Synthesis and study of "nonuniform" naphthylenephosphacyclophanes

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A method for the preparation of nionuniform phosphacyclophanes with two different naphthylene radicals and two phosphoramidite, phosphoramidate, or thiophosphoramidate residues in the molecule is proposed. The "nonuniform" phosphacyclophanes containing trivalent phosphorus are stable systems. Their oxidation or addition of sulfur to them changes the overall configuration of the molecules and decreases the stability of such systems.

Key words: dihydroxynaphthalenes, cyclophosphorylation, naphthylenephosphacyclophanes.

An important task of modern synthetic chemistry of organophosphorus compounds is the design of new types of phosphorus-containing macroheterocyclic cavity systems. The interest in these systems is due to the prospects of their use in the study of fundamental problems of the reactivity of phosphorus functional groups, the possibility of creating unusual supramolecular systems, studying the rules of molecular recognition, competing interactions in a system of identical phosphorus-containing groups, and so on. In addition, they can be used as molecular containers in solving various scientific, engineering, and medical problems.

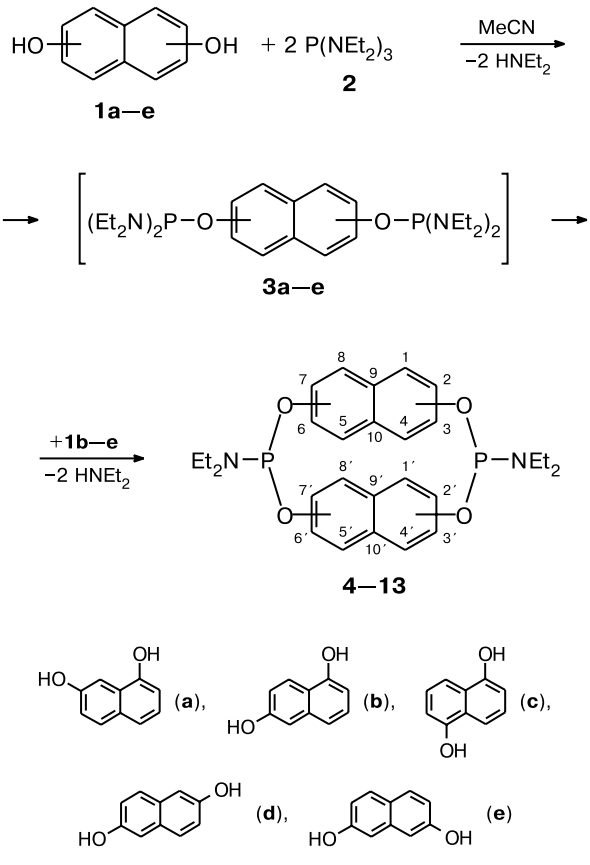
Previously,[1—3] we obtained the first representatives of phosphacyclophanes in whose molecules two identical naphthylene radicals are linked by *N*,*N*-dialkyl phosphoramidite, phosphoramidate, or thiophosphoramidate bridges. These compounds can be called "uniform" phosphacyclophanes. The purpose of the present study is to prepare analogous "nonuniform" systems containing different naphthylene radicals and to study their properties.

As the starting reagents, we chose dihydroxynaphthalenes with hydroxy groups located in different aromatic nuclei. Two of these compounds are asymmetric (1,7- and 1,6-dihydroxynaphthalenes **1a,b**) and the other three are symmetrical along various axes (1,5-, 2,6-, and 2,7-dihydroxynaphthalenes **1c—e**). Hexaethyl phosphorous triamide **2**, which reacts with bis-phenols in various solvents even at room temperature, was used as the phosphorylating reagent.[4]

The methods of synthesis includes two steps, namely, the preparation of bisphosphorylated dihydroxynaphthalenes and cyclophosphorylation of dibasic naphthols with these compounds (Scheme 1).

Acetonitrile was chosen as the solvent, because the final products are insoluble in it. The preparation and characteristics of compounds **3a—e** as thiophosphoramidates were described in our previous publication.[2,3] Note that in this case, of key importance is the time of complete bisphosphorylation of dihydroxynaphthalenes **1a—e**, which was determined from the ^{31}P NMR spectra

Scheme 1



4 (**3a**+**1b**), **5** (**3a**+**1c**), **6** (**3a**+**1d**), **7** (**3a**+**1e**), **8** (**3b**+**1c**), **9** (**3b**+**1d**), **10** (**3b**+**1e**), **11** (**3c**+**1d**), **12** (**3c**+**1e**), **13** (**3d**+**1e**)

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Table 1. Time required for complete bisphosphorylation of dihydroxynaphthalenes **1a—e** $P(NEt_2)_3$ in MeCN

Dihydroxynaphthalene*	τ/min
1a	20
1b	90
1c	20
1d	12
1e	12

* The concentration of the initial dihydroxynaphthalenes is 1 mol L^{-1}.

of the reaction mixtures (Table 1). The factor of time should be taken into account because dihydroxynaphthalene bis(phosphorodiamidites) are labile compounds; they tend to undergo dismutation giving uniform cyclic systems,[4] which can contaminate the target products.

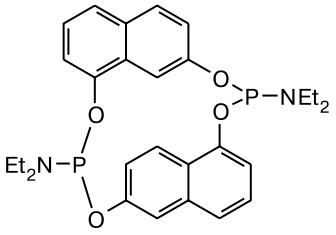
During bisphosphorylation, the signal at 117 ppm due to the $P(NEt_2)_3$ disappears from the ^{31}P NMR spectra; instead, a signal for the phosphorous ester diamide is accumulated at 132 ppm. During the period required for the completion of the first step, no dismutation takes place.

In the second step, cyclophosphorylation was over in 48 h at room temperature (≈20 °C), the products **4—13** formed in the reaction being separated from the solution as an oil. The cyclic phosphoramidites **4—13** thus formed, when dried *in vacuo*, were either oily products (**6**, **7**, **12**) or low-melting powders (**4**, **5**, **8—11**, **13**); they were readily soluble in CH_2Cl_2, C_6H_6, 1,4-dioxane, and Et_2O. The product yields were ~75%. The ^{31}P NMR spectra of compounds **4—13** exhibited singlets at about 140 ppm, which falls in the region typical of phosphorous ester diamides.

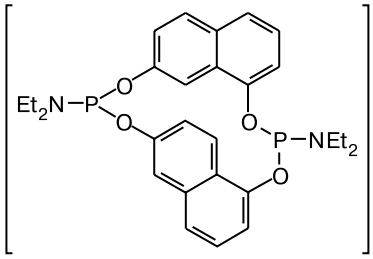
A distinctive feature of the derivatives based on 1,5- and 2,6-dihydroxynaphthalenes (**5**, **6**, **8**, **11**, and **13**) is the fact that the ^1H NMR signals of the aromatic part of the macrocyclic molecule do not shift upon the replacement of the second naphthyl fragment, whereas for analogous compounds based on other dihydroxynaphthalenes, these signals do shift. This can be attributed to the fact that, due to their structural features, these symmetrical naphthyl radicals form macrocycles having less degrees of freedom for conformational transitions.

It is noteworthy that cyclophosphorylation involving 1,7- and 1,6-dihydroxynaphthalenes can give two structural isomers of **4**, one with successive (1,6,1,7, isomer **A**) and one with pair (1,1,6,7, isomer **B**) linking of the naphthylene radicals.

However, we isolated only one structural isomer with successive connection of the hydroxy groups in the ring (**A**). This is indicated by the following facts. The ^{31}P NMR spectrum of compound **4** exhibited only one singlet, as both phosphorus atoms in the molecules of this isomer are magnetically equivalent. In addition, the ^1H and ^{13}C NMR spectra contained only one set of signals



4A



4B

and the chromatographic patterns had only one spot; this precluded the presence of an isomer mixture. It should be noted that our earlier synthesis of a "uniform" phosphocyclophane based on 1,7-dihydroxynaphthalene (**1a**) by the same procedure gave two structural isomers (1,7,1,7- and 1,1,7,7-isomers) with different spectral and physicochemical parameters.[3]

An interesting feature of the group of compounds based on 1,7-dihydroxynaphthalene is broadening of all signals in the ^1H NMR spectra. Neither the change of the solvent or temperature, nor an increase in the spectrometer operation frequency from 200 to 500 MHz results in a better resolution of the signals. We believe that this is related to the structure of the molecule, more precisely, to the presence of partially hindered conformations. The ^{13}C NMR spectra of these compounds corresponded to the proposed structures.

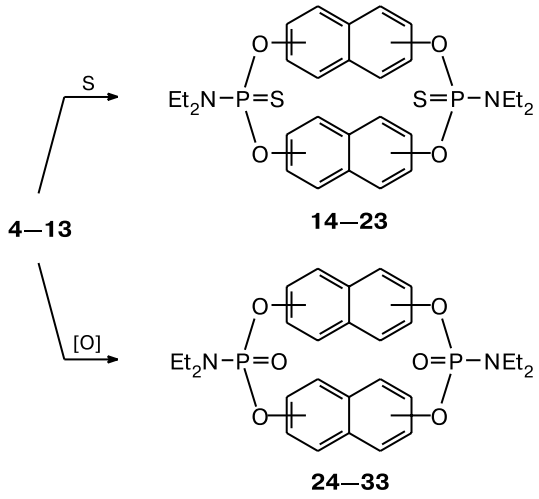
In addition, we also assumed that during storage in solution, the "nonuniform" phosphacyclophanes may tend to undergo symmetrization, *i.e.*, two "nonuniform" structures may be transformed into two "uniform" ones.[5] However, this reaction does not take place even within two months.

The MALDI-TOF mass spectrum of cyclophosphites **6** and **10** exhibits one peak with m/z 522.4, which is fully consistent with the calculated molecular mass for **6** and **10**.

In addition, comparison of "nonuniform" phosphacyclophanes with the "uniform" structures that we obtained previously[2,3] showed that the compounds derived from 1,5- and 2,6-dihydroxynaphthalenes **5**, **6**, **8**, **11**, and **13** have lower melting points than their symmetrical analogs.

In order to study the influence of the modification of the phosphorus unit on the chemical and structural properties of macrocyclic phosphites, we carried out their sulfurization and oxidation (Scheme 2).

Scheme 2



14, 24 (**3a**+**1b**), **15, 25** (**3a**+**1c**), **16, 26** (**3a**+**1d**), **17, 27** (**3a**+**1e**), **18, 28** (**3b**+**1c**), **19, 29** (**3b**+**1d**), **20, 30** (**3b**+**1e**), **21, 31** (**3c**+**1d**), **22, 32** (**3c**+**1e**), **23, 33** (**3d**+**1e**)

These reactions occurred at room temperature (≈20 °C) in CH_2Cl_2 over a period of 40 h.

Cyclothiophosphoramidates **14—23** were isolated by column chromatography. During isolation, the cyclic products underwent partial destruction, resulting in a lower yield. Unlike the "uniform" cyclothiophosphoramidates, which are powders, the nonuniform cyclothiophosphoramidates are oily products. Their ^{31}P NMR spectra show singlets at about 67 ppm, which is typical of thiophosphoramidates. Their individual character and the structure were proved unambiguously by TLC, ^{31}P and ^{1}H NMR spectroscopy, and elemental analysis.

The oxidation of phosphites **4—13** was accomplished by the complex hydrogen peroxide with urea. The resulting cyclophosphoramidates **24—33** were isolated in good yields by reprecipitation by hexane from a CH_2Cl_2 solution. They all were low-melting amorphous powders. Their ^{31}P NMR spectra showed singlets in the region of 1 ppm, which corresponds to most phosphoramidates. In the ^{1}H NMR spectra of the thiophosphates **14—17** and phosphates **24—27** derived from dihydroxynaphthalenes **1b—e**, the region of signals of the aromatic protons is markedly narrower than that in the spectra of analogous cyclophosphites. In our opinion, this is due to the increase in the rigidity of the aromatic cage of the molecule upon modification of the phosphorus fragment.

The change in the configuration of the phosphorus unit does not affect the resolution of the ^{1}H NMR signals for the group of rings based on 1,7-dihydroxynaphthalene (**1a**). The signals remain broadened at elevated temperatures and with a higher operation frequency of the spectrometer. The structures of phosphoramidates **24—33** were confirmed by ^{13}C NMR spectroscopy.

Table 2. Comparison of the steric energies of cyclophosphoramidites **4—13**, cyclothiophosphates **14—23**, and cyclophosphates **24—33**

Naphthylenes	$E_{ster} \cdot 10^{-19}$/J					
	Phosphite		Phosphorothioate		Phosphate	
1,7+1,6	**4**	29.1	**14**	91.6	**24**	83.3
1,7+1,5	**5**	33.8	**15**	93.5	**25**	92.2
1,7+2,7	**6**	30.8	**16**	95.8	**26**	84.4
1,7+2,6	**7**	37.3	**17**	89.0	**27**	82.1
1,6+1,5	**8**	33.7	**18**	90.6	**28**	86.4
1,6+2,7	**9**	44.4	**19**	86.3	**29**	79.7
1,6+2,6	**10**	30.3	**20**	85.5	**30**	84.3
1,5+2,6	**11**	30.8	**21**	80.5	**31**	80.2
1,5+2,7	**12**	39.1	**22**	89.9	**32**	86.1
2,6+2,7	**13**	32.3	**23**	85.4	**33**	82.4

The experiment showed that the cyclophosphates and, especially, cyclothiophosphates we synthesized are less stable than the corresponding cyclophosphites. In our opinion, the reason is in the change in electron density delocalization in the phosphorus unit and in the overall geometry of the cyclic molecule following the transition of phosphorus from the trivalent to pentavalent state. This was also supported by the computer MM2 optimization of the molecular geometry and steric energy in the gas phase [6] for cyclophosphites **4—13**, cyclothiophosphates **14—23**, and cyclophosphates **24—33**. It was shown that the steric energy of cyclophosphites is more than twice lower than this energy for the thio and oxo derivatives (Table 2).

Experimental

^{1}H NMR spectra of compounds **8—13**, **18—23**, and **28—33** were recorded on a Bruker AC-200 spectrometer, those of compounds **4—7**, **14—17**, and **24—27**, on a Bruker DRX-500 instrument; the ^{13}C NMR spectra of compounds **4—7**, **17**, and **24—27** were run on a Bruker AC-200 instrument operating at 80 MHz; the ^{31}P NMR spectra, on a Bruker WP-80SY spectrometer operating at 32.4 MHz. The standards used for recording the ^{1}H, ^{13}C, and ^{31}P NMR spectra were Me_4Si (internal) and 85% H_3PO_4 (external). Mass spectra were run on a Bruker Reflex III instrument by the laser-assisted desorption ionization technique (MALDI TOF) using $CHCl_3$ as the solvent and 2,4,6-trihydroxyacetophenone as the matrix. All syntheses were carried out under dry nitrogen using anhydrous solvents. The gas solid chromatography on a column was performed on silica gel L 100—250 μm, TLC was done on Silufol plates in 5 : 1 C_6H_6—dioxane (*A*); 3 : 1 C_6H_6—EtOH (*B*); and 5 : 1 $CHCl_3$—EtOH (*C*) solvent systems. The spots were visualized by iodine vapor or by burning.

The MM2 computations[6] for energy minimization were carried out using the Chem3D Ultra 7.0 program.

The physicochemical characteristics of the obtained compounds are listed in Table 3.

Cyclo[bis(naphthylenediethyl phosphoramidites)] (4—13). Dihydroxynaphthalene (**1a—e**) (0.648 g, 4 mmol) in 30 mL of

MeCN was added with stirring at ≈20 °C to phosphorous triamide **2** (2 g, 8 mmol). After a specified period of time (see Table 1), the other dihydroxynaphthalene (0.065 g, 4 mmol) in 20 mL MeCN was added to the reaction mixture. The mixture was stirred for 4 h and left for 48 h. The solution was decanted from the precipitate and the cyclophosphite was washed with MeCN and dried *in vacuo* for 2 h (70 °C, 1 Torr).

Cyclo[(1,7-naphthylene)(1,6-naphthylene)-bis(diethyl phosphoramidite)] (4). ^{1}H NMR ($CDCl_3$), δ: 1.06 (br.t, 12 H, CH_3, $^3J_{H,H}$ = 4.9 Hz); 3.15—3.45 (br.m, 8 H, CH_2N); 7.10—8.13 (br.m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.8 (s, 4 C, CH_3); 38.2 (dd, 4 C, CH_2N, $^2J_{P,C}$ = 24.5 Hz, $^3J_{P,C}$ = 5.1 Hz); 110.3 (d, C(8), $^3J_{P,C}$ = 6.1 Hz); 113.1 (d, C(2), $^3J_{P,C}$ = 5.2 Hz); 113.9 (d, C(2′), $^3J_{P,C}$ = 5.3 Hz); 114.1 (s, C(8′)); 116.9 (d, C(5′), $^3J_{P,C}$ = 6.2 Hz); 120.9 (s, C(7′)); 122.0 (s, C(6)); 122.4 (s, C(4)); 123.7 (s, C(9′)); 123.9 (s, C(4′)); 124.5 (s, C(5)); 126.9 (s, C(3′)); 127.1 (s, C(3)); 128.9 (s, C(9)); 135.2 (s, C(10)); 135.4 (s, C(10′)); 147.1 (d, C(1′), $^2J_{P,C}$ = 10.9 Hz); 149.1 (d, C(1), $^2J_{P,C}$ = 10.5 Hz); 149.7 (d, C(6′), $^2J_{P,C}$ = 11.6 Hz); 152.1 (d, C(7), $^2J_{P,C}$ = 11.3 Hz). ^{31}P NMR (CH_2Cl_2), δ: 140.7.

Cyclo[(1,7-naphthylene)(1,5-naphthylene)-bis(diethyl phosphoramidite)] (5). ^{1}H NMR ($CDCl_3$), δ: 1.02 (br.t, 12 H, CH_3, $^3J_{H,H}$ = 6.1 Hz); 3.12—3.48 (br.m, 8 H, CH_2N); 7.15—7.80 (br.m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.1 (s, 4 C, CH_3); 39.4

Table 3. Physicochemical characteristics of the synthesized cyclophosphoramidites **4—13**, cyclothiophosphates **14—23**, and cyclophosphates **24—33**

Compound	Yield (%)	M.p. /°C	R_f (system)	Found / Calculated (%)				Molecular formula	Mass spectrum	
				C	H	N	P		found, *m/z*, M	calculated, M
4	77	81—83	0.76 (*A*)	64.09 64.36	6.23 6.18	5.42 5.36	11.48 11.86	$C_{28}H_{32}N_2O_4P_2$		
5	71	Oil	0.71 (*A*)	— 	— 	— 	11.55 11.86	$C_{28}H_{32}N_2O_4P_2$		
6	75	76—78	0.74 (*A*)	64.12 64.36	6.21 6.18	5.46 5.36	11.46 11.86	$C_{28}H_{32}N_2O_4P_2$	522.59	522.21
7	71	Oil	0.76 (*A*)	— 	— 	— 	11.59 11.86	$C_{28}H_{32}N_2O_4P_2$		
8	72	Oil	0.70 (*A*)	— 	— 	— 	11.52 11.86	$C_{28}H_{32}N_2O_4P_2$		
9	77	99—101	0.69 (*A*)	— 	— 	— 	11.58 11.86	$C_{28}H_{32}N_2O_4P_2$		
10	78	111—113	0.61 (*A*)	64.13 64.36	6.22 6.18	5.40 5.36	11.48 11.86	$C_{28}H_{32}N_2O_4P_2$	522.59	522.19
11	71	72—73	0.69 (*A*)	— 	— 	— 	11.62 11.86	$C_{28}H_{32}N_2O_4P_2$		
12	73	Oil	0.77 (*A*)	64.10 64.36	6.22 6.18	5.48 5.36	11.55 11.86	$C_{28}H_{32}N_2O_4P_2$		
13	78	112—114	0.59 (*A*)	64.11 64.36	6.20 6.18	5.51 5.36	11.66 11.86	$C_{28}H_{32}N_2O_4P_2$		
14	55	120—122	0.79 (*A*)	57.59 57.32	5.60 5.50	4.68 4.77	10.55 10.56	$C_{28}H_{32}N_2O_4P_2S_2$		
15	49	Oil	0.71 (*A*), 0.62 (*B*)	— 	— 	— 	10.53 10.56	$C_{28}H_{32}N_2O_4P_2S_2$		
16	50	118—120	0.81 (*A*), 0.63 (*B*)	57.29 57.32	5.48 5.50	4.75 4.77	10.57 10.56	$C_{28}H_{32}N_2O_4P_2S_2$		
17	52	Oil	0.78 (*A*)	— 	— 	— 	10.59 10.56	$C_{28}H_{32}N_2O_4P_2S_2$		
18	53	126—128	0.69 (*A*)	57.44 57.32	5.59 5.50	4.81 4.77	10.56 10.56	$C_{28}H_{32}N_2O_4P_2S_2$	586.32	586.18
19	60	Oil	0.72 (*A*), 0.6 (*B*)	— 	— 	— 	10.55 10.56	$C_{28}H_{32}N_2O_4P_2S_2$		
20	51	106—108	0.80 (*A*)	— 	— 	— 	10.59 10.56	$C_{28}H_{32}N_2O_4P_2S_2$		
21	54	Oil	0.64 (*A*), 0.64 (*B*)	57.39 57.32	5.42 5.50	4.71 4.77	10.61 10.56	$C_{28}H_{32}N_2O_4P_2S_2$		
22	51	Oil	0.77 (*A*)	— 	— 	— 	10.59 10.59	$C_{28}H_{32}N_2O_4P_2S_2$		

(*to be continued*)

Table 3 (*continued*)

Compound	Yield (%)	M.p. /°C	R_f (system)	Found / Calculated (%)				Molecular formula	Mass spectrum	
				C	H	N	P		found, *m/z*, M	calculated, M
23	52	121—123	0.68 (*A*), 0.64 (*B*)	—	—	—	10.54 10.56	$C_{28}H_{32}N_2O_4P_2S_2$	586.32	586.12
24	92	122—124	0.61 (*B*), 0.89 (*C*)	—	—	—	11.20 11.17	$C_{28}H_{32}N_2O_6P_2$	554.29	554.09
25	94	118—120	0.88 (*C*)	60.78 60.64	5.65 5.82	4.97 5.05	11.26 11.17	$C_{28}H_{32}N_2O_6P_2$		
26	93	112—114	0.56 (*B*), 0.76 (*C*)	60.81 60.64	5.51 5.82	5.10 5.05	11.21 11.17	$C_{28}H_{32}N_2O_6P_2$		
27	92	Oil	0.79 (*C*)	—	—	—	11.29 11.17	$C_{28}H_{32}N_2O_6P_2$		
28	94	115—117	0.61 (*B*), 0.7 (*C*)	—	—	—	11.22 11.17	$C_{28}H_{32}N_2O_6P_2$		
29	92	106—108	0.84 (*C*)	60.59 60.64	5.80 5.82	5.10 5.05	11.18 11.17	$C_{28}H_{32}N_2O_6P_2$		
30	93	123—125	0.81 (*C*)	—	—	—	11.21 11.17	$C_{28}H_{32}N_2O_6P_2$		
31	90	114—116	0.58 (*B*), 0.72 (*C*)	60.68 60.64	5.73 5.82	5.15 5.05	11.21 11.17	$C_{28}H_{32}N_2O_6P_2$	554.29	554.18
32	93	92—93	0.84 (*C*)	60.6 60.64	5.84 5.82	5.09 5.05	11.21 11.17	$C_{28}H_{32}N_2O_6P_2$		
33	91	126—127	0.54 (*B*), 0.82 (*C*)	—	—	—	11.19 11.17	$C_{28}H_{32}N_2O_6P_2$		

(d, 4 C, CH_2N, $^2J_{P,C}$ = 25.1 Hz); 110.3 (d, C(8), $^3J_{P,C}$ = 6.3 Hz); 112.9 (d, C(2), $^3J_{P,C}$ = 5.9 Hz); 115.5 (d, C(2′), C(6′), $^3J_{P,C}$ = 6.1 Hz); 121.9 (d, C(6), $^3J_{P,C}$ = 6.1 Hz); 122.4 (s, C(4)); 122.9 (s, C(9′), C(10′)); 124.1 (s, C(5)); 125.9 (s, C(4′), C(8′)); 126.9 (s, C(3)); 129.1 (s, C(9)); 132.3 (s, C(3′), C(7′)); 135.4 (s, C(10)); 148.4 (d, C(1′), C(5′), $^2J_{P,C}$ = 9.9 Hz); 149.2 (d, C(1)); 151.8 (d, C(7), $^2J_{P,C}$ = 10.3 Hz). ^{31}P (CH_2Cl_2), δ: 140.8.

Cyclo[(1,7-naphthylene)(2,6-naphthylene)-bis(diethyl phosphoramidite)] (6). ^{1}H NMR ($CDCl_3$), δ: 1.04 (br.t, 12 H, CH_3, $^3J_{H,H}$ = 4.5 Hz); 3.16—3.40 (br.m, 8 H, CH_2N); 7.15—7.90 (br.m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.7 (s, 4 C, CH_3); 38.2 (d, 4 C, CH_2N, $^2J_{P,C}$ = 24.3 Hz); 110.1 (d, C(2), $^3J_{P,C}$ = 6.0 Hz); 110.3 (d, C(1′), C(5′)); 113.4 (d, C(8), $^3J_{P,C}$ = 5.8 Hz); 115.5 (d, C(3′,7′), $^3J_{P,C}$ = 5.2 Hz); 121.8 (s, C(6)); 122.2 (s, C(4)); 124.1 (s, C(5)); 128.5 (s, C(4′), C(8′)); 129.3 (s, C(3)); 129.4 (s, C(9)); 130.6 (s, C(9′), C(10′)); 131.3 (s, C(10)); 149.2 (d, C(1), $^2J_{P,C}$ = 11.5 Hz); 150.5 (d, C(2′), C(6′), $^2J_{P,C}$ = 11.9); 151.6 (d, C(7), $^2J_{P,C}$ = 11.5 Hz). ^{31}P NMR (CH_2Cl_2) δ: 140.9.

Cyclo[(1,7-naphthylene)(2,7-naphthylene)-bis(diethyl phosphoramidite)] (7). ^{1}H NMR ($CDCl_3$), δ: 1.02 (br.t, 12 H, CH_3, $^3J_{H,H}$ = 5.9 Hz); 3.25—3.41 (br.m, 8 H, CH_2N); 7.40—8.10 (br.m, 12 H, CH). ^{13}C NMR ($CDCl_3$), δ: 14.7 (s, 4 C, CH_3); 38.2 (d, 4 C, CH_2N, $^2J_{P,C}$ = 24.7 Hz); 110.3 (d, C(2), $^3J_{P,C}$ = 6.0 Hz); 113.4 (d, C(8), $^3J_{P,C}$ = 5.8 Hz); 114.5 (d, C(1′), C(8′), $^3J_{P,C}$ = 6.1 Hz); 119.7 (d, C(3′), C(6′)); 121.9 (s, C(6)); 122.3 (s, C(4)); 124.1 (s, C(5)); 126.4 (s, C(3)); 128.4 (s, C(4′), C(5′)); 129.1 (s, C(9)); 131.3 (s, C(10′)); 135.4 (s, C(9′), C(10)); 149.3 (d, C(1), $^2J_{P,C}$ = 11.8 Hz); 151.6 (d, C(7), $^2J_{P,C}$ = 12.1 Hz); 152.2 (d, C(2′), C(7′), $^2J_{P,C}$ = 12.0 Hz). ^{31}P NMR (CH_2Cl_2), δ: 140.8.

Cyclo[(1,6-naphthylene)(1,5-naphthylene)-bis(diethyl phosphoramidite)] (8). ^{1}H NMR ($CDCl_3$), δ: 1.13 (d, 12 H, CH_3, ^3J = 7.1 Hz); 3.39 (dd, 8 H, CH_2N, $^3J_{P,H}(1,1′)$ = 11.5 Hz, $^3J_{P,H}(7,5′)$ = 11.0 Hz); 7.07 (d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 6.7 Hz); 7.18 (d, 1 H, H(7), $^3J_{H(7),H(8)}$ = 8.5 Hz); 7.22 (d, 2 H, H(2′), H(6′), $^3J_{H(2′),H(6′)}$ = 7.8 Hz); 7.31 (t, 1 H, H(3), $^3J_{H(2),H(3)}$ = 6.7 Hz); 7.34 (t, 2 H, H(3′), H(7′), $^3J_{H(3′),H(4′)}$ = 7.7 Hz); 7.38 (d, 1 H, H(4), $^3J_{H(3),H(4)}$ = 7.5 Hz); 7.46 (s, 1 H, H(5)); 7.93 (d, 2 H, H(4′), H(8′), $^3J_{H(3′),H(4′)}$ = 7.7 Hz); 8.16 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 8.5 Hz). ^{31}P NMR (CH_2Cl_2), δ: 140.9.

Cyclo[(1,6-naphthylene)(2,6-naphthylene)-bis(diethyl phosphoramidite) (9). ^{1}H NMR ($CDCl_3$), δ: 1.13 (d, 12 H, CH_3, ^3J = 6.6 Hz); 3.33 (dd, 8 H, CH_2N, $^3J_{P,H}(1,2′)$ = 12.2 Hz, $^3J_{P,H}(6,6′)$ = 12.2 Hz); 7.08 (d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 6.6 Hz); 7.22 (d, 2 H, H(3′), H(7′), $^3J_{H(3′),H(4′)}$ = 9.2 Hz); 7.30 (t, 1 H, H(3), $^3J_{H(2),H(3)}$ = 6.6 Hz); 7.33 (d, 1 H, H(7), $^3J_{H(7),H(8)}$ = 8.8 Hz); 7.39 (d, 1 H, H(4), $^3J_{H(3),H(4)}$ = 7.7 Hz); 7.41 (s, 1 H, H(5)); 7.43 (s, 2 H, H(1′), H(5′)); 7.64 (d, 2 H, H(4′), H(8′), $^3J_{H(3′),H(4′)}$ = 9.2 Hz); 8.17 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 8.8 Hz). ^{31}P NMR (CH_2Cl_2), δ: 141.1.

Cyclo[(1,6-naphthylene)(2,7-naphthylene)-bis(diethyl phosphoramidite) (10). ^{1}H NMR ($CDCl_3$), δ: 1.09 (d, 12 H, CH_3, ^3J = 8.1 Hz); 3.32 (dd, 8 H, CH_2N, $^3J_{P,H}(1,2′)$ = 10.5 Hz, $^3J_{P,H}(6,7′)$ = 10.3 Hz); 7.06 (d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 7.3 Hz); 7.17 (d, 2 H, H(3′), H(6′), $^3J_{H(3′),H(4′)}$ = 8.8 Hz); 7.23 (d, 1 H, H(7), $^3J_{H(7),H(8)}$ = 8.5 Hz); 7.31 (t, 1 H, H(3), $^3J_{H(2),H(3)}$ = 7.3 Hz); 7.36 (s, 1 H, H(5)); 7.41 (s, 2 H, H(1′), H(8′)); 7.43 (d, 1 H, H(4), $^3J_{H(3),H(4)}$ = 7.7 Hz); 7.70 (d, 2 H, H(4′), H(5′),

$^3J_{H(3'),H(4')}$ = 8.8 Hz); 8.15 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 8.5 Hz). ^{31}P NMR (CH_2Cl_2), δ: 140.9.

Cyclo[(1,5-naphthylene)(2,6-naphthylene)-bis(diethyl phosphoramidite)] (11). ^{1}H NMR ($CDCl_3$), δ: 1.15 (t, 12 H, CH_3, ^3J = 7.2 Hz); 3.39 (m, 8 H, CH_2N); 7.21 (d, 2 H, H(3′), H(7′), $^3J_{H(3'),H(4')}$ = 9.1 Hz); 7.34 (d, 2 H, H(2), H(6), $^3J_{H(2),H(3)}$ = 7.1 Hz); 7.46 (s, 2 H, H(1′), H(5′)); 7.67 (t, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 8.3 Hz); 7.71 (d, 2 H, H(4′), H(8′), $^3J_{H(3'),H(4')}$ = 9.1 Hz); 7.94 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 8.3 Hz). ^{31}P NMR (CH_2Cl_2), δ: 141.2.

Cyclo[(1,5-naphthylene)(2,7-naphthylene)-bis(diethyl phosphoramidite)] (12). ^{1}H NMR ($CDCl_3$), δ: 1.10 (t, 12 H, CH_3, ^3J = 7.5 Hz); 3.34 (m, 8 H, CH_2N); 7.15 (d, 2 H, H(3′), H(6′), $^3J_{H(3'),H(4')}$ = 8.8 Hz); 7.18 (d, 2 H, H(2), H(6), $J_{H(2),H(3)}$ = 7.1 Hz); 7.34 (t, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 8.3 Hz); 7.36 (s, 2 H, H(1′), H(8′)); 7.69 (d, 2 H, H(4′), H(5′), $^3J_{H(3'),H(4')}$ = 8.8 Hz); 7.90 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 8.3 Hz). ^{31}P NMR (CH_2Cl_2), δ: 140.9.

Cyclo[(2,6-naphthylene)(2,7-naphthylene)-bis(diethyl phosphoramidite)] (13). ^{1}H NMR ($CDCl_3$), δ: 1.08 (t, 12 H, CH_3, ^3J = 7.0 Hz); 3.29 (m, 8 H, CH_2N); 7.16 (d, 2 H, H(3′), H(6′), $^3J_{H(3'),H(4')}$ = 8.9 Hz); 7.25 (d, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 9.2 Hz); 7.36 (s, 2 H, H(1′), H(8′)); 7.42 (s, 2 H, H(1), H(5)); 7.65 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 9.2 Hz); 7.70 (d, 2 H, H(4′), H(5′), $^3J_{H(3'),H(4')}$ = 8.9 Hz). ^{31}P NMR (CH_2Cl_2), δ: 141.2.

Cyclo[bis(naphthylene diethyl thiophosphoramidates)] (14—23). Sulfur (0.123 g, 3.8 mmol) was added to cyclophosphite (**4—13**) (1 g, 1.9 mmol) in 12 mL of CH_2Cl_2. The mixture was stirred for 2 h at ≈20 °C and left for 38 h. The solution was filtered, the solvent was removed in a vacuum of a water-aspirator pump, and the residue was chromatographed on a column, the products being eluted by a 7 : 1 C_6H_6—dioxane mixture. The isolated cyclothiophosphates were dried *in vacuo* for 2 h (70 °C, 1 Torr).

Cyclo[(1,7-naphthylene)(1,6-naphthylene)-bis(diethyl thiophosphoramidate)] (14). ^{1}H NMR ($CDCl_3$), δ: 1.16 (br.t, 12 H, CH_3, $^3J_{H,H}$ = 5.5 Hz); 3.15—3.31 (br.m, 8 H, CH_2N); 7.10—7.77 (br.m, 12 H, Ar). ^{31}P NMR (CH_2Cl_2), δ: 66.7.

Cyclo[(1,7-naphthylene)(1,5-naphthylene)-bis(diethyl thiophosphoramidate)] (15). ^{1}H NMR ($CDCl_3$), δ: 0.98 (br.t, 12 H, CH_3, $^3J_{H,H}$ = 5.9 Hz); 3.11—3.24 (br.m, 8 H, CH_2N); 6.90—8.00 (br.m, 12 H, Ar). ^{31}P NMR (CH_2Cl_2), δ: 66.6.

Cyclo[(1,7-naphthylene)(2,6-naphthylene)-bis(diethyl thiophosphoramidate)] (16). ^{1}H NMR ($CDCl_3$), δ: 1.10 (br.t, 12 H, CH_3, $^3J_{H,H}$ = 5.3 Hz); 3.45—3.61 (br.m, 8 H, CH_2N); 7.27—8.07 (br.m, 12 H, CH). ^{31}P NMR (CH_2Cl_2), δ: 67.0.

Cyclo[(1,7-naphthylene)(2,7-naphthylene)-bis(diethyl thiophosphoramidate)] (17). ^{1}H NMR ($CDCl_3$), δ: 1.10 (br.t, 12 H, CH_3, ^3J = 8.0 Hz); 3.39—3.52 (br.m, 8 H, CH_2N); 7.37—8.06 (br.m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.9 (s, 4 C, CH_3); 39.1 (d, 4 C, CH_2N, $^2J_{P,C}$ = 27.2 Hz); 110.9 (d, C(2), $^3J_{P,C}$ = 4.9 Hz); 113.2 (d, C(8), $^3J_{P,C}$ = 5.5 Hz); 115.1 (d, C(1′), C(8′), $^2J_{P,C}$ = 11.0 Hz); 120.4 (d, C(3′), C(6′), $^3J_{P,C}$ = 5.8 Hz); 121.0 (s, C(4)); 122.6 (s, C(6)); 125.2 (s, C(5)); 127.0 (s, C(3)); 129.2 (s, C(9)); 129.4 (s, C(4′), C(5′)); 131.9 (s, C(10′)); 134.9 (s, C(9′)); 136.9 (s, C(10)); 150.1 (d, C(1), $^2J_{P,C}$ = 11.2 Hz); 151.7 (d, C(7), $^3J_{P,C}$ = 11.0 Hz); 151.8 (d, C(2′), C(7′), $^2J_{P,C}$ = 10.9). ^{31}P NMR (CH_2Cl_2), δ: 66.9.

Cyclo[(1,6-naphthylene)(1,5-naphthylene)-bis(diethyl thiophosphoramidate)] (18). ^{1}H NMR ($CDCl_3$), δ: 1.18 (d, 12 H, CH_3, ^3J = 7.1 Hz); 3.54 (dd, 8 H, CH_2N, $^3J_{P,H}(1,1')$ = 9.9 Hz, $^3J_{P,H}(6,5')$ = 12.9 Hz); 7.32 (d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 6.7 Hz); 7.37 (d, 2 H, H(2′), H(6′), $^3J_{H(2'),H(6')}$ = 7.8 Hz); 7.39 (d, 1 H, H(7), $^3J_{H(7),H(8)}$ = 8.9 Hz); 7.42 (d, 1 H, H(4), $^3J_{H(3),H(4)}$ = 7.7 Hz); 7.52 (t, 1 H, H(3), $^3J_{H(2),H(3)}$ = 6.7 Hz); 7.56 (s, 1 H, H(5)); 7.74 (t, 2 H, H(3′), H(7′), $^3J_{H(3'),H(4')}$ = 9.1 Hz); 7.84 (d, 2 H, H(4′), H(8′), $^3J_{H(3'),H(4')}$ = 9.1 Hz); 8.03 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 8.9 Hz). ^{31}P NMR (CH_2Cl_2), δ: 66.7.

Cyclo[(1,6-naphthylene)(2,6-naphthylene)-bis(diethyl thiophosphoramidate)(19). ^{1}H NMR ($CDCl_3$), δ: 1.18 (d, 12 H, CH_3, ^3J = 6.7 Hz); 3.51 (dd, 8 H, CH_2N, $^3J_{P,H}(1,2')$ = 12.1 Hz, $^3J_{P,H}(6,6')$ = 11.0 Hz); 7.32 (d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 6.8 Hz); 7.37 (d, 2 H, H(3′), H(7′), $^3J_{H(3'),H(4')}$ = 9.16 Hz); 7.40 (t, 1 H, H(3), $^3J_{H(2),H(3)}$ = 6.8 Hz); 7.44 (d, 1 H, H(7), $^3J_{H(7),H(8)}$ = 8.8 Hz); 7.49 (s, 1 H, H(5)); 7.61 (d, 1 H, H(4), $^3J_{H(3),H(4)}$ = 7.6 Hz); 7.66 (s, 2 H, H(1′), H(5′)); 7.73 (d, 2 H, H(4′), H(8′), $^3J_{H(3'),H(4')}$ = 9.15 Hz); 8.03 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 8.8 Hz). ^{31}P NMR (CH_2Cl_2), δ: 67.4.

Cyclo[(1,6-naphthylene)(2,7-naphthylene)-bis(diethyl thiophosphoramidate) (20). ^{1}H NMR ($CDCl_3$), δ: 1.16 (t, 12 H, CH_3, ^3J = 7.2 Hz); 3.49 (dd, 8 H, CH_2N, $^3J_{P,H}(1,2')$ = 13.8 Hz, $^3J_{P,H}(6,7')$ = 13.2 Hz); 7.36 (d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 7.7 Hz); 7.41 (d, 1 H, H(7), $^3J_{H(7),H(8)}$ = 9.4 Hz); 7.53 (d, 2 H, H(3′), H(6′), $^3J_{H(3'),H(4')}$ = 8.8 Hz); 7.55 (t, 1 H, H(3), $^3J_{H(2),H(3)}$ = 7.7 Hz); 7.60 (d, 1 H, H(4), $^3J_{H(3),H(4)}$ = 7.8 Hz); 7.62 (s, 1 H, H(5)); 7.67 (s, 2 H, H(1′), H(8′)); 7.77 (d, 2 H, H(4′), H(5′), $^3J_{H(3'),H(4')}$ = 8.8 Hz); 8.04 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 9.4 Hz). ^{31}P NMR (CH_2Cl_2), δ: 67.1.

Cyclo[(1,5-naphthylene)(2,6-naphthylene)-bis(diethyl thiophosphoramidate)] (21). ^{1}H NMR ($CDCl_3$), δ: 1.20 (t, 12 H, CH_3, ^3J = 7.1 Hz); 3.55 (m, 8 H, CH_2N); 7.37 (d, 2 H, H(3′), H(7′), $^3J_{H(3'),H(4')}$ = 8.8 Hz); 7.42 (d, 2 H, H(2), H(6), $^3J_{H(2),H(3)}$ = 7.3 Hz); 7.44 (s, 2 H, H(1′), H(5′)); 7.62 (t, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 8.1 Hz); 7.75 (d, 2 H, H(4′), H(8′), $^3J_{H(3'),H(4')}$ = 8.8 Hz); 7.83 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 8.1 Hz). ^{31}P NMR (CH_2Cl_2), δ: 67.1.

Cyclo[(1,5-naphthylene)(2,7-naphthylene)-bis(diethyl thiophosphoramidate)] (22). ^{1}H NMR ($CDCl_3$), δ: 1.19 (t, 12 H, CH_3, ^3J = 6.8 Hz); 3.71 (m, 8 H, CH_2N); 7.32 (s, 2 H, H(1′), H(8′)); 7.38 (d, 2 H, H(3′), H(6′), $^3J_{H(3'),H(4')}$ = 8.7 Hz); 7.58 (d, 2 H, H(2), H(6), $^3J_{H(2),H(3)}$ = 7.1 Hz); 7.64 (t, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 8.3 Hz); 7.70 (d, 2 H, H(4′), H(5′), $^3J_{H(3'),H(4')}$ = 8.6 Hz); 7.83 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 8.3 Hz). ^{31}P NMR (CH_2Cl_2), δ: 66.8.

Cyclo[(2,6-naphthylene)(2,7-naphthylene)-bis(diethyl thiophosphoramidate)] (23). ^{1}H NMR ($CDCl_3$), δ: 1.03 (t, 12 H, CH_3, ^3J = 6.9 Hz); 3.41 (m, 8 H, CH_2N); 7.28 (d, 2 H, H(3′), H(6′), $^3J_{H(3'),H(4')}$ = 8.8 Hz); 7.36 (d, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 8.8 Hz); 7.54 (s, 2 H, H(1), H(5)); 7.66 (s, 2 H, H(1′), H(8′)); 7.74 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 8.8 Hz); 7.96 (d, 2 H, H(4′), H(5′), $^3J_{H(3'),H(4')}$ = 8.7 Hz). ^{31}P NMR (CH_2Cl_2), δ: 66.5.

Cyclo[bis(naphthylene diethyl phosphoramidates)] (24—33). The H_2O_2 complex with urea (commercial hydroperite) (0.348 g, 4.4 mmol) was added to cyclophosphite (**4—13**) (1 g, 1.9 mmol) in 12 mL of CH_2Cl_2. The mixture was stirred for 4 h at ≈20 °C and left for 36 h. Then the solution was cooled to −5 °C and filtered, the solvent was removed *in vacuo* down to a small volume, and 30 mL of hexane was added. After 24 h, the solution was decanted from the precipitate, and the residue was dried *in vacuo* for 2 h (70 °C, 1 Torr).

Cyclo[(1,7-naphthylene)(1,6-naphthylene)-bis(diethyl phosphoramidate)] (24). ^{1}H NMR ($CDCl_3$), δ: 1.08 (br.d, 12 H, CH_3, ^3J = 7.4 Hz); 3.39—3.48 (br.m, 8 H, CH_2N); 7.35—8.00 (br.m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 13.8 (s, 4 C, CH_3); 39.9 (d, 4 C, CH_2N, $^2J_{P,C}$ = 11.6 Hz); 110.7 (d, C(8), $^3J_{P,C}$ = 6.3 Hz); 113.9 (d, C(2′), $^3J_{P,C}$ = 7.0 Hz); 114.1 (s, C(8′)); 115.2 (d, C(2), $^3J_{P,C}$ = 6.6 Hz); 116.9 (d, C(5′), $^3J_{P,C}$ = 6.1 Hz); 120.5 (s, C(6)); 120.9 (s, C(7′)); 122.6 (s, C(9′)); 123.7 (s, C(4)); 123.9 (s, C(4′)); 124.1 (s, C(5)); 125.1 (s, C(3)); 126.9 (s, C(3′)); 129.8 (s, C(9)); 132.0 (s, C(10)); 135.4 (s, C(10′)); 147.1 (d, C(1′), $^3J_{P,C}$ = 6.3 Hz); 149.1 (d, C(1), $^2J_{P,C}$ = 12.3 Hz); 149.7 (d, C(6′), $^3J_{P,C}$ = 6.8 Hz); 149.9 (d, C(7), $^2J_{P,C}$ = 10.2 Hz). ^{31}P NMR (CH_2Cl_2), δ: 1.3.

Cyclo[(1,7-naphthylene)(1,5-naphthylene)-bis(diethyl phosphoramidate)] (25). ^{1}H NMR ($CDCl_3$), δ: 0.99 (br.d, 12 H, CH_3, ^3J = 7.3 Hz); 3.19—3.26 (br.m, 8 H, CH_2N); 7.35—8.12 (br.m, 12 H, CH). ^{31}P NMR (CH_2Cl_2), δ: 1.2.

Cyclo[(1,7-naphthylene)(2,6-naphthylene)-bis(diethyl phosphoramidate)] (26). ^{1}H NMR ($CDCl_3$), δ: 1.02 (br.t, 12 H, CH_3, J = 6.9 Hz); 3.00—3.22 (br.m, 8 H, CH_2N); 7.40—8.10 (br.m, 12 H, CH). ^{13}C NMR ($CDCl_3$), δ: 13.7 (s, 4 C, CH_3); 39.2 (d, 4 C, CH_2N, $^2J_{P,C}$ = 11.9 Hz); 110.3 (d, C(2), $^3J_{P,C}$ = 5.6 Hz); 113.4 (d, C(8), $^3J_{P,C}$ = 6.1 Hz); 114.5 (d, C(4′), C(8′), $^3J_{P,C}$ = 7.0); 119.7 (d, C(3′,7′), $^2J_{P,C}$ = 6.8 Hz); 121.9 (s, C(6)); 122.3 (s, C(4)); 124.1 (s, C(5)); 126.4 (s, C(3)); 128.4 (s, C(1′), C(5′)); 129.1 (s, C(9),C); 131.3 (s, C(10′)); 135.4 (s, C(10,9′)); 149.3 (d, C(1), $^2J_{P,C}$ = 9.5 Hz); 151.2 (d, C(2′), C(6′), $^2J_{P,C}$ = 10.0 Hz); 151.6 (d, C(7), CO). ^{31}P NMR (CH_2Cl_2), δ: 1.3.

Cyclo[(1,7-naphthylene)(2,7-naphthylene)-bis(diethyl phosphoramidate)] (27). ^{1}H NMR ($CDCl_3$), δ: 1.04 (br.d, 12 H, CH_3, ^3J = 7.0 Hz); 3.29—3.38 (br.m, 8 H, CH_2N); 7.33—8.09 (br.m, 12 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 13.7 (s, 4 C, CH_3); 39.7 (d, 4 C, CH_2N, $^2J_{P,C}$ = 9.8 Hz); 110.7 (d, C(2), $^3J_{P,C}$ = 6.6 Hz); 115.4 (d, C(8), $^3J_{P,C}$ = 5.9 Hz); 116.1 (d, C(1′), C(8′), $^3J_{P,C}$ = 6.0 Hz); 119.8 (d, C(3′), C(6′), $^3J_{P,C}$ = 6.5 Hz); 121.1 (s, C(6)); 124.1 (s, C(4)); 125.0 (s, C(5)); 126.8 (s, C(3)); 129.5 (s, C(4′), C(5′)); 129.8 (s, C(9)); 131.9 (s, C(10′)); 134.6 (s, C(10), C(9′)); 146.6 (d, C(1), $^2J_{P,C}$ = 11.0 Hz); 149.1 (d, C(7), J = 10.6 Hz); 149.2 (d, C(2′), C(7′), $^2J_{P,C}$ = 10.2 Hz). ^{31}P NMR (CH_2Cl_2), δ: 1.0.

Cyclo[(1,6-naphthylene)(1,5-naphthylene)-bis(diethyl phosphoramidate)] (28). ^{1}H NMR ($CDCl_3$), δ: 1.03 (d, 12 H, CH_3, ^3J = 5.6 Hz); 3.29 (dd, 8 H, CH_2N, $^3J_{P,H}(1,1′)$ = 11.0 Hz, $^3J_{P,H}(6,5′)$ = 11.7 Hz); 7.40 (d, 1 H, H(2)), $^3J_{H(2),H(3)}$ = 7.8 Hz); 7.51 (d, 2 H, H(2′), H(6′), $^3J_{H(2′),H(3′)}$ = 8.0 Hz); 7.60 (d, 1 H, H(7), $^3J_{H(7),H(8)}$ = 7.7 Hz); 7.68 (t, 1 H, H(3), $^3J_{H(3),H(4)}$ = 7.3 Hz); 7.70 (d, 1 H, H(4), $^3J_{H(3),H(4)}$ = 7.3 Hz); 7.75 (t, 2 H, H(3′), H(7′), $^3J_{H(2′),H(3′)}$ = 8.0 Hz, $^3J_{H(3′),H(4′)}$ = 9.5 Hz); 7.76 (s, 1 H, H(5)); 7.87 (d, 2 H, H(4′), H(8′), $^3J_{H(3′),H(4′)}$ = 9.5 Hz); 8.06 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 9.9 Hz). ^{31}P NMR (CH_2Cl_2), δ: 1.3.

Cyclo[(1,6-naphthylene)(2,6-naphthylene)-bis(diethyl phosphoramidate) (29). ^{1}H NMR ($CDCl_3$), δ: 1.08 (d, 12 H, CH_3, ^3J = 5.5 Hz); 3.31 (dd, 8 H, CH_2N, $^3J_{P,H}(1,2′)$ = 10.9 Hz, $^3J_{P,H}(6,6′)$ = 9.9 Hz); 7.32 (d, 2 H, H(3′), H(7′), $^3J_{H(3′),H(4′)}$ = 8.9 Hz); 7.35 (d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 7.6 Hz); 7.39 (t, 1 H, H(3), $^3J_{H(2),H(3)}$ = 7.6 Hz); 7.44 (d, 1 H, H(7), $^3J_{H(7),H(8)}$ = 8.9 Hz); 7.51 (s, 1 H, H(5)); 7.59 (d, 1 H, H(4)); 7.63 (s, 2 H, H(1′), H(5′)); 7.70 (d, 2 H, H(4′), H(8′), $^3J_{H(3′),H(4′)}$ = 9.0 Hz); 8.02 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 8.8 Hz). ^{31}P NMR (CH_2Cl_2), δ: 1.1.

Cyclo[(1,6-naphthylene)(2,7-naphthylene)-bis(diethyl phosphoramidate)] (30). ^{1}H NMR ($CDCl_3$), δ: 1.03 (t, 12 H, CH_3, ^3J = 5.4 Hz); 3.27 (dd, 8 H, CH_2N, $^3J_{P,H}(1,2′)$ = 12.7 Hz, $^3J_{P,H}(6,7′)$ = 11.6 Hz); 7.38 (dd, 1 H, H(7), $^3J_{H(7),H(8)}$ = 9.9 Hz); 7.41 (d, 1 H, H(2), $^3J_{H(2),H(3)}$ = 8.1 Hz); 7.49 (t, 1 H, H(3), $^3J_{H(2),H(3)}$ = 8.1 Hz); 7.57 (s, 3 H, H(5), H(1′), H(8′)); 7.71 (d, 1 H, H(4), ^3J = 7.8 Hz); 7.73 (d, 2 H, H(3′), H(6′), $^3J_{H(3′),H(4′)}$ = 8.5 Hz); 7.76 (d, 2 H, H(4′), H(5′), $^3J_{H(3′),H(4′)}$ = 8.5 Hz); 8.09 (d, 1 H, H(8), $^3J_{H(7),H(8)}$ = 9.9 Hz). ^{31}P NMR (CH_2Cl_2), δ: 1.2.

Cyclo[(1,5-naphthylene)(2,6-naphthylene)-bis(diethyl phosphoramidate)] (31). ^{1}H NMR ($CDCl_3$), δ: 1.04 (t, 12 H, CH_3, ^3J = 6.8 Hz); 3.29 (m, 8 H, CH_2N); 7.40 (s, 2 H, H(1′), H(5′)); 7.42 (d, 2 H, H(2), H(6), $^3J_{H(2),H(3)}$ = 6.9 Hz); 7.59 (d, 2 H, H(3′), H(7′), $^3J_{H(3′),H(4′)}$ = 8.9 Hz); 7.65 (t, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 8.2 Hz); 7.73 (d, 2 H, H(4′), H(8′), $^3J_{H(3′),H(4′)}$ = 8.9 Hz); 7.86 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 8.2 Hz). ^{31}P NMR (CH_2Cl_2), δ: 1.2.

Cyclo[(1,5-naphthylene)(2,7-naphthylene)-bis(diethyl phosphoramidate)] (32). ^{1}H NMR ($CDCl_3$), δ: 1.04 (t, 12 H, CH_3, ^3J = 7.4 Hz); 3.29 (m, 8 H, CH_2N); 7.25 (d, 2 H, H(3′), H(6′), $^3J_{H(3′)—H(4′)}$ = 8.7 Hz); 7.27 (d, 2 H, H(2), H(6), $^3J_{H(2),H(3)}$ = 6.9 Hz); 7.39 (t, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 8.8 Hz); 7.68 (s, 2 H, H(1′), H(8′)); 7.75 (d, 2 H, H(4′), H(5′), $^3J_{H(3′),H(4′)}$ = 8.7 Hz); 7.87 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 8.8 Hz). ^{31}P NMR (CH_2Cl_2), δ: 1.3.

Cyclo[(2,6-naphthylene)(2,7-naphthylene)-bis(diethylphosphoramidate)] (33). ^{1}H NMR ($CDCl_3$), δ: 1.06 (t, 12 H, CH_3, ^3J = 7.2 Hz); 3.27 (m, 8 H, CH_2N); 7.37 (d, 2 H, H(3′), H(6′), $^3J_{H(3′),H(4′)}$ = 8.9 Hz); 7.44 (d, 2 H, H(3), H(7), $^3J_{H(3),H(4)}$ = 8.8 Hz); 7.67 (s, 4 H, H(1), H(5), H(1′), H(8′)); 7.74 (d, 2 H, H(4), H(8), $^3J_{H(3),H(4)}$ = 8.8 Hz); 7.79 (d, 2 H, H(4′), H(5′), $^3J_{H(3′),H(4′)}$ = 8.9 Hz). ^{31}P NMR (CH_2Cl_2), δ: 1.2.

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