Pergamon

Tetrahedron: Asymmetry, Vol. 8, No. 22, pp. 3775–3784, 1997

Printed in Great Britain
PII: S0957-4166(97)00556-9
0957-4166/97 $17.00 + 0.00

Synthesis of 1′-(2-(diarylphosphino)1-naphthyl)isoquinolines; variation of the aryl substituent

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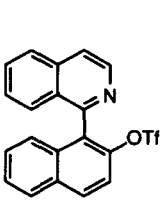
Abstract: A series of phosphinamines in which the aryl substituents are varied has been prepared from the known triflate **1** by palladium catalysed reaction with the appropriate secondary phosphine oxide followed by reduction with trichlorosilane. In four of the six cases attempted, resolution was successfully completed by fractional crystallisation of the diastereomeric cationic complexes formed with di-μ-chloro-bis[(*R*)-dimethyl(1-phenethyl)aminato-C^2,N]dipalladium, as previously described. The order of crystallisation was not predictable and in one case the specific rotation of the derived phosphine was anomalous, although the CD spectrum in the 220–350 nm region was as expected by comparison with the parent compound. © 1997 Elsevier Science Ltd

Introduction

In previous papers we have described the synthesis of a series of ligands based on the parent 1′-(2-(diphenylphosphino)1-naphthyl)isoquinoline.[1] In the simplest case, preparation involved coupling an intermediate triflate **1** with Ph_2PHO under Pd catalysis, followed by the reduction of the derived phosphine oxide with trichlorosilane.[2] In all cases to date, resolution was effected with the palladacycle derived from $PdCl_2$ and (*R*)- or (*S*)-N,N-dimethylnaphthylethylamine; the reasons for success with this particular resolving agent have been discussed.[1a,3] Pd complexes of the ligands have proved effective in asymmetric allylic alkylation[4] and also in asymmetric hydroboration.[5]

Significant recent effort has been directed to the effects of altering the electronic character of the ligand on reactivity and e.e. in asymmetric catalysis.[6] In the specific case of asymmetric hydroboration, Togni and co-workers have demonstrated that the substitution pattern on the pyrazole ring in complexes **2** has a significant effect on the enantioselectivity but less on the regioselectivity in the catalysed hydroboration of styrene with catecholborane.[7] Having developed a 'modular' ligand synthesis which was amenable to structural variation at several points, we were interested to discover the effects of variation in the P-aryl substituents of ligand **3** on catalysis. The present paper describes the straightforward synthesis of the ligands, and also some unpredicted observations made during the course of their resolution.



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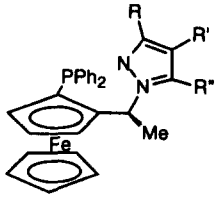

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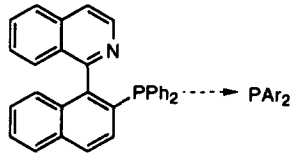

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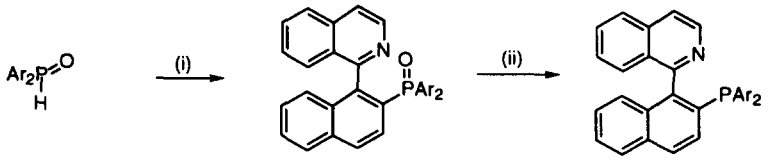
Ligand synthesis

A series of secondary phosphine oxides were prepared according to literature procedures[8] and used without further purification. For the phosphinylation step, considerable efforts were made to find a general procedure. In the original case, the product phosphine oxide was contaminated by the product of competing protolysis of the aryl–Pd bond. It was found that diisopropylethylamine as base was superior to triethylamine or $NaHCO_3$ reagents which had been reported previously, and that the solvent of choice for the reaction was DMSO rather than THF or DME. The optimum ratio of base to solvent was around 1:1, and under these conditions the mixture is biphasic at the reaction temperature of 90°C, with the Pd catalyst in the DMSO phase. Acidic impurities in the phosphine oxide precursor were particularly deleterious to the yield, hence it was necessary to work with rigorous exclusion of air. Results from this step and the following reduction with trichlorosilane are summarised in Scheme 1. In preliminary experiments it was demonstrated that compounds **8c** and **9c** could not be resolved, and hence no attempt was made to optimise their synthesis.



4a Ar = 3-MeC_6H_4
5a Ar = 3,5-diMeC_6H_3
6a Ar_2 = biphenylyl
7a Ar = 2-furyl
8a Ar = 3-CF_3
9a Ar = 3,5-di$CF_3C_6H_3$

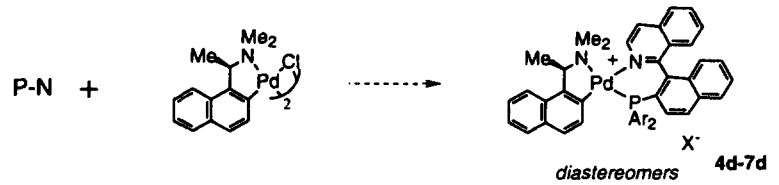
4b - 9b

4c : 63%
5c : 63%
6c : 73%
7c : 57%
[8c : 43%]
[9c : 50%]

Scheme 1. (i) Triflate **1**, iPr_2NEt, DMSO, (cat. Pd acetate, dppb or dppp, 4 mol percent), 90°C, 20 h; (ii) $HSiCl_3$, NEt_3, 4 h, reflux.

The resolution step was carried out as previously described, but with unpredictable results. For the 3-tolyl phosphine **4c**, procedures according to Scheme 2 led first to the crystallisation of one diastereomer of **4d** as the Cl^- salt, and the second as the PF_6^- salt. Over the course of the resolution the proportion of Et_2O in the $Et_2O/CHCl_3$ mixture was gradually increased in each crystallisation step. For the closely related 3,5-xylyl phosphine **5c**, the best results were obtained in the absence of KPF_6, and both diastereomers of **5d** were isolated as chloride salts.[9] For the biphenylyl phosphine **6c**, the original procedure led first to the isolation of a PF_6^- salt of one diastereomer of **6d**, and then the second diastereomer as its chloride. The same sequence was observed for the furylphosphine **7c**.

The absolute configuration of the parent ligand had been assigned by X-ray.[1a,10] Other members of the series have been similarly correlated, and (*R*)-(+) specific rotation at 589 nm in $CHCl_3$ was generally observed. This together with the recently described electrospray MS method[11] permitted the configuration of the new ligands to be defined, and the assignments were confirmed by the sense of asymmetric hydroboration with Rh complexes of the new ligands.[12] In the case of the furylphosphine **7c**, an anomaly was observed and these criteria would have demanded that the ligand was (*S*)-(+). This is indeed correct, as was defined by the CD spectrum of the ligand between 220 and 350 nm (Figure 1) in comparison to the parent compound (*S*)-(−)-**3** and the related phenanthridine (*R*)-(+)-**10**.



First crops	$[\alpha]_D^{20}$= −244, Cl^-	$[\alpha]_D^{20}$= +430, Cl^-	$[\alpha]_D^{20}$=-49, PF_6^-	$[\alpha]_D^{20}$=-216, PF_6^-
Second crops	$[\alpha]_D^{20}$= +170, Cl^-	$[\alpha]_D^{20}$=-242, PF_6^-	$[\alpha]_D^{20}$= +43, Cl^-	$[\alpha]_D^{20}$=+246, Cl^-

Scheme 2. Results of resolution experiments.

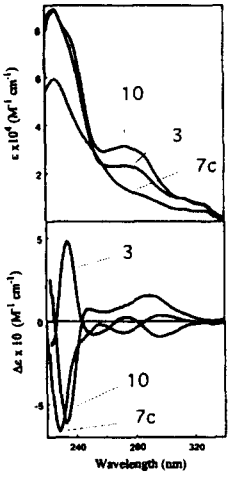
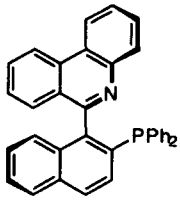


Figure 1. The UV (upper trace) and CD spectra (lower trace) of compounds (−)-**7c**, (*S*)-(−)-**3** and (*R*)-(+)-**10**, defining the absolute configuration of (−)-**7c** to be (*R*).



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Application of the new ligands in catalytic hydroboration has been carried out and will form part of a forthcoming full paper.[12]

Experimental section

General

Reactions were conducted under a dry argon atmosphere, using standard vacuum line techniques. Melting points were determined using a Reichert–Koffler block. NMR spectra were recorded on a Varian Gemini 200 and a Bruker AM250 or AMX 500 spectrometer. IR spectra were recorded on a

Perkin–Elmer Paragon 1000 spectrometer using KBr discs. Mass spectra were recorded on a Fison VG platform spectrometer or on a VG BIO Q triple quadrupole mass spectrometer equipped with a VG electrospray interface. GC analyses were performed on a Fison 8000 using a Chrompack WCOT Fused Silica column, CP-Chirasil-DEX CB column, 25 meters; injector temperature: 250°C; detector temperature: 275°C; inlet pressure: 2.90 psi. Specific rotations were measured with a Perkin–Elmer 241 spectrometer.

Materials

Reactions were carried out in solvents distilled from standard drying agents. Catecholborane (Aldrich) was distilled under reduced pressure before use. 5-Phenyl-5H-dibenzophosphole,[13] 1′-[1-(2-trifluoromethanesulfonylnaphthyl)]isoquinoline,[1] (*R*)-1′-(2-Diphenylphosphino-1-naphthyl)-isoquinoline,[1] di-μ-chloro-bis[(*R*)-dimethyl(1-phenethyl)aminato-C^2,N]dipalladium(II), and secondary phosphine oxides were prepared according to literature procedures. (*R*)-6′-(2-Diphenylphosphino-1-naphthyl)phenanthridine was a gift from Dr J. M. Valk.

Diarylphosphines: general procedure

DMSO was placed in a Schlenk tube, and argon was bubbled through for 20 min. To this was added 1′-[1-(2-trifluoromethanesulfonylnaphthyl)]isoquinoline,[2] $PAr_2(O)H$, dppp or dppb, $Pd(OAc)_2$, and diisopropylethylamine. The mixture was heated at 100°C for 20 h, added to dichloromethane, and subsequently washed with saturated Na_2CO_3 and three times with water. After drying over $MgSO_4$ and removal of the solvent *in vacuo*, a red–brown oil was obtained to which toluene was added. This suspension was transferred into a Schlenk tube under argon then $HSiCl_3$ and NEt_3 was added, leading to the evolution of white fumes. The solution was refluxed for 4 h and cooled with ice. To this was added carefully a 2 M NaOH solution. The layers were separated, and the water layer was extracted with dichloromethane three times. The organic layers were dried over $MgSO_4$ and concentrated *in vacuo*, giving a red–brown oil. The product was purified by chromatography on silica (eluent: CH_2Cl_2).

(rac)-1-(2-Di(3-methylphenyl)phosphino-1-naphthyl)isoquinoline ***4c***

From 40 ml of DMSO, 4 g of 1′-[1-(2-trifluoromethanesulfonylnaphthyl)]isoquinoline, 8 g of di(3-methylphenyl)phosphine oxide, 25 ml of diisopropylethylamine, 0.68 g of dppb, 0.36 g of $Pd(OAc)_2$, 250 ml of saturated Na_2CO_3, 3×250 ml of water, 8 ml of $HSiCl_3$, 16 ml of NEt_3, 100 ml of toluene, 400 ml of 2 M NaOH solution, 2.90 g (yield 63%) of phosphine **5** was obtained. M.p. 85°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, ^3J(H,H)=5.7 Hz, 1H; H_3), 7.94–7.88 (m, 3H), 7.76 (d, ^3J(H,H)=5.7 Hz, 1H; H_4), 7.61 (dd, ^3J(H,H)=6.8 and 6.8 Hz, 1H), 7.50–7.46 (m, 2H), 7.29–7.23 (m, 3H), 7.22–7.15 (m, 2H), 7.13–7.07 (m, 3H), 7.06–7.03 (m, 2H), 6.92 (dd, ^3J(H,H)=7.2 and 7.3 Hz, 1H), 6.91 (d, ^3J(H,H)=8.5 Hz, 1H), 2.26 (s, 3H; Me), 2.20 (s, 3H; Me); ^{13}C NMR (125.72 MHz, $CDCl_3$): 161.0 (d, J_{PC}=8.0 Hz; C_1), 144.4 (d, J_{PC}=33.0 Hz; $C_{2'}$), 142.6 (s; C_3), 137.8 (d, J_{PC}=17.9 Hz; *i*), 137.6 (d, J_{PC}=22.1 Hz; *i*′), 136.2–133.9 (m), 132.9 (d, J_{PC}=7.6 Hz; $C_{1'}$), 132–126 (m), 120.6 (s; C_4), 21.4 (s; Me), 21.3 (s; Me); ^{31}P NMR (101 MHz, $CDCl_3$): δ=−12.7; IR (KBr): ν=2910 cm^{-1} (C–H); MS (APCI+); m/z: 468 [m+1]; (467.5). Anal. Calcd for $C_{33}H_{26}PN$: C 84.77, H 5.61, N 3.00. Found: C 84.21, H 5.51, N 3.00.

(rac)-1-(2-Di(3,5-dimethylphenyl)phosphino-1-naphthyl)isoquinoline ***5c***

From 50 ml of DMSO, 5 g of 1′-[1-(2-trifluoromethanesulfonylnaphthyl)]isoquinoline, 11 g of di(3,5-dimethylphenyl)phosphine oxide, 40 ml of diisopropylethylamine, 0.85 g of dppb, 0.45 g of $Pd(OAc)_2$, 250 ml of saturated Na_2CO_3, three times 250 ml of water, 10 ml of $HSiCl_3$, 20 ml of NEt_3, 120 ml of toluene, 400 ml of 2 M NaOH solution, 3.90 g (yield 63%) of phosphine **6** was obtained. M.p. 94°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.73 (d, ^3J(H,H)=7.7 Hz, 1H; C_3), 7.95 (d, ^3J(H,H)=8.5 Hz, 1H; $C_{4'}$), 7.94 (d, ^3J(H,H)=7.5 Hz, 1H; $C_{8'}$), 7.93 (d, ^3J(H,H)=7.4 Hz, 1H; C_8), 7.78 (d, ^3J(H,H)=7.7 Hz, 1H; C_4), 7.62 (dd, ^3J(H,H)=7.4 and 7.4 Hz, 1H; C_7), 7.57 (dd, ^3J(H,H)=8.5 Hz, ^3J(P,H)=3.5 Hz, 1H; $C_{3'}$), 7.50 (dd, ^3J(H,H)=7.5 and 7.5 Hz, 1H; $C_{7'}$), 7.29 (dd, ^3J(H,H)=8.5

and 7.5 Hz, 1H; $C_{6'}$), 7.26 (d, ^3J(H,H)=7.4 Hz, 1H; C_5), 7.20 (dd, ^3J(H,H)=7.4 and 7.4 Hz, 1H; C_6), 7.14 (d, ^3J(H,H)=8.5 Hz, 1H; $C_{5'}$), 6.96 (s, 1H; Ar), 6.95 (s, 2H; Ar), 6.85 (s, 1H; Ar), 6.78 (s, 1H; Ar), 6.77 (s, 1H; Ar), 2.22 (s, 6H; Me), 2.15 (s, 6H; Me); ^{13}C NMR (125.72 MHz, $CDCl_3$): δ=160.5 (d, J_{PC}=8.0 Hz; C_1), 144.2 (d, J_{PC}=33.5 Hz; $C_{2'}$), 142.1 (s; C_3), 137.5 (s; Ar *i*+*i*′), 135.8–133.4 (m), 132.6 (d, J_{PC}=13.0 Hz; $C_{1'}$), 130.5 (s; $C_{3'}$), 131.7–130.8 (m), 130.1 (s; C_7), 129.8–126.4 (m), 120.2 (s; C_4), 21.2 (s; Me), 21.1 (s; Me); ^{31}P NMR (101 MHz, $CDCl_3$): δ=−12.4; IR (KBr): ν=2910 cm^{-1} (C–H); MS (APCI+); m/z: 496 [m+1] (495.6); Anal. Calcd for $C_{35}H_{30}PN$: C 84.82, H 6.10, N 2.83. Found: C 84.72, H 5.80, N 2.56.

(rac)-1-(2-P-Dibenzophospholyl-1-naphthyl)isoquinoline ***6c***

From 10 ml of DMSO, 1.25 g of 1′-[1-(2-trifluoromethanesulfonylnaphthyl)]isoquinoline, 1.25 g of dibenzophosphole oxide, 10 ml of diisopropylethylamine, 0.206 g of dppp, 0.112 g of $Pd(OAc)_2$, 50 ml of saturated Na_2CO_3, 3×50 ml of water, 4 ml of $HSiCl_3$, 8 ml of NEt_3, 50 ml of toluene, 200 ml of 2 M NaOH solution, 0.99 g (yield 73%) of phosphine **7** was obtained. M.p. 109°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.93 (d, ^3J(H,H)=5.8 Hz, 1H; H_3), 8.10–7.98 (m, 3H), 7.95 (d, ^3J(H,H)=7.8 Hz, 1H), 7.90 (d, ^3J(H,H)=5.8 Hz, 1H; H_4), 7.80 (d, ^3J(H,H)=8.1 Hz, 1H), 7.75 (dd, ^3J(H,H)=7.3 and 7.3 Hz, 1H), 7.67 (d, ^3J(H,H)=8.4 Hz, 1H), 7.62 (d, ^3J(H,H)=8.6 Hz, 1H; $H_{4'}$), 7.56 (dd, ^3J(H,H)=7.5 and 7.5 Hz, 1H), 7.50–7.40 (m, 4H), 7.33–7.30 (m, 2H), 7.22 (d, ^3J(H,H)=8.5, 1H), 6.66 (dd, ^3J(H,H)=8.5 Hz, ^3J(P,H)=3.0 Hz, 1H; $C_{3'}$); ^{13}C NMR (125.72 MHz, $CDCl_3$): δ=160.9 (d, J_{PC}=6.3 Hz; C_1), 145.1 (d, J_{PC}=34.3 Hz; $C_{2'}$), 144.6 (d, J_{PC}=26.0 Hz; phosphole), 143.1 (d, J_{PC}=10.9 Hz; phosphole), 142.3 (s; C_3), 136.2–129.7 (m), 134.1 (d, J_{PC}=18.8 Hz; $C_{1'}$), 131.2–130.5 (m), 129.3 (s, $C_{4'}$), 128.6–128.3 (m), 128.2 (s; $C_{3'}$), 127.9–121.0 (m), 120.6 (s, C_4); ^{31}P NMR (101 MHz, $CDCl_3$): δ=−20.0; IR (KBr): ν=1438 cm^{-1} (P–Ar); MS (APCI+); m/z: 438 [m+1]; (437.4). Anal. Calcd for $C_{31}H_{20}PN$: C 85.11, H 4.61, N 3.20. Found: C 84.86, H 4.23, N 2.93.

(rac)-1-(2-Di(2-furyl)phosphino-1-naphthyl)isoquinoline ***7c***

From 60 ml of DMSO, 4 g of 1′-[1-(2-trifluoromethanesulfonylnaphthyl)]isoquinoline, 8 g of di-(2-furyl)phosphine oxide, 40 ml of diisopropyl ethylamine, 0.66 g of dppp, 0.36 g of $Pd(OAc)_2$, 250 ml of saturated Na_2CO_3, 3×250 ml of water, 8 ml of $HSiCl_3$, 16 ml of NEt_3, 150 ml of toluene, 400 ml of 2 M NaOH solution, 2.35 g (yield 57%) of phosphine **8** was obtained. M.p. 135°C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.67 (d, ^3J(H,H)=5.7 Hz, 1H; H_3), 7.93 (d, ^3J(H,H)=8.6 Hz, 1H; $H_{3'}$), 7.91 (d, ^3J(H,H)=8.1 Hz, 1H; H_8), 7.85 (d, ^3J(H,H)=8.4 Hz, 1H; $H_{8'}$), 7.75 (d, ^3J(H,H)=5.7 Hz, 1H; H_4), 7.74 (d, ^3J(H,H)=8.6 Hz, 1H; $H_{4'}$), 7.66 (d, 1H, $^3J_{HH}$=1.7 Hz; furyl $H_{5'}$), 7.56 (dd, ^3J(H,H)=8.7 and 7.7 Hz, 1H; $H_{7'}$), 7.47 (dd, ^3J(H,H)=8.1 and 7.0 Hz, 1H; H_7), 7.32 (d, ^3J(H,H)=8.5 Hz, 1H; $H_{5'}$), 7.28 (d, ^3J(H,H)=1.7 Hz, 1H; furyl H_5), 7.27–7.22 (m, 2H, $H_{6+6'}$), 7.14 (d, ^3J(H,H)=8.5 Hz, 1H; H_5), 6.63 (dd, ^3J=2.7 and 1.7 Hz, 1H, furyl $H_{3'}$), 6.38 (ddd, ^3J=3.5, 2.7 and 1.7 Hz, 1H, furyl $H_{4'}$), 6.23 (dd, ^3J=2.7 and 1.7 Hz, 1H; furyl H_3), 6.00 (ddd, ^3J=3.5, 2.7 and 1.7 Hz, 1H, furyl $H_{3'}$); ^{13}C NMR (125.72 MHz, $CDCl_3$): 160.1 (d, J_{PC}=4.0 Hz; C_1), 150.4 (d, J_{PC}=29.0 Hz; furyl C_2), 150.3 (d, J_{PC}=29.0 Hz; furyl $C_{2'}$), 148.0 (s; furyl C_5), 147.6 (s; furyl C_5), 142.6 (s; C_3), 141.6 (d, J_{PC}=29.0 Hz; $C_{2'}$), 136.5–133.4 (m), 133.1 (d, J_{PC}=6.1 Hz; $C_{1'}$), 130.6 (s; $C_{7'}$), 129.8 (s; $C_{3'}$), 129.1 (s; $C_{4'}$), 129.0 (s; C_8), 126.7 (s; C_5), 128.4–126.9 (m), 122.4 (d, J_{PC}=27.0 Hz; furyl $C_{3'}$), 121.5 (d, J_{PC}=28.1 Hz; furyl C_3), 121.1 (s; C_4), 111.2 (d, J_{PC}=5.9 Hz; furyl $C_{4'}$), 110.6 (d, J_{PC}=6.4 Hz; furyl C_4); ^{31}P NMR (101 MHz, $CDCl_3$): δ=−56.6; IR (KBr): ν=1006, 816 cm^{-1}; MS (APCI+); m/z: 420 [m+1]; (419.4). Anal. Calcd for $C_{27}H_{18}PNO_2$: C 77.32, H 4.33, N 3.34. Found: C 76.97, H 4.12, N 3.14.

Synthesis of resolution complexes ***4d–7d****: general procedure*

A mixture of racemic phosphinamine **4c–7c** (3.8 mmol) and di-μ-chloro-bis[(*R*)-dimethyl(1-naphthylethyl)aminato-C^2,N]dipalladium(II) (1.3 g, 1.9 mmol) in MeOH (100 ml) under argon was stirred at room temperature overnight. The solution was concentrated to dryness to yield quantitatively a mixture of diastereomers of **4d–7d** as yellow solids. The mixture was dissolved in chloroform ,then 2.4 eq. of potassium hexafluorophosphate was added with a minimum of water. This was stirred

for 2 hours, dried over $MgSO_4$, concentrated *in vacuo*, and diethyl ether was added. After slow crystallisation, the solid was filtered off, washed with ether and dried. To the filtrate was added more ether, after further crystallisation the solid was filtered off, washed with ether and dried. This procedure was repeated several times. When crystallisation of the first diastereomer is nearly complete, the second diastereomer starts to crystallise.

Resolution of cis-[(R)-Dimethyl(1-naphthylethyl)aminato-C^2,N]-[(R) and (S)-1′-(2-di(3-methylphenyl)phosphino-1-naphthyl)isoquinoline] palladium(II) chloride/hexafluorophosphate ***4d***

The first diastereomer crystallises as a Cl^- salt, the second diastereosiomer crystallises as a PF_6^- salt. The yield depends on the scale and on the number of crystallisations (between 75% and 85% for both diastereomers).

First crystallised diastereomer (Cl^- salt): white solid; m.p. 181°C; $[\alpha]_D^{20}$=+430 (c=0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, CD_2Cl_2): δ=9.41 (d, ^3J(H,H)=6.2 Hz, 1H; H_3), 8.72 (d, ^3J(H,H)=8.6 Hz, 1H), 8.12 (d, ^3J(H,H)=8.5 Hz, 1H), 8.06 (d, ^3J(H,H)=8.3 Hz, 1H), 7.80 (d, ^3J(H,H)=6.2 Hz, 1H; H_4), 7.78 (d, ^3J(H,H)=8.5 Hz, 1H), 7.68–7.55 (m, 4H), 7.40 (dd, ^3J(H,H)=8.5 Hz, ^3J(P,H)=5.7 Hz, 1H; $H_{3'}$), 7.39–7.06 (m, 7H), 7.04 (d, ^3J(H,H)=8.5 Hz, 1H; $H_{4'}$), 6.98 (d, ^3J(H,H)=8.6 Hz, 1H; naphthylethylamine H_4), 6.95–6.60 (m, 4H), 6.48 (dd, ^3J(H,H)=8.6, ^3J(P,H)=7.3 Hz, 1H; naphthylethylamine H_3), 6.29 (d, J=12.8 Hz, 1H), 6.20 (dq, ^3J(H,H)=7.5 and 7.1 Hz, 1H; C*H*Me), 2.95 (d, ^3J=4.5 Hz, 3H; NMe), 2.67 (d, ^3J=5.1 Hz, 3H; NMe), 1.96 (d, ^3J(H,H)=7.2 Hz, 3H; CH*Me*), 1.90 (bs, 3H; Me), 1.26 (s, 3H; Me); ^{13}C NMR (125.72 MHz, CD_2Cl_2): 157.6 (s; C_1), 150.0, 143.9 (s; C_3), 140–122 (m), 71.9 (s; *C*HMe), 44.2 (s; NMe), 41.1 (s; NMe), 21.0 (s; 2 Me), 19.9 (s; 2 Me), 16.8 (s; CH*Me*); ^{31}P NMR (101 MHz, CD_2Cl_2): δ=29.3 (*S*); IR (KBr): ν=1107, 816 cm^{-1}; MS (electrospray); m/z: 771.2 [M^+]; (807.7).

Second crystallised diastereomer (PF_6^- salt): yellow solid; m.p. 217°C; $[\alpha]_D^{20}$=−242 (c=1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.78 (d, ^3J(H,H)=6.1 Hz, 1H; H_3), 8.13 (d, ^3J(H,H)=6.1 Hz, 1H; H_4), 8.12–8.06 (m, 2H), 7.85 (d, ^3J(H,H)=8.2 Hz, 1H), 7.70–7.60 (m, 4H), 7.48–7.27 (m, 9H), 7.17 (ddd, ^3J(H,H)=7.6 and 7.6, ^5J(P,H)=2.9 Hz, 1H; tolyl H_5), 7.14 (d, ^3J(H,H)=8.6 Hz, 1H), 7.04 (d, ^3J(H,H)=8.5 Hz, 1H; naphthylethylamine H_4), 6.94–6.74 (m, 4H), 6.53 (dd, ^3J(H,H)=8.5, ^4J(P,H)=5.8 Hz, 1H; naphthylethylamine H_3), 4.38 (dq, ^3J(H,H)=6.0 and 6.3 Hz, 1H), 2.94 (d, ^3J=1.8 Hz, 3H; NMe), 2.71 (d, ^3J=3.3 Hz, 3H; NMe), 2.07 (s, 3H; Me), 2.03 (bs, 3H; Me), 1.73 (d, ^3J(H,H)=6.3 Hz, 3H; CH*Me*); ^{13}C NMR (125.72 MHz, $CDCl_3$): 156.9 (s; C_1), 149.5, 149.1, 140.7 (s; C_3), 140–120 (m), 72.8 (s; *C*HMe), 51.9 (s; NMe), 47.8 (s; NMe), 23.9 (s; 2 Me), 21.0 (s; 2 Me), 20.5 (s; CH*Me*); ^{31}P NMR (101 MHz, $CDCl_3$): δ=39.8 (*S*), −142.9 (heptet, J(P,F)=711 Hz; PF_6); IR (KBr): ν=843 cm^{-1} (P–F); MS (electrospray); m/z: 771.2 [M^+]; (917.2). Anal. Calcd for $C_{47}H_{42}F_6N_2P_2Pd$: C 61.55, H 4.62, N 3.05. Found: C 61.95, H 4.74, N 2.90.

Resolution of cis-[(R)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(R) and (S)-1-(2-di(3,5-xylyl)-phosphino-1-naphthyl)isoquinoline] palladium(II) chloride/hexafluorophosphate ***5d***

The cis-[(*R*)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(*R*) and (*S*)-1′-(2-di(3,5-dimethylphenyl)phosphino-1-naphthyl)isoquinoline] palladium(II) chloride mixture was dissolved in the minimum of chloroform then some diethyl ether was added. After slow crystallisation, the solid was filtered off, washed with ether and dried. To the filtrate was added more ether and after crystallisation the solid was filtered off, washed with ether and dried *in vacuo*. This procedure was repeated several times. When the first diastereomer is nearly completely crystallised, the second diastereosiomer starts to crystallise. Both diastereomers crystallise as Cl^- salts (no KPF_6 was added). The yield depends on the scale and on the number of crystallisations (between 50% and 60% for each diastereomer).

First crystallised diastereomer (Cl^- salt): white solid; m.p. 203°C; $[\alpha]_D^{20}$=−244 (c=0.5, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.94 (d, ^3J(H,H)=6.1 Hz, 1H; H_3), 8.37 (d, ^3J(H,H)=6.1 Hz, 1H; H_4), 8.10 (d, ^3J=8.4 Hz, 1H), 8.06 (d, ^3J(H,H)=8.3 Hz, 1H), 7.94 (d, ^3J(H,H)=8.3 Hz, 1H), 7.70–7.62

(m, 4H), 7.40–7.28 (m, 7H), 7.09 (m, 2H), 7.03 (d, ^3J(H,H)=8.5 Hz, 1H; naphthylethylamine H_4), 7.13 (d, ^3J(H,H)=8.6 Hz, 1H), 6.60 (s, 1H), 6.57 (s, 1H), 6.54–6.47 (m, 2H), 4.34 (dq, ^3J=6.2 and 6.0 Hz, 1H; C*H*Me), 3.00 (d, ^3J=1.4 Hz, 3H; NMe), 2.72 (d, ^3J=3.1 Hz, 3H; NMe), 1.99 (s, 12H; 4 Me), 1.68 (d, ^3J=6.2 Hz, 3H; CH*Me*). ^{13}C NMR (125.72 MHz, $CDCl_3$): 156.9 (s; C_1), 149.9, 148.9, 141.3 (s; C_3), 139.1 (d, J(P,C)=13.0 Hz), 138.2 (m), 136.7 (d, J(P,C)=10.9 Hz; naphthylethylamine C_3); 73.1 (s; *C*HMe), 52.3 (s; NMe), 48.0 (s; NMe), 23.7 (s; CH*Me*), 21.0 (s; 2 Me), 20.7 (s; 2 Me); ^{31}P NMR (101 MHz, $CDCl_3$): δ=39.5 (*S*); IR (KBr): ν=1126, 811 cm^{-1}; MS (electrospray); m/z: 799 [M$^+$]; $C_{49}H_{46}ClN_2PPd$ (99.2).

Second crystallised diastereomer (Cl^- salt): white solid; m.p. 190°C; $[\alpha]_D^{20}$=+170 (c=1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.40 (d, ^3J(H,H)=6.2 Hz, 1H; H_3), 8.73 (d, ^3J(H,H)=8.6 Hz, 1H), 8.08 (d, ^3J(H,H)=7.5 Hz, 1H), 8.04 (d, ^3J(H,H)=8.3 Hz, 1H), 7.78–7.60 (m, 6H), 7.42–7.26 (m, 5H), 7.08 (dd, ^3J(H,H)=6.8 and 6.8 Hz, 1H), 6.96 (d, ^3J(H,H)=8.6 Hz, 1H), 6.74 (s, 1H), 6.43 (s, 1H), 6.24–6.17 (m, 3H, C*H*Me), 2.94 (d, ^3J=4.5 Hz, 3H; NMe), 2.69 (d, ^3J=5.0 Hz, 3H; NMe), 1.97 (d, ^3J(H,H)=7.2 Hz, 3H; CH*Me*), 1.90 (bs, 6H; 2 Me), 1.58 (s, 6H; 2 Me); ^{13}C NMR (125.72 MHz, $CDCl_3$): 157.3 (s; C_1), 149.1, 143.7 (s; C_3), 138.3 (d, J(P,C)=11.6 Hz), 138.2–122 (m), 71.6 (s; *C*HMe), 44.1 (s; NMe), 41.0 (s; NMe), 20.7 (s; 2 Me), 20.2 (s; 2 Me), 16.7 (s; CH*Me*); ^{31}P NMR (101 MHz, $CDCl_3$): δ=29.3 (*S*); IR (KBr): ν=1126, 814 cm^{-1}; MS (electrospray); m/z: 799 [M$^+$]; $C_{49}H_{46}ClN_2PPd$ (799.2).

*Resolution of cis-[(*R*)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(*R*) and (*S*)-1′-(2-P-dibenzophospholo-1-naphthyl)isoquinoline] palladium(II) hexafluorophosphate/chloride* ***6d***

The first diastereomer crystallises as a PF_6^- salt, the second diastereomer crystallises as a Cl^- salt. The yield depends on the scale and on the number of crystallisations (between 50 and 65% for each diastereomer).

First crystallised diastereomer (PF_6^- salt): yellow solid; m.p. 238°C; $[\alpha]_D^{20}$=−49 (c=1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ=9.08 (d, ^3J(H,H)=6.0 Hz, 1H; H_3), 8.68 (d, ^3J(H,H)=6.0 Hz, 1H; H_4), 8.32 (d, ^3J=8.3 Hz, 1H), 8.04 (d, ^3J(H,H)=8.1 Hz, 1H), 8.0–7.85 (m, 4H), 7.75 (dd, ^3J(H,H)=7.7 and 7.5 Hz, 1H), 7.70–7.60 (m, 3H), 7.50–7.35 (m, 6H), 7.30–7.22 (m, 3H), 7.21 (d, ^3J(H,H)=8.7 Hz, 1H), 7.13 (dd, ^3J(H,H)=8.3 and 8.0 Hz, 1H), 7.02 (d, ^3J(H,H)=8.7 Hz, 1H), 6.98 (d, ^3J(H,H)=8.4 Hz, 1H; naphthylethylamine H_4), 6.67 (m, 1H), 6.24 (dd, ^3J=8.4 and 6.6 Hz, 1H; naphthylethylamine H_3), 4.96 (dq, ^3J=6.3 and 6.1 Hz, 1H; C*H*Me), 2.92 (d, ^3J=1.9 Hz, 3H; NMe), 2.77 (d, ^3J=3.4 Hz, 3H; NMe), 1.67 (d, ^3J=6.1 Hz, 3H; CH*Me*). ^{13}C NMR (125.72 MHz, $CDCl_3$): 157.1 (s; C_1), 150–142 (5C), 141.9 (s; C_3), 140–122 (m), 73.5 (s; *C*HMe), 51.7 (s; NMe), 47.6 (s; NMe), 24.0 (s; CH*Me*); ^{31}P NMR (101 MHz, $CDCl_3$): δ=28.1 (*S*), −142.9 (heptet, J(P,F)=514 Hz; PF_6); IR (KBr): ν=1440 cm^{-1} (P–Ar), 842 cm^{-1} (P–F); MS (electrospray); m/z: 741 [M$^+$]; (741.2). Anal. Calcd for ($C_{45}H_{36}F_6N_2P_2Pd$+Et_2O): C 61.22, H 4.82, N 2.91. Found: C 60.95, H 4.68, N 2.93.

Second crystallised diastereomer (Cl^- salt): yellow solid; m.p. 219°C; $[\alpha]_D^{20}$=+43 (c=1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.89 (dd, ^3J(P,H)=13.5 Hz, ^3J(H,H)=8.6 Hz, 1H; $H_{3'}$), 8.16 (d, ^3J(H,H)=5.7 Hz, 1H; H_3), 8.10 (d, ^3J=8.6 Hz, 1H; $H_{4'}$), 8.01 (dd, ^3J(H,H)=7.9 and 7.3 Hz, 1H), 7.95–7.85 (m, 2H), 7.74 (d, ^3J(H,H)=7.8 Hz, 1H), 7.68–7.25 (m, 13H), 7.15 (dd, ^3J(H,H)=7.9 and 7.4 Hz, 1H), 7.10 (dd, ^3J(H,H)=7.5 and 7.5 Hz, 1H), 7.02 (d, ^3J(H,H)=8.6 Hz, 1H), 6.77 (d, ^3J(H,H)=8.6 Hz, 1H; naphthylethylamine H_4), 6.67 (dd, ^3J=7.6 and 7.5 Hz, 1H; naphthylethylamine H_3), 6.61 (m, 1H), 4.23 (dq, ^3J=6.2 and 6.2 Hz, 1H; C*H*Me), 2.86 (d, ^3J=3.3 Hz, 3H; NMe), 2.44 (s, 3H; NMe), 1.93 (d, ^3J=6.2 Hz, 3H; CH*Me*); ^{13}C NMR (125.72 MHz, $CDCl_3$): 157.7 (s; C_1), 150–142.3 (4 C), 142.1 (s; C_3), 136–133 (m), 132.7 (d, J(P,C)=23.2 Hz; $C_{3'}$), 132–120 (m), 73.3 (s; *C*HMe), 51.6 (s; NMe), 48.8 (s; NMe), 23.9 (s; CH*Me*); ^{31}P NMR (101 MHz, $CDCl_3$): δ=39.5 *(S)*; IR (KBr): ν=1439 cm^{-1} (P–Ar); MS (electrospray); m/z: 741 [M$^+$]; (741.2). Anal. Calcd for ($C_{45}H_{36}ClN_2PPd$+0.5 H_2O): C 68.71, H 4.74, N 3.56. Found: C 68.67, H 4.68, N 3.40.

Resolution of cis-[(R)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(R) and (S)-1-(2-difurylphosphino-1-naphthyl)isoquinoline] palladium(II) hexafluorophosphate/chloride 7d

The first diastereomer crystallises as a PF_6^- salt, the second diastereosiomer crystallises as a Cl^- salt. The yield depends on the scale and on the number of crystallisations (between 70 and 85% for each diastereomer).

First crystallised diastereomer (PF_6^- salt): white solid; m.p. 207°C; $[\alpha]_D^{20}=-216$ (c=1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.87 (d, ^3J(H,H)=6.2 Hz, 1H; H_3), 8.36 (d, ^3J(H,H)=6.2 Hz, 1H; H_4), 8.13 (dd, ^3J(H,H)=8.5, ^3J(P,H)=2.0 Hz, 1H; $H_{4'}$), 8.04 (d, ^3J(H,H)=8.3 Hz, 1H), 8.00 (d, ^3J(H,H)=8.3 Hz, 1H), 7.78–7.70 (m, 2H), 7.68–7.65 (m, 2H), 7.64 (m, 1H; furyl H_5), 7.45–7.35 (m, 4H), 7.32 (dd, ^3J(H,H)=8.6 and 8.3 Hz, 1H), 7.16 (d, ^3J(H,H)=8.4 Hz, 1H; naphthylethylamine H_4), 7.11 (d, ^3J(H,H)=8.6 Hz, 1H), 7.02 (m, 1H; furyl $H_{5'}$), 6.98 (d, ^3J(H,H)=8.5 Hz, 1H), 6.77 (dd, ^3J=3.1 and 3.0 Hz, 1H; furyl $H_{3'}$), 6.72 (m, 1H; furyl H_3), 6.60 (m, 1H; furyl H_4), 6.52 (dd, ^3J(H,H)=8.4, ^4J(P,H)=7.3 Hz, 1H; naphthylethylamine H_3), 5.87 (m, 1H; furyl $H_{4'}$), 4.33 (dq, ^3J=6.4 and 6.4 Hz, 1H; C*H*Me), 2.97 (d, ^3J=2.3 Hz, 3H; NMe), 2.73 (d, ^3J=3.7Hz, 3H; NMe), 1.63 (d, ^3J=6.4 Hz, 3H; CH*Me*). ^{13}C NMR (125.72 MHz, $CDCl_3$): 156.8 (d, J_{PC}=8.0 Hz; C_1), 150.3 (s; furyl C_5), 149.3 (s; furyl $C_{5'}$), 149.0, 146.2, 141.0 (s; C_3), 138.5–136.9 (m), 135.0 (d, J(P,H)=13.4 Hz; naphthylethylamine C_2), 134.2, 132.7–124 (m), 111.9 (s; furyl C_4), 110.9 (s; furyl $C_{4'}$), 73.7 (s; *C*HMe), 52.0 (s; NMe), 47.7 (s; NMe), 23.8 (s; CH*Me*); ^{31}P NMR (101 MHz, $CDCl_3$): δ=−0.6 *(S)*, −143.3 (heptet; PF_6); IR (KBr): ν=843 cm^{-1} (P–F); MS (electrospray); m/z: 723 [M^+]; (723.1). Anal. Calcd for ($C_{41}H_{34}F_6N_2O_2P_2Pd+H_2O$): C 55.51, H 4.09, N 3.16. Found: C 55.71, H 3.83, N 3.17.

Second crystallised diastereomer (Cl^- salt): yellow solid; m.p. 205°C; $[\alpha]_D^{20}=-246$ (c=1, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.60 (d, ^3J(H,H)=5.7 Hz, 1H; H_3), 7.97 (d, ^3J(H,H)=8.5 Hz, 1H; $H_{4'}$), 7.92 (d, ^3J=8.2 Hz, 1H), 7.66 (d, ^3J(H,H)=8.4 Hz, 1H; naphthylethylamine H_5), 7.64 (d, ^3J(H,H)=7.9 Hz, 1H), 7.63 (d, ^3J(H,H)=8.0 Hz, 1H; naphthylethylamine H_8), 7.62 (bs, 1H, furyl $H_{5'}$), 7.59 (dd, ^3J(H,H)=8.8 Hz, ^3J(P,H)=11 Hz, 1H; $H_{3'}$), 7.57 (d, ^3J(H,H)=8.4 Hz, 1H), 7.54 (dd, ^3J(H,H)=8.4 and 7.2 Hz, 1H), 7.47 (dd, ^3J(H,H)=8.4 and 7.4 Hz, 1H), 7.45 (d, ^3J(H,H)=5.7 Hz, 1H; H_4), 7.41 (bs, 1H, furyl $H_{3'}$), 7.37 (dd, ^3J(H,H)=8.0 and 7.4 Hz, 1H; naphthylethylamine H_7), 7.34 (dd, ^3J(H,H)=7.9 and 7.2 Hz, 1H), 7.33 (dd, ^3J(H,H)=8.4 and 7.4 Hz, 1H; naphthylethylamine H_6), 7.19 (dd, ^3J(H,H)=8.0 and 7.2 Hz, 1H), 7.09 (bs, 1H, furyl H_5), 7.00 (d, ^3J(H,H)=8.6 Hz, 1H; naphthylethylamine H_4), 6.89 (bs, 1H; furyl H_3), 6.87 (d, ^3J(H,H)=8.6 Hz, 1H), 6.53 (dd, ^3J=(H,H) 1.7 and 1.7 Hz, 1H; furyl $H_{4'}$), 6.38 (dd, ^3J(H,H)=8.4, ^3J(P,H)=7.6 Hz, 1H; naphthylethylamine H_3), 5.88 (bs, 1H; furyl H_4), 4.19 (dq, J=6.4 and 6.4 Hz, 1H; C*H*Me), 2.83 (d, ^3J=3.4 Hz, 3H; NMe), 2.19 (s, 3H; NMe), 2.03 (d, ^3J=(H,H) 6.4 Hz, 3H; CH*Me*). ^{13}C NMR (125.72 MHz, $CDCl_3$): 159.6 (s; C_1), 150–143 (m; 8C), 142.9 (s; C_3), 141.4 (d, J(P,H)=12.9 Hz; $C_{2'}$), 136.4, 135.8 (d, J(P,H)=12.5 Hz; naphthylethylamine C_2), 134.4, 133.2 (d, J(P,H)=10.8 Hz; $C_{1'}$), 132–120 (m), 111.4 (d, J(P,H)=8.1 Hz; furyl C_4), 110.8 (d, J(P,H)=8.8 Hz; furyl $C_{4'}$), 73.4 (s; *C*HMe), 51.2 (s; NMe), 48.9 (s; NMe), 24.1 (s; CH*Me*). ^{31}P NMR (101 MHz, $CDCl_3$): δ=+0.6 *(S)*; IR (KBr): ν=1010, 819 cm^{-1}; MS (electrospray); m/z: 723 [M^+]; (723.1). Anal. Calcd for ($C_{41}H_{34}ClN_2O_2PPd+2\ H_2O$): C 61.90, H 4.81, N 3.52. Found: C 62.24, H 4.48, N 3.49.

Decomplexation of the ligands

(S)-(-)-1′-(2-Di(3-methylphenyl)phosphino-1-naphthyl)isoquinoline (S)-4c

80 mg (0.2 mmol) of 1,2 bis(diphenylphosphino)ethane was added to a solution of cis-[(*R*)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(−)-1-(2-di(3-methylphenyl)phosphino-1-naphthyl)-isoquinoline] palladium(II) hexafluorophosphate, 155 mg (0.2 mmol) in dichloromethane (20 ml). The solution was stirred for 4 hours then the solvent removed *in vacuo* to leave a white solid. Toluene (20 ml) was added and the suspension stirred for 10 min. The solid was removed by filtration then the solvent removed *in vacuo* to give 84 mg (90%) of (−)-1′-(2-di-(3-methylphenyl)phosphino-1-naphthyl)isoquinoline as a white solid. $[\alpha]_D^{20}=-118$ (c=0.5, $CHCl_3$). If there are some traces of DPPE the product can be purified by chromatography on silica (eluent CH_2Cl_2).

(S)-(−)-1′-(2-Di(3,5-dimethylphenyl)phosphino-1-naphthyl)isoquinoline (S)-5c

The same procedure as for (−)-**4c** was followed from cis-[(*R*)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(−)-1-(2-di-(3,5-dimethylphenyl)phosphino-1-naphthyl)isoquinoline] palladium(II) chloride (first diastereomer) to give (−)-1-(2-di-(3,5-dimethylphenyl)phosphino-1-naphthyl)isoquinoline (88%) as a white solid. $[\alpha]_D^{20}=-53$ (c=1, $CHCl_3$).

(R)-(+)-1′-(2-P-Dibenzophospholo-1-naphthyl)isoquinoline (R)-6c

The same procedure as for (−)-**4c** was followed from cis-[(*R*)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(+)-1-(2-P-dibenzophospholo-1-naphthyl) isoquinoline] palladium(II) chloride to give (+)-1-(2-P-dibenzophospholo-1′-naphthyl)isoquinoline (91%) as a white solid. $[\alpha]_D^{20}=+240$ (c=0.5, $CHCl_3$).

(S)-(+)-1′-(2-Di(2-furyl)phosphino-1-naphthyl)isoquinoline (S)-7c

The same procedure as for (−)-**4c** was followed from cis-[(*R*)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(+)-1′-(2-di(2-furyl)phosphino-1-naphthyl)isoquinoline] palladium(II) hexafluorophosphate to give (+)-1′-(2-di(2-furyl)phosphino-1-naphthyl)isoquinoline (93%) as a white solid. $[\alpha]_D^{20}=+68$ (c=0.5, $CHCl_3$).

(R)-(−)-1′-(2-Di(2-furyl)phosphino-1-naphthyl)isoquinoline (R)-7c

The same procedure as for (−)-**4c** was followed from cis-[(*R*)-dimethyl(1-naphthylethyl)aminato-C^2,N]-[(−)-1′-(2-di(2-furyl)phosphino-1-naphthyl)isoquinoline] palladium(II) chloride to give (−)-1′-(2-di(2-furyl)phosphino-1-naphthyl)isoquinoline (88%) as a white solid. $[\alpha]_D^{20}=-69$ (c=0.5, $CHCl_3$).

Acknowledgements

We thank the Catalysis and Processes panel of EPSRC for support (to HD), Johnson–Matthey for a loan of palladium salts. Ms Tam Bui of the EPSRC National Chiroptical Spectroscopy, King's College, kindly recorded the spectra of Figure 1, arranged by Mark Hooper.

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(Received in UK 29 September 1997; accepted 30 October 1997)