Supplemental Data

Synthesis of the threo-epoxy (8R,9S,10R, syn-epoxy)- and erythro-epoxy (8R,9S,10S, anti-epoxy)-eicosanoates – The synthetic approach is outlined in Scheme S1. Addition of 1,7-octadiyne to undecanal via the corresponding lithium acetylide afforded propargylic alcohol **1** in 44–59% (unoptimized) yield, along with the bis-adduct (not shown). The ester functionality was installed onto **1** by use of methyl chloroformate to give **2**. Partial reduction of diyne **2** to *Z,Z*-diene **3** was achieved by hydrogenation with Lindlar's catalyst in 92% yield. The Sharpless asymmetric epoxidation (1) of allylic alcohol **3** in the presence of L-(+)-diisopropyl tartrate afforded a (ca 2:3) mixture of two epoxides **4** and **5**, in addition to the unreactive allylic alcohol, 10*R*-**3** (41%)**.** The two epoxides were separated by preparative TLC. Their stereochemical determination was made possible by comparison with *syn*-epoxy (*threo*-epoxy) alcohol **7**, which was obtained as a virtually single isomer by *syn*-selective hydroxyl-directed epoxidation (i.e., in the absence of tartrate ligand) of 10*R*-**3**. Titanium isopropoxide-mediated epoxidation (with *t*BuOOH) of Z-allylic alcohols are known to furnish high *syn* (*threo*) selectivity due to minimization of $A^{1,3}$ strain (1-3). Finally, standard hydrogenation of **4** and **7** delivered the corresponding methyl esters **6** and **8**, respectively. ^{1}H-NMR data for the *erythro* diastereomer **6** (360 MHz, $CDCl_3$): δ 3.67, 3H, s, OCH_3; 3.53, 1H, m, H10; 2.97, 1H, ddd, $J_{7a,8}$ = 6.9 Hz, $J_{7b,8}$ = 5.2 Hz, $J_{8,9}$ = 4.2 Hz, H8; 2.83, 1H, dd, $J_{8,9}$ = 4.2 Hz, $J_{9,10}$ = 7.7 Hz; 2.32 1H, t, H2; ~1.25-1.7, m H3-7, H11-19; 0.88, 3H, t, H20. NMR data for the *threo* diastereomer **8**: δ 3.67, 3H, s, OCH_3; 3.48, 1H, m, H10; 3.03, 1H, m, H8; 2.885, 1H, dd, $J_{8,9}$ = 4.4 Hz, $J_{9,10}$ = 7.9 Hz, H9; 2.32, 2H, t, H2; ~1.25-1.7, m H3-7, H11-19; 0.88, 3H, t, H20.

Of note, the 9,10 coupling constants for *erythro* and *threo* on NMR are too close to be diagnostic (7.7 versus 7.9 Hz). The epoxide protons H8 and H9 are both slightly downfield in the *threo* isomer (cf. Fig. 2). The published values for epoxidized 2-hydroxy-3*Z*-pentenol indicate that H3 (the equivalent of our H9) is downfield in *threo*, which agrees with our result, but H4 (the equivalent of our H8) has an identical chemical shift in *erythro* and *threo* (2).

On TLC of the methyl esters (hexane:ethyl acetate, 3:1), *erythro* was the less polar (higher Rf) diastereomer. On GC of the methyl ester TMS ether derivatives, the *erythro* diastereomer eluted later than *threo* (Results, main text).

References

1. Martin, V. S., S. S. Woodard, T. Katsuki, Y. Yamada, M. Ikeda, and K. B. Sharpless. 1981. Kinetic resolution of racemic allylic alcohols by enantioselective epoxidation - a route to substances of absolute enantiomeric purity. *J. Am. Chem. Soc.* **103**: 6237-6240.
2. Adam, W., A. Corma, T. I. Reddy, and M. Renz. 1997. Diastereoselective catalytic epoxidation of chiral allylic alcohols by the TS-1 and Ti-beta zeolites: Evidence for a hydrogen-bonded, peroxy-type loaded complex as oxidizing species. *J. Org. Chem.* **62**: 3631-3637.
3. Cui, M., W. Adam, J. H. Shen, X. M. Luo, X. J. Tan, K. X. Chen, R. Y. Ji, and H. L. Jiang. 2002. A density-functional study of the mechanism for the diastereoselective epoxidation of chiral allylic alcohols by the titanium peroxy complexes. *J. Org. Chem.* **67**: 1427-1435.

Scheme S1

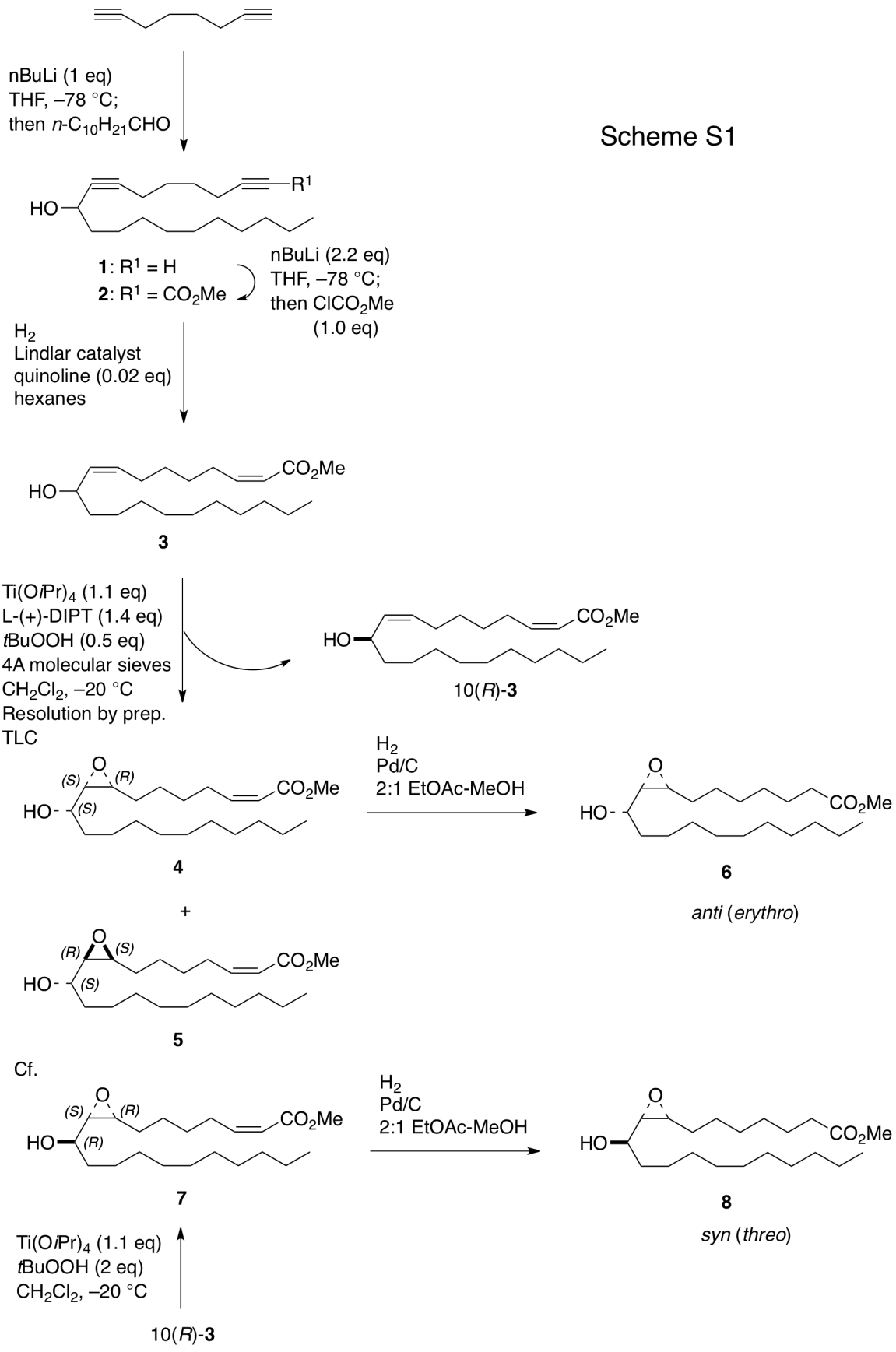

nBuLi (1 eq)
THF, –78 °C;
then n-C10H21CHO
HO
R1
1: R1 = H
2: R1 = CO2Me
nBuLi (2.2 eq)
THF, –78 °C;
then ClCO2Me
(1.0 eq)
H2
Lindlar catalyst
quinoline (0.02 eq)
hexanes
CO2Me
3
Ti(OiPr)4 (1.1 eq)
L-(+)-DIPT (1.4 eq)
tBuOOH (0.5 eq)
4A molecular sieves
CH2Cl2, –20 °C
Resolution by prep.
TLC
10(R)-3
H2
Pd/C
2:1 EtOAc-MeOH
(S)
(R)
4
6
anti (erythro)
+
5
Cf.
7
8
syn (threo)
Ti(OiPr)4 (1.1 eq)
tBuOOH (2 eq)
CH2Cl2, –20 °C
10(R)-3

Table S1. ^{1}H-NMR (500 MHz) of the 20:3ω6-derived epoxyalcohol methyl ester in $CDCl_3$

Chemical shift (ppm)	**# of protons**	**Multiplicity**	**Proton(s) [carbon no.]**	**Coupling constants (Hz)**
0.9	3	t	H20	$J_{19,20} = 7$
1.26-1.44	12	m	H4,5,6,17,18,19	
1.6-1.8	4	m	H3,7	
2.06	2	dt	H16	$J_{15,16} = 7.3$, $J_{16,17} = 7.3$
2.32	2	t	H2	$J_{2,3} = 7.5$
2.89	2	m	H13a, 13b	
2.96	1	dd	H9	$J_{8,9} = 4.1$, $J_{9,10} = 7.6$
3.03	1	ddd	H8	$J_{7a,8} = 6.8$, $J_{7b,8} = 5.5$, $J_{8,9} = 4$
3.68	3	s	-OCH3	
4.47	1	dt	H10	$J_{9,10} = J_{10,11} = 7.7$; $J_{9,OH} = 2$*
5.34	1	dt	H14	$J_{13,14} = 7.3$, $J_{14,15} = 11$
5.44	1	dt	H15	$J_{14,15} = 11$, $J_{15,16} = 7.3$
5.56	1	dd (unresolved)	H11	$J_{10,11} \approx J_{11,12} = \sim 10$
5.65	1	dt	H12	$J_{11,12} = 11$, $J_{12,13} = 7.7$

* The small extra coupling (designated as $J_{9,OH} = 2$), was not evident in other spectra acquired in $CDCl_3$ at 400 MHz.

Table S2. ^{1}H-NMR data on the 20:3ω6-derived epoxyalcohol methyl ester in C_6D_6

Chemical shift (ppm)	**# of protons**	**Multiplicity**	**Proton(s) [carbon no.]**	**Coupling constants (Hz)**
0.89	3	t	H20	$J_{19,20} = 6.9$
1.1-1.4	12	m	H4,5,6,17,18,19	
1.22	1	d	10-O<u>H</u>	J = 3.6
1.5-1.6	4	m	H3,7	
2.03	2	dt	H16	$J_{15,16} = 6.8$, $J_{16,17} = 6.8$
2.09	2	t	H2	$J_{2,3} = 7.5$
2.74	1	dt	H8	$J_{7,8} = 5.7$, $J_{8,9} = 4$
2.82	1	dd	H9	$J_{8,9} = 4$, $J_{9,10} = 7.4$
2.91	2	m	H13a, 13b	
3.36	3	s	-OCH3	
4.39	1	dt	H10	$J_{10,11} \approx J_{9,10} = 7.3$, $J_{10,OH} = 3.6$,
5.4-5.5	2	m	H12,15	
5.5-5.6	2	m	H11,14	

Supplemental Figure S1:

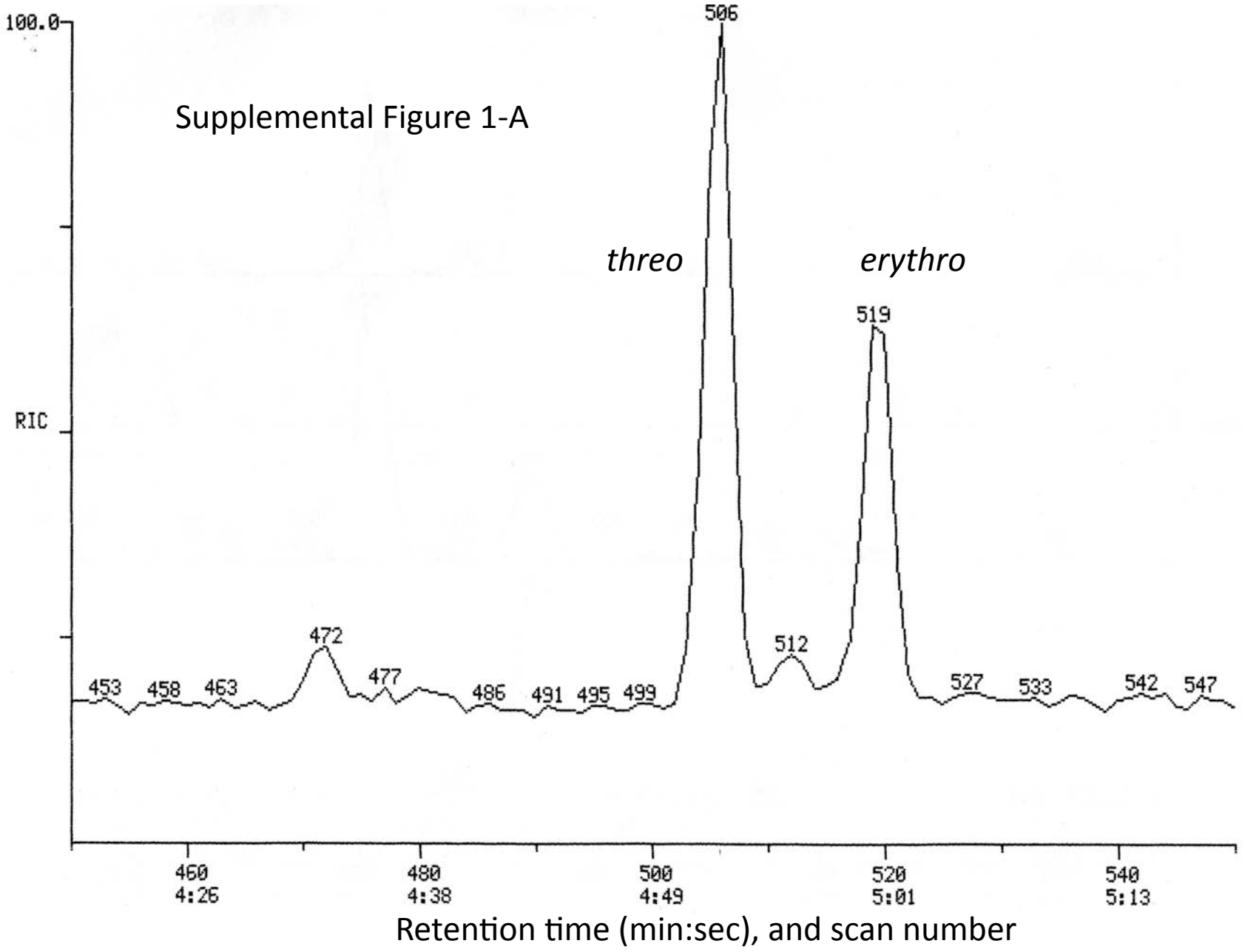
S1-A: Separation on gas chromatography of *threo* and *erythro* standards of 8*R*,9*S*-epoxy-10-hydroxy-eicosanoates as the methyl ester TMS ether derivative.

S1-B: Electron impact mass spectrum of authentic *threo* epoxyalcohol, 8*R*,9*S*-epoxy-10-hydroxy-eicosanoate as the methyl ester TMS ether derivative.

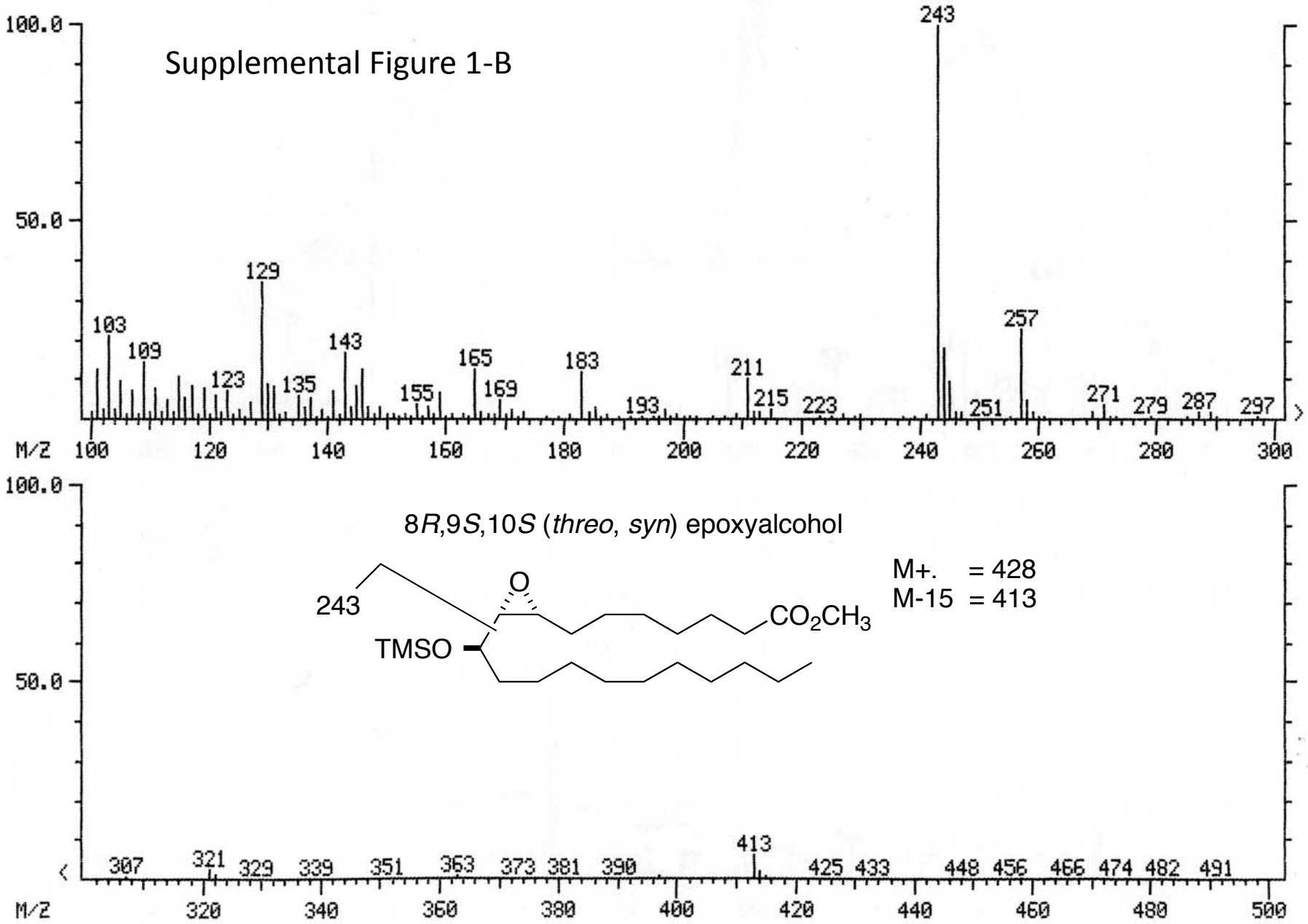
S1-C: Electron impact mass spectrum of authentic *erythro* epoxyalcohol, 8*R*,9*S*-epoxy-10-hydroxy-eicosanoate as the methyl ester TMS ether derivative.

S1-D: Electron impact mass spectrum of the epoxyalcohol (after hydrogenation, as the methyl ester TMS ether derivative) from the incubation of *P. homomalla* extracts with 20:3ω6. The retention time and mass spectrum match the authentic *erythro* diastereomer of 8*R*,9*S*-epoxy-10-hydroxy-eicosanoate.

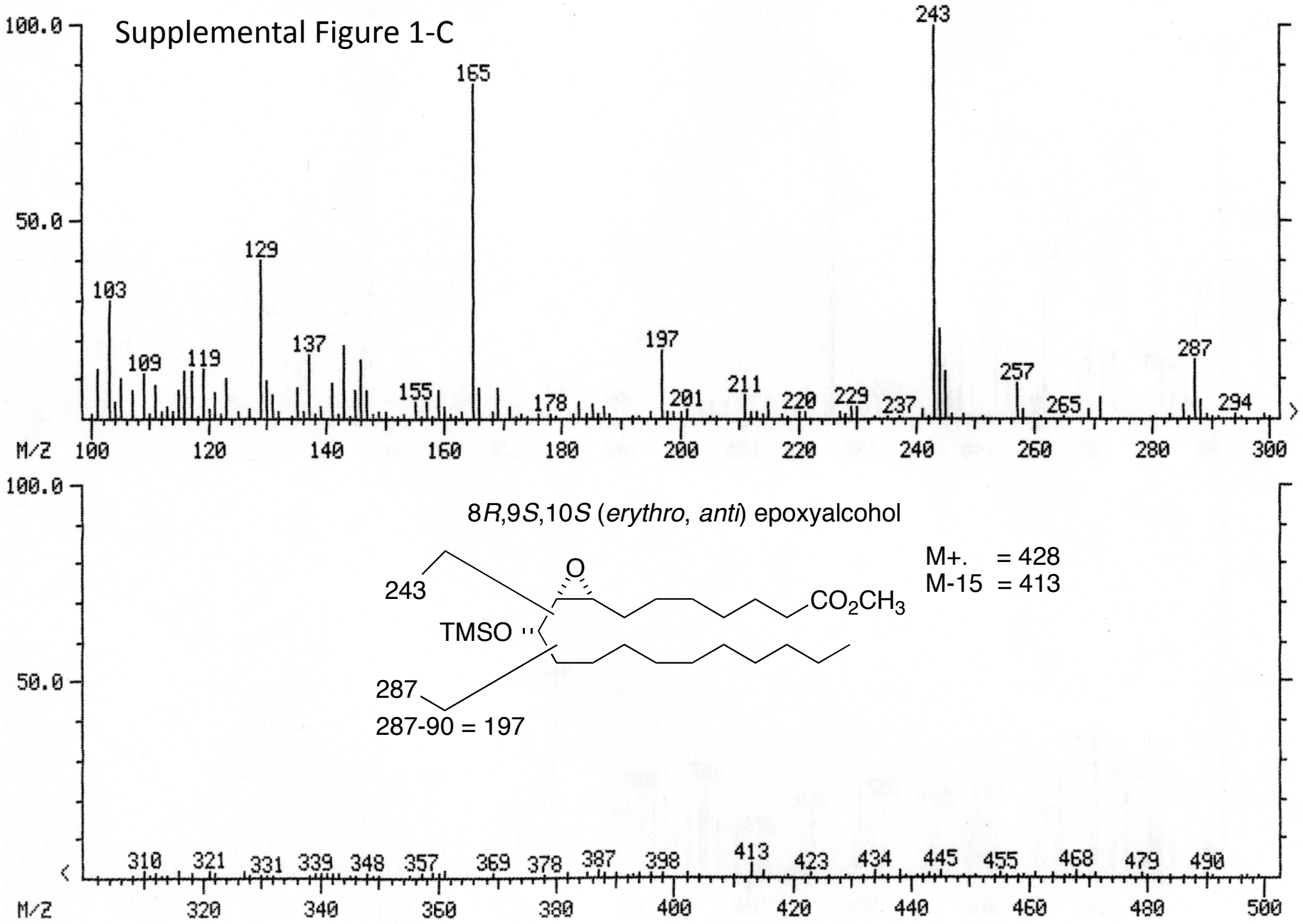
Figure S2-A: Separation on gas chromatography of *threo* and *erythro* standards of 8*R*,9*S*-epoxy-10-hydroxy-eicosanoate as the methyl ester TMS ether derivative.



S2-B: Electron impact mass spectrum of authentic *threo* epoxyalcohol, 8*R*,9*S*-epoxy-10-hydroxy-eicosanoate as the methyl ester TMS ether derivative.



S2-C: Electron impact mass spectrum of authentic *erythro* epoxyalcohol, 8*R*,9*S*-epoxy-10-hydroxy-eicosanoate as the methyl ester TMS ether derivative.



S2-D: Electron impact mass spectrum of the epoxyalcohol (after hydrogenation, as the methyl ester TMS ether derivative) from the incubation of *P. homomalla* extracts with 20:3ω6. The retention time and mass spectrum match the authentic *erythro* diastereomer of 8*R*,9*S*-epoxy-10-hydroxy-eicosanoate.

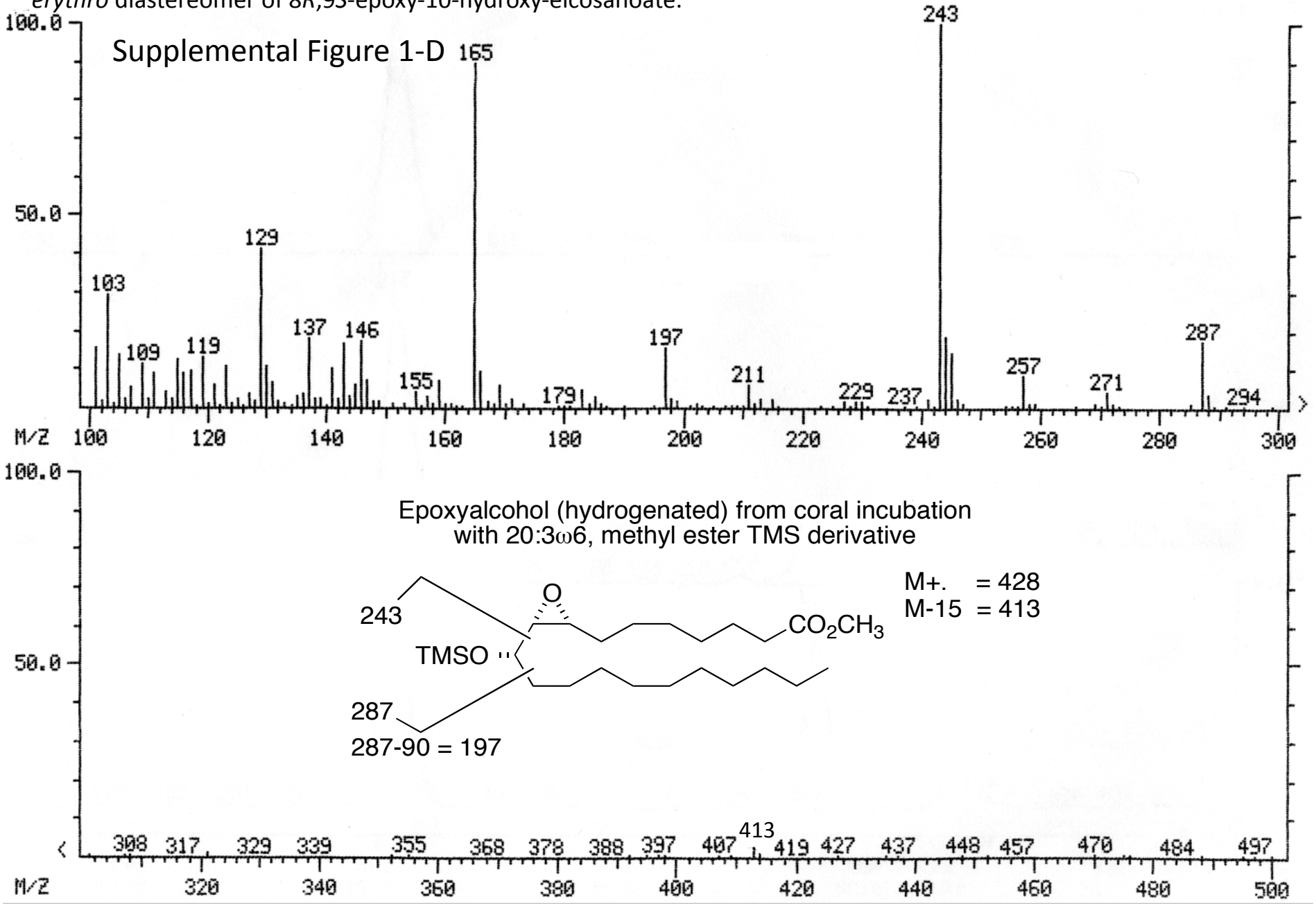


Figure S2

Mass spectrometric analysis of oxygen-18 incorporation in the epoxyalcohol product

Epoxyalcohol formed by biosynthesis from 20:3ω6 by *P. homomalla* extracts in the presence of $^{18}O_2$ gas. The product was purified from the $^{18}O_2$ incubation, hydrogenated, and analyzed as the PFB ester, TMS ether derivatives by GC-MS in the negative ion/chemical ionization mode. Partial mass spectral recordings of the prominent M-PFB ion of unlabeled epoxyalcohol (left side), and ^{18}O-labeled epoxyalcohol (right side).