

1 **Diphosphorus Ligands Containing a P-Stereogenic Phosphane and a Chiral Phosphite or**  
2 **Phosphorodiamidite – Evaluation in Pd-Catalysed Asymmetric Allylic Substitution Reactions**

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33 **ABSTRACT:**

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35 The synthesis of 14 new optically pure C<sub>1</sub>-symmetric phosphane–phosphinite (1–4), phosphane–  
36 phosphite (5–9) and phosphane–phosphorodiamidite (10–14) ligands is reported. The ligands were  
37 prepared through the condensation of (2-hydroxyphenyl)phenylphosphanes PPh(2-PhOH)R (R = Me,  
38 tBu and Ph) with chlorodiisopropylphosphane (1 and 2), chlorodiphenylphosphine (3 and 4), the  
39 chlorodioxaphosphine derived from both enantiomers of 1,1'-bi-2-naphthol (5–9) and the  
40 chlorodiazaphosphine derived from both enantiomers of N,N'-dimethyl-1,1'-binaphthyl-2,2'-diamine  
41 (10–14) in the presence of a base. With these ligands, cationic Pd complexes of the type [Pd(η<sup>3</sup>-  
42 C<sub>4</sub>H<sub>7</sub>)(PP')]PF<sub>6</sub> (Pd1–Pd14) were obtained and characterised; the crystal structures of Pd1, Pd2 and  
43 Pd13 were obtained. In solution, the complexes are present as mixtures of two diastereomers because of  
44 the lack of symmetry of the ligand and the presence of the methallyl group. The Pd complexes catalyse  
45 the allylic alkylation with dimethyl malonate and the amination with benzylamine of the model substrate  
46 rac-3-acetoxy-1,3-diphenyl-1-propene (I). For the alkylation, full conversions and good  
47 enantioselectivities (up to 96 % ee with Pd14) were observed.

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## 51 INTRODUCTION

52

53 Chiral phosphorus-based ligands have dominated asymmetric transition-metal homogeneous catalysis  
54 for more than 50 years.[1] Many of the most successful ligands are C<sub>2</sub>-symmetric diphosphanes,[2]  
55 which were initially thought to be superior ligands to monophosphanes or C<sub>1</sub>-symmetric ligands as the  
56 reduced number of intermediates and transition states in each step of a catalytic cycle would lead to  
57 higher enantioselectivities and simpler analysis of the results.

58 However, a much more complicated picture has now emerged. Although certain structural motifs lead to  
59 especially active and enantioselective ligands,[3] there will clearly never be a “universal ligand” suitable  
60 for all reactions and substrates. Therefore, all possible sources of structural diversity have been explored  
61 actively for the last two decades, and old dogmas and preconceptions have been revised or  
62 abandoned.[3,4] Nowadays, very active and enantioselective catalysts can contain ligands that are not  
63 phosphanes but possess one or more P–heteroatom bonds,[5] including many monophosphorus  
64 ligands.[6] It is also widely accepted that the previously ubiquitous C<sub>2</sub>-symmetric diphosphorus ligands  
65 (PP) are not better per se than their C<sub>1</sub>-symmetric counterparts (PP').[5a,5c,7] Finally, a strong  
66 resurgence of P-stereogenic ligands has also occurred.[4b,8] The extraordinary activity in the area of  
67 ligand design is understandable for the ever-increasing demand of optically pure compounds in  
68 pharmaceutical, agrochemical and other fields and is evident from the number of recent reviews[5b,7,9]  
69 and monographs[ 4] about the synthesis of chiral phosphorus-based ligands.

70 Only a few C<sub>1</sub>-symmetric diphosphorus ligands containing both a P-stereogenic phosphane and another  
71 phosphorus donor unit with a P–heteroatom bond have been reported.[10]

72 We have been working on the synthesis and catalytic applications of many chiral mono- and bidentate  
73 aminophosphane,[11] phosphinite,[12] phosphite[13] and phosphorodiamidite[14] ligands in several  
74 catalytic reactions. We have also been working on the synthesis and catalytic applications of P-  
75 stereogenic ligands.[12a,12b,15]

76 Therefore, it was deemed interesting to devote some effort to merge both areas of our previous research  
77 and prepare a few PP' (P = P-stereogenic phosphane; P' = phosphinite, phosphite or phosphorodiamidite)  
78 ligands and evaluate their catalytic potential. In this paper, we describe the synthesis of these ligands  
79 and their derived Pd complexes as well as their application as catalyst precursors in allylic substitution  
80 reactions.

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## 83 RESULTS AND DISCUSSION

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### 85 Ligand Synthesis

86 Upon analysing the possible routes to obtain modular P-stereogenic PP' ligands with an appropriate  
87 bridge to form bidentate ligands, it was concluded that a relatively easy way would be the condensation  
88 reaction between an electrophilic chlorophosphorus precursor and a configurationally stable P-  
89 stereogenic 2-hydroxyphenylphosphane in the presence of base. Such reactions would yield PP' ligands  
90 with rigid 2-oxyphenyl bridges between the two phosphorus atoms (Scheme 1).

91 An early paper of Pringle and Baker[16] described the preparation of one such ligand (see later),  
92 whereas Pizzano and coworkers have used this scaffold to prepare a series of phosphane–phosphite  
93 ligands and used them in Rh-[10f,10g,10l,17] and Ir-catalysed[10i,18] hydrogenations and in Rh-  
94 catalysed hydroformylation;[10l] however, only a few of their ligands possess a P-stereogenic  
95 phosphane moiety.

96 The required P-stereogenic 2-hydroxyphenylphosphanes are accessible as optically pure compounds by  
97 the well-known Jugé–Stephan method[19] starting from oxaphospholidine–borane A. Therefore, we  
98 started by reproducing the work of Stephan and co-workers,[20] who described the preparation of 2-  
99 hydroxyphenylphosphinite–borane B, and we obtained 2-hydroxyphenylphosphane C·BH<sub>3</sub> by treatment  
100 with excess methyllithium (Scheme 2).

101 A solution of B was also treated with excess tert-butyllithium to afford the corresponding 2-  
102 hydroxyphenylphosphane–borane C'·BH<sub>3</sub>. It has to be noted that it is very difficult[21] to introduce the  
103 tert-butyl group to a phosphane through the Jugé–Stephan method. However, in this case, it seems that  
104 the presence of an oxygen-containing group at the ortho position relative to the P atom facilitates the  
105 organolithium attack.[21a,21c] Phosphane–boranes C·BH<sub>3</sub> and C'·BH<sub>3</sub> were deboronated by treatment  
106 with tetrafluoroboric acid to yield the free phosphinophenols C and C' as air-sensitive semisolids. The  
107 absolute configurations of the phosphorus atoms, expected to be S, could be verified by the crystal  
108 structures of the Pd complexes of the ligands (described below). The preparation of the achiral  
109 phosphinophenol C'' was not required because it is commercially available. To complete the synthesis of  
110 the ligands, phosphinophenols C–C'' were treated with the appropriate chlorophosphorus precursors  
111 (either commercially available or described previously)[14] in the presence of amines as detailed in the  
112 Experimental Section. After the removal of the ammonium salts by filtration and exhaustive drying  
113 under vacuum, the desired PP' ligands were finally obtained as pasty solids. The ligands prepared in the  
114 present work are shown in Figure 1.

115 To the best of our knowledge, all of the prepared ligands are new except ligand 9, which was described  
116 by Baker and Pringle[16] and used by Pizzano and co-workers in Rh-catalysed hydrogenation.[17b] The  
117 ligands were characterised by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, which supported the structures  
118 depicted in Figure 1. In general, two doublets (4J<sub>P,P</sub> = 0–41 Hz) were observed in the <sup>31</sup>P{<sup>1</sup>H} NMR  
119 spectra, and the coupling constants are strongly dependent on the ligand. The coupling constants for the

120 phosphane–phosphinite ligands 1–4 are rather small (0–4 Hz), but those for phosphane–phosphite  
121 ligands 5–9 are much larger (15–42 Hz), whereas those for the phosphane–phosphorodiamidite ligands  
122 10–14 have intermediate values (7–16 Hz). As expected,[14a] small differences in the  $^{31}\text{P}\{^1\text{H}\}$  NMR  
123 chemical shifts for each of the members in the diastereomeric pairs 5/7, 6/8, 10/12 and 11/13 could be  
124 spotted. In the  $^1\text{H}$  NMR spectra of phosphane–phosphorodiamidite ligands 10–14, two doublets  
125 appeared for the two inequivalent N–Me groups coupled to the phosphorus atom, as previously reported  
126 for related compounds.[14a] A more thorough characterisation was not possible owing to the rapid  
127 degradation of the ligands by oxidation, hydrolysis, or both if they were not kept under a protective  
128 nitrogen atmosphere. Therefore, the ligands were not stored but used immediately for complexation to  
129 Pd as described in the following section.

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### 131 **Preparation of Pd Complexes**

132 The reaction of the Pd dimer D with 2 equiv. of ligand in dichloromethane in the presence of excess  
133 ammonium hexafluorophosphate[ 12b,12c] yielded the expected cationic complexes of the type  $[\text{Pd}(\eta^3\text{-}$   
134  $\text{C}_4\text{H}_7)(\text{PP}')]\text{PF}_6$  (Pd1–Pd14) as white or pale yellow solids after workup (Scheme 3).

135 The characterisation of solutions of the complexes by multinuclear ( $^{31}\text{P}\{^1\text{H}\}$ ,  $^1\text{H}$ , and in some cases  
136  $^{13}\text{C}\{^1\text{H}\}$ ) NMR spectroscopy revealed duplicate peaks indicative of the existence of two  
137 diastereoisomeric species owing to the lack of  $\text{C}_2$  symmetry of the bidentate ligand and the presence of  
138 the  $\eta^3$ -methallyl moiety, as previously observed for neutral complexes of the type  $[\text{Pd}(\eta^3\text{-C}_4\text{H}_7)\text{Cl}(\text{P})]$   
139 ( $\text{P}$  = chiral monophosphorus ligand).[12a,12c,14a,14c,22] The integration of the  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR  
140 spectra allowed the estimation of the diastereomeric ratio for each complex. There does not seem to be a  
141 simple correlation between the structures of the complexes and their diastereomeric ratios, which varied  
142 from 1:1 (Pd2, Pd4, Pd7, Pd12 and Pd14) to a maximum of 1:2.7 for Pd5. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra,  
143 two sharp pairs of doublets, one for each diastereomer, are indicative of AX spin systems. The  $2J_{\text{P},\text{P}'}$   
144 values are in the range previously reported for related compounds[14d,23] and follow the same trends as  
145 the  $4J_{\text{P},\text{P}'}$  values for the free ligands. The  $^{31}\text{P}$  coordination chemical shifts (CCS, defined as  $\delta_{\text{complex}} -$   
146  $\delta_{\text{free ligand}}$ ) of the phosphane fragments are approximately +30 ppm for the complexes, as expected. In  
147 contrast, the other phosphorus moiety shows a larger sensitivity to coordination The CCS values are  
148 approximately +40 ppm for phosphinite complexes Pd1–Pd4, +2 ppm for phosphite complexes Pd5–Pd9  
149 and –15 ppm for phosphorodiamidite complexes Pd10–Pd14. The shielding of the P atom of the  
150 phosphorodiamidite upon coordination is probably due to the low  $\sigma$  donation of this part of the ligand  
151 and has been reported for the complexation of other chiral phosphorodiamidite ligands.[14,24]  
152 In  $^1\text{H}$  NMR spectra, two sets of peaks associated with the aliphatic protons of each ligand are observed  
153 (see Experimental Section and Table S1 of the Supporting Information for details). For Pd10–Pd14  
154 bearing the phosphane–phosphorodiamidite ligands, two pairs of doublets, one for each isomer, account  
155 for the methyl groups of the diazaphosphepine part of the ligand. Interestingly, the  $3J_{\text{H},\text{P}}$  coupling  
156 constants are clearly different for the two methyl groups of each isomer (ca. 10 and 15 Hz), and the

157 same can be observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, in which  $2\text{J}_{\text{C,P}} \approx 12$  and  $30$  Hz. This suggests that  
158 the amino groups have a different orientation in solution with respect to the P–Pd bond, as observed in  
159 the solid state (vide infra) and for previously reported related compounds.[14d,24,25]

160 For the methallyl group, the  $^1\text{H}$  NMR spectra (Table S1) confirm the presence of two diastereomers.  
161 Hence, two singlets at  $\delta = 1.3\text{--}2.0$  ppm account for the methyl group, whereas two sets of four peak in  
162 the range  $\delta = 2.3\text{--}4.8$  ppm can be assigned to the four protons of the methallyl group. As  
163 expected,[14a,14d,22,23] the anti protons usually appear at higher fields ( $\delta = 2.3\text{--}3.8$  ppm) as doublets  
164 with coupling constants of ca.  $10$  Hz owing to the coupling with the phosphorus atom at the relative  
165 trans position. In a few cases, they appear as doublets of doublets, also coupled to the phosphorus atom  
166 at the cis position. At lower fields ( $\delta = 3.6\text{--}4.8$  ppm), two sets of syn protons appear as broad singlets,  
167 doublets, doublets of doublets or multiplets. For these protons, the coupling constants are smaller, as  
168 commonly found for comparable systems.[14a,14d,22,23] In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (Table S1), the  
169 methylene termini of the methallyl groups appeared as doublets or doublets of doublets owing to the  
170 coupling with one or two phosphorus atoms, respectively. The difference in the chemical shifts, which  
171 has been used to evaluate the asymmetry of the allyl bonding,[26] ranged from  $2.5$  ppm for one of the  
172 isomers of Pd3 to  $13.6$  ppm for one of the isomers of Pd2.

173 For Pd1, Pd2 and Pd13, single crystals suitable for X-ray diffraction studies were obtained by layering  
174 hexane on solutions of the complexes in dichloromethane. For all of these complexes, the structures are  
175 composed of discrete molecules of the cationic complex, hexafluorophosphate anions and  
176 dichloromethane molecules as well as adventitious water molecules for Pd13 separated by van der  
177 Waals distances. It is interesting to note that only one diastereomer was found in all of the crystals  
178 analysed. Representations of the molecular structures of Pd1 and Pd2 and a selection of bond lengths  
179 and angles are given in Figure 2.

180 For both structures, the palladium atom sits in a distorted square-planar geometry, coordinated to the  
181 two phosphorus atoms and to the terminal C atoms of the methallyl moiety. The metric parameters are in  
182 the ranges expected for cationic allylpalladium complexes.[12b,14d,22] For both structures, the Pd–  
183 Callyl distance trans to the phosphinite moiety is longer than the Pd–Callyl distance trans to the  
184 phosphane moiety, especially for Pd2. The same trend has been found for comparable complexes.[27]  
185 The X-ray structure of the phosphane–phosphorodiamidite complex Pd13 is depicted in Figure 3.  
186 The complex has a distorted square-planar geometry around the palladium atom, and the coordination  
187 positions are occupied by the two phosphorus atoms of the ligand and the two terminal atoms of the  
188 methallyl fragment. The distances and angles are similar to those for comparable complexes.[14d] The  
189 Pd–Callyl distance trans to the phosphorodiamidite fragment is longer than the Pd–Callyl distance trans  
190 to the phosphane moiety, as observed for complexes containing comparable phosphane–  
191 phosphoramidite ligands.[27] The two P–N bond lengths are different and in the range found for similar  
192 compounds.[14a,14c,14d] The values suggest a partial double-bond character, as found in related  
193 complexes.[14d] The sums of the bond angles around both nitrogen atoms are close to  $360^\circ$ ; therefore,

194 the coordination is close to planarity, as occurs for related complexes.[14d,25] The torsion angle of the  
195 binaphthyl group is 59.14°.

196 It is interesting to note that the longest Pd–Callyl distance in all the three crystal structures is always in  
197 the cis position with respect to the P-stereogenic phosphane group.

198 Pd-Catalysed Allylic Substitution The performance of the ligands 1–14 was tested in Pd-catalysed  
199 asymmetric allylic substitution reactions with the model substrate rac-3-acetoxy-1,3-diphenyl-1-propene  
200 (I) and the cationic palladium complexes Pd1–Pd14 (Scheme 4).

201 The studied allylic substitutions involved alkylation with the C-nucleophile derived from dimethyl  
202 malonate (DMM) in the presence of N,O-bis(trimethylsilyl)acetamide (BSA) and potassium acetate and  
203 amination with benzylamine. The obtained results are given in Table 1.

204 All of the complexes were active in the allylic alkylations and provided complete conversions in 24 h  
205 with 1 % of complex. A wide range of ee values (5–96 %) was obtained, in line with the results for other  
206 C1-symmetric diphosphorus ligands.[10d,27,28] The complexes with phosphane–phosphinite ligands,  
207 containing only the phosphorus atom as a stereogenic element (Table 1, Entries 1–4), led to the lowest  
208 enantioselectivities, and Pd4 achieved a moderate value of 45 % ee (Table 1, Entry 4). The results with  
209 the other complexes with two stereogenic elements (Table 1, Entries 5–14) allow the discussion of the  
210 match–mismatch effects between them. A general trend is that the enantioselectivities are considerably  
211 higher than those for complexes containing phosphane–phosphinite ligands, and this highlights the  
212 efficiency of the 1,1'-binaphthyl unit as a chiral inductor. Indeed, most of the ligands give very  
213 enantioselective systems that afford similar or better results than those with other phosphane–  
214 phosphite[10d,28a] or phosphane–phosphoramidite ligands[27] except Pd7, Pd11 and Pd13 (Table 1,  
215 Entries 7, 11 and 13). There is a match–mismatch effect between the absolute configurations of the 1,1'-  
216 bi-2-naphthyl fragment of the phosphite or phosphorodiamidite moiety and the stereogenic phosphorus  
217 atom. Clearly, the matched combination corresponds to the (Ra,SP) ligands (cf. Table 1, Entries 5 vs. 7,  
218 6 vs. 8, 10 vs. 12 and 11 vs. 13). The absolute configurations of the alkylation product are controlled by  
219 the absolute configuration of the phosphite or phosphorodiamidite part of the ligand; therefore, (Ra)  
220 ligands preferentially produce the (R)-alkylation product (Table 1, Entries 5, 6, 10 and 11), whereas (Sa)  
221 ligands give the (S)-alkylation product (Table 1, Entries 7–9 and 12–14). The same fact was observed by  
222 van Leeuwen and co-workers[10d] for related phosphane–phosphite ligands with a more flexible bridge.  
223 The only relevant difference between the Pstereogenic phosphane–phosphite (Table 1, Entries 5–9) and  
224 phosphane–phosphorodiamidite (Table 1, Entries 10–13) complexes is that the complexes bearing the  
225 tBu-containing phosphanes are more selective than the Me counterparts for the former (cf. Table 1,  
226 Entries 5 vs. 6 and 7 vs. 8), whereas the trend is the opposite for the latter (cf. Table 1, Entries 10 vs. 11  
227 and 12 vs. 13). The best results were obtained with Pd6, Pd9 and Pd14 (Table 1, Entries 6, 9 and 14), the  
228 latter two of which contain an achiral phosphane moiety.

229 Palladium complexes Pd1–Pd14 were also tested in the allylic amination of I with excess benzylamine.

230 The systems are much slower in the allylic amination than in the alkylation, as reported for related

231 phosphite–phosphoramidite ligands,[29] and the complexes with phosphane–phosphite ligands are  
232 totally inactive (Table 1, Entries 5–9). The other complexes led to low or moderate conversions at best.  
233 The complexes with phosphane–phosphinite ligands gave very poor enantioselectivities (Table 1,  
234 Entries 1–4), whereas those with phosphane–phosphorodiamidite ligands (Table 1, Entries 10–14) were  
235 slightly better. Complex Pd14, containing an achiral phosphane moiety, is clearly the best of the series  
236 in terms of activity and enantioselectivity. In this case, (R<sub>a</sub>) ligands gave preferentially the (S) amination  
237 product, which is the same sense of induction as in the alkylation reaction, as the amination product has  
238 the opposite absolute configuration to the alkylation product owing to a change of priority of the groups  
239 in the Cahn–Ingold–Prelog (CIP) rules.

240 To help to rationalise the absolute configurations of the substitution products of I, complex Pd6', bearing  
241 ligand 6 and the 1,3-diphenylallyl moiety, was prepared and characterised (Scheme 5).

242 This complex is one of the intermediates in the substitution of I with ligand 6. In solution, it is present as  
243 a mixture of two diastereomers in a 1:3.5 ratio, whereas this ratio was 1:2.3 for Pd6. Unfortunately, we  
244 were unable to obtain any crystals of Pd6' suitable for X-ray diffraction. From the crystal structure data  
245 of Pd1, Pd2 and Pd13, it seems that the phosphane (P) part exerts a lower trans influence than the other  
246 phosphorus moiety (P'). In principle, this means that the most electrophilic carbon atom of the allyl  
247 group and the one that will be preferentially attacked by the nucleophile will be the one at the cis  
248 position relative to the phosphane part. We assumed that the same trends would apply to the 1,3-  
249 diphenylallyl complexes and performed PM3-level calculations of the energies of the diastereomers of  
250 Pd6', Pd8', Pd9' and Pd14' (see Supporting Information). The absolute configuration of the substitution  
251 product resulting from the attack of the nucleophile at the allylic carbon atom cis to the phosphane  
252 moiety in the most stable isomer is coherent with the absolute configuration of the major enantiomer  
253 obtained experimentally.

254 We also studied the alkylations of cyclohexen-3-yl acetate (II) and cinnamyl acetate (III) with DMM  
255 (Scheme 6).

256 The more enantioselective catalysts Pd6 and Pd14 were chosen to study their potential in the alkylation  
257 of substrate II. As very low conversions and enantioselectivities were found within 24 h of reaction  
258 time, no more catalytic runs with this substrate were carried out. Finally, some of the complexes were  
259 tested in the alkylation of III. The complexes led to full conversions at 1 h reaction times, but, as  
260 expected,[12b] the achiral linear alkylation product (l) was favoured over the branched isomer (b). The  
261 full results can be found in Table S2 of the Supporting Information.

262



263 **CONCLUSIONS**

264

265 The preparation of 14 new, chiral phosphane–phosphinite, phosphane–phosphite and phosphane–  
266 phosphorodiamidite ligands has been reported. Most of them bear a stereogenic phosphorus atom and  
267 have been conveniently prepared by a condensation reaction between a phosphinophenol and a  
268 chlorophosphorus precursor. Many of the ligands include phosphite and phosphorodiamidite parts with a  
269 chiral 1,1'-binaphthyl moiety. The ligands have been designed to have one or two stereogenic elements  
270 to increase their modularity and to study the influence of the different combinations on the catalysis.

271 The cationic Pd complexes of the ligands with  $\eta^3$ -methallyl coligands have been prepared and  
272 characterised in solution by NMR spectroscopy and also by X-ray crystallography for Pd1, Pd2 and  
273 Pd13. They are good catalytic precursors for allylic substitutions (alkylation with DMM and amination  
274 with benzylamine) with substrates I, II and III. In the alkylation of I, all of the complexes gave full  
275 conversion to the alkylation product after 24 h, and very high enantioselectivities (up to 95 % ee) were  
276 obtained with Pd6 and Pd14. The stereochemical course of the reaction is coherent with the nucleophilic  
277 attack at the allylic carbon atom in cis position relative to the phosphane. Some match–mismatch effects  
278 have been identified, and it is the absolute configuration of the 1,1'-binaphthyl-based phosphite or  
279 phosphorodiamidite part of the ligand that dictates the absolute configuration of the alkylation product,  
280 but the phosphane part also has some influence on the level of enantioselection.

281 Given the results presented here and the high modularity of the ligands, we are currently preparing new  
282 ligands of the same type and using them and the reported ones in new catalytic reactions. The results of  
283 these studies will be reported in due course.

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286

287 **EXPERIMENTAL SECTION**

288

289 **General Data:** All compounds were prepared under a purified nitrogen atmosphere by standard Schlenk  
290 and vacuum-line techniques. The solvents were obtained from a solvent-purification system or purified  
291 by standard procedures[30] and kept under nitrogen.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and HSQC  $^1\text{H}$ – $^{13}\text{C}$  NMR  
292 spectra were recorded with 300 and 400 MHz spectrometers with  $\text{CDCl}_3$  as the solvent. The protons of  
293 the  $\text{BH}_3$  moieties of the phosphane–boranes appeared in the aliphatic region of the spectra as very broad  
294 bands and have not been assigned. For the Pd complexes, ma and mi refer to the major and minor  
295 diastereomers of the complexes, respectively. The IR spectra were recorded with samples in KBr, and  
296 the main absorption bands are expressed in  $\text{cm}^{-1}$ . High-resolution mass spectrometry analyses were  
297 performed with electrospray ionisation. The optical rotations were measured at room temperature with a  
298 sodium lamp at the sodium D-line wavelength (589.592 nm). In all cases, the solvent was  $\text{CH}_2\text{Cl}_2$ , and  
299 the concentration was 1 g/100 mL. The allylic substitution reactions of I were analysed with an HPLC  
300 instrument equipped with a multidiode array detector and fitted with an OD-H chiral column. The eluent  
301 was a 95:5 n-hexane/iPrOH mixture. The allylic alkylations of II and III were analysed by GC with a  
302 chromatograph equipped with a capillary column with He as the carrier gas and a flame-ionisation  
303 detector (FID). Phosphinite–borane B [prepared from 1,[19] which was prepared from (1R,2S)-(–)-  
304 ephedrine],[20] phosphane–borane C· $\text{BH}_3$ ,[20] the chlorodiazaphosphophepine derived from N,N'-  
305 dimethyl-1,1'-binaphthyl-2,2'-diamine,[14] Pd dimers D[31] and D'[32] and substrates I[33] and III[34]  
306 were prepared by literature procedures, whereas other reagents were used as received from commercial  
307 suppliers. CCDC 1461787 (for Pd1), 1461788 (for Pd2) and 1461789 (for Pd3) contain the  
308 supplementary crystallographic data for this paper. These data can be obtained free of charge from The  
309 Cambridge Crystallographic Data Centre.

310

311 **(S)-(tert-Butyl)(2-hydroxyphenyl)phenylphosphane–Borane (C'· $\text{BH}_3$ ):** Phosphinite–borane B (528  
312 mg, 2.1 mmol) was dissolved in diethyl ether (30 mL), and the mixture was cooled to  $-30^\circ\text{C}$ . A 1.6 M  
313 solution of tBuLi (3.1 mL, 5.0 mmol) was added by syringe, and the mixture was stirred for 1 h and left  
314 to warm to room temperature. Water (20 mL) was added carefully, the biphasic mixture was extracted  
315 with diethyl ether ( $3 \times 10$  mL), and the combined organic phases were washed with water (20 mL). The  
316 final organic phase was dried with anhydrous sodium sulfate and filtered, and the solvent was removed  
317 under vacuum to furnish the title product as an oil, yield 553 mg (97 %).  $^1\text{H}$  NMR (400 MHz):  $\delta$  = 8.06  
318 (s, br, 1 H), 7.79–7.74 (m, 2 H), 7.51–7.37 (m, 4 H), 7.24–7.19 (m, 1 H), 6.98 (ddd,  $J$  = 8.4, 5.2, 1.2 Hz,  
319 1 H), 6.88 (tm,  $J$  = 6.8 Hz, 1 H), 1.38 (d,  $^3J_{\text{H,P}}$  = 14.8 Hz, 9 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  =  
320 161.8–109.9 (C, CH, Ar), 32.2 (d,  $^1J_{\text{C,P}}$  = 32.7 Hz, C), 26.7 (d,  $^2J_{\text{C,P}}$  = 3.0 Hz,  $3 \times \text{CH}_3$ ) ppm.  
321  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$  = +26.6 (d, br,  $^1J_{\text{B,P}}$  = 71.0 Hz) ppm. HRMS: calcd. for  $\text{C}_{16}\text{H}_{21}\text{BOP}$  [M  
322 – H] $^+$  + 271.1417; found 271.1406.  $[\alpha]_{\text{D}}$  = +140.8 ( $\text{CH}_2\text{Cl}_2$ ,  $c$  = 1). HPLC analysis with a chiral column

323 indicated that the compound was essentially enantiopure (see HPLC trace in the Supporting  
324 Information).

325

326 **(S)-(2-Hydroxyphenyl)methylphenylphosphane (C)**: Phosphane–borane  $C \cdot BH_3$  (310 mg, 1.2 mmol)  
327 was dissolved in dichloromethane, and the solution was cooled to 0 °C.  $HBF_4 \cdot Et_2O$  (0.87 mL, 6.3  
328 mmol) was added rapidly by syringe, the mixture was vigorously stirred for 1 h and deoxygenated  
329 thoroughly, and a saturated aqueous  $NaHCO_3$  solution (10 mL) was added carefully. The organic layer  
330 was transferred to another flask, washed with thoroughly with deoxygenated water, dried with  
331 anhydrous sodium sulfate, filtered and brought to dryness under vacuum. The title product was obtained  
332 as an air-sensitive colourless oil, yield 200 mg (73 %). The characterisation data of this compound  
333 agreed with the data reported previously.[10f,35]

334

335 **(S)-(tert-Butyl)(2-hydroxyphenyl)phenylphosphane (C')**: The procedure was the same as that used to  
336 obtain C. From phosphane–borane  $C' \cdot BH_3$  (1000 mg, 3.7 mmol) and  $HBF_4 \cdot Et_2O$  (2.3 mL, 16.7 mmol),  
337 the title product was obtained as a colourless oil, yield 860 mg (90 %). The characterisation data of this  
338 compound agreed with the values reported previously.[36]  $^1H$  NMR (400 MHz):  $\delta$  = 7.74–7.70 (m, 2  
339 H), 7.67–7.64 (m, 1 H), 7.30–7.28 (m, 2 H), 7.25–7.23 (m, 3 H), 6.96–6.92 (m, 1 H), 1.28 (d,  $3J_{H,P}$  =  
340 13.6 Hz, 9 H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz):  $\delta$  = 161.0–115.3 (C, CH, Ar), 31.4 (d,  $1J_{C,P}$  = 7.8 Hz,  
341 C), 28.5 (d,  $2J_{C,P}$  = 13.8 Hz,  $CH_3$ ) ppm.  $^{31}P\{^1H\}$  NMR (162 MHz):  $\delta$  = –19.0 (s) ppm.

342

343 **Compound 1**: Hydroxyphosphane C (345 mg, 1.5 mmol) was dissolved in toluene (20 mL), and  
344 triethylamine (0.3 mL, 2.2 mmol) was added rapidly by syringe. To this mixture, a solution of  
345 chlorodiisopropylphosphane (0.24 mL, 1.5 mmol) in toluene (15 mL) was added dropwise over 15 min,  
346 and the suspension was stirred for 1 h. The ammonium salts were removed by filtration, and the filtrate  
347 was brought to dryness to afford the title product as a pasty, white solid, yield 445 mg (90 %).  $^1H$  NMR  
348 (400 MHz):  $\delta$  = 7.43–7.35 (m, 3 H), 7.30–7.27 (m, 3 H), 7.26–7.23 (m, 1 H), 7.10 (ddd,  $J$  = 7.6, 4.4, 1.6  
349 Hz, 1 H), 6.95 (tm,  $J$  = 7.6 Hz, 1 H), 1.90 (m, 1 H), 1.68 (m, 1 H), 1.54 (d,  $3J_{H,P}$  = 4.4 Hz, 3 H), 1.17  
350 (dd,  $3J_{H,P}$ ,  $3J_{H,H}$  = 10.8, 6.8 Hz, 3 H), 1.07 (dd,  $3J_{H,P}$ ,  $3J_{H,H}$  = 16.0, 7.6 Hz, 3 H), 0.94 (dd,  $3J_{H,P}$ ,  
351  $3J_{H,H}$  = 16.0, 7.2 Hz, 3 H), 0.82 (dd,  $3J_{H,P}$ ,  $3J_{H,H}$  = 11.2, 6.8 Hz, 3 H) ppm.  $^{31}P\{^1H\}$  NMR (162  
352 MHz):  $\delta$  = +145.1 (s), –37.5 (s) ppm.

353

354 **Compound 2**: The procedure was the same as that used to obtain 1. From hydroxyphosphane  $C'$  (284  
355 mg, 1.1 mmol), the title product was obtained as a white, pasty solid, yield 387 mg (94 %).  $^1H$  NMR  
356 (400 MHz):  $\delta$  = 7.52 (dt,  $J$  = 7.6, 2.0 Hz, 1 H), 7.41–7.35 (m, 3 H), 7.27–7.22 (m, 4 H), 6.94 (td,  $J$  = 7.6,  
357 1.2 Hz, 1 H), 2.01 (m, 1 H), 1.88 (m, 1 H), 1.23 (d,  $3J_{H,P}$  = 12.4 Hz, 9 H), 1.18 (dd,  $3J_{H,P}$ ,  $3J_{H,H}$  =  
358 11.2, 7.2 Hz, 3 H), 1.05 (dd,  $3J_{H,P}$ ,  $3J_{H,H}$  = 15.6, 7.2 Hz, 3 H), 0.86 (dd,  $3J_{H,P}$ ,  $3J_{H,H}$  = 15.6, 7.2 Hz,

359 3 H), 0.75 (dd, 3JH,P, 3JH,H = 11.6, 7.2 Hz, 3 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta = +145.9$  (d,  
360 4JP,P = 1.1 Hz), +2.0 (d, 4JP,P = 1.1 Hz) ppm.

361

362 **Compound 3:** The procedure was analogous to that used to obtain 1. From hydroxyphosphane C (130  
363 mg, 0.60 mmol) and chlorodiphenylphosphine (0.11 mL, 0.6 mmol), the title product was obtained as a  
364 white, pasty solid, yield 201 mg (84 %).  $^1\text{H}$  NMR (400 MHz):  $\delta = 7.80$ – $7.73$  (m, 2 H),  $7.72$ – $7.68$  (m, 1  
365 H),  $7.61$ – $7.48$  (m, 4 H),  $7.45$ – $7.17$  (m, 9 H),  $7.15$ – $7.10$  (m, 1 H), 7.01 (tm, J = 7.6 Hz, 1 H), 6.92 (t, br, J  
366 = 7.2 Hz, 1 H), 1.52 (d, 2JH,P = 4.4 Hz, 3 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta = +108.2$  (d, 4JP,P =  
367 2.1 Hz),  $-38.2$  (s) ppm.

368

369 **Compound 4:** The procedure was the same as that used to obtain 3. From hydroxyphosphane C' (242  
370 mg, 0.94 mmol), the title product was obtained as a white, pasty solid, yield 396 mg (95 %).  $^1\text{H}$  NMR  
371 (400 MHz):  $\delta = 7.64$ – $7.57$  (m, 3 H),  $7.37$ – $7.33$  (m, 6 H),  $7.30$ – $7.20$  (m, 8 H), 7.11 (m, 1 H), 7.04 (td, J =  
372 7.6, 1.2 Hz, 1 H), 1.24 (d, 3JH,P = 12.4 Hz, 9 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta = +108.6$  (d, 4JP,P  
373 = 3.6 Hz), +0.8 (d, 4JP,P = 3.4 Hz) ppm.

374

375 **Compound 5:** Hydroxyphosphane C (179 mg, 0.83 mmol) was dissolved in toluene (20 mL), and  
376 triethylamine (0.2 mL, 1.5 mmol) was added rapidly by syringe. To this mixture, a solution of the  
377 chlorodioxaphosphine derived from (R)-(+)-1,1'-bi(2-naphthol)[37] (291 mg, 0.83 mmol) in toluene  
378 (10 mL) was added dropwise over 15 min, and the suspension was stirred for 1 h. The ammonium salts  
379 were removed by filtration, and the filtrate was brought to dryness to afford the title product as a white  
380 solid, yield 343 mg (78 %).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta = +143.37$  (d, 4JP,P = 20.1 Hz),  $-36.50$  (d,  
381 4JP,P = 20.2 Hz) ppm.

382

383 **Compound 6:** The procedure was the same as that used to obtain 5. From hydroxyphosphane C' (245  
384 mg, 0.95 mmol), the title product was obtained as a white solid, yield 409 mg (75 %).  $^1\text{H}$  NMR (400  
385 MHz):  $\delta = 7.31$ – $7.09$  (m, 10 H), 7.04 (dd, J = 8.0, 4.0 Hz, 1 H), 6.86–6.78 (m, 5 H), 6.74–6.68 (m, 2 H),  
386 6.64–6.55 (m, 3 H), 0.88 (d, 3JH,P = 12.4 Hz, 9 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta = +144.31$  (d,  
387 4JP,P = 41.5 Hz), +1.30 (d, 4JP,P = 41.3 Hz) ppm.

388

389 **Compound 7:** The procedure was the same as that used to obtain 5 but with the  
390 chlorodioxaphosphine derived from (S)-(–)-1,1'-bi(2-naphthol). From hydroxyphosphane C (378 mg,  
391 1.75 mmol), the title product was obtained as a white solid, yield 770 mg (83 %).  $^1\text{H}$  NMR (400 MHz):  
392  $\delta = 7.99$  (d, J = 8.8 Hz, 1 H), 7.93 (t, J = 8.4 Hz, 1 H), 7.91 (t, J = 8.8 Hz, 1 H), 7.55 (d, J = 8.8 Hz, 1 H),  
393 7.52 (d, J = 8.8 Hz, 1 H), 7.47–7.41 (m, 4 H), 7.38 (d, J = 6.8 Hz, 2 H), 7.31–7.25 (m, 6 H), 7.22–7.08  
394 (m, 4 H), 1.57 (d, 2JH,P = 4.0 Hz, 3 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta = +143.45$  (d, 4JP,P = 16.7  
395 Hz),  $-37.38$  (d, 4JP,P = 16.7 Hz) ppm.

396 **Compound 8:** The procedure was the same as that used to obtain 7. From hydroxyphosphane C' (379  
397 mg, 1.47 mmol), the title product was obtained as a white solid, yield 660 mg (78 %). <sup>1</sup>H NMR (400  
398 MHz, C<sub>6</sub>D<sub>6</sub>): δ = 8.00 (d, J = 8.8 Hz, 1 H), 7.83 (t, J = 8.8 Hz, 2 H), 7.81–7.63 (m, 3 H), 7.66 (t, J = 8.8  
399 Hz, 2 H), 7.53 (d, J = 8.8 Hz, 1 H), 7.39 (dd, J = 8.4, 4.4 Hz, 1 H), 7.34–7.29 (m, 2 H), 7.27–7.18 (m, 5  
400 H), 7.15–7.02 (m, 3 H), 7.02 (t, J = 6.8 Hz, 1 H), 1.42 (d, 3J<sub>H,P</sub> = 12.4 Hz, 9 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR  
401 (162 MHz): δ = +142.33 (d, 4J<sub>P,P</sub> = 28.8 Hz), +0.80 (d, 4J<sub>P,P</sub> = 29.0 Hz) ppm.

402  
403 **Compound 9:** The procedure was the same as that used to obtain 7. From hydroxyphosphane C'' (242  
404 mg, 0.87 mmol), the title product was obtained as a white solid, yield 480 mg (93 %). The  
405 characterisation data of this compound agreed with the values reported previously.[16] <sup>1</sup>H NMR (400  
406 MHz): δ = 7.87 (d, J = 8.8 Hz, 1 H), 7.84 (d, J = 8.4 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 1 H), 7.68 (d, J = 8.8  
407 Hz, 1 H), 7.38–7.23 (m, 16 H), 7.21–7.12 (m, 4 H), 6.99 (t, J = 7.2 Hz, 1 H), 6.70 (ddd, J = 7.6, 4.0 Hz,  
408 1.6 Hz, 1 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz): δ = +143.21 (d, 4J<sub>P,P</sub> = 14.7 Hz), –16.00 (d, 4J<sub>P,P</sub> = 14.7  
409 Hz) ppm.

410  
411 **Compound 10:** Hydroxyphosphane C (134 mg, 0.62 mmol) was dissolved in toluene (20 mL), and  
412 triethylamine (0.2 mL, 1.5 mmol) and 4-dimethylaminopyridine (DMAP, 2 mg, 0.016 mmol) were  
413 added rapidly. To this mixture, a solution of the chlorodiazaphosphepine derived from (R)-N,N'-  
414 dimethyl-1,1'-binaphthyldiamine[14d] (0.62 mmol) in toluene (10 mL) was added dropwise over 15  
415 min, and the suspension was stirred for 1 h. The ammonium salts were removed by filtration, and the  
416 filtrate was brought to dryness to afford the title product as a white solid, yield 311 mg (90 %). <sup>1</sup>H NMR  
417 (400 MHz): δ = 7.93–7.84 (m, 4 H), 7.60 (d, J = 8.8 Hz, 1 H), 7.49 (d, J = 8.8 Hz, 1 H), 7.41–7.30 (m, 2  
418 H), 7.27–7.10 (m, 11 H), 6.98–6.95 (m, 2 H), 3.06 (d, 3J<sub>H,P</sub> = 13.6 Hz, 3 H), 2.89 (d, 3J<sub>H,P</sub> = 9.6 Hz, 3  
419 H), 1.35 (d, 2J<sub>H,P</sub> = 4.4 Hz, 3 H) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz): δ = +170.59 (d, 4J<sub>P,P</sub> = 7.0 Hz), –  
420 37.86 (d, 4J<sub>P,P</sub> = 6.8 Hz) ppm.

421  
422 **Compound 11:** The procedure was the same as that used to obtain 10. From hydroxyphosphane C' (206  
423 mg, 0.80 mmol), the title product was obtained as a white solid, yield 450 mg (94 %). <sup>1</sup>H NMR (400  
424 MHz): δ = 8.07–7.82 (m, 5 H), 7.71–7.58 (m, 3 H), 7.49–7.32 (m, 5 H), 7.29–6.98 (m, 8 H), 3.09 (d,  
425 3J<sub>H,P</sub> = 12.0 Hz, 3 H), 3.03 (d, 3J<sub>H,P</sub> = 14.0 Hz, 3 H), 1.03 (d, 3J<sub>H,P</sub> = 12.4 Hz, 9 H) ppm. <sup>31</sup>P{<sup>1</sup>H}  
426 NMR (162 MHz): δ = +172.16 (d, 4J<sub>P,P</sub> = 16.0 Hz), +0.23 (d, 4J<sub>P,P</sub> = 15.9 Hz) ppm. Compound 12:  
427 The procedure was the same as that used to obtain 10 but with the chlorodiazaphosphepine derived from  
428 (S)-N,N'-dimethyl-1,1'-binaphthyldiamine. From hydroxyphosphane C (162 mg, 0.75 mmol), the title  
429 product was obtained as a white solid, yield 371 mg (89 %). <sup>1</sup>H NMR (400 MHz): δ = 8.00 (dd, J = 8.8,  
430 2.4 Hz, 1 H), 7.96–7.92 (m, 2 H), 7.88 (d, J = 3.2 Hz, 1 H), 7.86 (d, J = 2.8 Hz, 1 H), 7.81 (d, J = 8.8 Hz,  
431 1 H), 7.67 (d, J = 8.8 Hz, 1 H), 7.62 (d, J = 9.2 Hz, 1 H), 7.46–7.32 (m, 4 H), 7.28–7.10 (m, 6 H), 7.07–  
432 6.95 (m, 3 H), 3.09 (d, 3J<sub>H,P</sub> = 9.6 Hz, 3 H), 3.05 (d, 3J<sub>H,P</sub> = 14.0 Hz, 3 H), 1.47 (d, 2J<sub>H,P</sub> = 4.0 Hz, 3

433 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta = +172.71$  (d,  $4\text{JP},\text{P} = 11.0$  Hz),  $-37.38$  (d,  $4\text{JP},\text{P} = 11.0$  Hz)  
434 ppm.

435

436 **Compound 13:** The procedure was the same as that used to obtain 12. From hydroxyphosphane C' (206  
437 mg, 0.80 mmol), the title product was obtained as a white solid, yield 380 mg (79 %).  $^1\text{H}$  NMR (400  
438 MHz):  $\delta = 7.57$  (dd,  $J = 8.8, 0.8$  Hz, 1 H), 7.45–7.39 (m, 4 H), 7.26–7.21 (m, 4 H), 7.12 (dd,  $J = 8.4, 1.2$   
439 Hz, 1 H), 7.08 (dd,  $J = 8.4, 1.2$  Hz, 1 H), 6.93 (ddt,  $J = 8.0, 4.4, 0.8$  Hz, 1 H), 6.90–6.61 (m, 8 H), 6.58  
440 (td,  $J = 7.2, 1.2$  Hz, 1 H), 2.73 (d,  $3\text{JH},\text{P} = 9.2$  Hz, 3 H), 2.62 (d,  $3\text{JH},\text{P} = 14.0$  Hz, 3 H), 0.91 (d,  $3\text{JH},\text{P} =$   
441  $12.0$  Hz, 3 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta = +171.34$  (d,  $4\text{JP},\text{P} = 8.9$  Hz),  $-0.67$  (d,  $4\text{JP},\text{P} = 8.9$   
442 Hz) ppm.

443

444 **Compound 14:** The procedure was the same as that used to obtain 12. From hydroxyphosphane C'' (223  
445 mg, 0.80 mmol), the title product was obtained as a white solid, yield 408 mg (82 %).  $^1\text{H}$  NMR (400  
446 MHz):  $\delta = 7.92$  (d,  $J = 8.8$  Hz, 1 H), 7.88 (d,  $J = 8.0$  Hz, 1 H), 7.86 (d,  $J = 8.0$  Hz, 1 H), 7.81 (d,  $J = 8.4$   
447 Hz, 1 H), 7.61 (d,  $J = 8.8$  Hz, 1 H), 7.41–7.10 (m, 19 H), 6.97 (t,  $J = 6.8$  Hz, 1 H), 6.75 (dd,  $J = 6.8, 4.8$   
448 Hz, 1 H), 2.92 (d,  $3\text{JH},\text{P} = 13.2$  Hz, 3 H), 2.89 (d,  $3\text{JH},\text{P} = 8.8$  Hz, 3 H) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162  
449 MHz):  $\delta = +170.48$  (d,  $4\text{JP},\text{P} = 10.2$  Hz),  $-17.51$  (d,  $4\text{JP},\text{P} = 10.5$  Hz) ppm.

450

451 **Complex Pd1:** Phosphane–phosphinite 1 (195 mg, 0.59 mmol), Pd dimer D (92 mg, 0.23 mmol) and  
452  $\text{NH}_4\text{PF}_6$  (191 mg, 1.17 mmol) were suspended in dichloromethane (20 mL), and the suspension was  
453 stirred vigorously for 2 h. Water (20 mL) was added, and the mixture was extracted with  
454 dichloromethane ( $3 \times 10$  mL). The combined organic phase was washed with water, dried with  
455 anhydrous  $\text{Na}_2\text{SO}_4$  and filtered, and the solvent was removed under vacuum. The crude product was  
456 recrystallised in dichloromethane/hexane to yield the title product as a white solid, yield 210 mg (71 %).  
457 Diastereomeric ratio: 1:1.8. IR:  $\tilde{\nu} = 2970, 2929, 1591, 1468, 1436, 1267, 1207, 1028, 899, 891, 839$   
458  $[\nu(\text{PF}_6^-)]$ , 774, 736, 558  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz):  $\delta = 7.61$  (t,  $J = 7.6$  Hz, 2 H), 7.51–7.30 (m, 11 H,  
459 Ar), 7.23–7.18 (m, 5 H, Ar), 4.50 (t,  $J = 4.0$  Hz, 1 H, ma), 4.47 (t,  $J = 3.6$  Hz, 1 H, mi), 4.35 (t,  $J = 4.4$   
460 Hz, 1 H, ma), 4.31 (t,  $J = 4.4$  Hz, 1 H, mi), 3.39 (d,  $J = 10.4$  Hz, 1 H, ma), 3.34 (d,  $J = 10.0$  Hz, 1 H, mi),  
461 2.99 (d,  $J = 10.0$  Hz, 1 H, mi), 2.88 (d,  $J = 10.0$  Hz, 1 H, ma), 2.46–2.23 (m, 4 H, ma + mi), 2.29 (d,  
462  $2\text{JH},\text{P} = 9.6$  Hz, 3 H, ma), 2.24 (d,  $2\text{JH},\text{P} = 9.2$  Hz, 3 H, mi), 1.89 (s, 3 H, ma), 1.84 (s, 3 H, mi), 1.22  
463 (dd,  $3\text{JH},\text{P}, 3\text{JH},\text{H} = 16.4, 7.2$  Hz, 3 H, ma), 1.15 (dd,  $3\text{JH},\text{P}, 3\text{JH},\text{H} = 18.4, 11.2$  Hz, 3 H, ma), 1.08 (dd,  
464  $3\text{JH},\text{P}, 2\text{JH},\text{H} = 7.2, 1.6$  Hz, 3 H, mi), 1.03 (dd,  $3\text{JH},\text{P}, 2\text{JH},\text{H} = 7.6, 3.2$  Hz, 3 H, mi), 0.98 (dd,  $3\text{JH},\text{P},$   
465  $3\text{JH},\text{H} = 19.6, 7.2$  Hz, 3 H, ma), 0.91 (dd,  $3\text{JH},\text{P}, 3\text{JH},\text{H} = 16.8, 7.2$  Hz, 3 H, mi), 0.85 (dd,  $3\text{JH},\text{P},$   
466  $2\text{JH},\text{H} = 16.0, 6.8$  Hz, 3 H, ma) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta = 158.3$ – $123.0$  (C, CH, Ar), 73.7  
467 (dd,  $2\text{JC},\text{P} = 30.5, 3.1$  Hz,  $\text{CH}_2$ , ma), 73.3 (dd,  $2\text{JC},\text{P} = 31.4, 2.2$  Hz,  $\text{CH}_2$ , mi), 64.6 (dd,  $2\text{JC},\text{P} = 30.2,$   
468  $2.1$  Hz,  $\text{CH}_2$ , mi), 64.2 (d,  $2\text{JC},\text{P} = 30.2$  Hz,  $\text{CH}_2$ , ma), 32.5 (d,  $1\text{JC},\text{P} = 11.3$  Hz, CH, mi), 32.3 (d,  
469  $1\text{JC},\text{P} = 10.3$  Hz, CH, ma), 30.5 (d,  $1\text{JC},\text{P} = 24.1$  Hz, CH, mi), 30.2 (d,  $1\text{JC},\text{P} = 25.3$  Hz, CH, mi), 24.2

470 (s, CH<sub>3</sub>, mi), 24.1 (s, CH<sub>3</sub>, Ma), 17.8–16.5 (m, 8 × CH<sub>3</sub>, ma + mi), 16.1 (d, 1JC,P = 28.3 Hz, CH<sub>3</sub>, mi),  
471 15.0 (d, 1JC,P = 29.1 Hz, CH<sub>3</sub>, ma) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz): δ = +190.81 (d, 2JP,P = 63.7 Hz,  
472 ma), +190.41 (d, 2JP,P = 63.8 Hz, mi), –6.49 (d, 2JP,P = 63.7 Hz, ma), –7.49 (d, 2JP,P = 63.7 Hz, mi)  
473 ppm. C<sub>23</sub>H<sub>33</sub>F<sub>6</sub>OP<sub>3</sub>Pd (638.82): calcd. C 43.24, H 5.21; found C 42.81, H 5.69.

474  
475 **Complex Pd2:** The procedure was the same as that used to prepare Pd1. From ligand 2 (180 mg, 0.48  
476 mmol) and Pd dimer D (76 mg, 0.19 mmol), the product was obtained as a white solid, yield 230 mg (89  
477 %). Diastereomeric ratio: 1:1. IR:  $\tilde{\nu}$  = 2966, 2873, 1591, 1466, 1434, 1265, 1201, 1097, 1074, 1028,  
478 899, 878, 839 [ $\nu$ (PF<sub>6</sub><sup>–</sup>)], 773, 747, 699, 558, 518 cm<sup>–1</sup>. <sup>1</sup>H NMR (400 MHz): δ = 7.76–7.42 (m, 2 H,  
479 Ar), 7.59–7.42 (m, 10 H, Ar), 7.22–6.99 (m, 6 H, Ar), 4.36 (d, J = 3.6 Hz, 2 H), 4.34 (m, 1 H), 3.64 (t, J  
480 = 4.4 Hz, 1 H), 3.42 (d, J = 10.0 Hz, 1 H), 2.90 (d, J = 10.0 Hz, 1 H), 2.87 (d, J = 10.0 Hz, 1 H), 2.61 (m,  
481 1 H), 2.48 (m, 2 H), 2.38 (d, J = 11.6 Hz, 1 H), 2.36 (m, 2 H), 1.86 (s, 3 H), 1.54 (s, 3 H), 1.48–1.26 (m,  
482 12 H), 1.42 (d, 3JH,P = 16.8 Hz, 9 H), 1.35 (d, 3JH,P = 16.4 Hz, 9 H), 1.19–1.07 (m, 12 H) ppm.  
483 <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz): δ = 159.2–115.0 (C, CH, Ar), 77.8 (dd, 2JC,P = 31.8, 3.1 Hz, CH<sub>2</sub>), 76.1  
484 (dd, 2JC,P = 31.1, 2.9 Hz, CH<sub>2</sub>), 64.2 (dd, 2JC,P = 28.3, 1.7 Hz, CH<sub>2</sub>), 62.9 (dd, 2JC,P = 28.5, 1.6 Hz,  
485 CH<sub>2</sub>), 35.6 (d, 1JC,P = 22.0 Hz, C), 34.8 (d, 1JC,P = 22.6 Hz, C), 32.5 (d, 1JC,P = 12.6 Hz, 2CH), 31.2  
486 (d, 1JC,P = 27.3 Hz, CH), 30.8 (d, 1JC,P = 27.1 Hz, CH), 28.4 (d, 2JC,P = 2.3 Hz, 3 × CH<sub>3</sub>), 28.3 (d,  
487 2JC,P = 2.5 Hz, 3 × CH<sub>3</sub>), 23.72 (s, CH<sub>3</sub>), 23.69 (s, CH<sub>3</sub>), 18.2 (d, 2JC,P = 5.6 Hz, CH<sub>3</sub>), 18.0 (d,  
488 2JC,P = 4.9 Hz, CH<sub>3</sub>), 17.8 (s, CH<sub>3</sub>), 17.5 (d, 2JC,P = 5.5 Hz, CH<sub>3</sub>), 17.4 (d, 2JC,P = 6.6 Hz, CH<sub>3</sub>),  
489 17.1 (s, CH<sub>3</sub>), 16.7 (d, 2JC,P = 2.7 Hz, CH<sub>3</sub>), 16.2 (s, CH<sub>3</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz): δ =  
490 +186.54 (d, 2JP,P = 59.6 Hz), +185.67 (d, 2JP,P = 59.8 Hz), +25.06 (d, 2JP,P = 59.6 Hz), +23.72 (d,  
491 2JP,P = 59.6 Hz) ppm. C<sub>26</sub>H<sub>39</sub>F<sub>6</sub>OP<sub>3</sub>Pd (680.90): calcd. C 45.86, H 5.77; found C 47.13, H 6.61.

492  
493 **Pd3:** The procedure was the same as that used to prepare Pd1. From ligand 3 (200 mg, 0.50 mmol) and  
494 Pd dimer D (78 mg, 0.20 mmol), the product was obtained as a white solid, yield 215 mg (76 %).  
495 Diastereomeric ratio: 1:1.3. IR:  $\tilde{\nu}$  = 3064, 3009, 2916, 1590, 1466, 1437, 1386, 1265, 1199, 1128, 1103,  
496 1079, 1027, 999, 894, 839 [ $\nu$ (PF<sub>6</sub><sup>–</sup>)], 777, 741, 693, 587, 558, 518, 475 cm<sup>–1</sup>. <sup>1</sup>H NMR (400 MHz): δ  
497 = 7.62–7.23 (m, Ar), 6.74 (m, Ar), 4.58 (t, J = 3.6 Hz, 1 H, mi), 4.55 (t, J = 4.0 Hz, 1 H, ma), 4.37 (t, J =  
498 4.0 Hz, 1 H, mi), 4.30 (t, J = 4.0 Hz, 1 H, ma), 3.48 (d, J = 10.0 Hz, 1 H, ma), 3.41 (d, J = 10.8 Hz, 1 H,  
499 mi), 3.21 (d, J = 10.0 Hz, 1 H, ma), 2.97 (d, J = 10.0 Hz, 1 H, mi), 2.35 (d, 2JH,P = 9.6 Hz, 3 H, ma),  
500 2.34 (d, 2JH,P = 9.6 Hz, 3 H, mi), 1.96 (s, 3 H, mi), 1.79 (s, 3 H, ma) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz):  
501 δ = 155.7–119.1 (C, CH, Ar), 72.4 (d, 2JC,P = 34.0 Hz, CH<sub>2</sub>, ma), 72.0 (d, 2JC,P = 23.8 Hz, CH<sub>2</sub>, mi),  
502 69.45 (d, 2JC,P = 26.3 Hz, CH<sub>2</sub>, mi), 69.37 (d, 2JC,P = 28.3 Hz, CH<sub>2</sub>, ma), 24.2 (s, CH<sub>3</sub>, mi), 24.1 (s,  
503 CH<sub>3</sub>, ma), 15.2 (d, 1JC,P = 27.1 Hz, CH<sub>3</sub>, mi), 14.3 (d, 1JC,P = 28.4 Hz, CH<sub>3</sub>, ma) ppm. <sup>31</sup>P{<sup>1</sup>H}  
504 NMR (162 MHz): δ = +151.53 (d, 2JP,P = 68.5 Hz, mi), +150.56 (d, 2JP,P = 68.2 Hz, ma), –5.06 (d,  
505 2JP,P = 68.0 Hz, ma), –5.87 (d, 2JP,P = 68.8 Hz, mi) ppm. C<sub>29</sub>H<sub>29</sub>F<sub>6</sub>OP<sub>3</sub>Pd (706.86): calcd. C 49.28,  
506 H 4.14; found C 49.64, H 4.58.

507 **Complex Pd4:** The procedure was the same as that used to prepare Pd1. From ligand 4 (150 mg, 0.34  
508 mmol) and Pd dimer D (53 mg, 0.13 mmol), the product was obtained as a white solid, yield 157 mg (81  
509 %). Diastereomeric ratio: 1:1. IR:  $\tilde{\nu}$  = 3061, 2960, 2865, 1590, 1567, 1466, 1436, 1398, 1369, 1310,  
510 1264, 1197, 1104, 1073, 1026, 999, 831 [ $\nu(\text{PF}_6^-)$ ], 773, 746, 694, 588, 558, 519, 481  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  
511 (400 MHz):  $\delta$  = 7.78–7.32 (m, 31 H, Ar), 7.17–7.07 (m, 4 H, Ar), 6.91–6.84 (m, 3 H, Ar), 4.44–4.40 (m,  
512 2 H), 4.14 (t,  $J$  = 4.0 Hz, 1 H), 3.91 (dd,  $J$  = 5.6, 4.0 Hz, 1 H), 3.48 (d,  $J$  = 12.4 Hz, 1 H), 3.45 (d,  $J$  =  
513 10.4 Hz, 1 H), 2.95 (d,  $J$  = 10.8 Hz, 1 H), 2.81 (d,  $J$  = 9.6 Hz, 1 H), 1.81 (s, 3 H), 1.75 (s, 3 H), 1.49 (d,  
514 3JH,P = 16.8 Hz, 9 H), 1.43 (d, 3JH,P = 16.8 Hz, 9 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  = 156.6–  
515 116.9 (C, CH, Ar), 74.6 (dd, 2JC,P = 33.5, 3.0 Hz, CH<sub>2</sub>), 70.8 (dd, 2JC,P = 28.0, 2.9 Hz, CH<sub>2</sub>), 68.4  
516 (dd, 2JC,P = 28.0, 2.5 Hz, CH<sub>2</sub>), 35.0 (d, 1JC,P = 21.7 Hz, C), 34.2 (d, 1JC,P = 22.0 Hz, C), 28.17 (d,  
517 2JC,P = 6.9 Hz, 3  $\times$  CH<sub>3</sub>), 28.11 (d, 2JC,P = 6.9 Hz, 3  $\times$  CH<sub>3</sub>), 23.96 (s, CH<sub>3</sub>), 23.86 (s, CH<sub>3</sub>) ppm.  
518  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$  = +148.71 (d, 2JP,P = 65.8 Hz), +148.45 (d, 2JP,P = 65.9 Hz), +29.74 (d,  
519 2JP,P = 65.8 Hz), +28.39 (d, 2JP,P = 65.8 Hz) ppm. C<sub>32</sub>H<sub>35</sub>F<sub>6</sub>O<sub>3</sub>Pd (748.94): calcd. C 51.32, H 4.71;  
520 found C 53.15, H 5.47.

521

522 **Complex Pd5:** The procedure was the same as that used to prepare Pd1. From ligand 5 (300 mg, 0.57  
523 mmol) and Pd dimer D (86 mg, 0.22 mmol), the product was obtained as a white solid, yield 270 mg (73  
524 %). Diastereomeric ratio: 1:2.7. IR:  $\tilde{\nu}$  = 3068, 1619, 1591, 1509, 1464, 1437, 1321, 1264, 1223, 1184,  
525 1068, 959, 841 [ $\nu(\text{PF}_6^-)$ ], 774, 750, 695, 608, 558, 500  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz):  $\delta$  = 8.17–8.13 (m,  
526 Ar), 8.09–7.98 (m, Ar), 7.79–7.75 (m, Ar), 7.62–7.30 (m, Ar), 7.24–7.15 (m, Ar), 7.07–6.98 (m, Ar),  
527 4.45 (d,  $J$  = 9.6 Hz, 1 H, mi), 4.25 (d,  $J$  = 8.8 Hz, 1 H, ma), 3.73 (d,  $J$  = 4.4 Hz, 2 H, ma + mi), 3.62 (d,  $J$   
528 = 16.8 Hz, 1 H, ma), 3.12 (d,  $J$  = 8.8 Hz, 1 H, mi), 3.00 (dd,  $J$  = 10.4, 2.8 Hz, 1 H, ma), 2.63 (d, br,  $J$  =  
529 11.6 Hz, 1 H, mi), 2.39 (d, 2JH,P = 10.0 Hz, 3 H, ma), 2.38 (d, 2JH,P = 10.0 Hz, 3 H, mi), 1.91 (s, 3 H,  
530 mi), 1.66 (s, 3 H, ma) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  = 153.5–119.2 (C, CH, Ar), 75.5 (dd, 2JC,P =  
531 46.0, 3.7 Hz, CH<sub>2</sub>, ma), 73.2 (dd, 2JC,P = 47.9, 3.8 Hz, CH<sub>2</sub>, mi), 69.8–69.4 (m, 2  $\times$  CH<sub>2</sub>, ma + mi),  
532 24.0 (s, CH<sub>3</sub>, ma), 23.8 (s, CH<sub>3</sub>, mi), 14.0 (d, 1JC,P = 28.9 Hz, CH<sub>3</sub>, mi), 13.2 (d, 1JC,P = 28.8 Hz,  
533 CH<sub>3</sub>, ma) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$  = +145.71 (d, 2JP,P = 102.5 Hz, mi), +145.64 (d, 2JP,P =  
534 102.9 Hz, ma), –4.21 (d, 2JP,P = 102.9 Hz, ma), –4.90 (d, 2JP,P = 102.7 Hz, mi) ppm.  
535 C<sub>37</sub>H<sub>31</sub>F<sub>6</sub>O<sub>3</sub>P<sub>3</sub>Pd (836.96): calcd. C 53.10, H 3.73; found C 52.78, H 4.46.

536

537 **Complex Pd6:** The procedure was the same as that used to prepare Pd1. From ligand 6 (380 mg, 0.66  
538 mmol) and Pd dimer D (105 mg, 0.27 mmol), the product was obtained as a white solid, yield 331 mg  
539 (70 %). Diastereomeric ratio: 1:1.8. IR:  $\tilde{\nu}$  = 3068, 2957, 2869, 1619, 1590, 1509, 1464, 1434, 1400,  
540 1322, 1264, 1225, 1184, 1068, 958, 927, 842 [ $\nu(\text{PF}_6^-)$ ], 773, 696, 609, 558  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz):  
541  $\delta$  = 8.25–8.02 (m, Ar), 7.89–7.87 (m, Ar), 7.78–6.80 (m, Ar), 4.29 (d,  $J$  = 8.8 Hz, 1 H, mi), 3.83 (d,  $J$  =  
542 17.2 Hz, 1 H, Ma), 3.68–3.59 (m, 3 H, 2  $\times$  ma + mi), 3.10 (d,  $J$  = 8.0 Hz, 1 H, ma), 2.65 (d,  $J$  = 8.8 Hz, 1  
543 H, mi), 2.47 (d,  $J$  = 16.4 Hz, 1 H, mi), 1.93 (s, 3 H, mi), 1.57 (d, 3JH,P = 17.2 Hz, 9 H, ma), 1.49 (d,



544 3JH,P = 16.4 Hz, 9 H, mi), 1.48 (s, 3 H, ma) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  = 154.7–115.7 (C, CH,  
545 Ar), 78.9 (dd, 2JC,P = 46.4, 2.3 Hz, CH<sub>2</sub>, ma), 75.9 (d, 2JC,P = 48.5 Hz, CH<sub>2</sub>, mi), 70.1 (dd, 2JC,P =  
546 27.4, 7.5 Hz, CH<sub>2</sub>, mi), 69.5 (dd, 2JC,P = 25.9, 7.1 Hz, CH<sub>2</sub>, ma), 36.0 (d, 1JC,P = 21.3 Hz, C, ma),  
547 35.4 (d, 1JC,P = 22.9 Hz, C, mi), 28.3 (d, 2JC,P = 6.5 Hz, 3 × CH<sub>3</sub>, mi), 28.2 (d, 2JC,P = 6.6 Hz, 3 ×  
548 CH<sub>3</sub>, ma), 23.7 (s, CH<sub>3</sub>, ma), 23.6 (s, CH<sub>3</sub>, mi) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$  = +144.42 (d, 2JP,P =  
549 = 97.8 Hz, ma), +143.67 (d, 2JP,P = 98.7 Hz, mi), +29.52 (d, 2JP,P = 98.8 Hz, mi), +28.76 (d, 2JP,P =  
550 97.2 Hz, ma) ppm. C<sub>40</sub>H<sub>37</sub>F<sub>6</sub>O<sub>3</sub>P<sub>3</sub>Pd (879.04): calcd. C 54.65, H 4.24; found C 54.23, H 5.06.

551  
552 **Complex Pd7:** The procedure was the same as that used to prepare Pd1. From ligand 7 (400 mg, 0.75  
553 mmol) and Pd dimer D (123 mg, 0.31 mmol), the product was obtained as a white solid, yield 398 mg  
554 (77 %). Diastereomeric ratio: 1:1. IR:  $\tilde{\nu}$  = 3066, 2957, 2924, 1619, 1591, 1509, 1464, 1437, 1322, 1264,  
555 1224, 1185, 1128, 1068, 958, 919, 832 [ $\nu(\text{PF}_6^-)$ ], 774, 741, 695, 608, 558, 500  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400  
556 MHz):  $\delta$  = 8.24–8.02 (m, 4 H, Ar), 7.73–7.18 (m, 17 H, Ar), 4.79 (d, J = 7.6 Hz, 1 H), 4.53 (d, J = 8.0  
557 Hz, 1 H), 3.79–3.64 (m, 3 H), 3.32 (d, J = 15.6 Hz, 1 H), 3.07 (d, J = 9.6 Hz, 1 H), 2.69 (d, J = 7.2 Hz,  
558 1H), 2.43 (d, 2JH,P = 9.6 Hz, 3 H), 2.35 (d, 2JH,P = 9.6 Hz, 3 H), 1.97 (s, 3 H), 1.68 (s, 3 H) ppm.  
559  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$  = +146.20 (d, 2JP,P = 103.2 Hz), +145.87 (d, 2JP,P = 102.7 Hz), –3.99  
560 (d, 2JP,P = 103.2 Hz), –5.42 (d, 2JP,P = 102.9 Hz) ppm. HRMS: calcd. For C<sub>37</sub>H<sub>31</sub>O<sub>3</sub>P<sub>2</sub>Pd [M –  
561 PF<sub>6</sub>]<sup>+</sup> 691.0777; found 691.0793.

562  
563 **Complex Pd8:** The procedure was the same as that used to prepare Pd1. From ligand 8 (285 mg, 0.50  
564 mmol) and Pd dimer D (72 mg, 0.18 mmol), the product was obtained as a white solid, yield 207 mg (65  
565 %). Diastereomeric ratio: 1:2.3. IR:  $\tilde{\nu}$  = 3065, 2961, 2869, 1619, 1590, 1509, 1464, 1435, 1400, 1368,  
566 1322, 1263, 1223, 1184, 1068, 958, 836 [ $\nu(\text{PF}_6^-)$ ], 774, 750, 696, 603, 558, 515  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400  
567 MHz):  $\delta$  = 8.26–8.13 (m, Ar), 8.13–7.87 (m, Ar), 7.78–7.71 (m, Ar), 7.61–7.29 (m, Ar), 7.09–7.01 (m,  
568 Ar), 4.43 (d, J = 8.8 Hz, 1 H, ma), 4.21 (dd, J = 9.2, 2.4 Hz, 1 H, mi), 3.67 (s, br, 1 H, Ma), 3.47 (s, br,  
569 1H, mi), 3.36 (d, J = 16.4 Hz, 1 H, mi), 3.29 (d, J = 17.2 Hz, 1 H, ma), 3.09 (d, J = 10.0 Hz, 1 H, ma),  
570 2.57 (dd, J = 10.0, 3.6 Hz, 1 H, mi), 1.83 (s, 3 H, mi), 1.63 (s, 3 H, Ma), 1.54 (d, 3JH,P = 17.2 Hz, 9 H,  
571 mi), 1.49 (d, 3JH,P = 16.8 Hz, 9 H, ma) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  = 153.8–118.2 (C, CH, Ar),  
572 75.4 (d, 2JC,P = 50.1 Hz, 2 × CH<sub>2</sub>, ma + mi), 70.7 (d, 2JC,P = 20.9 Hz, CH<sub>2</sub>, ma), 68.6 (d, 2JC,P = 19.9  
573 Hz, CH<sub>2</sub>, mi), 34.5 (d, 1JC,P = 20.5 Hz, C, mi), 34.2 (d, 1JC,P = 21.0 Hz, C, ma), 28.0 (d, 2JC,P = 6.9  
574 Hz, 3 × CH<sub>3</sub>, ma), 27.8 (d, 2JC,P = 6.5 Hz, 3 × CH<sub>3</sub>, mi), 23.82 (s, CH<sub>3</sub>, mi), 23.77 (s, CH<sub>3</sub>, ma) ppm.  
575  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$  = +146.99 (d, 2JP,P = 95.9 Hz, ma), +146.75 (d, 2JP,P = 96.7 Hz, mi),  
576 +32.10 (d, 2JP,P = 96.6 Hz, mi), +32.01 (d, 2JP,P = 96.1 Hz, ma) ppm. C<sub>40</sub>H<sub>37</sub>F<sub>6</sub>O<sub>3</sub>P<sub>3</sub>Pd (879.04):  
577 calcd. C 54.65, H 4.24; found C 54.53, H 4.71.

578

579

580

581 **Complex Pd9:** The procedure was the same as that used to prepare Pd1. From ligand 9 (320 mg, 0.54  
582 mmol) and Pd dimer D (81 mg, 0.21 mmol), the product was obtained as a white solid, yield 303 mg (80  
583 %). Diastereomeric ratio: 1:1.7. IR:  $\tilde{\nu}$  = 3061, 1619, 1590, 1509, 1463, 1437, 1323, 1265, 1224, 1184,  
584 1068, 958, 921, 841 [ $\nu(\text{PF}_6^-)$ ], 774, 749, 695, 609, 558, 517  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz):  $\delta$  = 8.24–8.19  
585 (m, Ar), 8.14–7.91 (m, Ar), 7.72–7.49 (m, Ar), 7.43–7.24 (m, Ar), 7.21–7.10 (m, Ar), 6.93–6.86 (m,  
586 Ar), 4.28 (d,  $J$  = 8.8 Hz, 1 H, mi), 4.10 (d,  $J$  = 8.8 Hz, 1 H, ma), 3.80 (d,  $J$  = 16.4 Hz, 1 H, ma), 3.74 (s,  
587 br, ma), 3.67 (s, br, mi), 3.33 (d,  $J$  = 16.4 Hz, 1 H, mi), 3.17 (dd,  $J$  = 10.4, 2.0 Hz, 1 H, ma), 2.78 (dd,  $J$  =  
588 10.0, 2.0 Hz, 1 H, mi), 1.96 (s, 3 H, mi), 1.70 (s, 3 H, ma) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  = 153.5–  
589 117.9 (C, CH, Ar), 75.2 (d,  $2J_{\text{C,P}}$  = 47.9 Hz,  $\text{CH}_2$ , mi), 70.4 (dd,  $2J_{\text{C,P}}$  = 28.0, 6.5 Hz,  $\text{CH}_2$ , ma), 70.0  
590 (dd,  $2J_{\text{C,P}}$  = 28.6, 7.5 Hz,  $\text{CH}_2$ , mi), 24.06 (s,  $\text{CH}_3$ , ma), 23.95 (s,  $\text{CH}_3$ , mi) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162  
591 MHz):  $\delta$  = +145.93 (d,  $2J_{\text{P,P}}$  = 100.9 Hz, ma), +145.66 (d,  $2J_{\text{P,P}}$  = 101.3 Hz, mi), +12.31 (d,  $2J_{\text{P,P}}$  =  
592 101.4 Hz, mi), +11.48 (d,  $2J_{\text{P,P}}$  = 100.9 Hz, ma) ppm.  $\text{C}_{42}\text{H}_{33}\text{F}_6\text{O}_3\text{P}_3\text{Pd}$  (899.03): calcd. C 56.11, H  
593 3.70; found C 55.47, H 3.5.

594  
595 **Complex Pd10:** The procedure was the same as that used to prepare Pd1. From ligand 10 (320 mg, 0.57  
596 mmol) and Pd dimer D (94 mg, 0.24 mmol), the product was obtained as a white solid, yield 315 mg (76  
597 %). Diastereomeric ratio: 1:2.4. IR:  $\tilde{\nu}$  = 3195, 3063, 2957, 1619, 1591, 1507, 1466, 1437, 1329, 1263,  
598 1198, 1131, 1090, 1026, 944, 901, 843 [ $\nu(\text{PF}_6^-)$ ], 751, 697, 633, 606, 558, 499  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400  
599 MHz):  $\delta$  = 8.16–8.07 (m, Ar), 8.02–7.91 (m, Ar), 7.84–7.82 (m, Ar), 7.71–7.38 (m, Ar), 7.32–7.13 (m,  
600 Ar), 7.10–7.05 (m, Ar), 6.88–6.79 (m, Ar), 4.08 (d,  $J$  = 6.4 Hz, 1 H, mi), 3.78 (d,  $J$  = 4.8 Hz, 1 H, ma),  
601 3.73 (m, 1 H, mi), 3.59 (d,  $J$  = 13.6 Hz, 1 H, ma), 3.38 (s, br, 1 H, ma), 3.31 (d,  $3J_{\text{H,P}}$  = 10.4 Hz, 3 H,  
602 ma), 3.14 (d,  $3J_{\text{H,P}}$  = 10.8 Hz, 3 H, mi), 3.05 (d,  $J$  = 10.4 Hz, 1 H, ma), 2.89 (d,  $3J_{\text{H,P}}$  = 14.8 Hz, 3 H,  
603 mi), 2.84 (s, br, 1 H, mi), 2.73 (d,  $3J_{\text{H,P}}$  = 14.8 Hz, 3 H, ma), 2.49 (d,  $J$  = 9.6 Hz, 1 H, mi), 2.25 (d,  
604  $2J_{\text{H,P}}$  = 9.2 Hz, 3 H, ma), 2.14 (d,  $2J_{\text{H,P}}$  = 9.2 Hz, 3 H, mi), 1.95 (s, 3 H, mi), 1.57 (s, 3 H, ma) ppm.  
605  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  = 155.1–120.4 (C, CH, Ar), 73.8 (d,  $2J_{\text{C,P}}$  = 43.6 Hz,  $\text{CH}_2$ , mi), 65.16  
606 (dd,  $2J_{\text{C,P}}$  = 30.0, 5.8 Hz,  $\text{CH}_2$ , ma), 65.11 (d,  $2J_{\text{C,P}}$  = 31.1 Hz,  $\text{CH}_2$ , mi), 39.58 (d,  $2J_{\text{C,P}}$  = 31.9 Hz,  
607  $\text{CH}_3$ , ma), 39.54 (d,  $2J_{\text{C,P}}$  = 30.2 Hz,  $\text{CH}_3$ , mi), 35.92 (d,  $2J_{\text{C,P}}$  = 12.2 Hz,  $\text{CH}_3$ , ma), 35.84 (d,  $2J_{\text{C,P}}$   
608 = 12.6 Hz,  $\text{CH}_3$ , mi), 24.0 (s,  $\text{CH}_3$ , ma), 23.9 (s,  $\text{CH}_3$ , mi), 13.4 (d,  $1J_{\text{C,P}}$  = 29.2 Hz,  $\text{CH}_3$ , mi), 12.5 (d,  
609  $1J_{\text{C,P}}$  = 28.6 Hz,  $\text{CH}_3$ , ma) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$  = +156.57 (d,  $2J_{\text{P,P}}$  = 85.2 Hz, mi),  
610 +155.95 (d,  $2J_{\text{P,P}}$  = 87.2 Hz, ma), –4.25 (d,  $2J_{\text{P,P}}$  = 87.2 Hz, ma), –5.92 (d,  $2J_{\text{P,P}}$  = 85.2 Hz, mi) ppm.  
611 HRMS: calcd. for  $\text{C}_{39}\text{H}_{37}\text{N}_2\text{O}_2\text{P}_2\text{Pd}$  [ $\text{M} - \text{PF}_6$ ] $^+$  717.1410; found 717.1435.

612  
613 **Complex Pd11:** The procedure was the same as that used to prepare Pd1. From ligand 11 (450 mg, 0.75  
614 mmol) and Pd dimer D (118 mg, 0.30 mmol), the product was obtained as a white solid, yield 375 mg  
615 (69 %). Diastereomeric ratio: 1:2.1. IR:  $\tilde{\nu}$  = 3063, 2959, 2870, 1619, 1591, 1507, 1466, 1434, 1329,  
616 1262, 1198, 1091, 944, 876, 842 [ $\nu(\text{PF}_6^-)$ ], 771, 748, 697, 633, 606, 558, 517  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400  
617 MHz):  $\delta$  = 8.19–7.86 (m, Ar), 7.71–7.40 (m, Ar), 7.39–7.11 (m, Ar), 7.06–6.95 (m, Ar), 4.34 (d,  $J$  = 6.0

618 Hz, 1 H, mi), 3.91 (s, br, 1 H, mi), 3.68 (d,  $J = 15.2$  Hz, 1 H, ma), 3.64 (dd,  $J = 9.2, 3.2$  Hz, 1 H, ma),  
619 3.34 (s, br, 1 H, ma), 3.28 (d,  $3J_{H,P} = 10.0$  Hz, 3 H, ma), 3.17 (d,  $J = 10.0$  Hz, 1 H, ma), 3.11 (d,  $3J_{H,P}$   
620  $= 10.4$  Hz, 3 H, mi), 3.01 (d,  $3J_{H,P} = 15.2$  Hz, 3 H, mi), 2.82 (d,  $3J_{H,P} = 14.4$  Hz, 3 H, ma), 2.45 (d,  $J =$   
621  $9.2$  Hz, 1 H, mi), 2.36 (d,  $J = 14.0$  Hz, 1 H, mi), 1.97 (s, 3 H, mi), 1.52 (d,  $3J_{H,P} = 16.8$  Hz, 9 H, ma),  
622 1.43 (d,  $3J_{H,P} = 16.8$  Hz, 9 H, mi), 1.33 (s, 3 H, ma) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz):  $\delta = 156.3$ – $121.8$   
623 (C, CH, Ar), 74.9 (d, CH<sub>2</sub>, mi), 65.4 (dd,  $2J_{C,P} = 27.3, 5.2$  Hz, CH<sub>2</sub>, ma), 64.6 (d,  $2J_{C,P} = 27.8$  Hz,  
624 CH<sub>2</sub>, mi), 39.85 (d,  $2J_{C,P} = 30.1$  Hz, CH<sub>3</sub>, mi), 39.75 (d,  $2J_{C,P} = 31.9$  Hz, CH<sub>3</sub>, ma), 36.49 (d,  $2J_{C,P} =$   
625  $11.3$  Hz, CH<sub>3</sub>, mi), 36.28 (d,  $2J_{C,P} = 11.2$  Hz, CH<sub>3</sub>, ma), 35.9 (d,  $1J_{C,P} = 21.1$  Hz, C, ma), 35.2 (d,  
626  $1J_{C,P} = 22.4$  Hz, C, mi), 28.6 (d,  $2J_{C,P} = 7.0$  Hz,  $3 \times$  CH<sub>3</sub>, mi), 28.2 (d,  $2J_{C,P} = 6.6$  Hz,  $3 \times$  CH<sub>3</sub>, ma),  
627 23.73 (s, CH<sub>3</sub>, mi), 23.70 (s, CH<sub>3</sub>, ma) ppm.  $^31P\{^1H\}$  NMR (162 MHz):  $\delta = +153.98$  (d,  $2J_{P,P} = 81.0$   
628 Hz, ma),  $+153.09$  (d,  $2J_{P,P} = 80.7$  Hz, mi),  $+27.73$  (d,  $2J_{P,P} = 80.7$  Hz, mi),  $+26.96$  (d,  $2J_{P,P} = 81.0$  Hz,  
629 ma) ppm. C<sub>42</sub>H<sub>43</sub>F<sub>6</sub>N<sub>2</sub>OP<sub>3</sub>Pd (905.12): calcd. C 55.73, H 4.79, N 3.09; found C 55.96, H 5.19, N 3.02.  
630

631 **Complex Pd12:** The procedure was the same as that used to prepare Pd1. From ligand 12 (300 mg, 0.54  
632 mmol) and Pd dimer D (84 mg, 0.21 mmol), the product was obtained as a white solid, yield 210 mg (58  
633 %). Diastereomeric ratio: 1:1. IR:  $\tilde{\nu} = 3064, 2962, 1619, 1592, 1507, 1467, 1438, 1329, 1275, 1200,$   
634  $1090, 944, 843$  [ $\nu(\text{PF}_6^-)$ ], 740, 697, 633, 605, 558, 509  $\text{cm}^{-1}$ .  $^1H$  NMR (400 MHz):  $\delta = 8.18$ – $7.04$  (m,  
635 4 H, Ar), 8.03– $7.88$  (m, 4 H, Ar), 7.83– $7.67$  (m, 5 H, Ar), 7.62– $7.33$  (m, 16 H, Ar), 7.31– $7.05$  (m, 13 H,  
636 Ar), 4.76 (d,  $J = 6.0$  Hz, 1 H), 4.50 (d,  $J = 4.0$  Hz, 1 H), 3.67 (d,  $J = 14.0$  Hz, 1 H), 3.53 (t,  $J = 4.4$  Hz, 1  
637 H), 3.38 (s, 1 H), 3.34 (d,  $J = 14.0$  Hz, 1 H), 3.15 (d,  $J = 10.4$  Hz, 1 H), 2.86 (d,  $3J_{H,P} = 14.8$  Hz, 3 H),  
638 2.68 (d,  $3J_{H,P} = 14.4$  Hz, 3 H), 2.54 (d,  $3J_{H,P} = 10.4$  Hz, 3 H), 2.51 (d,  $J = 8.0$  Hz, 1 H), 2.39 (d,  $3J_{H,P}$   
639  $= 10.4$  Hz, 3 H), 2.36 (d,  $2J_{H,P} = 10.0$  Hz, 3 H), 2.30 (d,  $2J_{H,P} = 9.6$  Hz, 3 H), 2.07 (s, 3 H), 1.66 (s, 3  
640 H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz):  $\delta = 154.6$ – $121.3$  (C, CH, Ar), 71.3 (d,  $2J_{C,P} = 39.9$  Hz, CH<sub>2</sub>),  
641 71.2 (d,  $2J_{C,P} = 40.3$  Hz, CH<sub>2</sub>), 67.2 (d,  $2J_{C,P} = 35.0$  Hz, CH<sub>2</sub>), 65.0 (d,  $2J_{C,P} = 34.6$  Hz, CH<sub>2</sub>), 39.6  
642 (d,  $2J_{C,P} = 31.8$  Hz, CH<sub>3</sub>), 39.4 (d,  $2J_{C,P} = 29.7$  Hz, CH<sub>3</sub>), 35.03 (d,  $2J_{C,P} = 11.8$  Hz, CH<sub>3</sub>), 35.00 (d,  
643  $2J_{C,P} = 12.1$  Hz, CH<sub>3</sub>), 24.2 (s, CH<sub>3</sub>), 24.1 (s, CH<sub>3</sub>), 16.3 (d,  $1J_{C,P} = 28.8$  Hz, CH<sub>3</sub>), 14.8 (d,  $1J_{C,P} =$   
644  $26.3$  Hz, CH<sub>3</sub>) ppm.  $^31P\{^1H\}$  NMR (162 MHz):  $\delta = +158.83$  (d,  $2J_{P,P} = 84.6$  Hz),  $+158.66$  (d,  $2J_{P,P} =$   
645  $85.2$  Hz),  $-3.16$  (d,  $2J_{P,P} = 84.7$  Hz),  $-4.95$  (d,  $2J_{P,P} = 85.1$  Hz) ppm. HRMS: calcd. for  
646 C<sub>39</sub>H<sub>37</sub>N<sub>2</sub>OP<sub>2</sub>Pd [M – PF<sub>6</sub>]<sup>+</sup> 717.1410; found 717.1437.  
647

648 **Complex Pd13:** The procedure was the same as that used to prepare Pd1. From ligand 13 (150 mg, 0.25  
649 mmol) and Pd dimer D (40 mg, 0.10 mmol), the product was obtained as a white solid, yield 122 mg (67  
650 %). Diastereomeric ratio: 1:2. IR:  $\tilde{\nu} = 3064, 2963, 1619, 1591, 1507, 1467, 1435, 1329, 1262, 1199,$   
651  $1090, 943, 842$  [ $\nu(\text{PF}_6^-)$ ], 774, 750, 697, 601, 557, 518  $\text{cm}^{-1}$ .  $^1H$  NMR (400 MHz):  $\delta = 8.15$ – $8.05$  (m,  
652 Ar), 7.99– $7.90$  (m, Ar), 7.86– $7.81$  (m, Ar), 7.73– $7.66$  (m, Ar), 7.58– $7.41$  (m, Ar), 7.31– $7.07$  (m, Ar),  
653 4.57– $4.53$  (m, 2 H, ma + mi), 3.68 (d,  $J = 14.0$  Hz, 1 H, ma), 3.33 (d,  $J = 14.0$  Hz, 1 H, mi), 3.20– $3.12$   
654 (m, 3 H,  $2 \times$  ma + mi), 2.84 (d,  $3J_{H,P} = 14.8$  Hz, 3 H, mi), 2.65 (d,  $3J_{H,P} = 14.4$  Hz, 3 H, ma), 2.38 (d,

655 3JH,P = 10.0 Hz, 3 H, ma), 2.22 (d, 3JH,P = 9.6 Hz, 3 H, mi), 2.03 (s, 3 H, mi), 1.61 (s, 3 H, ma), 1.50  
656 (d, 3JH,P = 16.4 Hz, 9 H, mi), 1.47 (d, 3JH,P = 16.4 Hz, 9 H, ma) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  =  
657 155.2–120.1 (C, CH, Ar), 73.4 (d, 2JC,P = 44.0 Hz, CH<sub>2</sub>, ma), 67.5 (d, 2JC,P = 22.6 Hz, CH<sub>2</sub>, ma),  
658 39.2 (d, 2JC,P = 30.9 Hz, CH<sub>3</sub>, ma), 35.1 (d, 2JC,P = 10.8 Hz, CH<sub>3</sub>, ma), 32.9 (d, 1JC,P = 19.6 Hz, C,  
659 mi), 32.3 (d, 1JC,P = 19.4 Hz, C, ma), 27.4 (d, 2JC,P = 6.3 Hz, 3 × CH<sub>3</sub>, mi), 27.1 (d, 2JC,P = 6.9 Hz, 3  
660 × CH<sub>3</sub>, ma), 23.9 (s, CH<sub>3</sub>, ma), 23.8 (s, CH<sub>3</sub>, mi) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$  = +157.80 (d,  
661 2JP,P = 77.6 Hz, ma), +154.36 (d, 2JP,P = 78.2 Hz, mi), +35.38 (d, 2JP,P = 78.2 Hz, mi), +35.34 (d,  
662 2JP,P = 77.4 Hz, ma) ppm. C<sub>42</sub>H<sub>43</sub>F<sub>6</sub>N<sub>2</sub>OP<sub>3</sub>Pd (905.12): calcd. C 55.73, H 4.79, N 3.09; found C  
663 53.22, H 5.01, N 3.08.

664  
665 **Complex Pd14:** The procedure was the same as that used to prepare Pd1. From ligand 14 (320 mg, 0.52  
666 mmol) and Pd dimer D (81 mg, 0.21 mmol), the product was obtained as a white solid, yield 303 mg (78  
667 %). Diastereomeric ratio: 1:1. IR:  $\tilde{\nu}$  = 3063, 1618, 1591, 1507, 1465, 1437, 1329, 1263, 1200, 1090,  
668 944, 842 [ $\nu(\text{PF}_6^-)$ ], 749, 697, 607, 558, 519  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz):  $\delta$  = 8.14 (d, J = 7.2 Hz, 1 H),  
669 8.12 (d, J = 6.4 Hz, 2 H), 8.09 (d, J = 6.4 Hz, 1 H), 8.00 (d, J = 3.6 Hz, 1 H), 7.98 (d, J = 4.0 Hz, 1 H),  
670 7.96 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 8.4 Hz, 1 H), 7.85 (d, J = 8.8 Hz, 1 H), 7.70 (q, J = 8.0 Hz, 2 H),  
671 7.73–7.36 (m, 20 H, Ar), 7.32–7.16 (m, 17 H, Ar), 7.12–7.08 (m, 2 H, Ar), 6.79 (m, 2 H, Ar), 4.31 (d, J  
672 = 6.0 Hz, 1 H), 3.99 (dd, J = 7.2, 2.4 Hz, 1 H), 3.86 (d, J = 13.6 Hz, 1 H), 3.61 (t, J = 4.4 Hz, 1 H), 3.41  
673 (s, br, 1 H), 3.32 (d, J = 13.6 Hz, 1 H), 3.22 (d, J = 10.4 Hz, 1 H), 2.99 (d, 3JH,P = 15.2 Hz, 3 H), 2.80  
674 (d, 3JH,P = 14.8 Hz, 3 H), 2.74 (dd, J = 10.4, 2.0 Hz, 1 H), 2.56 (d, 3JH,P = 10.8 Hz, 3 H), 2.35 (d,  
675 3JH,P = 10.4 Hz, 3 H), 2.02 (s, 3 H), 1.70 (s, 3 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  = 147.8–121.0  
676 (C, CH, Ar), 39.8 (d, 2JC,P = 28.0 Hz, CH<sub>3</sub>), 39.6 (d, 2JC,P = 31.2 Hz, CH<sub>3</sub>), 34.7 (d, 2JC,P = 17.0 Hz,  
677 CH<sub>3</sub>), 34.6 (d, 2JC,P = 17.0 Hz, CH<sub>3</sub>), 24.2 (s, CH<sub>3</sub>), 24.0 (s, CH<sub>3</sub>) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz):  $\delta$   
678 = +158.84 (d, 2JP,P = 84.7 Hz), +158.62 (d, 2JP,P = 83.3 Hz), +13.21 (d, 2JP,P = 83.3 Hz), 12.65 (d,  
679 2JP,P = 84.7 Hz) ppm. C<sub>44</sub>H<sub>39</sub>F<sub>6</sub>N<sub>2</sub>OP<sub>3</sub>Pd (925.11): calcd. C 57.12, H 4.25, N 3.03; found C 56.14, H  
680 4.56, N 3.03.

681  
682 **Complex Pd6':** The procedure was the same as that used to prepare Pd1. From ligand 6 (300 mg, 0.52  
683 mmol) and Pd dimer D' (135 mg, 0.2 mmol), the product was obtained as a white solid, yield 253 mg  
684 (62 %). Diastereomeric ratio: 1:3.5. IR:  $\tilde{\nu}$  = 3057, 2957, 1596, 1470, 1430, 1183, 1070, 957, 848  
685 [ $\nu(\text{PF}_6^-)$ ], 745, 561  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz):  $\delta$  = 8.47–6.18 (m, 40 H, Ar), 6.06–5.90 (m, 4 H, 2 ×  
686 ma + 2 × mi), 5.24–5.19 (m, 2 H, ma + mi), 1.43 (d, 3JH,P = 17.2 Hz, 9 H, ma), 1.08 (d, 3JH,P = 16.8  
687 Hz, 9 H, mi) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz):  $\delta$  = 154.8–118.5 (C, CH, Ar), 112.73 (d, 2JC,P = 7.9 Hz,  
688 CH), 112.60 (d, 2JC,P = 8.2 Hz, CH), 100.22 (d, 2JC,P = 4.5 Hz, CH), 99.86 (d, 2JC,P = 4.8 Hz, CH),  
689 86.36 (d, 2JC,P = 10.5 Hz, CH), 86.13 (d, 2JC,P = 10.7 Hz, CH), 36.79 (d, 1JC,P = 19.7 Hz, C, mi),  
690 36.72 (d, 1JC,P = 18.6 Hz, C, ma), 27.9 (d, 2JC,P = 6.2 Hz, 6 × CH<sub>3</sub>, ma + mi) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR  
691 (162 MHz):  $\delta$  = +139.57 (d, 2JP,P = 138.0 Hz, ma), +137.27 (d, 2JP,P = 144.5 Hz, mi), +29.87 (d, 2JP,P

692 = 138.0 Hz, ma), +26.75 (d, 2JP,P = 144.3 Hz, mi) ppm. HRMS: calcd. for C<sub>51</sub>H<sub>43</sub>O<sub>3</sub>P<sub>2</sub>Pd [M – PF<sub>6</sub>]<sup>+</sup>  
693 871.1716; found 871.1733.

694

695 **Allylic Alkylations with Dimethyl Malonate:** Under a nitrogen atmosphere, the appropriate Pd  
696 complex (0.01 mmol), the precursor I, II or III (1 mmol), dimethyl malonate (3 mmol), BSA (3 mmol)  
697 and KOAc (1 mg) were dissolved in dichloromethane (5 mL) in this precise order. The flask was  
698 covered with aluminium foil, and the mixture was stirred for the allotted time. To quench the reaction,  
699 diethyl ether (20 mL) and aqueous 10 % ammonium chloride solution (20 mL) were added. After  
700 extraction, the organic phase was dried with anhydrous sodium sulfate and filtered, and the solvent was  
701 removed in vacuo. The crude product was analysed by <sup>1</sup>H NMR spectroscopy to estimate the  
702 conversion. The crude product was dissolved in ethyl acetate, and the solution was passed through a  
703 column of silica to remove the metallic impurities. The eluent was removed in vacuo, and the residue  
704 was analysed by NMR spectroscopy and HPLC (alkylations of I) or GC (alkylations of II and III).

705

706 **Allylic Amination of I with Benzylamine:** Under a nitrogen atmosphere, the Pd complex (0.01 mmol),  
707 I (1 mmol) and benzylamine (3 mmol) were dissolved in dichloromethane (5 mL) in this precise order.  
708 The flask was covered with aluminium foil, and the mixture was stirred for 72 h. To quench the reaction,  
709 diethyl ether (20 mL) and aqueous 10 % ammonium chloride solution (20 mL) were added. After  
710 extraction, the organic phase was dried with anhydrous sodium sulfate and filtered, and the solvent was  
711 removed in vacuo. The crude product was analysed by <sup>1</sup>H NMR spectroscopy to estimate the  
712 conversion. The crude product was dissolved in ethyl acetate, and the solution was passed through a  
713 column of silica to remove the metallic impurities. The eluent was removed in vacuo, and the residue  
714 was analysed by NMR spectroscopy and HPLC.

715

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717

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720

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830 **Legends to figures**

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832 **Scheme 1.** Retrosynthetic route to the PP' ligands.

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834 **Scheme 2.** Preparation of PP' ligands 1–14.

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836 **Figure 1.** Prepared PP' ligands 1–14.

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838 **Scheme 3.** Preparation of Pd complexes Pd1–Pd14.

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840 **Figure 2.** ORTEP representations (thermal ellipsoids drawn at 50 % of probability level, H atoms and

841 PF<sub>6</sub> – anions removed for clarity) of Pd1 (left) and Pd2 (right). Distances [Å] and angles [°] for Pd1:

842 Pd–P(1) 2.2904(6), Pd–P(2) 2.2510(6), Pd–C(20) 2.206(3), Pd–C(21) 2.212(2), Pd–C(22) 2.159(2),

843 C(20)–C(21) 1.402(4), C(21)–C(22) 1.419(4), P(1)–Pd–Pd(2) 92.11(2), P(2)–Pd–C(22) 97.92(7), C(22)–

844 Pd–C(20) 67.19(10), C(20)–Pd–P(1) 102.67(8); for Pd2: Pd–P(1) 2.232(2), Pd–P(2) 2.286(3), Pd–C(24)

845 2.087(10), Pd–C(25) 2.299(12), Pd–C(26) 2.552(12), C(24)–C(25) 1.366(17), C(24)–C(26) 1.447(17),

846 C(24)–C(23) 1.365(15), P(1)–Pd–Pd(2) 94.67(9), P(1)–Pd–C(25) 125.6(3), C(25)–Pd–C(26) 61.1(4),

847 C(26)–Pd–P(2) 76.4(3).

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849

850 **Figure 3.** ORTEP representation (thermal ellipsoids drawn at 50 % of probability level, H atoms, water

851 molecules and the PF<sub>6</sub> – anion removed for clarity) of Pd13. Distances [Å] and angles [°]: Pd–P(1)

852 2.2568(13), Pd–P(2) 2.3192(14), Pd–C(39) 2.177(5), Pd–C(40) 2.189(6), Pd–C(41) 2.158(6), C(39)–

853 C(40) 1.428(9), C(40)–C(41) 1.376(8), C(40)–C(42) 1.517(9), P(1)–N(1) 1.683(4), P(1)–N(2) 1.656(5),

854 P(1)–Pd–P(2) 91.60(5), P(2)–Pd–C(39) 104.10(18), C(39)–Pd–C(41) 66.6(2), C(41)–Pd–P(1) 97.63(16),

855 ΣN(1) 346.7, ΣN(2) 357.1.

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857 **Scheme 4.** Allylic substitution reactions of I catalysed by Pd1–Pd14 complexes.

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859 **Scheme 5.** Preparation of complex Pd6'.

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861 **Scheme 6** Allylic alkylation of II and III catalysed by Pd complexes.

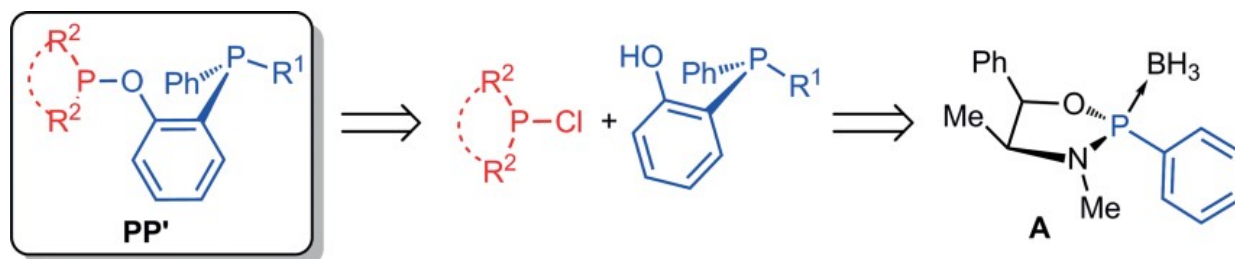
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863 SCHEME 1

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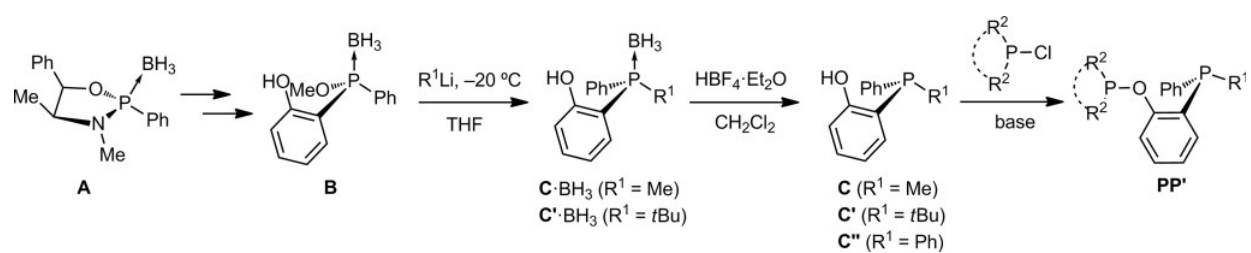


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## SCHEME 2

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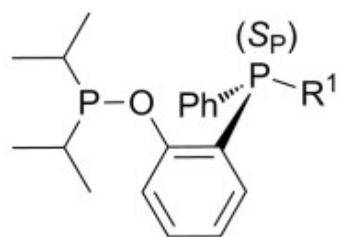
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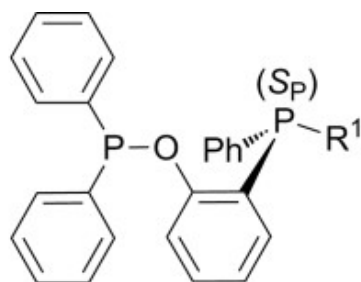
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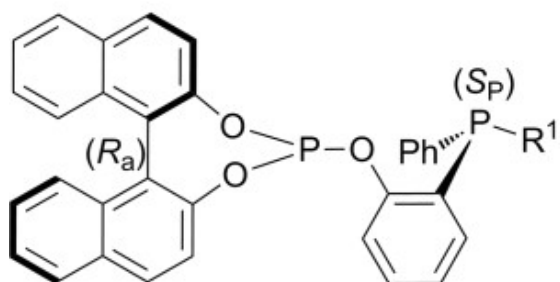
FIGURE 1



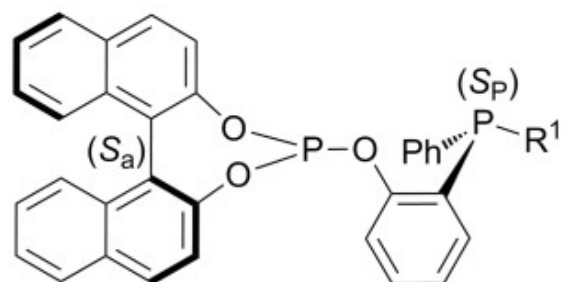
1 ( $R^1 = \text{Me}$ ); 2 ( $R^1 = t\text{Bu}$ )



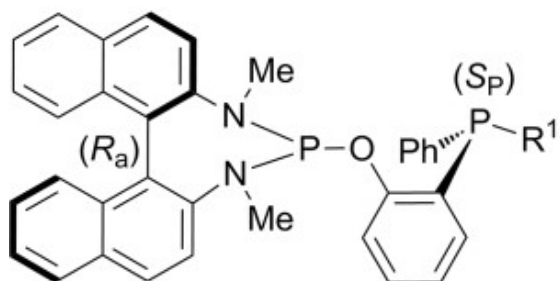
3 ( $R^1 = \text{Me}$ ); 4 ( $R^1 = t\text{Bu}$ )



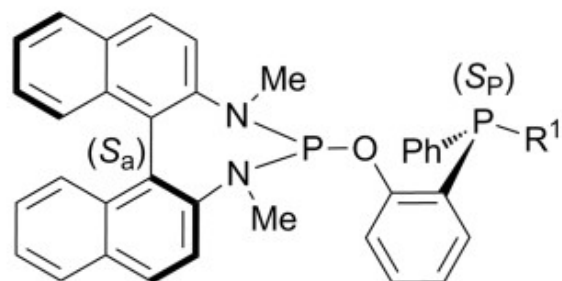
5 ( $R^1 = \text{Me}$ ); 6 ( $R^1 = t\text{Bu}$ )



7 ( $R^1 = \text{Me}$ ); 8 ( $R^1 = t\text{Bu}$ ); 9 ( $R^1 = \text{Ph}$ )



10 ( $R^1 = \text{Me}$ ); 11 ( $R^1 = t\text{Bu}$ )



12 ( $R^1 = \text{Me}$ ); 13 ( $R^1 = t\text{Bu}$ ); 14 ( $R^1 = \text{Ph}$ )

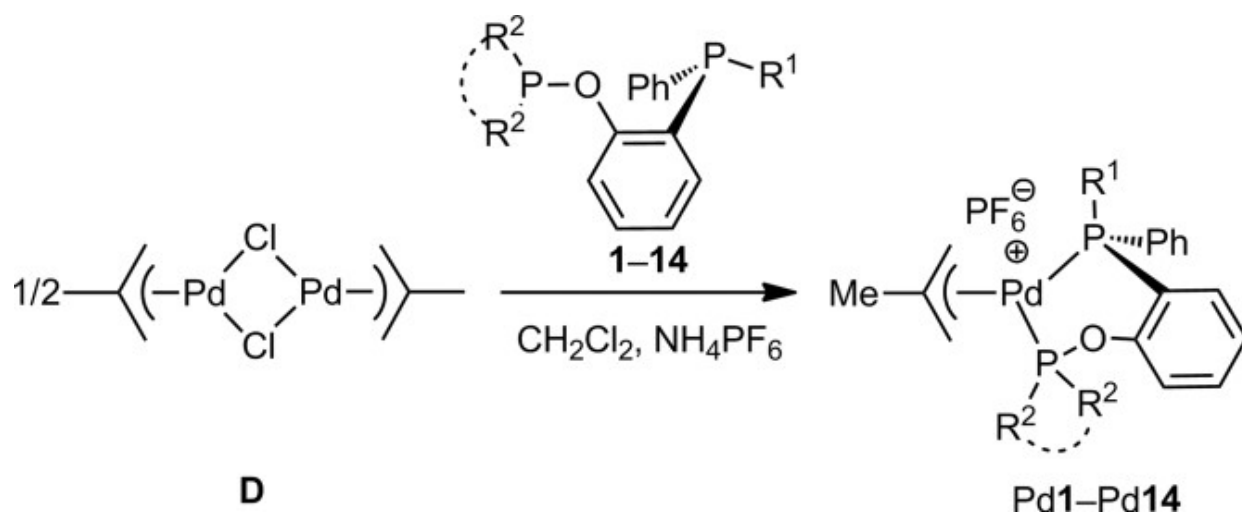
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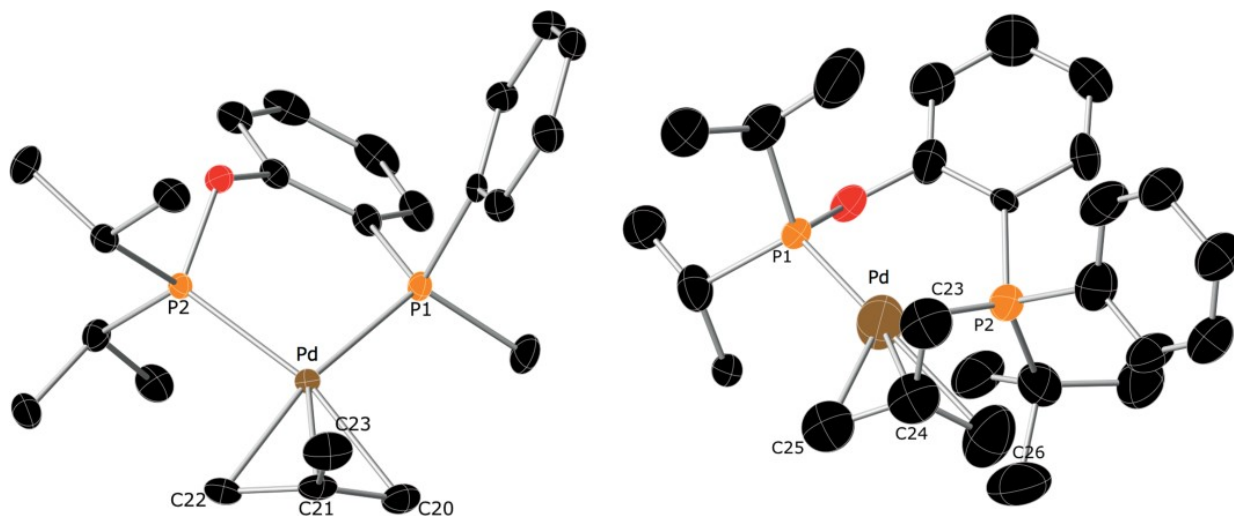
**SCHEME3**



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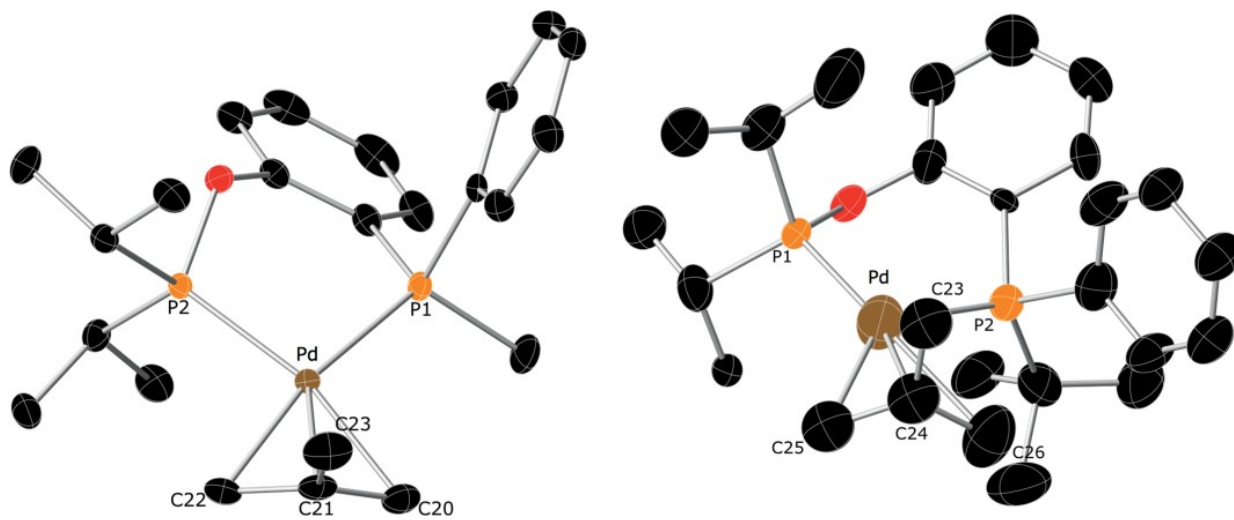
FIGURE 2





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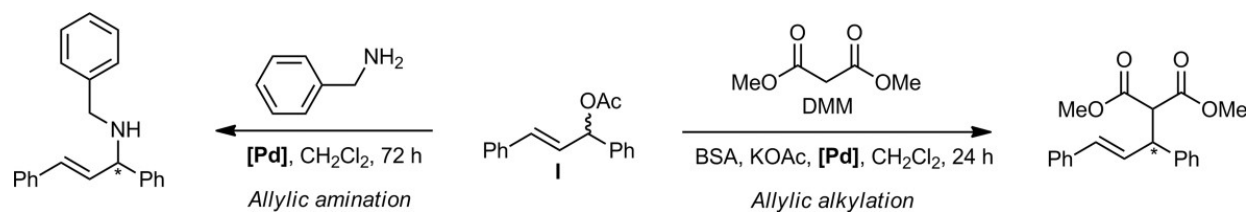
FIGURE 3.



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**SCHEME 4.**

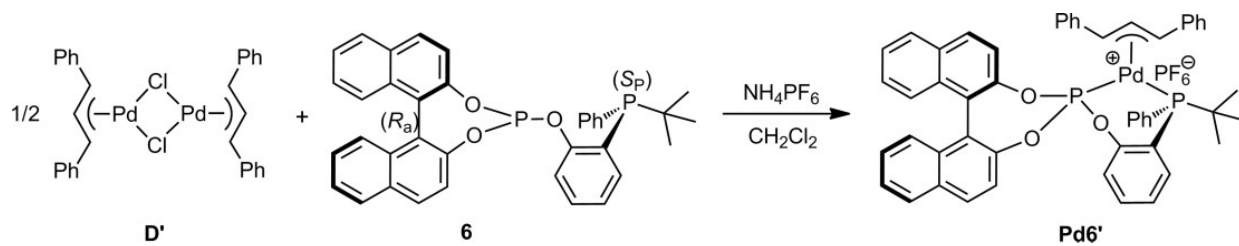
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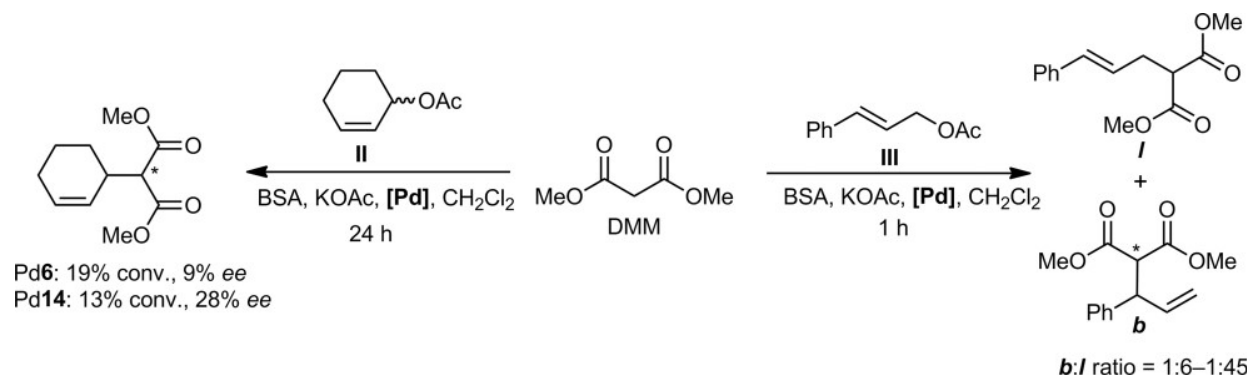
**SCHEME 5.**



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### SCHEME 6



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915 **Table 1** Results of asymmetric allylic substitutions of I with Pd1–Pd14.  
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Entry <sup>[a]</sup>	Pd complex	Alkylation Conv. [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>	Amination Conv. [%] <sup>[b]</sup>	ee [%] <sup>[c]</sup>
1	Pd1	>99	9 (S)	40	<5
2	Pd2	>99	5 (S)	20	8 (S)
3	Pd3	>99	11 (R)	10	<5
4	Pd4	>99	45 (R)	17	18 (S)
5	Pd5	>99	80 (R)	<5	–
6	Pd6	>99	94 (R)	<5	–
7	Pd7	>99	66 (S)	<5	–
8	Pd8	>99	81 (S)	<5	–
9	Pd9	>99	88 (S)	<5	–
10	Pd10	>99	82 (R)	31	18 (S)
11	Pd11	>99	56 (R)	40	37 (S)
12	Pd12	>99	73 (S)	61	42 (R)
13	Pd13	>99	50 (S)	70	39 (R)
14	Pd14	>99	96 (S)	80	70 (R)

[a] Conditions for allylic alkylations with DMM: Pd complex (0.01 mmol), I (1 mmol), dimethyl malonate (3 mmol), BSA (3 mmol) and KOAc (1 mg) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) at r.t. for 24 h; for allylic aminations with benzylamine: Pd complex (0.01 mmol), I (1 mmol) and benzylamine (3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) at r.t. for 72 h. [b] Conversion percentage expressed as I consumption, determined by NMR spectroscopy and HPLC. [c] Enantiomeric excesses determined by HPLC.

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