SUPPLEMENTARY DATA

Appendix A.

Preparation of compound **2b**: Compound (**2a**) (Labarre, *et al.*1984) (3g, 3.98 mmol) and phenol (4.49g, 47.8 mmol) were dissolved in 100 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, 1.91g, 47.8 mmol) in 50 mL of dry THF was quickly added under an argon atmosphere. The reaction was stirred for a further 30 days (in order to obtain full substitution and reasonable yield) at room temperature and was monitored by TLC on silica gel plates using CH_2Cl_2: ethyl acetate (12:1) as eluent. The reaction mixture was filtered to remove the sodium chloride, the THF removed under reduced pressure and the resulting oily crude subjected to column chromatography using CH_2Cl_2: ethyl acetate (12:1). Compound **(2b)** was isolated as white powder and crystallized from dichloromethane:ethylacetate:hexane (2:1:1) to give colourless crystals m.p. 120-121°C (yield 0.88 g, 18.2%). Analysis: Found: C, 57.02; H, 5.63; N, 11.06 %; M^+, 1212.9 $C_{58}H_{62}N_{10}O_8P_6$ requires: C, 57.43; H, 5.15; N, 11.55 %; M, 1213.

Preparation of compound **2c:** Compound (**2a**) (Labarre, *et al.*1984) (1g, 1.33 mmol) and 1,3-propanediol (0.405 g, 5.32 mmol) were dissolved in 50 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, 0.25 g, 10.6 mmol) in 50 mL of dry THF was quickly added under an argon atmosphere. The reaction was stirred for 21 h at room temperature and was monitored by TLC on silica gel plates using $CHCl_3$:ethyl acetate (3:1) as eluent. The reaction mixture was filtered to remove the sodium chloride, the THF removed under reduced pressure and the resulting white solid subjected to column chromatography using $CHCl_3$-ethyl acetate (3:1). The compound **(2c)** was isolated as a white powder and recrystallised from chloroform:hexane (1:1) to give colourless crystals, m.p. >250°C (yield: 0.33 g. 32%). Analysis: Found: C, 34.35; H, 6.2; N, 17.68. $(M+H)^+$, 764. $C_{22}H_{46}N_{10}O_8P_6$ requires: C, 34.56; H, 6.06; N, 18.32 M^+, 764.52.

Preparation of compound **2d**: 2,2-Dichloro-4,4,6,6-tetraphenylcyclotriphosphazene, m.p. 142-143°C (Acock *et al.*, 1964) (2g, 4 mmol), triethylamine (1.62 g,16 mmol) and 100 mL of chloroform were placed in a 500 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and spermine (0.81 g, 4 mmol) in 100 mL of chloroform was added under an argon atmosphere. The reaction was stirred for 2 h at room temperature and then refluxed 11 days and monitored by TLC on silica gel plates using CH_2Cl_2:THF

(15:1) as eluent. The reaction mixture was filtered to remove the triethylammonium chloride, the solvent removed under reduced pressure and the resulting reddish solid subjected to column chromatography. Two compounds were isolated, one of which, using dichloromethane as eluent was the starting material, the other using CH_2Cl_2:THF (15:1) as eluent was the product (**2d**). This was crystallised from dichloromethane:benzene (2:1) to give colourless crystals m.p. 208°C. (Yield 0.15 g, 3.45%). Analysis: Found: C, 64.05; H, 5.60; N, 12.25 $(M+H)^+$, 1084. $C_{58}H_{62}N_{10}P_6$ requires: C, 64.20; H, 5.76; N, 12.91 M^+, 1085.05.

Preparation of compound **2e:** Compound **(2a)** (Labarre, *et al.*1984) (1g, 1.33 mol) and excess of aniline (8.15g, 87.6 mmol) were refluxed for 5 h in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled to room temperature and then 100 mL of distilled water was added. The aqueous solution was extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, the solids removed by filtration and the solvent was then partially removed under reduced pressure. The products were precipitated on addition of 200 mL hexane and the precipitate was filtered. This purple solid was subjected to column chromatography using dichloromethane-ethyl acetate (1:1) as eluent. Two fractions were obtained. The first was isolated as a white powder (mp: 236 ^{o}C) (yield: 0.3g, 18.7%), the second as a white powder and this was recrystallized from dichloromethane-hexane (1:1) to give colourless crystals, mp: >250°C (yield: 0.2g, 12.3%). Analysis: *Found:* C, 56,47; H, 3.7; N, 19.74 %M^+, 1205.4 $C_{58}H_{70}N_{18}P_6$ *requires:* C,57.8; H, 5.85; N, 20.92 %M, 1205.17.

Preparation of compound **2f:** Compound **(2a)** (Labarre, *et al.*1984) (1g, 1.33 mol) and excess of pyrrolidine (2.4g, 30 mmol) in 50 mL of dry THF were refluxed for 48 h in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled to room temperature and 100 mL of distilled water was added. Compound **(2f)** was extracted from the aqueous solution with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4, the solids removed by filtration and the THF partially removed under reduced pressure. A yellowish solid was isolated and recrystallized from CH_2Cl_2:nitromethane (2:1) to give colourless crystals, mp = 250°C (yield: 0.48g, 35%). Analysis: *Found:* C, 49.46; H, 7.98; N, 24.01 %M^+, 1029.12 $C_{42}H_{86}N_{18}P_6$ *requires:* C, 49.02; H, 8.42; N, 24.50 %M, 1028.

Preparation of compound **2g:** 2,2-Dichloro-4,4,6,6-tetra-t-butylaminocyclotriphosphazene (Das *et al.*,1965) *(*4.5 g, 9.1 mmol), spermine (1.84 g, 9.1 mmol), triethylamine (3.68 g, 36 mmol) and 80 ml benzene in a 250 ml three-necked round-bottomed flask were refluxed 5 days and the reaction was followed by TLC on silica gel plates using CH_2Cl_2:THF (2:1). The reaction mixture was filtered

to remove the triethylammonium chloride, the solvent removed under reduced pressure and the resulting white solid subjected to column chromatography. Compound **(2g)** was isolated as a white powder and crystallized from dichloromethane:hexane (1:1) to give colourless crystals, m.p. 168-171°C (yield 0.9 g, 10%,). Analysis: Found: C, 47.98; H, 9.45; N, 23.89 %; M^{+}, 1045.5. $C_{42}H_{102}N_{18}P_{6}$ requires: C, 48.26; H, 9.84; N, 24.12 %; M, 1045.