A Novel Route to Phosphorus Bearing Axially Chiral Biaryls by Catalytic Asymmetric Cross Cyclotrimerization and a First Application in Asymmetric Hydrosilylation**

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Axially chiral biaryl units are of steadily growing interest and importance for academic as well as pharmaceutical drug research. Thus axial chirality is a fundamental basis for useful reagents and catalysts in asymmetric synthesis. The configuration at a biaryl axis can be a decisive factor in governing the pharmacological properties of a bioactive compound. In an excellent review Bringmann, Breuning and coworker classified the strategies of atroposelective synthesis of axially chiral biaryl compounds to their underlying concepts and evaluated critically their scope and limitation with reference to selected model reactions and applications.[1]

Apart from diastereoselective methods and those involving an optical resolution stage, there are only few direct catalytic asymmetric approaches to non-racemic axially chiral biaryls. Most popular examples are the cross-couplings[2] of aryl Grignard reagents[3], organolithiums[4] or arylboronic acids[5] with aryl halides. Another strategy involves a enantioposition-selective cross-coupling of achiral biaryl ditriflates.[6] Recently the asymmetric cleavage of dinaphtho[2,1-b:1′,2′-d]thiophene with a Grignard reagents was demonstrated, too.[7] Oxidative coupling of activated aromatics constitutes a special group of catalytic methods.[8] The opportunity to use a cycloaddition of arylpropiolates with gaseous acetylene in the presence of a nickel(0)/triphenylphosphine catalyst for

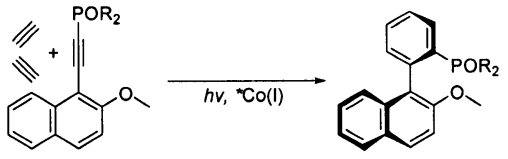
the preparation of compounds with axially chiral biaryl backbone was first realized by Mori and co-workers who synthesized a racemic biaryl in one elegant step.[9]

The asymmetric cross cyclotrimerization of alkynes with Ir or Rh complexes as a catalyst was shown as a powerful tool for the construction of axially chiral biaryl derivatives.[10]Very recently we discovered that our chiral cobalt(I) catalysts[11] under photochemical conditions which had been applied earlier to the synthesis of different pyridines[12] could be used for the preparation of axially chiral 2-aryl pyridines in particular.[13]

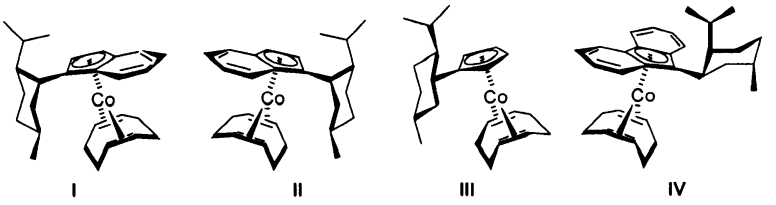
In addition to new insight into the reaction mechanism of our chiral cobalt(I) catalysis we have now significantly extended the scope of the method and herein report for the first time the use of a [2+2+2] cross cycloaddition reaction for the preparation of axially chiral biaryls bearing phosphorus functionalities. These compounds have huge potential as ligands in asymmetric catalysis and a first application in an asymmetric hydrosilylation was also successfully investigated.

We found our chiral cobalt(I) complexes to be useful for the synthesis of benzenes and biaryls as well. For example phenylpropynoic ethyl ester with gaseous acetylene in the presence of [cpCo(cod)] (η^5-cyclopentadienyl-η^4-cycloocta-1,5-diene-cobalt(I), 2 mol%) gave biphenyl-2-carboxylic acid ethyl ester in 87% yield after 24 h under irradiation with visible light (λ = 350-500 nm) at ambient temperature and pressure.

Based on these results, we synthesized a number of naphthyl derived alkynes bearing phosphoryl moieties which are suited to enter the reaction with acetylene and bulky enough to prevent self-trimerization (see Supporting Information). Converted with acetylene under above-mentioned reaction conditions, these new compounds gave axially chiral biaryls by cross coupling in moderate yields (Scheme 1). Using chiral half-sandwich Co^I complexes[11] as catalysts in order to achieve chiral induction complexes **I** and **II**: (–)-(*pS*)- and (+)-(*pR*)-(η^4-cycloocta-1,5-diene)(η^5-1-neomenthyl-indenyl)-cobalt were most effective (Scheme 2).



Scheme 1. Cross cyclotrimerization to axially chiral biaryls (R see in Table 1)



Scheme 2. Chiral cobalt(I) complexes employed.

Reactions with the chiral catalysts proceeded slower compared to the conventional catalyst [cpCo(cod)] (see Supporting Information) and exhibited difficulties frequently, e.g. oligomerization or the tendency of some substrates to char. However, in many cases reasonable yields and *ee* values were achieved under optimized conditions. Selected results are summarized in the Table 1.

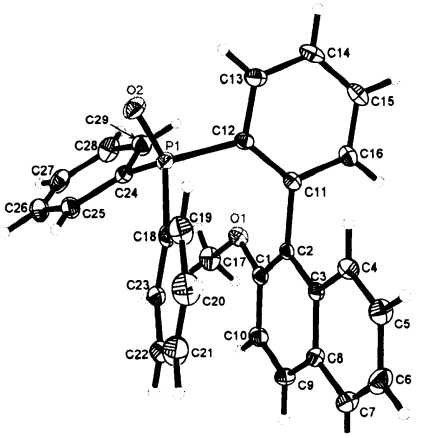
Table 1: Synthesis of axially chiral biaryls

Prod.[Conf]	POR_2	Cat.[a]	Reac. Cond.	Solvent	Yield [%][b]	Sel. [% ee][c]
$\mathbf{1}^S$	$PO(C_6H_5)_2$	**I**	45°C, 48 h	THF	49	79[d] (>99[e])
$\mathbf{1}^R$	$PO(C_6H_5)_2$	**II**	25°C, 24 h	THF	45	63
$\mathbf{2}^S$	$PO(p\text{-}CH_3O\text{-}C_6H_4)_2$	**I**	45°C, 24 h	THF	51	72[d] (>99[e])
$\mathbf{3}^S$	$PO[3,5\text{-}(CF_3)_2C_6H_3)]_2$	**I**	45°C, 24 h	THF	24	56
$\mathbf{4}^S$	$PO(t\text{-}C_4H_9)_2$	**I**	25°C, 48 h	THF	61	82[d] (>99[e])
$\mathbf{5}^S$	PO(1-Adamantyl)$_2$	**I**	25°C, 24 h	THF	44	83[d] (>99[e])
$\mathbf{6}^S$	$PO[(CH_3)_2N]_2$	**I**[f]	55°C, 12 h	THF	80	68
$\mathbf{1}^S$	$PO(C_6H_5)_2$	**III**	25°C, 48 h	Toluene	37	12
$\mathbf{1}^S$	$PO(C_6H_5)_2$	**IV**	25°C, 12 h	Toluene	8	12[d]

[a] 5 mol% cat. (see scheme 2). [b] Isolated yield. [c] Determined by HPLC on a chiral stationary phase (see the Supporting Information). [d] Measured in reaction mixture.[e] Determined after recrystallization.[f] Only 1 mol % cat.

Dynamic HPLC on a chiral stationary phase has proven that all the biarylic derivatives **1-6** exist in the form of two stable atropoisomeres, and no atropisomerization was observed at temperatures up to +60°C.

A relatively high enantiomeric excess of the products **1**, **2**, **4** and **5** allowed further enrichment by recrystallization. A homochiral crystal of the compounds **1**, **2** and **4** has been grown; both the



structures and the absolute configurations were unambiguously determined. One example is shown in Figure 1.

Figure 1. Crystal structure of [(-)-S-1-[2-(diphenyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene] **1** (crystallographic data are given in Supporting Information, table 4).

In all cases when the (–)-(*pS*)-catalyst **I** (Scheme 2) was employed (*S*)-enantiomers of biaryls **1-6** were found. We demonstrated that the products enriched with the opposite enantiomer are obtained by using (+)-(*pR*)-complex **II** as a catalyst from 1-(diphenyl-phosphinoylethynyl)-2-methoxy-naphthalene **1A** and acetylene. As expected, we received [(+)-*R*-1-[2-(diphenyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene] after 24 h at 25°C in THF with an enantiomeric excess of 63% and 45% yield (see Table 1).

An interesting feature of this reaction is the influence of temperature on the enantiomeric excess of the products. The *ee*s increase towards a certain maximum with temperature but then decrease again. Figure 2 shows the observed *ee* values against the reaction temperature in the case of derivative **1,** as an example.

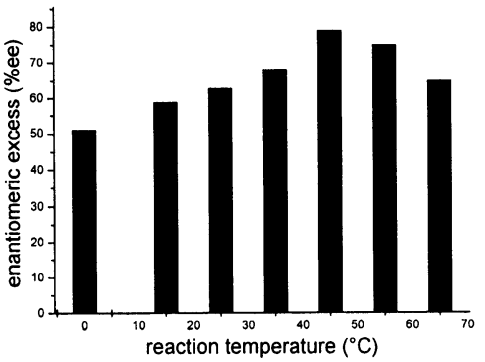
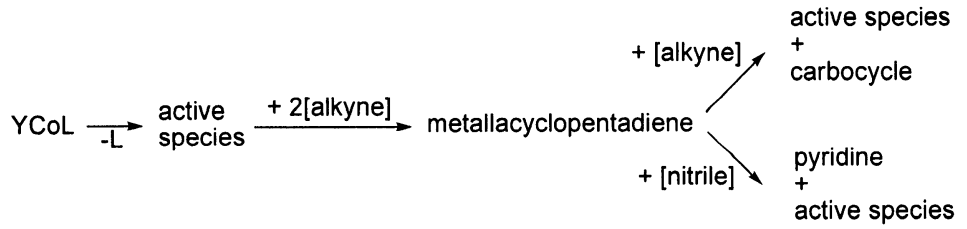


Figure 2. Development of the *ee* value against the reaction temperature

Every investigated reaction showed an individual point of inflexion, and required some optimization in order to find best conditions. In the case of the catalyst **I** and **II** THF is the solvent of choice; reactions in DME, dioxane, toluene showed slightly lower enantioselectivities and chemical yields. Other factors like the duration of irradiation, the extent of conversion and the amount of the catalyst were of little importance for the achieved *ee* values.

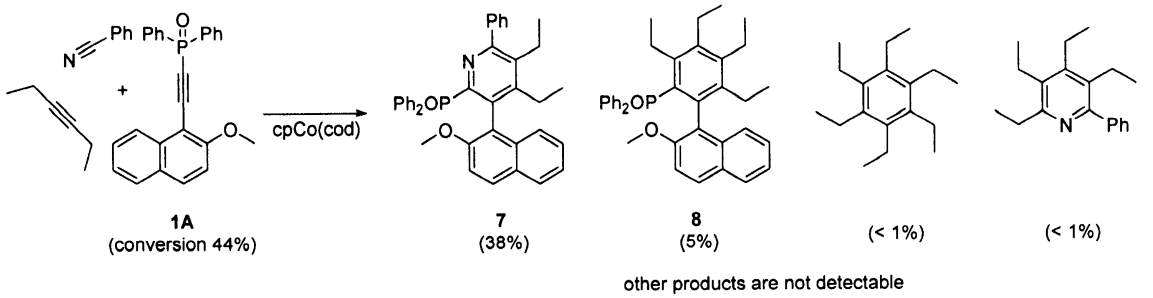
Following generally accepted mechanistic suggestions for the formation of pyridines and the corresponding benzenes as shown in scheme 3, in both cases an identical metallacyclopentadiene is generated which in the subsequent rate determining step reacts either with the nitrile or an additional

alkyne compound.[14] An interesting question concerning the formation of biaryls is to illustrate which alkyne compounds are involved in the formation of the intermediate cobaltacyclopentadiene.



Scheme 3. Generally accepted mechanistic suggestion

In order to clarify the origin of the optic induction and the nature of the intermediates, we introduced different starting materials including 3-hexyne and benzonitrile which were added to 1-(diphenyl-phosphinoylethynyl)-2-methoxy-naphthalene **1A**, in a ratio 1:1:1 with [cpCo(cod)] as catalyst (Scheme 4).



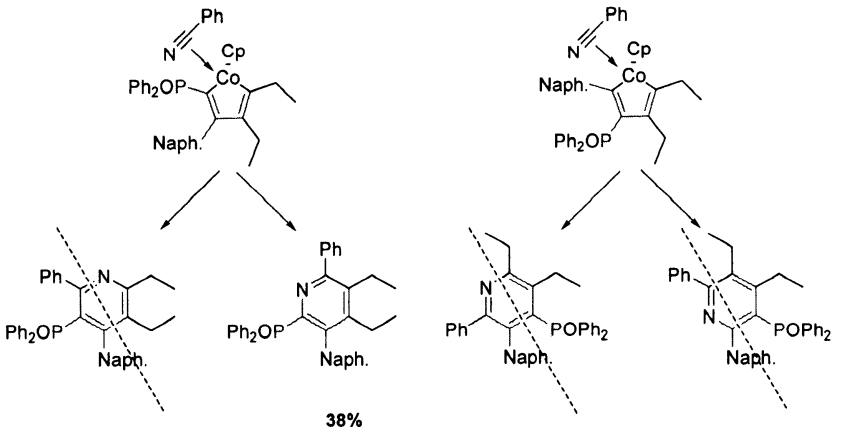
Scheme 4. Three-component cycloaddition.

Do only two hexyne molecules react at first or is the sterically more demanding alkyne **1A** involved in the formation of the metallacycle? The synthesis of pyridine **7** is only possible if substrate **1A** takes part in the formation of the cobaltacyclopentadiene intermediate.

As shown in scheme 4, at 44 % conversion of the used nitrile the pyridine **7** was isolated with 38% yield as a single regioisomer and the main product. The structure was confirmed by X-ray crystallography.[15] Only 5% yield of the benzene derivative **8** was determined by GC. Yields of other side products such as hexaethylbenzene and the 2,3,4,5-tetraethyl-6-phenyl-pyridine do not exceed 1% each.

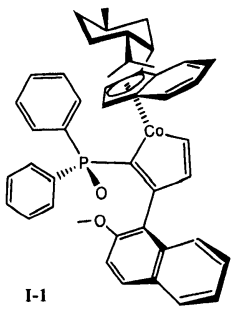
This ratio observed between pyridine **7** and carbocycle **8** conforms to the proposed mechanism[14c] according to which one single metallacyclopentadiene intermediate reacts faster with the nitrile than with the additional alkyne. This high selectivity allows us to rule out the tetraethyl-cobaltacyclopentadiene as an intermediate for the formation of the compounds **7** and **8**. As

illustrated in scheme 5, in addition we can rule out a cobaltacyclopentadiene intermediate in which the $POPh_2$ group is placed in ß-position to the Cobalt because the anticipated products are not formed.



Scheme 5. Possible intermediates and the corresponding products.

Following the idea of a single cobaltacyclopentadiene intermediate in the formation of pyridines and corresponding benzenes, as a result of our three-component experiment we suppose that employing the optically active catalyst **I** the cobaltacyclopentadiene **I-1** (Scheme 6) is the major diastereomeric intermediate which reacts with the sterically less hindered alkyne molecule to give axially chiral biaryls.

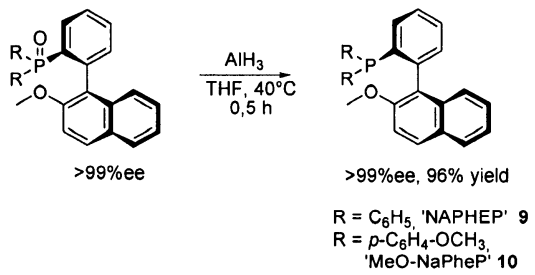


Scheme 6. The suggested cobaltacyclopentadiene intermediate **I-1**.

Possible origin of the asymmetric induction in this reaction can be the chirality transfer from the planar chiral neomenthylindenyl part of **I-1** to the 2-methoxynaphthyl group mediated by the chiral array of diastereotopic aryl groups at the phosphoryl moiety.

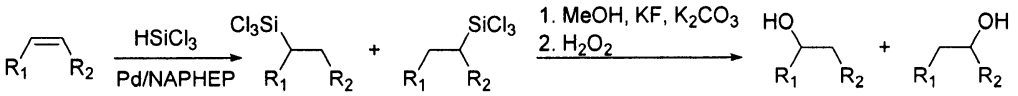
So far we demonstrated a novel and effective route to axially chiral biaryls bearing a phosphoryl moiety, but chiral phosphanes accessible by this route are even more interesting e.g. as ligands for asymmetric catalysis. The conversion of the chiral phosphine oxides prepared by [2+2+2] cross-

cyclotrimerization into the corresponding phosphanes is quite simple and practicable (Scheme 7). To demonstrate this and to synthesize axially chiral P-ligands we reduced the phosphine oxides **1** and **2** to the corresponding phosphanes **9** and **10** by means of AlH_3 in THF.[16,17] In contrast to the use of $LiAlH_4$[18] the reaction with AlH_3 proceeded smoothly and furnished the corresponding phosphane with 96% yield and without atropisomerization.



Scheme 7. Reduction to the corresponding chiral phosphane compound

In order to investigate whether our new compounds are suited as a ligand for asymmetric catalysis we compared compound **9** - our 'NAPHEP' ligand – with the well-studied MeO-MOP ligand from Hayashi et al.[19] The use of MOP/palladium catalytic systems was a first practical route for asymmetric hydrosilylation of alkenes. (Scheme 8)



Scheme 8. Asymmetric hydrosilylation

The phenyl/naphthyl incorporating framework in our NAPHEP might have some advantages over its binaphthyl counterpart. The dihedral angles of our less rigid biaryls can be easier self-tuned thus allowing better chiral geometry in the catalytically active palladium complex. Also the diminished electron donating properties of a phenyl ring can strongly influence the outcome of the catalytic reaction. The results (Table 2) with our NAPHEP as ligand in the hydrosilylation of linear and cyclic aliphatic alkenes and styrene are very similar to those obtained with MeO-MOP.[20] Overall, the first application of the new axially chiral compound - NAPHEP - as a ligand in an asymmetric catalysis could be demonstrated with good chemical yields and optical purities (up to 93%ee).

Table 2: Asymmetric hydrosilylation with Pd/NAPHEP as the catalytic system

Alkene	Yield[d]	2-/1-isomers ratio	Selectivity[e]

Alkene	Yield[d]	2-/1-isomers ratio	Selectivity[e]
1-Hexene[a]	61%	76:24	91% ee (*R*),
1-Octene[a]	59%	77:23	93% *ee* (*R*),
1-Phenylbut-4-ene[a]	53%	65:35	93% *ee* (*R*),
Norbornene[b]	96%	[f]	83% *ee* (*1S, 2S, 4R*)
Styrene[c]	85%	99:1	9% *ee* (*S*),

[a] Reaction conditions: 0.1mol% $[\pi\text{-PdCl}(C_3H_5)]_2$, 0.2mol% (*S*)-NAPHEP, without solvent, 40°C, 24 h. [b] Reaction conditions: 0.01mol% $[\pi\text{-PdCl}(C_3H_5)]_2$, 0.02mol% (*S*)-NAPHEP, without solvent, 0°C, 24 h. [c] Reaction conditions: 0.1mol% $[\pi\text{-PdCl}(C_3H_5)]_2$, 0.2mol% (*S*)-NAPHEP, without solvent, 0°C, 48 h. [d] Isolated yields of secondary alcohol. [e] Enantiomeric excess of the major enantiomer. [f] Only the formation of *exo*-2-silylated product was observed.

In principle NAPHEP could act as a monodentate P- or as a bidentate P,O-ligand. In the single crystal X-ray structure of the complex *trans*-$\{PdCl_2[(S)\text{-NAPHEP}]_2\}$[15] NAPHEP is coordinated as a monodentate ligand. Phosphorus atoms as well as chlorine atoms at palladium are adopting *trans* position to each other in the square-plane geometry of the complex. At the same time the benzannelated part of the naphthyl ring points towards the palladium atom and the methoxy group is in the remote side. This creates a chiral surrounding of the palladium for the origin of the outstanding enantioselectivity observed, similarly as supposed by Hayashi.[21]

Tests with our new axially chiral biaryl compounds in different catalytic reactions are underway in our laboratory.

In conclusion, we demonstrated a novel effective two step route to axially chiral biaryls. In a direct asymmetric cross cyclotrimerization using a chiral Cobalt(I) catalyst we created axially chiral biaryles bearing a phosphoryl moiety. By indirect proof we were able to clarify the origin of the optical induction and the nature of the central intermediate of the catalytic cycle. By subsequent reduction of the phosphoryl moiety to the corresponding phosphane we succeeded in an atomeconomically very efficient approach to chiral systems which clearly have a high potential to be used as axially chiral monodentate P- or as bidentate P,O-ligands. This has been exemplified by employing the novel NAPHEP as a monodendate acting new ligand in an asymmetric hydrosilylation reaction.

Experimental Section[15]

Cross trimerization – a representative example

Synthesis of (-)-S 1-[2-(Diphenyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene ***1****:*

A thermostated (45°C) reaction vessel was loaded with 1-(diphenyl-phosphinoylethynyl)-2-methoxy-naphthalene (1.15 g; 3 mmol), catalyst **I** (63 mg; 0.15 mmol), THF (30 mL) under

atmosphere of acetylene. The mixture was stirred and irradiated by two 460 W Phillips HPM 12 lamps ($\lambda_{max} \approx 420$ nm) for 48 h. The reaction was quenched by switching off the lamps and simultaneously letting in air. The conversion of the starting acetylene was determined by GC. The solvent was evaporated, the oily residue was purified on silica (ethyl acetate) to give (-)-*S*-1-[2-(diphenyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene **1** (639 mg, 49%) as a colorless solid. The optical purity was determined to be 79 % *ee* (HPLC). A recrystallization from ethyl acetate – hexane gave the product in enantiomerically pure state (391 mg, >99 % ee).

*Reduction to (-)-S [2-(2-Methoxy-naphthalen-1-yl)-phenyl]-diphenyl-phosphane (NAPHEP) **9**:*

Phosphine oxide **1** (266 mg, 0.612 mmol, >99 % ee) was dissolved in THF (5 mL) and AlH_3 (1.32 mL of a 0.5 M solution in THF, 0.652 mmol) was added dropwise. The mixture was stirred at 50°C for 30 minutes, cooled and dry methanol (0.1 mL) was added. The mixture was filtered through a pad of silica which was washed with THF (3 × 5 mL). The organic extract was evaporated and purified by flash chromatography eluting with hexane – ethyl acetate (9:1) to yield (-)-*S* [2-(2-Methoxy-naphthalen-1-yl)-phenyl]-diphenyl-phosphane (246 mg, 96%) as a colorless solid. The optical purity of the sample was determined to be >99 % ee (HPLC).

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[15] X-ray data for the compounds **1**, **2**, **4**, and **7** and experimental procedures for all synthesized are given in Supporting Information. CCDC 275232 (**1**), CCDC 275233 (**2**), CCDC 275234 (**4**), CCDC 275235 (**7**) and CCDC 287928 {$PdCl_2$[(*S*)-NAPHEP]$_2$} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

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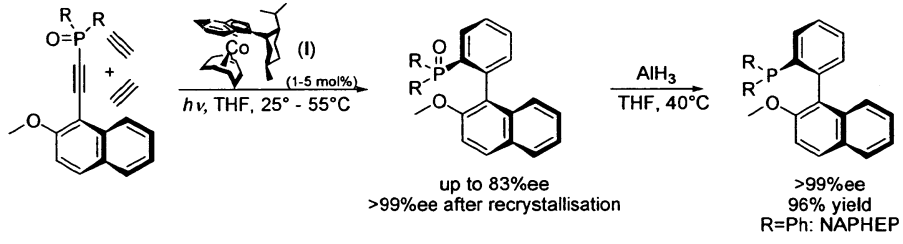
Chiral atropoisomers of phosphorus bearing biaryls are prepared through a cross cyclotrimerization of alkynes in the presence of chiral Co^{I} catalysts followed by recrystallisation and a simple reduction to corresponding phosphanes. In addition mechanistic investigations and results of employment the novel monodentate ligand 'NAPHEP' in asymmetric hydrosilylation are presented.



Barbara Heller*, Andrey Gutnov, Christine Fischer, Hans-Joachim Drexler, Anke Spannenberg, Dmitry Redkin, Corinna Sundermann, Bernd Sundermann

A Novel Route to Phosphorus Bearing Axially Chiral Biaryls by Catalytic Asymmetric Cross Cyclotrimerization and a First Application in Asymmetric Hydrosilylation

Keywords: asymmetric catalysis, atropoisomerism, P,O-ligands, axially chiral biaryl compounds, cross cyclotrimerization, cobalt.

Supporting Information

A Novel Route to Phosphorus Bearing Axially Chiral Biaryls by Catalytic Asymmetric Cross Cyclotrimerization and a First Application in Asymmetric Hydrosilylation

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General: The NMR spectra were recorded on a Bruker ARX 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{31}P, 162 MHz) spectrometer at 298 K. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residue of the deuterated solvent (deuterochloroform: δ 7.27 ppm for ^{1}H and δ 77.36 ppm for ^{13}C). Mass spectra were obtained with a Varian AMD-402 instrument at an ionizing voltage of 70 eV. Only characteristic fragments containing the isotopes of highest abundance are listed. Relative intensities in percentages are given in parentheses. Melting points were measured with a Büchi 540 melting point determination apparatus. Optical rotations were determined on a Gyromat-HP polarimeter. In all cases the enantiomeric excesses of products were analyzed by HPLC with a Liquid Chromatograph 1090 equipped with DAD (Hewlett Packard) and Chiralyser (IBZ Messtechnik GmbH, Hannover).

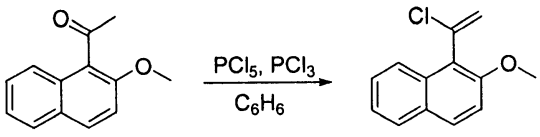
All reactions with sensitive materials were carried out in an argon atmosphere, using standard techniques in dry, oxygen-free solvents. All liquid reagents were distilled under argon prior to use. All solid compounds were recrystallized from degassed solvents. Chromatographic purifications were done with 240-400 mesh silica gel.

Diphenylchlorophosphine, di(t-butyl)chlorophosphine, methyl chloroformate, 1-ethynyl-naphthalene, BuLi, 3-hexyne, 2-butyne were purchased from Aldrich. Bis(dimethylamino)phosphoryl chloride was purchased from Strem.

1-Acetyl-2-methoxy-naphthalene,[22] 1-ethynyl-2-methyl-naphthalene,[23] bis-(3,5-bis-trifluoromethyl-phenyl)-chlorophosphine,[24] bis(4-methoxyphenyl)chlorophosphine,[24] bis(1-adamantyl)phosphinic chloride,[25] [CpCo(cod)][26] were synthesized according to known procedures.

I) Preparation of different naphthalens

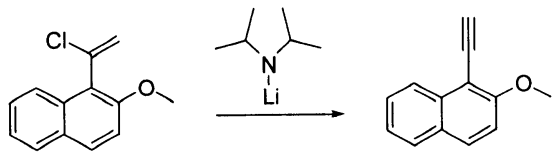
1-(1-Chloro-vinyl)-2-methoxy-naphthalene



PCl_5 (8.8 g, 41.7 mmol) was added to the solution of 1-acetyl-2-methoxy-naphthalene (7.7 g, 38.45 mmol) and PCl_3 (18.5 mL, 0.21 mol) in dry benzene (60 mL) at r.t. The reaction mixture was magnetically stirred for 24 h at r.t., and then carefully poured into ice (300 g). The organic fraction was extracted with ether (100 mL), washed with saturated $NaHCO_3$ solution, separated, and dried over Na_2SO_4. The solution was filtered through a pad of silica, and the solvent was removed in vacuo to give the crude product (8.24 g, 98% yield) as a pale-yellow oil. The compound was pure enough to be used for the next step, but could be crystallized from hexane to afford a colorless solid with m.p. 47-48°C.

HRMS calcd for $C_{13}H_{11}OCl$ 218.0493, found 218.0489 (delta -1.7); ^{1}H-NMR δ: 8.35 (d, 1H, J = 8.5Hz), 8.17 (d, 1H, J = 9.1Hz), 8.11 (d, 1H, J = 8.1Hz), 7.84 (m, 1H), 7.7 (m, 1H), 7.58 (d, 1H, J = 9.1Hz), 6.05 (dd, 2H, J = 0.99 and 197.4Hz), 4.3 (s, 3H); ^{13}C-NMR δ: 154.4, 134.6, 132.4, 131.3, 129.2, 128.5, 127.7, 124.7, 124.4, 122.4, 119.7, 113.7, 57.2;

1-Ethynyl-2-methoxy-naphthalene

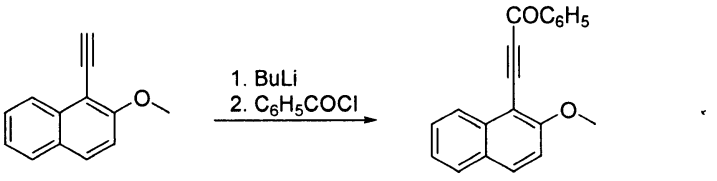


BuLi (1.6M solution in hexanes, 23 mL, 36.7 mmol) was added dropwise under stirring to the solution of diisopropylamine (4.45 g, 6.2 mL, 44 mmol) in THF (10 mL) at –78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to –78°C. A solution of 1-(1-chlorovinyl)-2-methoxy-naphthalene (3.1 g, 14.18 mmol) in THF (20 mL) was added slowly to the lithium diisopropylamide solution. The cooling bath was removed, and the mixture was stirred for 5 h at r.t. The reaction vessel was placed into an ice bath, and water (2 mL) was added carefully to the thick

slurry. After coagulation of inorganic phase, the organic layer was decanted, dried with Na_2SO_4, and filtrated through a pad of silica, being eluted with ether. The mother liquor was evaporated to dryness, and the solid residue was recrystallized from ethyl acetate - hexane to give 2.5 g (97% yield) of the title acetylene as white plates with m.p. 111-112°C.

HRMS calcd for $C_{13}H_{10}O$ 182.0726, found 182.0720 (delta -2.9); ^{1}H-NMR δ: 8.49 (dd, 1H, J = 0.6 and 8.5Hz), 8.01-7.95 (m, 2H), 7.75 (m, 1H), 7.57 (m, 1H), 7.40 (d, 1H, J = 9.1Hz), 4.2 (s, 3H), 3.97 (s, 1H); ^{13}C-NMR δ: 160.3, 135.3, 131.1, 128.8, 128.6, 128.0, 125.5, 124.7, 112.8, 105.3, 87.0, 78.7, 57.0.

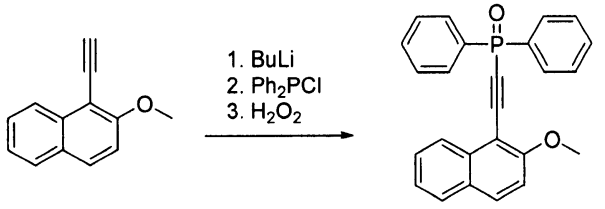
3-(2-Methoxy-naphthalen-1-yl)-1-phenyl-propynone



BuLi (1.6M solution in hexanes, 13 mL, 20.8 mmol) was added dropwise under stirring to the solution of 1-ethynyl-2-methoxy-naphthalene (3.64 g, 20 mmol) in THF (50 mL) at −78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to −78°C, whereupon benzoyl chloride (2.32 mL, 2.81 g, 20 mmol) was added dropwise. The temperature was raised to 0°C for 20 minutes, and water (0.5 mL) was added. The mixture was stirred for 5 min, filtered through a short pad of silica, and the solvent was evaporated in vacuo to afford a dark solid. The residue was purified on silica, eluting with Et_2O-hexane (1:1). Crystallization from ethyl acetate furnished 3.9 g (64% yield) of 3-(2-Methoxy-naphthalen-1-yl)-1-phenyl-propynone as yellow crystals (m.p. 137-138°C).

HRMS calcd for $C_{20}H_{14}O_2$ 286.0988, found 286.0982 (delta -2.2); ^{1}H-NMR δ: 8.46 (m, 2H), 8.40 (d, 1H, J = 8.5Hz), 8.01-7.32 (m, 8H), 4.16 (s, 3H); ^{13}C-NMR δ: 187.5, 162.5, 137.8, 135.4, 134.2, 133.8, 130.2, 128.9, 128.8, 128.8, 128.7, 125.4, 125.1, 112.5, 103.5, 97.3, 89.6, 57.0.

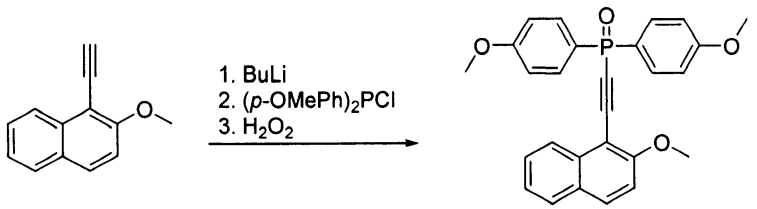
1-(Diphenyl-phosphinoylethynyl)-2-methoxy-naphthalene



BuLi (1.6M solution in hexanes, 26 mL, 41.6 mmol) was added dropwise under stirring to the solution of 1-ethynyl-2-methoxy-naphthalene (7.28 g, 40 mmol) in THF (80 mL) at −78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to −78°C, whereupon chlorodiphenylphosphine (8.8 g, 7.2 mL, 40 mmol) was added dropwise. The temperature was raised to 25°C for 30 minutes, and the reaction mixture was additionally stirred for 2 hours. The Schlenk flask was placed into an ice bath, and hydrogen peroxide (30% in water, 5 mL) was added carefully under vigorous stirring. The mixture was stirred for 30 min at r.t., dried with Na_2SO_4, and the resulted solution was filtered through a short pad of silica. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica (THF) to give 13.6 g (89%) of 1-(Diphenyl-phosphinoylethynyl)-2-methoxy-naphthalene.

HRMS calcd for $C_{25}H_{18}O_2P$ 381.1039, found 381.1034 (delta -1.2), M.p. 116-117°C (ethyl acetate / hexane); ^{1}H-NMR δ: 8.07 (dd, 1H, J = 0.6 and 8.5 Hz); 7.98-7.93 (m, 4H); 7.84 (d, 1H, J = 9.1Hz); 7.71 (d, 1H, J = 8.1Hz); 7.49-7.4 (m, 7H); 7.32-7.28 (m, 1H); 7.17 (d, 1H, J = 9.5Hz); 3.96 (s, 3H); ^{13}C-NMR δ: 162.1, 162.1; 136.1; 134.9; 134.7; 133.5; 133.3; 132.4; 132.4, 131.6; 131.5; 129.0; 128.9; 128.7; 128.5; 125.2; 125.0; 112.6; 103.4 (d, J = 3.8Hz); 103.4 (d, J = 30.5Hz); 92.2 (d, J = 172.6Hz); 56.9; ^{31}P-NMR δ: 8.9;

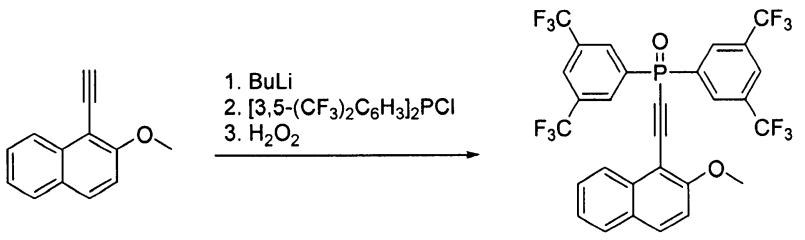
1-[Bis-(4-methoxy-phenyl)-phosphinoylethynyl]-2-methoxy-naphthalene



BuLi (1.6M solution in hexanes, 6.5 mL, 10.4 mmol) was added dropwise under stirring to the solution of 1-ethynyl-2-methoxy-naphthalene (1.82 g, 10 mmol) in THF (30 mL) at −78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to −78°C, whereupon bis(4-methoxyphenyl)chlorophosphine (2.81 g, 10 mmol) was added dropwise. The temperature was raised to 25°C for 30 minutes, and the reaction mixture was additionally stirred for 2 hours. The Schlenk flask was placed into an ice bath, and hydrogen peroxide (30% in water, 1.5 mL) was added carefully under vigorous stirring. The mixture was stirred for 30 min at r.t., dried with Na_2SO_4, and the resulted solution was filtered through a short pad of silica. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica (THF) to give 3.83 g (87%) of 1-[Bis-(4-methoxy-phenyl)-phosphinoylethynyl]-2-methoxy-naphthalene. M.p. 124-125°C (ethyl

acetate – hexane), HRMS calcd for $C_{27}H_{23}O_4P$ 442.1328, found 442.1316 (delta -2.9); ^{1}H-NMR δ: 8.37 (d, 1H, J = 8.3 Hz); 8.2-8.11 (m, 5H); 7.99 (d, 1H, J = 8.1Hz); 7.76-7.72 (m, 1H); 7.46 (d, 1H, J = 9.3 Hz); 7.24-7.2 (m, 4H); 4.25 (s, 3H), 4.07 (s, 6H); ^{13}C-NMR δ: 162.9; 162.9; 134.9; 133.5; 133.3; 133.1; 128.6, 128.6; 126.4; 125.3; 125.1; 124.9; 114.5; 114.4; 112.7; 103.6; 101.1; 100.8; 93.9; 92.2, 56.9, 55.7; ^{31}P-NMR δ: 8.6;

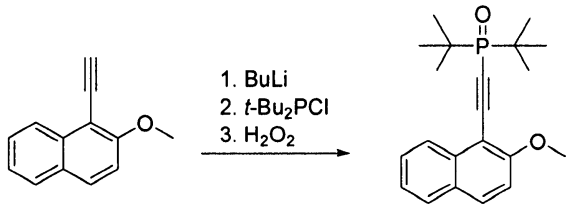
1-[Bis-(3,5-bis-trifluoromethyl-phenyl)-phosphinoylethynyl]-2-methoxy-naphthalene



BuLi (1.6M solution in hexanes, 6.5 mL, 10.4 mmol) was added dropwise under stirring to the solution of 1-ethynyl-2-methoxy-naphthalene (1.82 g, 10 mmol) in THF (30 mL) at –78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to –78°C, whereupon bis[3,5-bis(trifluoromethyl)phenyl]chlorophosphine (4.93 g, 10 mmol) was added dropwise. The temperature was raised to 25°C for 30 minutes, and the reaction mixture was additionally stirred for 2 hours. The Schlenk flask was placed into an ice bath, and hydrogen peroxide (30% in water, 1.5 mL) was added carefully under vigorous stirring. The mixture was stirred for 30 min at r.t., dried with Na_2SO_4, and the resulted solution was filtered through a short pad of silica. The solvent was evaporated in vacuo to afford a yellow oil, which was purified on silica (ethyl acetate / hexane 1:4) to give 5.71 g (90%) of 1-[Bis-(3,5-bis-trifluoromethyl-phenyl)-phosphinoylethynyl]-2-methoxy-naphthalene as a white crystalline solid.

HRMS calcd for $C_{29}H_{15}O_2F_{12}P$ 654.0613, found 654.0604 (delta -1.3); M.p. 162-163°C (ethyl acetate – hexane); ^{1}H-NMR δ: 8.72 (d, 4H, J = 13.7 Hz), 8.28-8.25 (m, 3H), 8.2 (d, 1H, J = 9.1Hz), 8.01 (d, 1H, J = 8.1Hz), 7.77-7.73 (m, 1H), 7.63-7.59 (m, 1H), 7.5 (d, 1H, J = 9.1Hz), 3.29 (s, 3H); ^{13}C-NMR δ: 163.3, 163.3, 137.0, 135.8, 134.9, 134.6, 133.6, 133.5, 133.3, 133.2, 133.0, 132.8, 132.6, 132.5, 131.6, 131.5, 129.3, 129.0, 128.5, 127.2, 126.9, 126.9, 125.4, 124.6, 124.5, 121.7, 119.0, 116.7, 112.2, 106.7, 106.3, 101.4, 89.8, 87.9, 56.8; ^{31}P-NMR δ: 2.2;

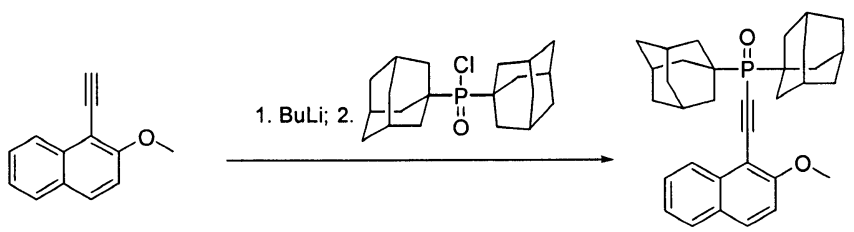
1-(Di-tert-butyl-phosphinoylethynyl)-2-methoxy-naphthalene



BuLi (1.6M solution in hexanes, 6.5 mL, 10.4 mmol) was added dropwise under stirring to the solution of 1-ethynyl-2-methoxy-naphthalene (1.82 g, 10 mmol) in THF (30 mL) at −78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to −78°C, whereupon chlorodi-*t*-butylphosphine (1.81 g, 1.9 mL, 10 mmol) was added dropwise. The temperature was raised to 25°C for 30 minutes, and the reaction mixture was additionally stirred for 12 hours. The Schlenk flask was placed into an ice bath, and hydrogen peroxide (30% in H_2O, 1.5 mL) was added carefully under vigorous stirring. The mixture was stirred for 30 min at r.t., dried with Na_2SO_4, and the resulted solution was filtered through a short pad of silica. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica (THF) to give 2.96 g (86%) of 1-(Di-tert-butyl-phosphinoylethynyl)-2-methoxy-naphthalene as a colorless crystalline solid.

HRMS calcd for $C_{21}H_{27}O_2P$ 342.1743, found 342.1733 (delta -3.0); M.p. 137-138°C (ethyl acetate – hexane); ^{1}H-NMR δ: 8.47 (d, 1H, J = 8.5Hz); 8.14 (d, 1H, J = 9.1Hz); 8.04 (d, 1H, J = 8.1Hz); 7.82 (m, 1H); 7.65 (m, 1H); 7.48 (d, 1H, J = 9.1Hz); 4.25 (s, 3H); 1.73 (d, 18H, J = 15.1Hz); ^{13}C-NMR δ: 161.7; 134.8; 132.5; 128.6; 128.5; 128.4; 125.2; 124.8; 112.7; 104.2 (d, J = 3.8Hz); 98.6 (d, J = 20Hz); 91.4 (d, J = 130.6Hz); 56.8; 36.6 (d, J = 72.5Hz); 26.9; ^{31}P-NMR δ: 49.2;

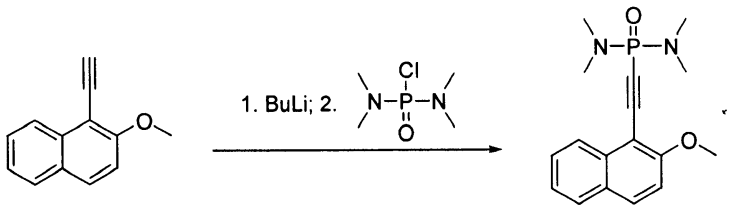
1-(Di-1-adamantyl-phosphinoylethynyl)-2-methoxy-naphthalene



BuLi (1.6M solution in hexanes, 26 mL, 41.6 mmol) was added dropwise under stirring to the solution of 1-ethynyl-2-methoxy-naphthalene (7.28 g, 40 mmol) in THF (100 mL) at −78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to −78°C, whereupon the solution of di-1-adamantylphosphinic chloride (14.12 g, 40 mmol) in THF (100 mL) was added dropwise. The temperature was raised to 25°C for 30 minutes, and the solution was stirred at reflux for 4 hours. The reaction mixture was cooled to 5°C, and water (1 mL) was added carefully under

stirring. The solution was filtered through a pad of silica, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica (ethyl acetate) to give 4.14 g (21%) of 1-(Di-1-adamantyl-phosphinoylethynyl)-2-methoxy-naphthalene as a colorless crystalline solid. HRMS calcd for $C_{33}H_{39}O_2P$ 498.2682, found 498.2676 (delta -1.2); M.p. 234-235°C (ethyl acetate); ^{1}H-NMR δ: 8.47 (dd, 1H, J = 0.6Hz and 8.5Hz); 8.9 (d, 1H, J = 9.1Hz); 8.0 (d, 1H, J = 8.1Hz); 7.77 (m, 1H); 7.6 (m, 1H); 7.45 (d, 1H, J = 9.1Hz); 4.21 (s, 3H); 2.89 (m, 12H); 2.28 (m, 6H); 2.01 (m, 12H); ^{13}C-NMR δ: 161.7; 135.0; 132.3; 128.6; 128.4; 125.4; 124.8; 112.7; 104.5 (d, J = 2.9Hz); 98.6 (d, J = 18.1Hz); 91.6; 90.3; 56.8; 40.9; 40.1; 37.1; 37.1; 28.3; 28.2; ^{31}P-NMR δ: 41.5;

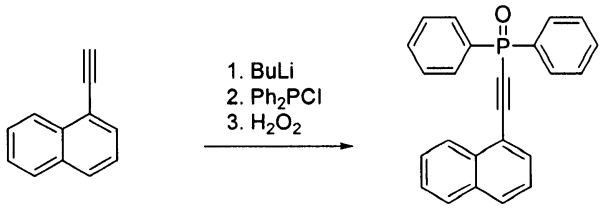
1-(Di-dimethylamino-phosphinoylethynyl)-2-methoxy-naphthalene



BuLi (1.6M solution in hexanes, 6.5 mL, 10.4 mmol) was added dropwise under stirring to the solution of 1-ethynyl-2-methoxy-naphthalene (1.82 g, 10 mmol) in THF (30 mL) at –78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to –78°C, whereupon bis(dimethylamino)phosphoryl chloride (1.71 g, 1.46 mL, 10 mmol) was added dropwise. The temperature was raised to 25°C for 30 minutes, and the reaction mixture was additionally stirred for 30 minutes. The solution was filtered through a short pad of silica, and concentrated in vacuo to an oily residue, which was further purified by column chromatography on silica (THF) to afford 2.59 g (82%) of 1-(Di-dimethylamino-phosphinoylethynyl)-2-methoxy-naphthalene as a yellowish crystalline solid.

HRMS calcd for $C_{17}H_{21}O_2N_2P$ 316.1335, found 316.1333 (delta -0.8); M.p. 105-106°C (ethyl acetate – hexane); ^{1}H-NMR δ: 8.46 (dd, 1H, J = 0.8Hz and 8.3Hz); 8.13 (d, 1H, J = 9.1Hz); 8.03 (d, 1H, J = 8.3Hz); 7.82-7.78 (m, 1H); 7.66-7.62 (m, 1H); 7.48 (d, 1H, J = 9.1Hz); 4.25 (s, 3H); 3.05 (d, 12H, J = 11.3Hz); ^{13}C-NMR δ: 161.3; 134.8; 132.5; 128.6; 128.6; 128.4; 125.9; 125.2; 124.8; 112.7; 104.0 (d, J = 4.8Hz); 96.0 (d, J = 41.0Hz); 90.9; 88.5; ^{31}P-NMR δ: 11.5;

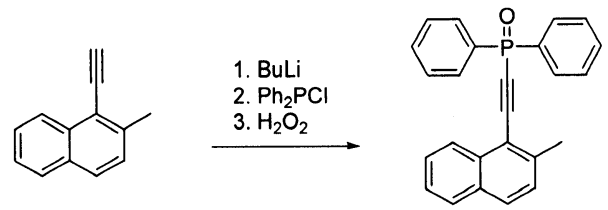
1-(Diphenyl-phosphinoylethynyl)-naphthalene



BuLi (1.6M solution in hexanes, 13 mL, 20.8 mmol) was added dropwise under stirring to the solution of 1-ethynyl-naphthalene (3.04 g, 2.84 mL; 20 mmol) in THF (60 mL) at −78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to −78°C, whereupon chlorodiphenylphosphine (4.4 g, 3.6 mL, 20 mmol) was added dropwise. The temperature was raised to 25°C for 30 minutes, and the reaction mixture was additionally stirred for 2 hours. The Schlenk flask was placed into an ice bath, and hydrogen peroxide (30% in water, 2.5 mL) was added carefully under vigorous stirring. The mixture was stirred for 30 min at r.t., dried with Na_2SO_4, and the resulted solution was filtered through a short pad of silica. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica (ethyl acetate) to give 6.15 g (87%) of 1-(Diphenyl-phosphinoylethynyl)-naphthalene.

HRMS calcd for $C_{24}H_{16}OP$ 351.0933, found 351.0925 (delta -2.4); M.p. 99-100°C (diethyl ether); ^{1}H-NMR δ: 8.52-8.5 (m, 1H); 8.28-8.19 (m, 5H); 8.14-8.11 (m, 2H); 7.85-7.7 (m, 9H); ^{13}C-NMR δ: 134.2; 133.7; 133.3; 133.0; 133.0; 132.7; 132.7; 131.8; 131.5; 131.4; 129.2; 129.1, 129.0; 128.1; 127.3; 126.0; 125.4; 117.8 (d, J = 4.8Hz), 104.4 (d, J = 29.6Hz), 88.9, 87.2; ^{31}P-NMR δ: 8.8;

1-(Diphenyl-phosphinoylethynyl)-2-methyl-naphthalene



BuLi (1.6M solution in hexanes, 5.06 mL, 8.1 mmol) was added dropwise under stirring to the solution of 1-ethynyl-2-methyl-naphthalene (1.339 g, 8.05 mmol) in THF (30 mL) at −78°C. The temperature was raised to 0°C for 20 minutes, and then cooled again to −78°C, whereupon chlorodiphenylphosphine (1.7 g, 1.39 mL, 8.05 mmol) was added dropwise. The temperature was raised to 25°C for 20 minutes, and the reaction mixture was additionally stirred for 2 hours. The Schlenk flask was placed into an ice bath, and hydrogen peroxide (30% in water, 1 mL) was added carefully under vigorous stirring. The mixture was stirred for 30 min at r.t., dried with Na_2SO_4, and the resulted solution was filtered through a short pad of silica. The solvent was removed in vacuo,

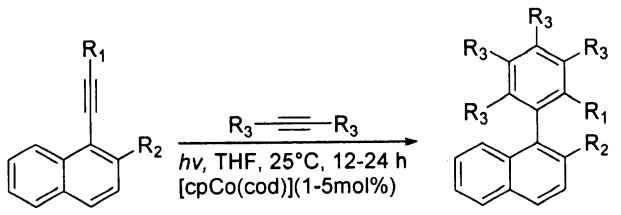
and the residue was purified by column chromatography on silica (ethyl acetate) to give 2.77 g (94%) of 1-(Diphenyl-phosphinoylethynyl)-2-methyl-naphthalene.

HRMS calcd for $C_{25}H_{18}OP$ 365.1090, found 365.1094 (delta 1.3); M.p. 92-93°C (ethyl acetate – hexane); ^{1}H-NMR δ: 8.46 (d, 1H, *J* = 8.3 Hz); 8.27-8.22 (m, 4H); 8.08-8.05 (m, 2H); 7.84-7.69 (m, 8H), 7.60 (d, 1H, *J* = 8.3Hz); 2.91 (s, 3H); ^{13}C-NMR δ: 142.8 (d, J = Hz), 134.4, 134.1, 133.2, 132.6, 132.6, 131.7, 131.5, 131.4, 131.1, 129.1, 129.0, 128.7, 128.3, 128.1, 126.4, 125.8, 116.4 (d, *J* = 3.8Hz); 103.6 (d, *J* = 30.5Hz); 93.2; 91.5; 21.9; ^{31}P-NMR δ: 8.7;

II) [2+2+2] cross cyclotrimerization

General procedure for the preparation of racemic as well as nonracemic biphenyls **1-6.**

A thermostated (e.g. 25°C) reaction vessel was loaded with a substituted acetylene such as 1-(Diphenyl-phosphinoylethynyl)-2-methoxy-naphthalene (1 mmol) and [cpCo(cod)] (11.6 mg, 0.05 mmol). THF (10 mL) was added, and the vessel was connected to an acetylene measuring and delivering device providing a constant pressure of acetylene. Alternatively, acetylene may simply be bubbled through the solution. If 2-butyne or 3-hexyne were used as a second component, the compounds (3 mmol) were injected under argon atmosphere. The mixture was stirred and irradiated by two 460-W Phillips HPM 12 lamps (λ ≈ 420 nm). The reaction was quenched by switching off the lamps and simultaneously letting in air. The extent of reaction, i.e. conversion of the starting substituted acetylene, was determined by GC. The solvent was evaporated, and the residue was purified on silica.



1-9 **10-20**

Scheme 9. Cross cyclotrimerization to racemic axially chiral biphenyls (R^{1-3} see in Table 1)

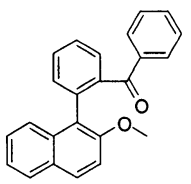
Table 3: Synthesis of racemic axially chiral biphenyls

R^1	R^2	R^3	Prod.	Reaction Cond.[a]	Yield[b]
COC_6H_5	OCH_3	H		2 mol% cat., 24h	69% [c]
$(C_6H_5)_2PO$	OCH_3	H	**1**	2 mol% cat., 24 h	52%
$(C_6H_5)_2PO$	OCH_3	C_2H_5		5 mol% cat., 24 h	76%
$(C_6H_5)_2PO$	OCH_3	CH_3		5 mol% cat., 24 h	26%

$(p\text{-}CH_3O\text{-}C_6H_4)_2PO$	OCH_3	H	**2**	5 mol% cat., 24 h	68%
$[3,5\text{-}(CF_3)_2C_6H_3)]_2PO$	OCH_3	H	**3**	1 mol% cat., 12 h	81%
$(t\text{-}C_4H_9)_2PO$	OCH_3	H	**4**	5 mol% cat., 24 h	74%
$(1\text{-Adamantyl})_2PO$	OCH_3	H	**5**	5 mol% cat., 24 h	55%
$[(CH_3)_2N]_2PO$	OCH_3	H	**6**	1 mol% cat., 12 h	80%
$(C_6H_5)_2PO$	H	CH_3		5 mol% cat., 24 h	79%
$(C_6H_5)_2PO$	CH_3	H		2 mol% cat., 12 h	81%

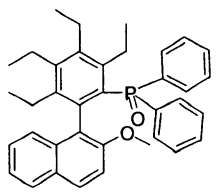
[a] [cpCo(cod)] as a catalyst in THF at 25°C. [b] Isolated yield. [c] Yield after chromatography

[2-(2-Methoxy-naphthalen-1-yl)-phenyl]-phenyl-methanone



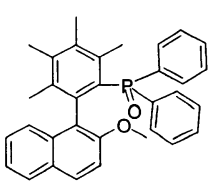
HRMS calcd for $C_{24}H_{18}O_2$ 338.1301, found 338.1296 (delta -1.6), M.p. 154-155°C (ethyl acetate/hexane), R_f = 0.4 (Et_2O/hexane 1:1). ^{1}H-NMR δ: 8.0-7.41 (m, 14H); 7.34 (d, 1H, *J* = 8.9Hz); 3.89 (s, 3H). ^{13}C-NMR δ: 197.9; 153.3; 140.9; 138.0; 136.1; 133.8; 132.8; 132.5, 130.7; 129.9; 129.9; 129.4; 129.2; 128.2; 127.9; 127.4; 126.9; 125.5; 123.7; 123.1; 112.7, 56.0.

1-[2-(Diphenyl-phosphinoyl)-3,4,5,6-tetraethyl-phenyl]-2-methoxy-naphthalene



HRMS calcd for $C_{37}H_{39}O_2P$ 546.2682, found 546.2678 (delta -0.8), M.p. 157-158°C (ethyl acetate/hexane), R_f = 0.59 (ethyl acetate). ^{1}H-NMR δ: 7.72 (d, 1H, *J* = 8.1 Hz), 7.68-7.63 (m, 2H); 7.56-7.39 (m, 7H); 7.16-7.09 (m, 3H); 6.98-6.93 (m, 2H); 6.9 (d, 1H, *J* = 9.1 Hz), 3.94 (s, 3H), 3.34-3.18 (m, 2H), 3.12-2.96 (m, 4H), 2.4-2.31 (m, 1H), 2.1-1.99 (m, 1H), 1.51-1.45 (m, 6H), 1.25 (t, 3H, *J* = 7.3Hz), 0.83 (t, 3H, *J* = 7.4Hz), ^{13}C-NMR δ: 154.2, 146.7, 146.7, 145.8, 145.8, 142.6, 142.5, 140.2, 140.1, 138.5, 137.6, 137.5, 137.4, 136.5, 135.2, 131.8, 131.8, 131.3, 131.2, 130.8, 130.7, 130.6, 130.5, 129.8, 129.8, 128.8, 127.8, 127.8, 127.6, 126.8, 126.7, 126.6, 125.8, 123.5, 123.0, 122.9, 111.8, 55.0, 26.2 (d, *J* = 5.7Hz), 23.7, 23.2, 22.1, 16.4, 16.3, 16.2, 14.9, ^{31}P-NMR δ: 31.2.

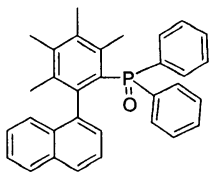
1-[2-(Diphenyl-phosphinoyl)-3,4,5,6-tetramethyl-phenyl]-2-methoxy-naphthalene



HRMS calcd for $C_{33}H_{31}O_2P$ 490.2056, found 490.2048 (delta -1.6), M.p. 233-234°C (ethyl acetate/hexane), R_f = 0.36 (ethyl acetate); ^{1}H-NMR δ: 7.81-7.72

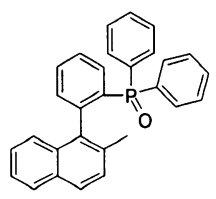
(m, 3H); 7.64-7.45 (m, 7H); 7.25-7.18 (m, 3H); 7.07-7.0 (m, 3H); 4.03 (s, 3H), 2.72 (s, 3H), 2.63 (s, 3H), 2.6 (s, 3H), 1.87 (s, 3H); ^{13}C-NMR δ: 153.9, 140.2, 140.1, 140.0, 137.6, 137.2, 137.1, 137.1, 137.0, 136.6, 136.6, 135.6, 134.5, 134.5, 134.3, 131.6, 131.4, 131.2, 131.1, 130.7, 130.7, 130.4, 130.0, 130.0, 128.9, 128.0, 127.9, 126.9, 126.8, 126.8, 125.7, 123.6, 112.1, 55.6, 21.9 (d, J = 6.7Hz), 18.1, 17.4, 17.2; ^{31}P-NMR δ: 31.4;
HPLC: AD-H(031), hexane/ethanol 95:5, 1mL/min, T_1 = 19.84 min, T_2 = 26.51 min.

1-[2-(Diphenyl-phosphinoyl)-3,4,5,6-tetramethyl-phenyl]-naphthalene



HRMS calcd for $C_{32}H_{28}OP$ 459.1872, found 459.1861 (delta -2.5), M.p. 194-195°C (ethyl acetate/hexane), R_f = 0.45 (ethyl acetate).
^{1}H-NMR δ: 7.7-7.68 (m, 1H); 7.62-7.58 (m, 2H); 7.52-7.49 (m, 2H); 7.45-7.39 (m, 6H); 7.29-7.25 (m, 1H); 7.19-7.14 (m, 3H); 7.07-7.03 (m, 2H), 2.63 (s, 3H), 2.57 (s, 3H), 2.54 (s, 3H), 1.84 (s, 3H), ^{13}C-NMR δ: 141.3, 141.2, 140.6, 140.5, 139.8, 139.8, 139.4, 139.4, 137.8, 137.1, 137.0, 136.8, 135.4, 134.4, 134.3, 134.2, 133.2, 132.7, 131.3, 131.2, 130.8, 130.7, 130.5, 129.9, 129.8, 129.7, 129.7, 129.4, 129.4, 128.9, 128.3, 127.5, 127.4, 127.3, 127.2, 127.1, 126.0, 125.7, 125.4, 22.4 (d, J = 6.7Hz), 18.2 (d, J = 1.9Hz), 17.8, 17.0. ^{31}P-NMR δ: 30.6; HPLC: AD-H(130), hexane/ethanol 95:5, 1mL/min, T_1 = 9.07 min, T_2 = 11.51 min.

1-[2-(Diphenyl-phosphinoyl)-phenyl]-2-methyl-naphthalene

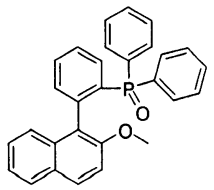


HRMS calcd for $C_{29}H_{23}OP$ 418.1481, found 418.1472 (delta -2.2), M.p. 163-164°C (ethyl acetate/hexane), R_f = 0.56 (ethyl acetate).
^{1}H-NMR δ: 8.07-8.01 (m, 1H); 7.93-7.87 (m, 3H); 7.83-7.74 (m, 3H); 7.67-7.63 (m, 1H); 7.59-7.43 (m, 7H); 7.39-7.35 (m, 1H); 7.3-7.26 (m, 2H); 7.16-7.11 (m, 2H), 2.48 (s, 3H), ^{13}C-NMR δ: 144.7, 144.6, 136.0, 136.0, 135.5, 134.8, 134.7, 134.0, 133.9, 133.0, 132.9, 132.7, 132.5, 132.4, 132.4, 132.2, 132.1, 131.7, 131.6, 131.6, 131.2, 131.1, 130.7, 130.7, 128.5, 128.4, 128.3, 128.2, 127.8, 127.6, 127.6, 127.5, 127.4, 126.5, 125.6, 124.6, 21.8. ^{31}P-NMR δ: 26.1, HPLC: AD-H(031), hexane/ethanol 98:2, 1.5mL/min, T_1 = 9.82 min, T_2 = 10.94 min.

Chiral complexes **I, II, III** or **IV** (see Figure 1) were taken to carry out the asymmetric version of the reaction. Products were purified chromatographically, and enantiomeric excess was analyzed by

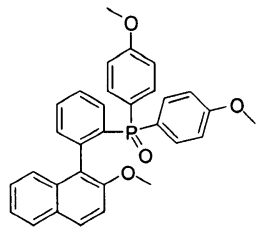
HPLC. For additional details see Table 1. Non-racemic samples of biphenyls **1**, **2**, **4**, **5** were enriched to optical purity >99% *ee* by one or two recrystallizations.

*One example: Synthesis of (-)-S 1-[2-(Diphenyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene **(1)**:*



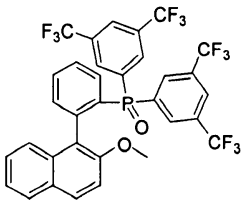
A thermostated (45°C) reaction vessel was loaded with 1-(diphenyl-phosphinoylethynyl)-2-methoxy-naphthalene (1.15 g; 3 mmol), catalyst **I** (63 mg; 0.15 mmol), THF (30 mL) under atmosphere of acetylene. The mixture was stirred and irradiated by two 460-W lamps ($\lambda \approx 420$ nm) for 48 h. The reaction was quenched by switching off the lamps and simultaneously letting in air. The conversion of the starting acetylene was determined by GC. The solvent was evaporated, the oily residue was purified on silica (ethyl acetate) to give (-)-*S*-1-[2-(diphenyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene **1** (639 mg, 49%) as a colorless solid. The optical purity was determined to be 79 %*ee* (HPLC). A recrystallization from ethyl acetate – hexane gave the product in enantiomerically pure state (391 mg, 30%, >99 %ee). HPLC: Chiralpack AD-H, hexane/ethanol 98:2, 2mL/min, T_1 = 28.81 min, T_2 = 38.68 min; $[\alpha]_D^{25}$ = -80.7° (c=0.56, $CHCl_3$); M.p. 149-150°C; ^{1}H NMR (400 MHz, $[D_1]CHCl_3$, 25°C): δ = 7.86-7.8 (m, 1H), 7.57-7.41 (m, 4H), 7.38-7.33 (m, 2H), 7.26-7.16 (m, 4H), 7.13-7.04 (m, 5H), 6.97-6.93 (m, 3H), 6.86 (d, 1H, *J* = 9.1Hz), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $[D_1]CHCl_3$, 25°C): δ = 135.0, 134.9, 133.4, 133.3, 132.3, 132.3, 132.2, 132.1, 131.9, 131.8, 131.3, 131.3, 131.1, 131.1, 130.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.6, 126.4, 125.8, 123.5, 112.3, 55.9; ^{31}P NMR (162 MHz, $[D_1]CHCl_3$, 25°C) δ: 27.9; HRMS calcd for $C_{29}H_{23}O_2P$ 434.1430, found 434.1422 (delta -1.9).

*1-[2-(Di-(4-methoxy-phenyl)-phosphinoyl)-phenyl]-2-methoxy-naphthalene **(2)***



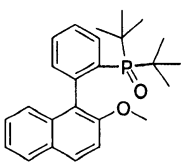
$C_{31}H_{27}O_4P$, MW = 494.52, M.p. 162-163°C (ethyl acetate/hexane), R_f = 0.41 (THF/ethyl acetate 1:1), $[\alpha]_D^{25}$ = –123.4° (c=0.36, in $CHCl_3$), >99% *ee*; ^{1}H-NMR δ: 7.97-7.92 (m, 1H); 7.53-7.41 (m, 4H); 7.28-7.23 (m, 2H); 7.1-7.0 (m, 5H); 6.9-6.87 (m, 2H); 6.58-6.55 (m, 2H); 6.32-6.29 (m, 2H). ^{13}C-NMR δ: 162.0 (d, *J* = 2.9Hz); 161.5 (d, *J* = 2.9Hz); 154.1, 140.9, 140.8, 134.9, 134.87, 134.0, 133.9, 133.8, 133.6, 133.4, 133.2, 133.1, 132.0, 132.0, 129.9, 128.7, 127.7, 127.6, 126.3, 125.9, 125.8, 125.0, 124.7, 123.9, 123.4, 123.3, 123.2, 113.6, 113.5, 113.1, 113.0, 112.5, 56.0, 55.6, 55.4, ^{31}P-NMR δ: 28.3; MS (70 eV), m/z: 494 (100) [M^+], 463 (89), 357 (67), 337 (50), 263 (64), 247 (24), 232 (56), 214 (41), 189 (27), 155 (17), 108 (16), 77 (13).
HPLC: Whelk 01 (S,S), hexane/ethanol 95:5, 2mL/min, T_1 = 32.76 min, T_2 = 42.55 min.

*1-[2-(Di-(3,5-bis-trifluoromethyl-phenyl)-phosphinoyl)-phenyl]-2-methoxy-naphthalene (**3**)*



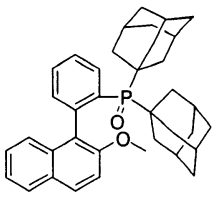
HRMS calcd for $C_{33}H_{19}O_2F_{12}P$ 706.0926, found 706.0941 (delta 2.1), M.p. 154-155°C (ethyl acetate/hexane), R_f = 0.79 (hexane/ethyl acetate 4:1). ^{1}H-NMR δ: 7.84-7.78 (m, 3H), 7.72-7.65 (m, 4H), 7.59-7.52 (m, 2H), 7.5 (d, 1H, *J* = 8.9Hz); 7.43-7.4 (m, 1H); 7.28-7.25 (m, 1H); 7.19-7.11 (m, 2H); 6.96 (d, 1H, *J* = 9.1Hz), 6.92-6.9 (m, 1H); 3.73 (s, 3H), ^{13}C-NMR δ: 154.9, 141.4, 141.3, 136.4, 135.6, 135.3, 134.6, 134.4, 134.3, 134.1, 134.0, 133.8, 133.6, 133.3, 132.1, 132.0, 131.8, 131.6, 131.5, 131.4, 131.3, 131.2, 130.5, 128.6, 128.5, 128.1, 127.9, 127.6, 125.7, 124.7, 124.3, 124.3, 122.0, 121.9, 121.6, 121.6, 112.6, 56.4. ^{31}P-NMR δ: 23.1, HPLC: Chiralpack OD, hexane/ethanol 99.5:0.5, 1mL/min, T_1 = 6.16 min, T_2 = 6.89 min.

*1-[2-(Di-tert-butyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene (**4**)*



HRMS calcd for $C_{25}H_{31}O_2P$ 394.2056, found 394.2053 (delta -0.9), M.p. 215-216°C (ethyl acetate/hexane), R_f = 0.51 (THF), $[\alpha]_D^{25}$ = +64.1° (c=1, in $CHCl_3$), >99% *ee*, ^{1}H-NMR δ: 7.76 (d, 1H, *J* = 9.1Hz); 7.69-7.64 (m, 2H); 7.52-7.47 (m, 1H); 7.39-7.34 (m, 1H); 7.26-7.03 (m, 5H); 3.72 (s, 3H); 1.22 (d, 1H, *J* = 13.1Hz); 0.99 (d, 1H, *J* = 13.5Hz), ^{13}C-NMR δ: 154.0; 144.3; 144.2; 136.1; 134.7; 134.6; 134.1; 132.3; 132.3; 132.2; 131.6; 130.8; 130.8; 129.4; 128.8; 128.3; 126.2; 125.8; 125.7; 125.2; 124.9; 124.8; 122.8; 116.7; 112.5; 55.8; 38.2 (d, *J* = 6.7Hz); 37.7 (d, *J* = 5.7Hz); 28.7 (d, *J* = 40Hz), ^{31}P-NMR δ: 52.9, HPLC: Chiralpack AD, hexane/isopropanol 98:2, 1mL/min, T_1 = 5.12 min, T_2 = 6.16 min.

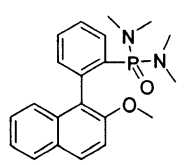
*1-[2-(Di-1-adamantyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene (**5**)*



HRMS calcd for $C_{37}H_{43}O_2P$ 550.2995, found 550.2985 (delta -1.8)$C_{37}H_{43}O_2P$, M.p. >300°C (ethyl acetate/hexane), R_f = 0.69 (ethyl acetate), $[\alpha]_D^{25}$ = +19.3° (c=1, in $CHCl_3$), >99% *ee*, ^{1}H-NMR δ: 8.06 (d, 1H, *J* = 9.1Hz); 7.99-7.92 (m, 2H); 7.84-7.8 (m, 1H); 7.72-7.67 (m, 1H); 7.56-7.45 (m, 2H); 7.41-7.33 (m, 3H), ^{13}C-NMR δ: 153.9, 144.7 (d, *J* = 3.8Hz), 134.7, 134.6, 134.1, 132.2, 132.1, 131.0, 130.6, 130.6, 130.2, 129.3, 128.8, 128.2, 126.3, 125.5, 125.4, 124.9, 124.9, 124.9, 122.7, 112.4, 55.8, 42.5, 42.3, 41.9, 41.7, 38.1, 38.1, 37.7, 37.6, 37.2, 37.0, 28.7, 28.6, 28.3, 28.2. ^{31}P-NMR δ: 44.6,

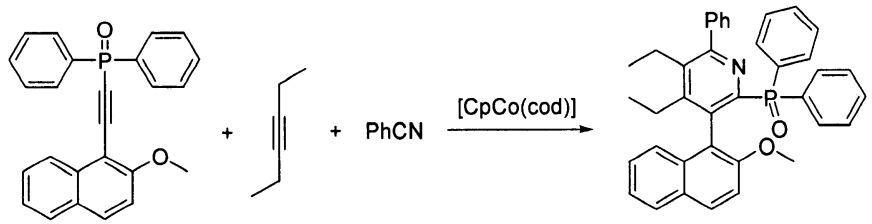
HPLC: Chiralpack AD, hexane/ethanol 98:2, 0.8mL/min, T_1 = 6.22 min, T_2 = 8.06 min.

*1-[2-(Bis-dimethylamino-phosphinoyl)-phenyl]-2-methoxy-naphthalene (**6**)*



$C_{21}H_{25}N_2O_2P$, MW = 368.41, R_f = 0.43 (THF), ^{1}H-NMR δ: 8.35-8.3 (m, 1H), 8.11 (d, 1H, *J* = 8.9Hz); 8.06-8.04 (m, 1H), 7.83-7.72 (m, 2H), 7.6 (d, 1H, *J* = 9.1Hz); 7.55-7.45 (m, 3H); 7.37-7.35 (m, 1H); 4.09 (s, 3H); 2.49 (d, 6H, *J* = 9.5Hz); 2.33 (d, 6H, *J* = 9.7Hz), ^{13}C-NMR δ: 154.3, 141.1 (d, *J* = 8.6Hz), 135.3, 135.2, 134.4, 133.7, 133.0, 132.9, 132.2, 131.3, 131.3, 129.3, 129.0, 128.1, 127.4, 127.3, 126.2, 125.9, 125.8, 125.4, 125.4, 123.5, 113.6, 56.6, 36.5 (q, *J* = 3.81Hz), ^{31}P-NMR δ: 29.6, MS (70 eV), m/z: 368 (100) [M^+], 337 (74), 324 (57), 309 (16), 294 (70), 279 (88), 266 (62), 249 (52), 232 (15), 215 (35), 202 (31), 189 (32), 169 (14), HPLC: Chiralpack AD, hexane/ethanol 98:2, 1mL/min, T_1 = 10.17 min, T_2 = 13.38 min.

*4,5-Diethyl-3-(2-methoxy-1-naphthyl)-6-phenyl-2-pyridyl(diphenyl)phosphane oxide (**7**)*



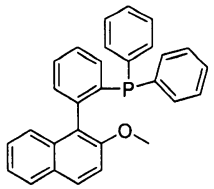
A thermostated (25°C) reaction vessel was loaded with 1-(Diphenyl-phosphinoylethynyl)-2-methoxy-naphthalene (382 mg, 1 mmol) and [cpCo(cod)] (11.6 mg, 0.05 mmol) under argon. THF (10 mL) was added, followed by 3-hexyne (115 µL, 1 mmol) and benzonitrile (103 µL, 1 mmol) and the mixture was stirred and irradiated by two 460-W lamps (λ ≈ 420 nm) for 24 hours. The reaction was quenched by switching off the lamps and simultaneously letting in air. The sample was analyzed by GC. The solvent was evaporated, and the residue was purified on silica (THF/hexane 1:1) to give the compound **7** (217 mg, 38%).

HRMS calcd for $C_{38}H_{34}O_2NP$ 567.2322, found 567.2330 (delta 1.4), M.p. 208-209°C (ethyl acetate/hexane), ^{1}H-NMR δ: 8.1 (d, 1H, *J* = 8.9 Hz); 8.0-7.93 (m, 3H), 7.8-7.55 (m, 8H); 7.51-7.44 (m, 5H), 7.38-7.33 (m, 3H), 7.2 (d, 1H, *J* = 8.3Hz); 3.11-3.01 (m, 2H), 2.74-2.65 (m, 1H), 2.57-2.49 (m, 1H), 1.31 (t, 3H, *J* = 7.5Hz), 1.07 (t, 3H, *J* = 7.5Hz); ^{13}C-NMR δ: 158.3, 158.1, 155.3, 153.2, 153.1, 152.1, 150.8, 141.6, 137.5, 137.5, 137.2, 137.0, 135.7, 134.9, 134.7, 134.3, 133.9, 132.7,

132.6, 132.5, 132.4, 130.9, 130.9, 130.8, 130.8, 130.5, 129.6, 128.9, 128.4, 128.2, 128.0, 127.8, 127.7, 127.7, 127.6, 126.5, 124.9, 123.4, 119.2, 113.0, 56.1, 23.4, 22.6, 15.7, 14.6; ^{31}P-NMR δ: 20.7.

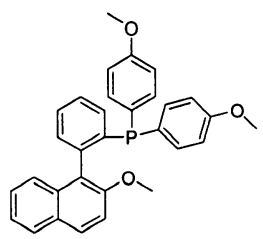
III) Reduction of the phoshine oxides to the corresponding phosphanes

*Reduction to (-)-S [2-(2-Methoxy-naphthalen-1-yl)-phenyl]-diphenyl-phosphane (NAPHEP) **9**:*



Phosphine oxide **1** (266 mg, 0.612 mmol, >99 %ee) was dissolved in THF (5 mL) and AlH_3 (1.32 mL of a 0.5 M solution in THF, 0.652 mmol) was added dropwise. The mixture was stirred at 50°C for 30 minutes, cooled and dry methanol (0.1 mL) was added. The mixture was filtered through a pad of silica which was washed with THF (3 × 5 mL). The organic extract was evaporated and purified by flash chromatography eluting with hexane – ethyl acetate (9:1) to yield (-)-*S* [2-(2-Methoxy-naphthalen-1-yl)-phenyl]-diphenyl-phosphane *(NAPHEP) **9*** (246 mg, 96%) as a colorless solid. The optical purity of the sample was determined to be >99 %ee (HPLC). HPLC: Chiralpack AD-H, hexane/ethanol 95:5, 1mL/min, T_1 = 17.32 min, T_2 = 21.27 min. M.p. 142-143°C (ethyl acetate); $[\alpha]_D^{25}$ = –40.9° (c=0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $[D_1]CHCl_3$, 25°C): δ = 7.77-7.74 (m, 1H), 7.69-7.67 (m, 1H), 7.38-7.34 (m, 1H), 7.28-6.93 (m, 17H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $[D_1]CHCl_3$, 25°C): δ = 154.6, 143.9, 143.5, 139.1, 139.0, 138.8, 138.6, 138.0, 137.9, 135.0, 134.3, 134.2, 134.1, 134.0, 133.8, 131.7, 131.7, 130.0, 129.6, 129.1, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 126.7, 125.7, 124.7, 124.6, 123.7, 113.0, 55.9; ^{31}P NMR (162 MHz, $[D_1]CHCl_3$, 25°C) δ: –13.5; HRMS calcd for $C_{29}H_{23}OP$ 418.1481, found 418.1473 (delta -1.8).

*[2-(-Methoxy-naphthalen-1-yl)-phenyl]-bis-(4-methoxy-phenyl)-phosphane (**10**)*



Phosphine oxide **2** (93 mg, 0.2 mmol, >99% *ee*) was dissolved in THF (3 mL) and AlH_3 (0.43 mL of an 0.5 M solution in THF, 0.21 mmol) was added dropwise. The mixture was stirred at 50°C for 30 minutes, cooled and dry methanol (0.1 mL) was added. The mixture was filtered through a pad of silica which was washed with THF (3 × 5 mL). The organic extract was evaporated and purified by flash chromatography eluting with hexane – ethyl acetate (2:1) to yield phosphine **10** (89 mg, 96% yield) as a colorless solid.

M.p. 153-154°C (ethyl acetate); $[\alpha]_D^{25}$ = –401° (c=0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $[D_1]CHCl_3$, 25°C): δ = 8.04-8.02 (m, 1H), 7.95-7.94 (m, 1H), 7.64-7.6 (m, 1H), 7.55-7.51 (m, 1H), 7.46-7.28

(m, 8H), 7.15-7.11 (m, 2H), 7.02-6.99 (m, 2H), 6.87-6.85 (m, 2H), 3.96 (s, 3H), 3.9 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $[D_1]CHCl_3$, 25°C): δ = 154.5, 143.1, 142.8, 135.6, 135.5, 135.4, 135.3, 134.2, 134.1, 131.6, 131.5, 129.8, 129.4, 129.1, 129.1, 129.0, 128.1, 127.9, 126.4, 125.6, 123.5, 117.2, 114.2, 114.1, 114.1, 114.1, 113.2, 56.0, 55.5, 55.5; ^{31}P NMR (162 MHz, $[D_1]CHCl_3$, 25°C) δ: –16.4; MS (70 eV), m/z : 478 (2) [M^+], 447 (100), 185 (9).

A sample of the substance was oxidized with H_2O_2 in THF solution, and the phosphine oxide was analyzed by HPLC to show the optical purity of >99% *ee*.

IV) NAPHEP as a ligand, catalytic asymmetric hydrosilylation

A mixture of thoroughly dried and degassed alkene (50 mmol), trichlorosilane (60 mmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (0.1-0.01 mol%), and (*S*)-(-)-MOPAN (0.2-0.02 mol%) was stirred at 0-40°C for 24-72 h (see Table 1 for details). The reaction mixture was distilled bulb-to-bulb under reduced pressure to give trichlorosilylalkanes. The compounds were converted quantitatively into corresponding trimethoxysilyl alkanes by dropwise addition to a suspension of KF (14.4 g, 0.25 mol) and $KHCO_3$ (50 g, 0.5 mol) in MeOH/THF (500 mL, 1:1) at 20°C. A liqiud sample was taken after 20 minutes to analyze the conversion and regioselectivity of the reaction (GC/MS). The mixture was then treated with 30% H_2O_2, and stirred for 12 hours at r.t. After filtration, the solvent was evaporated, and crude alcohols were purified by distillation (1-phenylethanol, *exo*-2-norborneol), flash chromatography (1-phenylbutan-2-ol), or by the preferential complexation with $CaCl_2$ (2-hexanol, 2-octanol) to remove primary alcohols. The enantiomeric excess was analyzed by chiral HPLC or GC (in the form of trifluoroacetic esters).

trans-[$PdCl_2${(*S*)-NAPHEP}$_2$]

$PdCl_2$ (8.9 mg, 0.05 mmol) and (*S*)-NAPHEP (42 mg, 0.1 mmol) were dissolved in acetonitrile (2 mL) under Argon, and the mixture was stirred for 2 hours. A single crystal suitable for X-ray investigation was grown by slow diffusion of diethyl ether into the acetonitrile solution.

V) Crystallographic Experimental Section

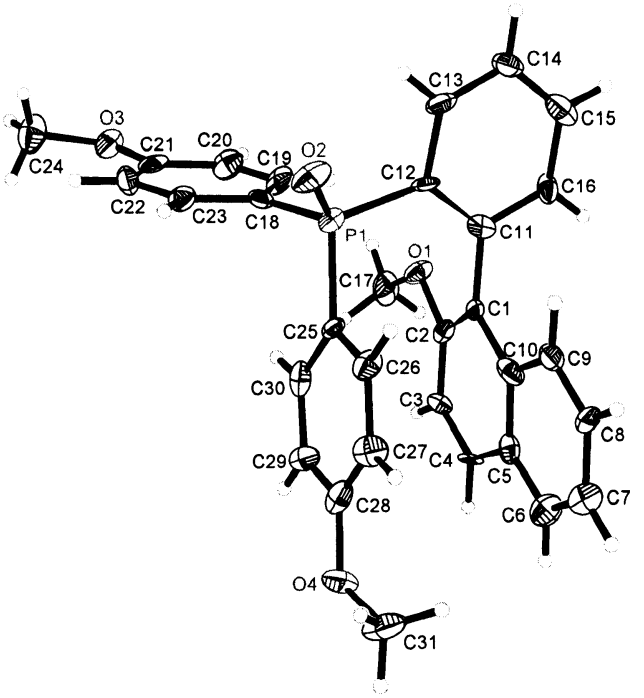


Figure 3. Crystal structure and numbering scheme of 1-[2-(Di-(4-methoxy-phenyl)-phosphinoyl)-phenyl]-2-methoxy-naphthalene **(2)**. (ellipsoids set at 50% probability level).

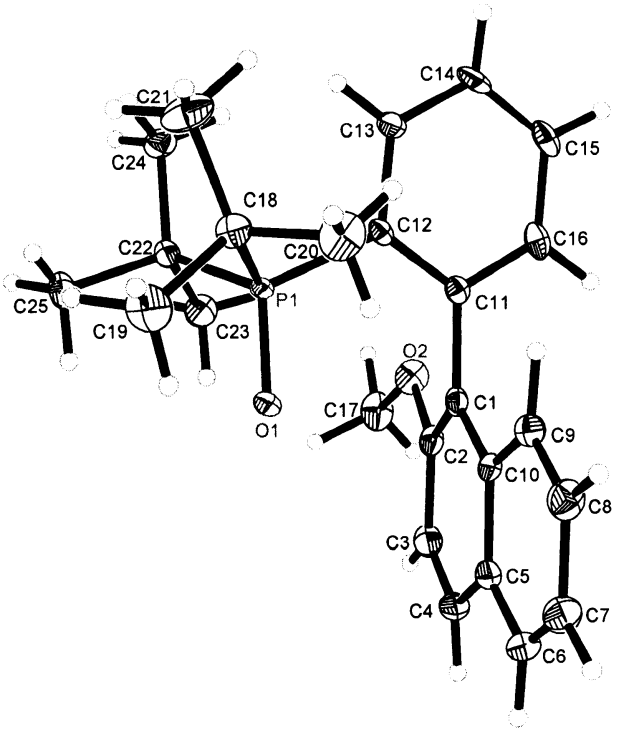


Figure 4. Crystal structure and numbering scheme of 1-[2-(Di-tert-butyl-phosphinoyl)-phenyl]-2-methoxy-naphthalene **4**. (ellipsoids set at 30% probability level).

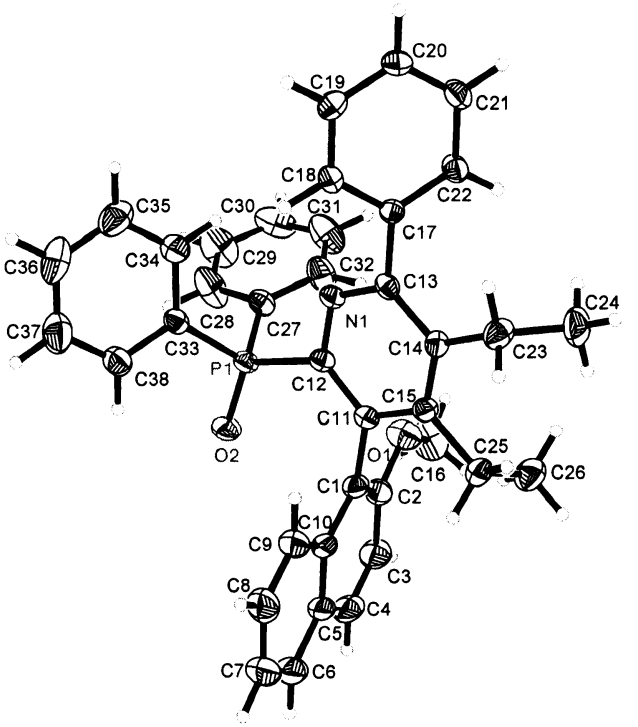


Figure 5. Crystal structure and numbering scheme of 4,5-Diethyl-3-(2-methoxy-1-naphthyl)-6-phenyl-2-pyridyl(diphenyl)phosphane oxide **7**. (ellipsoids set at 50% probability level).

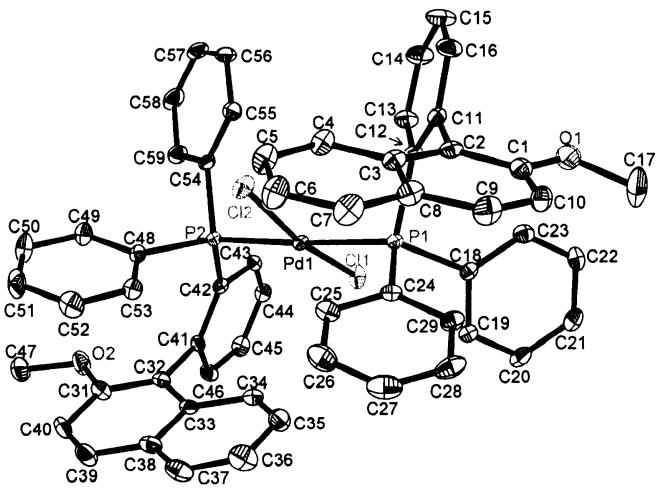


Figure 6. Crystal structure and numbering scheme of *trans*-[$PdCl_2${(*S*)-NAPHEP}$_2$. All hydrogens have been omitted for clarity. (ellipsoids set at 30% probability level).

Crystal structure determinations

Crystals of compounds **1, 2, 4, 7** and *trans*-[$PdCl_2${(*S*)-NAPHEP}$_2$ for the X-ray analyses were obtained by slow diffusion of pentane into a concentrated THF solution or slow evaporation of a concentrated ethyl acetate solution of phosphine oxides. Crystal data and details of the structure solution are summarised in Table 4.

For all compounds data were collected on a STOE-IPDS diffractometer using graphite monochromated Mo-Kα radiation. The structures were solved by direct methods (SHELXS-97)[27]

and refined by full matrix least squares techniques against F^2 (SHELXL-97)[28]. XP (Bruker-AXS) was used for structure representations.
The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed into theoretical positions and were refined by using the riding model. The weighting schemes are $\omega = 1/[\sigma^2(Fo^2) + (0.0808P)^2 + 0.0000P]$ for **1**, $\omega = 1/[\sigma^2(Fo^2) + (0.0000P)^2 + 0.0000P]$ for **2**, $\omega = 1/[\sigma^2(Fo^2) + (0.0745P)^2 + 0.0000P]$ for **4**, $\omega = 1/[\sigma^2(Fo^2) + (0.0061P)^2 + 0.0000P]$ for **7**, with $P = (Fo^2 + 2Fc^2)/3$ for $PdCl_2[(S)\text{-NAPHEP}]_2$.

CCDC 275232 (**1**), CCDC 275233 (**2**), CCDC 275234 (**4**), CCDC 275235 (**7**) and CCDC 287928 {$PdCl_2[(S)\text{-NAPHEP}]_2$} contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ,UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Table 4: Crystallographic and refinement data for **1**, **2**, **4**, **7**, and *trans*-[$PdCl_2${(*S*)-NAPHEP}$_2$

	1	**2**	**4**	**7**	Pd complex
Empirical formula	$C_{29}H_{23}O_2P$	$C_{31}H_{27}O_4P$	$C_{25}H_{31}O_2P$	$C_{38}H_{34}NO_2P$	$C_{58}H_{46}Cl_2O_2P_2Pd$
Formula weight	434.44	494.50	394.47	567.63	1014.19
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P1$	$P2_1/n$	$P2_1$
Unit cell dimensions					
a (Å)	10.346(2)	9.929(2)	8.098(2)	8.627(2)	10.169(2)
b (Å)	9.308(2)	13.264(3)	8.282(2)	16.928(3)	16.864(3)
c (Å)	11.713(2)	10.538(2)	9.493(2)	20.829(4)	14.648(3)
α [°]	90	90	98.71(3)	90	90
β [°]	98.08(3)	116.88(3)	96.06(3)	96.30(3)	104.79(3)
γ [°]	90	90	118.49(3)	90	90
V (Å^3)	1116.8(4)	1237.9(4)	541.4(2)	3023.5(10)	2428.8(8)
Z	2	2	1	4	2
D_{calc} (Mg/m^3)	1.292	1.327	1.210	1.247	1.387
μ (Mo Kα) (mm^{-1})	0.147	0.148	0.144	0.126	0.601
F(000)	456	520	212	1200	1040
Crystal size	0.5 x 0.4 x 0.4	0.2 x 0.1 x 0.1	0.4 x 0.2 x 0.2	0.4 x 0.3 x 0.2	0.5 x 0.3 x 0.3
Temperature (K)	200	200	200	293	200
Θ Range for data collection (°)	1.76 – 24.20	2.17 – 22.77	2.22 – 24.99	1.97 – 26.19	2.07 – 25.00
Index range (h,k,l)	-11/10, -10/10, -13/13	-10/0 - 14/14, -10/11	-9/9, -9/9, -11/11	-10/10, -20/20, -0/25	-12/12, -20/20, -17/17
Reflection collected	5964	5491	3235	10848	14545
Independent reflections	3327	3173	3235	5927	8557
Observed reflections	2920	1391	2975	2128	7383
Refined parameters	298	325	377	379	581
R1 (2σ(I))	0.0266	0.0537	0.0312	0.0427	0.0277
R1 (all data)	0.0329	0.1507	0.0347	0.1595	0.0365
wR2 (all data)	0.0712	0.0950	0.0771	0.0730	0.0509

Goodness of fit	0.645	0.669	0.763	0.679	0.874
Largest difference peak and hole (e/ Å)	0.122/-0.134	0.265/-0.250	0.220/-0.172	0.134/-0.190	0.382/-0.346

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