Supporting Information (experimental procedures and spectra data/copies) for

Concise Synthesis of (+)-*β*- and *γ*-Apopicropodophyllins, and Dehydrodesoxypodophyllotoxin

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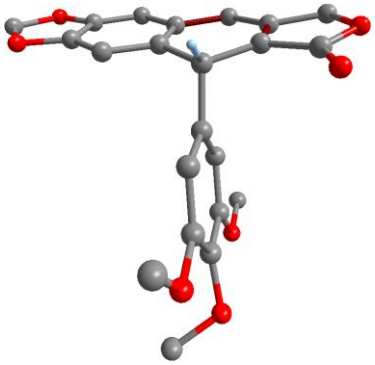


Table S1: X-ray crystal data of **5**•CH_2Cl_2

(selected H atoms and CH_2Cl_2 have been omitted for clarity)

Empirical formula	$C_{23}H_{22}O_7Cl_2$
Temperature (K)	297.16(10)
Crystal color	colorless
Formula weight	481.30
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	14.4878(12)
b (Å)	12.1979(8)
c (Å)	14.2602(12)
α (°)	90.00
β (°)	117.029(11)
γ (°)	90.00
V (Å ^{3})	2244.8(4)
Z	4
Density (calculated) (g/cm^3)	1.424
F (000)	1000.0
λ (Å)	1.54184
Reflections collected	8233
Independent reflections	4165
θ Range for data collection (°)	4.989-69.800
Index range	$-17 \leq h \leq 17$ $-14 \leq k \leq 7$ $-15 \leq l \leq 17$
Final R indices [I>2σ(I)]	R_1 = 0.0545, wR_2 = 0.1444
Largest difference peak and hole [e Å $^{-3}$]	0.367, –0.497

Table S2 ^{1}H NMR Data Comparison of β-Apopicropodophyllin

5 ($CDCl_3$, 300 MHz)	ref.[1] (Toste *et al.*) ($CDCl_3$, 300 MHz)	
δ_H (ppm), *J* (Hz)	δ_H (ppm), *J* (Hz)	$\Delta\delta$ (ppm)
6.72 *s*	6.71 *s*	+0.01
6.63 *s*	6.62 *s*	+0.01
6.37 *s*	6.36 *s*	+0.01
5.954 *s*	5.94 *d* (1.2)	
5.947 *s*	5.93 *d* (1.2)	
4.90 *d* (17.4)		
4.82 *d* (17.4)	4.82 *m* (3H)	
4.81 *s*		
3.86 *dd* (22.2, 3.9)	3.85 *dd* (22.5, 4.5)	+0.01
3.79 *s*	3.78 *s*	+0.01
3.78 *s*	3.77 *s*	+0.01
3.65 *dd* (22.2, 3.6)	3.63 *dd* (22.5, 4.5)	+0.02

Table S3 ^{1}H NMR Data Comparison of γ-Apopicropodophyllin

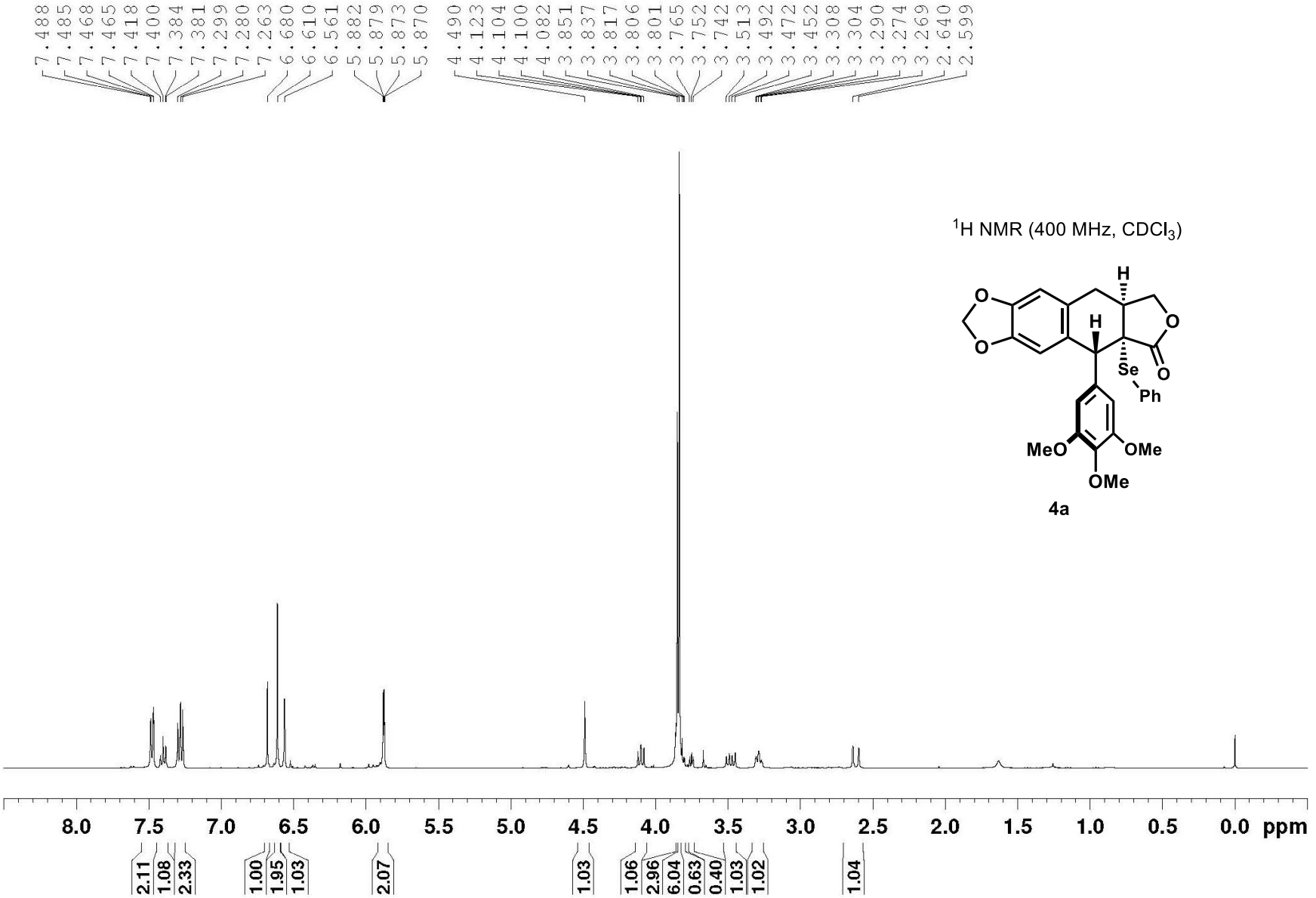
6 ($CDCl_3$, 300 MHz)	ref.[2] (Yamaguchi *et al.*) ($CDCl_3$, 300 MHz)	
δ_H (ppm), *J* (Hz)	δ_H (ppm), *J* (Hz)	$\Delta\delta$ (ppm)
6.77 *s*	6.77 *s*	0.00
6.52 brs	6.52 brs	0.00
5.97 *s*	5.97 *s*	0.00
4.70 *t* (8.7)	4.70 *dd* (8.8, 8.8)	0.00
4.01 *t* (8.7)	4.01 *dd* (8.8, 8.8)	0.00
3.92 *s*	3.92 *s*	0.00
3.83 *s*	3.84 *s*	–0.01
3.39 *td* (15.9, 8.7)	3.40 *m*	
2.94 *dd* (15.0, 6.9)	2.94 *dd* (16.0, 6.6)	0.00
2.79 *dd* (15.6, 15.3)	2.82 *d* (16.0)	–0.03

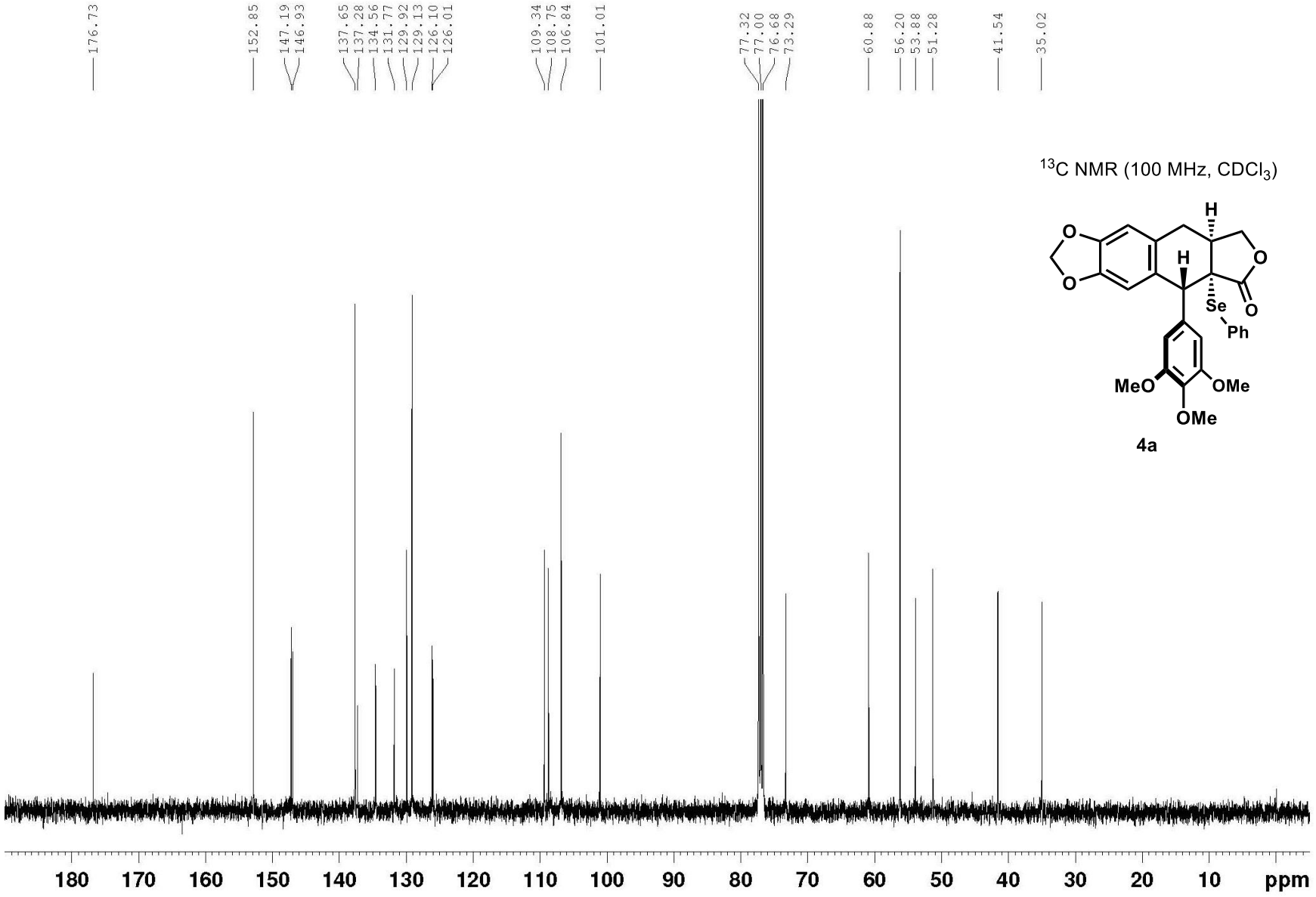
(1) Kennedy-Smith, J. J.; Young, L. A.; Toste, F. D. *Org. Lett.* **2004**, *6*, 1325.
(2) Kashima, T.; Tanoguchi, M.; Arimoto, M.; Yamaguchi, H. *Chem. Pharm. Bull.* **1991**, *39*, 192.

Table S4 ^{1}H NMR Data Comparison of Dehydrodesoxypodophyllotoxin

7 ($CDCl_3$, 400 MHz)	ref.[3] (Tanabe *et al.*) ($CDCl_3$, 400 MHz)	
δ_H (ppm), *J* (Hz)	δ_H (ppm), *J* (Hz)	$\Delta\delta$ (ppm)
7.70 *s*	7.70 *s*	0.00
7.21 *s*	7.21 *s*	0.00
7.12 *s*	7.12 *s*	0.00
6.55 *s*	6.55 *s*	0.00
6.09 *s*	6.09 *s*	0.00
5.38 *s*	5.38 *s*	0.00
3.97 *s*	3.97 *s*	0.00
3.84 *s*	3.84 *s*	0.00

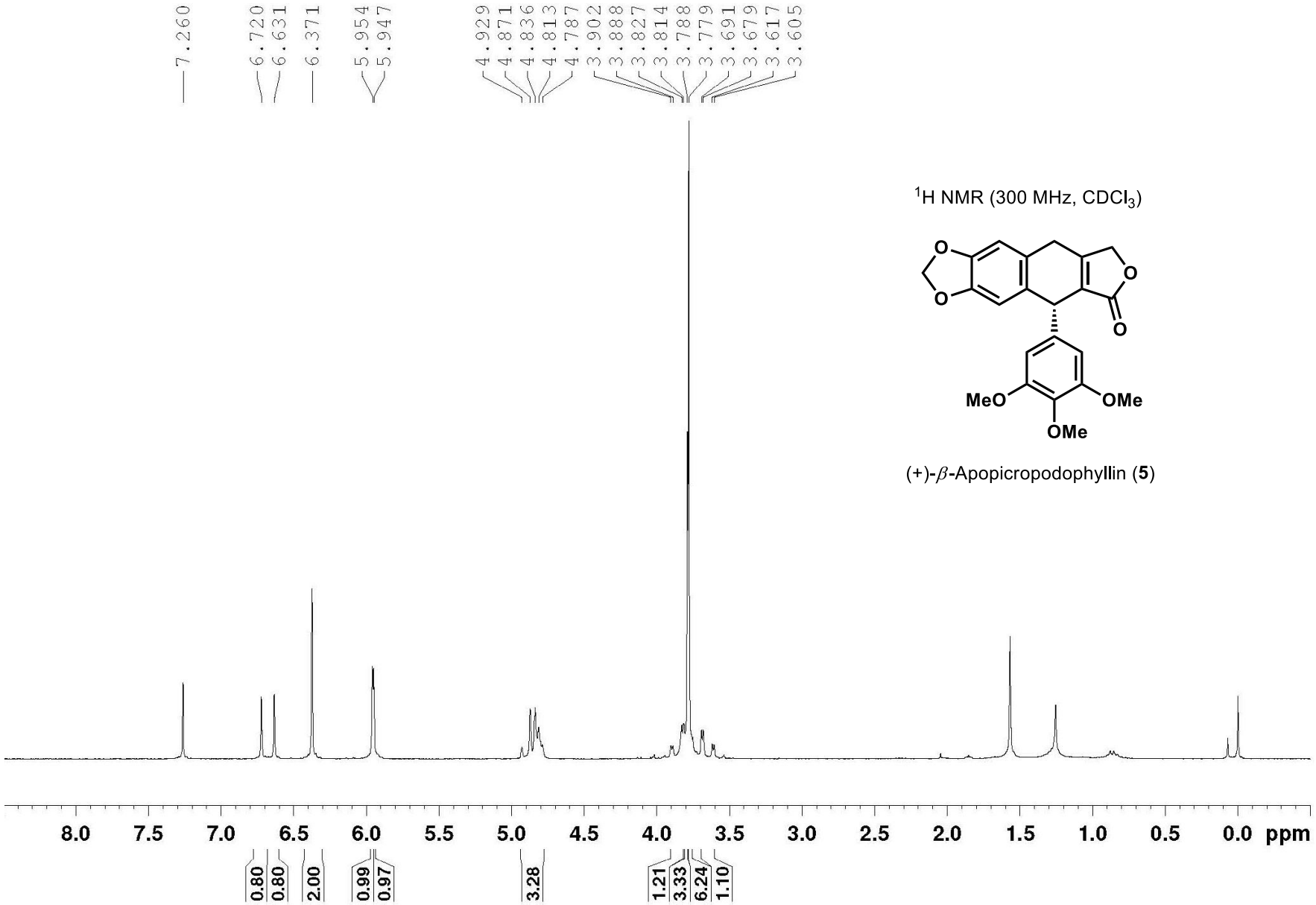
(3) Nishii, Y.; Yoshida, T.; Asano, H.; Wakasugi, K.; Morita, J.-i.; Aso, Y.; Yoshida, E.; Motoyoshiya, J.; Aoyama, H.; Tanabe, Y. *J. Org. Chem.* **2005**, *70*, 2667.


7.488
7.485
7.468
7.465
7.418
7.400
7.384
7.381
7.299
7.280
7.263
6.680
6.610
6.561
5.882
5.879
5.873
5.870
4.490
4.123
4.104
4.100
4.082
3.851
3.837
3.817
3.806
3.801
3.765
3.752
3.742
3.513
3.492
3.472
3.452
3.308
3.304
3.290
3.274
3.269
2.640
2.599
^{1}H NMR (400 MHz, CDCl$_3$)
H
O
O
H
O
Se
O
Ph
MeO
OMe
OMe
4a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.11
1.08
2.33
1.00
1.95
1.03
2.07
1.03
1.06
2.96
6.04
0.63
0.40
1.03
1.02
1.04



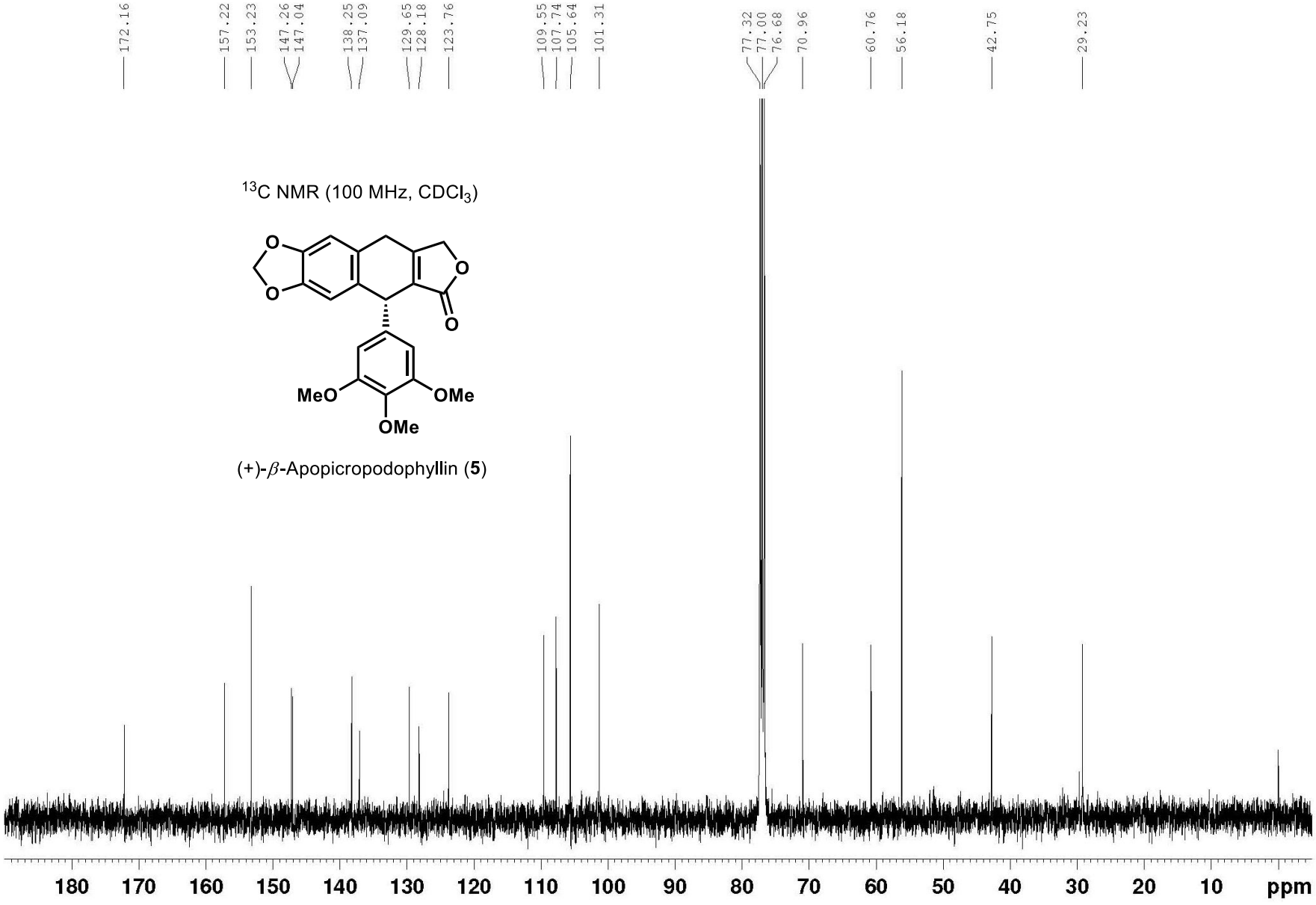
^{13}C NMR (100 MHz, $CDCl_3$)

4a



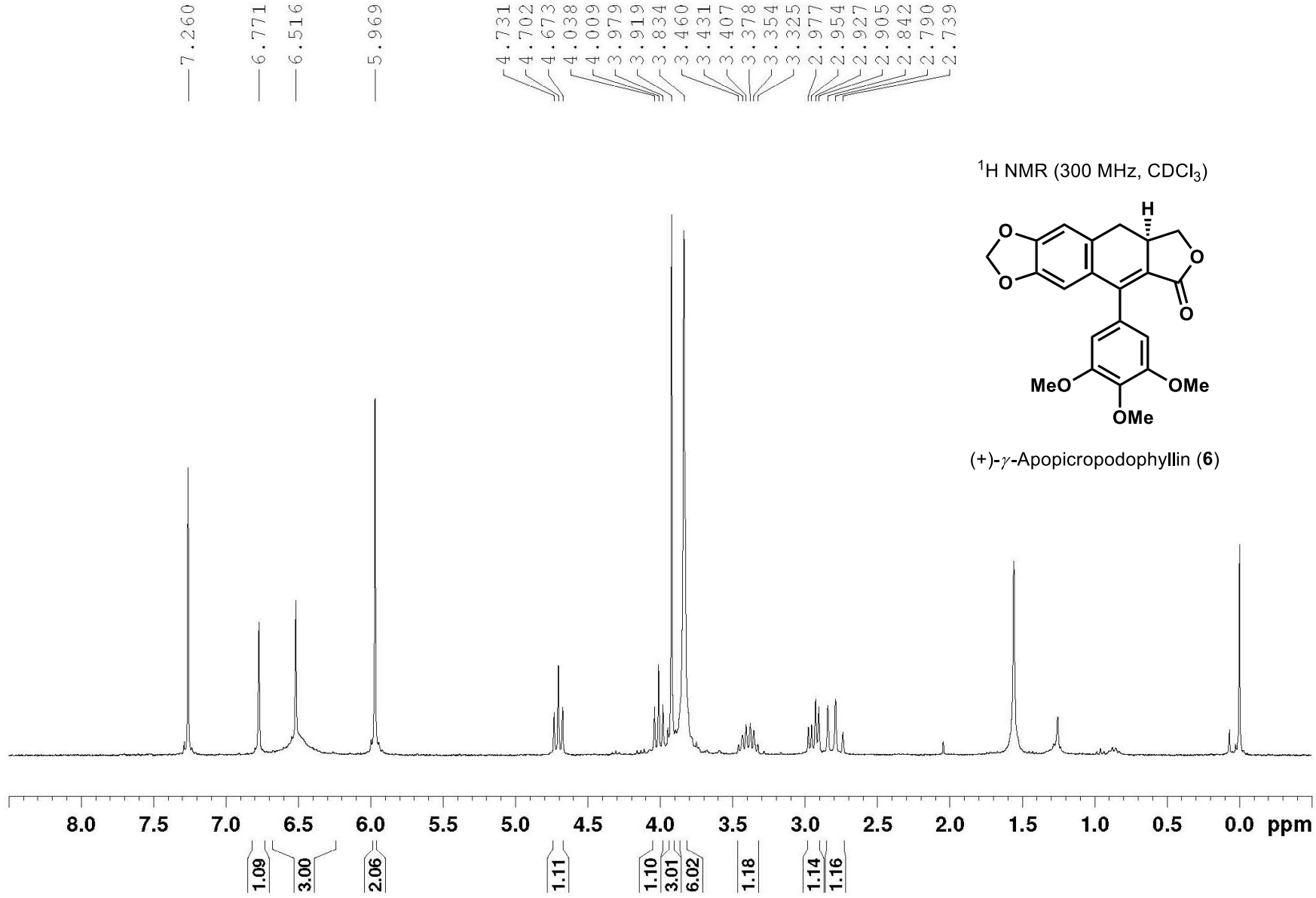
^{1}H NMR (300 MHz, $CDCl_3$)

(+)-β-Apopicropodophyllin (**5**)



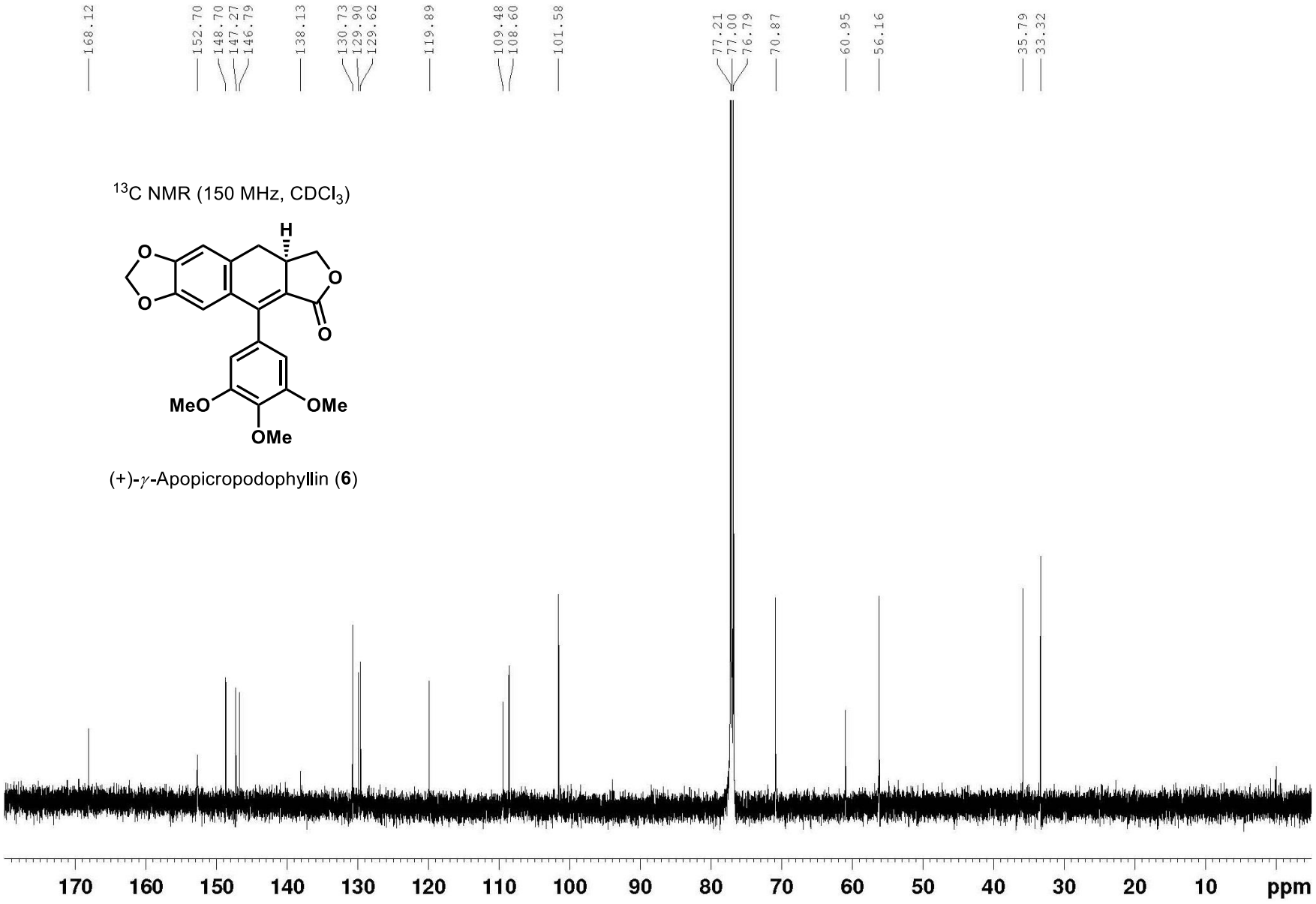
^{13}C NMR (100 MHz, $CDCl_3$)

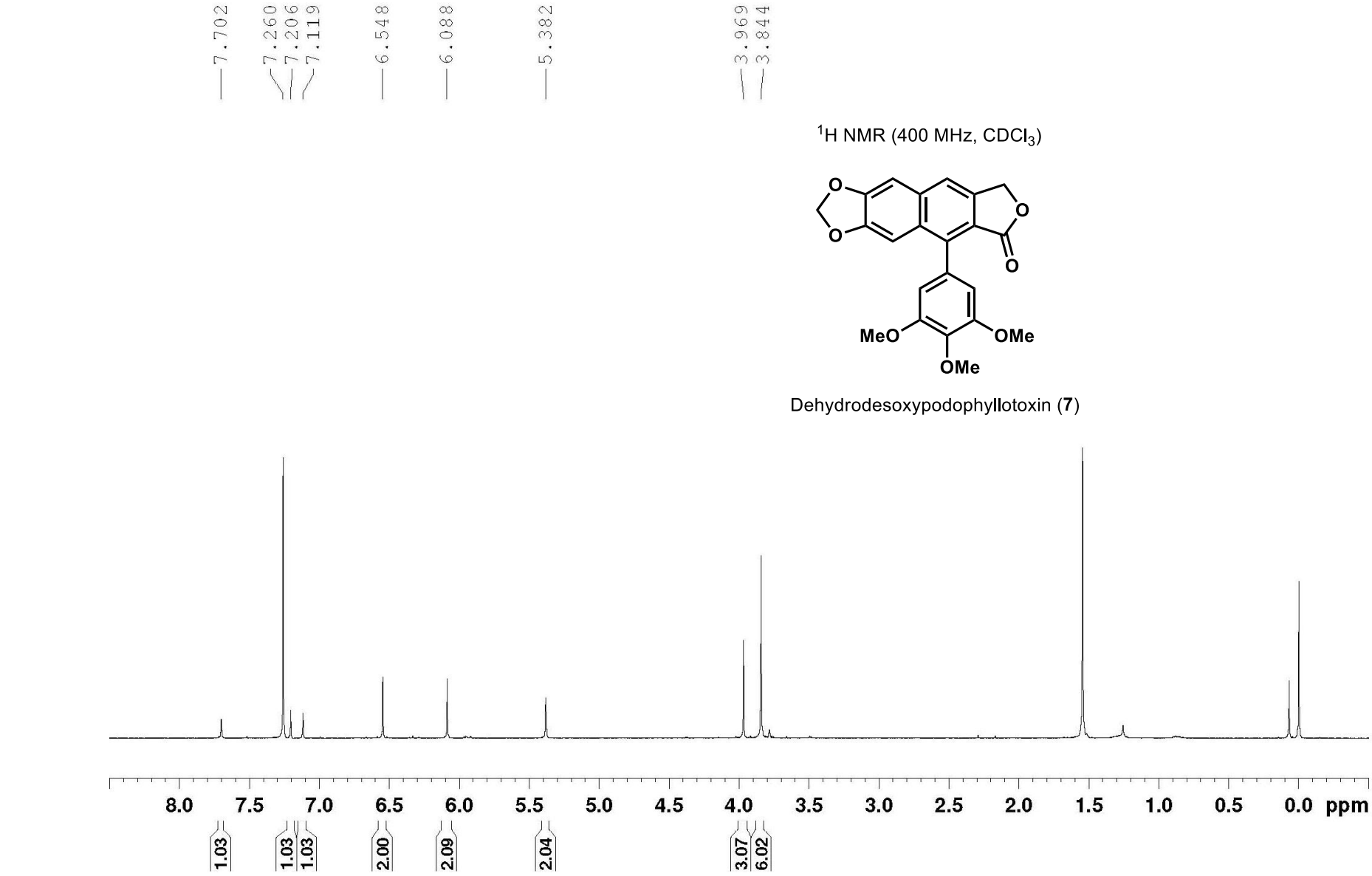
(+)-β-Apopicropodophyllin (**5**)



^{1}H NMR (300 MHz, $CDCl_3$)

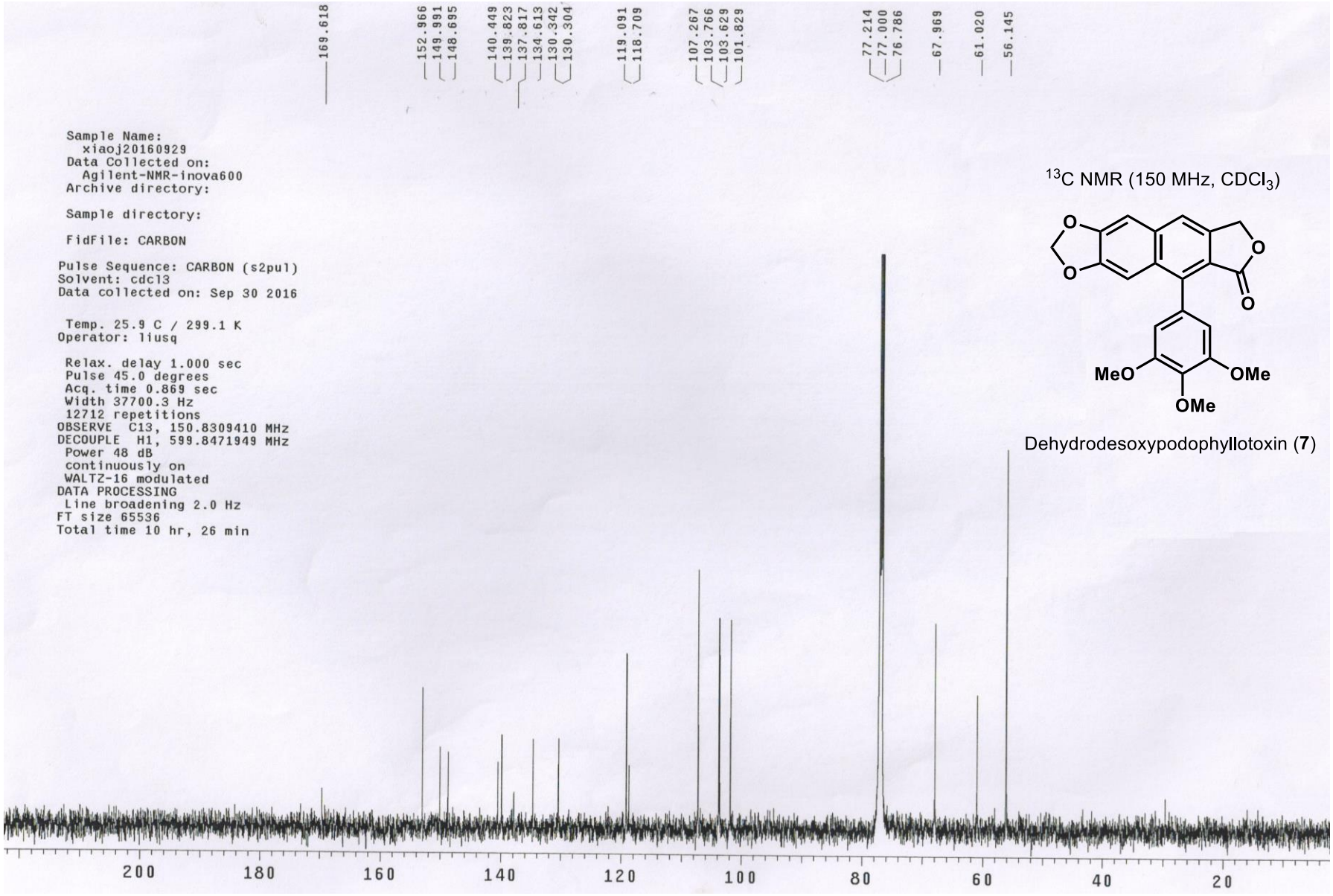
(+)-γ-Apopicropodophyllin (**6**)


168.12
152.70
148.70
147.27
146.79
138.13
130.73
129.90
129.62
119.89
109.48
108.60
101.58
77.21
77.00
76.79
70.87
60.95
56.16
35.79
33.32
^{13}C NMR (150 MHz, $CDCl_3$)
H
O
O
O
O
MeO
OMe
OMe
(+)-γ-Apopicropodophyllin (**6**)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



^{1}H NMR (400 MHz, $CDCl_3$)

Dehydrodesoxypodophyllotoxin (**7**)



^{13}C NMR (150 MHz, $CDCl_3$)

Dehydrodesoxypodophyllotoxin (**7**)