Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information 1

Asymmetric Amplification in Catalytic Enantioselective 1,2-Addition of Grignard Reagents to Enones

Francesca Caprioli, Ashoka V. R. Madduri, Adriaan J. Minnaard*, Syuzanna R. Harutyunyan*

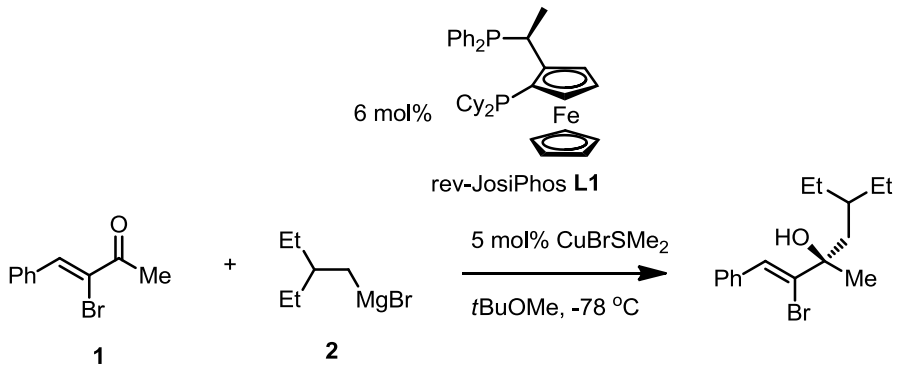
Contents

1. General information

General. Chiral ligands **rev-JosiPhos-L1, JosiPhos-L2, TaniaPhos-L3** and **WalPhos-L4** were donated by Solvias (Basel). **BINAP-L5**, CuBr·SMe_2 and $(C_6H_5CH_2CN)_2PdCl_2$ were purchased from Aldrich or Acros, and used without further purification. *t*BuOMe was purchased as anhydrous grade, stored on 4 Å MS and used without further purification. Solvents used were either technical grade (pentane) or distilled from the indicated drying agents (dichloromethane: P_2O_5.). CD_2Cl_2 and $CDCl_3$ were used for NMR. ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{31}P{^{1}H} NMR spectra were obtained with Varian VXR600 500 400 spectrometers equipped with a 5 mm *z*-gradient broadband probe. ^{1}H, ^{31}P and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) and were measured relative to the residual solvent peak (CD_2Cl_2 δ = 5.30 ppm for hydrogen atoms, δ = 53.5 ppm for carbon atoms, $CDCl_3$, δ = 7.26 ppm for hydrogen atoms, δ = 77.0 ppm for carbon atoms). ^{31}P chemical shifts are referenced to the standard PPh_3 (-9 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Due to ^{31}P coupling, resonances for certain carbon atoms in the phosphines listed below were observed as doublets. UV spectral data were obtained using a JASCO V630 DUAL BEAM spectrophotometer; CD spectra were obtained using a JASCO CD Spectropolarimeter J815. Progress of the reaction and conversion were determined by GC-MS (GC, HP6890: MS HP5973) with HP1 or HP5 columns (Agilent Technologies, Palo Alto, CA). Enantiomeric excesses (ee values) for **3** were determined by HPLC analysis using a Shimadzu LC 10AD*VP* HPLC equipped with a Shimadzu SPDM10A*VP* diode array detector and chiral columns as indicated. Sample injections were made using an HP 6890 Series Auto sample Injector. Exact mass spectra were recorded on a LTQ Orbitrap XL (ESI+) or on a DART Xevo G2 QTof. Optical rotations were measured in *t*BuOMe and CH_2Cl_2 on a Perkin Elmer 241 MC polarimeter with a 10 cm cell (concentration *c* given in g/mL). To calculate the error bars for optical rotation, each rotation measurement was done several times and the standard deviation for each sample is typically a few degrees. The uncertainties in the concentration of the samples were addressed by preparing the same sample 5 times. The standard deviation was found to be 5%. Overall the uncertainties of the optical rotation values are dominated by the uncertainties in the concentration of the corresponding samples. Therefore the error budget for the specific optical rotation values have a typical error of 5%. All the reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Reaction vessels were flame-dried prior to use. Flash chromatography was performed using Merck 60 Å 230-400 mesh silica gel. All organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure using a rotary evaporator.

All the NMR, ESI-MS and DART MS spectra are contained in SI 2.

2. 1,2-addition of Grignard reagents



Standard procedure for asymmetric catalytic 1,2-addition of Grignard reagents to enones.[1]

A Schlenk flask equipped with septum and stirring bar was charged with $CuBr{\cdot}SMe_2$ (0.015 mmol, mg, 5 mol%) and ligand **L1** (0.018 mmol, 6 mol%). Dry *t*BuOMe (3 mL) was added and the solution was stirred under nitrogen for 30 min. Then, the corresponding enone **1** (0.3 mmol in 1 mL *t*BuOMe) was added and the resulting solution was cooled to –78 °C. In a separate Schlenk, the corresponding Grignard reagent **2** (0.36 mmol, 1.2 equiv.) was diluted with *t*BuOMe (combined volume of 1 mL) under nitrogen and added dropwise to the reaction mixture over 3 h using a syringe pump. Once the addition was complete, the reaction mixture was monitored by TLC and GC-MS. The reaction was quenched by the addition of MeOH (1 mL) and saturated aqueous NH_4Cl (2 mL) and the mixture was warmed to rt, diluted with Et_2O and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 5 mL) and the combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel using mixtures of *n*-pentane and Et_2O as the eluent. The enantiomeric ratio was determined by chiral HPLC analysis, Chiralcel AD-H column, *n*-heptane *i*-PrOH 99 : 1, 40 °C, detection at 240 nm, retention times (min): 22.6 and 23.7.

Procedure for 1,2-addition of Grignard reagents to enones catalysed by a CuBr complex of scalemic rev-JosiPhos-L1:

Catalysts of varying enantiopurities (100, 80, 60, 40, 20 or 0% ee) were obtained by mixing the requisite ratios of equimolar stock solutions of the CuBr complexes of both enantiomers of rev-JosiPhos-**L1** in CH_2Cl_2. After stirring for 1 h, the solvent was removed *in vacuo* followed by addition of *t*BuOMe and stirring at rt for 5 h. The resulting suspension was centrifuged to

[1] A. V. R. Madduri, A. J. Minnaard and S. R. Harutyunyan, *Org. Biomol. Chem.*, 2012, **10**, 2878–2884.

provide a precipitate and a supernatant.[2] The supernatant was separated, evaporated, and the resulting residue was used to catalyze the 1,2-addition reaction of Grignard reagent **2** to enone **1**. We found that the enantioselectivity of the reactions catalyzed by 5 mol% of the supernatant of complexes with 80, 60, 40 and 20% ee was very similar to the results obtained with the enantiopure catalyst (5 mol% rev-JosiPhos-**L1**, 5 mol% of CuBr·SMe_2 in 3 ml of *t*BuOMe). When the supernatant/precipitate mixture was used in entirety as catalyst for the 1,2-addition, the reaction was found to proceed with somewhat lower ee but longer reaction time (48 h) and vigorous stirring was required due to the presence of a significant amount of the precipitate.

Table S1

Entry	CuBr-L1, ee (%)[a]	ee (%) 3 using supernatant [b] (conv. to product %)[c]	ee (%) 3 using supernatant/precipitate [d] (conv. to product %)[c]
1	100	96(96)	96 (96)
2	80	94(93)	90 (90)
3	60	92(92)	90 (93)
4	40	94(95)	90 (82)
5	20	94(92)	80 (75)
6	rac	2(51)	-

[a] Total of 5 mol% active catalyst present in the solution (using only supernatant). Reaction time 24 h. In case of using scalemic mixtures, the reaction time is 48 h. [b] The enantioselectivity of the reaction is determined by chiral HPLC. [c] Conversion was determined by GC-MS. [d] Total of catalyst loadings: 6.25 mol% of 80% ee, 8.33 mol% of 60% ee, 12.5 mol% of 40% ee, 25% of 20% ee)

[2] Cu-complex of rev-JosiPhos-**L1**with 20% ee needs to be centrifuged twice.

3. CuBr complex of Rev-JosiPhos-L1

Procedure for preparing CuBr complex of enantiopure rev-JosiPhos-L1

A solution of (*S,R*)-rev-JosiPhos-**L1** (0.006 mmol) and CuBr·SMe_2 (0.006 mmol) in *t*BuOMe (1.3 ml) in a Schlenk tube was stirred at rt for 1 h. The solvent was removed under vacuum and the resulting orange crude residue was washed with cold pentane to afford enantiopure CuBr-complex as an orange powder.

(*S,R*)-revJosiPhos-L1 CuBr enantiopure complex ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66 (m, 2H, ArH), 7.51 – 7.40 (m, 5H, ArH), 7.35 (m, 1H, ArH), 7.29 (t, *J*= 7.2 Hz, 2H, ArH), 4.34 (d, *J*= 9.5 Hz, 2H, FcH), 4.9 (s, 1H, FcH), 4.11 (s, 5H, FcH), 3.60 (m, 1H, CH), 2.63-0.86 (m, 25H, CyH and CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) δ -19.29 (m). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 16.0 (s, CH_3), 22.2 (s, 1C), 22.9 (s, 1C), 25.2 (d, *J* = 18.5 Hz, $2CH_2$), 25.9 (d, *J*=6.6, 1CH, $1CH_2$), 26.3 (bs, $1CH_2$), 27.1 (d, $1CH_2$), 29.2 (d, $1CH_2$), 29.6 (d, *J* = 4.1 Hz, $1CH_2$), 30.7 (d, $2CH_2$), 32.9 (d, 1CH), 34.3 (m,$1CH_2$), 38.1(d, *J* = 29.1 Hz, 1CH), 67.2 (s, 1CH), 68.1 (s, 1CH), 69.1 (s, 5CH), 72.8 (s, 1CH), 73.7(d, *J*= 29.1 Hz, 1C), 91.4 (d, 1C), 127.5 (d, *J* = 8.3 Hz, 2CH), 127.9 (d, *J* = 7.9 Hz, 2CH), 129.1 (d, 1CH), 130.1 (s, 1CH), 132.6 (d, *J* = 16.0 Hz, 2CH), 133.5 (d, J=15.5 Hz, 2CH). ESI-MS (CH_2Cl_2): 1472 [M^+ ($C_{72}H_{88}P_4Fe_2Cu_2Br_2$)], 1393 [$M^+$ - Br ($C_{72}H_{88}P_4Fe_2Cu_2Br$)], 698 [$M^+$ - Br + CH_3CN ($C_{35}H_{56}P_2FeCu$)]. ESI-MS (*t*BuOMe): 1472 [M^+ ($C_{72}H_{88}P_4Fe_2Cu_2Br_2$)], 1393 [$M^+$ - Br ($C_{36}H_{44}P_4Fe_2Cu_2Br$)], 736 [$M^+$ - $C_{36}H_{44}P_2FeCuBr$ ($C_{36}H_{44}P_2FeCuBr$)]. All isotopic patterns are in agreement with those calculated. Mp (decomposition) 198-200^{o}C.

Procedure for preparing CuBr complex of racemic rev-JosPhos-L1

Method A

Equimolar solutions of both enantiomers of CuBr complex of rev-JosiPhos-**L1** were prepared by mixing CuBr·SMe_2 (0.006 mmol) with enantiopure ligand (0.006 mmol) in 1.3 ml of a solvent (CH_2Cl_2 or *t*BuOMe) in a Schlenk tube and stirring at rt for 1h. Corresponding solutions were mixed together, stirred for additional hour to form the racemic complex. The precipitate was formed within that period. The solvent was removed under vacuum and the resulting crude residue was washed with cold pentane and dried to afford racemic CuBr complex of rev-JosiPhos-**L1**.

Method B

To a solution of (*S,R*)-rev-JosiPhos-**L1** (0.006 mmol) in 2.6 ml of CH_2Cl_2 (*R,S*)-rev-JosiPhos-**L1** (0.006 mmol) was added, followed by addition of $CuBr{\cdot}SMe_2$ (0.0125 mmol). The resulting solution was stirred at rt for 1 h. The precipitate formed within that period. The solvent was removed under vacuum and the resulting orange crude residue was washed with cold pentane to afford CuBr-complex of racemic rev-JosiPhos-**L1** as an orange powder.

CuBr complex (*S,R*)-(*R,S*) rev-JosiPhos-L1 racemate No NMR measurements were performed due to the very low solubility of the racemate in any organic solvent. ESI-MS (CH_2Cl_2): 1472 [M^+ ($C_{72}H_{88}P_4Fe_2Cu_2Br_2$), 1393 [$M^+$ - Br ($C_{36}H_{44}P_4Fe_2Cu_2Br$)], 698 [$M^+$ - Br + CH_3CN ($C_{35}H_{56}P_2FeCu$)]. All isotopic patterns are in agreement with those calculated. Mp (decomposition) 250-255^oC.

Precipitation studies

Solutions of CuBr complexes of rev-JosiPhos-**L1** (0.015 M) of varying enantiopurities (100, 70, 50, 20 and 0% ee) were obtained in *t*BuOMe using method **A** or **B** with stirring continuing for 12 h. Centrifugation of these solutions resulted in a precipitate and supernatant (an exception was the solution with 100% ee, which did not have any precipitate). The precipitate that starts forming after 20 min was not analyzed further due to low solubility. However the weight of the precipitate, in each case, was found to be approximately equivalent to twice the weight of the limiting enantiomer of the complex. Specific optical rotations and CD spectra obtained from the supernatants closely matched those from the enantiopure catalyst (Table S2 and Figure S1).

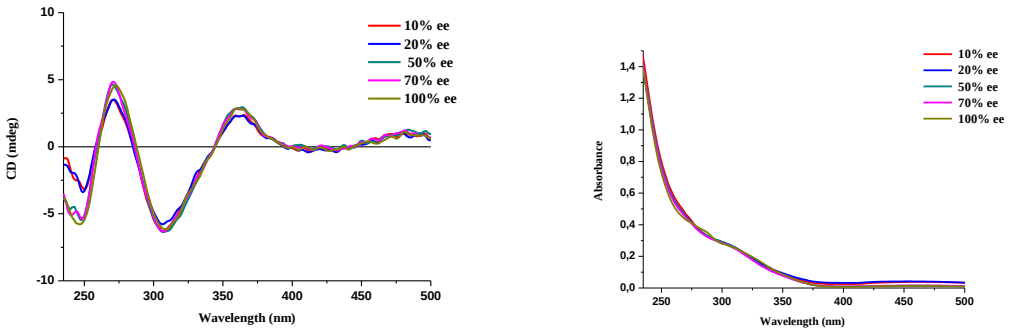
Table S2. Specific optical rotation values for the supernatants of scalemic CuBr rev-JosiPhos-**L1** in *t*BuOMe

Entry	Supernatant[a]	$[\alpha]_D^{20a}$	*c* (g/ml)	Precipitate[b]	$[\alpha]_D^{20b}$	*c*(g/ml)
1	20 % ee	-6	$1.0*10^{-3}$	-	-	-
2	40 % ee	-7	$2.9*10^{-3}$	-	-	-
3	60 % ee	-7	$5.0*10^{-3}$	-	-	-
4	80% ee	-7	$7.0*10^{-3}$	-	-	-
5	100% ee	-8	$7.1*10^{-3}$	-	-	-

[a]The optical rotation was measured in *t*BuOMe; [b] Precipitate was not soluble in any organic solvent

Figure S1: a) CD spectra of *t*BuOMe supernatants in CH_2Cl_2; **b)** UV spectra of supernatants in CH_2Cl_2.

a) **b)**



Isolation of rev-JosiPhos –L1 from supernatant of Cu-complex with 20% ee

The supernatant of CuBr complex of rev-Josiphos-**L1** obtained in *t*BuOMe was evaporated and solubilized in CH_2Cl_2 (0.005 M) followed by addition of 20 equiv of ethylenediamine at 0 ^oC. The resulting solution was stirred for 1 h at the same temperature. The reaction progress was followed by TLC (pentane /ethyl acetate). Purification by column chromatography (pentane /ethyl acetate) afforded the free ligand in 76% yield.

Supernatant of complex with 20% ee: $[\alpha]_D^{20a} = -6$ ($c = 9.3 \times 10^{-3}$ g/ml in *t*BuOMe)

CuBr-rev-JosiPhos-**L1** with 100% ee $[\alpha]_D^{20a} = -8$ ($c = 7.1 \times 10^{-3}$ g/ml in *t*BuOMe)

Free ligand from sample with 20% ee $[\alpha]_D^{20a} = -158$ ($c = 1.25 \times 10^{-3}$ g/ml in CH_2Cl_2)

rev-JosiPhos-**L1** with 100% ee $[\alpha]_D^{20a} = -163$ ($c = 2.76 \times 10^{-3}$ g/ml in CH_2Cl_2)

4. CuBr complex of JosiPhos-L2

Procedure for preparing CuBr complex of enantiopure JosiPhos-L2

A solution of (*R,S*)-JosiPhos-**L2** (0.006 mmol) and CuBr·SMe_2 (0.006 mmol) in *t*BuOMe (1.3 ml) in a Schlenk tube was stirred at rt for 30 min. The solvent was removed under vacuum and the resulting orange crude residue was washed with cold pentane to afford enantiopure CuBr-complex as an orange powder.

(*R,S*) - JosiPhos-L2 CuBr enantiopure complex ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.07 – 7.91 (m, 2H, ArH), 7.55 – 7.46 (m, 3H, ArH), 7.24-7.21 (m, 5H), 4.57 (m, 1H, FcH), 4.47 (t, 1H, FcH), 4.33-4.26 (m, 1H, FcH), 3.81 (s, 5H, FcH), 3.52-3.41 (m, 1H, CH), 2.22-0.95 (m, 25H, CyH and CH_3). ^{31}P NMR (CD_2Cl_2 at RT) δ, 5.74 (d, *J* = 193.1 Hz), -26.61 (d, *J* = 194.6 Hz); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 15.9 (s, CH_3), 26.4 (d, *J* = 18.7 Hz, $2CH_2$), 27.2 (dd, *J*=19.4, 11.9 Hz, 1CH, $1CH_2$), 27.8 (d, *J* = 8.1 Hz, $1CH_2$), 28.2 (d, *J* = 13.8 Hz, $1CH_2$), 29.23 (d, *J* = 6.0 Hz, $1CH_2$), 29.6 (d, *J* = 7.6 Hz, $1CH_2$), 30.7 (m, $2CH_2$), 32.1 (t, 2CH), 32.4 (d, *J* = 9.1 Hz, $1CH_2$), 70.3 (d, *J* = 4.1 Hz, 1CH), 70.8 (s, 5CH), 71.2 (d, *J*=8.3 Hz, 1CH), 73.5 (d, *J*= 29.1 Hz, 1C), 94.8 (d, *J*= 22.1 Hz, 1C), 128.7 (d, *J* = 8.3 Hz, 2CH), 128.9 (d, *J* = 10.3 Hz, 2CH), 129.3 (s, 1CH), 131.0 (s, 1CH), 132.8 (d, *J* = 14.0 Hz, 2CH), 135.5 (d, J=17.7 Hz, 2CH), 136.0 (m, 2C). ESI-MS (CH_2Cl_2): 1472 [M^+ ($C_{72}H_{88}P_4Fe_2Cu_2Br_2$)], 1393 [$M^+$ - Br ($C_{72}H_{88}P_4Fe_2Cu_2Br$)], 736 [$M^+$ - $C_{36}H_{44}P_2FeCuBr$ ($C_{36}H_{44}P_2FeCuBr$)], 698 [M^+ - Br + CH_3CN ($C_{35}H_{56}P_2FeCu$)]. ESI-MS (*t*BuOMe): 1472 [M^+ ($C_{72}H_{88}P_4Fe_2Cu_2Br_2$)], 1393 [$M^+$ - Br ($C_{36}H_{44}P_4Fe_2Cu_2Br$)], 736 [$M^+$ - $C_{36}H_{44}P_2FeCuBr$ ($C_{36}H_{44}P_2FeCuBr$)]. All isotopic patterns are in agreement with those of calculated. Mp (decomposition) 176-180 ^{o}C.

Procedure for preparing CuBr complex of racemic JosiPhos-L2

Method A

Equimolar solutions of both enantiomers of the CuBr complex of JosiPhos-**L2** were prepared by mixing CuBr·SMe_2 (0.006 mmol) with enantiopure ligand (0.006 mmol) in 1.3 ml of a solvent (*t*BuOMe or CH_2Cl_2) in a Schlenk tube and stirring at rt for 1 h. The corresponding solutions were mixed together, stirred for an additional hour to form the racemic complex (precipitate was formed when *t*BuOMe was used as a solvent). The solvent was removed under vacuum and the resulting crude residue was washed with cold pentane and dried to afford racemic CuBr complex of JosiPhos-**L2**.

Method B

(*R,S*)-JosiPhos-**L2** (0.006 mmol) was added to a solution of (*S,R*)-JosiPhos-**L2** (0.006 mmol) in 2.6 ml of CH_2Cl_2 followed by addition of $CuBr{\cdot}SMe_2$ (0.012 mmol). The resulting solution was stirred at rt for 1 h. No precipitate formed in this case. The solvent was removed under vacuum and the resulting orange crude residue was washed with cold pentane to afford CuBr-complex of racemic rev-JosiPhos-**L2** as an orange powder.

CuBr complex (*S,R*)-(*R,S*)-JosiPhos-L2 racemate ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.04 – 7.95 (m, 2H ArH), 7.57 – 7.16 (m, 3H, ArH), 7.35-7.19 (m, 5H), 4.57 (m, 1H, FcH), 4.47 (t, 1H, FcH), 4.33-4.26 (m, 1H, FcH), 3.82 (s, 5H, FcH), 3.54-3.45 (m, 1H. CH), 2.20-0.73 (m, 25H, CyH and CH_3). ^{31}P NMR (CD_2Cl_2 at RT) δ, 5.06 (d, *J* = 193.1 Hz), -26.79 (d, *J* = 194.6 Hz). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 15.6 (s, CH_3), 26.4 (d, *J* = 20.1 Hz, $2CH_2$), 27.2 (dd, *J*=21.3, 11.9 Hz, 1CH, $1CH_2$), 27.8 (d, *J* = 7.9 Hz, $1CH_2$), 28.2 (d, *J* = 13.7 Hz, $1CH_2$), 29.2 (d, *J* = 6.5 Hz, $1CH_2$), 29.5 (d, *J* = 7.6 Hz, $1CH_2$), 30.7 (m, $2CH_2$), 32.0 (t, 2CH), 32.5(d, *J* = 8.6 Hz, $1CH_2$), 70.3 (d, *J* = 4.3 Hz, 1CH), 70.8 (s, 5CH), 71.3 (d, *J*=8.3 Hz, 1CH), 73.7 (d, *J*= 28.5 Hz, 1C), 94.6 (d, *J*= 23.4 Hz, 1C), 128.7 (d, *J* = 8.3 Hz, 2CH), 129.0 (d, *J* = 10.3 Hz, 2CH), 129.3 (s, 1CH), 131.07 (s, 1CH), 132.8 (d, *J* = 14.1 Hz, 2CH), 135.5 (d, J=17.8 Hz, 2CH), 136.2 (m, 2C). ESI-MS (CH_2Cl_2): 1393 [M^+ - Br ($C_{72}H_{88}P_4Fe_2Cu_2Br$)], 698 [$M^+$ - Br + CH_3CN ($C_{35}H_{56}P_2FeCu$)]. All isotopic patterns are in agreement with those of calculated. Mp (decomposition) 215-220 ^oC.

Precipitation studies

CuBr complexes of JosiPhos-**L2** (0.015 M) of varying enantiopurities (100, 70, 50, 20 and 0% ee) were obtained in *t*BuOMe using either method **A** or **B** with stirring continuing for 12h (precipitate started to form after 5 h). Centrifugation of these solutions resulted in a precipitate and supernatant (an exception was solution with 100% ee, which did not have any precipitate).[3] The weight of the *t*BuOMe precipitate, in each case, was found to be approximately equivalent to twice the weight of the limiting enantiomer of the complex. Specific optical rotations and CD spectra (Table S3 and Figure S2) obtained from the supernatants closely matched those from the enantiopure catalyst except for the sample with 20% ee (Table S3, entry 2). Lower CD and rotation values obtained for samples with 20% ee can be attributed to the presence of tiny particles of the racemate in the supernatant which scatters the light. Therefore several cycles of centrifugation and precipitate removal were required (entry 1).

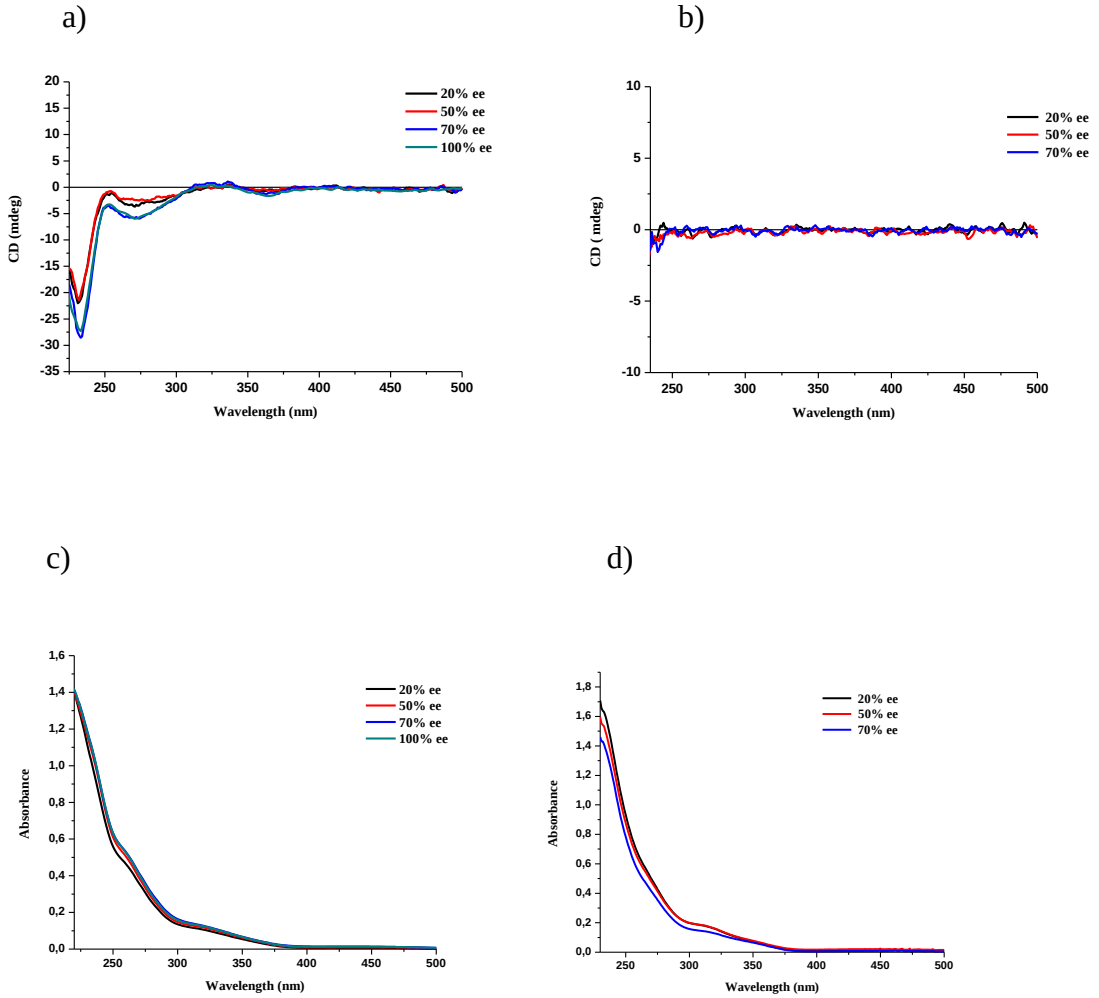
[3] The precipitate was soluble in CH_2Cl_2.

Table S3 Specific optical rotation values for the supernatants and precipitate of scalemic CuBr JosiPhos-**L2**

Entry	Supernatant[a]	$[\alpha]_D^{20a}$	*c* (g/ml)	Precipitate[b,c]	$[\alpha]_D^{20}$	*c* (g/ml)
1[d]	20% ee	-185	$1.0*10^{-3}$	20% ee	-13	$1.8*10^{-3}$
2	20% ee	-135	$2.8*10^{-3}$	-	-	-
3	50% ee	-191	$1.25*10^{-3}$	50% ee	-11	$1.3*10^{-3}$
4	70% ee	-192	$2.13*10^{-3}$	70% ee	-14	$1.35*10^{-3}$
5[e]	100% ee	-198	$4.0*10^{-3}$	-	-	-

[a]The optical rotation was measured in *t*BuOMe; [b]The optical rotation was measured in CH_2Cl_2.[c] The precipitate was washed with *t*BuOMe (2x5ml) and dried before preparing CH_2Cl_2 solution. [d] Sample with 20% ee needs to be centrifuged 2-3 times. [e] The value $[\alpha]_D^{20a}$ in CH_2Cl_2 was -341 *c (g/ml)*=2.6 $*10^{-3}$.

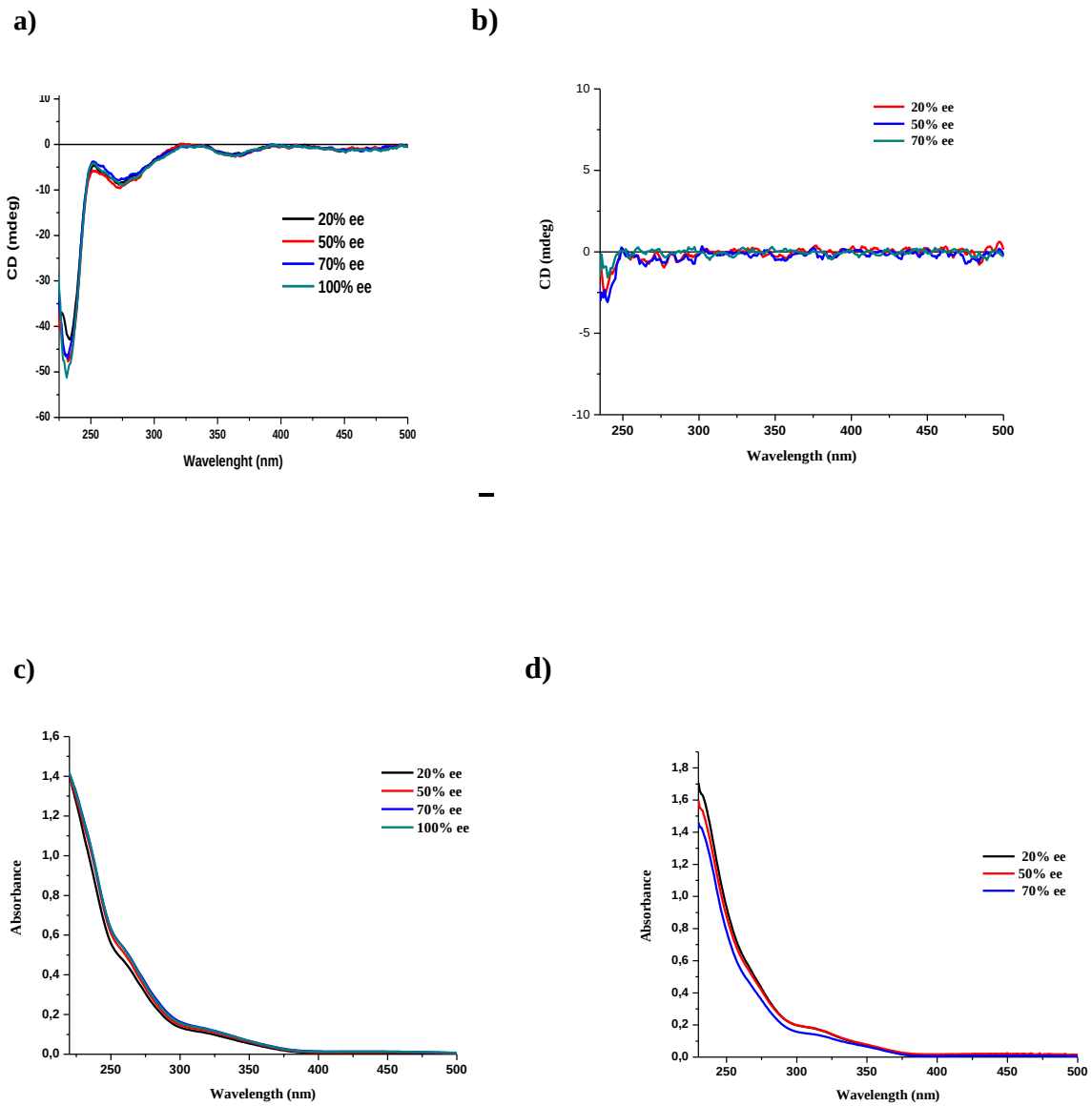
Figure S2: a) CD spectra of supernatants measured in *t*BuOMe; **b)** CD spectra of *t*BuOMe precipitates measured in CH_2Cl_2; c) UV spectra of supernatants in *t*BuOMe; d) UV spectra of precipitates in CH_2Cl_2.



Method C

To circumvent this problem we applied different approach. We prepared enantioenriched complexes (70, 50 and 20% ee) in CH_2Cl_2 using method **B**. After stirring for 2 h (no precipitation was observed) CH_2Cl_2 was evaporated to dryness. *t*BuOMe was added (0.025 M) followed by stirring at rt for 48 h. Centrifugation of these solutions resulted in a precipitate and a supernatant. CD spectra obtained from the supernatants closely matched those from the enantiopure catalyst (Figure S3).

Figure S3: a) CD spectra of supernatants measured in *t*BuOMe; **b)** CD spectra of precipitates measured in CH_2Cl_2; c) UV spectra of supernatants in *t*BuOMe; d) UV spectra of precipitates in CH_2Cl_2.



Isolation of JosiPhos –L2 from supernatant of Cu-complex with 50% and 20% ee

Enantioenriched complexes (50 and 20% ee) were prepared using method **A** and **C** respectively. The supernatant of the CuBr complex of Josiphos-**L2** obtained in *t*BuOMe was evaporated and solubilized in CH_2Cl_2 (0.005 M) followed by addition of 20 equiv of ethylenediamine at 0 ^oC. The resulting solution was stirred for 1 h at the same temperature. The reaction progress was followed by TLC (pentane /ethyl acetate, 9/1). Purification by column chromatography (pentane /ethyl acetate 9/1) afforded the free ligand (for yields see below). CD spectra of the ligand obtained from the copper complex with initial ee of 20% are shown in Figure S4.

Supernatant of complex with 50% ee: $[\alpha]_D^{20a}$ = -191 (c = 1.25 x 10^{-3} g/ml in *t*BuOMe)

Supernatant of complex with 20% ee: $[\alpha]_D^{20a}$ = -135 (c = 1.45 x 10^{-3} g/ml in *t*BuOMe)

CuBr-JosiPhos-**L2** with 100% ee $[\alpha]_D^{20a}$ = -198 (c= 4.0 x 10^{-3} g/ml in *t*BuOMe)

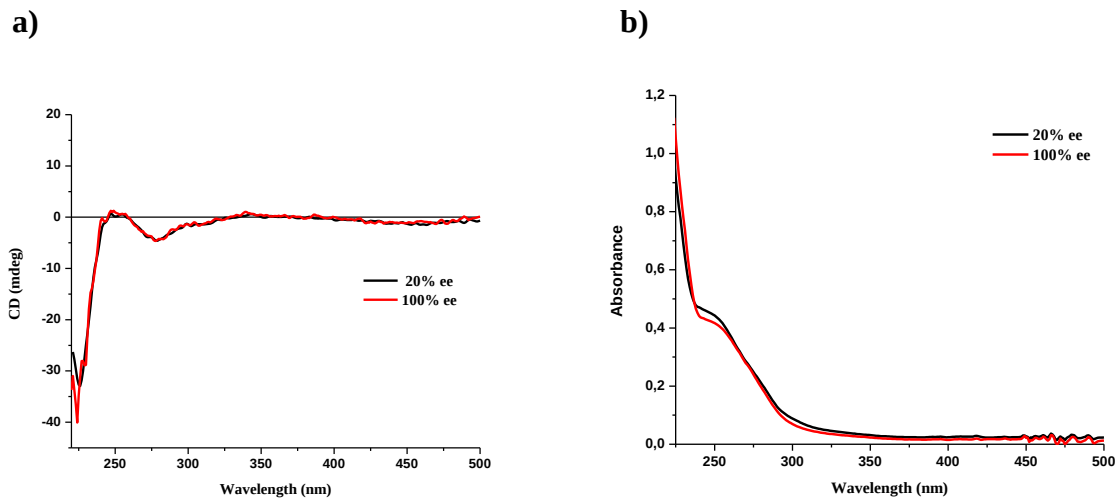
Free ligand from sample with 50% ee $[\alpha]_D^{20a}$ = -352 (c = 1.05 x 10^{-3} g/ml in CH_2Cl_2), 40% yield

Free ligand from sample with 20% ee $[\alpha]_D^{20a}$ = -363 (c = 0.95 x 10^{-3} g/ml in CH_2Cl_2), 82% yield

Free ligand from a precipitate of the sample with 50% ee $[\alpha]_D^{20a}$ = -5 (c = 2.5 x 10^{-3} g/ml in CH_2Cl_2), 98% yield

JosiPhos-**L2** with 100% ee $[\alpha]_D^{20a}$ = -370 (c = 1.3 x 10^{-3} g/ml in CH_2Cl_2)

Figure S4. a) CD spectra of an enantiopure ligand and of ligand isolated from supernatant of complex with 20% ee measured in CH_2Cl_2; **b)** UV spectra of the corresponding compounds.



Determination of the solubility for racemic and enantiopure Cu-complexes of JosiPhos-L2 in *t*BuOMe at rt.

CuBr complex of racemic JosiPhos-L2

A saturated solution of racemic complex of Josiphos-**L2** was prepared in *t*BuOMe (15 ml). The resulting heterogeneous mixture was stirred for 24 h at rt followed by centrifugation. The supernatant (15ml) was evaporated and 1 ml of CD_2Cl_2 was added to the residue. The ^{1}H and ^{31}P NMR analysis of the solution did not show any traces of the copper complex.

CuBr complex of enantiopure JosiPhos-L2

A saturated solution of the enantiopure complex of JosiPhos-**L2** was prepared in *t*BuOMe. The resulting heterogeneous solution was stirred for 24 h at rt followed by centrifugation. Two samples of 50 µl and 100 µl of supernatant solution were transferred in an Eppendorf, evaporated and dried under vacuum overnight, followed by weight determination.

100 µl sample $\rightarrow$ 7.1 mg

50 µl sample $\rightarrow$ 3.4 mg

Therefore the solubility of enantiopure the complex is 70 mg/ml and for the racemic complex less than 1 mg/15 ml (0.07 mg/ml).

5. CuBr complex of TaniaPhos-L3

Procedure for preparing CuBr complex of TaniaPhos-L3

Enantiopure, racemic and enantioenriched complexes of TaniaPhos-**L3** were prepared following the same procedures as described earlier for JosiPhos-**L2**.

(*R,R*)- TaniaPhos-L3 CuBr enantiopure complex ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.21 (t, 2H, ArH), 8.05 (bs, 2H, ArH), 7.59 – 7.40 (m, 6H, ArH), 7.33 (d, 2H, ArH), 7.23 (t, 1H, ArH), 7.06 (m, 3H, ArH), 6.99-6.96 (m, 1H, ArH), 6.90 (t, 2H, ArH), 6.65 (t, 1H, ArH), 6.39-6.34 (dt, 4H, ArH), 5.68 (d, 1H, CH), 4.95 (s, 1H, FcH), 4.61 (t, 1H, FcH), 4.13 (s, 1H, FcH), 4.05 (s, 5H,FcH), 1.96 (s, 6H, $2CH_3$). ^{31}P NMR (162 MHz, CD_2Cl_2) δ -26.4 – -29.4(m). ESI-MS (CH_2Cl_2): 843 [M^+ ($C_{44}H41P_2FeNCuBr$)], 764 [M^+ - Br + CH_3CN ($C_{44}H_{41}P_2FeNCuBr$)]. ESI-MS (*t*BuOMe): 843 [M^+ ($C_{44}H41P_2FeNCuBr$)]. All isotopic patterns are in agreement with those of calculated. Mp (decomposition) 187-200 ^{o}C.

(*R,R*)-(*S,S*) - TaniaPhos-L3 CuBr racemic complex ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.21 (bs, 2H, ArH), 8.04 (bs, 2H, ArH), 7.59 – 7.40 (m, 6H, ArH), 7.33 (bs, 2H, ArH),7.23 (t, 1H, ArH), 7.06 (m, 3H, ArH),), 6.99-6.96 (bs, 1H, ArH), 6.90 (t, 2H ArH), 6.64 (bs, 1H, ArH), 6.39-6.34 (d, 4H, ArH), 5.69 (bs, 1H, CH), 4.94 (s, 1H, FcH), 4.61 (s, 1H, FcH), 4.13 (s, 1H, FcH), 4.05 (s, 5H,FcH), 1.95 (s, 6H, $2CH_3$). ^{31}P NMR (162 MHz, CD_2Cl_2) δ -26.3 – -29.7 (m). ESI-MS (CH_2Cl_2): 1579 [M^+-Br ($C_{86}H_{78}P_4Fe_2N_2Cu_2Br$)], 791 [$M^+$-Br+ CH_3CN ($C_{43}H_{39}P_2FeNCuCH_3CN$)], 753 [$M^+$-Br-($C_{43}H_{39}P_2FeNCu$)]. All isotopic patterns are in agreement with those of calculated. Mp (decomposition) 206-243 ^{o}C.

Precipitation studies

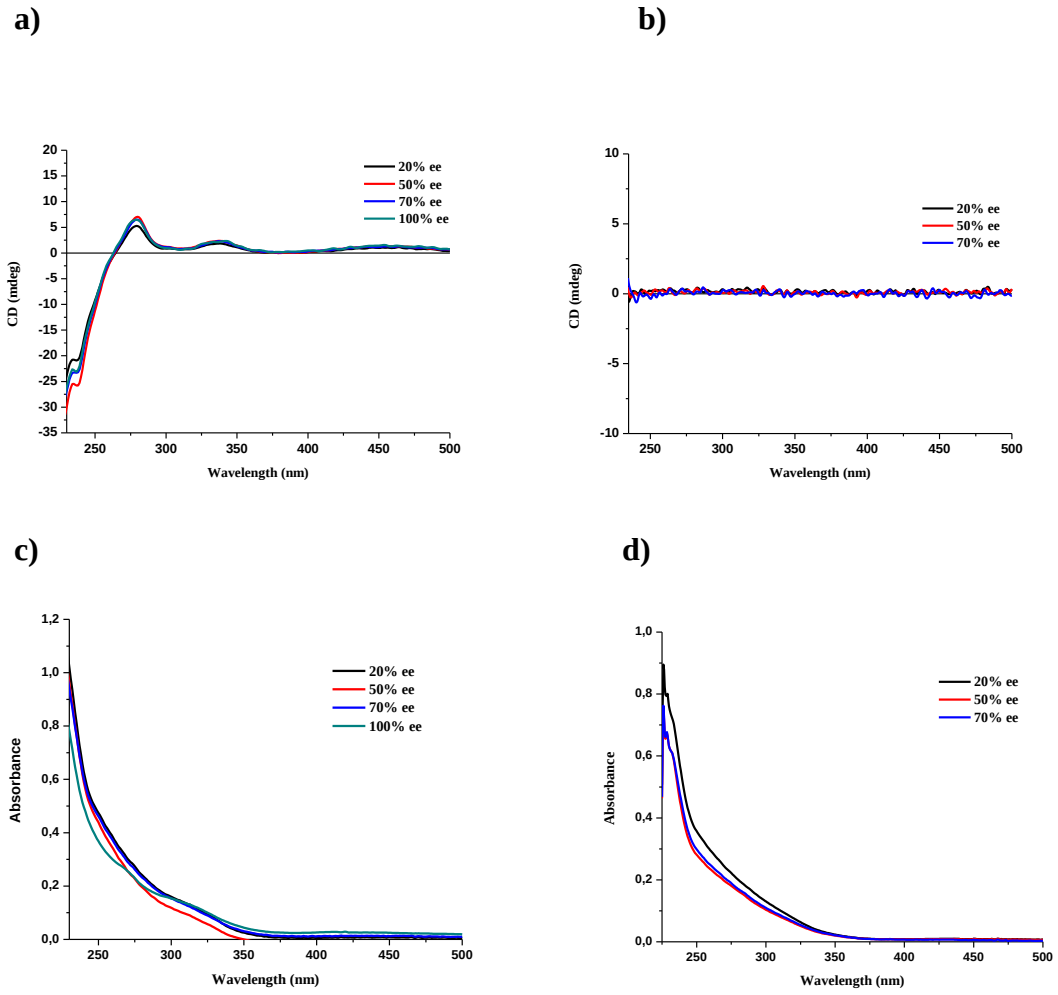
CuBr complexes of TaniaPhos-**L3** (0.015 M) of varying enantiopurities (100, 70, 50, 20 and 0% ee) were obtained in *t*BuOMe using method **B** with continuous stirring for 12 h. Centrifugation of these solutions resulted in a precipitate and supernatant (an exception was the solution with 100% ee, which did not have any precipitate).[3] The weight of the *t*BuOMe precipitate, in each case, was found to be approximately equivalent to twice the weight of the limiting enantiomer of the complex. Specific optical rotations and CD spectra (Table S4 and Figure S5) obtained from the supernatants were slightly lower than those obtained for the enantiopure complex. The lower CD and rotation values obtained for the samples can be attributed to the presence of tiny particles of the racemate in the supernatant solution which scatters the light.

Table S4 Specific optical rotation values for the supernatants and precipitates of scalemic CuBr TaniaPhos-**L3**

Entry	Supernatant[a]	$[\alpha]_D^{20a}$	*c* (g/ml)	Precipitate[b,c]	$[\alpha]_D^{20}$	*c* (g/ml)
1	20% ee	+125	$2.6*10^{-3}$	20 % ee	+9	$2.5*10^{-3}$
2	50% ee	+128	$3.8*10^{-3}$	50 % ee	+2	$2.4*10^{-3}$
3	70% ee	+122	$3.4*10^{-3}$	70 % ee	+44	$2.6*10^{-3}$
4[d]	100% ee	+155	$2.6*10^{-3}$	-	-	-

[a]The optical rotation was measured in *t*BuOMe; [b]The optical rotation was measured in CH_2Cl_2;[c] The precipitate was washed with *t*BuOMe (2x5 ml) and dried before preparing CH_2Cl_2 solution; [d]The value $[\alpha]_D^{20a}$ in CH_2Cl_2 was +166 *c* (g/ml)= $5.5 *10^{-3}$.

Figure S5: a) CD spectra of supernatants in *t*BuOMe; **b)** CD spectra of precipitates measured in CH_2Cl_2; **c)** UV spectra of supernatants in *t*BuOMe; **d)** UV spectra of precipitates in CH_2Cl_2.



Isolation of TaniaPhos –L3 from supernatant of Cu-complex with 20% ee

An enantioenriched complex (20% ee) was prepared in *t*BuOMe using method **B**. The supernatant of CuBr complex of TaniaPhos-**L3** obtained in *t*BuOMe was evaporated and solubilized in CH_2Cl_2 (0.005 M) followed by addition of 20 equiv of ethylenediamine at 0 ^oC. The resulting solution was stirred for 1 h at the same temperature and left to stir overnight at RT. The reaction progress was followed by TLC (pentane /ethyl acetate; 9/1). Purification by column chromatography (pentane /ethyl acetate) afforded the free ligand with 99% yield.

Supernatant of complex with 20% ee: $[\alpha]_D^{20a} = +120$ (c = 1.25 x 10^{-3} g/ml in *t*BuOMe)

CuBr-TaniaPhos-**L3** with 100% ee $[\alpha]_D^{20a} = +155$ (c= 2.6 x 10^{-3} g/ml in *t*BuOMe)

Free ligand from sample with 20% ee $[\alpha]_D^{20a} = +246$ (c = 2.5 x 10^{-3} g/ml in CH_2Cl_2)

TaniaPhos-**L3** with 100% ee $[\alpha]_D^{20a} = +267$ (c = 3.6 x 10^{-3} g/ml in CH_2Cl_2)

Determination of the solubility for racemic and enantiopure Cu-complexes of TaniaPhos-L3 in *t*BuOMe at rt.

CuBr complex of racemic TaniaPhos-L3

A saturated solution of racemic complex of TaniaPhos-**L3** was prepared in *t*BuOMe. The resulting heterogeneous mixture was stirred for 24 h at rt followed by centrifugation. Three samples of 100 µl of supernatant solution were transferred to an Eppendorf and dried under vacuum overnight, followed by weight determination.

sample 1 (200 µl) → 0.49 mg

sample 2 (200 µl) → 0.51 mg

sample 3 (100 µl) → 0.16 mg

CuBr complex of enantiopure TaniaPhos-L3

A saturated solution of enantiopure complex of TaniaPhos-**L3** was prepared *t*BuOMe. The resulting heterogeneous solution was stirred for 24 h at rt followed by centrifugation. Three samples of 100 µl of supernatant solution were transferred to an Eppendorf and dried under vacuum overnight, followed by weight determination.

sample 1 (200 µl) → 1.14 mg

sample 2 (200 µl) → 1.09 mg

sample 3 (100 µl) → 0.48 mg

Therefore the solubility of enantiopure the complex is 5.3 mg/ml and for the racemic 2.2 mg/ml.

6. CuBr complex of WalPhos-L4

Procedure for preparing CuBr complex of WalPhos-L4

Enantiopure and racemic complexes of WalPhos-**L4** were prepared in CH_2Cl_2 following the same procedures as described earlier for JosiPhos-**L2**.

(*R,S*)-WalPhos-L4 CuBr enantiopure complex ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.98 (bs, 1H, ArH), 7.76 (t, 2H, ArH), 7.47 (t, 2H, ArH), 7.44 – 7.35 (m, 7H, ArH), 7.22 (t, 1H, ArH), 6.87 (t, 1H, ArH), 4.23 (s, 5H, FcH), 4.11 (s, 1H, FcH), 3.98 (s, 1H, FcH), 3.14 (s, 1H, FcH), 2.65 (t, 1H, CH), 2.11 (bs, 2H, CyH), 1.92-0.85 (m, 23H, CyH and CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 14.5 (d, *J* = 135.0 Hz), 19.1 (d, *J* = 139.9 Hz). ESI-MS (CH_2Cl_2): 1545 [M^+-Br ($C_{84}H_{96}P_4Fe_2Cu_2Br$)], 812 [$M^+$- ($C_{42}H_{48}P_2FeCuBr$)], 733 [$M^+$-Br-($C_{42}H_{48}P_2FeCuBr$)]. All isotopic patterns are in agreement with those of calculated. Mp (decomposition) 245-252 ^oC.

(*R,R*)-(*S,S*) –WalPhos-L4 CuBr racemic complex ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.02 (bs, 1H, ArH), 7.75 (t, 2H, ArH), 7.47 (t, 1H, ArH), 7.22 (t, 1H, ArH), 7.44-7.35 (m, 7H, ArH), 7.22 (t, 1H, ArH), 6.87 (t, 1H, ArH), 4.22 (s, 5H, FcH), 4.10 (s, 1H, FcH), 3.97 (s, 1H, FcH), 3.13 (s, 1H, FcH), 2.65 (t, 1H, CH), 2.10 (t, 2H, CyH), 1.92 – 0.85 (m, 23H, CyH and CH_3). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 8.9 (d, *J* = 141.2 Hz), -24.6 (d, *J* = 138.5 Hz). ESI-MS (CH_2Cl_2): 1545 [M^+-Br ($C_{84}H_{96}P_4Fe_2Cu_2Br$)], 733 [$M^+$-Br-($C_{42}H_{48}P_2FeCu$)]. ESI-MS (*t*BuOMe): 1545 [M^+-Br ($C_{84}H_{96}P_4Fe_2Cu_2Br$)], 812 [$M^+$-($C_{42}H_{48}P_2FeCu$)], 733 [$M^+$-Br-($C_{42}H_{48}P_2FeCu$)]. All isotopic patterns are in agreement with those of calculated. Mp (decomposition) 212-218 ^oC.

Precipitation studies

CuBr complexes of WalPhos-**L4** (0.015 M) of varying enantiopurities (100, 70, 50, 20 and 0% ee) were obtained in *t*BuOMe using method **B** with continuous stirring for 12 h. Interestingly in this case the phenomenon was different: the complex of enantiopure WalPhos-**L4** precipitated out from *t*BuOMe solution while the complex of racemic WalPhos-**L4** was completely soluble in *t*BuOMe. Centrifugation of the heterogeneous solutions resulted in a precipitate and a supernatant. Specific optical rotations and CD spectra (Table S5 and Figure S6) showed that in contrast to previous results the supernatants were composed of nearly racemic complex while the precipitate was enantioenriched.

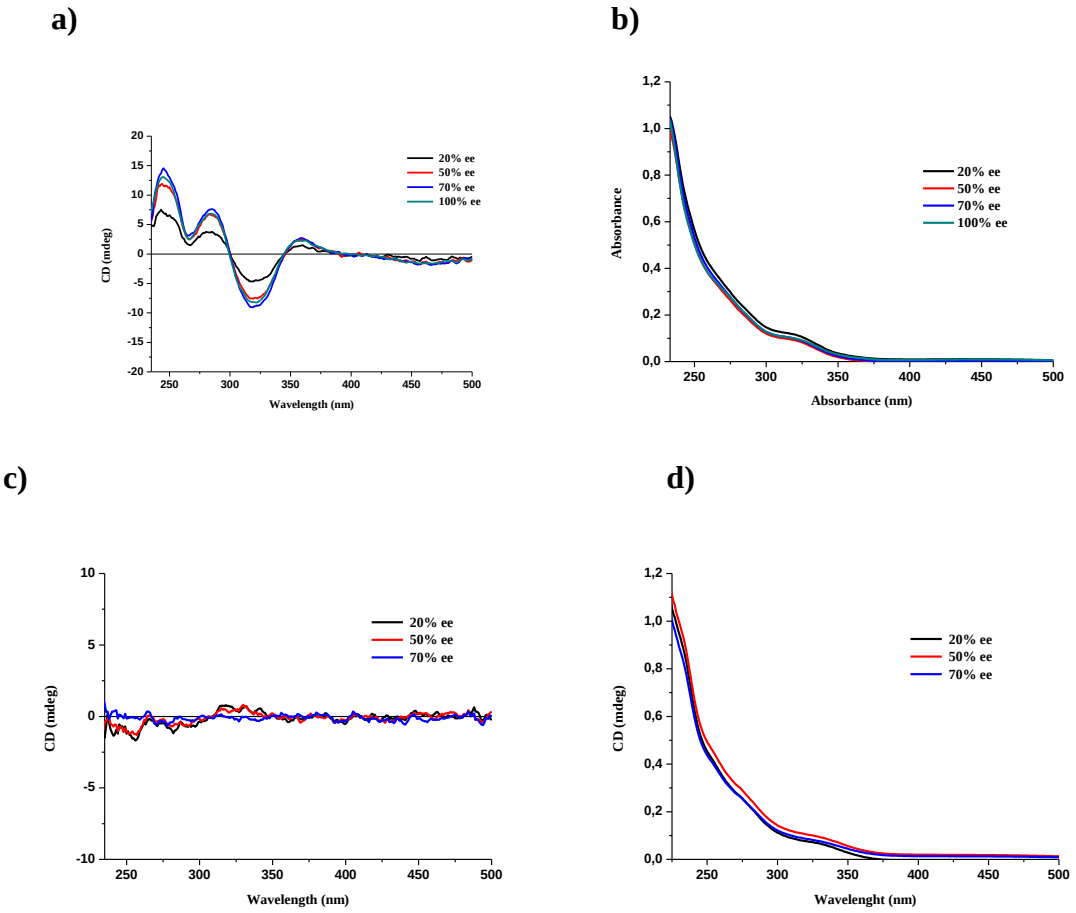
Table S5 Specific optical rotation values for the supernatants and precipitates of scalemic CuBr WalPhos-**L4**

Entry	Supernatant[a]	$[\alpha]_D^{20a}$	*c* (g/ml)	Precipitate[b]	$[\alpha]_D^{20}$	*c* (g/ml)
1	20 % ee	-6	$1.56*10^{-3}$	20% ee	-35	$5*10^{-3}$
2	50 % ee	-17	$1.52*10^{-3}$	50% ee	-72	$5.3*10^{-3}$

3	70 % ee	-8	$1.48*10^{-3}$	70% ee	-96	$4.1*10^{-3}$
4	-	-	-	100% ee	-99	$2.0*10^{-3}$

[a]The optical rotation was measured in *t*BuOMe; [b]The optical rotation was measured in CH_2Cl_2.

Figure S6: a) CD spectra of *t*BuOMe precipitates measured in CH_2Cl_2; **b)** UV spectra of precipitates measured in CH_2Cl_2; c) CD spectra of supernatants in *t*BuOMe; **b)** UV spectra of the supernatants in *t*BuOMe.



Isolation of WalPhos –L4 from supernatant of Cu-complex with 20% ee

Enantioenriched complex (20% ee) was prepared in *t*BuOMe using method **B**. The precipitate of the CuBr complex of WalPhos-**L4** obtained in *t*BuOMe was washed twice with the same solvent, dried and solubilized in CH_2Cl_2 (0.005 M) followed by addition of 20 equiv of ethylenediamine at 0 ^{o}C. The resulting solution was stirred for 1h at the same temperature and left to stir overnight at rt. The reaction progress was followed by TLC (pentane /ethyl acetate; 9:1). Purification by column chromatography (pentane /ethyl acetate) afforded the free ligand with 80% yield.

Free ligand from sample with 20% ee $[\alpha]_D^{20a} = -11$ (c = 0.71 x 10^{-3} g/ml in CH_2Cl_2)

WalPhos-**L4** with 100% ee $[\alpha]_D^{20a} = -13$ (c = 2.08 x 10^{-3} g/ml in CH_2Cl_2)

7. CuBr complex of BINAP-L5

Precipitation studies

Solution 1 (*R*) BINAP-L5 CuBr A solution of (*R*)-BINAP-**L5** (0.035 mmol; 22 mg) and CuBr·SMe2 (0.035 mmol; 6.58 mg) in CH_2Cl_2 (2.2 mL) in a Schlenk tube was stirred at rt for 1 h, the color of the solution changed from white to yellow.

Solution 2 (*S*) BINAP-L5 CuBr A solution of (*S*)-BINAP-**L5** (0.0128 mmol; 8 mg) and CuBr·SMe2 (0.0128 mmol; 2.6 mg) in CH_2Cl_2 (0.8 ml) in a Schlenk tube was stirred a rt for 1 h , the color of the solution changed from white to yellow.

CH_2Cl_2 was used due to the low solubility of both the enantiopure and racemic CuBr complexes of BINAP-**L5** in *t*BuOMe. From these standard solutions the corresponding enantioenriched and racemic mixtures (with a final of volume 1 ml) were prepared (50, 20, 70, 100% ee) followed by addition of 300 µl of *t*BuOMe to each mixture. All the solutions were mixed for 12 h and after 5h the precipitate started forming. Centrifugation of these solutions resulted in a precipitate and supernatant (an exception was solution with 100% ee, which did not have any precipitate). The precipitate was washed with *t*BuOMe (2x5 mL) and solubilised in a mixture of CH_3CN and MeOH.[4] The specific optical rotations are presented in Table S6. Although the phenomenon still persists (the precipitate is nearly racemic) the enantiopurity of the solution was not very high. The mixture of CH_2Cl_2/*t*BuOMe is probably not the optimal solvent mixture for the BINAP complex.

Table S6 Specific optical rotation values for the supernatants and precipitates of scalemic CuBr-BINAP-**L5**

Entry	Supernatant[a]	$[\alpha]_D^{20a}$	*c* (g/ml)	Precipitate[b]	$[\alpha]_D^{20}$	*c* (g/ml)
1	20% ee	-75	$2.9*10^{-3}$	20% ee	- 4	$0.8*10^{-3}$
2	50% ee	-154	$3.8*10^{-3}$	50% ee	- 4	$1.08*10^{-3}$
3	70% ee	-189	$4.0*10^{-3}$	70% ee	- 3.0	$0.6*10^{-3}$
4	100% ee	-195	$4.5*10^{-3}$	-	-	-

[a]The optical rotation was measured in CH_2Cl_2; [b]The optical rotation was measured in a mixture of CH_3CN/MeOH (5:1).

[4] The precipitate is not soluble in CH_2Cl_2.

Electronic Supplementary Material (ESI) for Chemical Communications

Determination of the solubility for racemic and enantiopure Cu-complexes of Binap-L5 in *t*BuOMe/ CH_2Cl_2 at RT.

CuBr complex of racemic Binap-L5

A saturated solution of the racemic complex of Binap-**L5** was prepared in a mixture of *t*BuOMe/CH_2Cl_2 (3:1). The resulting heterogeneous mixture was stirred for 24 h under nitrogen at rt. Three samples of 100 µl of supernatant were transferred to an Eppendorf and dried under vacuum overnight, followed by weight determination.

200 µl sample 1 → 2.25 mg

200 µl sample 2 → 1.97 mg

200 µl sample 3 → 1.6 mg

CuBr complex of enantiopure Binap-L5

A saturated solution of the enantiopure complex of Binap-**L5** was prepared in a mixture of *t*BuOMe/CH_2Cl_2 (3:1). The resulting heterogeneous mixture was stirred for 24 h under nitrogen at rt. Three samples of 100 µl of supernatant were transferred to an Eppendorf and dried under vacuum overnight, followed by weight determination.

100 µl sample 1 → 3.9 mg

100 µl sample 2 → 4.12 mg

100 µl sample 3 → 3.86 mg

Therefore the solubility of enantiopure the complex is 40 mg/ml and for the racemic complex 10 mg/ml.

8. $PdCl_2$ complex of JosiPhos-L2

Procedure for preparing $PdCl_2$ complex of enantiopure (*S,R*)-JosiPhos-L2

A solution of **(*S,R*)-JosiPhos-L2** ligand (0.006 mmol) and $(C_6H_5CH_2CN)_2PdCl_2$ (0.006 mmol) in CH_2Cl_2 (2 ml) in a Schlenk tube was stirred at rt for 24 h . The solvent was removed under vacuum and the residue was washed with cold pentane to afford the Pd-complex as a red powder.

Procedure for preparing $PdCl_2$ complex of racemic-JosiPhos-L2

$PdCl_2$-(*S,R*)-(*R,S*)-JosiPhos-**L2** racemate was prepared by mixing the enantiomers (*S,R*)-**L2** (0.006mmol), (*R,S*)-**L2** (0.006 mmol) and $(C_6H_5CH_2CN)_2PdCl_2$ (0.012 mmol) in 5 ml of CH_2Cl_2 in a Schlenk tube and stirring at rt for 24 h. The solvent was removed under vacuum and the residue was washed with cold pentane to afford the Pd-complex as a red powder.

(*S,R*)-JosiPhos-L2 $PdCl_2$ enantiopure complex ^{1}H NMR (500 MHz, cd_2cl_2) δ 8.28 (dd, *J* = 12.9, 3.8 Hz, 2H, ArH), 7.63 (s, 3H, ArH), 7.57 – 7.42 (m, 3H, ArH), 7.38 (d, *J* = 5.3 Hz, 2H, ArH), 4.64 (s, 1H, FcH), 4.41 (s, 1H, FcH), 4.20 (s, 1H, FcH), 3.73 (s, 5H, FcH), 3.30 (m, 1H,), 2.50 – 0.72 (m, 25H, CyH, and CH_3).^{31}P NMR (202 MHz, CD_2Cl_2) δ 71.3 (d, *J* = 5.0 Hz), 12.4 (d, *J* = 5.0 Hz). ESI-MS (CH_2Cl_2): 1505 [M^+ - Cl ($C_{72}H_{88}P_4Fe_2Pd_2Cl$)], 735 [$M^+$ - $C_{72}H_{88}P_4Fe_2Pd_2Cl_2$ - ($C_{36}H_{44}P_2FePdCl$)]. All isotopic patterns are in agreement with those calculated. Mp 156-167 ^oC.

(*S,R*)-(*R,S*) JosiPhos-L2 $PdCl_2$ racemic complex ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.28 (dd, *J* = 12.9, 3.8 Hz, 2H, ArH), 7.63 (s, 3H, ArH), 7.57 – 7.42 (m, 3H, ArH), 7.38 (d, *J* = 5.3 Hz, 2H, ArH), 4.64 (s, 1H, FcH), 4.41 (s, 1H, FcH), 4.20 (s, 1H, FcH), 3.73 (s, 5H, FcH), 3.30 (m, 1H,), 2.50 – 0.72 (m, 25H, CyH, and CH_3). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 77.1 (d, *J* = 5.0 Hz), 18.2 (d, *J* = 5.0 Hz,). ESI-MS (CH_2Cl_2): 1505 [M^+ - Cl ($C_{72}H_{88}P_4Fe_2Pd_2Cl$)], 735 [$M^+$ - $C_{72}H_{88}P_4Fe_2Pd_2Cl_2$ - ($C_{36}H_{44}P_2FePdCl$)]. All isotopic patterns are in agreement with those calculated. Mp 190-202 ^oC.

Precipitation studies

Solution 1 (*S,R*)-JosiPhos-L2 $PdCl_2$ - A solution of (*S,R*)-JosiPhos-**L2** (0.034 mmol) and $(C_6H_5CH_2CN)_2PdCl_2$ (0.034 mmol) in *t*BuOMe (2.2 mL) and CH_2Cl_2 (500 µl) in a Schlenk tube was stirred a rt for 24 h.

Solution 2 (*R,S*)-JosiPhos-L2 $PdCl_2$ - A solution of (*R,S*)-JosiPhos-**L2** (0.012 mmol) and $(C_6H_5CH_2CN)_2PdCl_2$ (0.012 mmol) in *t*BuOMe (0.8 mL) and CH_2Cl_2 (100 µl) in a Schlenk tube was stirred a rt for 24 h.

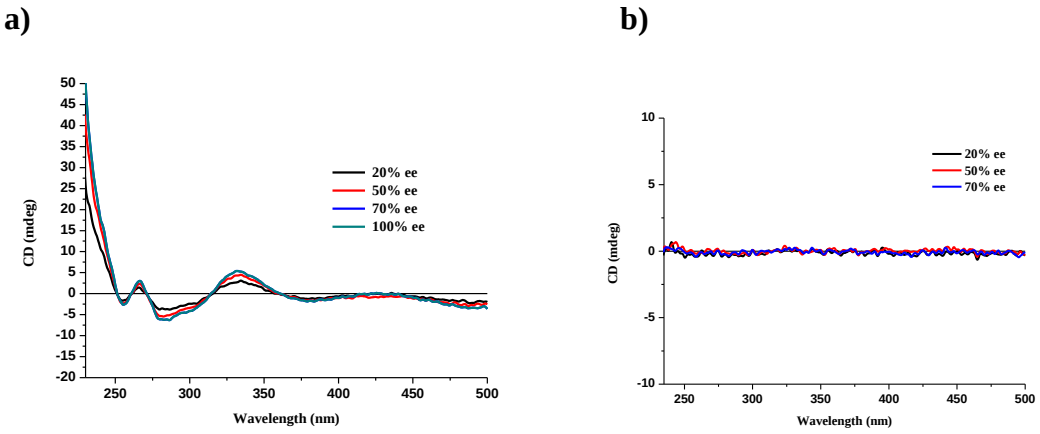
CH_2Cl_2 was added due to the low solubility of both the enantiopure and racemic Pd complexes of JosiPhos-**L2** in pure *t*BuOMe. From these standard solutions, the corresponding enantioenriched and racemic mixtures (100, 50, 20, 0% ee) were prepared with a final volume of 1 ml. All the solutions were mixed for 12 h. Centrifugation of these solutions resulted in a precipitate and supernatant (an exception was the solution with 100% ee, which did not have any precipitate). The precipitate was washed with *t*BuOMe (2x5 mL) and solubilised in CH_2Cl_2. The specific optical rotations and CD spectra are presented in Table S7 and Figure S7. Also for the Pd complex of JosiPhos-**L2** we found a similar phenomenon.

Table S7 Specific optical rotation values for the supernatants and precipitate of scalemic $PdCl_2$-JosiPhos-**L2**

Entry	Supernatant[a]	$[\alpha]_D^{20a}$	*c* (g/ml)	Precipitate[b]	$[\alpha]_D^{20}$	*c* (g/ml)
1	20% ee	-115	$2.1*10^{-3}$	20 % ee	-35	$2.3*10^{-3}$
2	50% ee	-122	$3.0*10^{-3}$	50 % ee	-13	$1.5*10^{-3}$
3	70% ee	-129	$4.8*10^{-3}$	70 % ee	-5	$0.9*10^{-3}$
4[b]	100% ee	-211	$4.8*10^{-3}$	-	-	-

[a]The optical rotation was measured in *t*BuOMe; [b]The optical rotation was measured in CH_2Cl_2.[c] The precipitate was washed with *t*BuOMe (2x5 ml) and dried before preparing CH_2Cl_2 solution.

Figure S7: a) CD spectra of supernatants measured *t*BuOMe; **b)** CD spectra of *t*BuOMe precipitates measured in CH_2Cl_2[a] .



Determination of the solubility for racemic and enantiopure Pd-complexes of JosiPhos-L2 in *t*BuOMe at rt.

Pd complex of racemic JosiPhos-L2

A saturated solution of racemic complex of JosiPhos-**L2** was prepared in a mixture of *t*BuOMe/CH_2Cl_2 (8:1). The resulting heterogeneous mixture was stirred for 24 h at rt followed by centrifugation. Three samples of 100 µl of supernatant solution were transferred to an Eppendorf and dried under vacuum overnight, followed by weight determination.

200 µl sample → 0.8 mg

200 µl sample → 0.3mg

200 µl sample → 0.4 mg

Pd complex of enantiopure JosiPhos-L2

A saturated solution of enantiopure complex of JosiPhos-**L2** was prepared *t*BuOMe. The resulting heterogeneous solution was stirred for 24 h at rt followed by centrifugation. Three samples of 100 µl of supernatant solution were transferred to an Eppendorf and dried under vacuum overnight, followed by weight determination.

100 µl sample → 1.3 mg

100 µl sample → 0.88 mg

100 µl sample → 1.52 mg

Therefore the solubility of enantiopure complex is 12 mg/ml and for the racemic complex 2.5 mg/ml.

9. $PdCl_2$ complex of TaniaPhos-L3

Procedure for preparing $PdCl_2$ complex of enantiopure (*R,R*)-TaniaPhos-L3

Enantiopure and racemic $PdCl_2$ complexes of TaniaPhos-**L3** were prepared as described earlier for the corresponding $PdCl_2$ complexes of JosiPhos-**L2**

(*R,R*)-TaniaPhos-L3 $PdCl_2$ enantiopure complex ^{31}P NMR (202 MHz, CD_2Cl_2) δ 14.1 (s), 8.0 (s). Mp 157-160°C. ESI-MS (CH_2Cl_2): 1691 [M^+ - Cl ($C_{86}H_{78}P_4Fe_2Pd_2Cl_4$)], 830 [$M^+$ - $C_{86}H_{78}P_4Fe_2Pd_2Cl_4$-($C_{43}H_{39}P_2FePdCl$)]. All isotopic patterns are in agreement with those of calculated. Mp 157-160 °C.

(*R,R*)-(*S,S*)-TaniaPhos-L3 $PdCl_2$ racemic complex ^{31}P NMR (202 MHz, CD_2Cl_2) δ 14.1 (s), 8.0 (s). ESI-MS (CH_2Cl_2): 1691 [M^+ - Cl ($C_{86}H_{78}P_4Fe_2Pd_2Cl_4$)], 830 [$M^+$ - $C_{86}H_{78}P_4Fe_2Pd_2Cl_4$-($C_{43}H_{39}P_2FePdCl$)]. All isotopic patterns are in agreement with those of calculated. Mp 195-198 °C.

Precipitation studies

Solution 1 (*R,R*)-TaniaPhos-L3- $PdCl_2$ - A solution of (*R,R*)-TaniaPhos-**L3** (0.032 mmol) and $(C_6H_5CH_2CN)_2PdCl_2$ (0.032 mmol) in *t*BuOMe (2.2 mL) and CH_2Cl_2 (600 µl) in a Schlenk tube was stirred a rt for 24 h.

Solution 2 (*S,S*)-TaniaPhos-L3- $PdCl_2$ - A solution of (*S,S*)-TaniaPhos-**L3** (0.012 mmol) and $(C_6H_5CH_2CN)_2PdCl_2$ (0.012 mmol) in *t*BuOMe (0.8 mL) and CH_2Cl_2 (300 µl) in a Schlenk tube was stirred a rt for 24 h.

CH_2Cl_2 was added due to the low solubility of both the enantiopure and racemic Pd complexes of TaniaPhos-**L3** in pure *t*BuOMe. From these standard solutions the corresponding enantioenriched and racemic mixtures (100, 50, 70, 20, 0% ee) were prepared with a final volume of 1 ml. All the solutions were mixed for 12 h. Centrifugation of these solutions resulted in a precipitate and a supernatant (an exception was solution with 100% ee, which did not have any precipitate). The precipitate was washed with *t*BuOMe (2x5 mL) and solubilised in CH_2Cl_2. The specific optical rotations are presented in Table S8.

Table S8 Specific optical rotation values for supernatants and precipitate of scalemic $PdCl_2$-TaniaPhos-**L3**

Entry	Supernatant[a]	$[\alpha]_D^{20a}$	*c* (g/ml)	Precipitate[b]	$[\alpha]_D^{20}$	*c* (g/ml)
1	20% ee	-117	$1.7*10^{-3}$	20% ee	18	$0.68*10^{-3}$
2	50% ee	-125	$2.1*10^{-3}$	50% ee	44	$0.58*10^{-3}$
3	70% ee	-144	$2.4*10^{-3}$	70% ee	42	$0.42*10^{-3}$
4[b]	100% ee	-148	$3.9*10^{-3}$	-	-	-

[a] The optical rotation was measured in *t*BuOMe;. [b]The optical rotation was measured in CH_2Cl_2; [c] The precipitate was washed with *t*BuOMe (2x5 ml) and dried before preparing CH_2Cl_2 solution.

Determination of the solubility for racemic and enantiopure Pd-complexes of TaniaPhos-L3 in *t*BuOMe at rt.

Pd complex of racemic TaniaPhos-L3

A saturated solution of racemic complex of TaniaPhos-**L3** was prepared in a mixture of *t*BuOMe/CH_2Cl_2 (8:1) The resulting heterogeneous mixture was stirred for 24 h at rt followed by centrifugation. Three samples of 100 µl of supernatant solution were transferred to an Eppendorf and dried under vacuum overnight, followed by weight determination.

400 µl sample → 0.08 mg

400 µl sample → 0.15mg

400 µl sample → 0.12 mg

Pd complex of enantiopure TaniaPhos-L3

A saturated solution of enantiopure complex of TaniaPhos-**L3** was prepared *t*BuOMe. The resulting heterogeneous solution was stirred for 24 h at rt followed by centrifugation. Three samples of 100 µl of supernatant solution were transferred to an Eppendorf and dried under vacuum overnight, followed by weight determination.

100 µl sample → 0.88 mg

100 µl sample → 1.2 mg

100 µl sample → 1.12 mg

Therefore the solubility of enantiopure complex is 14.4 mg/ml and for the racemic complex 0.3 mg/ml.

Electronic Supplementary Material (ESI) for Chemical Communications