ELECTRONIC SUPPLEMENTARY INFORMATION

Deduction of the SLE equations considering polymorphism phenomena

The isofugacity criteria establish that, in case of solid-liquid equilibrium (SLE), the fugacity of the compound f_i in both solid (*S*) and liquid (*L*) phases are equal.

$$f_i^{\rm S} = f_i^{\rm L}$$
 S1

Equation S1 can be written in terms of the standard fugacity of the compounds f_i^0 in each phase as follows:

$$x_{i}\gamma_{i}^{L}f_{i}^{L^{0}} = z_{i}\gamma_{i}^{S}f_{i}^{S^{0}} \longrightarrow \frac{x_{i}\gamma_{i}^{L}}{z_{i}\gamma_{i}^{S}} = \frac{f_{i}^{S^{0}}}{f_{i}^{L^{0}}}$$
S2

where x_i and z_i are mole fractions of the compound *i* in both liquid and solid phases, respectively, and γ_i^L and γ_i^S are the activity coefficients of both liquid and solid phases, respectively. It means that the temperature *T* of the system must be the same in both solid and liquid phases. This is attended considering a subcooled liquid state. The $x_i \gamma_i^L / z_i \gamma_i^S$ ratio can be calculated by the variation of the Gibbs energy ΔG as follows,

$$\Delta G = \mathbf{R}T \, \ln \frac{f_{i}^{S^{0}}}{f_{i}^{L^{0}}}$$

of the following process: heating the system from *T* to the melting temperature T_{fus} , followed by the complete melting and then cooling to the temperature *T*. The ΔG of such a process is calculated by Equation S4, knowing the variation of the enthalpy ΔH (Equation S5) and entropy ΔS (Equation S6) of the process, and considering the *n* solid-solid transitions.

 $\Delta G = \Delta H + T \Delta S$

$$\Delta H = \sum_{\text{tr}=1}^{n} \left(\int_{T}^{T_{\text{tr}}} Cp_{i}^{\text{S}} dT + \Delta_{\text{tr}} H \right) + \int_{T}^{T_{\text{fus}}} Cp_{i}^{\text{S}} dT + \Delta_{\text{fus}} H + \int_{T_{\text{fus}}}^{T} Cp_{i}^{\text{L}} dT + \sum_{\text{tr}=1}^{n} \left(\int_{T_{\text{tr}}}^{T} Cp_{i}^{\text{L}} dT \right)$$
S5

$$\Delta S = \sum_{\text{tr}=1}^{n} \left(\int_{T}^{T_{\text{tr}}} \frac{Cp_{\text{i}}^{\text{S}}}{T} dT + \frac{\Delta_{\text{tr}}H}{T_{\text{tr}}} \right) + \int_{T}^{T_{\text{fus}}} \frac{Cp_{\text{i}}^{\text{S}}}{T} dT + \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}} + \int_{T_{\text{fus}}}^{T} \frac{Cp_{\text{i}}^{\text{L}}}{T} dT + \sum_{\text{tr}=1}^{n} \left(\int_{T_{\text{tr}}}^{T} \frac{Cp_{\text{i}}^{\text{L}}}{T} dT \right)$$
S6

where $\Delta_{\text{fus}}H$ and T_{fus} are the melting enthalpy and temperature of the compound *i*, and $\Delta_{\text{tr}}H$ and T_{tr} are the solid-solid transitions enthalpy and temperature of the compound *i*. Knowing that the behavior of the heat capacity of the compound *i* in both liquid Cp_1^{L} and solid Cp_i^{S} phases as a function of the temperature is small¹⁻³ (in the range evaluated), Cp_1^{L} and Cp_i^{S} can be considered as constants as well as the variation of the heat capacity $\Delta_{\text{fus}}Cp = Cp^{\text{L}} - Cp^{\text{S}}$. Thus, the SLE can be determined by Equation S7 from $T_{\text{tr}} < T < T_{\text{fus}}$, by Equation S8 for $T < T_{\text{tr}}$, and analogously, in case of more than one solid-solid transition.

$$\ln\frac{x_{i}\gamma_{i}^{L}}{z_{i}\gamma_{i}^{S}} = \frac{\Delta_{\text{fus}}H}{R} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T}\right) + \frac{\Delta_{\text{fus}}C_{p}}{R} \left(\frac{T_{\text{fus}}}{T} - \ln\frac{T_{\text{fus}}}{T} - 1\right)$$
S7

$$\ln\frac{x_{i}\gamma_{i}^{L}}{z_{i}\gamma_{i}^{S}} = \frac{\Delta_{\text{fus}}H}{R} \left(\frac{1}{T_{\text{fus}}} - \frac{1}{T}\right) + \frac{\Delta_{\text{tr}}H}{R} \left(\frac{1}{T_{\text{tr}}} - \frac{1}{T}\right) + \frac{\Delta_{\text{fus}}C_{p}}{R} \left(\frac{T_{\text{fus}}}{T} - \ln\frac{T_{\text{fus}}}{T} - 1\right)$$
S8

Table S1. Melting temperatures $(T_{\text{fus}} / \text{K})$ and enthalpies $(\Delta_{\text{fus}}H / \text{kJ} \cdot \text{mol}^{-1})$ and solid-solid temperatures $(T_{\text{tr}} / \text{K})$ and enthalpies $(\Delta_{\text{tr}}H / \text{kJ} \cdot \text{mol}^{-1})$ of the pure compounds used in the modeling procedure and obtained in this work or from literature.

Compound	$T_{\rm fus}$	ref.	$\Delta_{ m fus} H$	ref.	$T_{\rm tr1}$	ref.		$\Delta_{tr1}H$	lit.	$T_{\rm tr2}$	ref.	$\Delta_{\rm tr2}H$	ref.
Trilaurin	319.39		116.45		308.25		4	86.00	4	288.75	4	69.80	4
Trimyristin	330.90		141.97	this work	319.05		4	106.00	4	305.75	4	81.90	4
Tripalmitin	338.98	this work	165.88		328.85		4	126.50	4	317.85	4	95.80	4
1-hexadecanol	322.61		33.60	5	321.89	the street		23.70	5	-		-	
1-octadecanol	331.42		40.10	6	330.55	uns work		26.50	6	-		-	

trilaurin (1) +				trilaurin (1)+	tr	trimyristin (1) +			
1-hexadecanol (2)			1-	octadecan	ol (2)	1-hexadecanol (2)				
x_1	Solidus	Liquidus	x_1	Solidus	Liquidus	x_1	Solidus	Liquidus		
	/ K	/ K		/ K	/ K		/ K	/ K		
0.000		322.61	0.000		331.42	0.000		322.61		
0.097	315.39	321.13	0.101	317.31	330.00	0.042	320.35	321.68		
0.197	315.44	319.48	0.197	317.42	328.56	0.100		319.98		
0.295	315.55	318.38	0.294	317.50	327.25	0.137		320.82		
0.402	315.96	317.30	0.395	317.67	325.84	0.192	320.11	322.05		
0.503		315.86	0.501	317.56	323.71	0.246	319.89	322.98		
0.592	315.85	316.28	0.597	318.01	321.73	0.394	319.11	324.71		
0.703	315.18	316.79	0.701	317.76	319.85	0.498	319.30	326.30		
0.781	315.06	317.15	0.790	317.76	318.67	0.594	318.99	326.78		
0.863	315.00	318.58	0.884	317.70	318.77	0.694	318.80	327.59		
1.000		319.39	1.000		319.39	0.778	319.10	328.24		
						0.894	323.55 ‡	329.24		
						1.000		330.90		
trimvristin (1) +							tripalmitin (1) +			
tı	rimyristin ((1) +	tı	ipalmitin ((1) +	tr	ipalmitin (1)+		
tr 1-	rimyristin (octadecan	(1) + ol (2)	tı 1-	ripalmitin (hexadecan	(1) + ol (2)	tr 1-	ipalmitin (octadecand	1) + ol (2)		
$\frac{\text{tr}}{1-x_1}$	rimyristin (octadecano <i>Solidus</i>	(1) + ol (2) <i>Liquidus</i>	$\frac{1}{x_1}$	^r ipalmitin (hexadecan <i>Solidus</i>	$\frac{(1) +}{liquidus}$	$\frac{1}{x_1}$	ipalmitin (octadecano <i>Solidus</i>	1) + ol (2) <i>Liquidus</i>		
$\frac{1}{x_1}$	rimyristin (octadecan) Solidus / K	(1) + ol (2) <i>Liquidus</i> /K	$\frac{1}{x_1}$	ipalmitin (hexadecan <i>Solidus</i> / K	(1) + ol (2) <i>Liquidus</i> /K	$\frac{\text{tr}}{1-x_1}$	ipalmitin (octadecand <i>Solidus</i> / K	1) + bl (2) Liquidus /K		
$\frac{1}{x_1}$	rimyristin (octadecand Solidus / K	(1) + ol (2) $Liquidus / K$ (331.42)	$\frac{1}{x_1}$	ipalmitin (hexadecan <i>Solidus</i> / K	(1) + ol (2) $Liquidus / K$ 322.61	$ \frac{\text{tr}}{1-x_1} $ 0.000	ipalmitin (octadecand Solidus / K	1) + bl (2) <i>Liquidus</i> /K 331.42		
$\frac{1}{x_1}$	imyristin (octadecano Solidus /K 325.99	$ \begin{array}{r} (1) + \\ ol (2) \\ Liquidus \\ /K \\ 331.42 \\ 329.88 \end{array} $		ipalmitin (hexadecan Solidus /K	(1) + ol (2) Liquidus / K 322.61 322.60		ipalmitin (octadecand Solidus /K 329.20	1) + bl (2) <i>Liquidus</i> /K 331.42 330.27		
	cimyristin (octadecand <i>Solidus</i> /K 325.99 326.26	$ \begin{array}{r} (1) + \\ oldsymbol{oldsymbol{olds}}{liquidus} \\ /K \\ 331.42 \\ 329.88 \\ 328.60 \\ \end{array} $		ipalmitin (hexadecan Solidus /K 322.90	(1) + ol (2) Liquidus/K322.61322.60328.69		ipalmitin (octadecand Solidus /K 329.20 328.90	1) + bl (2) <i>Liquidus</i> /K 331.42 330.27 329.80		
$ \begin{array}{r} tr \\ 1- \\ x_1 \\ 0.000 \\ 0.100 \\ 0.199 \\ 0.300 \\ \end{array} $	imyristin (octadecano Solidus /K 325.99 326.26 326.01	(1) + ol (2) <i>Liquidus</i> /K 331.42 329.88 328.60 327.28	$ \begin{array}{c} & \text{tr} \\ 1 - x_1 \\ \hline & x_1 \\ \hline & 0.000 \\ 0.050 \\ 0.101 \\ 0.201 \\ \end{array} $	ipalmitin (hexadecan Solidus /K 322.90 321.90	(1) + ol (2) Liquidus/K322.61322.60328.69331.98	$ \begin{array}{c} & \text{tr} \\ & 1 \\ & x_1 \\ & 0.000 \\ & 0.058 \\ & 0.099 \\ & 0.151 \\ \end{array} $	ipalmitin (octadecand Solidus /K 329.20 328.90	1) + bl (2) <i>Liquidus</i> /K 331.42 330.27 329.80 329.56		
$ \begin{array}{c} \text{tr}\\ 1-\\ x_1\\ 0.000\\ 0.100\\ 0.199\\ 0.300\\ 0.393\\ \end{array} $	imyristin (octadecand <i>Solidus</i> / <i>K</i> 325.99 326.26 326.01	(1) + ol (2) <i>Liquidus</i> /K 331.42 329.88 328.60 327.28 325.90	$ \begin{array}{c} & tr \\ & 1- \\ & x_1 \\ & 0.000 \\ & 0.050 \\ & 0.101 \\ & 0.201 \\ & 0.299 \\ \end{array} $	ipalmitin (hexadecan Solidus /K 322.90 321.90 321.93	(1) + ol (2) <i>Liquidus</i> /K 322.61 322.60 328.69 331.98 333.62	$ \begin{array}{c} & \text{tr} \\ & 1 \\ & x_1 \\ & 0.000 \\ & 0.058 \\ & 0.099 \\ & 0.151 \\ & 0.200 \\ \end{array} $	ipalmitin (octadecand Solidus /K 329.20 328.90 328.95	1) + bl (2) <i>Liquidus</i> / <i>K</i> 331.42 330.27 329.80 329.56 331.40		
$ \begin{array}{r} tr \\ 1- \\ x_1 \\ 0.000 \\ 0.100 \\ 0.199 \\ 0.300 \\ 0.393 \\ 0.493 \\ \end{array} $	imyristin (octadecand Solidus /K 325.99 326.26 326.01	(1) + ol (2) <i>Liquidus</i> / <i>K</i> 331.42 329.88 328.60 327.28 325.90 325.88	$ \begin{array}{c} & \text{tr} \\ 1- \\ x_1 \\ 0.000 \\ 0.050 \\ 0.101 \\ 0.201 \\ 0.299 \\ 0.408 \\ \end{array} $	ipalmitin (hexadecan Solidus /K 322.90 321.90 321.93 321.68	(1) + ol (2) <i>Liquidus</i> /K 322.61 322.60 328.69 331.98 333.62 334.75	$ \begin{array}{c} & \text{tr} \\ 1- \\ x_1 \\ 0.000 \\ 0.058 \\ 0.099 \\ 0.151 \\ 0.200 \\ 0.300 \\ \end{array} $	ipalmitin (octadecand <i>Solidus</i> / <i>K</i> 329.20 328.90 328.95 328.80	1) + bl (2) <i>Liquidus</i> /K 331.42 330.27 329.80 329.56 331.40 333.40		
$ \begin{array}{c} \text{tr}\\ 1-\\ x_1\\ 0.000\\ 0.100\\ 0.100\\ 0.199\\ 0.300\\ 0.393\\ 0.493\\ 0.592\\ \end{array} $	imyristin (octadecand <i>Solidus</i> / <i>K</i> 325.99 326.26 326.01 325.77	(1) + ol (2) <i>Liquidus</i> /K 331.42 329.88 328.60 327.28 325.90 325.88 326.73	$ \begin{array}{c} & tr \\ & 1- \\ & x_1 \\ \hline & 0.000 \\ & 0.050 \\ & 0.101 \\ & 0.201 \\ & 0.299 \\ & 0.408 \\ & 0.501 \\ \end{array} $	ipalmitin (hexadecan Solidus / K 322.90 321.90 321.93 321.68 321.90	(1) + ol (2) <i>Liquidus</i> /K 322.61 322.60 328.69 331.98 333.62 334.75 335.93	$ \begin{array}{c} & \text{tr} \\ 1- \\ x_1 \\ 0.000 \\ 0.058 \\ 0.099 \\ 0.151 \\ 0.200 \\ 0.300 \\ 0.401 \\ \end{array} $	ipalmitin (octadecand <i>Solidus</i> / <i>K</i> 329.20 328.90 328.95 328.80 329.50	1) + bl (2) <i>Liquidus</i> /K 331.42 330.27 329.80 329.56 331.40 333.40 333.40 334.79		
$ \begin{array}{c} \text{tr}\\ 1-\\ x_1\\ 0.000\\ 0.100\\ 0.199\\ 0.300\\ 0.393\\ 0.493\\ 0.592\\ 0.691\\ \end{array} $	imyristin (octadecand <i>Solidus</i> / <i>K</i> 325.99 326.26 326.01 325.77 325.65	(1) + ol (2) <i>Liquidus</i> /K 331.42 329.88 328.60 327.28 325.90 325.88 326.73 327.67	$ \begin{array}{c} & tr \\ & 1- \\ & x_1 \\ & 0.000 \\ & 0.050 \\ & 0.101 \\ & 0.201 \\ & 0.299 \\ & 0.408 \\ & 0.501 \\ & 0.597 \\ \end{array} $	ipalmitin (hexadecan Solidus /K 322.90 321.90 321.93 321.68 321.90 322.00	(1) + ol (2) <i>Liquidus</i> /K 322.61 322.60 328.69 331.98 333.62 334.75 335.93 336.61	$ \begin{array}{c} & \text{tr} \\ & 1- \\ & x_1 \\ & 0.000 \\ & 0.058 \\ & 0.099 \\ & 0.151 \\ & 0.200 \\ & 0.300 \\ & 0.401 \\ & 0.502 \\ \end{array} $	ipalmitin (octadecand <i>Solidus</i> / <i>K</i> 329.20 328.90 328.95 328.80 329.50 328.80	1) + bl (2) Liquidus /K 331.42 330.27 329.80 329.56 331.40 333.40 334.79 335.63		
$\begin{array}{c} \text{tr}\\ 1 \\ \hline x_1 \\ 0.000 \\ 0.100 \\ 0.199 \\ 0.300 \\ 0.393 \\ 0.493 \\ 0.592 \\ 0.691 \\ 0.793 \end{array}$	imyristin (octadecand <i>Solidus</i> / <i>K</i> 325.99 326.26 326.01 325.77 325.65 325.48	(1) + ol (2) <i>Liquidus</i> /K 331.42 329.88 328.60 327.28 325.90 325.88 326.73 327.67 328.90	$ \begin{array}{c} & tr \\ & 1- \\ & x_1 \\ \hline & 0.000 \\ & 0.050 \\ & 0.101 \\ & 0.201 \\ & 0.299 \\ & 0.408 \\ & 0.501 \\ & 0.597 \\ & 0.701 \\ \end{array} $	ipalmitin (hexadecan Solidus /K 322.90 321.90 321.68 321.68 321.90 322.00 321.82	(1) + ol (2) <i>Liquidus</i> /K 322.61 322.60 328.69 331.98 333.62 334.75 335.93 336.61 337.35	$ \begin{array}{c} \text{tr} \\ 1-\\ x_1\\ 0.000\\ 0.058\\ 0.099\\ 0.151\\ 0.200\\ 0.300\\ 0.401\\ 0.502\\ 0.595\\ \end{array} $	ipalmitin (octadecand <i>Solidus</i> / <i>K</i> 329.20 328.90 328.90 328.80 329.50 328.80 329.00	1) + bl (2) <i>Liquidus</i> /K 331.42 330.27 329.80 329.56 331.40 333.40 333.40 334.79 335.63 336.63		
$\begin{array}{c} \text{tr}\\ 1 \\ \hline x_1 \\ 0.000 \\ 0.100 \\ 0.199 \\ 0.300 \\ 0.393 \\ 0.493 \\ 0.592 \\ 0.691 \\ 0.793 \\ 0.878 \end{array}$	imyristin (octadecand <i>Solidus</i> / <i>K</i> 325.99 326.26 326.01 325.77 325.65 325.48 325.61	(1) + ol (2) <i>Liquidus</i> /K 331.42 329.88 328.60 327.28 325.90 325.88 326.73 327.67 328.90 329.52	$ \begin{array}{c} & \text{tr} \\ & 1- \\ & x_1 \\ & 0.000 \\ & 0.050 \\ & 0.101 \\ & 0.201 \\ & 0.299 \\ & 0.408 \\ & 0.501 \\ & 0.597 \\ & 0.701 \\ & 0.800 \\ \end{array} $	ipalmitin (hexadecan Solidus /K 322.90 321.90 321.93 321.68 321.90 322.00 321.82 330.45 ‡	(1) + ol (2) <i>Liquidus</i> /K 322.60 328.69 331.98 333.62 334.75 335.93 336.61 337.35 338.32	$ \begin{array}{c} \text{tr} \\ 1-\\ x_1 \\ 0.000 \\ 0.058 \\ 0.099 \\ 0.151 \\ 0.200 \\ 0.300 \\ 0.401 \\ 0.502 \\ 0.595 \\ 0.697 \\ \end{array} $	ipalmitin (octadecand <i>Solidus</i> / <i>K</i> 329.20 328.90 328.95 328.80 329.50 328.80 329.00 329.20	1) + bl (2) Liquidus /K 331.42 330.27 329.80 329.56 331.40 333.40 334.79 335.63 336.63 337.35		
$\begin{array}{c} \text{tr}\\ 1 \\ \hline x_1 \\ 0.000 \\ 0.100 \\ 0.199 \\ 0.300 \\ 0.393 \\ 0.493 \\ 0.592 \\ 0.691 \\ 0.793 \\ 0.878 \\ 1.000 \end{array}$	rimyristin (octadecand <i>Solidus</i> / <i>K</i> 325.99 326.26 326.01 325.65 325.65 325.48 325.61	(1) + ol (2) <i>Liquidus</i> / <i>K</i> 331.42 329.88 328.60 327.28 325.90 325.88 326.73 327.67 328.90 329.52 330.90	$ \begin{array}{c} & tr \\ & 1- \\ & x_1 \\ \hline & x_1 \\ \hline & 0.000 \\ & 0.050 \\ \hline & 0.101 \\ \hline & 0.201 \\ \hline & 0.299 \\ \hline & 0.408 \\ \hline & 0.501 \\ \hline & 0.597 \\ \hline & 0.701 \\ \hline & 0.800 \\ \hline & 0.894 \\ \hline \end{array} $	ipalmitin (hexadecan Solidus /K 322.90 321.90 321.93 321.68 321.90 322.00 321.82 330.45 ‡ 336.05 ‡	(1) + ol (2) <i>Liquidus</i> / <i>K</i> 322.61 322.60 328.69 331.98 333.62 334.75 335.93 336.61 337.35 338.32 338.85	$\begin{array}{c} & \text{tr} \\ 1 - \\ x_1 \\ 0.000 \\ 0.058 \\ 0.099 \\ 0.151 \\ 0.200 \\ 0.300 \\ 0.401 \\ 0.502 \\ 0.595 \\ 0.697 \\ 0.797 \end{array}$	ipalmitin (octadecand Solidus /K 329.20 328.90 328.90 328.80 329.50 328.80 329.00 329.20 332.05 ‡	1) + bl (2) Liquidus /K 331.42 330.27 329.80 329.56 331.40 333.40 334.79 335.63 336.63 337.35 338.16		
$\begin{array}{c} \text{tr}\\ 1 \\ \hline x_1 \\ 0.000 \\ 0.100 \\ 0.199 \\ 0.300 \\ 0.393 \\ 0.493 \\ 0.592 \\ 0.691 \\ 0.793 \\ 0.878 \\ 1.000 \end{array}$	imyristin (octadecand <i>Solidus</i> / <i>K</i> 325.99 326.26 326.01 325.77 325.65 325.48 325.61	(1) + ol (2) <i>Liquidus</i> /K 331.42 329.88 328.60 327.28 325.90 325.88 326.73 327.67 328.90 329.52 330.90	$ \begin{array}{c} & tr \\ & 1- \\ & x_1 \\ \hline & 0.000 \\ & 0.050 \\ & 0.101 \\ & 0.201 \\ & 0.299 \\ & 0.408 \\ & 0.501 \\ & 0.597 \\ & 0.701 \\ & 0.800 \\ & 0.894 \\ & 1.000 \\ \end{array} $	ipalmitin (hexadecan Solidus /K 322.90 321.90 321.93 321.68 321.90 322.00 321.82 330.45 ‡ 336.05 ‡	(1) + ol (2) <i>Liquidus</i> /K 322.61 322.60 328.69 331.98 333.62 334.75 335.93 336.61 337.35 338.32 338.85 338.98	$\begin{array}{c} & \text{tr} \\ 1 - \\ x_1 \\ 0.000 \\ 0.058 \\ 0.099 \\ 0.151 \\ 0.200 \\ 0.300 \\ 0.401 \\ 0.502 \\ 0.595 \\ 0.697 \\ 0.797 \\ 0.906 \end{array}$	ipalmitin (octadecand <i>Solidus</i> / <i>K</i> 329.20 328.90 328.90 328.80 329.50 328.80 329.00 329.20 332.05 ‡ 335.85 ‡	1) + bl (2) Liquidus /K 331.42 330.27 329.80 329.56 331.40 333.40 334.79 335.63 336.63 337.35 338.16 338.82		

Table S2. Experimental solid-liquid equilibrium data for the triacylglycerols + fatty alcohols systems for mole fraction x and temperature T for *solidus* and *liquidus* line.[†]

[†] Uncertainties for molar fraction and *liquidus* line temperature are \pm 0.001 and 0.38 K. Uncertainty for *solidus* line temperature measured by DSC and by microscopy [‡] is \pm 0.58 K.



Figure S1. Tammann plots of the experimental eutectic transition enthalpy $\Delta_{eut}H$ (\blacksquare) and linear regression (dashed lines) for the systems A) trilaurin (1) + 1-hexadecanol (2), B) trilaurin (1) + 1-octadecanol (2), C) trimyristin (1) + 1-hexadecanol (2), D) trimyristin (1) + 1-octadecanol (2), E) tripalmitin (1) + 1-hexadecanol (2), F) tripalmitin (1) + 1-octadecanol (2).

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