Supplementary Material for:

Second-generation products contribute substantially to the particle-phase organic material produced by β-caryophyllene ozonolysis

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1. Experimental conditions.

Expt	ΔHC (ppbv)	O_3 (ppbv)
1	1.7	50
2	6.7	50
3	13.3	50
4	46.4	50
5	1.7	100
6	6.7	100
7	13.3	100
8	46.4	100
9	1.7	200
10	6.7	200
11	13.3	200
12	46.4	200

Table S1. Experimental conditions. ΔHC is the concentration of β-caryophyllene consumed by reactions inside the chamber. O_3 concentration (in excess) is maintained constant by feedback control.

2. Operating conditions for UPLC-ToF-MS chromatography

Parameter	Condition
Injection	5 μL, 10 °C
Column	ACQUITY UPLC HSS T3, 1.8 μm, 2.1×50 mm, 40 ℃
Mobile phase	A: 0.1% (v/v) formic acid in water B: 0.1% (v/v) formic acid in methanol
Gradient	40% B, 1 min; 40% to 90% B in 3 min; kept at 90% B for 1 min; back to 40% B in 1 min; kept at 40% B for 1 min.
Flow rate	0.4 mL min^{-1}

Table S2. Conditions of ultra performance liquid chromatography (UPLC).

Parameter	For molecular formula determination		For fragmentation		For semi-quantification	
Ionization mode	ESI−	ESI+	ESI−	ESI+	ESI−	ESI+
ToF mass analyzer mode	W	W	W	W	V	V
Capillary voltage (V)	2800	3000	2800	3000	2800	3000
Aperture 1 voltage (V)	5	5	25	25	5	5
Acquisition range (*m/z*, Da)	100-1000	100-1000	100-1000	100-1000	100-400	100-400
Lock mass solution	Yes	Yes	Yes	Yes	No	No

Other conditions in ToF-MS include: cone voltage, 35 V; desolvation temperature, 300 ℃; source temperature, 120 ℃; cone gas, 20 L hr^{-1}; desolvation gas, 700 L hr^{-1}.

Table S3. Conditions of time-of-flight mass spectrometer (ToF-MS). Low aperture-1 voltage (5 V) was used to obtain intense peaks of quasi-molecular ions and adduct ions for molecular formula determination. High aperture-1 voltage (25 V) was used to obtain peaks of the fragments for structural elucidation. Mass calibration between *m*/z 100 and 1000 was carried out by direct infusion of a 15 mM sodium formate solution in 9:1 CH_3CN-H_2O. A 0.4 μM leucine enkephalin solution in 50:50 CH_3CN-H_2O was continuously infused through the reference spray probe as a lock for the *m*/*z* axis.

3. Extracted ion chromatograms (EICs)

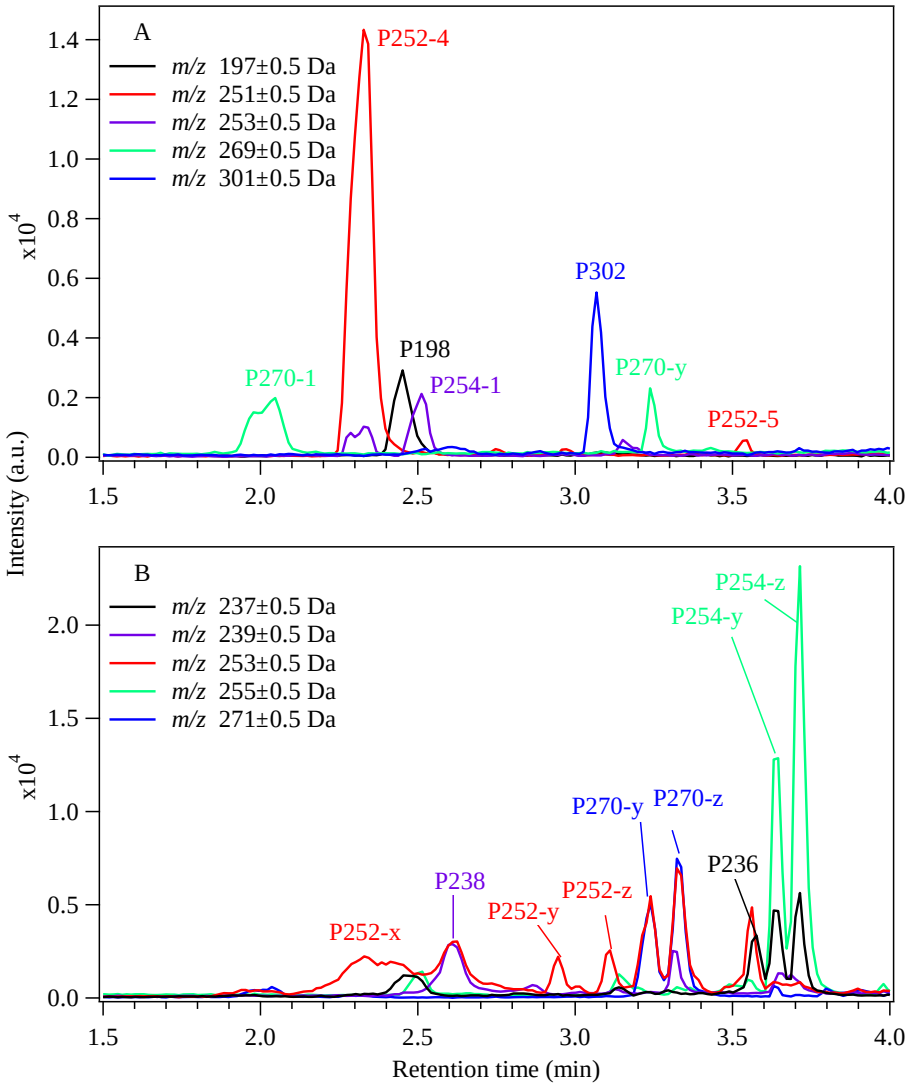

Figure S1. Extracted ion chromatograms (EICs) of the observed products in ESI− (Panel A) and ESI+ (Panel B). Each colored line represents the extracted signal of quasi-molecular ions ($[M-H]^-$ in ESI− mode and $[M+H]^+$ in ESI+ mode) within a 0.5 Da window. Labels of the products are as discussed in the caption of Figure 2. Some of the *m*/*z*-resolved peaks are fragment signals from a larger species. For example, in Panel B peaks at 3.2 and 3.3 min in the EIC of *m*/*z* 253 (red) are fragments from the EIC of *m*/*z* 271 (blue).

4. Adduct ions using acetic acid as the additive

ESI−				**[M+NaOOCCH$_3$-H]$^-$**	
product	rt (min)	Formula	measured	calculated	Δ(mDa)
P198	2.45	$C_{11}H_{18}O_3$	279.1239	279.1208	3.1
P252-4	2.33	$C_{14}H_{20}O_4$	333.1343	333.1314	2.9
P252-5	3.55	$C_{15}H_{24}O_3$	333.1654	333.1678	-3.4
P254-1	2.51	$C_{14}H_{22}O_4$	335.1511	335.1470	4.1
P270-1	2.05	$C_{14}H_{22}O_5$	351.1458	351.1419	3.9
P302	3.07	$C_{14}H_{22}O_7$	383.1118	383.1078	4.0
ESI+				**[M+CH$_3$OH+Na]$^+$**	
product	rt (min)	formula	measured	calculated	Δ(mDa)
P236	3.58	$C_{15}H_{24}O_2$	291.1933	291.1936	−0.3
P238	2.61	$C_{14}H_{22}O_3$	293.1805	293.1729	7.6
P252-*x*	2.33		-[a]	-	-
P252-*y*	2.95	$C_{15}H_{24}O_3$	307.1969	307.1885	8.4
P252-*z*	3.11		307.1978		9.3
P254-*y*	3.65	$C_{14}H_{22}O_4$	309.1671	309.1678	−0.7
P254-*z*	3.71		309.1683		0.5
P270-*y*	3.24	$C_{14}H_{22}O_5$	325.1584	325.1627	−4.3
P270-*z*	3.32		325.1585		−4.2

Table S4. Adduct ions of particle-phase products from the dark ozonolysis of β-caryophyllene, as detected by UPLC-ToF-MS with electrospray ionization (ESI) using acetic acid as the additive in the eluent. Retention times (rt) are listed. Measured and expected mass-to-charge (*m*/*z*) values as well as their difference are shown. Product label extenders "*x*", "*y*", and "*z*" are as discussed in the caption of Figure 2. [a]Adduct ions were not observed.

5. Mass spectra of products whose molecular formulas have been previously reported in the literature

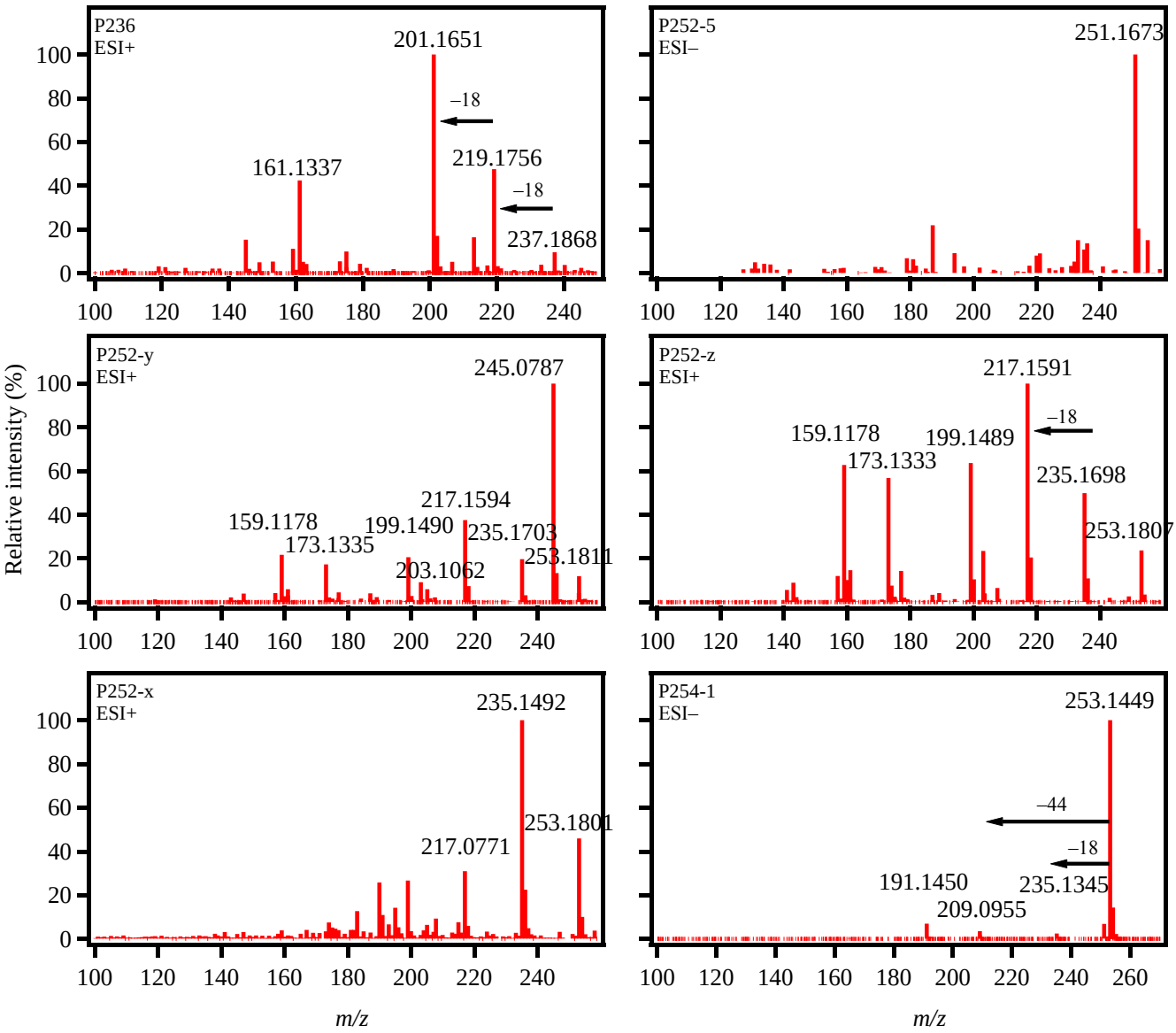

Figure S2. Mass spectra of particle-phase products whose molecular formulas have been previously reported in literature (first-generation). Structures of the products are provided in Figure 1 (panels B). Labels of the products are discussed in the caption of Figure 2. Solid arrows with the mass differences indicate the fragmentation that forms the different ions.

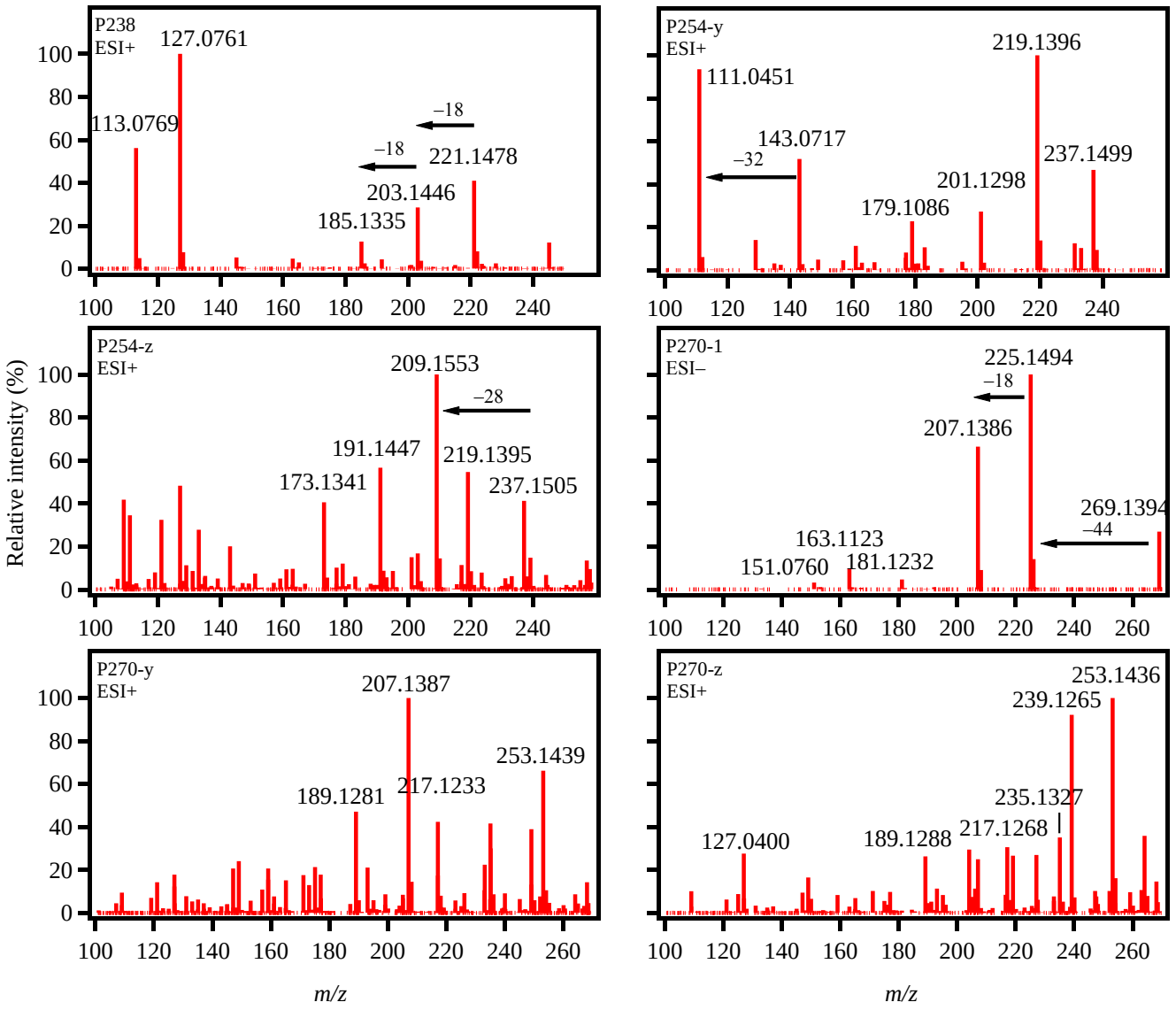

Figure S3. Mass spectra of particle-phase products whose molecular formulas have been previously reported in literature (second-generation). Structures of the products are provided in Figure 1 (panels C). Labels of the products are discussed in the caption of Figure 2. Solid arrows with the mass differences indicate the fragmentation that forms the different ions.

6. Reaction pathways in the formation of first-generation products

The first-generation products were formed from the Criegee intermediates (CIs) of β-caryophyllene with the nine-membered ring opened (i.e., ozonolysis on the endo-cyclic double bond). The CIs from alkene ozonolysis follow several different pathways (Kroll et al., 2002; Atkinson and Arey, 2003; Maksymiuk et al., 2009; Winterhalter et al., 2009), including (1) a stabilized Criegee intermediate (SCI) channel, (2) a vinyl hydroperoxide (VHP) channel, (3) an isomerization (ISO) channel, and (4) an ester channel.

The stabilized CIs can react with a number of common gas-phase molecules (Maksymiuk et al., 2009) such as H_2O (forming hydroperoxides, carbonyls, and organic acids), NO_2 (forming nitrate radicals and carbonyls), and carbonyls (forming secondary ozonides). We did not observe any secondary ozonides under our reaction conditions (i.e., no added NO_x and 40% RH). Therefore, the SCI channel here refers only to the reactions of stabilized CIs with H_2O. As illustrated in Figure S4, P236 can form via the SCI channel from the CIs produced by ozonolysis at the endo-cyclic double bond (Winterhalter et al., 2009).

In the VHP channel, the CIs rearrange via a 1,4-hydrogen shift to a vinyl hydroperoxide, which decompose to generate a keto alkyl radical ($RCOC^{\bullet}H_2$) and then react with O_2 to form a keto alkylperoxy radical ($RCOCH_2OO^{\bullet}$). This keto alkylperoxy radical reacts with other alkylperoxy radicals to form hydroxyl carbonyls and dicarbonyls, with O_2 as a by-product (Winterhalter et al., 2009). As depicted in Figure S4, products P252-2 and P252-3 can form via the VHP channel of these CIs (Winterhalter et al., 2009).

As shown in Figure S5, CI-2 follows a VHP channel to form a keto alkylperoxy radical ($RCOCH_2OO^{\bullet}$), which isomerizes to form a dicarboxylic acid (P254-1) with loss of formaldehyde (Jaoui et al., 2007; Winterhalter et al., 2009). This ISO pathway forming dicarboxylic acids is believed to be analogous to pinic acid formation from ring-opening CIs of monoterpenes (Ma et al., 2009; Winterhalter et al., 2009), with two possible routes of isomerization (Jenkin et al., 2000; Koch et al., 2000).

The ester channel involves rearrangement of a CI to form a dioxirane, which is followed by ring cleavage and formation of unsubstituted carboxylic acids and esters, as well as alkyl moiety with a loss of CO_2 (Kroll et al., 2001; Atkinson and Arey, 2003; Maksymiuk et al., 2009; Winterhalter et al., 2009). We did not observe esters in this study, probably due to their low yields (Nguyen et al., 2009); nevertheless, a carboxylic

acid (P252-5) was observed and is proposed to be formed via an ester channel (Scheme A, Figure S6) (Nguyen et al., 2009).

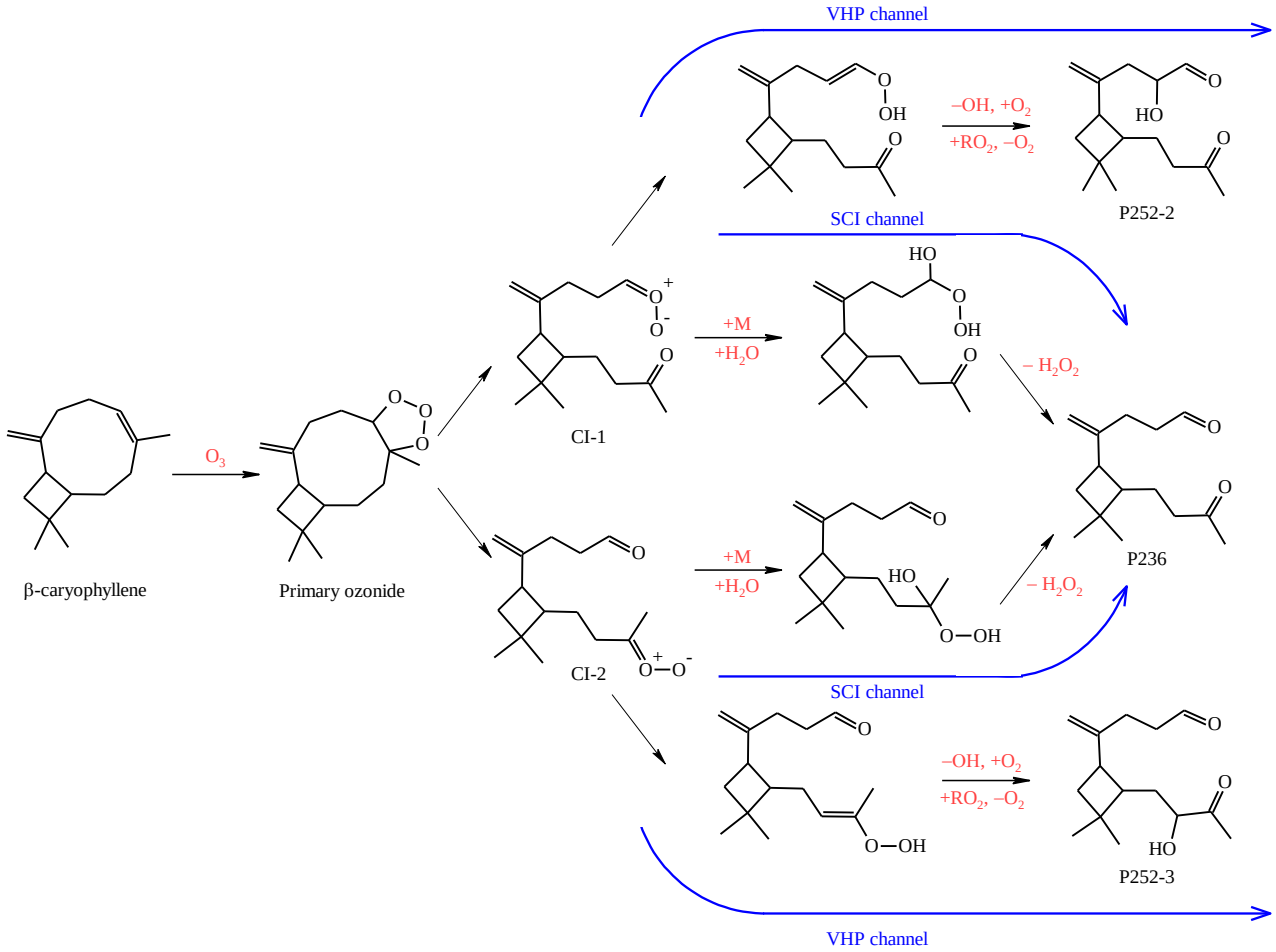

Figure S4. Proposed reactions leading to the first-generation products P236, P252-2, and P252-3 via VHP and SCI pathways. Labeling is as discussed in the caption of Figure 4.

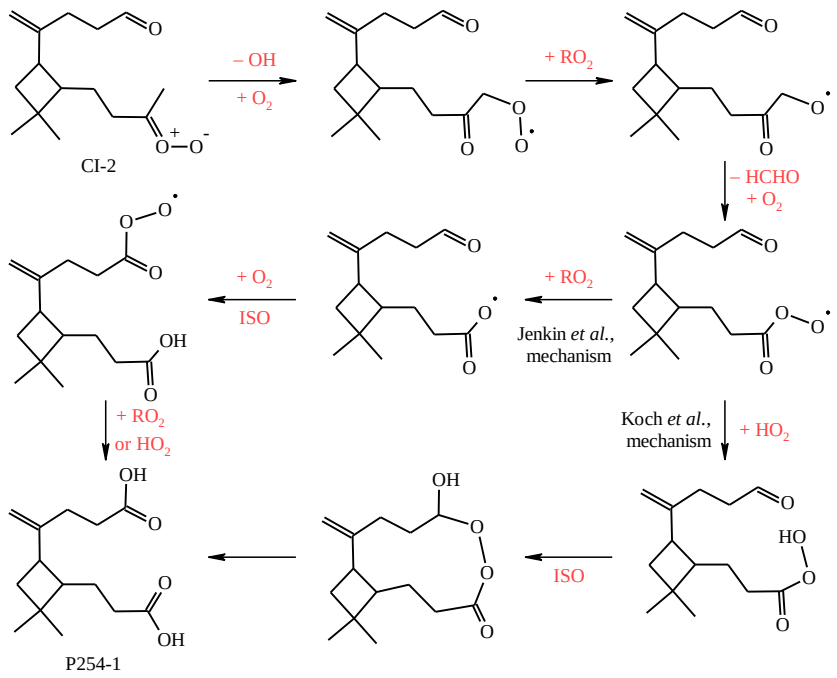

Figure S5. Proposed reaction pathways in the formation of the first-generation product P254-1 via ISO pathway starting from CI-2 of Figure S2.

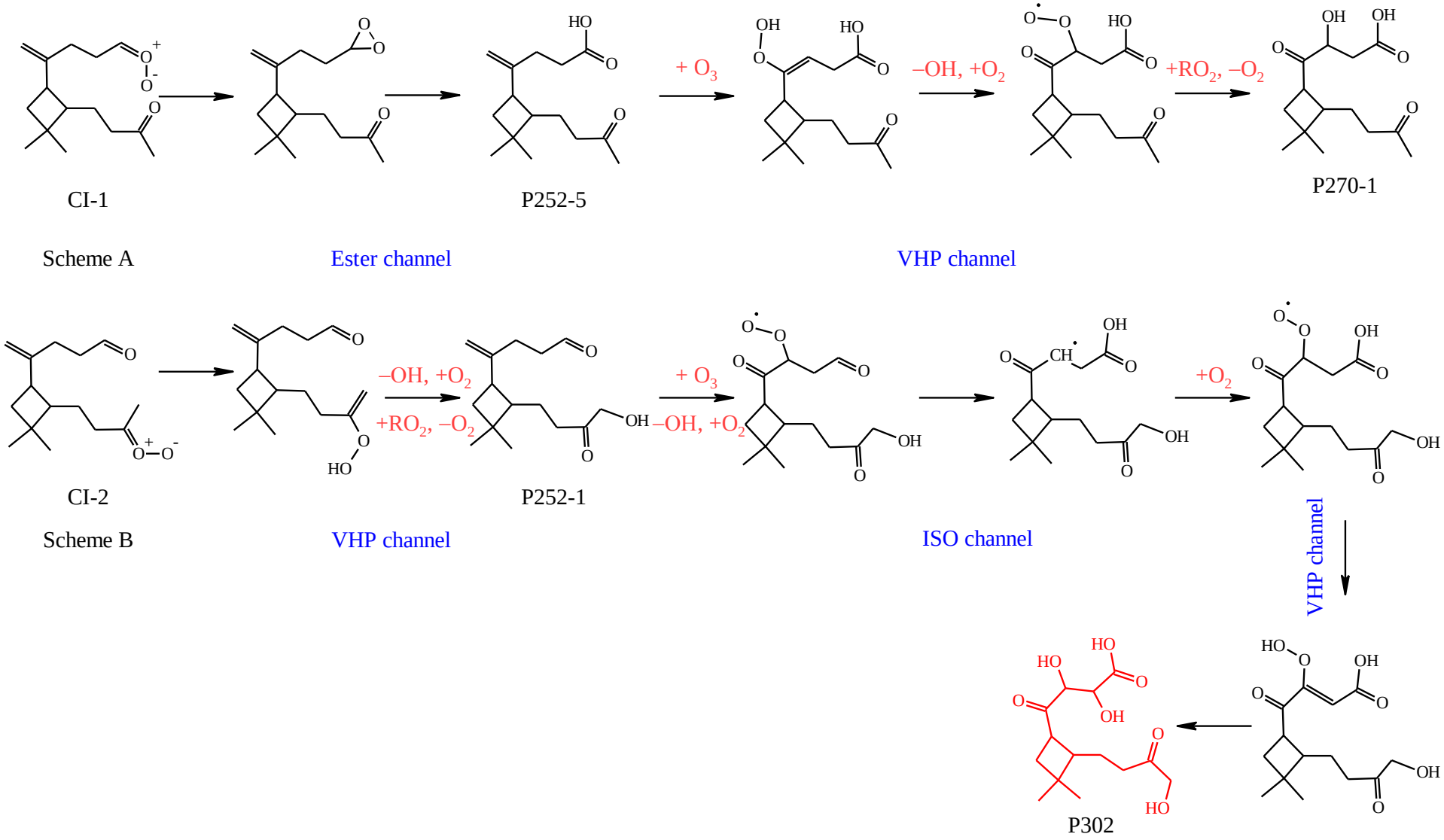

Figure S6. Proposed reaction pathways starting from CI-1 and CI-2 for the formation of the first-generation products P252-5 (Scheme A) and P252-1 (Scheme B) via ester and VHP pathways, respectively, as well as their further reactions to form P270-1 and P302 (Schemes D and E of Figure 4).

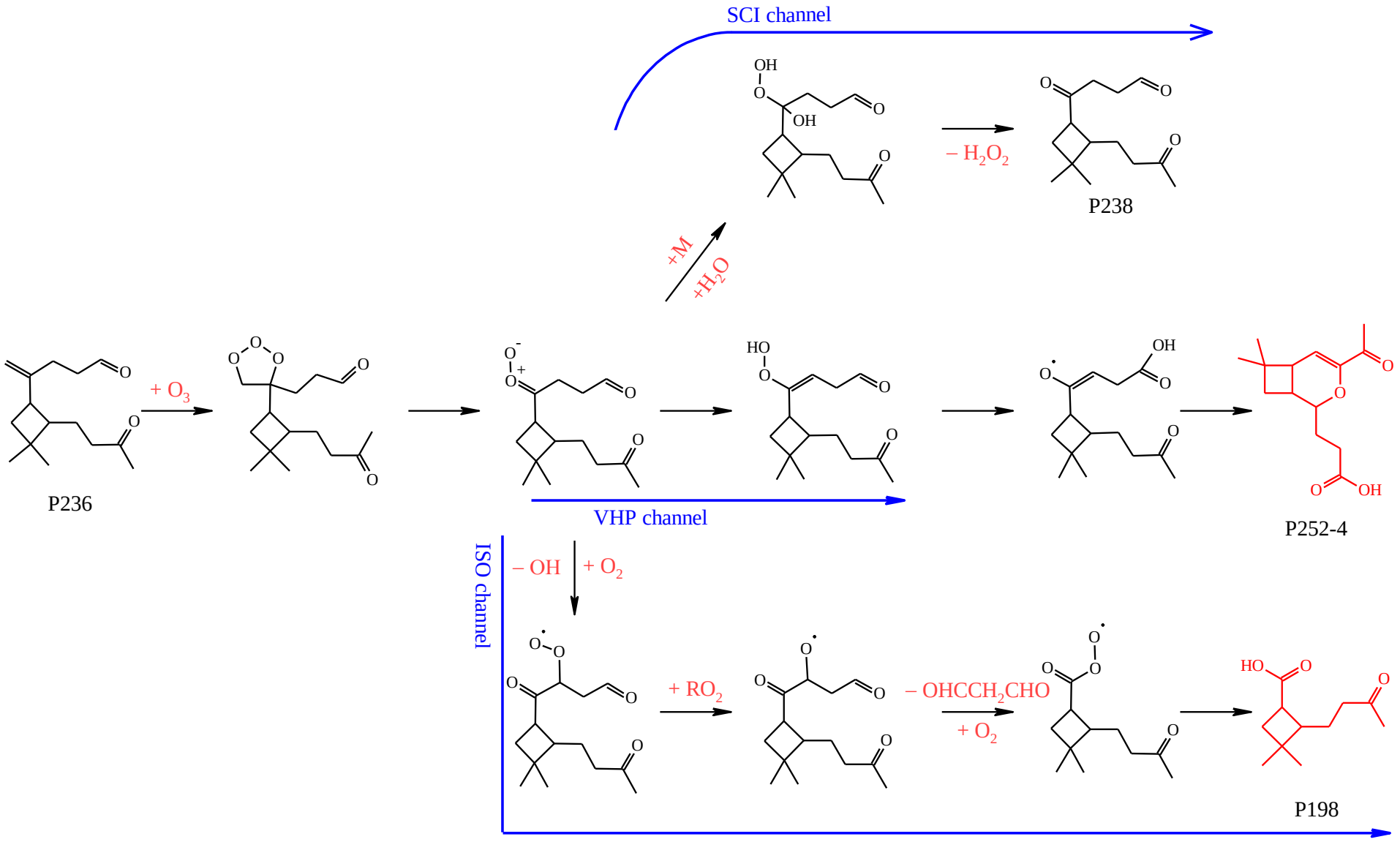

Figure S7. Proposed reaction pathways leading to the formation of the second-generation products P238, P252-1, and P198 from the first-generation product P236 (Scheme A of Figure 4).

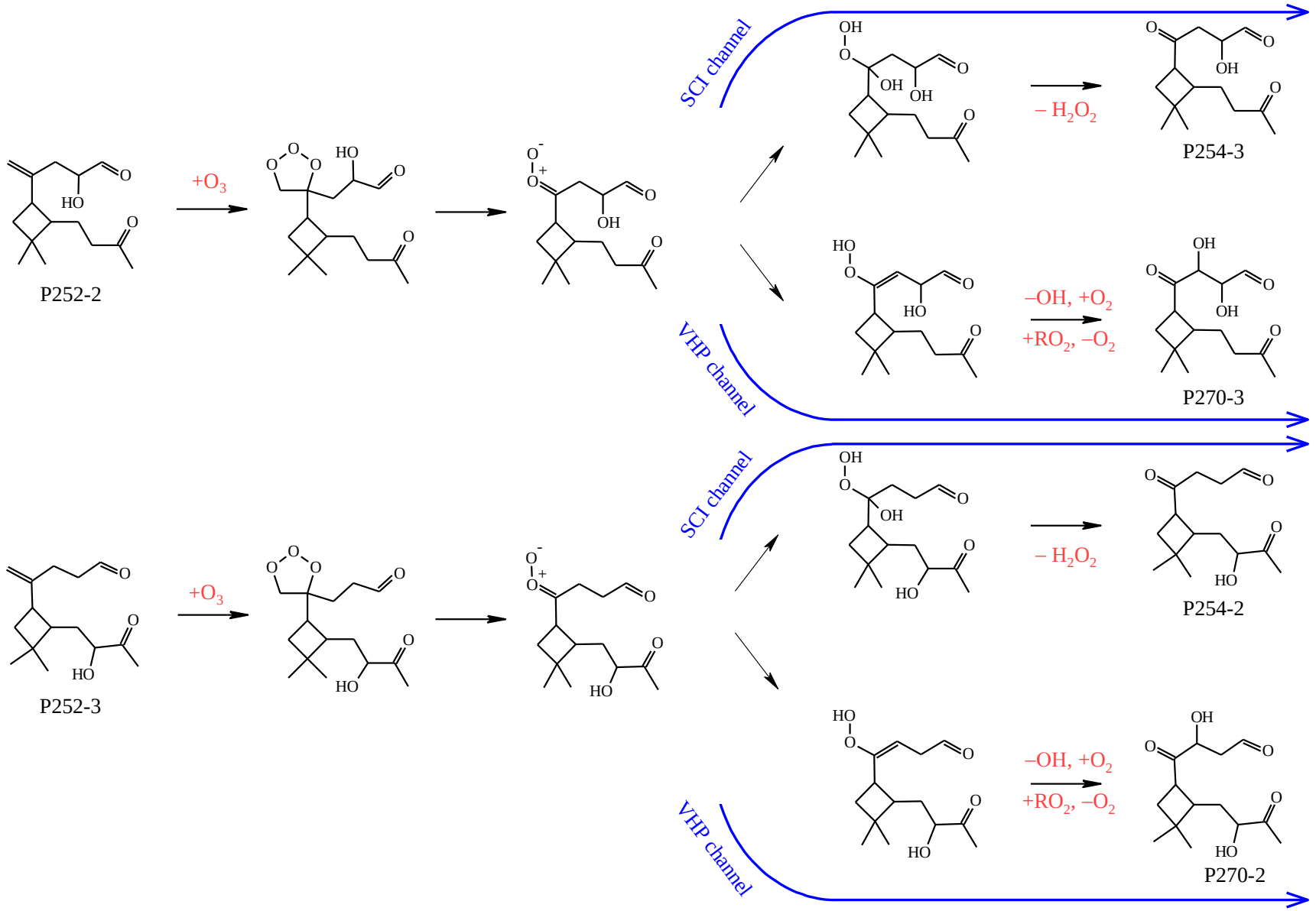

Figure S8. Proposed reaction pathways leading to the formation of second-generation products P254-2, P254-3, P270-2, and P270-3 from the first-generation products P252-2 and P252-3 (Schemes B and C of Figure 4).

7. References

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