

Supplementary Information

Organocatalytic aldol approach for protecting group-free asymmetric synthesis of (7*R'*)-parabenzlactone, (-)-hinokinin, (-)-yatein, (-)-bursehernin, (-)-pluviatolide, (+)-isostegane and allied lignans

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(7'R)-parabenzlactone (5)

Subject	Munakata group ¹ (-)-parabenzlactone	Wahälä group ² (500 MHz, CDCl ₃) (7'S)-parabenzlactone	Our work (400 MHz, CDCl ₃) (7'R)-parabenzlactone	
¹ H	Not reported	6.74 (d, <i>J</i> = 8.0 Hz, 1H, ArH)	6.74 – 6.70 (m, 1H)	
		6.70 (d, <i>J</i> = 1.5 Hz, 1H, ArH)	6.68 (d, <i>J</i> = 7.9 Hz, 1H)	
		6.68 (d, <i>J</i> = 8.0 Hz, 1H, ArH)	6.61 (d, <i>J</i> = 7.6 Hz, 2H)	
		6.67 (dd, <i>J</i> = 1.0, 8.0 Hz, 1H, ArH)	6.50 (dd, <i>J</i> = 9.8, 2.0 Hz, 2H),	
		6.61 (d, <i>J</i> = 1.0 Hz, 1H, ArH)		
		6.58 (dd, <i>J</i> = 1.5, 8.0 Hz, 1H, ArH)	5.97 (d, <i>J</i> = 1.44 Hz, 1H)	
		5.97 (<i>J</i> = 1.5 Hz, 1H, OCH ₂ O)		
		5.96 (<i>J</i> = 1.5 Hz, 1H, OCH ₂ O)		5.95 (d, <i>J</i> = 1.44 Hz, 1H)
		5.93 (<i>J</i> = 1.5 Hz, 1H, OCH ₂ O)		5.93 (d, <i>J</i> = 1.44 Hz, 1H)
		5.91 (<i>J</i> = 1.5 Hz, 1H, OCH ₂ O)		5.92 (d, <i>J</i> = 1.44 Hz, 1H)
		4.61 (dd, <i>J</i> = 2.8, 6.2 Hz, 1H, OHCH)		4.36 (m, 2H, (HO)CH + OCH)
		3.91 (m, 2H, OCH)		4.09 (dd, <i>J</i> = 9.5, 7.8 Hz, 1H, OCH)
		2.94–3.00 (m, 2H, ArCH)		2.80 (dd, <i>J</i> = 12.9, 4.2 Hz, 1H)
		2.90 (dd, <i>J</i> = 6.0, 12.0 Hz, 1H, OCH ₂ CH)		2.75 – 2.63 (m, 2H)
				2.54–2.60 (m, 1H, O=CCH)
		¹³ C NMR (CDCl ₃ , 125 MHz)		¹³ C NMR (CDCl ₃ , 101 MHz)
¹³ C	Not reported	178.9		178.7
		148.1, 147.6, 147.5, 146.3, 135.3, 131.2, 122.7, 119.4, 109.9, 108.2, 108.1, 106.2, 101.3, 100.9		148.0, 147.8, 147.5, 146.4, 135.4, 131.1, 122.2, 119.4, 116.1, 109.3, 108.2, 106.1, 101.2, 101.0
		75.5		73.7
		68.4		67.9
		45.1	46.3	
		43.7	43.5	
		35.1	35	
Optical rotation	[α] _D ²⁵ = -11.0 (c = 1.15, CHCl ₃), (-)-parabenzlactone	[α] _D ²² = -15.0 (c = 0.3, CHCl ₃), (7'S)-parabenzlactone	[α] _D ²⁵ = +25.9 (c = 0.42, CHCl ₃)	
State/M. P.	159–161 °C	155–158 °C	sticky colourless oil	

(-)- Hinokinin (6)

subject	Belletire group ³ (Frequency not provided)	Present study (¹ H NMR (400 MHz, CDCl ₃))
¹ H	6.75-6.66 (m, 2 H, ArH)	6.73 (d, <i>J</i> = 7.84 Hz, 1H)
		6.70 (d, <i>J</i> = 8.28 Hz, 1H)
	6.65-6.56 (m, 2 H, ArH)	6.63 (d, <i>J</i> = 1.7 Hz, 1H)
		6.60 (dd, <i>J</i> = 7.8, 1.7 Hz, 1H)
	6.50-6.42 (m, 2 H, ArH)	6.46 (m, 2H)
	5.925 (br s, 4 H, OCH ₂ O)	5.93 (m, 4H)
	4.118 (dd, <i>J</i> = 6.9, 9.1 Hz, 1 H, CHHOC=O)	4.13 (dd, <i>J</i> = 9.24, 6.84 Hz, 1H)
	3.850 (dd, <i>J</i> = 6.9, 9.1 Hz, 1 H, CHHOC=O)	3.86 (dd, <i>J</i> = 9.2, 6.92 Hz, 1H)
	2.978 (dd, <i>J</i> = 4.9, 13.9 Hz, 1 H, CHHCHCO ₂)	2.99 (dd, <i>J</i> = 14.1, 5.0 Hz, 1H)
	2.826 (dd, <i>J</i> = 4.9, 13.9 Hz, 1 H, CHHCHCO ₂)	2.84 (dd, <i>J</i> = 14.1, 7.2 Hz, 1H)
2.64-2.39 (m, 4 H, CH)	2.61 – 2.51 (m, 2H)	
	2.49- 2.42 (m, 2H)	
	(Frequency not provided)	¹³C NMR (101 MHz, CDCl₃)
¹³ C	178.391 (s)	178.4
	147.847 (s)	147.9
	146.441 (s)	146.5
	146.309 (s)	146.4
	131.652 (s)	131.6
	131.396 (s)	131.3
	122.205 (d)	122.2
	121.525 (d)	121.5
	109.424 (d)	109.4
	108.810 (d)	108.8
	108.293 (d)	108.4
	108.277 (d)	108.3
	101.007 (t)	101.0
	71.101 (t)	71.1
	46.427 (d)	46.5
	41.252 (d)	41.3
	38.274 (t)	38.4
34.777 (t)	34.8	

	Woodcock group ⁴	Magnusson group ⁵	Present Study
Optical rotation	$[\alpha]_D^{17} = -34.0$ (c = 0.981, CHCl ₃)	$[\alpha]_D^{23} = -34.7$ (c = 0.7, CHCl ₃)	$[\alpha]_D^{25} = -33.0$ (c = 1.0, CHCl ₃)
State/M.P.	65-66 °C	Colourless viscous oil	Colourless viscous oil

(-)-Yatein (8)

subject	Chen group ⁶	Enders group ⁷ (¹ H NMR (300 MHz, CDCl ₃)) [(+) - Yatein]	Our work (¹ H NMR (400 MHz, CDCl ₃))
¹ H	Not provided	6.69 (dd, 1 H, <i>J</i> = 1.0, 6.9 Hz, ArH)	6.69 (dd, <i>J</i> = 7.32, 0.96 Hz, 1H)
		6.49-6.46 (m, 2 H, ArH)	6.48 (dd, <i>J</i> = 8.24, 1.76 Hz, 1H)
		6.36 (s, 2 H, ArH)	6.45 (s, 1H)
		5.94 (dd, 2 H, <i>J</i> = 1.4, 3 Hz, OCH ₂ O)	6.36 (s, 2H)
		4.18 (dd, 1 H, <i>J</i> = 7.2, 9.3 Hz, CHHOC=O)	5.94 (d, <i>J</i> = 1.44 Hz, 1H)
		3.88 (dd, 1 H, <i>J</i> = 7.4, 9.0 Hz, CHHOC=O)	5.93 (d, <i>J</i> = 1.44 Hz, 1H)
		3.83 (s, 9H, OCH ₃)	4.18 (dd, <i>J</i> = 9.2, 7.1 Hz, 1H)
		3.06 (m, 1H, CHHCHCO ₂)	3.88 (dd, <i>J</i> = 9.1, 7.4 Hz, 1H)
		2.94 - 2.88 (m, 1H, CH)	3.83 (s, 9H)
		2.64 - 2.46 (m, 4H, CH ₂)	2.96-2.86 (m, 2H)
		¹³ C NMR (75 MHz, CDCl ₃)	¹³ C NMR (101 MHz, CDCl ₃)
¹³ C	Not provided	178.56	178.5
		153.24, 147.92, 146.40, 136.80, 133.34, 131.53, 121.54, 108.77, 108.31, 106.16, 101.10	153.3, 147.9, 146.4, 136.9, 133.3, 131.5, 121.5, 108.8, 108.3, 106.2, 101.1
		71.20	71.2
		60.88	60.9
		56.09	56.1
		46.44	46.5
		41.01	41.0
		38.33	38.4
		35.23	35.3
Optical rotation	[α] _D ²² = -30.0 (c 0.15, CHCl ₃)	[α] _D ²² = +30.6 (c = 1.10, CHCl ₃) For (+) - Yatein	[α] _D ²⁵ = -26.5 (c = 0.4, CHCl ₃)
State/M.P.	Not provided	Colourless oil	Yellowish gummy liquid

(+)- Isostagane (4)

Subject	Tomioka group ⁸	Enders group ⁷ (¹ H NMR (400 MHz, CDCl ₃)) [(-)- Isostagane]	Present study (¹ H NMR (400 MHz, CDCl ₃))
¹ H	6.3-6.7 (m, 3H)	6.63 (s, 1H, ArH)	6.70 (s, 1H)
		6.56 (s, 1 H, ArH)	6.623 (s,1H)
		6.55 (s, 1 H, ArH)	6.618 (s,1H)
	5.45 (d, 1H, J = 1 Hz)	5.93 (d, 1 H, J = 1.3 Hz, OCHHO)	6.01 (d, J = 1.5, 1H),
	5.39 (d, 1H, J = 1 Hz)	5.90 (d, 1 H, J = 1.3 Hz, OCHHO)	5.98 (d, J = 1.5, 1H)
	3.81 (s, 3H), 3.47 (s, 3H), 3.38 (s, 3H), 2.8-3.9 (m, 3H), 1.3-2.2 (m, 5H),	4.29 (dd, 1 H, J = 6.6, 8.2 Hz, CHHOC=O)	4.37 (dd, J = 8.5, 6.5 Hz, 1H),
		3.82 (s, 3 H, OCH ₃)	3.90 (s, 3H)
		3.81 (s, 3 H, OCH ₃)	3.88 (s, 3H)
		3.70 (dd, 1 H, J = 8.5, 11.0 Hz, CHHOC=O)	3.77 (dd, J = 11.1, 8.5 Hz, 1H)
		3.50 (s, 3 H, OCH ₃)	3.57 (s, 3H)
		3.06 (d, 1, H, J = 13.2 Hz, CHHCH ₂ CO ₂)	3.12 (d, J = 13.4 Hz, 1H)
		2.57 (d, 1 H, J = 12.9 Hz, CHHCH ₂ CO ₂)	2.63 (d, J = 13.1 Hz, 1H)
		2.32 (dd, 1 H, J = 9.6, 13.2 Hz, CHHCHCO ₂)	2.39 (dd, J = 13.1, 9.5 Hz, 1H)
		2.22 (dd, 1 H, J = 9.3, 13.6 Hz, CHHCHCO ₂)	2.29 (dd, J = 13.4, 9.2 Hz, 1H)
		2.17-2.00 (m, 2 H, CH)	2.12-2.07 (m, 2H)
	¹³ C NMR (75 MHz, CDCl ₃)	¹³ C NMR (200 MHz, CDCl ₃)	
¹³ C	Not provided	32.55	32.3
		34.39	34.1
		47.27	47.0
		50.33	50.1
		56.30	56.0
		61.07	60.8
		61.23	61.0
		70.31	70.1
		101.46	101.2
		107.74, 109.05, 112.02,126.70, 128.58, 132.74, 136.33, 146.16, 147.93, 152.14, 153.60	107.5, 108.8, 111.8, 126.4, 128.3, 132.4, 136.1, 140.8, 145.9, 147.7, 151.9, 153.4
176.83	176.6		
Optical rotation	[α] _D ²⁰ = +154.0 (c = 0.7, CHCl ₃)	[α] _D ²² = -156.9 (c = 2.8, CHCl ₃)	[α] _D ²⁵ = +151.0 (c = 0.6, CHCl ₃)
State/M.P.	Not provided	171-172 °C	Yellow oil

(-)-Brusehernin (10)

subject	Macmillan group ⁹ (¹ H NMR (500 MHz, CDCl ₃))	Our work (¹ H NMR (400 MHz, CDCl ₃))
¹ H	6.80 (d, <i>J</i> = 8.1 Hz, 1H, ArH)	6.79 (d, <i>J</i> = 8.0 Hz, 1H)
	6.70 (d, <i>J</i> = 7.9 Hz, 2H, ArH),	6.69 (d, <i>J</i> = 7.7 Hz, 2H)
	6.67 (d, <i>J</i> = 1.9 Hz, 1H, ArH)	6.66 (d, <i>J</i> = 2.0 Hz, 1H)
	6.47 (dd, <i>J</i> = 7.7, 1.7 Hz, 1H, ArH)	6.46 (dd, <i>J</i> = 7.8, 1.8 Hz, 1H),
	6.44 (d, <i>J</i> = 1.6 Hz, 1H, ArH)	6.43 (d, <i>J</i> = 1.7 Hz, 1H)
	5.94 (s, 1H, OCH ₂ O)	5.94 (d, <i>J</i> = 1.44 Hz, 1H)
	5.93 (s, 1H, OCH ₂ O)	5.93 (d, <i>J</i> = 1.44 Hz, 1H)
	4.13 (dd, <i>J</i> = 9.2, 6.7 Hz, 1H, OCH)	4.12 (dd, <i>J</i> = 9.1, 6.8 Hz, 1H)
	3.87 (s, 3H, OCH ₃)	3.87 (s, 3H)
	3.85 (s, 3H, OCH ₃)	3.84 (s, 3H)
	3.86-3.82 (m, 1H, OCH)	3.89-3.84 (m, 1H)
	2.98 (dd, <i>J</i> = 14.1, 5.1 Hz, 1H, ArCH)	2.97 (dd, <i>J</i> = 14.0, 5.1 Hz, 1H)
	2.90 (dd, <i>J</i> = 14.1, 7.0 Hz, 1H, ArCH)	2.89 (dd, <i>J</i> = 14.0, 7.0 Hz, 1H)
	2.64-2.54 (m, 2H, ArCH + OCH ₂ CH)	2.62 – 2.53 (m, 2H)
	2.52-2.44 (m, 2H, ArCH + O=CCH)	2.5 – 2.45 (m, 2H)
	¹³ C NMR (CDCl ₃ , 125 MHz)	¹³ C NMR (101 MHz, CDCl ₃)
¹³ C	178.8	178.7
	149.2, 148.04, 148.00, 146.5, 131.7, 130.2, 121.7, 121.5, 112.2, 111.2, 108.9, 108.4, 101.2,	149.0, 147.9, 147.6, 146.3, 131.6, 130.1, 121.5, 121.3, 112.0, 111.0, 108.7, 108.3, 101.1
	71.3	71.2
	56.0	55.8
	55.9	55.8
	46.7	46.5
	41.2	41.0
	38.5	38.3
	34.8	34.6
Optical rotation	[α] _D = -19.2 (c = 1.0, CHCl ₃)	[α] _D ²⁵ = -20.4 (c = 0.4 CHCl ₃)
Melting point	Colourless oil	colourless oil

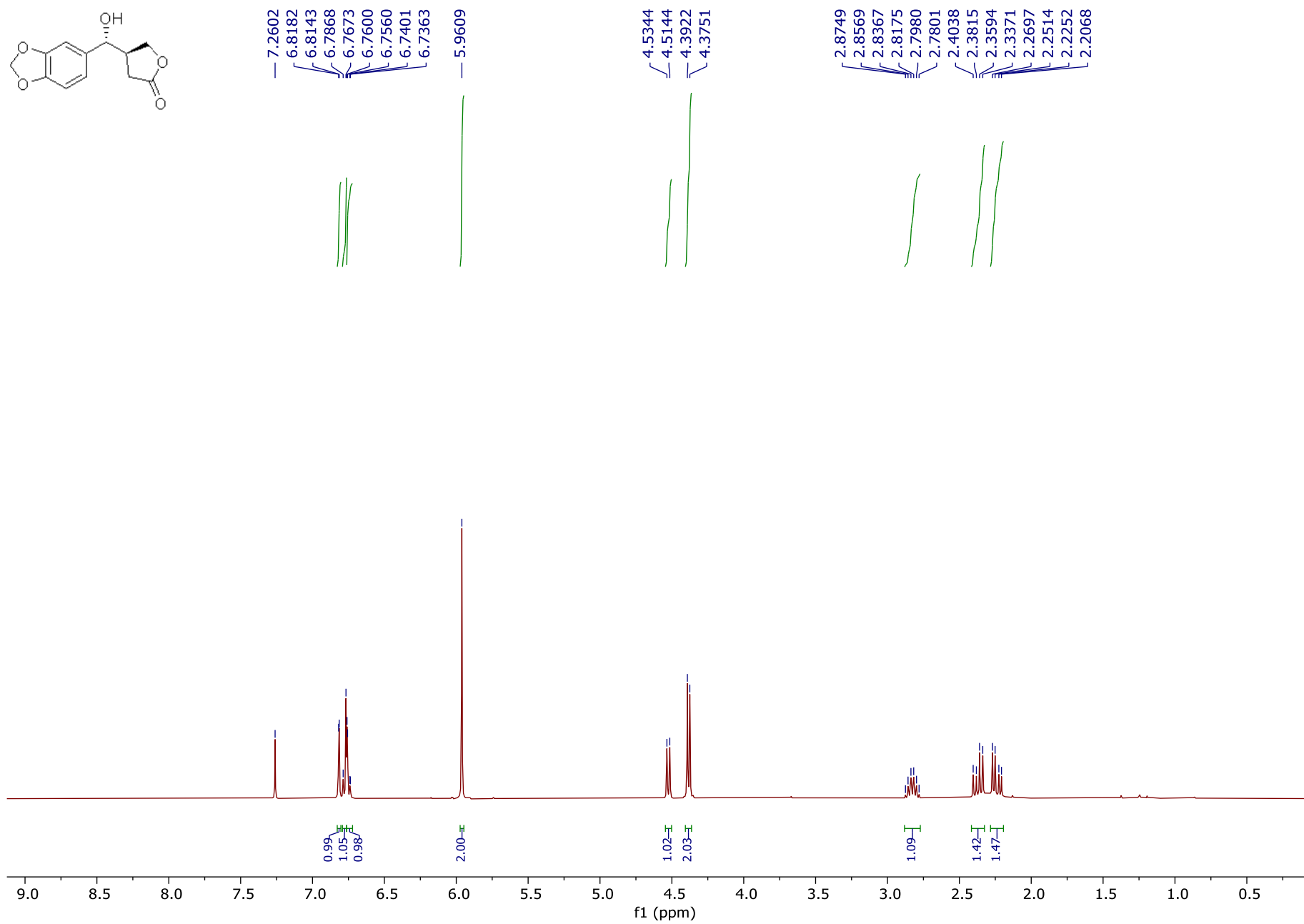
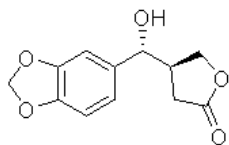
(-)-Pluviatolide (12):

Subject	Feringa group¹⁰ (Frequency not provided)	Our work (¹H NMR (400 MHz, CDCl₃))
¹H	6.86-6.82 (m, 1H, ArH)	6.84 (d, <i>J</i> = 8.0 Hz, 1H)
	6.72-6.60 (m, 3H, ArH)	6.69 (d, <i>J</i> = 8.3, 1H)
		6.66 (d, <i>J</i> = 2.0 Hz, 1H)
		6.63 (dd, <i>J</i> = 8.0, 2.0 Hz, 1H)
	6.48-6.45 (m, 2H, ArH)	6.45 (dd, <i>J</i> = 8.0, 1.76 Hz, 1H)
		6.44 (s, 1H)
	5.93 (s, 2H, OCH ₂ O)	5.93 (d, <i>J</i> = 1.24 Hz, 2H)
	5.65 (bs, 1H, OH)	5.52 (br s, 1H)
	4.16-4.08 (m, 1H, OCH)	4.11 (dd, <i>J</i> = 9.1, 6.9 Hz, 1H)
	3.90-3.82 (m, 1H, OCH)	3.88-3.82 (m, 1H)
	3.85 (s, 3H, OCH ₃)	3.85 (s, 3H)
	3.02-2.82 (m, 2H, ArCH)	2.96 (dd, <i>J</i> = 14.1, 5.1 Hz, 1H)
		2.89 (dd, <i>J</i> = 14.1, 6.7 Hz, 1H)
	2.63- 2.43 (m, 4H, ArCH + OCH ₂ CH + O=CCH)	2.65 – 2.53 (m, 2H)
2.51-2.42 (m, 2H)		
	Not provided	¹³C NMR (101 MHz, CDCl₃)
¹³C	178.76	178.7
	147.82,146.69,146.28,144.52, 131.62, 129.43,122.04,121.54,114.29,111.57, 108.80,108.28, 101.02	147.9, 146.7, 146.3, 144.5, 131.6, 129.4, 122.1, 121.6, 114.2, 111.5, 108.8, 108.3, 101.0,
	71.21	71.2
	55.88	55.9
	46.57	46.6
	41.0	41.0
	38.24	38.3
	34.6	34.6
Optical rotation	$[\alpha]_D^{23} = -30.1$ (c = 0.93, CHCl ₃)	$[\alpha]_D^{25} = -29.0$ (c = 1.0, CHCl ₃)
State/ M. P.	158-159 °C	Colourless Gummy oil

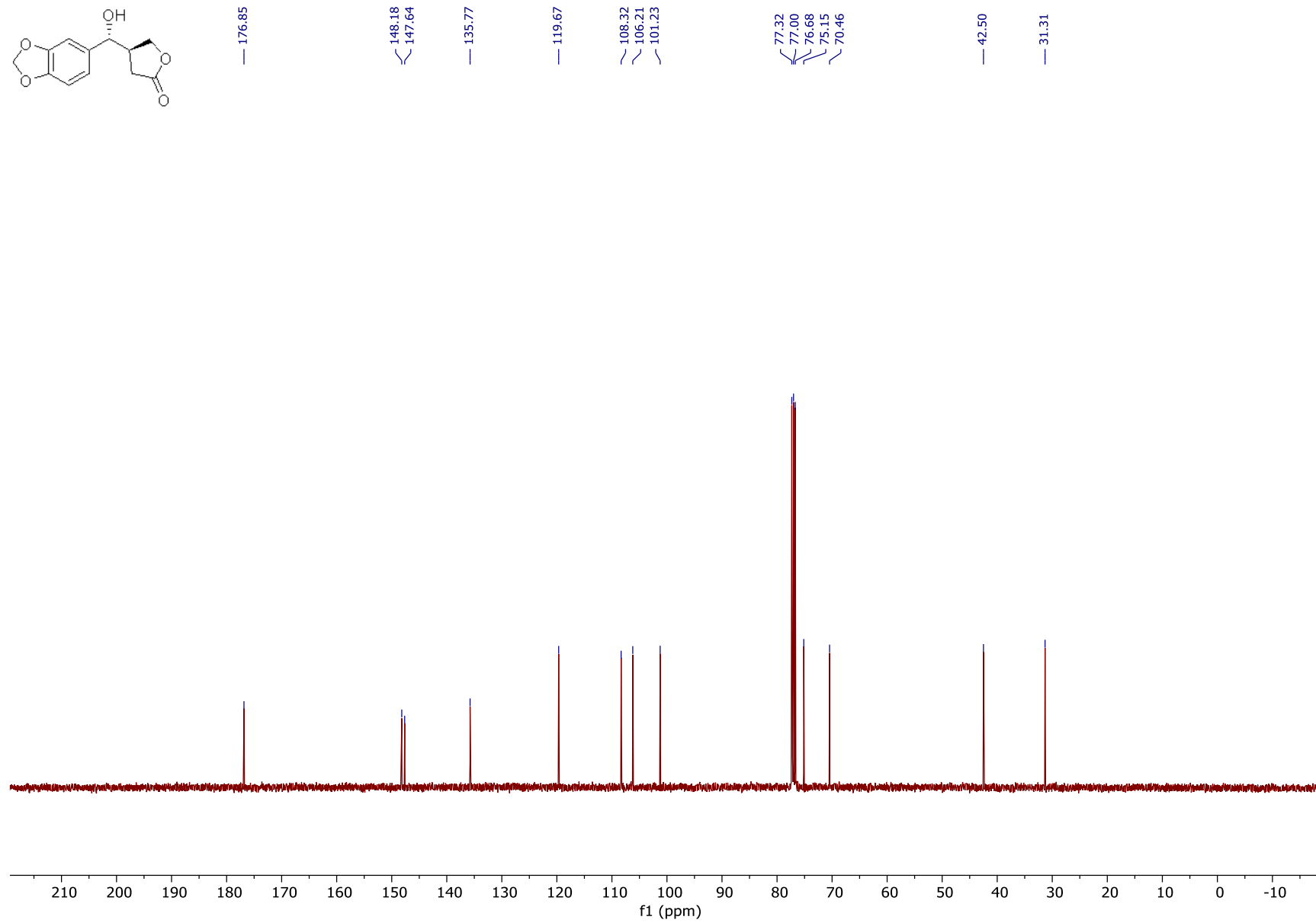
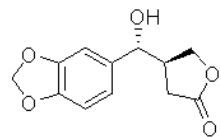
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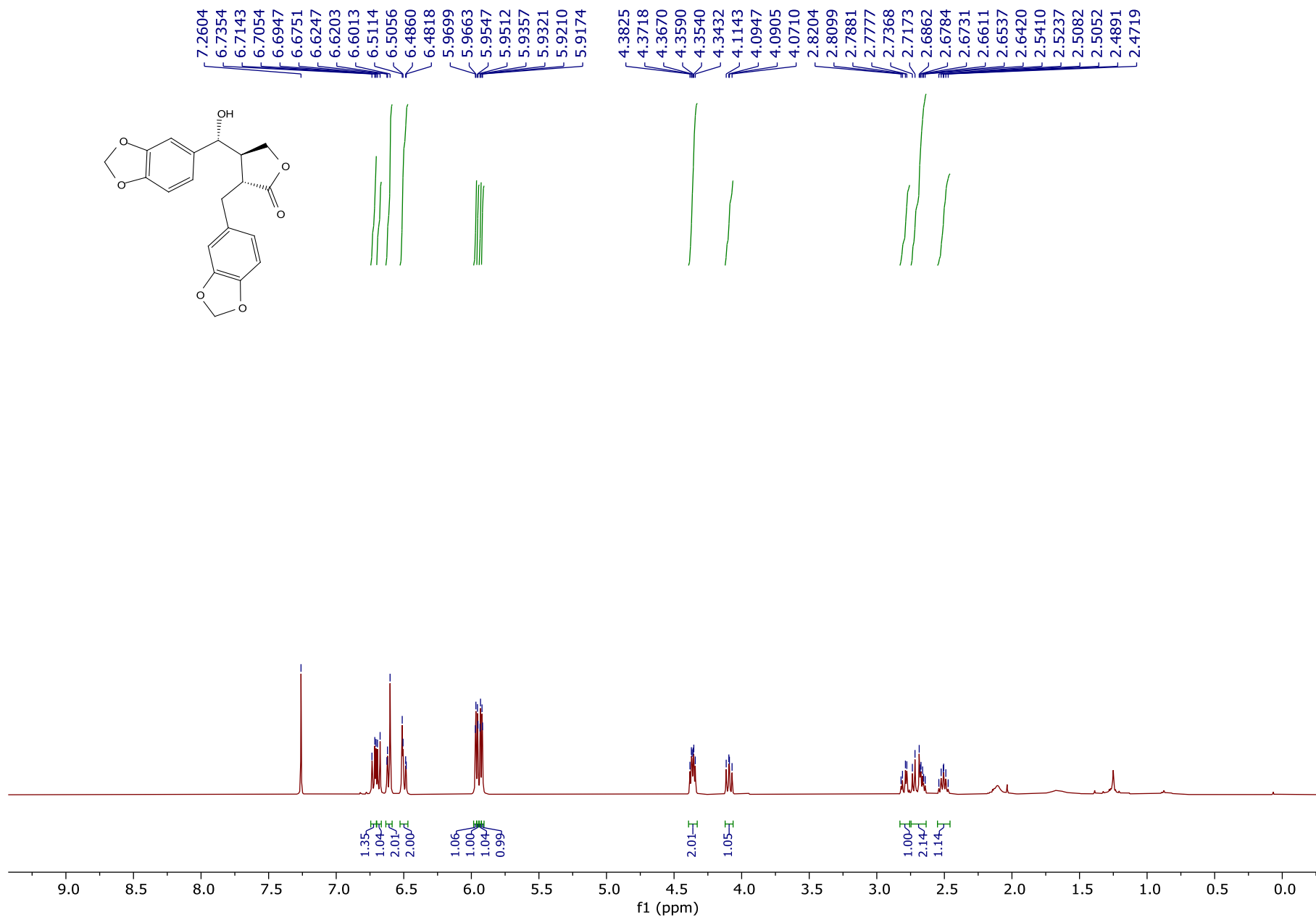
¹H NMR of lactone 13b (400 MHz, CDCl₃)



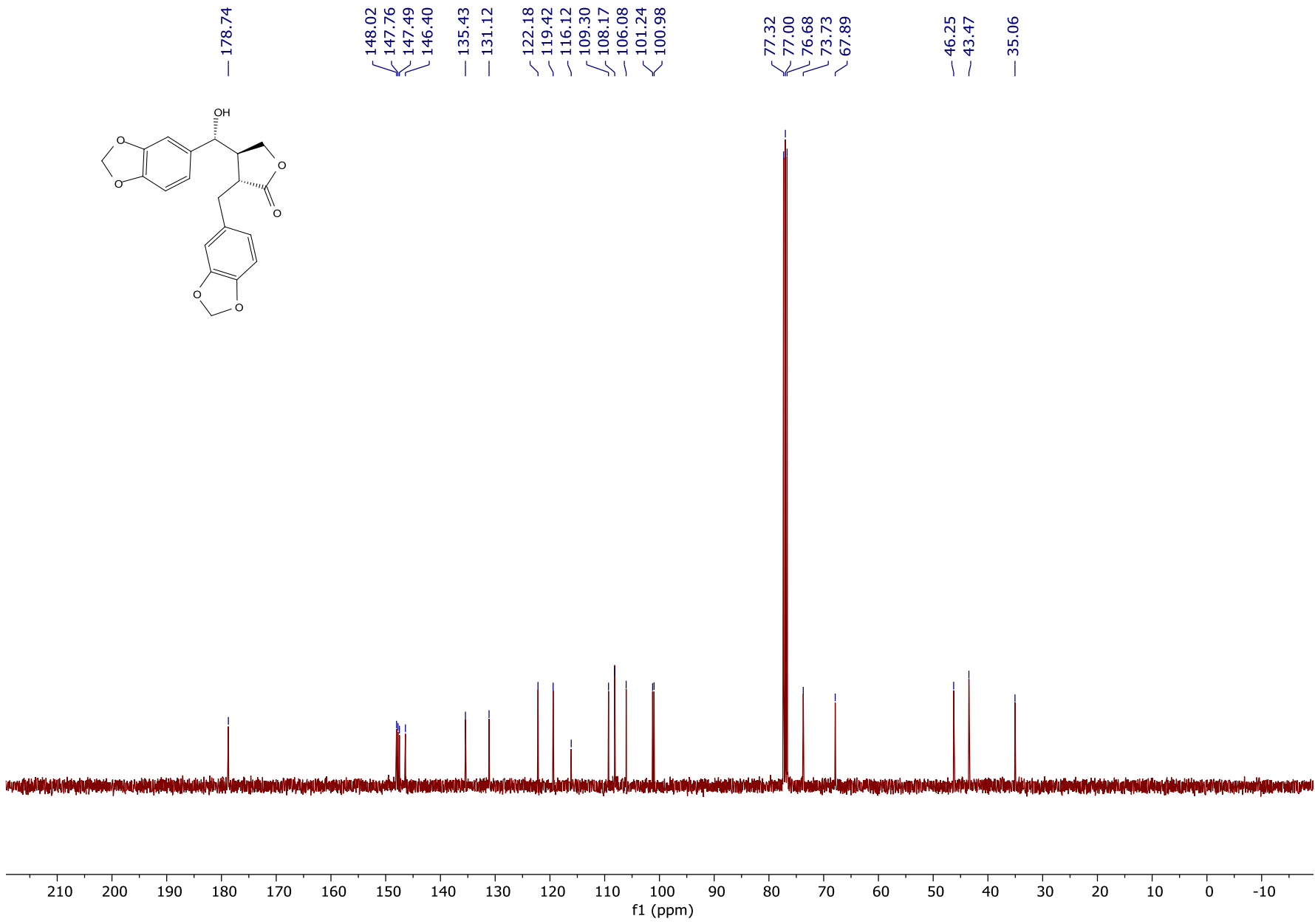
¹³C NMR of lactone 13b (101 MHz, CDCl₃)



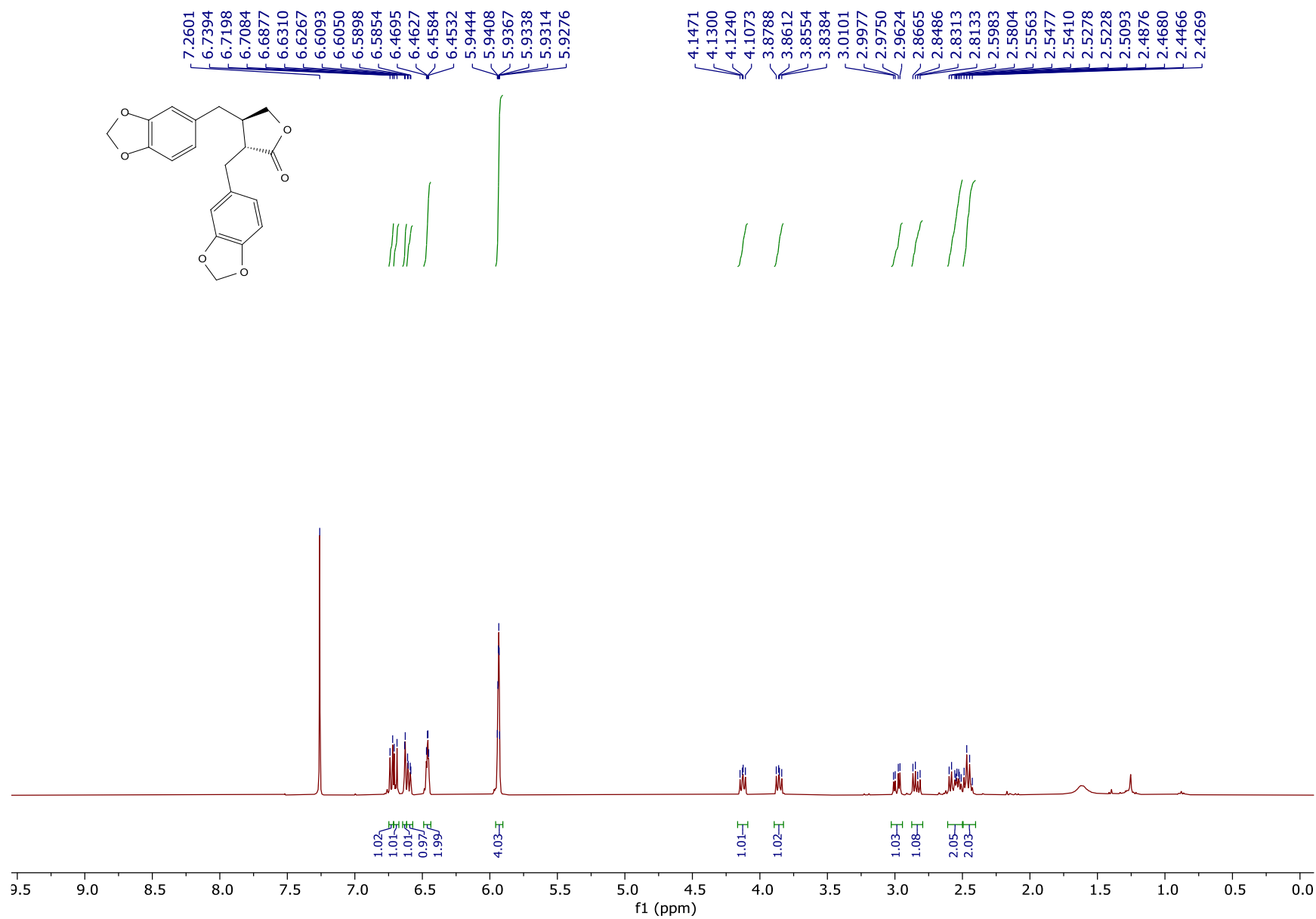
¹H NMR of (7'R)-Parabenzlactone 5 (400 MHz, CDCl₃)



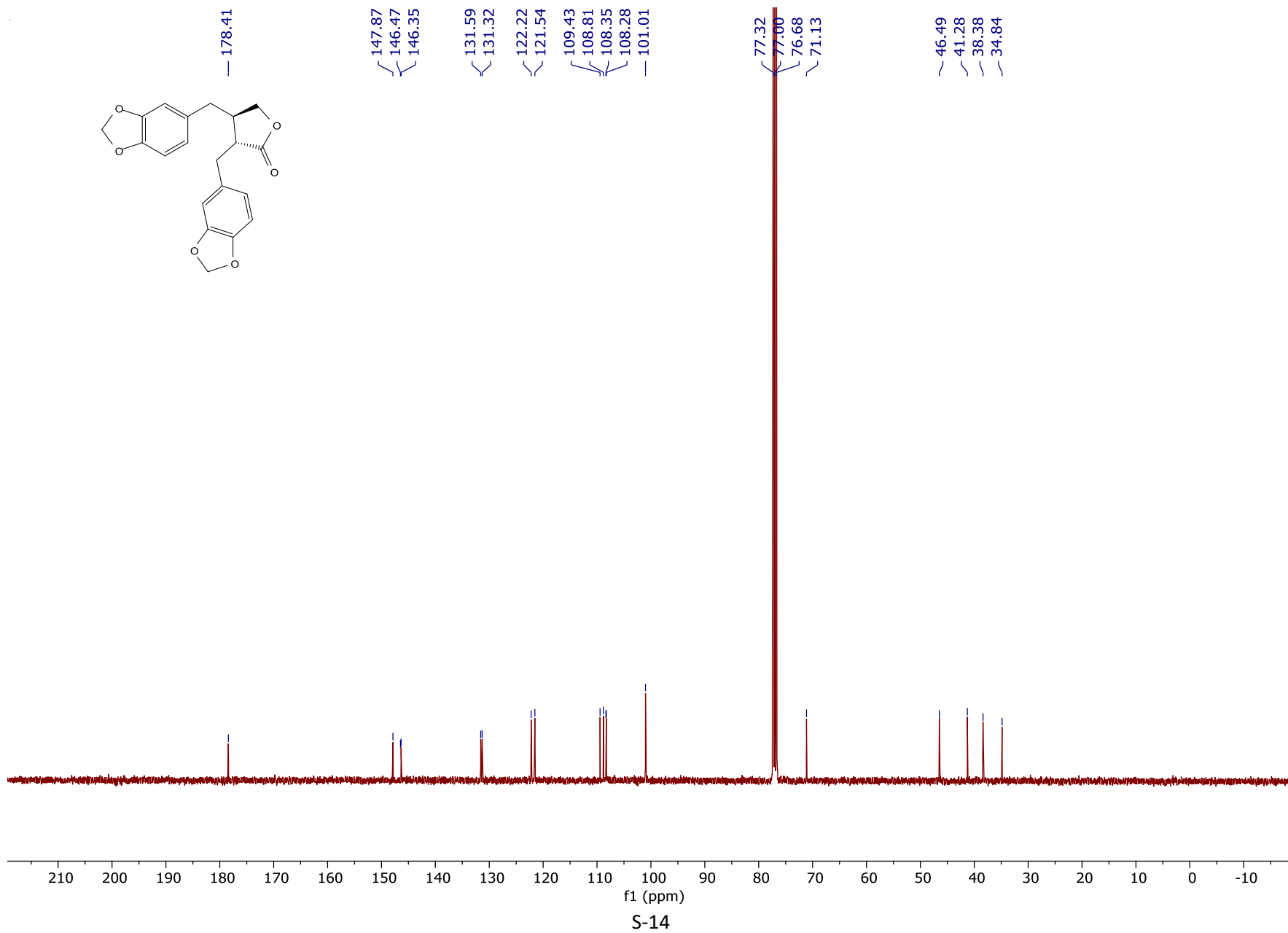
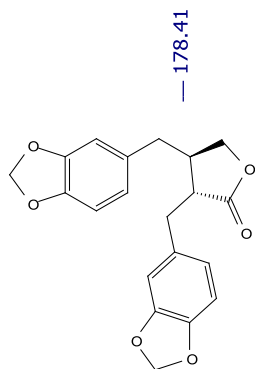
¹³C NMR of Parabenzlactone 5 (101 MHz, CDCl₃)



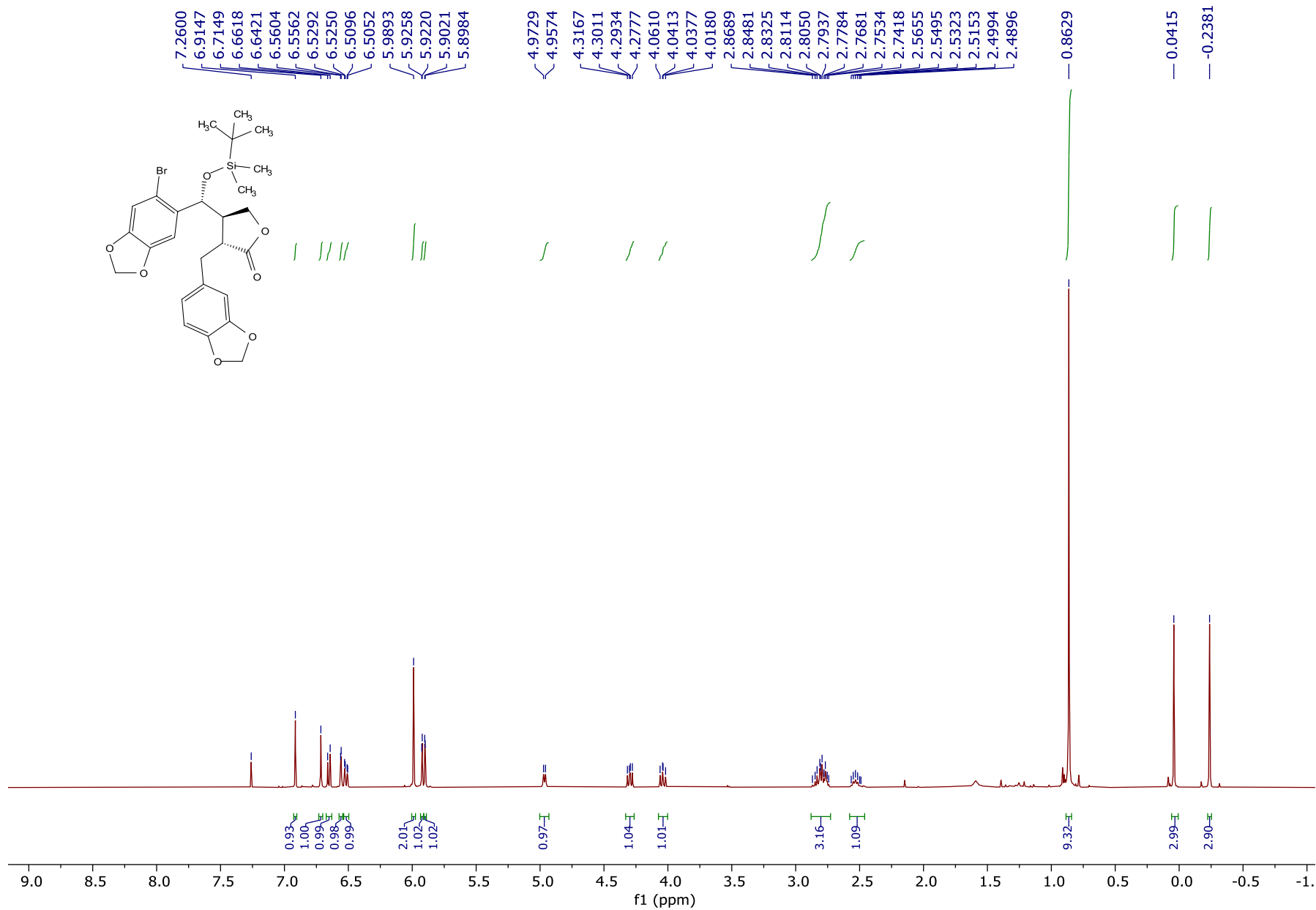
¹H NMR of Hinokinin 6 (400 MHz, CDCl₃)



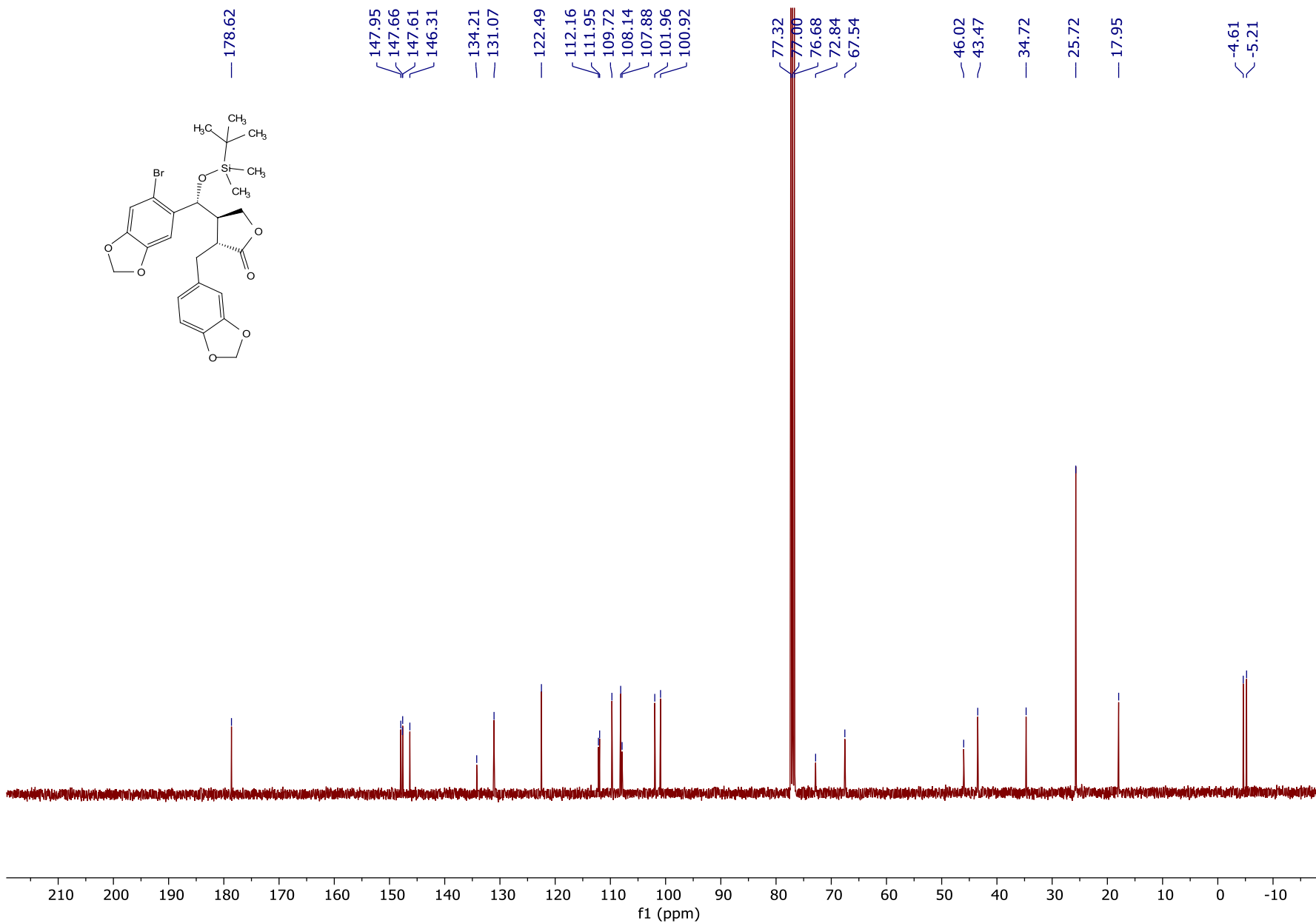
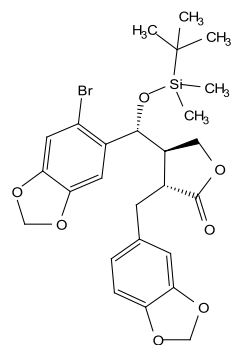
¹³C NMR of Hinokinin 6 (101 MHz, CDCl₃)



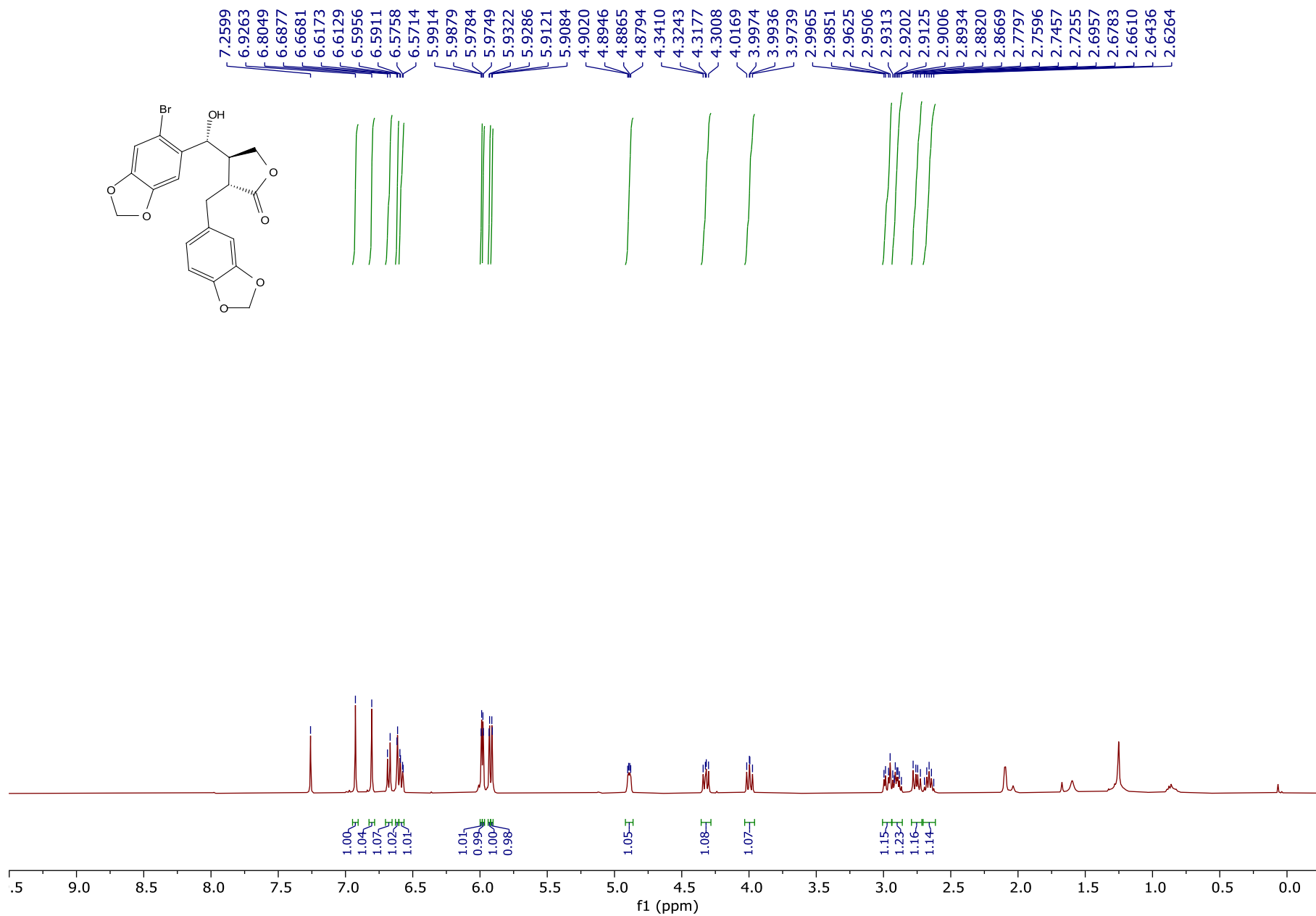
¹H NMR of compound 18 (400 MHz, CDCl₃)



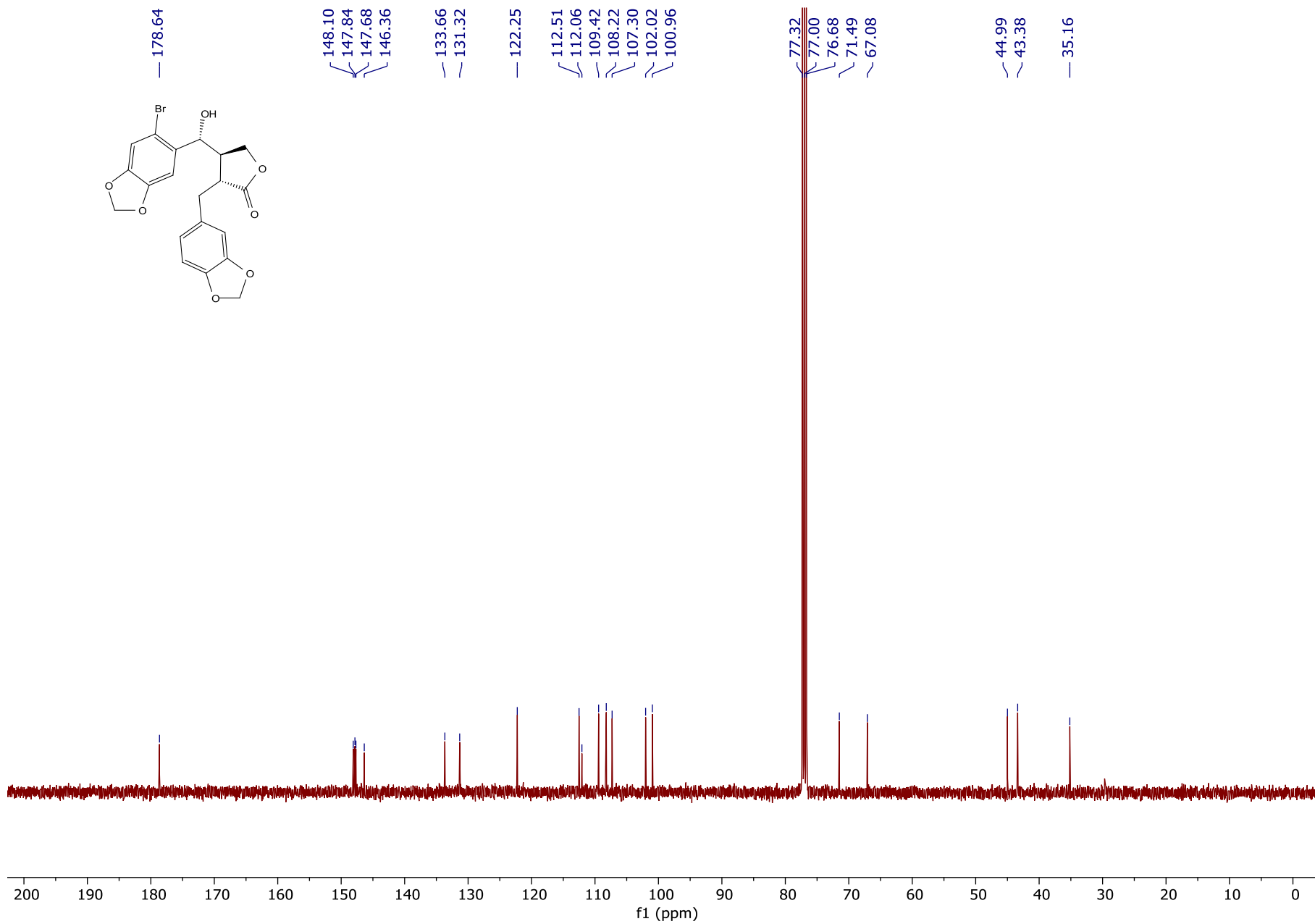
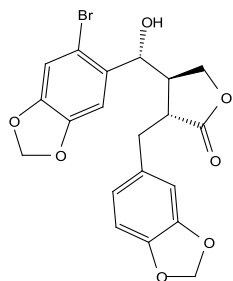
^{13}C NMR of compound 18 (101 MHz, CDCl_3)



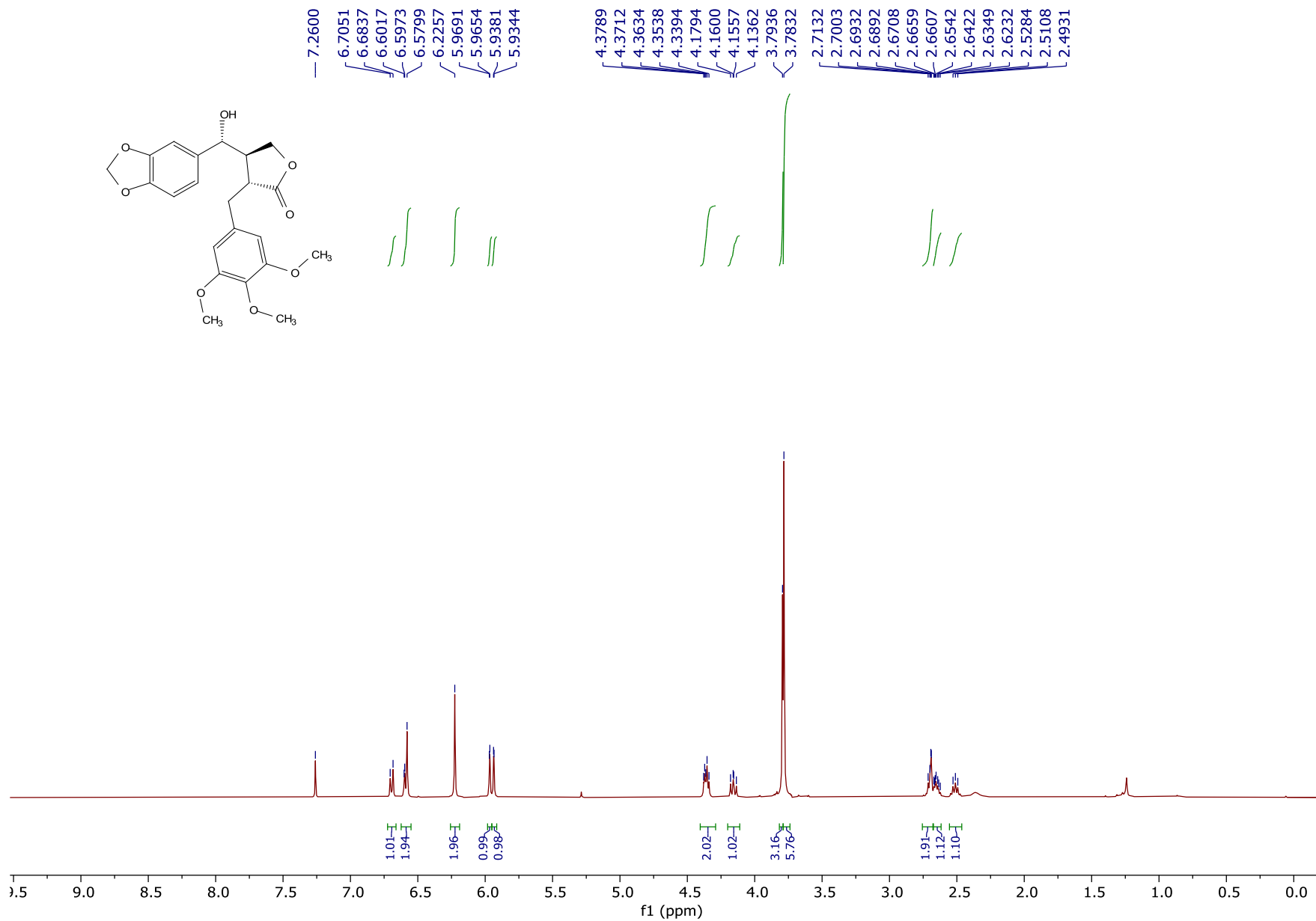
¹H NMR of Bromo-parabenzlactone 17 (400 MHz, CDCl₃)



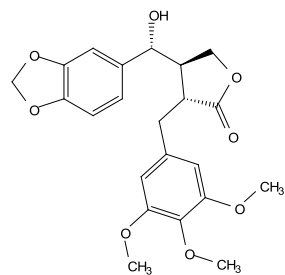
¹³C NMR of Bromo-parabenzlactone 17 (101 MHz, CDCl₃)



¹H NMR of (7'R)-Hydroxyatein 7 (400 MHz, CDCl₃)



¹³C NMR of (7'R)-Hydroxyatein 7 (101 MHz, CDCl₃)



— 178.74

— 153.12

— 148.18

— 147.65

— 136.70

— 135.39

— 133.09

— 119.58

— 107.93

— 106.04

— 105.95

— 101.41

— 77.32

— 77.00

— 76.68

— 74.36

— 68.33

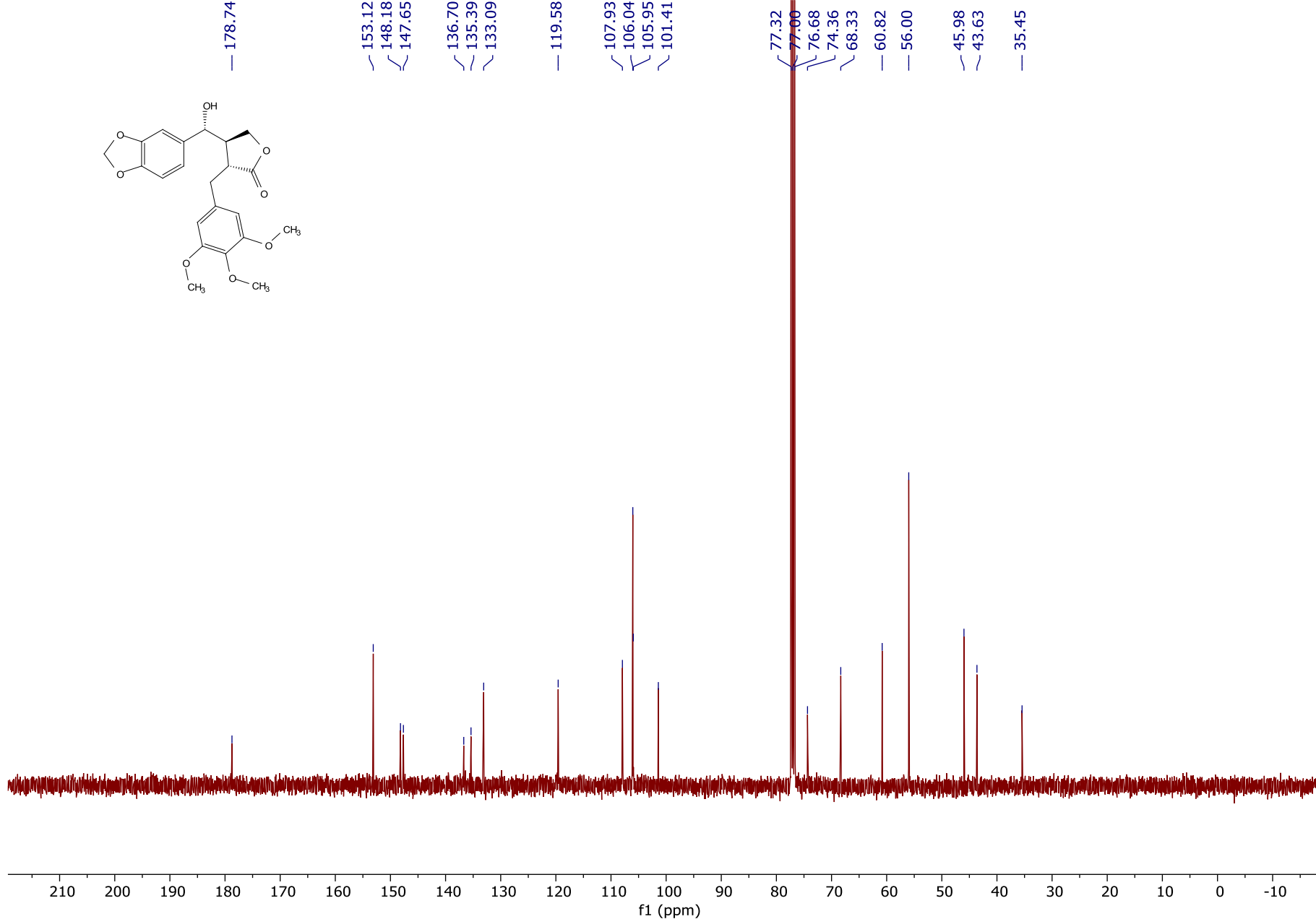
— 60.82

— 56.00

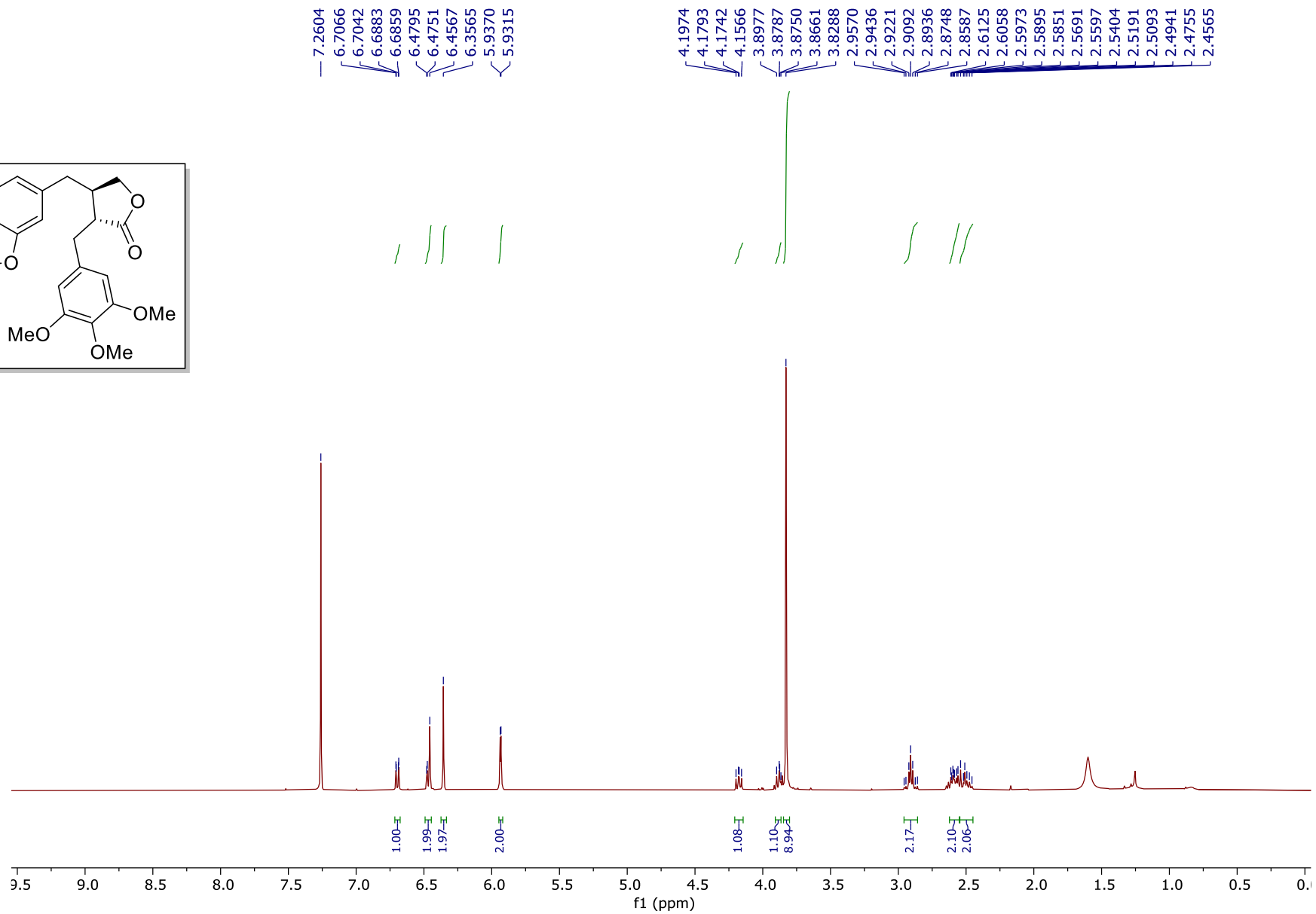
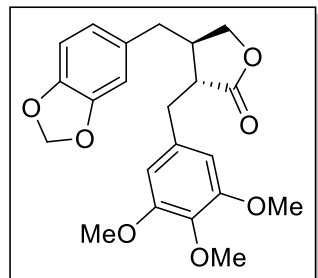
— 45.98

— 43.63

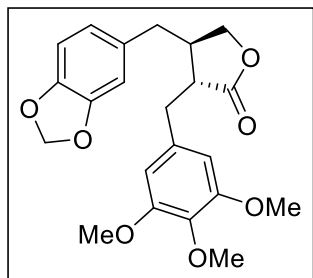
— 35.45



¹H NMR of (-)-Yatein 8 (400 MHz, CDCl₃)



¹³C NMR of (-)- yatein 8 (101 MHz, CDCl₃)



— 178.52

— 153.27
/ 147.94
— 146.42

— 136.88
/ 133.32
— 131.52

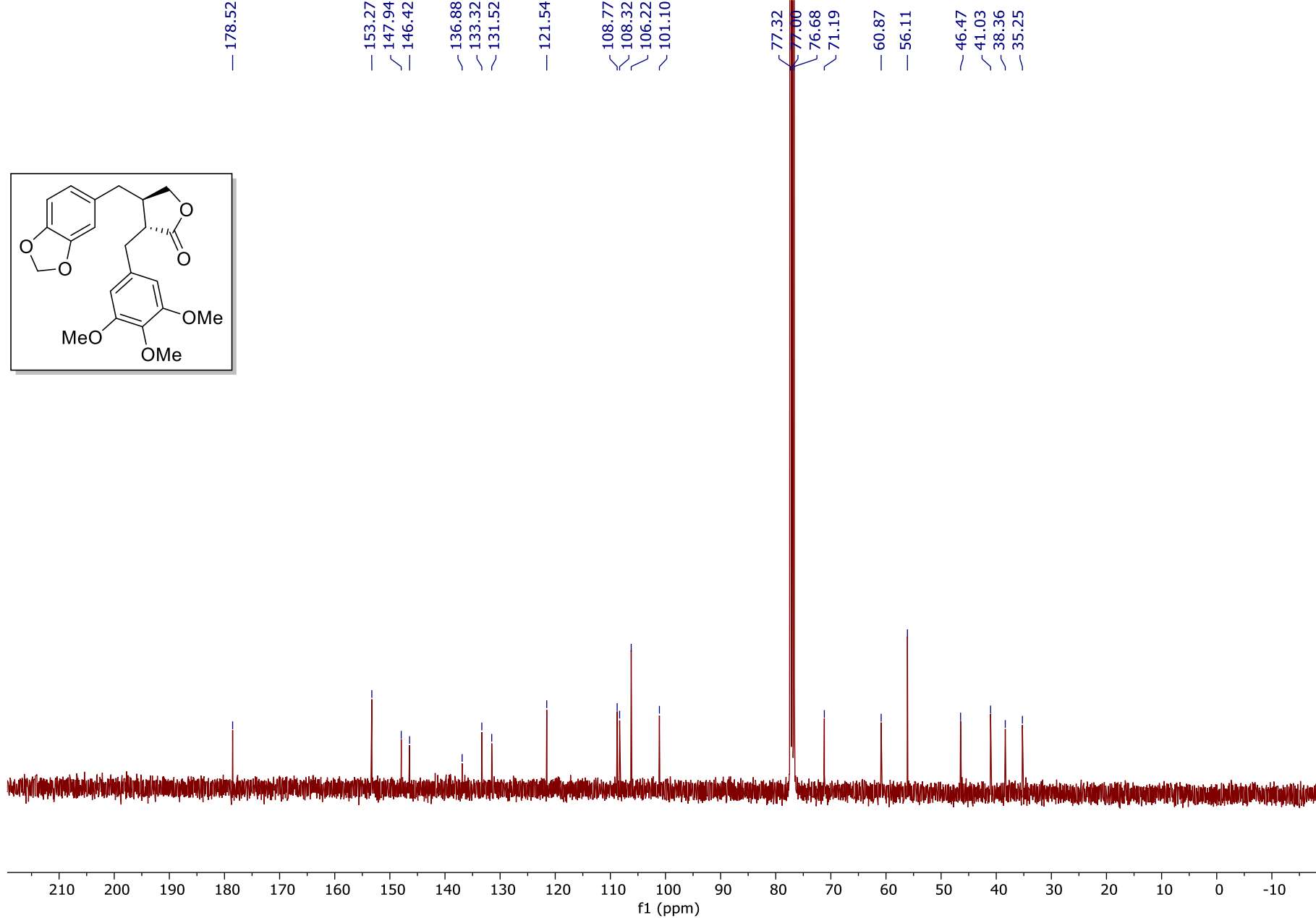
— 121.54

— 108.77
/ 108.32
/ 106.22
— 101.10

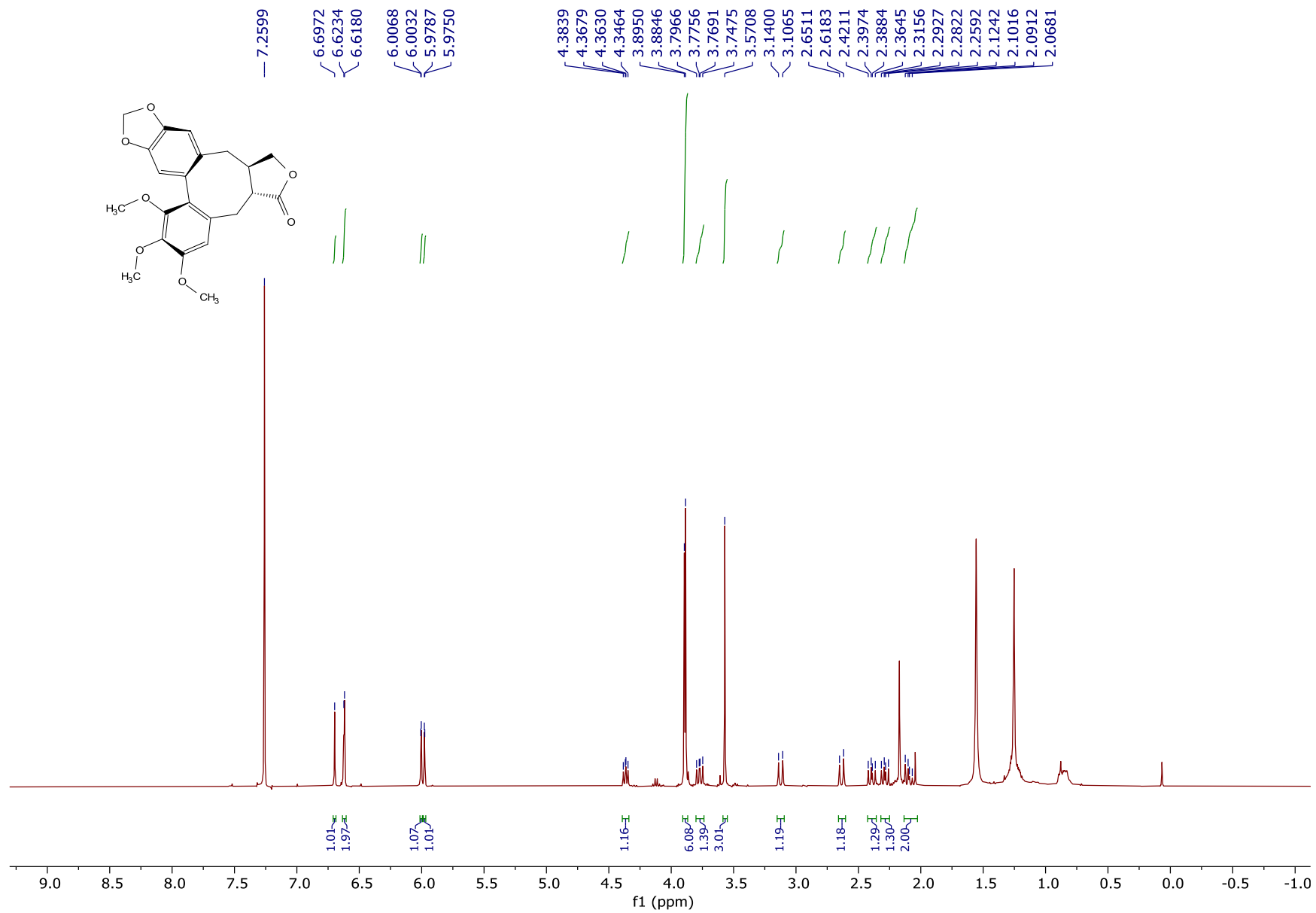
— 77.32
/ 77.00
/ 76.68
— 71.19

— 60.87
— 56.11

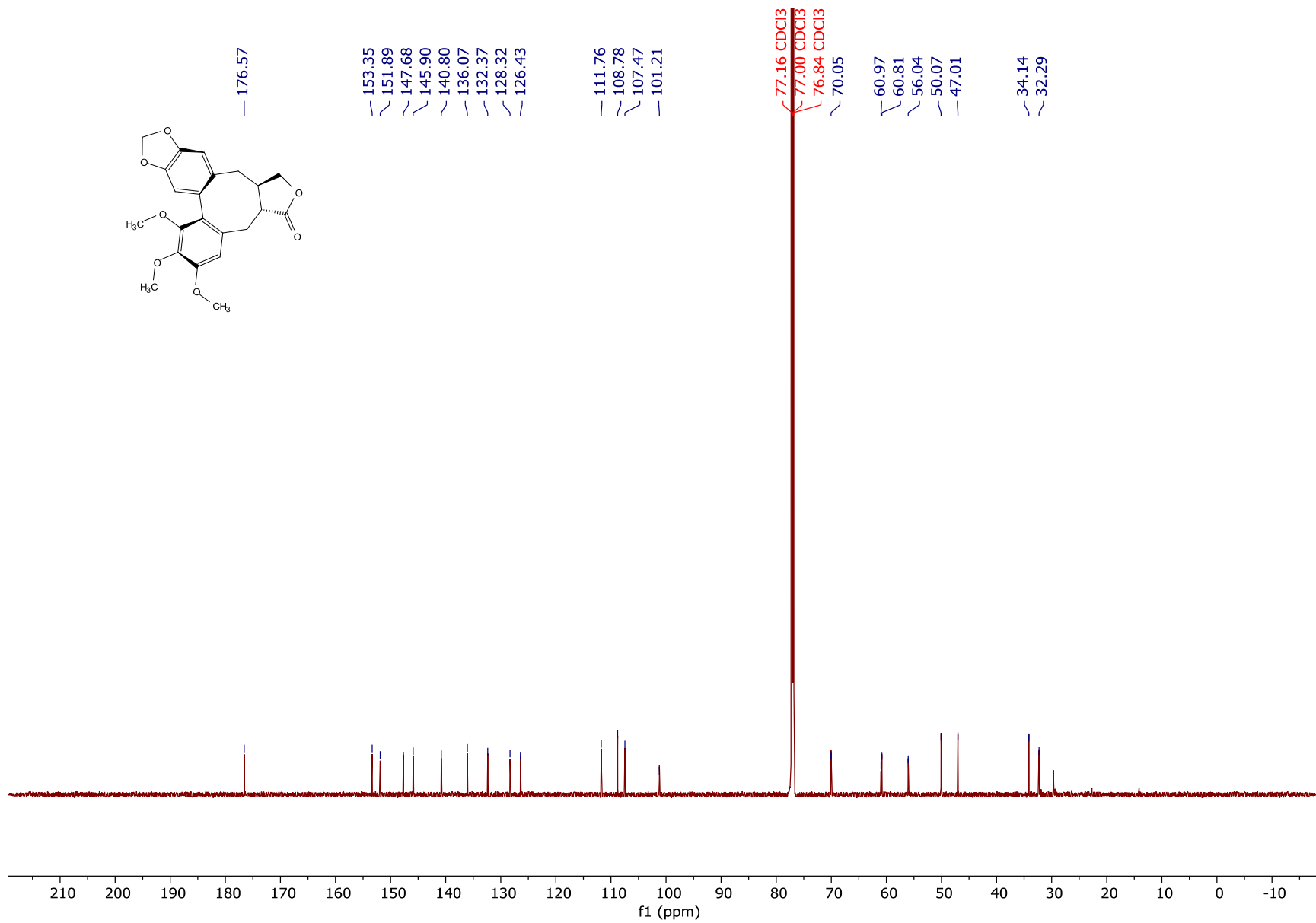
— 46.47
/ 41.03
/ 38.36
— 35.25



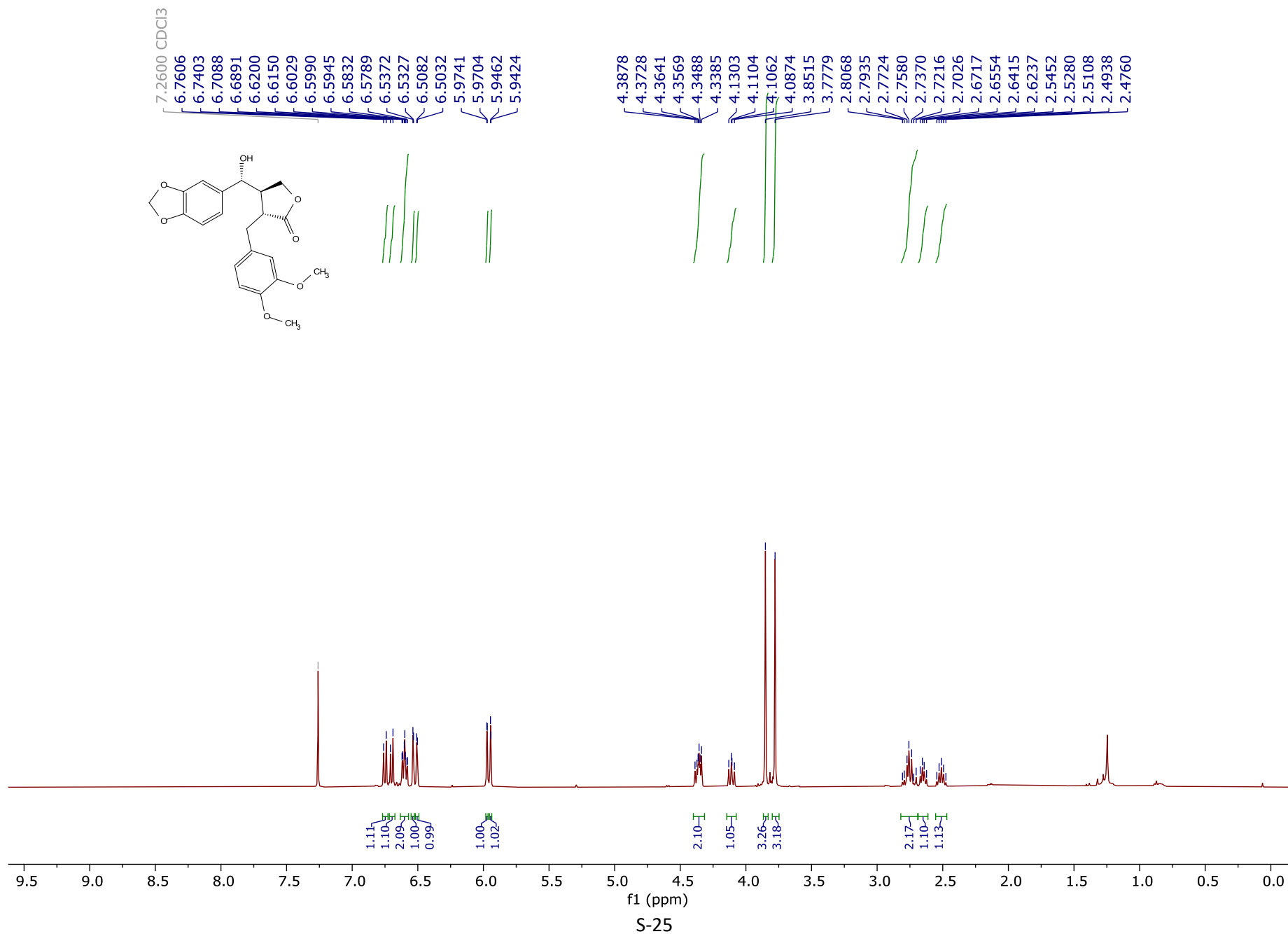
¹H NMR of (+)-Isostegane 4 (400 MHz, CDCl₃)



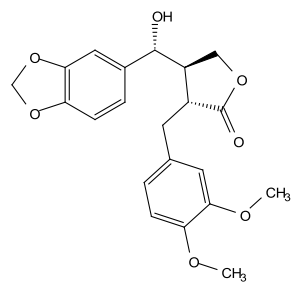
¹³C NMR of (+)-Isostegane 4 (202 MHz, CDCl₃)



¹H NMR of (7'R)-Hydroxybrusehernin 9 (400 MHz, CDCl₃)



¹³C NMR of (7'R)-Hydroxybrusehernin 9 (101 MHz, CDCl₃)



— 178.89

148.93
148.09
147.86
147.50

— 135.40

— 129.88

121.31
119.55

111.76
110.88

107.87
105.92

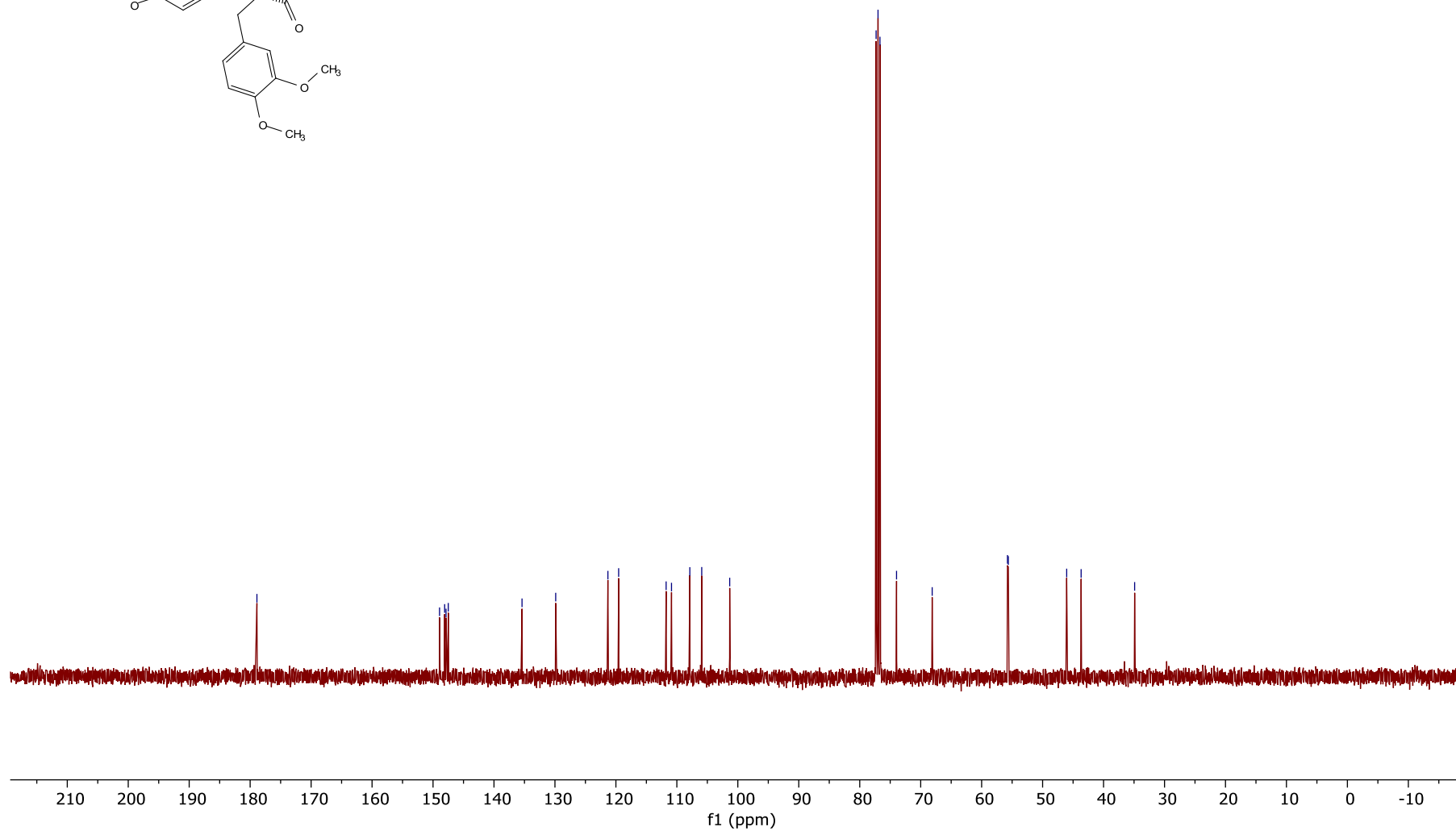
101.33

77.32
77.00
76.68
73.96
68.12

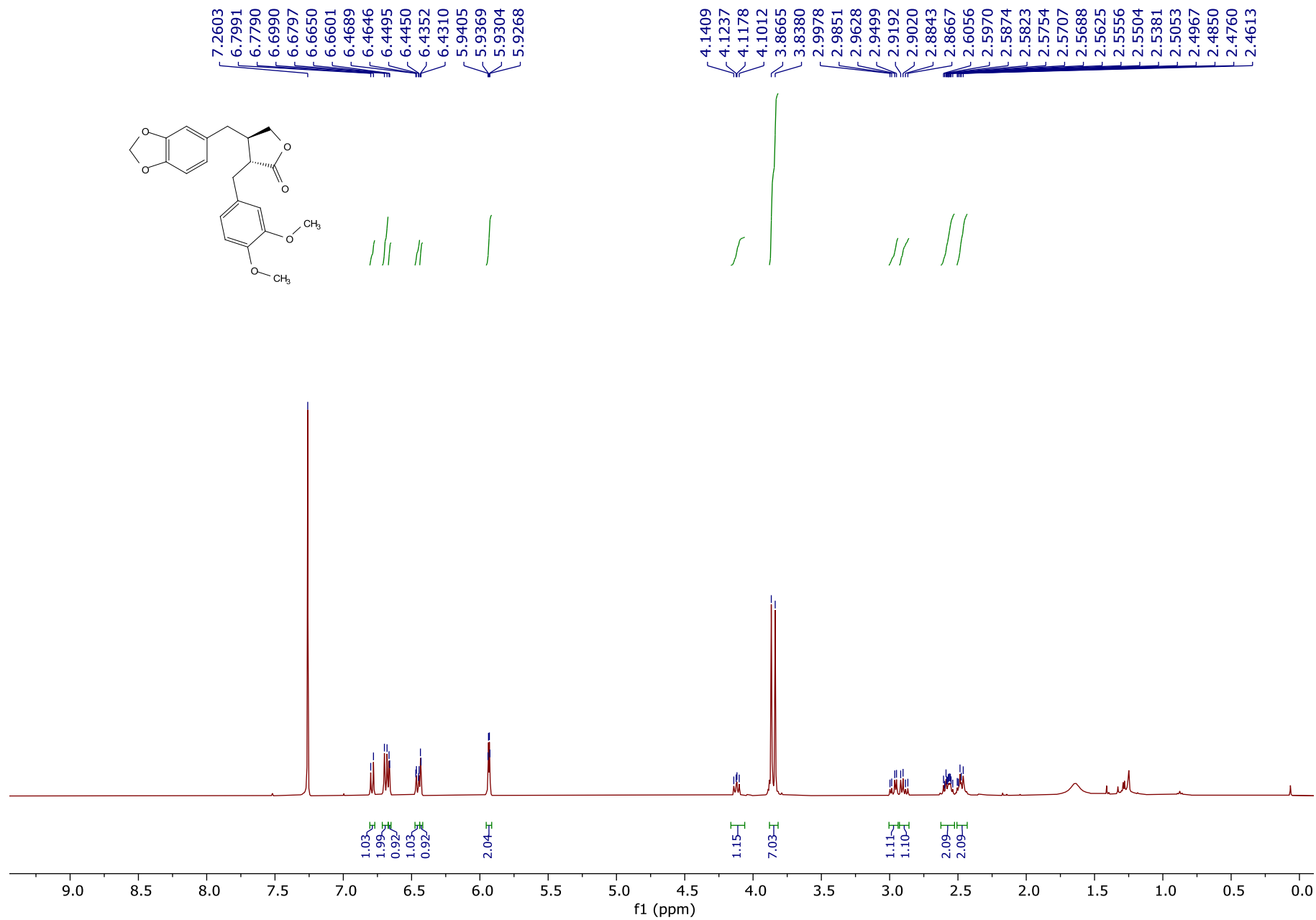
55.76
55.62

46.05
43.68

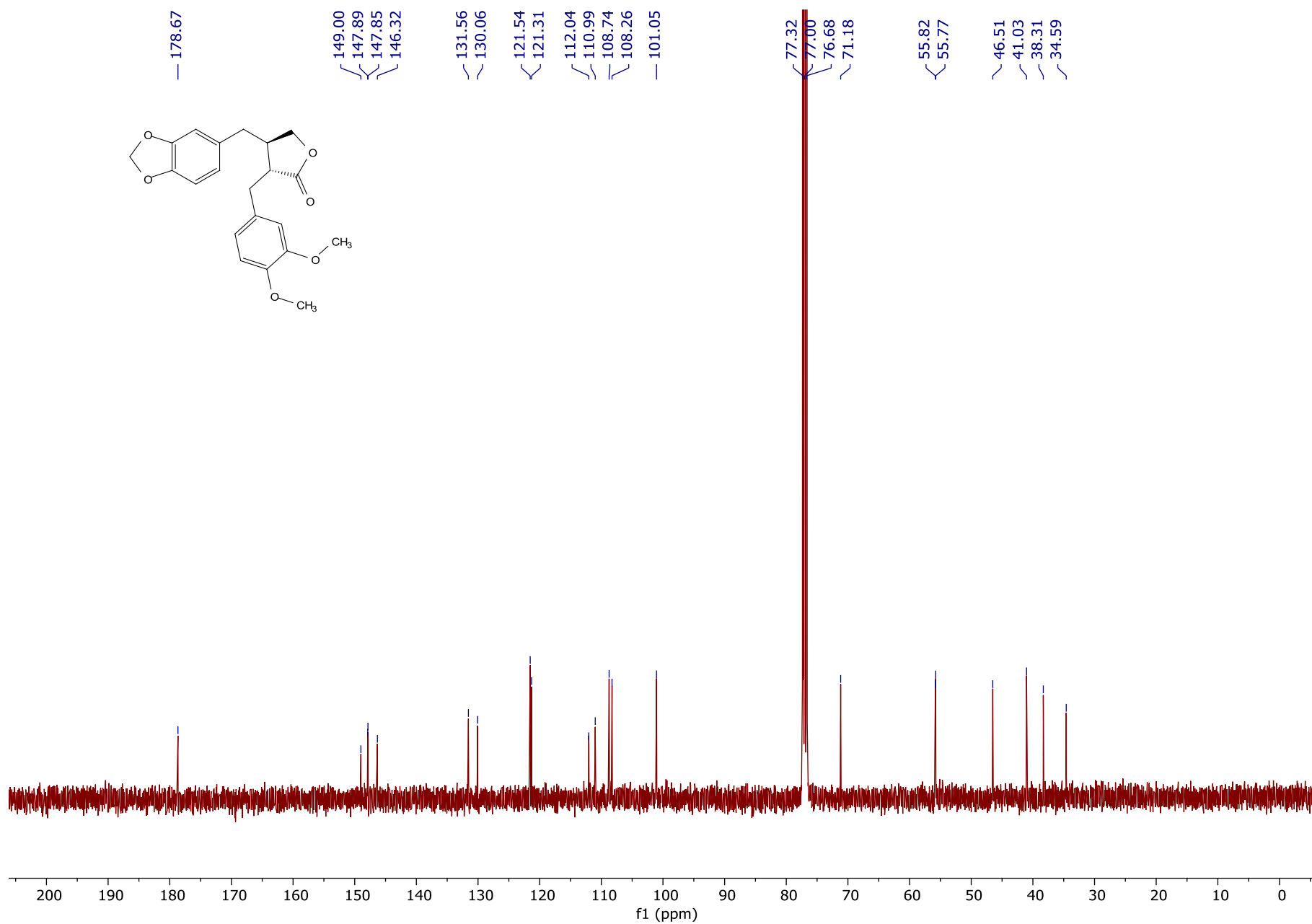
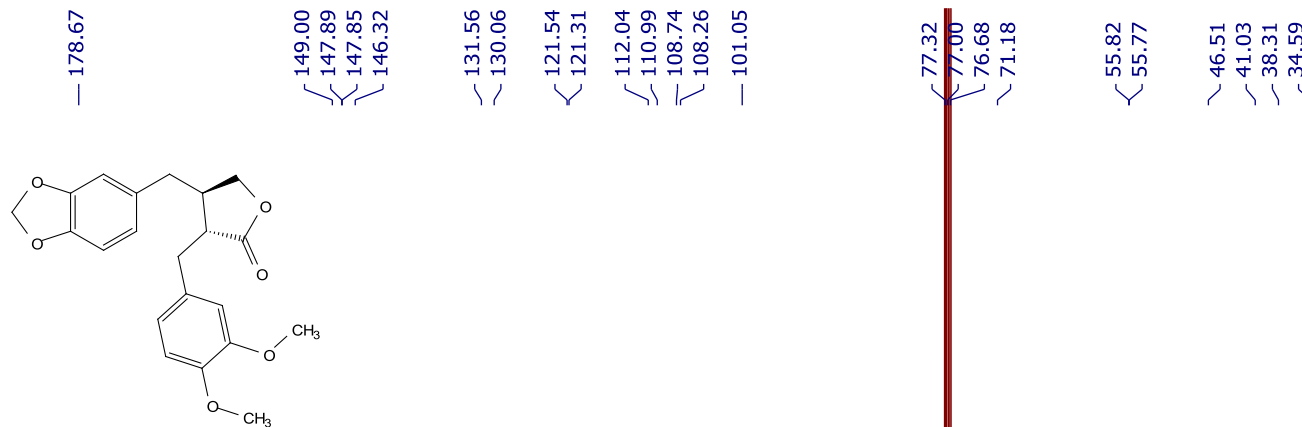
— 34.90



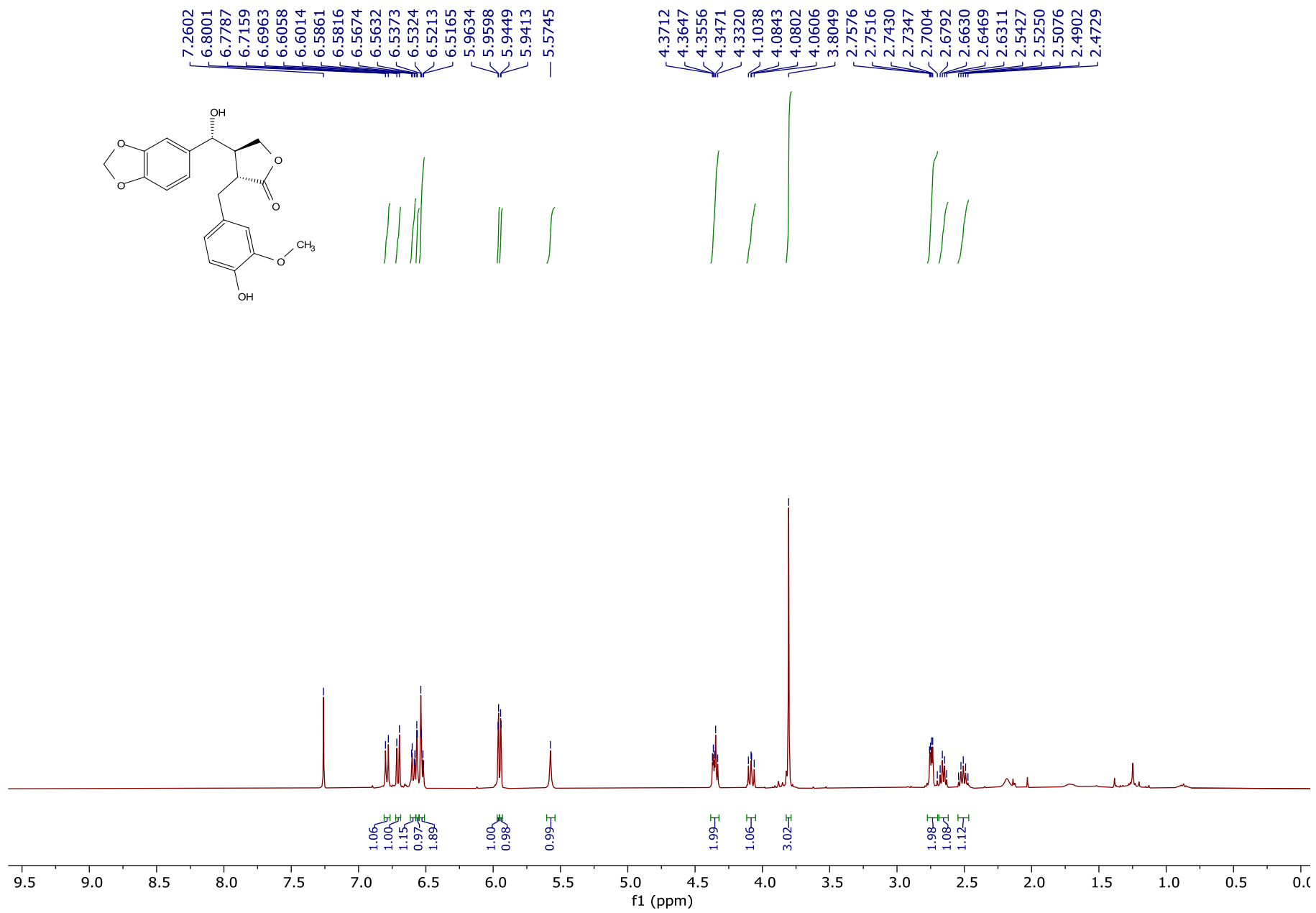
¹H NMR of (-)-Brusehernin 10 (400 MHz, CDCl₃)



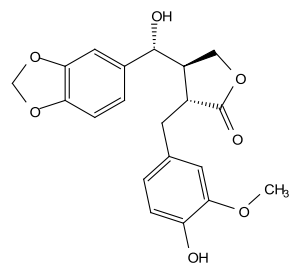
¹³C NMR of (-)-Brusehernin 10 (101 MHz, CDCl₃)



¹H NMR of (7'R)-Hydroxypluviatolide 11 (400 MHz, CDCl₃)



¹³C NMR of 7'-(R)-Hydroxypluviatolide 11 (101 MHz, CDCl₃)



— 178.95

148.04

147.45

146.58

144.44

— 135.47

— 129.26

122.00

119.50

114.16

111.32

108.01

106.02

101.28

77.32

77.00

76.68

73.85

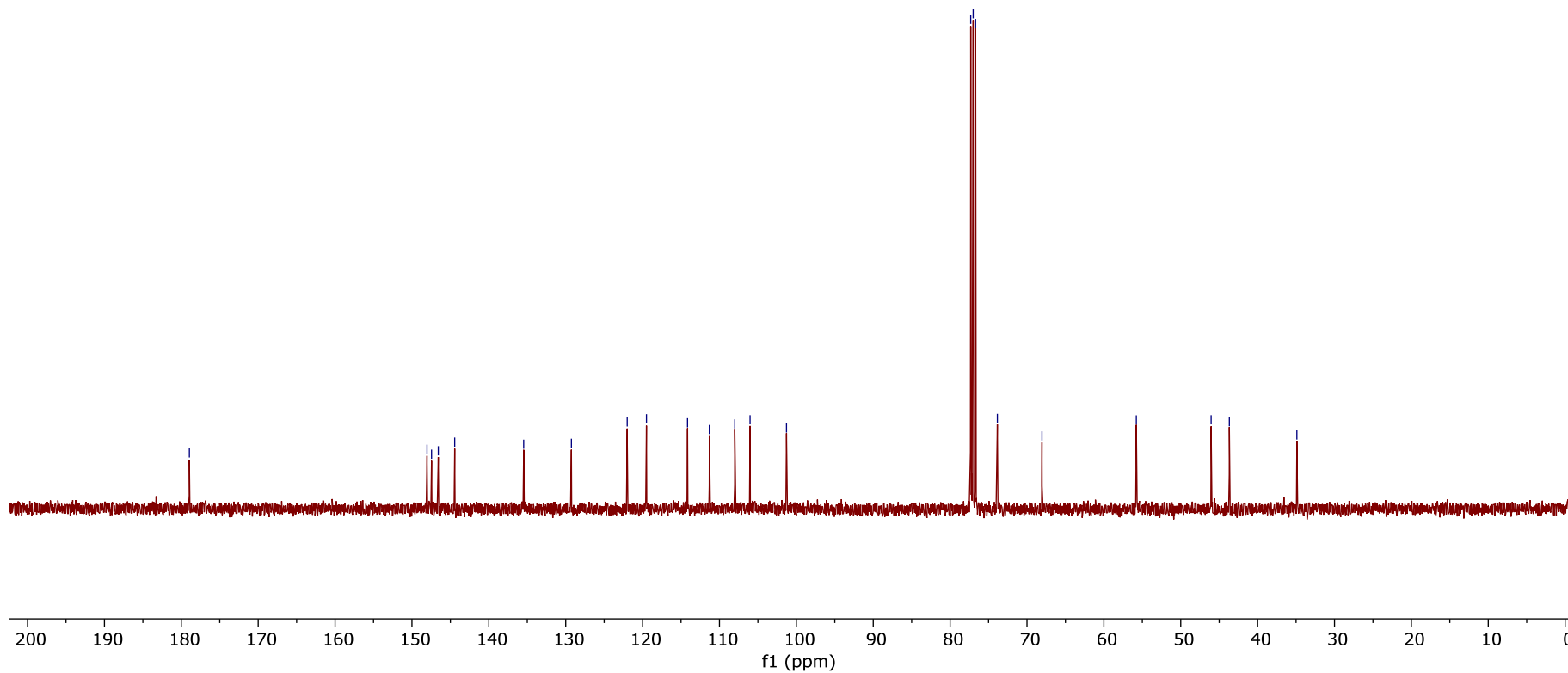
68.05

— 55.78

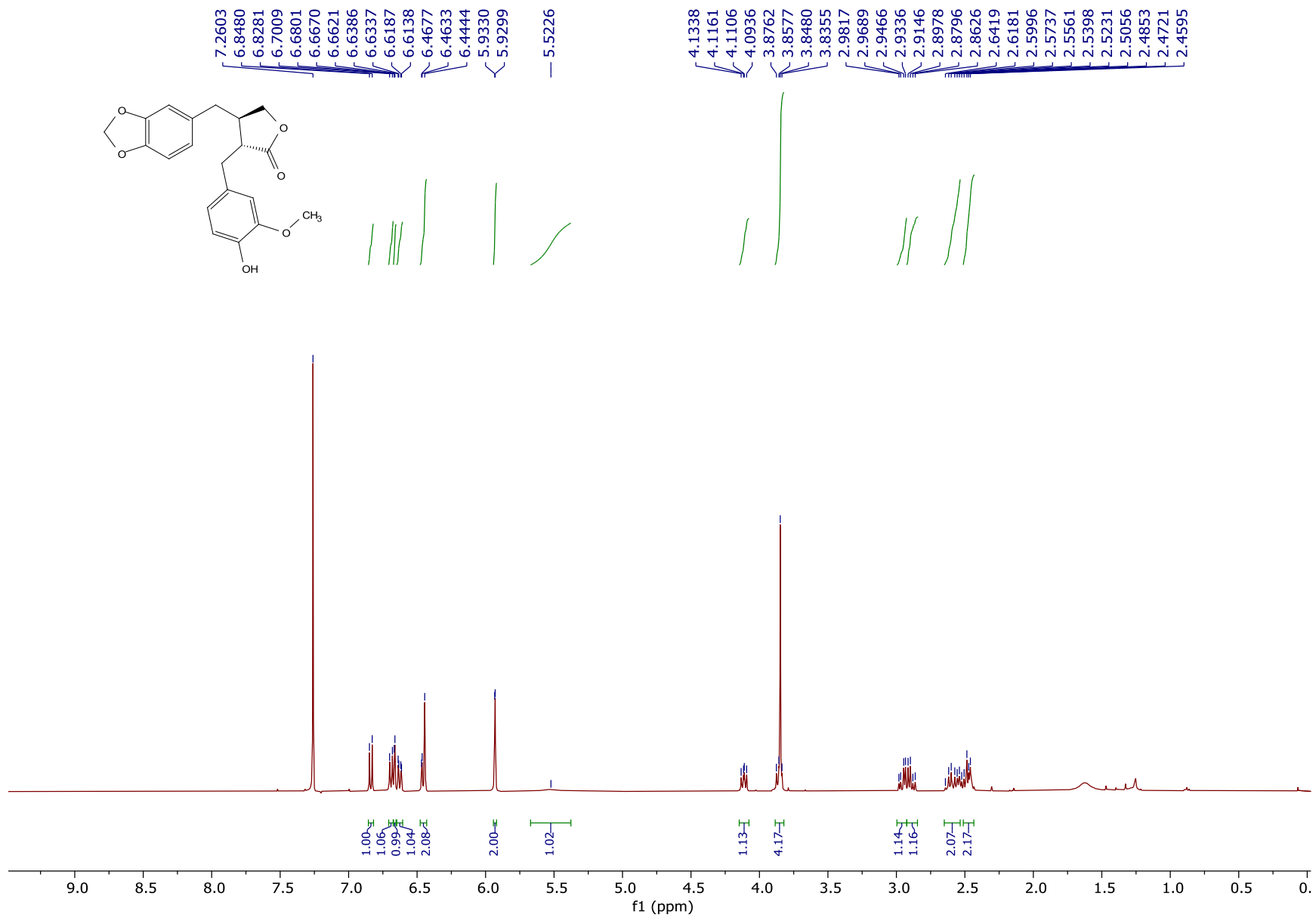
— 46.05

— 43.68

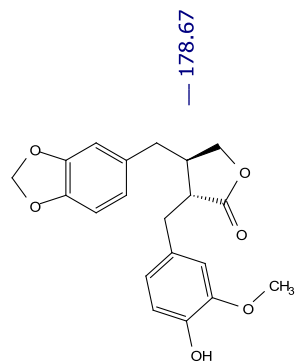
— 34.89



¹H NMR of (-)-Pluviatolide 12 (400 MHz, CDCl₃)



¹³C NMR of (-)-Pluviatolide 12 (101 MHz, CDCl₃)



178.67

147.89
146.69
146.36
144.56

131.62
129.46

122.10
121.57

114.26
111.53

108.82
108.33

101.06

77.34
77.02
76.71
71.21

55.89

46.62
41.02
38.32
34.64

