Asymmetric Ir^I-Catalysed Allylic Alkylation Of Monosubstituted Allylic Acetates With Phosphorus Amidites As Ligands

Björn Bartels,[a] Cristina García-Yebra,[a] and Günter Helmchen*[a]

Keywords: Iridium / Allylic substitution / Asymmetric catalysis / P ligands / Chirality

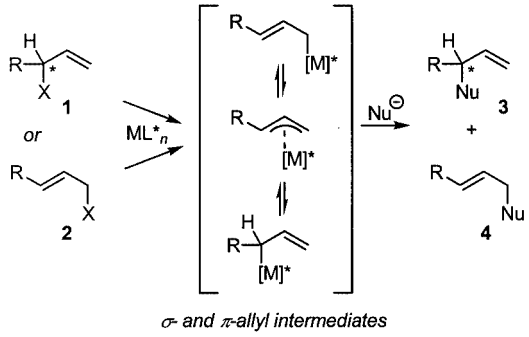
Monodentate phosphorus amidites derived from 2,2′-binaphthol and a variety of chiral amines were employed as ligands in Ir^I-catalysed allylic alkylations of unsymmetrically substituted allylic acetates. The enantio- and regioselectivities of these reactions were investigated. Phosphorus amidites of bulky secondary chiral amines induced enantioselectivities of up to 94% *ee* in reactions of linear substrates. Phosphorus amidites derived from chiral primary amines, which have not been previously employed in asymmetric catalysis, furnished improved regioselectivities. The use of LiCl as additive led to improved regio- and enantioselectivities.

Introduction

Transition-metal-catalysed asymmetric allylic substitutions are widely employed in organic synthesis.[1] Usually, symmetrically substituted allylic derivatives are used as substrates. Synthetically more easily accessible monosubstituted allylic substrates **1** or **2** (Scheme 1) are rarely employed because, in addition to enantioselectivity, regioselectivity in favour of branched chiral products **3** must be achieved. With palladium complexes as catalysts, linear products are generally produced. Only very recently have ligands been developed that give rise to the branched products **3** in special cases (R = CH_3 and R = aryl).[2] With alkyl-substituted substrates synthetically useful results have not been obtained so far. In contrast, Mo- or W-based catalysts preferentially give rise to branched products. High levels of reactivity and enantioselectivity were obtained within the limits stated for Pd complexes.[3] With Pd catalysts reactions proceed via π-allyl complexes which can isomerize via π-σ-π rearrangement or related processes so that branched and linear substrates yield the same products. Memory effects are known but are usually small.[4]

Memory effects for Mo- and W-catalyst are strongly dependent on the auxiliary ligand, nucleophile and substrate, and are poorely understood.[5]

Substitutions catalysed by Rh, Fe or Ru complexes proceed with a high degree of conservation of enantiomeric excess (*cee*). Intermediates of these reactions are σ- or π-allyl complexes which isomerize slowly compared to (allyl)Pd complexes.[6] As a consequence, enantiomerically enriched substrates **1**, even with achiral ligands, yield



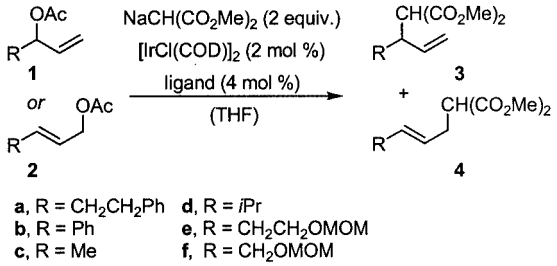
Scheme 1. General scheme for the metal-catalysed allylic substitution of monosubstituted allylic substrates

enantiomerically enriched products **3** via double inversion processes. Because of this, these metal ions appeared not to be suitable for asymmetric synthesis. Surprisingly, asymmetric synthesis was recently nevertheless accomplished with symmetrically substituted 1,3-diarylallyl derivatives.[7]

Ir^I-catalysed allylic substitutions, carried out with catalysts prepared by combining $[IrCl(COD)]_2$ with a π-acceptor ligand, usually triphenylphosphite, regioselectively furnish branched products **3** from both aryl- and alkyl-substituted allylic substrates (cf. Scheme 2).[8] Ir-based catalysis is of particular interest because of its broad scope concerning allylic substrates. Since 1997 we and others have studied enantioselective Ir^I-catalysed allylic substitutions using bidentate chiral phosphinooxazolines[9] and chiral phosphites and phosphorus amidites[10] as ligands. We have recently published a full account of our studies concerning the various factors affecting the steric course of the Ir^I-catalysed allylic substitution including characterisation of

[a] Organisch-chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: (internat.) +49-(0)6221/544-205
E-mail: g.helmchen@urz.uni-heidelberg.de

(allyl)Ir^{III} complexes related to the proposed intermediate species.[11]



Scheme 2. Substrates and typical conditions employed in the Ir^{I}-catalysed allylic alkylations

According to the previous work, the following aspects of the Ir^{I}-catalysed allylic alkylations are important: (a) There is a distinct memory effect with respect to regioselectivity, i.e., preference for the branched product **3** is higher with the branched substrate **1** than with the linear substrate **2**. (b) Similarly, substitution reactions with enantiomerically enriched acetates **1** catalysed by complexes containing achiral ligands proceed with partial conservation of enantiomeric purity. Because of this, a high level of enantioselectivity with a branched racemic substrate requires conditions that promote isomerisation at the level of the substrates or intermediates of the reaction. (c) It was found that phosphorus amidite and, less effectively, phosphite ligands promote isomerization of the intermediates. Furthermore, addition of LiCl gave rise to enhanced erosion of enantiomeric purity when enantiomerically pure acetates **1** were used as substrates. (d) Intermediate octahedral Ir^{III} complexes have been proposed to contain monodentate phosphorus and π-allyl ligands in mutual *cis* disposition due to the strong *trans* influence of these ligands. (e) Finally, it was demonstrated that the Ir^{I}-catalysed allylic alkylation proceeds via a double inversion process.[11]

Induced by the favourable properties of phosphorus amidites as ligands, we have carefully investigated their use in asymmetric allylic substitutions. Here we report results obtained with a variety of chiral phosphorus amidites. Phosphorus amidites are usually derived from secondary amines. In addition, we have investigated less bulky phosphorus amidites of primary amines.

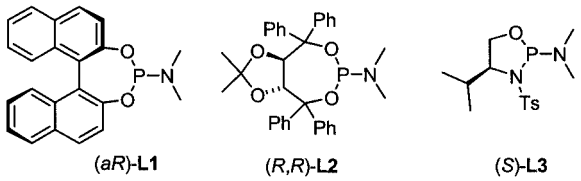
Results and Discussion

In the previous studies, tests of substrates with various leaving groups showed that acetates are best suited for Ir^{I}-catalyzed allylic substitutions.[11] Furthermore, aryl-substituted allylic derivatives invariably gave superior results. In order to gain a realistic assessment of the results, reactions with the alkyl-substituted compounds **1a** and **2a** (Scheme 2) were thoroughly studied and considered representative. Further studies using substrates **1b**−**f** and **2b**−**e** were then carried out in order to assess the scope of the method.

Use of Phosphorus Amidites Derived from Secondary Amines as Ligands

In the first set of experiments phosphorus amidites of widely differing types were tested as ligands (Table 1): **L1**,[12] **L2**,[13] known from the work of Feringa, and **L3**, prepared by standard procedures.[14]

Table 1. Allylic substitutions according to Scheme 2 with substrates (*rac*)-**1a** and **2a** using diverse chiral phosphorus amidites as ligands[a]



Entry	Substrate	Ligand	Temp. [°C]	Time [h]	Yield [%]	Ratio[b] **3:4**	*ee* [%][b] (*Conf.*)
1	**1a**	(*aR*)-**L1**	25	3	92	98:2	69 (*R*)
2	**1a**	(*R*,*R*)-**L2**	50	5	17	84:16	5 (*R*)
3	**1a**	(*S*)-**L3** [c]	25	72	31	96:4	9 (*R*)
4	**2a**	(*aR*)-**L1**	25	3	54	95:5	43 (*R*)
5	**2a**	(*R*,*R*)-**L2**	50	96	34	21:79	8 (*R*)
6	**2a**	(*S*)-**L3**[c]	50	96	26	39:61	7 (*S*)

[a] All reactions were carried out in THF as solvent at a 0.5 mmol scale [0.125 M] of allylic substrate with 2 equiv. of $NaCH(CO_2Me)_2$, 2 mol % of $[IrCl(COD)]_2$ and 4 mol % of the ligand. [b] Determined by HPLC. [c] Mixture of diastereomers (2.5:1); for details see Exp. Sect.

The ligand **L1**, derived from 2,2′-binaphthol (BINOL), gave the best results. This ligand was found to promote particularly fast isomerization of isomeric (allyl)Ir^{III} complexes and, therefore, enantio- and regioselectivities for both branched and linear substrates are similar (Table 1, entries 1 and 4). Based on these results, work was concentrated on phosphorus amidites derived from BINOL using the readily available, known compounds **L4**,[12b,15] **L5**,[16] **L6**,[15b,16] and **L7**[17] as ligands (Figure 1). The results obtained in alkylations of substrates (*rac*)-**1a** and **2a** are described in Table 2.

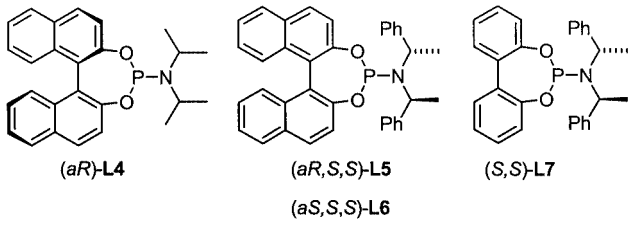


Figure 1. Some phosphorus amidite ligands derived from secondary amines

Reaction rates were distinctly lower with the bulky ligands **L4**−**L7** than with the comparatively small ligand **L1**. Regioselectivity was generally higher for the branched substrate **1a** than the linear substrate **2a**. However, while the difference was small with ligand **L1**, it was very pronounced

Table 2. Phosphorus amidites derived from secondary amines in Ir[I]-catalyzed allylic alkylation of substrates (*rac*)-**1a** and **2a** [a]

Entry	Substrate	Ligand	Temp. [°C]	Time [h]	Yield [%]	Ratio[b] **3:4**	*ee* [%] [b] (*Conf.*)
1	**1a**	(*aR*)-**L1**	25	3	92	98:2	**69 (*R*)**
2	**1a**	(*aR*)-**L4**	50	18	69	85:15	21 (*S*)
3	**1a**	(*aR*,*S*,*S*)-**L5**	50	18	85	86:14	27 (*S*)
4	**1a**	(*aS*,*S*,*S*)-**L6**	25	18	10	89:11	24 (*R*)
5	**1a**	(*S*,*S*)-**L7**	25	48	97	89:11	7 (*R*)
6	**2a**	(*aR*)-**L1**	25	3	54	95:5	43 (*R*)
7	**2a**	(*aR*)-**L4**	50	96	92	28:72	12 (*S*)
8	**2a**	(*aR*,*S*,*S*)-**L5**	50	96	49	30:70	23 (*S*)
9	**2a**	(*aS*,*S*,*S*)-**L6**	50	96	91	53:47	**77 (*R*)**
10	**2a**	(*S*,*S*)-**L7**	50	72	73	53:47	61 (*R*)

[a] All reactions were carried out in THF at a 0.5 mmol scale [0.125 M] with 2 equiv. of $NaCH(CO_2Me)_2$, 2 mol % $[IrCl(COD)]_2$ and 4 mol % of the ligand. [b] Determined by HPLC.

with **L4**−**L7**. There is no apparent trend with respect to enantioselectivity. Ligand **L1** performed best with the branched substrate (Table 2, entry 1), ligand **L6** gave an even better result with the linear substrate (entry 9), while the other bulky ligands **L4** and **L5** gave rise to low enantioselectivity (entries 7, 8). There is also no visible trend concerning the configurational course of the reaction. Even ligands **L1** and **L4**, with only a stereogenic axis, yield products with the opposite configuration (cf. entries 1, 2 and 6, 7). Similarly, the diastereomeric ligands **L5** and **L6** show widely differing influences without apparent pattern. Ligand **L7**, with only a stereogenic center, gave widely differing enantioselectivities for substrates **1a** and **2a** so that the relative influences of the BINOL moiety and the amine moiety are not apparent.

In view of the low reactivity found for ligands with bulky substituents at nitrogen, it was of interest to test phosphorus amidites derived from chiral primary amines in the allylic alkylation. It was hoped that enhanced reactivity might not only be due to the reduced steric bulk but also due to favorable hydrogen bonds between the NH group and the substrate. In previous work, we have obtained excellent results with such ligands in asymmetric hydrogenations.[18]

Use of Phosphorus Amidites Derived from Primary Amines as Ligands

The ligands **L8** to **L13** were synthesized by the standard procedure (Scheme 3) involving treatment of BINOL with phosphorus trichloride and further coupling of the product with the primary amine in the presence of two equivalents of NEt_3. Ligands **L8**−**L13** were obtained in 35−69% yield.

The results obtained with the new ligands in catalysis are summarised in Table 3. As anticipated, significant improvement, compared to the results obtained with ligands **L4**−**L6**, with respect to reactivity as well as regioselectivity was obtained. The enantioselectivity was almost the same as that achieved with **L1** (cf. entry 1 of Table 2 with entry 3 of Table 3) in the case of substrate **1a**. With substrate **2a** the degree of enantioselectivity was low (19−57% *ee*).

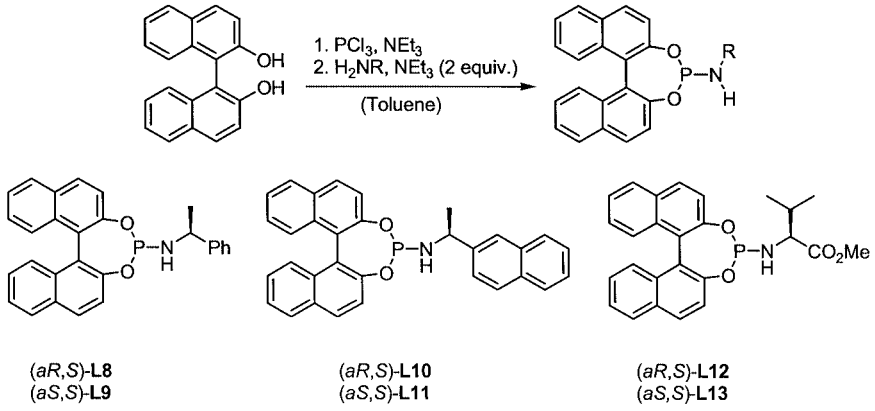
Table 3. Phosphorus amidites derived from primary amines as ligands in Ir[I]-catalyzed allylic alkylation of substrates (*rac*)-**1a** and **2a** [a]

Entry	Substrate	Ligand	Temp. [°C]	Time [h]	Yield [%]	Ratio[b] **3:4**	*ee* [%] [b] (*Conf.*)
1	**1a**	(*aR*,*S*)-**L8**	25	3	98	99:1	64 (*R*)
2	**1a**	(*aS*,*S*)-**L9**	25	5	96	96:4	27 (*S*)
3	**1a**	(*aR*,*S*)-**L10**	25	3	65	99:1	68 (*R*)
4	**1a**	(*aS*,*S*)-**L11**	25	18	60	99:1	18 (*S*)
5	**1a**	(*aR*,*S*)-**L12**	25	18	98	98:2	31 (*R*)
6	**1a**	(*aS*,*S*)-**L13**	25	18	94	98:2	19 (*S*)
7	**2a**	(*aR*,*S*)-**L8**	25	3	56	83:17	57 (*R*)
8	**2a**	(*aS*,*S*)-**L9**	25	5	67	88:12	38 (*S*)
9	**2a**	(*aR*,*S*)-**L10**	25	18	15	67:33	35 (*R*)
10	**2a**	(*aS*,*S*)-**L11**	25	18	40	67:33	19 (*S*)
11	**2a**	(*aR*,*S*)-**L12**	25	18	81	90:10	24 (*R*)
12	**2a**	(*aS*,*S*)-**L13**	25	18	53	72:28	39 (*S*)

[a] All reactions were carried out in THF at a 0.5 mmol scale [0.125 M] with 2 equiv. of $NaCH(CO_2Me)_2$, 2 mol % $[IrCl(COD)]_2$ and 4 mol % of the ligand. [b] Determined by HPLC.

Scope with Respect to Substrate

According to the results presented above, **L1** is the most suitable ligand for branched acetates (**1**), while the phosphorus amidite **L6** gives the best enantioselectivities but low regioselectivity for linear acetates (**2**).



Scheme 3. Phosphorus amidites derived from primary amines

Table 4. Allylic substitutions according to Scheme 2 using **L6** as ligand: variation of linear substrates **2** and effect of additives[a]

Entry	R, Substrate	Additive[b]	Temp. [°C]	Time	Yield [%]	Ratio[c] **3:4**	*ee* [%][d] (*Conf.*)
1	CH_2CH_2Ph, **2a**	–	50	4 d	91	53:47	77 (*R*)
2	CH_2CH_2Ph, **2a**	LiCl	50	4 d	84	65:35	92 (*R*)
3	Ph, **2b**	–	25	18 h	41	70:30	70 (*R*)
4	Ph, **2b**	LiCl	25	18 h	98	91:9	86 (*R*)
5	Me, **2c**	–	25	3 d	85	58:42	56 (*R*)
6	Me, **2c**	LiCl	25	3 d	96	75:25	82 (*R*)
7	*i*Pr, **2d**	–	25	4 d	25	30:70	78 (*R*)
8	*i*Pr, **2d**	LiCl	25	4 d	56	55:45	**94 (*R*)**
9	CH_2CH_2OMOM, **2e**	–	50	3 d	88	50:50	77 (*R*)
10	CH_2CH_2OMOM, **2e**	LiCl	50	3 d	79	65:35	83 (*R*)

[a] All reactions were carried out in THF at a 0.5 mmol scale [0.125 M] with 2 equiv. $NaCH(CO_2Me)_2$, 2 mol % $[IrCl(COD)]_2$ and 4 mol % (*aS*,*S*,*S*)-**L6**; a general procedure for the Ir^I-catalyzed allylic alkylation is described in the Exp. Sect. (see below). [b] One equivalent (relative to substrate) of additive was added before addition of the nucleophile. [c] Determined by GC/MS. [d] Determined by HPLC or GC.

L1 has previously been tested as chiral ligand in the Ir^I-catalyzed allylic alkylation of the branched aryl- and alkylallyl acetates **1a**–**f** (Scheme 2), giving rise to high values of regioselectivity (94–99%) and enantioselectivities of up to 86% *ee* (with **1a**) for the formation of branched products **3**.[11] In addition, ligand **L6** has now been tested in allylic alkylations of the linear acetates **2a**–**e**. The results are displayed in Table 4.

Enantiomeric excesses of between 56 and 78% *ee*, achieved using the standard reaction conditions, were promising (Table 4). Considering that halide ions can accelerate isomerization of allylic intermediates via σ-allyl complexes,[11,19] LiCl was added to the reaction mixtures. Indeed, addition of one equivalent of LiCl led to marked improvement, up to 82–94% *ee*. This additive also positively affected the regioselectivity of the process. Nevertheless, the regioselectivity of the substitution still has to be considerably improved, except in the case where R is Ph (**2b**).

Conclusion

A set of 13 chiral phosphorus amidite ligands has been tested in asymmetric Ir-catalyzed allylic alkylations of allylic substrates with widely differing substituents. The comparatively small ligand **L1** derived from BINOL and dimethylamine was optimal with respect to reactivity and regioselectivity. The particularly bulky ligand **L6**, derived from (*aS*)-BINOL and (*S*,*S*)-bis(1-phenylethyl)amine, gave rise to the highest enantioselectivity but relatively low degrees of regioselectivity and reactivity with linear allyl acetates. Improved results were obtained with LiCl as additive and with phosphorus amidites derived from secondary amines. With these ligands of a new type both reactivity and regioselectivity were considerably improved, although enantioselectivities were lower than with **L6**. Further research is required in order to fully explore the potential of chiral phosphorus amidites derived from primary amines.

Experimental Section

General: All reactions were carried out using dry solvents under an argon atmosphere. TLC: Macherey & Nagel Polygram Sil G/UV precoated sheets, treatment with I_2 or aqueous $KMnO_4$ solution for visualization of spots. Column chromatography: Fluka silica gel, grade 60 (0.04–0.063 mm) or aluminum oxide, activity IV. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker DRX 300 or DRX 500 instruments. ^1H NMR chemical shifts are relative to residual non-deuterated solvent in $CDCl_3$ (δ = 7.26 ppm) or [D_8]THF (δ = 1.72, 3.57 ppm). ^{13}C NMR shifts are quoted relative to the solvents $CDCl_3$ (δ = 77.0 ppm) and [D_8]THF (δ = 25.20, 67.20 ppm) and ^{31}P NMR shifts are relative to 85% H_3PO_4 (δ = 0.00 ppm). MS: JEOL, JMS-700. FAB: JEOL, JMS-700; matrix: 4-nitrobenzyl alcohol (NBA) or 4-nitrophenyl octyl ether (NPOE). Optical rotation: Perkin–Elmer P 241. GC: Hewlett Packard HP 5890 with Chiraldex γ-CD TA column (30 m × 0.25 mm). HPLC: Hewlett Packard HP 1090 with DAICEL Chiralcel ODH column (25 cm × 0.46 cm) in combination with DAICEL Chiralcel ODH precolumn (5 cm × 0.46 cm). Elemental analyses: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. The ligands **L1**,[12] **L2**,[13] **L4**,[12b,15] (*R*,*S*,*S*)-**L5**,[16] (*S*,*S*,*S*)-**L6**,[15b,16] and **L7**[17] were prepared according to published procedures. Allylic esters were prepared by reaction of the corresponding alcohols with acetic anhydride {**1a**,[20] (*E*)-**2a**,[11,21] (*E*)-**2b**,[22] (*E*)-**2c**,[23] (*E*)-**2d**[11] and (*E*)-**2e**[11]}. Compounds **3a**[11,24] **3b**,[22] **3c**,[6c,23] **3d**[25] and **3e**[11,26] have been described and characterised previously.

Synthesis of Phosphorus Amidites

Synthesis of L3: $P(NMe_2)_3$ (690 μL, 3.10 mmol) was added dropwise to a suspension of (*S*)-*N*-tosylvalinol (975 mg, 3.10 mmol) and NH_4Cl (7 mg, 0.10 mmol) in toluene (10 mL). The mixture was stirred for 18 h at 80 °C, then taken to room temperature and concentrated in vacuo to give a colourless oil, which gave colourless crystals of **L3** (2.5:1 mixture of diastereomers) upon treatment with CH_2Cl_2. Yield: 640 mg (63%). ^1H NMR (500.13 MHz, $CDCl_3$, 25 °C, values marked [*] belong to the minor diastereomer): δ = 0.46 (d, $^3J_{H,H}$ = 7.3 Hz, 3 H, Me_2CH), 0.74 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, Me_2CH), 0.93 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, Me_2CH)*, 1.04 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, Me_2CH)*, 1.95 (qqd, $^4J_{H,P}$ = 3.0, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 7.3 Hz, 1 H, Me_2CH), 2.31–2.40 (m, 1 H, Me_2CH)*, 2.42 (s, 3 H, MeC_6H_4), 2.43 (s, 3 H, MeC_6H_4)*, 2.64 (d, $^3J_{H,P}$ = 8.5 Hz,

6 H, NMe_2), 2.76 (d, $^3J_{H,P}$ = 9.8 Hz, 6 H, NMe_2)*, 2.95 (dddd, $^3J_{H,P}$ = 1.8, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 6.7, $^3J_{H,H}$ = 6.7 Hz, 1 H, Me_2CHCHN)*, 3.73−3.80 (m, 1 H, $Me_2CHCHCH_2O$)*, 3.97−4.04 (m, 2 H, Me_2CHCHN and $Me_2CHCHCH_2O$), 4.16 (ddd, $^3J_{H,H}$ = 6.7, $^3J_{H,P}$ = 6.7, $^2J_{H,H}$ = 9.2 Hz, 1 H, $Me_2CHCHCH_2O$)*, 4.30 (dd, $^3J_{H,H}$ = 6.7, $^2J_{H,H}$ = 9.2 Hz, 1 H, $Me_2CHCHCH_2O$), 7.28 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, *m*-C_6H_4), 7.31 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, *m*-C_6H_4)*, 7.80 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, *o*-C_6H_4)*, 7.82 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, *o*-C_6H_4) ppm. $^{13}C\{^1H\}$ NMR (75.47 MHz, [D$_8$]THF, values marked [*] belong to the minor diastereomer): δ = 14.9 (s, Me_2CH), 15.0 (s, Me_2CH), 18.70 (s, MeC_6H_4), 21.4 (s, Me_2CH), 37.0 (d, $^2J_{C,P}$ = 20.1 Hz, NMe_2), 63.4 (d, $^2J_{C,P}$ = 3.5 Hz, Me_2CHCHN), 67.7 (d, $^2J_{C,P}$ = 11.6 Hz, $Me_2CHCHCH_2O$), 127.9 (2d, $^4J_{C,P}$ = 2.8 Hz, *o*-C_6H_4), 128.6 (2d, $^4J_{C,P}$ = 6.2 Hz, *o*-C_6H_4)*, 130.1 (s, *m*-C_6H_4), 130.2 (s, *m*-C_6H_4)*, 141.5 (s, *ipso*-C_6H_4), 143.7 (s, *p*-C_6H_4) ppm. $^{31}P\{^1H\}$ NMR (202.47 MHz, $CDCl_3$, 25 °C): δ = 143.45 (s), 157.47 (s) ppm. MS (FAB): *m*/*z* (%) = 331 (69) [M^+ + 1], 286 (81) [M^+ − NMe_2]. HRMS (FAB): $M^+ = C_{14}H_{24}O_3N_2SP$ calcd. 331.1245; found 331.1270.

General Procedure for the Synthesis of Ligands L8−L13: The reactions were carried out in the vessel shown in Figure 2. In flask A, a solution of PCl_3 (305 μL, 3.50 mmol) in toluene (15 mL) was treated with triethylamine (975 μL, 7.00 mmol) and then 2,2′-binaphthol (1.00 g, 3.50 mmol). The mixture was stirred for 6 h at room temperature and then filtered into flask B. After washing the precipitate in flask A once with toluene (10 mL), the combined filtrates were cooled (0 °C). Triethylamine (975 μL, 7.00 mmol) and the corresponding primary amine (3.50 mmol) were added, and the mixture was stirred for 18 h at room temperature, after which it was filtered under argon, in order to remove NH_4Cl, and concentrated in vacuo. Products were purified by MPLC.

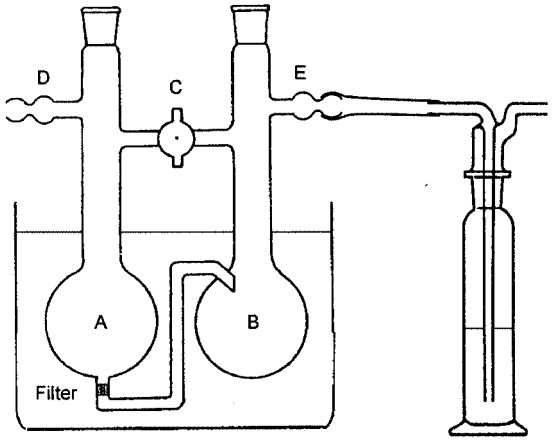


Figure 2. Two-flask system for isothermal addition of sensitive compounds.[27] The system consists of two flasks, A and B, connected by a capillary glass tube, provided with a sintered glass filter plate, and a wide-bore tube C containing a stopcock. Flask A is connected via D to an inert gas line and flask B through E to a bubbler filled with paraffin oil. Initially, stopcock C is open in order to provide equal pressure in flasks A and B. In flask A one of the reagents is prepared and transferred into flask B by closing stopcock C.

Synthesis of L8: Ligand **L8** was prepared according to the general procedure from (*aR*)-BINOL (1.00 g, 3.50 mmol) and (*S*)-phenylethylamine (450 μL, 424 mg, 3.50 mmol). The crude product was crystallized from CH_2Cl_2 and further subjected to MPLC on an aluminum oxide column [activity IV; 3 cm × 28 cm, flow 50 mL/min; eluent: petroleum ether/ethyl acetate (9:1)], previously deactivated by injection of NEt_3 (1 mL). Yield: 69% (1.04 g), colourless crystalline solid. $[\alpha]_D^{23}$ = −264.1 (*c* = 0.14, $CHCl_3$). ^1H NMR (500.13 MHz, [D$_8$]THF, 25 °C): δ = 1.45 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 4.40−4.50 (m, 1 H, $CHCH_3$), 5.09 (d, $^2J_{H,P}$ = 10.7 Hz, 1 H, NH), 6.80 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, arom. H), 7.17−7.39 (m, 11 H, arom. H), 7.49 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, arom. H), 7.82 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, arom. H), 7.89 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, arom. H), 7.91 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, arom. H), 7.98 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, [D$_8$]THF, 25 °C): δ = 26.0 (d, $^3J_{C,P}$ = 7.0 Hz, CH_3), 51.8 (d, $^2J_{C,P}$ = 26.8 Hz, $CHCH_3$), 122.7, 123.7 (both s, binaphthyl-*C*H), 124.2 (d, $J_{C,P}$ = 2.4 Hz, binaphthyl-*C*), 125.0 (d, $J_{C,P}$ = 4.7 Hz, binaphthyl-*C*), 125.2, 125.4, 126.6, 126.7 (all s, binaphthyl-*C*H), 127.1 (s, Ph-*C*H), 127.4 (s, Ph-*C*H), 127.4, 127.6 (both s, binaphthyl-*C*H), 129.0 (2s, Ph and binaphthyl-*C*H), 129.1, 130.0, 130.9 (all s, binaphthyl-*C*H), 132.0, 132.4, 133.7, 133.8 (all s, binaphthyl-*C*), 147.8 (d, $^3J_{C,P}$ = 1.9 Hz, Ph-*C*), 149.4 (d, $J_{C,P}$ = 4.7 Hz, binaphthyl-*C*), 150.8 (s, binaphthyl-*C*) ppm. $^{31}P\{^1H\}$ NMR (202.47 MHz, [D$_8$]THF, 25 °C): δ = 154.42 (s) ppm. MS (EI): *m*/*z* (%) = 435 (85) [M^+], 315 (63) [M^+ − $NHCHCH_3Ph$], 268 (48) [M^+ − $NHCHCH_3Ph$ − PO]. HRMS (EI) $M^+ = C_{28}H_{22}O_2NP$, calcd. 435.1388; found 435.1375. $C_{28}H_{22}NO_2P$ (435.46): C 77.23, H 5.09, N 3.22, P 7.11; found C 76.97, H 5.35, N 3.31, P 6.86.

Synthesis of L9: Ligand **L9** was prepared according to the general procedure from (*aS*)-BINOL (1.00 g, 3.50 mmol) and (*S*)-phenylethylamine (450 μL, 424 mg, 3.50 mmol). The crude product was purified by MPLC, first on a silica gel 60 column [3 cm × 25 cm, flow 70 mL/min; eluent: petroleum ether/ethyl acetate (9:1)] previously deactivated with NEt_3 (1 mL). The product obtained was subjected to a second MPLC purification on an aluminum oxide column [activity IV; 3 cm × 28 cm, flow 50 mL/min; eluent: petroleum ether/ethyl acetate (9:1)], previously deactivated with NEt_3 (1 mL). Yield: 35% (528 mg), colorless crystalline solid. $[\alpha]_D^{23}$ = +252.5 (*c* = 0.13, $CHCl_3$). ^1H NMR (500.13 MHz, [D$_8$]THF, 25 °C): δ = 1.46 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 4.43−4.53 (m, 1 H, $CHCH_3$), 5.09 (dd, *J* = 9.4, *J* = 9.7 Hz, 1 H, NH), 7.15−7.39 (m, 12 H, arom. H), 7.49 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, arom. H), 7.82 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, arom. H), 7.90 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, arom. H), 7.92 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, arom. H), 7.98 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, [D$_8$]THF, 25 °C): δ = 27.1 (d, $^3J_{C,P}$ = 3.8 Hz, CH_3), 51.8 (d, $^2J_{C,P}$ = 21.7 Hz, $CHCH_3$), 122.8, 123.6 (both s, binaphthyl-*C*H), 124.0 (d, $J_{C,P}$ = 2.4 Hz, binaphthyl-*C*), 125.0 (d, $J_{C,P}$ = 5.2 Hz, binaphthyl-*C*), 125.2, 125.4, 126.6 (all s, binaphthyl-*C*H), 126.7 (s, binaphthyl-*C*H), 126.8, 127.2 (both s, Ph-*C*H), 127.5, 127.6 (both s, binaphthyl-*C*H), 128.9 (s, Ph-*C*H), 129.1, 129.2, 130.2, 130.9 (all s, binaphthyl-*C*H), 131.9, 132.5, 133.8, 133.8 (all s, binaphthyl-*C*), 147.5 (d, $J_{C,P}$ = 4.3 Hz, Ph-*C*), 149.6 (d, $J_{C,P}$ = 5.2 Hz, binaphthyl-*C*), 150.8 (s, binaphthyl-*C*) ppm. $^{31}P\{^1H\}$ NMR (202.47 MHz, [D$_8$]THF, 25 °C): δ = 152.39 (s) ppm. MS (EI): *m*/*z* (%) = 435 (79) [M^+], 315 (66) [M^+ − $NHCHCH_3Ph$], 268 (46) [M^+ − $NHCHCH_3Ph$ − PO]. HMS (EI) $M^+ = C_{28}H_{22}O_2NP$ calcd. 435.1388; found 435.1378. $C_{28}H_{22}NO_2P$ (435.46): C 77.23, H 5.09, N 3.22, P 7.11; found C 77.14, H 5.23, N 3.36, P 6.86.

Synthesis of L10: Ligand **L10** was prepared according to the general procedure from (*aR*)-BINOL (1.00 g, 3.50 mmol) and (*S*)-1-(2-naphthyl)ethylamine (600 mg, 3.50 mmol). The crude product was purified twice by MPLC on a silica gel 60 column [3 cm × 25 cm, flow 70 mL/min; eluent: petroleum ether/ethyl acetate (9:1)] previ-

ously deactivated with NEt_3 (1 mL). Yield: 40% (679 mg), colorless crystals. $[\alpha]_D^{20} = -203.71$ ($c = 0.17$, $CHCl_3$). ^1H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 1.60 (d, $^3J_{H,H} = 7.35$ Hz, 3 H, CH_3), 3.54 (d, $^2J_{H,P} = 10.0$ Hz, 1 H, NH), 4.66−4.78 (m, 1 H, C*H*CH_3), 6.85 (d, $^3J_{H,H} = 8.6$ Hz, 1 H, arom. H), 7.20−7.30 (m, 2 H, arom. H), 7.36 (d, $^3J_{H,H} = 8.7$ Hz, 1 H, arom. H), 7.37−7.44 (m, 3 H, arom. H), 7.44−7.51 (m, 3 H, arom. H), 7.55 (d, $^3J_{H,H} = 8.7$ Hz, 1 H, arom. H), 7.73 (d, $^3J_{H,H} = 8.7$ Hz, 2 H, arom. H), 7.82−7.93 (m, 6 H, arom. H), 7.95 (d, $^3J_{H,H} = 9.4$ Hz, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 25.9 (d, $^3J_{C,P} = 7.5$ Hz, *C*H_3), 51.4 (d, $^2J_{C,P} = 26.4$ Hz, *C*HCH_3), 121.8 (d, $J_{C,P} = 2.0$ Hz, binaphthyl-*C*H), 122.5 (s, binaphthyl-*C*H), 123.6 (d, $J_{C,P} = 1.9$ Hz, binaphthyl-*C*), 124.1 (d, $J_{C,P} = 4.7$ Hz, binaphthyl-*C*), 124.2, 124.7, 124.8, 124.9, 125.8, 126.0, 126.1, 126.2, 126.8, 126.9, 127.7, 127.9, 128.2, 128.3, 128.3, 129.3, 130.2 (all s, aromatic-*C*H), 130.9, 131.4, 132.7, 132.75, 132.8, 133.4 (all s, aromatic-*C*), 143.6 (d, $J_{C,P} = 1.9$ Hz, naphthyl-*C*), 147.8 (d, $J_{C,P} = 2.1$ Hz, binaphthyl-*C*), 149.7 (d, $J_{C,P} = 1.9$ Hz, binaphthyl-*C*) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$, 25 °C): δ = 152.52 (s) ppm. MS FAB *m*/*z* (%) = 486 (55) [$M^+ + 1$], 485 (30) [M^+]. HMS (FAB) [$M^+ + 1$] = $C_{32}H_{25}NO_2P$ calcd. 486.1623; found 486.1629.

Synthesis of L11: Ligand **L11** was prepared according to the general procedure from (*aS*)-BINOL (1.00 g, 3.50 mmol) and (*S*)-1-(2-naphthyl)ethylamine (600 mg, 3.50 mmol). The crude product was purified by MPLC on a silica gel 60 column [3 cm × 25 cm, flow 70 mL/min; eluent: petroleum ether/ethyl acetate (95:5)] previously deactivated with NEt_3 (1 mL). The product obtained was submitted to a second MPLC purification on an aluminum oxide column [activity IV; 3 cm × 28 cm, flow 50 mL/min; eluent: petroleum ether/ethyl acetate (95:5)] previously deactivated with NEt_3 (1 mL). Yield: 60% (1.00 g), colorless crystals. $[\alpha]_D^{19} = +221.66$ ($c = 0.15$, $CHCl_3$). ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C): δ = 1.62 (d, $^3J_{H,H} = 6.8$ Hz, 3 H, CH_3), 3.56 (dd, $^3J_{H,H} = 6.6$, $^2J_{H,P} = 9.6$ Hz, 1 H, NH), 4.60−4.90 (m, 1 H, C*H*CH_3), 7.15−7.33 (m, 3 H, arom. H), 7.33−7.52 (m, 7 H, arom. H), 7.55 (d, $^3J_{H,H} = 8.8$ Hz, 1 H, arom. H), 7.71−8.02 (m, 8 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 26.6 (d, $^3J_{C,P} = 4.1$ Hz, CH_3), 50.5 (d, $^2J_{C,P} = 21.4$ Hz, *C*HCH_3), 121.8 (d, $J_{C,P} = 2.0$ Hz, binaphthyl-*C*H) 122.4 (s, binaphthyl-*C*H), 123.4 (d, $J_{C,P} = 2.7$ Hz, binaphthyl-*C*), 124.0 (d, $J_{C,P} = 4.8$ Hz, binaphthyl-*C*), 124.1, 124.5, 124.7, 124.8, 125.7, 126.0, 126.1, 126.1, 126.8, 126.9, 127.6, 127.9, 128.2, 128.2, 128.3, 129.4, 130.2 (all s, aromatic-*C*H), 130.8, 131.4, 132.5, 132.7, 132.7, 133.3 (all s, aromatic-*C*) 142.9 (d, $J_{C,P} = 4.1$ Hz, naphthyl-*C*), 147.6 (d, $J_{C,P} = 4.8$ Hz, binaphthyl-*C*), 149.3 (d, $J_{C,P} = 1.4$ Hz, binaphthyl-*C*) ppm. $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$, 25 °C): δ = 150.66 (s) ppm. MS (EI): *m*/*z* (%) = 485 (83) [M^+], 315 (33) [$M^+ - NHCHCH_3(C_{10}H_7)$], 268 (23) [$M^+ - NHCHCH_3(C_{10}H_7) - PO$]. HMS (EI) $M^+ = C_{32}H_{24}O_2NP$ calcd. 485.1545; found 485.1555.

Synthesis of L12: Ligand **L12** was prepared according to the general procedure with (*aR*)-BINOL (1.00 g, 3.50 mmol) and (*S*)-valine methyl ester (458 mg, 3.50 mmol). The crude product was purified by MPLC on a silica gel 60 column [3 cm × 25 cm, flow 70 mL/min; eluent: petroleum ether/ethyl acetate (9:1)] previously deactivated with NEt_3 (1 mL). The product thus isolated was submitted to a second MPLC purification on a aluminum oxide column [activity IV; 3 cm × 28 cm, flow 50 mL/min; eluent: petroleum ether/ethyl acetate (9:1)] previously deactivated with NEt_3 (1 mL). Yield: 44% (690 mg), colorless crystalline solid. $[\alpha]_D^{22} = -390$ ($c = 0.13$, $CHCl_3$). ^1H NMR (500.13 MHz, [D_8]THF, 25 °C): δ = 0.86 (d, $^3J_{H,H} = 6.7$ Hz, 3 H, *Me*$_2$CH), 0.94 (d, $^3J_{H,H} = 6.7$ Hz, 3 H, *Me*$_2$CH), 2.00 (dqq, $^3J_{H,H} = 6.4$, $^3J_{H,H} = 6.7$, $^3J_{H,H} = 6.7$ Hz, 1 H, Me$_2$C*H*), 3.69 (ddd, $^3J_{H,H} = 6.4$, $^3J_{H,H} = 11.7$, $^3J_{H,P} = 11.7$ Hz, 1 H, C*H*CO_2Me), 3.75 (s, 3 H, CO_2*Me*), 4.91 (d, $^2J_{H,P} = 11.7$ Hz, 1 H, NH), 7.21 (d, $^3J_{H,H} = 7.0$ Hz, 1 H, arom. H), 7.23 (d, $^3J_{H,H} = 7.0$ Hz, 1 H, arom. H), 7.30−7.36 (m, 3 H, arom. H), 7.37 (d, $^3J_{H,H} = 7.0$ Hz, 1 H, arom. H), 7.39 (d, $^3J_{H,H} = 7.0$ Hz, 1 H, arom. H), 7.50 (d, $^3J_{H,H} = 8.7$ Hz, 1 H, arom. H), 7.91−7.95 (m, 2 H, arom. H), 7.97 (d, $^3J_{H,H} = 8.7$ Hz, 1 H, arom. H), 7.99 (d, $^3J_{H,H} = 8.7$ Hz, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, [D_8]THF, 25 °C): δ = 18.1 (s, *Me*$_2$CH), 19.5 (s, *Me*$_2$CH), 33.0 (d, $^3J_{C,P} = 6.0$ Hz, Me$_2$*C*H), 51.8 (s, CO_2*Me*), 60.6 (d, $^2J_{C,P} = 28.7$ Hz, *C*HCO_2Me), 122.6, 124.0 (both arom. *C*H), 124.2 (s, arom. *C*), 125.1 (d, $J_{C,P} = 4.7$ Hz, arom. *C*), 125.3, 125.5, 126.6, 126.8, 127.4, 127.7, 129.1, 129.2, 130.1, 130.9 (all s, arom. *C*H), 132.2, 132.5, 133.7, 133.8 (all s, arom. *C*), 149.1 (d, $J_{C,P} = 4.7$ Hz, arom. *C*), 150.5 (s, arom. *C*), 174.0 (d, $^3J_{C,P} = 2.8$ Hz, *C*OOMe) ppm. $^{31}P\{^1H\}$ NMR (202.47 MHz, [D_8]THF, 25 °C): δ = 155.09 (s) ppm. MS (EI): *m*/*z* (%) = 445 (38) [M^+], 402 (73) [$M^+ - CH(CH_3)_2$], 386 (62) [$M^+ - CO_2CH_3$], 315 (100) [$M^+ - HNC(i\text{Pr})CO_2CH_3$], 268 (98) [$M^+ - HNC(i\text{Pr})CO_2CH_3 - PO$]. HMS (EI) $M^+ = C_{26}H_{24}O_4NP$ calcd. 445.1443; found 445.1439. $C_{26}H_{24}NO_4P$ (445.45): C 70.11, H 5.43, N 3.14, P 6.95; found C 70.29, H 5.61, N 3.06, P 6.88.

Synthesis of L13: Ligand **L13** was prepared according to the general procedure with (*aS*)-BINOL (1.00 g, 3.50 mmol) and (*S*)-valine methyl ester (458 mg, 3.50 mmol). The crude product was purified by MPLC, first on a silica gel 60 column [3 cm × 25 cm, flow 70 mL/min; eluent: petroleum ether/ethyl acetate (9:1)] previously deactivated with NEt_3 (1 mL). The resultant product was submitted to a second MPLC purification on an aluminum oxide column [activity IV; 3 cm × 28 cm, flow 50 mL/min; eluent: petroleum ether/ethyl acetate (9:1)] previously deactivated with NEt_3 (1 mL). Yield: 67% (1.05 g), colorless crystalline solid. $[\alpha]_D^{22} = +428$ ($c = 0.15$, $CHCl_3$). ^1H NMR (500.13 MHz, [D_8]THF, 25 °C): δ = 0.82 (d, $^3J_{H,H} = 7.0$ Hz, 3 H, *Me*$_2$CH), 0.94 (d, $^3J_{H,H} = 6.7$ Hz, 3 H, *Me*$_2$CH), 1.88−1.98 (m, 1 H, Me$_2$C*H*), 3.63 (ddd, $^3J_{H,H} = 4.7$, $^3J_{H,P} = 8.7$, $^3J_{H,H} = 13.0$ Hz, 1 H, C*H*CO_2Me), 3.65 (s, 3 H, CO_2*Me*), 4.85 (dd, $^3J_{H,H} = 11.4$, $^2J_{H,P} = 18.4$ Hz 1 H, NH), 7.18−7.40 (m, 7 H, arom. H), 7.49 (d, $^3J_{H,H} = 9.0$ Hz, 1 H, arom. H), 7.90−7.95 (m, 3 H, arom. H), 7.99 (d, $^3J_{H,H} = 8.7$ Hz, 1 H, arom. H) ppm. $^{13}C\{^1H\}$ NMR (125.77 MHz, [D_8]THF, 25 °C): δ = 17.5 (s, *Me*$_2$CH), 19.6 (s, *Me*$_2$CH), 33.2 (d, $^3J_{C,P} = 2.8$ Hz, Me$_2$*C*H), 51.6 (s, CO_2*Me*), 59.4 (d, $^2J_{C,P} = 13.2$ Hz, *C*HCO_2Me), 122.6, 123.0 (both arom. *C*H), 123.8 (d, $J_{C,P} = 2.4$ Hz, arom. *C*), 124.9 (d, $J_{C,P} = 4.7$ Hz, arom. *C*), 125.3, 125.5, 126.7, 126.8, 127.5, 127.6, 129.1, 129.2, 130.3, 131.0 (all s, arom. *C*H), 131.9, 132.5, 133.7, 133.7 (all s, arom. *C*), 149.8 (d, $J_{C,P} = 5.6$ Hz, arom. *C*), 150.6 (s, arom. *C*), 173.7 (d, $^3J_{C,P} = 3.3$ Hz, *C*OOMe) ppm. $^{31}P\{^1H\}$ NMR (202.47 MHz, [D_8]THF, 25 °C): δ = 149.23 (s) ppm. MS (EI): *m*/*z* (%) = 445 (61) [M^+], 402 (32) [$M^+ - CH(CH_3)_2$], 386 (60) [$M^+ - CO_2CH_3$], 315 (100) [$M^+ - HNC(i\text{Pr})CO_2CH_3$], 268 (51) [$M^+ - HNC(i\text{Pr})CO_2CH_3 - PO$]. HMS (EI) $M^+ = C_{26}H_{24}O_4NP$ calcd. 445.1443; found. 445.1449. $C_{26}H_{24}NO_4P$ (445.45): C 70.11, H 5.43, N 3.14, P 6.95; found C 70.28, H 5.68, N 3.10, P 6.94.

General Procedure for the Ir^I-Catalysed Allylic Alkylation: A solution of $[IrCl(COD)]_2$ (6.7 mg, 0.01 mmol) in THF (2 mL) was treated with substrate (0.50 mmol) and then ligand (0.02 mmol). The resultant solution was stirred for 5 min. If the reaction was run with additive, this was added at this point (0.50 mmol) and the solution stirred for a further 5 min. After that, a freshly prepared solution of dimethyl 2-sodiomalonate was added. This solution was prepared by suspending sodium hydride (24.0 mg, 1.00 mmol) in

THF (2 mL) and the dropwise addition of dimethyl malonate (115 μL, 1.00 mmol). The mixture was stirred under the stated reaction conditions, then water (4 mL) was added, and the mixture was extracted with diethyl ether (3 × 5 mL). The combined organic layers were washed with satd. NH_4Cl solution (10 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude product was purified by flash column chromatography to give a mixture of substitution products **3** and **4** as colourless oils. For analytical data see above.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. C. G.-Y. thanks the Alexander von Humboldt Foundation for a Postdoctoral Fellowship and the European Community for a Marie Curie Fellowship, program "Improving Human Research Potential and the Socio-economic Knowledge Base" under contract number HPMF-CT-2000-00905. We thank T. Leβmann and A. Spieβ for preparation of substrates, and Degussa AG for iridium salts.

[1] [1a] B. M. Trost, C. Lee, in *Catalytic Asymmetric Synthesis*, 2nd ed. (Ed.: I. Ojima) Wiley-VCH, New York, **2000**, pp. 593−649. [1b] A. Pfaltz, M. Lautens, in *Comprehensive Asymmetric Catalysis I−III* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**, pp. 833−884.

[2] [2a] S.-L. You, X.-Z. Zhu, Y.-M. Luo, X.-L. Hou, L.-X. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 7471−7472. [2b] R. Prétôt, A. Pfaltz, *Angew. Chem.* **1998**, *110*, 337−339; *Angew. Chem. Int. Ed.* **1998**, *37*, 323−325. [2c] B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1998**, *120*, 9074−9075. [2d] T. Hayashi, M. Kawatsura, Y. Uozumi, *Chem. Commun.* **1997**, 561−562. [2e] T. Hayashi, A. Ohno, S.-J. Lu, Y. Matsumoto, E. Fukuyo, K. Yanagi, *J. Am. Chem. Soc.* **1994**, *116*, 4221−4226. [2f] T. Hayashi, K. Kishi, A. Yamamoto, V. Ito, *Tetrahedron Lett.* **1990**, *31*, 1743−1746.

[3] Mo: [3a] B. M. Trost, K. Droga, I. Hachiya, T. Emura, D. L. Hughes, S. Krska, R. A. Reamer, M. Palucki, N. Yasuda, P. J. Reider, *Angew. Chem.* **2002**, *114*, 2009−2012; *Angew. Chem. Int. Ed.* **2002**, *41*, 1929−1932. [3b] O. Belda, N.-F. Kaiser, U. Bremberg, M. Larhed, A. Hallberg, C. Moberg, *J. Org. Chem.* **2000**, *65*, 5868−5870. [3c] B. M. Trost, I. Hachiya, *J. Am. Chem. Soc.* **1998**, *120*, 1104−1105. [3d] F. Glorius, A. Pfaltz, *Org. Lett.* **1999**, *1*, 141−144. W: [3e] G. C. Lloyd−Jones, A. Pfaltz, *Angew. Chem.* **1995**, *107*, 534−536; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 462−464.

[4] Pd: [4a] G. C. Lloyd-Jones, S. C. Stephen, M. Murray, C. P. Butts, Š. Vyskočil, P. Kočovský, *Chem. Eur. J.* **2000**, *6*, 4348−4357. [4b] G. C. Lloyd-Jones, S. C. Stephen, *Chem. Eur. J.* **1998**, *4*, 2539−2547.

[5] Mo: [5a] M. P. T. Sjögren, H. Frisell, B. Åkermark, P. O. Norrby, L. Eriksson, A. Vitagliano, *Organometallics* **1997**, *16*, 942−950. W: [5b] J. Lehmann, G. C. Lloyd-Jones, *Tetrahedron* **1995**, *51*, 8863−8874. [5c] H. Frisell, B. Åkermark, *Organometallics* **1995**, *14*, 561−563.

[6] Fe: [6a] Y. Xu, B. Zhou, *J. Org. Chem.* **1987**, *52*, 974−977. [6b] U. Eberhardt, G. Mattern, *Chem. Ber.* **1988**, *121*, 1531−1534. Rh: [6c] P. A. Evans, J. D. Nelson, *J. Am. Chem. Soc.* **1998**, *120*, 5581−5582. Ru: [6d] Y. Morisaki, T. Kondo, T.-A. Mitsudo, Y. Watanabe, *Organometallics* **1999**, *18*, 4742−4746. [6e] B. M. Trost, P. L. Fraisse, Z. T. Ball, *Angew. Chem.* **2002**, *114*, 1101−1103; *Angew. Chem. Int. Ed.* **2002**, *41*, 1059−1061.

[7] Y. Matsushima, K. Onitsuka, T. Kondo, T.-a. Mitsudo, S. Takahashi, *J. Am. Chem. Soc.* **2001**, *123*, 10405−10406.

[8] [8a] R. Takeuchi, M. Kashio, *J. Am. Chem. Soc.* **1998**, *120*, 8647−8655. [8b] R. Takeuchi, K. Tanabe, *Angew. Chem.* **2000**, *112*, 2051−2054; *Angew. Chem. Int. Ed.* **2000**, *39*, 1975−1978.

[9] J. P. Janssen, G. Helmchen, *Tetrahedron Lett.* **1997**, *38*, 8025−8026.

[10] [10a] B. Bartels, G. Helmchen, *Chem. Commun.* **1999**, 741−742. [10b] K. Fuji, N. Kinoshita, K. Tanaka, T. Kawabata, *Chem. Commun.* **1999**, 2289−2290. Note added in proof (February 10, 2003): After submission of our work, Ir^I-catalysed allylic aminations using ligand **L6** were reported: T. Ohmura, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 15164−15165.

[11] B. Bartels, C. García-Yebra, F. Rominger, G. Helmchen, *Eur. J. Inorg. Chem.* **2002**, 2569−2586.

[12] [12a] R. Hulst, N. Koen de Vries, B. L. Feringa, *Tetrahedron: Asymmetry* **1994**, *5*, 699−708. [12b] J. F. Jensen, B. Y. Svendsen, T. V. la Cour, H. L. Pedersen, M. Johannsen, *J. Am. Chem. Soc.* **2002**, *124*, 4558−4559.

[13] E. Keller, J. Mauer, R. Naasz, T. Schrader, A. Meetsma, B. L. Feringa, *Tetrahedron: Asymmetry* **1998**, *9*, 2409−2413.

[14] Ligand **L3** was isolated as a 2.5:1 mixture of diastereomers and used as such in catalysis.

[15] [15a] A. H. M. de Vries, A. Meetsma, B. L. Feringa, *Angew. Chem.* **1996**, *108*, 2526−2528; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2374−2376. [15b] L. A. Arnold, R. Imbos, A. Mandoli, A. H. M. de Vries, R. Naasz, B. L. Feringa, *Tetrahedron* **2000**, *56*, 2865−2878.

[16] B. L. Feringa, M. Poneschi, L. A. Arnold, R. Imbos, A. H. M. de Vries, *Angew. Chem.* **1997**, *109*, 2733−2736; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2620−2623.

[17] A. Alexakis, S. Rosset, J. Allamand, S. March, F. Guillen, C. Benhaim, *Synlett* **2001**, *9*, 1375−1378.

[18] M. Ostermeier, PhD Dissertation, Universität Heidelberg, Heidelberg, Germany, **2002**. Note added in proof (February 10, 2003): The particular effectiveness of phosphorus amidites is also described in recens work of other authors, cf.: D. Peña, A. J. Minnaard, A. H. M. de Vries, J. G. de Vries, B. L. Feringa, *Org. Lett.* **2003**, *5*, 475−478.

[19] For a recent review see: K. Fagnou, M. Lautens, *Angew. Chem. Int. Ed.* **2002**, *41*, 26−47.

[20] E. Keinan, E. Bosh, *J. Org. Chem.* **1986**, *51*, 4006−4016.

[21] Z. Rappoport, S. Winstein, W. G. Young, *J. Am. Chem. Soc.* **1972**, *94*, 2320−2329.

[22] J. L. Lehmann, G. C. Lloyd-Jones, *Tetrahedron* **1995**, *51*, 8863−8874; enantiomer analysis of **3b** by HPLC: Chiracel ODH column, length: 25 cm + 5 cm precolumn, flow: 0.5 mL min^{-1}, eluent: *n*hexane/*i*PrOH (99.5:0.5), **3b**: $t_R(R)$ = 28.9 min, $t_R(S)$ = 31.6 min; (*E*)-**4b**: t_R = 45.1 min, $[\alpha]_D^{24}$ = 27.2 (*c* = 0.85, $CHCl_3$) for **3b** with 86% *ee* (*R*).

[23] A. L. J. Beckwith, A. A. Zavitas, *J. Am. Chem. Soc.* **1986**, *108*, 8230−8234; enantiomer analysis of **3c** by GC: Chiraldex γ-CD TA column, length: 30 m, 100 kPa helium, flow 80 mL min^{-1}, 50−100 °C with 1 °C min^{-1}, then 20 min at 100 °C, **3c**: $t_R(R)$ = 35.7 min, $t_R(S)$ = 36.7 min; (*E*)-**4c**: t_R = 43.8 min $[\alpha]_D^{27}$ = 12.1 (*c* = 1.23, CH_2Cl_2) for **3c** with 85% *ee* (*R*).

[24] Enantiomer analysis of **3a** by HPLC: Chiracel ODH column, length: 25 cm + 5 cm precolumn, flow: 0.5 mL min^{-1}, eluent: *n*hexane/ *i*PrOH (99.5:0.5), **3a**: $t_R(R)$ = 32.2 min, $t_R(S)$ = 34.3 min; (*E*)-**4a**: t_R = 49.6 min $[\alpha]_D^{20}$ = 11.4 (*c* = 0.63, $CHCl_3$) for **3a** with 93% *ee* (*R*).

[25] Enantiomer analysis of **3d** by GC: Chiraldex γ-CD TA column, length: 30 m, 100 kPa helium, flow 80 mL min^{-1}, 50−100 °C with 1 °C min^{-1}, then 20 min at 100 °C, **3d**: $t_R(R)$ = 44.8 min, $t_R(S)$ = 46.3 min; (*E*)-**4d**: t_R = 56.7 min. $[\alpha]_D^{20}$ = 0.07 (*c* = 0.54, $CHCl_3$) for **3d** with 66% *ee* (*R*).

[26] Enantiomer analysis of **3e** by HPLC: Chiracel ODH column, length: 25 cm + 5 cm precolumn, flow: 0.5 mL min^{-1}, eluent: *n*hexane/ *i*PrOH (95:5), **3e**: $t_R(R)$ = 23.2 min, $t_R(S)$ = 24.6 min; (*E*)-**4e**: t_R = 28.9 min. $[\alpha]_D^{24}$ = −1.4 (*c* = 0.76, $CHCl_3$) for **3e** with 70% *ee* (*R*).

[27] This apparatus was invented in the senior author's group in the 1980s, cf. G. Wegner, PhD Dissertation, Universität Würzburg, Würzburg, Germany, **1987**. In the meantime, it has become widely known in the chemical community by oral communication.

Received November 6, 2002
[O02610]