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Regiodirected phosphorylation of 2,2′,7,7′-tetrahydroxydinaphthylmethane

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Abstract—The phosphorylation of 2,2′,7,7′-tetrahydroxydinaphthylmethane was studied and the influence of molecule pre-organization on the regioselectivity of functionalization was investigated. The reactions of 2,2′,7,7′-tetrahydroxydinaphthylmethane with phosphorous amides containing 1–3 amide bonds gave oligophosphorylated derivatives differing in the number and the nature of phosphorus fragments and in the size of phosphorus rings: tetraphosphorus macrocycles containing one 24-membered and two eight-membered phosphorus rings, triphosphorus compounds containing a phosphocine ring and two acyclic phosphorus fragments, and tetraphosphorylated derivatives with four phosphorus groups in the molecule. The possibility of controlling the regioselectivity of phosphorylation by using reagents differing in the number and activity of P–N bonds was demonstrated.

1. Introduction

Aromatic compounds are structural blocks used commonly to design macrocyclic receptor systems of different architecture. Some crown ethers, cyclophanes, cryptands, calixarenes, and cavitands represent sets of aromatic nuclei coupled in a definite way.[1] The chemical behavior of these compounds is due to the number and mutual arrangement of aromatic rings, links, and functional groups in the molecule.

Polyhydroxyaromatic compounds are of particular interest as structural blocks for the design of macrocyclic molecules, as they are easily modified, providing a route to complex polyfunctional receptor systems.[1] An example of compounds of this type is 2,2′,7,7′-tetrahydroxydinaphthylmethane **1** containing two naphthalene nuclei and four hydroxy groups, which is considered in this study. The presence of only one methylene bridge in molecule **1** suggests a priori different reactivities of the hydroxyl groups in positions 2,2′ and 7,7′, which may be the crucial factor in the control of the direction of their functionalization.

Compound **1** was prepared by Wolff[2] in 1893 by condensation of 2,7-dihydroxynaphthalene with 40% formaldehyde solution in an acid medium. In 1998, this reaction was studied in more detail by Kallmayer and Schroeder-Mann,[3] who found that the reaction gives a mixture of products. The replacement of acid catalysis by basic catalysis (a saturated solution of Na_2CO_3) allowed us to reduce the reaction time to 30 min and to carry out the process regioselectively.[4]

Modification of **1** has not been studied extensively. Only a few publications[5] describe tetrafunctionalization of **1** by means of 1,2-epoxy-3-chloropropane[5a,b] and *N*-chloroaniline.[5c]

Since functional derivatives of **1** may be useful for the design of macroheterocyclic receptor systems and ligands for metal complex catalysts, we started investigating the phosphorylation of this compound.[4] Using the reaction of 2,2′,7,7′-tetrahydroxydinaphthylmethane **1** with phosphorous amides as an example, we carried out the first study of the direction of functionalization of **1** and the possibility of its control.

2. Results and discussion

2.1. Pre-organization of 2,2′,7,7′-tetrahydroxydinaphthylmethane molecule

To evaluate the possible modification routes, we studied pre-organization of the molecule of tetrahydroxydinaphthylmethane **1**. The equilibrium geometry of compound **1** was

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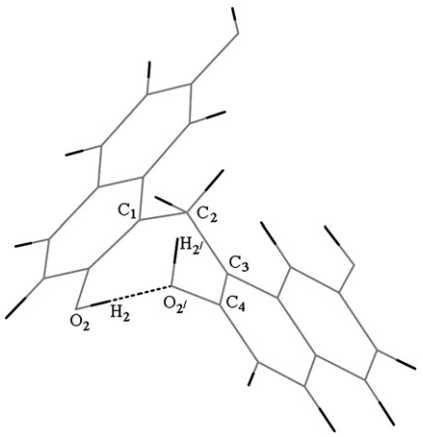


Figure 1. Equilibrium geometry of 2,2′,7,7′-tetrahydroxydinaphthylmethane **1** molecule based on AM1 calculations.

determined by semiempirical AM1 and Hartree–Fock (RHF approximation) calculations.[6] The absence of imaginary frequencies in the normal vibration spectrum served as the criterion for the correctness of the determined equilibrium geometry. The intensity distribution in the simulated IR spectra qualitatively reproduces the experimental one, which confirms the applicability of the chosen calculation techniques for predicting the structural and reactivity features of **1**.

The calculations predict the presence of a hydrogen bond[7] between the hydroxyl groups in positions 2,2′ (Fig. 1),[8] which is confirmed by a broad absorption band at 3500 cm^{-1} in the IR spectrum of dinaphthylmethane **1**.

Due to the hydrogen bond formation, the hydroxyl groups in positions 2,2′ are proximal to each other. The distance between the oxygen atoms O(2)–O(2′) is 3.20 Å and that between the atoms O(2)–H(2′) is 2.24 Å. The naphthyl fragments are arranged with respect to each other in such a way that the hydroxyl groups in positions 7,7′ are remote from each other. The distance between the oxygen atoms O(7)–O(7′) is 5.19 Å and the torsion angle C(1)C(2)C(3)C(4) is 116.4°.

This geometry of molecule **1** pre-determines the direction of its functionalization: the spatial proximity of the hydroxyl groups in positions 2,2′ promotes intramolecular reactions, whereas the remoteness of the hydroxyl groups in positions 7,7′ rules out these reactions but does not hamper intermolecular reactions.

In addition, control of the site of functionalization of dinaphthylmethane **1** was provided by the use of phosphorous amides **2a**–**h**, differing in the number of P–N bonds and, hence, in their reactivity toward phosphorylation.[9]

2.2. Phosphorylation of 2,2′,7,7′-tetrahydroxydinaphthylmethane 1 with phosphorous triamides

The reaction of **1** with phosphorous triamides **2a**,**b** was carried out in dioxane with variation of the reaction temperature (20–90 °C) and reactant ratio (**1**:**2**=1:2–20).

The presence of two pairs of hydroxyl groups in **1** with different reactivities assumes several possible pathways of development of reaction. Phosphorylation at C(2) and C(7) gives intermediate **3** (Scheme 1), upon which phosphocyclization results in intermediate **4**. Functionalization at C(7) first and then at C(2′) followed by cyclization provides a second route to **4**; phosphorylation at C(2), cyclization and then functionalization at C(7) provides the third.

Computer simulation of the process showed that the first pathway is preferable. The primary phosphorylation of the hydroxyl groups in positions 2 and 7 induces a change in the mutual arrangement of the naphthyl rings in space, and the torsion angle C(1)C(2)C(3)C(4) decreases to 109.9° in intermediate **3** (Scheme 1 and Fig. 2a). As a result, the phosphorodiamidite residue and hydroxyl groups in positions 2,2′, respectively, move toward each other in space. The O(2)–O(2′) distance decreases to optimum for phosphocyclization value 2.85 Å,[10] which induces fast cyclization to give intermediate **4** (Scheme 1 and Fig. 2b).

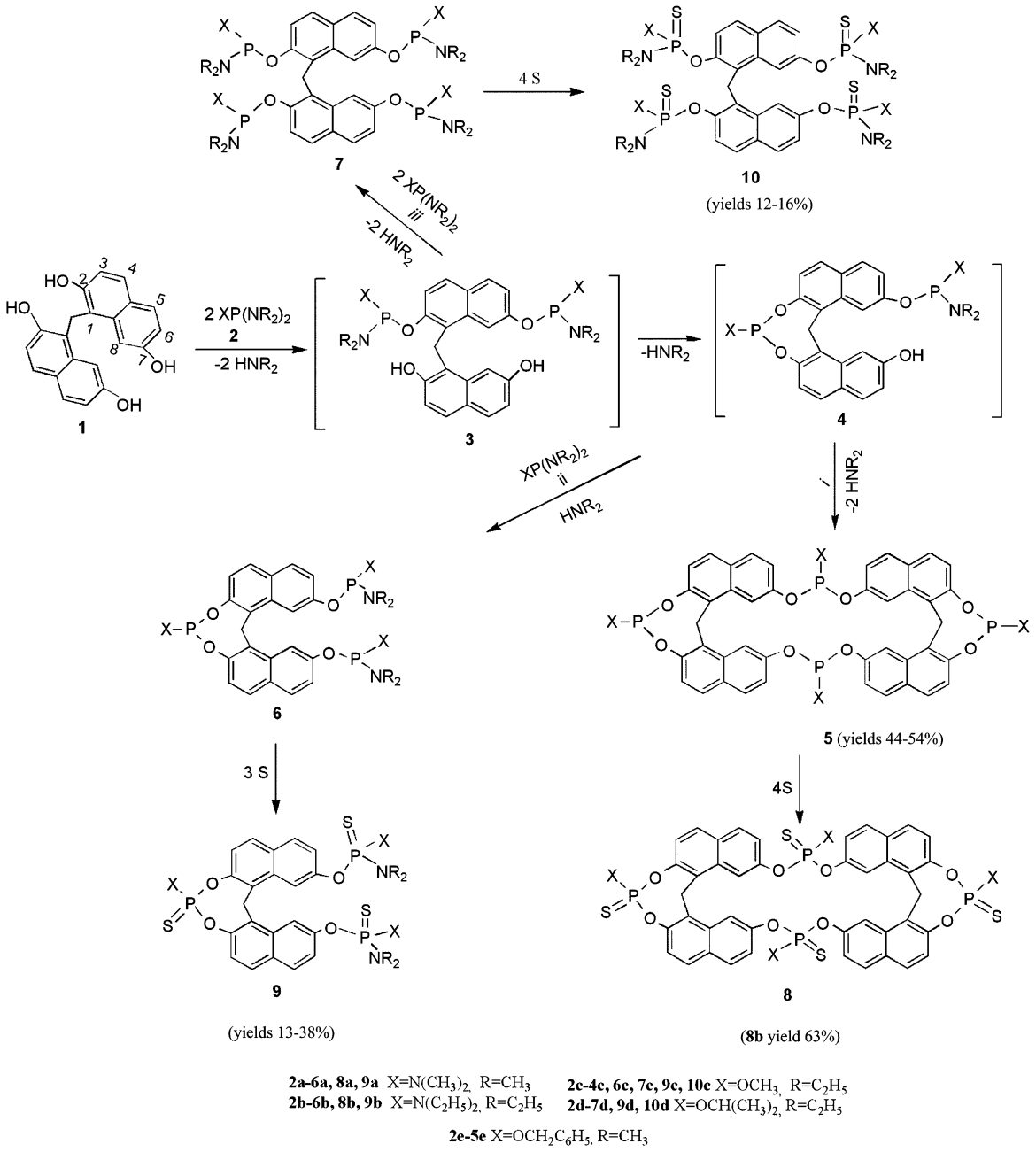
The calculation results are in good agreement with ^{31}P NMR spectroscopic data. For example, in the case of the reaction of dinaphthylmethane **1** with amide **2a** at 20 °C and **1**:**2a**=1:4, the ^{31}P NMR spectrum recorded 3 min after mixing the reactants exhibits, apart from the signal for **2a** (δ 122 ppm), two singlets with equal integrated intensities whose chemical shifts attest to cyclic phosphoromonoamidite (δ 139 ppm) and acyclic phosphorodiamidite (δ 135 ppm) fragments. The same ratio of the integrated intensities of these groups did not change for over the next 2 h. This formation of **4** after 20 min is indicative of a high rate of closure of the phosphocine ring and corresponds to structure **4**.

Upon closure of the phosphocine ring, the torsion angle C(1)C(2)C(3)C(4) decreases to 84.4°. This results in the rotation of the phosphorodiamidite group in position 7 away from the neighboring (7′) hydroxyl group. The distance between the O(7)–O(7′) atoms in intermediate **4** (Scheme 1 and Fig. 2b) increases to 6.45 Å, which completely rules out the possibility of intramolecular phosphocyclization.

The subsequent development of the process is determined by the content of phosphorous triamide in the reaction mixture. In the absence of phosphorous triamide, i.e., when the starting reactant ratio is **1**:**2**=1:2, two molecules of intermediate **4** undergo an intermolecular reaction to give macrophosphocyclic compound **5** containing three phosphorus rings, two eight-membered and one 24-membered (Scheme 1, i).

When the reaction mixture contains an additional amount of phosphorous triamide (**1**:**2**=1:>2), in addition to macrocycle **5**, the reaction gives compound **6** containing one phosphocine ring and two acyclic phosphorodiamidite fragments (Scheme 1, ii).

The predominance of a particular reaction product also depends on the size of the alkyl group at the N atoms of the phosphorylating reagent. For example, for R=Me and the reactant ratio **1**:**2**=1:3, compound **5a** (yield 54%) was the major reaction product, complete realization of pathway



Scheme 1. Phosphorylation of **1** with phosphorous triamides **2a**,**b** and alkyl phosphorodiamidites **2c**–**e**.

(ii) being attained only at the reactant ratio **1**:**2**=1:6. In the case where R=Et, compound **6b** (yield 95%) was the major reaction product even for **1**:**2**=1:3.

Due to the ease of closure of the phosphocine ring, we were unable to obtain tetraphosphorylated product **7** in considerable amounts (Scheme 1, iii) even with a 10-fold excess of phosphorous triamide. Studies of the reaction mixtures by MALDI and ^{31}P NMR spectroscopy have shown that in this case, too, triphosphorus derivative **6** is formed as the major product, while the content of tetraphosphorylated product **7** does not exceed 20%.

Note that raising the temperature did not influence the process direction much, but only increased the reaction rates.

Compound **5a** was precipitated from the reaction mixture as a dioxane complex. Pure compound **5b** could not be isolated even using preparative column and thin layer chromatography techniques. Elemental analysis data and the molecular weight of **5a** determined by MALDI corresponded to the theoretical values. The ^{31}P NMR spectrum of **5a** (Fig. 3a) exhibited two pairs of singlets with very similar chemical shifts and equal integrated intensities. The ^{1}H NMR spectrum (Fig. 3b) exhibited four doublets due to the methyl protons of the phosphamide groups, four H^{8} singlets, and doubling of the signals for the other aromatic protons (H^{3-6}) and the methylene bridge protons. In addition, the spectrum contained a singlet for the dioxane methylene protons. The integrated intensity ratio of the signals showed the presence of two dioxane molecules per

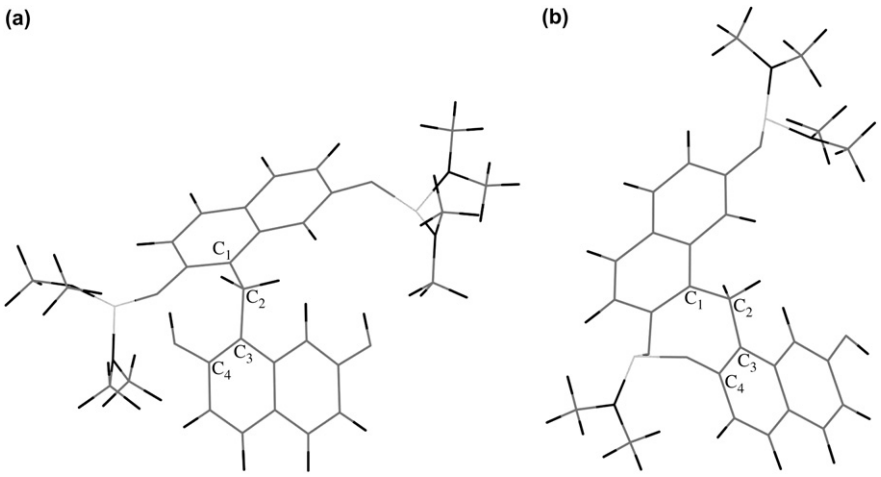


Figure 2. Equilibrium geometry of the molecules of intermediates **3** (a) and **4** (b). The calculations were done by the AM1 method.

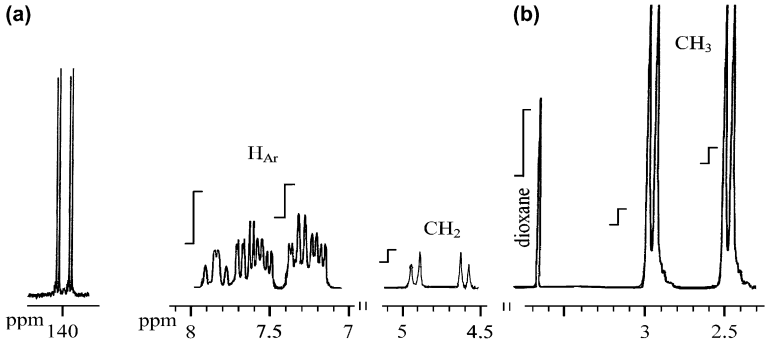


Figure 3. ^{31}P NMR (a) and ^{1}H NMR (b) spectra of compound **5a**.

macrocycle molecule. This was also confirmed by elemental analysis data.

The NMR spectral pattern corresponds to the optimized geometry of molecule **5a** (Fig. 4).

Sulfurization of compound **5a** does not induce substantial conformational changes in the molecule. The NMR spectroscopic parameters of the four-coordinate derivative **8** are similar to those of three-coordinate derivative **5a**.

Compounds **6a**,**b** resisted isolation in a pure state. They were subjected to sulfurization without isolation from the reaction mixture. Thio derivatives **9a**,**b** were isolated using preparative column chromatography. The composition and structure of **9a**,**b** were established based on the data of elemental analysis and MALDI and NMR spectra. For instance, the ^{31}P NMR spectrum of **9a** (Fig. 5a) exhibited three singlets, the higher-field one (δ 69.6 ppm) being due to the phosphocine phosphorus, while the lower-field signal (δ 80.5 ppm) corresponding to the phosphorus atoms of the acyclic phosphorodiamidate fragments. The integrated intensity ratio of the signals was 1:2, respectively. The high-field region of the ^{1}H NMR spectrum of **9a** (Fig. 5b) contained three doublets for the dimethylamide methyl groups with an integrated intensity ratio of 1:2:2, while the low-field part shows singlets for the methylene bridge protons and H^{8} aromatic protons, and four doublets for the other (H^{3-6}) aromatic protons. The integrated intensities of these

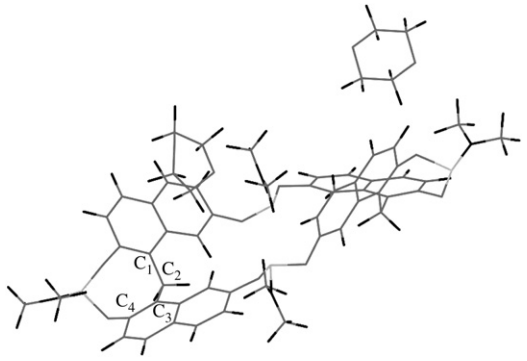


Figure 4. Equilibrium geometry of molecule **5a** found by AM1 calculations.

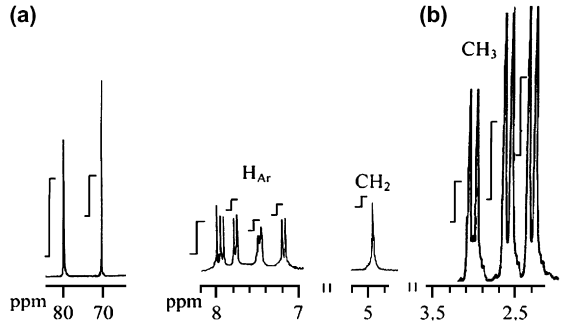


Figure 5. ^{31}P NMR (a) and ^{1}H NMR (b) spectra of compound **9a**.

signals corresponded to theoretical values. The MALDI spectra of **9a**,**b** exhibited one peak each corresponding to the calculated molecular weight.

2.3. Phosphorylation of 2,2′,7,7′-tetrahydroxydinaphthylmethane with phosphorodiamidites

The reactions of dinaphthylmethane **1** with phosphorodiamidites **2c**–**g** were carried out in acetonitrile at 20 °C with variable reactant ratio (**1**:**2**=1:2–10).

Alkyl phosphorodiamidites **2c**–**e** behaved similarly to phosphorous triamides **2a**,**b**. With a deficiency of the phosphorylating reagent (**1**:**2**=1:2), macrophosphocyclic compounds **5d**,**e** containing three phosphorus rings were formed (Scheme 1, i). The use of stoichiometric reactant ratios (**1**:**2**=1:4) gave rise to two major products: triphosphorus derivatives **6c**,**d** containing a phosphocine ring and two acyclic phosphoramidite fragments (ii), and tetraphosphorus derivatives **7c**,**d** containing four acyclic phosphoramidite fragments (iii). The formation of substantial amounts of tetraphosphorylated compounds **7c**,**d** is due to the lower reactivity of the P–N bond in monoamide fragments of primarily phosphorylated intermediates **3** compared to phosphorodiamidites,[9] which retards phosphocyclization (ii) and promotes route (iii). Note that in this case, phosphocyclization (i and ii) follows a classical route[9] including P–N bond cleavage and gives rise to phosphocine rings containing an exocyclic alkoxy group.

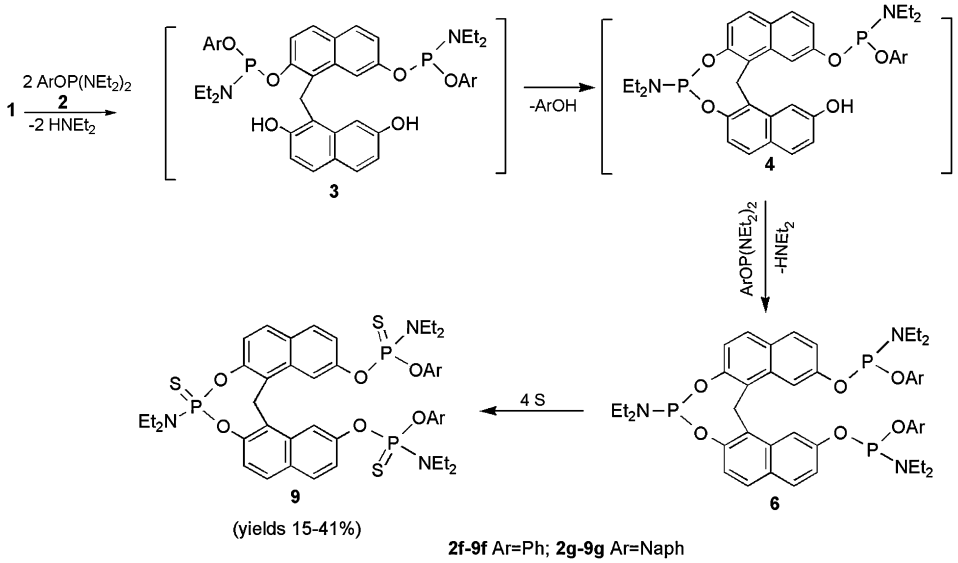
The behavior of aryl phosphorodiamidites **2f**,**g** differs from that described above. Phosphocyclization in intermediates **3f**,**g** occurs through cleavage of the P–O bond and ends in the formation of phosphocine rings containing an exocyclic amino group (Scheme 2).

This direction of polyol cyclophosphorylation with aromatic phosphorodiamidites is typical of polyhydroxyaromatic compounds with spatially proximate hydroxyl groups located in neighboring aromatic rings arranged in a certain way.[11]

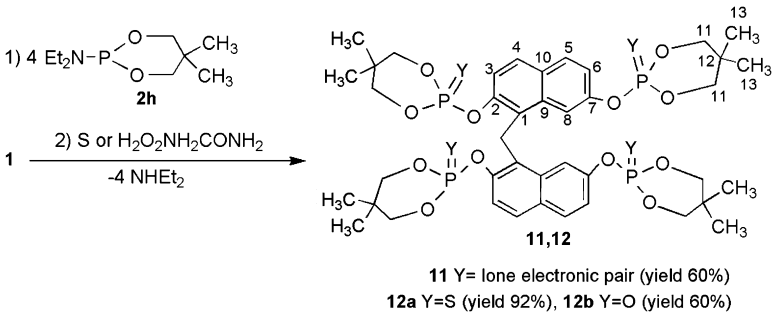
Intermediates **4f**,**g** do not undergo intermolecular interactions, which may be due both to steric factors and the relatively low reactivity of the P–N and P–O bonds in the diarylphosphoromonoamidite fragment in position 7. Therefore, irrespective of the reactant ratio, monophosphocyclic derivatives **6f**,**g** were formed as the major products (Scheme 2).

Macrocyclic compounds **5d**,**e** precipitated from reaction mixtures as complexes with two acetonitrile molecules. The ^{31}P NMR spectrum of compound **5d** exhibited three singlets with δ 125.8, 129.0, and 129.8 ppm and an integrated intensity ratio of 2:1:1, respectively, due to superposition of signals of the phosphorus atoms of 24-membered phosphorus ring. The ^{31}P NMR spectrum of **5e** showed two singlets with δ 123.4 and 125.8 ppm and equal integrated intensities due to superposition of signals of the phosphorus atoms of both 24-membered phosphorus ring and phosphocine cycles. The ^{1}H NMR spectra of **5d**,**e** contained no signals for dialkylamide protons but contained signals for the protons of alkoxy groups, methylene bridges, and aromatic nuclei.

Sulfur was added to compounds **6c**,**d**,**f**,**g** and **7c**,**d** without isolation from the reaction mixture. Sulfurization of **6c**,**d** and **7c**,**d** was carried out at 50 °C for 5 h, that of **6f**,**g** for 4 h at 20 °C. The four-coordinate derivatives **9c**,**d**,**f**,**g** and **10c**,**d** were isolated using column chromatography. The ^{31}P NMR spectra of **9c**,**d** showed two singlets with δ 61 and 74 ppm (**9c**), 58 and 71 ppm (**9d**), and 1:2 integrated intensity ratio; the ^{31}P NMR spectra of **10c**,**d** contained two singlets each with equal integrated intensities and very similar chemical shifts, δ 73 and 74 ppm; and the ^{31}P NMR spectra of **9f**,**g** showed singlets with δ 67 ppm. The ^{1}H NMR spectra of compounds **9c**,**d**,**f**,**g** and **10c**,**d** exhibited signals for all groups of protons with integrated intensities corresponding to theoretical values. However, the spectral pattern becomes more complicated due to the doubling of proton signals from the phosphorus fragments caused by diastereomeric anisotropy induced by the presence of several chiral phosphorus atoms in molecules **9c**,**d**,**f**,**g** and **10c**,**d**.



Scheme 2. Phosphorylation of **1** with aryl phosphorodiamidites **2f**,**g**.



Scheme 3. Phosphorylation of **1** with dioxaphosphorinane **2h**.

The elemental analysis data for **9c**,**d**,**f**,**g** and **10c**,**d** and the molecular weights in the MALDI spectra of **9c**,**d**,**f**,**g** and **10c**,**d** corresponded to the theoretical values.

2.4. Phosphorylation of 2,2′,7,7′-tetrahydroxydinaphthylmethane with 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane

The reaction of dinaphthylmethane **1** with 2-diethylamino-5,5-dimethyl-1,3,2-dioxaphosphorinane **2h** gave tetraphosphorylated derivative **11** as the major product. The presence of only one P–N bond in molecule **2h** ruled out the possibility of phosphocyclization. The reaction of **1** with **2h** was carried out in acetonitrile at 20 °C and at a stoichiometric reactant ratio of **1**:**2h**=1:4 (Scheme 3).

Tetraphosphorylated product **11** crystallized directly from the reaction mixture. The ^{31}P NMR spectrum of **11** exhibited two singlets with similar chemical shifts, 114.7 and 115.8 ppm, and equal integrated intensities. This is due to the non-equivalence of phosphorinane rings in positions 2,2′ and 7,7′, which was also manifested in the ^{1}H NMR spectrum of compound **11**. Indeed, the high-field spectral region contained two singlets for the axial and a singlet for the equatorial methyl protons, and two doublets for the axial and two multiplets for the equatorial methylene protons of the phosphorinane rings. The low-field part of the spectrum was similar to the ^{1}H NMR spectral pattern observed for triphosphorus derivatives **9**, namely, singlets for the methylene bridge protons and H^{8} aromatic protons and four doublets for the other (H^{3-6}) aromatic protons.

According to X-ray diffraction analysis, **11** (Fig. 6) crystallizes with the extended conformation characterized by the dihedral angle between planes of naphthyl rings equal to 90° and torsion angles C(1)C(1)C(11)C(12′) and C(1′)C(2′)C(11)C(12), which are almost identical and equal to 122.5° and 125.0°.

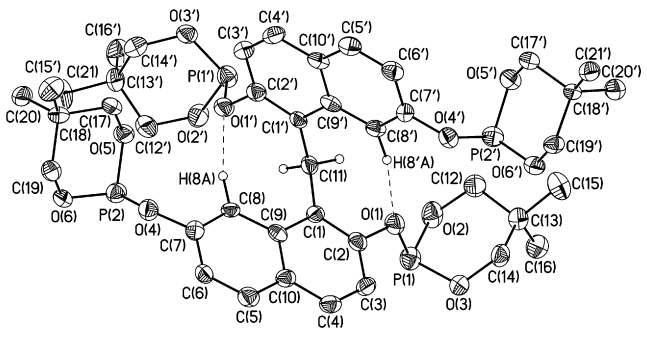


Figure 6. X-ray crystal structure of **11**.

The conformation observed in part can be the consequence of weak intramolecular C–H···O contacts, namely H(8′A)···O(1) and H(8A)···O(1′) with H···O distances and C–H···O angles equal to 2.45, 2.55 Å and 163–164°.

The addition of sulfur to tetraphosphorylated dinaphthylmethane **11** gave thio derivative **12a**, while oxidation of **11** with hydrogen peroxide afforded oxo derivative **12b**. The typical features of the NMR spectra of P(III)-phosphorylated dinaphthylmethane **11** are retained for the spectra of P(V)-derivatives **12a**,**b**, which attest to their structural analogy.

3. Conclusions

This study demonstrated the potential of regiodirected functionalization of 2,2′,7,7′-tetrahydroxydinaphthylmethane and an approach for controlling this regiochemistry. Directed phosphorylation of 2,2′,7,7′-tetrahydroxydinaphthylmethane gave a new family of phosphorus-containing aromatic compounds, including macrophosphocyclic systems. The subsequent research would deal with the use of polyphosphorylated dinaphthylmethane derivatives for the design of complicated supramolecular and coordination systems.

4. Experimental section

4.1. General

^{1}H NMR (TMS internal reference) and ^{31}P NMR spectra (85% H_3PO_4 external reference) of all compounds were recorded with a Bruker AC 300 instrument. ^{13}C NMR (TMS internal reference) spectra of **1**, **9b**, **10c**, and **11** were recorded with Bruker AC 200, and that of **8a** was performed with Bruker AC 600. MALDI-TOF mass spectra were measured with a Kratos Kompact MALDI II mass spectrometer (Shimadzu Europa GmbH) with N_2-laser source (λ=337 nm), positive polarity, and 20 kV acceleration voltage. All syntheses were carried out in dry solvents under argon. Compounds were purified by thin layer chromatography (TLC) on silica gel 100/160. Solvents were distilled before use and dried, as necessary, according to the literature procedures.

4.1.1. 2,2′,7,7′-Tetrahydroxydinaphthylmethane (1). Formalin (23%) (0.27 g, 8.91 mmol) was added to 2,7-dihydroxydinaphthalene (1.43 g, 8.91 mmol) in a saturated

solution of sodium carbonate (10 mL). The resulting suspension was stirred at room temperature for 30 min. Then Na_2CO_3 was precipitated by adding acetone (100 mL) to the reaction mixture. Acetone was evaporated and the product precipitated from the reaction mixture. The gray precipitate (1.48 g, 51%) was filtered off and dried for 5 h at 100–110 °C (1 mmHg). Mp 260–261 °C. ^{1}H NMR (300.1 MHz, CD_3OCD_3): δ 4.72 (s, 2H, CH_2), 6.86 (dd, $^3J_{HH}$=8.8 Hz, $^4J_{HH}$=2.65 Hz, 2H, H^3), 7.01 (d, $^3J_{HH}$=8.7 Hz, 2H, H^6), 7.52–7.65 (m, 6H, H^4, H^5, H^8), 8.45 (br s, 4H, OH) ppm. ^{13}C NMR (50.32 MHz, CD_3OCD_3): δ 22.05 (s, CH_2), 107.21 (s, C^8), 115.53 (s, C^3 or C^6), 115.86 (s, C^3 or C^6), 117.94 (s, C^1), 125.11 (s, C^{10}), 128.54 (s, C^4 or C^5), 130.71 (s, C^4 or C^5), 136.69 (s, C^9), 153.19 (s, C^2 or C^7), 156.20 (s, C^2 or C^7) ppm. ν_{max} (KBr) 3500, 1620, 1505, 1140 cm^{-1}. MS (MALDI): m/z=333 [M+H$^+$]. Anal. Calcd for $C_{21}H_{16}O_4$ (332.35): C, 75.89%; H, 4.85%. Found: C, 75.73%; H, 4.89%.

4.1.2. Macrocycle (5a). A solution of **1** (0.31 g, 0.93 mmol) and **2a** (0.31 g, 1.86 mmol) in dioxane (2 mL) was maintained at 20 °C for 48 h. The resulting precipitate was filtered off, washed with dioxane (2 mL), and dried under vacuum (1 mmHg, 110–115 °C). Compound **5a** (0.29 g, 54%) is a white powder. Mp 298–300 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 138.17 (s, 1P), 138.2 (s, 1P), 139.60 (s, 1P), 139.95 (s, 1P) ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.43 (d, $^3J_{HP}$=6.1 Hz, 6H, N–CH$_3$), 2.78 (d, $^3J_{HP}$=9.2 Hz, 6H, N–CH$_3$), 2.82 (d, $^3J_{HP}$=9.8 Hz, 6H, N–CH$_3$), 2.83 (d, $^3J_{HP}$=9.9 Hz, 6H, N–CH$_3$), 4.51 (dd, $^2J_{HH}$=16.3 Hz, $^5J_{HP}$=4.0 Hz, 1H, CH_2), 4.55 (dd, $^2J_{HH}$=15.9 Hz, $^5J_{HP}$=3.4 Hz, 1H, CH_2), 4.89 (d, $^2J_{HH}$=16.3 Hz, 1H, CH_2), 4.91 (d, $^2J_{HH}$=15.9 Hz, 1H, CH_2), 7.05 (d, $^3J_{HH}$=8.8 Hz, 2H, H^4 or H^5), 7.10 (d, $^3J_{HH}$=8.8 Hz, 2H, H^4 or H^5), 7.13 (d, $^3J_{HH}$=8.6 Hz, 2H, H^4 or H^5), 7.18 (d, $^3J_{HH}$=8.6 Hz, 2H, H^4 or H^5), 7.57 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 7.62 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 7.64 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 7.71 (dd, $^3J_{HH}$=8.8 Hz, $^4J_{HP}$=2.4 Hz, 2H, H^3 or H^6), 7.79 (s, 1H, H^8), 7.84 (s, 1H, H^8), 7.85 (s, 1H, H^8), 7.90 (s, 1H, H^8) ppm. ν_{max} (KBr) 2973, 2930, 2877, 1590, 1465, 1455, 1376, 1205, 1151, 1095, 1024, 990, 846, 788, 745 cm^{-1}. MS (MALDI): m/z=957 [M−2C$_4$H$_8$O$_2$+H$^+$]. Anal. Calcd for $C_{50}H_{48}N_4O_8P_4\cdot 2C_4H_8O_2$ (1133.35): C, 61.48%; H, 5.69%; N, 4.94%. Found: C, 61.00%; H, 6.05%; N, 4.43%.

4.1.3. Macrocycle (8). A suspension of **5a** (0.25 g, 0.22 mmol) and sulfur (0.03 g, 0.88 mmol) in a mixed solvent (benzene/chloroform=1:1, 2 mL) was stirred for 4 h at 70 °C. The resulting precipitate was filtered off, washed with benzene (2 mL), and dried under vacuum (1 mmHg, 110–115 °C). Compound **8** (0.15 g, 63%) is a white powder. Mp 240–241 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 69.91 (s, 2P) 68.34 (s, 2P). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.75 (d, $^3J_{HP}$=11.6 Hz, 6H, N–CH$_3$), 2.78 (d, $^3J_{HP}$=11.6 Hz, 6H, N–CH$_3$), 2.98 (d, $^3J_{HP}$=13.2 Hz, 6H, N–CH$_3$), 3.00 (d, $^3J_{HP}$=13.2 Hz, 6H, N–CH$_3$), 4.94 (s, 2H, CH_2), 4.98 (s, 2H, CH_2), 7.16 (d, $^3J_{HH}$=8.6 Hz, 2H, H^4 or H^5), 7.21 (d, $^3J_{HH}$=7.8 Hz, 2H, H^4 or H^5), 7.30 (d, $^3J_{HH}$=8.8 Hz, 2H, H^4 or H^5), 7.43 (d, $^3J_{HH}$=9.5 Hz, 2H, H^4 or H^5), 7.65 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 7.74 (d, $^3J_{HH}$=7.9 Hz, 2H, H^3 or H^6), 7.78 (d, $^3J_{HH}$=9.5 Hz, 2H, H^3 or H^6), 7.82 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 8.02 (s, 1H, H^8), 8.11 (s, 1H, H^8), 8.20 (s, 1H, H^8), 8.28 (s, 1H, H^8) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 25.13 (s, CH_2), 25.38 (s, CH_2), 37.55 (d, N–CH$_3$, $^2J_{CP}$=3.9 Hz), 37.62 (d, N–CH$_3$, $^2J_{CP}$=3.9 Hz), 37.82 (d, NCH$_3$, $^2J_{CP}$=2.6 Hz), 113.89 (s, C^8), 114.11 (s, C^8), 119.94 (s, C^3 or C^6), 120.19 (s, C^3 or C^6), 120.34 (s, C^3 or C^6), 120.75 (s, C^3 or C^6), 123.60 (s, C^1), 123.80 (s, C^1), 128.66 (s, C^4 or C^5), 129.03 (s, C^4 or C^5), 129.20 (s, C^4 or C^5), 130.05 (s, C^{10}), 130.49 (s, C^{10}), 133.27 (s, C^9), 133.59 (s, C^9), 149.57 (d, C–O–P, $^2J_{CP}$=5.7 Hz), 149.91 (d, C–O–P, $^2J_{CP}$=6.0 Hz), 150.18 (d, C–O–P, $^2J_{CP}$=6.0 Hz), 150.34 (d, C–O–P, $^2J_{CP}$=9.4 Hz) ppm. Anal. Calcd for $C_{50}H_{48}N_4O_8P_4S_4$: C, 55.34%; H, 4.46%; N, 5.16%. Found: C, 55.23%; H, 4.59%; N, 5.48%.

4.1.4. 2-Dimethylamino-2-thio-4,5;78-dinaphtho-13,13′-bis(tetramethyldiaminothiophosphoryl)-1,3,2-dioxaphosphocine (9a). A solution of **1** (0.09 g, 0.27 mmol) and **2a** (0.18 g, 1.11 mmol) in dioxane (4 mL) was maintained at 20 °C for 48 h. Dioxane and excess **2a** were removed under vacuum. The residue was dissolved in a solvent mixture (benzene/chloroform=1:1, 2 mL) and sulfur (0.03 g, 0.81 mmol) was added. The reaction mixture was stirred for 3 h at 20 °C. The solvents were evaporated under vacuum. The reaction product was isolated by column chromatography (silica gel, benzene/dioxane=5:1, R_f=0.61). Compound **9a** (0.08 g, 38%) is a yellow film. Mp 137–138 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 69.57 (s, 1P), 80.91 (s, 2P). ^{1}H NMR (300.1 MHz, C_6D_6): δ 2.39 (d, $^3J_{HP}$=12.1 Hz, 12H, N–CH$_3$), 2.50 (d, $^3J_{HP}$=12.4 Hz, 12H, N–CH$_3$), 2.64 (d, $^3J_{HP}$=13.2 Hz, 6H, N–CH$_3$), 4.89 (d, $^2J_{HH}$=16.1 Hz, 1H, CH_2), 5.12 (d, $^2J_{HH}$=16.1 Hz, 1H, CH_2), 7.00 (d, $^3J_{HH}$=9.1 Hz, 2H, H^4 or H^5), 7.30 (d, $^3J_{HH}$=9.1 Hz, 2H, H^3 or H^6), 7.44 (d, $^3J_{HH}$=8.8 Hz, 2H, H^4 or H^5), 7.52 (d, $^3J_{HH}$=8.4 Hz, 2H, H^3 or H^6), 8.07 (s, 2H, H^8) ppm. Anal. Calcd for $C_{31}H_{42}N_5O_4P_3S_3$: C, 50.46%; H, 5.74%; N, 9.49%; P, 12.59%. Found: C, 50.22%; H, 5.35%; N, 9.40%; P, 12.75%.

4.1.5. 2-Diethylamino-2-thio-4,5;78-dinaphtho-13,13′-bis(tetraethyldiaminothiophosphoryl)-1,3,2-dioxaphosphocine (9b). A solution of **1** (0.24 g, 0.72 mmol) and **2b** (0.71 g, 2.91 mmol) in dioxane (4 mL) was heated at 80–85 °C for 27 h. Then, a solution of sulfur (96 mg, 3.0 mmol) in benzene (1 mL) was added and the reaction mixture was stirred for 3 h at 60 °C. After cooling, hexane (4 mL) was added, the hexaethylthionophosphorotriamidate precipitate formed was filtered off, and the solvents were evaporated under vacuum. The product was isolated by column chromatography (benzene/dioxane=5:2, silica gel, R_f=0.68). Compound **9b** (0.21 g, 32%) is a yellow film. Mp 77–78 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 67.29 (s, 1P), 76.64 (s, 2P) ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.92 (t, $^3J_{HH}$=7.3 Hz, 12H, N–CH$_2$–*CH*$_3$), 1.13 (t, $^3J_{HH}$=7.0 Hz, 12H, N–CH$_2$–*CH*$_3$), 1.26 (t, $^3J_{HH}$=6.9 Hz, 6H, N–CH$_2$–*CH*$_3$), 3.02–3.21 (m, $^3J_{HP}$=13.9 and 12.4 Hz, 16H, N–*CH*$_2$–CH$_3$), 3.36 (m, $^3J_{HP}$=14.6 Hz, 4H, N–*CH*$_2$–CH$_3$), 4.85 (s, 2H, CH_2), 7.12 (d, $^3J_{HH}$=8.8 Hz, 2H, H^4 or H^5), 7.40 (d, $^3J_{HH}$=8.8 Hz, 2H, H^4 or H^5), 7.72 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 7.80 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 7.83 (s, 2H, H^8) ppm. ^{13}C NMR (121.5 MHz, $CDCl_3$): δ 13.70 (d, N–CH$_2$–*CH*$_3$, $^3J_{CP}$=2.7 Hz), 13.95 (d, N–CH$_2$–*CH*$_3$, $^3J_{CP}$=2.7 Hz), 14.14 (d, N–CH$_2$–*CH*$_3$, $^3J_{CP}$=3.9 Hz), 25.86 (s, CH_2), 39.90 (d, N–*CH*$_2$–CH$_3$,

$^2J_{CP}$=4.8 Hz), 40.33 (d, N–*CH*$_2$–CH$_3$, $^2J_{CP}$=4.7 Hz), 41.08 (d, N–*CH*$_2$–CH$_3$, $^2J_{CP}$=4.2 Hz), 114.12 (d, C^8, $^3J_{PC}$=5.9 Hz), 119.89 (d, C^3 or C^6, $^2J_{PC}$=4.9 Hz), 121.21 (d, C^3 or C^6, $^3J_{PC}$=4.3 Hz), 123.89 (s, C^1), 128.54 (s, C^4 or C^5), 128.77 (s, C^{10}), 129.79 (s, C^4 or C^5), 133.74 (s, C^9), 150.15 (d, C–O–P, $^2J_{PC}$=6.3 Hz), 150.32 (d, C–O–P, $^2J_{PC}$=11 Hz) ppm. ν_{max} (KBr) 2976, 2964, 2931, 1592, 1503, 1376, 1235, 1024, 950, 936, 840, 798, 725 cm^{-1}. MS (MALDI): *m*/*z*=879 [M+H$^+$]. Anal. Calcd for $C_{41}H_{62}N_5O_4P_3S_3$ (878.08): C, 56.08%; H, 7.12%; N, 7.98%; P, 10.58%. Found: C, 56.28%; H, 7.15%; N, 7.74%; P, 10.45%.

4.1.6. Macrocycle (5d). Phosphorodiamidite **2d** (0.20 g, 0.85 mmol) was added to a suspension of **1** (0.14 g, 0.43 mmol) in acetonitrile (4 mL). The reaction mixture was stirred for 5 days at 20 °C. Half of the solvent was evaporated and the precipitate was filtered off, washed with acetonitrile (3 mL), and dried under vacuum (1 mmHg, 110–115 °C). Compound **5d** (0.12 g, 55%) is a white powder. Mp 298–300 °C. ^{31}P NMR (121.5 MHz, CDCl$_3$): δ 125.8 (s, 2P), 129.0 (s, 1P), 129.8 (s, 1P) ppm. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 0.79 (d, $^2J_{HH}$=6.1 Hz, 3H, CH–*CH*$_3$), 0.90 (d, $^2J_{HH}$=6.6 Hz, 3H, CH–*CH*$_3$), 0.93 (d, $^2J_{HH}$=6.6 Hz, 3H, CH–*CH*$_3$), 0.97 (d, $^2J_{HH}$=6.1 Hz, 3H, CH–*CH*$_3$), 1.41 (d, $^2J_{HH}$=6.1 Hz, 6H, CH–*CH*$_3$), 1.43 (d, $^2J_{HH}$=6.0 Hz, 6H, CH–*CH*$_3$), 4.48 (d, $^2J_{HH}$=17.1 Hz, 2H, CH$_2$), 4.76 (m, $^2J_{HH}$=9.4 Hz, 2H, *CH*–(CH$_3$)$_2$), 4.78 (m, $^2J_{HH}$=9.4 Hz, 2H, *CH*–(CH$_3$)$_2$), 4.88 (d, $^2J_{HH}$=16.5 Hz, 2H, CH$_2$), 7.09 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.11 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.17 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.20 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.64 (d, $^3J_{HH}$=8.7 Hz, 2H, H^3 or H^6), 7.72 (d, $^3J_{HH}$=8.7 Hz, 2H, H^3 or H^6), 7.75 (d, $^3J_{HH}$=8.7 Hz, 2H, H^3 or H^6), 7.77 (d, $^3J_{HH}$=8.7 Hz, 2H, H^3 or H^6), 7.81 (s, 1H, H^8), 7.89 (s, 1H, H^8), 7.95 (s, 1H, H^8), 8.02 (s, 1H, H^8) ppm. Anal. Calcd for $C_{54}H_{52}O_{12}P_4$: C, 63.78%; H, 5.15%; P, 12.18%. Found: C, 63.45%; H, 5.36%; P, 12.08%.

4.1.7. Macrocycle (5e). Phosphorodiamidite **2e** (0.22 g, 0.97 mmol) was added to a suspension of **1** (0.16 g, 0.49 mmol) in acetonitrile (4 mL). The reaction mixture was stirred for 3 days at 20 °C. Half of the solvent was evaporated and the precipitate was filtered off, washed with acetonitrile (3 mL), and dried under vacuum (1 mmHg, 110–115 °C). Compound **5e** (0.14 g, 44%) is a pink powder. Mp 294–296 °C. ^{31}P NMR (121.5 MHz, CDCl$_3$): δ 121.9 (s, 2P), 127.1 (s, 2P) ppm. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 4.37 (d, $^2J_{HH}$=16.4 Hz, 2H, CH$_2$), 4.75 (d, $^2J_{HH}$=16.4 Hz, 2H, CH$_2$), 4.92 (d, $^2J_{HH}$=7.31 Hz, 4H, *CH*$_2$–C$_6$H$_5$), 5.17 (d, $^2J_{HH}$=7.31 Hz, 4H, *CH*$_2$–C$_6$H$_5$), 7.10 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.12 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.14 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.17 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.38–7.45 (m, 20H, OCH$_2$*C*$_6$*H*$_5$), 7.60 (d, $^3J_{HH}$=8.7 Hz, 2H, H^3 or H^6), 7.63 (d, $^3J_{HH}$=8.7 Hz, 2H, H^3 or H^6), 7.67 (d, $^3J_{HH}$=8.7 Hz, 2H, H^3 or H^6), 7.70 (d, $^3J_{HH}$=8.7 Hz, 2H, H^3 or H^6), 7.72 (s, 1H, H^8), 7.82 (s, 1H, H^8), 7.87 (s, 1H, H^8), 7.91 (s, 1H, H^8) ppm. ν_{max} (KBr) 2955, 2849, 1489, 1456, 1280, 1153, 1056, 997, 885, 755 cm^{-1}. MS (MALDI): *m*/*z*=1291 [M+H$^+$]. Anal. Calcd for $C_{70}H_{52}O_{12}P_4 \cdot 2CH_3CN$ (1290.29): C, 68.84%; H, 4.53%; P, 9.60%. Found: C, 68.58%; H, 4.11%; P, 9.25%.

4.1.8. 2-Diethylamino-2-thio-4,5;78-dinaphtho-13,13′-bis(diethylaminomethylthiophosphoryl)-1,3,2-dioxaphosphocine (9c) and 2,2′,7,7′-tetrakis(diethylaminomethylthiophosphoryl)dinaphthylmethane (10c). Phosphorodiamidite **2c** (0.50 g, 2.42 mmol) was added to a suspension of **1** (0.20 g, 0.61 mmol) in acetonitrile (3 mL). The reaction mixture was kept for 24 h at 20 °C, sulfur (0.08 g, 2.41 mmol) was added, and the reaction mixture was kept for 5 h at 50 °C. The solvent was evaporated and the products were separated by column chromatography (benzene/hexane=4:1, silica gel). Compound **9c**: R_f=0.22, yellow oil (60 mg, 13%). ^{31}P NMR (121.5 MHz, CDCl$_3$): δ 60.9 (s, 1P), 74.0 (s, 2P) ppm. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 0.91 (t, $^3J_{HH}$=6.8 Hz, 3H, N–CH$_2$–*CH*$_3$), 0.94 (t, $^3J_{HH}$=6.9 Hz, 3H, N–CH$_2$–*CH*$_3$), 1.07 (t, $^3J_{HH}$=6.9 Hz, 3H, N–CH$_2$–*CH*$_3$), 1.10 (t, $^3J_{HH}$=7.0 Hz, 3H, N–CH$_2$–*CH*$_3$), 3.02 (m, $^3J_{HP}$=14.0 Hz, 4H, N–*CH*$_2$–CH$_3$), 3.30 (m, $^3J_{HP}$=13.8 Hz, 4H, N–*CH*$_2$–CH$_3$), 3.54, 3.57 (2d, $^3J_{HP}$= 14.3 Hz and $^3J_{HP}$=13.7 Hz, 3H, O–CH$_3$), 3.70, 3.71 (2d, $^3J_{HP}$=13.7 Hz and $^3J_{HP}$=14.3 Hz, 3H, O–CH$_3$), 3.73, 4.00 (2d, $^3J_{HP}$=14.3 Hz, 3H, O–CH$_3$), 4.72 (d, $^2J_{HH}$=17.0 Hz, 1H, CH$_2$), 4.96 (d, $^2J_{HH}$=16.5 Hz, 1H, CH$_2$), 7.16 (d, $^3J_{HH}$=8.3 Hz, 2H, H^4 or H^5), 7.43 (d, $^3J_{HH}$=9.2 Hz, 2H, H^4 or H^5), 7.75 (d, $^3J_{HH}$=8.5 Hz, 2H, H^3 or H^6), 7.82 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 7.97 (s, 2H, H^8) ppm. MS (MALDI): *m*/*z*=755 [M+H$^+$]. Anal. Calcd for $C_{32}H_{41}N_2O_7P_3S_3$ (754.13): C, 50.92%; H, 5.48%; P, 12.31%. Found: C, 50.45%; H, 5.16%; P, 12.01%.

Compound **10c**: R_f=0.13, yellow oil (97 mg, 16%). ^{31}P NMR (121.5 MHz, CDCl$_3$): δ 74.2 (s, 2P), 73.6 (s, 2P) ppm. ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 0.93 (t, $^3J_{HH}$= 6.8 Hz, 6H, N–CH$_2$–*CH*$_3$), 0.98 (t, $^3J_{HH}$=6.9 Hz, 6H, N–CH$_2$–*CH*$_3$), 1.05 (t, $^3J_{HH}$=6.9 Hz, 6H, N–CH$_2$–*CH*$_3$), 1.10 (t, $^3J_{HH}$=7.0 Hz, 6H, N–CH$_2$–*CH*$_3$), 3.02 (m, $^3J_{HP}$=14.0 Hz, 8H, N–*CH*$_2$–CH$_3$), 3.32 (m, $^3J_{HP}$=13.7 Hz, 8H, N–*CH*$_2$–CH$_3$), 3.54 (d, $^3J_{HP}$=14.3 Hz, 3H, O–CH$_3$), 3.57 (d, $^3J_{HP}$= 13.7 Hz, 3H, O–CH$_3$), 3.71 (d, $^3J_{HP}$=14.3 Hz, 3H, O–CH$_3$), 4.11 (d, $^3J_{HP}$=14.3 Hz, 3H, O–CH$_3$), 4.72 (d, $^2J_{HH}$= 17.0 Hz, 1H, CH$_2$), 4.96 (d, $^2J_{HH}$=16.5 Hz, 1H, CH$_2$), 7.16–7.97 (m, 10H, H$_{Ar}$) ppm. ^{13}C NMR (121.5 MHz, CDCl$_3$): δ 14.09 (d, N–CH$_2$–*CH*$_3$, $^3J_{CP}$=6.9 Hz), 29.67 (s, CH$_2$), 39.90 (d, N–*CH*$_2$–CH$_3$, $^2J_{CP}$=4.8 Hz), 40.31 (d, N–*CH*$_2$–CH$_3$, $^2J_{CP}$=7.9 Hz), 53.35 (s, O–CH$_3$), 114.12 (s, C^8), 115.38 (s, C^8), 119.89 (d, C^3 or C^6, $^2J_{PC}$=3.9 Hz), 120.47 (d, C^3 or C^6, $^3J_{PC}$=3.3 Hz), 126.26 (s, C^{10}), 127.57 (s, C^4 or C^5), 128.61 (d, C^1, $^2J_{CP}$=10.8 Hz), 129.51 (s, C^4 or C^5), 134.15 (s, C^9), 147.56 (d, C–O–P, $^2J_{PC}$=5.3 Hz), 149.39 (d, C–O–P, $^2J_{PC}$=5.3 Hz) ppm. MS (MALDI): *m*/*z*=993 [M+H$^+$]. Anal. Calcd for $C_{41}H_{64}N_4O_8P_4S_4$ (992.26): C, 49.58%; H, 6.50%; N, 5.64%; P, 12.48%. Found: C, 49.08%; H, 6.45%; N, 5.48%; P, 12.15%.

4.1.9. 2-Diethylamino-2-thio-4,5;78-dinaphtho-13,13′-bis(diethylaminoisopropylthiophosphoryl)-1,3,2-dioxaphosphocine (9d) and 2,2′,7,7′-tetrakis(diethylaminoisopropylthiophosphoryl)dinaphthylmethane (10d). Phosphorodiamidite **2d** (0.61 g, 2.6 mmol) was added to a suspension of bisnaphthylmethane **1** (0.22 g, 0.65 mmol) in acetonitrile (4 mL). The reaction mixture was kept for 24 h at 20 °C, sulfur (0.08 g, 2.6 mmol) was added, and the reaction mixture was kept for 5 h at 50 °C. The solvent was evaporated and the products were separated by column

chromatography (benzene/hexane=4:1, silica gel). Compound **9d**: R_f=0.35, yellow oil (76 mg, 14%). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 58.07 (s, 1P), 70.55 (s, 2P) ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.88 (t, $^3J_{HH}$=7.0 Hz, 3H, N–CH_2–CH_3), 1.89 (t, $^3J_{HH}$=7.0 Hz, 3H, N–CH_2–CH_3), 1.07 (t, $^3J_{HH}$=6.7 Hz, 3H, N–CH_2–CH_3), 1.08 (t, $^3J_{HH}$=7.0 Hz, 3H, N–CH_2–CH_3), 1.19 (d, $^2J_{HH}$=5.8 Hz, 3H, CH–CH_3), 1.22 (d, $^2J_{HH}$=6.1 Hz, 3H, CH–CH_3), 1.27 (d, $^2J_{HH}$=6.4 Hz, 3H, CH–CH_3), 1.29 (d, $^2J_{HH}$=5.7 Hz, 3H, CH–CH_3), 1.33 (d, $^2J_{HH}$=6.1 Hz, 6H, CH–CH_3), 3.02 (m, $^3J_{HP}$=15.4 and 14.3 Hz, 4H, N–CH_2–CH_3), 3.28 (m, $^3J_{HP}$=13.2 Hz, 4H, N–CH_2–CH_3), 4.70 (d, $^2J_{HH}$=17.1 Hz, 1H, CH_2), 4.94 (d, $^2J_{HH}$=17.1 Hz, 1H, CH_2), 5.05 (m, $^2J_{HH}$=9.4 Hz, 3H, CH–$(CH_3)_2$), 7.16 (d, $^3J_{HH}$=8.5 Hz, 2H, H^4 or H^5), 7.44 (d, $^3J_{HH}$=8.5 Hz, 2H, H^4 or H^5), 7.74 (d, $^3J_{HH}$=8.8 Hz, 2H, H^3 or H^6), 7.82 (d, $^3J_{HH}$=9.2 Hz, 2H, H^3 or H^6), 7.91 (s, 1H, H^8), 7.95 (s, 1H, H^8) ppm. MS (MALDI): m/z=839 [M+H$^+$]. Anal. Calcd for $C_{38}H_{53}N_2O_7P_3S_3$ (838.22): C, 54.40%; H, 6.37%; N, 3.34%; P, 11.08%. Found: C, 54.10%; H, 6.15%; N, 3.50%; P, 11.20%.

Compound **10d**: R_f=0.21, yellow oil (86 mg, 12%). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 71.38 (s, 1P), 70.08 (s, 1P) ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.96–1.35 (m, $^3J_{HH}$=7.0 Hz, 24H, N–CH_2–CH_3), 1.43–1.50 (m, 24H, CH–CH_3), 3.17 (m, $^3J_{HP}$=15.4 and 14.3 Hz, 8H, N–CH_2–CH_3), 3.40 (m, $^3J_{HP}$=13.2 Hz, 8H, N–CH_2–CH_3), 4.63 (m, 2H, CH–$(CH_3)_2$), 4.80 (m, 2H, CH–$(CH_3)_2$), 4.93 (s, 2H, CH_2), 7.41 (d, $^3J_{HH}$=8.5 Hz, 2H, H^4 or H^5), 7.53 (br s, 4H, H_{Ar}), 7.61 (br s, 4H, H_{Ar}) ppm. MS (MALDI): m/z=1105 [M+H$^+$]. Anal. Calcd for $C_{49}H_{80}N_4O_8P_4S_4$ (1104.38): C, 53.24%; H, 7.30%; N, 5.07%; P, 11.21%. Found: C, 53.04%; H, 7.45%; N, 5.20%; P, 11.06%.

4.1.10. 2-Diethylamino-2-thio-4,5;78-dinaphtho-13,13′-bis(diethylaminophenylthiophosphoryl)-1,3,2-dioxaphosphocine (9f). A solution of dinaphthylmethane **1** (0.20 g, 0.60 mmol) and phosphorodiamidite **2f** (0.65 g, 2.41 mmol) in acetonitrile (4 mL) was kept at 20 °C for 24 h. The reaction mixture was treated with sulfur (0.08 g, 2.41 mmol) and stirred for 4 h at 20 °C. The solvent was evaporated and the product was isolated by column chromatography (silica gel, benzene/hexane=5:1, R_f=0.61). Compound **9f** is an orange film (0.23 g, 41%). Mp=128–129 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 67.11 (s, 3P) ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.89 (t, $^3J_{HH}$=7.0 Hz, 3H, N–CH_2–CH_3), 0.93 (t, $^3J_{HH}$=6.7 Hz, 3H, N–CH_2–CH_3), 1.09 (t, $^3J_{HH}$=7.0 Hz, 3H, N–CH_2–CH_3), 1.10 (t, $^3J_{HH}$= 7.3 Hz, 3H, N–CH_2–CH_3), 1.30 (t, $^3J_{HH}$=6.7 Hz, 6H, N–CH_2–CH_3), 3.09–3.15 (m, $^3J_{HP}$=11.9 and 12.5 Hz, 4H, N–CH_2–CH_3), 3.39 (m, $^3J_{HP}$=13.7 Hz, 8H, N–CH_2–CH_3), 4.90 (s, 2H, CH_2), 6.96 (m, 4H, Ph), 7.15 (d, $^3J_{HH}$=9.5 Hz, 1H, H^4 or H^5), 7.23 (d, $^3J_{HH}$=9.5 Hz, 1H, H^4 or H^5), 7.28–7.37 (m, 6H, Ph), 7.44 (d, $^3J_{HH}$=9.2 Hz, 1H, H^4 or H^5), 7.47 (d, $^3J_{HH}$=9.5 Hz, 1H, H^4 or H^5), 7.70 (d, $^3J_{HH}$= 8.8 Hz, 2H, H^3 or H^6), 7.74 (d, $^3J_{HH}$=9.2 Hz, 1H, H^3 or H^6), 7.82 (dd, $^3J_{HH}$=9.5 Hz, 1H, H^3 or H^6), 8.01 (s, 1H, H^8), 8.07 (s, 1H, H^8) ppm. ν_{max} (KBr) 2978, 2921, 2877, 1485, 1455, 1145, 1095, 1004, 990, 846, 798, 755 cm^{-1}. MS (MALDI): m/z=920 [M+H$^+$]. Anal. Calcd for $C_{45}H_{52}N_3O_6P_3S_3$ (919.22): C, 58.75%; H, 5.70%; N, 4.57%; P, 10.10%. Found: C, 59.05%; H, 5.78%; N, 4.51%; P, 9.98%.

4.1.11. 2-Diethylamino-2-thio-4,5;78-dinaphtho-13,13′-bis(diethylaminonaphthylthiophosphoryl)-1,3,2-dioxaphosphocine (9g). A solution of dinaphthylmethane **1** (0.15 g, 0.45 mmol) and phosphorodiamidite **2g** (0.57 g, 1.81 mmol) in acetonitrile (3 mL) was kept for 24 h at 20 °C. The reaction mixture was treated with sulfur (0.06 g, 1.81 mmol) and stirred for 4 h at 20 °C. The solvent was evaporated and the product was isolated by column chromatography (silica gel, benzene/hexane=4:1, R_f=0.58). Compound **9g** is an orange film (69 mg, 15%). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 67.11 (s, 3P) ppm. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.86 (t, $^3J_{HH}$=6.9 Hz, 3H, N–CH_2–CH_3), 0.93 (t, $^3J_{HH}$=7.0 Hz, 3H, N–CH_2–CH_3), 1.06 (t, $^3J_{HH}$=6.9 Hz, 3H, N–CH_2–CH_3), 1.11 (t, $^3J_{HH}$=6.9 Hz, 3H, N–CH_2–CH_3), 1.18 (t, $^3J_{HH}$=7.3 Hz, 6H, N–CH_2–CH_3), 3.08–3.28 (m, $^3J_{HP}$=14.6 and 12.1 Hz, 4H, N–CH_2–CH_3), 3.40 (m, $^3J_{HP}$=14.7 Hz, 8H, N–CH_2–CH_3), 4.84 (s, 2H, CH_2), 6.99–8.1 (m, 24H, H_{Ar}) ppm. ν_{max} (KBr) 2973, 2930, 2860, 1470, 1460, 1150, 1095, 1024, 990, 846, 788, 745 cm^{-1}. Anal. Calcd for $C_{53}H_{56}N_3O_6P_3S_3$: C, 62.40%; H, 5.53%; N, 4.12%; P, 9.11%. Found: C, 62.35%; H, 5.68%; N, 4.45%; P, 9.98%.

4.1.12. 2,2′,7,7′-Tetrakis(5″,5″-dimethyl-1″,3″,2″-dioxaphosphorinanoxy)dinaphthylmethane (11). A solution of dinaphthylmethane **1** (0.26 g, 0.77 mmol) and neopentyleneamide **2h** (0.63 g, 3.10 mmol) in acetonitrile (2.5 mL) was kept for 24 h at 20 °C. The colorless crystals that formed were filtered off and washed with a small portion of acetonitrile. Compound **11** (0.39 g, 60%) is a white powder. Mp 164–166 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 115.84 (s, 2P), 114.66 (s, 2P) ppm. ^{1}H NMR (300.1 MHz, $CDC1_3$): δ 0.72 (s, 6H, H^{13}), 0.75 (s, 6H, H^{13}), 1.28 (s, 12H, H^{13}), 3.34 (dd, $^2J_{HH}$=10.7 Hz, $^3J_{HP}$=21.8 Hz, 4H, H^{11e}), 3.37 (dd, $^2J_{HH}$=10.7 Hz, $^3J_{HP}$=21.3 Hz, 4H, H^{11e}), 4.17 (d, $^2J_{HH}$=9.8 Hz, 4H, H^{11a}), 4.32 (d, $^2J_{HH}$=10.7 Hz, 4H, H^{11a}), 4.91 (s, 2H, CH_2), 7.08 (d, $^3J_{HH}$=8.9 Hz, 2H, H^4 or H^5), 7.30 (d, $^3J_{HH}$=8.9 Hz, 2H, H^4 or H^5), 7.63 (d, $^3J_{HH}$=9.2 Hz, 2H, H^3 or H^6), 7.67 (d, $^3J_{HH}$=8.9 Hz, 2H, H^3 or H^6), 7.72 (s, 2H, H^8) ppm. ^{13}C NMR (121.5 MHz, $CDCl_3$): δ 22.57 (s, C^{13}), 22.67 (s, C^{13}), 23.55 (s, CH_2), 32.69 (s, C^{11}), 32.79 (s, C^{11}), 69.32 (s, C^{12}), 69.64 (s, C^{12}), 112.41 (d, C^8, $^2J_{PC}$=9.7 Hz), 118.84 (d, C^3 or C^6, $^2J_{PC}$=5.5 Hz), 118.96 (d, C^3 or C^6, $^3J_{PC}$=4.7 Hz), 125.04 (s, C^1), 127.42 (s, C^{10}), 127.67 (s, C^4 or C^5), 130.12 (s, C^4 or C^5), 134.79 (s, C^9), 148.881 (d, C–O–P, $^2J_{PC}$=6.6 Hz), 151.02 (d, C–O–P, $^2J_{PC}$=6.2 Hz) ppm. MS (MALDI): m/z=861 [M+H$^+$]. Anal. Calcd for $C_{41}H_{52}O_{12}P_4$ (860.24): C, 57.21%; H, 6.09%; P, 14.39%. Found: C, 56.98%; H, 6.42%; P, 14.26%.

4.1.13. 2,2′,7,7′-Tetrakis(2″-thio-5″,5″-dimethyl-1″,3″,2″-dioxaphosphorinanoxy)dinaphthylmethane (12a). A suspension of **11** (0.15 g, 0.17 mmol) and sulfur (0.02 g, 0.69 mmol) in a chloroform (1 mL)–benzene (1 mL) mixture was stirred for 2 h at 40 °C. Hexane (3 mL) was added to the reaction mixture, the precipitate was filtered off, and washed with hexane (5 mL). Compound **12a** (0.16 g, 92%) is a white powder. Mp 188–189 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 53.98 (s, 2P), 53.66 (s, 2P) ppm. ^{1}H NMR (300.1 MHz, $CDC1_3$): δ 0.75 (s, 6H, H^{14}), 0.83 (s, 6H, H^{14}), 1.23 (s, 6H, H^{14}), 1.29 (s, 6H, H^{14}), 3.72 (dd, $^2J_{HH}$=10.7 Hz, $^3J_{HP}$=23.2 Hz, 4H, H^{11e}), 3.87 (dd,

$^2J_{HH}$=11.1 Hz, $^3J_{HP}$=23.1 Hz, 4H, H^{11e}), 4.03 (d, $^2J_{HH}$=10.7 Hz, 4H, H^{11a}), 4.16 (d, $^2J_{HH}$=10.7 Hz, 4H, H^{11a}), 4.90 (s, 2H, CH_2), 7.42 (d, $^3J_{HH}$=8.7 Hz, 2H, H^4 or H^5), 7.50 (d, $^3J_{HH}$=8.9 Hz, 2H, H^4 or H^5), 7.74 (d, $^3J_{HH}$=8.9 Hz, 2H, H^3 or H^6), 7.81 (d, $^3J_{HH}$=8.9 Hz, 2H, H^3 or H^6), 7.82 (s, 2H, H^8) ppm. Anal. Calcd for $C_{41}H_{52}O_{12}P_4S_4$: C, 49.79%; H, 5.30%; P, 12.53%. Found: C, 50.09%; H, 5.45%; P, 12.38%.

4.1.14. 2,2′,7,7′-Tetrakis(2″-oxo-5″,5″-dimethyl-1″,3″,2″-dioxaphosphorinanoxy)dinaphthylmethane (12b). A suspension containing **11** (0.15 g, 0.17 mmol) and the hydrogen peroxide–urea adduct (0.064 g, 0.69 mmol) in chloroform (2 mL) was stirred for 4 h at 20 °C. The precipitate formed was filtered off, washed with water (20 mL), and the organic layer was separated. The solvent was evaporated and the residue was dried under vacuum (1 mmHg) at 70–80 °C. Compound **12b** (0.096 g, 60%) is a white powder. Mp 150–152 °C. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ −13.51 (s, 2P), −14.08 (s, 2P) ppm. ^{1}H NMR (300.1 MHz, $CDC1_3$): δ 0.75 (s, 6H, H^{14}), 0.87 (s, 6H, H^{14}), 1.24 (s, 6H, H^{14}), 1.29 (s, 6H, H^{14}), 3.73 (dd, $^2J_{HH}$=11.3 Hz, $^3J_{HP}$=22.9 Hz, 4H, H^{11e}), 3.87 (dd, $^2J_{HH}$=10.1 Hz, $^3J_{HP}$=22.9 Hz, 4H, H^{11e}), 4.04 (d, $^2J_{HH}$=10.7 Hz, 4H, H^{11a}), 4.16 (d, $^2J_{HH}$=11.0 Hz, 4H, H^{11a}), 4.89 (s, 2H, CH_2), 7.42 (d, $^3J_{HH}$=8.9 Hz, 2H, H^4 or H^5), 7.50 (d, $^3J_{HH}$=9.2 Hz, 2H, H^4 or H^5), 7.74 (d, $^3J_{HH}$=9.2 Hz, 2H, H^3 or H^6), 7.81 (d, $^3J_{HH}$=8.5 Hz, 2H, H^3 or H^6), 7.82 (s, 2H, H^8) ppm. MS (MALDI): m/z=925 [M+H$^+$]. Anal. Calcd for $C_{41}H_{52}O_{16}P_4$ (924.22): C, 53.25%; H, 5.67%; P, 13.40%. Found: C, 53.15%; H, 5.88%; P, 13.51%.

5. Supplementary material

The crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 620738. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 3 36 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Supplementary data

X-ray crystallographic data and structure refinement parameters for **11** and equilibrium geometry structures of **1**, **3a**, **4a**, and **5a**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.02.095.

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