SUPPLEMENTARY INFORMATION

Reaction of compound (3) with sodium phenoxide to form 1,1-(2'-amino-1'-ethoxy)-3-phenoxy-3,5,5-trichlorocyclotriphos-phazene (8a)

Compound (**3**)[5] (3.36 g, 10 mmol) and phenol (0.847 g, 9 mmol) were dissolved in 150 mL of dry THF in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.36 g, 9 mmol) in 10 mL of dry THF quickly added to the stirred solution under an argon atmosphere. The reaction mixture was stirred for a further 20 h at room temperature and the reaction was followed by TLC on silica gel plates using THF-hexane (1:2). The reaction mixture was filtered to remove sodium chloride, the solvent was removed under reduced pressure and the resulting colourless oil subjected to column chromatography using THF-hexane (1:2) as eluant. The product was crystallized from dichloromethane-hexane (1:4) to give white crystals of (**8a**) (yield 1.82 g, 46%, mp 146^{0}C), found: C, 24.47; H, 2.58; N, 14.10%; M, 392. $C_8H_{10}Cl_3N_4O_2P_3$ requires: C, 24.42; H, 2.56; N, 14.24%; M, 392. ^{1}H NMR ($CDCl_3$ solution): δ 4.38 (m, 4H, $POCH_2$), 7.26 (m, 1H p-OC_6H_5), 7.30 (m, 2H m-OC_6H_5), 7.38 (m, 2H o-OC_6H_5).

Reaction of compound (3) with pyrrolidine to form 1,1-(2'-amino-1'-ethoxy)-3-pyrrolidino-3,5,5-trichlorocyclotri-phosphazene (8b)

Pyrrolidine (0.426 g, 6 mmol in 20 ml of dry THF) was added dropwise from an addition funnel to a solution to compound (**3**)[5] (1.011 g, 3 mmol) dissolved in 20 mL of dry THF in a 100 mL three-necked round-bottomed flask and the reaction was stirred for 24 h at room temperature. The reaction mixture was then filtered, the solvent was removed under reduced pressure and the resulting colourless oil subjected to column chromatography using dichloromethane-hexane (1:1) as eluent. The oily product was crystallized from dichloromethane to give white crystals of (**8b**) (yield 0.4g, 36%, mp 178^{0}C), found: C, 19.44; H, 3.58; N, 18.87 %; M, 371. $C_6H_{13}Cl_3N_5OP_3$ requires: C, 19.45; H, 3.54; N, 18.90 %; M, 369. ^{1}H NMR ($CDCl_3$ solution): δ 1.89 (m, 4H, CH_2), 2.80 (broad d, 1H, NH), 3.26 (m, 2H, $NHCH_2$), 3.51 (m, 4H, $PNCH_2$), 4.40 (m, 2H, $POCH_2$).

Reaction of compound (4) with sodium phenoxide to form 1,1-(ethane-1',2'-dioxy)-3-phenoxy-3,5,5-trichlorocyclotriphosphazene (8e).

Compound (**4**)[1] (0.5 g, 1.48 mmol) and phenol (0.14 g, 1.48 mmol) were dissolved in 30 mL of dry THF in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.06 g, 1.48 mmol) in 10 mL of dry THF quickly added to the stirred solution under an argon atmosphere. The reaction mixture was stirred for a further 18 h at room temperature and the reaction was followed by TLC on silica gel plates using THF-hexane (3:1). The reaction mixture was filtered to remove sodium chloride, the solvent was removed under reduced pressure and the resulting colourless oil subjected to column chromatography using THF-hexane (3:1) as eluant. The product was crystallized from dichloromethane-light petroleum ether (40-60^{0}C) (2:5) to give white crystals of (**8e**) (yield 0.42 g, 72%, mp 142^{0}C), found: C, 24.40; H, 2.27; N, 10.42%; M, 393. $C_8H_9Cl_3N_3O_3P_3$ requires: C, 24.36; H, 2.30; N, 10.65%; M, 393. ^{1}H NMR ($CDCl_3$ solution): δ 4.38 (m, 4H, POCH2), 7.08-7.32 (m, 5H OC6H5).

Reaction of compound (4) with pyrrolidine to form 1,1-(ethane-1',2'-dioxy)-3-pyrrolidino-3,5,5-trichlorocyclotriphosphazene (8f).

Compound (**4**)[1] (0.5 g, 1.48 mmol) dissolved in 20 mL of dry THF in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.06 g, 1.48 mmol) in 10 mL of dry THF quickly added to the stirred solution under an argon atmosphere. Pyrrolidine (0.11 g, 1.48 mmol in 20 ml of dry THF) was added dropwise from an addition funnel to the solution and the reaction was stirred for a futher 24 h at room temperature. The reaction mixture was then filtered, the solvent was removed under reduced pressure and the resulting colourless oil subjected to column chromatography using dichloromethane-hexane (3:1) as eluent. The oily product was crystallized from dichloromethane to give white crystals of (**8f**) (yield 1.2 g, 22%, mp 143^{0}C), found: C, 19.44; H, 3.22; N, 15.01%; M, 369. $C_6H_{12}Cl_3N_4O_2P_3$ requires: C, 19.40; H, 3.26; N, 15.08%; M, 370. ^{1}H NMR ($CDCl_3$ solution): δ 1.89 (m, 4H, CH_2), 3.17 (m, 4H, $PNCH_2$), 4.30 (m, 4H, $POCH_2$).

X-ray crystallography

X-ray structure data were collected by means of combined phi and omega scans on a Bruker-Nonius KappaCCD area detector situated at the window of a rotating anode (λMo-k_α = 0.71073Å). The structures were solved by direct methods, SHELXS-97 and refined using SHELXL-97.[22] Hydrogen atoms were included in the refinement, but thermal parameters and geometry were constrained to ride on the atom to which they are bonded. The data were corrected for absorption effects using SORTAV.[23] The diffraction pattern arising from the crystal of **8c** examined was found to be a 180° rotation twin about the b axis. The data were integrated as two separate overlapping components and the structure refined against both these components using a batch scale factor to determine the relative contribution (which was found to be 47.6:52.4).

Table S1 Crystal data and refinement parameters for (**6a**), (**8a-c**), (**8e-f**)

	6a	**8a**	**8b**	**8c**	**8e**	**8f**
Empirical formula	$C_{10}H_{22}Cl_2N_3O_7P_3$	$C_8H_{10}Cl_3N_4O_2P_3$	$C_6H_{13}Cl_3N_5OP_3$	$C_3H_7Cl_3N_3O_3P_3$	$C_8H_9Cl_3N_3O_3P_3$	$C_6H_{12}Cl_3N_4O_2P_3$
Formula weight	460.12	393.46	370.47	332.38	394.44	371.46
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	7.9956(2)	17.2569(12)	8.231(3)	8.7423(4)	8.5409(2)	9.6475(2)
b (Å)	15.7971(5)	11.0110(8)	17.426(3)	8.0657(5)	17.1394(3)	8.1876(2)
c (Å)	14.8388(4)	7.9969(4)	9.8503(16)	17.2362(10)	10.6213(3)	17.5451(4)
α (°)	90	90	90	90	90	90
β (°)	101.751(2)	96.470(6)	94.76(3)	96.165(4)	109.5880(10)	98.544(2)
γ (°)	90	90	90	90	90	90
Volume (Å^3)	1834.97(9)	1509.86(17)	1408.1(7)	1208.34(12)	1464.83(6)	1370.50(5)
Z	4	4	4	4	4	4
Density (calc) (Mg/m^3)	1.666	1.731	1.748	1.827	1.789	1.800
Absorption coefficient (mm^{-1})	0.654	0.929	0.986	1.145	0.961	1.017
F(000)	952	792	752	664	792	752
Crystal size (mm)	0.14 × 0.08 × 0.06	0.20 × 0.18 × 0.04	0.16 × 0.14 × 0.03	0.50 × 0.15 × 0.01	0.20 × 0.10 × 0.02	0.50 × 0.20 × 0.20
θ_{max} (°)	27.47	27.50	27.50	27.49	27.50	27.50
Reflections collected	24562	22583	18678	2685	19576	12031
Independent reflections	4192	3453	3220	2685	3352	3115
R(int)	0.0446	0.0381	0.0799	0.0776	0.0397	0.0274
Final R indices $F^2>2\sigma F^2$	R1 = 0.0358 wR2 = 0.0805	R1 = 0.0850 wR2 = 0.2306	R1 = 0.0890 wR2 = 0.1635	R1 = 0.0983 wR2 = 0.2467	R1 = 0.0307 wR2 = 0.0760	R1 = 0.0256 wR2 = 0.0638
Δρ max / min (eÅ^{-3})	0.654 / –0.415	1.594 / –0.800	0.507 / –0.569	1.415 / –0.771	0.357 / –0.469	0.353 / –0.412

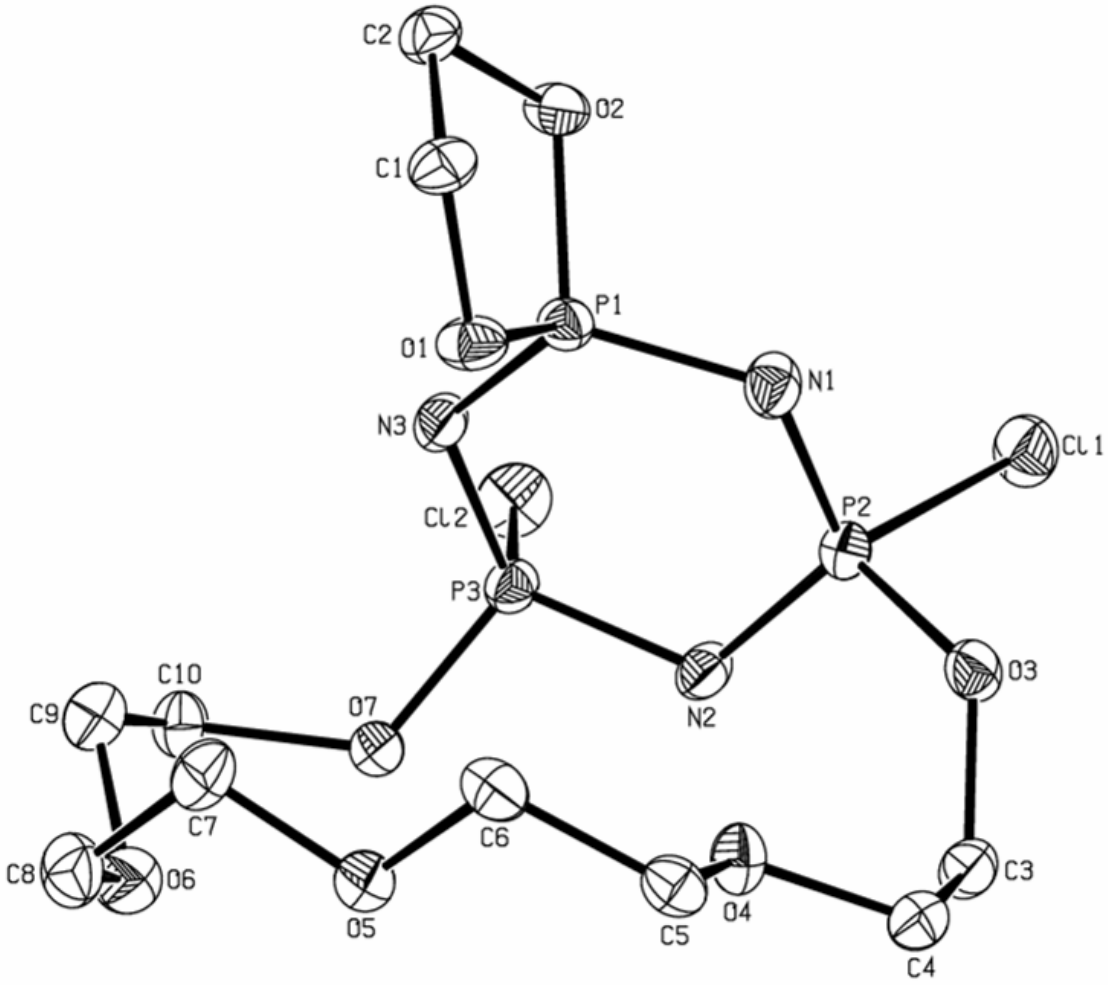

Figure S1. Crystal structure of compound (**6a**) is plotted at 50% probability.

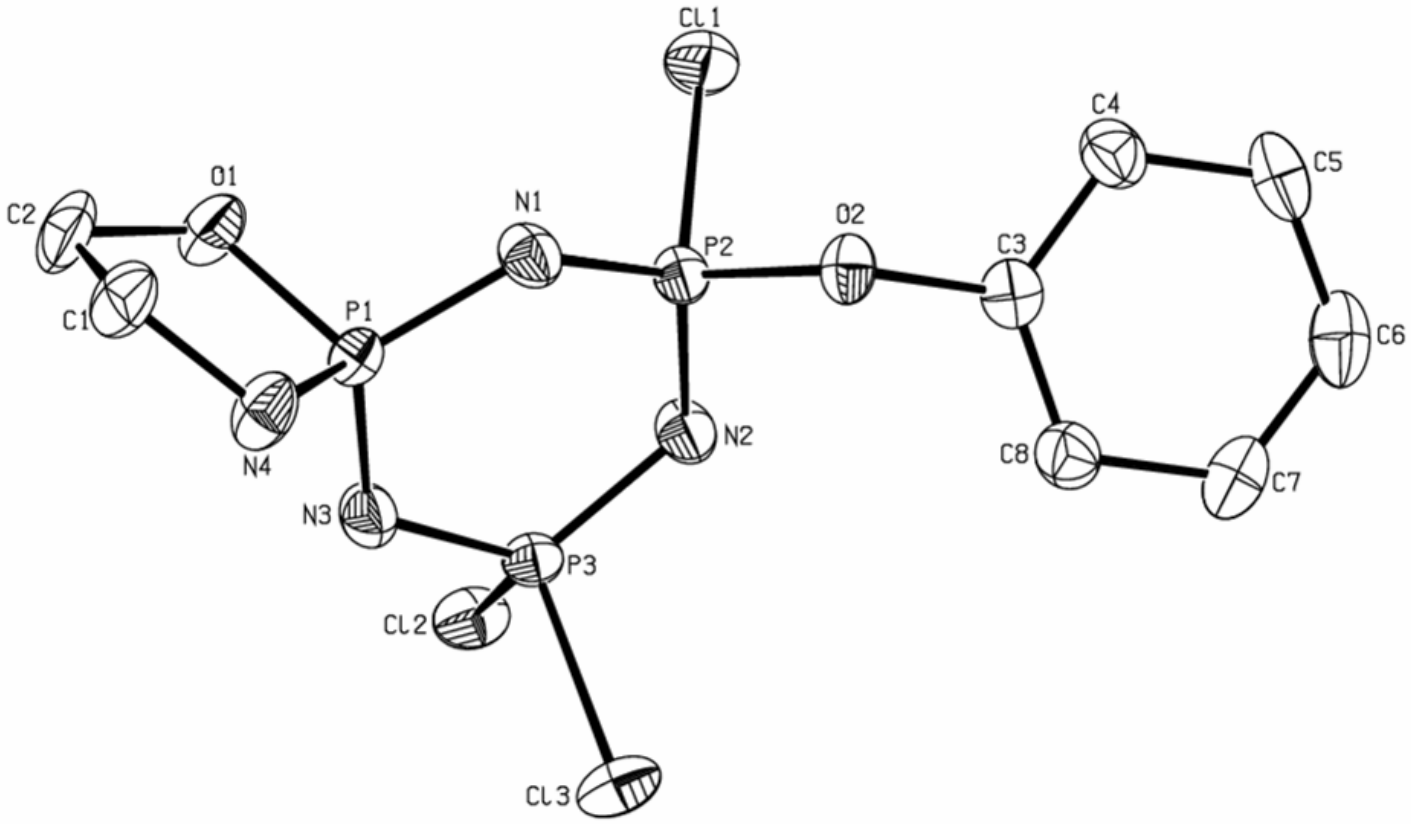

Figure S2. Crystal structure of compound (**8a**) is plotted at 50% probability.

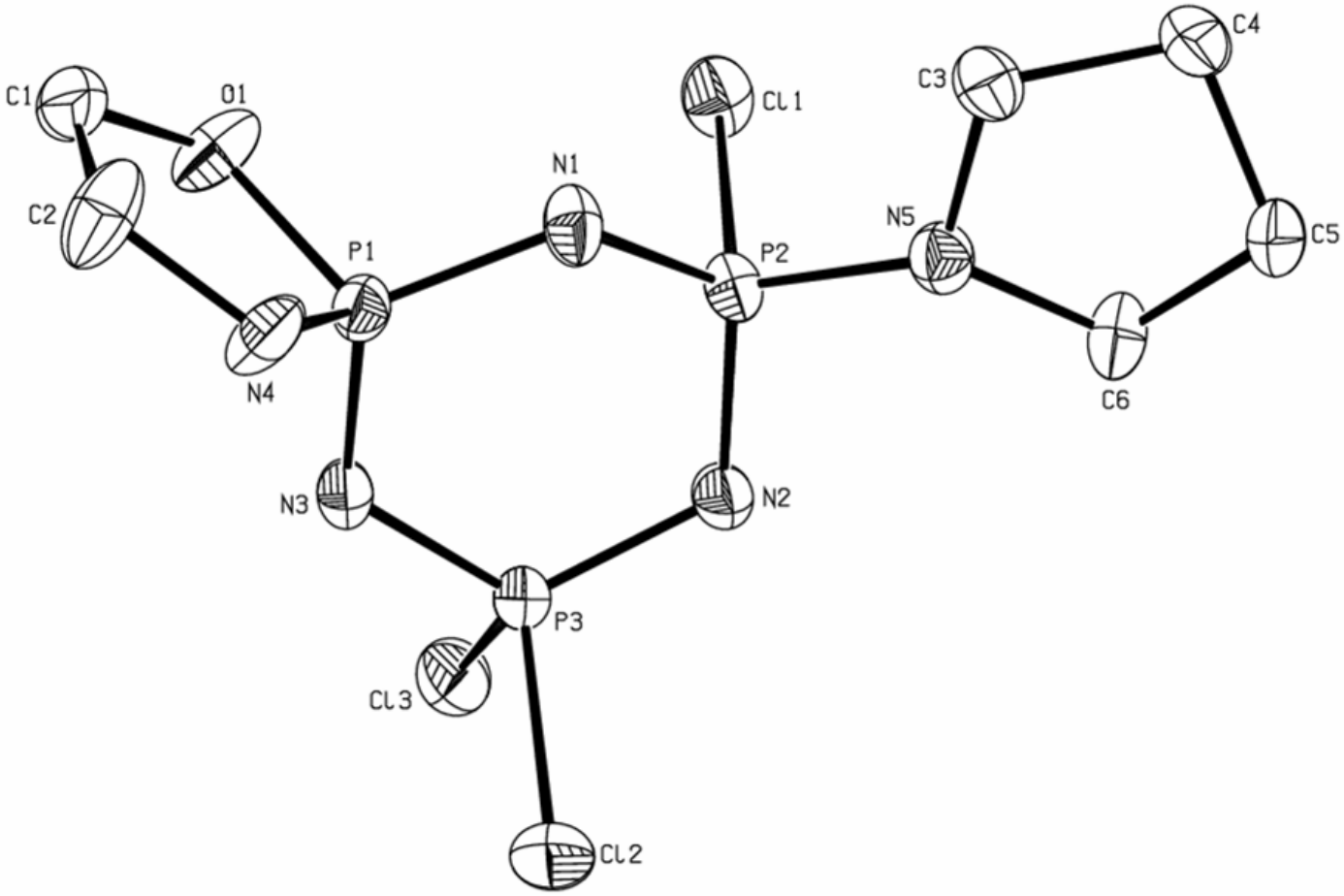

Figure S3. Crystal structure of compound (**8b**) is plotted at 50% probability.

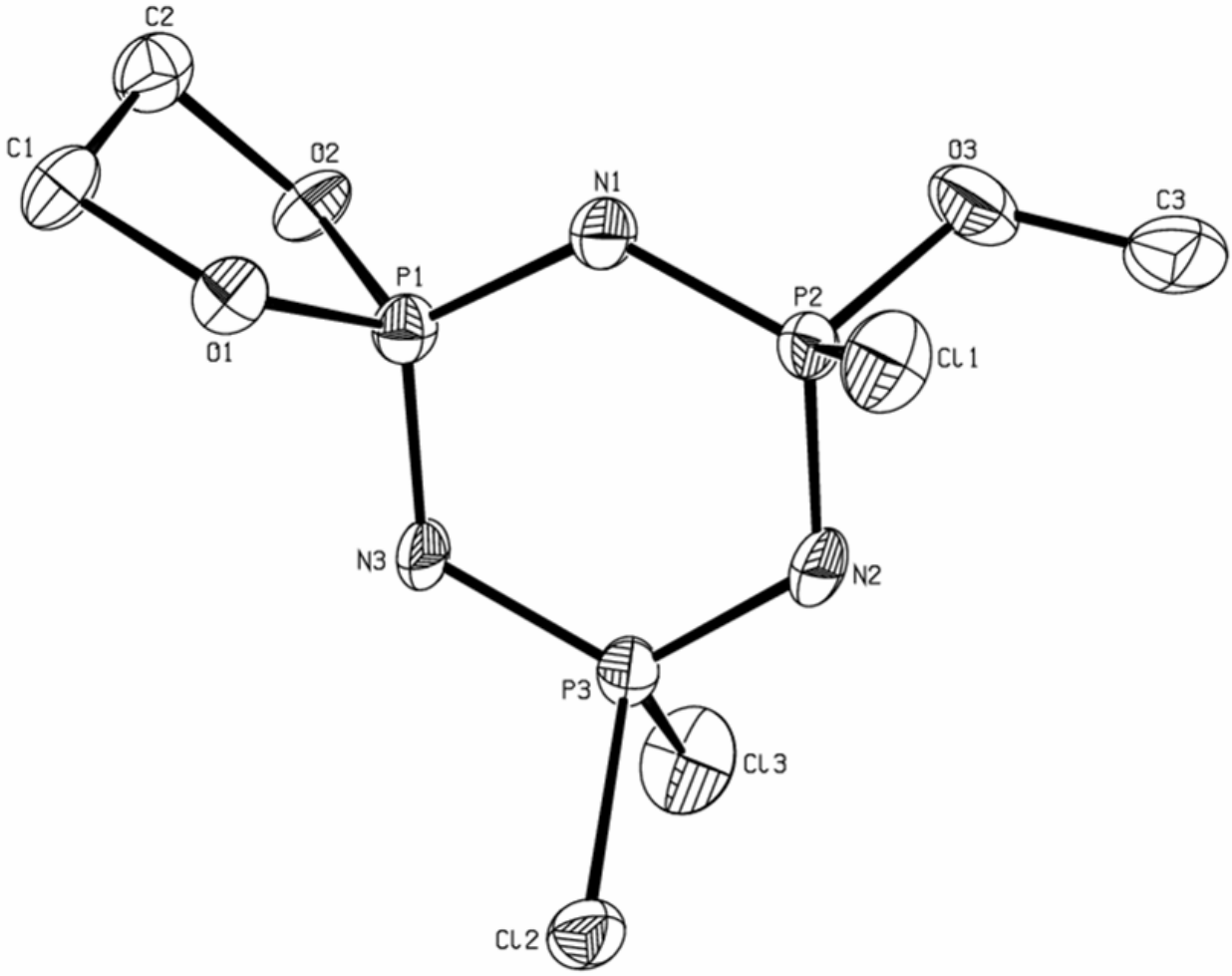

Figure S4. Crystal structure of compound (**8c**) is plotted at 50% probability.

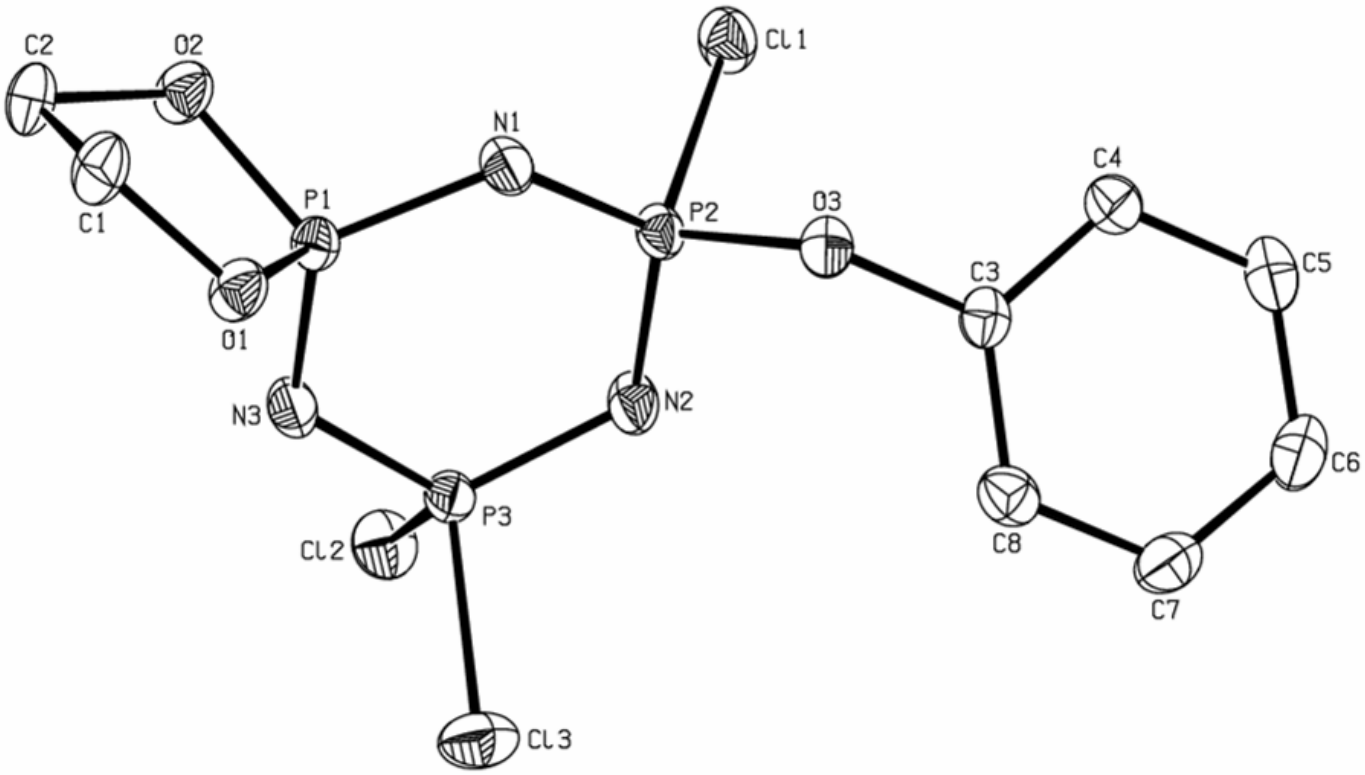

Figure S5. Crystal structure of compound (**8e**) is plotted at 50% probability.

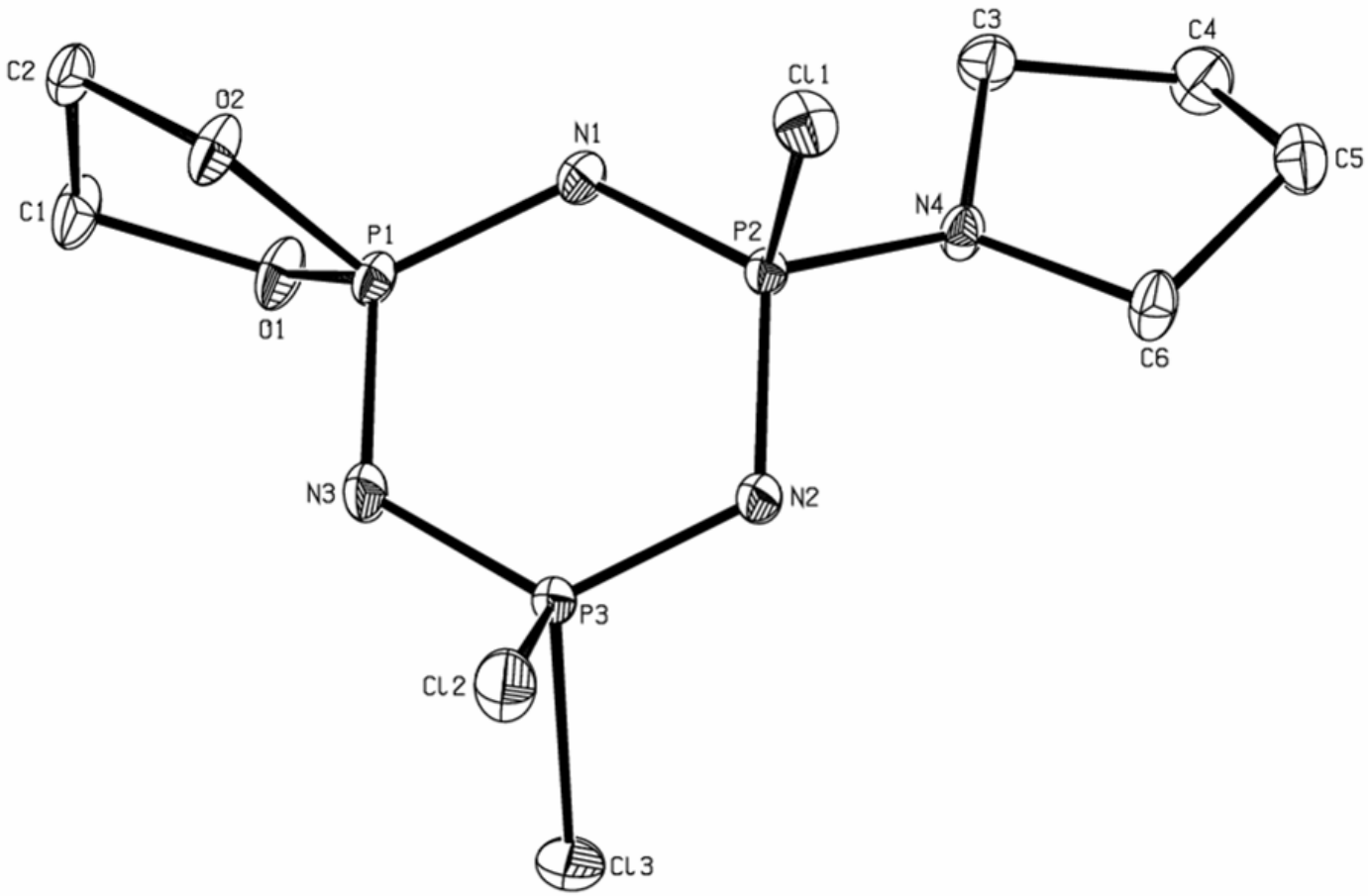

Figure S6. Crystal structure of compound (**8f**) is plotted at 50% probability.