Enantioselective Catalysis; 123:[1] Octaaldehyde Type Chelating Ligands – A Divergent Synthesis Approach to Easily Tunable Expanded Ligands for Enantioselective Catalysis

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Abstract: A broad range of optically active two-layer phosphanes was obtained by a divergent reaction sequence. Chirality was introduced into the ligands in the last step by easily performed Schiff base condensation of primary amines from the "chiral pool" and achiral octaaldehydes containing a bisphosphane core. The two achiral precursors are 1,2-ethylene- and *o*-phenylene-bridged bisphosphanes with four 3,5-dicarbaldehyde-substituted phenyls, synthesized in six steps. The resulting octaimine ligands have been used in Rh, Pd and Ni complexes in several model reactions of enantioselective catalysis giving low optical inductions.

Key words: two layer bisphosphanes, dendritic Schiff base ligands, divergent synthesis, enantioselective catalysis

Introduction

During the last decade a vast number of optically active phosphane ligands was synthesized and tested in different model systems of enantioselective homogeneous catalysis.[2] Most of these conventional ligands, such as diop,[3] prophos,[4] bppfa,[5] biphemp,[6] binap[7] or norphos,[8] are bis(diphenylphosphanyl) derivatives. In these ligands the chiral information is transferred to the catalytically active metal center via the arrangement of the phenyl rings of the diphenylphosphanyl groups. Due to the limited size, long range effects are not possible with these classical ligands.

Recently, we developed the concept of the expanded ligands.[9] In this approach optically active ligands with increased size are supposed to induce longe range selectivities in catalytic systems, such as the palladium catalyzed allylic alkylation of barbiturates.[10] The characteristics of expanded ligands are a strong chelating P,P skeleton derived e.g. from $Cl_2PCH_2CH_2PCl_2$ or *o*-$Cl_2PC_6H_4PCl_2$, non-chiral branching units for a space-filling construction and a final layer consisting of chiral functional groups (Figure). In this way it is possible to chirally shape the surroundings of the P atoms in a wide range. After coordination in a catalyst, an influence on the optical induction in enantioselective reactions is expected.

Up to now, such expanded ligands were synthesized in convergent reaction sequences. The preparation included lithiation steps of haloarene compounds and the addition of electrophilic components, e.g. chlorophosphanes. These steps usually were performed by metal-halogen exchange with butyllithium. Thus, base-sensitive groups and functionalities unstable against nucleophilic attack were not tolerated in these syntheses. Here we present a divergent reaction sequence allowing to introduce chiral functional groups (containing e.g. hydroxy groups) in the last reaction step. Therefore, an easy ligand tuning with

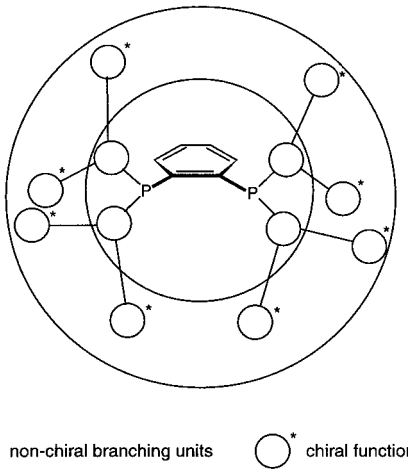


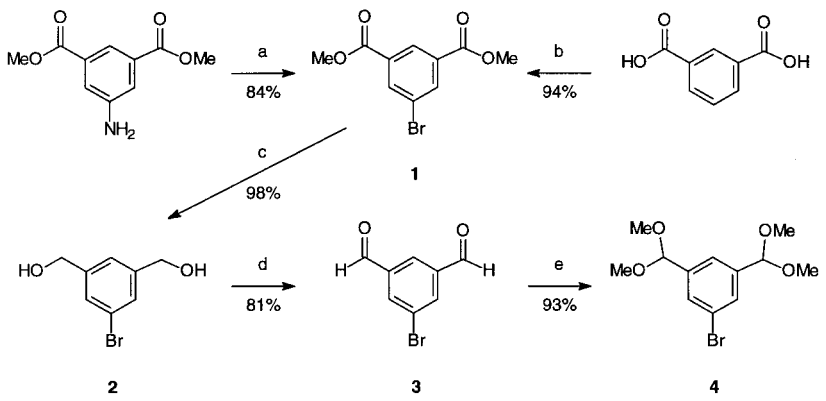
Figure. Structure of Expanded Ligands with Strong Chelating P,P Skeleton

optional interactions between ligand and substrate ("bifunctionalized catalysis"[11]) should be possible. The synthesis of sixteen optically active bisphosphanes, in which chirality is derived from enantiomerically pure primary amines by Schiff base condensation will be described. A prerequisite for this ultimate Schiff base condensation is the availability of the octaaldehyde type chelating P,P ligands octa-eth **6a** and octa-phen **6b**, the synthesis of which will be reported.[12]

Synthesis of the Aldehydes Octa-eth 6a and Octa-phen 6b

For a divergent reaction sequence based on Schiff base condensation, precursors with carbonyl groups are required to connect the chiral functionalities in the last step. We decided to branch the phenyl rings of the well known ligands $Ph_2PCH_2CH_2PPh_2$ and *o*-$Ph_2PC_6H_4PPh_2$ symmetrically with formyl groups in 3,5-position to get space filling ligand systems. By using formyl groups it should be easy to couple enantiomerically pure primary amines under mild conditions.

The aldehydes octa-eth **6a** and octa-phen **6b** were generated in a six-step synthesis starting from inexpensive commercially available compounds, such as isophthalic acid or dimethyl 5-aminoisophthalate. The latter substrate was transformed by a Sandmeyer reaction into dimethyl 5-bromoisophthalate **(1)** in 84% yield. Alternatively, **1** could be obtained in 94% yield by silver-catalyzed electrophilic



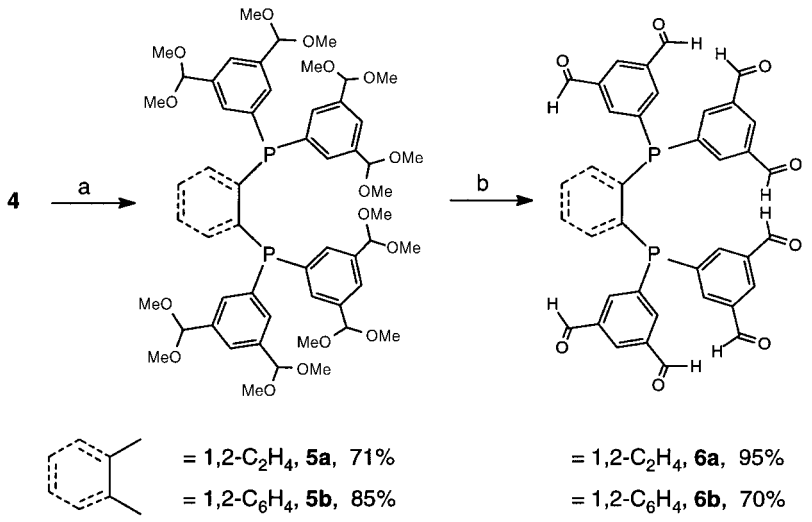
Reagents and conditions: (a) 1. $HBr/H_2O/NaNO_2$, 2. CuBr/HBr, O °C; (b) Ref. 13; (c) $LiAlH_4$/THF, –10 °C; (d) PCC/CH_2Cl_2, reflux; (e) $HC(OMe)_3$/MeOH/*p*-TosOH, reflux

Scheme 1

substitution of isophthalic acid with bromine under drastic conditions,[13] followed by acid-catalyzed esterification in methanol. The published reduction of **1** with a suspension of $LiAlH_4$ in THF[14] was optimized to give 3,5-bis(hydroxymethyl)bromobenzene **(2)** in 98% yield. Oxidation of **2** with pyridinium chlorochromate in dichloromethane gave 5-bromoisophthalaldehyde **(3)** in 81% yield,[15] which was transferred into its acetal **4** by an acidified trimethyl orthoformate/methanol mixture in 93% yield (Scheme 1).

After a halogen-metal exchange between butyllithium and the aryl bromide **4** an organolithium species was formed, which reacted with $Cl_2PCH_2CH_2PCl_2$ and *o*-$Cl_2PC_6H_4PCl_2$ to give the octaacetals **5a** and **5b**, respectively, as shown in Scheme 2. The octaacetal **5a** was recrystallized from dichloromethane/methanol to give a white solid, whilst **5b** could not be crystallized. Compound **5b** was purified by chromatography and directly used in the deprotection step. Deprotection of the acetal groups was performed by acid-catalyzed transacetalization in aqueous acetone. In the case of **5a**, a white precipitate formed, which turned slightly yellow, when working without light protection. Octa-eth **6a** is a fluffy powder, almost insoluble in most solvents and soluble only in traces in polar solvents such as DMF or DMSO. It was purified by washing with acetone, diethyl ether and dichloromethane. Octa-phen **6b** was isolated as a yellowish solid after recrystallization from dichloromethane/toluene (Scheme 2).

In the $^{31}P\{^1H\}$ NMR spectra only singlets were detected at $\delta = -12.5$ and –13.1 for **6a** and **6b**, respectively. In the ^1H NMR spectra the proton H-4' (between the two formyl groups) was shifted to low field (**6a**: $\delta = 8.33$; **6b**: $\delta = 8.30$). As expected, it gave a triplet due to coupling with the equivalent protons H-2' and H-6'. These protons appeared as doublets of triplets (coupling with the two phosphorus atoms: $^6J_{PH} = {}^3J_{PH} = 3.2$ Hz [**6a**]; 3.4 Hz [**6b**]), while in the $^1H\{^{31}P\}$ NMR spectra they were detected as doublets.



Reagents and conditions: (a) 1. BuLi/THF, –78 °C, 2. $TMEDA/Cl_2PCH_2CH_2PCl_2$, –78 °C → r.t.; (b) aq acetone/1 M HCl (**6a**) or *p*-TosOH (**6b**), r.t. → reflux

Scheme 2

Inclusions Causing Analytical Problems

Although at first glance the NMR and mass spectra of the octaaldehydes **6a** and **6b** looked clean, there were problems with their elemental analyses. Whereas **6a** is almost insoluble, **6b** is soluble in tetrahydrofuran and dichloromethane. Despite numerous recrystallizations from tetrahydrofuran elemental analyses of **6b** reproducibly gave H values, which were about 0.5% too high and C values, which were about 2.5% too low, indicating some water content. The C,H values did not improve significantly when drying of the samples was carried out in high vacuum at 80 °C instead of room temperature. A closer inspection revealed the presence of small amounts of tetrahydrofuran and dichloromethane in samples of **6b** which had been treated with these solvents, by ^{1}H NMR spectroscopy and chlorine elemental analysis in quantities of about 0.5 equivalents even after drying at 80 °C for two days.

The *o*-phenylene bridged octaaldehyde **6b** was subjected to a thermogravimetric and differential thermal analysis at normal pressure under nitrogen. It showed a significant loss of several mass percent between 120 and 140 °C combined with an endothermic peak, which can be associated with the loss of solvent and/or water. Samples which had been heated to 120–140 °C were shown to be free of solvents. Their H analyses turned out to be correct, the C analyses, however, still were too low. This was not unexpected as tetrahydrofuran has almost the same C content as **6b**. Some decomposition may have occurred during the harsh heating procedure.

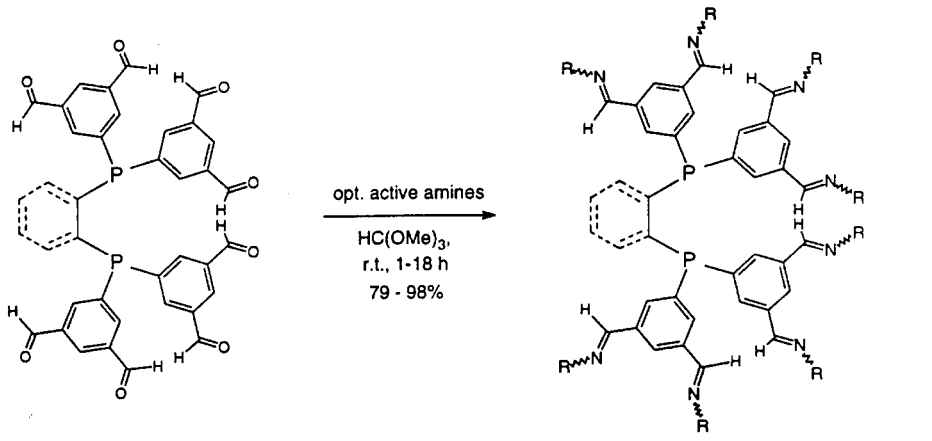
Obviously, solvents and/or water can be trapped in the branched structure of the aldehydes **6a** and **6b**. These inclusion phenomena were also observed for the octaimines to be described below. Unfortunately, these octaimines cannot be heated to higher temperatures without decomposition. Therefore, in the Experimental section the elemental analyses of these imines are left out. By adding the necessary amounts of water and/or solvent the elemental analysis can be fitted nicely (see Ref. 12).

The tendency to include solvents has also been found for other expanded compounds.[16] It may indicate a potential use of these branched aldehydes and imines as stationary phases in chromatography.

Synthesis of the Octaimine Ligands 7a–h and 8a–h

Starting with the octaaldehydes **6a** and **6b** and commercially available optically active amino alcohols, such as (*R*)-alaninol, (*R*)-2-aminobutan-1-ol, (*S*)-valinol, (*S*)-leucinol, (*S*)-phenylalaninol and (1*S*,2*S*)-2-amino-1-phenylpropan-1,3-diol or unfunctionalized amines such as (*S*)-1-phenylethylamine and (*R*)-1-cyclohexylethylamine as well as (8*R*,9*R*)-9-amino(9-deoxy)epicinchonine,[17] sixteen optically active expanded ligands were accessible by Schiff base condensation (Scheme 3).

The degassed octaaldehyde was suspended (**6a**) or dissolved (**6b**) in trimethyl orthoformate or trimethylorthoformate/methanol mixtures as dehydrating solvent and the amines were added at room temperature.[18] The formation of the imines was completed in a few hours, though typically reactions were run for 18 hours. After workup in all cases solids remained. The imine ligands could not be purified by chromatography on silica gel or alumina, because partial hydrolysis of the imine function led to the free amine and formyl groups. All attempts to recrystallize the ligands led to finely dispersed precipitates. When liquid amines were used as starting materials, the remaining solid residues were dried for several hours in high vacuo. The excess of solid amines was removed by adding



Scheme 3

diethyl ether to the solid residue and careful decanting of the ethereal layer. This procedure was repeated three times before the ligands were dried in high vacuo.

The FD/FAB mass spectra of the two-layer octaimine phosphanes **7** and **8** contained the molecular ions. The ^{1}H NMR spectra of **7** and **8** are complex, although the branching in 3,5-position arrange all the substituents in *meta* positions. However, *E*/*Z*-equilibria are possible with regard to the imine groups. As a consequence, a broadening of the peaks in the ^{1}H NMR spectra was observed. Furthermore, all the signals deriving from aromatic protons appeared doubled. There were two groups of signals for the equivalent H-2's and H-6's in *ortho* position and two separate signals for the H-4's in *para* position. The integration showed in all cases a 1:1 ratio. The splitting of the *ortho* protons (H-2' and H-6') as well as the azomethine protons, in principle, could arise from a diastereotopy within a phenyl substituent (hindered rotation) or from a diastereotopy of the two phenyl substituents bound to the same phosphorus atom (induced by the chiral imine substituents). The splitting of the *para* protons H-4', lying on the symmetry axis of the phenyl rings, is only in accord with the second explanation.

The ^{31}P NMR spectra showed singlets for all ligands, strongly dependent on the solvent used. Thus, **7f** and **8f** exhibited broad multiplets in $CDCl_3$, but sharp singlets in CD_3OD. In the IR spectra the strong carbonyl peak at 1700 cm^{-1} of the precursors **6a** and **6b** disappeared and the characteristic C=N peak of the imine ligands was found at 1640–1643 cm^{-1}. The spectroscopic data of the new octaimine ligands **7** and **8** are summarized in the Table.

Catalytic Results

Rhodium complexes, generated in situ from $[Rh(cod)Cl]_2$ and the given ligands were used as catalysts in the asymmetric hydrogenation of *Z*-α-*N*-acetamidocinnamic acid (**7a–g**, **8a–g**)[19] and the hydrosilylation of acetophenone with diphenylsilane (**7a,b,d,e,g**; **8a,b,e,h**).[20] Also in situ complexes were formed with $Pd(acac)_2$ for the palladium-catalyzed allylation of 1,5-dimethylbarbituric acid with allyl acetate (**7c–g**; **8c**,**e–h**)[10] and with anhydrous $NiCl_2$ for the nickel-catalyzed Grignard cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide (**7a–e**,**g**; **8a–e**,**g**,**h**).[21] For the catalytic procedures, the work-up and the determination of the chemical yield and the enantiomeric excess, the methods described in the literature were used.[10,19–21]

Enantioselective Hydrogenation of Z-α-N-Acetamidocinnamic Acid: The Rh-catalyzed hydrogenation of *Z*-α-*N*-acetamidocinnamic acid was carried out in methanol at 30 bar H_2 pressure. The average reaction time was 20 hours and the Rh:substrate ratio was 1:100. In all cases except **7h**, 100% hydrogenation was achieved. However, the optical inductions were low (0–6% ee).[12] No difference between the labile ethylene-bridged ligands **7** and the more rigid *o*-phenylene-bridged ligands **8** was recognized. Obviously, the chirality located at the surface of the ligands,

Table. Properties and Spectroscopic Data for Octaimine Type Expanded Ligands **7** and **8**

Product	mp (°C)	$[\alpha]_\lambda$ (*c*, solv.)	MS (FAB)	^{31}P NMR[a, b] δ (s)	^{1}H NMR[a, b] δ, *J* (Hz)
7a	110–115	(0.43, CH_2Cl_2) –50 (589 nm) –53 (578 nm) –62 (546 nm)	1448.2	13.1	8.41–8.07 (m, 12 H, Ar'), 7.79 (br s, 8 H, CHN), 7.47–7.22 (m, 40 H, Ph), 4.60–4.46 (m, 8 H, C*H*CH$_3$), 2.49–2.24 (m, 4 H, PCH$_2$CH$_2$P), 1.64–1.53 (m, 24 H, CHC*H*$_3$)
7b	76–80	(0.17, CH_2Cl_2) –115 (589 nm) –125 (578 nm) –146 (546 nm) –232 (436 nm)	1496.2	13.1	8.17 (s, 4 H, CHN), 8.15 (s, 4 H, CHN), 8.08 (s, 2 H, *p*-H), 8.06 (s, 2 H, *p*-H), 7.75 (m, 4 H, *o*-H), 7.44 (m, 4 H, *o*-H), 3.00–2.95 (m, 8 H, C*H*CH$_3$), 2.26 (s, 4 H, PCH$_2$CH$_2$P), 1.80–0.82 (m, 112 H, CHC*H*$_3$, cyclohexyl)
7c	146–148	(0.10, CH_2Cl_2) +83 (589 nm) +85 (578 nm) +100 (546 nm) +190 (436 nm)	1079.5	12.7	8.31 (s, 4 H, CHN), 8.27 (s, 4 H, CHN), 8.12 (s, 2 H, *p*-H), 8.08 (s, 2 H, *p*-H), 7.87–7.84 (m, 4 H, *o*-H), 7.84–7.82 (m, 4 H, *o*-H), 3.65–3.37 (m, 24 H, C*H*C*H*$_a$*H*$_b$OH), 2.29 (m, 4 H, PCH$_2$CH$_2$P), 1.19 (d, ^3J = 6.5 Hz, 24 H, CHC*H*$_3$)
7d	94–98	(0.44, MeOH) –3.9 (589 nm) –5.7 (578 nm) –4.1 (546 nm)	1191.7	12.7	8.29 (s, 4 H, CHN), 8.24 (s, 4 H, CHN), 8.17 (s, 2 H, *p*-H), 8.11 (s, 2 H, *p*-H), 7.90–7.88 (m, 4 H, *o*-H), 7.86–7.84 (m, 4 H, *o*-H), 3.71–3.56 (m, 16 H, CHC*H*$_a$*H*$_b$OH), 3.25–3.16 (m, 8 H, C*H*CH$_a$H$_b$OH), 1.68–1.43 (2 m, 16 H, C*H*$_a$*H*$_b$CH$_3$), 0.82 (m, 24 H, CH$_a$H$_b$C*H*$_3$)
7e	76–82	(0.17, MeOH) –39 (589 nm) –46 (578 nm) –52 (546 nm)	1304.8	13.6	8.16–7.40 (m, 20 H, CHN, Ar'), 4.00–3.90 (m, 8 H, C*H*$_a$H$_b$OH), 3.90–3.78 (m, 8 H, CH$_a$*H*$_b$OH), 3.14–2.94 (m, 8 H, C*H*CH$_a$H$_b$OH), 2.53–2.48 (m, 4 H, PCH$_2$CH$_2$P), 1.95–1.70 (m, 8 H, C*H*Me$_2$), 1.08–0.81 (m, 48 H, CH$_3$)

Table (continued)

Product	mp (°C)	$[\alpha]_\lambda$ (*c*, solv.)	MS (FAB)	^{31}P NMR[a, b] δ (s)	^{1}H NMR[a, b] δ, *J* (Hz)
7f	120–125	(0.49, CH_2Cl_2) –50 (589 nm) –53 (578 nm) –62 (546 nm)	1416.1	12.9	8.31 (s, 4 H, CHN), 8.28 (s, 4 H, CHN), 8.15 (br s, 2 H, *p*-H), 8.11 (br s, 2 H, *p*-H), 7.93–7.89 (m, 4 H, *o*-H), 7.89–7.85 (m, 4 H, *o*-H), 3.67–3.36 (m, 24 H, C*H*C*H*$_a$*H*$_b$OH), 2.49–2.39 (m, 4 H, PCH$_2$CH$_2$P), 1.61–1.20 (m, 24 H, C*H*$_a$*H*$_b$C*H*Me$_2$), 0.91–0.76 (m, 48 H, CH$_3$)
7g	69–73	(0.43, MeOH) –167 (589 nm) –177 (578 nm) –206 (546 nm)	1687.8	13.9	8.21–7.57 (m, 20 H, CHN, Ar'), 7.31–7.00 (m, 40 H, CH$_a$H$_b$*Ph*), 3.91–3.47 (m, 24 H, C*H*C*H*$_a$*H*$_b$OH), 2.98–2.76 (m, 16 H, C*H*$_a$*H*$_b$Ph), 2.44–2.37 (m, 4 H, PCH$_2$CH$_2$P)
7h	190–195	(1.2, MeOH) +97 (589 nm) +102 (578 nm) +118 (546 nm)	2826.8	13.4	8.82 (d, ^3J = 5.0 Hz, 8 H, H-2$_{qui}$), 8.34–8.06 (m, 36 H, CHN, Ar', H-5$_{qui}$, H-8$_{qui}$), 7.72–7.48 (m, 24 H, H-6$_{qui}$, H-7$_{qui}$, H-3$_{qui}$), 5.86–5.73 (m, 8 H, H-10$_{nu}$), 5.10–5.02 (m, 16 H, H-11$_{nu}$), 4.76 (br s, 8 H, H-9$_{nu}$), 3.07–2.65 (m, 40 H, H$_{nu}$), 2.31–2.25 (m, 8 H, H$_{nu}$), 2.12–2.09 (br s, 4 H, PCH$_2$CH$_2$P), 1.60–0.81 (m, 40 H, H$_{nu}$)[c]
8a	92–95	(0.58, CH_2Cl_2) –47 (589 nm) –49 (578 nm) –58 (546 nm)	1495.7	15.4	8.15–8.00 (m, 12 H, Ar´), 7.52 (br s, 8 H, CHN), 7.40–7.22 (m, 44 H, H-3–H-6, Ph), 4.42–4.31 (m, 8 H, C*H*CH$_3$), 1.52–1.48 (m, 24 H, CHC*H*$_3$)
8b	110–115	(0.16, CH_2Cl_2) –112 (589 nm) –120 (578 nm) –138 (546 nm)	1544.2	14.6	8.10 (t, ^4J = 1.5 Hz, 2 H, *p*-H), 8.06 (t, ^4J = 1.5 Hz, 2 H, *p*-H), 8.03 (s, 4 H, CHN), 8.01 (s, 4 H, CHN), 7.49 (dt, $^3J_{PH}$ = $^6J_{PH}$ = 3.8 Hz, ^4J = 1.5 Hz, 4 H, *o*-H), 7.44 (dt, $^3J_{PH}$ = $^6J_{PH}$ = 3.8 Hz, ^4J = 1.5 Hz, 4 H, *o*-H), 7.34–7.30 (m, 2 H, H-4, H-5), 7.23–7.19 (m, 2 H, H-3, H-6), 2.94–2.91 (m, 8 H, C*H*CH$_3$), 1.78–0.80 (m, 112 H, CHC*H*$_3$, cyclohexyl)
8c	170–175	(0.44, MeOH) +73 (589 nm) +74 (578 nm) +85 (546 nm)	1127.4	13.1	8.23 (s, 4 H, CHN), 8.21 (s, 4 H, CHN), 8.17 (s, 2 H, *p*-H), 8.14 (s, 2 H, *p*-H), 7.62–7.59 (m, 8 H, *o*-H), 7.41–7.38 (m, 2 H, H-4, H-5), 7.26–7.21 (m, 2 H, H-3, H-6), 3.64–3.38 (m, 24 H, C*H*C*H*$_a$*H*$_b$OH), 1.17 (d, ^3J = 6.2 Hz, 24 H, CHC*H*$_3$)
8d	82–83	(0.57, CH_2Cl_2) –2.8 (589 nm) –3.0 (578 nm) –3.5 (546 nm)	1239.9	14.9	8.22–7.32 (m, 24 H, CHN, H-3–H-6, Ar'), 3.70–3.55 (m, 16 H, CHC*H*$_a$*H*$_b$OH), 3.25–3.16 (m, 8 H, C*H*CH$_a$H$_b$OH), 1.65–1.36 (m, 16 H, C*H*$_a$*H*$_b$CH$_3$), 0.78 (m, 24 H, CH$_a$H$_b$C*H*$_3$)
8e	68–72	(0.18, MeOH) –40 (589 nm) –46 (578 nm) –51 (546 nm)	1351.8	14.6	8.22–7.34 (m, 24 H, CHN, H-3–H-6, Ar'), 4.11–3.68 (m, 16 H, CHC*H*$_a$*H*$_b$OH), 3.17–2.90 (m, 8 H, C*H*CH$_a$H$_b$OH), 1.99–1.74 (m, 8 H, C*H*Me$_2$), 1.06–0.80 (m, 48 H, CH$_3$)
8f	105–110	(0.2, MeOH) –46 (589 nm) –51 (578 nm) –58 (546 nm) –111 (436 nm)	1463.9	12.8	8.23–8.19 (m, 12 H, CHN, *p*-H), 7.64–7.59 (m, 8 H, *o*-H), 7.43–7.40 (m, 2 H, H-4, H-5), 7.33–7.30 (m, 2 H, H-3, H-6), 3.64–3.47 (m, 16 H, CHC*H*$_a$*H*$_b$OH), 3.40–3.34 (m, 8 H, C*H*CH$_a$H$_b$OH), 1.58–1.44 (m, 16 H, C*H*$_a$*H*$_b$CHMe$_2$), 1.36–1.28 (m, 8H, CH$_a$H$_b$(-*H*Me$_2$), 0.90–0.84 (m, 48 H, CH$_3$)
8g	83 (dec.)	(2.5, CH_2Cl_2) –34 (589 nm) –36 (578 nm) –42 (546 nm)	1736.8	14.9	8.21–7.60 (m, 24 H, CHN, H-3–H-6, Ar'), 7.20–7.07 (m, 40 H, CH$_a$H$_b$*Ph*), 3.88–3.40 (m, 24 H, C*H*C*H*$_a$*H*$_b$OH), 2.95–2.74 (m, 16 H, C*H*$_a$*H*$_b$Ph)
8h	82 (dec.)	(0.17, CH_2Cl_2) +70 (589 nm) +72 (578 nm) +82 (546 nm)	1864.2	13.3	8.25–7.55 (m, 24 H, CHN, H-3–H-6, Ar'), 7.39–7.25 (m, 40 H, CHOH*Ph*), 4.84–4.65 (m, 8 H, C*H*OHPh), 3.74–3.63 (m, 16 H, CHC*H*$_a$*H*$_b$OH), 3.28–3.23 (m, 8 H, C*H*CH$_a$H$_b$OH)

[a] Solvents for ^{31}P and ^{1}H NMR spectra: $CDCl_3$ for **7a, b, d, e, g, h, 8a–e, g;** CD_3OD for **7c, f, 8f, h**.
[b] The protons on the substituted four aromatic rings are indicated as Ar' for all 12 protons. Wherever assignments are possible they are referred specifically as *o*- and *p*-protons with reference to the phosphorus atom. Phenyl substituents on R containing 5 protons are abbreviated as Ph.
[c] qui = quinoline, nu = quinuclidine.

including the optional interactions between the hydroxy groups in the ligands and the substrate, did not lead to significant optical inductions.

Enantioselective Hydrosilylation of Acetophenone with Diphenylsilane: In the hydrosilylation of acetophenone with diphenylsilane, the catalysts were generated in situ in acetophenone [when **7d** was used, THF (2 mL) was added to form the in situ catalyst] and the Rh:substrate ratio was 1:200. All experiments were carried out under argon. The average reaction time was 66 hours (conversion checked by ^{1}H NMR). In all cases, the ethylene-bridged ligands **7** gave slightly higher optical inductions [**7a**: 2.8% ee (*R*); **7b**: 10.3% ee (*S*); **7e**: 18.1% ee (*S*)] than the analogous more rigid *o*-phenylene-bridged ligands **8** [**8a**: 2.4% ee (*R*); **8b**: 2.6% ee (*R*); **8e**: 0% ee].

Enantioselective Allylation of 1,5-Dimethylbarbituric Acid with Allylacetate: A detailed description of the results of octaimine ligands of type **7** and **8** is given in Ref. 10b. The newly synthesized ligands **7c–g** and **8c**,**e–h** induced enantioselectivities in the range of 5–11% ee. The average reaction time was 66 hours and the average chemical conversion about 70%.

Enantioselective Grignard Cross-Coupling of 1-Phenylethylmagnesium Chloride with Vinyl Bromide: Only racemates and low chemical conversions were obtained with in situ generated Ni-catalysts of octaimine type ligands.[12]

All manipulations involving phosphanes were performed under exclusion of air using standard Schlenk techniques under purified N_2. If organometallic reagents were involved, H_2O was also excluded. Solvents were dried and degassed according to standard procedures[22] and stored under N_2. H_2O and solvents for chromatography were degassed by bubbling N_2 through the fluids for at least 8 h. Chromatographic materials [silica gel 60 (65–200 μm), Merck], and alumina 90 (neutral, activity II–III, Merck) were saturated with N_2. TLC was performed on Merck silica gel 60 F_{254} plates (visualisation with UV light and $KMnO_4$ solution).

Melting points were determined using SMP-20 (Büchi) and are not corrected. Vibrational spectra were recorded on a Beckman spectrometer IR 4240 or a Bio-Rad FT-IR FTS 155 as films or as KBr pellets. For MS, the MAT 311 A (EI) and the MAT 95 (FD) apparatus (both Finnigan) were used. The intensities are relative to the basic peak (I = 100%), possible interpretations are given within brackets. Optical rotations were measured with a Perkin-Elmer model 241 polarimeter on the specified solutions in 1 dm cells at r.t. Elemental analyses were performed by the Mikroanalytisches Labor of the Universität Regensburg. ^{1}H NMR spectra were recorded using the following spectrometers: AW-80 (80 MHz, Bruker), AC 250 (250 MHz, Bruker) and ARX 400 (400 MHz, Bruker). The chemical shifts are given in units of the δ scale relative to internal TMS. Data are reported as follows: chemical shift, multiplicity, coupling constants in Hertz, integration and assignment. For the ^{31}P NMR spectra (^{1}H-decoupled), the ARX 400 (162 MHz), external standard 85% H_3PO_4, was used.
The following compounds were synthesized according to the literature: 1,2-bis(dichlorophosphanyl)ethylene,[23] *o*-bis(dichlorophosphanyl)-benzene,[24] (*8R*,*9R*)-(+)-9-amino-9-deoxyepicinchonine.[17] BuLi was purchased from Aldrich.

Dimethyl 5-Bromoisophthalate (1):
Commercial dimethyl 5-aminoisophthalate (40.0 g, 191 mmol) was dissolved at about 60 °C in half concentrated HBr (180 mL) contained in a beaker. After cooling in an ice-bath a microcrystalline suspension was obtained, to which a 2.5 M $NaNO_2$ solution (84 mL, 210 mmol) was added under vigorous stirring. The resulting yellow diazonium compound was transferred to a cooled dropping funnel (–5 °C) and added to a cooled solution (ice bath) of CuBr (36.4 g, 0.25 mmol) in concd HBr (100 mL) under vigorous stirring. Excessive foaming was prevented by adding some drops of *n*-butanol as defoaming agent when necessary. When the addition was completed, the solution was heated on a steam bath, until no further nitrogen emission was observed (about 1 h). After cooling, the acidic phase was extracted three times with Et_2O (250 mL). The ethereal layers were washed with H_2O (600 mL) and the H_2O layers extracted with Et_2O. The solvent was removed in vacuo and the yellowish crude product was dissolved in CH_2Cl_2 and passed through a pad of silica gel (10 × 6 cm). After removal of the solvent in vacuo **1** was obtained as a colorless solid (43.9 g, 161 mmol, 84%), mp 88–89 °C (Lit.[14] mp 88–89 °C).
^{1}H NMR (80 MHz, $CDCl_3$): δ = 8.6 (m, 1 H, H-2), 8.4 (m, 2 H, H-4, H-6), 4.0 (s, 6 H, OCH_3).
IR (KBr): ν = 3090 (ar. C–H), 2970 (aliph. C–H), 1730 (C=O), 1600, 1580 cm^{-1} (C=C).

3,5-Bis(hydroxymethyl)bromobenzene (2):
A solution of diester **1** (20.6 g, 75.4 mmol) in anhyd THF (80 ml) was added dropwise at –10 °C to a stirred suspension of $LiAlH_4$ (3.5 g, 92 mmol) in anhyd THF (200 mL). After the addition was complete, the mixture was boiled under reflux for 30 min. After cooling to r.t., excess $LiAlH_4$ was decomposed by dropwise addition of a satd aq Na_2SO_4 solution (30 mL). The ethereal layer was decanted and the precipitate was washed several times with Et_2O. The combined ethereal solutions were washed with brine (2 × 50 mL), dried (Na_2SO_4) and concentrated to give the colorless solid **2** (16.04 g, 73.9 mmol, 98%); mp 90–91 °C (Lit.[15] mp 90–91 °C).
^{1}H NMR (250 MHz, acetone-d_6): δ = 7.41 (m, 2 H, H-4, H-6), 7.31 (m, 1 H, H-2), 4.37 (d, ^3J = 5.6 Hz, 4 H, CH_2OH), 4.36 (t, ^3J = 5.6 Hz, 2 H, OH).
IR (KBr): ν = 3500–3000 (OH and ar. C–H); 2950, 2920, 2880, 2840 (aliph. C–H); 1600, 1580 cm^{-1} (ar. C=C).

5-Bromoisophthalaldehyde (3):
To a solution of pyridinium chlorochromate (48.0 g, 223 mmol) in CH_2Cl_2 (250 mL) was added **2** (15.0 g, 69 mmol) and refluxed for 4 h. After cooling to r.t., the organic phase was decanted and the black oily residue was treated twice with hot Et_2O (100 mL). The combined ethereal layers were reduced in vacuo to give a greenish black solution, which was passed through a silica gel column (6 × 10 cm) with Et_2O as eluent. After removal of the solvent 11.92 g (56 mmol, 81%) of the colorless, fluffy solid **3** remained; mp 125 °C (Lit.[15] mp 124 °C).
^{1}H NMR (80 MHz, $CDCl_3$): δ = 10.0 (s, 2 H, CHO), 8.2 (m, 3 H, ArH).
IR (KBr): ν = 3080 (ar. C–H), 2980, 2965, 2860 (aliph. C–H), 1700 (C=O), 1600, 1580 cm^{-1} (C=C).

3,5-Bis(dimethoxymethyl)bromobenzene (4):
To a solution of **3** (46.0 g, 216 mmol) in MeOH (500 mL) were added trimethyl orthoformate (100 mL) and *p*-TosOH (~20 mg). After refluxing this mixture for 2 h and cooling down to r.t., K_2CO_3 (0.3 g) was added and the solvent was removed. The viscous residue was distilled in vacuo yielding 61.7 g (202 mmol, 93%) of the colorless oil **4**; bp 111 °C/10^{-2} Torr.
^{1}H NMR (80 MHz, $CDCl_3$): δ = 7.6 (br s, 2 H, H-4, H-6), 7.5 (br s, 1 H, H-2), 5.4 (s, 2 H, OCHO), 3.30 (s, 12 H, OCH_3).
IR (film): ν = 3070 (ar. C–H), 2980, 2920, 2880 (aliph. C–H), 2820 (OCH_3), 1570 cm^{-1} (C=C).

$C_{12}H_{17}BrO_4$	calc.	C	47.23	H	5.61	Br	26.18
(305.2)	found		47.17		5.61		26.07

1,2-Bis{di[3',5'-bis(dimethoxymethyl)phenyl]phosphanyl}ethane (5a):
To a cooled solution (–78 °C) of **4** (18.32 g, 60 mmol) in anhyd THF (300 mL) were added dropwise BuLi (37.5 mL ,60 mmol, 1.6 M in hexane). After stirring the solution for 30 min at this temperature, TMEDA (9.0 mL, 60 mmol) and $Cl_2PCH_2CH_2PCl_2$ (3.48 g, 2.26 mL, 15 mmol) were added. The solution was allowed to warm up to r.t. within 12 h. The solvent was completely removed in vacuo and the residue was dissolved in Et_2O (200 mL). H_2O was added (20 mL) and the layers were separated. The ethereal layer was dried (Na_2SO_4), then passed through a silica gel pad (1 × 3 cm). After removal of the solvent, a yellowish oily residue remained, which was recrystallized from CH_2Cl_2/MeOH to give 10.5 g (10.6 mmol, 71%) of the colorless solid **5a**; mp 76 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.38 (m, 12 H, ArH), 5.32 (s, 8 H, OCHO), 3.226 and 3.233 (2 s, 48 H, OCH_3), 2.10 (t, J_{PH} = 4.3 Hz, 4 H, PCH_2CH_2P).
^{31}P NMR (162 MHz, $CDCl_3$): δ = –11.3 (s).
IR (KBr): ν = 3070 (ar. C–H), 2980, 2900 (aliph. C–H), 2850 (OCH_3), 1600, 1580 cm^{-1} (C=C).
MS (FD, acetone): *m*/*z* = 991.7 (MH^+).

$C_{50}H_{72}O_{16}P_2$	calc.	C	60.59	H	7.32
(991.1)	found		60.30		7.22

1,2-Bis{di[3',5'-bis(dimethoxymethyl)phenyl]phosphanyl}benzene (5b):
According to the procedure described above, a solution of **4** (12.21 g, 40 mmol) in THF (200 mL) was treated with BuLi (25 mL, 40 mmol, 1.6 M in hexane) at –78 °C and reacted with 1,2-$Cl_2PC_6H_4PCl_2$ (2.80 g, 10.0 mmol) to give 8.83 g (8.5 mmol, 85%) of the yellow viscous oil **5b**, which could not be crystallized. It was purified by chromatography on silica gel using Et_2O as a solvent.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (t, ^4J = 1.5 Hz, 4 H, H-4'), 7.24–7.19 (m, $^3J_{PH}$ = 3.8 Hz, ^4J = 1.5 Hz, 10 H, H-2', H-6', H-4, H-5), 7.00 (m, $^3J_{PH}$ = 4.8 Hz, ^3J = 5.3 Hz, ^4J = 1.9 Hz, ^5J = 0.4 Hz, 2 H, H-3, H-6), 5.26 (s, 8 H, OCHO), 3.23 (s, 24 H, OCH_3), 3.21 (s, 24 H, OCH_3).
^{31}P NMR (162 MHz, $CDCl_3$): δ = –12.4 (s).
MS (FD, acetone): *m*/*z* = 1038.4 (M^+).

$C_{54}H_{72}O_{16}P_2$	calc.	C	62.42	H	6.98
(1039.1)	found		61.04		6.59

1,2-Bis[di(3',5'-diformylphenyl)phosphanyl]ethane (6a):
The acetal phosphane **5a** (10.5 g, 10.6 mmol) was dissolved in aq degassed acetone (100 mL) to make a 0.1 M solution, which was acidified with a few drops of 1 N HCl. The clear yellowish solution was heated under reflux. Though a white solid precipitated after 2 to 3 h, it was necessary to reflux the suspension for an additional 15 h to deprotect all acetal functions. After cooling to r.t., the remaining off-white residue was filtered and washed successively with acetone, Et_2O and CH_2Cl_2. After drying in vacuo 6.26 g (10.1 mmol, 95%) of the fluffy solid **6a** remained; mp 170 °C (dec.).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.02 (s, 8 H, CHO), 8.33 (t, ^4J = 1.5 Hz, 4 H, *p*-H), 8.17 (dt, $^3J_{PH}$ = $^6J_{PH}$ = 3.2 Hz, ^4J = 1.5 Hz, 8 H, *o*-H), 2.50 (t, 4 H, PCH_2CH_2P).
^{31}P NMR (162 MHz, $CDCl_3$): δ = –12.5 (s).
IR (KBr): ν = 3060 (ar. C–H); 2960, 2920, 2850 (al. C–H); 2765 (CHO); 1700 (C=O); 1590 (C=C); 1460; 1425 (P-ar.); 1380; 1140; 1125; 885 cm^{-1}.
MS (FD, DMSO): *m*/*z* = 622.1 (M^+).

$C_{34}H_{24}O_8P_2$	calc.	C	65.60	H	3.89
(622.5)	found		62.94		4.36

1,2-Bis[di(3',5'-diformylphenyl)phosphanyl]benzene (6b):
Analogous to the description above compound **5b** was deprotected. The acetone solution was acidified with *p*-TosOH (~20 mg). After cooling to r.t., the solvents were removed in vacuo. The remaining residue was dissolved in CH_2Cl_2 and extracted with H_2O (2 × 3 mL). The organic layer was passed through a short pad of silica gel (1 × 3 cm) and Na_2SO_4 (2 × 3 cm). The pad was washed with an additional amount of CH_2Cl_2 (50 mL) and the solvents were removed. The remaining yellowish solid was recrystallized from THF/toluene (1:1) to give 4.00 g (6.0 mmol, 70%) of the product **6b**; mp 250 °C.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 8 H, CHO), 8.30 (t, ^4J = 1.5 Hz, 4 H, *p*-H), 7.91 (dt, $^3J_{PH}$ = $^6J_{PH}$ = 3.4 Hz, ^4J = 1.5 Hz, 8 H, *o*-H), 7.49 (dd, ^3J = 5.7 Hz, ^4J = 3.3 Hz, 2 H, H-4, H-5), 7.12 (ddt, $^3J_{PH}$ = $^4J_{PH}$ = 4.0 Hz, ^3J = 5.7 Hz, ^4J = 3.3 Hz, 2 H, H-3, H-6).
^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 190.2 (s, C=O), 140.5 (t, *J* = 11.5 Hz), 138.8 (t, *J* = 10.4 Hz), 138.5 (t, *J* = 5.2 Hz), 137.3 (t, *J* = 2.9 Hz), 134,6 (t, *J* = 3.4 Hz), 131.9 (s), 131.6 (s).
^{31}P NMR (162 MHz, $CDCl_3$): δ = –13.1 (s).
IR (KBr): ν = 3030 (ar. C–H), 2930, 2905, 2820 (aliph. C–H), 2710 (CHO), 1700 (C=O), 1580 (C=C), 1450, 1425 (P–ar.), 1410, 1360, 1235, 1130, 950, 870 cm^{-1}.
MS (FD, acetone): *m*/*z* = 670.2 (M^+).

$C_{38}H_{24}O_8P_2$	calc.	C	68.07	H	3.61
(670.6)	found		65.24		3.87

Octaimine Type Expanded Ligands 7 and 8; General Procedure:
Degassed trimethyl orthoformate (50 mL) or a MeOH/trimethyl orthoformate mixture (1:1, 50 mL) was added to the octaaldehydes **6a** and **6b**, respectively, under an inert gas atmosphere to give a slightly yellow solution using **6b** or a yellowish suspension using the almost insoluble octaaldehyde **6a**. Liquid amines were added in a molar ratio of up to 12:1 (50% excess for each formyl unit) at r.t. via a syringe, solid amines were dissolved in 10% excess of MeOH and added dropwise. After stirring at r.t. for 20 h, the solvents were removed in vacuo, at the end on a water bath. When liquid amines were used as starting materials, the remaining solid residue was dried for several hours in high vacuo. The excess of solid amines was removed by adding Et_2O to the solid residue and careful decanting of the ethereal layer. This procedure was repeated three times before the ligands were dried in high vacuo.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(S)-1''-phenylethylamine)-phenyl]phosphanyl}ethane **(7a)**: According to the General Procedure, **6a** (0.40 g, 0.64 mmol) and (*S*)-(-)-1-phenylethylamine (1.00 mL, 8.0 mmol) afforded 0.87 g (0.60 mmol, 93%) of **7a**; mp 110–115 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(R)-1''-cyclohexylethylamine)phenyl]phosphanyl}ethane **(7b)**: According to the General Procedure, **6a** (0.54 g, 0.87 mmol) and (*R*)-(–)-1-cyclohexylethylamine (1.5 mL, 10.2 mmol) yielded 1.17 g (0.78 mmol, 90%) of **7b**; mp 76–80 °C.

(+)-1,2-Bis{bis[3',5'-bis(N-methyliden-(R)-alaninol)phenyl]phosphanyl}ethane **(7c)**: According to the General Procedure, **6a** (0.51 g, 0.82 mmol) and (*R*)-(-)-alaninol (0.55 ml, 7.05 mmol) gave 0.89 g (0.76 mmol, 93%) of **7c**; mp 146–148 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methyliden-(R)-2''-aminobutan-1''-ol)phenyl]phosphanyl}ethane **(7d)**: According to the General Procedure, **6a** (0.39 g, 0.63 mmol) and (*R*)-(-)-2-aminobutan-1-ol (0.47 mL, 5.01 mmol) yielded 0.69 g (0.58 mmol, 92%) of **7d**; mp 94–98 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(S)-valinol)phenyl]phosphanyl}ethane **(7e)**: According to the General Procedure, **6a** (0.44 g, 0.70 mmol) and (*S*)-(+)-valinol (0.58 g, 5.65 mmol) gave 0.88 g (0.68 mmol, 97%) of **7e**; mp 76–82 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(S)-leucinol)phenyl]phosphanyl}ethane **(7f)**: According to the General Procedure, **6a** (0.54 g,

0.87 mmol) and (*S*)-(+)-leucinol (0.97 g, 8.20 mmol) afforded 1.20 g (0.85 mmol, 98%) of **7f**; mp 120–125 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(S)-phenylalaninol)phenyl]-phosphanyl}ethane **(7g)**: According to the General Procedure, **6a** (0.54 g, 0.87 mmol) and (*S*)-(–)-phenylalaninol (1.07 g, 7.07 mmol) yielded 1.21 g (0.72, mmol, 82%) of **7g**; mp 69–73 °C.

(+)-1,2-Bis{bis[3',5'-bis(N-methyliden-(8R,9R)-9-amino-9-deoxy-epicinchonine)phenyl]phosphanyl}ethane **(7h)**: According to the General Procedure, **6a** (0.50 g, 0.80 mmol) and (8*R*,9*R*)-(+)-9-amino(9-deoxy)epicinchonine (2.10 g, 7.16 mmol) yielded 2.15 g (0.76 mmol, 95%) of **7h**; mp 190–195 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(S)-1''-phenylethylamine)-phenyl]phosphanyl}benzene **(8a)**: According to the General Procedure, **6b** (1.00 g, 1.49 mmol) and (*S*)-(-)-1-phenylethylamine (1.83 mL, 14.3 mmol) gave 1.75 g (1.17 mmol, 79%) of **8a**; mp 92–95 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(R)-1''-cyclohexylethy-lamine)phenyl]phosphanyl}benzene **(8b)**: According to the General Procedure, **6b** (0.58 g, 0.86 mmol) and (*R*)-(–)-1-cyclohexylethylamine (1.03 mL, 7.0 mmol) afforded 1.10 g (0.71 mmol, 83%) of **8b**; mp 110–115 °C.

(+)-1,2-Bis{bis[3',5'-bis(N-methyliden-(R)-alaninol)phenyl]phosphanyl}benzene **(8c)**: According to the General Procedure, **6b** (0.75 g, 1.12 mmol) and (*R*)-(-)-alaninol (0.72 mL, 9.23 mmol) yielded 1.15 g (1.02 mmol, 91%) of **8c**; mp 170–175 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methyliden-(R)-2''-aminobutan-1''-ol)phenyl]phosphanyl}benzene **(8d)**: According to the General Procedure, **6b** (0.71 g, 1.06 mmol) and (*R*)-(–)-2-aminobutan-1-ol (1.88 mL, 20.0 mmol) yielded 1.29 g (1.04 mmol, 98%) of **8d**; mp 82–83 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(S)-valinol)phenyl]phosphanyl}benzene **(8e)**: According to the General Procedure, **6b** (0.50 g, 0.75 mmol) and (*S*)-(+)-valinol (0.63 g, 6.1 mmol) yielded 0.98 g (0.72 mmol, 97%) of **8e**; mp 68–72 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(S)-leucinol)phenyl]phosphanyl}benzene **(8f)**: According to the General Procedure, **6b** (0.50 g, 0.74 mmol) and (*S*)-(+)-leucinol (0.71 g, 6.06 mmol) gave 1.07 g (0.73 mmol, 98%) of **8f**; mp 105–110 °C.

(–)-1,2-Bis{bis[3',5'-bis(N-methylidene-(S)-phenylalaninol)phenyl]-phosphanyl}benzene **(8g)**: According to the General Procedure, **6b** (1.00 g, 1.49 mmol) and (*S*)-(–)-phenylalaninol (2.00 g, 13.2 mmol) yielded 2.44 g (1.41 mmol, 94%) of **8g**; mp 83 °C (dec.).

(+)-1,2-Bis{bis[3',5'-bis(N-methyliden-(1S,2S)-2-amino-1-phenyl-propane-1,3-diol)phenyl]phosphanyl}benzene **(8h)**: According to the General Procedure, **6b** (0.53 g 0.80 mmol) and (1*S*,2*S*)-(+)-2-amino-1-phenylpropane-1,3-diol (1.09 g, 6.5 mmol) yielded 1.44 g (0.77 mmol, 98%) of **8h**; mp 82 °C (dec.).

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