A general enantioselective route to the chamigrene natural product family

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Supplementary Data

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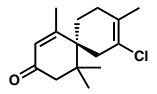
1. Methods

^{1}H NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz) or a Varian Inova 500 (at 500 MHz) instrument and are reported relative to the residual solvent peak (δ 7.26 for $CDCl_3$, 7.16 for C_6D_6, and δ 2.05 for acetone-d_6) or Me_4Si (δ 0.00) in the case of CCl_4. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian Mercury 300 (at 75 MHz), or a Varian Inova 500 (at 126 MHz) instrument and are reported relative the residual solvent peak (δ 77.0 for $CDCl_3$ and 128.06 for C_6D_6,). Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ ppm), as well as multiplicity and coupling constant (Hz) where applicable. ^{19}F NMR spectra were recorded on a Varian Inova 500 (at 470 MHz) instrument and are reported in terms of chemical shift (δ ppm) without the use of a reference peak. IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer and are reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-1010 polarimeter, using a 100 mm path-length cell.

2. Comparison of synthetic and published ^{1}H NMR, ^{13}C NMR, IR, and $[\alpha]_D$ data for the proposed structure of (+)-laurencenone B ((+)-7)



Proposed Structure of (+)-Laurencenone B ((+)-7)

Synthetic	**Natural**[1]
^{1}H NMR (500 MHz, acetone-d_6)	*^{1}H NMR (60, 250, or 360 MHz, acetone-d_6)*
(δ)	(δ)
5.80 (s, 1H)	5.90 (br s, 1H)
2.52–2.69 (br m, 2H)	2.70 (d, *J* = 18 Hz, 1H)
2.31 (dd, *J* = 0.98, 18.1 Hz, 1H)	1.6–2.3 (m, 6H)
2.19-2.27 (br m, 1H)	
2.02–2.16 (br m, 1H)	2.10 (d, *J* = 18 Hz, 1H)
1.88–2.02 (m, 2H)	
1.98 (d, *J* = 1.2 Hz, 3H)	1.98 (d, *J* = 2 Hz, 3H)
1.76–1.88 (br m, 1H)	
1.80 (br s, 3H)	1.75 (br d, *J* = ~4 Hz, 3H)
1.09 (s, 3H)	1.03 (s, 3H)
0.96 (s, 3H)	0.98 (s, 3H)
IR	*IR*

1. Kennedy, D. J.; Selby, I. A.; Thomson, R. H. *Phytochemistry* **1988**, *27*, 1761–1766.

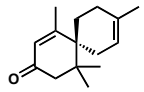
(cm^{-1}, selected values)	(cm^{-1})
1667	1670

Synthetic	**Semisynthetic**[2]
^{1}H NMR (500 MHz, $CDCl_3$)	*^{1}H NMR (250 MHz, $CDCl_3$)*
(δ)	(δ)
5.89 (s, 1H)	5.89 (br s, 1H)
2.50–2.69 (br m, 2H)	2.59 (AB m, 2H)
2.26 (br d, *J* = 18.3 Hz, 1H)	1.6–2.3 (m, 6H)
2.13–2.23 (br m, 1H)	
1.99–2.14 (br m, 2H)	
1.98 (d, *J* = 0.98 Hz, 3H)	1.98 (d, *J* = 0.9 Hz, 3H)
1.93 (ddd, *J* = 5.4, 12.3, 12.3, Hz, 1H)	
1.81 (br s, 3H)	1.81 (s, 3H)
1.72–1.80 (m, 1H)	
1.06 (s, 3H)	1.07 (s, 3H)
0.97(s, 3H)	0.97 (s, 3H)
^{13}C NMR (126 MHz, $CDCl_3$)	*^{13}C NMR ($CDCl_3$)*
(δ)	(δ)
198.2	198.04
168.6	168.38
129.6	129.64
127.5	127.54
126.2 (br)	126.23
48.8	48.90
46.3	46.38
40.4	40.45
36.3	36.33
30.4 (br)	30.37
30.1	30.22
24.8	24.80
23.9 (two overlapping CH_3 peaks)	23.89
	23.81
19.7	19.69
IR	*IR*
(cm^{-1}, selected values)	(cm^{-1})
3025	3000
2963	2950
2933	2900
2911 (shoulder)	
2880 (shoulder)	

2. Brennan, M. R.; Erickson, K. L; Minott, D. A.; Pascoe, K. O. *Phytochemistry* **1987**, *26*, 1053–1057.

2855	2850
1667	1660
1612	1610
$[\alpha]^{24}_{D}$	$[\alpha]^{25}_{D}$
+47.08° (c = 0.36, $CHCl_3$)	+58.3° (c = 0.36, $CHCl_3$)

3. Comparison of synthetic and published ^{1}H NMR, ^{13}C NMR, IR, and $[\alpha]_D$ data for (–)-laurencenone C (8)



(–)-Laurencenone C (8)

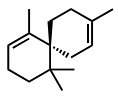
Synthetic	**Natural (original isolation)**[1]
^{1}H NMR (500 MHz, acetone-d_6)	*^{1}H NMR (60, 250, or 360 MHz, acetone-d_6)*
(δ)	(δ)
5.76 (br s, 1H)	5.95 (br s, 1H)
5.49–5.55 (br m, 1H)	5.62 (br s, 1H)
2.46–2.73 (br m, 1H)	2.75 (d, J = 18 Hz, 1H)
2.21–2.31 (br m, 1H)	2.2 (d, J = 18 Hz, 1H)
1.74–2.12 (br m, 6H)	1.6–2.3 (m, 6H)
1.97 (d, J = 1.5 Hz, 3H)	1.99 (d, J = 2 Hz, 3H)
1.65–1.69 (br m, 3H)	1.76 (br d, J = ~4 Hz, 3H)
1.03 (s, 3H)	1.03 (s, 3H)
0.93 (s, 3H)	0.97 (s, 3H)
IR	*IR*
(cm^{-1}, selected values)	(cm^{-1})
1667	1670

Synthetic	**Natural (second isolation)**[3]
^{1}H NMR (500 MHz, $CDCl_3$)	*^{1}H NMR (400 MHz, $CDCl_3$)*
(δ, selected values)	(δ)
5.87 (br s, 1H)	5.87 (s, 1H)
5.47–5.53 (br m, 1H)	5.50 (m, 1H)
1.97 (d, J = 1.5 Hz, 3H)	1.98 (s, 3H)
1.68 (br s, 3H)	1.68 (s, 3H)
1.03 (s, 3H)	1.03 (s, 3H)
0.95 (s, 3H)	0.95 (s, 3H)

3. Asakawa, Y.; Tori, M.; Masuya, T.; Frahm, J.-P. *Phytochemistry* **1990**, *29*, 1577–1584.

^{13}C NMR (126 MHz, $CDCl_3$)	*^{13}C NMR (22.5 or 100 MHz, $CDCl_3$)*
(δ)	(δ)
198.6	198.5
170.4	170.3
134.1	131.4
127.0	127.0
121.6	121.6
48.9	49.0
43.4	43.4
40.4	40.4
30.6 (br)	30.6
28.2	28.2
27.9	28.0
24.8	24.8
24.2	24.2
23.9 (br)	23.4
23.3	23.3
IR	*IR*
(cm^{-1}, selected values)	(cm^{-1})
1667	1660
1610	1610
$[\alpha]^{26}_D$	$[\alpha]_D$
–87.98° (*c* 1.00, $CHCl_3$)	–43° (*c* 1.0, $CHCl_3$)

4. Comparison of synthetic and published ^{1}H NMR, IR, and $[\alpha]_D$ data for (–)-α-chamigrene (5)



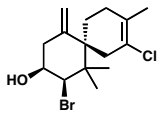
(–)-α-Chamigrene (5)

Synthetic	**Natural**[4]
^1H NMR (300 MHz, CCl_4)	*^1H NMR (CCl_4)*
(δ, selected values)	(δ)
5.36–5.43 (m, 1H)	5.3 (unresolved m, 2H)
5.23–5.29 (m, 1H)	
1.60–1.65 (m, part of a 14H m (1.55–2.02))	1.63 (br s, 6H)

4. Ohta, Y.; Hirose, Y. *Tetrahedron Lett*. **1968**, *9*, 2483–2485.

0.89 (s, 3H)	0.89 (s, 3H)
0.82 (s, 3H)	0.84 (s, 3H)
IR	*IR*
(cm^{-1}, selected values)	(cm^{-1})
1655	1655
832	830
810	810
800	800
760	760
$[\alpha]^{26}_{D}$	$[\alpha]_{D}$
–64.60° (*c* 0.21, $CHCl_3$)	–14.5° (*c* 0.21, $CHCl_3$)

5. Comparison of synthetic and published ^{1}H NMR data for (+)-elatol (1)



(+)-Elatol (1)

Synthetic	**Natural**[5]
^{1}H NMR (500 MHz, $CDCl_3$)	*^{1}H NMR (100 MHz, $CDCl_3$)*
(selected values)	*(published values from original isolation)*
(δ)	(δ)
5.13 (s, 1H)	5.12 (s, 1H)
4.80 (s, 1H)	4.80 (s, 1H)
4.61 (d, *J* = 2.9 Hz, 1H)	4.60 (d, *J* = 3 Hz, 1H)
4.13–4.17 (m, 1H)	4.16 (m, 1H)
1.70 (br s, 3H)	1.70 (m, 3H)
1.08 (s, 3H)	1.10 (s, 6H)
1.07 (s, 3H)	

5. Sims, J. J.; Lin, G. H. Y.; Wing, R. M. *Tetrahedron Lett*. **1974**, *15*, 3487–3490.

6. Natural Product Spectra

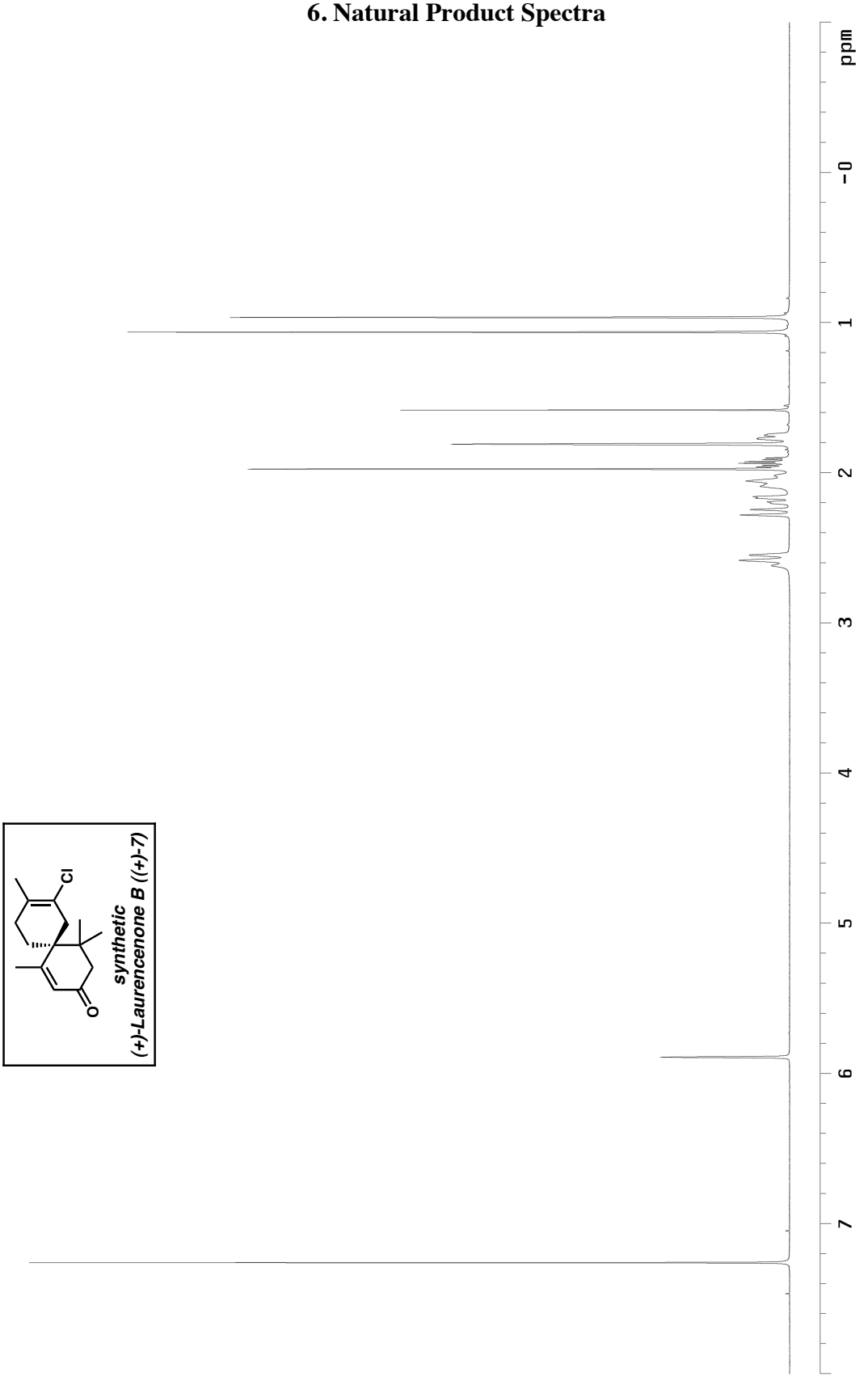
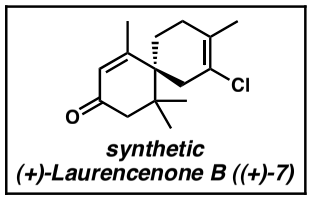


Figure S.1 ^{1}H NMR (500 MHz, $CDCl_3$) of synthetic (+)-laurencenone B ((+)-**7**).



synthetic
(+)-Laurencenone B ((+)-7)

Figure S.2 ^{1}H NMR (500 MHz, acetone-d_6) of synthetic (+)-laurencenone B ((+)-**7**).

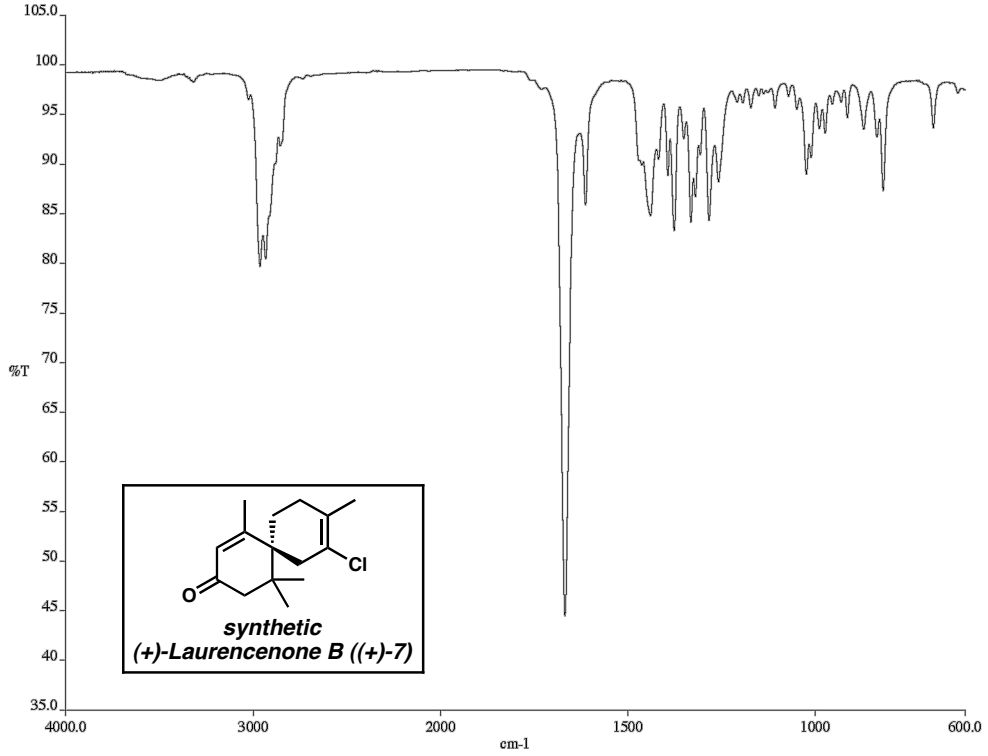


Figure S.3 Infrared spectrum (neat film/NaCl) of synthetic (+)-laurencenone B ((+)-**7**).

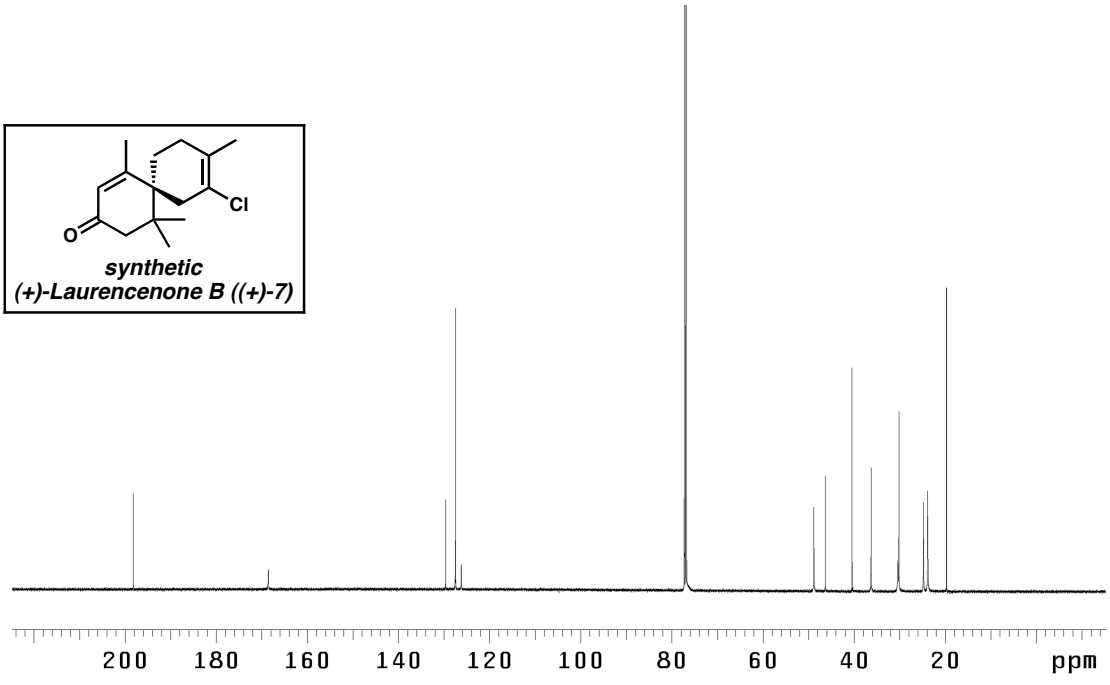


Figure S.4 ^{13}C NMR (126 MHz, $CDCl_3$) of synthetic (+)-laurencenone B ((+)-**7**).

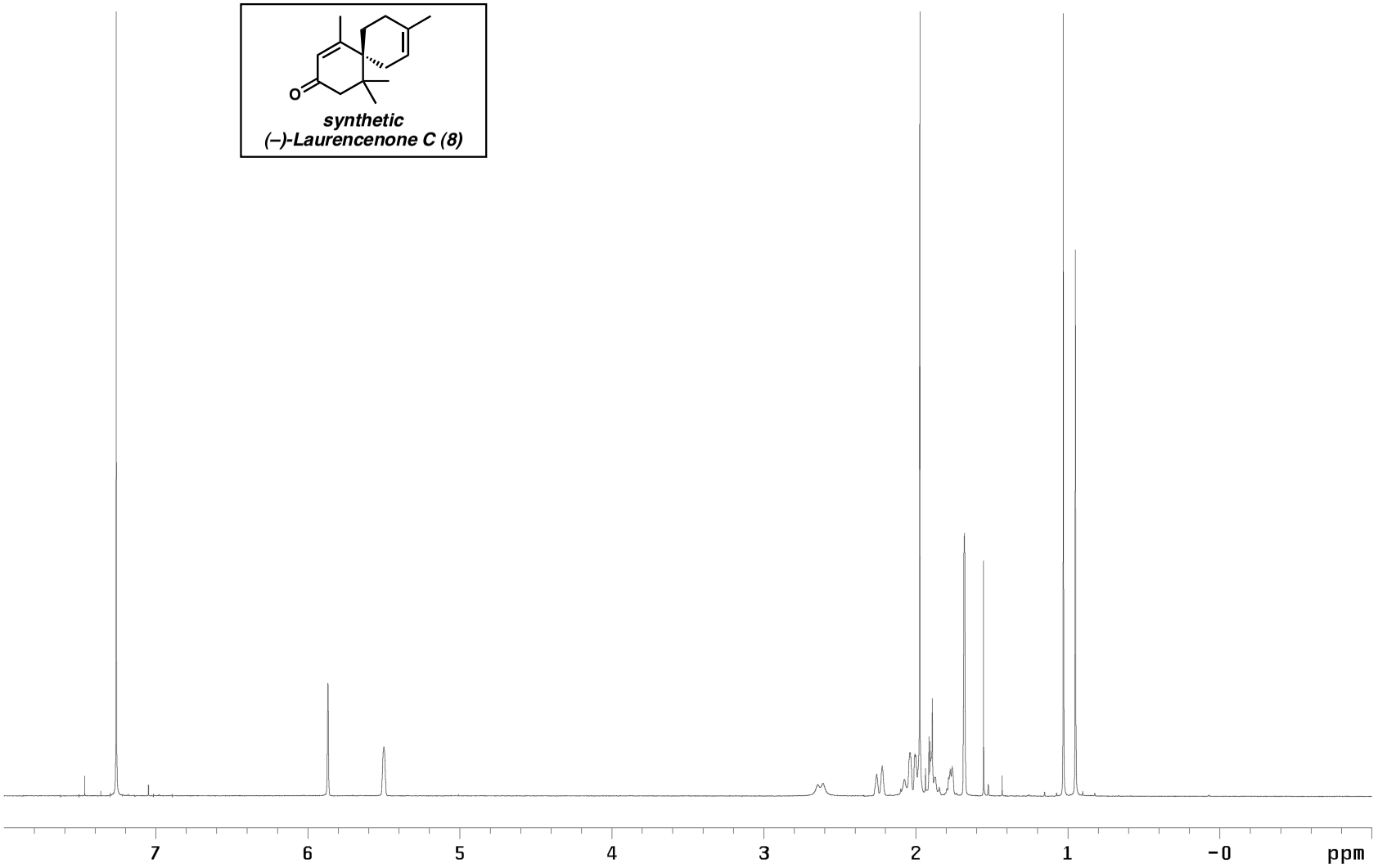


Figure S.5 ^{1}H NMR (500 MHz, $CDCl_3$) of synthetic (–)-laurencenone C (**8**).

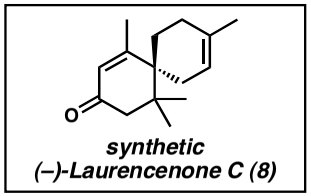


Figure S.6 ^{1}H NMR (500 MHz, acetone-d_6) of synthetic (–)-laurencenone C (**8**).

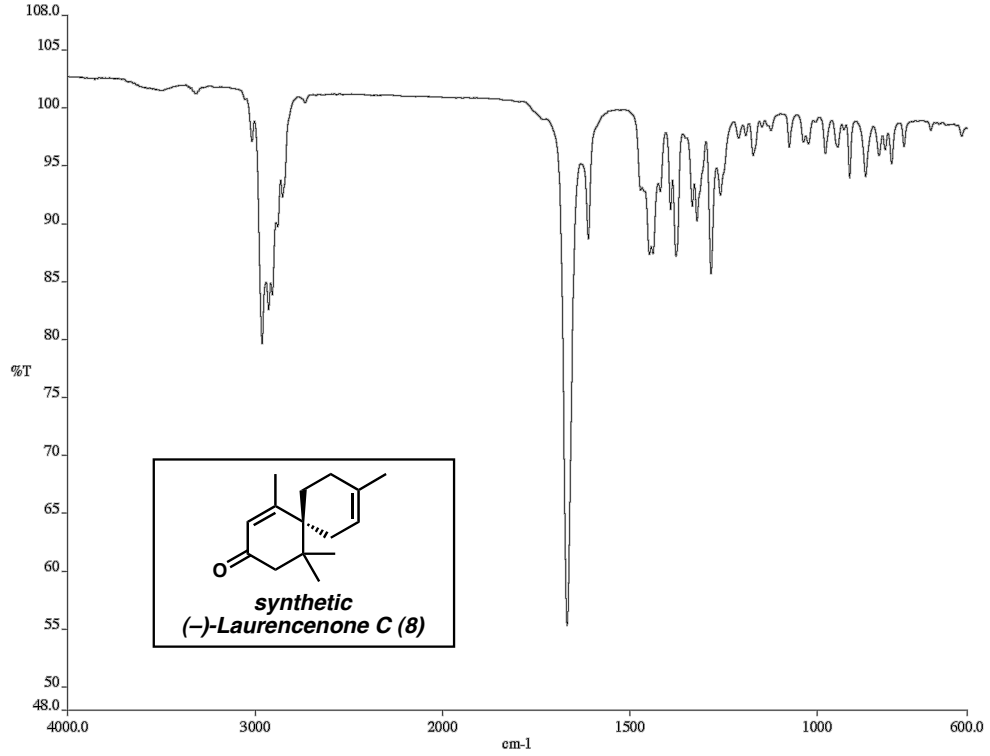


Figure S.7 Infrared spectrum (neat film/NaCl) of synthetic (–)-laurencenone C (**8**).

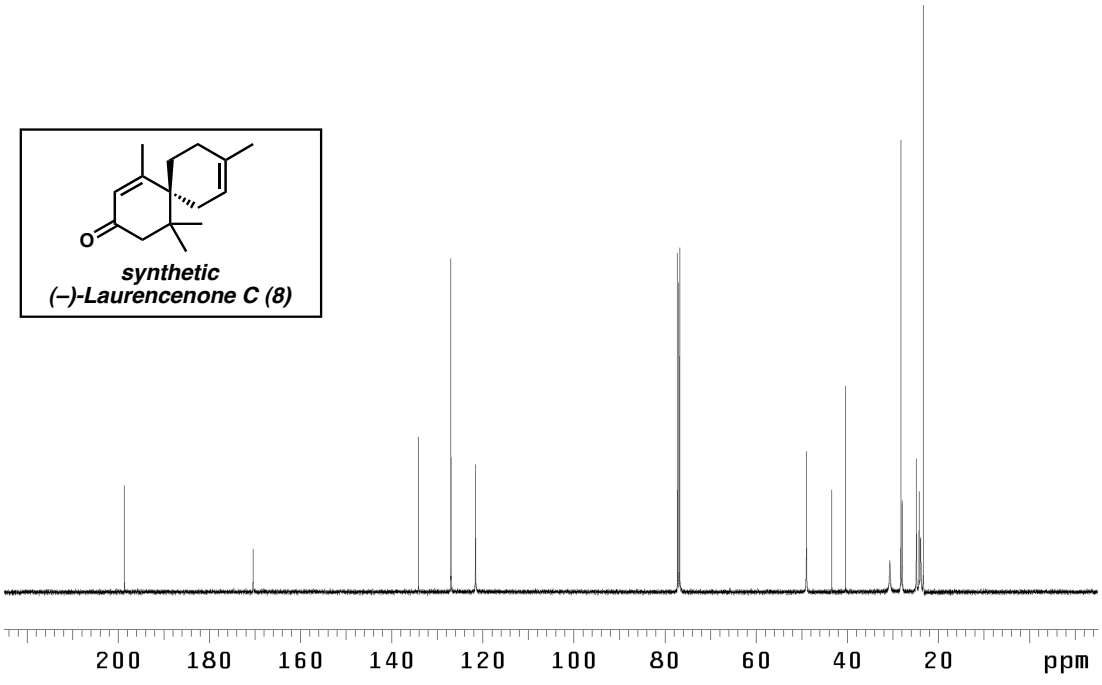


Figure S.8 ^{13}C NMR (126 MHz, $CDCl_3$) of synthetic (–)-laurencenone C (**8**).

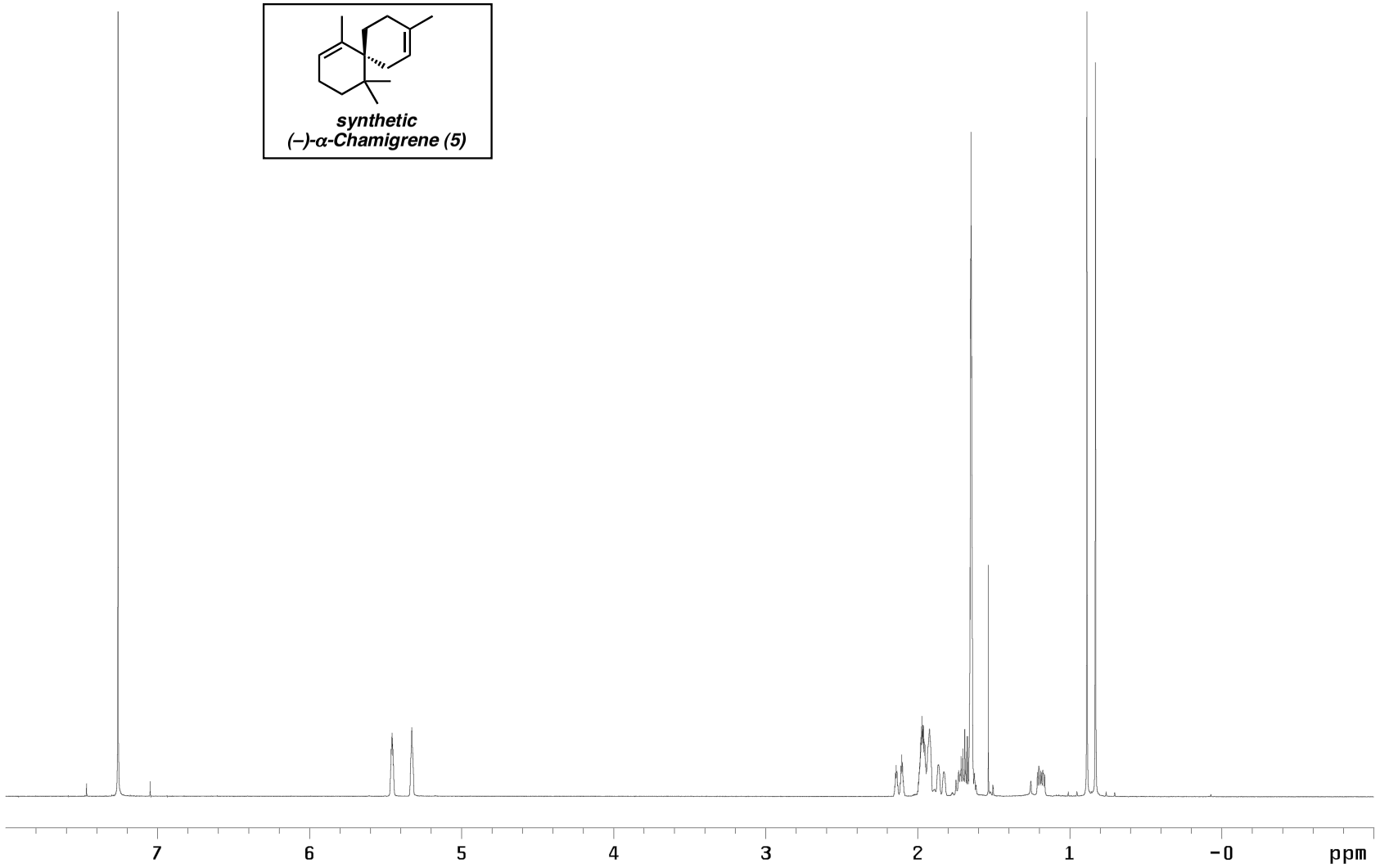


Figure S.9 ^{1}H NMR (500 MHz, $CDCl_3$) of synthetic (–)-α-chamigrene (**5**).

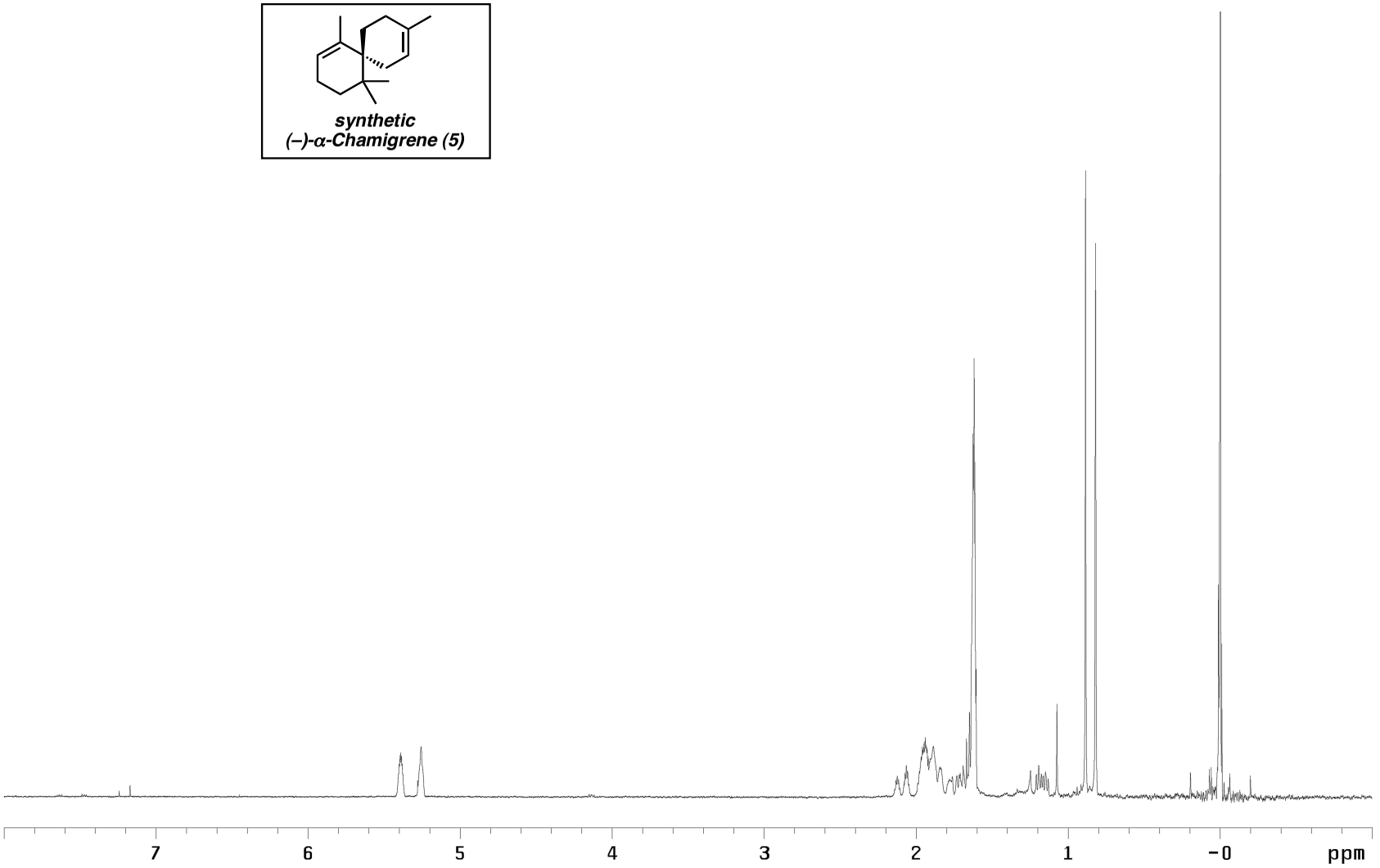


Figure S.10 ^{1}H NMR (300 MHz, CCl_4 with TMS as internal reference) of synthetic (–)-α-chamigrene (**5**).

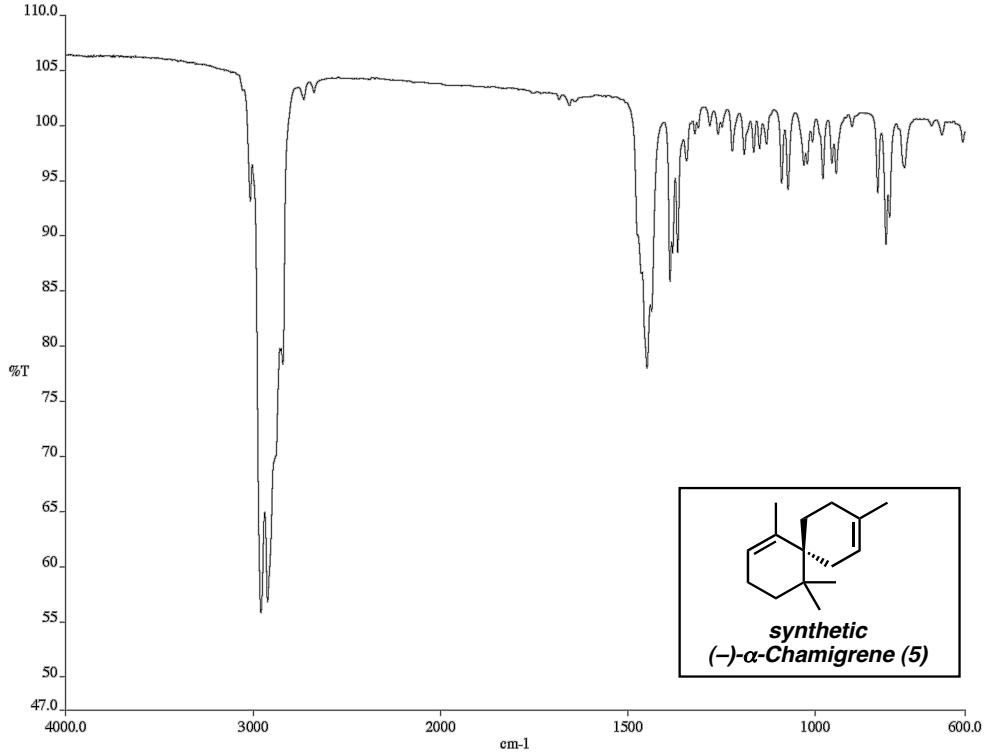


Figure S.11 Infrared spectrum (neat film/NaCl) of synthetic (–)-α-chamigrene (**5**).

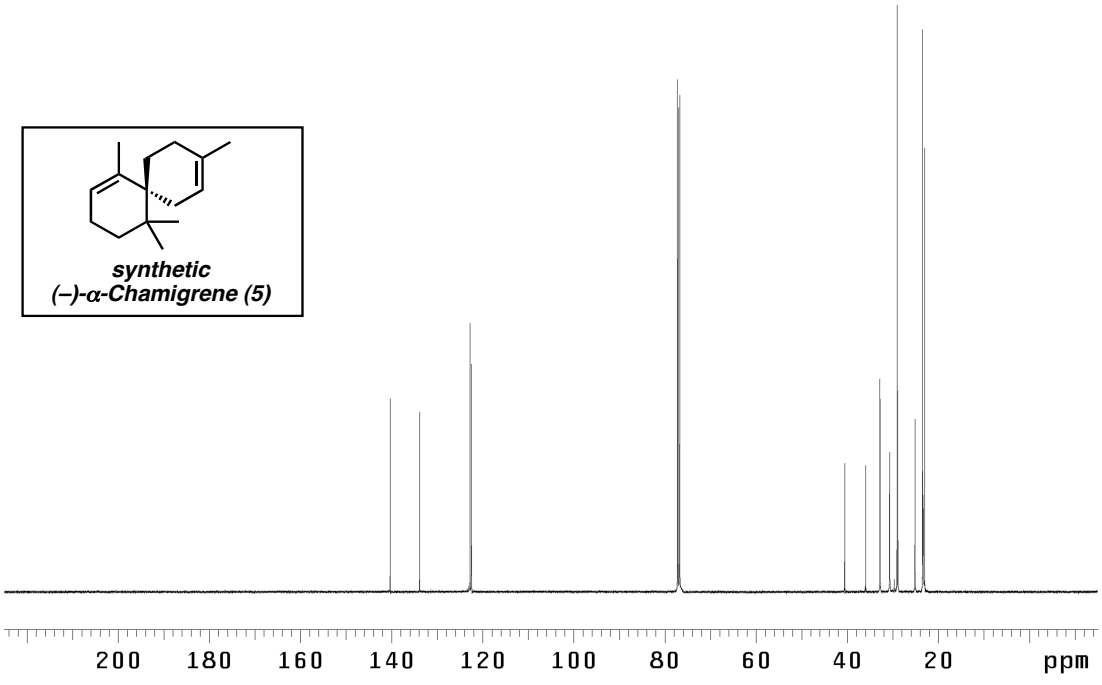


Figure S.12 ^{13}C NMR (126 MHz, $CDCl_3$) of synthetic (–)-α-chamigrene (**5**).

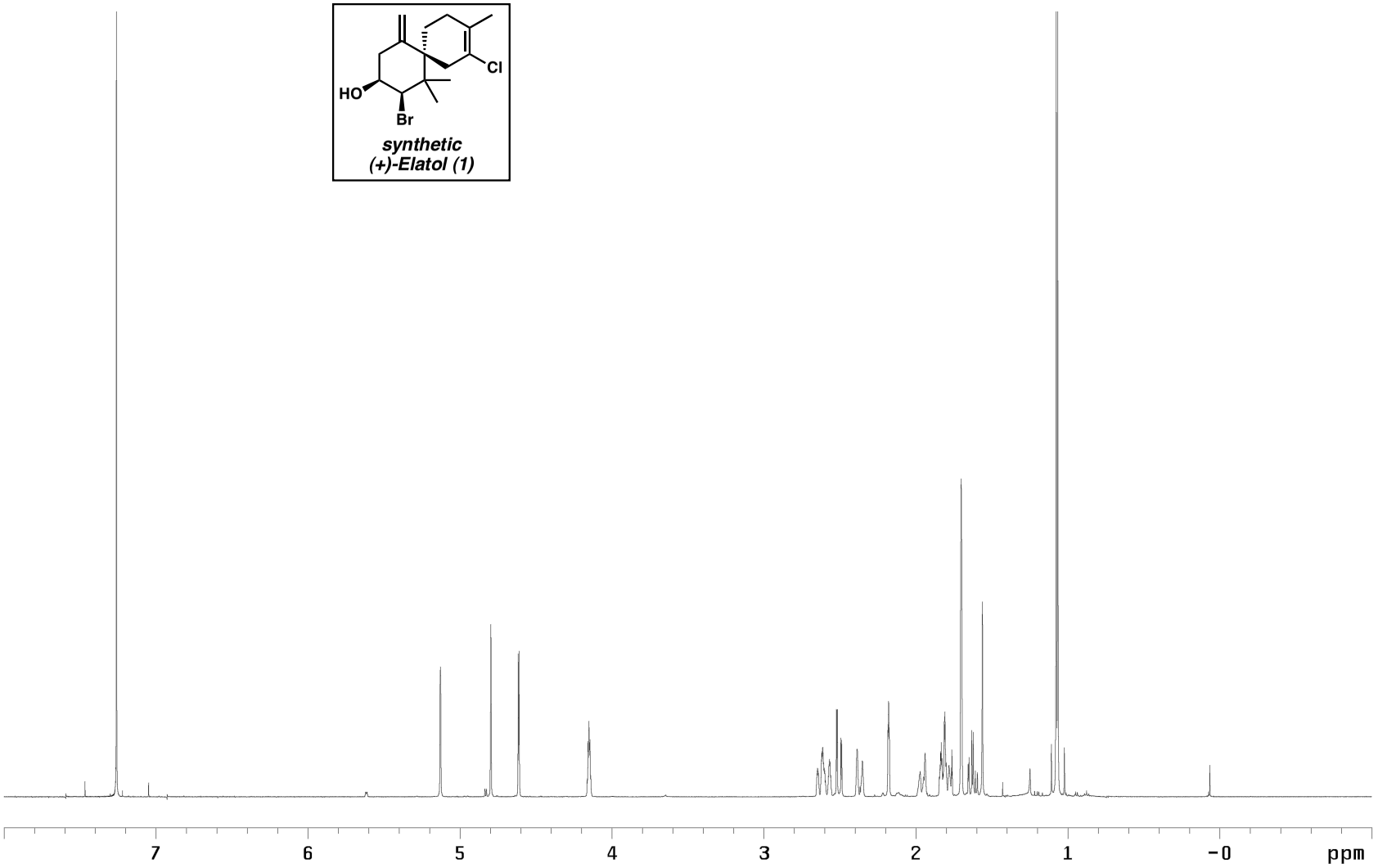


Figure S.13 ^{1}H NMR (500 MHz, $CDCl_3$) of synthetic (+)-elatol (**1**).

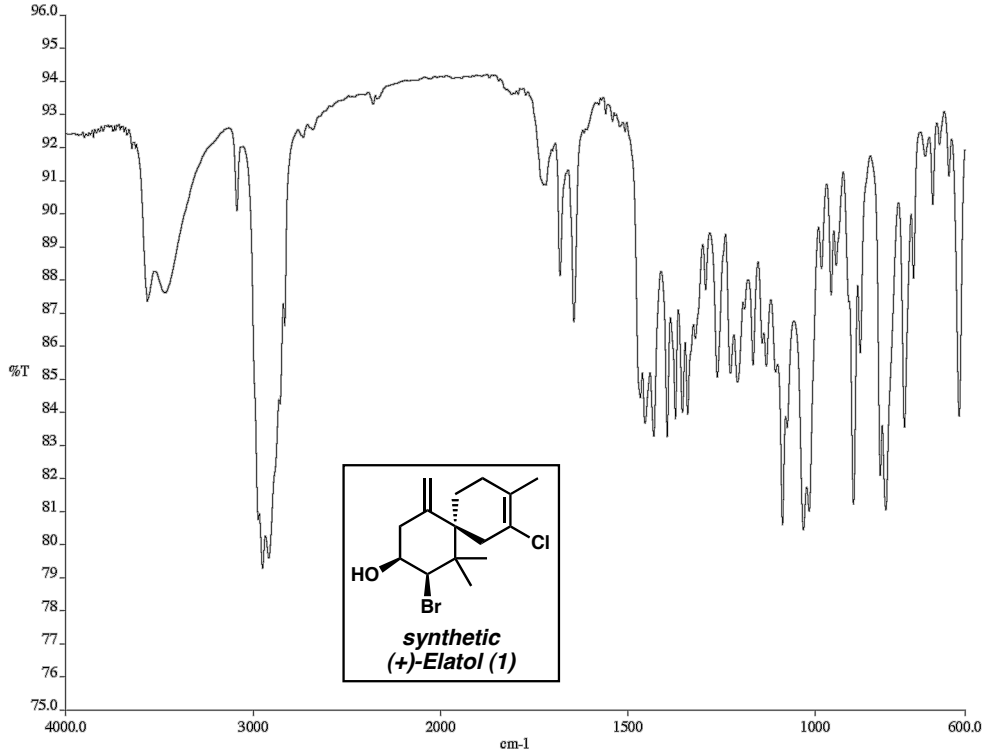


Figure S.14 Infrared spectrum (neat film/NaCl) of synthetic (+)-elatol (**1**).

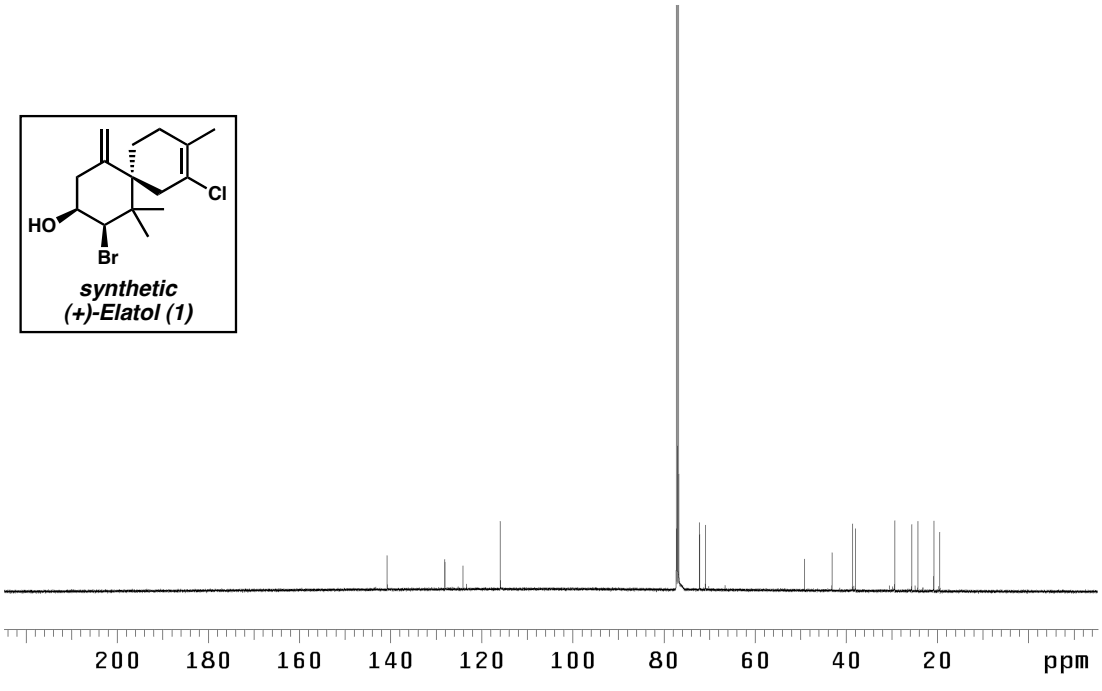


Figure S.15 ^{13}C NMR (126 MHz, $CDCl_3$) of synthetic (+)-elatol (**1**).

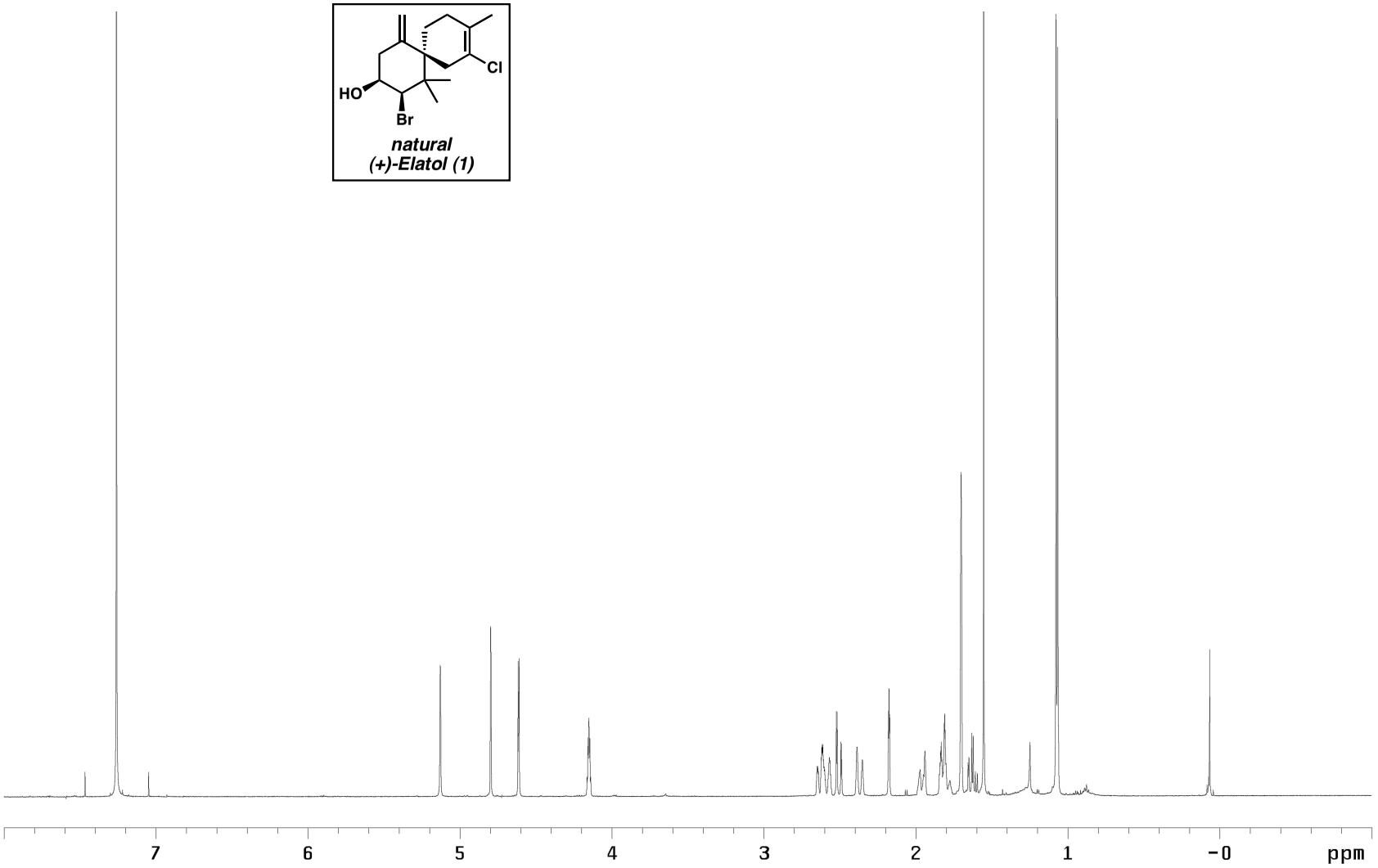


Figure S.16 ^{1}H NMR (500 MHz, $CDCl_3$) of a natural sample of (+)-elatol (**1**).

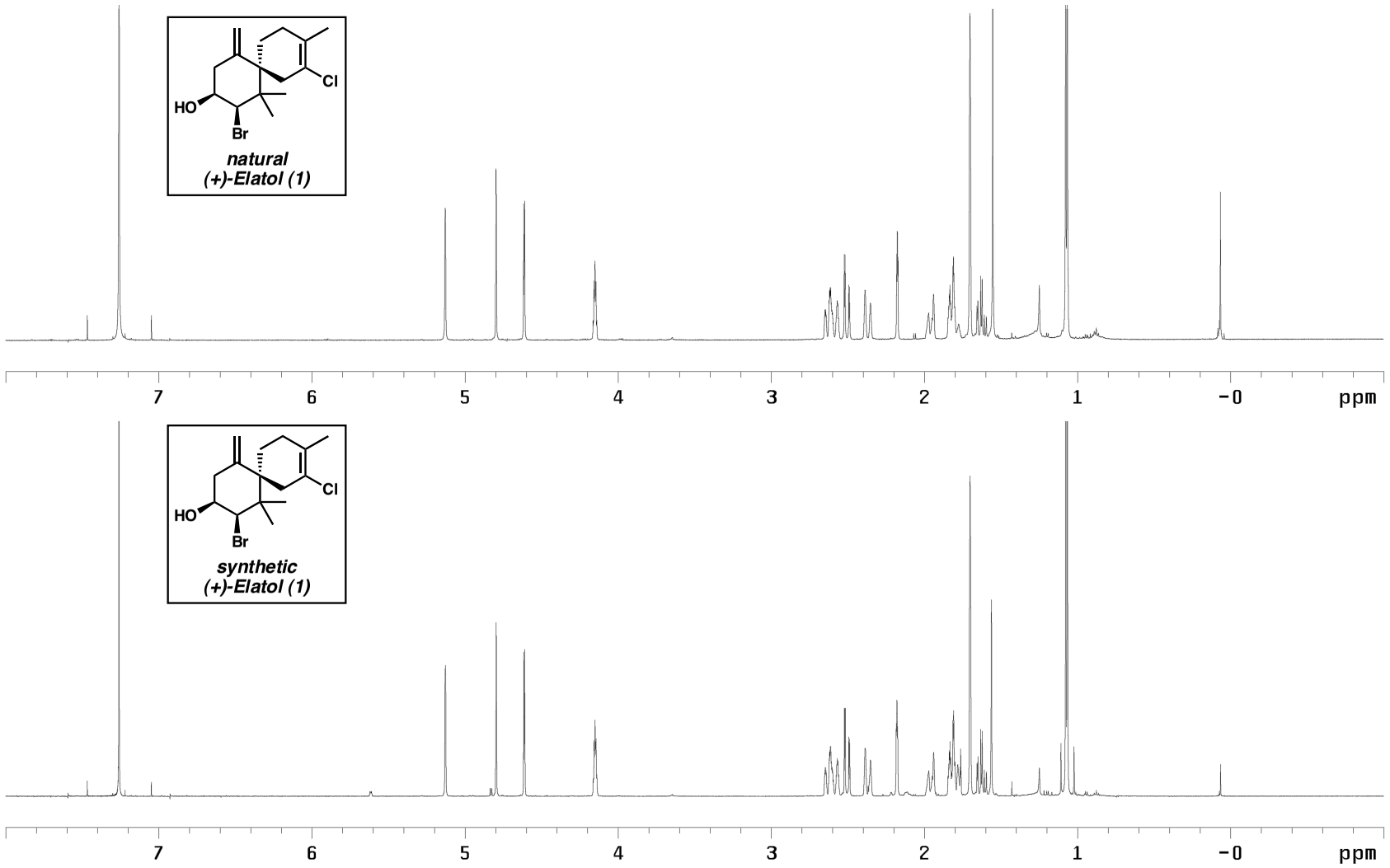


Figure S17 Overlay of ^{1}H NMR spectra (500 MHz, $CDCl_3$) of natural and synthetic (+)-elatol (**1**).