Electronic Supplementary Material (ESI) for Dalton Transactions.

Unexpected formation of ansa isomers enabled by phosphazene ring flexibility in the reactions of cyclotetraphosphazene with 1,2-ethanediol

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Table S1 Selected bond lengths (Å), bond angles (°) and conformational parameters for compounds **4A** and **4B**.

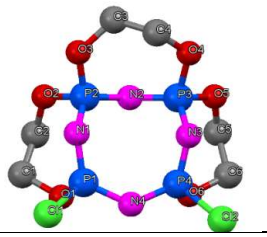
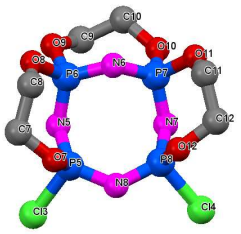
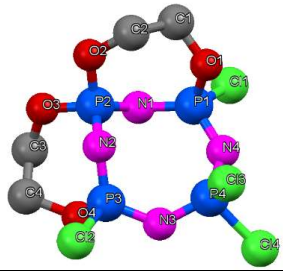
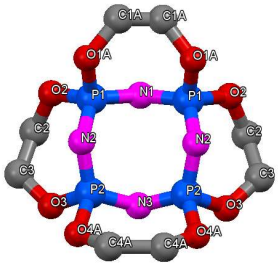
			
4-A		**4-B**	
P1-N1	1.562(3)	**P5-N5**	1.566(3)
P2-N2	1.576(3)	**P6-N6**	1.571(3)
P3-N3	1.585(3)	**P7-N7**	1.583(3)
P4-N4	1.560(3)	**P8-N8**	1.562(3)
N1-P2	1.586(3)	**N5-P6**	1.584(3)
N2-P3	1.581(3)	**N6-P7**	1.579(3)
N3-P4	1.569(3)	**N7-P8**	1.562(3)
N4-P1	1.564(3)	**N8-P5**	1.562(3)
O---O (avg.)	3.204	**O---O (avg.)**	3.201
Cl--Cl	5.231	**Cl--Cl**	5.212
P1-N1-P2	123.02(18)	**P5-N5-P6**	123.16(17)
P2-N2-P3	124.20(17)	**P6-N6-P7**	123.75(17)
P3-N3-P4	121.05(16)	**P7-N7-P8**	120.86(17)
P4-N4-P1	129.29(19)	**P8-N8-P5**	129.39(19)
N1-P2-N2	118.53(14)	**N5-P6-N6**	116.93(14)
N2-P3-N3	116.76(14)	**N6-P7-N7**	118.85(15)
N3-P4-N4	121.50(15)	**N7-P8-N8**	120.27(15)
N4-P1-N1	122.15(16)	**N8-P5-N5**	123.11(15)
P1-N1-P2-N2	-49.1(3)	**P5-N5-P6-N6**	51.3(3)
P2-N2-P3-N3	56.1(2)	**P6-N6-P7-N7**	-58.4(2)
P3-N3-P4-N4	-88.4(2)	**P7-N7-P8-N8**	87.4(2)
P4-N4-P1-N1	-28.9(4)	**P8-N8-P5-N5**	27.6(4)
N1-P2-N2-P3	-55.0(3)	**N5-P6-N6-P7**	52.6(3)
N2-P3-N3-P4	48.4(2)	**N6-P7-N7-P8**	-45.8(2)
N3-P4-N4-P1	33.8(3)	**N7-P8-N8-P5**	-34.3(3)
N4-P1-N1-P2	80.8(3)	**N8-P5-N5-P6**	159.02(17)
Selected Conformational Parameters			
Puckering amplitude, Q, for eight membered ring	1.176(3)	1.180(3)	
Max. Deviation (Å) phosphazene ring	-0.646(3) (N2)	-0.633(3) (N7)	

Table S2. Table S2 Selected bond lengths (Å), bond angles (°) and conformational parameters for compounds **3** and **5**.

			
3		**5**	
P1-N1	1.548(17)	**P1-N1**	1.571(3)
P2-N2	1.570(18)	**P1-N2**	1.570(5)
P3-N3	1.566(19)	**P2-N3**	1.569(3)
P4-N4	1.58(2)	**N1-P1**	1.571(3)
N1-P2	1.612(17)	**N2-P2**	1.577(4)
N2-P3	1.597(17)		
N3-P4	1.53(2)		
N4-P1	1.537(19)		
O---O (avg.)	3.142	**O---O (avg.)**	3.236
Cl---Cl (avg.)	5.296		
P1-N1-P2	121.4(10)	**P1-N1-P1**	121.7(3)
P2-N2-P3	122.1(10)	**P1-N2-P2**	120.2(3)
P3-N3-P4	129.1(14)	**P2-N3-P2**	120.9(3)
P4-N4-P1	134.6(18)	**N1-P1-N2**	118.9(2)
N1-P2-N2	114.6(9)	**N2-P2-N3**	119.7(2)
N2-P3-N3	119.8(10)		
N3-P4-N4	123.0(11)		
N4-P1-N1	122.4(12)	**P1-N1-P1-N2**	-51.7(5)
P1-N1-P2-N2	-55.7(16)	**P1-N2-P2-N3**	50.8(4)
P2-N2-P3-N3	87.2(16)	**N1-P1-N2-P2**	-50.8(4)
P3-N3-P4-N4	-56(2)	**N2-P2-N3-P2**	51.1(5)
P4-N4-P1-N1	-37(3)		
N1-P2-N2-P3	-50.2(15)		
N3-P4-N4-P1	39(3)		
N4-P1-N1-P2	82.6(17)	***Symmetry code#***	*1-x,y,z*
Selected Conformational Parameters			
Puckering amplitude, Q, for eight membered ring	1.07(2)	1.474(5)	
Max. Deviation (Å) phosphazene ring	-0.40(3) (N3)	-0.740(5) (N2/N2A)	

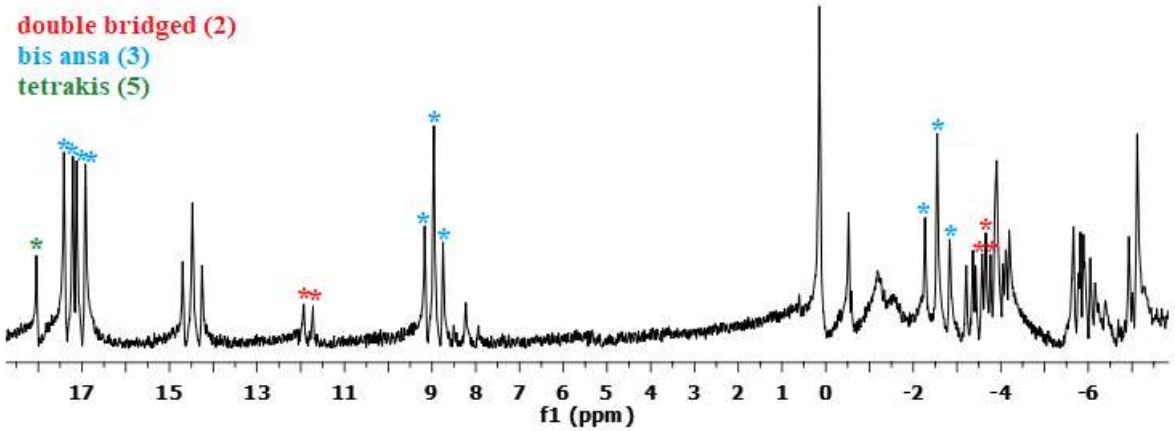


Figure S1. Proton-decoupled ^{31}P NMR spectrum of the reaction mixture (1:6 ratio).

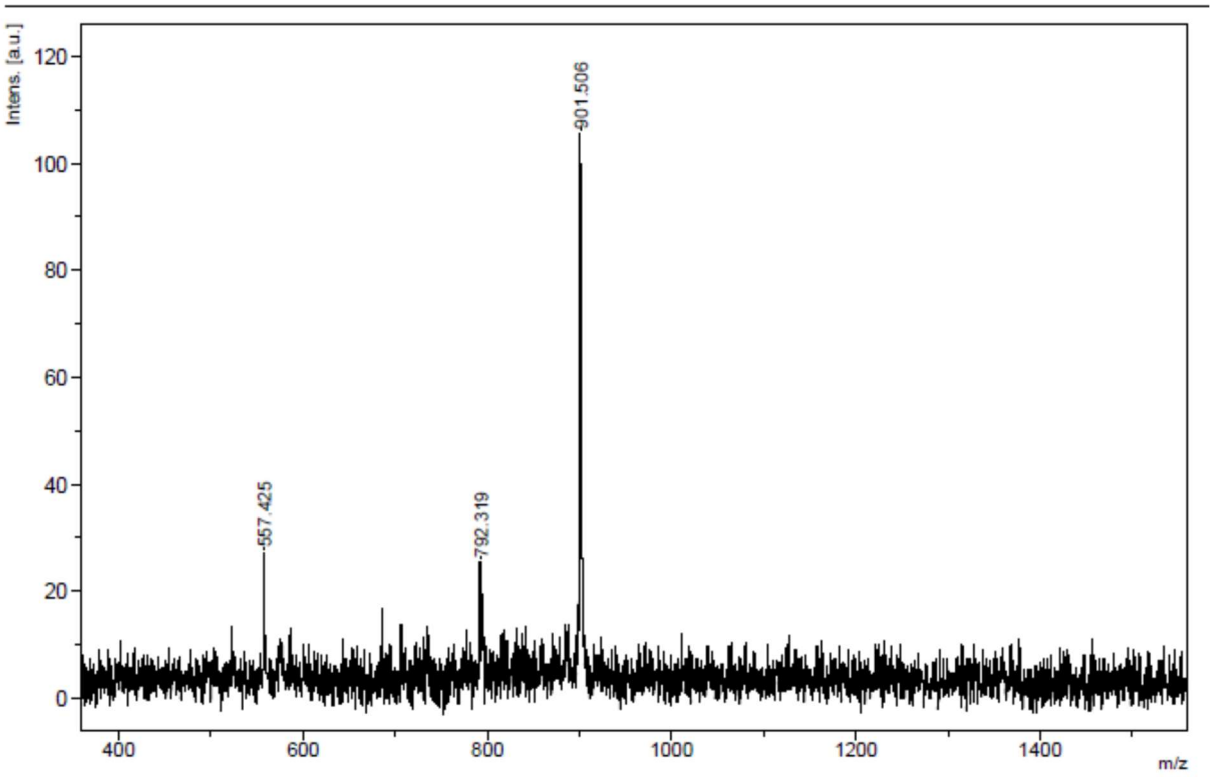


Figure S2. Mass spectrum of the compound **2**.

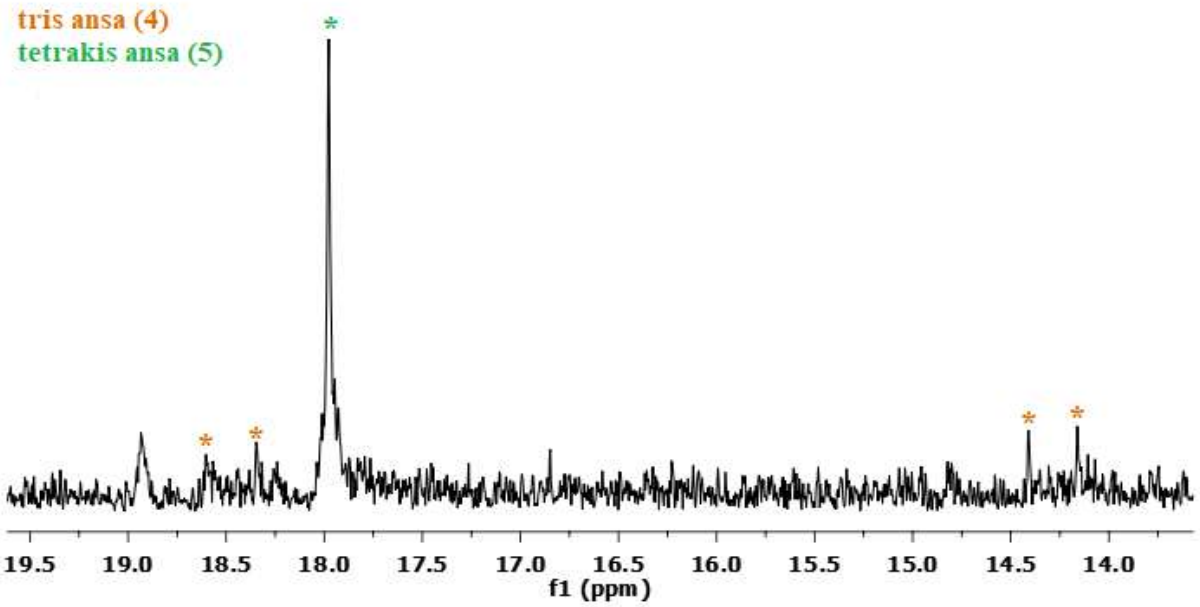


Figure S3. Proton-decoupled ^{31}P NMR spectrum of the reaction mixture (1:10 ratio).

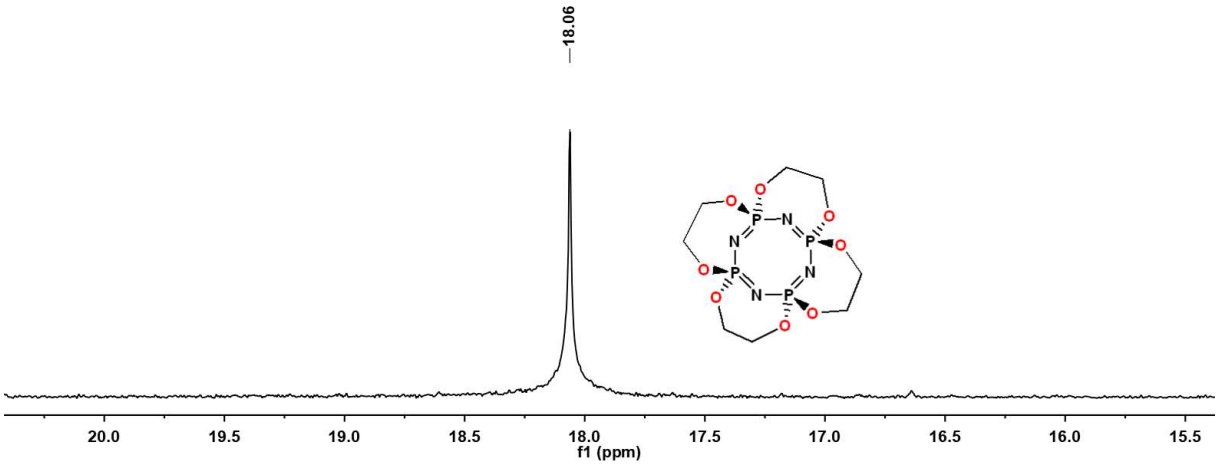


Figure S4. Proton-decoupled ^{31}P NMR A_4 type spectrum of compound **5**.

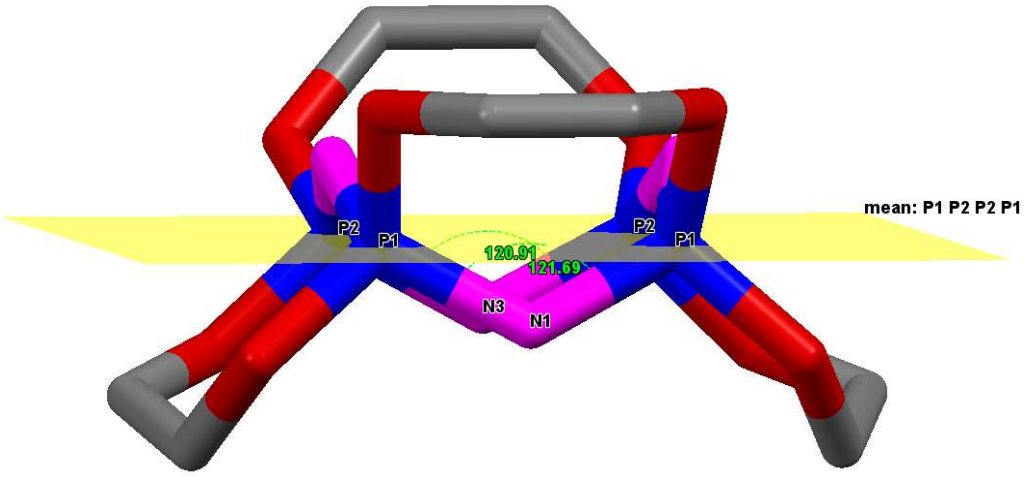


Figure S5. The arrangement of phosphorus atoms in the same plane and the representation of P-N-P angles in compound **5**.

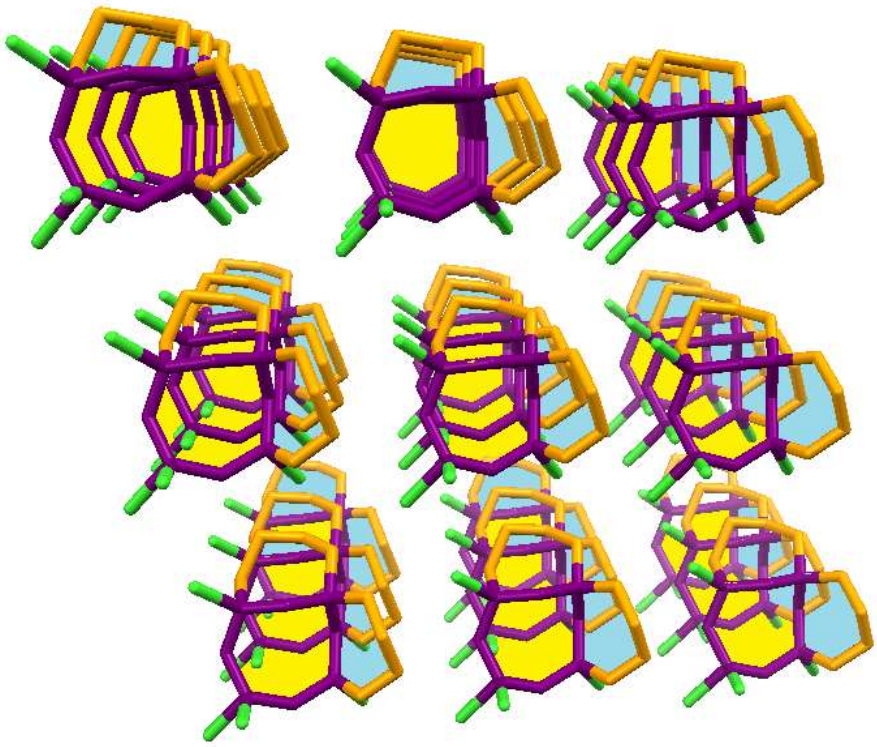


Figure S6. Perspective view in compound **3**; $(PN)_4$ ring was shown as purple color and ansa rings were depicted orange color. The space created by the $(PN)_4$ ring is marked in yellow, and the spaces created by the ansa rings are marked with turquoise.