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Phosphorus-Bearing Axially Chiral Biaryls by Catalytic Asymmetric Cross-Cyclotrimerization and a First Application in Asymmetric Hydrosilylation

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Abstract: A novel and efficient, two-step route to axially chiral biaryls is demonstrated. In a direct asymmetric cross-cyclotrimerization in the presence of a chiral cobalt(I) catalyst, axially chiral biaryls bearing phosphoryl moieties have been prepared, and through indirect evidence the authors have been able to clarify the origin of the stereochemical induction and the nature of the central intermediate in the catalytic cycle. By subsequent reduction of the phosphoryl moiety to the corresponding phosphine, a very efficient and atom-economical approach to chiral systems has been developed. These chiral systems clearly have great potential use as axially chiral monodentate P- or bidentate P,O-ligands, as has been demonstrated by the employment of the novel NAPHEP as a new monodentate acting ligand in an asymmetric hydrosilylation reaction.

Keywords: asymmetric catalysis · atropisomerism · biaryls · cobalt · cross-coupling

Introduction

Axial chirality is a fundamental basis for useful reagents and catalysts in asymmetric synthesis, so axially chiral biaryl units are of steadily growing interest and importance in both academic and pharmaceutical drug research. In an excellent and very recent review, Bringmann, Breuning, and co-workers classified the strategies for the atroposelective synthesis of axially chiral biaryl compounds by their underlying concepts and critically evaluated their scopes and limitations with reference to selected model reactions and applications.[1]

Apart from diastereoselective methods and those involving optical resolution stages, there are only a few direct catalytic asymmetric approaches to nonracemic, axially chiral biaryls, the most popular examples being cross-couplings[2] between aryl Grignard reagents,[3] organolithiums,[4] or arylboronic acids[5] and aryl halides. Another strategy involves enantioposition-selective cross-couplings of achiral biaryl bistriflates,[6] while the asymmetric cleavage of dinaphtho[2,1-*b*:1′,2′-*d*]thiophene with Grignard reagents has also recently been demonstrated.[7] Oxidative coupling of activated aromatics constitutes a special group of catalytic methods,[8] while the possibility of using cycloadditions of arylpropiolates with gaseous acetylene in the presence of a nickel(0)/triphenylphosphine catalyst for the preparation of compounds with axially chiral biaryl backbones was first accomplished by Mori and co-workers, who synthesized a racemic biaryl in one elegant step.[9]

Asymmetric cross-cyclotrimerizations of alkynes in the presence of Ir or Rh complexes as catalysts have been demonstrated to be powerful tools for the construction of axially chiral biaryl derivatives.[10] Very recently we discovered that application of our chiral cobalt(I) catalysts[11] (Scheme 1) under photochemical conditions, as previously applied in the synthesis of different pyridines,[12] could be used particularly successfully for the preparation of axially chiral 2-arylpyridines.[13]

Here we report the first use of [2+2+2] cross-cycloaddition reactions for the preparation of axially chiral biaryls bearing phosphorus functionalities. These compounds offer huge potential as ligands in asymmetric catalysis, so a first application in the asymmetric hydrosilylation of alkenes is also described.

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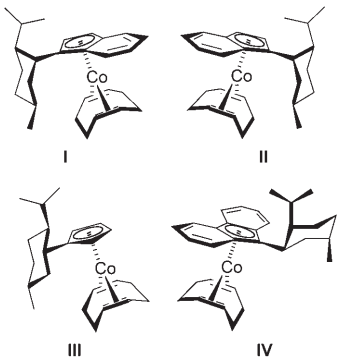
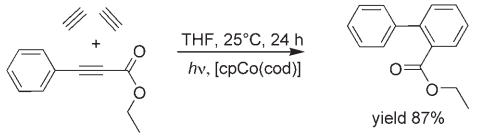


Scheme 1. Chiral cobalt(I) complexes.

Results and Discussion

Racemic axially chiral biphenyls: We had previously found cobalt(I) complexes to be useful for the synthesis of biaryls under irradiation with visible light (350–500 nm) at ambient temperature and pressure: ethyl phenylpropynoate and gaseous acetylene in the presence of [cpCo(cod)] (η^5-cyclopentadienyl-η^4-cycloocta-1,5-diene-cobalt(I)), for example, gave ethyl biphenyl-2-carboxylate in 87% yield. (Scheme 2).



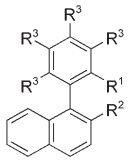
Scheme 2. Cobalt-catalyzed [2+2+2] cross-cycloaddition.

In view of these results, a number of new naphthyl-derived alkynes **1**–**9** (see Experimental Section) bearing phosphoryl moieties were prepared and used as templates for cycloadditions with acetylene, with self-trimerization being prevented by the steric bulkiness of the system. Upon cross-coupling with acetylene ($R^3 = H$), or alternatively with internal alkynes ($R^3 = CH_3$, C_2H_5), these compounds **1**–**9** gave the racemic axially chiral biaryls **10**–**20** in good yields, as summarized in Table 1.

With unsubstituted acetylene, benzene was observed as the single side product resulting from the homocoupling reaction. Nevertheless, the low chemoselectivity in the case of the biphenyls with $R^3 = H$ resulted in a biphenyls/benzene ratio in the range of 1:15–25, but causing practically no trouble, as C_6H_6 was easily removed by evaporation. The reactions with but-2-yne and hex-3-yne resulted in the corresponding biphenyls **12**, **13**, and **19**, with minimal formation of the undesired hexamethyl- and hexaethylbenzenes (< 5%, GC).

Dynamic HPLC (see Experimental Section) on a chiral stationary phase clearly showed that each of the biphenyl derivatives **10**–**20** exists in the form of two stable atropisomers, with no interconversion being observed at temperatures up to +60 °C.

Table 1. Synthesis of racemic axially chiral biphenyls.



Compd	R^1	R^2	R^3	[cpCo(cod)]/ mol %[a]	t/ h	Yield/ %[b]
10	COC_6H_5	OCH_3	H	2	24	69[c]
11	$PO(C_6H_5)_2$	OCH_3	H	2	24	52
12	$PO(C_6H_5)_2$	OCH_3	C_2H_5	5	24	76
13	$PO(C_6H_5)_2$	OCH_3	CH_3	5	24	26
14	$PO(p\text{-}CH_3OC_6H_4)_2$	OCH_3	H	5	24	68
15	$PO[3,5\text{-}(CF_3)_2C_6H_3)]_2$	OCH_3	H	1	12	81
16	$PO(tC_4H_9)_2$	OCH_3	H	5	24	74
17	PO(1-adamantyl)$_2$	OCH_3	H	5	24	55
18	$PO[(CH_3)_2N]_2$	OCH_3	H	1	12	80
19	$PO(C_6H_5)_2$	H	CH_3	5	24	79
20	$PO(C_6H_5)_2$	CH_3	H	2	12	81

[a] Amount of catalyst used in THF at 25 °C. [b] Isolated yield. [c] Yield after chromatography.

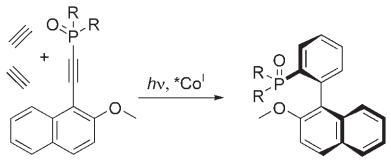
Chiral induction: For the induction of the chiral information, enantiomerically pure half-sandwich Co^I complexes **I** and **II** (see Scheme 1), (−)-(S_p)- and (+)-(R_p)-(η^4-cycloocta-1,5-diene)(η^5-1-neomenthyl-indenyl)-cobalt, were most effective. In many cases reasonable yields and *ee* values were achieved under optimized conditions (see Table 2).

The corresponding *S* enantiomers of biaryls were found in all cases in which the (-)-(S_p)-catalyst **I** was employed; however, as expected with use of the (+)-(R_p)-complex **II** as catalyst, we found that products enriched in the opposite enantiomers were obtained. Thus, after 24 h at 25°C in THF we synthesized (+)-(*R*)-1-[2-(diphenylphosphinoyl)-phenyl]-2-methoxynaphthalene with 63 and 45% *ee* by the reaction of 1-(diphenylphosphinoylethynyl)-2-methoxynaphthalene **2** and acetylene by using (+)-(R_p)-complex **II** as catalyst (see Table 2).

The relatively high enantiomeric excesses in the products **11**, **14**, **16**, and **17** allowed further enrichment by recrystallization. Homochiral crystals of compounds **11**, **14**, and **16** were grown, and both their structures and their absolute configurations have been unambiguously determined. One example is shown in Figure 1.

Influence of temperature and solvent: An interesting feature of this reaction is the influence of temperature on the enantiomeric excesses in the products: the *ee* values each 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 **11** as an example. Each investigated reaction showed an individual point of inflexion, and required some optimization in order to find the best conditions. THF is the solvent of choice in the case of the catalysts **I** and **II**; reactions in

Table 2. Synthesis of axially chiral biaryls.



Compd	R	Cat.[a]	Reaction conditions	Yield/ %[b]	Solvent	Sel./ % *ee*[c]
(*S*)-11	C_6H_5	**IV**	25 °C, 12 h	8	THF	12[d]
(*S*)-11	C_6H_5	**III**	25 °C, 48 h	37	THF	12
(*R*)-11	C_6H_5	**II**	25 °C, 24 h	45	THF	63
(*S*)-11	C_6H_5	**I**	45 °C, 48 h	49	THF	79[d] (>99[e])
(*S*)-14	*p*-$CH_3OC_6H_4$	**I**	45 °C, 24 h	51	THF	72[d] (>99[e])
(*S*)-15	3,5-$(CF_3)_2C_6H_3$	**I**	45 °C, 24 h	24	THF	56
(*S*)-16	*t*-C_4H_9	**I**	25 °C, 48 h	61	THF	82[d] (>99[e])
(*S*)-17	1-adamantyl	**I**	25 °C, 24 h	44	toluene	83[d] (>99[e])
(*S*)-18	$(CH_3)_2N$	**I**[f]	55 °C, 12 h	80	toluene	68

[a] 5 mol % cat. (see Scheme 1). [b] Isolated yield. [c] Determined by HPLC. [d] Measured in reaction mixture. [e] Determined after recrystallization. [f] 1 mol % cat.

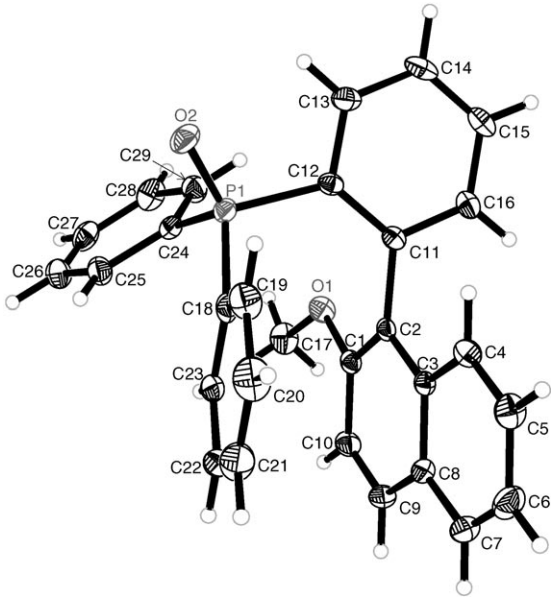


Figure 1. Crystal structure of [(−)-(*S*)-1-[2-(diphenylphosphinoyl)-phenyl]-2-methoxynaphthalene] (**11**; crystallographic data are given in the Experimental Section).[14]

DME, dioxane, or toluene showed slightly lower enantioselectivities and chemical yields. Other factors such as the duration of irradiation, the extent of conversion, and the amount of the catalyst were of little importance for the achieved *ee* values.

Reaction mechanism: Consistently with generally accepted mechanistic suggestions for the formation of pyridines and

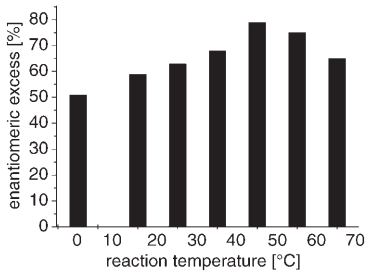
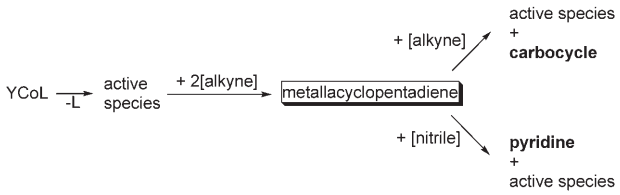


Figure 2. *ee* value against reaction temperature.

the corresponding benzenes (as shown in Scheme 3), an identical metallacyclopentadiene is generated in both cases, and in the subsequent rate-determining step this reacts



Scheme 3. Generally accepted mechanistic suggestion.

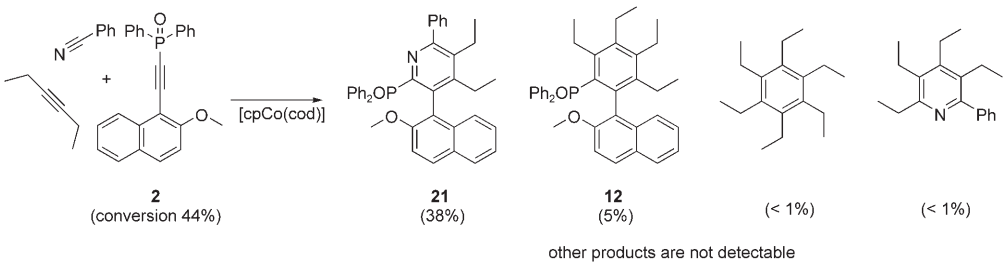
either with the nitrile or with an additional alkyne compound.[15] Since Co^I will not readily coordinate with a nitrile's lone-electron pair, only after metallacycle formation, when the metal exists as Co^{III}, will the nitrile coordinate and insert. An interesting challenge concerning the formation of biaryls is to identify which alkyne components are involved in the formation of the intermediate cobaltacyclopentadiene.

In order to clarify the origin of the stereochemical induction and the natures of the intermediates, we introduced different starting materials including hex-3-yne and benzonitrile, which were added to 1-(diphenylphosphinoylethynyl)-2-methoxynaphthalene (**2**) in a 1:1:1 ratio in the presence of [cpCo(cod)] as catalyst (Scheme 4).

Our experiment once more impressively demonstrated that the formation of cobaltacyclopentadiene from two alkynes is necessary for the formation of the pyridine product, to answer the question of whether only two hexyne molecules react at first, or whether the sterically more demanding alkyne **2** is involved in the formation of the metallacycle.

The finding of pyridine **21** as the major product is only possible if substrate **2** takes part in the formation of the cobaltacyclopentadiene intermediate.

As shown in Scheme 4, at 44 % conversion of the used nitrile the pyridine **21** was isolated in 38 % yield as a single regioisomer and also as the main product. The structure was confirmed by X-ray crystallography.[14] Only a 5 % yield of the benzene derivative **12** was determined by GC, and yields



Scheme 4. Three-component cycloaddition.

of other side products such as hexaethylbenzene and 2,3,4,5-tetraethyl-6-phenylpyridine do not exceed 1% each.

The observed ratio between pyridine **21** and carbocycle **12** supports the proposed mechanism,[15c] according to which one single metallacyclopentadiene intermediate reacts more rapidly 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 **21** and **12**. As illustrated in Scheme 5, we can also rule out a cobaltacyclopentadiene intermediate in which the $POPh_2$ group is located in the β-position to the cobalt because the anticipated products are not formed.

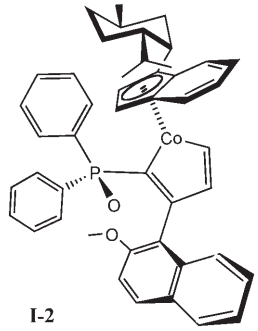
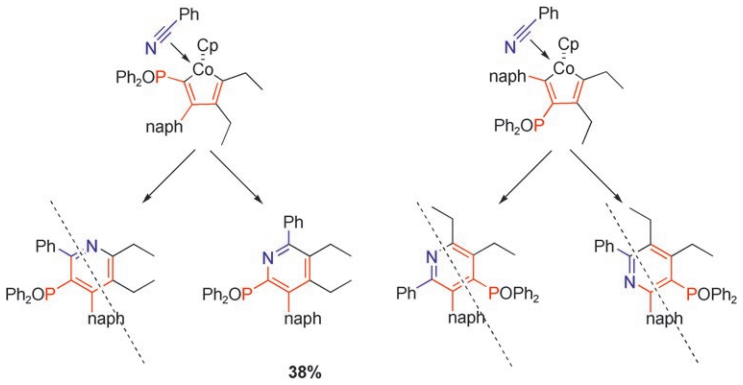


Figure 3. Suggested cobaltacyclopentadiene intermediate **I-2**.

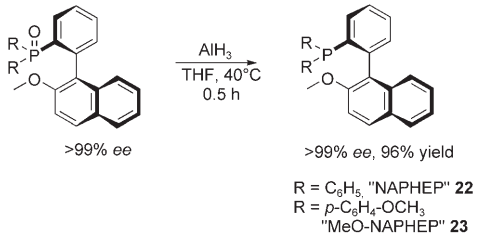


Scheme 5. Possible intermediates and the corresponding products.

Pursuing the idea of a single cobaltacyclopentadiene intermediate in the formation of pyridines and the corresponding benzenes, as a result of our three-component experiment we suppose that, with the employment of the optically active catalyst **I**, the cobaltacyclopentadiene **I-2** (Figure 3) is the major diastereomeric intermediate and reacts with the sterically less hindered alkyne molecule to give axially chiral biaryls.

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

Reduction to phosphines: We had so far demonstrated a novel and effective route to axially chiral biaryls bearing phosphoryl moieties, but chiral phosphines accessible by this route are even more interesting and potentially precious molecules in themselves as, for example, ligands for asymmetric catalysis. The conversion of the chiral phosphine oxides prepared by [2+2+2] cross-cyclotrimerization into the corresponding phosphines is quite simple and convenient. To demonstrate this and to synthesize axially chiral P-ligands we reduced the phosphine oxides **11** and **14** to the corresponding phosphines **22** and **23** by treatment with AlH_3 in THF (Scheme 6).[16,17] In contrast with the use of $LiAlH_4$,[18] the reaction with AlH_3 proceeded smoothly and furnished the corresponding phosphine in 96% yield and without atropisomerization.

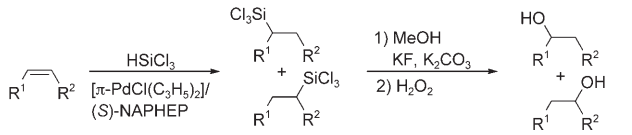


Scheme 6. Reduction to the corresponding chiral phosphines.

Application in asymmetric synthesis: In order to investigate whether our new compounds might be suited as ligands for asymmetric catalysis we compared compound **22**, our "NAPHEP" ligand, with the well studied MeO-MOP ligand of Hayashi et al.[19] The use of MOP/palladium catalytic systems was the first practical route for asymmetric hydrosilylation of alkenes.

The incorporation of phenyl/naphthyl moieties in the framework in our NAPHEP might offer it some advantages over its binaphthyl counterpart: the dihedral angles of our less rigid biaryls can be more easily self-tuned, thus allowing better adapted chiral geometry in the catalytically active palladium complex, while the diminished electron-donating properties of a phenyl ring may also strongly influence the outcome of a catalytic reaction. The results (Table 3) obtained with our NAPHEP as ligand in the hydrosilylation of alkenes 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 to proceed with good chemical yields and optical purities (up to 93% *ee*).

Table 3. Asymmetric hydrosilylation with Pd/(*S*)-NAPHEP.[a]



Alkene	*T*/ °C	Pd-cat./ mol%	NAPHEP/ mol%	Yield/ %[b]	2-/1-Isomers Ratio	Sel. [% *ee*][c]
hex-1-ene	40	0.1	0.2	61	76:24	91 (*R*)
oct-1-ene	40	0.1	0.2	59	77:23	93 (*R*)
1-phenyl-but-4-ene	40	0.1	0.2	53	65:35	93 (*R*)
norbornene	0	0.01	0.02	96	–[d]	83 (1*S*,2*S*,4*R*)

[a] Without solvent, 24 h. [b] Isolated yields of secondary alcohol. [c] *ee* of the major enantiomer. [d] Only *exo*-2-silylated product.

In principle, NAPHEP could act either 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*)-NAPHEP}$_2$] (Figure 4), NAPHEP is coordinated as a monodentate ligand, the phosphorus atoms and the chlorine atoms at palladium adopting *trans* relationships to one another in the square-planar geometry of the complex. At the same time, the benzannelated part of the naphthyl ring points towards the palladium atom while the methoxy group is on the remote side. This creates a chiral environment for the palladium for the origin of the outstanding observed enantioselectivity, similarly to the situation proposed by Hayashi.[21]

Conclusion

In summary, we have developed a novel and effective, two-step route to axially chiral biaryl ligands.

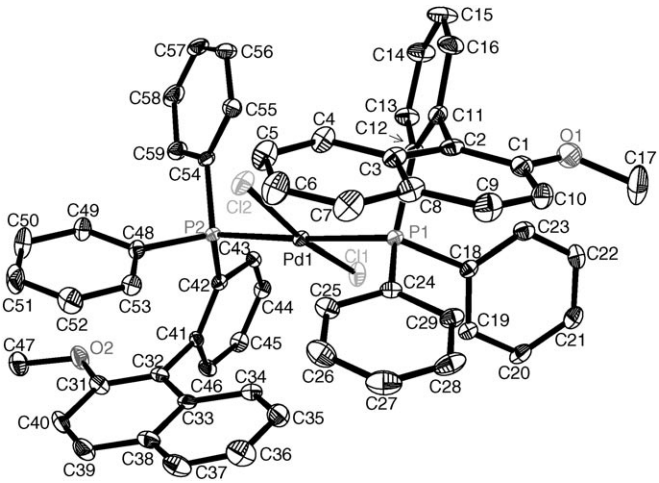


Figure 4. Crystal structure and numbering scheme of *trans*-[$PdCl_2${(*S*)-NAPHEP}$_2$. All hydrogens have been omitted for clarity (ellipsoids set at 30% probability level).[14]

In direct asymmetric cross-cyclotrimerizations using chiral cobalt(I) catalysts we created axially chiral biaryls bearing phosphoryl moieties. Mechanistic investigations detailing this [2+2+2] cycloaddition are presented.

Through subsequent reduction of the phosphoryl moieties to the corresponding phosphines we succeeded in developing a very efficient approach to chiral monodentate P- or bidentate P,O-ligands.

This has been demonstrated through the employment of the novel NAPHEP as a new, monodentate acting ligand in an asymmetric hydrosilylation reaction. Tests with our new axially chiral biaryl compounds in different catalytic reactions are underway in our laboratory.

Experimental Section

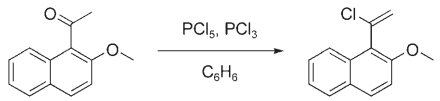
General methods: NMR spectra were recorded on a Bruker ARX 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{31}P, 162 MHz) spectrometer at 298 K. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residues of the deuteriated solvent (deuteriochloroform: $\delta = 7.27$ ppm for ^{1}H and $\delta = 77.36$ ppm for ^{13}C). Mass spectra were obtained with a MAT 95 XP 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 fitted with diode-array detector (DAD) (Hewlett–Packard) and Chiralyser (IBZ Messtechnik GmbH, Hannover). All reactions involving sensitive materials were carried out under argon, with use of 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 carried out with 240–400 mesh silica gel.

Diphenylchlorophosphine, di(*tert*-butyl)chlorophosphine, methyl chloroformate, 1-ethynyl-naphthalene, *n*BuLi, hex-3-yne, and but-2-yne were purchased from Aldrich. Bis(dimethylamino)phosphoryl chloride was purchased from Strem.

1-Acetyl-2-methoxynaphthalene,[22] 1-ethynyl-2-methylnaphthalene,[23] bis-[3,5-bis(trifluoromethyl)phenyl]-chlorophosphine,[24] bis(4-methoxyphenyl)chlorophosphine,[24] bis(1-adamantyl)phosphinic chloride,[25] and [CpCo(cod)][26] were synthesized by known procedures.

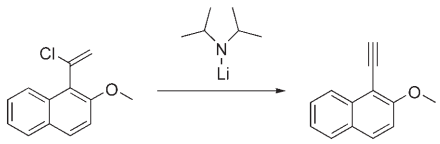
I) Preparation of different naphthalenes

1-(1-Chlorovinyl)-2-methoxynaphthalene: PCl_5 (8.8 g, 41.7 mmol) was added at RT to a solution of 1-acetyl-2-methoxynaphthalene (7.7 g,



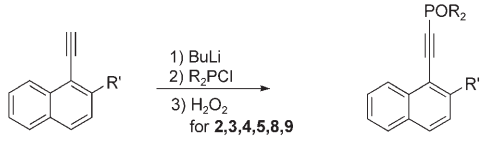
38.45 mmol) and PCl_3 (18.5 mL, 0.21 mol) in dry benzene (60 mL). The reaction mixture was magnetically stirred for 24 h at RT and was then carefully poured onto ice (300 g). The organic fraction was extracted with ether (100 mL), washed with saturated $NaHCO_3$ solution, separated, and dried over Na_2SO_4, the solution was filtered through a pad of silica gel, and the solvent was removed in vacuo to give the crude product (8.24 g, 98%) as a pale yellow oil. The compound was pure enough to be used for the next step, but could be recrystallized from hexane to afford a colorless solid. M.p. 47–48 °C; ^{1}H NMR ($CDCl_3$): δ = 8.35 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 9.1 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.84 (m, 1H), 7.7 (m, 1H), 7.58 (d, J = 9.1 Hz, 1H), 6.05 (dd, J = 0.99 and 197.4 Hz, 2H), 4.3 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): 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 ppm; HRMS: m/z: calcd for $C_{13}H_{11}OCl$: 218.0493; found: 218.0489 (δ = −1.7).

1-Ethynyl-2-methoxynaphthalene: n-BuLi (1.6 M solution in hexanes, 23 mL, 36.7 mmol) was added dropwise with stirring at −78 °C to a solu-



tion of diisopropylamine (4.45 g, 6.2 mL, 44 mmol) in THF (10 mL). The temperature was raised to 0 °C for 20 min, and the mixture was then again cooled to −78 °C. A solution of 1-(1-chlorovinyl)-2-methoxynaphthalene (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 RT. The reaction vessel was placed in an ice bath, and water (2 mL) was carefully added to the thick slurry. After deposition of the resulting solids, the organic layer was decanted, dried with Na_2SO_4, and filtered through a pad of silica gel, being eluted with Et_2O. The mother liquor was evaporated to dryness, and the solid residue was recrystallized from ethyl acetate/hexane to give the acetylene (2.5 g, 97%) as white plates. M.p. 111–112 °C; ^{1}H NMR ($CDCl_3$): δ = 8.49 (dd, J = 0.6, 8.5 Hz, 1H), 8.01–7.95 (m, 2H), 7.75 (m, 1H), 7.57 (m, 1H), 7.40 (d, J = 9.1 Hz, 1H), 4.2 (s, 3H), 3.97 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): 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 ppm; HRMS: m/z: calcd for $C_{13}H_{10}O$: 182.0726; found: 182.0720 (δ = −2.9).

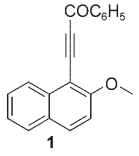
II) General procedure for preparation of acetylenes 1–9



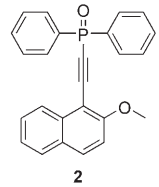
1-9

n-BuLi (1.6 M solution in hexanes, 6.5 mL, 10.4 mmol) was added dropwise with stirring at −78 °C to a solution of 1-ethynylnaphthalene (10 mmol) in THF (30 mL). The temperature was raised to 0 °C for 20 min, and the system was then again cooled to −78 °C, whereupon the appropriate electrophile (10 mmol) was added dropwise. The temperature was raised to 25 °C for 30 min, and the reaction mixture was additionally stirred for 2 h. To obtain the derivatives **2**–**5**, **8**, and **9** the Schlenk flask was then placed in an ice bath, and hydrogen peroxide (30% in water, 1.5 mL) was added carefully with vigorous stirring. The mixture was then stirred for a further 30 min at RT and finally dried with Na_2SO_4. The general workup procedure was as follows: the resulting solution was filtered through a short pad of silica gel, the solvent was evaporated in vacuo, and the residue was purified by chromatography.

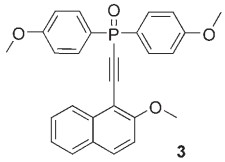
3-(2-Methoxynaphthalen-1-yl)-1-phenylprop-2-yn-1-one (1): Electrophile: C_6H_5COCl; 64% yield; m.p. 137–138 °C (ethyl acetate); ^{1}H NMR ($CDCl_3$): δ = 8.46 (m, 2H), 8.40 (d, J = 8.5 Hz, 1H), 8.01–7.32 (m, 8H), 4.16 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 187.5, 162.5, 137.8, 135.4, 134.2, 133.8, 130.2, 128.9, 128.8, 128.8, 128.7, 125.4, 125.1, 112.5, 103.5, 97.3, 89.6, 57.0 ppm; HRMS: m/z: calcd for $C_{20}H_{14}O_2$: 286.0988; found: 286.0982 (δ = −2.2).



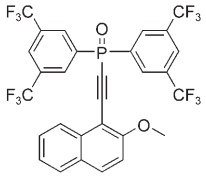
1-(Diphenylphosphinoylethynyl)-2-methoxynaphthalene (2): Electrophile: $(C_6H_5)_2PCl$; 89% yield; m.p. 116–117 °C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$): δ = 8.07 (dd, J = 0.6 and 8.5 Hz, 1H), 7.98–7.93 (m, 4H), 7.84 (d, J = 9.1 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.49–7.40 (m, 7H), 7.32–7.28 (m, 1H), 7.17 (d, J = 9.5 Hz, 1H), 3.96 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): 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 = 3.8 Hz), 103.4 (d, J = 30.5 Hz), 92.2 (d, J = 172.6 Hz), 56.9 ppm; ^{31}P NMR ($CDCl_3$): δ = 8.9 ppm; HRMS: m/z: calcd for $C_{25}H_{18}O_2P$: 381.1039; found: 381.1034 (δ = −1.2).



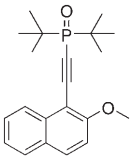
1-[Bis-(4-methoxyphenyl)phosphinoylethynyl]-2-methoxynaphthalene (3): Electrophile: $(p\text{-}CH_3OC_6H_5)_2PCl$; 87% yield; m.p. 124–125 °C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$): δ = 8.37 (d, J = 8.3 Hz, 1H), 8.2–8.11 (m, 5H), 7.99 (d, J = 8.1 Hz, 1H), 7.76–7.72 (m, 1H), 7.46 (d, J = 9.3 Hz, 1H), 7.24–7.20 (m, 4H), 4.25 (s, 3H), 4.07 ppm (s, 6H); ^{13}C NMR ($CDCl_3$): 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 ppm; ^{31}P NMR ($CDCl_3$): δ = 8.6 ppm; HRMS: m/z: calcd for $C_{27}H_{23}O_4P$: 442.1328; found: 442.1316 (δ = −2.9).



1-{Bis-[3,5-bis-(trifluoromethyl)phenyl]phosphinoylethynyl}-2-methoxynaphthalene (4): Electrophile: $[3,5\text{-}(CF_3)_2C_6H_5]_2PCl$; 90% yield; m.p. 162–163 °C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$): δ = 8.72 (d, J = 13.7 Hz, 4H), 8.28–8.25 (m, 3H), 8.2 (d, J = 9.1 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.77–7.73 (m, 1H), 7.63–7.59 (m, 1H), 7.5 (d, J = 9.1 Hz, 1H), 3.29 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$): 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 ppm; ^{31}P NMR ($CDCl_3$): δ = 2.2 ppm; HRMS: m/z: calcd for $C_{29}H_{15}O_2F_{12}P$: 654.0613; found: 654.0604 (δ = −1.3).



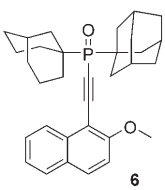
1-(Di-*tert*-butylphosphinoylethynyl)-2-methoxynaphthalene (5): Electrophile: $(t\text{Bu})_2PCl$; 86% yield; m.p. 137–138 °C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$): δ = 8.47 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 9.1 Hz, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.82 (m, 1H), 7.65 (m, 1H), 7.48 (d, J =



5

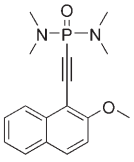
9.1 Hz, 1H), 4.25 (s, 3H), 1.73 ppm (d, J = 15.1 Hz, 18H); ^{13}C NMR ($CDCl_3$): δ = 161.7, 134.8, 132.5, 128.6, 128.5, 128.4, 125.2, 124.8, 112.7, 104.2 (d, J = 3.8 Hz), 98.6 (d, J = 20 Hz), 91.4 (d, J = 130.6 Hz), 56.8, 36.6 (d, J = 72.5 Hz), 26.9 ppm; ^{31}P NMR ($CDCl_3$): δ = 49.2 ppm; HRMS: m/z: calcd for $C_{21}H_{27}O_2P$: 342.1743; found: 342.1733 (δ = −3.0).

1-(Di-1-adamantylphosphinoylethynyl)-2-methoxynaphthalene (6): Electrophile: $(Ad)_2POCl$; 21% yield; m.p. 234–235°C (ethyl acetate); ^{1}H NMR ($CDCl_3$): δ = 8.47 (dd, J = 0.6 Hz and 8.5 Hz, 1H), 8.9 (d, J = 9.1 Hz, 1H), 8.0 (d, J = 8.1 Hz, 1H), 7.77 (m, 1H), 7.6 (m, 1H), 7.45 (d, J = 9.1 Hz, 1H), 4.21 (s, 3H), 2.89 (m, 12H), 2.28 (m, 6H), 2.01 ppm (m, 12H); ^{13}C NMR ($CDCl_3$): δ = 161.7, 135.0, 132.3, 128.6, 128.4, 125.4, 124.8, 112.7, 104.5 (d, J = 2.9 Hz), 98.6 (d, J = 18.1 Hz), 91.6, 90.3, 56.8, 40.9, 40.1, 37.1, 37.1, 28.3, 28.2 ppm; ^{31}P NMR ($CDCl_3$): δ = 41.5 ppm; HRMS: m/z: calcd for $C_{33}H_{39}O_2P$: 498.2682; found: 498.2676 (δ = −1.2).



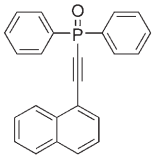
6

1-(Bis-dimethylaminophosphinoylethynyl)-2-methoxynaphthalene (7): Electrophile: $[(CH_3)_2N)_2PCl$; 82% yield; m.p. 105–106°C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$): δ = 8.46 (dd, J = 0.8 Hz, 8.3 Hz, 1H), 8.13 (d, J = 9.1 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.82–7.78 (m, 1H), 7.66–7.62 (m, 1H), 7.48 (d, J = 9.1 Hz, 1H), 4.25 (s, 3H), 3.05 ppm (d, J = 11.3 Hz, 12H); ^{13}C NMR ($CDCl_3$): 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 = 4.8 Hz), 96.0 (d, J = 41.0 Hz), 90.9, 88.5 ppm; ^{31}P NMR ($CDCl_3$): δ = 11.5 ppm; HRMS: m/z: calcd for $C_{17}H_{21}O_2N_2P$: 316.1335; found: 316.1333 (δ = −0.8).



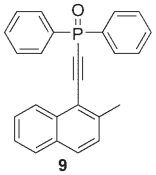
7

1-(Diphenylphosphinoylethynyl)-naphthalene (8): Electrophile: $(C_6H_5)_2PCl$; 87% yield; m.p. 99–100°C (diethyl ether); ^{1}H NMR ($CDCl_3$): δ = 8.52–8.50 (m, 1H), 8.28–8.19 (m, 5H), 8.14–8.11 (m, 2H), 7.85–7.7 ppm (m, 9H); ^{13}C NMR ($CDCl_3$): 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 = 4.8 Hz), 104.4 (d, J = 29.6 Hz), 88.9, 87.2 ppm; ^{31}P NMR ($CDCl_3$): δ = 8.8 ppm; HRMS: m/z: calcd for $C_{24}H_{16}OP$: 351.0933; found: 351.0925 (δ = −2.4).



8

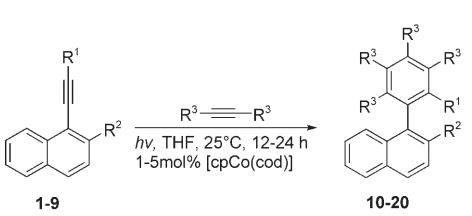
1-(Diphenylphosphinoylethynyl)-2-methylnaphthalene (9): Electrophile: $(C_6H_5)_2PCl$; 94% yield; m.p. 92–93°C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$): δ = 8.46 (d, J = 8.3 Hz, 1H), 8.27–8.22 (m, 4H), 8.08–8.05 (m, 2H), 7.84–7.69 (m, 8H), 7.60 (d, J = 8.3 Hz, 1H), 2.91 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): δ = 142.8, 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 = 3.8 Hz), 103.6 (d, J = 30.5 Hz), 93.2, 91.5, 21.9 ppm; ^{31}P NMR ($CDCl_3$): δ = 8.7 ppm; HRMS: m/z: calcd for $C_{25}H_{18}OP$: 365.1090; found: 365.1094 (δ = 1.3).



9

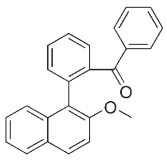
III) [2+2+2] Cross-cyclotrimerization

General procedure for the preparation of racemic biphenyls 10–20: A thermostated (e.g., 25°C) reaction vessel was loaded with a substituted acetylene—such as 1-(diphenylphosphinoylethynyl)-2-methoxynaphthalene (0.383 g, 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 but-2-yne or hex-3-yne were used as a second component, the compounds (3 mmol) were injected under argon. The mixture was stirred and irradiated with two 460 W Phillips HPM 12 lamps ($\lambda \approx 420$ nm). The reaction was quenched by switching off the lamps and simultaneously opening the vessel to the air. The progress of reaction—that is, conversion of the initial substituted acetylene—was determined by GC. The solvent was evaporated, and the residue was purified on silica gel.



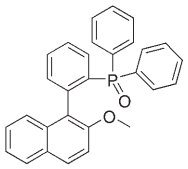
1-9 10-20

[2-(2-Methoxynaphthalen-1-yl)phenyl]phenylmethanone (10): M.p. 154–155°C (ethyl acetate/hexane); R_f = 0.4 (Et_2O/hexane 1:1); ^{1}H NMR ($CDCl_3$): δ = 8.0–7.41 (m, 14H), 7.34 (d, J = 8.9 Hz, 1H), 3.89 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): 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 ppm; HRMS: m/z: calcd for $C_{24}H_{18}O_2$: 338.1301; found: 338.1296 (δ = −1.6).



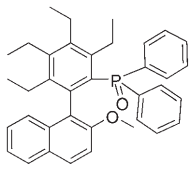
10

1-[2-(Diphenylphosphinoyl)phenyl]-2-methoxynaphthalene (11): M.p. 149–150°C; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.86–7.80 (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, J = 9.1 Hz, 1H), 3.54 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 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 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25°C): δ: 27.9 ppm; HRMS: m/z: calcd for $C_{29}H_{23}O_2P$: 434.1430; found: 434.1422 (δ = −1.9).



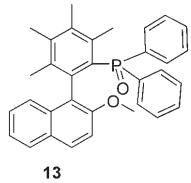
11

1-[2-(Diphenylphosphinoyl)-3,4,5,6-tetraethylphenyl]-2-methoxynaphthalene (12): M.p. 157–158°C (ethyl acetate/hexane); R_f = 0.59 (ethyl acetate); ^{1}H NMR ($CDCl_3$): δ = 7.72 (d, J = 8.1 Hz, 1H), 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, J = 9.1 Hz, 1H), 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, J = 7.3 Hz, 3H), 0.83 ppm (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$): 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 = 5.7 Hz), 23.7, 23.2, 22.1, 16.4, 16.3, 16.2, 14.9 ppm; ^{31}P NMR ($CDCl_3$): δ = 31.2 ppm; HRMS: m/z: calcd for $C_{37}H_{39}O_2P$: 546.2682; found: 546.2678 (δ = −0.8).



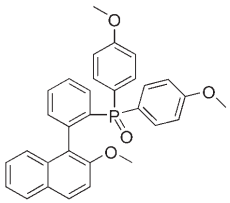
12

1-[2-(Diphenylphosphinoyl)-3,4,5,6-tetramethylphenyl]-2-methoxynaphthalene (13): M.p. 233–234°C (ethyl acetate/hexane); R_f = 0.36 (ethyl acetate); ^{1}H NMR ($CDCl_3$): δ = 7.81–7.72 (m, 3H), 7.64–7.45 (m, 7H), 7.25–7.18 (m, 3H), 7.07–7.00 (m, 3H), 4.03 (s, 3H), 2.72 (s, 3H), 2.63 (s, 3H), 2.6 (s, 3H), 1.87 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): 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 = 6.7 Hz), 18.1, 17.4, 17.2 ppm; ^{31}P NMR ($CDCl_3$): δ = 31.4 ppm; HRMS: m/z: calcd for $C_{33}H_{31}O_2P$: 490.2056; found: 490.2048 (δ = −1.6).



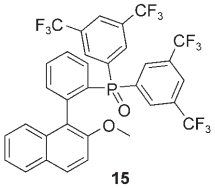
13

1-{2-[Bis-(4-methoxyphenyl)phosphinoyl]phenyl}-2-methoxynaphthalene (14): M.p. 162–163°C (ethyl acetate/hexane); R_f = 0.41 (THF/ethyl ace-

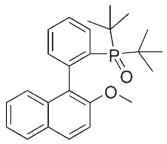

14

tate 1:1); ^{1}H NMR ($CDCl_3$): 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 ppm (m, 2H); ^{13}C NMR ($CDCl_3$): δ = 162.0 (d, J = 2.9 Hz), 161.5 (d, J = 2.9 Hz), 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 ppm; ^{31}P NMR ($CDCl_3$): δ = 28.3 ppm; 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).

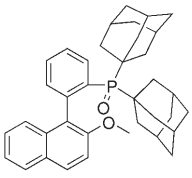
1-(2-{Bis-[3,5-bis-(trifluoromethyl)phenyl]phosphinoyl}phenyl)-2-methoxynaphthalene (15): M.p. 154–155 °C (ethyl acetate/hexane); R_f = 0.79 (hexane/ethyl acetate 4:1); ^{1}H NMR ($CDCl_3$): δ = 7.84–7.78 (m, 3H), 7.72–7.65 (m, 4H), 7.59–7.52 (m, 2H), 7.5 (d, J = 8.9 Hz, 1H), 7.43–7.40 (m, 1H), 7.28–7.25 (m, 1H), 7.19–7.11 (m, 2H), 6.96 (d, J = 9.1 Hz, 1H), 6.92–6.90 (m, 1H), 3.73 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): 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 ppm; ^{31}P NMR ($CDCl_3$): δ = 23.1 ppm; HRMS: m/z: calcd for $C_{33}H_{19}O_2F_{12}P$: 706.0926; found: 706.0941 (δ = 2.1).


15

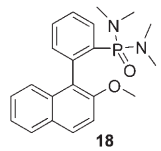
1-[2-(Di-*tert*-butylphosphinoyl)phenyl]-2-methoxynaphthalene (16): M.p. 215–216 °C (ethyl acetate/hexane); R_f = 0.51 (THF); ^{1}H NMR ($CDCl_3$): δ = 7.76 (d, J = 9.1 Hz, 1H), 7.69–7.64 (m, 2H), 7.52–7.47 (m, 1H), 7.39–7.34 (m, 1H), 7.26–7.03 (m, 5H), 3.72 (s, 3H), 1.22 (d, J = 13.1 Hz, 1H), 0.99 ppm (d, J = 13.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): 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 = 6.7 Hz), 37.7 (d, J = 5.7 Hz), 28.7 ppm (d, J = 40 Hz); ^{31}P NMR ($CDCl_3$): δ = 52.9 ppm; HRMS: m/z: calcd for $C_{25}H_{31}O_2P$: 394.2056; found: 394.2053 (δ = −0.9).


16

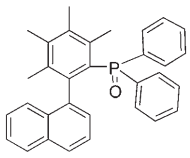
1-[2-(Di-1-adamantylphosphinoyl)phenyl]-2-methoxynaphthalene (17): M.p. >300 °C (ethyl acetate/hexane); R_f = 0.69 (ethyl acetate); ^{1}H NMR ($CDCl_3$): δ = 8.06 (d, J = 9.1 Hz, 1H), 7.99–7.92 (m, 2H), 7.84–7.80 (m, 1H), 7.72–7.67 (m, 1H), 7.56–7.45 (m, 2H), 7.41–7.33 ppm (m, 3H); ^{13}C NMR ($CDCl_3$): δ = 153.9, 144.7 (d, J = 3.8 Hz), 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 ppm; ^{31}P NMR ($CDCl_3$): δ = 44.6 ppm; HRMS: m/z: calcd for $C_{37}H_{43}O_2P$: 550.2995; found: 550.2985 (δ = −1.8).


17

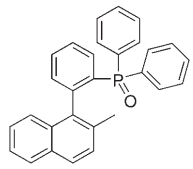
1-[2-(Bis-dimethylaminophosphinoyl)phenyl]-2-methoxynaphthalene (18): R_f = 0.43 (THF); ^{1}H NMR ($CDCl_3$): δ = 8.35–8.30 (m, 1H), 8.11 (d, J = 8.9 Hz, 1H), 8.06–8.04 (m, 1H), 7.83–7.72 (m, 2H), 7.6 (d, J = 9.1 Hz, 1H), 7.55–7.45 (m, 3H), 7.37–7.35 (m, 1H), 4.09 (s, 3H), 2.49 (d, J = 9.5 Hz, 6H), 2.33 ppm (d, J = 9.7 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ = 154.3, 141.1 (d, J = 8.6 Hz), 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 ppm (q, J = 3.81 Hz); ^{31}P NMR ($CDCl_3$): δ = 29.6 ppm; MS (70 eV): m/z: calcd for $C_{21}H_{25}N_2O_2P$: 368.41; found: 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).


18

1-[2-(Diphenylphosphinoyl)-3,4,5,6-tetramethylphenyl]naphthalene (19): M.p. 194–195 °C (ethyl acetate/hexane); R_f = 0.45 (ethyl acetate); ^{1}H NMR ($CDCl_3$): 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 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): 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 = 6.7 Hz), 18.2 (d, J = 1.9 Hz), 17.8, 17.0 ppm; ^{31}P NMR ($CDCl_3$): δ = 30.6 ppm; HRMS: m/z: calcd for $C_{32}H_{28}OP$: 459.1872; found: 459.1861 (δ = −2.5).

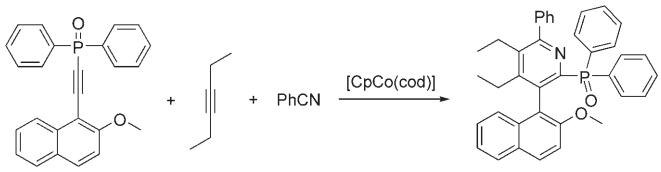

19

1-[2-(Diphenylphosphinoyl)phenyl]-2-methylnaphthalene (20): M.p. 163–164 °C (ethyl acetate/hexane); R_f = 0.56 (ethyl acetate); ^{1}H NMR ($CDCl_3$): 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 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): 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 ppm; ^{31}P NMR ($CDCl_3$): δ = 26.1 ppm; HRMS: m/z: calcd for $C_{29}H_{23}OP$: 418.1481; found: 418.1472 (δ = −2.2).


20

IV) Three-compound [2+2+2] cycloaddition

4,5-Diethyl-3-(2-methoxy-1-naphthyl)-6-phenyl-2-pyridyl-(diphenyl)phosphane oxide (21): A thermostated (25 °C) reaction vessel was loaded under argon with 1-(diphenylphosphinoylethynyl)-2-methoxy-



naphthalene (382 mg, 1 mmol) and [cpCo(cod)] (11.6 mg, 0.05 mmol). THF (10 mL) was added, followed by hex-3-yne (115 μL, 1 mmol) and benzonitrile (103 μL, 1 mmol), and the mixture was stirred and irradiated with two 460 W lamps ($\lambda \approx 420$ nm) for 24 h. The reaction was quenched by switching off the lamps and simultaneously opening the vessel to the air, the sample was analyzed by GC, the solvent was evaporated, and the residue was purified on silica gel (THF/hexane 1:1) to give compound **21** (217 mg, 38 %).

Compound 21: M.p. 208–209 °C (ethyl acetate/hexane); ^{1}H NMR ($CDCl_3$): δ = 8.1 (d, J = 8.9 Hz, 1H), 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, J = 8.3 Hz, 1H), 3.11–3.01 (m, 2H), 2.74–2.65 (m, 1H), 2.57–2.49 (m, 1H), 1.31 (t, J = 7.5 Hz, 3H), 1.07 ppm (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$): 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 ppm; ^{31}P NMR ($CDCl_3$): δ = 20.7 ppm; HRMS: m/z: calcd for $C_{38}H_{34}O_2NP$: 567.2322; found: 567.2330 (δ = 1.4).

V) Asymmetric cross-trimerization to give biphenyls 11–18

Chiral Co^{I} complexes **I**, **II**, **III**, or **IV** (see Scheme 1) were used to carry out the reaction. Products were purified chromatographically, and enantiomeric excesses were analyzed by HPLC. Nonracemic samples of biphenyls **11**, **14**, **16**, and **17** were enriched to optical purities of >99% *ee* by one or two recrystallizations.

When the (−)-(S_p)-catalyst **I** was employed, *S* enantiomers of biaryls **11**, **14**, **16**, and **17** were found in all cases. We demonstrated that products enriched in the opposite enantiomer were obtained with the use of (+)-(R_p)-complex **II**—from 1-(diphenylphosphinoylethynyl)-2-methoxy-naphthalene (**2**) and acetylene—as the catalyst. As expected, we obtained (+)-(*R*)-1-[2-(diphenylphosphinoyl)-phenyl]-2-methoxynaphthalene after 24 h at 25 °C in THF with an enantiomeric excess of 63% *ee* and in 45% yield (see Table 1).

Dynamic HPLC on a chiral stationary phase has shown that the biarylic derivatives **11**–**18** each exist in the form of two stable atropisomers, and no atropisomerization was observed at temperatures up to +60 °C.

General procedure

(−)-(*S*)-1-[2-(Diphenylphosphinoyl)phenyl]-2-methoxynaphthalene [(*S*)-11]: A thermostated (45 °C) reaction vessel was loaded with 1-(diphenylphosphinoylethynyl)-2-methoxynaphthalene (1.15 g, 3 mmol), catalyst **I** (63 mg, 0.15 mmol), and THF (30 mL) under acetylene. The mixture was stirred and irradiated with two 460 W lamps ($\lambda \approx 420$ nm) for 48 h. The reaction was quenched by switching off the lamps and simultaneously opening the vessel to the air, the degree of conversion of the starting acetylene was determined by GC, the solvent was evaporated, and the oily residue was purified on silica gel (ethyl acetate) to give (−)-(*S*)-1-[2-(diphenyl-phosphinoyl)-phenyl]-2-methoxynaphthalene (**2**, 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 form (391 mg, 30%, >99% *ee*). HPLC: Chiralpack AD-H, hexane/ethanol 98:2, 2 mL min^{-1}, t_1 = 28.81 min, t_2 = 38.68 min; $[\alpha]_D^{25} = -80.7$ (c = 0.56, $CHCl_3$).

1-{2-[Bis-(4-methoxyphenyl)phosphinoyl]phenyl}-2-methoxynaphthalene (14): $[\alpha]_D^{25} = -123.4$ (c = 0.36, $CHCl_3$), >99% *ee*; HPLC: Whelk 01 (*S*,*S*), hexane/ethanol 95:5, 2 mL min^{-1}, t_1 = 32.76 min, t_2 = 42.55 min.

1-(2-{Bis-[3,5-bis-(trifluoromethyl)phenyl]phosphinoyl}phenyl)-2-methoxy-naphthalene (15): HPLC: Chiralpack OD, hexane/ethanol 99.5:0.5, 1 mL min^{-1}, t_1 = 6.16 min, t_2 = 6.89 min.

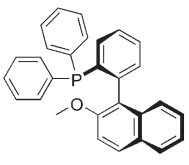
1-[2-(Di-*tert*-butylphosphinoyl)phenyl]-2-methoxynaphthalene (16): $[\alpha]_D^{25}$ = +64.1 (c = 1, $CHCl_3$), >99% *ee*, HPLC: Chiralcel AD, hexane/isopropanol 98:2, 1 mL min^{-1}, t_1 = 5.12 min, t_2 = 6.16 min.

1-[2-(Di-1-adamantylphosphinoyl)phenyl]-2-methoxynaphthalene (17): $[\alpha]_D^{25}$ = +19.3 (c = 1, $CHCl_3$), >99% *ee*, HPLC: Chiralpack AD, hexane/ethanol 98:2, 0.8 mL min^{-1}, T_1 = 6.22 min, T_2 = 8.06 min.

1-[2-(Bis-dimethylaminophosphinoyl)phenyl]-2-methoxynaphthalene (18): HPLC: Chiralpack AD, hexane/ethanol 98:2, 1 mL min^{-1}, t_1 = 10.17 min, t_2 = 13.38 min.

VI) Reduction of the phosphine oxides to the corresponding phosphines

(−)-(*S*)-[2-(2-Methoxynaphthalen-1-yl)phenyl]diphenylphosphine (NAPHEP, 22): Phosphine oxide **11** (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 min and cooled, and dry methanol (0.1 mL) was added. The mixture was filtered through a pad of silica gel, which was washed with THF (3×5 mL), and the organic extract was evaporated and purified by flash chromatography, with hexane/ethyl acetate (9:1) as eluent, to yield (−)-(*S*)-[2-(2-methoxynaphthalen-1-yl)-phenyl]-diphenylphosphine (NAPHEP, **22**, 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, 1 mL min^{-1}, 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, $CDCl_3$, 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 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 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 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = −13.5 ppm; HRMS: m/z: calcd for $C_{29}H_{23}OP$: 418.1481; found: 418.1473 (δ = −1.8).



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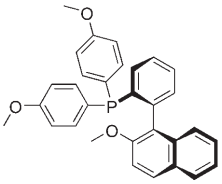
(−)-(*S*)-[2-(Methoxynaphthalen-1-yl)phenyl]bis(4-methoxyphenyl)phosphine (23): Phosphine oxide **14** (93 mg, 0.2 mmol, >99% *ee*) was dissolved in THF (3 mL), and AlH_3 (0.43 mL of an 0.5 M solution in THF, 0.21 mmol) was added dropwise. The mixture was stirred at 50 °C for 30 min and cooled, and dry methanol (0.1 mL) was added. The mixture was filtered through a pad of silica gel, which was washed through with THF (3×5 mL), and the organic extract was evaporated and purified by flash chromatography with hexane/ethyl acetate (2:1) as eluent to yield phosphine **23** (MeO-NAPHEP, 89 mg, 96%) 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, $CDCl_3$, 25 °C): δ = 8.04–8.02 (m, 1H), 7.95–7.94 (m, 1H), 7.64–7.60 (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 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 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 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C): δ = −16.4 ppm; MS (70 eV): m/z : 478 (2) $[M]^+$, 447 (100), 185 (9).



23

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

VII) 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*)-(−)-NAPHEP (0.2–0.02 mol%) was stirred at 0–40 °C for 24 h, and the reaction mixture was distilled bulb-to-bulb under reduced pressure to give trichlorosilylalkanes. These were converted quantitatively into the 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 liquid sample was taken after 20 min to analyze the degree of conversion and the regioselectivity of the reaction (GC/MS). The mixture was then treated with H_2O_2 (30%) and stirred for 12 h at RT. 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 their preferential complexation with $CaCl_2$ (hexan-2-ol, octan-2-ol) to remove primary alcohols. The enantiomeric excess was analyzed by chiral HPLC or GC (in the forms 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 h. A single crystal suitable for X-ray investigation was grown by slow diffusion of diethyl ether into the acetonitrile solution.

VIII) Crystallographic experimental section:[14]

See Figures 5–7

Crystal structure determinations: Crystals of compounds **11**, **14**, **16**, **21**, and *trans*-[$PdCl_2${(*S*)-naphep}$_2$] for X-ray analyses were obtained either by slow diffusion of pentane into a concentrated THF solution or by slow evaporation of a concentrated ethyl acetate solution of phosphine oxides. Crystal data and details of the structure solution are summarized in Table 4.

Data for all compounds were collected on a STOE-IPDS diffractometer with use of graphite monochromated $Mo_{K\alpha}$ radiation. The structures were solved by direct methods (SHELXS-97)[27] and refined by full-

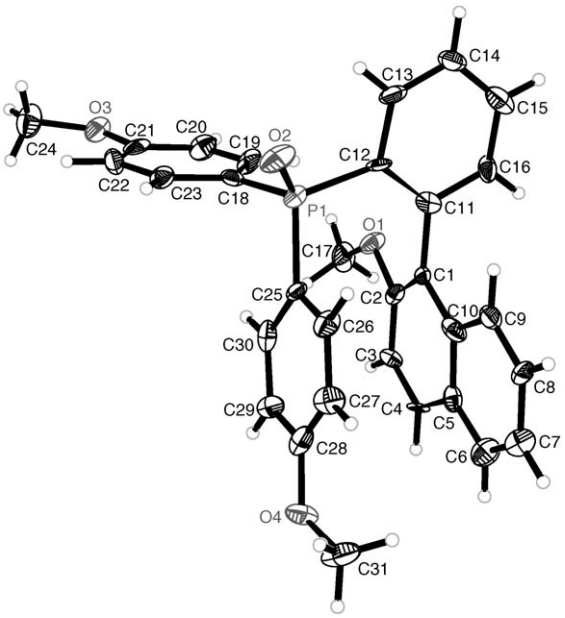


Figure 5. Crystal structure and numbering scheme of 1-{2-[bis-(4-methoxyphenyl)phosphinoyl]-phenyl}-2-methoxynaphthalene (**14**; ellipsoids set at 50% probability level).

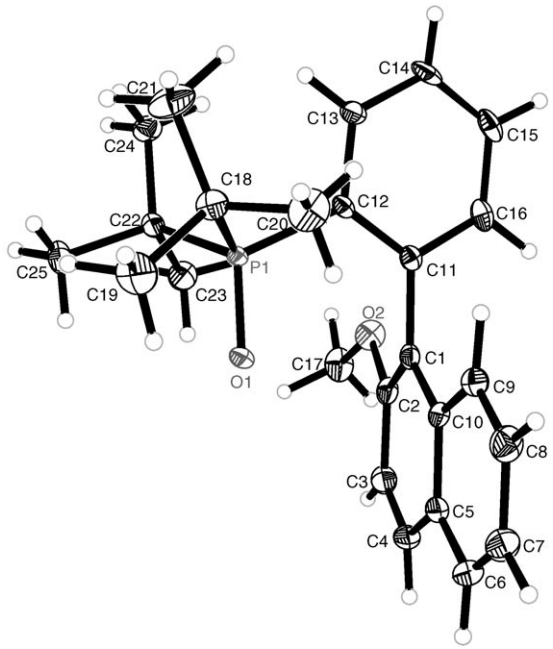


Figure 6. Crystal structure and numbering scheme of 1-[2-(di-*tert*-butylphosphinoyl)phenyl]-2-methoxynaphthalene (**16**; ellipsoids set at 30% probability level).

matrix, least-squares techniques against F^2 (SHELXL-97).[28] XP (Bruker-AXS) was used for structure representations.

Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed into theoretical positions and were refined with the aid of the riding model. The weighting schemes are:
$\omega = 1/[\sigma^2(F_o^2)+(0.0808P)^2+0.0000P]$ for **11**,
$\omega = 1/[\sigma^2(F_o^2)+(0.0000P)^2+0.0000P]$ for **14**,
$\omega = 1/[\sigma^2(F_o^2)+(0.0745P)^2+0.0000P]$ for **16**, and
$\omega = 1/[\sigma^2(F_o^2)+(0.0061P)^2+0.0000P]$ for **21**, with $P = (F_o^2+2F_c^2)/3$ for $[PdCl_2\{(S)\text{-naphep}\}_2]$.

CCDC-275232 (**11**), -275233 (**14**), -275234 (**16**), -275235 (**21**), and -287928 $[PdCl_2\{(S)\text{-naphep}\}_2]$ contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

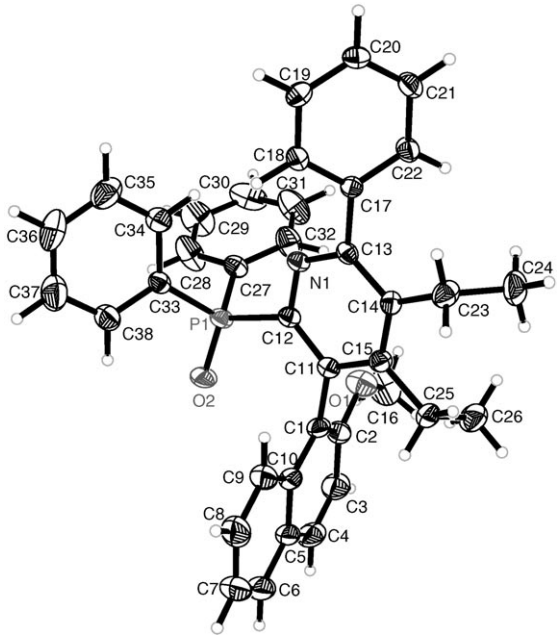


Figure 7. Crystal structure and numbering scheme of 4,5-diethyl-3-(2-methoxy-1-naphthyl)-6-phenyl-2-pyridyl(diphenyl)phosphane oxide (**21**; ellipsoids set at 50% probability level).

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Table 4. Crystallographic and refinement data for **11**, **14**, **16**, **21**, and *trans*-[$PdCl_2$\{(*S*)-NAPHEP\}$_2$].

	11	**14**	**16**	**21**	Pd complex
empirical formula	$C_{29}H_{23}O_2P$	$C_{31}H_{27}O_4P$	$C_{25}H_{31}O_2P$	$C_{38}H_{34}NO_2P$	$C_{58}H_{46}Cl_2O_2P_2Pd$
F_w	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
ρ_{calcd} [Mg m^{-3}]	1.292	1.327	1.210	1.247	1.387
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.147	0.148	0.144	0.126	0.601
F(000)	456	520	212	1200	1040
crystal size	0.5×0.4×0.4	0.2×0.1×0.1	0.4×0.2×0.2	0.4×0.3×0.2	0.5×0.3×0.3
T [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
refln colld	5964	5491	3235	10848	14545
indep reflns	3327	3173	3235	5927	8557
obsd reflns	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
GoF	0.645	0.669	0.763	0.679	0.874
largest difference peak and hole [e Å^{-3}]	0.122/−0.134	0.265/−0.250	0.220/−0.172	0.134/−0.190	0.382/−0.346

[1] G. Bringmann, A. J. P. Mortimer, P. A. Keller, M. J. Gresser, J. Garner, M. Breuning, *Angew. Chem.* **2005**, *117*, 5518–5563; *Angew. Chem. Int. Ed.* **2005**, *44*, 5384–5427.

[2] a) G. Bringmann, R. Walter, R. Weirich, *Angew. Chem.* **1990**, *102*, 106–119; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 977–991; b) T. Hayashi, in *Comprehensive Asymmetric Catalysis, Vol. II* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, pp. 887–907; c) M. Ogasawara, T. Hayashi, in *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), Wiley-VCH, New York, **2000**, 2nd ed., pp. 651–674; d) T. Hayashi, *J. Organomet. Chem.* **2002**, *653*, 41–45; e) P. Kočovský, Š. Vyskočil, M. Smrčina, *Chem. Rev.* **2003**, *103*, 3213–3245.

[3] a) T. Hayashi, K. Hayashizaki, T. Kiyoi, Y. Ito, *J. Am. Chem. Soc.* **1988**, *110*, 8153–8156; b) T. Hayashi, K. Hayashizaki, T. Kiyoi, Y. Ito, *Tetrahedron Lett.* **1989**, *30*, 215–218.

[4] M. Shindo, K. Koga, K. Tomioka, *J. Am. Chem. Soc.* 1992, **114**, 8732–8733.

[5] a) K. C. Nicolaou, H. Li, C. N. C. Boddy, J. M. Ramanjulu, T.-Y. Yue, S. Natarajan, X.-J. Chu, S. Bräse, F. Rübsam, *Chem. Eur. J.* **1999**, *5*, 2584–2601; b) J. Yin, S. L. Buchwald, *J. Am. Chem. Soc.* **2000**, *122*, 12051–12052; c) A.-S. Castanet, F. Colobert, P.-E. Broutin, M. Obringer, *Tetrahedron: Asymmetry* **2002**, *13*, 659–665; d) J. F. Jensen, M. Johannsen, *Org. Lett.* **2003**, *5*, 3025–3028; e) A. Herrbach, A. Marinetti, O. Baudoin, D. Guénard, F. Guéritte, *J. Org. Chem.* **2003**, *68*, 4897–4905; f) A. N. Cammidge, K. V. L. Crépy, *Tetrahedron* **2004**, *60*, 4377–4386; g) K. Mikami, T. Miyamoto, M. Hatano, *Chem. Commun.* **2004**, 2082–2083.

[6] a) T. Kamikawa, Y. Uozumi, T. Hayashi, *Tetrahedron Lett.* **1996**, *37*, 3161–3164; b) T. Kamikawa, T. Hayashi, *Tetrahedron* **1999**, *55*, 3455–3466.

[7] Y.-H. Cho, A. Kina, T. Shimada, T. Hayashi, *J. Org. Chem.* **2004**, *69*, 3811–3823.

[8] a) M. Smrčina, J. Poláková, Š. Vyskočil, P. Kočovský, *J. Org. Chem.* **1993**, *58*, 4534–4538; b) T. Osa, Y. Kashiwagi, Y. Yanagisawa, M. Bobbitt, *J. Chem. Soc. Chem. Commun.* **1994**, 2535–2537; c) M. Nakajima, I. Miyoshi, K. Kanayama, S. Hashimoto, M. Noji, K. Koga, *J. Org. Chem.* **1999**, *64*, 2264–2271; d) R. Irie, K. Masutani, T. Katsuki, *Synlett* **2000**, *10*, 1433–1436; e) S. Hon, C. Li, J. Kuo, N. B. Barhate, Y. Liu, Y. Wang, C. Chen, *Org. Lett.* **2001**, *3*, 869–872; f) C.-Y. Chu, D.-R. Hwang, S.-K. Wang, B.-J. Uang, *Chem. Commun.* **2001**, 980–981; g) Z. B. Luo, Q. Z. Liu, L. Z. Gong, X. Cui, A. Q. Mi, Y. Z. Jiang, *Angew. Chem.* **2002**, *114*, 4714–4717; *Angew. Chem. Int. Ed.* **2002**, *41*, 4532–4535; h) Y. Chen, S. Yekta, A. Yudin, *Chem. Rev.* **2003**, *103*, 3155–3211; i) X. Li, J. B. Hewgley, C. A. Mulrooney, J. Yang, M. C. Kozlowski, *Org. Chem.* **2003**, *68*, 5500–5511.

[9] Y. Sato, K. Ohashi, M. Mori, *Tetrahedron Lett.* **1999**, *40*, 5231–5234.

[10] a) T. Shibata, T. Fujimoto, K. Yokota, K. Takagi, *J. Am. Chem. Soc.* **2004**, *126*, 8382–8383; b) K. Tanaka, G. Nishida, A. Wada, K. Noguchi, *Angew. Chem.* **2004**, *116*, 6672–6674; *Angew. Chem. Int. Ed.* **2004**, *43*, 6510–6512; c) K. Tanaka, G. Nishida, M. Ogino, M. Hirano, K. Noguchi, *Org. Lett.* **2005**, *7*, 3119–3121; d) K. Tanaka, A. Wada, K. Noguchi, *Org. Lett.* **2005**, *7*, 4737–4739; e) T. Shibata, Y. Arai, Y. Tahara, *Org. Lett.* **2005**, *7*, 4955–4957.

[11] a) A. Gutnov, B. Heller, H.-J. Drexler, A. Spannenberg, G. Oehme, *Organometallics* **2003**, *22*, 1550–1553; b) A. Gutnov, H.-J. Drexler, A. Spannenberg, G. Oehme, B. Heller, *Organometallics* **2004**, *23*, 1002–1009.

[12] a) B. Heller, G. Oehme, *J. Chem. Soc. Chem. Commun.* **1995**, 179–180; b) B. Heller, B. Sundermann, H. Buschmann, H.-J. Drexler, J. You, U. Holzgrabe, E. Heller, G. Oehme, *J. Org. Chem.* **2002**, *67*, 4414–4422; c) B. Heller, B. Sundermann, C. Fischer, J. You, W. Chen, H.-J. Drexler, P. Knochel, W. Bonrath, A. Gutnov, *J. Org. Chem.* **2003**, *68*, 9221–9225.

[13] A. Gutnov, B. Heller, C. Fischer, H.-J. Drexler, A. Spannenberg, B. Sundermann, C. Sundermann, *Angew. Chem.* **2004**, *116*, 3883–3886; *Angew. Chem. Int. Ed.* **2004**, *43*, 3795–3797.

[14] X-ray data for compounds **11**, **14**, **16**, **21**, and *trans*-[$PdCl_2$\{(*S*)-naphep\}$_2$] and experimental procedures for all compounds synthesized are given in the Experimental Section.

[15] a) H. Bönnemann, *Angew. Chem.* **1978**, *90*, 517–526; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 565; b) K. P. C. Vollhardt, *Angew. Chem.* **1984**, *96*, 525–541; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539; c) B. Heller, D. Heller, G. Oehme, *J. Mol. Catal. A Chem.* **1996**, *110*, 211–219.

[16] H. Brown, N. M. Yoon, *J. Am. Chem. Soc.* **1966**, *88*, 1464–1472.

[17] S. Griffin, L. Heath, P. Wyatt, *Tetrahedron Lett.* **1998**, *39*, 4405–4406.

[18] L. J. Higham, E. F. Clarke, H. Müller-Bunz, D. G. Gilheany, *J. Organomet. Chem.* **2005**, *690*, 211–219.

[19] a) Y. Uozumi, T. Hayashi, *J. Am. Chem. Soc.* **1991**, *113*, 9887–9888; b) K. Yamamoto, T. Hayashi, in *Transition Metals for Organic Synthesis, Vol. II* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**, pp. 120–131; c) T. Hayashi, in *Comprehensive Asymmetric Catalysis, Vol. I* (Eds.: E. N. Jacobson, A. Pfaltz, H. Yamamoto), Springer, Berlin, Heidelberg, **1999**, pp. 319–333; d) Y. Uozumi, K. Kitayama, T. Hayashi, K. Yanagi, E. Fukuyo, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713–722.
[20] a) T. Hayashi, Y. Uozumi, *Pure Appl. Chem.* **1992**, *64*, 1911–1916; b) Y. Uozumi, K. Kitayama, T. Hayashi, *Tetrahedron: Asymmetry* **1993**, *4*, 2419–2422.
[21] Y. Uozumi, K. Kitayama, T. Hayashi, K. Yanagi, E. Fukuyo, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713–722.
[22] X. A. Dominguez, B. Gomez, J. Slim, D. Giesecke, E. B. Ureto, *J. Am. Chem. Soc.* **1954**, *76*, 5150–5150.
[23] G. T. Crisp, Y.-L. Jiang, *Synth. Commun.* **1998**, *28*, 2571–2576.
[24] A. L. Casalnuovo, T. V. RajanBabu, T. A. Ayers, T. H. Warren, *J. Am. Chem. Soc.* **1994**, *116*, 9869–9882.
[25] J. R. Goerlich, R. Schmutzler, *Phosphorus Sulfur and Silicon* **1995**, *102*, 211–215.
[26] H. Bönnemann, B. Bogdanoviæ, R. Brinkmann, B. Spliethoff, D. He, *J. Organomet. Chem.* **1993**, *451*, 23–31.
[27] G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, **1997**.
[28] G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997**.

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