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## **SYNTHESIS AND CHARACTERIZATION OF SOME TETRACYCLIC SPERMINE DERIVATIVES OF CYCLOTRIPHOSPHAZENE: THE FIRST EXAMPLES OF DISPIRANSA DERIVATIVES**

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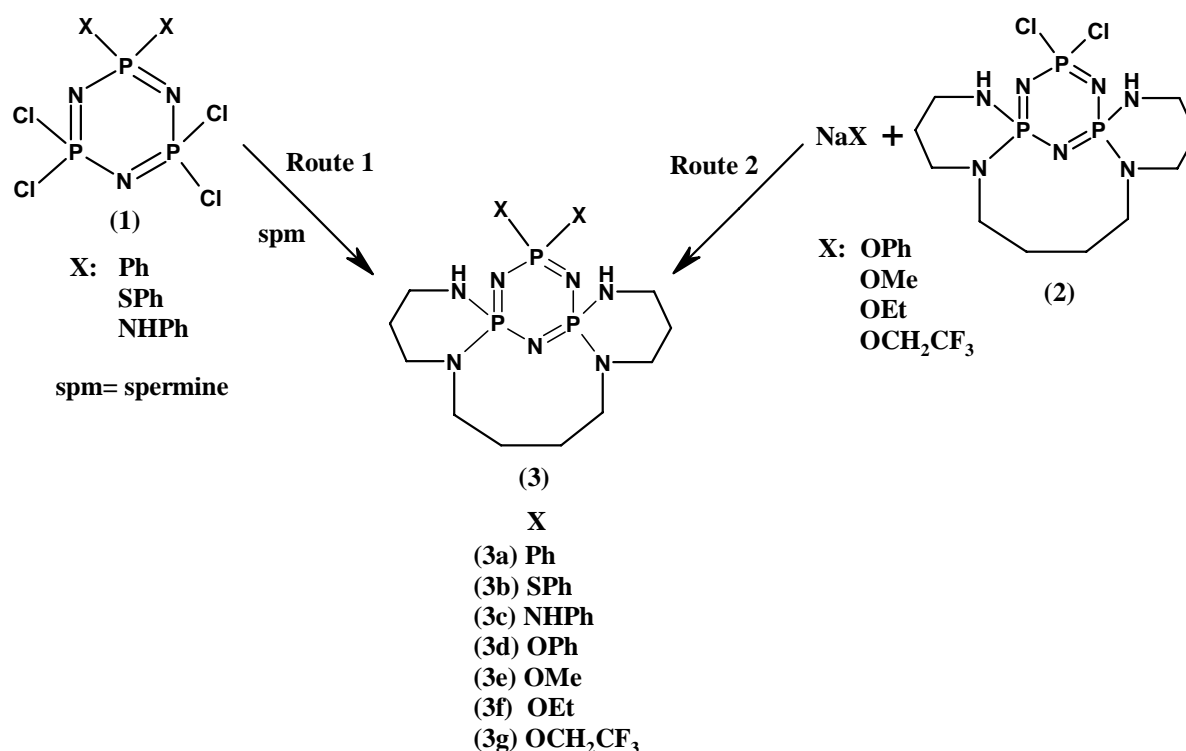
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**Abstract** – The synthesis and characterization is reported of a series of dispiransa cyclophosphazene derivatives based on the known compound  $N_3P_3X_2[HN(CH_2)_3N(CH_2)_4N(CH_2)_3NH]$ , (**2**) (where  $X = Cl$ ), to give a number of new compounds (**3a–g**) in which  $X = Ph, PhS, PhNH, PhO, MeO, EtO, CF_3CH_2O$ , respectively. Two synthetic routes were utilized: (i) reaction of spermine with the appropriate disubstituted cyclophosphazenes (**1**) to give compounds (**3a–c**) and (ii) using the chloro-precursor (**2**) in nucleophilic substitution reactions with nucleophiles to give compounds (**3d–g**). The structures of the compounds were determined by elemental analysis, mass spectrometry,  $^1H$  and  $^{31}P$  NMR spectroscopy.

## **INTRODUCTION**

The cyclophosphazenes probably are the best known and most intensively studied phosphorus-nitrogen compounds. Although a large number of cyclic phosphazenes with monofunctional or difunctional groups have been prepared and studied,<sup>1</sup> studies on a substitution with tetrafunctional group are relatively limited in the literature. The reactions of hexachlorocyclotriphosphazene,  $N_3P_3Cl_6$ , with the tetra-functional biogenic amine, spermine (spm), in aprotic solvents give rise to bridged dimer,  $[N_3P_3Cl_4(NHCH_2CH_2CH_2N)CH_2CH_2]_2$ ,<sup>2</sup> but in protic solvents such as  $CHCl_3$  give only a monomeric tetracyclic derivative,  $N_3P_3Cl_2(spm)$ .<sup>3</sup> During the last two decades, the reactions of bridged dimer,  $[N_3P_3Cl_4(NHCH_2CH_2CH_2N)CH_2CH_2]_2$ , with monofunctional and difunctional groups have been extensively studied.<sup>4</sup> A focus of recent work on bridged cyclophosphazenes has been given into the investigation of their stereogenic properties by X-ray crystallography and NMR spectroscopy.<sup>5</sup> To our

best knowledge, no reaction using compound (2) with any reagents has been carried out yet. But, the crystal structure of the compound (2) has been investigated. Compound (2), 2,2-dichloro-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatricyclohexadeca-2,4,6-triene, has a tetracyclic structure.<sup>3</sup> So, in this paper; we report the first examples of syntheses of novel tetracyclic derivatives (3a-g) using compounds (1) and (2) as a starting material. Two synthetic routes were utilized: (i) reaction of spermine with the appropriate disubstituted cyclophosphazenes (1) to give compounds (3a-c) (Route 1 in scheme 1) and (ii) using the chloro-precursor (2) in nucleophilic substitution reactions with nucleophiles to give compounds (3d-g) (Route 2 in scheme 1). The reaction of cyclophosphazenes with the monofunctional reagents (Ph, PhSH, PhNH<sub>2</sub>) give predominantly geminal products, whereas monofunctional alcohols (PhOH, EtOH, MeOH and CF<sub>3</sub>CH<sub>2</sub>OH) give predominantly nongeminal products.<sup>1b,6,7</sup> Therefore, route 1 was used to obtain compounds (3a-3c) and route 2 was used to obtain compounds (3d-g).

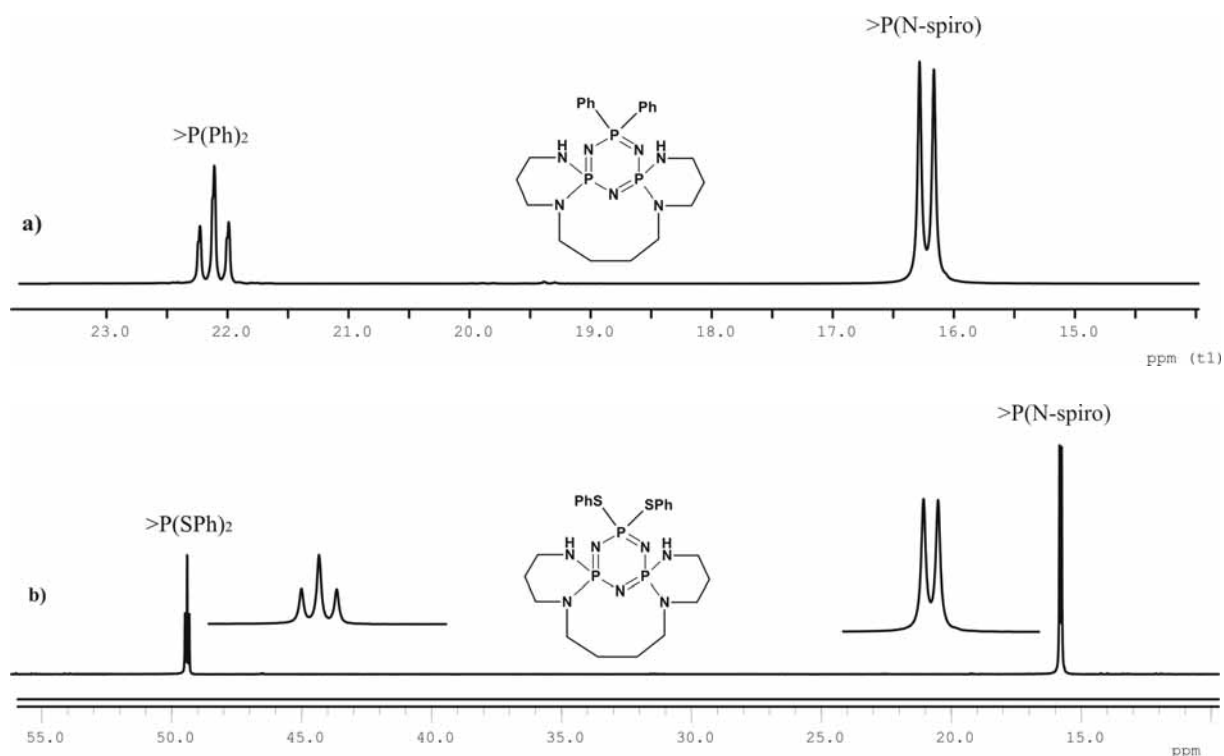


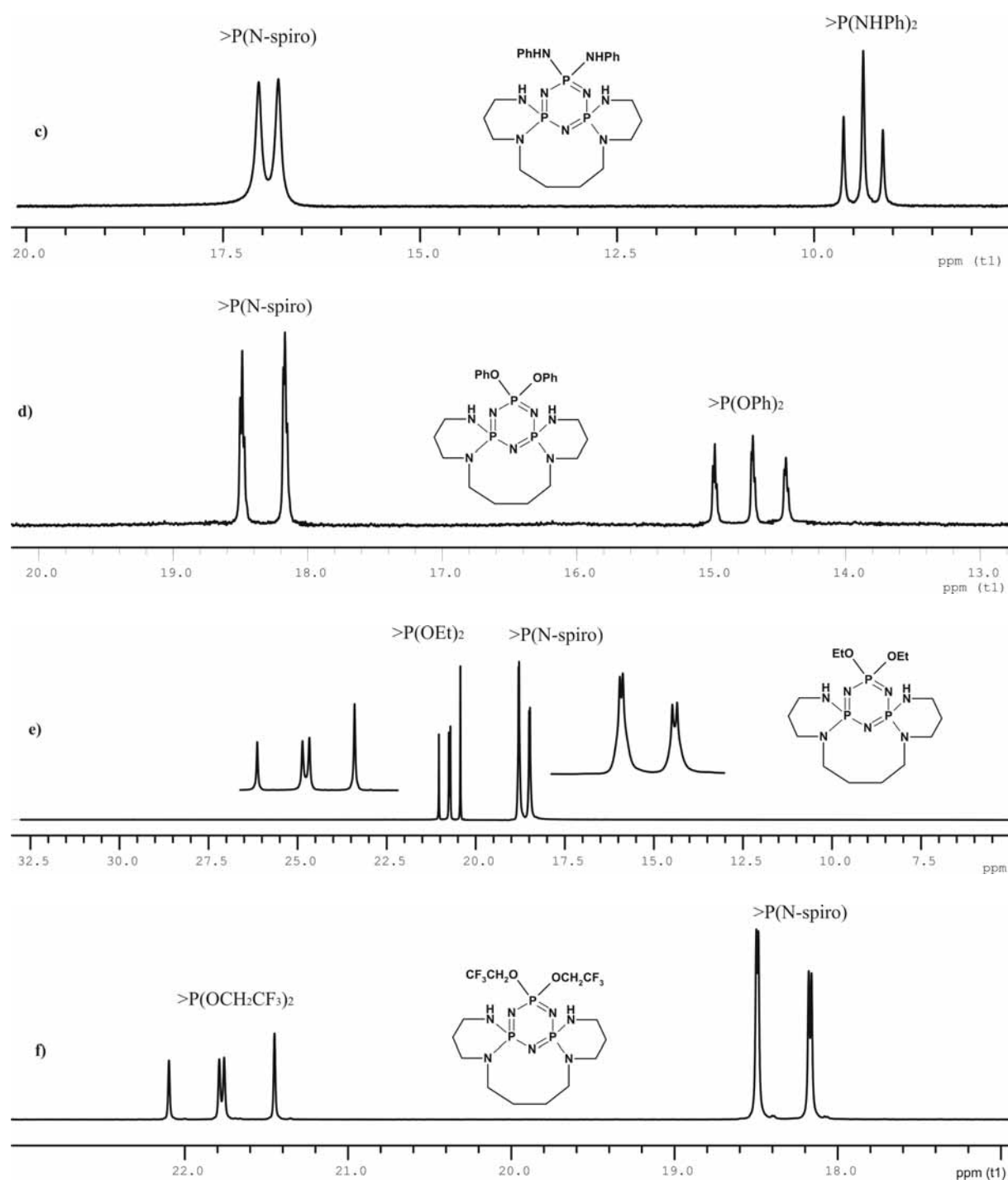
**Scheme 1**

## RESULTS AND DISCUSSION

Route 1 starts with di-substituted chlorocyclophosphazenes, N<sub>3</sub>P<sub>3</sub>Cl<sub>4</sub>X<sub>2</sub>, (1) {X= Ph, SPh, NHPH}, which react with spermine to give hexa-substituted derivatives, N<sub>3</sub>P<sub>3</sub>X<sub>2</sub>(spm) (3a-c). In these reactions,

only  $\text{CHCl}_3$  was used as a reaction medium and no apolar solvents were used because they may give rise to spermine-bridged compounds.<sup>5b</sup> In route 2, in presence of sodium hydride the compound (**2**), 2,2-dichloro-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatricyclohexadeca-2,4,6-triene, reacts with two molar equivalents of PhOH, MeOH, EtOH or  $\text{CF}_3\text{CH}_2\text{OH}$  giving rise to the compounds (**3d-g**) in THF. The structures of the compounds (**3a-g**) were determined by  $^1\text{H}$  and  $^{31}\text{P}$  NMR, mass spectrometry and elemental analysis are consistent with the proposed structures. The results are given in the experimental section. Compounds **2**, **3e** and **3g** are white crystals, however compounds **3a**, **3b**, **3c**, **3d** and **3f** are viscous oils. The proton decoupled  $^{31}\text{P}$  NMR spectra of compounds (**3a-g**) show that the nucleophiles had replaced the chlorine atoms of the  $\text{PCl}_2$  group. These compounds have  $\text{AX}_2$ ,  $\text{A}_2\text{X}$  or  $\text{AB}_2$  spin systems due to two different phosphorus environment within the molecules. The characteristic chemical shifts for the  $\text{P}(\text{Nspiro})$  in hexa-substituted  $\text{N}_3\text{P}_3\text{X}_2(\text{spm})$  appear at 15-19 ppm. But, chemical shifts for the  $\text{PX}_2$  ( $\text{X} = \text{Ph}, \text{PhS}, \text{PhNH}, \text{PhO}, \text{MeO}, \text{EtO}, \text{CF}_3\text{CH}_2\text{O}$ ) groups appear in different areas (Figure 1).  $^{31}\text{P}$  chemical shifts of phosphorus atom in cyclophosphazenes depends on the substitute group. The chemical shifts of the thiophenoxy substitute phosphazenes<sup>8</sup> are observed in a low field due to electron density of the phosphorus which scattered to the other atoms within the ring. The phenyl group (shown as **3a** in figure 1) increases the the shielding effect because of the magnetic anisotropy.<sup>5b</sup> Since the patterns of proton coupled  $^{31}\text{P}$  NMR spectra of compounds (**3a-g**) are very similar to those of the derivatives obtained by routes 1 and 2, we assume that all these spermine substituted phosphazenes contain the same tetracyclic system containing a dispiro-monoansa moiety.





**Figure 1.** Proton-decoupled  $^{31}\text{P}$  NMR spectra of the compound **a)** 3a, **b)** 3b, **c)** 3c, **d)** 3d, **e)** 3f, **f)** 3g

## EXPERIMENTAL

### 1. Materials

Hexachlorocyclotriphosphazene (a gift from the Shin Nisso Kako Co. Ltd.) was purified by fractional crystallization from *n*-hexane. The following chemicals were obtained from Merck; Spermine (97.0%),

THF ( $\geq 99.0\%$ ), *n*-hexane ( $\geq 96\%$ ), EtOAc ( $\geq 99.5\%$ ), NaH (60 % dispersion in mineral oil),  $\text{CH}_2\text{Cl}_2$  ( $\geq 99.0\%$ ), PhSh ( $\geq 98.0\%$ ),  $\text{C}_6\text{H}_6$  ( $\geq 99.5\%$ ),  $\text{PhNH}_2$  ( $\geq 99\%$ ), PhOH ( $\geq 99\%$ ),  $\text{CF}_3\text{CH}_2\text{OH}$  ( $\geq 99\%$ ),  $\text{CHCl}_3$  (99.0-99.4 %), MeOH ( $\geq 99\%$ ), EtOH ( $\geq 99\%$ ). All solvents used in this work were purified by conventional methods. THF was distilled over a sodium-potassium alloy under an atmosphere of dry argon. Solvents for NMR spectroscopy were obtained from Goss Scientific ( $\text{CDCl}_3$ ).

## 2. Methods

Elemental analyses were obtained using a Carlo Erba 1106 Instrument. Mass spectra were recorded on a VG Zab Spec GC-MS spectrometer using the fast atom bombardment (FAB) method (35 kV) with MNBA as the matrix and an AGILENT 1100 MSD LC/MS spectrometer using atmospheric pressure chemical ionization (APCI);  $^{35}\text{Cl}$  values were used for calculated masses. Analytical Thin Layer Chromatography (TLC) was performed on silica gel (Merck, Kieselgel 60, 0.25 mm thickness) with  $\text{F}_{254}$  indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 70-230 mesh; for 3g. crude mixture, 100g. silica gel was used in a column of 3 cm in diameter and 60 cm in length)  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded in  $\text{CDCl}_3$  solutions on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for  $^1\text{H}$  NMR and 85 %  $\text{H}_3\text{PO}_4$  as an external reference for  $^{31}\text{P}$ .

## 3. Synthesis

Compound (**2**) was prepared as in the literature.<sup>3</sup> All reactions were performed under a dry argon atmosphere.

### 3.1. Preparation of 2,2-diphenyl-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatricyclohexadeca-2,4,6-triene, (**3a**):

Spermine (1.88 g, 9.29 mmol) in  $\text{CHCl}_3$  (50 mL) was added dropwise over 0.5 h to a stirred mixture 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene (mp 95.5 °C) (2 g, 4.65 mmol)<sup>6b</sup> in  $\text{CHCl}_3$  (30 mL) in a 250 mL three-necked round-bottomed flask. The reaction mixture was stirred for 3 days at rt under an atmosphere of argon and then spermine tetrahydrochloride was filtered off and the solvent was removed under reduced pressure. The resulting white solid was subjected to column chromatography using  $\text{CH}_2\text{Cl}_2$ -THF (1:3) as mobil phase. Compound (**3a**) was isolated as oily product. (Yield 44 %), ( $R_f$  = 0.32  $\text{CH}_2\text{Cl}_2$ -THF 1:3 as eluent). Anal. Calcd for  $\text{C}_{22}\text{H}_{32}\text{N}_7\text{P}_3$ : C 54.21, H 6.62, N 20.11 %. Found: C 54.25, H 6.58, N 20.03%. MS(APCI): *m/z*:calcd for: 487. Found: 488.  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$ = 16.2 (2P, >P(Nspiro)); 22.10 (1P, >P(Ph));  $^2\text{J}(\text{PP})$  24 Hz. Spin system analysed as  $\text{AX}_2$  pattern.  $^1\text{H}$  NMR:  $\delta$ = 3.3-3.2 (m, 4H,  $\text{NCH}_2(\text{spiro})$ ); 3.0-2.95 (m,  $\text{NCH}_2(\text{bridge})$ ); 2.85-2.82 (m, 4H,  $\text{NHCH}_2(\text{spiro})$ ); 2.5(s, 2H, NH);

1.49-1.45 (m, 4H, CH<sub>2</sub>(bridge)); 1.7-1.8 (m, 4H, CH<sub>2</sub>(spiro)); 7.8-7.7 (m, 2H, *p*-CH(C<sub>6</sub>H<sub>5</sub>)); 7.5-7.4 (m, 8H, *o*-*m*-CH(C<sub>6</sub>H<sub>5</sub>)).

### 3.2. Preparation of 2,2-bis-thiophenoxy-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatricyclohexadeca-2,4,6-triene, (3b):

Spermine (1.58 g, 7.82 mmol) in CHCl<sub>3</sub> (50 mL) was added dropwise over 0.5 h to a stirred mixture 2,2-bis-thiophenoxy-4,4,6,6-tetrachlorocyclotriphosphazatriene (mp 93 °C)<sup>7b</sup> (1.95g, 3.93 mmol) in CHCl<sub>3</sub> (25 mL) in a 250 mL three-necked round-bottomed flask. The reaction mixture was stirred for 24 hours at rt under an atmosphere of argon and the reaction followed by TLC on silica gel plates using *n*-hexane-THF (2:1) as eluent. The reaction mixture was filtered to remove the spermine tetrahydrochloride, the solvent removed under reduced pressure and the resulting crude product subjected to column chromatography using *n*-hexane-THF (2:1) as mobile phase. Compound (3b) was isolated as oily product. (Yield 23 %). (*R*<sub>f</sub> = 0.25 *n*-hexane-THF 2:1 as eluent). Anal. Calcd for C<sub>22</sub>H<sub>32</sub>N<sub>7</sub>P<sub>3</sub>S<sub>2</sub>: C 47.91, H 5.85, N 17.78%. Found: C 47.87, H 5.88, N 17.82 %. MS(APCI): *m/z*:calcd for: 551. Found: 552. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 15.79 (2P, >P(Nspiro)); 49.40 (1P, >P(SPh)); <sup>2</sup>J(PP) 16.54 Hz. Spin system analysed as AX<sub>2</sub> pattern. <sup>1</sup>H NMR: δ = 3.6 (m, 4H, NCH<sub>2</sub> (spiro)); 3.3 (m, 4H, NCH<sub>2</sub> (spiro)); 2.8-2.7 (m, 4H, NHCH<sub>2</sub>(spiro)); 2.5(s, 2H, NH); 1.6-1.5 (m, 4H, CH<sub>2</sub>(bridge)); 1.71-1.68 (m, 4H, CH<sub>2</sub>(spiro)); 7.1-7.2 (m, 8H, *o*-*m*-CH(C<sub>6</sub>H<sub>5</sub>-S)); 7.6-7.5 (m, 8H, *p*-CH(C<sub>6</sub>H<sub>5</sub>-S)).

### 3.3. Preparation of 2,2-bis-anilino-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatricyclohexadeca-2,4,6-triene, (3c):

Spermine (0.87 g, 4.34 mmol) in CHCl<sub>3</sub> (30 mL) was added dropwise over 0.5 h to a stirred mixture 2,2-bis-anilino-4,4,6,6-tetrachlorocyclotriphosphazatriene (mp 209 °C),<sup>9</sup> (1.0 g, 2.17 mmol) in CHCl<sub>3</sub> (40 mL) in a 250 mL three-necked round-bottomed flask. The reaction mixture was stirred for 3 days at rt under an atmosphere of argon and the reaction followed by TLC on silica gel plates using THF-CH<sub>2</sub>Cl<sub>2</sub> (4:1) as eluent. The reaction mixture was filtered to remove the spermine tetrahydrochloride, the solvent removed under reduced pressure and the resulting crude product subjected to column chromatography using CH<sub>2</sub>Cl<sub>2</sub>-THF (4:1) as mobile phase. Compound (3c) was isolated as oily product. (Yield 19.6 %), (*R*<sub>f</sub> = 0.17 CH<sub>2</sub>Cl<sub>2</sub>-THF 1:3 as eluent). Anal. Calcd for C<sub>22</sub>H<sub>34</sub>N<sub>9</sub>P<sub>3</sub>: C 51.06, H 6.62, N 24.36%. Found: C 51.08, H 6.528, N 24.33 %. MS(APCI): *m/z*:calcd for: 517. Found: 518. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 16.9 (2P, >P(Nspiro)); 9.4 (1P, >P(NHPh)); <sup>2</sup>J(PP) 50.4 Hz. Spin system analysed as A<sub>2</sub>X pattern. <sup>1</sup>H NMR: δ = 3.4-3.3 (m, 4H, NCH<sub>2</sub>(spiro)); 3.1-3.0 (m, NCH<sub>2</sub>(bridge)); 2.85-2.8 (m, 4H, NHCH<sub>2</sub>(spiro)); 2.6(s, 4H, NH); 1.49-1.46 (m, 4H, CH<sub>2</sub>(bridge)); 1.7-1.8 (m, 4H, CH<sub>2</sub>(spiro)); 6.8-7.2 (m, 10H, NHPh moiety).

**3.4. Preparation of 2,2-bis-phenoxy-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatricyclohexadeca-2,4,6-triene, (3d):**

Compound (**2**)<sup>3</sup> (1 g, 2.47 mmol) and phenol (0.46 g, 4.94 mmol) were dissolved in dry THF (50 mL) in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.2 g, 4.94 mmol) in dry THF (40 mL) was added under an argon atmosphere. The reaction mixture was stirred for 24 h at rt and the reaction was followed by TLC on silica gel plates using CH<sub>2</sub>Cl<sub>2</sub>-THF (2:3) 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 CH<sub>2</sub>Cl<sub>2</sub>-THF (2:3) as mobile phase. Compound (**3d**) was isolated oily product. (Yield 15.6 %), (*R*<sub>f</sub> = 0.34 CH<sub>2</sub>Cl<sub>2</sub>-THF 2:3 as eluent). Anal. Calcd for C<sub>22</sub>H<sub>32</sub>N<sub>7</sub>O<sub>2</sub>P<sub>3</sub>: C 50.87, H 6.21, N 18.87 %. Found: C 50.80, H 6.25, N 18.82 %. MS(APCI): *m/z*:calcd for: 519, Found: 520. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 18.44 (2P, >P(Nspiro)); 14.78 (1P, >P(OPh)); <sup>2</sup>J(PP) 64.2 Hz. Spin system analysed as A<sub>2</sub>X pattern. <sup>1</sup>H NMR: δ = 3.9-3.6 (m, 4H, NCH<sub>2</sub>(spiro)); 3.7-3.2 (m, 4H, NCH<sub>2</sub>(bridge)); 2.95-2.86 (m, 4H, NHCH<sub>2</sub>(spiro)); 2.5(s, 2H, NH); 1.49-1.45 (m, 4H, CH<sub>2</sub>(bridge)); 1.71-1.81 (m, 4H, CH<sub>2</sub>(spiro)); 6.7-7.4 (m, 10H, OPh moiety).

**3.5. Preparation of 2,2-bis-methoxy-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatricyclohexadeca-2,4,6-triene, (3e):**

Compound (**2**)<sup>3</sup> (1 g, 2.47 mmol) and methanol (30ml) were dissolved in dry THF (30 mL) in a 250 mL three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.4 g, 9.9 mmol) in dry THF (20 mL) was added under an argon atmosphere. The reaction mixture was stirred for 24 h at rt and the reaction was followed by TLC on silica gel plates using CH<sub>2</sub>Cl<sub>2</sub>-THF (1:2) 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 CH<sub>2</sub>Cl<sub>2</sub>-THF (1:2) as mobile phase. Compound (**3e**) was isolated white powder. (Yield 41 %), (mp 180-181 °C), (*R*<sub>f</sub> = 0.25 CH<sub>2</sub>Cl<sub>2</sub>-THF 1:2 as eluent) and crystallised from CH<sub>2</sub>Cl<sub>2</sub>-THF (4:1). Anal. Calcd for C<sub>12</sub>H<sub>28</sub>N<sub>7</sub>O<sub>2</sub>P<sub>3</sub>: C 36.46, H 7.14, N 24.80 %. Found: C 36.40, H 7.02, N 24.58 %. MS(APCI): *m/z*:calcd for: 395, Found 396. <sup>31</sup>P NMR (CDCl<sub>3</sub>): 18.9 (2P, >P(Nspiro)); 23.78 (1P, >P(OMe)); <sup>2</sup>J(PP) 62.46 Hz. Spin system analysed as AX<sub>2</sub> pattern. <sup>1</sup>H NMR: δ=3.4 (m, 4H, NCH<sub>2</sub>(spiro)); 3.0 (m, 4H, NCH<sub>2</sub>(bridge)); 2.95 (m, 4H, NHCH<sub>2</sub>(spiro)); 2.4(s, 2H, NH); 1.45 (m, 4H, CH<sub>2</sub>(bridge)); 1.75-1.91 (m, 4H, CH<sub>2</sub>(spiro)); 3.6-3.7 (d, 6H, OCH<sub>3</sub>).

**3.6. Preparation of 2,2-bis-ethoxy-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatricyclohexadeca-2,4,6-triene, (3f):**

Compound (**2**)<sup>3</sup> (2g, 4.95 mmol) and EtOH (0.34 g, 7.42 mmol) were dissolved in dry THF (50 mL) in a 100 ml three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.29 g, 7.42 mmol) in dry THF (20 mL) was quickly added under an argon atmosphere. The reaction was stirred for 24 h at rt and was monitored by TLC on silica gel plates using THF-CH<sub>2</sub>Cl<sub>2</sub> (3:1) as eluent. The reaction mixture was filtered to remove the sodium chloride, the THF removed under reduced pressure and the resulting colourless oil was subjected to column chromatography using THF-CH<sub>2</sub>Cl<sub>2</sub> (3:1) as mobile phase. Compound (**3f**) was isolated as oily product. (Yield 10%). (*R*<sub>f</sub> = 0.12 CH<sub>2</sub>Cl<sub>2</sub>-THF 1:3 as eluent). Anal. Calcd for C<sub>14</sub>H<sub>32</sub>N<sub>7</sub>O<sub>2</sub>P<sub>3</sub>: C 39.72, H 7.62, N 23.16 %. Found: C 39.76, H 7.52, N 23.12 %. MS(APCI): *m/z*:calcd for: 422, Found: 423. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 18.64 (2P, > P(Nspiro)); 20.71 (1P, >P(OEt)); <sup>2</sup>J(PP) 61.36 Hz. Spin system analysed as AB<sub>2</sub> pattern. <sup>1</sup>H NMR: δ = 4.2-3.9 (m, 4H, CH<sub>3</sub>CH<sub>2</sub>O-); 3.5-3.2 (m, 4H, NCH<sub>2</sub>(spiro)); 3.0-2.7 (m, 4H, NCH<sub>2</sub>(bridge)); 2.9-2.8 (m, 4H, NHCH<sub>2</sub>(spiro)); 2.45(s, 2H, NH); 1.49-1.45 (m, 4H, CH<sub>2</sub>(bridge)); 1.7-1.8 (m, 4H, CH<sub>2</sub>(spiro)); 1.27 (m, 6H, <sup>3</sup>J(HH) 7.07 Hz, CH<sub>3</sub>CH<sub>2</sub>O-).

### 3.7. Preparation of 2,2-bis-(2',2',2'-trifluoroethoxy)-1,3,5,7,11,16,19-heptaaza-2,4,6-triphosphatri-cyclohexadeca-2,4,6-triene, (**3g**):

Compound (**2**)<sup>3</sup> (1g, 2.47 mmol) and 2,2,3-trifluoroethanol (0.49 g, 4.95 mmol) were dissolved in dry THF (50 mL) in a 100 ml three-necked round-bottomed flask. The reaction mixture was cooled in an ice-bath and NaH (60% oil suspension, 0.07 g, 4.95 mmol) in dry THF (20 mL) was quickly added under an argon atmosphere. The reaction was stirred for 24 h at rt and was monitored by TLC on silica gel plates using THF-CH<sub>2</sub>Cl<sub>2</sub> (4:1) as eluent. The reaction mixture was filtered to remove the sodium chloride, the THF removed under reduced pressure and the resulting colourless oil was subjected to column chromatography using THF-CH<sub>2</sub>Cl<sub>2</sub> (4:1) as eluent. Compound (**3g**) was isolated as oily and crystallized from CH<sub>2</sub>Cl<sub>2</sub>- EtOAc- *n*-hexane (3:1:2) to give colourless crystals, (mp 127 °C), (Yield: 0.52 g. 39.6%). Anal. Calcd for C<sub>14</sub>H<sub>26</sub>F<sub>6</sub>N<sub>7</sub>O<sub>2</sub>P<sub>3</sub>: C 31.65, H 4.93, N 18.45 %. Found: C 31.62, H 4.91, N 18.48 %. MS(APCI): *m/z*:calcd for: 531, Found: 532. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 18.4 (2P, > P(Nspiro)); 21.74 (1P, >P(OCH<sub>2</sub>CF<sub>3</sub>)); <sup>2</sup>J(PP) 64.8Hz. Spin system analysed as AX<sub>2</sub> pattern. <sup>1</sup>H NMR: δ = 4.21 (m, 4H, OCH<sub>2</sub>); 4.3 (m, 4H, NCH<sub>2</sub>(spiro)); 3.9 (m, 4H, NCH<sub>2</sub>(bridge)); 2.85 (m, 4H, CH<sub>2</sub>(bridge)); 2.5(s, 2H, NH); 1.50 (m, 4H, CH<sub>2</sub>(bridge)), 1.7-1.8 (m, 4H, CH<sub>2</sub>(spiro)).

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