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Graphical abstract.

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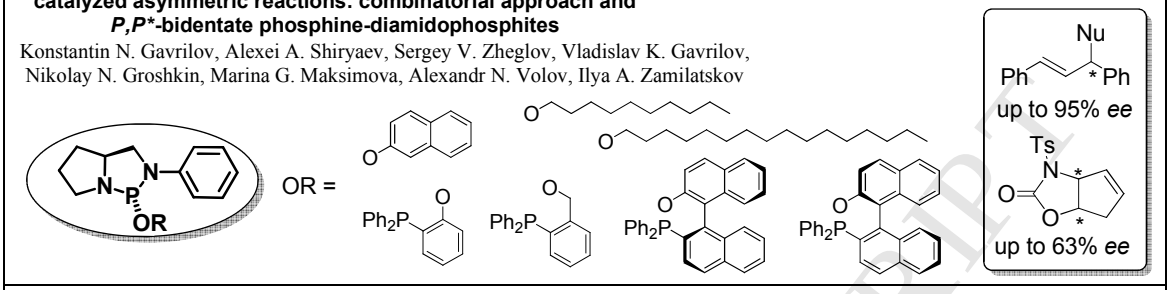

Nonsimple relationships between the *P**-chiral diamidophosphite and the arylphosphine moieties in Pd-catalyzed asymmetric reactions: combinatorial approach and *P,P**-bidentate phosphine-diamidophosphites

Konstantin N. Gavrilov,[a1] Alexei A. Shiryaev,[a] Sergey V. Zheglov,[a] Vladislav K. Gavrilov,[a] Nikolay N. Groshkin,[a] Marina G. Maksimova,[a] Alexandr N. Volov,[b] Ilya A. Zamilatskov [b]

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Abstract: A small family of *P,P**-bidentate C_1-symmetric ligands containing 1,3,2-diazaphospholidine rings with stereogenic phosphorus atoms has been prepared. Palladium catalytic systems with these phosphine-diamidophosphites afforded 95% and 63% *ee*s in asymmetric allylic substitution and desymmetrization processes, respectively. The influence of the nature of both the phosphine and diamidophosphite moieties of these compounds on the enantioselectivity is discussed. The "mixed-ligand approach" in Pd-catalyzed asymmetric allylation with participation of some new *P**-monodentate diamidophosphites and PPh_3 is also considered.

Keywords: Asymmetric allylic substitution; Desymmetrization; Palladium; Phosphine-diamidophosphites.

1. Introduction

Preparation of enantiopure or enantioenriched organic and organoelement compounds is a trend in synthetic chemistry. This is due to the practical importance of such substances as main components of pharmaceuticals, agrochemicals, food additives and perfumery compositions. Asymmetric synthesis involving the use of chiral catalysts is the main stream in the preparation of enantioenriched compounds. Such an approach was successfully effected, in particular, in enantioselective metal complex catalysis.[1-5] Activity and stereoselectivity of metal complex catalysts were significantly determined by a proper strategy of design and synthesis of the

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corresponding chiral ligands, first of all, phosphorus-containing ones, thousands of representatives of which were used in various asymmetric reactions.[1-10]

Beyond doubt, C_2-symmetric bis-phosphines are extremely powerful and versatile ligands for metal-mediated asymmetric transformations.[2,4,11,12] However, a sufficient number of facts have demonstrated that, regarding enantioselectivities, C_2-symmetric ligands are not necessarily intrinsically better than their analogs lacking any symmetry element. In certain cases, ligands with two different coordinating groups should allow for a better stereocontrol.[13,14] This has led to growing interest in the design, preparation and catalytic application of C_1-symmetric *P,P*-bidentate ligands. In particular, phosphorus compounds with phosphine and phosphite-type moieties are examples of nonsymmetric ligands that differ in the electronics and the sterics of their respective binding groups. Many of them are easier to prepare than bis-phosphines and they can induce high enantioselectivity and have desirable stability characteristics. These ligands have afforded excellent results in various asymmetric transformations, first of all in hydrogenation, hydroformylation and conjugate addition.[14,15]

Phosphine-phosphites and phosphine-phosphoramidites (where the phosphite-type moieties have three P–O bonds and two P–O bonds plus one P–N bond, respectively) are well-known groups of such unsymmetrical ligands.[14,15] To the best of our knowledge, there are no examples of phosphine-diamidophosphites (phosphite-type species with one P–O bond and two P–N bonds). It is rather important that diamidophosphites have different properties from phosphites or phosphoramidites. For example, nitrogen substituents create more steric bulk around the phosphorus than oxygen, since nitrogen substitution may be greater. Furthermore, the replacement of the oxygen atom in the first coordination sphere of the phosphorus by a nitrogen atom increases the electron density on the phosphorus center.[16,17] Inclusion of the phosphorus atom into a cyclic structure, in particular a five-membered 1,3,2-diazaphospholidine ring, is a key feature, since it increases its stability toward air and moisture. Also, these compounds display balanced electronic characteristics since they are both good π-acceptors (due to the accessibility of low-lying π^*_{PN} orbitals) as well as good σ-donors. The possibility of varying the nature of the substituents at the nitrogen and phosphorus atoms allows control over the steric and electronic parameters. Thus, interest in diamidophosphites with 1,3,2-diazaphospholidine rings for asymmetric catalysis lies not only in their robustness but also in the tunability of their donor- acceptors properties, as well as their geometry.[16-24]

Moreover, their modular nature allows a facile systematic variation of the configuration of the *C**- and, if the donor phosphorus atom is asymmetric, of the *P**-stereocentres. It is very important that in complexes with *P**-chirogenic ligands the asymmetric phosphorus atom binds directly to the metal atom. This factor eliminates potentially inefficient secondary transfer of

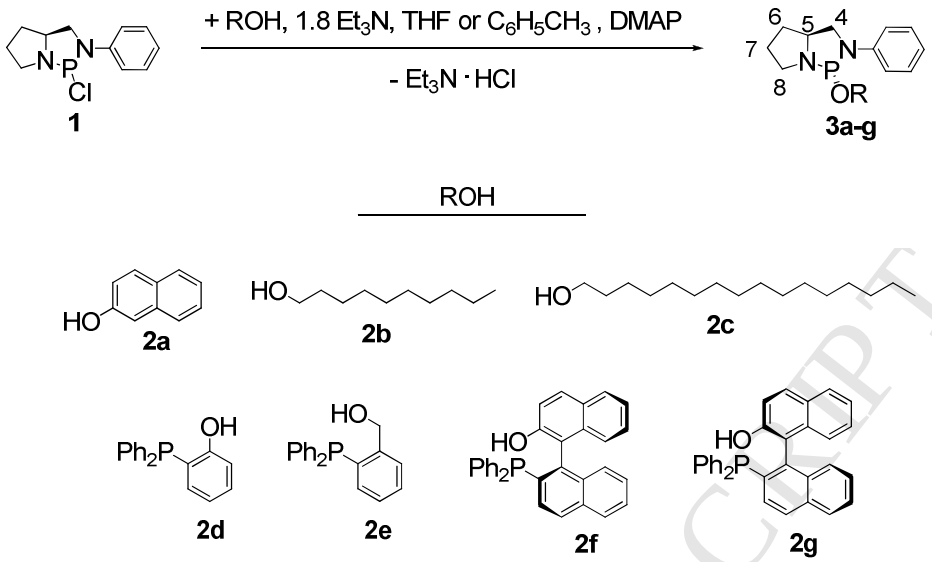
chirality from the ligand backbone and, thus, provides a more efficient chiral environment at the site where the enantioselection originates.[12,25,26] Note that phosphine-phosphites and phosphine-phosphoramidites with phosphine *P**-atoms were used successfully in Pd-catalyzed allylation, Rh-catalyzed hydroformylation, Rh- and Ir-catalyzed hydrogenation and some other enantioselective reactions.[14,15,27-34] At the same time, C_1-symmetric *P,P*-bidentate ligands bearing *P**-chirogenic phosphorus atoms in the phosphite-type moieties, are unknown.

In this paper, we report on the preparation of a small series of novel *P,P**-bidentate phosphine-diamidophosphites containing 1,3,2-diazaphospholidine rings, which we subsequently explored in Pd-catalyzed asymmetric allylation and desymmetrization reactions. The enantioselective Pd-catalyzed allylic substitution has emerged as a powerful synthetic tool, which is tolerant of various functional groups in the substrate and which operates with a wide range of nucleophiles. As a result, Pd-catalyzed allylic substitution is a versatile and highly efficient strategy in the total synthesis of enantiopure natural and unnatural products.[3,6,14,35-41] This is a common benchmark test for initial ligand screening. From a functional point of view, the enantiomeric excesses obtained are the simplest indexes for evaluating new chiral ligands.[14,40,42] It should be added that Pd-catalyzed desymmetrization of *N,N'*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate has been successfully used as a key step in the synthesis of mannostatin A and (-)-swainsonine.[3,36]

We also report the application of some new *P**-monodentate diamidophosphites and PPh_3 in Pd-catalyzed enantioselective processes using the so-called ”mixed-ligand approach”. This strategy has been exploited with success in Rh-catalyzed asymmetric reactions: it has been shown that the combination of two different *P*-monodentate ligands, in particular one chiral and the other achiral, may in certain situations afford a more stereoselective and/or more active catalyst.[43,44] Such an approach is less common for palladium catalysis.[45,46]

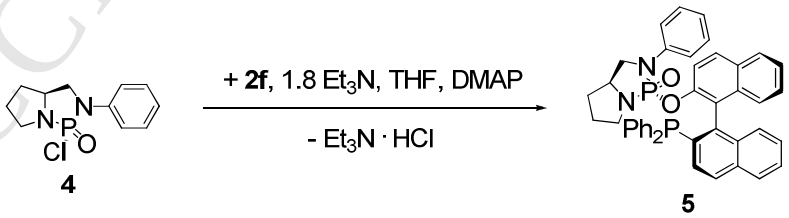
2. Results and discussion

The novel *P**-mono- and *P,P**-bidentate diamidophosphite ligands **3a-g** were prepared via condensation reactions between the phosphorylating reagent **1** and naphthalen-2-ol **2a**, alcohols **2b,c** or hydroxy-phosphines **2d-g** in THF or toluene in the presence of an excess of Et_3N as an HCl scavenger and DMAP as a catalyst. Scheme 1 shows the synthesis of these



Scheme 1. Synthesis of *P**-mono- and *P,P**-bidentate diamidophosphites **3a-g**.

compounds. The use of DMAP is advantageous, as it decreases the reaction time and also reduces the amount of byproducts.[47] However, in order to guarantee the elimination of possible impurities, the resulting mixtures were purified by chromatography through basic aluminum oxide. New stereoselectors were obtained as colorless oils for **3a,b** and **3d,e** and as white solids for **3c** and **3f,g** in good yields (74 - 86%). They can be stored under dry conditions at room temperature for at least a few months with minimal degradation. Ligands **3e-g** readily form solvates with toluene. Therefore, long time of high vacuum drying is required for the preparation of analytically pure material. Note that we turned our attention to design and synthesis of ligands **3b,c** with long-chain exocyclic substituents in view of the high efficiency of a similar *P**-chiral diamidophosphite stereoselector bearing a fluorous ponytail.[48] We also synthesized ligand **5** (Scheme 2) as a phosphine-diamidophosphate analog of **3f** with a P=O structural fragment.



Scheme 2. Synthesis of phosphine-diamidophosphate **5**.

Compounds **3a-g** and **5** have been fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, MALDI TOF/TOF or EI mass spectrometry as well as by elemental analysis, and the data collected are in accord with the structures proposed for them. In particular, all NMR

spectra suggest that the new *P,P**-bidentate phosphine-diamidophosphites show C_1-symmetry. ^{31}P NMR data are summarized in Table 1. In the ^{31} P NMR spectra **3d-g** two different phosphine

Table 1. ^{31}P NMR spectroscopic data for ligands **3a-g**, **5** and complexes **6d-f** in $CDCl_3$

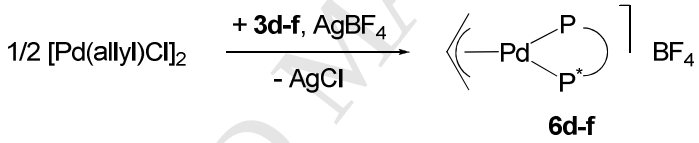
Compound	δ_P	$J_{P,P*}$, Hz
3a (96%) [a]	124.5 (s)	
(4%)	120.5 (s)	
3b	122.5 (s)	
3c	122.6 (s)	
3d (85%) [a]	125.9 (d), - 17.8 (d)	8.5
(15%)	117.6 (s), - 16.2 (s)	–
3e	120.0 (s), - 15.7 (s)	–
3f (84%) [a]	127.2 (s), - 12.9 (s)	–
(16%)	119.0 (s), - 14.4 (s)	–
3g (86%) [a]	130.6 (d), - 13.6 (d)	5.1
(14%)	117.2 (d), - 15.4 (d)	13.6
5	17.7 (s), - 13.5 (s)	–
6d (48%) [b]	137.7 (br. d), 11.4 (br. d)	79.4
(52%)	137.3 (br. d), 11.1 (br. d.)	81.8
6e (42%) [b]	127.8 (d), 12.8 (d)	65.5
(58%)	127.6 (d), 15.3 (d)	68.1
6f (85%) [a] (60%) [b]	132.7 (d), 22.5 (d)	63.2
(25%) [b]	131.9 (d), 24.0 (d)	63.7
(15%) [a] (11%) [b]	123.5 (d), 21.9 (d)	64.3
(4%) [b]	122.1 (d), 20.8 (d)	64.2

[a] Percentage of *P**-epimers.
[b] Percentage of *exo*- and *endo*-isomers.

and diamidophosphite moieties displayed two distinct singlets in a narrow range around δ_P - 12.9 – - 17.8 and 117.2 – 130.6 ppm, respectively. Compounds **3a**, **3d** and **3f,g** are mixtures of epimers with respect to the phosphorus stereocentre, and contain 84-96% of the major *P**-epimers, while ligands **3b**,**c** and **3e** are formed as single stereoisomers (Table 1). Ligands **3b**,**c** and **3e** and the major epimers of ligands **3a**, **3d** and **3f,g** have the *P**-stereocentres with the (*R*)-configuration. Indeed, the ^{13}C NMR spectra of these compounds are characterized by large spin-

spin coupling constants $^{2}J_{C(8),P}$ (32.4 – 38.4 Hz, see Experimental section). These values suggest an *anti*-orientation of the pseudoequatorial exocyclic substituent at the phosphorus atom and the -$(CH_2)_3$- part of the pyrrolidine fragment of the phosphabicyclic skeleton and, consequently, the *syn*-orientation of the phosphorus lone pair with respect to the C(8) atom. On the contrary, the minor epimers of **3a**, **3d** and **3f,g** contain asymmetric phosphorus atoms with the (*S*)-configuration, as evidenced by the fact that their ^{13}C NMR spectra have small coupling constants $^{2}J_{C(8),P}$ (3.2 – 4.5 Hz, see Experimental section).[18,20,22,48-50] It is worth noting that for both epimers of **3g** it is possible to observe the long range spin–spin coupling between two distant phosphorus atoms (Table 1) as new example of such quite rare phenomenon.[51] We did not establish the absolute configuration of the *P**-stereocentre in the structure of ligand **5**, nevertheless, considering the data presented in the literature on related compounds it can be assumed that this phosphine-diamidophosphate has an asymmetric phosphorus atom with the (*R*)-configuration.[52]

Compounds **3d-f** readily reacted with $[Pd(allyl)Cl]_2$ (CH_2Cl_2/THF, $AgBF_4$ as a chloride scavenger, room temperature, 3.5 h) to give cationic metallochelates **6d-f** of the type $[Pd(allyl)(L)]BF_4$ (Scheme 3). The AX systems were observed in the ^{31}P NMR spectra of

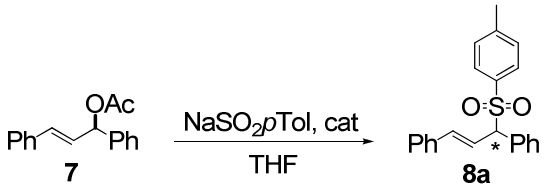


Scheme 3. Synthesis of cationic palladium complexes **6d-f**.

complexes **6d-f** due to the presence of the two different phosphine and diamidophosphite phosphorus atoms in the coordination sphere of the palladium. Duplication of the AX systems in the ^{31}P NMR spectra of complexes **6d-f** (Table 1) indicated the presence of their *exo*- and *endo*-isomers.[20,53] The MALDI TOF/TOF mass spectrometry and elemental analysis data (see Experimental section) were also in good agreement with the proposed structures of **6d-f**.

To investigate the ability of the present diamidophosphite ligands to induce enantioselectivity in catalytic processes, their performance in representative Pd-catalyzed asymmetric allylation and desymmetrization reactions has been examined. First, compounds **3a-f** and **6d-f** have been tested in Pd-catalyzed allylic sulfonylation of the substrate (*E*)-1,3-diphenylallyl acetate **7** as a test reaction (Table 2). The substrate was added to a solution

Table 2. Pd-catalyzed allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate **7** with sodium *para*-toluene sulfinate [a]



Entry	*Ligand*	*L/Pd*	*Yield (%)*	*Ee (%)* [b]
1	**3a**	1	95	69 (*S*)
2	**3a**	2	80	57 (*S*)
3	**3a**	1	72	10 (*S*) [c]
4	**3a**	2	70	11 (*S*) [d]
5	**3b**	1	80	80 (*S*)
6	**3b**	2	95	70 (*S*)
7	**3b**	1	23	20 (*S*) [e]
8	**3b**	2	25	30 (*S*) [f]
9	**3c**	1	51	77 (*S*)
10	**3c**	2	55	61 (*S*)
11	**3d**	1	93	2 (*S*)
12	**3d**	2	94	3 (*S*)
13	**3d**	1	90	5 (*S*) [g]
14	**3e**	1	25	57 (*S*)
15	**3e**	2	30	34 (*S*)
16	**3e**	1	26	68 (*S*) [h]
17	**3f**	1	80	55 (*S*)
18	**3f**	2	69	33 (*S*)
19	**3f**	**1**	**88**	**92 (*S*)** [i]
20	**3g**	1	25	60 (*R*)
21	**3g**	2	28	65 (*R*)

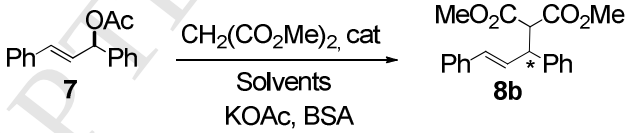
[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ in THF at room temperature for 48 h.
[b] Enantiomeric excess of **8a** was determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 4/1, 0.5 mL/min, 254 nm, *t*(*R*) = 16.3 min, *t*(*S*) = 18.5 min).
[c] Mixture of ligands **3a** and PPh_3 (0.005 mmol each).
[d] Mixture of ligands **3a** and PPh_3 (0.01 mmol each).
[e] Mixture of ligands **3b** and PPh_3 (0.005 mmol each).
[f] Mixture of ligands **3b** and PPh_3 (0.01 mmol each).
[g] With complex **6d** as the catalyst.
[h] With complex **6e** as the catalyst.
[i] With complex **6f** as the catalyst.

containing the palladium pre-catalyst $[Pd(allyl)Cl]_2$ and the appropriate ligand. Finally, the anhydrous sodium *para*-toluene sulfinate as the *S*-nucleophile was added to the reaction mixture. *P**-monodentate ligands **3a-c** demonstrated moderate to good levels of asymmetric induction (up to 69%, 80% and 77% *ee*, respectively, Table 2, entries 1, 5 and 9). The best asymmetric induction was achieved with L/Pd = 2 molar ratio in all cases. The hetero-combinations of PPh_3

and of the diamidophosphites **3a,b** behaved poorly in this reaction, providing sulfone (*S*)-**8a** with moderate or low yields and low enantiomeric excesses (see entries 3,4 and 7,8). The results obtained with *P,P**-bidentate phosphine-diamidophosphites **3d-g** demonstrated that the efficiency of these ligands differs dramatically. In particular, the palladium catalysts derived from **3d** showed excellent activity, but insignificant enantioselectivity (no more than 5% *ee*) regardless of the L/Pd molar ratio. At the same time, homologous ligand **3e** afforded a considerably greater asymmetric induction (up to 68% *ee*, Table 2, entries 11-16). Complex **6f** was the most efficient stereoselector, and (*S*)-**8a** was formed in 88% yield and 92% *ee* (Table 2, entry 19). Interestingly, the application of the hydroxy-phosphine **2f** (precursor of *P,P**-bidentate ligand **3f**) in the asymmetric sulfonylation process afforded **8a** in only 13% yield and 4% *ee* favoring the (*R*)-enantiomer; palladium complexes with phosphine-diamidophosphate **5** gave no conversion (see Supplementary data, Table S1, entries 1-4). Remarkably, compound **3g** induced reversal of the enantioselectivity in the synthesis of **8a**, compared to diastereomeric ligand **3f** (Table 2, entries 17-21).

In the next step, the novel diamidophosphites were studied in the traditional reaction between (*E*)-1,3-diphenylallyl acetate **7** and dimethyl malonate as the *C*-nucleophile. Dimethyl malonate was treated with **7** in the presence of $[Pd(allyl)Cl]_2$ and the corresponding ligand. As

Table 3. Pd-catalyzed allylic alkylation of (*E*)-1,3-diphenylallyl acetate **7** with dimethyl malonate [a]



Entry	*Ligand*	*L/Pd*	*Solvent*	*Conversion (%)*	*Ee (%)* [b]
1	**3a**	1	CH_2Cl_2	100	65 (*S*)
2	**3a**	2	CH_2Cl_2	100	73 (*S*)
3	**3a**	1	THF	78	71 (*S*)
4	**3a**	2	THF	90	70 (*S*)
5	**3a**	1	CH_2Cl_2	87	60 (*S*) [c]
6	**3a**	2	CH_2Cl_2	90	76 (*S*) [d]
7	**3a**	1	THF	0	- [c]
8	**3a**	2	THF	30	50 (*S*) [d]
9	**3b**	1	CH_2Cl_2	100	87 (*S*)
10	**3b**	2	CH_2Cl_2	100	86 (*S*)
11	**3b**	1	THF	75	82 (*S*)
12	**3b**	2	THF	100	92 (*S*)
13	**3b**	1	CH_2Cl_2	100	73 (*S*) [e]

14	**3b**	2	CH_2Cl_2	50	40 (*S*) [f]
15	**3b**	1	THF	30	75 (*S*) [e]
16	**3b**	2	THF	54	67 (*S*) [f]
17	**3c**	1	CH_2Cl_2	100	93 (*S*)
18	**3c**	2	CH_2Cl_2	100	90 (*S*)
19	**3c**	1	THF	87	87 (*S*)
20	**3c**	2	THF	70	84 (*S*)
21	**3d**	1	CH_2Cl_2	10	3 (*S*)
22	**3d**	2	CH_2Cl_2	16	2 (*S*)
23	**3d**	1	THF	0	-
24	**3d**	2	THF	0	-
25	**3d**	1	CH_2Cl_2	22	15 (*S*) [g]
26	**3d**	1	THF	0	- [g]
27	**3e**	1	CH_2Cl_2	100	47 (*S*)
28	**3e**	2	CH_2Cl_2	60	54 (*S*)
29	**3e**	1	THF	62	70 (*S*)
30	**3e**	2	THF	10	47 (*S*)
31	**3e**	1	CH_2Cl_2	71	50 (*S*) [h]
32	**3e**	1	THF	55	41 (*S*) [h]
33	**3f**	1	CH_2Cl_2	100	88 (*S*)
34	**3f**	**2**	**CH_2Cl_2**	**100**	**95 (*S*)**
35	**3f**	1	THF	40	34 (*S*)
36	**3f**	2	THF	35	35 (*S*)
37	**3f**	1	CH_2Cl_2	95	95 (*S*) [i]
38	**3f**	1	THF	46	80 (*S*) [i]
39	**3g**	1	CH_2Cl_2	80	33 (*R*)
40	**3g**	2	CH_2Cl_2	81	32 (*R*)
41	**3g**	1	THF	50	13 (*R*)
42	**3g**	2	THF	35	44 (*R*)

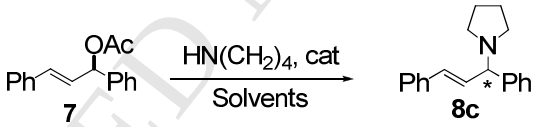
[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ at room temperature for 48 h (BSA, KOAc).
[b] The conversion of substrate **7** and enantiomeric excess of **8b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99/1, 0.3 mL/min, 254 nm, *t*(*R*) = 28.0 min, *t*(*S*) = 29.3 min).
[c] Mixture of ligands **3a** and PPh_3 (0.005 mmol each).
[d] Mixture of ligands **3a** and PPh_3 (0.01 mmol each).
[e] Mixture of ligands **3b** and PPh_3 (0.005 mmol each).
[f] Mixture of ligands **3b** and PPh_3 (0.01 mmol each).
[g] With complex **6d** as the catalyst.
[h] With complex **6e** as the catalyst.
[i] With complex **6f** as the catalyst.

seen from Table 3, both *P**-monodentate ligands **3b** and **3c** induced very good conversion and asymmetric induction (82-92% and 84-93% *ee* for (*S*)-**8b**, respectively, entries 9-12 and 17-20). The analogous palladium catalysts based on *P**-monodentate diamidophosphite **3a** with a naphthalen-2-ol fragment proved to be less efficient: no more than 73% *ee* was achieved in this case (Table 3, entries 1-4). Note that the 1:1 combination of **3a** and PPh_3 induced a peculiar outcome: the reaction rate and enantioselectivity were approximately the same in CH_2Cl_2, but

decreased in THF compared to **3a** alone (Table 3, entries 1-4 and 5-8). In addition, a decrease in the conversion and selectivity was observed for the hetero-combination **3b**/PPh_3 (compare entries 9-12 and 13-16). As in the case of the allylic sulfonylation, phosphine-diamidophosphite **3d** and phosphine-diamidophosphate **5** were completely inefficient (see Table 3, entries 21-26 and Supplementary data, Table S1, entries 9-12); compound **3e** showed moderate asymmetric induction again (*ee* varies from 41% to 70%, entries 27-32). Also, *P*,*P**-bidentate phosphine-diamidophosphite **3f** provided an excellent enantioselectivity (up to 95% *ee* for (*S*)-**8b**, Table 3, entry 34) and quantitative conversion. It is clear that CH_2Cl_2 is the solvent of choice (entries 33, 34 and 37). It is appropriate to mention here that under the same conditions hydroxy-phosphine **2f** (precursor of **3f**) gave malonate **8b** with a smaller conversion and asymmetric induction (53–57% *ee*) (Supplementary data, Table S1, entries 5, 6) as well as with opposite absolute configuration. Diastereomeric ligand **3g** afforded product (*R*)-**8b** with mediocre enantiomeric purity (13-44% *ee*) probably due to the mismatched combination of the (2*R*,5*S*)-stereocentres of the phosphabicyclic cores with the (S_a)-binaphthyl framework.

Table 4 shows the results obtained when pyrrolidine was used as the *N*-nucleophile.

Table 4. Pd-catalyzed allylic amination of (*E*)-1,3-diphenylallyl acetate **7** with pyrrolidine [a]



Entry	*Ligand*	*L/Pd*	*Solvent*	*Conversion (%)*	*Ee (%)* [b]
1	**3a**	1	CH_2Cl_2	100	62 (*R*)
2	**3a**	2	CH_2Cl_2	100	72 (*R*)
3	**3a**	1	THF	100	70 (*R*)
4	**3a**	2	THF	98	69 (*R*)
5	**3a**	1	CH_2Cl_2	100	22 (*R*) [c]
6	**3a**	2	CH_2Cl_2	100	50 (*R*) [d]
7	**3a**	1	THF	30	25 (*R*) [c]

8	**3a**	2	THF	40	35 (*R*) [d]
9	**3b**	1	CH_2Cl_2	100	80 (*R*)
10	**3b**	2	CH_2Cl_2	100	81 (*R*)
11	**3b**	1	THF	100	84 (*R*)
12	**3b**	2	THF	100	79 (*R*)
13	**3b**	1	CH_2Cl_2	63	68 (*R*) [e]
14	**3b**	2	CH_2Cl_2	65	43 (*R*) [f]
15	**3b**	1	THF	35	55 (*R*) [e]
16	**3b**	2	THF	32	57 (*R*) [f]
17	**3c**	1	CH_2Cl_2	100	87 (*R*)
18	**3c**	**2**	**CH_2Cl_2**	**100**	**89 (*R*)**
19	**3d**	1	CH_2Cl_2	55	35 (*R*)
20	**3d**	2	CH_2Cl_2	69	57 (*R*)
21	**3d**	1	THF	38	25 (*R*)
22	**3d**	2	THF	46	31 (*R*)
23	**3d**	1	CH_2Cl_2	26	25 (*R*) [g]
24	**3d**	1	THF	42	15 (*R*) [g]
25	**3e**	1	CH_2Cl_2	70	11 (*R*)
26	**3e**	2	CH_2Cl_2	80	9 (*R*)
27	**3e**	1	THF	55	5 (*R*)
28	**3e**	2	THF	70	13 (*R*)
29	**3e**	1	CH_2Cl_2	100	50 (*R*) [h]
30	**3e**	1	THF	99	60 (*R*) [h]
31	**3f**	1	CH_2Cl_2	100	65 (*R*)
32	**3f**	2	CH_2Cl_2	100	63 (*R*)
33	**3f**	1	THF	55	47 (*R*)
34	**3f**	2	THF	43	43 (*R*)
35	**3f**	1	CH_2Cl_2	100	44 (*R*) [i]
36	**3f**	1	THF	87	49 (*R*) [i]
37	**3g**	1	CH_2Cl_2	55	61 (*S*)
38	**3g**	2	CH_2Cl_2	56	55 (*S*)
39	**3g**	1	THF	89	38 (*S*)
40	**3g**	2	THF	54	43 (*S*)

[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ at room temperature for 48 h.
[c] The conversion of substrate **7** and enantiomeric excess of **8c** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*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).
[c] Mixture of ligands **3a** and PPh_3 (0.005 mmol each).
[d] Mixture of ligands **3a** and PPh_3 (0.01 mmol each).
[e] Mixture of ligands **3b** and PPh_3 (0.005 mmol each).
[f] Mixture of ligands **3b** and PPh_3 (0.01 mmol each).
[g] With complex **6d** as the catalyst.
[h] With complex **6e** as the catalyst.
[i] With complex **6f** as the catalyst.

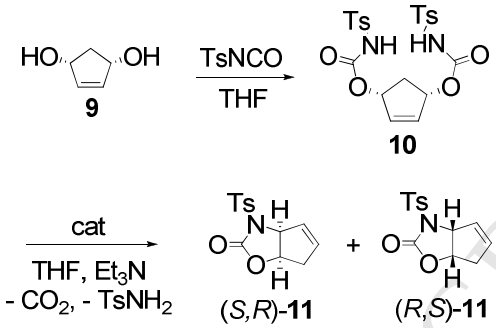
Catalytic performance in the Pd-catalyzed allylic amination of **7** with participation of *P**-monodentate ligands **3a-c** and pyrrolidine followed the same trend as for the allylic sulfonylation and alkylation of **7**. Moderate to good enantioselectivity was observed when employing diamidophosphites **3a-c** (up to 72%, 84% and 89% *ee*, respectively, Table 4, entries 2, 11 and

18). The resulting product **8c** proved to have the same (*R*)-configuration in all cases. In general, both the conversion of **7** and asymmetric induction were poorly sensitive to the L/Pd molar ratio and solvent, but for ligand **3c** CH_2Cl_2 is undoubtedly preferable. Again, the catalysts arising from the hetero-combinations of **3a**/PPh_3 and **3b**/PPh_3 were by far less active and stereoselective than with only **3a** or **3b** (entries 5-8 and 13-16). Ligand **5** with phosphine and diamidophosphate moieties exhibited very low conversion and enantioselectivity (Supplementary data, Table S1, entries 17-20). As for the *P,P**-bidentate phosphine-diamidophosphites **3d-g**, all of them gave amine (*R*)-**8c** ((*S*)-**8c** in the case of **3g**) with similar enantiomeric purity (57-65% *ee*) and modest to quantitative conversion. Although the L/Pd molar ratio and solvent do not have a profound influence on the efficiency of chiral transfer, for **3f,g** the highest results were obtained in CH_2Cl_2. As usual, ligand **3f** showed higher activity and enantioselectivity than its precursor **2f** (see Supplementary data, Table S1 and Table 4).

To understand, why the ”mixed-ligand approach”» was unsuccessful, we decided to study the Pd-π-allyl complexes which contain ligand **3b** or **3b** and PPh_3, as these are the key intermediates in the allylic substitution reactions studied.[3,54] The formation of the palladium complexes was investigated by adding **3b** (2 or 4 equiv.) or the **3b**/PPh_3 mixture (2 equiv. each) to a solution of $[Pd(allyl)Cl]_2$ (1 equiv.) in CD_2Cl_2. Complexation studies were then performed by means of ^{31}P NMR spectroscopy. Signals of both the *exo*- and *end*o-isomers of the neutral [Pd(allyl)(**3b**)Cl] complex were visible in the ^{31}P NMR spectrum of the resulting solution based on homo-combination at molar ratio **3b**/Pd = 1 (δ_P 121.9 and 121.5 ppm, 47% and 53%, respectively). When homo-combination at molar ratio **3b**/Pd = 2 was employed, two peaks (δ_P 117.9 and 116.8 ppm, 4% and 96%, respectively) of the cationic two-ligated specie $[Pd(allyl)(\mathbf{3b})_2]Cl$ was observed, also due to the presence of both isomers.[20] The ^{31}P NMR spectrum of the reaction mixture containing hetero-combination **3b**/PPh_3 showed a set of intensive singlets δ_P 104.2, 31.8, 25.2, 24.1, 21.3 and a minor AX system (δ_P 98.3 ppm, d and 38.7 ppm, d, $J_{P,P*}$ 30.9 Hz, 4%) which correspond, probably, to the expected hetero-complex [Pd(allyl)(PPh_3)(**3b**)]Cl. Thus, no selective formation of the hetero-complex was observed. It is, perhaps, one of the reasons for the rather low efficiency of the *P**-monodentate diamidophosphites/PPh_3 hetero-combinations in Pd-catalyzed asymmetric allylation. Indeed, the electronic disparity of the two different phosphorus ligands in the first coordination sphere of palladium is able to impact positively on the stereoselectivity of the reaction. In fact, the nucleophilic attack is expected to proceed preferentially *trans* to the ligand with the higher *trans*-influence, because of the higher electrophilicity of the corresponding π-allyl terminus.[46]

We evaluated the small *P**-chiral diamidophosphite ligand library in the Pd-catalyzed desymmetrization of *N,N'*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate **10** (Table 5). The

Table 5. Pd-catalyzed desymmetrization of *N*,*N'*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate **10** [a]



Entry	*Ligand*	*L/Pd*	*Yield (%)*	*Ee (%)* [b,c]
1	**3b**	1	49	12 (II)
2	**3b**	2	56	23 (II)
3	**3c**	1	39	15 (II)
4	**3c**	2	43	27 (II)
5	**3d**	1	76	30 (II)
6	**3d**	2	72	28 (II)
7	**3e**	1	59	12 (II)
8	**3e**	2	71	10 (II)
9	**3f**	1	87	45 (I)
10	**3f**	2	92	40 (I)
11	**3g**	**1**	**89**	**63 (II)**
12	**3g**	2	94	50 (II)

[a] All reactions were carried out with 5 mol% of $[Pd_2(dba)_3]\cdot CHCl_3$ in THF at 35 °C for 24 h.
[b] The enantiomeric excess of **11** was determined by HPLC (Kromasil 5-CelluCoat, C_6H_{14}/*i*-PrOH = 9/1, 2 mL/min, 219 nm, *t*(I) = 13 min, *t*(II) = 17 min).
[c] The absolute configuration of the product **11** was not assigned.

reaction was performed in THF in the presence of $[Pd_2(dba)_3]\cdot CHCl_3$ as the pre-catalyst. The stereochemistry of this transformation revealed some remarkable trends. In contrast to the Pd-catalyzed asymmetric allylic substitution of (*E*)-1,3-diphenylallyl acetate **7**, *P**-monodentate ligands **3b,c** provided poor asymmetric induction (12-27% *ee*, Table 5, entries 1-4). Similarly, with participation of the *P,P**-bidentate phosphine-diamidophosphites **3d,e** low enantioselectivity (no more than 30% *ee*, entries 5-8) was observed irrespective of the L/Rh molar ratio. The use of both diastereomers **3f,g** of the *P,P**-ligand with a binaphthyl backbone made it possible to obtain product **11** in good yield and the opposite absolute configuration (Table 5, entries 9-12). Unlike the allylation of **7**, in the Pd-catalyzed desymmetrization of

substrate **10**, compound **3g** afforded the resulting product **11** with a higher enantiomeric purity than diastereomeric ligand **3f** (up to 63% and 45% *ee*, respectively).

3. Conclusion

To sum up all of the above-considered data, the following conclusions can be drawn: i) we have designed and synthesized the first representatives of a novel class of C_1-symmetric *P,P*-bidentate ligands. These ligands have three main advantages: the diamidophosphite nature of their phosphite-type moieties, the *P**-chirogenic phosphorus atoms and the 1,3,2-diazaphospholidine rings with balanced electronic characteristics; ii) some new *P**-monodentate diamidophosphites **3a-c** with naphthyl or long-chain substituents have been successfully prepared. These ligands demonstrated moderate to high levels of asymmetric induction in Pd-catalyzed asymmetric allylation, but low enantioselectivity in Pd-catalyzed desymmetrization; iii) in accordance with the literature precedent [46] in Pd-catalyzed allylic substitution reactions, the hetero-combination of *P**-monodentate diamidophosphite/PPh_3, as a rule, induced a lower reaction rate and a diminished enantiomeric excess compared to the homo-combination of the corresponding diamidophosphite; iv) homologous *P,P**-bidentate phosphine-diamidophosphites **3d,e** with achiral phosphine moieties showed moderate-to-poor enantioselectivity, their catalytic performance is highly affected by the nature of the nucleophile. At the same time, diastereomeric *P,P**-bidentate phosphine-diamidophosphites **3f,g** are the most promising asymmetric inductors. In asymmetric Pd-catalyzed allylic substitution, **3f,g** and **3a-c** are very efficient and complementary groups of ligands, whereas in the Pd-catalyzed desymmetrization **3f,g** are substantially better stereoselectors than **3a-c**. As opposed to **3f**, its precursor **2f** and analog **5** with a P=O fragment provided much lower activity and enantioselectivity. Thus, the binaphthyl backbone in the efficient *P,P**-bidentate ligands **3f,g** forms an axially chiral phosphine basis and an additional *P**-donor atom and/or C*-stereocenters in the diamidophosphite species should be present in their structures for achieving high catalytic enantioselectivity.

Remarkably, in the Pd-mediated asymmetric allylic alkylation of (*E*)-1,3-diphenylallyl acetate **7** with dimethyl malonate, the best of the phosphine-phosphites and phosphine-phosphoramidites tested to date gave maximum *ee* values of 83% and 90%, respectively.[14,27,53] Hence, the enantioselectivity produced by phosphine-diamidophosphite **3f** (95% *ee*) is the best so far achieved in this reaction using unsymmetrical *P,P*-bidentate ligands with phosphine and phosphite-type moieties. As a whole, diastereomeric stereoselectors **3f,g** hold a noteworthy position among such ligands, and further studies to explore the scope of **3f,g** in other asymmetric catalytic reactions are currently in progress.

4. Experimental section

4.1. General comments

^{31}P, ^{13}C and ^{1}H NMR spectra were recorded on a Bruker MSL-300 (75.5 MHz for ^{13}C), a Bruker AMX 400 (162.0 MHz for ^{31}P, 100.6 MHz for ^{13}C and 400.13 MHz for ^{1}H) and a Bruker Avance III 600 (242.9 MHz for ^{31}P, 150.9 MHz for ^{13}C and 600.13 MHz for ^{1}H) instruments. Complete assignment of all the resonances in the ^{1}H and ^{13}C NMR spectra was achieved by the use of APT and DEPT techniques (together with COSY and HSQC techniques for compounds **3a**, **3e-g** and **5**) and published data. [18,20,30,31,49] Chemical shifts (ppm) were given relative to Me_4Si (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P NMR). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet); coupling constants ^{n}J in Hertz (Hz) integration, ”n” values are reported in the case of their unambiguous determination. IR spectra were recorded on a Specord M80 instrument. Mass spectra were recorded on a Varian MAT 311 spectrometer (EI) and a Bruker Daltonics Ultraflex spectrometer (MALDI TOF/TOF). 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.

All manipulations 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 benzophenone ketyl before use; dichloromethane was distilled from NaH. Triethylamine and pyrrolidine were distilled over KOH and then over a small amount of $LiAlH_4$ before use. Thin-layer chromatography was performed on E. Merck pre-coated silica gel 60 F254 and Macherey-Nagel Alugram Alox N/UV_{254} plates. Column chromatography was performed using silica gel MN Kieselgel 60 (230 – 400 mesh) and MN-Aluminum oxide, basic, Brockmann Activity 1. Phosphorylating reagents, (5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane **1**, (2*S*,5*S*)-2-chloro-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane-2-oxide **4** and ligands **3a-g**, **5** were prepared analogously to known procedures.[20,48,55,56] (2-(Diphenylphosphino)phenyl)methanol **2e** was prepared by the $NaBH_4$ reduction of 2-(diphenylphosphino)benzaldehyde.[57] (*R*)-2’-(Diphenylphosphino)-1,1’-binaphthyl-2-ol **2f** and (*S*)-2’-(diphenylphosphino)-1,1’-binaphthyl-2-ol **2g** were prepared in four steps, starting from the (*R*)- and (*S*)-BINOL, respectively.[58] The $[Pd(allyl)Cl]_2$, starting substrate **7**, and $[Pd_2(dba)_3]\cdot CHCl_3$ were obtained as published.[59,60] Pd-catalyzed reactions: allylic sulfonylation of (*E*)-1,3-diphenylallyl acetate **7** with sodium *para*-toluene sulfinate, alkylation

with dimethyl malonate, amination with pyrrolidine and desymmetrization of *N,N'*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate **10** were performed according to the appropriate procedures.[20,61, 23]

Naphthalen-2-ol **2a**, decan-1-ol **2b**, hexadecan-1-ol **2c**, 2-(diphenylphosphino)phenol **2d**, 2-(diphenylphosphino)benzaldehyde, (*R*)- and (*S*)-BINOL, DMAP (4-dimethylamino-pyridine), triphenylphosphine, sodium *para*-toluene sulfinate, dimethyl malonate, BSA (*N,O*-bis(trimethylsilyl) acetamide), *meso*-cyclopent-4-ene-1,3-diol **9** and tosyl isocyanate were purchased from Aldrich and Acros Organics and used without further purification.

4.2. General procedure for the preparation of ligands 3a-g and 5

A solution of the appropriate alcohol **2a-g** (2 mmol) in THF (for **2a-c** and **2f** in the case of ligand **5** synthesis) or toluene (for **2d-g**) (5 mL) was added dropwise to a vigorously stirred solution of the appropriate phosphorylating reagent **1** or **4** (2 mmol), Et_3N (0.5 mL, 3.6 mmol), and DMAP (0.025 g, 0.2 mmol) in the same solvent (10 mL). The mixture was then heated to boiling point, refluxed for 30 min (1 h 30 min in the case of ligand **5** synthesis), and cooled to 20 °C. The resulting suspension was filtered through a short plug of aluminum oxide, the column was washed twice with THF or toluene (6 mL), and the solvent evaporated under reduced pressure (40 Torr). The product was dried in vacuum (1 Torr) for 1h (16 h of further high vacuum (10^{-3} Torr) drying is necessary for the preparation of analytically pure samples of **3e-g**). Ligand **5** was additionally purified by column chromatography on aluminum oxide (CH_2Cl_2/hexane, 3:1).

*4.2.1. (2R,5S)-2-(Naphthalene-2-yloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**3a**).* Yield: 0.60 g (86%) as colorless oil. IR: ν_{max} ($CHCl_3$) 3038, 3021, 2923, 2851, 1464, 1432, 1078, 835, 740 cm^{-1}. ^1H NMR (600.13 MHz, $CDCl_3$, 24 °C): δ = 1.50-1.56 (m, 1 H, C(6)H), 1.83-1.90 (m, 2 H, C(7)H_2), 1.91-1.97 (m, 1 H, C(6)H), 3.13-3.16 (m, 1 H, C(4)H), 3.35-3.42 (m, 2 H, C(4)H and C(8)H), 3.64-3.67 (m, 1 H, C(5)H), 3.70-3.75 (m, 1 H, C(8)H), 6.96 (t, ^3J = 7.2 Hz, 1 H, CH_{Ph}), 7.12-7.16 (m, 3 H, CH_{Ar} and 2 CH_{Ph}), 7.31-7.36 (m, 3 H, CH_{Ar} and 2 CH_{Ph}), 7.38-7.41 (m, 1 H, CH_{Ar}), 7.43-7.46 (m, 1 H, CH_{Ar}), 7.69 (d, ^3J = 7.8 Hz, 1 H, CH_{Ar}), 7.72 (d, ^3J = 8.9 Hz, 1 H, CH_{Ar}), 7.80 (d, ^3J = 8.4 Hz, 1 H, CH_{Ar}). ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 26.4 (d, ^3J = 4.4 Hz, C(7)), 32.0 (s, C(6)), 48.0 (d, ^2J = 35.6 Hz, C(8)), 53.8 (d, ^2J = 7.9 Hz, C(4)), 62.9 (d, ^2J = 8.8 Hz, C(5)), 115.4 (d, ^3J = 12.8 Hz, CH_{Ph}), 117.7 (d, ^3J = 6.3 Hz, CH_{Naphth}), 119.4 (s, CH_{Ph}), 122.9 (d, ^3J = 3.5 Hz, CH_{Naphth}), 124.4 (s, CH_{Naphth}), 126.0 (s, CH_{Naphth}), 127.1 (s, CH_{Naphth}), 127.6 (s, CH_{Naphth}), 128.8 (s, CH_{Naphth}), 129.3 (s, CH_{Ph}), 130.2

(s, C_{Naphth}), 134.3 (s, C_{Naphth}), 145.3 (d, ^2J = 15.2 Hz, C_{Ph}), 151.6 (d, ^2J = 4.8 Hz, C_{Naphth}) (major epimer). MS (MALDI TOF/TOF): *m/z* (%) = 367 (41) $[M + H_2O + H]^+$, 177 (100) $[PhNHCH_2CH(CH_2)_3NH + H]^+$. Anal. Calcd for $C_{21}H_{21}N_2OP$: C, 72.40; H, 6.08; N, 8.04. Found: C, 72.67; H, 6.01; N, 8.16.

*4.2.2. (2R,5S)-2-(Decyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**3b**).* Yield: 0.57 g (79%) as colorless viscous oil. IR: ν_{max} ($CHCl_3$) 3033, 2953, 2920, 2870, 2861, 1441, 1378, 1065, 745 cm^{-1}. ^1H NMR (400.13 MHz , $CDCl_3$, 27 °C): δ = 0.87 (t, ^3J = 6.8 Hz, 3 H, CH_3), 1.17-1.32 (br. M, 14 H, $(CH_2)_7$), 1.46-1.53 (m, 2 H, CH_2); 1.60-1.66 (m, 1 H), 1.70-1.76 (m, 1 H), 1.79-1.85 (m, 1 H), 1.98-2.05 (m, 1 H) ($C(6)H_2$, $C(7)H_2$); 3.12-3.21 (m, 2 H, CH_2O); 3.48-3.60 (m, 2 H), 3.63-3.69 (m, 1 H), 3.71-3.76 (m, 1 H), 4.10-4.16 (m, 1 H) ($C(4)H_2$, C(5)H, $C(8)H_2$); 6.82 (t, ^3J = 7.2 Hz, 1 H, CH_{Ph}), 7.01 (br. d, ^3J = 7.4 Hz, 2 H, CH_{Ph}), 7.22 (t, ^3J = 7.6 Hz, 2 H, CH_{Ph}). ^{13}C NMR (75.5 MHz, $CDCl_3$, 26 °C): δ = 14.1 (s, CH_3), 22.7 (s, CH_2), 26.1 (s, CH_2), 26.2 (d, ^3J = 3.8 Hz, C(7)), 29.3 (s, CH_2), 29.4 (s, CH_2), 29.5 (s, CH_2), 29.6 (s, CH_2), 30.9 (d, ^3J = 3.8 Hz, CH_2), 31.9 (s, C(6)), 32.1 (s, CH_2), 48.8 (d, ^2J = 37.0 Hz, C(8)), 54.9 (d, ^2J = 6.8 Hz, C(4)), 62.3 (d, ^2J = 3.8 Hz, CH_2O), 63.3 (d, ^2J = 9.1 Hz, C(5)), 114.8 (d, ^3J = 12.1 Hz, CH_{Ph}), 118.7 (s, CH_{Ph}), 129.1 (s, CH_{Ph}), 145.9 (d, ^2J = 15.8 Hz, C_{Ph}). MS (EI, 70 eV): *m/z* (%) = 363 (16) $[M + H]^+$, 362 (37) $[M]^+$, 222 (91) $[M - C_{10}H_{20}]^+$, 205 (100) $[M - OC_{10}H_{21}]^+$. Anal. Calcd for $C_{21}H_{35}N_2OP$: C, 69.58; H, 9.73; N, 7.73. Found: C, 69.87; H, 9.92; N, 7.68.

*4.2.3. (2R,5S)-2-(Hexadecyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**3c**).* Yield: 0.66 g (74%) as milky-white waxy solid. IR: ν_{max} ($CHCl_3$) 3030, 2950, 2924, 2869, 2861, 1443, 1372, 1062, 745 cm^{-1}. ^1H NMR (400.13 MHz , $CDCl_3$, 25 °C): δ = 0.88 (t, ^3J = 6.4 Hz, 3 H, CH_3), 1.19-1.33 (br. M, 26 H, $(CH_2)_{13}$), 1.45-1.53 (m, 2 H, CH_2); 1.56-1.63 (m, 1 H), 1.70-1.76 (m, 1 H), 1.80-1.86 (m, 1 H), 1.98-2.05 (m, 1 H) ($C(6)H_2$, $C(7)H_2$); 3.13-3.22 (m, 2 H, CH_2O); 3.49-3.60 (m, 2 H), 3.64-3.69 (m, 1 H), 3.70-3.75 (m, 1 H), 4.10-4.16 (m, 1 H) ($C(4)H_2$, C(5)H, $C(8)H_2$); 6.81 (t, ^3J = 7.2 Hz, 1 H, CH_{Ph}), 7.0 (br. D, ^3J = 7.5 Hz, 2 H, CH_{Ph}), 7.22 (t, ^3J = 7.6 Hz, 2 H, CH_{Ph}). ^{13}C NMR (100.6 MHz, $CDCl_3$, 27 °C): δ = 14.0 (s, CH_3), 22.6 (s, CH_2), 25.9 (s, CH_2), 26.0 (d, ^3J = 3.8 Hz, C(7)), 29.1 (s, CH_2), 29.2 (s, CH_2), 29.4 (s, CH_2), 29.5 (s, CH_2), 29.6 (br. S, $(CH_2)_6$), 30.8 (d, ^3J = 3.3 Hz, CH_2), 31.8 (s, C(6)), 32.0 (s, CH_2), 48.6 (d, ^2J = 38.4 Hz, C(8)), 54.7 (d, ^2J = 7.1 Hz, C(4)), 62.2 (d, ^2J = 3.0 Hz, CH_2O), 63.1 (d, ^2J = 8.7 Hz, C(5)), 114.6 (d, ^3J = 11.7 Hz, CH_{Ph}), 118.6 (s, CH_{Ph}), 128.9 (s, CH_{Ph}), 145.7 (d, ^2J = 15.5 Hz, C_{Ph}). MS (MALDI TOF/TOF): *m/z* (%) = 465 (28) $[M + H_2O + H]^+$, 229 (100) $[M - OC_{16}H_{32} + Na]^+$, 177 (27) $[PhNHCH_2CH(CH_2)_3NH + H]^+$. Anal. Calcd for $C_{27}H_{47}N_2OP$: C, 72.60; H, 10.61; N, 6.27. Found: C, 72.90; H, 10.72; N, 6.45.

*4.2.4. (2R,5S)-2-(2-(Diphenylphosphino)phenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**3d**).* Yield: 0.82 g (85%) as colorless viscous oil. IR: ν_{max} ($CHCl_3$) 3053, 3031, 2922, 2854, 1460, 1440, 1077, 740 cm^{-1}. ^1H NMR (400.13 MHz , $CDCl_3$, 25 °C): δ = 1.45-1.52 (m, 1 H), 1.66-1.74 (m, 2 H), 1.78-1.85 (m, 1 H), ($C(6)H_2$, $C(7)H_2$); 2.98-3.11 (m, 2 H), 3.40-3.50 (m, 2 H), 3.60-3.66 (m, 1 H), ($C(4)H_2$, C(5)H, $C(8)H_2$); 6.85 (t, ^3J = 7.2 Hz, 1 H, CH_{Ar}), 6.93 (t, ^3J = 7.4 Hz, 1 H, CH_{Ar}), 6.96-7.04 (m, 3 H, CH_{Ar}), 7.19-7.37 (m, 14 H, CH_{Ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 26.3 (d, ^3J = 4.5 Hz, C(7)), 31.8 (s, C(6)), 48.0 (d, ^2J = 33.6 Hz, C(8)), 53.7 (d, ^2J = 6.8 Hz, C(4)), 62.9 (d, ^2J = 9.1 Hz, C(5)), 115.6 (d, ^3J = 13.6 Hz, CH_{PhN}), 119.3 (s, CH_{PhN}), 120.2 (dd, *J* = 10.2 Hz, *J* = 1.9 Hz, CH_{Ar}), 123.0 (s, CH_{Ar}), 128.1 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 129.1 (s, CH_{PhN}), 130.1 (s, CH_{Ar}), 133.6 (d, ^2J = 20.3 Hz, CH_{Ar}), 133.7 (d, ^2J = 20.4 Hz, CH_{Ar}), 134.3 (s, CH_{Ar}), 137.5 (d, ^1J = 12.6 Hz, C_{Ar}), 137.6 (d, ^1J = 12.7 Hz, C_{Ar}), 145.2 (d, ^2J = 15.4 Hz, C_{PhN}), 157.1 (dd, ^2J = 19.3 Hz, ^2J = 2.2 Hz, C_{Ar}) (major epimer) and 25.4 (d, ^3J = 3.8 Hz, C(7)), 28.4 (s, C(6)), 43.8 (d, ^2J = 4.5 Hz, C(8)), 51.5 (d, ^2J = 6.0 Hz, C(4)), 65.8 (d, ^2J = 11.3 Hz, C(5)), 117.3 (d, ^3J = 12.8 Hz, CH_{PhN}), 118.2 (s, CH_{PhN}), 120.7 (br. S, CH_{Ar}), 122.2 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 128.5 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 128.8 (s, CH_{PhN}), 129.9 (s, CH_{Ar}), 133.4 (d, ^2J = 19.4 Hz, CH_{Ar}), 133.5 (d, ^2J = 19.1 Hz, CH_{Ar}), 134.1 (s, CH_{Ar}), 136.4 (d, ^1J = 11.5 Hz, C_{Ar}), 136.2 (d, ^1J = 11.8 Hz, C_{Ar}), 146.5 (d, ^2J = 14.9 Hz, C_{PhN}), 158.5 (dd, ^2J = 18.7 Hz, ^2J = 2.3 Hz, C_{Ar}) (minor epimer). MS (MALDI TOF/TOF): *m/z* (%) = 501 (26) $[M + H_2O + H]^+$, 279 (100) $[Ph_2PC_6H_4OH + H]^+$, 177 (39) $[PhNHCH_2CH(CH_2)_3NH + H]^+$. Anal. Calcd for $C_{29}H_{28}N_2OP_2$: C, 72.19; H, 5.85; N, 5.81. Found: C, 72.32; H, 5.90; N, 5.65.

*4.2.5. (2R,5S)-2-(2-(Diphenylphosphino)phenylmethoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**3e**).* Yield: 0.83 g (84%) as colorless viscous oil. IR: ν_{max} ($CHCl_3$) 3055, 3029, 2922, 2850, 1460, 1443, 1065, 742 cm^{-1}. ^1H NMR (600.13 MHz , $CDCl_3$, 25 °C): δ = 1.54-1.60 (m, 1 H, C(6)H), 1.71-1.82 (m, 2 H, $C(7)H_2$), 1.94-2.0 (m, 1 H, C(6)H), 3.05-3.14 (m, 2 H, C(4)H and C(8)H), 3.50-3.57 (m, 2 H, C(4)H and C(8)H), 3.88-3.92 (m, 1 H, C(5)H), 4.72 (dd, $^2J_{H,H}$ = 13.4 Hz, $^3J_{H,P}$ = 5.4 Hz, 1 H, CHO), 4.99 (ddd, $^2J_{H,H}$ = 13.4 Hz, $^3J_{H,P}$ = 6.0 Hz, $^4J_{H,P}$ = 2.1 Hz, 1 H, CHO), 6.82 (t, ^3J = 6.4 Hz, 1 H, CH_{Ar}), 6.85 (t, ^3J = 7.2 Hz, 1 H, CH_{PhN}), 7.0 (d, ^3J = 7.4 Hz, 2 H, CH_{PhN}), 7.15 (t, ^3J = 7.2 Hz, 1 H, CH_{Ar}), 7.21-7.26 (m, 3 H, CH_{Ar} and 2 CH_{PhN}), 7.28-7.39 (m, 10 H, CH_{Ar}), 7.6-7.62 (m, 1 H, CH_{Ar}). ^{13}C NMR (150.9 MHz, $CDCl_3$, 23 °C): δ = 26.3 (d, ^3J = 4.1 Hz, C(7)), 32.1 (s, C(6)), 48.4 (d, ^2J = 37.6 Hz, C(8)), 54.9 (d, ^2J = 7.6 Hz, C(4)), 61.8 (dd, ^2J = 27.5 Hz, ^3J = 4.8 Hz, CH_2O), 63.2 (d, ^2J = 8.8 Hz, C(5)), 114.9 (d, ^3J = 12.2 Hz, CH_{PhN}), 118.8 (s, CH_{PhN}), 127.0 (d, *J* = 5.3 Hz, CH_{Ar}), 127.1 (s, CH_{Ar}), 128.6 (d, *J* = 6.9

Hz, CH_{Ar}), 128.7 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 128.9 (s, CH_{Ar}), 129.0 (s, CH_{PhN}), 132.6 (s, CH_{Ar}), 133.9 (d, ^2J = 19.8 Hz, CH_{Ar}), 134.1 (d, ^2J = 19.6 Hz, CH_{Ar}), 136.1 (d, ^1J = 9.8 Hz, C_{Ar}), 136.2 (d, ^1J = 10.1 Hz, C_{Ar}), 143.0 (dd, ^2J = 21.7 Hz, ^3J = 2.6 Hz, C_{Ar}), 145.7 (d, ^2J = 16.3 Hz, C_{PhN}). MS (MALDI TOF/TOF): *m/z* (%) = 535 (100) $[M + K]^+$, 497 (17) $[M + H]^+$. Anal. Calcd for $C_{30}H_{30}N_2OP_2$: C, 72.57; H, 6.09; N, 5.64. Found: C, 72.85; H, 6.16; N, 5.44.

*4.2.6. (2R,5S,R_a)-2-[1-(2-(Diphenylphosphino)naphthalene-1-yl)naphthalene-2-yloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**3f**)*. Yield: 1.01 g (77%) as white solid, m. p. 98-100 °C. IR: ν_{max} ($CHCl_3$) 3050, 3036, 2920, 2853, 1464, 1448, 1080, 833, 737 cm^{-1}. ^1H NMR (600.13 MHz, $CDCl_3$, 24 °C): δ = 1.51-1.57 (m, 1 H, C(6)H), 1.59-1.65 (m, 1 H, C(7)H), 1.67-1.72 (m, 1 H, C(7)H), 1.85-1.91 (m, 1 H, C(6)H), 2.55-2.61 (m, 1 H, C(8)H), 2.99-3.03 (m, 1 H, C(4)H), 3.19-3.25 (m, 1 H, C(8)H), 3.39 (t, ^3J = 8.1 Hz, 1 H, C(4)H), 3.79-3.84 (m, 1 H, C(5)H), 6.45 (d, ^3J = 7.8 Hz, 2 H, CH_{PhN}), 6.76 (t, ^3J = 7.5 Hz, 1 H, CH_{PhN}), 6.92 (d, ^3J = 8.4 Hz, 1 H, CH_{Ar}), 6.97 (t, ^3J = 7.8 Hz, 2 H, CH_{PhN}), 7.07-7.11 (m, 3 H, CH_{Ar}), 7.13-7.17 (m, 2 H, CH_{Ar}), 7.18-7.25 (m, 5 H, CH_{Ar}), 7.29-7.34 (m, 4 H, CH_{Ar}), 7.42 (dd, ^3J = 8.7 Hz, ^3J = 2.7 Hz, 1 H, CH_{Ar}), 7.48 (d, ^3J = 8.4 Hz, 1 H, CH_{Ar}), 7.52 (t, ^3J = 7.8 Hz, 1 H, CH_{Ar}), 7.88 (t, ^3J = 7.8 Hz, 2 H, CH_{Ar}), 7.91-7.94 (m, 2 H, CH_{Ar}). ^{13}C NMR (150.9 MHz, $CDCl_3$, 24 °C): δ = 26.0 (d, ^3J = 4.1 Hz, C(7)), 31.4 (s, C(6)), 47.6 (d, ^2J = 34.7 Hz, C(8)), 53.8 (d, ^2J = 7.2 Hz, C(4)), 62.4 (d, ^2J = 8.5 Hz, C(5)), 114.8 (d, ^3J = 12.7 Hz, CH_{PhN}), 118.8 (s, CH_{PhN}), 121.8 (d, J = 8.5 Hz, CH_{Ar}), 124.0 (s, CH_{Ar}), 125.9 (d, J = 7.4 Hz, CH_{Ar}), 126.1 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 127.6 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 128.1 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 128.9 (s, CH_{PhN}), 129.0 (s, CH_{Ar}), 129.2 (s, CH_{Ar}), 129.9 (s, C_{Ar}), 130.7 (s, CH_{Ar}), 133.1 (d, ^2J = 18.0 Hz, CH_{Ar}), 133.3 (d, J = 8.0 Hz, C_{Ar}), 133.5 (d, ^2J = 20.2 Hz, CH_{Ar}), 133.7 (s, C_{Ar}), 134.3 (s, C_{Ar}), 136.3 (d, J = 9.8 Hz, C_{Ar}), 138.3 (d, J = 14.0 Hz, C_{Ar}), 138.4 (d, J = 13.3 Hz, C_{Ar}), 142.2 (d, J = 35.5 Hz, C_{Ar}), 144.8 (d, ^2J = 16.2 Hz, C_{PhN}), 150.0 (s, C_{Ar}) (major epimer) and 27.9 (s, C(7)), 31.4 (s, C(6)), 42.4 (d, ^2J = 4.2 Hz, C(8)), 51.3 (d, ^2J = 6.0 Hz, C(4)), 65.3 (d, ^2J = 10.9 Hz, C(5)), 117.7 (d, ^3J = 12.1 Hz, CH_{PhN}), 120.6 (s, CH_{PhN}), 121.5 (d, J = 13.3 Hz, CH_{Ar}), 123.7 (s, CH_{Ar}), 125.3 (s, CH_{Ar}), 125.7 (s, CH_{Ar}), 125.8 (d, J = 5.3 Hz, CH_{Ar}), 127.0 (s, CH_{Ar}), 127.1 (s, CH_{Ar}), 128.1 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 129.3 (s, CH_{Ar}), 129.5 (s, C_{Ar}), 129.6 (s, CH_{PhN}), 130.3 (s, CH_{Ar}), 133.5 (d, ^2J = 19.8 Hz, CH_{Ar}), 133.6 (d, ^2J = 20.1 Hz, CH_{Ar}), 133.8 (s, C_{Ar}), 134.1 (s, C_{Ar}), 136.2 (d, J = 11.0 Hz, C_{Ar}), 137.7 (d, J = 13.0 Hz, C_{Ar}), 138.5 (d, J = 14.2 Hz, C_{Ar}), 142.5 (d, J = 35.1 Hz, C_{Ar}), 145.1 (d, ^2J = 13.7 Hz, C_{PhN}), 150.0 (s, C_{Ar}) (minor epimer). MS (MALDI TOF/TOF): *m/z* (%) = 677 (5) $[M + H_2O + H]^+$, 455 (15) $[(C_{10}H_6OH)C_{10}H_6PPh_2 + H]^+$, 437 (100) $[(C_{10}H_6)C_{10}H_6PPh_2]^+$, 229 (42) [M –

$(C_{10}H_5O)C_{10}H_6PPh_2 + Na]^+$. Anal. Calcd for $C_{43}H_{36}N_2OP_2$: C, 78.41; H, 5.51; N, 4.25. Found: C, 78.72; H, 5.26; N, 4.17.

*4.2.7. (2R,5S,S_a)-2-[1-(2-(Diphenylphosphino)naphthalene-1-yl)naphthalene-2-yloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**3g**).* Yield: 1.05 g (80%) as white solid, m. p. 104-106 °C. IR: ν_{max} ($CHCl_3$) 3050, 3037, 2922, 2853, 1464, 1447, 1078, 833, 738 cm^{-1}. ^1H NMR (600.13 MHz, $CDCl_3$, 24 °C): δ = 1.27-1.33 (m, 1 H, C(6)H), 1.37-1.49 (m, 3 H, C(6)H and C(7)H_2), 2.32-2.38 (m, 1 H, C(8)H), 2.84-2.95 (m, 3 H, C(4)H, C(5)H and C(8)H), 3.21 (t, ^3J = 7.8 Hz, 1 H, C(4)H), 6.81-6.86 (m, 3 H, CH_{PhN}), 6.89 (d, ^3J = 8.4 Hz, 1 H, CH_{Ar}), 7.02 (t, ^3J = 7.4 Hz, 1 H, CH_{Ar}), 7.06-7.19 (m, 9 H, 7 CH_{Ar} and 2 CH_{PhN}), 7.29 (t, ^3J = 8.1 Hz, 3 H, CH_{Ar}), 7.34 (t, ^3J = 7.8 Hz, 3 H, CH_{Ar}), 7.44-7.49 (m, 2 H, CH_{Ar}), 7.58 (d, ^3J = 8.4 Hz, 1 H, CH_{Ar}), 7.84-7.88 (m, 3 H, CH_{Ar}), 7.98 (d, ^3J = 8.4 Hz, 1 H, CH_{Ar}). ^{13}C NMR (150.9 MHz, $CDCl_3$, 25 °C): δ = 25.9 (d, ^3J = 3.9 Hz, C(7)), 30.8 (s, C(6)), 47.0 (d, ^2J = 32.4 Hz, C(8)), 52.9 (d, ^2J = 6.6 Hz, C(4)), 62.0 (d, ^2J = 8.0 Hz, C(5)), 115.2 (d, ^3J = 13.0 Hz, CH_{PhN}), 119.0 (s, CH_{PhN}), 122.6 (d, J = 8.0 Hz, CH_{Ar}), 124.0 (s, CH_{Ar}), 125.7 (s, CH_{Ar}), 125.8 (s, CH_{Ar}), 126.1 (s, CH_{Ar}), 126.4 (s, CH_{Ar}), 127.6 (d, J = 5.9 Hz, CH_{Ar}), 127.7 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 128.9 (s, CH_{PhN}), 129.4 (s, CH_{Ar}), 129.9 (s, C_{Ar}), 130.6 (d, J = 2.4 Hz, CH_{Ar}), 133.1 (d, ^2J = 18.9 Hz, CH_{Ar}), 133.4 (d, ^2J = 19.9 Hz, CH_{Ar}), 133.5 (s, C_{Ar}), 133.6 (s, C_{Ar}), 134.4 (s, C_{Ar}), 136.4 (d, J = 10.1 Hz, C_{Ar}), 137.8 (d, J = 13.7 Hz, C_{Ar}), 139.0 (d, J = 14.6 Hz, C_{Ar}), 142.5 (d, J = 35.8 Hz, C_{Ar}), 145.0 (d, ^2J = 15.4 Hz, C_{PhN}), 149.5 (s, C_{Ar}) (major epimer) and 27.5 (s, C(7)), 31.6 (s, C(6)), 43.4 (d, ^2J = 3.2 Hz, C(8)), 51.0 (d, ^2J = 6.3 Hz, C(4)), 65.5 (d, ^2J = 10.9 Hz, C(5)), 117.2 (d, ^3J = 13.3 Hz, CH_{PhN}), 120.2 (s, CH_{PhN}), 120.4 (d, J = 13.1 Hz, CH_{Ar}), 123.5 (s, CH_{Ar}), 125.5 (s, CH_{Ar}), 125.8 (d, J = 3.9 Hz, CH_{Ar}), 126.3 (s, CH_{Ar}), 126.7 (s, CH_{Ar}), 127.2 (d, J = 2.7 Hz, CH_{Ar}), 127.5 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 128.1 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 129.0 (s, CH_{Ar}), 129.2 (s, CH_{PhN}), 130.0 (s, C_{Ar}), 130.3 (d, J = 2.1 Hz, CH_{Ar}), 133.3 (s, C_{Ar}), 133.4 (s, C_{Ar}), 133.7 (dd, ^2J = 19.6 Hz, J = 2.4 Hz, C_{Ar}), 133.9 (d, ^2J = 20.7 Hz, CH_{Ar}), 134.3 (d, J = 3.5 Hz, C_{Ar}), 135.8 (d, J = 11.9 Hz, C_{Ar}), 137.3 (d, J = 13.0 Hz, C_{Ar}), 138.7 (d, J = 14.3 Hz, C_{Ar}), 142.6 (d, J = 34.1 Hz, C_{Ar}), 145.1 (d, ^2J = 16.9 Hz, C_{PhN}), 149.7 (s, C_{Ar}) (minor epimer). MS (MALDI TOF/TOF): *m/z* (%) = 677 (13) $[M + H_2O + H]^+$, 455 (10) $[(C_{10}H_6OH)C_{10}H_6PPh_2 + H]^+$, 437 (100) $[(C_{10}H_6)C_{10}H_6PPh_2]^+$, 229 (23) $[M - (C_{10}H_5O)C_{10}H_6PPh_2 + Na]^+$. Anal. Calcd for $C_{43}H_{36}N_2OP_2$: C, 78.41; H, 5.51; N, 4.25. Found: C, 78.61; H, 5.59; N, 4.09.

*4.2.8. (2R,5S,R_a)-2-[1-(2-(Diphenylphosphino)naphthalene-1-yl)naphthalene-2-yloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane-2-oxide (**5**).* Yield: 0.96 g (71%) as white solid,

m. p. 138-140 °C. IR: ν_{max} ($CHCl_3$) 3051, 3030, 2923, 2851, 1468, 1446, 1229, 1077, 830, 740 cm^{-1}. ^1H NMR (600.13 MHz, $CDCl_3$, 24 °C): δ = 1.61-1.66 (m, 1 H, C(6)H), 1.77-1.82 (m, 2 H, $C(7)H_2$), 1.92-1.97 (m, 1 H, C(6)H), 2.61-2.67 (m, 1 H, C(8)H), 3.13-3.17 (m, 1 H, C(4)H), 3.29-3.33 (m, 1 H, C(4)H), 3.40-3.45 (m, 1 H, C(5)H), 3.57-3.62 (m, 1 H, C(8)H), 6.53 (d, ^3J = 7.8 Hz, 2 H, CH_{PhN}), 6.79 (t, ^3J = 7.5 Hz, 1 H, CH_{PhN}), 6.85 (t, ^3J = 7.8 Hz, 2 H, CH_{PhN}), 6.92 (d, ^3J = 9.0 Hz, 1 H, CH_{Ar}), 7.03 (t, ^3J = 7.2 Hz, 2 H, CH_{Ar}), 7.13-7.21 (m, 7 H, CH_{Ar}), 7.24-7.29 (m, 2 H, CH_{Ar}), 7.31-7.36 (m, 2 H, CH_{Ar}), 7.37-7.41 (m, 2 H, CH_{Ar}), 7.55 (t, ^3J = 7.8 Hz, 1 H, CH_{Ar}), 7.62 (d, ^3J = 9.0 Hz, 1 H, CH_{Ar}), 7.84 (d, ^3J = 8.4 Hz, 1 H, CH_{Ar}), 7.89-7.94 (m, 2 H, CH_{Ar}), 7.98 (d, ^3J = 9.0 Hz, 1 H, CH_{Ar}). ^{13}C NMR (150.9 MHz, $CDCl_3$, 24 °C): δ = 25.7 (d, ^3J = 3.9 Hz, C(7)), 32.0 (d, ^3J = 3.9 Hz, C(6)), 46.7 (d, ^2J = 3.2 Hz, C(8)), 50.4 (d, ^2J = 19.3 Hz, C(4)), 56.3 (d, ^2J = 10.4 Hz, C(5)), 115.6 (d, ^3J = 5.1 Hz, CH_{PhN}), 119.0 (s, CH_{Ar}), 120.8 (s, CH_{PhN}), 124.9 (s, CH_{Ar}), 126.3 (d, J = 8.5 Hz, CH_{Ar}), 126.5 (s, CH_{Ar}), 126.8 (s, CH_{Ar}), 127.4 (s, CH_{Ar}), 127.6 (d, J = 2.7 Hz, CH_{Ar}), 127.7 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 128.1 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 128.8 (s, CH_{PhN}), 129.9 (s, CH_{Ar}), 130.5 (d, J = 2.4 Hz, CH_{Ar}), 133.1 (d, ^2J = 18.3 Hz, CH_{Ar}), 133.4 (d, ^2J = 20.4 Hz, CH_{Ar}), 133.7 (s, C_{Ar}), 134.2 (d, J = 1.5 Hz, C_{Ar}), 135.9 (d, J = 10.1 Hz, C_{Ar}), 137.9 (d, J = 13.0 Hz, C_{Ar}), 138.2 (d, J = 13.9 Hz, C_{Ar}), 140.7 (d, ^2J = 5.7 Hz, C_{PhN}), 141.0 (d, J = 35.5 Hz, C_{Ar}), 147.4 (dd, J = 7.9 Hz, J = 2.4 Hz, C_{Ar}). MS (MALDI TOF/TOF): *m/z* (%) = 675 (78) $[M + H]^+$, 437 (100) $[(C_{10}H_6)C_{10}H_6PPh_2]^+$, 177 (89) $[PhNHCH_2CH(CH_2)_3NH + H]^+$. Anal. Calcd for $C_{43}H_{36}N_2O_2P_2$: C, 76.55; H, 5.38; N, 4.15. Found: C, 76.76; H, 5.43; N, 4.24.

4.3. General procedure for the synthesis of the palladium complexes with ligands 3b and PPh_3 for the ^{31}P NMR experiments

Palladium complexes with diamidophosphite **3b** and PPh_3 were synthesized for the NMR investigations as follows: a solution of the diamidophosphite ligand or a solution of the mixture of ligands a) **3b** (0.016 g, 0.044 mmol), b) **3b** (0.032 g, 0.088 mmol), c) **3b** (0.016 g, 0.044 mmol) and PPh_3 (0.012 g, 0.044 mmol)) in CD_2Cl_2 (0.3 mL) was added dropwise to a stirred solution of $[Pd(allyl)Cl]_2$ ((0.008 g, 0.022 mmol) in each case) in CD_2Cl_2 (0.3 mL). The resulting solution (0.6 mL) was then transferred to an NMR tube and spectroscopic experiments were carried out.

4.4 General procedure for the synthesis of the cationic palladium complexes 6d-f

A solution of the corresponding *P,P**-bidentate ligand (0.2 mmol) in CH_2Cl_2 (2 mL) was added dropwise over 30 min to a stirred solution of $[Pd(allyl)Cl]_2$ (0.037 g, 0.1 mmol) in CH_2Cl_2 (1 mL) at 20 °C. The reaction mixture was stirred for a further 1 h at 20 °C. A solution of $AgBF_4$ (0.2 mmol, 0.039 g) in THF (2 mL) was added dropwise over 30 min to the resulting solution, and the reaction mixture was stirred for 1.5 h at 20 °C. The precipitate of AgCl formed was separated by filtration. Solvent excess was removed in vacuum (40 Torr) to a volume of ~0.3 mL, and ether (7 mL) was added. The precipitate formed was separated by centrifugation, washed with ether (2 × 5 mL), and dried in air and in vacuum (1 Torr).

*4.4.1. [Pd(allyl)(3d)]BF_4 (**6d**).* Yield: 0.13 g (91%) as sand-colored powder. MS (MALDI TOF/TOF): *m/z* (%) = 647 (94) $[M - BF_4 + H_2O]^+$, 629 (100) $[M - BF_4]^+$. Anal. Calcd for $C_{32}H_{33}BF_4N_2OP_2Pd$: C, 53.62; H, 4.64; N, 3.91. Found: C, 53.83; H, 4.59; N, 4.07.

*4.4.2. [Pd(allyl)(3e)]BF_4 (**6e**).* Yield: 0.14 g (94%) as sand-colored powder. MS (MALDI TOF/TOF): *m/z* (%) = 643 (68) $[M - BF_4]^+$, 602 (100) $[M - All - BF_4]^+$. Anal. Calcd for $C_{33}H_{35}BF_4N_2OP_2Pd$: C, 54.23; H, 4.83; N, 3.83. Found: C, 54.48; H, 4.68; N, 4.09.

*4.4.3. [Pd(allyl)(3f)]BF_4 (**6f**).* Yield: 0.17 g (95%) as light yellow powder. MS (MALDI TOF/TOF): *m/z* (%) = 805 (100) $[M - BF_4]^+$, 764 (28) $[M - All - BF_4]^+$. Anal. Calcd for $C_{46}H_{41}BF_4N_2OP_2Pd$: C, 61.87; H, 4.63; N, 3.14. Found: C, 62.02; H, 4.82; N, 2.88.

4.5. Catalytic reactions

4.5.1. Pd-catalyzed allylic sulfonylation of (E)-1,3-diphenylallyl acetate **7** *with sodium para-toluene sulfinate*. A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in THF (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min, then sodium *para*-toluene sulfinate (0.089 g, 0.5 mmol) was added and the reaction mixture stirred for a further 48 h, quenched with brine (3 mL) and extracted with THF (3 x 2 mL). The organic layer was washed with brine (2 x 2 mL) and dried over $MgSO_4$. The solvent was evaporated at reduced pressure (40 Torr). Crystallization of the residue from EtOH, followed by desiccation in vacuum (10 Torr, 12 h), gave (*E*)-1,3-diphenyl-3-tosylprop-1-ene **8a** as white crystals.[62,63] The enantiomeric excess of **8a** was determined by HPLC (Daicel Chiralcel OD-H column, C_6H_{14}/*i*-PrOH = 4/1, 0.5 mL/min, 254 nm, *t*(*R*) = 16.3 min, *t*(*S*) = 18.5 min).

4.5.2. Pd-catalyzed allylic alkylation of (E)-1,3-diphenylallyl acetate **7** *with dimethyl malonate*. A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (0.05 mL, 0.25 mmol) was added and the solution stirred for 15 min. Dimethyl malonate (0.05 mL, 0.44 mmol), BSA (0.11 mL, 0.44 mmol) and potassium acetate (0.002 g) were added. The reaction mixture was stirred for 48 h, diluted with CH_2Cl_2 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 **8b**. [64,65] 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, C_6H_{14}/*i*-PrOH = 99/1, 0.3 mL/min, 254 nm, *t*(*R*) = 28.0 min, *t*(*S*) = 29.3 min).

4.5.3. Pd-catalyzed allylic amination of (E)-1,3-diphenylallyl acetate **7** *with pyrrolidine*. A solution of $[Pd(allyl)Cl]_2$ (0.0019 g, 0.005 mmol) and the appropriate ligand (0.01 mmol or 0.02 mmol) in the appropriate solvent (1.5 mL) was stirred for 40 min. (*E*)-1,3-Diphenylallyl acetate (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 CH_2Cl_2 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-(1,3-diphenylallyl)pyrrolidine **8c**. [66,67] 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, C_6H_{14}/*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).

4.5.4. Pd-catalyzed desymmetrization of N,N'-ditosyl-meso-cyclopent-4-ene-1,3-diol biscarbamate **10**. A solution of $[Pd_2(dba)_3]\cdot CHCl_3$ (0.005 g, 0.005 mmol) and appropriate ligand (0.01 mmol or 0.02 mmol) in THF (1 mL) was stirred for 40 min. The resulting solution was brought to the 35 °C and a solution of *N,N'*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate **10** and Et_3N (14 µL, 0.099 mmol) in THF (0.5 mL) was added (compound **10** was prepared *in situ* as follows: to a solution of the *meso*-cyclopent-4-ene-1,3-diol **9** (0.01 g, 0.099 mmol) in THF (0.5 mL), tosyl isocyanate (35 µL, 0.232 mmol) was added; the mixture was stirred at room temperature for 15 min, heated to 55 °C for 1 h and cooled down to room temperature). The reaction mixture was stirred for 24 h. The solvent was removed at reduced pressure (40 Torr) and the residue was purified by flash chromatography on a short pad of silica gel (EtOAc/hexane,

1:4) and dried in vacuum (1 Torr) for 2 h gave the desired product **11** as a slightly brown solid.[68] The enantiomeric excess of **11** was determined by HPLC (Kromasil 5-CelluCoat column, C_6H_{14}/*i*-PrOH = 9/1, 2 mL/min, 219 nm, *t*(I) = 13 min, *t*(II) = 17 min).

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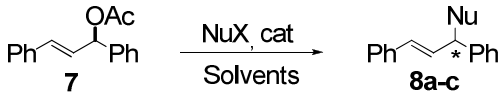
Tetrahedron

Nonsimple relationships between the *P**-chiral diamidophosphite and the arylphosphine moieties in Pd-catalyzed asymmetric reactions: combinatorial approach and *P,P**-bidentate phosphine-diamidophosphites

Konstantin N. Gavrilov, Alexei A. Shiryaev, Sergey V. Zheglov, Vladislav K. Gavrilov, Nikolay N. Groshkin, Marina G. Maksimova, Alexandr N. Volov, Ilya A. Zamilatskov

Supplementary data

Table S1. Pd-catalyzed allylic sulfonylation, alkylation and amination of (*E*)-1,3-diphenylallyl acetate **7** [a]



Nu = SO_2*p*Tol, X = Na, **8a**
Nu = $CH(CO_2Me)_2$, X = H, **8b**
Nu = $N(CH_2)_4$, X = H, **8c**

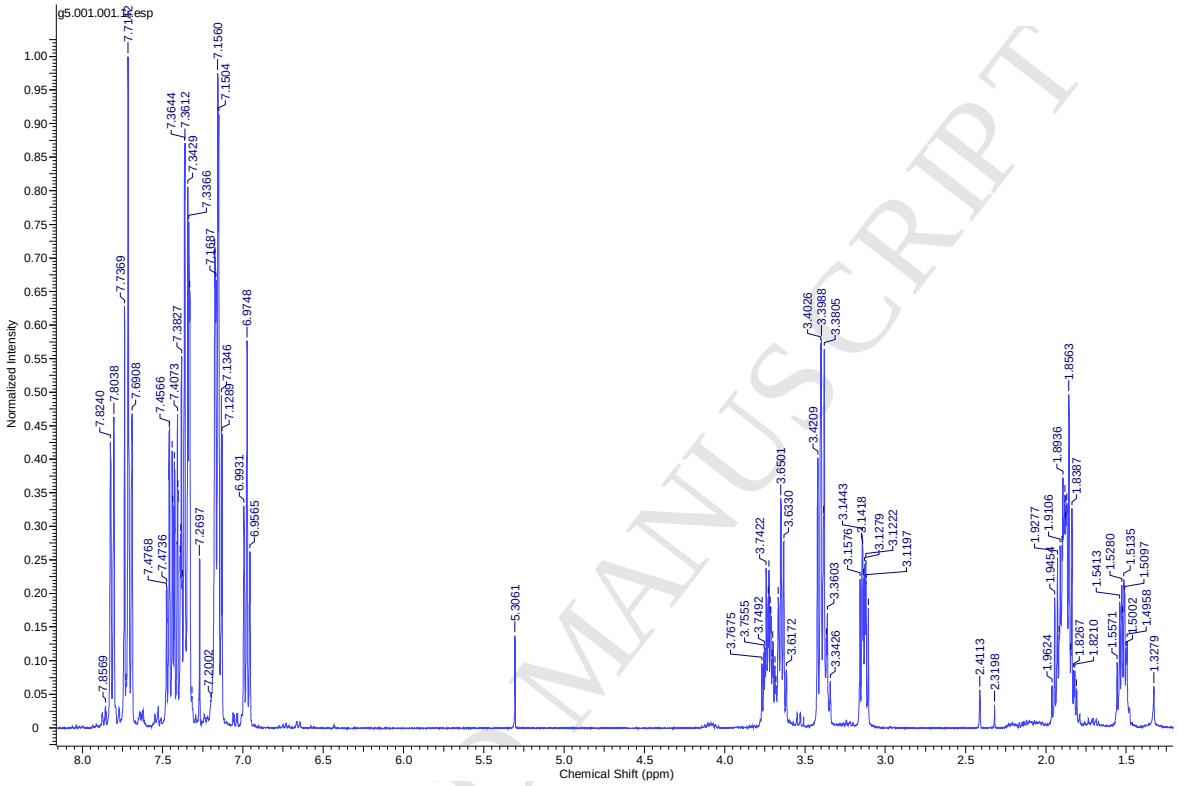
Entry	*Ligand*	*L/Pd*	*Solvent*	*Conversion (%)* [b]	*Ee (%)*
			allylic sulfonylation with sodium p-toluenesulfinate [c]		
1	**2f**	1	THF	0	-
2	**2f**	2	THF	13	4 (*R*)
3	**5**	1	THF	0	-
4	**5**	2	THF	0	-
			allylic alkylation with dimethyl malonate (BSA, KOAc) [d]		
5	**2f**	1	CH_2Cl_2	58	57 (*R*)
6	**2f**	2	CH_2Cl_2	31	53 (*R*)
7	**2f**	1	THF	0	-
8	**2f**	2	THF	0	-
9	**5**	1	CH_2Cl_2	50	2 (*S*)
10	**5**	2	CH_2Cl_2	55	5 (*S*)
11	**5**	1	THF	25	3 (*S*)
12	**5**	2	THF	40	4 (*S*)
			allylic amination with pyrrolidine [e]		
13	**2f**	1	CH_2Cl_2	78	24 (*R*)
14	**2f**	2	CH_2Cl_2	65	49 (*R*)
15	**2f**	1	THF	39	14 (*R*)
16	**2f**	2	THF	32	42 (*R*)
17	**5**	1	CH_2Cl_2	15	3 (*R*)
18	**5**	2	CH_2Cl_2	28	2 (*R*)
19	**5**	1	THF	13	3 (*R*)
20	**5**	2	THF	15	11 (*R*)

[a] All reactions were carried out with 2 mol% of $[Pd(allyl)Cl]_2$ at room temperature for 48 h.
[b] Isolated yield of **8a**.
[c] Enantiomeric excess of **8a** was determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 4/1, 0.5 mL/min, 254 nm, *t*(*R*) = 16.3 min, *t*(*S*) = 18.5 min).
[d] The conversion of substrate **7** and enantiomeric excess of **8b** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*i*-PrOH = 99/1, 0.3 mL/min, 254 nm, *t*(*R*) = 28.0 min, *t*(*S*) = 29.3 min).
[e] The conversion of substrate **7** and enantiomeric excess of **8c** were determined by HPLC (Daicel Chiralcel OD-H, C_6H_{14}/*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).

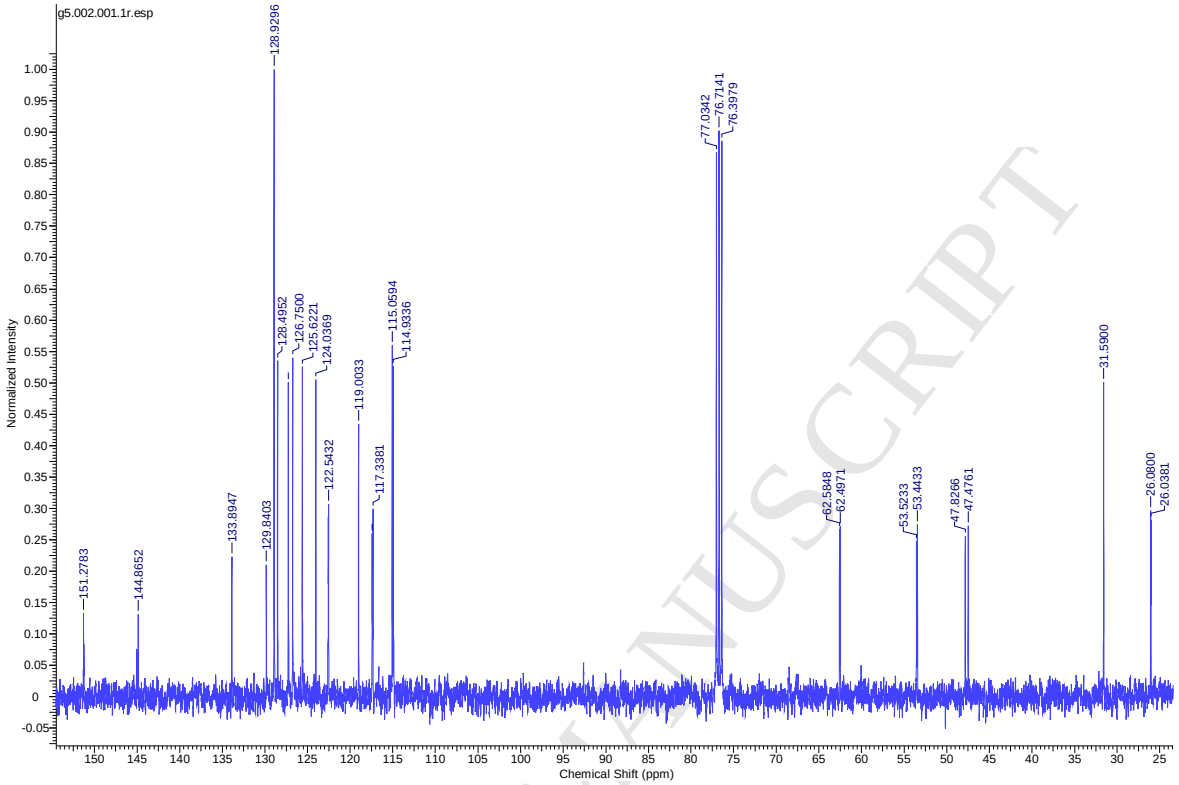
NMR spectra of new ligands

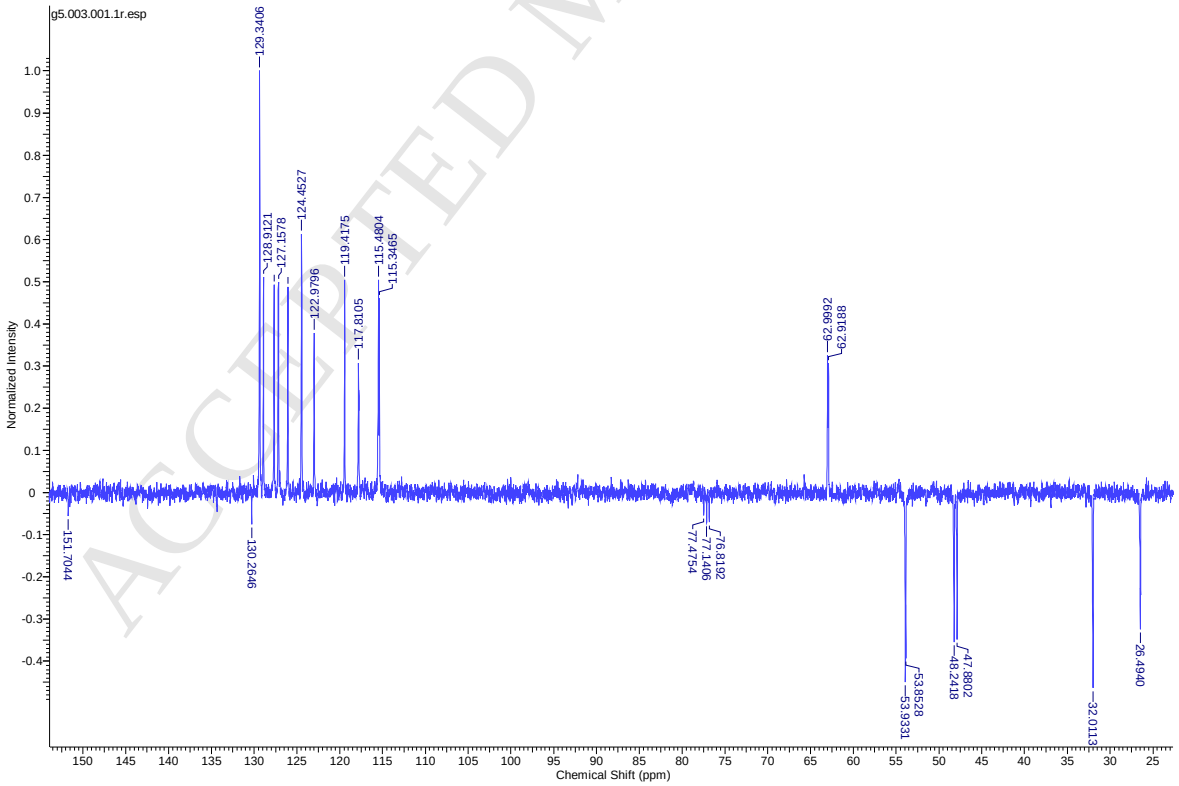
(2*R*,5*S*)-2-(Naphthalene-2-yloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3a)

^{1}H NMR (400.13 MHz, $CDCl_3$)

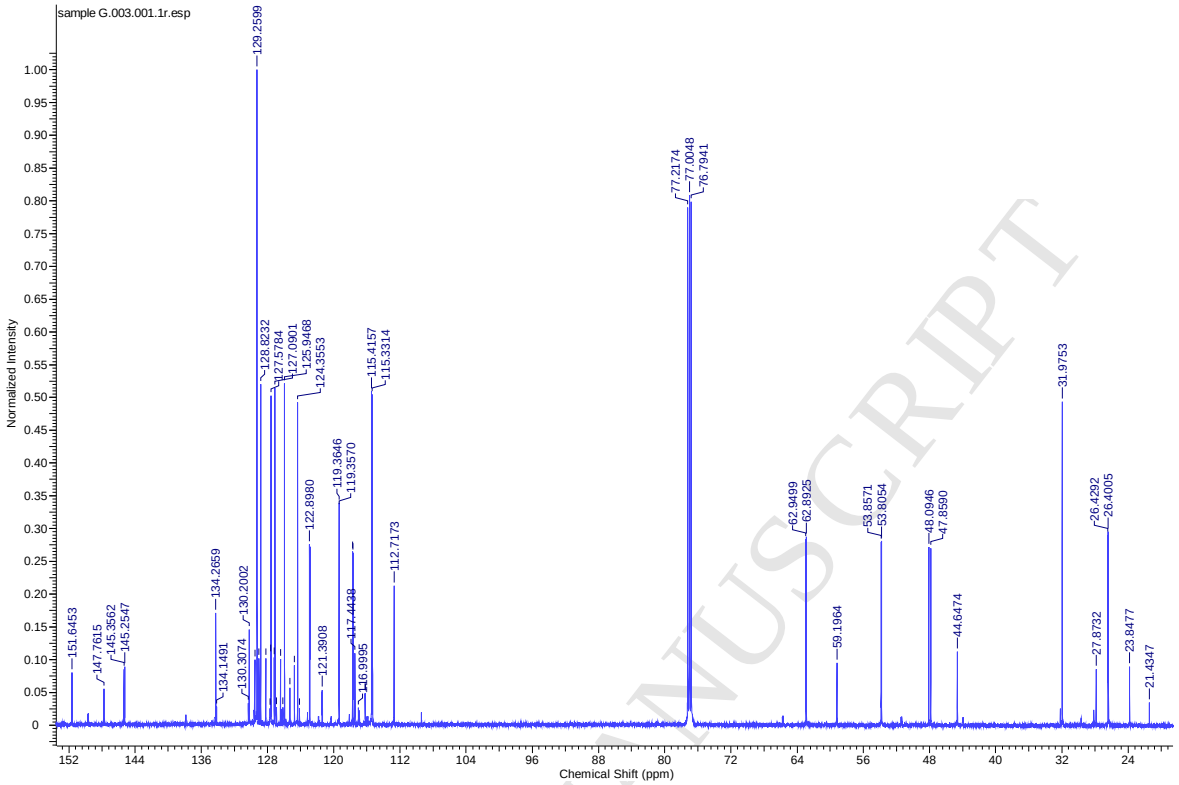


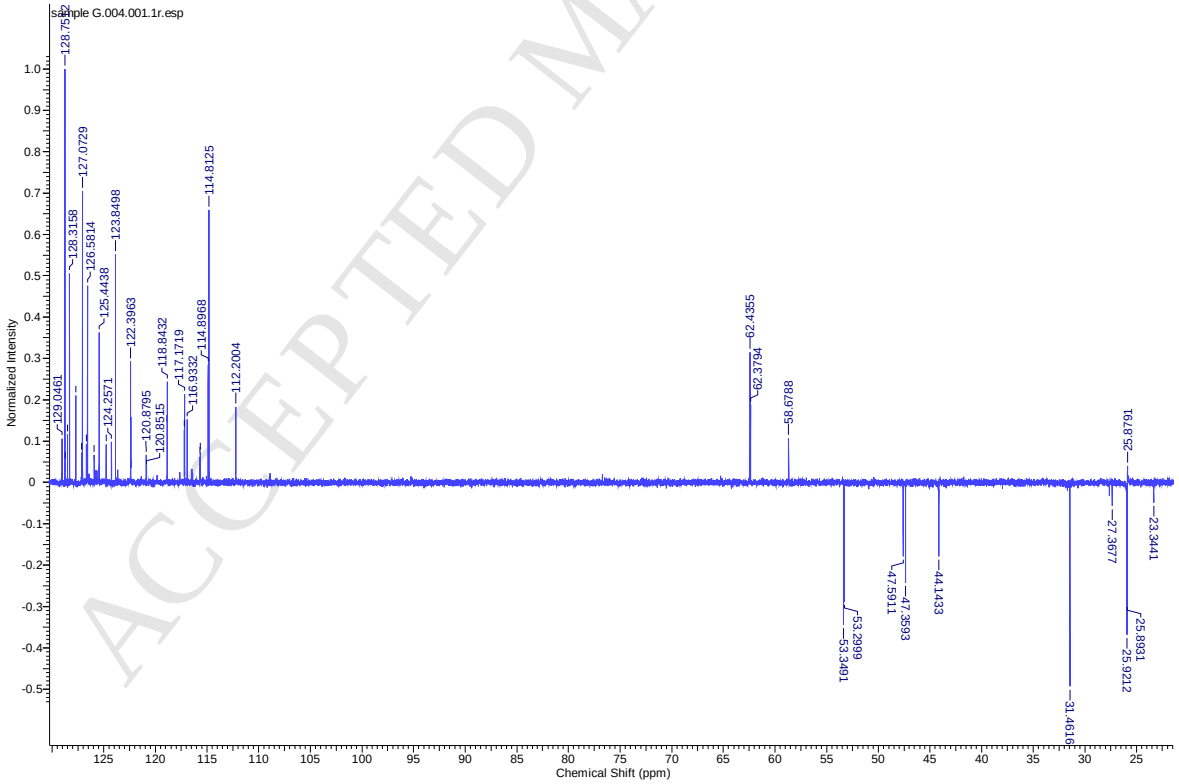
^{13}C NMR (100.6 MHz, $CDCl_3$)



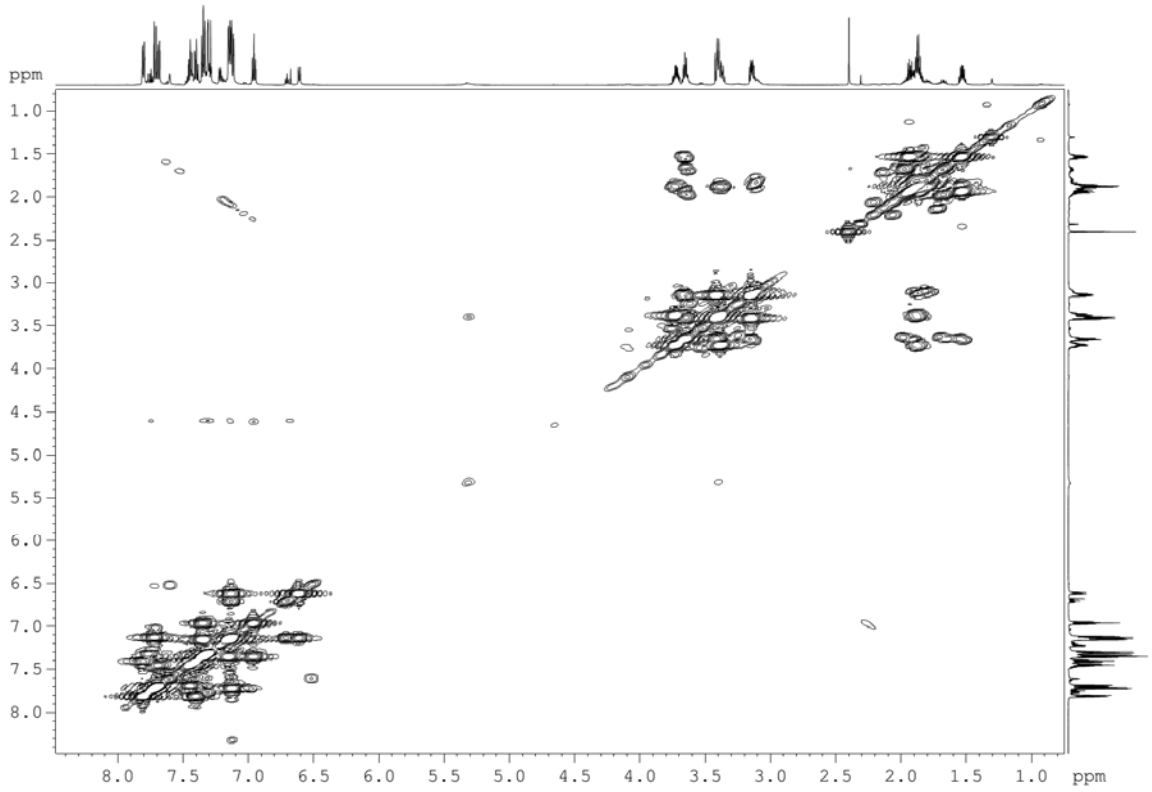


^{13}C NMR (150.9 MHz, $CDCl_3$)

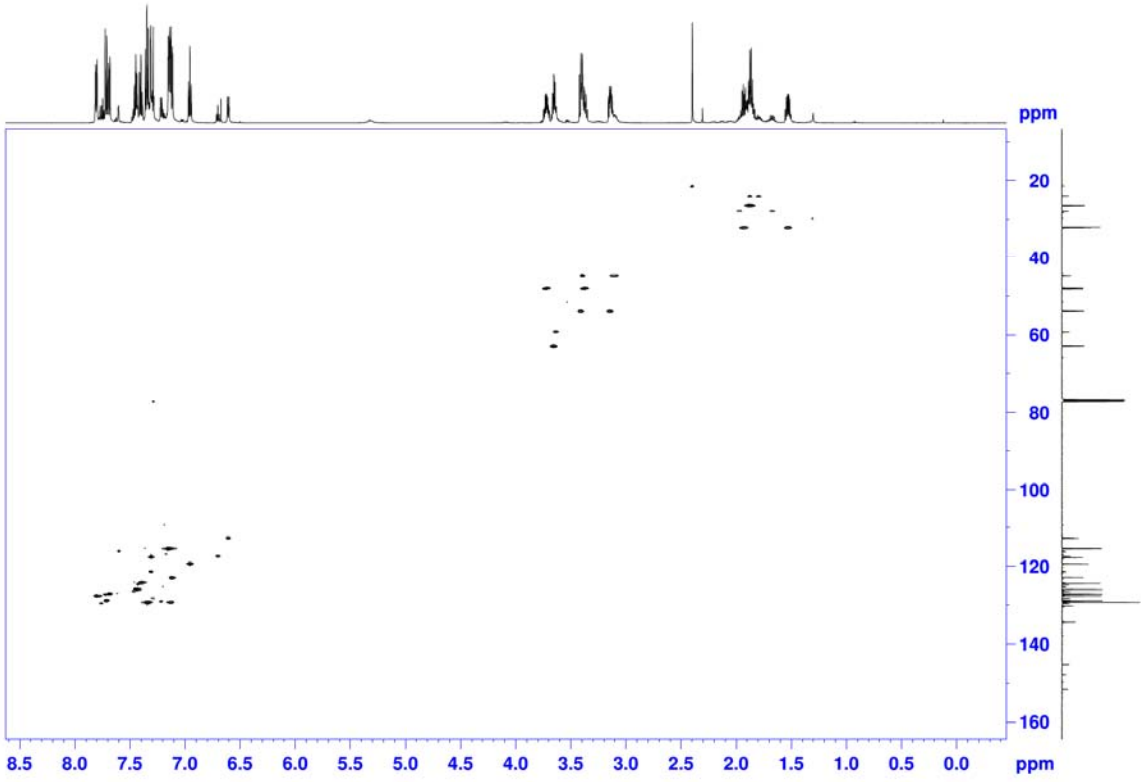




^{1}H -^{1}H 2D COSY (600.13 MHz, $CDCl_3$)

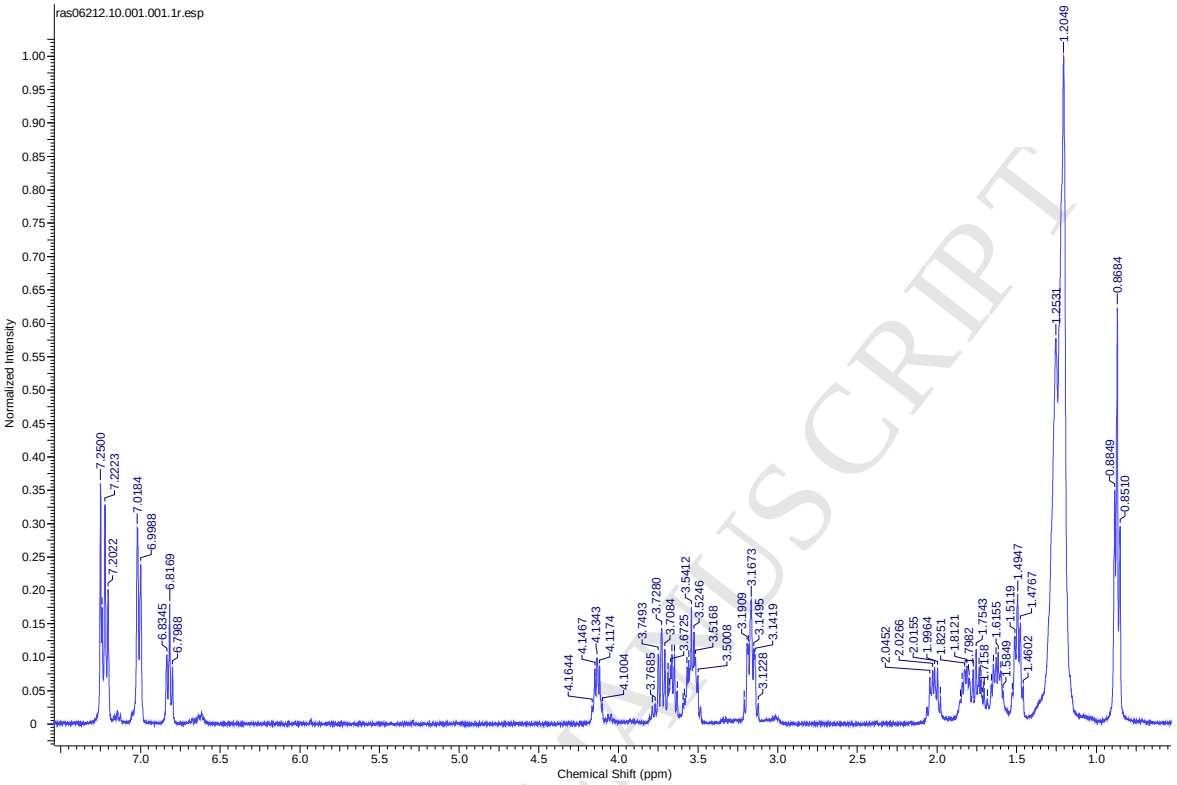


^{1}H -^{13}C HSQC (600.13 and 150.9 MHz, $CDCl_3$)

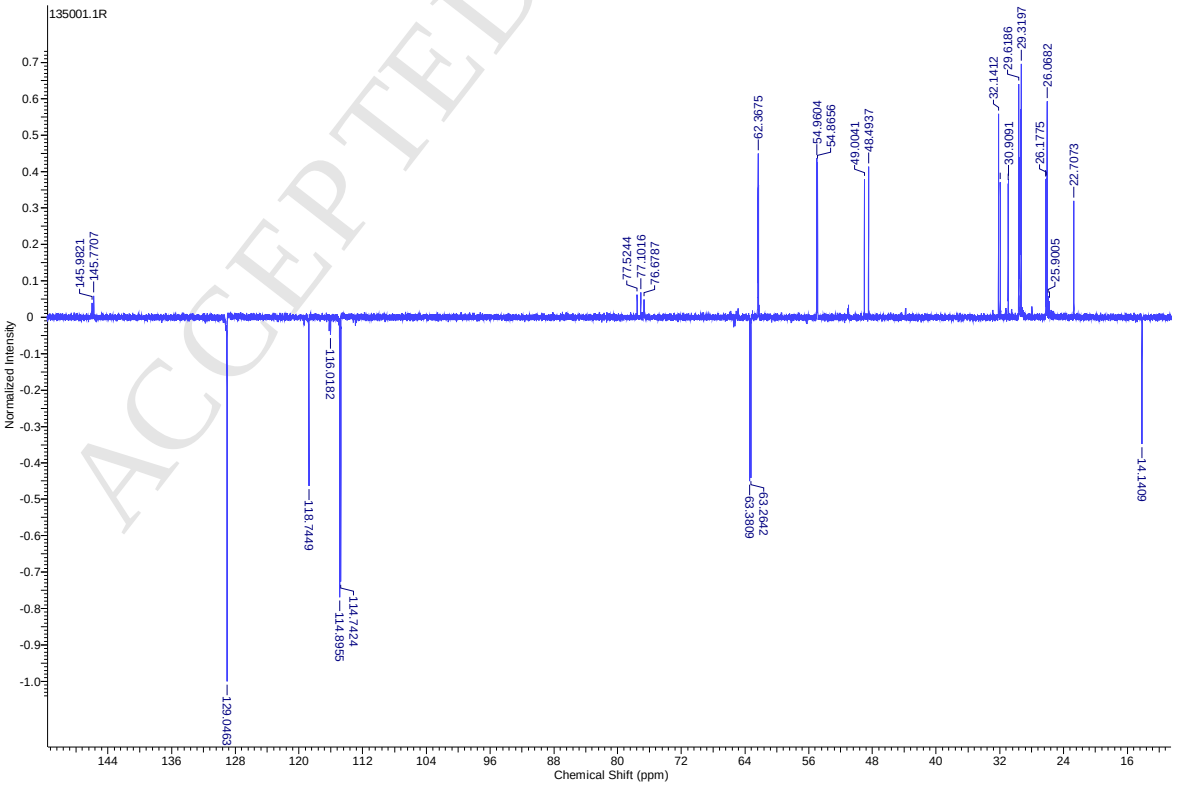


(2*R*,5*S*)-2-(Decyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3b)

^{1}H NMR (400.13 MHz, $CDCl_3$)

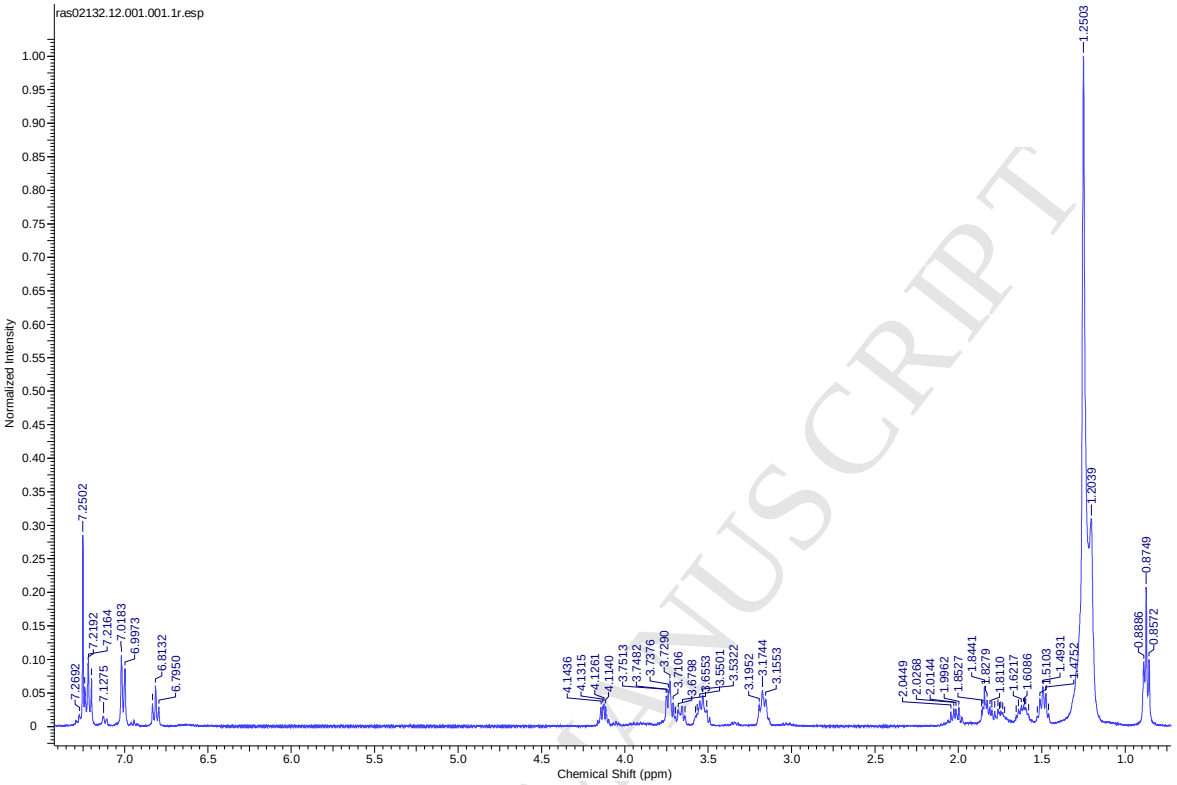


^{13}C NMR (75.5 MHz, $CDCl_3$)

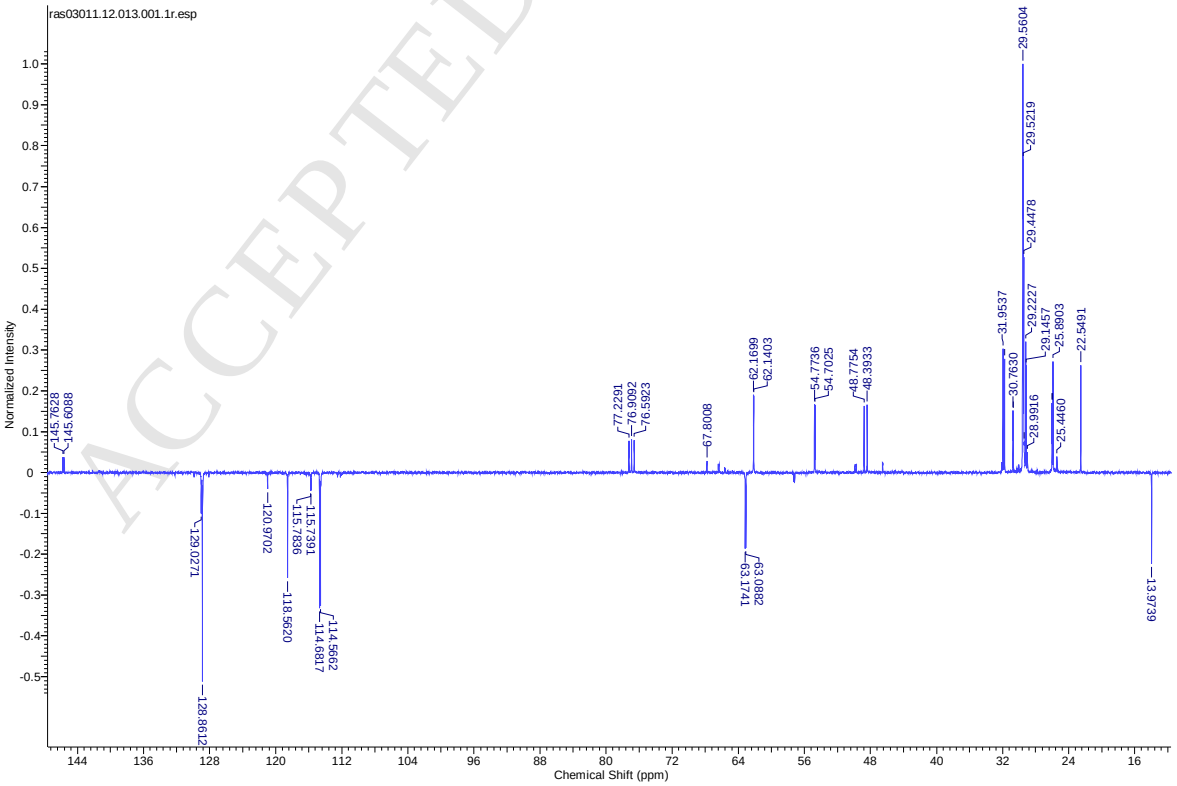


(*2R*,5*S*)-2-(Hexadecyloxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3c)

^{1}H NMR (400.13 MHz, $CDCl_3$)

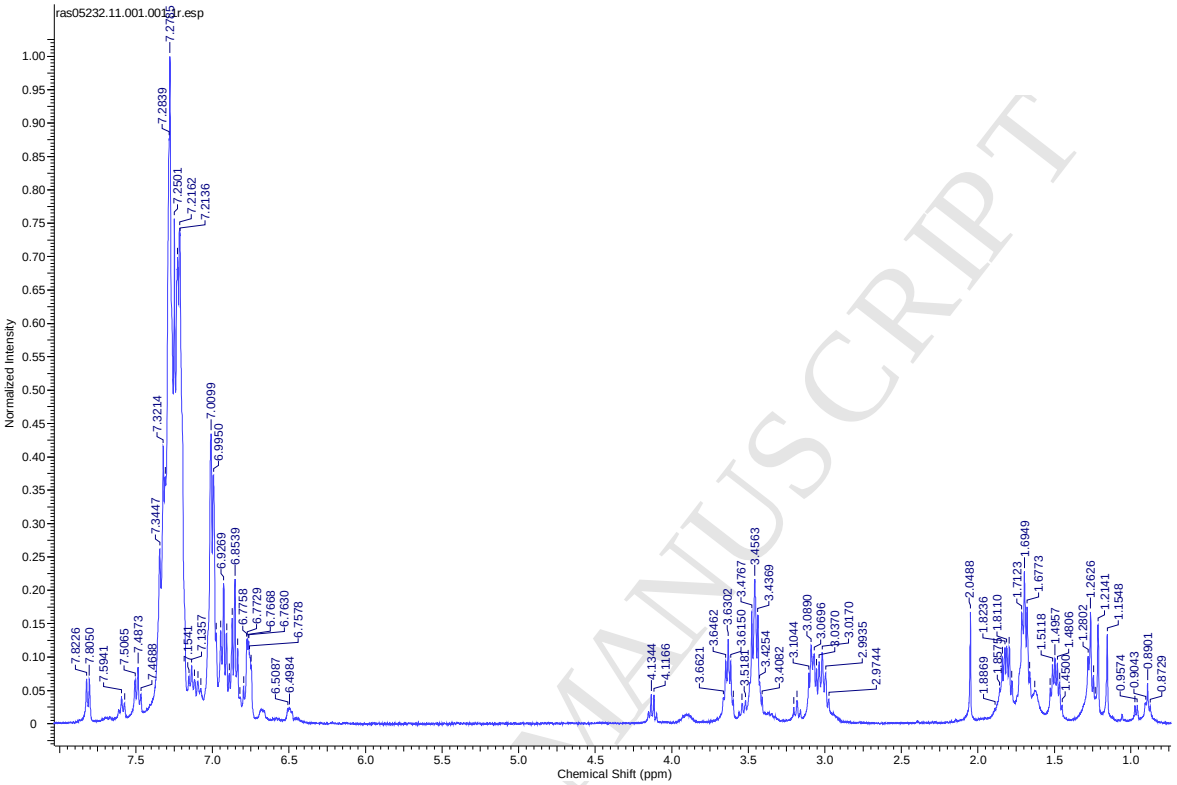


^{13}C NMR (100.6 MHz, $CDCl_3$)

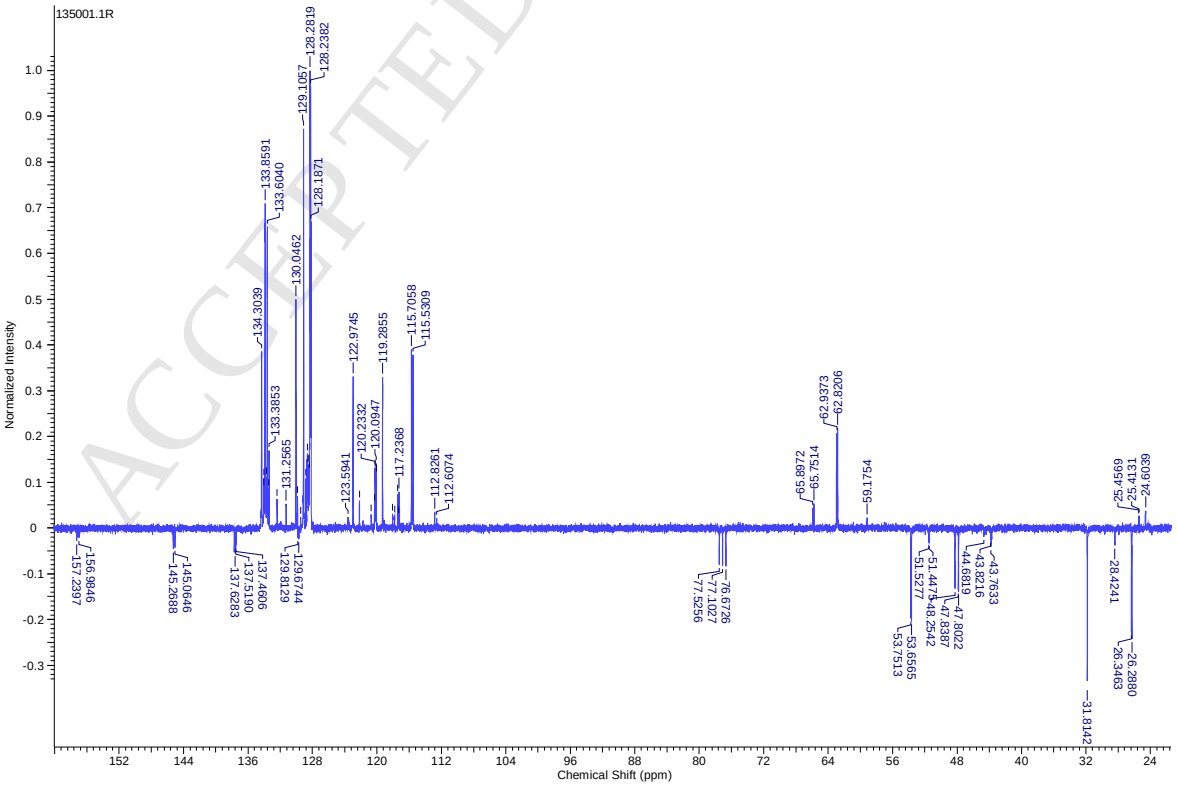


(2*R*,5*S*)-2-(2-(Diphenylphosphino)phenoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3d)

^{1}H NMR (400.13 MHz, $CDCl_3$)

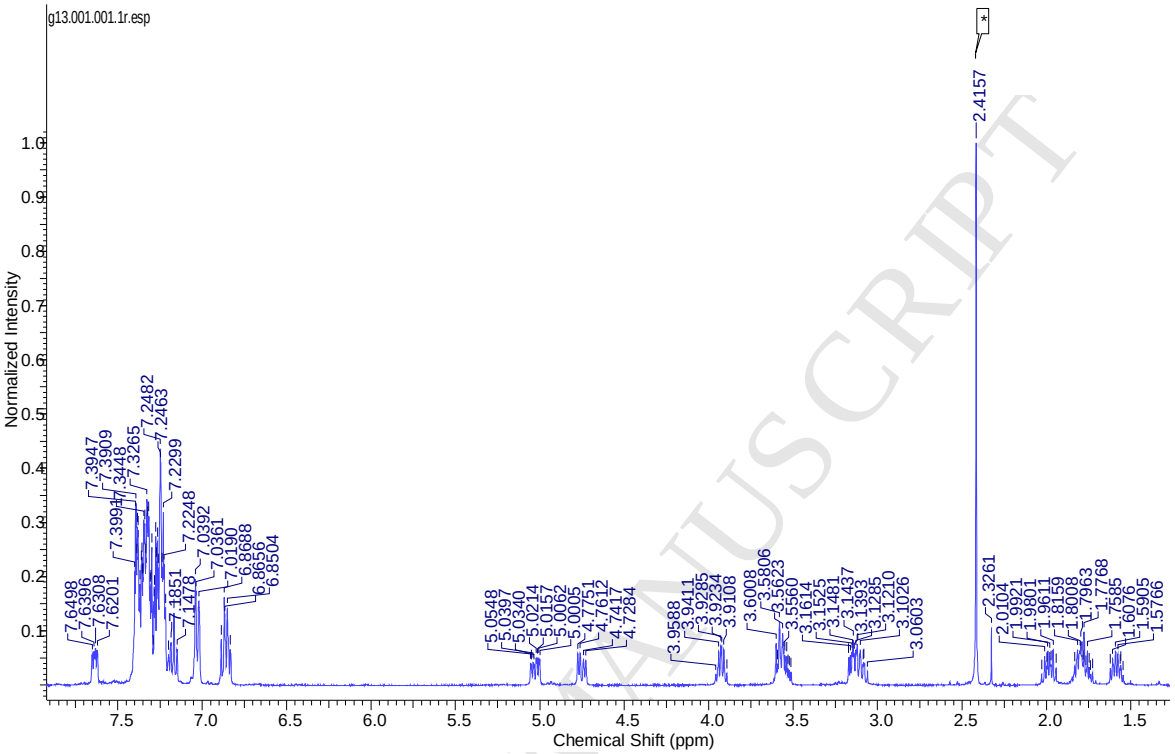


^{13}C NMR (75.5 MHz, $CDCl_3$)

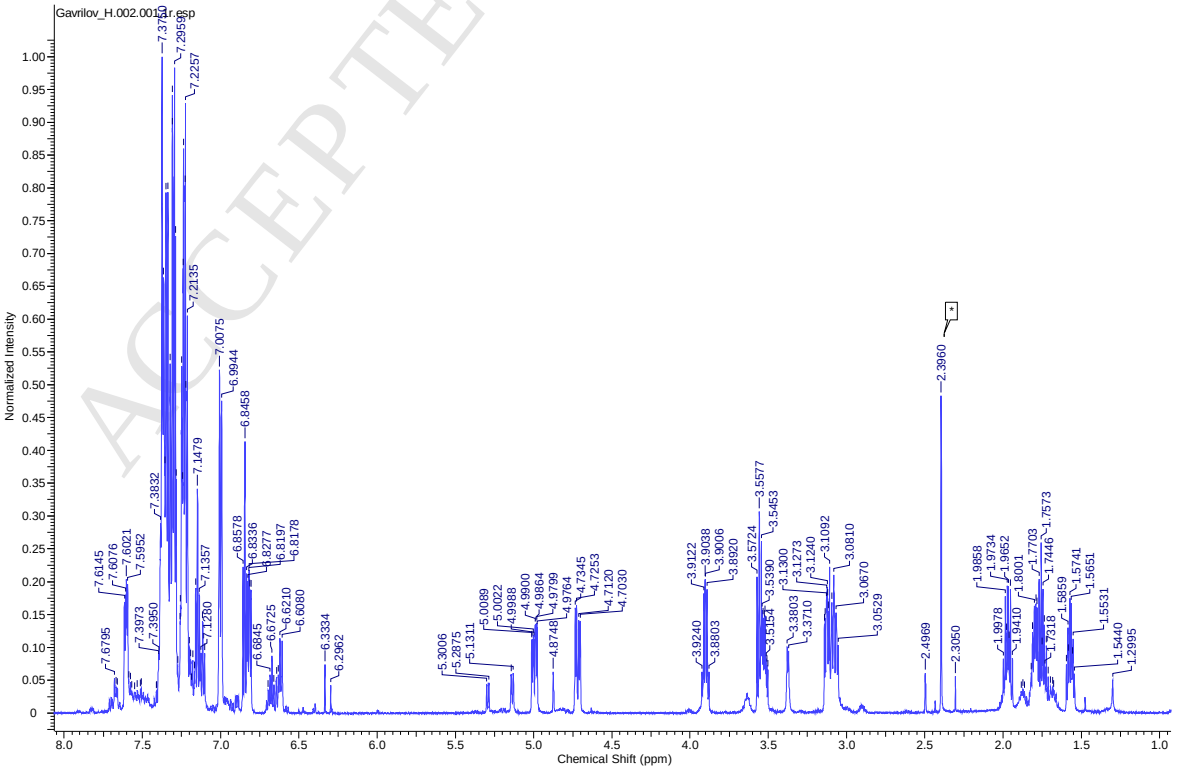


(2*R*,5*S*)-2-(2-(Diphenylphosphino)phenylmethoxy)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3e)

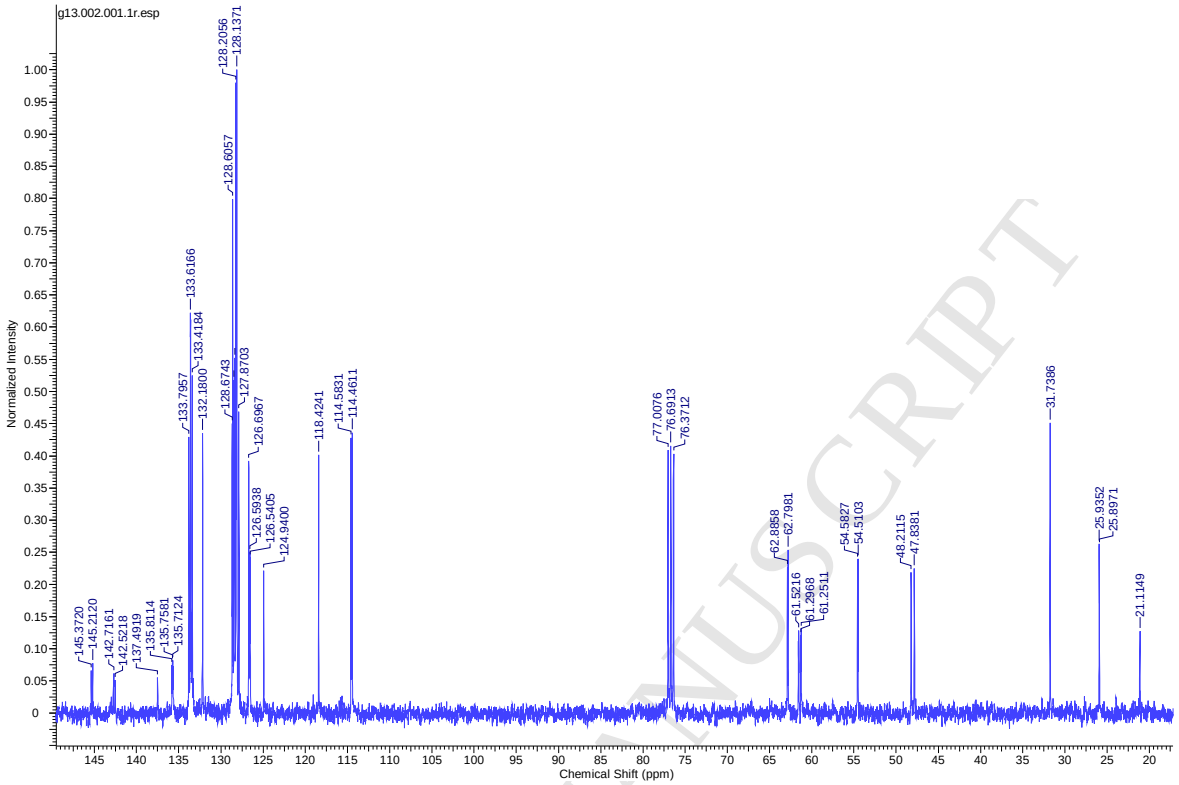
^{1}H NMR (400.13 MHz, $CDCl_3$)

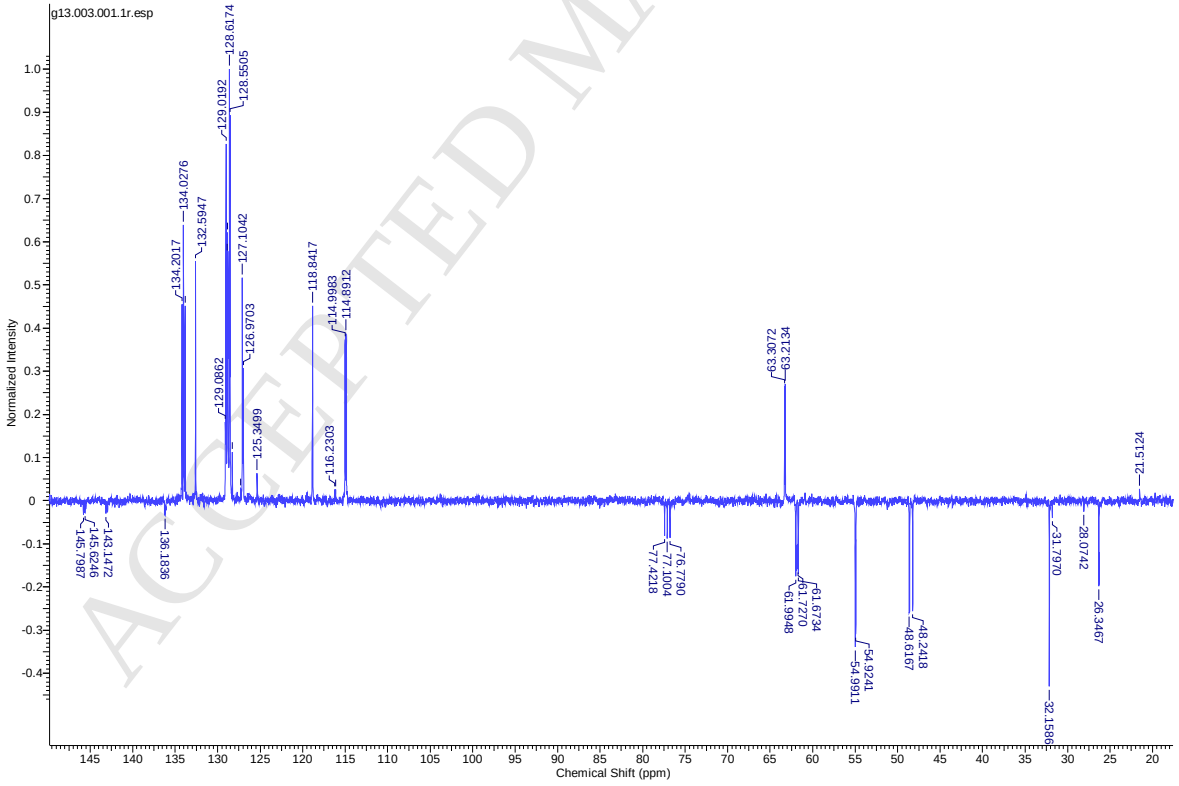


^{1}H NMR (600.13 MHz, $CDCl_3$)

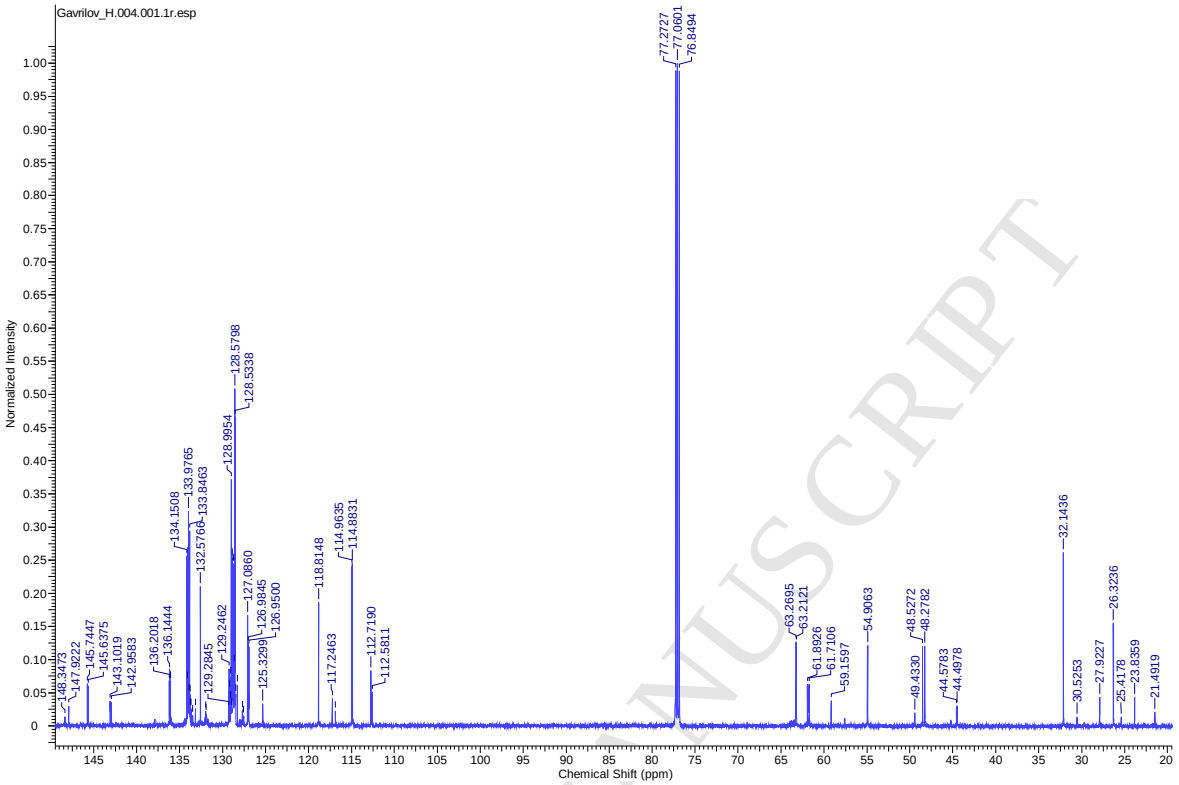


^{13}C NMR (100.6 MHz, $CDCl_3$)

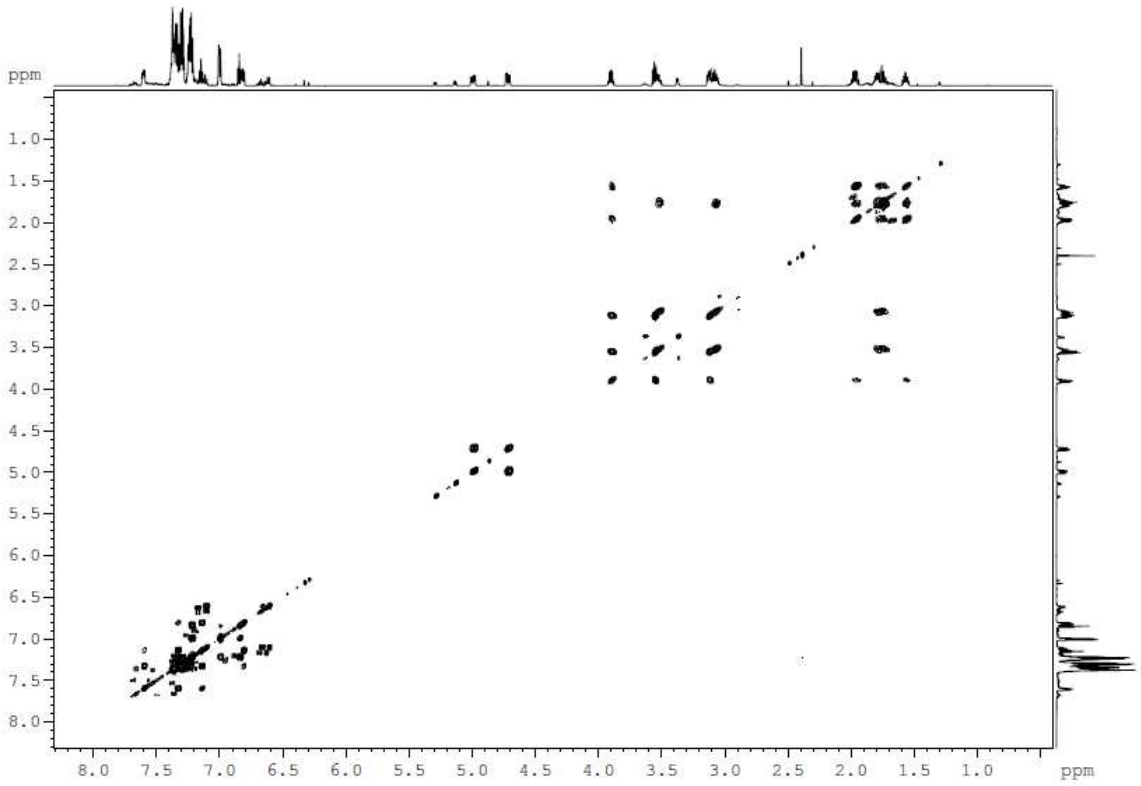




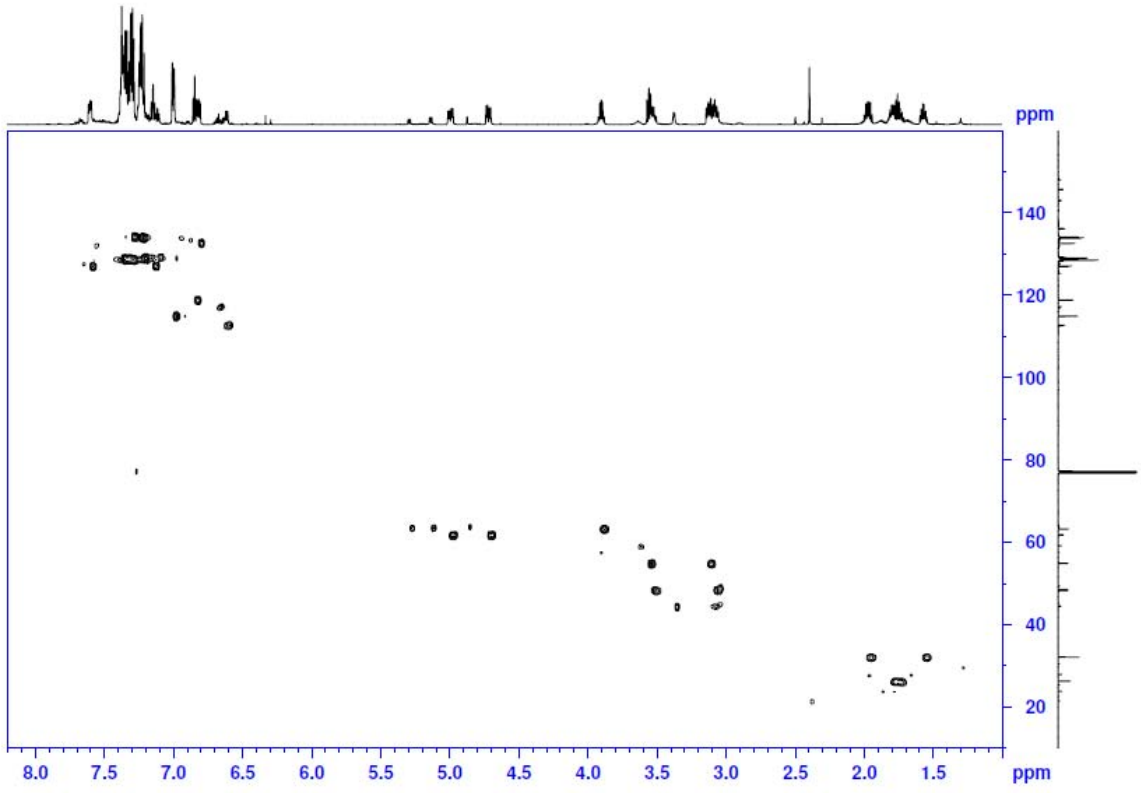
^{13}C NMR (150.9 MHz, $CDCl_3$)



^{1}H -^{1}H 2D COSY (600.13 MHz, $CDCl_3$)

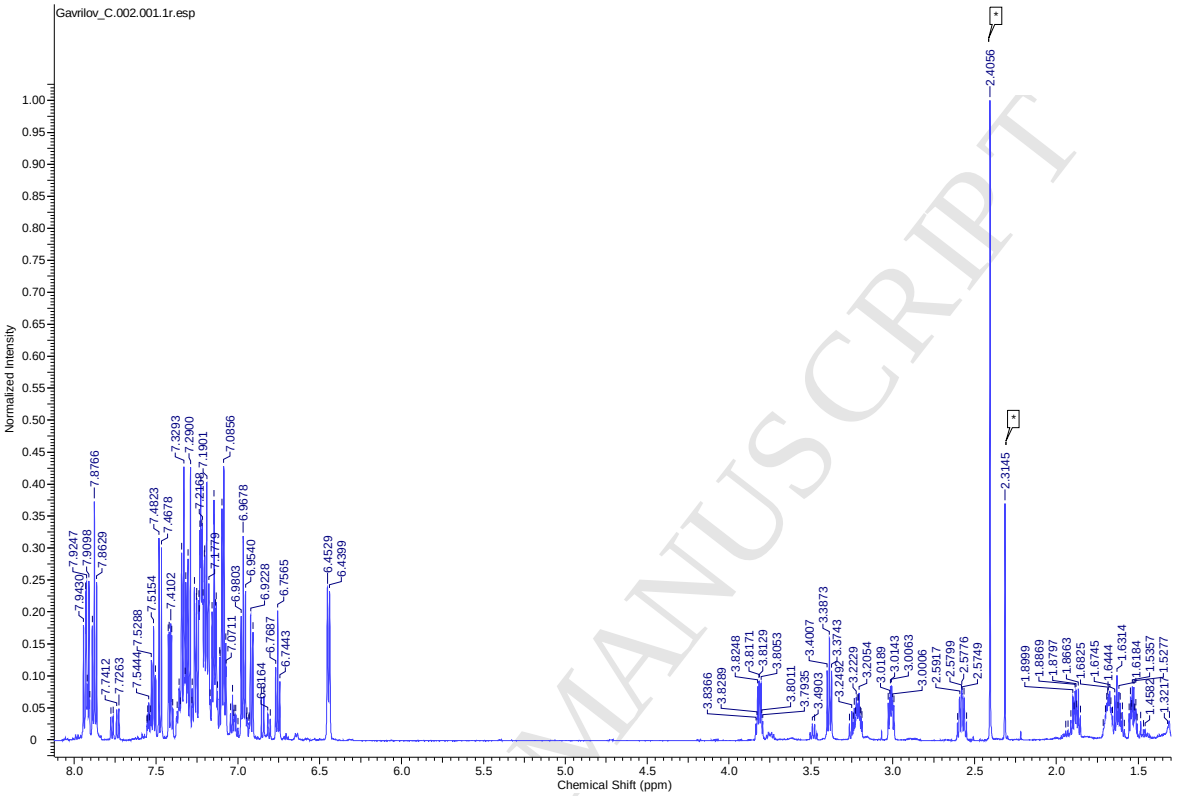


^{1}H -^{13}C HSQC (600.13 and 150.9 MHz, $CDCl_3$)



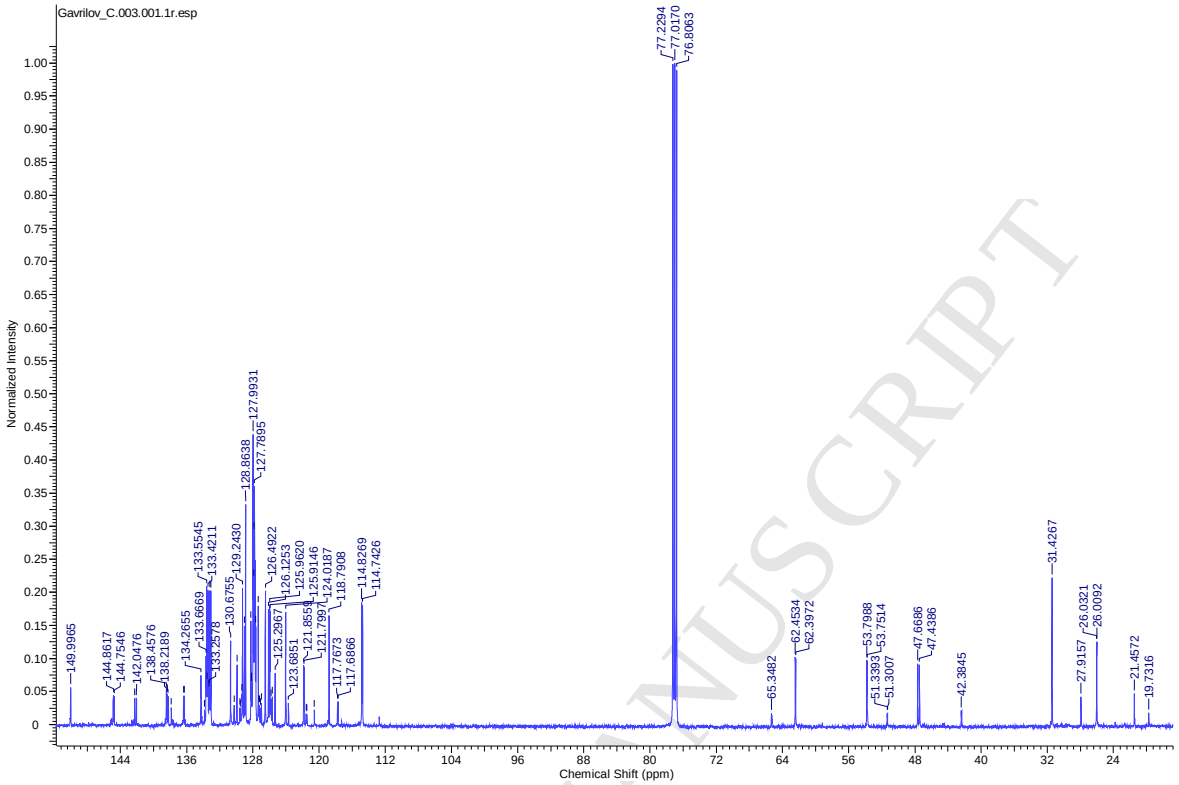
(2*R*,5*S*,R_a)-2-[1-(2-(Diphenylphosphino)naphthalene-1-yl)naphthalene-2-yloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3f)

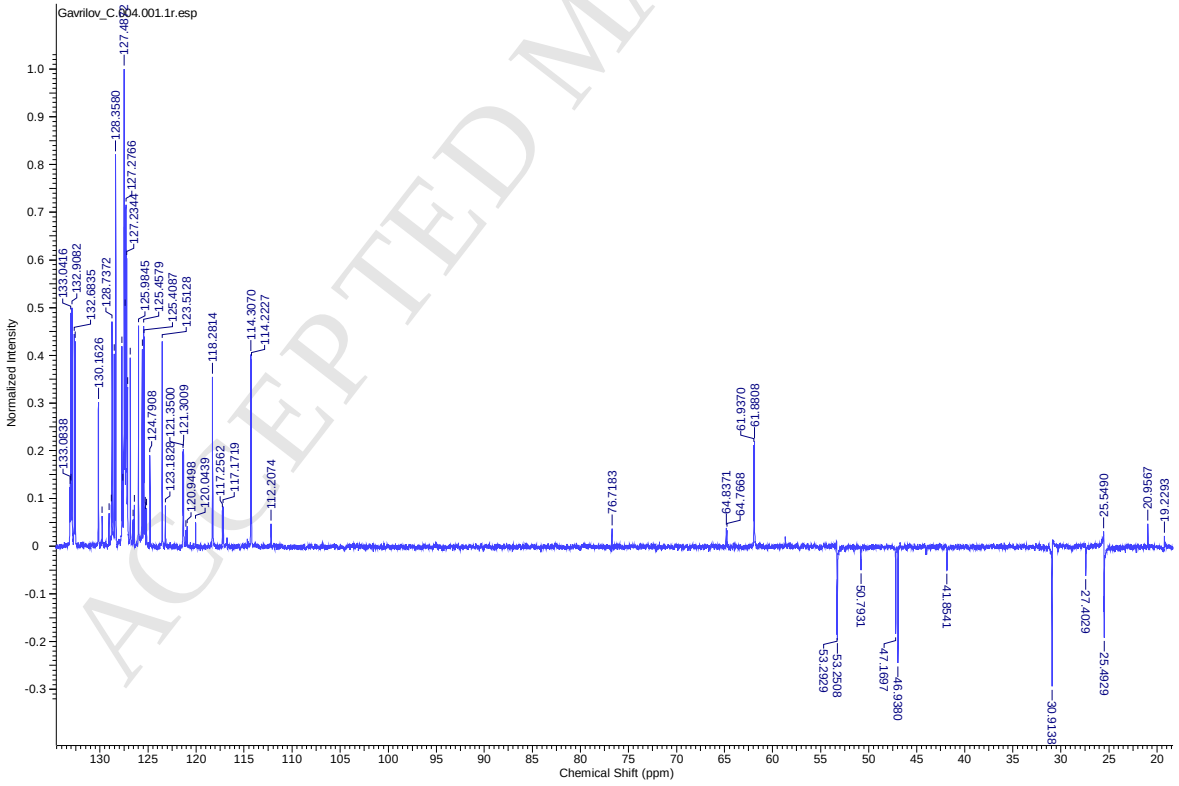
^{1}H NMR (600.13 MHz, $CDCl_3$)



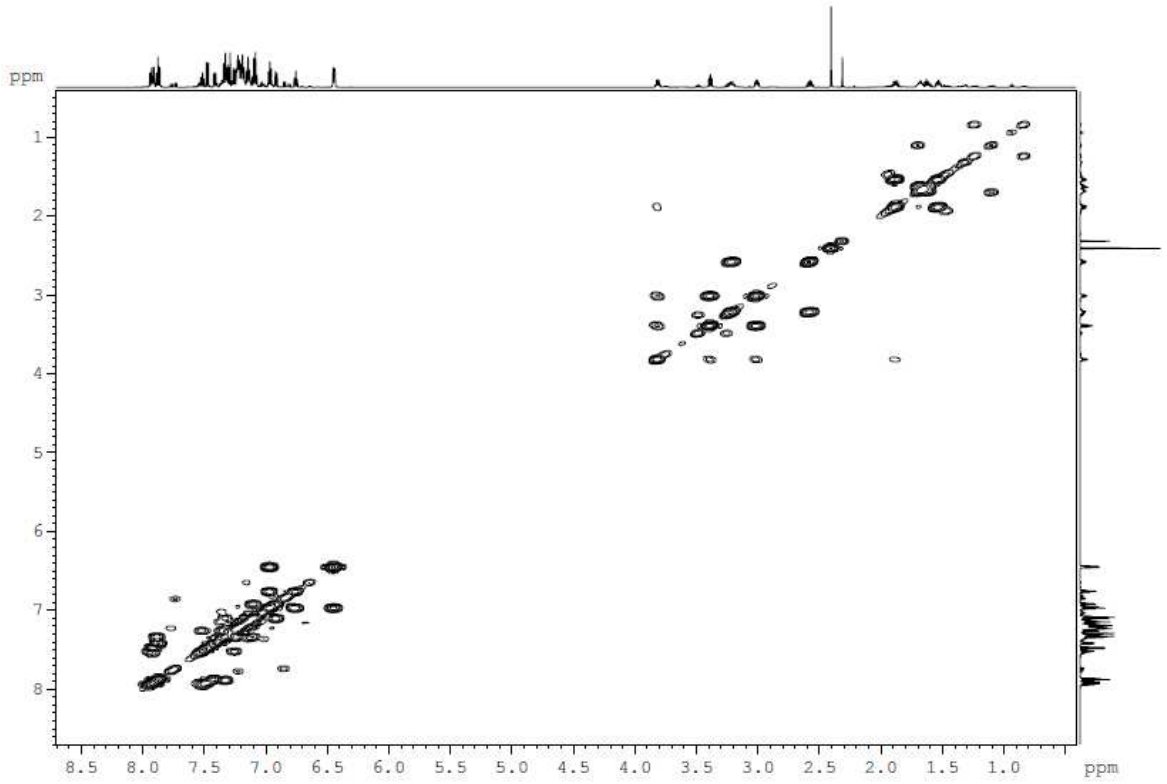
toluene

^{13}C NMR (150.9 MHz, $CDCl_3$)

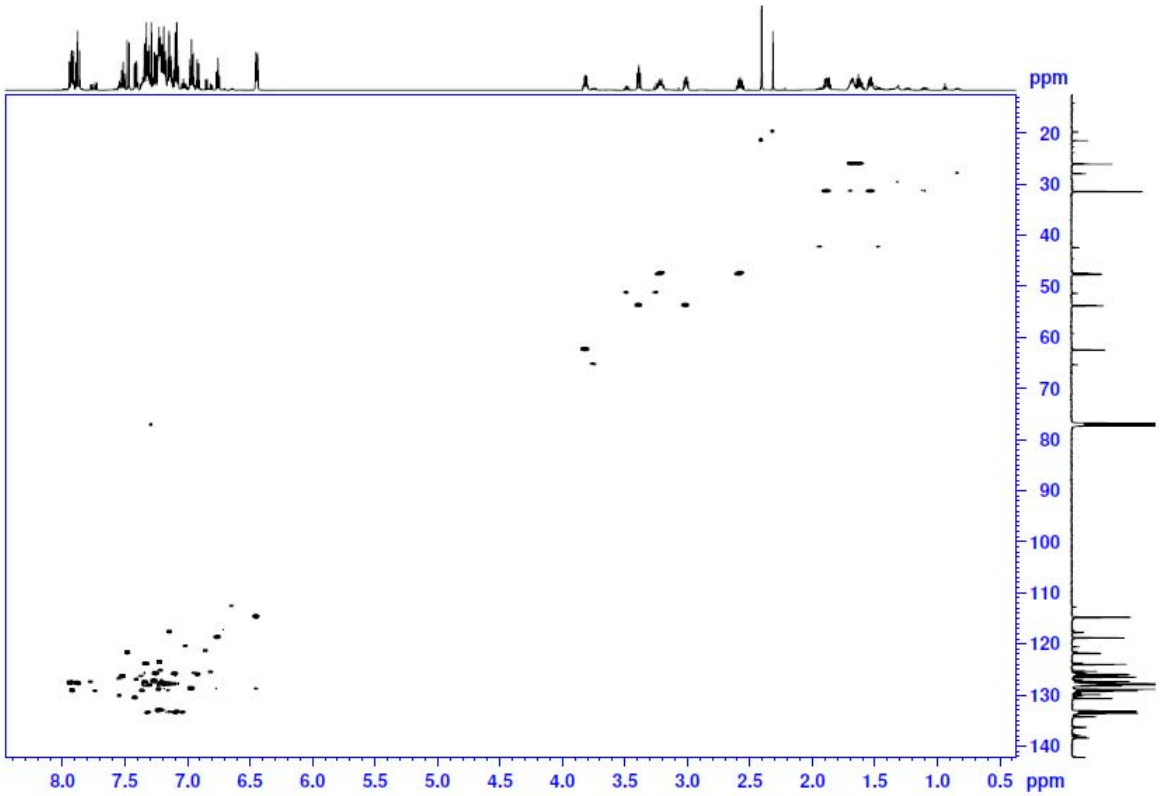




^{1}H -^{1}H 2D COSY (600.13 MHz, $CDCl_3$)

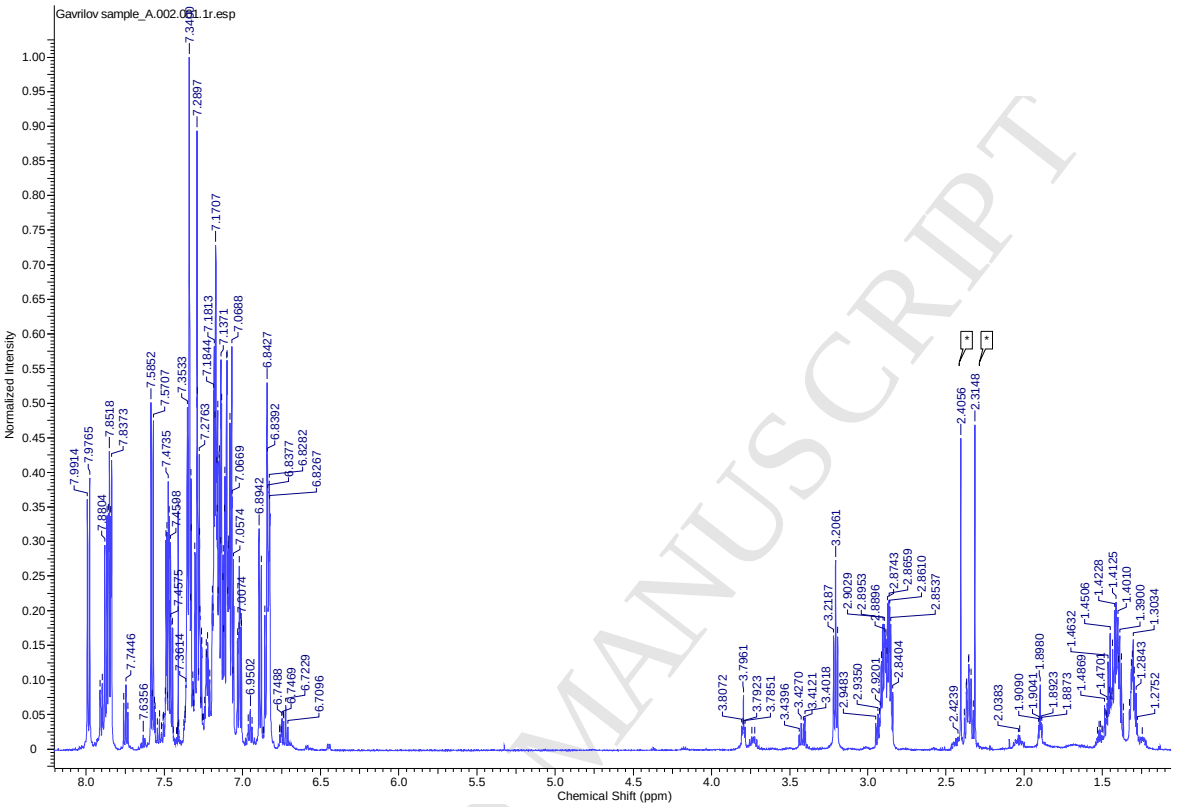


^{1}H -^{13}C HSQC (600.13 and 150.9 MHz, $CDCl_3$)



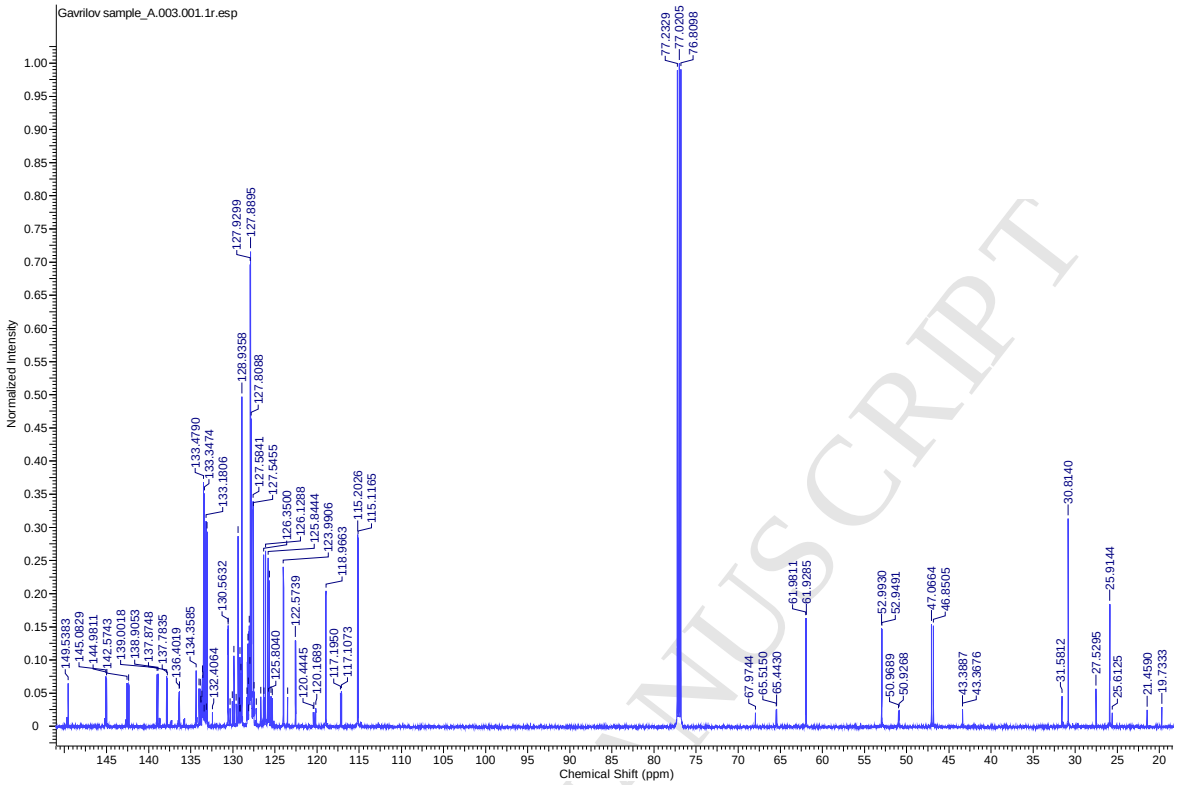
(2*R*,5*S*,S_a)-2-[1-(2-(Diphenylphosphino)naphthalene-1-yl)naphthalene-2-yloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (3g)

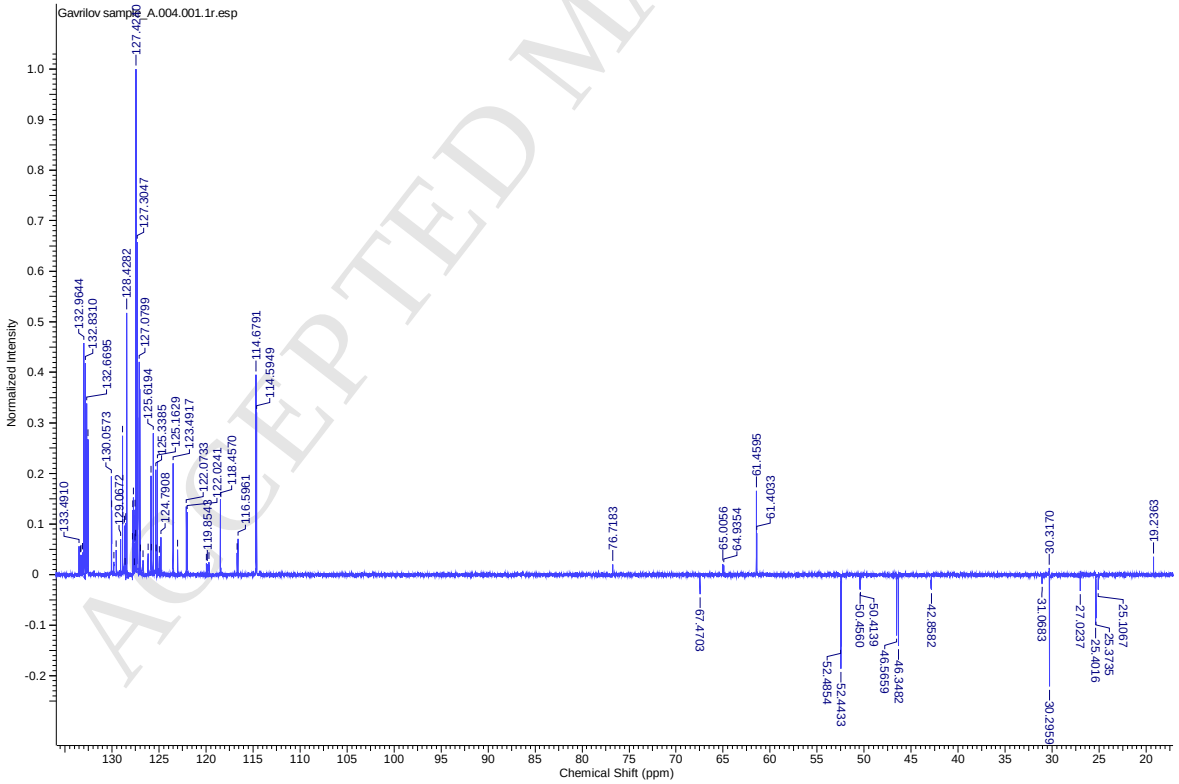
^{1}H NMR (600.13 MHz, $CDCl_3$)



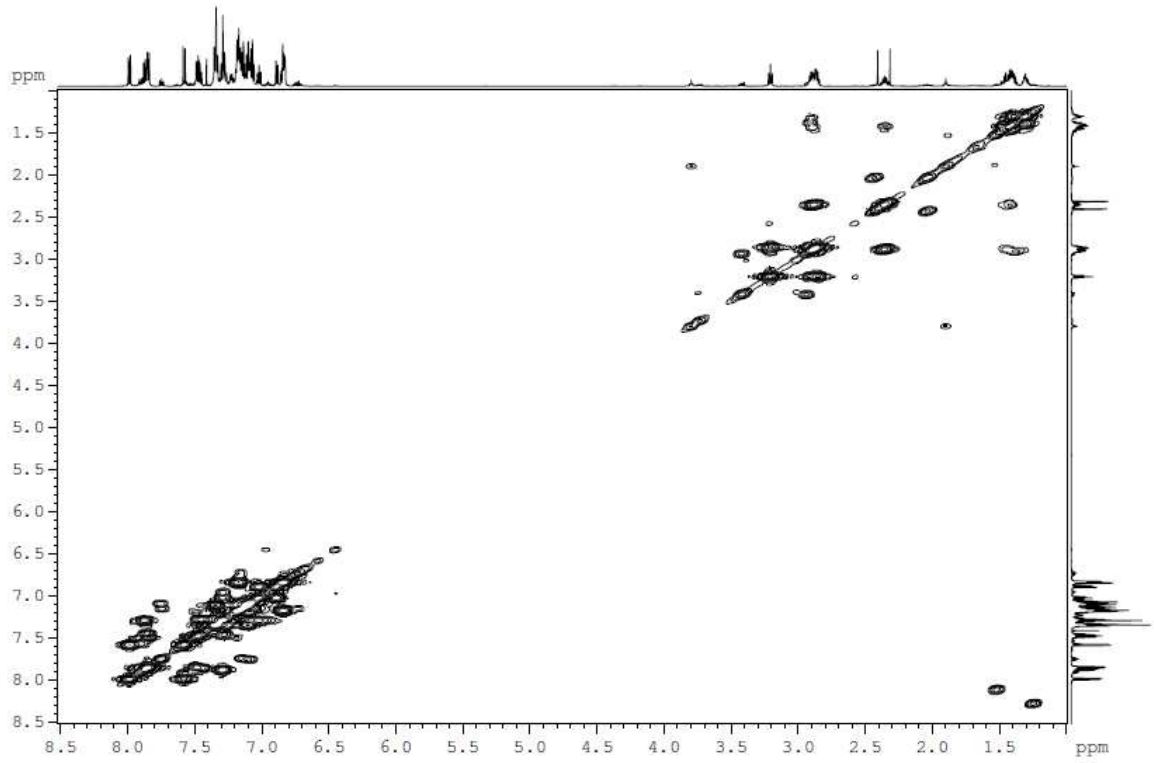
* toluene

^{13}C NMR (150.9 MHz, $CDCl_3$)

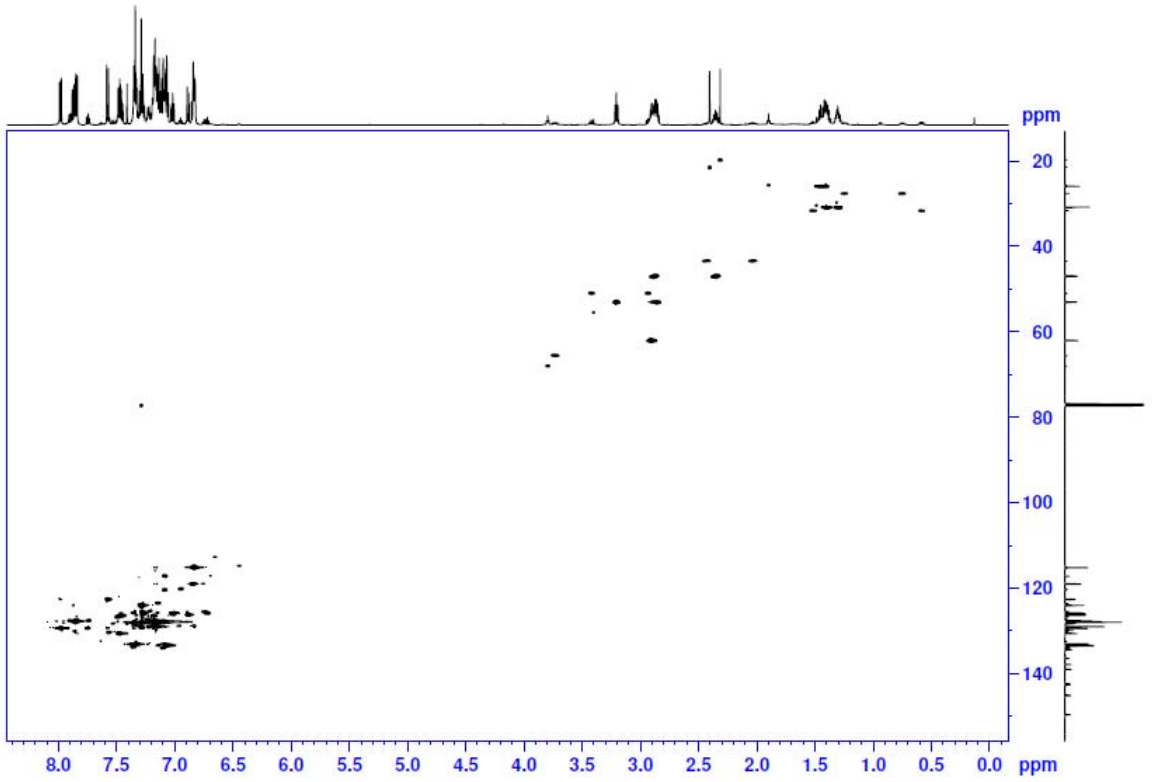




^{1}H -^{1}H 2D COSY (600.13 MHz, $CDCl_3$)

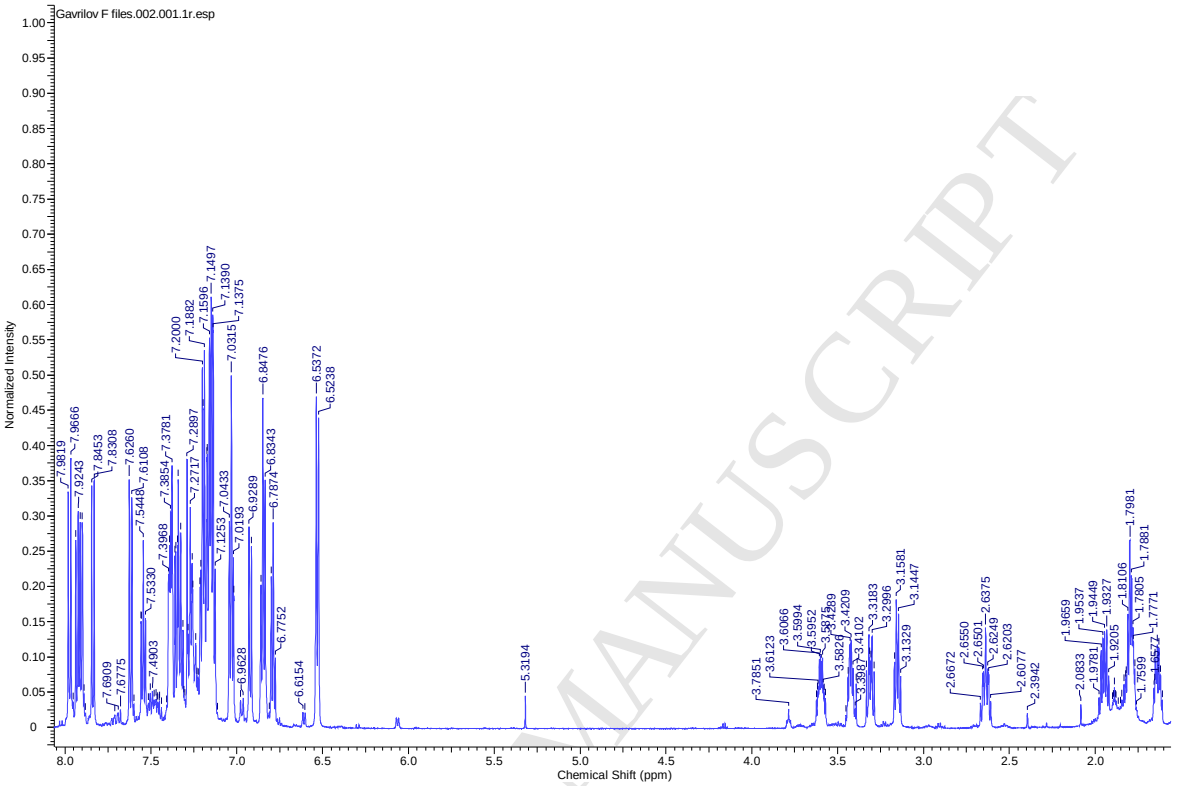


^{1}H -^{13}C HSQC (600.13 and 150.9 MHz, $CDCl_3$)

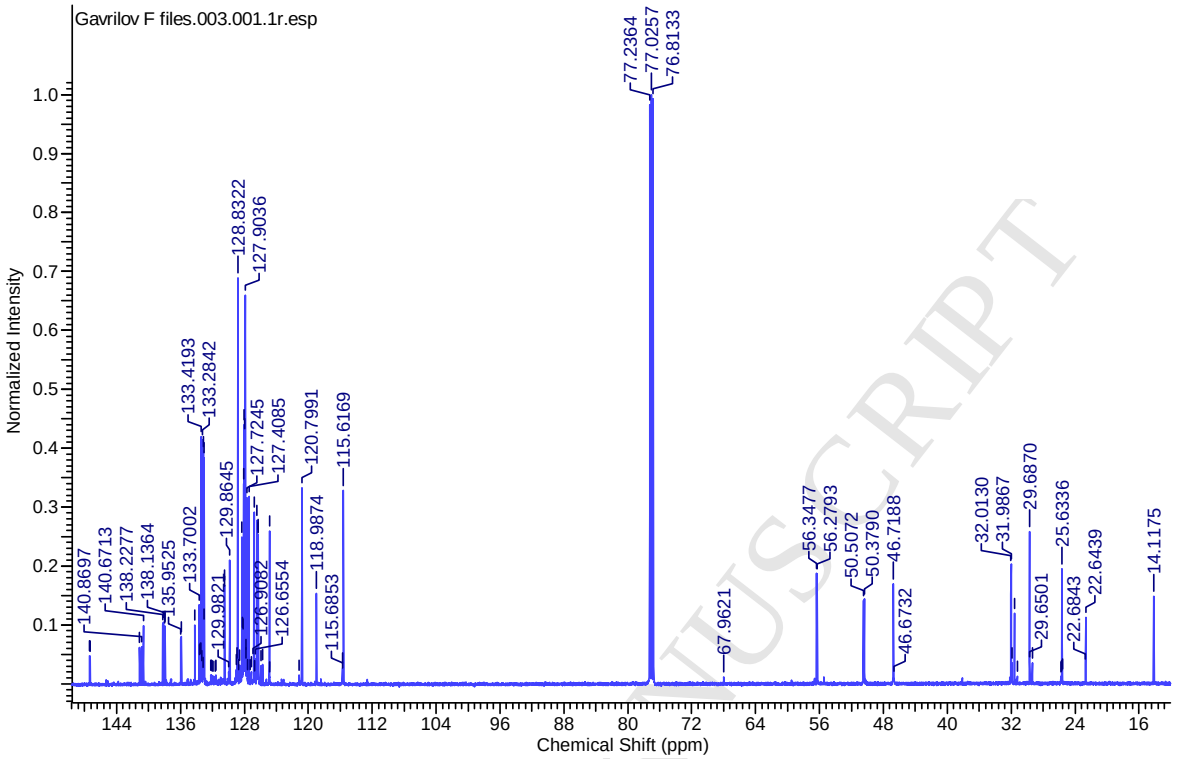


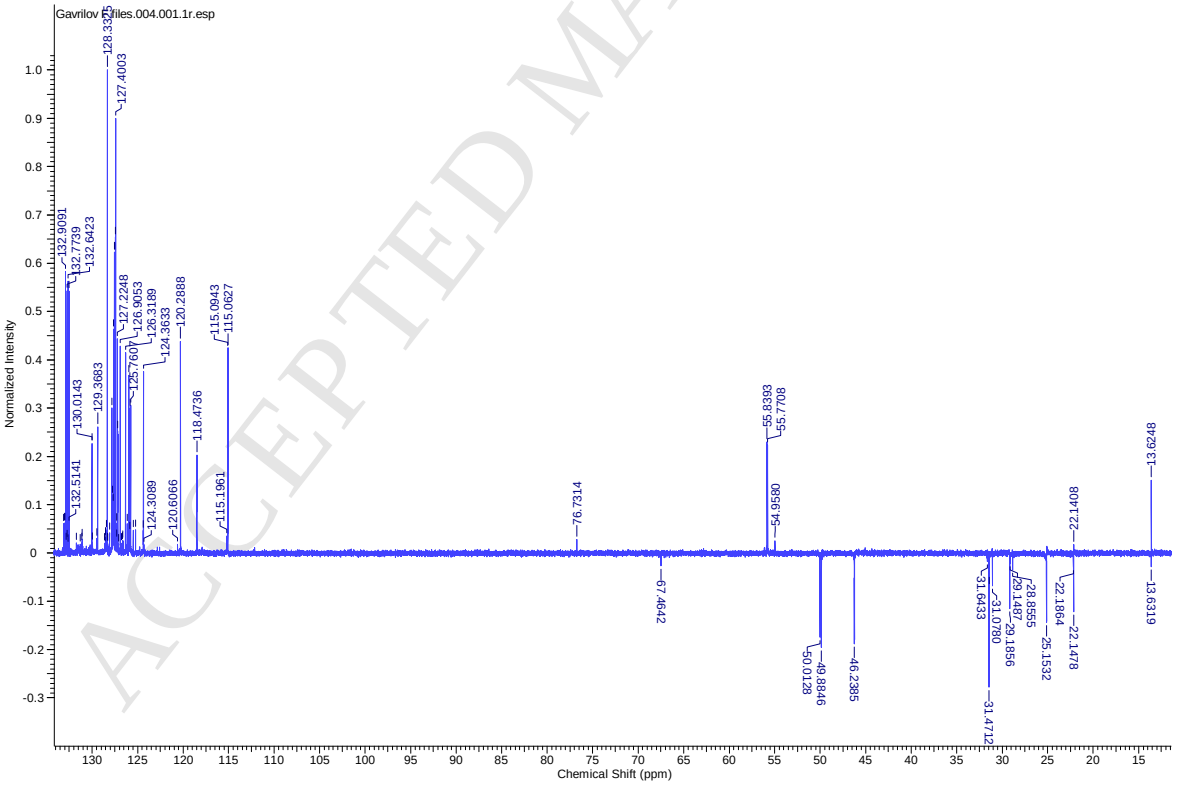
(2*R*,5*S*,R_a)-2-[1-(2-(Diphenylphosphino)naphthalene-1-yl)naphthalene-2-yloxy]-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane-2-oxide (5)

^{1}H NMR (600.13 MHz, $CDCl_3$)

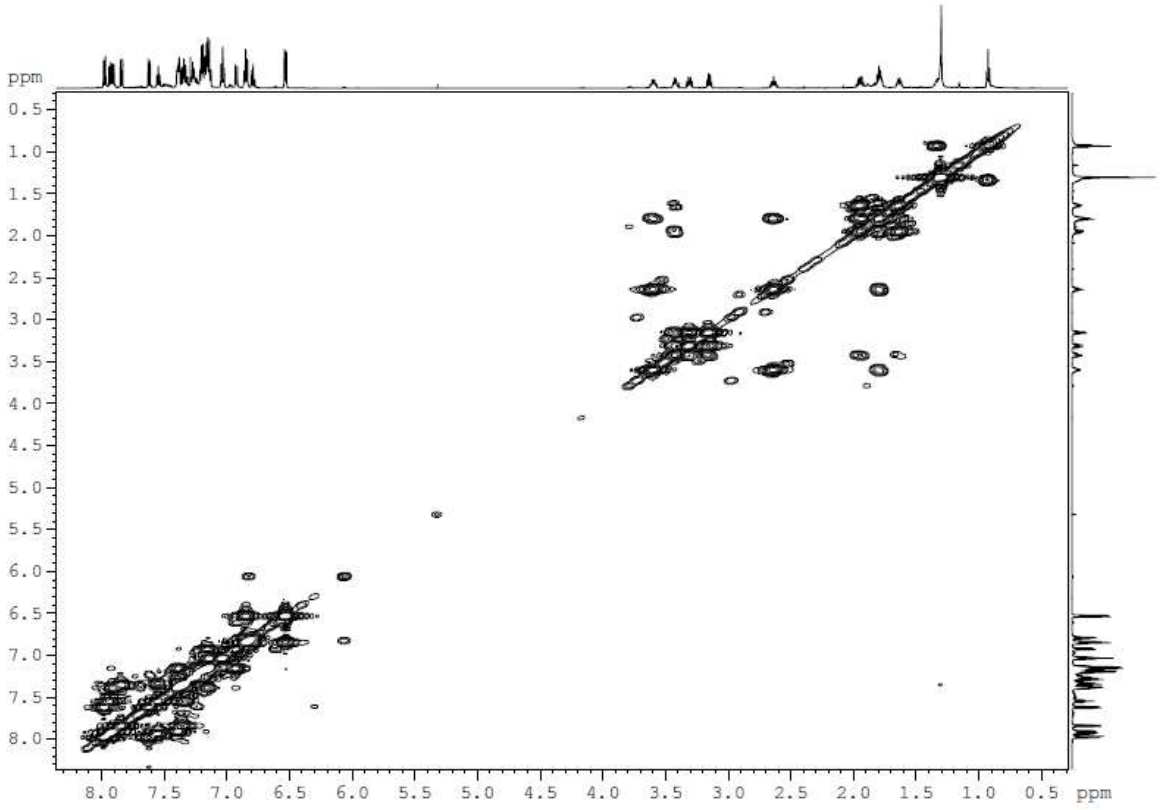


^{13}C NMR (150.9 MHz, $CDCl_3$)

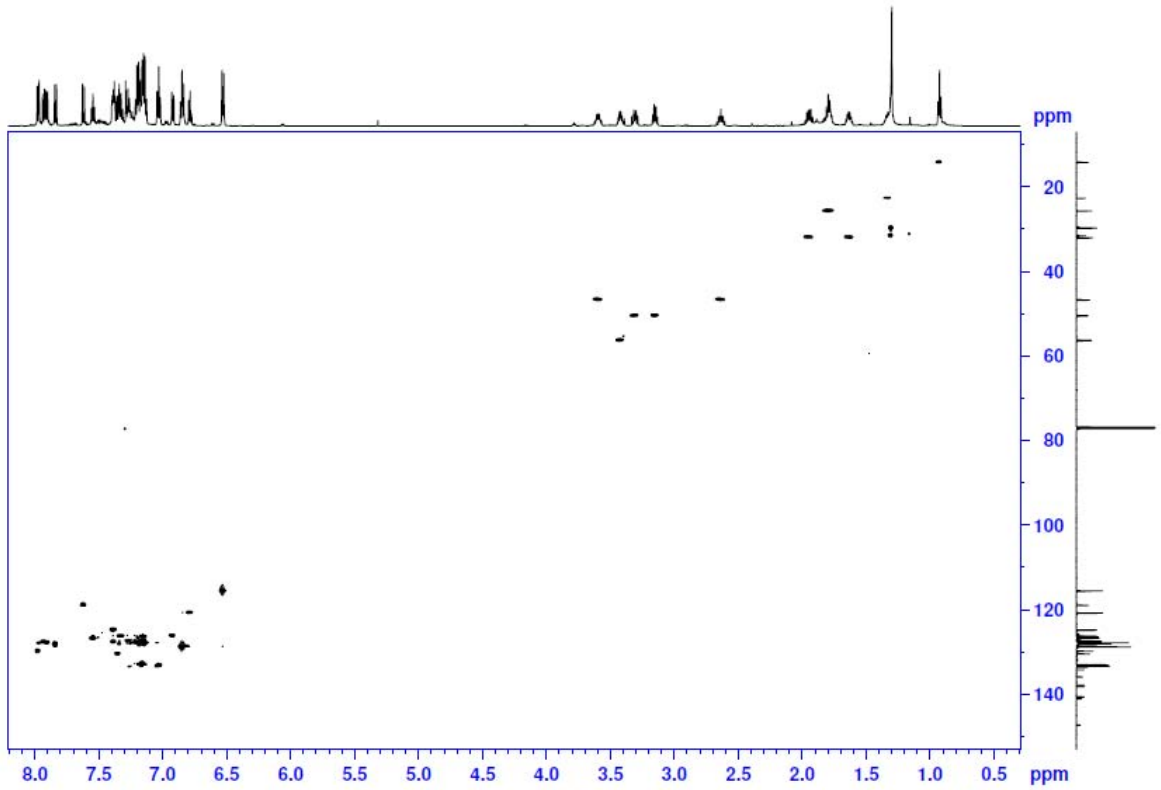




^{1}H -^{1}H 2D COSY (600.13 MHz, $CDCl_3$)



^{1}H -^{13}C HSQC (600.13 and 150.9 MHz, $CDCl_3$)



(±)-HPLC of 3-tosyl-3,3a,6,6a-tetrahydro-2H-cyclopenta[d]oxazol-2-one (11) (racemic) (Kromasil 5-CelluCoat column, C_6H_{14}/*i*-PrOH = 9/1, 2 mL/min, 219 nm, *t*(I) = 13 min, *t*(II) = 17 min)