Tetrahedron: *Asymmetry* 21 (2010) 1971–1982

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

A modular approach to a new class of phosphinohydrazones and their use in asymmetric allylic alkylation reactions

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ARTICLE INFO

Article history:
Received 4 May 2010
Accepted 18 May 2010
Available online 16 June 2010

ABSTRACT

A group of five phosphino hydrazones with a pendant binaphthyl unit as a chiral modifier has been synthesized from non-racemic 2,2′-bis(bromomethyl)-1,1′-binaphthyl and 3,3′-diiodo-2,2′-bis(bromomethyl)-1,1′-binaphthyl as the key intermediates. Their efficiency as chiral ligands in palladium-catalyzed allylic alkylation reactions has been investigated showing up to 95% ee under optimized conditions. X-ray diffraction structures of mono- and dimeric Pd complexes are also reported.

1. Introduction

It is well known that the selectivity in catalysis is highly dependent on a perfect fit of substrate structure, operating reaction mechanism, and nature of the catalyst. In order to obtain high stereoselectivity in asymmetric transformations, conditions have to be empirically developed usually on the basis of trial and error with modification of reaction conditions and stepwise adaptation of the ligand structure: with regard to the latter, a modular approach is highly desired providing an economic access to tailor-made ligands and the build-up of libraries. Along with popular bidentate P(III) ligands, P(III)–N(sp^3) or P(III)–N(sp^2) ligands[1] have also attracted much attention. Among these the family of oxazolinphospines **1** is prominent forming kinetically stable chelates and displaying outstanding enantioselectivity in various reactions particularly in allylic substitutions.[2] On the other hand the 2,2′-bridged binaphthyl moiety **2** forming distorted seven-membered azepine[3] and phosphepine[4] motifs with (pseudo) C_2 symmetry has found broad application in mono and bidentate ligands useful in asymmetric catalysis. Previous investigations have shown that azepine-based P–N ligands such as **4** and **5** displayed different degrees of enantioselectivity in various C–C coupling reactions. Allylic substitutions have been studied in detail revealing that the introduction of benzylic substituents in **5** gave, only in few cases, better ee The NMR investigation indicated that such crowded ligands are monodentate with coordination via the phosphorus. From this we concluded that replacement of the sp^3 nitrogen with an sp^2 nitrogen donor and a chiral modifier more distant from the coordination sites could increase the kinetic stability of the chelate concurrently reducing steric strain. The less pronounced chiral interaction in the substrate coordination sphere will eventually be counterbalanced by the introduction of additional substituents at the 3- and 3′-positions. To test this hypothesis, phosphino hydrazones **6** were chosen where the binaphthyl-based azepine unit is attached through a (rotatable) N–N σ bond to the bidentate sp^2-N–P(III) unit. The P,N donors will form conformatively stable six-membered chelates with only one degree of conformative freedom coming from the (freely) rotatable N–N bond. Substrates coordinating *trans* to the P atom will experience an interaction with the pending azepine unit. Fine tuning and/or extension of the chiral sphere can be achieved by further substitution at the 3- and 3′-positions with the aim of combining maximum asymmetric interaction with sufficient reactivity. Chiral ligands of type **3** have only recently been used in the asymmetric allylation (Fig. 1).[5]

2. Results and discussion

2.1. Synthesis of ligands

The synthesis of the parent compound **6** started from enantiopure 2,2′-bis(bromomethyl)-1,1′-binaphthyl **7** accessible either by various well-established optical resolution procedures of racemic **7**,[6] from non-racemic 2,2′-dihydroxy-1,1′-binaphthyl[7] or 1,1′-binaphthyl-2,2′-dicarboxylic acid[8] and subsequent stereoconservative transformations, or by asymmetric cross coupling.[9] (*R*)-**7** was refluxed with excess of Boc-hydrazine/triethylamine in THF to afford the cyclized product (*R*)-**8** in 75% yield. Deprotection (CF_3COOH, CH_2Cl_2, rt, 96%) and condensation with 2-diphenylphosphinobenzaldehyde ($MgSO_4$, CH_2Cl_2, rt, 97%) gave hydrazone **6** as a pale yellow foam, which could be handled under air without

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doi:10.1016/j.tetasy.2010.05.031

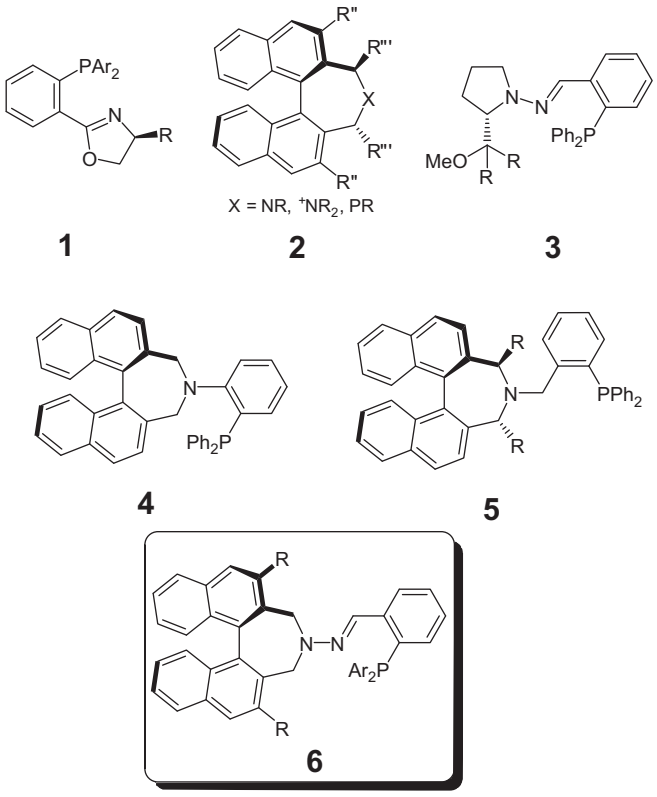


Figure 1. PN ligands

precautions. The electron-rich phosphine (*R*)-**10** was obtained similarly in 78% yield from 2-bis(3-anisyl)phosphinobenzaldehyde (Scheme 1).[10]

As an alternative approach a one-pot protocol[11] with preceding preparation of (*E*)-(2-(diphenylphosphino)benzylidene)hydrazine followed by cyclization with (*R*)-**7** furnished (*R*)-**6** in low yield (32%). Attempts to isolate the hydrazine intermediate were hampered from its readiness to form (1*E*,2*E*)-1,2-bis(2-(diphenylphosphino)benzylidene)hydrazine.

For the preparation of 3,3′-substituted binaphthyl units (Scheme 2) a reactive but stable key intermediate was required with the option of introducing substituents at a later stage of the synthesis. The diiodide (*R*)-**15** seemed suitable for this purpose. Its synthesis was based on the facile and high yielding orthometallation of the unprotected dicarboxylic acid (*R*)-**11** with Li-2,2,6,6-tetramethylpiperid (Li-TMP) and in situ reaction with Me_3SiCl[12] giving (*R*)-**12**[13,14] which was reduced (BH_3·THF, reflux) to afford (*R*)-**13**. Replacement of the Me_3Si-group by iodide (ICl)[15] and bromination of the dibenzylic alcohol (*R*)-**14** with PBr_3 at low temperature yielded (*R*)-**15** as a high-melting crystalline solid in 53% overall yield [from (*R*)-**11**]. (*R*)-**15** was cyclized with Boc-hydrazine and deprotected (CF_3COOH) to afford *N*-amino-substituted dihydroazepine (*R*)-**21** as a moderately stable intermediate which was treated with 2-diphenylphosphinobenzaldehyde/$MgSO_4$ to give (*R*)-**22** (72%). A subsequent Suzuki reaction[16] was applied to obtain 3,3′-substituted ligands (*R*)-**27** and (*R*)-**28** although in moderate yield. Alternatively, diphenyl- and dinaphthyl-substituted ligands were prepared via (*R*)-**23** and (*R*)-**25** or (*R*)-**24** and (*R*)-**26**, respectively, in significantly better overall yield [53% and 35%, respectively, from (*R*)-**20**]. Moreover, the synthesis of (*R*)-**17**–(*R*)-**19** from (*R*)-**22** was attempted. After effective two-fold iodo–lithio exchange (−78 °C, 5 min) treatment with Me_3SiCl gave (*R*)-**17** in fair yield (66%); while with Cl_3CCCl_3 exclusively the phosphine oxide of **18** was isolated (63%); its X-ray structure was determined (see below). With PhSSPh the desired product (*R*)-**19** was formed albeit in poor yield (10%). A one-step approach from (*R*)-**16** gave (*R*)-**17** in lower yield.

2.2. Asymmetric catalysis

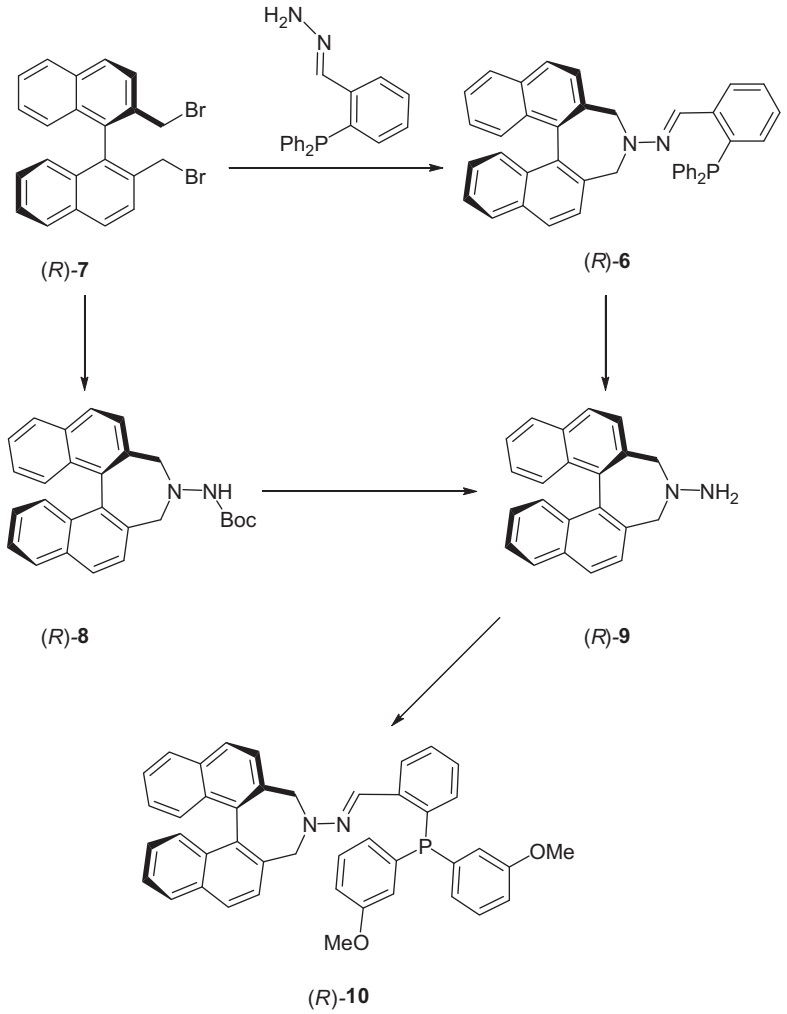
The group of new hydrazone-phosphine ligands was tested in prototypical asymmetric allylic substitution reactions (Scheme 3). In order to establish the optimal reaction conditions, ligand (*R*)-**6** was used first in the allylic alkylation of 1,3-diphenylprop-1-en-3-yl acetate with dimethylmalonate and BSA as base (reaction 1). Under standard conditions in CH_2Cl_2 with 1 mol % of 'Pd' as $[Pd(allyl)Cl]_2$ with Pd/Lig = 1:1 and a catalytic amount of KOAc the product was obtained in 90% yield and 67% ee with an (*S*)-configuration. As additives CsOAc and LiOAc proved to be superior. A strong dependence of ee from the Lig/Pd ratio was observed with an optimum of 0.5 mol % of ligand. Lowering the temperature to −10 °C resulted in a significant drop of yield and enantioselectivity. Among the four solvents tested so far the complexation ability was paralleled with a decrease of selectivity and an increase of reactivity giving the best result in toluene. The selection of a proper Pd precursor did not give an uniform picture; while with $Pd(OAc)_2$ the conversion was extremely slow with poor asymmetric induction (51%), $Pd_2(dba)_3$·$CHCl_3$ was the best choice in CH_2Cl_2 (1 mol % ligand), while [Pd(allyl)Cl] was superior in toluene (0.5 mol % ligand, 93% ee). Increasing the temperature to 40 °C resulted in some loss of enantioselectivity.

With optimized conditions in hand (Table 1, entry 15), ligands **10**, **17**, **27**, and **28** were investigated in reaction 1 (Table 2). With (*R*)-**10** slight improvement was observed (88% yield, 95% ee *S*) but with 3,3′-substituted ligands products with (*R*)-configuration were obtained albeit with low or moderate enantioselectivity and reactions became slow particularly when 0.5 mol % of ligand was used.

For this reversal of asymmetric induction several effects may act together (Scheme 4). Different substituents at the 3- and 3′-positions could prefer different conformations **I** and **II** by rotating the dinaphthoazepine moiety around the N–N bond. This in turn may shift the equilibrium of the substrate complexes and/or changing their relative reactivity toward the attacking nucleophile. In addition, the weak nitrogen coordination to Pd plays a role, particularly hampered when electron-withdrawing and/or bulky groups are present at the 3- and 3′-positions. We speculate that as a consequence, the mono- and dicoordinated 1:1 complexes (**B** and **A**) are coexisting in equilibrium. This could explain the detrimental effect of coordinating solvents on ee. Moreover, 2:1 complexes (**C**) with *P*-mono coordination might be involved particularly when excess of ligand being present.

Next, the more useful ligands were investigated for reactions 2–5 (Table 3). It turned out that reactions became generally slow particularly with 0.5 mol % of ligand. 3-Pentenyl-2-acetate showed a moderate degree of asymmetric induction (70–77% ee) at a low rate while cyclohexenyl acetate was even found to be almost inert with (*R*)-**10** and (*R*)-**17**. Cyclic substrates yielded largely racemic products, and only for the cycloheptenyl acetate (reaction 5) good asymmetric induction was observed.

Finally the allylation of a prochiral Schiff base (reaction 6) was investigated, a reaction where the new stereogenic center is generated in the approaching reagent. Having only a transient interaction of the pendant binaphthyl unit with the non-coordinated nucleophile, the degree of asymmetric induction should be low. A corresponding trend was indeed observed giving the highest induction of 15% ee with the most demanding ligand at the slowest conversion (Table 4).



Scheme 1. Synthesis of (*R*)-**6** and (*R*)-**10**.

2.3. Crystal structure analysis

To gain insight into structural peculiarities of this new group of P–N ligands their solid state structure was of interest. Unfortunately all attempts to obtain crystals suitable for crystal structure determination of free ligands failed; only the phosphine oxide of (±)-**18** gave single crystals of sufficient quality. For the sake of comparison, the structure of the unsubstituted binaphthyl-bridged benzylidenehydrazine (±)-**29**[17] was determined (Fig. 2a). As expected in both cases the hydrazone functionality showed *anti* geometry and phenyl rings and C=N–N units were close to coplanarity [deviation 12.2° and 10.5° for (±)-**18** and (±)-**29**, respectively]. The biaryl angle is slightly enlarged for (±)-**18** (57.4° vs 52.9°) which is attributed to some repulsion of proximate Cl substituents. Generally, both structures show similar geometric features irrespective of the presence of the diphenylphosphinoxy group and chloro substituents.

Next, Pd(II) complexes of **6** were investigated (Scheme 5). Complexes prepared in situ from Pd–allyl precursors and ligand showed complex mixtures of species in ^{1}H and ^{31}P NMR spectra with pronounced broadening of signals presumably caused by exchange phenomena and/or restricted rotation of phenyl rings. A neutral $PdCl_2$ complex of (*R*)-**6** gave suitable crystals and sharp signals in the NMR spectra, while attempts to obtain also crystals from cationic complexes with various counteranions failed. In the latter cases, complex NMR spectra indicated the presence of several slowly interconverting species. In contrast a complex prepared from racemic **6** crystallized readily as cationic dimer having bridging chloro substituents and two ligand molecules with opposite chirality (Fig. 2b). Although the kinetic stability of this species and its significance in a catalytic reaction are hardly to predict the ease of its formation prompted us to search for a non-linear effect of asymmetric induction.[18] Reaction 1 (Scheme 3) was performed using ligand **6** with 30%, 50%, 70%, and 100% enantiomeric purity. No significant deviation from linearity was observed, and products with 24.5%, 40.8%, 59.2%, and 91.8% ee, respectively, were obtained.

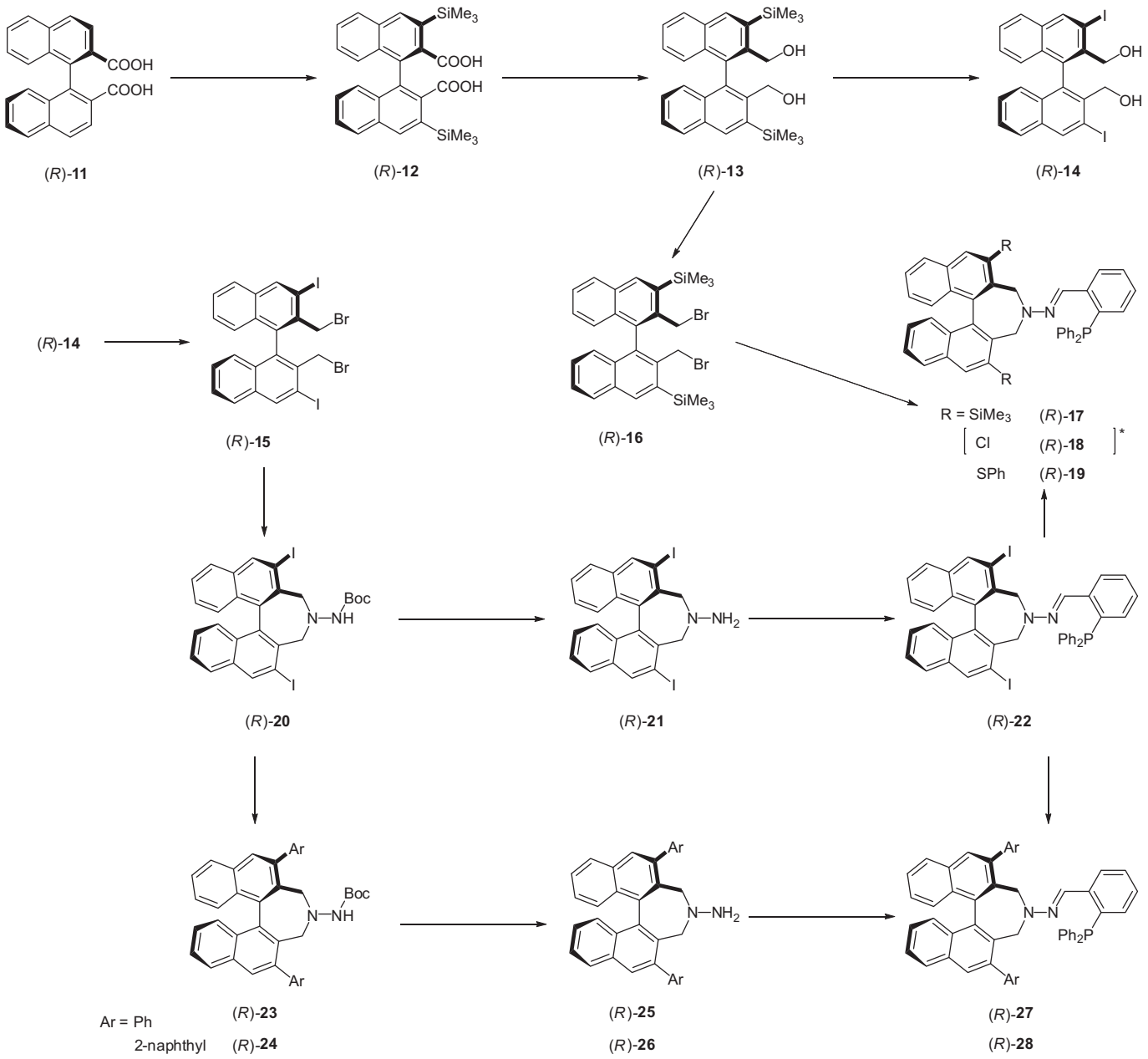
3. Conclusion

In conclusion, a flexible access to a new class of chiral PN ligands was developed and the first test reactions have been performed. While in selected cases, good reactivity and enantioselectivity (with up to 95% ee) were observed, the insufficient kinetic stability of the PN chelates limits their general usefulness in Pd-catalyzed allylic substitutions. Improvement via the introduction of electron-donating substituents proximate to the sp^2-N coordination site and application to other asymmetric transformations is currently in progress.

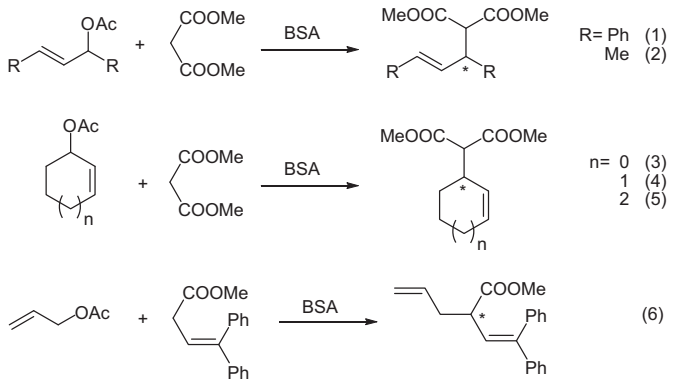
4. Experimental

4.1. General

Melting points: Kofler melting point apparatus, uncorrected. NMR: Bruker AVIII400 spectrometer at 400.27 MHz (^{1}H), 100.66



Scheme 2. Synthesis of 3,3′-disubstituted dinaphthoazepine ligands with hydrazone-phosphine functionalities. * Isolated as phosphine oxide, see text.



Scheme 3. Asymmetric allylation reactions.

Table 1
Optimization of the allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate (1)[a,b] using Pd/(*R*)-**6**

Entry	Pd precursor[c]	Lig/Pd	solvent	Additive	T (°C)	*t* (h)	Yield[d] (%)	ee[e] (%)
1	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1:1	CH_2Cl_2	KOAc	21	2.5	90	67
3	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1:1	CH_2Cl_2	CsOAc	21	1	92	75
2	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1:1	CH_2Cl_2	LiOAc	21	1.5	87	87
4	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	2:1	CH_2Cl_2	KOAc	21	1.5	82	36
5	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	0.5:1	CH_2Cl_2	KOAc	21	2.0	93	77
6	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1:1	CH_2Cl_2	KOAc	0	20	92	65
7	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1:1	CH_2Cl_2	KOAc	−10	45	56	57
8	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1:1	MeCN	KOAc	21	1	90	52
9	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1:1	THF	KOAc	21	3	93	62
10	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	1:1	Toluene	KOAc	21	5	93	81
11	$Pd(OAc)_2$	1:1	CH_2Cl_2	KOAc	21	96	80	51
12	$Pd_2(dba)_3{\cdot}CHCl_3$	1:1	CH_2Cl_2	KOAc	21	1.5	94	74
13	$Pd_2(dba)_3{\cdot}CHCl_3$	0.5:1	Toluene	CsOAc	21	3	90	81
14	$Pd_2(dba)_3{\cdot}CHCl_3$	0.5:1	Toluene	LiOAc	21	3.5	93	87
15	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	0.5:1	Toluene	LiOAc	21	16	84	**93**
16	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	0.5:1	Toluene	LiOAc	40	0.5	89	89
17	$Pd_2(dba)_3{\cdot}CHCl_3$	0.5:1	Toluene	LiOAc	21	3.5	93	87

[a] See Scheme 3.
[b] All reactions were run on a 1-mmol scale with BSA as base.
[c] 1 mol %.
[d] Isolated yield.
[e] (*S*)-Configuration.

Table 2
Allylic alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate (1)[a,b] and Pd/(*R*)-**10**, Pd/(*R*)-**17**, Pd/(*R*)-**27**, and Pd/(*R*)-**28**

Entry	Ligand	Lig/Pd[c]	*t* (h)	Yield[d] (%)	ee (%)
1	(*R*)-**10**	0.5:1	18	88	95 (*S*)
2	(*R*)-**17**	0.5:1	44	82	81 (*R*)
3	(*R*)-**17**	1:1	20	86	72 (*R*)
4	(*R*)-**17**	2:1	20	88	46 (*R*)
5	(*R*)-**27**	0.5:1	69	89	22 (*R*)
6	(*R*)-**27**	1:1	15	88	29 (*R*)
7	(*R*)-**27**	1:2	15	91	34 (*R*)
8	(*R*)-**28**	0.5:1	89	64	35 (*R*)
9	(*R*)-**28**	1:1	20	87	22 (*R*)
10	(*R*)-**28**	2:1	20	85	26 (*R*)

[a] See Scheme 3.
[b] All reactions were run on a 1-mmol scale in toluene at rt with BSA/LiOAc as base.
[c] 1 mol % of 'Pd' (as $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$) was used.
[d] Isolated yield.

MHz (^{13}C), and 162.02 MHz (^{31}P), respectively; chemical shifts δ are reported in ppm rel. to $CHCl_3$ (7.24 or 77.00 ppm, respectively). Coupling patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), p (pseudo), and b (broad). $^{13}C\{^1H\}$ NMR spectra are recorded in a *J*-modulated mode; coupling constants refer to P–C coupling; signals are assigned as C, CH_2, and CH_3; undesignated signals refer to CH-resonances. In spectral areas with extensive signal overlapping multiplets that could not be identified; these signals of unclear relationship are underlined, ignoring probable multiplet structures. MS: FINNIGAN MAT 8230 EI (70 eV). HRMS: FINNIGAN MAT 8230. For HPLC determination of chiral products a HP 1090 chromatograph equipped with a diode array detector was used. Optical rotations were measured with a Perkin–Elmer polarimeter 243 equipped with a 1-dm thermostated cell.

Petroleum ether, dichloromethane, and ethyl acetate were distilled, absolute THF from sodium benzophenone ketyl, Et_2O from $LiAlH_4$; dimethoxyethane (DME), dichloromethane, and trimethylamine from CaH_2; *n*-BuLi was used as 1.6 M solution in *n*-hexane (Aldrich). All the other chemicals were analytical grade and used without further purification. Column chromatography was performed on SiO_2, 40–63 μm. Reported procedures have been followed to obtain (*R*)-2,2′-bis(bromomethyl)-1,1′-binaphthyl,[8b] (*R*)-1,1′-binaphthyl-2,2′-dicarboxylic acid,[8] and 2-diphenylphosphinobenzaldehyde.[19]

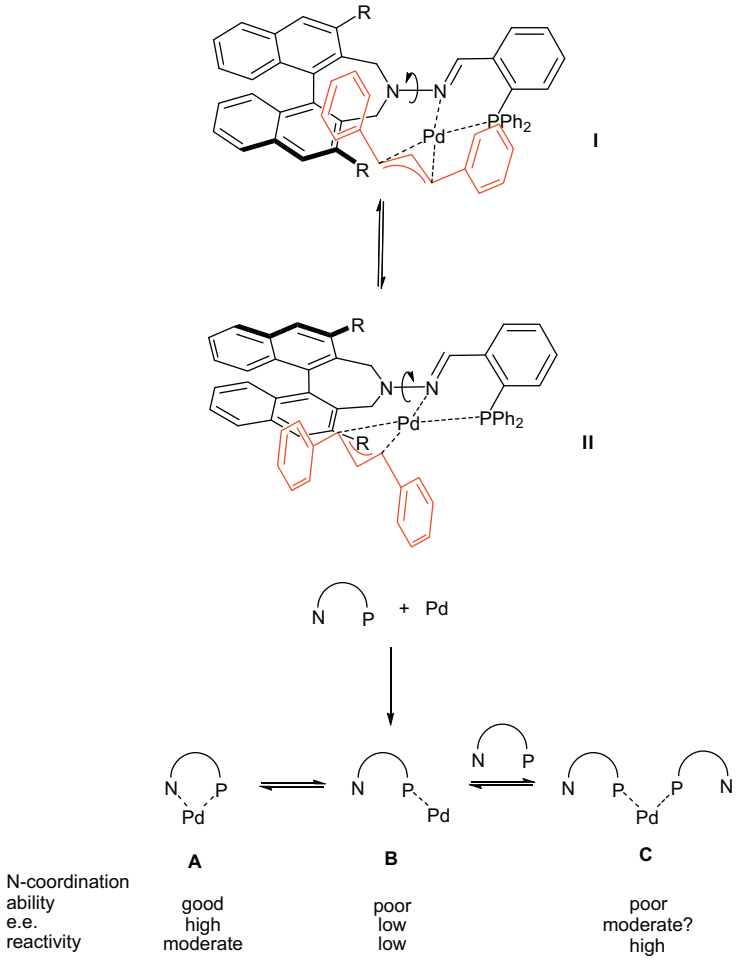
4.2. Synthesis

4.2.1. (*R*)-*tert*-Butyl-3,5-dihydro-4*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4-yl carbamate (*R*)-8

(*R*)-2,2′-Bis(bromomethyl)-1,1′-binaphthyl (220 mg, 0.5 mmol) and *N*-Boc-hydrazine (198 mg, 1.5 mmol, 3 equiv) were placed in an oven-dried Schlenk tube filled with argon. Freshly distilled abs THF (2 mL) was added and the mixture was degassed. Next, Et_3N (0.2 mL, 1.5 mmol, 3 equiv) was added and the mixture was stirred for 22 h at reflux. When TLC (Et_2O/petroleum ether, 50:50) indicated complete consumption of the starting material, water (2 mL) was added and the mixture was diluted with ethyl acetate (5 mL). The organic layer was separated, the aqueous layer was extracted with ethyl acetate (2 × 5 mL), and the combined organic phases were dried ($MgSO_4$). After evaporation of solvents, the crude product was crystallized from CH_2Cl_2/petroleum ether to yield 130 mg (63%) of pure (*R*)-**8**. Column chromatography (Et_2O/petroleum ether, 50:50) of the mother liquor afforded another fraction to give a total of 153 mg (75%) of (*R*)-**8** as a white crystalline solid; mp: 117–120 °C. $[\alpha]_D^{20} = -246$ (*c* 1.02, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 1.47 (s, 9H); 3.43 (d, J = 12.5 Hz, 2H); 3.95 (d, J = 12.5 Hz, 2H); 5.47 (br s, 1H); 7.25 (ddd, J = 8.3, 5.6, 1.1 Hz, 2H); 7.43 (d, J = 8.6 Hz, 2H); 7.45 (m, 2H); 7.60 (d, J = 8.3 Hz, 2H); 7.94 (d, J = 7.8 Hz, 2H); 7.96 (d, J = 8.2 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 28.36 (CH_3); 58.95 (CH_2); 80.26 (C); 125.74; 125.97; 127.42; 127.58; 128.31; 128.65; 131.45 (C); 132.28 (C); 133.35 (C); 135.11 (C); 154.35 (C) ppm. MS (150 °C) *m*/*z* (rel%): 410 (14, M^+). HRMS (ESI) calcd for $C_{27}H_{27}N_2O_2$: 411.2073, found: 411.2075.

4.2.2. (*R*)-3,5-Dihydro-4*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4-amine (*R*)-9

In a round-bottomed flask, (*R*)-**8** (1.20 g, 2.92 mmol) was dissolved in CH_2Cl_2 (4 mL) and a solution of TFA (4 mL) in CH_2Cl_2 (4 mL) was added. After stirring at rt. for 2 h, the reaction was quenched with saturated $NaHCO_3$ solution (8 mL) and the reaction mixture was extracted with CH_2Cl_2 (6 mL). The organic phase was washed with H_2O (8 mL) and brine (8 mL), dried over $MgSO_4$, and concentrated to give (*R*)-**9** as a white solid (989 mg, 99%, 92% purity by NMR); attempted purification by chromatography resulted



Scheme 4. Tentative interpretation of observed enantioselectivity.

Table 3
Allylic alkylations 2–5[a] with Pd/(*R*)-**6**, Pd/(*R*)-**10**, and Pd/(*R*)-**17** as catalyst

Entry	Reaction[b]	Ligand	Lig/Pd[c]	*t* (h)	Yield[d] (%)	ee (%)
1	2[e]	(*R*)-**6**	0.5:1	48	83	73 (*S*)
2	2	(*R*)-**6**	0.5:1	21	61	72 (*S*)
3	2	(*R*)-**6**	1:1	22	25	74 (*S*)
4	2[e]	(*R*)-**10**	0.5:1	21	24	77 (*S*)
5	2	(*R*)-**10**	1:1	22	48	70 (*S*)
6	2	(*R*)-**17**	1:1	22	3	—
7	3	(*R*)-**6**	0.5:1	48	13	4 (*R*)
8	3	(*R*)-**10**	0.5:1	84	82	4 (*R*)
9	3	(*R*)-**17**	1:1	48	74	20 (*R*)
10	4	(*R*)-**6**	0.5:1	48	19	2 (*S*)
11	4	(*R*)-**10**	0.5:1	84	n.r.	—
12	4	(*R*)-**17**	1:1	48	n.r	—
13	5	(*R*)-**6**	0.5:1	48	63	20 (*R*)
14	5	(*R*)-**10**	0.5:1	84	48	14 (*R*)
15	5	(*R*)-**17**	1:1	48	13	52 (*R*)

[a] All reactions were run on a 1-mmol scale in toluene at rt with BSA/LiOAc as base.
[b] see Scheme 3.
[c] With 1 mol % of 'Pd' (as $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$).
[d] Isolated yield.
[e] The corresponding carbonate was used as substrate.

Table 4
Allylic alkylation 6[a] with Pd/(*R*)-**6**, Pd/(*R*)-**27**, Pd/(*R*)-**28**, and Pd/(*R*)-**17** as catalyst

Entry	Reaction[b]	Ligand	Lig/Pd[c]	*t* (h)	Yield[d] (%)	ee (%)
1	6	(*R*)-**6**	1:1	72	47	2 (*S*)
2	6	(*R*)-**27**	1:1	72	32	11 (*S*)
3	6	(*R*)-**28**	1:1	72	40	11 (*S*)
4	6	(*R*)-**17**	1:1	72	23	15 (*S*)

[a] All reactions were run on a 1-mmol scale in toluene at rt with BSA/LiOAc as base.
[b] See Scheme 3.
[c] With 1 mol % of 'Pd' (as $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$).
[d] Isolated yield.

in significant decomposition. (An analytical sample of (±)-**9** was crystallized from CH_2Cl_2/petroleum ether; mp: 161–165 °C.) $[\alpha]_D^{20} = -505$ (*c* 1.01, $CHCl_3$). ^1H NMR (CD_3OD) δ: 3.77 (d, J = 12.9 Hz, 2H); 4.36 (d, J = 13.0 Hz, 2H); 4.85 (br s, 2H); 7.32 (ddd, J = 8.5, 6.6, 1.2 Hz, 2H); 7.38 (br d, J = 8.5 Hz, 2H); 7.56 (ddd, J = 8.1, 6.7, 1.4 Hz, 2H); 7.75 (d, J = 8.3 Hz, 2H); 8.07 (d, J = 8.4 Hz, 2 H); 8.16 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$) δ: 58.87 (CH_2); 126.95; 127.16; 127.38; 127.42 (C); 127.44; 128.63; 130.11; 131.28 (C); 134.32 (C); 135.70 (C); ppm. MS (50 °C) *m*/*z* (rel%): 310 (70, M^+). HRMS for $C_{22}H_{18}N_2$ calc. 310.1470, found 310.1467.

4.2.3. (*R*)-(*E*)-*N*-(2-(Diphenylphosphino)benzylidene)-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-6

(*R*)-*N*-Aminodinaphthoazepine **9** (300 mg, 0.968 mmol, 1.68 equiv) was dissolved in CH_2Cl_2 (6 mL). The solution was degassed and 2-diphenylphosphinobenzaldehyde (167 mg, 0.576 mmol) and $MgSO_4$ (132 mg, 1.1 mmol) were added. After stirring the mixture for 7 h at rt under argon, the suspension was filtered and the filtrate was extracted with water (6 mL). The organic layer was

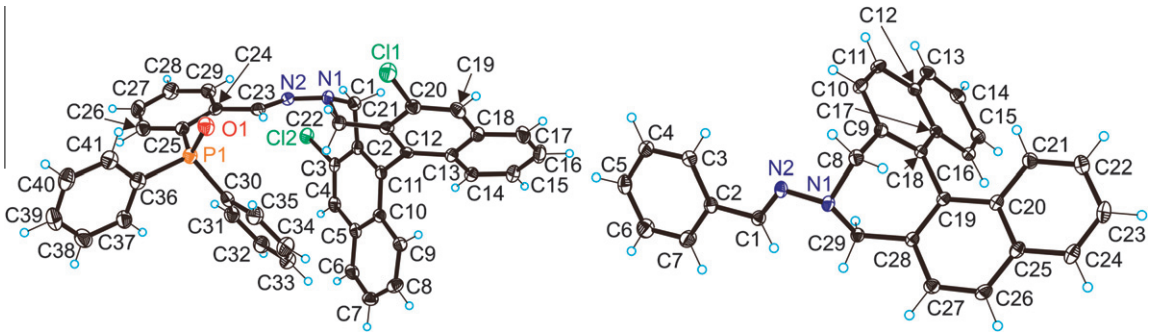
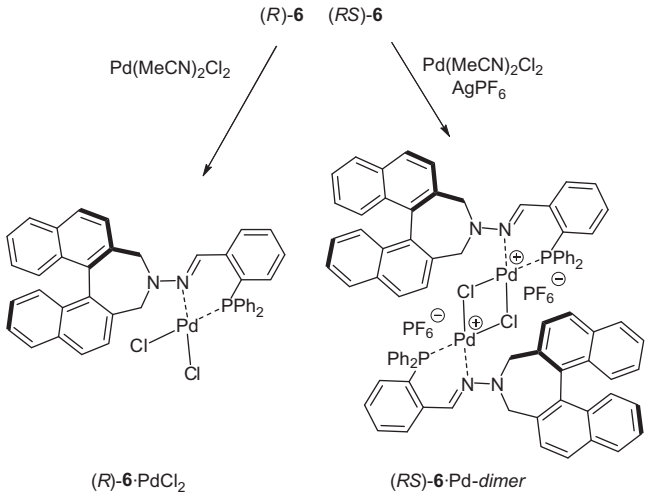


Figure 2a. Crystal structure of the phosphine oxide of (±)-**18** (left) and (±)-**29** (right). Co-crystallized solvent molecules are omitted for the sake of clarity. Selected bond distances (Å) and angles (°) for (±)-**18**: P1–O1 1.4919(18), N1–N2 1.380(3), C1–N1 1.483(3), C22–N1 1.488(3), C23–N2 1.287(3), $\Theta_{C2-C11-C12-C21}$ 57.4(3); for (±)-**29**: N1–N2 1.3840(13), N1–C8 1.4766(15), N1–C29 1.4799(14), N2–C1 1.2839(15), $\Theta_{C28-C19-C18-C9}$ 52.90(15).



Scheme 5. Synthesis of crystalline Pd(II) complexes of ligand **6**.

washed with brine (6 mL), dried over $MgSO_4$, and concentrated. Purification of the remaining residue by flash chromatography (4 g silica gel, 254 nm, 10 mL/min, petroleum ether/2-propanol, gradient 0→50%) yielded 326 mg (97%) of phosphinohydrazone (*R*)-**6** as a yellowish foam. (The racemic compound was obtained as a white solid; mp: 114–117 °C.) $[\alpha]_D^{20} = +106$ (*c* 1.00, $CHCl_3$). ^{1}H NMR (CD_2Cl_2) δ: 3.49 (d, J = 12.0 Hz, 2H); 4.39 (d, J = 12.0 Hz, 2H); 6.80 (ddd, J = 7.7, 5.0, 1.1 Hz, 1H); 6.85 (m, 1H); 7.03 (m, 2H); 7.11 (m, 1H); 7.14 (m, 2H); 7.28 (m, 4H); 7.35 (m, 4H);7.41 (d, J = 8.6 Hz, 2H); 7.43 (d, J = 8.3 Hz, 2H); 7.49 (ddd, J = 8.1, 6.7, 1.1 Hz, 2H); 7.75 (d, J = 4.5 Hz, 1H); 7.85 (ddd, J = 7.8, 3.9, 1.1 Hz, 1H); 7.93 (d, J = 8.3 Hz, 2H); 7.97 (d, J = 8.2 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 56.08 (CH_2); 125.60; 125.77; 125.81; 127.24; 127.44; 127.48; 128.12; 128.19; 128.25; 128.33; 128.51; 128.58; 131.45 (C); 133.20 (C); 133.31 (C); 133.43; 133.49; 133.50; 133.62; 133.84; 133.89; 134.03; 134.09; 134.21 (C); 134.62 (C); 136.83 (C, d, J = 10.5 Hz); 137.14 (C, d, J = 8.7 Hz); 139.92 (C, d, J = 17.3 Hz) ppm. ^{31}P NMR ($CDCl_3$) δ: −11.78 ppm. MS (ESI) 583.2 ($M+1^+$). HRMS for $C_{41}H_{32}N_2P$ calc. 583.2303, found 583.2315.

4.2.4. (*R*)-(*E*)-*N*-(2-(Bis(3-methoxyphenyl)phosphino)benzylidene)-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-10

(*R*)-*N*-Aminodinaphthoazepine **9** (165 mg, 0.532 mmol, 1.34 equiv) was dissolved in CH_2Cl_2 (2.5 mL). The mixture was degassed and 2-bis(3-methoxyphenyl)phosphinobenzaldehyde (139 mg, 0.397 mmol) and $MgSO_4$ (55 mg, 0.46 mmol) were added. After stirring for 20 h at rt under argon, the suspension was filtered and the filtrate was extracted with water (4 mL). The organic layer

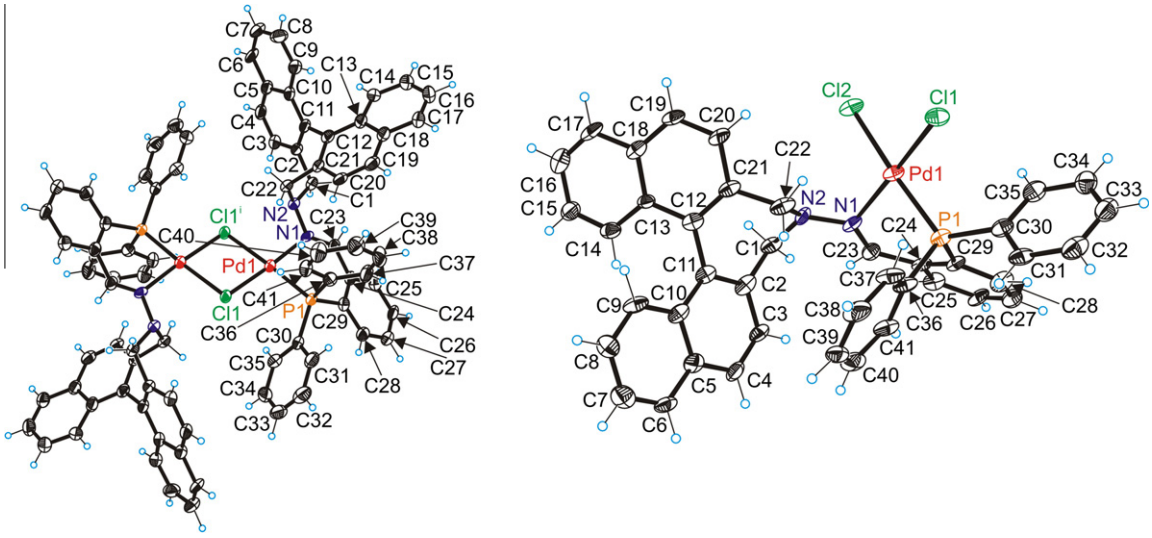


Figure 2b. X-ray diffraction structures of [((*R*)-**6**-(*S*)-**6**)Pd_2Cl_2]$^{2+}$ (left) and (*R*)-**6**$PdCl_2$ (right). Anions and solvent molecules are omitted for the sake of clarity. Selected bond distances (Å) and angles (°) for [((*R*)-**6**-(*S*)-**6**)Pd_2Cl_2]$^{2+}$: Pd1–N1 2.075(6), Pd1–P1 2.2315(18), Pd1–Cl1 2.3138(17), Pd–$Cl1^i$ 2.4304(16), N1–N2 1.412(8), N1–C23 1.277(9), $\Theta_{C2-C11-C12-C21}$ −55.1(9); for (*R*)-**6**$PdCl_2$: Pd1–N1 2.099(5), Pd1–P1 2.2191(18), Pd1–Cl1 2.2819(17), Pd–Cl2 2.3893(17), N1–N2 1.391(7), N1–C23 1.278(7), $\Theta_{C2-C11-C12-C21}$ −54.2(8).

was washed with brine (4 mL) and dried over $MgSO_4$. Concentration of the filtrate gave a semisolid residue, which was purified by column chromatography (petroleum ether/2-propanol, 90:10) to yield 200 mg (78%) of (*R*)-**10** as a white solid; mp: 94–98 °C. $[\alpha]_D^{20} = +100$ (*c* 0.984, CH_2Cl_2). ^1H NMR ($CDCl_3$) δ: 3.57 (s, 3H); 3.57 (d, *J* = 12.2 Hz, 2H); 3.70 (s, 3H); 4.39 (d, *J* = 12.3 Hz, 2H); 6.53 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H); 6.73 (m, 2H); 6.85 (m, 4H); 6.98 (m, 1H); 7.19 (ptd, *J* = 7.3, 1.0 Hz, 1H); 7.25 (m, 3H); 7.31 (ptd, *J* = 7.6, 1.0 Hz, 1H); 7.37 (d, *J* = 8.3 Hz, 2H); 7.43 (d, *J* = 8.7 Hz, 2H); 7.45 (m, 2H); 7.77 (d, *J* = 4.4 Hz, 1H); 7.81 (ddd, *J* = 7.9, 4.0, 1.3 Hz, 1H); 7.87 (d, *J* = 8.3 Hz, 2H); 7.92 (d, *J* = 8.3 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 55.03 (CH_3); 55.15 (CH_3); 56.10 (CH_2); 114.29 (d, *J* = 8.8 Hz); 118.91; 119.09; 119.11; 119.32; 125.60; 125.83; 125.91 (d, *J* = 4.5 Hz); 126.15; 126.26; 126.34; 126.45; 127.26; 127.45; 127.50; 128.28; 128.61); 128.70; 129.23 (d, *J* = 7.6 Hz); 129.54 (d, *J* = 8.0 Hz); 131.44 (C); 133.20 (C); 133.30; 133.34 (C); 133.49; 133.72; 133.92 (C); 134.64 (C); 138.47 (C); 138.58 (C); 138.73 (C); 138.82 (C); 140.07 (C, d, *J* = 18.0 Hz); 159.28 (C); 159.36 (C); 159.59 (C); 159.68 (C) ppm. ^{31}P NMR ($CDCl_3$) δ: −10.39 ppm. MS (ESI) *m*/*e*: 673 (M+MeOH$^+$); HRMS calcd for $C_{43}H_{36}N_2O_2P$: 643.2514, found: 643.2508.

4.2.5. (*R*)-3,3′-Bis(trimethylsilyl)-1,1′-binaphthyl-2,2′-dicarboxylic acid (*R*)-12

A solution of 2,2,6,6-tetramethylpiperidine (847 mg, 6 mmol, 1.01 mL) in dry THF (10 mL) was degassed and *n*-BuLi (3.75 mL, 6 mmol) was added dropwise at 0 °C under argon. After stirring for 20 min at the same temperature the solution was cooled to −78 °C and Me_3SiCl (1.09 g, 10 mmol, 1.27 mL) was added and stirring was continued for further 20 min. A degassed solution of (*R*)-**11** (342 mg, 1 mmol) in THF was added dropwise using a Teflon cannula. The reaction mixture was allowed to reach rt within 6–8 h. Hydrochloric acid (10 mL, 4 N) and Et_2O (20 mL) were added with stirring and the organic phase was separated. The aqueous phase was extracted with a second portion of Et_2O (10 mL) and the combined extracts were stirred with NaOH (20 mL, 1 M) for 15 min. The alkaline layer was separated and the procedure was repeated. The combined aqueous extracts were washed with Et_2O (20 mL) and acidified with HCl (6 M). The obtained mixture was extracted with Et_2O (2 × 50 mL) and the extracts were washed with water and brine and dried ($MgSO_4$). Removal of the solvent left 410 mg (84%) of (*R*)-**12** sufficiently pure for the next step. $[\alpha]_D^{20} = +204$ (*c* 1.00, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 0.41 (s, 18H); 7.02 (d, *J* = 8.3 Hz, 2H); 7.19 (m, 2H); 7.36 (m, 2H); 7.80 (d, *J* = 8.1 Hz, 2H); 8.11 (s, 2H); ~12.2 (br s, ~2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 0.11 (CH_3); 125.98; 126.84; 127.21; 127.67; 131.17 (C); 132.30 (C); 132.91 (C); 134.29 (C); 135.70; 141.15 (C); 175.22 (C) ppm. MS (ESI) *m*/*z*: 485.3 (M−H$^+$); HRMS calcd for $C_{28}H_{29}O_4Si_2$: 485.1604, found: 485.1611.

4.2.6. (*R*)-2,2′-Bis(hydroxymethyl)-3,3′-bis(trimethylsilyl)-1,1′-binaphthyl (*R*)-13

A solution of diacid (*R*)-**12** (972 mg, 2 mmol) in dry THF was degassed. Through a septum, BH_3·THF complex (8 mmol, 8 mL, 1 M in THF) was added and the reaction was refluxed under argon until TLC showed complete conversion (usually 20–24 h). Hydrochloric acid (2 mL, 2 M) was carefully added with external cooling to decompose the excess of borane. After evaporating the bulk of THF the residue was partitioned between CH_2Cl_2 (100 mL) and HCl (40 mL, 2 M). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The combined extracts were washed with water (50 mL) and brine and dried ($MgSO_4$). Evaporation and drying at an oil pump left 771 mg (84%) of (*R*)-**13**. Small amounts of an adhesive yellow impurity could be removed by washing with some cold petroleum ether; mp: 102–105 °C. $[\alpha]_D^{20} = +123$ (*c* 1.03, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 0.47 (s, 18H); 2.79 (br s, 2H); 4.18 (d, *J* = 11.6 Hz, 2H); 4.55 (d, *J* = 11.6 Hz, 2H); 6.93 (d, *J* = 8.4 Hz, 2H); 7.21 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 2H); 7.43 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 2H); 7.90 (d, *J* = 8.0 Hz, 2H); 8.20 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 0.91 (CH_3); 62.33 (CH_2); 126.03; 126.12, 127.04; 128.21; 132.33 (C); 133.51 (C); 135.76 (C); 136.42; 138.61 (C); 141.08 (C) ppm. MS (160 °C) *m*/*z* (rel%): 458 (8, M$^+$), 440 (3, M−18$^+$), 425 (59, M−18−15$^+$). HRMS (ESI) calcd for $C_{28}H_{33}O_2Si_2$: 457.2019, found: 457.2045.

4.2.7. (*R*)-2,2′-Bis(hydroxymethyl)-3,3′-diiodo-1,1′-binaphthyl (*R*)-14

A solution of ICl (487 mg, 3 mmol) in CH_2Cl_2 (10 mL) was added dropwise at −40 °C (15–30 min) to a solution of diol (*R*)-**13** (459 mg, 1 mmol) in CH_2Cl_2 (15 mL). After stirring for 2 h at the same temperature, $NaHSO_3$ solution (30 mL, 10%) was slowly added. During warm up a voluminous precipitate of product was formed. At rt this was filtered off and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic phases were dried ($MgSO_4$) and evaporated. The solid residue was washed with little Et_2O and dried in vacuo. Both fractions were found to be pure by ^1H NMR, total yield: 481–510 mg (85–90%); mp: 259–263 °C. $[\alpha]_D^{20} = +72.3$ (*c* 1.01, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 3.41 (br s, 2H); 4.16 (d, *J* = 12.2 Hz, 2H); 4.59 (d, *J* = 12.2 Hz, 2H); 6.88 (br d, *J* = 8.4 Hz, 2H); 7.25 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 2H); 7.47 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 2H); 7.80 (br d, *J* = 8.4 Hz, 2H); 8.59 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 65.96 (CH_2); 98.16 (C); 126.72; 126.97; 127.32; 127.49; 132.52 (C); 134.29 (C); 136.27 (C); 137.86 (C); 139.99 ppm. MS (210 °C) *m*/*z* (rel%): 566 (25, M$^+$). HRMS (ESI) calcd for $C_{22}H_{16}O_2I_2Na$: 588.9137, found: 588.9134.

4.2.8. (*R*)-2,2′-Bis(bromomethyl)-3,3′-diiodo-1,1′-binaphthyl (*R*)-15

At −40 °C, a solution of PBr_3 (700 mg, 2.59 mmol, 0.6 equiv 242 μL) in CH_2Cl_2 (5 mL) was added dropwise for 30 min to a solution of diol (*R*)-**14** (1.224 g, 2.16 mmol) in abs. THF (40 mL). Over 18 h the temperature was slowly raised to +10 °C. Water (3 mL) was added and the bulk of solvent was evaporated. The residue was partitioned between water (50 mL) and $CHCl_3$ (100 mL). Occasional gentle warming was necessary to ensure complete dissolution. The organic phase was separated, washed with brine, and dried (Na_2SO_4). Removal of solvent left a white solid which was dissolved in THF/$CHCl_3$ (40 + 40 mL) with heating. Partial evaporation of the solvent overnight yielded a first crop of crystalline product. The mother liquor was filtered over SiO_2 (2 × 10 cm) in CH_2Cl_2. Slow concentration gave a second crop of product. Additional amounts of the dibromide were obtained by column chromatography to yield a total of 1.17 g (78%) of (*R*)-**15** as a white powder. Mp: 281–283 °C. $[\alpha]_D^{20} = +74.7$ (*c* 1.01, THF). ^1H NMR ($CDCl_3$) δ: 4.30 (d, *J* = 10.1 Hz, 2H); 4.40 (d, *J* = 10.1 Hz, 2H); 6.96 (br d, *J* = 8.5 Hz, 2H); 7.27 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 2H); 7.49 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 2H); 7.80 (br d, *J* = 8.2 Hz, 2H); 8.64 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 38.44 (CH_2); 97.70 (C); 126.85; 127.36; 127.42; 127.89; 131.73 (C); 134.31 (C); 134.55 (C); 136.38 (C); 140.88 ppm. MS (250 °C) *m*/*z* (rel%): 694 (3.4)/692 (5.1)/690 (2.6) (isotopic pattern for M$^+$).

4.2.9. (*R*)-2,2′-Bis(bromomethyl)-3,3′-bis(trimethylsilyl)-1,1′-binaphthyl (*R*)-16

To a solution of diol (*R*)-**13** (1.078 g, 2.35 mmol) in abs. THF (70 mL) was added dropwise at −40 °C, PBr_3 (1.40 g, 5.17 mmol, 486 μL) dissolved in THF (12 mL). The orange-colored solution was slowly warmed up overnight and water (2 mL) was added at 0 °C. The bulk of solvent was evaporated and the residue was dissolved in CH_2Cl_2 (100 mL). The mixture was neutralized with sufficient sat. $NaHCO_3$ and the organic layer was separated. The aqueous layer was extracted once with CH_2Cl_2 (50 mL) and the

combined extracts were washed with water and brine and dried with $MgSO_4$. Evaporation yielded 925 mg (67%) of almost pure (*R*)-**16** as a colorless foam, which could not be crystallized (*note:* for (±)-**16**, mp: 162–165 °C). $[\alpha]_D^{20} = +98.3$ (*c* 1.00, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 0.53 (s, 18H); 4.33 (d, *J* = 10.3 Hz, 2H); 4.43 (d, *J* = 10.3 Hz, 2H); 7.00 (br d, *J* = 8.5 Hz, 2H); 7.22 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 2H); 7.46 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 2H); 7.89 (br d, *J* = 8.2 Hz, 2H); 8.22 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 1.22 (CH_3); 34.64 (CH_2); 126.76; 126.83; 127.33; 127.99; 132.54 (C); 132.89 (C); 136.13 (C); 137.44; 137.63 (C); 138.26 (C) ppm. MS (140 °C) *m*/*z* (rel%): 584 (28, M^+). HRMS (EI) calcd for $C_{28}H_{32}Br_2Si_2$: 584.0392, found: 584.0385.

4.2.10. (*R*)(*E*)-*N*-(2-(Diphenylphosphino)benzylidene)-2,6-bis(trimethylsilyl)-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-17

Method A: A suspension of 2-diphenylphosphinobenzaldehyde (61 mg, 0.21 mmol) and freshly dried $MgSO_4$ (26 mg, 0.22 mmol) was prepared in toluene (0.2 mL). Hydrazine monohydrate (10 μL, 0.2 mmol) in ethanol (0.3 mL) was added and the degassed mixture was stirred at 20 °C for 1 h. A solution of dibromide (*R*)-**16** (58 mg, 0.1 mmol) and triethylamine (35 μL, 0.25 mmol) in toluene (0.3 mL) was added and after degassing (2×), the reaction mixture was immersed into an oil bath (80–90 °C) and stirred for 48 h. For work-up CH_2Cl_2 (10 mL) and water (5 mL) were added. The aqueous phase was extracted with CH_2Cl_2 (5 mL) and the combined organic phases were washed with water and brine and dried ($MgSO_4$). After evaporation of solvents the residue was chromatographed on SiO_2 (1 × 40 cm) in CH_2Cl_2 (10→15%)/petroleum ether to give (*R*)-**17** as a colorless oil; yield: 25 mg (34%). $[\alpha]_D^{20} = -21.4$ (*c* 1.00, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 0.39 (s, 18H); 3.52 (d, *J* = 12.7 Hz, 2H); 4.75 (d, *J* = 12.7 Hz, 2H); 6.70 (m, 1H); 6.75 (m, 1H); 6.94 (m, 2H); 7.07 (m, 1H); 7.10 (m, 2H); 7.14–7.26 (m, 9H); 7.30 (bptd, *J* = 7.4, 1.0 Hz, 1H); 7.44 (m, 2H); 7.77 (d, *J* = 5.7 Hz, 1H); 7.92 (d, *J* = 8.3 Hz, 2H); 8.07 (ddd, *J* = 8.0, 4.1, 1.0 Hz, 1H); 8.09 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 0.68 (CH_3); 54.07 (CH_2); 124.65 (d, *J* = 3.5 Hz); 125.54; 126.19; 127.16 (d, *J* = 2.3 Hz); 127.38; 128.09; 128.17; 128.29; 128.46; 128.51; 128.53; 131.04 (d, *J* = 26.9 Hz); 132.10 (C); 133.08 (d, *J* = 3.8 Hz); 133.65 (d, *J* = 19.6 Hz); 133.77 (d, *J* = 15.4 Hz, C); 134.09 (d, *J* = 20.6 Hz); 135.11 (C); 135.87 (d, *J* = 9.6 Hz, C); 135.95; 136.25 (d, *J* = 10.8 Hz, C); 136.91 (C); 137.32 (C); 139.59 (d, *J* = 15.4 Hz, C) ppm. ^{31}P NMR ($CDCl_3$) δ: −12.26 (s) ppm. MS (ESI) *m*/*z*: 727.2 (M+1$^+$). HRMS calcd for $C_{47}H_{48}N_2PSi_2$: 727.3004, found: 727.3076.

Method B: To a degassed solution of (*R*)-**22** (84 mg, 0.1 mmol) was added *n*-BuLi solution (0.32 mL, 0.5 mmol) at −78 °C. After 5 min Me_3SiCl (108 mg, 1 mmol, 126 μL) was added to the orange solution and the reaction mixture was kept at this temperature for 1 h. After quenching with few drops of water and usual work-up with ethyl acetate the crude material was purified by column chromatography (SiO_2, 40 × 1.5 cm, in CH_2Cl_2/petroleum ether, 15:85) to give 48 mg (66%) of (*R*)-**17**.

4.2.11. (±)(*E*)-2,6-Dichloro-*N*-(2-(diphenylphosphoryl)benzylidene)-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (±)-18

A similar procedure as given for the synthesis of (*R*)-**17** (Method B) was applied except that $Cl_3C–CCl_3$ (1.25 equiv) was used as the electrophile. After chromatographic purification (SiO_2, 30 × 2 cm, CH_2Cl_2/petroleum ether, 15:85) phosphine oxide (*R*)-**18** was isolated in 63% yield, mp: >250 °C (dec.). ^1H NMR ($CDCl_3$) δ: 3.17 (d, *J* = 12.7 Hz, 2H): 5.05 (d, *J* = 12.8 Hz, 2H); 6.94 (tm, *J* = 7.5 Hz, 1H); 7.02 (ddd, *J* = 14.0, 7.6, 1.1 Hz, 1H); 7.11 (m, 2H); 7.15 (m, 1H); 7.24 (m, 4H); 7.36–7.54 (m, 8H); 7.60–7.66 (m, 2H); 7.83 (br d, *J* = 8.3 Hz, 2H); 8.00 (2 × s, 3H); 8.24 (ddd, *J* = 8.0, 4.0, 0.9 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$) δ: 51.30 (CH_2); 126.01 (d, *J* = 9.5 Hz); 126.34; 126.16 (d, *J* = 12.8 Hz); 126.96; 127.38 (2 × CH); 128.16 (d, *J* = 11.9 Hz); 128.44; 128.59 (d, *J* = 12.3 Hz); 128.78 (C); 129.78 (C); 130.02 (C); 131.09 (C); 131.30 (d, *J* = 2.8 Hz); 131.74 (d, *J* = 2.6 Hz); 131.82 (2 × d, *J* = 9.5 Hz); 132.15 (d, *J* = 22.8 Hz, C); 132.16 (d, *J* = 2.8 Hz); 132.98 (d, *J* = 11.9 Hz); 133.19 (d, *J* = 21.8 Hz, C); 133.42 (C); 134.04 (d, *J* = 7.1 Hz); 136.69 (C); 140.63 (d, *J* = 6.6 Hz, C) ppm. ^{31}P NMR ($CDCl_3$) δ: 30.74 (s) ppm. MS (ESI) *m*/*z*: 667.2 (M^+). HRMS calcd for $C_{41}H_{30}OCl_2N_2P$: 667.1467, found: 667.1475.

4.2.12. (*R*)-*tert*-Butyl 2,6-diiodo-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl carbamate (*R*)-20

Dibromide (*R*)-**15** (692 mg, 1 mmol), Boc-hydrazine (396 mg, 3 mmol) and Et_3N (303 mg, 3 mmol, 419 μL) were dissolved in abs. THF (10 mL) and abs. DMF (2 mL). After degassing, the mixture was stirred under argon at 60 °C (bath) for 72 h. After this time TLC (ethyl acetate/petroleum ether 20:80) showed >90% conversion. The reaction mixture was diluted with ethyl acetate (30 mL) and water was added (30 mL). After separation the organic phase was washed with water and brine and dried ($MgSO_4$). Removal of the solvent left 615 mg of crude (*R*)-**20** which was found to be pure enough for the next step (90–95% purity, corr. yield: 88%). $[\alpha]_D^{20} = -232$ (*c* 1.02, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 1.49 (s, 9H); 3.45 (d, *J* = 12.9 Hz, 2H); 4.51 (d, *J* = 13.0 Hz, 2H); 5.59 (br s, 1H); 7.19 (br d, *J* = 8.6 Hz, 2H); 7.24 (ddd, *J* = 7.9, 6.5, 1.3 Hz, 2H); 7.45 (ddd, *J* = 8.0, 6.5, 1.4 Hz, 2H); 7.80 (d, *J* = 8.2 Hz, 2H); 8.57 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 28.56 (CH_3); 61.37 (CH_2); 98.31 (C); 126.81 (2 × CH); 127.17; 127.41; 130.96 (C); 134.06 (C); 134.38 (C); 135.79 (C); 139.74 ppm ($C_{quart.}$, CO not observed). MS (ESI) *m*/*z*: 663.0 (M+1$^+$), HRMS: calcd for $C_{27}H_{25}I_2N_2O_2$: 663.0005, found: 662.9997.

4.2.13. (*R*)-2,6-Diiodo-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-21

Boc-hydrazine (*R*)-**20** (331 mg, 0.5 mmol) was dissolved in $CHCl_3$ (3 mL) and TFA (1 mL) was added. The solution was stirred at rt for 3 h after which TLC indicated complete conversion. The reaction mixture was carefully neutralized with sat. $NaHCO_3$, diluted with CH_2Cl_2 (25 mL), washed with water (30 mL) and brine, and dried (K_2CO_3). Removal of the solvent left 281 mg of crude (*R*)-**21** which was found to be pure enough for the next step (>97% purity by ^1H NMR; corr. yield: 97%). Chromatographic purification resulted in considerable loss of product due to pronounced sensitivity of the compound. (An analytical sample of the racemic compound crystallized from CH_2Cl_2, mp: 198–200 °C.) ^1H NMR ($CDCl_3$) δ: 3.33 (d, *J* = 12.8 Hz, 2H); 3.36 (br s, 2H); 4.45 (d, *J* = 12.8 Hz, 2H); 7.21 (m, 2H); 7.24 (m, 2H); 7.45 (ddd, *J* = 8.0, 6.1, 1.9 Hz, 2H); 7.80 (br d, *J* = 8.3 Hz, 2H); 8.57 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 63.74 (CH_2); 98.58 (C); 126.70; 126.77; 127.18; 127.43; 131.03 (C); 134.34 (C); 134.51 (C); 135.74 (C); 139.52 ppm. MS (EI, 150 °C) *m*/*z* (rel%): 562.1 (M^+, 12); 532.1 (62); HRMS: calcd for $C_{22}H_{16}I_2N_2$: 561.9403, found: 561.9385.

4.2.14. (*R*)(*E*)-*N*-(2-(Diphenylphosphino)benzylidene)-2,6-diiodo-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-22

To a degassed solution of diiodo hydrazine (*R*)-**21** (281 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) were added aldehyde (145 mg, 0.5 mmol) and $MgSO_4$ (120 mg, 1 mmol) and the mixture was stirred under argon at rt for 5 h. Extractive work-up with CH_2Cl_2/water left 378 mg of crude product which contained 11% of aldehyde. Chromatography on SiO_2 in CH_2Cl_2/petroleum ether (1:1), column 20 × 2 cm resulted in some decomposition and afforded 299 mg (72%) of (*R*)-**22** as a foam. ^1H NMR ($CDCl_3$) δ: 3.41 (d, *J* = 12.7 Hz, 2H); 5.00 (d, *J* = 12.7 Hz, 2H); 6.74 (ddd, *J* = 7.5, 5.2, 1.3 Hz, 1H); 6.91 (m, 1H); 7.06 (m, 2H); 7.11 (bpt, *J* ~7.4 Hz, 1H); 7.15 (bpt, *J* ~7.9 Hz, 2H); 7.20 (br d, *J* ~ 8.5 Hz, 2H); 7.22–7.30 (m, ~7H); 7.35 (bpt, *J* ~7.3 Hz, 1H); 7.45 (ddd, *J* = 8.0, 6.4, 1.6 Hz, 2H); 7.79

(d, J = 8.6 Hz, 2H); 7.91 (d, J = 5.8 Hz, 1H); 8.22 (ddd, J = 8.0, 4.0, 1.2 Hz, 1H); 8.52 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 59.19 (CH_2); 98.07 (C); 125.13 (d, J = 4.0 Hz); 126.70 (2 × CH); 127.14; 127.39; 127.70 (d, J = 2.0 Hz); 128.27; 128.34; 128.52; 128.63; 128.70; 128.80; 130.98 (C); 132.67 (d, J = 3.1 Hz); 134.00; 134.13; 134.20, 134.29 (C); 134.39; 134.41 (C); 134.57 (C); 134.63 (C); 134.75 (C); 135.45 (C); 135.84 (C); 135.93 (C); 136.01 (C); 136.10 (C); 139.31 (C, d, J = 16.7 Hz); 139.66 ppm. ^{31}P NMR ($CDCl_3$) δ: −12.36 (s) ppm. MS (ESI) m/z: 835.0. HRMS calcd for $C_{41}H_{30}I_2N_2P$: 835.0236, found: 835,0227.

4.2.15. (*R*)-*tert*-Butyl 2,6-diphenyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl carbamate (*R*)-23

Diiodide (*R*)-**20** (132 mg, 0.2 mmol) and benzene boronic acid (73 mg, 0.6 mmol) were mixed in DME (3 mL) and Cs_2CO_3 (147 mg, 0.45 mmol, in 0.2 mL of water) was added. After degassing $Pd(PPh_3)_4$ (24 mg, 10 mol %) was added and the reaction mixture was heated under argon. After about 20 h the color changed to brown and TLC indicated complete conversion. Work-up with ethyl acetate/water (20 + 20 mL), washing the organic phase with water and satd NaCl, drying with $MgSO_4$, and evaporation of solvent were followed by column chromatography (8 × 2 cm) in CH_2Cl_2/petroleum ether (50:50) to remove the catalyst. Elution with ethyl acetate/petroleum ether (20:80) gave 93 mg (84%) of (*R*)-**23** as a foam. (The racemic compound (±)-**23** crystallized; mp: 224–227 °C.) $[\alpha]_D^{20} = -121$ (c 0.64, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 1.27 (s, 9H); 3.33 (br d, J = 12.5 Hz, 2H); 4.13 (d, J = 12.5 Hz, 2H); 5.10 (br s, 1H); 7.27 (m, 2H); 7.38 (m, 2H); 7.42–7.51 (m, 8 H); 7.65 (bm, 4H); 7.94 (br d, J ~7.9 Hz, 2H); 7.97 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 28.17 (CH_3); 54.48 (CH_2); 79.60 (C); 126.00; 126.24; 127.27; 127.52; 128.35 (2 × CH); 129.52; 130.08; 130.17 (C); 130.84 (C); 132.83 (C); 136.39 (C); 140.23 (C); 140.69 (C) ppm. MS (EI, 50 °C) m/z (rel%): 562 (1, M^+). HRMS calcd for $C_{39}H_{34}N_2O_2$: 562.2620, found: 562.2609.

4.2.16. (*R*)-*tert*-Butyl 2,6-di(naphthalen-2-yl)-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-yl carbamate (*R*)-24

An analogous procedure as given for the synthesis of (*R*)-**23** was applied yielding 68% of (*R*)-**24** as a crystalline powder, mp: 165–166 °C. $[\alpha]_D^{20} = -60.0$ (c 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 0.99 (s, 9H); 3.44 (br d, d, J = 12.5 Hz, 2H); 4.25 (br d, J = 12.6 Hz, 2H); 5.19 (br s, 1H); 7.31 (ddd, J = 8.4, 6.7, 1.3 Hz, 2H); 7.46–7.54 (m, 8H); 7.78 (bm, 2H); 7.88 (m, 2H); 7.93 (d, J = 8.5 Hz, 2H); 7.96 (m, 2H); 7.99 (br d, J = 8.7 Hz, 2H); 8.10 (s, 2H); 8.24 (br s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 27.78 (CH_3); 54.56 (CH_2); 126.08 (2 × CH); 126.21; 126.26; 127.56; 127.60; 127.84; 128.26 (b); 128.44; 128.49 (b); 129.11(b); 129.75; 130.65 (C); 130.91 (C); 132.52 (C); 132.91 (C); 133.43 (C); 136.48 (C); 138.17 (C); 140.12 (C) ppm. MS (ESI) m/z: 663.2 ($M+1^+$). HRMS: calcd for $C_{49}H_{39}N_2O_2$: 663.3012, found: 663.3019.

4.2.17. (*R*)-2,6-Diphenyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-25

Boc-hydrazine (*R*)-**23** (90 mg, 0.16 mmol) was dissolved in $CHCl_3$ (1 mL) and TFA (0.25 mL) was added. The solution was stirred at rt for 2 h after which TLC (ethyl acetate/petroleum ether, 20:80) indicated complete conversion. The reaction mixture was carefully neutralized with sat. $NaHCO_3$, diluted with of CH_2Cl_2 (15 mL), washed with water (10 mL) and brine, and dried (K_2CO_3). Removal of the solvent left 58 mg of crude (*R*)-**25** which was found to be pure enough for the next step (>98% purity; corr. yield: 78%); (*note:* Attempted chromatographic purification resulted in considerable loss of product due to pronounced sensitivity of the compound. (±)-**25** was obtained crystalline; mp: 226–229 °C.) ^{1}H NMR ($CDCl_3$) δ: 2.73 (br s, 2H); 3.21 (d, J = 12.5 Hz, 2H); 4.08 (d, J = 12.5 Hz, 2H); 7.27 (m, 2H); 7.38 (m, 2H); 7.42–7.50 (m, 8H); 7.58 (br d, J ~7.3 Hz, 4H); 7.94 (br d, J = 8.3 Hz, 2H); 7.94 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 56.51 (CH_2); 125.88; 126.06; 127.21; 127.55; 128.29; 128.31; 129.17; 129.96; 130.91 (C); 130.93 (C); 132.69 (C); 136.35 (C); 140.46 (C); 141.15 (C) ppm. MS (ESI) m/z: 463.1 ($M+1^+$); HRMS calcd for $C_{34}H_{27}N_2$: 463.2174, found: 463.2192.

4.2.18. (*R*)-2,6-Di(naphthalen-2-yl)-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-26

An analogous procedure as given for the synthesis of (*R*)-**25** was applied yielding 75% of (*R*)-**26** as an off-white powder (purity >95%). ^{1}H NMR ($CDCl_3$) δ: 2.75 (br s, 2H); 3.31 (br d, J = 12.6 Hz, 2H); 4.16 (d, J = 12.7 Hz, 2H); 7.31 (m, 2H); 7.47–7.53 (m, 8H); 7.73 (br d, J ~8.4 Hz, 2H); 7.88 (m, 4H); 7.92 (d, J = 8.5 Hz, 2H); 7.98 (m, 2H); 8.05 (s, 2H); 8.06 (br s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 56.77 (CH_2); 125.98; 126.08; 126.12, 126.32; 127.60; 127.72; 127.78; 128.16; 128.34; 128.37; 128.71; 129.49; 131.04 (C); 131.19 (C); 132.50 (C); 132.76 (C); 133.36 (C); 136.44 (C); 138.75 (C); 140.41 (C) ppm. MS (ESI) m/z: 563.2 ($M+1^+$); HRMS calcd for $C_{42}H_{31}N_2$: 563.2487, found: 563.2506.

4.2.19. (*R*)(*E*)-*N*-(2-(Diphenylphosphino)benzylidene)-2,6-diphenyl-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-27

Method A: *N*-Aminodinaphthoazepine (*R*)-**25** (58 mg, 0.126 mmol) was dissolved in $CHCl_3$ (1 mL), the solution was degassed, and 2-diphenylphosphinobenzaldehyde (36 mg, 0.126 mmol) and $MgSO_4$ (30 mg, 0.25 mmol) were added. After stirring the mixture overnight at rt under argon the suspension was worked up with CH_2Cl_2 (10 mL) and water (10 mL). The organic layer was separated, washed with brine, and dried over $MgSO_4$. The filtrate was concentrated and the remaining residue was purified by column chromatography (SiO_2, CH_2Cl_2/petroleum ether, 30:70→50:50) to yield 76 mg (81%) of phosphinohydrazone (*R*)-**27** as a solid (>98% pure by NMR). $[\alpha]_D^{20} = +44.3$ (c 0.526, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ: 3.33 (d, J = 12.6 Hz, 2H); 4.63 (d, J = 12.6 Hz, 2H); 6.62 (bpt, J = 7.4 Hz, 1H); 6.72 (ddd, J = 6.8, 5.4, 1.0 Hz, 1H); 6.84 (m, 2H); 6.99 (m, 2H); 7.09 (m, 3H); 7.17 (m, 3H); 7.25–7.44 (m, 15H); 7.49 (m, 3H); 7.70 (ddd, J = 7.8, 4.0, 1.0 Hz, 1H); 7.87 (s, 2H); 7.93 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 51.81 (CH_2); 124.94 (d, J = 4.0 Hz); 125.80; 126.07; 127.19; 127.37 (d, J = 2.0 Hz); 127.61; 128.00; 128.07; 128.11 (2 × CH); 128.28; 128.35; 128.39; 128.44; 128.46; 128.65; 129.47; 129.85; 130.91 (C); 131.40 (C); 132.72 (C); 132.74; 132.78; 132.83; 133.09; 133.63; 133.77; 133.83; 133.96; 134.30 (C, d, J = 15.5 Hz); 135.65 (C); 135.70 (C); 135.74 (C); 135.80 (C); 135.95 (C); 139.36 (C, d, J = 16.2 Hz); 140.15 (C); 140.76 (C) ppm. ^{31}P NMR ($CDCl_3$) δ: −12.85 (s) ppm. MS (ESI) m/z: 735.3 ($M+1^+$). HRMS calcd for $C_{53}H_{40}N_2P$: 735.2929, found: 735.2933.

Method B: Diiodide (*R*)-**22** (83 mg, 0.1 mmol) and benzene boronic acid (37 mg, 0.3 mmol) were mixed in DME (2 mL) and Cs_2CO_3 (82 mg, 0.25 mmol, in 0.15 mL water) was added. After degassing $Pd(PPh_3)_4$ (12 mg, 10 mol %) was added and the reaction mixture was heated under argon for 24 h. Since the reaction was still heterogeneous and TLC showed only partial conversion another 12 mg (10 mol %) of $Pd(PPh_3)_4$ and 37 mg (0.3 mmol) of benzene boronic acid were added and heating was continued for further 48 h obtaining a clear yellow solution. Work-up with CH_2Cl_2/water (15 + 15 mL), washing with brine, and drying ($MgSO_4$) were followed by column chromatography (see above) to give 41 mg (56%) of (*R*)-**27**.

4.2.20. (*R*)(*E*)-*N*-(2-(Diphenylphosphino)benzylidene)-2,6-di(naphthalen-2-yl)-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]azepin-4(5*H*)-amine (*R*)-28

An analog procedure as applied for the synthesis of (*R*)-**27** was used yielding 69% of (*R*)-**26** as an off-white powder (purity >98%).

$[\alpha]_D^{20} = +62.8$ (*c* 0.53, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 3.43 (br s, 2H); 4.69 (br d, J = 12.5 Hz, 2H); 6.60 (pt, J = 7.3 Hz, 1H); 6.73 (ddd, J = 7.2, 5.9, 1.2 Hz, 1H); 6.79 (m, 2H); 6.88–7.01 (m, 7H); 7.09 (pt, J = 7.4 Hz, 1H); 7.14 (m, 1H); 7.31 (ddd, J = 8.2, 6.8, 1.2 Hz, 2H); 7.41 (d, J = 5.0 Hz, 1H); 7.45–7.58 (m, 11H); 7.79 (bm, 4H); 7.90 (m, 4H); 7.97 (d, J = 7.9 Hz, 2H); 7.97 (s, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 51.95 (CH_2); 125.11 (d, J = 3.6 Hz); 125.92 (d, J = 3.2 Hz); 126.13 (d, J = 3.6 Hz); 127.27 (d, J = 2.2 Hz); 127.59; 127.64; 127.70; 127.96; 128.03; 128.16; 128.23; 128.33; 128.49; 128.59; 128.66; 129.84; 131.00 (C); 131.55 (C); 132.55 (C); 132.71; 132.77 (C); 133.25; 133.34 (C); 133.47; 133.58; 133.78; 134.44 (C, d, J = 15.2 Hz); 135.46 (C); 135.51 (C); 135.55 (C); 135.60 (C); 135.99 (C, br); 138.41 (C); 139.19 (C, d, J = 15.6 Hz); 140.09 (C) ppm. ^{31}P NMR ($CDCl_3$) δ: −12.37 (s) ppm. MS (ESI) m/z: 835.3 ($M+1^+$). HRMS calcd for $C_{61}H_{44}N_2P$: 835.3242, found: 835.3217.

4.2.21. (2-(1,3-Dioxolan-2-yl)phenyl)bis(3-methoxyphenyl)phosphine

Magnesium (174 mg, 7.14 mmol, 1.07 equiv) was added to THF (1.2 mL) in an oven-dried Schlenk tube and the mixture was degassed. A single crystal of iodine was added, followed by the dropwise addition of a solution of 3-bromoanisole (1.25 g, 6.67 mmol) in THF (1.4 mL). After the addition was complete, the reaction mixture was stirred at reflux for 2 h. The solution of the Grignard reagent was allowed to cool to rt and added via a cannula to phosphorous trichloride (366 mg, 2.67 mmol, 0.4 equiv) in degassed THF (7.2 mL) at 0 °C. The reaction mixture was warmed to rt and stirred overnight. This solution of chlorobis(3-methoxyphenyl) phosphine was used directly in the following reaction.

Magnesium (146 mg, 6 mmol, 1.5 equiv) and THF (2.3 mL) were placed in an oven-dried Schlenk tube and the mixture was degassed. A single crystal of iodine was added, followed by the dropwise addition of 2-(2-bromophenyl)-1,3-dioxolane (916 mg, 4 mmol) dissolved in THF (4 mL). After the addition was complete, the reaction mixture was refluxed for 2 h. The solution of the Grignard reagent was cooled to rt and added *via* a cannula to the solution of chlorobis(3-methoxyphenyl)phosphine in degassed THF (9.8 mL) at 0 °C. The mixture was slowly warmed up and stirred overnight at 50 °C. The reaction mixture was concentrated, diluted with ethyl acetate (25 mL), and washed with water (2 × 20 mL) and saturated NH_4Cl (20 mL). After drying ($MgSO_4$) and evaporation, the crude product was purified by chromatography (ethyl acetate/petroleum ether, 10:90) to afford 190 mg (18%) of (2-(1,3-dioxolan-2-yl)phenyl)bis(3-methoxyphenyl)phosphine as an oil. ^1H NMR ($CDCl_3$) δ: 4.10 (s, 6H); 4.34 (m, 2H); 4.48 (m, 2H); 6.84 (d, J = 4.9 Hz, 1H); 7.23–7.27 (m, 6H); 7.42 (ddd, J = 7.7, 4.5, 1.4 Hz, 1H); 7.62–7.68 (m, 3H); 7.79 (ptd, J = 7.5, 1.4 Hz, 1H); 8.10 (ddd, J = 7.8, 4.1, 1.5 Hz, 1H) ppm. ^{31}P NMR ($CDCl_3$) δ: −14.66 (s) ppm.

4.2.22. 2-(Bis(3-methoxyphenyl)phosphino)benzaldehyde

(2-(1,3-Dioxolan-2-yl)phenyl)bis(3-methoxyphenyl)phosphine (176 mg, 0.447 mmol) was dissolved in acetone (4 mL) and the mixture was degassed. *p*-Toluenesulfonic acid monohydrate (5 mg) was added and the solution was refluxed for 3 h under argon. During this time, the yellow color of the final product developed. The product mixture was filtered through a short pad of SiO_2 (CH_2Cl_2) giving 139 mg (~80%) of a yellow oil (purity 95% by NMR). ^1H NMR ($CDCl_3$) δ: 3.73 (s, 6H); 6.82 (m, 2H); 6.84 (m, 2H); 6.98 (ddd, J = 8.3, 2.8, 1.0 Hz, 2H); 6.99 (m, 1H); 7.25 (m, 2H); 7.46 (m, 2H); 7.95 (m, 1H); 10.48 (d, J = 5.4 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$) δ: 55.16 (CH_2); 114.69 (2 × CH); 119.08; 119.30; 126.24; 126.44; 128.92; 129.68; 129.76; 130.59 (d, J = 3.9 Hz); 133.66; 133.91; 137.50 (d, J = 10.2 Hz, C); 138.49 (d, J = 14.7 Hz, C); 140.88 (d, J = 26.2 Hz, C); 159.67 (d, J = 9.2 Hz, C); 191.65 (d, J = 19.2 Hz) ppm. ^{31}P NMR ($CDCl_3$) δ: −10.03 ppm.

4.3. Catalytic experiments

For performing reactions 1–6 standard procedures were applied.[20] The enantiomeric purity of products was determined by HPLC (Chiralcel-ODH, 2-PrOH/*n*-hexane for reaction 1 and 6) or by ^1H NMR using a chiral shift reagent ($Eu(hfc)_3$ in $CDCl_3$ for reaction 2, 3, and 5).

4.4. Synthesis of Pd complexes

4.4.1. (*RS*)-6·Pd-dimer

To a degassed solution of $Pd(MeCN)_2Cl_2$ (14.1 mg, 0.0545 mmol) in CH_2Cl_2 (0.5 mL) was added *rac*-**6** (35 mg, 0.0545 mmol) at rt under argon. After 30 min, $AgPF_6$ (13.8 mg 0.0545 mmol) was added and stirring was continued for 1.5 h. Silver chloride was filtered off and the solvent was removed. The crude product was crystallized from CH_2Cl_2/benzene or $CDCl_3$ in orange prisms. Mp: 207–208 °C (dec.). ^1H NMR (CD_2Cl_2) δ: 3.70 (d, J = 12.3 Hz, 2H); 4.89 (br d, J = 12.3 Hz, 2H); 6.70 (br d, J = 7.7 Hz, 2H); 6.84 (dd, J = 12.1, 7.8 Hz, 1H); 7.22 (ddd, J = 8.0, 6.7, 1.2 Hz, 2H); 7.33 (br d, J = 8.7 Hz, 2H); 7.44 (ddd, J = 8.0, 6.7, 1.2 Hz, 2H); 6.30–7.47 (bm, ca. 6H); 7.55 (br s, 1H); 7.66 (d, J = 8.3 Hz, 2H); 7.57–7.77 (bm, ca. 6H); 7.87 (d, J = 8.3 Hz, 2H); 7.96 (bpt, J ~7.5 Hz, 1H) ppm. ^{31}P NMR (CD_2Cl_2) δ: 35.9 (br s) ppm.

4.4.2. (*R*)-6·PdCl$_2$

A solution of equimolar amounts of (*R*)-**6** with and $Pd(MeCN)_2Cl_2$ in $CHCl_3$ was layered with EtOH. After a few hours pale yellow needles formed which were completely converted into orange prisms within several days. Mp: 211–213 °C $[\alpha]_D^{20} = +618$ (*c* 0.0676 $CHCl_3$). ^1H NMR (CD_2Cl_2) δ: 3.67 (d, J = 12.7 Hz, 2H); 5.27 (d, J = 12.7 Hz, 2H); 6.78 (ddd, J = 11.0, 7.9, 1.0 Hz; 1H); 7.11 (d, J = 8.3 Hz, 2H); 7.19 (ddd, J = 8.3, 6.7, 1.3 Hz, 2H);7.19–7.33 (m, 8H); 7.40 (ddd, J = 8.0, 6.6, 1.0 Hz, 2H); 7.44 (br s, 1H); 7.46–7.57 (m, 6H); 7.68 (d, J = 8.3 Hz, 2H); 7.74 (m, 1H); 7.85 (d, J = 8.3 Hz, 2H) ppm. ^{13}C NMR (CD_2Cl_2) δ: 58.16 (CH_2); 119.07 (d, J = 50.2 Hz, C); 126.00 (d, J = 21.6 Hz, C); 126.58 (d, J = 32.4 Hz, C); 126.68 (2 × CH); 127.69; 127.90; 128.87; 128.88 (d, J = 12.0 Hz); 129.53; 130.22 (d, J = 11.6 Hz); 131.77 (d, J = 8.6 Hz); 131.84 (C); 131.86 (C); 132.36 (d, J = 3.0 Hz); 133.09 (d, J = 3.0 Hz); 133.67 (d, J = 2.5 Hz); 134.04 (C); 134.22 (d, J = 10.7 Hz); 134.61; 134.71; 134.74; 134.77; 134.88; 135.54 (C); 138.62 (d, J = 15.7 Hz, C); 141.63 (d, J = 8.7 Hz) ppm. ^{31}P NMR (CD_2Cl_2) δ: 29.56 (s) ppm.

4.5. Crystallographic structure determination

X-ray diffraction measurements were performed on X8 APEXII CCD diffractometer with graphite-monochromated MoKα radiation, λ = 0.71073 Å at 100(2) K. Single crystals were positioned at 35, 40, 40, and 35 mm from the detector and 1776, 2557, 1868, and 1055 frames were measured, each for 50, 20, 30, and 30 s over 1° scan width for (±)-**18**·$C_4H_8O_2$, (±)-**29**, $[((R)\text{-}\mathbf{6}\text{-}(S)\text{-}\mathbf{6})Pd_2Cl_2]^{2+}\cdot 2PF_6^+ \cdot 8CH_2Cl_2$ and $[((R)\text{-}\mathbf{6}Pd_2Cl_2]\cdot CHCl_3$, correspondingly. The data were processed using SAINT Plus software.[21] The structure was solved by direct methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were placed in geometrically calculated positions and refined as riding atoms in the subsequent least squares model refinements. The isotropic thermal parameters were estimated to be 1.2 times the values of the equivalent isotropic thermal parameters of the atoms to which hydrogens were bonded. The following software programs, computer, and tables were used: structure solution, SHELXS-97,[22] refinement, SHELXL-97,[23] molecular diagrams, ORTEP,[24] computer: Pentium IV; Tables 4.2.6.8 and 6.1.1.4 for scattering factors were taken from

the literature.[25] Details of crystal data, data collection, and refinement are as follows:[26]

(±)-**18**·$C_4H_8O_2$: $C_{45}H_{37}Cl_2N_2O_3P$, M_r = 755.64, monoclinic, space group $P2_1/n$ (no. 14), a = 13.8470(9), b = 10.0712(7), c = 27.1684(16) Å, V = 3754.3(4) Å^3, Z = 4, ρ_{calc} = 1.337 g/cm^3, μ = 0.260 mm^{-1}. Of 130,810 reflections collected up to θ_{max} = 25.5°, 6982 were independent, R_{int} = 0.162; final R indices: R_1 = 0.0480, wR_2 = 0.1045 (all data).

(±)-**29**: $C_{29}H_{22}N_2$, M_r = 398.49, monoclinic, space group $C2/c$ (no. 15), a = 11.1143(6), b = 16.3817(6), c = 22.9158(10) Å, V = 4086.7(3) Å^3, Z = 8, ρ_{calc} = 1.295 g/cm^3, μ = 0.076 mm^{-1}. Of 59,223 reflections collected up to θ_{max} = 30.1°, 6001 were independent, R_{int} = 0.055; final R indices: R_1 = 0.0447, wR_2 = 0.1114 (all data).

$[((R)$-**6**-(S)-**6**$)Pd_2Cl_2]^{2+} \cdot 2PF_6^+ \cdot 8CH_2Cl_2$: $C_{90}H_{76}Cl_{18}F_{12}N_4P_4Pd_2$, M_r = 2416.33, triclinic, space group P-1 (no. 2), a = 14.6409(11), b = 14.6437(11), c = 15.0967(12) Å, α = 113.405(5), β = 93.507(5), γ = 119.019(4)°, V = 2464.1(3) Å^3, Z = 1, ρ_{calc} = 1.628 g/cm^3, μ = 0.988 mm^{-1}. Of 60,424 reflections collected up to θ_{max} = 25.5°, 9019 were independent, R_{int} = 0.102; final R indices: R_1 = 0.0687, wR_2 = 0.2310 (all data).

$[((R)$-**6**$Pd_2Cl_2]\cdot CHCl_3$: $C_{42}H_{32}Cl_5N_2PPd$, M_r = 879.32, monoclinic, space group $P2_1$ (no. 4), a = 11.1254(12), b = 10.9705(13), c = 15.8822(19) Å, V = 1874.3(4) Å^3, Z = 2, ρ_{calc} = 1.558 g/cm^3, μ = 0.929 mm^{-1}. Of 36,163 reflections collected up to θ_{max} = 27.0°, 7893 were independent, R_{int} = 0.127; final R indices: R_1 = 0.0564, wR_2 = 0.0972 (all data).

Acknowledgments

We thank Alexander Roller for the collection of X-ray data and Mirjana Pacar for technical assistance. Two grants of the Estonian Science Foundation are gratefully acknowledged: 6706 and 8031.

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