

Figure S1. IR spectra of the blocking products

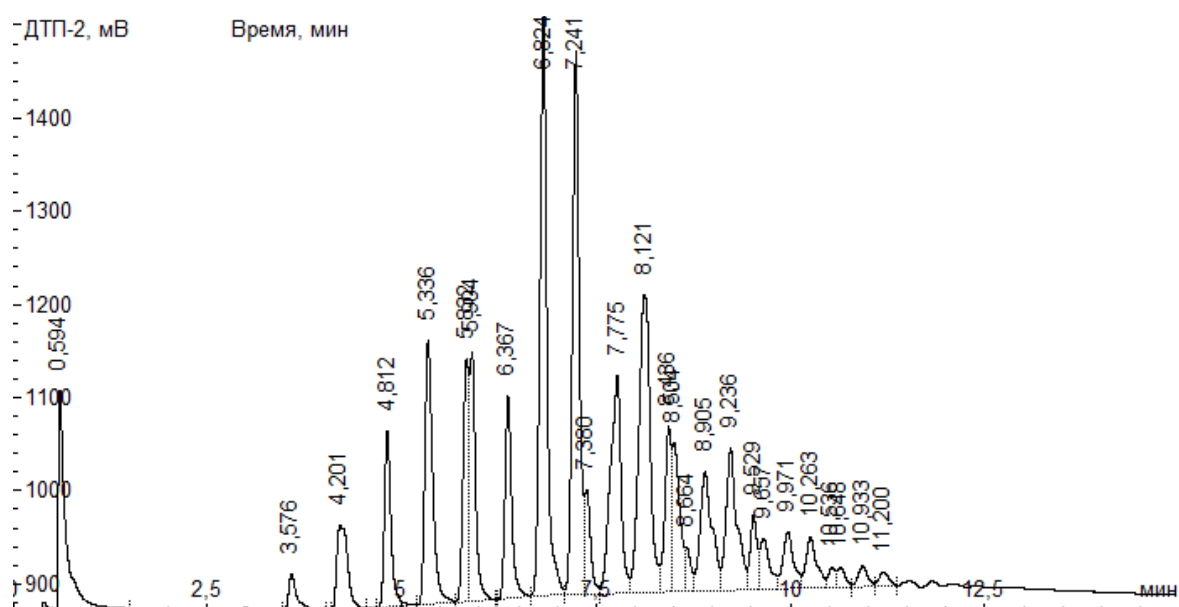
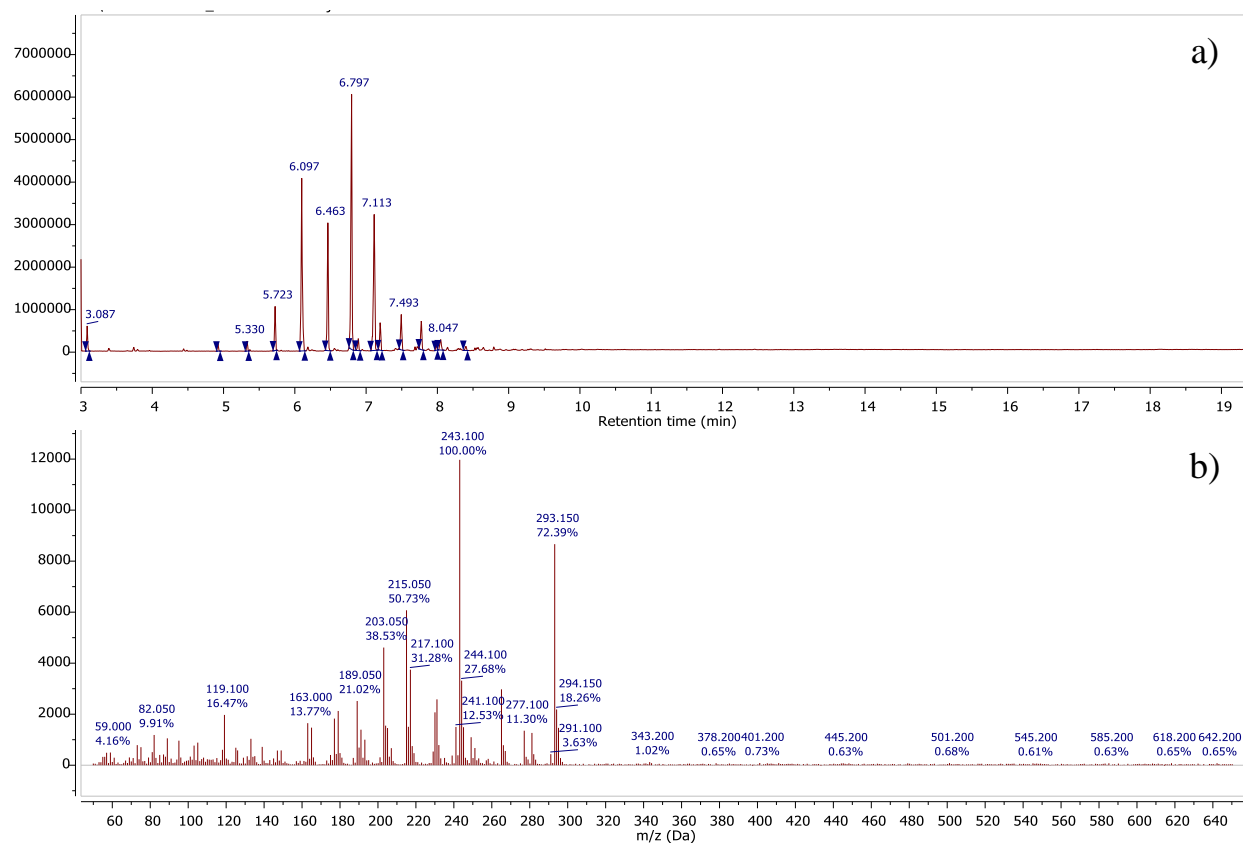
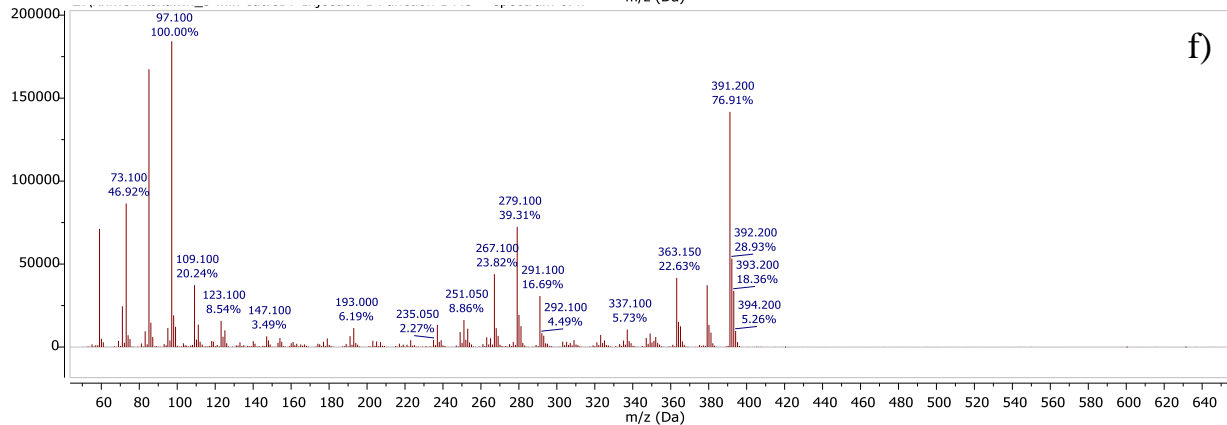
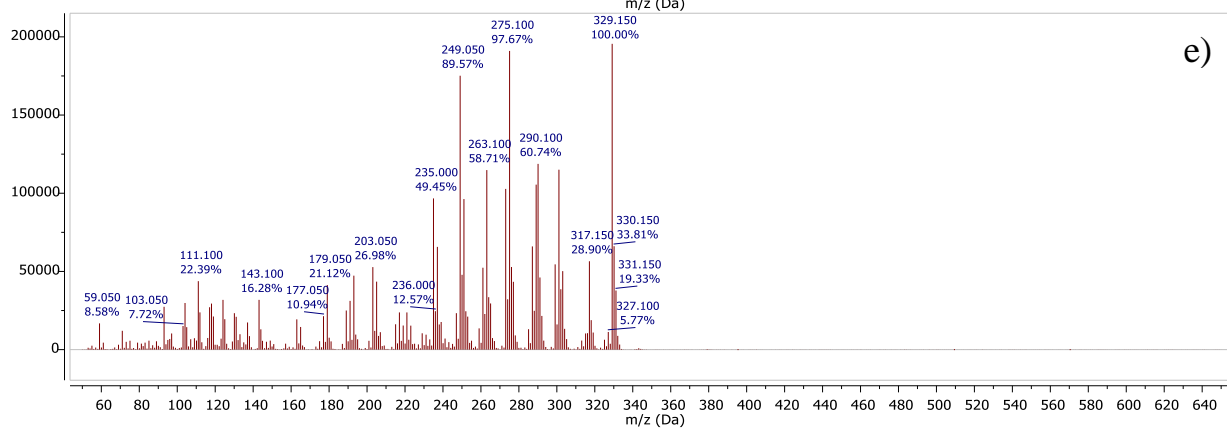
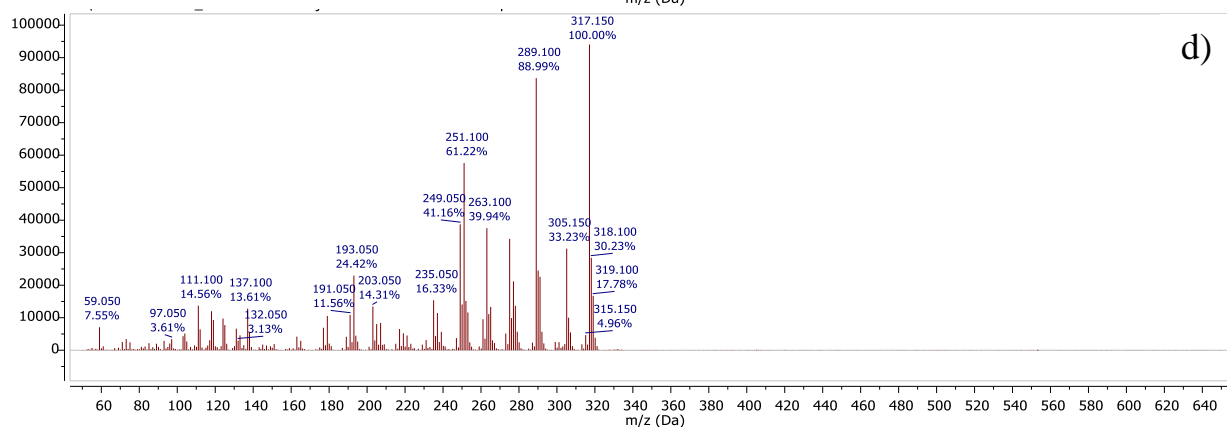
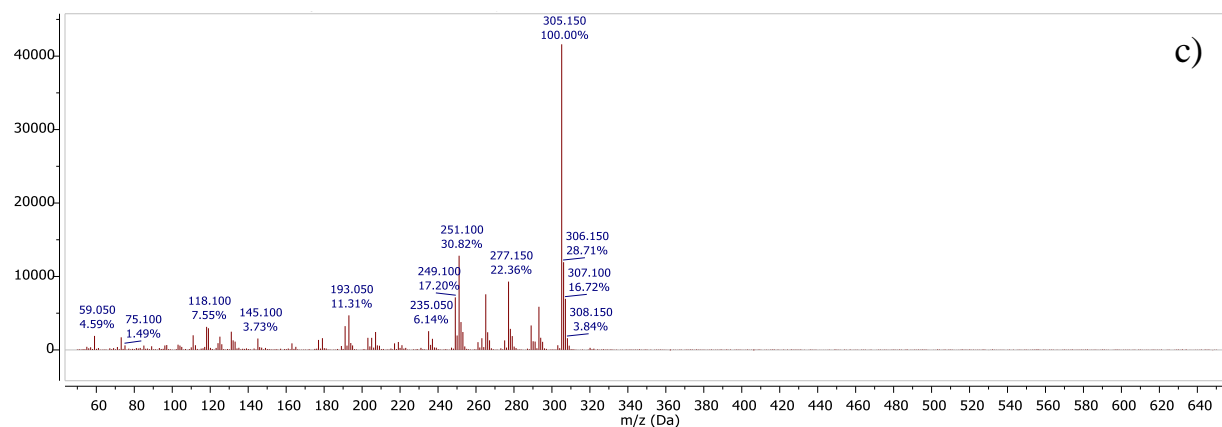


Figure S2. GLC of volatile products





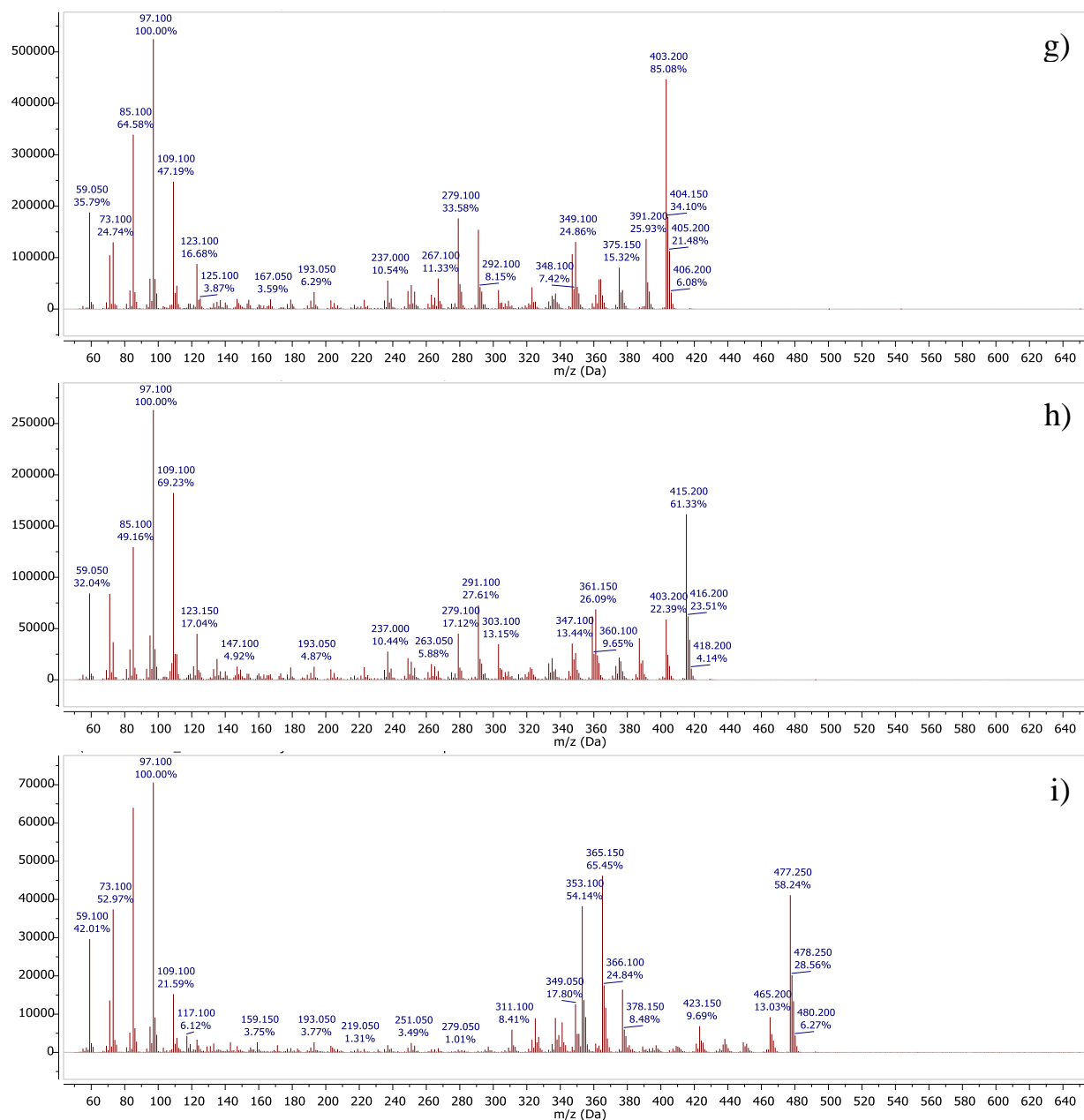
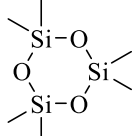
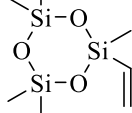
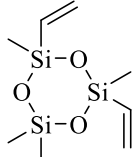
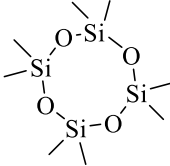
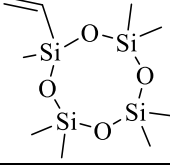
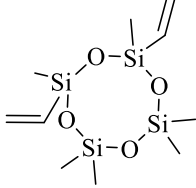
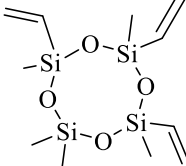
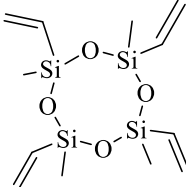
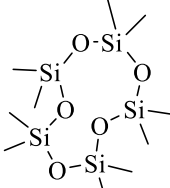
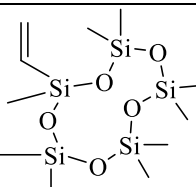
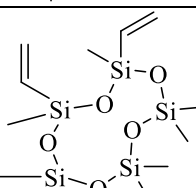


Figure S3. GC-MS spectrum of volatile products PDMS-75-Vin: a) general spectra, b) at 4.920 min, c) at 5.330 min, d) at 5.723 min, e) at 6.097 min, f) at 6.463 min, g) at 6.797 min, h) at 7.113 min, i) at 7.493 min

Table S1. Characteristics of cyclosilcosanes

№	m/z	Cycle	MM	Scheme	Boiling point, °C
1	219 [Si ₃ O ₃ C ₅ H ₁₅] ⁺	D ₃	234		134
2	213 [Si ₃ O ₃ C ₆ H ₁₅] ⁺	D ₂ V ₁	234		160

3	231 [Si ₃ O ₃ C ₇ H ₁₅] ⁺	D ₁ V ₂	246		185.6±13
4	281 [Si ₄ O ₄ C ₇ H ₂₁] ⁺	D ₄	296		175
5	293 [Si ₄ O ₄ C ₈ H ₂₁] ⁺	D ₃ V ₁	308		180
6	305 [Si ₄ O ₄ C ₉ H ₂₁] ⁺	D ₂ V ₂	320		219.9±23
7	317 [Si ₄ O ₄ C ₁₀ H ₂₁] ⁺	D ₁ V ₃	332		234±23
8	329 [Si ₄ O ₄ C ₁₁ H ₂₁] ⁺	V ₄	344		224
9	355 [Si ₅ O ₅ C ₉ H ₂₇] ⁺	D ₅	370		210
10	367 [Si ₅ O ₅ C ₁₀ H ₂₇] ⁺	D ₄ V ₁	382		257.5±23
11	379 [Si ₅ O ₅ C ₁₁ H ₂₇] ⁺	D ₃ V ₂	394		270.4±23

12	391 [Si ₅ O ₅ C ₁₂ H ₂₇] ⁺	D ₂ V ₃	406		283,1±23
13	403 [Si ₅ O ₅ C ₁₃ H ₂₇] ⁺	D ₁ V ₄	418		295.6±23
14	415 [Si ₅ O ₅ C ₁₄ H ₂₇] ⁺	V ₅	430		261-262
15	429 [Si ₆ O ₆ C ₁₁ H ₃₃] ⁺	D ₆	444		245
16	441 [Si ₆ O ₆ C ₁₂ H ₃₃] ⁺	D ₅ V ₁	456		304.5±25
17	453 [Si ₆ O ₆ C ₁₃ H ₃₃] ⁺	D ₄ V ₂	468		-
18	465 [Si ₆ O ₆ C ₁₄ H ₃₃] ⁺	D ₃ V ₃	480		-
19	477 [Si ₆ O ₆ C ₁₅ H ₃₃] ⁺	D ₂ V ₄	492		-

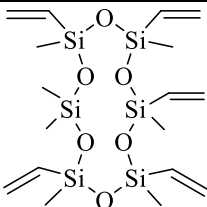
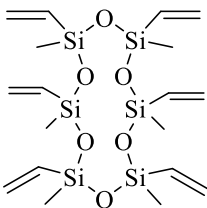
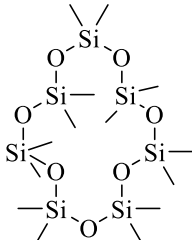
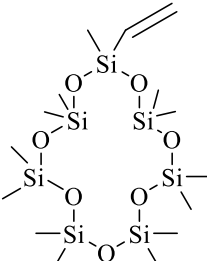
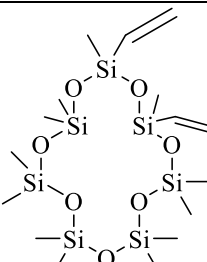
20	489 [Si ₆ O ₆ C ₁₆ H ₃₃] ⁺	D ₁ V ₅	504		-
21	501 [Si ₆ O ₆ C ₁₇ H ₃₃] ⁺	V ₆	516		320
22	503 [Si ₇ O ₇ C ₁₃ H ₃₉] ⁺	D ₇	518		336
23	515 [Si ₇ O ₇ C ₁₄ H ₃₉] ⁺	D ₆ V ₁	530		-
24	527 [Si ₇ O ₇ C ₁₅ H ₃₉] ⁺	D ₅ V ₂	542		-

Table S2. Detailed composition of cycles

Characteristics																											
№	MeVinSi(OMe) ₂ / Me ₂ Si(OEt) ₂	Composition of cyclosiloxanes, wt. %																									
		D ₃	D ₄	D ₅	D ₆	D _{n+1}	3 links		4 links			5 links				6 links					7 links		V ₃ V ₄ V ₅ V ₆ V _{n+1}				
							D ₂ V ₁	D ₁ V ₂	D ₃ V ₁	D ₂ V ₂	D ₁ V ₃	D ₄ V ₁	D ₃ V ₂	D ₂ V ₃	D ₁ V ₄	D ₅ V ₁	D ₄ V ₂	D ₃ V ₃	D ₂ V ₄	D ₁ V ₅	D ₆ V ₁	D ₅ V ₂					
1	100/0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6,0	76,0	15,5	2,0
2	25/75	*	17,5	6,0	1,5	*	*	*	31,0	15,5	2,5	10,0	7,0	2,0	*	2,5	2,0	*	*	-	*	*	-	-	-	-	-
3	50/50	*	3,5	*	*	-	*	1,5	19,5	30,0	17,5	4,0	10,0	6,5	3,0	*	*	1,0	*	*	-	*	-	-	*	-	-
4	75/25	-	-	-	-	-	-	1,5	2,5	15,0	40,0	-	-	3,0	3,0	-	*	1,5	2,5	2,5	-	-	-	23,0	5,5	-	-
5	100/0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	*	6,0	72,5	18,5	2,0
6	25/75	*	17,5	8,0	1,5	*	-	-	23,5	16,5	4,0	12,5	8,0	2,5	*	2,5	2,0	*	-	-	*	*	-	-	-	-	-
7	50/50	-	3,0	*	*	-	-	*	18,0	32,5	20,5	4,0	9,5	5,0	1,0	*	*	*	*	-	-	-	-	3,5	*	-	-
8	75/25	-	-	-	-	-	-	-	4,5	17,5	35,5	-	-	3,5	4,5	-	-	1,5	2,5	1,5	-	-	-	19,5	9,5	-	-

* ≤ 1

