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Highly Efficient and Versatile Phosphine-Phosphoramidite Ligands for Asymmetric Hydrogenation

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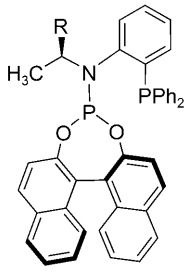
Abstract: A set of novel phosphine-phosphoramidite ligands possessing two elements of chirality have been prepared through a modular synthetic approach. The ligands (11b*S*)-*N*-[2-(diphenylphosphino)phenyl]-*N*-[(*S*)-1-phenylethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine [(S_a,S_c)-**1a**] and (11b*R*)-*N*-[2-(diphenylphosphino)phenyl]-*N*-[(*S*)-1-(1-naphthyl)ethyl]dinaphtho[2,1-*d*:1′,2′-*f*]-[1,3,2]dioxaphosphepin-4-amine [(S_a,S_c)-**1b**] are unique in providing enantioselectivities ≥96% *ee* and ≥94% *ee*, respectively, in mechanistically distinct hydrogenations of C=C, C=N and C=O double bonds in combination with three different transition metals (rhodium, iridium, and ruthenium, respectively). Particularly remarkable are the enantiomeric excesses up to 97% achieved in the iridium-catalyzed hydrogenation of 2-substituted quinolines, where (11b*S*)-*N*-[2-(diphenylphosphino)phenyl]-*N*-[(*S*)-1-(naphthalen-1-yl)ethyl]-8,9,10,11, 12,13,14,15-octahydrodinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine [(S_a,S_c)-**2**] proved to be the most selective ligand. Substantially lower *ee*s were obtained with the mismatched diastereomer (R_a,S_c)-**1b** and with the *N*-phenyl-substituted ligand **1c**, missing a second element of chirality.

Keywords: asymmetric catalysis; enantioselective hydrogenation; iridium; phosphine-phosphoramidite ligands; rhodium; ruthenium

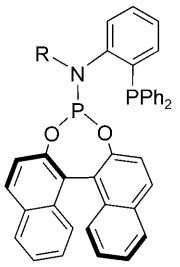
Asymmetric hydrogenation catalysed by transition metal complexes is a powerful tool for the synthesis of a variety of enantiomerically pure or enriched compounds and several industrial applications reflect its practical utility.[1] Although a plethora of ligands form efficient catalytic systems, most of them operate well only with specific metals or for certain functional groups, limiting the scope of their potential application.[1] Thus, new chiral ligands should ideally be able to generate highly active *and* enantioselective catalysts with different metal centres having a broad substrate acceptance (privileged ligands).[2] Moreover, such ligands should be accessible through a concise synthesis and easily modified in order to allow fine tuning of the lead structure.

In 2000, we introduced a family of phosphine-phosphoramidite ligands, QUINAPHOS, fulfilling these requisites.[3] Since then, several phosphine-phosphoramidites and other electronically dissymmetric P,P ligands having a phosphoramidite donor group have been reported and successfully used in catalysis.[4] Recently, Kostas et al. described the phosphine-phosphoramidite ligand Me-AnilaPhos **1d** and applied it in the Rh-catalysed hydrogenation of olefins with good results.[5] We report here that with the related, readily accessible ligands (S_a,S_c)-**1a, 1b** and **2** – bearing an additional stereocentre in the amine part – higher enantiomeric excesses are obtained as compared to (R_a)-**1c** and **1d**. Most notably, the new ligands give high to excellent asymmetric induction in mechanistically distinct hydrogenation reactions of C=C, C=N and C=O double bonds using Rh, Ir, and Ru catalysts, respectively.

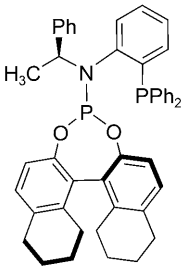
The synthetic route to ligands **1a–c** and **2** is depicted in Scheme 1. The aminophosphine key intermediates **4a–c** were prepared following the procedure of Liang et al.[6] In the first step, the Pd-catalysed Buchwald–Hartwig amination was applied to obtain the 2-fluoro-aniline derivatives **3a–c**. In the second step, phosphorylation of **3a–c** with potassium diphenylphosphide gave the desired products **4a–c** in good yields (52–60%) on a 10 g scale. Deprotonation of the amino function of **4a–c** with *n*-butyllithium/TMEDA and *in situ* reaction of the resulting lithium amide with phosphorochloridites **5** and **6** derived from (S_a)-BINOL or (R_a)-BINOL[7] and (S_a)-H_8-BINOL,[8] respectively, produced the phosphine-phosphoramidites **1a–c** and **2**. After filtration over basic alumina or a PTFE membrane and recrystallisation from CH_2Cl_2/



(S_a,S_c)-**1a**; R = Ph
(S_a,S_c)-**1b**; R = 1-naphthyl



(R_a,S_c)-**1b**; R = (*S*)-1-(1-naphthyl)-ethyl
(R_a)-**1c**; R = Ph
(R_a)-**1d**; R = Me (Me-AnilaPhos)[5]

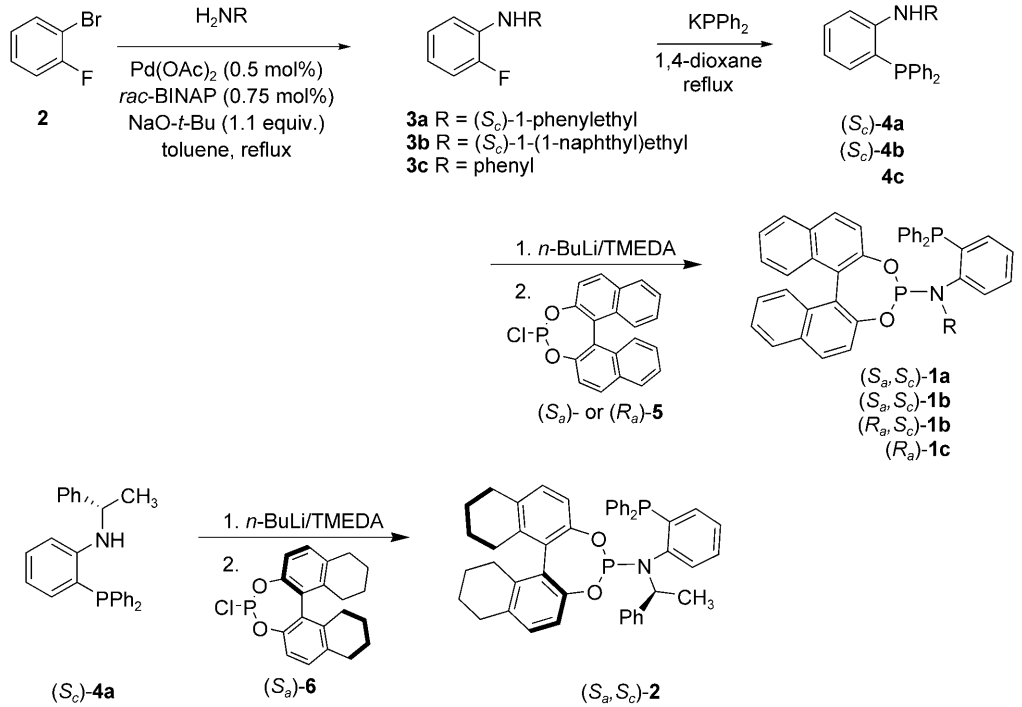


(S_a,S_c)-**2**

pentane or toluene/ethanol, the ligands **1a–c** and (S_a,S_c)-**2** were obtained in sufficient purity for catalytic application and in reasonable yields (37–66%).[9] The overall synthetic procedure is highly modular since diverse primary amines and phosphines can be introduced in the first and second step, as well as different phosphorus moieties in the last step.

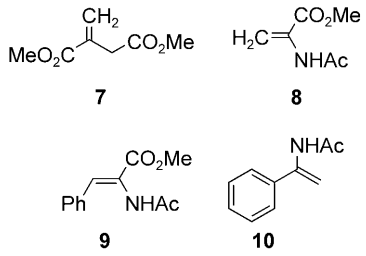
The catalytic potential of the new ligands was first evaluated in the Rh-catalysed hydrogenation of C=C double bonds using the corresponding [Rh(COD)L]X [L = **1a–c** or **2**; X = BF_4 or bis(trifluoromethylsulfonyl)amide, NTf_2; COD = 1,5-cyclooctadiene] complexes. In all reactions full conversion was obtained within one hour corresponding to TOFs $\geq 1000\ h^{-1}$ and high to excellent enantioselectivities were achieved (Table 1). The hydrogenation of the benchmark substrate dimethyl itaconate (**7**) with two diastereomers of **1b** clearly shows that the absolute configuration of the product is controlled by the axial chirality of the binaphthyl backbone (entry 1 *vs.* entry 2). Moreover, while (R_a,S_c)-**1b** resulted in a lower *ee* of 94% (mismatched diastereomer, entry 1), almost perfect enantioselectivity was achieved with (S_a,S_c)-**1b** (matched diastereomer, entry 2). Lower enantioinduction of 96% *ee* (*R*) was also obtained with the ligand (R_a)-**1c**, missing the additional stereocenter (entry 5). On the other hand, >99% *ee* was observed for all ligands with the additional stereocenter in *S*-configuration, irrespective of the substituent (**1a**/**1b**) or the BINOL backbone (**1a**/**2**) (entries 2–4).

Next, the scope of the complex [Rh(COD){(S_a,S_c)-**1a**}]BF_4 as hydrogenation catalyst was addressed using methyl α-acetamidoacrylate **8**, methyl α-acetamidocinnamate **9** and *N*-acetylphenylethylenamide **10** as representative substrates for dehydroamino acid derivatives and enamides, respectively. All these substrates could be rapidly hydrogenated with excellent enantioselectivity of ≥99% *ee* (entries 7–9).



Scheme 1. Synthesis of ligands **1a–c** and **2**.

Table 1. Rh-catalysed asymmetric hydrogenation of **7–10** with preformed complexes [Rh(COD)L]X.[a]



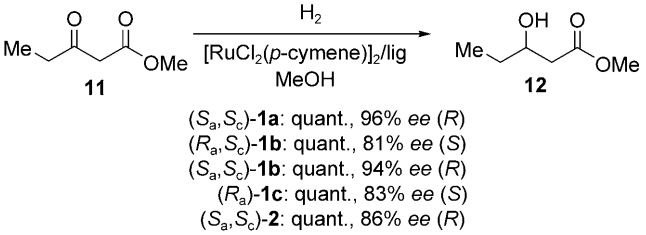
Entry	Ligand	Substrate	Conv. [%]	*ee* [%]
1[b]	(R_a,S_c)-**1b**	**7**	>99	94 (*R*)
2[b]	(S_a,S_c)-**1b**	**7**	>99	>99 (*S*)
3[c]	(S_a,S_c)-**1a**	**7**	>99	>99 (*S*)
4[b]	(S_a,S_c)-**2**	**7**	>99	>99 (*S*)
5[c]	(R_a)-**1c**	**7**	>99	96 (*R*)
6[c,d]	(S_a,S_c)-**1a**	**7**	>99	>99 (*S*)
7[c]	(S_a,S_c)-**1a**	**8**	>99	99 (*R*)
8[c]	(S_a,S_c)-**1a**	**9**	>99	99 (*R*)
9[c]	(S_a,S_c)-**1a**	**10**	>99	99 (*R*)

[a] *Reaction conditions:* 2 mL CH_2Cl_2, 1.0 mmol substrate, 0.1 mol% [Rh(COD)L]X, 10 bar H_2, 1 h, room temperature.
[b] X = NTf_2.
[c] X = BF_4.
[d] 5.0 mmol **7**, 0.02 mol% catalyst, 15 bar H_2, 32 min.

For a quantitative assessment of the catalytic activity of [Rh(COD){(S_a,S_c)-**1a**}] BF_4 the hydrogen consumption was monitored for substrate **7** by following the pressure drop at a catalyst loading of 0.02 mol%. An initial TOF of 14,100 h^{-1} could be estimated from the slope of the pressure curve and constant pressure was reached within 32 min, corresponding to a TOF_{av} of 9,400 h^{-1}. Offline analysis confirmed complete conversion and showed that the enantioselectivity remained at a high level even at this low catalyst loading (entry 6).

Next, the new ligands were applied in a typical Ru-catalysed hydrogenation using the β-keto ester **11** as benchmark substrate. The corresponding β-hydroxy ester **12** was obtained quantitatively after 16 h at 60 °C and 60 bar of H_2 in good to high enantiomeric excesses (Scheme 2). In this reaction the S_a,S_c diastereomers of **1a** and **1b** led again to the highest *ee*s (94% and 96%, respectively). Somewhat lower enantioselectivity (86%) was obtained with (S_a,S_c)-**2** comprising the H_8-BINOL backbone. Lower enantioselectivities in favour of the opposite enantiomer were achieved with (R_a)-**1c** (83%) and (R_a,S_c)-**1b** (81%) under the same conditions. Direct comparison of the two diastereomers of **1b** confirms again the pronounced cooperativity of the two stereoelements.

Substituted 1,2,3,4-tetrahydroquinolines are an important class of biologically active compounds.[10]

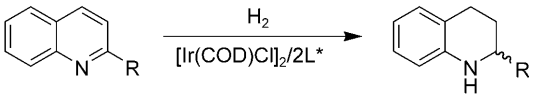


Scheme 2. Ru-catalysed hydrogenation of β-keto ester **11**.

Most recently, the asymmetric synthesis of tetrahydroquinolines with a chiral centre in two positions has been achieved by Ir-catalysed hydrogenation of 2-substituted quinolines. Benchmark ligands for this transformation are C_2-symmetrical bisphosphines like MeO-Biphep or H_8-BINAPO.[11] Mršić et al. applied the concept of mixing chiral monodentate phosphoramidites with achiral monodentate phosphines to this reaction obtaining up to 89% *ee*.[12] Encouraged by this report, we tested the new phosphine-phosphoramidite ligands in the same reaction (Table 2).

Using ligand (R_a)-**1c** under the conditions optimised by Wang et al.[11a] 2-methylquinoline **12a** was quantitatively hydrogenated with a moderate enantioselectivity of 67% *ee* in favour of the *S*-enantiomer (entry 1). However, a high *ee* of 96% (*R*) was obtained with (S_a,S_c)-**1a** (entry 2). The difference in performance between (S_a,S_c)-**1a** and (R_a)-**1c** is even more pronounced than in the Rh- and Ru-catalysed hydrogenation and underlines again the importance of the presence of a

Table 2. Ir-catalysed hydrogenation of 2-substituted quinolines.[a]



12a: R = Me
12b: R = Bu
12c: R = Ph

13a: R = Me
13b: R = Bu
13c: R = Ph

Entry	Ligand	Substrate	*t* [h]	Conv. [%]	*ee* [%]
1	(R_a)-**1c**	**12a**	16	>99	67 (*S*)
2	(S_a,S_c)-**1a**	**12a**	16	>99	96 (*R*)
3	(S_a,S_c)-**2**	**12a**	16	96	96 (*R*)
4	(S_a,S_c)-**1b**	**12a**	48	>99	97 (*R*)
5	(R_a,S_c)-**1b**	**12a**	48	>99	81 (*S*)
6	(S_a,S_c)-**1a**	**12b**	16	>99	94 (*R*)
7	(S_a,S_c)-**1b**	**12b**	48	>99	92 (*R*)
8	(S_a,S_c)-**2**	**12b**	48	84	97 (*R*)
9	(S_a,S_c)-**1a**	**12c**	16	>99	90 (*S*)
10	(S_a,S_c)-**1b**	**12c**	48	>99	89 (*S*)
11	(S_a,S_c)-**2**	**12c**	16	78	95 (*S*)

[a] *Reaction conditions:* 2 mL toluene, 1.0 mmol substrate, 1 mol% catalyst, 40 bar H_2, room temperature, catalyst formed *in situ* from $[Ir(COD)Cl]_2$ (0.5 mol%), ligand (1.1 mol%) and I_2 (5 mol%).

second element of chirality in (S_a,S_c)-**1a** to get high asymmetric induction. Enantioselectivities in the same range have been obtained also with (S_a,S_c)-**2** and (S_a,S_c)-**1b** (entries 3 and 4), whereas the R_a,S_c diastereomer of **1b** led preferentially to the opposite enantiomer with a reduced enantioselectivity of 81% (entry 5).

Ligands (S_a,S_c)-**1a**, (S_a,S_c)-**1b** and (S_a,S_c)-**2** resulted in high enantioselectivities also in the hydrogenation of 2-butylquinoline **12b** (94%, 92% and 97% *ee*, respectively, entries 6-8) as well as of 2-phenylquinoline **12c** (90%, 89% and 95% *ee*, respectively, entries 9–11). These values represent some of the highest enantioselectivities reported to date for the Ir-catalysed hydrogenation of quinolines.[11,12,13]

In summary, we have disclosed new phosphine-phosphoramidite ligands containing two elements of chirality, which can be prepared *via* a modular approach. (S_a,S_c)-**1a**, (S_a,S_c)-**1b** and (S_a,S_c)-**2** proved to be very efficient ligands for asymmetric Rh-catalysed hydrogenation of different classes of functionalised olefins with *ee*s $\geq$99% and TOFs up to 14,100 h^{-1}. High enantioselectivities have been achieved with (S_a,S_c)-**1a** and (S_a,S_c)-**1b** also in the Ru-catalysed hydrogenation of β-keto esters and in the Ir-catalysed asymmetric hydrogenation of 2-substituted quinolines. The ligand (S_a,S_c)-**2** resulted in enantioselectivities $\geq$95% both in the hydrogenation of 2-alkyl- and 2-arylquinolines. Experiments with the opposite diastereomers or ligands lacking the stereogenic centre substantiated the synergistic cooperativity of both elements of chirality in the (S_a,S_c) diastereomers. Hence, these ligands represent privileged structural motifs for asymmetric hydrogenation leading to high selectivities and activities in mechanistically distinct hydrogenations utilising different metal centres.

Experimental Section

General Remarks

All reactions were carried out under an inert atmosphere of dry and oxygen-free argon either with the use of standard Schlenk techniques or in a glovebox. All solvents were dried and distilled prior to use. NMR spectra were measured with a Bruker AV-600 or a Bruker DPX-300 spectrometer. Chemical shifts are given relative to TMS by using the solvent signal as internal reference for ^{1}H NMR as well as for ^{13}C NMR and H_3PO_4 (85%) as external reference for ^{31}P NMR spectroscopy. Mass spectra were recorded on a Finnigan MAT 8200 (MS and HR-MS-EI), Bruker FTICR-Apex III (HR-MS-ESI) or Finnigan MAT 95 (NBA, Cs^+ gun operating at 70 eV). Optical rotations were measured with a Jasco P-1020 polarimeter. Aniline was distilled under argon prior to use, 1-bromo-2-fluorobenzene, (*S*)-1-phenylethylamine, sodium *tert*-butoxide, *rac*-BINAP, palladium acetate and potassium diphenylphosphide (0.5 M in THF) were used as purchased. *n*-Butyllithium was titrated prior to use with *N*-benzylbenzamide.[14] Phosphorochloridites **5**[7] and **6**[8] were prepared according to literature procedures.

Synthesis of *N*-[(*S*)-1-Phenylethyl]-2-fluoraniline [(*S*)-3a]

To a yellow solution of $Pd(OAc)_2$ (67.3 mg, 0.30 mmol) and *rac*-BINAP (268.0 mg, 0.45 mmol) in toluene (30 mL), 1-bromo-2-fluorobenzene (60 mmol, 6.6 mL) and (*S*)-1-phenylethylamine (6.92 mL, 60 mmol) were successively added by syringe. As last component sodium *tert*-butoxide (70 mmol, 6.74 g) was added, whereby the solution turned immediately deep red. The mixture was refluxed for 4 d and the reaction was monitored by TLC. After complete consumption of 1-bromo-2-fluorobenzene, the reaction mixture was cooled down to room temperature and extracted with dichloromethane (3×15 mL). The combined organic phase was dried over $NaSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, pentane/ethyl acetate 10:1 R_f=0.64); yield: 84%, waxy solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.51 (d, J=6.6 Hz, 3H, CH_3), 4.26 (br, 1H, NH), 4.46 (m, 1H, CH), 6.40 (m, 1H, Ar), 6.52 (m, 1H, Ar), 6.78 (m, 1H, Ar), 6.92 (m, 1H, Ar), 7.20 (m, 1H, Ar), 7.31 (m, 4H, Ar); ^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ=25.1, 53.3, 113.2 (d, J=3.0 Hz), 114.2 (d, J=18.8 Hz), 116.5 (d, J=7.0 Hz), 124.4 (d, J=3.4 Hz), 125.8, 127.0, 128.7, 135.7 (d, J=11.4 Hz), 144.8, 151.4 (d, J=237.4 Hz); ^{19}F{^{1}H}-NMR ($CDCl_3$, 282 MHz): δ=−136.5; MS (EI): m/z (%)=215 (M^+, 54), 200 (55), 122 (13), 111 (67), 105 (100), 79 (14), 77 (21); HR-MS (ESI): m/z=215.111029, calcd. for $C_{14}H_{14}NF$: 215.111326; $[\alpha]_D^{20}$: +7.6 (*c* 0.55, CH_2Cl_2).

Synthesis of *N*-[(*S*)-1-(1-naphthyl)ethyl]-2-fluoraniline [(*S*)-3b]

The title compound was obtained by the procedure described above using (*S*)-1-(1-naphthyl)ethylamine (5.16 g, 30 mmol) as the amine and purified *via* column chromatography (SiO_2, pentane/ethyl acetate 20:1, R_f=0.54); yield: 93%, waxy solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.70 (d, J=6.5 Hz, 3H, CH_3), 4.42 (br, 1H, NH), 5.29 (m, 1H, CH), 6.29 (m, 1H, Ar), 6.54 (m, 1H, Ar), 6.74 (m, 1H, Ar), 6.98 (m, 1H, Ar), 7.41 (m, 1H, Ar), 7.57 (m, 3H, Ar), 7.76 (m, 1H, Ar), 7.91 (m, 1H, Ar), 8.16 (m, 1H, Ar); ^{13}C{^{1}H}-NMR (75 MHz, $CDCl_3$): δ=23.8, 49.5, 113.2 (d, J=3.4 Hz, Ar), 114.2 (d, J=18.9 Hz, Ar, CH), 116.5 (d, J=6.8 Hz), 122.5 (d, J=17.5 Hz), 124.5, 124.6, 125.6, 125.9, 126.2, 127.6, 129.2, 130.7, 134.2, 135.6 (d, J=11.5 Hz), 139.5, 151.5 (d, J=237.5 Hz); ^{19}F{^{1}H}-NMR ($CDCl_3$, 282 MHz): δ=−136.6; MS (EI): m/z (%)=265 (M^+, 27), 250 (9), 155 (100), 128 (8), 122 (6), 115 (5), 95 (3), 75 (2); HR-MS (ESI): m/z=265.126676, calcd. for $C_{18}H_{16}NF$ (M^+): 265.126401; $[\alpha]_D^{20}$: +166.6 (*c* 0.53, CH_2Cl_2).

Synthesis of *N*-Phenyl-2-fluoraniline (3c)

The title compound was obtained by the procedure described above using aniline (5.5 mL, 60 mmol) as the amine and purified *via* column chromatography (SiO_2, pentane/ethyl acetate 20:1, R_f=0.64); yield: 83% colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=5.79 (br, 1H, NH), 6.84 (m, 1H, Ar), 6.94–7.15 (m, 5H, Ar), 7.23–7.38 (m, 3H, Ar);

$^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): $\delta = 115.6$ ($J = 18.7$ Hz), 117.4 (d, $J = 2.1$ Hz), 118.8, 120.7 (d, $J = 6.9$ Hz), 121.9, 124.4 (d, $J = 3.8$ Hz), 129.6, 131.9 (d, $J = 11.1$ Hz), 142.3, 153.2 (d, $J = 242.0$ Hz); $^{19}F\{^1H\}$-NMR ($CDCl_3$, 282 MHz): $\delta = -132.1$; MS (EI): m/z (%) = 187 (M^+, 100), 167 (10), 159 (3), 77 (4), 51 (5); HR-MS (ESI): $m/z = 187.079730$, calcd. for $C_{12}H_{10}NF$ (M^+): 187.079554.

Synthesis of *N*-[(*S*)-1-phenylethyl]-2-diphenylphosphinoaniline [(*S*)-4a]

Potassium diphenylphosphide (50 mmol, 100 mL, 0.5 M in THF) was transferred into a Schlenk flask by means of a cannula. The solvent was removed under reduced pressure and a solution of **3a** (10.75 g, 50 mmol) in 1,4-dioxane (50 mL) was added *via* syringe. The orange solution was refluxed for 5 d and the reaction was monitored by ^{31}P NMR spectroscopy. After cooling to room temperature, the solvent was removed under reduced pressure, degassed water (40 mL) was added to the residue and the aqueous phase was extracted with dichloromethane (3×50 mL). The combined organic phase was dried over $NaSO_4$ and the solvent was removed under reduced pressure. The product was purified by column chromatography under an inert atmosphere (Al_2O_3 pH 9.5, pentane:$CH_2Cl_2 = 4:1$, $R_f = 0.45$); yield: 55%, colourless oil. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.26$ (d, $J = 6.4$ Hz, 3H), 4.38 (m, 1H, CH), 4.91 (m, 1H, NH), 6.29 (dd, $J = 5.1$ Hz, 8.4 Hz, 1H, Ar), 6.48 (t, $J = 7.5$ Hz, 1H, Ar), 6.75 (td, $J = 7.5$ Hz, 1.8 Hz, 1H, Ar), 6.95–7.20 (m, 7H, Ar), 7.29 (m, 9H, Ar); $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): $\delta = 25.3$, 53.6, 111.4 (d, $J = 2.0$ Hz), 117.1 (d, $J = 2.0$ Hz), 118.6 (d, $J = 2.0$ Hz), 125.8, 126.7, 128.52, 128.58, 128.68, 128.82, 128.85, 130.5, 133.6 (d, $J = 4.2$ Hz), 133.8 (d, $J = 4.2$ Hz), 134.6 ($J = 6.9$ Hz), 135.4 (d, $J = 7.9$ Hz), 135.5 (d, $J = 7.9$ Hz), 145.2, 149.7 (d, $J = 16.1$ Hz); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 125 MHz): $\delta = -19.9$; MS (EI): m/z (%) = 381 (M^+, 100), 367 (16), 366 (60), 304 (11), 303 (13), 288 (26), 277 (19), 276 (18), 261 (31), 198 (33), 194 (25), 183 (48), 181 (25), 167 (11), 105 (20), 77 (13); HR-MS (ESI): $m/z = 404.153860$, calcd. for $C_{26}H_{24}NPNa$ $(M+Na)^+$: 404.154180; $[\alpha]_D^{20}$: +122.7 (c 0.61, CH_2Cl_2).

Synthesis of *N*-[(*S*)-1-(1-Naphthyl)ethyl]-2-diphenylphosphinoaniline [(*S*)-4b]

Title compound was obtained by the procedure described above using **3b** (7.50 g, 30 mmol) instead of **3a**. The product was purified by recrystallisation from CH_2Cl_2/pentane at −18 °C and obtained as colourless crystals; yield: 52%. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.44$ (d, $J = 6.6$ Hz, 3H), 5.09 (m, 1H, NH), 5.21 (m, 1H, CH), 6.19 (m, 1H, Ar), 6.51 (m, 1H, Ar), 6.82 (m, 1H, Ar), 6.93 (m, 1H, Ar), 7.23–7.61 (m, 14H, Ar), 7.65 (m, 1H, Ar), 7.84 (m, 1H, Ar), 8.07 (m, 1H, Ar); $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$) $\delta = 23.9$, 49.7 , 111.5, 117.2, 118.6 (d, $J = 7.6$ Hz), 122.4 (d, $J = 8.5$ Hz), 125.4, 126.0 (d, $J = 8.5$ Hz), 127.4, 128.3, 128.7 (d, $J = 7.6$ Hz), 128.9 (d, $J = 5.7$ Hz), 129.2, 130.7 (d, $J = 5.7$ Hz), 133.7, 133.9, 134.1, 134.7 (d, $J = 7.6$ Hz), 135.4, 135.5, 135.6, 140.0, 149.5, 149.7; $^{31}P\{^1H\}$-NMR ($CDCl_3$, 125 MHz): $\delta = -18.8$; MS (EI): m/z (%) = 431 (M^+, 100), 416 (44), 338 (10), 304 (12), 303 (45), 288 (32), 276 (17), 261 (12), 198 (30), 183 (18), 155 (27), 153 (11), 77 (4); HR-MS (ESI): $m/z = 432.187562$, calcd. for $C_{26}H_{24}NPNa$ $(M+H)^+$: 432.187867; $[\alpha]_D^{20}$: +143.1 (c 0.62, CH_2Cl_2).

Synthesis of *N*-Phenyl-2-diphenylphosphinoaniline (4c)

The title compound was obtained by the procedure described above using **3c** (9.38 g, 50 mmol) instead of **3a**. The product was purified by recrystallisation from CH_2Cl_2/pentane at −18 °C and obtained as a white crystalline solid; yield: 60%. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 6.26$ (br, 1H, NH), 6.83–7.01 (m, 6H, Ar), 7.20–7.42 (m, 13H, Ar); $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): $\delta = 116.7$, 119.0, 121.1 (d, $J = 2.2$ Hz), 121.4, 124.5 ($J = 9.3$ Hz), 128.7, 128.8 (d, $J = 16.2$ Hz), 129.2, 130.0, 133.7 (d, $J = 19.4$ Hz), 134.6 (d, $J = 3.9$ Hz), 135.4 (d, $J = 8.7$ Hz), 142.7, 146.7 (d, $J = 18.7$ Hz); $^{31}P\{^1H\}$-NMR ($CDCl_3$, 125 MHz): $\delta = -19.2$; MS (EI): m/z (%) = 353 (41), 352 (M^+, 100), 274 (2), 272 (1), 198 (10), 183 (3), 167 (3), 77 (2); HR-MS (ESI): $m/z = 376.122556$, calcd. for $C_{24}H_{20}NPNa$ $(M+Na)^+$: 376.122800.

Synthesis of (11b*S*)-*N*-[2-(Diphenylphosphino)-phenyl]-*N*-[(*S*)-1-phenylethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine [(S_a,S_c)-1a]

To a solution of aminophosphine **4a** (762 mg, 2.0 mmol) in THF (10 mL), TMEDA (2.0 mmol, 0.29 mL) was added and the solution was cooled to −70 °C in dry ice bath. *n*-Butyllithium (2.0 mmol, 1.25 mL, 1.6 M in hexanes) was added dropwise causing the solution to turn yellow immediately. The mixture was stirred for 2 h and a solution of phosphorochloridite (*S*)-**5** (700 mg, 2.0 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure. The residue was taken up in toluene and filtered over basic alumina. Toluene was removed under reduced pressure and the crude product was purified by recrystallisation from CH_2Cl_2/pentane at −18 °C; yield: 49%; white, crystalline solid. ^1H NMR (600 MHz, $CDCl_3$): $\delta = 1.77$ (br, 3H, CH_3), 4.67 (br, 1H, CH), 6.6 (br, 1H, Ar), 6.75–7.64 (m, 26H, Ar), 7.87 (d, $J = 8.2$ Hz, 2H, Ar), 7.91 (d, $J = 8.2$ Hz, 2H, Ar); $^{13}C\{^1H\}$-NMR (150 MHz, $CDCl_3$): $\delta = 22.8$, 62.4, 122.3, 123.2, 124.1, 124.6 (d, $J = 52.7$ Hz), 125.9, 126.0, 127.0, 127.3, 127.5, 128.1, 128.2, 128.3 (d, $J = 5.1$ Hz), 128.45, 128.49, 129.0, 129.1, 129.5, 130.2, 131.1 (d, $J = 121.1$ Hz), 132.9, 133.5 (d, $J = 19.5$ Hz), 133.6 (d, $J = 19.5$ Hz), 136.3, 138.1 (d, $J = 13.6$ Hz), 139.3 (d, $J = 14.6$ Hz), 142.5, 149.6, 150.1; $^{31}P\{^1H\}$-NMR (250 MHz, $CDCl_3$): $\delta = -17.1$ (br), 140.1 (br); MS (EI): m/z (%) = 695 (M^+, 13), 590 (19), 381 (28), 380 (100), 302 (13); HR-MS (ESI): $m/z = 696.221585$, calcd. for $C_{46}H_{36}NO_2P_2$ $(M+H)^+$: 696.221104; $[\alpha]_D^{20}$: +127.0 (c 0.66, CH_2Cl_2).

Synthesis of (11b*S*)-*N*-[2-(Diphenylphosphino)-phenyl]-*N*-[(*S*)-1-(1-naphthyl)ethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine [(S_a,S_c)-1b]

The title compound was obtained by the procedure described above using toluene as the solvent, (*S*)-**4b** (214.8 mg, 0.5 mmol) and (*S*)-**5** (192.9 mg, 0.55 mmol). After 16 h, the reaction mixture was filtered through a PTFE membrane and the solvent removed under reduced pressure. The resi-

due was recrystallised from toluene/ethanol affording the product with a purity of 88% based on ^{31}P NMR; yield: 236 mg (66%). Analytically pure product was obtained after a second recrystallisation; yield: 19 mg (5%). ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta = 2.04$ (br, 3H, CH_3), 5.48 (br, 1H, CH), 6.38 (br, 2H, Ar), 6.69 (br, 1H, Ar), 6.92 (br, 1H, Ar) 7.81–6.69 (m, 28H, Ar), 8.26 (br, 1H, Ar); ^{13}C NMR (150 MHz, CD_2Cl_2): $\delta = 23.5$ (d, $J = 26.9$ Hz, CH_3), 60.2 (CH), 122.4 (Ar, CH), 123.2 (Ar, CH), 125.3 (Ar, CH), 125.9 (Ar, CH), 126.3 (Ar, CH), 126.5 (Ar, CH), 126.8 (Ar, CH), 127.2 (Ar, CH), 127.4 (Ar, CH), 128.3 (Ar, CH), 128.4 (Ar, CH), 128.6 (Ar, CH), 128.8 (Ar, CH), 129.0 (Ar, CH), 129.2 (Ar, CH), 129.3 (Ar, CH), 129.9 (Ar, CH), 130.7 (Ar, CH), 130.9 (Ar, C_q), 131.1 (Ar, CH), 131.9 (Ar, C_q), 133.1 (d, $J = 12.6$ Hz, Ar, C_q), 133.6 (d, $J = 19.6$ Hz, Ar, CH), 134.3 (Ar, C_q), 134.5 (d, $J = 19.6$ Hz, Ar, CH), 136.7 (Ar, CH), 138.6 (Ar, C_q), 138.8 (d, $J = 12.6$ Hz, Ar, C_q), 139.3 (Ar, C_q), 140.5 (Ar, C_q) 150.0 (Ar, C_q), 150.3 (Ar, C_q); ^{31}P{^{1}H}-NMR (121 MHz, $CDCl_3$): $\delta = -17.2$ (br), 138.4 (br); MS (EI): m/z (%) = 745 (M^+, 1), 448 (11), 447 (34), 433 (26), 432 (100), 431 (50), 430 (12), 416 (23), 287 (19), 286 (100), 268 (13), 257 (13), 239 (16), 155 (12); HR-MS (ESI): $m/z = 745.23021$, calcd. for $C_{50}H_{37}NO_2P_2$: 745.22941; $[\alpha]_D^{20}$: +166.3 (c 0.51, CH_2Cl_2).

Synthesis of (11b*R*)-*N*-[2-(Diphenylphosphino)-phenyl]-*N*-[(*S*)-1-(1-naphthyl)ethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine [(R_a,S_c)-1b]

The title compound was obtained by the procedure described above using (*R*)-**5** instead of (*S*)-**5**; yield: 44%, purity: 94% based on ^{31}P NMR. An analytical pure sample was obtained after a second recrystallisation; yield: 7%. Two sets of signals in a ratio of 1.3:1 were observed in the ^{1}H, ^{13}C NMR and ^{31}P NMR spectra due to two rotamers (referred to below as major and minor). *Major*: ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta = 1.77$ (br, 3H, CH_3), 5.62 (br, 1H, CH), 6.92 (br, 2H, Ar, major), 7.05–8.08 (m, 31H, Ar); ^{31}P{^{1}H}-NMR (250 MHz, $CDCl_3$): $\delta = -19.4$ (d, $J = 32.1$ Hz), 140.3 (d, $J = 32.1$ Hz). *Minor*: ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta = 1.70$ (br, 3H, CH_3), 5.96 (br, 1H, CH), 6.24 (br, 1H, Ar), 6.74 (br, 1H, Ar), 6.98 (br, 2H, Ar), 7.05–7.94 (m, 28H, Ar), 8.21 (br, 1H, Ar); ^{31}P{^{1}H}-NMR (250 MHz, $CDCl_3$): $\delta = -17.1$ (d, $J = 16.4$ Hz), 141.8 (d, $J = 16.4$ Hz); ^{13}C NMR (150 MHz, CD_2Cl_2): $\delta = 22.9$ (CH_3, minor), 23.9 (CH_3, major) 53.3 (CH, minor), 56.7 (CH, major), 121.6 (Ar, C_q), 122.3 (Ar, CH), 122.5 (Ar, CH), 122.8 (Ar, CH), 123.1 (Ar, CH), 123.7 (Ar, CH), 124.2 (Ar, C_q), 124.8 (Ar, CH), 125.0 (Ar, CH), 125.2 (Ar, CH), 125.3 (Ar, CH), 125.4 (Ar, CH), 125.6 (Ar, CH), 126.0 (Ar, CH), 126.3 (Ar, CH), 126.4 (Ar, CH), 126.7 (Ar, CH), 127.2 (Ar, CH), 127.4 (Ar, CH), 127.7 (Ar, CH), 127.9 (Ar, CH), 128.5 (Ar, CH), 128.7 (Ar, CH), 128.9 (Ar, CH) 129.1 (Ar, CH), 129.8 (Ar, CH), 129.9 (Ar, CH), 130.4 (Ar, CH), 130.8 (Ar, C_q), 131.0 (Ar, CH), 131.2 (Ar, C_q), 131.5 (Ar, C_q), 131.8 (Ar, C_q), 132.1 (Ar, C_q), 133.1 (Ar, C_q), 133.4 (Ar, CH), 133.9 (d, $J = 20$ Hz, Ar, CH), 134.2 (d, $J = 20$ Hz, Ar, CH), 134.6 (d, $J = 20$ Hz, Ar, CH), 135.2 (Ar, CH), 137.1 (Ar, CH), 138.3 (Ar, C_q), 139.1 (Ar, C_q), 139.6 (Ar, C_q), 140.1 (Ar, C_q), 149.6 (Ar, C_q), 150.3 (Ar, C_q), 151.2 (Ar, C_q); MS (EI): m/z (%) = 745 (M^+, 3), 448 (33), 447 (100), 433 (12), 431 (81), 430 (27), 417 (11), 416 (33), 287 (18), 286 (100), 268 (21), 257 (12), 239 (12), 155 (10); HR-MS (ESI): $m/z = 745.22966$, calcd. for $C_{50}H_{37}NO_2P_2$: 745.22941; $[\alpha]_D^{20}$: −83.3 (c 0.47, CH_2Cl_2).

Synthesis of (11b*S*)-*N*-[2-(Diphenylphosphino)phenyl]-*N*-[(*S*)-1-(naphthalen-1-yl)ethyl]-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine [(S_a,S_c)-2]

The title compound was obtained by the procedure described above using toluene as the solvent, (*S*)-**4a** and a slight excess (1.1 equiv.) of *n*-butyllithium, TMEDA and (*S*)-**6**. The pure product was obtained after one recrystallisation from toluene/ethanol; yield: 37% Two sets of signals in a ratio of 1.26:1 were observed in ^{31}P NMR due to two rotamers (referred to below as major and minor). For the same reason broad signals were observed partly in the ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.22$–1.76 (m, 11H, CH_3/CH_2), 2.03 (m, 2H, CH_2), 2.43 (m, 2H, CH_2), 2.68 (m, 4H, CH_2), 4.46 (br, 1H, CH), 6.09 (br, 1H, Ar), 6.47 (br, 1H, Ar), 6.72 (br, 1H, Ar), 6.79–7.23 (m, 16H, Ar); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 23.0$, 27.8, 28.1, 29.4, 29.5, 60.2, 118.9, 119.6, 126.7, 127.5, 128.1, 128.4, 128.48, 128.51, 128.57, 128.6, 128.8, 128.9, 129.0, 129.2, 129.4, 129.5, 133.4, 133.9, 138.1, 138.6, 138.7, 139.5, 139.6, 149.0; ^{31}P{^{1}H}-NMR (125 MHz, $CDCl_3$): $\delta = -17.1$, 136.2 (major); −17.1, 135.9 (minor); MS (EI): m/z (%) = 703.1 (M, 1), 382 (12), 381 (15), 380 (11), 337 (27), 183 (22), 92 (65), 91 (100); HR-MS (ESI): $m/z = 703.27555$, calcd. for $C_{44}H_{39}O_2NP_2$: 703.27636; $[\alpha]_D^{20}$: +30.3 (c 0.48, CH_2Cl_2).

Synthesis of (11b*R*)-*N*-[2-(Diphenylphosphino)phenyl]-*N*-phenyldinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine [(R_a)-1c]

The title compound was obtained by the procedure described above using THF as the solvent, *N*-phenyl-2-diphenylphosphinoaniline **4c** (706 mg, 2.0 mmol) and (*R*)-**5** (700 mg, 2.0 mmol). The crude product was purified by recrystallisation from toluene/ethanol; yield: 59%; white crystalline solid. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 6.85$ (m, 1H, Ar), 6.88–7.01 (m, 6H, Ar), 7.08 (m, 1H, Ar), 7.13–7.44 (m, 19H, Ar), 7.67 (d, $J = 8.7$ Hz, 1H, Ar), 7.84 (d, $J = 8.7$ Hz, 1H, Ar), 7.85 (d, $J = 8.2$ Hz, 1H, Ar), 7.89 (d, $J = 8.7$ Hz, 1H, Ar); ^{13}C{^{1}H}-NMR (150 MHz, $CDCl_3$): $\delta = 121.8$, 122.0, 122.2, 122.6, 124.3 (d, $J = 4.5$ Hz), 124.8 (d, $J = 56.9$ Hz), 125.9 (d, $J = 33.7$ Hz), 127.1 (d, $J = 34.3$ Hz), 127.3, 128.3 (d, $J = 14.2$ Hz), 128.4, 128.55 (d, $J = 16.8$ Hz), 128.58, 128.7, 129.6, 130.23, 130.25, 131.2 (d, $J = 116.6$ Hz), 132.8 (d, $J = 34.4$ Hz), 133.8 (d, $J = 18.8$ Hz), 134.1 (d, $J = 19.9$ Hz), 135.9, 138.0 (dd, $J = 159.1$ Hz, 11.1 Hz), 138.2 (d, $J = 12.5$ Hz), 145.6 (d, $J = 11.0$ Hz), 147.4 (dd, $J = 27.0$ Hz, 6.2 Hz), 148.8, 149.9; ^{31}P{^{1}H}-NMR (250 MHz, $CDCl_3$): $\delta = -15.5$ (d, $J = 34.7$ Hz), 141.4 (d, $J = 34.7$ Hz); MS (EI): m/z (%) = 667 (M^+, 93), 590 (100), 527 (17), 352 (26), 315 (12), 299 (12), 275 (11), 274 (14), 268 (25), 252 (12), 198 (12), 183 (10); HR-MS (ESI): m/z = 668.190283 ($C_{44}H_{32}NO_2P_2$), calcd. for $(M+H)^+$: 668.189413; $[\alpha]_D^{20}$: −78.1(c 0.56, CH_2Cl_2).

Synthesis of [Rh(COD){(S_a,S_c)-1a}] BF_4

To a solution of [Rh(COD)(acac)] (0.1 mmol, 31.2 mg) in THF (2 mL), $HBF_4 \cdot Et_2O$ (0.1 mmol, 13.6 μL) was added at

room temperature. After 15 min, a solution of (S_a,S_c)-**1a** (69.5 mg, 0.1 mmol) in THF (3 mL) was added dropwise. After 1 h the solution was concentrated under reduced pressure to 2 mL and the complex was precipitated by addition of diethyl ether (10 mL). The product was collected by filtration and washed with diethyl ether (3×5 mL); Yellow powder; yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (d, J = 7.2 Hz, 3H, CH_3), 1.84–2.68 (m, 8H, COD), 4.40 (m, 1H, COD), 4.64 (m, 1H, COD), 4.95 (m, 1H, CH), 5.26 (m, 1H, COD), 5.69 (m, 1H, COD), 6.39–8.17 (m, 31H, Ar); ^{31}P{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 16.8 (dd, J = 61.0 Hz, 142.3 Hz), 140.5 (dd, J = 61.0 Hz, 243.9 Hz); HR-MS (ESI pos): m/z = 906.213158, calcd. for $C_{54}H_{47}NO_2P_2Rh$ ([Rh(COD){(S_a,S_c)-**1a**}]$^+$): 906.214637.

Synthesis of [Rh(COD){(S_a,S_c)-1b}] NTf_2

A mixture of [Rh(COD)(acac)] (31.2 mg, 0.1 mmol) and bis(trifluoromethyl)sulfonamide (28.6 mg, 0.1 mmol) in ethanol (5 mL) was stirred until a clear yellow solution was obtained (*ca.* 10 min). A solution of (S_a,S_c)-**1b** (74.6 mg, 0.1 mmol) in THF (2 mL) was then added. The resulting orange reaction mixture was stirred for 30 min and then the solvent removed under reduced pressure. The residue was recrystallised from CH_2Cl_2 (1 mL) and pentane (10 mL). The product was collected by filtration and washed with pentane; orange powder; yield: 88%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.07 (br, 3H, CH_3), 1.70–2.40 (m, 8H, COD), 3.83 (m, 1H, COD), 4.34 (m, 1H, COD), 4.57 (m, 1H, CH), 5.49 (m, 1H, COD), 5.57 (m, 1H, COD), 6.99–8.02 (m, 35H, Ar); ^{31}P{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 13.4 (dd, J = 67.5 Hz, 135.1 Hz), 149.6 (dd, J = 67.5 Hz, 237.7 Hz); MS: m/z = 956.6, calcd. for $C_{58}H_{49}NO_2P_2Rh$ ([Rh(COD){(S_a,S_c)-**1b**}]$^+$): 956.9.

Synthesis of [Rh(COD){(R_a,S_c)-1b}] NTf_2

The title compound was obtained by the procedure described above using (R_a,S_c)-**1b** as the ligand; orange powder; yield: 82%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 1.17 (d, J = 7.0 Hz, 3H, CH_3), 1.99–2.47 (m, 8H, COD), 4.64 (m, 1H, COD), 4.95 (m, 1H, COD), 5.73 (m, 1H, CH), 5.89 (m, 1H, COD), 6.17 (m, 1H, COD), 6.68–8.18 (m, 35H, Ar); ^{31}P{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 14.3 (dd, J = 58.7 Hz, 141.1 Hz), 141.1 (dd, J = 58.7 Hz, 242.9 Hz); MS: m/z = 956.6, calcd. for $C_{58}H_{49}NO_2P_2Rh$ ([Rh(COD){(R_a,S_c)-**1b**}]$^+$): 956.9.

Synthesis of [Rh(COD){(S_a,S_c)-2}] NTf_2

Title compound was obtained by the procedure described above using (S_a,S_c)-**2** as the ligand; orange powder; yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, ^3J = 7.2 Hz, 3H, CH_3), 1.39–2.85 (m, 8H COD, 16H CH_2), 4.56 (m, 1H, COD), 4.98 (m, 1H, CH), 5.04 (m, 1H, COD), 5.67 (m, 1H, COD), 5.96 (m, 1H, COD), 6.57–7.54 (m, 23H, Ar); ^{31}P{^{1}H}-NMR (125 MHz, $CDCl_3$): = 15.0 (dd, J = 61.1 Hz, J = 142.0 Hz), 135.4 (dd, J = 61.1 Hz, J = 236.6 Hz); ^{19}F NMR (280 MHz, $CDCl_3$): δ = −79.4.

Synthesis of [Rh(COD){(R_a)-1c}] BF_4

Title compound was obtained by the procedure described for [Rh(COD){(S_a,S_c)-**1a**}] BF_4 using (R_a)-**1c** as the ligand; yellow powder; yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 (m, 1H, COD), 2.02 (m, 3H, COD), 2.60 (m, 3H, COD), 2.89 (m, 1H, COD), 4.13 (m, 1H, COD), 4.23 (m, 1H, COD), 5.77 (m, 1H, COD), 5.92 (m, 1H, COD), 6.32–8.46 (m, 31H, Ar); ^{31}P{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 23.3 (dd, J = 58.1 Hz, 142.7 Hz), 128.5 (dd, J = 58.1 Hz, 255.8 Hz); HR-MS (ESI pos): m/z = 878.182042, calcd. for $C_{52}H_{43}NO_2P_2Rh$ ([Rh(COD){(R_a)-**1c**)}]$^+$): 878.181858.

Typical Procedure for the Hydrogenation of Olefins

The substrate (1.0 mmol) was placed under argon in a stainless steel autoclave (10 mL) equipped with a glass inlet. A stock solution of [Rh(COD)(**1a**)]BF_4 in CH_2Cl_2 (2 mL, 0.5 mM) was transferred into the autoclave *via* syringe. After stirring for 20 min, the autoclave was pressurised with hydrogen (10 bar). After 1 h, the hydrogen pressure was carefully released. The reaction mixture was filtered over a pad of silica and analysed by chiral GC and NMR.

Typical Procedure for the Hydrogenation of Quinolines

To a solution of $[Ir(COD)Cl]_2$ (3.4 mg, 0.005 mmol) in toluene (1.5 mL) was added a solution of the ligand (0.011 mmol) in the same solvent (1.5 mL). After 30 min, the mixture was transferred under argon into a Schlenk tube containing the substrate (1.0 mmol) and iodine (12.6 mg, 0.05 mmol). The resulting solution was stirred for 30 min and transferred into a stainless steel autoclave (10 mL) equipped with a glass inlet. The autoclave was pressurised with hydrogen and stirred for 16 h. After releasing the hydrogen pressure, the reaction mixture was diluted with CH_2Cl_2 (5 mL) and extracted with saturated $NaHCO_3$ solution (10 mL). The aqueous phase was washed with CH_2Cl_2 (3×5 mL) and the organic phase dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was analysed by NMR and chiral GC or chiral HPLC.

Typical Procedure for the Hydrogenation of 11

$[RuCl_2(p\text{-cymene})]_2$ (0.005 mmol, 2.9 mg) was placed in Schlenk tube and a solution of **1a** (0.01 mmol, 6.9 mg) in toluene (1 mL) was added. The mixture was heated to 80 °C for 1 h and then the solvent removed under reduced pressure. The residue was dissolved in methanol (2.0 mL) and the substrate (1.0 mmol, 130.1 mg) was added. The mixture was transferred into a stainless steel high pressure autoclave (10 mL) equipped with a glass inlet. The autoclave was pressurised with hydrogen (60 bar) and stirred for 16 h at 60 °C. After releasing the hydrogen pressure, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2, filtered over a pad of silica and analysed by chiral GC and NMR.

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References

[1] a) *The Handbook of Homogenous Hydrogenation*, (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2006**; b) special issue on hydrogenation: *Acc. Chem. Res.* **2008**, *40*, 1237–1419; c) W. Tang, X. Zhang, *Chem. Rev.* **2003**, *103*, 3029–3070.

[2] T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691–1693.

[3] a) G. Franciò, F. Faraone, W. Leitner, *Angew. Chem.* **2000**, *112*, 1486–1488; *Angew. Chem. Int. Ed.* **2000**, *39*, 1428–1430; b) S. Burk, G. Franciò, W. Leitner, *Chem. Commun.* **2005**, 3460–3462; c) G. Franciò, F. Faraone, W. Leitner, in: *Asymmetric Synthesis with Chemical and Biological Methods*, (Eds.: D. Enders, K.-E. Jaeger), Wiley-VCH, Weinheim, **2007**, pp 250–277.

[4] a) N. W. Boaz, J. A. Ponasik, in: *Phosphorus Ligands in Asymmetric Catalysis*, (Ed. A. Börner), Wiley-VCH, Weinheim, **2008**, pp 453–476; b) F. Boeda, T. Beneyton, C. Crévisy, *Mini-Reviews in Organic Chemistry*, **2008**, *5*, 96–127; c) S. H. L Kok, T. T. L. Au-Yeung, H. Y. Cheung, W. S. Lam, S. S. Chan, A. S. C. Chan, in: *The Handbook of Homogenous Hydrogenation*, (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2006**, pp 883–994.

[5] K. A. Vallianatou, I. D. Kostas; J. Holz, A. Börner, *Tetrahedron Lett.* **2006**, *47*, 7947–7950.

[6] L.-C. Liang, W.-Y. Lee, C.-H. Hung, *Inorg. Chem.* **2003**, *42*, 5471–5473.

[7] G. Franciò, C. G. Arena, F. Faraone, C. Graiff, M. Lanfranchi, A. Tiripicchio, *Eur. J. Inorg. Chem.* **1999**, 1219–1227.

[8] A. Korostylev, D. Selent, A. Monsees, C. Borgmann, A. Börner, *Tetrahedron: Asymmetry* **2003**, *14*, 1905–1909.

[9] For most ligands one recrystallisation yields the pure ligands. Ligands (S_a,S_c)-**1b** and (R_a,S_c)-**1b** were obtained after one recrystallisation with a lower purity of 86% and 94%, respectively (based on ^{31}P NMR). Control experiments showed that the major impurity **4b** did not interfere with the *in situ* catalyst. Analytically pure (S_a,S_c)-**1b** and (R_a,S_c)-**1b** could be obtained after a second recrystallisation on the expense of the yield (see Experimental Section).

[10] A. R. Katritzky, S. Rachwal, B. Rachwal, *Tetrahedron* **1996**, *52*, 15031–15070.

[11] a) Y. G. Zhou, *Acc. Chem. Res.* **2007**, *40*, 1357–1366, and references cited therein; b) S. H. Chan, F. L. Lam, X. Li, L. Xu, W. Tang, F. L. Lam, W.-h. Lo, S.-B. Yu, Q.-H. Fan, A. S. C. Chan, *Tetrahedron: Asymmetry* **2007**, *18*, 2625–2631; c) C. Deport, M. Buchotte, K. Abecassis, H. Tadaoka, T. Ayad, T. Ohshima, J.-P. Genet, K. Mashima, V. Ratovelomanana-Vidal *Synlett* **2007**, 2743–2747; d) S.-M. Lu, C. Bolm *Adv. Synth. Catal.* **2008**, *350*, 1101–1105; e) X.-B. Wang, Y.-G. Zhou *J. Org. Chem.* **2008**, *73*, 5640–5642; .

[12] N. Mršić, L. Lefort, J. A. F. Boogers, A. J. Minnaard, B. L. Feringa, J. G. de Vries *Adv. Synth. Catal.* **2008**, *350*, 1081–1089.

[13] Very recently, Chan, Fan and co-workers reported the application of an extremely efficient ruthenium-diamine complex for the asymmetric hydrogenation of 2-alkylquinolines. However, modest enantioselectivity (79%) was obtained for **12c**: a) H. Zhou, Z. Li, Z. Wang, T. Wang, L. Xu, Y. He, Q.-H. Fan, J. Pan, L. Gu, A. S. C. Chan, *Angew. Chem.* **2008**, *120*, 8592–8595; *Angew. Chem. Int. Ed.* **2008**, *47*, 8464–8467; b) Z.-W. Li, T.-L. Wang, Y.-M. He, Z.-J. Wang, Q.-H. Fan, J. Pan, L.-J. Xu, *Org. Lett.* **2008**, *10*, 5265–5268.

[14] A. F. Burchat, J. M. Chong, N. Nielsen, *J. Organomet. Chem.* **1997**, *542*, 281–283.

