DOI: 10.1002/ejoc.200700249

Phosphoramidite quinaphos-Type Ligands for Highly Selective Ni-Catalysed Asymmetric C–C Bond Forming Reactions

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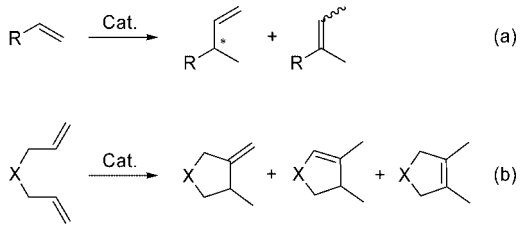
Keywords: Hydrovinylation / Cycloisomerisation / Phosphoramidites / Asymmetric catalysis / Ligand design

Monodentate quinaphos phosphoramidites bearing different substituents in the 2-position of the 1,2-dihydroquinoline backbone were synthesised and characterised. Computational, NMR spectroscopic and X-ray crystallographic methods were used for the elucidation of the structure in solution and in the solid state. Diastereomerically pure ligands were used in the nickel-catalysed asymmetric hydrovinylation of styrene as well as in the cycloisomerisation of diethyl diallylmalonate. Enantiomeric excesses up to 91 % for the hydrovinylation reaction and up to 46 % for the cycloisomerisation reaction were obtained, accompanied with unprecedented high activities and regioselectivities.

Introduction

The development of highly selective carbon–carbon bond forming reactions is still one of the major challenges in organic synthesis.[1] Especially, atom-economical coupling reactions are highly desirable as they avoid the formation of undesired byproducts, which leads to waste minimisation.[2] The hydrovinylation of olefins and the cycloisomerisation of 1,6-dienes are processes of this type with a still widely unexplored potential for organic synthesis. The transition-metal-catalysed hydrovinylation reaction is the formal addition of ethylene to an olefin and leads to the formation of high-value products containing – in the case of a prochiral olefin – a new stereogenic centre. A number of promising catalysts, especially nickel-based, have been found to catalyse efficiently the asymmetric hydrovinylation of styrene and other substrates.[3,4] Nevertheless, there is still a need for robust and easily accessible catalysts that provide high activities and selectivities. The transition-metal-catalysed cycloisomerisation of 1,6-dienes is formally an intramolecular olefin dimerisation reaction and leads mainly to five-membered carbo- or heterocyclic compounds, which also can contain a new stereogenic centre. Although a number of successful achiral systems catalysing the selective formation of the different 5-ring products have been reported,[5,6] asymmetric cycloisomerisation of dienes has been achieved very rarely (Scheme 1).[7]



Scheme 1. (a) Hydrovinylation of olefins (R = Ar, for example) and (b) cycloisomerisation of 1,6-dienes [X = $C(CO_2R)_2$, N–R, O, for example].

After their first successful applications by Feringa and coworkers in 1996,[8] phosphoramidites proved their potential as ligands in many different catalytic asymmetric transformations,[9,10] and they acquired a place in the set of so-called "privileged" ligands.[11] In 1999, Faraone and coworkers introduced a new family of phosphoramidites based on 1,2-dihydroquinoline as a readily accessible backbone for phosphoramidite ligands,[12] which formed the basis for the development of the quinaphos family in our group.[13,14] The quinaphos ligands offer the advantage of a modular synthesis with a high level of versatility. The groups at C-2 and C-8 as well as the diol functionality can be easily modified. In particular, the variation of the group at the C-2 stereogenic centre is straightforward as it is introduced during synthesis of the ligand. Furthermore, the coexistence of the central chirality in the 1,2-dihydroquinoline backbone with the axially chiral β-binaphthol moiety allows exploitation of cooperative effects in diastereomeric forms. Up to now, however, only quinaphos ligands with R = *n*Bu have been studied in detail in catalysis (Scheme 2).

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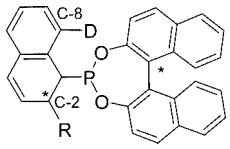


Scheme 2. The quinaphos ligand family with β-binaphthol as the diol moiety (D = Cl, OMe, PPh_2; R = alkyl or aryl, for example).

The quinaphos-type ligands already showed impressive results in different asymmetric catalytic reactions, such as the rhodium-catalysed hydroformylation of styrene,[15] the rhodium-[15] and ruthenium-catalysed[16] hydrogenation of alkenes and ketones, respectively, and the copper-catalysed conjugate addition of diethylzinc to enones.[17] Furthermore, monodentate derivatives are very promising candidates for challenging asymmetric nickel-catalysed olefin dimerisation reactions. We reported that Cl-quinaphos ligand **4** (D = Cl) bearing a *n*-butyl group in the 2-position can serve as an active and enantioselective catalyst for the hydrovinylation of styrene.[18] After this initial report, monodentate phosphoramidite ligands became widely used and successful ligands for the asymmetric hydrovinylation of olefins.[3,4a–4c] Motivated by the mechanistic analogy between the nickel-catalysed hydrovinylation and the cycloisomerisation of 1,6-dienes,[19,20] we also evaluated Cl-quinaphos phosphoramidites in the nickel-catalysed cyclisation of diethyl diallylmalonate as well as *N*,*N*-diallyl tosylamide and obtained high activities and regioselectivities accompanied with encouraging *ee* values.[7a,7b]

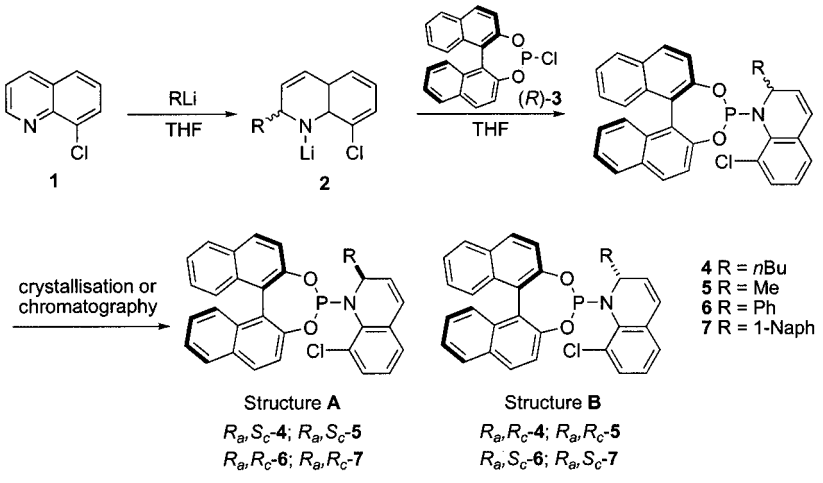
In this work, we report the synthesis and the characterisation of Cl-quinaphos derivatives bearing different substituents at the C-2 position and their applications in nickel-catalysed asymmetric C–C bond forming reactions. The aim of this study was to investigate the extent to which the catalytic performance of the ligand is affected by variation of the group in the 2-position. In particular, we were interested in the effect of cooperativity between the two elements of chirality of the ligand in these processes.

Results and Discussion

Ligand Synthesis

Cl-quinaphos phosphoramidites can be prepared by following the straightforward one-pot two-step procedure shown in Scheme 3.[12] 8-Chloroquinoline (**1**) was converted into the corresponding 1,2-dihydroquinoline amide **2** by addition of 1 equiv. of a lithium organic reagent to the C=N bond. The resulting lithium amide was then reacted with phosphorochloridite (*R*)-**3**, which was derived from enantiomerically pure (*R*)-β-binaphthol and PCl_3. After removing the lithium chloride byproduct, the quinaphos ligand was obtained as a 1:1 mixture of the two possible diastereoisomers. It is important to note that owing to the change in priority of the Cahn–Ingold–Prelog rules, the stereochemical descriptor for the central chirality is inverted for the same spatial arrangement of the diastereomers **A** and **B**. Separation of the diastereoisomers can be achieved either by crystallisation, extraction or column chromatography. The separation method needs to be optimised for each diastereomeric pair; thus, the purification step is currently the bottleneck that prevents the rapid preparation of a quinaphos library.

Besides the earlier described monodentate Cl-quinaphos **4** with an *n*-butyl group in the 2-position of the dihydroquinoline backbone,[12] we synthesised ligands **5**, **6** and **7** with R = methyl, phenyl and 1-naphthyl, respectively. Following the general procedure described above, methyl-substituted derivative **5** could be obtained in 59% yield as a 1:1 diastereomeric mixture. The (R_a,S_c)-isomer could be isolated from this mixture in a pure form as a white microcrystalline solid by recrystallisation from dichloromethane and ethanol at –20 °C in 32% yield.[21] The remaining mother liquor mainly contained the corresponding (R_a,R_c) isomer still contaminated with 10% of the (R_a,S_c)-configured ligand. Despite applying a number of possible purification methods, we were not able to obtain pure (R_a,R_c)-**5**. The diastereomeric mixture of corresponding phenyl-substituted ligand **6** was formed very smoothly in 91% yield. The



Scheme 3. Synthesis of monodentate quinaphos phosphoramidites.

separation of the diastereoisomers was achieved by column chromatography (*n*-pentane/THF) under inert gas conditions and led to the isolation of the (R_a,S_c) and the (R_a,R_c) isomer of **6** in 27 and 21% yield, respectively. Both diastereomers were obtained as white powders. The 1:1 diastereoisomeric mixture of 1-naphthyl derivative **7** could be isolated in 82% yield. The separation of the diastereoisomers was straightforward and (R_a,S_c)-**7** could be obtained in a pure form as a colourless solid in 37% yield after simple extraction of the mixture with dichloromethane. The mother liquor contained mainly (R_a,R_c)-**7**, which was purified by column chromatography (*n*-pentane/dichloromethane) and isolated in 33% yield.

Structural Analysis

Single crystals of the diastereomer of ligand **7**, which are poorly soluble in dichloromethane, were obtained from $CDCl_3$/*n*-pentane.[22] The resulting structure is shown in Figure 1. Selected bond lengths and angles are presented in Tables 1 and 2, respectively.

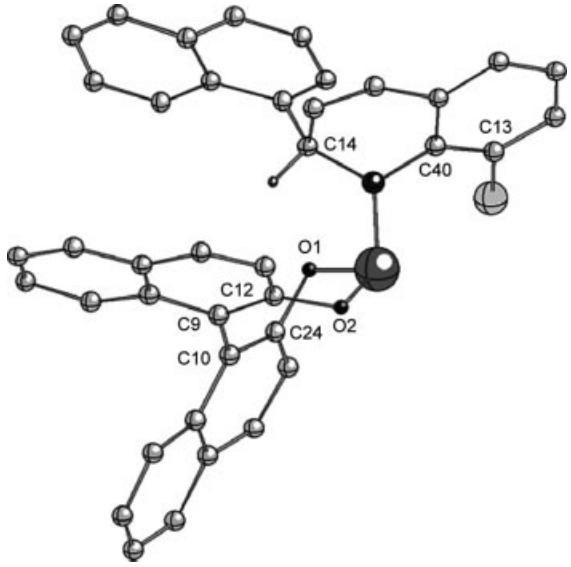


Figure 1. ORTEP of (R_a,S_c)-**7**.

Table 1. Selected bond lengths [Å] in (R_a,S_c)-**7**.

P1–O1	1.657(5)	N1–C14	1.473(9)
P1–O2	1.655(5)	N1–C40	1.414(9)
O1–C24	1.398(8)	C9–C10	1.512(10)
O2–C12	1.383(9)	C9–C12	1.378(9)
N1–P1	1.701(6)	C10–C24	1.362(10)

Table 2. Selected bond angles [°] in (R_a,S_c)-**7**.

N1–P1–O1	93.4(3)	N1–C14–C8	113.9(6)
N1–P1–O2	108.4(3)	N1–C14–C39	110.5(6)
O1–P1–O2	98.6(2)	N1–C40–C13	123.4(6)
C40–N1–C14	116.8(5)	N1–C40–C20	119.5(6)
C40–N1–P1	119.0(4)	O1–C24–C10	118.6(6)
C14–N1–P1	122.6(4)	O1–C24–C18	118.6(6)
P1–O1–C24	118.2(4)	O2–C12–C9	120.4(6)
P1–O2–C12	125.0(4)	O2–C12–C32	117.9(6)

The absolute configuration of the ligand could be assigned as (R_a,S_c), which corresponds to structure **B** in Scheme 3. This represents the same stereochemical arrangement as in ligand (R_a,R_c)-**4** which was characterised by X-ray diffraction previously.[12] The binaphthol moiety resides approximately on the opposite side with respect to the chlorine substituents to minimise possible steric repulsions. The torsion angle determining the axial chirality of the binaphthol backbone [τ(C12–C9–C10–C24)] has a value of –50.2° and is within the expected range. The nitrogen in (R_a,S_c)-**7** is almost trigonal planar, whereas nearly pyramidal nitrogen atoms were observed in *cis*-[Pt{(R_a,R_c)-**4**}$_2$I$_2$].[12]

A full stereochemical assignment of the diastereomers in solution was achieved by computational conformation analysis combined with a detailed NMR spectroscopic investigation that was carried out exemplary for (R_a,S_c)-**5** and (R_a,R_c)-**5**. The conformational minima for both ligands were calculated by using a combination of systematic and Monte-Carlo[23] conformational searches at the PM3 level followed by geometry optimisation by DFT calculations at the B3LYP/6-31G(d) level.[24] The resulting conformation with the lowest energy content of each diastereoisomer (Figure 2) was then compared with the results of 2D NOE NMR spectroscopic measurements. The calculated structures predicted NOE interactions between the protons at C-1/C-B and C-1/C-C for (R_a,S_c)-**5** and between the protons at C-3/C-B and C-3/C-C for (R_a,R_c)-**5**. Indeed, all these predicted NOE interactions were observed in the NMR spectroscopic experiments; this data clearly validates the stereochemical assignments and the calculated conformational minima in solution.

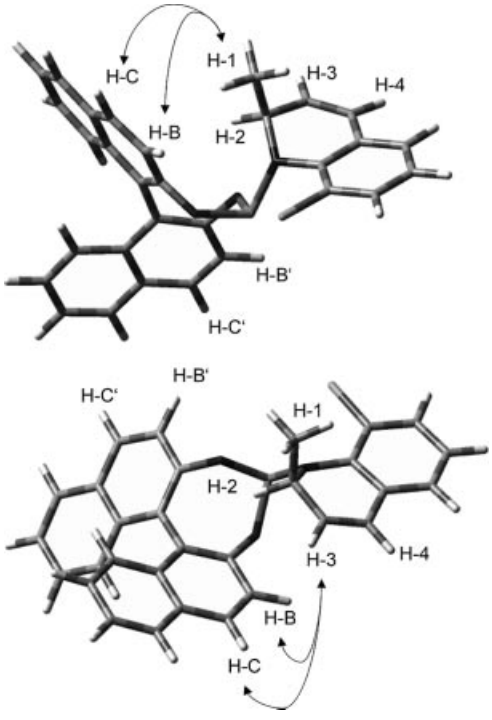


Figure 2. Calculated conformational minima of (R_a,S_c)-**5** (top) and (R_a,R_c)-**5** (bottom). The arrows show selected NOE interactions.

Gratifyingly, it was possible to identify the ^{31}P NMR chemical shift as a diagnostic tool for a reliable assignment of the stereochemical arrangement. All ligands show ^{31}P NMR spectroscopic signals in the range between 134 ppm and 145 ppm; the signals for the diastereomer corresponding to structure **A** is always found above, and those to **B** below, 140 ppm (Table 3). In contrast, the chemical shifts of the proton at C-2 cannot be used for the reliable assignment of the two diastereomeric structures.

Table 3. Comparison of selected NMR spectroscopic data.

Entry	Ligand	δ (^{31}P) [ppm]	δ [^{1}H(C-2)] [ppm]	Structure[a]
1	(R_a,S_c)-**4** (R = *n*Bu)	145.1	3.72	**A**
2	(R_a,R_c)-**4** (R = *n*Bu)	137.6	4.35	**B**
3	(R_a,S_c)-**5** (R = Me)	144.6	3.94	**A**
4	(R_a,R_c)-**5** (R = Me)	136.7	3.94	**B**
5	(R_a,R_c)-**6** (R = Ph)	143.2	5.23	**A**
6	(R_a,S_c)-**6** (R = Ph)	133.9	5.01	**B**
7	(R_a,R_c)-**7** (R = 1-Naph)	143.8	6.08	**A**
8	(R_a,S_c)-**7** (R = 1-Naph)	139.1	5.82	**B**

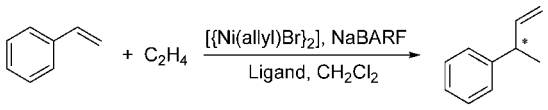
[a] As defined in Scheme 3.

Application in Asymmetric Catalysis

Ligands **5**–**7** were used in the nickel-catalysed asymmetric hydrovinylation of styrene and cycloisomerisation of diethyl diallylmalonate. For the hydrovinylation reaction, the catalyst was prepared in situ from [{Ni(allyl)Br}$_2$] and the phosphoramidite ligand with a nickel/phosphorus ratio of 1:1. Activation of the catalyst was achieved by adding a slight excess of NaBARF (BARF = [(B{[3,5-(CF$_3$)$_2$-C$_6$H$_3$]}$_4$)]) in the presence of styrene. Key results are shown in Table 4. For comparison, ligand **4** was included in this study and tested under the same benchmark conditions. With (R_a,R_c)-**4** at –35 °C and a styrene/nickel ratio of 300, full conversion and an *ee* value of 87% for the (*S*)-enantiomer was reached after 4 h (Table 4, Entry 1). However, owing to double bond isomerisation and oligomerisation of the primary product, the selectivity to the desired 3-phenyl-1-butene was only 53%. By lowering the reaction temperature to –78 °C, these side reactions could be effectively suppressed and **9** was obtained with a perfect selectivity and an *ee* value of 91% (Table 4, Entry 2). The simultaneous achievement of both excellent chemoselectivity and enantioselectivity under full conversion places this system among the best known catalysts for this transformation. To evaluate the catalyst activity, we ran a reaction with a reduced catalyst loading (**8**/Ni = 1000). A conversion of 42% after 4 h was observed, which corresponds to an average turnover frequency of 105 h^{-1} (Table 4, Entry 3), whereby only negligible loss in selectivity and *ee* was found. A strong miss-matched effect was observed as the corresponding (R_a,S_c) isomer led exclusively to styrene oligomerisation. Hence, only the diastereomers of **5**–**7** with identical spatial arrangement as (R_a,R_c)-**4** were tested in the hydrovinylation reaction.

Phenyl-substituted ligand **6** gave similar results as (R_a,R_c)-**4**. Full conversion was achieved within 4 h by using the (R_a,S_c)-isomer at –35 °C with **8**/Ni = 300 (Table 4, Entry 4). The selectivity with a value of 75% was somewhat higher with respect to that obtained with (R_a,R_c)-**4** under the same conditions, whereas the *ee* value was almost the same. The use of (R_a,S_c)-**6** as the ligand at lower reaction temperature provided perfect selectivity towards 3-phenyl-1-butene with an *ee* value of 90% (Table 4, Entry 5). Again, only a small reduction in the selectivity was observed by diminishing the catalyst loading to 0.1 mol-%. A conversion of 50% was observed, which corresponds to TOF = 125 h^{-1} (Table 4, Entry 6). A somewhat lower activity was observed with the catalyst based on (R_a,S_c)-**7** bearing a 1-naphthyl group in the 2-position (Table 4, Entry 7). At a reaction temperature of –78 °C and **8**/Ni = 400, 71% conversion was reached after 4 h (Table 4, Entry 8). The enantioselectivity was significantly lower (63%) relative to the values obtained with (R_a,R_c)-**4** and (R_a,S_c)-**6**, whereas the selectivity

Table 4. Hydrovinylation of styrene (**8**).[a]



8 **9**

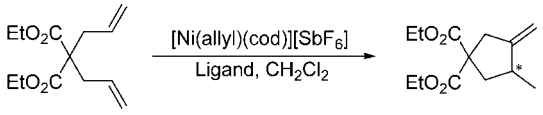
Entry	Ligand	*T* [°C]	**8**/Ni	Conversion [%]	Selectivity[b] [%]	*ee*[c] [%]
1	(R_a,R_c)-**4** (R = *n*Bu)	–35	300	>99	53	87 (*S*)
2	(R_a,R_c)-**4** (R = *n*Bu)	–78	400	99	99	91 (*S*)
3	(R_a,R_c)-**4** (R = *n*Bu)	–78	1000	42	97	90 (*S*)
4	(R_a,S_c)-**6** (R = Ph)	–35	300	>99	75	85 (*S*)
5	(R_a,S_c)-**6** (R = Ph)	–78	400	99	99	90 (*S*)
6	(R_a,S_c)-**6** (R = Ph)	–78	1000	50	96	86 (*S*)
7	(R_a,S_c)-**7** (R = 1-Naph)	–35	300	>99	29	49 (*S*)
8	(R_a,S_c)-**7** (R = 1-Naph)	–78	400	71	99	63 (*S*)
9	(R_a,S_c)-**7** (R = 1-Naph)	–78	1000	32	94	54 (*S*)

[a] $p(C_2H_4)$ = 1 bar; *t* = 4 h, Ni/L = 1. [b] Selectivity towards **9**. [c] Determined by chiral GC (Ivadex 7, 25 m, 60 °C, 1 °C min^{-1} up to 85 °C, 20 °C min^{-1} up to 180 °C).

towards **9** was at the same outstanding level (99%). In the presence of (R_a,S_c)-**7** at 0.1 mol-% catalyst loading, a TOF of 80 h^{-1} was obtained with 94% and 54% chemo- and enantioselectivity, respectively (Table 4, Entry 9).

For the cycloisomerisation of diethyl diallylmalonate (**10**), the catalyst was generated in situ by mixing equimolar amounts of the phosphoramidite ligand with [Ni(allyl)(cod)][SbF_6] at a catalyst loading of 5 mol-% with respect to the substrate. Subsequently, the substrate was added, and the reaction mixture was stirred at room temperature for the desired time. Table 5 shows representative results of this study. Preliminary observations[7b] showed that the relative configuration of the quinaphos ligand is again of crucial importance because, similar to the hydrovinylation reaction, only one diastereomer is able to impart high catalytic activity. Most intriguingly, the opposite spatial arrangement (structure **A** vs. **B**) is required for the intra- as compared with the intermolecular process. For instance, *n*-butyl-derivative (R_a,S_c)-**4** generated a highly active catalyst, which allowed the reaction to proceed with a lower limit of the turnover frequency (37 h^{-1}) and almost perfect regioselectivity (97%). The observed *ee* value was 46% (Table 5, Entry 1). The corresponding (R_a,R_c) diastereoisomer showed no activity at all. Ligand (R_a,R_c)-**6** resulted in a similar activity (TOF 36 h^{-1}) and selectivity (Table 5, Entry 3). Methyl derivative (R_a,S_c)-**5** afforded a very active catalytic system and full conversion was reached within 30 min, which corresponds to a lower limit for the turnover frequency of 40 h^{-1}. Product **11** was formed with 92% regioselectivity and 43% enantioselectivity (Table 5, Entry 2). Ligand (R_a,R_c)-**7** with a 1-naphthyl group in the 2-position provided slightly lower activity. A conversion of 89% was reached after one hour (TOF = 15 h^{-1}), whereas the resulting regioselectivity was a little bit higher (97%) and the enantioselectivity a little bit lower (39%) than that obtained with (R_a,S_c)-**5** (Table 5, Entry 4). As expected, diastereoisomer (R_a,S_c)-**7** showed no activity in the cycloisomerisation reaction. In summary, all four monodentate quinaphos ligands showed very good activities, excellent regioselectivities and comparably good enantioselectivities in the cycloisomerisation of **10**. These results compare well with the best catalytic systems known to date.[7]

Table 5. Cycloisomerisation of diethyl diallylmalonate (**10**).[a]



10 **11**

Entry	Ligand	*t* [h]	Conv. [%]	Sel.[b] [%]	*ee*[c] [%]
1	(R_a,S_c)-**4** (R = *n*Bu)	0.5	94	97	46 (–)
2	(R_a,S_c)-**5** (R = Me)	0.5	>99	92	43 (–)
3	(R_a,R_c)-**6** (R = Ph)	0.5	90	93	40 (–)
4	(R_a,R_c)-**7** (R = 1-Naph)	1	78	97	39 (–)

[a] *T* = 20 °C, **10**/Ni = 20, Ni/L = 1. [b] Regioselectivity towards **11**. [c] Determined by chiral HPLC (Chiracel OJ-H, *T* = 20 °C, *n*-heptane/2-propanol, 99.975:0.025, 0.5 mL min^{-1}, 203 nm).

Conclusions

The generality of the modular synthesis of quinaphos-type ligands was demonstrated by new monodentate Cl-quinaphos phosphoramidites **5**–**7** bearing a methyl, phenyl or 1-naphthyl group in the 2-position of the 1,2-dihydroquinoline backbone. The compounds were formed as 1:1 diastereomeric mixtures and could be separated into their individual diastereoisomers [except (R_a,R_c)-**5**, which still contained up to 10% of impurities] by crystallisation/extraction or column chromatography. X-ray diffraction allowed the elucidation of the absolute configuration of (R_a,S_c)-**7** and the structure in solution could be assigned by a combination of multinuclear NMR and computational methods.

The new ligands were used in two nickel-catalysed asymmetric C–C bond forming reactions: the hydrovinylation of styrene and the cycloisomerisation of diethyl diallylmalonate. In the hydrovinylation reaction, excellent results were obtained with phenyl and *n*-butyl derivatives (R_a,S_c)-**6** and (R_a,R_c)-**4**, respectively. TOFs between 105–125 h^{-1}, perfect selectivity towards the desired 3-phenyl-1-butene and very high *ee* values up to 91% were achieved. Ligand (R_a,S_c)-**7** bearing a 1-naphthyl group in the 2-position showed a somewhat reduced catalytic performance, probably because of steric reasons. Nickel catalysts based on (R_a,S_c)-**4**, (R_a,S_c)-**5**, (R_a,R_c)-**6** and (R_a,R_c)-**7** provided very promising and similar results in the cycloisomerisation of diethyl diallylmalonate. At 5 mol-% catalyst loading, these systems resulted in TOFs from 15 h^{-1} to >40 h^{-1}, selectivities towards *exo* methylenecyclopentane **11** between 92–97% and *ee*'s between 39–43%.

These results suggest that the substituent at C-2 of the monodentate quinaphos ligands is required to lock the conformation of the ligand, and hence, it controls the basic reactivity of the corresponding ligands. This is evident from the remarkable matched/mismatched effects observed with ligands **5**–**7**, where only diastereomers corresponding to structure **B** are suitable for intermolecular hydrovinylation, but structure **A** is the effective arrangement for the intramolecular cycloisomerisation reaction. For instance, diastereomer (R_a,S_c)-**4** forms a potent catalyst for styrene oligomerisation but is completely ineffective for styrene hydrovinylation. Interestingly, this is the diastereomer required for accomplishing efficiently the cycloisomerisation reaction. Conversely, (R_a,R_c)-**4** generates an active and extremely selective Ni-catalyst for the hydrovinylation of styrene, whereas it is not suitable for the cycloisomerisation.

The exact structure of the substituent has only a minor influence, which is understandable from the crystal structure of (R_a,S_c)-**7** and the calculated NMR spectroscopic structures of **5**. Both reveal that the substituent in the 2-position points away from the phosphorus lone pair of electrons and hence also from the expected position of the metal. The structural analysis further leads us to the conclusion that the group in the 8-position should have an influence on the catalytic performance as it should be rather close to the catalytic centre. A variation at this position is currently under investigation in our laboratories.

Experimental Section

General: All reactions were carried out under an atmosphere of dry and oxygen-free argon with the use of standard Schlenk techniques. All solvents were dried and distilled prior to use. NMR spectra were measured at room temperature with a Bruker AV-600 spectrometer. Chemical shifts are given relative to TMS by using the solvent signals as internal reference for ^{1}H NMR as well as ^{13}C NMR and H_3PO_4 (85%) as external reference for ^{31}P NMR spectroscopy. ^{1}H NOESY measurements were carried out by using a mixing time of 500 ms. 1-Naphthyllithium,[25] (*R*)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene [(*R*)-**3**],[12] [{Ni(allyl)Br}$_2$][26] and [Ni(allyl)(cod)][SbF_6][27] were prepared according literature procedures. 8-Chloroquinoline was purchased from TCI and distilled prior to use. All other reagents were ordered from Sigma–Aldrich. Styrene was distilled and diethyl diallylmalonate degassed by three freeze–pump–thaw cycles prior to use. Alkyllithium reagents were titrated with *N*-benzylbenzamide.[28] All other reagents were used as purchased.

2-Methyl-8-chloro-1-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]-dinaphthalen-4-yl)-1,2-dihydroquinoline (5): Methyllithium (1.48 M in diethyl ether, 2.9 mL, 4.2 mmol) was added dropwise at –78 °C to a solution of 8-chloroquinoline (0.5 mL, 3.9 mmol) in THF (10 mL). The reaction mixture was then warmed to –50 °C, stirred for 1 h and cooled down again to –78 °C. The resulting orange solution was added at –78 °C to a solution of (*R*)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene [(*R*)-**3**, 1.36 g, 3.9 mmol] in THF (3.0 mL). The reaction mixture was slowly warmed to room temp. and stirred for an additional 2 h. The solvent was evaporated, and the crude brown residue was suspended in toluene (12 mL) and filtered through a pad of celite. After evaporation of the solvent, the title compound was obtained as a yellow solid as a 1:1 diastereomeric mixture. This mixture was recrystallised from dichloromethane/EtOH. A white solid consisting of pure (R_a,S_c)-**5** (370 mg, 0.75 mmol, 32%) was obtained. The filtrate was evaporated to dryness, which resulted in a yellow solid (718 mg) that contained (R_a,R_c)-**5** contaminated with 10% of (R_a,S_c)-**5**. (R_a,S_c)-**5**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.82 (d, ^3J = 6. 8 Hz, 3 H), 3.94 (m, 1 H), 5.85 (dd, ^3J = 9.4 Hz, ^3J = 5.9 Hz, 1 H), 6.35 (d, ^3J = 9.4 Hz, 1 H), 7.00 (m, 1 H), 7.02 (m, 1 H), 7.25 (m, 1 H), 7.33 (m, 3 H), 7.44 (m, 4 H), 7.68 (d, ^3J = 8.8 Hz, 1 H), 7.90 (d, ^3J = 8.2 Hz, 1 H), 7.93 (d, ^3J = 8.8 Hz, 1 H), 7.96 (d, ^3J = 8.2 Hz, 1 H), 7.99 (d, ^3J = 8.7 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 18.9, 46.3, 122.2, 122.5, 122.8, 123.4, 124.0, 124.1, 124.8, 125.0, 125.1, 126.3, 126.4, 127.2, 127.3, 128.1, 128.2, 128.6, 128.7, 129.4, 130.0, 130.7, 131.2, 131.4, 131.7, 132.8, 133.0, 134.5, 135.2, 149.5 ppm. ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$): δ = 144.6 ppm. MS (CI): *m*/*z* (%) = 496 (9), 495 (8) $[M]^+$, 460 (5), 361 (16), 344 (10), 343 (38), 333 (7), 329 (8), 288 (20), 287 (100), 286 (13), 182 (12), 181 (5), 180 (27), 178 (20), 139 (5). HRMS (EI): calcd. for $C_{30}H_{21}ClNO_2P$ 493.09985; found 493.10020.

2-Phenyl-8-chloro-1-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]-dinaphthalen-4-yl)-1,2-dihydroquinoline (6): Phenyllithium (1.5 M in diethyl ether, 5.3 mL, 8.0 mmol) was added dropwise at –78 °C to a solution of 8-chloroquinoline (1.02 mL, 8.00 mmol) in THF (30.0 mL). The resulting solution was added at –78 °C to a solution of (*R*)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene [(*R*)-**3**, 2.79 g, 8.00 mmol] in THF (20 mL). The reaction mixture was stirred for 1 h at –78 °C and for 1 h at room temp. The solvent was evaporated, and the crude brown residue was suspended in toluene (20 mL) and filtered through a pad of celite. After evaporation of the solvent, the title compound was obtained as a yellow solid as a 1:1 diastereomeric mixture. The diastereomeric mixture (1.76 g, 3.17 mmol) was separated by column chromatography under inert gas conditions (Silicagel 60, 0.040–0.063 μm, THF/*n*-pentane, 1:10) and led to the isolation of (R_a,R_c)-**6** (476 mg, 0.86 mmol, 27%) and (R_a,S_c)-**6** (370 mg, 0.67 mmol, 21%). (R_a,R_c)-**6**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.23 (dd, ^3J = 6.4, ^4J = 2.5 Hz, 1 H), 6.23 (dd, ^3J = 9.3 Hz, ^3J = 6.4 Hz, 1 H), 6.46 (d, ^3J = 9.3 Hz, 1 H), 7.01–7.06 (m, 3 H), 7.08 (t, ^3J = 7.5 Hz, 1 H), 7.11 (d, ^3J = 8.7 Hz, 1 H), 7.24–7.29 (m, 3 H), 7.30–7.41 (m, 4 H), 7.44 (d, ^3J = 8.1 Hz, 1 H), 7.48–7.52 (m, 3 H), 7.57 (d, ^3J = 8.7 Hz, 1 H), 7.84 (d, ^3J = 8.1 Hz, 1 H), 7.99 (d, ^3J = 8.1 Hz, 1 H), 8.04 (d, ^3J = 8.7 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 52.6, 122.1, 122.2, 122.3, 123.8, 124.3, 124.8, 124.9, 125.2, 125.6, 125.8, 126.1, 126.4, 126.9, 127.2, 127.3, 128.3, 128.5, 129.6, 130.7, 131.0, 131.2, 131.2, 131.7, 131.8, 132.5, 133.0, 136.1, 136.2, 141.8, 149.0, 149.1 ppm. ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$): δ = 143.2 ppm. (R_a,S_c)-**6**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.01 (dd, ^3J = 5.8 Hz, ^4J = 2.5 Hz, 1 H), 6.08 (dd, ^3J = 9.5 Hz, ^3J = 5.8 Hz, 1 H), 6.81 (d, ^3J = 9.5 Hz, 1 H), 6.99 (d, ^3J = 7.7 Hz, 1 H), 7.05–7.08 (m, 2 H), 7.12 (t, ^3J = 7.6 Hz, 1 H), 7.22–7.31 (m, 2 H), 7.39–7.46 (m, 4 H), 7.48 (d, ^3J = 8.7 Hz, 1 H), 7.73 (d, ^3J = 8.8 Hz, 1 H), 7.92–7.98 (m, 4 H), 8.05 (d, ^3J = 8.8 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 52.2, 122.4, 122.5, 123.6, 125.0, 125.1, 125.2, 125.3, 125.6, 126.3, 126.4, 127.3, 127.3, 127.4, 127.4, 127.9, 128.1, 128.4, 128.6, 129.2, 129.6, 129.9, 130.9, 131.0, 131.1, 131.5, 131.9, 132.0, 132.1, 135.9, 139.8, 148.6, 149.2 ppm. ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$): δ = 133.9 ppm. HRMS (ESI+): calcd. for $C_{35}H_{23}ClNNaO_2P$ 578.105079; found 578.104713.

2-(1-Naphthalene)-8-chloro-1-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-1,2-dihydroquinoline (7): 8-Chloroquinoline (0.8 mL, 6.2 mmol) was rapidly added at room temp. to a solution of 1-naphthyllithium (0.33 M in THF, 19.6 mL, 6.2 mmol). The resulting dark brown solution was stirred for 1 h before it was added to a solution of (*R*)-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene [(*R*)-**3**, 2.17 g, 6.2 mmol] in THF (7.0 mL). After 2 h, the solvent was evaporated and the crude brown residue was suspended in toluene (15.0 mL) and filtered through a pad of celite. After evaporation of the solvent, the title compound was obtained as a yellow solid as a 1:1 diastereomeric mixture. The two diastereoisomers were separated by extraction with dichloromethane (15.0 mL). The compound insoluble in dichloromethane proved to be the (R_a,S_c) diastereoisomer and was obtained as a white solid (638 mg, 1.00 mmol, 37%). The filtrate was evaporated to dryness and a portion of the resulting solid (1.20 g, ≈70% desired product) was purified by column chromatography under inert gas conditions (Silicagel 60, 0.040–0.063 μm, dichloromethane/*n*-pentane, 1:5) to afford (R_a,R_c)-**7** as a white solid (175 mg, 0.29 mmol, 33%). (R_a,S_c)-**7**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.82 (t, ^3J = 4.5 Hz, 1 H), 5.94 (dd, ^3J = 9.6 Hz, ^3J = 5.6 Hz, 1 H), 6.37 (d, ^3J = 8.6 Hz, 1 H), 6.45 (m, 1 H), 6.53 (d, ^3J = 9.6 Hz, 1 H), 7.06 (m, 2 H), 7.12 (t, ^3J = 7.4 Hz, 1 H), 7.20 (m, 2 H), 7.25 (m, 1 H), 7.33 (m, 2 H), 7.41 (m, 3 H), 7.49 (d, ^3J = 8.9 Hz, 1 H), 7.57 (m, 3 H), 7.66 (d, ^3J = 8.7 Hz, 1 H), 7.89 (d, ^3J = 8.2 Hz, 1 H), 7.93 (d, ^3J = 8.8 Hz, 1 H), 8.10 (d, ^3J = 8.1 Hz, 1 H), 8.16 (d, ^3J = 8.7 Hz, 1 H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 50.9, 53.5, 122.0, 122.1, 122.2, 122.7, 123.3, 123.4, 123.8, 124.9, 125.0, 125.1, 125.5, 125.7, 125.8, 126.3, 126.5, 126.9, 127.3, 127.7, 127.9, 128.2, 128.4, 128.5, 129.4, 130.3, 130.6, 130.8, 130.9, 131.6, 131.7, 132.7, 133.1, 133.4, 134.8, 134.9, 137.6, 148.9, 149.9 ppm. ^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$): δ = 139.1 ppm. MS (CI): *m*/*z* (%) = 607 (1) $[M]^+$, 334 (6), 332 (12), 330 (7), 297 (5), 294 (14), 293 (36), 292 (94), 291 (82), 290 (100), 289 (27), 288 (11), 257 (14), 256 (77), 255 (49), 254 (15), 185 (24), 184 (6), 168 (17), 157 (29), 145 (12), 129 (16), 128 (8). (R_a,R_c)-**7**: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.08 (dd,

^3J = 6.6 Hz, ^4J = 2.7 Hz, 1 H), 6.16 (dd, ^3J = 9.5 Hz, ^3J = 6.6 Hz, 1 H), 6.32 (t, ^3J = 9.0 Hz, 2 H), 6.51 (d, ^3J = 9.0 Hz, 1 H), 6.62 (m, 1 H), 6.76 (d, ^3J = 8.5 Hz, 1 H), 6.96 (d, ^3J = 7.4 Hz, 1 H), 7.06 (m, 2 H), 7.17–7.27 (m, 5 H), 7.37 (m, 2 H), 7.40–7.42 (m, 2 H), 7.47 (dd, ^3J = 8.3 Hz, ^4J = 1. 6 Hz, 1 H), 7.56 (d, ^3J = 8.9 Hz, 1 H), 7.75 (d, ^3J = 8.2 Hz, 1 H), 7.80 (d, ^3J = 8.3 Hz, 1 H), 7.92 (d, ^3J = 8.3 Hz, 1 H), 7.98 (d, ^3J = 9.2 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 50.5, 121.3, 121.8, 121.9, 121.9, 122.5, 123.3, 124.1, 124.2, 124.7, 125.0, 125.4, 125.5, 125.6, 125.7, 125.8, 126.2, 126.3, 127.0, 127.5, 128.2, 128.3, 128.4, 128.8, 128.9, 130.0, 130.1, 130.4, 130.4, 130.6, 131.6, 131.9, 132.8, 133.4, 136.9, 137.1, 138.7, 148.3, 148.9 ppm. $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$): δ = 142.6 ppm. HRMS (ESI+): calcd. for $C_{39}H_{26}ClNO_2P$ 606.137569; found 606.138423.

General Procedure for a Typical Hydrovinylation Reaction: A solution of the ligand (0.012 mmol) in CH_2Cl_2 (2 mL) was added to a solution of $[Ni(allyl)Br]_2$ (0.006 mmol) in CH_2Cl_2 (1 mL) at room temp. under inert gas conditions. After 15 min, the solution was cooled to the desired reaction temperature and saturated with ethylene. Subsequently, styrene (**8**) and NaBARF (12.4 mg, 0.014 mmol) were added. The reaction mixture was stirred for 4 h and then quenched by the addition of aqueous ammonia (1 mL). The organic phase was washed with water (3 × 2 mL), dried with sodium sulfate and analysed by GC and chiral GC. Further details and modifications of the conditions are given in Table 4.

General Procedure for a Typical Cycloisomerisation Reaction: A solution of the ligand (0.03 mmol) in CH_2Cl_2 (5 mL) was added at room temp. to a solution of $[Ni(allyl)(cod)][SbF_6]$ (0.03 mmol) in CH_2Cl_2 (5 mL) under inert gas conditions. After 15 min, diethyl diallylmalonate (**10**, 0.6 mmol) was added by syringe to the yellow catalyst solution. The reaction mixture was stirred for the desired reaction time. The reaction was quenched by the addition of aqueous ammonia (1 mL). The organic phase was washed with water (3 × 2 mL), dried with sodium sulfate and analysed by GC and GC–MS. Further details and modifications of the conditions are given in Table 5.

For analysis by chiral HPLC the chlorinated solvent was replaced by *n*-heptane/2-propanol and the solution filtered through a pad of silica gel.

Acknowledgments

We are grateful to the European Community (contract NMP-3-CT-2003-505267, LIGBANK) and the Deutsche Forschungsgemeinschaft (SFB 380) for financial support. C. B. and C. J. D.-H. thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (GK 440), respectively, for predoctoral fellowships. Dr. J. Rubin-Preminger is acknowledged for collecting the X-ray data. We thank Dr. J. Klankermayer for helpful discussions, H. Eschmann for the HPLC measurements and K. Woike for technical assistance.

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V = 921.06 Å^3, λ = 0.71069 Å, μ(Mo-K_α) = 0.32 mm^{-1}, space group P1, Z = 2, δ(calc)= 1.220 g cm^{-3}, 12456 reflections measured, 8966 reflections unique, $R1$ = 0.0920, $wR2$ = 0.2475, GoF = 1.187. CCDC-637077 contains 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.

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Received: March 20, 2007
Published Online: May 8, 2007

