

Supporting Information

Simple access to 5-carboalkoxy-2,3-dihydro-4*H*-pyran-4-ones via domino acylative electrocyclization: First three step total synthesis of dihydronaphthopyran-4-one class of natural products

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X-ray Analysis of Compound **3ga**

Single crystal X-ray diffraction

A single crystal suitable for X-ray diffraction study was chosen carefully. The X-ray intensity measurements were done at room temperature (296 K) with Bruker SMART APEX-II CCD diffractometer using graphite monochromatic MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structure of the compound **3ga** was solved and all the non-hydrogen atoms were refined anisotropically using the SHELX-2013 program.¹ The remaining H atoms were placed in idealized geometrical positions and constrained to ride on their parent atoms. The thermal ellipsoidal and crystal packing figures were produced using the programs PLATON² and MERCURY³ respectively.

Crystal structure

The crystal data and refinement parameters of the compound **3ga** are summarized in Table 1. The hydrogen bonding interactions that stabilize the crystal structure are listed in Table 2. The compound **3ga** crystallizes in the non-centrosymmetric space group $P2_1/C$ which belongs to monoclinic crystal system. The asymmetric unit consists of two independent molecules, it is shown in the ORTEP diagram (Fig. 1). The structural superimposition was carried out to see any conformational changes on the molecular structure. All the non-hydrogen atoms of molecule (A and B) were used for the structural superimposition (Fig 2). The root mean square deviation (rmsd) between molecule A and B involving common atoms is 1.803 \AA . In molecule A and B, the thiophene ring is rotated in the opposite direction and other part of the molecule is nearly the same (Fig. 2). The crystal structure of the title compound is stabilized by weak intermolecular C–H...O interactions (Table 2).

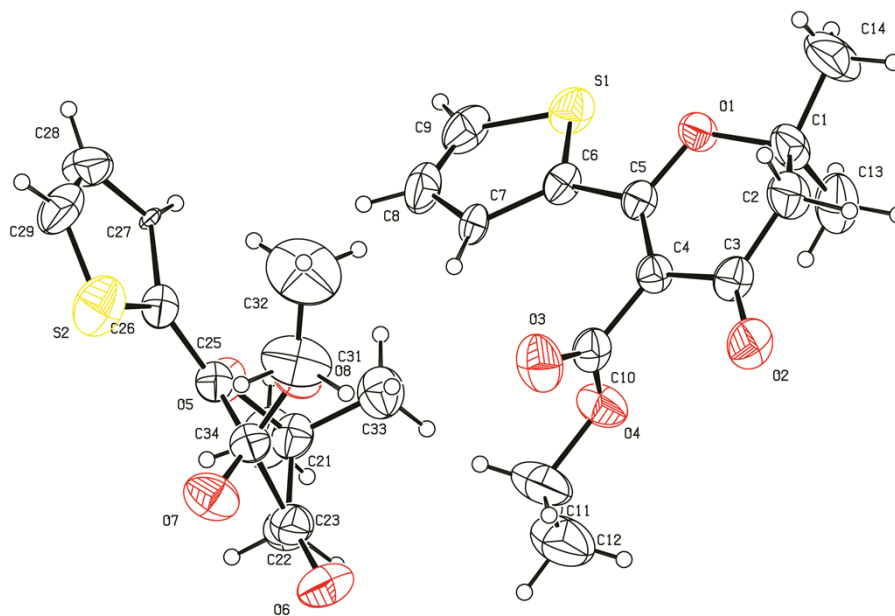


Fig 1. The ORTEP diagram of asymmetric unit of compound **3ga** with atom numbering scheme.

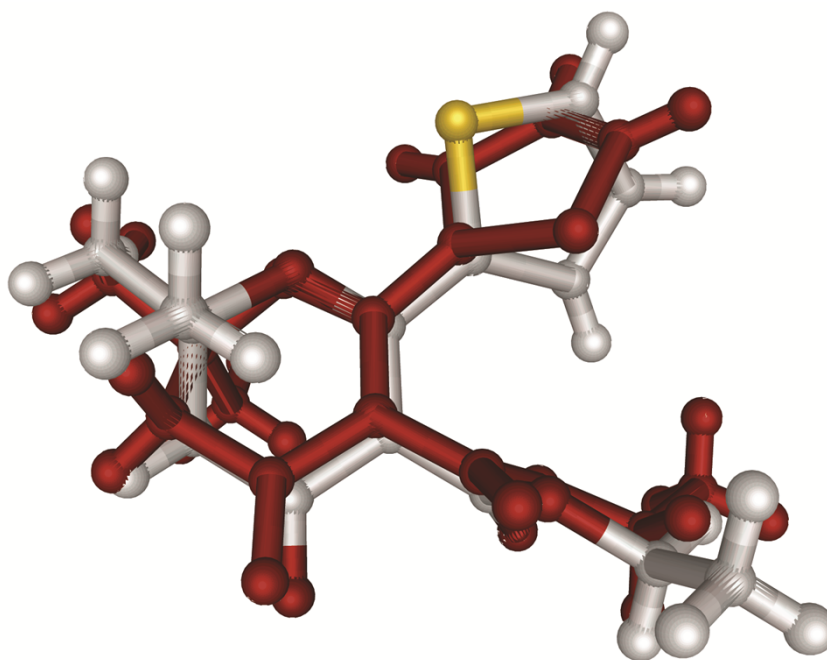


Fig 2. Structural superimposition of molecule A and B. (The molecule B in red colour).

Table 1. The crystal data and refinement parameters of compound **3ga**.

Compound	
Empirical formula	C ₁₄ H ₁₆ O ₄ S
Formula weight	280.33
T (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
a (Å)	10.4001(2)
b (Å)	20.6610(6)
c (Å)	13.5979(4)
α (°)	90
β (°)	91.972(2)
γ (°)	90
V (Å ³)	2920.14(13)
Z	4
Calculated density (Mg/m ³)	1.253
Absorption (mm ⁻¹)	0.114
F(0 0 0)	592
Crystal size (mm)	0.10 × 0.09 × 0.09
θ (°)	1.79– 21.89
Limiting indices	-10 ≤ h ≤ 10, -18 ≤ k ≤ 21, -14 ≤ l ≤ 14
Reflections collected/unique (R _{int})	18926/3508, (0.042)
(θ °) Completeness (%)	(25.242), 99.3 %
Refinement method F ²	full-matrix least-squares on F ²
Data/restraints /parameters	3508/0/345
Goodness-of-fit(GOF) on F ²	1.066
Final R indices [I > 2σ(I)]	R ₁ = 0.084, wR ₂ = 0.259
R indices (all data)	R ₁ = 0.1063, wR ₂ = 0.289
Largest difference in peak and hole (e Å ⁻³)	1.089 and -0.674

Table 2. H bond Table

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O7 ⁱ	0.97	2.62	3.567(8)	165.1
C9—H9···O2 ⁱⁱ	0.93	2.52	3.291(7)	140.7
Symmetric codes: (i) -x, y-1/2, -z+1/2; (ii) x+1, y, z.				

References:

1. G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.
2. A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.
3. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. v. d. Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.

Copies of ¹H NMR and ¹³C NMR Spectra

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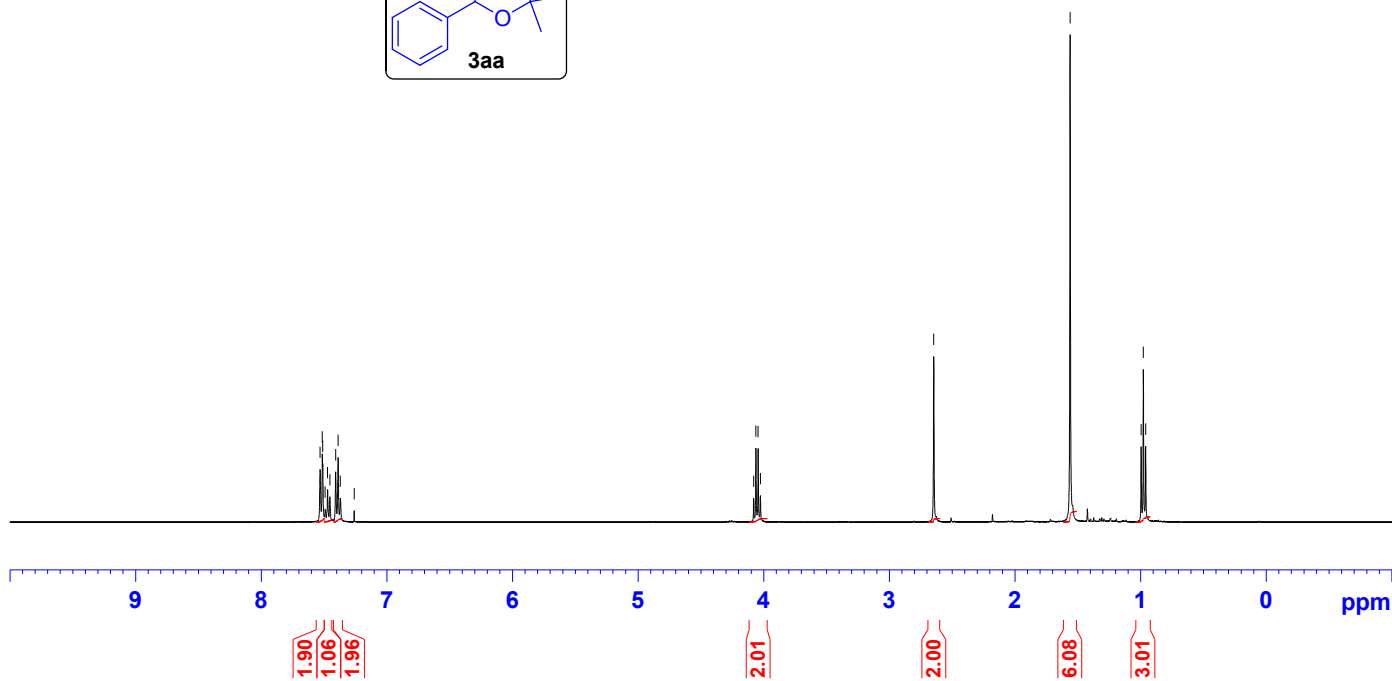
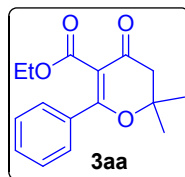
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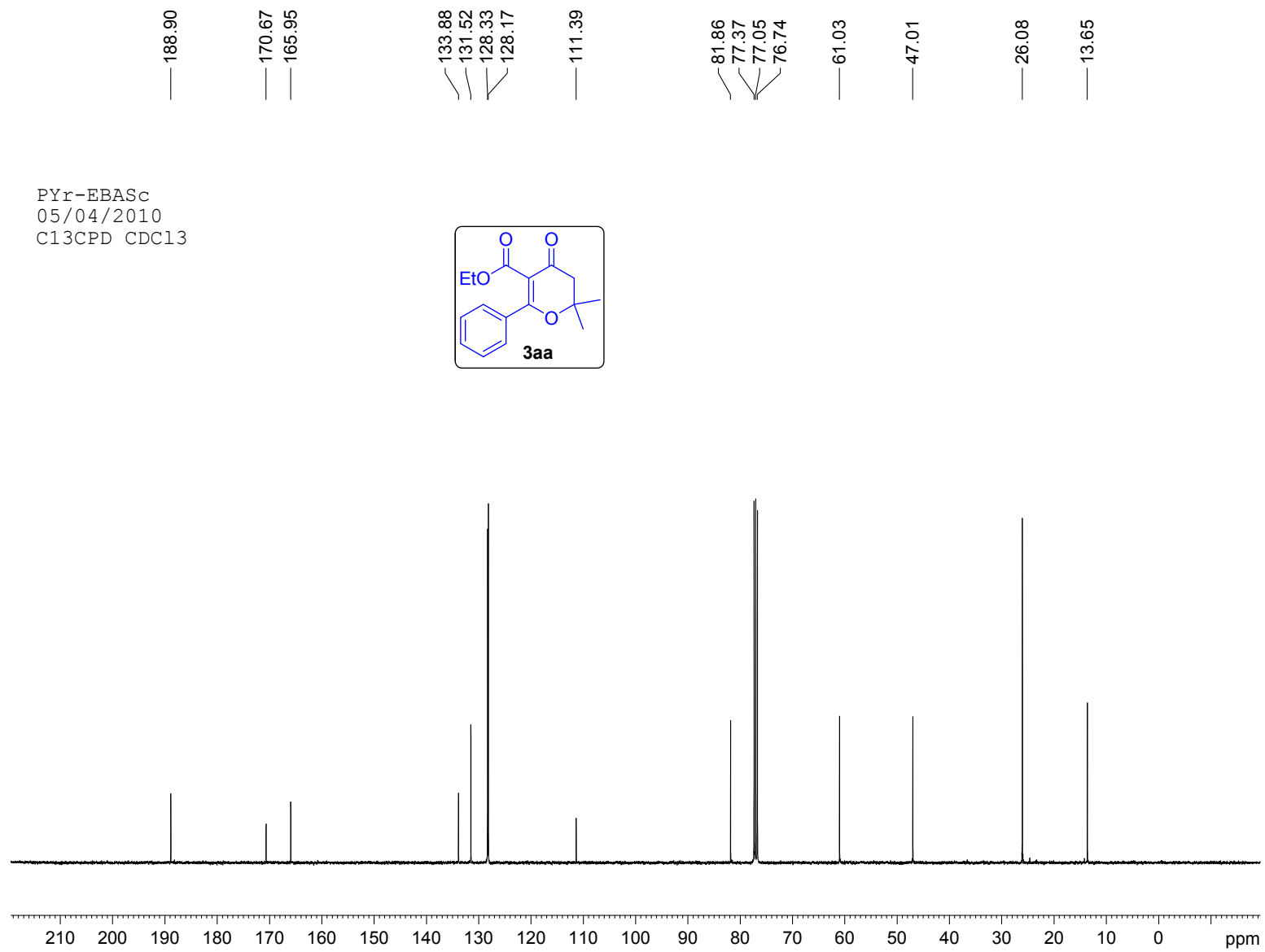
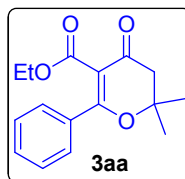
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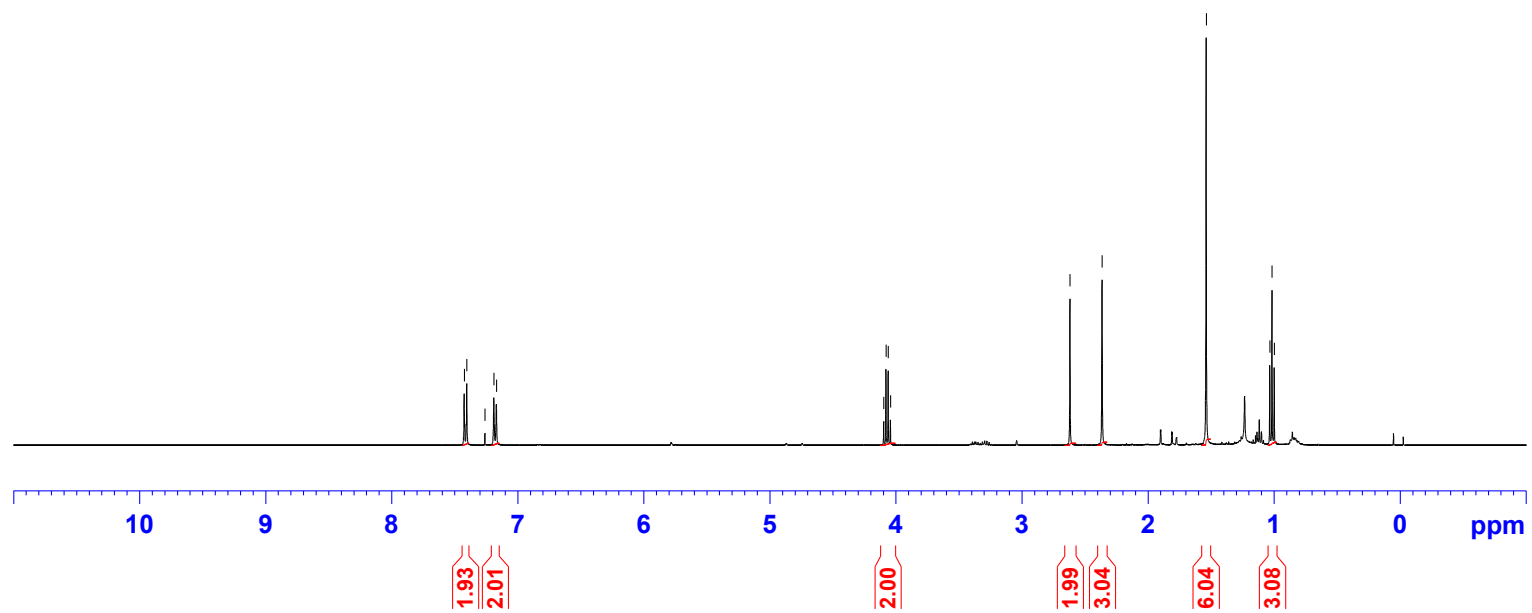
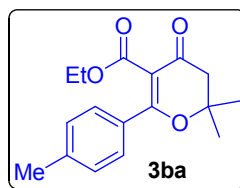
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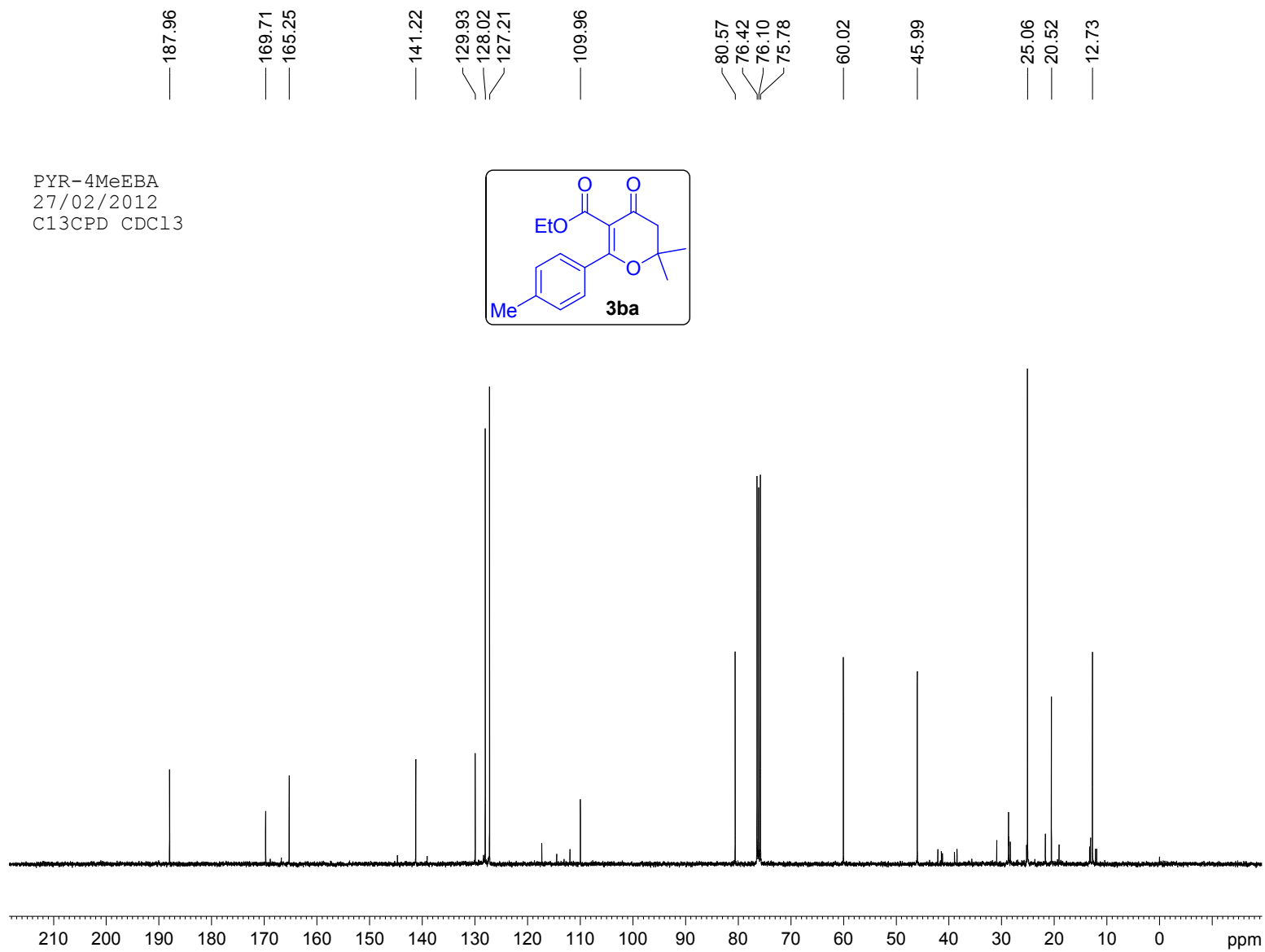
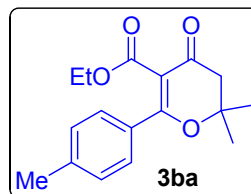
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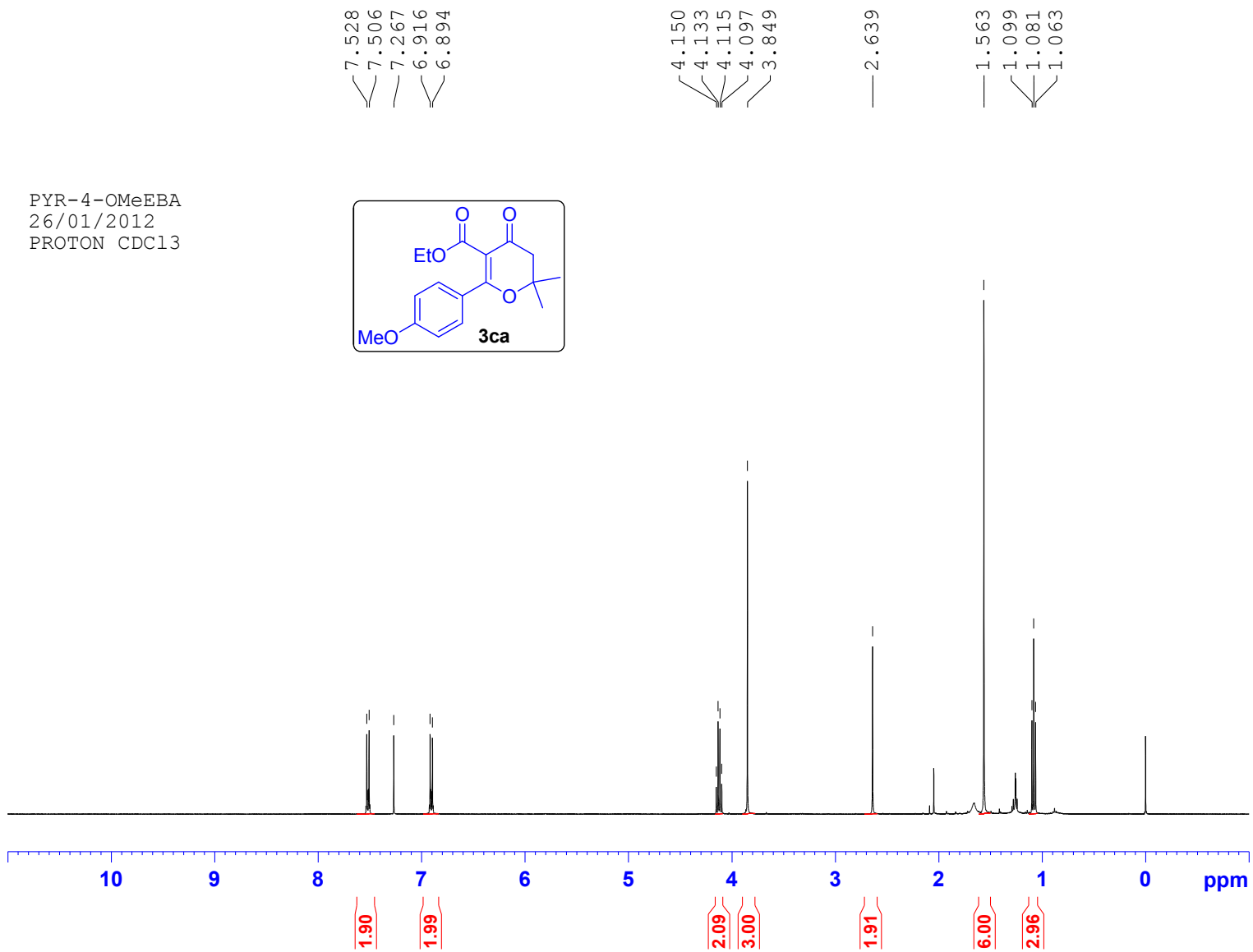
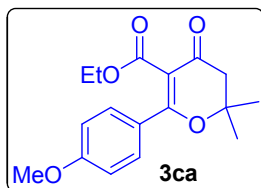
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PYR-4-OMeEBA
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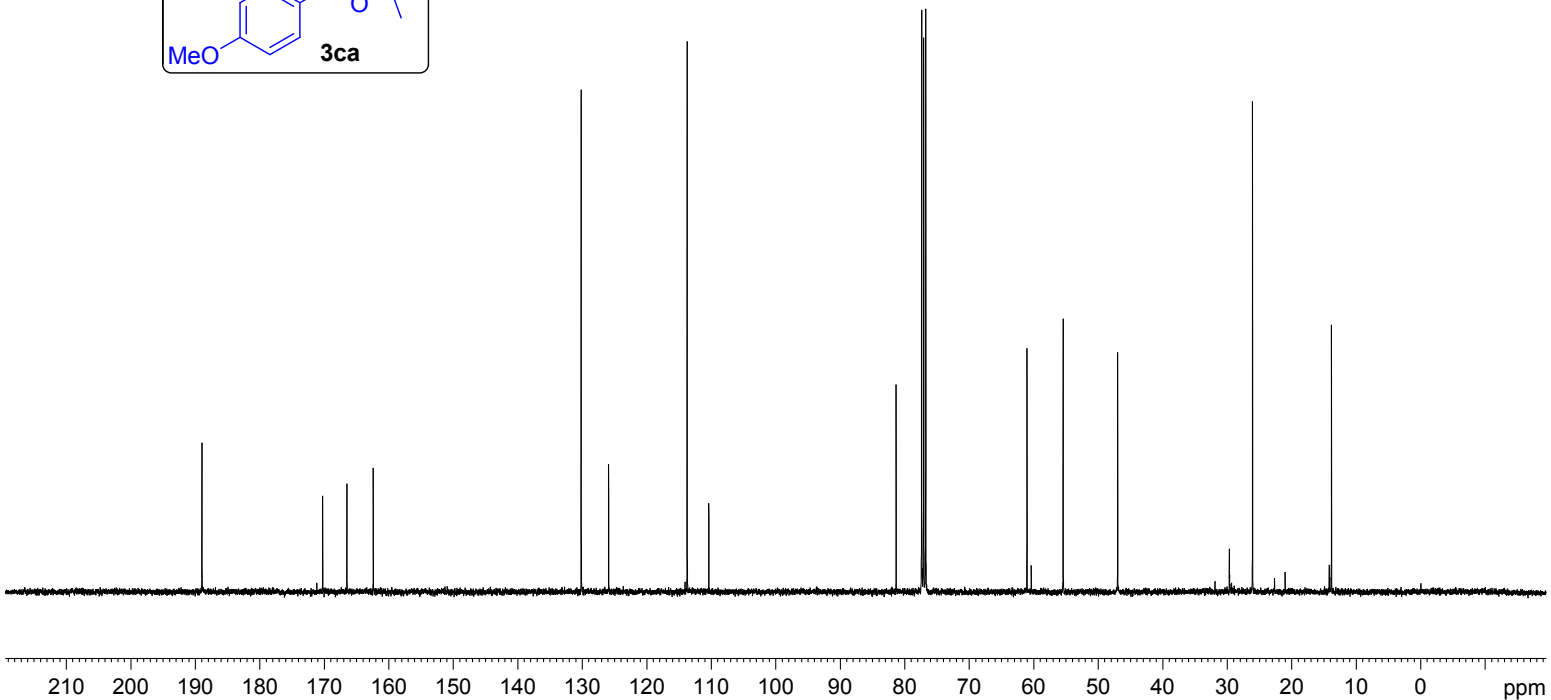
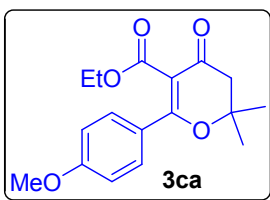
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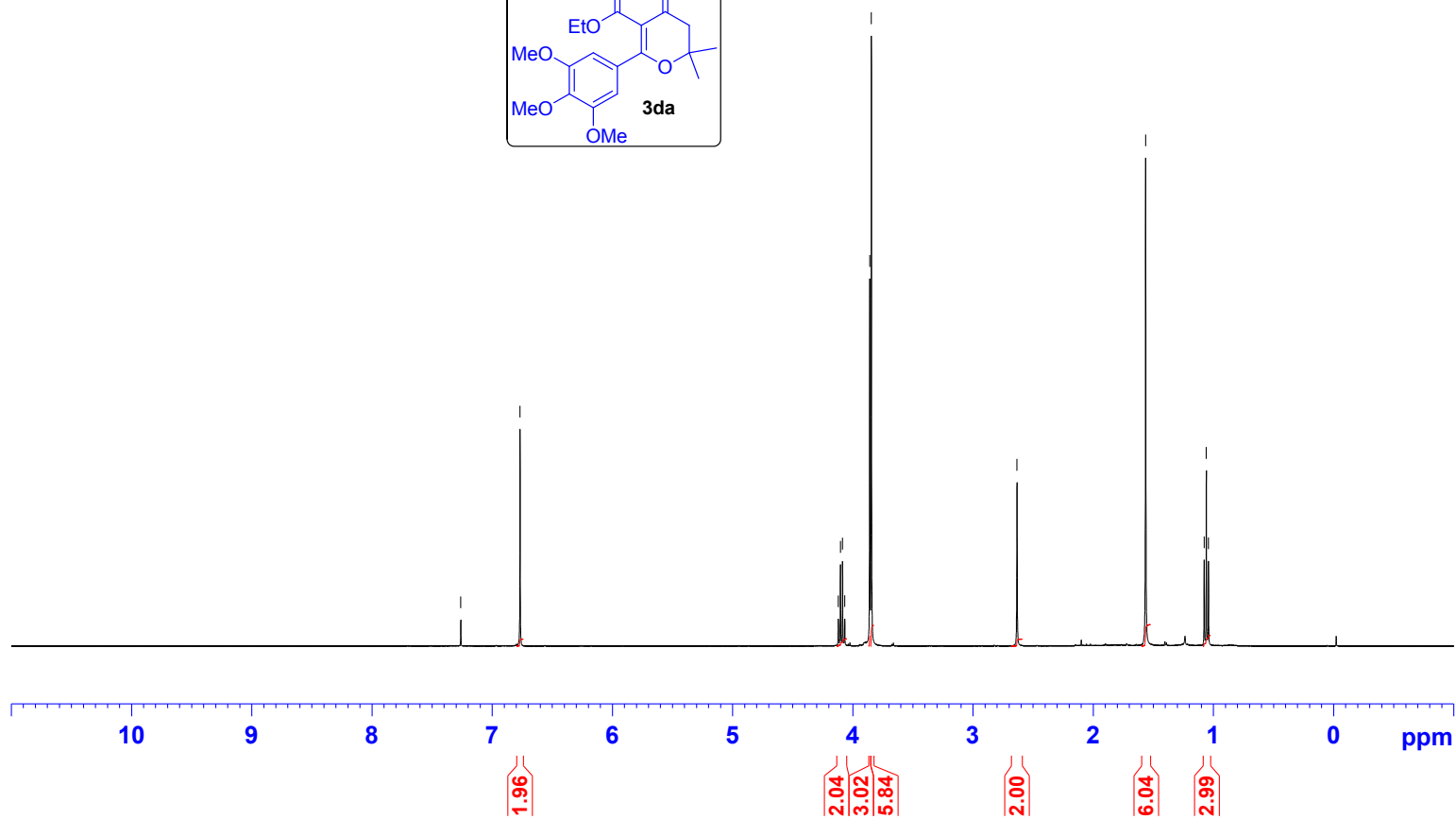
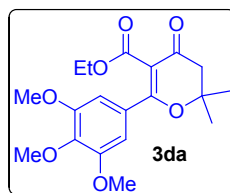
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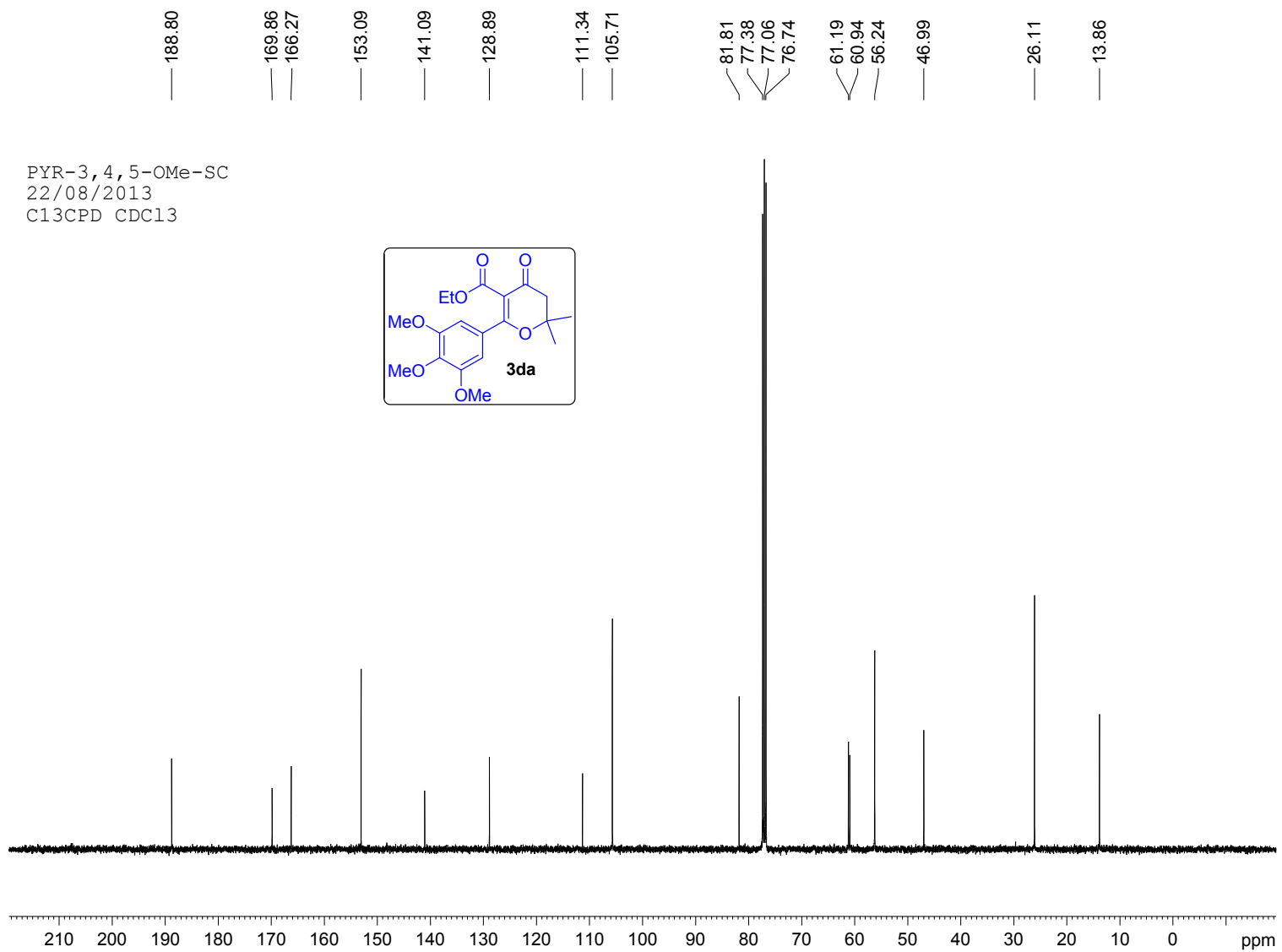
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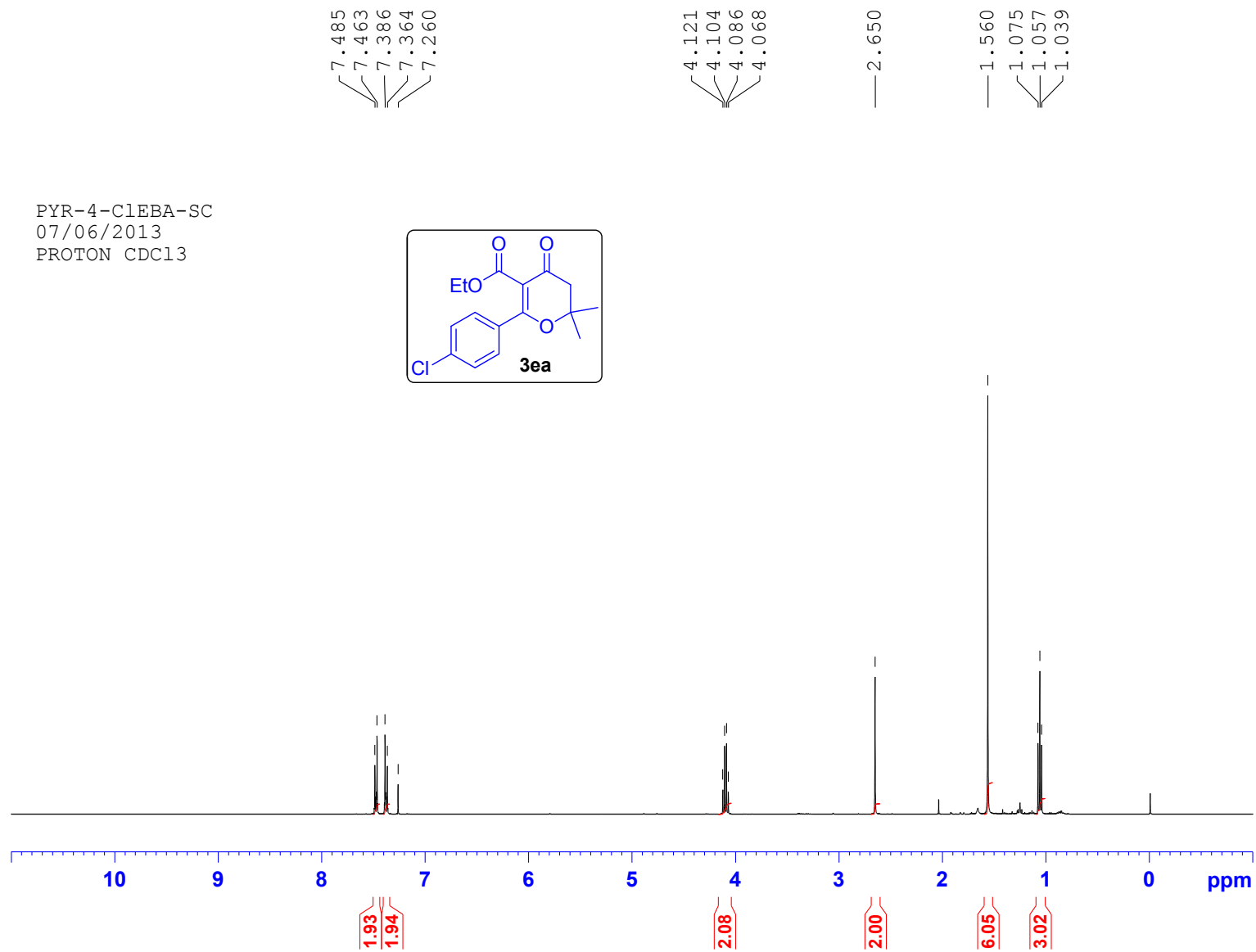
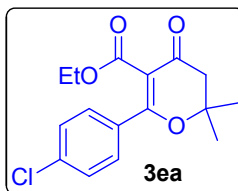
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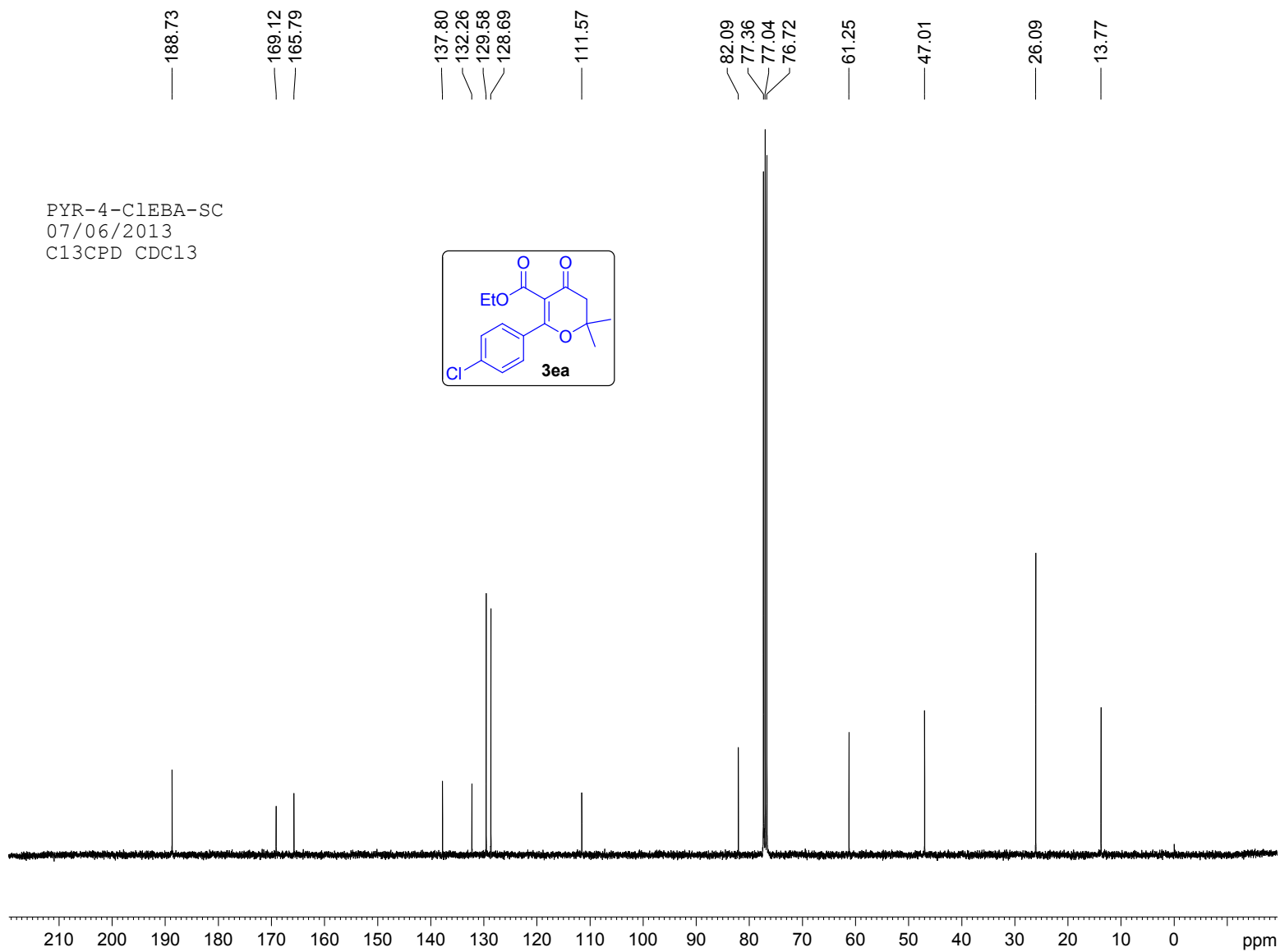
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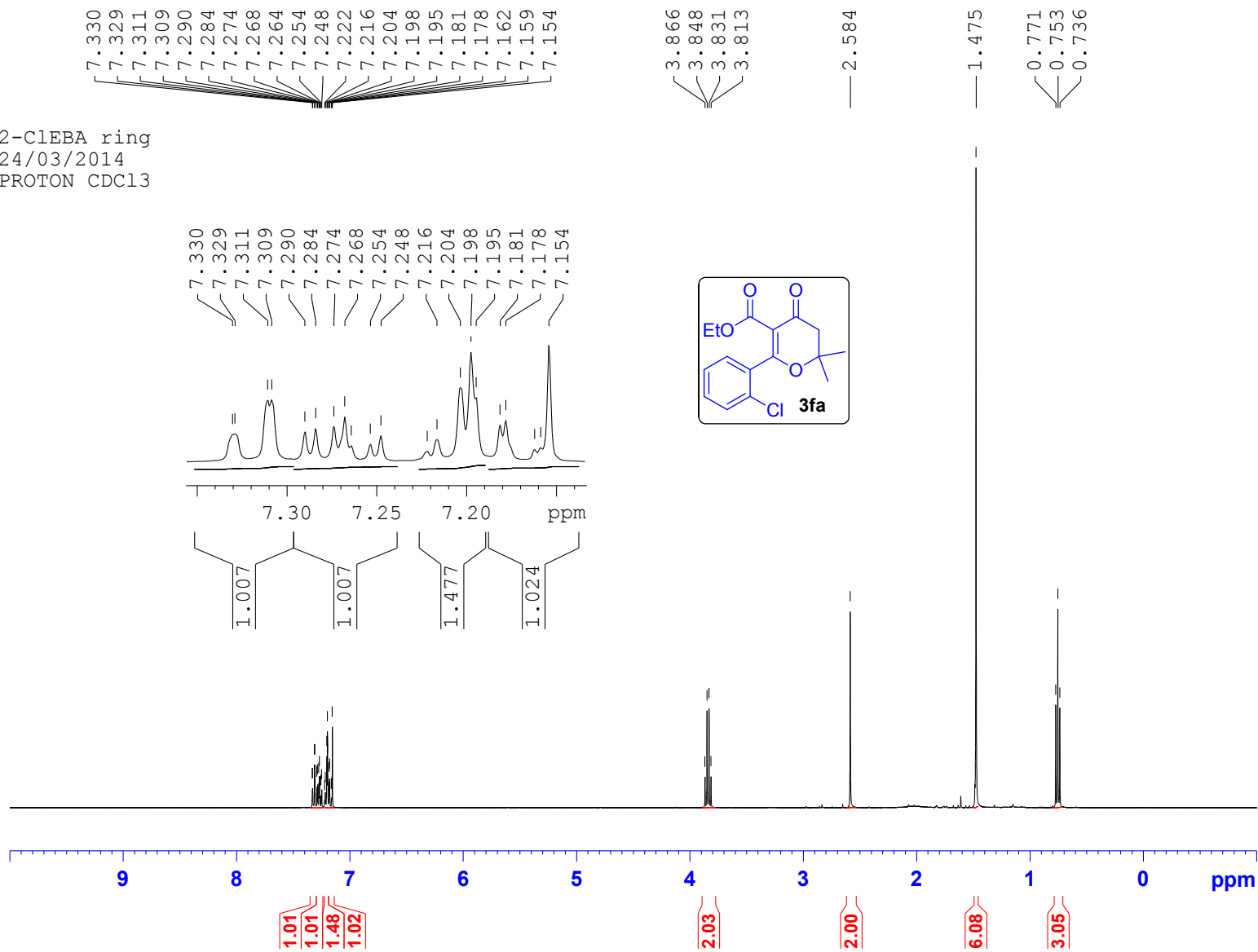


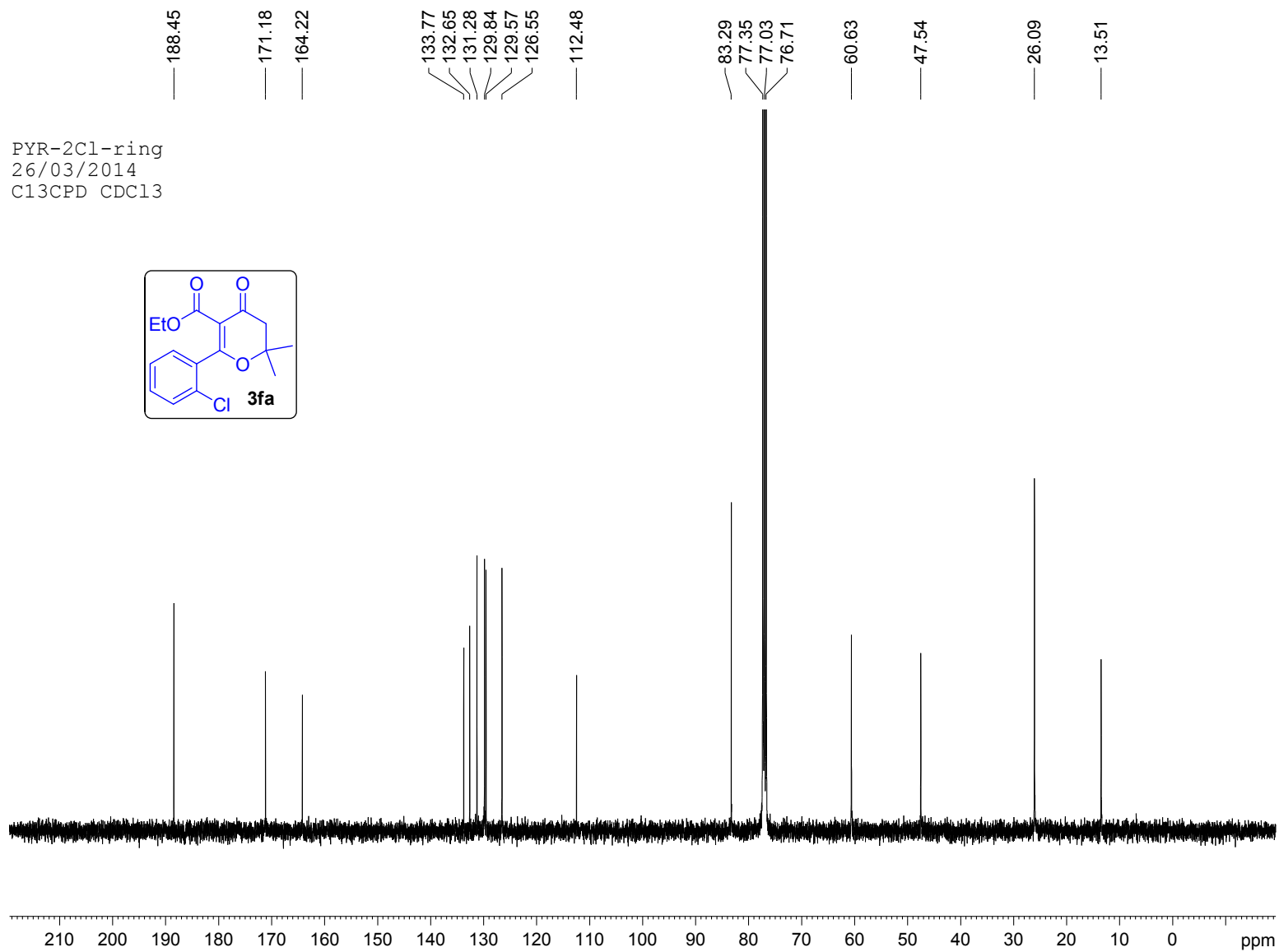
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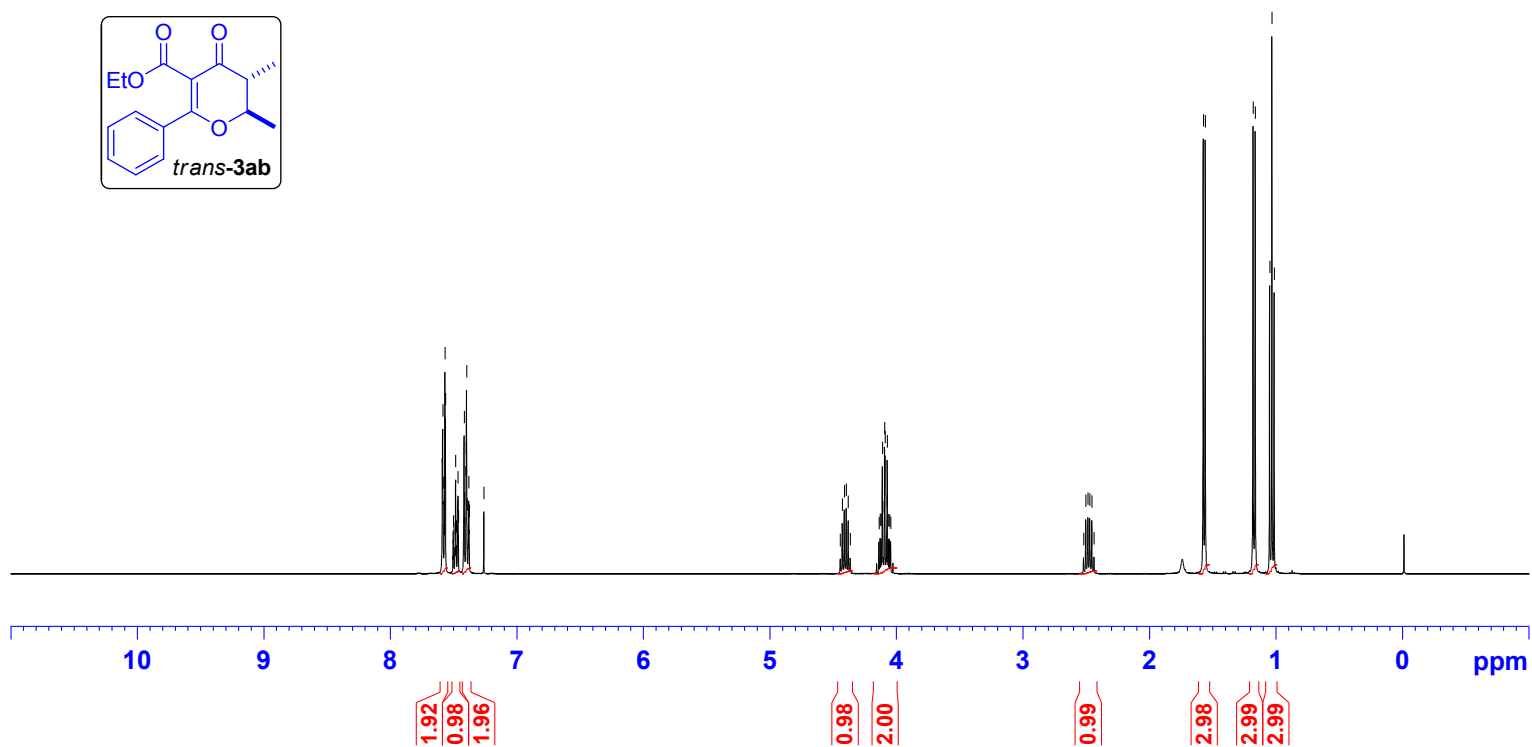
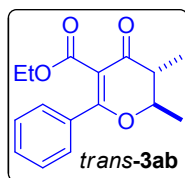
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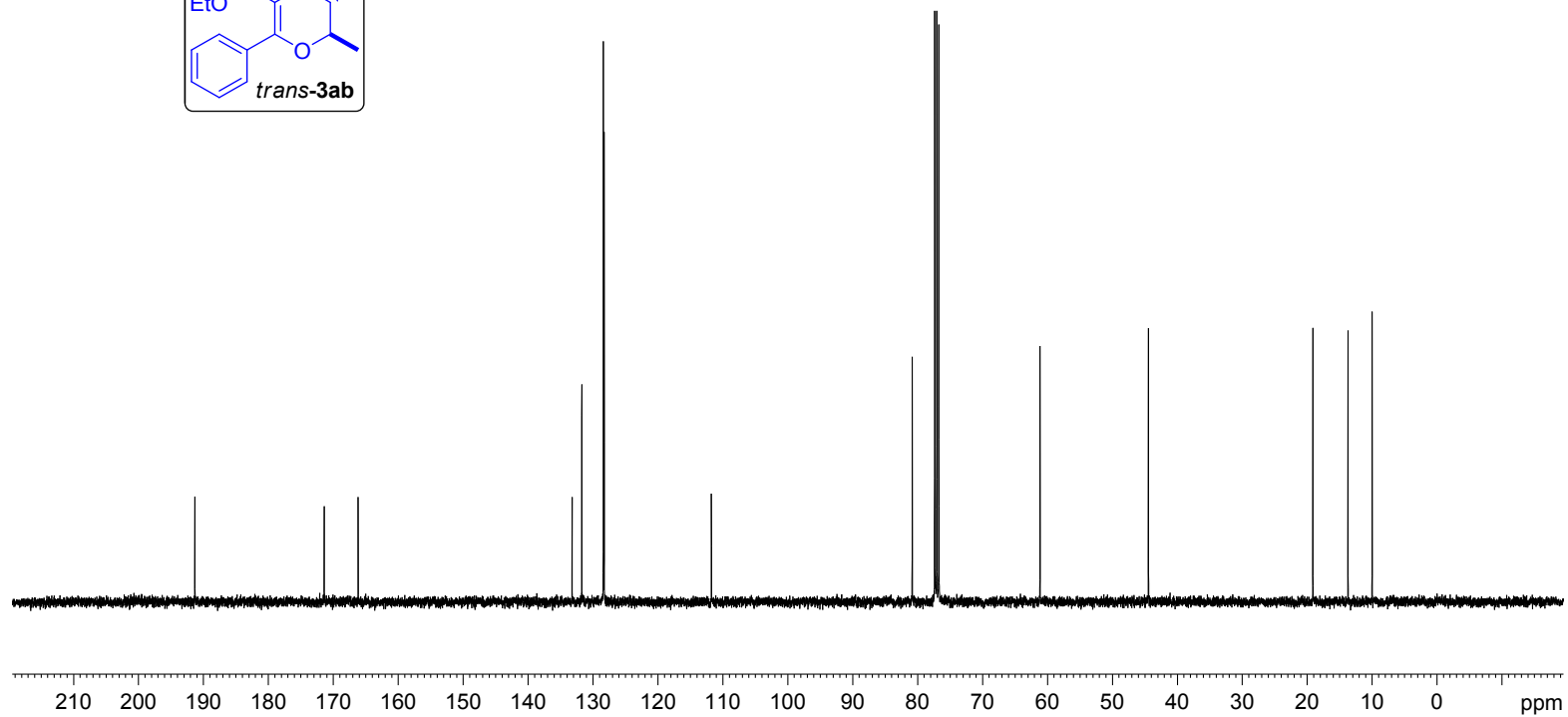
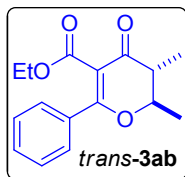
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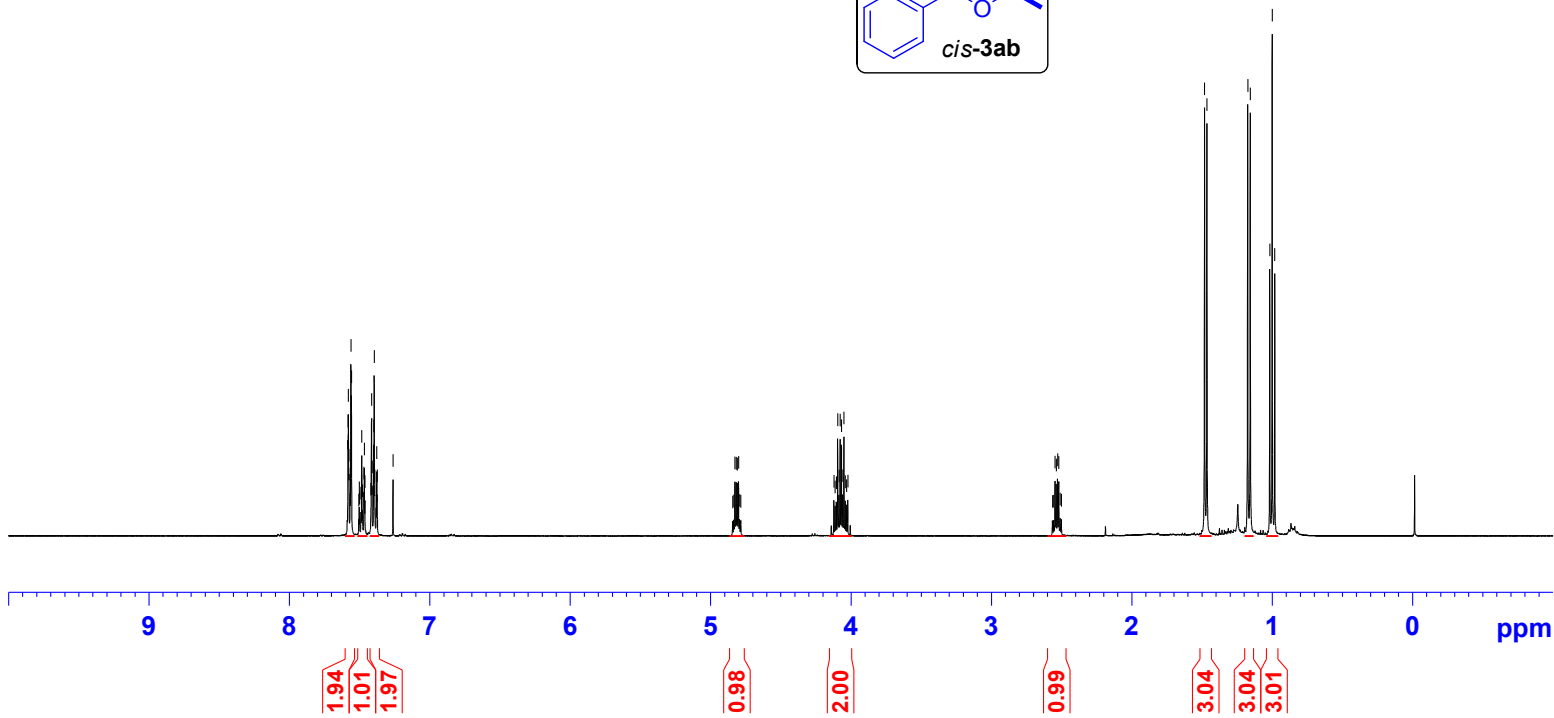
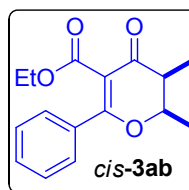
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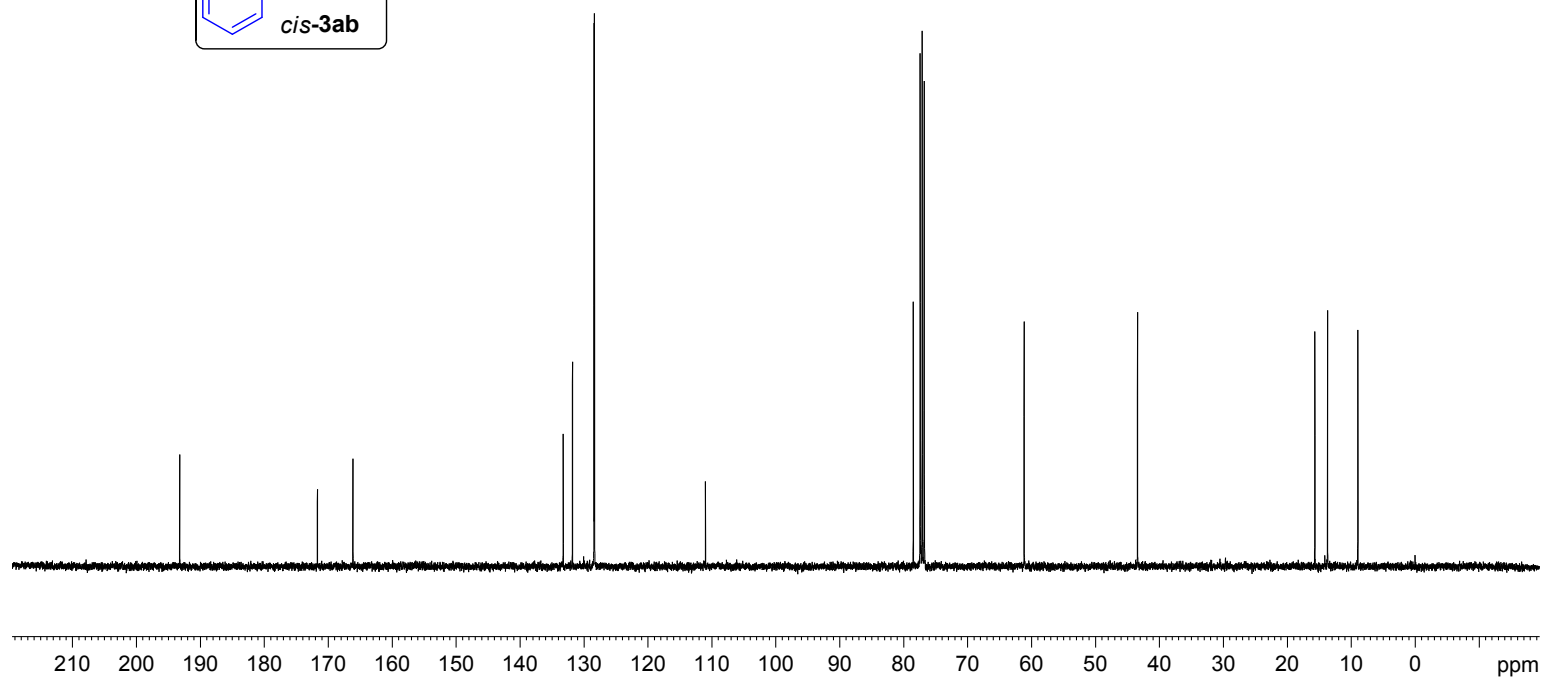
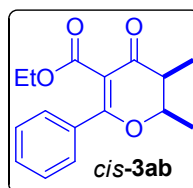
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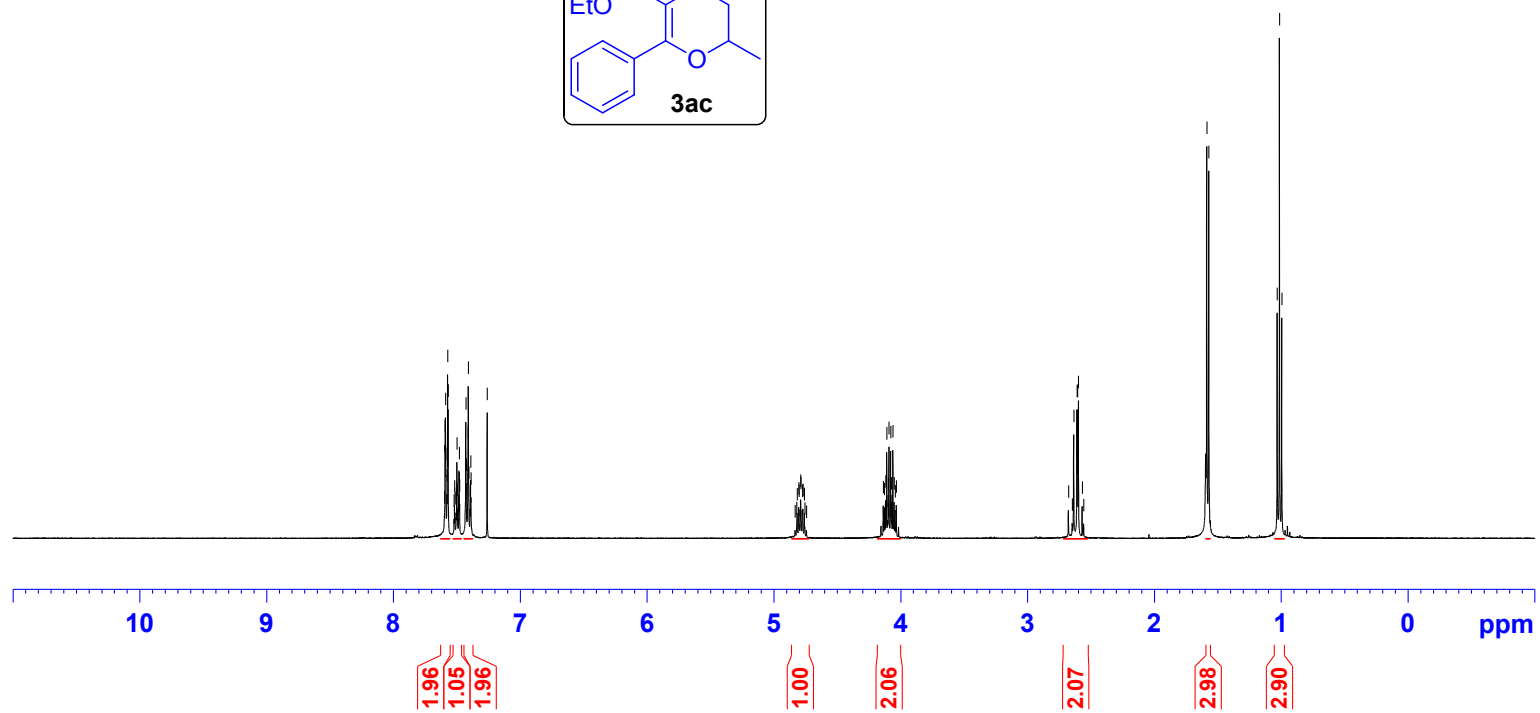
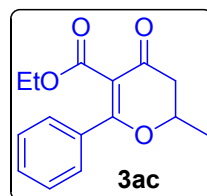
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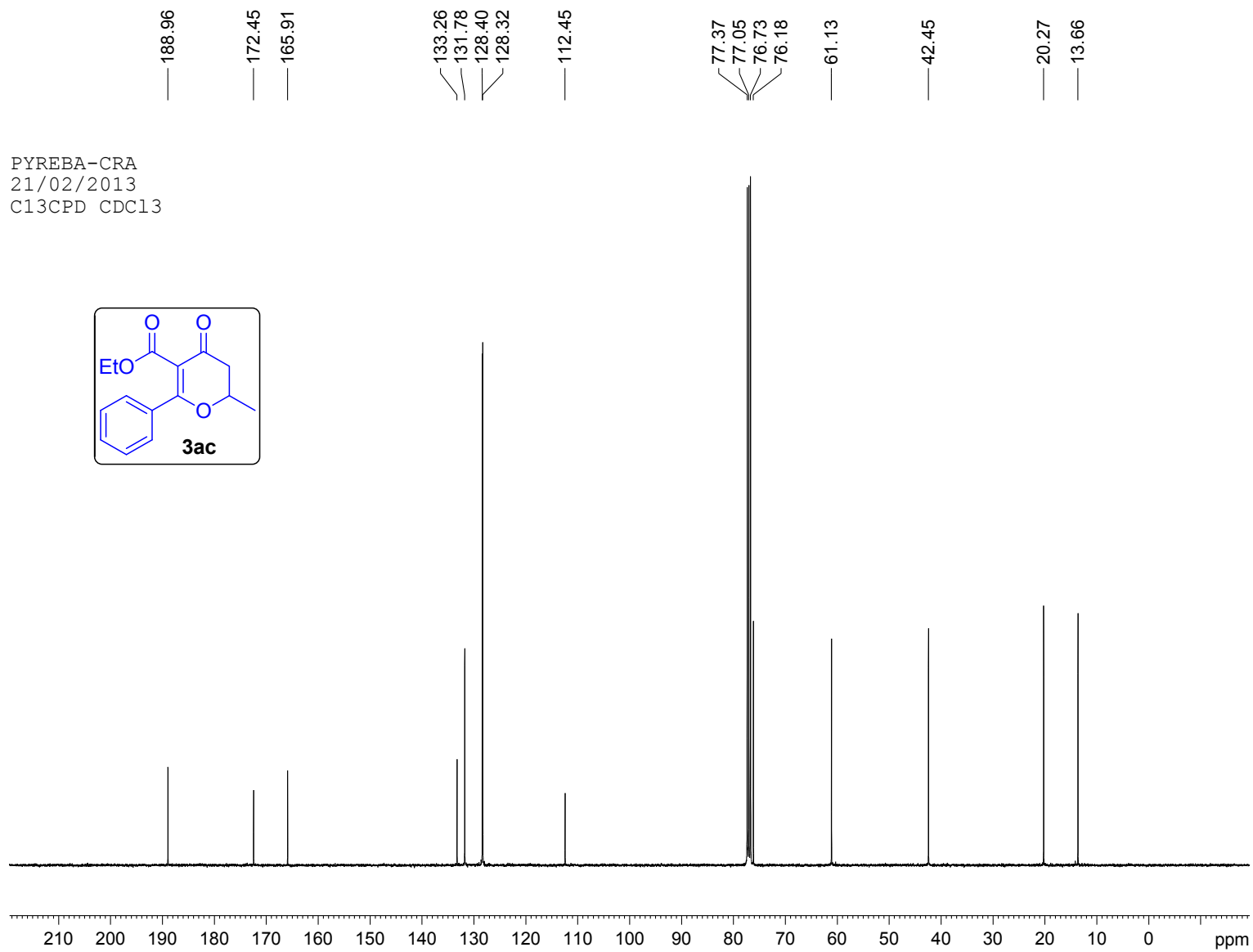
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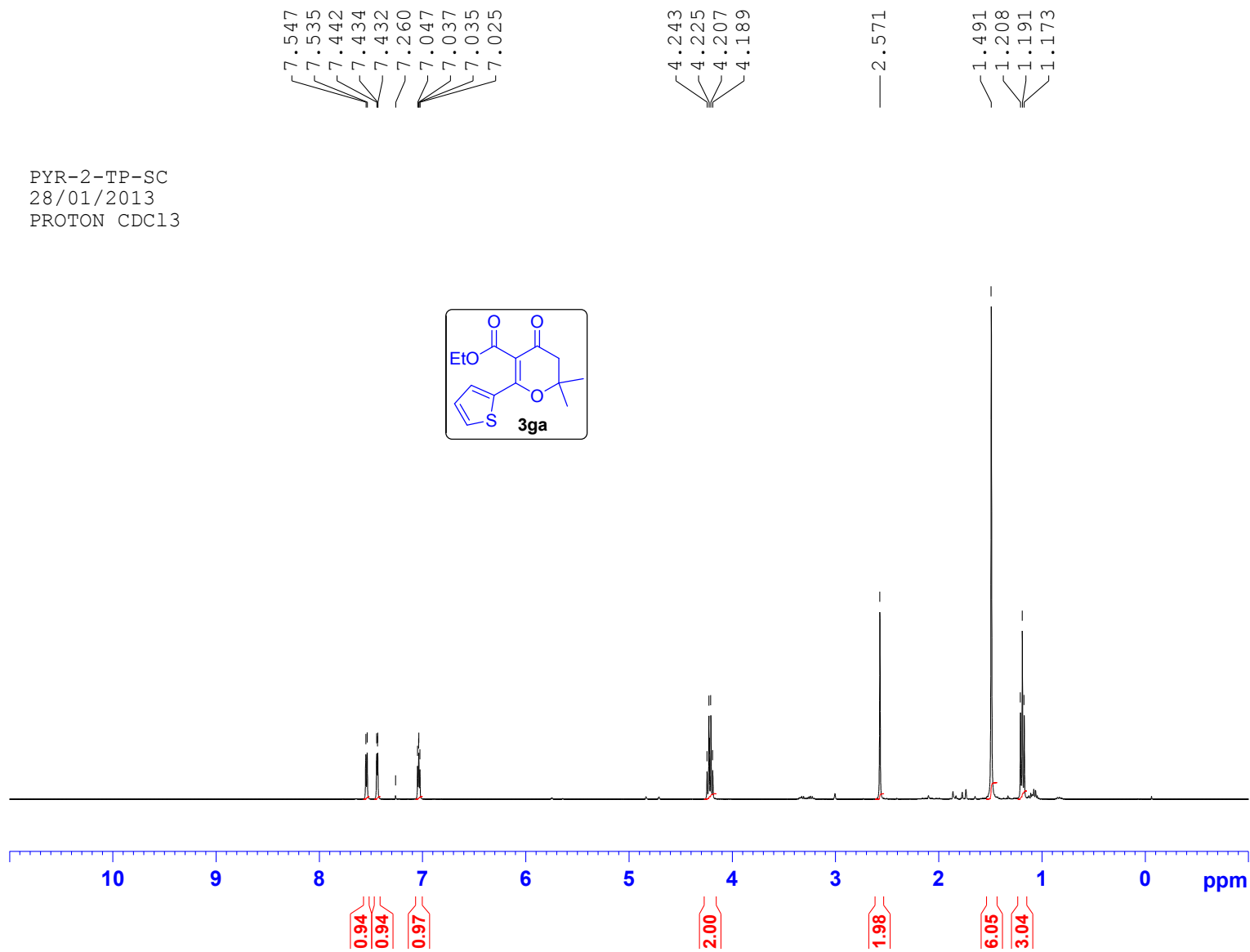
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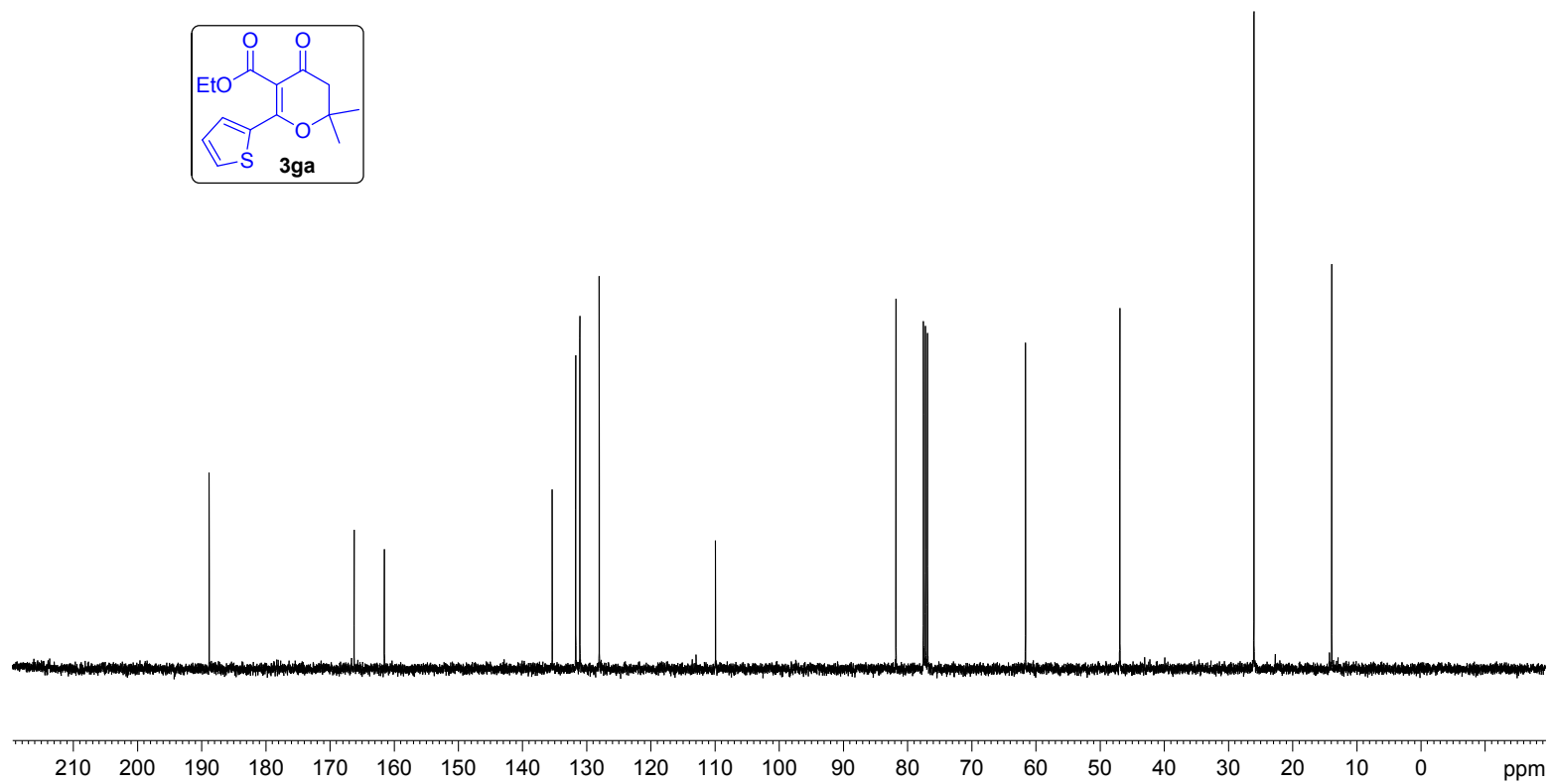
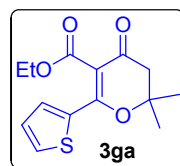


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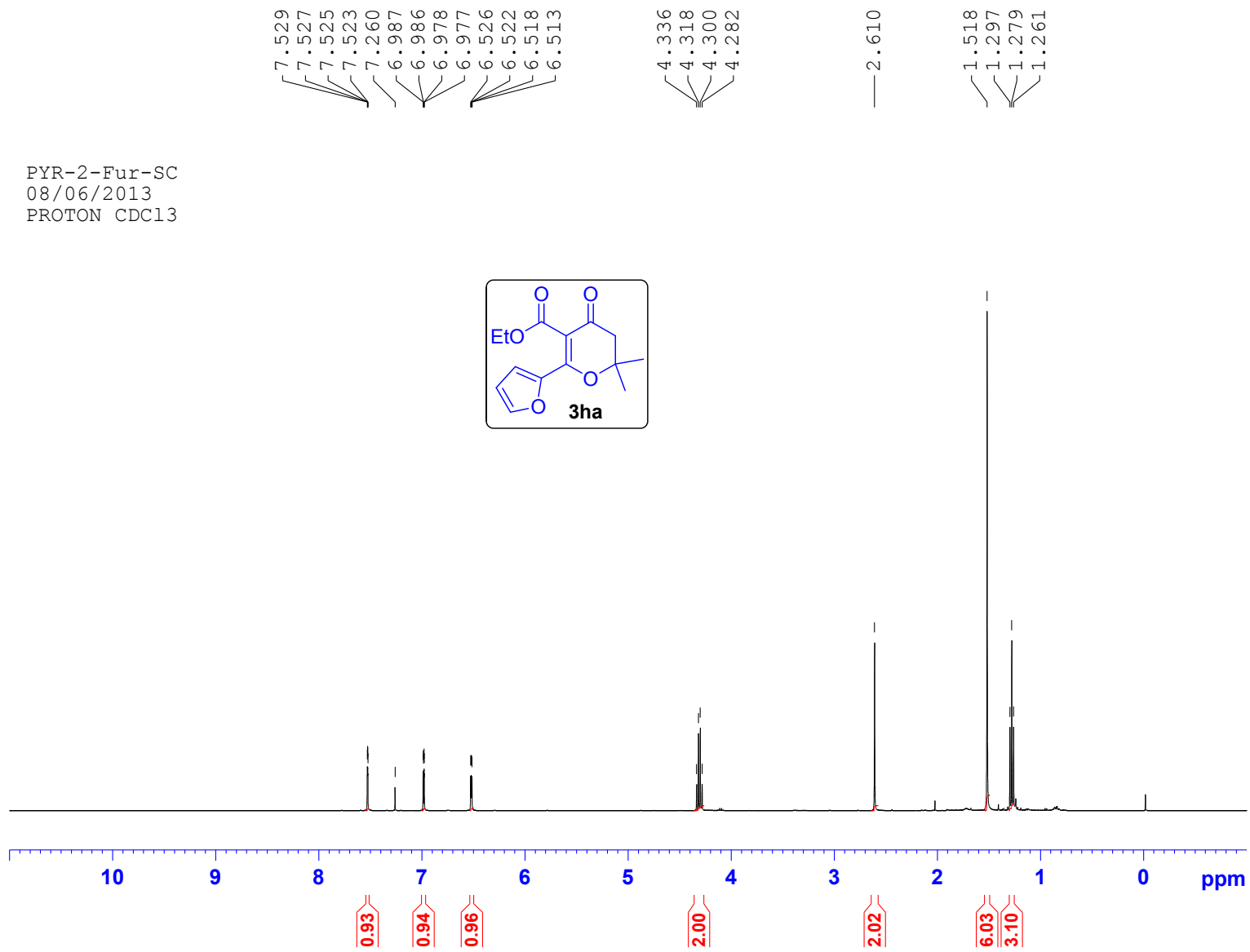


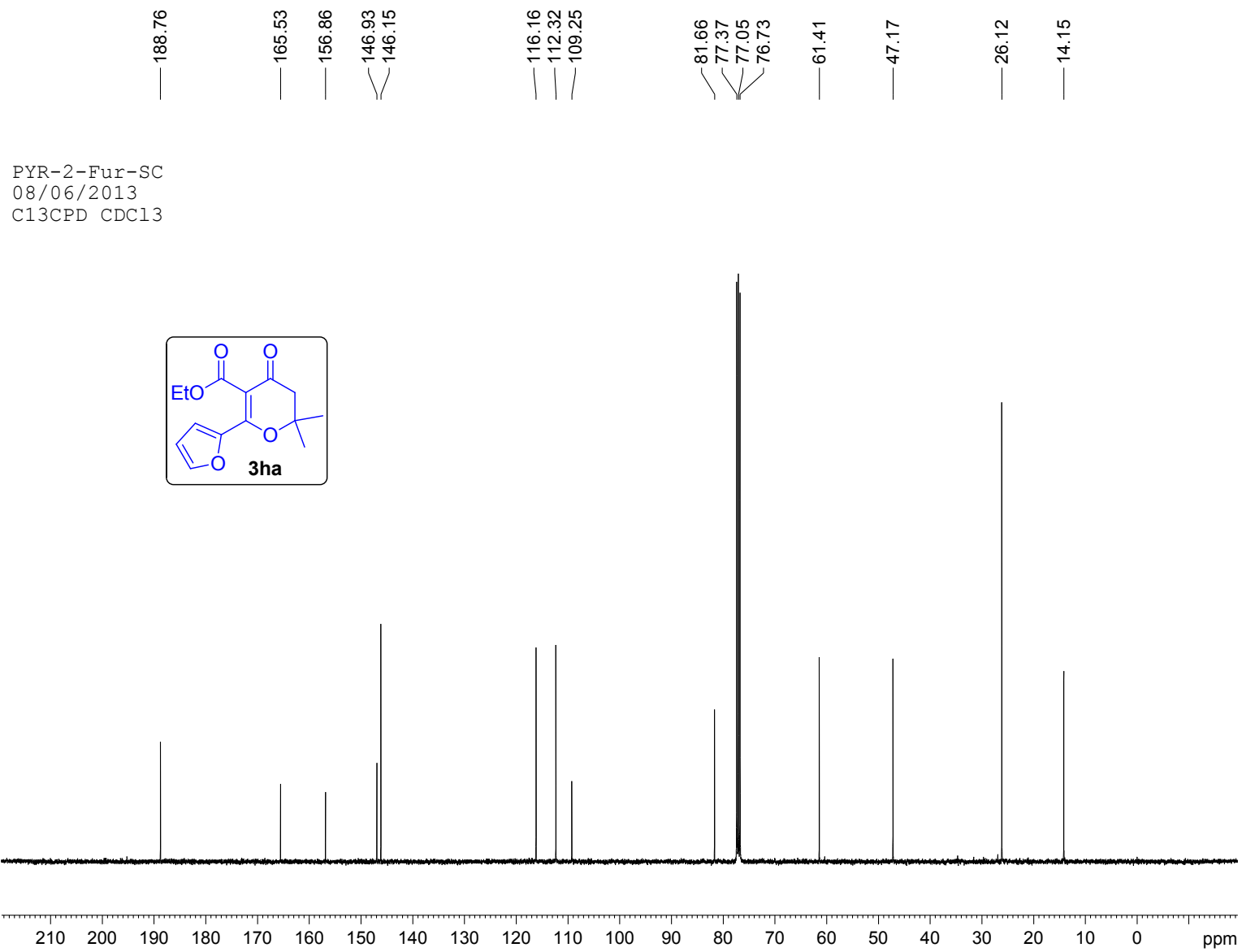
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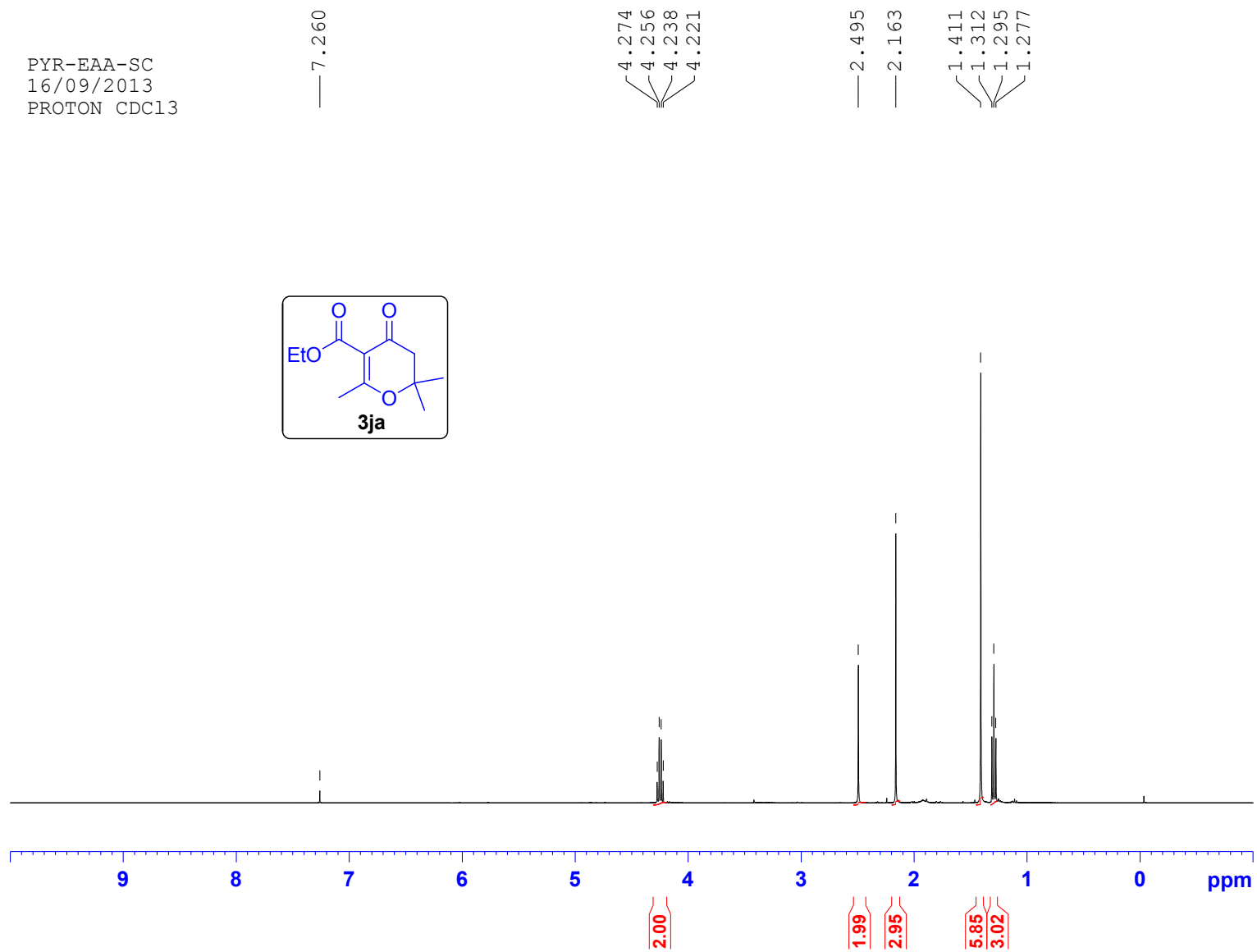
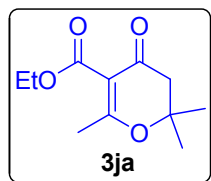


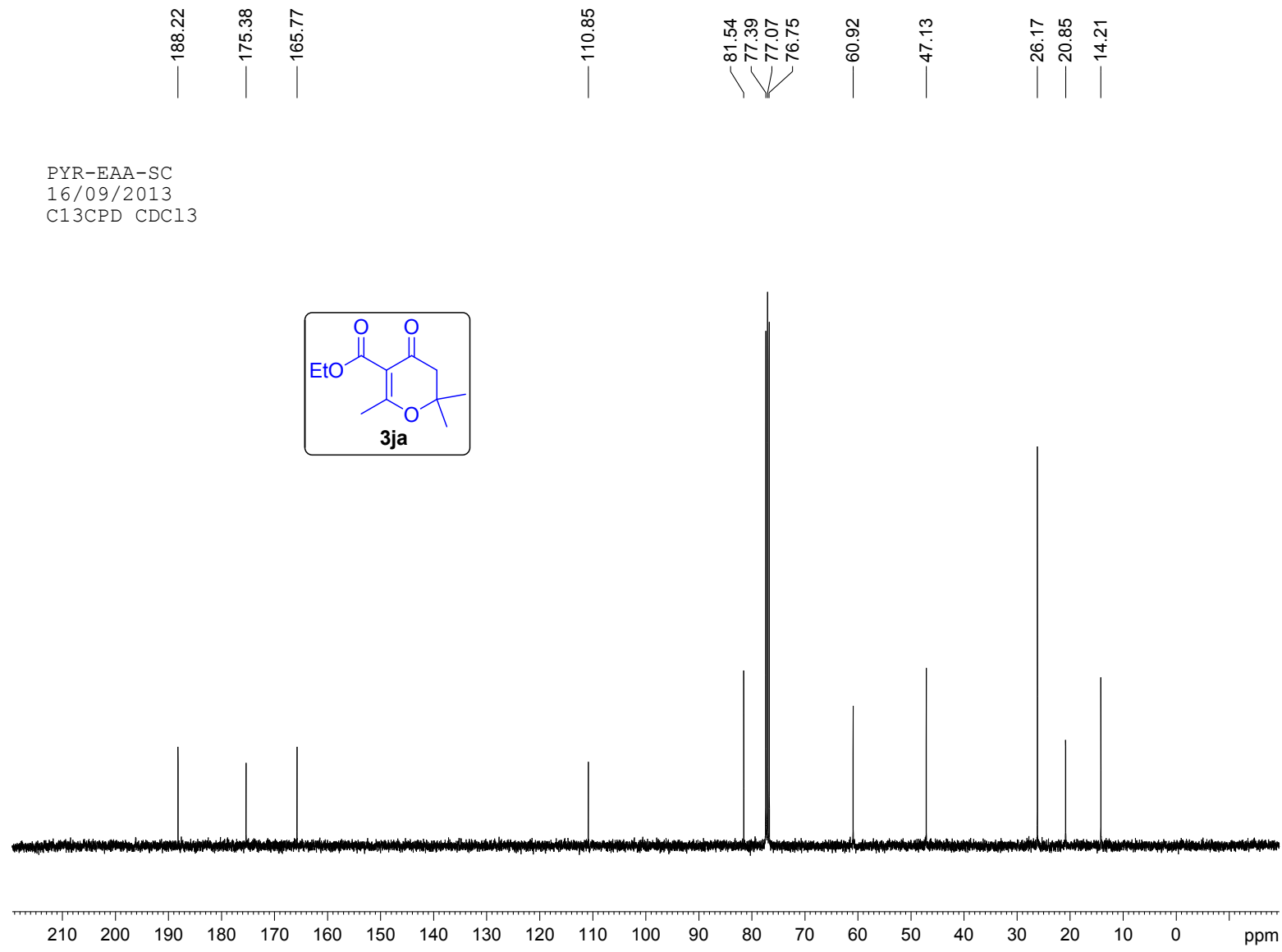
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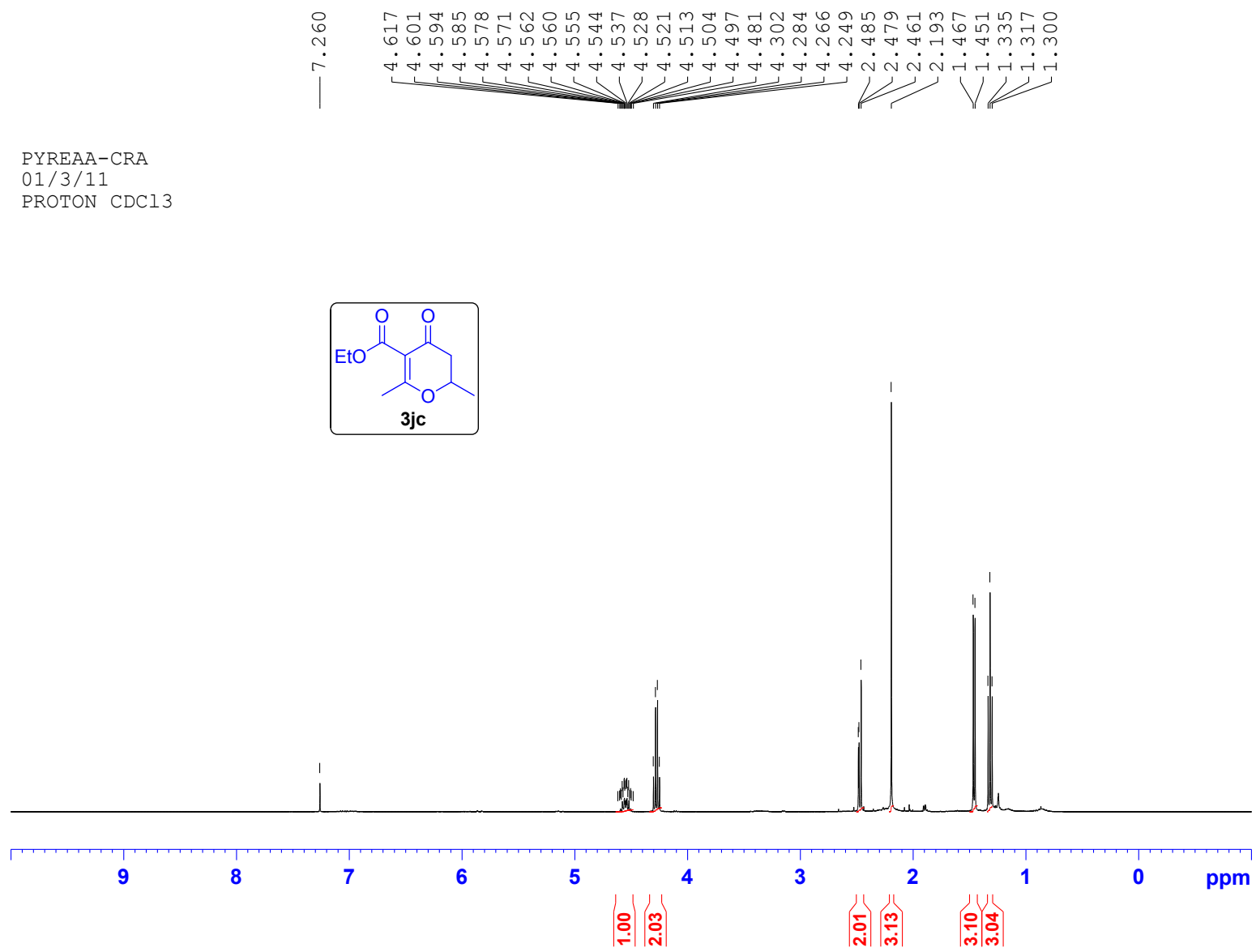


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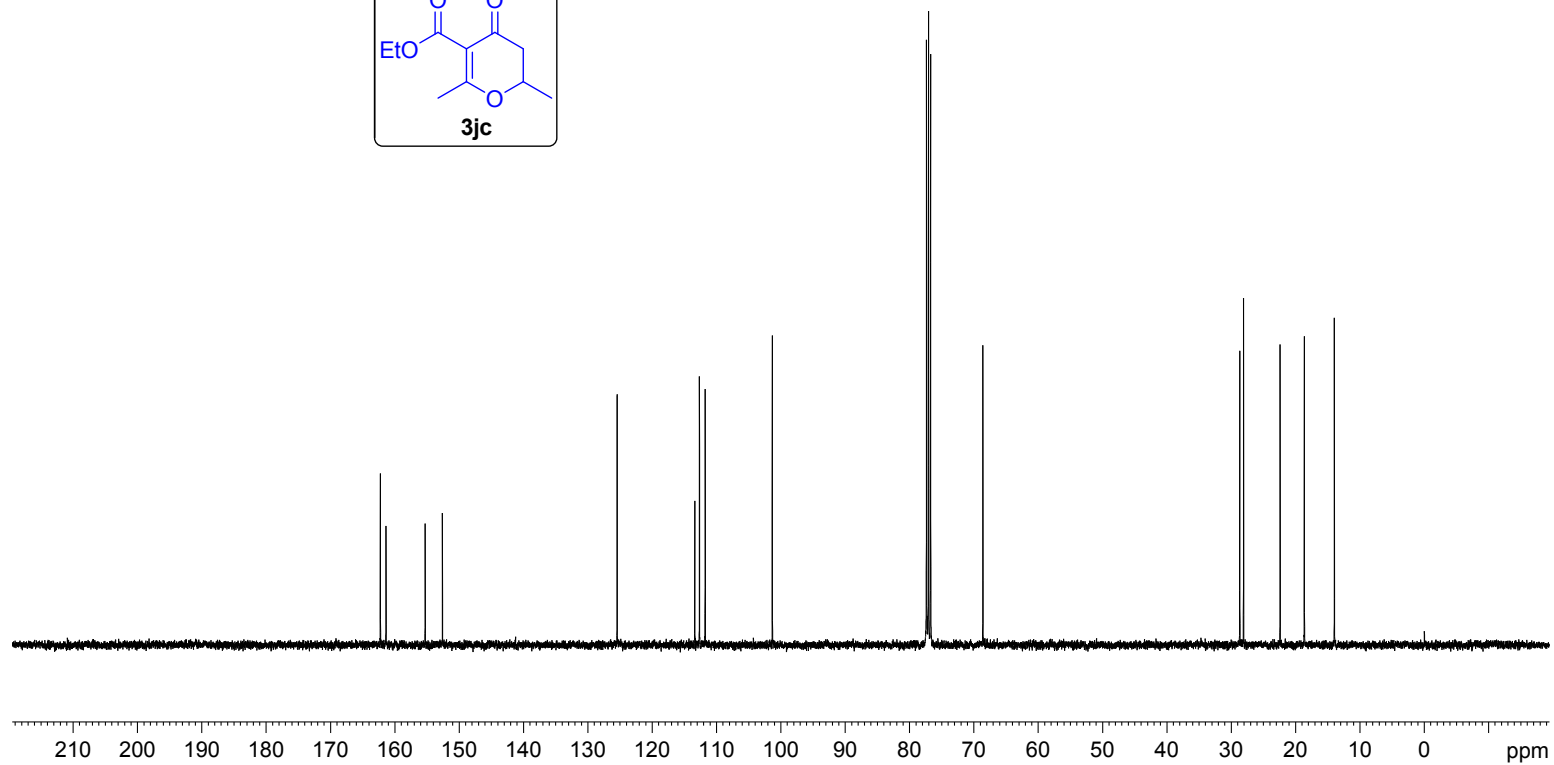
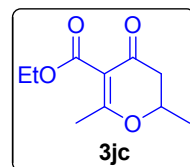
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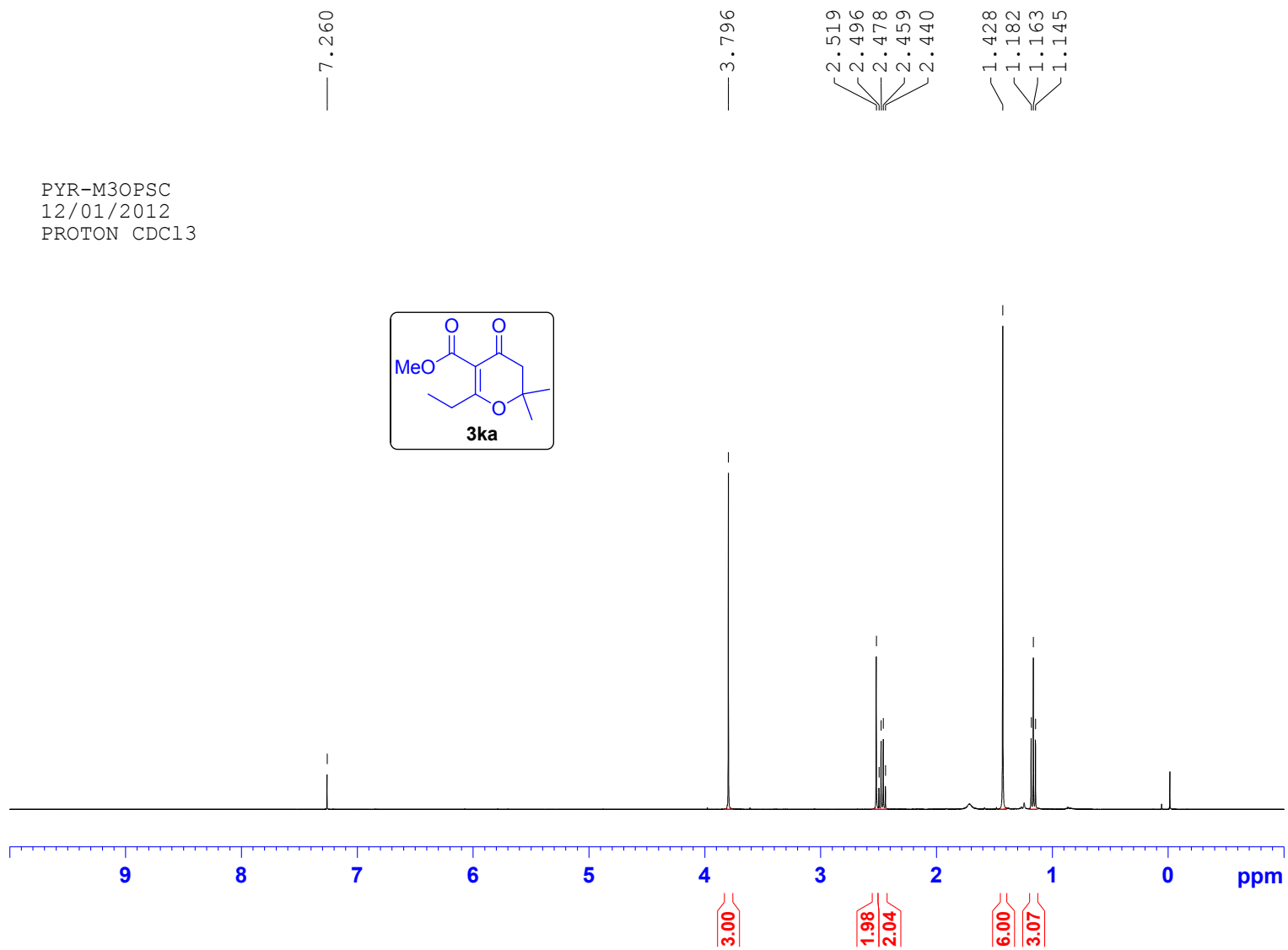
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PYR-M3OPSC
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PROTON CDC13



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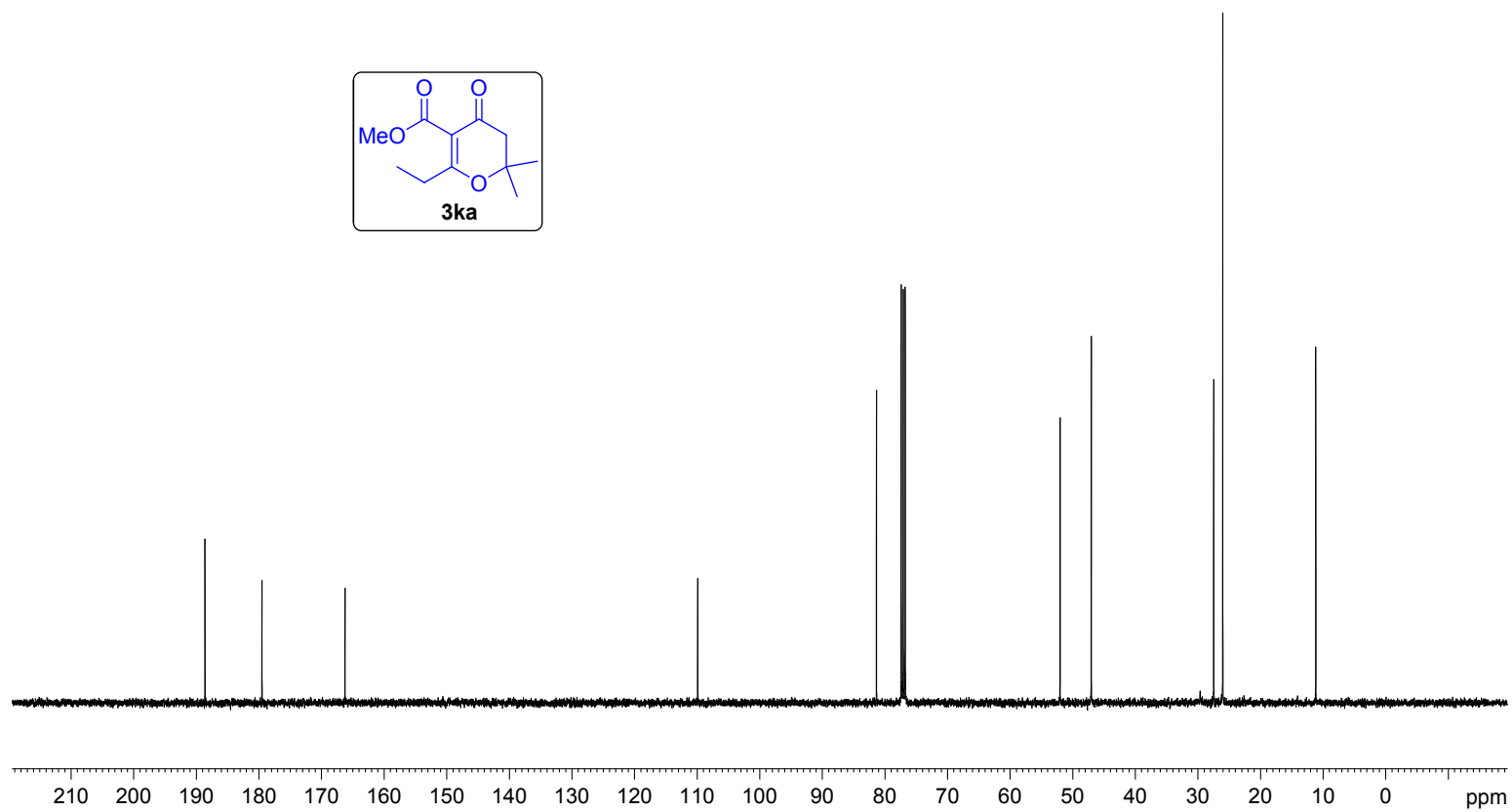
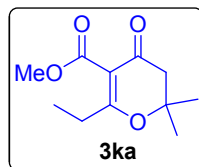
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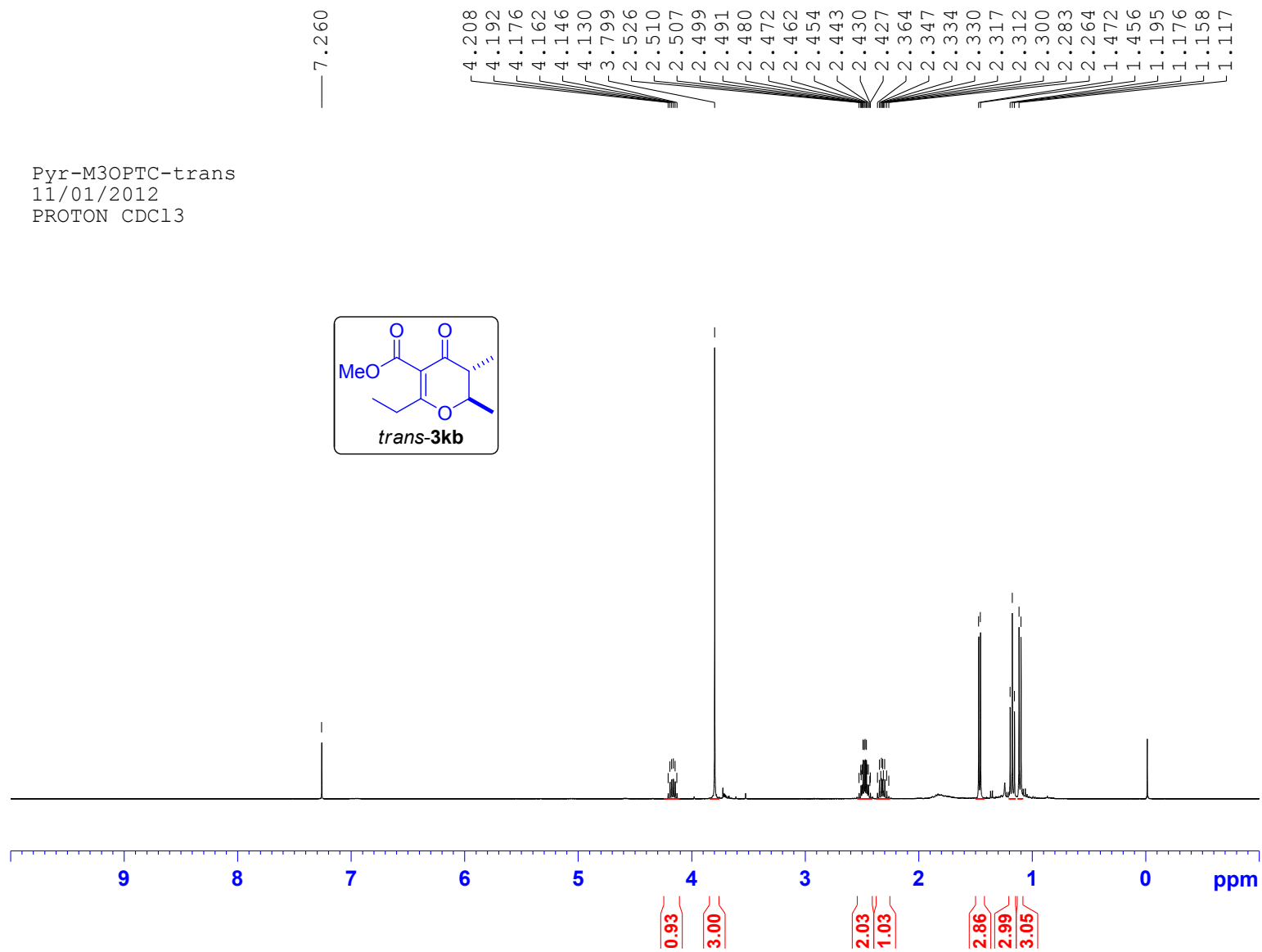
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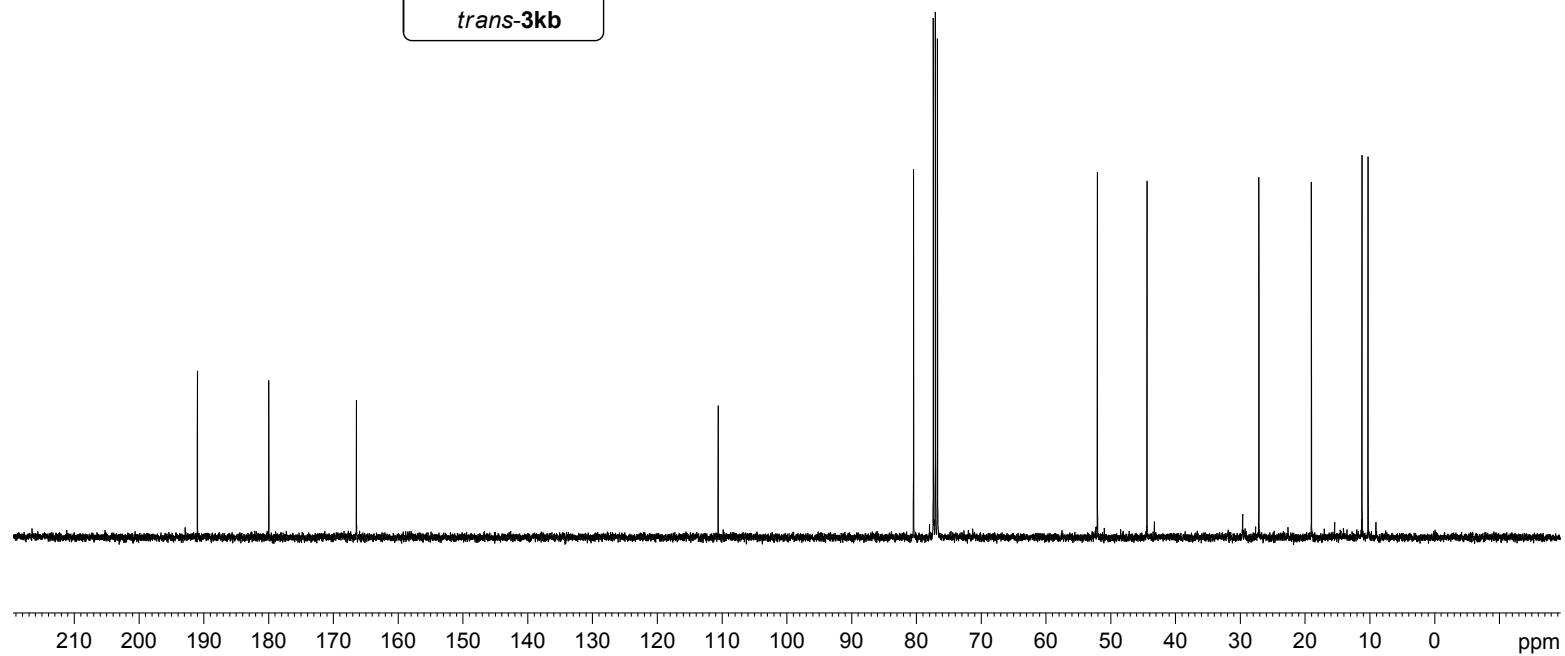
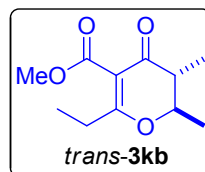
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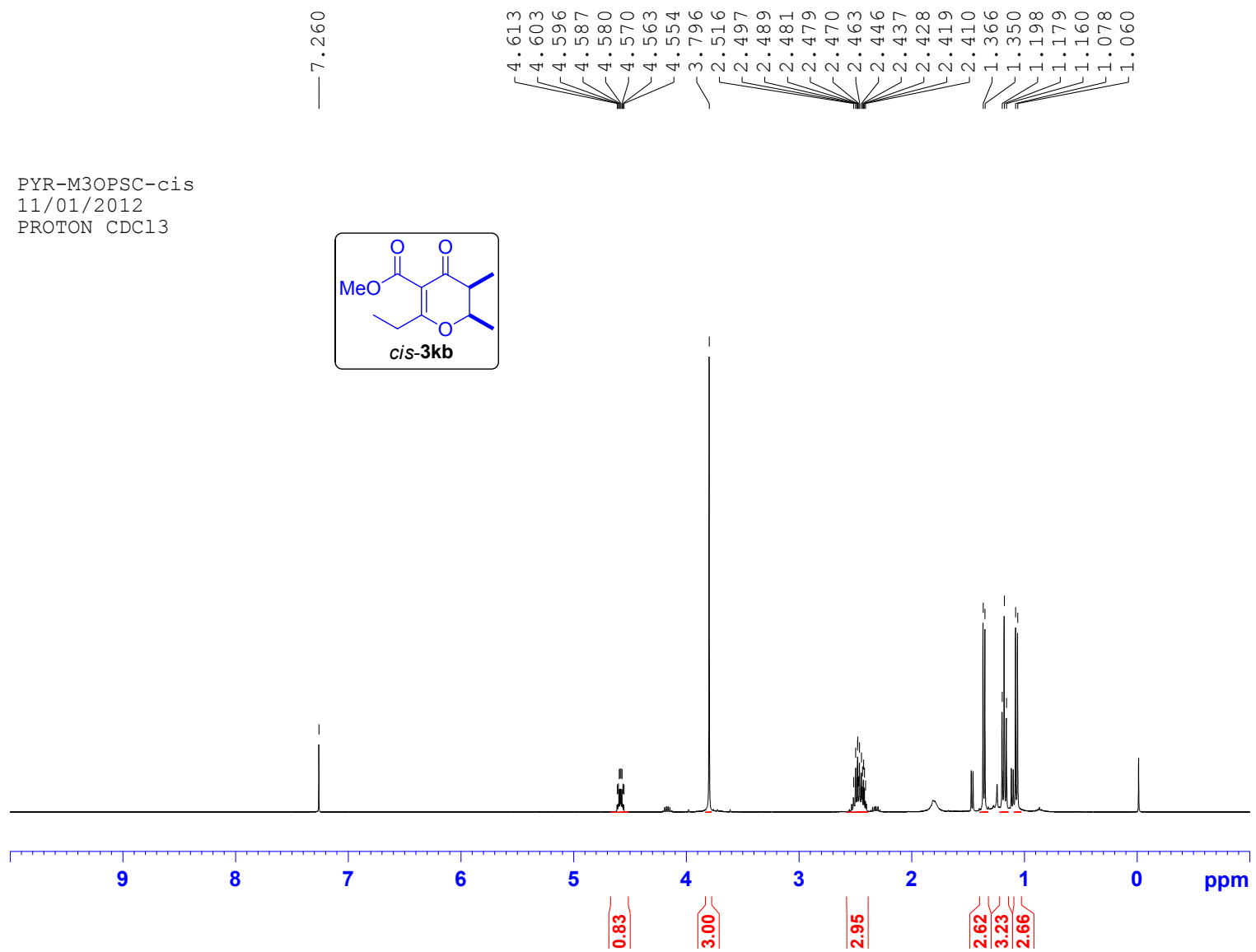
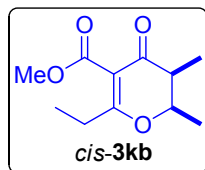
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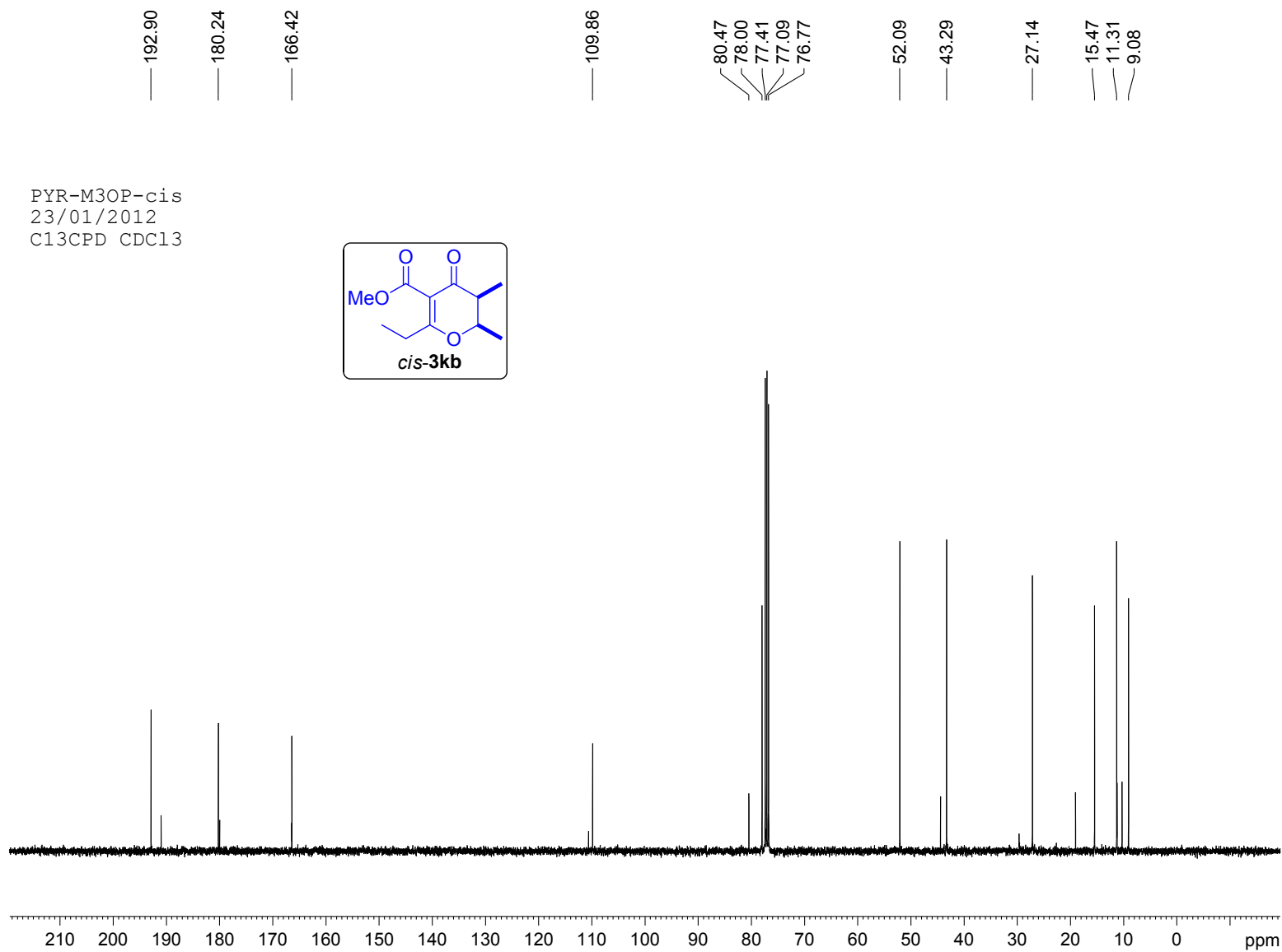
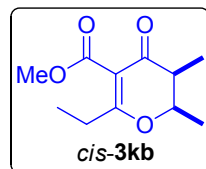
PYR-92 M3OP-trans
23/01/2012
C13CPD CDC13



PYR-M3OPSC-cis
11/01/2012
PROTON CDCl3



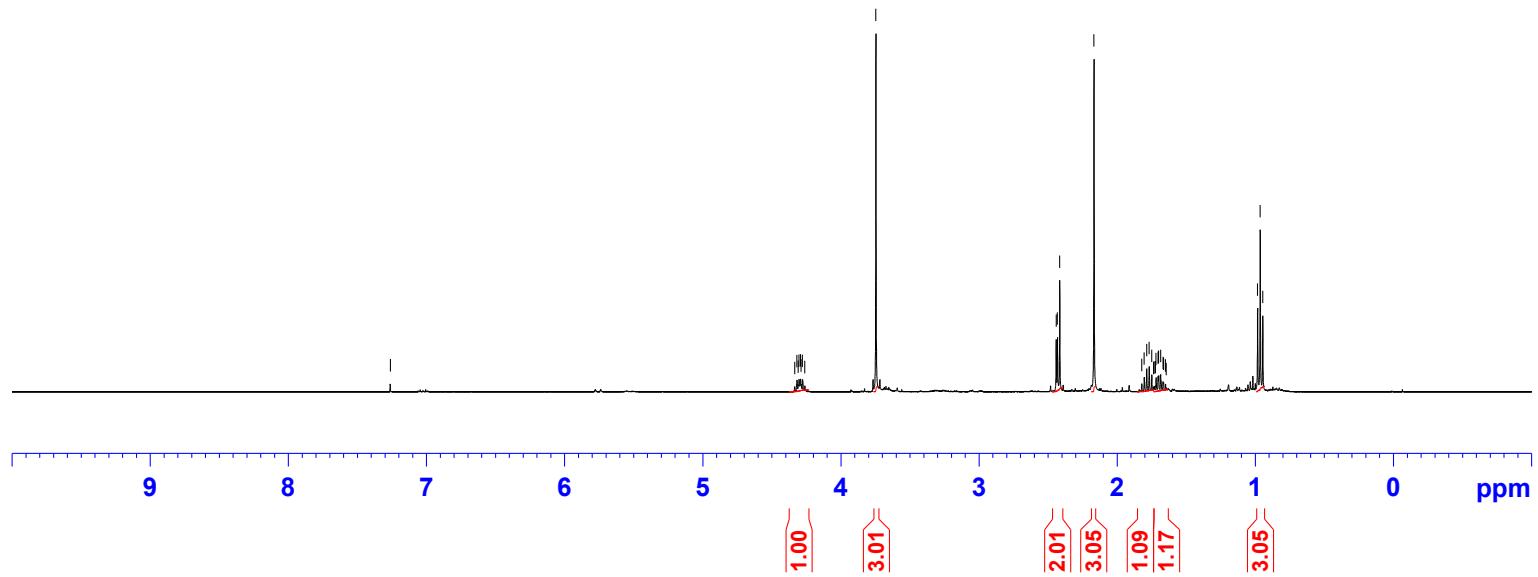
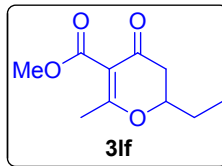
PYR-M3OP-cis
23/01/2012
C13CPD CDC13



PYR-297 HEP S-I
15/07/2013
PROTON CDC13

— 7.260

4.333
4.316
4.308
4.302
4.291
4.286
4.277
4.260
3.746
2.440
2.431
2.415
2.167
1.821
1.803
1.785
1.767
1.749
1.736
1.730
1.722
1.717
1.703
1.698
1.684
1.667
1.663
1.649
1.644
0.982
0.964
0.945



— 188.34
— 177.77
— 166.15

— 111.97

80.39
77.44
77.12
76.81

— 51.99

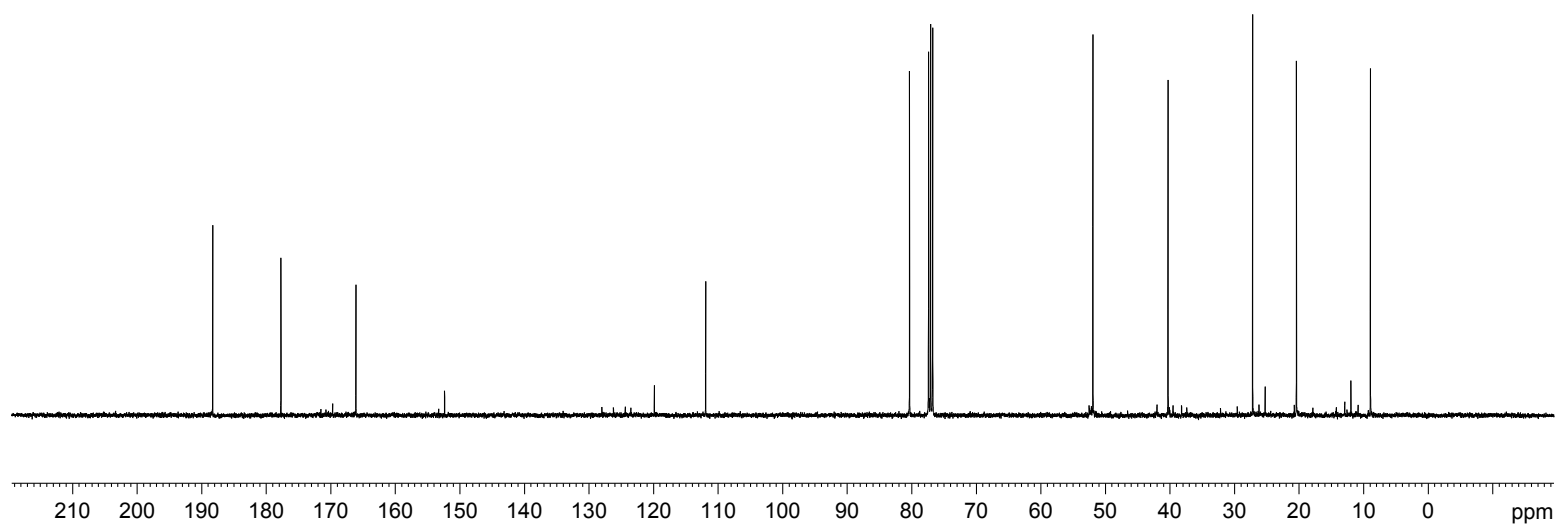
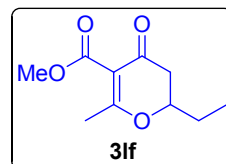
— 40.34

— 27.24

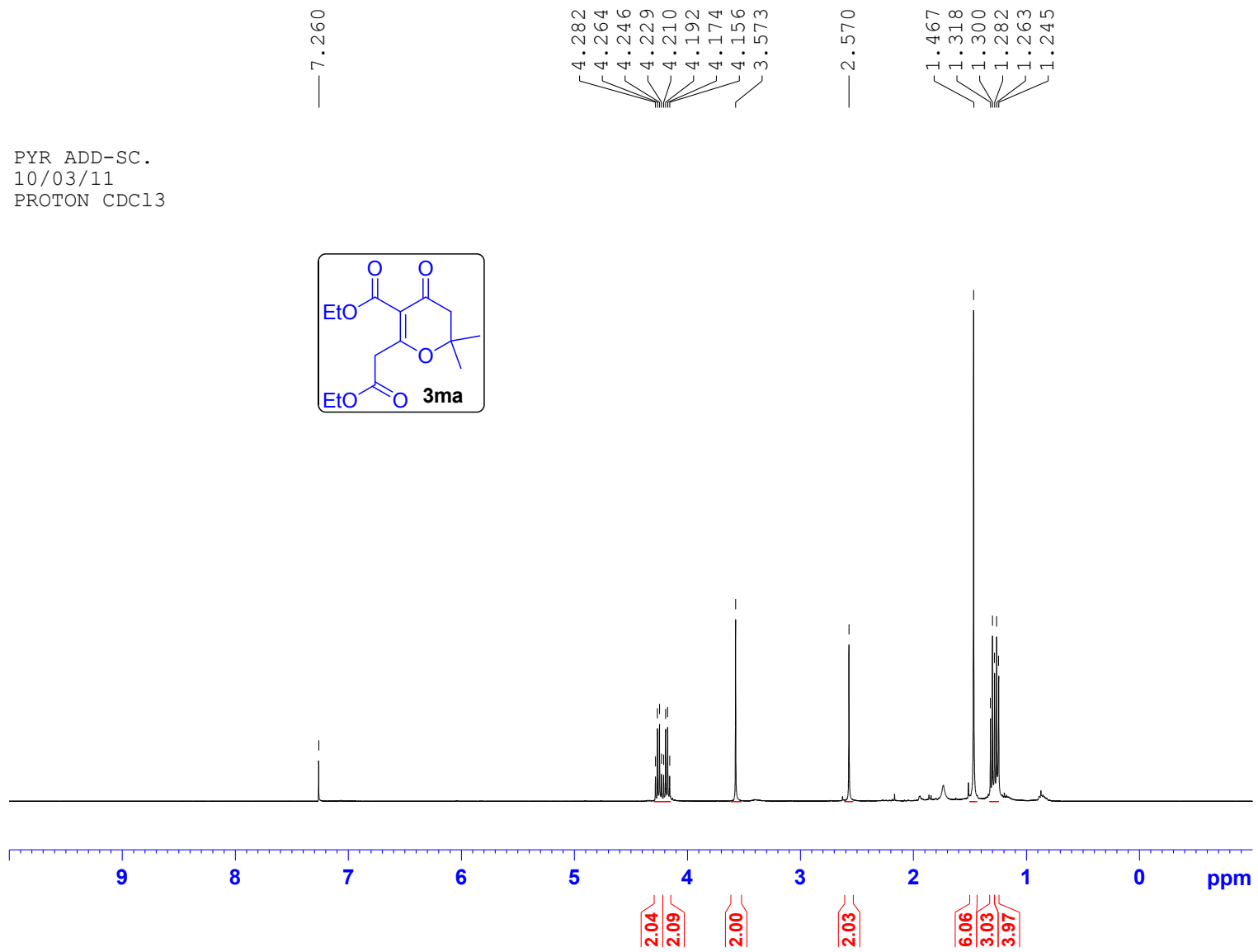
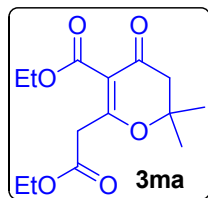
— 20.45

— 8.99

PYR-297 HEP S-I
15/07/2013
C13CPD CDC13

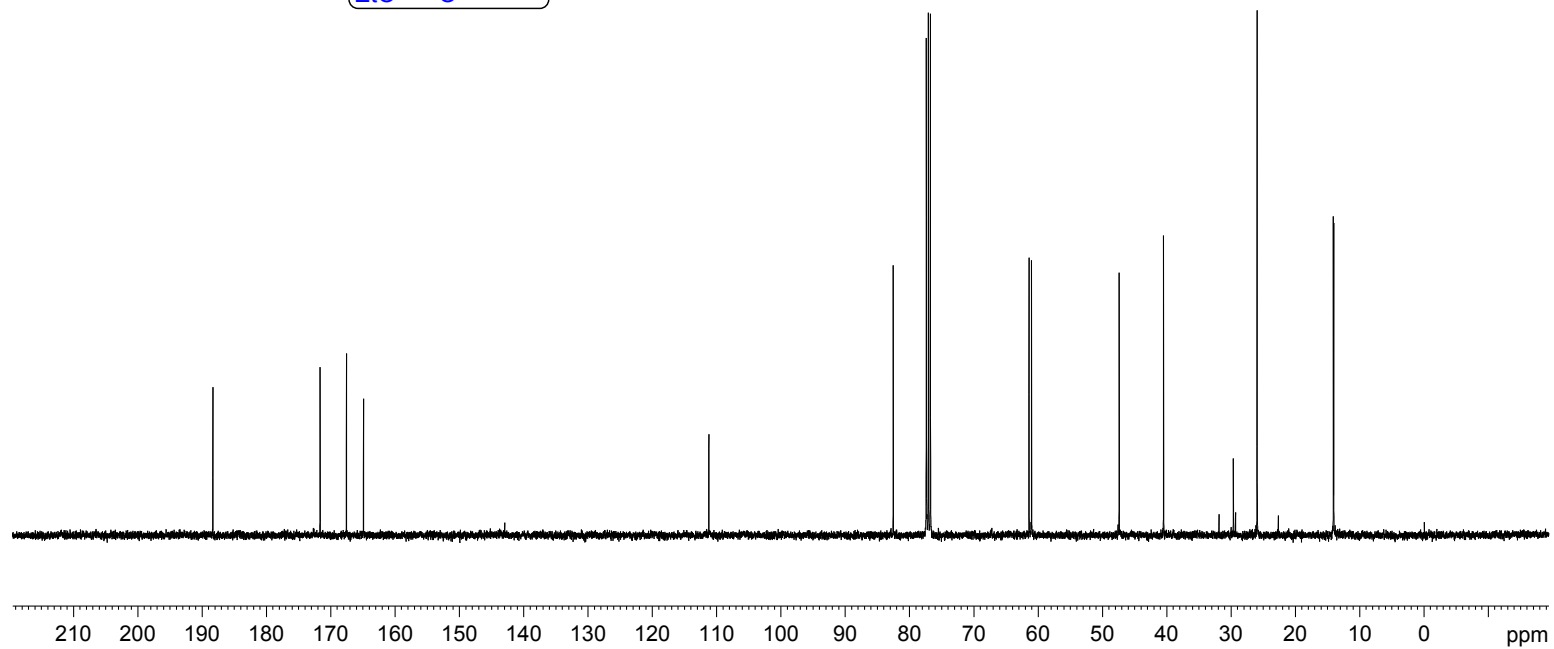
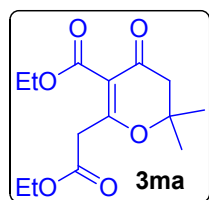


PYR ADD-SC.
10/03/11
PROTON CDC13

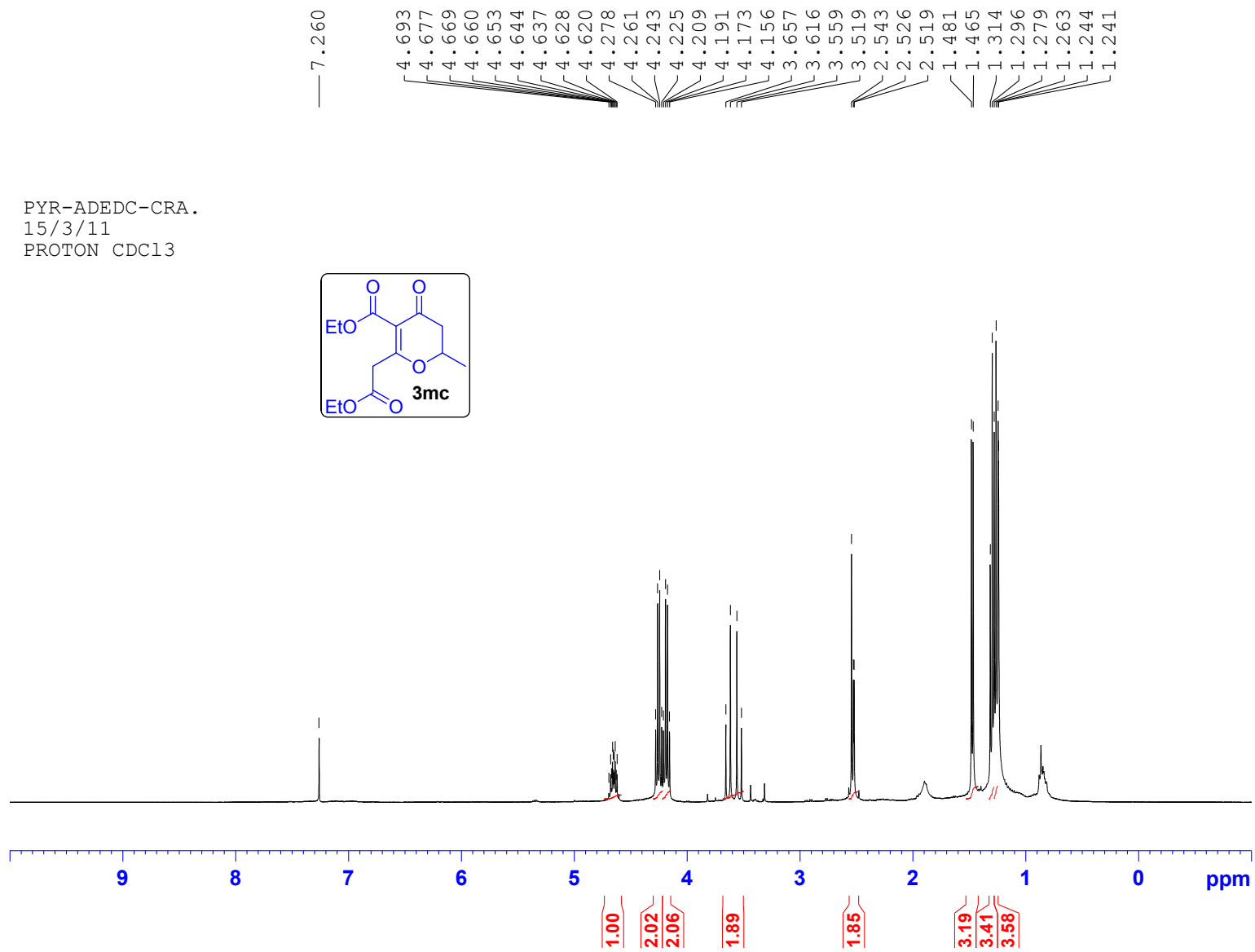
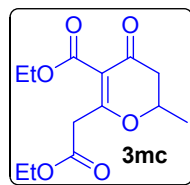


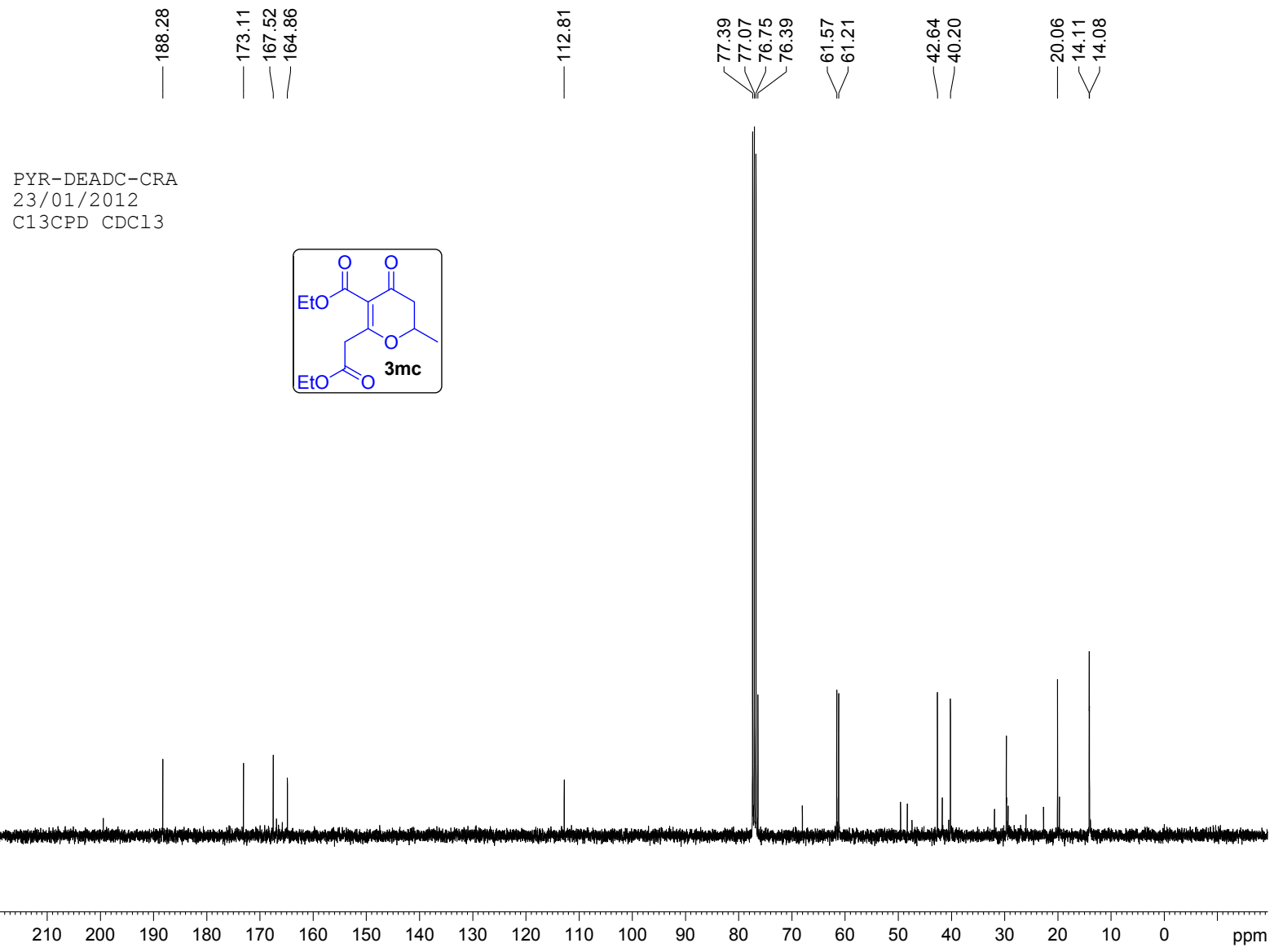
188.34
171.71
167.61
164.96
111.25
82.58
77.43
77.11
76.80
61.46
61.07
47.44
40.54
25.99
14.14
14.08

PYR-DEADC-SC
23/01/2012
C13CPD CDC13

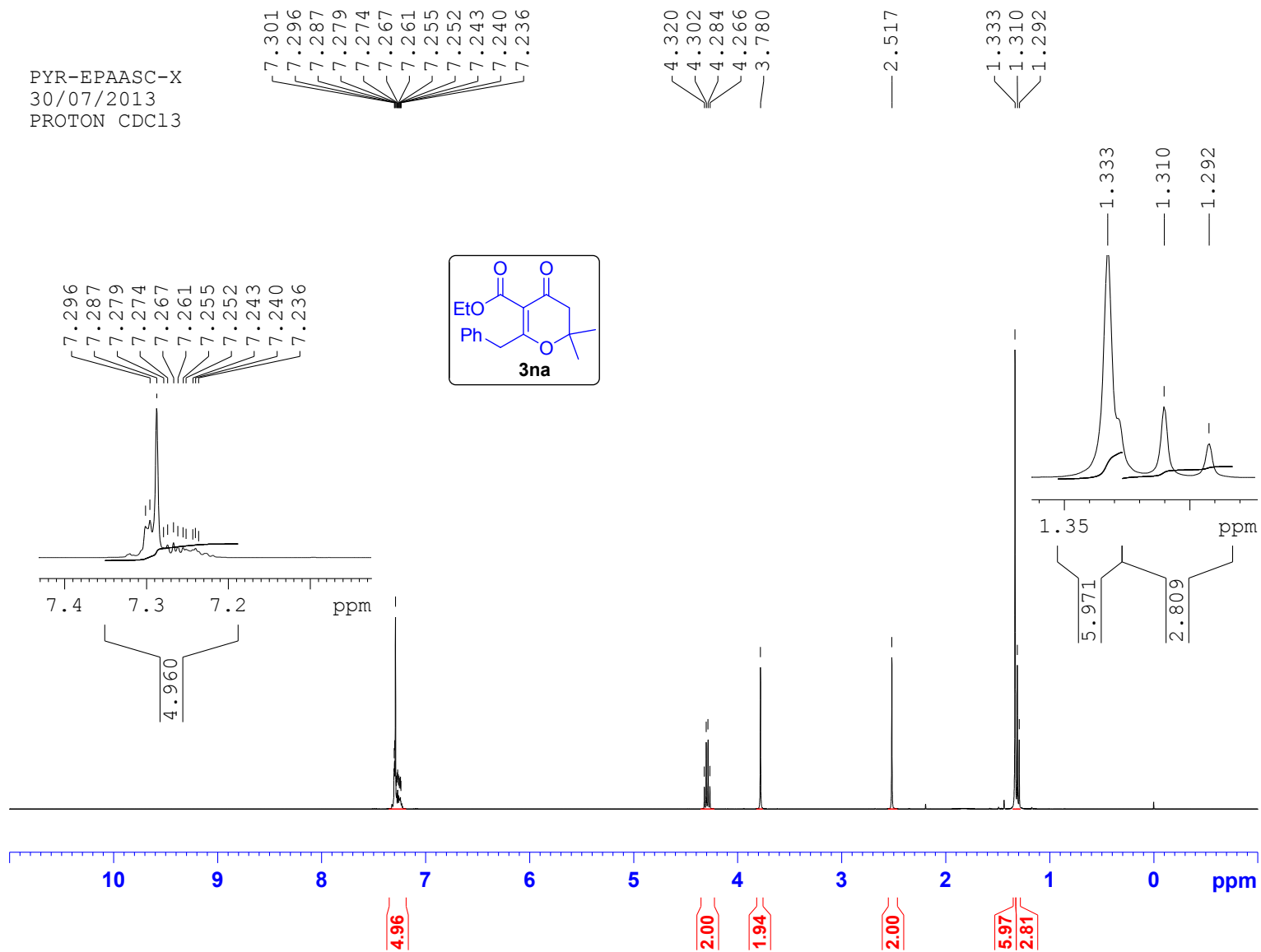


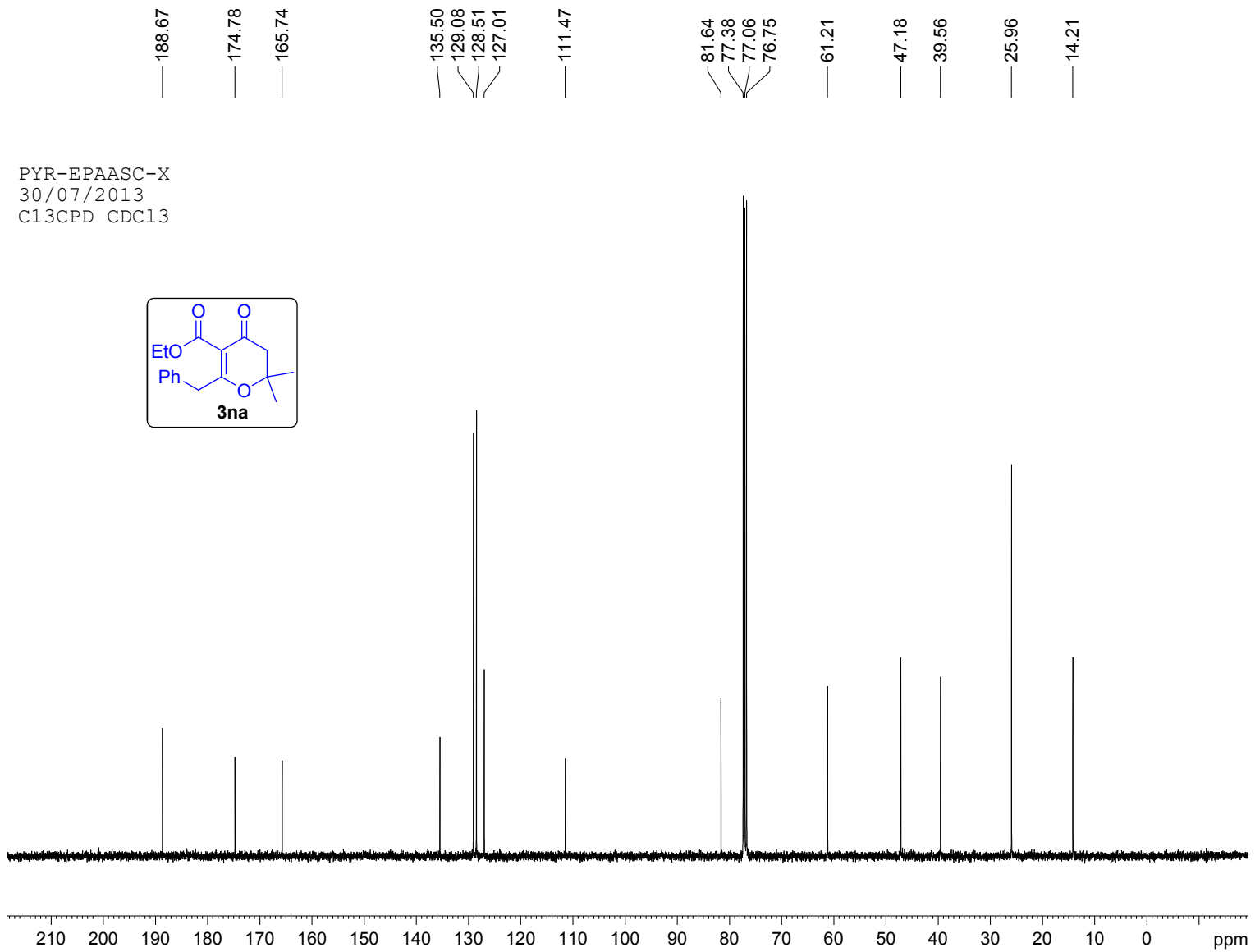
PYR-AEDDC-CRA.
15/3/11
PROTON CDC13



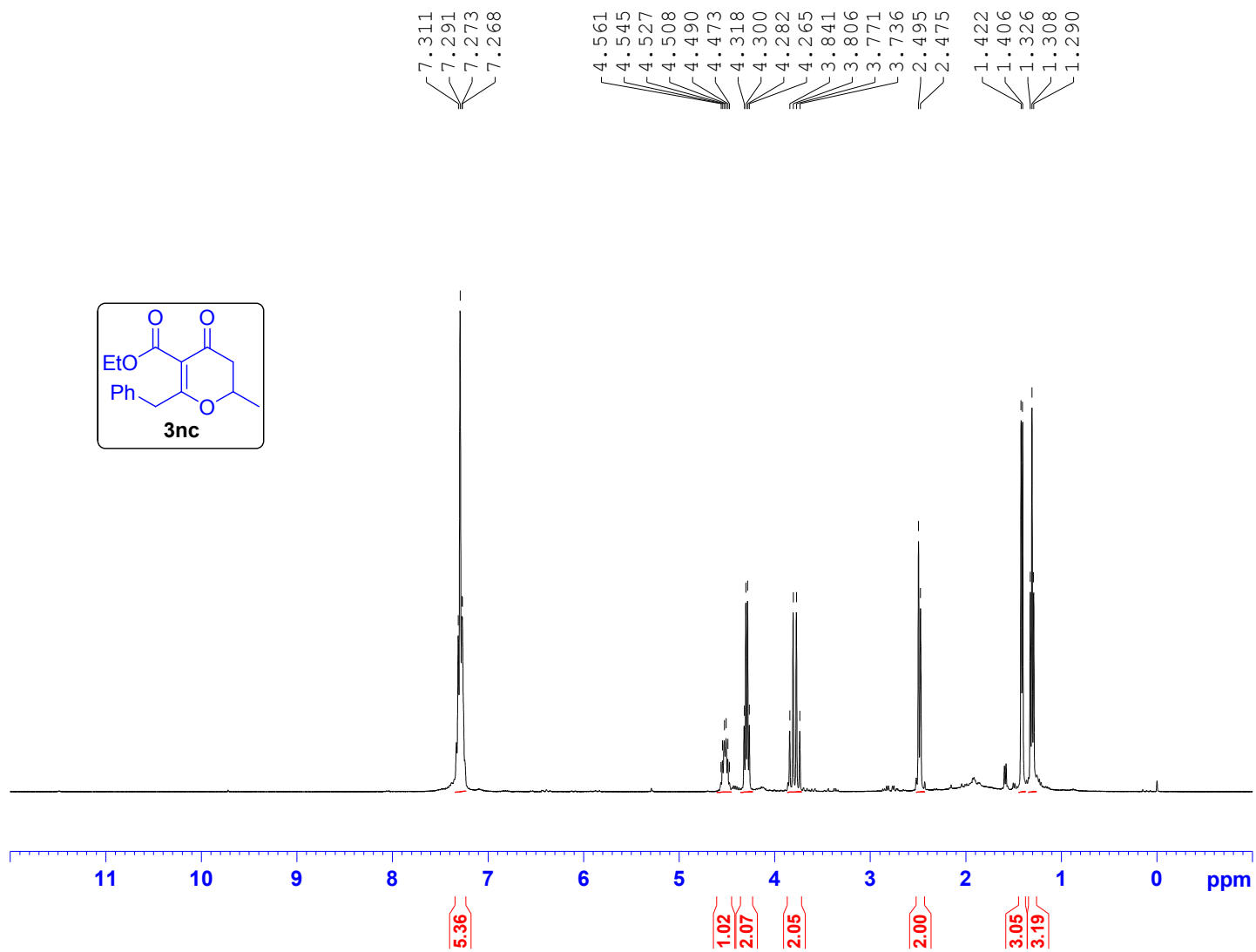


PYR-EPAASC-X
30/07/2013
PROTON CDC13

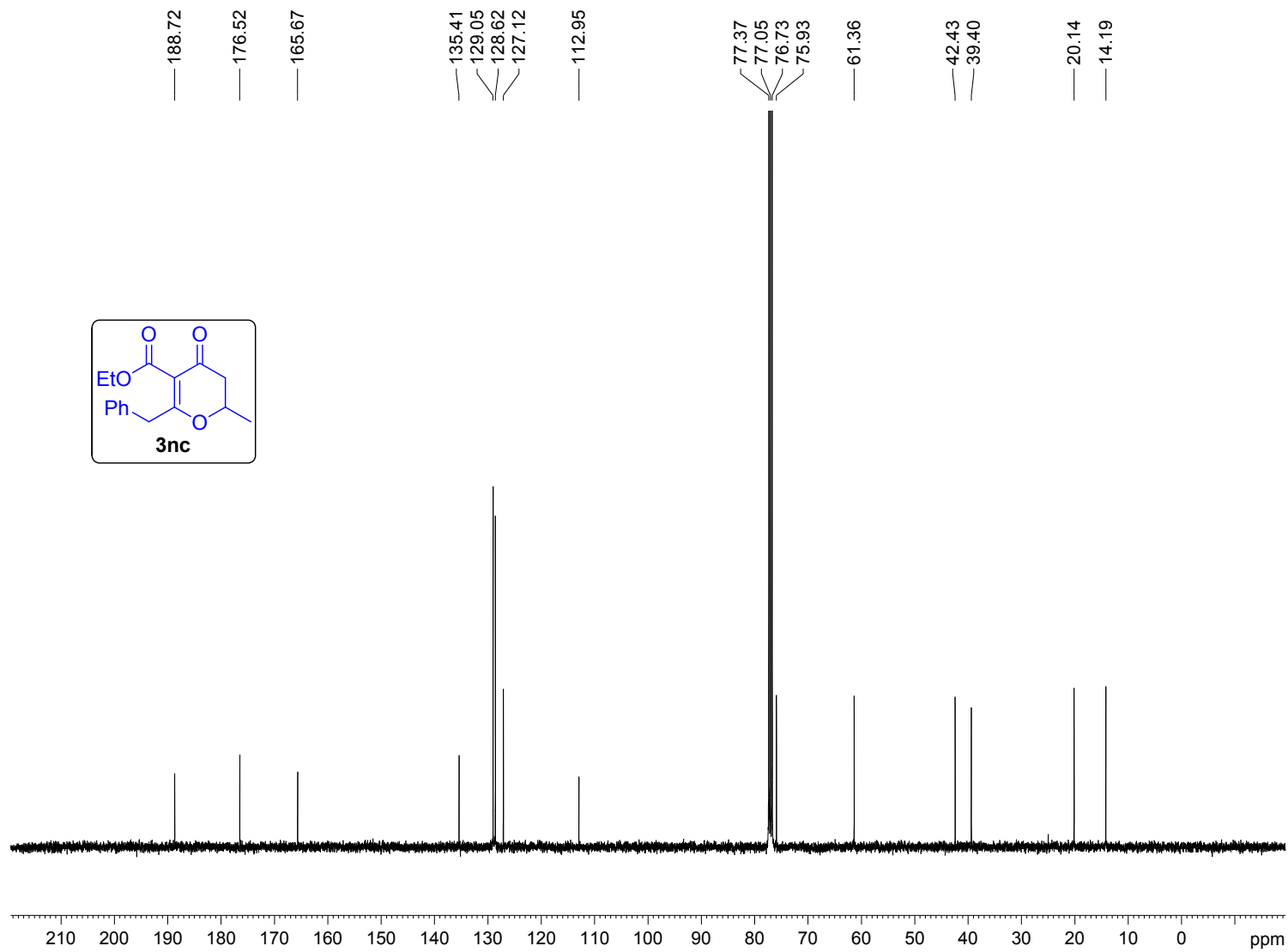




PYR-396 EPAA-CRC
PROTON CDC13 19.12.2013



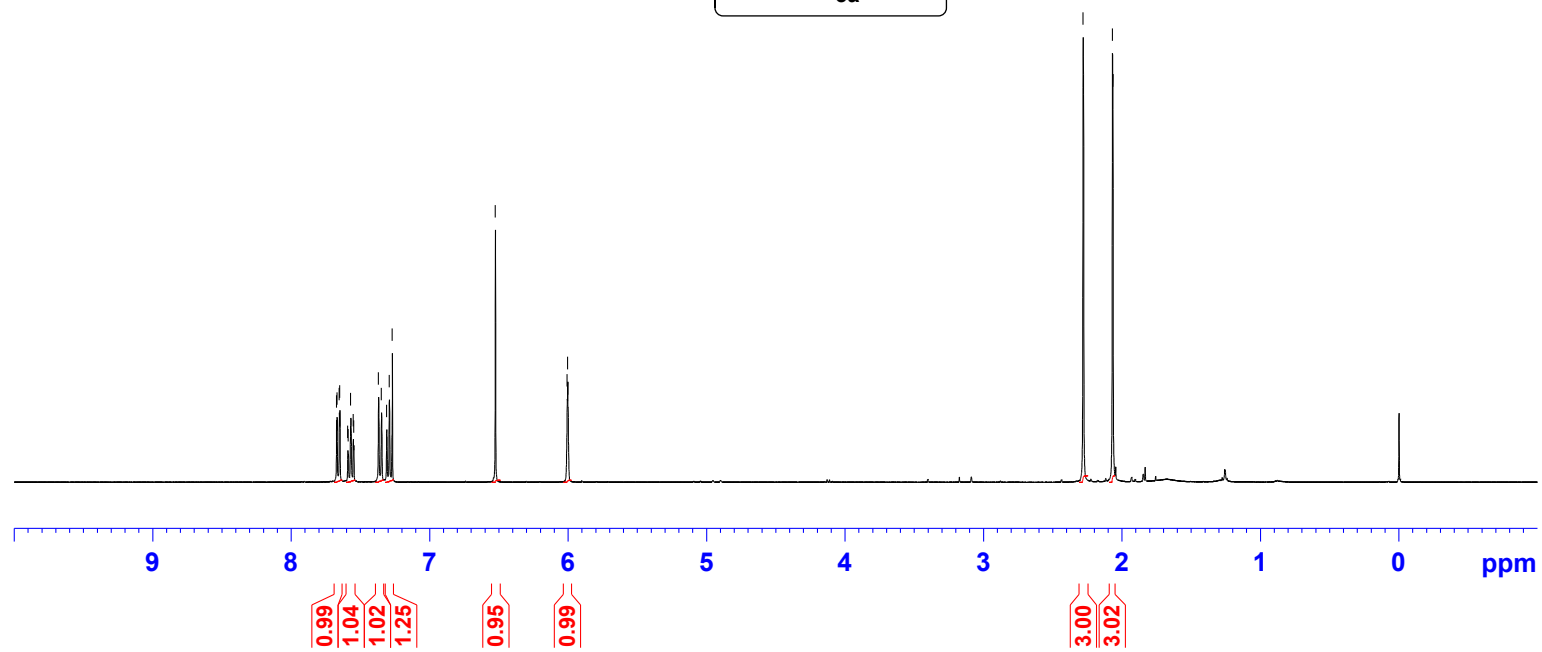
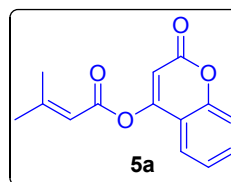
PYR-396 EPAA-CRC
C13CPD CDC13 19.12.2013



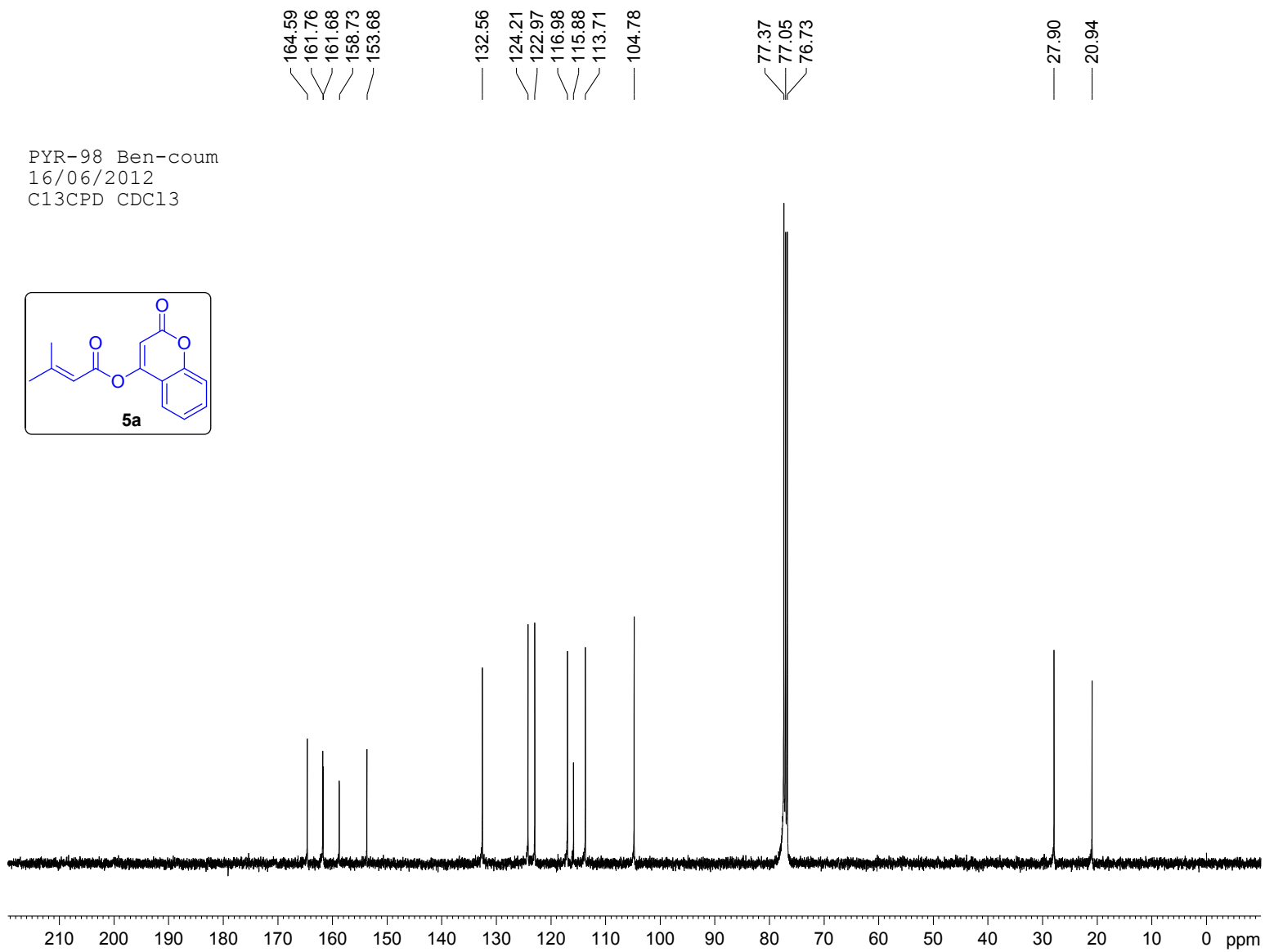
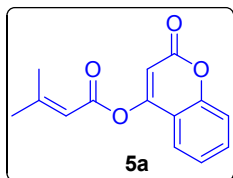
7.672
7.669
7.652
7.649
7.591
7.587
7.570
7.552
7.548
7.369
7.348
7.311
7.291
7.270
6.526
6.007
6.004
6.001

2.281
2.069

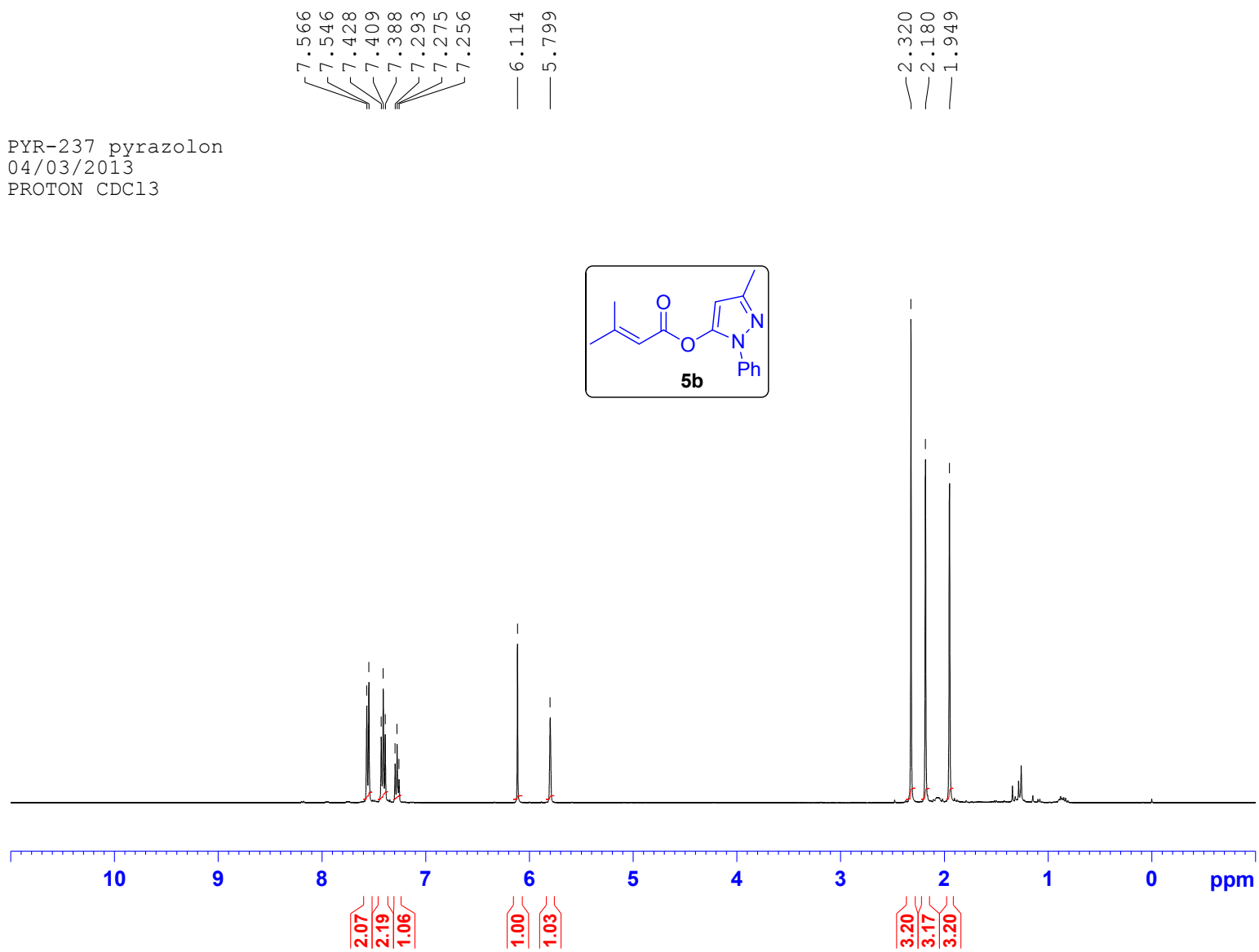
Pyr-11-98 BEN-COUM
11/01/2012
PROTON CDC13



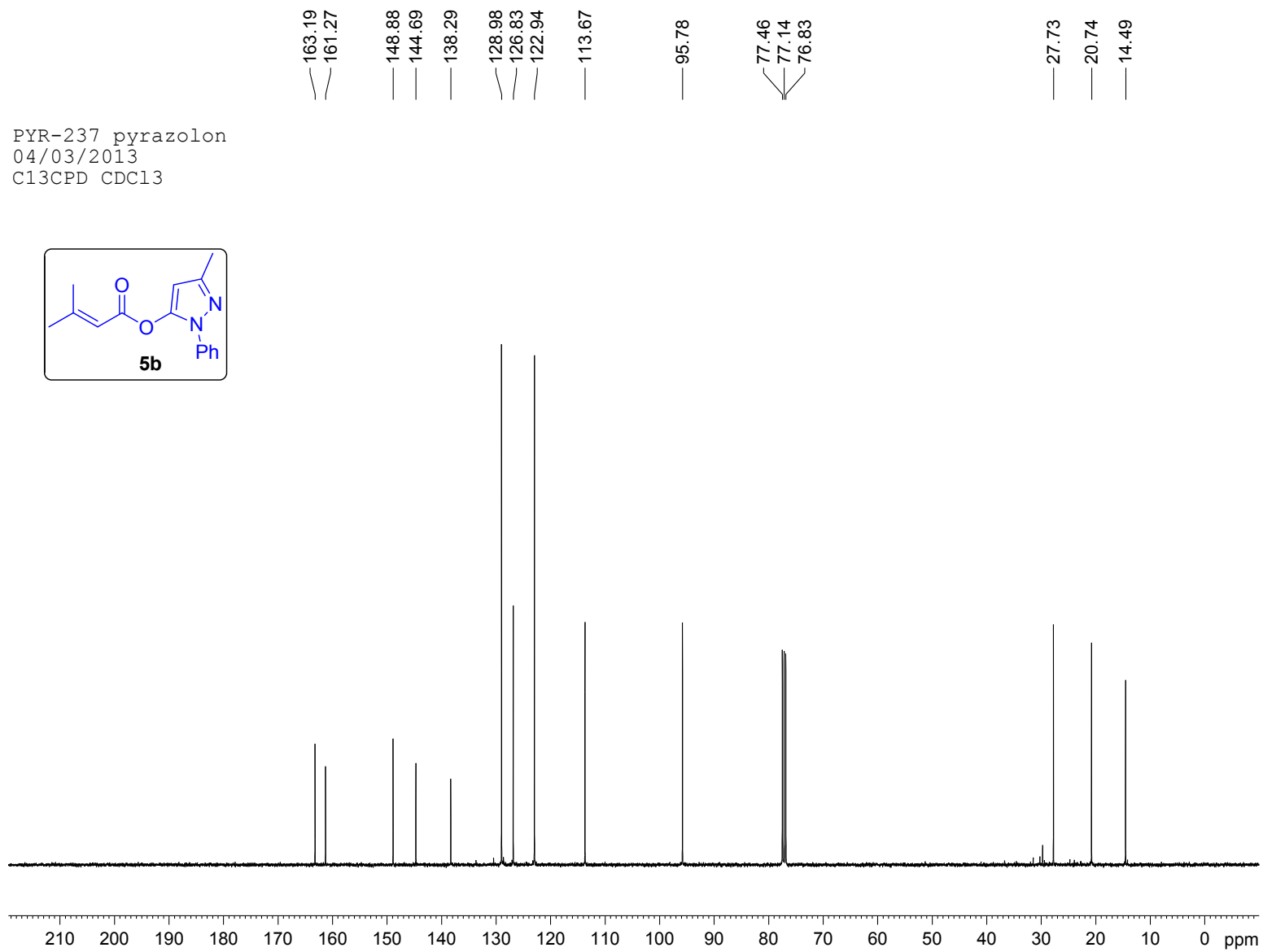
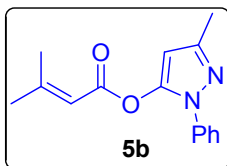
PYR-98 Ben-coum
16/06/2012
C13CPD CDCl3



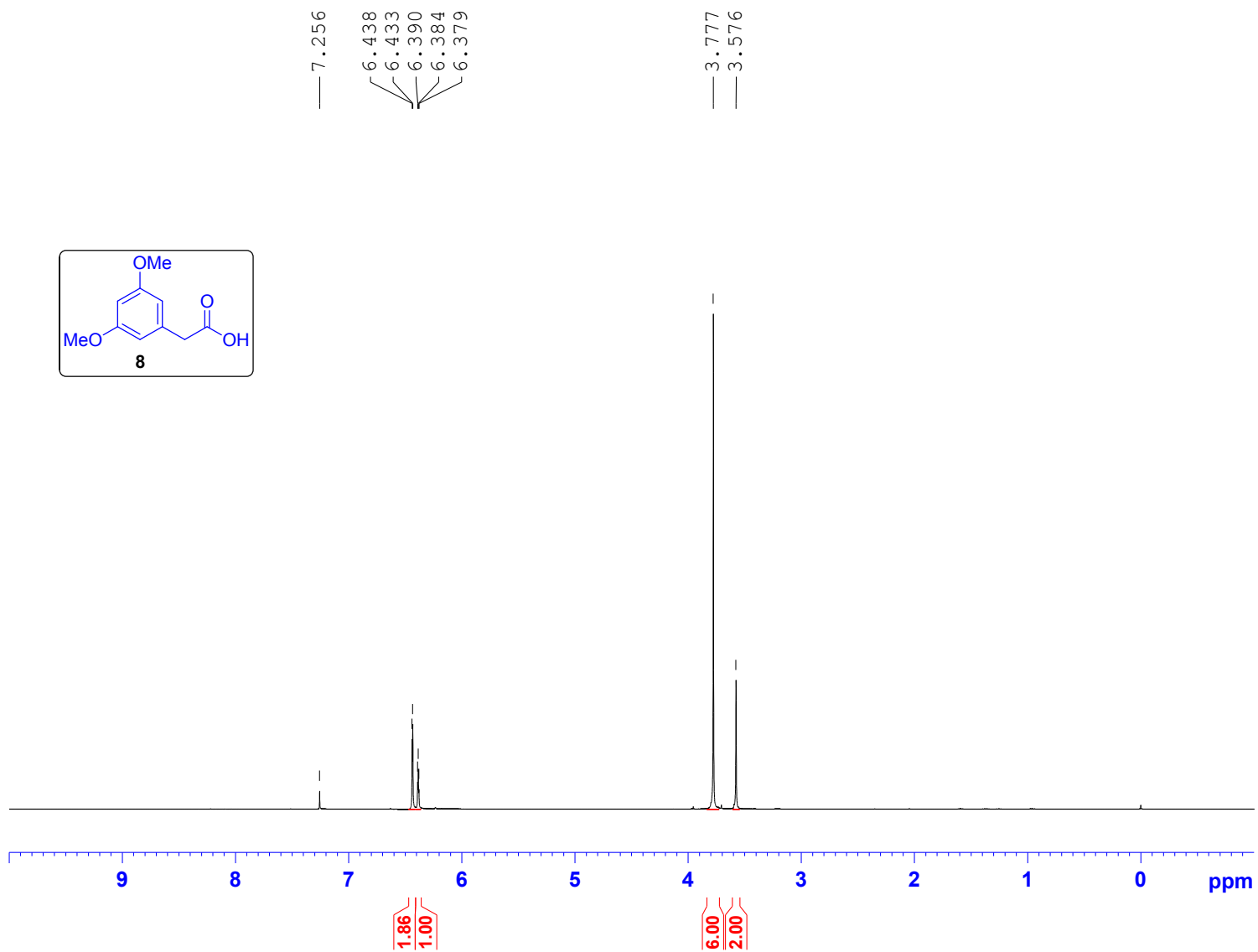
PYR-237 pyrazolon
04/03/2013
PROTON CDC13



PYR-237 pyrazolon
04/03/2013
C13CPD CDC13

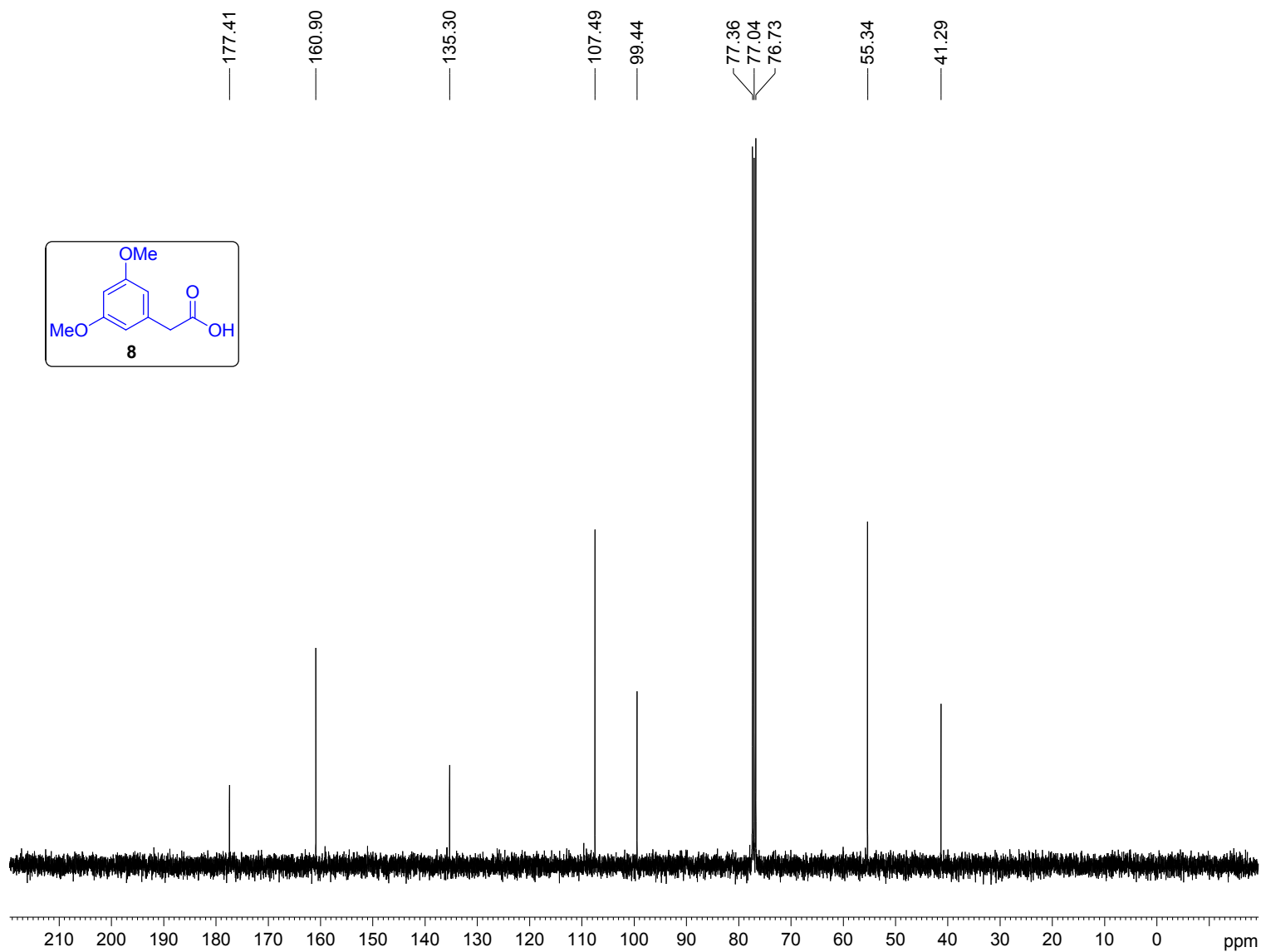
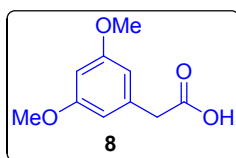


PYR-3,5-DMPAA 13/11/2013
PROTON CDC13

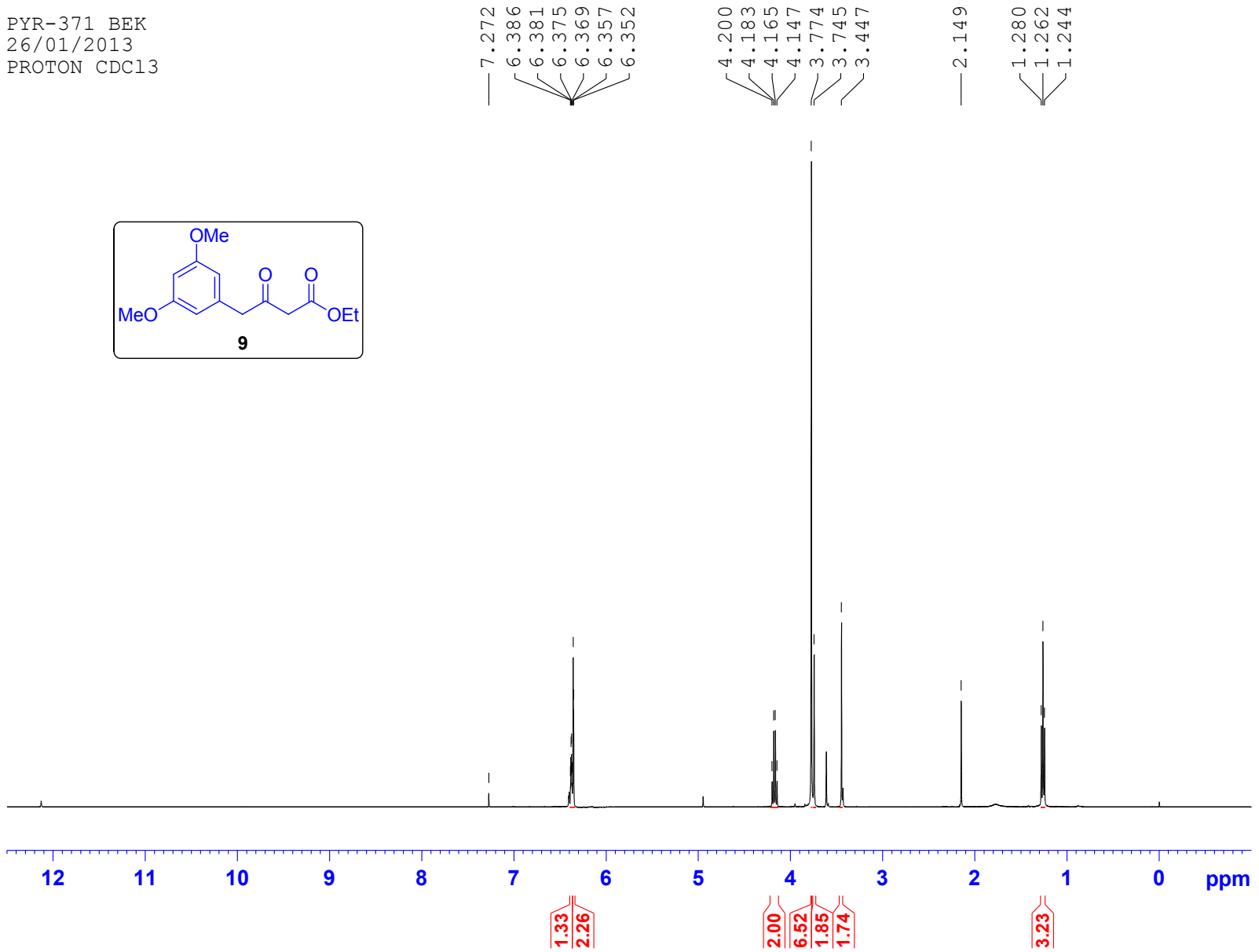
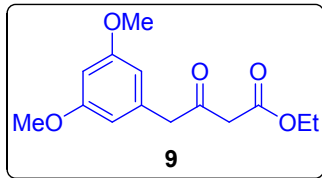


S51

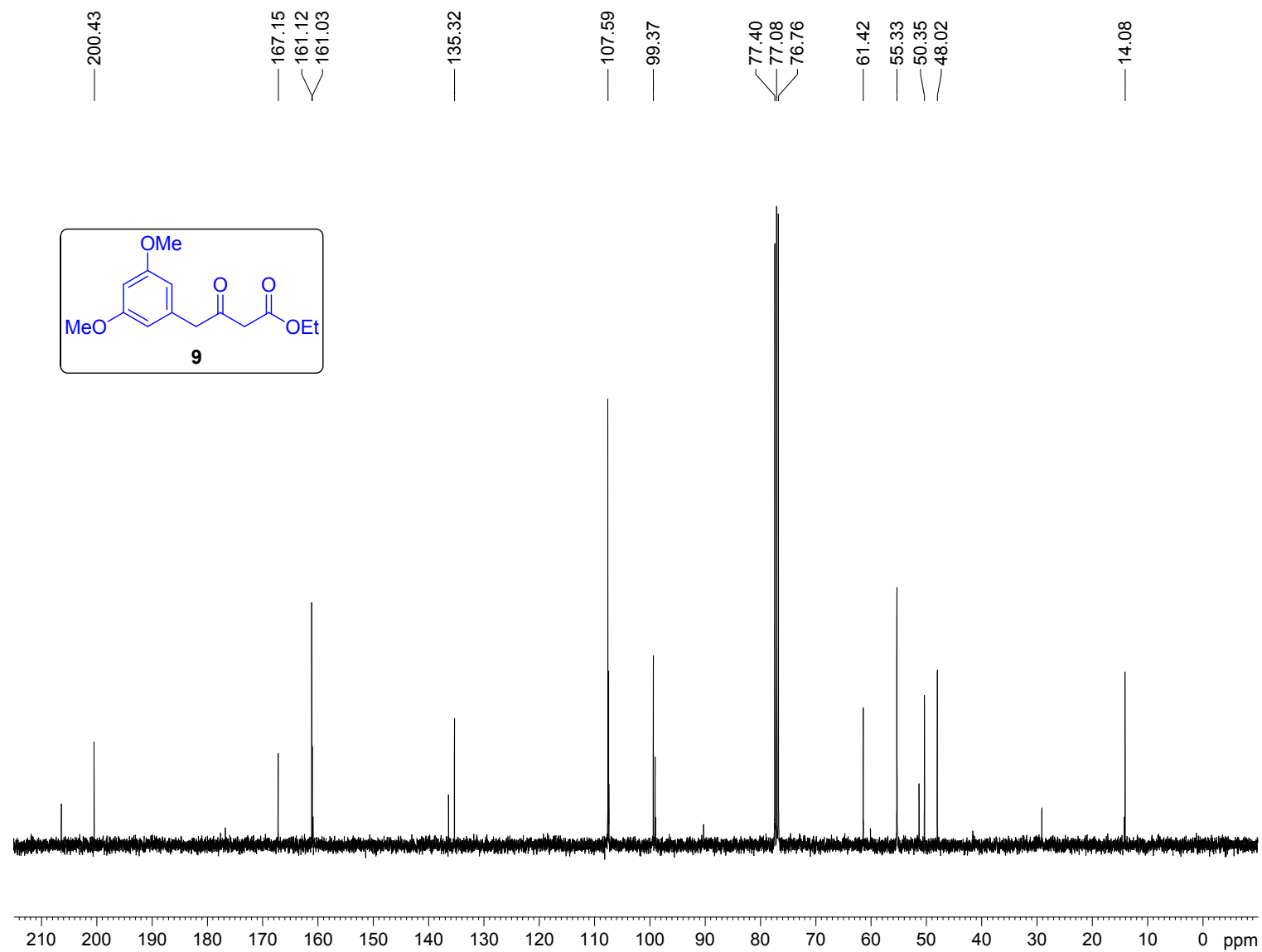
PYR-3,5-DMPAA
C13CPD CDC13



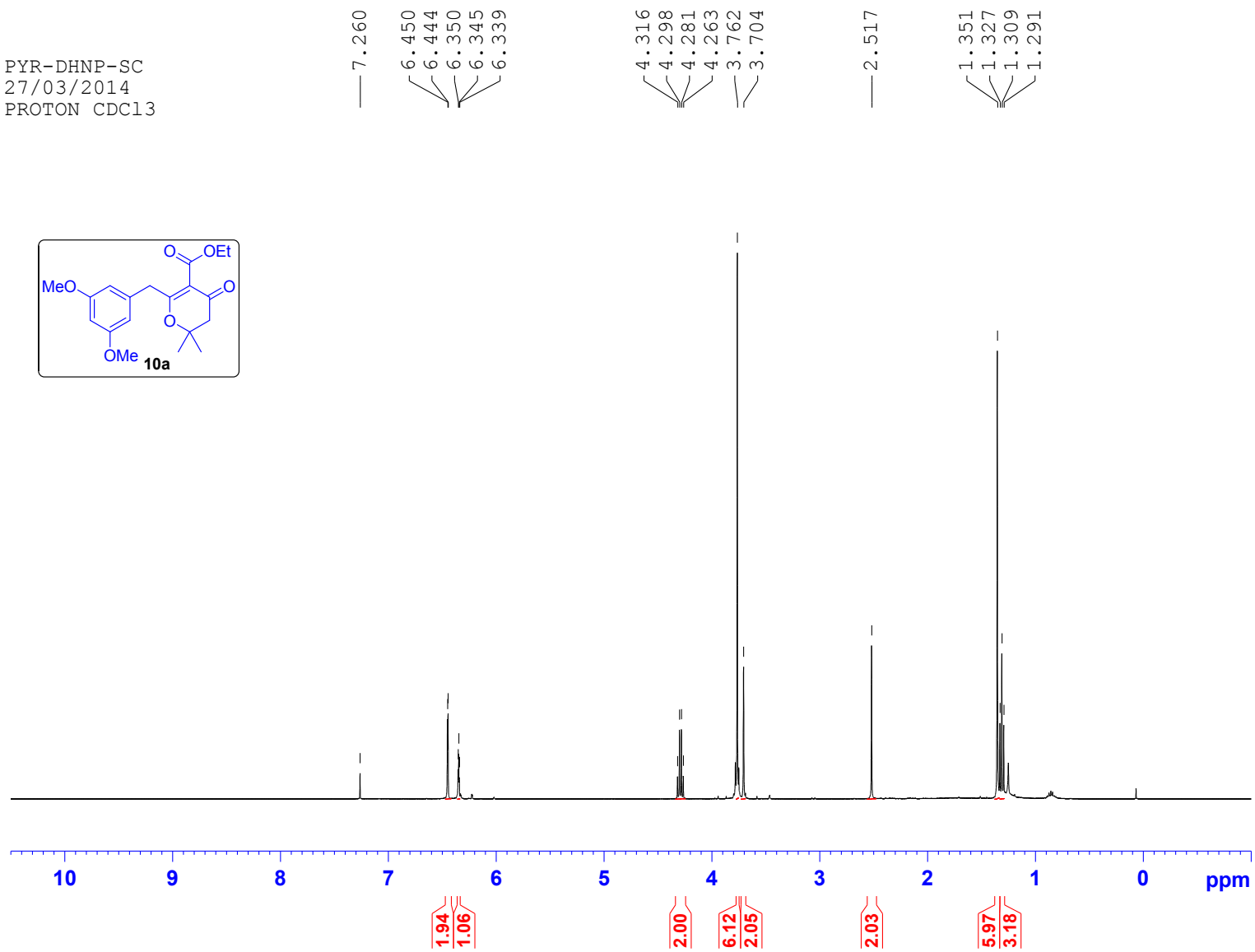
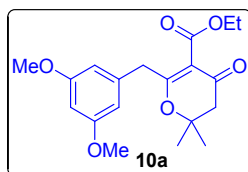
PYR-371 BEK
26/01/2013
PROTON CDC13



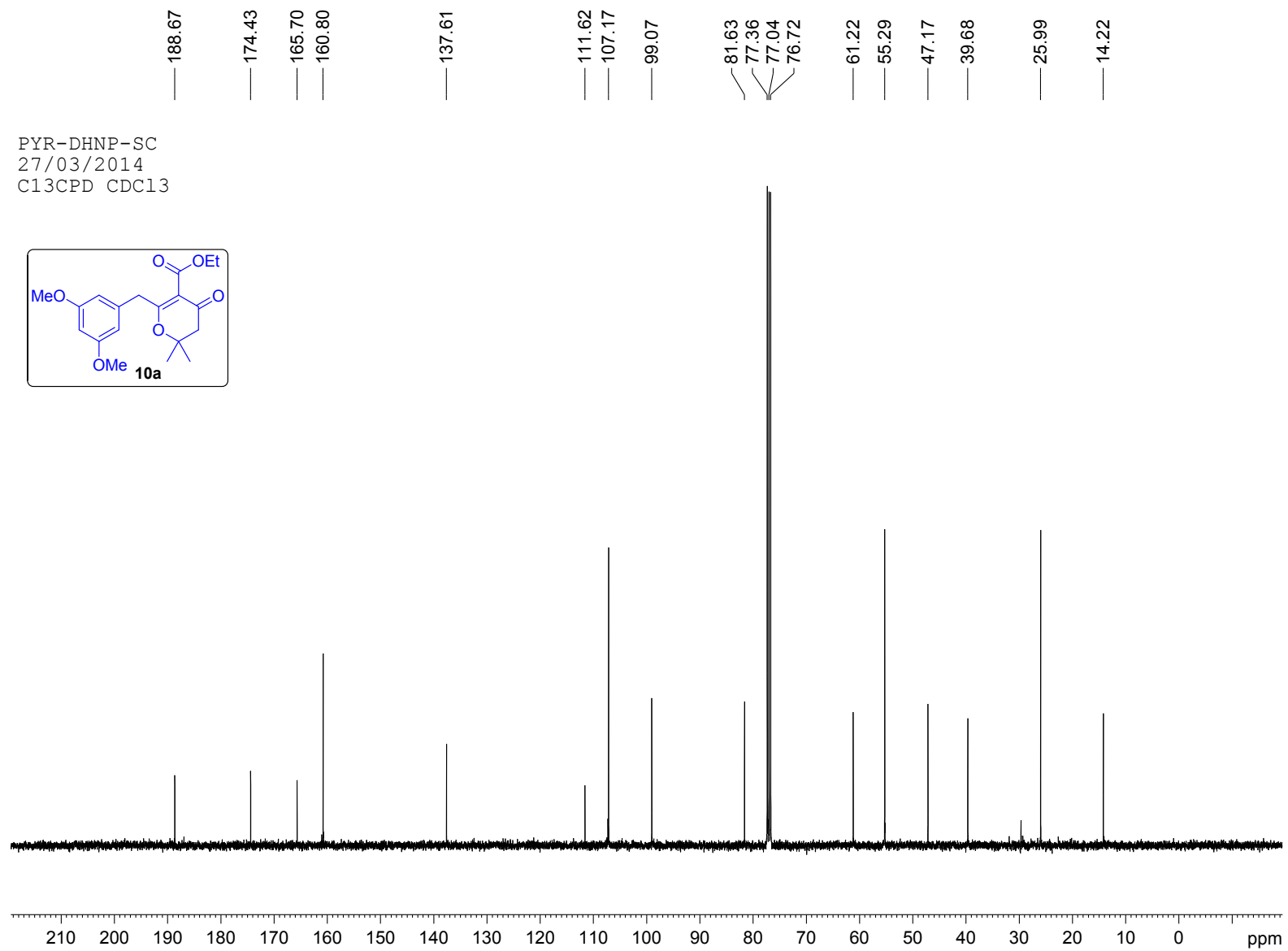
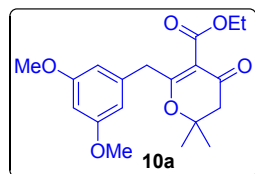
PYR-371 BEK
C13CPD CDCl3



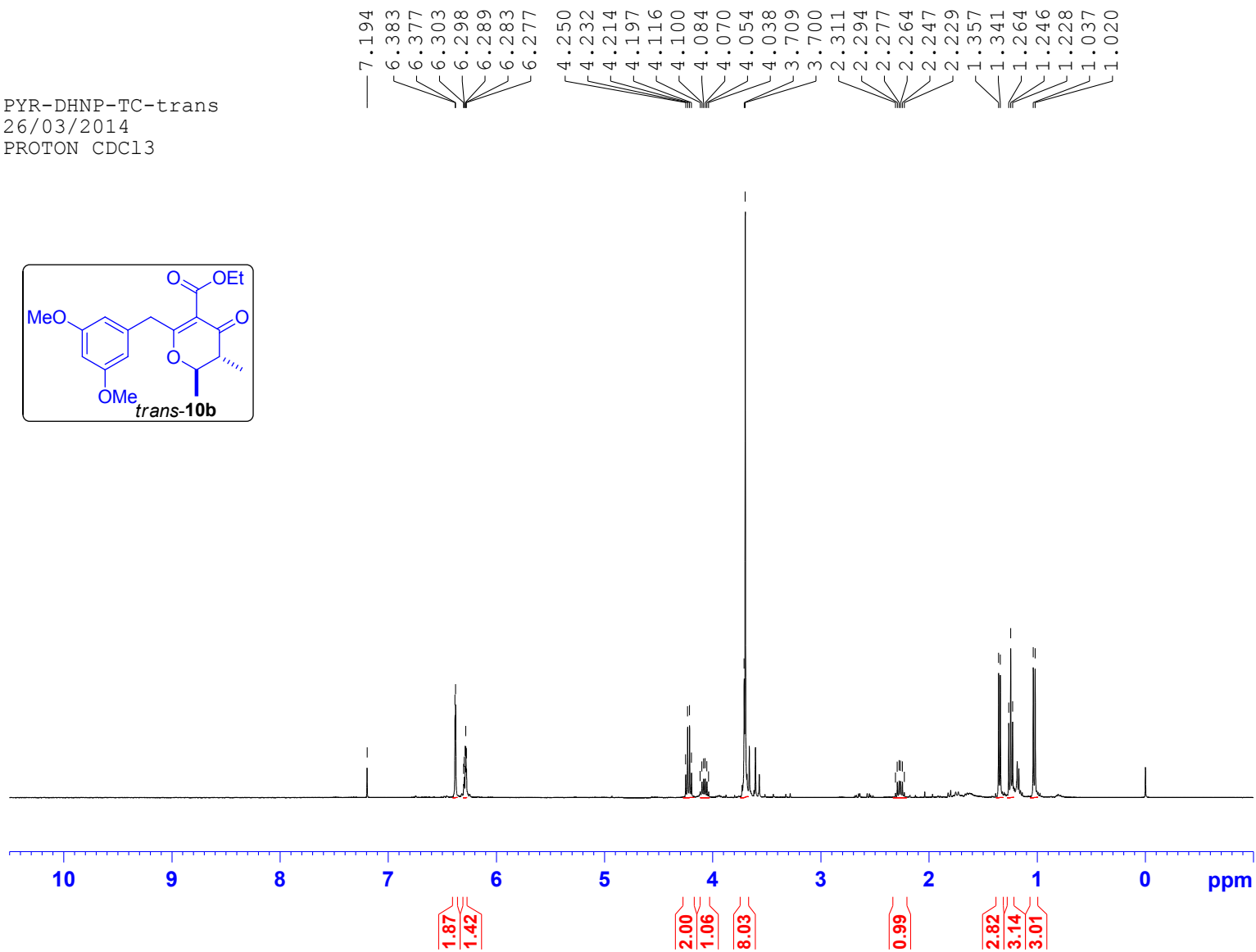
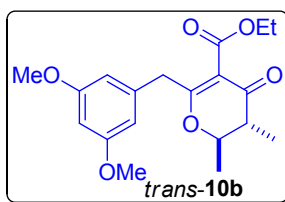
PYR-DHNP-SC
27/03/2014
PROTON CDC13

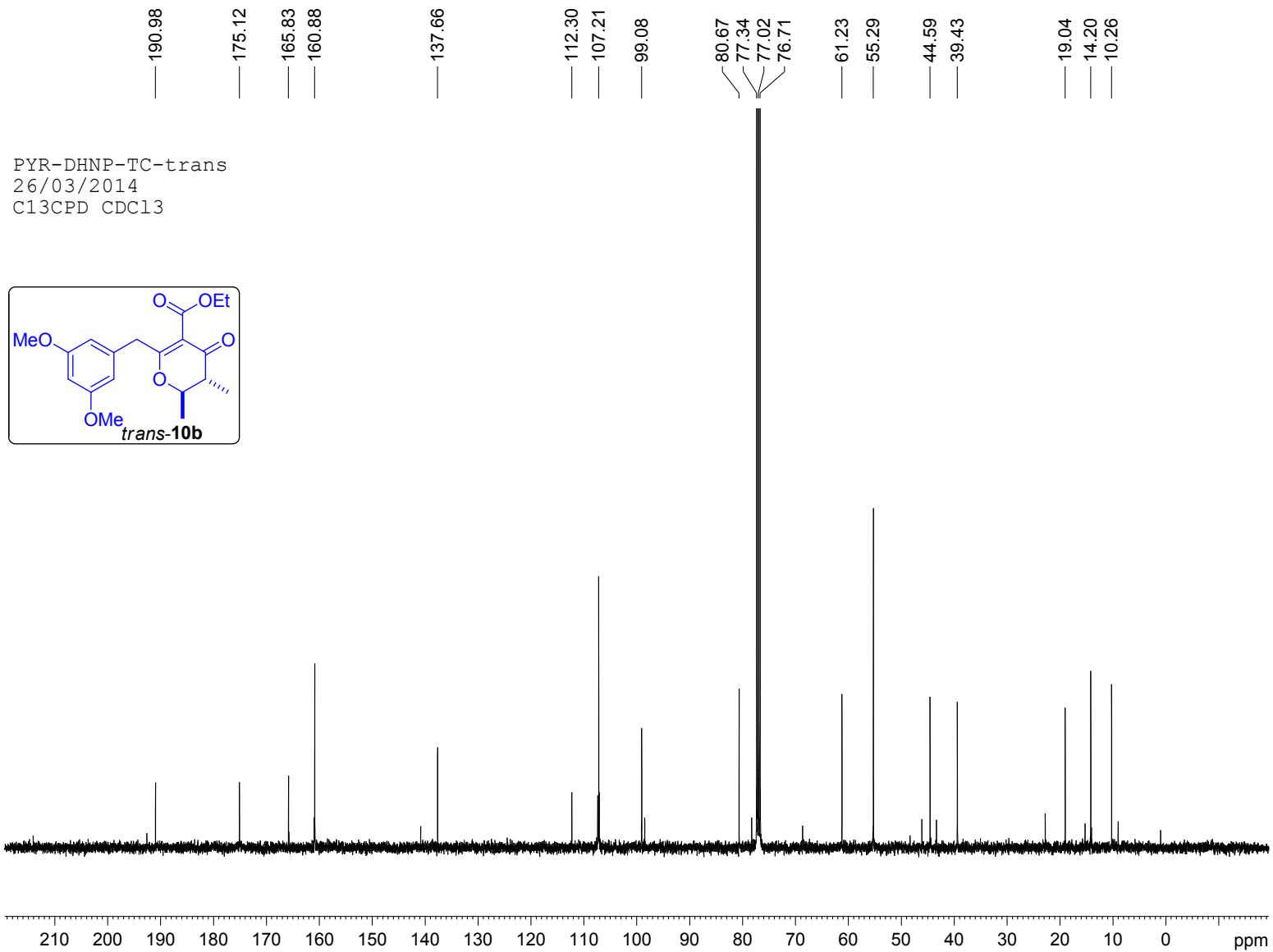


PYR-DHNP-SC
27/03/2014
C13CPD CDC13

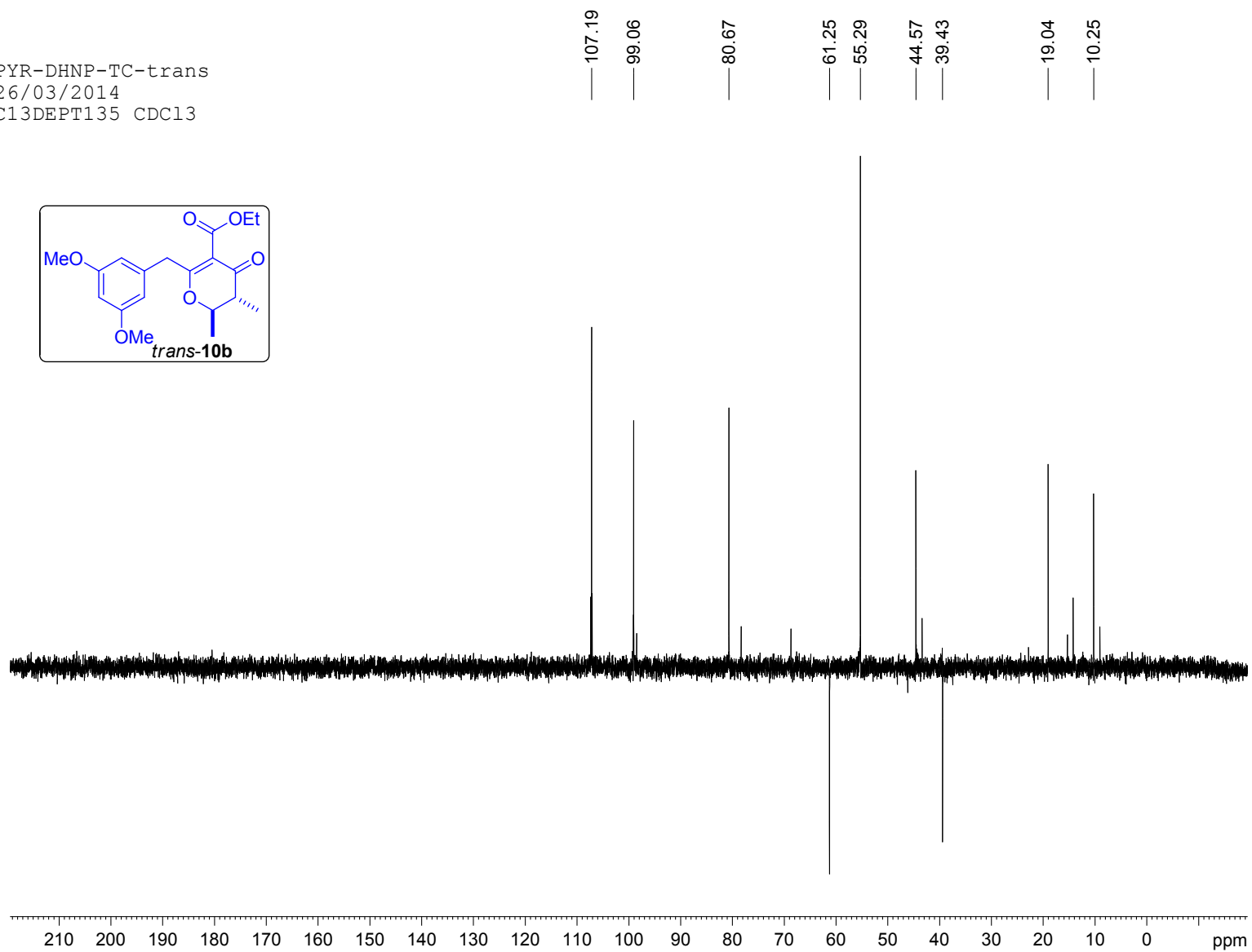
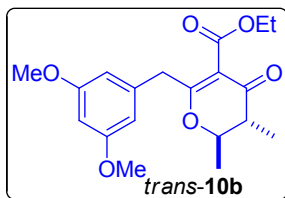


PYR-DHNP-TC-trans
26/03/2014
PROTON CDC13

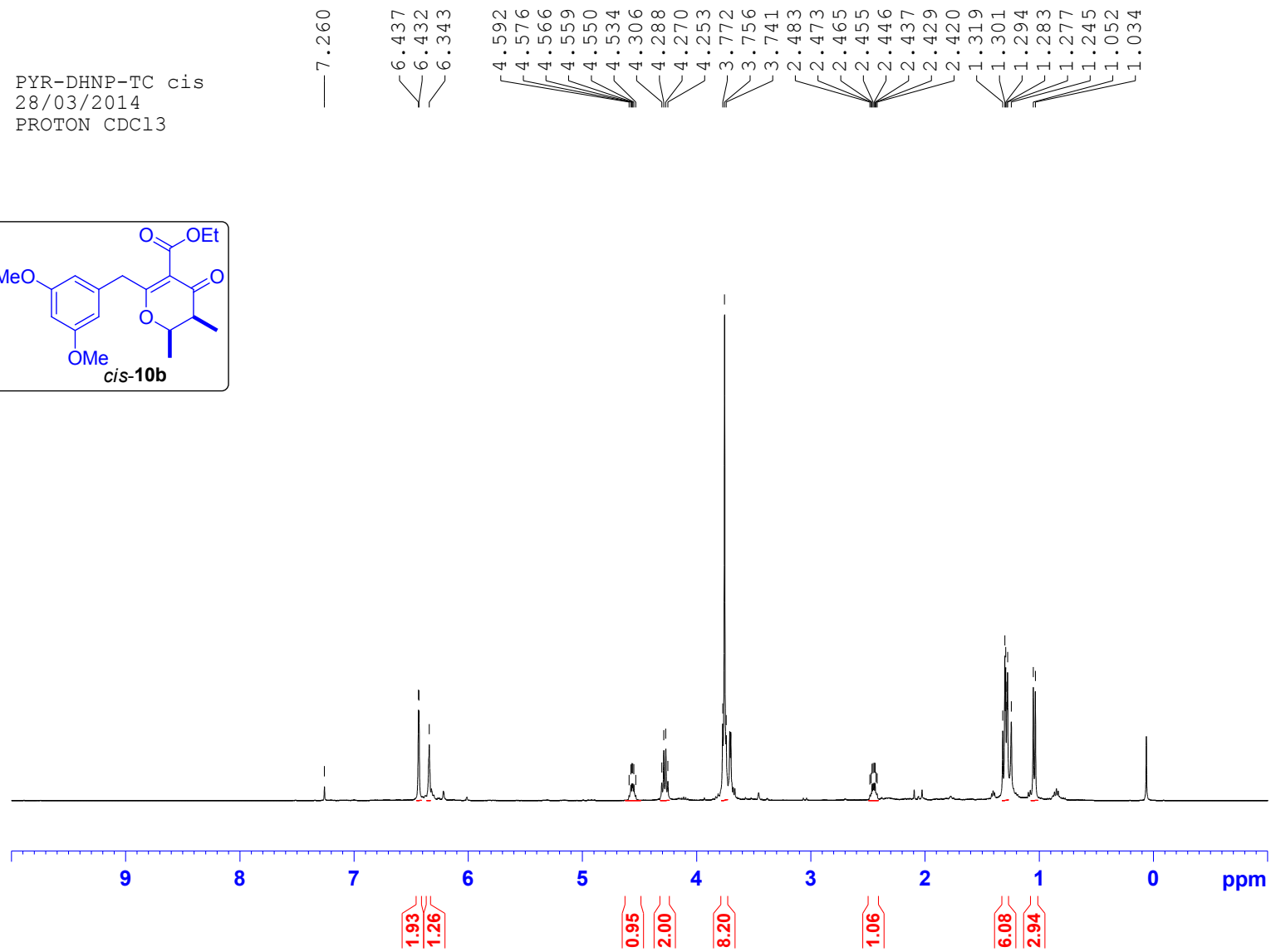
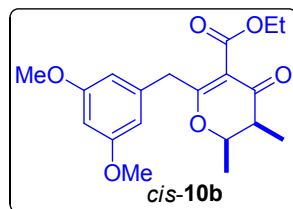




PYR-DHNP-TC-trans
26/03/2014
C13DEPT135 CDCl3

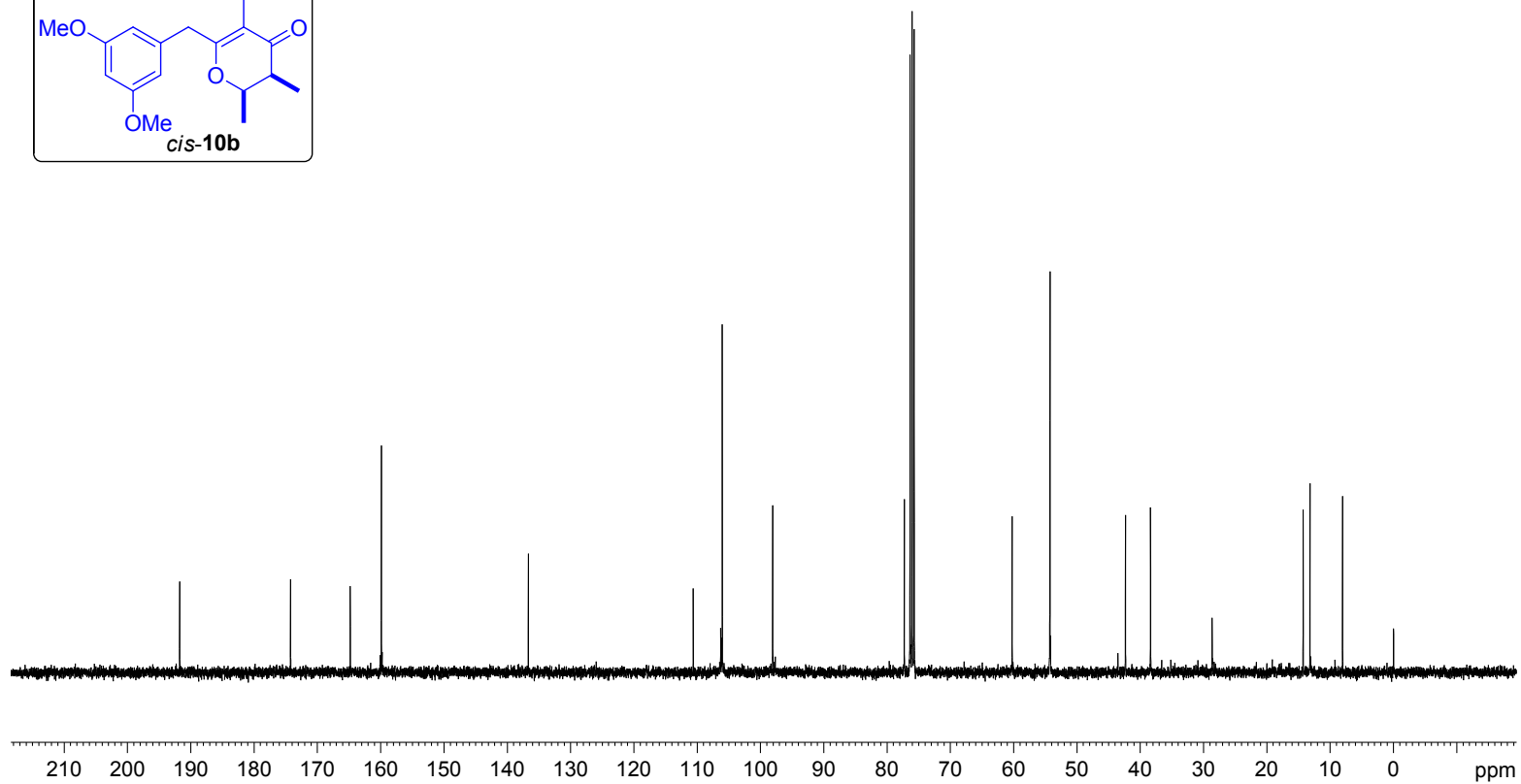
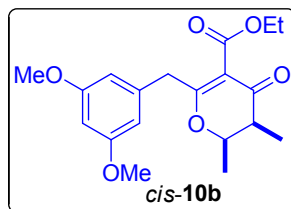


PYR-DHNP-TC cis
28/03/2014
PROTON CDC13

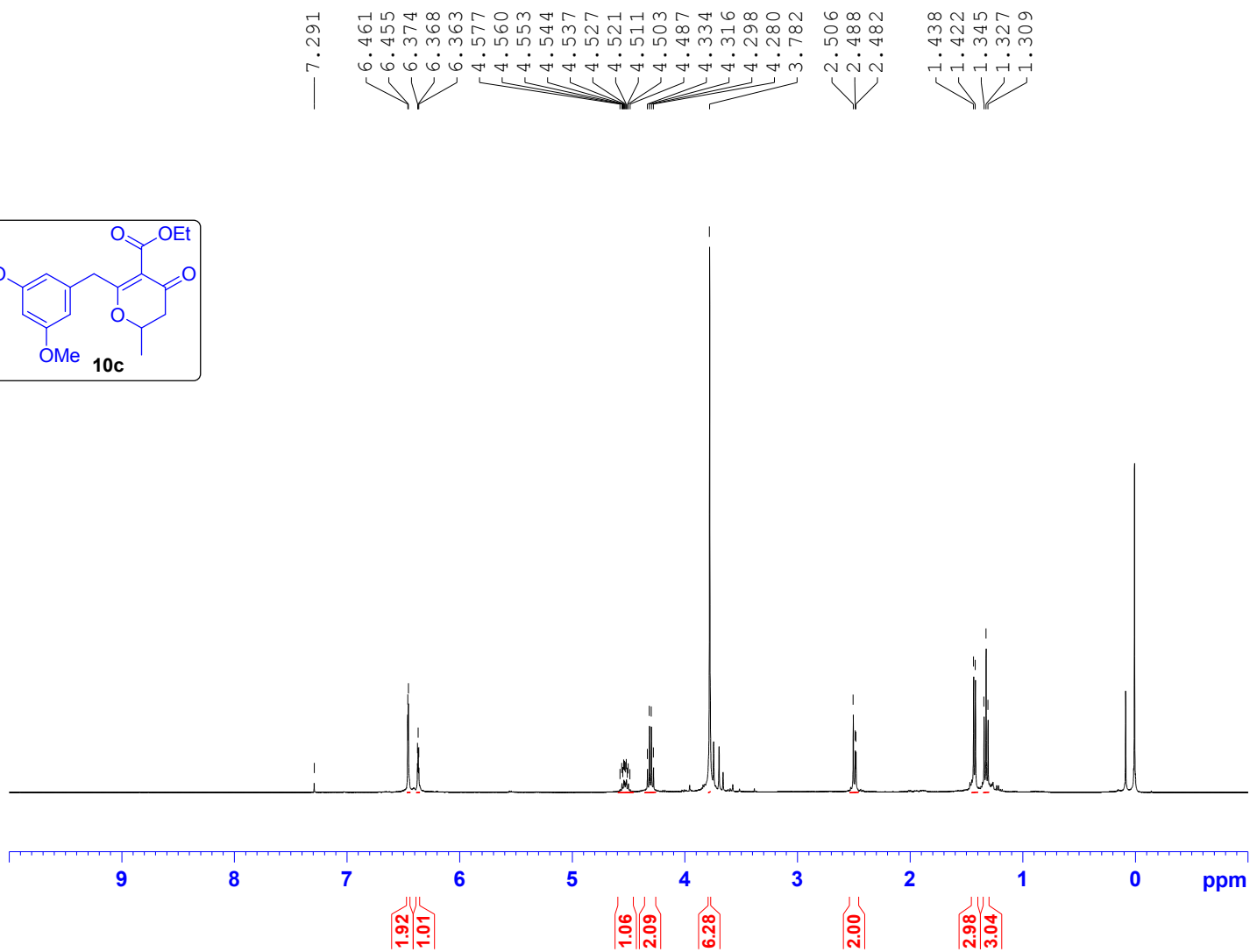
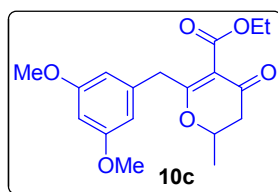


191.72
174.20
164.77
159.85
136.64
110.64
106.05
98.08
77.28
76.37
76.05
75.73
60.25
54.27
42.34
38.38
14.28
13.20
8.04

PYR-DHNP-TC cis
28/03/2014
C13CPD CDC13

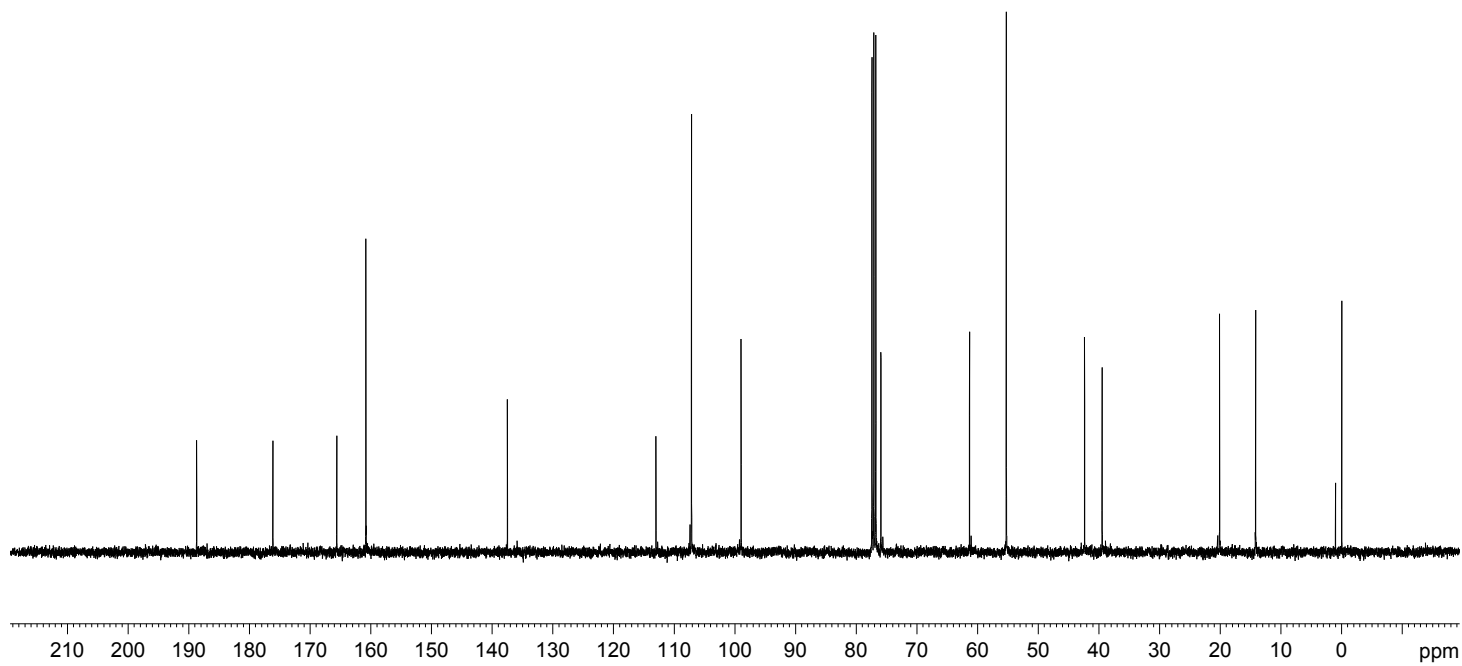
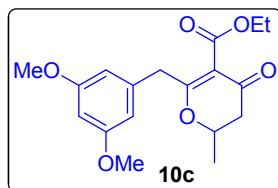


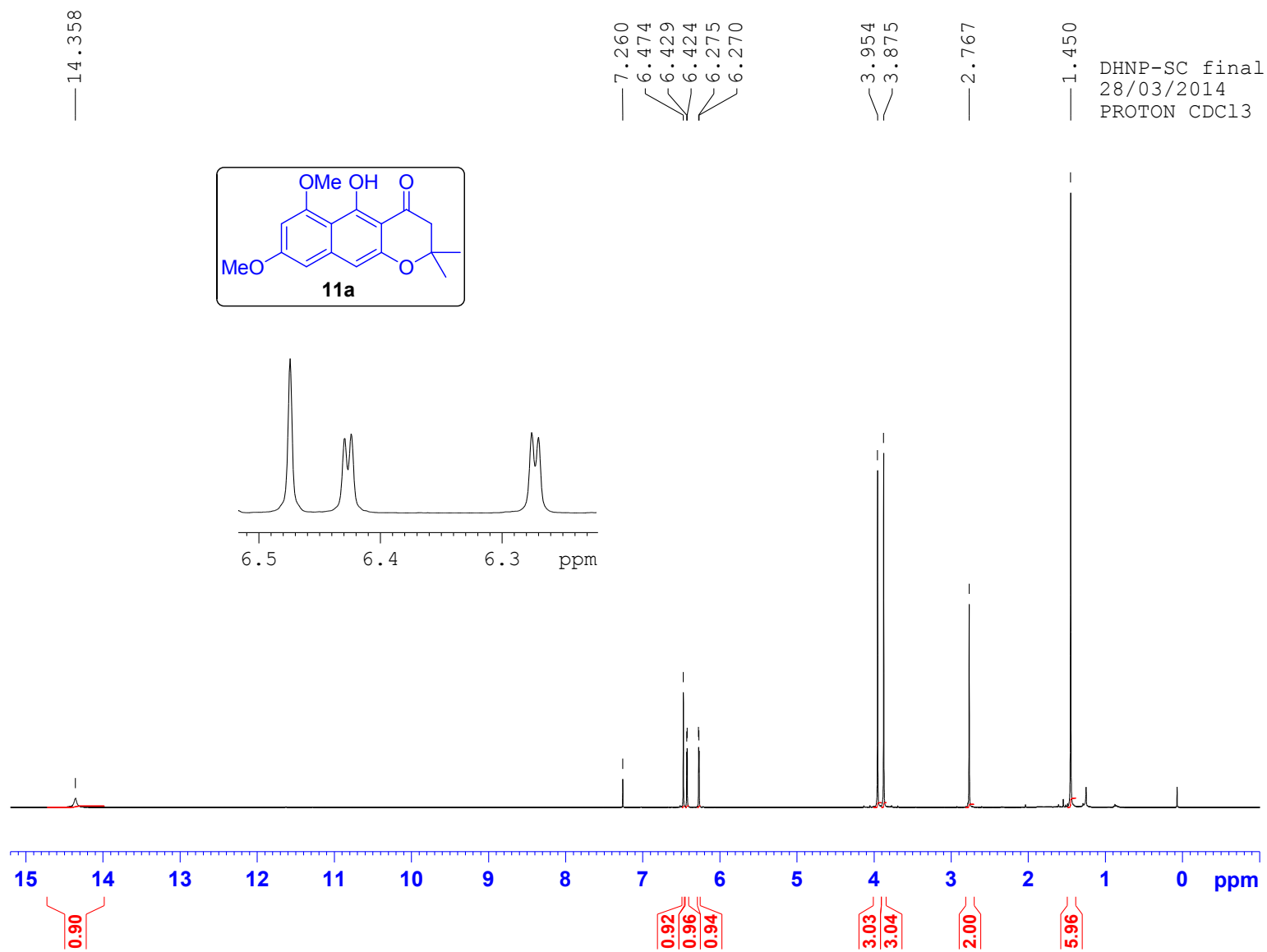
PYR-406 DMPAA-CRC
PROTON CDCl3 06/01/2014



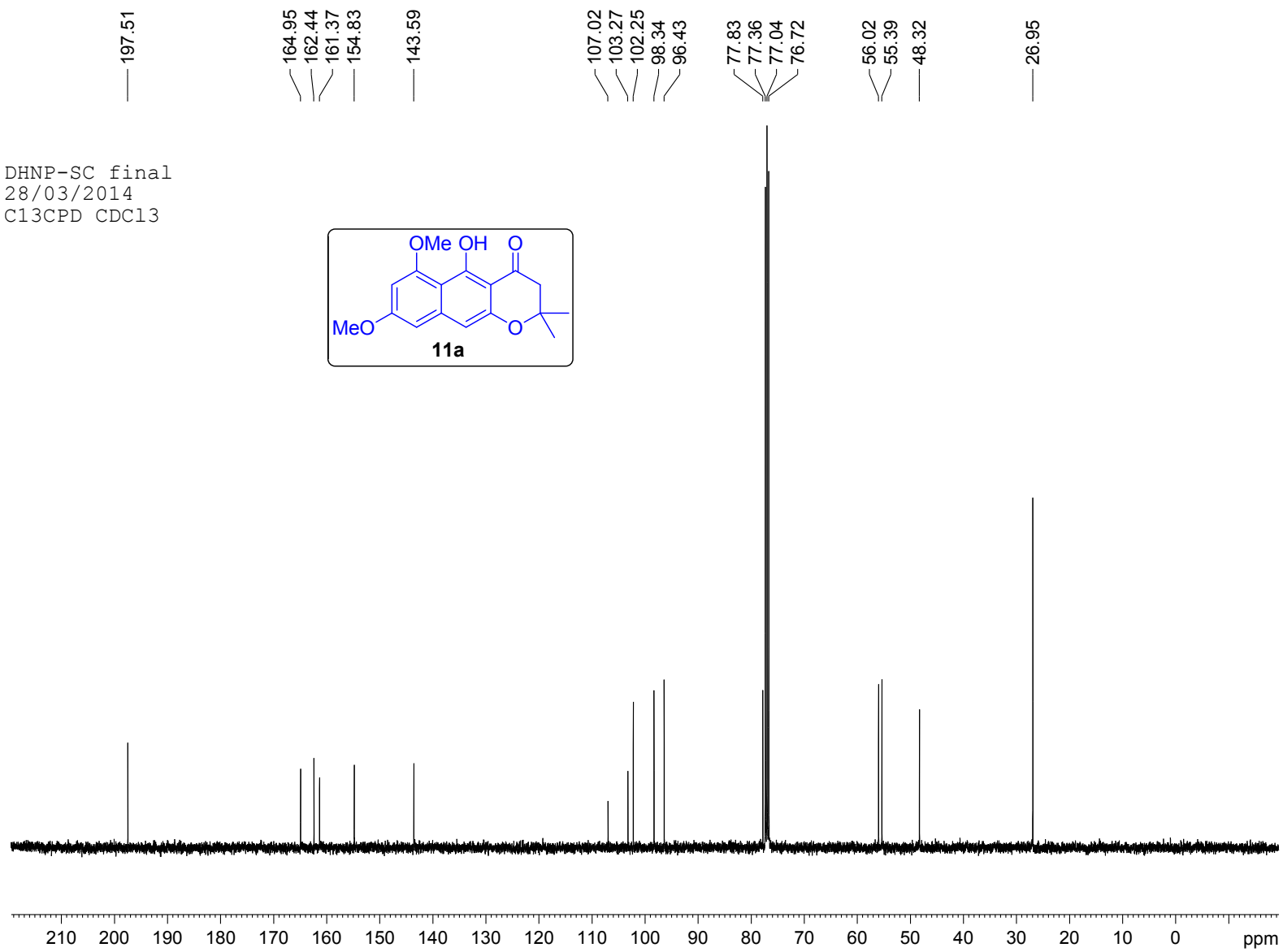
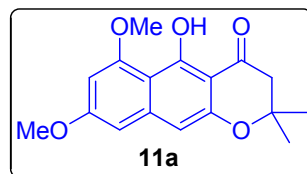
PYR-406 DMPAA-CRC
C13CPD CDC13 06/01/2014

188.73
176.16
165.63
160.85
137.52
113.03
107.17
99.00
77.43
77.11
76.80
75.95
61.34
55.28
42.39
39.49
20.13
14.19

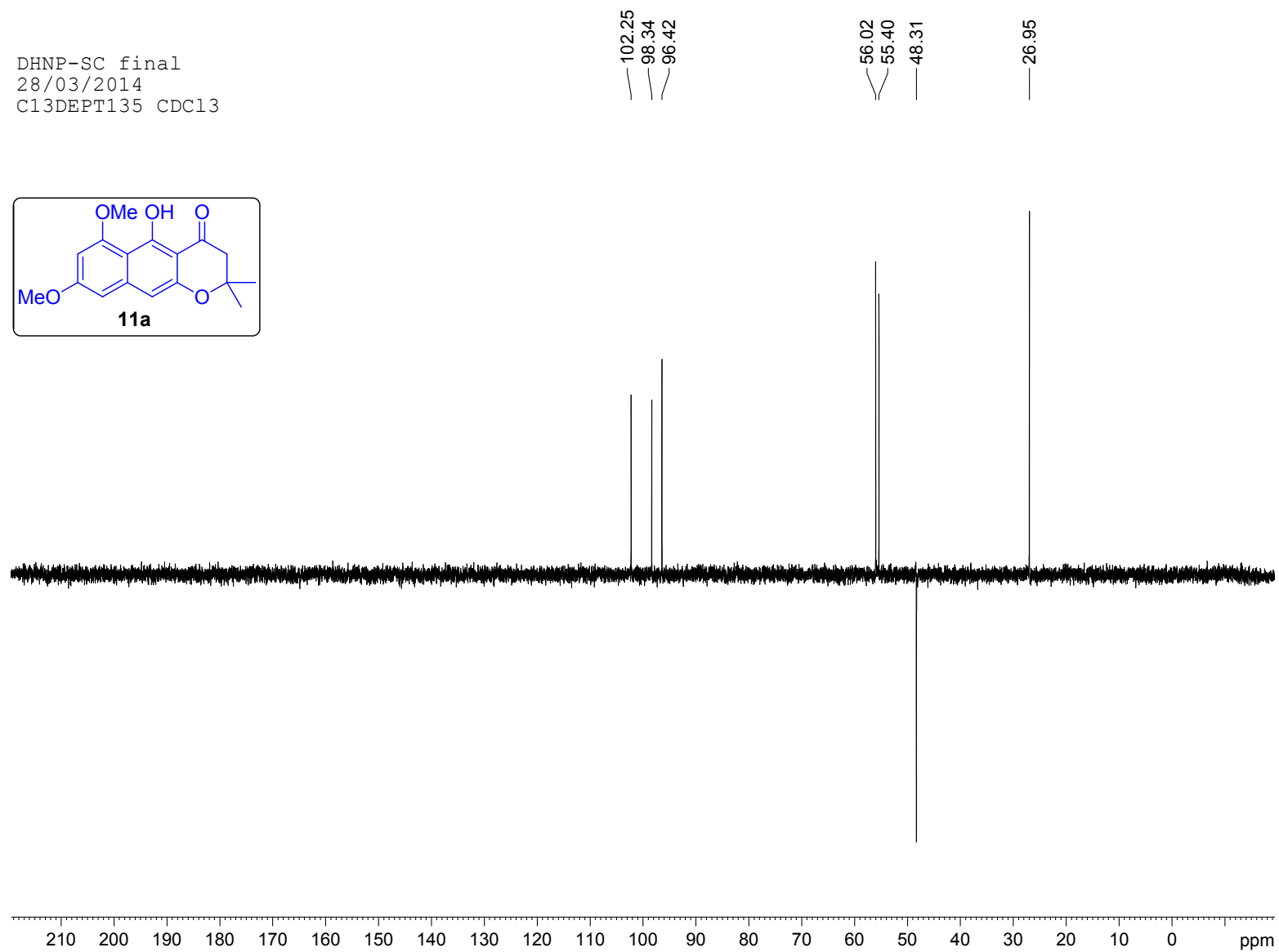
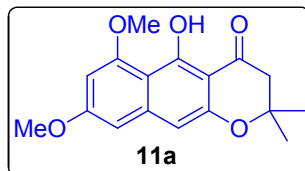




DHNP-SC final
28/03/2014
C13CPD CDC13



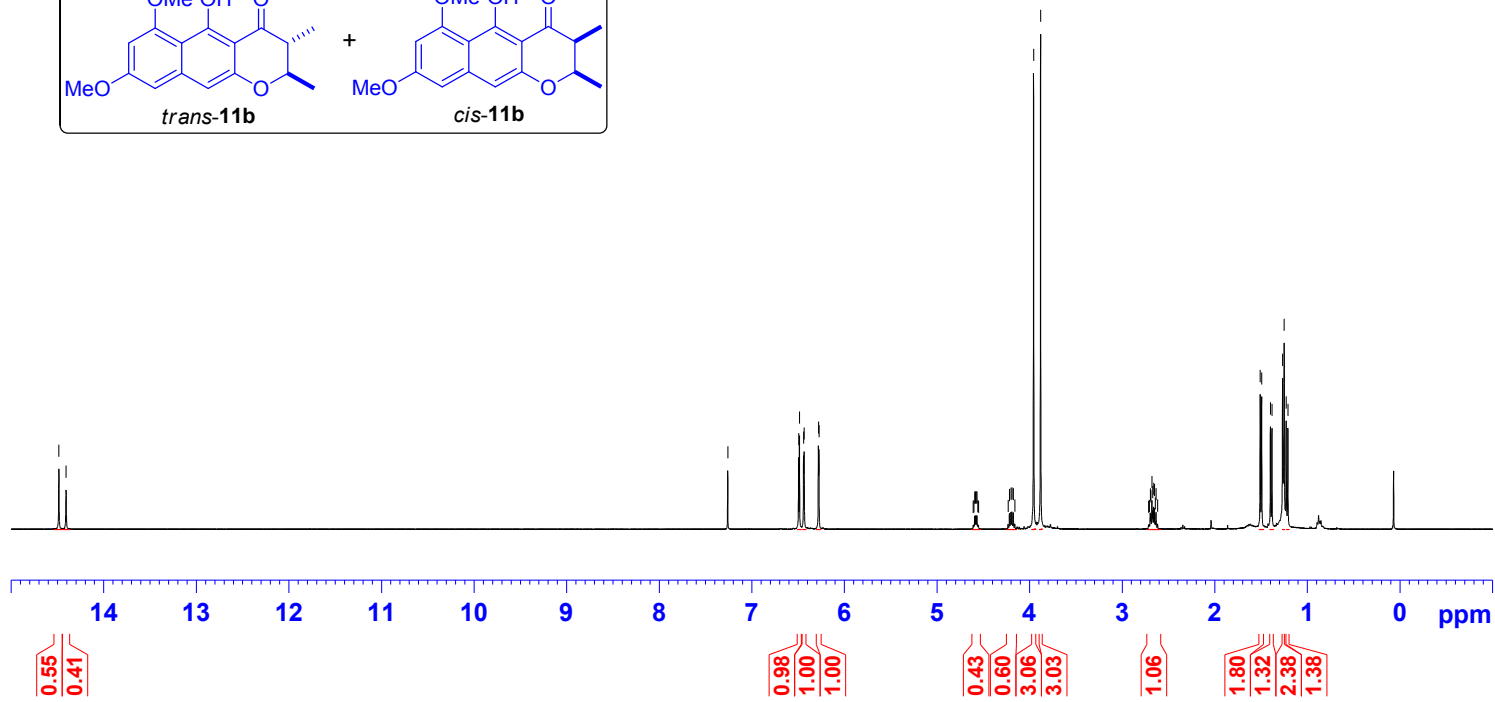
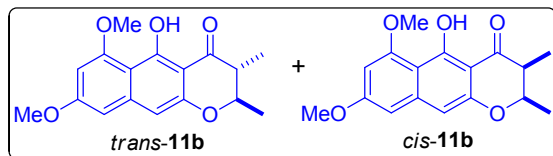
DHNP-SC final
28/03/2014
C13DEPT135 CDC13



14.484
14.406

DHNP-TC-C+T
28/03/2014
PROTON CDC13

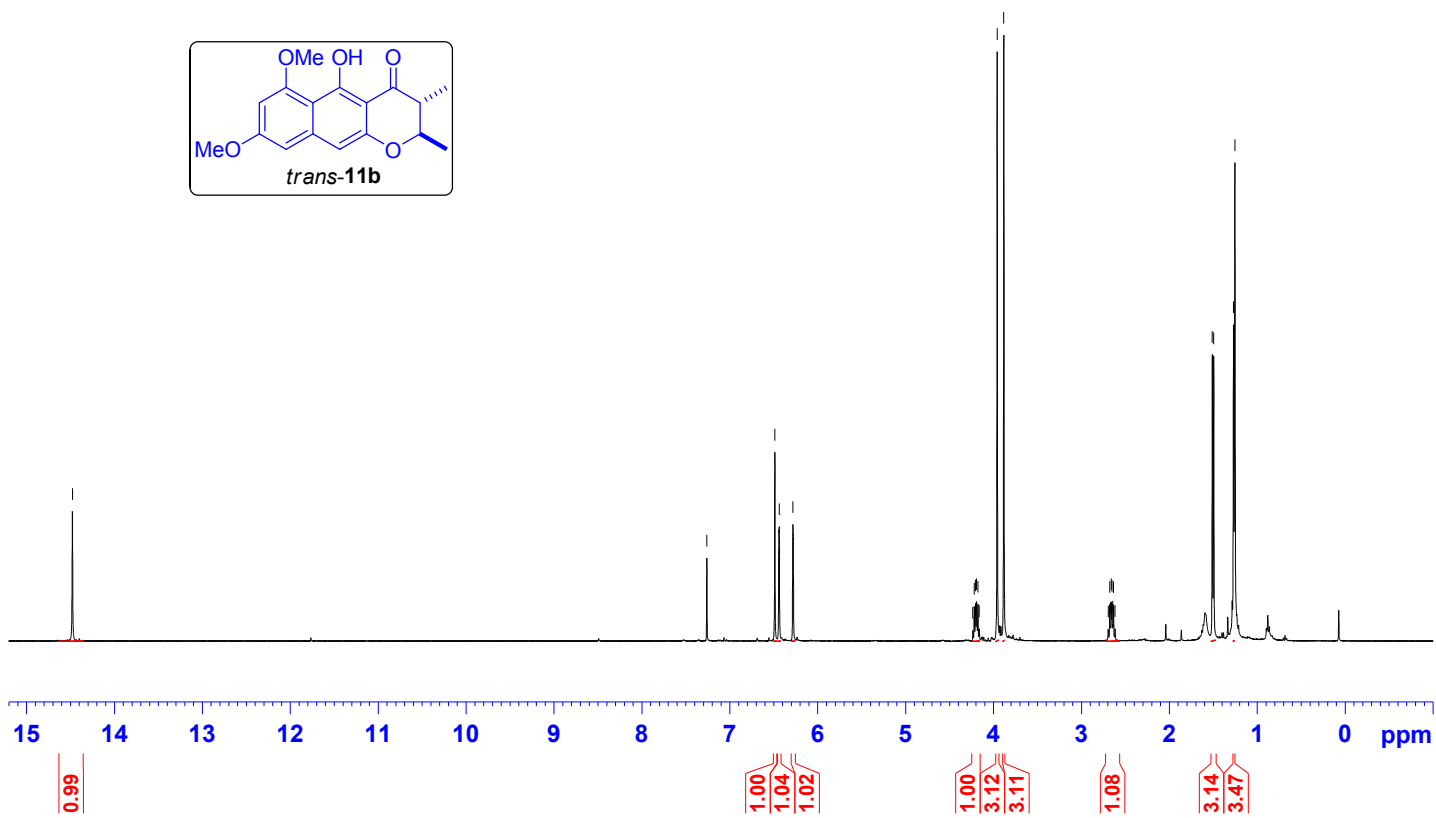
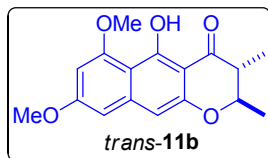
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6.494
6.485
6.440
6.435
6.280
6.275
4.609
4.600
4.592
4.584
4.576
4.568
4.560
4.551
4.232
4.217
4.201
4.191
4.175
4.159
3.956
3.881
2.715
2.707
2.696
2.689
2.678
2.670
2.660
2.652
2.643
2.634
2.616
1.509
1.493



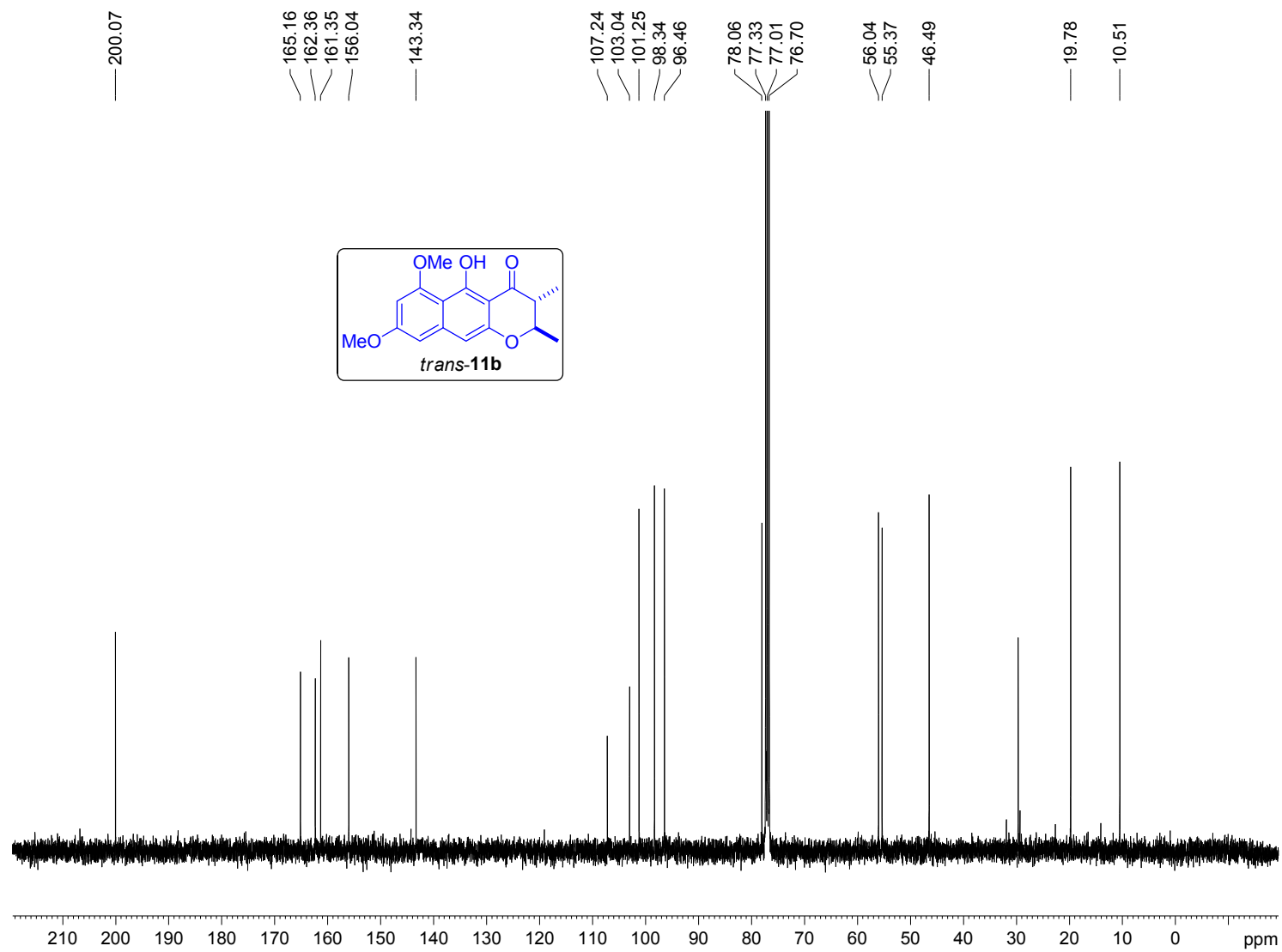
PYR-DHNP-TC-trans 02/05/2014
PROTON CDC13

— 14.474

7.260
6.486
6.436
6.281
4.233
4.218
4.202
4.191
4.176
4.160
3.957
3.881
2.694
2.676
2.668
2.659
2.651
2.642
2.633
2.616
1.509
1.494
1.269
1.253

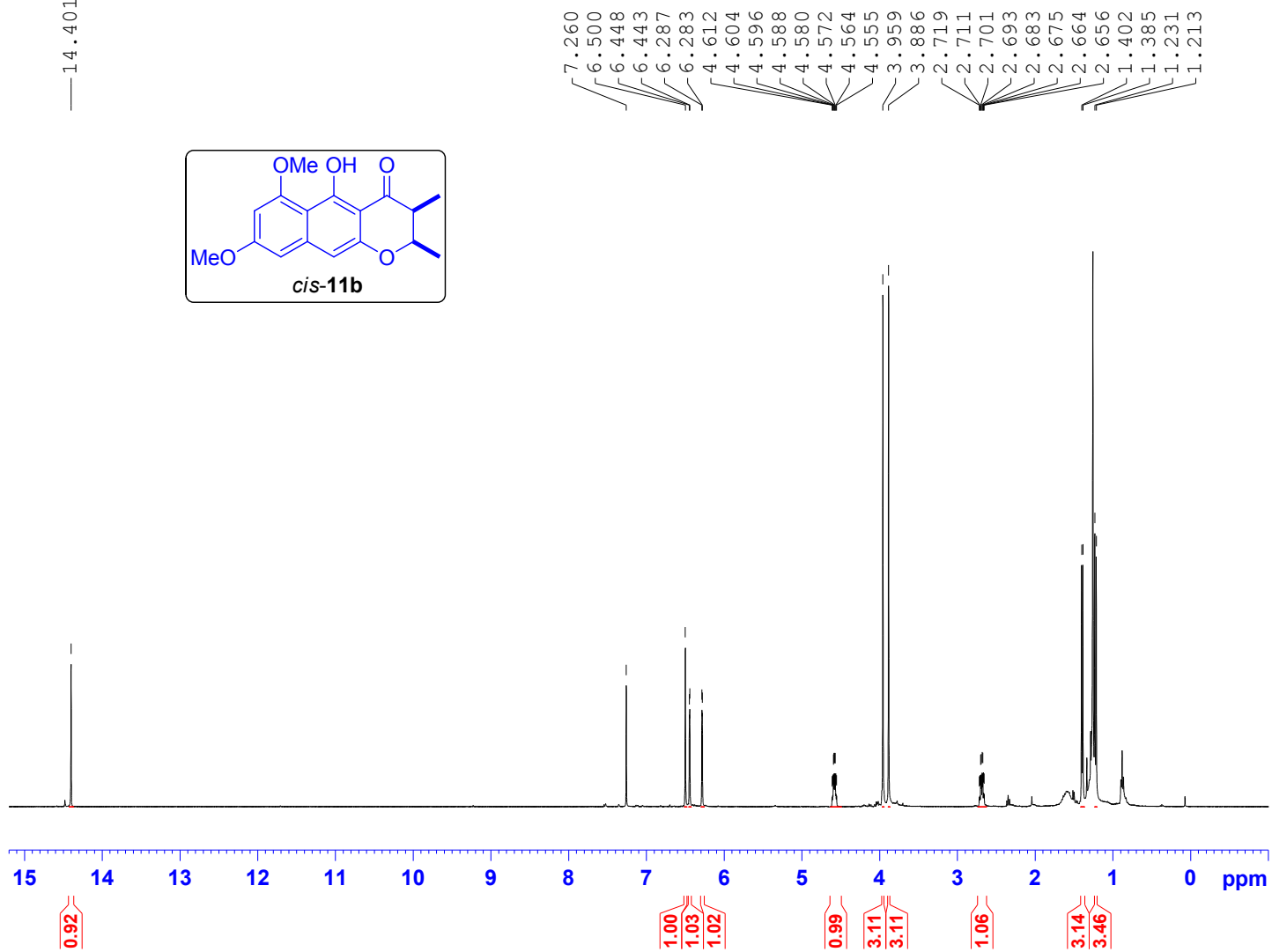
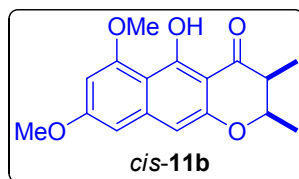


PYR-DHNP-TC-trans 02/05/2014
C13CPD CDCl3

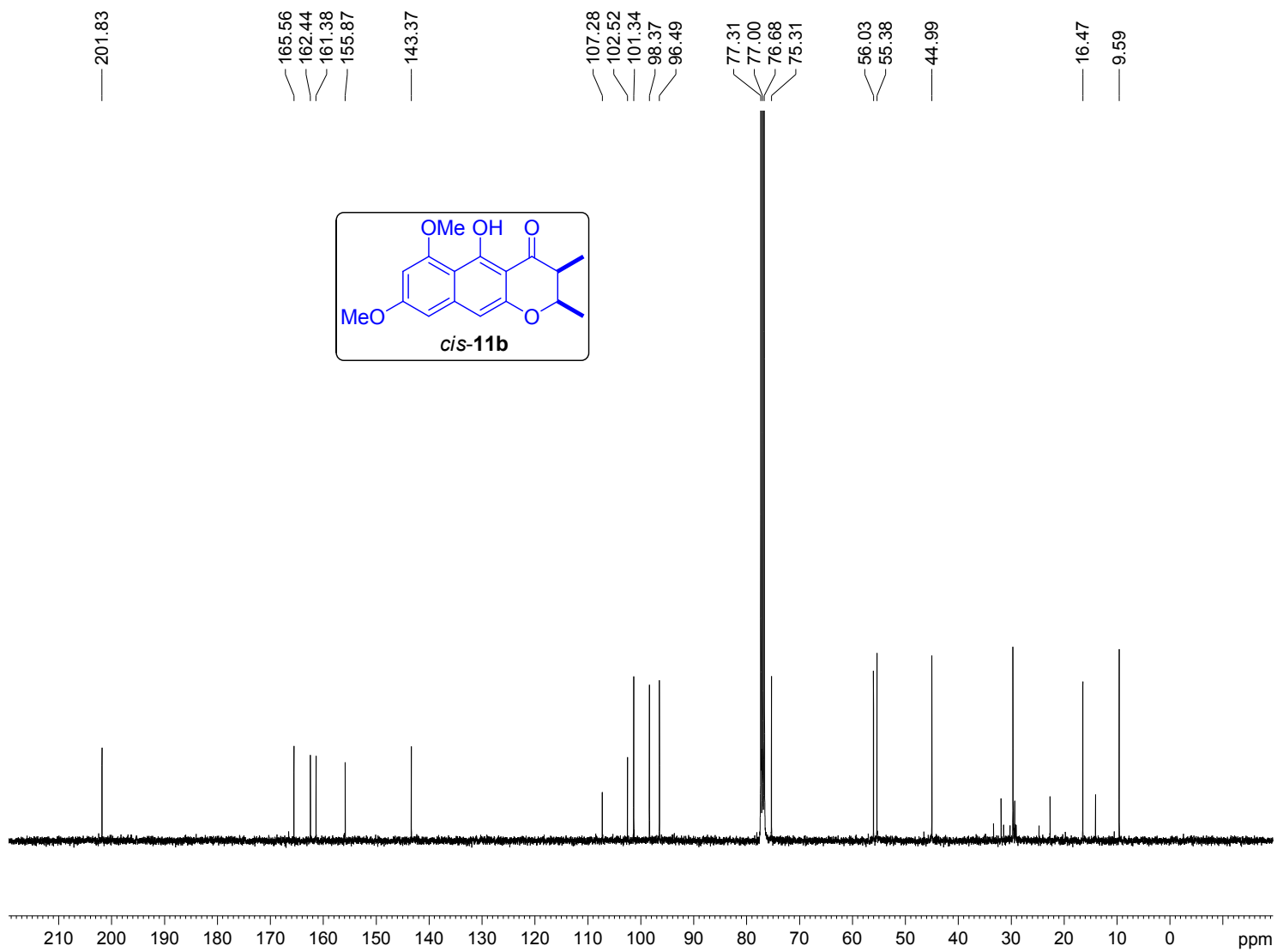


PYR-DHNP-TC-cis 02/05/2014
PROTON CDC13

— 14.401

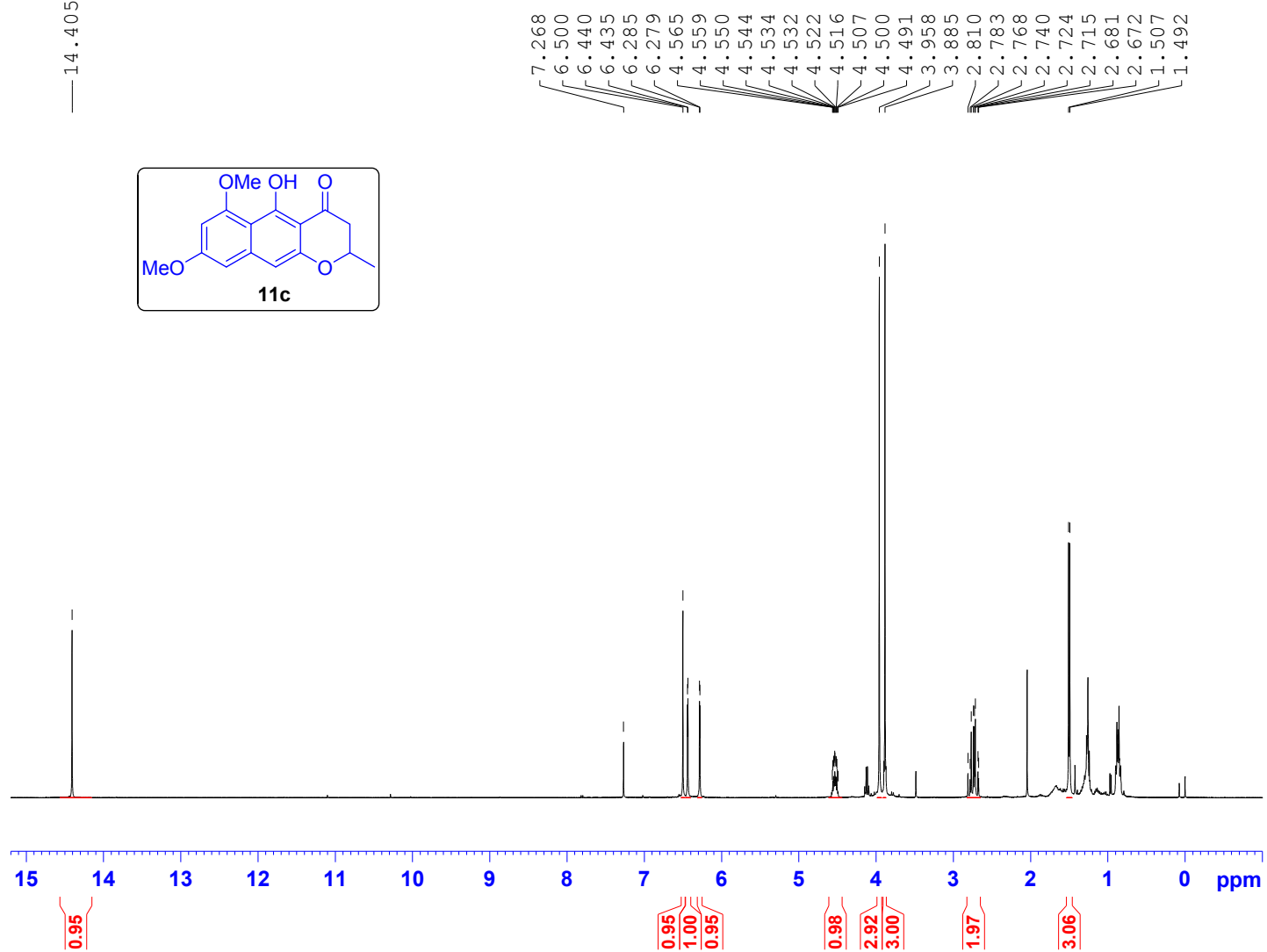
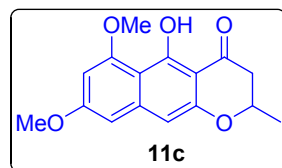


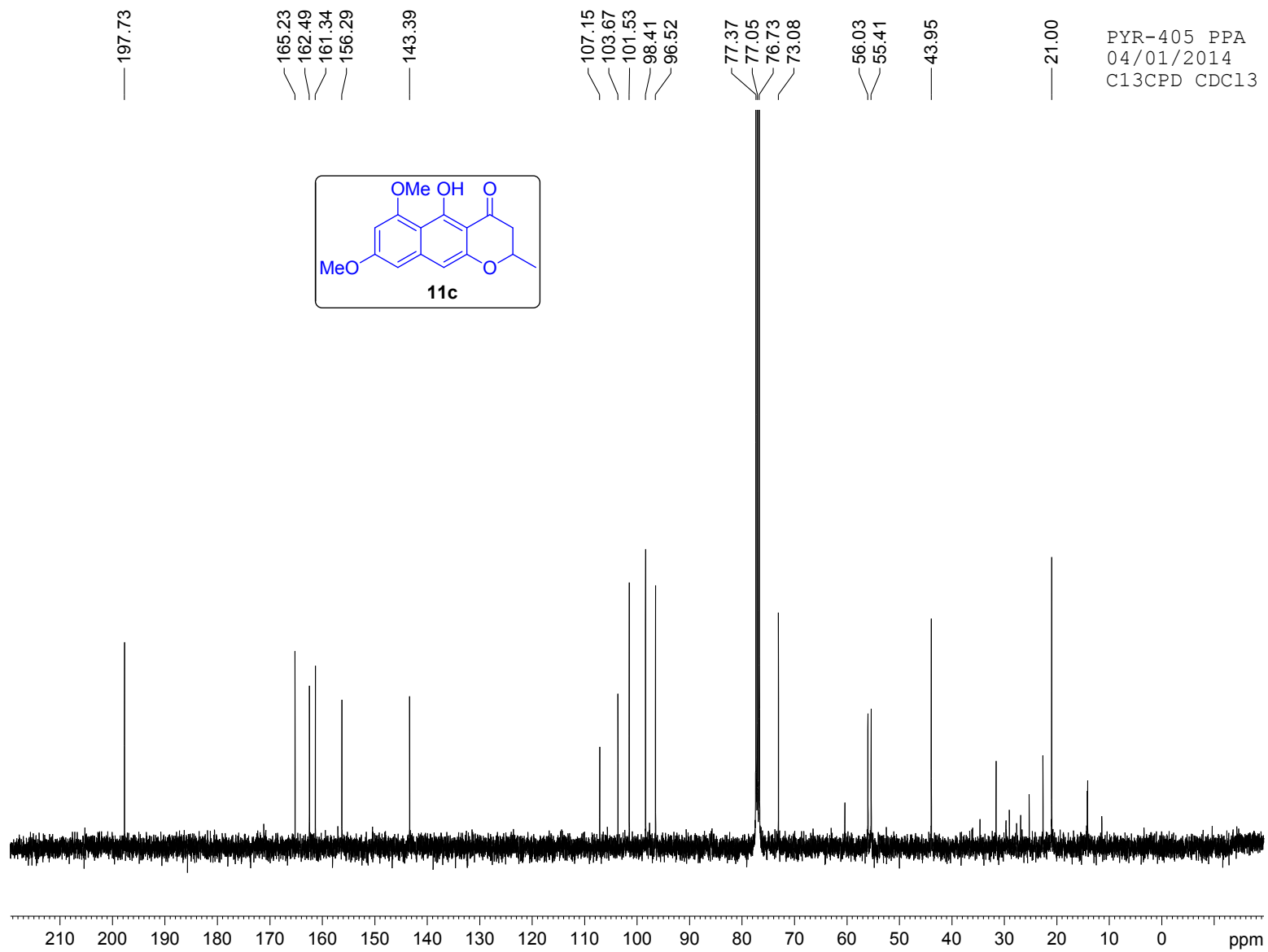
PYR-DHNP-TC-cis 02/05/2014
C13CPD CDC13



PYR-405 PPA
PROTON CDCl3 04.01.2014

— 14.405





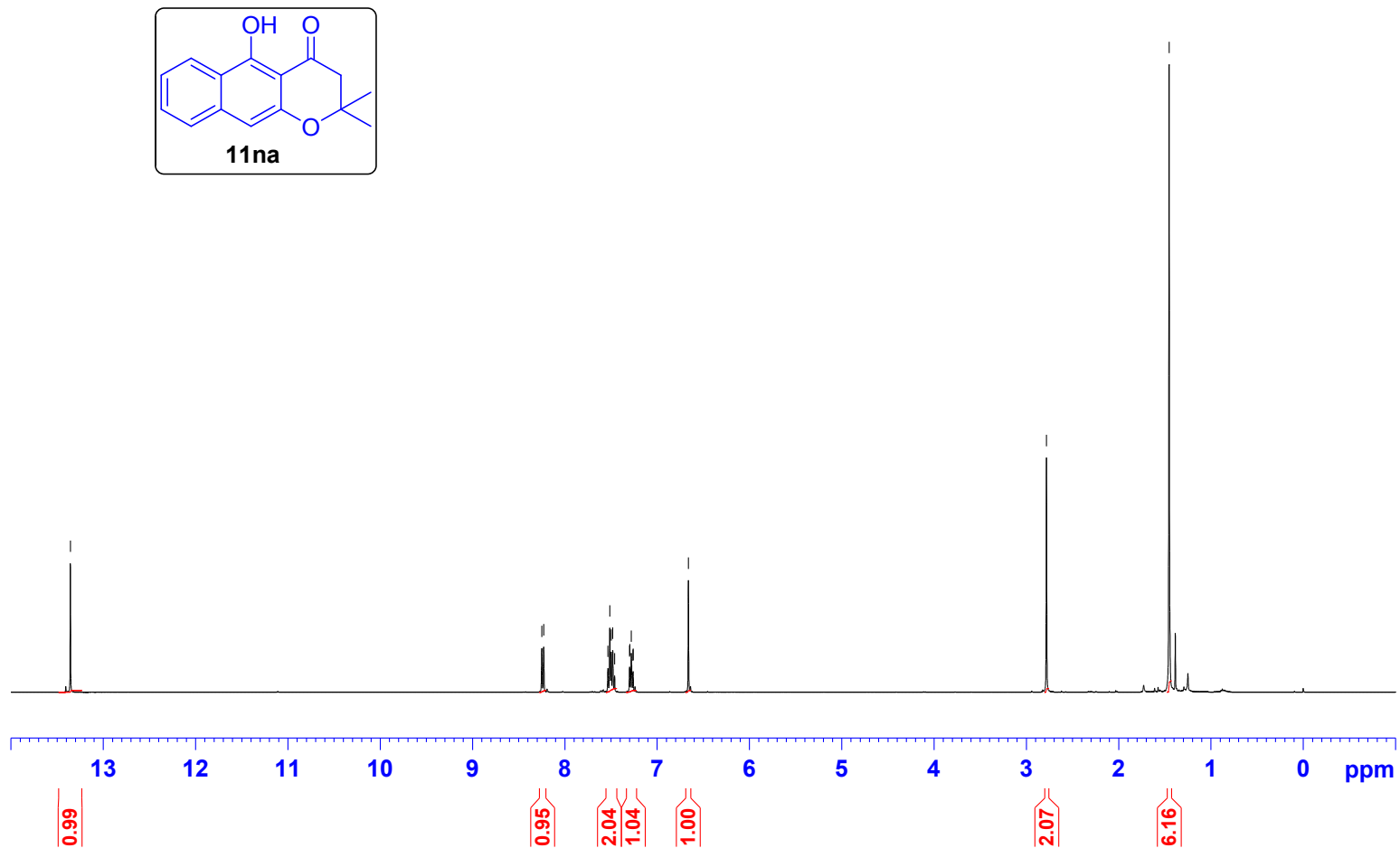
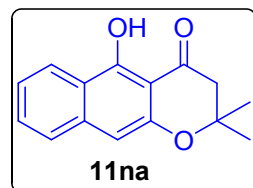
PYR-220a
PROTON CDC13

—13.355

8.249
8.229
7.532
7.513
7.497
7.480
7.460
7.300
7.297
7.280
7.262
7.260
6.661

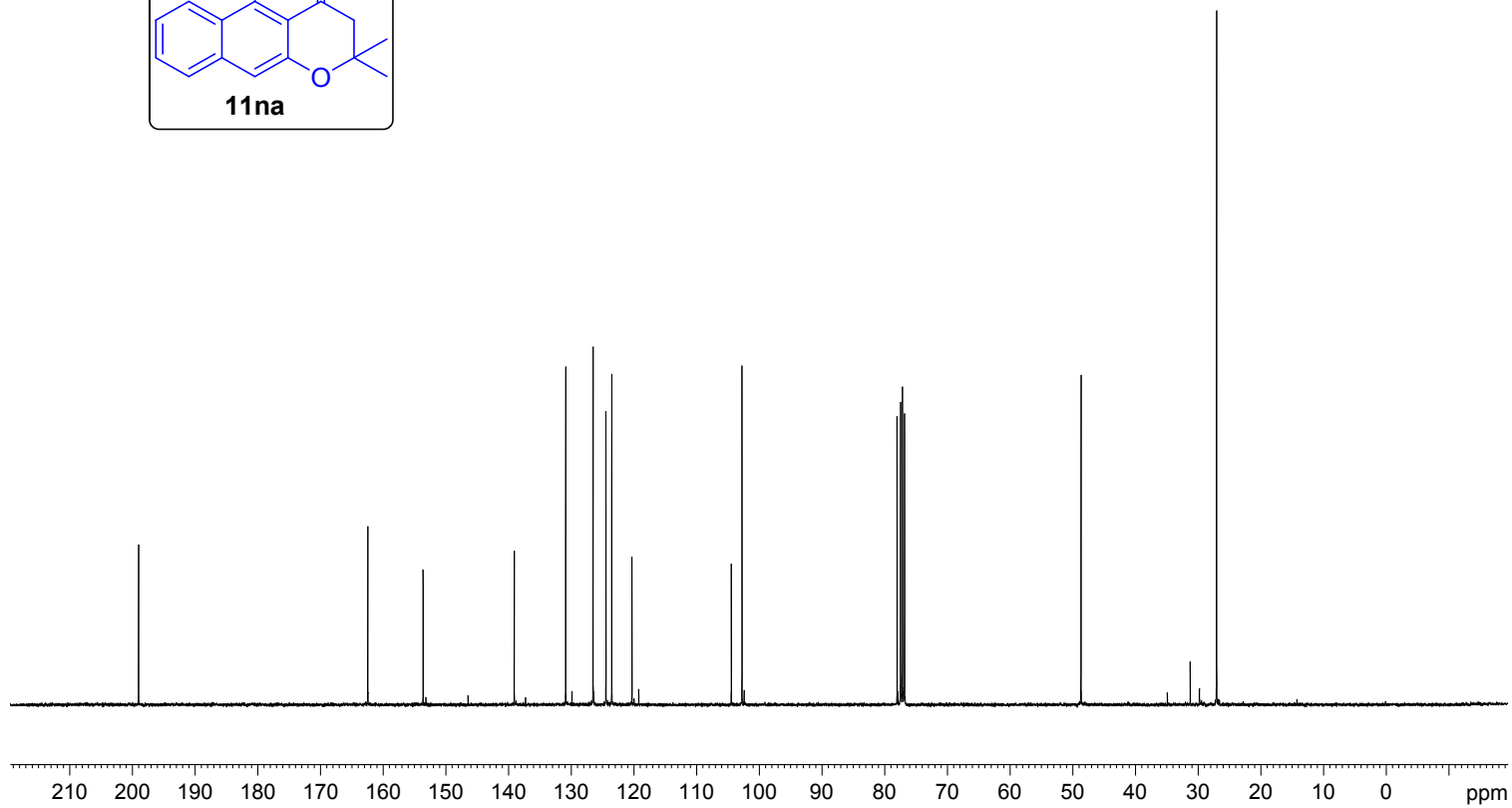
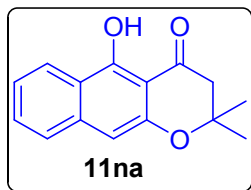
—2.781

—1.453

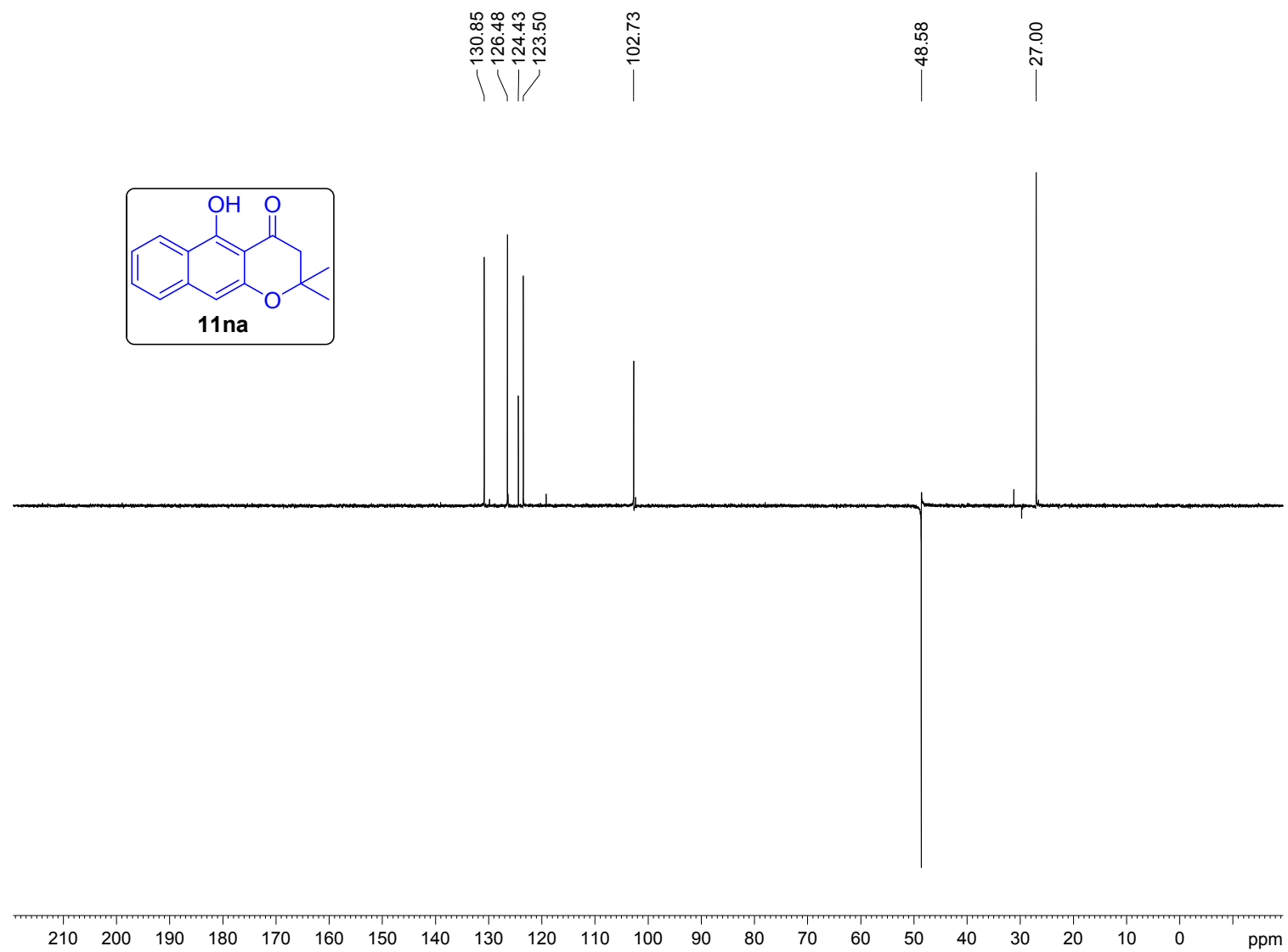


PYR -220a
C13CPD CDC13

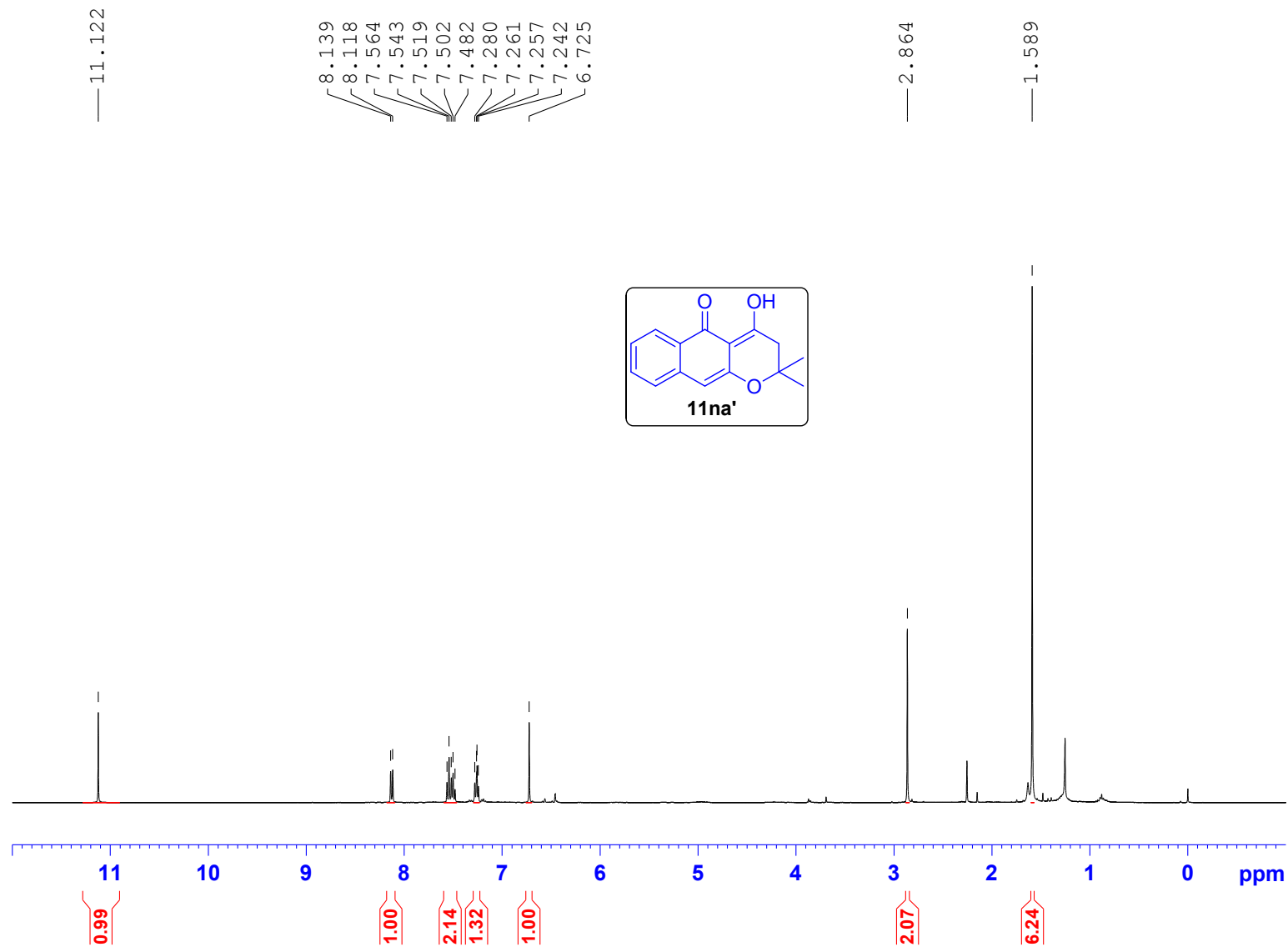
198.98
162.42
153.59
139.05
130.85
126.48
124.43
123.50
120.28
104.43
102.72
77.98
77.43
77.11
76.79
48.63
27.00



PYR -220a
C13DEPT135 CDC13



PYR-220b
PROTON CDC13



Pyr-220b
C13CPD CDC13

197.89

159.44

155.60

139.38

130.72

126.40

123.94

123.08

119.49

105.29

102.58

80.43

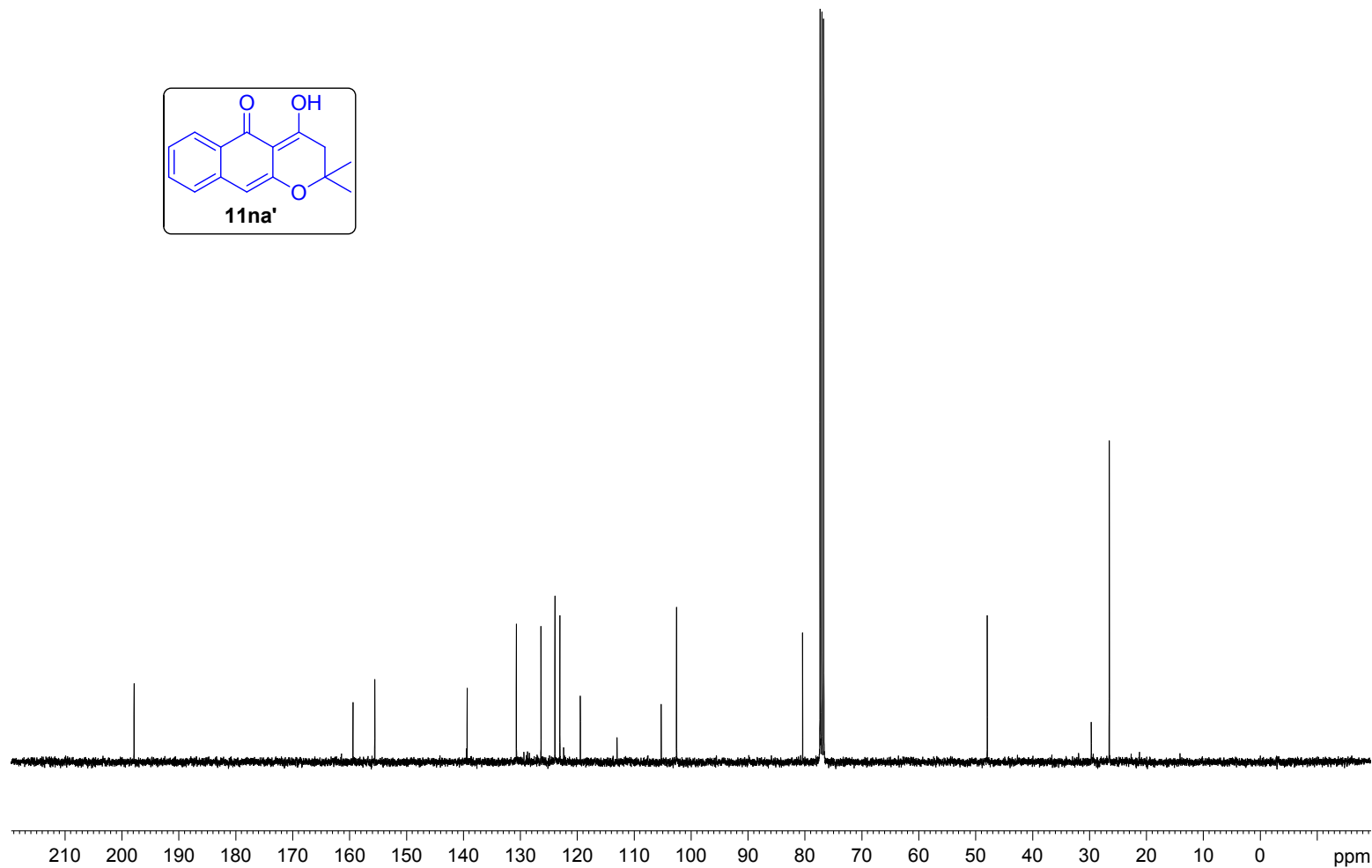
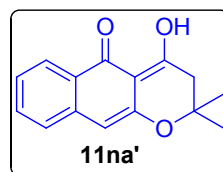
77.36

77.04

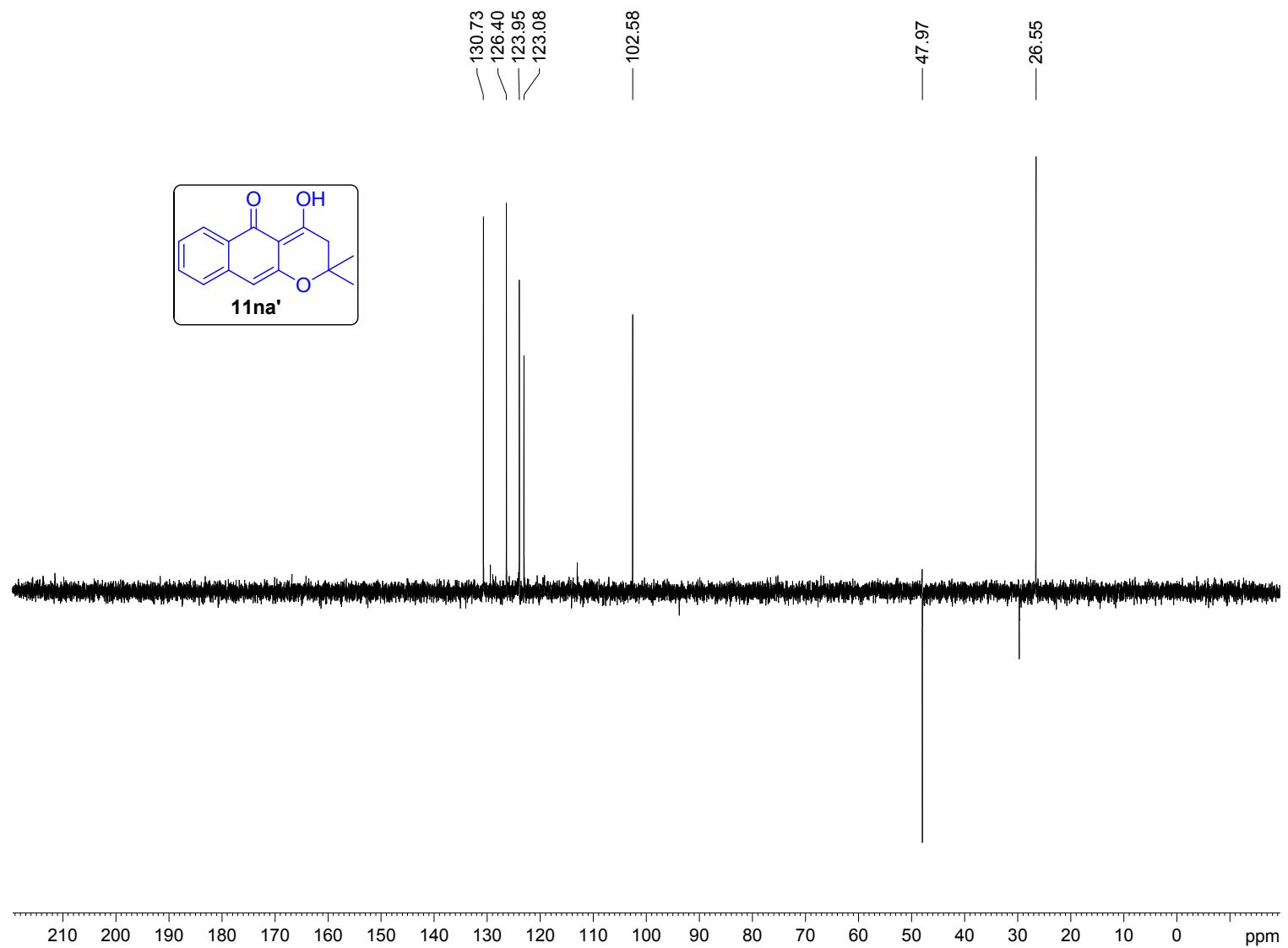
76.72

47.98

26.55

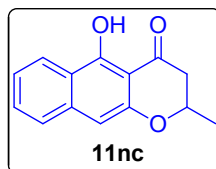


Pyr-220b
C13DEPT135 CDC13

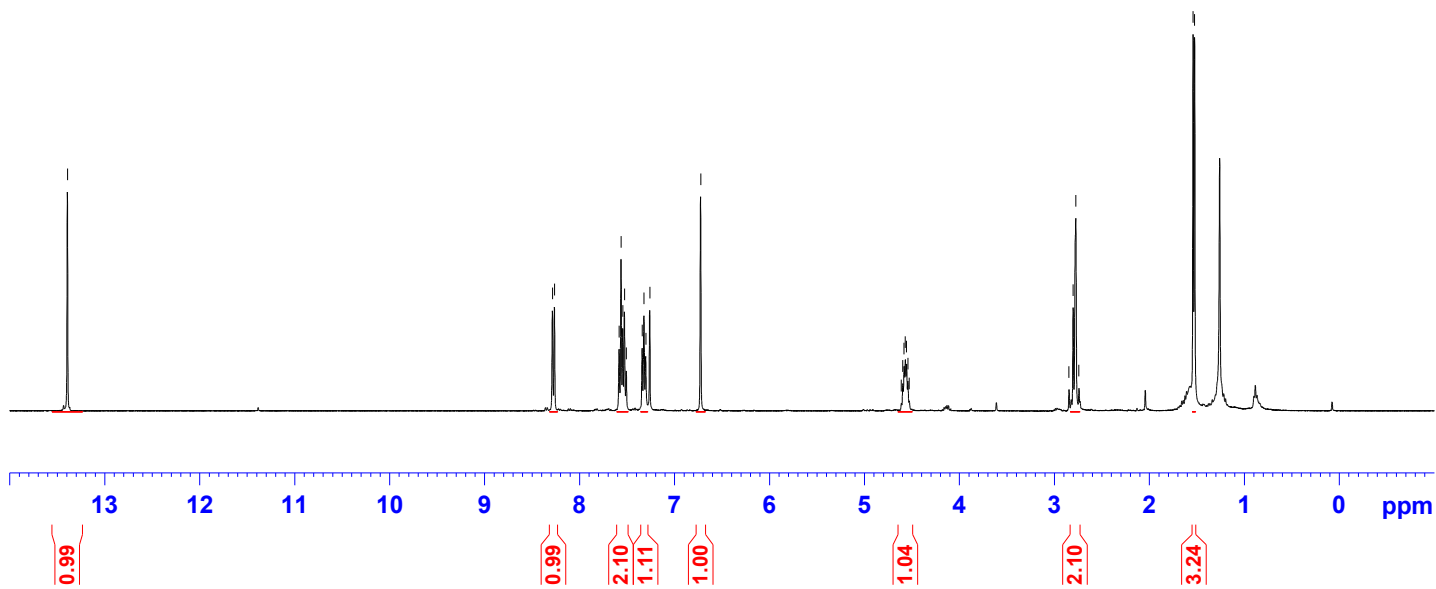


PA-DHNP-CR-Fr1
PROTON CDCl3 17/04/2013

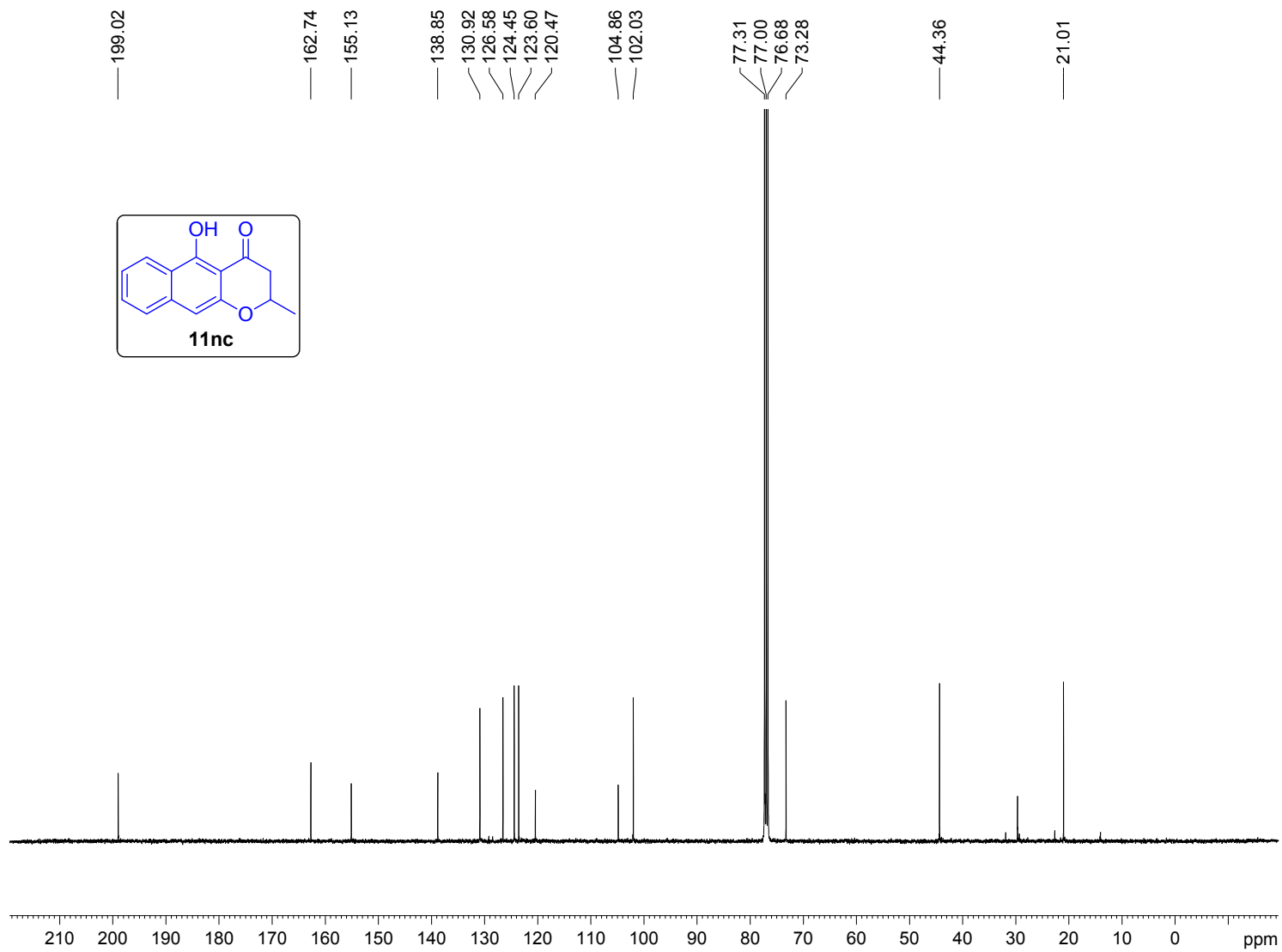
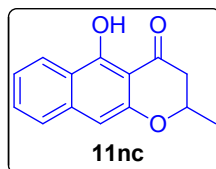
— 13.392



8.284
8.263
7.582
7.562
7.544
7.527
7.507
7.339
7.321
7.302
7.260
6.724
4.611
4.596
4.583
4.570
4.557
4.543
4.528
2.846
2.803
2.775
2.741
1.540
1.524



PA-DHNP-CR-Fr1
C13CPD CDCl3 17.04.2014



PA-DHNP-CR-Fr1
C13DEPT135 CDC13 17.04.2014

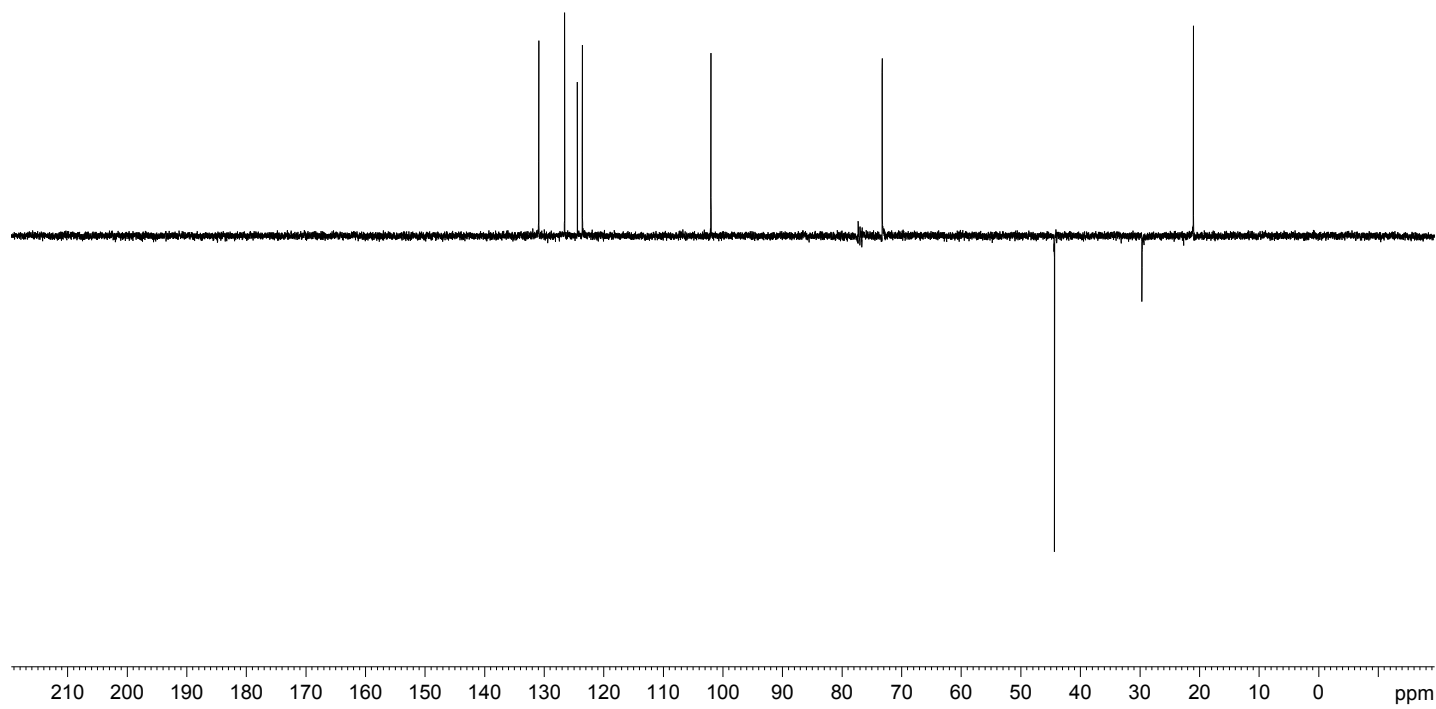
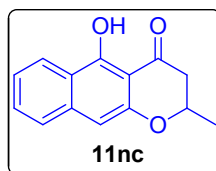
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126.59
124.45
123.61

102.03

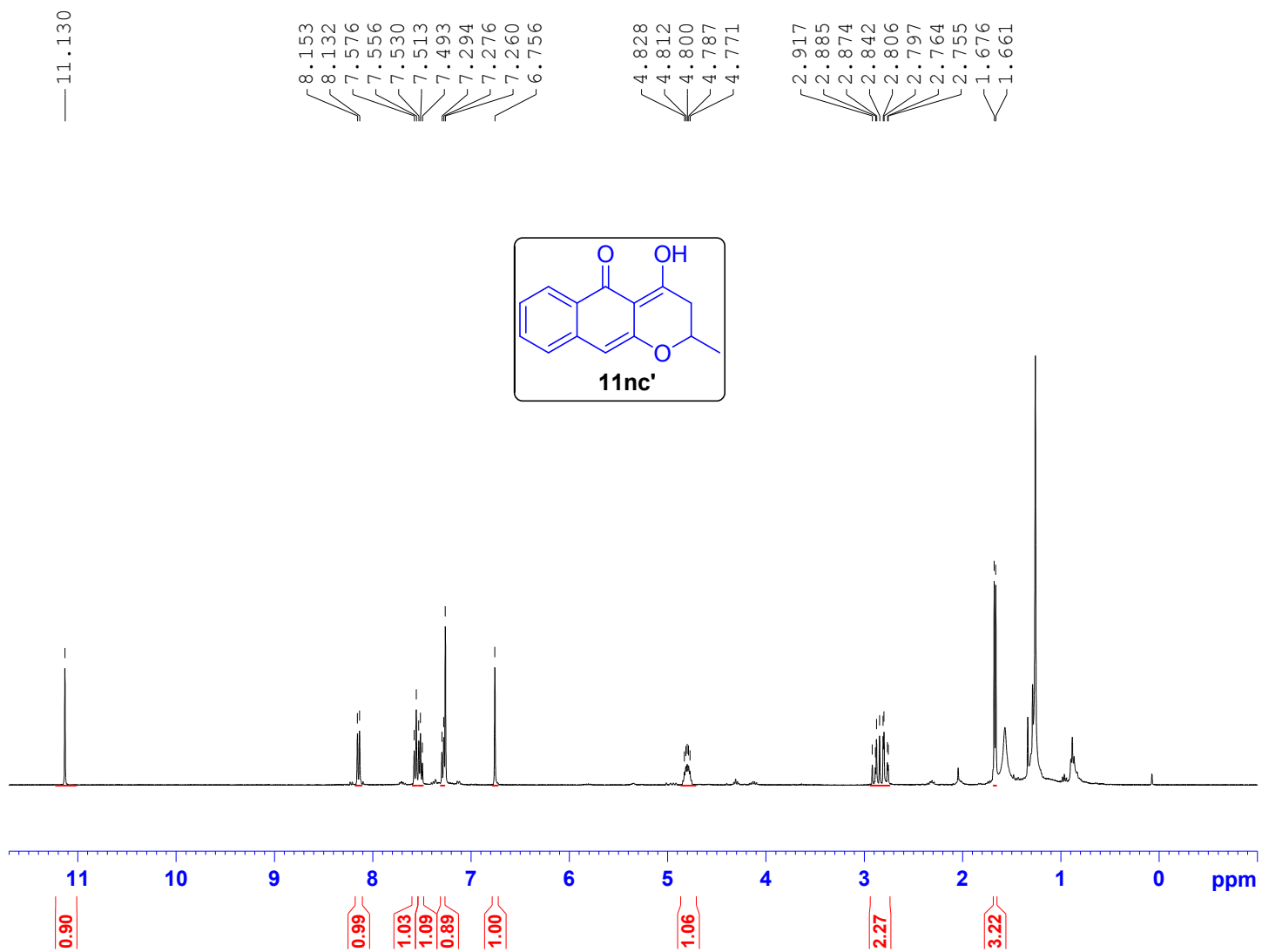
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44.36

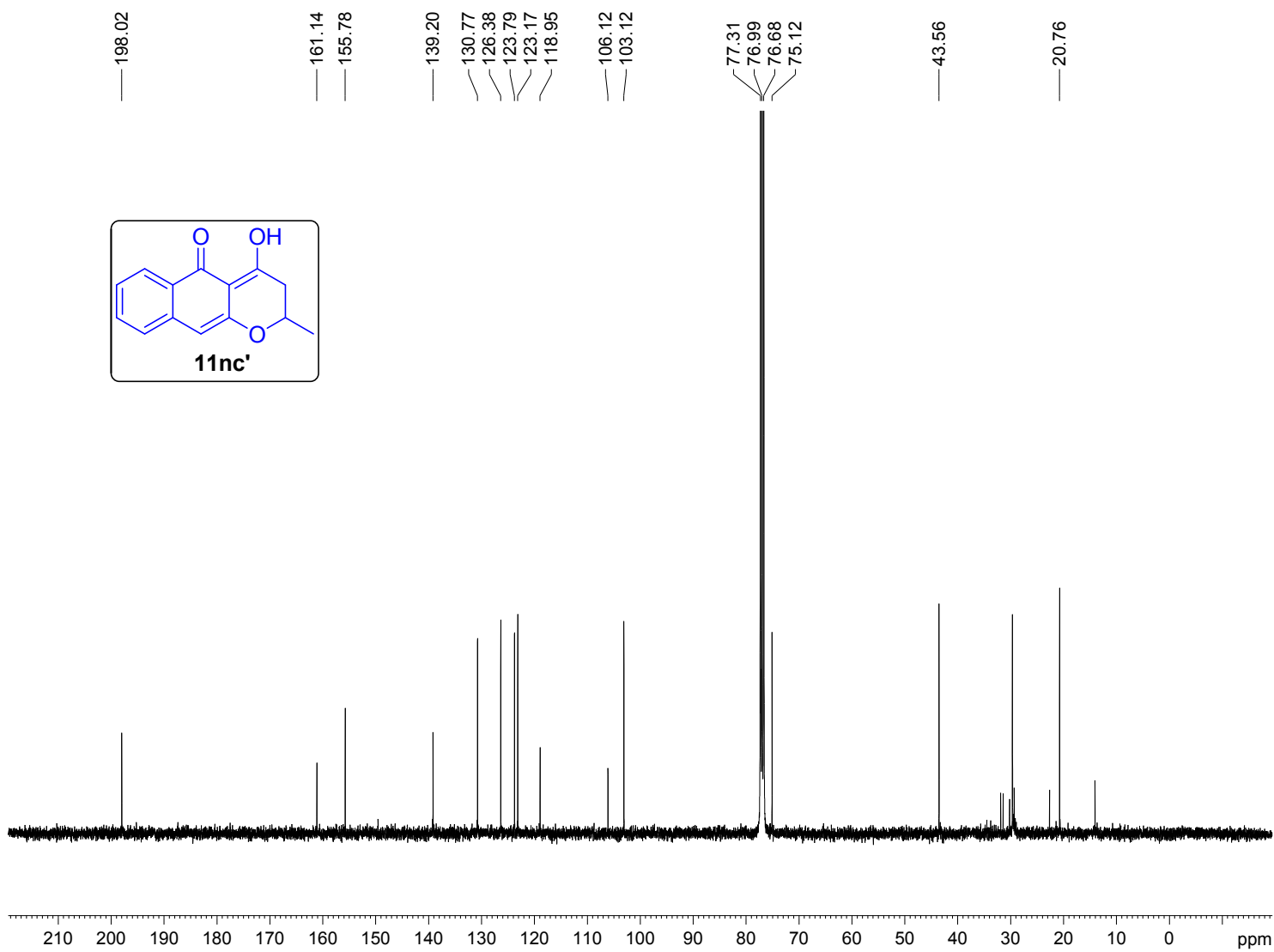
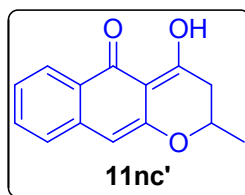
21.03



PA-DHNP-CR-Fr2 19/04/2014
PROTON CDC13



PA-DHNP-CR-Fr2 19/04/2014
C13CPD CDCl3



PA-DHNP-CR-Fr2
C13DEPT135 CDC13

130.78
126.39
123.79
123.18

103.11

75.12

43.55

20.78

