First Tetradeinate Diamidophosphite Based on [5,10,15,20-Tetrakis(4-hydroxyphenyl)porphyrinato]zinc: Synthesis, Spectral Features, Coordination, and Application in Asymmetric Pd-Catalyzed Reactions

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The synthesis of the tetradeinate diamidophosphite (L) containing four 1,3,2-diazaphospholidine rings and a porphyrin moiety, its characterization and application in asymmetric Pd-catalyzed reactions are reported. The best results (up to 63 % ee) were obtained for the Pd-catalyzed allylic alkylation of (E)-1,3-diphenylallyl acetate with dimethylmalonate. The complex L[Ru(p-cymene)Cl2]4 was synthesized in situ and characterized by spectroscopic data. The structure of the compounds obtained is discussed based on 1H, 13C, 13C DEPT, 31P, 1H-13C HSQC, 1H-13C HMBC, 1H-1H COSY, 1H-1H ROESY NMR spectroscopy, as well as UV-Vis and fluorescence spectroscopy.

Keywords: Asymmetric allylic substitution, palladium, diamidophosphites, ruthenium complexes, porphyrins.

Первый тетрадентатный диамидофосфит на основе 5,10,15,20-тетракис(4-гидроксифенил)порфирината цинка: синтез, спектральные особенности, координация и применение в асимметрических Pd-катализируемых реакциях

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В данной работе сообщается о синтезе, характеристиках и применении в асимметрических Pd-катализируемых реакциях тетрадентатного диамидофосфита (L), содержащего четыре 1,3,2-диазапфосфолидиновых колца и порфириновую часть. Наилучшие результаты (до 63 % энантиомерного избытка) были достигнуты для Pd-катализируемого аллильного алкилирования (E)-1,3-диэфенилаллиловой части с использованием диметилмалоната. Комплекс L[Ru(p-cymene)Cl2]4 был синтезирован in situ и характеризован спектральными данными. Структура полученных соединений обсуждается с привлечением данных 1H, 13C, 13C DEPT, 31P, 1H-13C HSQC, 1H-13C HMBC, 1H-1H COSY, 1H-1H ROESY ЯМР спектроскопии, а также УФ и флуоресцентной спектроскопии.

Ключевые слова: Асимметрическое аллильное замещение, палладий, диамидофосфиты, рутения комплексы, порфиринс.
**Introduction**

The current stage of the development of organic synthesis is characterized by the extensive use of chiral transition metal complexes as catalysts for the preparation of the organic and organoelement compounds with high enantiomeric purity. Such compounds are used as components of pharmaceuticals, agricultural crop protection products, food additives and fragrances.\(^{[1-7]}\) In turn, the current progress in the field of asymmetric catalysis is mainly determined by recent advances in the design and synthesis of chiral ligands, primarily phosphorus-containing ones, thousands of which were used in various asymmetric transformations.\(^{[1-12]}\) However, the vast majority of known chiral phosphorus ligands in the corresponding metal complexes are able to catalyze efficiently only a certain type of the asymmetric reaction. Only few ligands, the so-called “privileged” ones, can be successfully applied in diverse asymmetric transformations. Phosphoramidites are an excellent example of this type of ligands.\(^{[11]}\) Indeed, the binaphthol(biphenol)-based phosphoramidites are widely universal, readily accessible and very efficient stereoselectors. Therefore, the design and synthesis of new promising phosphorous-containing stereoselectors are ongoing and represent a serious challenge to researchers.

In general, phosphorous acid derivatives are a promising class of ligands due to their stability to oxidation, pronounced π-acceptor ability, ease of preparation and low cost. They can be obtained from readily available precursors by simple condensation, including parallel and solid-state syntheses.\(^{[5,7,11-17]}\) In addition, the presence of a chiral phosphorus atom as a donor center in the structure of such ligands often significantly increases the asymmetric induction in the catalytic reaction.\(^{[2,18-21]}\) Recently, chiral supramolecular derivatives of phosphorous acid based on porphyrins have attracted increasing attention.\(^{[22-37]}\)

We have previously reported the preparation of a series of chiral ligands – phosphorous acid derivatives, which were successfully applied in Pd-catalyzed allyl substitution reactions.\(^{[38-43]}\) In those cases, porphyrins were used both as achiral additives\(^{[38-41]}\) to increase enantioselectivity, and as starting substrates for phosphorylation.\(^{[42-44]}\) In a preliminary communication,\(^{[44]}\) we reported the synthesis of the first tetradentate diamidophosphate 1 (Figure 1) and its application in asymmetric Pd-catalyzed alkylation of cinnamyl acetate. This work is devoted to the synthesis of zinc-containing tetradentate diamidophosphate 2, its complexation with [Ru(p-cymene)Cl]₂, as well as the study of the photo-physical properties of ligands 1 and 2 and their application in a number of asymmetric Pd-catalyzed processes.

**Experimental**

\(^{31}\)P, \(^{13}\)C and \(^1\)H NMR spectra were recorded on a Bruker Avance III 600 (242.9 MHz for \(^{31}\)P, 150.9 MHz for \(^{13}\)C and 600.13 MHz for \(^1\)H) spectrometer. The assignment of the resonances in the \(^1\)H and \(^{13}\)C NMR spectra was achieved by the use of DEPT, COSY, ROESY, HSQC and HMBC techniques. Chemical shifts (ppm) were given relative to Me₄Si (\(^1\)H and \(^{13}\)C) and 85 % H₃PO₄ (\(^{31}\)P NMR). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet); coupling constants \(J\) in Hertz (Hz) integration, “n” values are reported in the case of their unambiguous determination. HPLC analyses were performed on Agilent 1100 and Stayer instruments using Chiralcel® and Kromasil® columns. Elemental analyses were performed on a CHN-microanalyzer Carlo Erba EA1108 CHNS-O. Electronic absorption spectra (EAS) were measured on Perkin Elmer Lambda 35 spectrophotometer, using quartz cuvettes of 1 cm pathlength. Luminescence spectra were measured on Fluorolog 3 instrument of Horiba Jobin Yvon, fitted with Hamamatsu R928 photomultiplier tube. Fluorescence quantum yield was measured by absolute method for the solutions in moisture free and non-degassed CH₂Cl₂ (optical density of the solution was not more...

![Figure 1. Structures of compounds 1 and 2.](image-url)
than 0.1 for the maximum of the most intensive Q band in quarts cuvette of 1 cm pathlength in order to avoid self-absorption effect).

Light of fluorescence was collected by Quanta-fl F-3029- sphere linked with Fluorolog 3 by Fiber-Optics adaptor FL-3000 produced by Horiba Jobin Yvon. Fluorescence quantum yields were calculated by FluoroEssence™ software of Horiba.

All reactions were carried out under a dry argon atmosphere in flame-dried glassware and in freshly dried and distilled solvents. For example, toluene and tetrahydrofuran were freshly distilled from sodium or calcium hydride before use; dichloromethane was distilled from CaH2, N,N-Dimethylformamide and pyrrolidine were distilled over KOH and then over a small amount of LiAlH4 before use. Thin-layer chromatography was performed on E. Merck pre-coated silica gel 60 (230 – 400 mesh) and MN-Aluminum oxide, basic, Brockmann Activity 1. 5,10,15,20-Tetrakis(4-hydroxyphenyl)porphine (1) was purchased from Aldrich and dried over P2O5 at 55 °C for 2 h before use. Phosphorylation reagent (5S)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3) was prepared and freshly distilled.[48] 5,10,15,20-Tetrakis(4-(2R,5S)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (1) and the appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis (Daicel Chiralcel OD-H column, C2H5OH/i-PrOH = 99/1, 0.3 mL/min, 254 nm, t(R) = 28.0 min, t(S) = 29.3 min).

Pd-Catalyzed allylic amination of substrate 8 with pyrrolidine. A solution of [Pd(allyl)Cl]2 (0.0019 g, 0.005 mmol) and the appropriate ligand (0.005 mmol or 0.0025 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. Substrate 8 (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then freshly distilled pyrrolidine (0.06 mL, 0.75 mmol) was added. The reaction mixture was stirred for 48 h, diluted with CH2Cl2 or THF (2 mL) and filtered through a thin layer of silica gel. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (E)-1-(3,1-diphenylallyl)pyrrolidine (12).[49,50] In order to evaluate ee and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis (Daicel Chiralcel OD-H column, C2H5OH/i-PrOH/HN(Et)2 = 200/1/0.1, 0.9 mL/min, 254 nm, t(R) = 5.0 min, t(S) = 6.1 min).

Pd-Catalyzed allylic alkylation of substrate 9 with reagent 10. A solution of [Pd(allyl)Cl]2 (0.0019 g, 0.005 mmol) and the appropriate ligand [(0.0025 mmol or 0.005 mmol or 0.01 mmol or 0.02 mmol) in toluene (1.5 mL) was stirred for 40 min. Substrate 9 (0.04 mL, 0.25 mmol) was added and the solution stirred for 15 min. Compound 10 (0.06 mL, 0.375 mmol), BSA (0.25 mL, 1 mmol) and zinc acetate (0.005 g) were added. The reaction mixture was stirred for 48 h, diluted with CH2Cl2 or toluene (2 mL) and filtered through a thin layer of silica gel. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing ethyl 1-cinnamyl-2-oxocyclohexanecarboxylate (13).[51] In order to evaluate ee and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis (Kromasil 5-CellulCoat, C4 2021, 70-78 14 126-130 mmol/L, 0.25 mmol, 0.14 mmol) and potassium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with CH2Cl2 or THF (2 mL) and filtered through a thin layer of silica gel. The filtrate was evaporated at reduced pressure (40 Torr) and dried in vacuum (10 Torr, 12 h) affording a residue containing (E)-dimethyl-2-(1,3-diphenylallyl)malonate (11).[47,48] In order to evaluate ee and conversion, the obtained residue was dissolved in an appropriate eluent mixture (8 mL) and a sample was taken for HPLC analysis (Daicel Chiralcel OD-H column, C2H5OH/i-PrOH = 99/1, 0.3 mL/min, 254 nm, t(R) = 28.0 min, t(S) = 29.3 min).

**Results and Discussion**

**Ligand Synthesis**

The new porphyrin-functionalized tetradiamidophosphite 2 was synthesized in one step through the reaction of the corresponding 5,10,15,20-tetrakis(4-hydroxyphenyl)porphine 3 with four equivalents of the phosphorylating reagent 4 in the presence of i-PrNEt as HCl scavenger in toluene (Scheme 1). The crude ligand was then purified by flash chromatography and have been fully characterized by a combination of NMR spectroscopic methods (H, 13C, 13C DEPT, 31P, 13C-H HSQC, 13C-H HMBC, 1H-H COSY and 1H-1H ROESY) as well as by elemental analysis. It gave us an opportunity to make a complete assignment of all 1H and 13C resonances (Scheme 1).

The 31P NMR spectrum of 2 in CD2Cl2, showed one singlet at δ 124.3 ppm, corresponding to the diaminophosphate phosphorus centers. According to the 31P and 13C NMR spectroscopy data, the exclusive formation of the stereodefined tetradiamidophosphite 2 with an (R)-configuration at the Pα-stereocenters occurred. In particular, the 13C spectrum of 2 is characterized by a large spin-spin coupling
Scheme 1. Synthesis of 2 and full assignment of all $^1$C and $^1$H resonances for the ligand.

constant $^2J_{CP} = 35.3$ Hz at δ 47.94 ppm, which is indicative of the syn-orientation of the phosphorus lone pair with respect to the PNCH$_2$ carbon atom. Correspondingly, the pseudoequatorial exocyclic substituent at the phosphorus atom and the -(CH$_2$)$_3$- of the pyrrolidine fragment of the phosphabicyclic skeleton are in the anti-arrangement (Figure 2).\[^{[52–58]}\]

**Figure 2.** Stereochemistry of the phosphabicyclic part in ligand 2 (X = exocyclic substituent).

**Photophysical Properties**

In order to clarify the photophysical properties of the new tetradeinate amidophosphite 2 and the previously reported\[^{[44,42]}\] 1 and 5–7 (Figure 3), electronic absorption (EAS) and fluorescence spectra were recorded. EAS of free base porphyrins contain four Q absorption bands corresponding to the split electronic transitions S$_0$–S$_1$ (Table 1). As for 6, absorption maxima of the Q bands are located at 515, 550, 591, and 648 nm. Q bands of 1, 7 are similar, with slight (no more than 2–3 nm) blue (7) and red (1) shifts. Zinc complexes 2, 5 possessing higher symmetry of the chromophore relative to the free base porphyrins exhibit only two Q bands with maxima at 548 and 586 nm for 5 and 550, 590 nm for 2. Soret bands corresponding to the electronic transition S$_0$–S$_2$, are observed at 418–422 nm for the studied compounds. The similarity of the spectra is determined by the common chromophore of meso-tetraarylporphine and by a weak influence of the peripheral substituents at benzene ring. Comparing the porphyrins 1, 7 and the zinc complexes 2, 5 it can be noted that an increase in the number of electron-donating amidophosphite substituents at the benzene rings of the porphyrin from one to four leads to a small bathochromic shift (3 nm) of the Soret band and slightly larger (from 3 to 5 nm) bathochromatic

**Figure 3.** Structures of compounds 5–7.
shifts of the Q bands. The effect of changing the type of the substituent from the triarylphosphite in 6 to diamidophosphite in 7 on their electronic spectra is even less appreciable. The weak impact of the substituents at benzene ring of tetraarylporphyrins on the chromophore properties is due to the low degree of π-electronic conjugation of the benzene rings with the tetrapyrrolic macrocycle being a result of their almost perpendicular orientation relative to the plane of the macrocycle.

Compounds 1, 2 and 5–7 manifest luminescence in the red visible region (Figure 4). Emission spectra of the free base porphyrins 1, 6, 7 contain two maxima at 650 and 720 nm. Zinc(II) porphyrins 2, 5 exhibit two maxima of fluorescence as well, however they are significantly blue shifted to 600 and 650 nm, as well as the Q absorption bands, due to the influence of metal cation on the electronic structure of the porphyrin core (Table 1). Quantum yields of fluorescence of free base porphyrins 1, 6, 7 are high enough (8–12 %) resembling that of the free base porphyrin. The emissions of fluorescence as well, however they are significantly blue shifted to 600 and 650 nm, as well as the Q absorption bands, due to the influence of metal cation on the electronic structure of the porphyrin core (Table 1). Quantum yields of fluorescence of free base porphyrins 1, 6, 7 are high enough (8–12 %) resembling that of the free base porphyrin.

Fluorescence quantum yields of zinc(II) porphyrins 2, 5 are typically lower (2.5–3.1 %) than that of the free base porphyrins 1, 6, 7. It can be explained by the increase of the intersystem crossing rate due to the effect of zinc cation leading to a decrease of the population of S1 level in favour of the triplet level T1. Such effect was described earlier for the analogous zinc(II) porphyrinates.[61]

**Complexation Results**

To examine the complexing capacity of tetradiamidophosphite 2, two coordination reactions were investigated. In particular, reaction of 2 with Pd(COD)Cl₂ (our standard precursor[39, 56, 57, 62] COD - cycloocta-1,5-diene) proceeded in CD₂Cl₂ and surprisingly resulted in insoluble polymeric residue. In order to shed light on the coordination properties of 2, we carried out the investigation of the ruthenium(II) complex obtained from the ligand. As a new precursor to study the coordination behavior of 2, [Ru(p-cymene)Cl₂] was selected, which is known to give stable complexes with phosphites, phosphoramidites[63–67] and cyclodiphosphazanes.[64–70] The complexation of the tetradiamidophosphite 2 with [Ru(p-cymene)Cl₂] in CD₂Cl₂ leads to neutral ruthenium complex 14 with a bridging function of the phosphorus ligand (Scheme 2). 31P NMR analyses confirmed the P-monodentate coordination mode. Indeed, the singlet at δ₃1P 103.0 ppm and the considerable coordination shift (Δδ₁₃P = −21.3 ppm) are observed in 31P NMR spectrum of in situ formed 14 in CD₂Cl₂. At the same time, a typical magnitude of δ₃1P lies in the range of 152–109 ppm for the complexes [LRu(p-cymene)Cl₂] with coordinated derivatives of phosphorous acid.[63–70] All 1H and 13C NMR signals were located by the same as for ligand 2 combination of NMR spectroscopic methods (Figure 4). It should be noted that the direct coordination of the phosphorus centers to the Ru atoms was also confirmed by a 13C NMR spectrum of complex 14, which contained phosphorus-coupled resonances of coordinated p-cymene ring. Noteworthy are the pronounced upfield coordination shifts (Δδ₁₃C > −35 ppm) of all p-cymene signals compared to the resonances in the spectrum of starting [Ru(p-cymene)Cl₂]₂. These results allowed us to conclude that tetradiamidophosphite 4 acts as a P₃P₃P₃P₃-tetradentate ligand with a bridging function of a porphyrin core.

**Asymmetric Pd-Catalyzed Allylic Substitution**

First of all, the new ligand 2 and the previously described ligand 1 were tested in the asymmetric palladium-catalyzed allylic alkylation of (E)-1,3-diphenylacetate (8), which is widely used as benchmark substrate (Scheme 3, Table 2). Both ligands showed moderate enantioselectivity.

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**Table 1.** Data of electronic absorption spectra, fluorescence spectra and quantum yields of fluorescence for compounds 1, 2 and 5–7 in CH₂Cl₂.

| Compound | λ maxima of EAS, nm | Fluorescence maxima, nm | Fluorescence quantum yield at 298 K |
|----------|---------------------|-------------------------|-----------------------------------|
| 1        | 421                 | 517, 554, 593, 649      | 656, 721                           | 11.7 %                     |
| 2        | 422                 | 550, 590                | 600, 649                           | 3.1 %                      |
| 5        | 419                 | 548, 586                | 597, 646                           | 2.5 %                      |
| 6        | 418                 | 515, 550, 591, 648      | 654, 717                           | 10.3 %                     |
| 7        | 418                 | 514, 549, 589, 645      | 652, 716                           | 8.0 %                      |

**Figure 4.** Fluorescence spectra of 1, 2 and 5–7 in CH₂Cl₂ (purple – 1, black – 2, green – 5, orange – 6, blue – 7).
Scheme 2. Synthesis of complex 14 in situ in CD$_2$Cl$_2$.

Figure 4. Full assignment of all $^{13}$C and $^1$H resonances for complex 14.

Scheme 3. Pd-Catalyzed allylic substitution of substrate 8 with dimethyl malonate or pyrrolidine.
The molar ratio L/Pd = $\frac{1}{2}$ and CH$_2$Cl$_2$ as the solvent are slightly preferable for both ligands. Undoubtedly, 2 gave better results in any conditions and the combination of 2 at L/Pd = $\frac{1}{2}$ and CH$_2$Cl$_2$ as the solvent allowed to obtain ee up to 63 % at 100 % conversion (entry 8).

Table 2. Pd-catalyzed allylic alkylation of (E)-1,3-diphenylallyl acetate (8) with dimethyl malonate.

| Entry | L     | L/Pd | Solvent | Conversion, % | ee, % |
|-------|-------|------|---------|---------------|-------|
| 1     | 1     | 1/4  | THF     | 59            | 24 (S) |
| 2     | 1     | 1/2  | THF     | 57            | 48 (S) |
| 3     | 1     | 1/4  | CH$_2$Cl$_2$ | 99     | 28 (S) |
| 4     | 1     | 1/2  | CH$_2$Cl$_2$ | 99     | 59 (S) |
| 5     | 2     | 1/4  | THF     | 100           | 46 (S) |
| 6     | 2     | 1/2  | THF     | 100           | 52 (S) |
| 7     | 2     | 1/4  | CH$_2$Cl$_2$ | 100     | 34 (S) |
| 8     | 2     | 1/2  | CH$_2$Cl$_2$ | 100     | 63 (S) |

In the next step, the chiral tetradeutate diamido phosphites 1 and 2 were evaluated in the traditional palladium-catalyzed allylic amination of (E)-1,3-diphenylacetate (8) with pyrrolidine as the N-nucleophile (Scheme 3, Table 3). As a whole, the catalytic performance in this process followed the same trend as for the allylic alkylation of 8. In particular, the amination process with participation of ligand 2 resulted in quantitative conversion in all cases (entries 5–8). The best result was obtained in CH$_2$Cl$_2$ as reaction medium at L/Pd = $\frac{1}{2}$ (entry 8). However, there is an inverse correlation between the L/Pd molar ratio and enantioselectivity in the amination of 8 with 1 (entries 1–2 and 3–4). The enantioselectivity was low in all cases.

Table 3. Pd-Catalyzed amination of (E)-1,3-diphenylallyl acetate (8) with pyrrolidine.

| Entry | L     | L/Pd | Solvent | Conversion, % | ee, % |
|-------|-------|------|---------|---------------|-------|
| 1     | 1     | 1/4  | THF     | 77            | 36 (R) |
| 2     | 1     | 1/2  | THF     | 72            | 27 (R) |
| 3     | 1     | 1/4  | CH$_2$Cl$_2$ | 98     | 20 (R) |
| 4     | 1     | 1/2  | CH$_2$Cl$_2$ | 99     | 14 (R) |
| 5     | 2     | 1/4  | THF     | 100           | 34 (R) |
| 6     | 2     | 1/2  | THF     | 100           | 40 (R) |
| 7     | 2     | 1/4  | CH$_2$Cl$_2$ | 100     | 38 (R) |
| 8     | 2     | 1/2  | CH$_2$Cl$_2$ | 100     | 46 (R) |

We also screened 2 in the Pd-catalyzed allylic alkylation of cinnamyl acetate (9) with ethyl 2-oxycyclohexene-1-carboxylate (10) as the C-nucleophile in a toluene solution (Scheme 4, Table 4). In this challenging process, a quaternary C*-stereocenter is generated on a carbon atom belonging to the nucleophile.[50,71] In all experiments almost quantitative conversion (96–98 %) of substrate 9 was observed and the resulting quaternary-substituted β-keto ether 13 had an (S)-configuration. The molar ratio L/Pd = 1 proved to be slightly more efficient with 60 % ee and 97 % conversion (entry 7). Surprisingly, in this catalytic reaction ligand 1 demonstrated better enantioselectivity but a lower conversion rate (entries 1–4).[44] Unlike the alkylation reaction with 2 the effect of the L/Pd molar ratio on the asymmetric induction was not unidirectional with ligand 1. We have no real explanation for these facts. The asymmetric induction of this reaction is difficult to control and a subtle difference in the structure of the diamidophosphate ligands could have a large effect on the enantioselectivity.

Table 4. Pd-catalyzed allylic alkylation of cinnamyl acetate (9) with ethyl 2-oxycyclohexene-1-carboxylate (10).

| Entry | L     | L/Pd | Conversion, % | ee, % |
|-------|-------|------|---------------|-------|
| 1     | 1     | 1/4  | 22            | 75 (S) |
| 2     | 1     | 1/2  | 50            | 62 (S) |
| 3     | 1     | 1/1  | 95            | 56 (S) |
| 4     | 1     | 2/1  | 60            | 76 (S) |
| 5     | 2     | 1/4  | 98            | 54 (S) |
| 6     | 2     | 1/2  | 96            | 46 (S) |
| 7     | 2     | 1/1  | 97            | 60 (S) |
| 8     | 2     | 2/1  | 98            | 48 (S) |

*Previously published results[44]

Conclusions

Thus, the synthesis of the new chiral tetradeutate diamidophosphate ligands on the basis of [5,10,15,20-tetakis(4-hydroxyphenyl)porphinato]zinc was successfully performed for the first time. Complete assignment of $^1$H and $^{13}$C NMR resonances of the ligand was implemented, and photophysical properties of the compound together with a number of related compounds were studied. Catalytic performance of the synthesized chiral tetradeutate diamidophosphites was investigated in asymmetric allyl substitution reactions of a number of model substrates. The catalytic reactions showed moderate enantioselectivity at high conversion. Nevertheless, the new ligands are of great interest from the viewpoints of coordination and supramolecular chemistry, which has successfully been demonstrated by the example of the L[Ru(p-cymene)Cl$_4$].

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