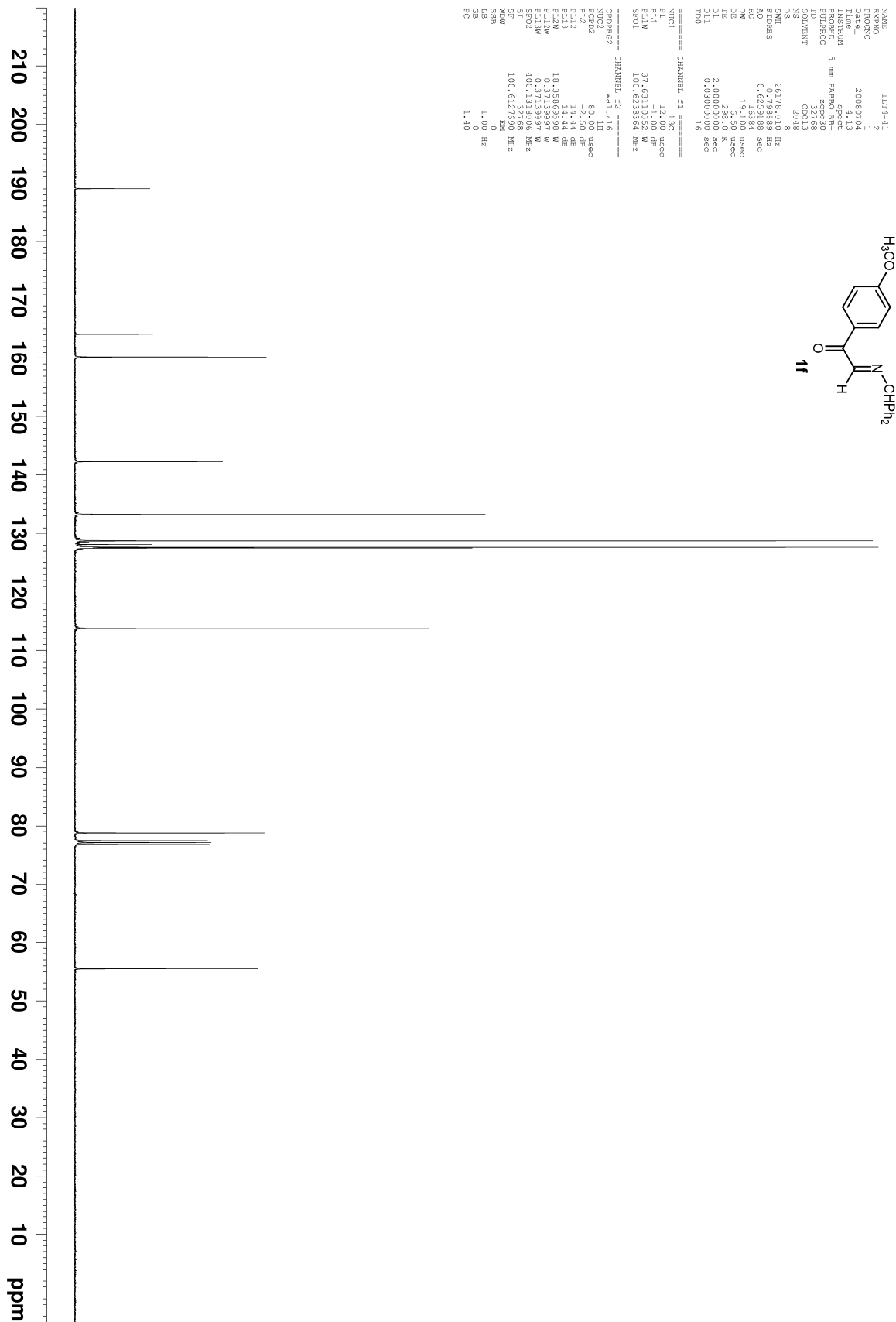
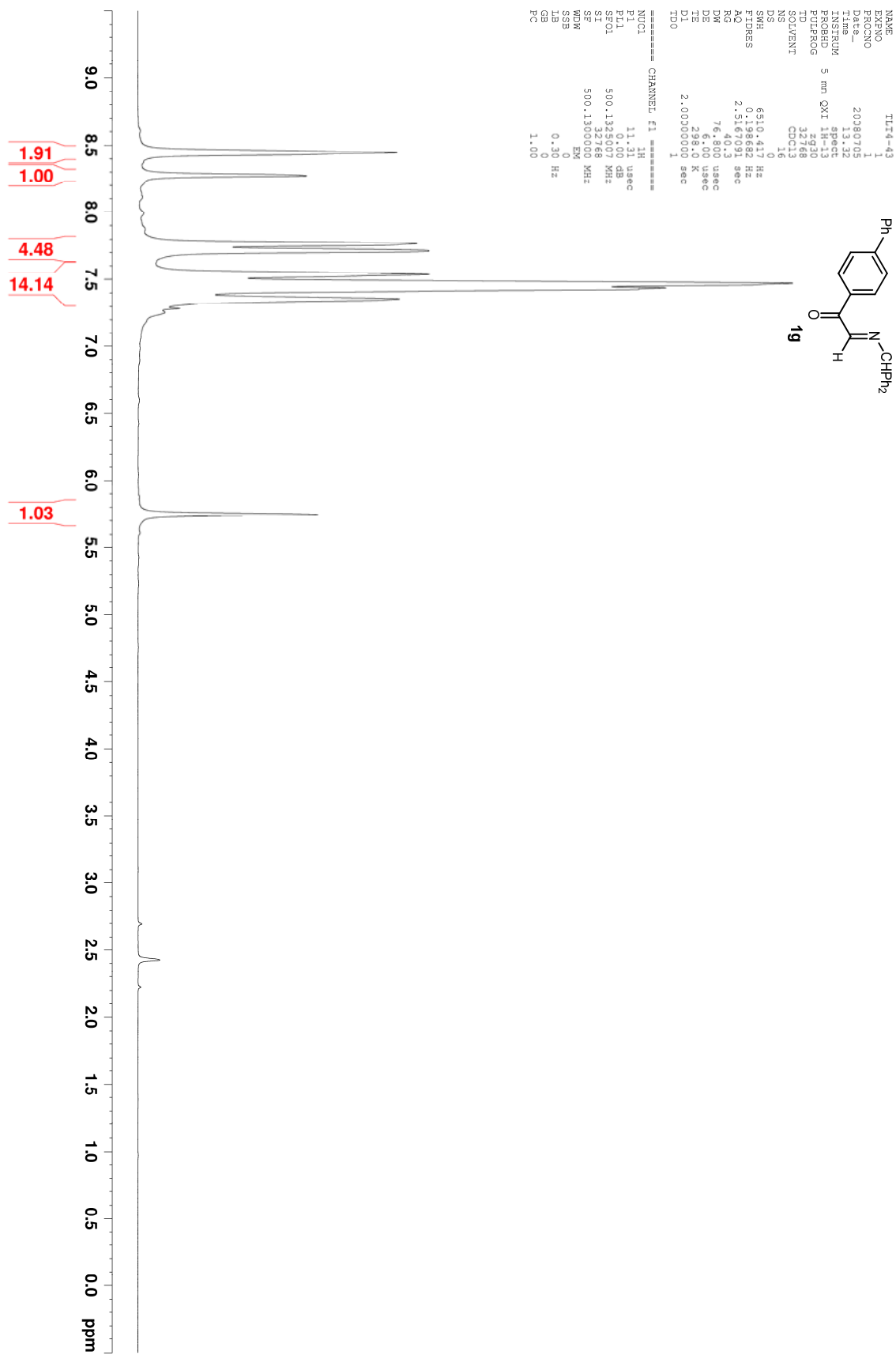


Figure 11. ^1H NMR (500 MHz, CDCl_3) of **1g**

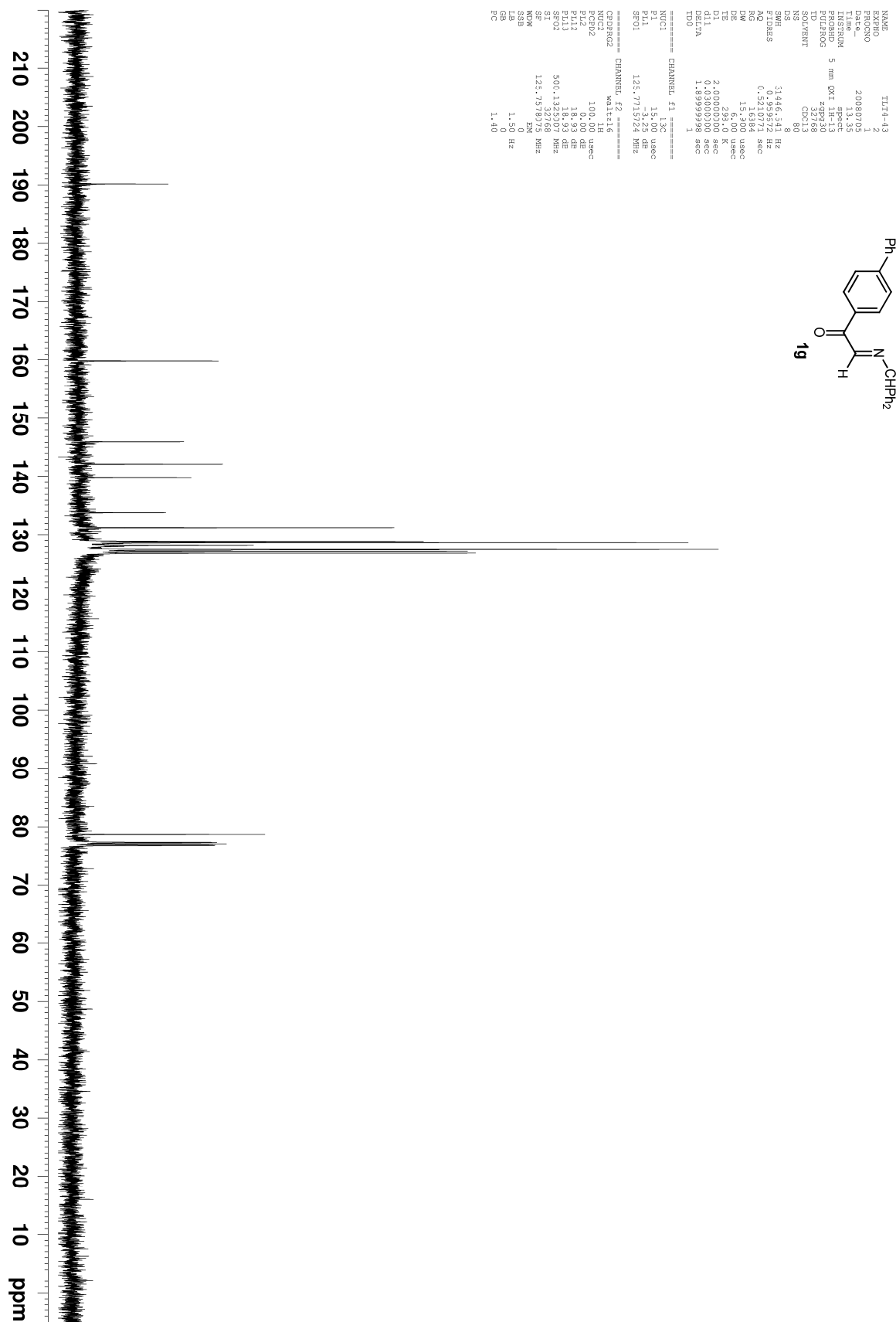
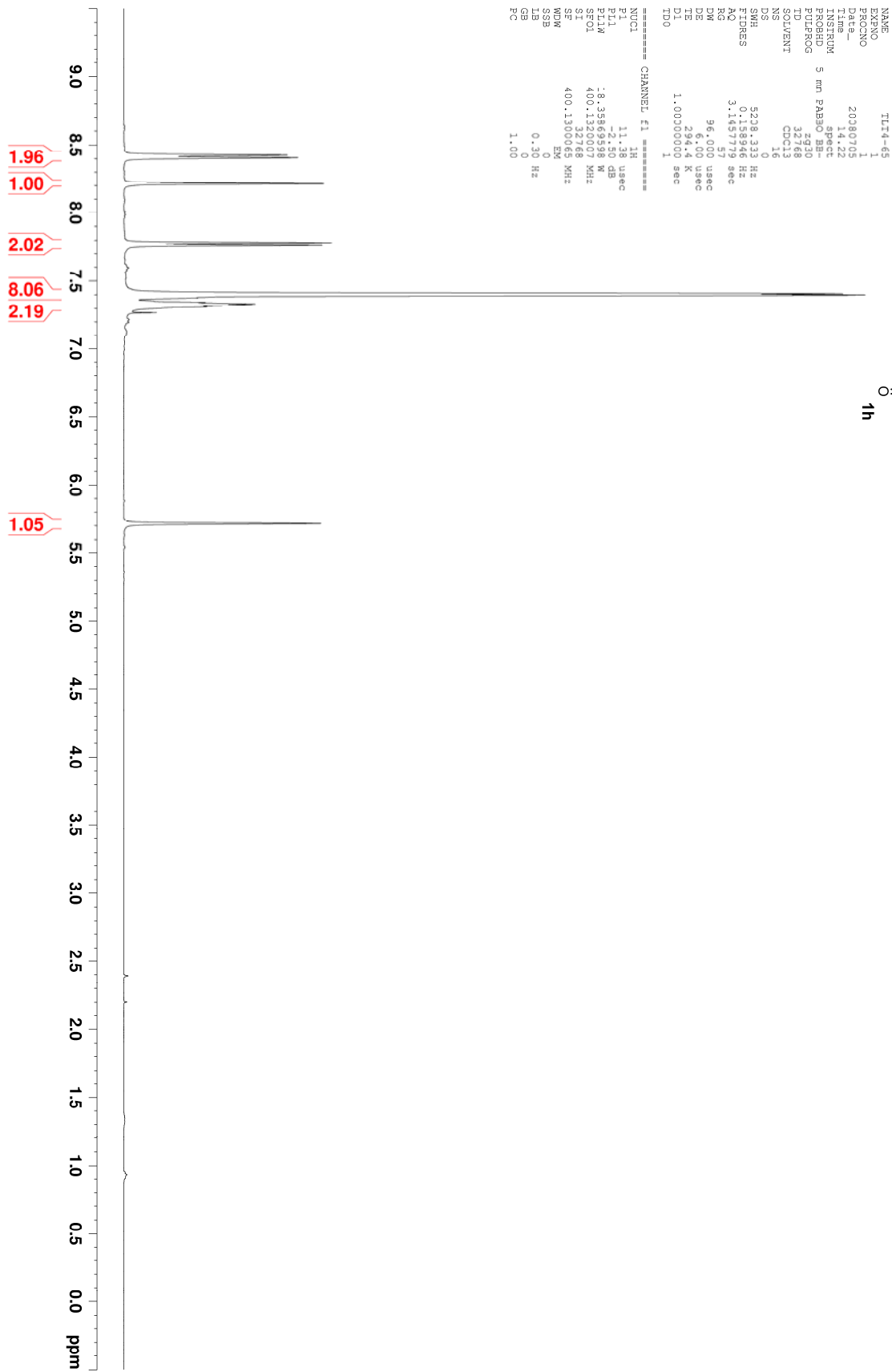


Figure 13. ¹H NMR (400 MHz, CDCl₃) of **1h**

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Figure 14. ^{13}C NMR (100 MHz, CDCl_3) of **1h**

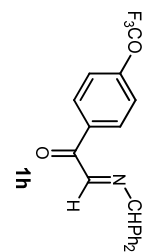
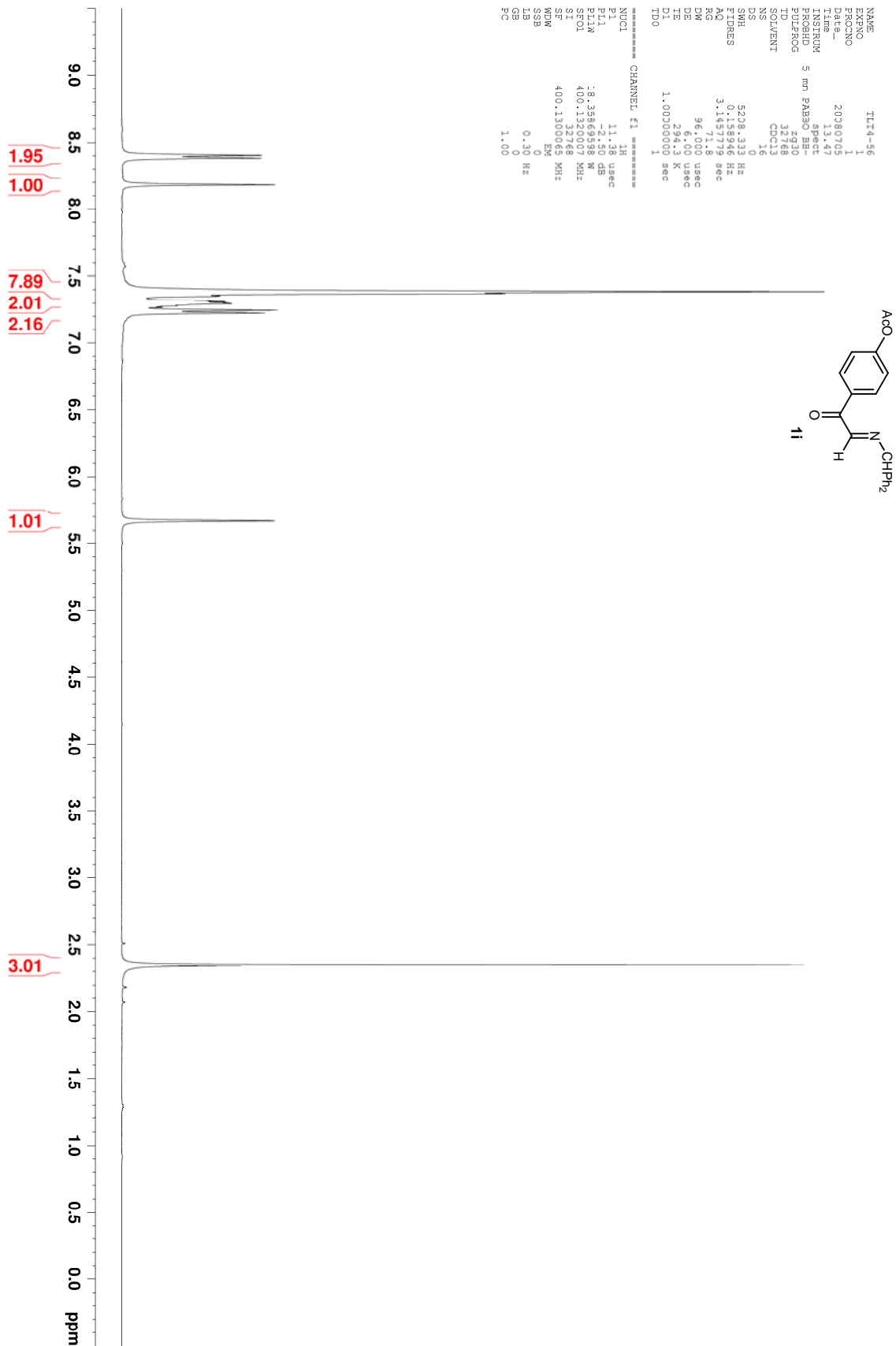


Figure 15. ¹H NMR (400 MHz, CDCl₃) of **11**

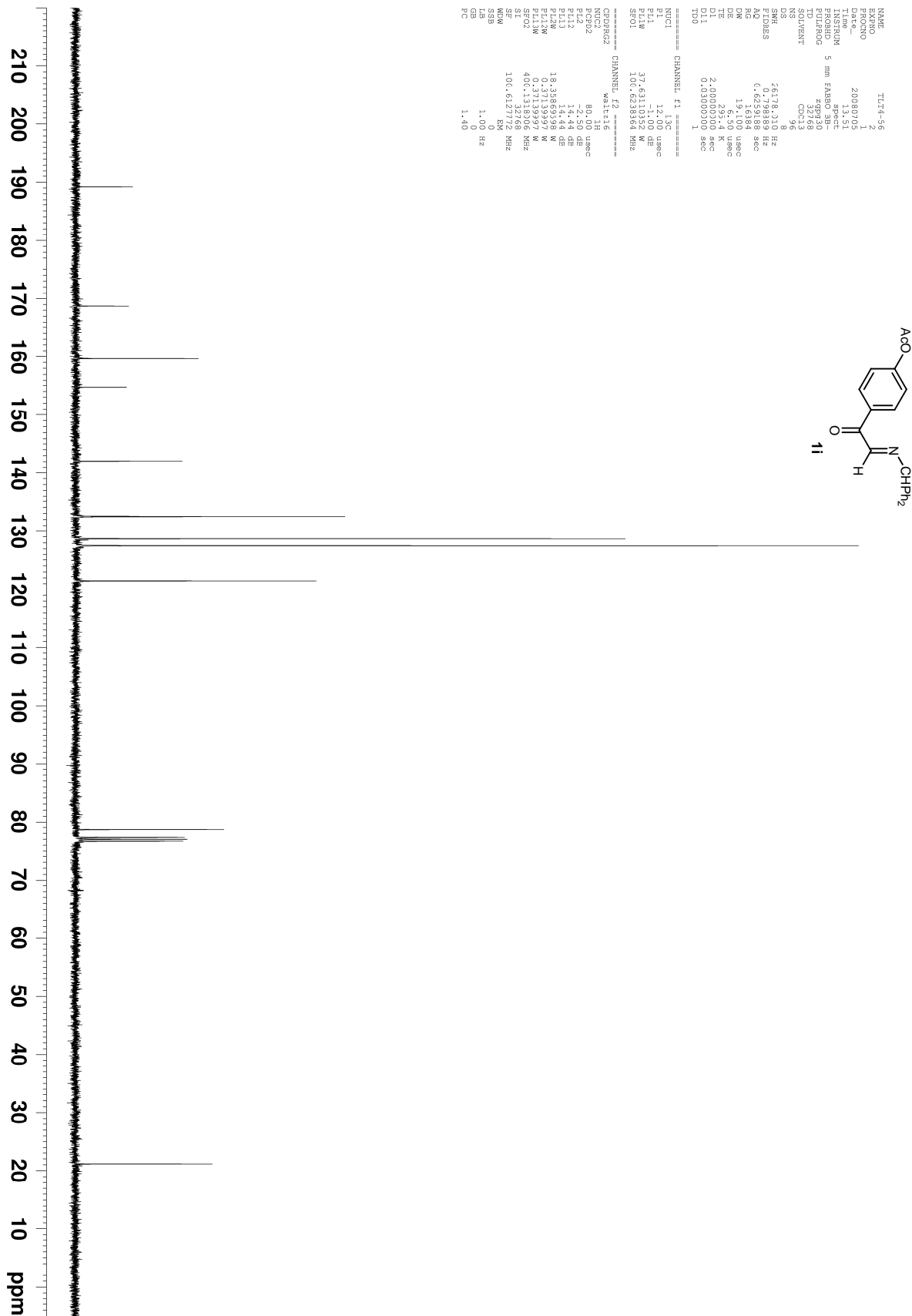
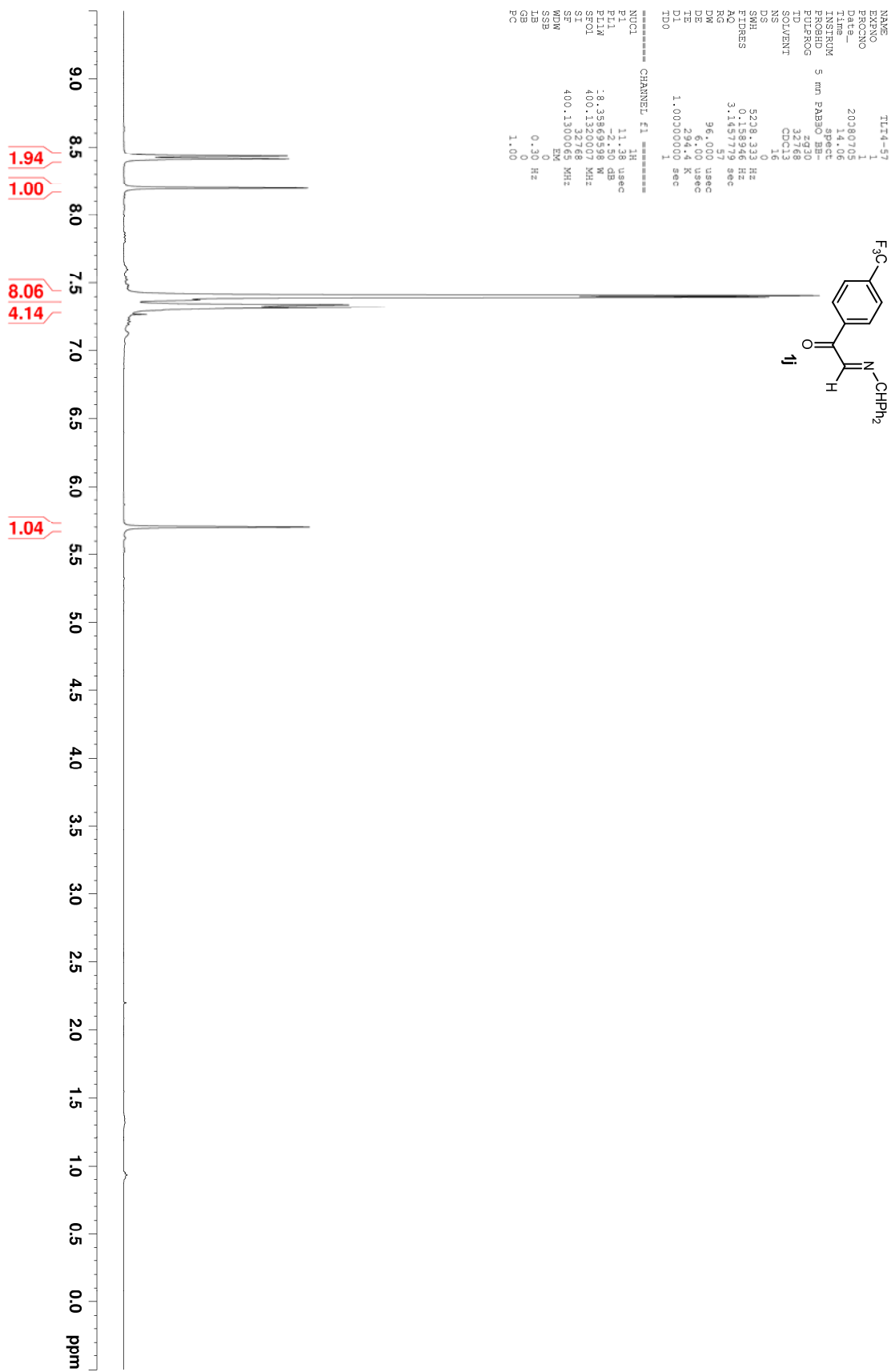


Figure 17. ^1H NMR (400 MHz, CDCl_3) of **1j**

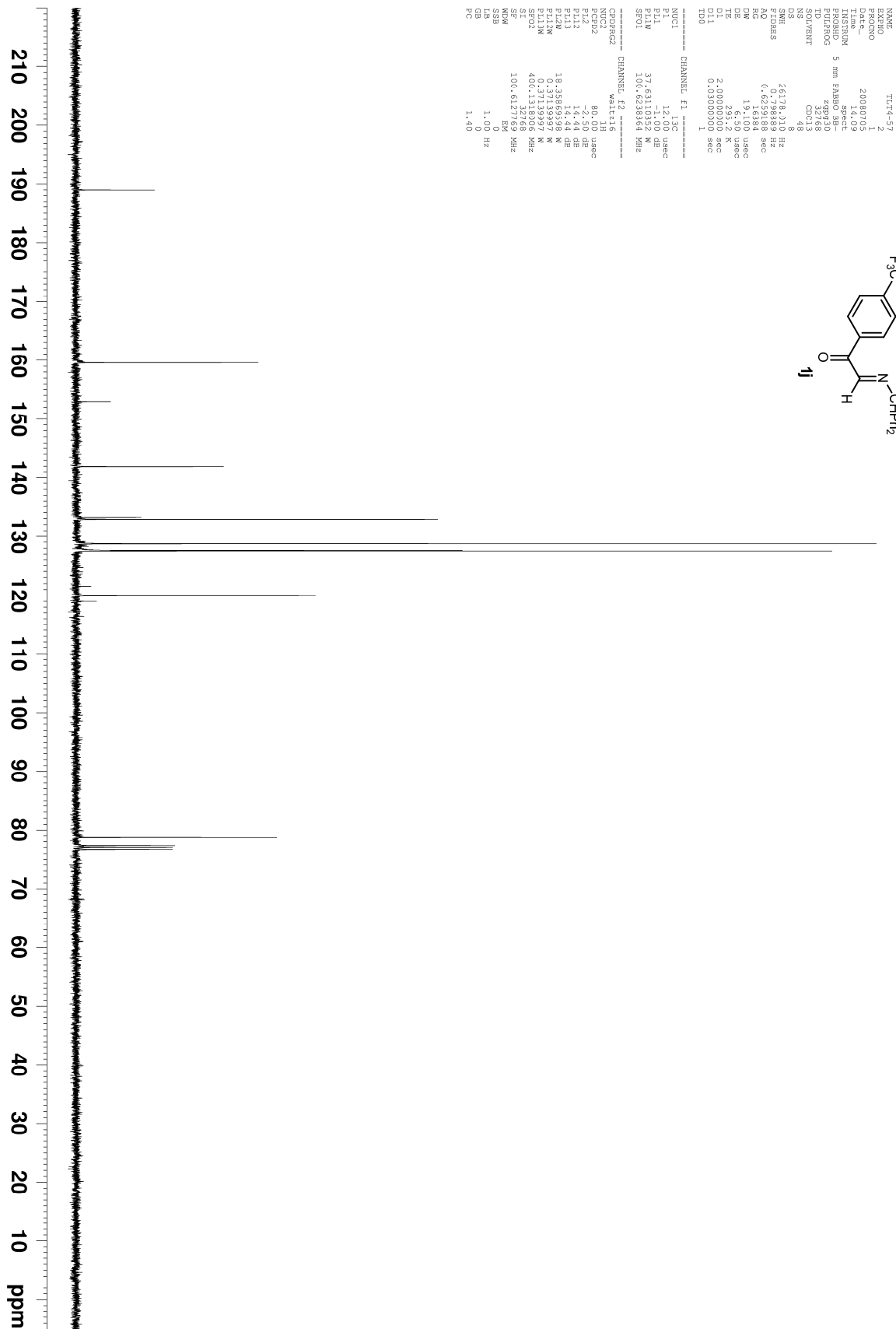
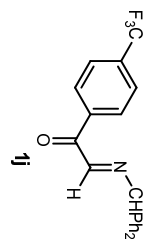


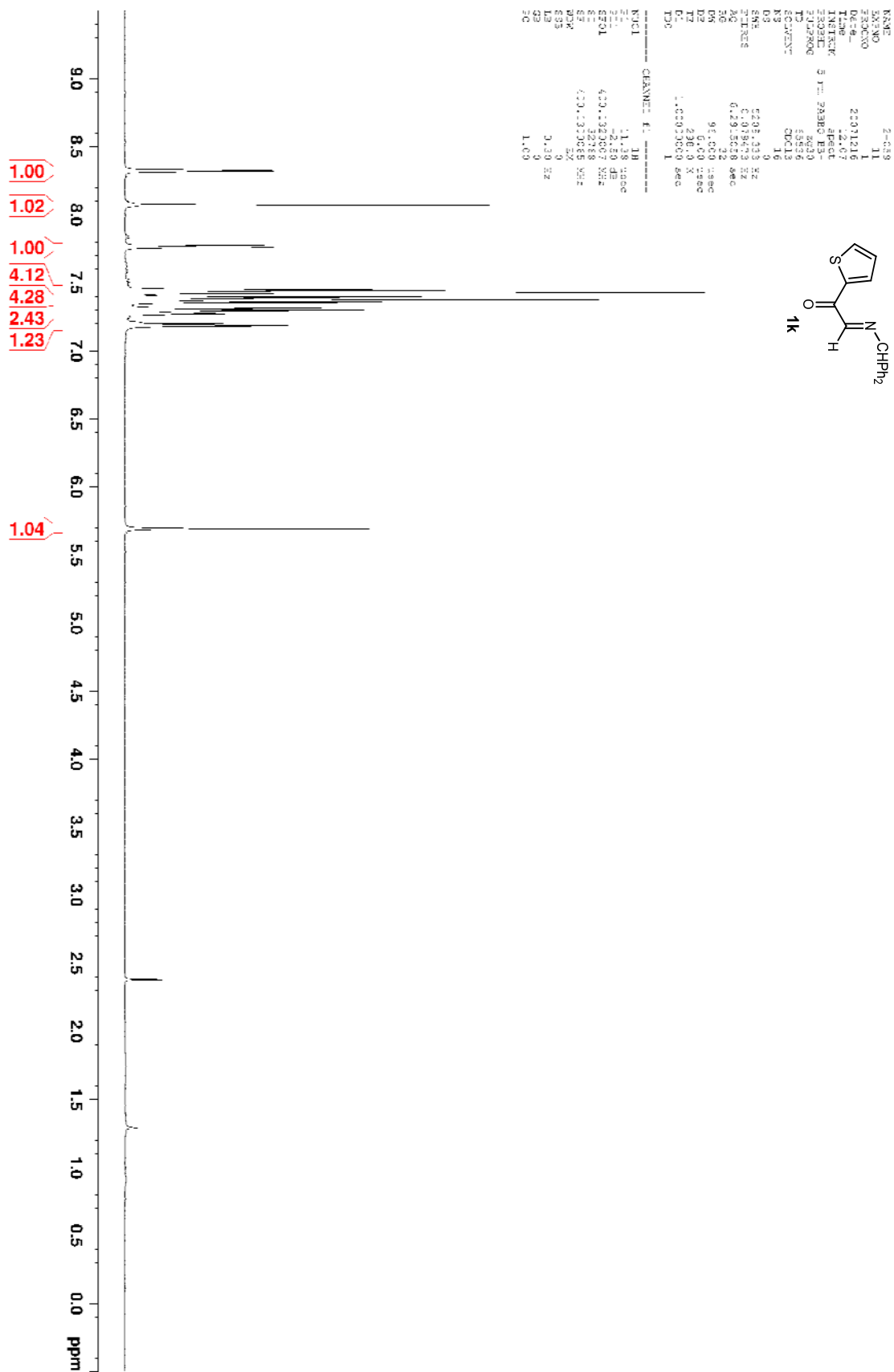
Figure 19. ^1H NMR (400 MHz, CDCl_3) of **1k**

Figure 20. ^{13}C NMR (100 MHz, CDCl_3) of **1k**

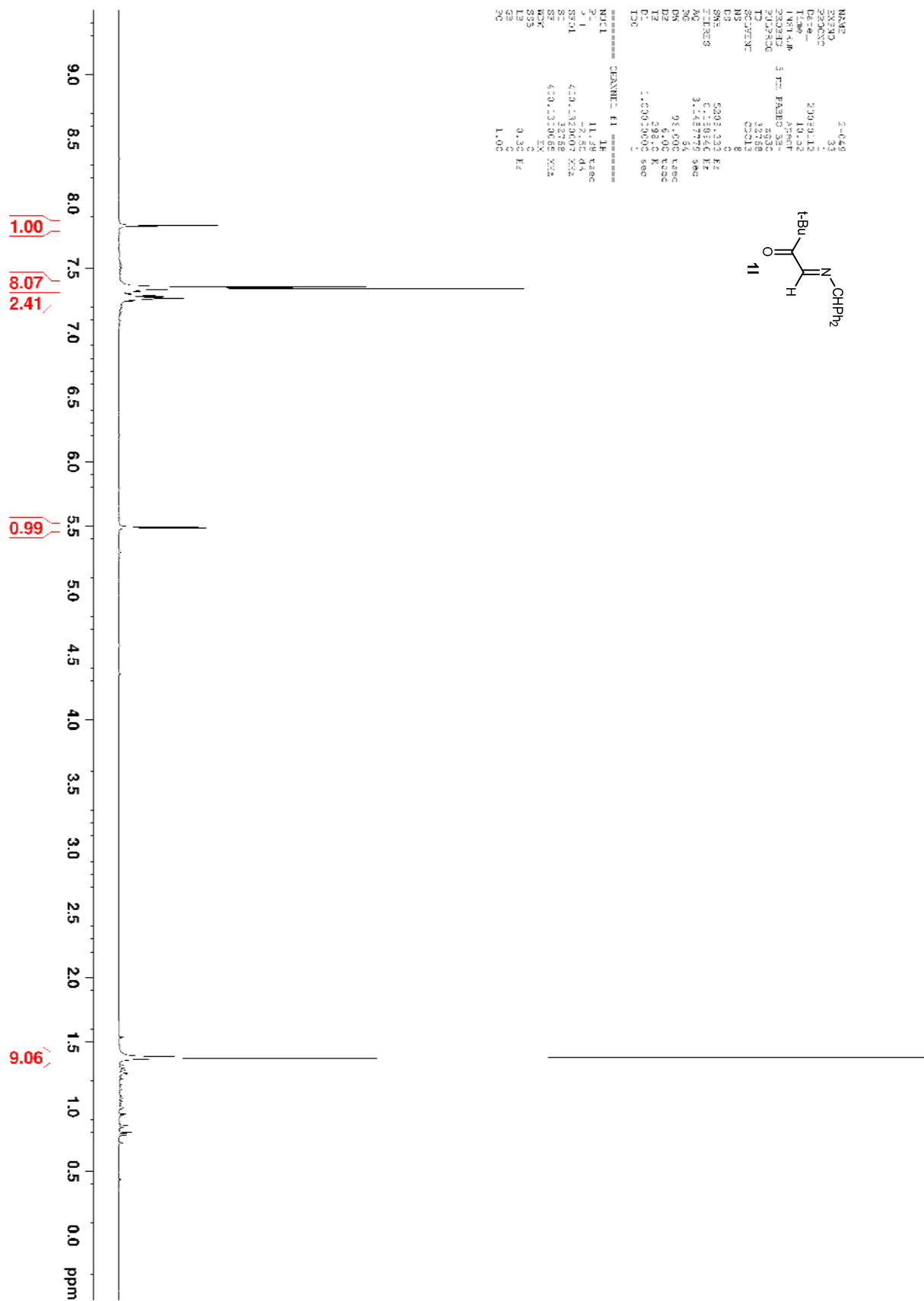
Figure 21. ¹H NMR (400 MHz, CDCl₃) of 11

Figure 22. ^{13}C NMR (100 MHz, CDCl_3) of **11**

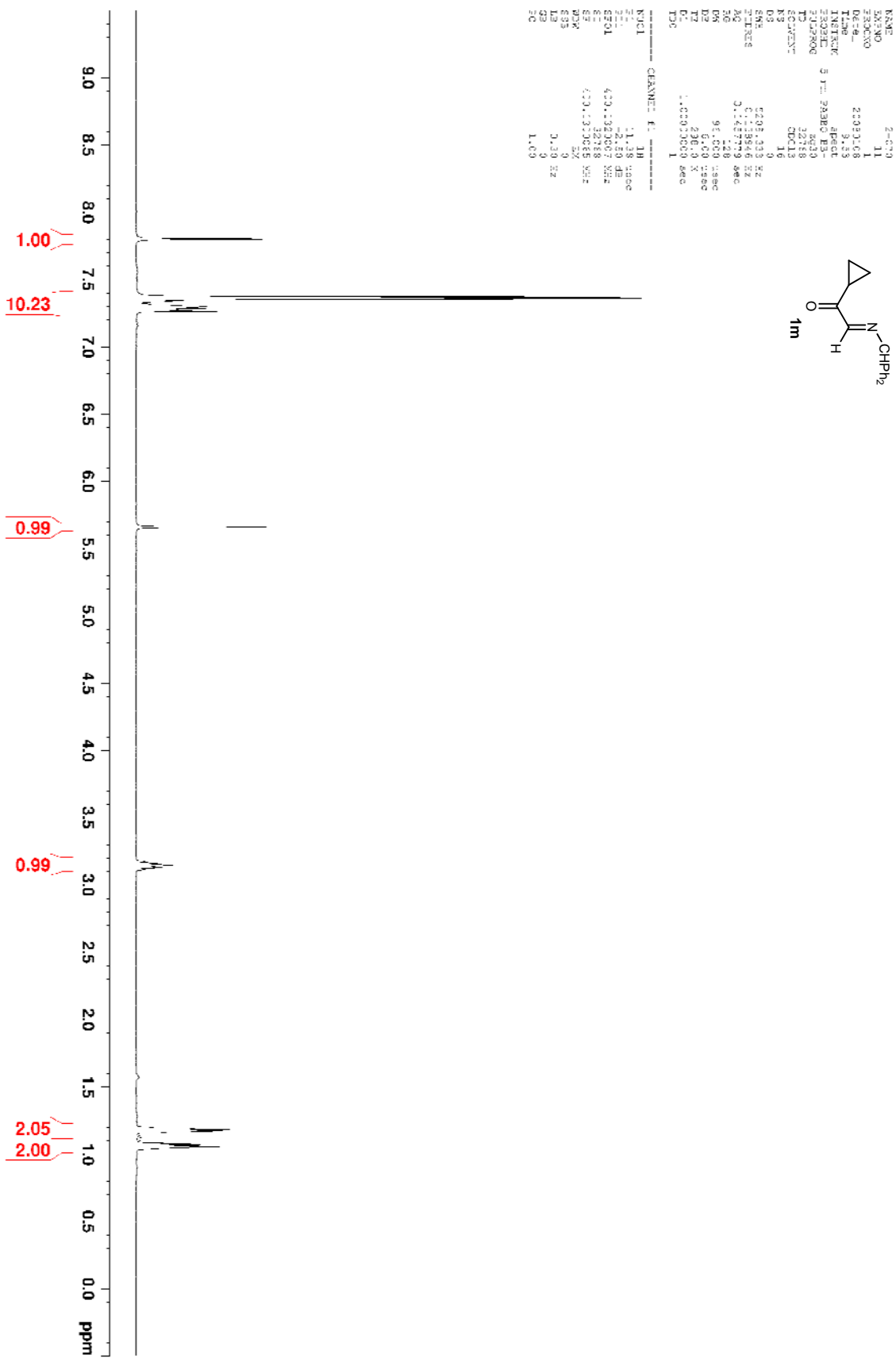
Figure 23. ^1H NMR (400 MHz, CDCl_3) of **1m**

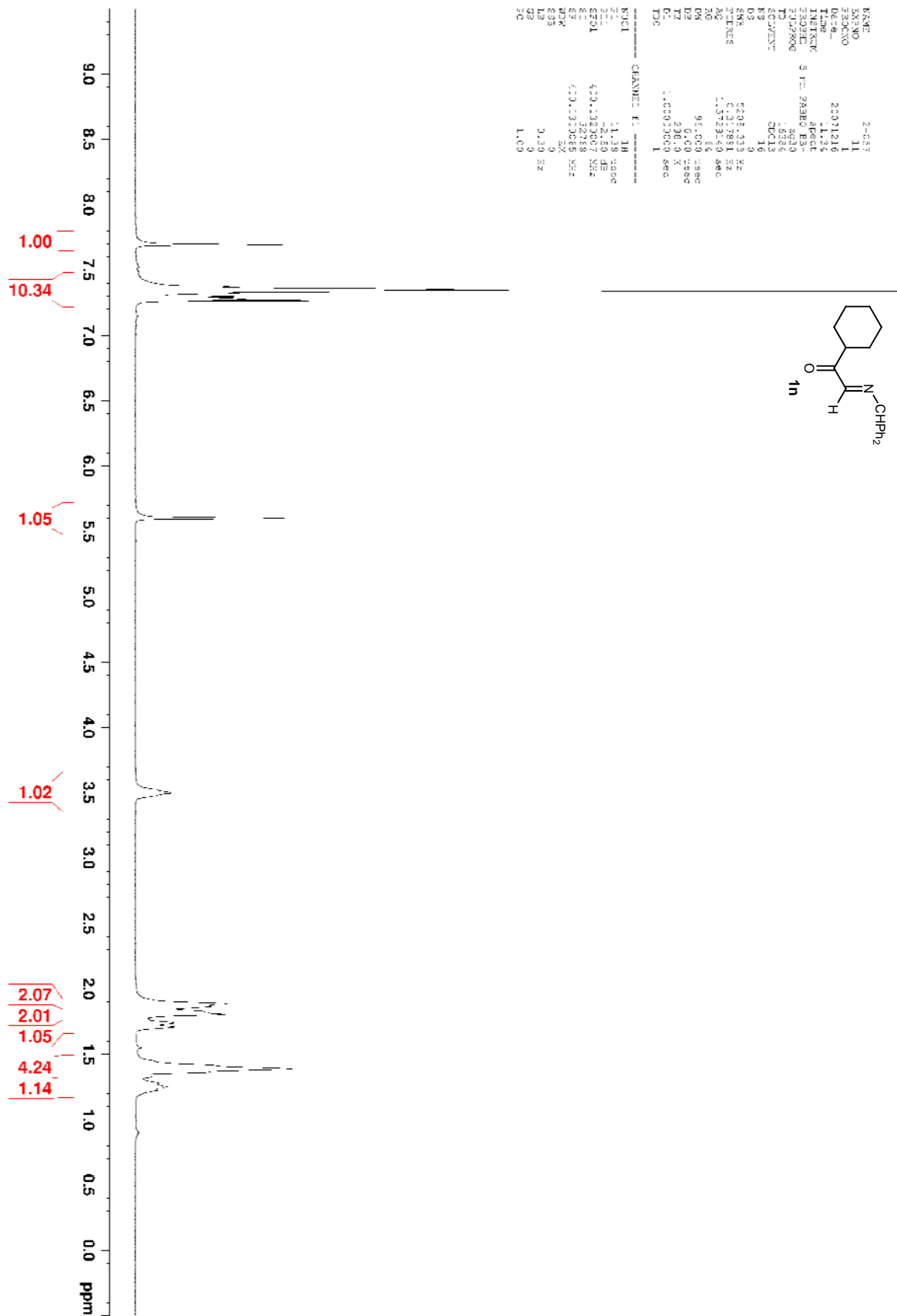
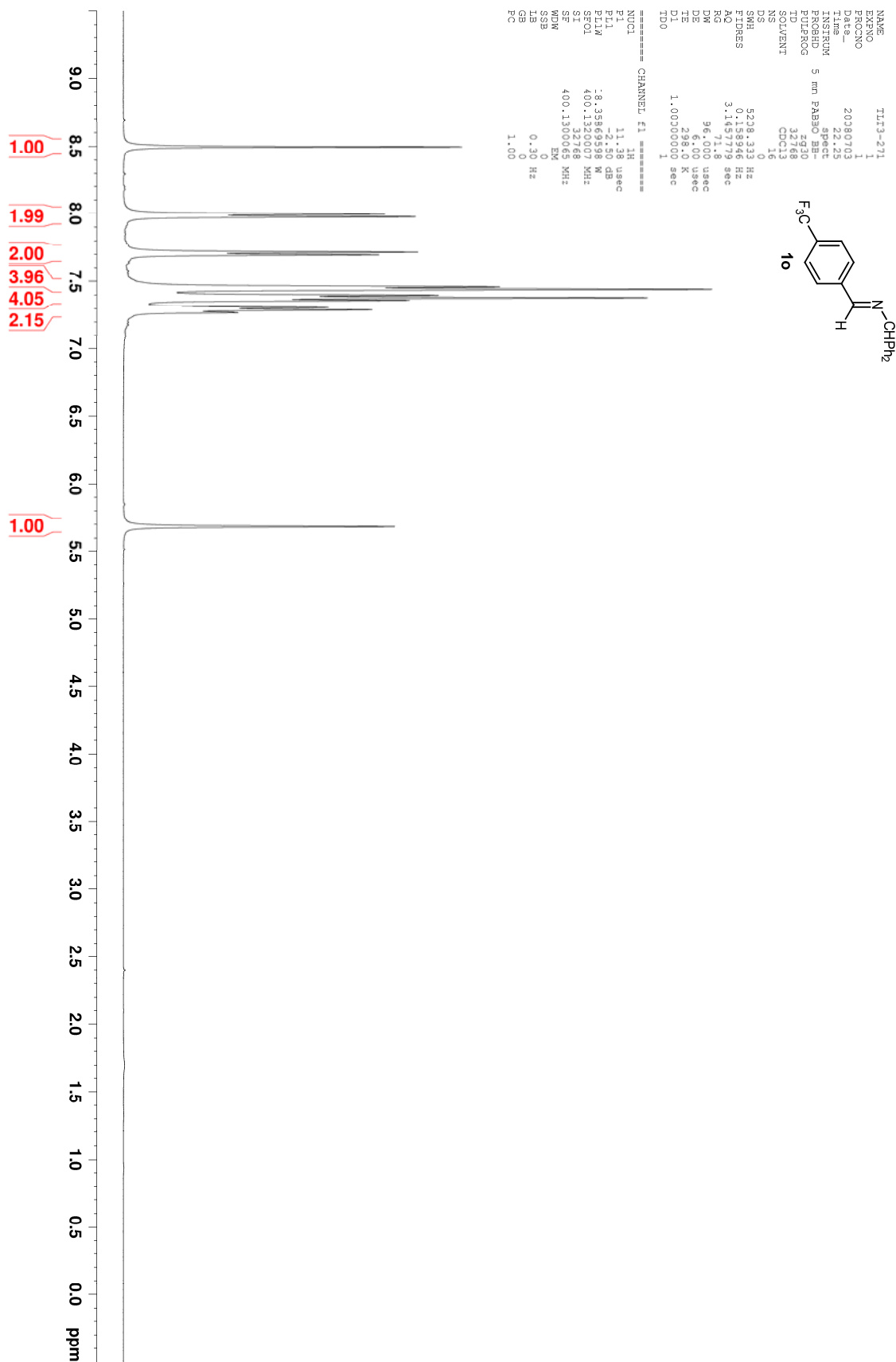
Figure 25. ¹H NMR (400 MHz, CDCl₃) of 1n

Figure 26. ^{13}C NMR (100 MHz, CDCl_3) of **1n**

Figure 27. ^1H NMR (400 MHz, CDCl_3) of **10**

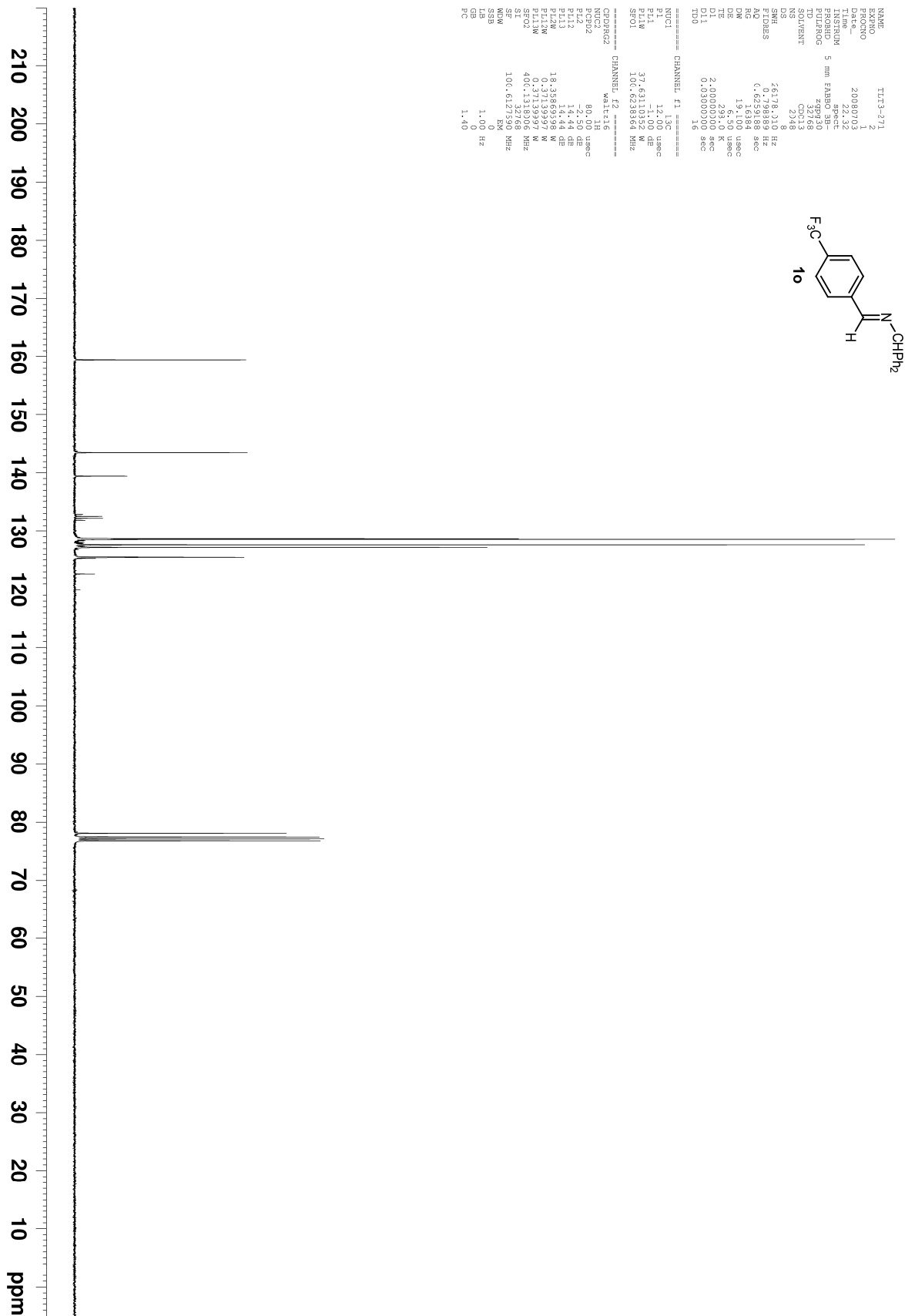
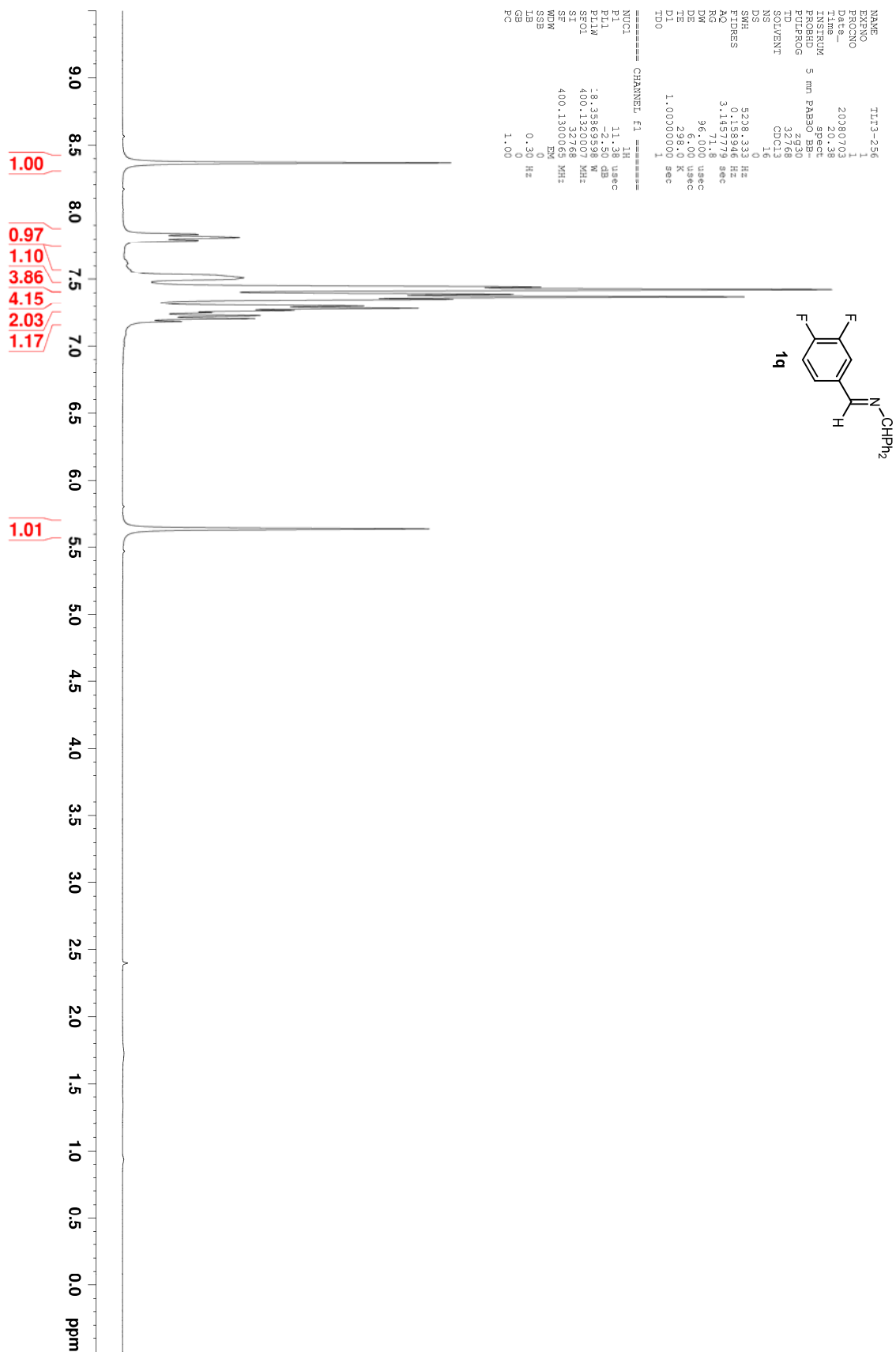


Figure 29. ¹H NMR (400 MHz, CDCl₃) of **1q**

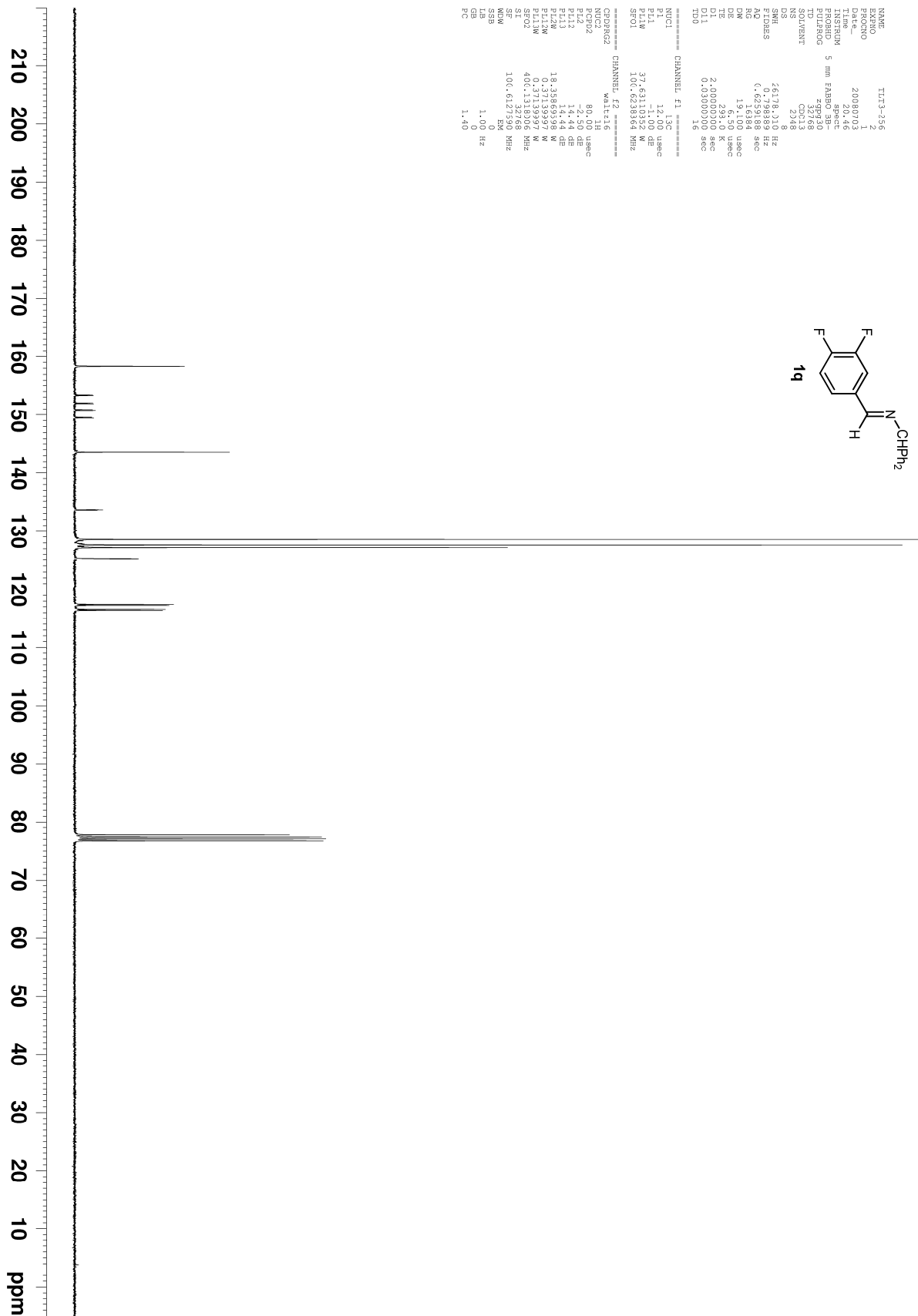
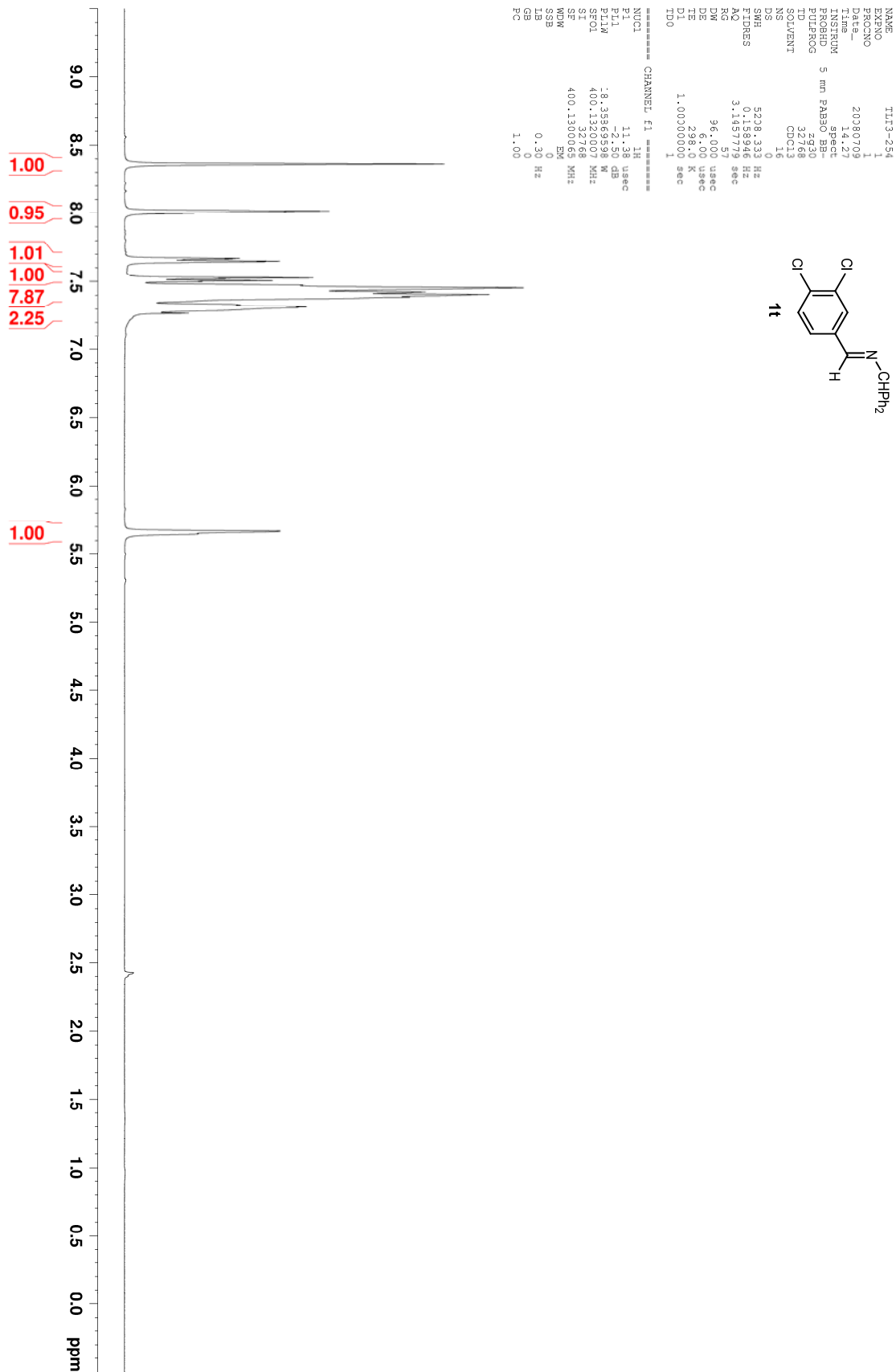


Figure 31. ^1H NMR (400 MHz, CDCl_3) of **1t**

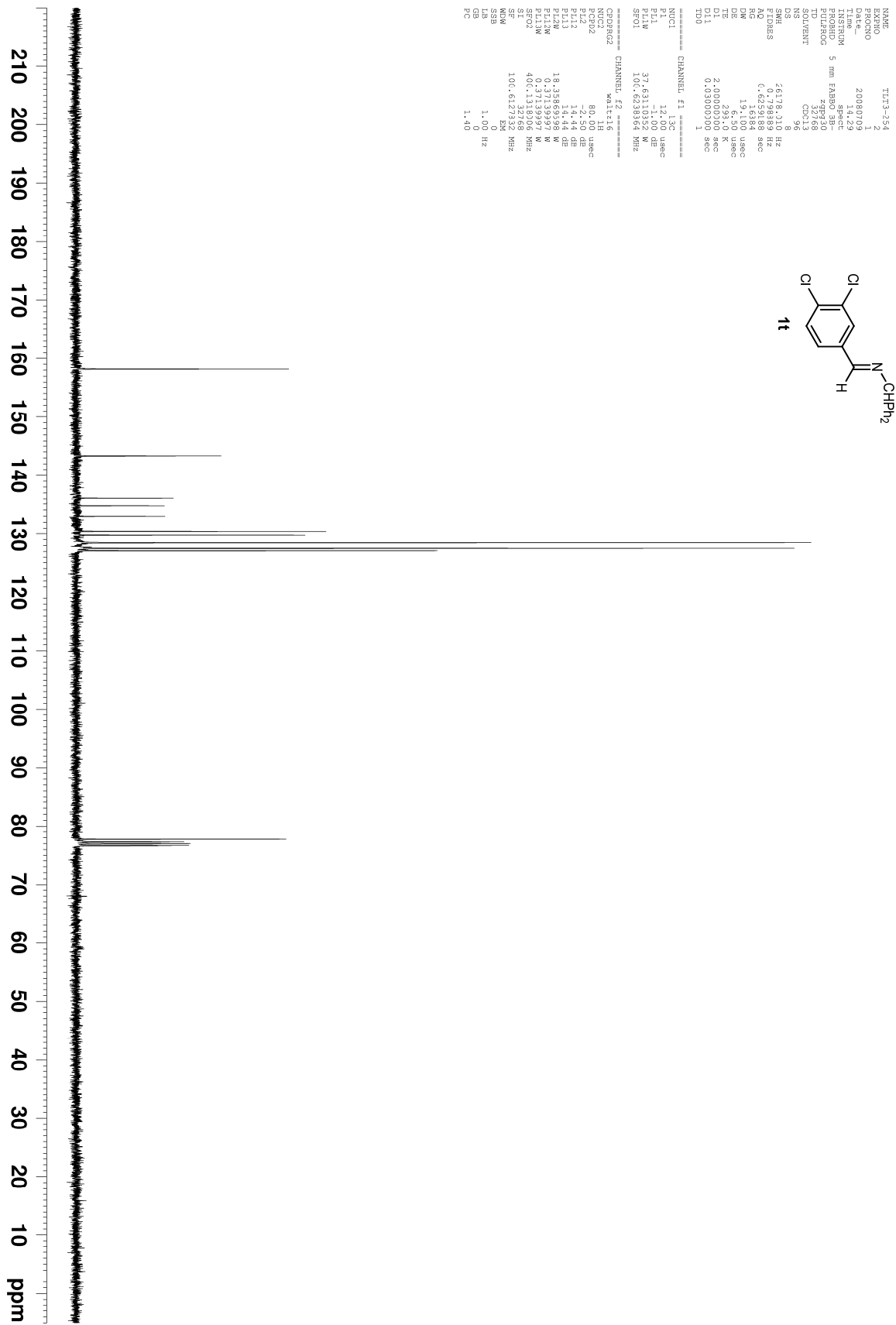
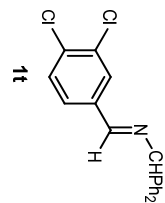
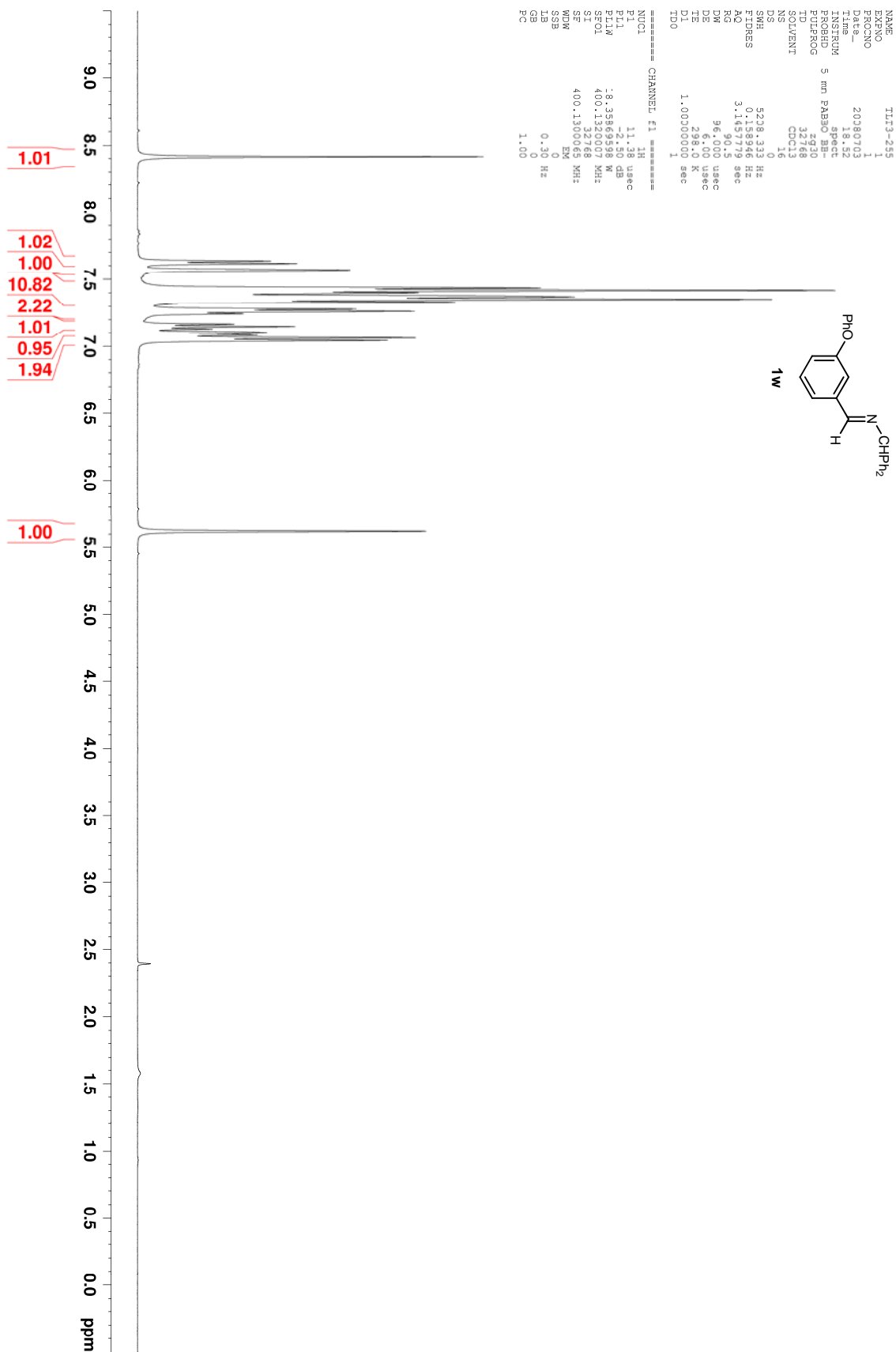


Figure 33. ¹H NMR (400 MHz, CDCl₃) of 1w

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Figure 34. ^{13}C NMR (100 MHz, CDCl_3) of **1w**

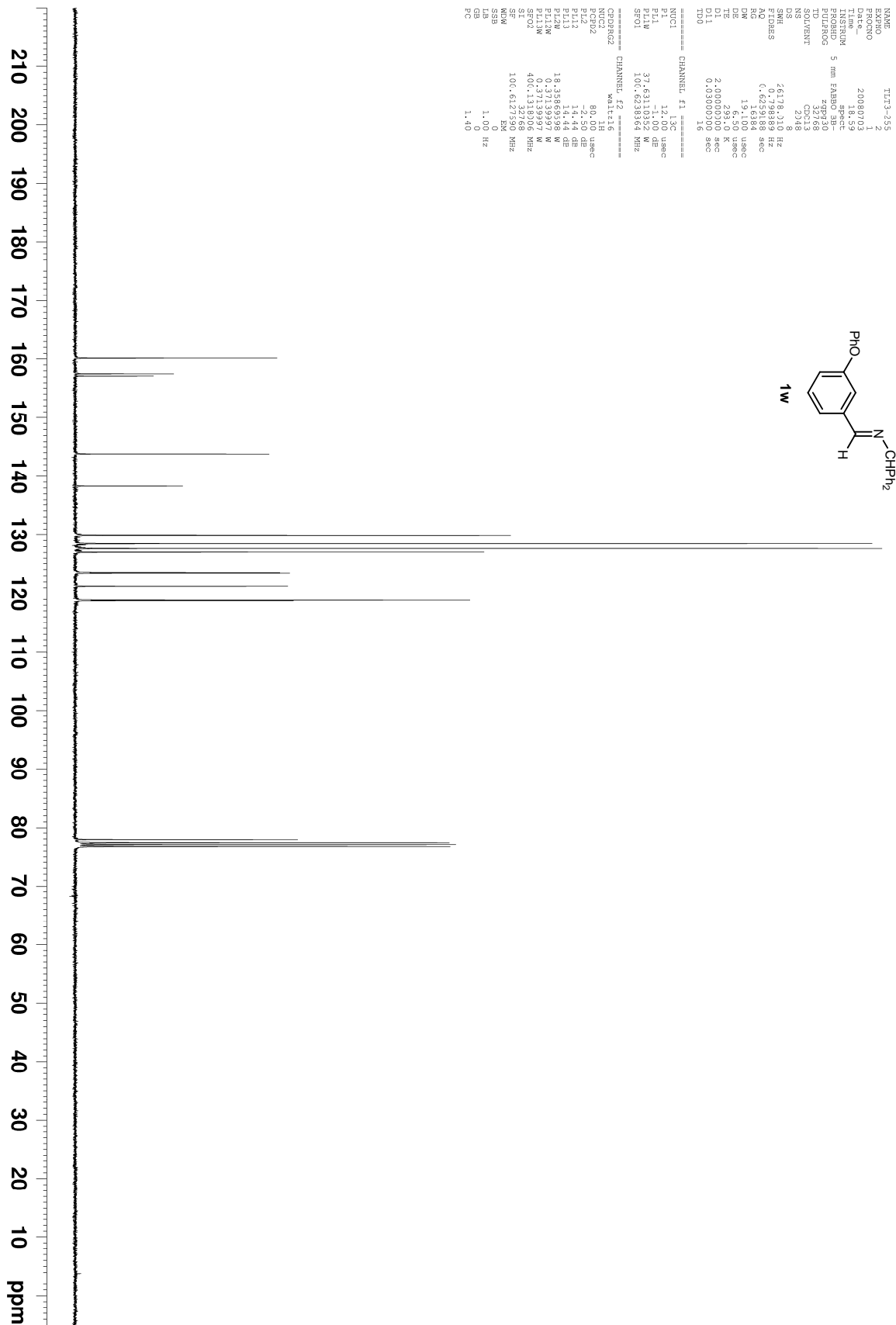
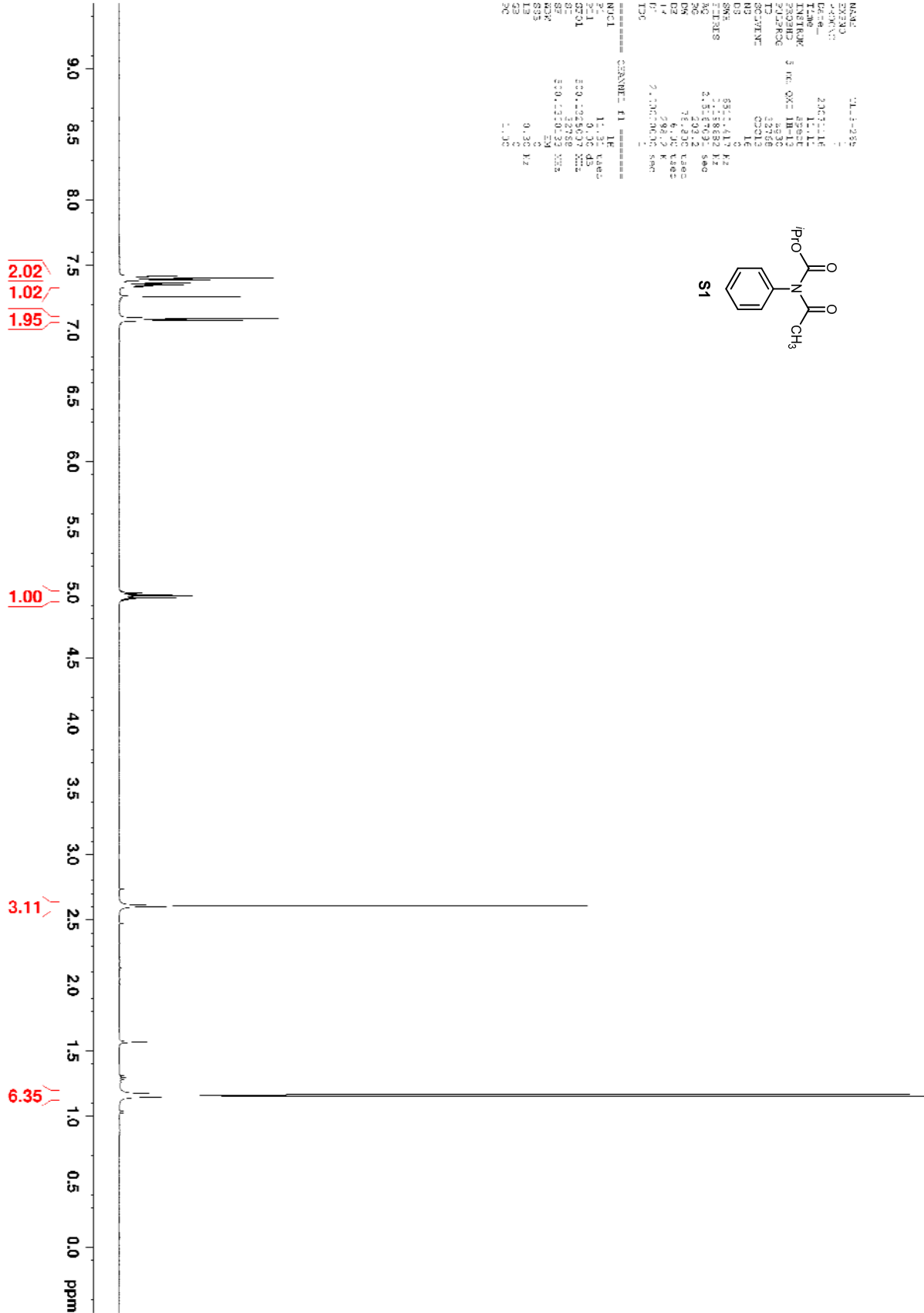
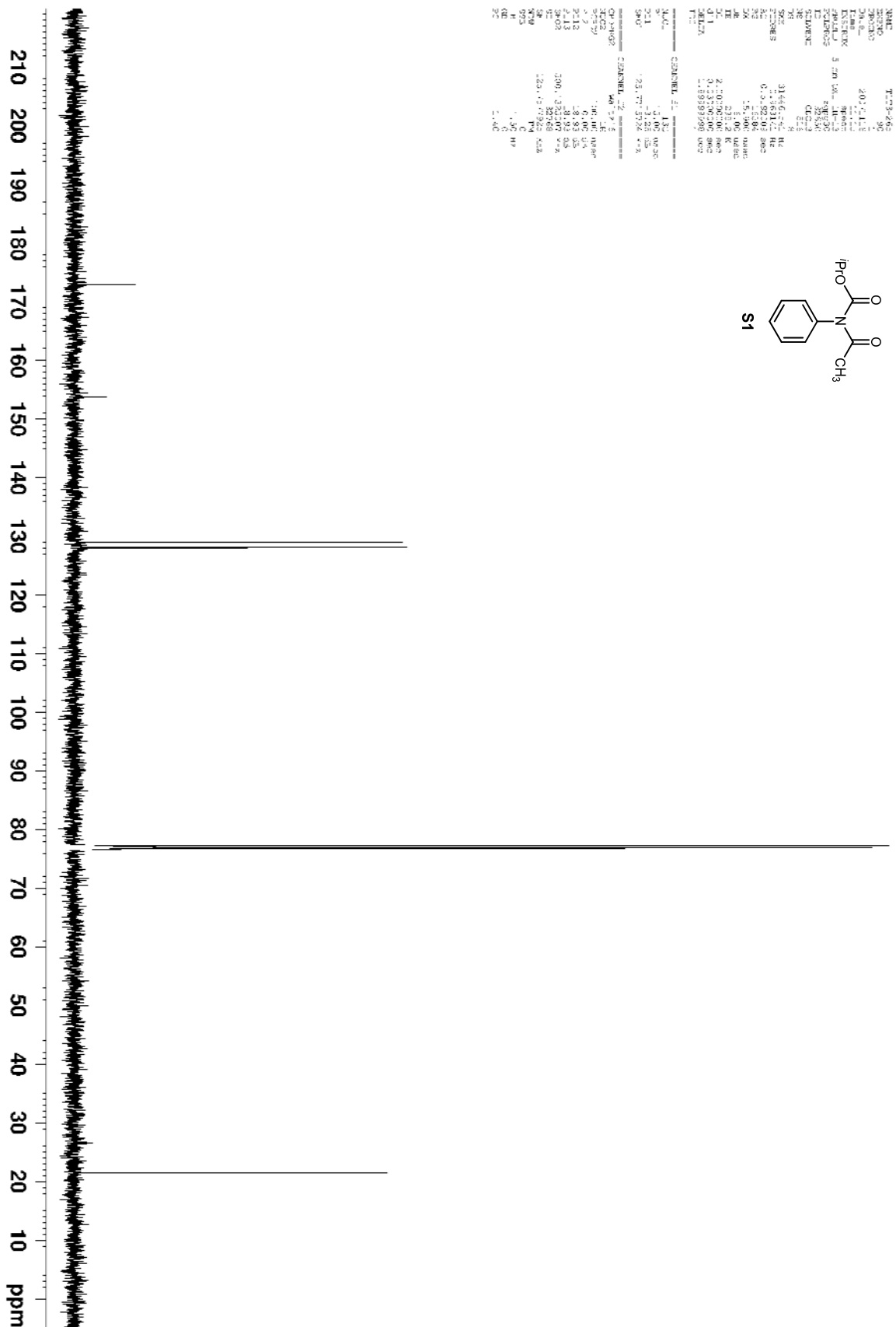


Figure 35. ¹H NMR (400 MHz, CDCl₃) of S1





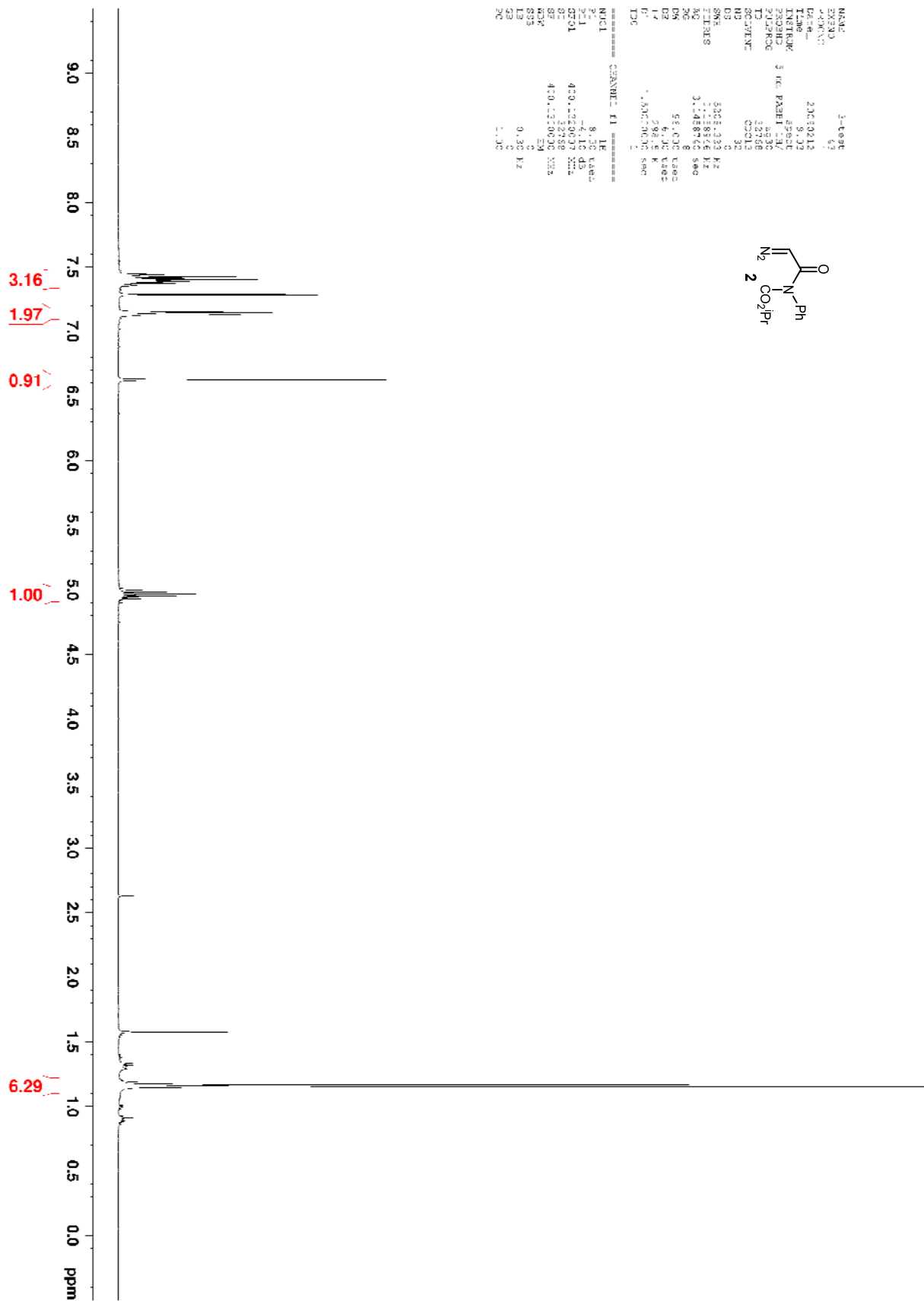
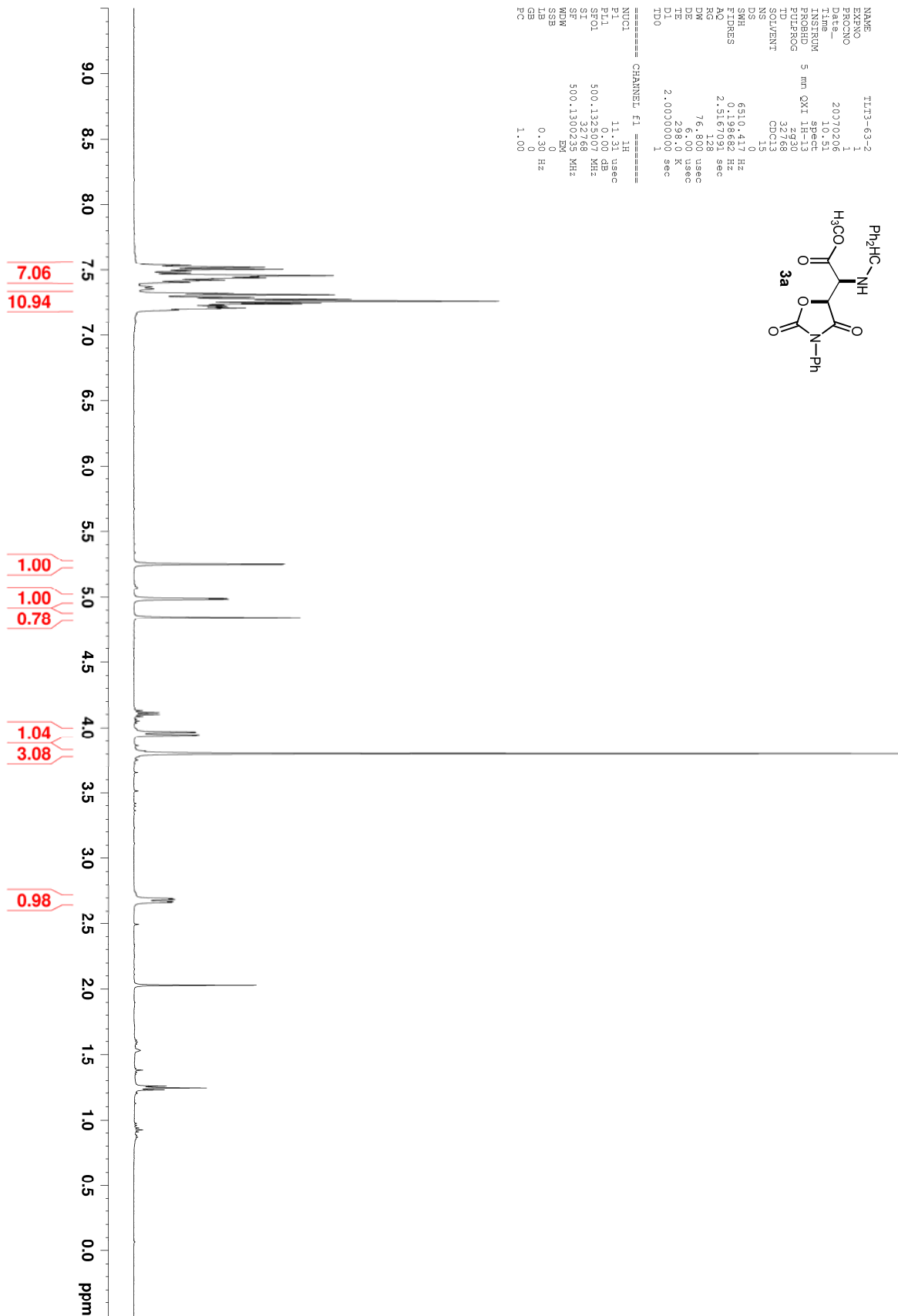


Figure 39. ¹H NMR (500 MHz, CDCl₃) of **3a**

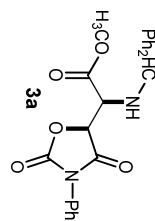
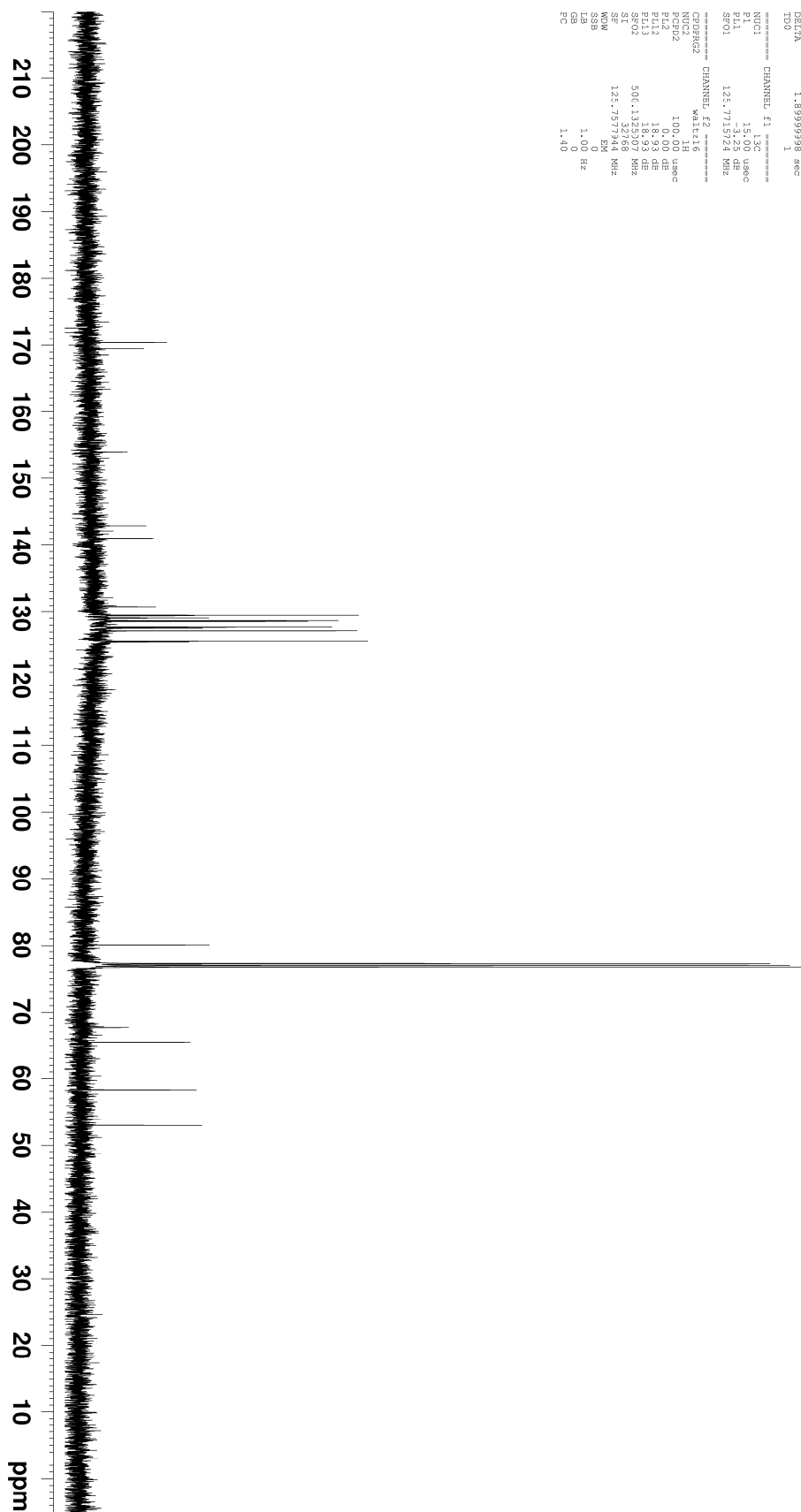
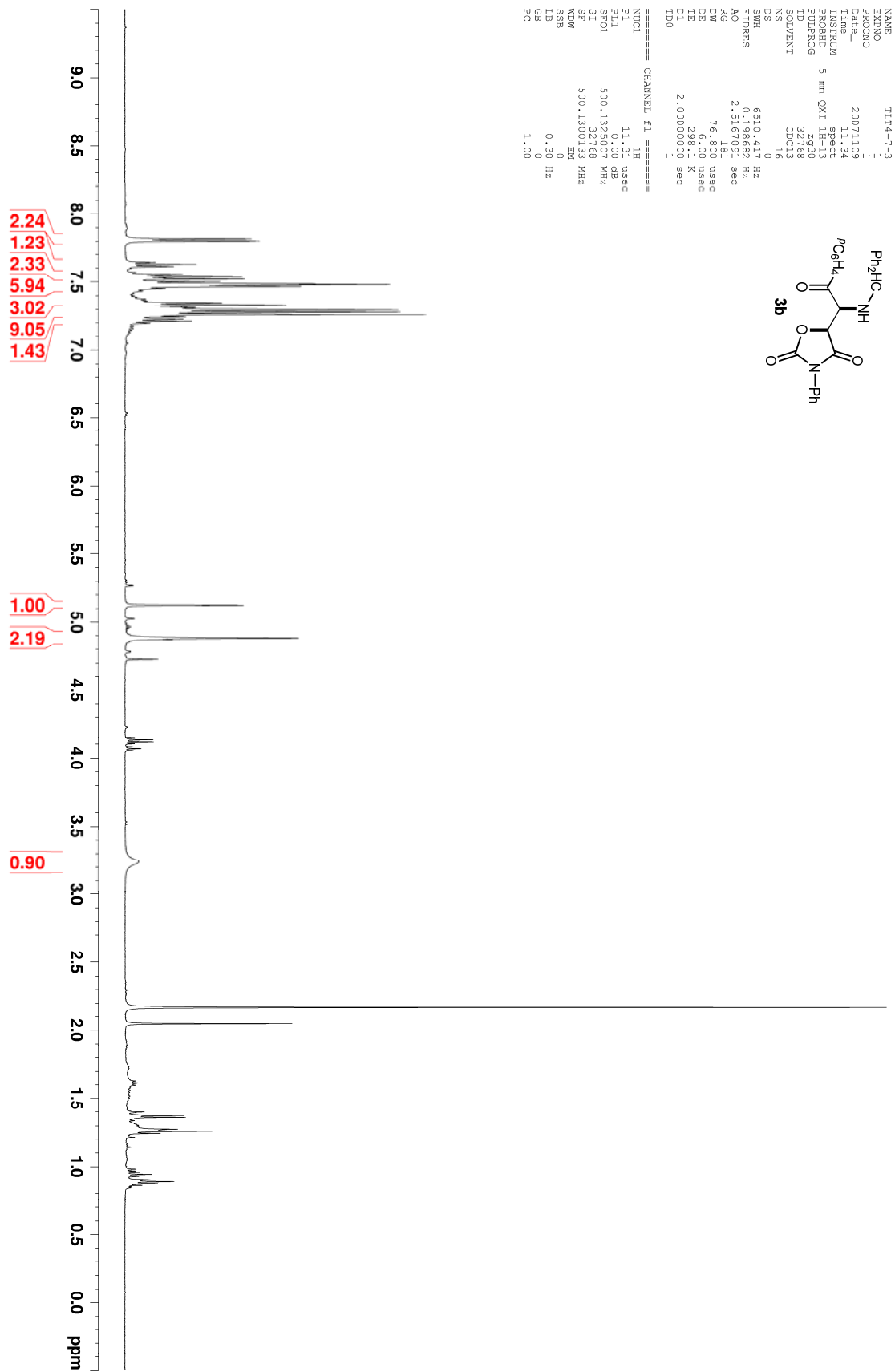


Figure 41. ¹H NMR (500 MHz, CDCl₃) of **3b**

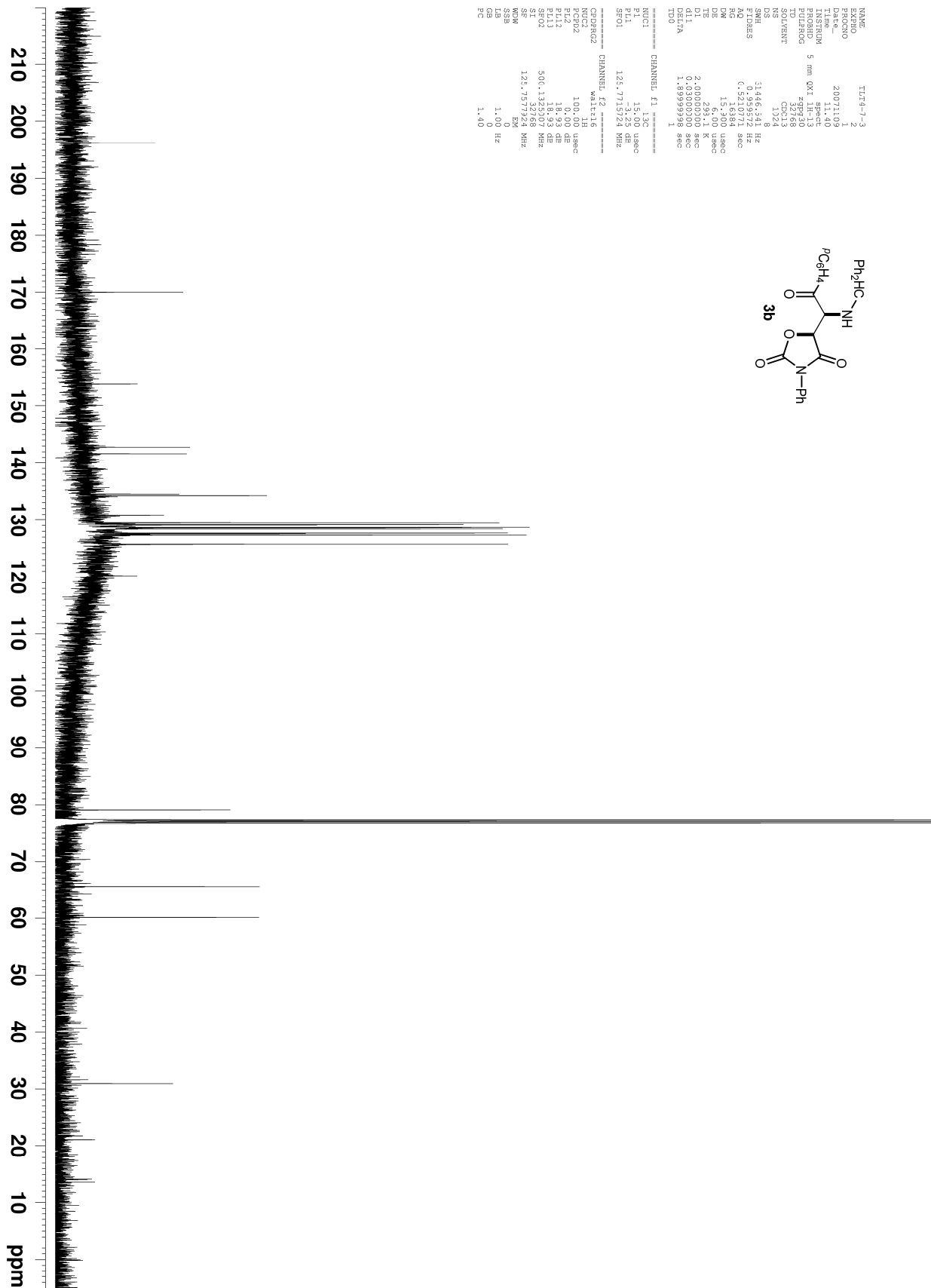
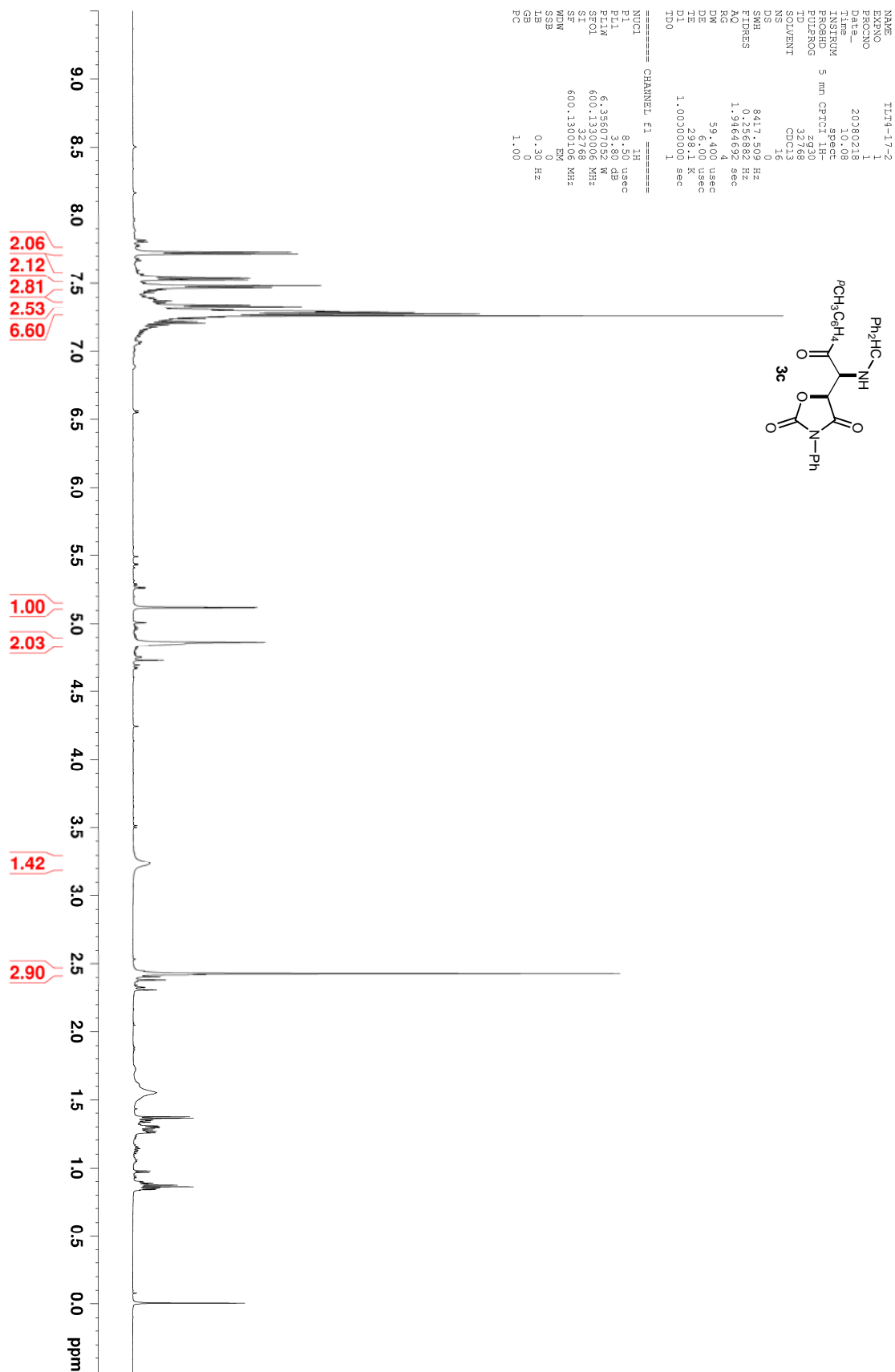


Figure 43. ¹H NMR (600 MHz, CDCl₃) of 3c

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Figure 44. ¹³C NMR (150 MHz, CDCl₃) of **3c**

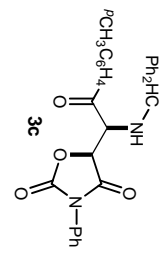
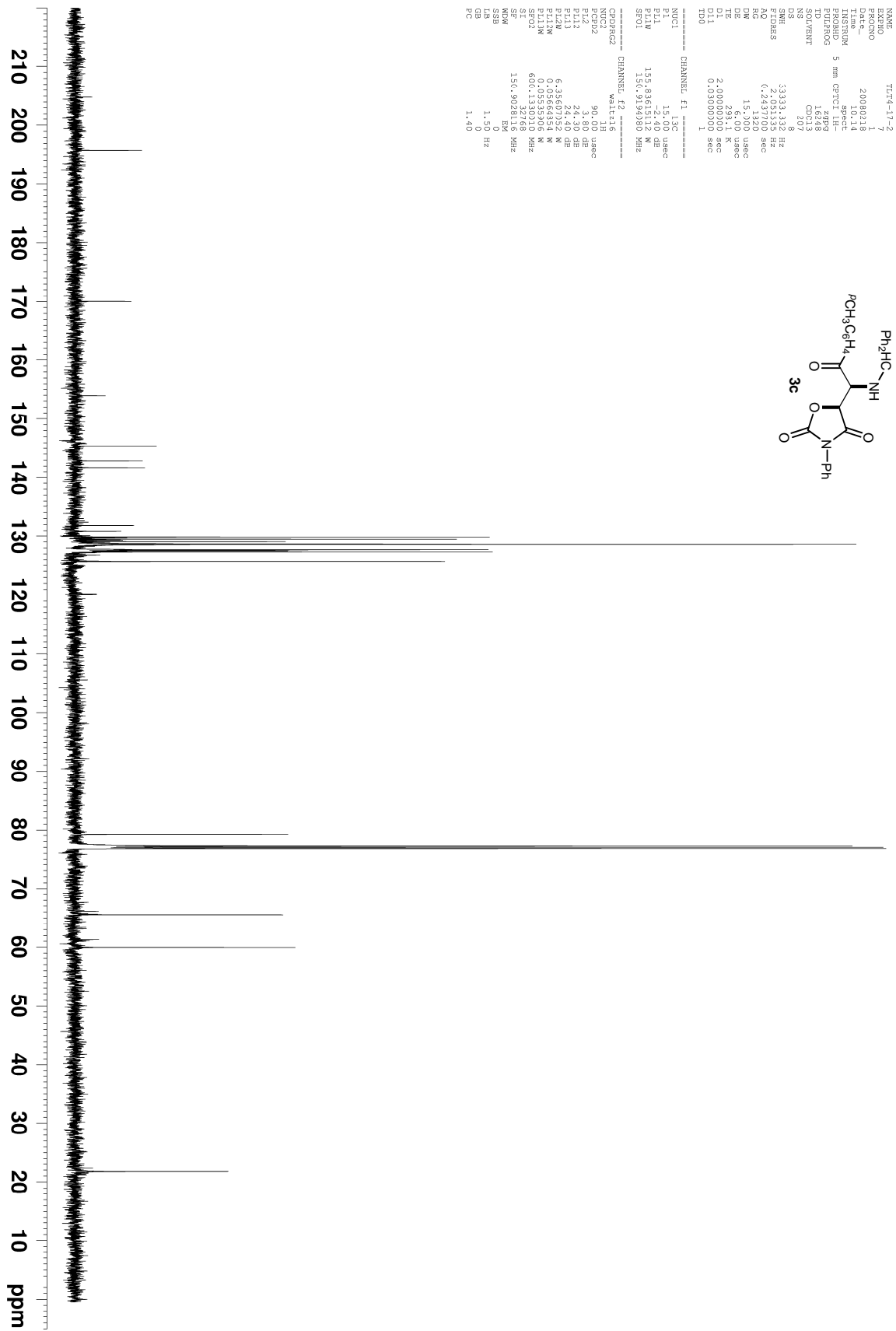
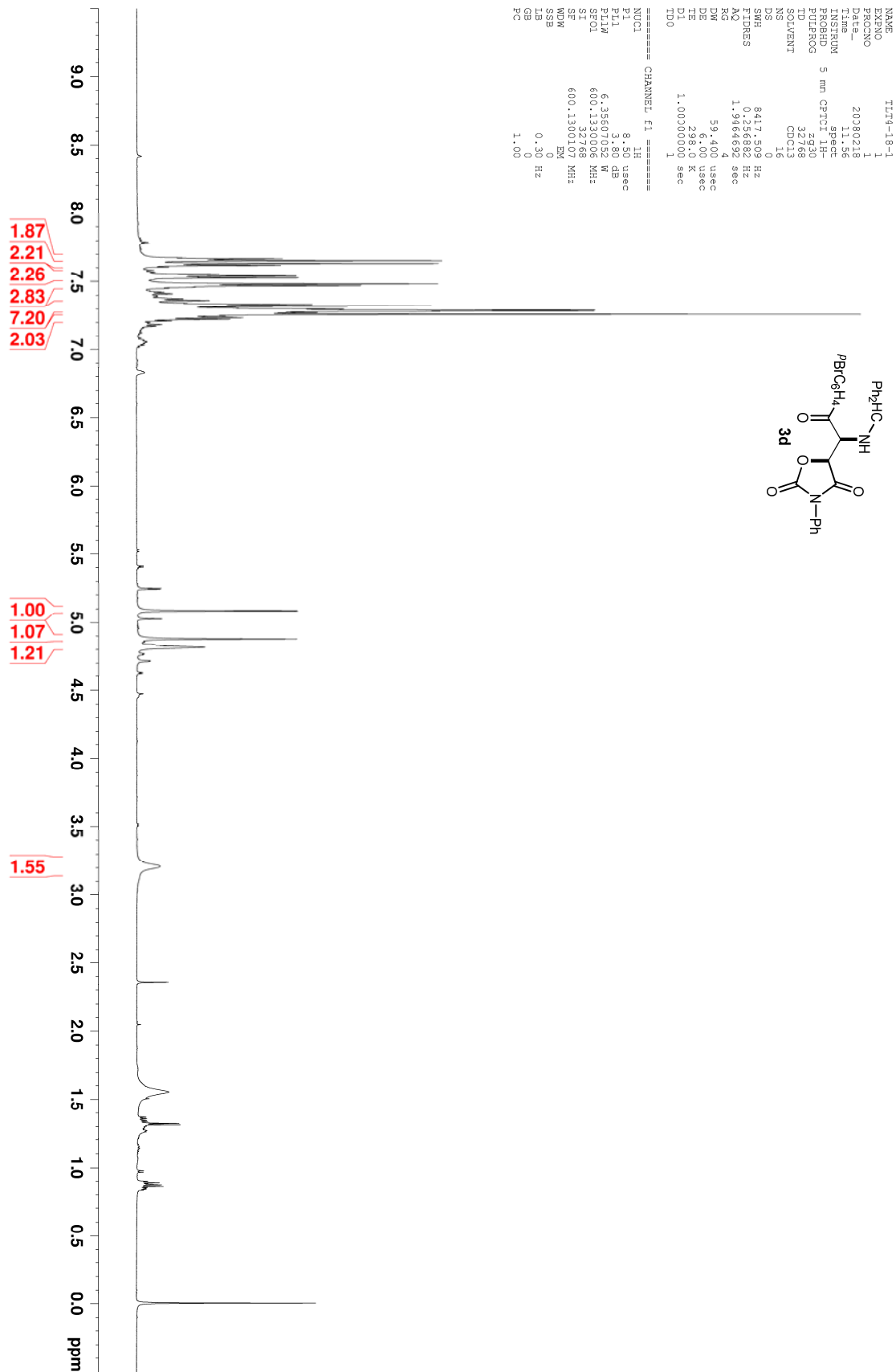


Figure 45. ¹H NMR (600 MHz, CDCl₃) of **3d**

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Figure 46. ^{13}C NMR (150 MHz, CDCl_3) of **3d**

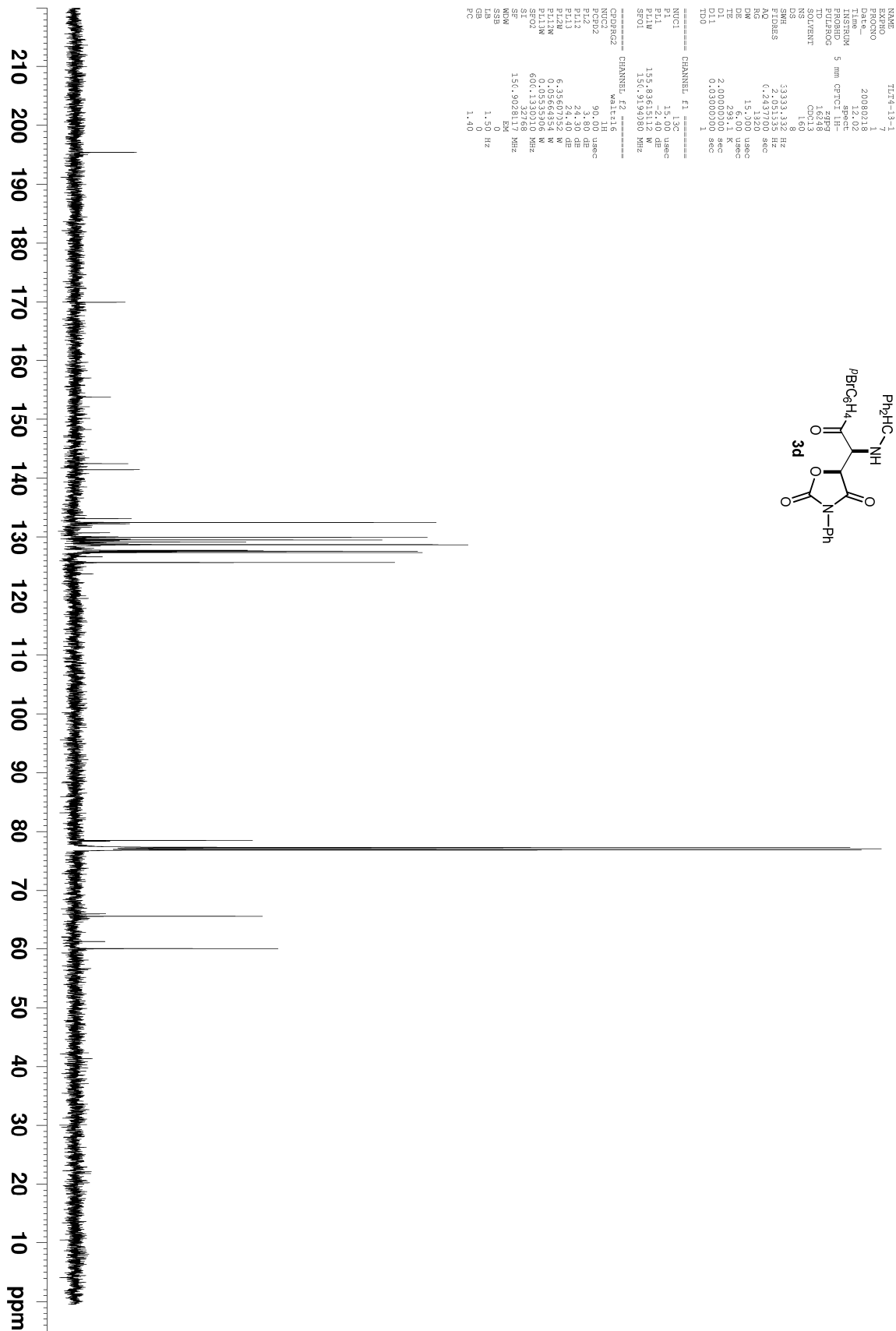
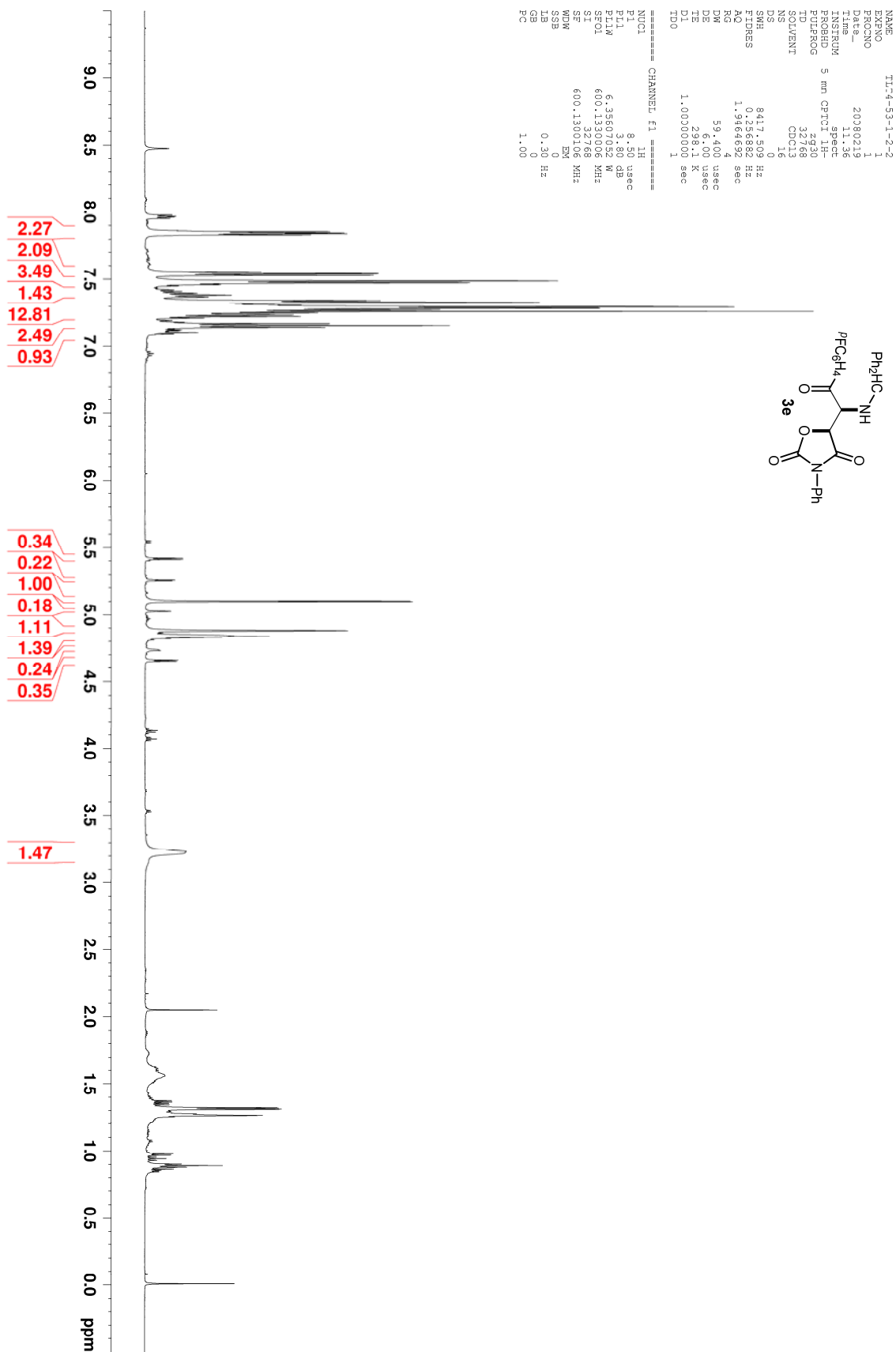
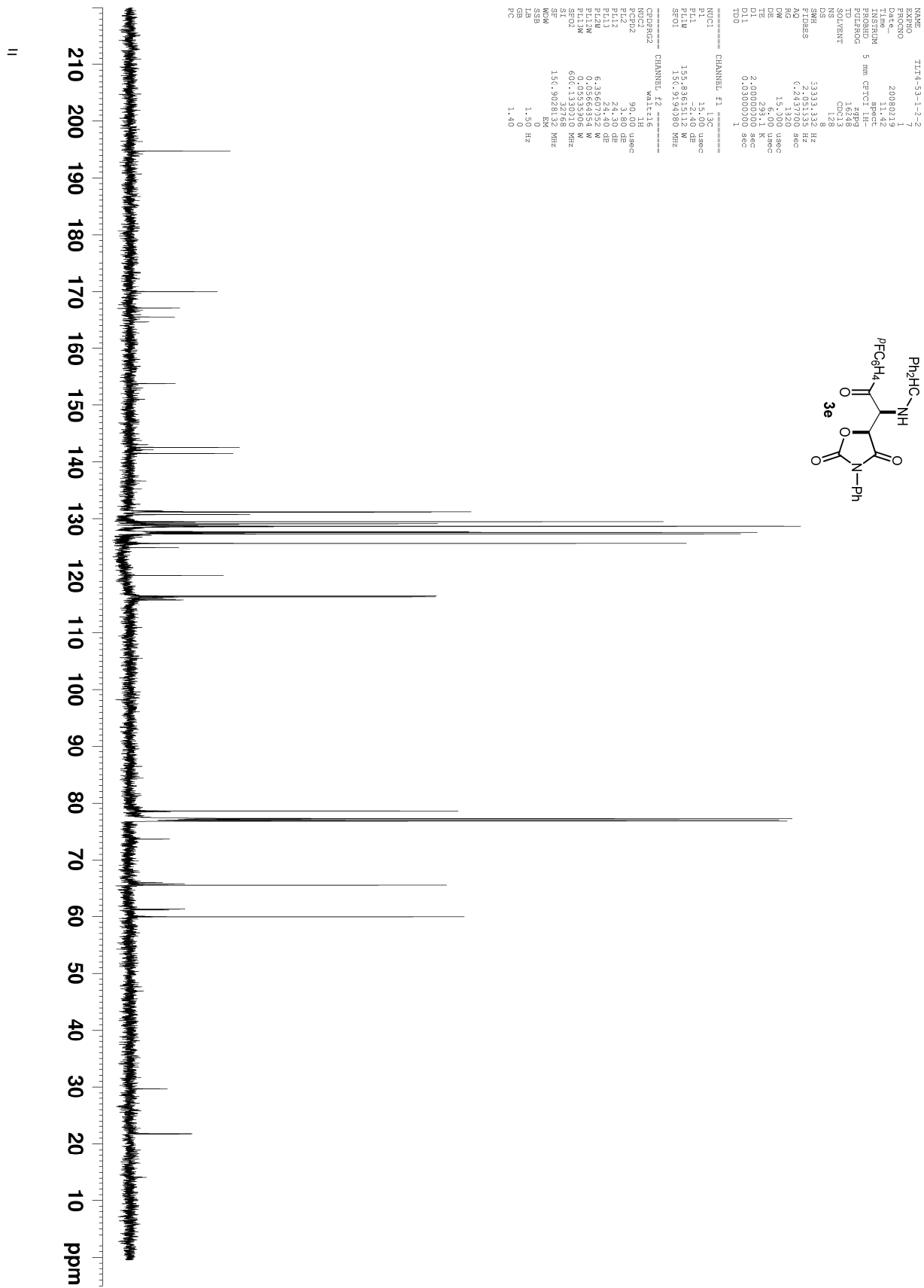


Figure 47. ¹H NMR (600 MHz, CDCl₃) of **3e**

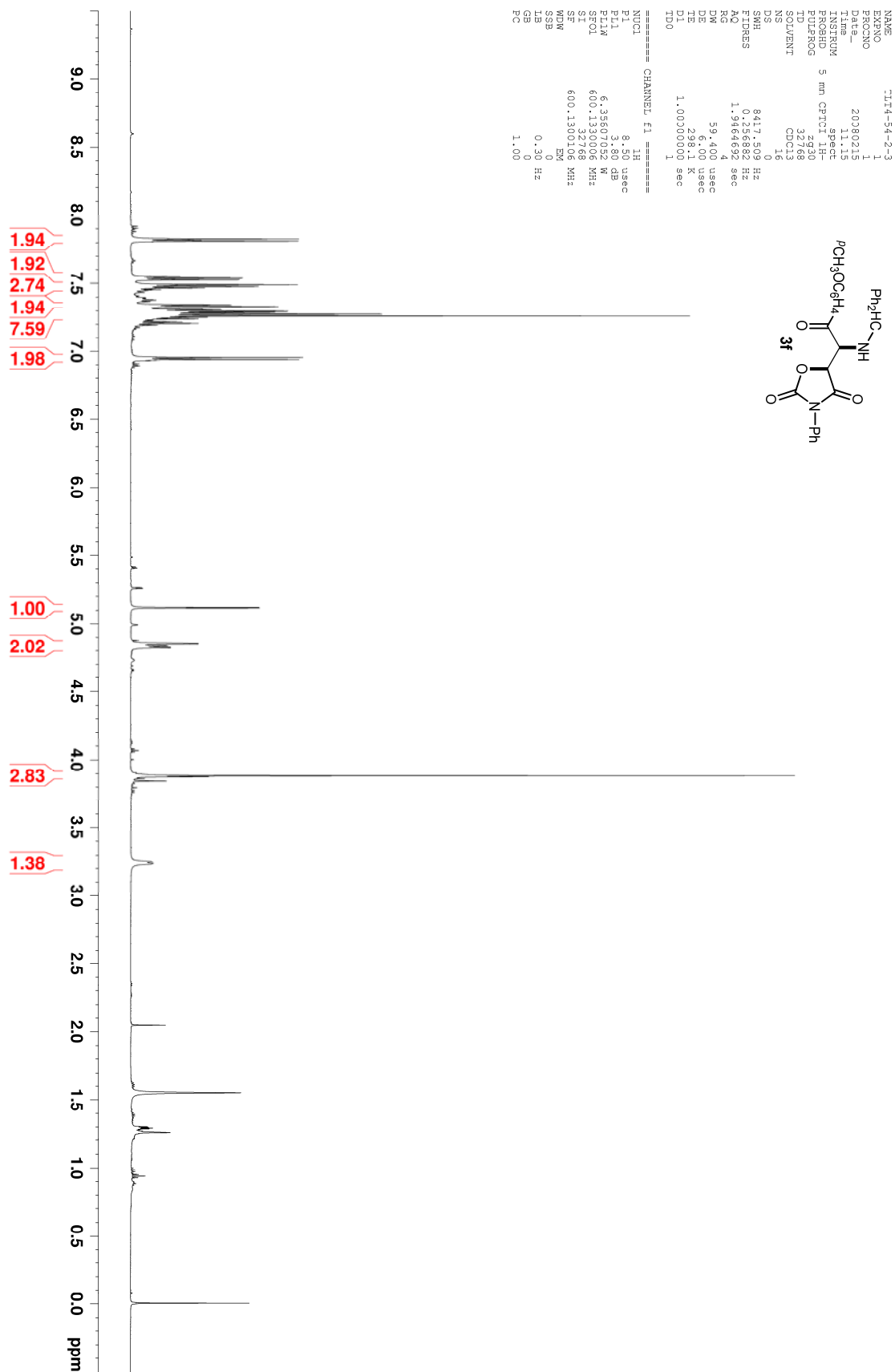


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D1            2.0000000000000000
D11           0.030000000000000000
TD0           1
    
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Figure 49. ¹H NMR (600 MHz, CDCl₃) of 3f

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Figure 50. ^{13}C NMR (150 MHz, CDCl_3) of **3f**

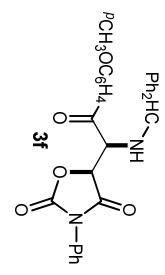
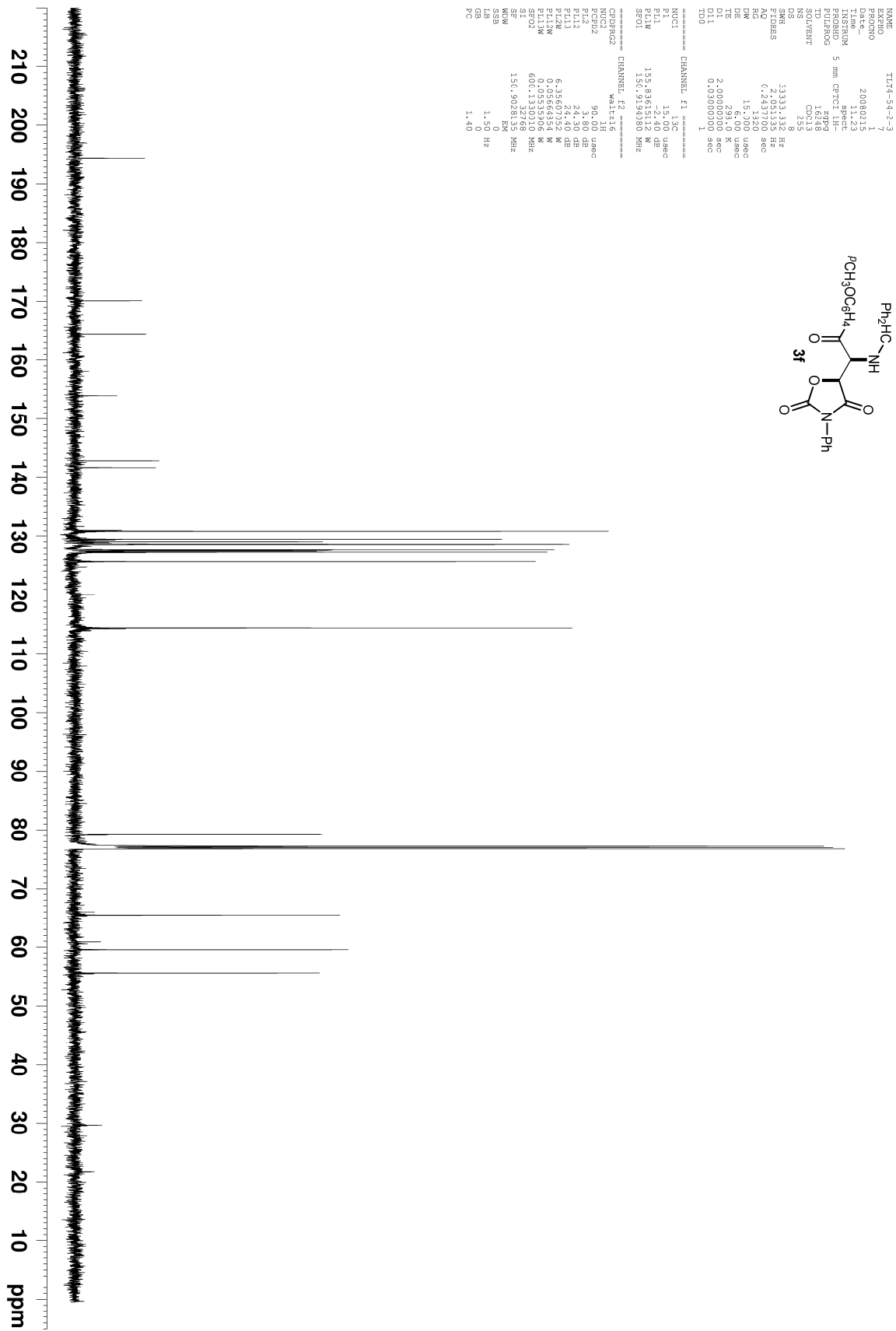
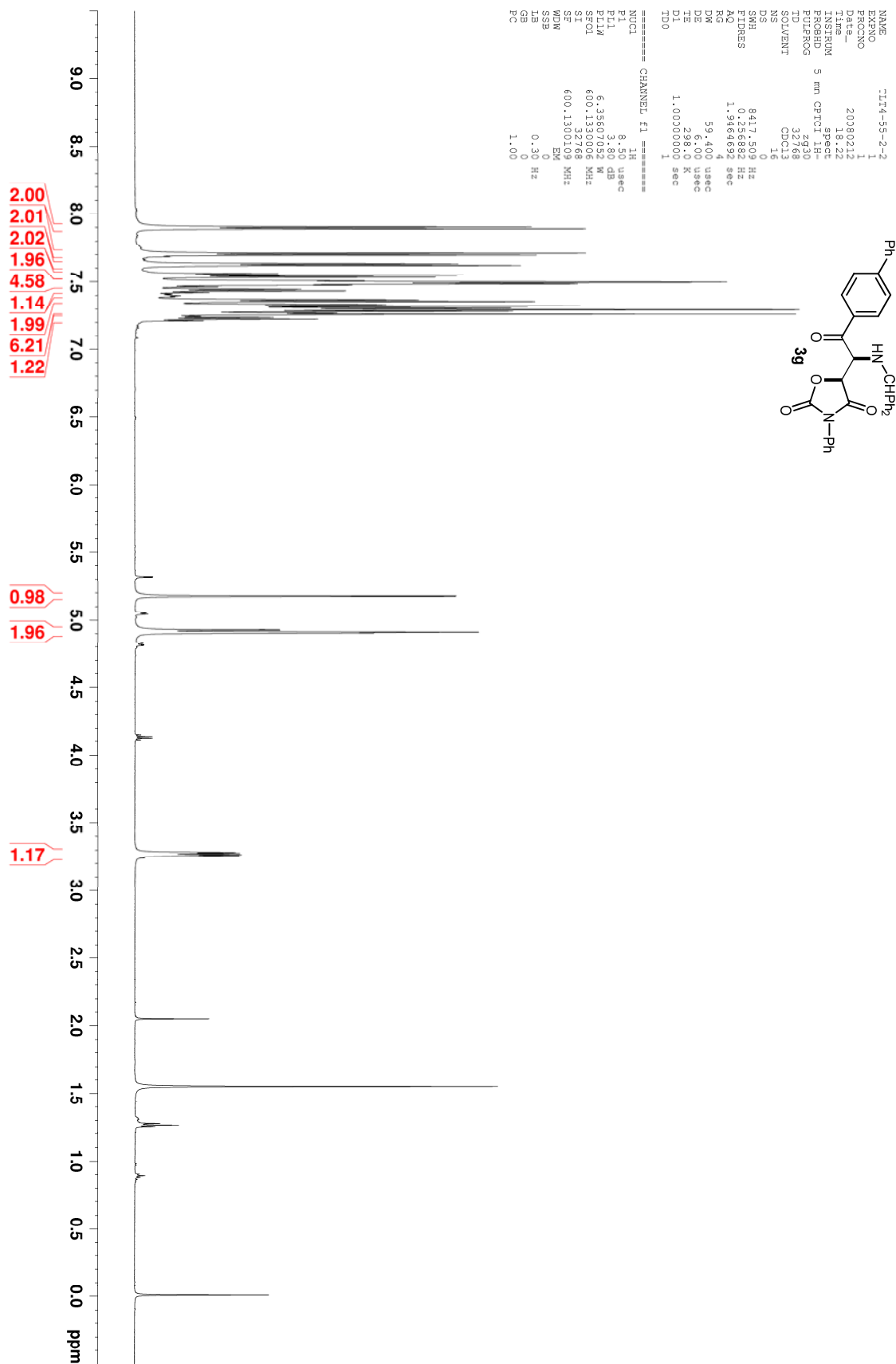
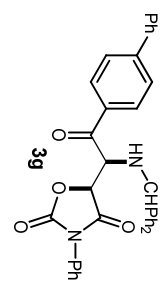
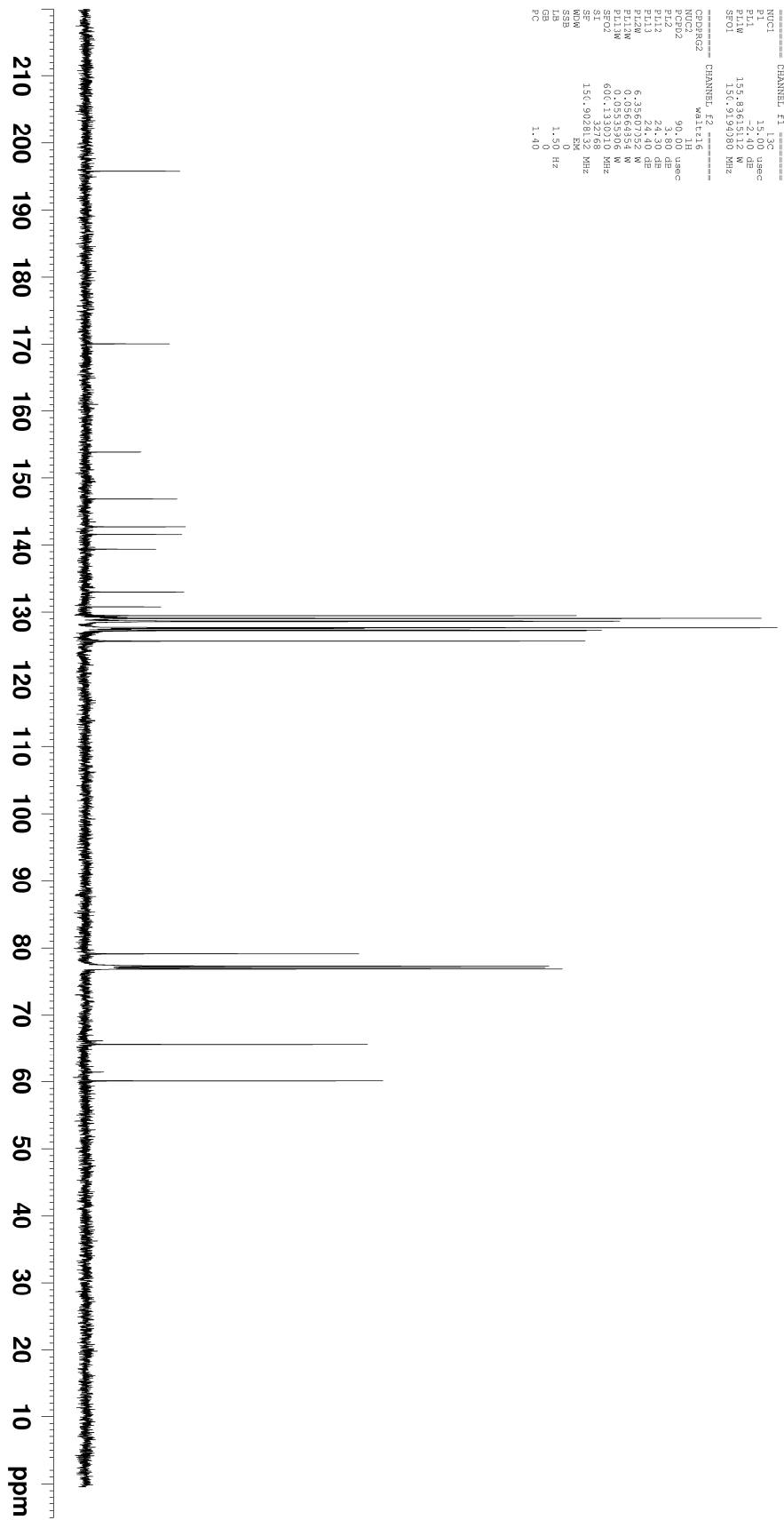


Figure 51. ¹H NMR (600 MHz, CDCl₃) of **3g**

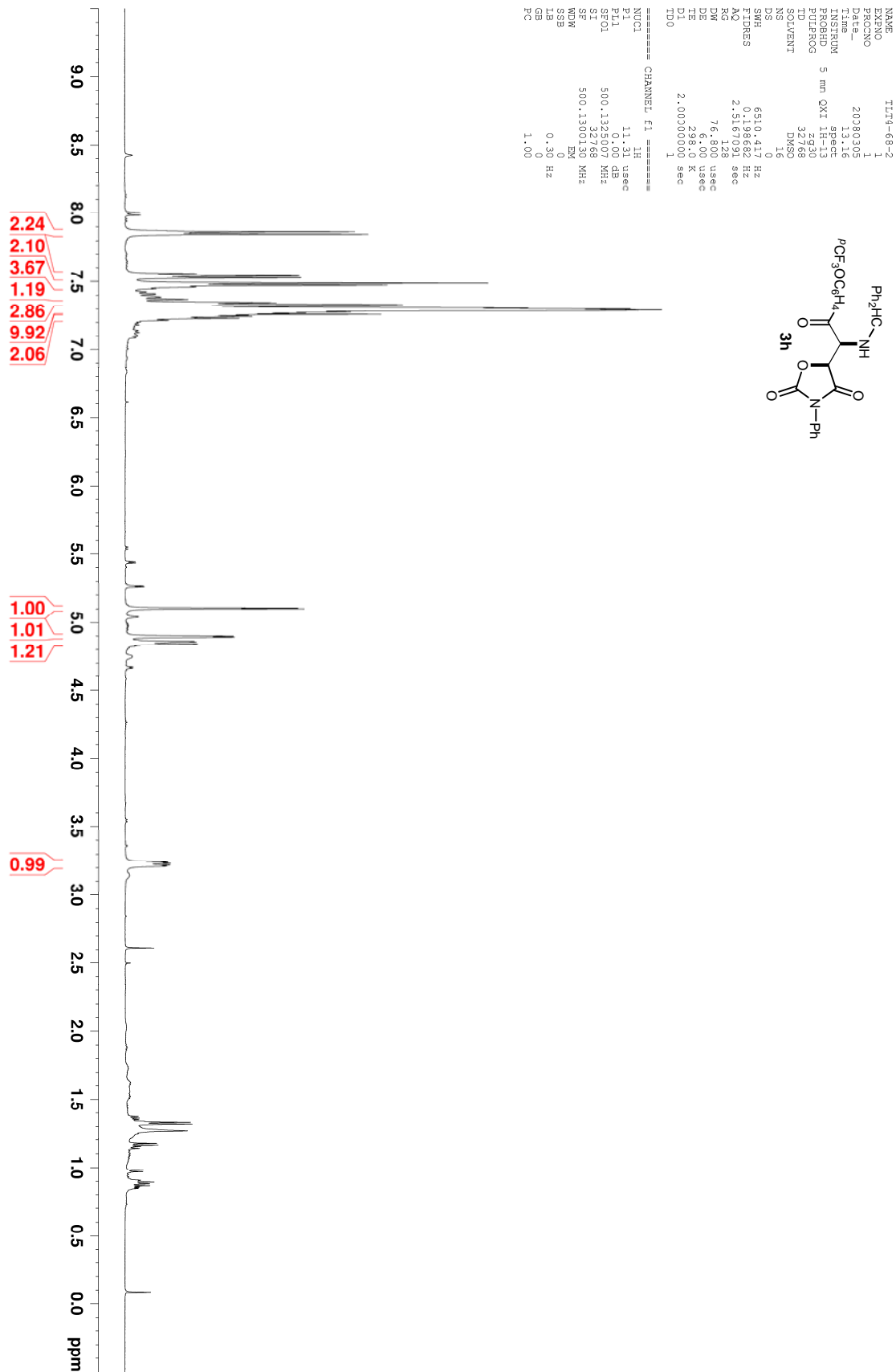


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D11           0.0300000 sec
TD0           1

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PL1           0.00 dB
PL12          15.8361412 dB
SFO1          15C.9194380 MHz

===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          1H
P2            9.00 usec
PL2           0.00 dB
PL12          24.30 dB
PL13          6.3827440 dB
PL14          0.0000000 dB
PL15          0.03664934 W
PL16          0.05535906 W
SFO2          600.1320000 MHz
SE           15C.9028132 MHz
RG            65536
GB            1.50 Hz
PC            0
FC            1.40
    
```

Figure 53. ¹H NMR (500 MHz, CDCl₃) of 3h

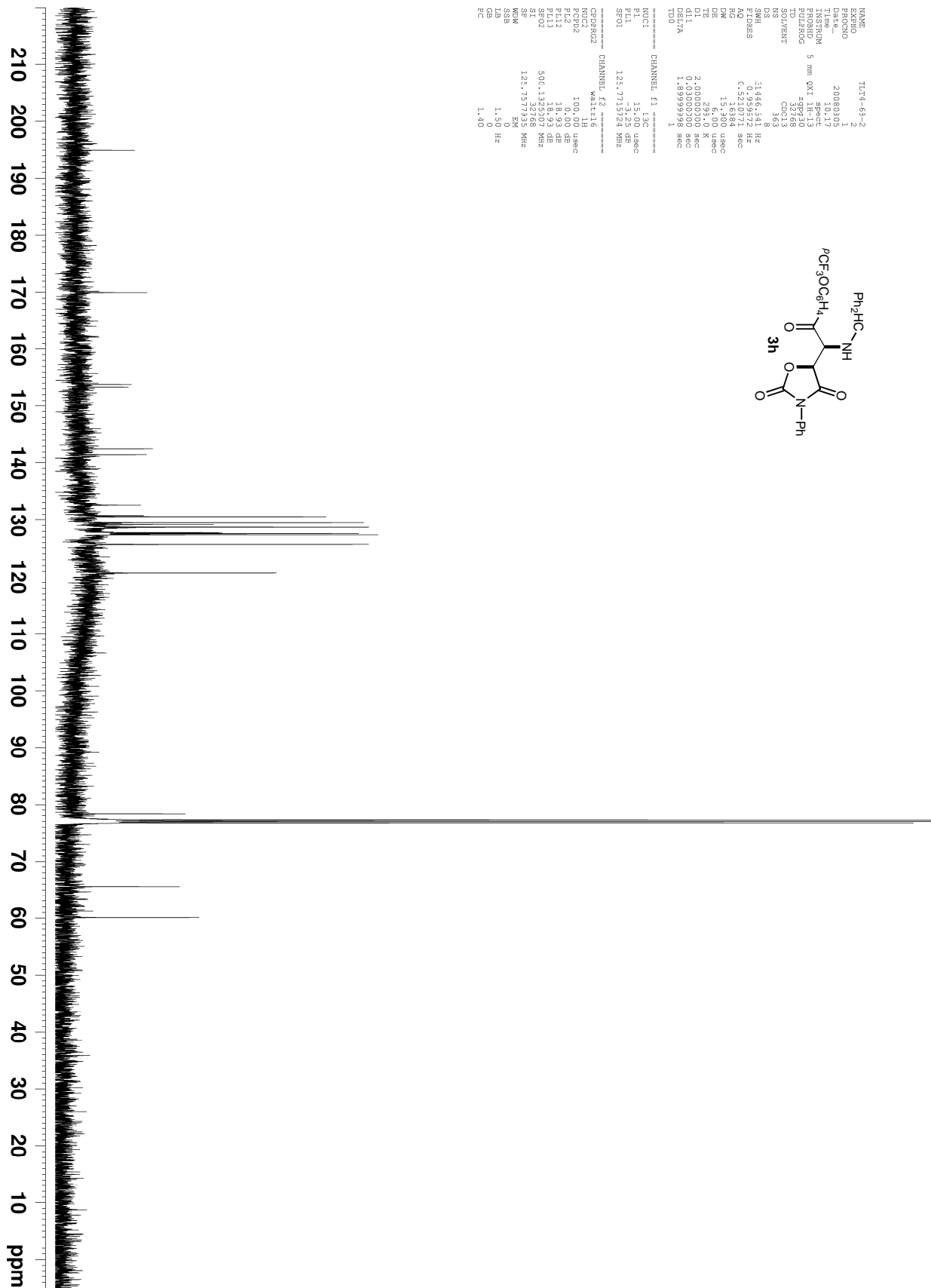
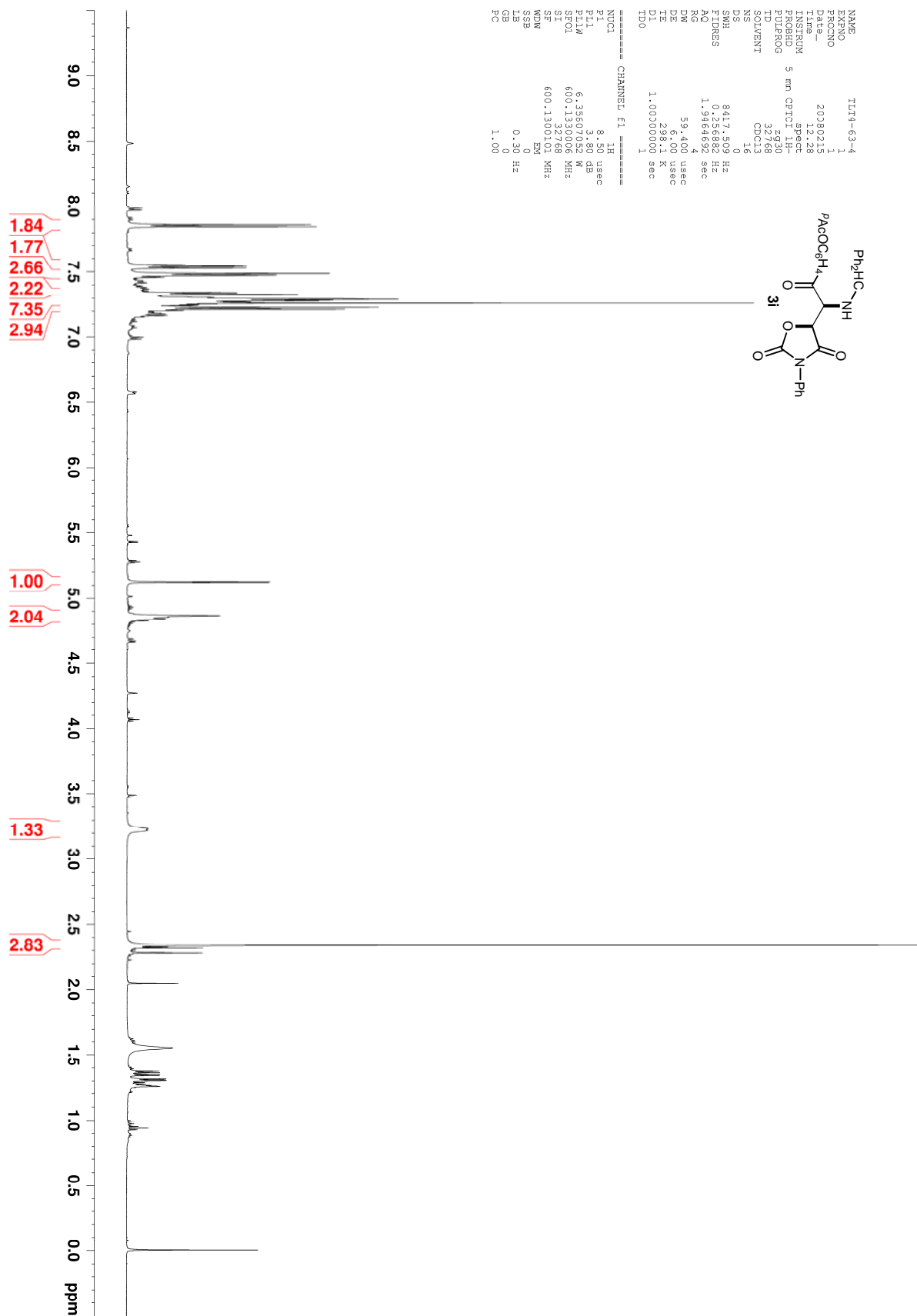


Figure 55. ¹H NMR (600 MHz, CDCl₃) of 3i

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Figure 56. ¹³C NMR (150 MHz, CDCl₃) of **3i**

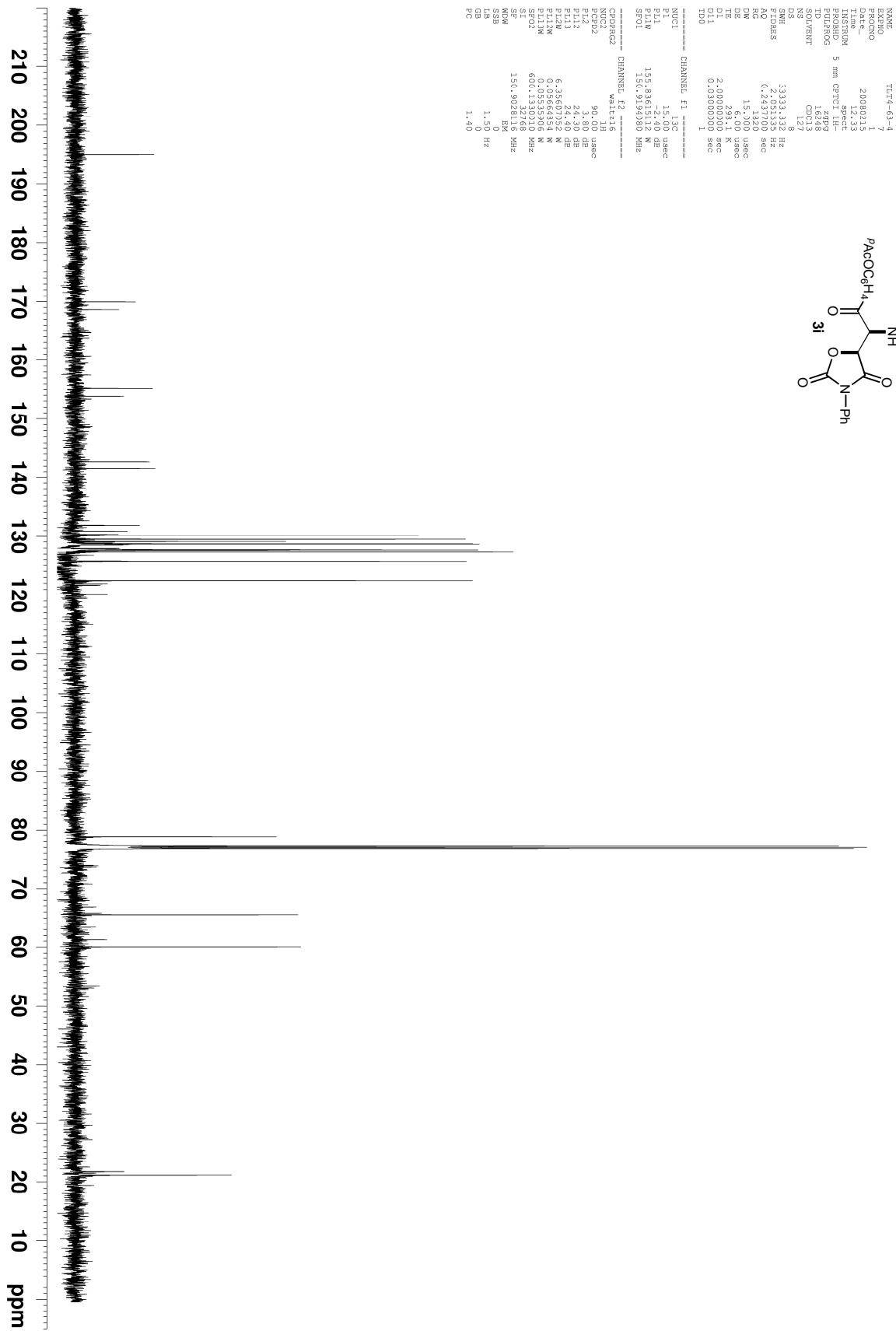
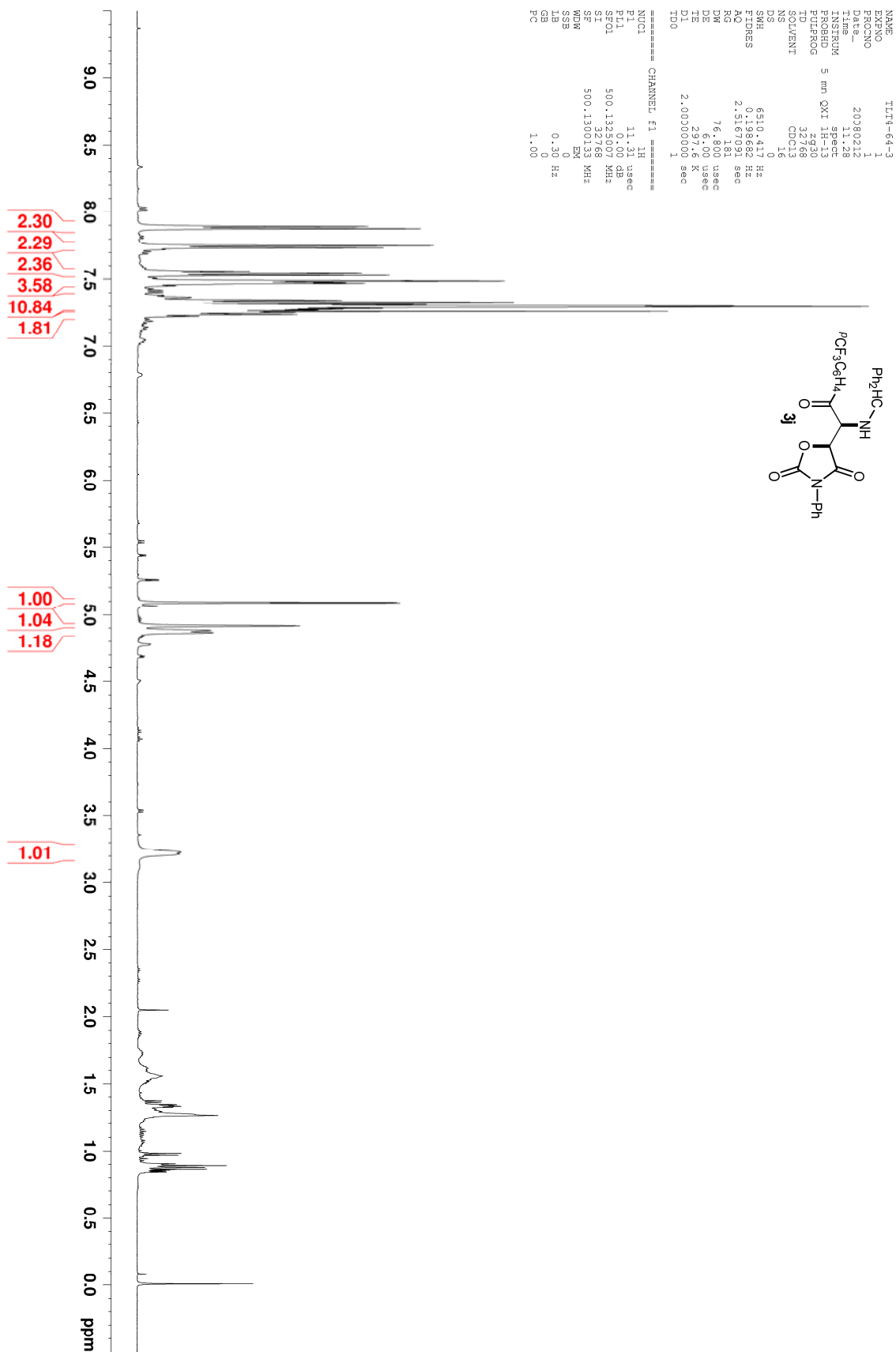


Figure S7. ¹H NMR (500 MHz, CDCl₃) of **3j**

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Figure 58. ¹³C NMR (125 MHz, CDCl₃) of **3j**

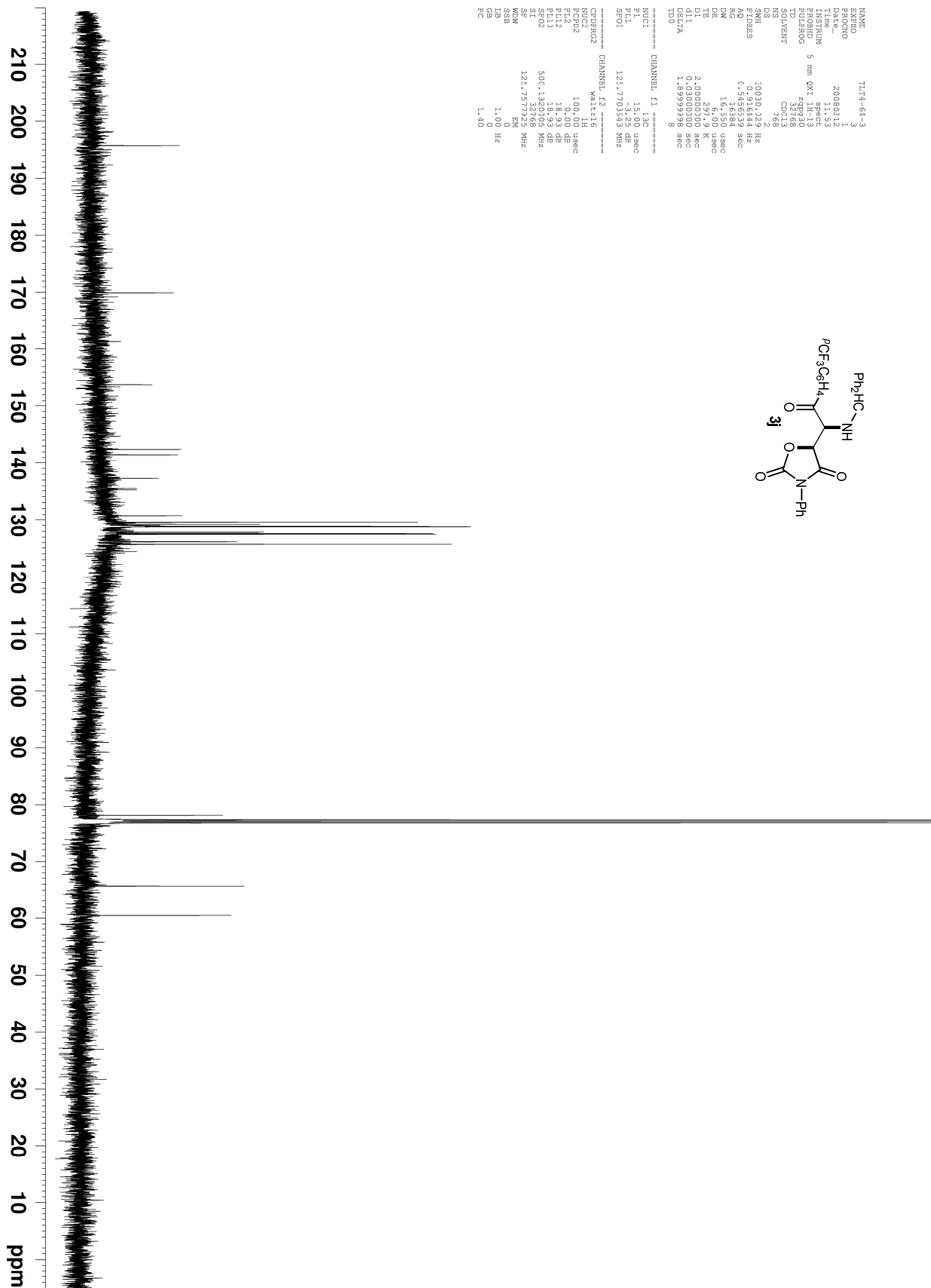
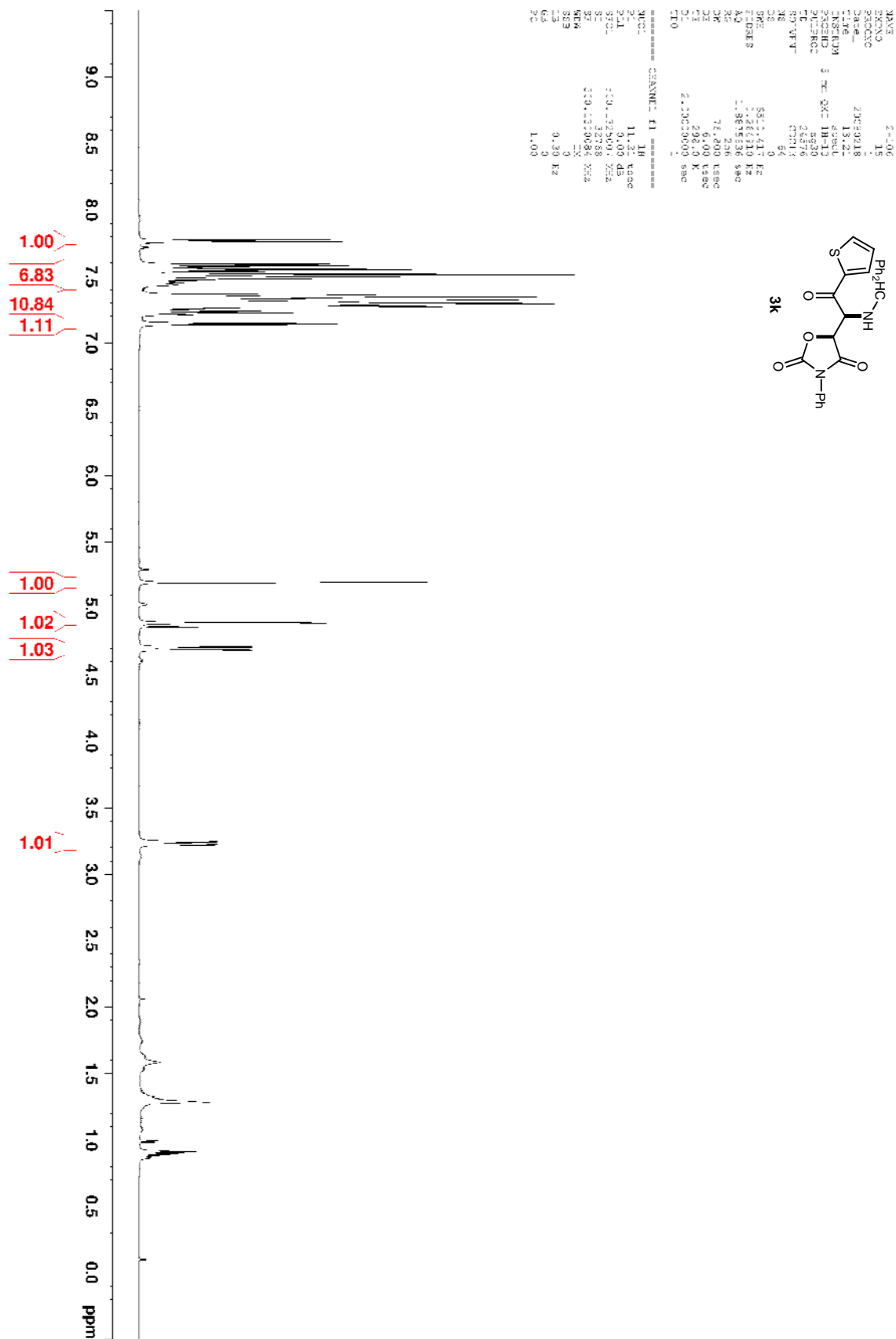
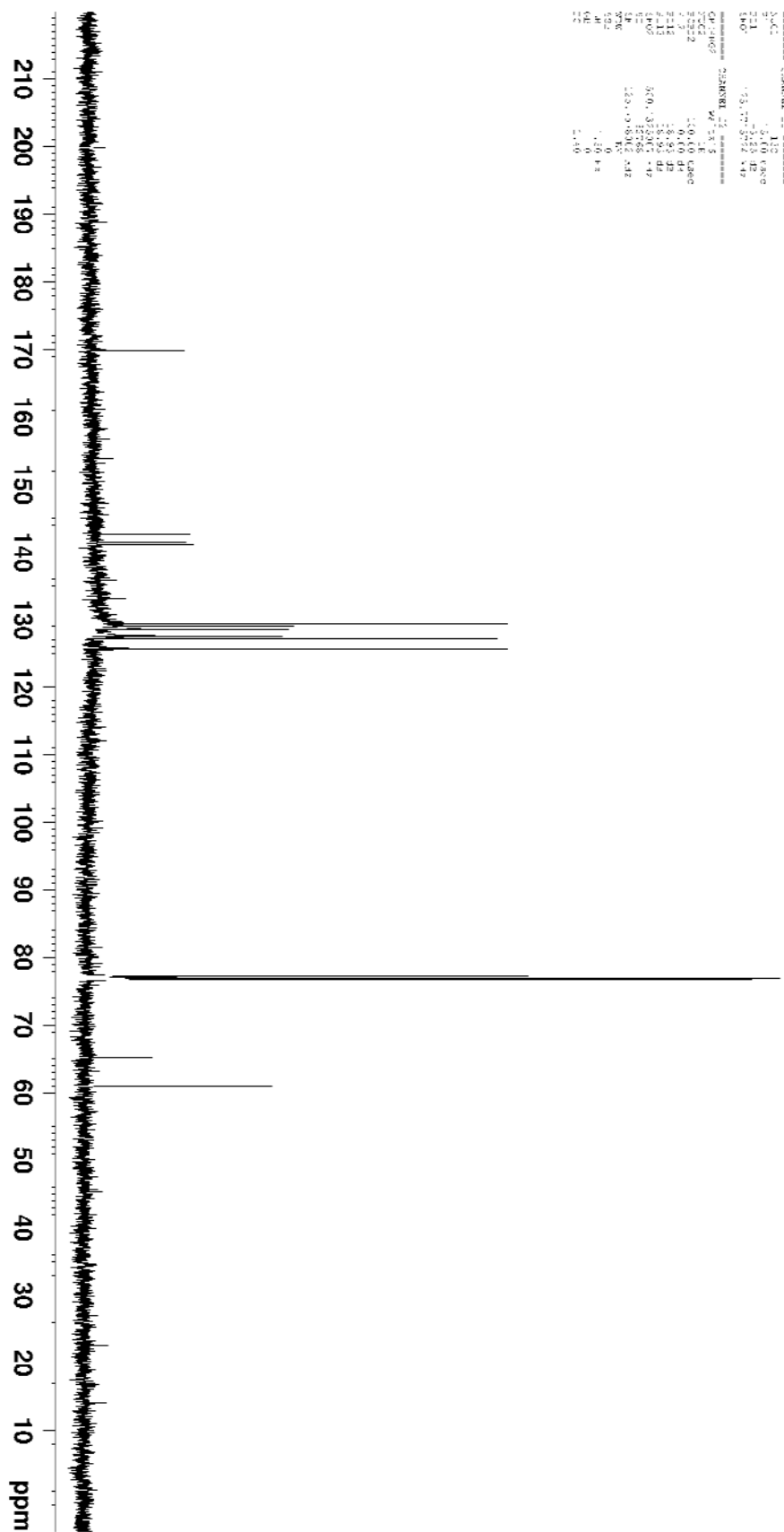


Figure 59. ¹H NMR (500 MHz, CDCl₃) of 3k

Johnston et al.
Figure 60. ^{13}C NMR (125 MHz, CDCl_3) of **3k**



NAME	2-115
EXPNO	12
PROCNO	2010222
F2	1.043
TIME	1.043
INSTRUM	gme 500
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	65536
DELTA	11.786
DELTA2	0.000000
DELTA3	0.000000
DELTA4	0.000000
DELTA5	0.000000
DELTA6	0.000000
DELTA7	0.000000
DELTA8	0.000000
DELTA9	0.000000
DELTA10	0.000000
DELTA11	0.000000
DELTA12	0.000000
DELTA13	0.000000
DELTA14	0.000000
DELTA15	0.000000
DELTA16	0.000000
DELTA17	0.000000
DELTA18	0.000000
DELTA19	0.000000
DELTA20	0.000000
DELTA21	0.000000
DELTA22	0.000000
DELTA23	0.000000
DELTA24	0.000000
DELTA25	0.000000
DELTA26	0.000000
DELTA27	0.000000
DELTA28	0.000000
DELTA29	0.000000
DELTA30	0.000000
DELTA31	0.000000
DELTA32	0.000000
DELTA33	0.000000
DELTA34	0.000000
DELTA35	0.000000
DELTA36	0.000000
DELTA37	0.000000
DELTA38	0.000000
DELTA39	0.000000
DELTA40	0.000000
DELTA41	0.000000
DELTA42	0.000000
DELTA43	0.000000
DELTA44	0.000000
DELTA45	0.000000
DELTA46	0.000000
DELTA47	0.000000
DELTA48	0.000000
DELTA49	0.000000
DELTA50	0.000000
DELTA51	0.000000
DELTA52	0.000000
DELTA53	0.000000
DELTA54	0.000000
DELTA55	0.000000
DELTA56	0.000000
DELTA57	0.000000
DELTA58	0.000000
DELTA59	0.000000
DELTA60	0.000000
DELTA61	0.000000
DELTA62	0.000000
DELTA63	0.000000
DELTA64	0.000000
DELTA65	0.000000
DELTA66	0.000000
DELTA67	0.000000
DELTA68	0.000000
DELTA69	0.000000
DELTA70	0.000000
DELTA71	0.000000
DELTA72	0.000000
DELTA73	0.000000
DELTA74	0.000000
DELTA75	0.000000
DELTA76	0.000000
DELTA77	0.000000
DELTA78	0.000000
DELTA79	0.000000
DELTA80	0.000000
DELTA81	0.000000
DELTA82	0.000000
DELTA83	0.000000
DELTA84	0.000000
DELTA85	0.000000
DELTA86	0.000000
DELTA87	0.000000
DELTA88	0.000000
DELTA89	0.000000
DELTA90	0.000000
DELTA91	0.000000
DELTA92	0.000000
DELTA93	0.000000
DELTA94	0.000000
DELTA95	0.000000
DELTA96	0.000000
DELTA97	0.000000
DELTA98	0.000000
DELTA99	0.000000
DELTA100	0.000000

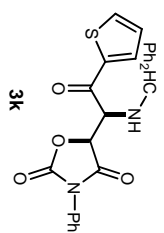


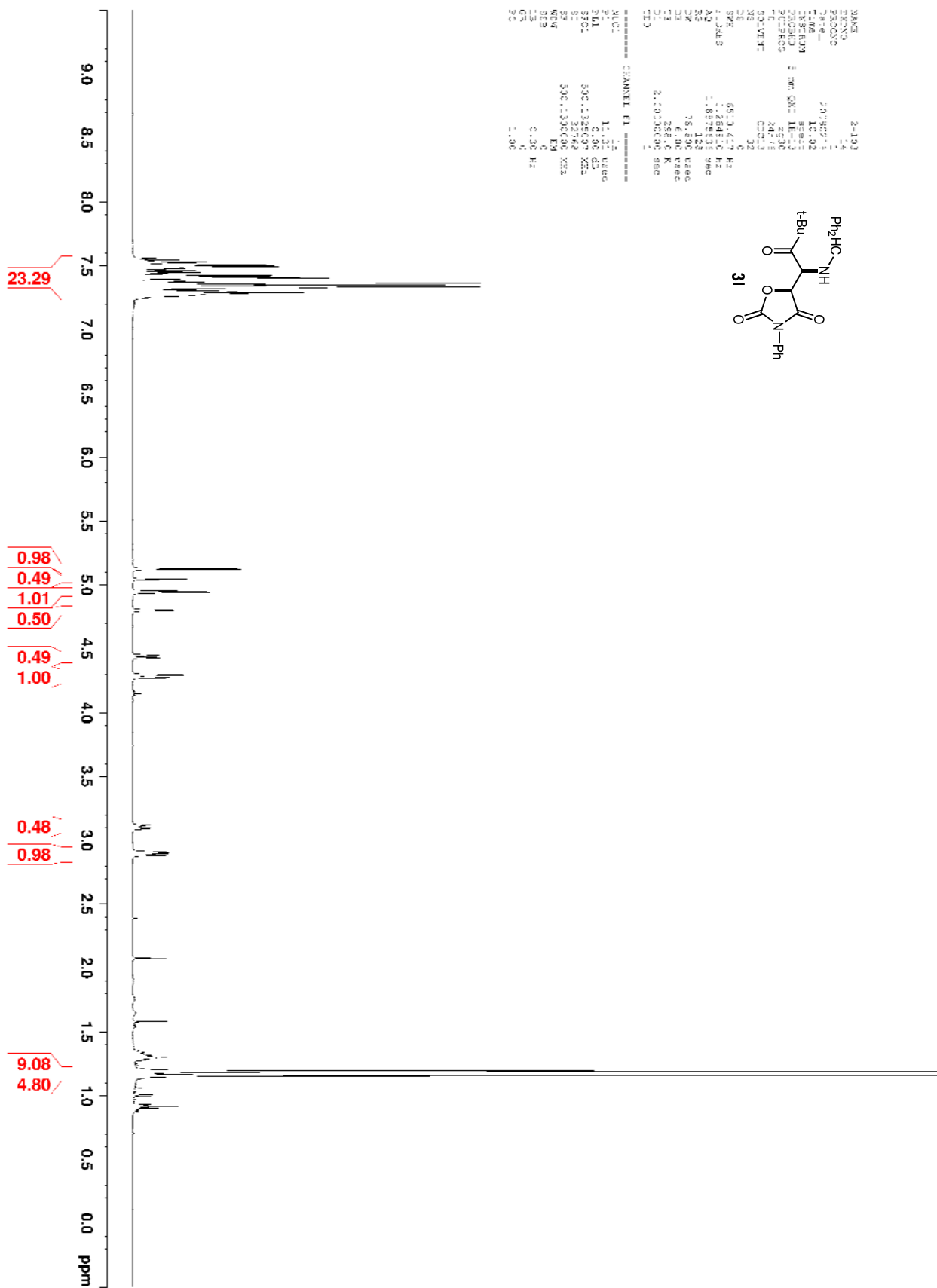
Figure 61. ^1H NMR (500 MHz, CDCl_3) of **31**

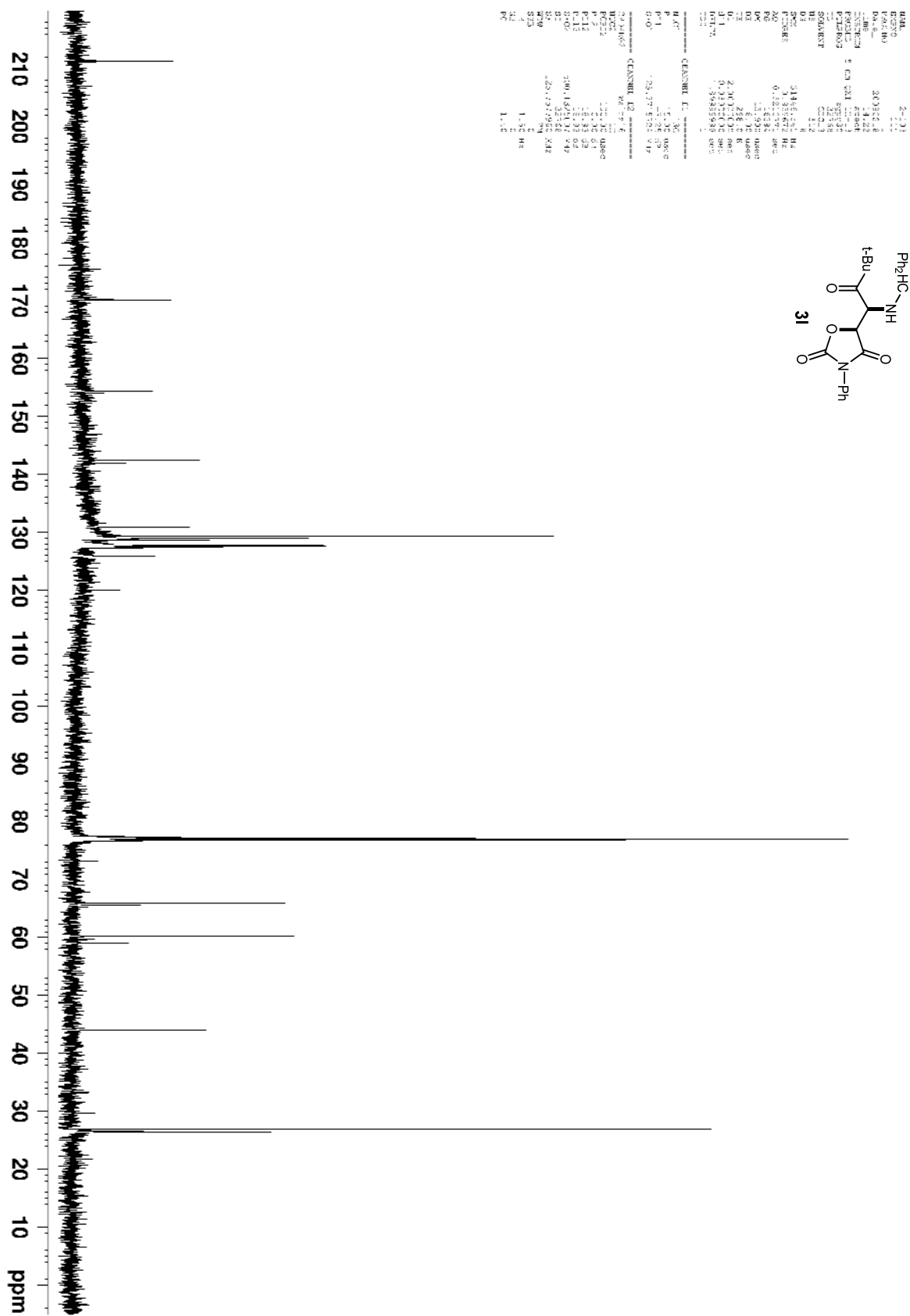
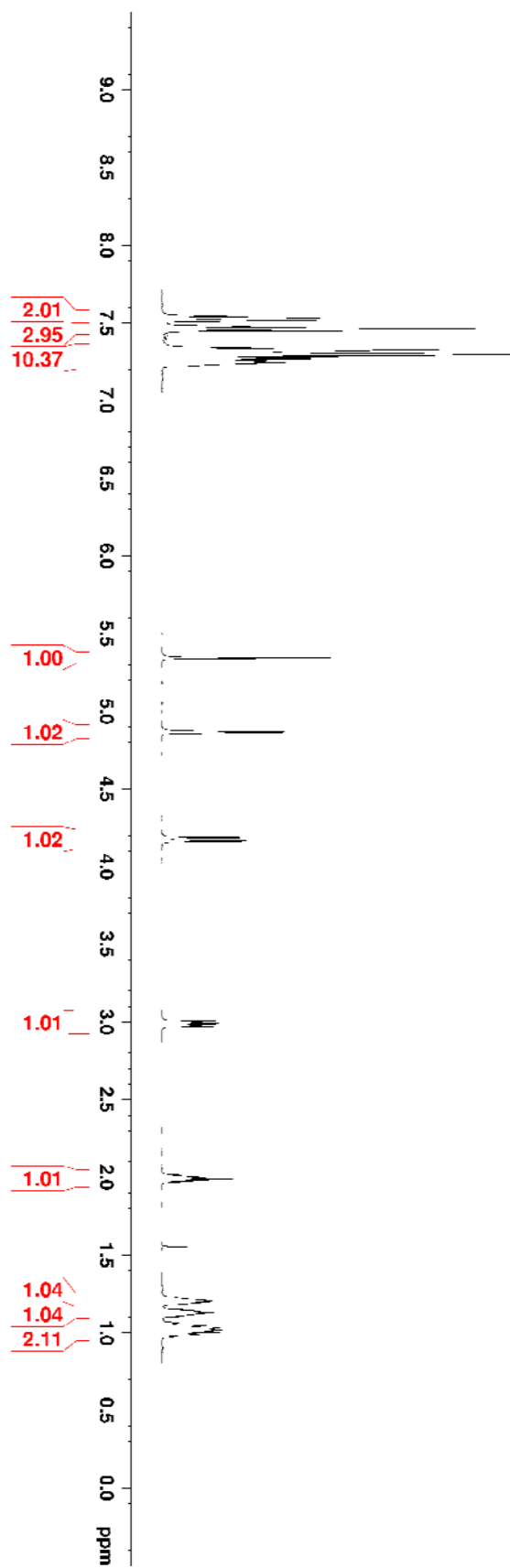
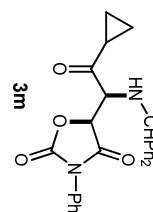
Figure 62. ^{13}C NMR (125 MHz, CDCl_3) of **31**

Figure 63. ^1H NMR (400 MHz, CDCl_3) of **3m**

```
NAME          2-(1-cyclopropyl-1-oxo-2-phenylaminoethyl)isoindolin-3-one
EXPNO         12
PROCNO        1
Date_         20190219
Time          10:14
INSTRUM       spect
PROBHD        5 mm QNP 1H 13
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS           64
DS           4
SWH           5577.417 Hz
AQ           1.1776247
RG           1284.500
AQ           1.2864500 SMC
RG           236
DS           4
WDW           EM
SSB           0
LB           3.00 Hz
GB           0
PC           2.1000000
TDC           5 sec
===== CHANNEL f1 =====
NUC1          13C
P1           12.00 usec
PL1          0.00 dB
SFO1         125.7613507 MHz
SI           32768
SF           125.7613507 MHz
WDW           EM
SSB           0
LB           3.00 Hz
GB           0
PC           1.00
```



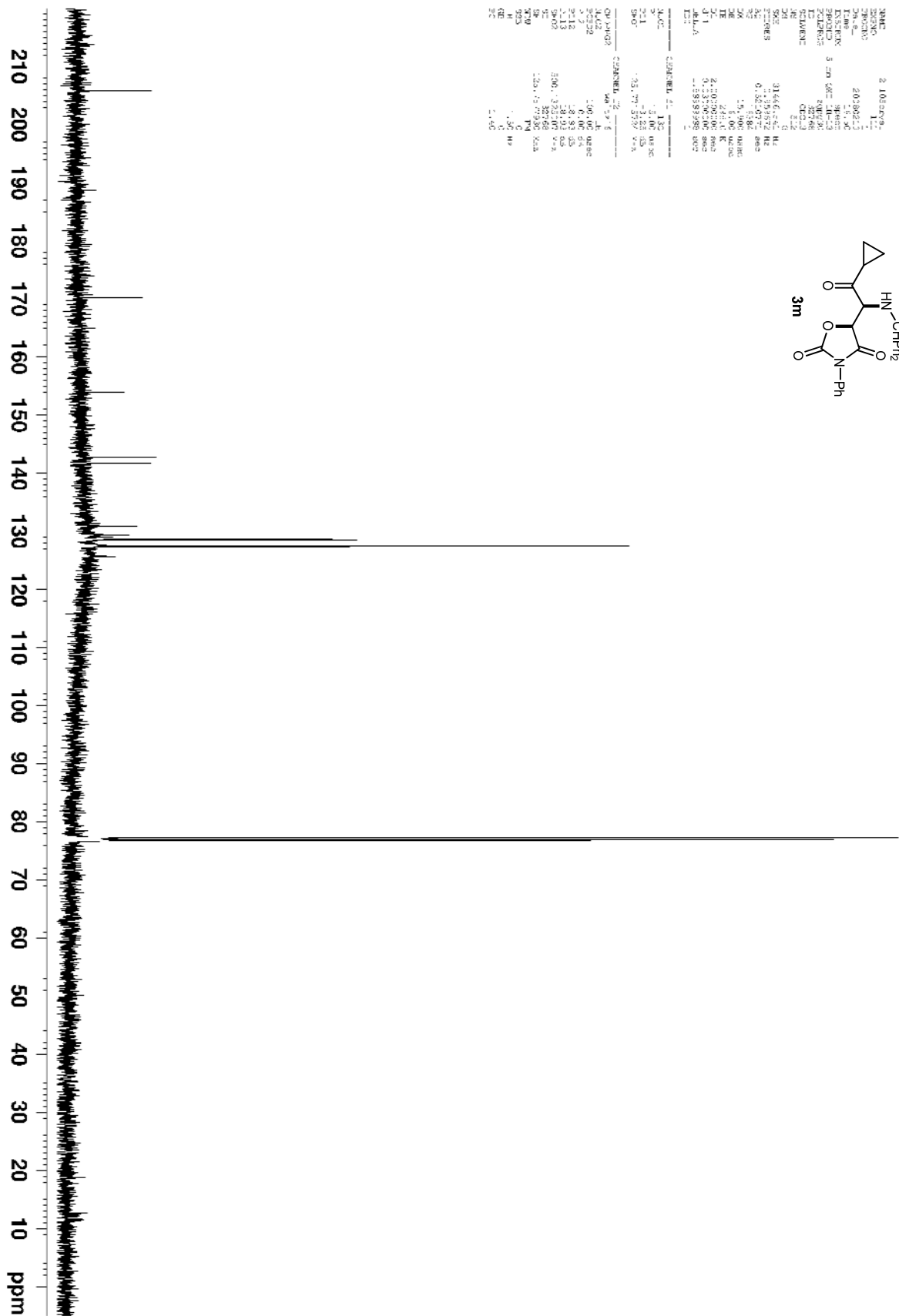
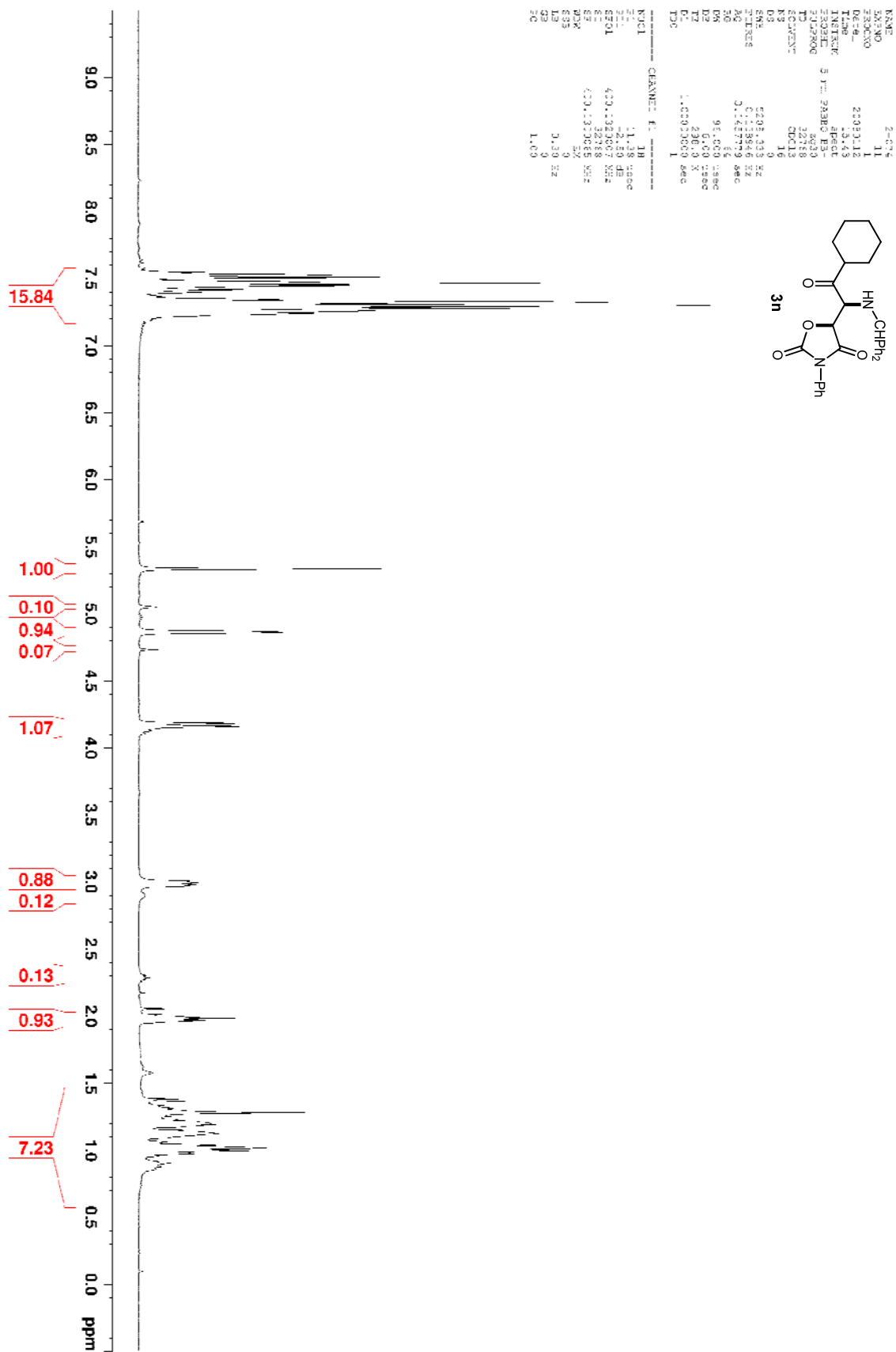


Figure 65. ¹H NMR (400 MHz, CDCl₃) of **3n**

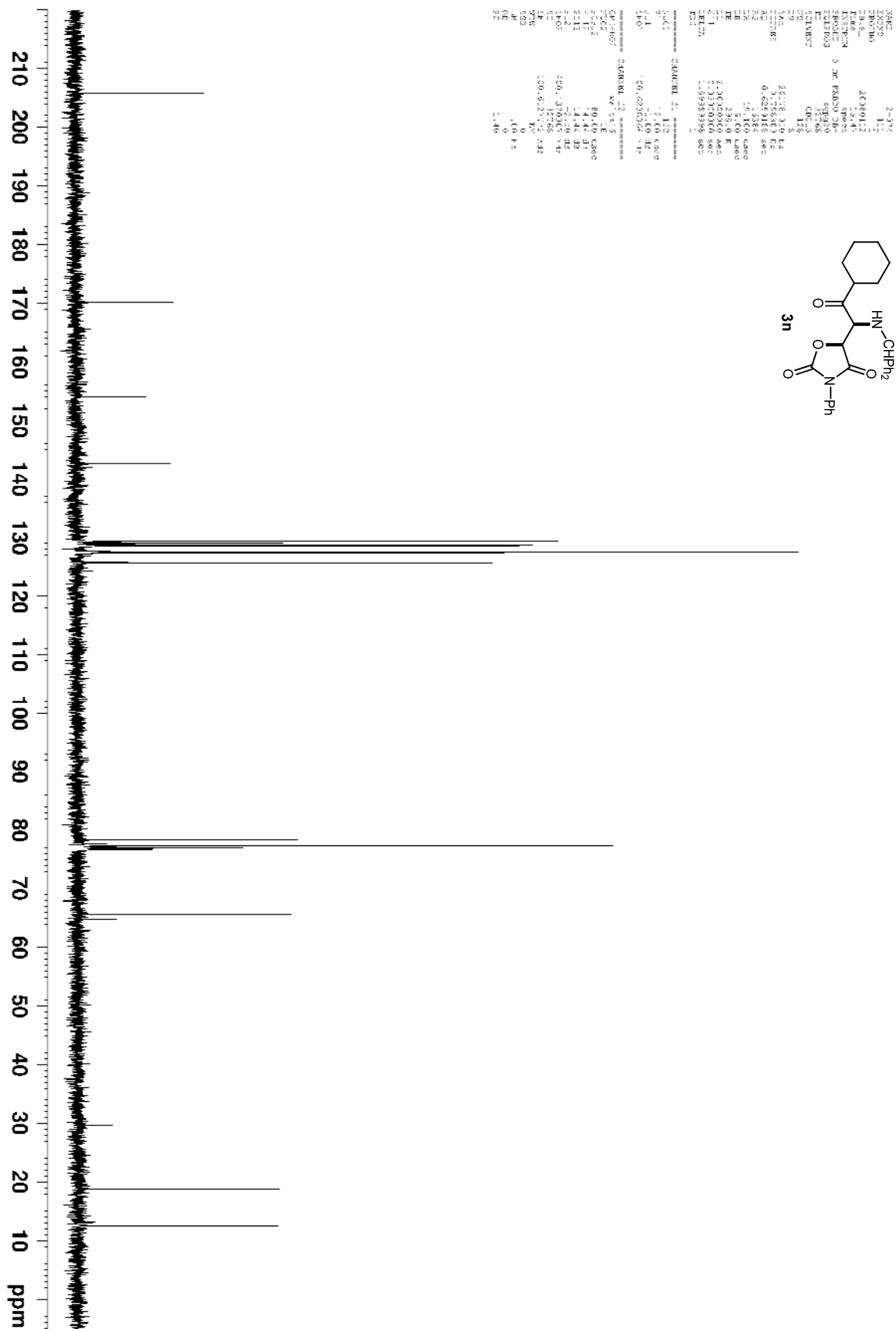
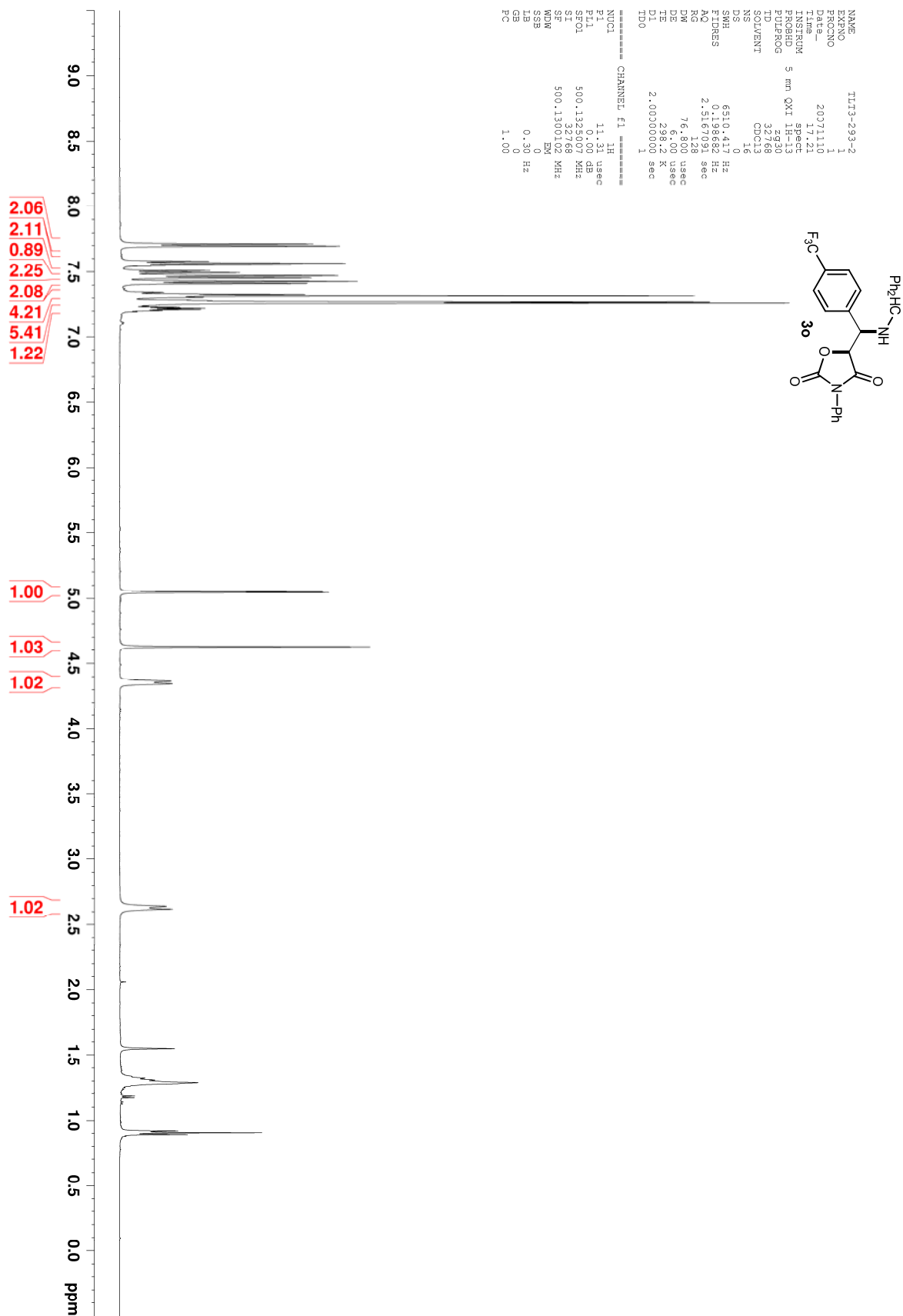
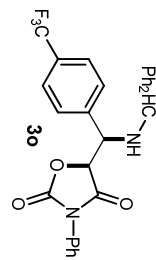


Figure 67. ¹H NMR (500 MHz, CDCl₃) of **30**



```
NAME          TIT3-291-2
EXPNO         2
PROCNO        1
Date_         20071110
Time          17:26
PROBHD        5 mm QNP 1H-13
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            259
DS            8
FIDRES        0.9546712 Hz
AQ            0.5210771 sec
RG            16384
AQ            1.6384 usec
DE            6.00 usec
TE            299.2 K
DELTA         0.0300000 sec
d11           1.8999998 sec
DELTA         1.8999998 sec
TD0           1
===== CHANNEL f1 =====
NUC1          13C
P1            13.00 usec
PL1           -1.20 dB
SFO1          125.771524 MHz
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
P2            10.00 usec
PL2           -1.00 dB
PL12          18.93 dB
PL13          594.133493 dB
SI            32768
SF            125.757333 MHz
RG            65536
AQ            1.2573333 sec
DE            1.00 usec
TE            1.40
=====
```

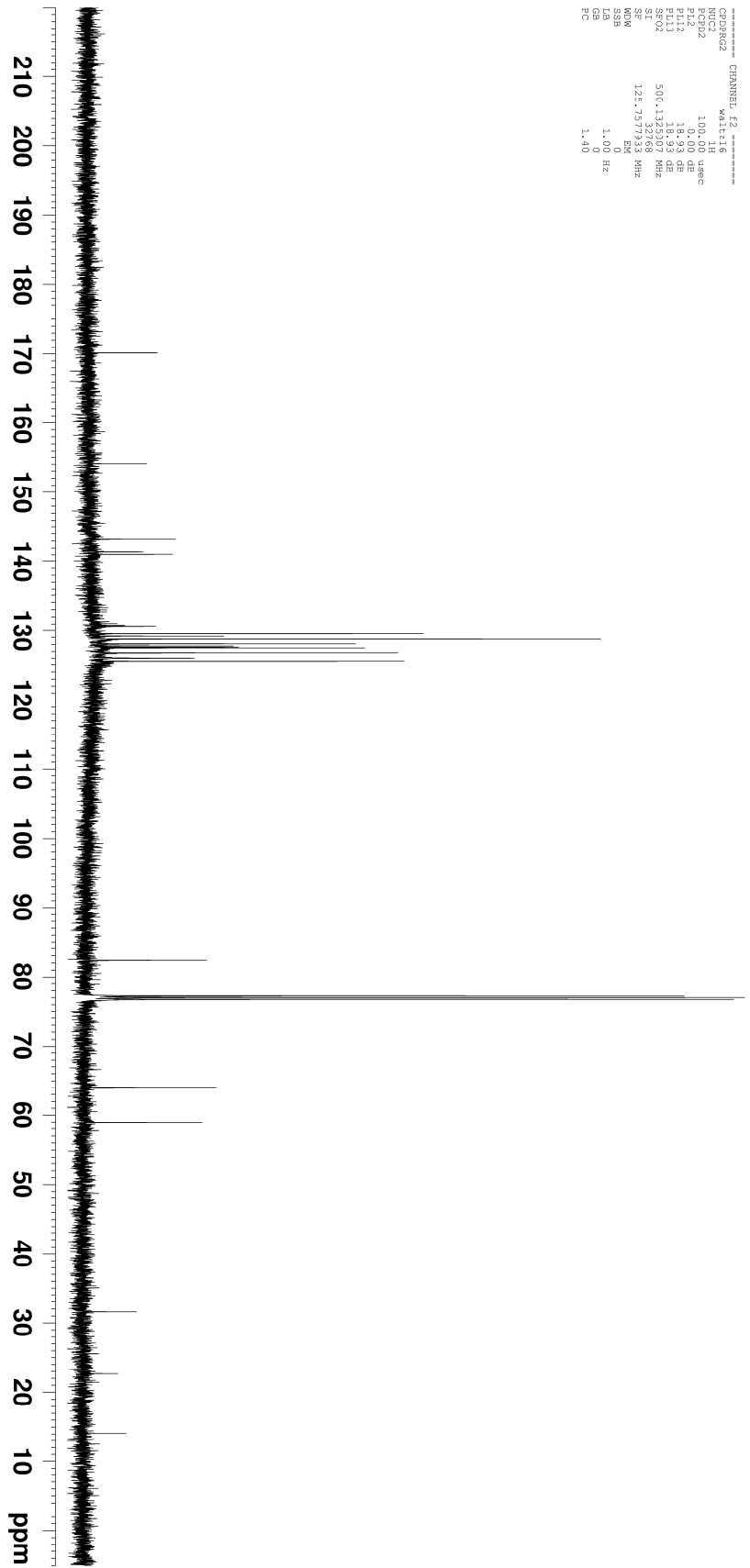
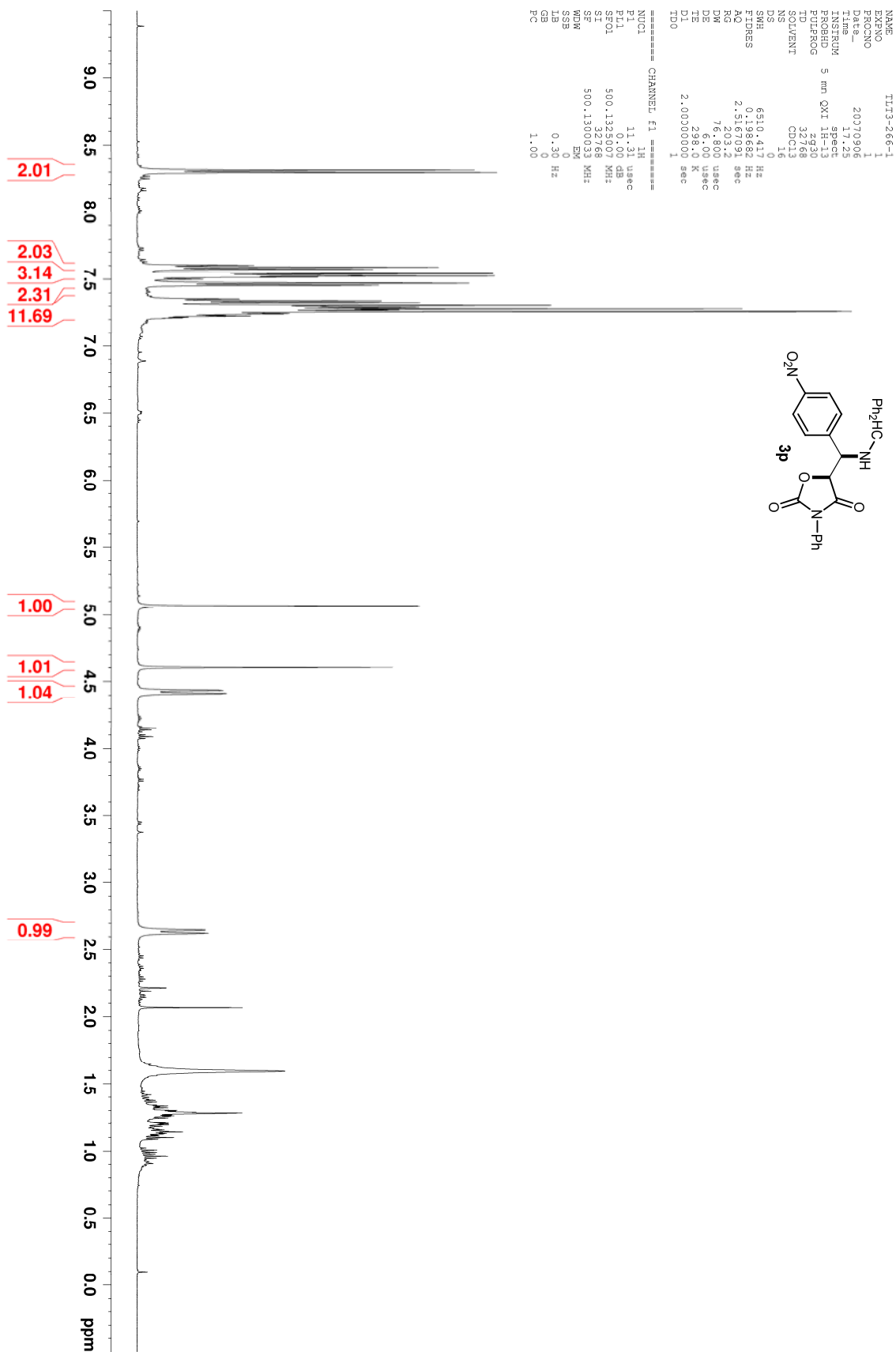


Figure 69. ¹H NMR (500 MHz, CDCl₃) of **3p**

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Figure 70. ¹³C NMR (125 MHz, CDCl₃) of **3p**

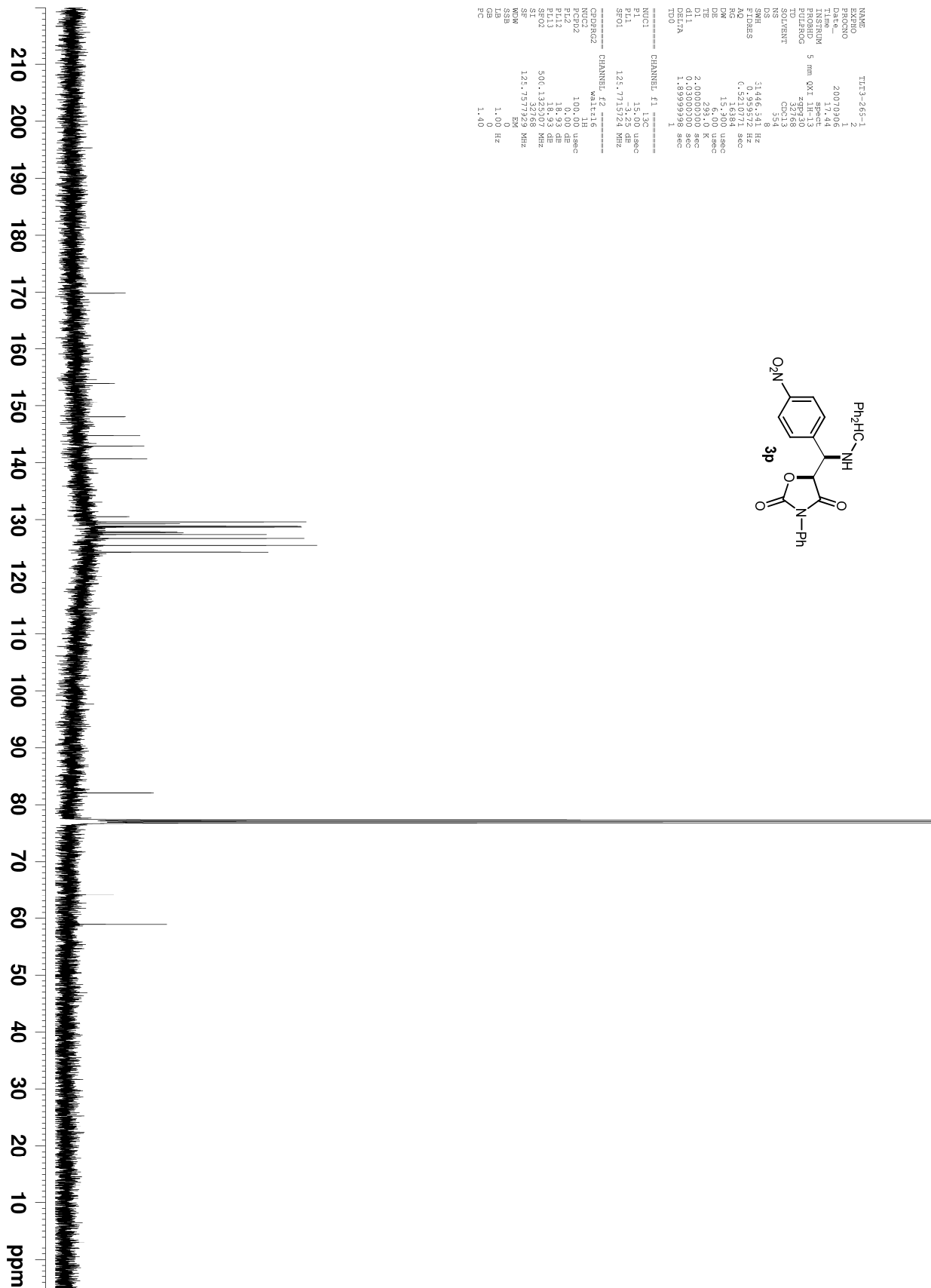
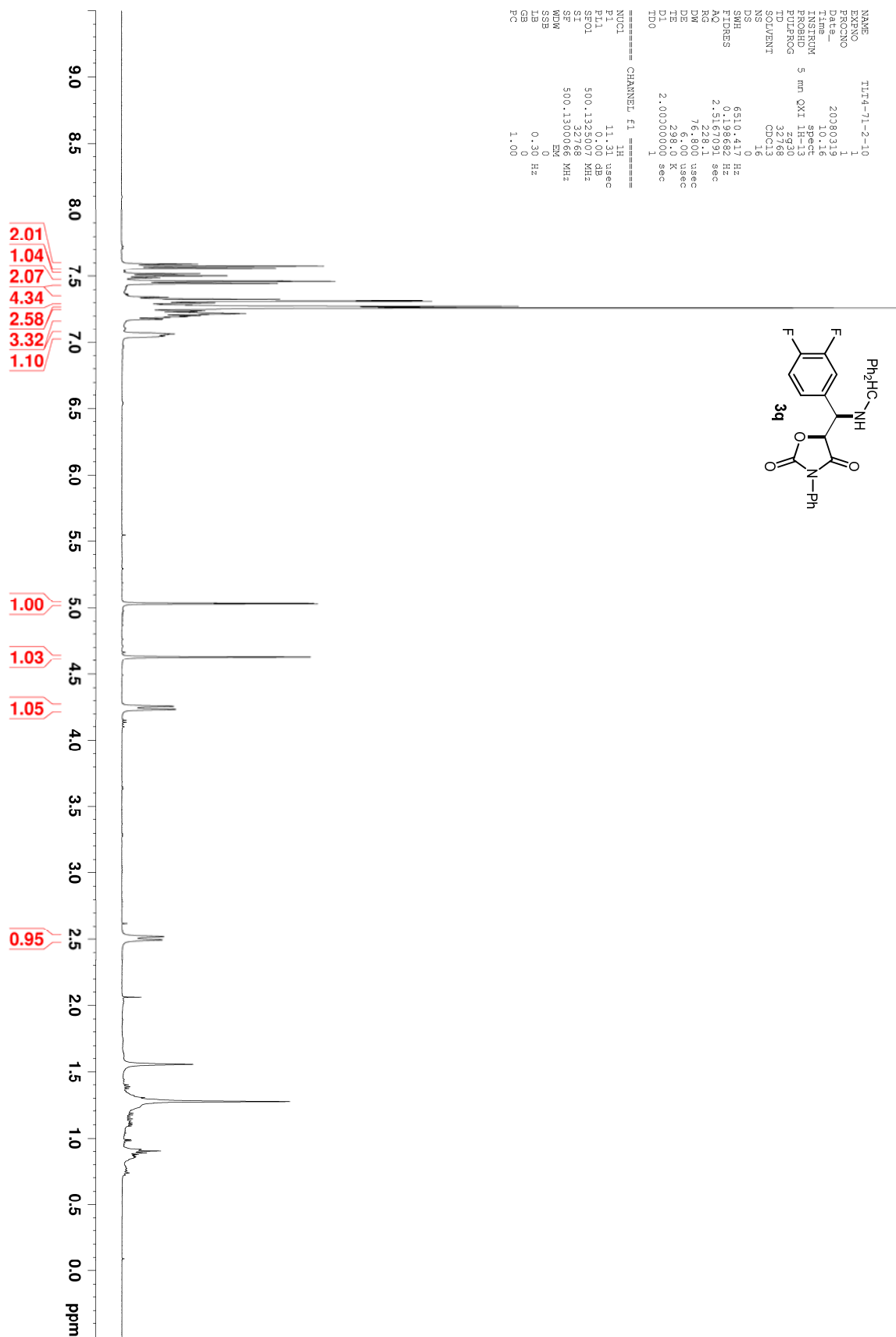


Figure 71. ¹H NMR (500 MHz, CDCl₃) of **3q**

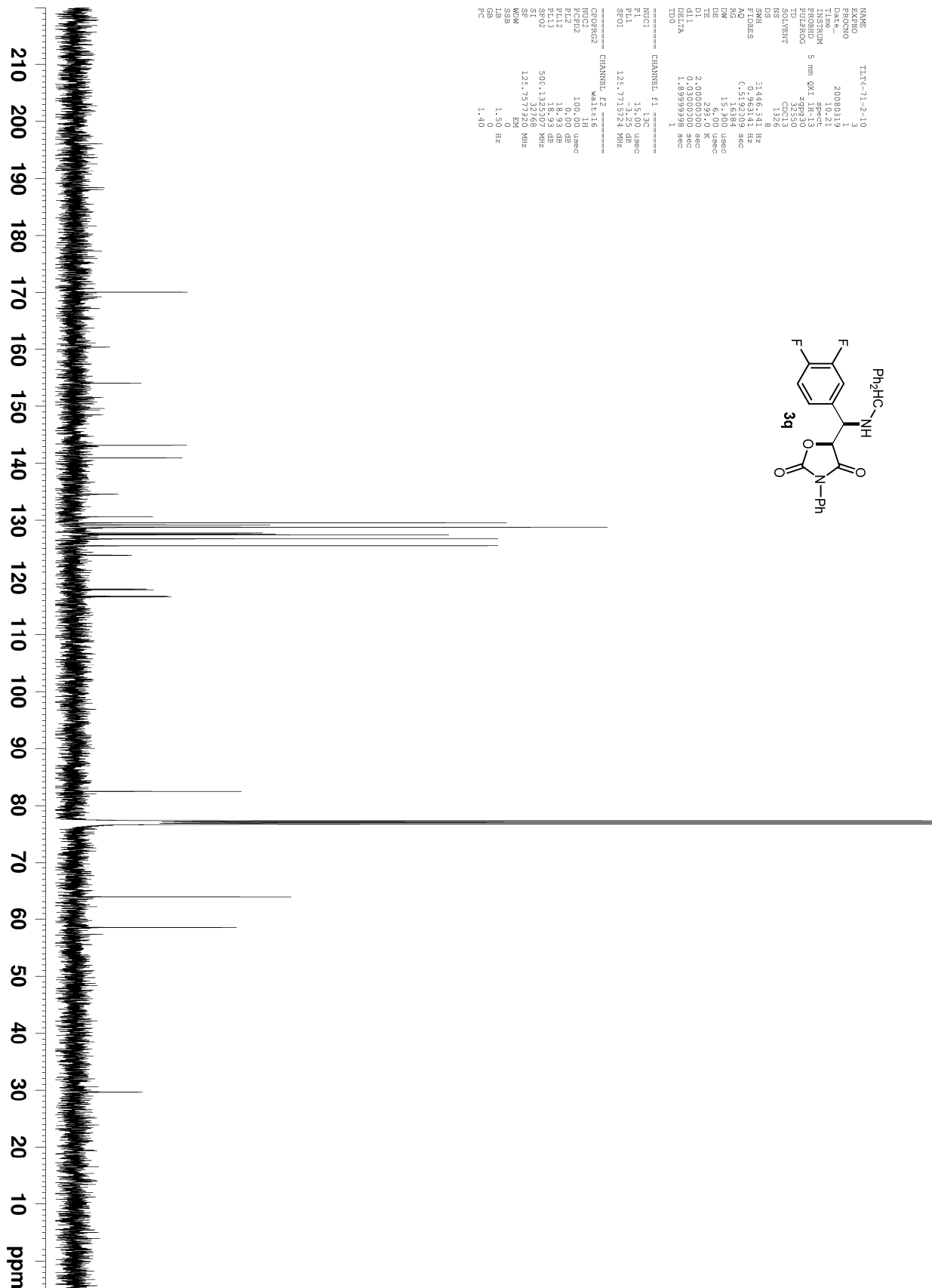
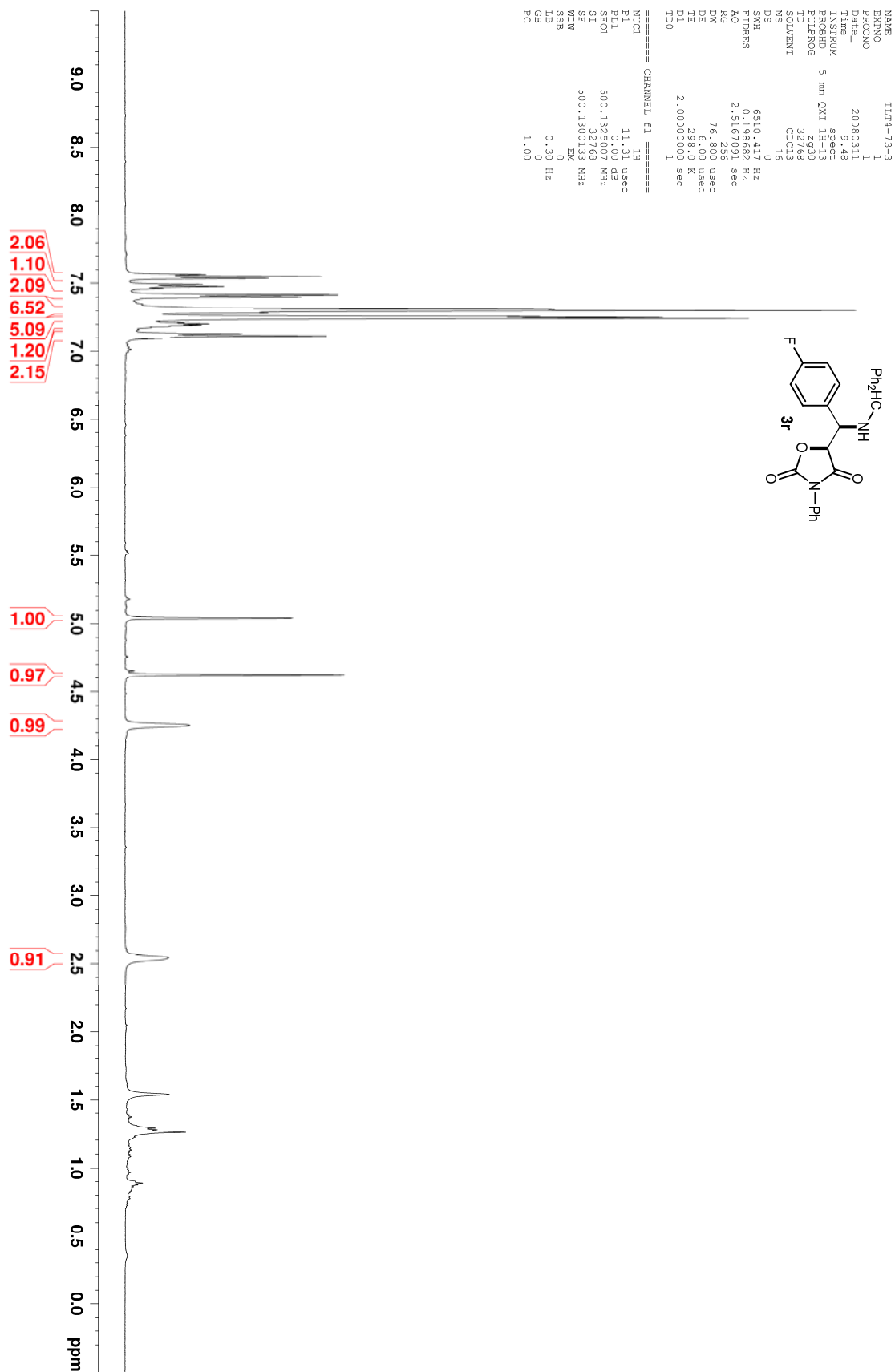


Figure 73. ¹H NMR (500 MHz, CDCl₃) of 3r

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Figure 74. ¹³C NMR (125 MHz, CDCl₃) of 3r

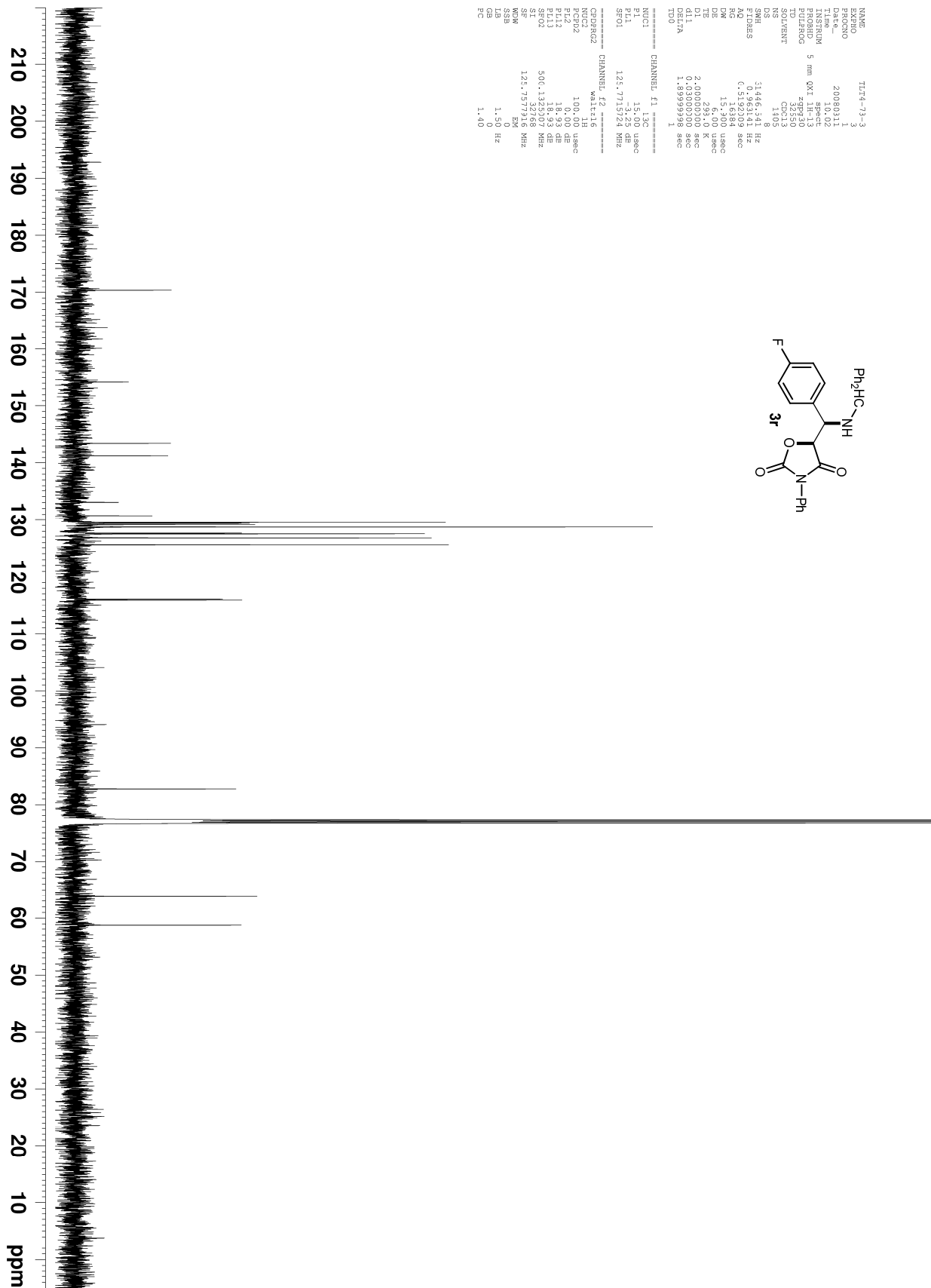
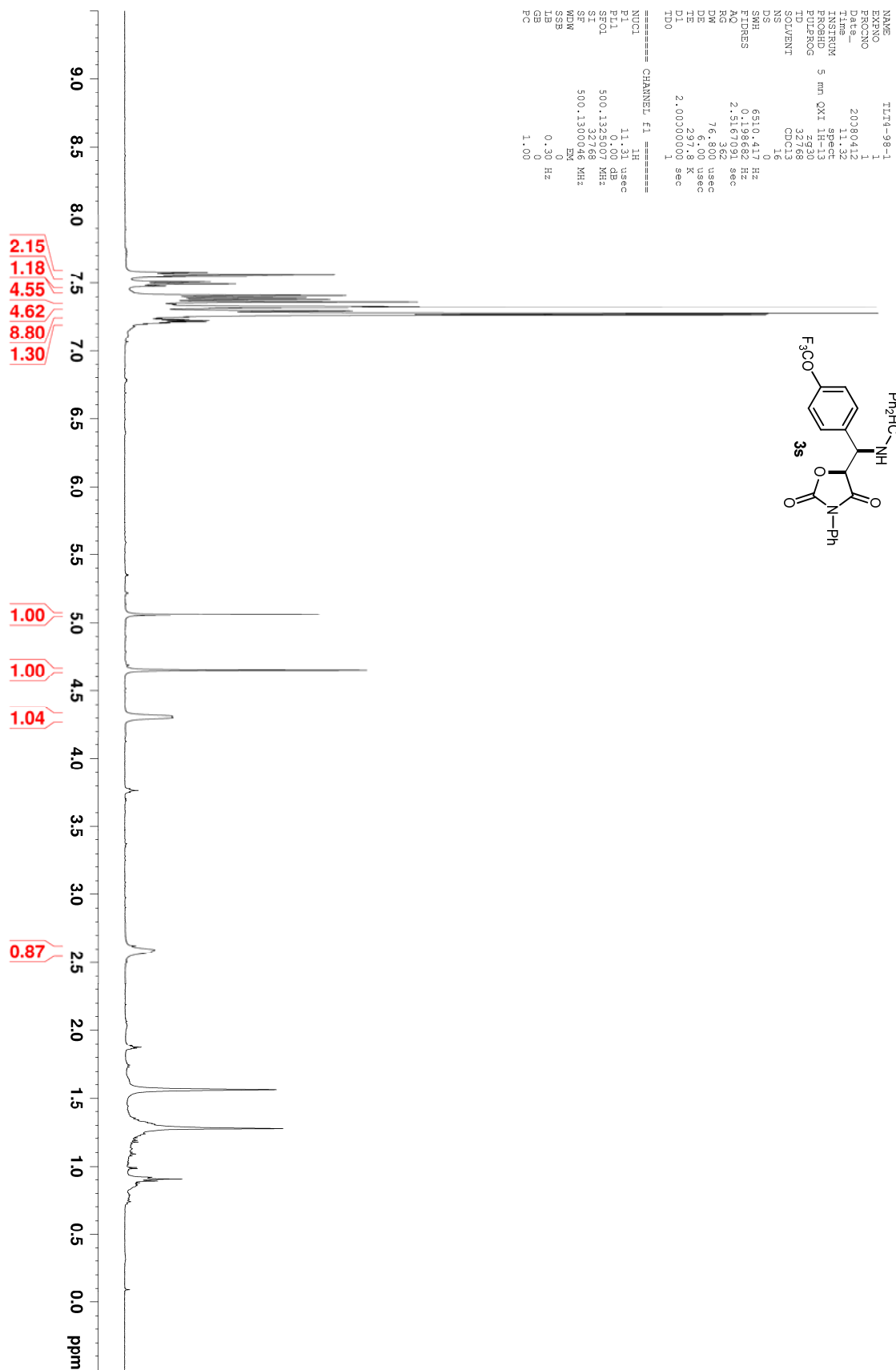


Figure 75. ¹H NMR (500 MHz, CDCl₃) of **3s**

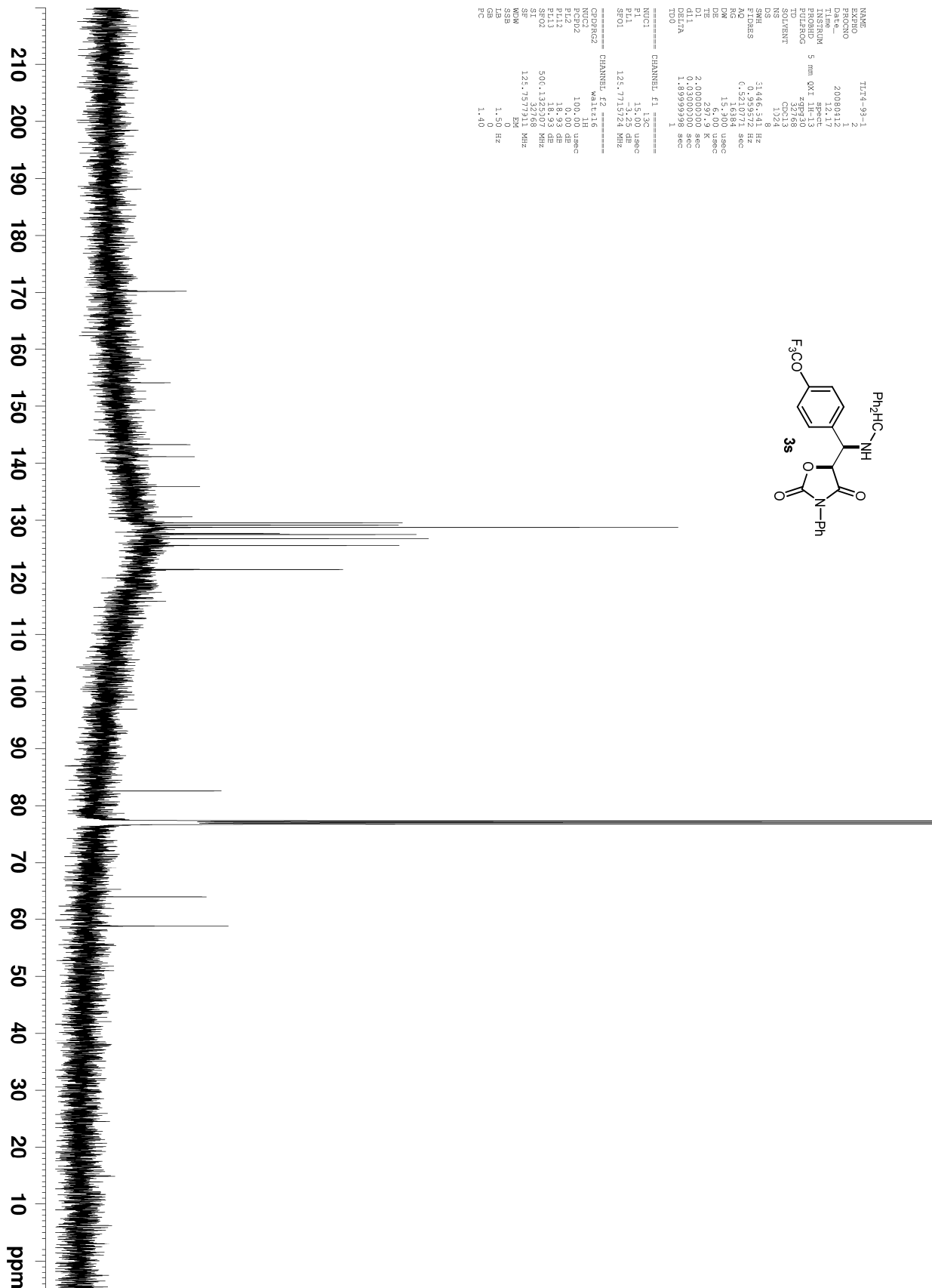
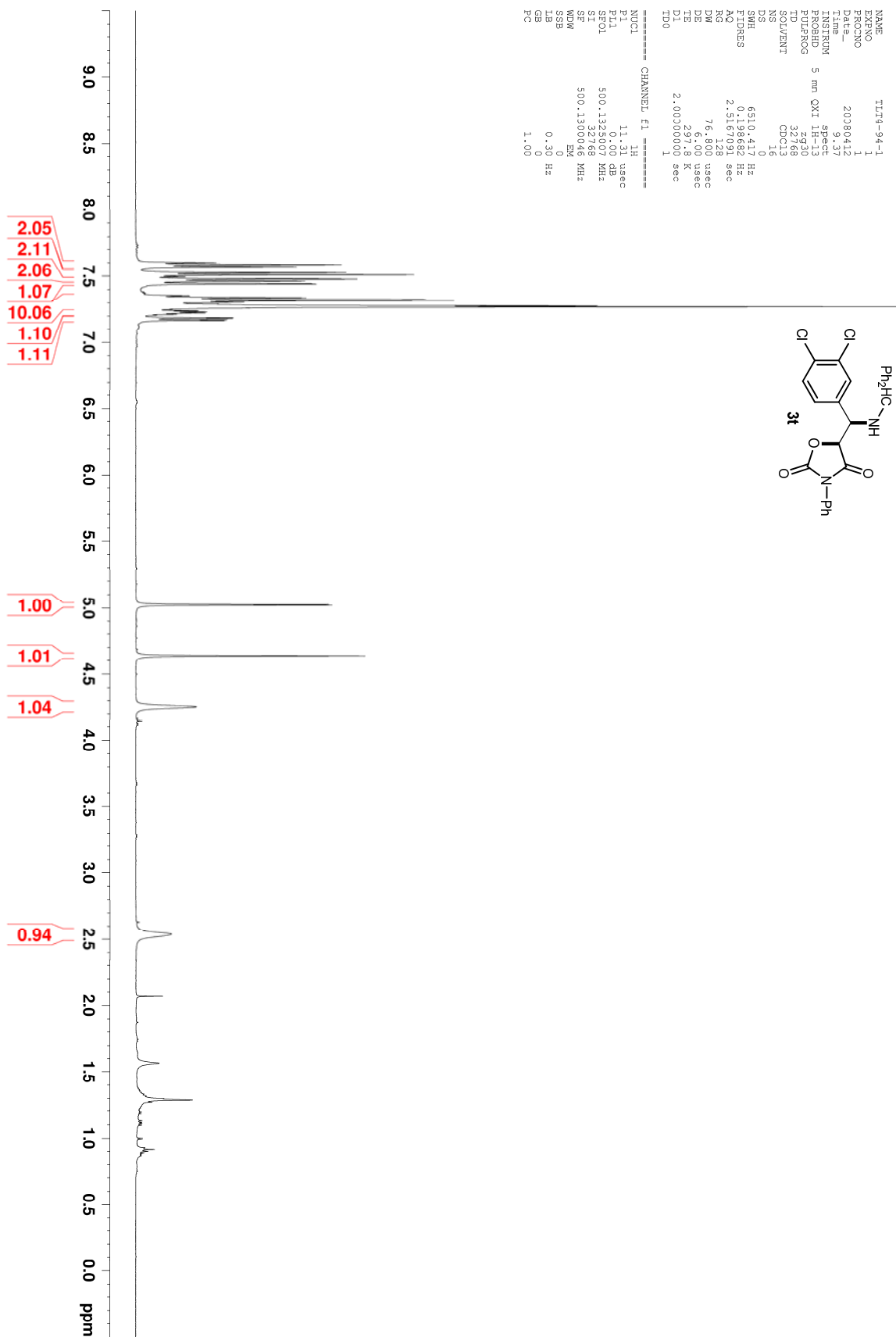


Figure 77. ¹H NMR (500 MHz, CDCl₃) of **3t**

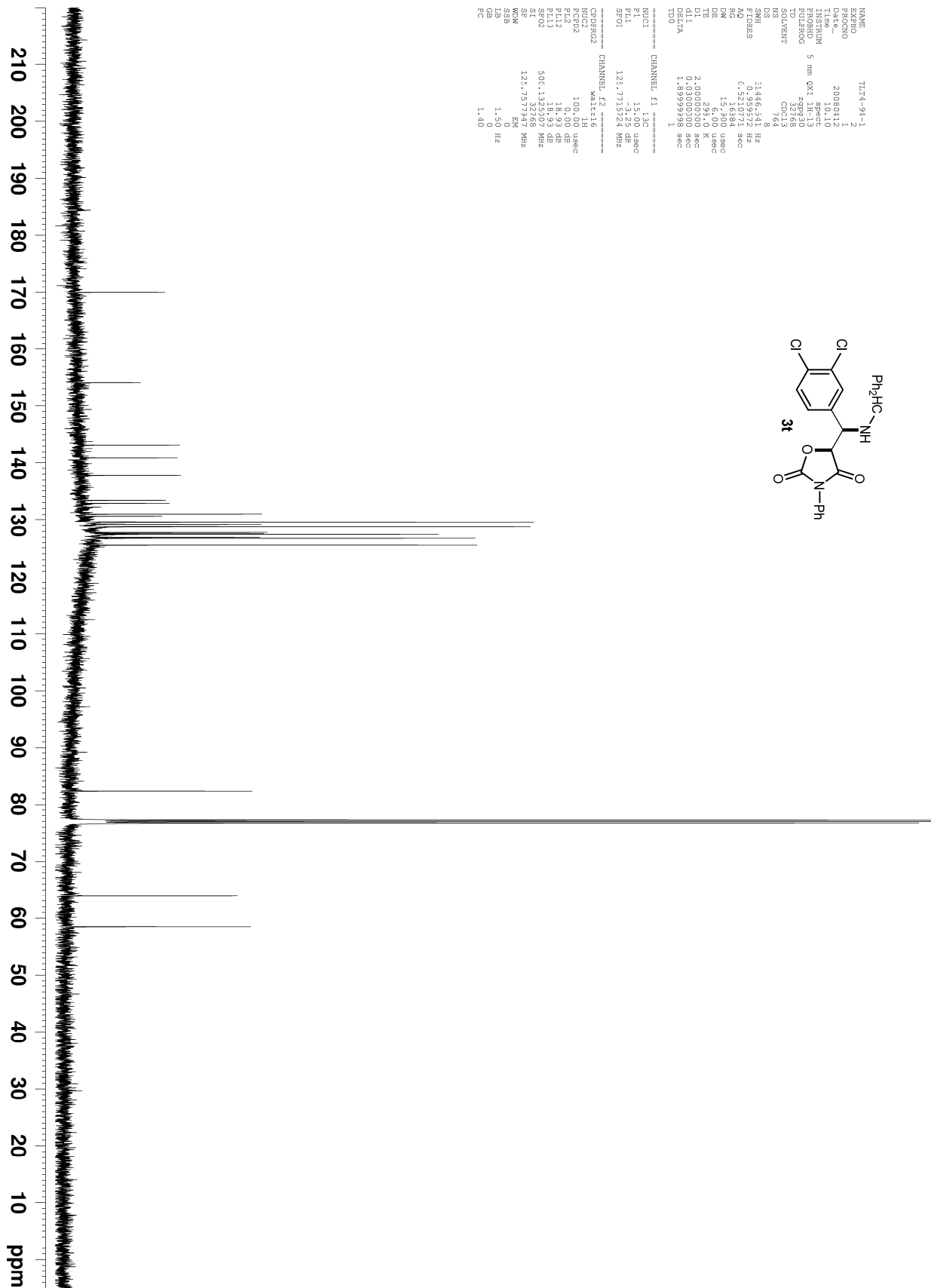
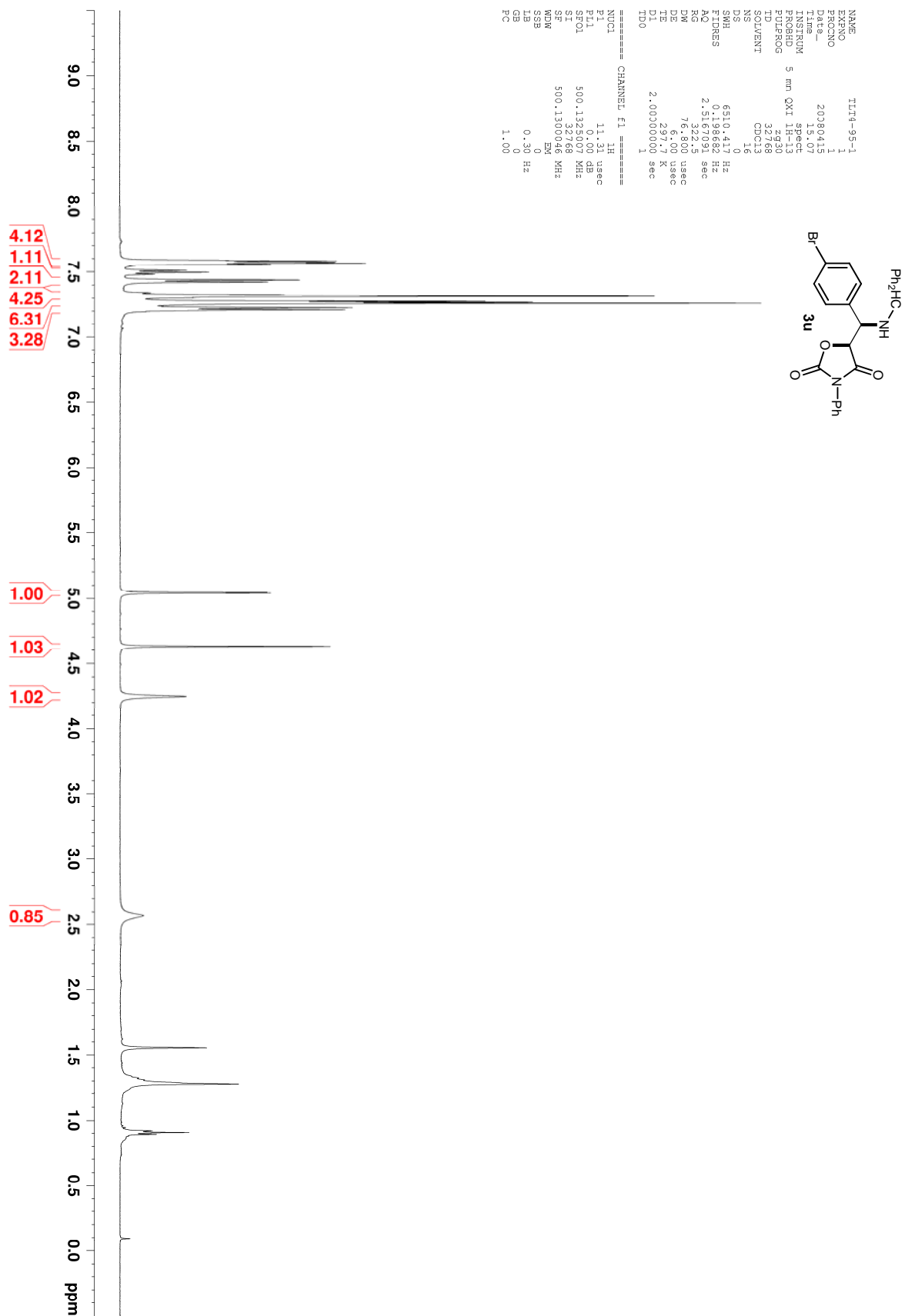


Figure 79. ¹H NMR (500 MHz, CDCl₃) of **3u**

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Figure 80. ^{13}C NMR (125 MHz, CDCl_3) of **3u**

Supporting Information

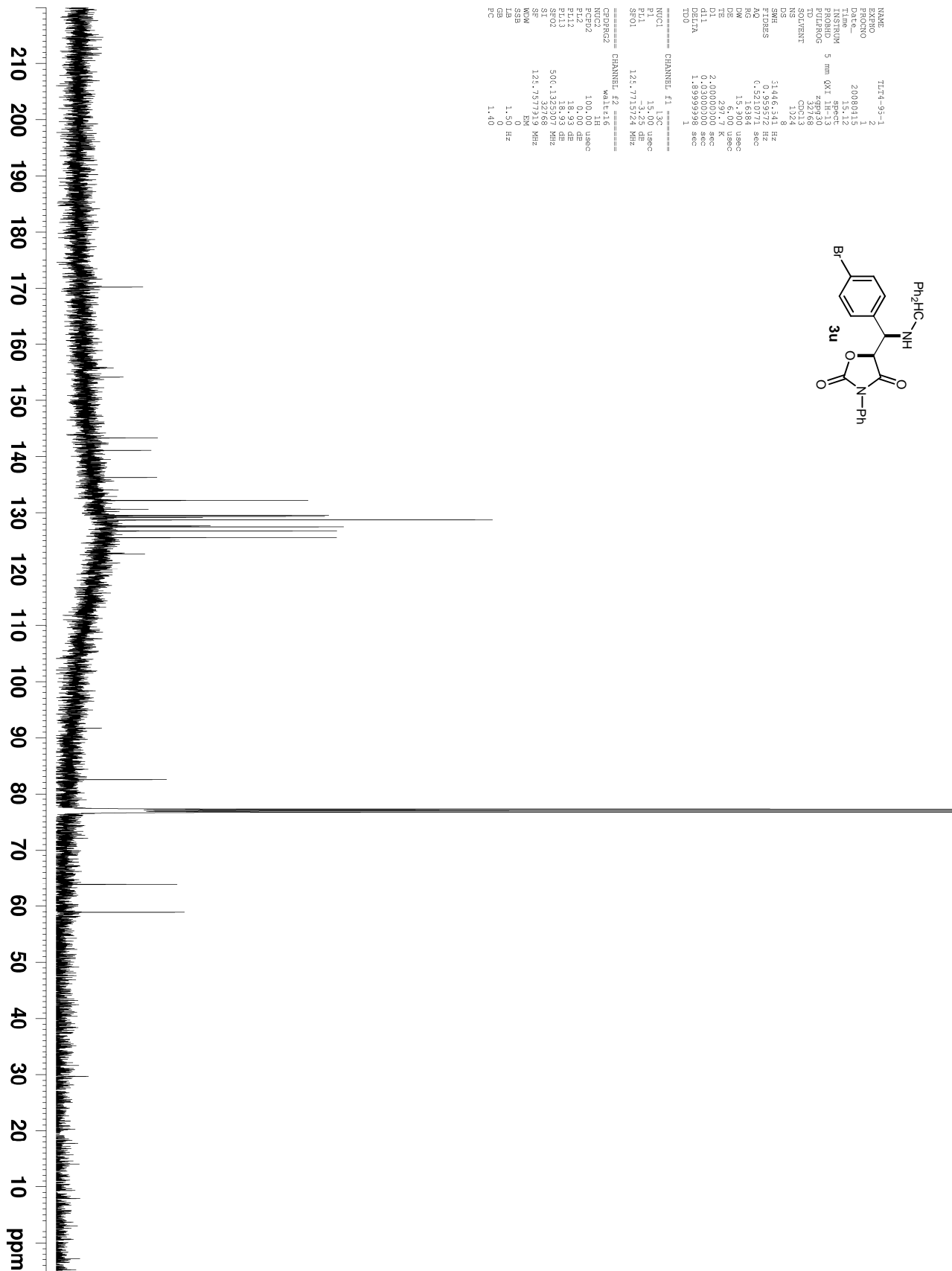
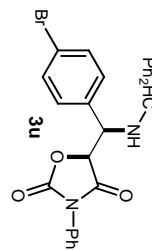
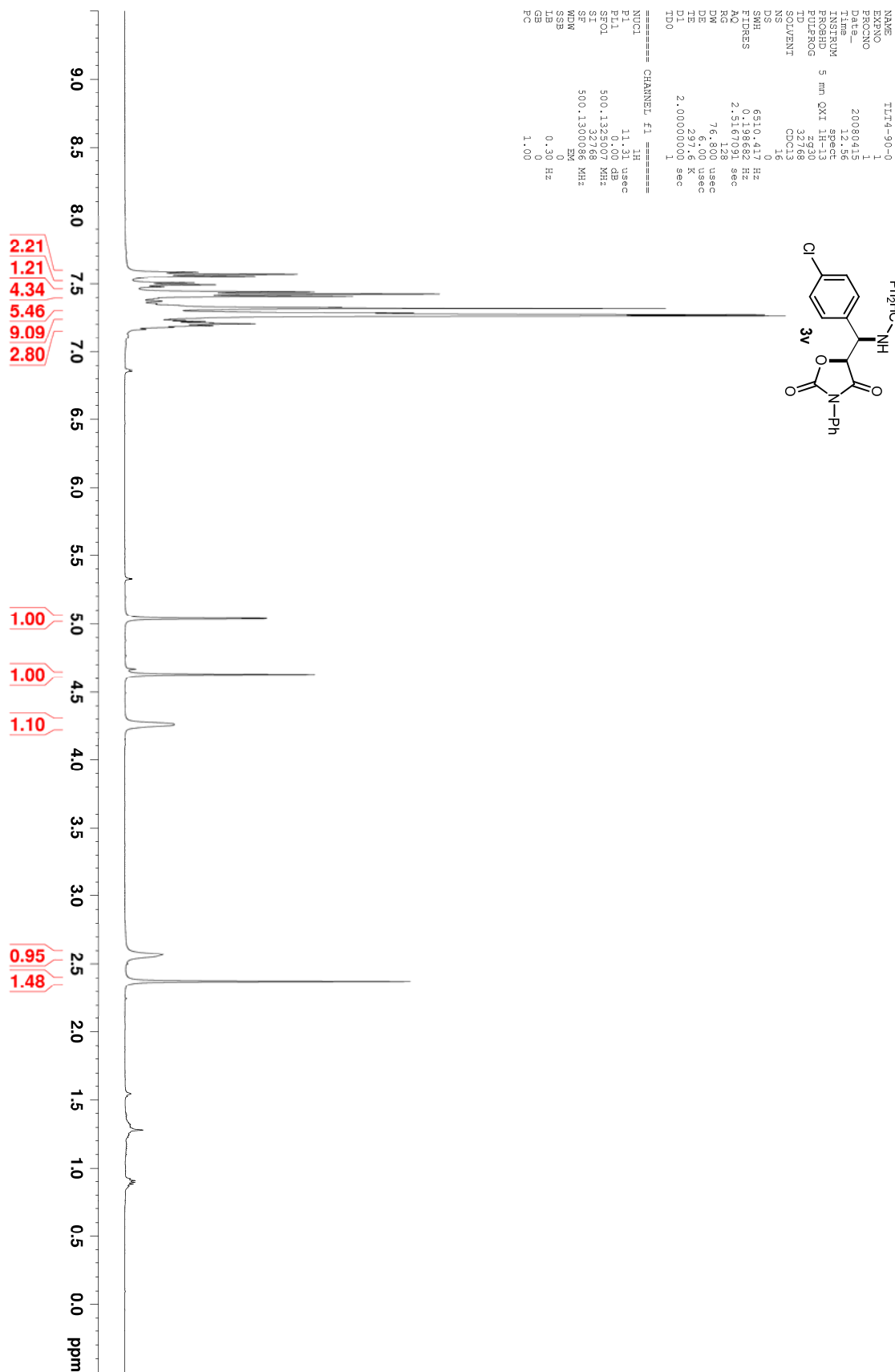


Figure 81. ^1H NMR (500 MHz, CDCl_3) of **3v**

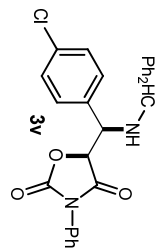
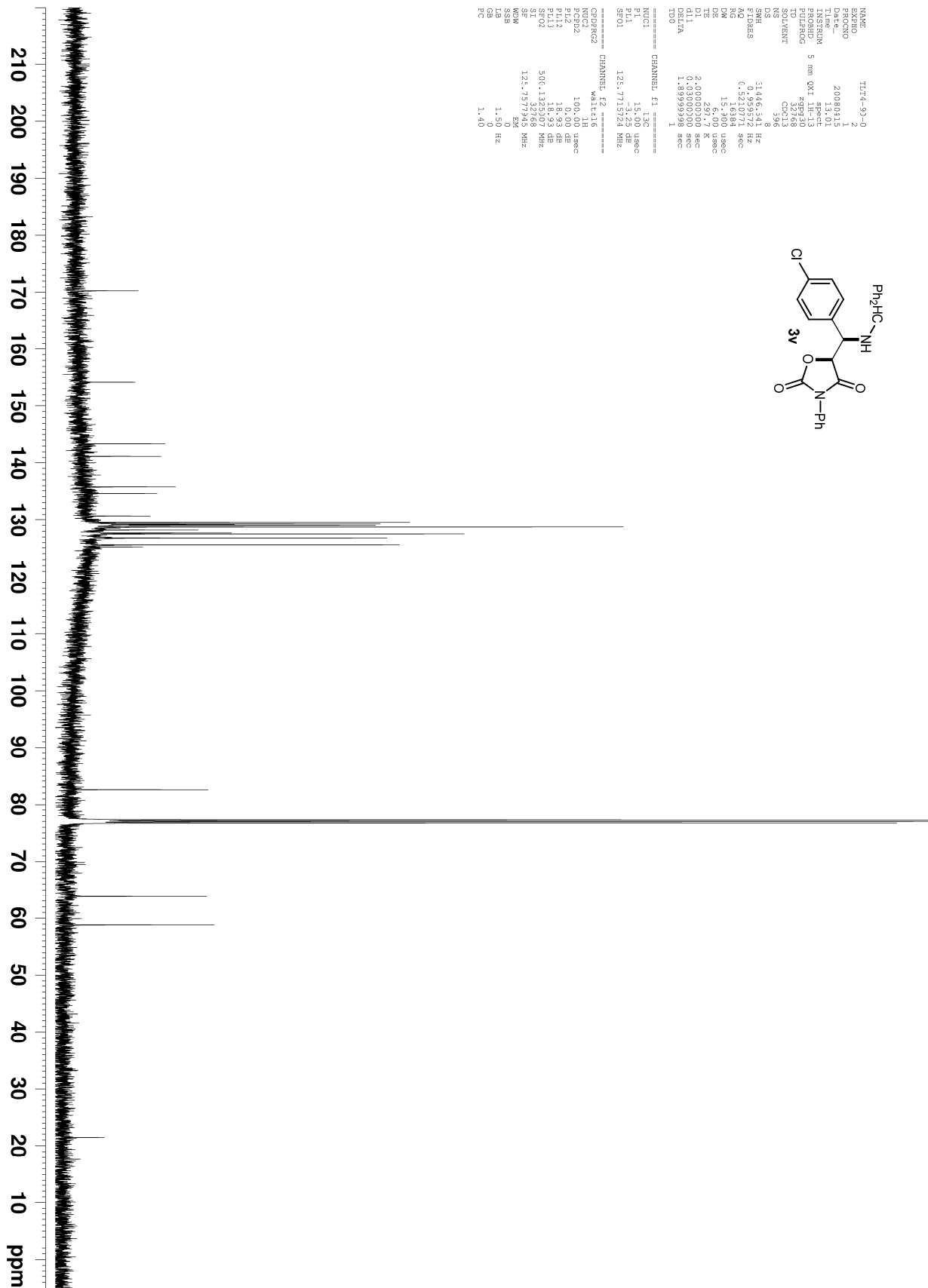
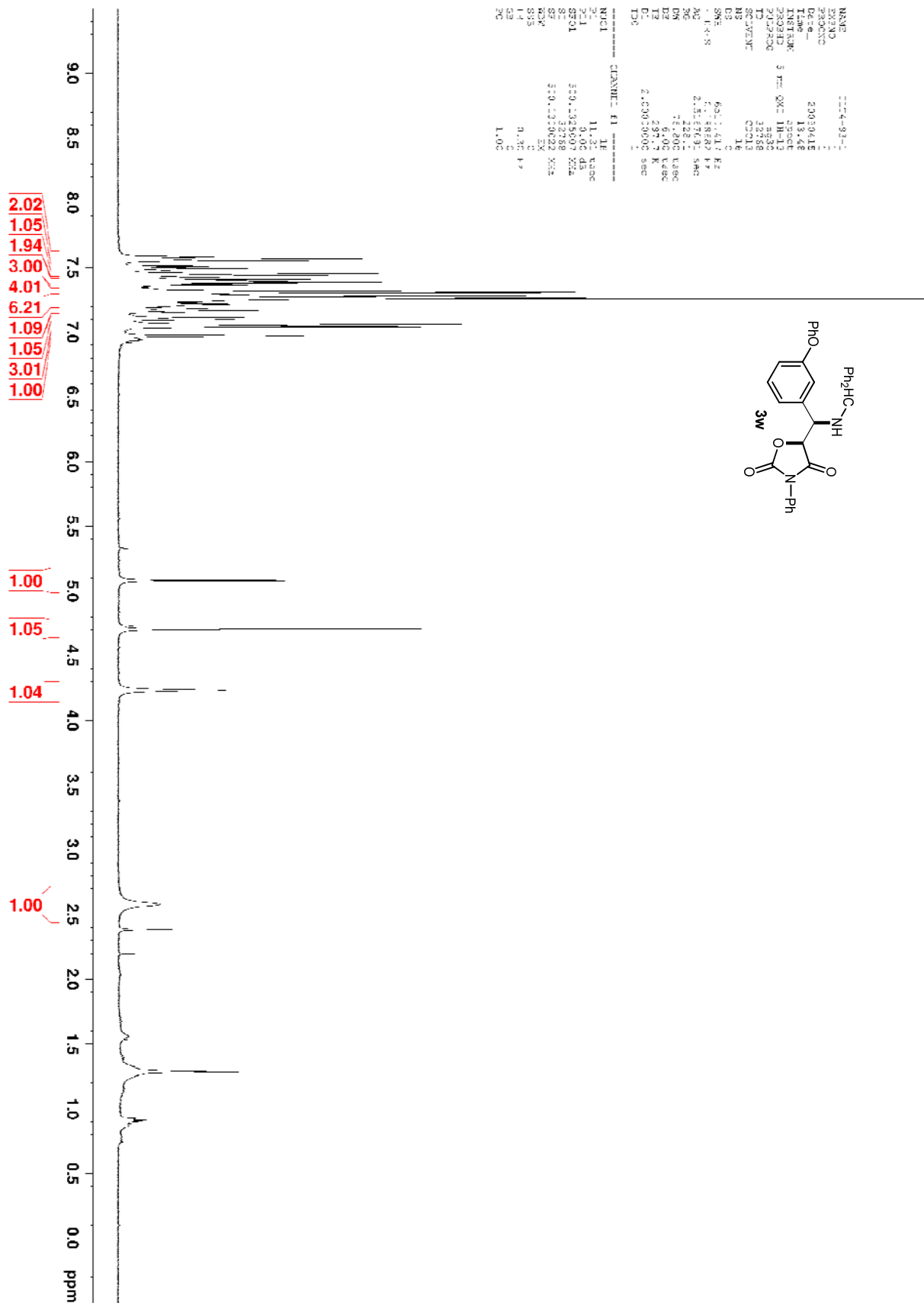


Figure 83. ¹H NMR (500 MHz, CDCl₃) of **3w**



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Figure 84. ¹³C NMR (125 MHz, CDCl₃) of **3w**

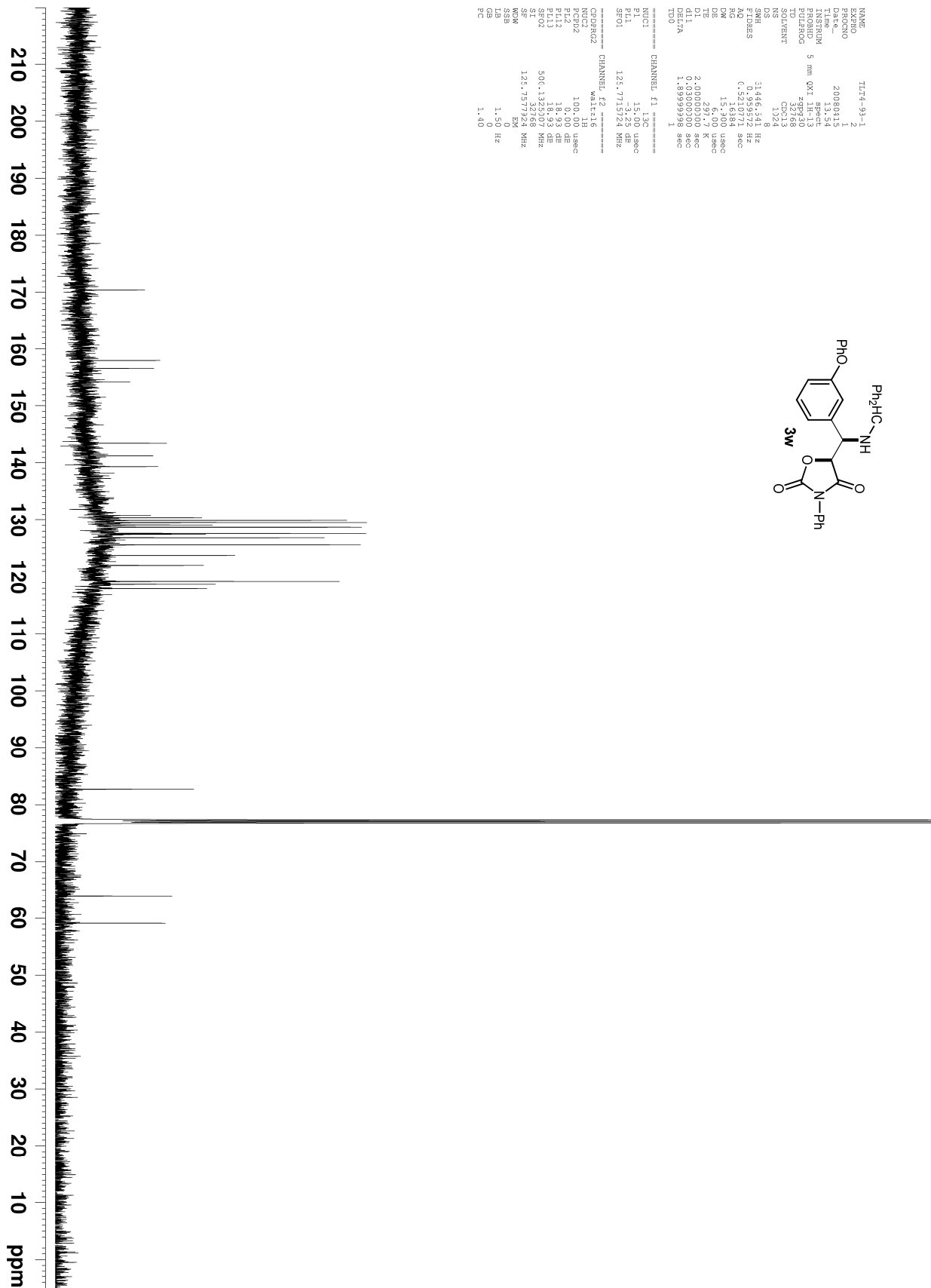


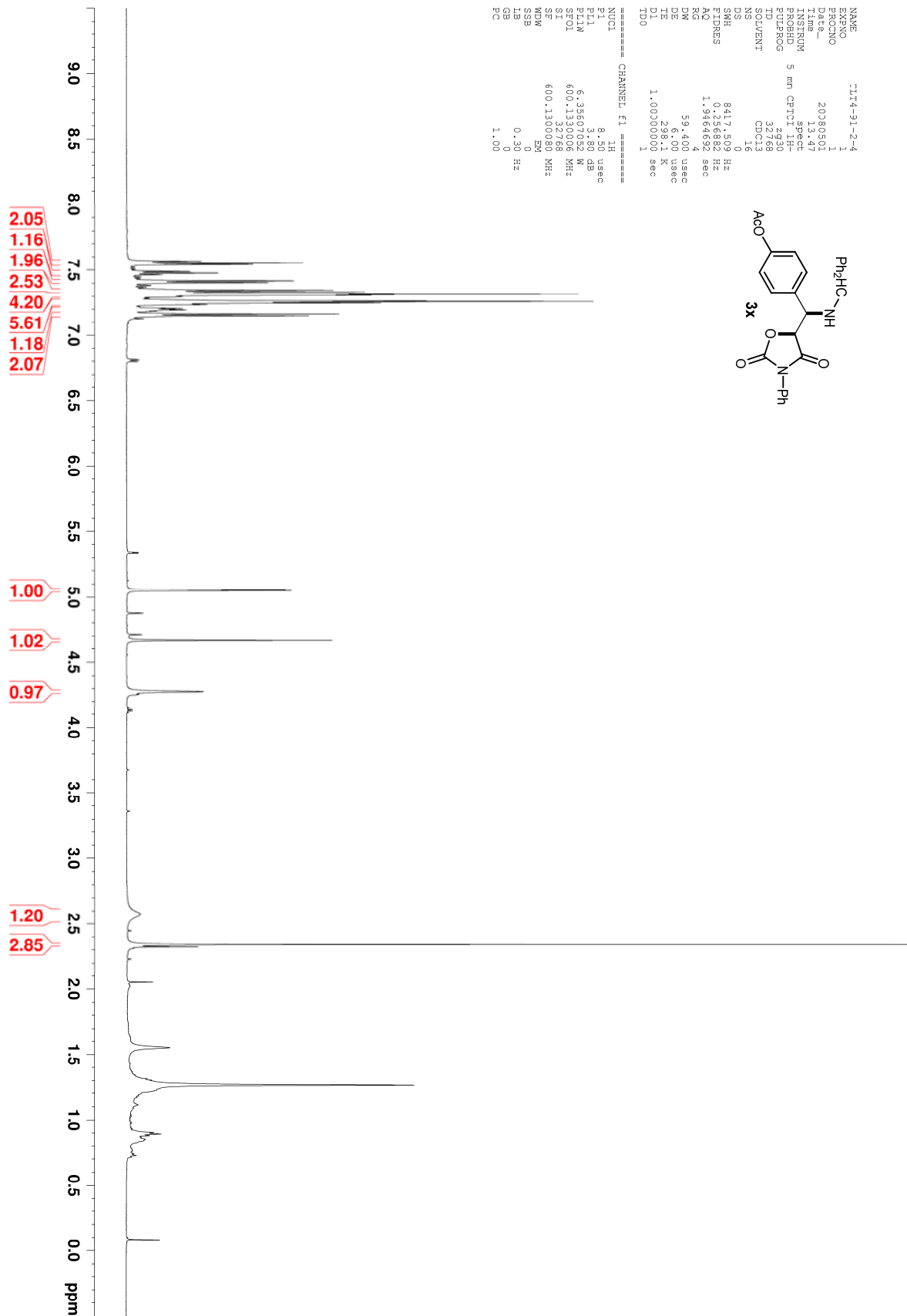
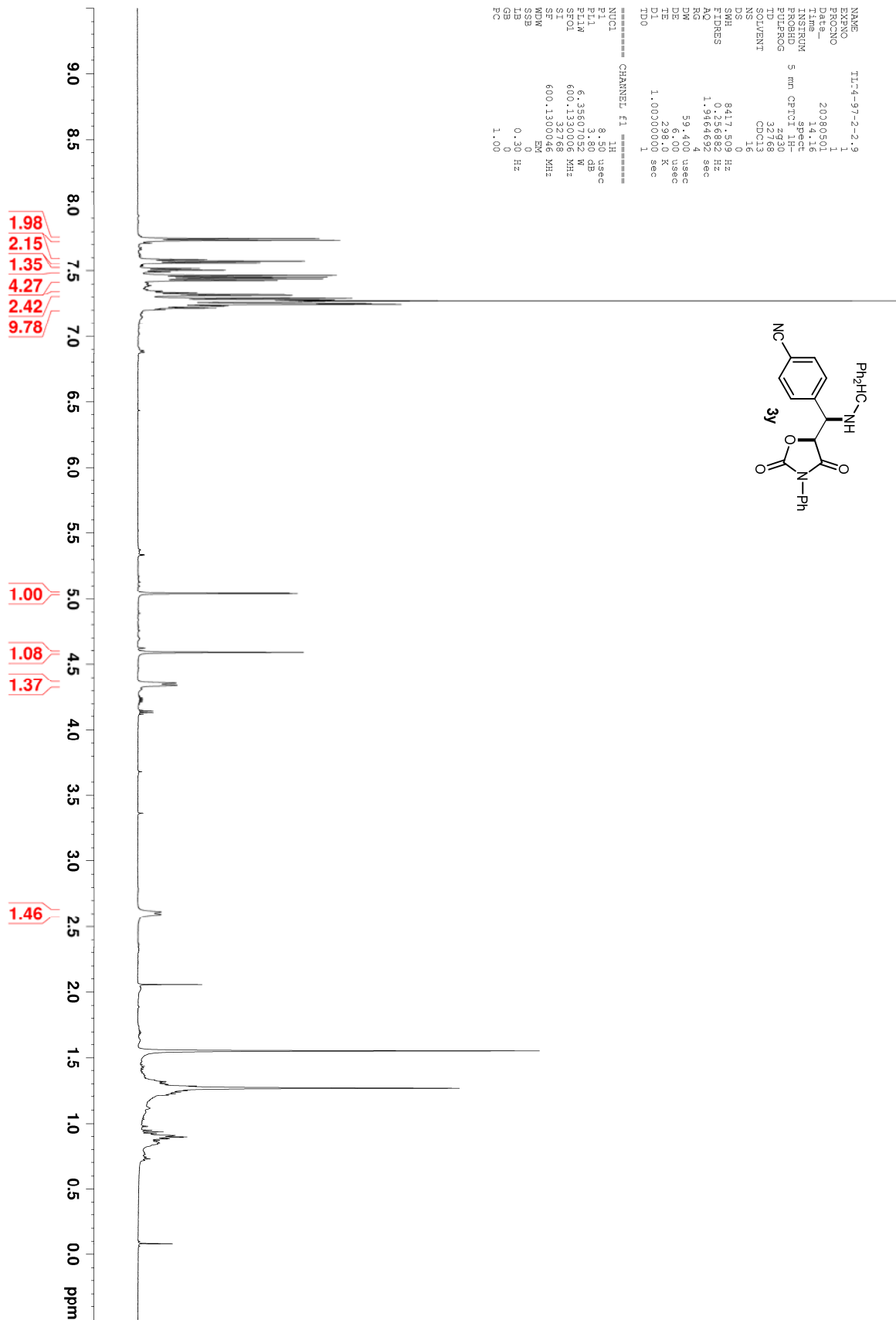
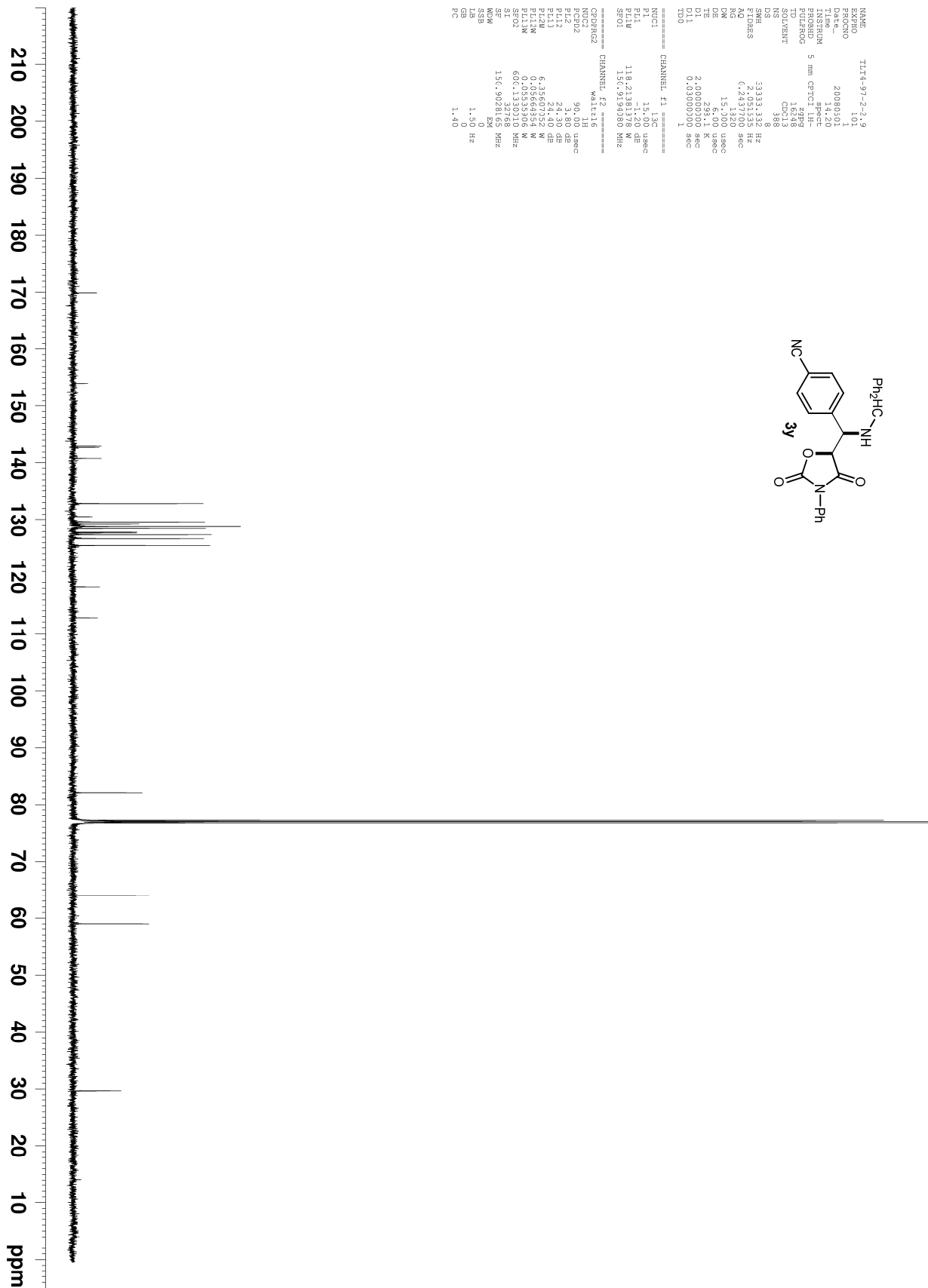
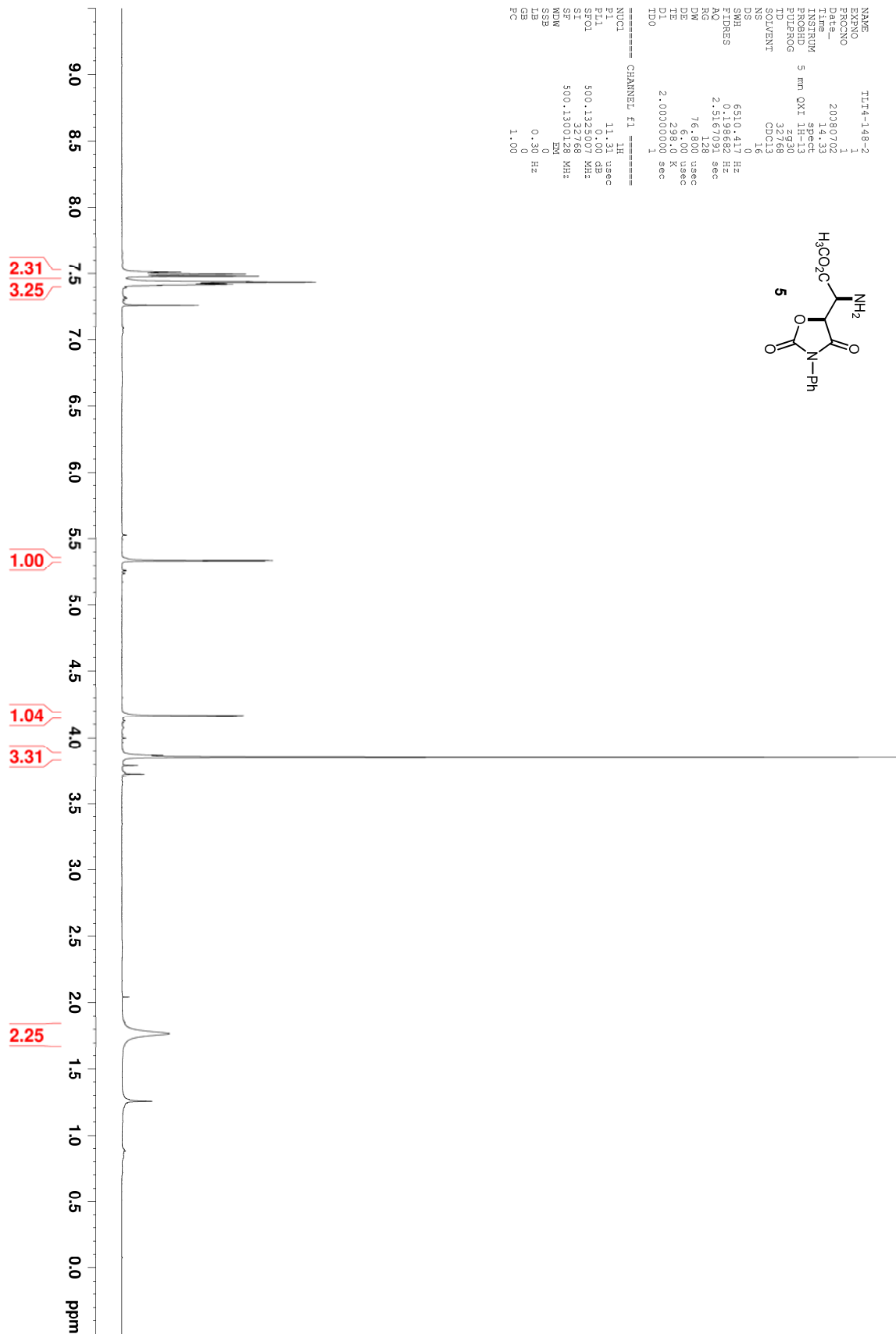
Figure 85. ¹H NMR (600 MHz, CDCl₃) of 3x

Figure 87. ¹H NMR (600 MHz, CDCl₃) of **3y**

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Figure 88. ^{13}C NMR (150 MHz, CDCl_3) of **3y**





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Figure 90. ^{13}C NMR (125 MHz, CDCl_3) of **5**

