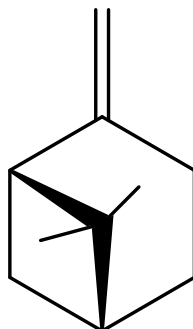
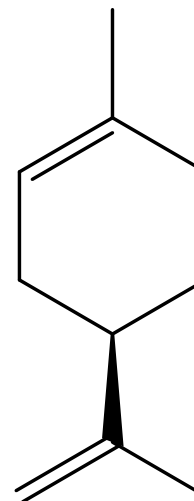


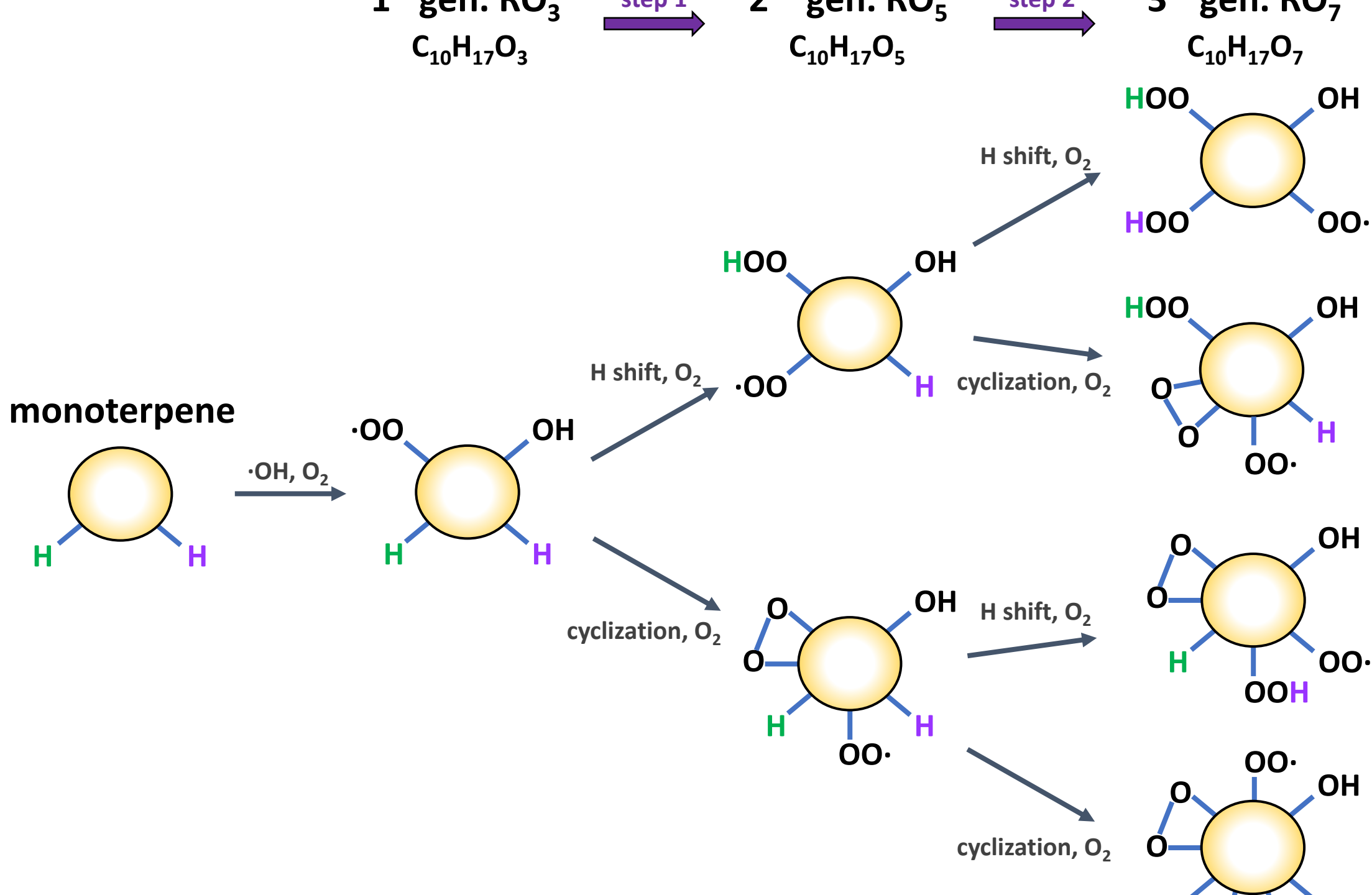
(+)- α -pinene

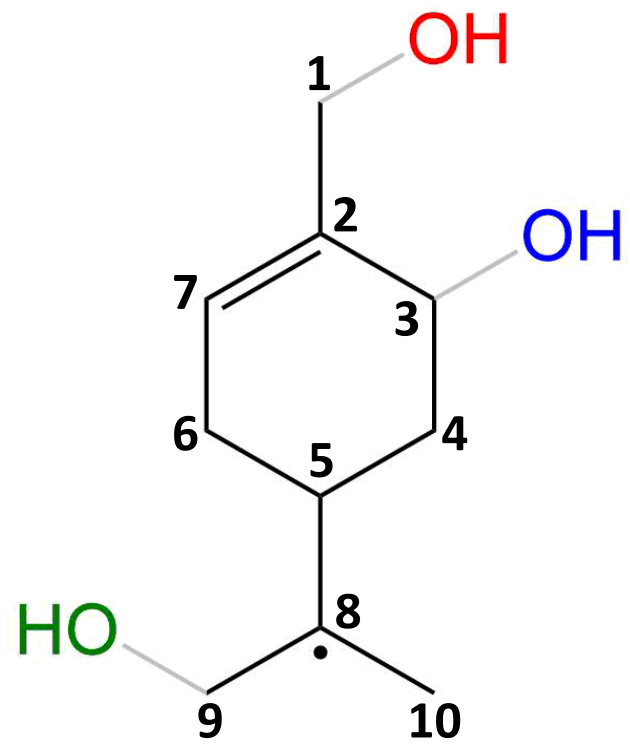


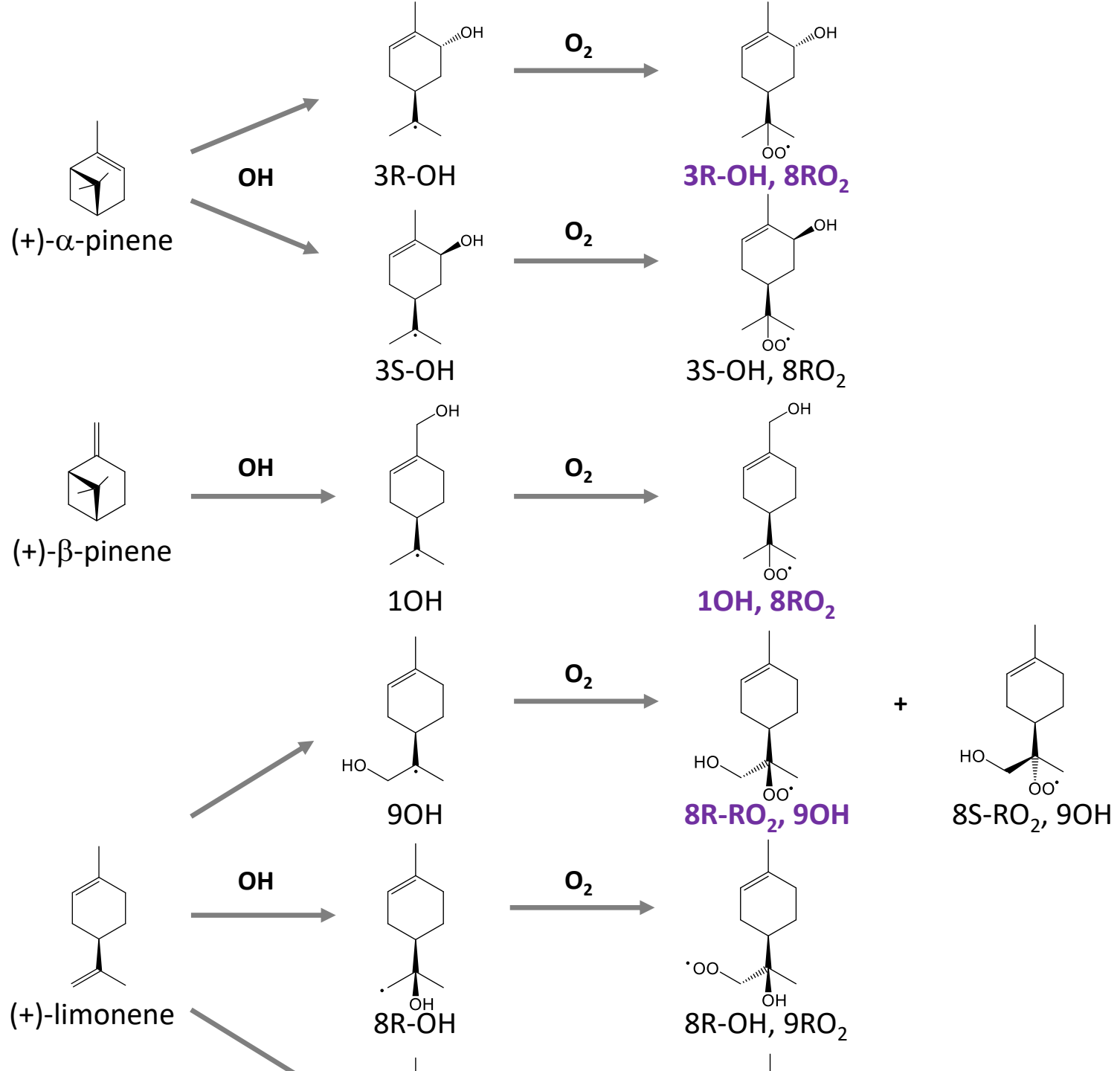
(+)- β -pinene

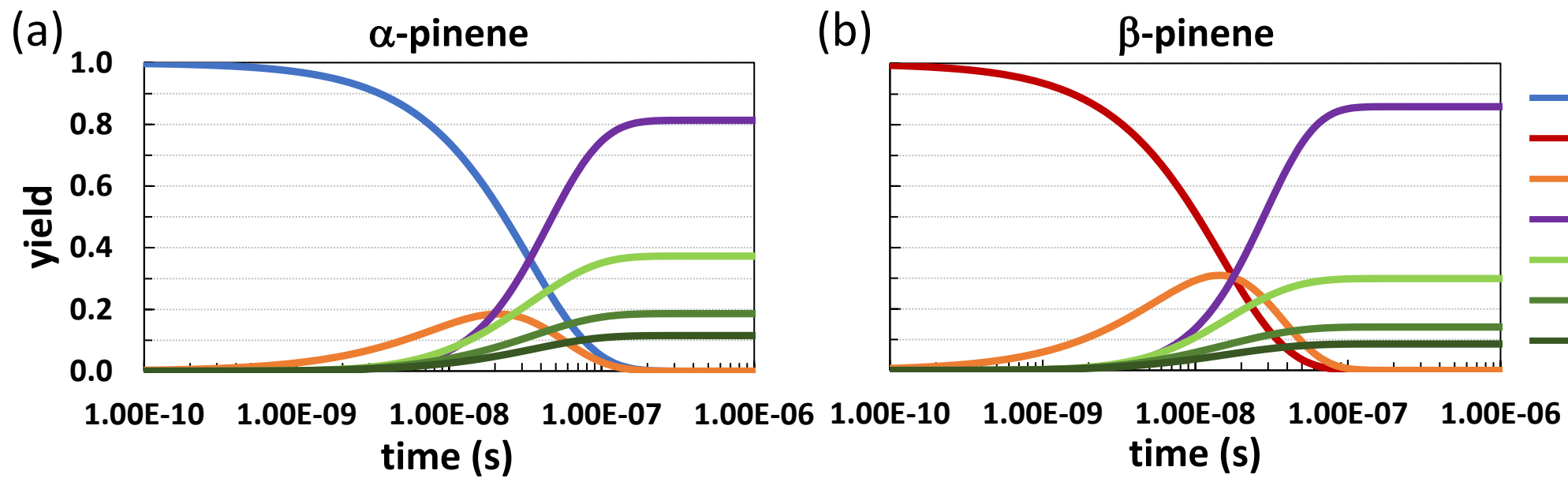


(+)-limonene









- α -pinene + OH
- β -pinene + OH
- HO-terpene·
- HO-terpene-OO·
- Ring Open $\Delta E_{\text{down}} = 100 \text{ cm}^{-1}$
- Ring Open $\Delta E_{\text{down}} = 200 \text{ cm}^{-1}$
- Ring Open $\Delta E_{\text{down}} = 300 \text{ cm}^{-1}$

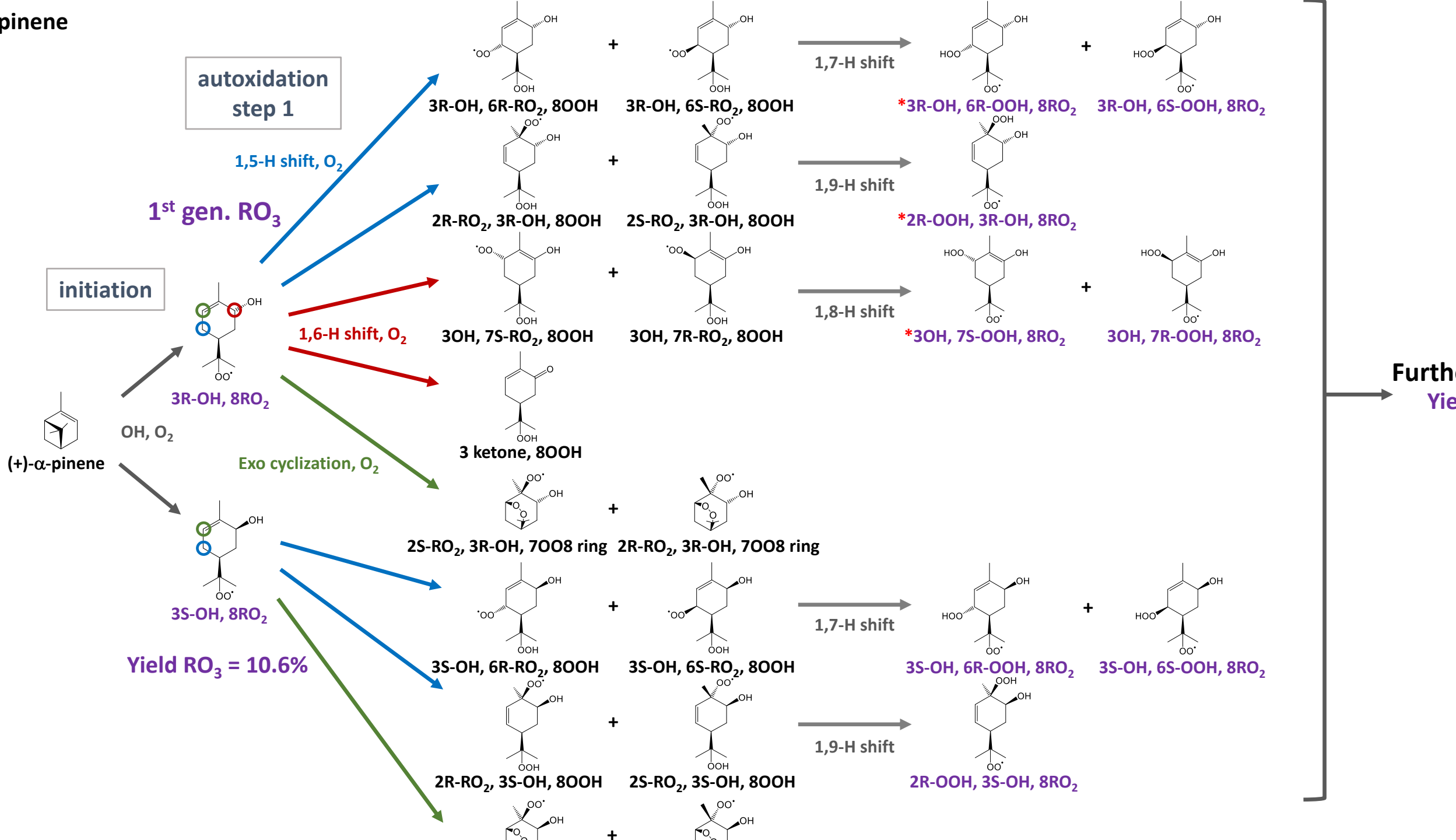
1,5-H shift rate constants (s^{-1})

	ω B97X-D/6-311++G**	ω B97X-D/aug-cc-pVTZ	M062x/aug-cc-pVTZ	CCSD(T)-F12a
α -pinene	2.3	3.1	11.9	1.1 ^a
β -pinene	2.7	4.7	14.9	1.4 ^a
limonene	6.4	7.8	15.8	4.0 ^b

6-exo-cyclization rate constants (s^{-1})

	ω B97X-D/6-311++G**	ω B97X-D/aug-cc-pVTZ	M062x/aug-cc-pVTZ	CCSD(T)-F12a
α -pinene	0.24	0.08	0.31	0.35 ^a
β -pinene	6.1	1.8	2.2	4.0 ^a
limonene	7.1	1.5	1.8	3.9 ^b

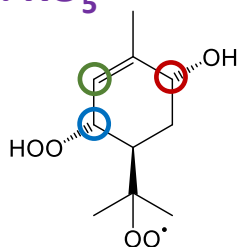
α -pinene



α -pinene

2nd gen. RO₅

autoxidation
step 2



3R-OH, 6R-OOH, 8RO₂

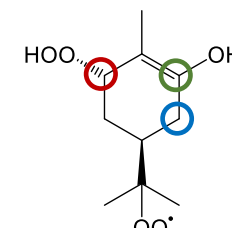
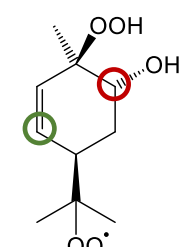
1,5-H shift, O₂

1,6-H shift, O₂

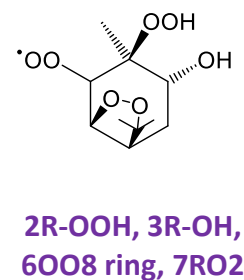
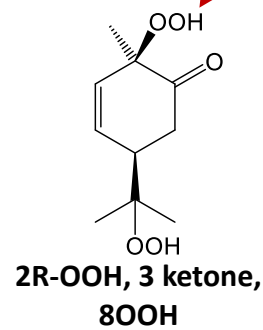
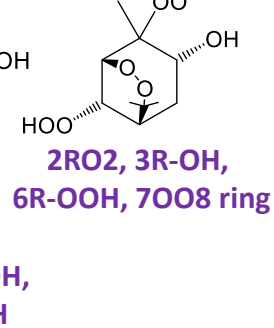
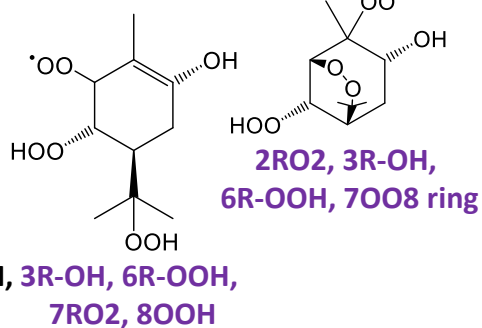
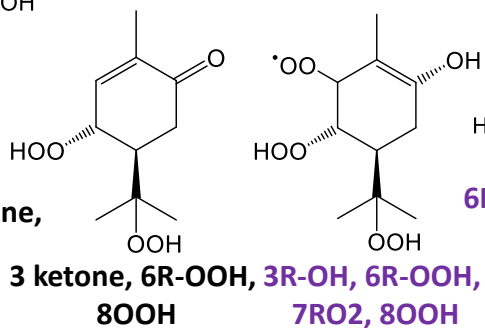
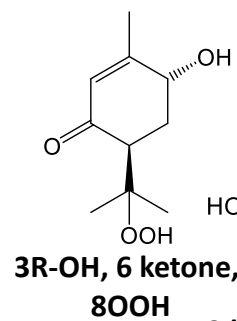
Exo cyclization, O₂

2R-OOH, 3R-OH, 8RO₂

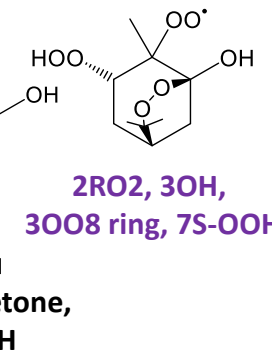
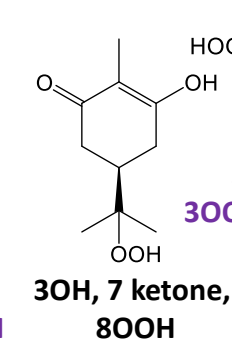
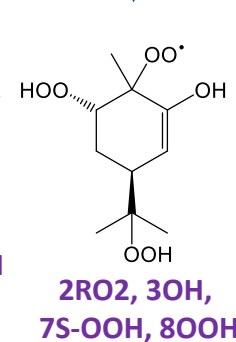
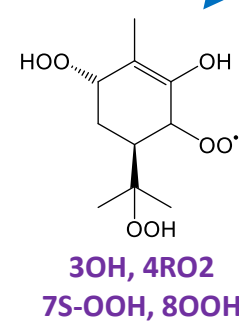
3OH, 7S-OOH, 8RO₂



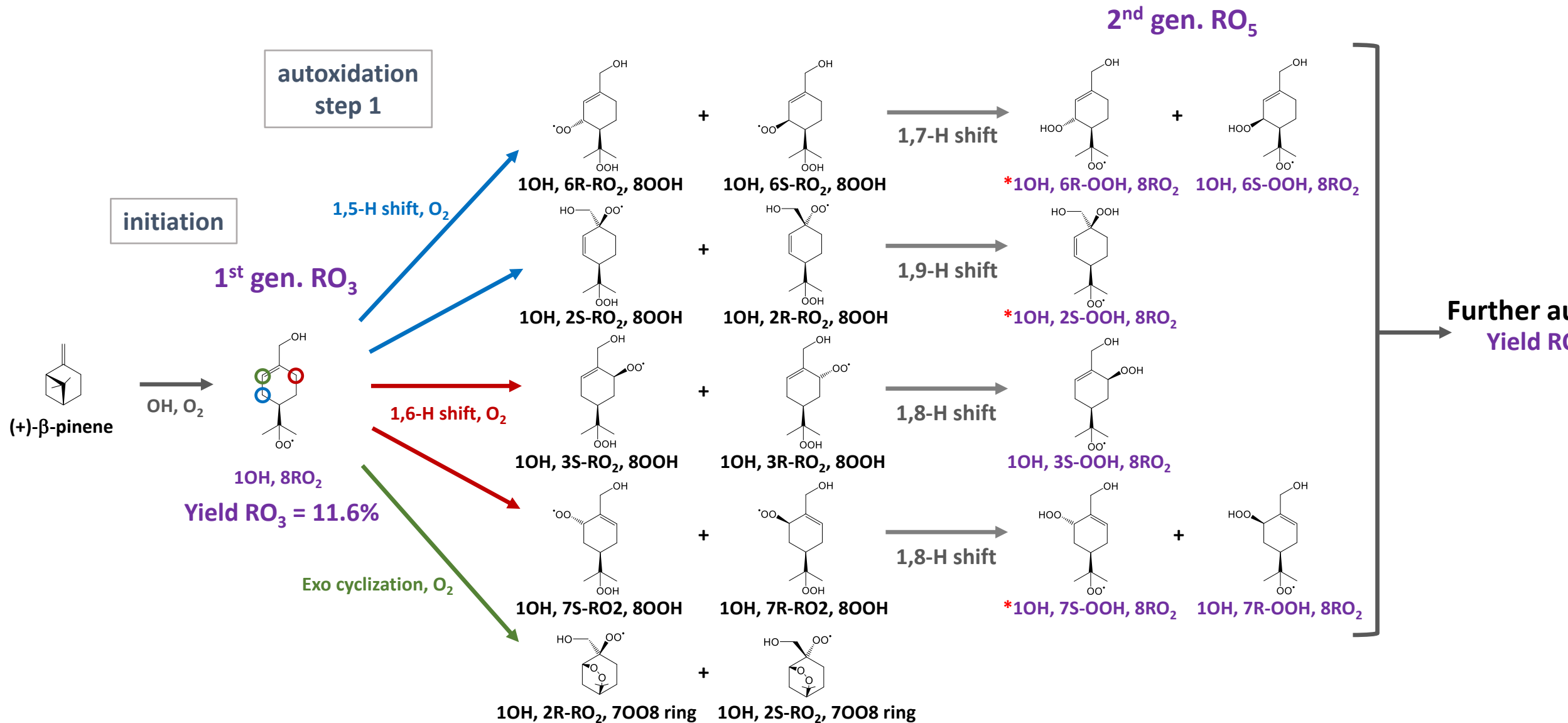
3rd gen. RO₇



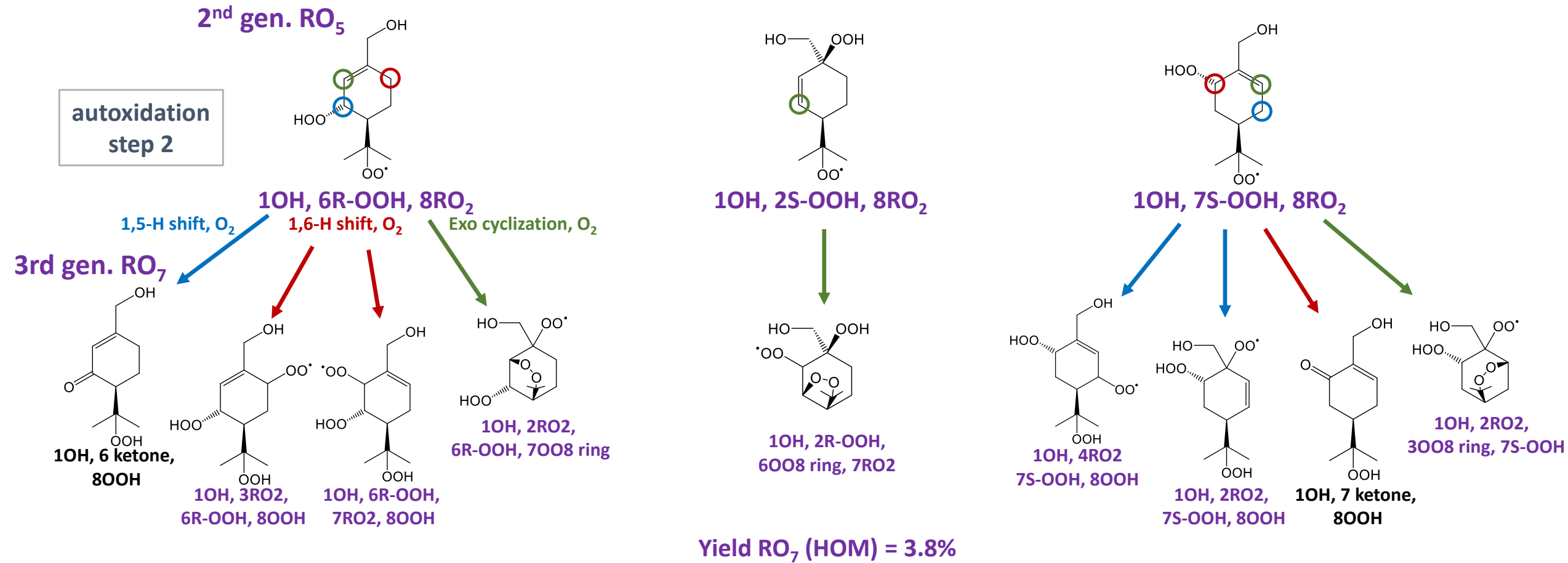
Yield RO₇ (HOM) = 4.6%



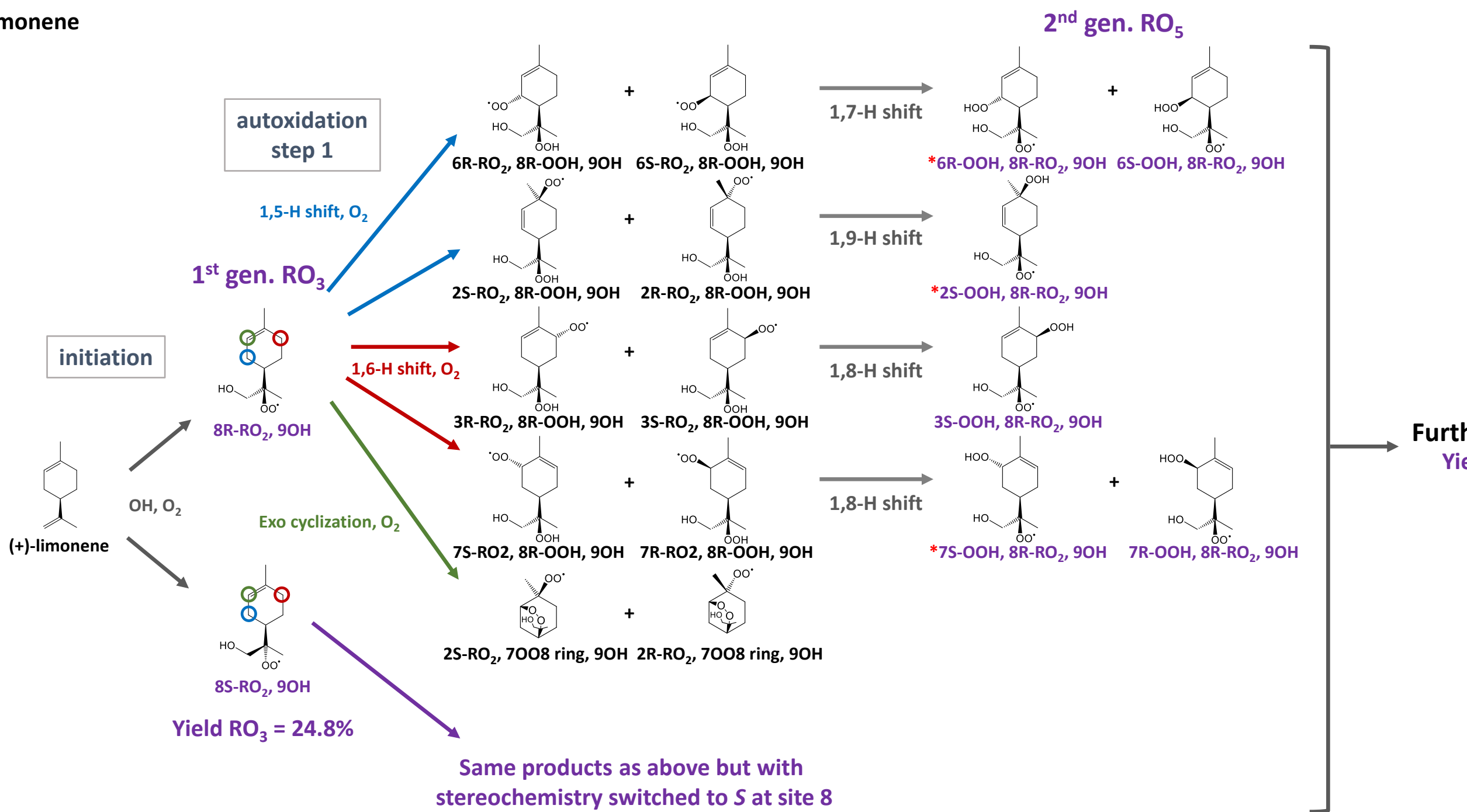
β -pinene



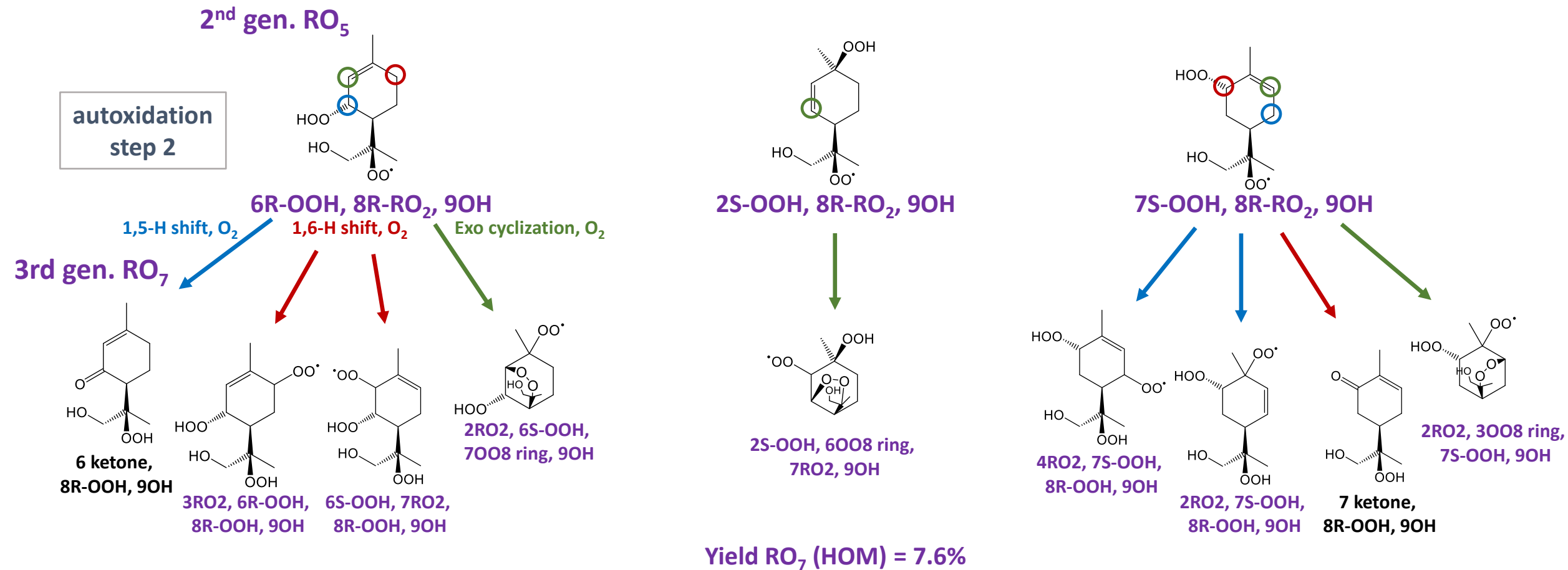
β -pinene

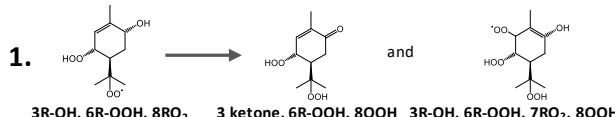
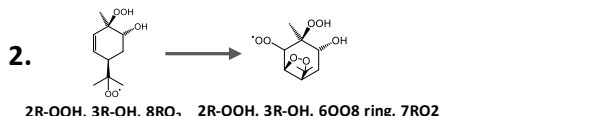
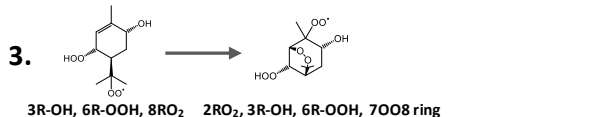
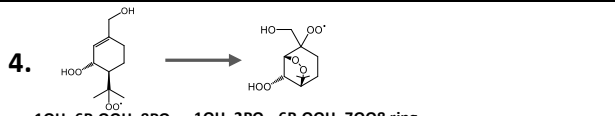
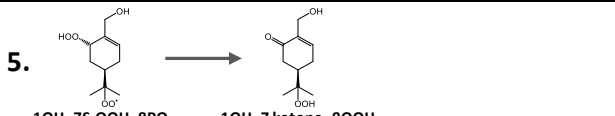
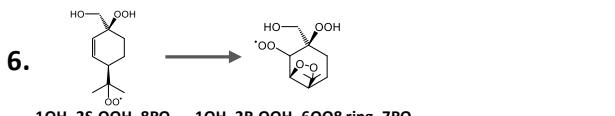
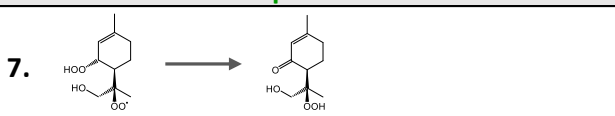
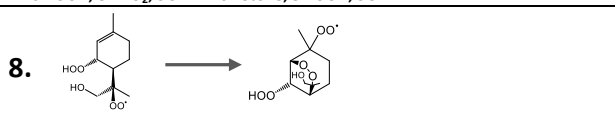
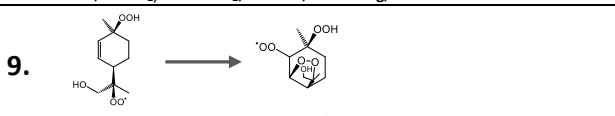


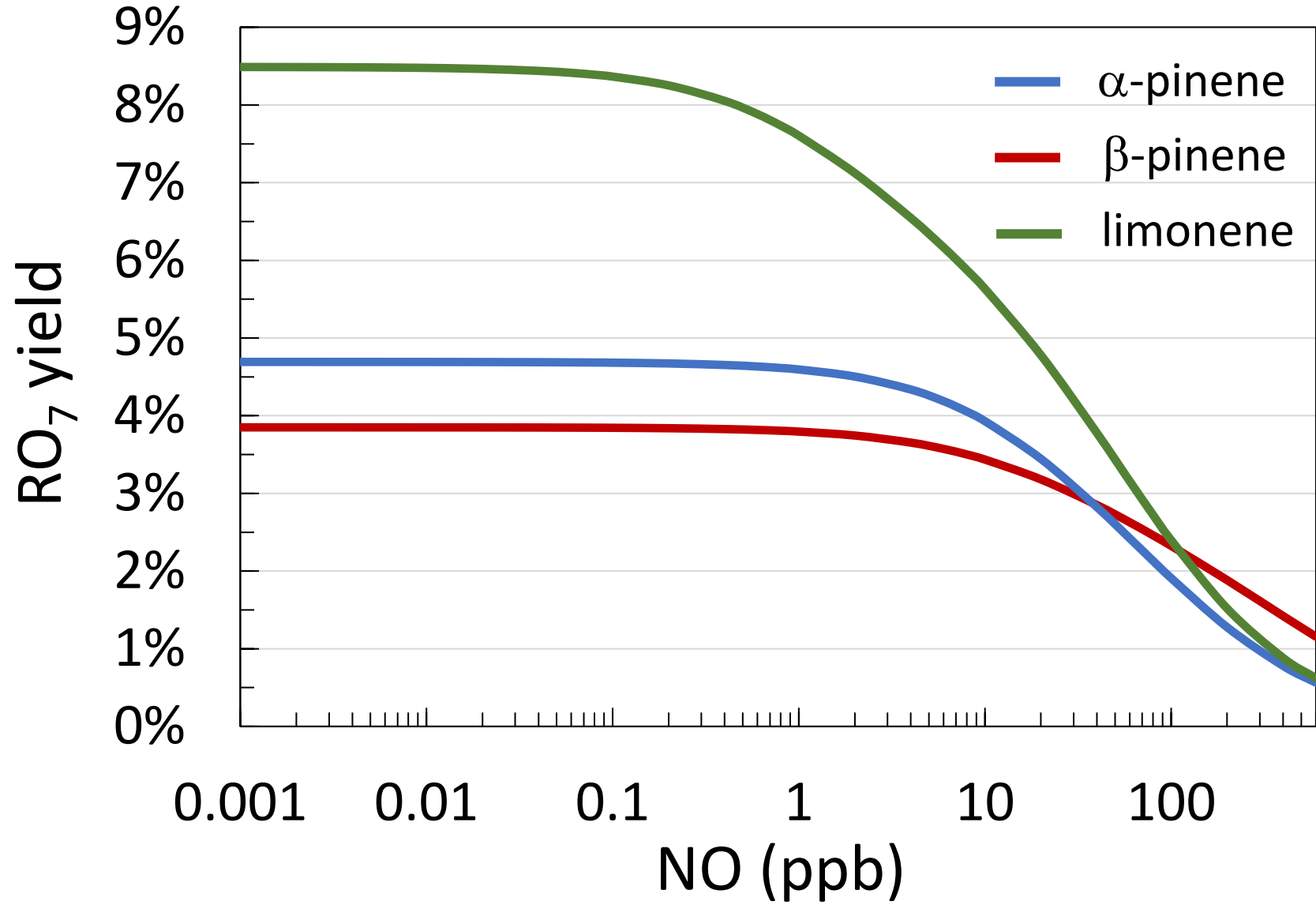
limonene



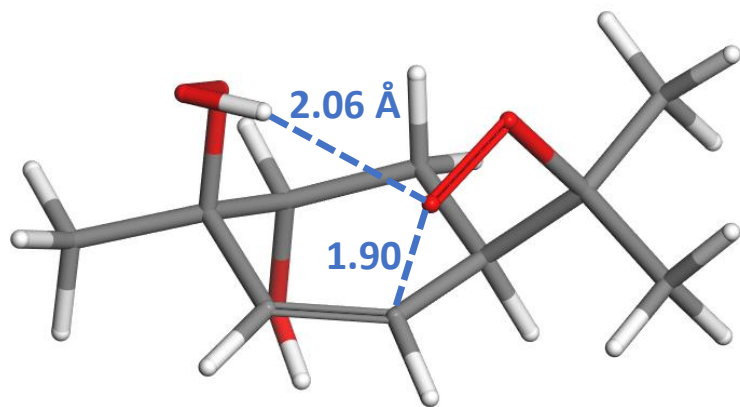
limonene



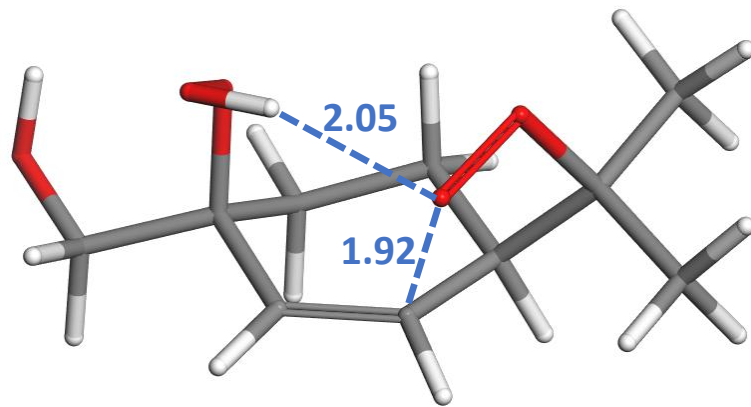
Reaction	Type	ΔG^\ddagger (kcal/mol)	k_{calc} (s ⁻¹)
α-pinene 2nd step autoxidation reactions			
<p>1. </p> <p>3R-OH, 6R-OOH, 8RO₂ 3 ketone, 6R-OOH, 8OOH 3R-OH, 6R-OOH, 7RO₂, 8OOH</p>	1,6-H shift	18.8	2.7E+01
<p>2. </p> <p>2R-OOH, 3R-OH, 8RO₂ 2R-OOH, 3R-OH, 6OO8 ring, 7RO₂</p>	5-exo cyc.	15.7	2.0E+01
<p>3. </p> <p>3R-OH, 6R-OOH, 8RO₂ 2RO₂, 3R-OH, 6R-OOH, 7OO8 ring</p>	6-exo cyc.	15.9	1.4E+01
β-pinene 2nd step autoxidation reactions			
<p>4. </p> <p>1OH, 6R-OOH, 8RO₂ 1OH, 2RO₂, 6R-OOH, 7OO8 ring</p>	6-exo cyc.	14.6	1.2E+02
<p>5. </p> <p>1OH, 7S-OOH, 8RO₂ 1OH, 7 ketone, 8OOH</p>	1,6-H shift	20.1	3.3E+01
<p>6. </p> <p>1OH, 2S-OOH, 8RO₂ 1OH, 2R-OOH, 6OO8 ring, 7RO₂</p>	5-exo cyc.	15.8	1.7E+01
limonene 2nd step autoxidation reactions			
<p>7. </p> <p>6R-OOH, 8R-RO₂, 9OH 6 ketone, 8R-OOH, 9OH</p>	1,5-H shift	20.2	1.3E+01
<p>8. </p> <p>6R-OOH, 8R-RO₂, 9OH 2RO₂, 6S-OOH, 7OO8 ring, 9OH</p>	6-exo cyc.	16.1	9.7E+00
<p>9. </p> <p>2S-OOH, 8R-RO₂, 9OH 2S-OOH, 6OO8 ring, 7RO₂, 9OH</p>	5-exo cyc.	16.2	7.9E+00



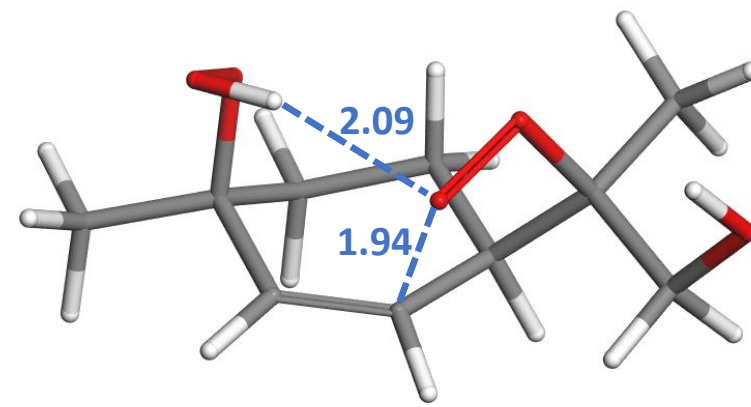
α -pinene



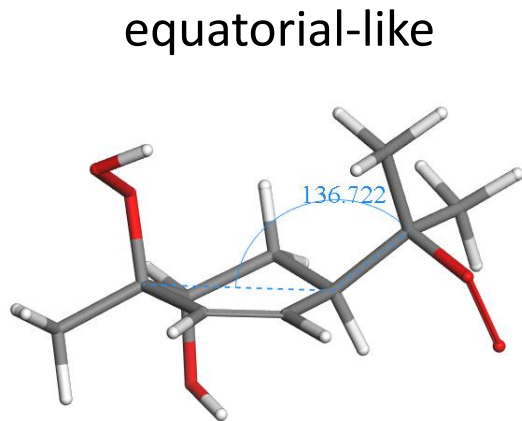
β -pinene



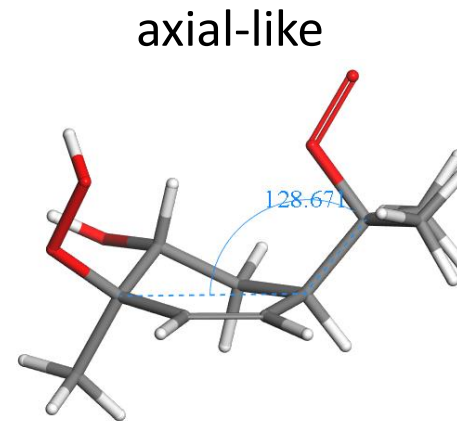
limonene



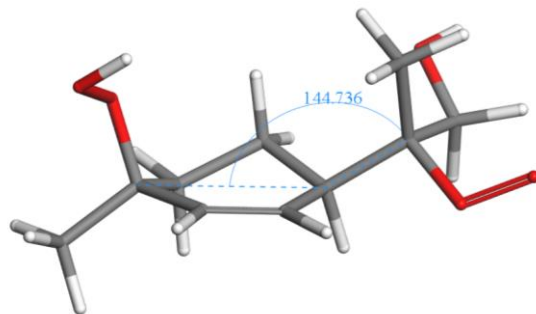
α -pinene
(2R-OOH,3R-OH,8RO₂)



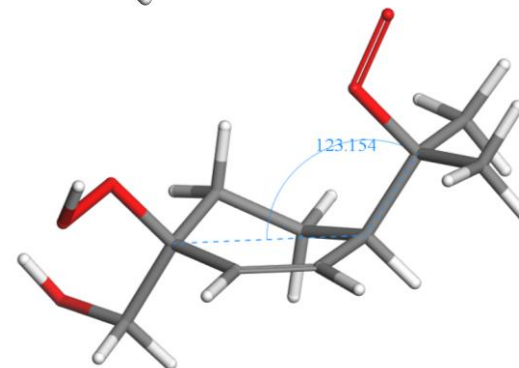
$\Delta G = 2.1$ kcal/mol



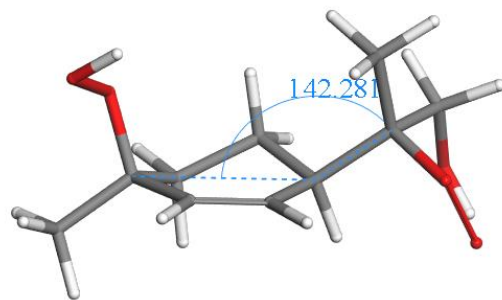
β -pinene
(1OH,2S-OOH,8RO₂)



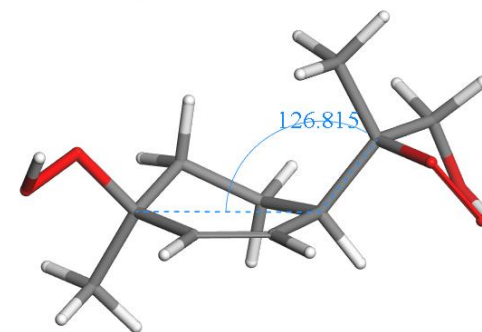
$\Delta G = 2.9$ kcal/mol



limonene
(2S-OOH,8R-RO₂,9OH)



$\Delta G = 2.5$ kcal/mol



TOC Graphic

