Palladium allylic complexes with enantiopure bis(diamidophosphite) ligands bearing a cyclohexane-1,2-diamine skeleton as catalysts in the allylic substitution reaction

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ABSTRACT:

A series of cationic allyl palladium complexes [Pd(h3-CH3-C3H5)(P-P)]X (X ¼ PF6, 2a-c, 2e; and X ¼ BPh4, 3a, 3b, 3d, 3e) and [Pd(h3-1,3-Ph2-C3H3)(P-P)]X (X ¼ PF6, 6b; and X ¼ BPh4, 7a) have been prepared. The bis(diamidophosphite) ligands (P-P) contain a diazaphospholidine terminal fragment derived from (R,R)- and (S,S)-N,N'-dibenzyl- and (R,R)-N,N'-dimethyl-cyclohexane-1,2-diamines and dialcoxy bridging fragment derived from (R,R)- and (S,S)-butanediol, (R,R)-cyclohexanediol, (4R,5R)- and (4S,5S)-4,5- di(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane and (R)- and (S)-binaphthol. Complexes [Pd(h3-CH3- C3H5l)P2]X (X ¼ PF6, 4f, 4g; and X ¼ BPh4, 5f), where P are monodentate diamidophosphite ligands with diazaphospholidine heterocyclic backbone obtained from (R,R)- and (S,S)-N,N'-dibenzylcyclohexane-1,2- diamine and alcoxy groups coming from (R)-phenyl-ethanol and (S)-borneol have been also prepared. Neutral palladium complexes [PdCl2(P-P)] (1a, 1c) were synthesized to prove the C2 symmetry of the P-P ligand. The new compounds were fully characterized in solution by NMR spectroscopy. The X-ray crystal structure determination for 2e-(R,R,Ral,Ral;R,R) and 1a-(S,S;Sal,Sal;S,S) has been achieved.

The new allyl-palladium complexes were applied in the asymmetric allylic substitution reaction of the benchmark substrate rac-3-acetoxy-1,3-diphenyl-1-propene with dimethyl malonate and benzylamine as nucleophiles in order to test their catalytic potential. The best results were obtained with the 3a-(R,R;Ral,- Ral;R,R) precursor (up to 84% ee) while complexes with the e ligand derived from the (R,R)-N,N'-dimethylcyclohexane- 1,2-diamine terminal fragment resulted inactive in the process. The influence of the nature and the absolute configuration of both the bridging and the terminal fragments of the bis(diamidophosphite) ligand on the asymmetric induction is discussed. A preliminary study of the anion effect (PF6 vs. BPh4 -) on the activity and the enantioselectivity of the Pd-catalysed allylic substitution has also been performed.

1. INTRODUCTION

The palladium-catalyzed asymmetric allylic substitution is a useful synthetic method for enantioselective formation of carboncarbon and carbon-heteroatom bonds [1]. The wide variety of chiral ligands for highly enantioselective allylic substitutions includes bidentate P- or N-based ligands, mixed bidentate P-N, P-S and P-P0 ligands and monodentate phosphorus donors [2]. Among P-donor ligands those with P-heteroatom bonds, such as phosphites (3P-O), phosphoramidites (2P-O, 1P-N) and diamidophosphites (2P-N, 1P-O) are good alternatives to chiral phosphines (3P-C), because they can be obtained straightforwardly through a modular approach by reacting chiral alcohols or amines with phosphorus halides, providing families of ligands with a large structural and stereochemical diversity. They also provide ample opportunity for fine-tuning their donor-acceptor and steric properties by incorporation of an heteroatom directly bound to the phosphorus atom and variation of the O- and N-containing chiral building blocks as well as the substituents on the N atom [3]. Bidentate phosphites [4] and mono- [5] and bisphosphoramidites [6] have been successfully applied in allylic alkylation reaction. The use of diamidophosphites is mostly focused on the P-stereogenic bis(diamidophosphite) ligands with 1,3,2-diazaphospholidine rings and several diols such as 1,4:3,6 dianhydro-D-manitol [7], N-benzyltartarimide [8], N-naphthyltartarimide [9], binaphthol [10], resorcinol and hydroquinone [11] as frameworks. Monodentate Pstereogenic diamidophosphites have also been found to be efficient ligands for palladium catalyzed asymmetric allylic substitution [12]. All of them contain a cyclic structure in which the phosphorus atom is part of the heterocyclic ring, this feature is responsible for an increase in ligand stability.

We have been interested in the synthesis of enantiopure monodentate and bidentate diamodophosphite ligands with heterocyclic fragments derived from N,N'-substituted cyclohexyldiamine and N,N'-dimethyl-1,1'-binaphthyldiamine and several chiral alcoxy groups.We have recently described the application of two different families of monodentate diamidophosphite ligands in the asymmetric Pd-catalyzed hydrovinylation reaction [13] and in the allylic substitution in ionic liquids [14]. The bidentate C2 diamidophosphite ligandswere applied in the Rh-catalyzed asymmetric hydrogenation of benchmark olefins attaining excellent enantioselectivities with most of them [15]. Cationc palladium complexes with bis(diamidophosphite) ligands containing N,N'-dimethyl-1,1'-binaphthyldiamine as heterocyclic terminal fragment have been tested as catalyitic precursors in the allylic substitution process affording enantiomeric excesses of up to 85% [16]. These results prompted us to explore the performance of the similar N,N'-substituted cyclohexyldiamine diamidophosphite ligands in the same reaction.

In this paper we describe the synthesis and characterization of new cationic methallyl palladium complexes [Pd(h3-2-CH3- C3H5)(P-P)][X], and [Pd(h3-2-CH3-C3H5)P2][X] with X ¼ PF6 or BPh4 , with the new cyclohexyldiamine based ligands a-(S,S;Sal,Sal; S), b-(R,R;Sal,Sal;R,R), c-(R,R;Ral;R,R) and e-(R,R;Ral,Ral;R,R). and the previously described ligands [15] as shown in Fig. 1. Not many examples of the coordination chemistry of this kind of ligands have been reported in the

literature so far [7a,13,16,17]. The new cationic palladium complexes have been used as catalytic precursors in the Pd-asymmetric allylic alkylation and amination of the model substrate, rac-3-acetoxy-1,3-diphenyl-1-propene, with the anion derived from dimethyl malonate and benzylamine as nucleophiles.

This group of complexes was suitable for the comparison of the influence of the nature and absolute configuration of both the terminal and bridging fragments of the bis(diamidophosphite) ligands on the asymmetric induction. In addition the effect of the different BPh_4^- and PF_6^- anions on the activity and enantioselectivity of the reaction has been evaluated. Moreover the importance of the monodentate or bidentate nature of the ligands and their influence on the activity and selectivity of the process can be discussed.

2. RESULTS AND DISCUSSION

2.1. Synthesis and characterization of diamidophosphite ligands

The new chiral C2-symmetric bis(diamidophosphite) ligands a, b, c, d and e depicted in Fig. 1 were synthesised via two consecutive condensation reactions from enantiomerically pure diamines and the corresponding diols in the presence of a base following our previously reported methods [15,16]. The chiral monodentate diamidophosphite ligands f and g (Fig. 1) were prepared as previously described by us [13]. As extensive manipulation led to ligand decomposition, they were used without purification in the formation of the corresponding palladium complexes. The preparation and characterization of the new a-(S,S;Sal,Sal;S,S), b-(R,R;Sal,Sal;R,R), c-(R,R;Ral;R,R) and e-(R,R;Ral,Ral;R,R) ligands is reported in the experimental section of this paper.

2.2. Synthesis and characterization of neutral complexes [PdCl2(PP)]

The reaction between [PdCl2(COD)] and two selected bis(diamidophosphite) ligands was studied in order to evaluate the coordination and the structural features of the ligands in an ideal environment of C2 symmetry. The reaction of equimolar amounts of the corresponding bis(diamidophosphite) (a-(S,S;Sal,Sal;S,S) or c- (R,R;Sal;R,R)) and [PdCl2(COD)] in toluene/dichloromethane solution at room temperature gave nearly quantitative yields of [PdCl2(P-P)], 1a-(S,S;Sal,Sal;S,S) and 1c-(R,R;Sal;R,R) (Scheme 1).

The 31P NMR spectra of the palladium complexes showed one phosphorus resonance at 111.4 ppm for 1a and at 101.7 ppm for 1c, shifted upfield with respect to the corresponding free bis(diamidophosphite) ligand and suggesting that the C2 symmetry of the free ligand is maintained upon coordination to the PdCl2 fragment. 13C NMR spectra for 1a and 1c showed the expected two signals for the four chiral carbon atoms of the cyclohexyldiamine ring. However, the signals of the four benzylic carbon atoms appeared as two pseudotriplets arising from the overlap of two doublets with very similar chemical shift and coupling constant (JCP ~7 Hz) indicating certain loss of the expected symmetry. It should be noted that the corresponding free ligands showed two doublets with very different coupling constants (about 40 and 20 Hz) [15]. 1H NMR for 1a and 1c showed more than four sets of signals belonging to the eight benzylic protons probably because of a different disposition of the aromatic rings of the benzylic groups in solution and in accordance with a partial loss of the symmetry of the ligand.

2.3. Synthesis and characterization of cationic allylpalladium complexes [Pd(h3-2-CH3-C3H4)(P-P)]X and [Pd(h3-2-CH3-C3H4)]P2]X

Reaction of the organometallic precursor [Pd(h3-2-CH3-C3H4)(m-Cl)]2 with the appropriate amount of ligand (2 equivalents for a-e, 4 equivalents for f-g) in the presence of an excess of sodium hexafluorophosphate afforded ionic allylpalladium complexes of general formula [Pd(h3-2-CH3-C3H4)(P-P)]PF6 (2a-c and 2e) and [Pd(h3-2-CH3-C3H4)]P2]PF6 (4f and 4g) (Scheme 2). Some

compounds with the BPh4 counterion, [Pd(h3-2-CH3-C3H4)(P-P)]BPh4 (3a, 3b, 3d and 3e) and [Pd(h3-2-CH3-C3H4)P2]BPh4 (5f) were also prepared by addition of a little excess of NaBPh4 in MeOH to a dichloromethane solution of the hexafluorophosphate compound.

The new compounds were obtained as white yellow solids in low to moderate yields, stable under inert atmosphere at room temperature and fully characterized in solid state and in solution by the usual techniques. Relevant NMR data are summarized in Table 1. 31P NMR spectroscopy confirms the existence of only one isomer in both kind of cationic complexes. Two sharp doublets showing a roof effect are observed in all compounds, indicating the loss of C2 symmetry of the Pd(P-P) or the PdP2 fragment in the presence of the allyl ligand as described for related cationic palladium methallyl bis(diamidosphosphite) [16] or monodentate diamidophosphite complexes [14,17]. Upon coordination to the palladium atom, the phosphorus atoms in both bidentate and monodentate diamidophosphite experience an upfield shift (5e17 ppm) with respect to the free ligand, probably due to their relative low s-donor character based on the high JPSe value previously reported [13,15]. Complexes containing different diastereoisomers of the same ligand, 2a-(S,S;Sal,Sal;S,S) and 2a- (R,R;Sal,Sal;R,R), 2b-(R,R;Ral,Ral;R,R) and 2b-R,R;Sal,Sal;R,R), 2c- (R,R;Ral;R,R) and 2c-R,R;Sal;R,R), showed slightly different 31P chemical shift and 2JPP coupling constants.

Bidimensional HSQC 1H-13C experiments were necessary to unequivocally assign 1H and 13C NMR spectra. 1H NMR spectra revealed the existence of a single palladium-allyl isomer for each complex, showing four signals for the terminal hydrogen atoms of the allyl moiety in accordance with the lack of symmetry of the complexes. The two signals of the anti protons usually appeared as doublets due to the coupling with the phosphorus atom in trans position (2a, 2b, 2e, 3a, 3b, 3d, 3e, 4f and 5f) while the two syn protons were observed as two broad singlets, but as doublets in 2b with smaller values of JHP compared to the anti ones. Obviously, the lack of symmetry can also be seen for the signals of the diamidophosphite ligands in complexes 2 and 3, giving some duplicated proton signals relative to the free ligands. All diastereotopic benzylic protons of the benzylcyclohexil fragment are different and accordingly up to six sets of signals are seen in the case of both diastereoisomers of 2c and five for 3d-(R,R;Ral,Ral;R,R). Some of these signals are well defined showing a triplet or a doublet of doublets pattern indicating that the diastereotopic benzylic protons have different coupling constants 3JPH. In complexes with the methylcyclohexil terminal fragment (2e and 3e), N-methyl protons appear as four doublets but in this case with very similar coupling constant values (3JHP around 15.0 Hz). Proton signals of the monodentate diamidophosphite ligands f and g are also duplicated in the spectrum of the allyl-palladium complexes 4f, 5f and 4g. It is worth noting that all the signals of cationic complexes containing BPh4 anion (3a, 3b, 3e and 5f) are shifted upfield compared to the corresponding complexes with PF6 anion (2a, 2b, 2e and 4f). This may be attributed to the local anisotropic effects associated with the presence of the phenyl groups in the BPh4 close enough to the complex cation in CDCl3 to shift the signals upfield. Similar results have been already reported in the literature for allyl-palladium complexes with nitrogen donor ligands suggesting ion-pairing in CDCl3 solution [19].

13C NMR spectra of palladium complexes with bidentate and monodentate diamidophosphite ligands show the terminal allylic carbon atoms as two well resolved doublet of doublets or broad doublets and the central carbon atom as a pseudotriplet because of the coupling with both phosphorus atoms. The larger differences between the chemical shifts of the terminal allylic carbon atoms appear in 2c-(R,R;Sal;R,R) (2.6 ppm) and in 4g-(R,R;Sal) (4.5 ppm). As reported in the experimental part, 13C NMR spectra show four doublets with two different coupling constant values corresponding to the benzylic carbon substituent of the cyclohexilamine fragment (2a-c, 3a, 3b, 3d, 4f, 5f and 4g) as well as for the methyl substituent in complexes with e ligand suggesting different orientations of these amino substituents with respect to the P-Pd bond as it has been previously reported [12,16,19].
Bidimensional NOESY experiments were performed for all the complexes (see supporting material). Only for complexes 2c- (R,R;Sal;R,R), 2e-(R,R;Ral,Ral;R,R) and 3e-(R,R;Ral,Ral;R,R) NOE contacts between the allyl fragment and the bis(diamidophosphite) ligand can be observed (see Fig. 2). Moreover in the NOESY experiment of 2e-(R,R;Ral,Ral;R,R) exchange signals between Hsyn- Hsyn, Hanti-Hanti, and Hsyn-Hanti protons were detected indicating that the dynamic behaviour takes place through the two well-known pseudorotation and h3-h1-h3 mechanisms [13,16]. On the other hand exchange signals between NMe groups have been also detected.

2.4. X-ray structures of 1a-(S,S;Sal,Sal;S,S) and 2e-(R,R;Ral,Ral;R,R)

Single crystals of 1a-(S,S;Sal,Sal;S,S) and 2e-(R,R;Ral,Ral;R,R) suitable for X-ray analysis were obtained by slow diffusion of hexane into a saturated dichloromethane solution of the complexes at room temperature or at 4 °C respectively. The molecular structure and a selection of bond lengths and angles are shown in Fig. 3 (1a- (S,S;Sal,Sal;S,S)) and Fig. 4 (2e-(R,R;Ral,Ral;R,R)). Both complexes have a slight distorted square planar geometry around the palladium atom. Bond distances and angles in the coordination sphere are in the range described for related cationic allyl palladium complexes [14,16].
The structure for 1a-(S,S;Sal,Sal;S,S) consists of discrete units of the neutral compound separated by typical van derWaals distances and is depicted in Fig. 3. The sligthly distorted square planar coordination of [PdP2Cl2] in 1a, showed the P-Pd-P bite angle close to 90° (90.76(4)°) and for the Cl-Pd-Cl angle a value of 92.43(4)° . The bridge of the bis(diamidophosphite) ligand is symmetrically located in relation to the coordination plane but the arrangement of the benzyl groups is not identical in each moiety of the ligand (Fig. 3b). The aromatic rings of the benzyl substituents of N3 and N4 are situated above and below the plane defined by atoms N4P2N3, with a trans disposition, while those of N1 and N2 are placed on the same side of the plane defined by atoms N1P1N2, with a cis disposition. This fact is also reflected, as depicted above, in the 1H NMR spectrum of the neutral complex in solution, in which more than four signals for the benzylic protons appear.
The structure for 2e-(R,R;Ral,Ral;R,R) consists of two similar non-equivalent discrete units of the cationic complex and hexafluorophosphate anions separated by typical van der Waals distances. One of the organometallic cations is depicted in Fig. 4. The two terminal carbon atoms of the allyl group are

approximately equidistant from the palladium centre. Moreover, the carboncarbon bond lengths of the h3-allyl group are nearly equal, which is in accordance with the similar chemical shifts observed in the 13C NMR spectra. No significant rotated orientation of the allyl group around the Pd-allyl axis is observed. The bite angle P-Pd-P is 102.51(9)° while the Ct-Pd-Ct angle is 67.4(4)° . This bite angle is smaller than that observed for the allylic complex containing a similar bidentate diamidophosphite ligand with the same bridge but with the bisdimethylbinaphthyldiamine terminal fragment (105.60(3)°) [16] and markedly different than that observed for complex 1a. This fact indicates that the presence of the two chlorine atoms leads to a narrower bite angle.

For both compounds the Pd-P distance is dependent on the bite angle of the ligand. As described by van Leeuwen and coworkers [20] for allylpalladium complexes with bidentate diphosphines a smaller bite angle results in a smaller Pd-P distance. It is 2.2172(11) Å for 1a and 2.276(2) Å for 2e. From the limited number of structures containing the PNNO skeleton, it should be noted that the P-N bond distances of the bis(diamidophosphite) coordinated ligand in complexes 2e and 1a are in the range of those described for both either mono and bidentate diamidophosphites in neutral and cationic allylic palladium complexes [13,14,16] and in boranediamidophosphite compounds [21]. The P-N bond distances for both compounds range between 1.641 Å and 1.678 Å and suggest partial multiple-bond character when compared to the normally accepted bond lengths (P-N bond, 1.77 Å and P]N bond 1.57 Å) [22]. Moreover the P-N bond lengths of the coordinated bis(diamidophosphite) ligands are smaller than those observed for similar free ligands [23].

2.5. Asymmetric allylic substitution reactions

To evaluate the potential of diamidophosphite ligands a-g in the asymmetric allylic substitution, the cationic palladium complexes [Pd(h3-2-CH3-C3H4)(P-P)]X, 2a-c, 3a, 3b, 3d, 3e, and [Pd(h3-2-CH3-C3H4)P2]X, 4f, 4g and 5f, were tested as catalytic precursors using the model substrate rac-3-acetoxy-1,3-diphenyl-1-propene (rac-I), with sodium dimethyl malonate and benzylamine as nucleophiles (Scheme 3). The reactions were performed in CH2Cl2 at room temperature for 24 h. Under these conditions, the allylic acetate rac-I was converted to the desired products II or III in variable yields. The results are summarized in Table 2.

When palladium complexes [Pd(h3-2-CH3-C3H4)(P-P)]X and [Pd(h3-2-CH3-C3H4)(P)2]X are used as precursors in the allylic alkylation reaction the conversion of the allylic acetate rac-I to the desired product II takes place in moderate to good yields (50e100% at 24 h reaction time). In general terms, the activity is lower than that reported for complexes with similar diamidophosphite ligands but with a terminal fragment derived from binaphtyldiamine [16]. Complexes 1e and 2e containing the methyl substituent in the cyclohexyldiamine fragment of the ligand were not active. This fact contrasts with the results of Wills et al., who reported that with similar monodentate diamidophosphine ligands the best activity and enantioselectivity was obtained with the N-methylated ligands [24].

A wide range of enantioselectivities (20e86% ee) was obtained with all the precursors tested in this work. The highest ee values appeared with complexes containing both diastereoisomers of a and the d ligands, which contain the shorter butanediol and ciclohexanediol bridging fragments (entries 1-4 and 11). In contrast, when the precursors contain the diamiophosphite ligand with the binaphthyldiamine terminal fragment the enantioselectivity increases when the bridging fragment is the long and rigid binaphtol, and decreases with the short and flexible bridging fragment derived from butanediol [16]. The absolute configuration of the reaction product II is determined by the absolute configuration of the carbons of the benzylcyclohexanediamine terminal group. In contrast, ligands with more rigid binaphtol bridge, this element determines the absolute configuration of the reaction product (entries 8 and 9).

A significant match-mismatch effect was observed between the configuration of the benzylcyclohexyldiamine and the diol derived bridge within each pair of the diastereoisomers of the ligands (entries 1 vs 2, 5 vs 6 and 8 vs 9) with 2a-(R,R;Sal,Sal;R,R), 2b- (R,R;Sal,Sal;R,R) and 2c-(R,R;Sal;R,R) being the matched combination with the hexafluorophosphate counterion. Matched and mismatched combinations of chirality elements were also found for similar ligands containing the binaphtyldiamine terminal fragment [16] and for P-stereogenic bis(diamidophosphite)-related ligands [10].

The allylic alkylation reaction catalyzed with palladium complexes stabilized by monodentate ligands [25] has been less studied. The results obtained with allyl palladium precursors [Pd(h3-2- CH3-C3H4)P2]X, 4f, 4g and 5f are also summarized in Table 2. Under the same catalytic conditions, up to 100% conversions were reached but with very low enantioselectivies. Here, the configuration of the major enantiomer was determined by the configuration of the cyclohexyldiamine fragment (entries 11 vs. 12). Therefore a beneficial effect for the asymmetric allylic alkylation reaction in terms of activity is observed for monodentate versus bidentate diamidophosphite ligands but does not happen the same for the enantioselectivity. These results contrast with those observed with cationic palladium complexes containing two similar monodentate diamidophosphites but with binaphthydiamine terminal fragments [16] and with monodentate P-stereogenic phosphanes [26]. Gavrilov [7e11,27] has applied libraries of bidentate P-stereogenic diamidophosphite ligands with 1,3,2-dizaphospholidine rings as terminal fragments and several diol-derived bridging fragments to the palladium-catalyzed asymmetric allylic alkylation process, achieving lower activity and better enantioselectivity than those described in this paper. The presence of the stereogenic phosphorous atom included in a rigid cycle attached to the metallic center may enhance the enantioselectivity of the catalytic systems.

Considering that some reports [18,28,29] describe that different counterions can affect the activity and enantioselectivity of the process, we compared the results obtained in the allylic alkylation reaction with complexes 2 and 3, which contain the hexafluorophosphate and tetraphenylborate respectively. In particular, comparing the results with the pair of complexes 2a-(S,S;Sal,Sal;S,S) and 3a-(S,S;Sal,Sal;S,S) better activity and enantioselectivity was obtained in the presence of the BPh_4 anion (entry 2 vs. 4) but the opposite was observed with precursors 2b-(R,R;Ral,Ral;R,R) and 3b-

(R,R;Ral,Ral;R,R) (entries 6 and 7). Literature concerned with anion effects in homogeneous catalysis suggests that larger boron anions can sometimes afford faster reactions [18]. Pregosin and coworkers [28] describe a substantial amount of ion pairing in dichlorometane solution and that the external BPh4 anion tends to be located in a remote position with respect the coordinated allyl ligand, so it is not surprising to find different anion effects between complexes containing different bisdiamidophosphite ligands.

We also tested the catalytic behaviour of the preformed complexes 2 and 3 in the allylic amination of rac-I using benzylamine as nucleophile. The results obtained are shown in Table 2. Similar or better activity is obtained in the amination than in the alkylation process with all the precursors except for 2a-(R,R;Sal,Sal;R,R) and 2b. Regarding the enantioselectivity, with complexes with diamidophosphites a and c similar or lower ee values are obtained respect to the alkylation process while those precursors with b ligand similar or higher values were found.

In general terms it can concluded that precursors with the BPh4 anion lead to better activities and that the best catalytic performance is obtained with 3a complexes in both alkylation and amination reactions. It is important to recall that the absolute configuration of the amination product with precursors containing ligands a and b is the same as for the alkylation reaction, although the CIP descriptor is inverted because of the change in the priority of the groups. However, in the case of the precursor 2c-(R,R;Sal;R,R) there is a change in the sense of the asymmetric induction between alkylation and amination (entry 7). This result is unexpected but has already been reported with phosphite [4c], phosphoramidite [30], diphosphine [31], and also diamidophosphite ligands. [7a,16].

Due to the low enantioselectivies attained in the alkylation process with monodentate diamidophosphite ligands, the study of the amination reaction with these precursors was not performed.

Complexes 2a and 2c were tested as catalyitic precursors using the cyclic substrate rac-3-acetoxy-1-cyclohexene (rac-IV), which is usually used as a model cyclic substrate, under the same conditions described above for the open acetate rac-I (Scheme 4).

The catalytic systems are less active and selective with the cyclic rac-IV substrate than with the model rac-I one in this process, achieving lower conversions and enantioselectivities.

2.6. Synthesis and characterization of cationic allylpalladium complexes [Pd(h3-(1,3-Ph2-C3H3)(P-P)]X

The Pd-catalyzed enantioselective nucleophilic substitution of rac-3-acetoxy-1,3-diphenyl-1-propene proceed via a cationic intermediate [Pd(h3-(1,3-Ph2-C3H3)(P-P)]þ.

As methallyl palladium complexes containing ligand a showed the best catalytic performance and ligand b showed the lowest selectivity out of all the complexes reported here, we prepared and characterized the putative diphenylallyl intermediates 6b and 7a (Scheme 5) to rationalize the catalytic results.

31P{1H} NMR spectra showed two sharp doublets with an AB pattern, revealing two different and strongly coupled phosphorus atoms (2J ¼ 140e152 Hz), indicating once again the loss of C2 symmetry of the bis(diamidophosphite) ligands in the allylic palladium complex.

The 1H NMR spectra of complexes 6b-(R,R;Ral,Ral;R,R) and 7a- (R,R;Sal,Sal;R,R) indicated the presence of only one species. Two different signals for the two terminal allylic protons appeared. A syn-syn configuration is suggested according to the NOESY experiments and to the triplet shown in the 1H NMR spectra for the central allylic hydrogen with coupling constants value of 12.9 Hz Hcentral-Hanti very similar to those described in the literature [32]. 13C NMR spectra showed that the chemical shift values of the two allylic terminal carbon atoms are substantially different compared to those observed for the parent methylallyl complexes 2a- (R,R;Sal,Sal;R,R) and 2b-(R,R;Ral,Ral;R,R) (92.3 and 85.4 for b, 93.7 and 82.6 for 7a). It is reported [33] that the difference between the chemical shifts of the two allylic terminal carbon atoms is a useful tool to evaluate the asymmetry of the allyl bonding. The larger difference observed for 2a is in good agreement with its better enantioselectivity in the alkylation process

3. CONCLUSIONS

Cationic allylic complexes [Pd(h3-2-CH3-C3H4)(P-P)]X (X ¼ PF6, BPh4) with both diastereoisomers of monodentate and bidentate diamidophosphite ligands a-f, based on disubstituted cyclohexane diamine, have been prepared and fully characterized. The X-ray structure for complex 2e-(R,R;Ral,Ral;R,R) suggests a partial multiple-bond character for thee P-N bond. The new complexes have been used as catalytic precursors in the allylic alkylation and amination reaction of the model substrate rac-3-acetoxy-1,3- diphenyl-1-propene showing good activity except for complexes containing the (R,R)-N,N'-dimethyl-cyclohexane-1,2-diamine terminal fragment that resulted inactive in the process. The best asymmetric induction has been achieved using 3a-(S,S;Sal,Sal;S,S) and 3a-(R,R;Ral,Ral;R,R) enantiomeric complexes as precursors leading to very similar activity (100%) and good ee values for alkylation (84%) and for amination (80%) reactions. The results obtained indicate that the presence of the different anions (PF6 , BPh4) influence both the activity and the enantioselectivity of the process. A marked match-mismatch effect has been observed for both diastereoisomers of complexes containing ligands b and c with a long bridging fragment. The absolute configuration of the major product depends on the configuration of the cyclohexyldiamine-derived terminal fragment when the bridge is flexible (ligands a and b), while with the more rigid bridging fragment (ligand d) it is the configuration of the binaphtholderived bridge that dictates the product configuration. These results allow us to conclude that for precursors containing bidentate diamidophopsphite ligands derived from disubstituted N,N'-cyclohexane-1,2-diamine the presence of the benzyl substituent and the short and flexible butanodiol-derived bridging fragment leads to the most efficient catalytic precursors in the allylic substitution reaction with the model substrate.

4. Experimental

4.1. General information

All manipulations were performed under a dry nitrogen atmosphere using standard vacuum-line Schlenk techniques. Anhydrous dichloromethane, tetrahydrofuran and toluene were obtained from a solvent purification system. NEt3 was distilled from CaH2 and collected over 4 Å molecular sieves before use. The diols, (S,S)-2,3- butanediol, (4R,5R) and (4S,5S) -4,5-di(hydroxymethyl)-2,2- dimethyl-1,3-dioxolane, (R)- and (S)-1,1'-bi-2-naphthol, (R)- and (S)-N,N'-dimethyl-1,1'-binaphthyl-2,2'-diamine and PCl3 were used as supplied. The dimeric palladium complex [Pd(h3-2-Me-C3H4)(m- Cl)]2 was prepared as described in the literature [34]. Bis(diamidophosphite) ligands a-(R,R;Ral,Ral;R,R), a-(R,R;Sal,Sal;R,R), b-(R,R;Ral,Ral;R,R), c-(R,R;Sal;R,R), d-(R,R;Ral,Ral;R,R), e-(R,R;Ral,Ral;R,R), as well as monodentate diamidophosphite ligands f-(R,R;Ral), f- (S,S;Ral) and g-(R,R;Sal) were prepared as previously described by us [15,16]. 1H and 13C (standard SiMe4), and 31P (standard H3PO4) NMR spectra were recorded on 400 MHz or 500 MHz spectrometers. High-resolution mass spectra were obtained on a time-of-flight instrument using electrospray ionization.

4.2. Synthesis of ligands

4.2.1. Synthesis of bis(diamidophosphite) ligands a-(S,S;Sal,Sal;S,S), b-(R,R;Sal,Sal;R,R) and c-(R,R;Ral;R,R)

(R,R)-N,N'-dibenzyl-1,2-cyclohexanediamine (1.06 g, 3.6 mmol) and NEt3 (1.50 mL, 10.8 mmol) were dissolved in 10 mL of toluene. PCl3 (0.40 mL, 4.6 mmol) dissolved in 5 mL of toluene was added drop wise at 0 C. The mixture was allowed to warm up to room temperature and was stirred for 2 h. The formation of the chlorodiazaphospholidine was monitored by 31P NMR spectroscopy (d ¼ 174.5 ppm) being complete after this period. The solvent and the excess of PCl3 were thoroughly removed under reduced pressure to afford a viscous oil. This oil was dissolved in toluene (10 mL) and 1.3 mL of NEt3 was added. The corresponding diol (1.8 mmol), ((S,S)-2,3-butanediol in toluene (10 mL), (4S,5S)-4,5-di(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane and (R)-1,1'-bi-2- naphthol in THF (10 mL)) was added dropwise at 0 C. After 4 h of stirring, the white precipitate of triethylamine hydrochloride was filtered off. The solvent was removed in vacuum and a yellowish oil was obtained and used without purification.

a-(S,S;Sal,Sal;S,S)

Yield: 970 mg (73%). [a]298 ¼ þ37.60 (c 1.0, CH2Cl2). 31P {1H} (CDCl3, 121,44 MHz), 1H NMR (CDCl3, 400 MHz) and 13C NMR (CDCl3, 100.6 MHz) were described for the enantiomer a-(R,R;Ral,-Ral;R,R) in previous work [15].

b-(R,R;Sal,Sal;R,R)

Yield: 594 mg (41%). [a]298 ¼ -44.00 (c 1.0, CH2Cl2). 31P{1H} NMR (101.25 MHz, CDCl3, d (ppm), J (Hz)): 136.3 (s). 1H NMR (400 MHz, CDCl3, d (ppm), J (Hz)): 7.43e7.11 (om, 32H, CH(Ar)), 4.38e4.17 (om, 6H, CH2(Bn)) 3.96e3.86 (om, 4H, 2CH2(Bn) þ 2OCH2), 3.84 (m, 2H, OCH), 3.56 (m, 2H, OCH2), 3.01 (m, 2H, CH(Cy)), 2.55 (m, 2H, CH(Cy)), 2.00e0.85 (om, 16H, CH2(Cy)), 1.39 (s, 6H, CH3). 13C{1H} NMR (100.0 MHz, CDCl3, d (ppm), J (Hz)): 140.9 (d, 3JCP ¼ 6.0, 2C, C(Ar)), 140.5 (d, 3JCP ¼ 3.0, 2C, C(Ar)), 129.0e125.0 (m, 20C, CH(Ar)), 109.4 (s, 1C, O2CMe2), 78.3 (d, 3JCP ¼ 3.0, 2C, OCH), 67.3 (d, 2JCP ¼ 7.0, 2C, CH(Cy)), 66.4 (d, 2JCP ¼ 8.0, 2C, CH(Cy)), 64.6 (d, 2JCP ¼ 9.0, 2C, OCH2), 50.1 (d, 2JCP ¼ 33.0, 2C, CH2(Bn)), 48.2 (d, 2JCP ¼ 14.0, 2C, CH2(Bn)), 30.3 (s, 2C, CH2(Cy)), 29.9 (s, 2C, CH2(Cy)), 27.1 (s, 2C, CH2(Cy)), 24.5 (s, 2C, CH2(Cy)), 24.2 (s, 2C, CH2(Cy)). HR-MS (ESI, m/z): calcd for C47H60N4O4P2 806.4090, found 807.4145 [MH]þ.

c-(R,R;Ral;R,R)

Yield: 435 mg (26%). [a]298 ¼ -41.55 (c 1.0, CH2Cl2). 31P{1H} NMR (101.25 MHz, CDCl3, d (ppm), J (Hz)): 139.2 (s). 1H NMR (400 MHz, C6D6, d (ppm), J (Hz)): 7.90e6.95 (om, 32H, CH(Ar)), 4.39e4.13 (om, 4H, CH2(Bn)) 3.80e3.66 (om, 2H, CH2(Bn)), 3.15 (dd, 2JHH ¼ 15.8, 3JHP ¼ 7.2, 2H, CH2(Bn)), 2.83 (m, 2H, CH(Cy)), 2.46 (m, 2H, CH(Cy)), 1.68e0.53 (om, 16H, CH2(Cy)). 13C{1H} NMR (100.0 MHz, C6D6, d (ppm), J (Hz)): 152.2 (d, 3JCP ¼ 5.0, 2C, C(Ar)), 141.7 (d, 2JCP ¼ 12.0, 2C, C(Ar)), 140.7 (d, 3JCP ¼ 4.0, 2C, C(Ar)), 135.1 (s, 2C, C(Ar)), 134.1 (s, 2C, C(Ar)), 130.4 (s, 2C, C(Ar)), 129.1e121.4 (om, 32C, CH(Ar)), 67.6 (d, 2JCP ¼ 7.0, 2C, CH(Cy)), 66.6 (d, 2JCP ¼ 7.0, 2C, CH(Cy)), 50.3 (d, 2JCP ¼ 33.0, 2C, CH2(Bn)), 48.4 (d, 2JCP ¼ 14.0, 2C, CH2(Bn)), 30.8 (d, 3JCP ¼ 3.0, 2C, CH2(Cy)), 30.6 (s, 2C, CH2(Cy)), 24.5 (s, 2C, CH2(Cy)), 24.3 (s, 2C, CH2(Cy)). HR-MS (ESI, m/z): calcd for C60H60N4O2P2 930.4192, found 931.4267 [MH]þ.

4.2.2. Synthesis of bis(diamidophosphite) ligand e-(R,R;Ral,Ral;R,R)

(R,R)-N,N'-dimethylcyclohexane-1,2-diamine (0.51 g, 3.6 mmol) and NEt3 (1.50 mL, 10.8 mmol) were dissolved in 10 mL of toluene. PCl3 (0.4 mL, 4.6 mmol) dissolved in 5 mL of toluene was added dropwise at 0 C. The mixture was allowed to warm up to room temperature and was stirred for 2 h. The formation of the chlorodiazaphospholidine was monitored by phosphorus NMR spectroscopy (d ¼ 175.4 ppm) being complete after this period. The solvent and the excess of PCl3 were thoroughly removed under reduced pressure to afford an oil. This oil was dissolved in toluene (10 mL) and DMAP (2.6 10 3 g, 0.021 mmol) was added. A solution of the stoichiometric amount of the diol (R,R)-2,3-butanediol (0.16 g, 1.8 mmol) and 1,3mL de NEt3 (9.0 mmol) in toluene (10 mL) was added dropwise in three portions at 0 C. After stirring overnight at room temperature, hexane (5 mL)was added and the white precipitate of triethylamine hydrochloride was filtered off. The solvent was removed in vacuum and a brownish oil was obtained and used without further purification.

Yield: 349 mg (45%); [a]298 ¼ -143.63 (c 1.0, CH2Cl2). 31P{1H} NMR (101.25 MHz, CDCl3, d (ppm), J (Hz)): 142.6 (s). 1H NMR (300 MHz, CD2Cl2, d (ppm), J (Hz)): 4.00 (m, 2H, OCH), 2.69 (d, 3JHP ¼ 13.5 6H, CH3(NMe)), 2.53 (d, 3JHP ¼ 14.2, 6H, CH3(NMe)), 2.04 (m, 2H, CH(Cy)), 1.78 (m, 2H, CH(Cy)), 1.42e0.94 (om, 16H, 16CH2(Cy)), 1.11 (d, 3JHH ¼ 6.2, 6H, CH3). 13C{1H} NMR (100.0 MHz, CDCl3, d (ppm), J (Hz)): 72.6 (dd, 2JCP ¼ 12.0, 3JCP ¼ 1.0, 2C, OCH), 69.3 (d, 2JCP ¼ 6.0, 2C, CH(Cy)), 66.0 (d, 2JCP ¼ 9.0, 2C, CH(Cy)), 33.1 (d, 2JCP ¼ 36.0, 2C, CH3(NMe)), 30.2 (d, 2JCP ¼ 11.0, 2C, CH3(NMe)), 29.5 (s, 2C, CH2(Cy)), 29,1 (d, 3JCP ¼ 4.0, 2C, CH2(Cy)), 24.3 (s, 2C, CH2(Cy)), 24.2 (s, 2C, CH2(Cy)), 16.3 (d, 3JCP ¼ 3.0, 2C, CH3). HR-MS (ESI, m/z): calcd for C20H40N4O2P2 430.2626, found 431.2694 [MH]þ.

4.3. Synthesis of palladium complexes

4.3.1. Synthesis of [PdCl2P2] 1a and 1c

To a solution of 155 mg (0.50 mmol) of [PdCl2(COD)] in 10 mL of toluene at 0 C, a solution of 0.50 mmol of the corresponding diamidophosphite ligand (a-(S,S;Sal,Sal;S,S) or c-(R,R;Sal;R,R)) in 10 Ml of CH2Cl2 was added. After 3 h stirring at room temperature, the resulting yellow solution was concentrated under vacuum and 10 mL of ether were added. The yellow precipitate was filtered and dried.

1a-(S,S;Sal,Sal;S,S)

Yield: 169 mg (37%). Mp: 192e202 C dec. 31P{1H} NMR (101.25 MHz, CDCl3, d (ppm), J (Hz)): 111.4 (s). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.57e7.00 (om, 20H, CH(Ar)), 5.11 (pt, 2JHH ¼ 3JHP ¼ 7.0, 1H, CH2(Bn)), 5.08 (pt, 2JHH ¼ 3JHP ¼ 7.0, 1H, CH2(Bn)), 4.64e4.50 (om, 4H, CH2(Bn)), 4.22 (pt, 2JHH ¼ 3JHP ¼ 5.9, 1H, CH2(Bn)), 4.19 (pt, 2JHH ¼ 3JHP ¼ 5.5, 1H, 1H, CH2(Bn)), 3.96 (m, 2H, OCH), 3.50 (m, 2H, CH(Cy)), 3.20 (m, 2H, CH(Cy)),1.90e0.81 (om, 16H, CH2(Cy), 0.84 (d, 3JHH ¼ 5.0, 6H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 140.7 (pt, 3JCP ¼ 2.5, 2C, C(Ar)), 140.3 (pt, 3JCP ¼ 1.9, 2C, C(Ar)), 129.4e126.2 (20C, CH(Ar)), 80.6 (pt, 2JCP ¼ 3JCP ¼ 5.0, 2C, OCH), 69.6 (bs, 2C, CH(Cy)), 65.6 (bs, 2C, CH(Cy)), 50.2 (pt, JCP ¼ 6.8, 2C, CH2(Bn)), 48.5 (pt, 2JCP ¼ 7.8, 2C, CH2(Bn)), 30.5 (bs, 2C, CH2(Cy)), 27.9 (bs, 2C, CH2(Cy)), 24.6 (bs, 2C, CH2(Cy)), 23.5 (bs, 2C, CH2(Cy)), 17.9 (pt, JCP ¼ 2.2, 2C, CH3). HR-MS (ESI, m/z): calcd for C44H56Cl2N4O2P2Pd 910.2290, found 875.2640 [M-Cl]þ. Anal. Calcd. for C44H56Cl2N4O2P2Pd: C 57.93, H 6.19, N 6.14%; found: C 56.71, H 6.85, N 6.44%.

1c-(R,R;Sal;R,R)

Yield: 177 mg (32%). Mp: 230e234 C dec. 31P{1H} NMR (121.4 MHz, Toluene/CH2Cl2, d (ppm), J (Hz)): 101.7 (s). 1H NMR (400 MHz, CDCl3, d (ppm), J (Hz)): 8.08e6.83 (om, 32H, CH(Ar)), 5.56 (pt, 2JHH ¼ 3JHP ¼ 8.1, 2H, CH2(Bn)), 5.52 (pt, 2JHH ¼ 3JHP ¼ 7.8, 1H, CH2(Bn)), 4.47 (d, 2JHH ¼ 17.6, 1H, CH2(Bn)), 3.46e3.26 (om, 4H, 2CH(Cy) þ 2CH2(Bn)), 3.02 (d, 2JHH ¼ 16.6, 2H, CH2(Bn)),

2.89 (m, 2H, CH(Cy)), 1.85e0.68 (ms, 16H, CH2(Cy). 13C{1H} NMR (100.6 MHz, CDCl3, d (ppm), J (Hz)): 147.6 (pt, 2JCP ¼ 6.3, 2C, OC(Ar)), 140.0 (pt, 3JCP ¼ 4.0, 2C, C(Ar)), 138.2 (pt, 3JCP ¼ 3.5, 2C, C(Ar)), 133.7 (s, 2C, C(Ar)), 131.0e119.5 (36C, 32CH(Ar) þ 4C(Ar), 71.5 (bs, 2C, CH(Cy)), 64,7 (bs, 2C, CH(Cy)), 53.0 (d, JCP ¼ 7.0, 2C, CH2(Bn)), 46.4 (pt, JCP ¼ 5.4, 2C, CH2(Bn)), 31.2 (bs, 2C, CH2(Cy)), 29.2 (bs, 2C, CH2(Cy)), 23.9 (bs, 2C, CH2(Cy)), 23.7 (bs, 2C, CH2(Cy)). MALDI-TOF-MS (m/z): calcd for C60H60Cl2N4O2P2Pd 1106.2603, found 1036.3 [M-2Cl]þ.

4.3.2. Synthesis of [Pd(h3-2-Me-C3H4)(P-P]PF6 (2a, 2b, 2c and 2e)

To a solution of the appropriate ligand (0.40 mmol) in toluene (10 mL) at 0 C a solution of [Pd(h3-2-Me-C3H4)(m-Cl)]2 (79 mg, 0.20 mmol) in CH2Cl2 (5 mL) was added dropwise. Then a solution of NaPF6 (67 mg, 0.40 mmol) in THF (5 mL) was added. After 3 h of stirring at room temperature, the solution was washed with deoxygenated water (2 4 mL). The organic phase was dried over anhydrous Na2SO4, filtered off and the solvent removed under reduced pressure. The white or yellow solid obtained was washed several times with diethyl ether or n-pentane and dried under reduced pressure.

2a-(R,R;Sal,Sal;R,R)

Yield: 246 mg (59%). Mp: 135e148 C dec. 31P{1H} NMR (121.2 MHz, CDCl3, d (ppm), J (Hz)): 134.7 (d, 2JPP ¼ 95.4), 132.6 (d, 2JPP ¼ 95.4). 1H NMR (500 MHz, CD2Cl2, d (ppm), J (Hz)): 7.41e7.05 (om, 20H, CH(Ar)), 4.59 (pt, 2JHH ¼ 3JHP ¼ 16.0 1H, CH2(Bn)), 4.44e4.20 (om, 7H, 5CH2(Bn) þ 2OCH), 4.07 (m, 2H, 2CH2(syn)), 3.92 (dd, 2JHH ¼ 15.0 3JHP ¼ 10.0, 1H, CH2(Bn)), 3.80 (dd, 2JHH ¼ 15.0 3JHP ¼ 7.0, 1H, CH2(Bn)), 3.00 (m, 1H, CH(Cy)), 2.91 (m, 1H, CH(Cy)), 2.85 (m, 2H, CH(Cy)), 2.52 (d, 2JHP ¼ 15.0, 1H, CH2(anti)), 2.23 (d, 2JHP ¼ 15.0,1H, CH2(anti)), 2.15e1.05 (om, 16H, CH2(Cy)), 1.42 (s, 3H, CH3(allyl)), 1.20 (d, 3JHH ¼ 6.0, 3H, CH3), 1.13 (d, 3JHH ¼ 6.5, 3H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 139.4 (pt, JCP ¼ 8.8 1C, C(allyl)), 138.4 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 138.3 (d, 3JCP ¼ 3.8, 1C, C(Ar)), 137.8 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 137.6 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 129.0e127.5 (20C, CH(Ar)), 79.8 (dd, 2JCP ¼ 34.4 3JCP ¼ 12.0, 1C, OCH), 76,7 (dd, 2JCP ¼ 31.2, 3JCP ¼ 10.0, 1C, OCH), 70.4 (dd, 2JCPtrans ¼ 42.5, 2JCPcis ¼ 5.0, 1C, CH2(allyl)), 69.4 (dd, 2JCPtrans ¼ 42.5, 2JCPcis ¼ 5.0, 1C, CH2(allyl)), 67.7 (d, 2JCP ¼ 3.8, 1C, CH(Cy)), 67.5 (d, 2JCP ¼ 3.8, 1C, CH(Cy)), 65.5 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 65.3 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 51.2 (d, 2JCP ¼ 18.8, 1C, CH2(Bn)), 50.3 (d, 2JCP ¼ 17.5, 1C, CH2(Bn)), 48.0 (d, 2JCP ¼ 7.5, 1C, CH2(Bn)), 47.7 (d, 2JCP ¼ 8.8, 1C, CH2(Bn)), 30.3 (d, 3JCP ¼ 1.3, 1C, CH2(Cy)), 30.1 (d, 3JCP ¼ 1.3, 1C, CH2(Cy)), 29.8 (s, 1C, CH2(Cy)), 29.7 (s, 1C, CH2(Cy)), 29.6 (s, 1C, CH2(Cy)), 29.5 (s, 1C, CH2(Cy)), 24.2 (d, 3JCP ¼ 7.5, 1C, CH2(Cy)), 23.9 (d, 3JCP ¼ 6.3 1C, CH2(Cy)), 23.4 (s, 1C, CH3(allyl)), 18.1 (d, 3JCP ¼ 1.3, 1C, CH3), 18.0 (d, 3JCP ¼ 1.3, 1C, CH3). HR-MS (ESI, m/z): calcd for C48H63N4O2P2Pd 895.3461, found 895.3460 [M]þ. Anal. Calc. for C48H63F6N4O2P3Pd: C 55.36, H 6.10, N 5.38%; found: C 55.11, H 6.26, N 5.46%.

2a-(S,S;Sal,Sal;S,S)

Yield: 104 mg (25%). Mp: 168e178 C dec. 31P NMR (101.2 MHz, CDCl3, d (ppm), J (Hz)): 135.2 (d, 2JPP ¼ 83.2),130.7 (d, 2JPP ¼ 83.2). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.87e7.05 (om, 20H, CH(Ar)), 4.50 (pt, 2JHH ¼ 3JHP ¼ 15.0, 1H, CH2(Bn)), 4.38e3.81 (om, 8H, 6CH2(Bn) þ 2OCH), 4.29 (bs, 2H, CH2(syn)), 4.23 (bs, 2H, CH2(syn)), 3.65 (dd, 2JHH ¼ 15.0, 3JHP ¼ 5.0, 1H, CH2(Bn)), 3.15e2.85 (om, 4H, 4CH(Cy)), 2.92 (d, 2JHP ¼ 15.0,1H, CH2(anti)), 2.69 (d, 2JHP ¼ 10.0, 1H, CH2(anti)), 2.20e1.06 (ms, 16H, CH2(Cy)), 1.62 (s, 3H, CH3(allyl), 1.20 (d, 3JHH ¼ 6.5, 3H, CH3), 1.16 (d, 3JHH ¼ 6.5, 3H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 140.2 (pt, JCP ¼ 7.5, 1C, C(allyl)), 138.9 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 138.7 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 138.5 (d, 3JCP ¼ 10.0, 1C, C(Ar)), 138.4 (d, 3JCP ¼ 8.8, 1C, C(Ar)), 129.2e126.7 (20C, CH(Ar)), 79.1 (pt, JCP ¼ 4.4, 1C, OCH), 78.1 (dd,

2c-(R,R;Ral;R,R)

Yield: 208 mg (42%). Mp: 191e197 C dec. 31P NMR (101.2 MHz, CDCl3, 298 K, d (ppm), J (Hz)): 138.4 (d, 2JPP ¼ 59.9), 133.4 (d, 2JPP ¼ 59.9). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 8.20e6.53 (om, 32H, CH(Ar)), 4.74 (pt, 2JHH ¼ 3JHP ¼ 16.0, 1H, CH2(Bn)), 4.50 (bs, 1H, CH2(syn)), 4.44 (bs, 1H, CH2(syn)), 4.38e3.77 (om, 3H, CH2(Bn)), 3.38 (d, 2JHP ¼ 10.0, 1H, CH2(anti)), 3.26 (m, 1H, CH(Cy)), 3.11 (m, 1H, CH(Cy)), 3.05e2.95 (om, 2H, 1CH2(anti) þ 1CH2(Bn)), 2.94 (dd, 2JHH ¼ 16.0, 3JHP ¼ 9.5, 1H, CH2(Bn)), 2.82e2.65 (om, 2H, 1CH2(Bn) þ 1CH(Cy)), 2.60e2.50 (om, 2H, 1CH2(Bn) þ 1CH(Cy)), 2.13e0.25 (om, 16H, CH2(Cy)), 1.76 (s, 3H, CH3(allyl) þ 3CH3(allyl)). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 152.8 (s, 1C, C(Ar)), 147.3 (d, 2JCP ¼ 3.8, 1C, C(Ar)), 147.1 (d, 2JCP ¼ 5.0, 1C, C(Ar)), 139.7 (pt, JCP ¼ 7.5, 1C, C(allyl)), 138.4 (d, 3JCP ¼ 3.8, 1C, C(Ar)), 138.3 (d, 3JCP ¼ 7.5, 1C, C(Ar)), 137.5 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 136.6 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 133.6e121.5 (37C, 5C(Ar) þ 32CH(Ar)), 76.6 (d, 2JCPtrans ¼ 35.0, 1C, CH2(allyl)), 74.2 (d, 2JCPtrans ¼ 36.3, 1C, CH2(allyl)), 66.2 (d, 2JCP ¼ 3.8, 1C, CH(Cy)), 65.9 (bs, 1C, CH(Cy)), 65.8 (d, 2JCP ¼ 2.5, 1C, CH(Cy)), 64.3 (bs, 1C, CH(Cy)), 49.1 (d, 2JCP ¼ 11.3, 1C, CH2(Bn)), 48.5 (d, 2JCP ¼ 15.0, 1C, CH2(Bn)), 46.5 (d, 2JCP ¼ 18.8, 1C, CH2(Bn)), 46.1 (d, 2JCP ¼ 18.8, 1C, CH2(Bn)), 29.9 (d, 3JCP ¼ 6.3, 1C, CH2(Cy)), 29.7 (s, 1C, CH2(Cy)), 29.5 (d, 3JCP ¼ 6.3, 1C, CH2(Cy)), 28.8 (s, 1C, CH2(Cy)), 24.3 (d, 3JCP ¼ 11.3, 1C, CH2(Cy)), 24.0 (s, 1C, CH2(Cy)), 23.7 (s, 1C, CH2(Cy)), 23.5 (s, 1C, CH2(Cy)), 23.2 (s, 1C, CH3(allyl)). HR-MS (ESI, m/z): calcd for C64H67N4O2P2Pd 1091.3774, found 1091.3779 [M]þ.

2c-(R,R;Sal;R,R)

Yield: 203 mg (41%). Mp: 196e202 C dec. 31P NMR (101.25 MHz, CDCl3, 298 K, d (ppm), J (Hz)): 139.0 (d, 2JPP ¼ 60.1), 133.0 (d, 2JPP ¼ 60.1). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 8.11e6.56 (om, 32H, CH(Ar)), 4.80 (pt, 2JHH ¼ 3JHP ¼ 16.0, 1H, CH2(Bn)), 4.58 (bs, 1H, CH2(syn)), 4.47 (bs, 1H, CH2(syn)), 4.36e4.17 (om, 2H, CH2(Bn)), 3.85 (dd, 2JHH ¼ 15.0, 3JHP ¼ 5.0, 1H,

CH2(Bn)), 3.30 (d, 2JHP ¼ 10.0, 1H, CH2(anti)), 3.02e2.77 (om, 4H, CH(Cy)), 2.75e2.61 (om, 2H, CH2(Bn)) 2.71 (bs,1H, CH2(anti)), 2.50 (dd, 2JHH ¼ 15.5, 3JHP ¼ 10.0, 1H, CH2(Bn)), 2.22 (dd, 2JHH ¼ 15.0, 3JHP ¼ 5.0, 1H, CH2(Bn)), 1.93 (s, 3H, CH3(allyl)), 1.91e0.68 (om, 16H, CH2(Cy). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 153.6 (s, 1C, C(Ar)), 152.8 (s, 1C, C(Ar)), 146.7 (d, 2JCP ¼ 5.0, 1C, C(Ar)), 146.5 (d, 2JCP ¼ 7.5, 1C, C(Ar)), 140.3 (pt, JCP ¼ 7,5, 1C, C(allyl)), 138.9 (d, 3JCP ¼ 6.3, 1C, C(Ar)), 138.2 (d, 3JCP ¼ 3.8, 1C, C(Ar)), 138.2 (d, 3JCP ¼ 2.5, 1C, C(Ar)), 138.1 (d, 3JCP ¼ 3.8, 1C, C(Ar)), 133.8 (s, 1C, C(Ar)), 131.2 (s, 1C, C(Ar)), 130.7 (s, 1C, C(Ar)), 130.3 (s, 1C, C(Ar)), 128.8e125.7 (32C, CH(Ar)), 76.3 (d, 2JCPtrans ¼ 37.5, 1C, CH2(allyl)), 73.7 (d, 2JCPtrans ¼ 37.5, 1C, CH2(allyl)), 70.5 (d, 2JCP ¼ 2.5, 1C, CH(Cy)), 68,9 (s, 1C, CH(Cy)), 66.2 (d, 2JCP. ¼1.3, 1C, CH(Cy)), 66.3 (d, 2JCP ¼ 1.3, 1C, CH(Cy)), 53.0 (d, 2JCP ¼ 22.5, 1C, CH2(Bn)), 50.0 (d, 2JCP ¼ 18.8, 1C, CH2(Bn)), 46.6 (d, 2JCP ¼ 7.5, 1C, CH2(Bn)), 46.1 (d, 2JCP ¼ 8.8, 1C, CH2(Bn)), 31.3 (d, 3JCP ¼ 2.5, 1C, CH2(Cy)), 30.9 (d, 3JCP ¼ 2.5, 1C, CH2(Cy)), 30.3 (d, 3JCP ¼ 8.8, 1C, CH2(Cy)), 30.1 (d, 3JCP ¼ 8.8, 1C, CH2(Cy)), 23.9 (s, 3C, CH2(Cy)), 23.65 (s, 1C, CH2(Cy)), 23.0 (s, 1C, CH3(allyl)). HR-MS (ESI, m/z): calcd for C64H67N4O2P2Pd 1091.3774, found 1091.3783 [M]þ. Anal. Calc. for C64H67F6N4O2P3Pd: C 62.11, H 5.46, N 4.53%; found: C 59.94, H 5.70, N 4.89%.

2e-(R,R;Ral,Ral;R,R)

Yield: 106 mg (36%). Mp: 172e180 C dec. 31P{1H} NMR (101.2 MHZ, CDCl3, d (ppm), J (Hz)): 131.6 (d, 2JPP ¼ 90.5), 128.7 (d, 2JPP ¼ 90.5). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 4.54 (m, 1H, OCH), 4.33 (m, 1H, OCH), 4.00 (bs, 1H, CH2(syn)), 3.91 (dd, 2JHH ¼ 15.0, 3JHH ¼ 5.0, 1H, CH2(syn)), 3.20 (d, 2JHP ¼ 15.0, 1H, CH2(anti)), 3.02 (d, 2JHP ¼ 15.0, 1H, CH2(anti)), 2.83 (d, 3JHP ¼ 15.3, 3H, CH3(NMe)), 2.80 (m, 2H, CH(Cy)), 2.74e2.41 (om, 2H, CH(Cy)), 2.66 (d, 3JHP ¼ 15.5, 3H, CH3(NMe)), 2.65 (d, 3JHP ¼ 15.5, 3H, CH3(NMe)), 2.54 (d, 3JHP ¼ 15.5, 3H, CH3(NMe)), 2.20e1.75 (om, 8H, CH2(Cy)), 1.85 (s, 3H, CH3(allyl), 1.62e0.99 (om, (8H, CH2(Cy)), 1.30 (d, 3JHH ¼ 4.0, 3H, CH3), 1.29 (d, 3JHH ¼ 4.0, 3H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 139.2 (pt, JCP ¼ 3.8, 1C, C(allyl)), 78.2 (t, 2JCP1 ¼ 2JCP2 ¼ 3.8, 1C, OCH), 77.3 (m, 1C, OCH), 70.7 (dd, 2JCPtrans ¼ 41.3, 2JCPcis ¼ 5.0, 1C, CH2(allyl)), 69.9 (dd, 2JCPtrans ¼ 38.8, 2JCPcis ¼ 6.3, 1C, CH2(allyl)), 68.7 (d, 2JCP ¼ 1.3, 1C, CH(Cy)), 68.3 (d, 2JCP ¼ 1.3, 1C, CH(Cy)), 64.4 (d, 2JCP ¼ 5.0, 2C, CH(Cy)), 32.6 (d, 2JCP ¼ 28.7, 1C, CH3(NMe), 32.3 (d, 2JCP ¼ 28.3, 1C, CH3(NMe), 29.3 (d, 2JCP ¼ 4.2, 1C, CH3(NMe), 29.1 (d, 2JCP ¼ 4.2, 1C, CH3(NMe)), 28.6 (d, 3JCP ¼ 3.8, 2C, CH2(Cy)), 28.2 (d, 3JCP ¼ 6.3, 1C, CH2(Cy)), 28.1 (d, 3JCP ¼ 6.3, 1C, CH2(Cy)), 24.3 (s, 1C, CH3(allyl)), 23.9 (bs, 4C, CH2(Cy)), 19.7 (pt, 2JCP ¼ 3JCP ¼ 2.5, 1C, CH3), 19.6 (pt, 2JCP ¼ 3JCP ¼ 2.5, 1C, CH3). HR-MS (ESI, m/z): calcd for C24H47N4O2P2Pd 591.2209, found 591.2207 [M]þ.

4.3.3. Synthesis of [Pd(h3-2-Me-C3H4)(P-P]BPh4 (3a, 3b, 3d and 3e)

To a solution of the corresponding diamidophosphite a, b, d, e (0.40 mmol) in toluene (10 mL) at 0 C a solution of [Pd(h3-2-Me- C3H4)(m-Cl)]2 (79 mg, 0.20 mmol) in CH2Cl2 (5 mL) was added dropwise

and then a solution of NaPF6 (67 mg, 0.40 mmol) in THF (5 mL). After 1 h of stirring at room temperature, a solution of NaBPh4 (204 mg, 0.60 mmol) in 20 mL of MeOH was added. The white solid formed on standing was filtered off and washed with deoxygenated water.

3a-(R,R;Ral,Ral;R,R)

Yield: 173.0 mg (35%). Mp: 172e178 C dec. 31P NMR (101.2 MHz, CDCl3, 298 K, d (ppm), J (Hz)): 135.6 (d, 2JPP ¼ 84.1), 130.7 (d, 2JPP ¼ 84.1). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.64e6.74 (om, 40H, CH(Ar)), 4.37 (pt, 2JHH ¼ 3JHP ¼ 15.0, 1H, CH2(Bn)), 4.26 (pt, 2JHH ¼ 3JHP ¼ 15.0, 1H, CH2(Bn)), 4.16e3.74 (om, 7H; 5H, CH2(Bn) þ 2H, OCH), 4.07 (om, 2H, CH2(syn)), 3.60 (dd, 2JHH ¼ 16.0, 3JHP ¼ 6.0, 1H, CH2(Bn)), 3.10e2.97 (om, 2H, CH(Cy)), 2.86 (m, 1H, CH(Cy)), 2.79 (m, 1H, CH(Cy)), 2.65 (d, 2JHP ¼ 10.0,1H, CH2(anti)), 2.52 (d, 2JHP ¼ 15.0, 1H, CH2(anti)), 2.04e0.86 (om, 16H, CH2(Cy)), 1.48 (s, CH3(allyl)), 1.15 (d, 3JHH ¼ 6.2, CH3) 1.11 (d, 3JHH ¼ 6.0, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 164.3 (q, 1JCB ¼ 49.0, 4C, CB(Ar)), 140.1 (pt, JCP ¼ 7.5, 1C, C(allyl)), 138.4 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 138.4 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 138.3 (d, 3JCP ¼ 10.0, 1C, C(Ar)), 138.2 (d, 3JCP ¼ 8.8, 1C, C(Ar)), 136.3e121.3 (om, 40C, CH(Ar)), 79.0 (pt, 2JCP ¼ 3JCP ¼ 5.0, 1C, OCH), 78.2 (dd, 2JCP ¼ 5.0, 3JCP ¼ 2.5, 1C, OCH), 71.8 (dd, 2JCPtrans ¼ 40.7, 2JCPcis ¼ 4.0, 1C, CH2(allyl)), 71.4 (dd, 2JCPtrans ¼ 40.8, 2JCPcis ¼ 4.2, 1C, CH2(allyl)), 69.3 (bs, 1C, CH(Cy)), 69.1 (bs, 1C, CH(Cy)), 65.7 (t, 2JCP ¼ 4.0, 2C, CH(Cy)), 51.9 (d, 2JCP ¼ 21.3, 1C, CH2(Bn)), 51.3 (d, 2JCP ¼ 20.1, 1C, CH2(Bn)), 47.8 (d, 2JCP ¼ 7.5, 1C, CH2(Bn)), 47,7 (d, 2JCP ¼ 8.8, 1C, CH2(Bn)), 30.5e29.7 (om, 4C, CH2(Cy)), 24.1 (s, 1C, CH2(Cy)), 24.0 (s, 1C, CH2(Cy)), 23.9 (s, 1C, CH2(Cy)), 23.8 (s, 1C, CH2(Cy)), 23.4 (s, 1C, CH3(allyl)), 18.9 (d, 3JCP ¼ 3.4, 1C, CH3), 18.8 (d, 3JCP ¼ 2.6, 1C, CH3). HR-MS (ESI, m/z): calcd for C48H63N4O2P2Pd 895.3461, found 895.3465 [M]þ.

3a-(S,S;Sal,Sal;S,S)

Yield: 190.0 mg (38%). Mp: 130e147 C. HR-MS (ESI, m/z): calcd for C48H63N4O2P2Pd 895.3461, found 895.3444 [M]þ. 31P {1H} (CDCl3, 121.4 MHz), 1H NMR (CDCl3, 500 MHz) and 13C NMR (CDCl3, 125.7 MHz) were described for 3a-(R,R;Ral,Ral;R,R) complex. HR-MS (ESI, m/z): calcd for C48H63N4O2P2Pd 895.3461, found 895.3444 [M]

3b-(R,R;Ral,Ral;R,R)

Yield: 200 mg (39%). Mp: 170e173 C dec. 31P{1H} NMR (101.2 MHz, CDCl3, d (ppm), J (Hz)): 121.5 (d, 2JPP ¼ 92.0), 118.7 (d, 2JPP ¼ 92.0). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.66e6.77 (om, 40H, CH(Ar)), 4.54e4.31 (om, 4H, 2OCH2 þ 2CH2(Bn)), 4.26e4.12 (ms, 4H, CH2(Bn)), 4.07 (dd, 2JHH ¼ 15.0 3JHP ¼ 10.0 1H, CH2(Bn)), 3.94 (bs, 1H, CH2(syn)), 3.84e3.68 (om, 3H, 1CH2(Bn) þ 2OCH), 3.80 (bs, 1H, CH2(syn)), 3.35 (m, 2H, 2OCH2), 3.07 (m, 2H, CH(Cy)), 2.86 (m,1H, CH(Cy)), 2.73 (m, 1H, CH(Cy)), 2.49 (d, 2JHH ¼ 15.0, 1H, CH2(anti)), 2.23 (d, 2JHH ¼ 15.0,

1H, CH2(anti)), 2.05e0.98 (om, 16H, CH2(Cy)), 1.60 (s, 3H, CH3(allyl)), 1.30 (s, 3H, CH3), 1.28 (s, 3H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 164.3 (q, 1JCB ¼ 48.8, 4C, CB(Ar)), 138.9 (pt, JCP ¼ 8.1 1C, C(allyl)), 138.0 (d, 3JCP ¼ 3.8 1C, C(Ar)), 137.8 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 137.7 (d, 3JCP ¼ 3.8, 1C, C(Ar)), 137.1 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 129.5e121.6 (40C, CH(Ar)), 111.2 (s, 1C, O2CMe2), 77.5 (d, 3JCP ¼ 3.8, 1C, OCH), 77.3 (d, 3JCP ¼ 2.5, 1C, OCH), 70.7 (dd, 2JCPtrans ¼ 43.8, 2JCPcis ¼ 3.8, 1C, CH2(allyl)), 69.2 (dd, 2JCPtrans ¼ 43.8, 2JCPcis ¼ 5.0, 1C, CH2(allyl)), 67.4 (d, 2JCP ¼ 16.3, 1C, OCH2), 66.9 (d, 2JCP ¼ 16.3, 1C, OCH2), 66.7 (s, 1C, CH(Cy)), 66.5 (s, 1C, CH(Cy)), 65.9 (d, 2JCP ¼ 6.3, 1C, CH(Cy)), 65.3 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 49.4 (d, 2JCP ¼ 18.8, 1C, CH2(Bn)), 48.7 (d, 2JCP ¼ 18.8, 1C, CH2(Bn)), 47.1 (d, 2JCP ¼ 11.3, 1C, CH2(Bn)), 46.8 (d, 2JCP ¼ 11.3, 1C, CH2(Bn)), 29.7e29.4 (4C, CH2(Cy)), 26.6 (s, 1C, CH3), 26.6 (s, 1C, CH3), 24.1 (d, 3JCP ¼ 3.8, 2C, CH2(Cy)), 23.9 (s, 1C, CH3(allyl)), 23.8 (d, 3JCP ¼ 1.3, 2C, CH2(Cy)). HR-MS (ESI, m/z): calcd for C51H67N4O4P2Pd 967.3672, found 967.3675 [M]þ.

3d-(R,R;Ral,Ral;R,R)

Yield: 104 mg (21%). Mp: 159e166 C dec. 31P{1H} NMR (101.2 MHZ, CDCl3, d (ppm), J (Hz)): 134.1 (d, 2JPP ¼ 87.1), 129.2 (d, 2JPP ¼ 87.1). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.72e6.68 (om, 40H, CH(Ar)), 4.43 (pt, 2JHH ¼ 3JHP ¼ 16.0, 1H, CH2(Bn)), 4.31 (pt, 2JHH ¼ 3JHP ¼ 15.0, 1H, CH2(Bn)), 4.14 (pt, 2JHH ¼ 3JHP ¼ 15.0, 1H, CH2(Bn)), 4.09e3.73 (om, 6H, 4CH2(Bn) þ 2OCH), 4.04 (bs, 1H, CH2(syn)), 4.01 (bs, 1H, CH2(syn)), 3.64 (dd, 2JHH ¼ 16.5, 3JHP ¼ 7.5, 1H, CH2(Bn)), 3.07 (m, 2H, CH(Cy)), 2.87 (m, 1H, CH(Cy)), 2.79 (m, 1H, CH(Cy)), 2.56 (d, 2JHP ¼ 10.0, 1H, CH2(anti)), 2.47 (d, 2JHP ¼ 15.0, 1H, CH2(anti)), 2.10e0.81 (om, 24H, 16CH2(Cy) þ 8CH2), 1.45 (s, 3H, CH3(allyl)). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 164.3 (q, 1JCB ¼ 48.8, 4C,CB(Ar)), 140.2 (pt, JCP ¼ 8.1, 1C, C(allyl)), 138.5 (s, 1C, C(Ar)), 138.4 (s, 1C, C(Ar)), 138.3 (s, 1C, C(Ar)), 138.2 (s, 1C, C(Ar)), 128.7e121.7 (40C, CH(Ar)), 80.1 (bs, 1C, OCH), 79.5 (bs, 1C, OCH), 71.7 (dd, 2JCPtrans ¼ 25.0, 2JCPcis ¼ 2.5 1C, CH2(allyl)), 71.4 (dd, 2JCPtrans ¼ 23.8, 2JCPcis ¼ 2.5, 1C, CH2(allyl)), 69.5 (bs, 1C, CH(Cy)), 69.1 (bs, 1C, CH(Cy)), 65.8 (pt, 2JCP ¼ 5.0, 2C, CH(Cy)), 52.4 (d, JCP ¼ 22.5, 1C, CH2(Bn)), 51.6 (d, JCP ¼ 20.0, 1C, CH2(Bn)), 47.8 (d, 2JCP ¼ 6.3, 1C, CH2(Bn)), 47.7 (d, 2JCP ¼ 8.8, 1C, CH2(Bn)), 32.6 (bs, 2C, CH2), 30.6 (s, 1C, CH2(Cy)), 30.2 (s, 1C, CH2(Cy)), 30.0 (d, 3JCP ¼ 8.8, 1C, CH2(Cy)), 29.9 (d, 3JCP ¼ 7.5, 1C, CH2(Cy)), 24.2e23.9 (6C, 2CH2 þ 4CH2(Cy)), 23.4 (s, 1C, CH3(allyl)). HR-MS (ESI, m/z): calcd for C50H65N4O2P2Pd 921.3618, found 921.3618 [M]þ.

3e-(R,R;Ral,Ral;R,R)

Yield: 91 mg (25%). Mp: 174e178 C dec. 31P{1H} NMR (101.2 MHZ, CDCl3, d (ppm), J (Hz)): 131.5 (d, 2JPP ¼ 90.4), 130.1 (d, 2JPP ¼ 90.4). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.88e6.87 (om, 20H, CH(Ar)), 4.34 (m,1H, OCH), 4.24 (m, 1H, OCH), 3.89 (bs, 1H, CH2(syn)), 3.80 (bs, 1H, CH2(syn)), 2.86 (d, 2JHP ¼ 15.0, 1H, CH2(anti)), 2.77 (m, 2H, CH(Cy)), 2.68 (d, 2JHP ¼ 15.0,

1H, CH2(anti)), 2.65 (d, 2JHP ¼ 14.4, 3H, CH3(NMe), 2.53 (d, 2JHP ¼ 14.6, 3H, CH3(NMe), 2.55e2.43 (om, 2H, CH(Cy)), 2.51 (d, 2JHP ¼ 14.5, 3H, CH3(NMe)), 2.45 (d, 2JHP ¼ 14.8, 3H, CH3(NMe), 2.06 (m, 4H, CH2(Cy)), 1.87 (m, 4H, CH2(Cy)),1.72 (s, 3H, CH3(allyl)),1.37e1.08 (m, 8H, CH2(Cy)),1.27 (d, 3JHP ¼ 5.0, 3H, CH3), 1.25 (d, 3JHP ¼ 5.0, 3H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 164.2 (q, 1JCB ¼ 48.8, 4C, CB(Ar)), 139.2 (pt, JCP ¼ 8.1, 1C, C(allyl)), 136.3 (s, 8C, CH(Ar)), 125.4 (s, 4C, CH(Ar)), 121.5 (s, 8C, CH(Ar)), 77.7 (m, 2C, OCH), 71.2 (dd, 2JCPtrans ¼ 38.3, 2JCPcis ¼ 6.3, 1C, CH2(allyl)), 69.6 (dd, 2JCPtrans ¼ 38.8, 2JCPcis ¼ 6.3, 1C, CH2(allyl)), 68.5 (d, 2JCP ¼ 2.5, 1C, CH(Cy)), 68.4 (d, 2JCP ¼ 1.3, 1C, CH(Cy)), 64.4 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 64.3 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 32.6 (d, 2JCP ¼ 20.0, 1C, CH3(NMe), 32.3 (d, 2JCP ¼ 18.8, 1C, CH3(NMe), 29.5 (d, 2JCP ¼ 5.0, 1C, CH3(NMe), 29.1 (d, 2JCP ¼ 6.3, 1C, CH3(NMe), 28.5 (d, 3JCP ¼ 2.5, 2C, CH2(Cy)), 28.1 (d, 3JCP ¼ 3.8, 1C, CH2(Cy)), 28.0 (d, 3JCP ¼ 5.0, 1C, CH2(Cy)), 24.3 (s, 1C, CH3(allyl)), 23.9 (s, 2C, CH2(Cy)), 23.8 (s, 1C, CH2(Cy)), 23.7 (s, 1C, CH2(Cy)), 19.7 (pt, 2JCP ¼ 3JCP ¼ 3.1, 2C, CH3). HR-MS (ESI, m/z): calcd for C24H47N4O2P2Pd 591.2209, found 591.2208 [M]þ.

4.3.4. Synthesis of [Pd(h3-2-CH3-C3H4)P2]PF6 (4f, 4g) and [Pd(h3-2-Me-C3H4)P2]BPh4 (5f)

To a solution of the appropriate ligand (0.80 mmol) in toluene (10 mL) at 0 °C a solution of [Pd(h3-2-CH3-C3H4)(m-Cl)]2 (79 mg, 0.20 mmol) in CH2Cl2 (5 mL) was added dropwise. Then a solution of NaPF6 (67 mg, 0.40 mmol) in THF (5 mL) was added. After 3 h of stirring at room temperature, the solution was washed with deoxygenated water (2 × 4 mL). The organic phase was dried over anhydrous Na2SO4, filtered off and the solvent removed under reduced pressure. The white or yellow solid obtained was washed several times with diethyl ether or n-pentane and dried under reduced pressure. In case of 4f treatment of the CH2Cl2/THF solution with a solution of NaBPh4 (204 mg, 0.60 mmol) in 20 mL of MeOH resulted in formation of a white or pale-yellow powder. The solid formed on standing was filtered off and washed with deoxygenated water.

4f-(R,R;Ral)

Yield: 117 mg (49%). Mp 171e177 °C dec. 31P{1H} NMR (101.2 MHz, CDCl3, d (ppm), J (Hz)): 124.0 (d, 2JPP ¼ 85.2), 122.2 (d, 2JPP ¼ 85.2). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.60e6.83 (om, 30H, CH(Ar), 5.36 (m, 1H, OCH), 5.27 (m, 1H, OCH), 4.54 (pt, 2JHH ¼ 3JHP ¼ 16.0, 1H, CH2(Bn)), 4.50 (bs, 1H, CH2(syn)), 4.41e3.97 (om, 5H, CH2(Bn)), 4.32 (bs, 1H, CH2(syn)), 3.17e2.94 (om, 2H, CH(Cy)), 3.00 (d, 3JHP ¼ 13.6, 1H, CH2(anti)), 2.88 (d, 3JHP ¼ 13.6, 1H, CH2(anti)), 2.81e2.54 (om, 4H, 2CH2(Bn) þ 2CH(Cy)), 2.07 (om, 2H, CH2(Bn)), 1.87 (s, 3H, CH3(allyl)), 1.74 (om, 2H, CH2(Bn)), 1.60 (om, 2H, CH2(Bn)),1.51e0.80 (om, 10H, CH2(Cy)), 1.33 (d, 3JHH ¼ 6.5, 3H, CH3), 1.22 (d, 3JHH ¼ 6.5, 3H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 142.6 (s, 1C, C(Ar)), 142.4 (s, 1C, C(Ar)), 139.6 (d, 3JCP ¼ 8.0, 1C, C(Ar)), 139.3 (d, 3JCP ¼ 9.0, 1C, C(Ar)), 138.8 (d, 3JCP ¼ 4.0, 1C, C(Ar)), 138.7e138.5 (2C, 1C(Ar) þ 1C(allyl)), 129.0e125.3

(30C, CH(Ar)), 75.2 (d, 2JCP ¼ 2.0, 1C, OCH), 75.1 (bs, 1C, OCH), 71.4 (dd, 2JCPtrans ¼ 42.0, 2JCPcis ¼ 4.0, 1C, CH2(allyl)), 70.8 (dd, 2JCPtrans ¼ 41.5, 2JCPcis ¼ 3.5, 1C, CH2(allyl)), 67.8 (bs, 1C, 1CH(Cy), 67.6 (bs, 1C, 1CH(Cy), 67.1 (pt, 2JCP ¼ 5.0, 2C, CH(Cy)), 50.8 (d, 2JCP ¼ 20.0, 1C, CH2(Bn)), 50.2 (d, 2JCP ¼ 19.0, 1C, CH2(Bn)), 47.2 (d, 2JCP ¼ 10.0, 1C, CH2(Bn)), 46.6 (d, 2JCP ¼ 10.0, 1C, CH2(Bn)), 30.6 (s, 1C CH2(Cy)), 30.6e30.4 (4C, CH2(Cy)), 26.1 (d, 3JCP ¼ 5.0, 1C, CH3), 25.8 (d, 3JCP ¼ 6.0, 1C, CH3), 24.3e23.8 (4C, CH2(Cy)), 23.4 (s, 1C, CH3(allyl)). HR-MS (ESI, m/z): calcd for C60H73N4O2P2Pd 1049.4244, found 1049.4251 [M]þ. Anal. Calcd. for C60H73F6N4O2P3Pd: C 60.28, H 6.15, N 4.69%; found: C 58.60, H 6.29, N 5.14%.

4g-(R,R;Sal)

Yield: 143 mg (57%). Mp: 179e184 C dec. 31P{1H} NMR (101.2 MHz, CDCl3, d (ppm), J (Hz)): 126.3 (d, 2JPP ¼ 76.2), 119.6 (d, 2JPP ¼ 76.2). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.65e6.75 (ms, 20H, CH(Ar)), 4.99 (dd, 2JHH ¼ 15.0, 3JHP ¼ 10.0, 1H, CH2(Bn)), 4.79 (pt, 2JHH ¼ 3J HP ¼ 16.5, 1H, CH2(Bn)), 4.49 (m, 1H, OCH), 4.45e3.85 (om, 6H, 5CH2(Bn) þ 1OCH), 4.24 (bs, 1H, CH2(syn)), 3.93 (bs, 1H, CH2(syn)) 3.76 (dd, 2JHH ¼ 16.5 3JHP ¼ 7.5, 1H, CH2(Bn)), 3.19 (m, 2H, CH(Cy)), 2.94 (m, 2H, CH(Cy)), 2.64 (d, 3JHP ¼ 15.0, 1H, CH2(anti)), 2.43e0.65 (ms, 30H,16CH2(Cy) þ 12CH2 þ 2CH(Cy)),1.90 (bs, 1H, CH2(anti)), 1.64 (s, 3H, CH3(allyl)), 0.99 (s, 3H, CH3), 0.90 (s, 6H, CH3), 0.84 (s, 3H, CH3), 0.80 (s, 3H, CH3), 0.47 (s, 3H, CH3). 13C {1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 138.9 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 138.7 (d, 3JCP ¼ 8.8, 1C, C(Ar)), 137.7e137.6 (3C, 2C(Ar) þ 1C(allyl)), 129.1e126.4 (20C, CH(Ar)), 84.3 (d, 2JCP ¼ 15.0, 1C, OCH), 83.4 (d, 2JCP ¼ 15.0, 1C, OCH), 74.8 (d, 2JCPtrans ¼ 42.5, 1C, CH2(allyl)), 70.3 (d, 2JCPtrans ¼ 41.3, 1C, CH2(allyl)), 68.8 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 67.8 (d, 2JCP ¼ 3.8, 1C, CH(Cy)), 65.8 (bs, 1C, CH(Cy)), 65.0 (bs, 1C, CH(Cy)), 50.3 (d, 2JCP ¼ 3.8, 1C, CH2(Bn)), 49.7 (d, 2JCP ¼ 5.0, 1C, CH2(Bn)), 47.4 (d, 2JCP ¼ 13.8, 2C, CH2(Bn)), 44.6 (s, 1C, CH), 44.4 (s, 1C, CH), 38.0 (d, 3JCP ¼ 5.0, 2C, CH2), 29.9 (bs, 1C, CH2(Cy)), 29.7 (bs, 1C, CH2(Cy)), 28.7 (s, 1C, CH2(Cy)), 28.4 (s, 1C, CH2(Cy)), 27.1 (bs, 2C, CH2), 26.7 (bs, 2C, CH2), 24.7 (d, 3JCP ¼ 6.3 2C, CH2(Cy)), 23.7 (d, 3JCP ¼ 2.5 2C, CH2(Cy)), 22.8 (s, 1C, CH3(allyl)), 19.8 (s, 1C, CH3), 19.7 (s, 1C, CH3), 18.9 (s, 2C, 2CH3), 14.3 (s, 1C, CH3), 13.4 (s, 1C, CH3). HRMS (ESI, m/z): calcd for C64H89N4O2P2Pd 1113.5496, found 1049.4251 [M]þHR-MS (ESI, m/z): 1113.5496 [M]þ.

5f-(S,S;Ral)

Yield: 118 mg (43%). Mp: 170e175 C dec. 31P{1H} NMR (101.2 MHz, CDCl3, d (ppm), J (Hz)): 120.7 (d, 2JPP ¼ 83.5), 115.9 (d, 2JPP ¼ 83.5). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.86e6.58 (m, 50H, CH(Ar)), 5.38 (m, 1H, OCH), 5.15 (m, 1H, OCH), 4.70 (pt, 2JHH ¼ 3JHP ¼ 15.0, 1H, CH2(Bn)), 4.42 (pt, 2JHH ¼ 3JHP ¼ 16.0, 1H, CH2(Bn)), 4.28e3.54 (om, 6H, CH2(Bn)), 4.17 (bs, 1H, CH2(syn)), 3.81 (bs, 1H, CH2(syn)), 3.28 (m, 2H, 2CH(Cy)), 2.83 (m, 2H, 2CH(Cy)), 2.50 (d,

3JHP ¼ 15.0, 1H, CH2(anti)), 2.08 (d, 3JHP ¼ 15.0, 1H, CH2(anti)), 2.03e0.79 (om, 16H, CH2(Cy)), 1.64e1.60 (om, 6H, 1CH3(allyl) þ 1CH3), 1.38 (d, 3JHH ¼ 6.5, 3H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 164.3 (q, 1JCB ¼ 48.4, 4C, CB(Ar)), 142.4 (d, 3JCP ¼ 1.3, 1C, C(Ar)), 142.1 (d, 3JCP ¼ 2.5, 1C, C(Ar)), 139.0 (d, 3JCP ¼ 6.3, 1C, C(Ar)), 138.8 (d, 3JCP ¼ 5.0, 1C, C(Ar)), 138.1 (pt, JCP ¼ 8.1, 1C, C(allyl)), 137.8 (d, 3JCP ¼ 3.8, 1C, C(Ar)), 137.6 (d, 3JCP ¼ 6.3, 1C, C(Ar)), 136.3 (s, 8C, CH(BPh4 -)), 129.0e125.5 (30C, CH(Ar)), 125.3 (s, 8C, CH(BPh4 -)), 121.6 (s, 4C, CH(BPh4 -)), 76.1 (dd, 2JCP ¼ 36.3, 4JCP ¼ 3.8, 1C, OCH), 75.6 (dd, 2JCP ¼ 20.6, 4JCP ¼ 14.4, 1C, OCH), 70.6 (dd, 2JCPtrans ¼ 36.3, 2JCPcis ¼ 2.5, 1C, CH2(allyl)), 70.2 (dd, 2JCPtrans ¼ 33.8, 2JCPcis ¼ 2.5, 1C, CH2(allyl)), 67.1 (d, 2JCP ¼ 5.0 1C, CH(Cy)), 67.0 (bs,1C, CH(Cy)), 66.3 (d, 2JCP ¼ 3.8, 1C, CH(Cy)), 66.0 (bs, 1C, CH(Cy)), 49.9 (d, 2JCP ¼ 18.8, 1C, CH2(Bn)), 47.6 (d, 2JCP ¼ 16.3, 1C, CH2(Bn)), 47.2 (d, 2JCP ¼ 15.0, 1C, CH2(Bn)), 46.9 (d, 2JCP ¼ 11.3, 1C, CH2(Bn)), 30.4 (d, 3JCP ¼ 6.3, 1C, CH2(Cy)), 29.6 (d, 3JCP ¼ 5.0, 1C, CH2(Cy)), 29.3 (bs, 1C, CH2(Cy)), 28.8 (d, 3JCP ¼ 2.5, 1C, CH2(Cy)), 25.2 (d, 3JCP ¼ 3.8, 1C, CH3), 24.7 (d, 3JCP ¼ 5.0, 1C, CH3), 24.3 (s, 1C, CH2(Cy)), 24.2 (s, 1C, CH2(Cy)), 23.8 (s, 1C, CH2(Cy)), 23.7 (s, 1C, CH2(Cy)), 23.3 (s, 1C, CH3(allyl)). HR-MS (ESI, m/z): calcd for C60H73N4O2P2Pd 1049.4244, found 1049.4246 [M]þ.

4.3.5. Synthesis of [Pd(h3-Ph2-C3H3)(P-P)]PF6 (6b) and [Pd(h3-Ph2C3H3)(P-P)]BPh4 (7a)

6b-(R,R;Ral,Ral;R,R)

To a solution of the b-(R,R;Ral,Ral;R,R) (0.40 mmol) in toluene (10 mL) at 0 C a solution of [Pd(h3-Ph2C3H3)(m-Cl)]2 (134 mg, 0.20 mmol) in CH2Cl2 (30 mL) was added dropwise. Then a solution of NaPF6 (67 mg, 0.40 mmol) in THF (10 mL) was added. After 3 h of stirring at room temperature, the solution was washed with deoxygenated water (2 4 mL). The organic phase was dried over anhydrous Na2SO4, filtered off and the solvent removed under reduced pressure. The white or yellow solid obtained was washed several times with diethyl ether or n-pentane and dried under reduced pressure. Yield: 365 mg (73%). Mp: 195e205 C dec. 31P{1H} NMR (101.2 MHz, CDCl3, d (ppm), J (Hz)): 120.2 (d, 2JPP ¼ 140.4), 117.3 (d, 2JPP ¼ 140.4). 1H NMR (500 MHz, CDCl3, d (ppm), J (Hz)): 7.94e6.75 (om, 30H, CH(Ar)), 6.57 (t, 3JHH ¼ 12.9, 1H, CHcentral(allyl)), 5.27e5.02 (m, 1H, CH2(Bn)), 5.20 (om, 1H, CH(anti), 5.09 (om, 1H, CH(anti), 4.63 (t, 2JHH ¼ 3JHP ¼ 16.5, 1H, CH2(Bn)), 4.47 (dd, 2JHH ¼ 15.2, 3JHP ¼ 6.8, 1H, CH2(Bn)), 4.40 (dd, 2JHH ¼ 15.8 3JHP ¼ 6.6, 1H, CH2(Bn)), 4.18e3.77 (om, 5H, 2OCH2 þ 3CH2(Bn)), 3.61 (m, 1H, OCH), 3.51e3.36 (m, 2H, 1OCH þ 1CH2(Bn)), 2.90 (m, 2H, CH(Cy)), 2.46 (m, 1H, CH(Cy)), 2.21e0.34 (ms, 19H, 1CH(Cy) þ 16CH2(Cy) þ 2OCH2), 1.06 (s, 3H, CH3), 1.02 (s, 3H, CH3). 13C{1H} NMR (125.7 MHz, CDCl3, d (ppm), J (Hz)): 139.3 (d, 3JCP ¼ 7.5, 1C, C(Ar)),138.8 (d, 3JCP ¼ 6.3, 1C, C(Ar)), 138.0 (dd, 3JCP1 ¼ 7.5, 3JCP2 ¼ 5.0, 1C, C(Ar, allyl)), 137.4 (d, 3JCP ¼ 10.0, 2C, C(Ar)), 137.0 (dd, 3JCP1 ¼ 7.5, 3JCP2 ¼ 5.0, 1C, C(Ar, allyl)), 134.5e125.3 (30C, CH(Ar)), 115.1 (pt, JCP ¼ 10.6, 1C, CHcentral(allyl)), 110.5 (s, 1C, O2CMe2), 92.3 (dd, 2JCPtrans ¼ 32.5, 2JCPcis ¼ 10.0, 1C, CH(allyl)), 85.4 (dd, 2JCPtrans ¼ 35.0, 2JCPcis ¼ 11.3, 1C, CH(allyl)), 77.2 (bs, 1C, OCH), 76.6 (bs, 1C, OCH), 68.6 (s, 1C, CH(Cy)),

67.1 (s, 1C, CH(Cy)), 65.8 (bs, 1C, OCH2), 65.7 (bs, 1C, OCH2), 63.8 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 63.4 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 50.7 (d, 2JCP ¼ 20.0, 1C, CH2(Bn)), 49.5 (d, 2JCP ¼ 18.8, 1C, CH2(Bn)), 46.2 (d, 2JCP ¼ 10.0, 1C, CH2(Bn)), 46.0 (d, 2JCP ¼ 8.8, 1C, CH2(Bn)), 30.7 (s, 1C, CH2(Cy)), 30.2 (s, 1C, CH2(Cy)), 27.6 (d, 3JCP ¼ 5.0, 1C, CH2(Cy)), 27.5 (d, 3JCP ¼ 5.0, 1C, CH2(Cy)), 26.3 (s, 1C, CH3), 26.1 (s, 1C, CH3), 24.1 (s, 1C, CH2(Cy)), 23.8 (s, 1C, CH2(Cy)), 23.7 (s, 1C, CH2(Cy)), 23.5 (s, 1C, CH2(Cy)). HR-MS (ESI, m/z): calcd for C62H73N4O4P2Pd 1105.4142, found 1105.4138 [M]þ. Anal. Calcd. for C62H73F6N4O4P3Pd: C 59.50, H 5.88, N 4.48%; found: C 56.98, H 5.92, N 4.52%.

7a-(R,R;Sal,Sal;R,R)

To a solution of a-(R,R;Sal,Sal;R,R) (0.40 mmol) in toluene (10 mL) at 0 C a solution of [Pd(h3-Ph2C3H3)(m-Cl)]2 (134 mg, 0.20 mmol) in CH2Cl2 (30 mL) was added dropwise. Then a solution of NaPF6 (67 mg, 0.40 mmol) in THF (10 mL) was added. After 1 h of stirring at room temperature, a solution of NaBPh4 (204 mg, 0.60 mmol) in 20 mL of MeOHwas added. The white solid formed on standingwas filtered off and washed with deoxygenated water.

Yield: 189 mg (35%). Mp: 175e178 C dec. 31P{1H} NMR (101.2 MHz, CDCl3, d (ppm), J (Hz)): 135.5 (d, 2JPP ¼ 152.4), 130.2 (d, 2JPP ¼ 152.4). 1H NMR (400 MHz, CDCl3, d (ppm), J (Hz)): 7.57e6.85 (om, 50H, CH(Ar)), 6.55 (t, 3JHH ¼ 12.9, 1H, CHcentral(allyl)), 4.92e4.67 (om, 1H, CH2(Bn), 4.74 (bs, 1H, CH(anti)), 4.49 (pt, 2JHH ¼ 3JHP ¼ 16.4, 1H, CH2(Bn)), 4.43e4.07 (om, 5H, 3CH2(Bn) þ 2OCH), 4.30 (bs, 1H, CH(anti)), 3.88e3.81 (om, 1H, CH2(Bn)), 3.47 (dd, 2JHH ¼ 16.0, 3JHP ¼ 8.0, 1H, CH2(Bn)), 3.26 (dd, 2JHH ¼ 16.0, 3JHP ¼ 26.0, 1H, CH2(Bn)), 2.71 (m, 1H, CH(Cy)), 2.64 (m, 1H, CH(Cy)), 2.50e0.67 (om, 18H, 16CH2(Cy) þ 2CH(Cy)), 0.92 (d, 3JHH ¼ 4.0, 3H, CH3), 0.77 (d, 3JHH ¼ 5.6, 3H, CH3). 13C{1H} NMR (100.6 MHz, CDCl3, d (ppm), J (Hz)): 164.2 (q, 1JCB ¼ 49.0, 4C, CB(Ar)),138.5 (d, 3JCP ¼ 7.0, 1C, C(Ar)), 137.3 (s, 1C, C(Ar)), 136.8 (s, 1C, C(Ar)), 136.3 (s, 1C, C(Ar)), 135.7 (dd, JCP1 ¼9.0, JCP2 ¼ 5.0, 1C, C(Ar, allyl)),134.8 (dd, 3JCP1 ¼8.5, 3JCP2 ¼ 6.5, 1C, C(Ar, allyl)), 129.8e121.7 (50C, CH(Ar)), 112.9 (pt, JCP ¼ 11.0, 1C, CHcentral (allyl)), 93.7 (dd, 2JCPtrans ¼ 36.2, 2JCPcis ¼ 8.0, 1C, CH(allyl)), 82.6 (dd, 2JCPtrans ¼ 40.0, 2JCPcis ¼ 10.0, 1C, CH(allyl)), 79.5 (dd, 2JCP ¼ 28.0, 3JCP ¼ 14.0, 2C, OCH), 69.8 (d, 2JCP ¼ 3.0, 1C, CH(Cy)), 69.7 (d, 2JCP ¼ 3.0, 1C, CH(Cy)), 63.3 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 62.3 (d, 2JCP ¼ 5.0, 1C, CH(Cy)), 51.9 (d, 2JCP ¼ 21.0, 1C, CH2(Bn)), 51.1 (d, 2JCP ¼ 20.0, 1C, CH2(Bn)), 47.8 (d, 2JCP ¼ 8.0, 1C, CH2(Bn)), 47.2 (d, 2JCP ¼ 10.0, 1C, CH2(Bn)), 31.1 (d, 3JCP ¼ 2.0, 1C, CH2(Cy)), 30.5 (bs, 1C, CH2(Cy)), 29.7 (bs, 1C, CH2(Cy)), 28.6 (s, 1C, CH2(Cy)), 27.9 (d, 3JCP ¼ 6.0, 1C, CH2(Cy)), 24.0 (s, 1C, CH2(Cy)), 23.8 (d, 3JCP ¼ 17.0, 1C, CH2(Cy)), 23.7(d, 3JCP ¼ 12.0, 2C, CH2(Cy)), 17.7 (s, 1C, CH3), 17.6 (s, 1C, CH3). HR-MS (ESI, m/z): calcd for C59H69N4O2P2Pd C62H73N4O4P2Pd 1033.3931, found 1033.3937 [M]þ.

Elemental analysis results of palladium complexes are generally outside the range viewed as adequate for establishing analytical purity. The presence of solvent molecules not removed after several hours

under vacuum and/or bad combustion of the solid samples are probably the reasons of these bad elemental analysis values. In the experimental part are only shown the microanalysis results that are acceptable.

31P{1H} NMR of complexes 2a-c, 2e, 4f, 4g and 6b show one heptuplet at d ¼ -144.0 ppm and 1J ¼ 715 Hz of the PF6 anion.

4.4. General procedure for palladium-catalyzed Allylic substitution

4.4.1. Allylic alkylation of rac-3-acetoxy-1,3-diphenyl-1-propene

Reactions were carried out into an Schlenk tube under N2 at 25 C. 0.01 mmol of the palladium precursor was dissolved in 8 mL of CH2Cl2. Then, 1 mmol of the substrate rac-3-acetoxy-1,3- diphenyl-1-propene and 1.5 mmol of Na(CH(COOMe)2) were added to the solution. The mixturewas stirred at room temperature for 24 h. At the end of the reaction, the mixture was diluted with diethyl ether, washed with ammonium chloride solution (3 10 mL) and water (2 10 mL). The organic phase was dried over anhydrous Na2SO4 and filtered off. After partially removing the solvent under reduced pressure, the solution was eluted through a short silica column with ethyl acetate. The conversion was determined by 1H NMR and the enantiomeric excess by HPLC on a Chiralcel-OD-H chiral column, using hexane/isopropanol 95/5 as eluent and a flow of 0.5 mL/min.

4.4.2. Allylic alkylation of rac-3-acetoxy-1-ciclohexene

The procedurewas analogous to that described for rac-3-acetoxy- 1,3-diphenyl-1-propene using rac-3-acetoxy-1-ciclohexene as substrate. Purificationwas performed by column chromatography (SiO2: ethyl acetate). The conversion and enantiomeric excess were determined by GC on a CHIRALDEX DM column.

4.4.3. Allylic amination of rac-3-acetoxy-1,3-diphenyl-1-propene

The procedure was analogous to that described for allylic alkylation of rac-3- acetoxy-1,3-diphenyl-1-propene, using 3 mmol of benzylamine as nucleophile and 4 mL of CH2Cl2. Conversion was determined by 1H NMR and enantiomeric excesses by HPLC on a Chiralcel-OD-H chiral column, using hexane/isopropanol 99/1 as eluent and a flow of 0.3 mL/min.

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935 **Legends to figures**

936

937 **Figure. 1** Diamidophosphite ligands P-P and P used in this work (new ligands in red). (For
938 interpretation of the references to colour in this figure legend, the reader is referred to the web version of
939 this article.)

940

941 **Scheme 1.** Synthesis of dichloropalladium complexes 1a and 1c.

942

943 **Scheme 2**. Synthesis of allyl palladium complexes 2a-c, 2e, 4f, 4g and 3a, 3b, 3d, 3e, 5f.

944

945 **Figure. 2** NOE contacts (blue) and exchange signals (red). (For interpretation of the references to
946 colour in this figure legend, the reader is referred to the web version of this article.)

947

948 **Figure. 3** a) Molecular view of the complex 1a-(S,S;Sal,Sal;S,S), (ellipsoids drawn at 50% probability
949 level). Hydrogen atoms have been omitted for clarity. b) lateral view of the coordination plane showing
950 the symmetric disposition of the ligand bridge. Selected distances (Å) and angles ( ): P1-Pd1
951 2.2254(10), P2-Pd1 2.2172(11), Cl1-Pd1 2.3729(11), Cl2-Pd1 2.3488(11), N1-P1 1.666(3), N2-P1
952 1.650(3), N3-P2 1.641(3), N4-P2 1.661(3), O1-P1 1.617(3), O2-P2 1.606(3); P2-Pd1-P1 90.79(4), Cl2-
953 Pd1-Cl1 92.43 (4), P2-Pd1-Cl2 88.00(4), P1-Pd1- Cl1 89.26(4).

954

955 **Figure. 4** Molecular view of the cation corresponding to the complex 2e-(R,R;Ral,Ral;R,R) (ellipsoids
956 drawn at 50% probability level). Hydrogen atoms and PF_6 anion have been omitted for clarity.
957 Selected distances (Å) and angles ( ): Pd(2)-C(21A) 2.177(11), Pd(2)-C(22A) 2.196(11), Pd(2)-C(23A)
958 2.173(11), Pd(2)-P(4) 2.262(3), Pd(2)-P(3) 2.276(2), P(3)-N(4A) 1.652(9), P(3)-N(3A) 1.672(8), P(4)-
959 N(1A) 1.654(9), P(4)-N(2A) 1.670(8), C(21A)-C(22A) 1.409(16), C(22A)-C(23A) 1.403(16); P(4)-
960 Pd(2)-P(3) 102.31(9), C(21A)-Pd(2)-C(23A) 67.4(4).

961

962 **Scheme 4.** Asymmetric Allylic Alkylation of rac-3-acetoxy-1-cyclohexene (rac-IV)
963 catalyzed by palladium complexes

964

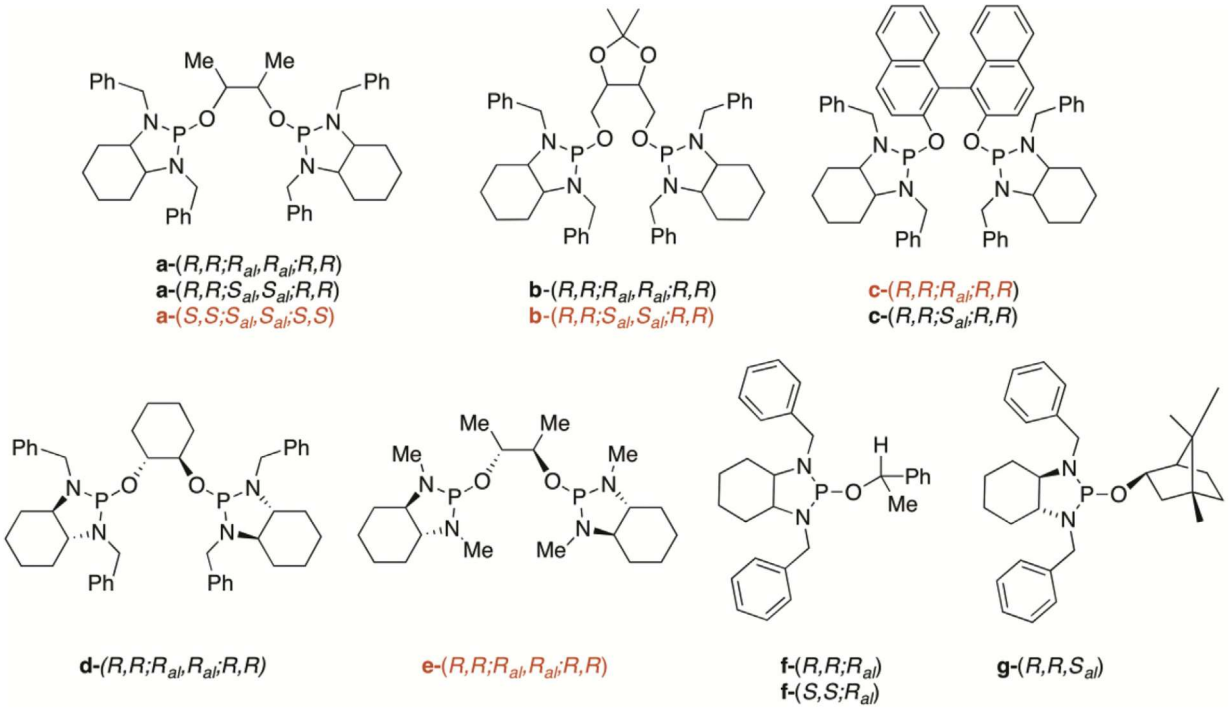
965 **Scheme 5.** Synthesis of allyl Palladium complexes 6b and 7a.

966

967 **FIGURE 1**

968

969



a-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)
a-(*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)
a-(*S,S;S*$_{al}$,*S*$_{al}$;*S,S*)

b-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)
b-(*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)

c-(*R,R;R*$_{al}$;*R,R*)
c-(*R,R;S*$_{al}$;*R,R*)

d-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)

e-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)

f-(*R,R;R*$_{al}$)
f-(*S,S;R*$_{al}$)

g-(*R,R,S*$_{al}$)

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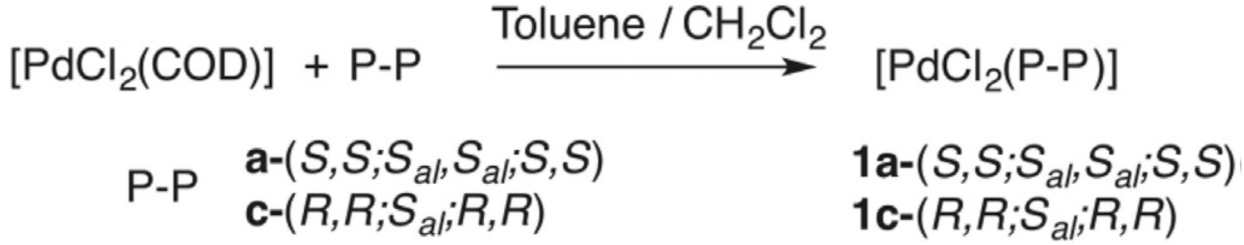
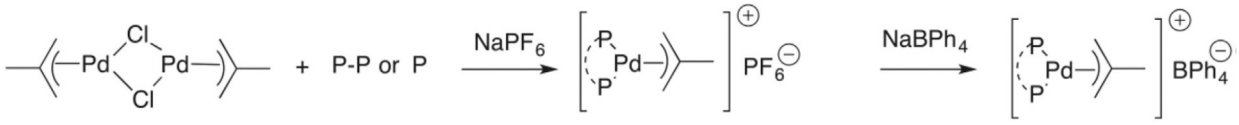
971

972

SCHEME 1.

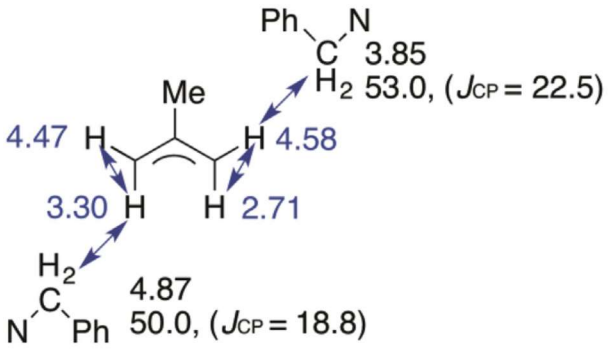

[PdCl2(COD)] + P-P
Toluene / CH2Cl2
[PdCl2(P-P)]
P-P
a-(S,S;Sal,Sal;S,S)
c-(R,R;Sal;R,R)
1a-(S,S;Sal,Sal;S,S)
1c-(R,R;Sal;R,R)

SCHEME 2

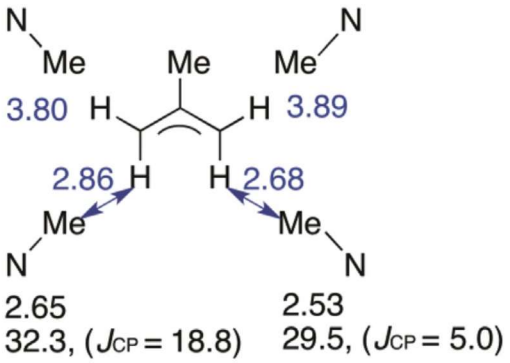


		a-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)	-	**3a-(***R,R;R*$_{al}$,*R*$_{al}$;*R,R)*
		a-(*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)	**2a-***(R,R;S*$_{al}$,*S*$_{al}$;*R,R)*	-
		a-(*S,S;S*$_{al}$,*S*$_{al}$;*S,S*)	**2a**-(*S,S;S*$_{al}$,*S*$_{al}$;*S,S*)	**3a**-(*S,S;S*$_{al}$,*S*$_{al}$;*S,S)*
		b-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)	**2b**-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)	**3b**-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)
	P-P	**b**-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)	**2b**-(*R,R;S*$_{al}$,*S*$_{al}$;*R,R*)	-
		c-(*R,R;R*$_{al}$;*R,R*)	**2c**-(*R,R;R*$_{al}$;*R,R*)	-
		c-(*R,R;S*$_{al}$;*R,R*)	**2c**-(*R,R;S*$_{al}$;*R,R)*	-
		d-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R)*	-	**3d**-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)
		e-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)	**2e**-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)	**3e**-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*)
		f-(*R,R;R*$_{al}$)	**4f**-(*R,R;R*$_{al}$)	-
	P	**f**-(*S,S;R*$_{al}$)	-	**5f**-(*S,S;R*$_{al}$)
		g-(*R,R;S*$_{al}$)	**4g**-(*R,R;S*$_{al}$)	-

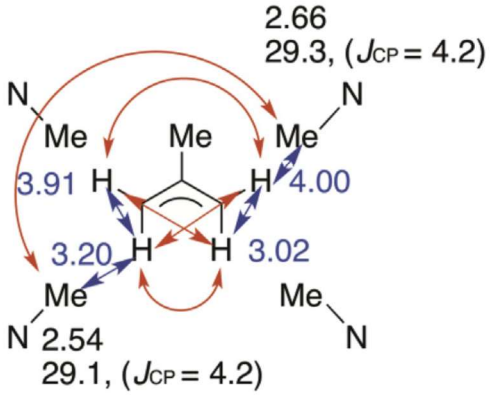
FIGURE 2



2c-(*R,R;S*$_{al}$*;R,R*)



3e-(*R,R;R*$_{al}$*,R*$_{al}$*;R,R*)

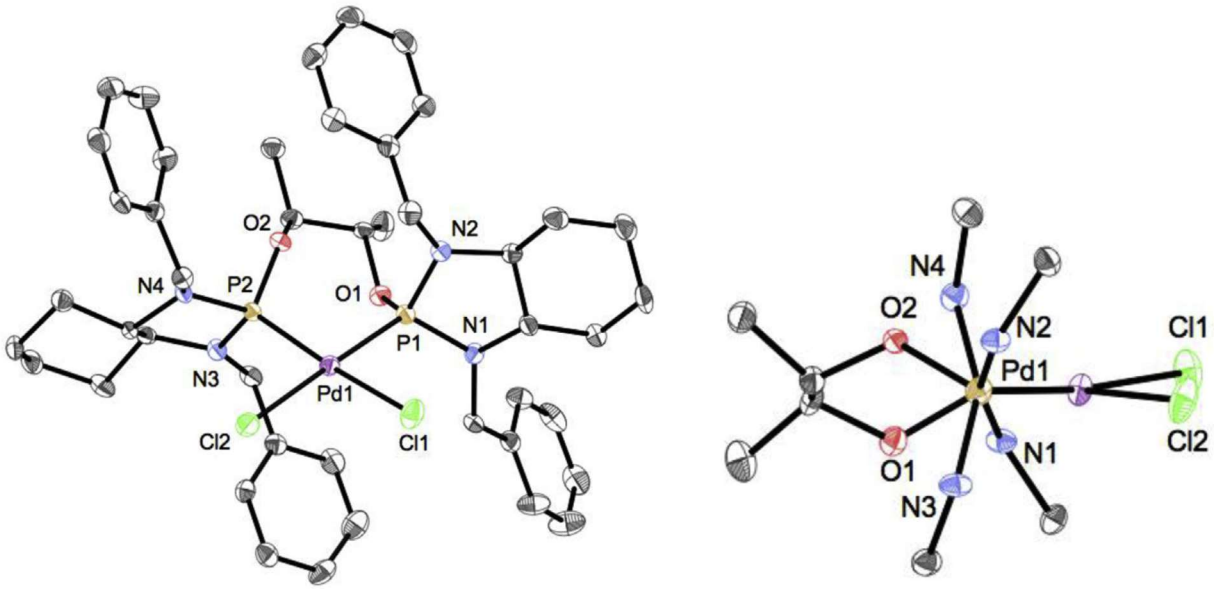


2e-(*R,R;R*$_{al}$*,R*$_{al}$*;R,R*)

988 **FIGURE 3**

989

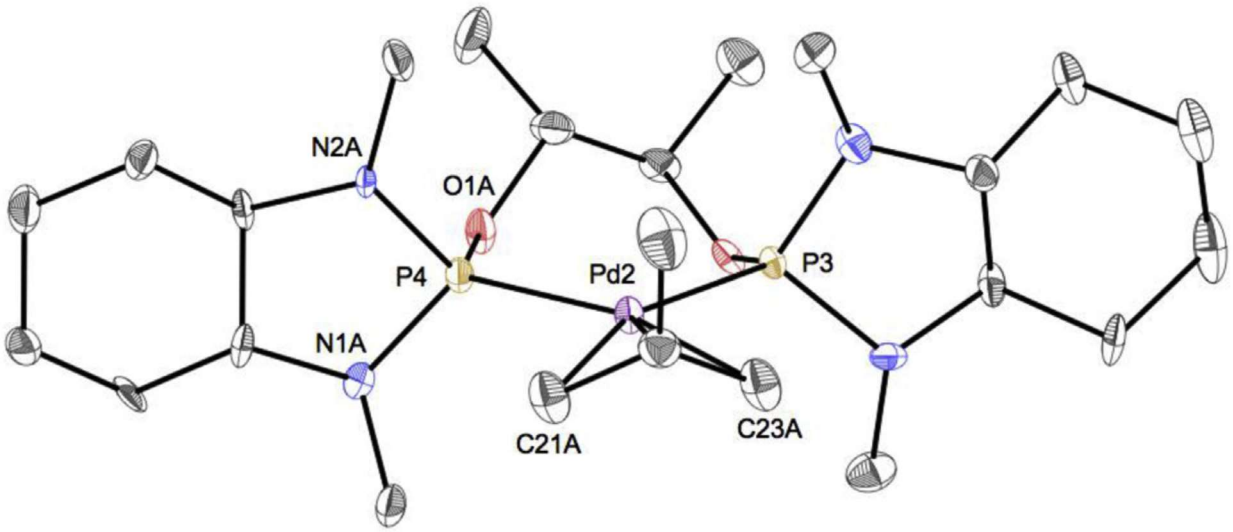
990



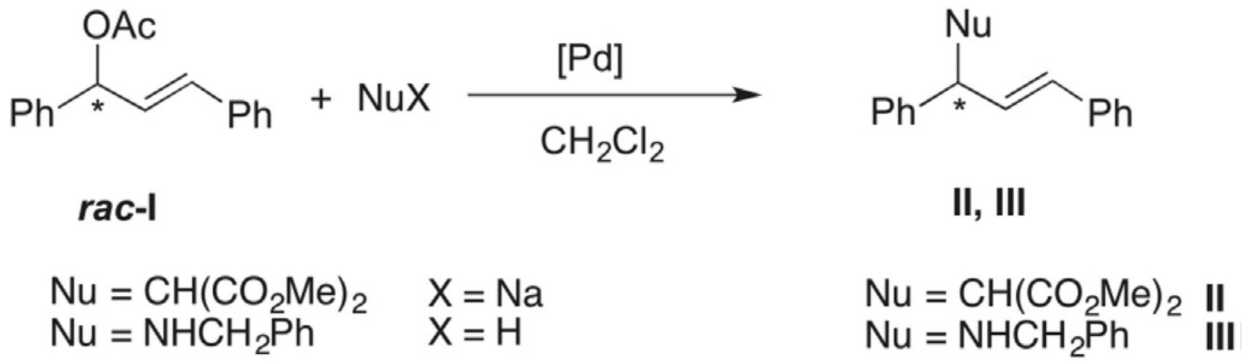
991

992

FIGURE 4



SCHEME 3



***rac*-I** **II, III**

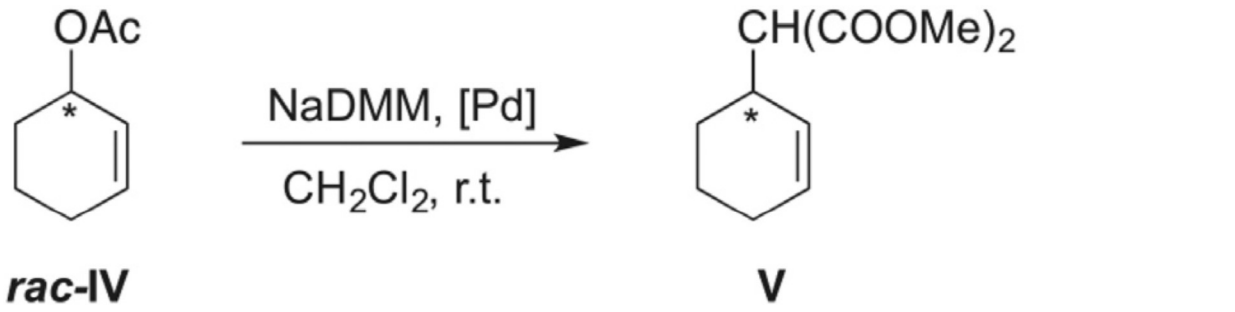
Nu = $CH(CO_2Me)_2$ X = Na
Nu = $NHCH_2Ph$ X = H

Nu = $CH(CO_2Me)_2$ **II**
Nu = $NHCH_2Ph$ **III**

1003 **SCHEME 4**

1004

1005



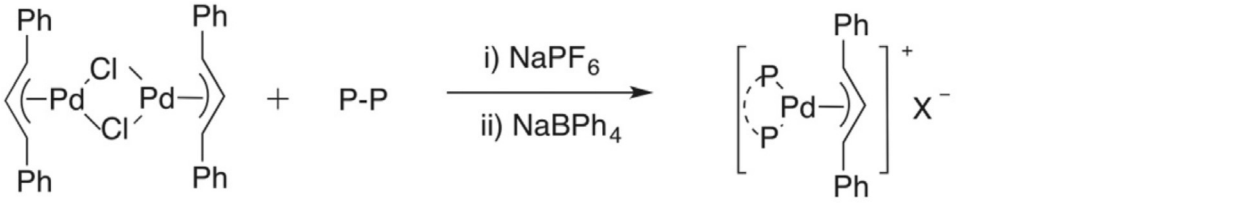
***rac*-IV** **V**

2a-($R,R;S_{al},S_{al};R,R$): Conv: 20%, ee 23% (*S*)
2c-($R,R;S_{al};R,R$): Conv: 25%, ee 10% (*R*)

1006

1007

FIGURE 5.



P-P **b**-(*R,R;R*$_{al}$,*R*$_{al}$;*R,R*) X = PF_6 **6b-**(*R,R;Ral,Ral;R,R*)
a-(*R,R;S*$_{al}$,*S*$_{al}$;*R,R*) X = BPh_4 **7a-**(*R,R;Sal,Sal;R,R*)

1019 **Table 1** Selected 31Pa and 1Ha NMR data for complexes 2a-c, 2e, 3a, 3b, 3d, 3e, 4f, 4g, 5f.

1020

Compound	$\delta^{31}P^{b}$ (complex)	$\delta\ ^{1}H^{c}$		
	[$\delta^{31}P$ (free ligand)]	H_{syn}	H_{anti}	CH_3(allyl)
2a-(*R,R*;S_{at},S_{at};*R,R*)	134.7 (*d*, 95.4) 132.6 (*d*, 95.4) [137.6 (*s*)]	4.07 (*om*)	2.52 (*d*, 15.0) 2.23 (*d*, 15.0)	1.42 (*s*)
2a-(*S,S*;S_{at},S_{at};*S,S*)	135.2 (*d*, 83.2) 130.7 (*d*, 83.2) [138.2 (*s*)]	4.29 (*bs*) 4.23 (*bs*)	2.92 (*d*, 15.0) 2.69 (*d*, 10.0)	1.62 (*s*)
3a-(*R,R*;R_{at},R_{at};*R,R*)	135.6 (*d*, 84.1)	4.07 (*om*)	2.65 (*d*, 10.0)	1.48 (*s*)
3a-(*S,S*;S_{at},S_{at};*S,S*)	130.7 (*d*, 84.1) [138.2 (*s*)]		2.52 (*d*, 15.0)	
2b-(*R,R*;S_{at},S_{at};*R,R*)	120.1 (*d*, 94.5) 117.7 (*d*, 94.5) [136.3 (*s*)]	4.13 (*bs*) 3.98 (*d*, 8.8)	2.73 (*d*, 15.0) 2.52 (*d*, 15.0)	1.69 (*s*)
2b-(*R,R*;R_{at},R_{at};*R,R*)	122.1 (*d*, 91.6) 120.8 (*d*, 91.6) [136.3 (*s*)]	4.18 (*d*, 9.2) 4.02 (*d*, 7.4)	2.85 (*d*, 11.3) 2.67 (*d*, 13.9)	1.77 (*s*)
3b-(*R,R*;R_{at},R_{at};*R,R*)	121.5 (*d*, 92.0) 118.7 (*d*, 92.0) [136.3 (*s*)]	3.94 (*bs*) 3.84 (*bs*)	2.49 (*d*, 15.0) 2.23 (*d*, 15.0)	1.60 (*s*)
2c-(*R,R*;S_{at};*R,R*)	139.0 (*d*, 60.1) 133.0 (*d*, 60.1) [139.3 (*s*)]	4.58 (*bs*) 4.47 (*bs*)	3.30 (*d*, 10.0) 2.71(*bs*)	1.93 (*s*)
2c-(*R,R*;R_{at};*R,R*)	138.4 (*d*, 59.9) 133.4 (*d*, 59.9) [139.2 (*s*)]	4.50 (*bs*) 4.44 (*bs*)	3.38 (*d*, 10.0) 3.01(*bs*)	1.76 (*s*)
3d-(*R,R*;R_{at},R_{at};*R,R*)	134.1 (*d*, 87.1) 129.2 (*d*, 87.1) [136.5 (*s*)]	4.04 (*bs*) 4.01 (*bs*)	2.56 (*d*, 10.0) 2.47 (*d*, 15.0)	1.45 (*s*)
2e-(*R,R*;R_{at},R_{at};*R,R*)	131.6 (*d*, 90.5) 128.7 (*d*, 90.5) [142.6 (*s*)]	4.00 (*bs*) 3.91 (*dd*, 15, 5)	3.20 (*d*, 15.0) 3.02 (*d*, 15.0)	1.85 (*s*)
3e-(*R,R*;R_{at},R_{at};*R,R*)	135.5 (*d*, 90.4) 130.1 (*d*, 90.4) [142.6 (*s*)]	3.89 (*bs*) 3.80 (*bs*)	2.86 (*d*, 15.0) 2.68 (*d*, 15.0)	1.72 (*s*)
4f-(*R,R*;R_{at})	124.0 (*d*, 85.2) 122.2 (*d*, 85.2) [135.2 (*s*)]	4.50 (*bs*) 4.32 (*bs*)	3.00 (*d*, 13.6) 2.88 (*d*, 13.6)	1.87 (*s*)
5f-(*S,S*;R_{at})	120.7 (*d*, 83.5) 115.9 (*d*, 83.5) [140.7 (*s*)]	4.17 (*bs*) 3.81 (*bs*)	2.50 (*d*, 15.0) 2.08 (*d*, 15.0)	1.63(*s*)
4g-(*R,R*;S_{at})	126.3 (*d*, 76.2) 119.6 (*d*, 76.2) [142.4 (*s*)]	4.24 (*bs*) 3.93 (*bs*)	2,64 (*d*, 15.0) 1.90 (*bs*)	1.64 (*s*)

[a] Chemical shifts in ppm; $^{31}P\{^{1}H\}$ (121,44 MHz, 298 K) and ^{1}H (400 MHz, 298 K) recorded in $CDCl_3$; coupling constants in Hz; overlapped signals assigned from gHSQC spectra; *s* (singlet), *d* (doublet), *t* (triplet), *br* (broad), *m* (multiplet), *o* (overlapped).

[b] multiplicity and J_{PP} in parenthesis.

[c] multiplicity and J_{HP} in parenthesis.

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1023

Table 2 Results of the asymmetric allylic substitution of rac-3-acetoxy-1,3-diphenyl-1-propene (rac-I).

Entry	Catalyst precursor	$NaCH(COOMe)_2$[a]		$BnNH_2$[b]	
		conv.%[c]	ee %[d]	conv.%[c]	ee %[d]
1	**2a**-(R,R-S_{at},S_{at};R,R)	70	86 (*S*)	30	65 (*R*)
2	**2a**-(S,S-S_{at},S_{at};S,S)	85	62 (*R*)	100	45 (*S*)
3	**3a**-(R,R;R_{at},R_{at};R,R)	100	84 (*S*)	100	80 (*R*)
4	**3a**-(S,S;S_{at},S_{at};S,S)	100	83 (*R*)	100	80 (*S*)
5	**2b**-(R,R;S_{at},S_a;R,R)	100	51 (*S*)	87	68 (*R*)
6	**2b**-(R,R;R_{at},R_{at};R,R)	98	36 (*S*)	45	72 (*R*)
7	**3b**-(R,R;R_{at},R_{at};R,R)	68	20 (*S*)	100	32 (*R*)
8	**2c**-(R,R;R_a;R,R)	82	32 (*S*)	100	37 (*R*)
9	**2c**-(R,R;S_{at};R,R)	78	55 (*R*)	100	35 (*R*)
10	**3d**-(R,R;R_{at},R_{at};R,R)	50	69 (*S*)	74	26 (*R*)
11	**4f**-(R,R;R_{at})	100	7 (*R*)		
12	**5f**-(S,S;R_{at})	100	7 (*S*)		
13	**4g**-(R,R;S_{at})	100	8 (*S*)		

[a] Reaction conditions: ***rac*-4**/$NaCH(COOMe)_2$/[Pd]/X = 1/1.5/0.01, 8 mL of CH_2Cl_2, 25 °C, 24 h.

[b] ***rac*-4**/Bn-NH_2/[Pd]/X = 1/3/0.01, 4 mL of CH_2Cl_2, 25 °C, 24 h.

[c] Conversions were determined by ^1H NMR spectroscopy.

[d] ee determined by HPLC, absolute configuration was determined by comparison with the known sign of specific rotation.