

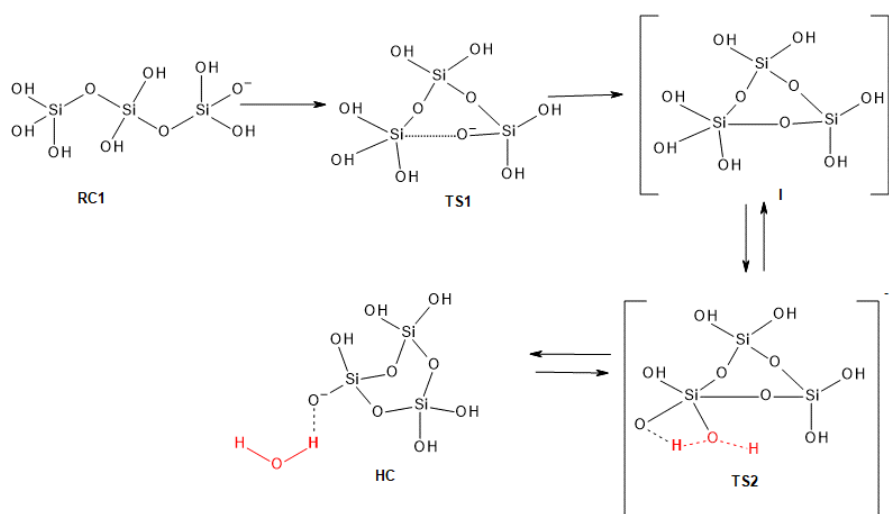
## Supporting Information

### **Impact of Organic Templates on the Selective Formation of Zeolite Oligomers**

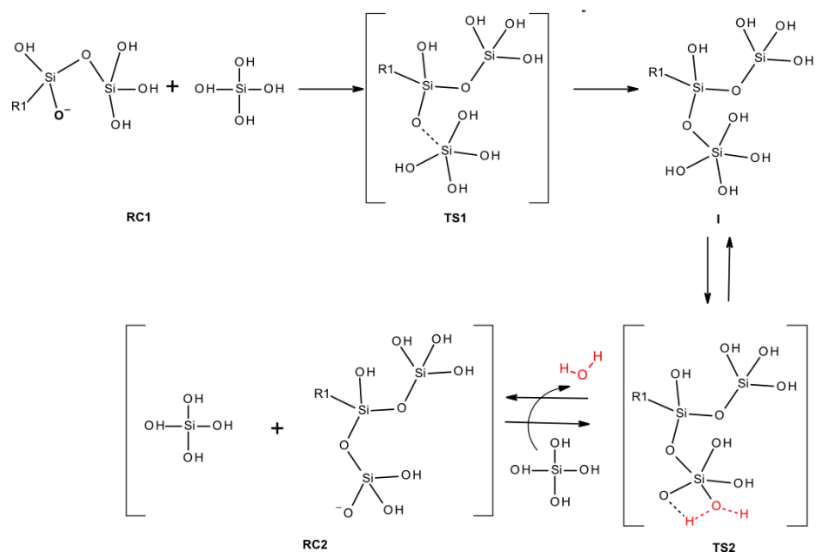
*Marine Ciantar, Thuat T. Trinh, Carine Michel, Philippe Sautet, Caroline Mellot-Draznieks,\* and Carlos Nieto-Draghi\**

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## Supporting information



**Scheme S1.** Anionic concerted mechanism for the formation of cyclic oligomers. This mechanism involves a first reactive complex (RC1) formed from anionic, followed by a transition state (TS1) and a five-coordinated intermediate (I). A second transition state (TS2) allows the formation of a hydrated complex (HC).

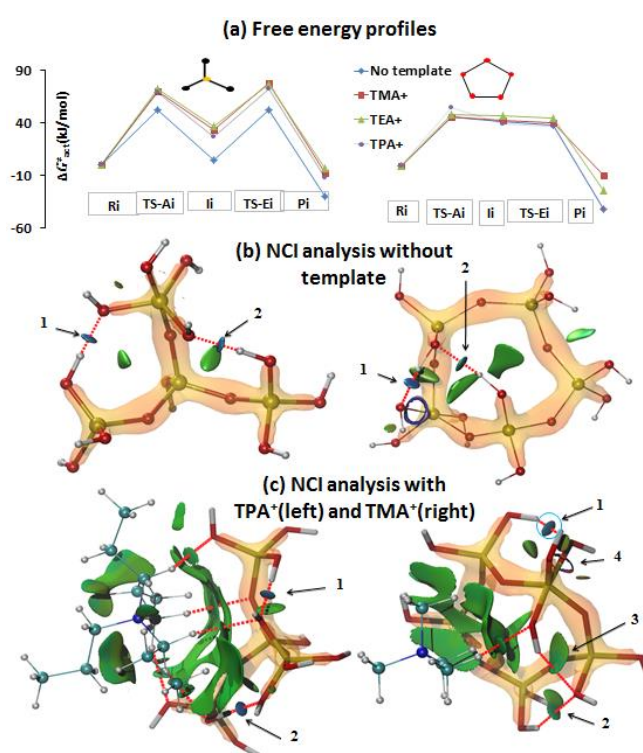


**Scheme S2.** Anionic concerted mechanism for the formation of branched oligomers. This new mechanism involves a first reactive complex (RC1) formed from anionic and neutral species, followed by a transition state (TS1) and a five-coordinated intermediate (I). A second transition state (TS2) allows the formation of a hydrated complex (HC). A neutral monomer combines with HC to form a reactive complex (RC2) with the release of a water molecule.

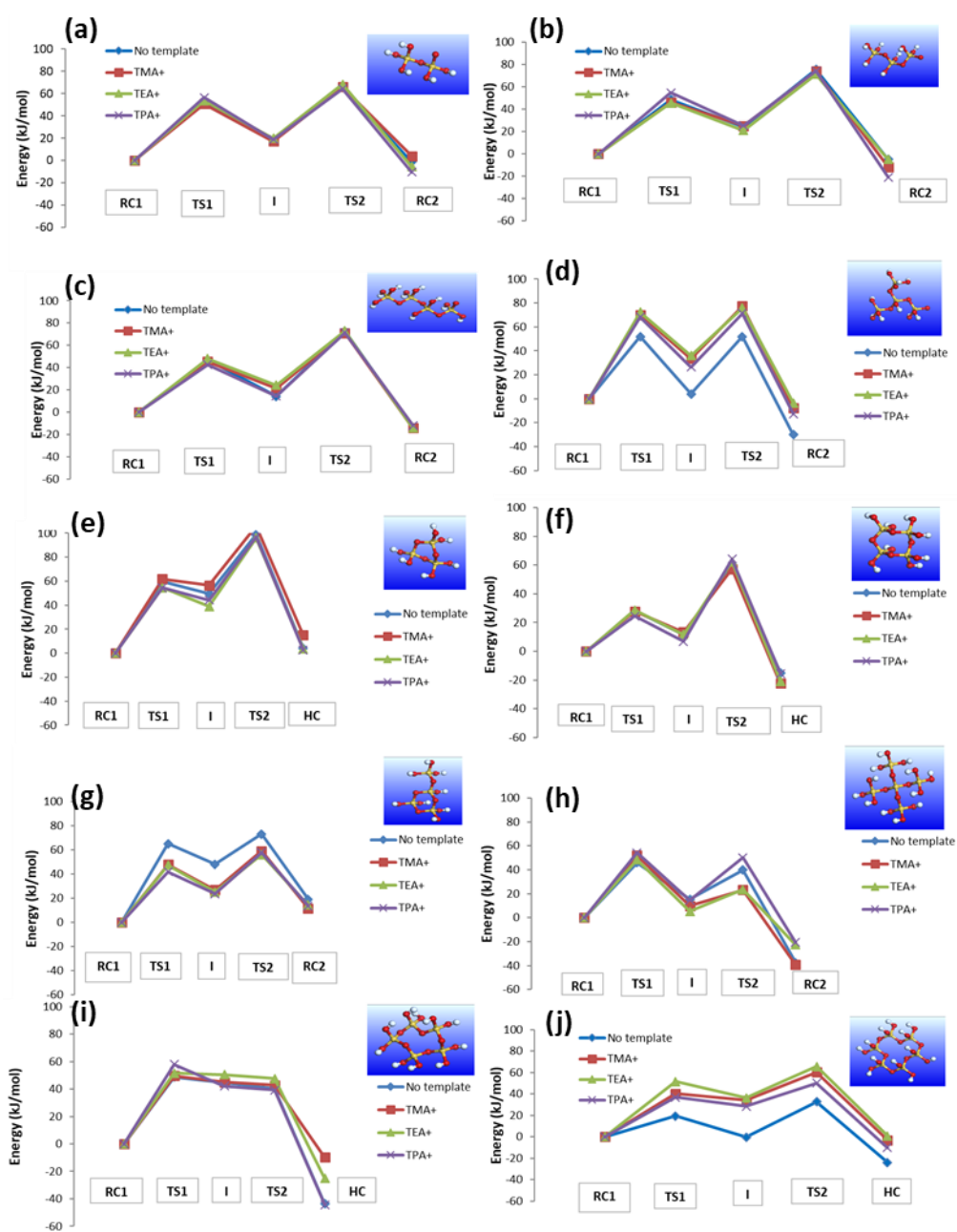
## SI Figures:

### NCI Analysis of the role of templates in the intramolecular H-bonds of pentacoordinated intermediates:

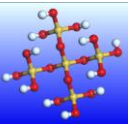
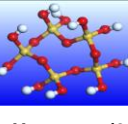


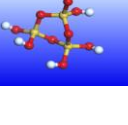

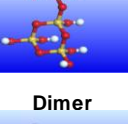
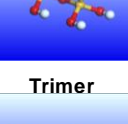

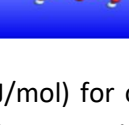
Further understanding of how the template influences the key pentacoordinated intermediate  $I_i$  (Scheme 1 in main text) can be provided using a Non-Covalent Interaction analysis (NCI)[1,2]. This is based on the electron density and the reduced density gradient and allow the identification of the specific interactions between the template and the pentacoordinated intermediate  $I_i$ . The branched intermediate is stabilized by two intramolecular H-bonds either in the absence or presence of a template (indicated by arrows in Figures S1.b and S1.c, respectively), pointing towards a minor role of  $TPA^+$  in this case. By contrast,  $TMA^+$  allows the formation of two additional intramolecular H-bonds upon the pentamer's cyclisation (Figure S1.c, right) to complement the two H-bonds formed in absence of a template (Figure S1.b right)



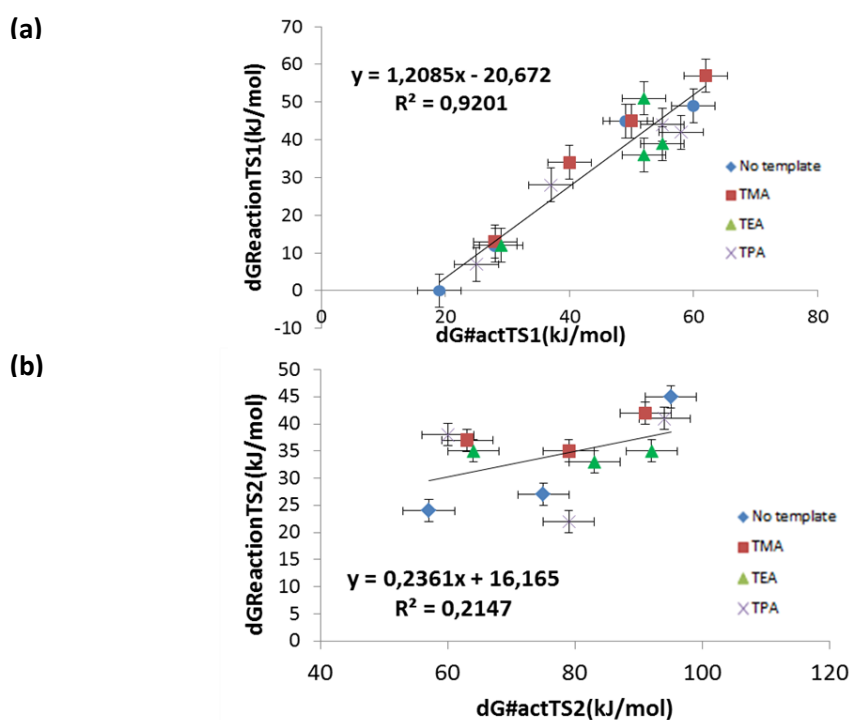
**Figure S1.** Comparison of branched tetramer (left) and cyclic pentamer (right). a) Free energy profiles from reactive complex ( $R_i$ ) to hydrated complex ( $P_i$ ) obtained with and without templates. NCI analysis for the conformation of oligomers without (b) and with (c)  $TPA^+$  or  $TMA^+$  template showing the intramolecular H-bonds (highlighted by arrows 1 to 4). Colours in figures (b) and (c) represent the different types of non-covalent interactions: H-bonds (blue); van der Waals (green).



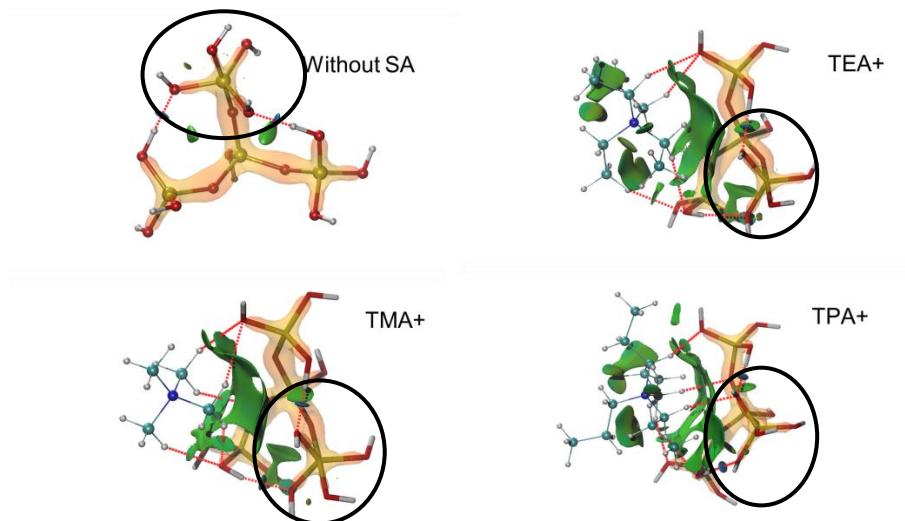
**Figure S2:** Comparison of the DFT activation barriers for different species with and without templates (TMA<sup>+</sup>, TPA<sup>+</sup> and TEA<sup>+</sup>).

	$\Delta G$	KJ/mol			
		States	No template (SA)	TMA+	TEA+
<b>Branched pentamer</b> 	RC1	0	0	0	0
	TS1	46	52	48	54
	I	15	10	5	15
	TS2	40	23	23	50
	RC2	-37	-39	-23	-21
<b>Cyclic Pentamer (5-ring)</b> 	RC1	0	0	0	0
	TS1	49	50	52	58
	I	45	45	51	42
	TS2	40	43	48	39
	HC	-44	-10	-25	-44
<b>Cyclic Hexamer (6-ring)</b> 	RC1	0	0	0	0
	TS1	19	40	52	37
	I	0	34	36	28
	TS2	33	60	65	50
	HC	-24	-3	1	-10
<b>Cyclic Tetramer (4-ring)</b> 	RC1	0	0	0	0
	TS1	28	28	29	25
	I	12	13	12	7
	TS2	60	57	62	64
	HC	-15	-22	-21	-15
<b>Cyclic Trimer (3-ring)</b> 	RC1	0	0	0	0
	TS1	60	62	55	55
	I	49	57	39	44
	TS2	99	106	96	97
	HC	4	15	4	3
<b>Branched tetramer</b> 	RC1	0	0	0	0
	TS1	52	70	72	68
	I	4	33	36	27
	TS2	52	77	76	71
	RC2	-30	-8	-4	-13
<b>Branched 3-ring</b> 	RC1	0	0	0	0
	TS1	65	48	47	42
	I	48	27	25	24
	TS2	73	59	56	58
	RC2	19	12	14	14
<b>Dimer</b> 	RC1	0	0	0	0
	TS1	53	51	54	57
	I	18	17	20	19
	TS2	65	66	68	64
	RC2	-1	4	-6	-10
<b>Trimer</b> 	RC1	0	0	0	0
	TS1	49	46	46	55
	I	24	25	21	25
	TS2	75	74	71	74
	RC2	-5	-12	-5	-21
<b>Tetramer</b> 	RC1	0	0	0	0
	TS1	47	45	48	43
	I	14	22	24	15
	TS2	73	71	73	71
	RC2	-14	-14	-14	-12

**Table S1:** Energies (kJ/mol) for oligomers until  $\text{Si}^6$  with all the intermediates species (RC1: reactive complex, TS1: transition state 1, I: Intermediate state, TS2: transition state 2, RC2 or HC: product complex or hydrated complex).



**Figure S3:** Brønsted-Evans-Polanyi relationship observed between the reactant complex RC1 and the intermediate I (a) and between I and RC2 (b) for **cyclic oligomers** as obtained from DFT calculations.



**Figure S4:** NCI Analysis for branched tetramer (Intermediate state) on the S2 scheme without and with templates (TEA+, TMA+ and TPA+). Colours in figures (b) and (c) represents different type of non-covalent interactions: H-bonds (blue); vdW (green). Template-oligomer vdW interactions (in green) produce a conformation (black circle) with a lot of intermolecular bonds on the penta-coordinated silicon, which disfavors the release of the water molecule required for the formation of the product structure.

Number	No template		TMA+		TEA+		TPA+		Reaction details			Species	Formula
	Forward	Reverse	Forward	Reverse	Forward	Reverse	Forward	Reverse					
1	0	28	0	28	0	28	0	28	esp22+esp23	↔	esp1	ESP1	Si(OH)4...Si(OH)3O-
2	53	35	50	34	49	36	50	36	esp1	↔	esp2	ESP2	[Si(OH)4-O-Si(OH)3]-
3	47	66	52	65	53	71	49	71	esp2	↔	esp3	ESP3	Si2O7H5-...H2O
4	0	30	0	34	0	19	0	20	esp3+esp22	↔	esp4+esp24	ESP4	Si(OH)4...Si2O6H5
5	49	25	46	21	46	25	55	30	esp4	↔	esp5	ESP5	[Si(OH)4-O-Si2O6H5]-
6	51	80	49	86	50	76	49	95	esp5	↔	esp6	ESP6	Si3O10H7-...H2O
7	0	29	0	35	0	40	0	21	esp6	↔	esp7+esp24	ESP7	Si3O9H7-O-(Δ)
8	60	11	62	5	55	16	55	11	esp7	↔	esp8	ESP8	[Si3O9H7-O-]-(Δ)
9	50	95	49	91	57	92	53	94	esp8	↔	esp9	ESP9	Si3O9H5-(Δ)...H2O
10	0	21	0	14	0	30	0	10	esp6+esp22	↔	esp10+esp24	ESP10	Si(OH)4...Si3O10H8
11	47	33	45	23	48	24	43	28	esp10	↔	esp11	ESP11	[Si(OH)3-O-Si3O10H8]-
12	59	87	49	85	49	87	56	83	esp11	↔	esp12	ESP12	Si4O13H9-...H2O
13	0	30	0	50	0	66	0	44	esp6+esp22	↔	esp13+esp24	ESP13	Si(OH)4...Si3O10H8 (+)
14	52	47	70	37	72	36	68	41	esp13	↔	esp14	ESP14	[Si(OH)3-O-Si3O10H8]- (+)
15	48	82	44	85	40	80	44	84	esp14	↔	esp15	ESP15	Si4O13H9-(+)...H2O
16	0	13	0	18	0	20	0	21	esp12	↔	esp16+esp24	ESP16	Si4O12H9-O-(0)
17	28	16	28	15	29	17	25	18	esp16	↔	esp17	ESP17	[Si4O12H9-O-]-(0)
18	48	75	44	79	50	83	57	79	esp17	↔	esp18	ESP18	Si4O12H7-(0)...H2O
19	0	33	0	16	0	17	0	23	esp12	↔	esp19+esp24	ESP19	Si4O12H9-O-(0-branched)
20	65	17	48	21	47	22	42	18	esp19	↔	esp20	ESP20	[Si4O12H9-O-]-(0 branched)
21	25	54	32	47	31	42	34	44	esp20	↔	esp21	ESP21	Si4O12H7-(0 branched)...H2O
22	0	21	0	14	0	30	0	10	esp12 + esp22	↔	esp28 + esp24	ESP22	Si(OH)4
23	47	33	45	23	48	24	43	28	esp28	↔	esp29	ESP23	Si(OH)3O-
24	59	87	49	85	49	87	56	83	esp29	↔	esp30	ESP24	H2O
25	0	13	0	18	0	20	0	21	esp30	↔	esp31+esp24	ESP25	OH-
26	49	4	50	5	52	1	58	16	esp31	↔	esp32	ESP26	H3O+
27	0	84	0	53	0	73	0	83	esp32	↔	esp33	ESP27	H+
28	0	0	0	0	0	0	0	0	esp15 + esp22	↔	esp34+esp24	ESP28	[Si(OH)3O...Si4O13H10]-
29	46	31	52	42	48	43	54	39	esp34	↔	esp35	ESP29	[[Si(OH)3-O-Si4O13H10]-]-
30	25	77	13	63	18	46	35	71	esp35	↔	esp36	ESP30	Si5O16H11...H2O
31	0	21	0	14	0	30	0	10	esp30 + esp 22	↔	esp37 + esp24	ESP31	Si5O15H9-(cyc)
32	47	33	45	23	48	24	43	28	esp 37	↔	esp38	ESP32	[Si5O15H9-]-(cyc)
33	59	87	49	85	49	87	56	83	esp38	↔	esp39	ESP33	Si5O15H9(cyc)...H2O
34	0	13	0	18	0	20	0	21	esp39	↔	esp40+esp24	ESP34	[Si(OH)3O...Si4O13H10]- (+)
35	19	19	40	6	52	16	37	9	esp40	↔	esp41	ESP35	[Si(OH)3O-Si4O13H10]- (+)
36	33	57	26	63	29	64	22	60	esp41	↔	esp42	ESP36	Si5O16H11-...H2O (+)
37	0	21	0	14	0	30	0	10	esp39 + esp22	↔	esp45+ esp24	ESP37	[Si(OH)3O...Si5O16H12]-
38	47	33	45	23	48	24	43	28	esp45	↔	esp46	ESP38	[Si(OH)3O-Si5O16H12]-
39	59	87	49	85	49	87	56	83	esp46	↔	esp47	ESP39	Si6O19H13...H2O
40	0	21	0	14	0	30	0	10	esp47 + esp22	↔	esp48 + esp24	ESP40	Si6O19H13-(cyc)
41	47	33	45	23	48	24	43	28	esp48	↔	esp49	ESP41	[Si6O19H13-](cyc)
42	59	87	49	85	49	87	56	83	esp49	↔	esp50	ESP42	Si6O18H11(cyc)...H2O
43	0	30	0	50	0	66	0	44	esp47 + esp22	↔	esp51 + esp24	ESP43	Si2O7H6...Si2O7H5-
44	52	47	70	37	72	36	68	41	esp51	↔	esp52	ESP44	[Si2O6H5-O-Si2O7H6]-
45	48	82	44	85	40	80	44	84	esp52	↔	esp53	ESP45	Heptamer reactif complex

46	0	30	0	50	0	66	0	44	esp47 + esp22	↔	esp54 + esp24	ESP46	Heptamer intermediate
47	52	47	70	37	72	36	68	41	esp54	↔	esp55	ESP47	Heptamer...H2O
48	48	82	44	85	40	80	44	84	esp55	↔	esp56	ESP48	Octamer reactif_complex
49	0	30	0	50	0	66	0	44	esp47 + esp22	↔	esp57 + esp24	ESP49	Octamer intermediate
50	52	47	70	37	72	36	68	41	esp57	↔	esp58	ESP50	Octamer Hydrated_product
51	48	82	44	85	40	80	44	84	esp58	↔	esp59	ESP51	Heptamer -2-beanchd-reactif-complex
52	0	21	0	14	0	30	0	10	esp15 + esp22	↔	esp60 + esp24	ESP52	Hepta -2-branched_Intermediate
53	47	33	45	23	48	24	43	28	esp60	↔	esp61	ESP53	Hepta -2-branched...H2O
54	59	87	49	85	49	87	56	83	esp61	↔	esp62	ESP54	Hepta -3-branched_reactif_complex
55	0	30	0	50	0	66	0	44	esp15 + esp3	↔	esp63 + esp24	ESP55	Hepta -3-branched_Intermediate
56	52	47	70	37	72	36	68	41	esp63	↔	esp64	ESP56	Hepta -3-branched...H2O
57	48	82	44	85	40	80	44	84	esp64	↔	esp62	ESP57	Isoheptamer_reactif_complex
58	0	30	0	50	0	66	0	44	esp30 + esp22	↔	esp242 + esp24	ESP58	Isoheptamer_Intermediate
59	52	47	70	37	72	36	68	41	esp242	↔	esp65	ESP59	Isoheptamer...H2O
60	48	82	44	85	40	80	44	84	esp65	↔	esp66	ESP60	Tetramer_2_branched_reactif_complex
61	0	21	0	14	0	30	0	10	esp62 + esp22	↔	esp67 + esp24	ESP61	Tetramer2branched_Intermediate
62	47	33	45	23	48	24	43	28	esp67	↔	esp68	ESP62	Tetramer2branched_Product
63	59	87	49	85	49	87	56	83	esp68	↔	esp66	ESP63	Tetramer2branched_reactif_complex
64	0	30	0	50	0	66	0	44	esp30 + esp22	↔	esp69 + esp24	ESP64	Isopentamer_reactif_complex
65	52	47	70	37	72	36	68	41	esp69	↔	esp70	ESP65	Isopentamer_Intermediate
66	48	82	44	85	40	80	44	84	esp70	↔	esp71	ESP66	Isopentamer...H2O
67	0	21	0	14	0	30	0	10	esp62 + esp22	↔	esp72 + esp24	ESP67	Isopentamer_reactif_complex
68	47	33	45	23	48	24	43	28	esp72	↔	esp73	ESP68	Isopentamer_Intermediate
69	59	87	49	85	49	87	56	83	esp73	↔	esp71	ESP69	Pentamer2branched_reactif_complex
70	0	30	0	50	0	66	0	44	esp62 + esp22	↔	esp74 + esp24	ESP70	Pentamer2branched_Intermediate
71	52	47	70	37	72	36	68	41	esp74	↔	esp75	ESP71	Pentamer2branched_product
72	48	82	44	85	40	80	44	84	esp75	↔	esp76	ESP72	Pentamer2branched_reactif_complex_v2
73	0	0	0	0	0	0	0	0	esp62 + esp22	↔	esp77 + esp24	ESP73	Pentamer2branched_Intermediate_V2
74	46	31	52	42	48	43	54	39	esp77	↔	esp78	ESP74	2,3Tetramerbranched_reactif_complex
75	25	77	13	63	18	46	35	71	esp78	↔	esp79	ESP75	2,3Tetramerbranched_Intermediate
76	0	21	0	14	0	30	0	10	esp36 + esp22	↔	esp80 + esp24	ESP76	2,3Tetramerbranched...H2O
77	47	33	45	23	48	24	43	28	esp80	↔	esp81	ESP77	2,2Tetramerbranched_reactif_complex
78	59	87	49	85	49	87	56	83	esp81	↔	esp79	ESP78	2,2Tetramerbranched_Intermediate
79	0	21	0	14	0	30	0	10	esp76 + esp22	↔	esp82 + esp24	ESP79	2,2Tetramerbranched_product
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81	59	87	49	85	49	87	56	83	esp83	↔	esp84	ESP81	2,2Tetramerbranched_Intermediate_V2
82	0	30	0	50	0	66	0	44	esp71 + esp22	↔	esp85 + esp24	ESP82	2,3pentamerbranched_reactif_complex
83	52	47	70	37	72	36	68	41	esp85	↔	esp86	ESP83	2,3pentamerbranched_Intermediate
84	48	82	44	85	40	80	44	84	esp86	↔	esp84	ESP84	2,3pentamerbranched...H2O
85	0	30	0	50	0	66	0	44	esp66 + esp22	↔	esp87 + esp24	ESP85	2,3pentamerbranched_reactif_complex-V2
86	52	47	70	37	72	36	68	41	esp87	↔	esp88	ESP86	2,3pentamerbranched_Intermediate_V2
87	48	82	44	85	40	80	44	84	esp88	↔	esp84	ESP87	2,3pentamerbranched_reactif_complex-V3
88	0	21	0	14	0	30	0	10	esp66 + esp22	↔	esp89 + esp24	ESP88	2,3pentamerbranched_Intermediate_V3
89	47	33	45	23	48	24	43	28	esp89	↔	esp90	ESP89	3dimerpentamerbranched_reactif_complex
90	59	87	49	85	49	87	56	83	esp90	↔	esp91	ESP90	3dimerpentamerbranched_Intermediate
91	0	30	0	50	0	66	0	44	esp39 + esp22	↔	esp92 + esp24	ESP91	3dimerpentamerbranched...H2O
92	52	47	70	37	72	36	68	41	esp92	↔	esp93	ESP92	3hexamerbranched_reactif_complex
93	48	82	44	85	40	80	44	84	esp93	↔	esp94	ESP93	3hexamerbranched_Intermediate



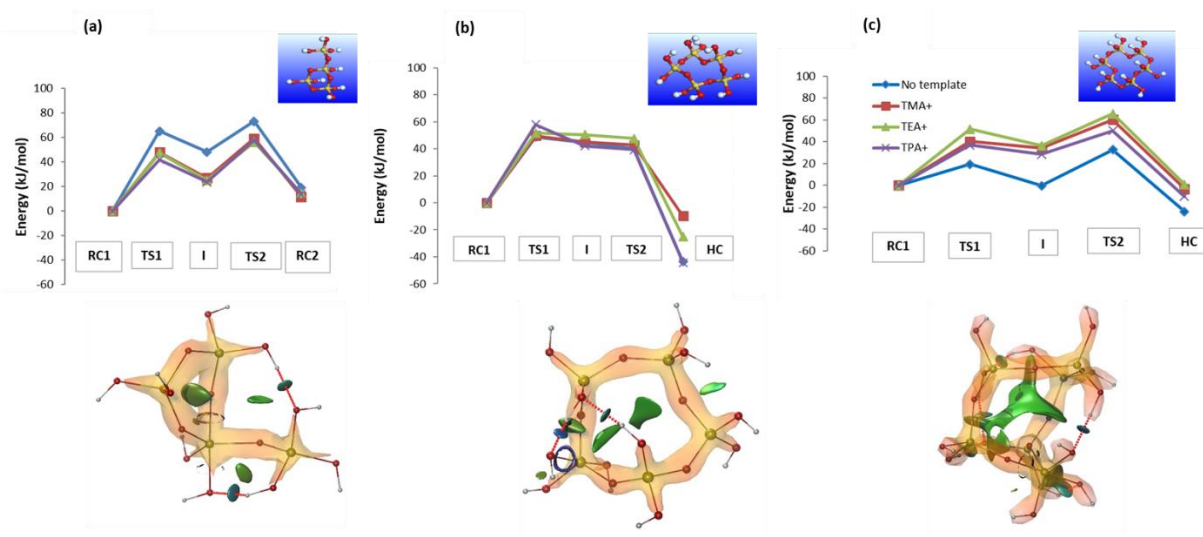
94	0	21	0	14	0	30	0	10	esp71 + esp22	↔	esp95 + esp24	ESP94	3hexamerbranched...H2O
95	47	33	45	23	48	24	43	28	esp95	↔	esp96	ESP95	3hexamerbranched_reactif_complex_V2
96	59	87	49	85	49	87	56	83	esp96	↔	esp94	ESP96	3hexamerbranched_Intermediate_V2
97	0	21	0	14	0	30	0	10	esp66 + esp22	↔	esp97 + esp24	ESP97	3hexamerbranched_reactif_complex_V3
98	47	33	45	23	48	24	43	28	esp97	↔	esp98	ESP98	3hexamerbranched_Intermediate_V3
99	59	87	49	85	49	87	56	83	esp98	↔	esp94	ESP99	2hexamerbranched_reactif_complex
100	0	30	0	50	0	66	0	44	esp39 + esp22	↔	esp99 + esp24	ESP100	2hexamerbranched_Intermediate
101	52	47	70	37	72	36	68	41	esp99	↔	esp100	ESP101	2hexamerbranched...H2O
102	48	82	44	85	40	80	44	84	esp100	↔	esp101	ESP102	2hexamerbranched_reactif_complex_V2
103	0	21	0	14	0	30	0	10	esp71 + esp22	↔	esp102 + esp24	ESP103	2hexamerbranched_Intermediate_V2
104	47	33	45	23	48	24	43	28	esp102	↔	esp103	ESP104	2,3,3Tetramer_reactif_complex
105	59	87	49	85	49	87	56	83	esp103	↔	esp101	ESP105	2,3,3Tetramer_Intermediate
106	0	30	0	50	0	66	0	44	esp79 + esp22	↔	esp104 + esp24	ESP106	2,3,3Tetramer...H2O
107	52	47	70	37	72	36	68	41	esp104	↔	esp105	ESP107	2,3,3Tetramer_reactif_complex_V2
108	48	82	44	85	40	80	44	84	esp105	↔	esp106	ESP108	2,3,3Tetramer_Intermediate_V2
109	0	0	0	0	0	0	0	0	esp76 + esp22	↔	esp107 + esp24	ESP109	4-ring2-(trimer)branched_reactif_complex
110	46	31	52	42	48	43	54	39	esp107	↔	esp108	ESP110	4-ring2-(trimer)branched_Intermediate
111	25	77	13	63	18	46	35	71	esp108	↔	esp106	ESP111	4-ring2-(trimer)branched...H2O
112	0	13	0	18	0	20	0	21	esp84	↔	esp109 + esp24	ESP112	4-ring2-(trimer)branched_reactif_complex_V2
113	28	16	28	15	29	17	25	18	esp109	↔	esp110	ESP113	4-ring2-(trimer)branched_Intermediate_V2
114	48	75	44	79	50	83	57	79	esp110	↔	esp111	ESP114	3,3isopentamerbranched_reactif_complex
115	0	13	0	18	0	20	0	21	esp102	↔	esp112 + esp24	ESP115	3,3isopentamerbranched_Intermediate
116	28	16	28	15	29	17	25	18	esp112	↔	esp113	ESP116	3,3isopentamerbranched...H2O
117	48	75	44	79	50	83	57	79	esp113	↔	esp111	ESP117	3,3isopentamerbranched_reactif_complex_V2
118	0	0	0	0	0	0	0	0	esp66 + esp22	↔	esp114 + esp24	ESP118	3,3isopentamerbranched_Intermediate_V2
119	46	31	52	42	48	43	54	39	esp114	↔	esp115	ESP119	2,2pentamerbranched_reactif_complex
120	25	77	13	63	18	46	35	71	esp115	↔	esp116	ESP120	2,2pentamerbranched_Intermediate
121	0	21	0	14	0	30	0	10	esp79 + esp22	↔	esp117 + esp24	ESP121	2,2pentamerbranched...H2O
122	47	33	45	23	48	24	43	28	esp117	↔	esp118	ESP122	2,2pentamerbranched_reactif_complex_V2
123	59	87	49	85	49	87	56	83	esp118	↔	esp116	ESP123	2,2pentamerbranched_Intermediate_V2
124	0	0	0	0	0	0	0	0	esp71 + esp22	↔	esp119 + esp24	ESP124	2,4pentamerbranched_reactif_complex
125	46	31	52	42	48	43	54	39	esp119	↔	esp120	ESP125	2,4pentamerbranched_Intermediate
126	25	77	13	63	18	46	35	71	esp120	↔	esp121	ESP126	2,4pentamerbranched...H2O
127	0	21	0	14	0	30	0	10	esp79 + esp22	↔	esp122 + esp24	ESP127	3heptamerbranched_reactif_complex
128	47	33	45	23	48	24	43	28	esp122	↔	esp123	ESP128	3heptamerbranched_Intermediate
129	59	87	49	85	49	87	56	83	esp123	↔	esp121	ESP129	3heptamerbranched_reactif_complex_V2
130	0	30	0	50	0	66	0	44	esp71 + esp22	↔	esp124 + esp24	ESP130	3heptamerbranched_Intermediate_V2
131	52	47	70	37	72	36	68	41	esp124	↔	esp125	ESP131	Isoheptamerbranched_reactif_complex
132	48	82	44	85	40	80	44	84	esp125	↔	esp126	ESP132	Isoheptamerbranched_Intermediate
133	0	21	0	14	0	30	0	10	esp94 + esp22	↔	esp127 + esp24	ESP133	Isoheptamerbranched...H2O
134	47	33	45	23	48	24	43	28	esp127	↔	esp128	ESP134	2,4hexamerbranched_reactif_complex
135	59	87	49	85	49	87	56	83	esp128	↔	esp56	ESP135	2,4hexamerbranched_Intermediate
136	0	21	0	14	0	30	0	10	esp101 + esp22	↔	esp129 + esp24	ESP136	2,4hexamerbranched...H2O
137	47	33	45	23	48	24	43	28	esp129	↔	esp130	ESP137	2,4hexamerbranched_reactif_complex_V2
138	59	87	49	85	49	87	56	83	esp130	↔	esp56	ESP138	2,4hexamerbranched_Intermediate_V2
139	0	21	0	14	0	30	0	10	esp94 + esp22	↔	esp131 + esp24	ESP139	3,4hexamerbranched_reactif_complex
140	47	33	45	23	48	24	43	28	esp131	↔	esp132	ESP140	3,4hexamerbranched_Intermediate
141	59	87	49	85	49	87	56	83	esp132	↔	esp133	ESP141	3,4hexamerbranched...H2O

142	0	30	0	50	0	66	0	44	esp47 + esp22	↔	esp239 + esp24	ESP142	4,4hexamerbranched_reactif_complex
143	52	47	70	37	72	36	68	41	esp239	↔	esp240	ESP143	4,4hexamerbranched_Intermediate
144	48	82	44	85	40	80	44	84	esp240	↔	esp133	ESP144	4,4hexamerbranched...H2O
145	0	30	0	50	0	66	0	44	esp101 + esp22	↔	esp134 + esp24	ESP145	4,5hexamerbranched_reactif_complex
146	52	47	70	37	72	36	68	41	esp134	↔	esp135	ESP146	4,5hexamerbranched_Intermediate
147	48	82	44	85	40	80	44	84	esp135	↔	esp136	ESP147	4,5hexamerbranched...H2O
148	0	30	0	50	0	66	0	44	esp94 + esp22	↔	esp137 + esp24	ESP148	2heptamerbranched_reactif_complex
149	52	47	70	37	72	36	68	41	esp137	↔	esp138	ESP149	2heptamerbranched_Intermediate
150	48	82	44	85	40	80	44	84	esp138	↔	esp136	ESP150	2heptamerbranched...H2O
151	0	30	0	50	0	66	0	44	esp94 + esp22	↔	esp139 + esp24	ESP151	2,5hexamerbranched_reactif_complex
152	52	47	70	37	72	36	68	41	esp139	↔	esp140	ESP152	2,5hexamerbranched_Intermediate
153	48	82	44	85	40	80	44	84	esp140	↔	esp141	ESP153	2,5hexamerbranched...H2O
154	0	0	0	0	0	0	0	0	esp94 + esp22	↔	esp142 + esp24	ESP154	4,5hexamerbranched_reactif_complex
155	46	31	52	42	48	43	54	39	esp142	↔	esp143	ESP155	4,5hexamerbranched_Intermediate
156	25	77	13	63	18	46	35	71	esp143	↔	esp144	ESP156	2heptamer-branched_reactif_complex
157	0	30	0	50	0	66	0	44	esp94 + esp22	↔	esp145 + esp24	ESP157	2heptamer-branched_Intermediate
158	52	47	70	37	72	36	68	41	esp145	↔	esp146	ESP158	4-ring2,3branched(3-dimer)_reactif_complex
159	48	82	44	85	40	80	44	84	esp146	↔	esp147	ESP159	4-ring2,3branched(3-dimer)_Intermediate
160	0	21	0	14	0	30	0	10	esp101 + esp22	↔	esp148 + esp24	ESP160	4-ring2,3branched(3-dimer)...H2O
161	47	33	45	23	48	24	43	28	esp148	↔	esp149	ESP161	2,3,4pentamerbranched_reactif_complex
162	59	87	49	85	49	87	56	83	esp149	↔	esp150	ESP162	2,3,4pentamerbranched_Intermediate
163	0	30	0	50	0	66	0	44	esp101 + esp22	↔	esp151 + esp24	ESP163	2,3,4pentamerbranched...H2O
164	52	47	70	37	72	36	68	41	esp151	↔	esp152	ESP164	2,3hexamerbranched_reactif_complex
165	48	82	44	85	40	80	44	84	esp152	↔	esp153	ESP165	2,3hexamerbranched_Intermediate
166	0	30	0	50	0	66	0	44	esp101 + esp22	↔	esp154 + esp24	ESP166	2,3hexamerbranched...H2O
167	52	47	70	37	72	36	68	41	esp154	↔	esp155	ESP167	3,4hexamerbranched_reactif_complex
168	48	82	44	85	40	80	44	84	esp155	↔	esp147	ESP168	3,4hexamerbranched_Intermediate
169	0	30	0	50	0	66	0	44	esp47 + esp22	↔	esp156 + esp24	ESP169	(3)trimerisopentamer_reactif_complex
170	52	47	70	37	72	36	68	41	esp156	↔	esp157	ESP170	(3)trimerisopentamer_Intermediate
171	48	82	44	85	40	80	44	84	esp157	↔	esp150	ESP171	(3)trimerisopentamer...H2O
172	0	13	0	18	0	20	0	21	esp84	↔	esp158 + esp24	ESP172	4-ring2branched,3(trimer)branched_reactif_complex
173	28	16	28	15	29	17	25	18	esp158	↔	esp159	ESP173	4-ring2branched,3(trimer)branched_Intermediate
174	48	75	44	79	50	83	57	79	esp159	↔	esp160	ESP174	4-ring2branched,3(trimer)branched...H2O
175	0	30	0	50	0	66	0	44	esp84 + esp22	↔	esp161 + esp24	ESP175	4-ring2branched,3(trimer)branched_reactif_complex_V2
176	52	47	70	37	72	36	68	41	esp161	↔	esp162	ESP176	4-ring2branched,3(trimer)branched_Intermediate_V2
177	48	82	44	85	40	80	44	84	esp162	↔	esp163	ESP177	2,3dimerbranched4-ring_reactif_complex
178	0	21	0	14	0	30	0	10	esp84 + esp22	↔	esp164 + esp24	ESP178	2,3dimerbranched4-ring_Intermediate
179	47	33	45	23	48	24	43	28	esp164	↔	esp165	ESP179	2,3dimerbranched4-ring...H2O
180	59	87	49	85	49	87	56	83	esp165	↔	esp166	ESP180	2,3dimerbranched4-ring_reactif_complex_V2
181	0	21	0	14	0	30	0	10	esp84 + esp22	↔	esp167 + esp24	ESP181	2,3dimerbranched4-ring_Intermediate_v2
182	47	33	45	23	48	24	43	28	esp167	↔	esp168	ESP182	2branched3trimerbranched4ring_reactif_complex
183	59	87	49	85	49	87	56	83	esp168	↔	esp141	ESP183	2branched3trimerbranched4ring_Intermediate
184	0	21	0	14	0	30	0	10	esp84 + esp22	↔	esp169 + esp24	ESP184	2branched3trimerbranched4ring...H2O
185	47	33	45	23	48	24	43	28	esp169	↔	esp170	ESP185	1,2branched3dimer4-ring_reactif_complex
186	59	87	49	85	49	87	56	83	esp170	↔	esp171	ESP186	1,2branched3dimer4-ring_Intermediate
187	0	21	0	14	0	30	0	10	esp160 + esp22	↔	esp172 + esp24	ESP187	1,2branched3dimer4-ring...H2O
188	47	33	45	23	48	24	43	28	esp172	↔	esp173	ESP188	2,4branched3dimer4-ring_reactif_complex
189	59	87	49	85	49	87	56	83	esp173	↔	esp174	ESP189	2,4branched3dimer4-ring_Intermediate

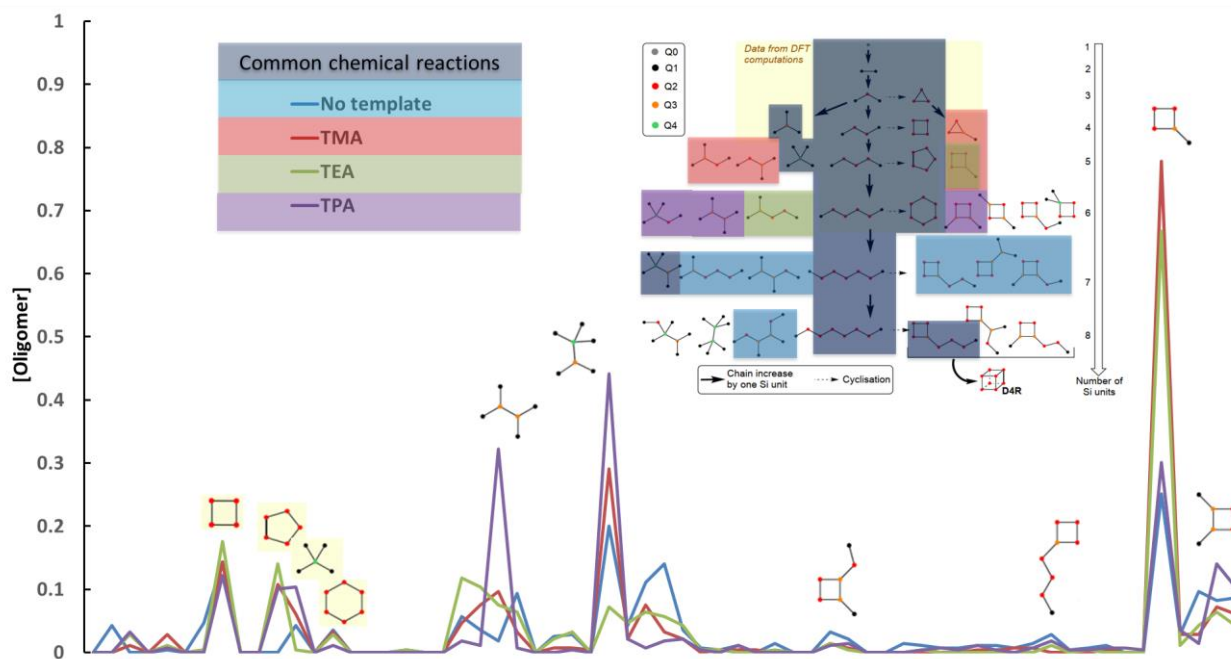
190	0	13	0	18	0	20	0	21	esp166	↔	esp175 + esp24	ESP190	2,4branched3dimer4-ring...H2O
191	28	16	28	15	29	17	25	18	esp175	↔	esp176	ESP191	4-ring2trimer4branched_reactif_complex
192	48	75	44	79	50	83	57	79	esp176	↔	esp174	ESP192	4-ring2trimer4branched_Intermediate
193	0	21	0	14	0	30	0	10	esp160 + esp22	↔	esp177 + esp24	ESP193	4-ring2trimer4branched...H2O
194	47	33	45	23	48	24	43	28	esp177	↔	esp178	ESP194	4-ring2tetramerbranched_reactif_complex
195	59	87	49	85	49	87	56	83	esp178	↔	esp179	ESP195	4-ring2tetramerbranched_Intermediate
196	0	13	0	18	0	20	0	21	esp169	↔	esp180 + esp24	ESP196	4-ring2tetramerbranched...H2O
197	28	16	28	15	29	17	25	18	esp180	↔	esp181	ESP197	4-ring2trimer3branched_reactif_complex
198	48	75	44	79	50	83	57	79	esp181	↔	esp179	ESP198	4-ring2trimer3branched_Intermediate
199	0	30	0	50	0	66	0	44	esp160 + esp22	↔	esp182 + esp24	ESP199	4-ring2trimer3branched...H2O
200	52	47	70	37	72	36	68	41	esp182	↔	esp183	ESP200	4-ring2tetramer_reactif_complex
201	48	82	44	85	40	80	44	84	esp183	↔	esp184	ESP201	4-ring2tetramer_Intermediate
202	0	30	0	50	0	66	0	44	esp160 + esp22	↔	esp185 + esp24	ESP202	4-ring2tetramer...H2O
203	52	47	70	37	72	36	68	41	esp185	↔	esp186	ESP203	4-ring2tetramer_reactif_complex_V2
204	48	82	44	85	40	80	44	84	esp186	↔	esp187	ESP204	4-ring2tetramer_Intermediate_V2
205	0	30	0	50	0	66	0	44	esp160 + esp22	↔	esp188 + esp24	ESP205	2,2bishexamerbranched_reactif_complex
206	52	47	70	37	72	36	68	41	esp188	↔	esp189	ESP206	2,2bishexamerbranched_Intermediate
207	48	82	44	85	40	80	44	84	esp189	↔	esp190	ESP207	2,2bishexamerbranched...H2O
208	0	30	0	50	0	66	0	44	esp111 + esp22	↔	esp191 + esp24	ESP208	2,2,3pentamerbranched_reactif_complex
209	52	47	70	37	72	36	68	41	esp191	↔	esp192	ESP209	2,2,3pentamerbranched_Intermediate
210	48	82	44	85	40	80	44	84	esp192	↔	esp193	ESP210	2,2,3pentamerbranched...H2O
211	0	0	0	0	0	0	0	0	esp111 + esp22	↔	esp194 + esp24	ESP211	2,3,3pentamerbranched_reactif_complex
212	46	31	52	42	48	43	54	39	esp194	↔	esp195	ESP212	2,3,3pentamerbranched_Intermediate
213	25	77	13	63	18	46	35	71	esp195	↔	esp196	ESP213	2,3,3pentamerbranched...H2O
214	0	30	0	50	0	66	0	44	esp111 + esp22	↔	esp197 + esp24	ESP214	2,2branched3(dimer)branched4-ring_reactif_complex
215	52	47	70	37	72	36	68	41	esp197	↔	esp198	ESP215	2,2branched3(dimer)branched4-ring_Intermediate
216	48	82	44	85	40	80	44	84	esp198	↔	esp199	ESP216	2,2branched3(dimer)branched4-ring...H2O
217	0	21	0	14	0	30	0	10	esp111 + esp22	↔	esp200 + esp24	ESP217	2,3branched3(dimer)branched4-ring_reactif_complex
218	47	33	45	23	48	24	43	28	esp200	↔	esp201	ESP218	2,3branched3(dimer)branched4-ring_Intermediate
219	59	87	49	85	49	87	56	83	esp201	↔	esp202	ESP219	2,3branched3(dimer)branched4-ring...H2O
220	0	21	0	14	0	30	0	10	esp169	↔	esp203 + esp24	ESP220	4-ring2branched_reactif_complex
221	47	33	45	23	48	24	43	28	esp203	↔	esp204	ESP221	4-ring2branched_Intermediate
222	59	87	49	85	49	87	56	83	esp204	↔	esp202	ESP222	4-ring2branched...H2O
223	0	0	0	0	0	0	0	0	esp101 + esp22	↔	esp205 + esp24	ESP223	4-ring2branched_reactif_complex_V2
224	46	31	52	42	48	43	54	39	esp205	↔	esp206	ESP224	4-ring2branched_Intermediate_V2
225	25	77	13	63	18	46	35	71	esp206	↔	esp207	ESP225	4-ring2branched_reactif_complex_V3
226	0	0	0	0	0	0	0	0	esp84 + esp22	↔	esp208 + esp24	ESP226	4-ring2branched_Intermediate_V3
227	46	31	52	42	48	43	54	39	esp208	↔	esp209	ESP227	2,4bis4-ringbranched_reactif_complex
228	25	77	13	63	18	46	35	71	esp209	↔	esp210	ESP228	2,4bis4-ringbranched_Intermediate
229	0	0	0	0	0	0	0	0	esp84 + esp22	↔	esp211 + esp24	ESP229	2,4bis4-ringbranched...H2O
230	46	31	52	42	48	43	54	39	esp211	↔	esp212	ESP230	2(Dimer)4-ringbranched_reactif_complex
231	25	77	13	63	18	46	35	71	esp212	↔	esp213	ESP231	2(Dimer)4-ringbranched_Intermediate
232	0	0	0	0	0	0	0	0	esp160 + esp22	↔	esp214 + esp24	ESP232	2(Dimer)4-ringbranched_Intermediate...H2O
233	46	31	52	42	48	43	54	39	esp214	↔	esp215	ESP233	1,2-4-ringbranched_reactif_complex
234	25	77	13	63	18	46	35	71	esp215	↔	esp216	ESP234	1,2-4-ringbranched_Intermediate
235	0	0	0	0	0	0	0	0	esp160 + esp22	↔	esp217 + esp24	ESP235	1,2-4-ringbranched...H2O
236	46	31	52	42	48	43	54	39	esp217	↔	esp218	ESP236	2,4-4-ringbranched_reactif_complex
237	25	77	13	63	18	46	35	71	esp218	↔	esp219	ESP237	2,4-4-ringbranched_Intermediate

238	0	30	0	50	0	66	0	44	esp18 + esp22	↔	esp220 + esp24	ESP238	2,4-4-ringbranched...H2O
239	52	47	70	37	72	36	68	41	esp220	↔	esp221	ESP239	Isoheptamerbranched_reactif_complex_V2
240	48	82	44	85	40	80	44	84	esp221	↔	esp222	ESP240	Isoheptamerbranched_Intermediate_V2
241	0	13	0	18	0	20	0	21	esp62	↔	esp223 + esp24	ESP241	H2O_bis
242	28	16	28	15	29	17	25	18	esp223	↔	esp224	ESP242	Isopentamer_reactif_complex
243	48	75	44	79	50	83	57	79	esp224	↔	esp222		
244	0	13	0	18	0	20	0	21	esp30	↔	esp225 + esp24		
245	28	16	28	15	29	17	25	18	esp225	↔	esp226		
246	48	75	44	79	50	83	57	79	esp226	↔	esp222		
247	0	0	0	0	0	0	0	0	esp222 + esp22	↔	esp227 + esp24		
248	46	31	52	42	48	43	54	39	esp227	↔	esp228		
249	25	77	13	63	18	46	35	71	esp228	↔	esp229		
250	0	21	0	14	0	30	0	10	esp222 + esp22	↔	esp230 + esp24		
251	47	33	45	23	48	24	43	28	esp230	↔	esp231		
252	59	87	49	85	49	87	56	83	esp231	↔	esp232		
253	0	30	0	50	0	66	0	44	esp222 + esp22	↔	esp233 + esp24		
254	52	47	70	37	72	36	68	41	esp233	↔	esp234		
255	48	82	44	85	40	80	44	84	esp234	↔	esp235		
256	0	30	0	50	0	66	0	44	esp222 + esp22	↔	esp236+ esp24		
257	52	47	70	37	72	36	68	41	esp236	↔	esp237		
258	48	82	44	85	40	80	44	84	esp237	↔	esp238		

**Table S2:** Complete list of equilibrium reactions for extended reaction pathway (until 8 Si atoms). First column corresponds to the ID number of each reaction considered. Columns two to nine corresponds to the activation barriers (in kJ.mol<sup>-1</sup>) of forward and backward reactions for no-templates and TMA<sup>+</sup>, TEA<sup>+</sup> and TPA<sup>+</sup> templates. Columns ten to twelve corresponds to the details of the reactions including the id of species as used in SPARKS code. Columns thirteen and fourteen corresponds to the ID code and name of the species considered in the study.



**Figure S5:** Energy barriers profiles and NCI Analysis (Intermediate state) for cyclic oligomerisation process (Scheme 1) without and with templates (TEA+, TMA+ and TPA+). Colours represents different type of non-covalent interactions: H-bonds (blue); vdW (green). We observe that the release water mechanism is fully dependent of cyclic oligomers size. It is thus difficult to predict the energy barriers with BEP models for cyclic species.



**Figure S6:** Steady state concentrations (in  $\text{mmol}\cdot\text{L}^{-1}$ ) of major chemical species calculated by kMC with the full-extended chemical reaction pathway (Scheme 2). **In the top right:** an extract of the full-extended chemical reaction pathway with the effect of the different templates on the reactions. In black colour: the common chemical reactions shared by all templates, blue colour: no template specific reactions, red colour: TMA specific reactions, green colour: TEA specific reactions, purple colour: TPA specific reactions.



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