Tanasri Bunlaksananusorn

Novel Synthesis of Chiral 1,2-Aminophosphine Ligands and Their Applications in Asymmetric Catalysis

München, 2003

Dissertation zur Erlangung des Doktorgrades
der Fakultät für Chemie und Pharmazie
der Ludwig-Maximilians-Universität München

Novel Synthesis of Chiral 1,2-Aminophosphine Ligands and Their Applications in Asymmetric Catalysis

Von

Tanasri Bunlaksananusorn

aus Yala, Thailand

München, 2003

Erklärung:

Diese Dissertation wurde im Sinne von § 13 Abs. 3 bzw. 4 der Promotionsordnung vom 29. Januar 1998 von Professor Dr. Paul Knochel betreut.

Ehrenwörtliche Versicherung:

Diese Dissertation wurde selbständig, ohne unerlaubte Hilfe erarbeit.

München, am 14.08.2003

Tanasri Bunlaksananusorn

Dissertation eingereicht am 14.08.2003

1. Gutachter: Prof. Dr. Paul Knochel
2 Gutachter: Prof. Dr. em. Wolfgang Steglich

Mündliche Prüfung am 25.09.2003

This work was carried out from March 2000 to October 2003 under the supervision of Professor Paul Knochel at the Fakultät für Chemie und Pharmazie, Ludwig-Maximilians-University, Munich.

I would like to thank Prof. Paul Knochel for giving me the opportunity to do my PhD in his group and his encouragement during my PhD work.

I also would like to thank Prof. Steglich for agreeing to be my "Zweigutacter", as well as Prof. Karaghiosoff, Prof. Pfändler, Prof. Zipse, Prof. Langhals for the interest shown in this manuscipt by accepting to be referees.

I would like to thank Ludwig-Maximilians-University of Munich for financial support.

I thank Dr. Lutz Ackerman and Frédéric Liron for the correction of this manuscript.

Vladimir Malakhov und Krystyna danke ich für die tatkräftige Unterstützung im Labor. Für die administrative Unterstützung bedanke ich mich bei Gabi Fried und Beatrix Cammelade.

Special thank go to my great lab mates Katja Tappe, Lionel Aufauvre, Andrei Gavriouchine, Viet Anh Vu and Yevgeniy Snitkovskyy for listening my songs and their invaluable help in the lab. I am indebted to Dr. Alain Louis Rodriguez for his precious help and his patience.

Furthermore, my appreciation is extended to all the members of AK Knochel who came and went throughout my PhD that have helped me with suggestion and support with their sympathy, which have made my time here in Germany great experience.

Finally, I would like to thank my mother, elder brothers and younger sister in Thailand for their great support through my time abroad.

Parts of this PhD have been published

[1] P. Knochel, A. Boudier, L. O. Bromm, E. Hupe, J. A. Varela, A. L. Rodriguez, C. Koradin, T. Bunlaksananusorn, H. Laaziri, F. Lhermitte, "Selective transformations mediated by main-group organometallics", *Pure Appl. Chem*. **2000**, *72*, 1699.

[2] A. L. Rodriguez, T. Bunlaksananusorn, P. Knochel, "Potassium *tert*-Butoxide Catalyzed Addition of Carbonyl Derivatives to Styrenes", *Org. Lett*. **2000**, *21*, 3285.

[3] T. Bunlaksananusorn, A. L. Rodriguez, P. Knochel, "*t*-BuOK-catalyzed addition of ketones and nitriles to vinylic silanes, phosphines and thio derivatives", *J. Chem. Soc., Chem. Commun.* **2001**, 745.

[4] P. Knochel, E. Hupe, W. Dohle, D. M. Lindsay, Q. Veronique, V. Bonnet, A. Boudier, F. Kopp, S. Demay, N. Seidel, M. I. Calaza, V. A. Vu, I. Sapountzis, T. Bunlaksananusorn, "Functionalized main-group organometallics for organic synthesis", *Pure Appl. Chem*. **2002**, *74***,** 11.

[5] T. Bunlaksananusorn, P. Knochel, "*t*-BuOK-catalyzed addition phosphines to functionalized alkenes: a convenient synthesis of polyfunctional phosphine derivatives", *Tetrahedron Lett*. **2002**, *43*, 5817.

[6] T. Bunlaksananusorn, K. Polborn, P. Knochel, "New P,N-Ligands for the Performance of Asymmetric Ir-Catalyzed Reactions", *Angew. Chem. Int. Ed.* **2003**, *42*, 3941.

[7] T. Bunlaksananusorn, A. P. Luna, M. Bonin, L. Micouin, P. Knochel, "New Applications of Camphor-Derived P,N-Ligands for Asymmetric Pd- and Ir-Catalyzed Reactions", *Synlett* **2003**, *in press*.

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Introduction

Results and Discussion

Experimental Section

1 Overview

The preparation of enantiomerically enriched compounds is an important and challenging area for synthetic chemists.[1] There are numerous examples, which stress the necessity for preparing enantiomerically enriched compounds. In 1996, two thirds of the 1200 drugs in the development stage were chiral and 51 % were developed as single enantiomers. The market for drugs of single enantiomers increased from $ 73 billion in 1996 to more than $ 96 billion in 1998.[2] In 2000, the worldwide sales for drug of single enantiomers reached $ 123 billion.[3] Therefore, the search for efficient syntheses of enantiomerically enriched compounds is an active area of research in both academic and industrial laboratories.[4]

There are three main approaches to synthesize single enantiomers:

- Synthesis from the chiral pool
- Resolution of racemic mixtures
- Asymmetric synthesis (the use of chiral reagents or auxiliaries[5] such as enzymes[6] non-metal-[7] or metal-based catalysts[8])

The approach *via* asymmetric catalysis has obvious advantages compared with the reagent and auxiliary methodologies,[5] since a small amount of an enantiomerically pure material produces large quantities of enantiopure material, thereby being economically more feasible.

One challenging topic in the research area of transition metal-catalyzed reactions is the development of chiral phosphine ligands. They are one of the most promising class of ligands in terms of stereoselectivity, rate and productivity. Phosphines coordinate metal atoms and can thereby create a chiral environment. They are also kinetically activating metal complexes toward ligand exchanges and therefore are facilitating catalytic processes.

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[1] a) J. D. Morrison, *Asymmetric Synthesis*, Academic Press, New York, **1983-1985**, *Vols. 1-5*; b) M. Nogradi, *Stereoselective Synthesis*, Wiley-VCH, Weinheim, **1955**.
[2] S. C. Stinson, *Chem. Eng. News*, **1999**, *77*, 101.
[3] S. C. Stinson, *Chem. Eng. News*, **2001,** *79*, 45.
[4] M. McCarthy, P. J. Guiry, *Tetrahedron* **2001**, *57*, 3809.
[5] R. A. Aitken, S. N. Kilenyi, *Asymmetric Synthesis*, Blackie, London, **1994**.
[6] C. –H. Wong, G. M. Whitesides, *Enzymes in Synthetic Organic Chemistry*, Pergamon Oxford, **1994**.
[7] M. S. Sigman, E. N. Jacobsen, *J. Am. Chem. Soc*. **1998**, *120*, 4901.
[8] a) M. Beller, C. Bolm, *Transition Metals for Organic Synthesis*, Wiley-VCH, Weinheim, **1998**; b) E. N. Jacobsen, A. Pfaltz, H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Springer, Berlin, **1999**.

1.1 Chiral P,P-ligands

In 1972, Kagan developed the ligand DIOP[9] and introduced the concept of C_2-symmetric ligands,[10] which reduces the number of possible catalyst-substrate conformations. Knowles (Nobel prize 2001)[11] and Horner developed DIPAMP,[12] a C_2-symmetric P-chirogenic phosphine ligand (see Chart 1). The discovery of DIPAMP enabled the first industrial asymmetric syntheses of amino acid (*S*)-DOPA, a drug used for treating Parkinson's disease. In this process a Rh-catalyzed asymmetric hydrogenation constitutes the key step.[13] In 1980, Noyori (Nobel Prize 2001)[14] reported an axially chiral ligand, BINAP.[15] The discovery of BINAP significantly expanded the scope of transition metal catalysts in asymmetric hydrogenations,[16] enantioselective reductions of various C=C and C=O double bonds[17] and also allowed the isomerization of allyl amines into enamines.[18]

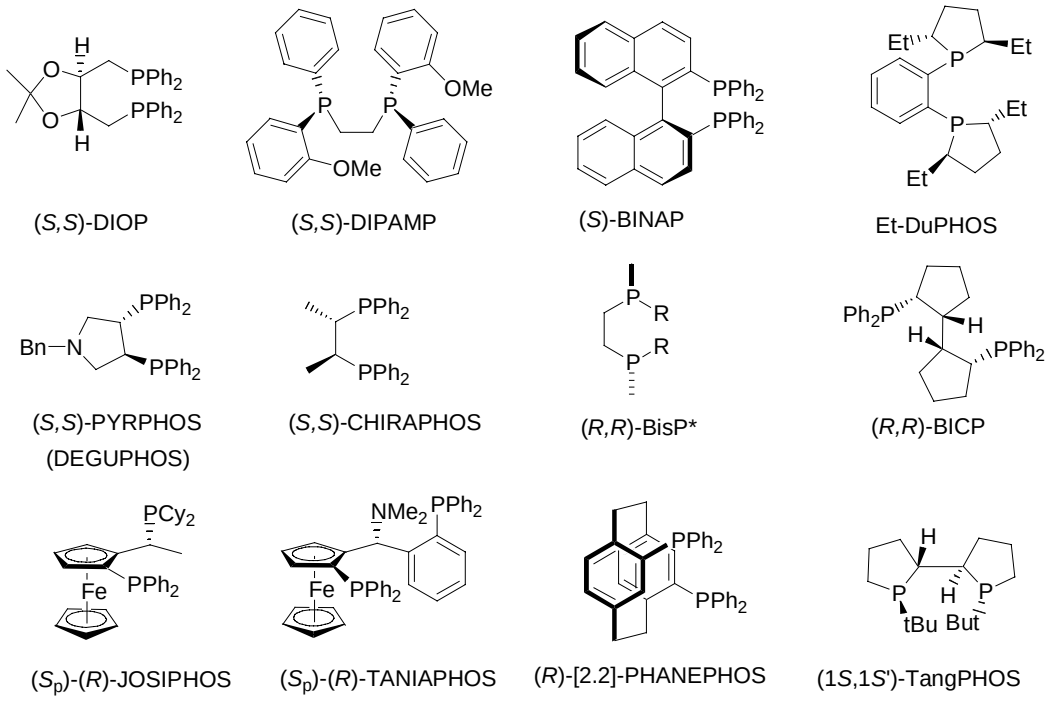
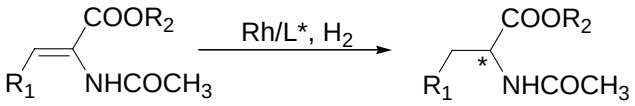


Chart 1. Chiral diphosphine ligands.

[9] H. B. Kagan, T. P. Dang, *J. Am. Chem. Soc*, **1972**, *94*, 6429.
[10] J. K. Whitesell, *Chem. Rev*. **1989**, *89*, 1581.
[11] W. S. Knowles, *Adv. Synth. Catal*. **2003**, *345*, 3.
[12] W. S. Knowles, *Acc. Chem. Res*. **1983**, *16*, 106.
[13] a) W. S. Knowles, M. J. Sabacky, B. D. Vineyard, *J. Chem. Soc., Chem. Commun*. **1972**, 10; b) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weinkauff, *J. Am. Chem. Soc*, **1977**, *99*, 5946.
[14] R. Noyori, *Adv. Synth. Catal*. **2003**, *345*, 15.
[15] R. Noyori, H. Takaya, *Acc. Chem. Res*. **1990**, *23*, 345.
[16] A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, R. Noyori, *J. Am. Chem. Soc*. **1980**, *102*, 7932.
[17] a) T. Ohta, H. Takaya, M. Kitamura, K. Nagai, R. Noyori, *J. Org. Chem*. **1987**, *52*, 3174; b) R. Noyori, T. Ohkuma, M. Kitamura, H. Takaya, N. Sayo, H. Kumobayashi, S. Akutagawa, *J. Am. Chem. Soc*. **1987**, *109*, 5856; c) R. Noyori, T. Ohkuma, *Angew. Chem.* **2001**, *113*, 40; *Angew. Chem. Int. Ed*. **2001**, *40*, 40.
[18] Tani, T. Yamagata, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita, R. Noyori, T. Otsuka, *J. Am. Chem. Soc*. **1984**, *106*, 5208.

Based on the discovery of DIOP, DIPAMP and BINAP, many new chiral diphosphine-based ligands were synthesized such as Et-DuPHOS,[19] (*S*,*S*)-PYRPHOS,[20] (*S*,*S*)-CHIRAPHOS,[21] (*R*,*R*)-BisP*,[22] (*R*,*R*)-BICP,[23] (S_p)-(*R*)-JOSIPHOS,[24] (S_p)-(*R*)-TANIAPHOS,[25] (*R*)-[2.2]-PHANEPHOS,[26] (1S,1*S*')TangPHOS.[27] They were extensively employed in asymmetric hydrogenation reactions of enamides (Table 1), giving rise to the corresponding amino acid derivatives with excellent enantioselectivities (> 96 % *ee*).[28]

Table 1. Enantioselective hydrogenation reactions of enamides.



L*	R_1	R_2	% *ee*
(*S*)-BINAP	C_6H_5	H	100 (*R*)
(*S*,*S*)-EtDuPHOS	C_6H_5	CH_3	>99 (*S*)
(*S*,*S*)-PYRPHOS	C_6H_5	H	99 (*R*)
(*S*,*S*)-CHIRAPHOS	C_6H_5	H	99 (*R*)
(*R*)-[2,2]PHANEPHOS	C_6H_5	CH_3	98 (*R*)
(*S*,*S*)-BisP*	H	CH_3	>99 (*R*)
(*R*,*R*)-BICP	C_6H_5	H	99 (*S*)
JOSIPHOS	C_6H_5	CH_3	96 (*S*)
TANIAPHOS	C_6H_5	CH_3	96 (*S*)
TangPHOS	C_6H_5	H	>99 (*R*)

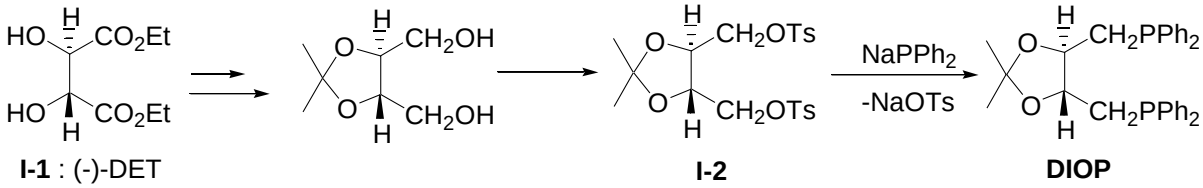
[19] M. J. Burk, *J. Am. Chem. Soc*. **1991**, *113*, 8518.
[20] a) U. Nagel, *Angew. Chem.* **1984**, *96*, 425; *Angew. Chem. Int. Ed*. **1985**, *23*, 435; b) U. Nagel, E. Kinzel, J. Andrade, G. Prescher, *Chem. Ber*. **1986**, *119*, 3326; c) U. Nagel, T. Krink, *Chem. Ber*. **1993**, *126*, 1091.
[21] M. D. Fryzuk, B. Bosnich, *J. Am. Chem. Soc*. **1977**, *99*, 6262.
[22] a) T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, *J. Am. Chem. Soc*. **1998**, *120*, 1635.
[23] G. Zhu, P. Cao, Q. Jiang, X. Zhang, *J. Am. Chem. Soc*. **1997**, *119*, 1799.
[24] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc*. **1994**, *116*, 4062.
[25] T. Ireland, G. Großheimann, C. Wieser-Jeunesse, P. Knochel, *Angew. Chem.* **1999**, *111*, 3397; *Angew. Chem. Int. Ed.* **1999**, *38*, 3212.
[26] P. J. Pye, K. Rossen, R. A. Reamer, N. N. Tsou, R. Volante, P. J. Reider, *J. Am. Chem. Soc*. **1997**, *119*, 6207.
[27] W. Tang, X. Zhang, *Angew. Chem.* **2002**, *114*, 1682; *Angew. Chem. Int. Ed.* **2002**, *41*, 1612.
[28] a) I. Ojima, *Catalytic Asymmetric Synthesis*, 2nd ed, VCH, Weinheim, **2000**; b) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, **1994**.

Chiral diphosphine ligands are also widely used in metal-mediated asymmetric reactions. Such ligands are generally prepared by:

- S_N2 reactions
- oxidative couplings
- Diels-Alder reactions
- Michael additions

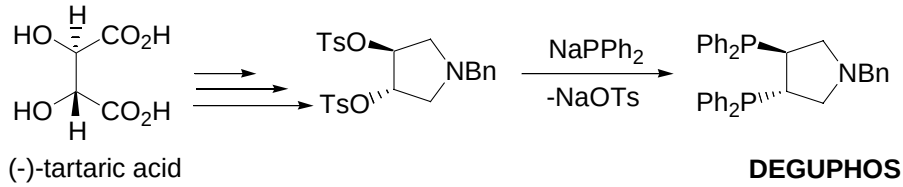
1.1.1 Synthesis *via* S_N2 reactions

Kagan's DIOP ligand,[9] which was applied in Rh-catalyzed hydrogenation reactions, was prepared from (-)-diethyl tartrate (DET, **I-1**) bearing the stereogenic information in the carbon backbone as outlined in Scheme 1. Sodium diphenylphosphide was employed in a S_N2 type reaction with the corresponding tosylate **I-2** to introduce the phosphorus moiety in the last reaction step of the sequence.



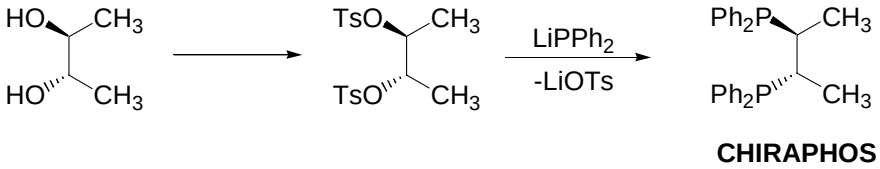
Scheme 1. Synthesis of DIOP.[9]

Nagel's DEGUPHOS and Bosnich's CHIRAPHOS are prepared following a similar synthetic pathway (Scheme 2 and 3). They are effective ligands for Rh-catalyzed enantioselective hydrogenation reactions.[29, 30]



Scheme 2. Synthesis of Nagel's DEGUPHOS.[20]

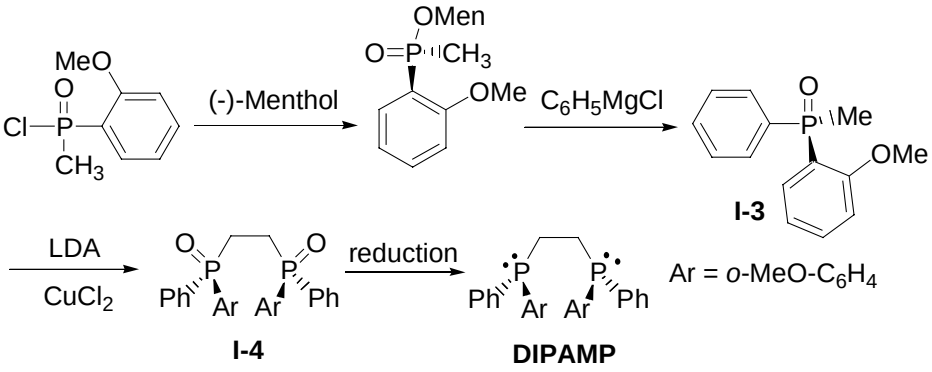
[29] V. Tararov, R. Kadyrov, A. Monsees, T. H. Riermeier, A. Börner, *Adv. Synth. Catal*. **2003**, *345*, 239.
[30] H. B. Kagan in *Asymmetric Synthesis*, *Vol. 5*, *Chiral Catalysis* (Ed.: J. D. Morrison), Academic Press, New York, **1985**, chap. 1.



Scheme 3. Synthesis of CHIRAPHOS.[21]

1.1.2 Synthesis *via* oxidative couplings

A new class of chiral C_2-symmetric P-chirogenic phosphine ligands was introduced by Knowles. The key step of this synthesis is the oxidative coupling of (*o*-methoxyphenyl)methylphenylphosphine oxide **I-3** after treatment with LDA using a copper salt to give the bis-phosphine oxide **I-4**. This precursor is converted to the DIPAMP ligand by reduction of **I-4** (Scheme 4).[31]



Scheme 4. Synthesis of Knowles's DIPAMP.[12]

Imamoto developed ligands based on the 1,2-bis-(alkylmethylphosphino)ethane framework (abbreviated BisP* with alkyl = *t*-butyl, 1-adamantyl, 1-methycyclohexyl, 1,1-diethylpropyl, cyclopentyl, cyclohexyl, isopropyl), which are obtained through oxidative coupling of the corresponding alkyldimethylphosphine-borane **I-5** in a one-pot synthesis starting from PCl_3. The chirality is elegantly introduced by a stereoselective deprotonation of phosphine-boranes **I-5** employing *s*-BuLi in the presence of (-)-sparteine (Scheme 5).[32] These ligands are precursors for efficient catalysts in the asymmetric hydrogenation of dehydroamino acids and itaconic acid derivatives.[33]

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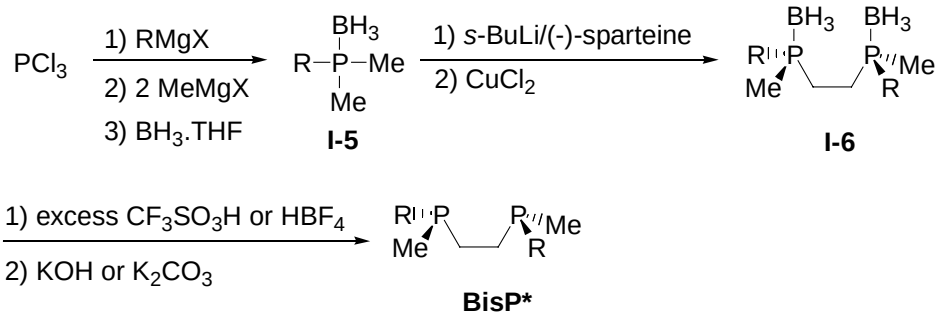
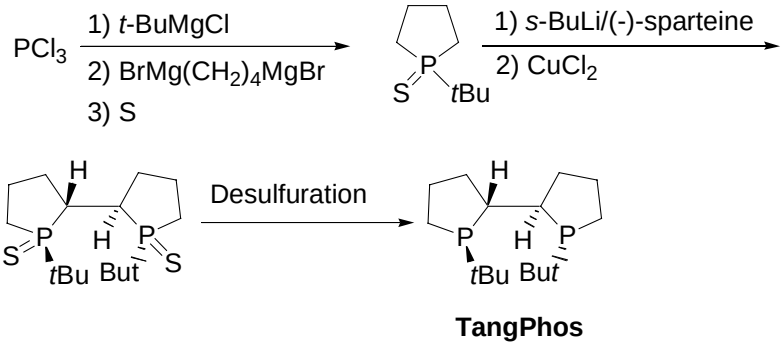
[31] B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, O. J. Weinkauff, *J. Am. Chem. Soc*. **1983**, *16*, 106.
[32] A. R. Muci, K. R. Campos, D. A. Evans, *J. Am. Chem. Soc*. **1995**, *117*, 9075.
[33] a) I. D. Gridnev, Y. Yamanoi, N. Higashi, H. Tsuruta, M. Yasutake, T. Imamoto, *Adv. Synth. Catal*. **2001**, *343*, 118; b) I. D. Gridnev, M. Yasutake, N. Higashi, T. Imamoto, *J. Am. Chem. Soc*. **2001**, *123*, 5268.



Scheme 5. Synthesis of Imamoto's BisP* ligands.[33]

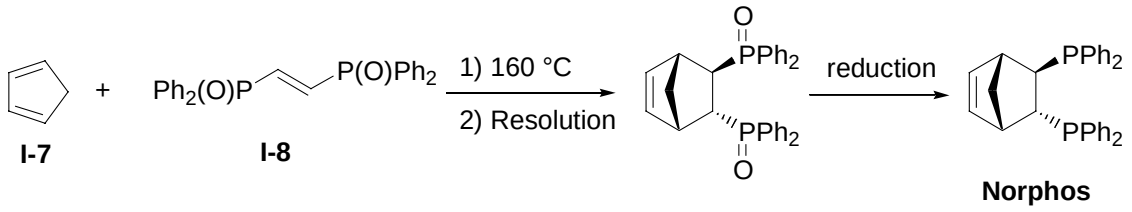
Similar enantioselective deprotonation followed by Cu-mediated oxidative coupling reactions were applied in the preparation of Zhang's TangPhos (Scheme 6).[34] Using this ligand, high enantioselectivities were observed for hydrogenation reactions of various substituted itaconic acid and aromatic enol acetate derivatives.[35]



Scheme 6. Synthesis of TangPhos.[34]

1.1.3 Synthesis *via* Diels-Alder reactions

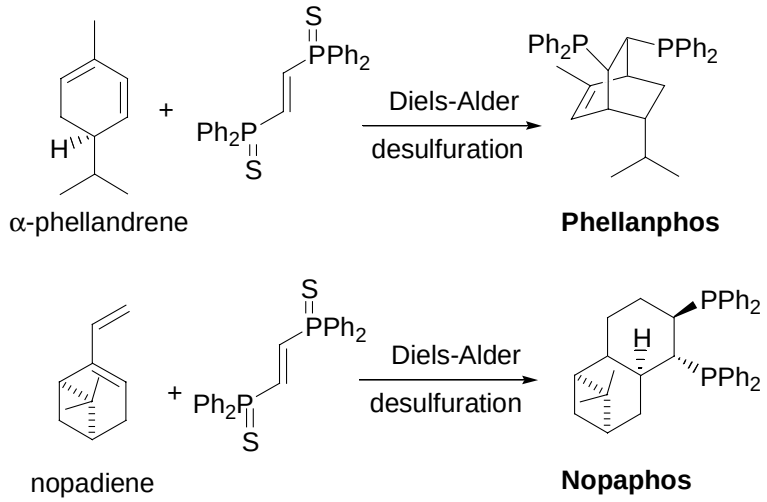
Diels-Alder reactions of a diene **I-7** and a dienophile **I-8** bearing two phosphorus atoms creates two stereogenic centers in α-position to the phosphorus atoms in only one step. Brunner's Norphos[36] was synthesized following this route as shown in Scheme 7.



Scheme 7. Synthesis of Brunner's Norphos.[36]

[34] W. Tang, X. Zhang, *Angew. Chem.* **2002**, *114*, 1682; *Angew. Chem. Int. Ed.* **2002**, *41*, 1612.
[35] W. Tang, D. Liu, X. Zhang, *Org. Lett*. **2003**, *5*, 205.
[36] a) H. Brunner, W. Pieronczyk, B. Schönhammer, K. Streng, I. Bernal, J. Korp, *Chem. Ber.* **1981**, *103*, 2280; b) H. Brunner, W. Pieronczyk, *Angew. Chem.* **1979**, *91*, 655; *Angew. Chem. Int. Ed.* **1979**, 1*8*, 620.

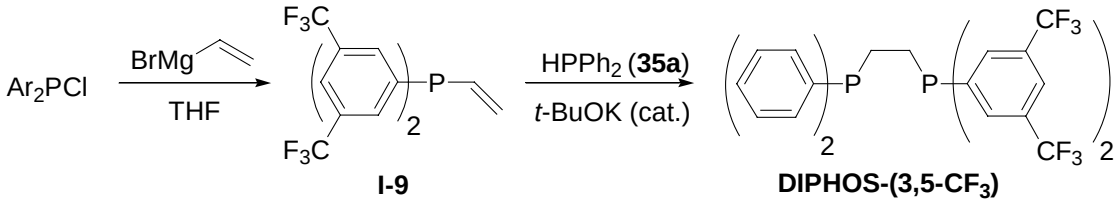
Kagan's Phellanephos[37] and Nopaphos[38] were also prepared based on Diels-Alder reactions starting from chiral dienes such as α-phellandrene or nopadiene. This method avoids the resolution of a ligand precursor. Complexes of these ligands were efficient in Rh-catalyzed hydrogenation of dehydroamino acids and itaconic acid derivatives (Scheme 8).



Scheme 8. Synthesis of Kagan's Nopaphos and Phellanphos.[37,38]

1.1.4 Synthesis *via* Michael additions

The base-mediated addition of a secondary phosphine across a carbon-carbon double bond of a diarylvinylphosphine **I-9** was used in the synthesis of DIPHOS-(3,5-CF_3), which can be applied for Rh-catalyzed enantioselective hydroformylation reactions.[39]

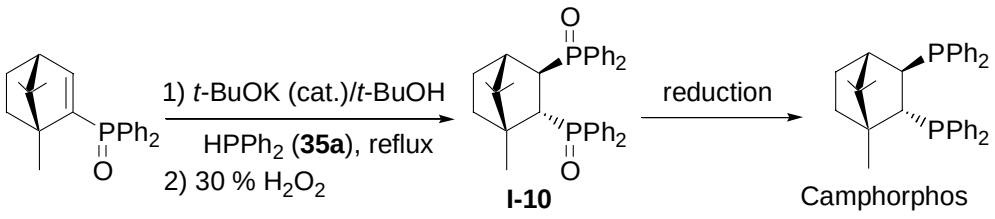


Scheme 9. Synthesis of DIPHOS-(3,5-CF_3).[39]

Helmchen and Krotz reported the preparation of Camphorphos by *t*-BuOK-mediated addition of diphenylphosphine (**35a**) to diphenylvinylphosphine oxide **I-10** *via* Michael

[37] M. Lauer, O. Samuel, H. B. Kagan, *J. Organomet.Chem*. **1979**, *177*, 309.
[38] O. Samuel, R. Couffignal, M. Lauer, S. Y. Zhang, H. B. Kagan, *Nouv. J. Chim*. **1981**, *5*, 15.
[39] C. P. Casey, E. L. Paulsen, E. W. Beuttenmueller, B. R. Proft, L. M. Petrovich, B. A. Matter, D. R. Powell, *J. Am. Chem. Soc*. **1997**, *119*, 11817.

addition. This ligand is effective in Rh-catalyzed asymmetric hydrogenation reactions (Scheme 10).[40]



Scheme 10. Synthesis of Helmchen's Camphorphos ligand.[40]

1.2 Chiral P,N-Ligands

During the last decade, chiral aminophosphine ligands (P,N-ligands) were successfully applied in metal-catalyzed asymmetric transformations.[41] Two reasons for their good performance are steric factors and the electronic differentiation[42] due to the presence of two different donor atoms in the ligand. The most successful classes of P,N-ligands are classified as follows:

- phosphinooxazoline ligands
- axially chiral aminophosphine ligands
- iminophosphine ligands
- phosphinopyridine ligands

1.2.1 Phosphinooxazoline ligands

C_2-symmetric chiral diphenylphosphines like DIOP, CHIRAPHOS and BINAP gave excellent results in asymmetric hydrogenation reactions but were disappointingly inefficient in allylic substitution reactions, particularly of cyclic substrates.[43] In the early 1990s, chiral phosphinooxazoline (PHOX) ligands possessing two different coordinating atoms were developed, which allowed a more selective regiocontrol compared to C_2-symmetric ligands. They proved to be highly effective ligands in Pd-catalyzed asymmetric allylic substitutions.[44]

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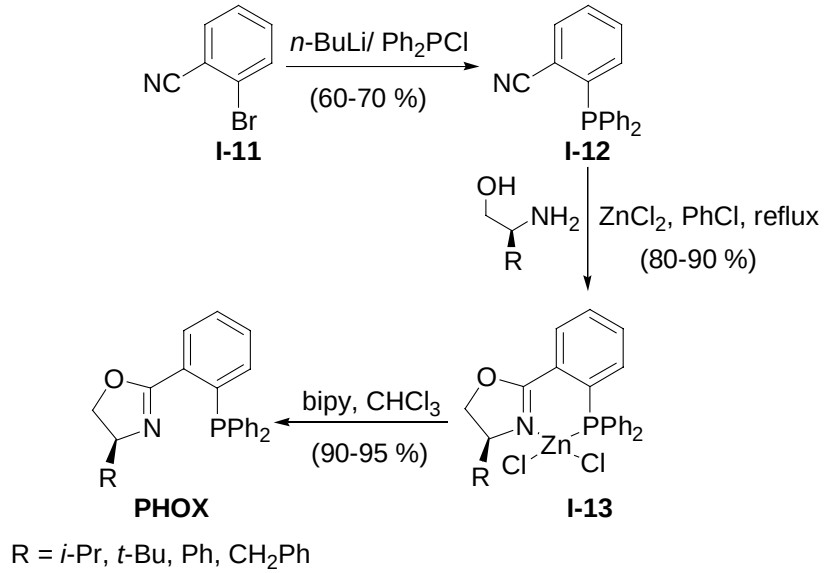
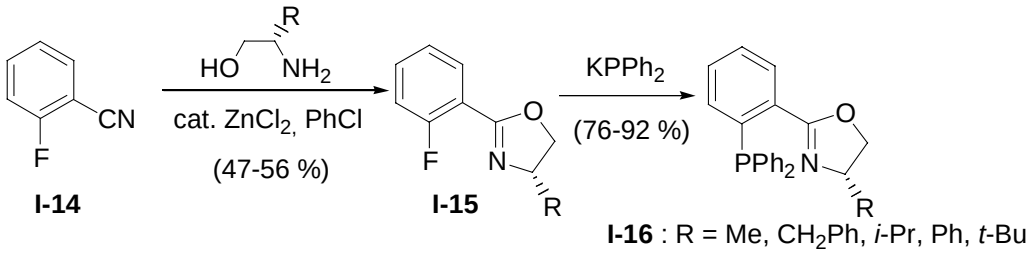
[40] A. Krotz, *Dissertation*, Universität Heidelberg, **1999**.
[41] H. Nishiyama in *Comprehensive Asymmetric Catalysis* (Eds: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, New York, **1999**, Vols. 1-3.
[42] J. W. Faller, K.-H Chao, H. H. Murray, *Organometallics*, **1984**, *3*, 1231.
[43] a) C. G. Frost, J. Howarth, J. M. J Williams, *Tetrahedron: Asymmetry* **1992**, *3* 1089; b) I. Starý, J. Zajiček, P. Kočovský, *Tetrahedron*, **1992**, *48*, 7229; c) B. M. Trost, *Acc. Chem. Res*. **1996**, *29*, 355.
[44] G. Helmchen, A. Pfaltz, *Acc. Chem. Res*. **2000**, *33*, 336.

Helmchen,[45] Pfaltz[46] and Williams[47] independently introduced chiral phosphinooxazoline ligands. In this synthesis, an aryllithium derivative prepared from 2-bromobenzonitrile (**I-11**) was first reacted with Ph_2PCl. The cyano compound **I-12** was subsequently treated with a chiral amino alcohol, thereby introducing the oxazoline moiety. $ZnCl_2$ complexes **I-13** were formed and treated with bipyridine, furnishing the corresponding PHOX ligands as shown in Scheme 11.



Scheme 11. Synthesis of PHOX-ligands following Pfaltz's method.[46]

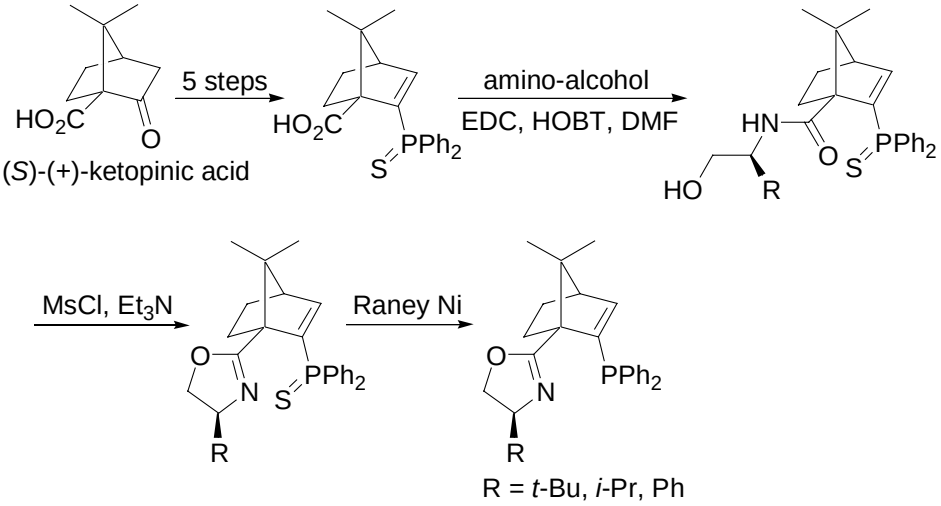
Williams prepared PHOX-ligands in a two step procedure. The reaction of *o*-fluorobenzonitriles **I-14** with amino alcohols in the presence of catalytic amounts of $ZnCl_2$ afforded the 2-(*o*-fluorophenyl)oxazolines **I-15**. The phosphino group is introduced by a nucleophilic aromatic substitution allowing the preparation of numerous different ligands **I-16** (Scheme 12).[48]



Scheme 12. Synthesis of PHOX-ligands following Williams's method.[47]

[45] a) J. Sprinz, G. Helmchen, *Tetrahedron Lett*. **1993**, *34*, 1769; b) G. Helmchen, S. Kudis, P. Sennhenn, H. Steinhagen, *Pure Appl. Chem*. **1997**, *69*, 513.
[46] a) P. von Matt, A. Pfaltz, *Angew. Chem*. **1993**, *105*, 614; *Angew. Chem. Int. Ed.* **1993**, *32*, 566; b) A. Pfaltz, *Acta Chem. Scand*. *B* **1996**, *50*, 189.
[47] a) G. J. Dawson, C. G. Frost, J. M. J. Williams, S. J. Coote, *Tetrahedron Lett*. **1993**, *34*, 3149; b) J. M. J. Williams, *Synlett* **1996**, 705.
[48] M. Peer, J. C. de Jong, M. Kiefer, T. Langer, H. Rieck, P. Sennhenn, J. Sprinz, H. Steinhagen, B. Wiese, G. Helmchen, *Tetrahedron* **1996**, *52*, 7547.

PHOX-ligands are highly effective in Pd-catalyzed asymmetric allylic substitutions,[49] Heck reactions[50] as well as Ir-catalyzed enantioselective hydrogenation reactions of trisubstituted alkenes[51] and imines.[52] Gilbertson reported the synthesis of chiral phosphinooxazoline ligands based on (1*S*)-(+)-ketopinic acid and their use in asymmetric Pd-catalyzed intermolecular Heck reactions (Scheme 13).[53]



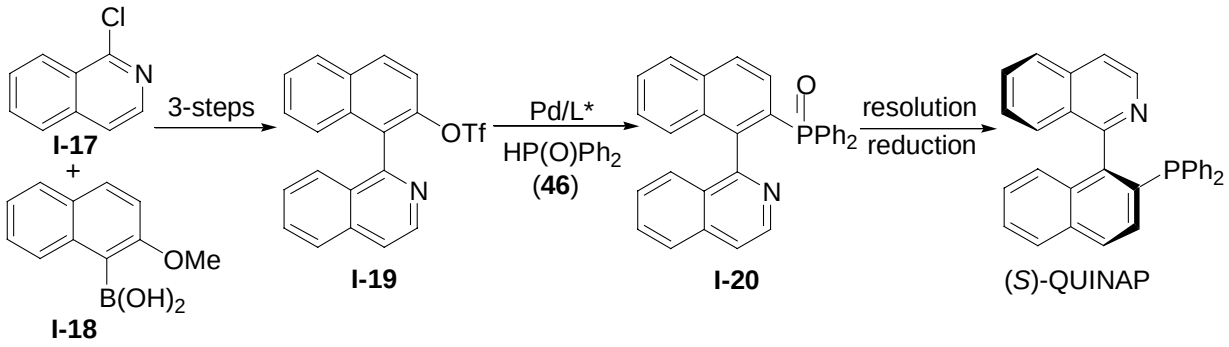
Scheme 13. Synthesis of chiral phosphinooxazoline ligands by Gilbertson.[53]

1.2.2 Axially chiral aminophosphine ligands

In 1993, Brown reported the synthesis and resolution of the axially chiral aminophosphine ligand QUINAP,[54] which was successfully employed in Rh-catalyzed hydroboration[55] and Pd-catalyzed allylic substitutions.[56] A multistep synthesis of the ligand was developed based on a Pd-catalyzed Suzuki reaction of 1-chloroquinoline (**I-17**) and the corresponding boronic acid **I-18**. Pd-catalyzed cross-coupling of aryl triflate **I-19** with $Ph_2P(O)H$ (**46**) led to the corresponding phosphine oxide **I-20**, which was subsequently reduced. (*S*)-QUINAP was obtained after resolution of aminophosphine as outlined in Scheme 14.

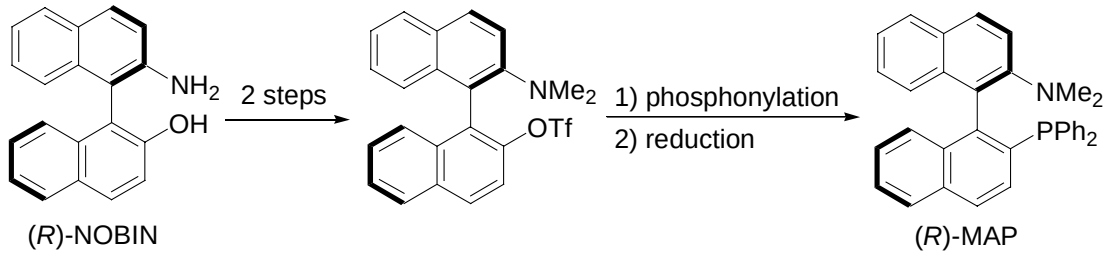
---

[49] a) H. Nishiyama in *Comprehensive Asymmetric Catalysis* (Eds: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **1999**, Vol. 2, Chapter 24; b) S. Kudis, G. Helmchen, *Angew. Chem.* **1998**, *110*, 3210; *Angew. Chem. Int. Ed.* **1998**, *37*, 3047.
[50] O. Loiseleur, M. Hayashi, M. Keenan, N. Schmees, A. Pfaltz, *J. Organomet. Chem.* **1999**, *576*, 16.
[51] A. Lightfoot, P. Schneider, A. Pfaltz, *Angew. Chem.* **1998**, *110*, 3047; *Angew. Chem. Int. Ed.* **1998**, *37*, 2897.
[52] S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz, *J. Am. Chem. Soc*. **1999**, *121*, 6421.
[53] S. R. Gilbertson, Z. Fu, *Org. Lett*. **2001**, *3*, 161.
[54] N. W. Alcock, J. M. Brown, D. I. Hulmes, *Tetrahedron: Asymmetry* **1993**, *4*, 743.
[55] a) J. M. Brown, D. I. Hulmes, T. P. Layzell, *J. Chem. Soc., Chem. Commun*. **1993**, 1673; b) J. M. Valk, G. A. Whitlock, T. P. Layzell, J. M. Brown, *Tetrahedron: Asymmetry* **1995**, *6*, 2593.
[56] J. M. Brown, D. I. Hulmes, P. J. Guiry, *Tetrahedron* **1994**, *50*, 4493.



Scheme 14. Synthesis of Brown's QUINAP.[54]

Recently, a new type of aminophosphine ligand, MAP was reported by Kočovský.[57] It can be regarded as a nitrogen analogue of Hayashi's MOP. The MAP ligand was prepared through a Pd-catalyzed coupling using $Ph_2P(O)H$ (**46**) and subsequent reduction with $HSiCl_3$ (Scheme 15).[58] Pd-complexes of (*R*)-MAP exhibited a dramatic acceleration in the Hartwig-Buchwald amination and in Suzuki reaction of aryl halides.[59]



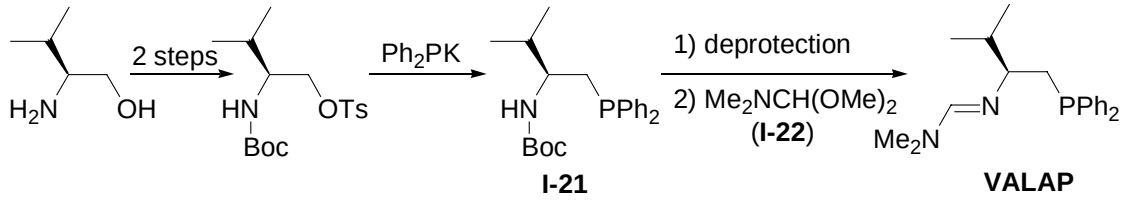
Scheme 15. Synthesis of Kočovský's MAP.[57]

1.2.3 Iminophosphine ligands

A new class of chiral amidinephosphine hybrid ligands, VALAP was easily accessible from a commercially available α-amino acid (L-valine) and its analogs. It was first developed by Morimoto.[60] A diphenylphosphino group was introduced *via* S_N2 reaction with potassium diphenylphosphide, yielding a diphenylphosphinoamine **I-21**, which was converted into VALAP by deprotection and reaction with *N*,*N*-dimethylformamide dimethyl acetal (**I-22**)

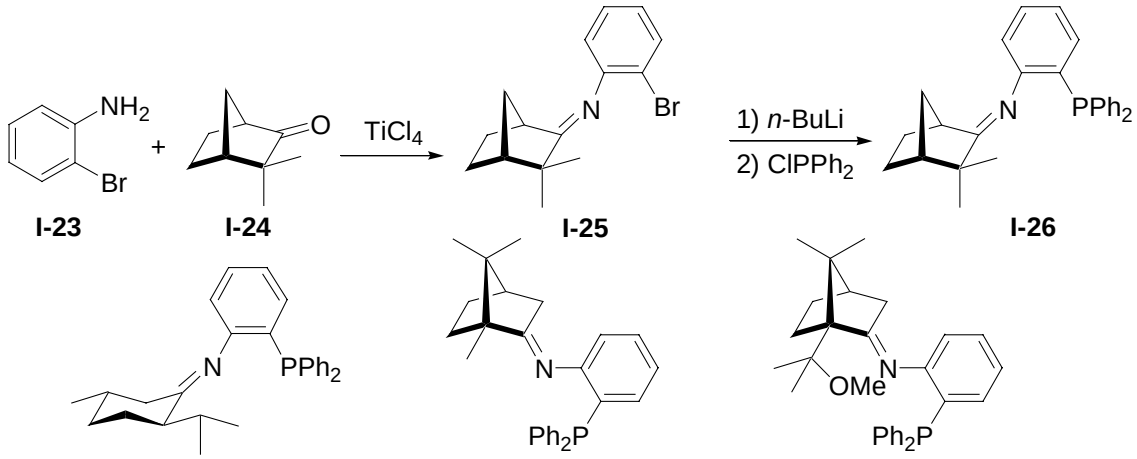
[57] a) S. Vyskočil, M. Smrčina, V. Hanuš, M. Polášek, P. Kočovský, *J. Org. Chem*. **1998**, *63*, 7738; b) K. Ding, Y. Wang, H. Yun, J. Liu, Y. Wu, M. Terada, Y. Okubo, K. Mikami, *Chem. Eur. J*. **1999**, *5*, 1734.
[58] a) S. Vyskočil, M. Smrčina, P. Kočovský, *Tetrahedron Lett*. **1998**, *39*, 9289; b) P. Kočovský, A. V. Malkov, S. Vyskočil, G. C. Lloyd-Jones, *Pure Appl. Chem*. **1999**, *71*, 1425.
[59] S. Vyskočil, I. Cisarova, J. Sejbal, I. Tislerova, M. Smrcina, G. C. Lloyd-Jones, S. C. Stephen, C. P. Butts, M. Murray, V. Langer, *J. Am. Chem. Soc*. **1999**, *121*, 7714.
[60] a) A. Saitoh, K. Achiwa, K. Tanaka, T. Morimoto, *J. Org. Chem*. **2000**, *65*, 4227; b) A. Saitoh, T. Morimoto, K, Achiwa, *Tetrahedron: Asymmetry* **1997**, *8*, 3567.

(Scheme 16). These iminophosphines are efficient chiral ligands for the Cu-catalyzed conjugated addition of diethylzinc to enones[61] and enantioselective Pd-catalyzed allylic substitutions.



Scheme 16. Synthesis of Morimoto's VALAP.[60]

Pd-catalyzed asymmetric Diels-Alder reactions were performed with considerably high enantioselectivity using Hiroi's chiral iminophosphine ligands derived from commercially available (+)-fenchone, (-)-menthone, (+)-camphor and (+)-ketopinic acid.[62] The imines were prepared by condensation of 2-bromoaniline (**I-23**) with (+)-fenchone (**I-24**) in the presence of $TiCl_4$. Lithiation of the bromo-aniline **I-25** with *n*-BuLi followed by phosphinylation with chlorodiphenylphosphine led to chiral iminophosphine ligands **I-26** as outlined in Scheme 17.

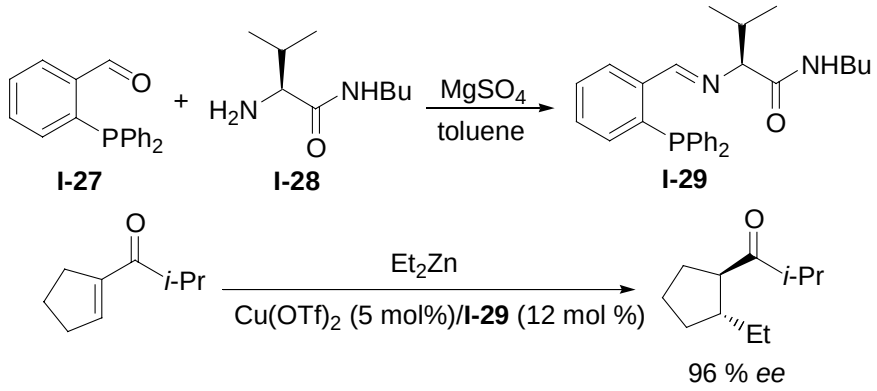


Scheme 17. Synthesis of chiral iminophosphines.[62]

Hoveyda reported recently Cu-promoted asymmetric additions of dialkylzinc species to acyclic aliphatic enones, trisubstituted cyclic enones[63] and unsaturated *N*-

[61] T. Morimoto, Y. Yamaguchi, M. Suzuki, A. Saitoh, *Tetrahedron Lett*. **2000**, *41*, 10025.
[62] K. Hiroi, K. Watanabe, *Tetrahedron: Asymmetry* **2001**, *12*, 3067.
[63] A. W. Hird, A. H. Hoveyda, *Angew. Chem*. **2003**, *115*, 1314; *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 1276.

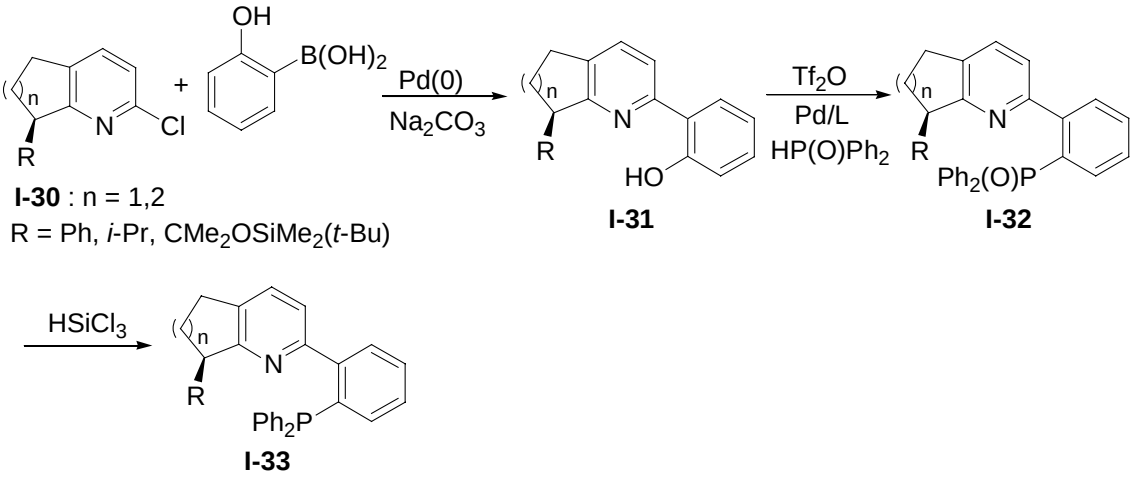
acyloxazolidinones.[64] High yields and excellent enantioselectivitites were observed using chiral iminophosphine ligands **I-29**, which were prepared through condensation of phosphinobenzaldehyde **I-27** with an amino acid derivative **I-28** in the presence of $MgSO_4$ as shown in Scheme 18.



Scheme 18. Synthesis of a chiral iminophosphine ligand according to Hoveyda.[63]

1.2.4 Phosphinoarylpyridine ligands

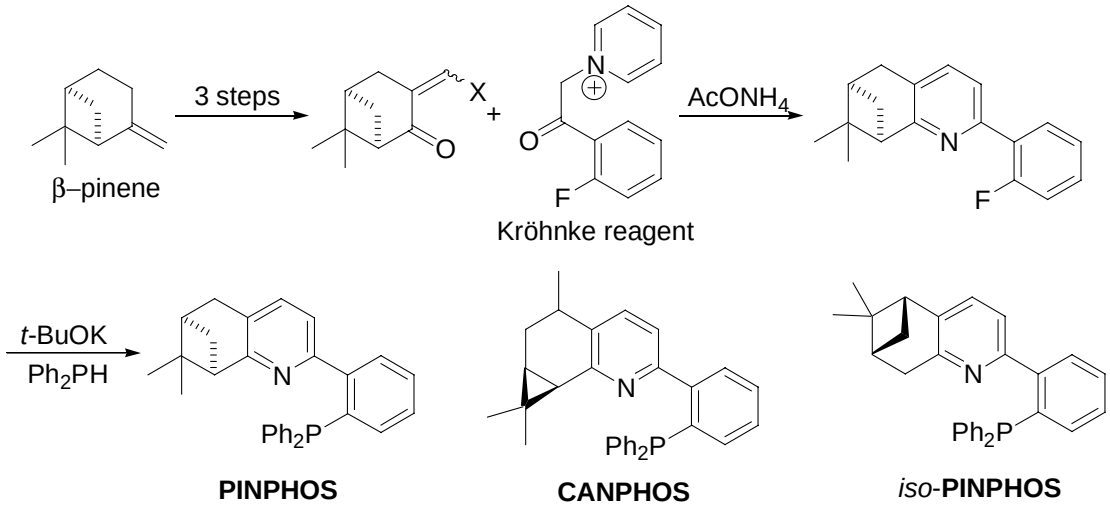
The first phosphinoarylpyridine ligands were reported by Ito.[65] The synthesis of chiral 2-phosphinoarylpyridines started from the corresponding chiral chloropyridines **I-30** (Scheme 19). Suzuki cross-coupling reactions afforded pyridylphenols **I-31**, which were converted into the desired chiral 2-phosphinoarylpyridines **I-33** after the reduction of the phosphine oxides **I-32**. Complexes of these ligands were found to be effective catalysts for Pd-catalyzed allylic substitutions.[66]



Scheme 19. Synthesis of chiral 2-phosphinoarylpyridine ligands.[65]

[64] a) H. Mizutani, S. J. Degrado, A. H. Hoveyda, *J. Am. Chem. Soc*. **2002**, *124*, 779; b) S. J. Degrado, H. Mizutani, A. H. Hoveyda, *J. Am. Chem. Soc*. **2002**, *124*, 13362.
[65] K. Ito, R. Kashiwagi, K. Iwasaki, T. Katsuki, *Synlett* **1999**, 1563.
[66] K. Ito, R. Kashiwagi, K. Iwasaki, T. Katsuki, *Synlett* **2001**, 284.

Kočovský developed the modular pyridine-type P,N-ligands PINPHOS, CANPHOS and *iso*-PINPHOS (Scheme 20). These ligands were synthesized from monoterpenes such as (-)-β-pinene, (+)-3-carene, (+)-2-carene and (-)-α-pinene, respectively *via* Kröhnke annulation as the key step.[67] They were applied in asymmetric Heck reactions.[68, 69]



Scheme 20. Synthesis of 2-phosphinoarylpyridine ligands by Kočovský.[68]

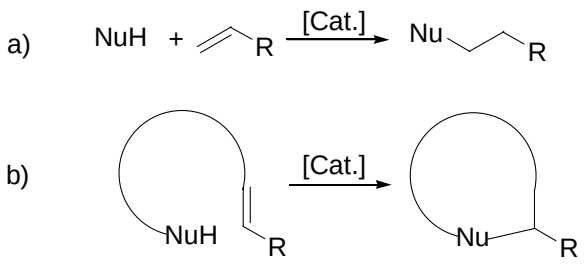
[67] F. Kröhnke, *Synthesis* **1976**, 1.
[68] A. V. Malkov, M. Bella, I. G. Stará, P. Kočovský, *Tetrahedron Lett*. **2001**, *42*, 3045.
[69] G. Chelucci, A. Saba, F. Soccolini, *Tetrahedron*, **2001**, *57*, 9989.

2 Objectives

The first objective of this work was the development of a new base-mediated formation of carbon-carbon bonds avoiding the formation of any side products. Based on cesium alkoxide-mediated additions of nitriles to alkynes previously developed in our group. The goal was to further explore this chemistry using functionalized alkenes instead.

Two main objectives were:

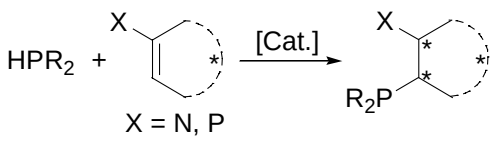
- ❖ the development of base-mediated inter- and intramolecular additions of nucleophiles to alkenes (Scheme 21)
- ❖ to explore the possibility to use this methodology for hydrophosphination reactions of alkenes



Scheme 21. Intermolecular and intramolecular addition of nucleophiles to alkenes.

Based on the hydrophosphination of olefins, another project was the preparation of chiral P,N- and P,P-ligands. The specific aim of this part was:

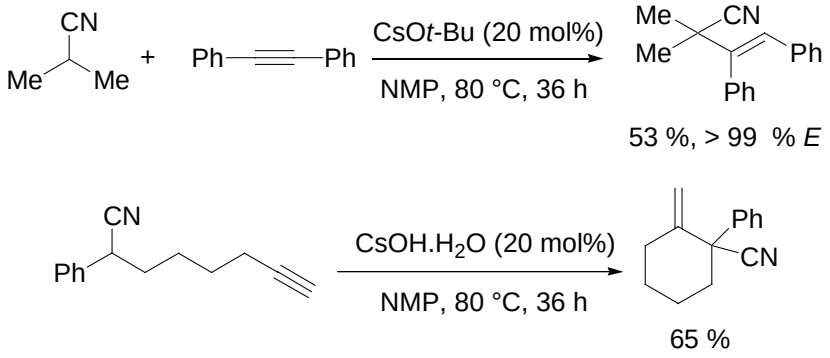
- ❖ to develop a protocol for the preparation of chiral P,N- and P,P-ligands using cheap precursors with chiral backbones (Scheme 22)
- ❖ to use these chiral P,N- and P,P-ligands in asymmetric catalysis



Scheme 22. Proposed preparation of chiral P,N- and P,P-ligands.

1 Addition of nucleophiles to alkenes

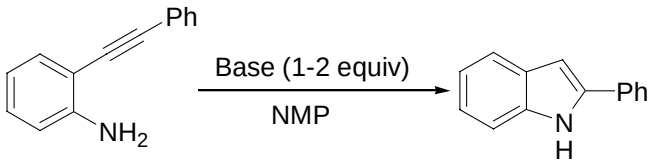
The metal-catalyzed formation of carbon-carbon bonds is an important synthetic tool, which avoids the formation of side products (atom economical reaction).[70] *Knochel* and *Koradin* showed that cesium alkoxides initiates in *N*-methylpyrrolidinone (NMP) inter- and intramolecular additions of nitriles to various alkynes leading to functionalized alkenes with good regio- and stereoselectivities as shown in Scheme 23.[71]



Scheme 23. Cesium alkoxide-mediated addition of nitriles to alkynes.

Recently, *Knochel* and *Rodriguez* have described a mild synthesis of 2-substituted indoles mediated by stoichiometric amounts of potassium or cesium bases in NMP (Table 2).[72]

Table 2. Na, K, Cs base-mediated cyclization reactions of an amino-alkyne.



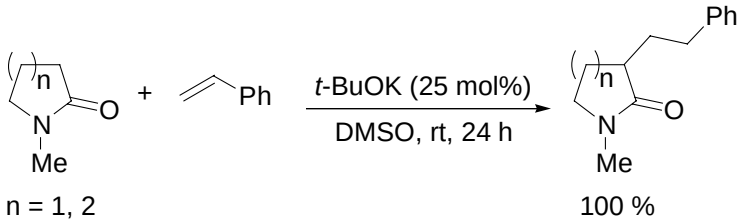
Base	T [°C]	T [h]	Yield [%]
NaH	60	8	<5
NaOEt	80	15	66
t-BuOK	**25**	**4**	**79**
KH	25	5	72
CsOH	90	5	68
t-BuOCs	25	5	71

[70] a) B. M. Trost, *Angew. Chem*. **1995**, *107*, 285; *Angew. Chem. Int. Ed.* **1995**, *34*, 259; b) B. M. Trost, *Science* **1991**, *254*, 1471; c) B. M. Trost, *Acc. Chem. Res*. **2002**, *35*, 695.
[71] C. Koradin, A. L. Rodriguez, P. Knochel, *Synlett* **2000**, 1452; b) C. Koradin, *Dissertation*, Ludwig-Maximilians-Universität, München, **2002**.
[72] A. L. Rodriguez, C. Koradin, W. Dohle, P. Knochel, *Angew. Chem*. **2000**, *112*, 2607; *Angew. Chem. Int. Ed.* **2000**, *39*, 2488.

In contrast, soluble potassium or cesium alkoxides such as *t*-BuOK or *t*-BuOCs as well as KH in NMP led to fast reactions at room temperature. Among these bases, *t*-BuOK in NMP afforded the highest chemical yield.

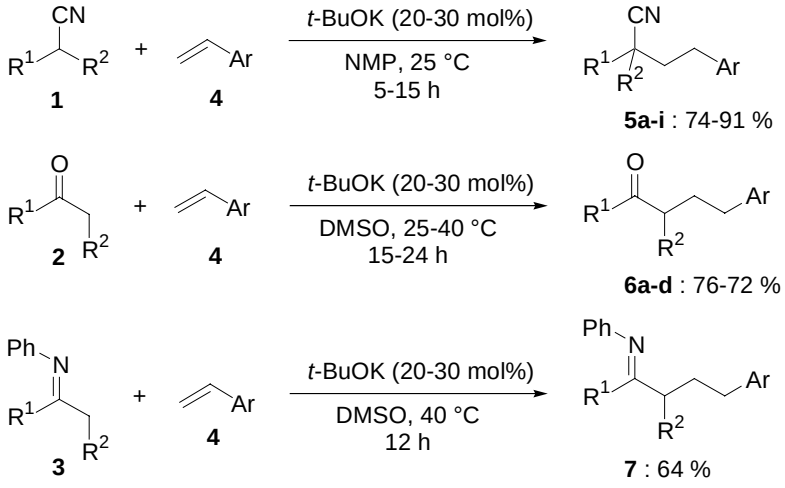
1.1 Addition of carbonyl derivatives to styrenes

The regioselective addition of organometallics to activated olefins such as styrenes is of great utility in polymer chemistry as well as carbometallation reactions.[73] However, only few reports described the addition of carbonyl compounds to styrene. Only, the *t*-BuOK-mediated addition of cyclic amides to styrene was reported (Scheme 24).[74]



Scheme 24. *t*-BuOK-mediated addition of cyclic amides to styrene.

Herein, we report a novel procedure for the addition of various carbonyl derivatives (nitriles (**1**), ketones (**2**), imines (**3**)) to styrenes **4** using substoichiometric amounts of potassium *tert*-butoxide (20-30 mol %) in dimethyl sulfoxide (DMSO) or NMP yielding the corresponding products **5-7** (Scheme 25).[75]



Scheme 25. Addition of carbonyl derivatives **1-3** to styrenes **4**.

[73] a) A. H. Hoveyda, N. M. Heron, in *Comprehensive Asymmetric Catalysis*, *Vol. I*, **1999**, Springer, Berlin, p. 431; b) I. Marek, *J. Chem. Soc., Perkin Trans I*, **1999**, 535; c) P. Knochel, in *Comprehensive Organic Synthesis*, B. M. Trost, I. Fleming, M. F. Semmelhack, Eds., **1991,** *Vol. 4*, Pergamon Press Oxford, p. 865.
[74] a) H. Pines, S. V. Kannan, J. Simonik, *J. Org. Chem.* **1971**, *36*, 2311; b) H. Pines, N. E. Sartoris, *J. Org. Chem*. **1969**, *34*. 2119.
[75] A. L. Rodriguez, T. Bunlaksananusorn, P. Knochel, *Org. Lett*. **2000**, *21*, 3285.

1.1.1 Nitriles as nucleophiles

Nitriles are the most reactive substrates, so that reactions were mostly completed at room temperature within 5-15 h using *t*-BuOK (20-30 mol%). A regioselective addition occurred to afford the addition products **5a-i** in 74-91 % yield (Table 3).

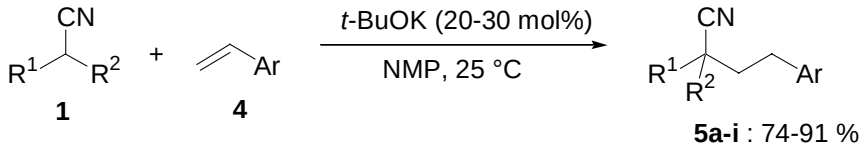
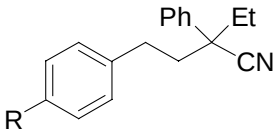
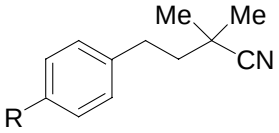
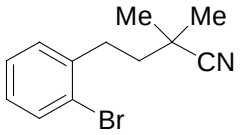
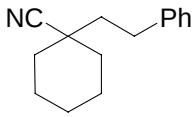
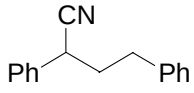
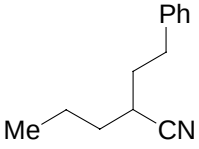


Table 3. *t*-BuOK-mediated addition of nitriles to styrenes.

Entry	Carbonyl compound	R^1	R^2	Ar	Time (h)	Product	Yield (%)[a]
							
1	**1a**	Ph	Et	C_6H_5	5	**5a**: R = H	77
2	**1a**	Ph	Et	*p*-F-C_6H_4	5	**5b**: R = F	78
							
3	**1b**	Me	Me	C_6H_5	5	**5c**: R = H	80
4	**1b**	Me	Me	*p*-F-C_6H_4	5	**5d**: R = F	79
5	**1b**	Me	Me	*p*-MeO-C_6H_4	15	**5e**: R = OMe	74
							
6	**1b**	Me	Me	*o*-Br-C_6H_4	2	**5f**	89
							
7	**1c**	-$(CH_2)_5$-		C_6H_5	15	**5g**	91[b]
							
8	**1d**	Ph	H	C_6H_5	15	**5h**	78[b,c]
							
9	**1e**	C_3H_7	H	C_6H_5	15	**5i**	78[b,c]

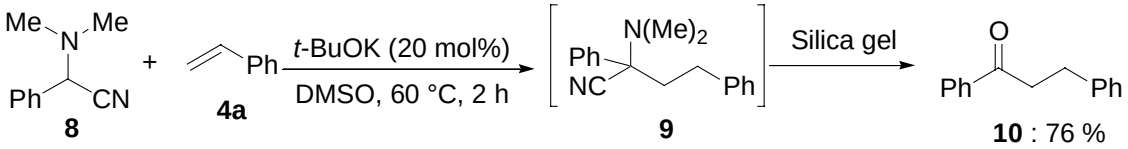
[a] Isolated yield of analytically pure product.

[b] The reaction was performed in DMSO.

[c] 10-15 % of double addition product was isolated.

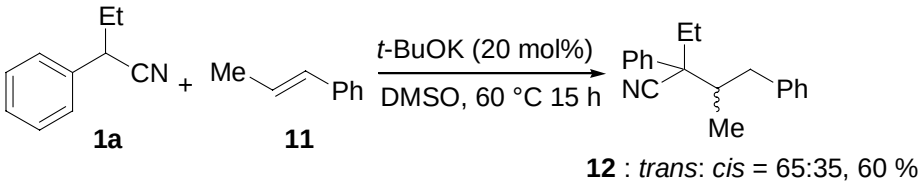
The presence of electron-withdrawing substituents such as a fluorine or a bromine atom on the aromatic ring shortened the reaction times considerably (2-5 h instead of 15 h). Nitriles on primary or secondary carbon atoms added smoothly to styrenes. However, in the case of primary nitriles double addition products (10-15 %) like 2,4-diphenyl-2-(2-phenylethyl)-butyronitrile (**5h´**) and 2,2-bis-2-(phenylethyl)pentanenitrile (**5i´**) were isolated in the case of primary nitriles (entries 8 and 9).

α-Dimethylaminophenylacetonitrile[76] (**8**) was added to styrene (**4a**), leading to the α-amino nitrile intermediate **9**, which was converted to ketone **10** by silica gel during the column chromatography (Scheme 26).



Scheme 26. The addition of α-dimethylaminophenylacetonitrile **8** to styrene **4a**.

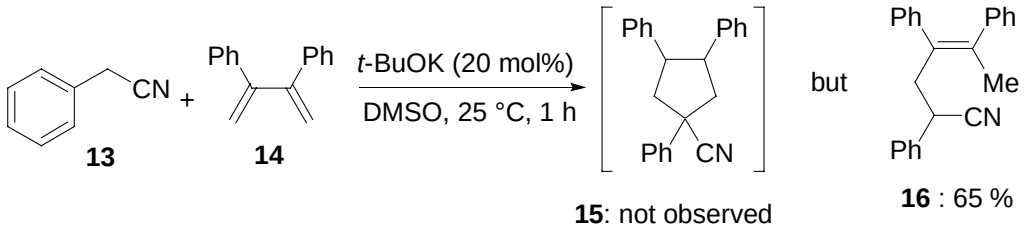
Nitrile **1a** was also reacted with a substituted styrene like *trans*-β-methylstyrene (**11**) in the presence of *t*-BuOK (20 mol%) in DMSO affording mixtures of the *cis* and *trans*-product **12** in satisfactory yield (Scheme 27).



Scheme 27. Addition of nitrile **1a** to *trans*-β-methylstyrene (**11**).

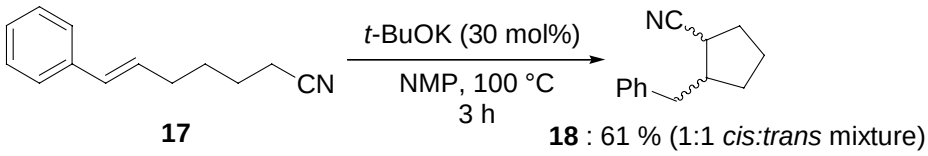
Interestingly, nitrile **13** underwent selectively mono-addition to the diene **14**, yielding the conjugated olefin **16** after isomerization. The cyclic double addition product **15** (5-endo-trig) was disfavored (Scheme 28).

[76] C. R. Hauser, H. M. Taylor, T. G. Ledford, *J. Am. Chem. Soc*. **1960**, *82*, 1786.



Scheme 28. Addition of nitrile **13** to 2,3-diphenyl-1,3-butadiene (**14**).

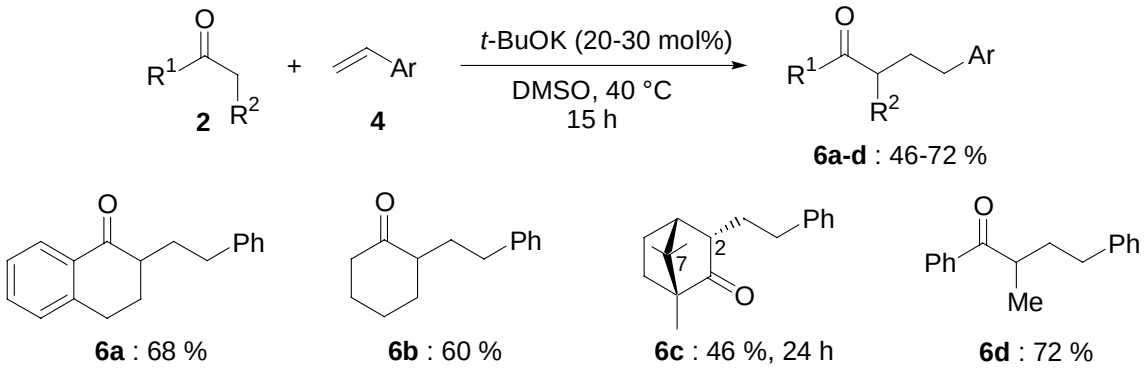
Furthermore, the addition to activated olefins can be performed intramolecularly. Thus, the treatment of 7-phenyl-6-hexenenitrile (**17**) with *t*-BuOK (30 mol%) in NMP (100 °C, 3 h) furnished the cyclopentanenitrile **18** in 61 % yield as a 1:1 mixture of *cis-trans* isomers (Scheme 29).



Scheme 29. *t*-BuOK-mediated intramolecular addition of nitrile **17**.

1.1.2 Ketones as nucleophiles

The addition of ketones to styrene was most efficient using DMSO as solvent since it was realized that NMP itself added to styrene under the more drastic reaction conditions.[74] The reaction temperature was crucial for the control of the formation of undesired double addition products and aldol side reaction of the ketones. When performing the reaction between 38-41 °C, a smooth addition reaction occurred, leading to the mono-addition products. Additionally, an excess ketone (3-4 equiv) was used in order to avoid a double addition reaction (Scheme 30).

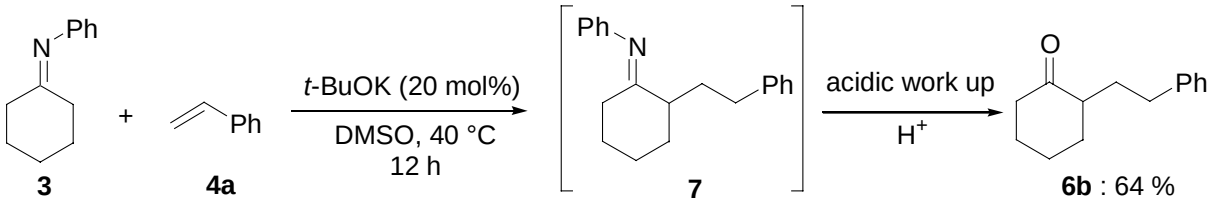


Scheme 30. Addition of various ketones to styrene.

For α-tetralone (**2a**), cyclohexanone (**2b**) and camphor (**2c**), only traces of double addition products were observed and the reactions proceeded cleanly (Scheme 30). The stereochemistry of **6c** was confirmed through NOESY experiments (H_2 correlates with H_7). In the case of ethyl phenyl ketone (**6d**), 8 % of the double addition product 1,4-diphenyl-2-methyl-2-(2-phenylethyl)butan-1-one (**6d´**) was isolated.

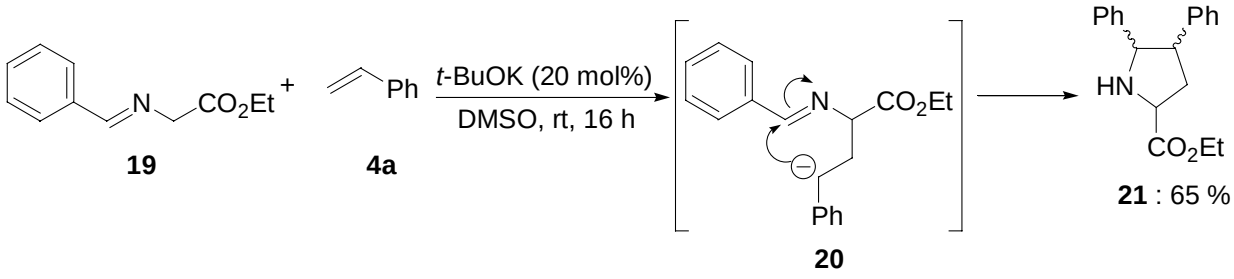
1.1.3 Imines as nucleophiles

The addition of imine **3** to styrene (**4a**) was as well achieved at 40 °C, providing substituted imine **7**, which was converted to ketone **6b** in satisfactory yield by acidic hydrolysis (Scheme 31).



Scheme 31. Addition of imine **3** to styrene (**4a**) leading to the ketone **6b**.

Deprotonation of alanine ester imine **19**[77] with *t*-BuOK in DMSO, followed by the addition of styrene (**4a**) led presumably to intermediate **20**, which exclusively underwent selective cyclization to yield pyrrolidine **21**[78] as a mixture of diastereomers in 65 % yield (Scheme 32).

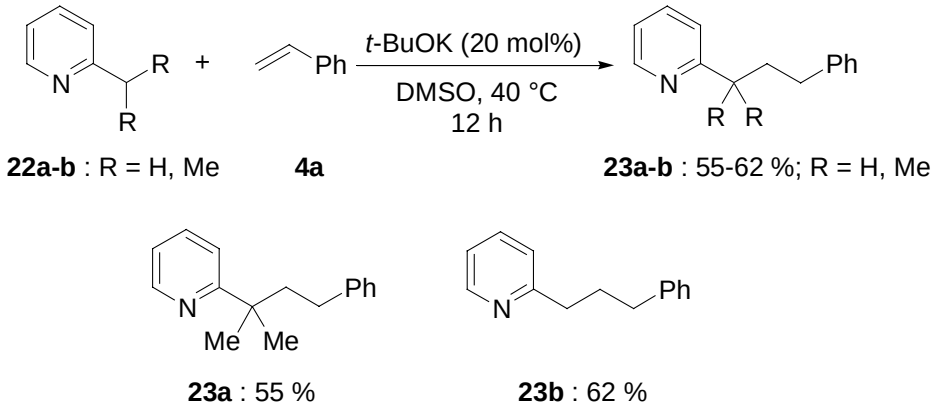


Scheme 32. Preparation of pyrrolidine **21**.

[77] G. Tarzia, C. Balsamini, G. Spadoni, E. Duranti, *Synthesis* **1988**, 514.
[78] R. Henning, U. Lerch, H. Urbach, *Synthesis* **1989**, 265.

1.1.4 Other nucleophiles

The synthesis of quaternary 2-picolinic carbons is a challenge since several natural products and biologically active compounds bear such a quaternary picolinic carbon.[79] Thus, 2-isopropylpyridine (**22a**) was converted using *t*-BuOK (20 mol%) in DMSO to substituted pyridine **23a** in 55 % yield as shown in Scheme 33. Furthermore, under these conditions, 2-methylpyridine (**22b**) smoothly underwent addition to styrene (**4a**), furnishing substituted pyridine **23b** in satisfactory yield.[80]



22a-b : R = H, Me **4a** **23a-b** : 55-62 %; R = H, Me

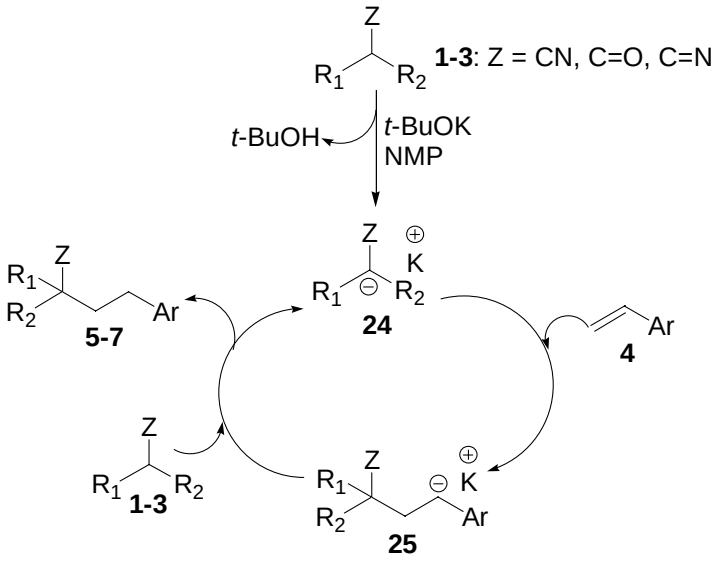
23a : 55 % **23b** : 62 %

Scheme 33. Synthesis of substituted pyridines **23a-b**.

1.1.5 Mechanism

The addition of carbonyl derivatives **1-3** to styrenes was examined. The reaction intermediate seems not to be a radical because the reaction of nitrile **1a** with styrene **4** proceeds even in the presence of 2,6-di-*tert*-butyl-4-methylphenol (radical inhibitor). Thus, we proposed an anionic mechanism for the addition of carbonyl derivatives to styrenes (Scheme 34).

[79] E. Pasquinet, P. Rocca, F. Marsais, A. Godard, G. Quéguiner, *Tetrahedron* **1998**, *54*, 8771.
[80] H. Pines, B. Notari, *J. Am. Chem. Soc*. **1960**, *82*, 2209



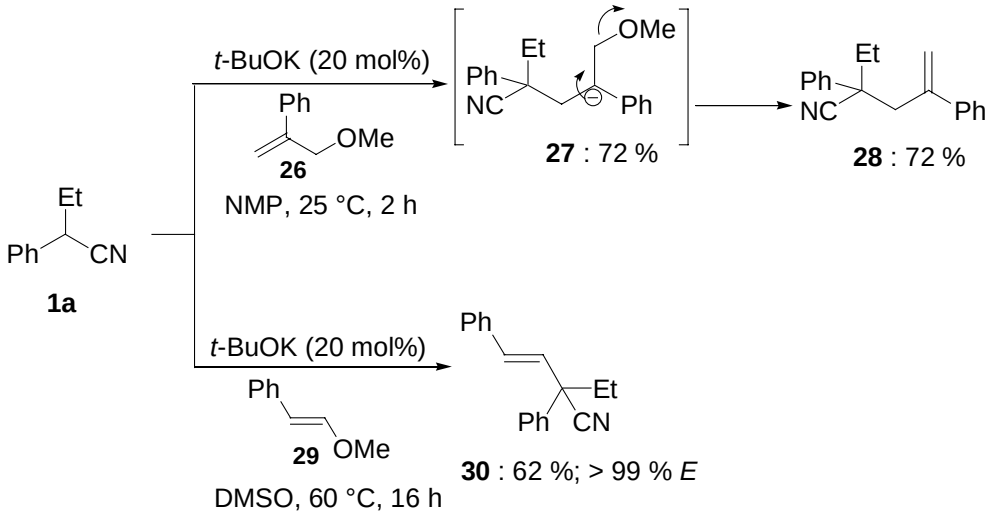
Scheme 34. Proposed mechanism for the addition of carbonyl derivatives to styrenes.

As outlined in Scheme 34, anion **24** is formed by deprotonation using *t*-BuOK (pK_a of *t*-BuOH in DMSO = 32).[81] Subsequently, anion **24** attacked styrene **4** as a nucleophile to form anion **25**, which is protonated by carbonyl derivatives **1-3** (pK_a of representative nitriles ca. 22, pK_a of representative ketones ca. 25).

1.1.6 Addition-elimination reactions

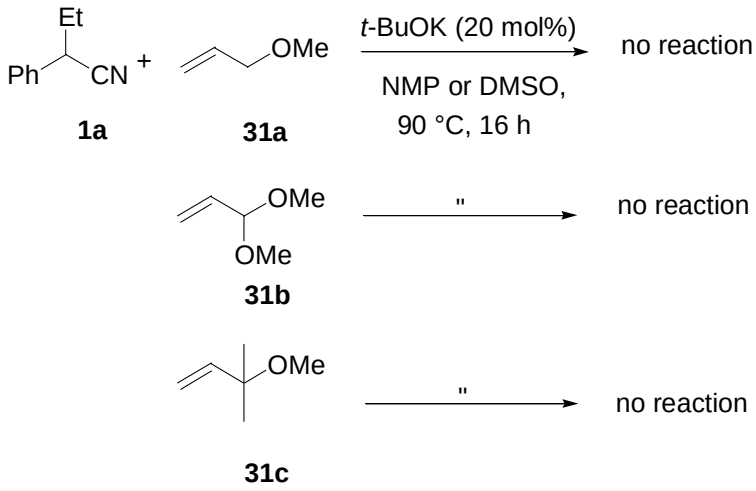
A smooth catalytic allylation of nitrile **1a** using methyl 2-phenyl-2-propenyl ether (**26**) occurred under mild conditions, leading exclusively to the substitution product **28** with good yield. Interestingly, the addition of nitrile **1a** to β-methoxystyrene (**29**) furnished product **30** with high *E*-selectivity. We tentatively propose that this reaction occurs *via* an addition-elimination mechanism as shown in Scheme 35.

[81] F. G. Bordwell, *Acc. Chem. Res*, **1988**, *21*, 456.



Scheme 35. Preparation of products **28** and **30** *via* an addition-elimination mechanism.

However several attempts to add nitrile **1a** to various allyl methoxy derivatives **31a-c** gave only disapointing results (Scheme 36).



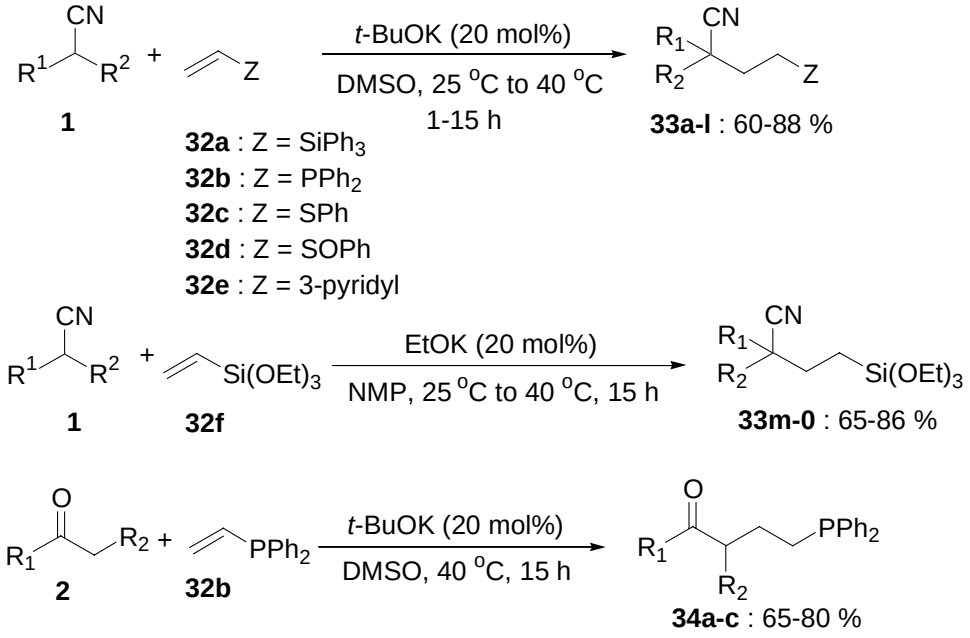
Scheme 36. Attempts to add nitrile **1a** to various allyl methoxy derivatives **31a-c**.

1.1.7 Summary

We developed a synthetic method allowing the inter- and intramolecular addition of nitriles, ketones, imines and substituted pyridines to styrenes in the presence of substoichiometric amounts of *t*-BuOK (20 mol%). The reactions occurred in polar solvents such as DMSO or NMP yielding the corresponding adducts with good regioselectivities and yields. The addition-elimination reaction of the allylic ether **26** and alkenyl ether **29** using nitriles **1a** led to product **28** and **30** in good yields (with a high stereoselectivity for **30**).

1.2 Addition of carbonyl derivatives to functionalized alkenes

The conjugate addition of deprotonated nitriles or ketones to activated alkenes of type **32** (Z = electron-withdrawing group) is a well-known reaction (Michael addition).[82] Stabilized nucleophiles like enolates usually not add to moderately activated vinylic derivatives of type **32** (Z = SiR_3, SR or PR_2). Only highly reactive organolithium compounds add to such Michael-acceptors.[83] Thus, an addition of nitriles and ketones to various functionalized alkenes (such as **32a-f**) would be desirable. The reaction proceeds smoothly and allows for the preparation of various functionalized molecules (Scheme 37).



Scheme 37. Preparation of functionalized nitriles **33a-o** and ketones **34a-c**.

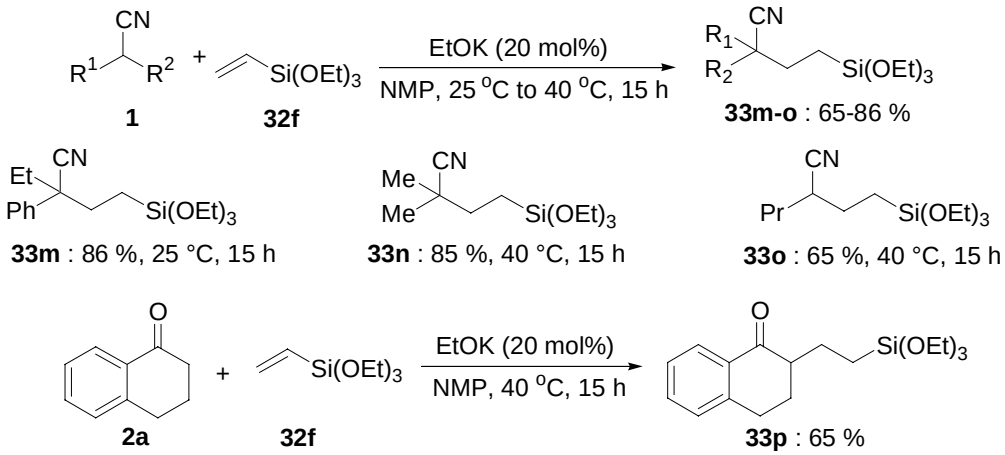
1.2.1 Addition of nitriles to functionalized alkenes

A range of nitriles was added to triphenylvinylsilane (**32a**), diphenylvinylphosphine (**32b**), phenyl vinyl sulfide (**32c**), phenyl vinyl sulfoxide (**32d**) and 3-vinylpyridine (**32e**) through substoichiometric amounts of *t*-BuOK (20 mol%) in DMSO, leading to the corresponding Michael-adducts **33a-l** in 60-88 % yield (Table 4). Thus, 2-phenylbutyronitrile (**1a**) (entry 1, Table 1) added to triphenylvinylsilane (**32a**) within 15 h at 40 °C in the

[82] a) M. E. Jung in *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and M. F. Semmelhack, **1991**, *Vol. 4*, p. 1; b) P. Perlmutter, *Conjugate Addition Reactions in Organic Synthesis*, Pergamon Press, **1992**.
[83] a) L. F. Casan, H. G. Brooks, *J. Am. Chem. Soc.* **1952**, *74*, 4582; b) D. Seebach, R. Bürstinghaus, B. T. Gröbel, M. Kolb, *Liebigs Ann. Chem.* **1977**, 830; c) T. H. Chan, E. Chang, E. Vinokur, *Tetrahedron Lett.* **1970**, 1137; d) J. Yoshida, S. Nakatani, S. Isoe, *J. Org. Chem.* **1989**, *54*, 5655; e) N. H. Andersen, P. F. Duffy, A. D. Denniston, D. B. Grotjahn, *Tetrahedron Lett.* **1978**, *19*, 4315; f) D. Seebach, *Synthesis* **1969**, 17.

presence of *t*-BuOK (20 mol%), leading to the addition product **33a** in 60 % yield. The related cyclohexanecarbonitrile (**1c**) added to **32a** under the same reaction conditions, affording adduct **33b** in 76 % yield (entry 2). Vinyl phosphine **32b** usually undergoes reluctantly addition of nucleophiles[84] and efficient additions were only observed to vinylic phosphine oxide derivatives or alkenylphosphonium salts.[85] Using reaction conditions developed herein, various nitriles **1** added to diphenylvinylphosphine (**32b**) smoothly (25 °C, 1 h), leading to the desired products **33c-d** in 81-88 % yield. Double addition product **33e** was obtained in 80 % yield in case of primary nitrile **1e**. Nitriles like **1a**, **1c** and **1e** added also to phenyl vinyl thioether **32c**, affording the Michael-adducts **33f-h** in 60-78 % yield (entries 6-8). The corresponding sulfoxide **32d** were added using nitrile **1a-b** under similar conditions (40 °C, 1 h), furnishing the sulfoxides **33i-j** in 70-82 % yield (entries 9-10). Interestingly, these nitriles **1a-b** also added to heterocyclic alkenes such as 3-vinylpyridine (**32e**) providing the substituted pyridines **33k-l** in 63-78 % yield (entries 11-12).

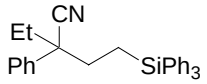
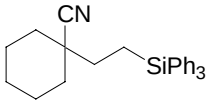
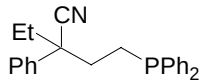
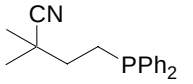
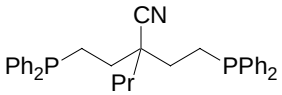
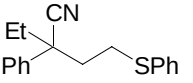
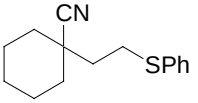
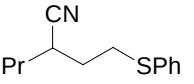
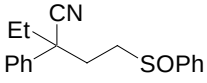
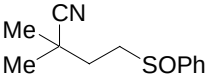
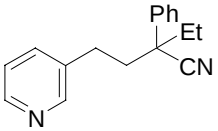
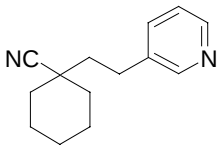
Secondary nitriles **1a-b**, primary nitriles **1e** and α-tetralone (**2a**) added similarly to triethoxyvinylsilane (**32f**). However, in this case potassium ethoxide (20 mol%) was used to avoid alkoxide exchanges on silicon (Scheme 38). These products have potential as precursors for the preparation of functionalized silicon containing compounds.



Scheme 38. Preparation of functionalized silicone containing compounds.

[84] M. S. Rahman, J. W. Steed, K. K. Hii, *Synthesis* **2000**, 1320.
[85] R. M. Cory, D. M. T. Chan, Y. M. A. Naguib, M. H. Rastall, R. M. Renneboog, *J. Org. Chem.* **1980**, *45*, 1852.

Table 4. *t*-BuOK-mediated addition of nitriles **1** to functionalized alkenes **32a-e** in DMSO.

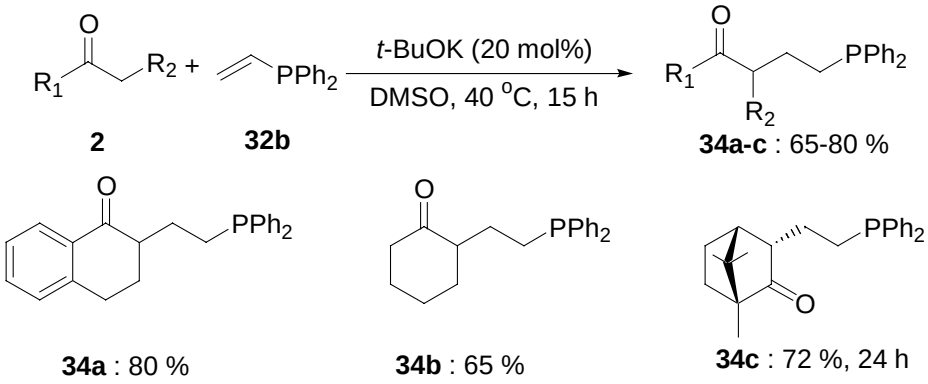
Entry	R^1	R^2	Z	(°C, h)	Product	Yield (%)[a]
1	Ph	Et	**32a**	40, 15	 **33a**	60
2	-$(CH_2)_5$-		**32a**	40, 15	 **33b**	76
3	Ph	Et	**32b**	25, 1	 **33c**	88
4	Me	Me	**32b**	25, 1	 **33d**	81
5	C_3H_7	H	**32b**	25, 1	 **33e**	80
6	Ph	Et	**32c**	25, 4	 **33f**	78
7	-$(CH_2)_5$-		**32c**	25, 1	 **33g**	75
8	C_3H_7	H	**32c**	70, 15	 **33h**	60[b]
9	Ph	Et	**32d**	40, 15	 **33i**	82
10	Me	Me	**32d**	40, 15	 **33j**	70
11	Ph	Et	**32e**	25, 15	 **33k**	78
12	-$(CH_2)_5$-		**32e**	60, 15	 **33l**	63

[a] Isolated yield of analytically pure product.

[b] Using excess of **32c** (3 equiv) in order to avoid double addition.

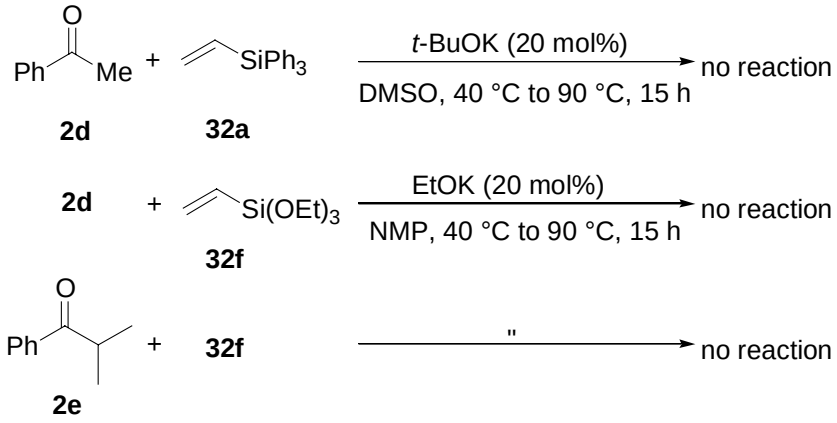
1.2.2 Addition of ketones to vinyl phosphines

Interestingly, ketones like *α*-tetralone (**2a**), camphor (**2b**) and cyclohexanone (**2c**) also underwent efficient Michael-addition at 40 °C (12 h), leading to the keto-phosphines **34a-c** in respectively 80 %, 72 % and 65 % yield. For **34c** only the *endo*-isomer was obtained and the stereochemisty was determined by NOESY experiments (Scheme 39).[86]



Scheme 39. Preparation of keto-phosphines.

Unfortunately, all attempts to prepare functionalized silicone containing compounds through addition of ketones to **32a** and **32f** failed, even under harsh reaction conditions (heating to 90 °C) as illustrated in Scheme 40.



Scheme 40. Attempts to prepare silicon containing ketone compounds.

[86] T. Bunlaksananusorn, A. L. Rodriguez, P. Knochel, *J. Chem. Soc., Chem. Commun*. **2001**, 745.

1.2.3 Summary

we have described a novel *t*-BuOK-mediated addition of nitriles to various moderately active Michael-acceptors **32a-f** allowing the preparation of new functionalized silanes, phosphines and thioethers. In the case of diphenylvinylphosphine (**32b**), the addition of ketones proceeded also well.

1.3 Hydrophosphination of alkenes

Tertiary phosphines are an important class of compounds, which are widely employed both as ligands for transition metal complexes and in various catalytic processes.[87] Thus, there is a considerable interest in developing new methodologies allowing for the formation of carbon-phosphorus bonds. However, taking "green chemistry"- and "atom economy"-principles into consideration, a route such phosphines through addition of secondary phosphines to alkenes would be desirable. This reaction can be carried out in the presence of a radical initiators,[88] strong basic conditions[89] or transition metal catalysis.[90] The use of phosphine-borane complexes is also possible and enables selective hydrophosphinations.[91]

1.3.1 Hydrophosphination of functionalized alkenes

We used the results from our earlier studies (Chapter 1.2) for the hydrophosphination of functionalized alkenes of type **32**. We have used either Ph_2PH (**35a**) or an aliphatic dialkylphosphine like dicyclohexylphosphine (**35b**), in the presence of substoichiometric amounts of *t*-BuOK (20 mol%) in DMSO (Scheme 41).[92]

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[87] L. Brandsma, S. F. Vasilesky, H. D. Verkruijsse, *Application of Transition Metal Catalysts in Organic Synthesis*; Springer-Verlag: Berlin, Heidelberg, New York, **1999**

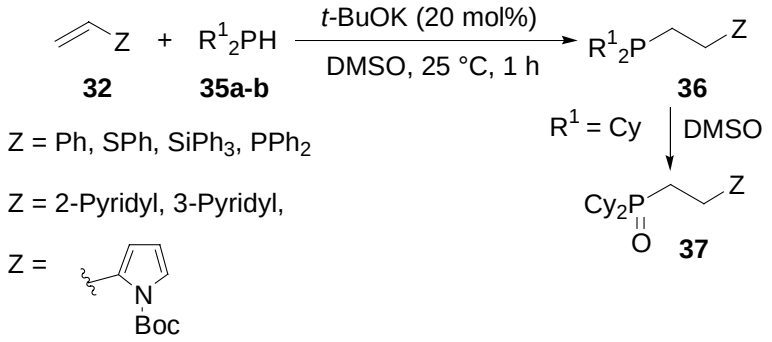
[88] a) B. Therrien, A. König, T. R. Ward, *Organometallics* **1999**, *18*, 1565; b) T. N. Mitchell, K. Heesche *J. Organomet. Chem.* **1991**, *409*, 163; c) B. Therrien, T. R. Ward, *Angew. Chem.* **1999**, *111*, 418; *Angew. Chem. Int. Ed.* **1999**, *38*, 405.

[89] a) G. Knühl, P. Sennhenn, G. Helmchen, *J. Chem. Soc., Chem. Commun*. **1995**, 1845; b) R. A. Khachatryan, S. V. Sayadyan, N. Y. Grigoryan, M. G. Indzhikyan, *Zh. Obshch. Khim.* **1988**, *58*, 2472; c) S. N. Arbuzova, N. K. Gusarova, S. F. Malysheva, L. Brandsma, A. I. Albanov, B. A. Trofimov, *Zh. Obshch. Khim.* **1996**, *66*, 56; d) C. P. Casey, E. L. Paulsen, E. W. Beuttenmueller, B. R. Proft, B. A. Matter, D. R. Powell, *J. Am. Chem. Soc*. **1999**, *121*, 63

[90] a) M. O. Shulyupin, M. A. Kazankova, I. P. Beletskaya, *Org. Lett*. **2002**, *4*, 761; b) M. R. Douglass, T. J. Mark, *J. Am. Chem. Soc*. **2000**, *122*, 1824; c) K. Takaki, M. Takeda, G. Koshoji, T. Shishido, K. Takehira, *Tetrahedron Lett*. **2001**, *42*, 6357.

[91] a) K. Bourumeau, A. –C. Gaumont, J. –M. Denis, *Tetrahedron Lett.* **1997**, *38*, 1923; b) K. Bourumeau, A. –C. Gaumont, J. –M. Denis, *J. Organomet. Chem.* **1997**, *529*, 205.

[92] T. Bunlaksananusorn, P Knochel, *Tetrahedron Lett*. **2002**, *43*, 5817.

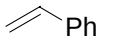
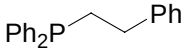
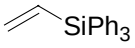
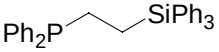
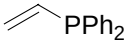
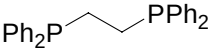
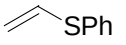
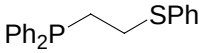
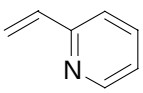
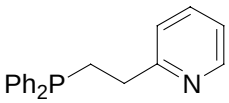
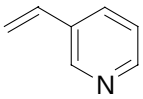
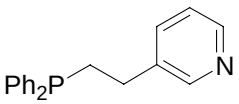
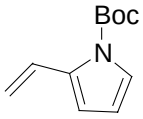
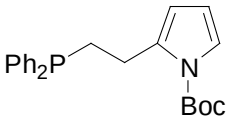
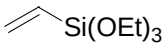
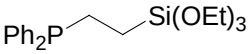
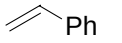
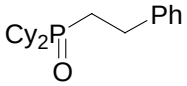


Scheme 41. Preparation of polyfunctionalized phosphine derivatives.

Thus, styrene (**4a**) reacted very rapidly with Ph_2PH (**35a**) in the presence of *t*-BuOK (25 °C, 1 h), leading to the phosphine **36a** in 83 % yield (entry 1, Table 5). Activated alkenes like vinyl silane **32a**, vinyl phosphine **32b** and vinylic thioether **32c** reacted under similar reaction conditions furnishing the polyfunctionalized phosphines **36b-d** (entries 2-4) in 80-90 % yield. Heterocyclic compounds such as 2-vinylpyridine (**32g**), 3-vinylpyridine (**32e**) and *N*-protected pyrrole **32h** also reacted with Ph_2PH (**35a**), leading to potential P,N-ligands (**36e-g**; 63-68 %, entries 5-7). Whereas 2-vinylpyridine (**32g**), bearing an unsaturated vinylic imine unit was expected to react well (25 °C, 1 h, entry 5), we observed that the isomeric cross-conjugated 3-vinylpyridine (**32e**) was converted equally fast (25 °C, 1 h, entry 6). Triethoxyvinylsilane (**32f**) reacted in the presence of EtOK (used instead of *t*-BuOK in order to avoid alkoxide scrambling), leading to the phosphine **36h**, which might be used to attach a phosphine unit on silica gel.[93] The reaction with Cy_2PH (**35b**) proceeded similarly. However, the sensitive intermediate dicyclohexylphosphine adduct was oxidized by DMSO, leading to the phosphine oxide **37** in 73 % yield (entry 9).

[93] G. Tsiavaliaris, S. Haubrich, C. Merckle, J. Blümel, *Synlett* **2001**, 391.

Table 5. Functionalized phosphines **36a-h** and phosphine oxide **37** obtained by *t*-BuOK-mediated addition of phosphines **35a-b** to styrene (**4a**) and functionalized alkenes **32** in DMSO at 25 °C.

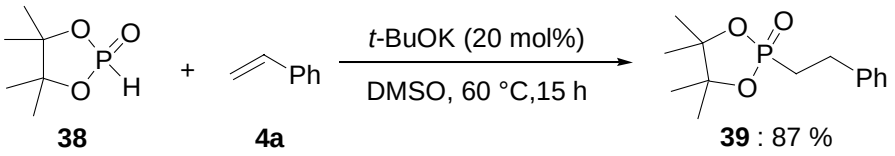
Entry	Alkenes	Phosphines	Product	Yield (%)[a]
		$HPPh_2$		
1	**4a**	**35a**	**36a**	83
				
2	**32a**	**35a**	**36b**	88
				
3	**32b**	**35a**	**36c**	90
				
4	**32c**	**35a**	**36d**	80
				
5	**32g**	**35a**	**36e**	63
				
6	**32e**	**35a**	**36f**	65
				
7	**32h**	**35a**	**36g**	68
				
8	**32f**	**35a**	**36h**	81[b]
		Cy_2PH		
9	**4**	**35b**	**37**	73

[a] Isolated yield of analytically pure product.

[b] EtOK (20 mol %) in NMP was used.

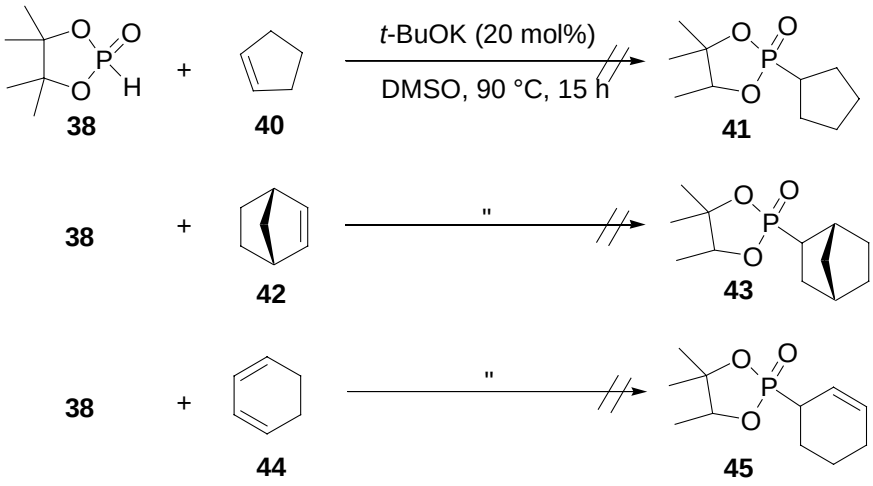
Our methodology allowed also the smooth addition of the five membered cyclic phosphonate, cyclic hydrogen phosphonate **38**[94] to styrene (**4a**), affording the phosphonate adduct **39** in 87 % yield (Scheme 42).

[94] a) L. –B. Han, F. Mirzaei, C. –Q. Zhao, M. Tanaka, *J. Am. Chem. Soc*. **2000**, *122*, 5407; b) F. Mirzaei, L. –B. Han, M. Tanaka, *Tetrahedron Lett*. **2001**, *42*, 297.



Scheme 42. Hydrophosphorylation of styrene (**4a**).

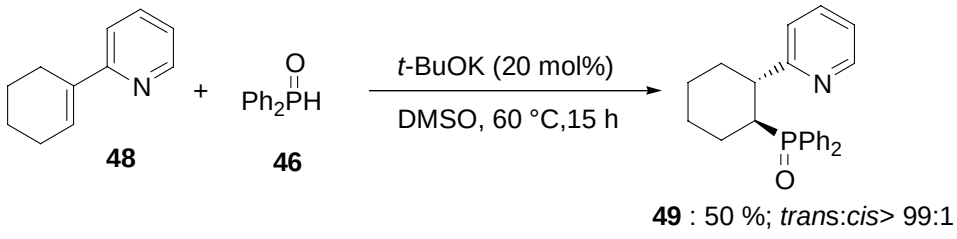
Unfortunately, treatment of various alkenes **40**, **42** and **44** under the conditions described above did not lead to the expected products **41**, **43** and **45**. Complexe mixtures were obtained as judged by ^{31}P NMR spectroscopy (Scheme 43).



Scheme 43. Attempts to prepare cyclic phosphonates **41**, **43** and **45**.

1.3.2 Addition of phosphine oxides to trisubstituted alkenes

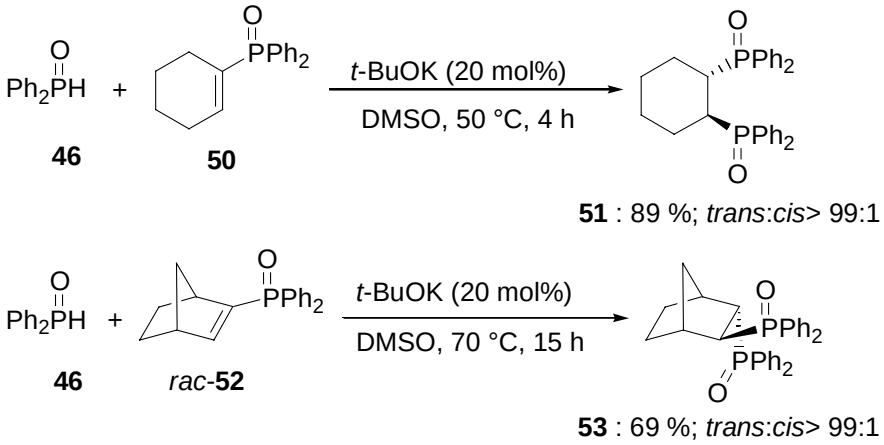
Addition of Ph_2PH (**35a**) to trisubstituted unsaturated pyridines like **48**[95] was only achieved after long reaction times (70 °C, 16 h). Mixtures of the aminophosphine oxide adduct **49** and the corresponding aminophosphine were obtained. However, diphenylphosphine oxide (**46**) reacted faster and afforded selectively *trans*-adduct **49** in 50 % yield as a single diastereoisomer (Scheme 44).[96]



Scheme 44. Preparation of 1,2-aminophosphine oxide **49**.

[95] a) P. Gros, Y. Fort, P. Caubère, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 570; b) H. L. Lochte, P. F. Kruse, E. N. Wheeler, *J. Am. Chem. Soc*. **1953**, *75*, 4477.
[96] S. Demay, *Dissertation*, Ludwig-Maximilians-Universität München, **2001**.

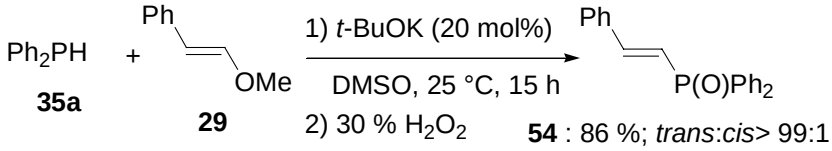
1,2-Diphosphine oxides were easily prepared by this method. Thus, the addition of $Ph_2P(O)H$ (**46**) to trisubstituted cyclohexenylphosphine oxide **50** led to the C_2-symmetrical phosphine oxide **51**[97] in 89 % yield (*trans*:*cis* > 99:1). A similar addition of $Ph_2P(O)H$ (**46**) to bisphosphine oxide **52** furnished the diphenylphosphine oxide *rac*-**53**[40,98] in 69 % yield (*trans*:*cis*> 99:1) as shown in Scheme 45.



Scheme 45. Preparation of *rac*-1,2 diphenylphosphine oxides **51** and **53**.

1.3.3 Addition-elimination reactions

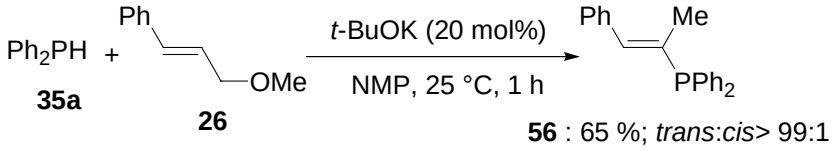
Addition-elimination reactions are also feasible. Remarkably, the reaction of Ph_2PH (**35a**) with β-methoxystyrene (**29**) led to **54**, which is usually prepared through Pd or Ni-catalyzed addition of diphenylphosphine to an alkyne.[99] Our addition-elimination process led stereoselectively in 86 % yield to the *trans*-adduct **54** (J_{trans} = 22.0 Hz) in Scheme 46.



Scheme 46. Preparation of vinylic phosphine oxide **54**.

[97] S. Demay, F. Volant, P. Knochel, *Angew. Chem.* **2001**, *113*, 1272; *Angew. Chem. Int. Ed.* **2001**, *40*, 1235.
[98] E. P. Kyba, R. E. Davis, P. N. Juri, K. R. Shirley, *Inorg. Chem*. **1981**, *20*, 3616.
[99] M. A. Kazankova, I. V. Efimova, A. N. Kochetkov, V. V. Afanas'ev, I. P. Beletskaya, P. H. Dixneuf, *Synlett* **2001**, 497.

Also the hydrophosphination of *trans*-3-methoxy-1-phenyl-1-propene[100] **26** using Ph_2PH (**35a**) led to the regioselective formation of substituted phosphine **56** in moderate yield at room temperature (Scheme 47). We tentatively propose that this reaction occurs *via* an addition-elimination mechanism.



Scheme 47. Preparation of substituted phosphine **56**.

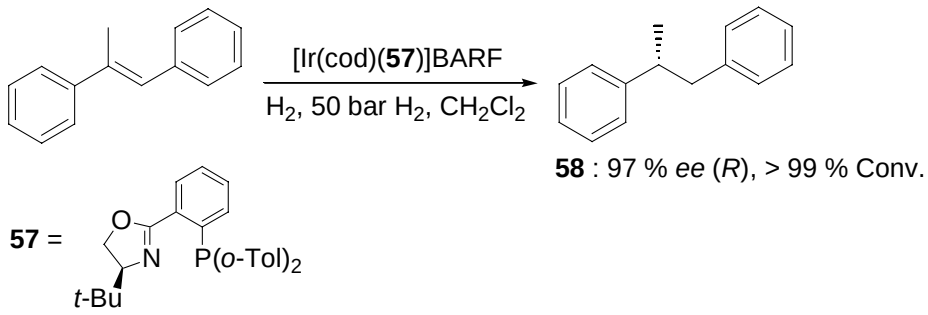
1.3.4 Summary

A new convenient and environmentally benign method for the preparation of C-P bonds was developed through *t*-BuOK-mediated hydrophosphination using phosphines, phosphine oxides to functionalized alkenes **32a-g** under mild conditions. This method was applied for the preparation of *rac*-1,2-aminophosphine oxide **49**, *rac*-1,2-diphosphine oxides **51** and **53**. Furthermore, the addition-elimination reaction of Ph_2PH (**35a**) with allylic ether **26** and alkenyl ether **29** led to substituted phosphine oxide **54** and phosphine **56** in good yields with high steroselectivities under mild reaction conditions.

2 Synthesis of chiral P,N-ligands and their applications in asymmetric catalysis

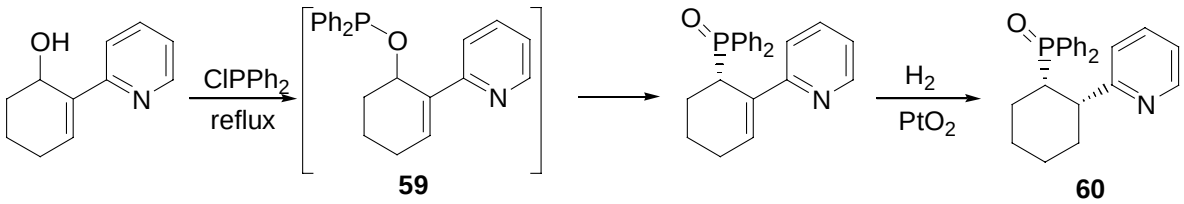
Transition metal complexes of heterobidentate ligands such as (phosphinoaryl)-oxazolines[44], QUINAP[54] and MAP[59] are valuable catalysts for a number of asymmetric reactions, particulary in areas where traditional C_2-symmetrical ligands failed. Many other P,N-ligands were also reported in the literature and enabled interesting transformations in asymmetric catalysis.[101] Among these P,N-ligands, Pfaltz's chiral phosphinooxazoline ligands proved to be especially efficient in Ir-catalyzed asymmetric hydrogenation reactions of olefins. These Ir-complexes are readily prepared, air-stable and easy to handle (Scheme 48).[102]

[100] J. G. Duboudin, B. Jousseaume, *J. Organomet. Chem*. **1979**, *168*, 1.
[101] F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, *Chem. Rev*. **2000**, *100*, 2159; b) P. Espinet, K. Soulantica, *Coord. Chem. Rev*. **1999**, *193-195*, 499.
[102] A. Pfaltz, J. Blankenstein, R. Hilgraf, E. Hörmann, S. McIntyre, F. Menges, M. Schönleber, S. P. Smidt, B. Wüstenberg, N. Zimmermann, *Adv. Synth. Catal*. **2003**, *345*, 33.



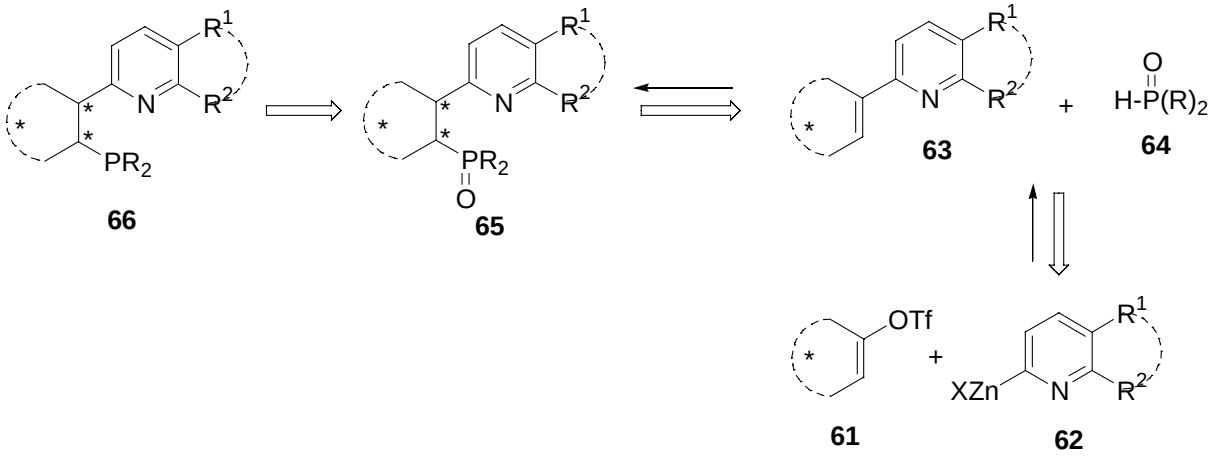
Scheme 48. Asymmetric hydrogenation using Pfaltz's chiral phosphinooxazoline **58**.

Knochel and *Demay* described the preparation of *cis*-aminophosphine oxide containing a pyridine ring *via* [2,3]-sigmatropic rearrangement of allylic phosphinite **59**, followed by reduction of the alkene, leading to *cis*-aminophosphine oxide **60**. Unfortunately, the reduction of the phosphine oxide moiety in **60** was unsuccessful despite variation of the reducing reagent (Scheme 49).[96]



Scheme 49. The preparation of *cis*-aminophosphine oxide **60**.

Based on our previous preparation of *rac-trans*-aminophosphine oxide **49** (Scheme 46), we turned our attention to the preparation of novel chiral P,N-ligands of type **66**, starting from readily available chiral building blocks, like (+)-camphor (**67**) and (+)-nopinone (**68**). These ligands may display properties analogous to Brown's QUINAP and Pfaltz's chiral phosphinooxazoline **57**, since they would chelate the metal as a six-membered ring. Our synthetic approach is outlined in Scheme 50.

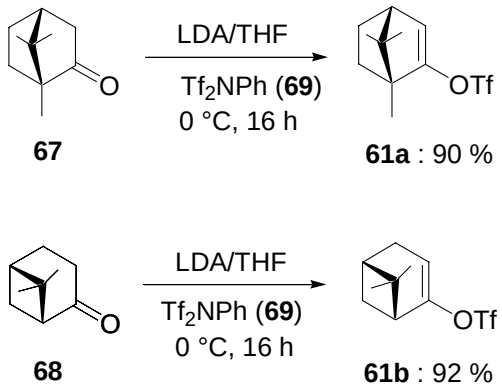


Scheme 50. Preparation of chiral aminophosphine oxides of type **66**.

As proposed in Scheme 52, the aminophosphine oxides **65** will be prepared using a *t*-BuOK-mediated addition of phosphine oxides **64** to alkenylpyridines **63**. This will be synthesized *via* a Negishi cross-coupling of chiral alkenyl triflates **61** with alkenylpyridylzinc halides **62**. The reduction of **65** will give rise to chiral aminophosphines **66**.

2.1 Preparation of chiral alkenyl triflates 61

The preparation of alkenyl triflates **61a-b** are described in the literature.[103] Treatment of the enolate anions of commerically available (+)-camphor (**67**) and (+)-nopinone (**68**) with *N*-phenyltrifluoromethanesulfonamide (**69**) in THF at 0 °C led to the desired alkenyl triflates **61a-b** in 90-92 % yield (Scheme 51).

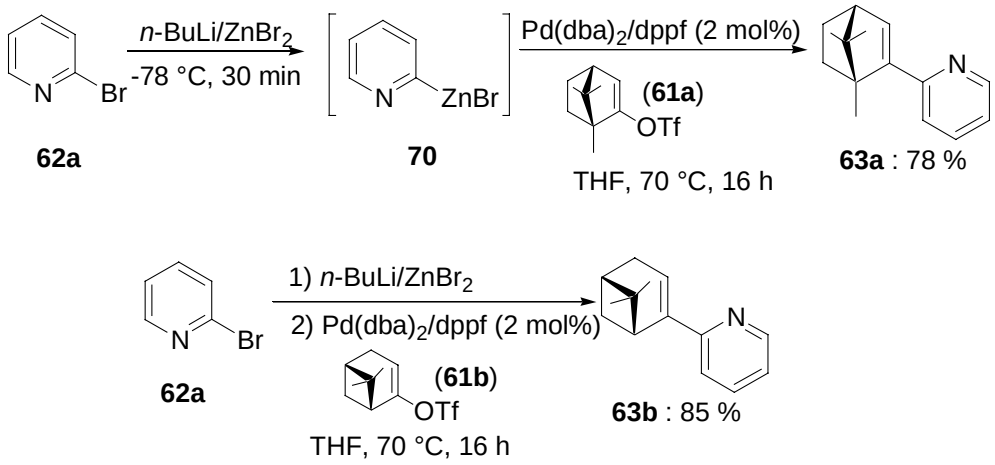


Scheme 51. Preparation of alkenyl triflates **61a-b**.

[103] J. E. Mc Murry, W. J. Scott, *Tetrahedron Lett*. **1983**, *24*, 979.

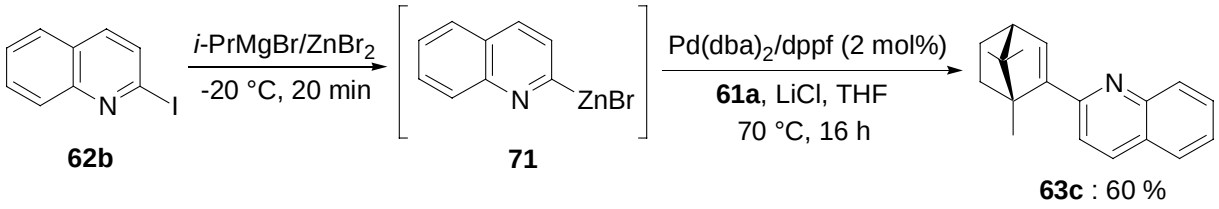
2.2 Negishi cross-coupling of pyridylzinc reagents 70-71

The chiral alkenyl triflates **61a-b** underwent smooth Negishi cross-coupling reactions[104] with 2-pyridylzinc bromide **70** prepared from commercially available 2-bromopyridine (**62a**) by direct Br-Li exchange, affording the desired 2-alkenylpyridines **63a-b** in 78-85 % yield (Scheme 52).



Scheme 52. Preparation of 2-alkenylpyridines **63a-b**.

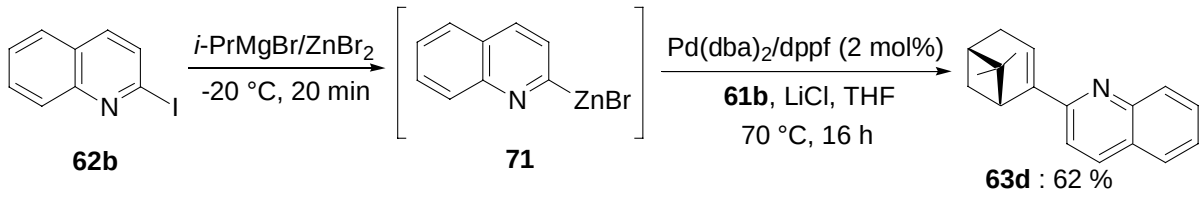
For 2-iodoquinoline[105], we observed only the substitution of the iodine by the butyl group at –78 °C using *n*-BuLi or *t*-BuLi. This problem was solved by using a Grignard reagent prepared *via* a Mg-I exchange.[106] 2-Alkenylquinoline **63c** was obtained in satisfactory yield (60 %) through Pd-catalyzed cross-coupling of 2-quinolylzinc bromide **71** with alkenyl triflate **61a** in the presence of LiCl (Scheme 53).



Scheme 53. Preparation of 2-alkenylquinoline **63c**.

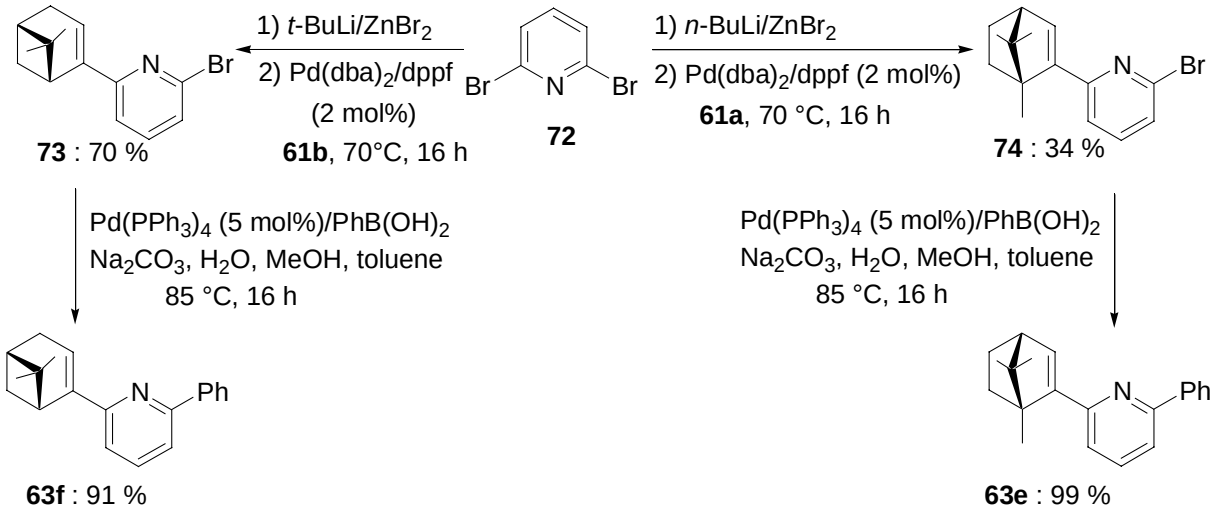
[104] a) E. -I. Negishi, *Acc. Chem. Res*. **1982**, *15*, 340; b) E. –I. Negishi in *Metal-Catalyzed Cross Coupling Reactions* (Eds. : F. Diederich, P. J. Stang), Wieley-VCH, Weinheim, **1998**, chap. 1; c) E. Erdik, *Tetrahedron* **1992**, *48*, 9577.
[105] R. C. Corcoran, S. H. Bang, *Tetrahedron Lett*. **1990**, *31*, 6757.
[106] F. Trécourt, G. Breton, V. Bonnet, F. Mongin, F. Marsais, G. Quéguiner, *Tetrahedron* **2000**, *56*, 1349.

The organozinc bromide **71** was also treated with alkenyl triflate **62b** under similar reaction conditions as shown in Scheme 53, giving 2-alkenylquinoline **63d** in 62 % yield (Scheme 54).



Scheme 54. Preparation of 2-alkenylquinoline **63d**.

Our attention was directed towards the preparation of substituted bromopyridine **73-74**. A method developed by Cai[107] allows for the formation of mono-metallated species. Subsequent transmetallation with anhydrous zinc bromide followed by Negishi cross-coupling reactions,[108] led to the expected coupling products **73-74** in 34-70 % yield. Afterwards, the bromopyridines **73-74** underwent a Suzuki cross-coupling with phenylboronic acid in the presence of a catalytic amount of $Pd(PPh_3)_4$ to give 2-alkenyl-6-phenylpyridines **63e-f** in high yields (Scheme 55).[109]

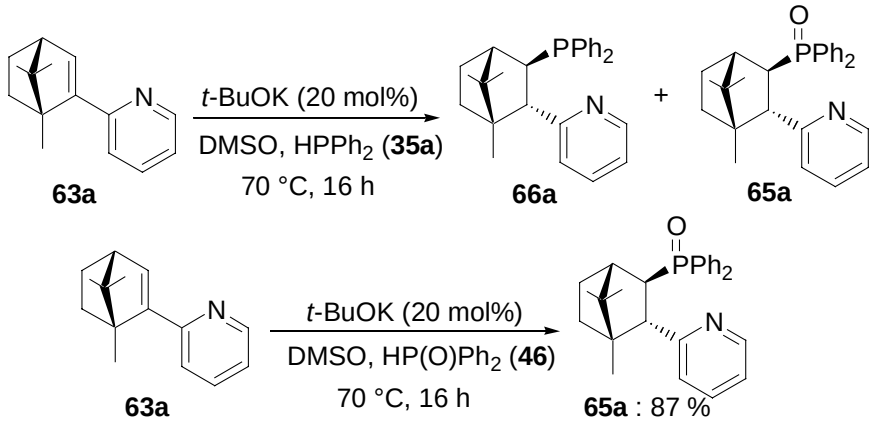


Scheme 55. Preparation of 6-phenyl-2-alkenylpyridines **63e-f**.

[107] a) D. Cai, D. L. Hughes, T. R. Verhoeven, *Tetrahedron Lett*. **1996**, *37*, 2537; b) M. A. Peterson, J. R. Mitchell, *J. Org. Chem*. **1997**, *62*, 8237.
[108] M. Alami, J. –F. Peyrat, L. Belachmi, J. -D. Brion, *Eur. J. Org. Chem*. **2001**, *22*, 4207.
[109] G. Chelucci, N. Culeddu, A. Saba, R. Valenti, *Tetrahedron: Asymmetry* **1999**, *10*, 3537.

2.3 Hydrophosphination of alkenylpyridines 63a-f

Initailly, treatment of alkenylpyridine **63a** with Ph_2PH (**35a**) using *t*-BuOK in DMSO led to both P,N-ligand **66a** and aminophosphine oxide **65a** in a ratio of **65a**:**66a** = 80:20 by ^{31}P NMR spectroscopy. Attempts to purify the mixture by recrystallization or column chromatography either using silica gel or alumina oxide was unsuccessful. We considered that it would be possible to carry out the hydrophosphination with $Ph_2P(O)H$ (**46**), followed by reduction of **65a** to **66a**. Fortunately, the addition of **46** to alkenylpyridine **63a** in the presence of substoichiometric amounts of *t*-BuOK (20 mol%) in DMSO furnished aminophosphine oxide **65a** in 87 % as a single diastereomer (Scheme 56).



Scheme 56. Preparation of aminophosphine oxide **65a**.

The *trans* stereochemistry of **65a** was confirmed by x-ray analysis as shown in Figure 1.

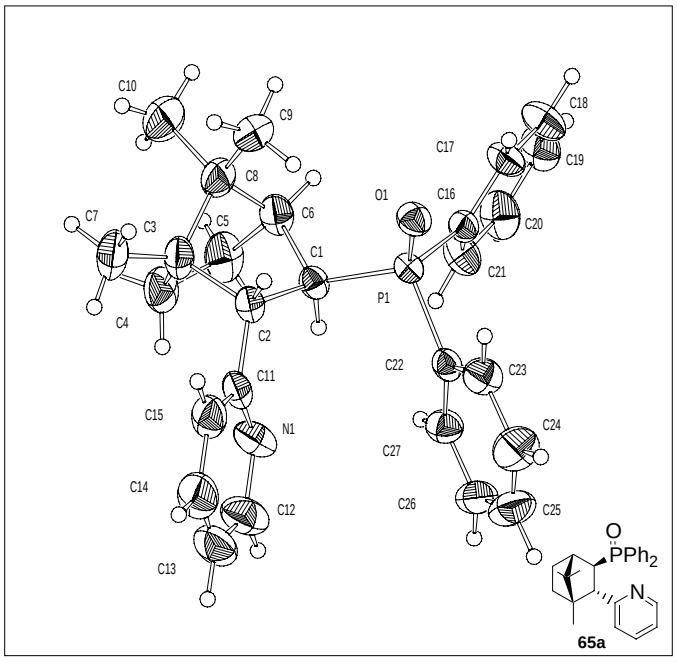
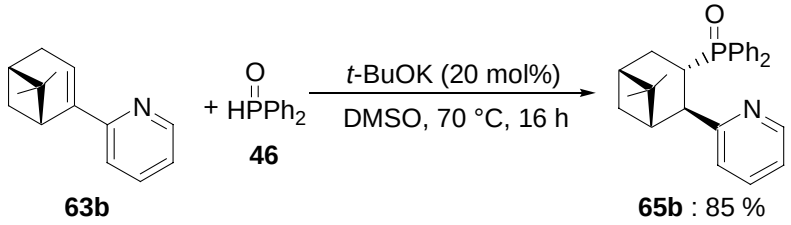


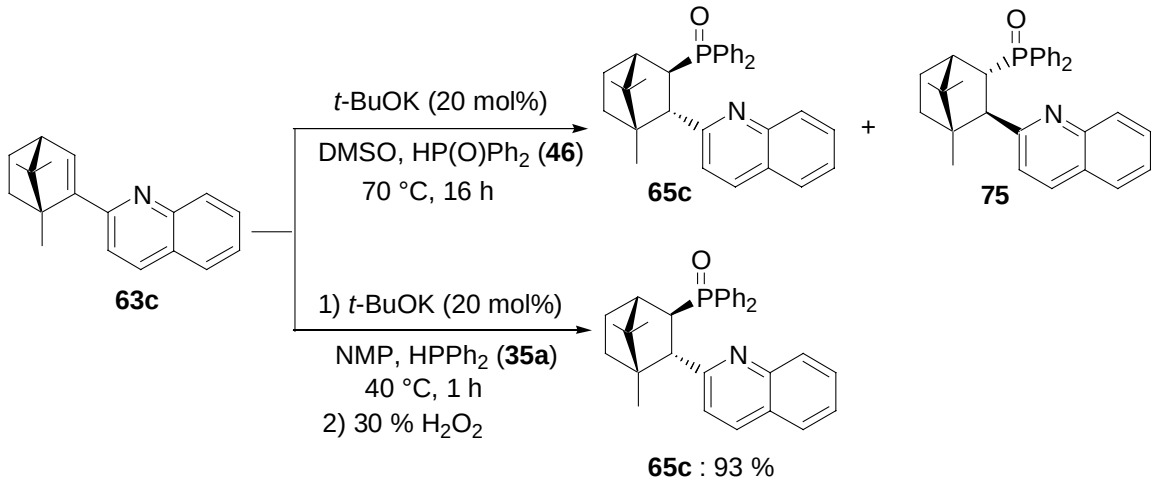
Figure 1. X-ray structure of the aminophosphine oxide **65a**.

Under the same conditions, chiral alkenylpyridine **63b** underwent smooth hydrophosphination with $Ph_2P(O)H$ (**46**), giving *trans*-**65a** in 85 % yield (Scheme 57). Assignment of the stereochemistry was viable by NOESY experiments.



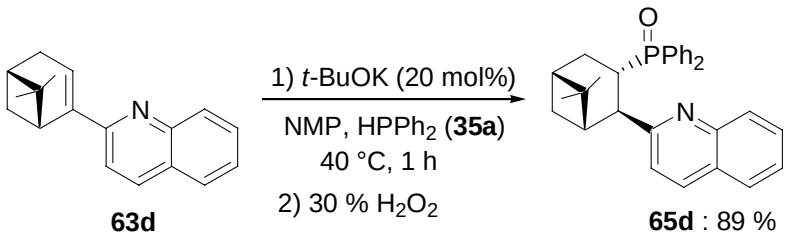
Scheme 57. Preparation of aminophosphine oxide **65b**.

Interestingly, for the 2-alkenylquinoline **63c**, diastereomer **75** was also detected by ^{31}P NMR spectroscopy applying the standard reaction conditions (ratio of **65c**:**75** = 88:12). Attempts to separate this diastereomers by column chromatography or isomerization under basic conditions failed. Surprisingly, changing the solvent from DMSO to NMP and the $Ph_2P(O)H$ (**46**) to Ph_2PH (**35a**) allowed for the formation of **65c** as a single diastereomer in high yield under mild conditions (Scheme 58). The sterochemistry was determined by NOESY experiments.



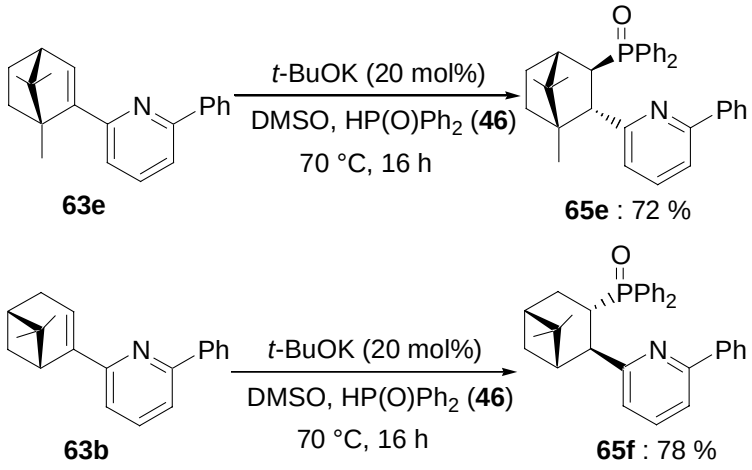
Scheme 58. Preparation of aminophosphine oxide **65c**.

Aminophosphine oxide **65d** was synthesized with good yield (89 %) by the addition of Ph_2PH (**35a**) to 2-alkenylquinoline **63d** in the presence of *t*-BuOK (20 mol%) in NMP at 25 °C, for 1 h. Only one diastereomer was observed by ^{31}P NMR spectroscopy (Scheme 59).



Scheme 59. Preparation of aminophosphine oxide **65d**.

Furthermore, we have prepared aminophosphine oxides of type **65e-f** by introducing a phenyl group in the 6 position of the pyridine ring.[110] Thus, a new class of aminophosphine oxides **65e-f** was prepared under mild conditions, leading to aminophosphine oxides **65e-f** in good yields (Scheme 60). The stereochemistry of **65e** was assigned by comparison with **65a** and NOESY experiments. The structure of aminophosphine oxide **65f** was determined by x-ray analysis as shown in Figure 2.



Scheme 60. Preparation of aminophosphine oxide **65e-f**.

[110] a) G. Chelucci, S. P. Deriu, A. Saba, R. Valenti, *Tetrahedron: Asymmetry* **1999**, *10*, 145; b) G. Chelucci, S. Medici, A. Saba, A. *Tetrahedron: Asymmetry* **1999**, *10*, 543; c) G. Chelucci, S. Medici, A. Saba, A. *Tetrahedron: Asymmetry* **1997**, *8*, 3183.

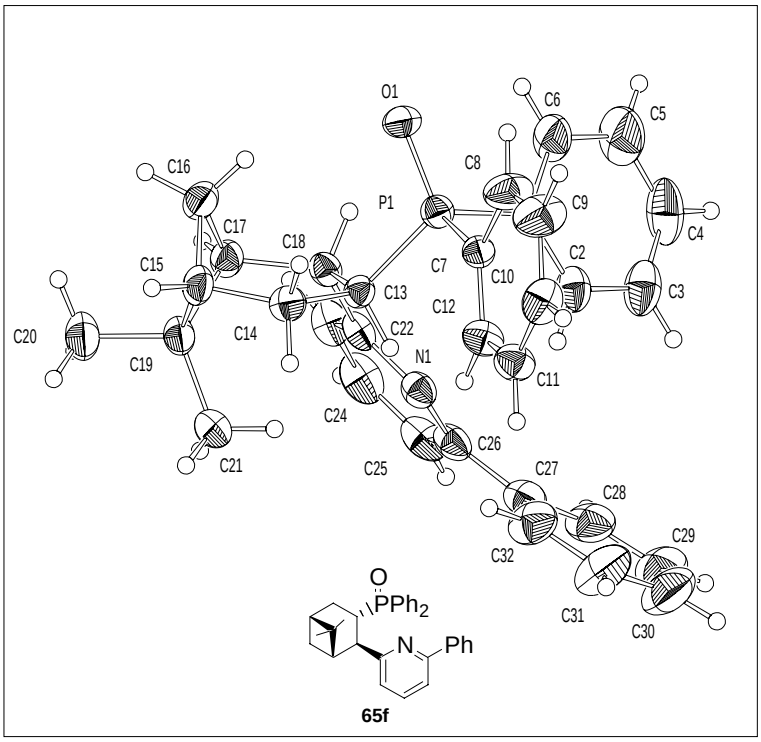
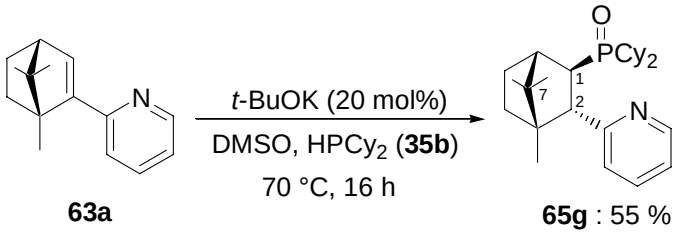


Figure 2. X-ray structure of aminophosphine oxide **65f**.

Moreover, the addition of Cy_2PH (**35b**) to vinylpyridine **63a** provided only aminophosphine oxide **65g** after aqueous workup due to the air sensitivity of aminophosphine **66g** (Scheme 61). The stereochemisty was assigned on the basis of its ^1H-^1H NOESY experiments, which showed a correlation between H_2 and H_7.

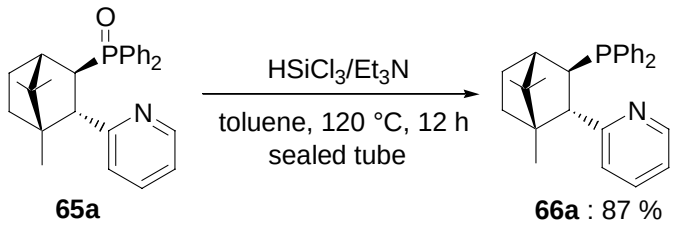


Scheme 61. Preparation of electron rich aminophosphine oxide **65g**.

2.4 Reduction of phosphine oxides 65a-g

Having novel aminophosphine oxides **65a-g** in hands, we have investigated the reduction of phosphine oxides to phosphines.[111] The reduction of **65a** was achieved with $HSiCl_3$ and Et_3N in toluene upon heating to 120 °C, yielding chiral aminophosphine **66a** (Scheme 62).

[111] U. Yasuhiro, A. Tanahashi, S.-Y. Lee, T. Hayashi, *J. Org. Chem*. **1993**, *58*, 1945.



65a **66a** : 87 %

Scheme 62. Reduction of phosphine oxide **65a**.

No isomerization could be detected during the reduction step. The stereochemistry was determined by x-ray analysis of the phosphine-borane complex of **66a** as shown in Figure 3.

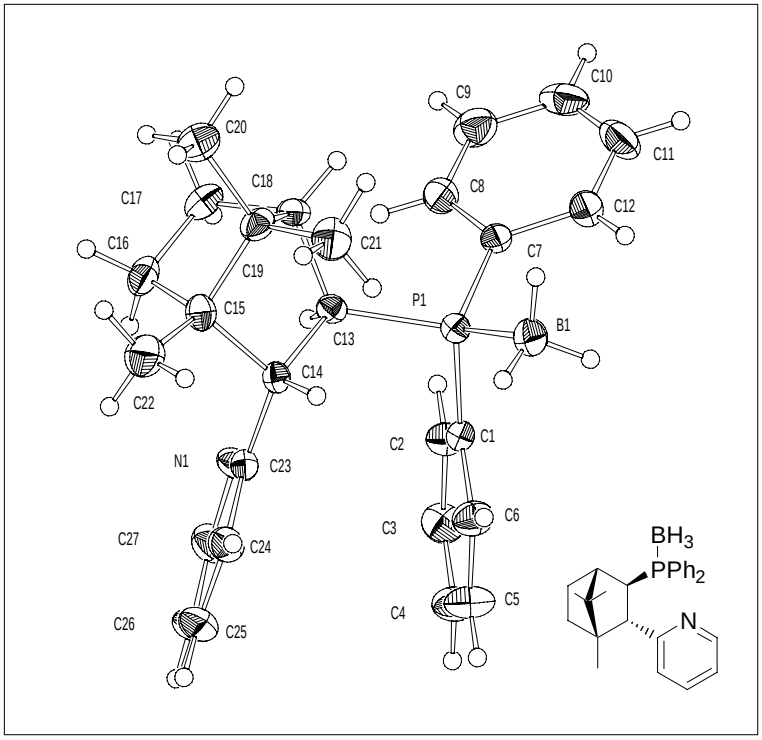
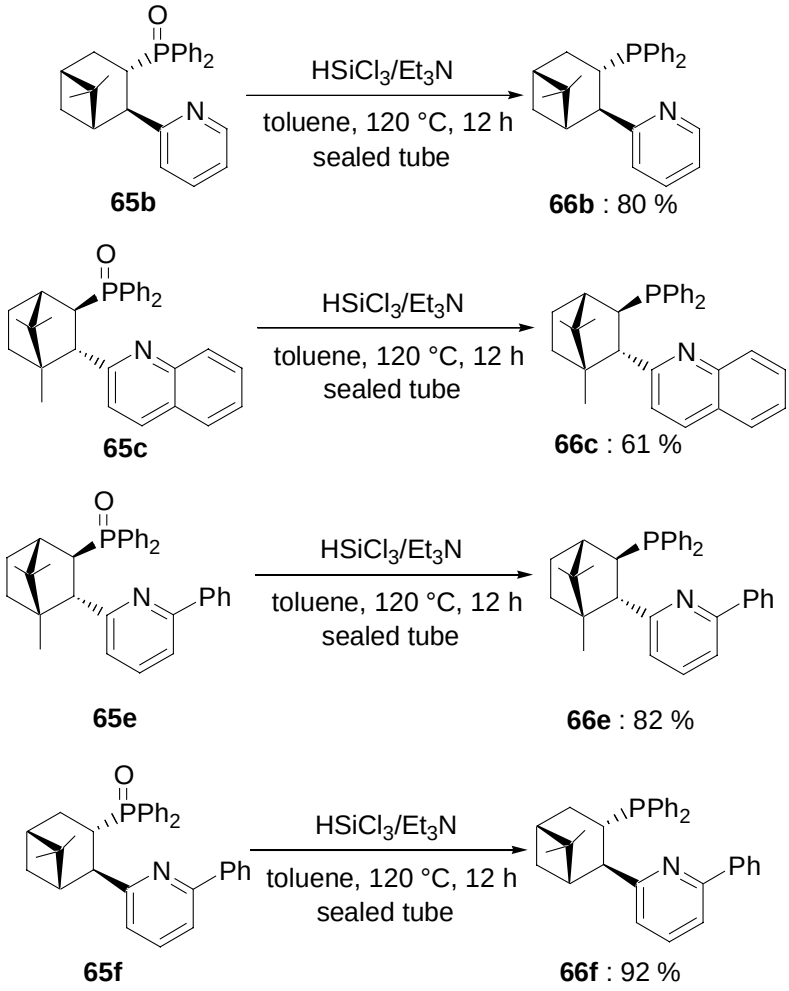


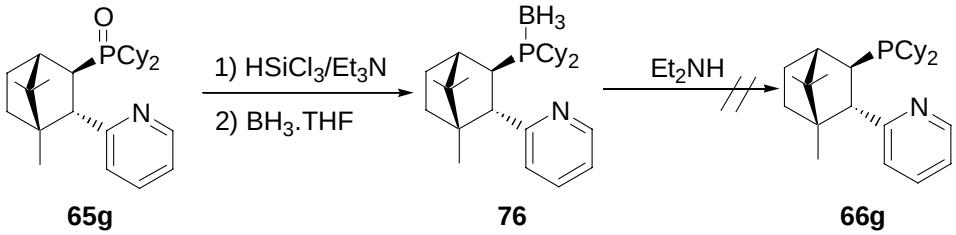
Figure 3: X-ray structure of phosphine-borane complex of **66a**.

Under these reaction conditions, phosphine oxides **66b-c** and **65e-f** were reduced to furnish the desired chiral P,N-ligands **66b-c** and **66e-f** in 61-92 % yield as outlined in Scheme 63.



Scheme 63. Reduction of aminophosphine oxides **65b-c** and **65e-f** with $HSiCl_3$.

For the reduction of aminophosphine oxide **65g** to **66g**, the crude reaction mixture did not show the formation of any by-products. Unfortunately, after careful workup under argon, a new resonance was observed in the ^{31}P spectrum in a ratio 50:50 (**66g**:**65g**). Attempts to prepare the phosphine-borane complex **76** followed by deprotection of the borane using Et_2NH[112] were unsuccessful. Unfortunately, only phosphine oxide **65g** was observed (Scheme 64).

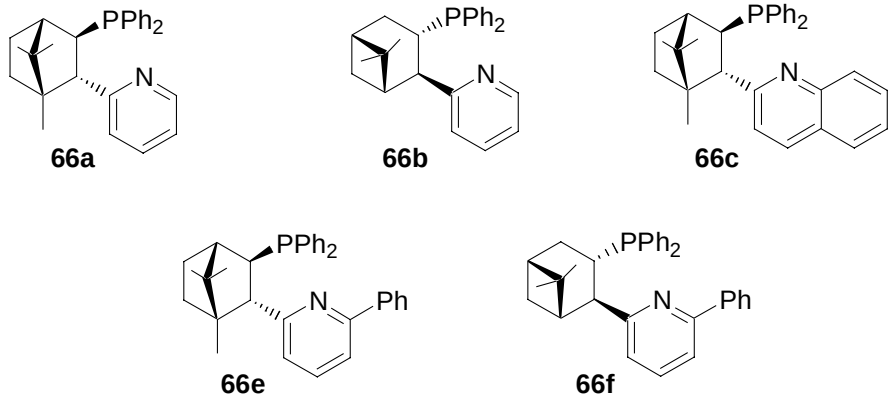


Scheme 64. Attempted preparation of P,N-ligand **66g**.

[112] M. Lotz, *Dissertation*, Ludwig-Maximilians-Universität München, **2002**.

2.5 Applications in asymmetric catalysis

For clarity, the structure of the chiral P,N-ligands **66a-c** and **66e-f** are provided in Scheme 65.

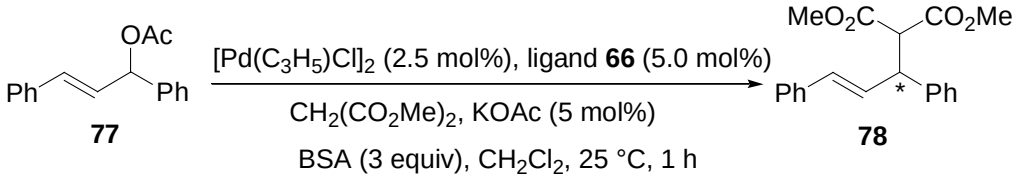


Scheme 65. Overview of novel chiral P,N-ligands **66a-c** and **66e-f**.

2.5.1 Pd-catalyzed enantioselective allylic substitution

The Pd-catalyzed allylation is a widely studied reaction[113] With the novel chiral ligands **66** in hands, we examined their applications in Pd(0)-catalyzed allylic substitution reactions of racemic 1,3-diphenylprop-2-1-yl acetate (±)-**77** with dimethyl malonate employing Trost's procedure.[114] $[Pd(C_3H_5)Cl]_2$ was used as the catalyst precursor in the presence of a mixture of dimethyl malonate, *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and potassium acetate in CH_2Cl_2. The results are summarized in Table 6.

Table 6. Asymmetric allylic Pd(0)-catalyzed substitution of racemic substrate **77** with dimethyl malonate.



[113] a) B. M. Trost, D. L. Van Vranken, *Chem. Rev*. **1996**, *96*, 395; b) A. Heumann, M. Réglier, *Tetrahedron* **1995**, *51*, 975.
[114] B. M. Trost, D. J. Murphy, *Organometallics* **1985**, *4*, 1143.

Entry	L*	Solvent	*ee* (%)[a]	Yield (%)[b]
1	**66a**	CH_2Cl_2	96 (*R*)	75
2	**66a**	Et_2O	86 (*R*)	73
3	**66b**	CH_2Cl_2	72 (*S*)	88
4	**66c**	CH_2Cl_2	68 (*S*)	85
5	**66e**	CH_2Cl_2	41 (*R*)	65
6	**66f**	CH_2Cl_2	80 (*S*)	78

[a] Determined by HPLC analysis (Daicel Chiralcel OD-H, *n*-heptane: *i*-PrOH, 98:2).
[b] Isolated yield of analytically pure product.

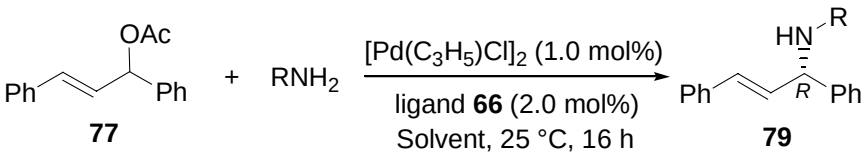
In all cases, the reaction was carried out at 25 °C for 1 h, leading to the allylated malonate **78** with high yields (entries 1-6, Table 6). Excellent enantioselectivity was achieved using chiral P,N-ligand **66a** with a camphor backbone (96 % *ee*, entry 1). The enantioselectivity decreased changing the solvent from CH_2Cl_2 to Et_2O (86 % *ee*, instead of 96 % *ee*, entries 1 and 2). It should be noted that ligands **66b** and **66e** gave a significant level of stereodifferentiation but the opposite configuration in **78** (entries 3 and 5). A dramatic effect of decreasing enantioselectivity compared with **66a** was observed in the presence of ligands bearing a quinoline ring or a 6-phenyl substituted pyridine ring (entries 4 and 6).

2.5.2 Pd-catalyzed enantioselective allylic amination

The Pd-catalyzed allylic amination is a well-established process in organic synthesis.[115] We applied Pfaltz's conditions[116] using benzylamine, the sodium salts of *p*-toluenesulfonamide or benzoylhydrazine as nucleophiles. Ligand **66b** was found to be the most effective ligand for the Pd-catalyzed allylic amination (compare entries 1 and 2, Table 7). With benzylamine, a good enantioselectivity (87 % *ee*) was obtained in toluene (compare entries 2, 3 and 4). Various nucleophiles such as benzoylhydrazine and *p*-toluenesulfonamide reacted to give the expected product with moderate enantioseletivities (entries 5-7) as shown in Table 7.

[115] M. Johannsen, K. A. Jørgensen, *Chem. Rev*. **1998**, *98*, 1689.
[116] P. von Matt, O. Loiseleur, G. Koch, A. Pfaltz, C. Lefeber, T. Feucht, G. Helmchen, *Tetrahedron: Asymmetry* **1994**, *5*, 573.

Table 7. Pd-catalyzed allylic amination of 1,3-diphenylallyl acetate **77**.



Entry	L*	Nucleophile	Solvent	*ee* (%)[a]	Yield (%)[b]
1	**66a**	$PhCH_2NH_2$	THF	-	-
2	**66b**	$PhCH_2NH_2$	THF	80	72
3	**66b**	$PhCH_2NH_2$	CH_2Cl_2	63	93
4	**66b**	$PhCH_2NH_2$	toluene	87	95
5	**66b**	$PhCONHNH_2$	toluene	54	50
6	**66b**	$PhCONHNH_2$	THF	69	72
7	**66b**	$TsNH^-Na^+$	THF	51	20[c]

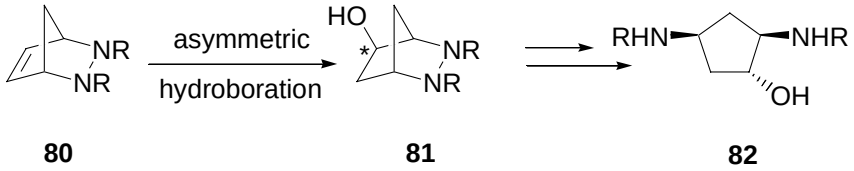
[a] Determined by HPLC analysis (Daicel Chiralcel OD-H, *n*-heptane: *i*-PrOH, 98:2).

[b] Isolated yield of analytically pure product.

[C] 70 °C, overnight.

2.5.3 Ir-catalyzed asymmetric hydroboration of *meso*-bicyclic hydrazine

Recently, *Micouin* and *Bonin* developed a straightforward access to polysubstituted diaminocyclopentanes **82** based on the desymmetrization of *meso*-bicyclic hydrazines **80** *via* Rh- or Ir-catalyzed asymmetric hydroboration.[117]



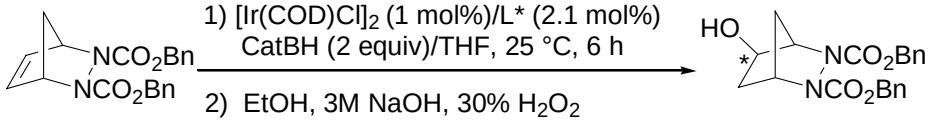
Scheme **66**. Desymmetrization of *meso*-bicyclic hydrazines **80**.

Micouin has used chiral ligand **66** for an Ir-catalyzed asymmetric hydroboration of hydrazine **80a** with catecholborane (CatBH)[117] and has obtained *exo*-alcohol **81a** as shown in Table 8. Using the same experimental conditions, ligand **66a** proved to be the most effective ligand in this transformation. The stereochemical outcome in this reaction was the same as the

[117] a) A. P. Luna, M. -A. Ceschi, M. Bonin, L. Micouin, H. -P. Husson, *J. Org. Chem*. **2002**, *67*, 3522.

one previously reported for the hydroboration of norbornene.[118] Surprisingly, no enantioselectivity and only low conversions were observed when ligands with a 6-phenyl substituted pyridine backbone were used (entries 4-5).

Table 8. Ir-catalyzed hydroboration of compound **80a**.

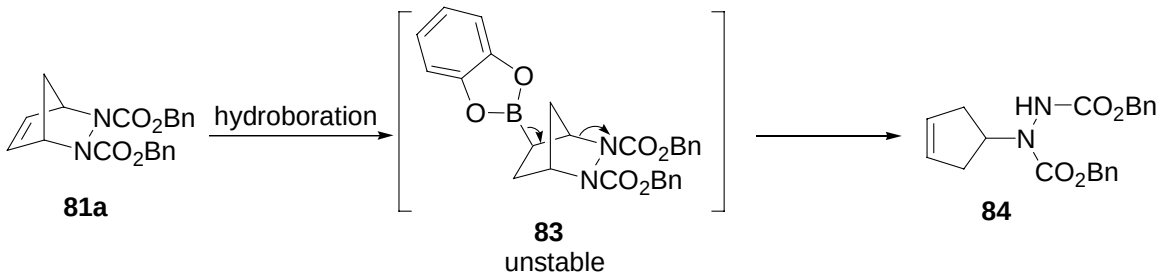


80a *exo*-alcohol **81a**

Entry	L*	*ee* (%)[a]	Yield (%)[b]
1	**66a**	58 (1*S*, 4*R*, 5*R*)	57
2	**66b**	44 (1*S*, 4*R*, 5*R*)	67
3	**66c**	13 (1*S*, 4*R*, 5*R*)	43
4	**66e**	rac	23
5	**66f**	rac	40

[a] Determined by HPLC analysis (Chiralpack column AD, *n*-hexane: *i*-PrOH, 80:20).
[b] Isolated yield of analytically pure product.

With respect to the activity of the iridium complexes, it is quite intriguing that no chemical yields higher than 70 % were obtained despite of full conversion in most of the cases. Generally 10-15 % of side products **84** were generated. This was probably due to the instability of the intermediate borane **83**, which underwent ring opening of the bicyclic hydrazine **83** to cyclopentene **84** as shown in Scheme 67.



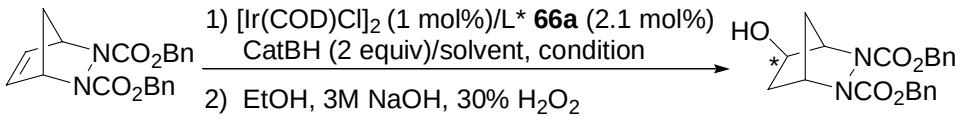
81a **83** unstable **84**

Scheme 67. Ring opening of bicyclic hydrazine **83**.

[118] T. Hayashi in *Comprehensive Asymmetric Catalysis* (Eds: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **1999**.

Next, we have optimized the reaction conditions using chiral ligand **66a**. The results are summarized in Table 9. Thus, lowering the reaction temperature was not possible since no significant reaction occurred at –20 °C (entry 1, Table 9). A solvent variation to toluene led to a lower conversion (30 yield) and 65 % *ee* (entry 2) whereas a change to DME provided the *exo*-alcohol **81a** in 63 % yield and 67 % *ee* (entry 3). In order to improve the reaction yield we increased the catecholborane concentration (entries 4 and 5) and obtained our best result with a 0.6 M solution of CatBH (76 % yield, 71 % *ee*, entry 5). Compared with previous studies using (*R*,*S*)-Josiphos,[119] the use of the novel ligand **66a** represented an improvement of yield and a slight improvement in enantioselectivity (from 64 % *ee* to 71 % *ee*).

Table 9. Influene of solvent and temperature for Ir-catalyzed hydroboration of **80a**.



80a *exo*-alcohol **81a**

Entry	L*	Molarity	Solvent	T [°C, h]	*ee* (%)[a]	Yield (%)[c]
1	**66a**	0.25	THF	-20, 16	-	-
2	**66a**	0.25	toluene	0, 4	65[b]	30
3	**66a**	0.25	DME	0, 4	67[b]	63
4	**66a**	0.25	THF	25, 4	71[b]	61
5	**66a**	0.6	THF	0, 4	71[b]	76
6	(*R*,*S*)-Josiphos	0.6	THF	0, 4	64[d]	60

[a] Determined by HPLC analysis (Chiralpack column AD, *n*-hexane: *i*-PrOH, 80:20).

[b] The absolute configuration of the major enantiomer has been established to be (1*S*,4*R*,5*R*).

[c] Isolated yield of analytically pure product.

[d] The absolute configuration of the major enantiomer has been established to be (1*R*,4*S*,5*S*).

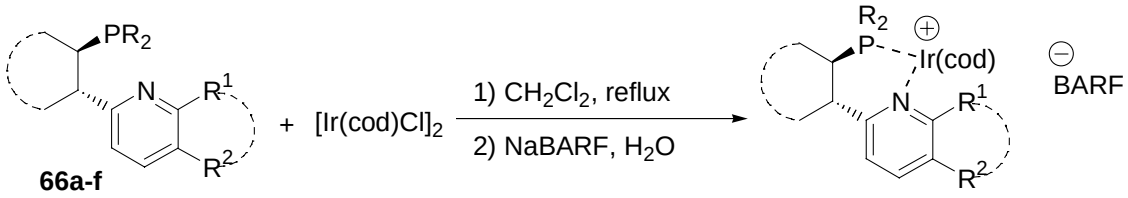
2.5.4 Ir-catalyzed asymmetric hydrogenation of trisubstituted alkenes

Iridium phosphinooxazoline complexes have proven to be highly effective catalysts for enantioselective hydrogenation reactions of olefins including unfunctionalized alkenes.[120]

[119] A. P. Luna, M. Bonin, L. Micouin, H.-P. Husson, *J. Am. Chem. Soc*. **2002**, *124*, 12098.

[120] a) P. Schnider, G. Koch, R. Prétôt, G. Wang, F. M. Bohnen, C. Krüger, A. Pfaltz, *Chem. Eur. J*. **1997**, *3*, 887; b) D. G. Blackmond, A. Lightfoot, A. Pfaltz, T. Rosner, P. Schnider, N. Zimmermann, *Chirality* **2000**, *12*, 442.

Following Pfaltz's procedure,[121] Ir-complexes **85a-f** were readily prepared by heating a solution of $[Ir(cod)Cl]_2$ and the respective P,N-ligand **66** in CH_2Cl_2. The chloride ion was exchanged with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARF) in a biphasic CH_2Cl_2-H_2O system. The resulting orange BARF salts can be purified by column chromatography on silica gel. The complexes were stable towards oxygen and moisture (Scheme 68).



85a : **66a**.Ir(cod)BARF; 89 %
85b : **66b**.Ir(cod)BARF; 85 %
85c : **66c**.Ir(cod)BARF; 88 %
85d : **66e**.Ir(cod)BARF; 88 %
85e : **66g**.Ir(cod)BARF; 75 %

Scheme 68. Preparation of Ir-complexes **85a-e**.

The x-ray analysis of cationic Ir-complex **85a** is shown in Figure 4.

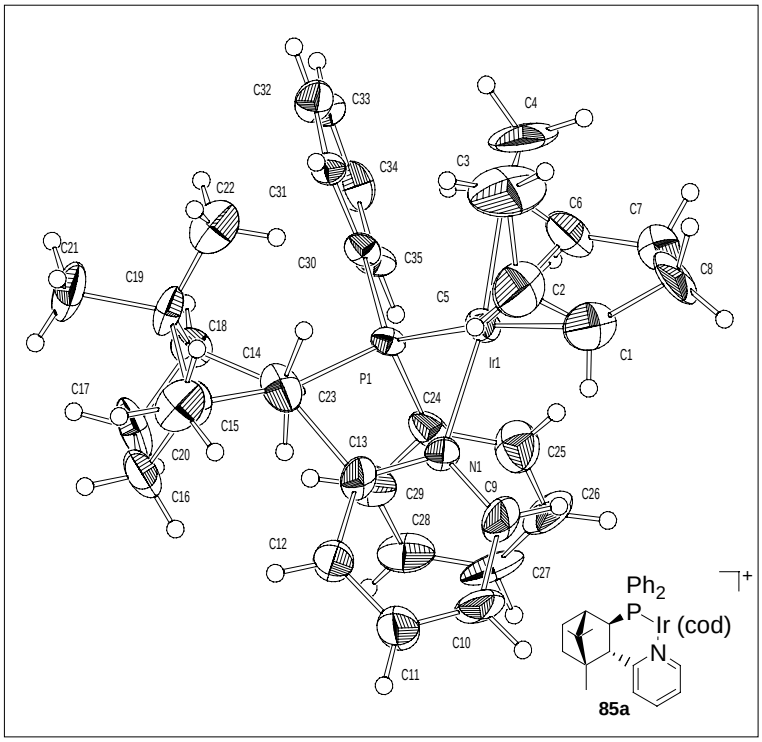


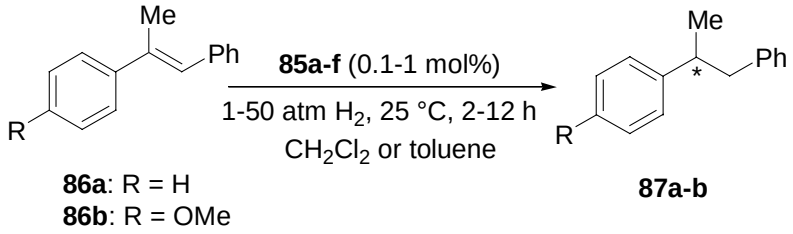
Figure 4. X-ray structure of Ir-complex **85a**.

[121] A. Lightfoot, P. Schnider, A. Pfaltz, *Angew. Chem.* **1998**, *110*, 3047; *Angew. Chem. Int. Ed.* **1998**, *37*, 2897.

Having succeeded in the preparation of iridium complexes **85a-e**, a systematic study of these complexes in Ir-catalyzed hydrogenation reactions of (*E*)-1,2-diphenylpropene (**86a**) and 2-(4-methoxyphenyl)-1-phenyl-1-propene (**86b**) was performed (Table 10).[122] Ir-catalyzed hydrogenation of (*E*)-1,2-diphenylpropene (**86a**) and 2-(4-methoxyphenyl)-1-phenyl-1-propene (**86b**) was studied at 25 °C in the presence of complexes **85a-e** (0.1-1 mol%). A slow reaction was observed in CH_2Cl_2 but an excellent conversion was obtained in toluene (entries 1 and 2), leading to (*S*)-1,2-diphenylpropane (**87a**) with complete conversion within 12 h and 95 % *ee*. Remarkably, the pressure could be reduced to 1 bar of H_2 leading to (*S*)-**87a** (95 % *ee*) in 91 % conversion (entry 4). Decreasing of the catalyst loading to 0.5 mol% still led to a conversion of 90 % with 95 % *ee* within 2 h at 25 °C (entry 5). Catalyst **85d**, in which the pyridyl group bears an additional phenyl substituent in the 6 position proved to be unreactive (entry 6). Also the replacement of the PPh_2 group of the catalyst **85a** by a PCy_2 group (catalyst **85e**, entry 7) led to a moderate conversion (only 80 % under 1 bar of H_2, 25 °C, 12 h) and 80 % *ee*. However, complex **85c** with a quinolyl group led to high conversions and high enantioselectivities (entries 8-13). The high activity of this catalyst allowed the performance of the reaction under a pressure of 1 bar of H_2 (entries 10, 11 and 12). The loading of the catalyst could be reduced to 0.5 mol%. However, with 0.1 mol% catalyst **85c**, no conversion was observed under a pressure of 1 bar of H_2 but 92 % conversion and 95 % *ee* were obtained under a pressure of 50 bar of H_2 (entries 12 and 13). This might be due to a deactivation of the catalyst through the formation of an catalytically inactive hydride-bridged trimer.[123] Catalyst **85b** provided hydrogenated product (*R*)-**87a** with the opposite configuration (80 % *ee*), although with low conversion (26 % after 2 h at 25 °C, entry 14). Similar results were obtained with 2-(4-methoxyphenyl)-1-phenyl-1-propene (**86b**) (entry 15-18). Complex **85c** was by far the most active catalyst (entries 15 and 16).

[122] T. Bunlaksananusorn, K. Polborn, P. Knochel, *Angew. Chem.* **2000**, *112*, 1027; *Angew. Chem. Int. Ed.* **2003**, *115*, 4071.
[123] R. H. Crabtree, *Acc. Chem. Res*. **1979**, *12*, 331.

Table 10. Ir-catalyzed enantioselective hydrogenation of *E*-1,2-diphenylpropene (**86a**) and 2-(4-methoxyphenyl)-1-phenyl-1-propene (**86b**) in toluene at 25 °C.



86a: R = H
86b: R = OMe

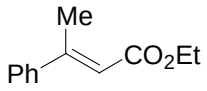
87a-b

Entry	Catalyst (Mol%)	Substrate	Reaction Conditions (bar, h)	% Conversion	*ee* (%)[a]
1	**85a** (1.0)	**86a**	(50, 12)	44	93.5 (*S*)[b]
2	**85a** (1.0)	**86a**	(50, 12)	100	95.0 (*S*)
3	**85a** (0.5)	**86a**	(50, 12)	100	95.0 (*S*)
4	**85a** (1.0)	**86a**	(1, 5)	91	95.0 (*S*)
5	**85a** (0.5)	**86a**	(1, 2)	90	95.0 (*S*)
6	**85d** (1.0)	**86a**	(50, 12)	6	-
7	**85e** (1.0)	**86a**	(1, 12)	80	80.0 (*S*)
8	**85c** (1.0)	**86a**	(50, 12)	100	95.0 (*S*)
9	**85c** (1.0)	**86a**	(50, 2)	100	94.0 (*S*)
10	**85c** (1.0)	**86a**	(1, 5)	100	95.0 (*S*)
11	**85c** (0.5)	**86a**	(1, 2)	96	96.0 (*S*)
12	**85c** (0.1)	**86a**	(1, 12)	1	-
13	**85c** (0.1)	**86a**	(50, 12)	92	95.0 (*S*)
14	**85b** (1.0)	**86a**	(50, 2)	26	80.0 (*R*)
15	**85a** (1.0)	**86b**	(50, 2)	87	91.0 (*S*)
16	**85c** (1.0)	**86b**	(50, 2)	100	94.7(*S*)
17	**85c** (1.0)	**86b**	(1, 2)	76	94.0 (*S*)

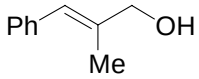
[a] The enantiomeric excess was determined by chiral HPLC (Daicel Chiracel OJ column).

[b] The reaction was performed in CH_2Cl_2.

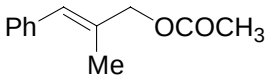
Additionally, other substrates, such as ethyl 3-phenylbutenoate (**88**), 2-methyl-3-phenylallyl alcohol (**89**) and 2-methyl-3-phenylallyl acetate (**90**) were also hydrogenated in the presence of catalyst **85c** (1 mol%; 50 bar of H_2, 25 °C, 12 h). The desired products were obtained with moderate to good enantioselectivities (58-80 % *ee*; see Scheme 69).



88 : 65 % conv., 58 % *ee*



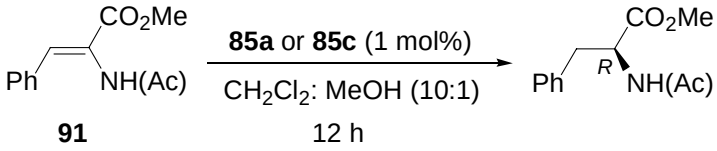
89 : 94 % conv., 69 % *ee*



90 : 100 % conv., 80 % *ee*

Scheme 69. Ir-catalyzed hydrogenation of unsaturated substrates using catalyst **85c**.

The hydrogenation of unsaturated enamides such as **91** to amino acid derivatives such as **92** is of special interest. This enantioselective hydrogenation was extensively studied using Rh-catalysts.[28] To our knowledge, no enantioselective Ir-catalyzed hydrogenation of these substrates was reported. We found that the hydrogenation of **91** under standard conditions (50 bar of H_2, 25 °C, 12 h) in CH_2Cl_2:MeOH (10:1) in the presence of the chiral Ir-catalyst **85a** and **85c** provided phenylalanine derivative **92** in 100 % conversion and with 95.4 % *ee* and 95.3 % *ee*, respectively. Moreover, when the reaction was carried out the higher temperature of 50 °C and at just 1 bar of H_2, full conversion and an excellent enantiomeric excess of 96.5 % *ee* were observed (Scheme 70).



91

92 : with **85a** : 100 % conv., 95.4 % *ee*; 50 bar H_2, rt

92 : with **85a** : 100 % conv., 96.5 % *ee*; 1 bar H_2, 50 °C

92 : with **85c** : 100 % conv., 95.3 % *ee*; 50 bar H_2, rt

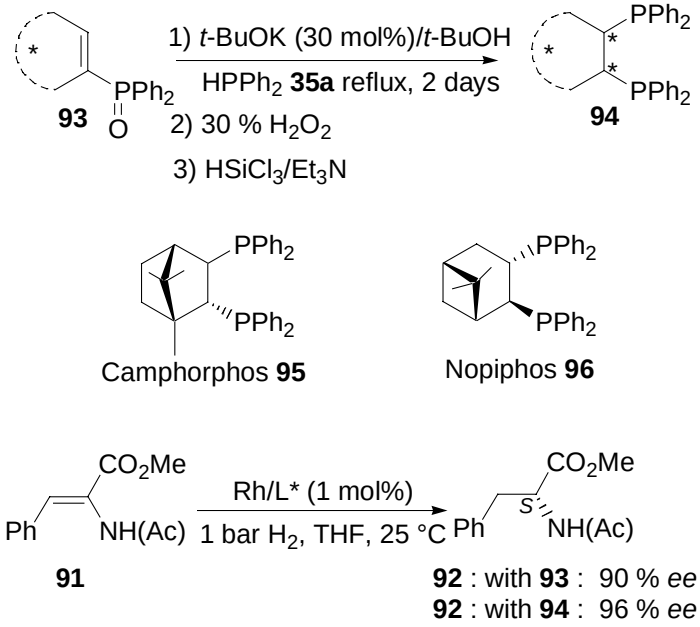
Scheme 70. Ir-catalyzed hydrogenation of dehydroamino acids using catalyst **85a** and **85c**.

2.6 Summary

In summary, novel chiral P,N ligands **66a-e** have been prepared in high yields through *t*-BuOK-mediated addition of phosphine oxides to vinylpyridines **63a-e**. They gave rise to Ir-complexes, which exhibit high enantioselectivity in the hydrogenation reactions of (*E*)-1,2-diphenylpropene (**86a**) leading to the hydrogenated product **87a** with up to 95 % *ee*. Remarkably, several of these Ir-catalyzed reactions could be performed under 1 bar of H_2 showing the high activity of these catalysts. For the first time P,N-ligands could be used for the asymmetric Ir-catalyzed hydrogenation of dehydroamino acid derivatives such as (*Z*)-α-(acetamido)cinnamate **91** with high enantioselectivity.

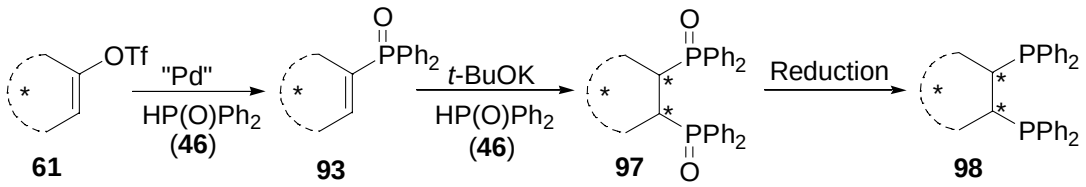
3 Preparation of chiral P,P-ligands and their applications in asymmetric catalysis

Chiral diphosphine ligands are widely used in various metal-catalyzed asymmetric reactions. *Helmchen* and *Krotz* reported the preparation of the modular 1,2-diphenylphosphine ligands. Camphorphos **95** and Nopiphos **96** were reported using Michael acceptors such as vinylphosphine oxides **93** and Ph_2PH (**35a**) in the presence of 30 mol% *t*-BuOK (1M in *t*-BuOH), followed by the reduction of the phosphine oxides. These ligands are efficient in Rh-catalyzed asymmetric hydrogenation of (*Z*)-α-(acetamido)cinnamate **91**, leading to phenylalanine derivative **92** with high enantioselectivities (90-96 % *ee*) as shown in Scheme 71.[40]



Scheme 71. Preparation of Camphorphos **95** and Nopinophos **96** and their applications in a asymmetric hydrogenation reactions.

Thus, the syntheses of **95** and **96** prompted us to prepare chiral P,P-ligands using our optimised conditions for the preparation of chiral P,N-ligands **66** as described in chapter 2. Our synthetic approach is outlined in Scheme 72.

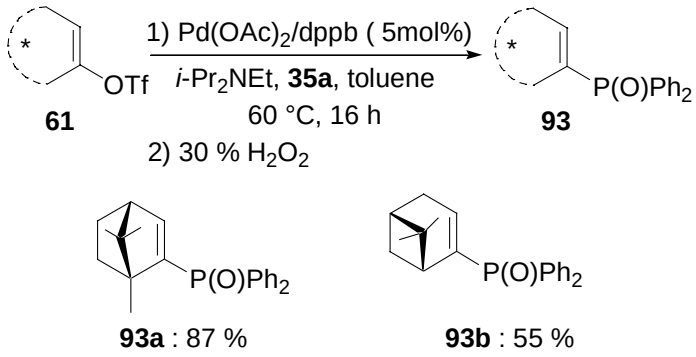


Scheme 72. Proposed preparation of chiral P,P-ligands **98**.

As proposed in Scheme 72, vinylphosphine oxides **93** is synthesized by Pd-catalyzed cross-coupling of alkenyl triflates **61** with $Ph_2P(O)H$ (**46**). The hydrophosphination of vinylphosphine oxides **93** with $Ph_2P(O)H$ (**46**) in the presence of substoichiometric amounts of *t*-BuOK leads to 1,2-diphenylphosphine oxides **97**. Reduction of **97** gives the desired chiral P,P-ligands **98**.

3.1 Preparation of alkenylphosphine oxides 93

Pd-catalyzed cross-coupling of alkenyl triflates **61** with $HPPh_2$ (**35a**) was described by Gilbertson.[124] Applying these reaction conditions, alkenylphosphine oxides **93a-b** were prepared in 55-87 % yield as shown in Scheme 73.

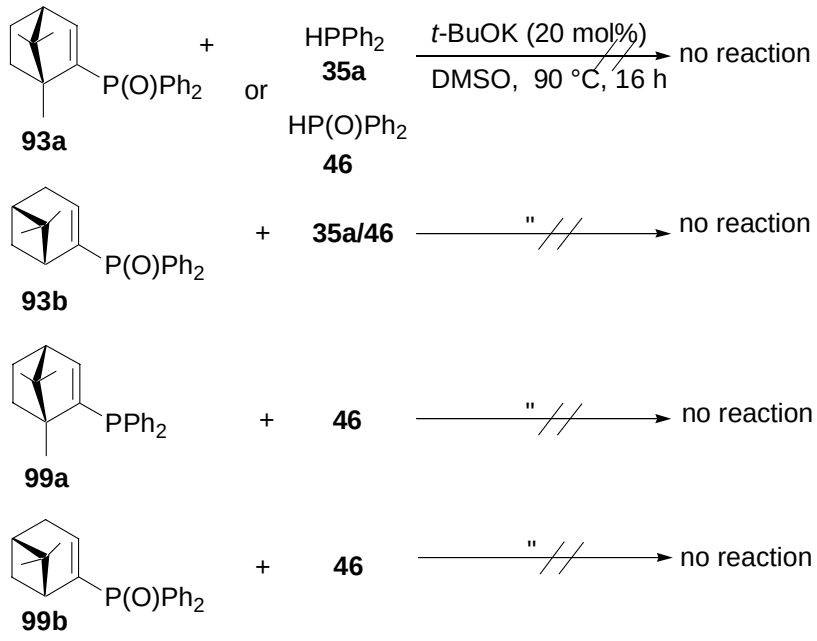


Scheme 73. Preparation of alkenylphosphine oxides **93a-b**.

3.2 Hydrophosphination of 93a-b and 99a-b

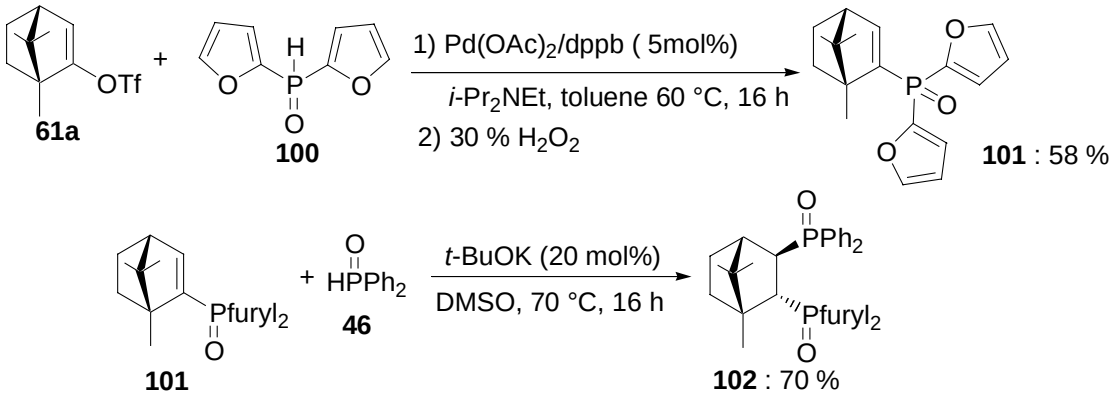
Attempts to prepare Camphorphos **95** and Nopiphos **96** using our optimised conditions failed even after heating to 90 °C for 16 h. The use of excess *t*-BuOK (1-2 equiv) remained also unsuccessful. Changing the substrate from alkenylphosphine oxide **93a** to alkenylphosphine **99a**, in order to avoid a steric hindrance, led to the same disappointing results as illustrated in Scheme 74.

[124] S. R. Gilbertson, Z. Fu, G. W. Starkey, *Tetrahedron Lett*. **1999**, *40*, 8509.



Scheme 74. Attempts to prepare Camphorphos **95** and Nopiphos **96**.

Assuming that the steric hindrance of the substituents on the phosphine oxide was accounting for this failure, we changed the substituents on the phosphine oxide from phenyl to 2-furyl. The cross-coupling of **100** with alkenyl triflate **61a** proceeded smoothly giving *trans*-1,2-diphosphine oxide **102** in 70 % yield (Scheme 75). The x-ray crystal structure of *trans*-**102** is shown in Figure 5.



Scheme 75. Preparation of chiral 1,2-diphosphine oxide **102**.

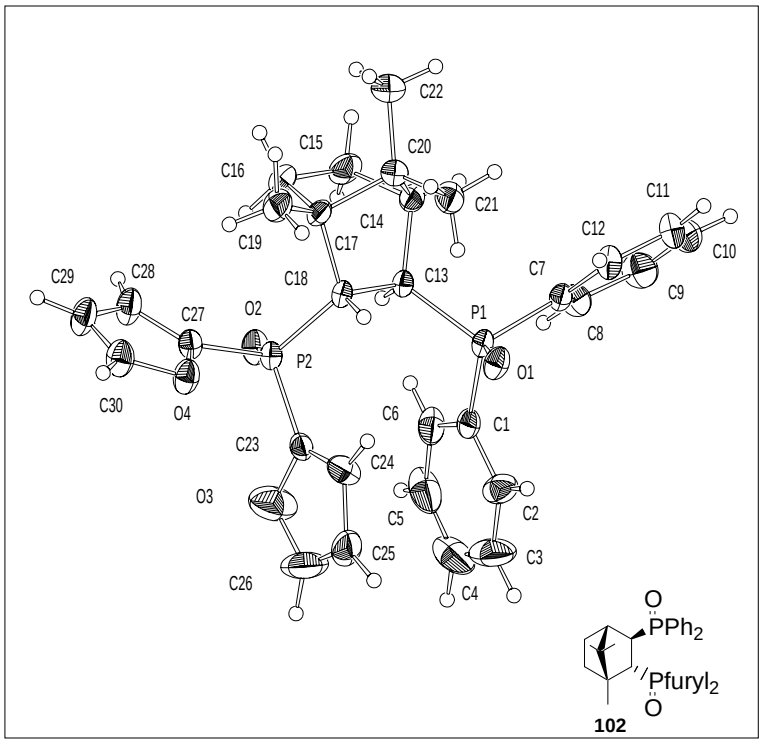
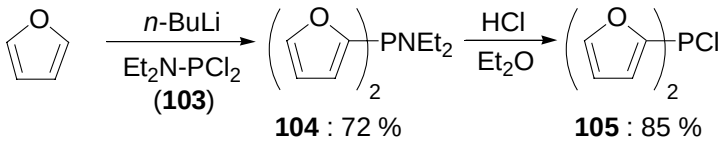


Figure 5. X-ray crystal structure of chiral 1,2-diphosphine oxide **102**.

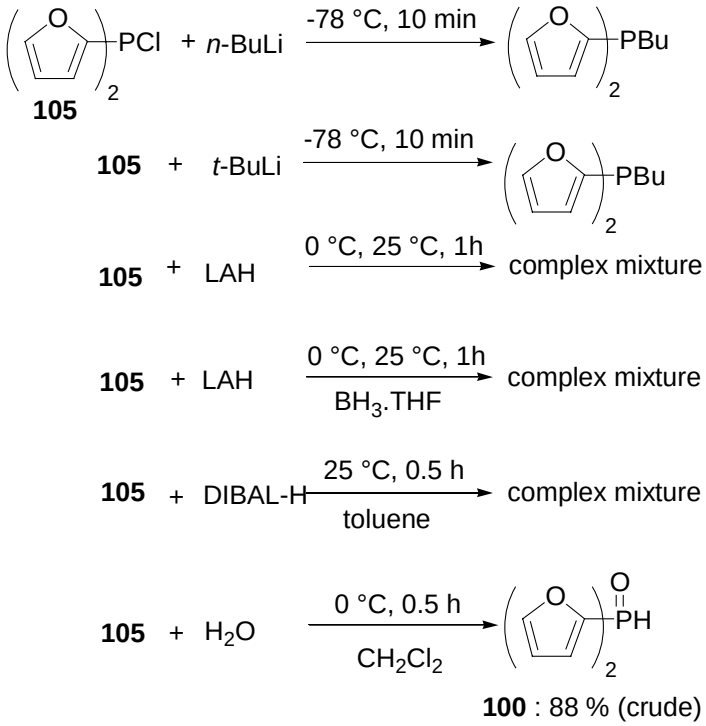
3.3 Preparation of di-2-furylphosphine oxide 100

Attempts to convert di-2-furylphosphine chloride (**105**)[125], prepared according to the literature (Scheme 76),[126] to di-2-furylphosphine oxide (**100**) were unsuccessful. Complex reaction mixtures were observed by ^{31}P NMR spectroscopy and the results are summarized in Scheme 77. Finally, we found that addition of water to di-2-furylphosphine chloride (**105**) in CH_2Cl_2 at 0 °C led to crude di-2-furylphosphine oxide (**100**) in 88 % yield. Attempts to purify **100** by column chromatography failed.



Scheme 76. Preparation of di-2-furylphosphine chloride **105**.

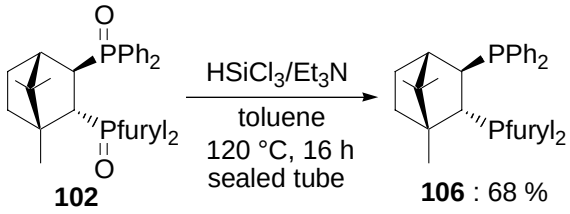
[125] a) N. G. Andersen, R. Mcdonald, B. A. Keay, *Tetrahedron: Asymmetry* **2001**, *12*, 263; b) G. Markl, J. Amrhein, T. Stoiber, U. Striebl, P. Kreitmeier, *Tetrahedron*, **2002**, 58, 2551.
[126] a) A. L. Casalnuovo, T. V. Rajanbabu, T. A. Ayers, T. H. Warren, *J. Am. Chem. Soc*. **1994,** *116*, 9869; b) M. P. Johnson, S. Tripett*, J. Chem. Soc., Perkin Trans. 1*, **1982**, 191.



Scheme 77. Attempts to prepare di-2-furylphosphine oxide (**100**).

3.4 Reduction of chiral 1,2-diphosphine oxide 102

Reduction of chiral diphosphine oxide **102** using standard conditions ($HSiCl_3$, Et_3N, toluene, 120 °C, 16 h)[112] furnished chiral 1,2-diphosphine **106** in satisfactory yield (Scheme 78).

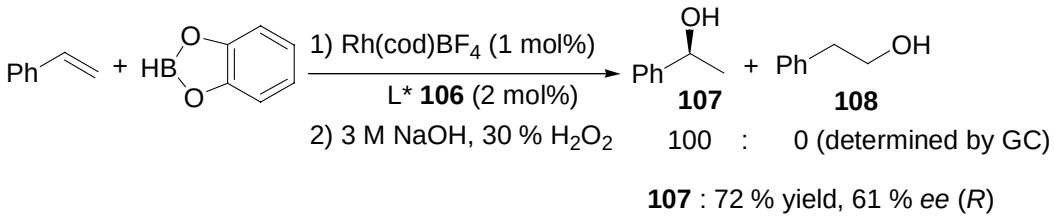


Scheme 78. Preparation of chiral P,P-Ligand **106**.

3.5 Applications in asymmetric catalysis

3.5.1 Rh-catalyzed hydroboration of styrene using ligand 106

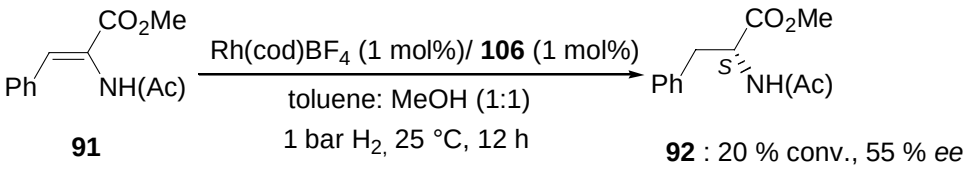
The hydroboration of alkenes is a valuable reaction in organic synthesis.[127] The first examples of Rh-catalyzed asymmetric hydroboration were reported by Burgess[128] and Suzuki.[129] In 1993, Brown's QUINAP was shown to be an effective ligand in Rh-catalyzed hydroboration of arylalkenes.[130] Applying Brown's conditions, the hydroboration of styrene using ligand **106** and $Rh(cod)BF_4$ proceeded with high regioselectivity for the branched alcohol **107** in 72 % yield and moderate enantioselectivity (61 % *ee*, Scheme 79).



Scheme 79. Hydroboration of styrene using ligand **106**.

3.5.2 Rh-catalyzed enantioselective hydrogenation of methyl (*Z*)-α-(acetamido)cinnamate 91

Rh-catalyzed hydrogenation of (*Z*)-α-(acetamido)cinnamate **91** using ligand **106** was explored.[131] The reaction was rather slow and we observed low enantioselectivity in the hydrogenated product **92** (55 % *ee*, Scheme 80).



Scheme 80. Rh-catalyzed hydrogenation of dehydroamino-acids using ligand **106**.

[127] A. Pelter, K. Smith, H. C. Brown, *Borane Reagent*, Academic Press, New York, **1988**.
[128] a) K. Burgess, M. J. Ohlmeyer, *J. Org. Chem*. **1988**, *53*, 5179; b) K. Burgess, W. A. van der Donk, M. J. Ohlmeyer, *Tetrahedron: Asymmetry* **1991**, *2*, 613.
[129] M. Sato, N. Miyaura, A. Suzuki, *Tetrahedron Lett*. **1990**, *31*, 231.
[130] J. M. Valk, G. A. Whitlock, T. O. Layzell, J. M. Brown, *Tetrahedron: Asymmetry* **1995**, *6*, 2593.
[131] T. Ireland, *Dissertation*, Ludwig-Maximilians-Universität München, **1999**.

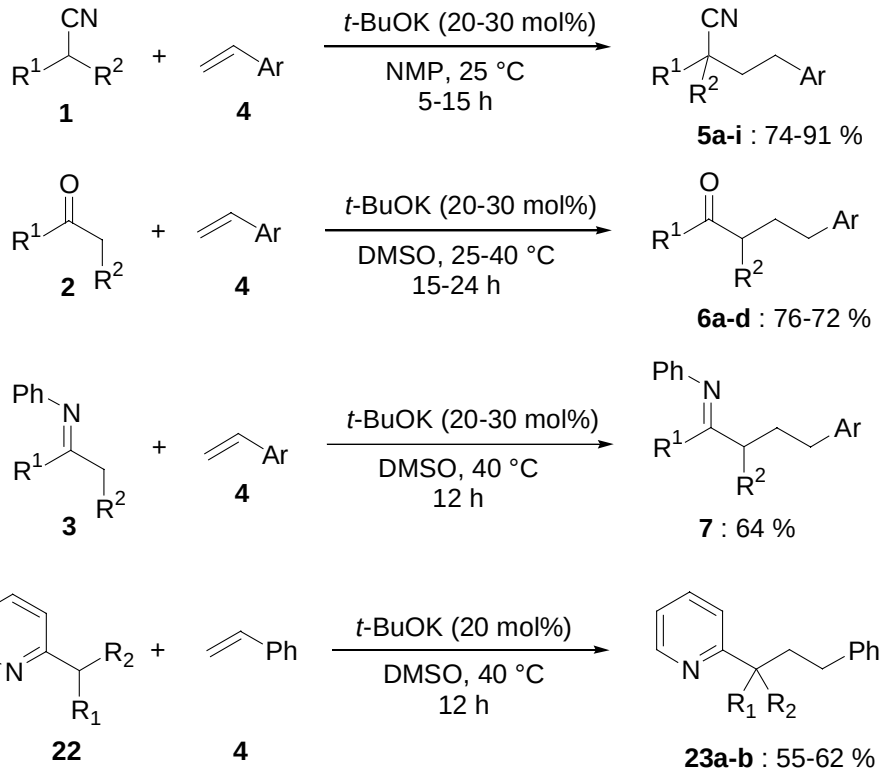
3.6 Summary

We have described the preparation of chiral diphosphine ligand **106** through addition of $Ph_2P(O)H$ (**46**) to alkenylphosphine oxide **101** in the presence of substoichiometric amounts of *t*-BuOK (20 mol%) in DMSO. Applications in asymmetric catalysis such as Rh-catalyzed hydroboration of styrene and hydrogenation of (*Z*)-α-(acetamido)cinnamate **91** using chiral ligand **106** gave only moderate enantioselectivities.

4. Summary and Outlook

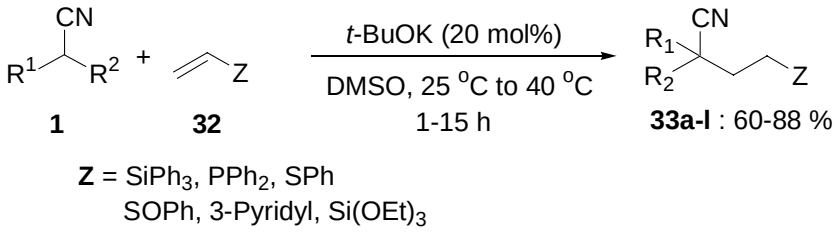
This work focused on new methods for the synthesis of chiral P,N- and P,P-ligands as well as their applications in asymmetric synthesis.

In the first part, we have found that potassium enolates of nitriles **1**, ketones **2**, imine **3** or pyridines **22** generated catalytically using *tert*-BuOK in DMSO or NMP have a high nucleophilicity in these solvents and add readily to various styrenes in good yields allowing an unique catalytic phenylethylation reaction (Scheme 81).



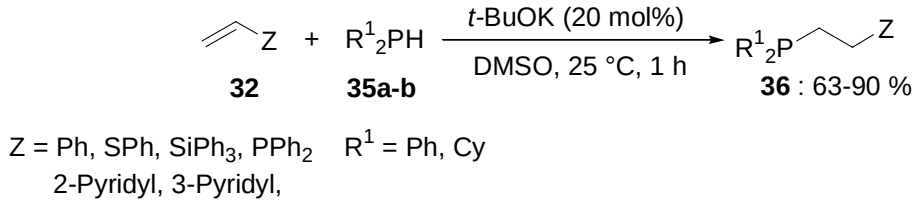
Scheme 81. *t*-BuOK-mediated addition of various nucleophiles to styrene.

Furthermore, we developed an efficent protocol for the addition of nitriles to various moderately active Michael-acceptors allowing the preparation of new functionalized silanes, phosphines, pyridines and thioethers (Scheme 82). Up to now, only highly reactive organolithium species were used to successfully these moderately active Michael-acceptors.



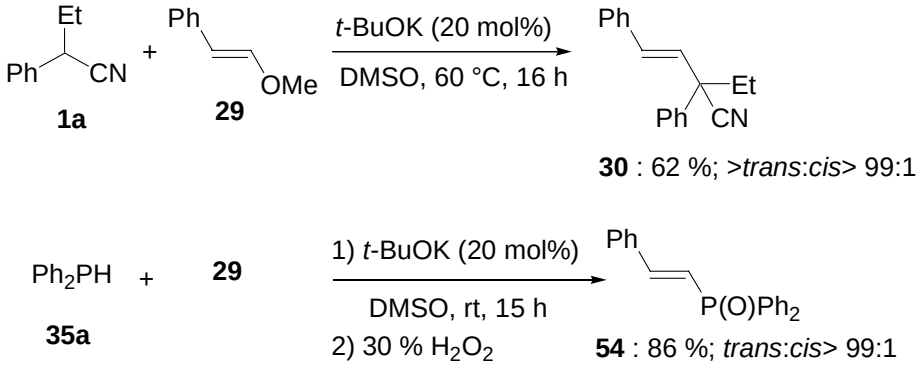
Scheme 82. Addition of nitriles to various functionalized alkenes **32**.

The hydrophosphination of functionalized alkenes was developed under mild conditions, providing high yields and selectivities for the *anti*-Markovnikov products (Scheme 83). No transition metal catalysts was needed to be used, which makes this transformation economically benign.



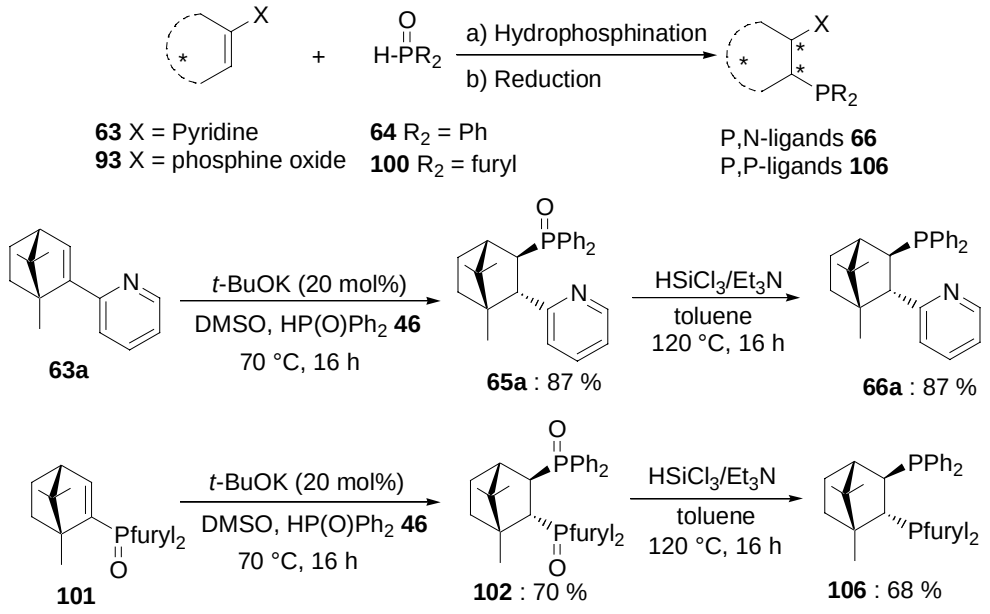
Scheme 83. Hydrophosphination of functionalized alkenes **32**.

Interestingly, the catalytic vinylation of nitrile **1a** and diphenylphosphine (**35a**) *via* an addition-elimination mechanism led to high stereoselectivities for vinylated products and good yields (Scheme 84). During this reaction, MeOH is the only by-product. It would be desirable to develop a general protocol for the preparation of functionalized vinyl-substituted products by further investigations of substrate and leaving group scope.



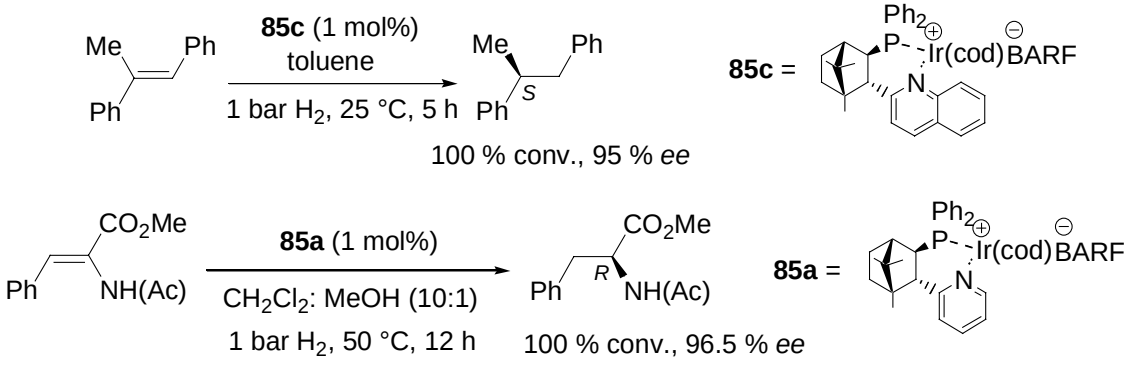
Scheme 84. Preparation of vinyl-substituted nitrile **30** and phosphine oxide **54**.

In the second part of this work, we applied the hydrophosphination to the synthesis of various chiral alkenylpyridines **63** and alkenylphosphine oxides **93** from cheap chiral backbones such as (+)-camphor, thereby providing new chiral P,N-ligands **66** and P,P-ligand **106** as outlined in Scheme 85.



Scheme 85. Synthesis of chiral P,N- and P,P-ligands.

Among these P,N-ligands **66**, **66a** and **66c** were found to be efficient ligands for Ir-catalyzed enantioselective hydrogenation reactions of trisubstituted alkenes. For the first time, the Ir-catalyzed asymmetric hydrogenation of (*Z*)-α-(acetamido)cinnamate was achieved, leading to high enantioselectivities under a pressure of 1 bar of H_2 at 25-50 °C as shown in Scheme 86.



Scheme 86. Application in Ir-catalyzed enantioselective hydrogenation.

We described a new synthesis of chiral P,N- and P,P-ligands. Further improvements in the variation of the chiral building block and the electronic nature of the pyridine ring might improve the enantioselectivities in various asymmetric reactions.

1 General Conditions

All reactions were carried out with magnetic stirring and, if air or moisture sensitive, in flame-dried glassware under argon. Syringes which were used to transfer reagents and solvents were purged with argon prior to use.

Solvents

Solvents were dried according to standard methods by distillation over drying agents as stated below and were stored under argon: DMSO (CaH_2), THF (Na/benzophenone), triethylamine (KOH), CH_2Cl_2 and toluene (Na).

Reagents

- Reagents of >98 % purity were used as obtained.
- *n*-Butyllithium was used as 1.5 M solution in hexane.
- *t*-Butyllitihum was used as 1.5 M solution in pentane.
- 1.7 M $ZnBr_2$ solution was prepared by drying $ZnBr_2$ (30.5 g, 0.14 mol) under vacuum at 120 °C for 5 h. After cooling to rt, dry THF (80 mL) was added and stirring was continued until the salt was dissolved.
- Diisopropylamine was distilled from CaH_2.

The following reagents were prepared according to literature: $Pd(dba)_2$[132], dppf[133], 2-iodoquinoline[105], dimethylaminophenylacetonitrile[76], *tert*-butyl 2-formyl-1*H*-pyrrole-1-carboxylate[134], *trans*-3-methoxy-1-phenyl-1-propene[135], 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane-2-oxide[136], *N*-cyclohexylideneaniline[137], dibenzyl 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate[138], (6*E*)-7-phenyl-6-heptenenitrile[139], ethyl benzylideneaminoacetate[140] and $Rh(COD)_2BF_4$.[141]

- Organolithium and organomagnesium solutions were titrated using Paquette's method.[142]

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[132] Y. Takahashi, T. Ito, S. Sakai, *J. Chem. Soc., Chem. Commun*. **1970**, 1065.
[133] J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, J. C. Smart, *J. Organomet. Chem*. **1971**, *27*, 241.
[134] L. F. Tietze, G. Kettschau, K. Heitmann, *Synthesis* **1996**, 851.
[135] J. G. Duboudin, B. Jousseaume, *J. Organomet.Chem*. **1979**, *168*, 1
[136] A. Munoz, C. Hubert, J. –L. Luche, *J. Org. Chem*. **1996**, *61*, 6015.
[137] B. Capon, Z. P. Wu, *J. Org. Chem*. **1990**, *55*, 2317.
[138] J. A. Moore, R. Muth, R. Sorace, *J. Org. Chem*. **1974**, *39*, 3799.
[139] B. Lipshutz, P. A. Blomgren, S. –K. Kim, *Tetrahedron Lett*. **1999**, *40*, 197.
[140] J. Haddow, C. J. Suckling, Hamish C. S. Wood, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1297.
[141] M. D. Fryzuk, B. J. Bosnich, *J. Am. Chem. Soc*. **1977**, *99*, 6262.
[142] H. –S. Lin, L. A. Paquette, *Synth. Commun*. **1994**, *24*, 2503.

Chromatography

- Thin layer chromatography (TLC) was performed using aluminium plates coated with SiO_2 (Merck 60, F-254). TLC plates were viewed under UV light and /or by treatment with one of the solutions below followed by heating with a heat gun:

  -$KMNO_4$ (0.3 g), K_2CO_3 (20 g), KOH (0.3 g) in water (300 mL).

  Phosphomolybdic acid (5.0 g), $Ce(SO_4)_2$ (2.0 g), conc. H_2SO_4 (12 mL) in water (230 mL).
- Flash column chromatography was performed using SiO_2 (0.040-0.063 mm) from Merck.
- Gas chromatgraphy (GC): Hewlett-Packard 6890. Chiral columns: Chiralsil DEX CB (25m x 250 μm x 0.25 μm, Chrompack) or Chiralsil L-Val (25 m x 0.12 μm x 0.22 mm fused silica WCOT). Carrier gas: H_2.
- High performance liquid chromatography (HPLC): Apparatus from Gynkotec firm with autosample and a diode array UV-VIS detector. Chiral column: Chiracel OD, OB, AD, OJ (*Dacel Chemical Industries*) with *n*-heptane/2-propanol as a mobile phase.
- Racemic compounds were used to choose the operating conditions for the resolution of the enantiomer and diastereomer peaks.

Analytical data

- **Melting point** were determined on a Büchi B-540 apparatus and are uncorrected.
- **NMR** spectra were recorded on Brucker ARX 200, Ac 300 or WH 400 instruments. Chemical shifts are reported as δ-values in ppm relative to the deuterated solvent peak: $CDCl_3$ (δ_H 7.27, δ_C 77.0). For ^{31}P NMR, 85 % phosphoric acid was used as an external standard. For the characterization of the observed signal multiplicities the following abbrevations were applied: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).
- **Optical rotation** were measured on a Perkin-Elmer 241 polarimeter.
- **Infrared** spectra were recorded between 4000 and 400 cm^{-1} on a Nicolet 510 or Perkin-Elmer 281 spectrophotometer.
- **Electron impact masss** (EI, 70 eV) spectra were recorded on a Varian MAT CH 7A instrument. High resolution mass spectra (HRMS) were recorded on a Varian MAT 711 instrument.
- **Elemental analysis** was carried out on a Heraeus CHN-Rapid-Elementanalyzer I at the microanalytical laboratories of the Department für Chemie und Pharmazie, Ludwig-Maximilians Universität München.

2 Typical Procedures (TP)

2.1 TP 1: Typical procedure for *t*-BuOK-mediated addition reactions of carbonyl derivatives to styrenes

Method A: To a stirred solution of *t*-BuOK (56 mg, 0.5 mmol, 25 mol%) in NMP (2 mL) was added under argon a mixture of cyclohexanecarbonitrile (**1c**) (164 mg, 1.5 mmol) and styrene **4** (208 mg, 2 mmol). The reaction mixture was stirred for 16 h at 25 °C. Water (3 mL) and CH_2Cl_2 (25 mL) were added and the resulting solution was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

Method B: The reaction was carried out as above using DMSO instead of NMP as the solvent. To a stirred solution of *t*-BuOK (45 mg, 0.4 mmol, 20 mol%) in DMSO (2.5 mL) was added α-tetralone (**2a)** (877 mg, 6 mmol) and styrene **4** (208 mg, 2 mmol). The reaction mixture was vigorously stirred for 15 h at 40 °C. Following the workup procedure, as described for Method A, purification by flash chromatography yielded the desired product.

2.2 TP 2: Typical procedure for *t*-BuOK-mediated addition reactions of carbonyl derivatives to substituted styrenes

To a stirred solution of *t*-BuOK (45 mg, 0.4 mmol, 20 mol%) in DMSO (2.0 mL) was added the nitrile (2 mmol), followed by the substituted styrene (2 mmol). After stirring for the required time, the reaction was quenched with saturated, aqueous NH_4Cl (4 mL). The aqueous phase was extracted with CH_2Cl_2 (25 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.3 TP 3: Typical procedure for *t*-BuOK-mediated addition reactions of substituted pyridines to styrenes

To a stirred solution of *t*-BuOK (44 mg, 0.4 mmol, 20 mol%) in DMSO (2.0 mL) was added 2-isopropylpyridine (**22a**) (242 mg, 2 mmol), followed by styrene **4** (210 mg, 2 mmol). The reaction mixture was vigorously stirred for 0.5 h at 25 °C and quenched with saturated, aqueous NH_4Cl (5 mL). The aqueous phase was extracted with CH_2Cl_2. The combined

organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.4 TP 4: Typical procedure for addition-elimination reactions of nitriles to methoxystyrenes

To a stirred solution of *t*-BuOK (0.4 mmol, 30 mol%) in NMP (2.0 mL) was added 2-phenylbutyronitrile (**1a**) (145 mg, 1.0 mmol), followed by methyl 2-phenyl-2-propenyl ether (**26**) (1.0 mmol). The reaction mixture was stirred at 25 °C for 2 h. Water (3 mL) was added and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.5 TP 5: Typical procedure for *t*-BuOK-mediated addition reactions of nitriles to functionalized alkenes

To a stirred solution of *t*-BuOK (0.8 mmol, 20 mol%) in DMSO (2.0 mL) were added 2-phenylbutyronitrile (**1a**) (1.5 mmol), and triphenylvinylsilane (**32a**) (429 mg, 1.5 mmol). The reaction mixture was vigorously stirred at 40 °C for 1 h. Water (4 mL) was added and the mixture extracted with CH_2Cl_2 (2 x 15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.6 TP 6: Typical procedure for *t*-BuOK-mediated addition reactions of carbonyl derivatives to triethoxyvinylsilane

To a stirred solution of EtOK (252 mg, 3.0 mmol, 20 mol%) in NMP (15 mL) was added isobutyronitrile (**1b**) (1.38 g, 20 mmol), followed by triethoxyvinylsilane (**32f**) (2.85 g, 15 mmol). The reaction mixture was stirred at 40 °C for 16 h. Water (10 mL) was added and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.7 TP 7: Typical procedure for *t*-BuOK-mediated addition of ketones to diphenylvinylphosphine

To a stirred solution of *t*-BuOK (45 mg, 0.4 mmol, 20 mol%) in DMSO (2.0 mL) was added the ketone (6.0 mmol) and diphenylvinylphosphine (**32b**) (424 mg, 2.0 mmol). The reaction mixture was stirred at 40 °C for 15 h. Water (5 mL) was added and the mixture extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.8 TP 8: Typical procedure for the hydrophosphination of functionalized alkenes

To a stirred solution of *t*-BuOK (45 mg, 0.4 mmol, 20 mol%) in DMSO (2 mL) were successively added Ph_2PH **35a** (424 mg, 2 mmol) and phenyl vinyl sulfide **32c** (272 mg, 2 mmol). The reaction was stirred at 25 °C. After stirring for the required time for full conversion, the reaction was quenched with saturated, aqueous NH_4Cl (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.9 TP 9: Typical procedure for the preparation of alkenyl triflates[103]

n-BuLi (6.7 mL, 1.5 M in hexane, 10 mmol) was added to a solution of diisopropylamine (1.7 mL, 12 mmol) in THF (40 mL) at –78 °C and stirred for 30 min. Then a solution of ketone (10 mmol) in THF (20 mL) was added dropwise and stirred at –78 °C, for 1 h. A solution of Tf_2NPh (**69**) (3.82 g, 10.7 mmol) in THF (20 mL) was then added and the reaction was stirred at 0 °C for 14 h. The reaction mixture was quenched with saturated, aqueous NH_4Cl (30 mL) and extracted with Et_2O (3 x 40 mL). The organic phase was washed with water, brine and dried over $MgSO_4$. Purification by flash chromatography yielded the desired product.

2.10 TP 10: Typical procedure for the preparation of alkenylphosphine oxides from ketones[124]

Alkenyl triflate (3 mmol), Ph_2PH (**35a**) (596 mg, 3.2 mmol), and *N*,*N*-diisopropylethylamine (1.4 mL, 8 mmol) were dissolved in toluene (10 mL). $Pd(OAc)_2$ (34 mg, 0.15 mmol, 5 mol%)

and 1,4-bis(diphenylphosphino)butane (64 mg, 0.15 mmol, 5 mol%) in toluene (4 mL) were added and the mixture was stirred at 40 °C. After stirring for the required time for full conversion, 30 % H_2O_2 (2 mL) was added at 0°C and the mixture was allowed to warm up to 25 °C within 1 h. The mixture was diluted with CH_2Cl_2 (30 mL) and washed with water and brine. The solution was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo*. Purification by flash chromatography yielded the desired product.

2.11 TP 11: Typical procedure for Negishi cross-coupling reactions

A solution of *n*-BuLi (13.4 mL, 1.5 M in hexane, 20 mmol) was added dropwise at –78 °C to a solution of 2-bromopyridine (**62a**) (20 mmol) in THF (20 mL). The reaction mixture was stirred at –78 °C for 30 min, then a solution of $ZnBr_2$ (12.4 mL, 1.7 M in THF, 21 mmol) was added dropwise. After 15 min at –78 °C, the reaction mixture was allowed to warm up to rt for 30 min, then a solution of the alkenyl triflate (10 mmol), $Pd(dba)_2$ (115 mg, 0.2 mmol, 2 mol%), dppf (111 mg, 0.2 mmol, 2 mol%) in THF (15 mL) was added dropwise. The reaction mixture was heated to reflux (70 °C) for 15 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (40 mL) and the aqueous phase was extracted with Et_2O (3 x 60 mL). The organic phase was washed with brine and dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.12 TP 12: Typical procedure for Suzuki cross-coupling reactions[109]

A solution of bromopyridine (0.50 mmol) and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol, 4 mol%) in toluene (2 mL) was treated with a solution of Na_2CO_3 (106 mg, 1 mmol) in H_2O (1 mL) followed by a solution of $PhB(OH)_2$ (64 mg, 0.53 mmol) in MeOH (1 mL). The mixture was stirred at 85 °C for 16 h. After cooling to 25 °C, a solution of concentrated aqueous NH_3 (0.25 mL) in saturated Na_2CO_3 (2.5 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. Removal of the solvent *in vacuo* gave a residue which was purified by flash column, yielding the desired product.

2.13 TP 13: Typical procedure for the preparation of chiral 1,2-aminophosphine oxide 65 and chiral 1,2-diphosphine oxide 102

To a stirred solution of *t*-BuOK (22 mg, 0.2 mmol, 20 mol%) in DMSO (1 mL) were successively added under argon, $Ph_2P(O)H$ (**46**) (202 mg, 1 mmol) and 2-alkenylpyridine (1 mmol) in DMSO (2 mL). The reaction mixture was stirred at 70 °C for 15 h. After cooling to rt, water (5 mL) and CH_2Cl_2 were added (20 mL). The organic phase was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the desired product.

2.14 TP 14: Typical procedure for the reduction of phosphine oxides to phosphines[111]

A tube was charged with the phosphine oxide (0.5 mmol), toluene (15 mL), trichlorosilane (0.5 mL, 10 equiv, 5 mmol) and triethylamine (1.4 mL, 20 equiv, 10 mmol) under argon, sealed and heated for 16 h at 120 °C. After cooling to 25 °C, the reaction mixture was transferred to a 100 mL-flask filled with argon. Toluene and excess trichlorosilane were evaporated *in vacuo*. The residue was dissolved in toluene (15 mL) and carefully quenched with degassed 10 % aqueous $NaHCO_3$ (3 mL). The separated organic phase was filtered and transferred by cannulation in a second flask flushed with argon. Toluene was evaporated *in vacuo* and the residue was washed with Et_2O (30 mL). After filtration, remaining solvents were evaporated *in vacuo*, yielding the desired product.

2.15 TP 15: Typical procedure for Ir-complexes 85[121]

To a two-necked flask fitted with a reflux condensor was added the P,N-ligand (0.1 mmol), $[Ir(cod)Cl]_2$ (34 mg, 0.05 mmol) and CH_2Cl_2 (5 mL) The solution was heated to reflux at 45 °C for 1 h until ^{31}P NMR indicated that the ligand was consumed. After cooling to 25 °C, Na[BARF] (131 mg, 0.15 mmol) was added, followed by H_2O (5 mL) and the resulting two-phase mixture was stirred vigorously for 30 min. The seperated aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with H_2O (10 mL) and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography, yielding the Ir-complex as an orange solid.

2.16 TP 16: Typical procedure for Pd-catalyzed allylic substitution reactions

Ligand **66a** (10 mg, 25 μmol, 5.0 mol%), $[Pd(C_3H_5)Cl]_2$ (4.6 mg, 12.5 μmol, 2.5 mol%) and potassium acetate (2.5 mg, 25 μmol, 5.0 mol%) were dissolved in CH_2Cl_2 (1 mL) and stirred at rt for 15 min. 3-Acetoxy-1,3-diphenyl-propene (**77**) (126 mg, 0.5 mmol) in CH_2Cl_2 (2 mL), dimethyl malonate (0.2 mL, 1.5 mmol) and *N*,*O*-bistrimethylsilylacetamide (305 mg, 1.5 mmol) were added. The reaction mixture was stirred at 25 °C for 2 h. The reaction was quenched with saturated aqueous NH_4Cl (2 mL) and extracted with Et_2O (3 x 15 mL). The organic phase phase was washed with saturated aqueous $NaHCO_3$ (3 mL), water, brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded **78**.

2.17 TP 17: Typical procedure for Pd-catalyzed allylic amination reactions

$[Pd(C_3H_5)Cl]_2$ (1.5 mg, 4 μmol, 1.0 mol%) and ligand **66b** (3.1 mg, 8 μmol, 2.0 mol%) were dissolved in toluene (1 mL) and stirred at rt for 10 min. A solution of 3-acetoxy-1,3-diphenyl-propene (**77**) (100 mg, 0.4 mmol) in toluene (3 mL) was added and stirring was maintained for 15 min. Benzylamine (86 mg, 0.8 mmol) was added. The resulting solution was stirred at 25 °C for 12 h. The reaction was quenched with saturated aqueous NH_4Cl (2 mL) and extracted with Et_2O (3 x 15 mL). The combined organic phases were washed with water, brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded **79**.

2.18 TP 18: Typical procedure for Ir-catalyzed hydroboration reactions of *meso*-bicyclic hydrazine 80a[118]

$[Ir(COD)Cl]_2$ (3.4 mg, 5 μmol, 1 mol%), Ligand **66a** (4.2 mg, 11 μmol, 2.1 mol%) and **80a** (182 mg, 0.5 mmol) were placed under argon in a flame-dried Schlenk tube. THF (0.85 mL) was degassed at –50 °C and added to the mixture at this temperature. The reaction was stirred at rt for 30 min and cooled to 0 °C. Catecholborane (0.11 mL, 1 mmol) was added at 0 °C and stirred for 4 h. EtOH (0.5 mL), 3 M NaOH (0.85 mL) and 30 % H_2O_2 (0.5 mL) were added and stirred at 25 °C for 16 h. The reaction mixture was extracted with EtOAc (3 x 10 mL). The organic phase was washed with 1 M NaOH (5 x 10 mL), brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography yielded the *exo*-alcohol **81a**.

2.19 TP 19: Typical procedure for Ir-catalyzed enantioselective hydrogenation reactions of trisubstituted alkenes

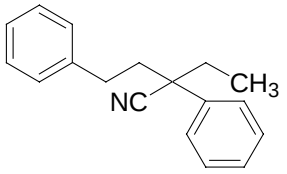
Ir-complex catalyst **85** (1 mol%), *E*-1,2-diphenylpropene (**86a**) (78 mg, 0.4 mmol) and toluene (2 mL) were placed into an autoclave. The autoclave was sealed and pressurized to 50 bar of H_2, and the mixture was stirred for 2 h at 25 °C. The solvent was removed and the crude product was passed through a short pad of silica gel column with pentane as the eluent. After evaporation of the solvent, (*S*)-**87a** was obtained in quantitative yield.

2.20 TP 20: Typical procedure for Ir-catalyzed enantioselective hydrogenation reactions of α-acetamidocinnamate ester 91

Ir-complex catalyst **85a** (4.7 mg, 3 μmol, 1 mol%), methyl (*Z*)-α-(acetamido)cinnamate **91** (66 mg, 0.3 mmol), CH_2Cl_2 (3 mL) and MeOH (0.3 mL) were placed in an autoclave. The autoclave was sealed and pressurized to 1 bar of H_2 and the mixture was stirred at 50 °C for 2 h. CH_2Cl_2 and MeOH were removed and the crude product was passed through a short silica gel column with Et_2O as eluent. After evaporation of the solvent, (*R*)-**92** was obtained in quantitative yield.

3 Addition of nucleophiles to styrenes

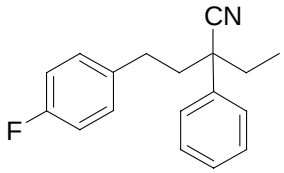
Synthesis of 2-ethyl-2,4-diphenylbutyronitrile (5a)



Prepared according to TP 1 (Method A) from 2-phenylbutyronitrile (**1a**) (290 mg, 2.0 mmol), *t*-BuOK (56 mg, 0.5 mmol, 25 mol%) in NMP (2 mL) and styrene (**4a**) (312 mg, 3.0 mmol). Reaction time: 5 h at 25 °C. Purification by flash chromatography (CH_2Cl_2) yielded **5a** (403 mg, 81 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.16 (m, 10H), 2.89 (dd, *J* = 12.7 Hz, 4.3 Hz, 1H), 2.57-1.98 (m, 5H), 1.04 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3, 138.5, 129.5, 129.0, 128.8, 128.3, 126.7, 126.5, 122.6, 49.5, 43.2, 34.8, 32.3, 10.2.
IR (KBr, cm^{-1}): 2235, 1602, 1584, 1495, 1455, 761, 700.
MS (EI, 70 eV): 249 (M^+, 34), 145 (10), 105 (100), 91 (39), 77 (8), 51 (4).
$C_{18}H_{19}N$ HRMS: Calcd.: 249.1517.
Found: 249.1508.

Synthesis of 2-ethyl-4-(4-fluorophenyl)-2-phenylbutyronitrile (5b)



Prepared according to TP 1 (Method A) from 2-phenylbutyronitrile (**1a**) (363 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in NMP (2 mL) and 4-fluorostyrene (**4b**) (244 mg, 2.0 mmol). Reaction time: 5 h at 25 °C. Purification by flash chromatography (10% CH_2Cl_2 in pentane) yielded **5b** (416 mg, 78 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.33 (m, 5H), 7.10-6.92 (m, 4H), 2.83-2.72 (m, 1H), 2.44-1.92 (m, 5H), 0.96 (t, *J* = 7.2 Hz, 3H).

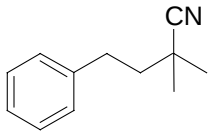
^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0 (d, *J* = 242.6 Hz), 138.2, 136.7 (d, *J* = 3.2 Hz), 130.1, 130.0, 129.4, 128.3, 126.4, 122.5, 115.8, 115.5, 49.4, 43.2, 34.6, 31.4, 10.0.

IR (KBr, cm^{-1}): 2236, 1601, 1510, 1494, 1449, 1222, 1157, 826, 758, 700.

MS (EI, 70 eV): 267 (M^+, 65.2), 123 (100), 109 (34).

$C_{18}H_{18}FN$	Calcd.:	C, 80.87	H, 6.79	N, 5.24
	Found:	C, 80.81	H, 6.43	N, 5.15

Synthesis of 2,2-dimethyl-4-phenylbutyronitrile (5c)



Prepared according to TP 1 (Method A) from isobutyronitrile (**1b**) (228 mg, 3.3 mmol), *t*-BuOK (79 mg, 0.7 mmol) in NMP (5 mL) and styrene (**4a**) (447 mg,4.3 mmol). Reaction time: 15 h at 25 °C. Purification by flash chromatography (CH_2Cl_2) yielded **5c** (457 mg, 80 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.25 (m, 5H), 2.68-2.60 (m, 2H), 1.70-1.62 (m, 2H), 1.24 (s, 6H).

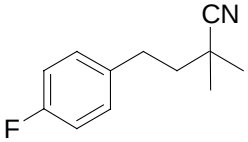
^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3, 129.0, 128.8, 126.7, 125.2, 43.4, 32.9, 32.2, 27.1.

IR (KBr, cm^{-1}): 2233, 1603, 1498, 1471, 1455, 1370, 1207, 753, 703.

MS (EI, 70 eV): 173 (M^+, 21), 105 (63), 91 (100), 69 (39).

$C_{12}H_{15}N$	HRMS:	Calcd.:	173.1204.
		Found:	173.1198.

Synthesis of 4-(4-fluorophenyl)-2,2-dimethylbutyronitrile (5d)



Prepared according to TP 1 (Method A) from isobutyronitrile (**1b**) (138 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in NMP (2 mL) and 4-fluorostyrene (**4b**) (244 mg, 2.0 mmol). Reaction time: 5 h at 25 °C. Purification by flash chromatography (20% CH_2Cl_2 in pentane) yielded **5d** (302 mg, 79 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07-6.98 (m, 2H), 6.88-6.79 (m, 2H), 1.70-1.60 (m, 2H), 2.69-2.58 (m, 2H), 1.26 (s, 6H).

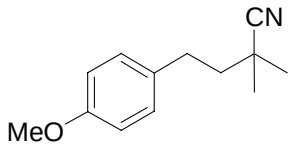
^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0 (d, J = 242.6 Hz), 137.0 (d, J = 3.2 Hz), 130.2, 130.1, 125.1, 115.8, 115.5, 43.4, 32.8, 31.3, 26.9.

IR (KBr, cm^{-1}): 1601, 1511, 1472, 1458, 1372, 1222, 1158, 832.

MS (EI, 70 eV): 191 (M^+, 16), 123 (21) (100).

$C_{12}H_{14}FN$	HRMS:	Calcd.:	191.1110.		
		Found:	191.1120.		
$C_{12}H_{14}FN$		Calcd.:	C, 75.36	H, 7.38	N, 7.32
		Found:	C, 75.50	H, 7.34	N, 7.45

Synthesis of 4-(4-methoxyphenyl)-2,2-dimethylbutyronitrile (5e)



Prepared according to TP 1 (Method A) from isobutyronitrile (**1b**) (276 mg, 4.0 mmol), *t*-BuOK (56 mg, 0.5 mmol) in NMP (3 mL) and 4-methoxystyrene (**4c**) (402 mg, 3 mmol). Reaction time: 15 h at 25 °C. Purification by flash chromatography (CH_2Cl_2) yielded **5e** (450 mg, 74 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (m, 2H), 6.74 (m, 2H), 3.68 (s, 3H), 2.68-2.60 (m, 2H), 1.72-1.66 (m, 2H), 1.30 (s, 6H).

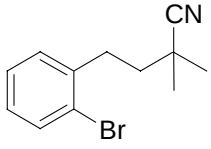
^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 133.3, 129.6, 125.3, 114.4, 55.6, 43.7, 32.8, 31.3, 27.1.

IR (KBr, cm^{-1}): 2233, 1613, 1584, 1513, 1463, 1301, 1248, 1178, 1035, 822.

MS (EI, 70 eV): 203 (M^+, 45), 135 (12), 121 (100).

$C_{13}H_{17}NO$	HRMS:	Calcd.:	203.1310.
		Found:	203.1310.

Synthesis of 4-(2-bromophenyl)-2,2-dimethylbutyronitrile (5f)



Prepared according to TP 1 (Method B) from isobutyronitrile (**1b**) (183 mg, 2.0 mmol), *t*-BuOK (42mg, 0.37 mmol) in DMSO (2 mL) and 2-bromostyrene (**4d**) (183 mg, 1 mmol). Reaction time: 2 h at 25 °C. Purification by flash chromatography (CH_2Cl_2) yielded **5f** (223 mg, 89 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.40 (m, 1H), 7.16-7.14 (m, 2H), 7.02-6.95 (m, 1H), 2.85-2.78 (m, 2H), 1.74-1.66 (m, 2H), 1.34 (s, 6H).

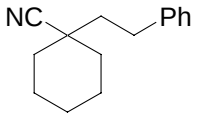
^{13}C NMR (75 MHz, $CDCl_3$): δ 140.5, 133.3, 130.8, 128.5, 128.2, 125.1, 124.6, 41.5, 32.7, 32.6, 27.0.

IR (KBr, cm^{-1}): 2234, 1471, 1440, 1371, 1232, 1206, 1028, 753.

MS (EI, 70 eV): 253 (32), 183 (44), 172 (100), 103 (48).

$C_{12}H_{14}NBr$ HRMS: Calcd.: 251.0310.
Found: 251.0309.

Synthesis of 1-(2-phenylethyl)cyclohexanecarbonitrile (5g)



Prepared according to TP 1 (Method A) from cyclohexanecarbonitrile (**1c**) (164 mg, 1.5 mmol), *t*-BuOK (56 mg, 0.5 mmol) in NMP (2 mL) and styrene (**4a**) (208 mg, 2.0 mmol). Reaction time: 16 h at 25 °C. Purification by flash chromatography (30% CH_2Cl_2 in pentane) yielded **5g** (291 mg, 91 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.00 (m, 5H), 2.80-2.65 (m, 2H), 2.10-1.90 (m, 2H), 1.80-1.44 (m, 7H), 1.28-1.04 (m, 3H).

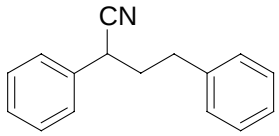
^{13}C NMR (75 MHz, $CDCl_3$): δ 141.5, 128.9, 128.7, 126.6, 123.9, 43.0, 39.5, 36.1, 31.3, 25.8, 23.5.

IR (KBr, cm^{-1}): 2230, 1604, 1497, 1453, 753, 701.

MS (EI, 70 eV): 213 (M^+, 18), 109 (82), 105 (71), 91 (100).

$C_{15}H_{19}N$ HRMS: Calcd.: 213.1517.
Found: 213.1518.

Synthesis of 2,4-diphenylbutyronitrile (5h)



Prepared according to TP 1 (Method B) from phenylacetonitrile (**1d**) (937 mg, 8.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and styrene (**4a**) (208 mg, 2.0 mmol). Reaction time: 16 h at 25 °C. Purification by flash chromatography (15% Et_2O in pentane) yielded **5h** (345 mg, 78 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.20 (m, 10H), 3.85-3.73 (m,1H), 2.95-2.76 (m, 2H), 2.40-2.13 (m, 2H).

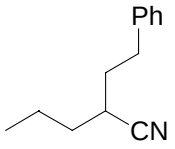
^{13}C NMR (75 MHz, $CDCl_3$): δ 140.0, 136.0, 129.5, 129.1, 128.8, 128.5, 127.6, 126.9, 121.0, 37.7, 36.9, 33.4.

IR (KBr, cm^{-1}): 2241, 1602, 1495, 1454, 1029, 750, 698.

MS (EI, 70 eV): 221 (M^+, 100), 130 (47), 116 (14), 104 (8).

$C_{16}H_{15}N$ HRMS: Calcd.: 221.1204.
Found: 221.1200.

Synthesis of 2-(2-phenylethyl)pentanenitrile (5i)



Prepared according to TP 1 (Method B) from pentanenitrile (**1e**) (2.74 g, 33 mmol), *t*-BuOK (0.45 g, 4 mmol) in DMSO (2.0 mL) and styrene (**4a**) (1.04 g, 10 mmol). Reaction time: 16 h at 25 °C. The crude product was distilled under reduced pressure, yielding **5i** (1.46 g, 78 %) as a colourless oil.

Bp: 30 °C (0.5 mm Hg).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.20 (m, 5H), 3.00-2.85 (m, 1H), 2.83-2.70 (m, 1H), 2.60-2.45 (m, 1H), 2.05-1.80 (m, 2H), 1.75-1.35 (m, 4H), 0.96 (t, J = 7 Hz, 3H).

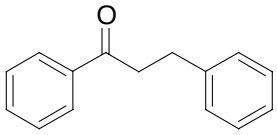
^{13}C NMR (75 MHz, $CDCl_3$): δ 140.6, 129.0, 128.7, 126.7, 122.4, 34.6, 34.3, 33.6, 31.1, 20.7, 13.9.

IR (KBr, cm^{-1}): 2960, 2933, 2236, 2182, 1603, 1497, 1455, 1381, 749, 700.

MS (EI, 70 eV): 187 (M^+, 18), 137 (27.6), 105 (35.1), 91 (100).

$C_{13}H_{17}N$ HRMS: Calcd.: 187.1360.
Found: 187.1353.

Synthesis of 1,3-diphenyl-1-propanone (10)



Prepared according to TP 1 (Method B) from α-dimethylaminophenylacetonitrile (**8**) (320 mg, 2.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (3.0 mL) and styrene (**4a**) (208 mg, 2.0 mmol). Reaction time: 2 h at 60 °C. Purification by flash chromatography (30% CH_2Cl_2 in pentane) yielded **10** (319 mg, 76 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90-7.85 (m, 2H), 7.50-7.10 (m, 8H), 3.21 (t, J = 7.7 Hz, 2H), 2.98 (t, J = 7.7 Hz, 2H).

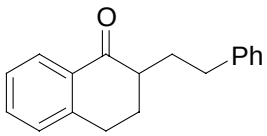
^{13}C NMR (75 MHz, $CDCl_3$): δ 199.6, 141.7, 137.2, 133.4, 129.0, 128.9, 128.8, 128.4, 126.5, 40.8, 30.5.

IR (KBr, cm^{-1}): 1655, 1595, 1495, 1449, 1365, 1292, 1209, 1185, 974, 702.

MS (EI, 70 eV): 210 (M^+, 68.8), 105 (100), 77 (38).

$C_{15}H_{14}O$ HRMS: Calcd.: 210.1045.
Found: 210.1044.

Synthesis of 2-(2-phenylethyl)-3,4-dihydro-1(2*H*)-naphthalenone (6a)



Prepared according to TP 1 (Method B) from α-tetralone (**2a**) (438 mg, 3.0 mmol), *t*-BuOK (4 mg, 0.4 mmol) in DMSO (2.5 mL) and styrene (**4a**) (210 mg, 2.0 mmol). Reaction time: 15 h at 40 °C. Purification by flash chromatography (CH_2Cl_2) yielded **6a** (340 mg, 68 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.30 (m, 1H), 7.18-7.02 (m, 7H), 2.88-2.80 (m, 2H), 2.72-2.54 (m, 2H), 2.41-2.30 (m, 1H), 2.26-2.08 (m, 2H), 1.85-1.60 (m, 2H).

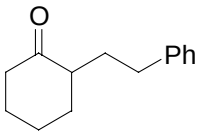
^{13}C NMR (75 MHz, $CDCl_3$): δ 198.9, 142.8, 141.0, 132.1, 131.5, 127.6, 127.4, 127.3, 126.3, 125.5, 124.8, 45.7, 32.1, 30.3, 27.4, 27.3.

IR (KBr, cm^{-1}): 1681, 1601, 1496, 1454, 1226, 740, 700.

MS (EI, 70 eV): 250 (M^+, 4), 159 (14), 146 (100), 131 (13), 115 (5), 104 (4), 91 (13).

$C_{18}H_{18}O$ HRMS: Calcd.: 250.1358.
Found: 250.1451.

Synthesis of 2-(2-phenylethyl)cyclohexanone (6b)



Prepared according to TP 1 (Method B) from cyclohexanone (**2b**) (588 mg, 6.0 mmol), *t*-BuOK (67 mg, 0.6 mmol) in DMSO (2.5 mL) and styrene (**4a**) (209 mg, 2.0 mmol). Reaction time: 5 h at 40 °C. Purification by flash chromatography (CH_2Cl_2) yielded **6b** (242 mg, 60 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.06 (m, 5H), 2.55 (t, *J* = 9 Hz, 2H), 2.36-1.92 (m, 6H), 1.82-1.28 (m, 5H).

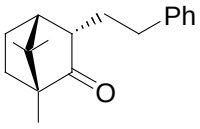
^{13}C NMR (75 MHz, $CDCl_3$): δ 213.5, 142.6, 128.8, 128.7, 126.2, 50.3, 42.5, 34.4, 33.6, 31.6, 28.4, 25.3.

IR (KBr, cm^{-1}): 1708, 1602, 1496, 1450, 1128, 749, 700.

MS (EI, 70 eV): 202 (M^+, 9.7), 111 (14), 98 (100), 91 (25), 77 (37).

$C_{14}H_{18}O$ HRMS: Calcd.: 202.1358.
Found: 202.1372.

Synthesis of 1,7,7-trimethyl-3-(2-phenylethyl)bicyclo[2.2.1]heptan-2-one (6c)



Prepared according to TP 1 (Method B) from camphor (**2c**) (912 mg, 6.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2.5 mL) and styrene (**4a**) (210 mg, 2.0 mmol). Reaction time: 15 h at 40 °C. Purification by flash chromatography (3% Et_2O in pentane) yielded **6c** (236 mg, 46%) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-7.07 (m, 5H), 2.70-2.50 (m, 2H), 2.35-2.25 (m, 1H), 2.08-1.92 (m, 2H), 1.80-1.40 (m, 4H), 1.28-1.16 (m, 1H), 0.92 (s, 3H), 0.81 (s, 3H), 0.76 (s, 3H).

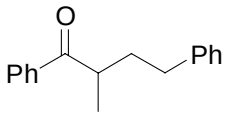
^{13}C NMR (75 MHz, $CDCl_3$): δ 221.7, 142.1, 128.7, 126.3, 59.0, 54.7, 49.4, 46.5, 46.2, 34.5, 31.5, 29.5, 20.5, 19.9, 19.7, 10.0.

IR (KBr, cm^{-1}): 1738, 1603, 1496, 1373, 750, 700.

MS (EI, 70 eV): 256 (M^+, 9), 152 (100), 137 (17), 124 (30), 91 (24), 83 (21).

$C_{18}H_{24}O$	HRMS:	Calcd.:	256.1827.
		Found:	256.1831.
$C_{18}H_{24}O$		Calcd.:	C, 84.32 H, 9.44
		Found:	C, 84.52 H, 9.55

Synthesis of 2-methyl-1,4-diphenyl-1-butanone (6d)



Prepared according to TP 1 (Method B) from 1-phenyl-propan-1-one (**2d**) (214 mg, 1.6 mmol), *t*-BuOK (36 mg, 0.32 mmol) in DMSO (3 mL) and styrene (**4a**) (250 mg, 2.4 mmol). Reaction time: 5 h at 40 °C. Purification by flash chromatography (CH_2Cl_2) yielded **6d** (274 mg, 72 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96-7.90 (m, 2H), 7.62-7.56 (m, 1H), 7.52-7.44 (m, 2H), 7.36-7.20 (m, 5H), 3.53 (m, 1H), 2.71 (t, J = 7.7 Hz, 2H), 2.32-2.18 (m, 1H), 1.88-1.76 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H).

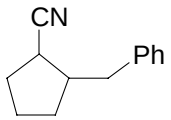
^{13}C NMR (75 MHz, $CDCl_3$): δ 204.4, 142.2, 137.0, 133.3, 129.0, 128.9, 128.8, 128.7, 126.4, 40.2, 35.6, 33.9, 17.7.

IR (KBr, cm^{-1}): 1681, 1596, 1579, 1495, 1448, 1376, 1226, 974, 748, 700.

MS (EI, 70 eV): 239 (M^++1, 1.7), 238 (M^+, 10), 147 (22), 134 (100), 105 (72), 91 (44), 77 (28).

$C_{17}H_{18}O$ HRMS: Calcd.: 238.1358.
Found: 238.1326.

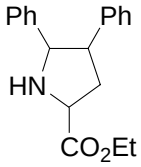
Synthesis of 2-benzylcyclopentanecarbonitrile (18)



Prepared according to TP 1 (Method B) from (6*E*)-7-phenyl-6-heptenenitrile (**17**) (180 mg, 0.97 mmol), *t*-BuOK (43 mg, 0.4 mmol) in NMP (4 mL). Reaction time: 2 h at 100 °C. Purification by flash chromatography (CH_2Cl_2) yielded **18** (109 mg, 61 %) as a mixture of diastereomers (ratio of *cis*:*trans* = 1:1)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-6.90 (m, 5H), 2.80-1.00 (m, 10H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 140.7, 139.7, 129.4, 129.1, 128.9, 126.9, 126.7, 47.7, 45.8, 40.3, 38.5, 34.2, 34.1, 31.5, 30.7, 30.6, 24.1, 23.2.
MS (EI, 70 eV): 185 (M^+, 7), 156 (6), 117 (15.5), 91 (100).
$C_{13}H_{15}N$ HRMS: Calcd.: 185.1204.
Found: 185.1193.

Synthesis of ethyl 4,5-diphenyl-2-pyrrolidinecarboxylate (21)



Prepared according to TP 1 (Method B) from ethyl (*E*)-phenylmethylidenecarbamate (**19**) (2.29 g, 12 mmol) and styrene (**4a**) (1.25 g, 12 mmol). Reaction time: 16 h at 25 °C. Purification by flash chromatography (33% Et_2O in pentane) yielded **21** (2.30 g, 65 %) as a mixture of diastereomers.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-6.95 (m, 10H), 4.30-4.00 (m, 4H), 3.15-3.00 (m, 1H), 2.75-2.50 (m, 2H), 2.20-2.10 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 176.1, 142.6, 140.9, 128.8, 128.5, 128.2, 127.6, 127.3, 127.1, 69.8, 61.5, 59.1, 54.8, 39.1, 14.7.

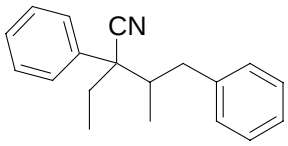
IR (KBr, cm^{-1}): 1737, 1494, 1454, 1202, 1028, 756.

MS (EI, 70 eV): 296 ($[M+H]^+$, 1.6), 295 (5.0), 222 (45), 205 (12), 191 (100), 117 (51).

$C_{19}H_{21}NO_2$ HRMS: Calcd.: 296.1651.

Found: 296.1657. $[M+H]^+$

Synthesis of 2-ethyl-3-methyl-2,4-diphenylbutyronitrile (12)



Prepared according to TP 2 from 2-phenylbutyronitrile (**1a**) (290 mg, 2.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and (*E*)-1-phenylpropene (**11**) (236 mg, 2.0 mmol). Reaction time: 16 h at 60 °C. Purification by flash chromatography (20% CH_2Cl_2 in pentane) yielded **12** (316 mg, 60 %) as a mixture of *cis* and *trans*-products.

Ratio of *cis*:*trans* = 35:65 (by ^{1}H NMR: integration of resonances for CH_3).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-6.80 (m, 10H), 3.20-1.70 (m, 5H), 0.98 (d, *J* = 5.9 Hz, 3H, *cis*-diastereomer), 0.77 (t, *J* = 7.2 Hz, 3H, *trans*-diastereomer), 0.71 (t, *J* = 7.2 Hz, 3H, *cis*-diastereomer), 0.56 (d, *J* = 6.5 Hz, 3H, *trans*-diastereomer).

^{13}C NMR (75 MHz, $CDCl_3$): δ 140.6, 140.5, 138.6, 137.9, 129.6, 129.4, 129.3, 129.2, 128.9, 128.7, 128.2, 128.1, 127.1, 127.0, 126.7, 126.5, 121.9, 121.5, 54.9, 54.6, 45.3, 44.9, 39.5, 39.4, 31.6, 31.1, 15.6, 15.1, 10.4, 10.3.

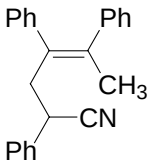
IR (KBr, cm^{-1}): 2233, 1602, 1495, 1454, 1382, 760, 746, 700.

MS (EI, 70 eV): 263 (M^+, 12.6), 145 (47), 130 (6), 119 (51), 91 (100).

$C_{19}H_{21}N$ HRMS: Calcd.: 263.1652.

Found: 263.1674.

Synthesis of 2,4,5-triphenyl-4-hexenenitrile (16)

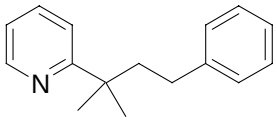


Prepared according to TP 2 from phenylacetonitrile (**13**) (234 mg, 2.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and 2,3-diphenyl-1,3-butadiene (**14**) (412 mg, 2.0 mmol).

Reaction time: 1 h at 25 °C. Purification by flash chromatography (2% Et_2O in pentane) yielded **16** (420 mg, 65 %) as a mixture of *cis* and *trans*-products.
Ratio of *cis*:*trans* = 10:90 (by ^{1}H NMR: integration of resonances for CH_3).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-6.80 (m, 15H), 3.56 (dd, *J* = 8.7, 7.1 Hz, 1H), 3.27 (dd, *J* = 13.7, 8.7 Hz, 1H), 2.95 (ddd, *J* = 13.7, 7.1, 0.7 Hz, 1H), 1.97 (s, 3H, *trans*-isomer), 1.80 (s, 3H, *cis*-isomer).
^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2, 141.4, 138.5, 136.1, 132.7, 130.3, 129.4, 129.2, 128.5, 128.0, 127.8, 126.9, 126.5, 121.0, 41.5, 36.4, 21.7.
IR (KBr, cm^{-1}): 2241, 1598, 1491, 1454, 1442, 1026, 1012, 765.
EI (70 eV): 323 (M^+, 6), 207 (100), 129 (5).
$C_{24}H_{21}N$ HRMS: Calcd. 323.1674.
Found 323.1661.

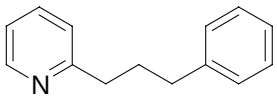
Synthesis of 2-(1,1-dimethyl-3-phenylpropyl)pyridine (23a)



Prepared according to TP 3 from 2-isopropylpyridine (**22a**) (242 mg, 2.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and styrene (**4a**) (208 mg, 2.0 mmol). Reaction time: 0.5 h at 25 °C. Purification by flash chromatography (7% Et_2O in pentane) yielded **23a** (248 mg, 55 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (ddd, *J* = 2.9, 1.9, 0.9 Hz, 1H), 7.55-7.48 (m, 1H), 7.26-6.96 (m, 7H), 2.32-2.23 (m, 2H), 2.00-1.90 (m, 2H), 1.33 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 168.3, 149.2, 143.4, 136.5, 128.7, 128.6, 125.9, 121.1, 120.3, 46.0, 41.0, 31.8, 28.3.
IR (KBr, cm^{-1}): 2962, 2861, 1587, 1569, 1475, 1454, 1362, 790, 747, 727.
MS (EI, 70 eV): 225 (M^+, 0.4), 210 (2), 134 (16), 121 (100), 106 (12), 91 (8), 78 (3), 69 (2).
$C_{16}H_{19}N$ Calcd.: C, 85.28 H, 8.50 N, 6.22
Found: C, 85.46 H, 8.84 N, 6.22

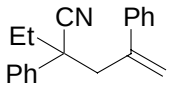
Synthesis of 2-(3-phenylpropyl)pyridine (23b)



Prepared according to TP 3 from 2-methylpyridine (**22b**) (186 mg, 2.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and styrene (**4a**) (208 mg, 2.0 mmol). Reaction time: 16 h at 40 °C. Purification by flash chromatography (15% CH_2Cl_2 in pentane) yielded **23b** (244 mg, 62 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50-8.42 (m, 1H), 7.50 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.25-6.99 (m, 7H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.06-1.94 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 162.3, 149.6, 142.5, 136.6, 128.8, 128.6, 126.1, 123.1, 121.3, 38.2, 35.9, 31.8.
IR (KBr, cm^{-1}): 1590, 1568, 1496, 1474, 1434, 748, 700.
MS (EI, 70 eV): 198 ($[M+H]^+$, 0.5), 93 (100).
$C_{14}H_{15}N$ HRMS: Calcd.: 198.1283.
Found: 198.1282. $[M+H]^+$

Synthesis of 2-ethyl-2,4-diphenyl-4-pentenenitrile (21)

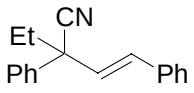


Prepared according to TP 4 from 2-phenylbutyronitrile (**1a**) (145 mg, 1.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in NMP (2.0 mL) and methyl 2-phenyl-2-propenyl ether (**26**) (148 mg, 1.0 mmol). Reaction time: 3 h at 25 °C. Purification by flash chromatography (25 % CH_2Cl_2 in pentane) yielded **21** (188 mg, 72 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.08 (m, 10H), 5.22 (d, *J* = 1.2 Hz, 1H), 5.05 (t, *J* = 1.2 Hz, 1H), 3.09 (dd, *J* = 14.1, 0.9 Hz, 1H, AB system), 3.00 (dd, *J* = 14.1, 0.9 Hz, 1H, AB system), 2.00-1.76 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 142.0, 138.0, 128.9, 128.5, 127.9, 127.8, 126.9, 126.7, 122.1, 119.1, 49.7, 46.5, 33.8, 10.0.
IR (KBr, cm^{-1}): 2235, 1626, 1494, 1448, 1384, 907.
MS (EI, 70 eV): 261 (M^+, 46), 144 (100), 117 (66).

$C_{19}H_{19}N$ HRMS: Calcd.: 261.1517.
Found: 261.1518.

Synthesis of 2-ethyl-2,4-diphenyl-4-pentenenitrile (30)[71]

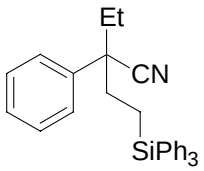


Prepared according to TP 4 from 2-phenylbutyronitrile (**1a**) (290 mg, 2.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and β-methoxystyrene (**29**) (268 mg, 2.0 mmol). Reaction time: 16 h h at 60 °C. Purification by flash chromatography (2% Et_2O in pentane) yielded **30** (306 mg, 62 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.28 (m, 10H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 2.31-2.17 (m, 2H), 1.14 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 139.4, 136.2, 131.9, 129.5, 129.4, 129.1, 128.7, 128.5, 127.1, 126.7, 121.3, 50.9, 34.0, 10.3.
IR (KBr, cm^{-1}): 2237, 1599, 1494, 1448, 1383, 966, 746.

4 Addition of carbonyl derivatives to functionalized alkenes

Synthesis of 2-ethyl-2-phenyl-4-triphenylsilanylbutyronitrile (33a)



Prepared according to TP 5 from 2-phenylbutyronitrile (**1a**) (218 mg, 1.5 mmol), *t*-BuOK (33 mg, 0.3 mmol) in DMSO (2.0 mL) and triphenylvinylsilane (**32a**) (430 mg, 1.5 mmol). Reaction time: 15 h at 40 °C. Purification by flash chromatography (15% CH_2Cl_2 in pentane) yielded **33a** (388 mg, 60 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.19 (m, 20H), 2.11-1.69 (m, 4H), 1.55-1.42 (m, 1H), 1.12-0.99 (m, 1H), 0.77 (t, *J* = 7.4 Hz, 3H).

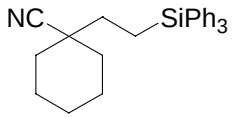
^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2, 135.9, 134.66, 130, 129.2, 128.4, 128.1, 126.7, 122.7, 51.8, 35.9, 34.2, 10.2, 9.0.

IR (KBr, cm^{-1}): 2233, 1111, 740, 714, 700.

MS (EI, 70 eV): 431 (M^+, 0.1), 403 (12), 259 (100).

$C_{30}H_{29}NSi$	HRMS:	Calcd.:	431.2069.		
		Found:	431.2027.		
$C_{30}H_{29}NSi$		Calcd.:	C, 83.48	H, 6.77	N, 3.24
		Found:	C, 83.64	H, 6.70	N, 3.16

Synthesis of 2-[2-(triphenylsilyl)ethyl]cyclohexanecarbonitrile (33b)



Prepared according to TP 5 from cyclohexanecarbonitrile (**1c**) (218 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and triphenylvinylsilane (**33a**) (573 mg, 2.0 mmol). Reaction time: 15 h at 40 °C. Purification by flash chromatography (25% CH_2Cl_2 in pentane) yielded **33b** (600 mg, 76 %) as a white solid.

Mp: 111.5-111.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49-7.25 (m, 15H), 1.98-1.88 (m, 2H), 1.70-1.43 (m, 9H), 1.14-0.97 (m, 3H).

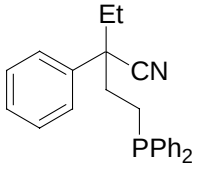
^{13}C NMR (75 MHz, $CDCl_3$): δ 135.9, 134.7, 130.0, 128.4, 124.0, 41.4, 35.6, 35.3, 25.9, 23.5, 8.2.

IR (KBr, cm^{-1}): 2232, 1448, 1428, 1111, 737, 715.

MS (EI, 70 eV): 395 (M^+, 0.1), 367 (14), 299 (17), 259 (100), 181 (12).

$C_{27}H_{29}NSi$	Calcd.:	C, 81.97	H, 7.39	N, 3.54
	Found:	C, 82.04	H, 7.33	N, 3.40

Synthesis of 4-diphenylphosphanyl-2-ethyl-2-phenylbutyronitrile (33c)



Prepared according to TP 5 from 2-phenylbutyronitrile (**1a**) (44 mg, 3.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and diphenylvinylphosphine (**32b**) (424 mg, 2.0 mmol). Reaction time: 1 h at 25 °C. Purification by flash chromatography (2% Et_2O in pentane) gave **33c** (628 mg, 88 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.15 (m, 15H), 2.19-1.65 (m, 6H), 0.77 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2-137.6 (m), 133.4-132.7 (m), 129.3, 129.1, 129.0-128.9 (m), 128.2, 126.5, 122.3, 50.4 (d, *J* = 13.2 Hz), 37.2 (d, *J* = 21.0 Hz), 34.6, 23.7 (d, *J* = 12.0 Hz), 10.1.

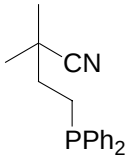
^{31}P NMR (81 MHz) δ -15.4.

IR (KBr, cm^{-1}): 2236, 1493, 1481, 1433, 1096, 1027, 740.

MS (EI, 70 eV): 357 (M^+, 21), 342 (13), 275 (100), 224 (21), 183 (38).

$C_{24}H_{24}NP$	HRMS:	Calcd.:	357.1646.		
		Found:	357.1660.		
$C_{24}H_{24}NP$		Calcd.:	C, 80.65	H, 6.77	N, 3.92
		Found:	C, 80.64	H, 6.83	N, 3.90

Synthesis of 4-diphenylphosphanyl-2,2-dimethylbutyronitrile (33d)



Prepared according to TP 5 from isobutyronitrile (**1b**) (207 mg, 3.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and diphenylvinylphosphine (**32b**) (424 mg, 2.0 mmol). Reaction time: 1 h at 25 °C. Purification by flash chromatography (5% Et_2O in pentane) yielded **33d** (455 mg, 81 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.02 (m, 10H), 2.19-2.09 (m, 2H), 1.59-1.49 (m, 2H), 1.24 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9 (d, *J* = 18.0 Hz), 129.3, 129.0, 128.9, 125, 37.7 (d, *J* = 19.6 Hz), 33.6 (d, *J* = 13.7 Hz), 26.8, 24.0 (d, *J* = 12.3 Hz).

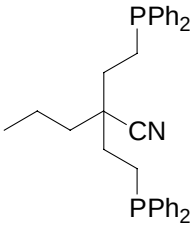
^{31}P NMR (81 MHz) δ –15.0.

IR (KBr, cm^{-1}): 2233, 1481, 1470, 1433, 739, 697.

MS (EI, 70 eV): 281 (M^+, 58.5), 266 (3), 225 (100), 182 (54), 152 (6), 108 (14).

$C_{18}H_{20}NP$	HRMS:	Calcd.:	281.1333.		
		Found:	281.1323.		
$C_{18}H_{20}NP$		Calcd.:	C, 76.85	H, 7.17	N, 4.98
		Found:	C, 76.95	H, 7.14	N, 5.00

Synthesis of 2,2-bis[2-(diphenylphosphino)ethyl]pentanenitrile (33e)



Prepared according to TP 5 from pentanenitrile (**1e**) (498 mg, 6.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (3 mL) and diphenylvinylphosphine (**32b**) (424 mg, 2.0 mmol). Reaction time: 1 h at 25 °C. Purification by flash chromatography (2% Et_2O in pentane) furnished the nitrile **33e** (811 mg, 80 %) as a white solid.

Mp: 113-114 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.21 (m, 20H), 1.95-1.85 (m, 4H), 1.62-1.50 (m, 4H), 1.46-1.36 (m, 2H), 1.24-1.10 (m, 2H), 0.80 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.1-137.8 (m), 133.2 (d, J = 2.2 Hz), 132.9 (d, J = 2.2 Hz), 129.3, 129.0 (d, J = 6.8 Hz), 123.7, 42.6, 38.2, 32.2, 31.9, 22.9, 22.8, 17.9, 14.4.

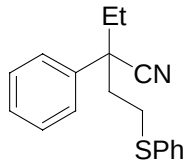
^{13}P NMR (81 MHz) δ –14.8.

IR (KBr, cm^{-1}): 2232, 1480, 1433, 739.

MS (EI, 70 eV): 507 (M^+, 14), 464 (100), 225 (100), 182 (54).

$C_{33}H_{35}NP_2$	HRMS:	Calcd.:	507.2245.		
		Found:	507.2234.		
$C_{33}H_{35}NP_2$		Calcd.:	C, 78.09	H, 6.95	N, 2.76
		Found:	C, 77.77	H, 6.90	N, 2.64

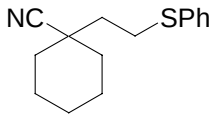
Synthesis of 2-ethyl-2-phenyl-4-(phenylsulfanyl)butyronitrile (33f)



Prepared according to TP 5 from 2-phenylbutyronitrile (**1a**) (145 mg, 1.0 mmol), *t*-BuOK (23 mg, 0.2 mmol) in DMSO (2 mL) and phenyl vinyl sulfide (**32c**) (136 mg, 1.0 mmol). Reaction time: 4 h at 25 °C. Purification by flash chromatography (30% CH_2Cl_2 in pentane) yielded **33f** (278 mg, 78 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.10 (m, 10H), 2.30 (ddd, *J* = 13.7, 12.3, 4.6 Hz, 1H), 2.55 (ddd, *J* = 13.7, 12.3, 4.6 Hz, 1H), 2.08-1.83 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 137.1, 135.2, 129.1, 129.0, 128.1, 126.2, 126.0, 121.6, 48.8, 40.2, 34.3, 28.8, 9.5.
IR (KBr, cm^{-1}): 2236, 1583, 1481, 1449, 1439, 1086, 1025, 759, 700.
MS (EI, 70 eV): 281 (M^+, 53), 137 (100), 109 (26).
$C_{18}H_{19}NS$ HRMS: Calcd.: 357.1646.
Found: 357.1660.

Synthesis of 1-[2-(phenylsulfanyl)ethyl]cyclohexanecarbonitrile (33g)



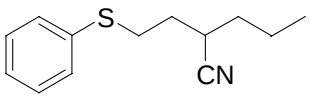
Prepared according to TP 5 from cyclohexanecarbonitrile (**1c**) (110 mg, 1.0 mmol), *t*-BuOK (23 mg, 0.2 mmol) in DMSO (2 mL) and phenyl vinyl sulfide (**32c**) (136 mg, 1.0 mmol). Reaction time: 2 h at 25 °C. Purification by flash chromatography (30% CH_2Cl_2 in pentane) gave **33g** (184 mg, 75 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.19 (m, 5H), 3.14-3.05 (m, 2H), 2.06-1.55 (m, 9H), 1.33-1.11 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 135.8, 129.7, 129.5, 126.7, 123.3, 40.4, 39.4, 35.9, 28.9, 25.7, 23.3.
IR (KBr, cm^{-1}): 2231, 1583, 1481, 1451, 1440, 1089, 1025, 739.

MS (EI, 70 eV): 246 ([M+H]$^+$, 16), 168 (2), 137 (52), 123 (41), 110 (35), 109 (22).

$C_{15}H_{19}NS$ HRMS: Calcd.: 245.1238.
Found: 245.1244.

Synthesis of 2-[2-(phenylsulfanyl)ethyl]pentanenitrile (33h)

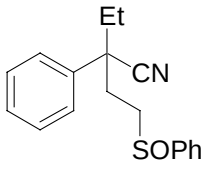


Prepared according to TP 5 from pentanenitrile (**1e**) (2.74 g, 33.0 mmol), *t*-BuOK (224 mg, 2.0 mmol) in DMSO (2.0 mL) and phenyl vinyl sulfide (**32c**) (1.36 g, 10.0 mmol). Reaction time: 16 h at 70 °C. Purification by flash chromatography (2% Et_2O in pentane) furnished **33h** (1.31 g, 60 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32-7.10 (m, 5H), 3.12-3.00 (m, 1H), 2.97-2.80 (m, 1H), 2.77-2.64 (m, 1H), 1.93-1.66 (m, 2H), 1.60-1.30 (m, 4H), 0.85 (t, *J* = 7 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 135.5, 130.3, 129.5, 127.0, 122.0, 34.4, 32.1, 31.7, 30.6, 20.7, 13.9.
IR (KBr, cm^{-1}): 2237, 1583, 1481, 1439, 1091, 1025, 740.
MS (EI, 70 eV): 220 ([M+H]$^+$, 14), 219 (M$^+$, 100), 124 (48), 110 (29), 109 (13).

$C_{13}H_{17}NS$	HRMS:	Calcd.:	219.1082.			
		Found:	219.1084.			
$C_{13}H_{17}NS$		Calcd.:	C, 71.18	H, 7.81	N, 6.39	S, 14.62
		Found:	C, 71.20	H, 7.85	N, 6.26	S, 14.60

Synthesis of 2-ethyl-2-phenyl-4-(phenylsulfinyl)butyronitrile (33i)



Prepared according to TP 5 from 2-phenylbutyronitrile (**1a**) (436 mg, 3.0 mmol), *t*-BuOK (224 mg, 2.0 mmol) in DMSO (2.0 mL) and phenyl vinyl sulfoxide (**32d**) (304 mg, 2.0 mmol). Reaction time: 1 h at 40 °C. Purification by flash chromatography (20% CH_2Cl_2 in pentane) yielded **33i** (487 mg, 82 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.13 (m, 10H), 2.80-2.26 (m, 3H), 2.17-1.77 (m, 3H), 0.80 (dt, *J* = 12.2, 7.4 Hz, 3H).

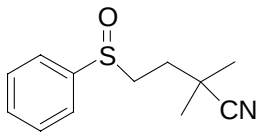
^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 143.1, 136.9, 131.5, 131.4, 129.7, 129.6, 129.5, 128.6, 128.5, 126.3, 126.2, 124.3, 124.2, 121.6, 52.3, 51.7, 48.5, 35, 34.8, 32.7, 31.9.

IR (KBr, cm^{-1}): 2236, 1494, 1444, 1086, 1046, 749.

MS (EI, 70 eV): 297 ($[M+H]^+$, 3), 297 (10), 280 (100), 144 (62), 126 (92), 116 (74), 105 (24), 91 (87), 77 (37).

$C_{18}H_{19}SON$ HRMS: Calcd.: 297.1187.
Found: 297.1205.

Synthesis of 2,2-dimethyl-4-(phenylsulfinyl)butyronitrile (33j)



Prepared according to TP 5 from isobutyronitrile (**1b**) (207 mg, 3.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and phenyl vinyl sulfoxide (**32d**) (304 mg, 2.0 mmol). Reaction time: 16 h at 40 °C. Purification by flash chromatography (Et_2O) yielded **33j** (309 mg, 70 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70-7.50 (m, 5H), 3.12-3.00 (m, 1H), 2.92-2.81 (m, 1H), 2.09-1.98 (m, 1H), 1.85-1.73 (m, 1H), 1.40 (s, 3H), 1.34 (s, 3H).

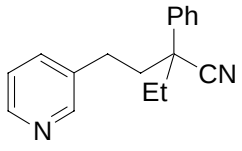
^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 131.6, 129.8, 124.3, 124.2, 52.6, 33.0, 32.2, 27.0, 26.8.

IR (KBr, cm^{-1}): 2234, 1475, 1444, 1086, 1045, 750.

MS (EI, 70 eV): 221 (M^+, 17), 204 (19), 126 (100), 125 (48), 109 (10), 97 (10), 78 (43).

$C_{12}H_{15}NOS$ HRMS: Calcd.: 221.0874.
Found: 221.0866.

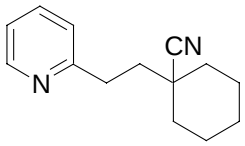
Synthesis of 2-ethyl-2-phenyl-4-(3-pyridinyl)butyronitrile (33k)



Prepared according to TP 5 from 2-phenylbutyronitrile (**1a**) (218 mg, 2.0 mmol), *t*-BuOK (34 mg, 0.3 mmol) in DMSO (1.5 mL) and 2-vinylpyridine (**32e**) (210 mg, 1.5 mmol). Reaction time: 1 h at 25 °C. Purification by flash chromatography (20% CH_2Cl_2 in pentane) yielded **33k** (293 mg, 78 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (m, 1H), 8.26 (m, 1H), 7.45-7.22 (m, 6H), 7.14-7.05 (m, 1H), 2.70-2.63 (m, 1H), 2.39-1.80 (m, 5H), 0.85 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 150.0, 148.1, 137.9, 136.4, 136.1, 129.5, 128.4, 126.3, 123.8, 122.3, 49.4, 42.6, 34.7, 29.4, 10.0.
IR (KBr, cm^{-1}): 1576, 1494, 1480, 1449, 1424, 1028, 762, 716, 702.
MS (EI, 70 eV): 250 (M^+, 67.2), 235 (1.8), 144 (10), 106 (100), 92 (38).
$C_{17}H_{18}N_2$ HRMS: Calcd.: 250.1470.
Found: 250.1454.

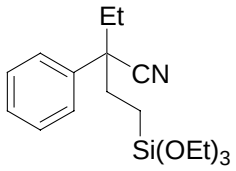
Synthesis of 1-[2-(2-pyridinyl)ethyl]cyclohexanecarbonitrile (33l)



Prepared according to TP 5 from cyclohexanecarbonitrile (**1c**) (328 mg, 3.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and 3-vinylpyridine (**32e**) (210 mg, 2.0 mmol). Reaction time: 15 h at 60 °C. Purification by flash chromatography (30% Et_2O in pentane) yielded **33l** (240 mg, 56 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41-8.37 (m, 2H), 7.47-7.43 (m, 1H), 7.16 (m, 1H), 2.80-2.70 (m, 2H), 2.05-1.90 (m, 2H), 1.80-1.45 (m, 7H), 1.30-1.05 (m, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 150.1, 148.1, 136.8, 136.3, 123.9, 123.6, 42.5, 39.5, 36.1, 28.5, 25.7, 23.4.
IR (KBr, cm^{-1}): 2934, 2859, 2230, 1576, 1479, 1452, 1424, 716.
MS (EI, 70 eV): 214 (M^+, 32), 159 (48), 106 (100), 92 (43), 77 (8), 65 (20).
$C_{14}H_{18}N_2$ HRMS: Calcd.: 214.1470.
Found: 214.1466.

Synthesis of 2-ethyl-2-phenyl-4-(triethoxysilyl)butyronitrile (33m)



Prepared according to TP 6 from 2-phenylbutyronitrile (**1a**) (290 mg, 2.0 mmol), EtOK (33 mg, 0.4 mmol) in NMP (2 mL) and triethoxyvinylsilane (**32f**) (571 mg, 3.0 mmol). Reaction time: 15 h at 25 °C. Purification by flash chromatography (0.5% Et_2O in pentane) yielded **33m** (576 mg, 86 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.18 (m, 5H), 3.68 (q, *J* = 7.0 Hz, 6H), 2.08-1.75 (m, 4H), 1.11 (t, *J* = 7.0 Hz, 9H), 0.83 (t, *J* = 7.4 Hz, 3H), 0.71 (dd, *J* = 14.0, 4.4 Hz), 1H), 0.34 (dd, *J* = 14.0, 4.4 Hz, 1H).

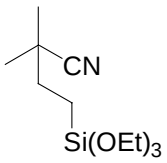
^{13}C NMR (75 MHz, $CDCl_3$): δ 138.3, 129.1, 127.9, 126.6, 122.5, 58.7, 51.4, 34.7, 34, 18.6, 10.1, 6.4.

IR (KBr, cm^{-1}): 2236, 1494, 1449, 1390, 1166, 1102, 1079, 962, 762, 701.

MS (EI, 70 eV): 335 (M^+, 0.2), 307 (14), 292 (10), 263 (2), 163 (100), 135 (13), 119 (47).

$C_{18}H_{29}NO_3Si$ HRMS: Calcd: 335.1917.
Found: 335.1915.

Synthesis of 2,2-dimethyl-4-(triethoxysilyl)butyronitrile (33n)



Prepared according to TP 6 from isobutyronitrile (**1b**) (1.38 g, 20.0 mmol), EtOK (0.25 g, 3.0 mmol) in NMP (15 mL) and triethoxyvinylsilane (**32f**) (2.85 g, 15.0 mmol). Reaction time: 15 h at 40 °C. The resulting oil was distilled under reduced pressure to yield **33n** (3.30 g, 85 %) as a colourless oil.

Bp: 65 °C (2.9×10^{-5} mmbar).

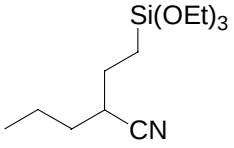
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.67 (q, *J* = 7.0 Hz, 6H), 1.54-1.45 (m, 2H), 1.17 (s, 6H), 1.08 (t, *J* = 7.0 Hz, 9H), 0.67-0.57 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 125.2, 58.8, 34.9, 34.4, 26.3, 18.6, 6.5.

IR (KBr, cm^{-1}): 2234, 1471, 1391, 1369, 1197, 1167, 1908, 962, 780.

$C_{12}H_{25}NO_3Si$	Calcd.:	C, 55.56	H, 9.71	N, 5.40
	Found:	C, 55.82	H, 10.13	N, 5.66

Synthesis of 2-[2-(triethoxysilyl)ethyl]pentanenitrile (33o)



Prepared according to TP 6 from pentanenitrile (**1e**) (3.33 g, 40.0 mmol), EtOK (337 mg, 4.0 mmol) in NMP (20 mL) and triethoxyvinylsilane (**32f**) (3.81 g, 20.0 mmol). Reaction time: 15 h at 40 °C. The resulting oil was distilled under reduced pressure to provide **33o** (3.55 g, 65 %) as a colourless oil

Bp: 81 °C (0.5 mmHg).

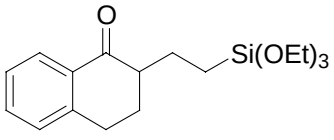
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (q, *J* = 7.0 Hz, 6H), 2.55-2.43 (m, 1H), 1.70-1.30 (m, 6H), 1.16 (t, *J* = 7.0 Hz, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.85-0.74 (m, 1H), 0.70-0.58 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 122.6, 58.8, 34.5, 34.2, 26.4, 20.7, 18.6, 13.9, 8.6.

IR (KBr, cm^{-1}): 2237, 1390, 1167, 1103, 1081, 960, 790.

$C_{13}H_{27}NO_3Si$	Calcd.:	C, 57.10	H, 9.95	N, 5.12
	Found:	C, 57.40	H, 10.32	N, 5.38

Synthesis of 2-[2-(triethoxysilyl)ethyl]-3,4-dihydro-1(2*H*)-naphthalenone (33p)



Prepared according to TP 6 from *α*-tetralone (**2a**) (5.84 g, 40 mmol), EtOK (337 mg, 4.0 mmol) in NMP (20 mL) and triethoxyvinylsilane (**32f**) (3.81 g, 20 mmol). Reaction time: 15 h at 40 °C. The resulting oil was distilled under reduced pressure to yield **33p** (4.37 g, 65 %) as a pale yellow oil.

Bp: 130 °C (9 x 10^{-5} mbar).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (m, 1H), 7.40-7.00 (m, 3H), 3.76 (q, *J* = 7.1 Hz, 6H), 3.00-2.80 (m, 2H), 2.45-2.30 (m, 1H), 2.25-2.10 (m, 1H), 2.08-1.75 (m, 2H), 1.67-1.50 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 9H), 0.75-0.60 (m, 2H).

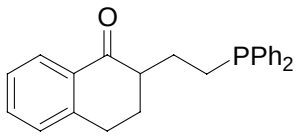
^{13}C NMR (75 MHz, $CDCl_3$): δ 200.5, 49.9, 133.4, 133.0, 129.0, 127.7, 126.8, 58.7, 49.9, 28.7, 28.1, 23.1, 18.6, 7.9.

IR (KBr, cm^{-1}): 1683, 1601, 1454, 1390, 1293, 1225, 1167, 1103, 1079, 958.

MS (EI, 70 eV): 336 (M^+, 2), 308 (7), 291 (32), 261 (8), 146 (100).

$C_{18}H_{28}O_4Si$ HRMS: Calcd.: 336.1757.
Found: 336.1741.

Synthesis of 2-[2-(diphenylphosphino)ethyl]-3,4-dihydro-1(2*H*)-naphthalenone (34a)



Prepared according to TP 7 from *α*-tetralone (**2a**) (877 mg, 6.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and diphenylvinylphosphine (**32b**) (424 mg, 2.0 mmol). Reaction time: 15 h at 40 °C. Purification by flash chromatography (5% Et_2O in pentane) yielded **34a** (573 mg, 80 %) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (m, 1H), 7.45-7.05 (m, 13H), 2.95-2.80 (m, 2H), 2.60-2.45 (m, 1H), 2.20-1.50 (m, 6H).

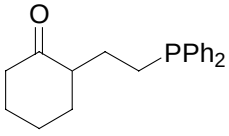
^{13}C NMR (75 MHz, $CDCl_3$): δ 200.2, 138.8-138.5 (m), 133.2 (d, *J* = 18.5 Hz), 133.1 (d, *J* = 18.5 Hz), 129.1, 128.9 (d, *J* = 6.8 Hz), 127.8, 127.0, 48.7 (d, *J* = 7.0 Hz), 28.9, 28.8, 26.6 (d, *J* = 18.0 Hz), 25.7 (d, *J* = 11.0 Hz).

IR (KBr, cm^{-1}): 1681, 1600, 1454, 1433, 1226, 740.

MS (EI, 70 eV): 358 (M^+, 12), 329 (27), 199 (37), 183 (43), 108 (34).

$C_{24}H_{23}OP$ HRMS: Calcd.: 358.1487.
Found: 358.1483.

Synthesis of 2-[2-(diphenylphosphino)ethyl]cyclohexanone (34b)



Prepared according to TP 7 from cyclohexanone (**2b**) (588 mg, 6.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (2.0 mL) and diphenylvinylphosphine (**32b**) (424 mg, 2.0 mmol). Reaction time: 15 h at 40 °C. Purification by flash chromatography (5% Et_2O in pentane) furnished **34b** (403 mg, 65 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.00 (m, 10 H), 2.50-1.00 (m, 13 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 213.3, 139.2-138.8 (m), 133.2 (d, J = 5.6 Hz), 133.2 (d, J = 5.6 Hz), 128.9-128.7 (m), 52.0 (d, J = 12.6 Hz), 42.5, 34.4, 28.4, 26.4 (d, J = 17.3 Hz), 26.0 (d, J = 11.0 Hz), 25.3.

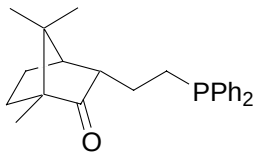
^{13}P NMR (81 MHz) δ -15.1.

IR (KBr, cm^{-1}): 1707, 1481, 1447, 1433, 1126, 740.

MS (EI, 70 eV): 310 (M^+, 68), 281 (84), 239 (19), 229 (29), 215 (40), (100), 182 (77).

$C_{20}H_{23}OP$ HRMS: Calcd.: 310.1487.
Found: 310.1460.

Synthesis of 3-[2-(diphenylphosphino)ethyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (34c)



Prepared according to TP 7 from (+)-camphor (**2c**) (1.21 g, 8.0 mmol),), *t*-BuOK (44 mg, 0.4 mmol) in DMSO (3.0 mL) and diphenylvinylphosphine (**32b**) (424 mg, 2.0 mmol). Reaction time: 15 h at 40 °C. Purification by flash chromatography (pentane) yielded **34c** (514 mg, 72 %) as a white solid.

Mp: 80-82 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.20 (m, 10H), 2.44-2.35 (m, 1H), 2.22-1.76 (m, 4H), 1.68-1.48 (m, 2H), 1.40-1.08 (m, 3H), 0.90 (s, 3H), 0.79 (s, 3H), 0.76 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 221.2, 138.9-138.7 (m), 133.3-132.9 (m), 129.1-128.8 (m), 59.1, 50.9 (d, J = 12.5 Hz), 46.5, 46.1, 31.4, 26.8 (d, J = 11.3 Hz), 24.1 (d, J = 18.0 Hz), 20.4, 19.7 (d, J = 15.5 Hz), 9.92.

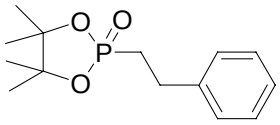
^{13}P NMR (81 MHz) δ -15.6.

IR (KBr, cm^{-1}): 1738, 1482, 1434, 1094, 1043, 740.

$C_{24}H_{29}OP$ Calcd.: C, 79.33 H, 8.26
Found: C, 78.93 H, 8.07

5 Hydrophosphination of functionalized alkenes

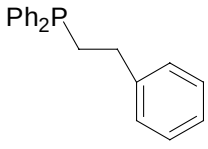
Synthesis of 4,4,5,5-tetramethyl-2-(2-phenylethyl)-1,3,2-dioxaphospholane 2-oxide (39)



Prepared according to TP 8 from 4,4,5,5-tetramethyl-[1,3,2]dioxaphospholane 2-oxide (**38**) (328 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2.0 mL) and styrene (**4a**) (208 mg, 2.0 mmol). Reaction time: 15 h at 60 °C. Purification by flash chromatography (65% Et_2O in pentane) yielded **39** (467 mg, 87 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.10 (m, 5H), 3.02-2.90 (m, 2H), 2.16-2.02 (m, 2H), 1.43 (s, 6H), 1.27 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3 (d, J = 18.2 Hz), 128.9, 128.4, 126.7, 88.4, 30.5 (d, J = 130.6 Hz), 29.3 (d, J = 4.1 Hz), 25.1 (d, J = 3.8 Hz), 24.4 (d, J = 5.2 Hz).
^{31}P NMR (81 MHz): δ 43.6.
IR (KBr, cm^{-1}): 1454, 1376, 1257, 1137, 962, 931, 875.
MS (EI, 70 eV): 268 (M^+, 48.6), 253 (3.3), 186 (78.3), 104 (100), 91 (10), 84 (73.7).
$C_{14}H_{21}O_3P$ HRMS: Calcd.: 268.1228.
Found: 268.1234.

Synthesis of diphenyl(2-phenylethyl)phosphine (36a)



Prepared according to TP 8 from Ph_2PH (**35a**) (522 mg, 3.0 mmol), *t*-BuOK (67 mg, 0.6 mmol) in DMSO (3 mL) and styrene (**4a**) (430 mg, 3.0 mmol). Reaction time: 60 °C for 15 h. Purification by flash chromatography (pentane) yielded **36a** (722 mg, 83 %) as a pale yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.00 (m, 15H), 2.70-2.55 (m, 2H), 2.40-2.20 (m ,2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 143.0 (d, *J* = 13.5 Hz), 138.4 (d, *J* = 15.0 Hz), 133.1 (d, *J* = 15.0 Hz), 129.2-128.6 (m), 126.5, 32.5 (d, *J* = 22.5 Hz), 30.5 (d, *J* = 15 Hz).

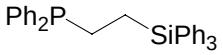
^{31}P NMR (81 MHz) δ -14.7.

IR (KBr, cm^{-1}): 1495, 1480, 1453, 1433, 1027, 737.

MS (EI, 70 eV): 290 (M^+, 49.6), 289 (100), 262 (31.2), 199 (23.2), 183 (23.2), 121 (37.8), 108 (3.9).

$C_{20}H_{19}P$ HRMS: Calcd.: 290.1224.
Found: 290.1200.

Synthesis of diphenyl[2-(triphenylsilyl)ethyl]phosphine (36b)



Prepared according to TP 8 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and triphenylvinylsilane (**32a**) (573 mg, 2.0 mmol). Reaction time: 25 °C for 1 h. Purification by flash chromatography (15% CH_2Cl_2 in pentane) yielded **36b** (831 mg, 88 %) as a white solid.

Mp: 132-133 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57-7.30 (m, 25 H), 2.26-2.16 (m, 2 H), 1.57-1.45 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.4 (d, *J* = 15.0 Hz), 136.1, 134.9, 133.3 (d, *J* = 15.0 Hz), 129.9, 129.1, 128.8 (d, *J* = 7.5 Hz), 128.4, 21.8 (d, *J* = 12.6 Hz), 9.1 (d, *J* = 11.4 Hz).

^{31}P NMR (81 MHz) δ -7.5.

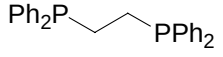
IR (KBr, cm^{-1}): 1480, 1148, 1110, 1026, 742, 712.

MS (EI, 70 eV): 472 (M^+, 35), 259 (100), 183 (13).

$C_{32}H_{29}PSi$ HRMS: Calcd.: 472.1776.
Found: 472.1762.

$C_{32}H_{29}PSi$ Calcd.: C, 81.32 H, 6.18
Found: C, 81.16 H, 6.20

Synthesis of [2-(diphenylphosphino)ethyl](diphenyl)phosphine (36c)



Prepared according to TP 8 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and diphenylvinylphosphine (**32b**) (424 mg, 2.0 mmol). Reaction time: 25 °C for 1 h. Water was added and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo.* The crude product was washed with cold pentane to give **36c** (716 mg, 90 %) as a white solid.

Mp: 139.5-141.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.30 (m, 20 H), 2.16 (t, *J* = 4.1 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5 (t, *J* = 6.6 Hz), 133.2 (t, *J* = 9.3 Hz), 129.1-128.8 (m), 24.3 (d, *J* = 2.6 Hz).

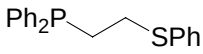
^{31}P NMR (81 MHz) δ -11.5.

IR (KBr, cm^{-1}): 1480, 1432, 1161, 1098, 1067, 1025, 740, 727.

MS (EI, 70 eV): 398 (M^+, 35), 370 (46), 289 (74), 262 (43), 183 (65).

$C_{26}H_{24}P_2$ HRMS: Calcd.: 398.1353.
Found: 398.1341.

Synthesis of diphenyl[2-(phenylsulfanyl)ethyl]phosphine (36d)



Prepared according to TP 8 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and phenyl vinyl sulfide (**32c**) (272 mg, 2.0 mmol). Reaction time: 25 °C for 1 h. Purification by flash chromatography (pentane) yielded **36d** (515 mg, 80 %) as a white solid.

Mp: 86.5-87.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.00 (m, 15 H), 2.95-2.80 (m, 2 H), 2.35-2.22 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.0 (d, *J* = 12.7 Hz), 136.3, 133.2 (d, *J* = 18.8 Hz), 129.8, 129.3 (d, *J* = 7.5 Hz), 129.1 (d, *J* = 7.5 Hz), 126.5, 30.6 (d, *J* = 15.0 Hz), 28.6 (d, *J* = 15.0 Hz).

^{13}P NMR (81 MHz) δ -16.0.

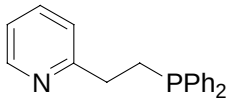
IR (KBr, cm^{-1}): 1480, 1434, 1254, 1091, 1023, 739.

MS (EI, 70 eV): 322 (M^+, 48), 289 (84), 262 (100), 245 (17.4), 185 (37).

$C_{20}H_{19}PS$ HRMS: Calcd.: 322.0945.
Found: 322.0933.

$C_{20}H_{19}PS$ Calcd.: C, 74.51 H, 5.94
Found: C, 74.65 H, 5.92

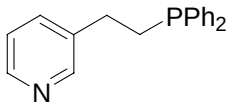
Synthesis of 2-[2-(diphenylphosphino)ethyl]pyridine (36e)



Prepared according to TP 8 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and 2-vinylpyridine (**32g**) (315 mg, 3.0 mmol). Reaction time: 25 °C for 1 h. Purification by flash chromatography (30% Et_2O in pentane) yielded **36e** (378 mg, 65 %) as a white solid.

Mp: 58.8-60 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.45-8.35 (m, 1H), 7.44-7.16 (m, 11H), 6.98-6.90 (m, 2H), 2.86-2.73 (m, 2H), 2.47-2.35 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 162.1 (d, J = 13.4 Hz), 149.6, 138.8 (d, J = 13.1 Hz), 136.8, 133.3, 133.0, 129.0-128.8 (m), 123.1, 121.6, 34.9 (d, J = 17.8 Hz), 28.4 (d, J = 12.5 Hz).
^{31}P NMR (81 MHz) δ -19.6.
IR (KBr, cm^{-1}): 1592, 1567, 1471, 1433, 1152, 997, 740.
MS (EI, 70 eV): 291 (M^+, 10.6), 214 (100).
$C_{19}H_{18}NP$ HRMS: Calcd.: 291.1177.
Found: 291.1179.

Synthesis of 3-[2-(diphenylphosphino)ethyl]pyridine (36f)



Prepared according to TP 8 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and 3-vinylpyridine (**32e**) (210 mg, 2.0 mmol). Reaction time: 25 °C for 1 h. Purification by flash chromatography (50% Et_2O in pentane) yielded **36f** (367 mg, 63 %) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40-8.35 (m, 2H), 7.50-7.20 (m, 12H), 2.72-2.60 (m, 2H), 2.33-2.24 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 149.9, 147.7, 138.4, 138.3, 136.2, 133.1 (d, J = 18.7 Hz), 129.2, 128.9 (d, J = 6.4 Hz), 123.8, 30.2 (d, J = 13.7 Hz), 29.5 (d, J = 18.0 Hz).

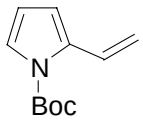
^{31}P NMR (81 MHz) δ -15.3.

IR (KBr, cm^{-1}): 1574, 1479, 1433, 1423, 1190, 1096, 1026, 794, 739, 712.

MS (EI, 70 eV): 290 ($[M-H]^+$, 100), 277 (4.7), 263 (18.7), 214 (4), 199 (24.7), 183 (30.8), 121 (36.2).

$C_{19}H_{18}NP$ HRMS: Calcd.: 291.1177.
Found: 291.1168.

Synthesis of *tert*-butyl 2-vinyl-1*H*-pyrrole-1-carboxylate (32h)[134]

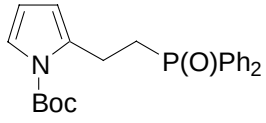


Methyltriphenylphosphonium bromide (8.57 g, 24.0 mmol) was suspended in THF (100 mL). The mixture was cooled to 0 °C and treated with *n*-BuLi (15 mL, 1.5 M in hexane, 22 mmol). After stirring at 0 °C for 1 h, the mixture was cooled to –78 °C, and *tert*-butyl 2-formyl-1*H*-pyrrole-1-carboxylate[94] (3.90 g, 20.0 mmol) in THF (20 mL) was added. After additional stirring at –78 °C for 15 min, the mixture was allowed to warm up to rt and was stirred for 3 h. The mixture was diluted with H_2O and extracted with Et_2O. The combined organic extracts were washed with H_2O, brine and dried over $MgSO_4$. The crude product was purified by flash chromatography (2% Et_2O in pentane) to furnish **32h** (2.51 g 65 %) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20-7.10 (m, 2H), 6.40-6.30 (m, 1H), 6.05 (t, J = 3.3 Hz, 1H), 5.44 (dd, J = 17.6, 1.6 Hz, 1H), 5.03 (dd, J = 11.1, 1.6 Hz, 1H), 1.52 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 134.9, 124.8, 122.2, 113.7, 111.2, 111.1, 28.4.

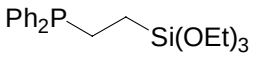
Synthesis of *tert*-butyl 2-[2-(diphenylphosphoryl)ethyl]-1*H*-pyrrole-1-carboxylate (36g)



Prepared according to TP 8 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and 2-vinyl-pyrrole-1-carboxylic acid *tert*-butyl ester (**32h**) (386 mg, 2.0 mmol) After stirring at 25 °C for 1 h, 30 % H_2O_2 was added at 0 °C and warmed up to 25 °C for 30 min. Purification by flash chromatography (33% CH_2Cl_2 in pentane) yielded **36g** (537 mg, 68 %) as a yellow foam.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77-7.65 (m, 4H), 7.50-7.32 (m, 6H), 7.04 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.98-5.86 (m, 2H), 3.15-3.03 (m, 2H), 2.64-2.50 (m, 2H), 1.46 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 149.6, 134.8 (d, *J* = 17.8 Hz), 133.1 (d, *J* = 98.0 Hz), 132.5, 132.1 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 9.3 Hz), 129.0 (d, *J* = 11.7 Hz), 121.6, 112.0, 110.4, 84.0, 29.8 (d, *J* = 70.3 Hz), 28.3, 21.7.
^{31}P NMR (81 MHz) δ 34.0.
IR (KBr, cm^{-1}): 1738, 1493, 1437, 1334, 1118, 1064, 997, 847, 723.
MS (EI, 70 eV): 395 (M^+, 15), 322 (9), 295 (68), 202 (100).
$C_{23}H_{26}NO_3P$ HRMS: Calcd.: 395.1650.
Found: 395.1659.

Synthesis of diphenyl[2-(triethoxysilyl)ethyl]phosphine (36h)



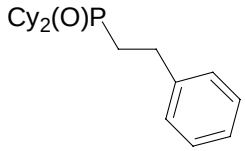
Prepared according to TP 8 from Ph_2PH (**35a**) (3.72 g, 20.0 mmol), EtOK (337 mg, 4.0 mmol) in NMP (20 mL) and triethoxyvinylsilane (**32f**) (3.80 g, 20.0 mmol). Reaction time: 25 °C for 1 h. The resulting oil was distilled under reduced pressure yielded **36h** (6.09 g, 81 %) as a colourless oil

Bp: 150 °C ($150x10^{-5}$ mbar).
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.12 (m, 10 H), 3.65 (q, *J* = 7 Hz, 6 H), 2.05-1.95 (m, 2 H), 1.07 (t, *J* = 7.1 Hz, 9H), 0.65-0.5 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 139.1 (d, *J* = 14 Hz), 133.2 (d, *J* = 18.1 Hz), 128.9-128.7 (m), 58.9, 20.9 (d, *J* = 13.4 Hz), 18.7, 6.5 (d, *J* = 11.7 Hz).
^{31}P NMR (81 MHz) δ -8.0.
IR (KBr, cm^{-1}): 1481, 1434, 1389, 1260, 1165, 1102, 1079, 958, 773, 740.

MS (EI, 70 eV): 376 (M^+, 38), 347 (6), 271 (7), 186 (79.1), 163 (100) 135 (9), 119 (20), 108 (16).

$C_{20}H_{29}O_3PSi$ HRMS: Calcd.: 376.1606.
Found: 376.1624.

Synthesis of dicyclohexyl(2-phenylethyl)phosphine oxide (37)



Prepared according to TP 8 from dicyclohexylphosphine (**35b**) (397 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and styrene (**4a**) (208 mg, 2.0 mmol). Reaction time: 25 °C for 16 h. Purification by flash chromatography (Et_2O) yielded **37** (464 mg, 73 %) as a white solid.

Mp: 62-68 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.10 (m, 5H), 2.95-2.80 (m, 2H), 2.00-1.00 (m, 24H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2 (d, J = 12.8 Hz), 128.9, 128.3, 126.6, 36.8 (d, J = 67.5 Hz), 28.4 (d, J = 3.5 Hz), 27.0 (d, J = 2.1 Hz), 26.9 (d, J = 1.5 Hz), 26.4, 26.0 (d, J = 2.9 Hz), 25.6.

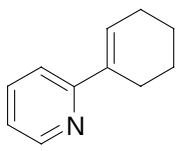
^{31}P NMR (81 MHz) δ 46.2.

IR (KBr, cm^{-1}): 1497, 1448, 1227, 1149, 890, 853, 773, 754, 706.

MS (EI, 70 eV): 319 ($[M+H]^+$, 31), 235 (75.8), 214 (100), 132 (46.8).

$C_{20}H_{31}OP$ HRMS: Calcd.: 318.2113.
Found: 318.2115.

Synthesis of 2-(1-cyclohexen-1-yl)pyridine (48)[95]

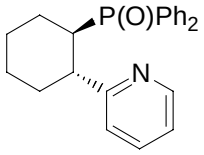


To 1-(2-pyridyl)cyclohexanol[95] (4.02 g, 22.7 mmol) was slowly added H_2SO_4 (5 mL, 90 mmol) with vigorous stirring at 0 °C. After stirring at 25 °C for 15 min, the solution was poured onto ice and neutralized with 50 % NaOH. The reaction mixture was extracted with

Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (5% Et_2O in pentane) gave **48** (2.53 g, 70 %) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.47 (m, 1H), 7.26-7.20 (m, 1H), 6.96 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 6.61-6.57 (m, 1H), 2.44-2.36 (m, 2H), 2.20-2.10 (m, 2H), 1.74-1.52 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4, 149.1, 136.9, 136.5, 128.8, 121.6, 119.2, 26.3, 26.2, 23.2, 22.5.
IR (KBr, cm^{-1}): 1643, 1584, 1564, 1467, 1432, 1277, 1153, 1136, 774, 751.
MS (EI, 70 eV): 159 (M^+, 100), 144 (57), 130 (57), 117 (18).

Synthesis of diphenyl[2-(2-pyridinyl)cyclohexyl]phosphine oxide (48)

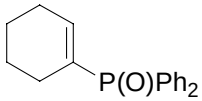


Prepared according to TP 8 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), and 2-(1-cyclohexen-1-yl)pyridine (**48**) (318 mg, 2.0 mmol). After stirring at 60 °C for 15 h, 30 % H_2O_2 was added at 0 °C and the mixture was allowed to warm up to 25 °C for 30 min. The crude product was washed with cold pentane to give **9** (361 mg, 50 %) as a white solid.

Mp: 132-143 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10-8.00 (m, 1H), 7.75-7.58 (m, 2H), 7.50-7.20 (m, 5H), 7.10-6.90 (m, 5H), 6.58-6.48 (m, 1H), 3.30-3.15 (m, 1H), 3.10-2.85 (m, 1H), 1.80-1.50 (m, 6H), 1.45-1.25 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 162.8, 149.2, 136.1, 134.6-133.4 (m), 131.2 (d, *J* = 2.6 Hz), 130.8 (d, *J* = 8.8 Hz), 130.3 (d, *J* = 2.6 Hz), 128.7 (d, *J* = 11.0 Hz), 127.9 (d, *J* = 11.0 Hz), 124.7, 121.8, 45.1 (d, *J* = 3.2 Hz), 39.8 (d, *J* = 71.0 Hz), 34.4 (d, *J* = 10.8 Hz), 26.2-25.9 (m).
^{31}P NMR (81 MHz) δ 32.8.
IR (KBr, cm^{-1}): 1589, 1472, 1436, 1180, 1114, 1071, 740, 710.
MS (EI, 70 eV): 361 (M^+, 6.4), 284 (98), 201 (15), 160 (100).
$C_{23}H_{24}NOP$ HRMS: Calcd.: 361.1596.
Found: 361.1584.
$C_{23}H_{24}NOP$ Calcd.: C, 76.43 H, 6.69 N, 3.88

Found: C, 76.08 H, 6.77 N, 3.72

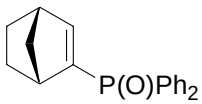
Synthesis of 1-cyclohexen-1-yl(diphenyl)phosphine oxide (49)[124]



Prepared according to TP 10 from 1-cyclohexen-1-yl trifluoromethanesulfonate (**61c**)[104] (1.79 g, 7.8 mmol), Ph_2PH (**35a**) (1.45 g, 7.8 mmol), *i*-Pr_2NEt (4 mL, 23 mmol) in toluene (20 mL). $Pd(OAc)_2$ (90 mg, 0.4 mmol, 5.1 mol%), dppb (170 mg, 0.4 mmol, 5.1 mol%) in toluene (10 mL) were added and the mixture was stirred at 60 °C for 15 min. 30 % H_2O_2 was added and stirred at 25 °C for 15 min. Purification by flash chromatography (30% Et_2O in CH_2Cl_2) yielded **49** (1.58 g, 72 %) as a foam.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66-7.32 (m, 10H), 6.40-6.26 (m, 1H), 2.16-2.06 (m, 4H), 1.64-1.52 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7 (d, *J* = 8.4 Hz), 132.3 (d, *J* = 9.4 Hz), 132.1 (d, *J* = 98.8 Hz), 132.0 (d, *J* = 2.5 Hz), 131.9 (d, *J* = 101.3 Hz), 128.8 (d, *J* = 11.9 Hz), 26.7 (d, *J* = 14.3 Hz), 24.9 (d, *J* = 9.3 Hz), 22.5 (d, *J* = 8.3 Hz), 21.8.
^{31}P NMR (81 MHz): δ 30.2.

Synthesis of bicyclo[2.2.1]hept-2-en-2-yl(diphenyl)phosphine oxide (49)[124]



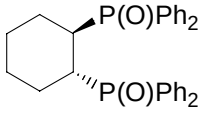
Prepared according to TP 10 from 1-cyclohexen-1-yl trifluoromethanesulfonate (**61d**)[104] (789 mg, 3.26 mmol), Ph_2PH (**35a**) (652 mg, 3.5 mmol), *i*-Pr_2NEt (1.74 mL, 10 mmol) in toluene (20 mL). $Pd(OAc)_2$ (36 mg, 0.16 mmol, 5 mol%), dppb (68 mg, 0.16 mmol, 5 mol%) in toluene (10 mL) were added and the mixture was stirred at 60 °C for 15 min. 30 % H_2O_2 was added and stirred at 25 °C for 15 min. Purification by flash chromatography (30% Et_2O in CH_2Cl_2) achieved **49** (617 mg, 60 %) as a foam.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.40 (m, 10H), 6.62 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.22 (s, 1H), 3.07 (s, 1H), 1.80-1.56 (m, 3H), 1.28 (m, 1H), 1.16-1.00 (m, 2H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 152.0 (d, *J* = 7.5 Hz), 141.1 (d, *J* = 103.8 Hz), 133.0-132.1 (m), 131.7-131.4 (m), 128.4-128.2 (m), 49.5 (d, *J* = 4.6 Hz), 44.3-44.1 (m), 24.9, 24.6 (d, *J* = 2.9 Hz).

^{31}P NMR (81 MHz): δ 23.8.

Synthesis of [2-(diphenylphosphoryl)cyclohexyl](diphenyl)phosphine oxide (50)



Prepared according to TP 8 from $Ph_2P(O)H$ (**46**) (323 mg, 1.6 mmol), *t*-BuOK (34 mg, 0.3 mmol) in DMSO (2 mL) and alkenylphosphine oxide **49** (479 mg, 1.7 mmol). Reaction time: 50 °C for 4 h. The crude product was washed with cold pentane to give **50** (689 mg, 89%) as a yellow solid.

Mp: 242-245 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70-7.20 (m, 20H), 2.75-2.3 (m, 4H), 2.00-1.65 (m, 4H), 1.60-1.40 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 133.6-132.4 (m), 132.0, 131.8, 131.4-131.3 (m), 129.2-129.0 (m), 32.9-31.2 (m), 23.3, 22.4.

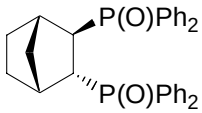
^{31}P NMR (81 MHz): δ 37.9.

IR (KBr, cm^{-1}): 2221, 1437, 1192, 1114, 724.

MS (EI, 70 eV): 485 ($[M+H]^+$, 3), 283 (100), 201 (60).

$C_{30}H_{30}O_2P$	HRMS:	Calcd.:	484.1721.		
		Found:	484.1778.		
$C_{30}H_{30}O_2P$		Calcd.:	C, 76.43	H, 6.69	N, 3.88
		Found:	C, 76.08	H, 6.77	N, 3.72

Synthesis of [3-(diphenylphosphoryl)bicyclo[2.2.1]hept-2-yl](diphenyl)phosphine oxide (52)



Prepared according to TP 8 from $Ph_2P(O)H$ (**46**) (202 mg, 1.0 mmol), *t*-BuOK (23 mg, 0.2 mmol) in DMSO (5 mL) and alkenylphosphine oxide **51** (294 mg, 1.0 mmol). The reaction mixture was stirred at 70 °C for 15 h. Purification by flash chromatography (33% Et_2O in CH_2Cl_2) yielded **52** (342 mg, 69 %) as a white solid.

Mp: 320-321 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.65 (m, 4H), 7.60-7.48 (m, 4H), 7.45-7.33 (m, 6H), 7.12-6.95 (m, 6H), 3.80-3.65 (m, 1H), 3.28 (dd, *J* = 15.3, 5.7 Hz, 1H), 2.50-2.00 (m, 4H), 1.75-1.40 (m, 2H), 1.26-1.10 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 135.8-132.0 (m), 131.6-130.5 (m), 128.9-128.5 (m), 41.4, 40.2 (d, *J* = 54.8 Hz), 39.7, 39.3 (d, *J* = 4.1 Hz), 38.3 (d, *J* = 3.8 Hz), 30.6 (d, *J* = 14.0 Hz), 26.0 (d, *J* = 5.5 Hz).

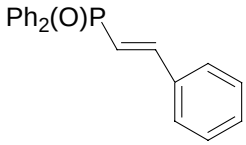
^{31}P NMR (81 MHz) δ 33.1 (d, *J* = 9.5 Hz), 30.2 (d, *J* = 9.5 Hz).

IR (KBr, cm^{-1}): 1437, 1180, 1115, 1071, 721, 700.

MS (EI, 70 eV): 496 (M^+, 6.4), 295 (100), 267 (9.4), 201 (50).

$C_{31}H_{30}O_2P_2$ HRMS: Calcd.: 496.1721.
Found: 496.1686.

Synthesis of diphenyl[(*E*)-2-phenylethenyl]phosphine oxide (54)



Prepared according to TP 4 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), *t*-BuOK (45 mg, 0.4 mmol) in DMSO (2 mL) and β-methoxystyrene (**29**) (805 mg, 6.0 mmol). After stirring at 25 °C for 15 h, 30 % H_2O_2 was added at 0 °C and warmed up to 25 °C for 30 min. Purification by flash chromatography (33% CH_2Cl_2 in pentane) yielded **54** (523 mg, 86 %) as a white solid.

Mp: 158-163 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83-7.70 (m, 4 H), 7.60-7.32 (m, 12H), 6.85 (dd, *J* = 22.0, 17.0 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.9 (d, *J* = 3.5 Hz), 135.4 (d, *J* = 17.8 Hz), 133.4 (d, *J* = 105.0 Hz), 132.2 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 10 Hz), 130.5, 129.5-128.9 (m), 119.7 (d, *J* = 105.0 Hz).

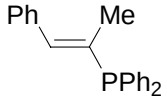
^{31}P NMR (81 MHz) δ 25.4.

IR (KBr, cm^{-1}): 1607, 1437, 1182, 1120, 999, 812, 742.

MS (EI, 70 eV): 304 (M^+, 100), 277 (3), 227 (28), 202 (52), 180 (31).

$C_{20}H_{17}OP$ HRMS: Calcd.: 304.1017.
Found: 304.1000.

Synthesis of diphenyl[(1*E*)-2-phenyl-1-propenyl]phosphine (56)



Prepared according to TP 4 from Ph_2PH (**35a**) (372 mg, 2.0 mmol), *t*-BuOK (44 mg, 0.4 mmol) in NMP (3.0 mL) and methyl 2-phenyl-2-propenyl ether (**26**) (148 mg, 1.0 mmol). Reaction time: 1 h at 25 °C. Purification by flash chromatography (pentane) yielded **56** (393 mg, 65 %) as a white solid.

Mp: 70-73 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.18 (m, 15H), 6.46-6.43 (m, 1H), 2.29 (t, *J* = 0.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 151.5 (d, *J* = 24.0 Hz), 143.1 (d, *J* = 7.0 Hz), 139.7 (d, *J* = 9.2 Hz), 133.1 (d, *J* = 18.8 Hz), 129.0-128.4 (m), 126.3, 20.0 (d, *J* = 24.0 Hz).

^{31}P NMR (81 MHz) δ -24.6.

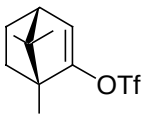
IR (KBr, cm^{-1}): 1478, 1432, 1025, 751, 738.

MS (EI, 70 eV): 301 ($[M-H]^+$, 100).

$C_{21}H_{19}P$ HRMS: Calcd.: 302.1224.
Found: 302.1224.

6 Synthesis of novel chiral P,N-ligands

Synthesis of (1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yltrifluoromethanesulfonate (61a)[103]



Prepared according to TP 9. A solution of (+)-camphor (1.52 g, 10 mmol) in THF (15 mL) was added to a solution of LDA (10 mmol) in THF (40 mL) at –78 °C and stirred for 1 h. A solution of *N*-phenyltrifluoromethanesulfonimide (**69**) (3.82 g, 10.7 mmol) in THF (20 mL) was then added, and the reaction was stirred at 0 °C for 14 h. The residue was purified by flash chromatography (pentane) to give **61a** (2.56 g, 90 %) as a colourless liquid.

$[\alpha]^{23}_{D}$: + 8.63 (*c* 1.07, $CHCl_3$).

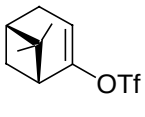
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.59 (d, *J* = 3.9 Hz, 1H), 2.37 (t, *J* = 3.9 Hz, 1H), 1.90-1.80 (m, 1H), 1.65-1.54 (m, 1H), 1.30-1.22 (m, 1H), 1.12-1-03 (m,1H), 0.95 (s, 3H), 0.85 (s, 3H), 0.71 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 118.9 (q, *J* = 318.0 Hz), 118.0, 57.3, 54.2, 50.5, 31.2, 25.7, 20.0, 19.3, 9.8.

IR (KBr, cm^{-1}): 1623, 1423, 1391, 1212, 1142, 1111.

MS (EI, 70 ev): 284 (M^+, 22), 151 (20), 123 (100), 95 (38), 81 (31), 55 (24).

Synthesis of (1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yltrifluoromethanesulfonate (61b)[143]



Prepared according to TP 9. A solution of (+)-nopinone (1.80 g, 13 mmol) in THF (20 mL) was added to a solution of LDA (13 mmol) in THF (50 mL) at –78 °C and stirred for 1 h. A solution of *N*-phenyltrifluoromethanesulfonimide (**69**) (5.00 g, 14 mmol) in THF (20 mL) was then added, and the reaction was stirred at 0 °C for 14 h. The residue was purified by flash chromatography (pentane) to give **61b** (3.23 g, 92 %) as a colourless liquid.

$[\alpha]^{26}_{D}$: +23.5 (*c* 0.545, $CHCl_3$).

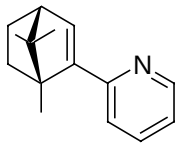
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.46 (m, 1H), 2.50-2.40 (m, 1H), 2.35-2.00 (m, 4H), 1.35-1.20 (m, 4H), 0.86 (s, 3H).

[143] L. R. Subramanian, H. Bentz, M. Hanack, *Synthesis* **1973**, 293.

^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4, 118.9 (q, *J* = 315.0 Hz), 111.8, 46.7, 40.5, 40.1, 32.1, 28.6, 25.9, 21.2.

IR (KBr, cm^{-1}): 1667, 1421, 1247, 1208, 1143, 1063, 1042.

Synthesis of 2-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]pyridine (63a)[109]



Prepared according to TP 11. A solution of *n*-BuLi (14 mL, 20 mmol) was added dropwise at –78 °C to a solution of 2-bromopyridine (**62a**) (3.16 g, 20 mmol) in THF (20 mL). The reaction mixture was stirred at –78 °C for 30 min, then a solution of $ZnBr_2$ (13 mL, 21 mmol) was added dropwise. After 15 min at –78 °C, the reaction mixture was allowed to warm up to rt for 30 min, the solution of the alkenyl triflate **61a** (2.84 g, 10 mmol), $Pd(dba)_2$ (0.12 g, 0.2 mmol), dppf (0.11 g, 0.2 mmol) in THF (10 mL) was added dropwise. The reacture mixture was refluxed (70 °C) for 15 h. The crude product was purified by flash chromatography (20% Et_2O in pentane), affording **63a** (1.66 g, 78 %) as a pale yellow liquid.

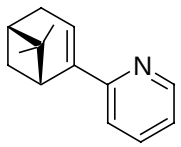
$[\alpha]^{27}_D$: -176.4 (*c* 1.825, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.48 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.20 (m, 1H), 6.97 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 6.26 (d, *J* = 3.3 Hz, 1H), 2.35 (t, *J* = 3.6 Hz, 1H), 1.92-1.82 (m, 1H), 1.68-1.56 (m, 1H), 1.40-1.28 (m, 1H), 1.17 (s, 3H), 1.08-0.96 (m, 1H), 0.81 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 157.8, 149.8, 149.4, 136.1, 135.9, 121.5, 121.3, 57.3, 55.3, 52.2, 32.1, 26.0, 20.1, 14.5, 12.8.

IR (KBr, cm^{-1}): 2953, 2872, 1583, 1560, 1464, 1430, 1385, 775.

Synthesis of 2-[(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]pyridine (63b)



Prepared according to TP 11. A solution of *n*-BuLi (4 mL, 6 mmol) was added dropwise at –78 °C to a solution of 2-bromopyridine (**62a**) (948 mg, 6 mmol) in THF (10 mL). The

reaction mixture was stirred at –78 °C for 30 min, then a solution of $ZnBr_2$ (4.2 mL, 7 mmol) was added dropwise. After 15 min at –78 °C, the reaction mixture was allowed to warm up to 25 °C for 30 min, the solution of the alkenyl triflate **61b** (810 mg, 3 mmol), $Pd(dba)_2$ (34.5 mg, 60 μmol), dppf (33.6 mg, 60 μmol) in THF (10 mL) was added dropwise. The reaction mixture was heated to reflux (70 °C) for 15 h. The crude product was purified by flash chromatography (5% Et_2O in pentane), affording **63a** (531 mg, 89 %) as a pale yellow liquid.

$[\alpha]^{23}_D$: -27.0 (*c* 0.725, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.46 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 7.48 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.32-7.25 (m, 1H), 6.97 (ddd, *J* = 7.5, 4.8, 0.9 Hz, 1H), 6.30-6.26 (m, 1H), 3.03-2.97 (m, 1H), 2.48-2.32 (m, 4H), 1.30 (s, 3H), 1.21 (d, *J* = 8.7 Hz, 1H), 0.79 (s, 3H).

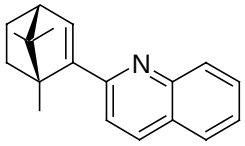
^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 149.4, 147.8, 136.4, 124.5, 121.6, 119.3, 43.2, 41.1, 38.2, 32.4, 31.9, 26.6, 21.3.

IR (KBr, cm^{-1}): 1624, 1585, 1562, 1432, 1465, 1365, 770.

MS (EI, 70 eV): 198 (M+, 47), 184 (100), 156 (14).

$C_{14}H_{17}N$ HRMS: Calcd.: 199.1361.
Found: 199.1388.

Synthesis of 2-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]quinoline (63c)



Prepared according to TP 11. To a solution of 2-iodoquinoline (**62b**) (2.55 g, 10 mmol) in THF (20 mL) was slowly added *i*-PrMgCl (9.4 mL, 1.38 M in THF, 13 mmol) at –20 °C. After 20 min at –20 °C. $ZnBr_2$ (8.2 mL, 1.7 M in THF, 14 mmol) was added dropwise and the mixture was slowly warmed up to 25 °C for 30 min. A solution of the alkenyl triflate **61a** (1.42 g, 5 mmol), $Pd(dba)_2$ (57.5 mg, 0.1 mmol, 2 mol%), dppf (55.4 mg, 0.1 mmol, 2 mol%), LiCl (0.63 g, 15 mmol) in THF (20 mL) was added dropwise. The reacture mixture was heat to reflux (70 °C) for 15 h. The crude product was purified by flash chromatography (5% Et_2O in pentane), affording **63c** (0.79 g, 60 %) as a white solid.

Mp: 96-98 °C.

$[\alpha]^{23}_D$: -181.3 (*c* 0.45, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98-7.86 (m, 2H), 7.62-7.50 (m, 2H), 7.40-7.28 (m, 2H), 6.44 (d, *J* = 3.6 Hz, 1H), 2.39 (t, *J* = 3.6 Hz, 1H), 1.95-1.84 (m, 1H), 1.70-1.61 (m, 1H), 1.48-1.37 (m, 1H), 1.35 (s, 3H), 1.07-0.98 (m, 1H), 0.83 (s, 3H), 0.77 (s, 3H).

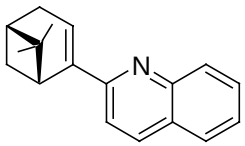
^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5, 150.1, 148.3, 137.8, 135.6, 130.0, 129.4, 127.6, 127.0, 125.9, 120.2, 57.1, 55.7, 52.5, 32.1, 26.2, 20.2, 19.9, 13.1.

IR (KBr, cm^{-1}): 1600, 1500, 1424, 1232, 1107, 820, 765.

MS (EI, 70 eV): 263 (M^+, 70), 248 (100), 220 (62).

$C_{19}H_{21}N$ HRMS Calcd.: 263.1674.
Found: 263.1658.

Synthesis of 2-[(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]quinoline (63d)



Prepared according to TP 11. To a solution of 2-iodoquinoline (**62b**) (2.55 g, 10 mmol) in THF (20 mL) was slowly added *i*-PrMgCl (9.4 mL, 1.38 M in THF, 13 mmol) at –20 °C, After 20 min at –20 °C. $ZnBr_2$ (8.2 mL, 1.7 M in THF, 14 mmol) was added dropwise and the solution slowly warmed up to 25 °C for 30 min. A solution of the alkenyl triflate **61b** (1.35 g, 5 mmol), $Pd(dba)_2$ (57.5 mg, 0.1 mmol, 2 mol%), dppf (55.4 mg, 0.1 mmol, 2 mol%), LiCl (0.63 g, 15 mmol) in THF (20 mL) was added dropwise. The reacture mixture was refluxed (70 °C) for 15 h. The crude product was purified by flash chromatogrphy (5% Et_2O in pentane), affording **63d** (0.77 g, 62 %) as a pale yellow foam.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.88 (m, 2H), 7.65-7.48 (m, 3H), 7.36-7.30 (m, 1H), 6.50-6.44 (m, 1H), 3.40-3.34 (m, 1H), 2.53-2.40 (m, 3H), 2.18-2.08 (m, 1H), 1.35 (s, 3H), 1.25 (d, *J* = 8.7 Hz, 1H), 0.81 (s, 3H).

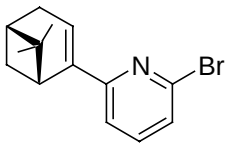
^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 147.2, 146.9, 134.6, 128.6, 128.1, 126.2, 125.9, 125.1, 124.6, 116.7, 41.3, 39.7, 36.9, 31.3, 30.5, 25.3, 20.0.

IR (KBr, cm^{-1}): 1612, 1598, 1503, 1427, 1365, 1269, 1141, 1119, 805, 782, 753.

MS (EI, 70 ev): 249 (M^+, 59), 234 (75.5), 206 (100), 180 (55.9), 167 (43.3).

$C_{18}H_{19}N$ HRMS: Calcd.: 249.1501.
Found: 249.1517.

Synthesis of 2-bromo-6-[(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]pyridine (73)



Prepared according to TP 11. A solution of *t*-BuLi (4 mL, 1.5 M in pentane, 20 mmol) was added dropwise at –78 °C to a solution of 2,6-dibromopyridine (**72**) (2.37 g, 10 mmol) in THF (50 mL). The reaction mixture was stirred at –78 °C for 30 min, then a solution of $ZnBr_2$ (13 mL, 21 mmol) was added dropwise. After 15 min at –78 °C, the reaction mixture was allowed to warm up to 25 °C for 30 min. The solution of the alkenyl triflate **61b** (1.35 g, 5 mmol), $Pd(dba)_2$ (57.5 mg, 0.1 mmol), dppf (55.4 mg, 0.1 mmol) in THF (25 mL) was added dropwise. The reacture mixture was heated to reflux (70 °C) for 15 h. The crude product was purified by flash chromatogrphy (2 %Et_2O in pentane), affording **73** (0.97 g, 70 %) as a pale yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (t, *J* = 7.8 Hz, 1H), 7.24-7.14 (m, 2H), 6.48-6.42 (m, 1H), 2.93 (dd, *J* = 5.7, 1.5 Hz, 1H), 2.48-2.36 (m, 3H), 2.14-2.08 (m, 1H), 1.31 (s, 3H), 1.18 (d, *J* = 9 Hz, 1H), 0.77 (s, 3H).

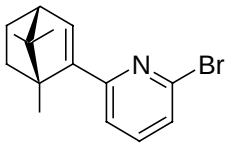
^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 146.3, 142.1, 138.8, 126.5, 125.7, 117.6, 42.9, 40.9, 38.3, 32.5, 31.9, 26.6, 21.4.

IR (KBr, cm^{-1}): 1621, 1574, 1545, 1434, 1160, 1122, 782.

MS (EI, 70 ev): 278 ($[M+H]^+$, 70), 236 (100), 154 (46).

$C_{14}H_{16}BrN$ HRMS: Calcd.: 277.0466.
Found: 277.0476.

Synthesis of 2-bromo-6-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]pyridine (74)[109]

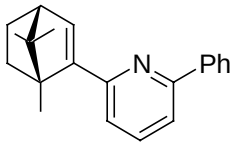


Prepared according to TP 11. A solution of *n*-BuLi (4 mL, 6 mmol) was added dropwise at –78 °C to a solution of 2,6-dibromopyridine (**72**) (1.42 g, 6 mmol) in THF (40 mL). The reaction mixture was stirred at –78 °C for 30 min, then a solution of $ZnBr_2$ (4.7 mL, 7 mmol)

was added dropwise. After 15 min at –78 °C, the reaction mixture was allowed to warm up to 25 °C for 30 min. A solution of the alkenyl triflate **61a** (0.85 mg, 3 mmol), $Pd(dba)_2$ (35 mg, 60 μmol), dppf (34 mg, 60 μmol) in THF (20 mL) was added dropwise. The reacture mixture was refluxed (70 °C) for 15 h. The crude product was purified by flash chromatography (pentane), affording **73** (297 mg, 34 %) as a pale yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.7 Hz, 1H), 7.20-7.12 (m, 2H), 6.37 (d, *J* = 3.3 Hz, 1H), 2.34 (t, *J* = 3.6 Hz, 1H), 1.94-1.82 (m, 1H), 1.64-1.55 (m, 1H), 1.36-1.28 (m, 1H), 1.20 (s, 3H), 1.08-0.98 (m, 1H), 0.78 (s, 3H), 0.75 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 148.3, 141.6, 138.3, 137.7, 125.2, 119.7, 57.3, 55.2, 52.2, 31.9, 26.0, 20.0, 19.9, 12.7.
IR (KBr, cm^{-1}): 1575, 1543, 1432, 1387, 1158, 1117, 985, 787.

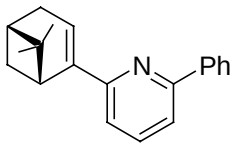
Synthesis of 2-phenyl-6-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]pyridine (63e)[109]



Prepared according to TP 12. A solution of (1*R*, 4*R*)-2-(pyridin-2yl)-1,7,7-trimethylbicyclo[2.2.1]-2-heptene (**74**) (146 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (23 mg, 20 μmol) in toluene (2 mL) was treated with a solution of Na_2CO_3 (106 mg, 1 mmol) in H_2O (1 mL), followed by a solution of $PhB(OH)_2$ (65 mg, 0.53 mmol) in MeOH (1 mL). The mixture was stirred at 85 °C for 16 h. The crude product was purified by flash chromatography (2% Et_2O in pentane) to give **63e** (143 mg, 99 %) as a pale yellow oil.

$[\alpha]^{21}_D$: -166.5 (*c* 0.585, $CHCl_3$).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10-7.96 (m, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.48-7.28 (m, 4H), 7.20 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.31 (d, *J* = 3.3 Hz, 1H), 2.37 (t, *J* = 3.6 Hz, 1H), 1.94-1.82 (m, 1H), 1.68-1.60 (m, 1H), 1.48-1.42 (m, 1H), 1.31 (s, 3H), 1.08-0.98 (m, 1H), 0.83 (s, 3H), 0.78 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 154.7, 148.6, 138.8, 135.5, 127.6, 127.5, 125.8, 118.3, 116.1, 55.7, 54.1, 50.9, 30.7, 24.8, 18.7, 18.5, 11.7.

Synthesis of 2-[(1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl]-6-phenylpyridine (63f)



Prepared according to TP 12. A solution of 2-bromo-6-[(1*R*,5*S*)-6,6-dimethyl-bicyclo[3.1.1]hept-2-en-2-yl]pyridine (**73**) (0.42 g, 1.5 mmol) and $Pd(PPh_3)_4$ (69.3 mg, 60 µmol) in toluene (3 mL) was treated with a solution of Na_2CO_3 (318 mg, 3 mmol) in H_2O (2 mL), followed by a solution of $PhB(OH)_2$ (207 mg, 1.7 mmol) in MeOH (2 mL). The mixture was stirred at 85 °C for 16 h. The crude product was purified by flash chromatography (2 % Et_2O in pentane) to give **63f** (375 mg, 91 %) as a colourless liquid.

$[\alpha]^{25}_D$: -13.2 (*c* 0.56, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02-7.96 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.48-7.24 (m, 5H), 6.50-6.46 (m, 1H), 3.17 (dd, *J* = 5.7, 1.5 Hz, 1H), 2.40 (m, 3H), 2.52-2.49 (m, 1H), 1.34 (s, 3H), 1.24 (d, *J* = 8.7 Hz, 1H), 0.82 (s, 3H).

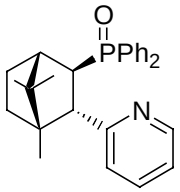
^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5, 156.4, 147.9, 140.2, 137.1, 129.0, 128.9, 127.3, 124.4, 118.1, 117.3, 43.0, 41.1, 38.3, 32.5, 31.9, 26.8, 21.4.

IR (KBr, cm^{-1}): 1587, 1565, 1456, 1365, 760.

MS (EI, 70 eV): 275 (M^+, 100), 260 (78), 232 (85).

$C_{20}H_{21}N$ HRMS: Calcd.: 275.1674.
Found: 275.1679.

Synthesis of 2-[(1*S*,2*S*,3*R*,4*S*)-3-(diphenylphosphoryl)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine (65a)



Prepared according to TP 13. To a stirred solution of *t*-BuOK (22.4 mg, 0.2 mmol) in DMSO (1 mL) were successively added under argon, $Ph_2P(O)H$ (**46**) (202 mg, 1 mmol) and alkenylpyridine **63a** (213 mg, 1 mmol) in DMSO (2 mL). The reaction mixture was stirred at 70 °C for 15 h. The oily residue was purified by flash chromatography (10% Et_2O in CH_2Cl_2),

affording the aminophosphine oxide **65a** (361 mg, 87 %) as a crystalline colourless compound.

Mp: 132-139 °C.

$[\alpha]^{23}_D$: +78.9 (*c* 0.56, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (m, 1H), 7.96-7.86 (m, 2H), 7.52-7.36 (m, 5H), 7.32-7.24 (m, 1H), 7.10-6.88 (m, 4H), 6.67 (m, 1H), 3.71 (dd, *J* = 8.4, 6.3 Hz, 1H), 3.50 (ddd, *J* = 20.7, 8.7, 2.1 Hz, 1H), 2.20 (d, *J* = 9.2, 3.8 Hz, 1H), 1.96-1.80 (m, 2H), 1.72-1.60 (m, 1H), 1.41 (s, 3H), 1.20-1.08 (m, 1H), 0.92 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 148.5, 135.4, 134.6 (d, *J* = 94.0 Hz), 133.4 (d, *J* = 94.0 Hz), 131.6-131.3 (m), 130.7 (d, *J* = 2.7 Hz), 128.9 (d, *J* = 11 Hz), 127.7 (d, *J* = 11 Hz), 125.6, 121.4, 53.3 (d, *J* = 2.9 Hz), 52.2 (d, *J* = 5.1 Hz), 51.0, 48.1, 45.2 (d, *J* = 70.4 Hz), 32.3 (d, *J* = 13.7 Hz), 28.2, 21.2, 20.2, 14.5.

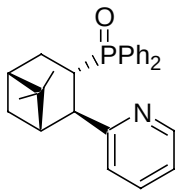
^{31}P NMR (81 MHz, $CDCl_3$): δ 32.8.

IR (KBr, cm^{-1}): 1589, 1478, 1433, 1390, 1206, 1147, 740.

MS (EI, 70 eV): 415 (M^+, 6), 332 (30), 214 (100).

$C_{27}H_{30}NOP$	HRMS:	Calcd.:	415.2065.		
		Found:	415.2061.		
$C_{27}H_{30}NOP$		Calcd.:	C, 78.05	H, 7.28	N, 3.37
		Found:	C, 77.82	H, 7.17	N, 3.27

Synthesis of 2-[(1*S*,2*R*,3*S*,5*R*)-3-(diphenylphosphoryl)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]pyridine (65b)



Prepared according to TP 13. To a stirred solution of *t*-BuOK (0.18 g, 1.6 mmol) in DMSO (15 mL) were successively added under argon, $Ph_2P(O)H$ (**46**) (1.64 g, 8.1 mmol) and alkenylpyridine **63b** (1.61 g, 8.1 mmol) in DMSO (15 mL). The reaction mixture was stirred at 70 °C for 15 h. The crude product was purified by flash chromatography on silica gel (5% Et_2O in CH_2Cl_2), affording the aminophosphine oxide **65b** (2.76 g, 85 %) as a white solid.

Mp: 57-63 °C.

$[\alpha]^{26}_D$: -24.0 (*c* 0.56, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29-8.25 (m 1H), 8.00-7.90 (m, 2H), 7.60-7.52 (m, 2H), 7.44-7.40 (m, 3H), 7.22-7.16 (m, 1H), 7.02-6.88 (m, 3H), 6.84-6.76 (m, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 4.80-4.67 (m, 1H), 3.72 (ddd, *J* = 22.0, 6.6, 2.7 Hz, 1H), 2.40-2.12 (m, 4H), 1.93-1.85 (m, 1H), 1.72 (d, *J* = 9.9 Hz, 1H), 1.01 (s, 3H), 0.72 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6 (d, *J* = 2.7 Hz), 147.2, 135.9, 133.8 (d, *J* = 82.0 Hz), 132.5 (d, *J* = 82.0 Hz), 131.8-131.6 (m), 131.0 (d, *J* = 2.7 Hz), 128.9 (d, *J* = 11.2 Hz), 127.6 (d, *J* = 11.2 Hz), 123.9, 121.0, 48.3 (d, *J* = 5.6 Hz), 46.6, 40.7 (d, *J* = 3.8 Hz), 39.1, 30.9, 27.9, 26.5 (d, *J* = 2.1 Hz), 25.2 (d, *J* = 71.0 Hz), 22.7.

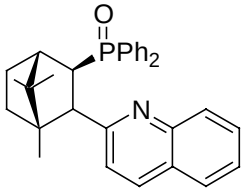
^{31}P NMR (81 MHz, $CDCl_3$): δ 38.4.

IR (KBr, cm^{-1}): 1589, 1473, 1437, 1191, 1117.

MS (EI, 70 ev): 401 (M^+, 13), 283 (18), 200 (100).

$C_{26}H_{28}NOP$ HRMS: Calcd.: 401.1906.
Found 401.1906.

Synthesis of 2-[(1*S*,2*S*,3*R*,4*S*)-3-(diphenylphosphoryl)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]quinoline (65c)



Prepared according to TP 13. To a stirred solution of *t*-BuOK (22.4 mg, 0.2 mmol) in NMP (1 mL) were successively added under argon, Ph_2PH (**35a**) (186.2 mg, 1 mmol) and alkenylpyridine **63c** (289 mg, 1 mmol) in NMP (2 mL). The reaction mixture was stirred at 40 °C for 1 h. The crude product was purified by flash chromatography on silica gel (5% Et_2O in CH_2Cl_2), affording the aminophosphine oxide **65c** (432 mg, 93 %) as a white solid.

Mp: 70-78 °C.

$[\alpha]^{28}_D$: +83.4 (*c* 0.525, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.80 (m, 3H), 7.70-7.55 (m, 3H), 7.44-6.55 (m, 6H), 6.78-6.58 (m, 4H), 4.01 (t, *J* = 7.5 Hz, 1H), 3.58 (dd, *J* = 20, 2.1 Hz, 1H), 2.17 (dd, *J* = 9.3, 3.8 Hz, 1H), 1.93-1.60 (m, 3H), 1.35 (s, 3H), 1.18-0.95 (m, 1H), 0.85 (s, 3H), 0.75 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1, 147.5, 135.1, 134.9 (d, *J* = 96.0 Hz), 133.1 (d, *J* = 96.0 Hz), 131.6-131.4 (m), 130.4 (d, *J* = 2.7 Hz), 129.6-128.8 (m), 127.6-127.4 (m), 127.2, 125.9, 123.9, 54.2 (d, *J* = 2.4 Hz), 52.7 (d, *J* = 4.6 Hz), 51.3, 48.0, 45.0 (d, *J* = 70.0 Hz), 32.4 (d, *J* = 14.0 Hz), 28.3, 21.2, 20.2, 14.9.

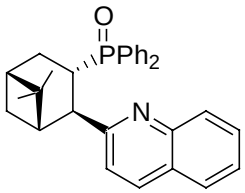
^{31}P NMR (81 MHz, $CDCl_3$): δ 32.9.

IR (KBr, cm^{-1}): 1600, 1503, 1437, 1194, 1114, 837.

MS (EI, 70 eV): 465 (M^+, 3), 382 (7), 264 (100).

$C_{31}H_{32}NOP$	HRMS:	Calcd.:	465.2222.		
		Found:	465.2245.		
$C_{31}H_{32}NOP$		Calcd.:	C, 79.97	H, 6.93	N, 3.01
		Found:	C, 79.64	H, 6.94	N, 3.05

Synthesis of (1*S*,2*R*,3*R*,5*R*)-6,6-Dimethyl-2-(2-naphthyl)bicyclo[3.1.1]hept-3-yl(diphenyl) phosphine oxide (65d)



Prepared according to TP 13. To a stirred solution of *t*-BuOK (15.7 mg, 0.14 mmol) in NMP (1 mL) were successively added under argon, Ph_2PH (**35a**) (130 mg, 0.7 mmol) and alkenylpyridine **63c** (174 mg, 0.7 mmol) in NMP (2 mL). The reaction mixture was stirred at 40 °C for 1 h. The crude product was purified by flash chromatography (10% Et_2O in CH_2Cl_2), affording the aminophosphine oxide **65d** (281 mg, 89 %) as a foam.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05-7.94 (m, 3H), 7.70-7.54 (m, 5H), 7.50-7.34 (m, 4H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.79-6.62 (m, 3H), 5.16-5.04 (m, 1H), 3.84 (ddd, *J* = 22.0, 6.3, 2.7 Hz, 1H), 2.45-2.12 (m, 4H), 1.97-1.89 (m, 1H), 1.79 (d, *J* = 9.3 Hz, 1H), 1.01 (s, 3H), 0.71 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 162.1 (d, *J* = 2.7 Hz), 146.6, 135.7, 133.9 (d, *J* = 95.0 Hz), 132.5 (d, *J* = 95.0 Hz), 131.9-131.6 (m), 130.8 (d, *J* = 2.3 Hz), 129.2-128.9 (m), 127.6-127.3 (m), 126.9, 126.1, 121.8, 47.3-47.1 (m), 40.9 (d, *J* = 3.8 Hz), 39.4, 31.2, 27.9, 26.5 (d, *J* = 2.1 Hz), 25.0 (d, *J* = 71.0 Hz), 22.5.

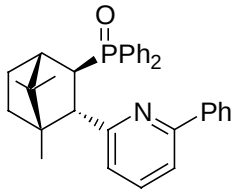
^{31}P NMR (81 MHz, $CDCl_3$): δ 38.4.

IR (KBr, cm^{-1}): 1618, 1602, 1437, 1190, 1117, 720, 700.

EI (70 eV): 451 (M^+, 11), 382 (8), 356 (2), 283 (5), 250 (100), 201 (12).

$C_{30}H_{30}NOP$ HRMS: Calcd.: 451.2044.
Found: 451.2065.

Synthesis of 2-[(1*S*,2*R*,3*S*,4*S*)-3-(diphenylphosphoryl)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]-6-phenylpyridine (65e)



Prepared according to TP 13. To a stirred solution of *t*-BuOK (12 mg, 0.1 mmol) in DMSO (2 mL) were successively added under argon, $Ph_2P(O)H$ (**46**) (101 mg, 0.7 mmol) and alkenylpyridine **63e** (144 mg, 0.5 mmol) in DMSO (2 mL). The reaction mixture was stirred at 70 °C for 16 h. The crude product was purified by flash chromatography (10% Et_2O in CH_2Cl_2), affording the aminophosphine oxide **65e** (177 mg, 72 %) as a white solid.

Mp: 69-72 °C.

$[\alpha]^{22}_D$: -68.9 (*c* 0.505, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09-7.96 (m, 2H), 7.84-7.74 (m, 2H), 7.48-7.24 (m, 10H), 6.96-6.88 (m, 1H), 6.80-6.72 (m, 2H), 6.61 (m, 1H), 3.95 (m, 1H), 3.53 (ddd, *J* = 10.5, 4.2, 0.9 Hz, 1H), 2.22 (dd, *J* = 4.8, 2.1 Hz, 1H), 2.00-1.88 (m, 2H), 1.74-1.70 (m, 1H), 1.40 (s, 3H), 1.22-1-13 (m, 1H), 0.93 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 155.2, 140.0, 136.4, 135.5, 134.8, (d, *J* = 96.0 Hz), 133.2 (d, *J* = 96.0 Hz), 131.6-131.4 (m), 130.7 (d, *J* = 2.3 Hz), 129.1, 128.8 (d, *J* = 11.0 Hz), 127.6 (d, *J* = 11.0 Hz), 126.9, 124.0, 117.8, 53.6 (d, *J* = 2.9 Hz), 52.1 (d, *J* = 5.2 Hz), 51.1, 48.1, 45.4 (d, J = 70 Hz), 32.6 (d, *J* = 13.7 Hz), 28.4, 21.1, 20.2, 14.6.

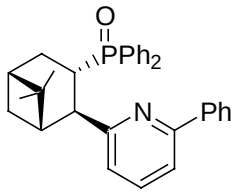
^{31}P NMR (81 MHz, $CDCl_3$): δ 32.6.

IR (KBr, cm^{-1}): 1570, 1438, 1195, 1115.

MS (EI, 70 eV): 477 (M^+, 7), 276 (100).

$C_{33}H_{34}NOP$ HRMS: Calcd.: 491.2378.
Found: 491.2380.

Synthesis of 2-[(1*S*,2*R*,3*S*,5*R*)-3-(diphenylphosphoryl)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-6-phenylpyridine (65f)



Prepared according to TP 13. To a stirred solution of *t*-BuOK (34 mg, 0.3 mmol) in DMSO (2 mL) were successively added under argon, $Ph_2P(O)H$ (**46**) (303 mg, 1.5 mmol) and vinylpyridine **63f** (412 mg, 1.5 mmol) in DMSO (4 mL). The reaction mixture was stirred at 70 °C for 16 h. The crude product was purified by flash chromatography (5% Et_2O in CH_2Cl_2), affording the aminophosphine oxide **65f** (558 mg, 78 %) as a white solid.

Mp: 67-73 °C.

$[\alpha]^{29}_D$: +59.2 (*c* 0.76, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04-7.86 (m, 4H), 7.52-7.20 (m, 10 H), 6.94-6.56 (m, 4H), 5.00-4.88 (m, 1H), 3.78 (ddd, *J* = 22.0, 6.6, 2.7 Hz, 1H), 2.44-2.12 (m, 4H), 1.94-1.88 (m, 1H), 1.68 (d, *J* = 9.6 Hz, 1H), 1.03 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6 (d, *J* = 2.3 Hz), 154.4, 140.2, 136.9, 133.8 (d, *J* = 95.0 Hz), 132.5 (d, *J* = 95.0 Hz), 131.8-131.5 (m), 130.9 (d, *J* = 2.7 Hz), 129.1 (d, *J* = 3.2 Hz), 128.9, 127.5 (d, *J* = 11.3 Hz), 126.9, 122.4, 117.4, 48.3 (d, *J* = 5.8 Hz), 46.9, 40.9 (d, *J* = 4.1 Hz), 39.3, 31.4, 28.0, 26.6 (d, *J* = 2.0 Hz), 25.4 (d, *J* = 71.0 Hz), 24.9, 23.0.

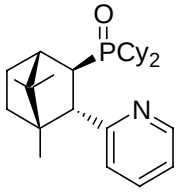
^{31}P NMR (81 MHz, $CDCl_3$): δ 37.9.

IR (KBr, cm^{-1}): 1590, 1571, 1445, 1191, 1117.

MS (EI, 70 eV): 477 (M^+, 7), 276 (100).

$C_{32}H_{32}NOP$ HRMS: Calcd.: 477.2222.
Found: 477.2213.

Synthesis of 2-[(1*S*,2*S*,3*R*,4*S*)-3-(dicyclohexylphosphoryl)-1,7,7-trimethylbicyclo[2.2.1]-hept-2-yl]pyridine (65g)



Prepared according to TP 13. To a stirred solution of *t*-BuOK (23 mg, 0.2 mmol) in DMSO (2 mL) were successively added under argon, Cy_2PH (**35b**) (0.2 mL, 1 mmol) and alkenylpyridine **63a** (213 mg, 1 mmol) in DMSO (3 mL). The reaction mixture was stirred at 70 °C for 16 h. The crude product was purified by flash chromatography (5% Et_2O in CH_2Cl_2), affording the aminophosphine oxide **65h** (235 mg, 55 %) as a white solid.

Mp: 128-132 °C.

$[\alpha]^{27}_D$: +14.7 (*c* 0.475, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 5.3, 2 Hz, 1H), 7.36 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.94-6.88 (m, 2H), 3.35 (ddd, *J* = 18.3, 8.4, 2.1 Hz, 1H), 2.66 (dd, *J* = 8.4, 5.1 Hz, 1H), 2.00-0.48 (m, 35H), 0.80-(-0.08) (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.3, 148.9, 135.9, 126.1, 121,8, 53.3 (d, *J* = 3.9 Hz), 51.7 (d, *J* = 5.0 Hz), 50.6, 48.3 (d, *J* = 2.1 Hz), 41.1 (d, *J* = 58.1 Hz), 39.4 (d, *J* = 43.4 Hz), 38.6 (d, *J* = 43.4 Hz), 32.2 (d, *J* = 11.8 Hz), 28.2-26.4 (m), 21.4, 20.1, 14.6.

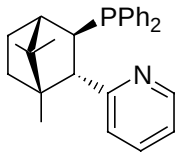
^{31}P NMR (81 MHz, $CDCl_3$): δ 50.8.

IR (KBr, cm^{-1}): 1589, 1449, 1163.

MS (EI, 70 eV): 427 (M^+, 3), 344 (17), 214 (100).

$C_{27}H_{42}NOP$ HRMS: Calcd.: 427.3004.
Found: 427.2997.

Synthesis of 2-[(1*S*,2*S*,3*R*,4*S*)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]pyridine (66a)



Prepared according to TP 14 from phosphine oxide **65a** (208 mg, 0.5 mmol) in toluene (15 mL), trichlorosilane (0.1 mL, 10 equiv, 5 mmol) and triethylamine (1.4 mL, 20 equiv, 10 mmol). Reaction time: 16 h at 120 °C. After filtration, the residue was dried under high vacuum, furnishing the aminophosphine ligand **66a** (174 mg, 87 %) as a viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38-8.34 (m, 1H), 7.48-7.40 (m, 2H), 7.27-6.97 (m, 7H), 6.80-6.64 (m, 3H), 6.46-6.40 (m, 1H), 3.33-3.24 (m, 1H), 3.06-2.95 (m, 1H), 1.95-1.60 (m, 4H), 1.44 (s, 3H), 1.20-1.12 (m, 1H), 0.94 (s, 3H), 0.72 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.6, 147.0, 139.0 (d, *J* = 15.0 Hz), 136.3 (d, *J* = 15.0 Hz), 133.6, 133.6-133.1 (m), 131.4 (d, *J* = 17.3 Hz), 127.3-126.7 (m), 126.1 (d, *J* = 7.6 Hz), 123.6, 119.3, 55.6 (d, *J* = 9.9 Hz), 50.4 (d, *J* = 3.85 Hz), 50.0, 48.1 (d, *J* = 12.5 Hz), 42.6 (d, *J* = 13.7 Hz), 29.9 (d, *J* = 7.3 Hz), 27.3, 20.0, 19.8 (d, *J* = 20.0 Hz), 13.4.

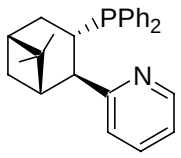
^{31}P NMR (81 MHz, $CDCl_3$): δ -2.1.

IR (KBr, cm^{-1}): 1589, 1478, 1433, 1112, 740.

MS (EI, 70 eV): 399 (M^+, 27), 316 (39), 214 (100), 183 (59).

$C_{27}H_{30}NP$ HRMS: Calcd.: 399.2116.
Found: 399.2116.

Synthesis of 2-[(1*S*,2*R*,3*S*,5*R*)-3-(diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]pyridine (66b)



Prepared according to TP 14 from phosphine oxide **65b** (539 mg, 1.4 mmol) in toluene (20 mL), trichlorosilane (1.4 mL, 14 mmol) and triethylamine (3.9 mL, 28.0 mmol). Reaction time: 16 h at 120 °C. After filtration, the residue was dried under high vacuum, furnishing the aminophosphine ligand **66b** (431 mg, 80 %) as a viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24-8.20 (m, 1H), 7.66-7.58 (m, 2H), 7.32-7.12 (m, 6H), 6.88-6.68 (m, 5H), 4.34-4.22 (m, 1H), 3.35 (ddd, *J* = 18.3, 6.0, 2.4, 1H), 2.44-2.20 (m, 3H), 1.92-1.74 (m, 2H), 1.41 (d, *J* = 8.7 Hz, 1H), 1.02 (s, 3H), 0.79 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 162.4 (d, *J* = 2.6 Hz), 146.2, 136.8 (d, *J* = 15.5 Hz), 136.2 (d, *J* = 15.5 Hz), 134.1-132.6 (m), 132.7 (d, *J* = 18.7 Hz), 127.6-127.1 (m), 126.2 (d, *J* = 7.0 Hz), 122.0, 119.1, 50.7 (d, *J* = 2.6 Hz), 47.8 (d, *J* = 4.9 Hz), 40.6 (d, *J* = 2.3 Hz), 38.1 (d, *J* = 1.6 Hz), 30.4 (d, *J* = 17.8 Hz), 30.0, 26.5, 21.7, 21.4 (d, *J* = 8.1 Hz).

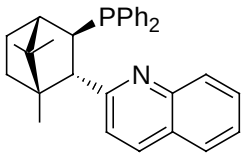
^{31}P NMR (81 MHz, $CDCl_3$): δ 10.5.

IR (KBr, cm^{-1}): 1588, 1565, 1472, 1431, 1386.

MS (EI, 70 eV): 385 (M^+, 6), 308 (48), 200 (100).

$C_{26}H_{28}NP$ HRMS: Calcd.: 385.1959.
Found: 385.1992.

Synthesis of 2-[(1*S*,2*R*,3*S*,4*S*)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]quinoline (66c)



Prepared according to TP 14 from phosphine oxide **65c** (233 mg, 0.5 mmol) in toluene (8 mL), trichlorosilane (0.5 mL, 5.0 mmol) and triethylamine (1.4 mL, 10.0 mmol). Reaction time: 16 h at 120 °C. After filtration, the residue was dried under high vacuum, furnishing the aminophosphine ligand **66c** (137 mg, 61 %) as a viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (m, 1H), 7.60-7.20 (m, 9H), 7.06-6.98 (m, 2H), 6.60-6.40 (m, 4H), 3.65 (t, *J* = 8.1 Hz, 1H), 3.16 (m, 1H), 1.92-1.72 (m, 4H), 1.40 (s, 3H), 1.08-1.00 (m, 1H), 0.88 (s, 3H), 0.72 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.1, 146.3, 139.2 (d, *J* = 15.0 Hz), 136.1 (d, *J* = 15.0 Hz), 133.5-133.1 (m), 131.4 (d, *J* = 17.2 Hz), 128.3, 127.4-126.8 (m), 126.0-125.8 (m), 125.4, 124.2, 122.2, 56.4 (d, *J* = 10.1 Hz), 50.9 (d, *J* = 3.8 Hz), 50.5, 48.1 (d, *J* = 12.8 Hz), 42.3 (d, *J* = 13.7 Hz), 30.0 (d, *J* = 7.4 Hz), 27.4, 20.0, 19.7, 13.7.

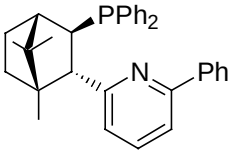
^{31}P NMR (81 MHz, $CDCl_3$): δ -1.5.

IR (KBr, cm^{-1}): 1618, 1600, 1435, 834.

MS (EI, 70 eV): 449 (M^+, 28), 366 (17), 264 (100), 156 (33).

$C_{31}H_{32}NP$ HRMS: Calcd.: 449.2272.
Found: 449.2301.

Synthesis of 2-[(1*S*,2*R*,3*S*,4*S*)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]-6-phenylpyridine (65e)



Prepared according to TP 14 from phosphine oxide **65e** (201 mg, 0.4 mmol) in toluene (15 mL), trichlorosilane (0.4 mL, 4 mmol) and triethylamine (1.2 mL, 8.0 mmol). Reaction time: 16 h at 120 °C. After filtration, the residue was dried under high vacuum, furnishing the aminophosphine ligand **66e** (156 mg, 82 %) as a viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.92 (m, 2H), 7.48-6.96 (m, 12H), 6.80-6.60 (m, 3H), 6.32 (m, 1H), 3.62 (t, *J* = 8.1 Hz, 1H), 3.02-2.92 (m, 1H), 1.96-1.68 (m, 4H), 1.38 (s, 3H), 1.12-1.00 (m, 1H), 0.88 (s, 3H), 0.68 (s, 3H).

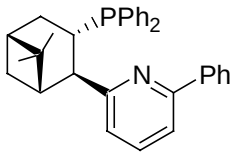
^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 153.7, 139.2 (d, *J* = 15.0 Hz), 138.9, 136.2 (d, *J* = 15.0 Hz), 134.5, 133.3 (d, *J* = 18.8 Hz), 131.4 (d, *J* = 18.8 Hz), 127.6-127.2 (m), 126.8, 126.1 (d, *J* = 8.0 Hz) 125.6, 122.3, 115.7, 55.7 (d, *J* = 10.0 Hz), 50.4 (d, *J* = 4.1 Hz), 50.3, 48.1 (d, *J* = 12.8 Hz), 42.4 (d, *J* = 13.4 Hz), 30.1 (d, *J* = 7.0 Hz), 27.4, 19.9, 19.7, 13.5.

^{31}P NMR (81 MHz, $CDCl_3$): δ -2.1.

MS (EI, 70 eV): 475 (M^+, 26), 392 (18), 290 (100), 182 (32).

$C_{33}H_{34}NP$ HRMS: Calcd.: 475.2429.
Found: 475.2447.

Synthesis of 2-[(1*S*,2*R*,3*S*,5*R*)-3-(diphenylphosphino)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-6-phenylpyridine (66f)



Prepared according to TP 14 the phosphine oxide **65e** (229 mg, 0.48 mmol) in toluene (15 mL), trichlorosilane (0.48 mL, 4.8 mmol) and triethylamine (1.4 mL, 9.6 mmol). Reaction time: 16 h at 120 °C. After filtration, the residue was dried under high vacuum, furnishing the aminophosphine ligand **66f** (204 mg, 92 %) as a viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00-7.94 (m, 2H), 7.68-7.60 (m, 2H), 7.42-7.20 (m, 10H), 6.82-6.66 (m, 3H), 6.61 (m, 1H), 4.64-4.54 (m, 1H), 3.44-3.32 (m, 1H), 2.44-2.28 (m, 3H), 1.96-1.80 (m, 2H), 1.44-1.36(m, 1H), 1.04 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9 (d, *J* = 2.3 Hz), 153.0, 138.9, 136.9 (d, *J* = 15.5 Hz), 136.1 (d, *J* = 15.5 Hz), 135.0, 133.2 (d, *J* = 18.8 Hz), 132.7 (d, *J* = 18.8 Hz), 127.6-127.2 (m), 126.1 (d, *J* = 7.4 Hz), 125.6, 120.5, 115.5, 50.7 (d, *J* = 19.0 Hz), 47.7 (d, *J* = 5.2 Hz), 40.7 (d, *J* = 2.5 Hz), 38.4, 30.6 (d, *J* = 18.5 Hz), 30.3, 26.6, 21.9, 21.4 (d, *J* = 8.3 Hz).

^{31}P NMR (81 MHz, $CDCl_3$): 10.1.

MS (EI, 70 eV): 461 (M^+, 2), 384 (5), 276 (100).

$C_{32}H_{32}NP$ HRMS: Calcd.: 461.2272.
Found: 461.2241.

7 Synthesis of novel chiral P,P-ligands

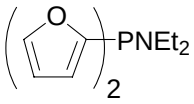
Synthesis of diethylphosphoramidous dichloride (103)[96]

$Et_2N\text{-}PCl_2$

A solution of Et_2NH (62 mL, 600 mmol) was added dropwise to a solution of PCl_3 (26 mL, 300 mmol) dissolved in ether (300 mL) at –20 °C within 1.5 h. The amonium salt precipitated. The reaction was warmed up to 25 °C and stirred for 5 h. The precipitate was filtered off rapidly and washed twice with ether (200 mL). The solvent was removed *in vacuo*. The residue was distilled at 45 °C under 0.8 mbar to give **103** as a colourless liquid (39.2 g, 75 % yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.33-3.21 (m, 4H), 1.11 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 40.6 (d, *J* = 22.4 Hz), 13.1 (d, *J* = 4.7 Hz).
^{31}P NMR (81 MHz): δ 163.8.

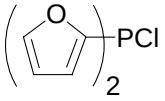
Synthesis of bis(2-furyl)(diethylamino)phosphine (104)[96]



A suspension of 2-furyllithium was prepared by slow addition of *n*-BuLi (68 mL, 1.6 M in hexane,102 mmol) to a solution of furane (9 mL, 124 mmol) in THF (50 mL) at –30 °C. The mixture was stirred at rt for 1 h and then slowly added to a solution of Et_2NPCl_2 (**103**) (10 g, 56 mmol) in THF (40 mL) at –30 °C. After 1 h at –30 °C, the brown mixture was stirred for 12 h at rt. Solvents were evaporated *in vacuo* and the residue was distilled at 80-90 °C under 0.5 mbar, yielding bis(2-furyl)(diethylamino)phosphine (**104**) (9.6 g, 72 % yield) as a slightly yellow oil, which was stored under argon at 0 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 1.8 Hz, 0.6 Hz, 2H), 6.55-6.53 (m, 2H), 6.34-6.31 (m, 2H), 3.10-2.97 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 154.0 (d, *J* = 9.5 Hz), 145.1 (d, *J* = 3.5 Hz), 117.5 (d, *J* = 21 Hz), 109.3 (d, *J* = 4.1 Hz), 43.4 (d, *J* = 15.5 Hz), 13.3 (d, *J* = 3.8 Hz).
^{31}P NMR (81 MHz): δ 14.8.

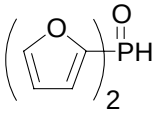
Synthesis of Bis(2-furyl)phosphine chloride(105)[96]



Dry HCl, generated from NH_4Cl (24.6 g, 460 mmol) and concentrated H_2SO_4 (25.0 mL, 460 mmol), was passed through a solution of bis(2-furyl)diethylaminophosphine (**104**) (11 g, 46 mmol) in ether (230 mL). After 0.5 h, the amine hydrochloride was filtered under argon through celite to provide a solution of bis(2-furyl)phosphine chloride (**105**) which was concentrated *in vacuo*. The residue was distilled at 80-90 °C under 0.4-0.5 mbar, affording chlorodifurylphosphine **105** (7.8 g, 85 % yield) as a pale yellow liquid.

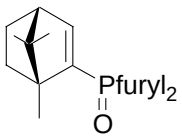
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77-7.76 (m, 2H), 7.05-7.03 (m, 2H), 6.50-6.47 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$): δ 150.7 (d, J = 33.4 Hz), 149.3 (d, J = 3.5 Hz), 123.4 (d, J = 30.5 Hz), 116.6 (d, J = 6.5 Hz).
^{31}P NMR (81 MHz): δ 18.1.
IR (KBr, cm^{-1}): 1554, 1459, 1198, 1120, 1013, 763.

Synthesis of di(2-furyl)phosphine oxide (100)



To a solution of bis(2-furyl)phosphine chloride (**105**) (1.2 g, 6.0 mmol) in CH_2Cl_2 (20 mL) was added H_2O (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h. CH_2Cl_2 and H_2O were added, and the resulting solution was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product **100** showed the presence of the expected product (δ = -17.0 ppm in ^{31}P NMR and GC MS; mass peak at 182) and was used in the next step without purification.

Synthesis of di(2-furyl)(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)phosphine oxide (101)



Prepared according to TP 10 from alkenyll triflate **61a** (341 mg, 1.2 mmol), difurylphosphine oxide (**100**) (255 mg, 1.4 mmol), *i*-Pr_2NEt (0.6 mL, 3 mmol) in toluene (8 mL). $Pd(OAc)_2$ (13.5 mg, 60 μmol), dppb (25.6 mg, 60 μmol) in toluene (2 mL) were added and the mixture was stirred at 60 °C for 15 min. 30 % H_2O_2 was added and the mixture was stirred at 25 °C for 15 min. Purification by flash chromatography (20% Et_2O in CH_2Cl_2) furnished **101** (220 mg, 58 %) as a yellow foam.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64-7.61 (m, 2H), 7.09 (ddd, *J* = 3.3, 2.1, 0.6 Hz, 1H), 6.98 (ddd, *J* = 3.3, 2.1, 0.6 Hz, 1H), 6.63 (dd, *J* = 12.9, 3.3 Hz, 1H), 6.47-6.42 (m, 2H), 2.44-2.40 (m, 1H), 1.88-1.80 (m, 1H), 1.55-1.46 (m, 1H), 1.23-1.10 (m, 1H), 1.04-0.94 (m, 4H), 0.78 (s, 3H), 0.71 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1 (d, *J* = 9.0 Hz), 147.8 (d, *J* = 10.8 Hz), 146.7-146.6 (m, 1H), 145.8 (d, *J* = 10.8 Hz), 139.3 (d, *J* = 117.2 Hz), 121.2-120.8 (m), 110.0-109.8 (m), 57.4 (d, *J* = 5.5 Hz), 55.8 (d, *J* = 9.3 Hz), 52.4 (d, *J* = 13.7 Hz), 30.7, 22.7 (d, *J* = 3.2 Hz), 18.3, 18.0, 10.7.

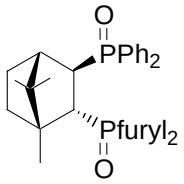
^{31}P NMR (81 MHz, $CDCl_3$): δ 0.3.

IR (KBr, cm^{-1}): 1553, 1461, 1368, 1208, 1133, 1007, 911, 883.

EI (70 eV): 317 ($[M+H]^+$, 18.7), 316 (M^+, 96), 301 (77), 273 (100).

$C_{18}H_{21}O_3P$ HRMS: Calcd.: 316.1221.
Found: 316.1228.

Synthesis of [(1*R*, 2*S*,3*R*,4*S*)-3-(diphenylphosphoryl)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl][di(2-furyl)]phosphine oxide (102)



Prepared according to TP 13. To a stirred solution of *t*-BuOK (22 mg, 0.2 mmol) in DMSO (2 mL) were successively added under argon, $Ph_2P(O)H$ (**46**) (130 mg, 0.7 mmol) and di(2-furyl)(1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)-phosphine oxide (**101**) (316 mg, 1.0 mmol) in DMSO (2 mL). The reaction mixture was stirred at 60 °C for 16 h. The crude product was purified by flash chromatography (50% Et_2O in CH_2Cl_2), affording the diphosphine oxide **102** (363 mg, 70 %) as a white solid.

Mp: 271-273 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66-7.52 (m, 5H), 7.38-7.20 (m, 7H), 6.89 (ddd, *J* = 3.3, 1.8, 0.6 Hz, 1H), 6.45 (ddd, *J* = 3.3, 1.8, 0.6 Hz, 1H), 6.37-6.34 (m, 1H), 5.92-5.89 (m, 1H), 3.50-3.32 (m, 2H), 2.48-2.38 (m, 1H), 1.80-1.52 (m, 3H), 1.40-1.14 (m, 1H), 1.04 (s, 3H), 0.60 (s, 3H), 0.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.7 (d, *J* = 99.3 Hz), 148.0-147.9 (m), 145.9 (d, *J* = 99.3 Hz), 135.3 (d, *J* = 24.7 Hz), 134.0 (d, *J* = 24.7 Hz), 131.5-131.1 (m), 128.7-128.4 (m), 122.6-122.0 (m), 111.5 (d, *J* = 8.5 Hz), 111.3 (d, *J* = 8.5 Hz), 52.0, 51.2 (d, *J* = 12.0 Hz), 49.9 (d, *J* = 5.0 Hz), 47.6 (d, *J* = 44.0 Hz), 46.5 (d, *J* = 4.5 Hz), 41.5 (d, *J* = 65.1 Hz), 31.4 (d, *J* = 14.1 Hz), 31.2 (d, *J* = 6.2 Hz), 19.8, 19.7.

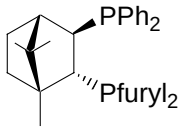
^{31}P NMR (81 MHz, $CDCl_3$): δ 26.3 (d, *J* = 7.7 Hz), 9.8 (d, *J* = 7.7 Hz).

IR (KBr, cm^{-1}): 1460, 1438, 1200, 1133, 1012, 913, 771, 751, 714.

EI (70 ev): 518 (M^+, 15), 337 (61.2), 317 (100), 201 (29.9).

$C_{30}H_{32}O_4P_2$	HRMS	Calcd.:	518.1776.	
		Found:	518.1760.	
$C_{30}H_{32}O_4P_2$		Calcd.:	C, 69.49	H, 6.22
		Found:	C, 69.06	H, 6.45

Synthesis of [(1*R*,2*S*,3*R*,4*S*)-3-(diphenylphosphino)-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl][di(2-furyl)]phosphine (106)



Prepared according to TP 14 from 1,2-diphenylphosphine oxide **102** (207 mg, 0.4 mmol) in toluene (7 mL), trichlorosilane (0.4 mL, 4 mmol) and triethylamine (1.4 mL, 10 mmol). Reaction time: 16 h at 120 °C. After filtration, the residue was dried under high vacuum, furnishing the 1,2-diphenylphosphine ligand **106** (132 mg, 68 %) as a foam.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.48 (m, 1H), 7.32-7.04 (m, 11H), 6.60-6.54 (m, 1H), 6.28-6.20 (m, 2H), 5.80-5.72 (m, 1H), 3.40-3.28 (m, 1H), 2.48-2.36 (m, 1H), 2.24-2.12 (m, 1H), 1.84-1.70 (m, 1H), 1.40-1.20 (m, 2H), 0.89 (s, 3H), 0.84-0.72 (m, 1H), 0.58 (s, 3H), 0.31 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 150.8 (d, *J* = 18.5 Hz), 148.2 (d, *J* = 12.3 Hz), 145.3, 138.5-138.1 (m), 134.3 (d, *J* = 21.0 Hz), 131.6 (d, *J* = 21.0 Hz), 127.5-126.6 (m), 120.8 (d, *J* = 24.5 Hz), 119.6 (d, *J* = 25.7 Hz), 109.7-109.5 (m), 50.2-50.0 (m), 49.3-48.1 (m), 43.9-43.3 (m), 30.6 (d, *J* = 2.6 Hz), 29.3 (d, *J* = 23.9 Hz), 18.7, 12.8.

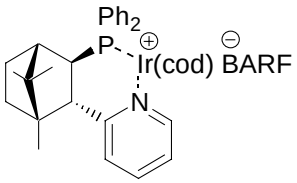
^{31}P NMR (81 MHz, $CDCl_3$): δ 8.00 (d, *J* = 2.3 Hz) and –57.5.

EI (70 ev): 486 (M^+, 100), 350 (39), 252 (49), 165 (41).

$C_{30}H_{32}O_2P_2$ HRMS Calcd.: 486.1878.
Found: 486.1870.

8 Preparation of Ir-complexes 85

Synthesis of Ir-BARF complex (85a)



Prepared according to TP 15. The P,N-ligand **66a** (0.1 mmol, 40 mg), $[Ir(cod)Cl]_2$ (33.6 mg, 0.05 mmol) and CH_2Cl_2 (5mL) were heated to reflux at 45 °C for 1 h, until ^{31}P NMR indicated that the ligand was consumed. After cooling to 25 °C, Na[BARF] (130 mg, 0.15 mmol) was added, followed by H_2O (5 mL), and the resulting two-phase mixture was stirred vigorously for 30 min. The residue was purified by column chromatography (50% CH_2Cl_2 in pentane) to afford **85a** (136 mg, 88 %) as an orange solid.

Mp: 173-177 °C.

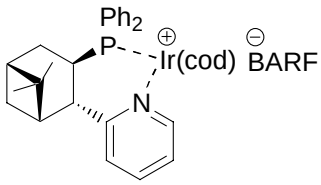
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44-8.40 (m, 1H), 7.68-7.04 (m, 25 H), 4.78 (dd, *J* = 23.0, 11.3 Hz, 1H), 4.44-4.36 (m, 1H), 4.10-4.00 (m, 1H), 3.85-3.76 (m, 1H), 3.26-3.16 (m, 1H), 2.12-1.96 (m, 10H), 2.92-1.02 (m, 7H), 1.09 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (75 MHz, CDCl3): δ 163.5-161.1 (m), 151.7, 139.7, 135.2, 134.6 (d, *J* = 12.6 Hz), 133.6 (d, *J* = 9.3 Hz), 132.1, 131.8, 130.3-128.6 (m), 126.7, 123.5, 123.1, 122.8, 117.8 (d, *J* = 3.8 Hz), 93.9 (d, *J* = 8.8 Hz), 92.5 (d, *J* = 14.6 Hz), 66.4, 63.6, 61.5 (d, *J* = 7.4 Hz), 51.0, 49.0 (d, *J* = 8.7 Hz), 46.9 (d, *J* = 3.8 Hz), 46.2, 45.9, 37.3, 34.0 (d, *J* = 15.2 Hz), 28.7, 28.2, 26.7, 22.5, 20.7, 14.2.

^{31}P NMR (81 MHz, $CDCl_3$): δ 18.9.

$C_{67}H_{54}BF_{24}IrNP$	Calcd.:	C, 51.48	H, 3.48	N, 0.90
	Found:	C, 51.55	H, 3.39	N, 0.84

Synthesis of Ir-BARF complex (85b)



Prepared according to TP 15. The P,N-ligand **66b** (30 mg, 78 μmol,), $[Ir(cod)Cl]_2$ (26 mg, 39 μmol) and CH_2Cl_2 (5mL) were heated to reflux at 45 °C for 1 h, until ^{31}P NMR indicated that the ligand was consumed. After cooling to 25 °C, Na[BARF] (106 mg, 0.12 mmol) was added, followed by H_2O (5 mL), and the resulting two-phase mixture was stirred vigorously for 30 min. The residue was purified by column chromatography (50% CH_2Cl_2 in pentane) to afford **85b** (106 mg, 88 %) as an orange solid.

Mp: 85-90 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.62-8.54 (m, 1H), 7.80-7.00 (m, 25H), 4.86-4.62 (m, 1H), 4.56-4.42 (m, 1H), 4.36-4.20 (m, 1H), 3.90-3.78 (m, 1H), 3.10-2.90 (m, 1H), 2.80-1.00 (m, 18H), 0.85 (s, 3H).

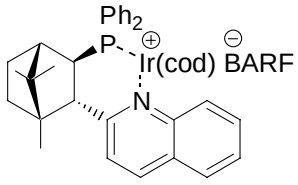
^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8-159.7 (m), 137.8 (d, J = 52.0 Hz), 133.7, 133.1 (d, J = 9.6 Hz), 131.3-127.6 (m), 123.2-120.3 (m), 116.5-116.4 (m), 83.1 (d, J = 3.8 Hz), 72.3, 66.5, 50.5 (d, J = 6.8 Hz), 41.9 (d, J = 8.7 Hz), 39.5-34.3 (m), 30.3, 27.2-26.2 (m), 23.9-23.1 (m).

^{31}P NMR (81 MHz, $CDCl_3$): δ 11.7.

MS (FAB): m/z = 686 (M^+, 23), 606 (100), 574 (57).

$C_{34}H_{40}IrNP$	HRMS:	Calcd.:	686.2528.
		Found:	686.2530.

Synthesis of Ir-BARF complex (85c)



Prepared according to TP 15. The P,N-ligand **66c** (98.8 mg, 0.22 mmol,), $[Ir(cod)Cl]_2$ (74 mg, 0.11 mmol) and CH_2Cl_2 (10 mL) were heated to reflux at 45 °C for 1 h, until ^{31}P NMR indicated that the ligand was consumed. After cooling to 25 °C, Na[BARF] (297 mg, 0.34 mmol) was added, followed by H_2O (10 mL), and the resulting two-phase mixture was stirred vigorously for 30 min. The residue was purified by column chromatography (50% CH_2Cl_2 in pentane) to afford **85c** (312 mg, 88 %) as an orange solid.

Mp: 165-169 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.43-8.39 (m, 1H), 7.68-7.04 (m, 27H), 4.77 (dd, *J* = 23.0, 11.0, 1H), 4.44-4.36 (m, 1H), 4.10-4.00 (m, 1H), 3.84-3.76 (m, 1H), 3.26-3.16 (m, 1H), 2.60-1.84 (m, 11H), 1.72-1.16 (m, 6H), 1.09 (s, 3H), 0.98 (s, 3H).

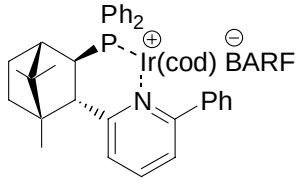
^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2-162.8 (m), 153.4, 141.4, 137.9 (d, *J* = 53 Hz), 136.9, 136.4 (d, *J* = 12.5 Hz), 135.3 (d, *J* = 9.4 Hz), 133.8 (d, *J* = 1.7 Hz), 133.5 (d, *J* = 2.1 Hz), 132.1-130.3 (m), 128.4, 126.6, 125.2-124.6 (m), 121.2, 119.6-119.5 (m), 95.6 (d, *J* = 8.7 Hz), 94.3 (d, *J* = 14.9 Hz), 68.2, 65.3, 63-3 (d, *J* = 7.5 Hz), 52.8, 50.7 (d, *J* = 8.5 Hz), 48.6 (d, *J* = 3.8 Hz), 47.9, 47.6, 39.1 (d, *J* = 3.6 Hz), 36.3, 35.9, 35.6 (d, *J* = 7.3 Hz), 30.5, 29.9, 28.9, 28.5 (d, *J* = 1.7 Hz), 24.3, 22.4.

^{31}P NMR (81 MHz, $CDCl_3$): δ 18.9.

MS (FAB): m/z = 751 ($[M+H]^+$, 100), 666 (14).

$C_{39}H_{44}IrNP$ HRMS: Calcd.: 750.2634.
Found: 750.2841.

Synthesis of Ir-BARF complex (85d)



Prepared according to TP 15. The P,N-ligand **66e** (152 mg, 0.32 mmol), $[Ir(cod)Cl]_2$ (107 mg, 0.16 mmol) and CH_2Cl_2 (4 mL) were heated to reflux at 45 °C for 1 h, until ^{31}P NMR indicated that the ligand was consumed. After cooling to 25 °C, Na[BARF] (297 mg, 0.34 mmol) was added, followed by H_2O (4 mL), and the resulting two-phase mixture was stirred

vigorously for 30 min. The residue was purified by column chromatography (50% CH_2Cl_2 in pentane) to afford **85e** (461 mg, 88 %) as an orange solid.

Mp: 86-92 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72-7.12 (m, 30H), 4.42 (t, *J* = 7.1 Hz, 1H), 4.03 (t, *J* = 7.1 Hz, 1H), 3.92-3.70 (m, 2H), 2.42-2.24 (m, 1H), 2.16-1.82 (m, 6H), 1.74-1.60 (m, 2H), 1.38-0.76 (m, 8H), 0.70 (s, 3H), 0.60-0.44 (m, 1H), 0.41 (s, 3H).

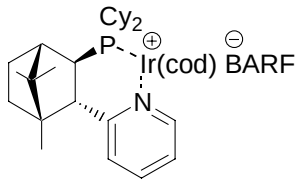
^{13}C NMR (75 MHz, $CDCl_3$): δ 163.3-159.7 (m), 137.9, 137.1, 135.3 (d, *J* = 10.8 Hz), 133.8, 131.6, 130.9 (d, *J* = 2.4 Hz), 130.7 (d, *J* = 10.5 Hz), 130.1 (d, *J* = 1.1 Hz), 129.3, 128.9-128.5 (m), 128.1-128.0 (m), 127.7-127.6 (m), 127.2 (s, *J* = 101 Hz), 125.3, 124.9, 124.3, 12.9, 122.2, 121.7, 121.1, 116.5-116.4 (m), 87.7, 80.0 (d, *J* = 2.9 Hz), 70.8 (d, *J* = 23.9 Hz), 63.4, 55.5 (d, *J* = 3.9 Hz), 49.5, 46.7 (d, *J* = 6.7 Hz), 44.4 (d, *J* = 5.3 Hz), 39.6 (d, *J* = 27.3 Hz), 36.6, 34.7 (d, *J* = 5.5 Hz), 31.5 (d, *J* = 8.3 Hz), 27.1, 26.3, 22.0 (d, *J* = 4.1 Hz), 19.7 (d, *J* = 24.8 Hz), 13.9.

^{31}P NMR (81 MHz, $CDCl_3$): δ 19.9.

MS (FAB): m/z = 776 (100), 666 (40).

$C_{41}H_{46}IrNP$ HRMS: Calcd.: 776.2997.
Found: 776.2998.

Synthesis of Ir-BARF complex (85e)



Prepared according to TP 15. The P,N-ligand **66e** (113 mg, 0.3 mmol,), $[Ir(cod)Cl]_2$ (101 mg, 0.15 mmol) and CH_2Cl_2 (4 mL) were heated to reflux at 45 °C for 1 h, until ^{31}P NMR indicated that the ligand was consumed. After cooling to 25 °C, Na[BARF] (297 mg, 0.34 mmol) was added, followed by H_2O (4 mL), and the resulting two-phase mixture was stirred vigorously for 30 min. The residue was purified by column chromatography (50% CH_2Cl_2 in pentane) to afford **85e** (354 mg, 75 %) as an orange solid.

Mp: 154-160 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ 8.60-8.52 (m, 1H), 7.80-7.20 (m, 15H), 5.00-4.90 (m, 1H), 4.80-4.60 (m, 1H), 4.30-4.18 (m, 1H), 4.10-3.98 (m, 1H), 3.76-3.60 (m, 1H), 2.60-2.40 (m, 2H), 2.30-0.98 (m, 43H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1-161.1 (m), 152.0, 139.7, 135.2, 130.3-128.6 (m), 126.7, 124.8, 123.1, 122.9, 119.5, 117.8 (d, *J* = 0 3.8 Hz), 89.8 (d, *J* = 8.1 Hz), 87.2 (d, *J* = 14.5 Hz), 64.9, 61.7 (d, *J* = 6.4 Hz), 50.6, 48.5 (d, *J* = 7.7 Hz), 47.9, 41.7-40.5 (m), 33.4, 31.6, 31.0, 30.4, 29.6, 28.3-25.9 (m), 26.1, 25.9, 21.5, 20.5, 14.1.

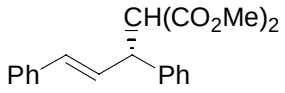
^{31}P NMR (81 MHz, $CDCl_3$): δ 14.3.

MS (FAB): m/z = 776 ($[M+H]^+$, 100), 600 (22).

$C_{35}H_{54}IrNP$ HRMS: Calcd.: 712.3623.
Found: 712.3625.

9 Applications in asymmetric catalysis

Synthesis of *trans*-(*R*)-methyl 2–carbomethoxy-3,5-diphenylpent-4-enolate (78)[114]



Prepared according to TP 16. Ligand **66a** (10 mg, 25 μmol, 5.0 mol%), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.6 mg, 12.5 μmol, 2.5 mol%) and potassium acetate (3.5 mg, 25 μmol, 5.0 mol%) were dissolved in CH_2Cl_2 (1 mL) and stirred at 25 °C for 15 min. 3-Acetoxy-1,3-diphenyl-propene (**77**) (126 mg, 0.5 mmol) in CH_2Cl_2 (2 mL), dimethyl malonate (0.2 mL, 1.5 mmol) and *N*, *O*-bistrimethylsilylacetamide (0.4 mL, 1.5 mmol) were added. The reaction mixture was stirred at 25 °C for 1 h. The crude product was purified by flash chromatography (5% EtOAc in pentane), affording (*R*)-**78** (122 mg, 75 %, 96 % *ee*) as a white solid.

HPLC (Chiralcel OD-H, *n*-heptane/*i*-PrOH 98/2, 0.4 mL/min, 215 nm): t_r/min = 25.0 (*R*), 27.1 (*S*).

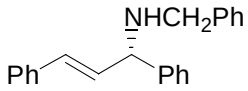
Mp: 93-95 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.06 (m, 10H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.25 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.19 (dd, *J* = 10.9, 8.4 Hz, 1H), 3.88 (d, *J* = 10.9 Hz, 1H), 3.61 (s, 3H), 3.43 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 167.7, 140.2, 136.8, 131.8, 129.1, 128.7, 128.4, 127.8, 127.5, 127.1, 126.3, 57.6, 52.5, 52.3, 49.1.

IR (KBr, cm^{-1}): 1760, 1738, 1495, 1454, 1370, 1158.

Synthesis of (*R*,*E*)-N-benzyl-(1,3-diphenyl-2-propenyl)amine (79)[116]



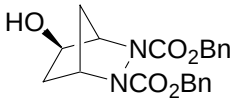
Prepared according to TP 17. $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (1.5 mg, 4.0 μmol, 1.0 mol%) and ligand **66b** (3.1 mg, 8.0 μmol, 2.0 mol%) were dissolved in toluene (1 mL) and stirred at room temperature for 10 min. A solution of 3-acetoxy-1,3-diphenyl-propene (**77**) (100 mg, 0.4 mmol) in toluene (3 mL) was added and stirring was maintained for 15 min. Benzylamine (86 mg, 0.8 mmol) was added. The resulting solution was stirred at 25 °C for 12 h. The crude product was purified by flash chromatography (20 %Et_2O in pentane), affording (*R*)-**79** (114 mg, 95 %, 87 % *ee*) as a a pale yellow oil.

HPLC (Chiralcel OD-H, *n*-heptane/*i*-PrOH 95/5, 0.5 mL/min, 215 nm): t_r/min = 45.0 (*R*), 48.8 (*S*).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.08 (m, 15H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.24 (dd, *J* = 15.9, 7.2 Hz, 1H), 4.32 (d, *J* = 7.5 Hz, 1H), 3.73 (*J* = 15.6 Hz, 1H, AB system), 3.69 (*J* = 15.6 Hz,1, AB system), 1.60 (br s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 140.8, 137.4, 133.0, 130.7, 129.0, 128.9, 128.8, 128.6, 127.8, 127.7, 127.6, 127.3, 126.8, 65.0, 51.8.

Synthesis of dibenzyl 5-hydroxy-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (81a)[118]



Prepared according to TP 18, $[Ir(cod)Cl]_2$ (3.4 mg, 5 μmol, 1 mol%), ligand **66a** (4.2 mg, 10.5 μmol, 2.1 mol%) and **80a** (182 mg, 0.5 mmol) were placed under argon in a flame-dried Schlenk tube. THF (0.85 mL) was degassed at –50 °C and added to the mixture at this temperature. The reaction was stirred at room temperature for 30 min and cooled to 0 °C. Catecholborane (0.11 mL, 1 mmol) was added at 0 °C and stirred for 4 h. EtOH (0.5 mL), 3 M NaOH (0.85 mL) and 30 % H_2O_2 (0.5 mL) were added and stirred at 25 °C for 16 h. The

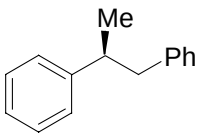
crude product was purified by flash chromatography (50% EtOAc in cyclohexane), affording (1*R*,4*R*,5*R*)-**81a** (145 mg, 76 %, 71 % *ee*) as a colourless liquid.

HPLC (Chiralcel AD, *n*-hexane/*i*-PrOH 80/20, 0.8 mL/min, 220 nm): t_r/min = 14.6 (1*S*,4*R*,5*R*), 16.4 (1*R*, 4*S*,5*S*).

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.35 (m, 10H), 5.16 (m, 4H), 4.68 (s, 1H), 4.52 (s, 1H), 4.28 (s, 1H), 2.04-1.98 (m, 2H), 1.97 (d, *J* = 10.5 Hz, 1H), 1.54 (d, *J* = 10.5 Hz, 1H), 1.46 (dt, *J* = 13.7, 2.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 155.0, 135.9, 135.8, 128.3, 128.0, 70.4, 68.2, 68.1, 64.3, 59.6, 38.0, 34.0.

Synthesis of (*S*)-1,2-diphenylpropane (87a)[121]



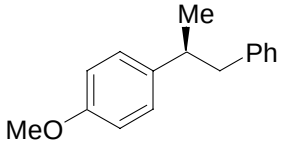
Prepared according to TP 19. Catalyst **85c** (6.5 mg, 4 μmol, 1 mol%), and *E*-1,2-diphenyl-propene (**86a**) (77 mg, 0.4 mmol) in toluene (2 mL) were added into the autoclave. The autoclave was sealed and pressurized to 50 bar H_2 and the mixture was stirred at rt for 2 h. After the crude product was passed through a short column (pentane), (*S*)-**87a** was obtained in quantitative yield, 95 % *ee* as a colourless oil.

HPLC (Chiralcel OJ, *n*-heptane/*i*-PrOH 99/1, 0.5 mL/min, 215 nm): t_r/min = 13.1 (*R*), 16.1 (*S*).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-6.96 (m, 10H), 2.98-2.82 (m, 2H), 2.74-2.64 (m, 1H), 1.16 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.4, 141.2, 129.6, 128.7, 128.5, 127.4, 126.4, 126.2, 45.4, 42.3, 21.5.

Synthesis of (*E*)-2-(4-methoxyphenyl)-1-phenylpropane (87b)[121]



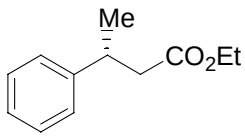
Prepared according to TP 19. Catalyst **85c** (3.3 mg, 2 μmol, 1 mol%), and *E*-1-phenyl-2-(4-methoxyphenyl)-1-propene (**86b**) (45 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) were added into the autoclave. The autoclave was sealed and pressurized to 50 bar H_2 and the mixture was stirred at rt for 2 h. After the crude product was passed through a short column (pentane), (*S*)-**87b** was obtained in quantitative yield, 95.2 % *ee* as a colourless oil.

HPLC (Chiralcel OJ, *n*-heptane/*i*-PrOH 95/5, 0.5 mL/min, 215 nm): t_r/min = 13.1 (*R*), 16.1 (*S*).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-6.96 (m, 7H), 6.76-6.72 (m, 2H), 3.70 (s, 3H), 2.92-2.78 (m, 2H), 2.70-2.62 (m, 1H), 1.13 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2, 141.3, 139.5, 129.6, 128.5, 128.3, 126.2, 114.1, 55.6, 45.7, 41.4, 21.8.

Synthesis of 3-phenylbutanoate (88)[121]



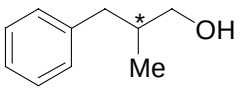
Prepared according to TP 19. Catalyst **85c** (7.3 mg, 4.5 μmol, 1 mol%), and ethyl *trans*-β-methylcinnamate **86b** (85 mg, 0.45 mmol) in toluene (1 mL) were added into the autoclave. The autoclave was sealed and pressurized to 50 bar H_2, and the mixture was stirred at rt for 2 h. After the crude product passed through the short column (pentane), (*S*)-**87b** was obtained in 58 % *ee* as a pale yellow oil.

HPLC (Chiralcel OB, *n*-heptane/*i*-PrOH 99.5/0.5, 0.5 mL/min, 215 nm): 13.3 (*R*), 15.2 (*S*) min.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.08 (m, 5H), 3.99 (q, *J* = 7.2 Hz, 2H), 3.25-3.14 (m, 1H), 2.56-2.40 (m, 2H), 1.22 (d, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 146.1, 128.9, 127.1, 126.8, 60.6, 43.4, 36.9, 22.2, 14.6.

Synthesis of 3-phenyl-2-methylallyl alcohol (89a)[121]



Prepared according to TP 19, Catalyst **85c** (7.0 mg, 4.3 μmol, 1 mol%), and *trans*-2-methyl-3-phenyl-2-propen-1-ol (**89**) (64 mg, 0.43 mmol) in toluene (0.5 mL) were added to the autoclave. The autoclave was sealed and pressurized to 50 bar H_2 and the mixture was stirred at rt for 16 h. After the crude product passed through the short column (33% Et_2O in pentane), **89a** was obtained in 69 % *ee* as a colourless oil.

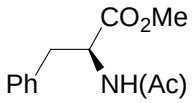
HPLC (Chiralcel OD-H, *n*-heptane/*i*-PrOH 95/5, 0.5 mL/min, 215 nm): 16.5/18.9 min.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.06 (m, 5H), 3.48-3.36 (m, 2H), 2.68 (dd, *J* = 13.5, 6.2 Hz, 1H), 2.35 (dd, *J* = 13.5, 8.1 Hz, 1H), 1.94-1.80 (m, 1H), 1.31 (br s, 1H), 0.85 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 141.0, 129.5, 128.6, 126.3, 68.1, 40.1, 38.2, 16.8 ppm.

For 3-phenyl-2-methylallyl acetate (**90a**) was hydrolyzed ($MeOH/K_2CO_3$) to 3-phenyl-2-methylallyl alcohol (**89a**, 80 % *ee*).

Synthesis of *N*-acetylphenylalanine methyl ester (92)[112]



Prepared according to TP 20. Catalyst **85a** (4.7 mg, 3.0 μmmol, 1 mol%), methyl (*Z*)-α-(acetamido)cinnamate **91** (65 mg, 0.3 mmol), CH_2Cl_2 (3 mL) and MeOH (0.3 mL) were charged in an autoclave. The autoclave was sealed and pressurized to 1 bar of H_2, and the mixture was stirred at 50 °C for 2 h. After evaporation of the solvent, (*S*)-**92** was obtained in quantitative yield and 96.5 % *ee* as a white solid.

GC (140 °C, column): t_r/min = 10.5 (*R*), 11.5 (*S*).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.14 (m, 3H), 7.02-7.00 (m, 2H), 6.04 (d, *J* = 7.2 Hz, 1H), 4.84-4.76 (m, 1H), 3.64 (s, 3H), 3.12-2.96 (m, 2H), 1.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 169.0, 135.3, 128.6, 127.9, 126.4, 52.5, 51.6, 37.1, 22.4.

10 Data for the x-ray crystallography analyses

Data related to the aminophosphine oxide 65a

Empirical formular	$C_{27}H_{30}NOP$
Formular weight	415.49
Temperature	295 (2)K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1$ (No.4)
Unit cell dimensions	a = 9.438(2) Å
	b = 12.063(14) Å β = 103.508 (13)°
	c = 10.701(9) Å
Volume	1184.6 (3) Å ^{3}
Z	2
Density (calculated)	1.165 Mg/m^3
Absorption coefficient	0.134 mm^{-1}
F(000)	444
Crystal size	0.27 x 0.43 x 0.53 mm
Theta range for data collection	6.80 to 23.99 deg
Index ranges	-10≤h≤10, -13≤k≤13, -12≤l≤12
Reflections collected	4489
Independent reflections	3611 [R (int) = 0.0161]
Absorption correction	
Max. and min. transmission	0.9969 and 0.7934
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2373/274/1
Goodness-of-fit on F^2	1.101
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0447
R indices (all data)	R1 = 0.0970, wR2 = 0.1022
Absolute structure parameter	-0.04 (10)
Largest diff. Peak and hole	0.280 and –0.136 Å ^{3}

Data related to the aminophosphine oxide 65d

Empirical formular	$C_{32}H_{32}NOP$
Formular weight	477.56
Temperature	295 (2)K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P2_1$ (No.2)
Unit cell dimensions	a = 10.856(2) Å α = 105.86 (2)°
	B = 11.450(2) Å β = 92.166 (15)°
	C = 12.027(2) Å γ = 113.13 (2)°
Volume	1304.6 (4) $Å^3$
Z	2
Density (calculated)	1.216 Mg/m^3
Absorption coefficient	0.130 mm^{-1}
F(000)	508
Crystal size	0.20 x 0.33 x 0.53 mm
Theta range for data collection	2.95 to 23.98 deg
Index ranges	$-12\leq h\leq 12$, $-13\leq k\leq 12$, $0\leq l\leq 13$
Max. and min. transmission	0.9996 and 0.9760
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2465/318/0
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1054
R indices (all data)	R1 = 0.0792, wR2 = 0.1207
Absolute structure parameter	
Largest diff. Peak and hole	0.176 and –0.219 $Å^3$

Data related to the phosphine-borane complex of 66a

Empirical formular	$C_{27}H_{33}BNP$
Formular weight	413.32
Temperature	295 (2)K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No.2)
Unit cell dimensions	a = 9.5277(15) Å
	B = 12.1999(15) Å
	C = 19.917(3) Å
Volume	2315.1 (6) $Å^3$
Z	4
Density (calculated)	1.186 Mg/m^3
Absorption coefficient	0.133 mm^{-1}
F(000)	888
Crystal size	0.20 x 0.33 x 0.57 mm
Theta range for data collection	2.37 to 23.97 deg
Index ranges	$-10\leq h\leq 10$, $-13\leq k\leq 13$, $-22\leq l\leq 22$
Reflections collected	4263
Independent reflections	3596 [R (int) = 0.0158]
Absorption correction	
Max. and min. transmission	0.9977 and 0.9767
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2460/275/0
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0813
R indices (all data)	R1 = 0.0378, wR2 = 0.0853
Absolute structure parameter	-0.01 (10)
Largest diff. Peak and hole	0.135 and –0.160 $Å^3$

Data related 1,2-diphosphine oxide (102)

Empirical formular	$C_{30}H_{32}O_4P_2$
Formular weight	518.50
Temperature	295 (2)K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No.19)
Unit cell dimensions	a = 8.105 (4) Å
	b = 8.729 (3) Å
	C = 37.158 (12) Å
Volume	2628.9 (17) $Å^3$
Z	4
Density (calculated)	1.310 Mg/m^3
Absorption coefficient	0.200 mm^{-1}
F(000)	1096
Crystal size	0.23 x 0.43 x 0.57 mm
Theta range for data collection	2.57 to 23.98 deg
Index ranges	$-9\leq h\leq 9$, $-9\leq k\leq 9$, $-42\leq l\leq 42$
Reflections collected	4774
Independent reflections	4082 [R (int) = 0.0126]
Absorption correction	
Max. and min. transmission	0.9952 and 0.7830
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2541/328/0
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1061
R indices (all data)	R1 = 0.0487, wR2 = 0.1128
Absolute structure parameter	-0.01 (11)
Largest diff. Peak and hole	0.333 and –0.278 $Å^3$

11 Abbreviations

Ac	Acetyl
Bp	Boiling point
br	Broad
Bn	Benzoyl
BARF	Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
BSA	*N*,*O*-Bistrimethylsilylacetamide
t-Bu	*tert*-Butyl
Boc	*tert*-Butoxycarbonyl
Bu	Butyl
COD	1,4-Cyclooctadiene
Cy	Cyclohexyl
Calcd.	Calculated
cat.	Catalytic
Conv.	Conversion
°C	Degree celcious
δ	Chemical shift
dppb	1,4-Bisdiphenylphosphinobutane
DMSO	Dimethylsulfoxide
dppe	1,2-Bisdiphosphinoethane
dppf	1,1´-Bisdiphenylphosphinoferrocene
dba	Dibenzylideneacetone
DIBAL-H	Diisobutylaluminium hydride
Et	Ethyl
EI	electron ionization
equiv.	Equivalent
ee	Enantiomeric excess
FG	Functional group
GC	Gas chromatography
h	Hour
HRMS	High resolution mass
Hz	Hertz
HPLC	High performance liquid chromatography
IR	Infrared

i-Pr	*iso*-Propyl
J	Coupling constant
LDA	Lithium diisopropylamide
M	Molar
Me	Methyl
min	Minute
Mp	Melting point
mL	Millilitre
MS	Mass spectroscopy
M^+	Molecular ion peak
m	Multiplet
mL	Millilitre
mmol	Millimole
NMP	N-methyl-pyrrolidone
NMR	Nuclear magnetic resonance
NuH	Nucleophiles
Ph	Phenyl
q	Quartet
rac.	Racemic
rt	Room temperature
s	Singlet
t	Triplet
Tf	Triflate
tlc	Thin layer chromatography
TP	Typical procedure
THF	Tetrahydrofuran

CURRICULUM VITAE

Name: Tanasri Bunlaksananusorn
Date of birth: 23 December 1974
Nationality: Thai

EDUCATIONAL BACKGROUND

2000 to present: **PhD Student at Ludwig-Maximilians-University, Munich under the guidance of Prof. Dr. Paul Knochel**
Thesis Title: "Novel Synthesis of Chiral 1,2-Aminophosphine Ligands and Their Applications in Asymmetric Catalysis"

1997-1999: **Master of Science** (Organic Chemistry) at the Mahidol University (Bangkok, Thailand) under the guidance of Prof. Dr. Manat Pohmakotr
Thesis Title: "Spirocyclic System via Intramolecular Acylation of α-Sulfinyl Carbanions: A Convenient Synthesis of Spiro[4.n]Alk-2-Ene-1,6-Diones and Spiro[5.n]Alk-2-Ene-1,7-Diones"

1993-1997: **Bachelor of Science** (Chemistry) at Mahidol University (Bangkok, Thailand)

TRAINING AND WORK EXPERIENCES

May 2003: Pratikum in Bayer Chemicals (Leverkusen)

Jan 2003-Feb 2003: Exchange Student in CNRS UMR 8638 (Faculty of pharmacy of Paris) under the guidance of Dr. Laurent Micouin

2000-2003: Teaching and lab-courses for organic chemistry students at the Ludwig-Maximilians-University, Munich

PUBLICATIONS & PATENT

[1] Bunlaksananusorn, T.; Pohmakotr, M.; Tuchinda, P. "A general strategy to spiro[4.*n*]alk-2-ene-1,6-diones and spiro[5.*n*]alk-2-ene-1,7-diones via intramolecular acylation of α-sulfinyl carbanions" *Tetrahedron Lett.* **2000**, *41*, 377.
[2] Knochel, P.; Boudier, A.; Bromm, L. O.; Hupe, E.; Varela, J. A.; Rodriguez, A. L; Koradin, C.; Bunlaksananusorn, T.; Laaziri, H.; Lhermitte, F. "Selective transformations mediated by main-group organometallics" *Pure Appl. Chem.* **2000**, *72*, 1699.
[3] Rodriguez, A. L.; Bunlaksananusorn, T.; Knochel, P. "Potassium *tert*-Butoxide Catalyzed Addition of Carbonyl Derivatives to Styrenes" *Org. Lett.* **2000**, *21*, 3285.

[4] Bunlaksananusorn, T.; Rodriguez, A. L.; Knochel, P. "*t*-BuOK-catalyzed addition of ketones and nitriles to vinylic silanes, phosphines and thio derivatives" *J. Chem. Soc., Chem. Commun.* **2001**, 745.
[5] Knochel, P.; Hupe, E.; Dohle, W.; Lindsay, D. M.; Veronique, Q.; Bonnet, V.; Boudier, A.; Kopp, F.; Demay, S.; Seidel, N.; Calaza, M. I.; Vu, V. A.; Sapountzis, I.; Bunlaksananusorn, T. "Functionalized main-group organometallics for organic synthesis" *Pure Appl. Chem*. **2002**, *74***,** 11.
[6] Bunlaksananusorn, T.; Knochel, P. "*t*-BuOK-catalyzed addition phosphines to functionalized alkenes: a convenient synthesis of polyfunctional phosphine derivatives" *Tetrahedron Lett*. **2002**, *43*, 5817.
[7] Bunlaksananusorn, T.; Polborn, K.; Knochel, P. "New P,N-Ligands for the Performance of Asymmetric Ir-Catalyzed Reactions" *Angew. Chem., Int. Ed*. **2003**, *42*, 3941.
[8] Bunlaksananusorn, T.; Luna, A. P.; Bonin, M.; Micouin, L.; Knochel, P. "New Applications of Camphor-Derived P,N-Ligands for Asymmetric Pd- and Ir-Catalyzed Reactions", *Synlett* **2003**, *in press*.

ORAL COMMUNICATION & POSTERS

Poster/June 2003: "*t*-BuOK-Catalyzed Addition Phosphines to Functionalized Alkenes: A Convenient Synthesis of Polyfunctional Phosphine Derivatives"
Bunlaksananusorn, T.; Knochel, P. Heidelberg Forum of Molecular Catalysis 2003, Heidelberg

Talk/January 2003: "Asymmetric Hydroboration in Organic Syntheses" at the Ludwig-Maximilians-University, Munich

Poster/July 2001: "Potassium *tert*-Butoxide Catalzyed Addtion of Nitriles, Ketones and Phosphines to Vinylic Silanes, Phosphines and Thio Derivatives"
Bunlaksananusorn, T.; Knochel, P. OMCOS-11, Taipei, Taiwan

Poster/December 2000: "The Catalytic Addition of Carbonyl Derivatives to Styrenes"
Bunlaksananusorn, T.; Knochel, P. 4th Sigma-Aldrich Symposium So Cress, Spa Belgium

Languages: Thai (Mother Tongue)
English (Fluent written and spoken)
German (Mitte Stufe 2)