Supporting information

First total synthesis of natural varioxiranol A

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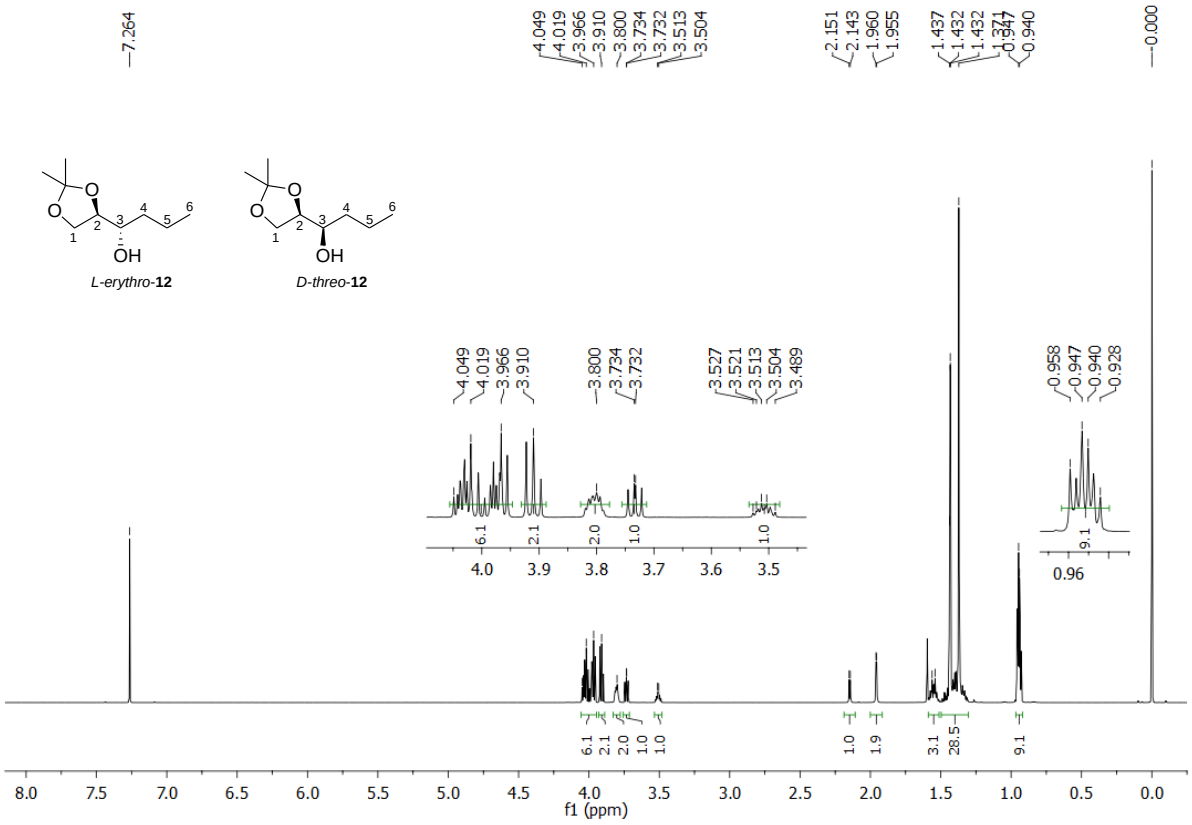
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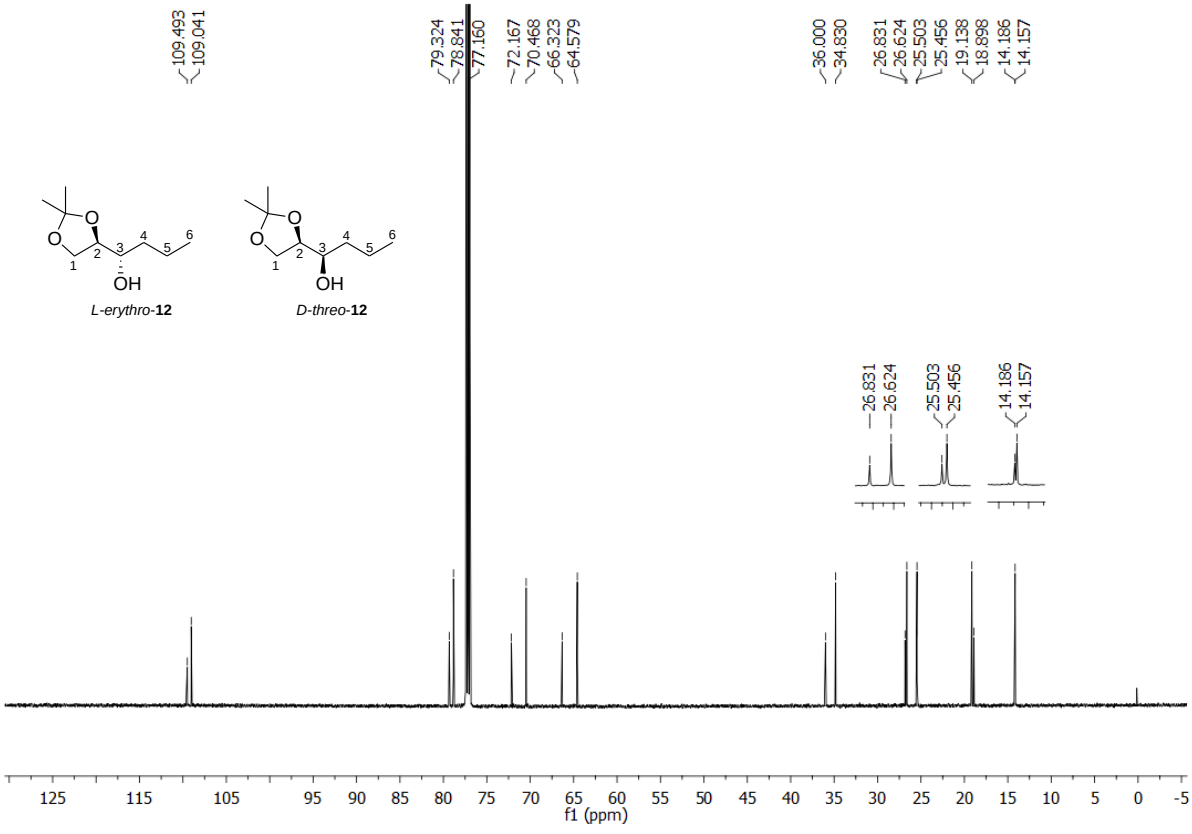
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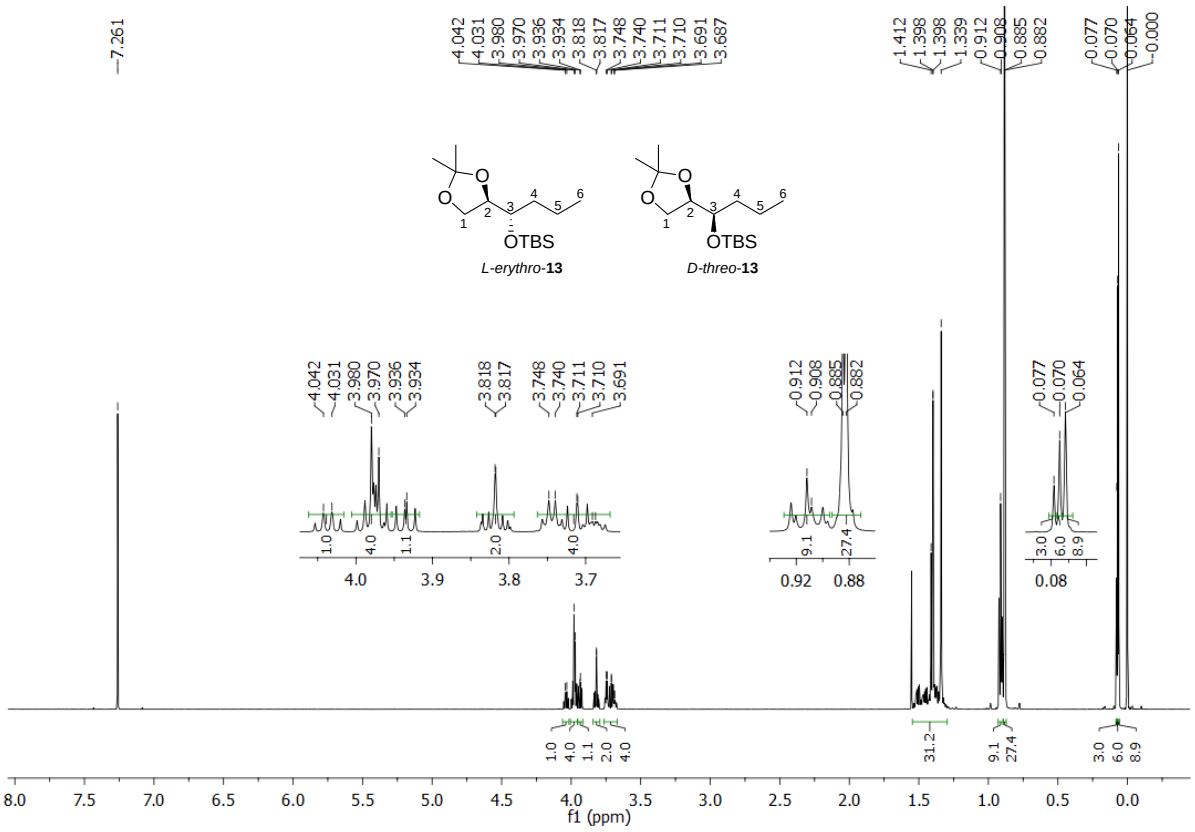
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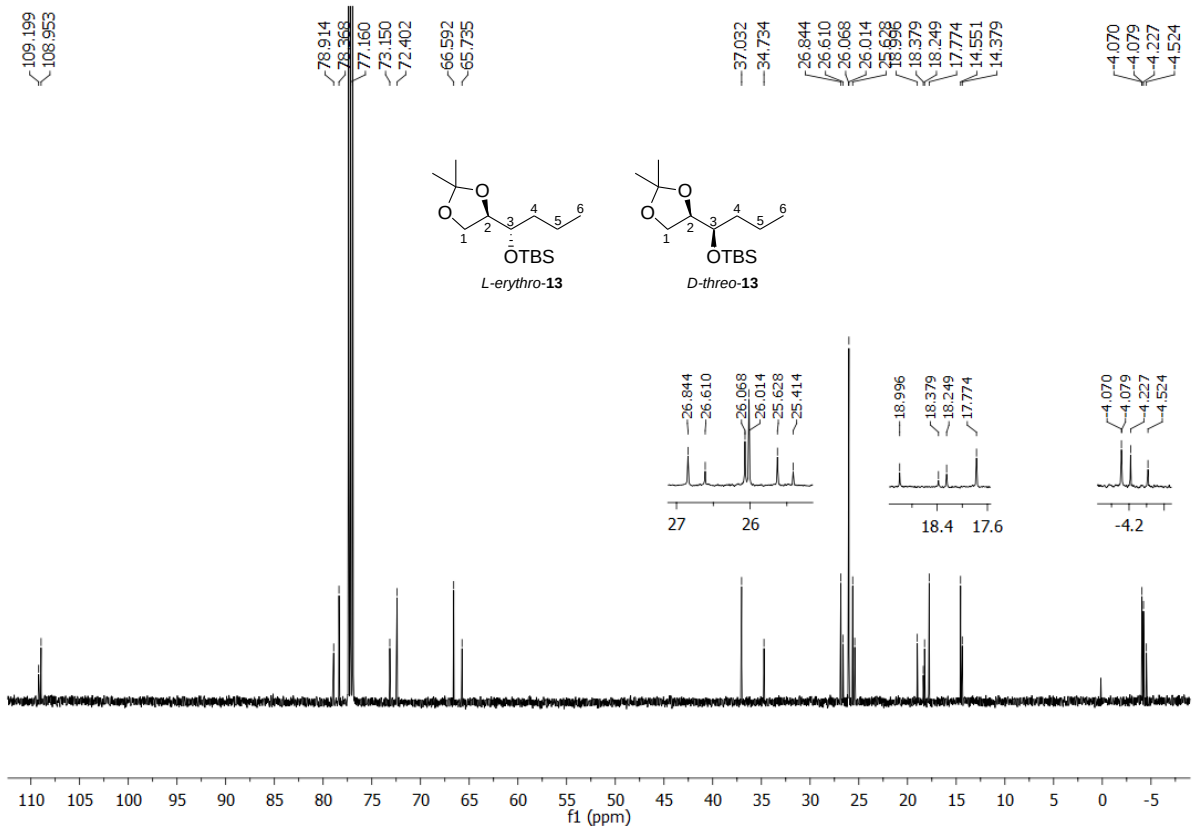
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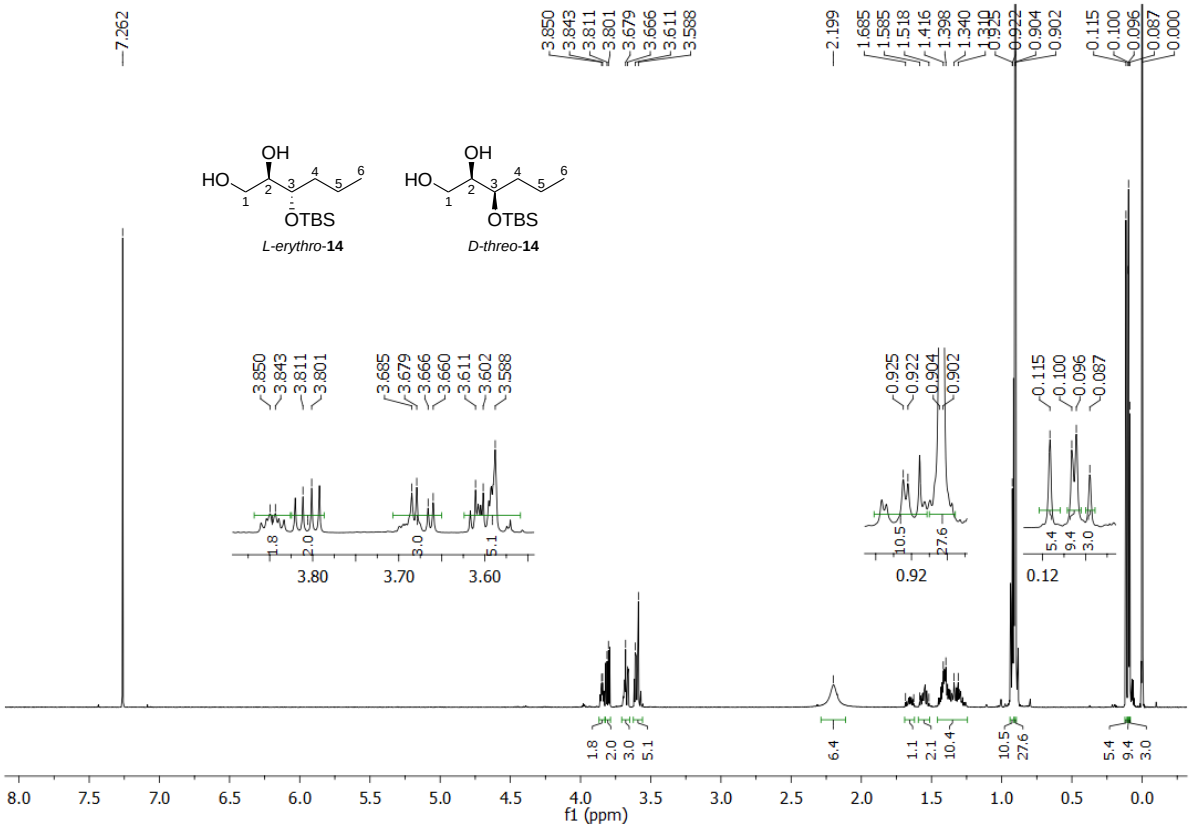
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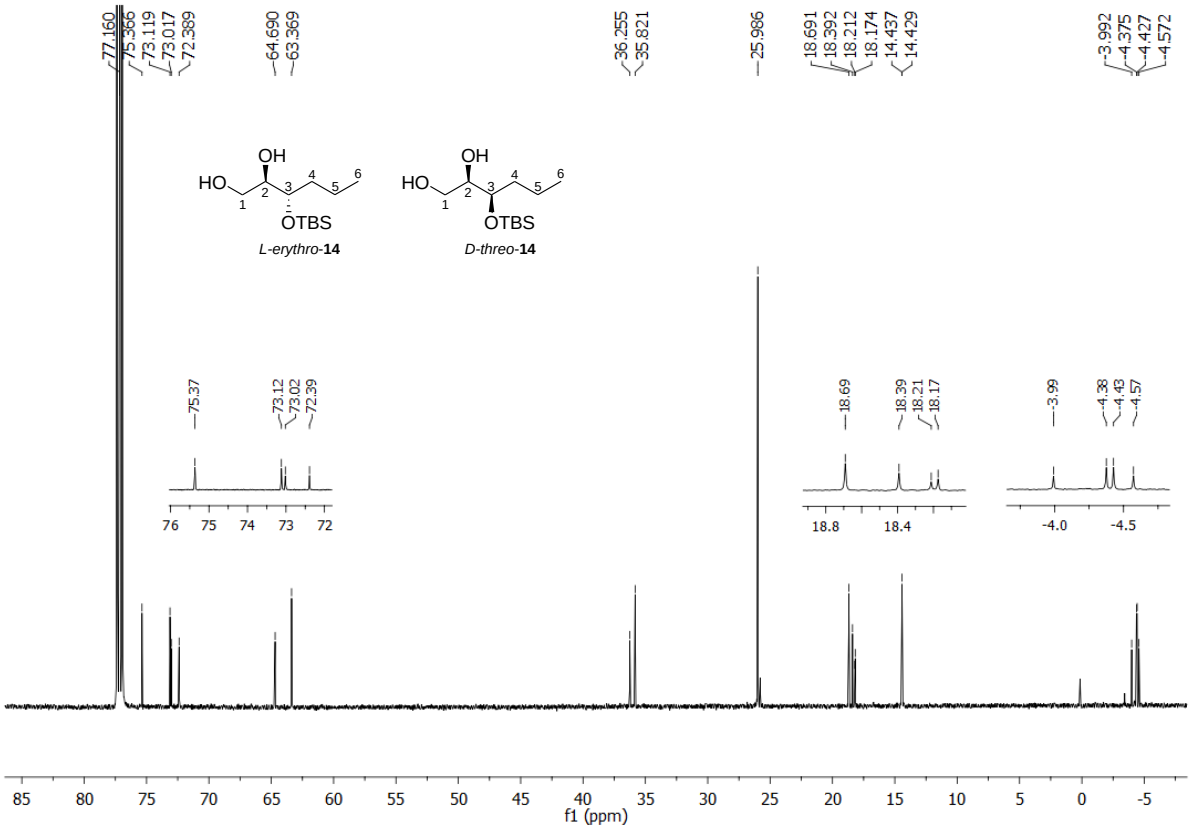
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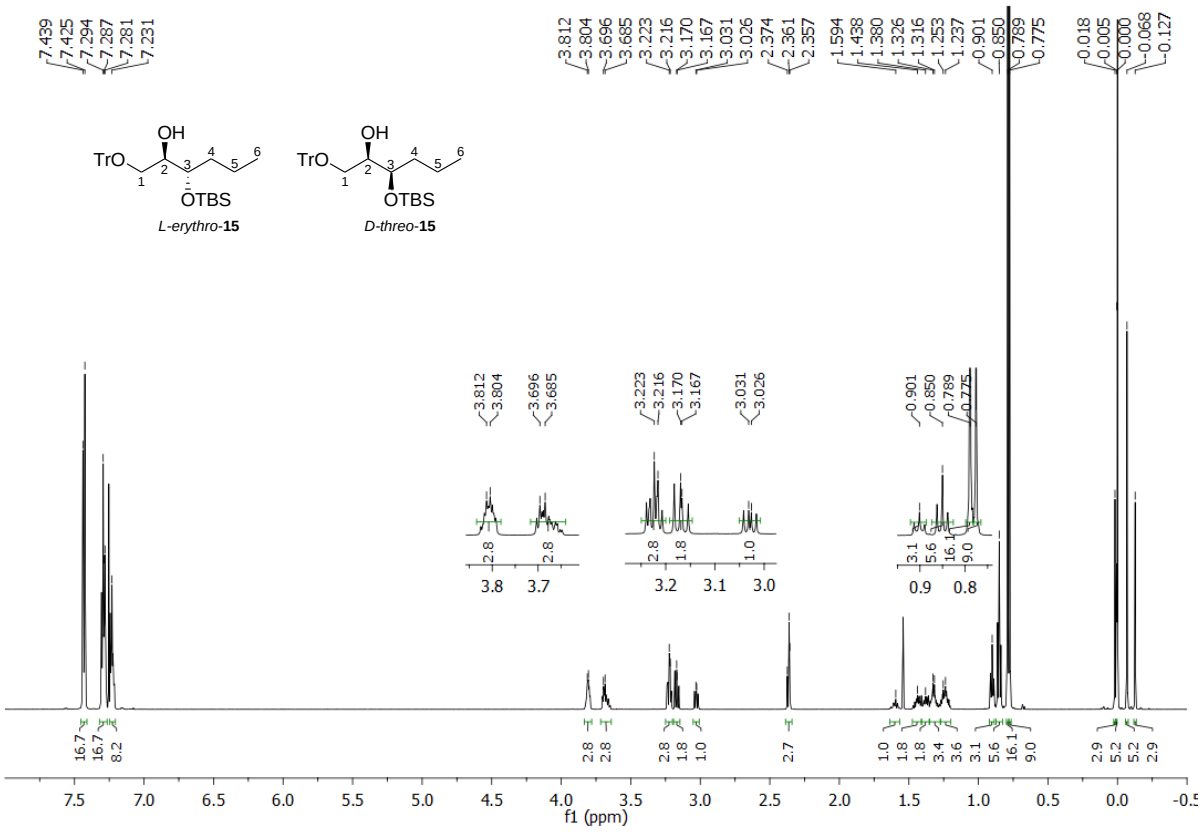
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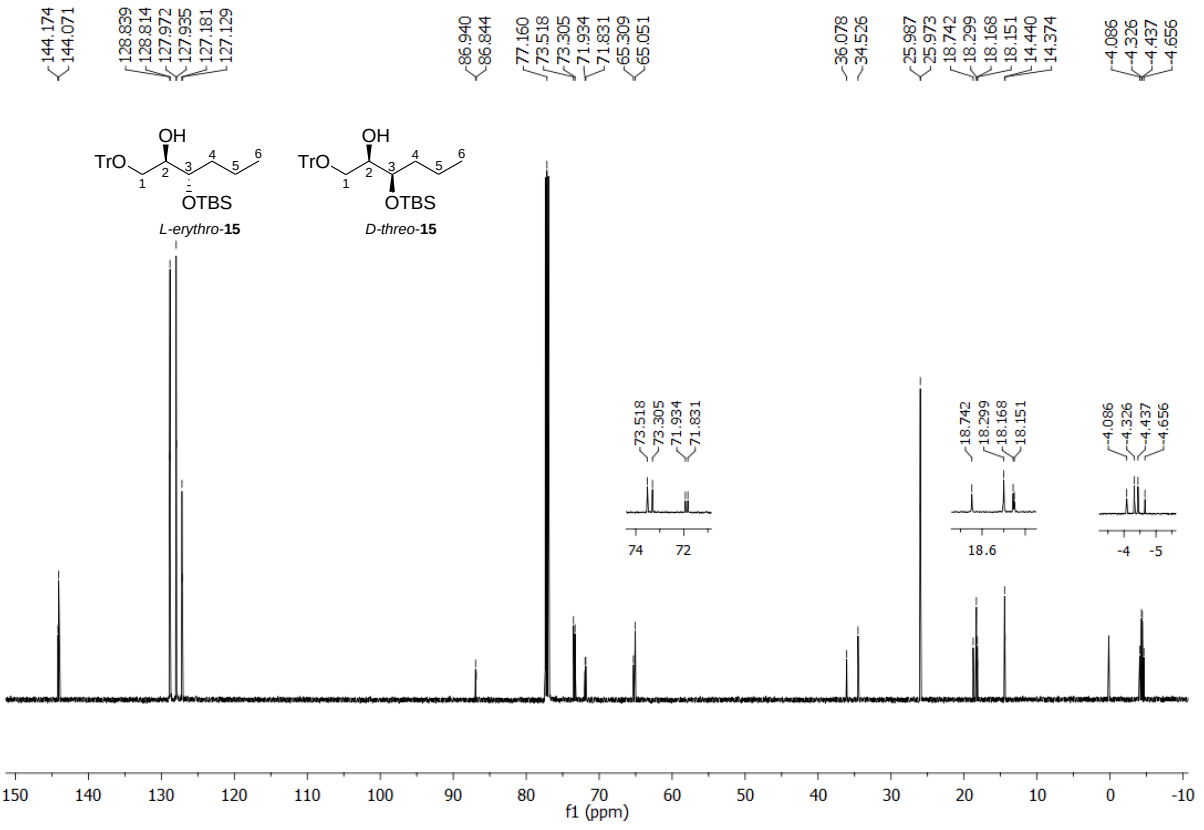
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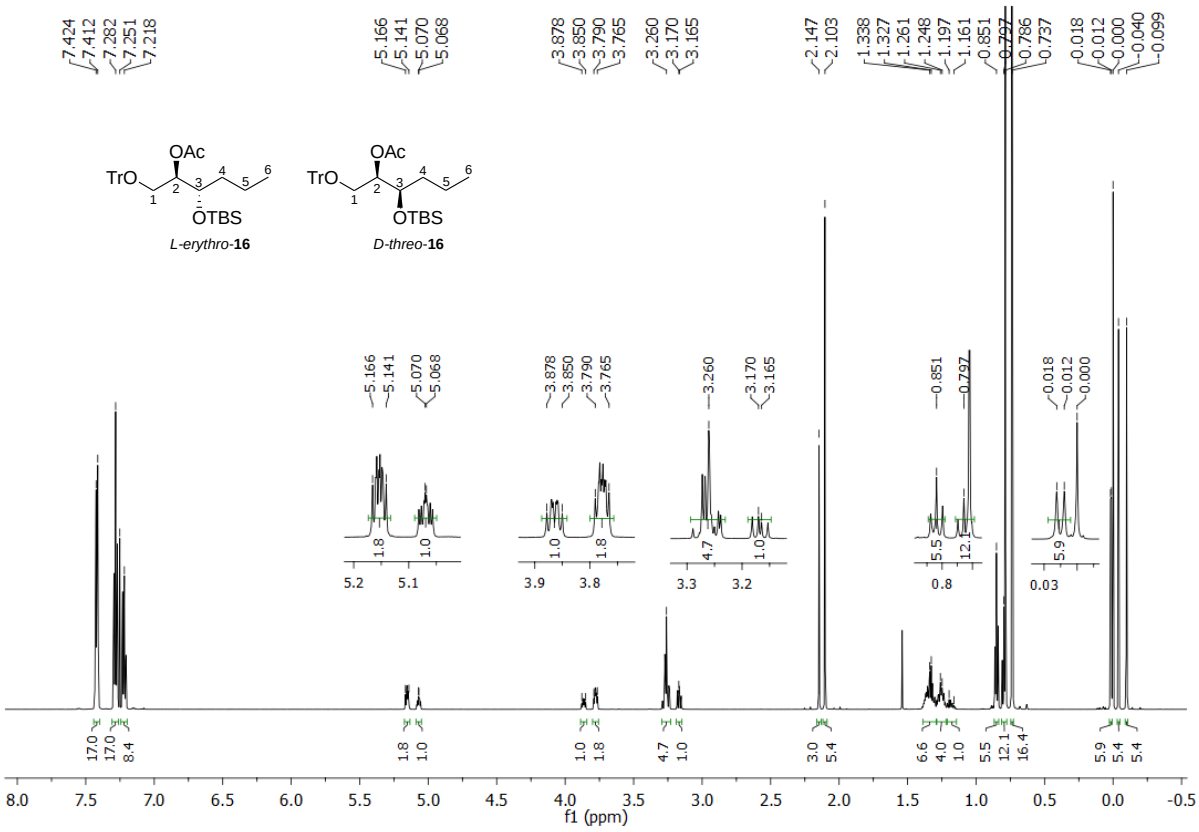
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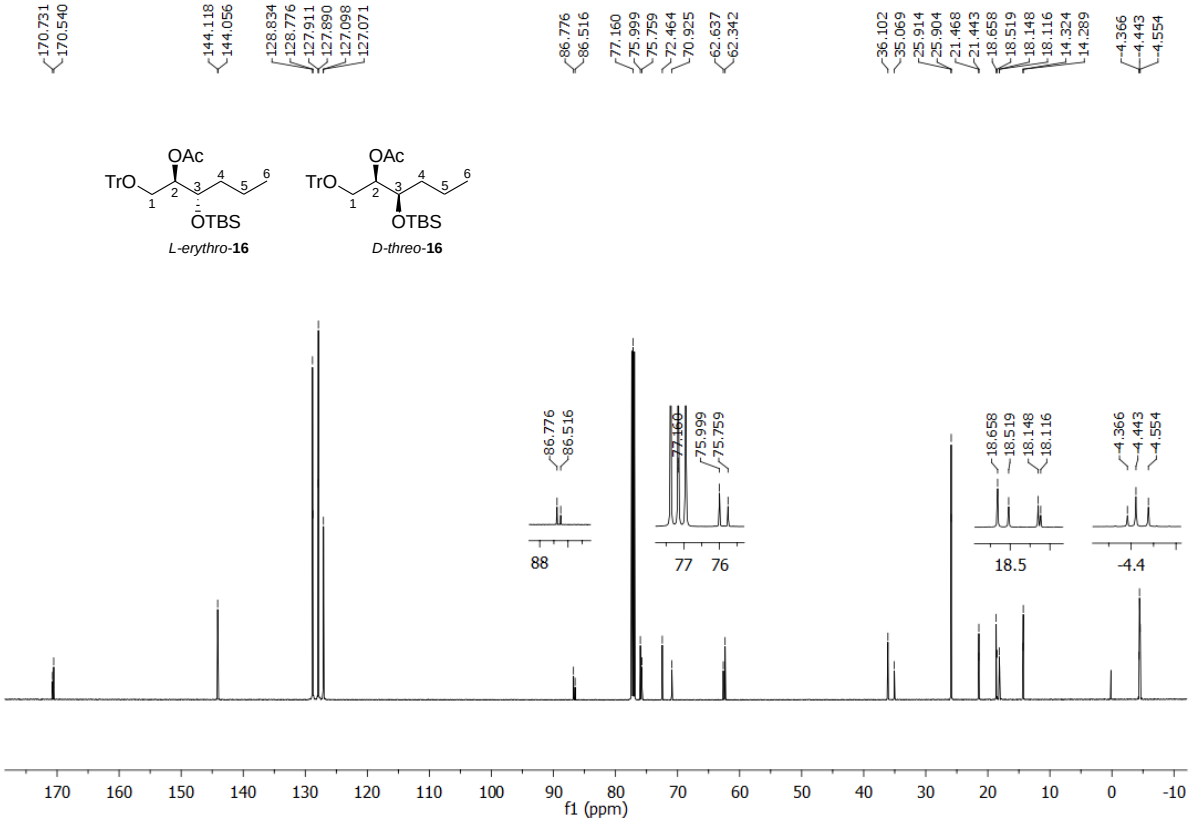
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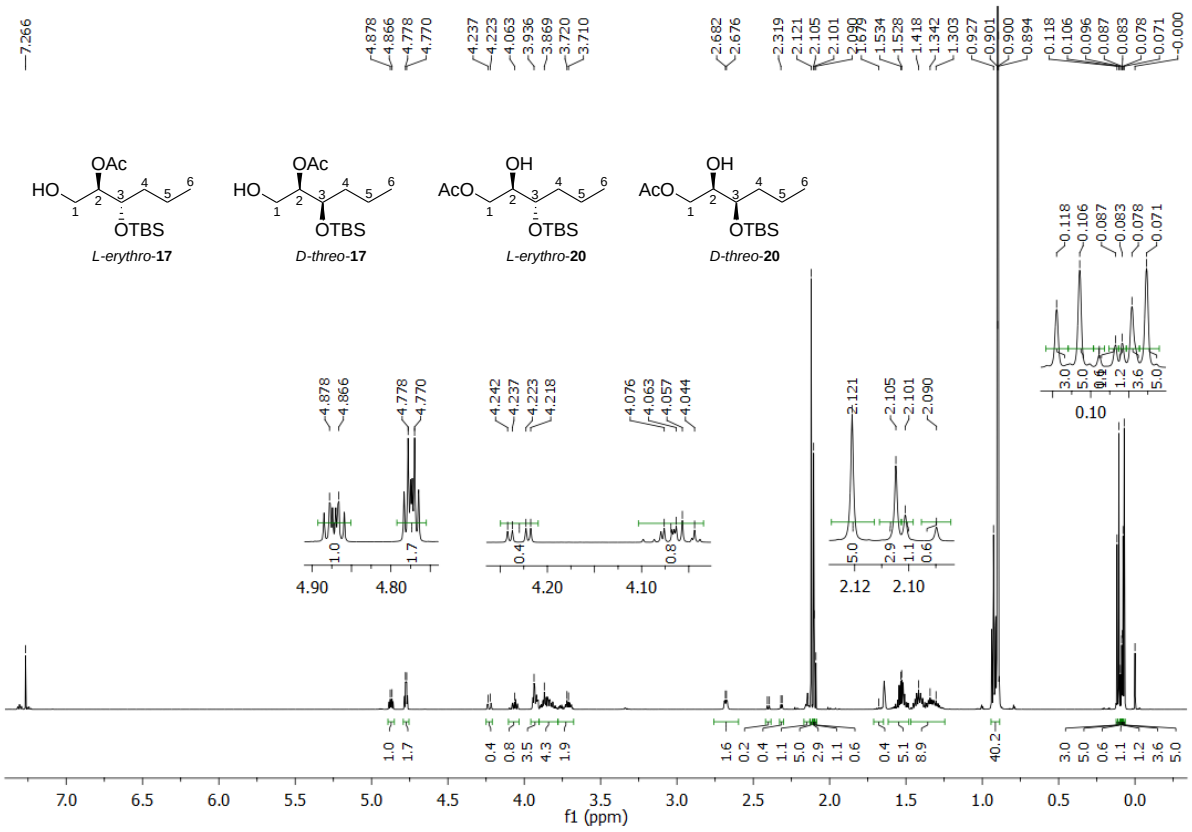
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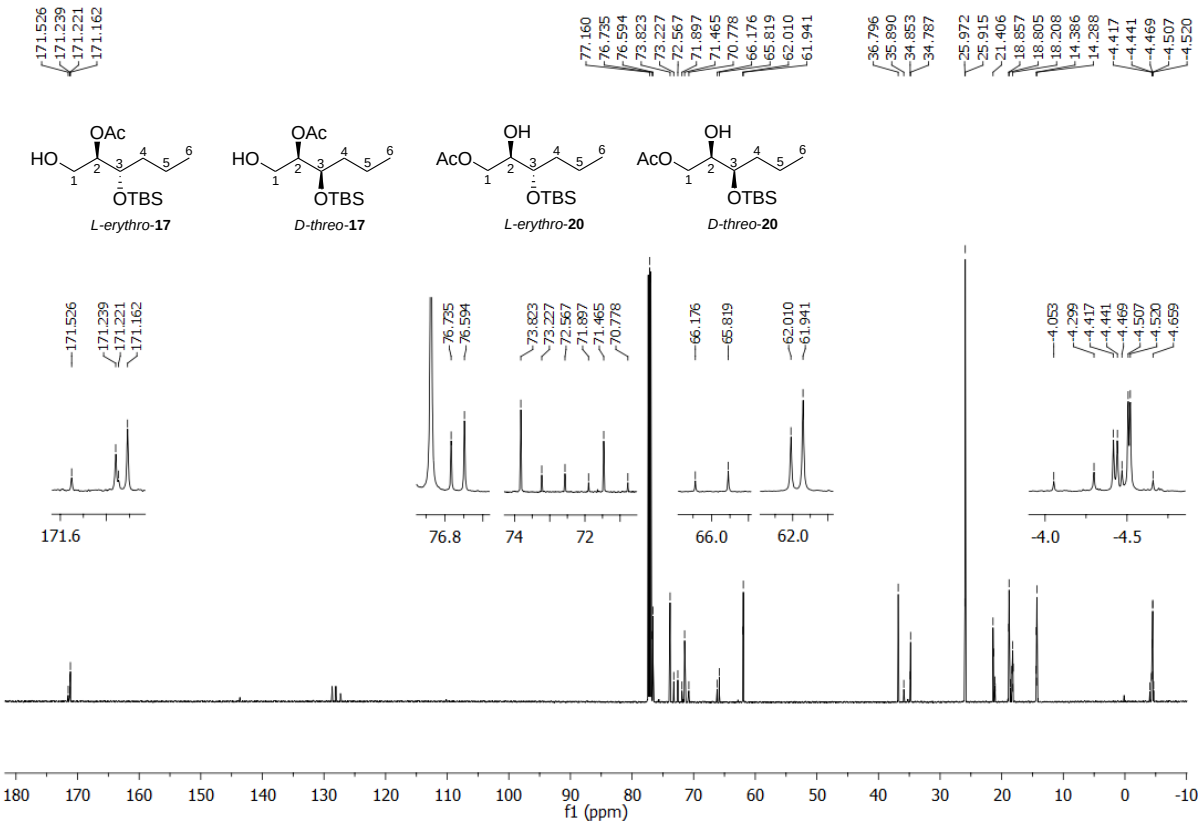
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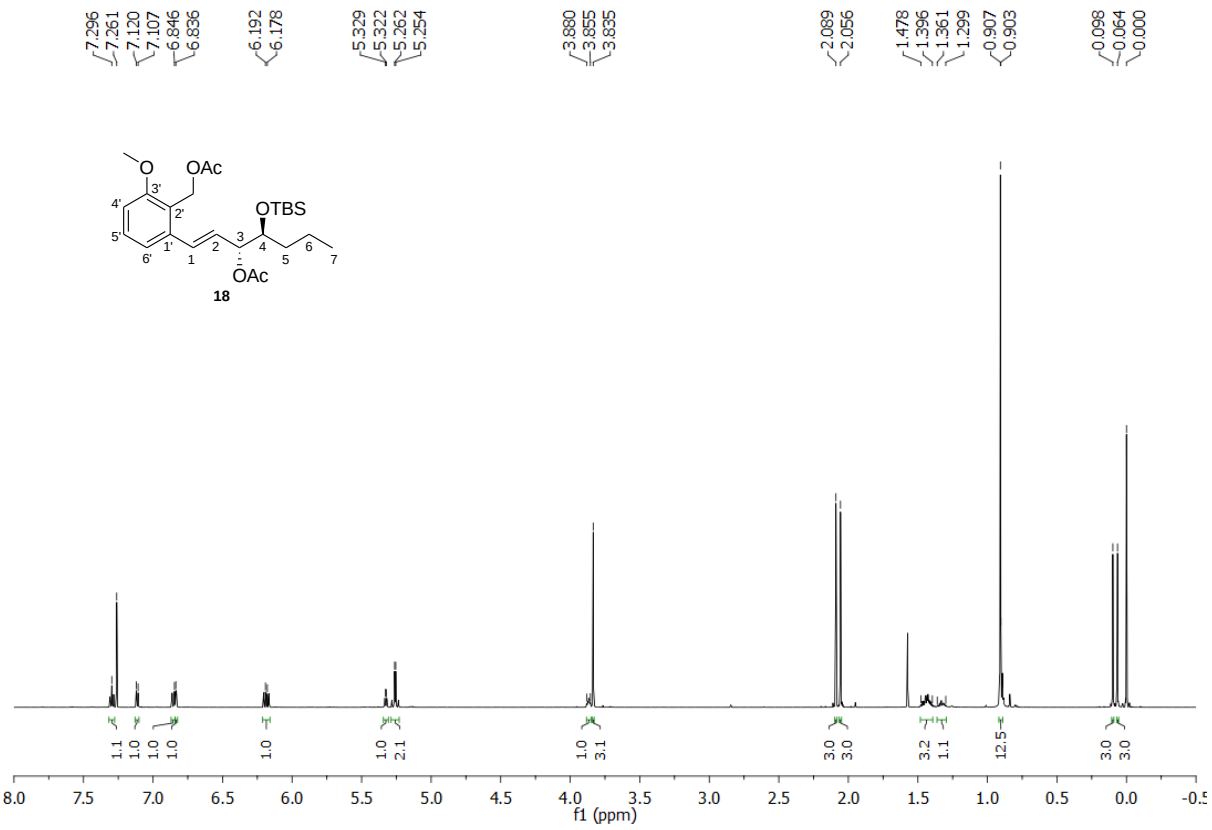
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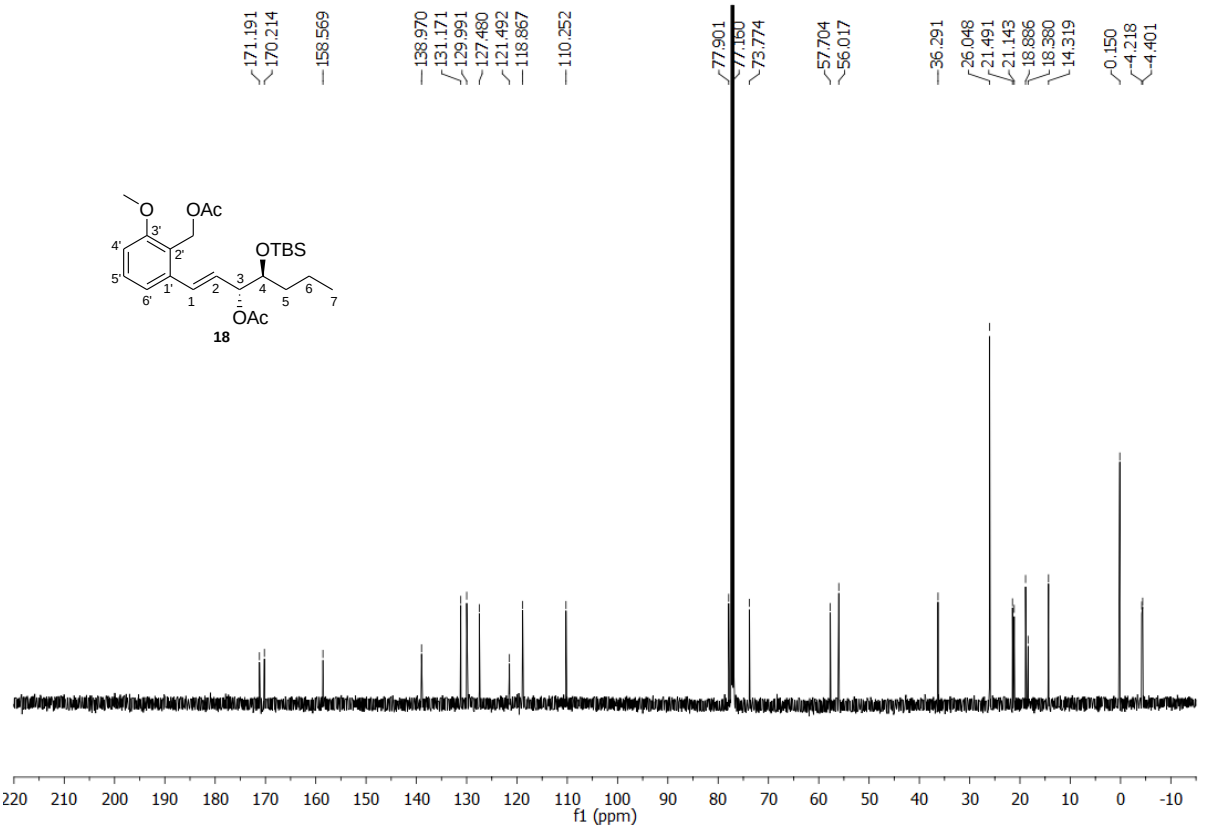
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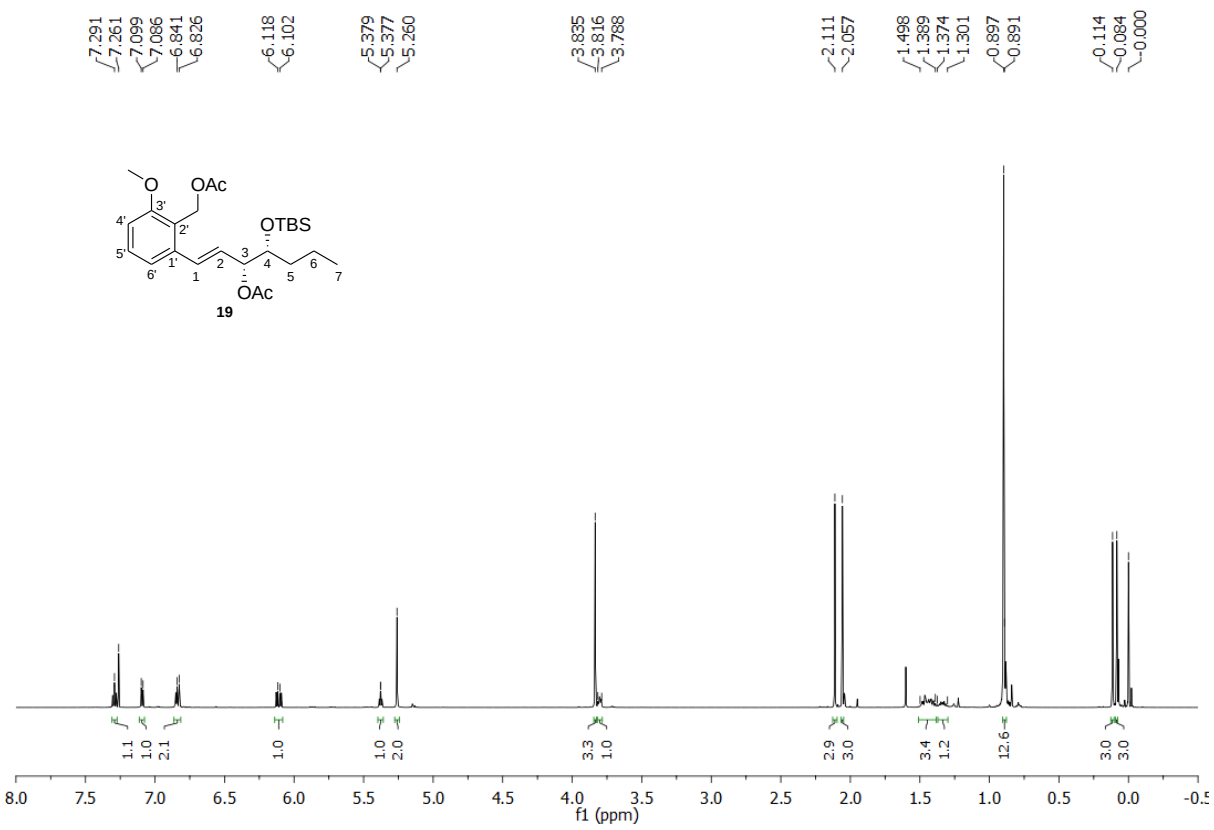
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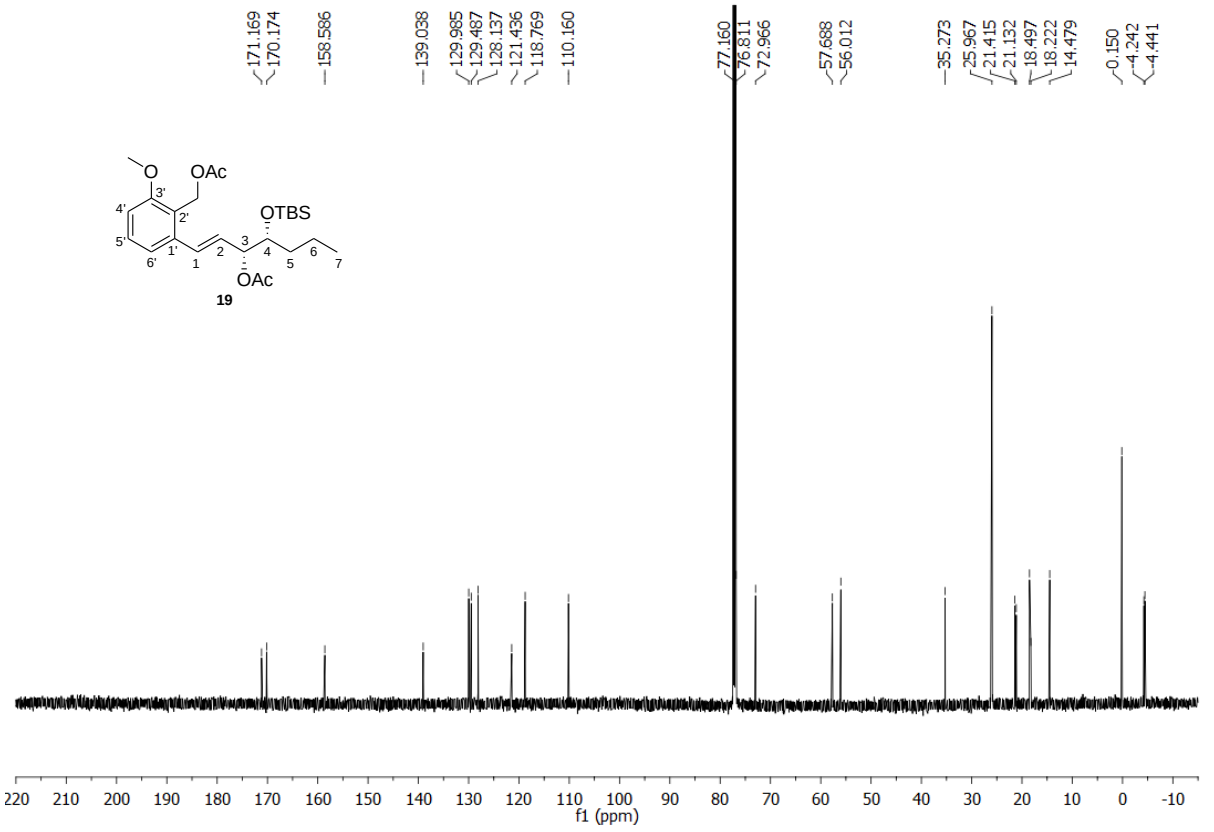
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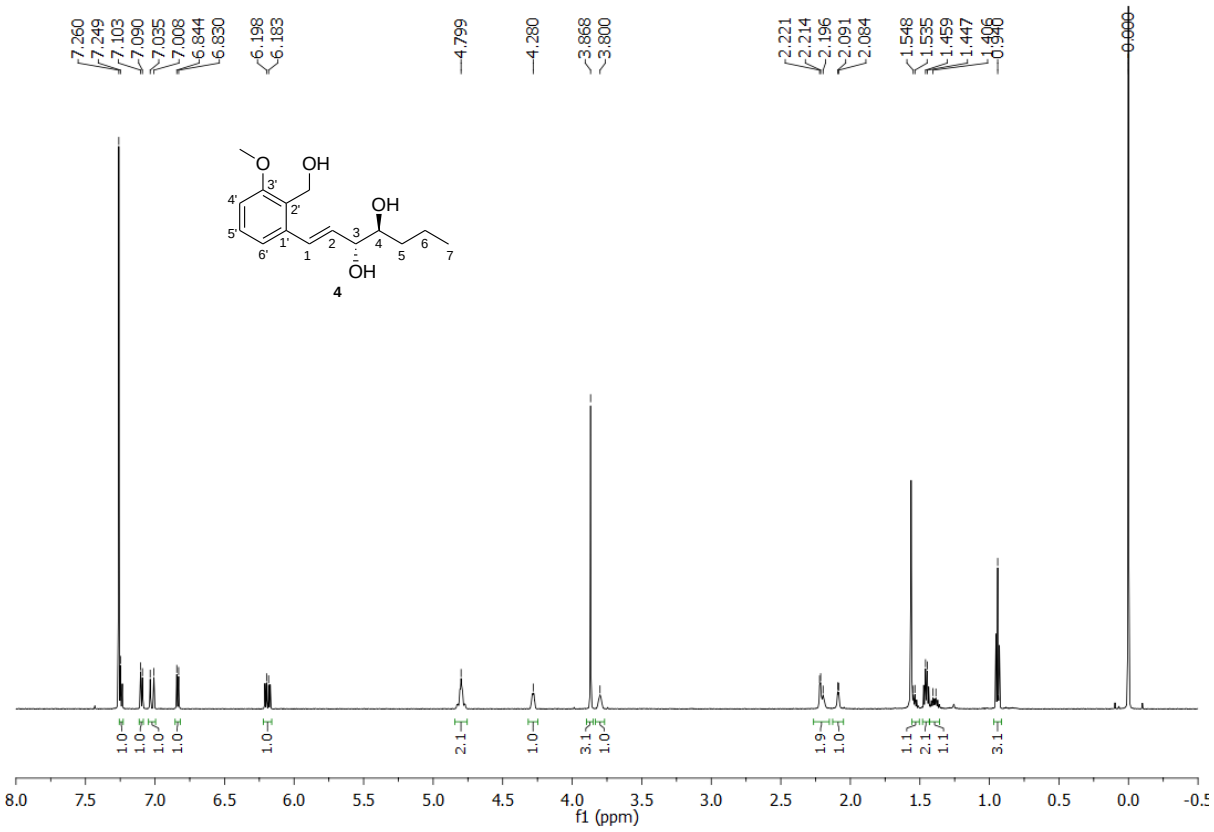
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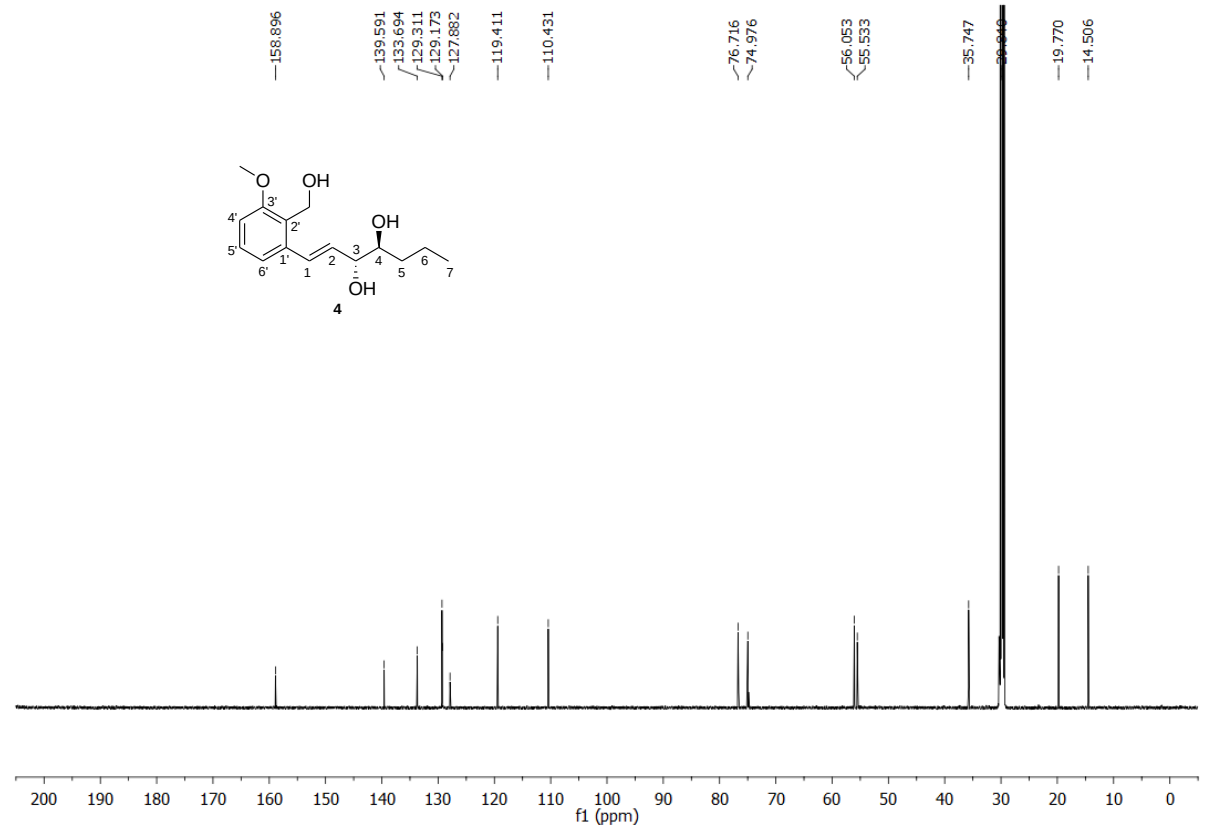
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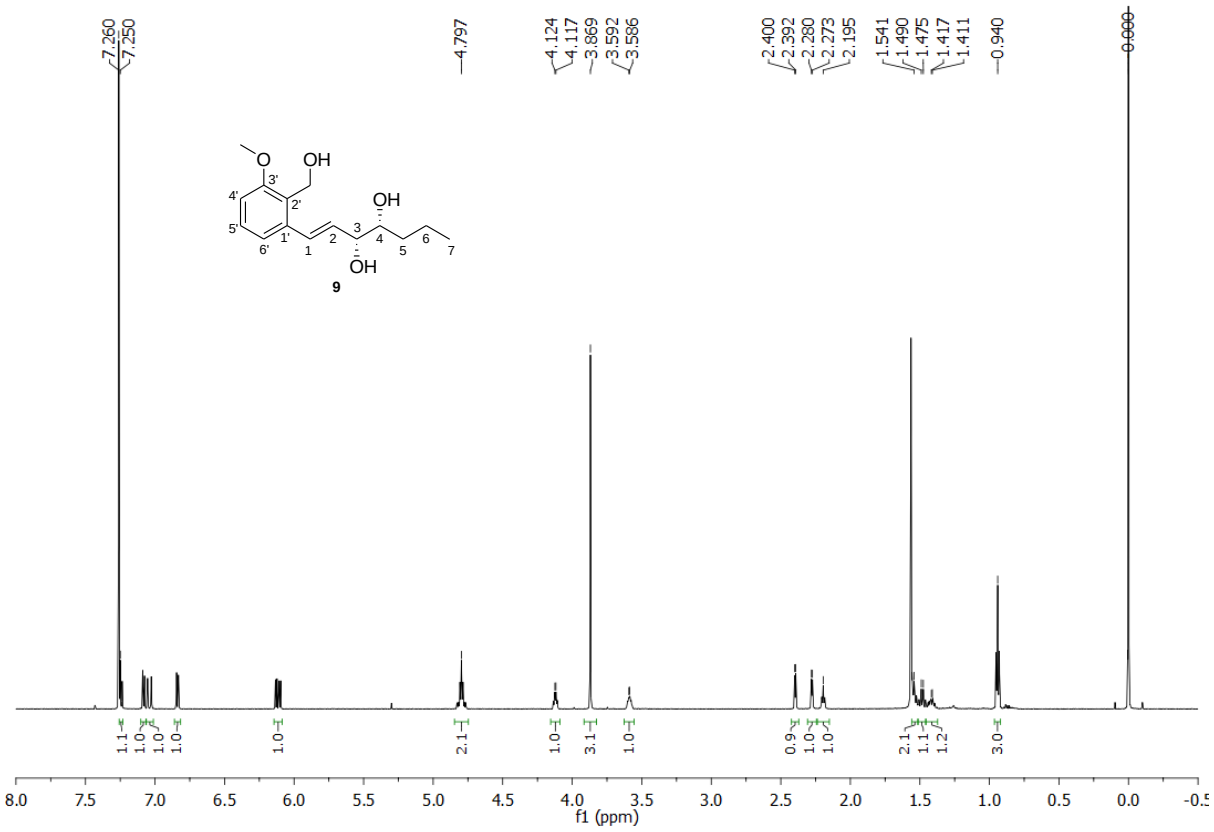
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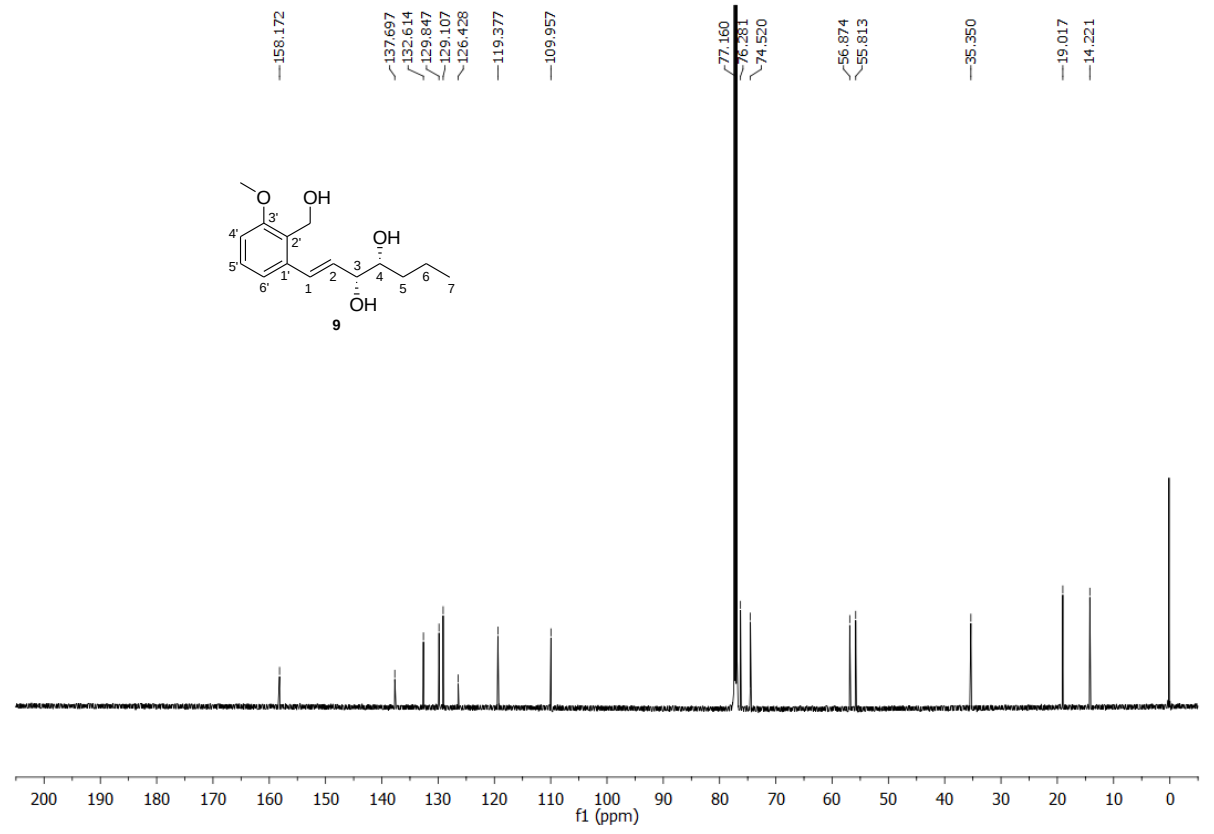
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OH
OH
OH
9
f1 (ppm)

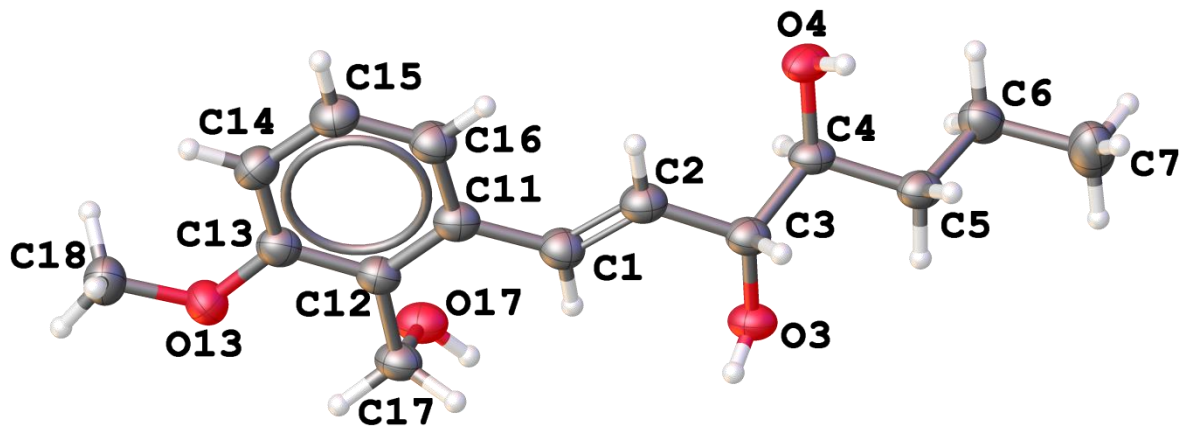
Table S1 Crystal data and structure refinement for compounds **4** and **9**

	4	**9**
Empirical formula	$C_{15}H_{22}O_4$	$C_{15}H_{22}O_4$
Formula weight /g mol^{-1}	266.32	266.32
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
Temperature /K	100	100
Crystal size /mm	0.24 × 0.03 × 0.02	0.42 × 0.07 × 0.02
Z	2	4
a / Å	11.3505(4)	12.4108(1)
b / Å	4.9503(2)	5.0577(1)
c / Å	13.0003(6)	22.8288(2)
β /°	104.764(4)	101.593(2)
V /Å^3	706.35(5)	1403.73(1)
ρ_{calc}/g cm^{-3}	1.252	1.260
μ /mm^{-1}	0.730	0.735
F(000)	288.0	576.0
Radiation	CuKα , (λ = 1.54186 Å)	CuKα, (λ = 1.54186 Å)
2Θ range for data collection/°	7.032 to 145.314	7.270 to 143.468
Index ranges	-11 ≤ h ≤ 14,	-15 ≤ h ≤ 14,
	-5 ≤ k ≤ 6,	-3 ≤ k ≤ 6,
	-16 ≤ l ≤ 10	-25 ≤ l ≤ 28
Data/restraints/parameters	2407/1/178	4184/13/368
Goodness-of-fit on F^2	1.038	0.987
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1206	R_1 = 0.0317, wR_2 = 0.0722
R indices (all data)	R_1 = 0.0534, wR_2 = 0.1272	R_1 = 0.0367, wR_2 = 0.0755
Flack parameter (x)	0.3(2)	-0.08(5)
Hooft parameter (y)	0.07(11)	-0.02(5)
CCDC No.	1892452	1892453

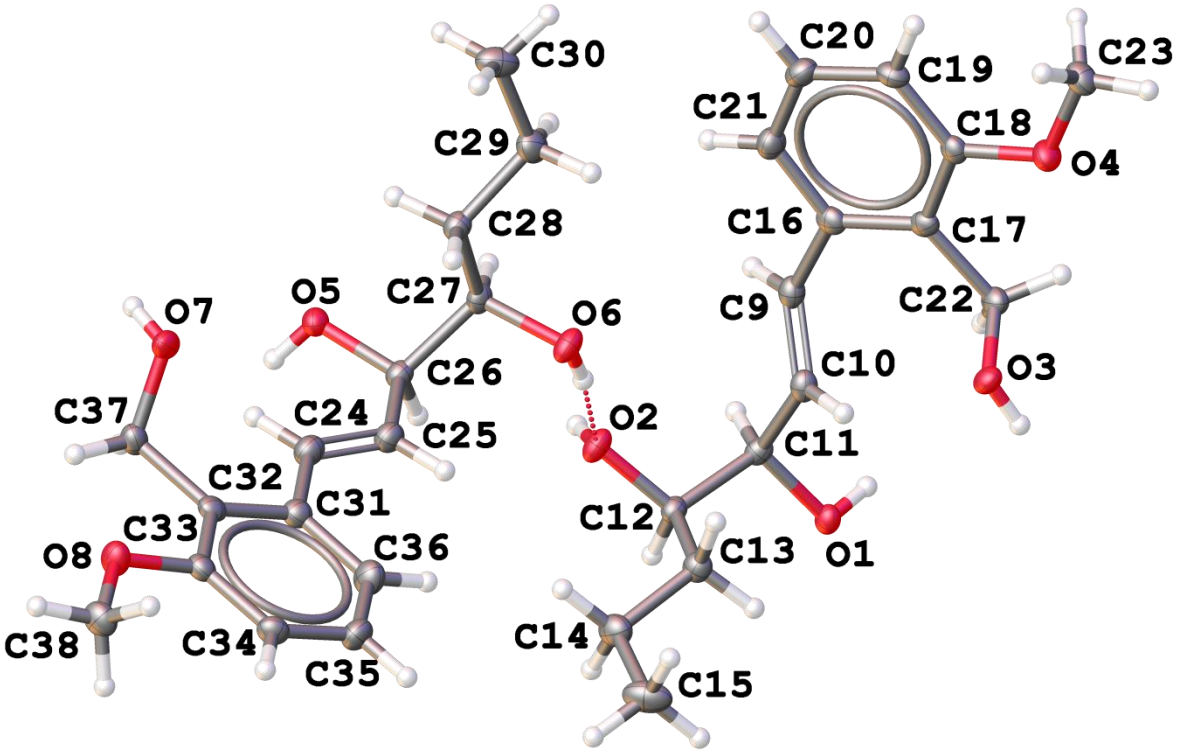
Table S2 Hydrogen bonds parameters of **4** and **9**

D–H···A	Symmetry code	d(D–H) Å	d(H–A) Å	d(D–H) Å	<(D–H–A) °
4					
O3–H3···O7	*x*, -1+*y*, *z*	0.84	1.88	2.683(3)	159
O4–H4···O4	2-*x*, -1/2+*y*, 1-*z*	0.84	1.96	2.799(2)	175
O17–H17···O3	1-*x*, 1/2+*y*, 1-*z*	0.84	1.85	2.682(3)	176
9					
O1–H11···O3	*x*, 1+*y*, *z*	0.83	1.91	2.720(3)	168
O2–H21···O6	*x*, 1+*y*, *z*	0.81	1.98	2.775(3)	166
O3–H31···O1	1-*x*,-1/2 +*y*, -*z*	0.81	1.93	2.734(3)	173
O5–H51···O7	*x*, 1+*y*, *z*	0.83	1.96	2.752(3)	157
O6–H61···O2		0.82	1.98	2.782(3)	167
O7–H71···O5	1-*x*,-1/2 +*y*, 1-*z*	0.81	1.98	2.776(3)	171

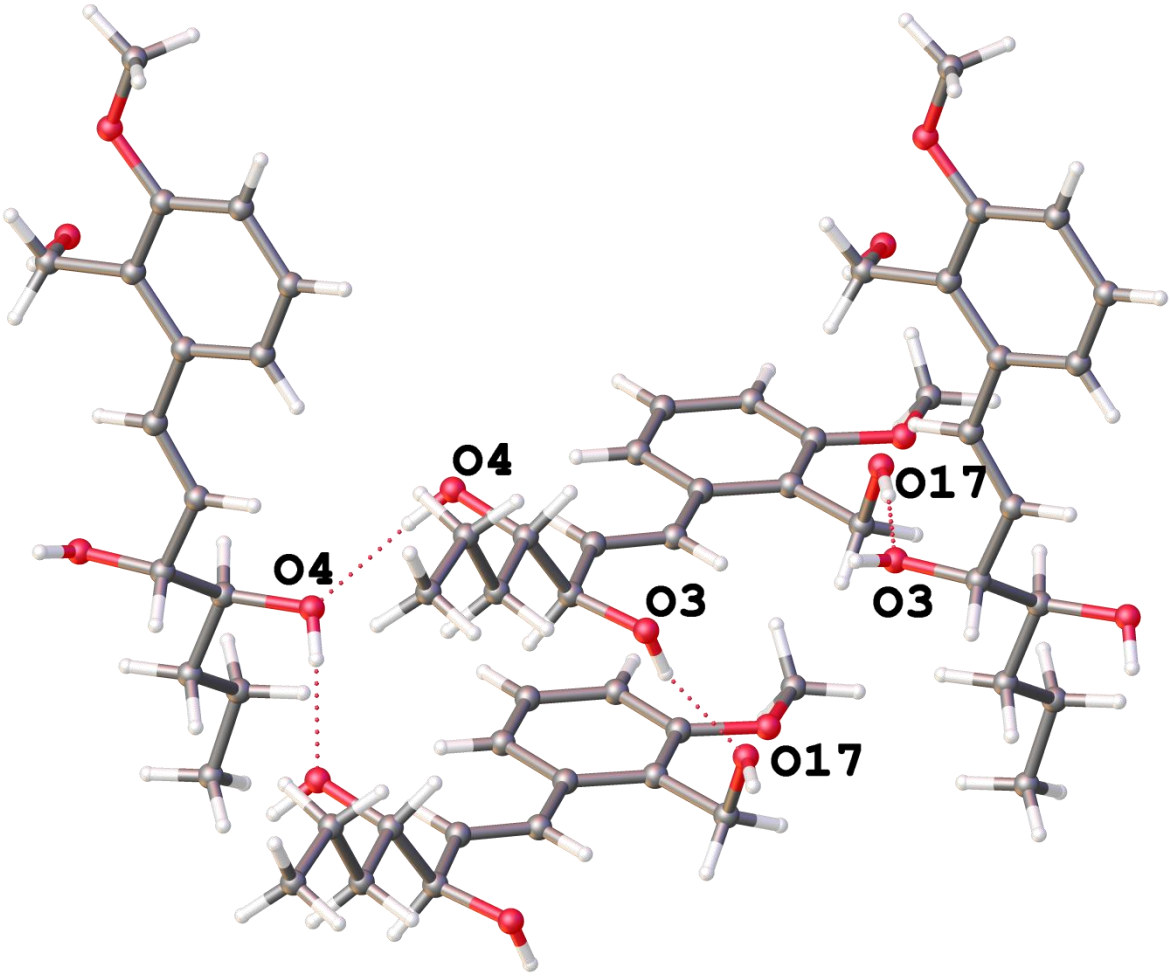
ORTEP-like drawing of **4**



ORTEP-like drawing of **9**



Hydrogen bond network in crystal structure of **4**



Hydrogen bond network in crystal structure of **9**