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The synthesis and extraction properties of new 2-(phosphorylalkyl)- and 2-(phosphorylalkenyl)-substituted 1,8- and 1,6-naphthyridines

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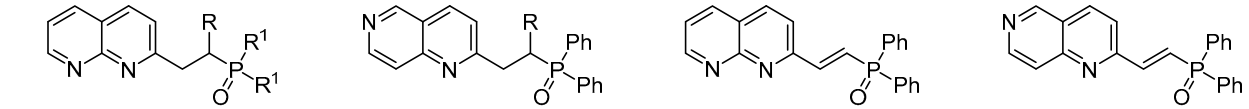


New 1,8- and 1,6-naphthyridines containing a phosphoryl group in the side chain were synthesized *via* Friedländer reaction by combining the appropriate aminonicotinic aldehydes and phosphoryl ketones in alcohol medium in the presence of basic catalysts (pyrrolidine or KOH). A series of phosphoryl-substituted 1,8-naphthyridines effectively extracted uranium(VI) from neutral aqueous solutions containing lanthanide(III) into 1,2-dichloroethane.

Keywords: phosphoryl-substituted 1,8(1,6)-naphthyridines, extraction, *f*-elements, Friedländer reaction.

Derivatives of 1,8- and 1,6-naphthyridines, synthesized over the recent decades, have attracted the attention of researchers by many potential applications in biomedicine,[1,2] catalysis,[3] design of luminescent chemosensors and markers.[4] Recently it was also found that 2-phosphoryl-substituted 1,8-naphthyridines can be successfully used for the extraction of lanthanides from carbonate-containing media.[5] We have previously demonstrated that 2-(phosphorylalkyl)-substituted 1,8- and 1,6-naphthyridines can be successfully obtained from phosphoryl ketones in a Friedländer reaction.[6–8]

A Friedländer reaction between the appropriate nicotinic aldehydes and phosphoryl ketones was used in this work for the synthesis of a range of new 1,8- and 1,6-naphthyridine derivatives containing a phosphoryl moiety in the side chain. The obtained compounds **1b**,**c**,**e**,**f**, **2a**,**b**, **3**, **4** (Fig. 1) were used for studying the extraction of uranium (VI) and lanthanides(III) from neutral aqueous solutions. The relationship between the ligand structure and the extraction ability was identified. The extractive properties of previously described naphthyridines **1a**, **2c** were also studied for more accurate estimation of the effect of structure on extraction parameters.

The phosphorylated naphthyridines **1b**–**f**, **2b** were synthesized by refluxing phosphoryl ketones **5b**–**f** with a slight excess of aminonicotinic aldehydes **6**, **7** in ethanol under argon atmosphere in the presence of pyrrolidine (1.20 equiv) and H_2SO_4 (0.05 equiv) as a regioselective catalyst[6–9]

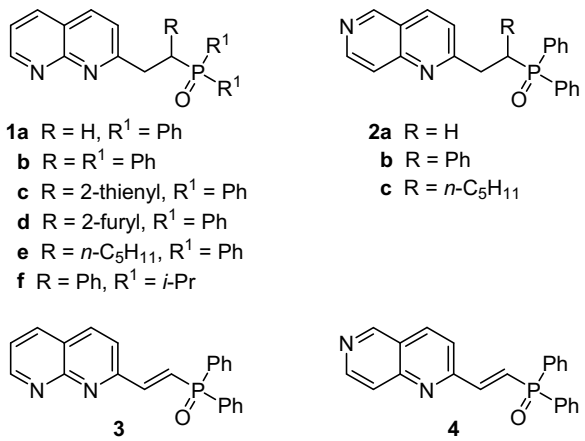
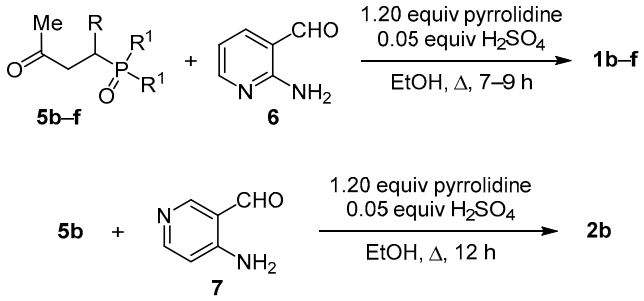


Figure 1. Derivatives of 1,8- and 1,6-naphthyridines containing a phosphoryl group in the side chain.

Scheme 1

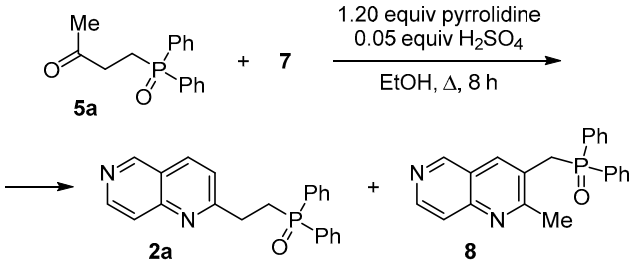


5 b R = R^1 = Ph; **c** R = 2-thienyl, R^1 = Ph; **d** R = 2-furyl, R^1 = Ph
e R = *n*-C_5H_{11}, R^1 = Ph; **f** R = Ph, R^1 = *i*-Pr

(Scheme 1). Despite the fact that the Friedländer reaction with unsymmetrical ketones may lead to the formation of a mixture of 2- and 2,3-substituted naphthyridines,[10,11] the reaction of aldehydes **6**, **7** with phosphoryl ketones **5b**–**f** under these conditions produced only a single regioisomer (Scheme 1).

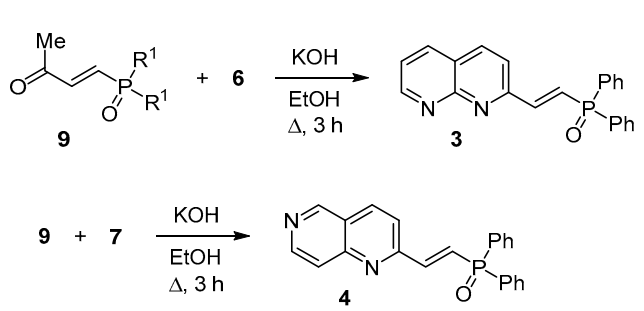
Only the reaction of phosphoryl ketone **5a** with aldehyde **7** gave a mixture of isomeric naphthyridines **2a** and **8** in 70 and 30% yields, respectively, according to ^{31}P NMR data (Scheme 2). The individual compounds **2a** and **8** could be isolated by fractional crystallization of this mixture in 11 and 2% yields, respectively.

Scheme 2



The preparation of naphthyridines **3** and **4** by using pyrrolidine as catalyst was complicated due to side reactions that were likely caused by the addition of this amine at the double bond of the starting phosphoryl enone **9**.[12] For this reason, KOH was used as catalyst[13] (Scheme 3), although it caused partial resinification of the reaction mixture and decreased the product yields.

Scheme 3



The composition and structure of the obtained compounds were confirmed by elemental analysis, data of vibrational spectroscopy and multinuclear NMR spectroscopy, as well as X-ray structural analysis in the case of compound **8**.

IR spectra of the substituted 1,8-naphthyridines **1b**–**f** featured strong absorption bands at 1605–1609 and 1499–1503 cm^{-1}, and a medium intensity absorption band at ~1550 cm^{-1}, which were characteristic for 1,8-naphthyridine nucleus and belonged to the mixed vibrations of ν(C–C)+ν(C–N)+δ(C–H).[14–16] A strong line in the Raman spectra at ~1370 cm^{-1} (mixed vibration of ν(C–C)+δ(C–H)) and absorption bands at ~780 and ~540 cm^{-1} (interpreted as "breathing" vibrations of the naphthyridine system (with participation of both nitrogen atoms) coupled with δ(CH) also were in good agreement with the structure of 1,8-naphthyridine system.[16] The main differences in vibrational frequencies of 1,6- and 1,8-naphthyridines were due to the lower degree of symmetry in the molecules of 1,6-naphthyridines.[14,15]

The spectra of naphthyridines **2a**–**c** exhibited the main spectral characteristics of 1,6-naphthyridines: a strong IR absorption band at 1613 cm^{-1} matched by a weak Raman line, a strong Raman line at ~1590 cm^{-1} matched by a weaker IR absorption band, as well as an IR absorption band at ~1550 cm^{-1} and Raman lines at ~1370 and ~540 cm^{-1}. For naphthyridines **3**, **4** containing a double bond in the linker, the ν(C=C) vibrations were likely mixed with the similar ring vibration frequencies. Thus, the spectra in the range of 1700–1600 cm^{-1} were somewhat different from the spectra of naphthyridines **1b**–**f**, **2a**,**b**, and the band at ~1610 cm^{-1} can be assigned to a vibration containing contribution of ν(C=C).

Identification of vibrations due to the thiophene and furan substituents in compounds **1c**,**d** was impossible, because the series of absorption bands of these rings were close to the vibration frequencies of the naphthyridine system, while the ν(C–S) absorption band in the region of ~700 cm^{-1} overlapped with the intense absorption bands due to the deformation vibrations of phenyl rings. The ν(P=O) vibrations were observed at a frequency typical for diphenylphosphoryl group, at 1185–1175 cm^{-1} in all the studied naphthyridines except compound **8**, which differed from the other studied naphthyridines by having a short linker (the spectrum of compound **8** contained absorption bands at 1186 and 1168 cm^{-1}). Compound **1f** contained isopropyl substituents instead of phenyl groups at the phosphorus atom, and thus had a lower vibration frequency, with the ν(P=O) absorption at 1145 cm^{-1}.

^{1}H and ^{13}C–{^{1}H} NMR signals were interpreted based on a set of 2D NMR experiments (^{1}H–^{1}H COSY, HMQC, and HMBC). The CH_2 group within the –CH_2CHR– linker connecting the naphthyridine system with the phosphoryl group in compounds **1b**–**e**, **2b** was next to an asymmetric carbon atom, therefore its signal was a part of ABMX system in ^{1}H NMR spectra, where M and X were respectively the H and P nuclei of CHP(O)Ph_2 fragment, or ABM system in ^{1}H–{^{31}P} NMR spectra. The reason for this effect was the prochiral nature of CH_2 group, according to the

concept described by Hanson.[17] The hydrogen atoms in this moiety were diastereotopic and, thus, anisochronic (i.e., characterized by different chemical shifts) in achiral medium. It should be noted that the molecules of naphthyridines **1b**–**e**, **2b** contained another prochiral center, the phosphorus atom, thus the phenyl substituents bonded to this center must also be diastereotopic. This was manifested both in ^{1}H, ^{1}H–{^{31}P} spectra, as well as in ^{13}C–{^{1}H} spectra, which featured doubled ^{13}C NMR signals of the aromatic rings linked to phosphorus (the *ortho*, *meta*, *para*, and *ipso* atoms).

In the case of naphthyridine **1f**, the prochiral centers were not only the phosphorus atom and methylene carbon atom in the –CH_2CHPh– linker, but also both α-carbon atoms of the isopropyl groups. Therefore, isopropyl groups themselves and CH_3 substituents at each of these groups will be diastereotopic. This created conditions for the manifestation of so-called double magnetic nonequivalence in the respective NMR spectra.[18] Indeed, ^{1}H NMR spectrum of compound **1f** in $CDCl_3$ solution contained two multiplets (double septets) of the methine protons in isopropyl groups and four double doublets belonging to the methyl group protons. These multiplets in ^{1}H–{^{31}P} NMR spectrum of naphthyridine **1f** were transformed into two septets and four doublets, respectively. The double magnetic nonequivalence effect was similarly observed also in ^{13}C–{^{1}H} NMR spectrum of compound **1f**, which showed two doublets belonging to anisochronic α-carbon atoms of isopropyl fragments and four doublets of carbon atoms in the magnetically nonequivalent methyl groups of these substituents. Thus, naphthyridine **1f** belongs to a rare type of structures where a system of prochiral centers giving rise to double magnetic nonequivalence in NMR spectra contains not only the usual carbon atoms,[18–20] but also a tetracoordinated pentavalent phosphorus atom.*

The structure of naphthyridine **8** was additionally confirmed by X-ray structural analysis (Fig. 2). According to the obtained data, the geometry parameters for compound **8** were quite close to those of the previously described 2-[(1-diphenylphosphoryl-1-methyl)ethyl]-1,6-naphthyridine (**10**).[8] In both cases we should note the cissoid configuration of the P=O group relative to the naphthyridine moiety. The pseudotorsion angle OPC(14)C(15) in the structure of naphthyridine **8** was equal to 5.9°, while in the structure of the analogous compound **10** it was 3.0°.[8]

The properties of naphthyridines **1a**–**f**, **2a**–**c**, **3**, **4** with regard to the extraction of *f*-elements were studied by using the extraction of uranium(VI) and lanthanides(III) from neutral aqueous solutions into 1,2-dichloroethane as an example. Since the values of distribution ratios found for lanthanides had no significant differences, only the data for europium and uranium are discussed further (Table 1).

When considering the correlation between the structure of phosphoryl-substituted naphthyridine and its efficiency

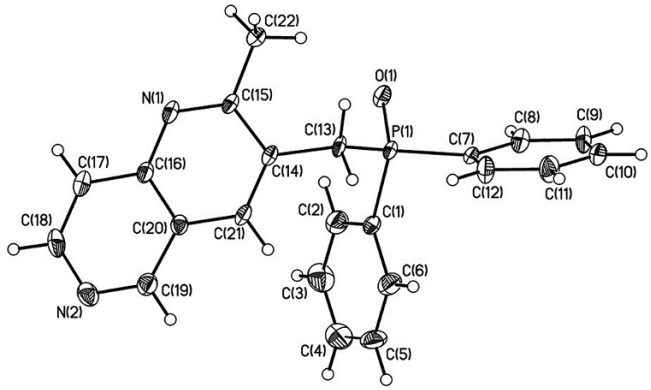


Figure 2. The molecular structure of compound **8** with atoms represented by thermal vibration ellipsoids of 50% probability.

in the extraction of U(VI) and Eu(III) ions, first of all the substantial difference between the isomeric 1,8- and 1,6-naphthyridines should be noted when comparing the pairs of compounds **1a**–**2a**, **1b**–**2b**, **1e**–**2c** (Table 1). The D_M values in these pairs differed by several times. Obviously, the main reason for different extraction ability between the isomers **1**–**2** was the difference in their coordinating ability.

Thus, it is known that the phosphorylated 1,8-naphthyridines showed tridentate ONN-coordination in complexes with lanthanide salts.[22] The coordinating properties of phosphoryl-substituted 1,6-naphthyridines have not been studied, however, it can be expected from their structure that complex formation with lanthanides will occur either by monodentate interaction with the cation *via* P=O→M bond, or by O,N-bidentate coordination. Obviously, the stability of complexes is higher in the case of tridentate interaction, compared to mono– and bidentate coordination, and thus the extraction efficiency with 1,8-naphthyridines will be higher than with the isomeric 1,6-naphthyridines.

The complex formation between phosphoryl-substituted 1,8- and 1,6-naphthyridines and uranyl cations has not yet been investigated. However, the efficiency of uranium(VI) extraction by some 1,8-naphthyridines (ligands **1a**,**e**,**f**, Table 1) is so high that participation of both ring nitrogen atoms in coordination with uranyl cation/cations is assumed.

It should be noted that the extraction efficiency was much lower and nearly identical in the case of specially synthesized model isomers **3** and **4**, where the naphthyridine moiety and the phosphoryl group were linked by a –CH=CH– fragment (Table 1). According to

Table 1. Extraction properties of 2-phosphoryl-substituted 1,8- and 1,6-naphthyridines **1a**–**f**, **2a**–**c**, **3**, **4**

Compound	Distribution ratios*		Compound	Distribution ratios	
	D_{Eu}	D_U		D_{Eu}	D_U
1a	3.9	125	**2a**	< 0.1	48
1b	< 0.1	5.8	**2b**	< 0.1	0.21
1c	< 0.1	1.5	**2c**	< 0.1	2.6
1e	8.9	186	**3**	< 0.1	1.5
1f	1.8	436	**4**	< 0.1	0.76

* $D_M = [M_{org}]/[M_{aq}]$, where M – metal.

*The phenomenon of double magnetic nonequivalence in NMR spectra of systems containing a prochiral phosphorus atom was first reported by M. I. Kabachnik with coworkers.[21]

conformational analysis data, the presence of a double bond in the linker prevented simultaneous coordination of the oxygen atom of phosphoryl group and nitrogen atom/ atoms of the naphthyridine moiety to one metal cation. It should be also pointed out that the D_M values for ligands **3** and **4** (Table 1) were close to the D_M value of phosphine oxide $(p\text{-Tol})_2P(O)CH_2Ph$ determined under the same experimental conditions: $D_{Eu} < 0.1$ and $D_U = 7.24$.

The introduction of substituent R at the α-position of $–CH_2CHR–$ linker had a substantial effect on the extraction efficiency. The substituent altered not only the lipophilic properties of extragent, but also the stability of extracted complexes by changing the basicity of phosphoryl group, and thus also the strength of the P=O→M coordination bond. The inductive effect of $p\text{-}C_5H_{11}$ substituent increased the phosphoryl group basicity (as well as ligand lipophilicity), while the introduction of a phenyl or thienyl* substituent decreased the basicity of the P=O group (when comparing the D_M values in the series of ligands **1a**–**c**,**e** and **2a**–**c**).

The replacement of phenyl substituents at the phosphorus atom with more electron-donating isopropyl substituents (ligands **1b**,**f**) increased the basicity of P=O group, thus improving the stability of the extracted complexes and raising the D_U and D_{Eu} values of extractant **1f** (Table 1).

The obtained results showed that the 2-phosphoryl-substituted 1,8-naphthyridines **1a**,**e**,**f** were effective and selective extractants for the recovery of uranium and can be used for the extraction of trace amounts of uranium from aqueous solutions of lanthanides.

Thus, we have used the Friedländer reaction to synthesize a range of new 2-phosphorylethyl-substituted 1,8- and 1,6-naphthyridines from the respective nicotinic aldehydes and phosphoryl-substituted ketones. The composition and molecular structure of the products were established from elemental analysis, vibrational (IR, Raman) spectroscopy and multinuclear (^1H, ^{31}P, ^{13}C) NMR spectroscopy. Several of the obtained 1,8-naphthyridines effectively extracted uranium from neutral aqueous solutions into 1,2-dichloroethane. The extraction efficiency depended on the nature of substituents at the phosphorus atom, as well as the substituent at the α-position of the ethylene linker between the naphthyridine system and the phosphoryl group.

Experimental

IR spectra in the range of 400–4000 cm^{-1} were recorded on a Bruker Tensor 37 FTIR spectrometer in KBr pellets. Raman spectra in the range of 100–3500 cm^{-1} were recorded on a Jobin-Yvon LabRAM 300 spectrometer, equipped with a microscope and laser CCD detector. The He–Ne laser emission line with 632.8 nm was used for excitation at a power not higher than 2 mW. ^1H and $^{13}C–\{^1H\}$ NMR spectra of compounds **1d**, **2b**, **8** were acquired on a Bruker Avance 400 spectrometer (400 and 100 MHz, respectively). ^1H and $^{13}C–\{^1H\}$ NMR spectra for the rest of the compounds were acquired on a Bruker Avance 600 spectrometer (600 and 125 MHz, respectively). $^1H–\{^{31}P\}$ and $^{31}P–\{^1H\}$ NMR spectra were acquired on a Bruker Avance 400 spectrometer (400 and 162 MHz, respectively). The solvent was $CDCl_3$, the concentration of solutions was 0.025 mol/l (compound **8**) or 0.1 mol/l (the rest of the compounds). Residual solvent signals were used as internal standard in ^1H and ^{13}C NMR spectra (7.26 ppm for ^1H nuclei, 77.0 ppm for ^{13}C nuclei), 85% H_3PO_4 was used as external standard in ^{31}P NMR spectra. Elemental analysis was performed at the Laboratory of Microanalysis, Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences; the content of C, H, and N was determined on a Carlo Erba 1106 instrument, the content of P and S was determined according to published procedures.[23] Melting points were determined in open capillaries on a Stanford Research Systems MPA120 EZ-melt automated melting point apparatus and were not corrected. Ethanol was of anhydrous grade, purchased from Scharlau, pyrrolidine was purchased from Acros Organics, H_2SO_4 was of chemically pure grade (98% assay). All other solvents were purified by standard procedures prior to use. The reaction progress was controlled by ^{31}P NMR spectra of the reaction mixtures. Phosphoryl ketones **5a**–**f** and **9** were synthesized according to literature,[8,24] nicotinic aldehydes **6**, **7** – according to another published procedure.[25]

Synthesis of 2-phosphoryl-substituted 1,8- and 1,6-naphthyridines 1b–f, **2a,b, 8** (General method).[6–8] A mixture of phosphoryl ketone **5a**–**f** (2.50 mmol) and aminonicotinic aldehyde **6** or **7** (2.63 mmol, 1.05 equiv) was treated with EtOH (10 ml) and 2 ml of ethanol solution containing pyrrolidine (0.26 g, 3.00 mmol, 1.20 equiv) and H_2SO_4 (13 mg, 0.13 mmol, 0.05 equiv). The obtained mixture was stirred and refluxed for 7–12 h. The precipitate that formed in the reaction mixture was separated, washed, and recrystallized. If precipitate was absent after the reaction completion, ethanol was removed at reduced pressure (12 mmHg), the residue was dissolved in $CHCl_3$ (20 ml), the solution was washed with water (3×20 ml), dried over anhydrous Na_2SO_4, evaporated to dryness at reduced pressure, and recrystallized. The obtained product was dried at reduced pressure (120–140°C, 12 mmHg) for 2–4 h.

Naphthyridines **1a**[7], **2c**,[8] and the phosphine oxide $(p\text{-Tol})_2P(O)CH_2Ph$[26] were synthesized and purified according to the respective procedures. Compound **2c** was characterized by vibrational spectra that were not previously reported.[8]

2-[(2-Diphenylphosphoryl-2-phenyl)ethyl]-1,8-naphthyridine (1b) was obtained from phosphoryl ketone **5b** (0.70 g, 2.01 mmol) and aldehyde **6** (0.26 g, 2.13 mmol). The reaction time was 9 h. Yield 0.70 g (81%), white fine crystalline powder, mp 254–256°C ($CHCl_3$–EtOAc, 1:3). IR spectrum, ν, cm^{-1}: 1608, 1560, 1548, 1499, 1453, 1437 (Ph), 1185, 1174 (P=O), 1119, 1102, 1072, 847, 811, 753, 716, 697, 549, 534. Raman spectrum, ν, cm^{-1}: 1604, 1593, 1372, 1193, 1048, 1038, 1029, 1000 (Ph), 811, 779, 755, 692, 617, 536. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.72 (1H, ddd, $^2J = 14.6$, $^3J = 4.4$, $^3J_{HP} = 8.3$) and 3.78 (1H, ddd,

* Compound **1d** with a furyl substituent was not studied due to its low stability.

^2J = 14.6, ^3J = 10.6, $^3J_{HP}$ = 8.5, C$\underline{H}_2$CH); 4.75 (1H, ddd, ^3J = 5.0, ^3J = 10.4, $^2J_{HP}$ = 5.4, $CH_2C\underline{H}$); 7.01 (1H, t, ^3J = 6.9, H-4 CPh); 7.05 (2H, t, ^3J = 7.3, H-3,5 CPh); 7.06 (1H, d, ^3J = 8.7, H-3); 7.22 (2H, td, ^3J = 7.5, $^4J_{HP}$ = 2.3, H-3,5 PPh); 7.31 (1H, t, ^3J = 7.5, H-4 PPh); 7.36 (2H, d, ^3J = 7.3, H-2,6 CPh); 7.41 (1H, dd, ^3J = 7.9, ^3J = 4.2, H-6); 7.44–7.52 (5H, m, H PPh); 7.82 (1H, d, ^3J = 8.2, H-4); 8.04 (1H, dd, ^3J = 7.9, ^4J = 1.3, H-5); 8.06–8.13 (2H, m, H-2,6 PPh); 9.08 (1H, dd, ^3J = 3.9, ^4J = 1.6, H-7). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 3.73 (1H, dd, ^2J = 14.6, ^3J = 5.1) and 3.78 (1H, dd, ^2J = 14.7, ^3J = 10.7, C$\underline{H}_2$CH); 4.75 (1H, dd, ^3J = 4.8, ^3J = 10.1, $CH_2C\underline{H}$); 7.01 (1H, t, ^3J = 6.9, H-4 CPh); 7.05 (2H, t, ^3J = 7.7, H-3,5 CPh); 7.06 (1H, d, ^3J = 8.3, H-3); 7.22 (2H, t, ^3J = 7.5, H-3,5 PPh); 7.31 (1H, t, ^3J = 7.5, H-4 PPh); 7.36 (2H, d, ^3J = 7.0, H-2,6 CPh); 7.41 (1H, dd, ^3J = 8.0, ^3J = 4.3, H-6); 7.44–7.52 (5H, m, H PPh); 7.82 (1H, d, ^3J = 8.2, H-4); 8.05 (1H, dd, ^3J = 8.0, ^4J = 1.1, H-5); 8.06–8.13 (2H, m, H-2,6 PPh); 9.09 (1H, dd, ^3J = 3.8, ^4J = 1.4, H-7). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 38.8 ($\underline{C}H_2CH$); 45.6 (d, $^1J_{CP}$ = 67.4, $CH_2\underline{C}H$); 121.2 (C-4a); 121.6 (C-6); 123.8 (C-3); 126.8 (d, $^5J_{CP}$ = 2.2, C-4 CPh); 128.0 (d, $^3J_{CP}$ = 12.2, C-3,5 PPh); 128.1 (d, $^4J_{CP}$ = 1.1, C-3,5 CPh); 128.7 (d, $^3J_{CP}$ = 11.1, C-3,5 PPh); 130.1 (d, $^3J_{CP}$ = 5.5, C-2,6 CPh); 130.9 (d, $^2J_{CP}$ = 8.8, C-2,6 PPh); 131.2 (d, $^4J_{CP}$ = 2.8, C-4 PPh); 131.5 (d, $^2J_{CP}$ = 8.3, C-2,6 PPh); 131.6 (d, $^4J_{CP}$ = 2.2, C-4 PPh); 131.7 (d, $^1J_{CP}$ = 94.5, C-1 PPh); 132.1 (d, $^1J_{CP}$ = 99.5, C-1 PPh); 135.7 (d, $^2J_{CP}$ = 5.0, C-1 CPh); 136.8 (C-4); 136.9 (C-5); 153.3 (C-7); 155.7 (C-8a); 163.4 (d, $^3J_{CP}$ = 13.3, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 33.5. Found, %: C 76.97; H 5.34; N 6.61; P 7.26. $C_{28}H_{23}N_2OP$. Calculated, %: C 77.41; H 5.34; N 6.45; P 7.13.

2-{[2-Diphenylphosphoryl-2-(thiophen-2-yl)]ethyl}-1,8-naphthyridine (1c) was obtained from phosphoryl ketone **5c** (0.88 g, 2.48 mmol) and aldehyde **6** (0.31 g, 2.53 mmol). The reaction time was 7 h. Yield 0.60 g (55%), white fine crystalline powder, mp 251–253°C (2-PrOH). IR spectrum, ν, cm^{-1}: 1607, 1550, 1503, 1436 (Ph), 1249, 1174 (P=O), 1145, 1121, 1093, 853, 796, 727, 715, 696, 594, 564, 529. Raman spectrum, ν, cm^{-1}: 1595, 1431, 1375, 1001 (Ph), 840, 783, 731, 669, 618, 537. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.66 (1H, ddd, ^2J = 14.5, ^3J = 4.8, $^3J_{HP}$ = 7.4) and 3.69 (1H, ddd, ^2J = 14.5, ^3J = 10.3, $^3J_{HP}$ = 7.4, C$\underline{H}_2$CH); 5.10 (1H, ddd, ^3J = 4.8, ^3J = 10.7, $^2J_{HP}$ = 6.3, $CH_2C\underline{H}$); 6.68 (1H, dd, ^3J = 3.8, ^3J = 4.9, H-4'); 6.92–6.95 (2H, m, H-3',5'); 7.12 (1H, d, ^3J = 8.3, H-3); 7.28 (2H, dt, ^3J = 7.7, $^4J_{HP}$ = 3.0, H-3,5 Ph); 7.34–7.38 (1H, m, H-4 Ph); 7.41 (1H, dd, ^3J = 8.0, ^3J = 4.4, H-6); 7.43–7.48 (3H, m, H 3,4,5 Ph); 7.57–7.63 (2H, m, H-2,6 Ph); 7.86 (1H, d, ^3J = 8.2, H-4); 8.04–8.09 (3H, m, H-5, H-2,6 Ph); 9.08 (1H, dd, ^3J = 4.2, ^4J = 2.0, H-7). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 3.67 (1H, dd, ^2J = 14.2, ^3J = 5.0) and 3.70 (1H, dd, ^2J = 14.4, ^3J = 9.8, C$\underline{H}_2$CH); 5.11 (1H, dd, ^3J = 5.6, ^3J = 9.7, $CH_2C\underline{H}$); 6.66–6.71 (1H, m, H-4'); 6.92–6.97 (2H, m, H-3',5'); 7.13 (1H, d, ^3J = 8.2, H-3); 7.29 (2H, t, ^3J = 7.4, H-3,5 Ph); 7.36 (1H, t, ^3J = 7.3, H-4 Ph); 7.42 (1H, dd, ^3J = 8.0, ^3J = 4.2, H-6); 7.44–7.49 (3H, m, H-3,4,5 Ph); 7.61 (2H, d, ^3J = 7.5, H-2,6 Ph); 7.87 (1H, d, ^3J = 8.2, H-4); 8.03–8.10 (3H, m, H-5, H-2,6 Ph); 9.08 (1H, dd, ^3J = 3.9, ^4J = 1.7, H-7). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 39.8 ($\underline{C}H_2CH$); 41.0 (d, $^1J_{CP}$ = 69.7, $CH_2\underline{C}H$); 121.3 (C-4a); 121.6 (C-6); 123.8 (C-3); 124.8 (d, $^4J_{CP}$ = 2.8, C-5'); 126.5 (d, $^4J_{CP}$ = 2.8, C-4'); 127.7 (d, $^3J_{CP}$ = 6.6, C-3'); 128.1 (d, $^3J_{CP}$ = 11.6, C-3,5 Ph); 128.8 (d, $^3J_{CP}$ = 11.6, C-3,5 Ph); 131.0 (d, $^2J_{CP}$ = 8.8, C-2,6 Ph); 131.3 (d, $^1J_{CP}$ = 95.1, C-1 Ph); 131.5 (d, $^4J_{CP}$ = 3.9, C-4 Ph); 131.5 (d, $^2J_{CP}$ = 8.3, C-2,6 Ph); 131.7 (d, $^1J_{CP}$ = 100.6, C-1 Ph); 131.8 (d, $^4J_{CP}$ = 2.8, C-4 Ph); 136.9 (C-4); 137.0 (C-5); 137.3 (d, $^2J_{CP}$ = 6.1, C-2'); 153.3 (br. s, C-7); 155.7 (C-8a); 163.1 (d, $^3J_{CP}$ = 13.3, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 32.6. Found, %: C 70.97; H 4.83; N 6.35; P 7.12; S 7.34. $C_{26}H_{21}N_2OPS$. Calculated, %: C 70.89; H 4.81; N 6.36; P 7.03; S 7.28.

2-{[2-Diphenylphosphoryl-2-(furan-2-yl)]ethyl}-1,8-naphthyridine (1d) was obtained from phosphoryl ketone **5d** (1.01 g, 2.98 mmol) and aldehyde **6** (0.37 g, 3.03 mmol) The reaction time was 8 h. Yield 0.66 g (52%), white crystalline powder, mp 215–216°C ($CHCl_3$–hexane, 1:5). IR spectrum, ν, cm^{-1}: 1607, 1549, 1503, 1436 (Ph), 1178 (P=O), 1148, 1122, 1101, 856, 812, 750, 728, 699, 549, 526. Raman spectrum, ν, cm^{-1}: 1609, 1594, 1551, 1496, 1374, 1002 (Ph), 822, 797, 783, 732, 690, 645, 618, 537. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.65 (1H, ddd, ^2J = 14.6, ^3J = 4.4, $^3J_{HP}$ = 7.8) and 3.78 (1H, ddd, ^2J = 14.6, ^3J = 11.0, $^3J_{HP}$ = 7.7, C$\underline{H}_2$CH); 4.96 (1H, ddd, ^3J = 4.4, ^3J = 11.0, $^2J_{HP}$ = 8.3, $CH_2C\underline{H}$); 6.04–6.07 (2H, m, H-3',4'); 7.10–7.12 (1H, m, H-5'); 7.20 (1H, d, ^3J = 8.3, H-3); 7.31–7.37 (2H, m, H-3,5 Ph); 7.39–7.49 (5H, m, H-6, H-3,4,5,4' Ph); 7.58–7.65 (2H, m, H-2,6 Ph); 7.92 (1H, d, ^3J = 8.3, H-4); 7.96–8.03 (2H, m, H-2,6 Ph); 8.07 (1H, dd, ^3J = 8.1, ^4J = 1.9, H-5); 9.06 (1H, dd, ^3J = 4.3, ^4J = 1.9, H-7). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 3.66 (1H, dd, ^2J = 14.6, ^3J = 4.0) and 3.77 (1H, dd, ^2J = 14.6, ^3J = 11.0, C$\underline{H}_2$CH); 4.96 (1H, dd, ^3J = 4.4, ^3J = 10.9, $CH_2C\underline{H}$); 6.04–6.08 (2H, m, H-3',4'); 7.10–7.12 (1H, m, H-5'); 7.20 (1H, d, ^3J = 8.2, H-3); 7.34 (2H, t, ^3J = 7.4, H-3,5 Ph); 7.38–7.49 (5H, m, H-6, H-3,4,5,4' Ph); 7.59–7.64 (2H, m, H-2,6 Ph); 7.91 (1H, d, ^3J = 8.3, H-4); 7.96–8.02 (2H, m, H-2,6 Ph); 8.07 (1H, dd, ^3J = 8.1, ^4J = 1.7, H-5); 9.06 (1H, dd, ^3J = 4.2, ^4J = 2.0, H-7). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 36.6 ($\underline{C}H_2CH$); 40.2 (d, $^1J_{CP}$ = 69.0, $CH_2\underline{C}H$); 109.4 (d, $^3J_{CP}$ = 5.9, C-3'); 110.4 (d, $^4J_{CP}$ = 2.2, C-4'); 121.3 (C-4a); 121.6 (C-6); 123.4 (C-3); 128.1 (d, $^3J_{CP}$ = 12.5, C-3,5 Ph); 128.7 (d, $^3J_{CP}$ = 11.7, C-3,5 Ph); 131.1 (d, $^2J_{CP}$ = 9.5, C-2,6 Ph); 131.3 (d, $^1J_{CP}$ = 95.4, C-1 Ph); 131.5 (d, $^2J_{CP}$ = 8.8, C-2,6 Ph); 131.6 (d, $^4J_{CP}$ = 2.9, C-4 Ph); 131.6 (d, $^1J_{CP}$ = 100.5, C-1 Ph); 131.8 (d, $^4J_{CP}$ = 2.2, C-4 Ph); 136.9 (C-5); 137.0 (C-4); 141.9 (d, $^4J_{CP}$ = 2.9, C-5'); 149.0 (d, $^2J_{CP}$ = 7.3, C-2'); 153.3 (C-7); 155.7 (C-8a); 163.2 (d, $^3J_{CP}$ = 13.2, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 31.8. Found, %: C 73.50; H 4.94; N 6.61; P 7.39. $C_{26}H_{21}N_2O_2P$. Calculated, %: C 73.57; H 4.99; N 6.60; P 7.30.

2-[(2-Diphenylphosphoryl)hept-1-yl]-1,8-naphthyridine (1e) was obtained from phosphoryl ketone **5e** (0.68 g, 1.96 mmol) and aldehyde **6** (0.26 g, 2.13 mmol). The reaction time was 8 h. Yield 0.58 g (63%), white fine crystalline powder, mp 194–195°C (EtOAc–cyclohexane, 1:4). IR spectrum, ν, cm^{-1}: 1609, 1549, 1500, 1454, 1438 (Ph),

1371, 1307, 1263, 1179 (P=O), 1118, 1102, 1073, 854, 794, 780, 758, 714, 700, 566, 543. Raman spectrum, ν, cm^{-1}: 1610, 1594, 1576, 1550, 1374, 1045, 1031, 1000 (Ph), 782, 693, 617, 536. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.64 (3H, t, ^3J = 6.8, CH_3); 0.92–1.08 (4H, m, $C\underline{H}_2C\underline{H}_2CH_3$); 1.10–1.36 (2H, m, $C\underline{H}_2(CH_2)_2CH_3$); 1.55–1.77 (2H, m, $C\underline{H}_2(CH_2)_3CH_3$); 3.31 (1H, ddd, ^2J = 15.3, ^3J = 8.2, $^3J_{HP}$ = 12.8) and 3.43 (1H, ddd, ^2J = 15.3, ^3J = 5.4, $^3J_{HP}$ = 12.0, $C\underline{H}_2CH$); 3.67–3.73 (1H, m, $CH_2C\underline{H}$); 7.15–7.20 (2H, m, H-3,5 Ph); 7.22 (1H, d, ^3J = 8.3, H-3); 7.20–7.24 (1H, m, H-4 Ph); 7.44 (1H, dd, ^3J = 8.0, ^3J = 4.4, H-6); 7.42–7.49 (3H, m, H-3,4,5 Ph); 7.79–7.84 (2H, m, H-2,6 Ph); 7.90 (1H, d, ^3J = 8.0, H-4); 7.86–7.91 (2H, m, H-2,6 Ph); 8.10 (1H, dd, ^3J = 8.0, ^4J = 1.8, H-5); 9.10 (1H, dd, ^3J = 4.2, ^4J = 2.0, H-7). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 0.65 (3H, t, ^3J = 6.7, CH_3); 0.92–1.10 (4H, m, $C\underline{H}_2C\underline{H}_2CH_3$); 1.10–1.40 (2H, m, $C\underline{H}_2(CH_2)_2CH_3$); 1.54–1.79 (2H, m, $C\underline{H}_2(CH_2)_3CH_3$); 3.31 (1H, dd, ^2J = 15.3, ^3J = 8.2) and 3.43 (1H, dd, ^2J = 15.3, ^3J = 5.4, $C\underline{H}_2CH$); 3.66–3.74 (1H, m, $CH_2C\underline{H}$); 7.15–7.20 (2H, m, H-3,5 Ph); 7.22 (1H, d, ^3J = 8.5, H-3); 7.20–7.25 (1H, m, H-4 Ph); 7.44 (1H, dd, ^3J = 7.8, ^3J = 4.2, H-6); 7.43–7.50 (3H, m, H-3,4,5 Ph); 7.80–7.84 (2H, m, H-2,6 Ph); 7.87–7.91 (2H, m, H-2,6 Ph); 7.90 (1H, d, ^3J = 8.4, H-4); 8.10 (1H, dd, ^3J = 8.1, ^4J = 1.9, H-5); 9.10 (1H, dd, ^3J = 4.2, ^4J = 1.9, H-7). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 13.8 (CH_3); 22.1 ($\underline{C}H_2CH_3$); 27.2 (d, $^3J_{CP}$ = 8.9, $\underline{C}H_2(CH_2)_2CH_3$); 28.2 ($\underline{C}H_2(CH_2)_3CH_3$); 31.7 ($\underline{C}H_2CH_2CH_3$); 36.0 (d, $^1J_{CP}$ = 70.8, $CH_2\underline{C}H$); 36.8 ($\underline{C}H_2CH$); 121.2 (C-4a); 121.5 (C-6); 123.7 (C-3); 128.2 (d, $^3J_{CP}$ = 11.1, C-3,5 Ph); 128.5 (d, $^3J_{CP}$ = 11.0, C-3,5 Ph); 130.9 (d, $^2J_{CP}$ = 8.8, C-2,6 Ph); 131.0 (d, $^4J_{CP}$ = 2.2, C-4 Ph); 131.0 (d, $^2J_{CP}$ = 8.8, C-2,6 Ph); 131.4 (d, $^4J_{CP}$ = 2.2, C-4 Ph); 132.7 (d, $^1J_{CP}$ = 94.0, C-1 Ph); 132.9 (d, $^1J_{CP}$ = 94.9, C-1 Ph); 136.8 (C-5); 136.9 (C-4); 153.3 (C-7); 155.7 (C-8a); 164.3 (d, $^3J_{CP}$ = 9.9, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 36.4. Found, %: C 75.54; H 6.77; N 6.56; P 7.24. $C_{27}H_{29}N_2OP$. Calculated, %: C 75.68; H 6.82; N 6.54; P 7.23.

2-[(2-Diisopropylphosphoryl-2-phenyl)ethyl]-1,8-naphthyridine (1f) was obtained from phosphoryl ketone **5f** (0.56 g, 2.00 mmol) and aldehyde **6** (0.26 g, 2.13 mmol). The reaction time was 9 h. Yield 0.55 g (75%), white fine crystalline powder, mp 205–206°C ($CHCl_3$–hexane, 1:4). IR spectrum, ν, cm^{-1}: 1605, 1548, 1501, 1454, 1145 (P=O), 887, 857, 816, 780, 748, 702, 634, 542. Raman spectrum, ν, cm^{-1}: 1604, 1584, 1550, 1454, 1372, 1038, 1004 (Ph), 783, 751, 537. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.88 (3H, dd, ^3J = 7.3, $^3J_{HP}$ = 15.1) and 1.44 (3H, dd, ^3J = 7.4, $^3J_{HP}$ = 14.8, $CH(C\underline{H}_3)_2$); 1.10 (3H, dd, ^3J = 7.3, $^3J_{HP}$ = 14.5) and 1.47 (3H, dd, ^3J = 7.2, $^3J_{HP}$ = 14.5, $CH(C\underline{H}_3)_2$); 1.85 (1H, d sept, ^3J = 7.4, $^2J_{HP}$ = 14.8, $C\underline{H}Me_2$); 2.39 (1H, d sept, ^3J = 7.2, $^2J_{HP}$ = 14.4, $C\underline{H}Me_2$); 3.68 (1H, ddd, ^2J = 14.2, ^3J = 11.7, $^3J_{HP}$ = 5.3) and 3.79 (1H, ddd, ^2J = 14.3, ^3J = 3.4, $^3J_{HP}$ = 5.8, $C\underline{H}_2CH$); 4.12 (1H, ddd, ^3J = 11.5, ^3J = 3.6, $^2J_{HP}$ = 5.3, $CH_2C\underline{H}$); 6.93 (1H, d, ^3J = 8.2, H-3); 7.10 (1H, t, ^3J = 6.9, H-4 Ph); 7.15 (1H, t, ^3J = 7.4, H-3,5 Ph); 7.39–7.43 (3H, m, H-6, H-2,6 Ph); 7.83 (1H, d, ^3J = 8.2, H-4); 8.06 (1H, dd, ^3J = 8.0, ^4J = 1.8, H-5); 9.07 (1H, dd, ^3J = 4.1, ^4J = 1.9, H-7). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 0.88 (3H, d, ^3J = 7.4) and 1.44 (3H, d, ^3J = 7.4, $CH(C\underline{H}_3)_2$); 1.10 (3H, d, ^3J = 7.3) and 1.47 (3H, d, ^3J = 7.3, $CH(C\underline{H}_3)_2$); 1.85 (1H, sept, ^3J = 7.3, $C\underline{H}Me_2$); 2.40 (1H, sept, ^3J = 7.4, $C\underline{H}Me_2$); 3.68 (1H, dd, ^2J = 14.2, ^3J = 11.6) and 3.79 (1H, dd, ^2J = 14.2, ^3J = 3.5, $C\underline{H}_2CH$); 4.12 (1H, dd, ^3J = 11.6, ^3J = 3.4, $CH_2C\underline{H}$); 6.93 (1H, d, ^3J = 8.2, H-3); 7.10 (1H, tm, ^3J = 7.2, H-4 Ph); 7.15 (1H, tm, ^3J = 7.2, H-3,5 Ph); 7.38–7.44 (3H, m, H-6, H-2,6 Ph); 7.83 (1H, d, ^3J = 8.2, H-4); 8.06 (1H, dd, ^3J = 8.1, ^4J = 2.0, H-5); 9.07 (1H, dd, ^3J = 3.8, ^4J = 1.2, H-7). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 16.0 (d, $^2J_{CP}$ = 2.2, CH_3); 16.5 (d, $^2J_{CP}$ = 1.7, CH_3); 17.2 (d, $^2J_{CP}$ = 2.8, CH_3); 17.7 (d, $^2J_{CP}$ = 2.2, CH_3); 26.6 (d, $^1J_{CP}$ = 63.0, $\underline{C}HMe_2$); 26.7 (d, $^1J_{CP}$ = 59.7, $\underline{C}HMe_2$); 39.8 ($\underline{C}H_2CH$); 41.8 (d, $^1J_{CP}$ = 55.8, $CH_2\underline{C}H$); 121.1 (C-4a); 121.5 (C-6); 123.6 (C-3); 126.9 (d, $^5J_{CP}$ = 1.7, C-4 Ph); 128.4 (br. s, C-3,5 Ph); 129.8 (d, $^3J_{CP}$ = 5.0, C-2,6 Ph); 136.6 (C-4); 137.0 (C-5); 137.2 (d, $^2J_{CP}$ = 5.0, C-1 Ph); 153.3 (C-7); 155.8 (C-8a); 163.8 (d, $^3J_{CP}$ = 12.7, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 56.5. Found, %: C 72.19; H 7.49; N 7.64; P 8.49. $C_{22}H_{27}N_2OP$. Calculated, %: C 72.11; H 7.43; N 7.64; P 8.45.

2-[(2-Diphenylphosphoryl)ethyl]-1,6-naphthyridine (2a) was obtained from phosphoryl ketone **5a** (2.15 g, 7.90 mmol) and aldehyde **7** (1.03 g, 8.43 mmol). The reaction time was 8 h. The product was isolated by repeated recrystallization from a mixture of compounds **2a** and **8**. Yield 0.31 g (11%), white fine crystalline powder, mp 173–174°C (EtOAc). IR spectrum, ν, cm^{-1}: 1613, 1591, 1557, 1483, 1467, 1437 (Ph), 1401, 1229, 1179 (P=O), 1119, 1108, 969, 944, 854, 775, 755, 726, 695, 546. Raman spectrum, ν, cm^{-1}: 1610, 1590, 1571, 1559, 1468, 1373, 1352, 1341, 1156, 1026, 995 (Ph), 789, 684, 675, 614, 536. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.91–2.99 (2H, m, $CH_2C\underline{H}_2P$); 3.33–3.40 (2H, m, $C\underline{H}_2CH_2P$); 7.38 (1H, d, ^3J = 8.5, H-3); 7.43–7.47 (4H, m, H-3,5 Ph); 7.48–7.52 (2H, m, H-4 Ph); 7.77–7.83 (5H, m, H-8, H-2,6 Ph); 8.12 (1H, d, ^3J = 8.5, H-4); 8.72 (1H, d, ^3J = 5.9, H-7); 9.19 (1H, br. s, H 5). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 2.91–3.00 (2H, m, $CH_2C\underline{H}_2P$); 3.32–3.42 (2H, m, $C\underline{H}_2CH_2P$); 7.38 (1H, d, ^3J = 8.4, H-3); 7.42–7.47 (4H, m, H-3,5 Ph); 7.48–7.53 (2H, m, H-4 Ph); 7.77–7.84 (5H, m, H-8, H-2,6 Ph); 8.12 (1H, d, ^3J = 8.4, H-4); 8.72 (1H, d, ^3J = 5.9, H-7); 9.19 (1H, br. s, H-5). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 28.3 (d, $^1J_{CP}$ = 71.9, $CH_2\underline{C}H_2P$); 30.8 (d, $^2J_{CP}$ = 1.1, $\underline{C}H_2CH_2P$); 121.7 (C-8); 122.5 (C-4a); 123.2 (C-3); 128.7 (d, $^3J_{CP}$ = 11.6, C-3,5 Ph); 130.8 (d, $^2J_{CP}$ = 9.4, C-2,6 Ph); 131.8 (d, $^4J_{CP}$ = 2.2, C-4 Ph); 132.7 (d, $^1J_{CP}$ = 99.5, C-1 Ph); 135.8 (C-4); 147.0 (C-7); 150.1 (C-8a); 152.4 (C-5); 165.6 (d, $^3J_{CP}$ = 13.8, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 32.0. Found, %: C 74.01; H 5.14; N 7.76; P 8.57. $C_{22}H_{19}N_2OP$. Calculated, %: C 73.73; H 5.34; N 7.82; P 8.64.

2-[(2-Diphenylphosphoryl-2-phenyl)ethyl]-1,6-naphthyridine (2b) was obtained from phosphoryl ketone **5b** (0.87 g, 2.50 mmol) and aldehyde **7** (0.31 g, 2.53 mmol). The reaction time was 12 h. Yield 0.82 g (76%), white fine crystalline powder, mp 183–184°C (MeCN, followed by EtOAc). IR spectrum, ν, cm^{-1}: 1613, 1592, 1557, 1483, 1438 (Ph), 1400, 1175 (P=O), 1120, 1102, 1071, 845, 754, 724, 716, 697, 593, 549. Raman spectrum, ν, cm^{-1}: 1605, 1593, 1559, 1376, 1193, 1001 (Ph), 791, 692, 617, 542.

^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.72 (1H, ddd, ^2J = 15.0, ^3J = 5.8, $^3J_{HP}$ = 8.9) and 3.74 (1H, ddd, ^2J = 14.9, ^3J = 8.8, $^3J_{HP}$ = 8.8, C$\underline{H}_2$CH); 4.55 (1H, ddd, ^3J = 6.0, ^3J = 8.9, $^2J_{HP}$ = 6.7, $CH_2C\underline{H}$); 7.02–7.11 (3H, m, H-3,4,5 CPh); 7.09 (1H, d, ^3J = 8.4, H-3); 7.21–7.27 (2H, m, H-3,5 PPh); 7.29–7.36 (3H, m, H-2,6 CPh, H-4 PPh); 7.43–7.54 (5H, m, H PPh); 7.83 (1H, d, ^3J = 5.9, H-8); 7.91 (1H, dd, ^3J = 8.4, ^4J = 0.6, H-4); 7.99–8.07 (2H, m, H-2,6 PPh); 8.70 (1H, d, ^3J = 5.9, H-7); 9.09 (1H, br. s, H-5). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 3.72 (1H, dd, ^2J = 15.1, ^3J = 5.8) and 3.74 (1H, dd, ^2J = 14.9, ^3J = 8.9, C$\underline{H}_2$CH); 4.55 (1H, dd, ^3J = 6.0, ^3J = 8.7, $CH_2C\underline{H}$); 7.02–7.07 (1H, m, H-4 CPh); 7.08 (2H, t, ^3J = 7.3, H-3,5 CPh); 7.09 (1H, d, ^3J = 8.4, H-3); 7.24 (2H, t, ^3J = 7.5, H-3,5 PPh); 7.29–7.36 (3H, m, H-4 PPh, H-2,6 CPh); 7.43–7.53 (5H, m, H PPh); 7.83 (1H, d, ^3J = 5.9, H-8); 7.91 (1H, d, ^3J = 8.4, H-4); 8.00–8.07 (2H, m, H-2,6 PPh); 8.70 (1H, d, ^3J = 5.9, H-7); 9.09 (1H, br. s, H-5). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 39.1 (C$\underline{H}_2$CH); 45.6 (d, $^1J_{CP}$ = 67.5, $CH_2C\underline{H}$); 121.7 (C-8); 122.3 (C-4a); 123.9 (C-3); 127.0 (d, $^5J_{CP}$ = 2.2, C-4 CPh); 128.0 (d, $^3J_{CP}$ = 11.7, C-3,5 PPh); 128.2 (d, $^4J_{CP}$ = 2.2, C-3,5 CPh); 128.7 (d, $^3J_{CP}$ = 11.7, C-3,5 PPh); 129.9 (d, $^3J_{CP}$ = 5.1, C-2,6 CPh); 131.0 (d, $^2J_{CP}$ = 8.8, C-2,6 PPh); 131.3 (d, $^4J_{CP}$ = 2.2, C-4 PPh); 131.4 (d, $^2J_{CP}$ = 8.8, C-2,6 PPh); 131.7 (d, $^1J_{CP}$ = 94.6, C-1 PPh); 131.7 (d, $^4J_{CP}$ = 2.2, C-4 PPh); 132.0 (d, $^1J_{CP}$ = 100.5, C-1 PPh); 135.3 (C-4); 135.6 (d, $^2J_{CP}$ = 5.1, C-1 CPh); 146.8 (C-7); 150.1 (C-8a); 152.4 (C-5); 164.5 (d, $^3J_{CP}$ = 12.5, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 33.2. Found, %: C 77.27; H 5.24; N 6.31; P 7.09. $C_{28}H_{23}N_2OP$. Calculated, %: C 77.41; H 5.34; N 6.45; P 7.13.

2-[(2-Diphenylphosphoryl)hept-1-yl]-1,6-naphthyridine (2c). IR spectrum, ν, cm^{-1}: 1613, 1591, 1558, 1483, 1467, 1437 (Ph), 1403, 1374, 1339, 1311, 1232, 1179 (P=O), 1116, 844, 715, 700, 636, 568, 551, 542. Raman spectrum, ν, cm^{-1}: 1614, 1594, 1559, 1469, 1375, 1340, 1030, 1000 (Ph), 791, 676, 618, 542.

***trans*-2-[(2-Diphenylphosphoryl)vinyl]-1,8-naphthyridine (3)**. A solution of aldehyde **6** (0.36 g, 2.94 mmol) and phosphoryl ketone **9** (0.74 g, 2.74 mmol) in EtOH (5 ml) was treated with KOH (8 mg, 0.14 mmol) as 20% aqueous solution. The mixture was refluxed for 3 h. The precipitate that formed upon cooling was recrystallized from EtOH and dried for 2 h at reduced pressure (120°C, 12 mmHg). Yield 0.43 g (44%), white crystalline powder, mp 269–270°C (EtOH). IR spectrum, ν, cm^{-1}: 1610, 1596, 1547, 1501, 1437 (Ph), 1185 (P=O), 1119, 1103, 994, 838, 822, 807, 778, 750, 743, 722, 693, 580, 549, 524, 517. Raman spectrum, ν, cm^{-1}: 1608 (C=C), 1592, 1376, 1274, 998 (Ph), 776, 691, 614, 533. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.44–7.50 (5H, m, H-6, H-3,5 Ph); 7.51–7.55 (2H, m, H-4 Ph); 7.62 (1H, d, ^3J = 8.3, H-3); 7.76–7.82 (4H, m, H-2,6 Ph); 7.82 (1H, dd, ^3J = 16.9, $^3J_{HP}$ = 18.3, C$\underline{H}$=CHP); 8.01 (1H, dd, ^3J = 16.7, $^2J_{HP}$ = 24.7, CH=C$\underline{H}$P); 8.19 (1H, dd, ^3J = 8.1, ^4J = 2.0, H-5); 8.24 (1H, d, ^3J = 8.2, H-4); 9.13 (1H, dd, ^3J = 4.1, ^4J = 2.1, H-7). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 7.44–7.51 (5H, m, H-6, H-3,5 Ph); 7.51–7.57 (2H, m, H-4 Ph); 7.63 (1H, d, ^3J = 8.3, H-3); 7.77–7.82 (4H, m, H-2,6 Ph); 7.82 (1H, d, ^3J = 17.4, C$\underline{H}$=CHP); 8.01 (1H, d, ^3J = 16.8, CH=C$\underline{H}$P); 8.20 (1H, dd, ^3J = 8.1, ^4J = 1.7, H-5); 8.24 (1H, d, ^3J = 8.2, H-4); 9.13 (1H, dd, ^3J = 4.1, ^4J = 1.9, H-7). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 122.5 (C-6); 122.9 (C-4a); 123.0 (C-3); 128.2 (d, $^1J_{CP}$ = 99.5, CH=$\underline{C}$HP); 128.7 (d, $^3J_{CP}$ = 12.2, C-3,5 Ph); 131.4 (d, $^2J_{CP}$ = 9.9, C-2,6 Ph); 132.1 (d, $^4J_{CP}$ = 2.2, C-4 Ph); 132.5 (d, $^1J_{CP}$ = 105.0, C-1 Ph); 136.9 (C-5); 138.4 (C-4); 145.2 (d, $^2J_{CP}$ = 3.3, $\underline{C}$H=CHP); 154.5 (C-7); 155.8 (C-8a); 160.0 (d, $^3J_{CP}$ = 17.7, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 23.8. Found, %: C 74.11; H 4.80; N 7.65; P 8.64. $C_{22}H_{17}N_2OP$. Calculated, %: C 74.15; H 4.81; N 7.86; P 8.69.

***trans*-2-[(2-Diphenylphosphoryl)vinyl]-1,6-naphthyridine (4)** was obtained analogously to compound **3** from aldehyde **7** (0.22 g, 1.80 mmol) and phosphoryl ketone **9** (0.46 g, 1.70 mmol). After heating for 3 h, the solvent was removed by evaporation at reduced pressure and the solid residue was treated as described in the procedure for preparation of compound **3**. Yield 0.24 g (40%), white fine crystalline powder, mp 204–206°C (EtOAc). IR spectrum, ν, cm^{-1}: 1611, 1587, 1550, 1483, 1438 (Ph), 1400, 1234, 1196, 1183 (P=O), 1160, 1120, 1099, 1071, 1001, 829, 785, 755, 739, 721, 693, 561, 547, 530, 523, 513. Raman spectrum, ν, cm^{-1}: 1620, 1610 (C=C), 1591, 1574, 1554, 1371, 1332, 1184, 1161, 1029, 1002 (Ph), 790, 693, 617, 540. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.49–7.54 (4H, m, H-3,5 Ph); 7.55–7.59 (2H, m, H-4 Ph); 7.68 (1H, d, ^3J = 8.5, H-3); 7.76 (1H, dd, ^3J = 17.0, $^3J_{HP}$ = 18.6, C$\underline{H}$=CHP); 7.80 (1H, dd, ^3J = 17.0, $^3J_{HP}$ = 22.9, CH=C$\underline{H}$P); 7.79–7.84 (4H, m, H-2,6 Ph); 7.88 (1H, d, ^3J = 5.9, H-8); 8.33 (1H, d, ^3J = 8.5, H-4); 8.76 (1H, d, ^3J = 5.9, H-7); 9.28 (1H, br. s, H-5). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 7.51 (4H, t, ^3J = 7.3, H-3,5 Ph); 7.55–7.60 (2H, m, H-4 Ph); 7.68 (1H, d, ^3J = 8.4, H-3); 7.76 (1H, d, ^3J = 17.0, C$\underline{H}$=CHP); 7.81 (1H, d, ^3J = 16.7, CH=C$\underline{H}$P); 7.80–7.84 (4H, m, H-2,6 Ph); 7.89 (1H, d, ^3J = 6.0, H-8); 8.33 (1H, d, ^3J = 8.5, H-4); 8.77 (1H, d, ^3J = 6.0, H-7); 9.28 (1H, br. s, H-5). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 122.1 (C-8); 122.8 (C-3); 123.3 (C-4a); 128.8 (d, $^3J_{CP}$ = 12.2, C-3,5 Ph); 128.9 (d, $^1J_{CP}$ = 98.4, CH=$\underline{C}$HP); 131.5 (d, $^2J_{CP}$ = 9.9, C-2,6 Ph); 132.2 (d, $^1J_{CP}$ = 107.3, C-1 Ph); 132.2 (d, $^4J_{CP}$ = 2.2, C-4 Ph); 136.9 (C-4); 145.5 (d, $^2J_{CP}$ = 3.3, $\underline{C}$H=CHP); 147.4 (C-7); 150.4 (C-8a); 152.8 (C-5); 157.1 (d, $^3J_{CP}$ = 17.7, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 23.8. Found, %: C 74.05; H 4.74; N 7.77; P 8.55. $C_{22}H_{17}N_2OP$. Calculated, %: C 74.15; H 4.81; N 7.86; P 8.69.

3-[(Diphenylphosphoryl)methyl]-2-methyl-1,6-naphthyridine (8) was obtained after the isolation of compound **2a** from the reaction mixture. The residue obtained after evaporation of the combined filtrates was repeatedly recrystallized. Yield 50 mg (2%), white crystalline solid, mp 199–200°C (EtOAc–hexane). IR spectrum, ν, cm^{-1}: 1617, 1586, 1559, 1479, 1439, 1401, 1234, 1212, 1186, 1168, 1135, 1121, 1108, 1093, 1070, 944, 915, 831, 819, 742, 719, 691, 577, 543, 517, 506, 478, 460. Raman spectrum, ν, cm^{-1}: 1616, 1590, 1575, 1558, 1400, 1371, 1361, 1025, 996 (Ph), 741, 682, 663, 615, 438. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.65 (3H, s, CH_3); 3.86 (2H, d, $^2J_{HP}$ = 13.5, CH_2); 7.47–7.54 (4H, m, H-3,5 Ph); 7.57–7.63 (2H, m, H-4 Ph); 7.69–7.76 (4H, m, H-2,6 Ph); 7.79 (1H, d,

^3J = 6.0, H-8); 7.88 (1H, d, $^4J_{HP}$ = 2.8, H-4); 8.68 (1H, d, ^3J = 5.9, H-7); 9.02 (1H, br. s, H-5). ^{1}H–{^{31}P} NMR spectrum, δ, ppm (*J*, Hz): 2.65 (3H, s, CH_3); 3.86 (2H, s, CH_2); 7.50 (4H, t, ^3J = 7.5, H-3,5 Ph); 7.60 (2H, t, ^3J = 7.4, H-4 Ph); 7.73 (4H, d, ^3J = 7.2, H-2,6 Ph); 7.79 (1H, d, ^3J = 5.9, H-8); 7.88 (1H, s, H-4); 8.68 (1H, d, ^3J = 5.9, H-7); 9.02 (1H, br. s, H-5). ^{13}C–{^{1}H} NMR spectrum, δ, ppm (*J*, Hz): 24.4 (CH_3); 34.8 (d, $^1J_{CP}$ = 64.9, CH_2); 121.2 (C-8); 122.4 (d, $^4J_{CP}$ = 1.6, C-4a); 125.9 (d, $^2J_{CP}$ = 8.0, C-3); 128.9 (d, $^3J_{CP}$ = 11.2, C-3,5 Ph); 131.1 (d, $^2J_{CP}$ = 9.6, C-2,6 Ph); 131.7 (d, $^1J_{CP}$ = 101.7, C-1 Ph); 132.4 (d, $^4J_{CP}$ = 2.4, C-4 Ph); 136.7 (d, $^3J_{CP}$ = 4.8, C-4); 146.8 (C-7); 148.9 (d, $^5J_{CP}$ = 1.6, C-8a); 152.1 (C-5); 164.0 (d, $^3J_{CP}$ = 4.0, C-2). ^{31}P–{^{1}H} NMR spectrum, δ, ppm: 28.9. Found, %: C 73.81; H 5.34; N 7.77; P 8.61. $C_{22}H_{19}N_2OP$. Calculated, %: C 73.73; H 5.34; N 7.82; P 8.64.

X-ray structural analysis of compound 8. Crystals of compound **8** (*M* 358.38) suitable for X-ray structural analysis were obtained by isothermal evaporation of its solution in EtOAc–hexane mixture. X-ray structural analysis was performed on a Bruker SMART APEX II CCD diffractometer (MoKα-radiation, graphite monochromator, ω-scanning). The structure was solved by direct method and refined by method of least squares in anisotropic full matrix approximation by F^2_{hkl}. The hydrogen atom positions were calculated geometrically and refined in isotropic approximation by the "rider" model. All calculations were performed with the SHELXTL PLUS software suite.[27] The complete X-ray structural dataset for compound **8** has been deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1483897).

Investigation of the extraction properties. 1,2-Dichloroethane of chemically pure grade was used without additional purification as the organic solvent. Solutions of extractants at 0.01 mol/l concentration were prepared from accurately weighed samples. The initial aqueous U(VI) and lanthanide(III) solutions were prepared by dissolving the respective perchlorates in water, followed by the addition of NH_4ClO_4. The initial concentrations of metal ions were $4\cdot10^{-6}$ mol/l, the concentration of NH_4ClO_4 was 1 mol/l. The phases were contacted at room temperature by agitation with a stirrer at 60 rpm for 1 h, which is sufficient for establishing constant values of distribution ratios. The concentration of lanthanides(III) and U(VI) in the initial and equilibrated aqueous solutions was determined by mass spectrometry with inductively coupled plasma ionization of samples (ICP-MS), using a Thermo Elemental X-7 mass spectrometer according to a published method.[28] The content of elements in the organic phase was determined after reextraction with a 0.1 M solution of hydroxyethylidenediphosphonic acid. The distribution ratios for the elements were calculated as ratios of the equilibrium concentration in the organic and aqueous phases ($D_M = [M_{org}]/[M_{aq}]$). The error of the determined D_M values did not exceed 5%.

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