

Table S1: Temperatures of maximum desorption with 20 s averaging (in K) and experimental saturation vapor pressures^a of the calibration compounds (PEG6, PEG7 and PEG8).

Compound	run 1	run 2	run 3	p_{sat} (Pa) ^a
$\text{C}_{12}\text{H}_{26}\text{O}_7$	316.82	316.80	317.32	3.05×10^{-5}
$\text{C}_{14}\text{H}_{30}\text{O}_8$	337.99	336.87	337.52	1.29×10^{-6}
$\text{C}_{16}\text{H}_{34}\text{O}_9$	352.07	349.29	356.85	9.20×10^{-8}

^a The experimental saturation vapor pressures were taken from Krieger et al.^{S1}

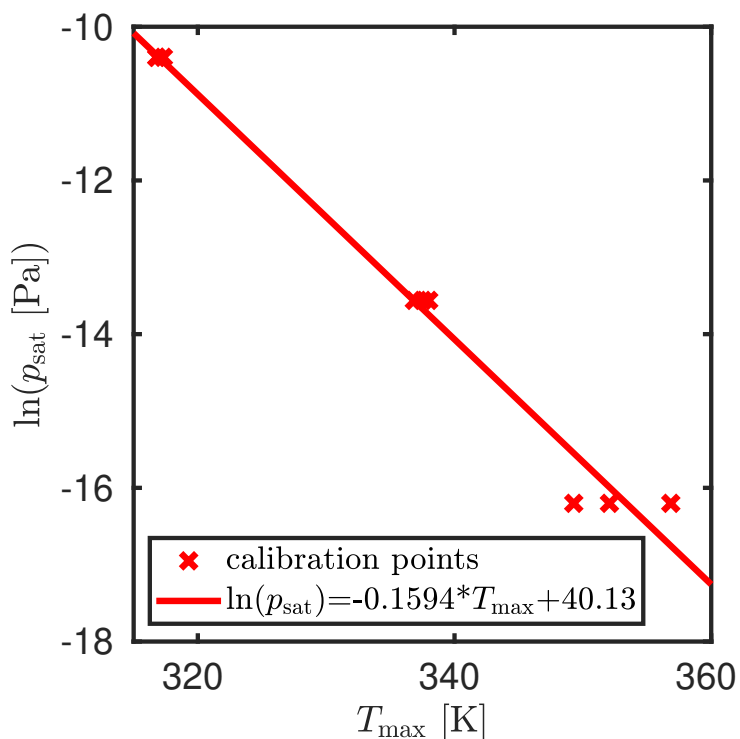


Figure S1: Calibration of the 20 s averaged thermograms at 298.15 K. The compounds used in the calibration are polyethylene glycols (PEG) $\text{C}_{12}\text{H}_{26}\text{O}_7$, $\text{C}_{14}\text{H}_{30}\text{O}_8$ and $\text{C}_{16}\text{H}_{34}\text{O}_9$ (PEG6, PEG7 and PEG8, respectively). The values used in the calibration are shown in Table S1.

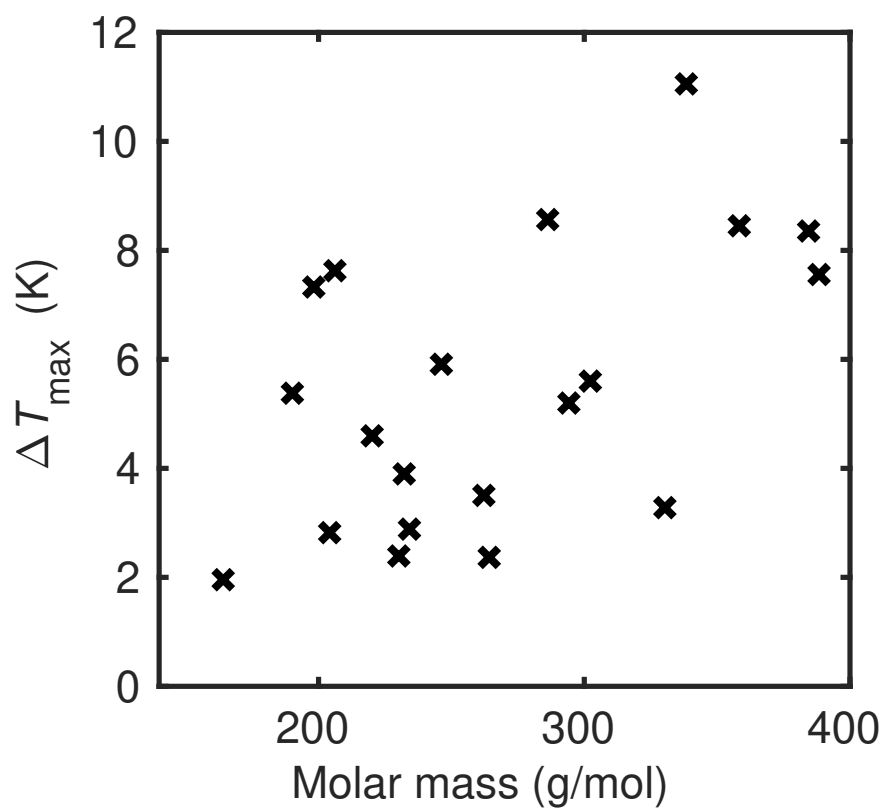


Figure S2: Difference between the highest and lowest T_{\max} values in the 6 measurement cycles as a function of molar mass. Compounds thought to be products of thermal decomposition were not included.

2 S1 Conformer selection

3 To reduce the computational costs, we tested omitting conformers that contain intramolecu-
4 lar H-bonds already after the initial conformer sampling step. All distances between H-bond
5 donors and acceptors were measured in Spartan14.^{S2} We then removed all conformers that
6 contained at least one donor-acceptor distance $< 2.2 \text{ \AA}$. Doing this, we were able to omit
7 up to 98 % of the original conformers before starting density functional theory (DFT) cal-
8 culations using TURBOMOLE.^{S3} The reduction is significant especially in large monomers
9 and dimers that have thousands of unique conformers.

10 In cases, where we did not find conformers containing no intramolecular H-bonds (after
11 COSMO*conf* calculations), a new calculation was performed using the full set of conformers
12 as input to COSMO*conf*. This way all conformers containing a single intramolecular H-bond
13 are included in the initial conformer set.

14 Table S2 shows the number of conformers containing no intramolecular H-bonds we found
15 using two initial conformer sets: one with all conformers found in systematic conformer search
16 ("all") and the other with no conformers that contain intramolecular H-bonds ("0 H-bonds").
17 The same COSMO*conf* template was then used to optimize all conformers in the conformer
18 sets and to remove duplicate conformers. With both initial conformer sets, COSMO*conf*
19 produced a similar number of final conformers containing no intramolecular H-bonds. The
20 largest difference in the saturation vapor pressure in our test calculations was a factor of
21 7.34, indicating that too many conformers were removed from the initial conformer set. For
22 the other molecules, the small differences between the two conformer sets is caused by the
23 removal of conformers with similar chemical potentials, in which different conformers were
24 omitted depending on other conformers in the remaining conformer set.

Table S2: Comparison of saturation vapor pressures (p_{sat}) calculated using all conformers (all) or conformers containing no intramolecular H-bonds (0 H-bonds) as the input conformer set in *COSMOconf*.

	# 0 H-bond conformers		p_{sat} [Pa]		difference
	0 H-bonds	all	0 H-bonds	all	
$\text{C}_4\text{H}_4\text{O}_5$ -iso2	5	6	1.06×10^{-1}	1.05×10^{-1}	1.01
$\text{C}_8\text{H}_{12}\text{O}_6$ -iso4	7	8	7.68×10^{-6}	6.30×10^{-6}	1.22
$\text{C}_{10}\text{H}_{14}\text{O}_8$ -iso2	18	15	1.03×10^{-6}	1.04×10^{-6}	0.99
Isomers from Kurtén et al., ^{S4} calculated using the BP_TZVPD_FINE_19 parametrization					
$\text{C}_{10}\text{H}_{16}\text{O}_9$	> 40	> 40	6.63×10^{-8}	2.26×10^{-8} ^b	2.94
$\text{C}_{10}\text{H}_{16}\text{O}_{10}$	10	10	1.97×10^{-9}	1.97×10^{-9} ^b	1.00
$\text{C}_{20}\text{H}_{30}\text{O}_{10}$ -iso1	> 40	> 40	1.29×10^{-10}	1.76×10^{-11} ^b	7.34
$\text{C}_{20}\text{H}_{30}\text{O}_{10}$ -iso2	> 40	> 40	8.72×10^{-10}	8.74×10^{-10} ^b	1.00

^b Hyttinen et al.^{S5}

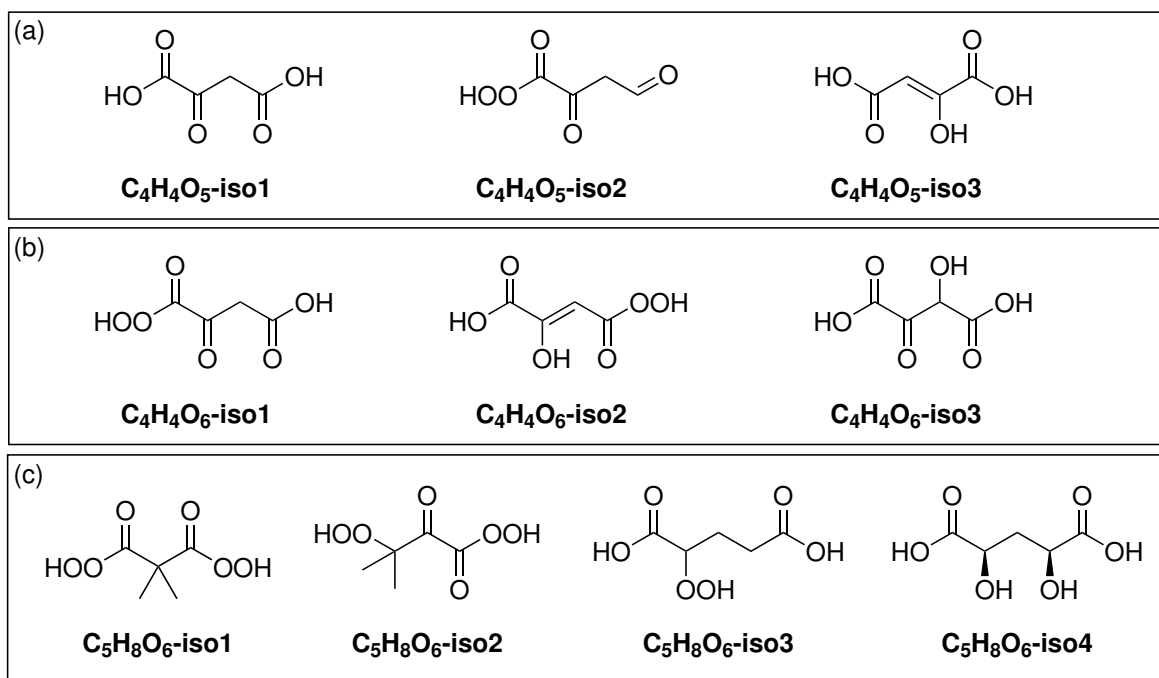


Figure S3: Structures of the studied (a) C₄H₄O₅, (b) C₄H₄O₆ and (c) C₅H₈O₆ isomers.

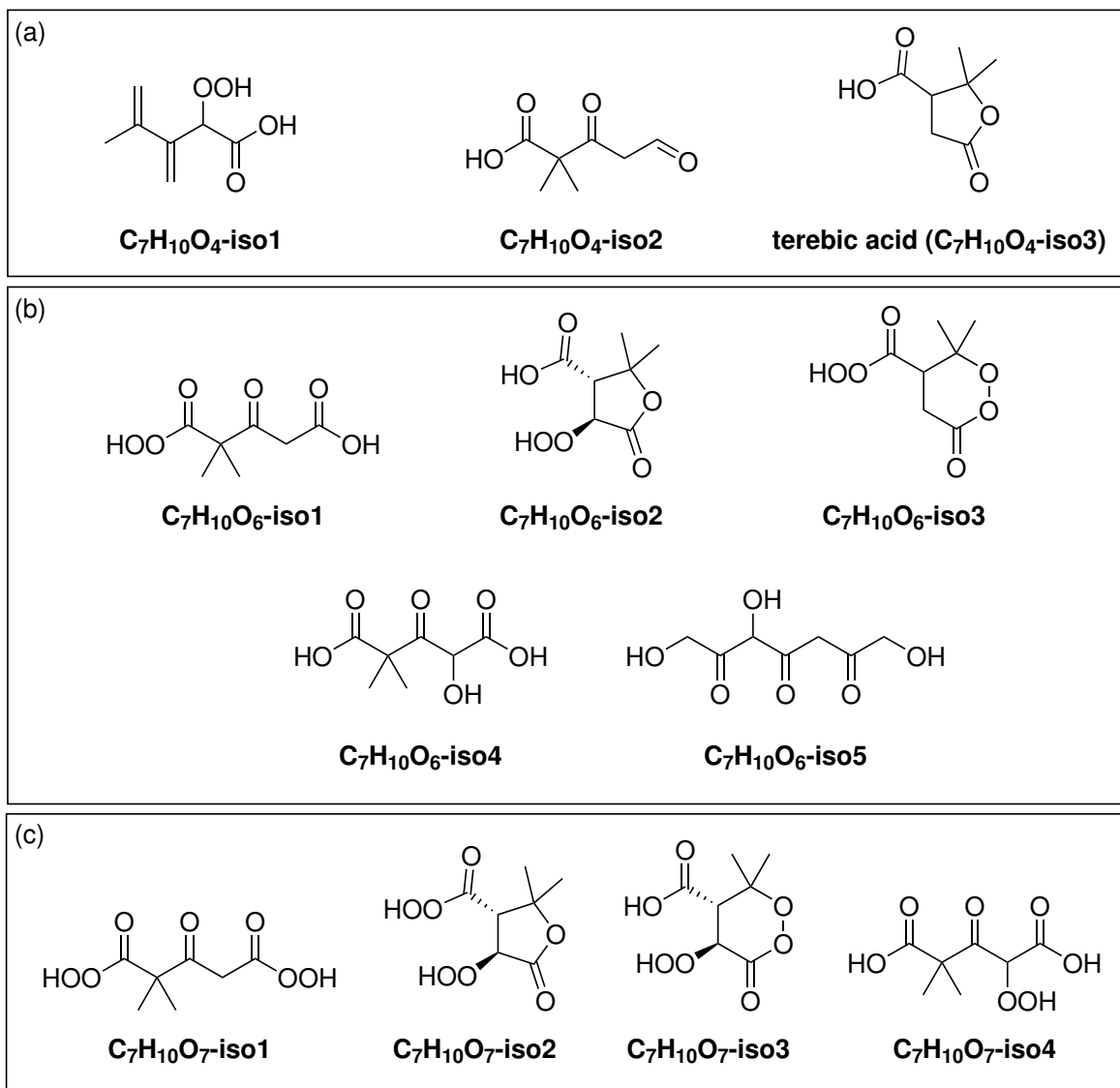


Figure S4: Structures of the studied (a) C₇H₁₀O₄, (b) C₇H₁₀O₆ and (c) C₇H₁₀O₇ isomers. Additional isomers for C₇H₁₀O₄ and C₇H₁₀O₆ are shown in Figures S10a and S10b, respectively, as products of thermal decomposition.

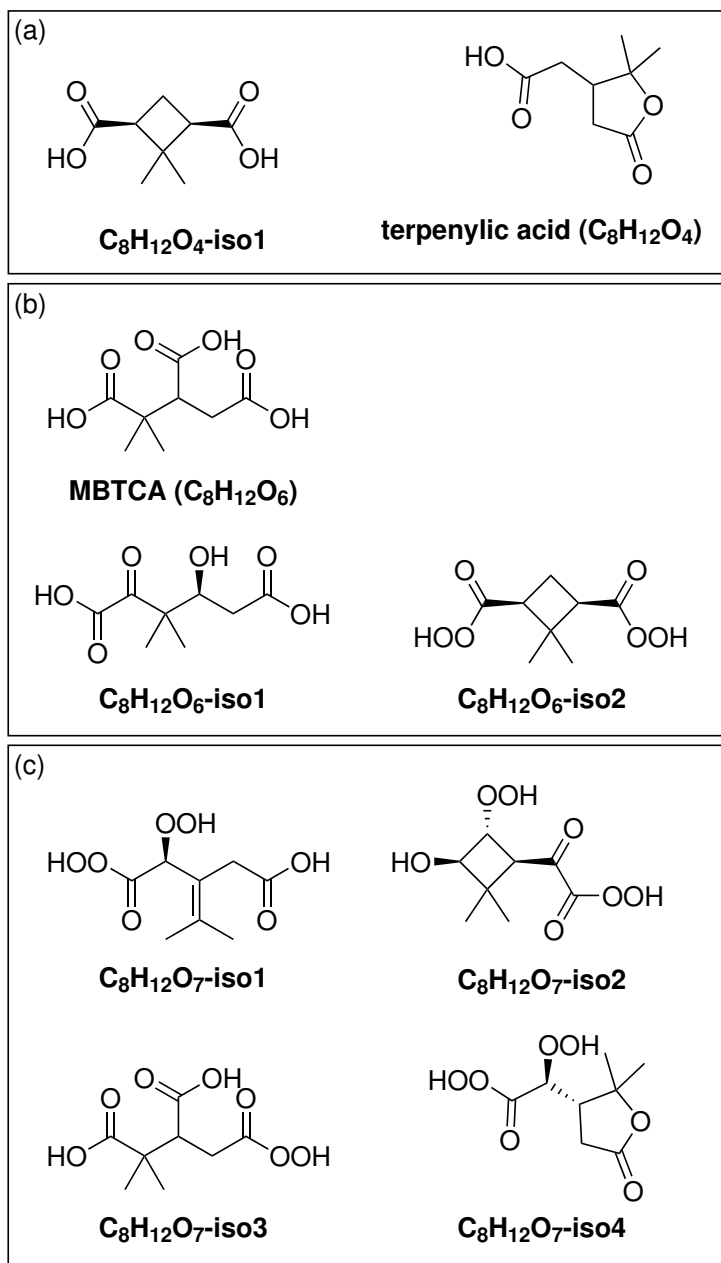


Figure S5: Structures of the studied (a) C₈H₁₂O₄, (b) C₈H₁₂O₆ and (c) C₈H₁₂O₇ isomers. Additional isomers for C₈H₁₂O₄ and C₈H₁₂O₆ are shown in Figures S11a and S11b, respectively, as products of thermal decomposition.

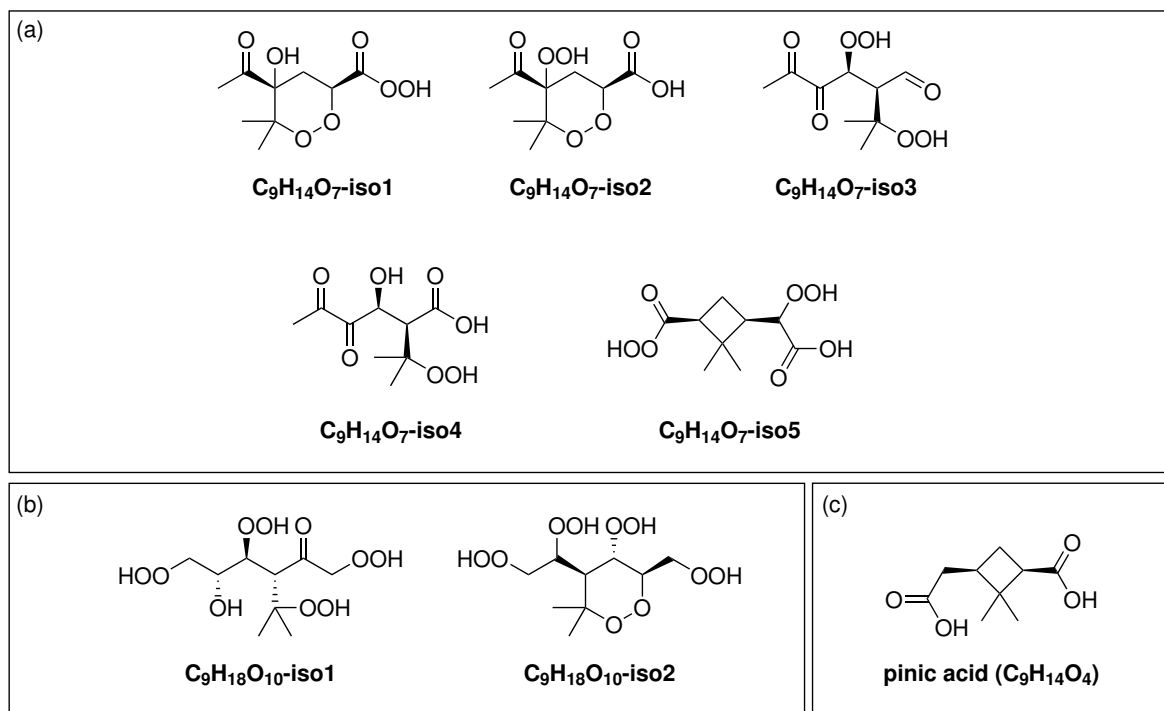


Figure S6: Structures of the studied (a) C₉H₁₄O₇, (b) C₉H₁₈O₁₀ and (c) C₉H₁₄O₄ isomers.

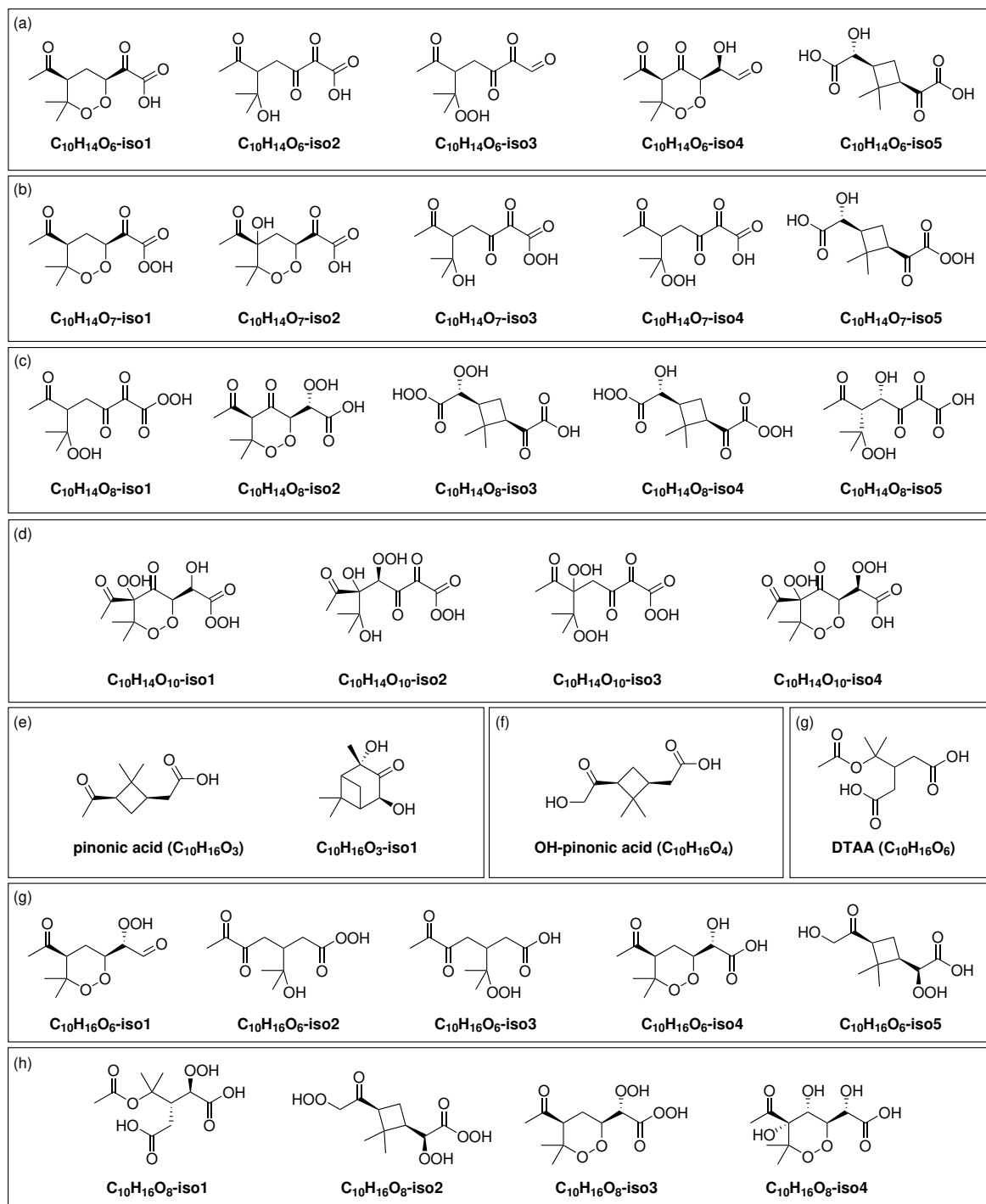


Figure S7: Structures of the studied (a) C₁₀H₁₄O₆, (b) C₁₀H₁₄O₇, (c) C₁₀H₁₄O₈, (d) C₁₀H₁₄O₁₀, (e) C₁₀H₁₆O₃, (f) C₁₀H₁₆O₄, (g) C₁₀H₁₆O₆ and (h) C₁₀H₁₆O₈ isomers.

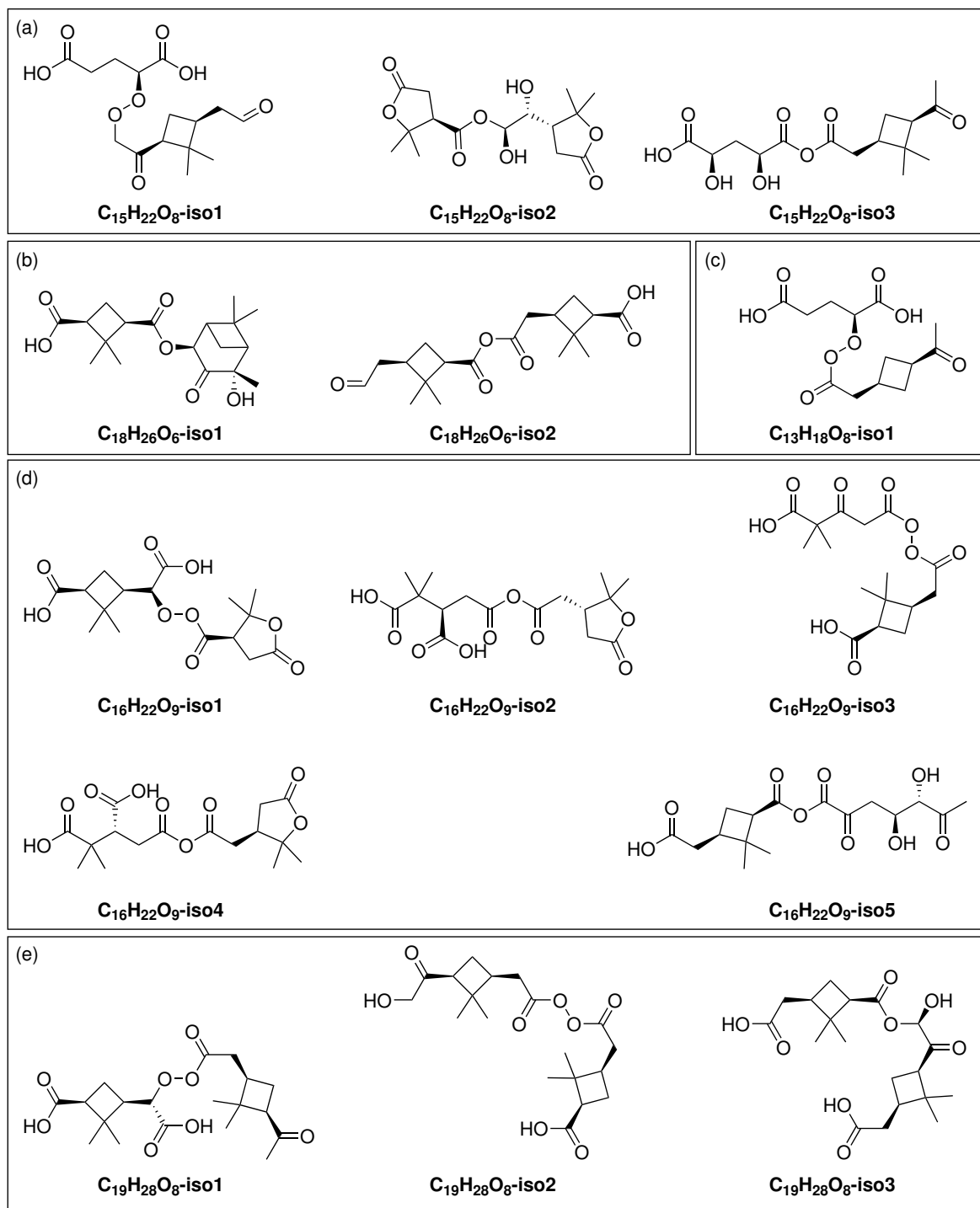


Figure S8: Structures of the studied (a) C₁₅H₂₂O₈, (b) C₁₈H₂₆O₆, (c) C₁₃H₁₈O₈, (d) C₁₆H₂₂O₉ and (e) C₁₉H₂₈O₈ dimer isomers.

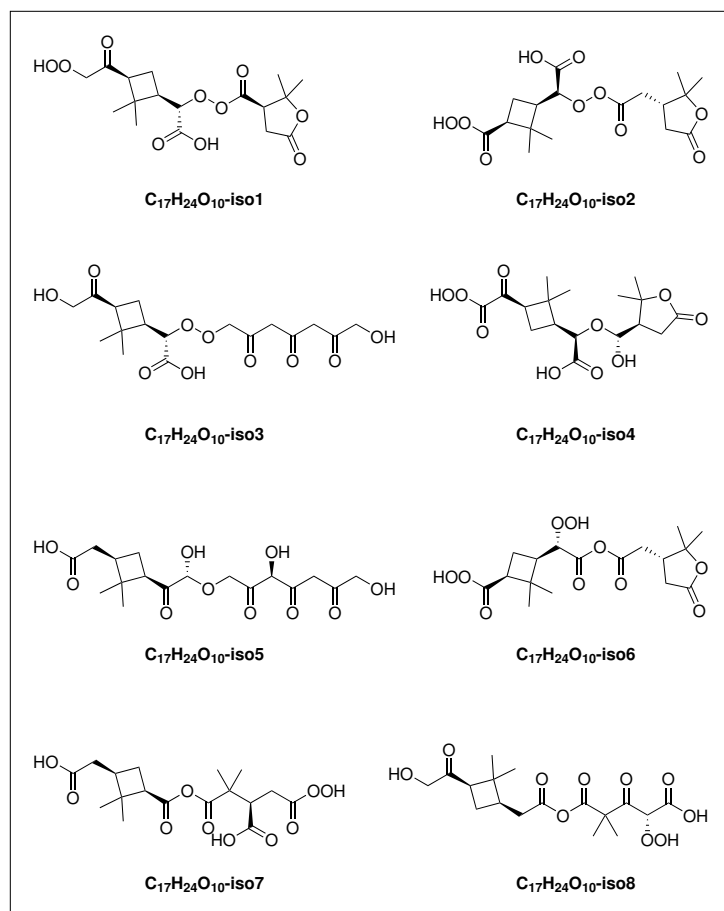


Figure S9: Structures of the studied C₁₇H₂₄O₁₀ dimer isomers.

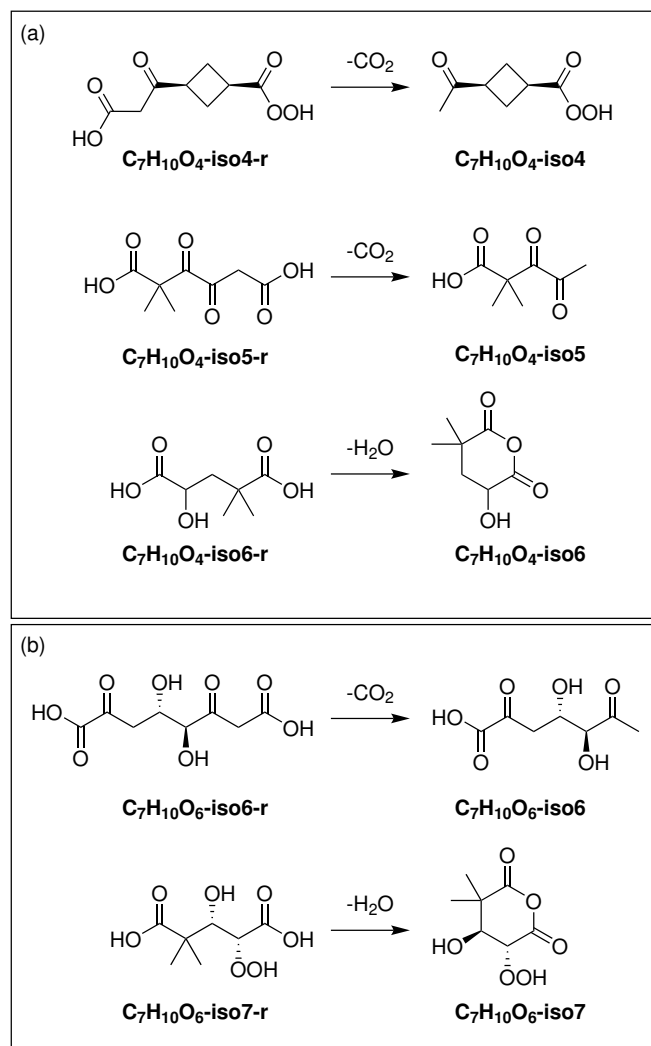


Figure S10: Structures of possible thermal decomposition products of (a) $\text{C}_7\text{H}_{10}\text{O}_4$ and (b) $\text{C}_7\text{H}_{10}\text{O}_6$, and the corresponding reactants of the decomposition reactions. Note that the reactants (labeled with "-r") have different elemental compositions than indicated by their names.

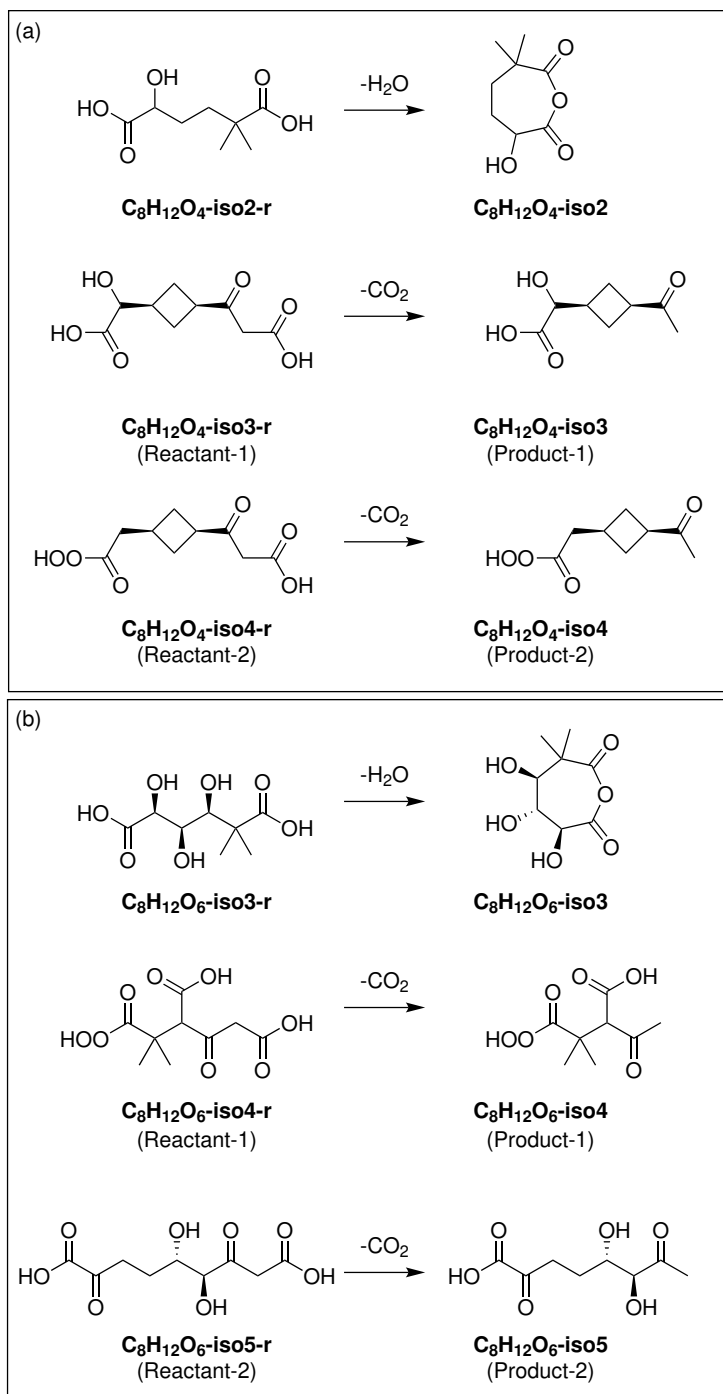


Figure S11: Structures of possible thermal decomposition products of (a) $\text{C}_8\text{H}_{12}\text{O}_4$ and (b) $\text{C}_8\text{H}_{12}\text{O}_6$, and the corresponding reactants of the decomposition reactions. Note that the reactants (labeled with "-r") have different elemental compositions than indicated by their names.

Table S3: Monomers that form the studied dimer isomers.

Monomers		Dimer
$C_5H_8O_6 + C_8H_{12}O_4$	$\xrightarrow{-2OH}$	$C_{13}H_{18}O_8$ -iso1
$C_5H_8O_6 + C_{10}H_{16}O_4$	$\xrightarrow{-2OH}$	$C_{15}H_{22}O_8$ -iso1
$C_7H_{10}O_4 + C_8H_{12}O_4$	\rightarrow	$C_{15}H_{22}O_8$ -iso2
$C_5H_8O_6 + C_{10}H_{16}O_3$	$\xrightarrow{-H_2O}$	$C_{15}H_{22}O_8$ -iso3
$C_8H_{12}O_4 + C_{10}H_{16}O_3$	$\xrightarrow{-H_2O}$	$C_{18}H_{26}O_6$ -iso1
$C_9H_{14}O_4 + C_9H_{14}O_4$	$\xrightarrow{-2OH}$	$C_{18}H_{26}O_6$ -iso2
$C_7H_{10}O_4 + C_9H_{14}O_7$	$\xrightarrow{-2OH}$	$C_{16}H_{22}O_9$ -iso1
$C_8H_{12}O_4 + C_7H_{10}O_7$	$\xrightarrow{-2OH}$	$C_{16}H_{22}O_9$ -iso2
$C_9H_{14}O_4 + C_7H_{10}O_7$	$\xrightarrow{-2OH}$	$C_{16}H_{22}O_9$ -iso3
$C_8H_{12}O_4 + C_8H_{12}O_6$	$\xrightarrow{-H_2O}$	$C_{16}H_{22}O_9$ -iso4
$C_9H_{14}O_4 + C_7H_{10}O_6$	$\xrightarrow{-H_2O}$	$C_{16}H_{22}O_9$ -iso5
$C_{10}H_{16}O_3 + C_9H_{14}O_7$	$\xrightarrow{-2OH}$	$C_{19}H_{28}O_8$ -iso1
$C_9H_{14}O_4 + C_{10}H_{16}O_6$	$\xrightarrow{-2OH}$	$C_{19}H_{28}O_8$ -iso2
$C_9H_{14}O_4 + C_{10}H_{14}O_4$	\rightarrow	$C_{19}H_{28}O_8$ -iso3
$C_7H_{10}O_4 + C_{10}H_{16}O_8$	$\xrightarrow{-2OH}$	$C_{17}H_{24}O_{10}$ -iso1
$C_8H_{12}O_4 + C_9H_{14}O_8$	$\xrightarrow{-2OH}$	$C_{17}H_{24}O_{10}$ -iso2
$C_7H_{10}O_6 + C_{10}H_{16}O_6$	$\xrightarrow{-2OH}$	$C_{17}H_{24}O_{10}$ -iso3
$C_7H_{10}O_4 + C_{10}H_{14}O_6$	\rightarrow	$C_{17}H_{24}O_{10}$ -iso4
$C_7H_{10}O_6 + C_{10}H_{14}O_4$	\rightarrow	$C_{17}H_{24}O_{10}$ -iso5
$C_8H_{12}O_4 + C_9H_{14}O_7$	$\xrightarrow{-H_2O}$	$C_{17}H_{24}O_{10}$ -iso6
$C_9H_{14}O_4 + C_8H_{12}O_7$	$\xrightarrow{-H_2O}$	$C_{17}H_{24}O_{10}$ -iso7
$C_{10}H_{16}O_4 + C_7H_{10}O_7$	$\xrightarrow{-H_2O}$	$C_{17}H_{24}O_{10}$ -iso8

Table S4: COSMO*therm*-estimated saturation vapor pressures (p_{sat}) and enthalpies of vaporization (ΔH_{vap}) of all studied monomers, dimers and reactants of thermal decomposition at 298.15 K.

Molecule name	Molar mass [g/mol]	p_{sat} [Pa]	ΔH_{vap} [kJ/mol]
Monomers			
C ₄ H ₄ O ₅ -iso1	132.07	6.64×10^{-2}	84.45
C ₄ H ₄ O ₅ -iso2	132.07	1.06×10^{-1}	83.11
C ₄ H ₄ O ₅ -iso3	132.07	3.02×10^{-2}	91.57
C ₄ H ₄ O ₆ -iso1	148.07	1.87×10^{-3}	101.47
C ₄ H ₄ O ₆ -iso2	148.07	5.47×10^{-3}	97.32
C ₄ H ₄ O ₆ -iso3	148.07	1.39×10^{-3}	102.18
C ₇ H ₁₀ O ₄ -iso1	158.15	1.32×10^{-2}	95.31
C ₇ H ₁₀ O ₄ -iso2	158.15	1.46×10^{-1}	83.55
terebic acid (C ₇ H ₁₀ O ₄ -iso3)	158.15	3.00×10^{-3}	93.99
C ₇ H ₁₀ O ₄ -iso4	158.15	1.55	68.17
C ₇ H ₁₀ O ₄ -iso5	158.15	6.54×10^{-1}	77.52
C ₇ H ₁₀ O ₄ -iso6	158.15	3.04×10^{-1}	79.24
C ₅ H ₈ O ₆ -iso1	164.11	1.58	71.20
C ₅ H ₈ O ₆ -iso2	164.11	2.29×10^{-2}	90.90
C ₅ H ₈ O ₆ -iso3	164.11	3.85×10^{-6}	127.28
C ₅ H ₈ O ₆ -iso4	164.11	2.86×10^{-7}	139.38
C ₈ H ₁₂ O ₄ -iso1	172.18	9.32×10^{-4}	104.54
C ₈ H ₁₂ O ₄ -iso2	172.18	1.23×10^{-2}	88.26
C ₈ H ₁₂ O ₄ -iso3	172.18	5.49×10^{-4}	102.45
C ₈ H ₁₂ O ₄ -iso4	172.18	1.84×10^{-3}	98.45
terpenylic acid (C ₈ H ₁₂ O ₄)	172.18	1.72×10^{-4}	104.55
C ₁₀ H ₁₆ O ₃ -iso1	184.23	2.06×10^{-1}	87.00

Table S4 – continued from previous page

Molecule name	Molar mass [g/mol]	p_{sat} [Pa]	ΔH_{vap} [kJ/mol]
pinonic acid ($\text{C}_{10}\text{H}_{16}\text{O}_3$)	184.23	3.86×10^{-3}	95.55
$\text{C}_7\text{H}_{10}\text{O}_6$ -iso1	190.15	1.40×10^{-4}	111.13
$\text{C}_7\text{H}_{10}\text{O}_6$ -iso2	190.15	1.30×10^{-4}	110.73
$\text{C}_7\text{H}_{10}\text{O}_6$ -iso3	190.15	3.19×10^{-2}	82.84
$\text{C}_7\text{H}_{10}\text{O}_6$ -iso4	190.15	6.09×10^{-6}	124.93
$\text{C}_7\text{H}_{10}\text{O}_6$ -iso5	190.15	1.27×10^{-7}	136.70
$\text{C}_7\text{H}_{10}\text{O}_6$ -iso6	190.15	7.29×10^{-7}	132.58
$\text{C}_7\text{H}_{10}\text{O}_6$ -iso7	190.15	6.05×10^{-3}	93.22
OH-pinonic acid ($\text{C}_{10}\text{H}_{16}\text{O}_4$)	200.23	1.01×10^{-5}	122.23
$\text{C}_8\text{H}_{12}\text{O}_6$ -iso2	204.17	7.48×10^{-3}	92.88
$\text{C}_8\text{H}_{12}\text{O}_6$ -iso3	204.17	5.48×10^{-6}	124.92
$\text{C}_8\text{H}_{12}\text{O}_6$ -iso4	204.17	6.30×10^{-6}	120.62
MBTCA ($\text{C}_8\text{H}_{12}\text{O}_6$)	204.17	3.20×10^{-7}	138.42
$\text{C}_7\text{H}_{10}\text{O}_7$ -iso1	206.15	1.83×10^{-6}	127.84
$\text{C}_7\text{H}_{10}\text{O}_7$ -iso2	206.15	2.03×10^{-4}	108.90
$\text{C}_7\text{H}_{10}\text{O}_7$ -iso3	206.15	6.97×10^{-3}	94.64
$\text{C}_7\text{H}_{10}\text{O}_7$ -iso4	206.15	8.43×10^{-6}	125.11
$\text{C}_8\text{H}_{12}\text{O}_7$ -iso1	220.17	2.65×10^{-8}	145.36
$\text{C}_8\text{H}_{12}\text{O}_7$ -iso2	220.17	7.27×10^{-7}	137.07
$\text{C}_8\text{H}_{12}\text{O}_7$ -iso3	220.17	8.30×10^{-8}	142.88
$\text{C}_8\text{H}_{12}\text{O}_7$ -iso4	220.17	2.22×10^{-6}	127.22
$\text{C}_{10}\text{H}_{14}\text{O}_6$ -iso1	230.21	2.47×10^{-6}	123.40
$\text{C}_{10}\text{H}_{14}\text{O}_6$ -iso2	230.21	1.06×10^{-5}	122.16
$\text{C}_{10}\text{H}_{14}\text{O}_6$ -iso3	230.21	1.65×10^{-4}	109.08

Table S4 – continued from previous page

Molecule name	Molar mass [g/mol]	p_{sat} [Pa]	ΔH_{vap} [kJ/mol]
C ₁₀ H ₁₄ O ₆ -iso4	230.21	6.12×10^{-3}	93.31
C ₁₀ H ₁₄ O ₆ -iso5	230.21	6.77×10^{-8}	142.53
C ₁₀ H ₁₆ O ₆ -iso1	232.23	4.79×10^{-5}	114.46
C ₁₀ H ₁₆ O ₆ -iso2	232.23	7.11×10^{-6} (3.6×10^{-2} i)	125.84
C ₁₀ H ₁₆ O ₆ -iso3	232.23	1.24×10^{-5} (9.3×10^{-4} i)	122.44
C ₁₀ H ₁₆ O ₆ -iso4	232.23	4.25×10^{-6}	126.26
C ₁₀ H ₁₆ O ₆ -iso5	232.23	7.38×10^{-9}	152.48
DTAA (C ₁₀ H ₁₆ O ₆)	232.23	2.72×10^{-6}	128.78
C ₉ H ₁₄ O ₇ -iso1	234.20	3.68×10^{-7}	134.89
C ₉ H ₁₄ O ₇ -iso2	234.20	4.16×10^{-6}	126.52
C ₉ H ₁₄ O ₇ -iso3	234.20	1.16×10^{-5}	121.45
C ₉ H ₁₄ O ₇ -iso4	234.20	7.86×10^{-7}	134.75
C ₉ H ₁₄ O ₇ -iso5	234.20	3.21×10^{-8}	145.82
C ₁₀ H ₁₄ O ₇ -iso1	246.21	1.99×10^{-6}	127.51
C ₁₀ H ₁₄ O ₇ -iso2	246.21	4.14×10^{-7}	138.05
C ₁₀ H ₁₄ O ₇ -iso3	246.21	2.85×10^{-6}	127.50
C ₁₀ H ₁₄ O ₇ -iso4	246.21	2.28×10^{-6}	128.28
C ₁₀ H ₁₄ O ₇ -iso5	246.21	3.36×10^{-8}	148.67
C ₁₀ H ₁₄ O ₈ -iso1	262.21	6.29×10^{-7}	133.04
C ₁₀ H ₁₄ O ₈ -iso2	262.21	1.03×10^{-6}	132.94
C ₁₀ H ₁₄ O ₈ -iso3	262.21	4.60×10^{-8}	145.63
C ₁₀ H ₁₄ O ₈ -iso4	262.21	1.04×10^{-8}	150.49
C ₁₀ H ₁₄ O ₈ -iso5	262.21	2.69×10^{-8}	148.43

ⁱKurtén et al.^{S4}

Table S4 – continued from previous page

Molecule name	Molar mass [g/mol]	p_{sat} [Pa]	ΔH_{vap} [kJ/mol]
$\text{C}_{10}\text{H}_{16}\text{O}_8\text{-iso1}$	264.22	4.32×10^{-8}	149.32
$\text{C}_{10}\text{H}_{16}\text{O}_8\text{-iso2}$	264.22	1.94×10^{-8}	149.88
$\text{C}_{10}\text{H}_{16}\text{O}_8\text{-iso3}$	264.22	1.62×10^{-7}	138.41
$\text{C}_{10}\text{H}_{16}\text{O}_8\text{-iso4}$	264.22	4.46×10^{-8}	148.82
$\text{C}_9\text{H}_{18}\text{O}_{10}\text{-iso1}$	286.23	1.64×10^{-11}	182.20
$\text{C}_9\text{H}_{18}\text{O}_{10}\text{-iso2}$	286.23	2.43×10^{-9}	159.49
$\text{C}_{10}\text{H}_{14}\text{O}_{10}\text{-iso1}$	294.21	1.63×10^{-10}	167.55
$\text{C}_{10}\text{H}_{14}\text{O}_{10}\text{-iso2}$	294.21	1.81×10^{-8}	151.20
$\text{C}_{10}\text{H}_{14}\text{O}_{10}\text{-iso3}$	294.21	1.19×10^{-8}	152.74
$\text{C}_{10}\text{H}_{14}\text{O}_{10}\text{-iso4}$	294.21	1.29×10^{-9}	159.26
Thermal decomposition reactants			
$\text{C}_7\text{H}_{10}\text{O}_4\text{-iso4-r}$	202.16	5.47×10^{-7}	129.96
$\text{C}_7\text{H}_{10}\text{O}_4\text{-iso5-r}$	202.16	1.74×10^{-4}	113.21
$\text{C}_7\text{H}_{10}\text{O}_4\text{-iso6-r}$	176.16	2.70×10^{-5}	121.40
$\text{C}_8\text{H}_{12}\text{O}_4\text{-iso2-r}$	190.19	5.54×10^{-6}	128.99
$\text{C}_8\text{H}_{12}\text{O}_4\text{-iso3-r}$	216.18	2.28×10^{-9}	154.76
$\text{C}_8\text{H}_{12}\text{O}_4\text{-iso4-r}$	216.18	3.32×10^{-7}	134.07
$\text{C}_7\text{H}_{10}\text{O}_6\text{-iso6-r}$	234.16	2.52×10^{-11}	169.09
$\text{C}_7\text{H}_{10}\text{O}_6\text{-iso7-r}$	208.16	5.40×10^{-8}	146.36
$\text{C}_8\text{H}_{12}\text{O}_6\text{-iso3-r}$	222.19	1.40×10^{-11}	177.75
$\text{C}_8\text{H}_{12}\text{O}_6\text{-iso4-r}$	248.18	3.28×10^{-11}	169.43
No experimental p_{sat}			
pinic acid ($\text{C}_9\text{H}_{14}\text{O}_4$)	186.20	2.57×10^{-4}	109.58
Dimers			

Table S4 – continued from previous page

Molecule name	Molar mass [g/mol]	p_{sat} [Pa]	ΔH_{vap} [kJ/mol]
C ₁₃ H ₁₈ O ₈ -iso1	302.27	1.87×10^{-10}	167.55
C ₁₅ H ₂₂ O ₈ -iso1	330.32	2.06×10^{-11}	175.86
C ₁₅ H ₂₂ O ₈ -iso2	330.32	1.27×10^{-12}	181.47
C ₁₅ H ₂₂ O ₈ -iso3	330.32	2.42×10^{-11}	178.93
C ₁₆ H ₂₂ O ₉ -iso1	358.33	9.15×10^{-12}	180.50
C ₁₆ H ₂₂ O ₉ -iso2	358.33	4.32×10^{-13}	192.59
C ₁₆ H ₂₂ O ₉ -iso3	358.33	1.10×10^{-9}	166.08
C ₁₆ H ₂₂ O ₉ -iso4	358.33	5.03×10^{-13}	191.80
C ₁₆ H ₂₂ O ₉ -iso5	358.33	9.20×10^{-12}	185.72
C ₁₇ H ₂₄ O ₁₀ -iso1	388.36	3.12×10^{-13}	190.29
C ₁₇ H ₂₄ O ₁₀ -iso2	388.36	3.96×10^{-14}	200.56
C ₁₇ H ₂₄ O ₁₀ -iso3	388.36	4.25×10^{-14}	208.97
C ₁₇ H ₂₄ O ₁₀ -iso4	388.36	3.93×10^{-15}	210.91
C ₁₇ H ₂₄ O ₁₀ -iso5	388.36	2.17×10^{-14}	213.43
C ₁₇ H ₂₄ O ₁₀ -iso6	388.36	5.27×10^{-13}	190.36
C ₁₇ H ₂₄ O ₁₀ -iso7	388.36	5.77×10^{-13}	194.38
C ₁₇ H ₂₄ O ₁₀ -iso8	388.36	8.56×10^{-13}	195.08
C ₁₈ H ₂₆ O ₆ -iso1	338.39	4.08×10^{-7}	141.43
C ₁₈ H ₂₆ O ₆ -iso2	338.39	1.19×10^{-7}	140.03
C ₁₉ H ₂₈ O ₈ -iso1	384.41	5.14×10^{-12}	186.15
C ₁₉ H ₂₈ O ₈ -iso2	384.41	2.17×10^{-10}	174.36
C ₁₉ H ₂₈ O ₈ -iso3	384.41	3.26×10^{-12}	189.87

Table S5: Experimental T_{\max} values from 6 subsequent thermal desorptions in Kelvin.

compound	cycle 2	cycle 3	cycle 4	cycle 5	cycle 6	cycle 7
$C_4H_4O_5$	343.74	348.67	346.32	351.78	345.86	354.61
$C_4H_4O_6$	448.78	449.11	448.40	447.60	447.66	442.00
$C_7H_{10}O_4$	344.74	346.32	346.32	348.36	348.18	348.97
$C_5H_8O_6$	350.75	351.33	351.33	352.49	352.30	352.71
$C_9H_{12}O_3$	444.53	444.26	446.58	438.11	441.76	-
$C_8H_{12}O_4$	350.45	353.98	352.82	352.49	351.98	355.35
$C_{10}H_{16}O_3$	327.84	325.69	327.82	325.16	326.01	325.00
$C_9H_{14}O_4$	348.30	344.93	344.93	346.53	-	-
$C_7H_{10}O_6$	346.64	350.17	350.03	351.98	348.66	352.02
$C_{10}H_{14}O_4$	388.44	393.09	393.09	394.35	391.85	387.02
$C_8H_{12}O_6$	357.10	358.71	358.71	359.92	359.75	359.76
$C_7H_{10}O_7$	353.35	354.00	354.00	356.04	348.41	354.77
$C_8H_{12}O_7$	346.64	349.08	350.58	348.36	350.36	351.24
$C_{10}H_{14}O_6$	358.33	357.11	357.06	356.04	355.94	356.66
$C_{10}H_{16}O_6$	335.45	335.05	335.84	336.12	333.00	332.22
$C_9H_{14}O_7$	358.33	357.74	360.61	360.62	359.56	360.31
$C_{10}H_{14}O_7$	350.45	353.60	353.98	355.68	355.36	356.36
$C_{10}H_{14}O_8$	350.45	350.17	350.17	352.49	352.70	353.67
$C_{10}H_{16}O_8$	362.06	363.58	364.43	363.97	362.50	362.81
$C_9H_{18}O_{10}$	370.09	375.04	375.04	375.90	372.43	378.66
$C_{10}H_{14}O_{10}$	362.86	365.65	365.92	368.06	364.73	364.16
$C_{13}H_{18}O_8$	390.00	391.69	391.69	392.00	388.10	386.40
$C_{15}H_{22}O_8$	383.11	385.54	385.05	383.94	383.30	382.26
$C_{18}H_{26}O_6$	363.16	365.96	368.19	374.22	368.89	371.33
$C_{16}H_{22}O_9$	393.99	393.61	393.61	395.00	392.30	386.55
$C_{19}H_{28}O_8$	377.94	386.30	385.54	380.06	381.45	-
$C_{17}H_{24}O_{10}$	390.00	397.56	394.53	-	-	-
$C_{20}H_{34}O_{10}$	379.96	385.54	385.54	383.94	387.95	382.36

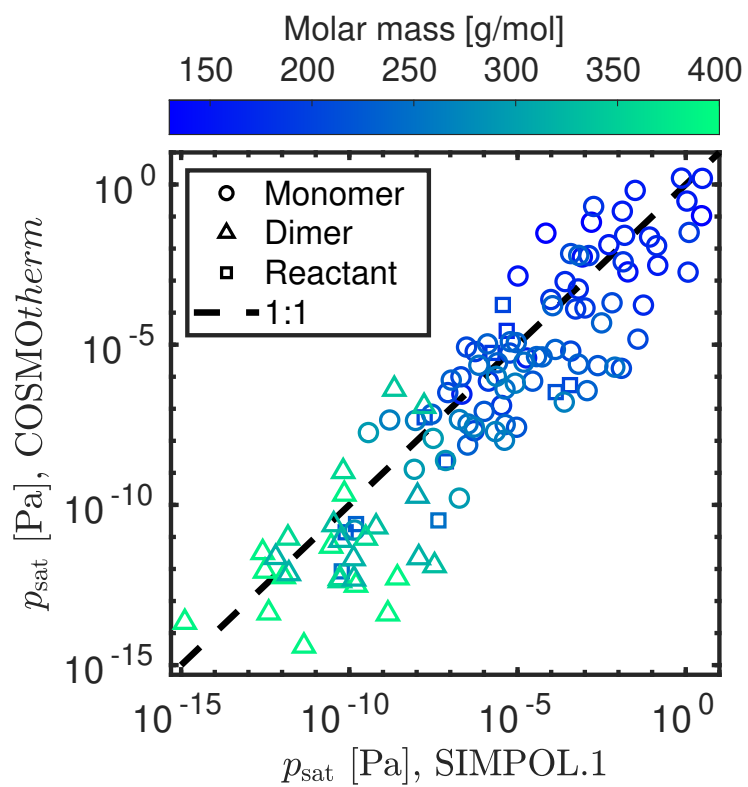


Figure S12: Saturation vapor pressures of all studied monomers, dimers and thermal decomposition reactants estimated using COSMOTHERM and SIMPOL.1 at 298.15K.

25 S2 The effect of dimer formation on COSMO $therm$ sat- 26 uration vapor pressures

27 The size-dependence of S in equation 4 was tested using polyethylene glycol (PEG; $H(OC_2H_4)_mOH$)
28 molecules with $m=2-8$ (see Figure S13). We see that S is clearly higher when the p_{sat} value
29 of the PEG is estimated using PEG1 than using only PEG2-PEG7. This result is likely
30 caused by the relatively low COSMO $therm$ -estimated p_{sat} of PEG1 (if a logarithmic size
31 dependence is assumed for the p_{sat} of the PEG series). No clear correlation is seen between
32 S and the monomer size (PEG or α -pinene-derived monomers) with the exception of PEG1
33 (see Figure S13). The SIMPOL.1 group-contribution method predicts $S = 6.5 \times 10^{-4}$ for all
34 PEG dimerization reactions.

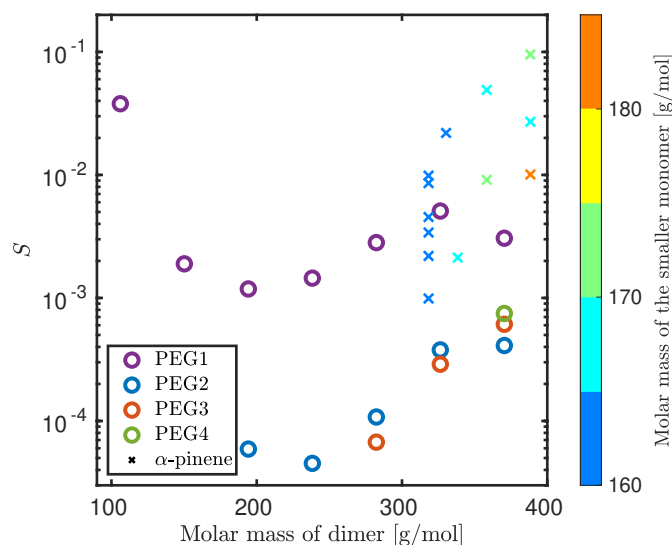


Figure S13: Molar mass dependence of S in COSMO $therm$ -derived saturation vapor pressures of polyethylene glycols (PEG2-PEG8) and α -pinene-derived acid anhydride dimers. The colors indicate the size of the smaller monomer used to form the dimer. E.g., PEG8 can be formed from dimerization of PEG1 and PEG7, PEG2 and PEG6, PEG3 and PEG5, or two PEG4 molecules, giving four different values of S .

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