Pergamon

Tetrahedron 56 (2000) 2879–2888

TETRAHEDRON

New Chiral Oxazoline-Phosphite Ligands for the Enantioselective Copper-Catalyzed 1,4-Addition of Organozinc Reagents to Enones

Iris H. Escher and Andreas Pfaltz*

Department of Chemistry, University of Basel, St. Johanns-Ring 19, CH-4056 Basel, Switzerland

Received 8 November 1999; accepted 20 January 2000

Abstract—A series of new *P*,*N*-ligands with a binaphthyl and an oxazoline moiety were prepared, which are efficient ligands for the enantioselective copper-catalyzed 1,4-addition of organozinc reagents to enones. Increasing the steric bulk in the 3,3′-position of binaphthyl from an H to a biphenylyl moiety improved the ee from 65 to 94% in the reaction of diethylzinc with cyclopentenone.

Introduction

The conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds is an attractive and widely used tool for C–C bond formation.[1] A number of chiral auxiliaries and stoichiometric reagents are known that allow high stereocontrol in the 1,4-addition.[2] On the other hand, the development of enantioselective catalytic versions[1c] of this transformation has met great difficulties. Although various chiral copper[3,4] or nickel[5] catalysts have been reported in the early nineties, which gave promising enantioselectivities in certain cases, all these catalysts were not really practical because of low catalytic efficiency and a very limited application range. However, one catalytic system originally introduced by Alexakis,[6] the combination of an organozinc reagent and a copper complex with a chiral phosphorus ligand, has recently undergone a remarkable development. Using chiral phosphoramidites such as **2**, Feringa et al.[7] achieved very high enantioselectivities in the conjugate addition of various organozinc reagents to a range of cyclohexenones. Alexakis found a TADDOL-derived phosphite ligand **1** which induces up to 96% ee in the reaction of diethylzinc with cyclohexenone.[8] Although these catalysts give excellent results with cyclohexenone derivatives, the enantioselectivities in analogous 1,4-additions to cyclopentenone are disappointingly low. Moreover, cyclopentenone poses additional problems related to the lower reactivity and the tendency to undergo a Michael reaction with the enolate resulting from the conjugate addition of the organozinc reagent. Therefore, the yields are often low with this substrate[9] (Fig. 1).

Inspired by Feringa's results, we tested the oxazoline-phosphite **4a** and the corresponding (*S*,*S*)-diastereomer **4b**, which we had originally developed for enantio- and regiocontrol in palladium-catalyzed allylic substitution,[10] as controller ligands in the copper-catalyzed conjugate addition of organozinc reagents to enones. The results showed

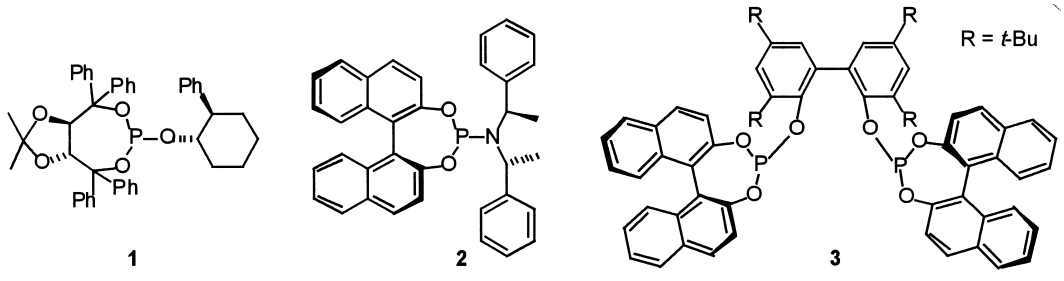


Figure 1.

Keywords: asymmetric induction; addition reactions; oxazolines; copper and compounds.
* Corresponding author. Tel.: +41-61-267-1108; fax: +41-61-267-1103; e-mail: andreas.pfaltz@unibas.ch

0040–4020/00/$ - see front matter
PII: S0040-4020(00)00143-5

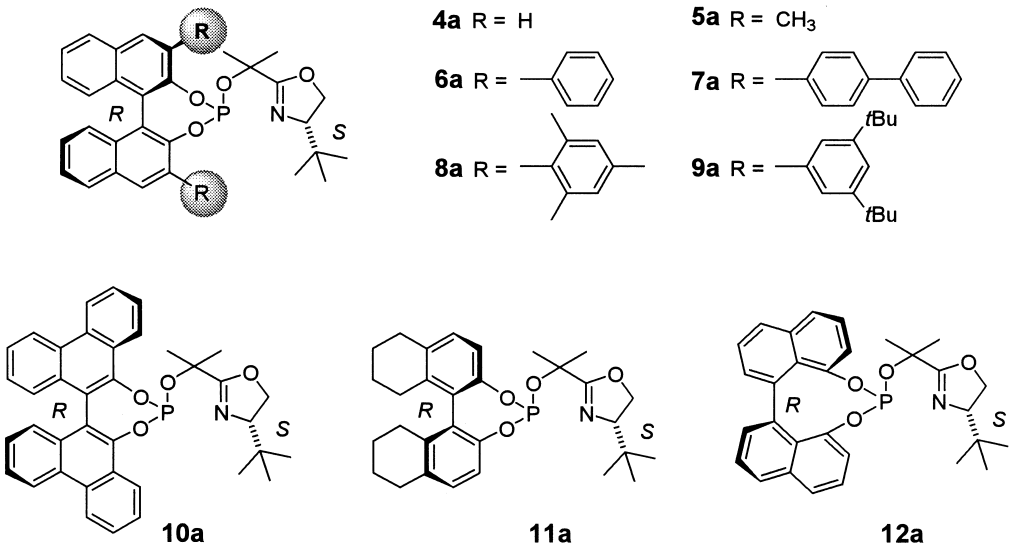


Figure 2. All ligands are illustrated as the (*R*,*S*)-diastereomers (a), the (*S*,*S*)-diastereomers (b) were also synthesized.

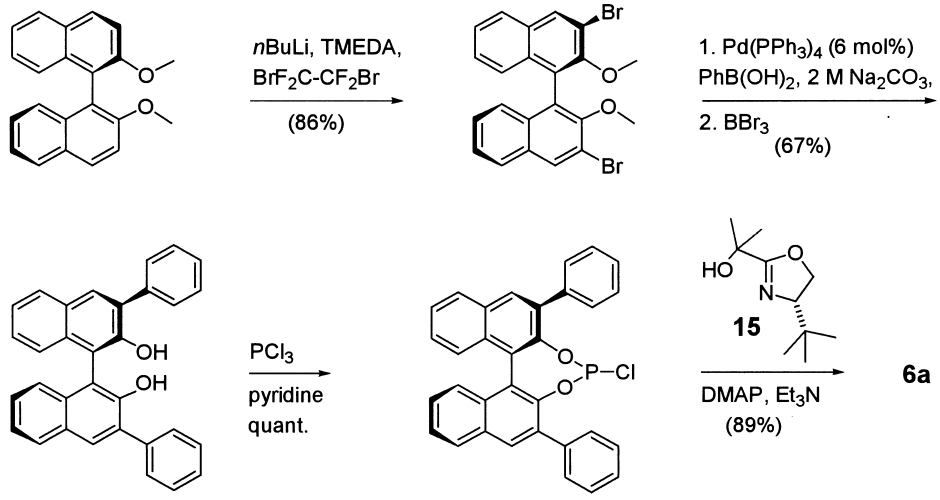
that both the chiral oxazoline and the chiral phosphite unit have a significant influence on the enantioselectivity. While the (*R*,*S*)-ligand **4a** gave the (*R*)-product in 52% ee in the reaction of diethylzinc with cyclohexenone, use of the (*S*,*S*)-diastereomer led to the (*S*)-product in 9% ee.[11] Introduction of two *ortho* methyl groups in the binaphthyl system (ligand **5a**) strongly increased the ee to 90%. The highest ee (up to 96%) was obtained with ligand **5a** in the reaction of dimethylzinc with cyclohexenone. Although cyclopentenone gave only 52% ee with Et_2Zn and ligand **5a**, this value was still significantly higher than the enantioselectivity observed with Feringa's ligands. Therefore, we decided to vary the structure of the biaryl unit in a systematic manner, hoping that we would find an effective ligand for 1,4-additions to cyclopentenone. Here we report the results of this study which show that it is indeed possible to achieve high enantioselectivities of >90% ee with this notoriously difficult substrate. Very recently, after completion of our work, Chan et al. reported another very effective ligand, the diphosphite **3**, which gave up to 89% ee in the reaction of diethylzinc with cyclopentenone.[12]

Results and Discussion

In order to investigate the influence of substituents in the 3,3′-position of the binaphthyl backbone, a series of ligands **4**–**10** was synthesized. In addition, the octahydrobinaphthyl derivatives **11a** and **11b** and ligands **12a** and **12b**, containing a 1,1′-binaphthyl-8,8′-diyl unit, were also prepared. (Fig. 2)

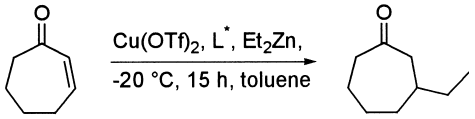
In the key step of the synthesis, the chiral binaphthol derivative was reacted with PCl_3 followed by treatment of the resulting chlorophosphite with the oxazoline alcohol **15** which led to the product in 12 to 91% yield (Procedure A, Scheme 1). For all the structures shown the (*R*,*S*)- as well as the (*S*,*S*)-diastereomers, designated by **a** and **b**, were synthesized.

According to Cram's procedure the methyl substituents in ligand **5** were introduced by *ortho*-lithiation and subsequent addition of methyl iodide.[13] For ligands **6**–**9** the substituents in the 3,3′-position were attached by a Suzuki coupling



Scheme 1.

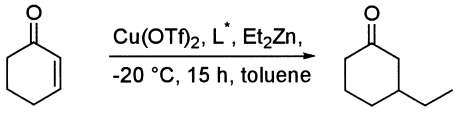
Table 1. 1,4-Addition of diethylzinc to cycloheptenone (all reactions were carried out under argon. 2–3 mol% of $Cu(OTf)_2$ were used. A copper to ligand ratio of 1:1.2 was applied)



Entry	Ligand	Yield[a] (%)	ee[b] **a** (%)	Ligand	Yield[a] (%)	ee[b] **b** (%)
1	**4a**	97	79 (+)	**4b**	95	31 (−)
2	**5a**	96	80 (+)	**5b**	97	20 (+)
3	**6a**	63	77 (+)	**6b**	83	67 (−)
4	**7a**	93	62 (+)	**7b**	99	83 (−)
5	**8a**	66	21 (−)	**8b**	96	82 (+)
6	**9a**	99	16 (+)	**9b**	99	44 (+)
7	**10a**	99	14 (−)	**10b**	97	94 (+)
8	**11a**	96	78 (+)	**11b**	99	48 (−)
9	**12a**	92	81 (+)	**12b**	96	12 (−)

[a] Determined by GC, using dodecane as an internal standard.
[b] Determined by GC (TBCD(β)).

Table 2. 1,4-Addition of diethylzinc to cyclohexenone (all reactions were carried out under argon. 2–3 mol% of $Cu(OTf)_2$ were used. A copper to ligand ratio of 1:1.2 was applied)



Entry	Ligand	Yield[a] (%)	ee[b] (%)	Ligand	Yield[a] (%)	ee[b] (%)
1	**4a**	91[c]	54 (*R*)	**4b**	99	34 (*S*)
2	**5a**	96[c]	90 (*R*)	**5b**	99	40 (*S*)
3	**6a**	69	66 (*R*)	**6b**	93	79 (*S*)
4	**7a**	95	48 (*R*)	**7b**	97	86 (*S*)
5	**8a**	99	16 (*R*)	**8b**	99	57 (*R*)
6	**9a**	99	43 (*R*)	**9b**	92	42 (*R*)
7	**10a**	90	37 (*S*)	**10b**	99	72 (*R*)
8	**11a**	99	63 (*R*)	**11b**	98	33 (*S*)
9	**12a**	95	79 (*R*)	**12b**	96	32 (*S*)

[a] Determined by GC, using dodecane as an internal standard.
[b] Determined by GC (Lipodex A).
[c] Stopped after 3 h.

procedure (Scheme 1).[14] Except for **7**, which required the protected 3,3′-diiodobinaphthol[15] as the precursor, the 3,3′-dibromo-2,2′-dimethoxy-1,1′-binaphthyl was reacted in high yields with the appropriate aromatic boronic acid.[16]

The 9,9′-biphenanthrol skeleton of **10** was synthesized in a solid state reaction according to a method by Toda, employing $[Fe(DMF)_3Cl_2][FeCl_4]$ as the coupling reagent.[17] Optical resolution was achieved via a tartaric acid derivative.[18] The ee (99%) of 9,9′-biphenanthrol was determined by HPLC analysis.[19] In the synthesis of ligand **11**, enantiomerically pure BINOL was partially hydrogenated in acetic acid at 10 bar of H_2 using 20 mol% of PtO_2 as catalyst in quantitative yield in 2 h. Racemic 8,8′-dimethoxy-1,1′-binaphthyl, the backbone of **12**, was prepared by *ortho*-lithiation and subsequent oxidative coupling.[20] Optical resolution was achieved by reacting the diol with (*S*)-*O*-acetylmandelic acid[21] and separating the crude mixture of diastereomers by preparative HPLC.[22] After cleavage of the chiral auxiliary with KOH/methanol, both enantiomers were isolated in enantiomerically pure form. The ee was determined by HPLC analysis.[23] To couple 8,8′-dihydroxy-1,1′-binaphthyl successfully with oxazoline alcohol **15** it emerged that slow addition of PCl_3 was crucial (procedure B). Otherwise both hydroxy groups reacted with PCl_3 giving rise to a bis(phosphite) rather than the desired cyclic phosphite.

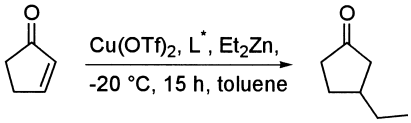
To evaluate these ligands we screened their copper complexes as catalysts in the 1,4-addition of diethylzinc to cyclic enones of varying ring size. In a typical procedure 2–3 mol% of $Cu(OTf)_2$ and a copper to ligand ratio of 1:1.2 were applied in the addition of diethylzinc (1.3 equiv.) to the corresponding enone. The reaction was usually carried out in toluene at −20°C for 15 h.

All ligands formed catalysts, which were highly reactive in the reaction with cycloheptenone (Table 1). Enantiomeric excesses of >80% were obtained with ligands **5a**, **7b**, **8b** and **12a**. The best result was obtained using ligand **10b** (94% ee, 98% yield). There is no obvious correlation between increasing steric bulk in the 3,3′-position in the ligand structure and the resulting ee. Surprisingly, the product configuration was reversed going from ligand **7b** (*S*,*S*) to **8b** (*S*,*S*) while the ee values were almost identical.

Excellent yields and high enantioselectivities were also obtained in the 1,4-addition of diethylzinc to cyclohexenone (Table 2). The best ee was achieved using ligand **5a** (90%). The best ee for the opposite enantiomer (86%) was obtained with **7b.** Independent of the diastereomer used, ligands **8**, **9** and **10** gave the same major enantiomer in the reaction. Again, there is no obvious correlation between increasing steric bulk in the 3,3′-position of the ligand structure and observed ee.

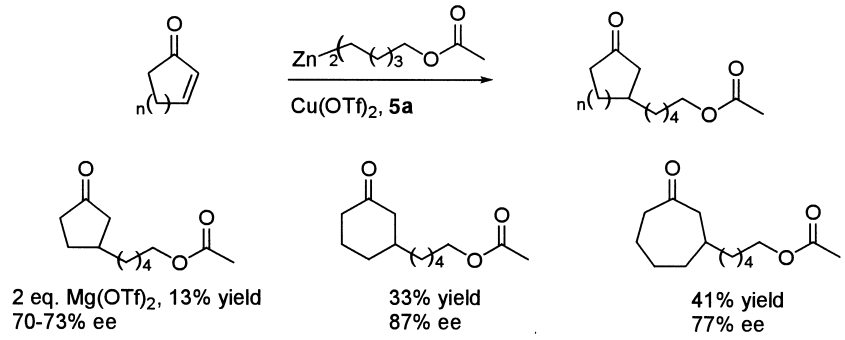
Not surprisingly the yields were only moderate in the catalytic addition of diethylzinc to cyclopentenone (20 to 70%, Table 3). This is a general problem with this substrate. The reaction goes to full conversion, but in addition to ethylcyclopentanone, products comprising more than one cyclopentanone unit are formed. Apparently the reactive zinc enolate, resulting from the 1,4-addition of diethylzinc, reacts with another molecule of cyclopentenone, leading to

Table 3. 1,4-Addition of diethylzinc to cyclopentenone (2–3 mol% of $Cu(OTf)_2$ were used. A copper to ligand ratio of 1:1.2 was applied)



Entry	Ligand	Yield[a] (%)	ee[b] (%)	Ligand	Yield[a] (%)	ee[b] (%)
1	**4a**	56	65 (*R*)	**4b**	40	13 (*S*)
2	**5a**	52	72 (*R*)	**5b**	22	24 (*S*)
3	**6a**	49	91 (*R*)	**6b**	57	83 (*S*)
4	**7a**	41	94 (*R*)	**7b**	44	83 (*S*)
5	**8a**	7	25 (*S*)	**8b**	37	19 (*R*)
6	**9a**	54	24 (*S*)	**9b**	42	7 (*R*)
7	**10a**	37	41 (*S*)	**10b**	44	54 (*R*)
8	**11a**	41	60 (*R*)	**11b**	40	42 (*S*)
9	**12a**	69	90 (*R*)	**12b**	63	32 (*S*)

[a] Determined by GC, using undecane as an internal standard.
[b] Determined by GC (Ivadex 7).

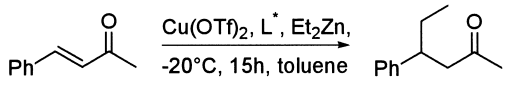


Scheme 2.

complex mixtures of products. Yields given in the table were determined by quantitative GC-analysis, using tridecane as internal standard. The yields of purified products were 10–20% lower because of the difficult separation from side products and the high volatility of the product. Ligand **12a** led to the best yield (69%), ligand **7a** to the best enantioselectivity (94% ee). In general the (*R*,*S*)-diastereomers **4a**–**12a** give higher enantioselectivity than the (*S*,*S*)-diastereomers **4b**–**12b**. Accordingly for this substrate the (*R*,*S*)-ligands can be considered as the 'matched' diastereomers. Ligands **6a** and **7a**, containing phenyl- or biphenyl groups in *ortho* position of the binaphthyl unit, gave the highest enantioselectivities (91 and 94% ee). More bulky substituents such as mesityl- or 3,5-di-*tert*-butylphenyl groups (ligands **8** and **9**) proved to be detrimental to the enantioselectivity. Taking high yield and high ee into consideration the best result was achieved with ligand **12a** (69% yield, 90% ee, entry 9).

In contrast to Grignard reagents, a broad spectrum of functionality is tolerated by diorganozinc reagents. Taking advantage of this feature, a functionalized diorganozinc reagent was used in the 1,4-addition to cyclopentenone, -hexenone and -heptenone using ligand **5a**. The results are summarized in Scheme 2. Although moderate to good enantioselectivities could be obtained, conversions and yields were low because of the low reactivity of the functionalized organozinc reagent.

Table 4. 1,4-Addition of diethylzinc to 4-phenyl-3-buten-2-one (2–3 mol% of $Cu(OTf)_2$ were used. A copper to ligand ratio of 1:1.2 was applied)



Entry	Ligand	Yield[a] (%)	ee[b] (%)
1	**4a**	55	15 (*S*)[c]
2	**4b**	29	12 (*R*)
3	**5a**	47	4 (*S*)[c]
4	**7a**	66	34 (*S*)
5	**7b**	90	58 (*S*)
6	**8b**	70	59 (*S*)
7	**9a**	89	31 (*S*)
8	**9b**	99	87 (*S*)
9	**10b**	68	37 (*S*)

[a] Determined by GC, using 1,2,4-triethylbenzene as an internal standard.
[b] Determined by HPLC.
[c] Stopped after 3 h.

In order to extend the range of substrates for these catalysts, we also studied 1,4-addition of diethylzinc to *trans*-4-phenyl-3-buten-2-one (Table 4). In this case, by far the best result was obtained with ligand **9b**, which gave excellent yield and promising enantioselectivity (99% yield, 87% ee, entry 8).

Conclusion

Our results show that the new oxazoline-phosphites described herein are effective ligands for enantiocontrol in the conjugate addition of organozinc reagents to enones. Good results were obtained for cyclic enones as well as for an acyclic substrate, 4-phenyl-3-buten-2-one. Optimization of the ligand structure led to a catalyst affording up to 94% ee in the 1,4-addition of diethylzinc to cyclopentenone, which is the highest ee reported to date for this substrate. Considering the modular construction and the straightforward synthesis of these ligands, it should be possible to develop tailored ligands for other substrates which so far have given unsatisfactory results.

Experimental

Optical rotation was measured by Perkin–Elmer PE-141 polarimeter at 589 nm. Melting points were measured on a Büchi 512 apparatus. NMR spectra were recorded on either a Varian XL-300 (300 MHz) or a Bruker DRX 500 (500 MHz). Chemical shifts are reported in ppm from tetramethylsilane with the solvent reference as internal standard ($CDCl_3$: δ 7.24 for ^{1}H- and δ 77.0 for ^{13}C NMR; triphenylphosphate: δ −18 for ^{31}P NMR). Infrared spectra were recorded on a Perkin–Elmer 1600 FT-spectrometer. Mass spectra were obtained with a Varian VG-70-250 instrument. High resolution mass spectrometry was performed at the 'Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr' (Germany). $Cu(OTf)_2$ was purchased from FLUKA. Enones were purchased from ALDRICH and purified by distillation or column chromatography prior to use. Reactions were conducted in flame-dried glassware under an inert gas atmosphere of argon. In order to obtain reproducible enantioselectivities in the 1,4-addition of diethylzinc to enones it proved necessary to handle $Cu(OTf)_2$ in a glove box. All yields obtained in the 1,4-addition of diorganozinc reagents to enones were determined by quantitative GC-analysis. To confirm the values, products

were isolated and purified by flash chromatography. For ethylcyclohexanone and ethylcycloheptanone the yields of purified products were 5 to 7% lower than the GC-values. The difference was more significant (8–22%) for ethylcyclopentanone due to the difficult separation from side-products and the high volatility of the product.

Procedure A. {2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}[(*R*)-3,3′-diphenylbinaphthyl-2,2′-diyl]-phosphite (6a)

In a dry 50 mL Schlenk tube (*R*)-3,3′-diphenyl-2,2′-dihydroxy-1,1′-binaphthyl (0.55 g, 1.1 mmol) was dissolved under argon in freshly distilled toluene (15 mL). PCl_3 (0.16 mL, 1.8 mmol) and pyridine (0.45 mL, 5.6 mmol) were added. A white precipitate was formed. The reaction was stirred at 95°C for 18 h. Afterwards the heterogeneous mixture was filtered under argon, and all volatile components were removed at reduced pressure. ^{31}P NMR showed exclusively one peak at 177.8 ppm for the chlorophosphite. In a second 50 mL Schlenk tube DMAP (0.15 g, 1.2 mmol) and Et_3N (1.6 mL, 11.4 mmol) were diluted in 10 mL of dry toluene. At −78°C the chlorophosphite was added as a solution in toluene (25 mL) over 2 h by means of a dropping funnel. The oxazoline alcohol **15** (0.23 g, 1.2 mmol) was added as a solid subsequently. The reaction was allowed to warm to room temperature and stirred for 36 h. Celite (2 g) was added to the reaction mixture and the solvent was removed at reduced pressure. The crude product absorbed by Celite was purified by column chromatography on aluminium oxide (basic) using hexane/dichloromethane 1:4 for elution (R_f=0.6). Product **6a** was obtained as a colorless solid in 89% yield (0.66 g).

Procedure B. {2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}[(*R*)-1,1′-binaphthyldihydrox-8,8′-diyl]-phosphite (12a)

In a dry 50 mL Schlenk tube 8,8′-dihydroxy-1,1′-binaphthyl (0.5 g, 1.7 mmol) and pyridine (0.7 mL, 8.7 mmol) were stirred under argon in freshly distilled toluene (5 mL). By means of a syringe pump PCl_3 (0.2 mL, 2.3 mmol) was added as a solution in toluene (5 mL) over 5 h. The reaction mixture was stirred for 14 h at room temperature. After a filtration under argon, all volatile components were removed under reduced pressure. ^{31}P NMR showed exclusively one peak at 178.8 ppm for the chlorophosphite. For coupling with **15** see procedure A. The crude product was purified by column chromatography on aluminium oxide (neutral) using hexane/dichloromethane 1:3 for elution, affording **12a** as a colorless solid in 28% yield (243 mg).

General procedure for the copper-catalyzed 1,4-addition

$Cu(OTf)_2$ (15.2 mg, 0.04 mmol, 3.0 mol%) was weighed in the glove box. Ligand **6a** (33 mg, 0.05 mmol, 3.6 mol%) and dry toluene (10 mL) were added. The solution was stirred for 1 h at room temperature under an argon atmosphere. The reaction was cooled to −20°C. Cyclopentenone (113 mg, 1.4 mmol) was added followed by Et_2Zn (1.8 mL, 1.3 equiv., 1 M in toluene) which was added dropwise within 2 min. After stirring for 15 h at −20°C the reaction mixture was hydrolyzed by addition of saturated NH_4Cl and NH_3 (32%) solutions (2 mL each). *n*-Undecane (194 mg, 1.2 mmol) as internal standard was added and the mixture was allowed to warm up to room temperature. After dilution with water and Et_2O (2 mL each) and stirring for 10 min., an aliquot of the organic phase was taken, filtered through a pad of cotton and analyzed by GC (49% yield and 91% ee). The aqueous phase was separated and extracted with Et_2O (3×3 mL). The combined organic phases were dried over $MgSO_4$. Most of the solvent was removed at reduced pressure. The crude product was purified by gradient flash column chromatography (silica-gel, 2×15 cm, going from pentane (to remove the toluene) to pentane/diethyl ether 4:1) to afford 65.0 mg (42%) of 3-ethylcyclopentanone as a colorless liquid.

(−)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*R*)-binaphthyl-2,2′-diyl]phosphite (4a). 65% yield, colorless solid, $\alpha_D^{25}=-359.8$ (*c* 0.49, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (s, $C(CH_3)_3$, 9H), 1.66 (s, $C(CH_3)_2$, 3H), 1.72 (s, $C(CH_3)_2$, 3H), 3.93–3.99 (m, 1H, CH), 4.19–4.33 (m, 2H, CH_2), 7.19–7.50 (m, 8H), 7.88–7.95 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.8 $C(CH_3)_3$, 28.2 (d, J_{CP}=6.6 Hz, $C(CH_3)_2$), 28.4 (d, J_{CP}=7.4 Hz, $C(CH_3)_2$), 33.8 $C(CH_3)_3$, 69.6 CH_2, 75.7 (d, J_{CP}=11.1 Hz, $C(CH_3)_2$), 75.8 CH, 121.9 CH, 122.0 CH, 123.1 (d, J_{CP}=2.4 Hz, C), 124.4 (d, J_{CP}=5.4 Hz, C), 124.6 CH, 124.8 CH, 125.8 CH, 126.1 CH, 127.0 CH, 127.1 CH, 128.2 CH, 128.3 CH, 129.3 CH, 130.0 CH, 131.1 C, 131.5 C, 132.6 C, 132.8 C, 148.0 (d, J_{CP}=2.3 Hz, C–O), 148.1 (d, J_{CP}=4.7 Hz, C–O), 168.2 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 150.3. IR (KBr) ν (cm^{-1}) 2962, 2907, 1665, 1620, 1591, 1508, 1464, 1462, 1385, 1367, 1327, 1299, 1258, 1157, 1128, 1071, 1027, 969, 944, 908, 887, 865, 851, 829. MS (EI) *m/z* (rel int%) 499 (M^+, 67), 442 (15), 374 (14), 332 (91), 315 (7), 268 (79), 239 (32), 226 (9), 168 (100), 111 (27), 82 (10), 69 (11), 57 (28), 41 (23). HRMS *m/z* calculated for $C_{30}H_{30}NO_4P$ (M^+) 499.1912, found 499.1907.

(+)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*S*)-binaphthyl-2,2′-diyl]phosphite (4b). 30% yield, colorless solid, mp 94°C, $\alpha_D^{25}=+269.0$ (*c* 3.10, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (s, $C(CH_3)_3$, 9H), 1.65 (s, $C(CH_3)_2$, 3H), 1.75 (s, $C(CH_3)_2$, 3H), 3.95–4.00 (m, 1H), 4.20–4.35 (m, 2H), 7.22–7.52 (m, 8H), 7.89–7.96 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.8 $C(CH_3)_3$, 28.1 (d, J_{CP}=7.9 Hz, $C(CH_3)_2$), 28.2 (d, J_{CP}=5.7 Hz, $C(CH_3)_2$), 33.9 $C(CH_3)_3$, 69.7 CH_2, 75.7 CH, 77.2 $C(CH_3)_2$, 121.9 CH, 122.4 CH, 123.2 C, 124.5 (d, J_{CP}=3.1 Hz, C), 124.6 CH, 124.8 CH, 125.8 CH, 126.0 CH, 126.9 CH, 127.0 CH, 128.1 CH, 128.2 CH, 129.3 CH, 130.0 CH, 131.1 C, 131.4 C, 132.7 C, 132.8 C, 147.9 (d, J_{CP}=2.3 Hz, C–O), 148.0 (d, J_{CP}=3.7 Hz, C–O), 168.3 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 151.5. IR (KBr) ν (cm^{-1}) 3060, 2973, 1620, 1590, 1509, 1464, 1385, 1366, 1327, 1256, 1156, 1128, 1071, 1045, 979, 944, 853. MS (EI) *m/z* (rel int%) 499 (M^+, 88), 442 (21), 374 (15), 332 (77), 268 (100), 239 (46), 226 (15), 168 (98), 110 (19), 82 (15), 69 (11), 57 (53), 41 (39). HRMS *m/z* calculated for $C_{30}H_{30}NO_4P$ (M^+) 499.1912, found 499.1904. Chlorophosphite intermediate: ^{31}P NMR (121 MHz, $CDCl_3$) δ 178.0.

(−){2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*R*)-(3,3′-dimethyl)binaphthyl-2,2′-diyl]phosphite (5a). 68% yield, colorless solid, $\alpha_D^{25}=-379.0$ (*c* 0.92, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, $C(CH_3)_3$, 9H), 1.69 (s, $C(CH_3)_2$, 6H), 2.59 (s, $Ar(CH_3)$, 6H), 3.93 (dd, *J*=7.3 and 10.1 Hz, CH, 1H), 4.12–4.32 (m, CH_2, 2H), 7.12–7.37 (m, 6H), 7.75–7.83 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.43 (d, *J*=2.1 Hz, $Ar(CH_3)$), 17.95 $Ar(CH_3)$, 25.80 $C(CH_3)_3$, 28.25 (d, J_{CP}=7.7 Hz, $C(CH_3)_2$), 28.39 (d, J_{CP}=7.5 Hz, $C(CH_3)_2$), 33.87 $C(CH_3)_3$, 69.56 CH_2, 75.88 CH, 75.90 (d, J_{CP}=11.4 Hz, $C(CH_3)_2$), 122.88 C, 122.91 C, 124.73 CH, 124.78 CH, 124.86 CH, 125.11 CH, 127.02 CH, 127.07 CH, 127.33 CH, 127.47 CH, 129.18 CH, 129.54 CH, 130.26 C, 130.28 C, 130.78 C, 131.08 C, 131.36 C, 131.48 C, 131.76 C, 147.03 (d, J_{CP}=2.5 Hz, C–O), 148.03 (d, J_{CP}=5.8 Hz, C–O), 168.34 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 149.3. IR (KBr) ν (cm^{-1}) 2956, 2869, 1670, 1596, 1477, 1414, 1364, 1334, 1244, 1206, 1148, 1120, 1100, 1095, 980, 957, 901, 881, 860. MS (EI) *m*/*z* (rel int%) 527 (M^+, 45), 470 (42), 376 (18), 360 (67), 345 (26), 296 (71), 280 (12), 252 (14), 168 (69), 151 (100), 110 (10), 83 (33). HRMS *m*/*z* calculated for $C_{32}H_{34}NO_4P$ (M^+) 527.2225 found 527.2205. Chlorophosphite intermediate: ^{31}P NMR (121 MHz, $CDCl_3$) δ 175.7.

(+){2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*S*)-(3,3′-dimethyl)binaphthyl-2,2′-diyl]phosphite (5b). 26 % yield, colorless solid, $\alpha_D^{25}=+339.1$ (*c* 0.45, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, $C(CH_3)_3$, 9H), 1.68 (s, $C(CH_3)_2$, 3H), 1.69 (s, $C(CH_3)_2$, 3H), 2.59 (s, $Ar(CH_3)$, 6H), 3.95 (dd, *J*=7.7 and 10.1 Hz, CH, 1H), 4.19 (t, *J*=8.2 Hz, 1H), 4.28 (dd, *J*=8.7 and 10.1 Hz, 1H), 7.13–7.36 (m, 5H), 7.75–7.83 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.45 (d, *J*=2.3 Hz, $Ar(CH_3)$), 18.01 $Ar(CH_3)$, 25.83 $C(CH_3)_3$, 28.17 $C(CH_3)_2$), 28.29 $C(CH_3)_2$), 28.40 $C(CH_3)_2$), 33.83 $C(CH_3)_3$, 69.56 CH_2, 75.86 CH, 75.88 (d, J_{CP}=11.1 Hz, $C(CH_3)_2$), 124.59 CH, 124.69 C, 124.77 C, 124.86 CH, 125.11 CH, 127.00 CH, 127.10 CH, 127.33 CH, 127.46 CH, 129.15 CH, 129.53 CH, 130.23 C, 130.26 C, 130.68 C, 131.03 C, 131.33 C, 131.47 C, 131.72 C, 147.01 (d, J_{CP}=2.6 Hz, C–O), 148.01 (d, J_{CP}=5.3 Hz, C–O), 168.34 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 148.9. IR (KBr) ν (cm^{-1}) 2955, 2868, 1671, 1502, 1478, 1462, 1414, 1384, 1364, 1334, 1241, 1209, 1148, 1127, 1102, 1085, 980, 954, 907, 881, 862, 803, 767, 747. MS (EI) *m*/*z* (rel int%) 528 (M^+, 53), 470 (100), 376 (12), 360 (59), 345 (20), 296 (60), 253 (11), 168 (41), 151 (14), 95 (11), 57 (13). HRMS *m*/*z* calculated for $C_{32}H_{34}NO_4P$ (M^+) 527.2225 found 527.2216.

(−)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*R*)-(3,3′-diphenyl)binaphthyl-2,2′-diyl]phosphite (6a). 89% yield, colorless solid, mp 106°C, $\alpha_D^{25}=-365.6$ (*c* 0.94, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.65 (s, $C(CH_3)_3$, 9H), 0.82 (s, CH_3, 3H), 1.14 (s, CH_3, 3H), 3.42 (t, *J*=8.1 Hz, 1H), 3.60 (dd, *J*=7.6 and 9.9 Hz, 1H), 3.78 (dd, *J*=8.5 and 9.8 Hz, 1H), 7.23–7.30 (m, 2H), 7.34–7.38 (m, 3H), 7.41–7.47 (m, 7H), 7.71–7.73 (m, 4H), 7.92–7.95 (m, 2H), 7.98–7.99 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.59 $C(CH_3)_3$, 26.56 (d, J_{CP}=11.5 Hz, $C(CH_3)_2$), 27.83 (d, J_{CP}=3.9 Hz, $C(CH_3)_2$), 33.67 $C(CH_3)_3$, 69.05 CH_2, 75.54 CH, 75.82 (d, J_{CP}=14.6 Hz, $C(CH_3)_2$), 124.22 CH, 124.26 CH, 125.05 CH, 125.34 CH, 125.92 CH, 126.15 CH, 126.99 CH, 127.24 CH, 128.11 CH, 128.20 CH, 128.32 CH, 130.59 CH, 130.27 CH, 130.61 CH, 131.10 C, 131.27 C, 132.32 C, 132.45 C, 134.85 C, 134.90 C, 138.04 C, 138.73 C, 145.13 (d, J_{CP}=4.4 Hz, C–O), 145.42 (d, J_{CP}=2.0 Hz, C–O), 168.19 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 150.7. IR (KBr) ν (cm^{-1}) 3054, 2954, 1666, 1409, 1151, 989, 951, 881, 848, 765, 750, 698. MS (EI) *m*/*z* (rel int%) 651 (M^+, 100), 594 (11), 566 (2), 526 (6), 500 (6), 484 (72), 465 (21), 420 (42), 389 (7), 315 (5), 215 (2), 168 (78), 110 (7), 57 (15). Anal. calcd for $C_{42}H_{38}NO_4P$ C, 77.40%; H, 5.88%. Found C, 77.43%; H, 5.83%.

(+)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*S*)-(3,3′-diphenyl)binaphthyl-2,2′-diyl]phosphite (6b). 89% yield, colorless solid, mp 121°C, $\alpha_D^{20}=+311.7$ (*c* 0.46, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (s, $C(CH_3)_3$, 9H), 0.93 (s, CH_3, 3H), 1.12 (s, CH_3, 3H), 3.57–3.59 (m, 2H), 3.72–3.73 (m, 1H), 7.24–7.38 (m, 4H), 7.40–7.49 (m, 8H), 7.66–7.74 (m, 4H), 7.91–7.95 (m, 2H), 7.97–7.98 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.60 $C(CH_3)_3$, 26.48 (d, J_{CP}=11.9 Hz, $C(CH_3)_2$), 27.85 (d, J_{CP}=1.3 Hz, $C(CH_3)_2$), 33.63 $C(CH_3)_3$, 68.89 CH_2, 75.43 CH, 75.68 (d, J_{CP}=14.0 Hz, $C(CH_3)_2$), 124.16 C, 124.19 C, 125.03 CH, 125.31 CH, 125.67 C, 125.75 C, 125.88 CH, 126.11 CH, 127.01 CH, 127.17 CH, 127.97 CH, 128.05 CH, 128.21 CH, 128.32 CH, 130.09 CH, 130.28 CH, 130.51 CH, 131.10 C, 131.22 C, 132.34 C, 132.49 C, 134.84 C, 134.99 C, 138.02 C, 138.68 C, 145.23 (d, J_{CP}=2.3 Hz, C–O), 145.50 (d, J_{CP}=4.4 Hz, C–O), 168.10 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 150.6. IR (KBr) ν (cm^{-1}) 3052, 2952, 2363, 1665, 1497, 1454, 1407, 1362, 1247, 1210, 1179, 1153, 1129, 987, 951, 883, 846, 800, 764, 749, 701. MS (EI) *m*/*z* (rel int%) 651 (M^+, 100), 594 (10), 526 (6), 501 (9), 484 (66), 465 (18), 420 (48), 389 (7), 315 (5), 215 (1), 168 (41), 110 (7), 57 (24). HRMS *m*/*z* calculated for $C_{42}H_{38}NO_4P$ (M^+) 651.2538, found 651.2535.

(−)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-{(*R*)-[3,3′-bis(4-biphenylyl)](binaphthyl-2,2′-diyl} phosphite (7a). 48% yield, colorless solid, mp 125°C. $\alpha_D^{25}=-301.0$ (*c* 0.89, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.56 (s, $C(CH_3)_3$, 9H), 0.89 (s, $C(CH_3)_2$, 3H), 1.18 (s, $C(CH_3)_2$, 3H), 3.38 (t, *J*=8.2 Hz, 1H), 3.53 (dd, *J*=10.1 and 7.8 Hz, 1H), 3.72 (dd, *J*=10.1 and 8.7 Hz, 1H), 7.32–7.39 (m, 4H), 7.42–7.51 (m, 6H), 7.61–7.72 (m, 8H), 7.83–7.85 (m, 4H), 7.96–8.00 (m, 3H), 8.06–8.14 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.54 $C(CH_3)_3$, 26.69 (d, J_{CP}=11.3 Hz, $C(CH_3)_2$), 27.91 (d, J_{CP}=3.9 Hz, $C(CH_3)_2$), 33.54 $C(CH_3)_3$, 69.06 CH_2, 75.57 CH, 75.85 (d, J_{CP}=14.3 Hz, $C(CH_3)_2$), 125.14 CH, 125.42 CH, 126.02 CH, 126.24 CH, 126.64 CH, 126.89 CH, 127.07 CH, 127.10 CH, 127.18 CH, 127.26 CH, 127.35 CH, 127.43 CH, 127.51 CH, 128.28 CH, 128.39 CH, 128.76 CH, 128.82 CH, 128.87 CH, 130.02 CH, 130.47 CH, 130.65 CH, 130.75 CH, 131.19 C, 131.39 C, 132.44 C, 132.59 C, 134.53 C, 137.05 C, 137.81 C, 139.91 C, 140.30 C, 140.54 C, 141.01 C, 141.29 C, 145.29 (d, J_{CP}=2.2 Hz, C–O), 145.62 (d, J_{CP}=4.9 Hz, C–O), 168.10 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 150.5. IR (KBr) ν (cm^{-1}) 3054, 3028, 2953, 1666, 1488, 1420, 1396, 1364, 1249, 1196, 1178, 1151, 1132, 1077, 1008, 989, 950, 884, 848, 838, 799, 766, 751, 737, 694. MS (EI) *m*/*z* (rel int %) 803 (M^+, 84), 746 (12), 653 (10), 636 (100), 617 (25), 572 (54), 555 (3), 544 (5), 483

(5), 465 (5), 418 (4), 391 (5), 286 (6), 168 (81), 149 (5), 110 (58), 82 (25), 69 (26). Anal. calcd for $C_{54}H_{46}NO_4P$ C, 80.68%; H, 5.77%. Found C, 80.49%; H, 5.88%. Chlorophosphite intermediate: ^{31}P NMR (121 MHz, $CDCl_3$) δ 176.3.

(+)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-{(*S*)-[3,3′-bis(4-biphenylyl)]binaphthyl-2,2′-diyl} phosphite (7b). 62% yield, colorless solid, mp 121°C, $\alpha_D^{25}=+252.5$ (*c* 1.19, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 0.59 (s, 9H), 0.93 (s, 3H), 1.13 (s, 3H), 3.41–3.49 (m, 2H), 3.63 (dd, *J*=12.3 and 13.2 Hz, 1H), 7.18–7.38 (m, 6H), 7.41–7.48 (m, 7H), 7.65–7.71 (m, 7H), 7.76–7.80 (m, 4H), 7.93–7.98 (m, 2H), 8.03–8.05 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.37 C(CH_3)$_3$, 26.37 (d, J_{CP}=11.9 Hz, C(CH_3)$_2$), 27.93 (d, J_{CP}=4.0 Hz, C(CH_3)$_2$), 33.50 $C(CH_3)_3$, 68.87 CH_2, 75.29 CH, 75.72 (d, J_{CP}=14.1 Hz, $C(CH_3)_2$), 124.25 C, 125.11 CH, 125.41 CH, 125.79 C, 125.84 C, 125.98 CH, 126.21 CH, 126.58 CH, 126.84 CH, 127.05 CH, 127.34 CH, 127.39 CH, 128.25 CH, 128.37 CH, 128.81 CH, 128.86 CH, 130.35 CH, 130.59 CH, 130.70 CH, 131.14 C, 131.29 C, 132.37 C, 132.52 C, 134.41 C, 134.62 C, 136.97 C, 137.73 C, 139.91 C, 140.19 C, 140.60 C, 140.88 C, 145.24 C–O, 145.61 (d, J_{CP}=4.0 Hz, C–O), 167.98 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 150.6. IR (KBr) ν (cm^{-1}) 3053, 3027, 2954, 2903, 2867, 1599, 1665, 1487, 1449, 1419, 1395, 1364, 1248, 1207, 1196, 1178, 1151, 1131, 1077, 988, 950, 883, 837, 766, 750, 736, 693. MS (EI) *m/z* (rel int %) 803 (M^+, 100), 746 (23), 678 (5), 636 (83), 617 (17), 572 (54), 543 (4), 465 (4), 391 (5), 318 (5), 286 (13), 262 (6), 215 (2), 168 (60), 110 (63), 82 (17), 69 (18), 57 (37). Anal. calcd for $C_{54}H_{46}NO_4P$ C**,** 80.68%; H, 5.77%. Found C, 80.75%; H, 5.84%.

(−)-{2′-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-{(*R*)-[3,3′-bis(2,4,6-trimethylphenyl)]binaphthyl-2,2′-diyl}-phosphite (8a). 88% yield, colorless solid, mp 223°C, $\alpha_D^{23}=-125.7$ (*c* 0.52, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.75 (s, C(CH_3)$_3$, 9H), 1.03 (s, C(CH_3)$_2$, 3H), 1.12 (s, C(CH_3)$_2$, 3H), 1.99 (s, $ArCH_3$, 3H), 2.08 (s, $ArCH_3$, 6H), 2.21 (s, $ArCH_3$, 3H), 2.30 (s, $ArCH_3$, 3H), 2.32 (s, $ArCH_3$, 3H), 3.49–3.60 (m, 2H), 3.74 (dd, *J*=7.6 and 9 Hz, 1H), 6.90–6.94 (m, 4H), 7.23–7.28 (m, 2H), 7.36–7.45 (m, 4H), 7.75–7.76 (m, 2H), 7.85–7.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.34 $ArCH_3$, 20.66 $ArCH_3$, 21.06 $ArCH_3$, 21.28 $ArCH_3$, 21.41 $ArCH_3$, 22.45 $ArCH_3$, 25.62 C(CH_3)$_3$, 27.35 (d, J_{CP}=9.1 Hz, C(CH_3)$_2$), 27.40 (d, J_{CP}=9.0 Hz, C(CH_3)$_2$), 33.59 $C(CH_3)_3$, 68.89 CH_2, 75.54 CH, 75.56 (d, J_{CP}=14.7 Hz, $C(CH_3)_2$), 123.20 C, 123.25 C, 124.68 CH, 124.96 CH, 125.57 CH, 125.77 CH, 127.17 CH, 127.28 CH, 127.68 CH, 127.74 CH, 127.92 CH, 128.16 CH, 128.22 CH, 130.85 CH, 130.96 CH, 133.41 C, 136.40 C, 136.57 C, 136.63 C, 137.59 C, 137.74 C, 145.98 CO, 147.06 CO, 168.46 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 148.1. IR (KBr) ν (cm^{-1}) 2954, 2920, 2866, 1666, 1612, 1495, 1212, 1149, 1125, 991, 958, 941, 882, 846, 806, 750, 698. MS (EI) *m/z* (rel int %) 735 (M^+, 63), 678 (63), 568 (32), 549 (9), 531 (3), 504 (21), 487 (6), 471 (7), 455 (4), 368 (2), 259 (3), 243 (14), 229 (4), 216 (4), 169 (100), 112 (7), 69 (8). Anal. calcd for $C_{48}H_{50}NO_4P$ C, 78.34%; H, 6.85%. Found C, 78.19%; H, 6.79%. Chlorophosphite intermediate: ^{31}P NMR (121 MHz, $CDCl_3$) δ 173.1.

(+)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-{(*S*)-[3,3′-bis(2,4,6-trimethylphenyl)]binaphthyl-2,2′-diyl}phosphite (8b). 91% yield, colorless solid, mp 130°C, $\alpha_D^{23}=+73.6$ (*c* 1.08, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.75 (s, C(CH_3)$_3$, 9H), 1.09 (s, C(CH_3)$_2$, 3H), 1.19 (s, C(CH_3)$_2$, 3H), 2.06 (s, $ArCH_3$, 3H), 2.08 (s, $ArCH_3$, 3H), 2.09 (s, $ArCH_3$, 3H), 2.29 (s, $ArCH_3$, 3H), 2.33 (s, $ArCH_3$, 3H), 2.35 (s, $ArCH_3$, 3H), 3.49 (dd, *J*=6.4 and 8.5 Hz, 1H), 3.56–3.64 (m, 2H), 6.91–6.94 (m, 4H), 7.23–7.29 (m, 2H), 7.33–7.46 (m, 4H), 7.75 (s, 2H), 7.85–7.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.31 $ArCH_3$, 20.67 $ArCH_3$, 21.03 $ArCH_3$, 21.37 $ArCH_3$, 21.46 $ArCH_3$, 22.46 $ArCH_3$, 25.62 C(CH_3)$_3$, 26.96 (d, J_{CP}=4.0 Hz, C(CH_3)$_2$), 27.00 (d, J_{CP}=11.0 Hz, C(CH_3)$_2$), 33.65 $C(CH_3)_3$, 68.64 CH_2, 75.31 CH, 75.46 ($C(CH_3)_2$), 122.74 C, 124.72 CH, 125.02 CH, 125.29 CH, 125.63 CH, 125.82 CH, 127.17 CH, 127.24 CH, 127.57 CH, 127.62 CH, 127.96 CH, 128.03 CH, 128.22 CH, 130.70 CH, 130.93 CH, 131.30 C, 131.50 C, 131.60 C, 133.47 C, 134.10 C, 134.49 C, 135.13 C, 136.40 C, 136.74 C, 136.79 C, 137.54 C, 146.36 C, 167.29 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 148.1. IR (KBr) ν (cm^{-1}) 2957, 2920, 2868, 1665, 1611, 1495, 1479, 1404, 1262, 1211, 1150, 1129, 957, 941, 882, 846, 806, 750, 728, 698. MS (EI) *m/z* (rel int%) 735 (M^+, 100), 678 (72), 608 (6), 585 (9), 566 (29), 549 (7), 504 (17), 487 (7), 471 (8), 455 (4), 259 (3), 243 (16), 229 (5), 216 (4), 168 (32), 152 (18), 112 (10), 83 (11). Anal. calcd for $C_{48}H_{50}NO_4P$ C, 78.34%; H, 6.85%. Found C, 78.22%; H, 6.91%.

(−)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-{(*R*)-[3,3′-bis(3,5-di-*tert*-butylphenyl)]binaphthyl-2,2′-diyl}phosphite (9a). 46% yield, colorless solid, mp 167°C, $\alpha_D^{21}=-282.1$ (*c* 0.31, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.63 (s, C(CH_3)$_3$, 9H), 0.72 (s, CH_3, 3H), 1.07 (s, CH_3, 3H), 1.36 (s, ArC(CH_3)$_3$, 18H), 1.37 (s, ArC(CH_3)$_3$, 18H), 3.17–3.31 (m, 1H), 3.48–3.62 (m, 2H), 7.21–7.3 (m, 1H), 7.37–7.46 (m, 8H), 7.50–7.58 (dd, *J*=1.8 and 14.0 Hz, 2H), 7.93–8.05 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.75 C(CH_3)$_3$, 26.34 (d, J_{CP}=11.0 Hz, C(CH_3)$_2$), 27.89 C(CH_3)$_2$, 31.55 ArC(CH_3)$_3$, 31.67 ArC(CH_3)$_3$, 33.52 $C(CH_3)_3$, 34.94 Ar$C(CH_3)_3$, 68.66 CH_2, 75.35 $C(CH_3)_2$, 75.51 CH, 121.05 CH, 121.49 CH, 124.19 C, 124.24 C, 124.30 C, 124.38 CH, 124.66 CH, 124.91 CH, 125.21 CH, 125.68 CH, 125.89 CH, 127.08 CH, 127.14 CH, 128.18 CH, 128.25 CH, 130.08 CH, 130.73 CH, 131.18 C, 131.28 C, 132.28 C, 135.64 C, 136.29 C, 136.30 C, 137.25 C, 137.63 C, 145.31 (d, J_{CP}=2.0 Hz, C–O), 145.70 (d, J_{CP}=2.0 Hz, C–O), 150.16 C, 150.35 C, 167.96 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 149.1. IR (KBr) ν (cm^{-1}) 2962, 2904, 2868, 1669, 1595, 1477, 1456, 1401, 1363, 1207, 982, 967, 906, 886, 828, 800, 749. MS (EI) *m/z* (rel int%) 875 (M^+, 100), 818 (5), 708 (21), 644 (4), 563 (4), 539 (2), 507 (3), 168 (32). Anal. calcd for $C_{58}H_{70}NO_4P$ C, 79.51%; H, 8.05%. Found C, 79.42%; H, 8.09%. Chlorophosphite intermediate: ^{31}P NMR (121 MHz, $CDCl_3$) δ 175.6.

(+)-{2-[(4′*S*)-(4′-tert-Butyloxazolin-2′-yl)]-2-methylethyl}-{(*S*)-[3,3′-bis(3,5-di-*tert*-butylphenyl)]binaphthyl-2,2′-diyl}phosphite (9b). 85% yield, colorless solid, mp 113°C. $\alpha_D^{21}=+163.9$ (*c* 0.41, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.59 (s, C(CH_3)$_3$, 9H), 0.63 (s, CH_3, 3H), 1.00 (s, CH_3, 3H), 1.28 (s, ArC(CH_3)$_3$, 18H), 1.29 (s, ArC(CH_3)$_3$, 18H), 2.87–2.97 (m, 1H), 3.38–3.47 (m, 2H), 7.31–7.43 (m,

10H), 7.48–7.49 (m, 2H), 7.85 (s, 2H), 7.87–7.9 (m, 1H), 7.91 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.45 C(CH_3)$_3$, 26.15 (d, J_{CP}=10.8 Hz, C(CH_3)$_2$), 28.12 (d, J_{CP}=2.6 Hz, C(CH_3)$_2$, 31.63 ArC(CH_3)$_3$, 31.63 ArC(CH_3)$_3$, 33.60 C(CH_3)$_3$, 34.94 ArC(CH_3)$_3$, 68.35 CH_2, 75.28 CH, 75.35 (d, J_{CP}=16.4 Hz, C(CH_3)$_2$), 121.20 CH, 121.49 CH, 124.27 C, 124.41 CH, 124.56 CH, 124.91 CH, 125.24 CH, 125.68 CH, 125.93 CH, 127.09 CH, 128.17 CH, 128.24 CH, 130.20 CH, 130.72 CH, 131.18 C, 131.20 C, 132.28 C, 132.32 C, 135.80 C, 136.35 C, 136.48 C, 137.55 C, 137.82 C, 145.34 (d, J_{CP}=2.7 Hz, C–O), 145.71 (d, J_{CP}=4.0 Hz, C–O), 150.07 C, 150.38 C, 168.37 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 150.67. IR (KBr) ν (cm^{-1}) 2961, 2903, 2867, 1666, 1594, 1477, 1455, 1401, 1362, 1246, 1180, 1152, 982, 964, 906, 885, 828, 800, 749. MS (EI) *m/z* (rel int%) 875 (M^+, 100), 818 (7), 708 (26), 644 (4), 581 (2), 563 (5), 539 (3), 507 (5), 419 (1), 339 (1), 215 (1), 168 (27), 110 (3). Anal. calcd for $C_{58}H_{70}NO_4P$ C, 79.51%; H, 8.05%. Found C, 79.39%; H, 8.10%.

(+)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*R*)-9,9′-biphenanthryl-10,10′-diyl]phosphite (10a). 20% yield, colorless solid, mp 79°C, α_D^{24}=+343.6 (*c* 0.79, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (s, C(CH_3)$_3$, 9H), 1.45 (s, CH_3, 3H), 1.62 (s, CH_3, 3H), 3.96 (dd, *J*=7.5 and 10.1 Hz, 1H), 4.14–4.28 (m, 2H), 7.10–7.23 (m, 2H), 7.29–7.37 (m, 2H), 7.43–7.55 (m, 2H), 7.57–7.77 (m, 4H), 8.52–8.55 (m, 2H), 8.63–8.71 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.89 C(*C*H_3)$_3$, 28.15 (d, J_{CP}=5.0 Hz, C(*C*H_3)$_2$), 28.44 (d, J_{CP}=8.1 Hz, C(*C*H_3)$_2$, 33.91 *C*(CH_3)$_3$, 69.85 CH_2, 75.92 CH, 76.14 (d, J_{CP}=10.4 Hz, *C*(CH_3)$_2$), 120.70 C, 121.67 C, 121.75 C, 122.35 CH, 122.66 CH, 122.76 C, 122.86 CH, 123.47 CH, 124.47 CH, 125.38 CH, 125.61 CH, 126.18 CH, 126.35 CH, 126.37 CH, 126.39 CH, 127.01 CH, 127.33 CH, 127.55 C, 128.08 CH, 128.16 CH, 128.28 C, 128.31 C, 128.54 C, 131.25 (C–O), 131.55 (d, J_{CP}=5.2 Hz, C–O), 168.73 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 155.2. IR (KBr) ν (cm^{-1}) 2956, 2929, 2854, 1674, 1591, 1489, 1448, 1365, 1129, 1107, 979, 875, 805, 757, 744. MS (EI) *m/z* (rel int%) 599 (M^+, 42), 542 (18), 501 (2), 432 (33), 368 (100), 339 (18), 168 (11), 110 (14). Anal. calcd for $C_{38}H_{34}NO_4P$ C, 76.11%; H, 5.71%. Found C, 76.24%; H, 5.83%. Chlorophosphite intermediate: ^{31}P NMR (121 MHz, $CDCl_3$) δ 181.6.

(−)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*S*)-9,9′-iphenanthryl-10,10′-diyl]phosphite (10b). 16% yield, colorless solid, mp 105°C. α_D^{23}=−378.5 (*c* 0.62, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (s, C(CH_3)$_3$, 9H), 1.54 (s, CH_3, 3H), 1.57 (s, CH_3, 3H), 3.96 (dd, *J*=7.4 and 10.1 Hz, 1H), 4.15–4.29 (m, 2H), 7.15–7.23 (m, 2H), 7.29–7.37 (m, 2H), 7.42–7.49 (m, 2H), 7.57–7.71 (m, 4H), 7.42–8.45 (m, 1H), 8.49–8.52 (m, 1H), 8.63–8.71 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.82 C(*C*H_3)$_3$, 27.29 (C(*C*H_3)$_2$), 27.38 (C(*C*H_3)$_2$), 32.89 *C*(CH_3)$_3$, 68.78 CH_2, 74.97 CH, 75.10 (d, J_{CP}=11.6 Hz, *C*(CH_3)$_2$), 119.25 C, 120.35 C, 121.25 CH, 121.69 CH, 121.75 CH, 121.85 CH, 122.29 CH, 123.62 CH, 124.36 CH, 124.61 CH, 125.15 CH, 125.38 CH, 126.03 CH, 126.32 CH, 126.53 CH, 127.11 CH, 127.17 CH, 127.30 C, 127.32 C, 128.0 CH, 130.50 C, 130.64 C, 143.85 (C–O), 144.92 (d, J_{CP}=6.2 Hz, C–O), 167.51 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 155.46. IR (KBr) ν (cm^{-1}) 2956, 2932, 2867, 1673, 1591, 1489, 1448, 1365, 1157, 1128, 1107, 1036, 978, 875, 806, 757, 727. MS (EI) *m/z* (rel int%) 599 (M^+, 64), 542 (9), 514 (1), 474 (1), 432 (100), 417 (65), 368 (75), 339 (23), 326 (5), 184 (2), 168 (21), 110 (6). Anal. calcd for $C_{38}H_{34}NO_4P$ C, 76.11%; H, 5.71%. Found C, 76.02%; H, 5.59%.

(−)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*R*)-(5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl)]phosphite (11a). 12% yield, colorless solid, mp 116°C. α_D^{25}=−174.3 (*c* 0.60, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (s, C(CH_3)$_3$, 9H), 1.40–1.58 (m, 2H), 1.57 (s, CH_3, 3H), 1.64 (s, CH_3, 3H), 1.65–1.76 (m, 6H), 2.15–2.28 (m, 2H), 2.52–2.80 (m, 6H), 3.84 (dd, *J*=7.4 and 10.2 Hz, 1H), 4.25–4.07 (m, 2H), 6.80–7.00 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.50 CH_2, 22.68 CH_2, 22.78 CH_2, 25.84 C(*C*H_3)$_3$, 27.75 CH_2, 27.81 CH_2, 28.17 (d, J_{CP}=6.6 Hz, C(*C*H_3)$_2$), 28.37 (d, J_{CP}=8.3 Hz, C(*C*H_3)$_2$), 29.18 CH_2, 29.27 CH_2, 33.86 *C*(CH_3)$_3$, 69.40 CH_2, 75.32 (d, J_{CP}=12.3 Hz, *C*(CH_3)$_2$), 75.81 CH, 118.94 CH, 119.30 CH, 128.13 C, 128.69 CH, 129.09 CH, 129.62 C, 133.59 C, 134.43 C, 137.32 C, 138.27 C, 145.99 C, 146.84 C, 168.29 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 145.5. IR (KBr) ν (cm^{-1}) 2934, 2865, 1678, 1469, 1365, 1250, 1232, 1218, 1159, 1124, 987, 967, 938, 842, 819, 790, 762. MS (EI) *m/z* (rel int%) 507 (M^+, 54), 492 (3), 450 (11), 427 (2), 382 (14), 356 (4), 340 (27), 321 (4), 300 (7), 276 (5), 259 (3), 248 (4), 233 (3), 215 (3), 168 (100), 152 (2), 110 (6), 57 (7). HRMS *m/z* calculated for $C_{30}H_{38}NO_4P$ (M^+) 507.2538, found 507.2540.

(+)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*S*)-(5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl-2,2′-diyl)]phosphite (11b). 19% yield, colorless solid, mp 67°C, α_d^{25}=+75.3 (*c* 1.26, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (s, C(CH_3)$_3$, 9H), 1.51–1.60 (m, 2H), 1.62 (s, CH_3, 3H), 1.71 (s, CH_3, 3H), 1.70–1.80 (m, 6H), 2.15–2.36 (m, 2H), 2.55–2.88 (m, 6H), 3.93 (dd, *J*=7.4 and 10.1 Hz, 1H), 4.16–4.27 (m, 2H), 6.84–6.86 (m, 1H), 6.99–7.06 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.49 CH_2, 22.68 CH_2, 22.76 CH_2, 25.81 C(*C*H_3)$_3$, 27.75 CH_2, 27.78 CH_2, 27.81 (d, J_{CP}=8.9 Hz, C(*C*H_3)$_2$), 28.32 (d, J_{CP}=5.5 Hz, C(*C*H_3)$_2$), 29.17 CH_2, 29.23 CH_2, 33.91 *C*(CH_3)$_3$, 69.58 CH_2, 75.32 (d, J_{CP}=11.9 Hz, *C*(CH_3)$_2$), 75.65 CH, 118.94 CH, 119.27 CH, 128.17 C, 128.66 CH, 129.08 CH, 129.65 C, 133.49 C, 134.34 C, 137.32 C, 138.18 (d, J_{CP}=1.0 Hz, C–O), 145.97 (d, J_{CP}=3.0 Hz, C–O), 146.87 C, 168.47 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 144.3. IR (KBr) ν (cm^{-1}) 2933, 2865, 1669, 1466, 1437, 1355, 1268, 1249, 1231, 1156, 1131, 977, 938, 880, 838, 794, 766. MS (EI) *m/z* (rel int%) 507 (M^+, 44), 492 (5), 450 (29), 422 (6), 382 (36), 357 (6), 340 (54), 323 (10), 293 (5), 276 (12), 248 (10), 235 (4), 215 (6), 168 (100), 152 (3), 110 (13). Anal. calcd for $C_{30}H_{38}NO_4P$ C, 70.99%; H, 7.55%. Found C, 70.76%; H, 7.48%. Chlorophosphite intermediate: ^{31}P NMR (121 MHz, $CDCl_3$) δ 169.7.

(−)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*R*)-(1,1′-binaphthyl-8,8′-diyl)]phosphite (12a). 28% yield, colorless solid, mp 75°C, α_D^{23}=−422.1 (*c* 0.56, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (s, C(CH_3)$_3$, 9H), 1.42 (s, C(CH_3)$_2$, 3H), 1.48 (s, C(CH_3)$_2$, 3H), 3.87 (dd, *J*=7.4 and 10.1 Hz, 1H), 4.09–4.24 (m, 2H), 6.64 (dd, *J*=1.2 and 6.9 Hz, 1H), 6.89 (dd, *J*=1.0 and 6.9 Hz, 1H),

7.15–7.19 (m, 1H), 7.25–7.47 (m, 5H), 7.69–7.80 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.44 C(CH_3)$_3$, 27.29 (d, J_{CP}=7.5 Hz, C(CH_3)$_2$), 27.59 (d, J_{CP}=6.7 Hz, C(CH_3)$_2$), 33.47 $C(CH_3)_3$, 69.06 CH_2, 75.46 CH, 75.78 (d, J_{CP}=12.8 Hz, $C(CH_3)_2$), 120.09 CH, 120.23 CH, 120.95 CH, 124.44 CH, 124.51 CH, 124.69 CH, 124.75 CH, 125.08 CH, 125.84 CH, 125.91 CH, 126.56 CH, 130.08 C, 134.78 C, 134.99 C, 139.09 C, 140.10 C, 146.47 (d, J_{CP}=7.8 Hz, C–O), 148.15 (d, J_{CP}=7.7 Hz, C–O), 167.86 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 138.0. IR (KBr) ν (cm^{-1}) 3049, 2956, 2903, 1670, 1568, 1454, 1381, 1364, 1228, 1158, 1129, 1071, 981, 899, 827, 761, 734. MS (EI) *m/z* (rel int%) 499 (M^+, 31), 442 (1), 332 (44), 284 (5), 268 (33), 252 (4), 239 (12), 189 (35), 168 (100), 152 (2), 110 (4), 57 (11), 41 (7). Anal. calcd for $C_{30}H_{30}NO_4P$ C, 72.13%; H, 6.05%. Found C, 72.18%; H, 6.11%.

(+)-{2-[(4′*S*)-(4′-*tert*-Butyloxazolin-2′-yl)]-2-methylethyl}-[(*S*)-(1,1′-binaphthyl-8,8′-diyl)]phosphite (12b). 11% yield, colorless solid, mp 94°C, α_D^{25}=+279.8 (*c* 0.30, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (s, C(CH_3)$_3$, 9H), 1.40 (s, C(CH_3)$_2$, 3H), 1.45 (s, C(CH_3)$_2$, 3H), 3.88 (dd, *J*=7.5 and 10.0 Hz, 1H), 4.08–4.23 (m, 2H), 6.62 (dd, *J*=1.1 and 7.0 Hz, 1H), 6.88 (dd, *J*=0.7 and 6.9 Hz, 1H), 7.13–7.48 (m, 6H), 7.68–7.81 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.65 C(CH_3)$_3$, 27.50 (d, J_{CP}=6.0 Hz, C(CH_3)$_2$), 27.90 (d, J_{CP}=7.0 Hz, C(CH_3)$_2$), 33.78 $C(CH_3)_3$, 69.55 CH_2, 75.69 CH, 76.15 (d, J_{CP}=11.2 Hz, $C(CH_3)_2$), 120.53 CH, 121.13 CH, 124.72 CH, 124.84 CH, 124.95 CH, 125.06 CH, 125.40 CH, 126.19 CH, 126.81 CH, 126.97 CH, 130.34 CH, 130.38 CH, 135.06 C, 135.09 C, 139.47 C, 146.86 C–O, 148.49 C–O, 168.43 C=N. ^{31}P NMR (121 MHz, $CDCl_3$) δ 137.7. IR (KBr) ν (cm^{-1}) 2957, 1672, 1570, 1455, 1383, 1364, 1267, 1229, 1158, 1129, 966, 898, 836, 827, 767. MS (EI) *m/z* (rel int%) 499 (M^+, 20), 332 (79), 315 (6), 284 (16), 268 (50), 252 (7), 239 (33), 226 (7), 189 (57), 168 (100), 152 (3), 110 (9), 57 (28), 41 (18). Anal. calcd for $C_{30}H_{30}NO_4P$ C, 72.13%; H, 6.05%. Found C, 72.22%; H, 6.11%.

3-(5′-Acetoxypentyl)cyclopentanone. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22–1.52 (m, 6H), 1.54–1.70 (m, 2H), 1.72–1.87 (m, 2H), 2.06 (s, 3H), 2.14–2.30 (m, 3H), 2.35–2.50 (m, 2H), 4.11 (t, *J*=6.6 Hz, 2H, H_2CO). ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.9 CH_3, 25.9, 27.4, 28.4, 29.4, 35.5, 37.1, 38.4, 45.2, 64.4 H_2CO, 171.1 CO_2, 219.6 C=O. IR (NaCl) ν (cm^{-1}) 3460, 2930, 2858, 1740 bs, 1241, 1366, 1160, 1039. MS (EI) *m/z* (rel int%) 213 (M^+, 1), 183 (1), 169 (1), 152 (6), 137 (1), 123 (5), 109 (15), 95 (16), 83 (100), 67 (14), 55 (33), 43 (52), 29 (8). HRMS *m/z* calculated for $C_{12}H_{21}O_3$ (MH^+) 213.1490, found 213.1487. Yield GC Restek Rtx-1701, 30 m, 0.6 bar H_2, 60–80, 1°/min, 80–250, 30°/min, t_r=26.8 min, internal standard *n*-dodecane. ee GC Chiraldex B-TA, 30 m, 0.25 mm, 0.6 bar H_2, 60–120°C, 8°/min, 120–180, 1°/min, t_r=48.4/48.6 min minor/major enantiomer, estimated error ±5% (not completely base-line-separated).

3-(5′-Acetoxypentyl)cyclohexanone. ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.06 (s, CH_3, 3H), 1.17–2.46 (m, 17H), 4.06 (t, *J*=6.7 Hz, H_2CO, 2H).^{13}C NMR (50 MHz, $CDCl_3$) δ 20.6 CH_3, 24.9 CH_2, 25.6 CH_2, 25.9 CH_2, 28.1 CH_2, 30.0 CH_2, 36.0 CH_2, 38.6 CH, 41.1 CH_2, 47.8 CH_2, 64.0 H_2CO, 170.8 CO_2, 211.5 C=O. IR (NaCl) ν (cm^{-1}) 3467, 2922, 2855, 1733, 1711, 1450, 1367, 1238, 1033. MS (EI) *m/z* (rel int%) 226 (M^+, 0.3), 166 (3), 149 (3), 123 (10), 110 (5), 97 (100), 81 (10), 69 (19), 55 (43). HRMS *m/z* calculated for $C_{13}H_{23}O_3$ (MH^+) 227.1647, found 227.1649. For GC-analysis see Ref. 10.

3-(5′-Acetoxypentyl)cycloheptanone. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25–1.33 (m, 8H), 1.43–1.68 (m, 6H), 1.85–1.94 (m, 3H), 2.05 (s, 3H, CH_3), 2.44–2.50 (m, 3H), 4.05 (t, *J*=6.6 Hz, H_2CO, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.0 CH_3, 24.3 CH_2, 26.0 CH_2, 26.5 CH_2, 28.4 CH_2, 28.5 CH, 35.9 CH_2, 36.8 CH_2, 37.1 CH_2, 43.9 CH_2, 49.8 CH_2, 64.5 H_2CO, 171.2 CO_2, 214.5 C=O. IR (NaCl) ν (cm^{-1}) 3422, 2930, 2858, 1738, 1700, 1448, 1367, 1242, 1125, 1045. MS (EI) *m/z* (rel int%) 240 (M^+, 1), 198 (2), 180 (4), 162 (7), 151 (6), 137 (9), 122 (24), 111 (100), 95 (32), 81 (25), 67 (26), 55 (165), 43 (68), 29 (11). HRMS *m/z* calculated for $C_{14}H_{25}O_3$ (MH^+) 241.1803, found 241.1805. For GC-analysis see Ref. 10.

Acknowledgements

Special thanks go to Mrs. K. Radkowski, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, for her help with the ligand syntheses. I. E. thanks the 'Verband der chemischen Industrie' for a fellowship. Financial support by the Swiss National Science Foundation is gratefully acknowledged.

References

1. (a) Perlmutter, P. In *Conjugate Addition Reactions in Organic Synthesis*, Tetrahedron Organic Chemistry Series, Vol. 9; Baldwin, J. E.; Magnus, P. D., Eds.; Pergamon Press: Oxford, 1992. (b) Yamamoto, Y. In *Houben-Weyl*, 4th ed., E21, Vol. 4; Helmchen, G; Hoffmann, R. W.; Mulzer, J.; Schaumann, E., Eds.; Thieme: Stuttgart, 1996; Chapter 1.5.2.1. (c) Tomioka, K.; Nagaoka, Y. In *Comprehensive Asymmetric Catalysis*, Vol. 3; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer-Verlag: Berlin/Heidelberg, 1999; Chapter 31.1.

2. Rossiter, B. E.; Swingle, N. M. *Chem. Rev.* **1992**, *92*, 771.

3. (a) Ahn, K. H.; Klassen, R. B.; Lippard, S. *J. Organometallics* **1990**, *9*, 3178. (b) Van Klaveren, M.; Lambert, F.; Eijkelkamp, D. J. F. M.; Grove, D. M.; van Koten, G. *Tetrahedron Lett.* **1994**, *35*, 6135. (c) Van Koten, G. *Pure Appl. Chem.* **1994**, *66*, 1455. (d) Spescha, M.; Rihs, G. *Helv. Chim. Acta* **1993**, *76*, 1219. (e) Kanai, M.; Tomioka, K. *Tetrahedron Lett.* **1995**, *36*, 4275. (f) Tanaka, K.; Matsui, J.; Suzuki, H. *J. Chem. Soc., Perkin Trans. I* **1993**, 153.

4. Zhou, Q.-L.; Pfaltz, A. *Tetrahedron* **1994**, *50*, 4467.

5. (a) Soai, K.; Okudo, M.; Okamoto, M. *Tetrahedron Lett.* **1991**, *32*, 95. (b) Bolm, C.; Ewald, M.; Felder, M. *Chem. Ber.* **1992**, *125*, 1205. (c) de Vries, A. H. M.; Imbos, R.; Feringa, B. L. *Tetrahedron: Asymmetry* **1997**, *8*, 1467. (d) Corma, A.; Iglesias, M.; Martín, M. V.; Rubio, J.; Sánches, F. *Tetrahedron: Asymmetry* **1992**, *3*, 845.

6. Alexakis, A.; Frutos, J. C.; Mangeney, P. *Tetrahedron: Asymmetry* **1993**, *4*, 2427.

7. Feringa, B. L.; Pineschi, M.; Arnold, A.; Imbos, R.; de Vries, A. H. M. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2620.

8. Alexakis, A.; Vastra, J.; Burton, J.; Benhaim, C.; Mangeney, P. *Tetrahedron Lett.* **1998**, *39*, 7869.
9. Keller, E.; Maurer, J.; Naasz, R.; Schader, T.; Meetsma, A.; Feringa, B. L. *Tetrahedron: Asymmetry* **1998**, *9*, 2409.
10. Prétôt, R.; Lloyd-Jones, G. C.; Pfaltz, A. *Pure Appl. Chem.* **1998**, *70*, 1035.
11. Knöbel, A. K. H.; Escher, I. H.; Pfaltz, A. *Synlett* **1997**, 1429.
12. Yan, M.; Chan, A. S. C. *Tetrahedron Lett.* **1999**, *40*, 6645.
13. (a) Cram, D. J. *J. Org. Chem.* **1980**, *49*, 391. (b) Cox, P. J.; Wang, W.; Snieckus, V. *Tetrahedron Lett.* **1992**, *33*, 2253.
14. (a) Suzuki A. *Pure Appl. Chem.* **1994**, *66*, 213 method A. (b) Simonsen, K. B.; Gothelf, K. V.; Jørgensen, K. A. *J. Org. Chem.* **1998**, *63*, 7536.
15. Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org. Chem.* **1981**, *56*, 625.
16. (a) Morgan, J.; Pinhey, J. T. *J. Chem. Soc. Perkin Trans. I* **1990**, 715. (b) Hawthorne, M. F. *J. Org. Chem.* **1958**, *23*, 1576.
17. Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, *54*, 3007.
18. Toda, F.; Tanak, K. *J. Org. Chem.* **1988**, *53*, 3607.
19. Ee (HPLC): Chiralpak OP+, 25 cm, methanol, 0.5 mL/min, 20°C, t_r=26.7 (*S*)/27.7 min (*R*).
20. Artz, S. P.; de Grandpre, M. P.; Cram, D. J. *J. Org. Chem.* **1985**, *50*, 1486.
21. Fuji, K.; Kawabata, T.; Kuroda, A. *J. Org. Chem.* **1995**, *60*, 1914.
22. Prep. HPLC: Nucleosil-5-100-C18/A, 12.5 cm, methanol/water 75:25, 0.8 mL/min, 35°C. De (HPLC): Chiralpak AD, 25 cm, *n*-heptane/2-propanol 80:20, 0.5 mL/min, 25°C, t_r=11.4 (*S*,*S*,*S*) 35% yield, t_r=21.4 (*S*,*R*,*S*) min 32% yield.
23. Ee (HPLC): Chiralpak AD, 25 m, *n*-heptane/2-propanol 80:20, 0.5 mL/min, 25°C, t_r=23.9 (*R*) min, *t*=29.4 (*S*) min.