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Synthesis of New Chiral Phosphine Ligands and Their Applications in Asymmetric Catalysis

von

Murthy Narasimha Cheemala

aus

Eluru, India

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Erklärung

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Ehrenwörtliche Versicherung

Diese Dissertation wurde selbständig, und ohne unerlaubte Hilfe erarbeitet.

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Murthy Narasimha Cheemala

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4. Cheemala, M. N.; Knochel, P. "Synthesis of New Ferrocenyl P,N-ligands and their Applications in Asymmetric Catalysis" *Manuscript in Preparation.*

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To my parents

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1. General Introduction

Molecular chirality plays a key role in science and technology.[1] Many organic compounds are chiral and many enantiomerically pure compounds are widely used in the preparation of cosmetics, flavours, pesticides, vitamins and pharmaceuticals.[2] There are many examples which stress the necessity for preparing enantiomerically pure compounds. For example, the market for single enantiomer drugs in 1996 was $ 73 billion, which increased to $ 96 billion in 1998 and to $ 123 billion in 2000. The market for enantiopure materials continues to increase[3]; hence the search for efficient ways to access enantiomerically enriched compounds is still an active area of research to synthetic organic chemists.[4]

To access enantiomerically pure compounds there are four main approaches.

1. Resolution of a racemic mixture
2. Synthesis from a chiral pool and synthesis using a chiral auxiliary[5]
3. Synthesis using biocatalysts (enzymes, cell cultures and antibody)[6]
4. Asymmetric catalysis using a man made chiral catalyst.

Among this variety of methods, asymmetric catalysis has proved to be an ideal method to prepare naturally and nonnaturally occurring chiral compounds in large quantities by using small amounts of chiral catalyst.

In the past three decades, many metal complexes using various chiral ligands have been found that catalyze various reactions with impressive enantioselectivities. However, despite the impressive progress in this area, the design of suitable chiral ligands for a particular application remains a formidable task.[7] Hence the design of new chiral ligands for

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[1] Noyori, R. *Adv. Synth. Catal.* **2003**, *345*, 15.

[2] a) Gawley, R. E.; Aube, J. *Principles of Asymmetric Synthesis*; 1996, Pergamon: Oxford, p 1 b) *Chirality in Industry: The Commercial Manufacture and Applications of Optically Active Compounds*; Collins, A. N., Sheldrake, G. N., Crosby, G., Eds.; Wiley-Interscience: New York, 1992. c) Sheldon, R. A. *Chirotechnology. Industrial Synthesis of Optically Active Compounds*; Dekker, M., Ed.; New York, 1993. d) Scott, J. W. In *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley-Interscience: New York, 1991, Vol. 19, p 209-226. e) Crossley, R. *Tetrahedron* **1992**, *48*, 8155.

[3] a) Stinson, S. C. *Chem. Eng. News* **1999**, *77*, 101. (b) Stinson, S. C. *Chem. Eng. News* **2001**, *79*, 45.

[4] McCarthy, M.; Guiry, P. J. *Tetrahedron*, **2001**, *57*, 3809.

[5] Aitken, R. A.; Kilenyi, S. N. *Asymmetric synthesis;* Blackie: London, **1994**.

[6] Wong, C.-H.; Whitesides, G. M. *Enzymes in Synthetic Organic Chemsitry;* Pergamon: Oxford, 1994.

[7] Pfaltz, A.; Drury, W. J., III; *Proc. Nat. Acad. Sci.* **2004**, *101*, 5723.

asymmetric catalysis is a highly active field of research[8] that concentrates especially, on chiral P,P and P,N-ligands, since this type of ligands plays a wide role in transition-metal-catalyzed asymmetric reactions.

1.1 Chiral P,P-ligands

The concept of C_2-symmetry in ligands was first introduced when Kagan developed the ligand DIOP.[9] The main advantage of having a C_2-symmetrical axis in ligands is that it reduces the number of possible competing, diastereomeric transition states.[10] In 1980, Noyori reported an axially chiral ligand, BINAP, which expanded the scope of transition-metal-catalyzed asymmetric hydrogenations.[11,12] Since then many chiral P,P-ligands have been prepared and have played a successful role in transition-metal-catalyzed asymmetric reactions. BPPM[13] (Achiwa), CHIRAPHOS[14] (Bosnich), DuPHOS[15] (Burk), BICP[16] (Zhang), PHANEPHOS[17] (Rossen), PENNPHOS[18] (Zhang), BIPHEMP[19] (Schönholzer), P-PHOS[20] (Chan), SEGPHOS[21] (Mikami) and TANGPHOS[22] (Zhang) are some of the successful examples in this field (Figure 1).

[8] a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis;* Wiely: New york, 1994. b) Ohkuma, T.; Kitamura, M.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: Weinheim, 2000, p 1. c) Splinder, F.; Blaser, H.-U. In *Transition Metals for Organic Synthesis*, 2nd ed.; Beller, M., Bolm, c., Eds.; Wiley-VCH: Weinheim, 2004, Vol. 2, p 113-123. d) Blaser, H.-U.; Splider, F. In *Comprehensive Asymmetric Catalysis;* Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 1999, Vol. 1, pp 247-265.
[9] Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429.
[10] Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.
[11] a) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. b) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345.
[12] a) Ohta, T.; Takaya, H.; Kitamura, M.; Nagai, K.; Noyori, R. *J. Org. Chem.* **1987**, *52*, 3174. b) Noyori, R.; Ohkuma, T.; Kitamura, M.; Takaya, H.; Sayo, N.; Kumobayashi, H.; Akutagawa, S. *J. Am. Chem. Soc.* **1987**, *109*, 5856. c) Noyori, R.; Ohkuma, T. *Angew. Chem, Int. Ed.* **2001**, *40*, 40.
[13] Achiwa, K. J. *J. Am. Chem. Soc.* **1976**, *98*, 8256.
[14] Fryzuk, M. D.; Bosnich, B. J. *J. Am. Chem. Soc.* **1977**, *99*, 6262.
[15] Burk, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 8518.
[16] Zhu, G.; Cao, P.; Jiang, Q.; Zhang, Q. *J. Am. Chem. Soc.* **1997**, *119*, 1799.
[17] Pye, P. J.; Rossen, K.; Reaner, R. A.; Tsou, N. N.; Volante, R. P.; Reider, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 6207.
[18] Jiang, Q.; Jiang, Y.; Xiao, D.; Cao, P.; Zhang, X. *Angew. Chem. Int. Ed.* **1998**, *37*, 1100.
[19] Schmid, R.; Cereghetti, M.; Heiser, B.; Schönholzer, P. *Helv. Chim. Acta* **1998**, *71*, 897.
[20] Pai, C.; Lin, C.; Chen, C.; Chan, A. S. C. *J. Am. Chem. Soc.* **2000**, *122*, 11513.
[21] Hatano, M.; Terada, M.; Mikami, K. *Angew. Chem. Int. Ed.* **2001**, *40*, 249.
[22] Tang, W.; Zhang, X. *Angew. Chem. Int. Ed.* **2002**, *41*, 1612.

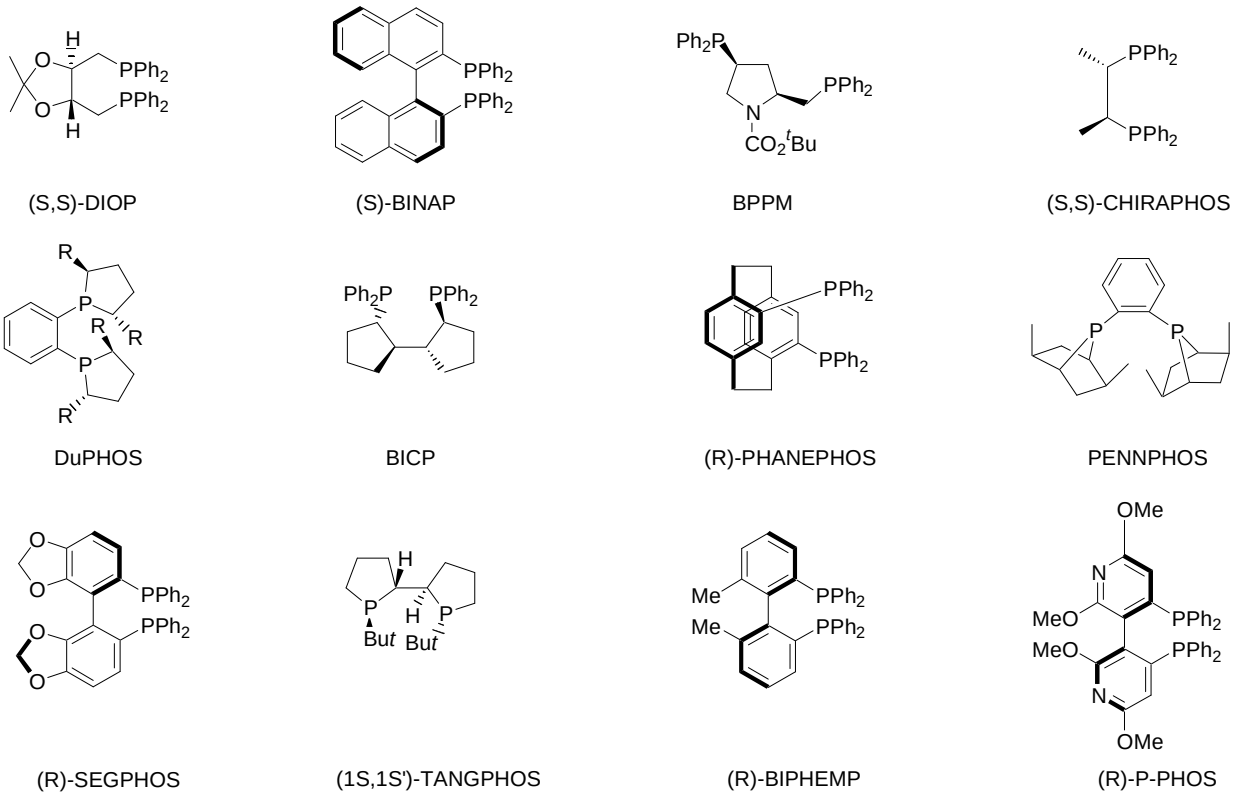
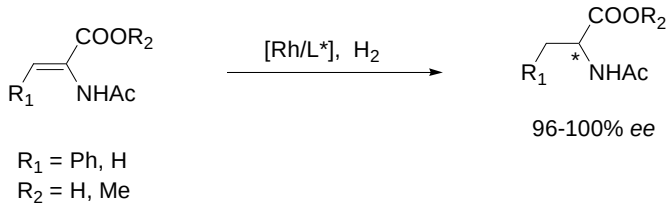


Figure 1. Chiral diphosphine ligands

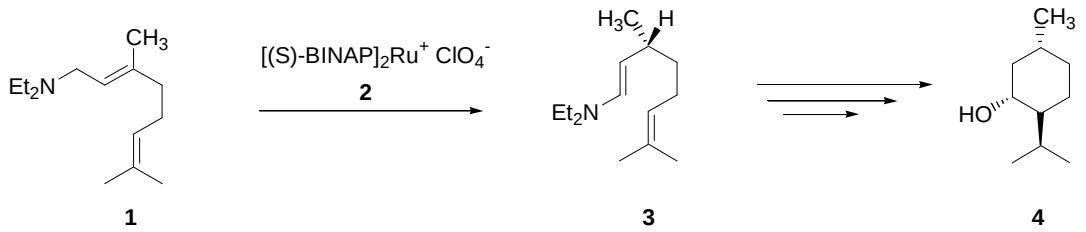
These ligands were extensively employed in Rh-catalyzed asymmetric hydrogenation of enamides giving rise to the corresponding amino acid derivatives with high enantioselectivities (Scheme 1).[23]



Scheme 1. Asymmetric hydrogenation of enamides using chiral diphosphine ligands

One of the outstanding industrial achievements using these chiral ligands in asymmetric catalysis is the widely known Takasago's industrial synthesis of (–)-menthol (**4)** starting from myrcene. The crucial step is asymmetric isomerization of diethylgeranylamine (**1)** to 3-(*R*)-citronellal enamine (**3)** using the catalyst [(*S*)-BINAP]$_2$Ru$^+$ClO$_4^-$ (**2**) (Scheme 2).[24]

[23] Ojima, I. *Catalytic Asymmetric Synthesis*, 2nd ed.; Wiley-VCH: Weinhem, 2000.
[24] a) Tani, T.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, T. *J. Am. Chem. Soc.* **1984**, *106*, 5208.



Scheme 2. Takasago's industrial synthesis of (−)-menthol using (*S*)-Binap.

1.1.1 Ferrocenyl P,P-ligands

Since the discovery of ferrocene in 1951,[25] its fascinating sandwich structure has caught the attention of chemists as a potential platform for the preparation of new ligands for asymmetric catalysis.[26] A very interesting structural feature in ferrocene chemistry is planar chirality. This means that compounds substituted at positions 1 and 2 with different groups are chiral because of the loss of plane of symmetry (Figure 2).

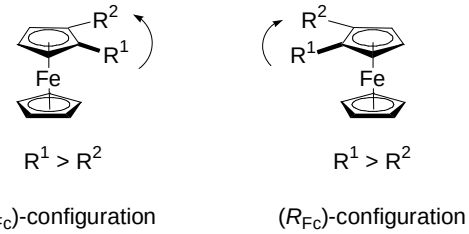


Figure 2. Planar chirality in 1,2-disubstituted ferrocene

The pioneering work of Ugi[27] *et al.* on the C_2-functionalization of enantiopure *N*,*N*-dimethyl-1-ferrocenylethylamine, in which planar chirality was introduced into the ferrocene backbone using a diastereoselective *ortho* lithiation with an appropriate chiral *ortho*-directing group and subsequent *in situ* trapping with an electrophile has become a standard methodology for the preparation of such compounds. In 1974 Hayashi reported the first example of a planar-chiral enantiopure ferrocenyl phosphine by introducing the ligand PPFA (*N*,*N*-dimethyl-1-[2-(diphenylphosphino)ferrocenyl]ethylamine.[28] Its high reactivity was a

[25] Kelay, T. J.; Pauson, P. J. *Nature* **1951**, *168*, 1039.
[26] For reviews see a) Hayashi, T. In *Organic Synthesis: An Interdisciplinary Challenges*; Streith, J., Prinzbach, H., Schill, G., Eds.; Blackwell: London, 1985, p 35-42. b) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395. c) Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101. d) Arrayás, R. G.; Adiro, J.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 7674.
[27] Markarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389.
[28] Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, 4405.

landmark in the development of chiral ferrocene ligands for asymmetric catalysis. Josiphos,[29] Taniaphos,[30] Walphos[31] and Bophoz[32] are some successful examples (Figure 3).

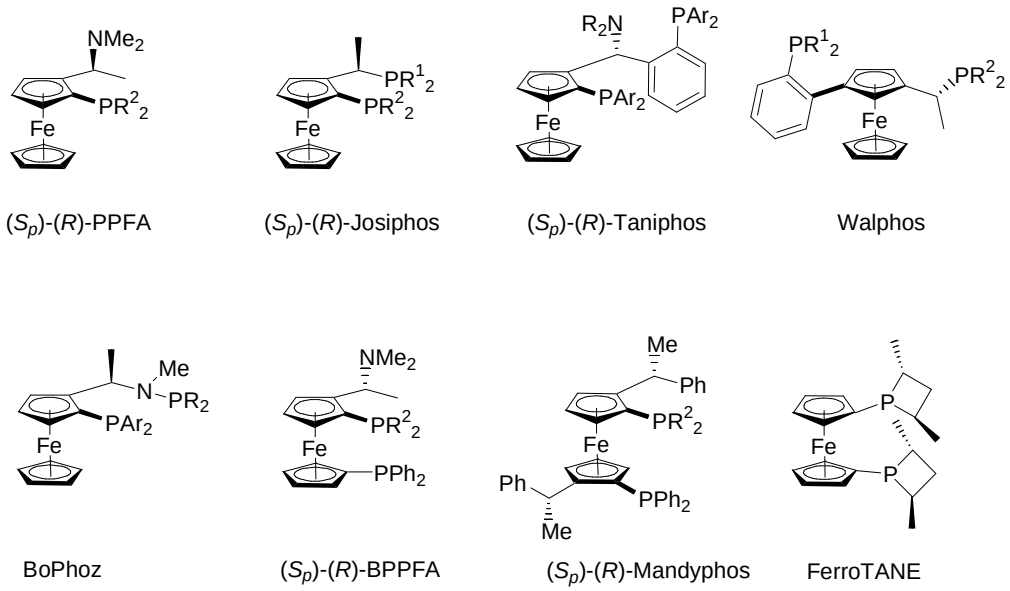
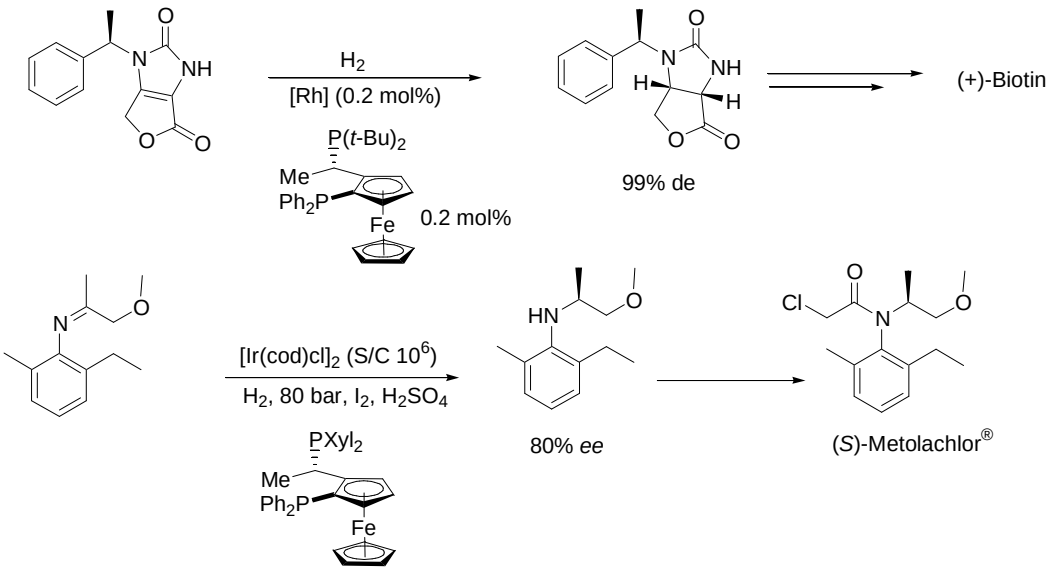


Figure 3. Chiral ferrocenyl P,P-ligands.

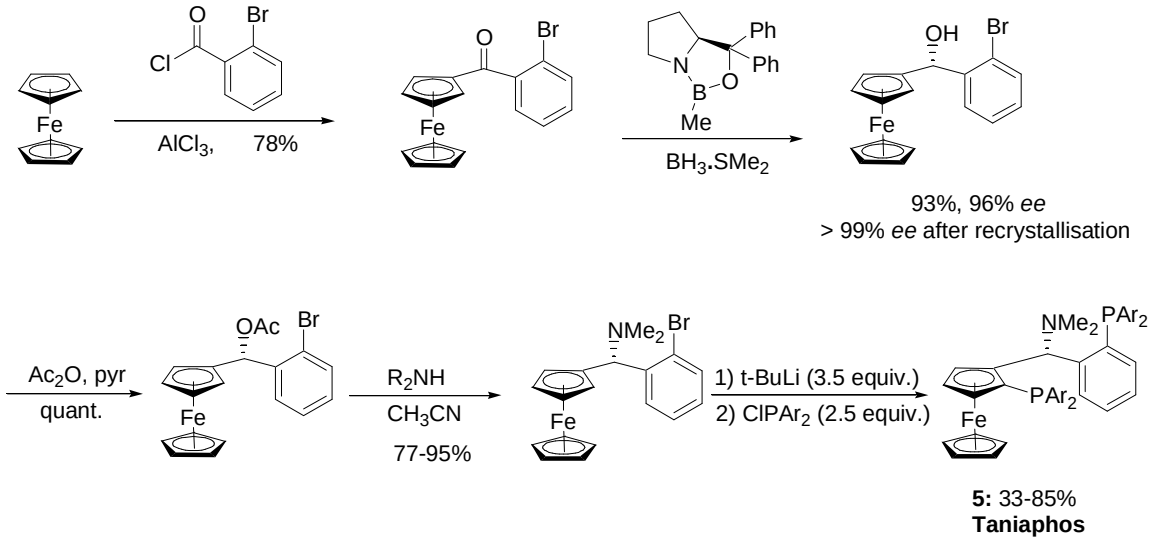
These ligands were successfully applied in Rh, Ru, Ir, and Pd-catalyzed asymmetric reactions providing high enantioselectivities and also noteworthy applications in industrial chemistry.[26c] One of the intensive application to mention here is the preparation of (+)–Biotin (Lonza AG)[33,34] and (*S*)-Metolachlor® (Syngenta)[33,35] using Josiphos by transition-metal-catalyzed hydrogenation reactions (Scheme 3).

[29] Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc*. **1994**, *116*, 4062.
[30] Ireland, T. Grossheimann, G.; Wiesser-Jeunesse, C.; Knochel, P. *Angew. Chem. Int. Ed.* **1999**, *38*, 3212.
[31] Sturm, T.; Weissensteiner, W.; Spindler, F. *Adv. Synth. Catal*. **2003**, *345*, 160.
[32] Boaz, N. W.; Debenham, S. D.; Mackeniz, E. B.; Large, S. E: *Org. Lett.* **2002**, *4*, 2421.
[33] Togni, A. *Angew. Chem. Int. Ed.* **1996**, *35*, 1475.
[34] McGarrity, J.; Spindler, F.; Fuchs, R.; Eyer, M (Lonza AG), EP-A624587A2, **1995**, [Chem. ABstr. 1995, 122P8111369q].
[35] Spindler, F.; Pugin, B.; Jalett, H.-P.; Buser, U. P.; Blaser, H.-U. In *Catalysis of Organic Reactions*, Malz, Jr., R. E. Ed.; Dekker: New York, 1996, Vol. 68, p 153.



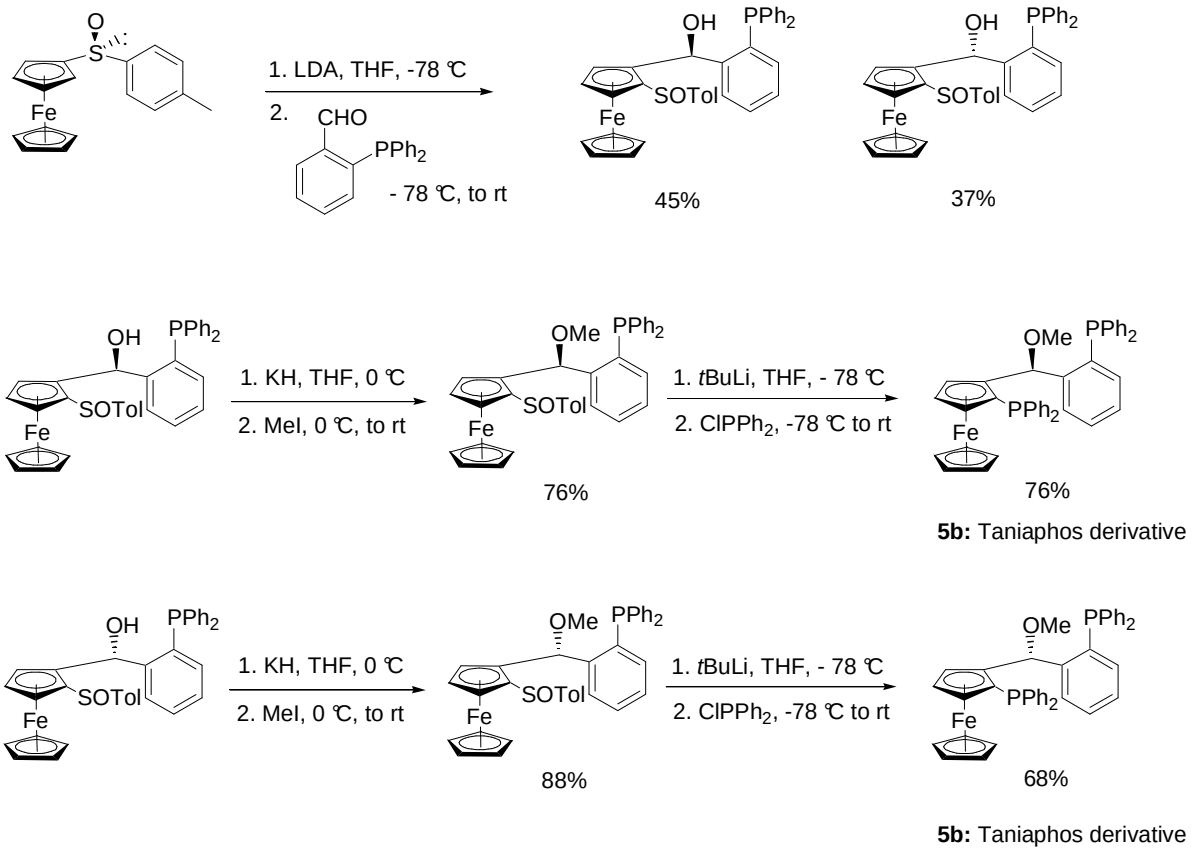
Scheme 3. Industrial preparation of (–)-Biotin and (*S*)-Metolachlor® using ferrocenyl P,P-ligand Josiphos.

Another very successful ferrocenyl ligand, reported by Knochel *et al*,[30] which has found broad applications in transition-metal-catalyzed asymmetric catalysis, is Taniaphos (**5**). This ligand was prepared *via* diastereoselective *ortho*-lithiation using Ugi's amine (Scheme 4).



Scheme 4. Preparation of Taniaphos

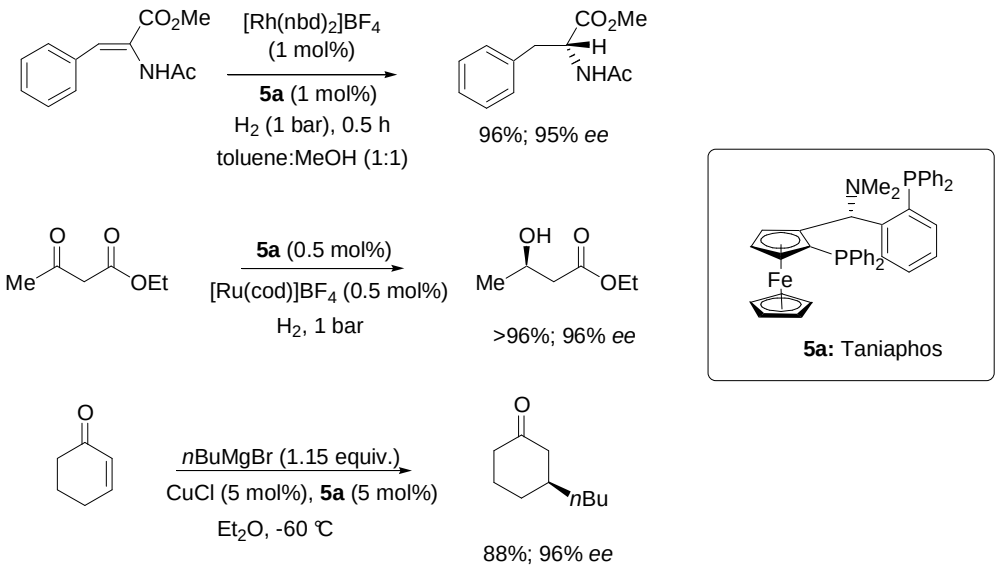
The second generation of Taniaphos was later prepared by replacing the dimethylamino group with a methoxy group at the α-position. This was prepared *via* diastereoselective *ortho*-lithiation using a sulfoxide (Scheme 5)[36].



Scheme 5. Synthesis of second generation Taniaphos *via* sulfoxide approach

Taniaphos has been successfully applied in Rh and Ru-catalyzed hydrogenation of olefins, β-keto esters,[37] Cu-catalyzed 1,4-addition of cyclic and acyclic unsaturated ketones[38], and aldol, Mannich-type reactions (Scheme 6).[39]

[36] Lotz, M.; Polborn, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2002**, *41*, 4708.
[37] Ireland, T.; Tappe, K.; Grossheimann, G.; Knochel, P. *Chem. Eur. J.* **2002**, *8*, 843.
[38] a) Feringa, B. L.; Badorrey, R.; Pena, Diego.; Harutyunyan, S. R.; Minnaard, A. J. *Proc. Natl. Acad. Sci.* **2004**, *101*, 5834. b) Spindler, F.; Malan, C.; Lotz, M.; Kesselgruber, M.; Pittelkow, U.; Rivas-Nass, A.; Briel, O.; Blaser, H.-U. *Tetrahedron: Asymmetry*, **2004**, *15*, 2299. c) Kreis, M.; Friedmann, C. J.; Braese, S. *Chem. Eur. J.* **2005**, *11*, 7387. d) Llamas, T.; Gomez-Arrayas, R.; Carretero, J. C. *Org. Lett.* **2006**, *8*, 1795. e) Lopez, F.; Van Zijl, A. W.; Minnaard, A. J.; Feringa, B. L. *Chem. Commun.* **2006**, 409. f) Zhao, D.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 14440. g) Geurts, K.; Fletcher, S. P.; Feringa, B. L. *J. Am. Chem. Soc.* **2006**, *128*, 15572. h) Chuzel, O.; Deschamp, J.; Chausteur, C.; Riant, O. *Org. Lett.* **2006**, *8*, 5943.
[39] Oisaki, K.; Zhao, D.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2006**, *128*, 7164.



Scheme 6. Application of Taniaphos in asymmetric catalysis.

1.2 Chiral P,N-ligands

P,N-ligands are another important class in chiral ligands. To date, many P,N-ligands have been prepared and successfully applied in asymmetric catalysis.[40] The success of these mixed donor ligands in metal-catalyzed asymmetric catalysis arises from the fact that they are a class of hemi labile ligands possessing a combination of hard and soft donor atoms.[41] Therefore, the different features associated with each donor atom provide a unique reactivity to their metal complexes.[42] Axially chiral aminophosphines such as Quinap,[43] MAP,[44] PINAP[45], Pyphos[46], phosphoryloxazolines such as PHOX[47], iminophosphine ligands[48] such as VALAP[49] and phosphinoarylpyridine ligands[50] such as PINPHOS, CANPHOS,[51] are representative examples of the variety of classes in this area (Figure 4).

[40] Nishiyama, H. *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999, Vols. 1-3.
[41] Chelucci, G.; Orrù, G.; Pinna, G. A. *Tetrahedron* **2003**, *59*, 9471.
[42] a) Espinet, P.; Soulantica, K. *Coord. Chem. Rev.* **1999**, *193-195*, 499. b) Molina, P.; Arques, A.; García, A.; Ramríez de Arellano, M. C. *Eur. J. Inorg. Chem.* **1998**, 1359 and references therein.
[43] Alcock, N. W.; Brown, J. M. *Tetrahedron Asymmetry:* **1993**, *4*, 743.
[44] Vyskočil, S.; Cisarova, I.; Sejbal, J.; Tislerova, I.; Smrcina, M.; Lloyd-Jones, G. C.; Stephen, S. C.; Butts, C. P.; Murray, M.; Langer, V. *J. Am. Chem. Soc.* **1999**, *121*, 7714.
[45] Knöpfel, T. F.; Aschwanden, P.; Ichikawa, T.; Watanabe, T.; Carreira, E. M. *Angew. Chem. Int. Ed.* **2004**, *43*, 5971.
[46] Kwong, F. Y.; Yang, Q.; Mak, T. C. W.; Chan, A. S. C.; Chan, K. S. *J. Org. Chem.* **2002**, *67*, 2729.
[47] Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336.
[48] a) Hird, A. W.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 1276. b) Hiroi, K.; Watanabe, K.; *Tetrahedron: Asymmetry* **2001**, *12*, 3067.
[49] a) Saitoh, A.; Achiwa, K.; Tanaka, K.; Morimoto, T.; *J. Org. Chem.* **2000**, *65*, 4227. b) Saitoh, A.; Morimoto, T.; Achiwa, K. *Tetrahedron: Asymmetry* **1997,** *8*, 3567.
[50] a) Bunlaksananusorn, T.; Polborn, K.; Knochel, P. *Angew. Chem. Int. Ed.* **2003**, *42*, 3941. b) Kasier, S.; Smidt, S. P.; Pfaltz, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 5194.

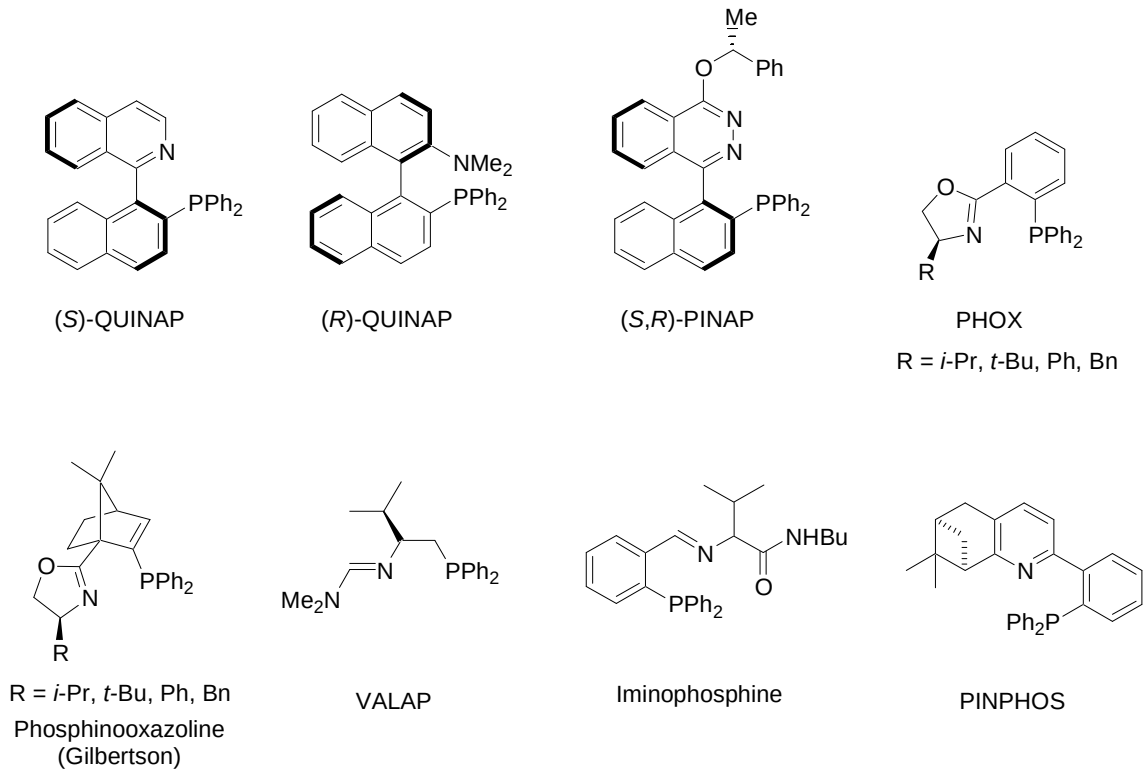


Figure 4. Chiral P, N-ligands

These chiral P,N-ligands have been successfully applied in Pd-catalyzed asymmetric alkylations[52] and asymmetric Heck reactions,[53] Rh-catalyzed asymmetric hydroboration reactions,[54] Cu-catalyzed conjugated addition of dialkylzinc species to enones[55] and Ir-catalyzed asymmetric hydrogenation reactions.[56] Among these chiral P,N-ligands, phosphanyloxazolines (**6**) have proved to be the most efficient chiral ligands for metal-catalyzed asymmetric reactions. The syntheses of chiral phosphinoxazolines were reported independently, by Helmchen,[57] Pflatz,[58] and Williams[59]. The synthesis of PHOX ligands reported by Pfaltz *et al.* is shown in scheme 7.

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[51] a) Malkov, A. V.; Bella M. Stará, I. G. Kočovský, P. *Tetrahedron Lett.* **2001**, *42*, 3045. b) Chelucci, G.; Saba, A.; Soccolini, F. *Tetrahedron* **2001**, *57*, 9989.

[52] Lautens, M. A.; Pfaltz, A.; *Allylic Substitution Reactions*:. *Comprehensive Asymmetric Catalysis;* Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Heidelberg, 1999; Vol. 2, Chapter 24.

[53] a) de Meijere, A.; Meyer, F. E. *Angew. Chem. Int. Ed.* **1994**, *33*, 3279. b) Loiseleur, O.; Meier, P.; Pfaltz, A. *Angew. Chem. Int. Ed.* **1996**, *35*, 200. c) Ripa, L.; Hallberg, A. *J. Org. Chem.* **1997**, *62*, 595. d) Shibasaki, M.; Vogel, E. M.; Ohshima, T. *Adv. Synth. Catal.* **2004**, *346*, 1533.

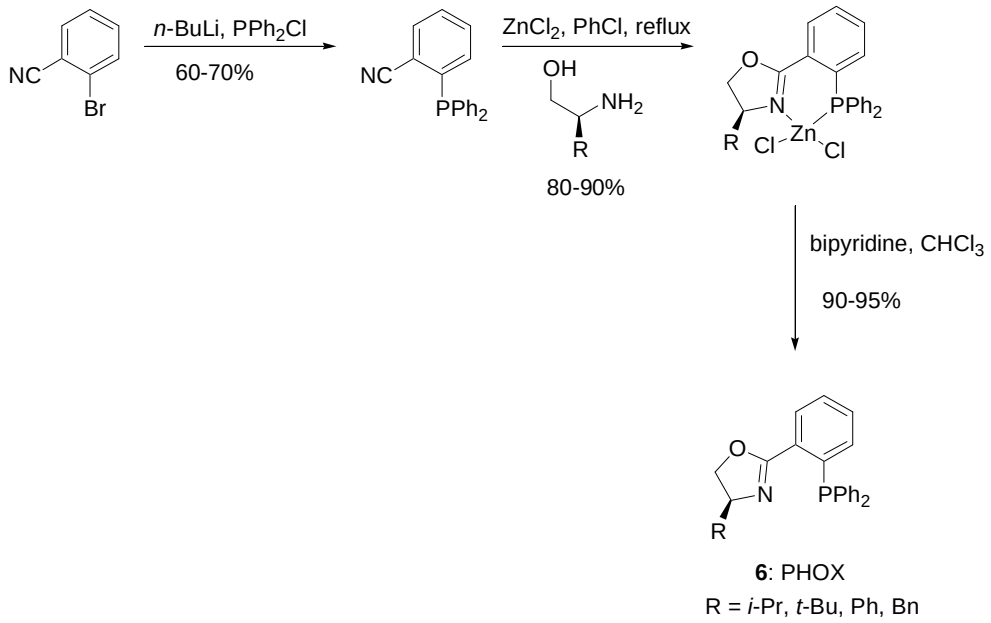
[54] Carroll, A.-M.; O'Sullivan, T. P.; Guiry, P. J. *Adv. Synth. Catal*. **2005**, *347*, 609.

[55] a) Mizutani, H.; Degrado, S. J.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 779. b) Degrado, S. J.; Mizutani, A.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 13362.

[56] Källström, K.; Munslow, I.; Andersson, P. G. *Chem. Eur. J.* **2006**, *12*, 3194.

[57] a) Spring. J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769. b) Helmchen, G.; Kudis, S.; Sennhenn, P.; Steinhagen, H. *Pure Appl. Chem.* **1997**, *69*, 513.

[58] a) von Matt, P.; Pflatz, A. *Angew. Chem. Int. Ed.* **1993**, *32*, 566. b) Pfaltz, A. *Acta Chem. Scand. B* **1996**, *50*, 189.



Scheme 7. Synthesis of PHOX-ligands by Pfaltz's method

1.2.1 Chiral Ferrocenyl P,N-ligands

Similar to the chiral ferrocenyl P,P-ligands, many chiral P,N-ligands based on the ferrocene backbone have been prepared and found successful applications in asymmetric catalysis.[26] Ferrcocenyl oxazolinylphosphine (Fc-PHOX) its analogues,[60] PPFA, [28,40] and PPFA-type ligands[61] have proved to be the most successful ligands for asymmetric catalysis. Fc-PHOX ligands have been successfully applied in an amazing variety of enatioselective processes. Some of the successful applications to mention here are Pd-catalyzed asymmetric Heck reactions,[62] Cu-catalyzed asymmetric 1,3-dipolar addition reactions,[63] Ru and Ir-catalyzed hydrogenation reactions (Scheme 8).[64]

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[59] a) Dawson, G. J.; Frost, C. G.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1993**, **34**, 3149. b) Williams, J. M. J. *Synlett* **1996**, 705.

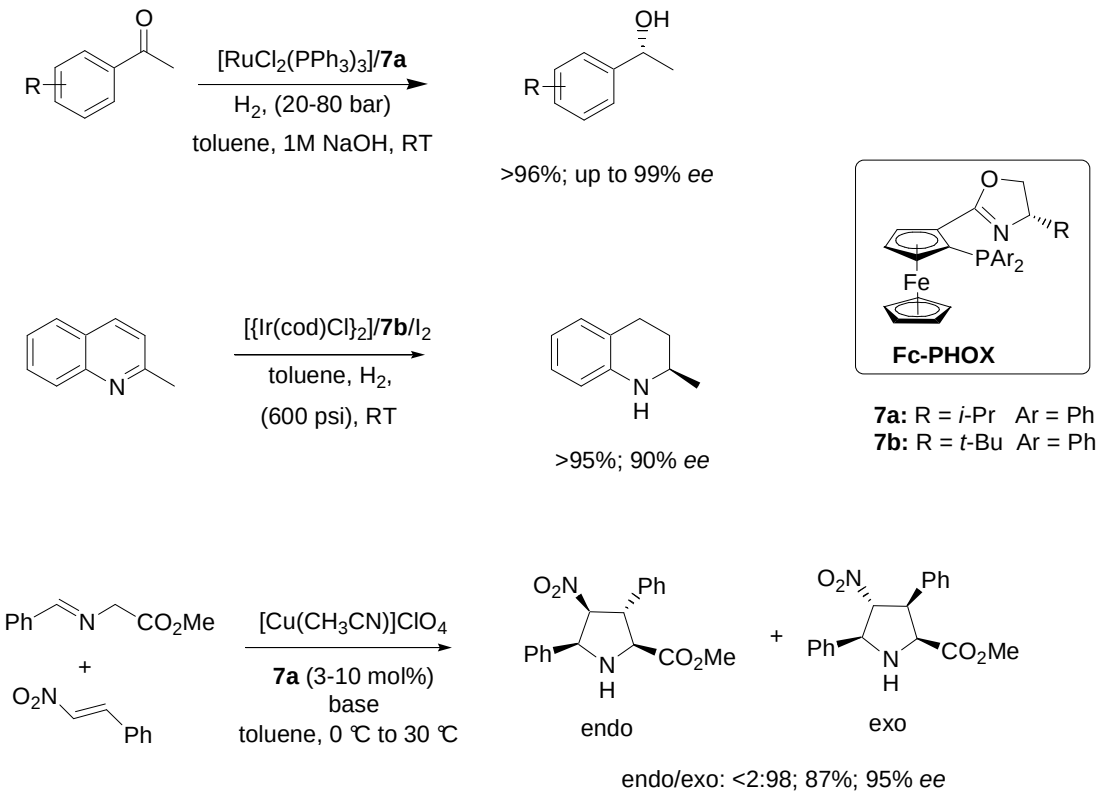
[60] Sutcliffe, O. B.; Bryce, M. R. *Tetrahedron: Asymmetry* **2003**, *14*, 2297.

[61] a) Chen, W.; Mbafor, W.; Roberts, S. M.; Whittall, J. *Tetrahedron: Asymmetry* **2006**, *17*, 550. b) Cammidge, A. N.; Crépy, K. V. L. *Tetrahedron* **2004**, *60*, 4377. c) Bringmann, G.; Hamm, A.; Schraut, M. *Org. Lett.* **2003**, *5*, 2805. d) Böttcher, A.; Schmalz, H.-G. *Synlett* **2003**, 1595. e) Wang, M.-C.; Liu, L.-T.; Hua, Y.-Z.; Zhang, J.-S.; Shi, Y.-Y.; Wang, D.-K. *Tetrahedron: Asymmetry* **2005**, *16*, 2531. f) Matsumura, S.; Maeda, Y.; Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **2003**, *125*, 8862.

[62] a) Deng, W.-P.; Hou, X.-L.; Dai, L.-X.; Dong, X.-W. *Chem. Commun.* **2000**, 1483. b) Tu.; T.; Deng, W.-P.; Hou, X.-L.; Dai, X.-L.; Dong, X.-C. *Chem. Eur. J.* **2003**, *9*, 3073. c) Kiely, D. Guiry, P. J. *J. Organomet. Chem.* **2003**, *687*, 545. d) Tu, T.; Hou, X.-L.; Dai, X.-L. *Org. Lett.* **2003**, *5*, 3651.

[63] a) Gao, W.; Zhang, X.; Raghunath, M. *Org. Lett.* **2005**, *7*, 4241. b) Yan, X.-X.; Peng, Q.; Zhang, Y.; Zhang, K.; Hong, W.; Hou, X.-L.; Wu, Y.-D. *Angew. Chem. Int. Ed.* **2006**, *45*, 1979.

[64] Ru-catalyzed reactions a) Naud, F.; Malan, C.; Splinder, F.; Rüggeberg, C.; Schmidt, T. Blaser, H.-U. *Adv. Synth. Catal.* **2006**, 348, 47. b) Tellers, D. M.; Bio, M.; Song, Z. J.; McWilliams, J. C.; Sun, Y. *Tetrahedron: Asymmetry* **2006**, *17*, 550. c) Nishibayashi, Y.; Yamauchi, A.; Onodera, G.; Uemura, S. *J. Org. Chem.* **2003**, *68*, 5875. Ir-catalyzed reactions d) Lu, S.-M.; Han, X.-W.; Zhou, Y.-G. *Adv. Synth. Catal.* **2004**, *346*, 909. e)



Scheme 8. Applications of Fc-PHOX ligands in asymmetric catalysis

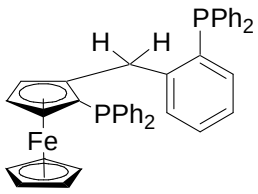
2. Objectives

As shown in the previous section, Taniaphos and its analogues compounds are important ligands in asymmetric catalysis. To further explore this class of compounds, the main objectives of this work were firstly the development of new chiral P,P- or P,N-ligands based on the Taniaphos structure, and secondly to study their applications in transition-metal-catalyzed asymmetric reactions.

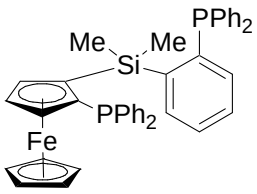
2.1 Ferrocenyl P,P-ligands

The first objective of this work was to prepare the new chiral ferrocenyl P,P-ligand **8** (Figure 5) in enantiomerically pure form and use this ligand in asymmetric catalysis.

Giernoth, R.; Krumn, M. S. *Adv. Synth. Catal.* **2004**, *346*, 989. f) Onodera, G.; Nishibayashi, Y.; Uemura, S. *Angew. Chem. Int. Ed.* **2006**, *45*, 3819.



5c: Taniaphos derivative

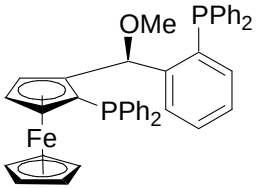


8

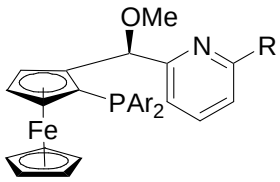
Figure 5. New chiral ferrocenyl P,P-ligand **8**

2.2 Chiral Ferrocenyl P,N-ligand

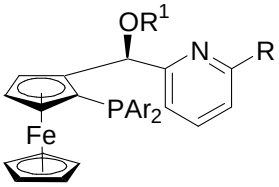
Based on the progress in the synthesis of new chiral P,N-ligands and their successful applications in asymmetric catalysis, it was of interest to prepare chiral P,N-ligands based on the Taniaphos structure. The objectives of this work were to synthesize new chiral ferrocenyl P,N-ligands **9** and **10** (Figure 6) by replacing one of the phosphines by a *N*-donor group such as pyridine in Taniaphos and to test their efficiency in asymmetric catalysis.



5b: Taniaphos derivative



9

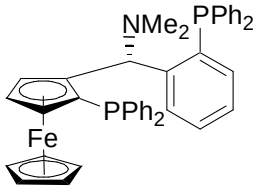


10

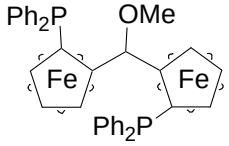
Figure 6. New chiral ferrocenyl P,N-ligands **9** and **10**

2.3 Bis-ferrocenyl P,P-ligands

The third objective of this work was to prepare the new ferrocenyl ligand **11** (Figure 7), which bares structural similarities to Taniaphos and to apply this ligand in metal-catalyzed asymmetric reactions.



5a: Taniaphos

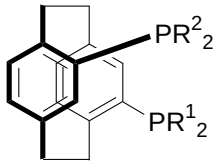


11

Figure 7. New chiral bis-ferrocenyl P,P-ligand **11**

2.4. Chiral Paracyclophane P,P-ligands

The final objective was to synthesize new paracyclophane diphosphines of type **12**, (Figure 8) bearing two different kinds of phosphines and test their efficiency in asymmetric catalysis.



12

R^1 = Ph

R^2 = 4-F-C_6H_4

= 3,5-$(CF_3)_2$-C_6H_3

= 3,5-$(CH_3)_2$-C_6H_3

Figure 8. New paracyclophane diphosphines of type **12**

Results and Discussion

1. Synthesis of Planar Chiral Ferrocenyl P,P-ligand and their applications in asymmetric catalysis

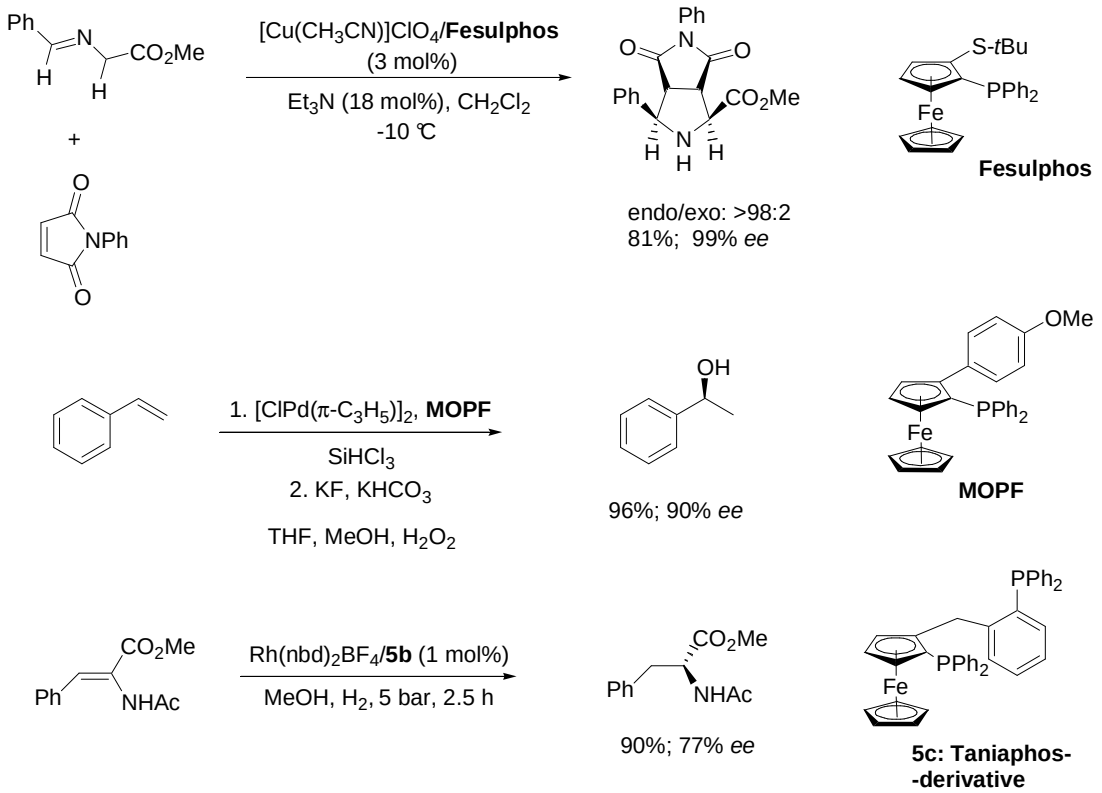
1.1. Introduction

1.1.1 Chiral ferrocenyl ligands with planar chirality

In recent years many chiral ferrocenyl ligands have been prepared and have found broad applications in asymmetric catalysis. Many of the chiral ferrocenyl ligands developed, possess both planar and central chiralities, although there are some examples such as Fesulphos[65], MOPF[66] and Taniaphos derivatives[37], showing only planar chirality. Fesulphos is a bidentate P,S-ligand and has been successfully applied in asymmetric catalysis. Whereas, Mopf (monophosphine) and Taniaphos derivative **5b** (bisphosphine) have found limited applications in asymmetric catalysis due to the moderate selectivities observed (Scheme 9).

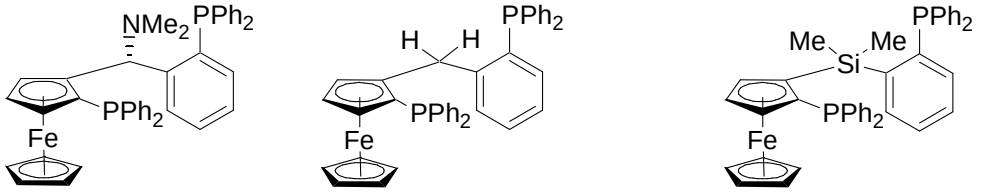
[65] García Mancheño, O.; Priego, J.; Cabrera, S.; Gómez Arrayás, R.; Llamas, T.; Carretero, J, C. *J. Org. Chem.* **2003**, *68*, 3679.

[66] a) Jensen, J. F.; Johannsen, M. *Org.Lett.* **2003**, 5, 3025. b) Jensen, J. F.; Søtofte, I.; Sørensen, H. O.; Johannsen, M. *J. Org. Chem.* **2003**, *68*, 1258.



Scheme 9. Applications of Fesulphos, MOPF and Taniaphos-derivative **5c** in asymmetric catalysis.

In order to further explore planar chiral ferrocenyl ligands such as **5c**, our goal was to prepare ligand **8** (Figure 9) and investigate its properties in asymmetric catalysis.



5a: Taniaphos **5c** **8**

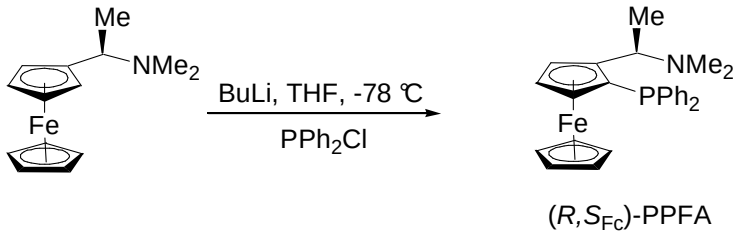
Figure 9. New chiral ferrocenyl ligand **8** for asymmetric catalysis

1.1.2. Synthesis of 1,2-disubstituted ferrocenes via diastereoselective *ortho*-metallation

Chiral 1,2-disubstituted ferrocenes have found much attention since these building blocks have emerged as a premiere structural ligand motif in metal-catalyzed asymmetric reactions.[67] In 1970, Ugi reported the first example of diastereoselective *ortho*-lithiation on

[67] Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377.

N,N-dimethylamino-1-ferrocenylethylamine using the *N*,*N*-dimethylamino group as an *ortho*-directing group (Scheme 10).[68]



Scheme 10. Diastereoselective *ortho*-lithiation on Ugi amine.

In addition to Ugi's amine, a large number of other chiral *ortho*-directing groups have been described such as sulfoxides,[69] acetals,[70] oxazolines,[71] azepines,[72] pyrrolidines,[73] hydrazones,[74] sulfoximines,[75] imidazolines[76] and phosphine oxides.[77] Among these, the Ugi amine method, the oxazoline approach, and the sulfoxide approach are the most widely used strategies for the preparation of chiral 1,2-ferrocenes (Figure 10).

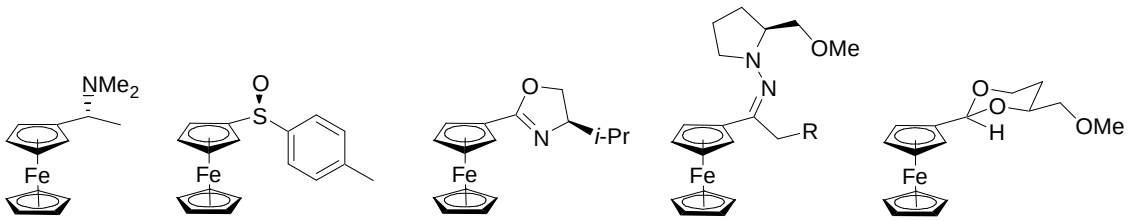
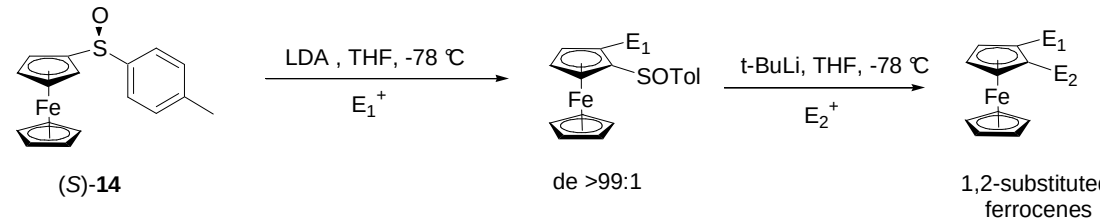


Figure 10. Directing groups for the diastereoselective *ortho*-lithiation on ferrocenes.

The Kagan sulfoxide approach has significantly enlarged the possibilities for preparing structurally diverse 1,2-substituted ferrocenes. The major advantage of this method is that, after a diastereoselective *ortho*-lithiation and substitution, the sulfoxide group can be removed

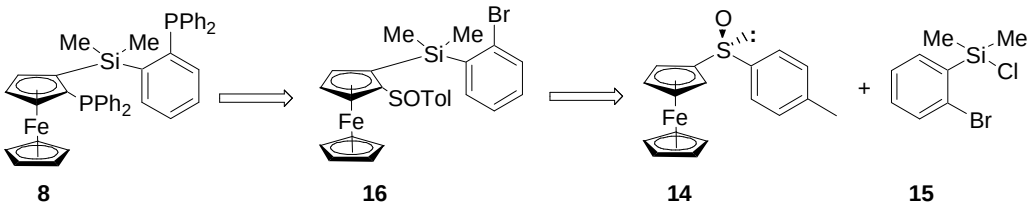
[68] Gokel, G.; Marquarding, D.; Ugi, I. J. *J. Org. Chem.* **1972**, *37*, 3052.
[69] Rebière, F.; Riant, O.; Ricard, L.; Kagan, H. B. *Angew. Chem. Int. Ed.* **1993**, *32*, 568.
[70] Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc*. **1993**, *115*, 5835.
[71] a) Richards, C. J.; Damalidis, T.; Hibbis, D. E.; Hursthouse, M. B. *Synlett* **1995**, 74. b) Sammakia, T.; Latham, H. A.; Schaad, D. R. *J. Org. Chem*. **1995**, *60*, 10.
[72] Wildhalm, M.; Mereiter, K.; Bourghida, M. *Tetrahedron: Asymmetry* **1998**, *9*, 2983.
[73] Farrell, Y.; Goddard, R.; Guiry, P. J. *J. Org. Chem*. **2002**, *67*, 4209.
[74] Enders, D.; Peters, R.; Lochtman, R.; Raabe, G. *Angew. Chem. Int. Ed*. **1999**, *38*, 2421.
[75] Bolm, C.; Kesselgruber, M.; Muñiz, K.; Raabe, G. *Organometallics* **2000**, *19*, 1648.
[76] Peters, R.; Fischer, D. F. *Org. Lett*. **2005**, *7*, 4137.
[77] Nettekoven, U.; Widhalm, M.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M.; Mereiter, K. Lutz, M. *Organometallics* **2000**, *19*, 2299.

by *tert*-butyllithium mediated C-S cleavage and the resulting ferrocenyllithium can be reacted with an electrophile (Scheme 11).[78]



Scheme 11. Preparation of 1,2-disubstituted ferrocenes *via* Kagan sulfoxide approach

Ligand **8** could therefore be formed in enantiomerically pure form using Kagan's sulfoxide as shown retrosynthetically in scheme 12.



Scheme 12. Synthetic approach to chiral ferrocenyl P,P-ligand **8**

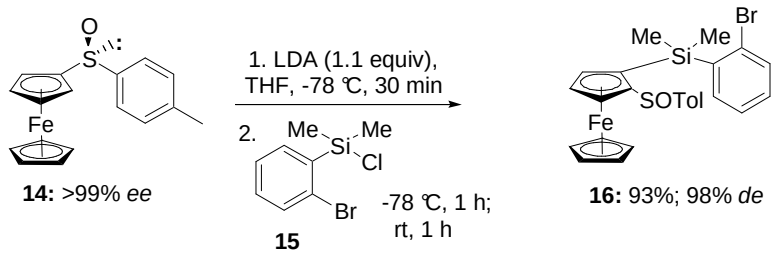
The diphosphine **8** can be prepared by the consecutive, onepot exchange of bromine and sulfoxide on **16**, followed by the addition of chlorodiphenylphosphine. Substrate **16** can be prepared *via* the diastereoselective lithiation of **14**.

1.2. Synthesis of Chiral Planar Ferrocenyl P,P-ligand 8

1.2.1. Diastereoselective *ortho*-lithiation

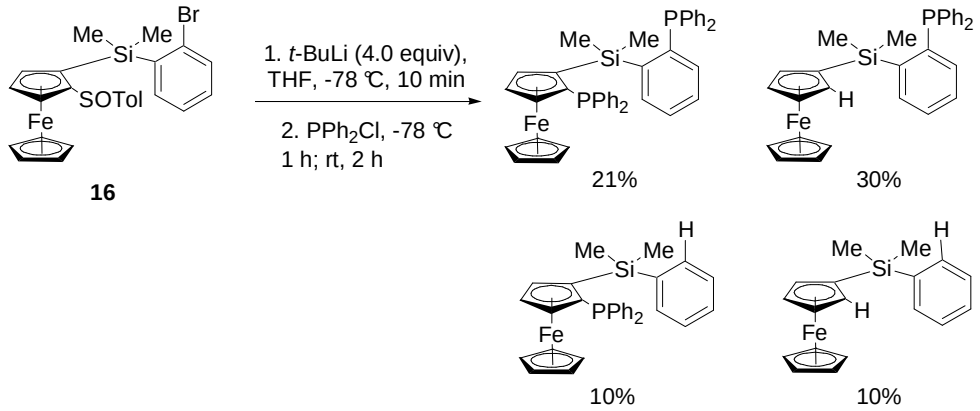
The diastereoselective *ortho*-lithiation on the Kagan sulfoxide **14** using LDA proceeded with >98% de. The resulting ferrocenyllithium was reacted with **15**[79] at -78 °C to furnish the corresponding ferrocenyl silane compound **16** in 93% yield and 98% de (Scheme 13).

[78] a) Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502. b) Riant, O. ; Argouarch, G. ; Guillaneux, D. ; Samuel, D. ; Kagan, H. B. *J. Org. Chem.* **1998**, *63*, 3511.
[79] Acemoglu, M. *J. Lable Compd. Radiopharm.* **2002**, *45*, 361.



Scheme 13. Diasteroselective *ortho*-lithiaton of **14** and reaction with electrophile **15**

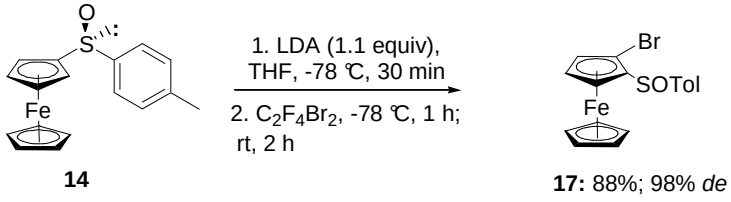
Treatment of **16** with *t*-BuLi (4.2 equiv) in THF at -78 °C, followed by the addition of chlorodiphenylphosphine led to a mixture of compounds that contained mono and disubstituted phosphines as well as the protolysis product (Scheme 14).



Scheme 14. Exchange of sulfoxide and bromine using *t*-BuLi

1.2.2. Optimization for selective Sulfoxide-Lithium exchange

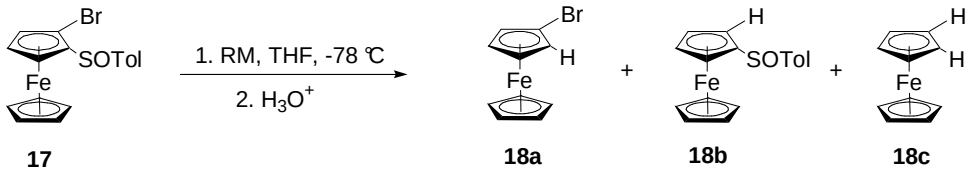
Since we are obtaining a complex mixture with the simultaneous exchange on **16** using *t*BuLi, we decided to perform a stepwise exchange of the sulfoxide and bromine. We screened some organomagnesium reagents and organolithium reagents for a selective exchange of the sulfoxide. For this study we have chosen the (R_{Fc},*S*)-(*p*-tolylsulfinyl)-2-bromoferrocene **17** as a test substrate. The bromoferrocene **17** can be synthesized *via* diastereoselective *ortho*-lithiation of sulfoxide **14**, followed by the addition of 1,1,2,2-tetrafluoro-1,2-dibromoethane (Scheme 15).



Scheme 15. Preparation of bromo-sulfoxide **17**

With the test substrate in hand, we screened several organomagnesium and lithium reagents, the results are summarized in Table 1.

Table 1. Screening of organometallic reagents for a selective sulfoxide-lithium exchange on **17**



17 **18a** **18b** **18c**

Entry	Organometallic reagent (RM)	Product (%)[a]		
		18a	**18b**	**18c**
1	*t*-BuLi (2.2 equiv)	–	–	45
2	*n*-BuLi (1.1 equiv)	–	75	<5
3	*i*-PrMgCl (1.1equiv)	25	5	Traces
4	PhMgCl (1.1 equiv)	–	–	–
5	PhLi (1.1 equiv)	75	4	<1

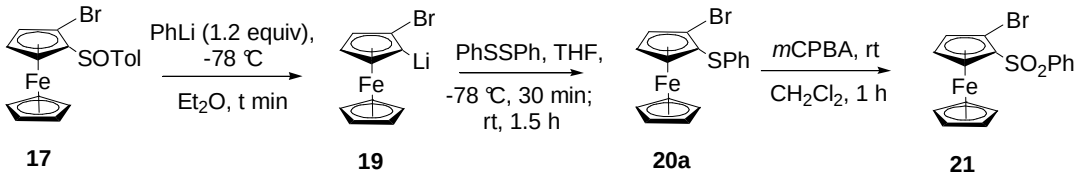
[a] yields refers to the isolated products

Sulfoxide/lithium-exchange using *t*-BuLi (-78 °C, 10 min) on **17** led to complete exchange of both the bromine and the sulfoxide and gave product **18c** in 90% yield (entry 1). Whereas, *n*-BuLi (-78 °C, 15 min) selectively exchanged the bromine, providing the product **18b** in 75% yield (entry 2). Very poor exchange rate was observed with *i*-PrMgCl (-50 °C, 1 day), but, after long reaction times, we also observed the partial exchange of bromine (entry 3). No exchange (neither bromine nor sulfoxide) was observed with PhMgCl (entry 4). Exchange of sulfoxide using PhLi[80] (-78 °C, 10 min) proceeded selectively and afforded the desired product **18a** in 75% yield. We also noticed a partial exchange of bromine and also traces of product **18c** (entry 5).

Although exchange of the sulfoxide using PhLi proceeded selectively, the stability of the α-bromoferrocenyllithium species to racemization was unknown. Quenching of the ferrocenyllithium species **19** with diphenyldisulfide as an electrophile using various reaction times gave the ferrocenyl sulfide **20a** in 30-72% yield. Measurement of the enantiopurity of the sulfone **21** formed via oxidation with *m*-CPBA gave an indication of the stability of bromo-lithium species **19** (Table 2).

[80] Kloetzing, R.J.; Knochel, P. *Tetrahedron: Asymmetry* **2006**, *17*, 116.

Table 2. Verifying the configurational stability of α-bromoferrocenyllithium species **19**

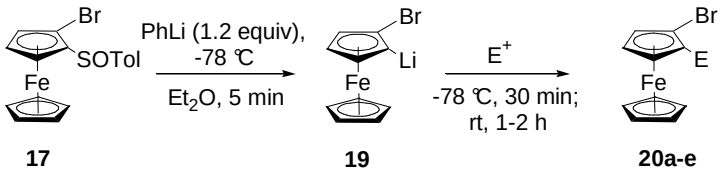


17 **19** **20a** **21**

Entry	Quenching the lithium species at *t* (min)	Product **20a**	Product **21**	
		yield(%)[a]	yield(%)[a]	*ee*(%)[b]
1	5	72	90	97
2	10	70	91	86
3	15	66	90	64
4	20	50	85	49
5	60	30	92	Rac

[a] isolated yield of analytically pure sample. [b] enantioselectivity was measured by chiral HPLC using a chiralcel OD-H column

As the time before the bromo-lithium species was quenched with the electrophile was increased (5 to 60 min), the enantioselectivity of the desired product **21** dropped. It may be that **19** was undergoing a halogen dance[81] and thus led to racemization of the product. A possible disadvantage of this method is that the lithium species **19** must be quenched with very reactive electrophiles. To examine the scope of this method, the lithium species **19** was quenched with a variety of electrophiles to form **20a-e** in 69-79% yield (Scheme 16). Compound **20c** is an especially interesting building block for many cross-coupling reactions and can be accessed only by using this method.



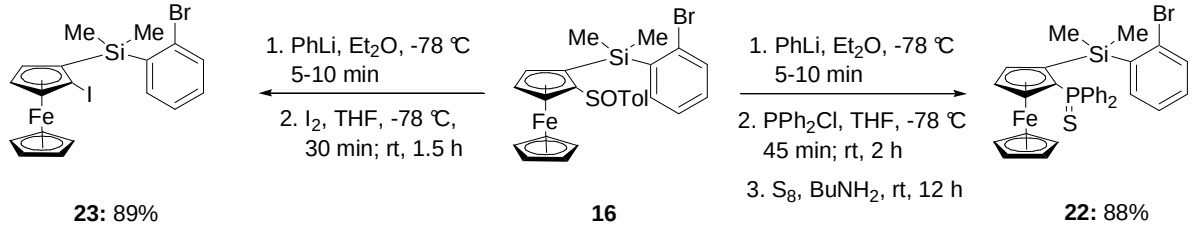
17 **19** **20a-e**

20a: E = SPh 72%
20b: E = CHO 69%
20c: E = I 70%
20d: E = $SiMe_3$ 70%
20e: E = $P(S)Ph_2$ 79%

Scheme 16. Preparation of bromoferrocenes of type **20** by the reaction of the lithium species **19** with various electrophiles

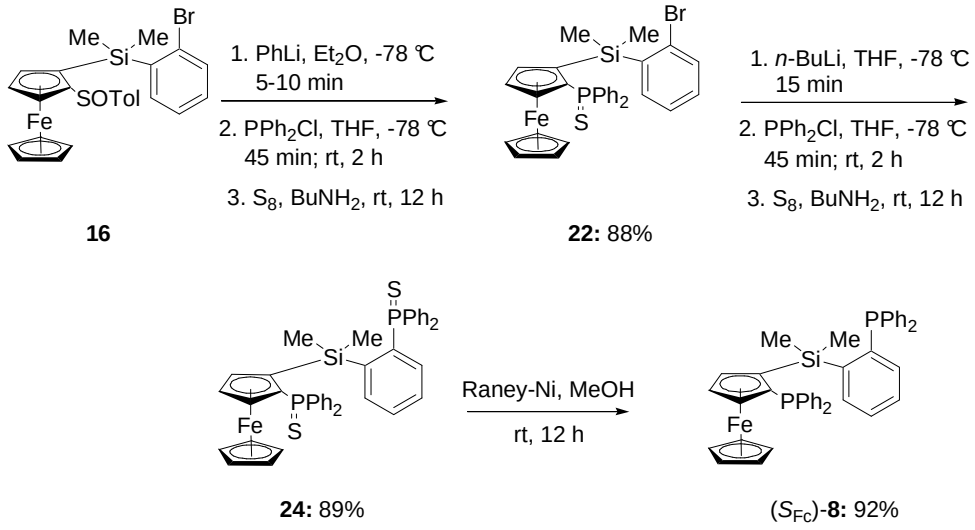
[81] Schnürch, M.; Spina, M.; Khan, F. A.; Mihovilovic, M. D.; Stanetty, P. *Chem. Soc. Rev.* **2007**, *36*, 1046.

Application of these findings to silyl ferrocene derivative **16**, phenyllithium proved to be the appropriate reagent for the selective sulfoxide/lithium-exchange (Scheme 17). The sulfoxide/lithium-exchange on **16** using PhLi, followed by the addition of chlorodiphenylphosphine and *in situ* protection of the resulting phosphine with sulfur (S_8, $BuNH_2$), provided the thionophosphine compound **22** in 88% yield (Scheme 17).



Scheme 17. Selective sulfoxide/lithium exchange on the substrate **16** using phenyllithium

Further, bromine/lithium-exchange on **22** using *n*-BuLi, followed by reaction with chlorodiphenylphosphine and protection of the phosphine with sulfur, provided the air-stable diphosphine disulfide **24** in 89% yield. Deprotection of diphosphine disulfide **24** was smoothly accomplished using Raney-Ni[82] in methanol, leading to the diphosphine **8** in 92% yield (Scheme 18).



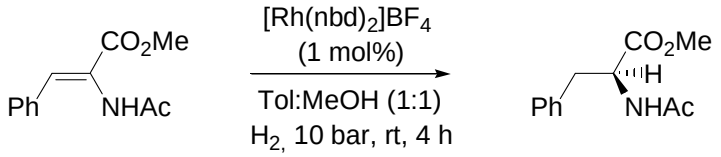
Scheme 18. Preparation of chiral ferrocenyl P,P-ligand **8**

[82] a) C. Korff, G. Helmchen, *Chem. Commun.* **2004,** 530. b) D. Liu, W. Tang, X. Zhang, *Org. Lett.* **2004,** *6*, 513.

1.3. Applications in asymmetric catalysis

1.3.1. Rh-catalyzed hydrogenation of olefins

Exploration of the efficiency of this new chiral ferrocenyl P,P-ligand **8** in the Rh-catalyzed hydrogenation of α-acetamidocinnamate **25** to phenylalanine derivative **26** was conducted. Despite the hydrogenation reaction being quantitative, no selectivity was observed in the desired product **26** (Scheme 19).

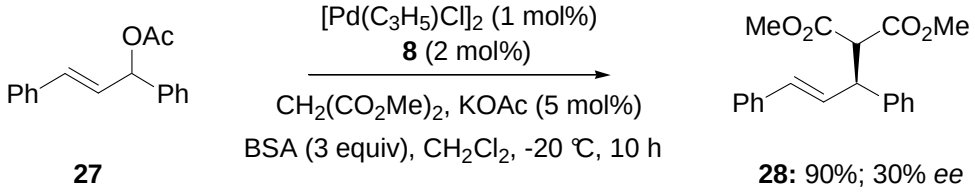


25 **26:** >95%; rac.

Scheme 19. Application of **8** in Rh-catalyzed hydrogenation of **25**

1.3.2. Pd-catalyzed asymmetric allylic alkylations

The application of **8** in Pd(0)-catalyzed allylic substitution reactions of racemic 1,3-diphenylprop-2-en-1-yl acetate (±)-**27** with dimethylmalonate employing Trost's procedure[83] was investigated. $[Pd(C_3H_5)Cl]_2$ 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. Reaction at -20 °C using the ligand **8** provided the desired compound **28** in 90% yield and 30% *ee* (Scheme 20).



27 **28:** 90%; 30% *ee*

Scheme 20. Pd-catalyzed allylic alkylation using ferrocenyl ligand **8**

1.4. Conclusion

In conclusion, the synthesis of the chiral P,P-ligand **8** was achieved. We have shown that phenyllithium is the most efficient reagent for a selective sulfoxide/lithium-exchange on bromoferrocenyl sulfoxide **17**. Furthermore, we have applied this methodology to the synthesis of various ferrocene derivatives of type **20**. The ligand **8** was applied to Rh-

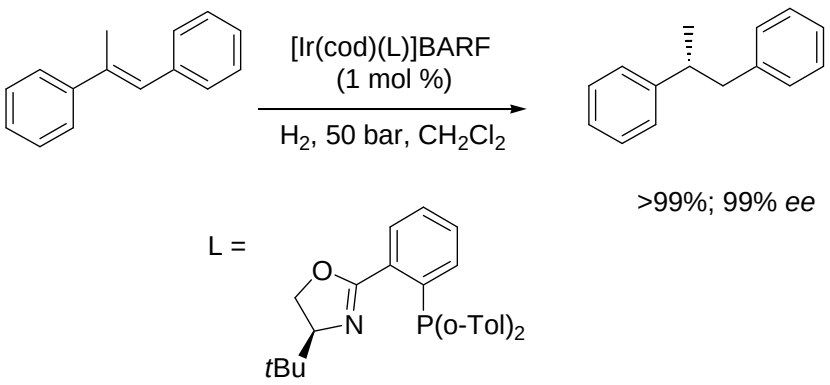
[83] Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143.

catalyzed asymmetric hydrogenations and Pd-catalyzed allylic alkylations and very poor selectivities were observed. One of the possible reasons for the poor enantioselectivity using ligand **8** is that the C-Si bond is so long that the two donor phosphines are too far away from each other to form a favourable bite angle in the complex with the transition metal.

2. Synthesis of Chiral Ferrocenyl P,N-ligands and their Application in Asymmetric Catalysis.

2.1 Introduction

Chiral P,N-ligands are one of the most important classes of chiral ligands because they have proved to be efficient in transition-metal-catalyzed asymmetric reactions, particularly in areas where C_2-symmetrical ligands failed.[84] During the past two decades an increasing number of P,N-ligands and their catalysts were reported for a wide range of asymmetric reactions and improved the efficiency of existing processes. 2-Phosphinylphenyloxazoline ligands, one of the most successful chiral P,N-ligands, were reported by Pfaltz *et al.*[7] These ligands have proved to be especially efficient in Ir-catalyzed asymmetric hydrogenation reactions of olefins (Scheme 21).[85]

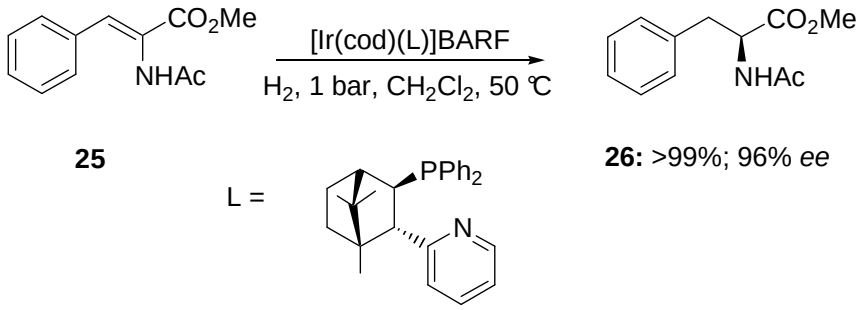


Scheme 21. Asymmetric hydrogenation of olefins using Pflatz's chiral phospineoxazoline ligand

In addition to this Ir-catalyzed hydrogenation of olefins, Knochel *et al.* have demonstrated the iridium catalyzed hydrogenation of enamides such as **25** to amino acid derivatives **26** using a

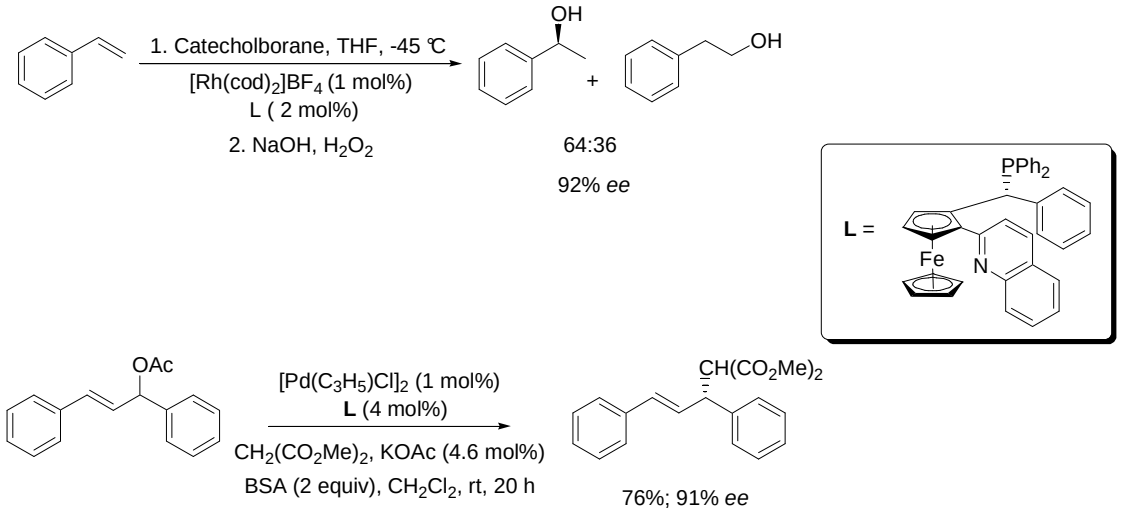
[84] Espinet, P.; Soulantica, K. *Coord. Chem. Rev*. **1999**, *193-195*, 499.
[85] Pfaltz, A.; Jörg, B.; Hilgraf, R.; Hörmann, E.; McIntyre, S.; Menges, F.; Schönleber, M.; Smidt, S. P.; Wüstenberg, B.; Zimmermann, N. *Adv. Synth. Catal.* **2003**, *345*, 33.

chiral terpene-derived P,N-ligand. This is of interest as it allows for the potential Ir-catalyzed formation of highly enantiomerically pure nonnatural α-amino acid derivatives, which have previously been extensively studied using Rh and Ru-catalysts (Scheme 22).



Scheme 22. Ir-catalyzed reduction of enamide **25** using the chiral terpene-derived P,N-ligand

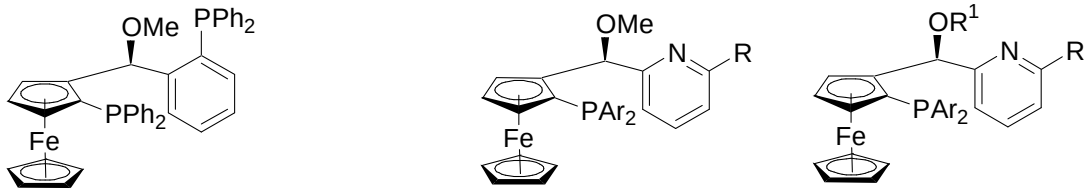
Recently, our group reported a ferrocenyl P,N-ligand with both planar and central chiralities and found very good applications in Rh-catalyzed hydroboration reactions and Pd-catalyzed asymmetric allylic alkylation reactions (Scheme 23).[86]



Scheme 23. Ferrocenyl P,N-ligands for asymmetric catalysis.

This impressive progress on the successful applications of P,N-ligands in asymmetric catalysis encouraged us to design and synthesize a new chiral P,N-ligand for asymmetric catalysis. The aim of this work was to synthesize chiral P,N-ligands analogous to Taniaphos, which possess both planar and central chirality elements and have a $–NMe_2$ or a –OMe group in the side chain. The ligand structure is described in figure 11.

[86] Kloetzing, R. J.; Lotz, M.; Knochel P. *Tetrahedron: Asymmetry* **2003**, *14*, 255.



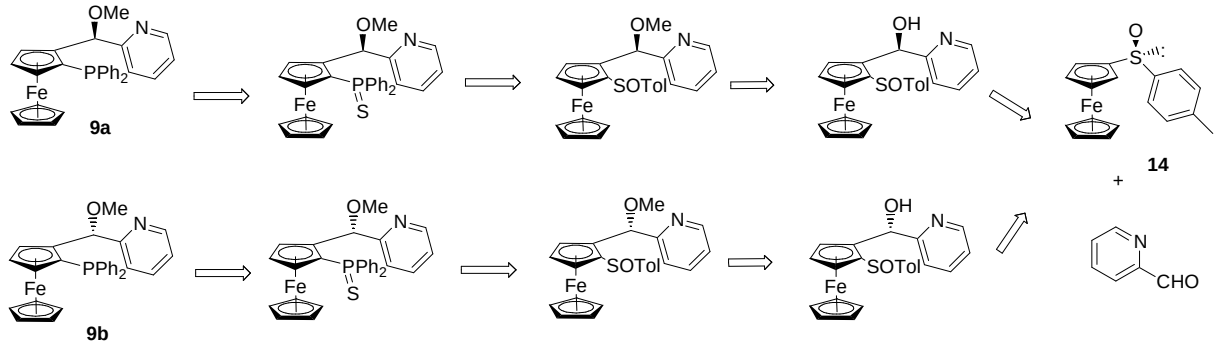
5b: Taniaphos derivative **9** R = H, Ph, *t*Bu **10** R^1 = Bn, H

Figure 11. New ferrocenyl P,N-ligands **9-10**

2.2. Synthesis of P,N-ligands 9 and 10

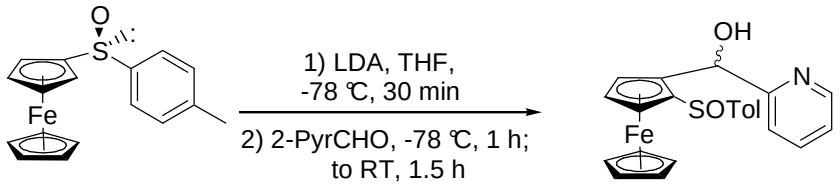
2.2.1 Synthesis of ferrocenyl ligands 9 and 10 with a pyridine ring as a *N*-donor

Initially we tried to synthesize the P,N-ligands **9-10** *via* a classical route.[36] The phosphines **9a-b** can be prepared by the deprotection of the corresponding sulfides. The phosphine sulfides can be prepared *via* the sulfoxide-lithium exchange of the corresponding ferrocenyl sulfoxide. The methyl ether can be prepared through the *O*-methylation of the corresponding alcohol which can be prepared by through the diastereoselective *ortho*-lithiation of the sulfoxide **14** (Scheme 24).



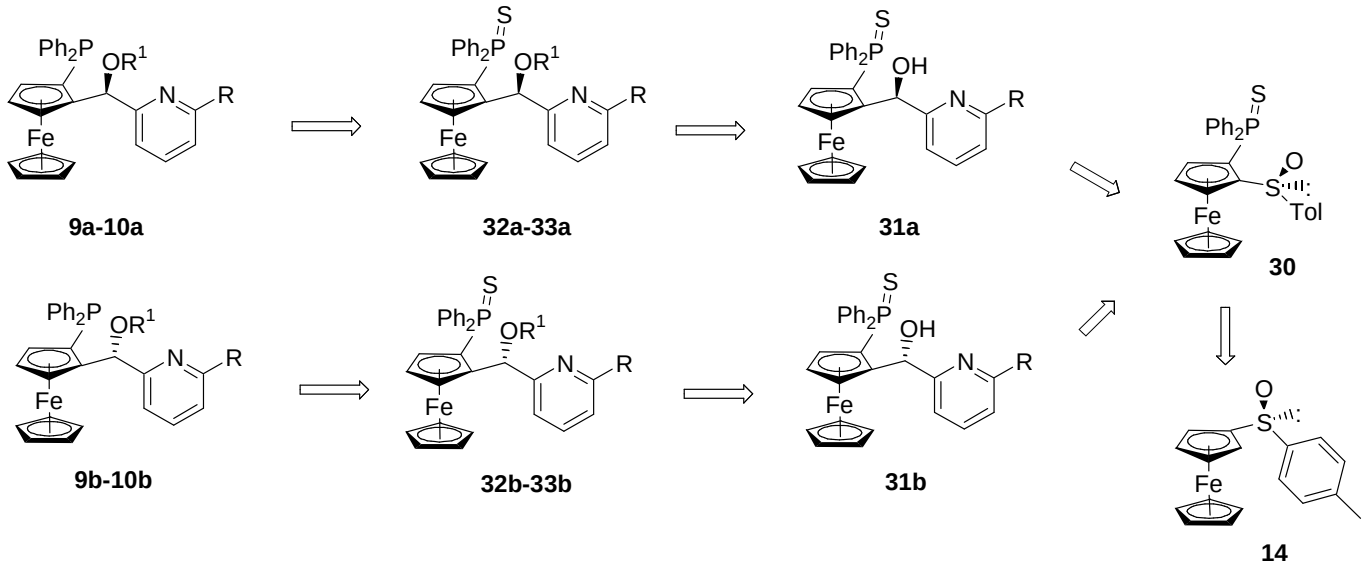
Scheme 24. Classical approach to the P,N-ligands **9a-b**

Thus, treating the Kagan sulfoxide **14** with LDA at -78 °C for 30 min, followed by the addition of 2-pyridinecarboxaldehyde, resulted in the alcohol **29** (Scheme 25). This alcohol was quite unstable at room temperature and turned black immediately after isolation.



Scheme 25. Preparation of pyridyl alcohol **29**

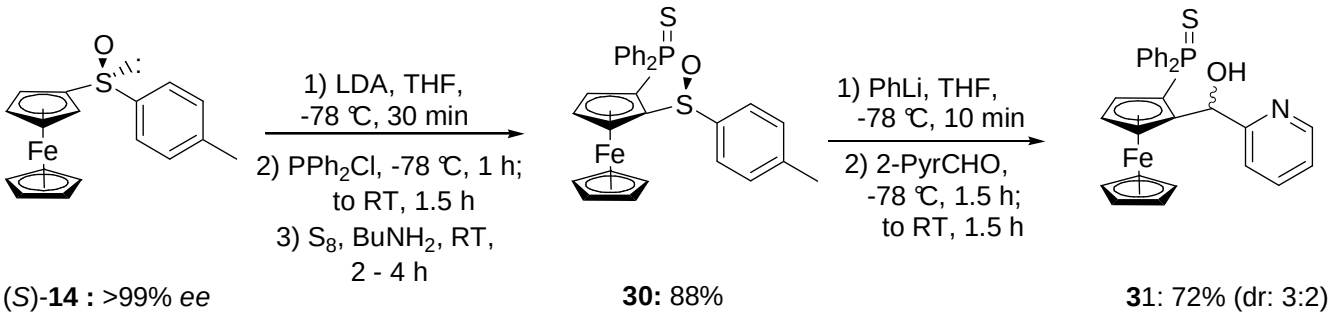
Because we met the difficulties to isolate **29**, we changed our synthetic pathway towards the P,N-ligands of type **9** and **10**. Our new synthetic approach is outlined in the Scheme 26.



Scheme 26. Novel synthetic approach to the chiral ferrocenyl P,N-ligands **9-10**

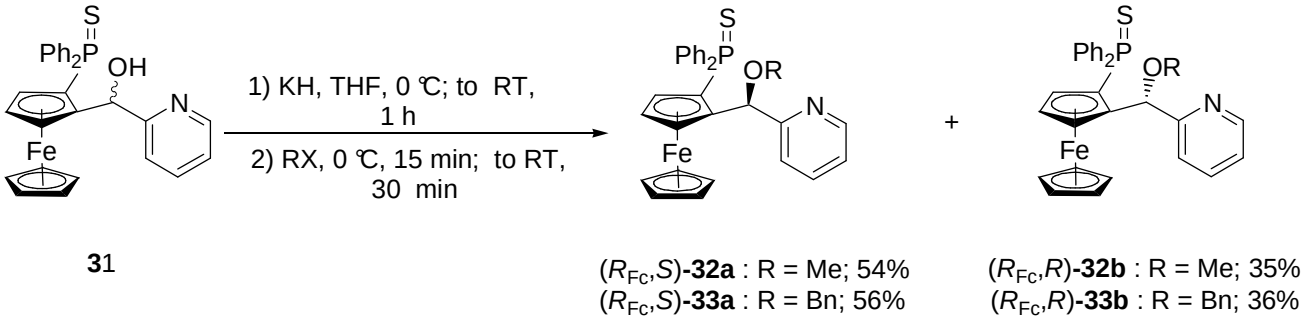
The phosphine sulfides **32a-33a** and **32b-33b** could be prepared by *O*-alkylation of the alcohols **31a-b**. These alcohols can be synthesized through the sulfoxide-lithium exchange on **30**, followed by the addition of the 2-pyridinecarboxaldehydes. Phosphine sulfide **30** can be prepared *via* the diastereoselective *ortho*-metallation of Kagan sulfoxide **14**. Deprotection of phosphine sulfides **32a-33b** will furnish chiral P,N-ligands **9-10**.

The diastereoselective lithiation of **14** using LDA, followed by the addition of chlorodiphenylphosphine, led to an air sensitive phosphine, which was *in situ* protected with sulfur leading to the thianophosphinyl ferrocene **30** in 88% yield. Performance of a sulfoxide/lithium-exchange using phenyllithium, followed by the addition of 2-pyridinecarboxaldehyde, led to a 3:2 mixture of diastereomeric ferrocenyl alcohols **31a** and **31b** as **31** in 72% yield (Scheme 27).



Scheme 27. Preparation of pyridyl alcohol **31**

This inseparable mixture of alcohols **31** was alkylated with MeI leading to the separable ferrocenyl methyl ethers **32a** and **32b** in 54% and 35% yield respectively (Scheme 28). In a similar manner, the alcohol mixture **31** was benzylated using KH and benzyl bromide, leading to separable benzyl ethers **33a** and **33b** in 56% and 36% yield respectively (Scheme 28).



Scheme 28. Preparation of protected ferrocenyl ligands **32a-33b**

The stereochemistry of the two ferrocenyl ethers **32a** and **32b** at the α-centre was determined by X-ray analysis of the phosphine sulfide **32b** as shown in figure 12.[87]

[87] a) For more details about atomic coordinates, bond lengths, bond angles Cambridge database number **CCDC 627426**.

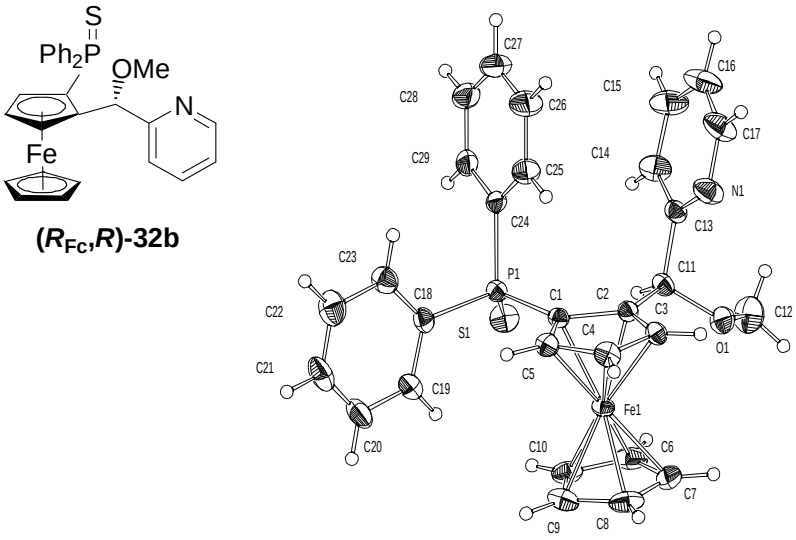
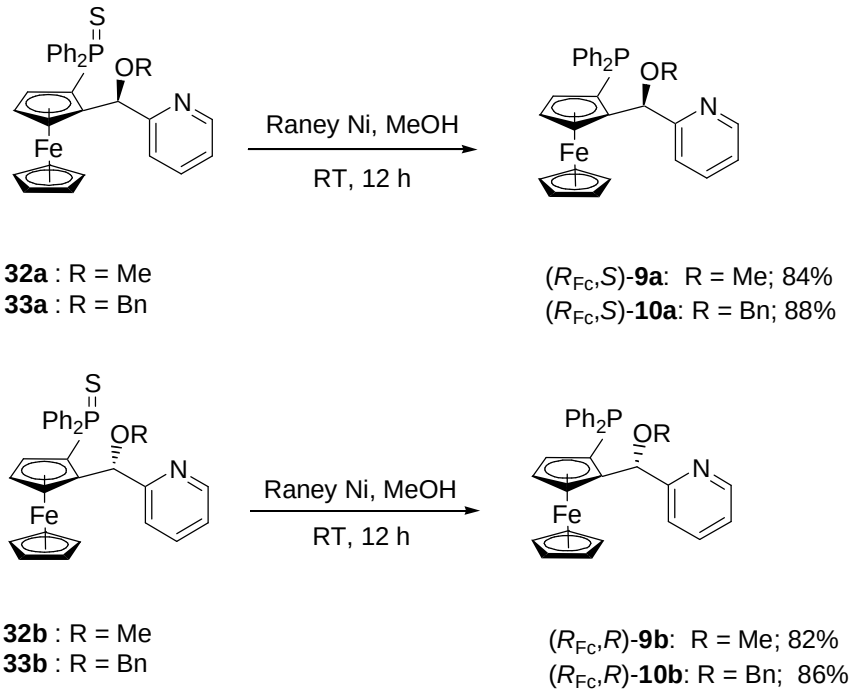


Figure 12. ORTEP drawing of **32b**.

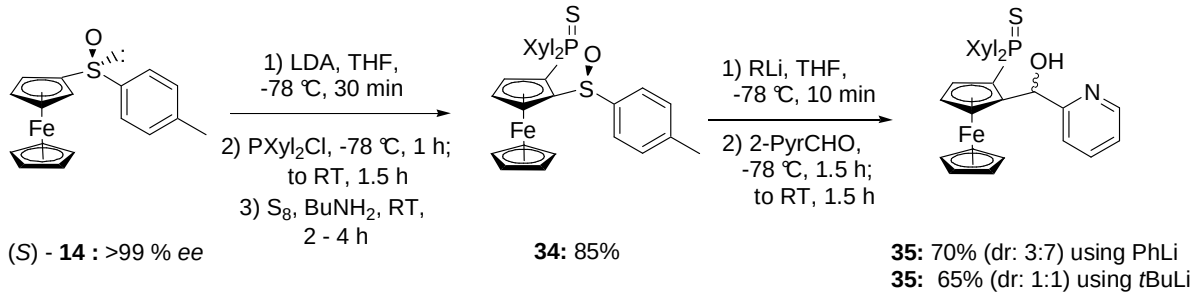
The reduction of the phosphine sulfides **32a-33b** was achieved smoothly with Raney-Ni in MeOH at 25 °C for 12 h, to furnish the air-stable chiral P,N-ligands **9a-10b** in 82-88% yield (Scheme 29). These ligands are quite stable towards air.



Scheme 29. Deprotection of phosphine sulfides **32a-b** and **33a-b**

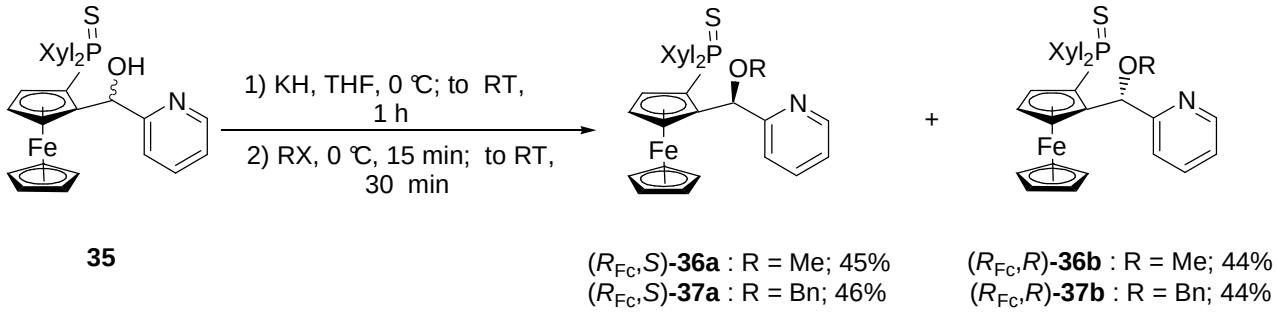
Furthermore, we have prepared the ferrocenyl P,N-ligands of type **9c-d** and **10c-d** by changing the aromatic group on the phosphorus (Scheme 32). Thus, treating the sulfoxide **14**

with LDA, followed by the addition of chlorobis(3,5-dimethylphenyl)phosphine, led to the sulfoxide **34** in 85% yield. Performing the sulfoxide-lithium exchange with PhLi, followed by the addition of 2-pyridinecarboxaldehyde, provided the mixture of diastereomeric alcohols **35** in 3:7 ratio ((R_{Fc},*S*):(R_{Fc},*R*)). On the other side, the diastereoselectivity of the alcohols changed to 1:1, when we performed the sulfoxide-lithium exchange using *t*BuLi, followed by the addition of pyridine-2-carboxaldehyde (Scheme 30).



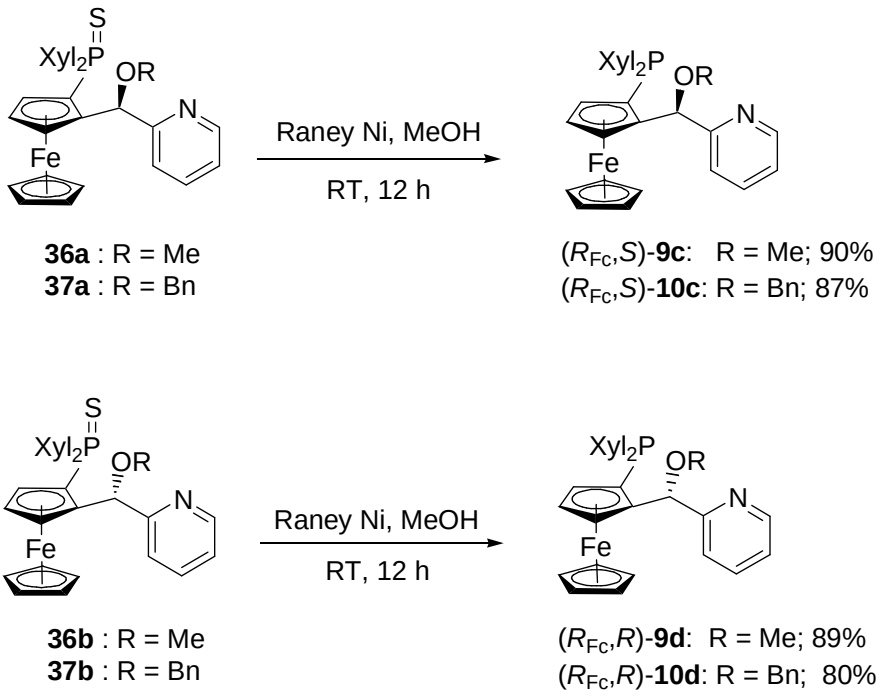
Scheme 30. Preparation of ferrocenyl alcohol **35**

O-alkylation of the alcohol mixture **35** using KH and CH_3I or $PhCH_2Br$ led to the corresponding separable methyl ethers **36a** (45%), **36b** (44%) and benzyl ethers **37a** (46%), **37b** (44%) respectively (Scheme 31).



Scheme 31. Preparation of ferrocenyl ethers **36a-b** and **37a-b**

Reduction of the phosphine sulfides **36a-b** and **37a-b** using Raney-Ni in methanol furnished the corresponding phosphine **9c-d** and **10c-d** in 80-90% yield (Scheme 32).



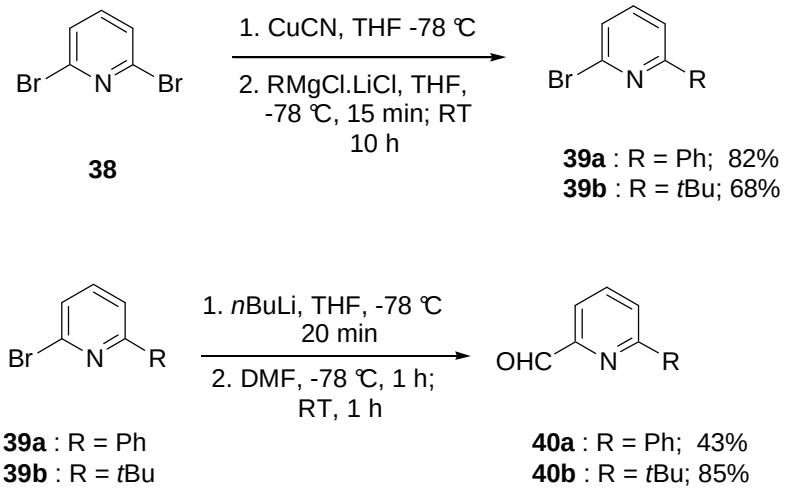
Scheme 32. Preparation of the P,N-ligands **9c-d** and **10c-d**

2.2.2. Synthesis of ferrocenyl P,N-ligands 9-10 with substituted pyridine as a *N*-donor

In addition, we directed our attention towards the preparation of chiral P,N-ligands having substituted pyridines as a *N*-donor group. We synthesized some 2-pyridine aldehydes with various substituents at the 6-position.

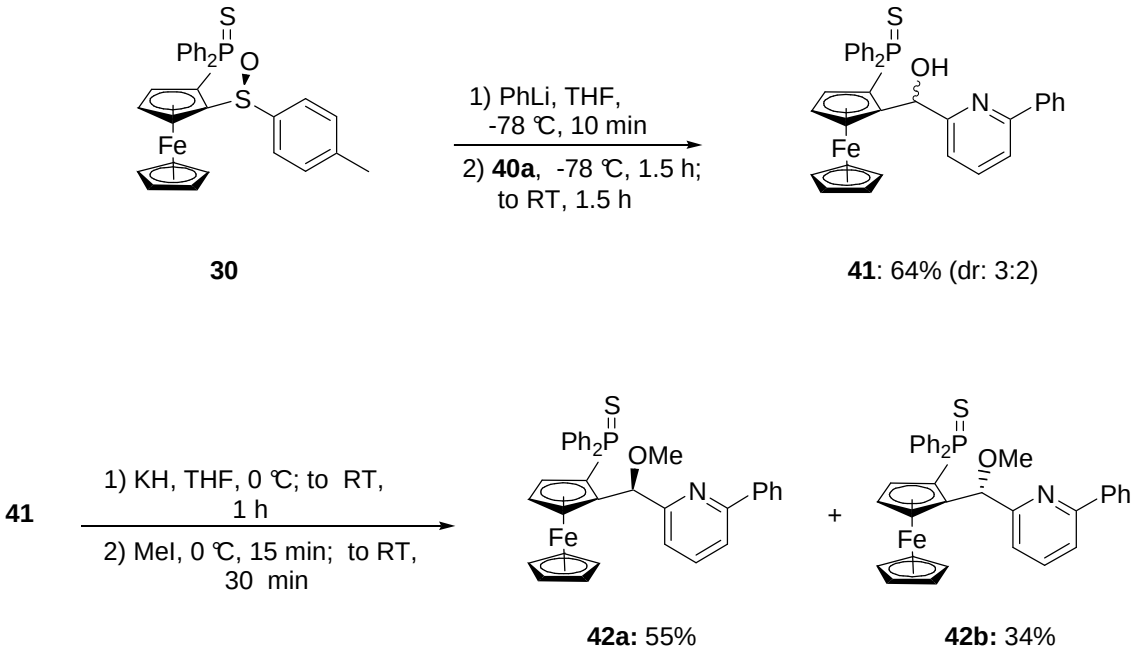
Treating 2,6-dibromopyridine with a fourfold excess of 2:1 PhMgCl·LiCl/CuCN mixture provided 6-phenyl-2-bromopyridine **39a** in 82% yield.[88] In a similar manner, reacting 2,6-dibromopyridine with *t*BuMgCl·LiCl, afforded 6-*t*butyl-2-bromopyridine **39b** in 68% yield. The bromine-lithium exchange on substrates **39a** and **39b** using *n*BuLi, followed by the addition of DMF, furnished the 2-pyridine aldehydes **40a** and **40b** in 43% and 82% yield, respectively (Scheme 33).[89]

[88] Bell, W. T.; Hu, L.-Y.; Patel, S. V. *J. Org. Chem.* **1987,** *52*, 3847.
[89] Ziessel, R. *New J. Chem.* **1996**, *20*, 919.



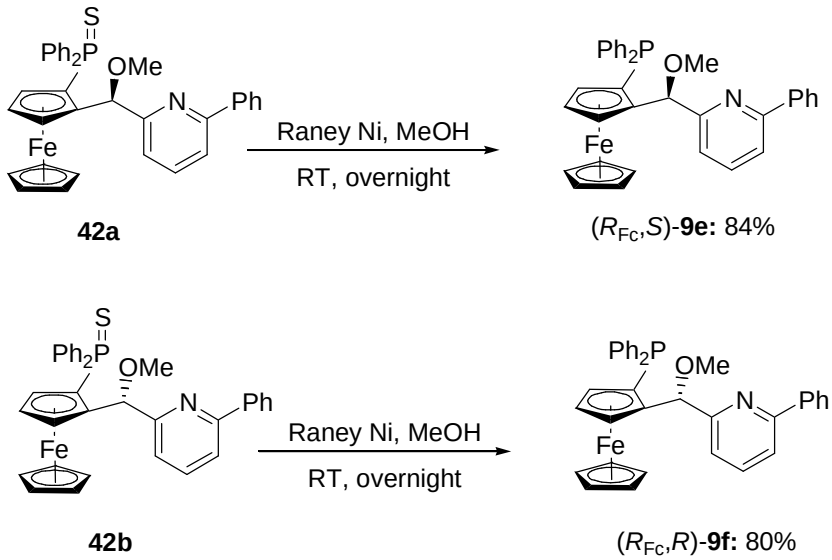
Scheme 33. Synthesis of 6-substittuted 2-pyridine aldehydes.

With the precursors in hands, we started our investigation towards the preparation of the new P,N-ligand derivatives of type **9** and **10** with substituted pyrdines as *N*-donors. Exchange of the sulfoxide on substrate **30** using PhLi at -78 °C, followed by the addition of **40a**, led to the two diastereomeric alcohols **41a** and **41b** as an inseparable diastereomeric mixture **41** in 64% yield. The diastereomeric mixture **41** was treated with KH and CH_3I, to afford the readily separable methyl ethers **42a** and **42b** in 55% and 34% yield, respectively (Scheme 34).



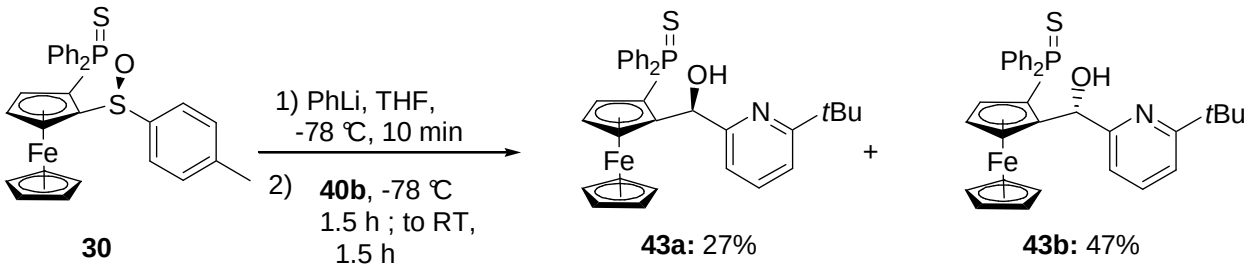
Scheme 34. Preparation of 6-phenylpyridyl-substituted P,N-ligands **42a-b**.

The deprotection of the two phosphine sulfides **42a** and **42b** was performed using Raney-Ni in MeOH at room temperature overnight, furnishing the corresponding phosphines **9e** and **9f** in 80-84% yield (Scheme 35).



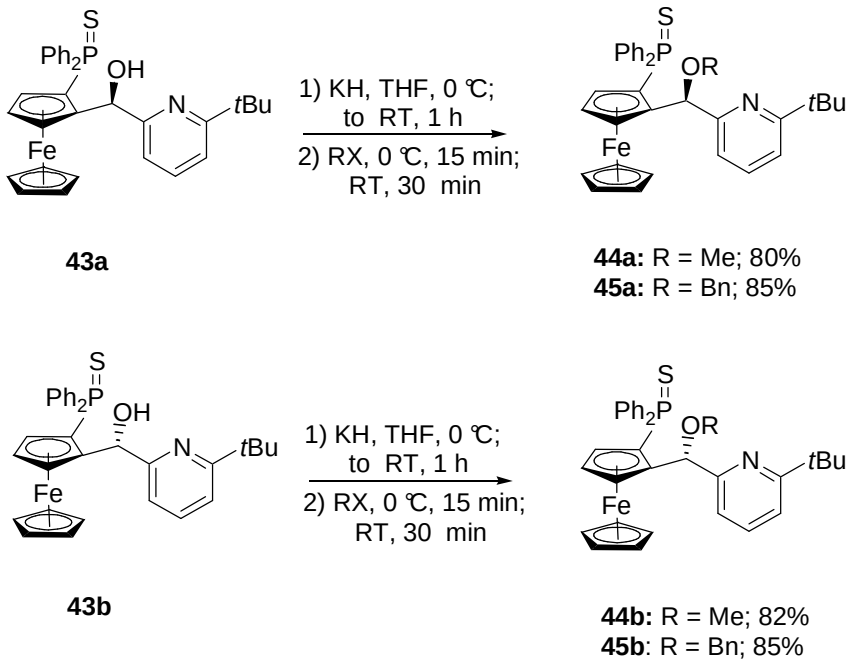
Scheme 35. Preparation of the chiral P,N-ligands **9e** and **9f**

Surprisingly, when we treated the ferrocenylsulfoxide **30** with PhLi at -78 °C, followed by the addition of 6-*t*butyl-2-pyridinecarboxaldehyde **40b**, we obtained the two diastereomeric alcohols **43a** and **43b** as separable compounds in 27% and 47% yield respectively (Scheme 35). Furthermore, the diastereoselectivity of the reaction was opposite to the other analogues **31a-b**, **35a-b** and **41a-b** (Scheme 27 and 31). The (R_{Fc},*R*) compound was obtained as the major diastereomeres and the (R_{Fc},*S*)-compound as the minor one (Scheme 36). This change in the diastereoselectivity may be because of the sterical hindrance of the *t*-butyl group.



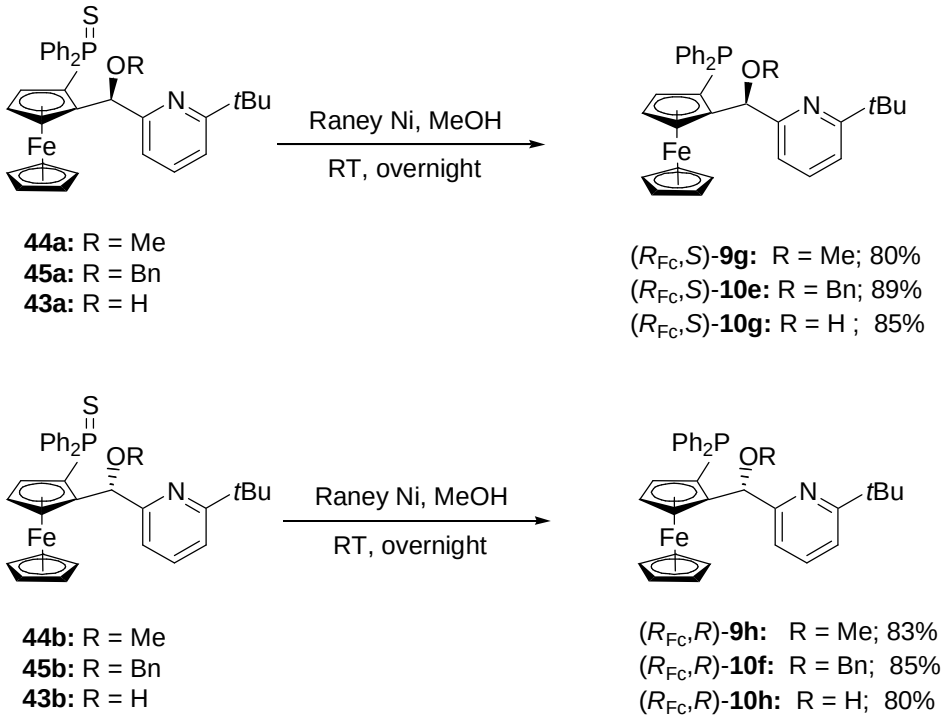
Scheme 36. Preparation of the phosphine sulfide **43a-b**

Treating the two ferrocenyl alcohols **43a** and **43b** individually with KH and MeI or BnBr provided the corresponding methyl ethers **44a** and **44b** in 80% and 82% yield and benzyl ethers **45a-b** in 85% yield respectively (Scheme 37). The stereochemistry of both diastereomers was deduced from their ^{1}H, ^{13}C NMR data when compared to that of compounds **32a** and **32b**.



Scheme 37. Synthesis of phosphine sulfides **44a-b** and **45a-b**

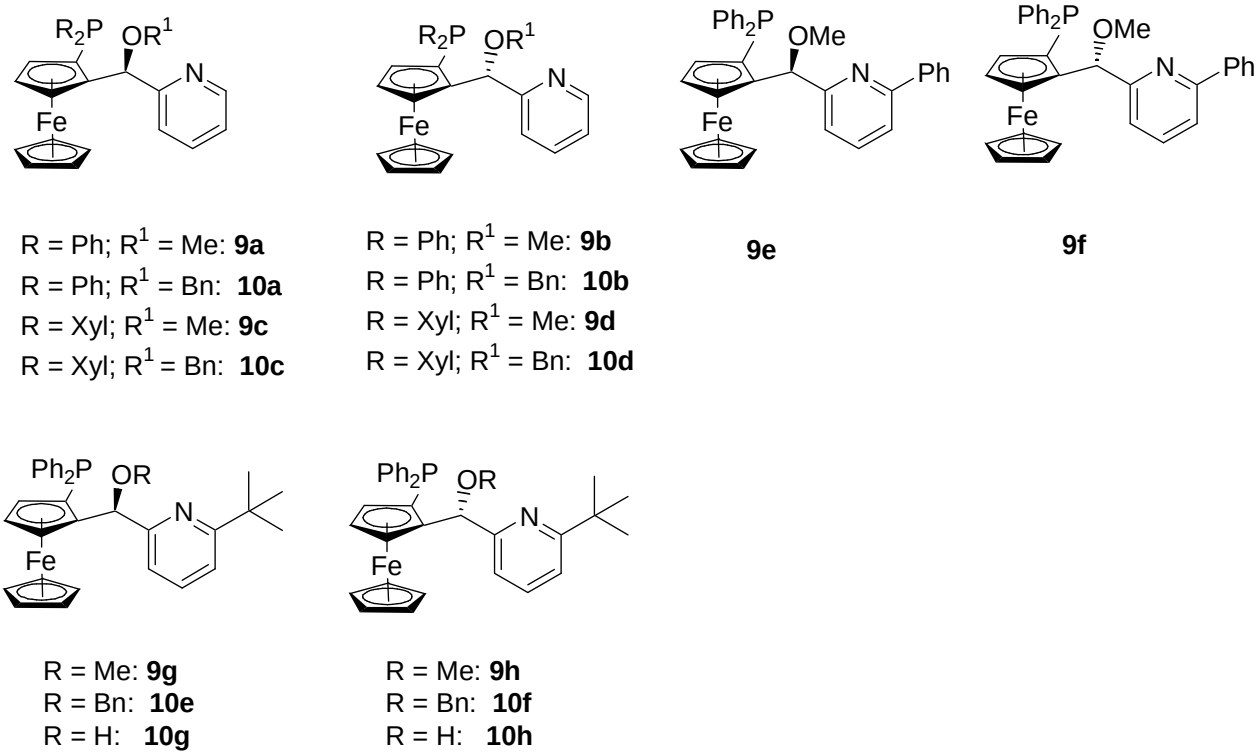
Desulfurization of the compounds **44a-b** and **45a-b** was smoothly accomplished using Raney-Ni in MeOH, furnishing the chiral phosphines **9g-h** and **10e-f** in 80-89% yield (Scheme 38). We then investigated the reduction of the phosphine sulfides of the ferrocenyl alcohols **43a** and **43b**. For this reason, we subjected the two ferrocenyl alcohols **43a-b** under similar conditions (Raney-Ni, MeOH, rt, overnight) and obtained the corresponding phosphines **10g** and **10h** in 85% and 80% yields, respectively (Scheme 38).



Scheme 38. Preparation of phosphines **9g-h** and **10e-h**

2.3. Applications in asymmetric catalysis

For clarity, the structure of the chiral P,N-lignads **9a-h** and **10a-h** is depicted in Scheme 39.

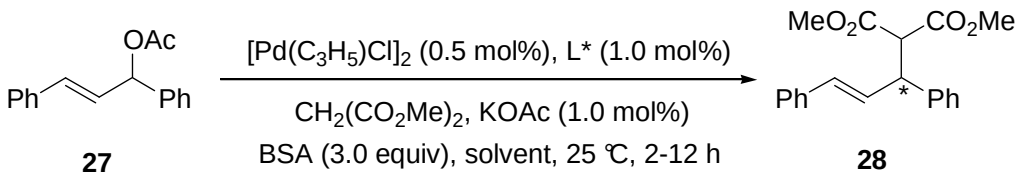


Scheme 39. Overview of novel chiral P,N-ligands **9a-h** and **10a-h**

2.3.1. Pd-catalyzed asymmetric allylic alkylation

With the novel chiral ligands **9a-h** and **10a-h** in hand, we examined their applications in Pd(0)-catalyzed allylic substitution reactions of racemic 1,3-diphenylprop-2-en-1-yl acetate (±)-**27** with dimethylmalonate, employing $[Pd(C_3H_5)Cl]_2$ as the catalyst precursor in the presence of a mixture of dimethylmalonate, *N*,*O*-bis(trimethylsilyl)acetamide (BSA), and potassium acetate in a solvent. The results are summarized in Table 3.

Table 3. Pd(0)-catalyzed asymmetric allylic substitution of **27** with dimethyl malonate.



27 **28**

Entry	L*	Solvent	T[h]	Yield (%)[a]	*ee*[b]
1	(R_{Fc},*S*)-**9a**	THF	6	89	70(*R*)
2	(R_{Fc},*S*)-**9a**	toluene	4	94	79(*R*)
3	(R_{Fc},*S*)-**9a**	CH_2Cl_2	6	90	89(*R*)
4[c]	(R_{Fc},*S*)-**9a**	CH_2Cl_2	12	90	97(*R*)
5	(R_{Fc},*S*)-**10a**	CH_2Cl_2	6	90	82(*R*)
6	(R_{Fc},*S*)-**9c**	CH_2Cl_2	6	91	89(*R*)
7	(R_{Fc},*S*)-**10c**	CH_2Cl_2	6	87	85(*R*)
8	(R_{Fc},*R*)-**9b**	CH_2Cl_2	8	69	25(*S*)
9	(R_{Fc},*R*)-**10b**	CH_2Cl_2	8	60	20(*S*)
10	(R_{Fc},*R*)-**9d**	CH_2Cl_2	8	65	25 (*S*)
11	(R_{Fc},*R*)-**10d**	CH_2Cl_2	8	55	28(*S*)
12	(R_{Fc},*S*)-**9e**	CH_2Cl_2	10	90	78(*R*)
13	(R_{Fc},*R*)-**9f**	CH_2Cl_2	10	85	30(*S*)
14	(R_{Fc},*S*)-**9g**	CH_2Cl_2	1	73	65(*R*)
15	(R_{Fc},*S*)-**10e**	CH_2Cl_2	1	75	64(*R*)
16	(R_{Fc},*S*)-**10g**	CH_2Cl_2	2	58	35(*R*)
17	(R_{Fc},*R*)-**9h**	CH_2Cl_2	1	92	94(*S*)
18	(R_{Fc},*R*)-**10f**	CH_2Cl_2	1	94	94(*S*)
19	(R_{Fc},*R*)-**10h**	CH_2Cl_2	2	90	66(*S*)

[a] Isolated yields of analytically pure product. [b] Enantioselectivity was determined by HPLC using a chiralcel OD-H column. [c] Reaction was performed at -20 °C

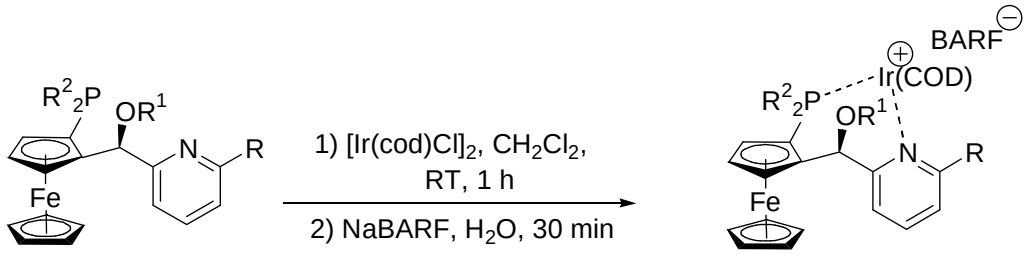
The results can be summarized as follows: high conversions and enantioselectivities were achieved in dichloromethane. Ligands bearing (*S*)-configuration at the α-centre, generally provided good reaction rates and enantioselectivities (entries 1-7 and 12). Exceptionally, in the case of P,N-ligands with a *t*-butyl group on the pyridine ring the (*R*)-isomers provided higher enantioselectivities compared to (*S*)-isomers (up to 94% *ee*; entries 14-19). The P,N-ligands bearing an alcohol group at the α-centre, such as **10g** and **10h**, provided mediocre results compared to the corresponding alkyl ethers **9g-h** and **10g-h** (entries 16 and 19). These results show the necessity of *O*-alkyl groups in creating a sterical environment capable of providing high enantioselectivities. The difference in the reactivity of both diastereomers (R_{Fc},*S*) and (R_{Fc},*R*), is clearly supporting the concept of substrate and catalyst matched and mismatched interactions.

2.3.2. Ir-catalyzed asymmetric hydrogenation of olefins

With encouraging results from the Pd(0)-catalyzed asymmetric allylic alkylation reactions with the P,N-ligands **9a-h** and **10a-h**, we then tested the efficiency of these new P,N-ligands in the Ir-catalyzed asymmetric hydrogenation of olefins.

Following, Pfaltz's procedure,[90] iridium complexes **46a-46g** and **47a-47g** were readily prepared by reacting a solution of $[Ir(cod)Cl]_2$ and the (R_{Fc},*S*)-P,N-ligand or (R_{Fc},*R*)-P,N-ligand in CH_2Cl_2 at room temperature for 1 h. The chloride ion was exchanged with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate using NaBARF in a biphasic CH_2Cl_2-H_2O system. The resulting orange BARF salts can be purified by silica gel column chromatography. These complexes were stable towards oxygen and moisture. The iridium-complexes **46a-g** were prepared by using $[Ir(cod)Cl]_2$ and the (R_{Fc},*S*)-P,N-ligand (Scheme 40 and Table 4)

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



R = H, Ph, *t*Bu
R^2 = Ph, Xyl
R^1 = Me, Bn

46a-g

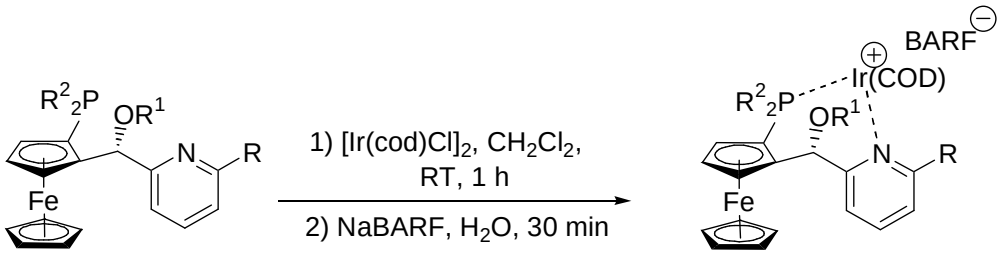
Scheme 40. Preparation of iridium complexes **46a-g**

Table 4. Preparation of Ir-catalysts **46a-g** using the (R_{Fc},*S*)-P,N-ligands.

Entry	Ligand	R	R^1	R^2	Yield[a]	Product
1	**9a**	H	Me	Ph	90	**46a**
2	**10a**	H	Bn	Ph	90	**46b**
3	**9c**	H	Me	(3,5-dimethylphenyl)	92	**46c**
4	**10c**	H	Bn	(3,5-dimethylphenyl)	89	**46d**
5	**9e**	Ph	Me	Ph	82	**46e**
6	**9g**	*t*Bu	Me	Ph	89	**46f**
7	**10e**	*t*Bu	Bn	Ph	88	**46g**

[a] Isolated yield of analytically pure product.

Using the similar procedure mentioned above, iridium complexes **47a-g** were prepared by using (R_{Fc},*R*)-P,N-ligand (Scheme 41 and Table 5).



R = H, Ph, *t*Bu
R^1 = Me, Bn
R^2 = Ph, Xyl

47a-g

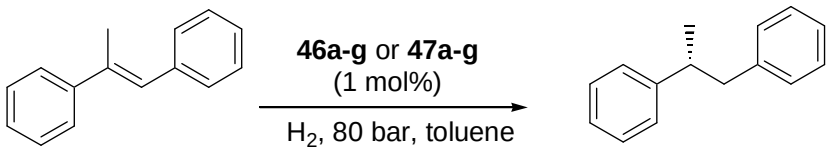
Scheme 41. Preparation of iridium complexes **47a-g**

Table 5. Preparation of Ir-catalysts **46a-g** using the (R_{Fc},*R*)-P,N-ligands.

Entry	Ligand	R	R^1	R^2	Yield[a]	Product
1	**9b**	H	Me	Ph	89	**47a**
2	**10b**	H	Bn	Ph	88	**47b**
3	**9d**	H	Me	(3,5-dimethylphenyl)	93	**47c**
4	**10d**	H	Bn	(3,5-dimethylphenyl)	90	**47d**
5	**9f**	Ph	Me	Ph	80	**47e**
6	**9h**	*t*Bu	Me	Ph	88	**47f**
7	**10f**	*t*Bu	Bn	Ph	80	**47g**

[a] Isolated yield of analytically pure product.

Applying these iridium complexes **46a-g** and **47a-g** in the asymmetric hydrogenation of olefin **48** gave disappointing results giving only traces of the product even at high hydrogen pressures and in different solvent systems (e.g. methanol, toluene, CH_2Cl_2, DMF etc) (Scheme 42).



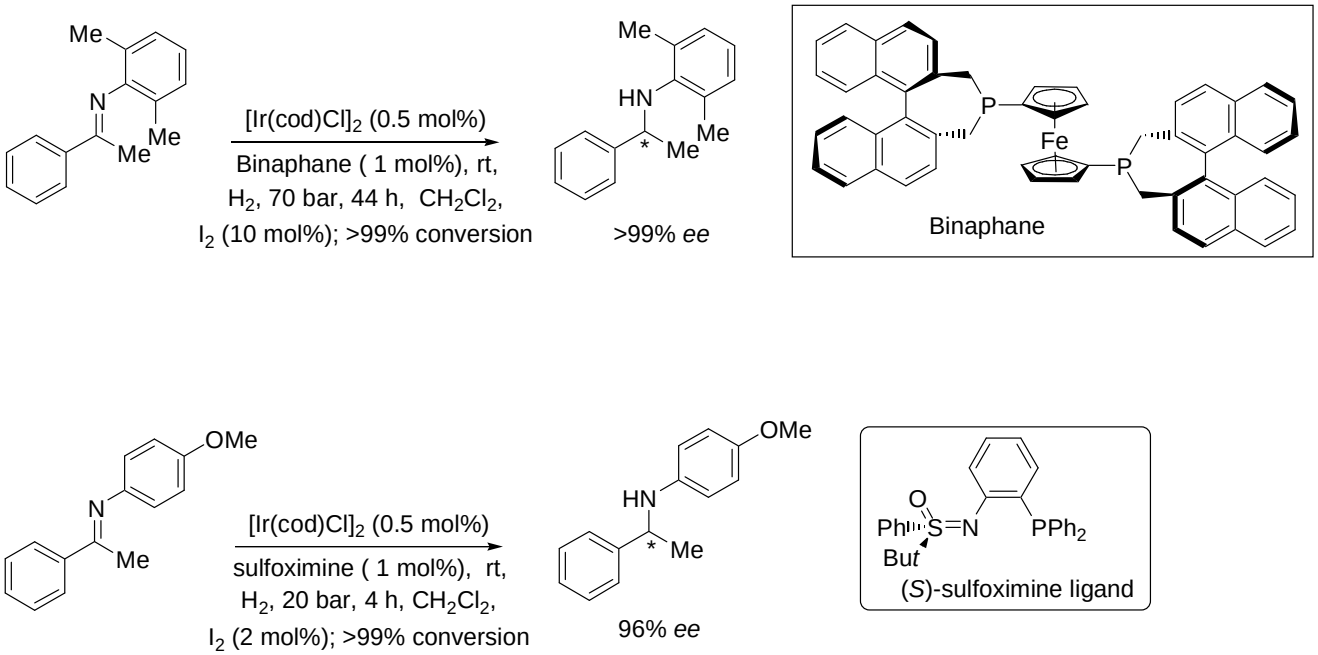
Scheme 42. Asymmetric hydrogenation of olefin **48** using the iridium complex **46a**

2.3.3. Ir-catalyzed asymmetric imine hydrogenation

Asymmetric synthesis of chiral amines is an important synthetic task since these structural units are widely used in pharmaceutical and agrochemical substances.[91] Recently, the catalytic asymmetric hydrogenation of imines has drawn much attention since it proves to be one of the most efficient ways to form chiral amines. In the past decade, many efficient catalysts using different transition metals, such as Ti,[92] Rh,[93] and Ru[94] were developed for the highly enantioselective imine hydrogenation. Although many efficient catalysts have been developed for the asymmetric imine hydrogenation, most of them were suitable only for

[91] a) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999,** *99*, 1069. b) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029. c) Blaser, H.-U.; Malan, C.; Pugin, B.; Spinder, F.; Steiner, H.; Studer, M. *Adv. Synth. Catal.* **2003,** *345*, 103.
[92] a) Verdaguer, X.; Lange, U. E. W.; Reding, M. T.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996,** *118*, 6784. b) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. c) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992,** *114*, 7562. d) Hanson, M. C.; Buchwald, S. L. *Org. Lett.* **2000,** *2*, 713.
[93] a) Mao, J.; Baker, D. C. *Org. Lett.* **1999**, *1*, 841. b) Xiao, D. Zhang, X. *Org. Lett*, **1999**, 1679. c) Becalski, A. G.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G.-J.; Rettig, S. R. *Inorg. Chem.* **1991**, *30*, 5002.
[94] a) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916. b) Cobley, C. J.; Henschke, J. P. *Adv. Synth. Catal.* **2003**, *345*, 195. c) Oppolzer, W.; Wills, M.; Starkemann, M.; Bernardinelli, G. *Tetrahedron Lett.* **1990,** *31*, 4117.

cyclic substrates. The reduction of acyclic imines with high enantioselectivities is still a major challenge in this field.[95] Chiral iridium complexes based on P,P or P,N-ligands have been successfully applied as catalysts for the highly enantioselective hydrogenation of imines.[96] One of the most notable examples was reported by Zhang *et al.* in the hydrogenation of acyclic imines that gave up to 99% *ee* using Ir/F-Binaphane catalysts.[97] Furthermore, Bolm *et al.* reported a highly enantioselective Ir-catalyzed hydrogenation of *N*-aryl ketimines using sulfoximine ligands (P,N-ligands) with I_2 as an additive[98] (Scheme 43).



Scheme 43. Ir-catalyzed asymmetric reduction of *N*-aryl ketimines

We investigated the efficiency of the new iridium complexes **46a-46g** and **47a-47g** in asymmetric imine hydrogenation. For this purpose, *N*-Phenylethylidene amine **50a** was

[95] Ohkuma, T.; Kitamura, M.; Noyori, R. In *Catalytic Asymmetric Synthesis;* Ojima, I., Ed.; Wiley-VCH: Weinheim, 2000, p 1.

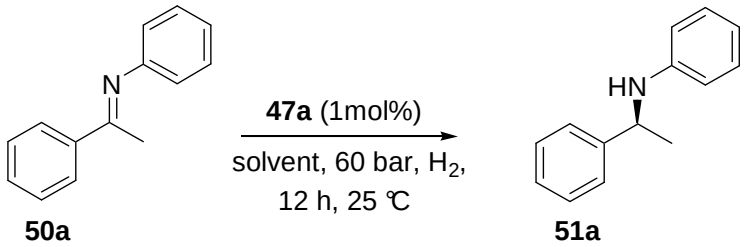
[96] a) Trifonova, A.; Diesen, J. S.; Chapman, C. J.; Anderson, P. G. *Org. Lett.* **2004,** *6*, 3825. b) Olinas, M.; Pfaltz, A.; Cozzi, P. G.; Leitner, W. *J. Am. Chem. Soc.* **2004,** *126*, 16142. c) Iwadate, N.; Yoshida, K.; Imamoto, T. *Org. Lett.* **2006,** *8*, 2289. d) Guiu, E.; Aghmiz, M.; Diaz, Y.; Claver, C.; Meseguer, B.; Militzer, C.; Castillon, S. *Eur. J. Org. Chem.* **2006,** 627. d) Spindler, F.; Blaser, H.-U. *Adv. Synth. Catal.* **2001,** *343*, 68. e) Schnider, P.; Koch, G.; Prétôt, R.; Wang, G.; Bohnen, F. M.; Krüger, C.; Pfaltz, A. *Chem. Eur. J.* **1997,** *3*, 887. f) Jiang, X.-B.; Minnaard, A. J.; Hessen, B.; Feringa, B. L.; Duchateau, A. L. L.; Andrien, J. G. O.; Boogers, J. A. F.; Vries, d. J. G. *Org. Lett.* **2003,** *5*, 1503. g) Kainz, S.; Brinkmann, A.; Leitner, W.; Pfaltz, A. *J. Am. Chem. Soc.* **1999,** *121*, 6421. h)Wang, W.-B.; Lu, S.-M.; Yang, P.-Y.; Han, X.-W.; Zhou, Y.-G. *J. Am. Chem. Soc.* **2003,** *125*, 10536. i) Dervisi, A.; Carcedo, C.; Ooi, L.-L. *Adv. Synth. Catal.* **2006,** *348*, 175. j) Vargas, S.; Rubio, M.; Suárez, A.; Río, D. D.; Álvarez, E.; Pizzano, A. *Organometallics* **2006, 25,** 961. k). Zhu, G.; Zhang, X. *Tetrahedron: Asymmetry* **1998**, *9*, 2415.

[97] Xiao, D.; Zhang, X. *Angew. Chem. Int. Ed.* **2001**, *40*, 3425.

[98] Moessner, C.; Bolm, C. *Angew. Chem. Int. Ed.* **2005**, *44*, 7564.

chosen as the test substrate and hydrogenation reaction was performed at 60 bar pressure using 1 mol% of **47a** as the standard catalyst. The results are summarized in Table 6.

Table 6. Asymmetric hydrogenation of imine **50a** using catalyst **47a** and testing the effect of solvents



50a **51a**

Entry	Solvent	Conversion (%)[a]	*ee*(%)[b,c]
1	toluene	96	11
2	CH_2Cl_2	55	6
3	MeOH	23	39
4	Tol:MeOH (4:1)	72	67
5	Tol:MeOH (1:1)	63	56
6	Tol:MeOH (10:1)	80	23
7	Tol:*i*PrOH (4:1)	89	2
8	Tol:*t*BuOH (4:1)	63	56

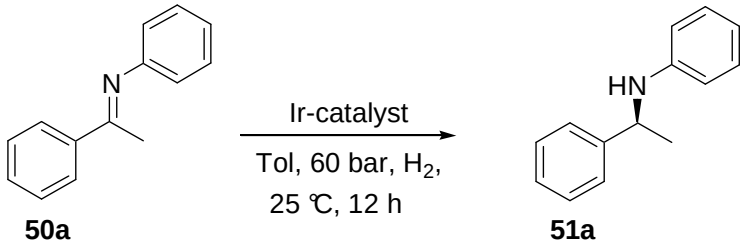
[a] Conversion was measured by chiral GC or by ^{1}H NMR. [b] Enantioselectivity was determined by chiral GC using a DEX-CB column.
[c] Configuration was assigned by comparing the literature values.

Hydrogenation of imine **50a** in toluene provided the corresponding amine **51a** in 96% conversion, but only in 11% *ee* (entry 1). We also noticed that very polar solvents (e.g. methanol) or less polar solvents (e.g. CH_2Cl_2) tremendously decreased the reaction rate and enantioselectivity (entries 2-3). Interestingly, performing the hydrogenation of imine **50a** in a mixed solvent system such as toluene:methanol (4:1) showed a remarkable improvement in enantioselectivity from 11 to 67% *ee* but decreased the conversion of the amine **51a** (entry 4). Increasing the portion of methanol in the solvent mixture of toluene/methanol or replacing the methanol by 2-propanol or *t*-butanol led to only mediocre conversions and poor

enantioselectivities of the amine **51a** (entries 5-8). It turned out that a toluene:methanol (4:1) mixture only provided the improved selectivities in the hydrogenation of imine **50a**.

For a systematic approach, we initially tested all the iridium complexes **47a-47g** in the hydrogenation of imine **50a** using the reaction conditions from the above screenings. We conducted the hydrogenation of **50a** in toluene:methanol (4:1) at 60 bar pressure using the catalysts **47a-g** (Table 7).

Table 7. Ir-catalyzed enantioselective hydrogenation of imine **50a** using **47a-g**



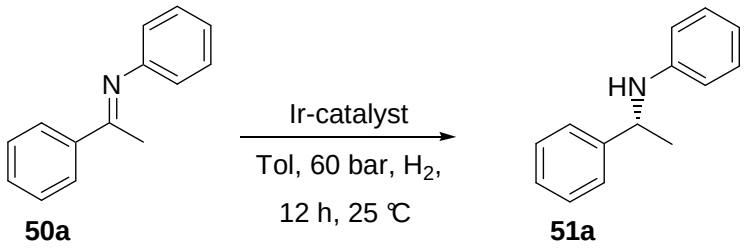
50a **51a**

Entry	Catalyst	Conv(%)[a]	*ee*(%)[b,c]
1	**47a**	72	67
2	**47b**	75	65
3	**47c**	70	65
4	**47d**	79	65
5	**47e**	20	10
6	**47f**	40	18
7	**47g**	34	18

[a] Conversion was measured by ^{1}H-NMR analysis or by chiral GC.[b] Enantioselectivity was determined by chiral GC using a DEX-CB column.
[c] Configuration was assigned by comparing the literature values

Ir-complexes **47a-47d** which have no substitution on the pyridine ring of the P,N-ligand provided better enantioselectivities and moderate conversions in the hydrogenation of imine **50a** (entries 1-4). Ir-complexes **47e-47g** with substitution on the pyridine ring of P,N-ligands provided poor conversions and selectivities (entries 5-7). Under similar conditions (toluene/methanol (4:1), H_2, 60 bar, rt), we examined the efficiency of Ir-catalysts **46a-46g** in the hydrogenation of imine **50a** (Table 8).

Table 8. Ir-catalyzed enantioselective hydrogenation of imine **50a** using **46a-g.**



50a **51a**

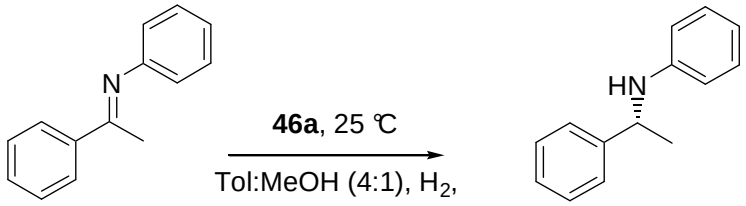
Entry	Catalyst	Conv(%)[a]	*ee*(%)[b,c]
1	**46a**	100	82
2	**46b**	100	82
3	**46c**	100	80
4	**46d**	100	80
5	**46e**	50	26
6	**46f**	21	6
7	**46g**	30	5

[a] Conversion was measured by ^{1}H-NMR analysis or by chiral GC.[b] Enantioselectivity was determined by chiral GC using a DEX-CB column.
[c] Configuration was assigned by comparing the literature values

Ir-catalysts with (*S*)-configuration at the α-center and no substitution on the pyridine ring of the P,N-ligand, provided improved results in the reduction of imine **50a**. Reduction of imine **50a** using the iridium catalysts **46a-d** proceeded quantitatively and provided the amine **51a** in 80-82% *ee* (entries 1-4), whereas the Ir-catalysts **46e-f** with substitutions on the pyridine ring of P,N-ligands provided low selectivities and conversions (entries 5-7).

To trace out the most efficient reaction conditions for the imine hydrogenation, we performed the hydrogenation of imine **50a** using the catalyst **46a** at low hydrogen pressures and low catalyst loadings (Table 9). Decreasing the hydrogen pressure from 60 to 10 bar didn't effect the conversion; it rather improved the enantioselectivity of amine **51a** from 82 to 84% *ee* (entries 1-5). Hydrogenation at 1 bar hydrogen pressure resulted in long reaction timings (entry 5). Decreasing the catalyst loading from 1 mol% to 0.5 mol% increased the reaction time but retained the enantioselectivity at 84% *ee* (entry 6). We observed a decrease in enantioselectivity when the catalyst loading was lower to 0.25 mol% (entry 7).

Table 9. Effect of the catalyst loading and hydrogen pressure on the hydrogenation of imine **50a** using the catalyst **46a**



50a **51a**

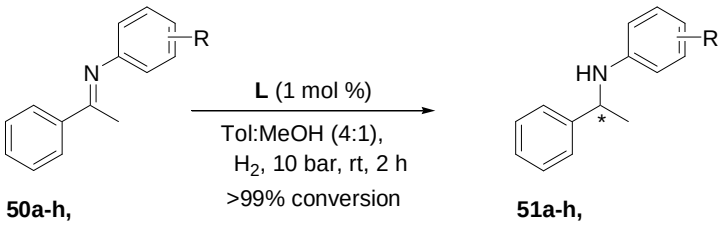
Entry	Catalyst loading (mol %)	Pressure (bar)	Time [h]	Conversion [%][a]	*ee*(%)[b]
1	1	60	2	100	82
2	1	40	2	100	83
3	1	20	2	100	84
4	1	10	2	100	84
5	1	1	21	75	84
6	0.5	10	3	100	84
7	0.25	10	12	100	80

[a] Conversion was measured by chiral GC or ^{1}H NMR. [b]. Enantioselectivity was determined by chiral GC using a DEX-CB column.

Among all catalysts **46a-g**, **47a-g** the iridium catalysts **46a**, **46b**, **46c** and **46d** provided better results under optimized conditions (toluene:MeOH (4:1), 10 bar H_2, 2 h; 80-84% *ee*). In order to further improve this asymmetric imine hydrogenation, we performed the hydrogenation of various imines with different aryl substituents attached to the nitrogen atom of the imine, using the catalysts **46a-46b** (Table 10). We noticed that reduction of imines with electron-rich aromatic groups on the imine nitrogen proceeded well and provided improved enantioselectivities (entries 2-6). Imines having *ortho*-substituted aromatic groups on the nitrogen atom gave mediocre conversions and enantioselectivities (entries 8-9). Interestingly,

the hydrogenation of the imine **52a** (R = 3,5-dimethyl) gave the best results, providing the corresponding secondary amine (*R*)-**53a**[99] in 93-94% *ee* (entry 10).

Table 10. Asymmetric hydrogenation of imines **50a-h** and **52a** using the Ir-complexes **46a** and **46b**



50a-h, **51a-h,**

Entry	Imine	R	Product [a]	*ee* (%)[b]	
				L = **46a**	L = **46b**
1	**50a**	H	**51a**	84(*R*)	84(*R*)
2	**50b**	4-MeO	**51b**	88(*R*)	88(*R*)
3	**50c**	4-Me	**51c**	84	84
4	**50d**	3,4-dioxymethylene	**51d**	90	90
5	**50e**	3,4,5-trimethoxy	**51e**	89	87
6	**50f**	3,4-dimethyl	**51f**	90	89
7	**50g**	3,4-dimethoxy	**51g**	81	80
8[c]	**50h**	2,4-dimethyl	**51h**	83	80
9[d]	**50i**	2-MeO	**51i**	54	50
10	**52**	3,5-dimethyl	**53a**	94(*R*)	93(*R*)

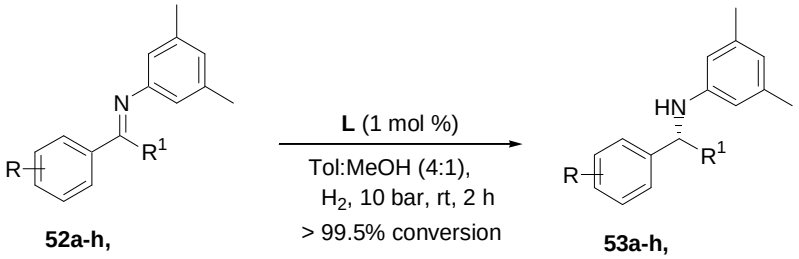
[a] In all cases full conversion was achieved in 2-4 h. [b] Enantioselectivity was determined by HPLC (chiracel OD-H) or by GC using a chiral Dex-CB column. [c] Reaction time is 10 h; isolated yield is 84% [d] Reaction time is 12 h; isolated yield is 50%.

To envisage the effect of functional groups on the imine hydrogenation, we investigated the hydrogenation on a series of imines of type **52** using the catalysts **46a** and **46b** (Table 11). Imines **52b-52h** were smoothly reduced under the optimized conditions and provided the corresponding secondary amines **53b-53h** in 84-94% *ee* (Table 9). Imines with electron donating groups (entries 2, 3, 4 and 7) provided better enantioselectivities compared to electron withdrawing groups (entry 5). Reduction of the imine **52h** which was derived from

[99] Kwong, F. Y.; Buchwald, S. L. *Org Lett*. **2003,** *5*, 793.

tetralone also proceeded well and the corresponding amine **53h** was obtained in 84% *ee* (entry 8).

Table 11. Asymmetric hydrogenation of imines **52a-h** using the Ir-complexes **46a** and **47a**



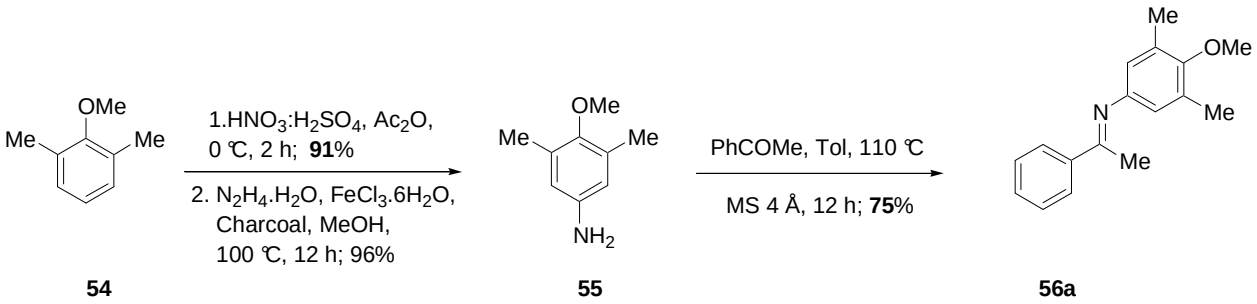
Entry	Imine	R	R^1	Product[a]	*ee*(%)[b]	
					L = **46a**	L = **46b**
1	**52a**	H	Me	**53a**	94	93
2	**52b**	4-MeO	Me	**53b**	94	93
3	**52c**	4-Me	Me	**53c**	93	92
4	**52d**	3-OMe	Me	**53d**	94	89
5	**52e**	4-Cl	Me	**53e**	91	88
6	**52f**	4-Ph	Me	**53f**	88	82
7	**52g**	H	Et	**53g**	94	94
8	**52h**	$-(CH_2)_3-$	Me	**53h**	84	84

[a] In all cases full conversion was achieved. [b] enantioselectivity was determined by HPLC using a chiralcel OD-H column or by AD-column.

Although high enantioselectivities were achieved in the hydrogenation of imines of type **52**, the removal of the 3,5-dimethylphenyl group from the amine **53** was difficult. In general, secondary amines with 4-methoxy or 2-methoxyphenyl on the nitrogen atom of the amine can be cleaved under practical conditions to provide chiral primary amines.[100] Since the imines with *N*-(4-methoxyphenyl) group **50b**, **50e**, **50g** and *N*-(2-methoxyphenyl) group **50i** provided the corresponding amines in moderate enantioselectivities (entries 2; 5, 7, and 9 of Table 10), we searched for another substrate. We thought that *N*-aryl imine **56a** with a 3,5-dimethyl-4-methoxyphenyl group on the imine nitrogen could also be the ideal substrate for the

[100] For the cleavage of 4-methoxy *N*-phenyl groups see a) Shang, G.; Yang, Q.; Zhang, X. *Angew. Chem. Int. Ed.* **2006**, *45*, 5194. b) Palacios, F.; Aparicio, D.; García, J.; Rodríguez, E. *Eur. J. Org. Chem.* **1998**, 1413. c) Taniyama, D.; Hasegawa, M.; Tomika, K. *Tetrahedron Lett.* **2006**, *47*, 821. for the cleavage of 2-methoxy *N*-phenyl groups see ref 15

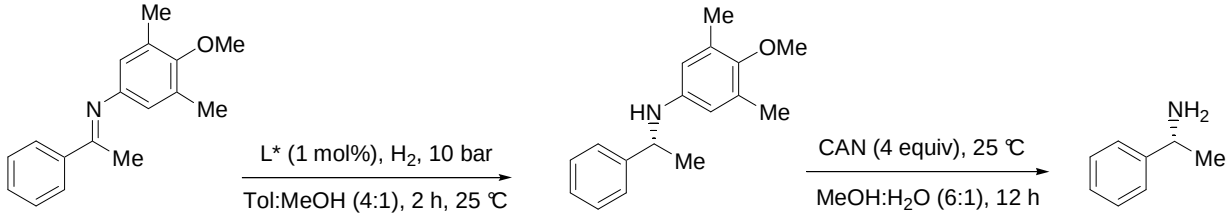
deprotection to provide primary amines. Imine **56a** was synthesized as showed in the following scheme (Scheme 44).



54 **55** **56a**

Scheme 44. Synthesis of the imine **56a**

To our delight, imine **56a** could be smoothly reduced using the Ir-catalysts **46a** and **46b**, furnishing the corresponding secondary amine **57a** in 92-94% *ee*. As we anticipated, deprotection of the 3,5-dimethyl-4-methoxyphenyl group on the amine **57a** was accomplished by using cerium ammonium nitrate (CAN; $Ce(NH_4)_2(NO_3)_6$) in MeOH:H_2O (6:1), providing the chiral primary amine (*R*)-**58** in 85% yield and 94% *ee* (Scheme 45).



56a **(*R*)-57a** **(*R*)-58**

L * = **46a**: 96%; 94% *ee*
L * = **46b:** 95%; 92% *ee*

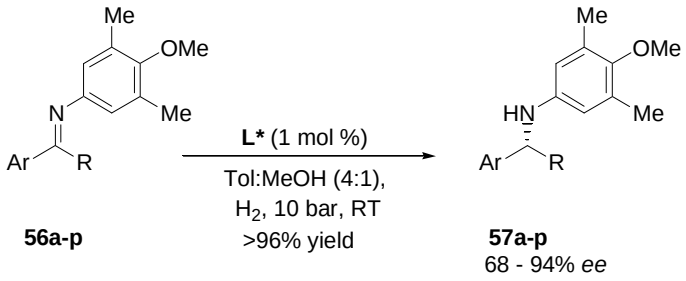
85%; 94% *ee*

Scheme 45. Asymmetric hydrogenation of imine **56a** using the Ir-catalysts **46a** and **46b** and subsequent deprotection to primary amine **58**

To extend the scope of this asymmetric imine hydrogenation, we examined the reduction of various imines of type **56** using the Ir-catalysts **46a** and **46b** (Table 12). The results are summarized as follows. Both electron donating (entries 2, 3, 4, 7, 8, 12 and 13) and electron withdrawing substituents (entries 5, 6, 9, 10, 11 and 14) provided high enantioselectivities (80-94% *ee*; Table 10) in hydrogenation. Imines with electron withdrawing groups on the aromatic ring provided higher enantioselectivities compared to electron donating groups. Among the electron-rich imines, imines with *meta*- and *ortho*-substitution provided better enantioselectivities compared to *para*-substitution (entries 2, 4, 8 and 3, 7). Reduction of the

imine derived from tetralone **56o** provided the secondary amine in 84% *ee*, whereas the indanone derived imine **56p** provided the corresponding amine only in 70% *ee*

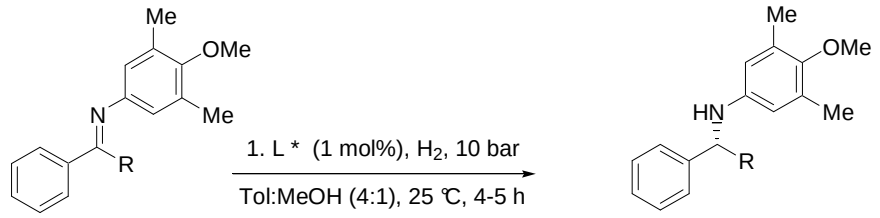
Table 12. Asymmetric hydrogenation of imines **56a-p** using the Ir-complex **46a** and **46b**



Entry	Imine	Ar	R	Product	time [h][a]	*ee*(%)[b]	
						46a	**46b**
1	**56a**	Ph	Me	**57a**	2	94	92
2	**56b**	4-Me-C_6H_4	Me	**57b**	2	86	85
3	**56c**	3-MeC_6H_4	Me	**57c**	2	94	93
4	**56d**	2-Me-C_6H_4	Me	**57d**	6	94	94
5	**56e**	4-MeCO_2-C_6H_4	Me	**57e**	4	94	92
6	**56f**	4-CF_3-C_6H_4	Me	**57f**	2	89	88
7	**56g**	4-MeO-C_6H_4	Me	**57g**	2	85	84
8	**56h**	3-MeO-C_6H_4	Me	**57h**	2	86	82
9	**56i**	3-F-C_6H_4	Me	**57i**	2	93	91
10	**56j**	4-Cl-C_6H_4	Me	**57j**	4	92	92
11	**56k**	3-Cl-C_6H_4	Me	**57k**	2	90	90
12	**56l**	4-Ph-C_6H_4	Me	**57l**	2	92	90
13	**56m**	2-naphthyl	Me	**57m**	2	93	93
14	**56n**	3-CH_3CO-C_6H_4	Me	**57n**	2	80	80
15	**56o**	Ph	-$(CH_2)_3$-	**57o**	2	84	84
16[c]	**56p**	Ph	-$(CH_2)_2$-	**57p**	12	70	68

[a] Time to achieve full conversion. [b] Enatioselectivity was determined by HPLC using chiracel OD-H column or AD-column. [c] Only 70% conversion was achieved even after 12 h at rt.

The asymmetric imine hydrogenation with catalysts **46a** and **46b** can also be applied to various kinds of imines bearing a side-chain at the α–position. Thus, imines **56q-s** underwent a smooth hydrogenation and the respective secondary amines **57q-s** were obtained in 92-95% *ee* (Scheme 46).



56q : R = Et
56r : R = Pent
56s : R = $(CH_2)_2Ph$

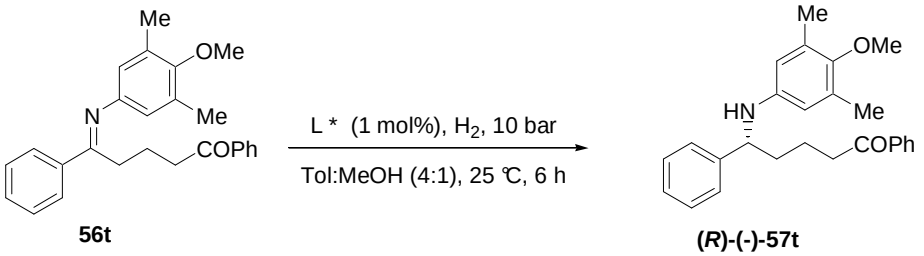
R= Et; **57q** L * = **46a:** 96%; 94% *ee*
L* = **46b:** 95%; 92% *ee*

R = Pent; **57r** L * = **46a:** 98%; 95% *ee*
L* = **46b:** 95%; 94% *ee*

R = $(CH_2)_2Ph$; **57s** L * = **46a:** 98%; 95% *ee*
L* = **46b:** 95%; 95% *ee*

Scheme 46. Reduction of imines **56q**, **56r** and **56s** with side-chains at the α-position using the catalysts **46a** and **46b**

Interestingly, reduction of the imine **56t** bearing a remote keto group proceeded chemo-selectively and quantitatively, yielding the corresponding amine **57t** in 99% *ee* (Scheme 47). No over-reduction of the ketone functionality was observed in this reaction.

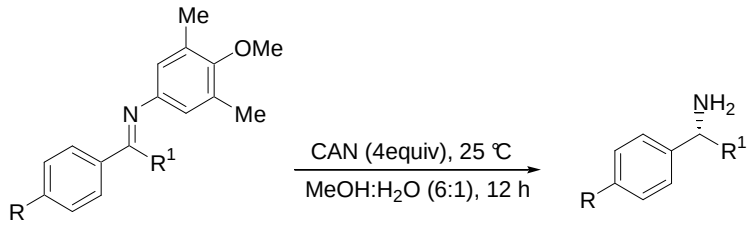


56t **(*R*)-(-)-57t**

L * = **46a:** 95%; 99% *ee*
L* = **46b:** 95%; 98% *ee*

Scheme 47. Chemoselective hydrogenation of imine **56t** using the Ir-catalysts **46a** and **46b**

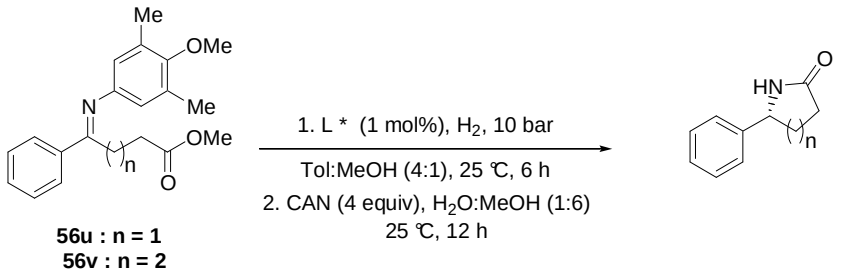
Deprotection of the functionalized amines of type **56** was also accomplished by using CAN to furnish the corresponding (*R*)-primary amines in good yields (Scheme 48).



(*R*)-59: R = Cl, R^1 = Me: 82%; 92% *ee*
(*R*)-60: R = CO_2Me R^1 = Me: 87%; 94% *ee*
(*R*)-61: R = H R^1 = Et: 80%; 94% *ee*
(*R*)-62: R = H R^1 = Pent 78%; 95% *ee*

Scheme 48. Preparation of chiral primary amine **59-62**

Furthermore, we extended this protocol to the asymmetric synthesis of chiral γ- and δ-lactams.[101-102] Thus, the imines **56u** and **56v** bearing a remote ester group were subjected to the asymmetric hydrogenation, and after subsequent deprotection of the *N*-aromatic group, the 5-phenyl-2-pyrrolidinone **63** and 6-phenyl-2-piperidinone **64** were obtained in 74% yield, 92% *ee* and 78% yield, 97% *ee* respectively (Scheme 49).



56u : n = 1
56v : n = 2

n = 1; **(*R*)-(+)-63** L * = **46a:** 74%; 92% *ee*
L* = **46b:** 72%; 90% *ee*

n = 2; **(*R*)-(+)-64** L * = **46a:** 78%; 97% *ee*
L* = **46b:** 72%; 96% *ee*

Scheme 49. Synthesis of γ- and δ-lactams **63** and **64**

Hydrogenation of disubstituted imines **56w-y** under optimized reaction conditions was then investigated (Scheme 50). Unlike the mono substituted imines, disubstituted imines with electron donating groups provided improved enantioselectivities compared to the electron withdrawing imine (Scheme 50).

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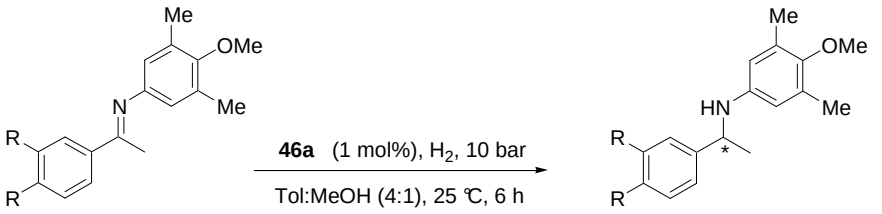
[101] for the asymmetric synthesis of γ-lactams, a) Ramachnadran, P. V.; Burghardt, T. E. *Chem. Eur. J.* **2005,** *11,* 4387. b) Vivienne, B. C.; Page, M. I.; Korn, S. R.; Monteith, M. *Chem. Commun.* **1999**, *8*, 721. c) Ward, B. D.; Risler, H.; Weitershaus, K.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Inorg. Chem.* **2000**, *45*, 7777.

[102] for the asymmetric synthesis of δ-lactams, a) Burke, A. J.; Davies, S. G.; Garner, A. C.; McCarthy, T. D.; Roberts, P. M.; Smith, A. D.; Rodriguez-Solla, H.; Vickers, R. J. *Org. Biomol. Chem.* **2004**, *2*, 1387. b) Davis, F. A.; Chao, B.; Fang, T.; Szewczyk, J. M. *Org. Lett.* **2000**, *2*, 1041. c) Davis, F. A.; Szewczyk, J. M. *Tetrahedron Lett.* **1998**, *39*, 5951.



56w: R = Cl:
56x: R = OMe
56y: R = Me

57w: R = Cl: 96%; 87% *ee*
57x: R = OMe 96%; 92% *ee*
57y: R = Me 98%; 94% *ee*

Scheme 50. Hydrogenation of disubstituted imines **56w-y**

2.4. Conclusion

In conclusion, the novel synthesis of P,N-ligands **9a-g** and **10a-g** in high yields was achieved. Their iridium complexes **46a-g** and **47a-g** were prepared and applied in asymmetric imine hydrogenation. Various *N*-arylketimines were reduced using the Ir-catalysts **46a** and **46b** in high conversions and enantioselectivities (up to 99% *ee*). We also described the synthesis of chiral primary amines and γ- and δ-lactams via this asymmetric imine hydrogenation.

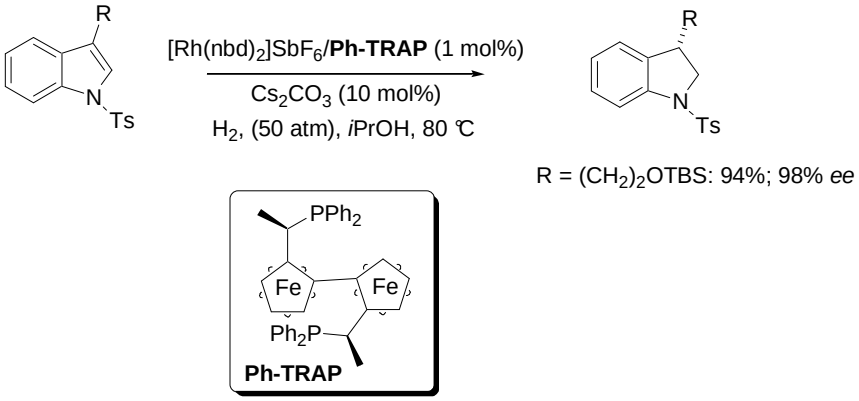
3. Preparation of bis-ferrocenyl P,P ligands and their applications in asymmetric catalysis

3.1. Introduction

Although many chiral ferrocene ligands have been prepared for various transition-metal-catalyzed asymmetric reactions, only few ligands with two ferrocenyl groups (bis-ferrocenyl ligands) have been reported. Trap,[103] Pigiphos,[104] and Trost's chiral pocket ligand[105] are the only reported examples in this category. Among these bis-ferrocenyl P,P-ligands, ligand TRAP proved to be a very efficient ligand for asymmetric catalysis. Trap has been successfully applied in Rh-catalyzed asymmetric hydrogenation of indoles[106] and

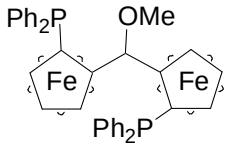
[103] Sawamura, M.; Hamashima, H.; Sugawara, M.; Kuwano, R.; Ito, Y. *Organometallics* **1995**, *14*, 4549.
[104] a) Barbaro, P.; Togni, A. *Organometallics* **1995**, *14*, 3570. b) Ladini, L.; Togni, A. *Chem Commun.* **2003**, 30. c) Sadow, A. D.; Togni, A. *J. Am. Chem. Soc.* **2005**, *127*, 17012.
[105] a) Trost, B. M.; Schroeder, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 6759. b) Yan, X.-X.; Liang, C.-G.; Zhang, Y.; Hong, W.; Cao, B.-X.; Dai, L.-X.; Hou, X.-L. *Angew. Chem. Int. Ed.* **2005**, *44*, 4435.
[106] Kuwano, R.; Sato, K.; Kurokawa, T.; Karube, T.; Ito, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7614. b) Kuwano, R.; Kaneda, K.; Ito, T.; Sato, K.; Kurokawa, T.; Ito, Y. *Org. Lett.* **2004**, *6*, 2213.

hydrosilylation of prochiral ketones,[107] and Rh and Pd-catalyzed asymmetric allylic alkylations[108] (Scheme 51).



Scheme 51. Applications of Trap in asymmetric catalysis.

Based on this successful work, we decided to design a bis-ferrocenyl ligand for asymmetric catalysis. The ligand structure is shown in figure 13. The α-carbon in the ligand structure is a chirotopic center.



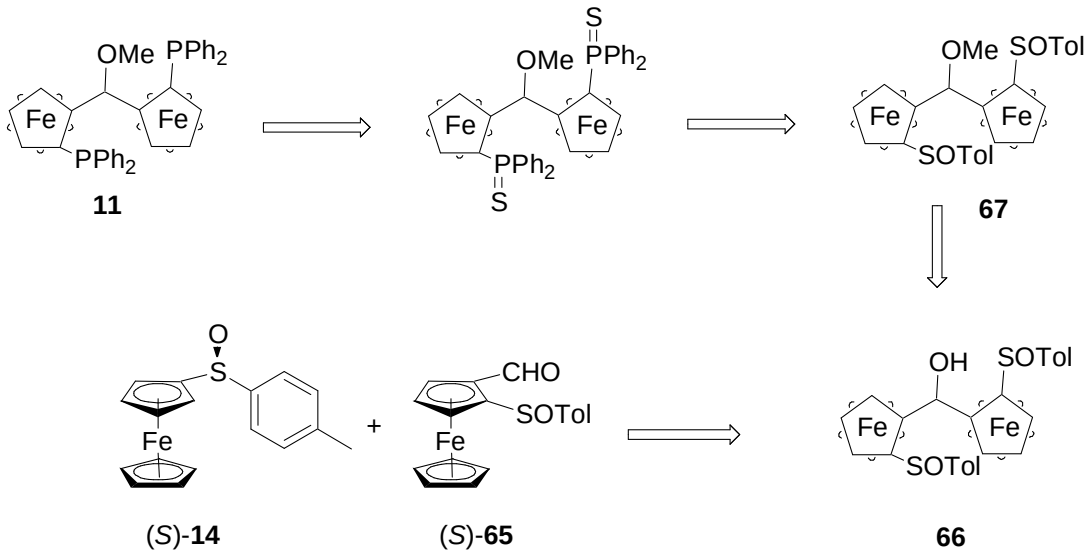
11

Figure 13. Structure of new bis-ferrocenyl ligands **11**

3.2. Synthesis of bis-ferrocenyl P,P-ligand 11

The synthetic approach for the ligand **11** is shown in the scheme 52. The bis-ferrocenyl phosphine **11** can be prepared through the reduction of the corresponding phosphine sulfides. The phosphine sulfides can be prepared via the sulfoxide-lithium exchange on **67**, followed by the addition of chlorodiarylphosphines. The methyl ether can be prepared by *O*-methylation of the corresponding alcohol **66** which can be prepared via the diastereoselective *ortho*-lithiation of **14**, followed by the addition of **65**.

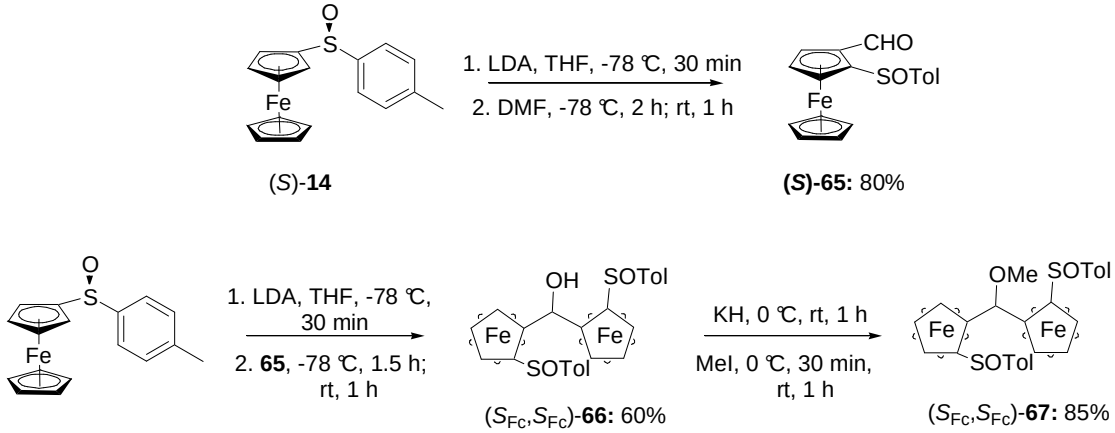
[107] Kuwano, R.; Uemura, T.; Saitoh, M.; Ito, Y. *Tetrahedron: Asymmetry* **2004**, *15*, 2263.
[108] a) Sawamura, M.; Sudoh, M.; Itoh, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3309. b) Nowicki, A.; Mortreux, A.; Agbossou-Niedercorn, F. *Tetrahedron: Asymmetry* **2005**, *16*, 1295.



(*S*)-**14** (*S*)-**65**

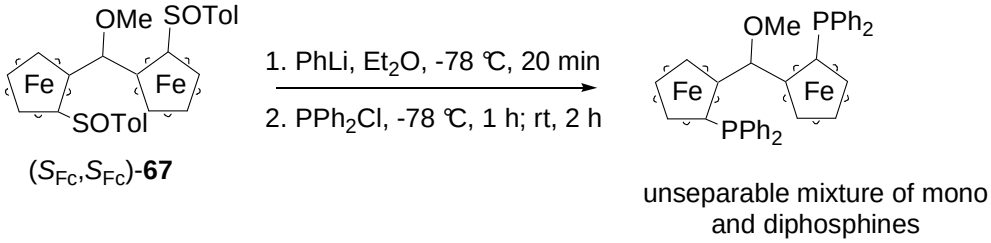
Scheme 52. Synthetic approach to the bis-ferrocenyl ligand **11**

Diastereoselective *ortho*-lithiation on sulfoxide **14**, followed by the addition of DMF, led to the aldehyde **65** in 80% yield. Addition of this aldehyde **65** to the lithiated species generated from the diastereoselective metallation of **14**, provided the bis-ferrocenyl alcohol **66** in 60% yield. *O*-methylation of **66** using KH and MeI led to the bis-ferrocenyl ether **67** in 85% yield (Scheme 53).



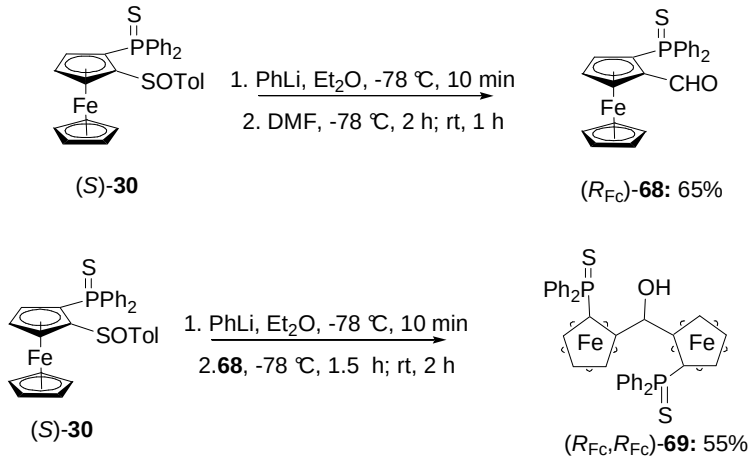
Scheme 53. Preparation of bis-ferrocenyl ether **67**

Exchange of the sulfoxide using phenyllithium or *tert*-butyllithium, followed by the addition of chlorodiphenylphosphine led to an inseparable mixture of mono and disubstituted phosphines (Scheme 54).



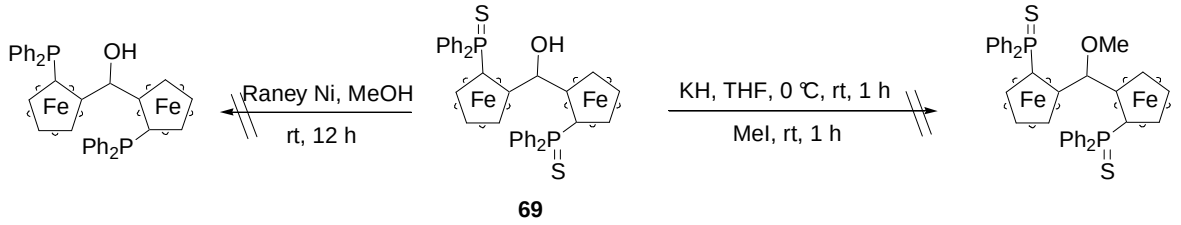
Scheme 54. Performance of sulfoxide/lithium exchange on **67**

Since compound **67** provided an inseparable mixture in the reaction with $ClPPh_2$ after the sulfoxide/lithium exchange, we changed our synthetic approach to ligand **11**. Starting our synthesis from the sulfoxide **30**, performance of sulfoxide-lithium exchange of **30** using PhLi, followed by the addition of DMF, furnished the ferrocenyl aldehyde **68** in 65% yield. Sulfoxide-lithium exchange on **30** using PhLi, followed by the addition of **68** led to the bis-ferrocenyl alcohol **69** in 55% yield (Scheme 55).



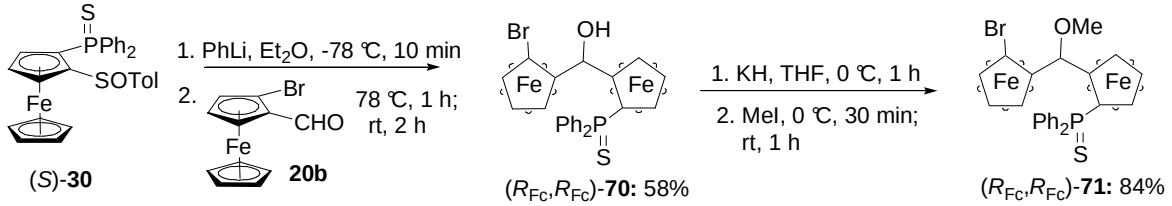
Scheme 55. Preparation of bis-ferrocenyl alcohol **69**

We couldn't accomplish the *O*-methylation of the alcohol **69** under any known reaction conditions. In addition, attempted deprotection on the bisphosphine sulfide **69** using Raney-Ni in MeOH resulted in no conversion (Scheme 56).



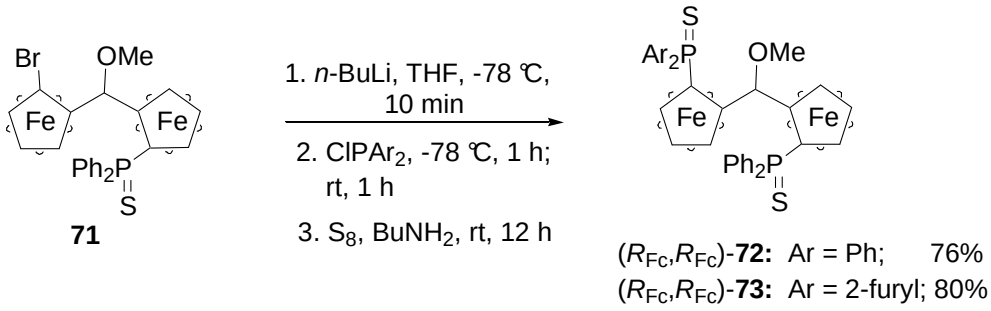
Scheme 56. Attempts to prepare the bis-ferrocenyl ether from **69**

Keeping these problems from the above two synthetic approaches in mind, the following synthesis was attempted. Sulfoxide-lithium exchange on the substrate **30**, followed by the addition of bromoferrocenyl aldehyde **20b**, led to the bis-ferrocenyl alcohol **70** in 58% yield. *O*-methylation of **70** using KH and MeI led to the bis-ferrocenyl ether **71** in 84% yield (Scheme 57).



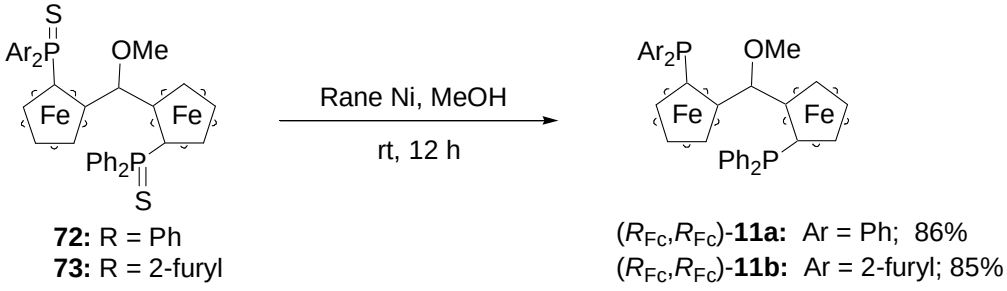
Scheme 57. Preparation of bis-ferrocenyl ether **71**

The bromine-lithium exchange on **71** using *n*-BuLi, followed by the addition of chlorodiphenylphosphine or bis-2-furyl phosphine, gave the bis-ferrocenyl phosphine sulfides **72** and **73** in 76 and 80% yields, respectively (Scheme 58).



Scheme 58. Preparation of bis-ferrocenyl phosphine sulfides **72** and **73**

Deprotection of the phosphine sulfides **72** and **73** using Raney-Ni in methanol provided the corresponding bisphosphines **11a-b** in 76-80% yield, respectively (Scheme 59)

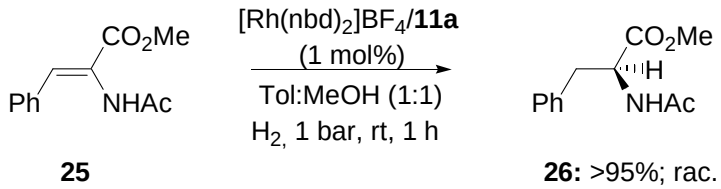


Scheme 59. Preparation of bis-ferrocenyl phosphines **11a** and **11b**

3.3 Applications in asymmetric catalysis

3.3.1 Rh-catalyzed hydrogenation of olefins

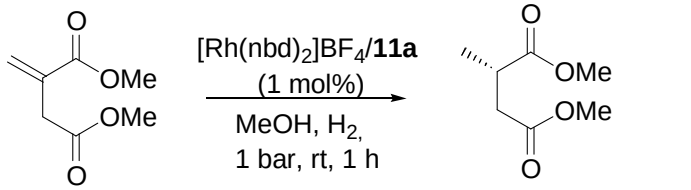
With the two bis-ferrocenyl ligands **11a-11b** in hand, we applied them in Rh-catalyzed hydrogenation of α-acetamidocinnamate **25** to yield the phenylalanine derivative **26**. Hydrogenation of **25** using **11a** proceeded quantitatively, but racemic product was obtained (Scheme 60).



25 **26:** >95%; rac.

Scheme 60. Application of **11a** in Rh-catalyzed hydrogenation of **25**

We also tested the efficiency of **11a** in the Rh-catalyzed hydrogenation of dimethyl itaconate **74**. The desired product **75** was obtained quantitatively but only in 18% *ee* (Scheme 61).



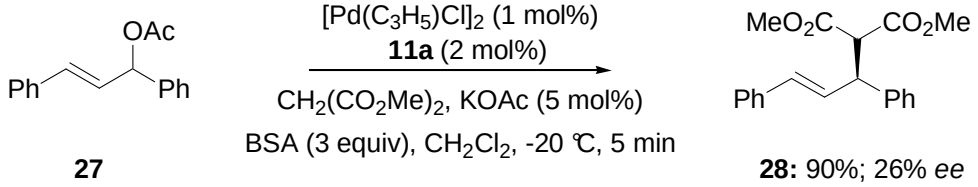
74 **75:** 90%; 18% *ee*

Scheme 61. Rh-catalyzed hydrogenation of dimethyl itaconate **75**

Application of ligand **11b** in the above reactions resulted in no reactions.

3.3.2. Pd-catalyzed asymmetric allylic alkylation

We then examined the efficiency of new ferrocenyl ligand **11a** in Pd(0)-catalyzed asymmetric alkylation on the racemic substrate **27** using dimethylmalonate as a nuecleophile. We observed complete conversion in 5 minutes, however, a very low selectivity was achieved (Scheme 62).



27 **28:** 90%; 26% *ee*

Scheme 62. Asymmetric allylic alkylation using the ligand **11a**

3.4. Conclusion

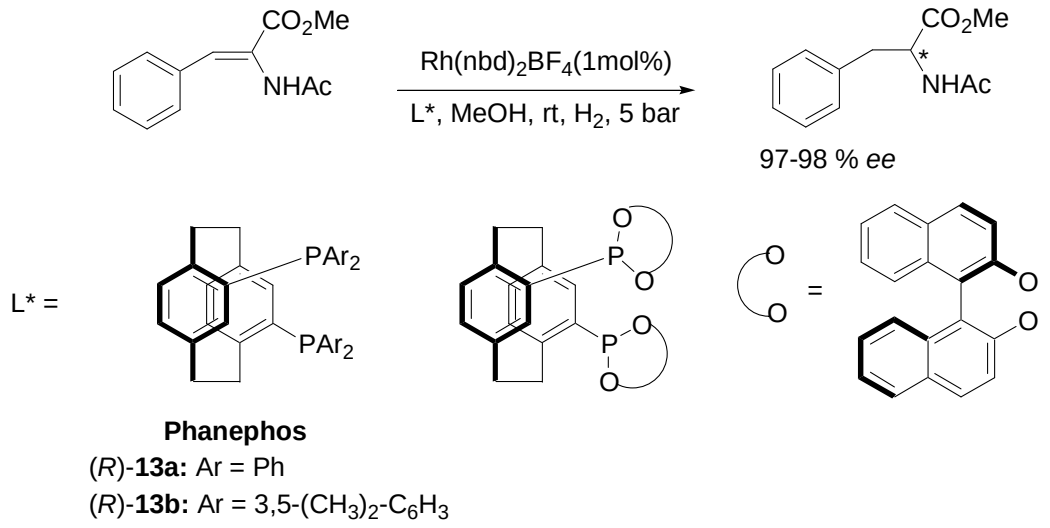
In conclusion, we prepared the new bis-ferrocenyl ligands **11** in good yields. Although the ligands formed very active catalysts, as shown by quantitative conversions and low reaction times, low enantioselectivities were observed.

4. Synthesis of new paracyclophane phosphines and their applications in asymmetric catalysis

4.1 Introduction

The [2,2]paracyclophane backbone serves as a powerful tool to develop new and efficient ligands for the asymmetric catalysis.[109] The chiral [2,2]phanephos **13,** a C_2 symmetric bisphosphine, is one of the most successful chiral ligands with a rigid paracyclophane backbone (Scheme 63). It has been efficiently used in Rh-catalyzed hydrogenation of dehydroamino acids,[17] allylic acids,[110] Ru-catalyzed hydrogenation of β-ketoesters,[111] aromatic ketones[112] and Pd-catalyzed amination reactions.[113] The chiral C_2-symmetrical phosphinites based on the paracyclophane backbone have also proved to be very efficient catalysts for Rh-catalyzed hydrogenation of *N*-acetyl dehydroamino acids and esters (Scheme 63).[114]

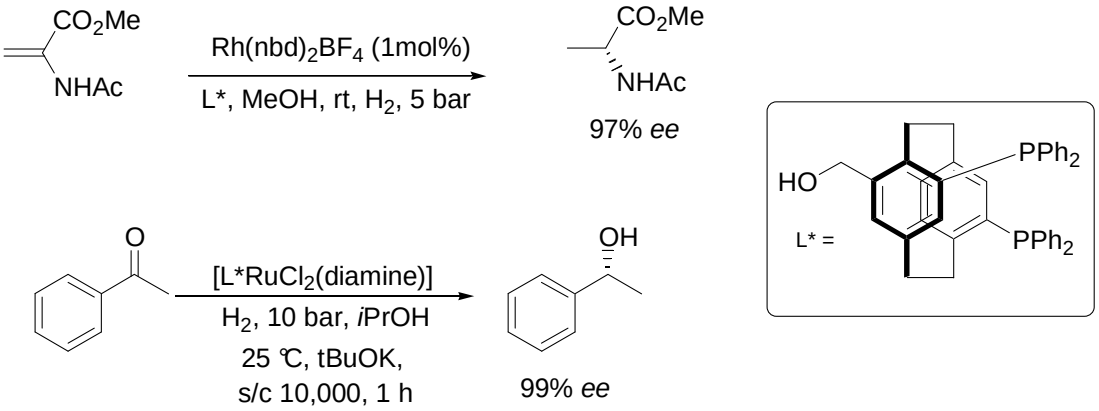
[109] Gibson, S. E.; Knight, J. D. *Org. Biomol. Chem.* **2003,** *1*, 1256.
[110] Boulton, L. T.; Lennon, I. C. ; McCague, R. *Org. Biomol. Chem.* **2003,** *1*, 1094.
[111] Pye, P. J.; Rossen, K. ; Reamer, R. A.; Volante, R. P; Reider, P. J. *Tetrahedron Lett.* **1998**, *39*, 4441.
[112] Burk, M. J.; Hems, W. P.; Herzburg, D.; Malan, C.; Zanotti-Gerosa, A. *Org. Lett.* **2000**, *2*, 4173.
[113] Rossen, K.; Pye, P. J.; Maliakal, A. Volante, R. P. *J. Org. Chem*. **1997**, *62*, 6462.
[114] Zanotti-Gerosa, A.; Malan, C.; Herzburg, D. *Org. Lett.* **2001**, *3*, 3687.



Phanephos
(*R*)-**13a:** Ar = Ph
(*R*)-**13b:** Ar = 3,5-$(CH_3)_2$-C_6H_3

Scheme 63. Applications of C_2-symmetrical paracyclophane phosphines in asymmetric catalysis

Hems *et al.* prepared various non-C_2-symmetrical paracyclophane phosphines by introducing substituents on one of the aromatic ring of Phanephos **12**. These ligands showed an indistinguishable performance to the original Phanephos **12** in Rh-catalyzed hydrogenation of dehydroamino acids and Ru-catalyzed hydrogenation of acetophenone (Scheme 63).[115]

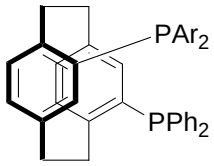


Scheme 63. Applications of non-C_2-symmetrical paracyclophane phosphines in Rh and Ru-catalyzed hydrogenation reactions

4.2 Synthesis of new paracyclophane phosphines

[115] Dominguez, B.; Canotti-Gerosa, A.; Hems, W. *Org. Lett.* **2004,** *6,* 1927.

However, apart from this fascinating work, paracyclophane phosphines bearing two different kinds of aryl phosphines have not been synthesized until now. Our aims of this work were to synthesize the new diphosphines of type **12** based on the paracyclophane backbone and test their efficiency in asymmetric catalysis. This work also allows us to study the electronic properties of different phosphines to elucidate the effect of the phosphines on asymmetric catalysis. The new ligands structure is depicted in Figure 14.

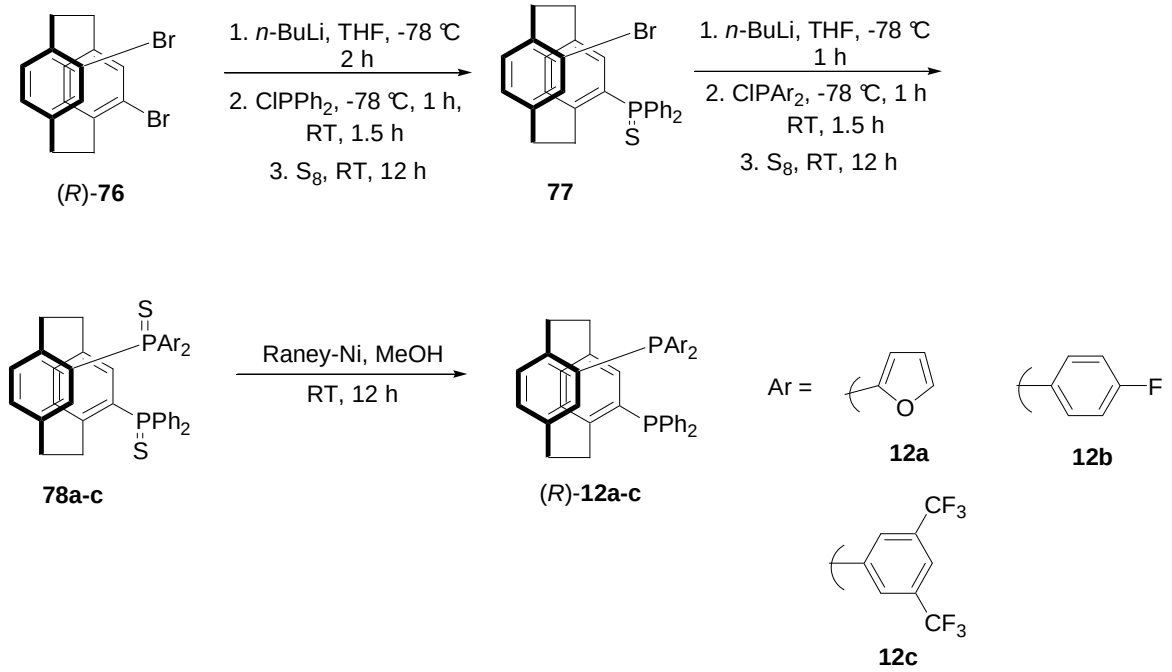


12

Figure 14. New paracyclophane phosphines of type **12**

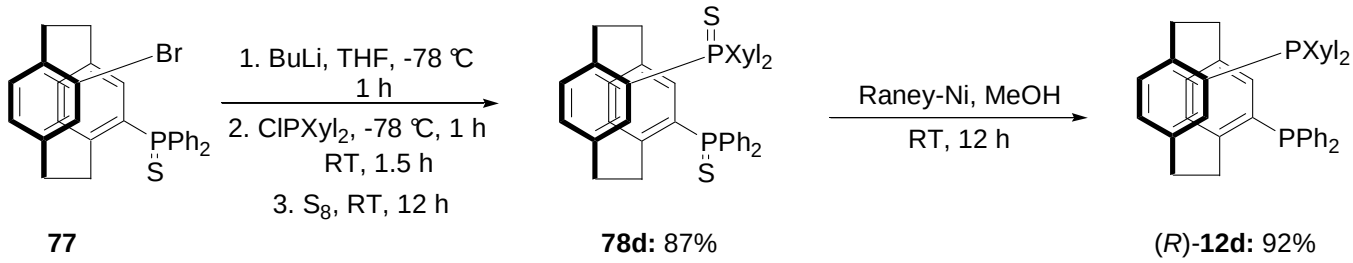
The corresponding monometallation on chiral dibromide **76**[116] using *n*-BuLi for 2 h at -78 °C, followed by the addition of chlorodiphenylphosphine led to an air sensitive diphenyphosphine derivative which was *in situ* protected with sulfur leading to the air stable phosphine sulfide **77** in 85% yield. Bromine/lithium-exchange on substrate **77** using *n*-BuLi at -78 °C for 1 h, followed by reaction with various chlorodiarylphosphines and *in situ* protection the resulting phosphine with sulfur, provided the bisphosphine sulfides **78a-78c** in 50-86% yields. The deprotection of the phosphine sulfides was accomplished using Raney-Ni in MeOH (25 °C, 12 h) to obtain the diphosphines **12a-c** in 20-66% yields (Scheme 65).[117]

[116] a) For the preparation of the dibromide see the ref. (109) and for the preparation of racemic dibromide see b) Reich, H. J.; Cram, D. J. *J. Am. Chem. Soc.* **1969**, *91*, 3527.
[117] Ph. D thesis, Maud gayral, Oxford University.



Scheme 65. Preparation of new paracyclophane based ligands **12a-c**.

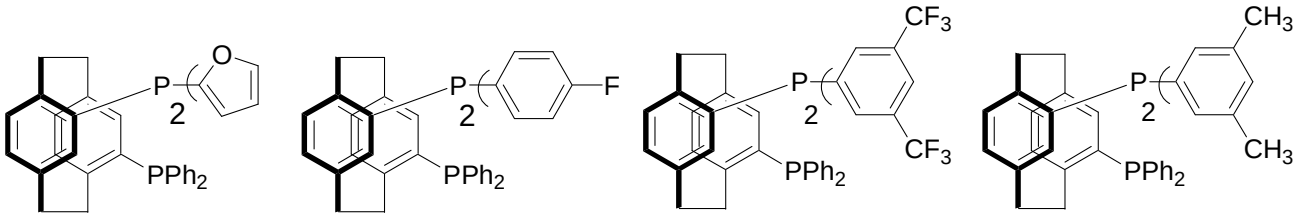
In addition, we required also a mixed bisphosphine bearing an electron-rich aromatic group on the phosphorous such as 3,5-dimethylphenyl group. Thus, we prepared the diphosphine **12d**, in the similar way to the synthesis as described in Scheme 65. The bromine-lithium exchange on substrate **77**, using *n*-BuLi, followed by reaction with chlorobis(3,5-dimethylphenyl)phosphine and *in situ* protection with sulfur, provided the bisphosphinesulfide **78d** in 86% yield. The deprotection of **78d** was performed by using Raney-Ni in MeOH at room temperature, and provided the phosphine **12d** in 92% yield (Scheme 66).



Scheme 66. Preparation of the paracyclophane phosphine **12d**

4.3 Applications in asymmetric catalysis.

For clarity, the structure of chiral P,P-ligands **12a-d** are shown in Scheme 67.

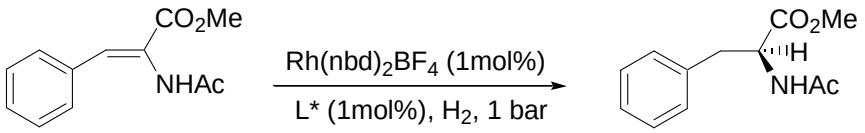


(*R*)-**13a** (*R*)-**13b** (*R*)-**13c** (*R*)-**13d**

Scheme 67. Overview of new chiral paracyclophane based P,P-ligands **12a-d**

4.3.1 Rh-catalyzed asymmetric hydrogenation reactions

Having these P,P-ligands in hand, we sought to investigate their efficiency in Rh-catalyzed asymmetric hydrogenation of *N*-acetyl methyl cinnamate **25**. Since ligand **12a** is very unstable and oxidized rapidly, we couldn't apply this ligand in asymmetric catalysis. The ligands **12b-d** gave mixed results in asymmetric hydrogenation of cinnamate **25**. The ligand **12d** proved to be efficient for the hydrogenation of **25** and gave the desired compound **26** in quantitative yield and 90% *ee* (Scheme 68).

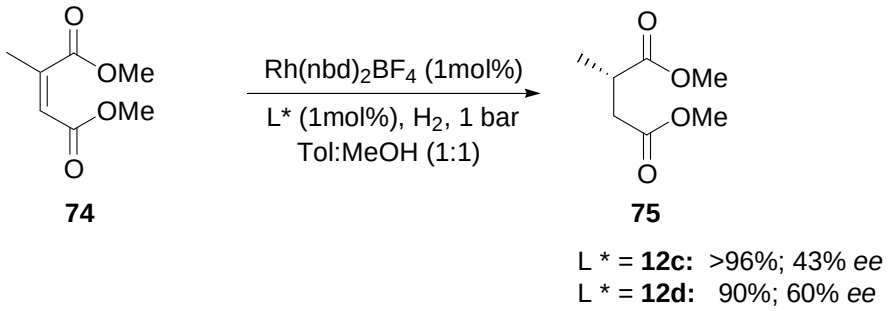


25 **26**

L * = **12b** : 60%; 18% *ee*
L * = **12c** : 95%; 30% *ee*
L* = **12d** : 95%; 90% *ee*

Scheme 68. Rh-catalyzed hydrogenation of *N*-acetyl dehydroamino acids using the ligands **12b-d**

Applying these ligands in Rh-catalyzed hydrogenation of dimethylitaconate, also resulted in moderate enantioselectivities (Scheme 69).



Scheme 69. Rh-catalyzed hydrogenation of dimethyl itaconate using the ligands **12c** and **12d**.

4.3.2 Ru-Catalyzed Hydrogenation of Prochiral Ketones

Enantiomerically pure alcohols serve as important intermediates in drug design. A direct approach to single enantiomer alcohols through catalytic reduction of ketones is most attractive, and various methods have been introduced.[118] Owing to the inherent atom-economical nature of the hydrogenation reactions, hydrogenation of prochiral ketones is one of the most facile routes for generating single enantiomer alcohols. Recently, a ground-breaking discovery by Noyori and co-workers, found that phosphine-ruthenium-diamine complexes are very effective catalysts for the hydrogenation of ketones and aldehydes.[119] Significantly, this method allowed the development of many efficient catalysts for highly enantioselective hydrogenation of a wide range of prochiral ketones.[120] Thus, we sought to investigate the efficiency of these new ligands **12b-d** in ruthenium catalyzed hydrogenation of prochiral ketones. We prepared various phosphine-ruthenium-diamine complexes **79a-c** and

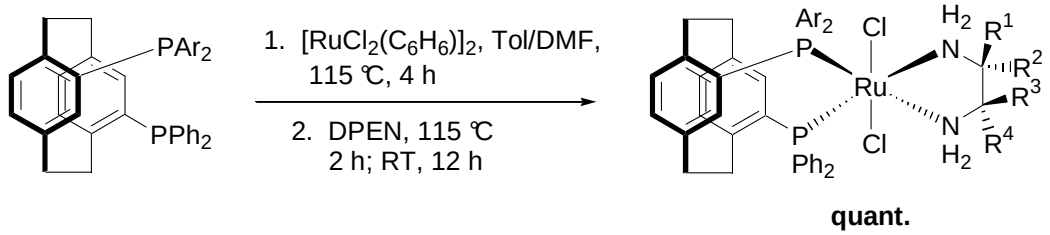
[118] Hydroboration: a) Itsuno, S.; Nakano, M.; Miyazaki, K.; Masuda, H.; Ito, K.; Hirao, A.; Nakahama, S. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2039. b) Corey, E. J.; Bakshi, R. K.; Shibata, S. *J. Am. Chem. Soc*. **1987**, *109*, 5551. c) Singh, V. K. *Synthesis* **1991**, 605. d) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc*. **1989**, *111*, 3426. e) Brown, J. M.; Hulmes, D. I.; Layzell, T. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1673
Hydrosilylation: f) Brunner, H.; Nishiyama, H.; Itoh, K. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 1993, Chapter 6. g) Sun, J.; Buchwald, S. L. *J. Am. Chem. Soc*. **1999**, *121*, 5640.
Hydrogen transfer: h) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res*. **1997**, *30*, 97 and references therein. i) Jiang, Y.; Jiang, Q.; Zhang, X. *J. Am. Chem. Soc*. **1998**, *120*, 3817. j) Murata, K.; Ikariya, T.; Noyori, R. *J. Org. Chem*. **1999**, *64*, 2186 k) Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1999**, *18*, 2291.

[119] a) Ohkuma, T.; Ooka, H.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 2675. b) Ohkuma, T.; Ooka, H.; Yamakawa, M.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 10417.

[120] a) Ohkuma, T.; Ooka, H.; Yamakawa, M.; Ikariya, T.; Noyori, R. *J. Org. Chem.* **1996**, *61*, 4872. b) Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1703. c) Ohkuma, T.; Koizumi, M.; Doucet, H.; Pham, T.; Kozawa, M.; Murata, K.; Katayama, E.; Yokozawa, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1998**, *120*, 13529. d) Noyori, R.; Ohkuma, T. *Angew. Chem. Int. Ed.* **2001**, *40*, 40. e) Wu, J.; Chen, H.; Kwok, W.-H.; Guo, R.-W.; Zhou, Z.-Y.; Yeung, C.-H.; Chan, A. S. C. *J. Org. Chem.* **2002**, *67*, 7908. f) Cao, P.; Zhang, X. *J. Org. Chem.* **1999**, *64*, 2127. g) Ohkuma, T.; Koizumi, M.; Ikehira, H.; Yokozawa, T.; Noyori, R. *Org. Lett*. **2000**, *2*, 659. h) Ohkuma, T.; Koizumi, M.; Yoshida, M.; Noyori, R. *Org. Lett.* **2000**, *2*, 1749. i) Noyori, R.; Ohkuma, T. *Pure Appl. Chem*. **1999**, *71*, 1493. j) Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem. Int. Ed.* **1999**, *38*, 495.

80a-c using chiral 1,2-diphenylethylenediamines. The ruthenium complexes were prepared analogous to the literature procedure.[113] Heating a mixture of diphosphine **12b-d** and $[RuCl_2(C_6H_6)]_2$ in toluene/DMF for 4 h at 115 °C, followed by the addition of chiral diamine and heating the mixture for 2 h at 115 °C provided the ruthenium complexes **79a-c** and **80a-c** in quantitative yields (Table 11). Catalysts **79a-c** were prepared using (*R*,*R*)-1,2-diphenylethylenediamine, whereas the catalysts **80a-c** were prepared by using (*S*,*S*)-1,2-diphenylethylenediamine.

Table. 13 Preparation of Ru-complexes using the chiral diamine and the ligands **79a-c** and **80a-c**.



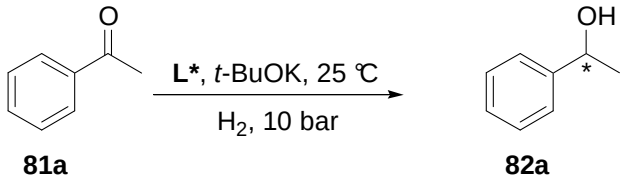
quant.

Entry	Ar	Ligand	Diamine[a]	Product[b]
1	4-F-C_6H_4	**12b**	(*R*,*R*)-DPEN	**79a**
2	4-F-C_6H_4	**12b**	(*S*,*S*)-DPEN	**80a**
3	3,5-$(CF_3)_2$-C_6H_3	**12c**	(*R*,*R*)-DPEN	**79b**
4	3,5-$(CF_3)_2$-C_6H_3	**12c**	(*S*,*S*)-DPEN	**80b**
5	3,5-$(CH_3)_2$-C_6H_3	**12d**	(*R*,*R*)-DPEN	**79c**
6	3,5-$(CH_3)_2$-C_6H_3	**12d**	(*S*,*S*)-DPEN	**80c**

[a] DPEN = Diphenylethylenediamine. [b] all product was obtained in quantitative yield.

We started our investigation on the ketone hydrogenation using the novel ruthenium complexes **79a-c** and **8a-0c** and acetophenone as the model substrate under standard reaction conditions (*i*-PrOH solvent, 10 bar H_2, *t*-BuOK/Ru : 25/1, 1.0-2.0 M solutions)[120-121] (Table 14). Preliminary results indicate that the hydrogenation of acetophenone **81a** using ruthenium complexes **79a-c** led to poor conversions and enantioselectivities (entries 1-3). On the other hand the ruthenium complexes **80a-c** provided better enantioselectivities in the hydrogenation of acetophenone **81a** (entries 4-6). Among the ruthenium precatalysts **80a-c**, catalyst **80c** proved to be the most efficient catalyst for the asymmetric hydrogenation of acetophenone **81a** and furnished the corresponding alcohol **82a** in 97% *ee* (entry 6-10).

Table 14. Hydrogenation of acetophenone **81a** using the ruthenium precatalysts **79a-80c**[a].



81a **82a**

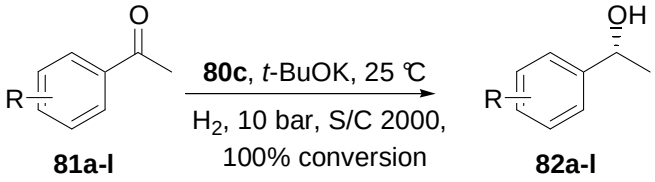
Entry	Catalyst	S/C[a]	Time[h]	Conv(%)[b]	*ee*[c]
1	**79a**	500	12	45	14(*S*)
2	**79b**	500	12	54	22(*S*)
3	**79c**	500	12	55	25(*S*)
4	**80a**	500	12	50	43(*R*)
5	**80b**	500	12	70	80(*R*)
6	**80c**	500	1	100	97(*R*)
7	**80c**	1000	1	100	97(*R*)
8	**80c**	2000	1	100	97(*R*)
9	**80c**	5000	1.5	100	97(*R*)
10	**80c**	10000	2	100	95(*R*)

[a] S/C: Substrate/Catalyst [b] Conversion was measured by chiral GC or by ^{1}H-NMR.[c] Enantioselectivity was determined using chiral GC-DEX-CB column

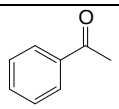
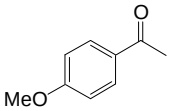
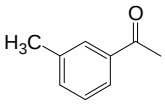
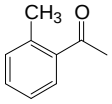
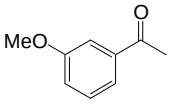
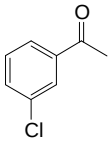
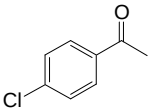
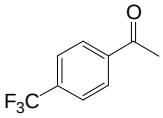
These results indicated that the stereochemistry of the diamine played a major role in providing high conversions and enantioselectivities in ketone hydrogenation. The efficiency of this ruthenium-complex **80c** in ketone hydrogenation was investigated by decreasing the catalyst loadings. Increasing the ratio of substrate/catalyst to 10000 provided the alcohol **82a** in quantitative yield but diminished the enantioselectivity to 95% *ee* (entries 7-10 of Table 14).

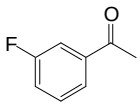
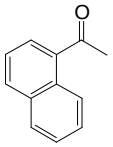
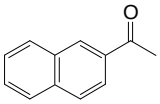
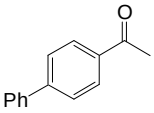
Then we investigated the scope of ketone substrates for the asymmetric hydrogenation using the Ru-catalyst **80c**. Various types of substituted acetophenones were reduced in high conversions providing the corresponding chiral alcohols in high enantioselectivities. The results are listed in Table 15.

Table 15. Asymmetric hydrogenation of substituted acetophenones using the Ru-catalyst **80c**[a]



81a-l **82a-l**

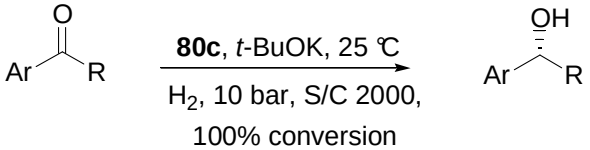
Entry	Substrate	Time[h]	Product[b]	*ee*(%)[c]
1	 **81a**	1	**82a**	97
2	 **81b**	1.5	**82b**	96
3	 **81c**	1	**82c**	97
4	 **81d**	2	**82d**	94
5	 **81e**	1.5	**82e**	97
6	 **81f**	1.5	**82f**	97
7	 **81g**	1	**82g**	96
8	 **81h**	1	**82h**	94

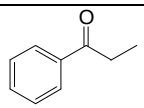
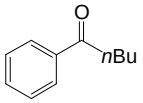
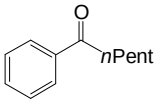
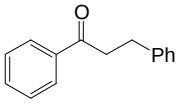
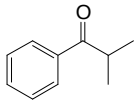
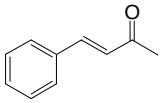
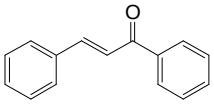
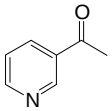
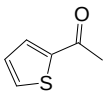
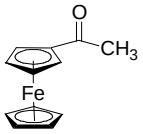
9	 **81i**	1	**82i**	96
10	 **81j**	2	**82j**	97
11	 **81k**	2	**82k**	97
12	 **81l**	2	**82l**	94

[a] Reactions were performed with 1M solution of ketone in *i*-PrOH at S/C 2000/1 and *t*-BuOK (base/Ru = 25/1). [b] In all cases full conversion was achieved. [c] Enantiomeric excess was determined by chiral GC or chiral HPLC.

In order to further explore the substrate scope, we investigated the asymmetric hydrogenation of ketones bearing different types of side-chains at the α-position. Elongation of the side chain of the ketone from methyl to ethyl, *n*-butyl, *n*-pentyl or benzyl doesn't affect the reactivity and provided the corresponding secondary alcohols in 90-97% *ee* (entries 1-4 of Table 16). Introducing branching at the α-position of the ketone led to long reaction times and poor selectivities (entry 5). Furthermore, we examined the chemoselective hydrogenation of α,β-unsaturated ketones of type **85a-b** (entries 6-7; Table 16). Ketone **85a** was smoothly reduced to afford the allylic alcohol **86a** in 95% *ee* (entry 6) whereas the ketone **85b** furnished the secondary alcohol **86b** in 37% *ee* (entry 7). We also extended the hydrogenation of ketones using the Ru-catalyst **80c** to hetero-aromatic ketones **87**, **88** and **91** and obtained the corresponding alcohols in excellent enantioselectivities (entries 8-10; Table 16).

Table 16. Asymmetric hydrogenation of aryl and heteroaryl ketones using the Ru-catalyst **80c**.[a]

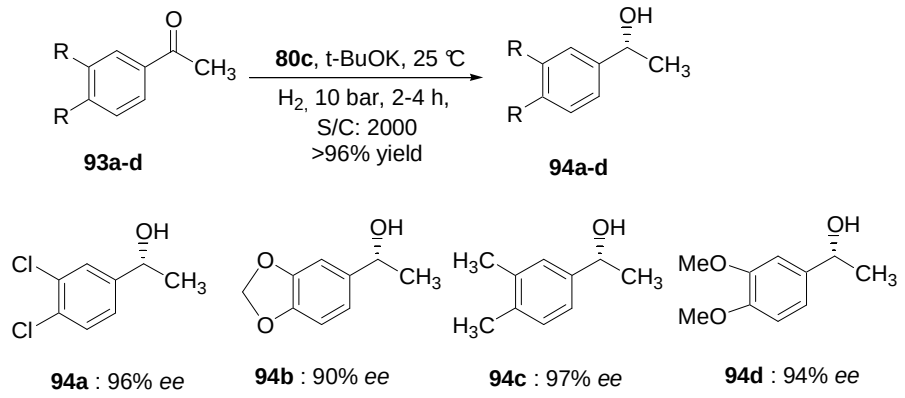


Entry	Substrate	Time[h]	Product[b]	*ee*(%)[c]
1	 **83a**	1.5	**84a**	97
2	 **83b**	1.5	**84b**	97
3	 **83c**	1.5	**84c**	94
4	 **83d**	2	**84d**	90
5	 **83e**	5	**84e**	38
6	 **85a**	1	**86a**	94
7	 **85b**	2	**86b**	37
8	 **87**	3	**88**	96
9	 **89**	2.5	**90**	93
10	 **91**	4	**92**	92

[a] Reactions were performed with 1M solution of ketone in *i*-PrOH at S/C 2000/1 and *t*-BuOK (base/Ru = 25/1). [b] In all cases full conversion was achieved. [c] Enantiomeric excess was determined by chiral GC or chiral HPLC.

To broaden the application of this ruthenium catalyzed hydrogenation using the catalyst **80c**, we performed the hydrogenation on disubstituted acetophenones **93a-d** and obtained the respective alcohols **94a-d** in good enantioselectivities. Reduction of the ketone **93d** bearing

two methoxy groups on 3,4 positions of the aromatic ring was accomplished smoothly providing the alcohol **94d** in 94% *ee*, which is a precursor for the synthesis of (−)-Salsolidine (Scheme 70).[121]



Scheme 70. Asymmetric hydrogenation of disubstituted acetophenone using the Ru-catalyst **80c**

4.4. Conclusion

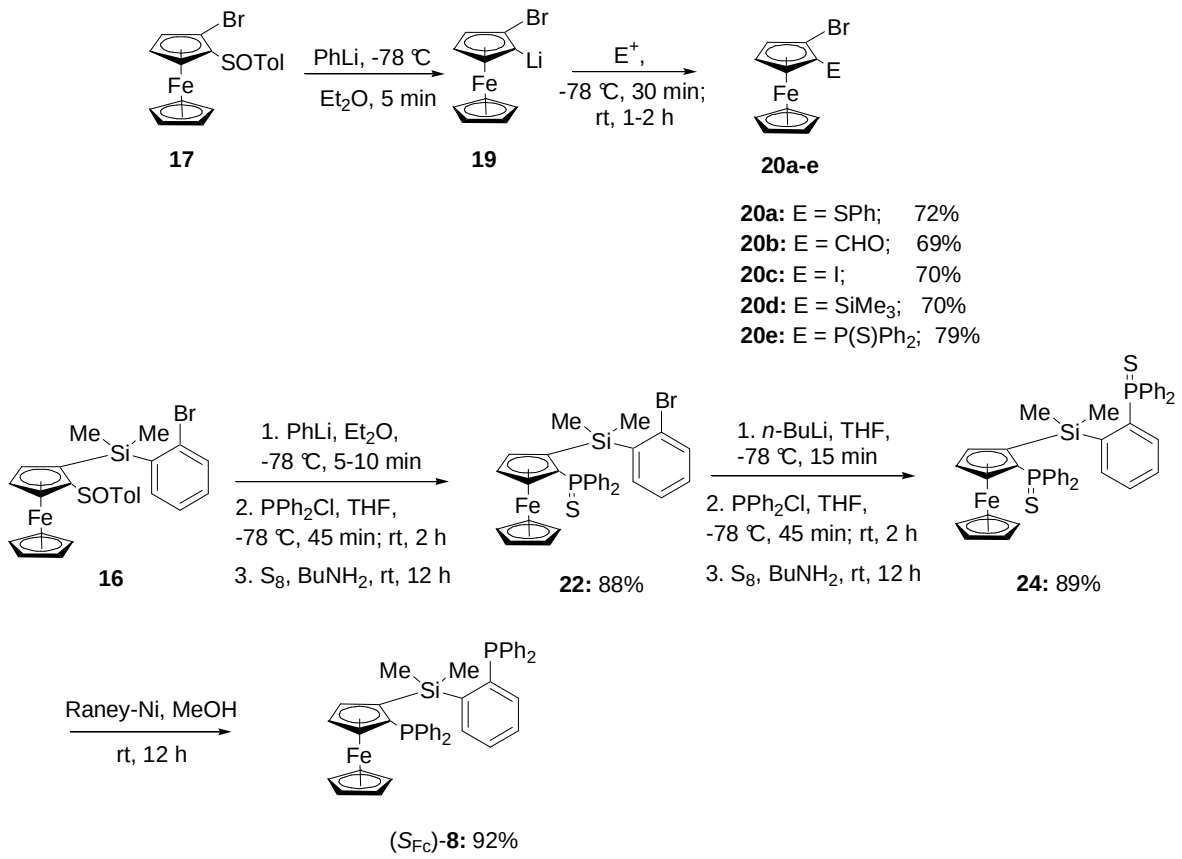
In conclusion, we have synthesized new paracyclophane based diphosphine ligands **12a-d**. By tuning the electronic properties of the phosphines, we were able to demonstrate the ligand **12d** as the more efficient one for transition-metal catalyzed asymmetric reactions. The possible reason for the difference in the reactivity of the ligands **12c** and **12d** in asymmetric catalysis could be that the (3,5-trifluoromethylphenyl) group on the phosphine of the ligand **12c** is an electron poor group. This may lead to an increase in the Lewis acidity on the transition metal, thereby decreasing the reactivity and selectivities in the asymmetric reactions. The ruthenium complex **80c** which was derived from **12d** and (*S*,*S*)-1,2-DPEN provided high enantioselectivities in hydrogenation of aromatic and hetero-aromatic ketones, quite comparable to the C_2-symmetrical dixylylphosphine **13b**.

[121] Ponzo, V. L.; Kaufman, T. S. *Tetrahedron Lett.* **1995**, *36*, 9105.

5. Summary and Outlook

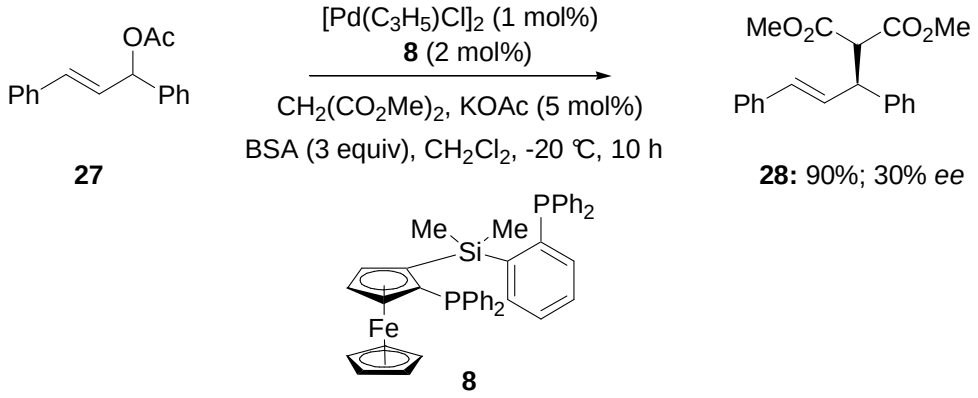
This work focused on the preparation of new chiral ligands and studies concerning their applications in asymmetric catalysis.

In the first project, we described the synthesis of a chiral planar ferrocenyl P,P-ligand **8** through the selective sulfoxide-lithium exchange. Performing the sulfoxide-lithium exchange on 1,2-bromo-ferrocenyl sulfoxide **17** using PhLi, followed by the addition of several electrophiles led to the bromo substituted 1,2-chiral ferrocenes of type **20** (Scheme 71).



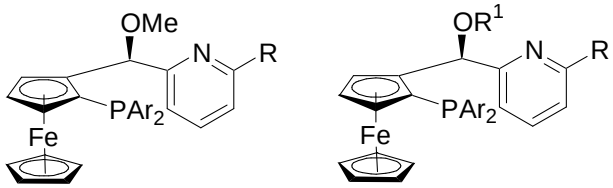
Scheme 71. Preparation of bromo ferrocenes of type **20** and chiral planar ferrocenyl ligand **8** through selective sulfoxide-lithium exchange using PhLi

The ferrocenyllithium species **19** was unstable and undergoes racemization for long reaction times. We extended this selective-sulfoxide lithium exchange to synthesize the chiral planar ferrocenyl P,P-ligand **8**. This ligand gave poor enantioselecetivities in Pd(0)-catalyzed asymmetric allylic alkylation (Scheme 72).



Scheme 72. Application of ferrocenyl P,P-ligand **8** in Pd(0)-catalyzed allylic alkylation

In the second project, the synthesis of various novel chiral P,N-ligands of type **9**-**10** was demonstrated. Various chiral P,N-ligands with or without substitutions on the pyridine ring were described (Figure 15).



9a-h

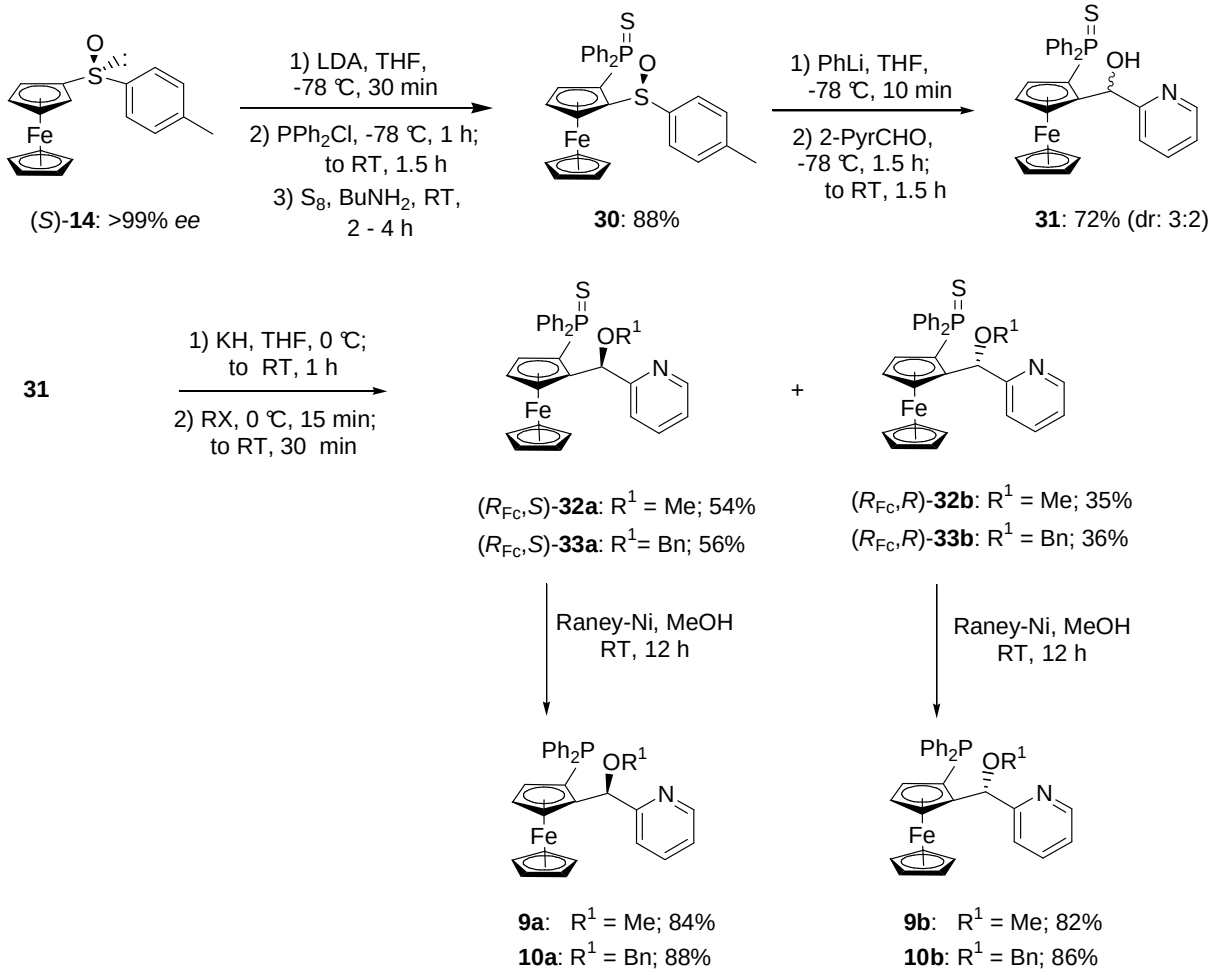
R = H, *t*Bu, Ph
Ar = Ph, Xyl

10a-h

R = H, *t*Bu, Ph
R^1 = Bn, H

Figure 15. New ferrocenyl P,N-ligands of type **9** and **10** for asymmetric catalysis.

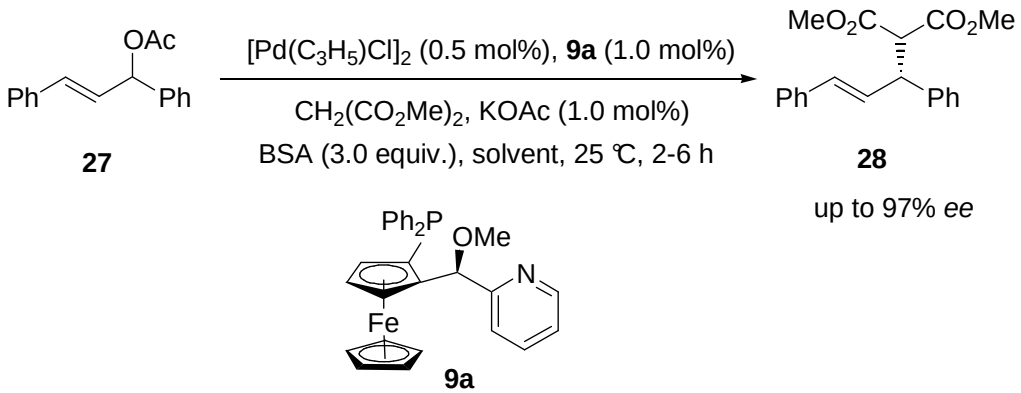
The P,N-ligands of type **9** and **10** were synthesized *via* the diastereoselective *ortho*-lithiation of ferrocenyl sulfoxide **14** (Scheme 73).



Scheme 73. Synthesis of chiral ferrocenyl P,N-ligands **9a-b** and **10a-b**

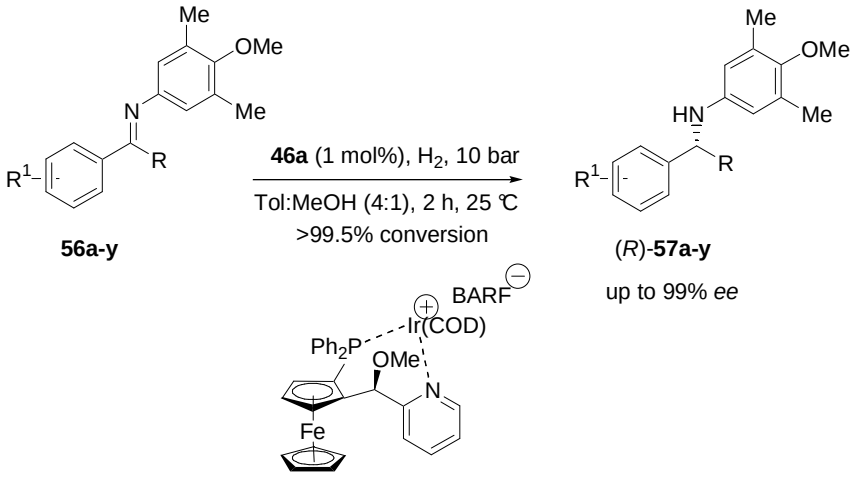
The stereochemistry of the two ferrocenyl ethers **32a** and **32b** at the α-center was determined by X-ray analysis of the phosphine sulfide **32b**.

These chiral ferrocenyl P,N-ligands were applied successfully in Pd(0)-catalyzed asymmetric allylic alkylations of **27** and provided the desired product **28** in up to 97% *ee* (Scheme 74).



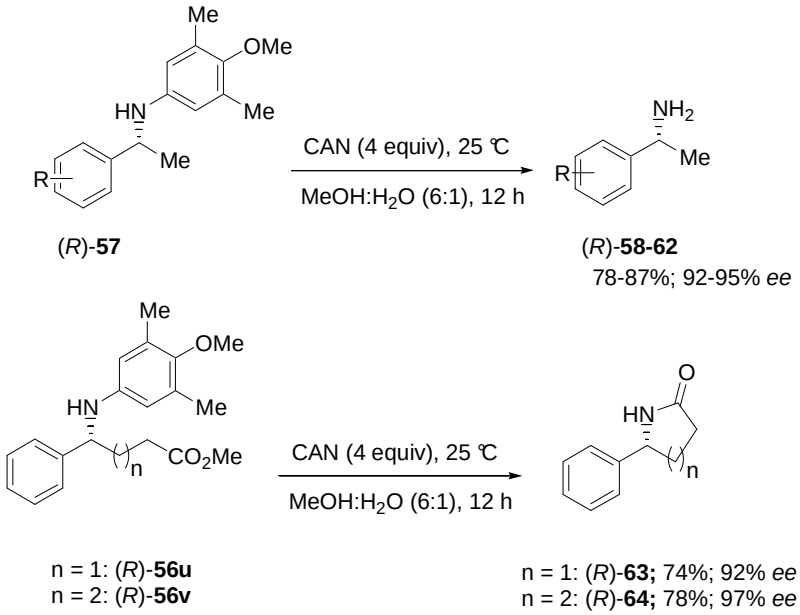
Scheme 74. Application of new P,N-ligands **9-10** in asymmetric allylic alkylations

Further, we applied these P,N-ligands **9a-g** and **10a-g** in Ir-catalyzed asymmetric hydrogenation of imines. The P,N-ligands **9a**, **10a**, **9c**, and **9d** were found to be efficient ligands for the iridium catalyzed imine hydrogenation under mild conditions. Iridium complexes based on these P,N-ligands **46a-d** provided high enantioselectivities in the hydrogenation of various *N*-(3,5-dimethyl-4-methoxy)phenyl-1-phenyl ethylidene amines of type **56** that up to 99% *ee* (Scheme 75).



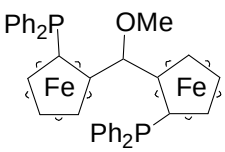
Scheme 75. Hydrogenation of imine **56** using the Ir-catalysts **46a**

We also demonstrated the deprotection of *N*-(3,5-dimethyl-4-methoxy)phenyl group on the amines of type **57** under practical conditions which lead to the various chiral primary amines and lactams (Scheme 76).

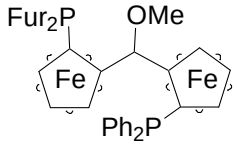


Scheme 76. Deprotection of *N*-aromatic group and synthesis of chiral amines and lactams

In the third project we described the synthesis of bis-ferrocenyl ligands of type **11** and their applications in asymmetric catalysis (Figure 16). These ligands provided disappointing results in asymmetric hydrogenations and allylic alkylations.



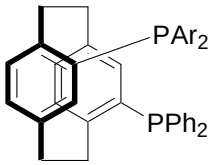
11a



11b

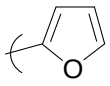
Figure 16. New bis-ferrocenyl P,P-ligands **11a** and **11b**

In the final project we demonstrated the synthesis of new paracyclophane phosphines **12a-d** (Figure 17).

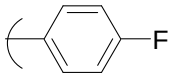


(*R*)-**12a-d**

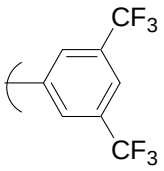
Ar =



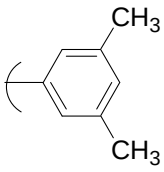
12a



12b



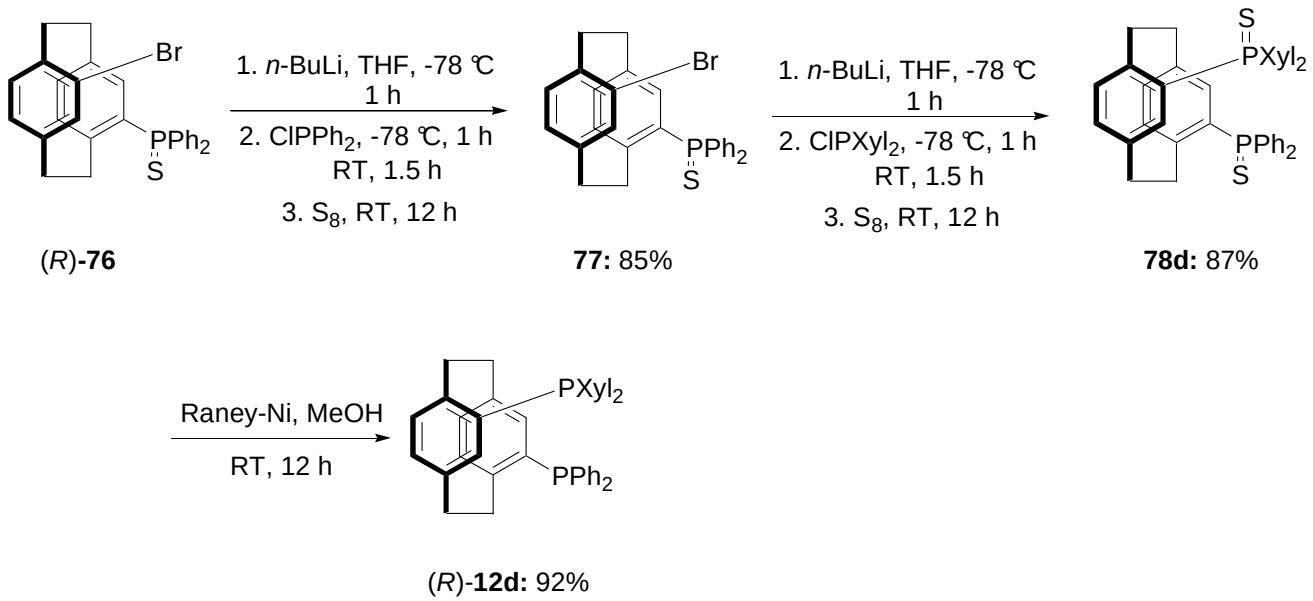
12c



12d

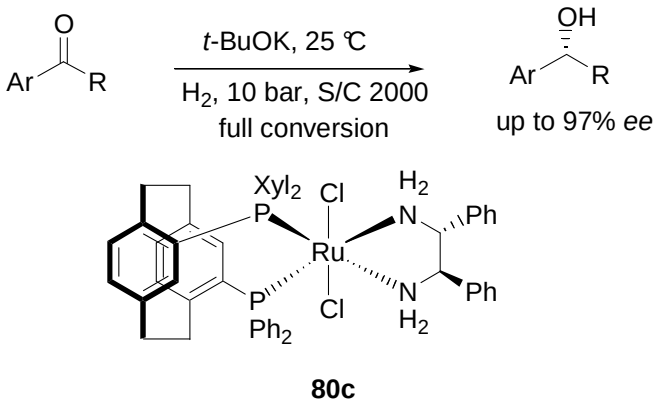
Figure 17. New paracyclophane based diphosphines **12a-d**

The ligand **12d** was synthesized as outlined in the scheme 77.



Scheme 77. Synthesis of new paracyclophane diphosphine **12d**

Among these P,P-ligands **12a-d**, ligand **12d** proved to be an efficient ligand for Ru-catalyzed hydrogenation of various prochiral ketones (Scheme 78). The ruthenium-diamine complex **80c** which was derived from ligand **12d** provided high conversions and enantioselectivities in the hydrogenation of different aromatic and hetero-aromatic ketones up to 97% *ee* (Scheme 78).



Scheme 78. Asymmetric hydrogenation of aromatic and hetero-aromatic ketones using Ru-catalyst **80c**

Experimental Section

1. General conditions

All reactions were carried out with a magnetic stirring and, if air or moisture sensitive, in a flamed-dried glassware under a nitrogen or an argon atmosphere. The syringes which were used to transfer the reagents and the solvents were purged with nitrogen or argon prior to use.

Solvents

The solvents were dried according to standard methods by distillation over drying agents as stated below and were stored under argon or nitrogen. Dichloromethane and toluene were predried over calcium chloride and were distilled from calcium hydride. DMF was heated at reflux for 14 h over calcium hydride and was distilled. Diisopropylamine and *i*-PrOH were distilled from potassium hydride. Ethanol was treated with phthalic anhydride (25 g/L) and sodium, heated at reflux for 6 h and distilled. Methanol was treated with magnesium turnings (20 g/L), heated at reflux for 6 h and distilled. Tetrahydrofuran (THF) was continuously heated at reflux and freshly distilled from sodiumbenzophenone ketyl under nitrogen.

Reagents

Reagents of >98% purity were used as obtained.
n-Butyllithium was used as a solution in hexane.
t-Butyllithium was used as a solution in pentane.
Lithium Diisopropylamine was prepared by adding *n*-BuLi (1.5 M; 1.10 equiv.) to a 2.0 M solution of diisopropylamine (1.32 equiv.) in THF at -78 °C and then stirring at room temperature for 30 min. It was used, as it is in lithiation reactions.
Phenyl lithium was prepared by adding *n*-BuLi (1.5 M; 1.10 equiv.) to a 0.2 M solution of iodobenzene (1.0 equiv) in diethyl ether at 0 °C and then stirred at room temperature for 30 min. It was used, as it is in exchange and lithiation reactions.
The following reagents and substances were prepared according to the literature procedures:
Sulfoxide (**14**), 1,3-Diphenyl-3-acetoxypropen (**27**),[122] chloro dixylylphosphine,[123] bis 2-furylphsophine,[124] and NaBARF[125]
Content determination of organometallic reagents
The organo lithium and organo magnesium solutions were titrated using the method of Paquette[126] and Knochel[127] prior to use.

Chromatography

Thin layer chromatography (TLC) was performed using aluminium plates covered with SiO_2 (Merck 60, F-254). The chromatograms were developed under UV light and/or by treatment of the TLC plate with one of the solutions below followed by gentle heating with a heat gun:
-$KMnO_4$ (0.3 g), K_2CO_3 (20 g) and KOH (0.3 g) in water (300 mL)

---

[122] Hayashi, T. ; Yamamoto, A. ; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301.
[123] Wu, J.; Chen, H.; Kwok, H.; Lam, K. H.; Zhou, Z. Y.; Yeung, C. H.; Chan, A. S. C. *Tetrahedron Lett.* **2002**, *43*, 1539.
[124] Demay, S. Dissertation, Ludwig-Maximilins-Universität München, **2001**
[125] Reger, D. L.; Wright, T. D.; Little, C. A.; Lamba, J. J. S.; Smith, M. D. *Inorg. Chem.* **2001**, *40*, 3810
[126] Lin, H.-S.; Paquette, L. A. *Synth. Commun*. **1994**, *24*, 2503.
[127] Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, *5*, 890.

-Phosphormolybdic acid (5.0 g), $Ce(SO_4)_2$ (2.0 g) and conc. H_2SO_4 (12 mL) in water (230 mL)
Flash column chromatography was performed using SiO_2 60 (0.040-0.063 mm; 230-400 mesh ASTM) or Al_2O_3 (grade III) from Merck. The diameters of the columns and the amount of silica gel were calculated according to the recommendations of W. C: Still.[128]

Analytical data

Melting points were uncorrected and measured on a Büchi B-540 apparatus.
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) and Benzene-d_6 (δ_H: 7.16, δ_C: 128.0).
For the characterization of the observed signal multiplicities the following abbreviations were applied: s (singlet), d (doublet), dd (double doublet), t (triplet), dt (double triplet), m (multiplet), br (broad).
Optical rotation values were measured on the Perkin-Elmer 241 polarimeter.
Infrared spectra were recorded from 4000-400 cm^{-1} on a Nicolet 510 FT-IR or a Perkin-Elmer 281 IR spectrometer. The absorption bands are reported in wave number (cm^{-1}). For the band characterization the following abbreviation were applied: br (broad), s (strong), m (medium), w (weak).
Gas Chromatography (GC): Hewlett-Packard 6890. Cjiral columns: Chirasil-Dex-CB (25 mm x 0.25 nm), Chirasil-L-val (25 m x 0.12 μm x 0.22 mm fused silica WCOT)). Carrier gas H_2.
High Performance Liquid Chromatography (HPLC) was performed using Gynkotec-HPLC with a diode-array UV-VIS detector. Chiral columns: OD-H, OD, OJ and AD (Diacel Chemical Industries) with *n*-heptane/*i*-propanol as a mobile phase. Racemic compounds were used for optimizing the operating conditions for the resolution of the enantiomer and diastereomer peaks.
Electron impact mass (EI, 70 ev) specta were recorded on Finnigan MAT 95Q or Finnigan 90 instrument. High resolution mass spectra (HRMS) were recorded on the same instrument. The combination of gas chromatography with mass spectroscopic detection, a GC/MS from Hewlett-Packard HP 6890/MSD 5973 was used.
Elemental Analysis was carried out on a Heraeus CHN-Rapid-Elementanalyzer in the microanalytical laboratories of the Department für Chemie und Pharmazie, Ludwig-Maxmilians Universität München.

2. Typical Procedures

Typical procedure for the diastereoselective *ortho*-lithiation of ferrocene 14 (TP 1)

A 250 mL Schlenk flask under an argon atmosphere was charged with ferrocenyl sulfoxide **14** (5 mmol, 1.0 equiv.) in THF (50 mL) and added freshly prepared lithium diisopropylamine (2.0 M in THF; 2.75 mL; 1.1 equiv) at -78 °C. The reaction mixture was stirred at -78 °C for 30 min and then electrophile (1.10-1.20 equiv) was added. The reaction mixture was stirred at -78 °C for 1-1.5 h and then warm up to room temperature and stirred for 2 h. The reaction mixture was quenched with a saturated aqueous NH_4Cl solution (20 mL) and the aqueous layer was washed with Et_2O (4 x 25 mL). The combined organic extracts were washed with water, brine and then dried over $MgSO_4$. After evaporation of the solvents, the crude product was purified by column chromatography.

[128] Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Typical procedure for the sulfoxide-lithium exchange on bromo ferrocenes of type 17 using PhLi (TP 2)

A 10 mL Schlenk flask under argon atmosphere, was charged with 1-bromo ferrocenyl sulfoxide **17** (1.0 mmol) was dissolved in THF (5.0 mL). This solution was added to a freshly prepared solution of phenyllithium (0.2 M in diethylether; 1.20 equiv) at -78 °C. After stirring the reaction mixture are -78 °C for 5 min, electrophile (1.10-1.20 equiv) was added and stirred for 30-45 min. Then the reaction mixture was warmed to room temperature and stirred for 1-2 h. Reaction mixture was quenched with saturated aqueous NH_4Cl solution (5 mL) and the aqueous layer was extracted with Et_2O (4 x 10 mL). The combined organic extracts were washed with water, brine and dried over $MgSO_4$. Evaporation of the solvents and purification by column chromatography afforded the desired bromoferrocenes of type **20**.

Typical procedure for the preparation of ferrocenyl alcohols through the sulfoxide-lithium exchange (TP 3)

A Schlenk flask under an argon atmosphere was charged with ferrocenyl sulfoxide **30** or **34** (10 mmol, 1.0 equiv.) in THF and cooled to −78 °C. A solution of freshly prepared PhLi in ether (0.20 M in ether, 1.20 equiv.) was slowly added and the reaction mixture was stirred at −78 °C for 10 min. 2-Pyridinecarboxaldehyde (1.20 equiv) was added dropwise at −78 °C and reaction mixture was stirred for 1.5 h then at room temperature for 1.5 h-2 h. After quenching the reaction mixture with a saturated NH_4Cl solution (25 mL), the aqueous layer was extracted with diethyl ether (4 x 30 mL). The combined organic layers were washed with water, brine, dried over $MgSO_4$ and evaporated under reduced pressure. Purification of the residue by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) afforded the two diastereomeric alcohols as a separable or inseparable mixture.

Typical procedure for preparation of ferrocenyl ethers (TP 4):

A 50 mL Schlenkflask under an argon atmosphere was charged with KH (1 30 equiv) in THF and cooled to 0 °C. A solution of ferrocenyl alcohol (1.0 equiv) in THF was slowly added and the mixture was stirred at room temperature for 1 h. Methyliodide (1.20 equiv) or benzylbromide (1.20 equiv.) was then added dropwise at 0 °C and the reaction mixture was stirred at this temperature for 10 min then at room temperature for 30 min. After quenching the reaction mixture with a saturated NH_4Cl solution, aqueous layer was extracted with diethyl ether. The combined organic layers were washed with water, brine, dried over $MgSO_4$ and evaporated under reduced pressure. Crude product was purified by flash chromatography to furnish the ferrocenyl ethers as solids.

Typical procedure for the desulfurization of phosphine sulfides (TP 5).

An argon flushed 50 mL Schlenk flask was loaded with Raney Ni slurry (Raney Ni in water; (P,N-ligand: 10 equiv; P,P-ligand 25 equiv)). Raney Ni was washed with MeOH (4 × 15 mL). To this flask was then transferred a solution of the protected ligand in THF (2-4 mL), then added 25 mL MeOH and stirred at room temperature under argon atmosphere for 12 h (conversion was monitored by ^{31}Pnmr). The reaction mixture was filtered under argon. The Raney Ni residue was washed with THF (4 × 10 mL). The combined filtrate was concentrated under reduced pressure to afford the pure product as a yellow solid and stored under argon.

Typical procedure for the preparation of ferrocenyl P,N-iridium complexes 46a-g and 47a-g (TP 6).

A 25 mL Schlenk flask under an argon atmosphere, was charged with P,N-ligand (0.50 mmol), $[Ir(cod)Cl]_2$ (0.25 mmol, 0.50 equiv.) in CH_2Cl_2 (5 mL) and stirred at room temperature for 1 h. NaBARF (0.75 mmol, 1.50 equiv.) was added followed by water (5 mL) and the resulting two-phase reaction mixture was stirred vigorously for 30 min. The separated aqueous layer was extracted with CH_2Cl_2 (4 × 15 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. The residue was purified by column chromatography (CH_2Cl_2 as an eluent) yielding the Ir-complexes as a bright orange solid.

Typical procedure for the preparation of *N*-arylimines (TP7).

A 250 mL round-bottomed flask was filled with a ketone (10.0 mmol), an amine (12.0 mmol) and molecular sieves (4 Å, 8 g) in toluene (60 mL). The reaction mixture was refluxed until full conversion was reached (conversion was monitored by GC). The reaction mixture was filtered through celite, solvent was evaporated and the crude product was further purified by column chromatography or vacuum distillation or recrystallization to afford the desired product.

Typical procedure for the Ir-catalyzed hydrogenation of the imines (TP 8):

A 10 mL Schlenk flask under an argon atmosphere was loaded with Ir-complex (0.005 mmol) and imine (0.5 mmol) in Toluene:MeOH (4:1). The mixture was stirred at room temperature for 10-15 min. Then the solution was transferred under argon to an autoclave which was equipped with a glass tube and a stirring bar. The autoclave was then purged three times with hydrogen (5 bar) and finally pressurized to 10 bar. The reaction mixture was stirred for the indicated period of time until full conversion was achieved. Then the hydrogen gas was released, evaporated the solvents and filtered through a short pad of silica gel
Conversion was checked by ^{1}H-NMR/GC and enantioselectivity was determined using either Chiral GC or Chiral HPLC.

Typical procedure for the preparation of chiral primary amines and lactams (TP 9)

The secondary amine of type **57** (0.4 mmol) was dissolved in MeOH:H_2O (6:1; 21 mL) and cerium ammonium nitrate (CAN; 4 equiv; 1.6 mmol) was added at 0 °C. Then the reaction mixture was warmed to room temperature and stirred for overnight. The reaction mixture washed with CH_2Cl_2 (5 mL) and the aqueous layer was made alkaline using aqueous NaOH solution (2.0 M). The aqueous layer was washed with ethylacetate (4 x 15 mL) and the combined organic extracts were washed with water, brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by chromatography afforded the primary amines and lactams.

Typical procedure for the preparation of ruthenium-diamine complexes 79a-c and **80a-c of paracyclophane phosphines (TP 10)**

In a 10 mL Schlenk falsk P,P-ligand (0.01 mmol) and $[Ru(C_6H_5)Cl]_2$ (0.005 mmol) were dissolved in a mixture of toluene (2 mL) and DMF (1.5 mL) under an argon atmosphere. The mixture was heated at 115 °C for 4 h and then chiral diamine (0.01 mmol) was added and continued the stirring at 115 °C for 2 h. The reaction mixture was cooled to room temperature

and stirred for overnight. Evaporated the solvents under reduced pressure and the mixture was washed with CH_2Cl_2:Et_2O (1:1; 4 mL) under argon. Evaporation of the solvents, afforded the desired ruthenium-diamine complex of the paracyclophane phosphine (**79a-c** or **80a-c**). These complexes are used in the ketone hydrogenation without any further purification.

Typical procedure for the Ru-catalyzed hydrogenation of the ketones (TP 11)

A 10 mL Schlenk flask was charged with the ruthenium precatalyst of type **79** or **80** (0.002 mmol) and ketone (4 mmol) and dry *i*PrOH (4 mL) under argon atmosphere. The mixture was stirred at room temperature for 15 min then transferred under argon to an autoclave which was equipped with a glass tube and a stirring bar. The autoclave was then purged three times with hydrogen (5 bar) and finally pressurized to 10 bar. The reaction mixture was stirred for the indicated period of time until full conversion was achieved. Then the hydrogen gas was released, evaporated the solvents and filtered through a short pad of silica gel
Conversion was checked by ^{1}H-NMR/GC and enantioselectivity was determined using either Chiral GC or Chiral HPLC.

Typical procedure for the Pd(0)-catalyzed asymmetric alkylation on racemic 27 (TP 12)

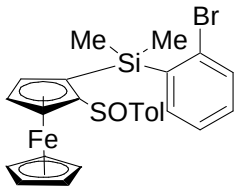
A 10 mL Schlenk flask was filled with ferrocenyl ligand (1.0 mol %), $[Pd(C_3H_5)Cl]_2$ (1.0 mg; 0.5 mol %) and CH_2Cl_2 (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 10 min. 3-Acetoxy-1,3-diphenyl-propene **27** (126 mg; 0.5 mmol), dimethylmalonate (0.2 mL; 1.5 mmol), *N*,*O*-bistrimethylsilylacetamide (305 mg; 1.5 mmol) and potassium acetate (0.5 mg; 1.0 mol%) were added successively. The reaction mixture was stirred for 1 h-12 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (2 mL) and extracted with CH_2Cl_2 (4 x 10 mL). The organic phase was washed with water, brine, dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography yielded **28**.

Typical procedure for the Rh-catalyzed hydrogenations (TP 13)

A 10 mL Schlenk flask was charged with the chiral ligand (1 mol %) and $[Rh(nbd)_2]BF_4$ (3.7 mg, 1 mol %) in toluene/methanol (5:1). Then added a solution of substarte **25** or **74** in methanol (4 mL) and stirred for 15 min at room temperature. The mixture was transferred to an autoclave which was equipped with a glass tube and a stirring bar. The autoclave was then purged three times with hydrogen (5 bar) and finally pressurized to the required pressure. The reaction mixture was stirred for the indicated period of time until full conversion was achieved. Then the hydrogen gas was released, evaporated the solvents and filtered through a short pad of silica gel, afforded the desired product **26** or **75**.
Conversion was checked by ^{1}H-NMR/GC and enantioselectivity was determined using either Chiral GC or HPLC.

3. Preparation of new planar chiral ferrocenyl P,P-ligand 8

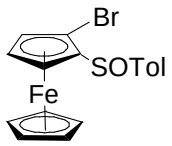
(S_{Fc}, *S*)-[2-((2-Bromophenyl)dimethylsilyl)-ferrocen-1-yl]-*p*-tolylsulfoxide (16)



Prepared according to **TP1** using sulfoxide **14** (1.62 g; 5.0 mmol), LDA (2.75 mL, 5.50 mmol; 1.10 equiv.), and 2-bromophenyldimethylchlorosilane **15** (1.50 g, 6.0 mmol; 1.2 equiv) as an electrophile. After the typical work-up, the crude product was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1), provided the desired compound (2.50 g, 4.65 mmol, 93 %) as a yellow solid.

MP: 146.5-148.5 °C
$[\alpha]_D^{20}$ = +20.1 (c = 0.2, acetone)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.59-7.58 (m, 2H), 7.45-7.44 (m, 2H), 7.27-7.24 (m, 3H), 7.17-7.15 (m, 2H), 4.56 (s, 1H), 4.46 (s, 1H), 4.35 (s, 1H), 4.24 (s, 5H), 2.41 (s, 3H), 1.04 (s, 3H), 0.79 (s, 3H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 140.9, 139.6, 137.9, 132.4, 130.6, 130.0, 129.2, 126.3, 125.1, 78.7, 73.3, 71.6, 71.5, 70.1, 21.4, 0.74, -0.58 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3435 (br, s), 2920 (w), 1578 (w), 1411 (m), 1175 (m), 1048 (m), 810 (s), 757 (m).
MS (70 eV, EI): *m/z* (%) = 536 (M^+, 68), 523 (47), 522 (100), 520 (90), 398 (11).
HRMS (EI): *m/z* calcd. for: [$C_{25}H_{25}{}^{79}BrFe^{32}SSiO$] 535.9928, found: 535..9912.

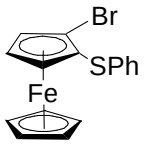
(R_{Fc}, *S*)-[1-Bromo-2-ferrocen-1-yl]-*p*-tolylsulfoxide (17)



Prepared according to **TP1** using sulfoxide **14** (1.62 g, 5.0 mmol), LDA (2.75 mL, 5.50 mmol; 1.10 equiv.), and 1,1,2,2-tetrafluorodibromoethane (1.56 g; 6.0 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1), provided the desired compound (1.78 g, 4.41 mmol, 88 %) as a brown solid

MP: 85.8-88.9 °C
$[\alpha]_D^{20}$ = +9.5 (c = 0.2, acetone)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.72-7.69 (m, 2H), 6.90-6.88 (m, 2H), 4.18 (dd, *J* = 1.3 Hz, 2.2 Hz, 1H), 4.05 (s, 5H), 3.85 (q, *J* = 1.3 Hz, 1H), 3.63 (t, *J* = 2.7 Hz, 1H), 1.98 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 142.2, 140.7, 129.4, 125.5, 93.6, 77.5, 73.5, 72.5, 68.4, 68.2 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (m), 3078 (w), 1641 (w), 1490 (w), 1191 (m), 1034 (s), 813 (m), 627 (m).
MS (70 eV, EI): *m/z* (%) = 402 (M^+, 100), 386 (14), 324 (19), 250 (57), 217 (57), 185 (31).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{15}{}^{79}BrFe^{32}SO$] 401.9376, found: 401.9340.

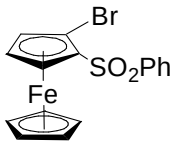
(R_{Fc})-[2-Bromo-2-ferrocen-1-yl]-phenylsulfide (20a)



Prepared according to **TP2**, using sulfoxide **17** (403 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et_2O; 1.20 equiv) and diphenyldisulfide (262 mg; 1.20 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, *n*-pentane), provided the desired compound (269 mg, 0.72 mmol, 72 %) as a pale yellow solid.

MP: 66.7-67.0 °C
$[\alpha]_D^{20}$ = –6.0 (c = 0.2, acetone)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.23-7.22 (m, 2H), 6.98-6.93 (m, 2H), 6.86-6.81 (m, 1H), 4.34 (dd, *J* = 1.3 Hz, 2.6 Hz, 1H), 4.20 (dd, *J* = 1.7 Hz, 2.6 Hz, 1H), 4.04 (s, 5H), 3.77 (t, *J* = 2.6 Hz, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 139.9, 129.0, 126.7, 125.5, 85.9, 77.9, 73.8, 72.5, 72.4, 68.7 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3435 (s), 1627 (m), 1478 (m), 1394 (m), 1106 (w), 1024 (m), 1001 (m), 827 (m), 740 (m).
MS (70 eV, EI): *m/z* (%) = 372 (M^+, 100), 292 (12), 258 (23), 203 (20), 171 (43).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{13}{}^{79}BrFe^{32}S$] 371.9271, found: 371.9273.

(R_{Fc})-[2-Bromo-2-ferrocen-1-yl]-phenylsulfone (21)

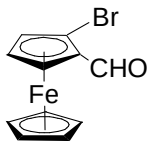


To a 50 mL round-bottomed flask was added ferrocenylsulfide **20a** (186 mg; 0.5 mmol) and CH_2Cl_2 (10 mL). This solution was added slowly to a solution of mCPBA (345 mg, 2.0 mmol; 4.0 equiv) in CH_2Cl_2 (5 mL). After the addition the reaction mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was quenched with 2.0 M aqueous solution of $NaHSO_3$ (20 mL) and the aqueous layer was extracted with CH_2Cl_2 (4 x 10 mL). The combined organic extracts were washed with water, brine, dried over MgSO4 and concentrated *in vacum*. The residue was purified by flash chromatography (silica gel, *n*-pentane), furnished the desired compound (190 mg, 0.47 mmol, 94 %) as a pale yellow solid.

MP: 66.4-68.9 °C
$[\alpha]_D^{20}$ = –2.3 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 8.09-8.06 (m, 2H), 6.91-6.89 (m, 3H), 4.66 (dd, *J* = 1.7 Hz, 2.7 Hz, 1H), 4.33 (s, 5H), 4.12-4.11 (m, 1H), 3.67 (t, *J* = 2.9 Hz, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 143.2, 132.7, 128.9, 127.6, 89.3, 76.8, 74.6, 73.5, 70.0, 69.9 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (m), 1637 (w), 1445 (m), 1322 (s), 1200 (m), 1146 (s), 1088 (m), 938 (m), 724 (s), 612 (s).
MS (70 eV, EI): *m/z* (%) = 404 (M^+, 62), 324 (100), 258 (5), 204 (28), 202 (25).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{13}{}^{79}BrFe^{32}SO_2$] 403.9169, found: 403.9149.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.3 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C);

t_r = 44.9 min [minor], t_r = 51.0 min [major]; 97% *ee*.

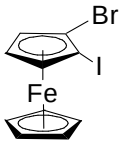
(R_{Fc})-[2-Bromo-2-ferrocen-1-yl]-aldehyde (20b)



Prepared according to **TP2**, using sulfoxide **17** (403 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et_2O; 1.20 equiv), and DMF (1.0 mL; 1.30 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, *n*-pentane:Et_2O (10:1)), provided the desired compound (202 mg, 0.69 mmol, 69 %) as a dark red oil.

$[\alpha]_D^{20}$ = –692 (c = 0.15, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 10.24 (s, 1H), 4.62 (s, 1H), 4.26 (s, 1H), 3.85 (s, 6H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 191.4, 80.3, 76.5, 74.6, 72.2, 70.9, 66.8 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3436 (w), 1681 (s), 1438 (m), 1224 (m), 987 (m), 828 (m), 749 (m).
MS (70 eV, EI): *m/z* (%) = 292 (M^+, 66), 212 (100), 184 (33), 156 (4), 128 (51).
HRMS (EI): *m/z* calcd. for: [$C_{11}H_9{}^{79}BrFeO$] 291.9186, found: 291.9179.

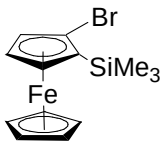
(R_{Fc})-[2-Bromo-2-ferrocen-1-yl]-Iodide (20c)



Prepared according to **TP2**, using sulfoxide **17** (403 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et_2O; 1.2 equiv), and I_2 (304 mg; 1.2 mmol; 1.2 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, *n*-pentane), provided the desired compound (274 mg, 0.70 mmol, 70 %) as a pale yellow solid.

MP: 85.5-83.6 °C
$[\alpha]_D^{20}$ = –1.8 (c = 0.2, acetone)
^{1}H-NMR (600 MHz, C_6D_6): δ = 4.52 (s, 1H), 4.42 (s, 1H), 4.22 (s, 5H), 4.19 (s, 1H) ppm.
^{13}C-NMR (150 MHz, C_6D_6): δ = 84.5, 73.7, 73.6, 73.3, 69.6, 68.4 ppm.
IR (KBr-pressling): υ_{max} (cm^{-1}) = 2900 (w), 1690 (m), 1633 (s), 1569 (m), 1468 (m), 1312 (m), 1100 (m), 1028 (m), 845 (s), 779 (s).
MS (70 eV, EI): *m/z* (%) = 390 (M^+, 100), 183 (17), 128 (74), 127 (12).
HRMS (EI): *m/z* calcd. for: [$C_{10}H_8{}^{79}BrFeI$] 389.8203, found: 389.8188.

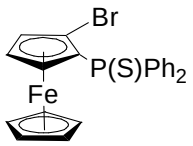
(R_{Fc})-[2-Bromo-2-ferrocen-1-yl]-trimethylsilane (20d)



Prepared according to **TP2**, using sulfoxide **17** (403 mg; 1.0 mmol), phenyllithium (6.0 mL; 0.2 M in Et_2O; 1.20 equiv), and trimethylchlorosilane (0.2 mL; 1.20 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, *n*-pentane), provided the desired compound (236 mg, 0.70 mmol, 70 %) as a pale yellow oil.

$[\alpha]_D^{20}$ = –1.0 (c = 0.2, acetone)
^{1}H-NMR (300 MHz, C_6D_6): δ = 4.41 (s, 1H), 4.40 (s, 1H), 4.18 (s, 5H), 4.17 (s, 1H), 0.21 (s, 9H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 82.5, 73.7, 73.0, 72.8, 67.6, 67.2 ,-0.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2910 (w), 1600 (w), 1558 (m), 1468 (m), 1229 (m), 1100 (m), 1028 (m), 845 (s), 779 (s), 698 (m).
MS (70 eV, EI): *m/z* (%) = 335 (M^+, 100), 258 (77), 195 (14), 121 (25).
HRMS (EI): *m/z* calcd. for: [$C_{13}H_{17}{}^{79}BrFeSi$] 335.9632, found: 335.9640.

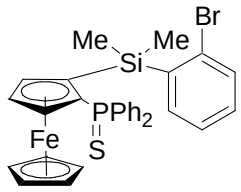
(R_{Fc})-[2-Bromo-2-ferrocen-1-yl]-trimethylsilane (20e)



Prepared according to **TP2**, using sulfoxide **17** (403 mg; 1.0 mmol), phenyllithium (6.0 mL; 0.2 M in Et_2O; 1.20 equiv). The reaction mixture was stirred at -78 °C for 5 min, and then $ClPPh_2$ (0.2 mL; 1.20 mmol; 1.20 equiv) was added as an electrophile. The reaction mixture was stirred 30 min at -78 °C and then at room temperature for 1 h. A solution of sulphur (320 mg; 10.0 equiv) in butylamine (1.0 mL) was added to the reaction mixture. Then reaction mixture was stirred at room temperature for 4-5 h and added saturated aqueous NH_4Cl solution (10 mL). The aqueous layer was extracted with Et_2O (4 x 15 mL) and the combined organic extracts were washed with HCl (2.0 M), water, brine, dried over $MgSO_4$, and concentrated *in vacum*. The crude product was purified by column chromatography (silica gel, *n*-pentane:Et_2O (10:1)), furnished the desired compound (380 mg, 0.79 mmol, 70 %) as a pale yellow solid.

MP: 125.5-123.6 °C
$[\alpha]_D^{20}$ = –4.2 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.64-7.54 (m, 4H), 7.15-7.10 (m, 6H), 4.64-4.62 (m, 1H), 4.54-4.53 (m, 1H), 4.42 (s, 5H), 4.29 (s, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 134.6 (d, *J* = 87.1 Hz), 132.8 (d, *J* = 85.6 Hz), 131.4 (d, *J* = 11.0 Hz), 131.0 (d, *J* = 10.6 Hz), 129.2 (d, *J* = 2.9 Hz), 129.0 (d, *J* = 2.9 Hz), 127.6 (d, *J* = 12.7 Hz), 127.1 (d, *J* = 13.0 Hz), 82.8 (d, *J* = 10.1 Hz), 79.2 (d, *J* = 90.2 Hz), 78.2 (d, *J* = 10.8 Hz), 72.5 (d, *J* = 9.7 Hz), 72.0 (d, *J* = 7.6 Hz), 71.9 ppm.
IR (KBr-pressling): υ_{max} (cm^{-1}) = 2914 (br, w), 1689 (w), 1646 (m), 1598 (m), 1219 (m), 1109 (m), 898 (s), 778 (s), 645 (s).
MS (70 eV, EI): *m/z* (%) = 480 (M^+, 12), 448 (100), 337 (64), 183 (30)**.**
HRMS (EI): *m/z* calcd. for: [$C_{22}H_{18}{}^{79}BrFeP^{32}S$] 479.9400, found: 479.9412.

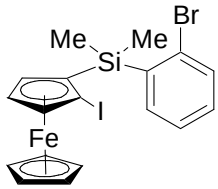
(S_{Fc})-[2-((2-Bromophenyl)dimethylsilyl)]-1-phosphinothioylferrocene (22)



Prepared according to **TP2**, using sulfoxide **17** (538 mg; 1.0 mmol), phenyllithium (6 mL; 0.2 M in Et_2O; 1.20 equiv). The reaction mixture was stirred at -78 °C for 10 min, and then $ClPPh_2$ (0.2 mL; 1.20 mmol; 1.2 equiv) was added as an electrophile. The reaction mixture was stirred 30 min at -78 °C and then at room temperature for 1 h. A solution of sulfur (320 mg; 10 equiv) in butylamine (1.0 mL) was added to the reaction mixture. Then reaction mixture was stirred at room temperature for 4-5 h and added saturated aqueous NH_4Cl solution (10 mL). The aqueous layer was extracted with Et_2O (4 x 15 mL) and the combined organic extracts were washed with HCl (2.0 M), water, brine, dried over $MgSO_4$, and concentrated *in vacum*. The crude product was purified by column chromatography (silica gel, *n*-pentane:Et_2O (8:1)), furnished the desired compound (542 mg, 0.88 mmol, 88 %) as a yellow solid.

MP: 121.4-122.8 °C
$[\alpha]_D^{20}$ = +9.2 (c = 0.2, acetone)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.99-7.94 (m, 2H), 7.75-7.69 (m, 2H), 7.58 (dd, *J* = 7.5 Hz, 1.8 Hz, 1H), 7.21 (d, *J* = 1.8 Hz, 1H), 7.02-6.99 (m, 3H), 6.92-6.90 (m, 4H), 6.70-6.66 (m, 1H), 4.40-4.39 (m, 1H), 4.27 (s, 5H), 4.10-4.09 (m, 1H), 3.92-3.91 (m, 1H), 1.00 (s, 3H), 0.86 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 140.8, 137.9, 135.7 (d, *J* = 16.0 Hz), 134.8 (d, *J* = 15.1 Hz), 132.9, 132.7 (d, *J* = 10.3 Hz), 132.3 (d, *J* = 10.5 Hz), 131.3, 130.9 (d, *J* = 3.1 Hz), 130.7, 128.1, 127.9 (d, *J* = 3.9 Hz), 127.8, 126.3, 82.8 (d, *J* = 12.8 Hz), 82.2 (d, *J* = 96.9 Hz), 78.3 (d, *J* = 14.4 Hz), 74.5 (d, *J* = 18.2 Hz), 72.1 (d, *J* = 9.7 Hz), 70.7, 1.9, 1.4 ppm.
^{31}P-NMR (81 MHz, CDCl3): δ = +41.33 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3435 (br, s), 2923 (w), 1628 (w), 1436 (w), 1101 (m), 811 (m), 717 (m), 616 (w).
MS (70 eV, EI): *m/z* (%) = 614 (M^+, 63), 601 (18), 599 (17), 217 (100).
HRMS (EI): *m/z* calcd. for: [$C_{30}H_{28}{}^{79}BrFeP^{32}SSi$] 613.9951, found: 613.9950.

(S_{Fc})-[2-((2-Bromophenyl)dimethylsilyl)]-1-iodo-ferrocene (23)

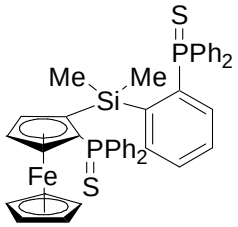


Prepared according to **TP2**, using sulfoxide **17** (270 mg; 0.5 mmol), phenyllithium (3 mL; 0.2 M in Et_2O; 1.20 equiv) and I_2 (152 mg, 0.6 mmol; 1.20 equiv) as an electrophile. After the typical work-up, the crude product was purified by column chromatography (silica gel, *n*-pentane), furnished the desired compound (234 mg, 0.45 mmol, 89 %) as a yellow solid.

MP: 110.0-112.4 °C
$[\alpha]_D^{20}$ = +4.8 (c = 0.2, acetone)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.50-7.48 (m, 1H), 7.17-7.13 (m, 3H), 4.70 (q, *J* = 1.3 Hz, 1H), 4.38 (t, *J* = 2.2 Hz, 1H), 4.22 (s, 5H), 4.18 (dd, *J* = 1.3 Hz, 2.6 Hz, 1H), 0.98 (s, 3H), 0.72)s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 139.7, 137.8, 132.6, 130.8, 126.2, 113.6, 88.7, 79.3, 73.6, 72.8, 72.7, 71.2, 1.0, 0.2 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 2920 (m), 1628 (w), 1599 (m), 1346 (w), 1001 (m), 811 (m), 707 (m).
MS (70 eV, EI): *m/z* (%) = 524 (M^+, 90), 318 (20), 303 (25), 181 (100), 121 (68).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{18}{}^{79}BrFe^{127}ISi$] 523.8755, found: 523.8767.

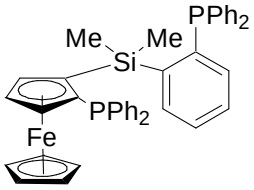
(S_{Fc})-[2-(((2-Phosphiothioyl)phenyl))dimethylsilyl)]-1-phosphinothioyl-ferrocene (24)



A 25 mL Schlenk flask was charged with phosphinesulfide **22** (616 mg; 1.0 mmol) and THF (5 mL) under argon atmosphere. *n*BuLi (1.6 M; 0.70 mL; 1.10 mmol) was added at -78 °C dropwise to the above solution and stirred the resulted lithium species for 15 min. $ClPPh_2$ (0.20 mL; 1.20 mmol; 1.20 equiv) was added as an electrophile and the reaction mixture was stirred 30 min at -78 °C and then at room temperature for 1 h. A solution of sulfur (320 mg; 10 equiv) in butylamine (1.0 mL) was added to the reaction mixture and the reaction mixture was stirred at room temperature for 4-5 h and added a saturated aqueous NH_4Cl solution (10 mL). The aqueous layer was extracted with Et_2O (4 x 15 mL) and the combined organic extracts were washed with HCl (2.0 M), water, brine, dried over $MgSO_4$, and concentrated *in vacum*. The crude product was purified by column chromatography (silica gel, *n*-pentane:Et_2O (6:1)), furnished the desired compound (670 mg, 0.89 mmol, 89%) as a yellow solid.

MP: 212.4-213.8 °C
$[\alpha]_D^{20}$ = +2.9 (c = 0.2, acteone)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.90-7.75 (m, 2H), 7.61-7.54 (m, 7H), 7.50-7.40 (m, 12H), 732-7.26 (m, 3H), 4.38-4.36 (m, 2H), 4.29 (s, 5H), 3.83-3.81 (m, 1H), 0.66 (s, 3H), 0.18 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 145.4 (d, *J* = 18.3 Hz), 140.0 (d, *J* = 16.5 Hz), 138.4 (d, *J* = 87.5 Hz), 135.4 (d, *J* = 9.9 Hz), 135.2 (d, *J* = 87.3 Hz), 134.8 (d, *J* = 3.6 Hz), 134.6 (d, *J* = 87.5 Hz), 134.3 (d, *J* = 9.5 Hz), 133.7 (d, *J* = 3.1 Hz), 132.51 (d, *J* = 13.7 Hz), 132.5 (d, *J* = 10.1 Hz), 132.4 (d, *J* = 14.5 Hz), 132.2 (d, *J* = 10.5 Hz), 128.1 (d, *J* = 3.5 Hz), 88.1 (d, *J* = 87.6 Hz), 81.2 (d, *J* = 2.7 Hz), 80.0 (d, *J* = 2.9 Hz), 71.6 (d, *J* = 9.1 Hz), 70.4, 70.2 (d ; *J* = 8.9 Hz), 4.6, 4.1 ppm
^{31}P-NMR (81 MHz, CDCl3): δ = +41.33 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3430 (br, s), 2910 (m), 1500 (m), 1460 (m), 1219 (w), 1101 (m), 810 (m), 798 (m).
MS (70 eV, EI): *m/z* (%) = 752 (M^+, 13), 689 (25), 688 (50), 687 (100), 656 (8).
HRMS (EI): *m/z* calcd. for: [$C_{42}H_{38}FeP_2{}^{32}S_2Si$] 752.1009, found: 752.1013.

(S_{Fc})-[2-(((2-Diphynlphosphiono)phenyl))dimethylsilyl)]-1-diphenylphosphinoferrocene (8)

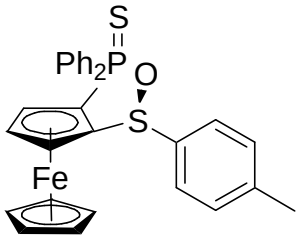


Prepared according to TP5, using the phosphinesulfide 24 (150 mg, 0.20 mmol) and Raney-Ni (765 mg, 13 mmol; 65.0 equiv.) in MeOH (25 mL). After evaporation of the solvent, the diphosphine (127 mg, 0.18 mmol; 92%) obtained as a yellow solid.

MP: 88.5-91.2 °C
$[\alpha]_D^{20}$ = +2.0 (c = 0.2, acteone)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.90-7.75 (m, 2H), 7.61-7.54 (m, 7H), 7.50-7.40 (m, 12H), 732-7.26 (m, 3H), 4.38-4.36 (m, 2H), 4.29 (s, 5H), 3.83-3.81 (m, 1H), 0.66 (s, 3H), 0.18 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 145.4 (d, *J* = 18.3 Hz), 140.0 (d, *J* = 16.5 Hz), 138.4 (d, *J* = 87.5 Hz), 135.4 (d, *J* = 9.9 Hz), 135.2 (d, *J* = 87.3 Hz), 134.8 (d, *J* = 3.6 Hz), 134.6 (d, *J* = 87.5 Hz), 134.3 (d, *J* = 9.5 Hz), 133.7 (d, *J* = 3.1 Hz), 132.51 (d, *J* = 13.7 Hz), 132.5 (d, *J* = 10.1 Hz), 132.4 (d, *J* = 14.5 Hz), 132.2 (d, *J* = 10.5 Hz), 128.1 (d, *J* = 3.5 Hz), 88.1 (d, *J* = 87.6 Hz), 81.2 (d, *J* = 2.7 Hz), 80.0 (d, *J* = 2.9 Hz), 71.6 (d, *J* = 9.1 Hz), 70.4, 70.2 (d ; *J* = 8.9 Hz), 4.6, 4.1 ppm
^{31}P-NMR (81 MHz, CDCl3): δ = -21.60, -10.61 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3430 (br, s), 2910 (m), 1500 (m), 1460 (m), 1219 (w), 1101 (m), 810 (m), 798 (m).
MS (70 eV, EI): *m/z* (%) = 688 (M^+, 13), 687 (25), 524 (100), 412 (45).
HRMS (EI): *m/z* calcd. for: [$C_{42}H_{38}FeP_2Si$] 688.1567, found: 688.1573.

4. Preparation of new ferrocenyl P,N-ligands 9-10

(S_{Fc})-1-((*S*)-*p*-Tolylsulfinyl)-2-(diphenylphosphinothioyl) ferrocene (30):

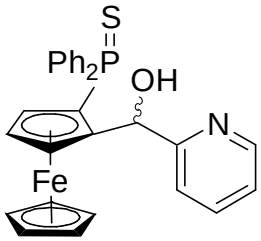


Prepared according to the typical procedure **TP1**, using sulfoxide **14** (6.48 g, 20.0 mmol) in THF (200 mL) and LDA (11.0 mL; 22.0 mmol; 1.1 equiv.). The reaction mixture was stirred for 30 min at −78 °C and chloro diphenylphosphine (5.30 g, 24.0 mmol, 1.20 equiv.) was added slowly at −78 °C. The reaction mixture was stirred at −78 °C for 1.5 h then warmed to room temperature and stirred for 1.5 h. A solution of sulfur (1.92 g, 60.0 mmol, 3.0 equiv.) in butylamine (3 mL) was added to the reaction mixture at room temperature and stirred for 2-4 h (protection was monitored by ^{31}P-NMR). After quenching the reaction mixture with a saturated NH_4Cl solution, aqueous layer was extracted with dichloromethane (4 × 100 mL). The combined organic layers were washed with 2N HCl, water, brine, dried over $MgSO_4$ and evaporated under reduced pressure. Purification by flash chromatography (silica gel, *n*-

pentane:Et_2O 1:1) of the residue provided the desired compound (9.50 g, 17.60 mmol, 88 %) as a pale brown solid.

MP: 120.3-121.3 °C
$[\alpha]_D^{20}$ = −306 (c = 0.08, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 8.35-8.23 (m, 4H), 7.94 (d, *J* = 7.8 Hz, 2H) 7.24-7.15 (m, 6H) 6.92 (d, *J* = 7.5 Hz, 2H) 4.56-4.51 (m, 1H) 4.24-4.21 (m, 1H) 4.20 (s, 5H), 4.14-4.00 (m, 1H), 2.09 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 143.0, 141.6, 135.4 (d, *J* = 28.8 Hz), 134.2 (d, *J* = 28.2), 133.52 (d, *J* = 24.1 Hz), 133.51 (d, *J* = 1.8 Hz), 132.1 (d, *J* = 3.5 Hz), 131.8 (d, *J* = 2.9 Hz), 129.7, 128.8 (d, *J* = 1.8 Hz), 128.6 (d, *J* = 7.6 Hz), 81.3, 80.0, 77.4 (d, *J* = 12.9 Hz), 72.5, 72.0 (d, *J* = 7.6 Hz), 71.9 (d, *J* = 10.0 Hz), 21.5 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.45 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, s), 1630 (br, w), 1436 (w), 1041 (m), 717 (m).
MS (70 eV, EI): *m/z* (%) = 540 (M^+, 26), 524 (22), 401 (100).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{25}P^{56}FeO^{32}S_2$] 540.0434, found: 540.0417

Preparation of (R_{Fc})-1-(Diphenylphosphinothioyl)-2-(α-hydroxypyridyl)methylferrocene (31):



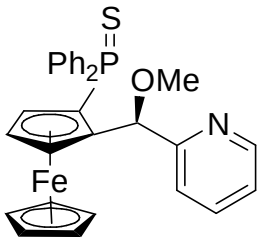
Prepared according to the typical procedure **TP3**, using ferrocenyl sulfoxide **30** (10.0 mmol, 5.40 g) in THF (10 mL), PhLi (0.20 M, 60 mM, 12.0 mmol, 1.20 equiv.) in diethylether, and 2-Pyridinecarboxaldehyde (2.30 mL, 24.0 mmol, 1.20 equiv.) as an electrophile. After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) afforded the two diastereomeric alcohols **31a** and **31b** (3.69 g, 7.20 mmol, 72 %) as an inseparable mixture **31** in 6:4 ratio (by ^{31}P-NMR).

^{1}H-NMR (200 MHz, C_6D_6): δ = 8.29-8.19 (m, 1H), 7.93-7.86 (m, 4H), 7.76-7.72 (m, 1H), 7.65-7.54 (m, 4H), 7.39-7.35 (m, 1H), 7.01-6.80 (m, 16H), 6.44-6.36 (m, 3H), 5.32 (d, *J* = 9.0 Hz, 1H), 4.96 (d, *J* = 6.0 Hz, 1H), 4.65 (s, 1H), 4.48 (s, 5H), 4.32 (s, 6H), 3.93-3.91 (m, 2H), 3.64-3.61 (m, 2H) ppm.
^{31}P-NMR (81 MHz, C_6D_6): +42.6 (minor, 40 %), +43.5 (major, 60%) ppm.

Preparation of ferrocenyl methyl ethers 32a and 32 b:

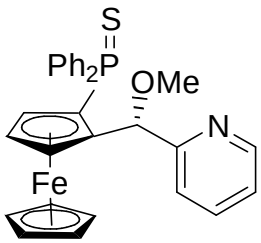
Prepared according to the typical procedure **TP4**, using KH (104 mg, 2.60 mmol, 1.30 equiv.) in THF (4 mL), ferrocenyl alcohol **31** (dr 6:4, 1.01 g, 2.0 mmol) in THF (20 mL) and CH_3I (341 mg, 2.40 mmol, 1.20 equiv.). The reaction mixture was quenched with a saturated NH_4Cl solution (10 mL) and the aqueous layer was extracted with diethylether (4 x 20 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) to furnish the two methyl ethers **32a** (566 mg, 1.07 mmol, 54 %) and **32b** (367 mg, 0.70 mmol, 35 %) yellow solids.

(R_{Fc})-1-(Diphenylphosphinothioyl)-2-((*S*)-α-methoxypyridyl)methylferrocene (32a):



MP: 217.9-218.4 °C
$[\alpha]_D^{20}$ = −25.8 (c = 0.22, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 8.50-8.42 (m, 1H), 8.08-7.95 (m, 4H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.13-7.03 (m, 7 H), 6.71-6.67 (m, 1 H), 6.64 (s, 1H), 4.35 (s, 5H), 4.10-4.08 (m, 1H), 3.94 (dd, *J* = 2.2 Hz, 4.0 Hz, 1H), 3.77 (dd, *J* = 2.2 Hz, 4.0 Hz, 1H), 2.92 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 161.4, 149.1, 136.4 (d, *J* = 88.0 Hz), 135.7, 134.8 (d, *J* = 87.0 Hz), 132.8 (d, *J* = 4.7 Hz), 132.7 (d, *J* = 4.7 Hz), 130.9 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 2.9 Hz), 128.2, 127.9, 122.3, 122.2, 92.6 (d, *J* = 11.8 Hz), 80.8, 75.8 (d, *J* = 94.5 Hz), 75.5 (d, *J* = 12.9 Hz), 72.9 (d, *J* = 8.8 Hz), 71.7, 69.1 (d, *J* = 10.5 Hz), 56.7 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.74 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, s), 1630 (br, w), 1589 (s), 1436 (br, s), 3436 (m), 1099 (s), 819 (w), 715 (s), 502 (s).
MS (70 eV, EI): *m/z* (%) = 523 (M^+, 28), 458 (68), 428 (100), 288 (14).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{26}P^{56}FeNO^{32}S$] 523.0822, found: 523.0837

(R_{Fc})-1-(Diphenylphosphinothioyl)-2-((*R*)-α-methoxypyridyl)methylferrocene (32b):

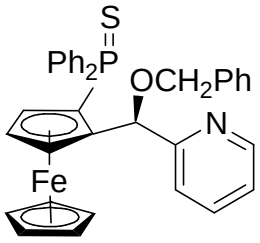


MP: 199.3-200.8 °C
$[\alpha]_D^{20}$ = −21.7 (c = 0.18, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 8.25-8.23 (m, 1H), 7.92-7.84 (m, 2H), 7.40-7.33 (m, 2H), 7.20-7.17 (m, 1H), 7.04-6.95 (m, 3H), 6.84-6.79 (m, 1H), 6.73-6.63 (m, 3 H), 6.60 (s, 1 H), 6.38-6.33 (m, 1H), 5.30 (dd, *J* = 1.8 Hz, 4.0 Hz, 1 H), 4.50 (s, 5 H), 4.02 (dd, *J* = 2.3 Hz, 4.0 Hz, 1H), 3.57 (dd, *J* = 2.3 Hz, 4.0 Hz, 1H), 3.30 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 160.0, 149.6, 135.6 (d, *J* = 60.0 Hz), 134.8, 134.5 (d, *J* = 60.0 Hz), 132.6 (d, *J* = 10.6 Hz), 132.1 (d, *J* = 10.6 Hz), 131.0 (d, *J* = 2.9 Hz), 130.2 (d, *J* = 2.9 Hz), 127.8, 127.6, 124.1, 121.9, 95.5 (d, *J* = 11.8 Hz), 79.5, 74.4 (d, *J* = 12.3 Hz), 73.3 (d, *J* = 94.5 Hz), 72.4 (d, *J* = 9.5 Hz), 71.4, 69.5 (d, *J* = 10.2 Hz), 56.6 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.59 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, m), 1588 (w), 1436 (s), 1158 (s), 1099 (s), 819 (m), 615 (s).
MS (70 eV, EI): *m/z* (%) = 523 (M^+, 25), 458 (60), 428 (100), 426(32).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{26}P^{56}FeNO^{32}S$] 523.0822, found: 523.0855

Preparation of ferrocenyl benzyl ethers 33a and 33b:

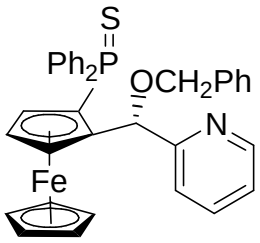
Prepared according to the typical procedure **TP4**, using KH (104 mg, 2.60 mmol, 1.30 equiv.) in THF (4 mL), ferrocenyl alcohol **31** (dr 6:4, 1.01 g, 2.0 mmol) in THF (20 mL) and Benzyl bromide (411 mg, 2.40 mmol, 1.20 equiv). The reaction mixture was quenched with a saturated NH_4Cl solution (10 mL), the aqueous layer was extracted with diethylether (4 x 20 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) to furnish the two benzyl ethers **33a** (649 mg, 1.08 mmol, 54 %) and **33b** (433 mg, 0.72 mmol, 36 %) as yellow solids.

(R_{Fc})-1-(Diphenylphosphinothioyl)-2-(((*S*)-α-benzyloxy)pyridyl))methylferrocene (33a):



MP: 173.1-175.0 °C
$[\alpha]_D^{20}$ = −62.6 (c = 0.3, CH_2Cl_2).
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.36-8.27 (m, 1 H), 7.74-7.67 (m, 2 H), 7.47-7.26 (m, 8 H), 7.20-7.12 (m, 4H), 7.06-6.96 (m, 3H), 6.82-6.74 (m, 1 H), 6.50 (s, 1H), 5.20 (s, 1H), 4.50 (dd, *J* = 11.6 Hz, 22.0 Hz, 2H), 4.34 (s, 1H), 4.33 (s, 5 H), 3.60 (s, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.9, 138.4, 135.7, 134.3 (d, *J* = 49.6 Hz), 133.1 (d, *J* = 49.2 Hz), 132.0 (d, *J* = 11.0 Hz), 131.6 (d, *J* = 11.0 Hz), 131.1 (d, *J* = 2.8 Hz), 130.4 (d, *J* = 2.8 Hz), 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 124.1, 122.3, 94.2 (d, *J* = 11.9 Hz), 76.8, 74.4 (d, *J* = 12.8 Hz), 72.6 (d, *J* = 94.6 Hz), 71.4 (d, *J* = 9.4 Hz), 71.0, 70.9, 69.4 (d, *J* = 10.6 Hz) ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.98 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, s), 3056 (br, w), 1589 (m), 1436 (s), 1102 (s), 1052 (s), 819 (w), 750 (m), 715 (s), 695 (s)..
MS (70 eV, EI): *m/z* (%) = 599 (M^+, 36), 534 (38), 429 (100), 288 (41), 154 (40).
HRMS (EI): *m/z* calcd. for: [$C_{35}H_{30}P^{56}FeNO^{32}S$] 599.1135, found: 599.1120

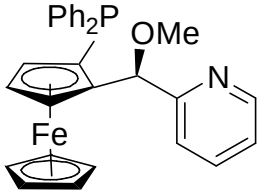
(R_{Fc})-1-(Diphenylphosphinothioyl)-2-(((*R*)-α-benzyloxy)pyridyl))methylferrocene (33b):



MP: 129.7-130.8 °C
$[\alpha]_D^{20}$ = −48.0 (c = 0.3, CH_2Cl_2).
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.79-7.68 (m, 2H), 7.53-7.29 (m, 8H), 7.21-7.13 (m, 4H), 7.10-7.04 (m, 3H), 6.82 (s, 1H), 6.53 (s, 1H), 5.23 (s, 1H), 4.53 (q, *J* = 11.7 Hz, 2H), 4.40-4.37 (m, 1H), 4.36 (s, 5H), 3.63 (s, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.2, 149.1, 138.7, 136.0, 134.5 (d, *J* = 49.8 Hz), 133.4 (d, *J* = 49.8 Hz), 132.3 (d, *J* = 10.5 Hz), 131.9 (d, *J* = 10.5 Hz), 131.4 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 3.3 Hz), 128.5, 128.3, 128.1, 127.9, 127.8, 124.4, 122.5, 94.5 (d, *J* = 11.7 Hz), 77.1,

74.7 (d, *J* = 12.2 Hz), 72.9 (d, *J* = 94.5 Hz), 71.6 (d, *J* = 9.4 Hz), 71.3, 69.7 (d, *J* = 10.5 Hz) ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.96 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3435 (b, s), 1629 (b, w), 1436 (s), 1101 (s), 821 (m), 714 (s), 694 (s).
MS (70 eV, EI): *m/z* (%) = 599 (M^+, 10), 534 (8), 429 (27), 428 (100), 427 (25)
HRMS (EI): *m/z* calcd. for: [$C_{35}H_{30}P^{56}FeNO^{32}S$] 599.1122, found: 599.1158

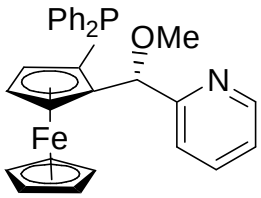
(*R*$_{Fc}$)-1-(Diphenylphosphino)-2-(((*S*)-α-methoxy)pyridyl))methylferrocene (9a):



Prepared according to **TP5** from Raney-Ni (1. 5 g, 24.0 mmol, 30 equiv.) and **32a** (420 mg, 0.80 mmol) in MeOH (50 mL) and obtained as a yellow solid (331 mg, 0.67 mmol, 84 %).

MP: 120.3-122.4 °C
[α]$_D^{20}$ = +234 (c = 0.1, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.69-8.68 (m, 1H) 7.75-7.69 (m, 2H), 7.63-7.51 (m, 4H), 7.39-7.38 (m, 2H), 7.30-7.22 (m, 5H), 5.49 (d, *J* = 3.3 Hz, 1H), 4.23-4.20 (m, 1H), 4.03 (s, 1H), 3.81 (s, 5H), 3.36 (s, 1H), 2.93 (s, 3H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.6, 148.7, 135.2 (d, *J* = 21.5 Hz), 132.4 (d, *J* = 18.3 Hz), 132.3, 130.8, 129.0, 128.7, 128.0 (d, *J* = 8.0 Hz), 127.63 (d, *J* = 6.5 Hz), 127.4, 122.6, 121.8, 95.6 (d, *J* = 24.0 Hz), 82.3, 73.8 (d, *J* = 9.5 Hz), 71.2, 70.5, 69.8, 69.2, 68.7 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -21.17 ppm.
IR(neat): υ_{max} (cm^{-1}) = 2920 (w), 1728 (w), 1586 (m), 1428 (m), 1126 (m), 1080 (s), 1105 (s), 810 (s), 748 (s), 698 (s).
MS (70 eV, EI): *m/z* (%) = 491 (M^+, 39), 427 (28), 426 (100), 396 (32), 262 (30), 154 (37).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{26}P^{56}FeNO$] 491.1101, found: 491.1108

(*R*$_{Fc}$)-1-(Diphenylphosphino)-2-(((*R*)-α-methoxy)pyridyl))methylferrocene (9b):

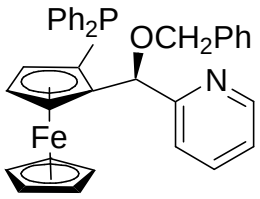


Prepared according to **TP4** from Raney-Ni (1.5 g, 24.0 mmol, 30 equiv.) and **32b** (420 mg, 0.80 mmol) in MeOH (50 mL), and obtained as a yellow solid (325 mg, 0.66 mmol, 82 %).

MP: 140.2-144.0 °C
[α]$_D^{20}$ = +214 (c = 0.1, CH_2Cl_2)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.07 (m, 1H), 7.71-7.70 (m, 1H), 7.49 (br s, 2H), 7.33-7.28 (m, 3H), 7.12-6.94 (m, 4H), 6.79-6.76 (m, 3H), 5.39 (s, 1H), 4.66 (s, 1H), 4.31-4.26 (m, 1H), 4.10 (s, 5H), 3.65 (s, 1H), 3.34 (s, 3H) ppm.

^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.3, 148.5, 139.1 (d, *J* = 9.2 Hz), 137.5 (d, *J* = 9.2 Hz), 135.8, 135.0 (d, *J* = 21.3 Hz), 131.9 (d, *J* = 18.5 Hz), 128.9, 127.9 (d, *J* = 8.0 Hz), 127.5 (d, *J* = 6.4 Hz), 127.0, 122.0, 121.7, 92.9 (d, *J* = 24.7 Hz), 82.8 (d, *J* = 9.8 Hz), 76.5 (d, *J* = 9.6 Hz), 71.7 (d, *J* = 4.2 Hz), 70.0 (d, *J* = 3.4 Hz), 69.7, 68.7, 68.1 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -21.25 ppm.
IR(neat): υ_{max} (cm^{-1}) = 2928 (w), 1725 (w), 1586 (m), 1430 (m), 1162 (m), 1087 (s), 1104 (s), 816 (s), 744 (s), 698 (s).
MS (70 eV, EI): *m/z* (%) = 491 (M^+, 47), 427 (28), 426 (100), 396 (37), 262 (38), 154 (50).
HRMS (EI): *m/z* calcd. for: [$C_{29}H_{26}P^{56}FeNO$] 491.1101, found: 491.1110.

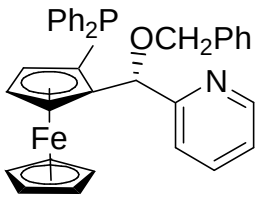
(R_{Fc})-1-(Diphenylphosphino)-2-(((*S*)-α-benzyloxy)pyridyl))methylferrocene (10a):



Prepared according to **TP4** from Raney-Ni (1.5 g, 24.0 mmol; 30 equiv.) and **33a** (480 mg, 0.80 mmol) in MeOH (50 mL), and obtained as a yellow solid (402 mg, 0.71 mmol, 88 %).

MP: 49.8-53.5 °C
$[\alpha]_D^{20}$ = +230 (c = 0.1, CH_2Cl_2)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.71-8.70 (m, 1H), 7.77-7.74 (m, 1H), 7.65-7.61 (m, 3H), 7.39-7.38 (m, 3H), 7.30-7.28 (m, 1H), 7.24-7.16 (m, 5H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 2H), 6.74-6.73 (m, 2H), 5.88 (s, 1H), 4.31 (d, *J* = 10.9 Hz, 1H), 4.26 (t, *J* = 2.6 Hz, 1H), 4.22 (s, 1H), 4.13 (d, *J* = 10.9 Hz, 1H), 3.90 (s, 1H), 3.83 (s, 5H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.7, 140.5 (d, *J* = 10.0 Hz), 137.9 (d, *J* = 10.2 Hz), 137.6, 135.4 (d, *J* = 22.0 Hz), 132.4 (d, *J* = 18.0 Hz), 129.1, 128.4, 128.1 (d, *J* = 1.7 Hz), 128.0, 127.9, 127.8 (d, *J* = 1.7 Hz), 127.4, 127.4, 122.8, 122.3, 95.1 (d, *J* = 26 Hz), 76.5 (d, *J* = 10.6 Hz), 71.9 (d, *J* = 4.5 Hz), 71.7, 70.5, 70.49 (d, *J* = 3.4 Hz), 70.0, 69.8 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -21.58 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3054 (br, w), 2858 (br, w), 1587 (m), 1432 (m), 1047 (s), 817 (m), 739 (s), 690 (s).
MS (70 eV, EI): *m/z* (%) = 567 (M^+, 38), 502 (87), 461 (57), 396 (100), 276 (33), 154 (34).
HRMS (EI): *m/z* calcd. for: [$C_{35}H_{30}P^{56}FeNO$] 567.1414, found: 567.1389

(R_{Fc})-1-(Diphenylphosphino)-2-(((*R*)-α-benzyloxy)pyridyl))methylferrocene (10b):

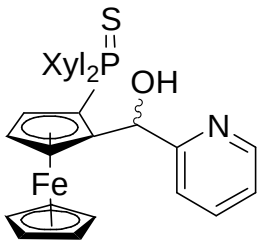


Prepared according to **TP4** from Raney-Ni (1.5 g, 24.0 mmol; 30 equiv.) and **33b** (482 mg, 0.80 mmol) in MeOH (50 mL), and obtained as a yellow solid (390 mg, 0.69 mmol, 86 %).

MP: 58.0-60.2 °C
$[\alpha]_D^{20}$ = +134 (c = 0.1, CH_2Cl_2)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05-8.03 (m, 1H), 7.51-7.42 (m, 4H), 7.39-7.27 (m, 7H), 7.20-7.18 (m, 1H), 7.04-7.01 (m, 1H), 6.95-6.91 (m, 2H), 6.79-6.71 (m, 3H), 5.71 (d, *J* = 2.1 Hz, 1H), 4.80-4.79 (m, 1H), 4.53 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.28 (t, *J* = 2.3 Hz, 1H), 4.05 (s, 5H), 3.70-3.69 (m, 1H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.7, 148.4, 139.3 (d, *J* = 9.2 Hz), 138.6, 137.6 (d, *J* = 9.6 Hz), 135.9, 135.2 (d, *J* = 21.3 Hz), 131.9 (d, *J* = 18.2 Hz), 128.9 (d, *J* = 0.8 Hz), 128.3, 127.9 (d, *J* = 7.8 Hz), 127.6, 127.5, 127.4 (d, *J* = 2.2 Hz), 127.0, 122.1, 121.8 (d, *J* = 1.5 Hz), 95.9 (d, *J* = 24.3 Hz), 80.7 (d, *J* = 7.3 Hz), 73.8 (d, *J* = 10.5 Hz), 71.3 (d, *J* = 4.8 Hz), 70.8, 69.9, 69.1, 69.0 (d, *J* = 4.5 Hz) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -22.49 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3050 (w), 2860 (w), 1586 (m), 1432 (m), 1066 (m), 1026 (m), 815 (m), 740 (s), 692 (s), 614 (m).
MS (70 eV, EI): *m/z* (%) = 568 ($[M+H]^+$, 38), 567 (M^+, 100), 502 (58), 461 (47), 385 (83), 276 (41), 212 (72).
HRMS (EI): *m/z* calcd. for: [$C_{35}H_{30}P^{56}FeNO$] 567.1414, found: 567.1436

Preparation of (R_{Fc})-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(α-hydroxypyridyl)methylferrocene (35):



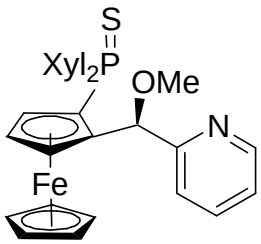
Prepared according to the typical procedure **TP3**, using ferrocenyl sulfoxide **35** (6.00 g, 10.0 mmol) in THF (10 mL), *t*-BuLi (1.50 M, 14.7 mL, 22.0 mmol, 2.20 equiv.), and 2-pyridinecarboxaldehyde (2.30 mL, 24.0 mmol, 1.20 equiv.) as an electrophile. After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) afforded the two diastereomeric alcohols **35a** and **35b** (3.69 g, 6.50 mmol, 65 %) as an inseparable mixture **35** in 5:5 ratio (by ^{31}P-NMR).

^{1}H-NMR (200 MHz, C_6D_6): δ = 8.29-8.19 (m, 1H), 7.93-7.86 (m, 4H), 7.76-7.72 (m, 1H), 7.65-7.54 (m, 4H), 7.39-7.35 (m, 1H), 7.01-6.80 (m, 16H), 6.44-6.36 (m, 3H), 5.32 (d, *J* = 9.0 Hz, 1H), 4.96 (d, *J* = 6.0 Hz, 1H), 4.65 (s, 1H), 4.48 (s, 5H), 4.32 (s, 6H), 3.93-3.91 (m, 2H), 3.64-3.61 (m, 2H) ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = 43.09 (51 %), 43.83 (49 %).

Preparation of ferrocenyl methyl ethers 36a and 36 b:

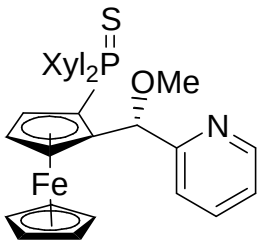
Prepared according to the typical procedure **TP4**, using KH (95 mg, 2.25 mmol, 1.50 equiv.) in THF (4 mL), ferrocenyl alcohol **35** (dr 5:5, 850 mg, 1.5 mmol) in THF (10 mL) and CH_3I (0.12 mL, 1.80 mmol, 1.20 equiv.). The reaction mixture was quenched with a saturated NH_4Cl solution (10 mL) and the aqueous layer was extracted with diethylether (4 x 20 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) to furnish the two methyl ethers **36a** (393 mg, 0.67 mmol, 45%) and **36b** (256 mg, 0.66 mmol, 44%) as yellow solids.

(R_{Fc})-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((*S*)-α-methoxy)pyridyl))methyl-ferrocene (36b):



MP: 88 °C (sublimation)
$[\alpha]_D^{20}$ = −25.8 (c = 0.22, acetone).
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.54-8.52 (m, 1H), 7.93-7.91 (m, 2H), 7.83-7.80 (m, 2H), 7.53 (tt, *J* = 1.0 Hz, 7.8 Hz, 1H), 7.12 (ddd, *J* = 1.9 Hz, 7.7 Hz, 1H), 6.78-6.77 (m, 2H), 6.68 (dddd, *J* = 1.3 Hz, 4.8 Hz, 7.4 Hz, 1H), 6.64 (s, 1H), 4.35 (s, 5H), 4.33-4.32 (m, 1H), 4.03-4.02 (m, 1H), 4.00-3.99 (m, 1H), 2.99 (s, 3H), 2.04 (s, 6H), 2.03 (s, 6H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 161.5, 149.2, 137.6 (d, *J* = 12.9 Hz), 137.4 (d, *J* = 13.0 Hz), 136. 4 (d, *J* = 86.8 Hz), 135.7, 134.8 (d, *J* = 84.2 Hz), 132.9 (d, *J* = 3.0 Hz), 132.7 (d, *J* = 3.2 Hz), 130.7 (d, *J* = 10.5 Hz), 130.6 (d, *J* = 10.9 Hz), 122.5, 122.3, 92.5 (d, *J* = 11.4 Hz), 80.6, 76.3 (d, *J* = 93.6 Hz), 75.4 (d, *J* = 12.3 Hz), 73.1 (d, *J* = 8.9 Hz), 71.7, 69.2 (d, *J* = 10.3 Hz), 56.7, 21.15 (d, *J* = 0.8 Hz), 21.1 (d, *J* = 0.8 Hz) ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.31 ppm..
IR(KBr): υ_{max} (cm^{-1}) = 3635 (w), 2920 (m), 1587 (m), 1431 (m), 1121 (m), 1073 (s), 846 (m), 689 (s), 670 (s).
MS (70 eV, EI): *m/z* (%) = 579 (M^+, 32), 515 (27), 514 (80), 485 (31), 484 (100), 482 (22), 154 (17).
HRMS (EI): *m/z* calcd. for: [$C_{33}H_{34}P^{56}FeNO^{32}S$] 579.1448, found: 579.1457

(R_{Fc})-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((*R*)-α-methoxy)pyridyl))methyl-ferrocene (36b):



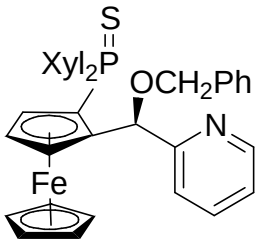
MP: 99.3-100.1 °C
$[\alpha]_D^{20}$ = −21.7 (c = 0.18, acetone).
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.32-8.30 (m, 1H), 7.75-7.72 (m, 2H), 7.27 (tt, *J* = 1.0 Hz, 7.7 Hz, 1H), 7.14-7.12 (m, 2H), 6.74 (s, 1H), 6.66 (ddd, *J* = 1.8 Hz, 7.7 Hz, 2H), 6.53 (s, 1H), 6.33 (dddd, *J* = 1.3 Hz, 4.7 Hz, 7.5 Hz, 1H), 5.36-5.35 (m, 1H), 4.58 (s, 5H), 4.06-4.05 (m, 1H), 3.78-3.77 (m, 1H), 3.28 (s, 3H), 1.97 (s, 6H), 1.80 (s, 6H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 160.2, 149.5, 137.6 (d, *J* = 13.0 Hz), 137.3 (d, *J* = 13.3 Hz), 135. 6 (d, *J* = 86.5 Hz), 134.8 (d, *J* = 84.8 Hz), 134.6, 132.9 (d, *J* = 3.2 Hz), 132.4 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 10.7 Hz), 130.0 (d, *J* = 10.7 Hz), 124.3, 121.9, 95.4 (d, *J* = 11.5 Hz), 79.5, 74.6 (d, *J* = 12.1 Hz), 74.1 (d, *J* = 93.7 Hz), 72.4 (d, *J* = 9.2 Hz), 71.4, 69.3 (d, *J* = 10.4 Hz), 56.5, 21.1 (d, *J* = 0.8 Hz), 21.0 (d, *J* = 0.8 Hz) ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.31 ppm.

IR(KBr): υ_{max} (cm^{-1}) = 3325 (w), 2918 (m), 1586 (m), 1467 (m), 1432 (m), 1122 (m), 1088 (m), 848 (m), 814 (m), 690 (s), 662 (s).
MS (70 eV, EI): *m/z* (%) = 523 (M^+, 25), 458 (60), 428 (100), 426(32).
HRMS (EI): *m/z* calcd. for: [$C_{33}H_{34}P^{56}FeNO^{32}S$] 579.1488, found: 579.1467

Preparation of ferrocenyl benzyl ethers 37a and 37b:

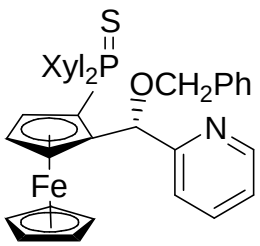
Prepared according to the typical procedure **TP4**, using KH (95 mg, 2.25 mmol, 1.50 equiv.) in THF (4 mL), ferrocenyl alcohol **35** (dr 5:5, 850 mg, 1.5 mmol) in THF (10 mL) and $PhCH_2Br$ (312 mg, 1.80 mmol, 1.20 equiv.). The reaction mixture was quenched with a saturated NH_4Cl solution (10 mL) and the aqueous layer was extracted with diethylether (4 x 20 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1) to furnish the two methyl ethers **37a** (455 mg, 0.69 mmol, 46%) and **37b** (435 mg, 0.66 mmol, 44%) yellow solids.

(R_{Fc})-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((*S*)-α-benzyloxy)pyridyl))methyl-ferrocene (37a):



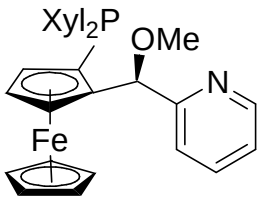
MP: 222.6-223.9 °C
$[\alpha]_D^{20}$ = −10.8 (c = 0.2, acetone).
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.68 (s, 1H), 7.67 (s, 1H), 7.58 (s, 1H), 7.41-6.66 (m, 10H), 6.63 (s, 2H), 6.47 (s, 1H), 4.31 (s, 1H), 4.18 (s, 2H), 4.05 (s, 5H), 3.89 (s, 1H), 3.75 (s, 1H), 2.28 (s, 6H), 2.09 (s, 6H), ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.3, 138.5, 137.5 (d, *J* = 13.0 Hz), 136.2, 134.6 (d, *J* = 89.2 Hz), 133.7 (d, *J* = 86.4 Hz), 132.9, 130.1 (d, *J* = 10.7 Hz), 129.9 (d, *J* = 11.6 Hz), 127.8, 127.6, 126.8, 123.2, 122.8, 78.5, 75.3 (d, *J* = 12.2 Hz), 74.8 (d, *J* = 95 Hz), 73.2, 71.4, 71.1, 69.5 (d, *J* = 11.2 Hz), 21.5, 21.4 ppm
^{31}P-NMR (81 MHz, C_6D_6): δ = +43.10 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3345 (br, w), 2917 (w), 1588 (m), 1433 (m), 1195 (m), 1051 (s), 848 (m), 690 (s), 675 (s).
MS (70 eV, EI): *m/z* (%) = 655 (M^+, 45), 590 (11), 564 (17), 485 (30), 484 (100).
HRMS (EI): *m/z* calcd. for: [$C_{39}H_{38}P^{56}FeNO^{32}S$] 655.1761, found: 655.1783

(R_{Fc})-1-Bis(3,5-dimethylphenylphosphinothioyl)-2-(((*R*)-α-benzyloxy)pyridyl))methyl-ferrocene (37b):



MP: 129.7-130.8 °C
$[\alpha]_D^{20}$ = −12.7 (c = 0.2, acetone).
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.33 (brs, 1H) 7.36 (s, 2H), 7.23-7.19 (m, 6H), 7.12 (s, 1H), 7.02 (s, 1H), 6.98 (brs, 1H), 6.76 (s, 1H), 6.67 (m, 2H), 6.46 (s, 1H), 5.16 (brs, 1H), 4.50-4.42 (m, 2H), 4.27 (s, 6H), 3.53 (s, 1H), 2.25 (s, 6H), 2.01 (s, 6H), ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 148.9, 138.6, 137.7 (d, *J* = 11.9 Hz), 137.3 (d, *J* = 12.2 Hz), 134.0 (d, *J* = 86.0 Hz), 133.3 (d, *J* = 85.1 Hz), 133.2, 132.7, 129.9 (d, *J* = 11.2 Hz), 129.6 (d, *J* = 10.7 Hz), 128.5, 128.4, 127.7, 124.5, 76.8, 74.8 (d, *J* = 12.1 Hz), 73.3 (d, *J* = 92.1 Hz), 71.7, 71.2, 69.6 (d, *J* = 12.0 Hz), 21.5 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +43.08 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3435 (b, s), 2912 (w), 1586 (m), 1433 (m), 1121 (m), 848 (m), 690 (s), 661 (s).
MS (70 eV, EI): *m/z* (%) = 655 (M^+, 15), 485 (28), 484 (100), 483 (30), 154 (14).
HRMS (EI): *m/z* calcd. for: [$C_{39}H_{38}P^{56}FeNO^{32}S$] 655.1761, found: 655.1758

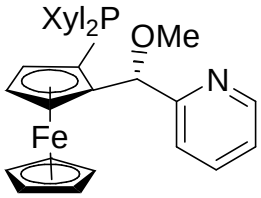
(R_{Fc})-1-Bis(3,5-dimethylphenylphosphino)-2-(((*S*)-α-methoxy)pyridyl))methylferrocene (9c):



Prepared according to **TP5** from Raney-Ni (1.1 g, 18.0 mmol; 30 equiv.) and **36a** (347 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (297 mg, 0.54 mmol, 90%).

MP: 112.3-113.2 °C
$[\alpha]_D^{20}$ = +16.2 (c = 0.2, acetone)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.55-8.47 (m, 1H) 7.42-7.31 (m, 2H), 6.83-6.66 (m, 3H), 6.25-6.20 (m, 4H), 5.45 (s, 1H), 4.25-4.18 (m, 1H), 4.13 (s, 1H), 3.80 (s, 5H), 3.35 (s, 1H), 2.85 (s, 3H), 2.31 (s, 6H), 2.28 (s, 6H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.2, 147.6, 133.5 (d, *J* = 22.1 Hz), 132.0 (d, *J* = 19.1 Hz), 131.1, 129.8, 129.0, 127.9, 127.2 (d, *J* = 9.1 Hz), 126.6, 126.2 (d, *J* = 6.7 Hz), 121.5, 120.2, 96.2 (d, *J* = 25.2 Hz), 81.3, 71.8 (d, *J* = 8.2 Hz), 71.2 (d, *J* = 9.8 Hz), 71.0, 68.5 (d, *J* = 6.7 Hz), 69.2, 68.7, 23.5, 21.7 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -20.46 ppm.
IR(neat): υ_{max} (cm^{-1}) = 2911 (w), 1658 (w), 1522 (m), 1435 (s), 1246 (m), 1080 (s), 865 (s), 724 (s), 695 (s).
MS (70 eV, EI): *m/z* (%) = 547 (M^+, 46), 482 (44), 480 (100), 260 (11).
HRMS (EI): *m/z* calcd. for: [$C_{33}H_{34}P^{56}FeNO$] 547.1727, found: 547.1711

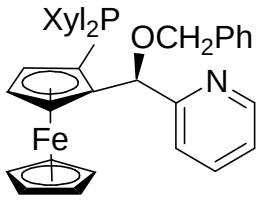
(R_{Fc})-1-Bis(3,5-dimethylphenylphosphino)-2-(((*R*)-α-methoxy)pyridyl))methylferrocene (9d):



Prepared according to **TP4** from Raney-Ni (1.1g, 18.0 mmol; 30 equiv.) and **36b** (347 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (286 mg, 0.49 mmol, 82 %).

MP: 140.2-144.0 °C
$[\alpha]_D^{20}$ = +22.1 (c = 0.2, acetone)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.11-8.07 (m, 1H) 7.75-7.72 (m, 1H), 6.91-6.80 (m, 3H), 6.77-6.72 (m, 1H), 6.21-6.19 (m, 4H), 5.40 (s, 1H), 4.85-4.80 (m, 1H), 4.43 (s, 1H), 4.05 (s, 5H), 3.65-3.59 (m, 1H), 2.91 (s, 3H), 2.32 (s, 6H), 2.26 (s, 6H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.0, 146.6, 133.5 (d, *J* = 21.0 Hz), 133.2 (d, *J* = 18.2 Hz), 132.1, 130.2, 130.0, 128.7 (d, *J* = 9.5 Hz), 127.9, 126.0 (d, *J* = 5.9 Hz), 124.2, 121.5, 121.2, 94.1 (d, *J* = 25.0 Hz), 80.2, 71.8 (d, *J* = 8.1 Hz), 71.6, 71.0 (d, *J* = 8.8 Hz), 66.7, 68.2, 67.5, 24.2, 23.2 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -20.25 ppm.
IR(neat): υ_{max} (cm^{-1}) = 2982 (w), 1754 (w), 1628 (m), 1545 (m), 1368 (m), 1022 (m), 1104 (s), 964 (s), 728 (s), 699 (s).
MS (70 eV, EI): *m/z* (%) = 547 (M^+, 28), 482 (24), 480 (100), 365 (43), 260 (18).
HRMS (EI): *m/z* calcd. for: [$C_{33}H_{34}P^{56}FeNO$] 547.1727, found: 547.1719.

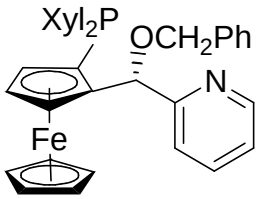
(R_{Fc})-1-Bis(3,5-dimethylphenylphosphino)-2-(((*S*)-α-benzyloxy)pyridyl))methylferrocene (10c):



Prepared according to **TP4** from Raney-Ni (1.1 g, 18.0 mmol, 30 equiv.) and **37a** (395 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (335 mg, 0.53 mmol, 89 %).

MP: 69.1-70.5 °C
$[\alpha]_D^{20}$ = +14.5 (c = 0.2, acetone)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.75-8.72 (m, 1H), 7.71-7.66 (m, 4H), 7.54-7.48 (m, 3H), 7.11-6.99 (m, 3H), 6.35-6.25 (m, 4H), 5.82-5.79 (m, 1H), 4.32-4.26 (m, 2H), 4.15 (s, 1H), 4.05-3.96 (m, 2H), 3.81 (s, 5H), 2.31 (s, 6H), 2.30 (s, 6H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.6, 141.0 (d, *J* = 10.1 Hz), 138.2, 137.8 (d, *J* = 22.1 Hz), 134.8 (d, *J* = 10.2 Hz), 132.2, 130.6 (d, *J* = 17.2 Hz), 128.4 (d, *J* = 2.1 Hz), 128.2, 127.9, 127.5, 126.9, 126.4 (d, *J* = 2.1 Hz), 126.1, 125.8, 122.7, 122.1, 96.2 (d, *J* = 25.8 Hz), 75.9 (d, *J* = 11.2 Hz), 72.8 (d, *J* = 5.4 Hz), 71.8 (d, *J* = 4.5 Hz), 71.0, 70.8, 70.2, 69.8, 23.9, 22.1 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -21.46 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3065 (br, w), 2926 (br, w), 1648 (m), 1444 (s), 1168 (s), 954 (m), 817 (m), 675 (s).
MS (70 eV, EI): *m/z* (%) = 623 (M^+, 38), 558 (25), 452 (100), 260 (35).
HRMS (EI): *m/z* calcd. for: [$C_{39}H_{38}P^{56}FeNO$] 623.2040, found: 623.2039

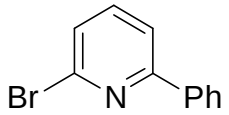
(R_{Fc})-1-Bis(3,5-dimethylphenylphosphino)-2-(((*R*)-α-benzyloxy)pyridyl))methylferrocene (10d):



Prepared according to **TP4** from Raney-Ni (1.1 g, 18.0 mmol; 30 equiv.) and **33b** (395 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (300 mg, 0.48 mmol, 80 %).

MP: 55.6-60.9 °C
$[\alpha]_D^{20}$ = +14.3 (c = 0.2, acetone)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 8.45-8.41 (m, 1H), 7.81-7.79 (m, 2H), 7.65-7.60 (m, 2H), 7.58-7.46 (m, 4H), 7.10-6.90 (m, 3H), 6.29-6.25 (m, 3H), 5.64-5.60 (m, 1H), 4.82-4.77 (m, 2H), 4.34-4.31 (m, 1H), 4.22-4.20 (m, 1H), 3.98 (s, 6H), 2.35 (s, 6H), 2.33 (s, 6H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 160.6, 145.2 (d, *J* = 11.2 Hz), 138.6 (d, *J* = 10.5 Hz), 137.9 (d, *J* = 22.0 Hz), 135.2 (d, *J* = 10.8 Hz), 132.2, 131.2 (d, *J* = 16.9 Hz), 128.4,127.8 (d, *J* = 2.3 Hz), 126.8 (d, *J* = 8.2 Hz), 126.5, 126.0, 125.1 (d, *J* = 2.4 Hz), 125.9, 124.8, 122.1, 122.0, 95.4 (d, *J* = 26.0 Hz), 76.2 (d, *J* = 13.0 Hz), 74.0, 72.7 (d, *J* = 4.4 Hz), 71.0, 70.2, 69.8, 69.0, 24.2, 22.7 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = -22.49 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3065 (w), 2925 (w), 1646 (m), 1538 (m), 1026 (s), 914 (m), 862 (m), 699 (s), 672 (m).
MS (70 eV, EI): *m/z* (%) = 623 (M^+, 65), 558 (11), 452 (100), 260 (35), 155 (32).
HRMS (EI): *m/z* calcd. for: [$C_{39}H_{38}P^{56}FeNO$] 623.2040, found: 623.2053

2-Bromo-6-phenylpyridine 39a

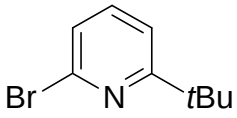


Under an argon atmosphere, a 250 mL Schlenk flask was charged with CuCN (2.35 g, 26.2 mmol, 1.05 equiv) and THF (30 mL). This suspension was treated with a solution of PhMgCl·LiCl (32 mL, 1.65 M, 52.8 mmol, 2.1 equiv) at –78 °C. After 20 minutes stirring, 2,6-dibromopyridine **38** (5.92 g, 25 mmol, 1 equiv) in THF (30 mL) was slowly added. When the addition was completed, the reaction mixture was warmed up to room temperature and stirring for 12 h. The reaction mixture was quenched with an aqueous solution of NH_3:NH_4Cl (6:4; 20 mL). Extracted the aqueous layer with Et_2O (4 x 30 mL), the combined organic layers were washed with water, brine and dried over $MgSO_4$. Purification of the crude mixture was was performed by flash chromatography (silica gel, *n*-pentan) and gave the desired product as a colourless oil (4.8 g, 20.5 mmol, 82 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (m, 2H), 7.67 (dd, *J* = 0.8 Hz, 7.7 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.49-7.38 (m, 4H) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.5, 142.1, 138.9, 137.6, 129.6, 128.8, 126.9, 126.3, 118.9 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 2850 (w), 1546 (m), 1429 (m), 1124 (m), 1051 (m), 982 (m), 781 (s).
MS (70 eV, EI) *m/z* (%) = 233 (M^+, 69), 154 (100), 127 (36).
HRMS (EI): *m/z* calcd. for [$C_{11}H_8N^{79}Br$] 232.9840, found: 232.9843.

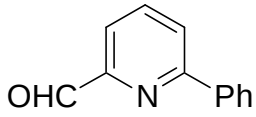
2-Bromo-6-*tert*Butylpyridine 39a



Under an argon atmosphere, a 250 mL Schlenk flask was charged with CuCN (2.35 g, 26.2 mmol, 1.05 equiv) and THF (30 mL). This suspension was treated with a solution of *t*BuMgCl·LiCl (32 mL, 1.65 M, 52.8 mmol, 2.1 equiv) at –78 °C. After 20 minutes stirring, 2,6-dibromopyridine **38** (5.92 g, 25 mmol, 1 equiv) in THF (30 mL) was slowly added. When the addition was completed, the reaction mixture was warmed up to room temperature and stirring for 12 h. The reaction mixture was quenched with an aqueous solution of NH_3:NH_4Cl (6:4; 20 mL). Extracted the aqueous layer with Et_2O (4 x 30 mL), the combined organic layers were washed with water, brine and dried over $MgSO_4$. Purification of the crude mixture was performed by flash chromatography (silica gel, *n*-pentan) and gave the desired product as a colourless oil (17.8 mmol, 3.8 g, 68 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 7.7 Hz, 1H), 7.26-7.23 (m, 2H), 1.33 (s, 9H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 171.2, 141.2, 138.4, 124.9, 117.8, 37.6, 30.0 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 2964 (s), 1580 (s), 1553 (s), 1398 (s), 1114 (s), 852 (m), 794 (s).
MS (70 eV, EI) *m/z* (%) = 213 (M^+, 23), 200 (99), 198 (100), 171 (18), 118 (14).
HRMS (EI): *m/z* calcd. for [$C_9H_{12}N^{79}Br$] 213.0153, found: 213.0142.

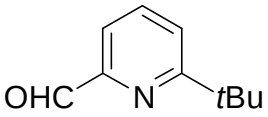
Preparation of 6-Phenyl-2-pyridylcarboxaldehyde 40a



A 100 mL Schlenk flask, under an argon atmosphere, was charged with 2-Bromo-6-phenylpyridine **39a** (4.37 g, 18.6 mmol, 1 equiv) and THF (20 mL). The *n*BuLi (12.4 mL, 1.58 M, 19.5 mmol, 1.05 equiv) was added slowly to the above solution at –78 °C. After stirring for 15 minutes, DMF (2.2 mL, 27.9 mmol, 1.5 equiv) was slowly added and the reaction mixture was stirred for 2 hours at -78 °C before warming to room temperature. The reaction mixture was quenched at room temperature with an aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O (4 x 10 mL) and the combined organic layers were washed with water, brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the crude mixture by flash chromatography (silica gel, *n*-pentan:Et_2O (10:1)), afforded the desired product as a colourless oil (15.8 mmol, 2.91 g, 85 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.17 (s, 1H), 8.09-8.06 (m, 2H), 7.97-7.88 (m, 3H), 7.54-7.43 (m, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 193.9, 157.9, 152.7, 138.1, 137.8, 129.6, 128.9, 127.0, 124.4, 119.7 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3401 (br, w), 2849 (w), 1071 (s), 1452 (m), 1027 (s), 1217 (s), 761 (s), 693 (m).
MS (70 eV, EI) *m/z* (%) = 183 (M^+, 81), 154 (100), 127 (34), 77 (16).
HRMS (EI): *m/z* calcd. for [$C_{12}H_9NO$] 183.0684, found: 183.0692.

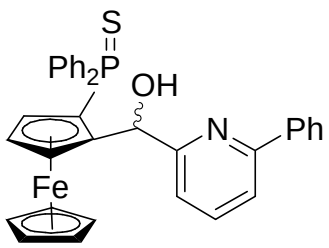
Preparation of 6-*tert*Butyl-2-pyridylcarboxaldehyde 40b



A 100 mL Schlenk flask, under an argon atmosphere, was charged with 2-Bromo-6-*tert*butylpyridine **39b** (3.3 g, 15.5 mmol, 1 equiv) and THF (20 mL). The *n*BuLi (10.3 mL, 1.58 M, 16.3 mmol, 1.05 equiv) was added slowly to the above solution at –78 °C. After stirring for 15 minutes, DMF (1.8 mL, 23.25 mmol, 1.5 equiv) was slowly added and the reaction mixture was stirred for 2 hours at -78 °C before warming to room temperature. The reaction mixture was quenched at room temperature with an aqueous solution of NH_4Cl. The aqueous layer was extracted with Et_2O (4 x 10 mL) and the combined organic layers were washed with water, brine and dried over $MgSO_4$. Evaporation of the solvent and purification of the crude mixture by flash chromatography (silica gel, *n*-pentan:Et_2O (10:1)), afforded the desired product as a colourless oil (13.2 mmol, 2.15 g, 85 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 10.07 (s, 1H), 7.77-7.76 (m, 2H), 7.57-7.44 (m, 1H), 1.40 (s, 9H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 194.5, 170.0, 151.9, 137.0, 123.4, 118.3, 37.6, 30.0 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 2961 (s), 1547 (s), 1502 (s), 1386 (s), 1114 (s), 830 (m), 760 (s).
MS (70 eV, EI) *m/z* (%) = 163 (M^+, 34), 148 (100), 118 (12), 91 (5).
HRMS (EI): *m/z* calcd. for [$C_{10}H_{13}NO$] 163.0997, found: 163.0976.

(R_{Fc})-1-Diphenylphosphinothioyl-2-[α-hydroxy(6-phenylpyridyl)]-methylferrocene 41



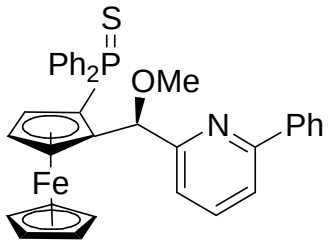
Prepared according to the typical procedure **TP3**, using ferrocenyl sulfoxide **30** (10.0 mmol, 5.40 g) in THF (10 mL), PhLi (0.20 M, 60 mM, 12.0 mmol, 1.20 equiv.) in diethylether, and 6-phenyl-2-pyridinecarboxaldehyde **40a** (2.20 g, 12.0 mmol, 1.1 equiv) as an electrophile. After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-

pentane:Et_2O 6:1) afforded the two diastereomeric alcohols **41a** and **41b** (3.79 g, 6.40 mmol, 64%) as an inseparable mixture **41** in 6:4 ratio (by ^{31}P-NMR).

^{1}H-NMR (200 MHz, C_6D_6): δ = 8.04-7.96 (m, 2H), 7.93-7.75 (m, 6H), 7.69-7.63 (m, 2H), 7.58-7.47 (m; 3H), 7.26-7.13 (m, 6H), 7.04-6.93 (m, 9H), 6.82-6.72 (m, 10H), 6.37 (d, *J* = 11.0 Hz, 1H), 5.87 (d, *J* = 10.0 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.68-4.63 (m, 1H), 4.45 (s, 5H), 4.29 (s, 5H), 3.93-3.85 (m, 2H), 3.60-3.55 (m, 2H) ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +43.6 (60 %), +42.6 (40 %) ppm.

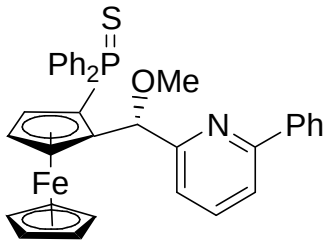
Preparation of ferrocenyl methyl ethers 42a and 42b
Prepared according to the typical procedure **TP4**, using KH (60 mg, 1.50 mmol, 1.50 equiv.) in THF (3 mL), ferrocenyl alcohol **41** (576 mg, 0.98 mmol, 1.0 equiv.) in THF (3 mL) and CH_3I (0.5 mL, 8.0 mmol, 8.0 equiv.). The reaction mixture was quenched with a saturated NH_4Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 15 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 6:1) to furnish the two methyl ethers **42a** (322 mg, 0.54 mmol, 55 %) and **42b** (198 mg, 0.33 mmol, 34 %) as yellow solids.

(R_{Fc})-1-Diphenylphosphinothioyl-2-[(*S*)-α-methoxy(6-phenylpyridyl)]-methylferrocene 42a



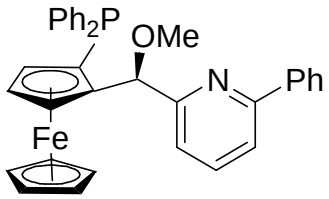
MP: 141.2-143.8 °C
$[\alpha]_D^{20}$ = -28 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.25-8.23 (m, 2H), 8.08-7.98 (m, 4H), 7.45-7.19 (m, 5H), 7.07-7.04 (m, 7H), 6.70 (s, 1H), 4.31 (s, 5H), 4.20-4.18 (m, 1H), 3.89 (dd, *J* = 2.1 Hz, 4.0 Hz, 1H), 3.76-3.74 (m, 1H), 2.99 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 161.2, 156.6, 139.5, 136.9, 136.5 (d, *J* = 88.2 Hz), 134.8 (d, *J* = 84.6 Hz), 132.8 (d, *J* = 3.4 Hz), 132.7 (d, *J* = 3.7 Hz), 130.9 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 3.8 Hz), 129.2, 129.0, 127.9, 127.2, 120.8, 118.8, 92.6 (d, *J* = 11.6 Hz), 81.0, 75.8 (d, *J* = 94.6 Hz), 75.5 (d, *J* = 12.3 Hz), 73.1 (d, *J* = 8.8 Hz), 71.6, 69.0 (d, *J* = 10.0 Hz), 56.8 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.8 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3436 (m), 2925 (s), 1630 (w), 1446 (m), 1437 (m), 1101 (m), 759 (m), 693 (m).
MS (70 eV, EI) *m/z* (%) = 599 (M^+, 100), 534 (22), 504 (100), 502 (16), 286 (16).
HRMS (EI): *m/z* calcd. for [$C_{32}H_{32}P^{56}FeO^{32}SN$] 599.1135, found: 599.1129.

(R_{Fc})-1-Diphenylphosphinothioyl-2-[(*S*)-α-methoxy(6-phenylpyridyl)]-methylferrocene 42b



MP: 100-110 °C
$[\alpha]_D^{20}$ = -31 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.40-7.98 (m, 6H), 7.45-7.20 (m, 5H), 7.13-7.09 (m, 7H), 6.72 (s, 1H), 5.32-5.30 (m, 1H), 4.50 (s, 5H), 4.25-4.20 (m, 1H), 3.81-3.79 (m, 1H), 3.20 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 162.4, 158.2, 140.5, 138.2, 137.2 (d, *J* = 87.2 Hz), 135.2 (d, *J* = 84.8 Hz), 133.2 (d, *J* = 3.8 Hz), 132.9 (d, *J* = 4.0 Hz), 132.6 (d, *J* = 3.9 Hz), 131.4 (d, *J* = 4.0 Hz), 129.2, 128.4, 121.2, 119.2, 93.0 (d, *J* = 11.8 Hz), 81.5, 76.2 (d, *J* = 95.0 Hz), 76.1 (d, *J* = 13.2 Hz), 73.7 (d, *J* = 9.0 Hz), 72.4, 69.2 (d, *J* = 10.4 Hz), 61.2 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +41.2 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3440 (m), 2900 (s), 1629 (w), 1446 (m), 1400 (m), 1100 (m), 792 (m), 698 (s).
MS (70 eV, EI) *m/z* (%) = 599 (M^+, 100), 532 (20), 504 (82), 502 (20), 286 (36).
HRMS (EI): *m/z* calcd. for [$C_{32}H_{32}P^{56}FeO^{32}SN$] 599.1135, found: 599.1130.

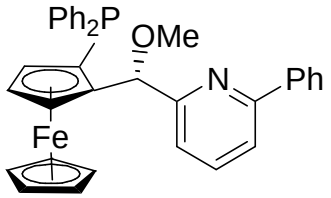
(R_{Fc})-1-diphenylphoshphino-2-[(*S*)-α-methoxy(6-phenylpyridyl)]methylferrocene 9e



Prepared according to **TP5** from Raney-Ni (1.10 g, 18.0 mmol, 30 equiv.) and **42a** (360 mg; 0.6 mmol) in MeOH (40 mL), and obtained as a yellow solid (286 mg, 0.51 mmol, 84%).

MP: 112-114 °C
$[\alpha]_D^{20}$ = -20 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.14-7.92 (m, 6H), 7.16-7.42 (m, 5H), 7.02-7.05 (m, 7H), 6.68 (s, 1H), 4.32 (s, 5H), 4.21-4.22 (m, 1H), 3.88-3.91 (m, 1H), 3.76-3.78 (m, 1H), 2.96 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 157.2, 154.2, 137.2, 135.1, 134.5 (d, *J* = 80.0 Hz), 132.8 (d, *J* = 78.2 Hz), 131.4 (d, *J* = 3.2 Hz), 130.7 (d, *J* = 2.4 Hz), 129.4 (d, *J* = 3.1 Hz), 129.2 (d, *J* = 2.2 Hz), 128.4, 128.1, 126.8, 126.7, 126.5, 118.2, 116.8, 91.2 (d, *J* = 10.4 Hz), 80.9, 74.6 (d, *J* = 88 Hz), 74.5 (d, *J* = 11.3 Hz), 72.8 (d, *J* = 8.0 Hz), 70.8, 68.5 (d, *J* = 10.8 Hz), 56.4 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3421 (m), 2924 (s), 1572 (s), 1638 (m), 1512 (m), 1108 (m), 791 (m), 698 (m).
MS (70 eV, EI) *m/z* (%) = 567 (M^+, 18), 534 (24), 504 (100), 501 (36).
HRMS (EI): *m/z* calcd. for [$C_{35}H_{30}P^{56}FeON$] 567.1414, found: 567.1428.

(R_{Fc})-1-diphenylphoshphino-2-[(*R*)-α-methoxy(6-phenylpyridyl)]methylferrocene 9f



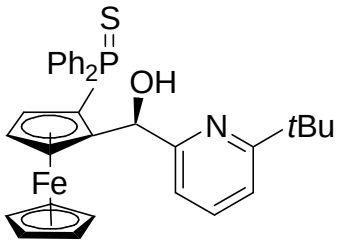
Prepared according to **TP5** from Raney-Ni (1.1 g, 18.0 mmol; 30 equiv.) and **42b** (360 mg; 0.6 mmol) in MeOH (40 mL), and obtained as a yellow solid (274 mg, 0.48 mmol, 80 %).

MP: 152-153 °C
$[\alpha]_D^{20}$ = -19 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.02-7.92 (m, 6H), 7.44-7.30 (m, 5H), 7.06-7.03 (m, 7H), 6.70 (s, 1H), 4.92 (s, 1H), 4.40 (s, 5H), 3.92-3.91 (m, 1H), 3.78-3.77 (m, 1H), 3.10 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 158.2, 156.1, 138.1, 135.4, 135.1 (d, *J* = 80.0 Hz), 132.4 (d, *J* = 81.0 Hz), 131.6 (d, *J* = 3.1 Hz), 131.1 (d, *J* = 2.8 Hz), 130.4 (d, *J* = 2.8 Hz), 130.1 (d, *J* = 2.0 Hz), 128.6, 128.4, 127.9, 127.8, 127.6, 119.4, 118.2, 92.4 (d, *J* = 10.8 Hz), 81.2, 74.9 (d, *J* = 84 Hz), 74.8 (d, *J* = 11.4 Hz), 73.2 (d, *J* = 8.2 Hz), 70.9, 68.8 (d, *J* = 11.0 Hz), 58.2 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3400 (m), 2947 (s), 1565 (s), 1600 (m), 1547 (m), 1100 (m), 790 (m), 645 (m).
MS (70 eV, EI) *m/z* (%) = 567 (M^+, 48), 534 (25), 504 (100), 501 (86).
HRMS (EI): *m/z* calcd. for [$C_{35}H_{30}P^{56}FeON$] 567.1414, found: 567.1419.

Preparation of ferrocenyl alcohols 43a and 43b

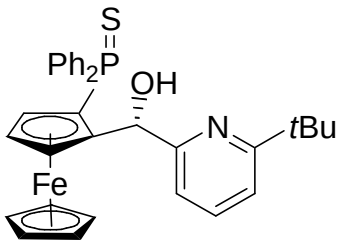
Prepared according to the typical procedure **TP3**, using ferrocenyl sulfoxide **30** (5.40 g, 10.0 mmol) in THF (10 mL), PhLi (0.20 M, 60 mL, 12.0 mmol, 1.20 equiv.) in diethylether, and 6-(*tert*-butyl)-2-pyridylcarbaldehyde **40b** (1.98 g, 12.0 mmol, 1.20 equiv) as an electrophile. After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 6:1) afforded the two diastereomeric alcohols **43a** (1.54 g; 2.70 mmol, 27%) and **43b** (2.67 g; 4.70 mmol, 47%) as yellow solids.

(R_{Fc})-1-Diphenylphosphinothioyl-2-[(*S*)-α-hydroxy(6-phenylpyridyl)]-methylferrocene 43a



MP: 111-112 °C
$[\alpha]_D^{20}$ = -68.2 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.96-7.90 (m, 2H), 7.73-7.67 (m, 2H), 7.54-7.52 (m, 1H), 7.05-6.92 (m, 7H), 6.76 (dd, *J* = 0.8 Hz, 7.8 Hz, 1H), 6.47 (d, *J* = 9.2 Hz, 1H), 5.05 (d, *J* = 8.9 Hz, 1H), 4.51-4.49 (m, 1H), 4.26 (s, 5H), 3.95-3.94 (m, 1H), 3.70-3.69 (m, 1H), 1.34 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 167.4 161.6, 136.4, 135.8 (d, *J* = 87.4 Hz), 134.2 (d, *J* = 85.8 Hz), 132.8 (d, *J* = 10.8 Hz), 132.3 (d, *J* = 10.8 Hz), 131.2 (d, *J* = 3.1 Hz), 130.9 (d, *J* = 3.1 Hz), 128.1, 127.9, 118.9, 117.2, 97.1 (d, *J* = 11.8 Hz), 75.0 (d, *J* = 12.4 Hz), 74.2 (d, *J* = 9.2 Hz), 74.1 (d, *J* = 92.7 Hz), 71.7, 71.4, 69.5 (d, *J* = 10.2 Hz), 37.4, 30.3 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +43.6 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3435 (br, s), 2956 (m), 1575 (m), 1437 (s), 1104 (s), 750.4 (s), 714 (s), 693 (s), 509 (s).
MS (70 eV, EI) *m/z* (%) = 565 (M^+, 65), 501 (31), 500 (100), 482 (97), 210 (20).
HRMS (EI): *m/z* calcd. for [$C_{32}H_{32}P^{56}FeO^{32}SN$] 565.1292, found: 565.1301.

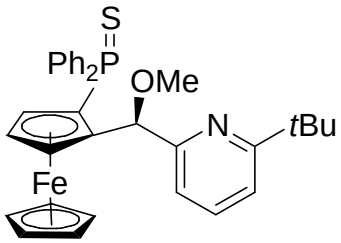
(R_{Fc})-1-diphenylphoshphinothioyl-2-[(*R*)-α-hydroxy(6-*tert*-butylpyridyl)]methyl ferrocene 43b



MP: 167-169 °C
$[\alpha]_D^{20}$ = -63.25 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.96-7.91 (m, 2H), 7.65-7.60 (m, 2H), 7.09-6.94 (m, 6H), 6.89-6.85 (m, 2H), 6.76-6.71 (m, 2H), 5.13 (d, *J* = 5.6 Hz, 1H), 4.68-4.67 (m, 1H), 4.50 (s, 5H), 3.97-3.96 (m, 1H), 3.64-3.63 (m, 1H), 1.24 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 167.5, 160.7, 136.3, 136.0 (d, *J* = 85.8 Hz), 135.2 (d, *J* = 86.0 Hz), 132.6 (d, *J* = 10.5 Hz), 132.4 (d, *J* = 10.5 Hz), 131.1 (d, *J* = 3.3 Hz), 130.8 (d, *J* = 3.0 Hz), 128.1, 127.9, 119.1, 117.2, 99.4 (d, *J* = 12.3 Hz), 74.3 (d, *J* = 11.9 Hz), 73.8 (d, *J* = 94.9 Hz), 72.1 (d, *J* = 9.5 Hz), 71.4, 69.4 (d, *J* = 10.9 Hz), 68.5, 37.3, 30.1 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.5 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3430 (br, s), 2963 (s), 1574 (s), 1436 (s), 1102 (s), 716 (s), 693 (s), 490 (s).
MS (70 eV, EI) *m/z* (%) = 565 (M^+, 72), 501 (34), 500 (99), 482 (100).
HRMS (EI): *m/z* calcd. for [$C_{32}H_{32}P^{56}FeO^{32}SN$] 565.1292, found: 565.1278.

Preparation of ferrocenyl methyl ethers 44a and 44b

(R_{Fc})-1-Diphenylphoshphinothioyl-2-[(*S*)-α-methoxy(6-*tert*-butylpyridyl]methyl ferrocene 44a

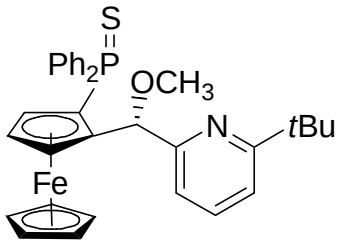


Prepared according to the typical procedure **TP4**, using KH (19 mg, 0.5 mmol, 1.5 equiv) in THF (1 mL), ferrocenyl alcohol **43a** (170 mg, 0.30 mmol, 1.0 equiv) in THF (2 mL) and CH_3I (0.1 mL, 1.6 mmol, 5.0 equiv). After quenching the reaction mixture with a saturated NH_4Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 10 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 6:1) to furnish the methyl ether **44a** (139 mg, 0.24 mmol, 80%) as a yellow solid.

MP: 196-198 °C
$[\alpha]_D^{20}$ = -49 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.07-7.97 (m, 4H), 7.38-7.36 (m, 1H), 7.23-7.19 (m, 1H), 7.06-7.04 (m, 6H), 6.99-6.97 (m, 1H), 6.52 (s, 1H), 4.35-4.33 (m, 1H), 4.32 (s, 5H), 3.95-3.94 (m, 1H), 3.77-3.75 (m, 1H), 2.92 (s, 3H), 1.43 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.7, 160.0, 136.5 (d, *J* = 88.2 Hz), 136.3, 134.9 (d, *J* = 85.0 Hz), 132.8 (d, *J* = 10.6 Hz), 132.7 (d, *J* = 10.7 Hz), 130.9 (d, *J* = 3.1 Hz), 130.6 (d, *J* = 3.1 Hz), 127.9, 127.7, 120.0, 117.9, 92.6 (d, *J* = 11.8 Hz), 81.0, 75.9 (d, *J* = 94.2 Hz), 75.5 (d, *J* = 12.4 Hz), 73.1 (d, *J* = 9.1 Hz), 71.5, 69.1 (d, *J* = 10.3 Hz), 56.5, 37.8, 30.6 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.89 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3436 (w), 2957 (m), 1575 (m), 1437 (s), 1162 (m), 1103 (s), 822 (m), 751 (m), 693 (s), 513 (m).
MS (70 eV, EI) *m/z* (%) = 580 ($[M+H]^+$, 31), 579 (M^+, 76), 564 (12), 514 (38), 485 (34), 484 (100), 482 (35).
HRMS (EI): *m/z* calcd. for [$C_{33}H_{34}P^{56}FeO^{32}SN$] 579.1448, found: 579.1440.

(R_{Fc})-1-Diphenylphoshphinothioyl-2-[(*R*)-α-methoxy(6-*tert*-butylpyridyl]methyl ferrocene 44b

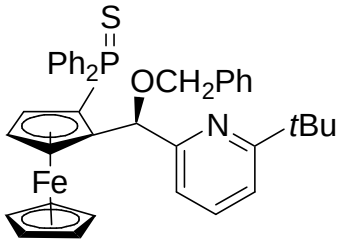
Prepared according to the typical procedure **TP4**, using KH (30 mg, 1.25 mmol, 1.5 equiv) in THF (1.5 mL), ferrocenyl alcohol **43b** (284 mg, 0.50 mmol, 1.0 equiv) in THF (2 mL) and CH_3I (0.1 mL, 1.8 mmol, 3.5 equiv). After quenching the reaction mixture with a saturated NH_4Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 15 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 6:1) to furnish the methyl ether **44b** (239 mg, 0.41 mmol, 82%) as a yellow solid.



MP: 159-161 °C
$[\alpha]_D^{20}$ = -41 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.90-7.84 (m, 2H), 7.31-7.26 (m, 2H), 7.03-6.92 (m, 4H), 6.85-6.80 (m, 1H), 6.73-6.62 (m, 4H), 6.57 (s, 1H), 5.32-5.31 (m, 1H), 4.52 (s, 5H), 4.03 (q, *J* = 2.3 Hz, 1H), 3.55 (q, *J* = 2.1 Hz, 1H), 3.27 (s, 3H), 1.33 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.5, 158.2, 135.7 (d, *J* = 86.4 Hz), 135.4, 134.8 (d, *J* = 85.7 Hz), 132.6 (d, *J* = 10.7 Hz), 132.0 (d, *J* = 10.3 Hz), 131.9 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 3.1 Hz), 127.9, 127.6, 121.3, 117.0, 95.5 (d, *J* = 11.9 Hz), 79.4, 74.3 (d, *J* = 12.2 Hz), 73.2 (d, *J* = 94.5 Hz), 72.6 (d, *J* = 9.2 Hz), 71.4, 69.3 (d, *J* = 10.4 Hz), 37.6, 30.3, 56.4 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.4 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3436 (w), 2955 (m), 1575 (m), 1434 (s), 1158 (m), 1098 (s), 748 (s), 693 (s), 519 (m).
MS (70 eV, EI) *m/z* (%) = 579 (M^+, 64), 515 (12), 514 (34), 484 (100), 482 (34).
HRMS (EI): *m/z* calcd. for [$C_{33}H_{34}P^{56}FeO^{32}SN$] 579.1448, found: 579.1432.

Preparation of ferrocenyl benzylethers 45a-b

(R_{Fc})-1-Diphenylphoshphinothioyl-2-[(*S*)-α-benzyloxy(6-*tert*-butylpyridyl]methyl ferrocene 45a



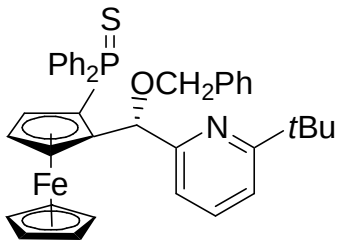
Prepared according to the typical procedure **TP4**, using KH (19 mg, 0.5 mmol, 1.5 equiv) in THF (1 mL), ferrocenyl alcohol **43a** (170 mg, 0.30 mmol, 1.0 equiv) in THF (2 mL) and $PhCH_2Br$ (260 mg, 1.6 mmol, 5.0 equiv). After quenching the reaction mixture with a saturated NH_4Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 15 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 6:1) to furnish the benzyl ether **45a** (169 mg, 0.25 mmol, 85%) as a yellow solid.

MP: 165.3-166.3 °C
$[\alpha]_D^{20}$ = −85 (c = 0.2, acetone).

^{1}H-NMR (400 MHz, C_6D_6): δ = 8.05-7.91 (m, 4H), 7.46-7.45 (m, 1H), 7.05-6.78 (m, 14H), 4.68-4.61 (m, 1H), 4.39-4.38 (m, 1H), 4.31 (s, 5H), 4.18-4.12 (m, 1H), 3.98-3.96 (m, 1H), 3.89-3.78 (m, 1H), 1.46 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.2, 157.6, 139.7, 138.9, 135.0 (d, *J* = 86.9 Hz), 134.8 (d, *J* = 86.3 Hz), 134.0, 132.0 (d, *J* = 10.8 Hz), 131.6 (d, *J* = 10.3 Hz), 130.8 (d, *J* = 10.8 Hz), 130.2 (d, *J* = 10.8 Hz), 128.0, 127.9, 127.6 (d, *J* = 12.7 Hz), 127.4 (d, *J* = 11.4 Hz), 120.9, 117.1, 94.5 (d, *J* = 11.7 Hz), 77.4, 74.0 (d, *J* = 12.1 Hz), 73.2 (d, *J* = 95.5 Hz), 72.6 (d, *J* = 9.1 Hz), 70.9, 70.4, 69.5 (d, *J* = 10.4 Hz), 37.4, 30.0 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.71 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, s), 2958 (w), 1629 (w), 1575 (m), 1479 (m), 1437 (m), 1103 (m), 1101 (s), 823 (m), 750 (m), 715 (m), 694 (m).
MS (70 eV, EI): *m/z* (%) = 655 (M^+, 19), 565 (19), 564 (47), 485 (28), 484 (100).
HRMS (EI): *m/z* calcd. for: [$C_{39}H_{38}P^{56}FeO^{32}SN$] 655.1761, found: 655.1742

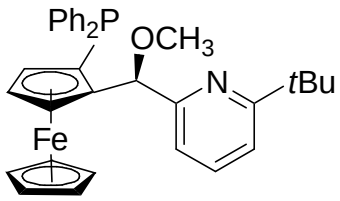
(R_{Fc})-1-Diphenylphoshphinothioyl-2-[(*R*)-α-benzyloxy(6-*tert*-butylpyridyl]methyl ferrocene 45b

Prepared according to the typical procedure **TP4**, using KH (19 mg, 0.5 mmol, 1.5 equiv) in THF (1 mL), ferrocenyl alcohol **43b** (170 mg, 0.30 mmol, 1.0 equiv) in THF (2 mL) and $PhCH_2Br$ (260 mg, 1.6 mmol, 5.0 equiv). After quenching the reaction mixture with a saturated NH_4Cl solution (5 mL) and the aqueous layer was extracted with diethylether (4 x 15 mL). After the typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 6:1) to furnish the benzyl ether **45b** (169 mg, 0.25 mmol, 85%) as a yellow solid.



MP: 181.0-181.9 °C
$[\alpha]_D^{20}$ = −80 (c = 0.2, acetone).
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.89-7.84 (m, 2H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.33-7.28 (m, 2H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.11-6.95 (m, 5H), 6.85-6.82 (m, 2H), 6.74-6.65 (m, 4H), 5.32-5.31 (m, 1H), 4.56 (d, *J* = 11.2 Hz, 1H), 4.47 (d, *J* = 11.4 Hz, 1H), 4.44 (s, 5H), 4.05-4.04 (m, 1H), 3.59-3.58 (m, 1H), 1.34 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.5, 158.5, 139.7, 139.6, 135.8 (d, *J* = 86.8 Hz), 135.4, 134.7 (d, *J* = 86.3 Hz), 132.6 (d, *J* = 10.8 Hz), 132.0 (d, *J* = 10.8 Hz), 130.9 (d, *J* = 10.8 Hz), 130.1 (d, *J* = 10.8 Hz), 128.4, 128.3, 127.8 (d, *J* = 12.3 Hz), 127.6 (d, *J* = 11.4 Hz), 121.3, 117.1, 95.5 (d, *J* = 11.5 Hz), 77.6, 74.3 (d, *J* = 12.1 Hz), 73.2 (d, *J* = 94.5 Hz), 72.6 (d, *J* = 9.1 Hz), 71.4, 70.9, 69.3 (d, *J* = 10.3 Hz), 37.6, 30.3 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = +42.31 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, s), 2956 (m), 1574 (m), 1160 (m), 1101 (s), 821 (m), 749 (s), 713 (s), 694 (s).
MS (70 eV, EI): *m/z* (%) = 655 (M^+, 10), 485 (32), 484 (100), 483 (84), 427 (11).
HRMS (EI): *m/z* calcd. for: [$C_{39}H_{38}P^{56}FeO^{32}SN$] 655.1761, found: 655.1757

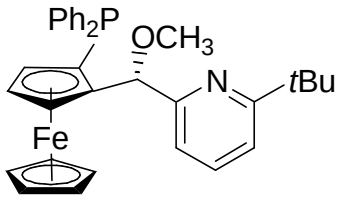
(R_{Fc})-1-Diphenylphoshphino-2-[(*S*)-α-methoxy(6-*tert*-butylpyridyl]methylferrocene 9g



Prepared according to the typical procedure **TP5**, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and **44a** (232 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (175 mg, 0.32 mmol, 80 %).

MP: 55-57 °C
$[\alpha]_D^{20}$ = +29 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.78-7.74 (m, 2H), 7.54-7.50 (m, 2H), 7.36-7.34 (m, 1H), 7.25-7.22 (m, 1H), 7.14-7.07 (m, 5H), 7.05-6.98 (m, 2H), 5.89 (d, *J* = 2.9 Hz, 1H), 4.20-4.19 (m, 1H), 4.08 (t, *J* = 2.6 Hz, 1H), 4.00 (s, 5H), 3.95-3.94 (m, 1H), 2.99 (s, 3H), 1.46 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.4, 160.4, 141.6 (d, *J* = 10.9 Hz), 139.0 (d, *J* = 9.9 Hz), 136.4, 136.0 (d, *J* = 22.1 Hz), 132.9 (d, *J* = 18.2 Hz), 129.2, 128.3, 127.9, 127.5, 119.3, 117.9, 93.9 (d, *J* = 24.8 Hz), 83.7 (d, *J* = 8.8 Hz), 72.4 (d, *J* = 4.9 Hz), 70.9 (d, *J* = 3.9 Hz), 70.3, 69.7, 69.4 (d, *J* = 59.0 Hz), 56.5, 37.7, 30.6 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3436 (m), 2955 (m), 1576 (m), 1433 (m), 1085 (m), 820 (m), 742 (m), 696 (m), 489 (m).
MS (70 eV, EI) *m/z* (%) = 548 ($[M+H]^+$, 38), 547 (M^+, 100), 532 (53), 395 (19), 347 (22), 210 (22).
HRMS (EI): *m/z* calcd. for [$C_{33}H_{34}P^{56}FeON$] 547.1727, found: 547.1719.

(R_{Fc})-1-Diphenylphoshphino-2-[(*R*)-α-methoxy(6-*tert*-butylpyridyl]methylferrocene 9h

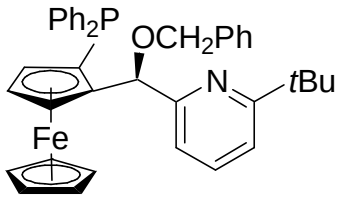


Prepared according to the typical procedure **TP5**, using Raney-Ni (1.1 g, 18.0 mmol; 30 equiv.) and **44b** (348 mg, 0.60 mmol) in MeOH (40 mL), and obtained as a yellow solid (273 mg, 0.50 mmol, 83%).

MP: 142-144 °C
$[\alpha]_D^{20}$ = +21 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.66-7.61 (m, 2H), 7.10-7.07 (m, 4H), 7.04-7.00 (m, 1H), 6.87-6.73 (m, 6H), 5.70 (d, *J* = 2.1 Hz, 1H), 4.93-4.92 (m, 1H), 4.17 (s, 5H), 4.14-4.11 (m, 1H), 3.77-3.76 (m, 1H), 3.20 (s, 3H), 1.25 (s, 9H) ppm.

^{13}C-NMR (100 MHz, C_6D_6): δ = 168.0, 160.1, 141.0 (d, *J* = 11.7 Hz), 139.1 (d, *J* = 11.2 Hz), 136.2, 135.8 (d, *J* = 22.3 Hz), 132.2 (d, *J* = 17.6 Hz), 129.1, 128.2, 127.7, 127.0, 119.2 (d, *J* = 0.8 Hz), 117.3, 97.0 (d, *J* = 24.0 Hz), 82.9 (d, *J* = 8.0 Hz), 74.8 (d, *J* = 12.0 Hz), 71.4 (d, *J* = 4.9 Hz), 70.3, 69.7, 69.4 (d, *J* = 58.4 Hz), 56.6, 37.4, 30.2 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = -20.5 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3436 (w), 2956 (m), 1574 (m), 1449 (m), 1156 (m), 1093 (s), 821 (m), 749 (m), 698 (m), 504 (m).
MS (70 eV, EI) *m/z* (%) = 548 ($[M+H]^+$, 40), 547 (M^+, 100), 532 (46), 394 (44), 332 (26), 210 (39).
HRMS (EI): *m/z* calcd. for [$C_{33}H_{34}P^{56}FeON$] 547.1727, found: 547.1737.

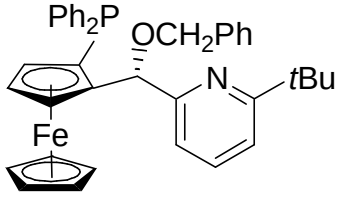
(R_{Fc})-1-Diphenylphoshphino-2-[(*S*)-α-benzyloxy(6-*tert*-butylpyridyl]methylferrocene 10e



Prepared according to the typical procedure **TP5**, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and **45a** (265 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (224 mg, 0.36 mmol, 89 %).

MP: 112.8-114.2 °C
$[\alpha]_D^{20}$ = +209 (c = 0.30, CH_2Cl_2).
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.76-7.62 (m, 2H), 7.46-7.40 (m, 3H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.12-7.11 (m, 3H), 7.01-6.97 (m, 7H), 6.82-6.80 (m, 2H), 6.20 (d, J = 3.2 Hz, 1H), 4.52-4.49 (m, 1H), 4.24-4.22 (m, 2H), 4.11 (t, *J* = 2.2 Hz, 1H), 3.99 (s, 6H), 1.48 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.4, 160.5, 141.5 (d, *J* = 10.3 Hz), 139.1 (d, *J* = 11.5 Hz), 138.7, 136.5, 136.0 (d, *J* = 22.3 Hz), 133.0 (d, J = 17.4 Hz), 129.2 (d, J = 0.8 Hz), 128.4, 128.3, 128.1 (d, J = 5.8 Hz), 128.0, 127.5, 127.1, 119.7, 118.0, 93.7 (d, *J* = 25.7 Hz), 82.1 (d, *J* = 8.9 Hz), 77.3 (d, *J* = 11.4 Hz), 72.5 (d, *J* = 5.3 Hz), 71.6, 71.2 (d, *J* = 3.8 Hz), 70.3, 70.0, 37.8, 30.6 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = -21.22 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, m), 2956 (m), 1573 (m), 1452 (m), 1434 (m), 1087 (m), 1062 (m), 820 (m), 748 (s), 696 (s).
MS (70 eV, EI): *m/z* (%) = 623 (M^+, 30), 532 (19), 518 (34), 517 (100), 439 (13), 347 (13), 332 (51).
HRMS (EI): *m/z* calcd. for: [$C_{39}H_{38}P^{56}FeON$] 623.2040, found: 623.2021

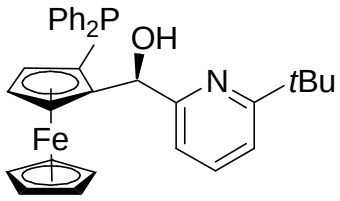
(R_{Fc})-1-Diphenylphoshphino-2-[(*R*)-α-benzyloxy(6-*tert*-butylpyridyl]methylferrocene 10f



Prepared according to the typical procedure **TP5**, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and **45b** (265 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (212 mg, 0.34 mmol, 85%).

MP: 120.5-121.7 °C
$[\alpha]_D^{20}$ = +105 (c = 0.26, CH_2Cl_2).
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.65-7.60 (m, 2H), 7.46-7.44 (m, 2H), 7.24-7.20 (m, 2H), 7.14-7.10 (m, 6H), 6.85-6.74 (m, 6H), 5.97 (d, *J* = 2.4 Hz. 1H), 4.92-4.90 (m, 1H), 4.50 (s, 2H), 4.15-4.13 (m, 1H), 4.12 (s, 5H), 3.80-3.79 (m, 1H), 1.27 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.0, 160.3, 141.5 (d, *J* = 12.0 Hz), 139.4, 139.1 (d, *J* = 11.5 Hz), 136.3, 135.8 (d, *J* = 22.1 Hz), 132.2 (d, *J* = 17.6 Hz), 129.1 (d, *J* = 0.8 Hz), 128.5, 128.2 (d, *J* = 0.8 Hz), 128.2, 127.8, 127.6, 127.0, 119.4, 117.4, 97.0 (d, *J* = 27.4 Hz), 81.0 (d, *J* = 8.4 Hz), 74.8 (d, *J* = 12.6 Hz), 71.4 (d, *J* = 4.6 Hz), 71.0, 70.4, 69.9 (d, *J* = 4.2 Hz), 69.7, 37.4, 30.2 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = -20.61 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, m), 2950 (m), 1585 (m), 1476 (m), 1434 (m), 1049 (m), 818 (m), 747 (m), 709 (m).
MS (70 eV, EI): *m/z* (%) = 623 (M^+, 96), 532 (44), 518 (38), 517 (100), 451 (41), 394 (41), 332 (84).
HRMS (EI): *m/z* calcd. for: [$C_{39}H_{38}P^{56}FeON$] 623.2040, found: 623.2040

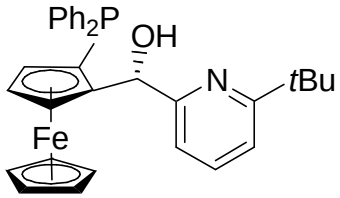
(R_{Fc})-1-Diphenylphoshphino-2-[(*S*)-α-hydroxy(6-*tert*-butylpyridyl]methylferrocene 10g



Prepared according to the typical procedure **TP5**, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and **43a** (226 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (182 mg, 0.34 mmol, 85%).

MP: 98-100 °C
$[\alpha]_D^{20}$ = -41.2 (c = 0.3, CH_2Cl_2)
^{l}H-NMR (400 MHz, C_6D_6): δ = 7.96-7.91 (m, 2H), 7.69-7.52 (m, 3H), 7.06-6.96 (m, 6H), 6.77-6.74 (m, 1H), 6.42 (s, 1H), 5.04 (s, 1H), 4.48-4.40 (m, 1H), 4.28 (s, 5H), 3.94-3.92 (m, 1H), 3.69-3.65 (m, 1H), 1.32 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 169.2, 161.2, 142.6 (d, *J* = 10.9 Hz), 140.1 (d, *J* = 11.8 Hz), 138.2, 137.1 (d, *J* = 23.1 Hz), 133.2 (d, *J* = 20 Hz), 130.1, 129.6, 128.1, 127.4, 120.1 (d, *J* = 1.1 Hz), 116.9, 96.9 (d, *J* = 25.2 Hz), 83.1 (d, *J* = 8.5 Hz), 75.2 (d, *J* = 12.2 Hz), 71.7 (d, *J* = 5.0 Hz), 70.8, 70.1, 69.6 (d, *J* = 58.2 Hz), 37.2, 30.3 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = -20.0 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3436 (br, s), 2882 (s), 1572 (s), 1409 (s), 1112 (m), 747 (m), 698 (s).
MS (70 eV, EI) *m/z* (%) = 533 (M^+, 40), 501 (28), 500 (66), 482 (100).
HRMS (EI): *m/z* calcd. for [$C_{32}H_{32}P^{56}FeON$] 533.1571, found: 533.1578.

(R_{Fc})-1-Diphenylphoshphino-2-[(*R*)-α-hydroxy(6-*tert*-butylpyridyl]methylferrocene 10h

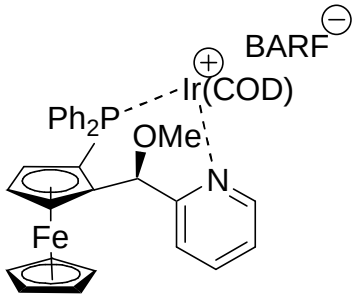


Prepared according to the typical procedure **TP5**, using Raney-Ni (720 mg, 12.0 mmol; 30 equiv.) and **43b** (226 mg, 0.40 mmol) in MeOH (30 mL), and obtained as a yellow solid (171 mg, 0.32 mmol, 80%).

MP: 101-104 °C
$[\alpha]_D^{20}$ = -49.8 (c = 0.3, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.95-7.91 (m, 2H), 7.70-7.61 (m, 2H), 7.08-7.00 (m, 6H), 6.91-6.88 (m, 2H), 6.75-6.70 (m, 2H), 5.14 (s, 1H), 4.69-4.67 (m, 1H), 4.20 (s, 5H), 3.96-3.90 (m, 1H), 3.62-3.60 (m, 1H), 1.20 (s, 9H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.8, 160.1, 141.5 (d, *J* = 12.1 Hz), 139.5 (d, *J* = 11.2 Hz), 135.9, 136.2 (d, *J* = 21.9 Hz), 132.4 (d, *J* = 18 Hz), 129.9, 128.5, 127.9, 127.2, 119.5 (d, *J* = 1.0 Hz), 116.8, 96.5 (d, *J* = 24.1 Hz), 82.5 (d, *J* = 8.0 Hz), 75.0 (d, *J* = 12.0 Hz), 71.5 (d, *J* = 4.9 Hz), 70.4, 69.5, 69.4 (d, *J* = 58.0 Hz), 37.4, 30.1 ppm.
^{31}P-NMR (81 MHz, C_6D_6): δ = -23.4 ppm.
IR (KBr): ν_{max} (cm^{-1}) = 3449 (br, s), 2990 (m), 1570 (s), 1400 (s), 1100 (s), 726 (s), 699 (s).
MS (70 eV, EI) *m/z* (%) = 533 (M^+, 30), 501 (32), 500 (48), 482 (100).
HRMS (EI): *m/z* calcd. for [$C_{32}H_{32}P^{56}FeON$] 533.1571, found: 533.1577.

5. Preparation of iridium complexes 46a-g and 47a-g

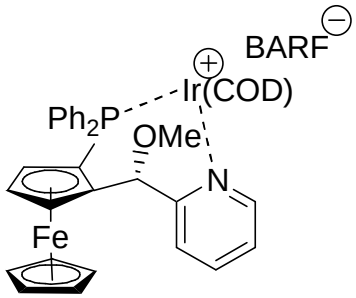
Iridium complex (46a):



Prepared according to **TP6** from P,N-ligand **9a** (246 mg, 0.50 mmol), $[Ir(cod)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) afforded the iridium complex **46a** (746 mg, 90%) as a bright orange solid.

MP: 184.3-185.4 °C
$[\alpha]_D^{20}$ = +69 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.78-8.77 (m, 1H), 8.17-8.06 (m, 2H), 7.94-7.84 (m, 3H), 7.74-7.69 (m, 7H), 7.64-7.45 (m, 7H), 7.33-7.30 (m, 3H), 6.95-6.82 (m, 3H), 4.96-4.91 (m, 1H), 4.48 (t, *J* = 2.6 Hz, 1H), 4.15-4.08 (m, 3H), 3.79-3.68 (m, 1H), 3.70 (s, 2H), 3.13 (s. 4H), 2.66-2.29 (m, 5H), 2.16-1.80 (m, 3H), 1.68-1.27 (m, 4H), ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 164.9, 161.7 (q, *J* = 53.7 Hz), 149.8, 137.1 (q, *J* = 291.2 Hz), 135.6 (d, *J* = 14.4 Hz), 134.8, 132.7 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 2.8 Hz), 129.9 (d, *J* = 58.8 Hz), 129.2 (d, *J* = 11.2 Hz), 129.1 (q, *J* = 2.7 Hz), 128.7 (q, *J* = 2.9 Hz), 128.6, 128.4 (q, *J* = 2.7 Hz), 126.2, 125.9, 123.6, 123.2, 120.5, 117.5 (q, *J* = 4.0 Hz), 94.0-93.6 (m), 81.9 (d, *J* = 1.9 Hz), 73.3 (d, *J* = 2.3 Hz), 71.5 (d, *J* = 55.4 Hz), 70.4, 70.1 (d, *J* = 6.3 Hz), 69.9 (d, *J* = 8.5 Hz), 67.4, 65.1, 58.4, 36.2 (d, *J* = 4.1 Hz), 32.9 (d, *J* = 1.9 Hz), 28.5 (d, *J* = 1.8 Hz), 26.6 (d, *J* = 2.2 Hz) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2930 (w), 1272 (w), 1354 (s), 1273 (s), 1111 (s), 1096 (s), 887 (m), 716 (m), 668 (s).
MS (FAB): 793 ($[M+H]^+$, 41), 792 (M^+, 100), 791 (63), 650 (21).
HRMS (EI): *m/z* calcd. for: [$C_{37}H_{38}PNO^{193}Ir^{56}Fe$]: 792.1660, found 792.1658

Iridium complex (47a):

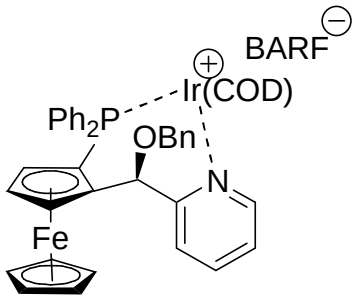


Prepared according to **TP6** from P,N-ligand **9b** (246 mg, 0.50 mmol), $[Ir(cod)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) afforded the iridium complex **47a** (736 mg, 89%) as a bright orange solid.

MP: 189.3-190.9 °C
$[\alpha]_D^{20}$ = +50 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.71-7.70 (m, 7H), 7.56-7.33 (m, 12H), 7.55-7.20 (m, 1H), 7.12-7.07 (m, 2H), 6.81 (s, 1H), 6.77-6.73 (m, 2H), 6.64-6.61 (m, 1H), 5.04-5.03 (m, 1H), 4.66-4.63 (m, 1H), 4.56-4.47 (m, 2H), 4.38 (s, 4H), 4.24-4.14 (m, 2H), 3.67-3.66 (m, 1H), 3.56 (s, 3H), 2.62-2.40 (m, 5H), 2.18-2.13 (m, 1H), 1.84-1.74 (m, 2H), 1.55 (s, 1H), , 1.26 (s, 1H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.8, 161.7 (q, *J* = 50.1 Hz), 149.2, 138.8, 134.5, 132.8 (d, *J* = 10.0 Hz), 131.9 (d, *J* = 2.6 Hz), 131.4, 131.3 (d, *J* = 11.3 Hz), 130.9, 130.7 (d, *J* = 2.4 Hz), 129.4 (d, *J* = 2.7 Hz), 129.0 (q, *J* = 2.9 Hz), 128.8 (d, *J* = 6.5 Hz), 128.7-128.0 (m), 128.6, 125.7 (d, *J* = 32.0 Hz), 125.0, 124.5, 123.2, 121.8, 120.5, 117.4, 92.8 (d, *J* = 13.3 Hz), 91.7 (d, *J* = 16.2 Hz), 88.6 (d, *J* = 11.6 Hz), 85.5 (d, *J* = 1.7 Hz), 73.2 (d, *J* = 1.9 Hz), 71.8 (d, *J* = 6.1 Hz), 71.2, 69.4 (d, *J* = 6.7 Hz), 67.4, 66.9, 60.6, 58.0, 35.1 (d, *J* = 4.0 Hz), 32.3 (d, *J* = 2.2 Hz), 31.0 (d, *J* = 2.3 Hz), 27.4 (d, *J* = 1.9 Hz) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.6 ppm

IR (neat): υ_{max} (cm^{-1}) = 2925 (w), 1609 (w), 1353 (m), 1273 (s), 1156 (s), 1122 (s), 1095 (s), 887 (m), 838 (m), 715 (m), 668 (m).
MS (ESI): 793 ($[M+H]^+$, 41), 792 (M^+, 100), 790 (65), 452 (11).
HRMS (ESI): *m/z* calcd. for: [$C_{37}H_{38}P^{56}FeNO^{193}Ir$] 792.1670, found: 792.1639

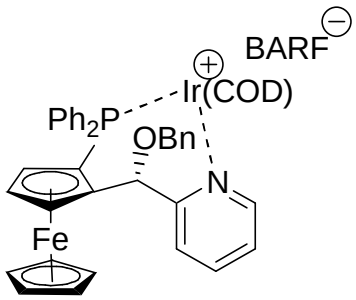
Iridium complex (46b):



Prepared according to **TP6** from P,N-ligand **10a** (284 mg, 0.50 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) provided the iridium complex **46b** (780 mg, 90%) as a bright orange solid.

MP: 178.1-180.7 °C
$[\alpha]_D^{20}$ = +54 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.77-8.75 (m, 1H), 8.13-8.09 (m, 2H), 8.03-8.02 (m, 1H), 7.96-7.92 (m, 1H), 7.78-7.72 (m, 8H), 7.61-7.60 (m, 3H), 7.52 (br, s, 3H), 7.48-7.44 (m, 1H), 7.41-7.34 (m, 8H), 6.95-6.87 (m, 3H), 5.05-5.04 (m, 1H), 4.87-4.86 (m, 2H), 4.51 (t, *J* = 2.6 Hz, 1H), 4.22-4.19 (m, 1H), 4.07 (t, *J* = 2.6 Hz, 1H), 3.98-3.97 (m, 1H), 3.65-3.64 (m, 1H), 3.13 (s, 4H), 2.52-2.48 (m, 2H), 2.35-2.29 (m, 1H), 2.09-2.00 (m, 2H), 1.79-1.75 (m, 1H), 1.57-1.52 (m, 3H), 1.23 (m, 2H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.1, 161.7 (q, *J* = 50.1 Hz), 149.7, 136.4, 135.5 (d, *J* = 14.0 Hz), 134.8-134.7 (m), 133.4 (q, *J* = 360.1 Hz), 132.7 (d, *J* = 2.2 Hz), 130.8 (d, *J* = 2.6 Hz), 130.0 (d, *J* = 58.7 Hz), 129.2 (d, *J* = 11.0 Hz), 129.1 (q, *J* = 2.9 Hz), 128.9, 128.7 (q, *J* = 2.8 Hz), 128.6, 127.2, 126.1, 125.9, 123.8, 123.2, 120.5, 117.5-117.4 (m), 94.6 (d, *J* = 14.2 Hz), 94.0 (d, *J* = 6.8 Hz), 93.9, 78.6 (d, *J* = 1.8 Hz), 73.3 (d, *J* = 2.2 Hz), 72.3, 71.7 (d, *J* = 55.0 Hz), 70.4, 70.2 (q, *J* = 8.2 Hz), 67.0, 65.5, 35.7 (d, *J* = 4.5 Hz), 32.2 (d, *J* = 1.9 Hz), 28.7 (d, *J* = 2.1 Hz), 26.9 (d, *J* = 2.3 Hz) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.6 ppm
IR (neat): υ_{max} (cm^{-1}) = 2927 (w), 1608 (w), 1353 (m), 1272 (s), 1117 (s), 1000 (w), 886 (m), 838 (m), 712 (m), 668 (m), 681 (m).
MS (ESI): 869 ($[M+H]^+$, 44), 868 (M^+, 100), 866 (49), 584 (10), 391 (5).
HRMS (ESI): *m/z* calcd. for: [$C_{43}H_{42}P^{56}FeNO^{193}Ir$] 868.1938, found: 868.1964

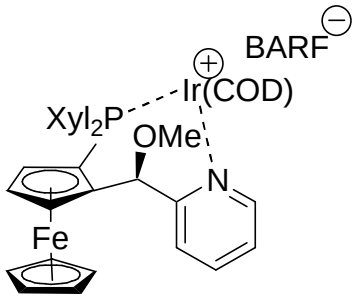
Iridium complex (47b):



Prepared according to **TP6** from P,N-ligand **10b** (284 mg, 0.5 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Flash chromatographical purification (silica gel, CH_2Cl_2) provided the iridium complex **47** (763 mg, 88%) as a bright orange solid.

MP: 71.5-75.7 °C
$[\alpha]_D^{20}$ = +27 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.72-7.70 (m, 8H), 7.57-7.40 (m, 16H), 7.24-7.20 (m, 1H), 7.12-7.08 (m, 2H), 6.96 (s, 1H), 6.78-6.73 (m, 2H), 6.64-6.60 (m, 1H), 5.18-5.17 (m, 1H), 4.80-4.77 (m, 1H), 4.66-4.57 (m, 3H), 4.53-4.48 (m, 1H), 4.34 (s, 4H), 4.29-4.23 (m, 1H), 4.20-4.15 (m, 1H), 3.71-3.69 (m, 1H), 2.54-2.13 (m, 7H), 1.92-1.77 (m, 3H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.8, 161.7 (q, *J* = 50.0 Hz), 149.3, 138.9, 136.4, 134.8 (br, s), 132.8 (d, *J* = 9.8 Hz), 131.9 (d, *J* = 2.5 Hz), 131.27 (d, *J* = 11.3 Hz), 131.26 (d, *J* = 54.0 Hz), 130.8 (d, *J* = 2.5 Hz), 129.4-129.3 (m), 129.1 (t, *J* = 3.0 Hz), 129.0, 128.9-128.7 (m), 128.5-128.4 (m), 127.5, 126.8 (q, *J* = 365.0 Hz), 125.9, 125.6, 123.2, 122.2, 117.5-117.4 (m), 93.4 (d, *J* = 13.0 Hz), 91.9 (d, *J* = 15.7 Hz), 88.7 (d, *J* = 12.1 Hz), 82.9, 73.2 (d, *J* = 1.4 Hz), 72.3, 71.7 (d, *J* = 6.3 Hz), 71.2, 69.8 (d, *J* = 7.2 Hz), 67.3, 66.7 (d, *J* = 57.0 Hz), 61.2, 34.5 (d, *J* = 3.5 Hz), 31.7 (d, *J* = 2.3 Hz), 31.6 (d, *J* = 2.3 Hz), 27.9 (d, *J* = 2.2 Hz) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +5.71 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2928 (w), 1609 (m), 1353 (m), 1273 (s), 1117 (s), 1001 (m), 839 (m), 669 (m), 682 (m).
MS (ESI): 869 ($[M+H]^+$, 44), 868 (M^+, 100), 866 (46), 584 (18).
HRMS (ESI): *m/z* calcd. for: [$C_{43}H_{42}P^{56}FeNO^{193}Ir$] 868.1938, found: 868.1948

Iridium complex (46c):

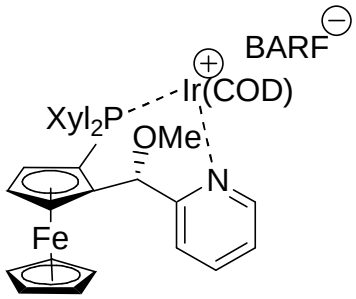


Prepared according to **TP6** from P,N-ligand **9c** (275 mg, 0.50 mmol), $[Ir(cod)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) afforded the iridium complex **46c** (787 mg, 0.46 mmol; 92%) as a bright orange solid.

MP: 189.3-191.4 °C

$[\alpha]_D^{20}$ = +60 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.75-8.72 (m, 1H), 8.15-8.10 (m, 4H), 7.79-7.68 (m, 6H), 7.54-7.42 (m, 6H), 7.00-6.75 (m, 4H), 6.45-6.40 (m, 3H), 4.80-4.75 (m, 2H), 4.22-4.18 (m, 4H), 3.80-3.65 (m, 2H), 3.75 (s, 1H), 3.18 (s, 3H), 2.65-2.25 (m, 6H), 2.45 (s, 6H), 2.38 (s, 6H), 2.20-1.80 (m, 3H), 1.67-1.25 (m, 4H), ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.9, 162.7 (q, *J* = 54.2 Hz), 150.1, 135.2 (q, *J* = 290.7 Hz), 135.0, 134.8, 132.7 (d, *J* = 3.1 Hz), 130.8 (d, *J* = 3.1 Hz), 130.2 (d, *J* = 61.2 Hz), 129.2 (d, *J* = 11.2 Hz), 129.1 (q, *J* = 3.7 Hz), 128.7-128.6 (m), 127.8 (q, *J* = 3.2 Hz), 125.2, 125.0, 123.6-121.0 (m), 116.8 (q, *J* = 3.6 Hz), 94.0-93.6 (m), 82.5 (d, *J* = 1.9 Hz), 73.5 (d, *J* = 2.3 Hz), 71.8 (d, *J* = 58.5 Hz), 70.4, 70.1 (d, *J* = 6.3 Hz), 70.0, 68.2, 66.2, 58.2, 36.5 (d, *J* = 3.8 Hz), 33.2 (d, *J* = 2.1 Hz), 28.9 (d, *J* = 2.1 Hz), 26.6 (d, *J* = 2.2 Hz), 25.4, 23.5 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2945 (w), 1445 (w), 1345 (s), 1269 (m), 1156 (s), 1009 (s), 716 (m), 668 (s).
MS (FAB): 849 ($[M+H]^+$, 22), 848 (M^+, 100), 782 (63), 620 (22).
HRMS (EI): *m/z* calcd. for: [$C_{41}H_{46}PNO^{193}Ir^{56}Fe$]: 848.2296, found 848.2305

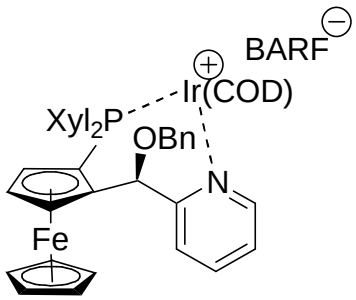
Iridium complex (47c):



Prepared according to **TP6** from P,N-ligand **9d** (275 mg, 0.50 mmol), $[Ir(cod)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) afforded the iridium complex **47c** (804 mg, 0.47 mmol; 93%) as a bright orange solid.

MP: 192.6-193.0 °C
$[\alpha]_D^{20}$ = +61.0 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05-7.97 (m, 1H), 7.77-7.65 (m, 4H), 7.58-7.40 (m, 7H), 6.90-6.65 (m, 6H), 6.58-6.32 (m, 5H), 5.11-5.01 (m, 1H), 4.48-4.01 (m, 4H), 3.80-3.68 (m, 2H), 3.22 (s, 3H), 2.66-2.26 (m, 6H), 2.45 (s, 6H), 2.38 (s, 6H), 2.18-1.81 (m, 2H), 1.67-1.18 (m, 5H), ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.0, 161.4 (q, *J* = 50.8 Hz), 152.1, 133.7 (q, *J* = 297.4 Hz), 133.0, 132.9 (d, *J* = 3.1 Hz), 132.7, 131.8 (d, *J* = 1.8 Hz), 131.0 (d, *J* = 58.5 Hz), 129.8 129.4 (q, *J* = 4.1 Hz), 128.7 (d, *J* = 11.2 Hz), 127.0 (q, *J* = 4.0 Hz), 125.2-124.8 (m), 123.0-120.8 (m), 114.2 (q, *J* = 2.7 Hz), 95.4-93.0 (m), 82.5 (d, *J* = 1.9 Hz), 75.4 (d, *J* = 2.3 Hz), 72.1 (d, *J* = 55.8 Hz), 71.0 (d, *J* = 6.3 Hz), 70.4, 70.0, 69.2, 68.5, 58.2, 36.5 (d, *J* = 3.9 Hz), 33.1 (d, *J* = 2.2 Hz), 29.2 (d, *J* = 2.9 Hz), 26.7 (d, *J* = 2.4 Hz), 25.4, 23.5 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.0 ppm
IR (neat): υ_{max} (cm^{-1}) = 3006 (w), 2825 (m), 1611 (w), 1345 (m), 1229 (s), 1198 (m), 1010 (s), 967 (m), 875 (m), 668 (m).
MS (FAB): 849 ($[M+H]^+$, 21), 848 (M^+, 100), 782 (22).
HRMS (EI): *m/z* calcd. for: [$C_{41}H_{46}PNO^{193}Ir^{56}Fe$]: 848.2296, found 848.2292

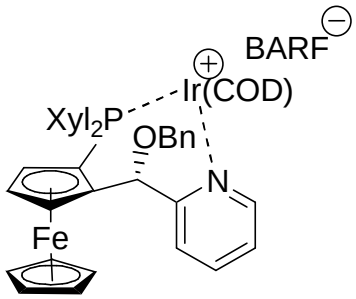
Iridium complex (46d):



Prepared according to **TP6** from P,N-ligand **10c** (312 mg, 0.50 mmol), $[Ir(cod)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) provided the iridium complex **46d** (796 mg, 0.45 mmol; 89%) as a bright orange solid.

MP: 188.2-190.1 °C
$[\alpha]_D^{20}$ = +48.9 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.68-8.64 (m, 1H), 8.44-7.99 (m, 10H), 7.95-7.82 (m, 4H), 7.80-7.70 (m, 4H), 7.60-7.32 (m, 6H), 6.95-6.87 (m, 3H), 4.90-4.88 (m, 1H), 4.87-4.86 (m, 1H), 4.78-4.55 (m, 2H), 4.22-4.19 (m, 1H), 4.00-3.95 (m, 2H), 3.13 (s, 5H), 2.50-2.48 (m, 2H), 2.39 (s, 6H), 2.37 (s, 6H), 2.30-2.00 (m, 2H), 1.75-1.44 (m, 4H), 1.23 (s, 2H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.0, 160.7 (q, *J* = 52.5 Hz), 150.1, 135.2, 135.0-134.0 (m), 133.2 (q, *J* = 287.0 Hz), 132.1 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 2.6 Hz), 130.0 (d, *J* = 60.1 Hz), 129.5, 129.2 (q, *J* = 2.9 Hz), 128.9 (d, *J* = 11.2 Hz), 128.7 (q, *J* = 2.8 Hz), 128.2, 127.9, 126.8, 126.2, 124.2, 123.7, 121.2, 119.5-116.4 (m), 94.5 (d, *J* = 13.1 Hz), 93.8 (d, *J* = 7.0 Hz), 93.5, 78.6, 73.2 (d, *J* = 2.8 Hz), 72.1, 71.0 (d, *J* = 56.3 Hz), 70.8, 70.3 (q, *J* = 8.2 Hz), 69.2, 67.5, 35.7 (d, *J* = 2.9 Hz), 32.7 (d, *J* = 1.9 Hz), 28.6 (d, *J* = 2.7 Hz), 26.9 (d, *J* = 2.1 Hz), 23.3, 22.8 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.4 ppm
IR (neat): υ_{max} (cm^{-1}) = 2918 (w), 1765 (m), 1644 (w), 1482 (m), 1399 (m), 1186 (s), 992 (w), 886 (m), 742 (s), 698 (s), 681 (s).
MS (ESI): 925 ($[M+H]^+$, 64), 924 (M^+, 100), 825 (19), 620 (10)..
HRMS (ESI): *m/z* calcd. for: [$C_{47}H_{50}P^{56}FeNO^{193}Ir$] 924.2609, found: 924.2629

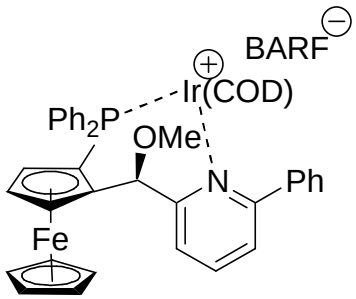
Iridium complex (47d):



Prepared according to **TP6** from P,N-ligand **10d** (312 mg, 0.50 mmol), $[Ir(cod)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) provided the iridium complex **47d** (804 mg, 0.45 mmol; 90%) as a bright orange solid.

MP: 154.2-155.7 °C
$[\alpha]_D^{20}$ = +42.8 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.08-8.01 (m, 1H), 8.44-7.90 (m, 12H), 7.88-7.66 (m, 7H), 7.55-7.48 (m, 5H), 6.95-6.85 (m, 3H), 5.11-5.08 (m, 1H), 4.89-4.85 (m, 1H), 4.64 (s, 2H), 4.38-4.15 (m, 2H), 3.83 (s, 6H), 2.55-2.50 (m, 2H), 2.35 (s, 6H), 2.32 (s, 6H), 2.30-1.58 (m, 6H), 1.28-1.20 (m, 2H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.4, 160.2 (q, *J* = 54.1 Hz), 149.2, 135.2-134.8 (m), 133.2 (q, *J* = 275.8 Hz), 132.0 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 3.8 Hz), 129.8 (d, *J* = 60.1 Hz), 129.4, 128.9 (q, *J* = 3.2 Hz), 128.9, 128.2 (q, *J* = 3.1 Hz), 127.9 (d, *J* = 12.1 Hz), 127.9-123.5 (m), 120.9-115.2 (m), 95.4 (d, *J* = 12.8 Hz), 94.2 (d, *J* = 6.8 Hz), 93.0, 78.6 (d, *J* = 2.2 Hz), 73.0, 72.1, 71.0 (d, *J* = 58.1 Hz), 70.9, 70.2 (q, *J* = 8.2 Hz), 68.7, 67.2, 36.5 (d, *J* = 2.8 Hz), 32.6 (d, *J* = 1.9 Hz), 28.6 (d, *J* = 2.2 Hz), 27.4 (d, *J* = 2.1 Hz), 24.2, 23.8 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +8.56 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3008 (w), 1609 (m), 1425 (m), 1365 (s), 1135 (s), 981 (s), 839 (m), 785 (s), 670 (m), 654 (s).
MS (ESI): 925 ($[M+H]^+$, 12), 924 (M^+, 100), 825 (22), 620 (25)..
HRMS (ESI): *m/z* calcd. for: [$C_{47}H_{50}P^{56}FeNO^{193}Ir$] 924.2609, found: 924.2608

Iridium complex (46e):

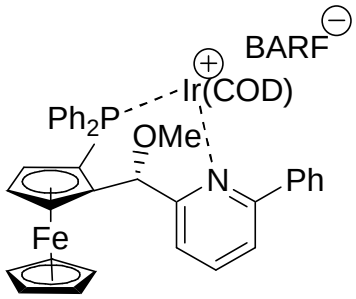


Prepared according to **TP6** from P,N-ligand **9e** (350 mg, 0.50 mmol), $[Ir(cod)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) afforded the iridium complex **46e** (764 mg, 0.41 mmol; 82%) as a bright orange solid.

MP: 221.8-223.4 °C
$[\alpha]_D^{20}$ = +28.8 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.70-8.67 (m, 1H), 8.11-7.88 (m, 8H), 7.81-7.55 (m, 10H), 7.45-7.33 (m, 11H), 6.95-6.82 (m, 1H), 4.96-4.90 (m, 1H), 4.45 (t, *J* = 2.2 Hz, 1H), 4.11-4.00 (m, 3H), 3.79-3.68 (m, 3H), 3.21 (s. 5H), 2.67-2.29 (m, 5H), 2.15-1.81 (m, 2H), 1.68-1.27 (m, 3H), ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.2, 160.9 (q, *J* = 51.2 Hz), 150.2, 135.0 (q, *J* = 278.9 Hz), 135.0, 134.8 (d, *J* = 14.2 Hz), 132.7, 130.8 (d, *J* = 2.8 Hz), 130.2 (d, *J* = 55.4 Hz), 129.2-127.8 (m), 126.2 (d, *J* = 11.4 Hz), 125.0 (d, *J* = 2.8 Hz), 123.8, 122.9, 121.2, 116.7 (q, *J* = 5.9 Hz), 94.8-93.0 (m), 81.9, 73.0 (d, *J* = 2.8 Hz), 71.2 (d, *J* = 56.2 Hz), 70.2, 70.0 (d, *J* = 5.8 Hz), 69.5 (d, *J* = 7.2 Hz), 66.8, 64.3, 56.7, 36.2 (d, *J* = 4.1 Hz), 33.8 (d, *J* = 3.1 Hz), 28.5 (d, *J* = 1.8 Hz), 26.6 (d, *J* = 2.2 Hz) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2998 (w), 1465 (m), 1542 (m), 1268 (m), 1225 (s), 1165 (s), 1028 (s), 912 (m), 878 (m), 792 (m), 765 (m).
MS (ESI): 869 ($[M+H]^+$, 2), 868 (M^+, 100), 852 (18), 782 (15), 685 (22).

HRMS (ESI): *m/z* calcd. for: [$C_{43}H_{42}PNO^{193}Ir^{56}Fe$]: 868.1938, found 868.1922

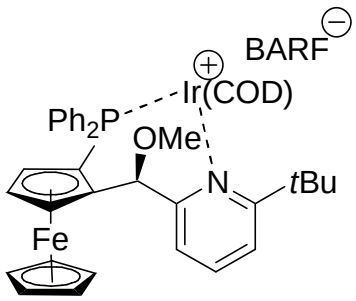
Iridium complex (47e):



Prepared according to **TP6** from P,N-ligand **9f** (350 mg, 0.50 mmol), $[Ir(cod)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol, 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) afforded the iridium complex **47e** (745 mg, 0.40 mmol; 80%) as a bright orange solid.

MP: 199.0-201.2 °C
$[\alpha]_D^{20}$ = +24.3 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.10-8.07 (m, 1H), 7.98-7.71 (m, 10H), 7.69-7.48 (m, 11H), 7.40-7.10 (m, 7H), 6.88-6.86 (m, 2H), 5.11-5.06 (m, 1H), 4.52-4.47 (m, 1H), 4.32-4.22 (m, 3H), 3.91-3.88 (m, 2H), 3.80-3.75 (m, 1H), 3.43 (s. 5H), 2.65-2.25 (m, 4H), 2.15-1.80 (m, 3H), 1.68-1.27 (m, 3H), ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.0, 160.0 (q, *J* = 52.7 Hz), 148.5, 134.3 (q, *J* = 282.1 Hz), 134.0, 134.2 (d, *J* = 14.6 Hz), 133.7 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 11.4 Hz), 132.7-130.2 (m), 130.4-126.6 (m), 125.8 (d, *J* = 2.8 Hz), 125.0 (d, *J* = 10.8 Hz), 124.2, 123.2, 121.8, 118.2 (q, *J* = 6.1 Hz), 95.2-93.1 (m), 82.5 (d, *J* = 11.8 Hz), 73.0 (d, *J* = 2.8 Hz), 71.0 (d, *J* = 55.4 Hz), 70.8, 70.0 (d, *J* = 5.8 Hz), 69.4 (d, *J* = 6.7 Hz), 67.4, 65.8, 57.2, 37.4 (d, *J* = 3.8 Hz), 32.1 (d, *J* = 3.2 Hz), 28.5 (d, *J* = 1.9 Hz), 27.2 (d, *J* = 2.5 Hz) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +9.6 ppm
IR (neat): υ_{max} (cm^{-1}) = 3002 (br, w), 2999 (w), 1676 (w), 1556 (m), 1344 (m), 1298 (s), 1199 (s), 1009 (s), 965 (s), 898 (m), 856 (m), 695 (m).
MS (ESI): 869 ($[M+H]^+$, 12), 868 (M^+, 100), 852 (11), 625 (22).
HRMS (ESI): *m/z* calcd. for: [$C_{43}H_{42}PNO^{193}Ir^{56}Fe$]: 868.1938, found 868.1935

Iridium complex (46f):

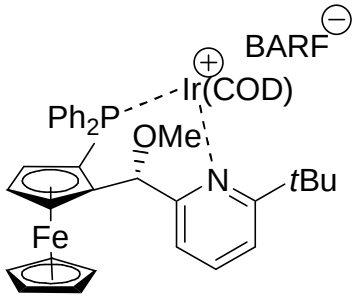


Prepared according to **TP6** from P,N-ligand **9g** (302 mg, 0.50 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash

chromatography (silica gel, CH_2Cl_2) provided the iridium complex **46f** (790 mg, 0.45 mmol; 89%) as a bright orange solid.

MP: 128.1-129.7 °C
$[\alpha]_D^{20}$ = +63.4 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.76-8.66 (m, 2H), 8.24-8.05 (m, 3H), 7.98-7.75 (m, 9H), 7.60-7.54 (m, 6H), 7.40-7.32 (m, 4H), 6.95-6.87 (m, 3H), 5.00-4.88 (m, 3H), 4.50 (t, *J* = 2.2 Hz, 1H), 4.12-4.05 (m, 2H), 3.98-3.95 (m, 1H), 3.65-3.64 (m, 2H), 3.25 (s, 3H), 2.50-2.47 (m, 2H), 2.34-2.29 (m, 1H), 2.09-2.00 (m, 1H), 1.79-1.75 (m, 1H), 1.57-1.52 (m, 3H), 1.98 (s, 9H), 1.23 (m, 2H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.2, 162.1 (q, *J* = 50.1 Hz), 151.7, 138.2, 135.5 (d, *J* = 14.0 Hz), 135.0 (q, *J* = 371.1 Hz), 134.5-133.6 (m), 132.5 (t, *J* = 2.1 Hz), 130.8 (d, *J* = 2.6 Hz), 129.8 (d, *J* = 57.6 Hz), 129.2 (d, *J* = 10.9 Hz), 129.0, 128.8 (q, *J* = 3.2 Hz), 128.7 (q, *J* = 2.8 Hz), 128.2, 127.7, 126.2, 125.9-121.0 (m), 117.5-117.0 (m), 95.6 (d, *J* = 14.0 Hz), 94.2 (d, *J* = 7.1 Hz), 93.5, 78.8 (s), 73.0 (d, *J* = 2.1 Hz), 72.8, 71.0 (d, *J* = 54.0 Hz), 70.2, 70.0 (q, *J* = 8.0 Hz), 68.2, 66.5, 34.8 (d, *J* = 5.2 Hz), 31.0 (d, *J* = 1.9 Hz), 28.7 (d, *J* = 2.1 Hz), 26.9 (d, *J* = 2.3 Hz), 14.5, 11.8 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +8.45 ppm
IR (neat): υ_{max} (cm^{-1}) = 3008 (br, w), 2998 (w), 1665 (w), 1592 (m), 1156 (m), 1222 (s), 1177 (s), 980 (m), 886 (m), 728 (m), 662 (m).
MS (ESI): 849 ($[M+H]^+$, 40), 848 (M^+, 100), 820 (15), 657 (24).
HRMS (ESI): *m/z* calcd. for: [$C_{41}H_{46}P^{56}FeNO^{193}Ir$] 848.2283, found: 848.2275

Iridium complex (47f):

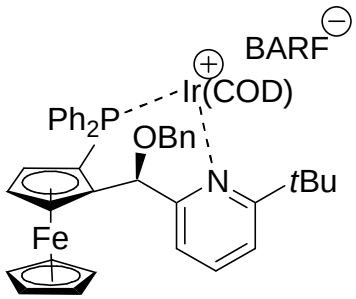


Prepared according to **TP6** from P,N-ligand **9h** (302 mg, 0.50 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) provided the iridium complex **47f** (774 mg, 0.44 mmol; 88%) as a bright orange solid.

MP: 167.5-171.2 °C
$[\alpha]_D^{20}$ = +38.0 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.65-7.68 (m, 9H), 7.57-7.50 (m, 2H), 7.24-7.22 (m, 3H), 7.20-6.99 (m, 8H), 6.96 (s, 1H), 6.75-6.70 (m, 1H), 6.64-6.60 (m, 1H), 5.19-5.16 (m, 1H), 4.75-4.77 (m, 1H), 4.64-4.55 (m, 2H), 4.54-4.47 (m, 2H), 4.30 (s, 4H), 4.29-4.23 (m, 2H), 4.22-4.20 (m, 1H), 3.71-3.69 (m, 1H), 2.54-2.13 (m, 7H), 2.01 (s, 9H), 1.92-1.77 (m, 2H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 161.8, 161.0 (q, *J* = 51.2 Hz), 148.7, 139.2-136.4 (m), 134.5, 132.7 (d, *J* = 10.2 Hz), 131.9 (d, *J* = 2.7 Hz), 131.2 (d, *J* = 52.2 Hz), 131.0 (d, *J* = 10.8 Hz), 130.8 (d, *J* = 2.5 Hz), 129.4-129.0 (m), 128.9-128.7 (m), 128.5, 128.0, 128.2, 127.5, 126.8 (q, *J* = 366.1 Hz), 126.2, 125.2, 122.8, 122.2, 120.0-118.4 (m), 93.2 (d, *J* = 12.2 Hz), 92.1 (d, *J* = 14.2 Hz), 89.2 (d, *J* = 11.7 Hz), 82.0 (d, *J* = 1.4 Hz), 73.2, 72.3, 71.7 (d, *J* = 6.8

Hz), 71.0, 69.7 (d, *J* = 7.0 Hz), 67.0, 66.7 (d, *J* = 57.0 Hz), 58.4, 32.9 (d, *J* = 3.2 Hz), 31.7 (d, *J* = 2.3 Hz), 31.2 (d, *J* = 2.3 Hz), 27.9 (d, *J* = 2.2 Hz) 16.2, 14.8 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +5.66 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3002 (br, w), 2918 (w), 1542 (m), 1655 (m), 1292 (m), 1212 (s), 1156 (s), 1045 (m), 925 (s), 839 (m), 798 (m).
MS (ESI): 849 ($[M+H]^+$, 50), 848 (M^+, 100), 817 (10), 620 (11).
HRMS (ESI): *m/z* calcd. for: [$C_{41}H_{46}P^{56}FeNO^{193}Ir$] 848.2283, found: 848.2285

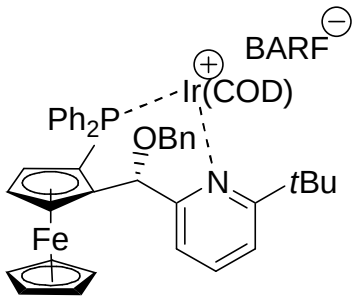
Iridium complex (46g):



Prepared according to **TP6** from P,N-ligand **10g** (340 mg, 0.50 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Purification by flash chromatography (silica gel, CH_2Cl_2) provided the iridium complex **46g** (811 mg, 0.44 mmol, 88%) as a bright orange solid.

MP: 164.2-169.5 °C
$[\alpha]_D^{20}$ = +48.4 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.88-8.82 (m, 2H), 8.15-8.00 (m, 4H), 7.95-7.82 (m, 6H), 7.75-7.60 (m, 6H), 7.42-7.22 (m, 4H), 7.12-6.90 (m, 6H), 6.75-6.62 (m, 3H), 5.11-5.06 (m, 1H), 4.88-4.80 (m, 2H), 4.50-4.48 (m, 1H), 4.22 (s, 4H), 3.98-3.97 (m, 1H), 3.65-3.64 (m, 1H), 2.52-2.40 (m, 2H), 2.32-2.29 (m, 2H), 2.09-2.00 (m, 2H), 11.79-1.75 (m, 1H), 1.64 (s, 9H), 1.57-1.50 (m, 3H), 1.22 (m, 2H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 163.2, 160.6 (q, *J* = 50.1 Hz), 149.7, 136.4, 135.5 (d, *J* = 14.0 Hz), 134.8-134.7 (m), 133.4 (q, *J* = 360.1 Hz), 132.7 (d, *J* = 2.2 Hz), 130.8 (d, *J* = 2.6 Hz), 130.0 (d, *J* = 58.7 Hz), 129.2 (d, *J* = 11.0 Hz), 129.1 (q, *J* = 2.9 Hz), 128.9, 128.7 (q, *J* = 2.8 Hz), 128.6, 127.2, 126.1, 125.9, 123.8, 123.2, 120.5, 117.5-117.4 (m), 94.6 (d, *J* = 14.2 Hz), 94.0 (d, *J* = 6.8 Hz), 93.9, 78.6 (d, *J* = 1.8 Hz), 73.3 (d, *J* = 2.2 Hz), 72.3, 71.7 (d, *J* = 55.0 Hz), 70.4, 70.2 (q, *J* = 8.2 Hz), 67.0, 65.5, 35.7 (d, *J* = 4.5 Hz), 32.2 (d, *J* = 1.9 Hz), 28.7 (d, *J* = 2.1 Hz), 26.9 (d, *J* = 2.3 Hz), 16.5, 14.2 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +8.4 ppm
IR (neat): υ_{max} (cm^{-1}) = 2914 (w), 1608 (w), 1554 (m), 1275 (s), 1192 (s), 1024 (w), 925 (m), 886 (m), 768 (m), 681 (m).
MS (ESI): 925 ($[M+H]^+$, 11), 924 (M^+, 100), 902 (12), 789 (27), 584 (10).
HRMS (ESI): *m/z* calcd. for: [$C_{47}H_{50}P^{56}FeNO^{193}Ir$] 924.2596, found: 9242595

Iridium complex (47g):

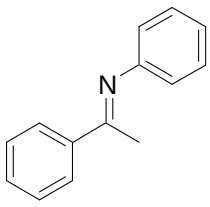


Prepared according to **TP6** from P,N-ligand **10f** (340 mg, 0.50 mmol), $[Ir(COD)Cl]_2$ (168 mg, 0.25 mmol) and NaBARF (665 mg, 0.75 mmol; 1.50 equiv.). Flash chromatographical purification (silica gel, CH_2Cl_2) provided the iridium complex **47g** (740 mg, 0.40 mmol; 80%) as a bright orange solid.

MP: 122.5-128.7 °C
$[\alpha]_D^{20}$ = +42.1 (c = 0.2, CH_2Cl_2)
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 6H), 7.55-7.45 (m, 12H), 7.22-7.20 (m, 4H), 7.10-6.99 (m, 3H), 6.78-6.70 (m, 5H), 6.64-6.60 (m, 1H), 5.20-5.15 (m, 1H), 4.80-4.78 (m, 2H), 4.66-4.57 (m, 1H), 4.53-4.48 (m, 1H), 4.34 (s, 4H), 3.72-3.69 (m, 1H), 2.54-2.10 (m, 7H), 1.92-1.75 (m, 3H), 1.68 (s, 9H), 1.22 (m, 2H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 160.5, 160.0 (q, *J* = 50.0 Hz), 149.3, 138.9, 136.4, 134.8 (br, s), 132.8 (d, *J* = 9.8 Hz), 131.9 (d, *J* = 2.5 Hz), 131.27 (d, *J* = 11.3 Hz), 131.26 (d, *J* = 54.0 Hz), 130.8 (d, *J* = 2.5 Hz), 129.4-129.3 (m), 129.1 (t, *J* = 3.0 Hz), 129.0, 128.9-128.7 (m), 128.5-128.4 (m), 127.5, 126.8 (q, *J* = 365.0 Hz), 125.9, 125.6, 123.2, 122.2, 117.5-117.4 (m), 93.4 (d, *J* = 13.0 Hz), 91.9 (d, *J* = 15.7 Hz), 88.7 (d, *J* = 12.1 Hz), 82.9, 73.2 (d, *J* = 1.4 Hz), 72.3, 71.7 (d, *J* = 6.3 Hz), 71.2, 69.8 (d, *J* = 7.2 Hz), 67.3, 66.7 (d, *J* = 57.0 Hz), 61.2, 34.5 (d, *J* = 3.5 Hz), 31.7 (d, *J* = 2.3 Hz), 31.6 (d, *J* = 2.3 Hz), 27.9 (d, *J* = 2.2 Hz) 17.2, 15.3 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +7.601 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3002 (br, w), 2999 (w), 1642 (m), 1554 (m), 1456 (m), 1275 (s), 1122 (s), 966 (m), 888 (m), 768 (m), 742 (m), 681 (m).
MS (ESI): 925 ($[M+H]^+$, 21), 924 (M^+, 100), 902 (16), 789 (30), 584 (11).
HRMS (ESI): *m/z* calcd. for: [$C_{47}H_{50}P^{56}FeNO^{193}Ir$] 924.2596, found: 924.2612

6. Synthesis of *N*-arylimines

N-phenyl-1-phenylethylideneamine (50a)[129]

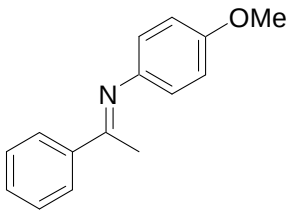


Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and aniline (12.0 mmol, 1.12 g, 1.1 mL; 1.20 equiv.). Recrystallisation from *n*-pentane, afforded the desired imine (1.42 g, 7.30 mmol, 73%) as a yellow crystalline solid.

[129] Schnider, P.; Koch, G.; Prétôt, R.; Wang, G.; Bohnen, F. M.; Krüger, C.; Pfaltz, A. *Chem. Eur. J.* **1997,** *3,* 887.

MP: 38-39 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 7.5 Hz, 2.1 Hz, 2H), 7.44-7.40 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 7.3 Hz, 2H), 2.18 (s, 3H) ppm.

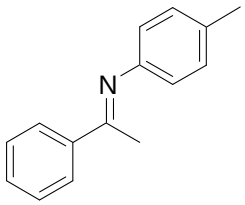
***N*-(4-methoxy)phenyl-1-phenylethylideneamine (50b)**[130]



Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 4-methoxy aniline (12.0 mmol, 1.48 g; 1.20 equiv.). Recrystallisation from *n*-pentane:EtOAc, afforded the desired imine (1.42 g, 6.29 mmol, 63%) as a yellow crystalline solid.

MP: 87.3-87.9 °C.
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98-7.95 (m, 2H) 7.45-7.43 (m, 3H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.30 (s, 3H) ppm.

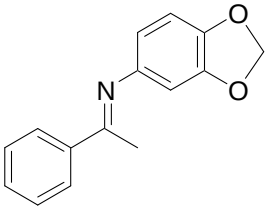
***N*-(4-methyl)phenyl-1-phenylethylideneamine (50c)[2]:**



Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 4-methyl aniline (12.0 mmol, 1.29 g; 1.20 equiv.). Recrystallisation from *n*-pentane:EtOAc, afforded the desired imine (1.57 g, 7.50 mmol, 75%) as a yellow solid.

MP: 41-42 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98-7.96 (m, 2H), 7.49-7.44 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H), 2.20 (s, 3H) ppm.

***N*-(3,4-Dioxymethylene)phenyl-1-phenylethylideneamine (50d)**

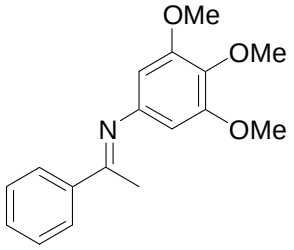


[130] Barluenga, J. ; Fernández, A. M. ; Aznar, F. ; Valdés, C. *Chem. Eur. J.* **2004,** *10*, 494.

Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,4-dioxymethylene aniline (12.0 mmol, 1.65 g; 1.20 equiv.). Recrystallisation from MeOH, afforded the desired imine (1.82 g, 7.61 mmol, 76%) as a pale brown solid.

MP: 118.3-120.0 °C.
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96-7.93 (m, 2H), 7.48-7.39 (m, 3H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.37 (d, *J* = 2.2 Hz, 1H), 6.24 (dd, *J* = 2.2 Hz, 8.1 Hz, 1H), 5.90 (s, 2H), 2.26 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.3, 150.0, 146.0, 143.7, 139.4, 130.5, 128.4, 127.1, 111.8, 108.3, 101.6, 101.0, 17.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3065 (w), 2889 (w), 1616 (m), 1481 (s), 1339 (m), 1240 (s), 1177 (s), 1031 (s), 938 (s), 848 (s).
MS (70 eV, EI): *m/z* (%) = 239 (M^+, 57), 224 (100), 225 (15), 162 (8), 121 (9).
HRMS (EI): *m/z* calcd. for: [$C_{15}H_{13}NO_2$] 239.0946, found: 239.0958.

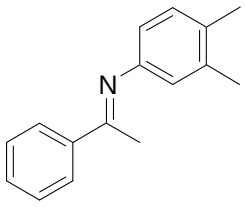
***N*-(3,4,5-Trimethoxy)phenyl-1-phenylethylideneamine (50e)**



Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,4,5-trimethoxy aniline (12.0 mmol, 2.20 g; 1.20 equiv.). Recrystallisation from *n*-pentane:EtOAc, afforded the desired imine (2.25 g, 7.89 mmol, 79%) as a yellow solid.

MP: 96.1-97.9 °C.
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.97-7.94 (m, 2H), 7.45-7.42 (m, 3H), 6.02 (s, 2H), 3.86 (s, 3H), 3.83 (s, 6H), 2.28 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.0, 153.6, 147.8, 139.2, 130.5, 128.5, 128.3, 127.1, 96.6, 61.0, 56.0, 17.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3855 (w), 3752 (w), 2951 (w), 1636 (m), 1581 (s), 1496 (s), 1411 (s), 1233 (s), 1119 (s), 1011 (s), 768 (s), 696 (s).
MS (70 eV, EI): *m/z* (%) = 285 (M^+, 66), 270 (100), 242 (3), 226 (3), 146 (3), 103 (5).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{19}NO_3$] 285.1365, found: 285.1361.

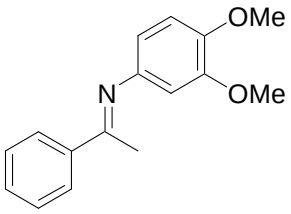
***N*-(3,4-Dimethyl)phenyl-1-phenyl ethylidene amine (50f)**



Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,4-dimethyl aniline (12.0 mmol, 1.45 g; 1.20 equiv.). Purification by vacuum distillation (160 °C, 0.1 mbar) afforded the desired imine (1.70 g, 7.58 mmol, 76%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98-7.95 (m, 2H), 7.46-7.43 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.60-6.53 (m, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.3, 149.3, 139.6, 137.1, 131.2, 130.3, 130.0, 128.3, 127.1, 120.8, 116.7, 19.9, 19.1, 17.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3866 (w), 3745 (w), 2920 (w), 1631 (s), 1602 (m), 1491 (s), 1450 (m), 1365 (m), 1241 (s), 1204 (m), 819 (m), 758 (s), 685 (s).
MS (70 eV, EI): *m/z* (%) = 223 (M^+, 72), 208 (100), 146 (4), 105 (8).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{17}N$] 223.1361, found: 223.1352.

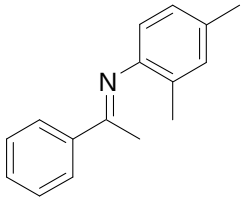
***N*-(3,4-Dimethoxy)phenyl-1-phenylethylideneamine (50g)**



Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,4-dimethoxy aniline (12.0 mmol, 1.84 g; 1.20 equiv.). Recrystallisation from *n*-pentane:EtOAc, afforded the desired imine (1.91 g, 7.50 mmol, 75%) as a yellow solid.

MP: 91.6-92.6 °C.
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98-7.93 (m, 2H), 7.48-7.41 (m, 3H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 6.32 (dd, *J* = 2.7 Hz, 8.8 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 2.27 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.0, 149.4, 145.2, 139.5, 133.0, 130.4, 128.3, 127.1, 111.7, 110.7, 104.3, 56.1, 55.8, 17.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3855 (w), 3075 (w), 2842 (w), 1700 (w), 1623 (m), 1576 (m), 1501 (s), 1228 (s), 1133 (s), 1024 (s), 856 (s), 770 (s), 704 (s).
MS (70 eV, EI): *m/z* (%) = 255 (M^+, 97), 240 (100), 196 (3), 122 (4), 103 (4).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{17}NO_2$] 255.1259, found: 255.1255.

***N*-(3,5-Dimethyl)phenyl-1-phenylethylideneamine (50h)**

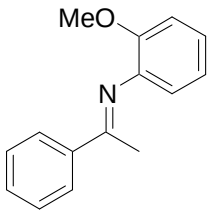


Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 2,4.dimethyl aniline (12.0 mmol, 1.45 g, 1.48 mL; 1.20 equiv.). Purification by vacuum distillation (85 °C, 0.1 mbar), afforded the desired imine (1.75 g, 7.80 mmol, 78%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.45-7.28 (m, 5H), 7.21-7.18 (m, 1H), 6.92 (s, 2H), 2.38 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.2, 150.5, 138.5, 132.1, 132.0, 130.3, 128.3, 127.1, 124.9, 117.0, 21.3, 17.4, 16.8 ppm.

IR (neat): υ_{max} (cm^{-1}) = 2924 (w), 1682 (w), 1633 (s), 1589 (s), 1450 (m), 1367 (m), 1274 (s), 1150 (m), 1029 (m), 845 (s), 763 (s), 672 (s).
MS (70 eV, EI): *m/z* (%) = 223 (M^+, 44), 207 (88), 208 (100), 105 (25), 103 (9).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{17}N$] 223.1361, found: 223.1371.

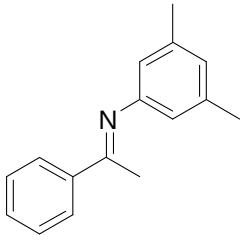
***N*-(3,5-Dimethyl)phenyl-1-phenylethylideneamine (50i)**[131]



Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 2-methoxy aniline (12.0 mmol, 1.48 g; 1.20 equiv.). Purification by vacuum distillation (140 °C, 0.1 mbar), afforded the desired imine (1.58 g, 7.00 mmol, 70%) as a yellow solid.

MP: 42.4 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.99-7.94 (m, 3H), 7.41-7.34 (m, 2H), 7.01 (dd, *J* = 2.0 Hz, 7.9 Hz, 1H), 6.93-6.85 (m, 2H), 6.77 (dd, *J* = 2.0 Hz, 7.7 Hz, 1H), 3.71 (s, 3H), 2.13 (s, 3H) ppm.

***N*-(3,5-Dimethyl)phenyl-1-phenylethylideneamine (52a)**

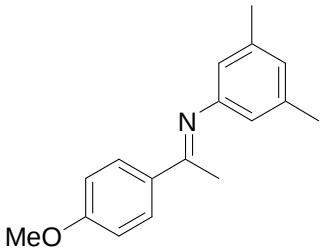


Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,5.dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar), afforded the desired imine (1.72 g, 7.79 mmol, 78%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98-7.95 (m, 2H), 7.49-7.43 (m, 3H), 6.73 (s, 1H), 6.43 (s, 2H), 2.32 (s, 6H), 2.24 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.2, 151.5, 138.5, 133.1, 130.3, 128.3, 127.1, 124.9, 117.0, 21.3, 17.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2915 (w), 1682 (w), 1633 (s), 1589 (s), 1450 (m), 1367 (m), 1274 (s), 1150 (m), 1029 (m), 845 (s), 763 (s), 672 (s).
MS (70 eV, EI): *m/z* (%) = 223 (M^+, 84), 208 (100), 105 (15), 103 (6), 77 (11).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{17}N$] 223.1361, found: 223.1364.

***N*-(3,5-Dimethyl)phenyl-1-(4-methoxylphenyl)ethylideneamine (52b)**

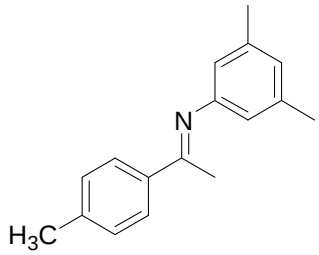
[131] Barluenga, J.; Fernandez, M. A.; Aznar, F. ; Valdes, C. *Chem. Eur. J.* **2004**, *10*, 494.



Prepared according to **TP7** from 4-methoxy acetophenone (10.0 mmol, 1.50 g) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by recrystalliation (*n*-pentane:MeOH), afforded the desired imine (1.90 g; 7.50 mmol, 75%) as a orange yellow solid.

MP: 62.3-64.6°C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.96-7.92 (m, 2H), 6.96-6.91 (m, 2H), 6.72 (s, 1H), 6.43 (s, 2H), 3.85 (s, 3H), 2.30 (s, 6H), 2.21 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.8, 161.7, 151.0, 138.9, 138.5, 129.0, 124.9, 117.4, 113.6, 55.4, 21.3, 17.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2915 (w), 1631 (s), 1592 (s), 1512 (m), 1365 (m), 1246 (s), 1171 (s), 1026 (s), 827 (s), 688 (s).
MS (70 eV, EI): *m/z* (%) = 253 (M^+, 49), 239 (13), 238 (100), 105 (5).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{19}N$] 253.1467 found: 253.1479.

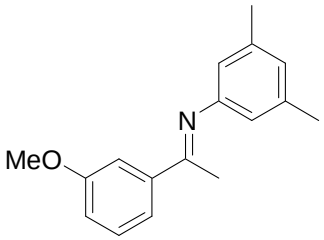
***N*-(3,5-Dimethyl)phenyl-1-(4-methylphenyl)ethylideneamine (52c)**



Prepared according to **TP7** from 4-methylacetophenone (1.34 g; 1.33 mL, 10.0 mmol,) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar), afforded the desired imine (1.71 g; 7.20 mmol, 72%) as a yellow solid.

MP: 59.1-61.7 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.91-7.87 (m, 2H), 7.29-7.27 (m, 2H), 6.75 (s, 1H), 6.50 (s, 2H), 2.43 (s, 3H), 2.33 (s, 6H), 2.25 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.2, 151.3, 140.7, 138.5, 136.6, 129.0, 127.2, 124.9, 117.2, 26.5, 21.3, 17.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3029 (w), 1635 (s), 1588 (s), 1364 (s), 1272 (s), 1149 (m), 1031 (m), 841 (s), 810 (s), 736 (m), 688 (s).
MS (70 eV, EI): *m/z* (%) = 237 (M^+, 64), 222 (100), 105 (8).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{19}N$] 237.1517 found: 237.1522.

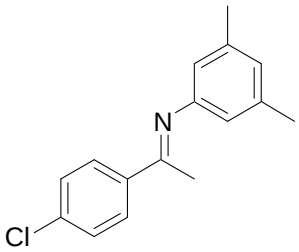
***N*-(3,5-Dimethyl)phenyl-1-(3-methoxyphenyl)ethylideneamine (52d)**



Prepared according to **TP7** from 3-methoxy acetophenone (10.0 mmol, 1.50 g, 1.38 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Recrystallisation of the crude product in methnaol, afforded the desired imine (1.87 g; 7.40 mmol, 74%) as a yellow solid.

MP: 57.7-59.0 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.59-7.57 (m, 1H), 7.51-7.48 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.01 (dddd, *J* = 7.9 Hz, 2.6 Hz, 0.9 Hz, 1H), 6.73 (s, 1H), 6.43 (s, 2H), 3.87 (s, 3H), 2.31 (s, 6H), 2.23 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.0, 159.7, 151.4, 140.9, 139.0, 138.6, 129.2, 124.9, 119.8, 117.0, 111.8, 55.4, 21.3, 17.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3008 (w), 2910 (w), 1633 (s), 1584 (s), 1447 (m), 1277 (s), 1029 (s), 848 (s), 794 (s), 672 (s).
MS (70 eV, EI): *m/z* (%) = 253 (M^+, 66), 238 (100), 146 (5), 105 (6).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{19}NO$] 253.1467, found: 253.1469.

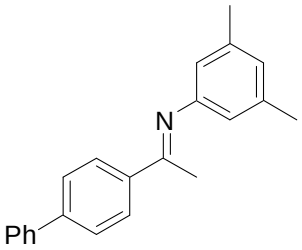
***N*-(3,5-Dimethyl)phenyl-1-(4-chlorophenyl)ethylideneamine (52e)**



Prepared according to **TP7** from 4-chloro acetophenone (10.0 mmol, 1.54 g, 1.29 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar), afforded the desired imine (2.29 g; 8.90 mmol; 89%) as a pale yellow crystalline solid.

MP: 105.3-107.4 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.91-7.88 (m, 2H), 7.42-7.38 (m, 2H), 6.73 (s, 1H), 6.40 (s, 2H), 2.31 (s, 6H), 2.21 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.8, 151.3, 138.6, 137.9, 136.5, 128.5, 125.0, 116.9, 21.3, 17.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2919 (br, w), 1635 (s), 1587 (s), 1399 (m), 1270 (m), 1152 (m), 1008 (s), 840 (s), 768 (s), 676 (s).
MS (70 eV, EI): *m/z* (%) = 259 (M^+, 22), 257 (63), 242 (100), 105 (22), 79 (10).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{16}NCl$] 257.0971, found: 257.0975.

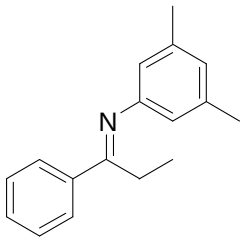
***N*-(3,5-Dimethyl)phenyl-1-(4-phenylphenyl)ethylideneamine (52f)**



Prepared according to **TP7** from 4-phenyl acetophenone (10.0 mmol, 1.96 g) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Recrystallisation of the crude product in *n*-pentane, afforded the desired imine (1.95 g; 6.50 mmol, 65%) as a pale yellow solid.

MP: 121.9-123.1 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.07-8.02 (m, 2H), 7.70-7.64 (m, 4H), 7.49-7.44 (m, 3H), 6.75 (s, 1H), 6.45 (s, 2H), 2.33 (s, 6H), 2.28 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.8, 151.4, 143.1, 140.4, 138.3, 135.8, 128.8, 127.7, 127.6, 127.1, 127.0, 124.9, 117.1, 21.3, 17.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3860 (w), 3747 (m), 3039 (br, w), 2915 (br, w), 1773 (w), 1625 (s), 1558 (s), 1540 (s), 1458 (s), 1398 (m), 1272 (m), 843 (s), 763 (s), 685 (s).
MS (70 eV, EI): *m/z* (%) = 299 (M^+, 52), 284 (100), 152 (3), 105 (7).
HRMS (EI): *m/z* calcd. for: [$C_{22}H_{21}N$] 299.1674, found: 299.1667.

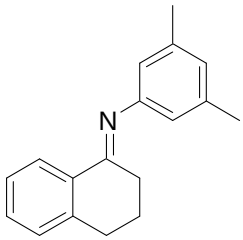
***N*-(3,5-Dimethyl)phenyl-1-phenylpropylideneamine (52h)**



Prepared according to **TP7** from propiophenone (10.0 mmol, 1.34 g, 1.34 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Purification by vacuum distillation (120 °C, 0.1 mbar), afforded the desired imine (1.66 g; 7.00 mmol, 70%) as a pale yellow oil.

^{1}H-NMR (300 MHz, C_6D_6): δ = 8.04-8.02 (m, 2H), 7.26-7.19 (m, 3H), 6.75 (s, 1H), 6.45 (s, 2H), 2.50 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 6H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 165.1, 151.0, 138.2, 133.2, 130.4, 128.2, 127.6, 126.5, 117.4, 21.0, 17.2, 13.0 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2920 (w), 1705 (m), 1600 (s), 1290 (s), 1029 (m), 848 (m), 795 (m), 699 (m).
MS (70 eV, EI): *m/z* (%) = 237 (M^+, 25), 223 (100), 209 (90), 121 (70), 91 (19).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{19}N$] 237.3395, found: 237.3404.

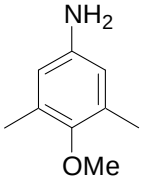
***N*-(3,5-Dimethyl)phenyl-1-(1,2,3,4-tertahydro)naphthyliedeneamine (52h)**



Prepared according to **TP7** from α-tetralone (10.0 mmol, 1.46 g, 1.33 mL) and 3,5-dimethyl aniline (12.0 mmol, 1.45 g, 1.49 mL; 1.20 equiv.). Recrystallisation of the crude product (*n*-pentane:ethylacetate (10:1)), afforded the desired imine (1.79 g; 7.20 mmol, 72%) as a brown solid.

MP: 83.5-84.6 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.33-8.30 (m, 1H), 7.36 (ddd, *J* = 7.5 Hz, 1.6 Hz, 1H), 7.31-7.26 (m, 1H), 7.20-7.18 (m, 1H), 6.70 (s, 1H), 6.40 (s, 2H), 2.90 (t, *J* = 6.2 Hz, 2H), 2.54 (dd, *J* = 7.2 Hz, 6.2 Hz, 2H), 2.30 (s, 6H), 1.96-1.87 (m, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.4, 151.4, 141.3, 138.5, 133.8, 133.3, 130.6, 128.6, 126.4, 124.7, 117.1, 30.0, 29.9, 22.9, 21.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2921 (w), 1631 (s), 1588 (s), 1454 (m), 1290 (s), 1035 (m), 840 (s), 765 (s), 662 (s).
MS (70 eV, EI): *m/z* (%) = 249 (M^+, 100), 221 (61), 121 (7), 105 (8), 77 (13).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{19}N$] 249.1517 found: 249.1513.

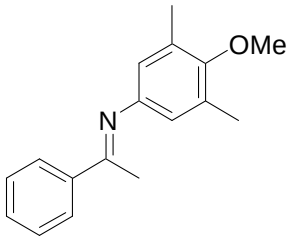
Preparation of 2,6-Dimethyl-4-amino anisole (55)



A 1.0 L flask was charged with 2,6-dimethyl-4-nitro anisole (180 mmol, 32.6 g), active charcoal (20%, 36.0 mmol, 434 mg), $FeCl_3.6H_2O$ (10%, 18.0 mmol, 4.90 g), MeOH (500 mL) and refluxed. While the reaction mixture was refluxing, $NH_2NH_2 \cdot H_2O$ (1.8 mol, 57.5 g, 55.8 mL) was added slowly and continued stirring for overnight. Reaction mixture was cooled to room temperature, filtered and washed with MeOH (3 × 100 mL). Evaporated the filtrate under reduced pressure, filtered the residue through a short pad of silica gel and washed with ether to afford the amine in 96 % yield as a pale yellow crystalline solid.

MP: 62-64 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.45-6.45 (m, 2H), 4.02 (br, 2H, NH), 3.68 (s, 3H), 2.25-2.21 (m, 6H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 150.5, 140.9, 131.8, 116.1, 60.2, 16.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3400 (s), 2955 (m), 1623 (w), 1472 (m), 1212 (m), 1013 (s), 796 (m).
MS (70 eV, EI): *m/z* (%) = 151 (M^+, 88), 137 (26), 136 (100), 108 (47), 93 (28).
HRMS (EI): *m/z* calcd. for: [$C_9H_{13}NO$] 151.0997, found 151.0999.

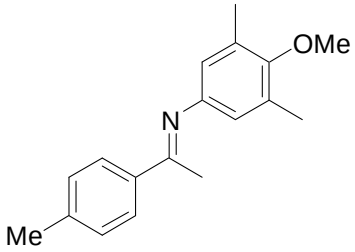
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenylethylideneamine (56a)**



Prepared according to **TP7** from acetophenone (10.0 mmol, 1.20 g, 1.16 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by vacuum distillation (140 °C, 0.1 mbar), afforded the desired imine (1.90 g, 7.50 mmol, 75%) as a yellow solid.

MP: 65.5-66.7 °C.
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98-7.95 (m, 2H) 7.46-7.43 (m, 3H), 6.48 (s, 2H), 3.70 (s, 3H), 2.28 (s, 6H), 2.27 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.6, 150.2, 140.4, 133.1, 130.6, 128.5, 128.4, 127.3, 119.8, 59.9, 17.5, 16.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2945 (m), 2822 (w), 1686 (w), 1629 (s), 1471 (m), 1448 (s), 1278 (s), 1213 (s), 1007 (s), 874 (m), 766 (s), 692 (s).
MS (70 eV, EI): *m/z* (%) = 253 (M^+, 32), 238 (100), 223 (2), 194 (2), 91 (10).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{19}NO$] 253.1467, found: 253.1462.

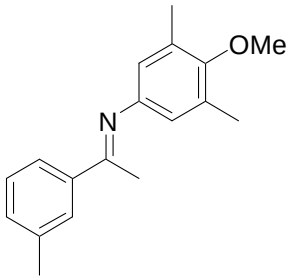
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-methyl)phenylethylideneamine (56b)**



Prepared according to **TP7** from 4-methyl acetophenone (1.34 g; 1.33 mL, 10.0 mmol,) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 20:1 (2% Et_3N)), furnished the desired imine (1.85 g, 6.9 mmol, 69 %) as a yellow oil.

^{1}H-NMR (300 MHz, C_6D_6): δ = 8.02-7.99 (m, 2H), 7.07-7.04 (m, 2H), 6.51 (s, 2H), 3.44 (s, 3H), 2.23 (s, 3H), 2.12 (s, 6H), 1.97 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 164.0, 153.4, 148.4, 140.3, 137.6, 131.3, 129.1, 127.6, 119.9, 59.4, 21.2, 16.8, 16.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2921 (br, w), 1631 (m), 1594 (m), 1477 (m), 1364 (m), 1275 (m), 1216 (s), 1182 (m), 1010 (s), 872 (m), 816 (s).
MS (70 eV, EI): *m/z* (%) = 267 (M^+, 42), 253 (15), 252 (100), 119 (2), 117 (2).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO$] 267.1623, found: 267.1631.

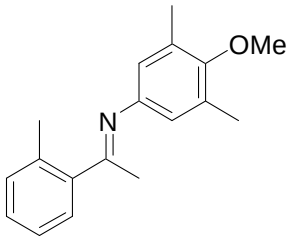
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methyl)phenylethylideneamine (56c)**



Prepared according to **TP7** from 3-methyl acetophenone (10.0 mmol, 1.34 g, 1.33 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)) afforded the desired imine (1.95 g, 7.29 mmol, 73%) as a yellow oil.

^{1}H-NMR (300 MHz, C_6D_6): δ = 7.99 (s, 1H) 7.84-7.81 (m, 1H), 7.18-7.16 (m, 1H), 7.07-7.04 (m, 1H), 6.52 (s, 2H), 3.43 (s, 3H), 2.24 (s, 6H), 2.17 (s, 3H), 1.97 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 164.3, 153.5, 148.3, 140.2, 137.8, 131.3, 131.2, 128.3, 128.2, 124.9, 119.9, 59.4, 21.4, 16.9, 16.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2922 (w), 1631 (m), 1477 (m), 1282 (m), 1217 (s), 1010 (m), 875 (m), 694 (s).
MS (70 eV, EI): *m/z* (%) = 267 (M^+, 42), 252 (100), 133 (2), 118 (4).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO$] 267.1623, found: 267.1628.

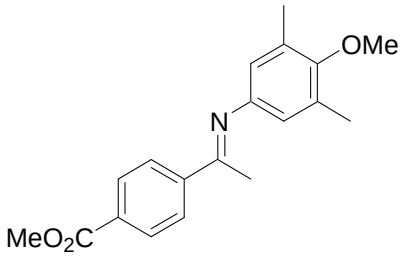
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-methylphenyl) ethylidene amine (56d):**



Prepared according to **TP7** from 2-methyl acetophenone (10.0 mmol, 1.34 g, 1.30 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)), afforded the desired imine (1.98 g, 7.40 mmol, 74%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.33-7.30 (m, 1H), 7.12-7.10 (m, 2H), 6.87-6.86 (m, 1H), 6.55 (s, 2H), 3.44 (s, 3H), 2.24 (s, 6H), 2.06 (s, 3H), 1.92 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.1, 153.7, 148.0, 140.1, 135.9, 131.5, 129.6, 128.6, 127.8, 125.8, 119.5, 59.4, 29.2, 20.5, 16.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2925 (w), 1641 (m), 1479 (s), 1217 (s), 1009 (s), 871 (m), 744 (s).
MS (70 eV, EI): *m/z* (%) = 268 ($[M+H]^+$, 12), 267 (M^+, 88), 252 (100), 135 (15), 130 (31), 91 (56).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO$] 267.1623, found: 267.1614.

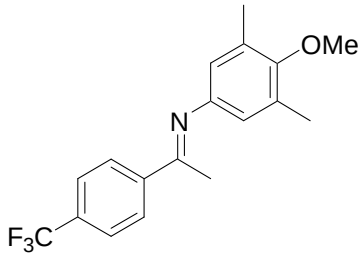
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-carbomethoxy)phenylethylideneamine (56e)**



Prepared according to **TP7** from methyl 4-acetyl-benzoate (10.0 mmol, 1.78 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)), provided the desired imine (2.33 g, 7.50 mmol, 75%) as a bright yellow solid.

MP: 90.0-92.4 °C.
^{1}H-NMR (300 MHz, C_6D_6): δ = 8.21-8.19 (m, 2H), 7.97-7.95 (m, 2H), 6.46 (s, 2H), 3.52 (s, 3H), 3.43 (s, 3H), 2.20 (s, 6H), 1.84 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 166.4, 163.6, 153.8, 147.7, 143.8, 132.1, 131.4, 129.8, 127.5, 119.8, 59.4, 51.7, 16.8, 16.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2955 (w), 1718 (s), 1627 (m), 1437 (m), 1272 (s), 1112 (s), 1007 (s), 768 (s), 696 (s) ppm.
MS (70 eV, EI): *m/z* (%) = 311 (M^+, 56), 296 (100), 132 (11).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{21}NO_3$] 311.1521, found: 311.1515.

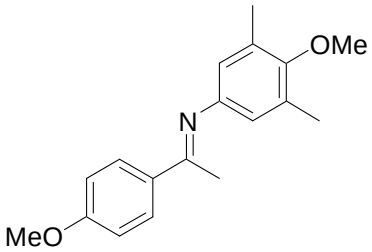
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-trifluoromethyl)phenylethylideneamine (56f)**



Prepared according to **TP7** from 4-trifluoromethyl acetophenone (10.0 mmol, 1.88 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by vacuum distillation (160 °C, 0.1 mbar), afforded the desired imine (2.70 g, 8.40 mmol, 84%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.98-7.95 (m, 2H), 7.46-7.43 (m, 2H), 6.48 (s, 2H), 3.70 (s, 3H), 2.28 (s, 6H), 2.27 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.0, 152.3, 146.7, 132.0 (q, *J* = 16.8 Hz), 131.3, 128.6, 127.5 (q, *J* = 283.3 Hz), 127.4, 125.2 (q, *J* = 3.6 Hz), 119.3, 59.9, 17.4, 16.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2935 (br, w), 1633.2 (m), 1478 (m), 1326 (s), 1220 (s), 1124 (s), 1111 (s), 1011 (s), 843 (s), 605 (m).
MS (70 eV, EI): *m/z* (%) = 321 (M^+, 48), 306 (100), 302 (2), 171 (2), 91 (5).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{18}NF_3O$] 321.1340, found: 321.1329.

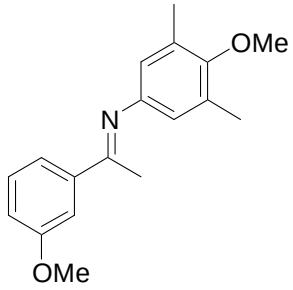
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-methoxy)phenylethylideneamine (56g)**



Prepared according to **TP3** from 4-methoxy acetophenone (10.0 mmol, 1.50 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Recrystallisation from MeOH, afforded the desired imine (1.98 g, 6.99 mmol, 70%) as a yellow solid.

MP: 62.3-64.6 °C.
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.96-7.92 (m, 2H), 6.96-6.91 (m, 2H), 6.40 (s, 2H), 3.85 (s, 3H), 3.45 (s, 3H), 2.24 (s, 6H), 2.00 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 165.9, 160.8, 151.4, 145.6, 133.4, 129.4, 127.8, 120.6, 114.6, 55.9, 55.6, 16.6, 16.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2915 (w), 1631 (s), 1592 (s), 1512 (m), 1365 (m), 1246 (s), 1171 (s), 1026 (s), 827 (s), 688 (s).
MS (70 eV, EI): *m/z* (%) = 283 (M^+, 49), 268 (100), 105 (10).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO_2$] 283.1572, found: 283.1571.

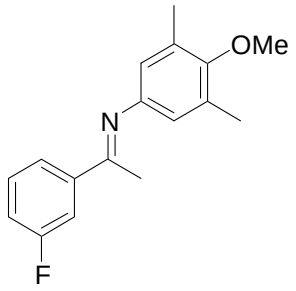
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methoxy)phenylethylideneamine (56h)**



Prepared according to **TP7** from 3-methoxy acetophenone (10.0 mmol, 1.50 g, 1.38 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 20:1 (2% Et_3N)), furnished the desired imine (1.98 g, 7.0 mmol, 70%) as a yellow oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.59-7.57 (m, 1H), 7.51-7.48 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.01 (dddd, *J* = 0.9 Hz, 2.6 Hz, 7.9 Hz, 1H), 6.60 (s, 2H), 3.80 (s, 3H), 3.65 (s, 3H), 2.41 (s, 6H), 2.20 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 164.3, 153.5, 148.3, 140.2, 137.8, 131.3, 131.2, 128.3, 128.2, 124.9, 119.9, 60.1, 55.4, 17.2, 16.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3001 (w), 2910 (w), 1633 (s), 1584 (s), 1447 (m), 1277 (s), 1029 (s), 848 (s), 794 (s), 672 (s).
MS (70 eV, EI): *m/z* (%) = 283 (M^+, 59), 268 (100), 105 (11).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO_2$] 283.1572, found: 283.1584.

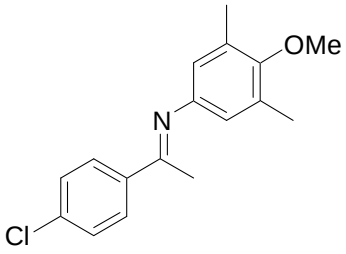
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propylidene amine (56i)**



Prepared according to **TP7** from 3-fluoro acetophenone (10.0 mmol, 1.38 g, 1.23 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)), provided the desired imine (2.06 g, 7.59 mmol, 76%) as a yellow oil.

^{1}H-NMR (300 MHz, C_6D_6): δ = 7.84-7.79 (m, 1H), 7.65-7.62 (m, 1H), 7.00-6.84 (m, 2H), 6.44 (s, 2H), 3.43 (s, 3H), 2.22 (s, 6H), 1.81 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 163.4 (d, *J* = 245.0 Hz), 163.0 (d, *J* = 3.0 Hz), 153.7, 147.6, 142.5 (d, *J* = 7.5 Hz), 131.4, 129.9 (d, *J* = 7.7 Hz), 123.1 (d, *J* = 2.8 Hz), 119.8, 117.1 (d, *J* = 22.0 Hz), 114.4 (d, *J* = 23.0 Hz), 59.4, 16.7, 16.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2937 (br, w), 1691 (w), 1633 (m), 1585 (m), 1481 (m), 1440 (s), 1266 (s), 1217 (s), 1010 (m), 867 (s), 784 (s), 686 (s).
MS (70 eV, EI): *m/z* (%) = 271 (M^+, 44), 256 (100), 120 (5).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{18}NFO$] 271.1372, found:271.1363.

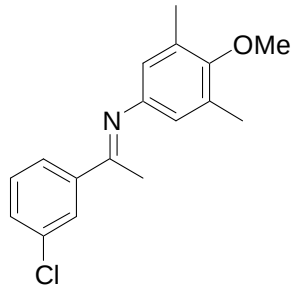
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-chloro)phenylethylideneamine (56j)**



Prepared according to **TP7** from 4-chloro acetophenone (10.0 mmol, 1.54 g, 1.29 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)), afforded the desired imine (2.16 g, 7.51 mmol, 75%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.90-7.87 (m, 2H), 7.44-7.37 (m, 2H), 6.40 (s, 2H), 3.70 (s, 3H), 2.27 (s, 6H), 2.20 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.0, 153.1, 146.9, 138.0, 136.4, 131.2, 128.4, 119.4, 59.8, 17.2, 16.1 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2936 (br, w), 1631 (m), 1589 (m), 1477 (m), 1398 (w), 1272 (w), 1219 (s), 1091 (s), 1011 (s), 830 (s), 756 (m).
MS (70 eV, EI): *m/z* (%) = 287 (M^+, 38), 274 (30), 272 (100), 91 (5).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{18}N^{35}ClO$] 287.1077, found: 287.1078.

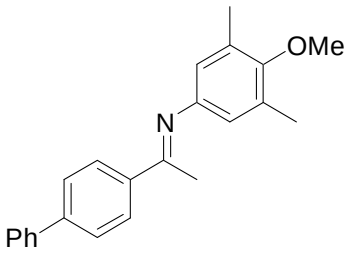
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-chloro)phenylethylideneamine (56k)**



Prepared according to **TP7** from 3-chloro acetophenone (10.0 mmol, 1.54 g, 1.29 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 40:1 (2% Et_3N)), afforded the desired imine (2.16 g, 7.51 mmol, 75%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.90-7.84 (m, 2H), 7.65-7.60 (m, 1H), 7.00-6.88 (m, 1H), 6.40 (s, 2H), 3.48 (s, 3H), 2.22 (s, 6H), 1.80 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.0, 152.8, 146.2, 138.1, 136.0, 130.4, 129.4, 129.0, 128.6, 126.2, 119.4, 59.6, 17.0, 16.1 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2912 (br, w), 1615 (m), 1509 (s), 1382 (m), 1272 (m), 1206 (m), 1091 (m), 868 (s), 790 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 287 (M^+, 30), 274 (55), 272 (100), 91 (15).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{18}N^{35}ClO$] 287.1077, found: 287.1066.

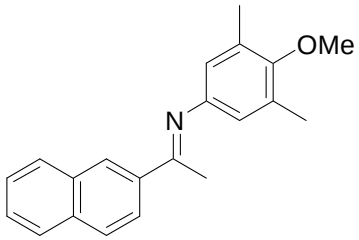
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-phenyl)phenylethylideneamine (56l)**



Prepared according to **TP7** from 4-phenyl acetophenone (10.0 mmol, 1.96 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Recrystallisation from *n*-pentane, afforded the desired imine (2.47 g, 7.50 mmol, 75%) as a yellow solid.

MP: 96.3-97.3 °C
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.12-8.09 (m, 2H), 7.55-7.53 (m, 2H), 7.51-7.48 (m, 2H), 7.25-7.18 (m, 3H), 6.55 (s, 2H), 3.45 (s, 3H), 2.26 (s, 6H), 2.00 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 163.9, 153.6, 148.2, 143.3, 140.9, 139.0, 131.4, 129.1, 128.1, 127.8, 127.5, 127.2, 120.0, 59.4, 16.8, 16.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2929 (w), 1623 (m), 1595 (m), 1214 (s), 1066 (s), 870 (s), 765 (s), 693 (s).
MS (70 eV, EI): *m/z* (%) = 329 (M^+, 52), 314 (100), 207 (6), 157 (5).
HRMS (EI): *m/z* calcd. for: [$C_{23}H_{23}NO$] 329.1780, found: 329.1765.

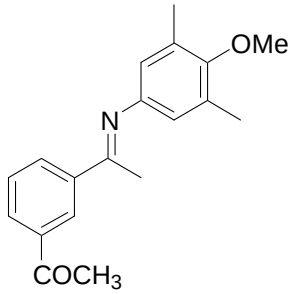
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-naphthyl) ethylidene amine (56m)**



Prepared according to **TP7** from 2-acetyl naphthalene (10.0 mmol, 1.70 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 80:1 (2% Et_3N)), afforded the desired imine (1.94 g, 6.39 mmol, 64%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.56 (dd, *J* = 1.8 Hz, 8.8 Hz, 1H) 8.23-8.22 (m, 1H), 7.74-7.62 (m, 3H), 7.37-7.30 (m, 2H), 6.56 (s, 2H), 3.45 (s, 3H), 2.26 (s, 6H), 2.05 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.1, 153.6, 148.3, 137.6, 134.9, 133.5, 131.4, 129.1, 128.2, 128.1, 128.0, 127.2, 126.4, 124.9, 119.9, 59.4, 16.7, 16.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2912 (w), 1641 (m), 1489 (s), 1207 (s), 1109 (s), 789 (m), 690 (s).
MS (70 eV, EI): *m/z* (%) = 304 ($[M+H]^+$, 11), 303 (M^+, 48), 288 (100), 151 (6).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{21}NO$] 303.1623, found: 303.1622.

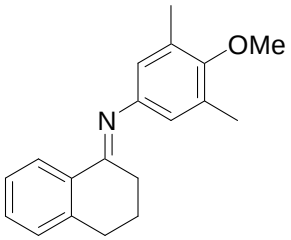
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-acetylphenyl) ethylidene amine (56n)**



Prepared according to **TP7** from 1,3-diacetyl benzene (10.0 mmol, 1.62 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 20:1 (2% Et_3N)), furnished the desired imine (2.07 g, 7.0 mmol 70%) as a yellow oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.13-8.08 (m, 1H), 7.98-7.69 (m, 2H), 7.39-7.38 (m, 1H), 6.52 (s, 2H), 3.43 (s, 3H), 2.61 (s, 3H), 2.24 (s, 3H), 2.20 (s, 6H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 199.6, 164.3, 153.6, 148.8, 140.2, 137.9, 131.6, 131.4, 128.4, 128.3, 125.0, 119.5, 59.4, 26.9, 16.9, 16.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2924 (w), 1611 (m), 1497 (s), 1207 (s), 1109 (m), 870 (m), 764 (s).
MS (70 eV, EI): *m/z* (%) = 295 (M^+, 78), 280 (100), 263 (29), 136 (30).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{21}NO_2$] 295.1572, found: 295.1577.

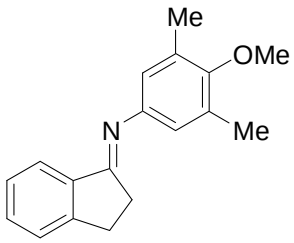
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(1,2,3,4-tetrahydro) naphthylidene amine (56o)**



Prepared according to **TP7** from α-tetralone (10.0 mmol, 1.46 g, 1.33 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Recrystallisation from *n*-pentane:EtOAc, afforded the desired imine (1.79 g, 6.41 mmol, 64%) as a brown solid.

MP: 85.3-86.4 °C.
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.32-8.29 (m, 1H), 7.35 (ddd, *J* = 7.5 Hz, 1.7 Hz, 1H), 7.30-7.27 (m, 1H), 7.20-7.16 (m, 1H), 6.46 (s, 2H), 3.70 (s, 3H), 2.89 (t, *J* = 6.2 Hz, 2 H), 2.58-2.54 (m, 2H), 2.27 (s, 6H), 1.93-1.87 (m, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 165.8, 153.0, 141.3, 133.8, 133.4, 131.2, 130.7, 128.7, 126.4, 119.7, 59.8, 30.0, 29.9, 23.0, 16.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2927 (m), 1625 (s), 1596 (m), 1453 (m), 1219 (s), 1004 (s), 872 (s), 766 (s).
MS (70 eV, EI): *m/z* (%) = 279 (M^+, 48), 264 (100), 129 (8).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{21}NO$] 279.1623, found: 279.1634.

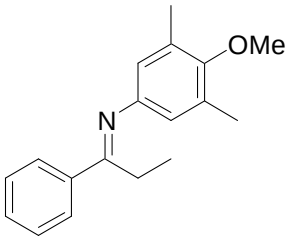
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(1,2,3,4-tetrahydro) naphthylidene amine (56p)**



Prepared according to **TP7** from α-indanone (10.0 mmol, 1.38 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 20:1 (2% Et_3N)), furnished the desired imine (1.86 g, 7.00 mmol 70%) as a dark brown oil.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.28-8.19 (m, 1H), 7.35 (ddd, *J* = 7.4 Hz, 1.6 Hz, 1H), 7.28-7.25 (m, 1H), 7.11-7.10 (m, 1H), 6.42 (s, 2H), 3.68 (s, 3H), 2.89 (t, *J* = 6.2 Hz, 2H), 2.56 (t, *J* = 6.7 Hz, 2H), 2.24 (s, 6H), 1.93-1.87 (m, 2H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 164.2, 152.0, 141.3, 133.2, 133.0, 131.4, 130.8, 128.2, 125.9, 120.0, 59.6, 30.6, 29.4, 16.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2907 (m), 1600 (s), 1575 (s), 1386 (m), 1112 (m), 1005 (m), 985 (m), 862 (s).
MS (70 eV, EI): *m/z* (%) = 265 (M^+, 18), 250 (100), 129 (12), 116 (72).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{19}NO$] 265.1467, found: 265.1488.

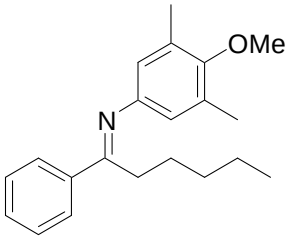
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propylidene amine (56q)**



Prepared according to **TP7** from propiophenone (10.0 mmol, 1.34 g, 1.34 mL) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 80:1 (2% Et_3N)), afforded the desired imine in (2.09 g, 7.81 mmol, 78%) as a yellow oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 8.02-8.00 (m, 2H), 7.24-7.19 (m, 3H), 6.53 (s, 2H), 3.43 (s, 3H), 2.52 (q, *J* = 7.7 Hz, 2H), 2.23 (s, 6H), 0.89 (t, *J* = 7.7 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 169.4, 153.4, 148.2, 138.6, 131.4, 130.2, 128.6, 128.0, 119.4, 59.4, 23.0, 16.4, 13.1 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2980 (w), 1705 (m), 1600 (s), 1220 (m), 1110 (m), 795 (m), 699 (m).
MS (70 eV, EI): *m/z* (%) = 267 (M^+, 75), 252 (100), 238 (99), 111 (20), 91 (29).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO$] 267.1623, found: 267.1629.

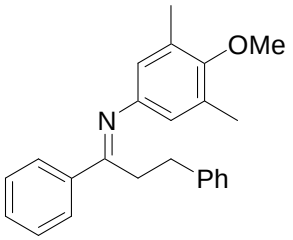
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl hexylidene amine (56r)**



Prepared according to **TP7** from n-hexanophenone (10.0 mmol, 1.76 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 100:1 (2% Et_3N)), afforded the desired imine (2.23 g, 7.21 mmol, 72%) as a yellow oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.27-7.25 (m, 2H), 7.19-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.66 (s, 2H), 3.37 (s, 3H), 2.42-2.38 (m, 2H), 2.17 (s, 6H), 1.59-1.57 (m, 2H), 1.20-1.17 (m, 4H), 0.85 (t, *J* = 7.7 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 169.5, 153.6, 149.5, 144.0, 131.1, 128.7, 127.2, 126.7, 116.2, 59.5, 39.3, 32.1, 28.6, 22.9, 16.7, 15.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2990 (w), 1745 (m), 1600 (s), 1225 (m), 1010 (m), 699 (m).
MS (70 eV, EI): *m/z* (%) = 309 (M^+, 40), 294 (18), 253 (99), 238 (100), 151 (30).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{27}NO$] 309.2093, found: 309.2094.

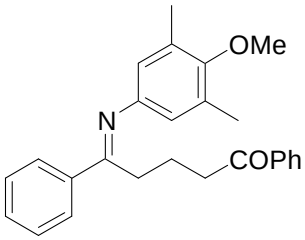
***N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl hexylidene amine (56s)**



Prepared according to **TP7** from 1,3-diphenylpropiophenone (10.0 mmol, 2.54 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 100:1 (2% Et_3N)), afforded the desired imine (2.11 g, 7.41 mmol, 74%) as a yellow oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.28-7.15 (m, 6H), 7.10-6.90 (m, 4H), 6.50 (s, 2H), 3.41 (s, 3H), 2.62-2.58 (m, 2H), 2.31-2.29 (m, 2H), 2.20 (s, 6H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 168.5, 164.4, 148.5, 144.0, 132.0, 131.1, 129.8, 129.4, 129.3, 128.6, 127.2, 126.7, 116.2, 59.5, 27.6, 22.9, 16.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2982 (w), 1815 (m), 1643 (s), 1460 (m), 1225 (m), 1125 (m), 814 (m), 765 (m), 699 (m).
MS (70 eV, EI): *m/z* (%) = 343 (M^+, 20), 267 (40), 253 (19), 238 (100), 151 (10).
HRMS (EI): *m/z* calcd. for: [$C_{24}H_{25}NO$] 343.1936, found: 343.1954.

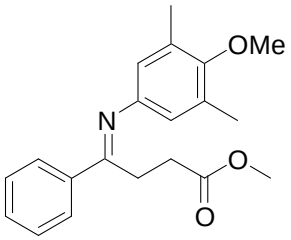
5-[(*N*-(3,5-Dimethyl-4-methoxy)phenyl)imino]-1,5-diphenylpentan-1-one (56t)



Prepared according to **TP7** from 1,5-diphenyl-1,5-pentanedione (10.0 mmol, 2.52 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g;, 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 4:1 (2% Et_3N)), provided the desired imine (2.70 g, 7.0 mmol, 70%) as a dark brown oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.76-7.74 (m, 2H), 7.22-6.99 (m, 8H), 6.82 (s, 2H), 3.32 (s, 3H), 3.09-3.04 (m, 2H), 2.11 (s, 6H), 1.82-1.75 (m, 2H), 1.60-1.53 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 198.7, 161.7, 153.8, 149.5, 144.0, 137.5, 134.4, 132.7, 131.1, 130.7, 128.8, 128.2, 127.0, 114.0, 59.5, 38.6, 34.6, 23.8, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3360 (m), 2949 (w), 1700 (s), 1680 (s), 1635 (m), 1189 (s), 1100 (s), 760 (s), 685 (s).
MS (70 eV, EI): *m/z* (%) = 385 (M^+, 42), 280 (45), 266 (80), 253 (88), 238 (100).
HRMS (EI): *m/z* calcd. for: [$C_{26}H_{27}NO_2$] 385.2042, found: 385.2038.

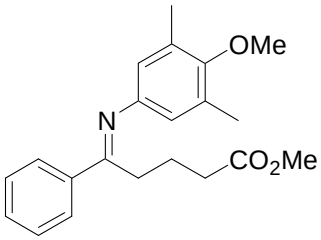
Methyl 4-[(*N*-(3,5-dimethyl-4-methoxyphenyl))imino]-4-phenylbutanoate (56u)



Prepared according to **TP7** from methyl 3-benzoylpropionate (10.0 mmol, 1.92 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 5:1 (2% Et_3N)), provided the desired imine (2.24 g, 6.89 mmol, 69%) as a dark brown oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.19-7.17 (m, 2H), 7.10-7.00 (m, 3H), 6.50 (s, 2H), 3.39 (s, 3H), 3.34 (s, 3H), 2.52 (t, *J* = 6.4 Hz, 2H), 2.31-2.29 (m, 2H), 2.20 (s, 6H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 172.8, 166.8, 153.6, 147.7, 138.3, 130.4, 128.7, 128.2, 127.9, 119.3, 59.4, 51.2, 33.4, 32.3, 16.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2950 (w), 1735 (s), 1686 (s), 1219 (s), 1165 (s), 1009 (m), 758 (s), 690 (s).
MS (70 eV, EI): *m/z* (%) = 325 (M^+, 99), 310 (43), 266 (28), 250 (45), 238 (100).
HRMS (EI): *m/z* calcd. for: [$C_{20}H_{23}NO$] 325.1678, found: 325.1662.

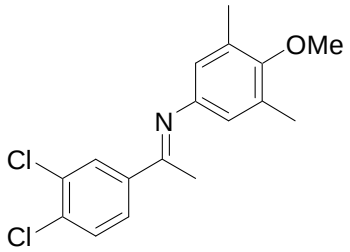
Methyl 5-[(*N*-(3,5-dimethyl-4-methoxyphenyl))imino]-5-phenylpentanoate (56v)



Prepared according to **TP7** from methyl 4-benzoylbutanoate (10.0 mmol, 2.06 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethyl ether 5:1 (2% Et_3N)), provided the desired imine (2.37 g, 6.99 mmol, 70%) as a dark brown oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.80-7.77 (m, 2H), 7.13-7.03 (m, 3H), 6.90 (s, 2H), 3.32 (s, 3H), 3.28 (s, 3H), 2.55 (t, *J* = 6.4 Hz, 2H), 2.23 (s, 6H), 2.17-2.13 (m, 2H), 2.00-1.94 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 173.1, 167.0, 153.0, 145.9, 137.4, 132.7, 130.0, 128.5, 127.8, 120.2, 59.7, 50.9, 33.4, 33.0, 19.5, 18.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2945 (w), 1700 (s), 1686 (s), 1189 (s), 1165 (s), 798 (s), 650 (s).
MS (70 eV, EI): *m/z* (%) = 339 (M^+, 60), 324 (25), 308 (27), 266 (65), 253 (55), 238 (100).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{25}NO_3$] 339.1834, found: 339.1845.

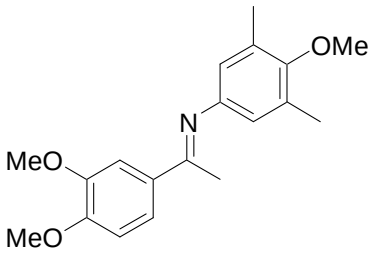
***N*-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethoxy)phenyl ethylideneamine (56W)**



Prepared according to **TP7** from 3,4-dichlorocetophenone (10.0 mmol, 1.89 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g, 1.20 equiv.). Purification by recrystallisation from methanol provided the desired imine (2.29 g, 7.11 mmol, 71 %) as a yellow oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 8.24 (d, *J* = 2.8 Hz, 1H), 7.94 (dd, *J* = 8.4 Hz, 2.1 Hz, 1H), 7.09-7.01 (m, 1H), 6.60 (s, 2H), 3.51 (s, 3H), 2.27 (s, 6H), 2.05 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 164.0, 148.5, 146.2, 140.1, 138.5, 135.2, 134.4, 128.3, 121.0, 120.1, 111.2, 59.4, 17.0, 16.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2925 (w), 1620 (w), 1562 (m), 1418 (s), 1366 (s), 1299 (m), 1007 (m), 808 (s), 712 (s).
MS (70 eV, EI): *m/z* (%) = 321 (M^+, 25), 307 (10), 306 (100), 171 (27).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{17}Cl_2NO$] 321.0687, found: 313.1665.

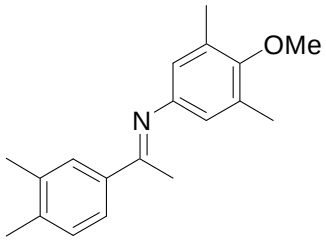
***N*-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethoxy)phenyl ethylideneamine (56x)**



Prepared according to **TP7** from 3,4-dimethoxyacetophenone (10.0 mmol, 1.80 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by recrystallisation from methanol provided the desired imine (2.23 g, 7.22 mmol, 72%) as a white solid.

MP: 115.9-117.1 °C
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.05 (d, *J* = 2.1 Hz, 1H), 7.40 (dd, *J* = 8.3 Hz, 2.1 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 2H), 3.49 (s, 3H), 3.43 (s, 3H), 3.40 (s, 3H), 2.25 (s, 6H), 2.05 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 163.5, 157.5, 152.3, 150.1, 148.5, 133.1, 131.4, 128.3, 121.0, 120.1, 110.8, 59.4, 55.44, 55.41, 16.7, 16.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2935 (w), 2959 (w), 1620 (w), 1594 (m), 1583 (s), 1510 (s), 1452 (m), 1414 (s), 1267 (s), 1217 (s), 1153 (s), 1018 (s), 867 (s), 765 (m).
MS (70 eV, EI): *m/z* (%) = 314 ($[M+H]^+$, 12), 339 (M^+, 55), 299 (18), 298 (100), 268 (6).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{23}NO_3$] 313.1678, found: 313.1665.

***N*-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethoxy)phenyl ethylideneamine (56y)**

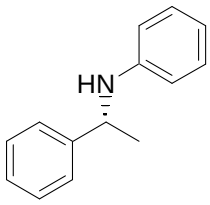


Prepared according to **TP7** from 3,4-dimethylacetophenone (10.0 mmol, 1.48 g) and 3,5-dimethyl-4-methoxy aniline (12.0 mmol, 1.81 g; 1.20 equiv.). Purification by flash chromatography (silica gel; *n*-pentane:diethylether 60:1 (2% Et_3N)), provided the desired imine (1.83 g, 6.50 mmol, 65%) as a yellow oil.

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.38-7.22 (m, 2H), 6.91-6.82 (m, 1H), 6.61 (s, 2H), 3.40 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.25 (s, 6H), 2.05 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 163.0, 158.5, 150.3, 149.2, 148.5, 132.8, 131.9, 128.3, 121.0, 120.2, 111.2, 59.4, 17.4, 17.2, 16.7, 16.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2912 (w), 1645 (w), 1600 (m), 1512 (m), 1478 (m), 1400 (s), 1297 (s), 1125 (m), 1008 (m), 875 (m), 795 (s).
MS (70 eV, EI): *m/z* (%) = 281 (M^+, 65), 266 (100), 265 (10), 151 (16), 146 (70).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{23}NO$] 281.1780, found: 281.1781.

7. Asymmetric Hydrogenation of Imines

(*R*)-*N*-phenyl-1-phenyl ethyl amine (51a)[132]

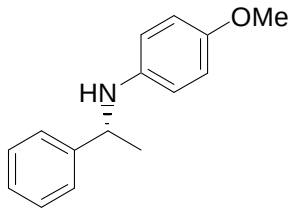


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50a** (98 mg; 0.50 mmol) and obtained as a yellow oil (95 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = −3.9 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.06 (dd, *J* = 8.9 Hz, 7.4 Hz, 2H), 6.65 (t, *J* = 7.4 HZ, 1H), 6.50 (d, *J* = 7.9 Hz, 2H), 4.48 (q, *J* = 6.9 Hz, 1H), 3.95 (br, NH), 1.50 (d, *J* = 7.1 HZ, 3H) ppm.
The enantiomer ratio was determined by Chiral GC DEX-CB Column (100 °C (5 min), 5 °C/min 160 °C (50 min)); t_r = 20.9 min [minor], t_r = 21.1 min [major]; 84% *ee*.

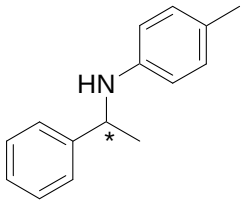
(*R*)-*N*-(4-methoxy)phenyl-1-phenyl ethylidene amine (51b)[3]

[132] Iwadate, N.; Yoshida, K.; Imamoto, T. *Org. Lett.* **2006,** *8*, 2289;



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50a** (113 mg; 0.50 mmol) and obtained as a yellow oil (108 mg, 0.47 mmol, 95%)
$[\alpha]_D^{20}$ = +1.3 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.21-7.10 (m, 4H), 7.05-7.00 (m, 1H), 6.69-6.64 (m, 2H), 6.73-6.72 (m, 2H), 4.17 (q, *J* = 6.6 Hz, 1H), 3.54 (s, 3H), 3.31 (br, 1H, -NH), 1.13 (d, *J* = 6.85 Hz, 3H) ppm.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 ml/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C); t_r = 14.9 min [major], t_r = 16.2 min [minor]; 88% *ee*.

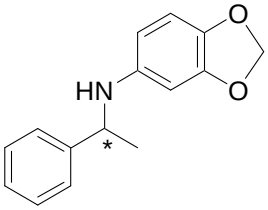
***N*-(4-methyl)phenyl-1-phenyl ethyl amine (51c)**[133]



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50c** (105 mg; 0.50 mmol) and obtained as a yellow oil (100 mg, 0.48 mmol, 95%).

$[\alpha]_D^{20}$ = +48.2 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.35-7.30 (m, 2H), 7.25-7.20 (m, 3H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.45 (d, *J* = 8.0 Hz, 2H), 4.42 (q, *J* = 6.7 Hz, 1H), 3.52 (br, NH), 2.20 (s, 3H), 1.52 (d, *J* = 6.8 Hz, 3H) ppm.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 ml/min, heptane/iPrOH: 90/10, λ = 215 nm, 25 °C); t_r = 13.0 min [major], t_r = 14.5 min [minor]; 85% *ee*.

***N*-(3,4,-Dioxymethylene)phenyl-1-phenyl ethyl amine (51d)**

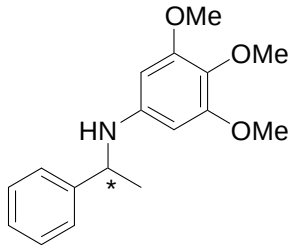


[133] Kwong, F. Y.; Buchwald, S. L. *Org. Lett*, **2003,** *5*, 793.

Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50d** (120 mg; 0.50 mmol) and obtained as a pale white solid. (111 mg, 0.46 mmol, 92%)

MP: 104.2-106.1 °C.
$[\alpha]_D^{20}$ = −11.4 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34-7.12 (m, 5H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.10 (d, *J* = 2.1 Hz, 1 H), 5.91 (dd, *J* = 2.1 Hz, 8.2 Hz, 1 H), 5.72 (s, 2H), 4.31 (q, *J* = 6.6 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 147.8, 144.2, 141.7, 139.6, 128.3, 126.7, 125.6, 108.1, 105.6, 100.2, 96.6, 54.6, 24.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3421 (m), 2956 (w), 1638 (w), 1519 (m), 1481 (s), 1352 (m), 1292 (m), 1204 (s), 1036 (s), 928 (s), 789 (m), 696 (s).
MS (70 eV, EI): *m/z* (%) = 241 (M^+, 92), 226 (54), 137 (100), 105 (86), 79 (17).
HRMS (EI): *m/z* calcd. for: [$C_{15}H_{15}NO_2$] 241.1103, found: 241.1084.
The enantiomer ratio was determined by Chiral GC DEX-CB Column (160 °C, const; 100 min); t_r = 40.2 min [minor], t_r = 41.0 min [major]; 90% *ee*.

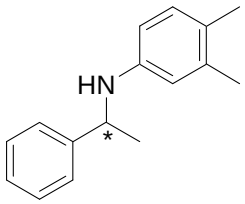
***N*-(3,4,5-trimrthoxy)phenyl-1-phenyl ethyl amine (51e)**



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50e** (143 mg; 0.50 mmol) and obtained as a viscous oil. (135 mg, 0.47 mmol, 94%)

$[\alpha]_D^{20}$ = −30.2 (c = 0.50, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.18-7.17 (m, 1H), 7.11-7.10 (m, 3H), 7.02-6.98 (m, 1H), 5.64 (s, 2H), 4.18 (q, *J* = 6.8 Hz, 1H), 3.75 (s, 3H), 3.47 (br, 1H, NH), 3.36 (s, 6H), 1.16 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 154.7, 146.0, 144.2, 131.7, 128.8, 127.1, 126.1, 92.5, 60.7, 55.8, 54.1, 24.9 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3376 (br, w), 2933 (w), 1609 (m), 1507 (m), 1420 (m), 1231 (s), 1117 (s), 1005 (m), 764 (m), 700 (s).
MS (70 eV, EI): *m/z* (%) = 287 (M^+, 84), 272 (72), 182 (21), 168 (97), 105 (100).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}NO_3$] 287.1521, found: 287.1498.
The enantiomer ratio was determined by HPLC using Chiralcel OJ column (flow rate 1.0 mL/min, heptane/iPrOH: 85/15, λ= 215 nm, 25 °C); t_r = 44.2 min [major], t_r = 55.2 min [minor]; 89% *ee*.

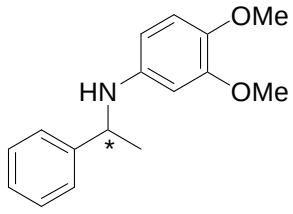
***N*-(3,4,-Dimethyl)phenyl-1-phenyl ethyl amine (51f)**



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50f** (112 mg; 0.50 mmol) and obtained as a yellow oil (108 mg, 0.48 mmol, 92%)

$[\alpha]_D^{20}$ = −20.9 (c = 1.0, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.17-7.16 (m, 1H), 7.10-7.06 (m, 3H), 7.00-6.96 (m, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.24-6.21 (m, 2H), 4.23 (q, *J* = 6.8 Hz, 1H), 3.40 (br, 1H, NH), 1.97 (s, 3H), 1.96 (s, 3H), 1.12 (d, *J* = 6.6 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 145.9, 145.8, 136.7, 130.3, 128.6, 126.8, 126.0, 124.9, 115.6, 112.3, 53.5, 18.7, 24.8, 20.0 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3406 (br, w), 2964 (m), 2920 (m), 1617 (s), 1500 (s), 1447 (m), 1317 (m), 801 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 225 (M^+, 51), 210 (100), 121 (32), 120 (10), 106 (13), 105 (46).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{19}N$] 225.1517, found: 225.1510.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 14.4 min [minor], t_r = 17.5 min [major]; 90% *ee*.

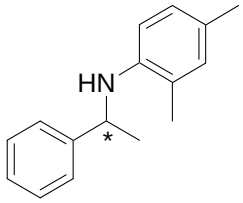
***N*-(3,4,-Dimethoxy)phenyl-1-phenyl ethyl amine (51g)**



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50g** (128 mg; 0.50 mmol) and obtained as a yellow oil (122 mg, 0.47 mmol, 95%)

$[\alpha]_D^{20}$ = −34.2 (c = 0.55, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.19-7.18 (m, 1H), 7.12-7.08 (m, 3H), 7.02-6.98 (m, 1H), 6.52 (d, *J* = 8.7 Hz, 1H), 5.97 (d, *J* = 2.7 Hz, 1H), 5.93 (dd, *J* = 2.7 Hz, 8.6 Hz, 1H), 4.20 (br, 1H, NH), 4.17 (q, *J* = 6.6 Hz, 1H), 3.40 (s, 3H), 3.36 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 151.2, 146.0, 142.8, 142.5, 128.7, 126.9, 126.0, 115.3, 104.9, 100.6, 57.0, 55.4, 54.1, 24.9 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3384 (m), 2961 (m), 2829 (m), 1616 (m), 1511 (s), 1448 (m), 1223 (s), 1165 (s), 1023 (m), 760 (m).
MS (70 eV, EI): *m/z* (%) = 257 (M^+, 100), 242 (73), 153 (20), 138 (43), 105 (54).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{19}NO_2$] 257.1416, found: 257.1415.
The enantiomer ratio was determined by HPLC using Chiralcel OJ column (flow rate 1.0 mL/min, heptane/iPrOH: 85/15, λ= 215 nm, 25 °C); t_r = 34.5 min [minor], t_r = 39.5 min [major]; 81% *ee*.

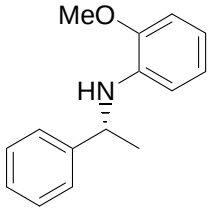
***N*-(2,4,-Dimethyl)phenyl-1-phenyl ethyl amine (51h)**



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50h** (112 mg; 0.50 mmol) and obtained as a yellow oil (95 mg, 0.42 mmol, 84%)

$[\alpha]_D^{20}$ = −10.1 (c = 0.40, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.22-7.18 (m, 2H), 7.16-7.06 (m, 3H), 6.45 (s, 2H), 6.16 (s, 1H), 4.17 (q, *J* = 7.0 Hz, 1H), 3.87 (brs, NH, 1H), 1.98 (s, 3H), 1.96 (s, 3H), 1.14 (d, *J* = 7.0 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 145.4, 142.6, 131.2, 129.5, 129.2, 128.5, 127.6, 126.4, 121.2, 54.5, 25.6, 24.9, 16.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3362 (m), 2928 (m), 1624 (m), 1500 (s), 1464 (m), 1165 (s), 1082 (m), 760 (m), 673 (s).
MS (70 eV, EI): *m/z* (%) = 225 (M^+, 22), 210 (100), 121 (12), 105 (64).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{19}N$] 225.1517, found: 225.1520.
The enantiomer ratio was determined by HPLC using Chiralcel OJ column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 10.3 min [minor], t_r = 16.3 min [major]; 83% *ee*.

(*R*)-*N*-(2-methoxy)phenyl-1-phenyl ethyl amine (51i)[134]

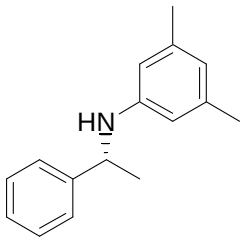


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **50i** (114 mg; 0.50 mmol) and obtained as a yellow oil (57 mg, 0.25 mmol, 50%)

$[\alpha]_D^{20}$ = +4.2 (c = 0.20, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.37 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.65 (t, *J* = 7.9 Hz, 1H), 6.60 (t, *J* = 7.8 Hz, 1H), 6.35 (d, *J* = 7.9 Hz, 1H), 4.60 (brs, NH, 1H), 4.47 (q, *J* = 6.7 Hz, 1H), 3.88 (s, 3H), 1.57 (s, 3H) ppm.
The enantiomer ratio was determined by GC using Chiralsil DEX-CB column (100 °C (7 min) 5 °C/min 160 °C (60 min), const;); t_r = 14.9 min [major], t_r = 16.2 min [minor]; 54% *ee*.

(*R*)-*N*-(3,5,-Dimethyl)phenyl-1-phenyl ethyl amine (53a)[135]

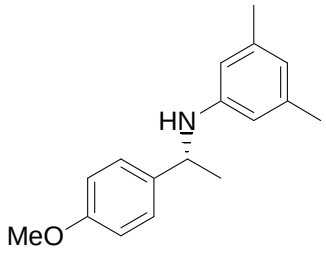
[134] Pei, D.; Wang, Z.; Wei, S.; Zhang, Y.; Sun, J. *Org. Lett.* **2006**, *8*, 5413.
[135] Kwong, F. Y.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 793.



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **52a** (112 mg; 0.50 mmol) and obtained as a pale yellow oil (106 mg, 0.47 mmol, 94%)

$[\alpha]_D^{20}$ = −12.8 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.25-7.23 (m, 2H), 7.18-7.13 (m, 2H), 7.08-7.06 (m, 1H), 6.37 (s, 1H), 6.16 (s, 2H), 4.32 (q, *J* = 7.0 Hz, 1H), 3.71 (br, 1H, NH), 2.13 (s, 6H), 1.21 (d, *J* = 7.1 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 147.6, 145.8, 138.5, 128.8, 127.0, 126.1, 120.0, 112.0, 53.5, 24.8, 21.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3406 (br, w), 2914 (w), 1597 (s), 1512 (m), 1452 (m), 1336 (m), 1184 (m), 822 (m), 696 (m).
MS (70 eV, EI): *m/z* (%) = 225 (M^+, 39), 210 (100), 121 (34), 120 (10), 105 (42).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{19}N$] 225.1517, found: 225.1511.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 9.7 min [minor], t_r = 11.0 min [major]; 94% *ee*.

(*R*)-*N*-(3,5,-Dimethyl)phenyl-1(4-methoxyphenyl)ethyl amine (53b)

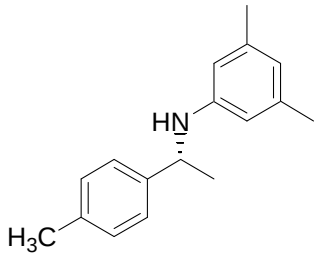


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **52b** (120 mg; 0.50 mmol) and obtained as a yellow oil (112 mg, 0.47 mmol, 94%).

$[\alpha]_D^{20}$ = +10.8 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.29-7.23 (m, 2H), 6.91-6.85 (m, 2H), 6.47 (s, 1H), 6.28 (s, 2H), 4.90-4.40 (m, 1H), 3.63 (brs, 1H), 3.40 (s, 3H), 2.25 (s, 6H), 1.33 (d, *J* = 6.6 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 157.7, 146.6, 137.1, 136.5, 125.8, 118.4, 112.9, 110.6, 53.3, 51.5, 23.6, 20.3 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3390 (m), 2961 (w), 1602 (s), 1507 (s), 1341 8s), 1029 (s), 825 (s).
MS (70 eV, EI): *m/z* (%) = 255 (M^+, 16), 135 (100), 121 (11), 105 (8).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}NO$] 255.1618, found: 255.1609.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 13.9 min [minor], t_r = 15.7 min [major]; 94% *ee*.

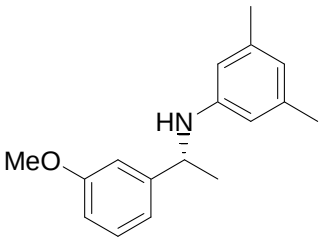
(*R*)-*N*-(3,5,-Dimethyl)phenyl-1(4-methylphenyl)ethyl amine (53c)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **52c** (119 mg; 0.50 mmol) and obtained as a yellow oil (115 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +12.3 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.13 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.33 (s, 1H), 6.13 (s, 2H), 4.31 (q, *J* = 6.2 Hz, 1H), 3.50 (brs, 1H), 2.10 (s, 6H), 2.06 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 147.8, 142.9, 138.3, 136.1, 129.4, 126.0, 119.6, 111.8, 53.1, 24.8, 21.5, 20.9 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3395 (br, w), 2920 (br, w), 1597 (s), 1507 (m), 1473 (m), 1336 (m), 1184 (m), 1109 (w), 814 (s), 721 (w), 690 (m).
MS (70 eV, EI): *m/z* (%) = 239 (M^+, 89), 225 (14), 224 (100), 121 (48), 119 (72).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}N$] 239.1674, found: 239.1678.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 9.2 min [minor], t_r = 10.3 min [major]; 93% *ee*.

(*R*)-*N*-(3,5,-Dimethyl)phenyl-1(3-methoxyphenyl)ethyl amine (53d)

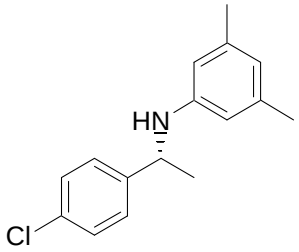


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **52d** (127 mg; 0.50 mmol) and obtained as a pale yellow oil (121 mg, 0.47 mmol, 95%).

$[\alpha]_D^{20}$ = +10.5 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.07 (t, J = 8.0 Hz, 1H), 6.99-6.97 (m, 1H), 6.87-6.85 (m, 1H), 6.61 (dddd, *J* = 0.9 Hz, 2.7 Hz, 8.0 Hz, 1H), 6.32 (s, 1H), 6.13 (s, 2H), 4.33-4.25 (m, 1H), 3.50 (brs, 1H), 3.30 (s, 3H), 2.10 (s, 6H), 1.17 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 160.5, 147.8, 147.7, 138.4, 129.7, 119.7, 118.3, 112.1, 112.0, 111.8, 54.5, 53.4, 24.8, 21.5 ppm.

IR (neat): υ_{max} (cm^{-1}) = 3403 (br, w), 2918 (w), 1600 (s), 1482 (m), 1335 (m), 1251 (s), 1043 (s), 820 (s), 690 (s).
MS (70 eV, EI): *m/z* (%) = 255 (M^+, 45), 240 (100), 135 (32), 121 (40), 105 (16), 91 (8).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}NO$] 255.1623, found: 255.1624.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 17.4 min [minor], t_r = 19.9 min [major]; 94% *ee*.

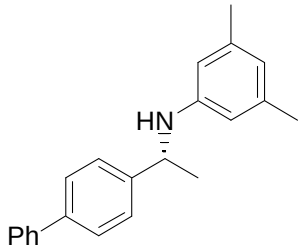
(*R*)-*N*-(3,5,-Dimethyl)phenyl-1(4-chlorophenyl)ethyl amine (53e)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **52e** (129 mg, 0.50 mmol) and obtained as a yellow crystalline solid (122 mg, 0.47 mmol, 94%).

MP: 44.2-46.4 °C
$[\alpha]_D^{20}$ = +8.0 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.07-7.03 (m, 2H), 6.91-6.86 (m, 2H), 6.33 (s, 1H), 6.04 (s, 2H), 4.12 (q, *J* = 6.6 Hz, 1H), 3.40 (brs, 1H), 2.10 (s, 6H), 1.02 (d, *J* = 6.6 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 147.3, 144.3, 138.5, 132.5, 128.8, 127.4, 119.9, 111.8, 52.6, 24.6, 21.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3390 (m), 2853 (w), 1597 (m), 1486 (m), 1336 (m), 1207 (m), 1184 (m), 1086 (m), 1011 (m), 817 (s), 781 (m), 690 (m).
MS (70 eV, EI): *m/z* (%) = 259 (M^+, 73), 244 (100), 139 (42), 121 (58), 103 (21).
HRMS (EI): *m/z* calcd. for: [$C_{16}H_{18}N^{35}Cl$] 259.1128, found: 259.1128.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 10.6 min [minor], t_r = 13.7 min [major]; 91% *ee*.

(*R*)-*N*-(3,5,-Dimethyl)phenyl-1(4-phenylphenyl)ethyl amine (53f)

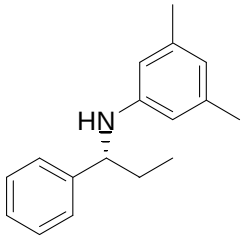


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **52f** (150 mg; 0.50 mmol) and obtained as a yellow oil (142 mg, 0.47 mmol, 94%).

$[\alpha]_D^{20}$ = +8.0 (c = 0.6, CH_2Cl_2)

^{1}H-NMR (300 MHz, C_6D_6): δ = 7.44-7.39 (m, 3H), 7.26-7.22 (m, 1H), 7.20-7.05 (m, 5H), 6.30 (s, 1H), 6.20 (s, 2H), 4.35 (q, *J* = 6.6 Hz, 1H), 3.50 (brs, 1H), 2.10 (s, 6H), 1.20 (d, *J* = 6.6 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 147.8, 145.0, 141.5, 140.2, 138.6, 128.9, 127.7, 127.4, 127.3, 126.6, 120.0, 111.9, 53.1, 24.9, 21.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3392 (m), 2863 (w), 1590 (m), 1470 (s), 1330 (m), 1107 (m), 1100 (m), 1011 (m), 897 (s), 780 (m), 690 (m).
MS (70 eV, EI): *m/z* (%) = 301 (M^+, 55), 286 (54), 181 (100), 165 (16), 121 (18).
HRMS (EI): *m/z* calcd. for: [$C_{22}H_{23}N$] 301.1830, found: 301.1832.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 16.3 min [minor], t_r = 13.6 min [major]; 88% *ee*.

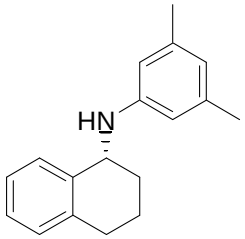
(*R*)-*N*-(3,5,-Dimethyl)phenyl-1phenyl-propylamine (53g)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **52g** (119 mg; 0.50 mmol) and obtained as a brown oil (115 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +12.0 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.28-7.20 (m, 2H), 7.18-7.05 (m, 3H), 6.25 (s, 1H), 6.16 (s, 2H), 4.31 (t, *J* = 6.7 Hz, 1H), 3.71 (br, 1H, NH), 2.10 (s, 6H), 1.55-1.50 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 147.8, 145.8, 139.1, 128.7, 127.0, 126.7, 120.1, 112.7, 55.2, 25.0, 23.2, 21.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3390 (br, w), 2920 (m), 1600 (m), 1455 (m), 1120 (m), 1009 (s), 845 (m), 765 (m), 690 (s).
MS (70 eV, EI): *m/z* (%) = 239 (M^+, 20), 210 (100), 165 (29), 121 (18).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}N$] 239.1674, found: 239.1680.
The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 9.2 min [major], t_r = 10.2 min [minor]; 94% *ee*.

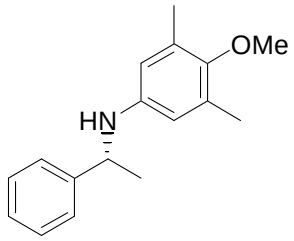
(*R*)-*N*-(3,5,-Dimethyl)phenyl-1(1,2,3,4-dihydro)naphthylamine (53h)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **52h** (125 mg; 0.50 mmol) and obtained as a brown oil (118 mg, 0.47 mmol, 94%).

$[\alpha]_D^{20}$ = +20.8 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.40-7.37 (m, 1H), 7.09-7.03 (m, 2H), 6.97-6.95 (m, 1H), 6.43 (s, 1H), 6.20 (s, 2H), 4.49-4.46 (m, 1H), 3.38-3.36 (m, 1H), 2.62-2.49 (m, 2H), 2.22 (s, 6H), 1.81-1.74 (m, 1H), 1.70-1.58 (m, 2H), 1.47-1.42 (m, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 148.1, 138.9, 138.7, 137.6, 129.7, 129.1, 127.3, 126.3, 119.6, 111.4, 51.3, 29.6, 29.2, 21.7, 19.7 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3402 (br, w), 3019 (m), 2919 (m), 1595 (s), 1510 (m), 1447 (m), 1337 (m), 1183 (m), 817 (s), 742 (s), 689 (s).
MS (70 eV, EI): *m/z* (%) = 251 (M^+, 63), 249 (12), 131 (70), 129 (12), 121 (100), 105 (6), 91 (17).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}N$] 251.1674, found: 251.1670.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 9.4 min [major], t_r = 10.3 min [minor]; 84% *ee*.

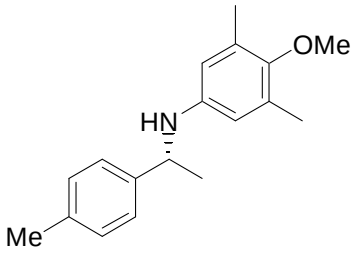
(*R*)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl ethyl amine (57a)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56a** (127 mg; 0.50 mmol) and obtained as a pale yellow solid (121 mg, 0.47 mmol, 95%).

$[\alpha]_D^{20}$ = −6.3 (c = 0.6, CH_2Cl_2)
MP: 86.3 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.39-7.29 (m, 4H), 7.25-7.22 (m, 1H), 6.21 (s, 2H), 4.41 (q, *J* = 6.7 Hz, 1H), 3.62 (s, 3H), 2.15 (s, 6H), 1.49 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.0, 145.2, 143.0, 131.2, 128.6, 126.8, 125.9, 113.6, 59.9, 54.1, 24.7, 16.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3381 (m), 2924 (br, m), 1609 (m), 1487 (s), 1190 (s), 1006 (s), 830 (m), 701 (m).
MS (70 eV, EI): *m/z* (%) = 255 (M^+, 100), 240 (87), 136 (77), 105 (98).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}NO$] 255.1623, found: 255.1627.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 1.0 mL/min, heptane/iPrOH: 80/20, λ= 215 nm, 25 °C); t_r = 6.4 min [minor], t_r = 7.6 min [major]; 94% *ee*.

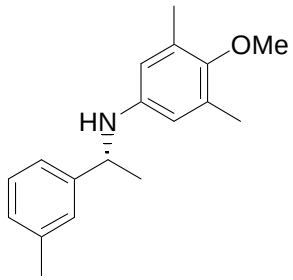
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-methyl)phenyl ethyl amine (57b)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56b** (134 mg; 0.50 mmol) and obtained as a viscous oil (128 mg, 0.47 mmol, 95%).

$[\alpha]_D^{20}$ = + 3.8 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.19-7.15 (m, 2H), 7.00-6.97 (m, 2H), 6.17 (s, 2H), 4.29 (q, *J* = 6.6 Hz, 1H), 3.40 (br, 1H, NH), 3.38 (s, 3H), 2.09 (s, 6H), 2.12 (s, 3H), 1.23 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 149.5, 143.8, 143.1, 136.2, 131.0, 129.5, 126.1, 114.0, 59.5, 53.5, 25.0, 21.0, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3392 (br, w), 2923 (w), 1608 (m), 1487 (m), 1340 (w), 1219 (s), 1135 (w), 1044 (m), 1009 (s), 835 (m), 815 (s).
MS (70 eV, EI): *m/z* (%) = 269 (M^+, 85), 253 (47), 151 (24), 136 (50), 119 (100).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{23}NO$] 269.1780, found: 269.1783.
The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 11.4 min [minor], t_r = 12.5 min [major]; 86% *ee*.

(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methyl)phenyl ethyl amine (57c):

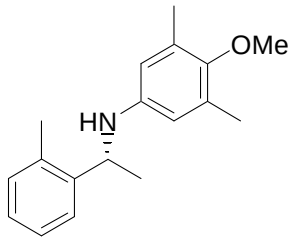


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56c** (134 mg; 0.50 mmol) and obtained as a viscous yellow oil (129 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +4 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.12-7.10 (m, 3H), 6.90-6.88 (m, 1H), 6.18 (s, 2H), 4.29 (q, *J* = 6.9 Hz, 1H), 3.42 (br, 1H, NH), 3.37 (s, 3H), 2.17 (s, 6H), 2.11 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 149.5, 146.2, 143.8, 138.2, 131.1, 128.8, 127.8, 126.7, 123.3, 114.0, 59.5, 53.9, 25.1, 21.5, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3396 (br, w), 2923 (w), 1607 (s), 1486 (s), 1222 (s), 1189 (m), 1009 (m), 835 (m), 784 (m).
MS (70 eV, EI): *m/z* (%) = 271 ($[M+2H]^+$, 9), 270 ($[M+H]^+$, 100), 213 (5).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{24}NO$]; $[M+H]^+$: 270.1858, found: 270.1846

The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 10.2 min [major], t_r = 11.8 min [minor]; 94% *ee*.

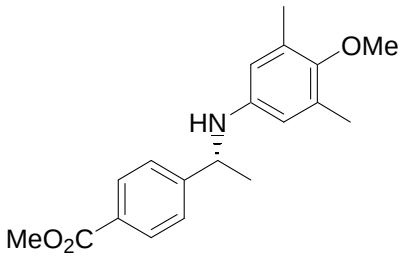
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-methyl)phenyl ethyl amine (57d):



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56d** (134 mg; 0.50 mmol) and obtained as a viscous yellow oil (128 mg, 0.47 mmol, 95%).

$[\alpha]_D^{20}$ = +1.8 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (300 MHz, C_6D_6): δ = 7.41-7.39 (m, 1H), 7.10-7.05 (m, 1H), 7.03-7.01 (m, 2H), 6.09 (s, 2H), 4.50 (q, *J* = 6.7 Hz, 1H), 3.37 (brs, 4H), 2.22 (s, 3H), 2.16 (s, 6H), 1.18 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 149.5, 143.7, 143.5, 134.8, 131.1, 130.8, 126.9, 126.8, 125.1, 113.7, 59.5, 50.1, 22.7, 18.9, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3406 (br, w), 2964 (m), 2920 (m), 1617 (s), 1500 (s), 1447 (m), 1317 (m), 801 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 269 (M^+, 100), 254 (72), 151 (35), 136 (51), 119 (68), 91 (13).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{23}NO$] 269.1780, found: 269.1774.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 13.9 min [major], t_r = 15.7 min [minor]; 94% *ee*.

(*R*)-(+)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-carbomethoxy)phenyl ethyl amine (57e)



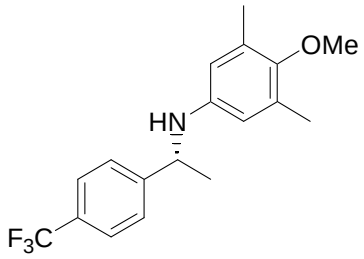
Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56e** (156 mg; 0.50 mmol) and obtained as a yellow solid (150 mg, 0.48 mmol, 96%).

MP: 113.7-115.2 °C
$[\alpha]_D^{20}$ = +23.3 (c = 0.6, CH_2Cl_2)

^{1}H-NMR (400 MHz, C_6D_6): δ = 8.09-8.07 (m, 2H), 7.15-7.14 (m, 2H), 6.08 (s, 2H), 4.18 (q, *J* = 6.8 Hz, 1H), 3.47 (s, 3H), 3.36 (s, 3H), 3.34 (br, 1H, NH), 2.16 (s, 6H), 1.08 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 166.5 151.4, 149.7, 143.4, 131.2, 130.3, 129.5, 126.1, 114.0, 59.5, 53.6, 51.4, 24.6, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3350 (m), 2994 (w), 1713 (s), 1605 (m), 1431 (m), 1279 (s), 1220 (s), 1114 (s), 1009 (s), 831 (s), 764 (s), 712 (s).
MS (70 eV, EI): *m/z* (%) = 313 (M^+, 94), 298 (90), 163 (100), 136 (80), 150 (41).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{23}NO_3$] 313.1678, found: 313.1679.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 25.2 min [minor], t_r = 28.9 min [major]; 94% *ee*.

(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-trifluoromethyl)phenyl ethyl amine (57f)

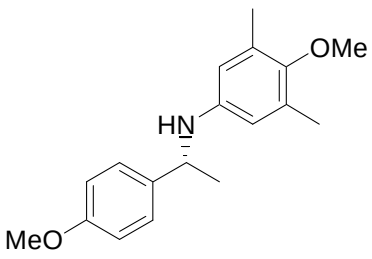


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56f** (161 mg; 0.50 mmol) and obtained as a yellow oil (155 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +10.2 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 2H), 4.45 (q, *J* = 6.7 Hz, 1H), 3.60 (s, 3H), 2.14 (s, 6H), 1.50 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.4, 149.3, 142.3, 131.4, 129.6 (q, *J* = 32.3 Hz), 126.3, 125.6 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.0 Hz), 113.8, 59.9, 54.1, 24.7, 16.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3349 (m), 2966 (w), 1605 (m), 1488 (m), 1323 (s), 1222 (s), 1155 (s), 1062 (s), 1005 (s), 835 (s), 607 (m).
MS (70 eV, EI): *m/z* (%) = 323 (M^+, 100), 308 (77), 293 (11), 173 (33), 150 (21), 136 (4).
HRMS (EI): *m/z* calcd.for: [$C_{18}H_{20}F_3NO$] 323.1497, found: 323.1481.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 14.4 min [minor], t_r = 18.5 min [major]; 89% *ee*.

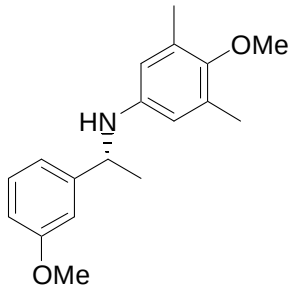
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-methoxy)phenyl ethyl amine (57g)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56g** (142 mg; 0.50 mmol) and obtained as a viscous yellow oil (136 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +6.4 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.26-7.21 (m, 2H), 6.74-6.72 (m, 2H), 6.02 (s, 2H), 4.04 (q, *J* = 6.8 Hz, 1H), 3.85 (br, 1H, NH), 3.75 (s, 3H), 3.60 (s, 3H), 2.12 (s, 6H), 1.32 (d, *J* = 6.6 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 158.5, 151.6, 138.0, 136.4, 129.5, 122.4, 120.9, 114.1, 59.7, 55.2, 52.4, 24.9, 16.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3406 (br, w), 2964 (m), 2920 (m), 1617 (s), 1500 (s), 1447 (m), 1317 (m), 801 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 285 (M^+, 50), 270 (20), 151 (30), 135 (100).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{23}NO_2$] 285.1729, found: 285.1719.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 11.3 min [minor], t_r = 12.9 min [major]; 85% *ee*.

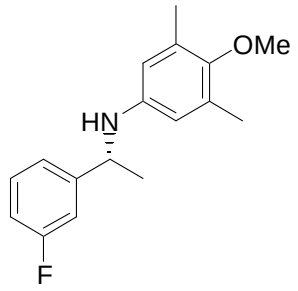
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-methoxy)phenyl ethyl amine (57h):



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56h** (142 mg; 0.50 mmol) and obtained as a viscous oil (133 mg, 0.47 mmol, 94%).

$[\alpha]_D^{20}$ = −4.6 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.23-7.11 (m, 1H), 6.98-6.71 (m, 2H), 6.67-6.60 (m, 1H), 6.10 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 1H), 3.71 (br, 1H, NH), 3.66 (s, 3H), 3.46 (s, 3H), 2.10 (s, 6H), 1.46 (d, *J* = 7.0 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 158.1, 153.0, 138.2, 136.9, 130.1, 125.0, 122.4, 121.0, 113.9, 112.8, 59.2, 55.1, 53.8, 25.7, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3416 (br, w), 2954 (m), 2922 (m), 1607 (s), 1487 (s), 1319 (m), 801 (m), 689 (s).
MS (70 eV, EI): *m/z* (%) = 285 (M^+, 41), 270 (80), 151 (10), 135 (100).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{23}NO_2$] 285.1729, found: 285.1731.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 18.7 min [minor], t_r = 21.5 min [major]; 86% *ee*.

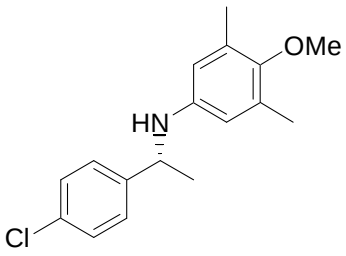
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-fluoro)phenyl ethyl amine (57i)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56i** (136 mg; 0.50 mmol) and obtained as a yellow oil (128 mg, 0.47 mmol, 94%).

$[\alpha]_D^{20}$ = −12 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.03-7.00 (m, 1H), 6.91-6.88 (m, 2H), 6.72-6.67 (m, 1H), 6.08 (s, 2H), 4.14 (q, *J* = 6.8 Hz, 1H), 3.37 (s, 3H), 3.28 (br, 1H, NH), 2.16 (s, 6H), 1.07 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 163.7 (d, *J* = 245.5 Hz), 149.7, 149.6 (d, *J* = 6.1 Hz), 143.4, 131.2, 130.3 (d, *J* = 7.9 Hz), 121.7 (d, *J* = 2.6 Hz), 113.9, 113.8 (d, *J* = 21.3 Hz), 113.0 (d, *J* = 21.6 Hz), 59.5, 53.4 (d, *J* = 1.8 Hz), 24.7, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3389 (br, w), 2927 (w), 1608 (m), 1485 (s), 1222 (s), 1009 (s), 835 (m), 784 (s), 696 (s).
MS (70 eV, EI): *m/z* (%) = 275 ($[M+2H]^+$, 7), 274 ($[M+H]^+$, 100), 193 (5).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{21}NFO$]; $[M+H]^+$: 274.1607, found: 274.1595
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 14.6 min [minor], t_r = 18.0 min [major]; 93% *ee*.

(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-chloro)phenyl ethyl amine (57j)

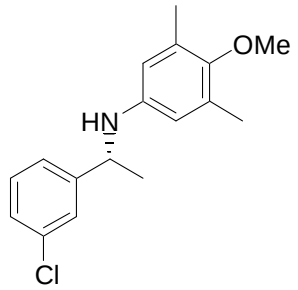


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56j** (144 mg; 0.50 mmol) and obtained as a yellow oil (139 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +8.3 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.13-7.08 (m, 2H), 6.95-6.91 (m, 2H), 6.07 (s, 2H), 4.10 (q, *J* = 6.6 Hz, 1H), 3.38 (s, 3H), 3.27 (br, 1H, NH), 2.17 (s, 6H), 1.06 (d, *J* = 7.1 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 149.7, 144.5, 143.4, 132.6, 131.2, 128.9, 127.5, 114.0, 59.5, 53.1, 24.8, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2926 (w), 1608 (m), 1487 (s), 1337 (w), 1222 (s), 1090 (m), 1010 (s), 825 (s), 730 (m), 695 (m).
MS (70 eV, EI): *m/z* (%) = 289 (M^+, 87), 276 (20), 274 (69), 150 (28), 139 (100), 136 (83).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{20}N^{35}ClO$] 289.1233, found: 289.1227.

The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 13.7 min [minor], t_r = 17.1 min [major]; 92% *ee*.

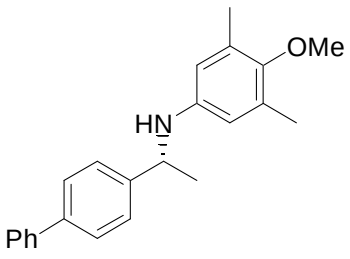
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-chloro)phenyl ethyl amine (57k)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56k** (144 mg; 0.50 mmol) and obtained as a yellow oil (139 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +11.2 (c = 0.4, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.06-7.01 (m, 1H), 6.90-6.71 (m, 2H), 6.69-6.60 (m, 1H), 6.10 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 1H), 3.36 (s, 3H), 3.21 (br, 1H, NH), 2.11 (s, 6H), 1.04 (d, *J* = 6.9 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 151.2, 137.6, 136.4, 132.8, 130.9, 127.9, 127.4, 127.0, 125.9, 112.6, 59.6, 53.8, 25.4, 16.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2926 (w), 1606 (s), 1412 (m), 1262 (s), 1191 (m), 1010 (s), 945 (s), 781 (m), 695 (m).
MS (70 eV, EI): *m/z* (%) = 289 (M^+, 61), 274 (32), 150 (22), 139 (100), 121 (26).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{20}N^{35}ClO$] 289.1233, found: 289.1228.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 14.2 min [minor], t_r = 18.4 min [major]; 90% *ee*.

(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(4-phenyl)phenyl ethyl amine (57l)

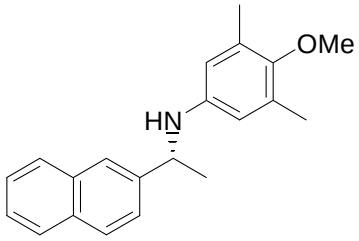


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56l** (165 mg; 0.50 mmol) and obtained as a pale yellow powder (157 mg, 0.47 mmol, 95%).

MP: 156.2-157.9 °C
$[\alpha]_D^{20}$ = +48.7 (c = 0.6, CH_2Cl_2)

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.47-7.43 (m, 4H), 7.31-7.27 (m, 2H), 7.21-7.17 (m, 2H), 7.13-7.09 (m, 1H), 6.20 (s, 2H), 4.34 (q, *J* = 6.7 Hz, 1H), 3.43 (br, 1H, NH), 3.38 (s, 3H), 2.19 (s, 6H), 1.24 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 149.6, 145.2, 143.7, 141.5, 140.2, 131.2, 129.0, 127.7, 127.4, 127.3, 126.6, 114.0, 59.5, 53.5, 25.0, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3354 (w), 2924 (w), 1604 (m), 1484 (s), 1217 (s), 998 (s), 827 (s), 767 (s), 699 (s).
MS (70 eV, EI): *m/z* (%) = 331 (M^+, 41), 316 (24), 181 (100), 165 (19), 151 (26), 136 (32).
HRMS (EI): *m/z* calcd. for: [$C_{23}H_{25}NO$] 331.1936, found: 331.1930.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 17.5 min [minor], t_r = 23.1 min [major]; 92% *ee*.

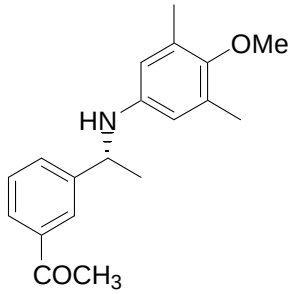
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(2-naphthyl) ethyl amine (57m)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56m** (152 mg; 0.50 mmol) and obtained as a pale yellow oil (144 mg, 0.47 mmol, 94%).

$[\alpha]_D^{20}$ = −22.4 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (600 MHz, C_6D_6): δ = 7.73 (s, 1H), 7.63-7.60 (m, 3H), 7.35 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.24-7.21 (m, 2H), 6.20 (s, 2H), 4.43 (q, *J* = 6.7 Hz, 1H), 3.53 (br, NH, 1H), 3.35 (s, 3H), 2.14 (s, 6H), 1.27 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C-NMR (150 MHz, C_6D_6): δ = 149.6, 143.8, 143.6, 134.2, 133.3, 131.2, 128.7, 128.1, 127.9, 126.2, 125.6, 124.8, 124.6, 114.0, 59.5, 54.0, 24.9, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3405 (br, w), 2864 (m), 2910 (m), 1687 (s), 1510 (s), 1477 (m), 1297 (m), 891 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 305 (M^+, 56), 290 (30), 155 (100), 136 (35).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{23}NO$] 305.1780, found: 305.1785.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 9.1 min [minor], t_r = 10.2 min [major]; 92% *ee*.

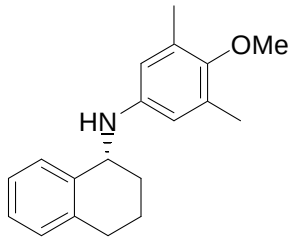
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(3-acetyl)phenyl ethyl amine (57n)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56n** (148 mg; 0.50 mmol) and obtained as a dark brown oil (138 mg, 0.46 mmol, 92%).

$[\alpha]_D^{20}$ = −14.8 (c = 0.50, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.94-7.90 (m, 2H), 7.82-7.54 (m, 3H), 7.29-7.25 (m, 2H), 6.10 (s, 2H), 4.10 (q, *J* = 7.0 Hz, 1H), 3,54 (br, NH, 1H), 3.38 (s, 3H), 2.18 (s, 6H), 1.26 (d, *J* = 7.0 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 196.5, 151.2, 137.6, 134.6, 131.5, 128.2, 127.4, 127.0, 126.8, 112.5, 59.4, 53.5, 26.5, 25.4, 16.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3405 (br, w), 2864 (m), 2910 (m), 1687 (s), 1510 (s), 1477 (m), 1297 (m), 891 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 297 (M^+, 100), 282 (91), 267 (10), 178 (13), 147 (85), 136 (90).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{23}NO_2$] 297.1729, found: 297.1735.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 17.2 min [minor], t_r = 19.5 min [major]; 80% *ee*.

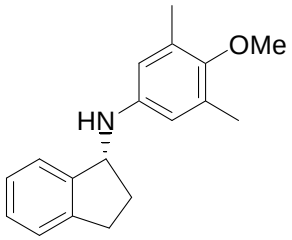
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(1,2,3,4-tetrahydro)naphthyl amine (57o)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56o** (139 mg; 0.50 mmol) and obtained as a brown oil (129 mg, 0.46 mmol, 92%).

$[\alpha]_D^{20}$ = +18.4 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.44-7.42 (m, 1H), 7.10-7.06 (m, 2H), 6.98-6.95 (m, 1H), 6.20 (s, 2H), 4.46-4.39 (m, 1H), 3.50 (s, 3H), 3.23 (br, 1H, NH), 2.63-2.46 (m, 2H), 2.26 (s, 6H), 1.81-1.59 (m, 3H), 1.52-1.42 (m, 1H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 149.5, 144.0, 139.0, 137.5, 131.3, 129.7, 129.1, 127.3, 126.3, 113.6, 59.6, 51.8, 29.6, 29.1, 19.6, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2929 (w), 1605 (m), 1487 (m), 1222 (s), 1010 (s), 835 (m), 742 (s).
MS (70 eV, EI): *m/z* (%) = 281 (M^+, 62), 151 (46), 131 (100), 129 (12), 91 (18).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{23}NO$] 281.1780, found: 281.1780.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 9.2 min [major], t_r = 10.2 min [minor]; 84% *ee*.

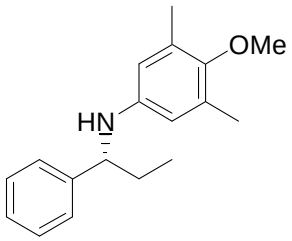
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-(1,2,3,4-tetrahydro)naphthyl amine (57p)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56p** (133 mg; 0.50 mmol) and obtained as a dark brown oil (73 mg, 0.27 mmol, 54%).

$[\alpha]_D^{20}$ = +4.9 (c = 0.4, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.46-7.43 (m, 1H), 7.10-6.99 (m, 3H), 6.20 (s, 2H), 4.44-4.40 (m, 1H), 3.52 (s, 3H), 3.23 (br, 1H, NH), 2.66-2.44 (m, 2H), 2.28 (s, 6H), 1.81-1.52 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 150.1, 144.2, 140.0, 137.5, 131.4, 129.9, 129.1, 127.3, 125.9, 112.6, 59.6, 51.8, 29.6, 19.6, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2949 (w), 1622 (m), 1475 (s), 1298 (m), 1010 (m), 895 (m), 694 (m).
MS (70 eV, EI): *m/z* (%) = 267 (M^+, 35), 165 (31), 131 (100), 129 (12), 91 (18).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{21}NO$] 267.1623, found: 267.1630.
The enantiomer ratio was determined by HPLC using Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 19.2 min [major], t_r = 20.1 min [minor]; 70% *ee*.

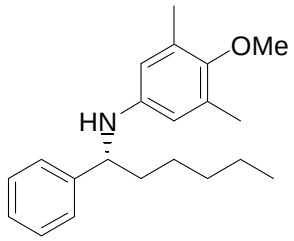
(*R*)–*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl propyl amine (57q)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56q** (134 mg; 0.50 mmol) and obtained as a pale yellow oil (129 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +2.0 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.18-7.17 (m, 1H), 7.13-7.09 (m, 3H), 7.02-6.98 (m, 1H), 6.10 (s, 2H), 4.04 (t, *J* = 6.6 Hz, 1H), 3.43 (br, 1H, NH), 3.30 (s, 3H), 2.10 (s, 6H), 1.55-1.48 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 149.5, 144.8, 144.0, 131.1, 128.7, 127.0, 126.7, 114.0, 60.1, 59.5, 31.9, 16.5, 10.9 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3394 (br, w), 2930 (m), 1608 (m), 1487 (s), 1220 (s), 1009 (s), 835 (m), 750 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 269 (M^+, 21), 240 (100), 136 (9), 91 (15).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{23}NO$] 269.1780, found: 269.1791.
The enantiomer ratio was determined by HPLC using Chiralcel AD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 10.4 min [major], t_r = 12.4 min [minor]; 94% *ee*.

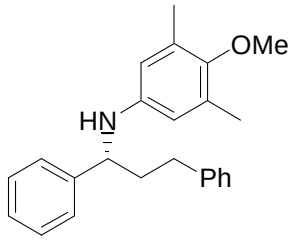
(*R*)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl-hexylamine (57r)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56r** (155 mg; 0.50 mmol) and obtained as a yellow oil (153 mg, 0.49 mmol, 98%).

$[\alpha]_D^{20}$ = +2.4 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.24-7.22 (m, 2H), 7.14-7.12 (m, 2H), 7.04-7.00 (m, 1H), 6.18 (s, 2H), 4.18 (t, *J* = 7.1 Hz, 1H), 3.52 (br, NH), 3.34 (s, 3H), 2.14 (s, 6H), 1.58-1.52 (m, 2H), 1.32-1.15 (m, 6H), 0.82 (t, *J* = 7.0 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 149.5, 145.3, 144.0, 131.1, 128.7, 127.0, 126.7, 114.0, 59.5, 58.8, 39.3, 32.1, 26.4, 22.9, 16.5, 14.2 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2928 (m), 1608 (m), 1488 (m), 1222 (s), 1011 (m), 832 (m), 755 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 327 (M^+, 37), 241 (100), 226 (8), 117 (17).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{29}NO$] 311.2249, found: 311.2248.
The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 11.0 min [minor], t_r = 12.3 min [major]; 95% *ee*.

(*R*)-*N*-(3,5-Dimethyl-4-methoxy)phenyl-1-phenyl-hexylamine (57s)

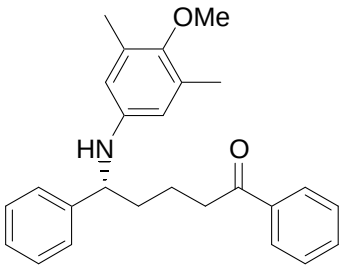


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56s** (172 mg; 0.50 mmol) and obtained as a yellow oil (169 mg, 0.49 mmol, 98%).

$[\alpha]_D^{20}$ = +6.9 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.44-7.14 (m, 6H), 7.00-6.82 (m, 4H), 6.18 (s, 2H), 4.16 (t, *J* = 7.1 Hz, 1H), 3.50 (br, NH, 1H), 3.43 (s, 3H), 2.80-2.69 (m, 2H) 2.34 (s, 6H), 2.12 (t, *J* = 7.0 Hz, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 149.5, 146.5, 145.3, 144.0, 138.2, 131.1, 130.3, 128.7, 127.0, 126.7, 125.4, 114.2, 59.5, 58.8, 26.4, 24.2, 16.5, ppm.
IR (neat): υ_{max} (cm^{-1}) = 2918 (m), 1600 (m), 1425 (m), 1202 (s), 1142 (m), 864 (m), 698 (s).
MS (70 eV, EI): *m/z* (%) = 345 (M^+, 41), 241 (100), 226 (22), 117 (71).
HRMS (EI): *m/z* calcd. for: [$C_{24}H_{27}NO$] 345.2093, found: 345.2081.

The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 11.0 min [minor], t_r = 12.3 min [major]; 95% *ee*.

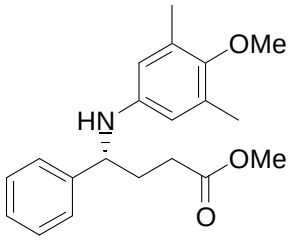
(*R*) –5-[(*N*-(3,5-Dimethyl-4-methoxy)phenyl)amino]-1,5-diphenylpentan-1-one (57t)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56t** (193 mg; 0.50 mmol) and obtained as a dark brown oil (184 mg, 0.47 mmol, 95%).

$[\alpha]_D^{20}$ = −11 (c = 0.4, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.82-7.80 (m, 2H), 7.28-7.26 (m, 2H), 7.18-7.17 (m, 1H), 7.14-7.11 (m, 2H), 7.09-7.02 (m, 3H), 6.24 (s, 2H), 4.25 (t, *J* = 6.7 Hz, 1H), 3.83 (br, NH), 3.37 (s, 3H), 2.48-2.46 (m, 2H), 2.17 (s, 6H), 1.87-1.81 (m, 1H), 1.68-1.59 (m, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 198.7, 149.5, 145.1, 144.0, 137.5, 132.7, 131.1, 128.8, 128.6, 128.2, 127.0, 126.7, 114.0, 59.5, 58.7, 38.6, 37.8, 21.0, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3010 (w), 1788 (m), 1685 (s), 1129 (m), 1155 (s), 1009 (m), 795 (m).
MS (70 eV, EI): *m/z* (%) = 389 ($[M+2H]^+$, 22), 388 ($[M+H]^+$, 100), 237 (15).
HRMS (EI): *m/z* calcd. for: [$C_{26}H_{30}NO_2$] 388.2270, found: 388.2277.
The enantiomer ratio was determined by HPLC using a Chiralcel AD column (flow rate 0.2 mL/min, heptane/iPrOH: 80/20, λ= 215 nm, 25 °C); t_r = 57.0 min [major], t_r = 64.5 min [minor]; 99% *ee*.

(*R*)-Methyl 4-[(*N*-(3,5-dimethyl-4-methoxy)phenyl)amino]-4-phenyl butanoate (57u)

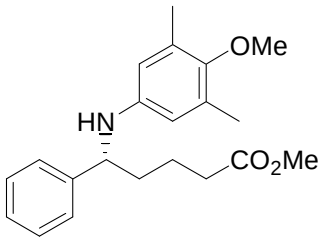


Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56u** (163 mg; 0.50 mmol) and obtained as a brown oil (154 mg, 0.47 mmol, 94%).

$[\alpha]_D^{20}$ = +21 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.17 (s, 1H), 7.13-7.09 (m, 2H), 7.04-7.00 (m, 2H), 6.19 (s, 2H), 4.24 (t, *J* = 6.8 Hz, 1H), 3.72 (br, NH), 3.35 (s, 3H), 3.30 (s, 3H), 2.80 (t, *J* = 6.8 Hz, 1H), 2.53 (t, *J* = 6.4 Hz, 1H), 2.21-2.16 (m, 2H), 2.15 (s, 6H) ppm.

^{13}C-NMR (100 MHz, C_6D_6): δ = 173.5, 149.6, 143.7, 132.8, 131.1, 128.8, 128.5, 126.6, 114.0, 59.4, 58.1, 51.1, 33.6, 31.1, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3393 (br, w), 2949 (w), 1732 (s), 1488 (s), 1220 (s), 1162 (s), 1009 (s), 837 (m), 750 (s), 700 (s).
MS (70 eV, EI): *m/z* (%) = 327 (M^+, 37), 241 (100), 226 (8), 117 (17).
HRMS (EI): *m/z* calcd. for: [$C_{20}H_{25}NO_3$] 327.1834, found: 327.1825.
The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 80/20, λ= 215 nm, 25 °C);
t_r = 19.5 min [major], t_r = 25.3 min [minor]; 92% *ee*.

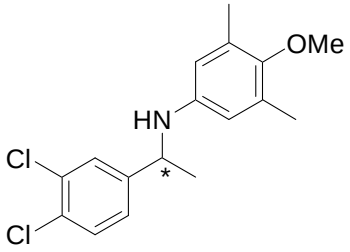
(*R*)-Methyl 5-[(*N*-(3,5-dimethyl-4-methoxy)phenyl)amino]-4-phenyl pentanoate (57v)



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56v** (170 mg; 0.50 mmol) and obtained as a yellow oil (164 mg, 0.48 mmol, 96%).

$[\alpha]_D^{20}$ = +8 (c = 0.6, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.21-7.19 (m, 2H), 7.16-7.12 (m, 2H), 7.05-7.03 (m, 1H), 6.19 (s, 2H), 4.17 (t, *J* = 6.2 Hz, 1H) 3.62 (br, NH), 3.37 (s, 3H), 3.30 (s, 3H), 2.17 (s, 6H), 2.04-2.01 (m, 2H), 1.68-1.64 (m, 1H), 1.53-1.51 (m, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 173.1, 149.5, 144.8, 143.8, 131.1, 128.7, 127.1, 126.6, 113.9, 59.5, 58.4, 50.9, 38.4, 33.6, 22.0, 16.5 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2949 (w), 1732 (s), 1684 (m), 1488 (m), 1222 (s), 1152 (m), 1010 (m), 753 (m), 700 (s).
MS (70 eV, EI): *m/z* (%) = 341 (M^+, 100), 310 (13), 241 (45), 240 (46), 225 (18).
HRMS (EI): *m/z* calcd. for: [$C_{21}H_{27}NO_3$] 341.1991, found: 341.1979.
The enantiomer ratio was determined by HPLC using a Chiralcel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 80/20, λ= 215 nm, 25 °C); t_r = 16.1 min [minor], t_r = 17.3 min [major]; 98% *ee*.

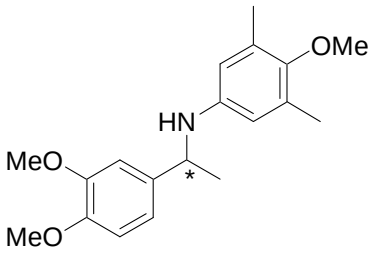
***N*-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethyl)phenyl ethylamine (57w)**



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **57w** (162 mg; 0.50 mmol) and obtained as a yellow oil (156 mg, 0.48 mmol, 96%)

$[\alpha]_D^{20}$ = +18.2 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.51-7.45 (m, 2H), 6.94 (s, 1H), 6.10 (s, 2H), 4.11 (q, *J* = 6.8 Hz, 1H), 3.88 (brs, NH, 1H), 3.43 (s, 3H), 2.22 (s, 6H), 2.00 (d, *J* = 7.0 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 152.2, 145.2, 140.5, 136.2, 135.2, 134.1, 132.2, 130.5, 125.2, 114.0, 56.6, 55.5, 16.7, 16.0 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2992 (w), 1664 (m), 1592 (m), 1434 (m), 1325 (m), 1212 (m), 1062 (s), 879 (s), 76o (m), 654 (s).
MS (70 eV, EI): *m/z* (%) = 323 (M^+, 59), 268 (19), 253 (100), 151 (16).
HRMS (EI): *m/z* calcd. for: [$C_{17}H_{19}NOCl_2$] 323.0844, found: 323.0852.

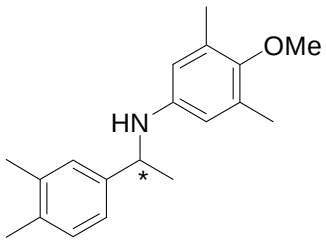
***N*-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethoxy)phenyl ethylamine (57x)**



Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56x** (157 mg; 0.50 mmol) and obtained as a yellow oil (149 mg, 0.47 mmol, 94%)

$[\alpha]_D^{20}$ = +12.7 (c = 0.5, CH_2Cl_2)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.21 (d, *J* = 2.2 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.10-7.05 (m, 1H), 6.11 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 1H), 3.90 (brs, NH, 1H), 3.51 (s, 3H), 3.43 (s, 3H), 3.40 (s, 3H), 2.25 (s, 6H), 1.08 (d, *J* = 6.9 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 152.5, 147.2, 145.2, 141.0, 135.6, 132.4, 126.2, 124.2, 120.4, 112.8, 56.8, 56.6, 56.3, 56.2, 23.7, 16.6 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2935 (w), 2959 (w), 1620 (w), 1594 (m), 1583 (s), 1510 (s), 1452 (m), 1414 (s), 1267 (s), 1217 (s), 1153 (s), 1018 (s), 867 (S), 765 (m).
MS (70 eV, EI): *m/z* (%) = 314 ($[M+H]^+$, 12), 339 (M^+, 55), 299 (18), 298 (100), 268 (6).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{25}NO_3$] 313.1678, found: 313.1665.

***N*-(3,5-dimethyl-4-methoxyphenyl)-1-(3,4-dimethyl)phenyl ethylamine (57y)**



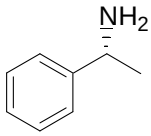
Prepared according to the typical procedure **TP8**, using the iridium catalyst **46a** (9.0 mg; 0.05 mmol) and imine **56y** (140 mg; 0.50 mmol) and obtained as a yellow oil (134 mg, 0.47 mmol, 94%)

$[\alpha]_D^{20}$ = +4.5 (c = 0.5, CH_2Cl_2)

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.22-7.18 (m, 1H), 7.10-7.06 (m, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.32 (s, 2H), 4.12 (q, *J* = 7.0 Hz, 1H), 3.85 (brs, NH, 1H), 3.42 (s, 3H), 2.34 (s, 3H), 2.30 (s, 3H), 2.25 (s, 6H), 1.00 (d, *J* = 7.0 Hz, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 151.2, 140.2, 139.2, 135.4, 128.3, 124.2, 120.1, 111.2, 59.4, 55.2, 23.2, 21.5, 16.7, 16.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 2912 (w), 1645 (w), 1585 (m), 1464 (m), 1398 (m), 1208 (m), 1118 (s), 1002 (s), 879 (s), 765 (m).
MS (70 eV, EI): *m/z* (%) = 283 (M^+, 25), 268 (21), 253 (100), 151 (12).
HRMS (EI): *m/z* calcd. for: [$C_{19}H_{25}NO$] 283.1936, found: 283.1665.

8. Synthesis of Chrial Primary Amines and Lactams

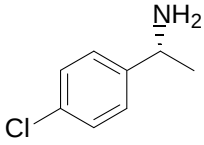
(*R*)–α-methyl benzylamine (58)[136]



Prepared according to the typical procedure **TP9**, using the chiral secondary amine **57a** (102 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (42 mg, 0.34 mmol, 85%).

$[\alpha]_D^{20}$ = +28.9 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 6.8 Hz, 3H), 1.68 (br, 2H), 4.25 (q, *J* = 6.8 Hz, 1H), 7.30-7.43 (m, 5H) ppm.

(*R*)–α-methyl benzylamine (59)[137]

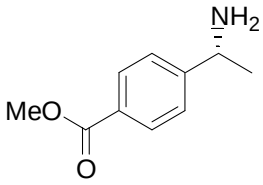


Prepared according to the typical procedure **TP9**, using the chiral secondary amine **57j** (116 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (51 mg; 0.33 mmol, 82%).

$[\alpha]_D^{20}$ = +18.9 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.48 (d, *J* = 7.0 Hz, 3H), 1.62 (br, 2H), 4.21 (q, *J* = 6.9 Hz, 1H), 7.15-7.17 (m, 2H), 7.87-7.99 (m, 2H) ppm.

(*R*)–Methyl-4-(1-aminoethyl)benzoate ester (60)[138]

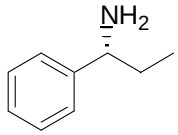
[136] Chi, Y.; Zhou, Y.; Zhang, X. *J. Org. Chem.* **2003,** *10*, 4120.
[137] Mereyala, H. B.; Pola, P. *Tetrahedron: Asymmetry* **2003,** *14*, 2683.
[138] Shawn, I. P.; McWilliams, J.; Secord, C.; Elizabeth, A.; Dale, M. R.; Todd, N. D.; Kress, M. H. *Tetrahedron Lett.* **2006,** *47*, 6409.



Prepared according to the typical procedure **TP9**, using the chiral secondary amine **57e** (126 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (63 mg; 0.35 mmol, 87%).

$[\alpha]_D^{20}$ = +21.9 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.99-7.87 (m, 2H), 7.17-7.15 (m, 2H), 4.20 (q, *J* = 6.9 Hz, 1H), 3.38 (s, 3H), 1.60 (br, 2H), 1.48 (d, *J* = 7.0 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 166.8, 151.4, 129.1, 127.0, 126.1, 52.6, 51.8, 25.8 ppm.
MS (70 eV, EI): *m/z* (%) = 179 (M^+, 18), 121 (20), 107 (18), 106 (100), 91 (2).
HRMS (EI): *m/z* calcd. for: [$C_{10}H_{13}NO_2$] 179.2158, found: 179.2165.

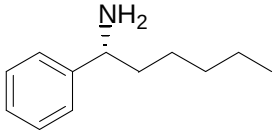
(*R*)-1-Phenyl-1-propylamine (61)[7]



Prepared according to the typical procedure **TP9**, using the chiral secondary amine **57q** (108 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (44 mg; 0.32 mmol, 80%).

^{1}H-NMR (300 MHz, $CDCl_3$): 7.39-7.15 (m, 5H), 3.80 (t, *J* = 6.8 Hz, 1H), 1.75 (m, 2H), 1.60 (s, 2H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): 144.2, 131.1, 127.0, 126.4, 55.0, 32.5, 12.5 ppm.
$[\alpha]_D^{20}$ = + 10.8 (c = 1.0, EtOH)
MS (70 eV, EI): *m/z* (%) = 135 (M^+, 2), 121 (10), 106 (100), 91 (40).
HRMS (EI): *m/z* calcd. for: [$C_9H_{13}N$] 135.1048 found 135.1040

(*R*)-(+)-1-Phenyl-1-hexanamine (62)[139]



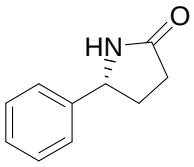
Prepared according to the typical procedure **TP9**, using the chiral secondary amine **57r** (125 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a pale yellow oil (55 mg; 0.31 mmol, 78%).

$[\alpha]_D^{20}$ = +4.8 (c = 1.6, EtOH)
^{1}H-NMR (300 MHz, $CDCl_3$): 7.32-7.10 (m, 5H), 3.85 (t, *J* = 6.8 Hz, 1H), 1.80-1.00 (m, 10H), 0.84 (t, *J* = 7.0 Hz, 1H) ppm.

[139] Bataille, P.; Paterne, M.; Brown, E. *Tetrahedron: Asymmetry* **1998,** *9*, 2181.

^{13}C-NMR (75 MHz, $CDCl_3$): 144.0, 131.1, 127.0, 126.7, 55.1, 14.1, 38.5, 32.6, 27.1, 22.5 ppm.
MS (70 eV, EI): *m/z* (%) = 177 (M^+, 5), 160 (6), 118 (12), 106 (100), 91 (36).
HRMS (EI): *m/z* calcd. for: [$C_{12}H_{19}N$] 177.1517 found 177.1521

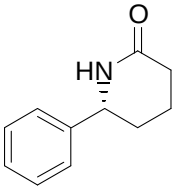
(*R*)-5-Phenylpyrrolidin-2-one (63)[140]



Prepared according to the typical procedure **TP9**, using the chiral secondary amine **57u** (131 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a pale yellow oil (46 mg; 0.29 mmol, 72%).

$[\alpha]_D^{20}$ = +41.0 (c = 0.4, CH_2Cl_2)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.97-2.11 (m, 1H), 2.40-2.72 (m, 3H), 4.82 (t, *J* = 7.0 Hz, 1H), 6.70 (brs, NH), 7.34-7.48 (m, 5H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 30.9, 31.4, 58.2, 125.8, 127.8, 128.9, 143.0, 178.9 ppm.
MS (70 eV, EI): *m/z* (%) = 161 (M^+, 67), 117 (100), 104 (8), 77 (17).
HRMS (EI): *m/z* calcd. for: [$C_{10}H_{11}NO$] 161.0841, found: 161.0843.
The enantiomer ratio was determined by Chiral GC using a Chiral DEX-CB column (100 °C (5), 5 °C/min to 160 °C (60)) t_r = 36.7 min [major], t_r = 41.0 min [minor]; 92% *ee*.

(*R*)-6-Phenylpiperidin-2-one (64)[141]



Prepared according to the typical procedure **TP9**, using the chiral secondary amine **57v** (137 mg; 0.40 mmol) and cerium ammonium nitrate (880 mg; 1.6 mmol; 4.0 equiv) and obtained as a yellow oil (55 mg; 0.31 mmol, 78%).

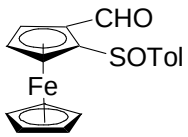
MP: 118-119 °C
$[\alpha]_D^{20}$ = +40.0 (c = 2.0, $CHCl_3$)
^{1}H-NMR (400 MHz, C_6D_6): δ = 1.19-1.27 (m, 2H), 1.42-1.48 (m, 2H), 2.04-2.11 (m, 1H), 2.15-2.22 (m, 1H), 3.94-3.97 (m, 1H), 6.80 (br, s, NH), 6.98-7.06 (m, 3H), 7.09-7.13 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 19.6, 31.2, 32.1, 57.3, 126.4, 127.5, 128.7, 143.7, 171.4 ppm.
IR (neat): υ_{max} (cm^{-1}) = 3266 (br, w), 2955 (w), 1655 (s), 1623 (s), 1478 (s), 1355 (s), 1175 (m), 737 (s), 695 (s).

[140] Ramachandran, P. V.; Burghardt, T. E. *Chem. Eur. J.* **2005,** *11*, 4387.
[141] Davis, F. A.; Chao, B.; Fang, T.; Szewczyk, J. M. *Org. Lett.* **2000**, *2*, 1041.

MS (70 eV, EI): *m/z* (%) = 176 ($[M+H]^+$, 12), 175 (M^+, 100), 119 (26), 106 (34), 98 (10), 77 (11).
HRMS (EI): *m/z* calcd. for: [$C_{11}H_{13}NO$] 175.0997 found 175.0989
The enantiomer ratio was determined by Chiral GC using a Chiral DEX-CB column (100 °C (5), 5 °C/min to 160 °C (60))
t_r = 38.7 min [minor], t_r = 40.8 min [major]; 97% *ee*.

9. Synthesis of bisferrocenyl P,P-ligands

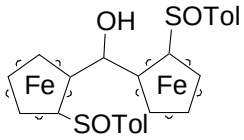
(*S*$_{Fc}$, *S*)-[2-(Formyl)-ferrocen-1-yl]-*p*-tolylsulfoxide (65)



Prepared according to the **TP1** using sulfoxide **14** (1.30 g; 4.0 mmol), THF (40 mL), LDA (2.2 mL, 4.4 mmol). The reaction mixture stirred at -78 °C for 30 min and added DMF (0.45 mL; 6.0 mmol; 1.5 equiv) as an electrophile and stirred for 1h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h before quenching with a Sat. NH_4Cl solution (20 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1), provided the desired compound (1.13 g, 3.20 mmol, 80 %) as a red solid.

MP: 149.1-149.8 °C
[α]$_D^{20}$ = −188 (c = 0.1, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 11.05 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.4 Hz, 2H), 4.81 (s, 1H), 4.34 (s, 1H), 4.17 (s, 5H), 3.98-3.97 (m, 1H), 1.89 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 191.7, 144.4, 140.6, 129.9, 124.0, 98.5, 79.4, 73.8, 72.5, 71.7, 70.3, 21.0 ppm.
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, w), 3093 (w), 1673 (s), 1435 (m), 1227 (m), 1033 (s), 817 (m), 754 (m).
MS (70 eV, EI): *m/z* (%) = 352 (M^+, 100), 335 (21), 244 (54), 211 (20).
HRMS (EI): *m/z* calcd. for: [$C_{18}H_{16}{}^{56}FeO_2{}^{32}S$] 352.0220, found: 352.0211

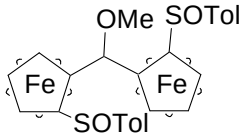
(*S*$_{Fc}$)-1-[(*S*)-*p*-Tolylsulfinyl]-2-[α-hydroxy-((*S*$_{Fc}$)-1-((*S*)-*p*-tolylsulfinyl))ferrocenyl]met- -hylferrocene (66)



Prepared according to the **TP1** using sulfoxide **14** (260 mg; 0.80 mmol), THF (8 mL), LDA (0.44 mL; 0.88 mmol, 1.1 equiv). The reaction mixture stirred at -78 °C for 30 min and added ferrocenyl aldehyde **65** (340 mg; 0.96 mmol; 1.2 equiv) as an electrophile and stirred for 1.5 h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h before quenching with a saturated aquesous NH_4Cl solution (15 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, Et_2O), provided the bisferrocenyl alcohol **66** (243 mg, 0.48 mmol, 60 %) as a yellow solid.

MP: 129.1-130.2 °C
$[\alpha]_D^{20}$ = −4.2 (c = 0.1, acetone)
^{1}H-NMR (300 MHz, C_6D_6): δ = 8.26-8.24 (m, 2H), 7.95-7.92 (m, 2H), 7.11-7.04 (m, 4H), 6.01 (d, *J* = 12.0 Hz, 1H), 5.90 (d, *J* = 11.5 Hz, 1H), 4.94-4.90 (m, 2H), 4.20 (s, 5H), 4.09-4.06 (m, 1H), 3.99 (s, 5H), 3.89-3.80 (m, 2H), 3.77-3.74 (m, 1H), 2.10 (s, 3H), 2.06 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 148.5, 147.2, 146.8, 145.4, 135.2, 134.7, 130.2, 127.8, 99.9, 99.0, 85.4, 84.7, 77.8, 76.2, 76.0, 74.5, 73.2, 72.4, 71.9, 71.2, 70.9, 24.2, 23.8 ppm.
IR (KBr): υ_{max} (cm^{-1}) = 3463 (br, w), 2793 (m), 1665 (m), 1598 (m), 1435 (m), 1389 (m), 1212 (m), 1063 (s), 817 (m), 754 (m).
MS (70 eV, EI): *m/z* (%) = 676 (M^+, 60), 659 (100), 324 (55), 211 (10).
HRMS (EI): *m/z* calcd. for: [$C_{35}H_{32}{}^{56}Fe_2O_3{}^{32}S_2$] 676.0492, found: 676.0500

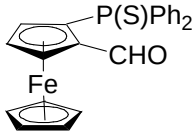
(S_{Fc})-1-[(*S*)-*p*-Tolylsulfinyl]-2-[α-methoxy-((S_{Fc})-1-((*S*)-*p*-tolylsulfinyl))ferrocenyl]met- -hylferrocene (67)



Prepared according to the typical procedure **TP4**, using KH (19 mg, 0.45 mmol, 1.50 equiv.) in THF (2.0 mL), bisferrocenyl alcohol **66** (203 mg, 0.3 mmol) in THF (1.0 mL) and CH_3I (135 mg; 0.05 mL, 0.90 mmol, 3.0 equiv). After quenching the reaction mixture with a saturated aqueous NH_4Cl solution (5 mL) and typical work-up, the residue was purified by flash chromatography (silica gel, Et_2O) to furnish the methyl ether **68** (176 mg, 0.26 mmol, 85 %) as a yellow solid.

MP: 140.6-142.1 °C
$[\alpha]_D^{20}$ = −6.4 (c = 0.1, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 8.16 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 4H), 5.91 (s, 1H), 4.92-4.90 (m, 1H), 4.40-4.36 (m, 1H), 4.17 (s, 5H), 4.40-3.97 (m, 1H), 3.90 (s, 5H), 3.88-3.86 (m, 1H), 3.82-3.81 (m, 1H), 3.77-3.75 (m, 1H), 3.74 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 146.2, 144.2, 141.3, 141.1, 130.2, 130.1, 125.6, 124.2, 99.1, 98.8, 80.2, 79.4, 75.4, 74.8, 74.2, 72.5, 72.0, 71.9, 71.0, 70.2, 70.0, 59.7, 23.0, 21.2 ppm
IR(KBr): υ_{max} (cm^{-1}) = 3436 (br, w), 3086 (w), 1632 (w), 1492 (w), 1108 (m), 1089 (s), 1039 (s), 813 (s).
MS (70 eV, EI): *m/z* (%) = 690 (M^+, 7), 628 (17), 625 (19), 507 (32), 506 (98), 384 (30), 383 (100).
HRMS (EI): *m/z* calcd. for: [$C_{36}H_{34}{}^{56}Fe_2O_3{}^{32}S_2$] 690.0648, found: 690.0608

(R_{Fc})-1-(Diphenylphosphinothioyl)-2-ferrocenylcarboxaldehyde (68)

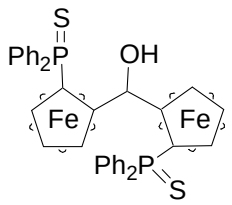


Prepared according to the **TP3** using sulfoxide **30** (1.62 g; 3.0 mmol), THF (40 mL), PhLi (18 mL, 3.6 mmol). The reaction mixture stirred at -78 °C for 10 min and added DMF (0.35 mL;

6.0 mmol; 1.5 equiv) as an electrophile and stirred for 1h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 1 h before quenching with a Sat. NH_4Cl solution (20 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 1:1), provided the desired compound (840 mg, 1.95 mmol, 65 %) as a red oil.

$[\alpha]_D^{20}$ = +68.1 (c = 0.1, acetone).
^{1}H-NMR (300 MHz, C_6D_6): δ = 11.25 (s, 1H), 7.88-7.80 (m, 2H), 7.72-7.65 (m, 2H), 7.05-7.00 (m, 3H), 6.92-6.89 (m, 3H), 5.17-5.15 (m, 1H), 4.21 (s, 5H), 4.04-4.03 (m, 1H), 3.82-3.80 (m, 1H) ppm.
^{13}C-NMR (75 MHz, C_6D_6): δ = 193.4, 135.7 (d, *J* = 87.1 Hz), 133.9 (d, *J* = 85.6 Hz, 1H), 132.4 (d, *J* = 11.0 Hz), 132.0 (d, *J* = 10.6 Hz), 131.4 (d, *J* = 2.9 Hz), 131.4 (d, *J* = 2.9 Hz), 128.6 (d, *J* = 12.7 Hz), 128.1 (d, *J* = 13.0 Hz), 83.9 (d, *J* = 10.1 Hz), 80.2 (d, *J* = 90.2 Hz), 79.2 (d, *J* = 10.8 Hz), 72.8 (d, *J* = 9.7 Hz), 72.3 (d, *J* = 7.6 Hz), 72.0 ppm.
IR(neat): υ_{max} (cm^{-1}) = 3436 (br, w), 2921 (w), 1664 (s), 1437 (m), 1243 (m), 1101 (m), 830 (w), 717 (m), 656 (m).
MS (70 eV, EI): *m/z* (%) = 430 (M^+, 100), 402 (39), 365 (29), 338 (17), 337 (82).
HRMS (EI): *m/z* calcd. for: [$C_{23}H_{19}{}^{56}FeOP^{32}S$] 430.0244, found: 430.0239

(R_{Fc})-1-Diphenylphosphinothioyl-2-[α-hydroxy-((R_{Fc})-1-(diphenylphosphinothioyl)) ferrocenyl]methylferrocene (69)

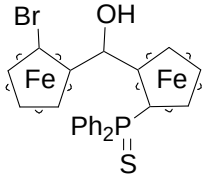


Prepared according to the **TP3** using sulfoxide **30** (270 mg; 0.5 mmol), THF (5 mL), PhLi (3 mL; 0.6 mmo, 1.2 equiv). The reaction mixture stirred at -78 °C for 10 min and ferrocenylaldehyde **68** (259 mg; 0.6 mmol; 1.2 equiv) as an electrophile and stirred for 1.5 h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 2 h before quenching with a saturated aqueous NH_4Cl solution (10 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 10:1), provided the desired compound (230 mg, 0.28 mmol, 55 %) as a yellow solid.

MP: 281 °C (decomposed)
$[\alpha]_D^{20}$ = +12 (c = 0.1, acetone).
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.74-7.60 (m, 4H), 7.48-7.25 (m, 16H), 6.20 (d, *J* = 12.5 Hz, 1H), 5.81 (d, *J* = 11.5 Hz, 1H), 4.74-4.73 (m, 2H), 4.66-4.65 (m, 2H), 4.30 (s, 5H), 4.27 (s, 5H), 3.31-3.28 (m, 2H), 3.19-3.15 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 139.1 (d, *J* = 86.8 Hz), 137.4 (d, *J* = 87.9 Hz), 137.3 (d, *J* = 86.3 Hz), 135.9 (d, *J* = 86.0 Hz), 133.7 (d, *J* = 10.9 Hz), 133.5 (d, *J* = 7.9 Hz), 132.6 (d, *J* = 8.0 Hz), 131.7 (d, *J* = 11.4 Hz), 131.2 (d, *J* = 2.8 Hz), 130.9 (d, *J* = 3.8 Hz), 130.0 (d, *J* = 2.9 Hz), 129.1 (d, *J* = 3.2 Hz), 128.9 (d, *J* = 9.9 Hz), 126.9 (d, *J* = 11.1 Hz), 98.6 (d, *J* = 13.2 Hz), 96.0 (d, *J* = 10.5 Hz), 76.9 (d, *J* = 13.1 Hz), 75.4 (d, *J* = 9.2 Hz), 75.0, 74.8 (d, *J* = 94.9 Hz), 73.7 (d, *J* = 11.2 Hz), 73.0 (d, *J* = 9.9 Hz), 72.9 (d, *J* = 9.8 Hz), 71.9 (d, *J* = 5.4 Hz), 71.8 (d, *J* = 92.8 Hz), 71.9, 71.2, 69.9 (d *J* = 11.9 Hz), 69.1 (d, *J* = 10.6 Hz) ppm
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, s), 1619 (m), 1452 (m), 1338 (m), 1100 (m), 828 (m), 797 (m), 714 (m), 694 (m).
MS (70 eV, EI): *m/z* (%) = 832 (M^+, 40), 817 (100), 695 (14), 445 (29).

HRMS (EI): *m/z* calcd. for: [$C_{18}H_{16}{}^{56}FeO_2{}^{32}S$] 832.0538, found: 832.0530

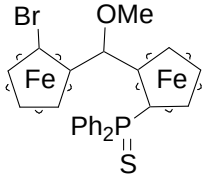
(R_{Fc})-1-Bromo-2-[α-hydroxy-((R_{Fc})-1-(diphenylphosphinothioyl)) ferrocenyl]methyl-ferrocene (70)



Prepared according to the **TP3** using sulfoxide **30** (1.10 g; 2.0 mmol), THF (10 mL), PhLi (11 mL; 2.2 mmol). The reaction mixture stirred at -78 °C for 10 min and added 1-bromo-2-ferrocenylcarboxaldehyde **20b** (645 mg; 2.2 mmol; 1.2 equiv) as an electrophile and stirred for 1h at -78 °C. The reaction mixture was warmed to room temperature and stirred for 2 h before quenching with a saturated aqueous NH_4Cl solution (20 mL). After the typical work-up, the crude product was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 8:1), provided the desired compound (807 mg, 1.16 mmol, 58%) as a yellow solid.

MP: 171-172.8 °C
$[\alpha]_D^{20}$ = +61.2 (c = 0.2, acetone).
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.74-7.60 (m, 4H), 7.48-7.25 (m, 16H), 6.20 (d, *J* = 12.5 Hz, 1H), 5.81 (d, *J* = 11.5 Hz, 1H), 4.74-4.73 (m, 2H), 4.66-4.65 (m, 2H), 4.30 (s, 5H), 4.27 (s, 5H), 3.31-3.28 (m, 2H), 3.19-3.15 (m, 2H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 138.7 (d, *J* = 89.5 Hz), 136.4 (d, *J* = 85.2 Hz), 134.2 (d, *J* = 10.5 Hz), 134.0 (d, *J* = 10.7 Hz), 132.0 (d, *J* = 3.0 Hz), 131.4 (d, *J* = 2.8 Hz), 129.2 (d, *J* = 12.1 Hz), 128.5 (d, *J* = 13.1 Hz), 95.2 (d, *J* = 12.1 Hz), 91.4, 81.2, 77.2 (d, *J* = 12.2 Hz), 75.2 (d, *J* = 95.2 Hz), 73.8, 73.0 (d, *J* = 9.1 Hz), 72.1, 71.9, 70.5, 70.0 (d, *J* = 10.5 Hz), 67.2, 66.7 ppm
^{31}P-NMR (81 MHz, C_6D_6): δ =+43.19 ppm
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3440 (br, w), 2972 (w), 1678 (m), 1629 (w), 1400 (m), 1378 (m), 1101 (s), 925 (s), 832 (s), 797 (s), 614 (s)
MS (70 eV, EI): *m/z* (%) = 694 (M^+, 100), 677 (70), 382 (10).
HRMS (EI): *m/z* calcd. for: [$C_{33}H_{28}Fe_2P^{32}SO^{79}Br$] 693.9481, found: 693.9491.

(R_{Fc})-1-Bromo-2-[α-methoxy-((R_{Fc})-1-(diphenylphosphinothioyl)) ferrocenyl]methyl-ferrocene (71)

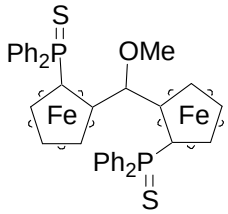


Prepared according to the typical procedure **TP4**, using KH (60 mg, 1.50 mmol, 1.50 equiv.) in THF (2 mL), ferrocenyl alcohol **70** (698 mg, 1.0 mmol) in THF (3 mL) and CH_3I (215 mg; 0.1 mL, 1.50 mmol, 1.50 equiv.). After quenching the reaction mixture with a saturated NH_4Cl and typical work-up, the residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 4:1) to furnish the methyl ether **71** (597 mg, 0.84 mmol, 84%) as a yellow solid.

MP: 181.6-182.6 °C

$[\alpha]_D^{20}$ = +85 (c = 0.2, acetone).
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.07-7.98 (m, 4H), 7.06-7.03 (m, 6H), 6.43 (s, 1H), 4.33-4.29 (m, 2H), 4.21 (s, 5H), 4.20-4.19 (m, 1H), 4.09 (s, 5H), 3.99-3.97 (m, 1H), 3.88-3.87 (m, 2H), 3.12 (s, 3H) ppm.
^{13}C-NMR (100 MHz, C_6D_6): δ = 136.5 (d, *J* = 86.8 Hz), 135.3 (d, *J* = 84.7 Hz), 132.8 (d, *J* = 10.7 Hz), 132.7 (d, *J* = 10.7 Hz), 130.9 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 2.9 Hz), 127.93 (d, *J* = 12.1 Hz), 127.9 (d, *J* = 12.8 Hz), 94.3 (d, *J* = 11.9 Hz), 91.2, 79.1, 75.3 (d, *J* = 12.2 Hz), 74.5 (d, *J* = 94.2 Hz), 72.9, 72.8 (d, *J* = 8.5 Hz), 71.9, 71.4, 69.6, 69.3 (d, *J* = 10.5 Hz), 66.2, 65.7, 56.3 ppm
^{31}P-NMR (81 MHz, C_6D_6): δ = +41.90 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, s), 2930 (w), 1629 (w), 1436 (m), 1231 (m), 1101 (s), 823 (s), 717 (s), 694 (s)
MS (70 eV, EI): *m/z* (%) = 708 (M^+, 100), 413 (20), 382 (60).
HRMS (EI): *m/z* calcd. for: [$C_{33}H_{28}Fe_2P^{32}SO^{79}Br$] 707.9637, found: 707.9613.

(R_{Fc})-1-Diphenylphosphinothioyl-2-[α-methoxy-((R_{Fc})-1-(diphenylphosphinothioyl)) ferrocenyl]methylferrocene (72)

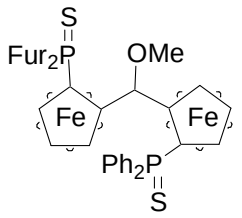


A 25 mL Schlenk flask was charged with bisferrocenylether **71** (355 mg; 0.5 mmol) and THF (3 mL). The reaction mixture was cooled to -78 °C and *n*BuLi (1.6 M solution in pentane; 0.35 mL, 0.55 mmol, 1.1 equiv) and stirred for 15 min. Chlorodiphenylphosphine (168 mg; 0.15 mL, 0.75 mmol, 1.5 equiv) was added and at -78 °C and the reaction mixture was stirred for 1 h before warming to the room temperature. The reaction mixture was stirred at room temperature for 1 h and then sulfur (S_8; 160 mg; 5.0 mmol, 10 equiv) was added a solution in butylamine (2 mL) and the reaction mixture was stirred for 12 h at room temperature. Sat. Nh4Cl was added to the reaction mixture and the aqueous layer was extracted with diethylether (4 x 15 mL). The combined organic layers were washed with water, brine, dried over MgSO4 and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 4:1) to furnish bisphsophne sulfide **72** (323 mg, 0.38 mmol, 76%) as a yellow solid.

MP: 223.4-225.0 °C
$[\alpha]_D^{20}$ = +57.6 (c = 0.2, acetone)
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.11-7.70 (m, 8H), 7.20-6.85 (m, 12H), 6.33 (s, 1H), 4.61-4.42 (m, 2H), 4.25 (s, 5H), 4.07 (s, 5H), 3.87 (s, 3H), 3.66-3.56 (m, 2H), 3.48-3.30 (m, 2H) ppm.
^{13}C-NMR (150 MHz, C_6D_6): δ = 137.1 (d, *J* = 85.4 Hz), 136.4 (d, *J* = 87.5 Hz), 136.3 (d, *J* = 85.3 Hz), 134.8 (d, *J* = 86.2 Hz), 132.8 (d, *J* = 10.6 Hz), 132.7 (d, *J* = 8.3 Hz), 132.6 (d, *J* = 8.0 Hz), 132.4 (d, *J* = d, 10.5 Hz), 130.95 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 3.8 Hz), 130.44 (d, *J* = 3.6 Hz), 130.4 (d, *J* = 2.6 Hz), 128.3 (d, *J* = 9.6 Hz), 127.6 (d, *J* = 11.3 Hz), 98.6 (d, *J* = 12.9 Hz), 96.0 (d, *J* = 10.5 Hz), 75.9 (d, *J* = 12.9 Hz), 75.0 (d, *J* = 9.0 Hz), 74.9, 74.5 (d, *J* = 92.9 Hz), 73.7 (d, *J* = 12.2 Hz), 73.0 (d, *J* = 9.9 Hz), 72.6 (d, *J* = 9.8 Hz), 71.4 (d, *J* = 4.7 Hz), 71.1 (d, *J* = 98.8 Hz), 71.3, 71.2, 68.9 (d *J* = 10.9 Hz), 68.1 (d, *J* = 10.6 Hz), 59.8 ppm
^{31}P-NMR (81 MHz, CDCl3): δ = +43.98, +41.46 ppm.

IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, s), 1629 (m), 1436 (m), 1101 (m), 1004 (m), 820 (m), 717 (m), 694 (m).
MS (70 eV, EI): *m/z* (%) = 846 (M^+, 100), 782 (3), 695 (5), 630 (87), 445 (25), 324 (46).
HRMS (EI): *m/z* calcd. for: [$C_{46}H_{40}Fe_2P_2O^{32}S_2$] 846.0695, found: 846.0668.

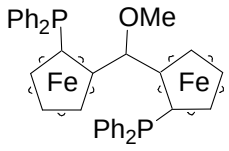
(R_{Fc})-1-Diphenylphosphinothioyl-2-[α-methoxy-((R_{Fc})-1-(bis(2-furylphosphinothioyl)) ferrocenyl]methylferrocene (73)



A 25 mL Schlenk flask was charged with bisferrocenylether **71** (355 mg; 0.5 mmol) and THF (3 mL). The reaction mixture was cooled to -78 °C and *n*BuLi (1.6 M solution in pentane; 0.35 mL, 0.55 mmol, 1.1 equiv) and stirred for 15 min. Chlorobis(2-furyl)phosphine (152 mg; 0.75 mmol, 1.5 equiv) was added and at -78 °C and the reaction mixture was stirred for 1 h before warming to the room temperature. The reaction mixture was stirred at room temperature for 1 h and then sulfur (160 mg; 5.0 mmol, 10 equiv) was added a solution in butylamine (2 mL) and the reaction mixture was stirred for 12 h at room temperature. Sat. NH_4Cl was added to the reaction mixture and the aqueous layer was extracted with diethylether (4 x 15 mL). The combined organic layers were washed with water, brine, dried over MgSO4 and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 4:1) to furnish bisphsophne sulfide **73** (332 mg, 0.40 mmol, 80%) as a red solid.

MP: 206.9-207.6 °C
$[\alpha]_D^{20}$ = +35.8 (c = 0.2, acetone)
^{1}H-NMR (400 MHz, C_6D_6): δ = 8.01-7.98 (m, 2H), 7.86-7.82 (m, 2H), 7.25 (t, *J* = 3.3 Hz, 1H), 7.13 (t, *J* = 2.8 Hz, 1H), 7.08-7.01 (m, 8H), 6.41 (s, 1H), 5.93-5.91 (m, 2H), 4.56-4.52 (m, 3H), 4.39 (s, 5H), 4.12 (s, 5H), 3.83-3.82 (m, 1H), 3.76 (s, 3H), 3.71-3.70 (m, 1H), 3.54-3.53 (m, 1H) ppm.
^{13}C-NMR (100 MHz, $CDCl_3$): δ = 151.3 (d, *J* = 98.0 Hz), 150.0 (d, *J* = 92.2 Hz), 147.3 (d, *J* = 7.0 Hz), 147.2 (d, *J* = 7.0 Hz), 137.0 (d, *J* = 85.0 Hz), 136.6 (d, *J* = 87.8 Hz), 132.8 (d, *J* = 8.1 Hz), 132.7 (d, *J* = 8.4 Hz), 130.4 (d, *J* = 2.8 Hz), 130.3 (d, *J* = 3.0 Hz), 127.9 (d, *J* = 2.8 Hz), 127.7 (d, *J* = 13.2 Hz), 122.3 (d, *J* = 13.3 Hz), 122.1 (d, *J* = 11.4 Hz), 111.4 (d, *J* = 9.1 Hz), 111.1 (d, *J* = 9.5 Hz), 98.5 (d, *J* = 15.6 Hz), 96.3 (d, *J* = 10.3 Hz), 75.9 (d, *J* = 13.5 Hz), 74.5 (d, *J* = 92.8 Hz), 74.9 (d, *J* = 92.7 Hz), 74.4 (d, *J* = 9.3 Hz), 74.4, 73.3 (d, *J* = 13.5 Hz), 72.3 (d, *J* = 10.9 Hz), 71.48, 71.47, 69.7 (d, *J* = 11.6 Hz), 68.4 (d, *J* = 10.6 Hz), 59.4 ppm
^{31}P-NMR (81 MHz, CDCl3): δ = +44.04, +10.81 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, s), 1631 (m), 1436 (m), 1158 (m), 1101 (m), 1003 (m), 757 (s), 691 (s), 658 (m).
MS (70 eV, ESI): *m/z* (%) = 826 (M^+, 27), 795 (100), 645 (55), 397 (7).
HRMS (EI): *m/z* calcd. for: [$C_{42}H_{36}{}^{56}Fe_2P_2{}^{32}S_2O_3$] 826.0280, found: 826. 0293.

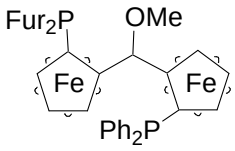
(R_{Fc})-1-Diphenylphosphino-2-[α-methoxy-((R_{Fc})-1-(diphenylphosphino))ferrocenyl]methylferrocene (11a)



A 25 mL Schlenk flask was charged with bisferrocenylether **71** (355 mg; 0.5 mmol) and THF (3 mL). The reaction mixture was cooled to -78 °C and *n*BuLi (1.6 M solution in pentane; 0.35 mL, 0.55 mmol, 1.1 equiv) and stirred for 15 min. Chlorodiphenylphosphine (168 mg; 0.15 mL, 0.75 mmol, 1.5 equiv) was added and at -78 °C and the reaction mixture was stirred for 1 h before warming to the room temperature. The reaction mixture was stirred at room temperature for 1 h and then sulfur (S_8; 160 mg; 5.0 mmol, 10 equiv) was added a solution in butylamine (2 mL) and the reaction mixture was stirred for 12 h at room temperature. Sat. Nh4Cl was added to the reaction mixture and the aqueous layer was extracted with diethylether (4 x 15 mL). The combined organic layers were washed with water, brine, dried over MgSO4 and concentrated in vacuum. The residue was purified by flash chromatography (silica gel, *n*-pentane:Et_2O 4:1) to furnish bisphsophne sulfide **72** (323 mg, 0.38 mmol, 76%) as a yellow solid.

MP: 123.0-124.0 °C
$[\alpha]_D^{20}$ = +17.6 (c = 0.2, acetone)
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.80-7.71 (m, 2H), 7.62-7.39 (m, 6H), 7.15-7.05 (m, 12H), 5.63-5.61 (m, 1H), 4.34-4.29 (m, 2H), 3.95-3.94 (m, 2H), 3.91 (s, 5H), 3.80 (s, 8H), 3.67-3.66 (m, 1H), 2.99-2.96 (m, 1H) ppm.
^{13}C-NMR (150 MHz, C_6D_6): δ = 139.1 (d, *J* = 13.0 Hz), 137.2(d, *J* = 12.1 Hz), 137.0 (d, *J* = 2.1 Hz), 136.5 (d, *J* = 13.0 Hz), 134.8 (d, *J* = 22.1 Hz), 132.0 (d, *J* = 11.8 Hz), 129.6 (d, *J* = 11.2 Hz), 129.0 (d, *J* = 22.1 Hz), 128.9 (d, *J* = 5.5 Hz), 128.6 (d, *J* = 21.8 Hz), 127.4 (d, *J* = 6.2 Hz), 126.2 (d, *J* = 22.6 Hz), 126.0 (d, *J* = 3.2 Hz), 122.1 (d, *J* = 3.4 Hz), 111.6 (d, *J* = 10.2 Hz), 106.0 (d, *J* = 10.5 Hz), 74.5 (d, *J* = 24.2 Hz), 74.0 (d, *J* = 22.9 Hz), 73.9 (d, *J* = 13.1 Hz), , 73.5 (d, *J* = 12.9 Hz), 72.7 (d, *J* = 13.1 Hz), 72.2 (d, *J* = 5.6 Hz), 72.0 (d, *J* = 6.0 Hz), 71.0 70.5 (d, *J* = 14.9 Hz), 69.7, 69.2, 67.3 (d *J* = 5.9 Hz), 67.1 (d, *J* = 4.2 Hz), 57.6 ppm
^{31}P-NMR (81 MHz, CDCl3): δ = -19.58 (d, *J* = 7.6 Hz), -23.95 (d, *J* = 6.9 Hz) ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, s), 3068 (w), 1629 (w), 1434 (m), 1107 (m), 1002 (m), 818 (m), 742 (s), 698 (s).
MS (70 eV, EI): *m/z* (%) = 782 (M^+, 14), 717 (15), 630 (90), 446 (30), 445 (100), 379 (8).
HRMS (EI): *m/z* calcd. for: [$C_{46}H_{40}Fe_2OP_2$] 782.1253, found: 782.1241.

(*R*$_{Fc}$)-1-Diphenylphosphino-2-[α-methoxy-((*R*$_{Fc}$)-1-(bis(2-furylphosphino))ferrocenyl] methylferrocene (11b)



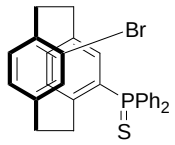
Prepared according to **TP5**, using bisferrocenylsulfide **73** (165 mg; 0.20 mmol) in THF (2 mL) and Raney-Ni (Raney Ni in water; 704 mg; 12 mmol, 60 equiv) in MeOH (25 mL) and obtained the desired product **11b** (130 mg, 0.17 mmol, 85%) as a yellow solid.

MP: 126.3-129.0 °C
$[\alpha]_D^{20}$ = +27.0 (c = 0.2, acetone)

^{1}H-NMR (600 MHz, C_6D_6): δ = 7.64 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 5.9 Hz, 2H), 7.13-7.04 (m, 7H), 6.84 (s, 1H), 6.14 (s, 1H), 6.04 (s, 1H), 5.67 (t, *J* = 4.7 Hz, 1H), 5.00 (s, 1H), 4.56 (s, 1H), 4.53 (s, 1H), 4.29-4.25 (m, 1H), 4.08 (s, 5H), 4.06 (s, 1H), 3.79-3.77 (s, 1H), 3.57 (s, 5H), 3.15 (s, 3H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 154.0 (d, *J* = 12.9 Hz), 153.4 (d, *J* = 11.8 Hz), 146.3 (d, *J* = 1.9 Hz), 140.6 (d, *J* = 11.8 Hz), 139.2 (d, *J* = 13.0 Hz), 135.3 (d, *J* = 21.1 Hz), 133.8 (d, *J* = 19.9 Hz), 128.7 (d, *J* 0 1.8 Hz), 128.3 (d, *J* = 6.0 Hz), 128.2 (d, *J* = 6.9 Hz), 128.0 (d, *J* = 21.2 Hz), 120.7 (d, *J* = 29.3 Hz), 120.7 (d, *J* = 3.4 Hz), 120.6 (d, *J* = 3.4 Hz), 110.8 (d, *J* = 8.5 Hz), 110.7 (d, *J* = 6.5 Hz), 101.7 (d, *J* = 33.0 Hz), 97.2 (d, *J* = 24.3 Hz), 76.1 (d, *J* = 13.4 Hz), 74.3 (d, *J* = 12.9 Hz), 74.2 (d, *J* = 13.0 Hz), 73.0 (d, *J* = 6.0 Hz), 72.3 (d, *J* = 2.2 Hz), 70.4 (d, *J* = 6.0 Hz), 70.3, 70.2, 69.2 (d, *J* = 15.2 Hz), 68.5 (d, *J* = 5.6 Hz), 65.9, 57.3 ppm
^{31}P-NMR (81 MHz, CDCl3): δ = -10.07, -17.68 ppm.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, s), 3050 (m), 1630 (w), 1434 (m), 1251 (m), 1001 (m), 807 (s), 742 (s), 696 (s).
MS (70 eV, EI): *m/z* (%) = 752 (M^+, 13), 689 (25), 688 (50), 687 (100), 656 (8).
HRMS (EI): *m/z* calcd. for: [$C_{42}H_{38}FeP_2{}^{32}S_2Si$] 752.1009, found: 752.1013.
IR (KBr-Pressling): υ_{max} (cm^{-1}) = 3436 (br, m), 2926 (m), 1434 (m), 1154 (w), 1108 (m), 1085 (s), 1004 (s), 817 (m), 744 (s), 698 (m).
MS (70 eV, EI): *m/z* (%) = 762 (M^+, 27), 610 (13), 446 (35), 445 (100), 425 (23).
HRMS (EI): *m/z* calcd. for: [$C_{42}H_{36}{}^{56}Fe_2P_2O_3$] 762.0838, found: 762.0821.

10. Synthesis of new paracyclophane based diphsophines

(*R*)-4-Bromo-12-diphenylphosphinothioyl[2.2]paracyclophane (77):

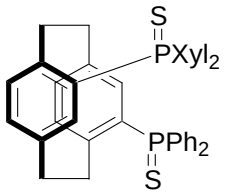


Dibromide **76** (1.83 g; 5.0 mmol) and THF (15 mL) were added to a 50 mL Schlenk flask under argon atmosphere. *n*BuLi (1.5 M in pentane; 3.70 mL, 5.50 mmol) was added slowly to the above solution at -78 °C and stirred for 1 h. $ClPPh_2$ (1.33 g; 6.0 mmol, 1.20 equiv) was added and stirred for 1 h at -78 °C. The reaction mixture was warned to room temperature and stirred for 1.5 h. Sulfur (1.60 g; 50.0 mmol, 10 equiv) was added to the reaction mixture and stirred for overnight at room temperature. The reaction mixture was quenched with a saturated NH_4Cl solution (20 mL) and the aqueous layer was extracted with CH_2Cl_2 (4 x 30 mL). The combined organic layers were washed with water, brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography (silicagel, *n*pentane:Et_2O (10:1)), afforded the desired compound as a white solid (2.14 g; 4.25 mmol, 85%).

MP: 148.1-148.9 °C
$[\alpha]_D^{20}$ = –22.9 (c = 0.4, $C\tilde{H}_2Cl_2$)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.83-7.71 (m, 5H), 7.48-7.35 (m, 6H), 6.65-6.53 (m, 5H), 3.60-3.49 (m, 2H), 3.39-3.35 (m, 1H), 3.01-2.97 (m, 1H), 2.90-2.71 (m, 4H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 145.0 (d, *J* = 8.6 Hz) 141.6, 138.6 (d, *J* = 13.0 Hz), 138.5, 136.9 (d, *J* = 3.1 Hz), 136.3, 135.5 (d, *J* = 11.8 Hz), 134.6 (d, *J* = 86.2 Hz), 133.4, 132.9 (d, *J* = 10.6 Hz), 132.8 (d, *J* = 11.8 Hz), 132.2 (d, *J* = 84.6 Hz), 131.9 (d, *J* = 10.2 Hz), 131.3 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 3.0 Hz), 131.1, 128.1 (d, *J* = 12.4 Hz), 128.0, (d, *J* = 12.4 Hz), 127.8 (d, *J* = 87.2 Hz), 127.2, 35.4, 34.7 (d, *J* = 4.9 Hz), 33.7 (d, *J* = 1.1 Hz), 31.92 ppm.

^{31}P-NMR (81 MHz, $CDCl_3$): δ = +40.44 ppm.
IR(neat): υ_{max} (cm^{-1}) = 3440 (br, w), 2912 (w), 1629 (s), 1425 (m), 1325 (m), 1102 (m), 789 (s), 656 (s).
MS (70 eV, EI): *m/z* (%) = 504 (37), 502 (M^+, 34), 321 (18), 320 (100), 319 (16), 209 (10), 183 (11).
HRMS (EI): *m/z* calcd. for: [$C_{28}H_{24}{}^{79}BrP^{32}S$] 502.0520, found: 502.0512

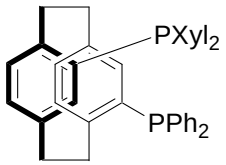
(*R*)-4-Bis(3,5-dimethylphenyl)phosphinothioyl-12-diphenylphosphinothioyl[2.2]paracyc--lophane (78d)



Monophosphine sulfide **77** (755 mg; 1.50 mmol) and THF (5 mL) were added to a 25 mL Schlenk flask under argon atmosphere. *n*BuLi (1.5 M in pentane; 1.2 mL, 1.70 mmol) was added slowly to the above solution at -78 °C and stirred for 2 h. chlorobis(3,5-dimethylphenyl)phosphine (500 mg; 1.80 mmol, 1.20 equiv) was added and stirred for 1 h at -78 °C. The reaction mixture was warned to room temperature and stirred for 1.5 h. Sulfur (482 mg; 15.0 mmol, 10 equiv) was added to the reaction mixture and stirred for overnight at room temperature. The reaction mixture was quenched with a sat. NH_4Cl solution (10 mL) and the aqueous layer was extracted with CH_2Cl_2 (4 x 15 mL). The combined organic layers were washed with water, brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography (silicagel, npentane:Et_2O (5:1)), afforded the desired compound as a white solid (910 mg; 1.30 mmol, 87%).

MP: 291 °C
$[\alpha]_D^{20}$ = ~ –20.9 (c = 0.4, CH_2Cl_2)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.96-7.93 (m, 2H), 7.73-7.69 (m, 2H), 7.51-7.47 (m, 5H), 7.33-7.31 (m, 4H), 7.26-7.23 (m, 2H), 7.10-7.08 (m, 2H), 7.02 (brs, 1H), 6.72-6.69 (m, 2H), 6.66-6.63 (m, 2H), 3.42-3.47 (m, 2H), 3.33-3.26 (m, 2H), 2.86-2.80 (m, 2H), 2.71-2.66 (m, 2H), 2.31 (s, 6H), 2.23 (s, 6H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 144.93 (d, *J* = 9.6 Hz), 144.9 (d, *J* = 9.6 Hz), 139.6 (d, *J* = 13.3 Hz), 139.4 (d, *J* = 13.2 Hz), 137.5 (d, *J* = 12.9 Hz), 137.3 (d, *J* = 13.2 Hz), 136.6 (d, *J* = 3.6 Hz), 136.5 (d, *J* = 3.7 Hz), 136.1 (d, *J* = 11.7 Hz), 135.9 (d, *J* = 12.3 Hz), 135.7 (d, *J* = 83.3 Hz), 135.0 (d, *J* = 83.8 Hz), 134.7 (d, *J* = 11.8 Hz), 134.4 (d, *J* = 12.0 Hz), 133.2 (d, *J* = 10.5 Hz), 133.0 (d, *J* = 3.1 Hz) 132.7 (d, *J* = 3.5 Hz), 131.6 (d, *J* = 10.3 Hz), 131.5 (d, *J* = 84.8 Hz), 131.2 (d, *J* = 84.8 Hz), 131.1 (d, *J* = 3.1 Hz), 130.9 (d, *J* = 10.1 Hz), 130.9 (d, *J* = 2.8 Hz), 129.3 (d, *J* = 10.1 Hz), 127.9 (d, *J* = 12.5 Hz), 127.8 (d, *J* = 87.7 Hz), 127.8 (d, *J* = 12.5 Hz), 127.7 (d, *J* = 88.7 Hz), 35.4 (t, *J* = 5.2 Hz), 33.8 (d, *J* = 16.0 Hz), 21.8 (d, *J* = 0.9 Hz), 21.5 (d, *J* = 0.9 Hz) ppm
^{31}P-NMR (81 MHz, $CDCl_3$): δ = +38.71, +38.39 ppm.
IR(neat): υ_{max} (cm^{-1}) = 3441 (br, w), 2785 (w), 1594 (m), 1447 (m), 1389 (m), 1101 (m), 874 (s), 725 (s), 696 (s).
MS (70 eV, EI): *m/z* (%) = 696 (M^+, 45), 521 (28), 320 (100), 309 (12), 183 (21).
HRMS (EI): *m/z* calcd. for: [$C_{44}H_{42}P_2{}^{32}S_2$] 696.2203, found: 696.2211

(*R*)-4-Bis(3,5-dimethylphenyl)phosphino-12-diphenylphosphino[2.2]paracyclophane (12d):



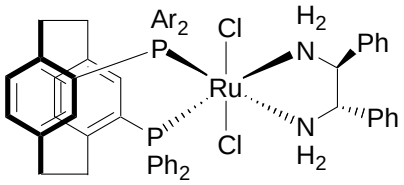
Prepared according to **TP5**, by using bisphosphinesulfide **78d** (698 mg; 1.0 mmol) and Raney-Ni (3.8 g; Raney-Ni in water) in MeOH (60 mL) and the bisphosphine **13d** was obtained as a white solid (583 mg; 0.92 mmol, 92%).

MP: 211.0-212.2 °C
$[\alpha]_D^{20}$ = −22.4 (c = 0.4, CH_2Cl_2)
^{1}H-NMR (600 MHz, $CDCl_3$): δ = 7.47-7.44 (m, 2H), 7.41-7.36 (m, 5H), 7.24-7.20 (m, 5H), 7.04-7.02 (m, 3H), 6.65-6.63 (m, 1H), 6.57-6.48 (m, 6H), 3.02-2.89 (m, 6H), 2.63-2.54 (m, 2H), 2.35 (s, 6H), 2.18 (s, 6H) ppm.
^{13}C-NMR (150 MHz, $CDCl_3$): δ = 143.3 (d, *J* = 14.7 Hz), 143.1 (d, *J* = 15.1 Hz), 139.5 (d, *J* = 12.1 Hz), 139.4 (d, *J* = 13.9 Hz), 139.3 (d, *J* = 6.1 Hz), 138.9 (d, *J* = 7.1 Hz), 138.2 (d, *J* = 12.2 Hz), 138.1 (d, *J* = 12.6 Hz), 137.5 (d, *J* = 17.5 Hz), 137.4 (d, *J* = 16.9 Hz), 137.3 (d, *J* = 7.9 Hz), 137.2 (d, *J* = 8.7 Hz), 135.9 (d, *J* = 0.9 Hz), 135.7 (d, *J* = 0.9 Hz), 134.2 (d, *J* = 6.8 Hz), 134.1 (d, *J* = 6.1 Hz), 133.4 (d, *J* = 22.8 Hz), 133.3 (d, *J* = 22.8 Hz), 133.0 (d, *J* = 20.4 Hz), 132.7 (d, *J* = 8.7 Hz), 132.3 (d, *J* = 6.8 Hz), 131.3 (d, *J* = 1.1 Hz), 130.6 (d, *J* = 20.9 Hz), 130.3 (d, *J* = 0.9 Hz), 129.3 (d, *J* = 0.8 Hz), 128.5 (d, *J* = 0.8 Hz), 128.3 (d, *J* = 22.7 Hz), 128.2 (d, *J* = 22.0 Hz), 35.8 (d, *J* = 18.7 Hz), 35.7 (d, *J* = 19.0 Hz), 33.2 (d, *J* = 2.6 Hz), 33.0 (d, *J* = 2.5 Hz), 21.4, 21.2 ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): δ = 0.69, 0.03 ppm
IR(neat): υ_{max} (cm^{-1}) = 3444 (br, w), 2019 (w), 1655 (s), 1450 (s), 1210 (s), 876 (s), 765 (m), 667 (m), 586 (m).
MS (70 eV, EI): *m/z* (%) = 632 (M^+, 14), 428 (32), 320 (100), 309 (11).
HRMS (EI): *m/z* calcd. for: [$C_{44}H_{42}P_2$] 632.2762, found: 632.2777

11. Preparation of ruthenium-diamine complexes 79a-c and 80a-c

Prepartation of ruthenium-diamine complexes of 12b

Prparation of the ruthenium complex 79a:



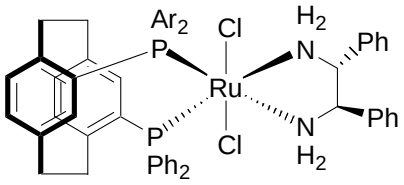
Ar = 4-F-phenyl

Prepared according to **TP10**, using the ligand **12b** (25 mg; 0.041 mmol; 1.0 equiv), $[RuCl(C_6H_6)]_2$ (9.4 mg; 0.021 mmol) and (*S*,*S*)-1,2-diphenylethylenediamine (8.9 mg; 0.041 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

^{1}H-NMR (200 MHz, $CDCl_3$): 8.45-7.82 (m, 21H), 7.32-6.44 (m, 13 H), 4.50-3.51 (m, 5H), 2.53-1.80 (m, 9H) ppm.

^{31}P-NMR (81 MHz, $CDCl_3$): +43.65 (d, *J* = 25.0 Hz), +40.36 (d, *J* = 25.2 Hz) ppm.

Prparation of the ruthenium complex 80a:



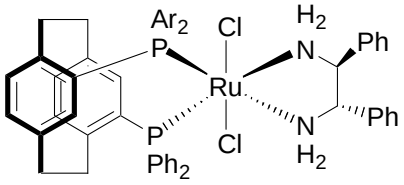
Ar = 4-F-phenyl

Prepared according to **TP10**, using the ligand **12b** (25 mg; 0.041 mmol; 1.0 equiv), $[RuCl(C_6H_6)]_2$ (9.4 mg; 0.021 mmol) and (*S*,*S*)-1,2-diphenylethylenediamine (8.9 mg; 0.041 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

^{1}H-NMR (200 MHz, $CDCl_3$): 8.54-8.00 (m, 20H), 7.50-6.65 (m, 14H), 4.55-3.55 (m, 5H), 2.60-2.48 (m, 4H), 2.10-1.88 (m, 5H) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): +44.11 (d, *J* = 25.1 Hz), +41.88 (d, *J* = 24.2 Hz) ppm.

Prepartation of ruthenium-diamine complexes of 12c

Prparation of the ruthenium complex 79c:

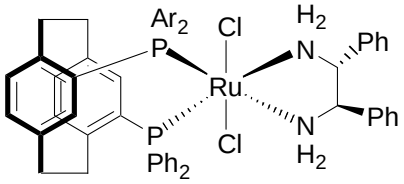


Ar = 3,5-$(CF_3)_2$-phenyl

Prepared according to **TP10**, using the ligand **12c** (20 mg; 0.024 mmol; 1.0 equiv), $[RuCl(C_6H_6)]_2$ (5.5 mg; 0.012 mmol) and (*S*,*S*)-1,2-diphenylethylenediamine (5.2 mg; 0.024 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

^{1}H-NMR (200 MHz, $CDCl_3$): 8.55-8.08 (m, 12H), 8.00-7.95 (m, 4H), 7.75-6.60 (m, 14H), 6.60-6.51 (m, 2H), 4.48-4.30 (m, 2H), 2.85-2.46 (m, 6H), 1.81-1.64 (m, 6H) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): +48.16 (d, *J* = 28.9 Hz), +45.79 (d, *J* = 27.0 Hz) ppm.

Prparation of the ruthenium complex 80b:



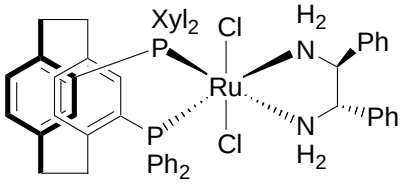
Ar = 3,5-$(CF_3)_2$-phenyl

Prepared according to **TP10**, using the ligand **12c** (20 mg; 0.024 mmol; 1.0 equiv), $[RuCl(C_6H_6)]_2$ (5.5 mg; 0.012 mmol) and (*S*,*S*)-1,2-diphenylethylenediamine (5.2 mg; 0.024 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

^{1}H-NMR (200 MHz, $CDCl_3$): 8.68-7.98 (m, 16H), 7.80-6.90 (m, 14H), 6.66-6.54 (m, 2H), 4.55-4.38 (m, 2H), 3.01-2.67 (m, 4H), 2.60-2.55 (m, 2H), 2.00-1.60 (m, 6H) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): +46.10 (d, *J* = 26.1 Hz), +43.20 (d, *J* = 26.2 Hz) ppm.

Prepartation of ruthenium-diamine complexes of 12d

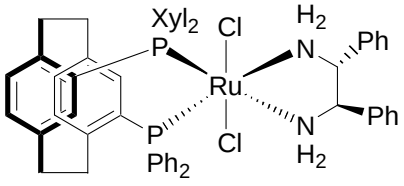
Prparation of the ruthenium complex 79c:



Prepared according to **TP10**, using the ligand **12d** (50 mg; 0.07 mmol; 1.0 equiv), $[RuCl(C_6H_6)]_2$ (16 mg; 0.035 mmol) and (*R*,*R*)-1,2-diphenylethylenediamine (15 mg; 0.07 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

^{1}H-NMR (200 MHz, $CDCl_3$): 8.46-8.20 (m, 3H), 8.01-7.45 (m, 3H), 7.40-7.25 (m, 4H), 7.20-7.11 (m, 7H), 7.00-6.85 (m, 7H), 6.70-6.68 (m, 1H), 6.60-6.58 (m, 1H), 6.50-6.39 (m, 6H), 4.50-4.48 (m, 1H), 4.11-4.10 (m, 1H), 2.76-2.69 (m, 2H), 2.62-2.50 (m, 2H), 2.29 (s, 6H), 2.12 (s, 6H), 1.94-1.87 (m, 2H), 1.71-1.66 (m, 2H).
^{31}P-NMR (81 MHz, $CDCl_3$): +48.16 (d, *J* = 28.9 Hz), +44.79 (d, *J* = 27.0 Hz) ppm.

Prparation of the ruthenium complex 80c:

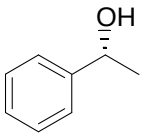


Prepared according to **TP10**, using the ligand **12d** (50 mg; 0.07 mmol; 1.0 equiv), $[RuCl(C_6H_6)]_2$ (16 mg; 0.035 mmol) and (*S*,*S*)-1,2-diphenylethylenediamine (15 mg; 0.07 mmol; 1.0 equiv) and obtained as a purple coloured solid in quantitative yield. The residue was used for hydrogenations without any further purification.

^{1}H-NMR (200 MHz, $CDCl_3$): 8.36-8.34 (m, 2H), 8.30-8.26 (m, 1H), 8.10-8.05 (m, 1H), 8.00-7.92 (m, 1H), 7.40-7.25 (m, 4H), 7.20-7.10 (m, 8H), 7.05-6.90 (m, 7H), 6.76 (s, 1H), 6.60-6.54 (m, 2H), 6.47-6.36 (m, 5H), 4.50-4.48 (m, 1H), 4.19-4.12 (m, 1H), 2.86-2.70 (m, 2H), 2.60-2.55 (m, 2H), 2.23 (s, 6H), 2.02 (s, 6H), 1.95-1.86 (m, 2H), 1.71-1.66 (m, 2H) ppm.
^{31}P-NMR (81 MHz, $CDCl_3$): +47.46 (d, *J* = 28.1 Hz), +44.19 (d, *J* = 27.1 Hz) ppm.

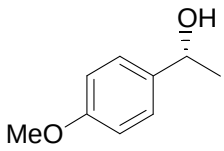
12. Asymmetric hydrogenation of ketones and olefins

(*R*)-1-Phenylethanol (82a):



$[\alpha]_D^{20}$ = +40.4 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, CDCl3): δ = 7.20-7.29 (m, 5H), 4.66 (q, **J** = 6.5 Hz, 1H), 2.80 (brs, 1H), 1.30 (d, *J* = 6.4 Hz, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 146.4, 128.8, 127.7, 125.9, 70.6, 25.6 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 30 °C/min 160 °C (30 min)); 8.5 min (*R*), 8.9 (*S*). 97% *ee.*

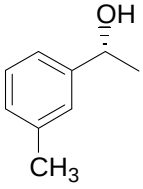
(*R*)-1-(4-Methoxyphenyl)ethanol (82b):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 4-methoxy-acetophenone **81b** (600 mg; 4.0 mmol) and obtained as colourless oil (584 mg; 3.84 mmol, 96%)

$[\alpha]_D^{20}$ = +43.6 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31-7.26 (m, 2H), 6.89-6.86 (m, 2H), 4.84 (q, *J* = 6.4Hz, 1H), 3.79 (s, 3H), 1.47 (d, *J* = 6.4 Hz, 3H), 1.83 (brs, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.0, 138.0, 126.6, 113.8, 69.9, 55.3, 25.0 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (60 min), Const.); 26.0 min (*R*), 30.0 (*S*). 96% *ee.*

(*R*)-1-(3-Methylphenyl)ethanol (82c):

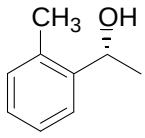


Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 3- methyl-acetophenone **81c** (537 mg; 0.54 mL, 4.0 mmol) and obtained as colourless oil (523 mg; 3.84 mmol, 96%)

$[\alpha]_D^{20}$ = +64.2 (c= 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.27-7.22 (m, 1H), 7.19-7.15 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 4.85 (q, *J* = 6.5 Hz, 1H), 2.36 (s, 3H), 1.88 (s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 145.8, 138.1, 128.4, 128.2, 126.1, 122.4, 70.4, 25.1, 21.4 ppm.

Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 30 °C/min 160 °C (30 min)); 9.5 min (*R*), 9.7 (*S*). 97% *ee.*

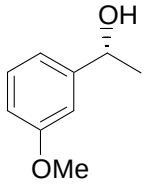
(*R*)-1-(2-Methylphenyl)ethanol (82d):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **81d** (537 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (534 mg; 3.92 mmol, 98%)

$[\alpha]_D^{20}$ = +48.2 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.52-7.49 (m, 1H), 7.26-7.21 (m, 1H), 7.19-7.13 (m, 2H), 5.12 (q, *J* = 6.4 Hz, 1H), 2.34 (s, 3H), 1.82 (s, 1H), 1.46 (d, *J* = 6.4 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 143.8, 134.2, 130.3, 127.1, 126.3, 124.4, 66.8, 23.9, 18.9 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (15 min), 5 °C/min 160 °C (30 min)); 20.1 min (*R*), 22.1 (*S*). 94% *ee.*

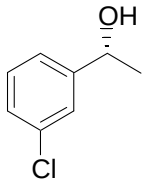
(*R*)-1-(3-Methoxyphenyl)ethanol (82e):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 3- methoxy-acetophenone **81e** (601 mg; 0.55 mL, 4.0 mmol) and obtained as colourless oil (584 mg; 3.84 mmol, 96%)

$[\alpha]_D^{20}$ = +54.8 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.2 Hz, 1H), 6.97-6.95 (m, 2H), 6.83 (dddd, *J* = 1.0 Hz, 2.6 Hz, 8.2 Hz, 1H), 4.88 (q, *J* = 6.5 Hz, 1H), 3.83 (s, 3H), 2.00 (brs, 1H), 1.50 (d, *J* = 6.5 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 159.7, 147.6, 129.5, 117.6, 112.8, 110.1, 70.3, 55.2, 25.1 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (60) const; 29.8 min (*R*), 34.7 (*S*). 97% *ee.*

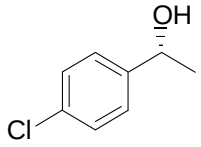
(*R*)-1-(3-Chlorophenyl)ethanol (82f):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 3- chloro-acetophenone **81f** (618 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (601 mg; 3.84 mmol, 96%)

$[\alpha]_D^{20}$ = +42.4 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.37-7.36 (m, 1H), 7.26-7.21 (m, 3H), 4.89-4.82 (m, 1H), 1.98 (d, *J* = 3.5 Hz, 1H), 1.47 (d, *J* = 6.5 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 147.8, 134.3, 129.7, 127.5, 125.6, 123.5, 69.8, 25.2 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (10 min), 50 °C/min 160 °C (30 min)); 12.9 min (*R*), 13.2 (*S*). 97% *ee.*

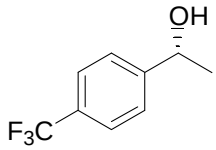
(*R*)-1-(4-Chlorophenyl)ethanol (82g):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 4- chloro-acetophenone **81g** (618 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (614 mg; 3.92 mmol, 98%)

$[\alpha]_D^{20}$ = +26.8 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.30-7.28 (m, 2H), 6.90-6.87 (m, 2H), 4.82 (q, *J* = 6.7 Hz, 1H), 1.24 (brs, 1H), 1.30 (d, *J* = 6.8 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 158.2, 136.5, 124.8, 112.1, 68.2, 24.5 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (130 °C (60 min), Const.); 9.2 min (*R*), 10.7 (*S*). 96% *ee.*

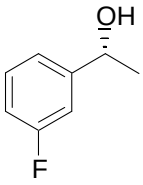
(*R*)-1-(4-Trifluoromethylphenyl)ethanol (82h):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 4- trifluoromethyl-acetophenone **81h** (753 mg; 4.0 mmol) and obtained as colourless oil (715 mg; 3.76 mmol, 94%)

$[\alpha]_D^{20}$ = +34.9 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.61-7.59 (m, 2H), 7.49-7.46 (m, 2H), 4.98-4.91 (m, 1H), 1.98 (d, *J* = 3.3 Hz, 1H), 1.49 (d, *J* = 6.3 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.7 (q, *J* = 1.4 Hz), 129.6 (q, *J* = 32.3 Hz), 125.6, 125.4 (q, *J* = 3.9 Hz), 124.1 (q, *J* = 271.6 Hz), 69.8, 25.4 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 30 °C/min 160 °C (30 min)); 9.3 min (*R*), 9.7 (*S*). 94% *ee.*

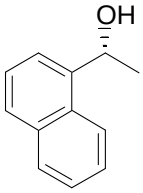
(*R*)-1-(3-Fluorophenyl)ethanol (82i):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 3- fluoro-acetophenone **81i** (552 mg; 0.49 mL, 4.0 mmol) and obtained as colourless oil (532 mg; 3.80 mmol, 95%)

$[\alpha]_D^{20}$ = +42.4 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.23-7.19 (m, 1H), 7.05-7.00 (m, 2H), 6.90-6.85 (m, 1H), 4.81 (q, *J* = 6.5 Hz, 1H), 1.96 (brs, 1H), 1.40 (d, *J* = 6.5 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 163.0 (d, *J* = 246.1 Hz), 148.5 (d, *J* = 6.4 Hz), 129.9 (d, *J* = 7.7 Hz), 120.9 (d, *J* = 2.6 Hz), 114.2 (d, *J* = 21.2 Hz), 112.3 (d, *J* = 21.2 Hz), 69.7 (d, *J* = 2.1 Hz), 25.2 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (10 min), 50 °C/min 160 °C (20 min)); 8.5 min (*R*), 10.1 (*S*). 96% *ee.*

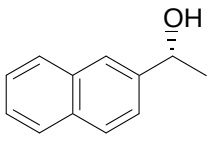
(*R*)-1-(1'-Naphtyhl)ethanol (82j):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **81j** (681 mg; 0.61 mL, 4.0 mmol) and obtained as colourless oil (661 mg; 3.84 mmol, 96%)

$[\alpha]_D^{20}$ = +68.8 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.13-8.12 (m, 1H), 7.89-7.86 (m, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.55-7.45 (m, 3H), 5.70-5.62 (m, 1H), 2.02 (d, *J* = 2.8 Hz, 1H), 1.67 (d, *J* = 6.57 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 141.3, 133.8, 130.2, 128.9, 127.9, 126.0, 125.6, 125.5, 123.1, 122.0, 67.1, 24.3 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (115 °C (15 min), 15 °C/min 160 °C (60 min)); 26.8 min (*S*), 27.4 (*R*). 96% *ee.*

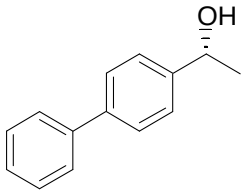
(*R*)-1-(2'-Naphthyl)ethanol (82k):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 1- naphthyl-acetophenone **81k** (681 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (675 mg; 3.92 mmol, 98%)

$[\alpha]_D^{20}$ = +60.4 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.84-7.80 (m, 4H), 7.51-7.44 (m, 3H), 5.05 (q, *J* = 6.5 Hz, 1H), 1.98 (brs, 1H), 1.58 (d, *J* = 6.2 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 143.2, 133.3, 132.9, 128.3, 127.9, 127.6, 126.1, 125.8, 123.8, 123.7, 70.5, 25.1 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (115 °C (15 min), 15 °C/min 160 °C (60 min)); 25.5 min (*R*), 26.3 (*S*). 97% *ee.*

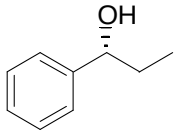
(*R*)-1-(4-Phenylphenyl)ethanol (82l):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 4- phenyl-acetophenone **81l** (785 mg; 4.0 mmol) and obtained as colourless oil (769 mg; 3.88 mmol, 97%)

$[\alpha]_D^{20}$ = +51.0 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.60-7.57 (m, 4H), 7.46-7.41 (m, 4H), 7.37-7.32 (m, 1H), 4.95 (q, *J* = 6.5 Hz, 1H), 1.87 (brs, 1H), 1.54 (d, *J* = 6.5 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 144.8, 140.8, 140.4, 128.7, 127.2, 127.1, 125.8, 70.1, 25.1 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 5 °C/min 160 °C (60 min)); 40.6 min (*R*), 42.7 (*S*). 94% *ee.*

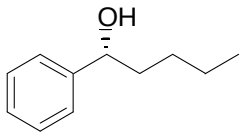
(*R*)-1-Phenylpropanol (84a):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and propiophenone **83a** (537 mg; 0.54 mL, 4.0 mmol) and obtained as colourless oil (523 mg; 3.84 mmol, 96%)

$[\alpha]_D^{20}$ = +32.4 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.36-7.26 (m, 5H), 4.60 (t, *J* = 6.5 Hz, 1H), 1.94 (brs, 1H), 1.84-1.76 (m, 2H), 0.93 (t, *J* = 6.5 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 144.6, 128.4, 127.4, 125.9, 76.0, 31.9, 10.1 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (60 min), Const.); 11.9 min (*R*), 13.2 (*S*). 97% *ee.*

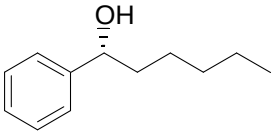
(*R*)-1-Phenylpentanol (84b):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **83b** (649 mg; 0.66 mL, 4.0 mmol) and obtained as a colourless oil (624 mg; 3.80 mmol, 95%)

$[\alpha]_D^{20}$ = +28.9 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.31-7.29 (m, 4H), 7.25-7.21 (m, 1H), 4.61 (t. *J* = 7.2 Hz, 1H), 1.84 (brs, 1H), 1.78-1.62 (m, 2H), 1.38-1.16 (m, 4H), 0.85 (t, *J* = 7.1 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 144.9, 128.4, 127.4, 125.9, 74.7, 38.8, 28.0, 22.6, 14.0 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (15 min), 5 °C/min 160 °C (45)); 24.3 min (*S*), 24.4 (*R*). 97% *ee*.

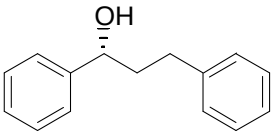
(*R*)-1-Phenylhexanol (84c):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **83c** (713 mg; 4.0 mmol) and obtained as a colourless oil (714 mg; 3.84 mmol, 96%)

$[\alpha]_D^{20}$ = +36.0 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.34-7.24 (m, 5H), 4.63-4.62 (m, 1H), 1.86 (d, *J* = 3.1 Hz, 1H), 1.79-1.60 (m, 2H), 1.45-1.27 (m, 6H), 0.89-0.84 (m, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 145.0, 128.4, 127.4, 125.9, 74.5, 39.1, 31.7, 25.5, 22.5, 14.0 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (15 min), 5 °C/min 160 °C (45)); 26.6 min (*S*), 26.7 (*R*). 94% *ee*.

(*R*)-1,3-Diphenylpropanol (84d):

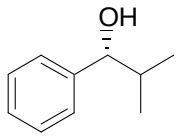


Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **83d** (841 mg; 4.0 mmol) and obtained as colourless oil (815 mg; 3.84 mmol, 96%)

$[\alpha]_D^{20}$ = +41.2 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.36-7.19 (m, 10H), 4.72-4.66 (m, 1H), 2.76-2.67 (m, 2H), 2.20-1.98 (m, 2H), 1.90 (d, *J* = 3.6 Hz, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 144.5, 141.7, 128.5, 128.4, 128.3, 127.6, 125.9, 125.8, 73.9, 40.4, 32.0 ppm.

Enantiomeric excess was determined by chiral HPLC using a chiracel OD-H column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 22.7 min [minor], t_r = 25.5 min [major]; 90% *ee*.

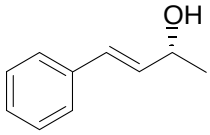
(*R*)-1-Phenyl-2-methylpropanol (84e):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **83e** (593 mg; 0.60 mL, 4.0 mmol) and obtained as colourless oil (541 mg; 3.60 mmol, 90%)

$[\alpha]_D^{20}$ = +12.8 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.35-7.23 (m, 5H), 4.34 (d, *J* = 7.1 Hz, 1H), 1.98-1.89 (m, 2H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 143.6, 128.1, 127.3, 126.5, 80.0, 35.2, 19.0, 18.2 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (110 °C (30 min), 5 °C/min 160 °C (45)); 17.9 min (*R*), 18.6 (*S*). 38% *ee*.

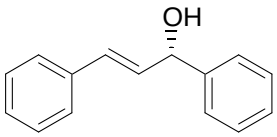
(*R*)-(*E*)-4-Phenyl-3-buten-2-ol (86a):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **85a** (585 mg; 4.0 mmol) and obtained as colourless oil (563 mg; 3.80 mmol, 90%)

$[\alpha]_D^{20}$ = +36.8 (c=1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.41-7.30 (m, 4H), 7.28-7.22 (m, 1H), 6.58 (dd, *J* = 0.9 Hz, 15.9 Hz, 1H), 6.27 (dd, *J* = 6.4 Hz, 15.8 Hz, 1H), 4.55-4.46 (m, 1H), 1.71 (brs, 1H), 1.39 (d, *J* = 6.4 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 136.7, 133.5, 129.4, 128.5, 127.6, 126.4, 68.9, 23.4 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (115 °C (20 min), 5 °C/min 160 °C (30)); 18.8 min (*R*), 19.7 (*S*). 94% *ee*.

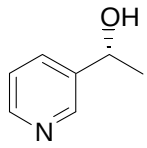
(*R*)-(*E*)-1,3-Diphenyl-2-propen-1-ol (86b):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **85b** (833 mg; 0.52 mL, 4.0 mmol) and obtained as colourless oil (816 mg; 3.88 mmol, 98%)

$[\alpha]_D^{20}$ = +2.0 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.46-7.21 (m, 10H), 6.69 (d, *J* = 0.9 Hz, 15.8 Hz, 1H), 6.38 (d, *J* = 6.4 Hz, 15.8 Hz, 1H), 5.38 (d, *J* = 6.4 Hz, 1H), 2.12 (brs, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 142.7, 136.5, 131.5, 130.5, 128.6, 128.5, 127.8, 127.7, 126.6, 126.3, 75.1 ppm.
Enantiomeric excess was determined by chiral HPLC using a chiracel OD column (flow rate 0.5 mL/min, heptane/iPrOH: 90/10, λ= 215 nm, 25 °C); t_r = 14.8 min [minor], t_r = 19.1 min [major]; 37% *ee*.

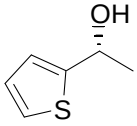
(*R*)-1-(3-Pyridyl)ethanol (88):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **87** (484 mg; 0.44 mL, 4.0 mmol) and obtained as colourless oil (483 mg; 3.92 mmol, 98%)

$[\alpha]_D^{20}$ = +21.8 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.50-8.42 (m, 2H), 7.71 (tt, *J* = 7.9 Hz, 1.7 Hz, 1H), 7.27-7.23 (m, 1H), 4.91 (q, *J* = 6.6 Hz, 1H), 2.98 (brs, 1H), 1.49 (d, *J* = 6.5 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 148.4, 147.2, 141.3, 133.3, 123.5, 67.8, 25.2 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (40 °C (15 min), 3 °C/min 160 °C (60 min)); 45.8 min (*R*), 46.8 (*S*). 96% *ee*.

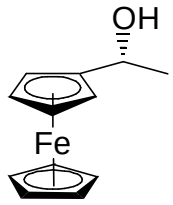
(*R*)-1-(2-Thienyl)ethanol (90):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **89** (505 mg; 0.43 mL, 4.0 mmol) and obtained as colourless oil (502 mg; 3.92 mmol, 98%)

$[\alpha]_D^{20}$ = +16.4 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.22 (dd, *J* = 1.6 Hz, 4.6 Hz, 1H), 6.98-6.94 (m, 2H), 5.16-5.08 (m, 1H), 2.06 (brs, 1H), 1.59 (d, *J* = 6.4 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.8, 126.6, 124.4, 123.1, 66.2, 25.2 ppm.
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (15 min), 5 °C/min 160 °C (60 min)); 12.4 min (*R*), 14.5 (*S*). 92% *ee*.

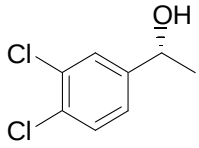
(*R*)-1-Ferrocenylethanol (92):



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 2- methyl-acetophenone **91** (912 mg; 4.0 mmol) and obtained as colourless oil (865 mg; 3.76 mmol, 94%)

$[\alpha]_D^{20}$ = –30.2 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 4.58-4.50 (m, 1H), 4.22-4.20 (m, 2H), 4.18 (s, 5H), 4.15 (t, *J* = 1.9 Hz, 2H), 1.85 (d, *J* = 4.7 Hz, 1H), 1.43 (d, *J* = 6.3 Hz, 1H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 94.5, 68.3, 67.9, 67.8, 66.1, 66.1, 65.6, 23.7 ppm.
Enantiomeric excess was determined by chiral HPLC using a chiracel OJ column (flow rate 0.6 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 34.8 min [major], t_r = 37.2 min [minor]; 94% *ee*.

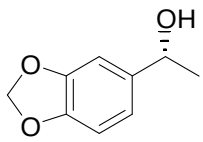
1-(3', 4'- Dichlorophenyl)ethanol (94a)[142]:



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 3,4-dichloroacetophenone **93a** (756 mg; 4.0 mmol) and obtained as colourless oil (745 mg; 3.92 mmol, 98%)

$[\alpha]_D^{20}$ = +35.8 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 2.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.18 (dddd, *J* = 0.6 Hz, 2.1 Hz, 8.3 Hz, 1H), 4.84 (q, *J* = 6.5 Hz, 1H), 1.91 (brs, 1H), 1.45 (d, *J* = 6.6 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 146.0, 132.5, 131.2, 130.4, 127.5, 124.7, 69.2, 25.3 ppm.
MS (70 eV, EI): *m/z* (%) = 190 (M^+, 35), 175 (100), 147 (47), 111 (70).
HRMS (EI): *m/z* calcd. for: [$C_8H_8OCl_2$] 189.9952, found: 189.9953
Enantiomeric excess was determined by chiral GC using DEX-CB column (160 °C (60 min), const.); 6.6 min (*R*), 7.1 (*S*). 97% *ee*.

1-(3', 4'- Dioxymethylenephenyl)ethanol (94b)[143]:

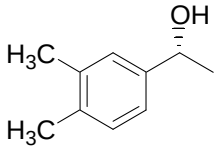


[142] Mao, J.; Wan, B.; Wu, F.; Lu, S. *Tetrahedron Lett.* **2005**, *46*, 7341.
[143] Koul, S.; Koul, J. L.; Sing, B.; Kapoor, M.; Parshad, R.; Manhas, K. S.; Taneja, S. C.; Qazi, G. N. *Tetrahedron: Asymmetry* **2005**, *16*, 2575.

Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 3,4-dioxymethyleneacetophenone **93b** (657 mg; 4.0 mmol) and obtained as colourless oil (625 mg; 3.76 mmol, 94%)

$[\alpha]_D^{20}$ = +42.6 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.87 (d, *J* = 1.8 Hz, 1H), 6.80 (dddd, *J* = 0.5 Hz, 1.8 Hz, 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 2H), 6.80 (q, *J* = 6.4 Hz, 1H), 1.90 (brs, 1H), 1.44 (d, *J* = 6.40 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 147.7, 146.8, 139.9, 118.6, 108.0, 106.0, 100.9, 70.2, 25.1 ppm.
MS (70 eV, EI): *m/z* (%) = 166 (M^+, 71), 151 (97), 148 (12), 123 (27), 93 (100).
HRMS (EI): *m/z* calcd. for: [$C_9H_{10}O_3$] 166.0630, found: 166.0623
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 5 °C/min 160 °C (60)); 19.7 min (*R*), 20.1 (*S*). 90% *ee*.

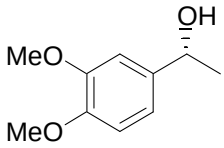
1-(3', 4'- Dimethylphenyl)ethanol (94c)[144]:



Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 3,4-dimethyl-acetophenone **93c** (593 mg; 0.59 mL, 4.0 mmol) and obtained as colourless oil (583 mg; 3.88 mmol, 97%)

$[\alpha]_D^{20}$ = +50.0 (c = 1.0, $CHCl_3$)
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.15 (brs, 1H), 7.12-7.09 (m, 2H), 4.84 (q, *J* = 6.7 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.85 (brs, 1H), 1.48 (d, *J* = 6.4 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 143.3, 136.6, 135.7, 129.7, 126.7, 122.7, 70.2, 25.0, 19.8, 19.4 ppm.
MS (70 eV, EI): *m/z* (%) = 150 (M^+, 43), 135 (82), 107 (100), 91 (49).
HRMS (EI): *m/z* calcd. for: [$C_{10}H_{14}O$] 150.1045, found: 150.1035
Enantiomeric excess was determined by chiral GC using DEX-CB column (100 °C (7 min), 5 °C/min 160 °C (60)); 15.4 min (*R*), 15.7 (*S*). 96% *ee*.

1-(3', 4'- Di´methoxyphenyl)ethanol (94d)[145]



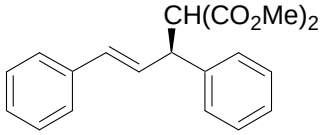
Prepared according to the typical procedure **TP11**, using ruthenium catalysts **80c** (2.1 mg; 0.002 mmol) and 3,4-dimethoxy-acetophenone **93d** (721 mg; 4.0 mmol) and obtained as colourless oil (714 mg; 3.92 mmol, 98%)

$[\alpha]_D^{20}$ = +49.6 (c = 1.0, $CDCl_3$)

[144] Kagechika, H.; Himi, T.; Namikawa, K.; Kawachi, E.; Hashimoto, Y.; Shudo, K. *J. Med. Chem.* **1989**, *32*, 1098.
[145] Zaitsev, A. B.; Adolfsson, H. *Org. Lett.* **2006**, *8*, 5129.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.92 (d, *J* = 2.0 Hz, 1H), 6.87-6.86 (m, 1H), 6.83 (s, 1H), 4.86-4.79 (m, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 1.86 (d, *J* = 2.2 Hz, 1H), 1.47 (d, *J* = 6.7 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.0, 148.3, 138.5, 117.5, 111.0, 108.6, 70.2, 55.9, 55.8, 25.0 ppm.
MS (70 eV, EI): *m/z* (%) = 182 (M^+, 59), 167 (100), 139 (81), 124 (13).
HRMS (EI): *m/z* calcd. for: [$C_{10}H_{14}O_3$] 182.0943, found: 182.0923
Enantiomeric excess was determined by chiral GC using DEX-CB column (120 °C (120 min), const); 46.5 min (*R*), 50.5 (*S*). 94% *ee*.

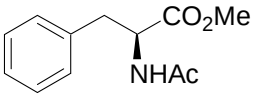
Synthesis of *trans*-(*S*)-methyl2-carbomethoxy-3,5-diphenylpent-4-enolate (28)



Preared according to **TP12**, using ligand **9h** (3 mg, 0.0055 mmol) and 3-Acetoxy-1,3-diphenyl-propene **27** (126 mg; 0.5 mmol), dimethylmalonate (0.2 mL; 1.5 mmol) and (*S*)-**28** obtained as a white solid (149 mg, 0.46 mmol; 92%).

MP: 94.1-94.8 °C
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.25-7.00 (m, 10H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.25 (dd, *J* = 15.8 Hz, 8.4 Hz, 1H), 4.15 (dd, *J* = 10.5, 8.8 Hz, 1H), 3.88 (d, *J* = 10.5 Hz, 1H), 3.55 (s, 3H), 3.45 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 168.1, 167.5, 139.9, 136.0, 131.5, 129.1, 128.7, 128.1, 127.5, 127.3, 126.9, 126.3, 57.9, 52.8, 52.0, 49.1ppm.
Enantiomeric excess was determined by chiral HPLC using a chiracel OD-H column (flow rate 0.6 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 34.8 min (*R)*, t_r = 37.2 min (*S*); 94% *ee*.

Synthesis of *N*-acetylphenylalaninmethylester (26)[146]

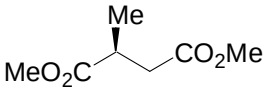


Preared according to **TP13**, using ligand **13d** (6.4 mg, 0.0011 mmol) in MeOH (1 mL) and 2-acetamidoacrylicacidmethylester **25** (219 mg, 1.0 mmol) in MeOH (4 mL) at 5 bar H_2 pressure and obtained the desired compound **26** as colourless solid (211 mg, 0.95 mmol; 95%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.32-7.17(m, 3H), 7.13-7.04 (m, 2H), 6.06 (brs, 1H), 4.87 (brs, 1H), 3.70 (s, 3H), 3.20-3.00 (m, 2H), 1.97 (s, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 172.0, 169.7, 135.8, 129.2, 128.5, 127.0, 53.1, 52.3, 37.8, 23.2 ppm.
Enantiomeric excess was determined by GC using a chirlsil L-Val column (140 °C const;) t_r = 11.6 min (*R)*, t_r = 12.5 min (*S*); 90% *ee*.

Synthesis of 2-methylsuccinicaciddimethylester (75)[147]

[146] Glaser, R.; Vainas, B. *J. Organomet. Chem.* **1976**, *121*, 249.



Preared according to **TP13**, using ligand **13d** (6.4 mg, 0.0011 mmol) in MeOH (1 mL) and 2-acetamidoacrylicacidmethylester **74** (158 mg, 1.0 mmol) in MeOH (4 mL) at 5 bar H_2 pressure and obtained the desired compound **75** as colourless oil (144 mg, 0.90 mmol; 90%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.66 (s, 3H), 3.64 (s, 3H), 2.99-2.85 (m, 1H), 2.74-2.65 (m, 1H), 2.40-2.38 (m, 1H), 1.20 (d, *J* = 7.1 Hz, 3H) ppm.
^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.1, 172.7, 52.0, 51.8, 37.8, 36.1, 16.5 ppm.
Enantiomeric excess was determined by chiral HPLC using a chiracel OD-H column (flow rate 0.6 mL/min, heptane/iPrOH: 95/5, λ= 215 nm, 25 °C); t_r = 34.8 min (*R)*, t_r = 37.2 min (*S*); 60% *ee*.

[147] Behrens, U.; Burk, M. J.; Gerlach, A.; Hems, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 1981.

13. Data for the x-ray crystallography analysis

Crystallographic data of 4b:

Empirical Formula : $C_{29}H_{26}FeNOPS$

Formular weight : 523.39

Temperature [°C] : 295 (2)K

Wavelength : 0.71073 Å

Crystal system : Monoclinic

Space group : $P2_1$

Unit cell dimensions : a = 9.0830 (18) Å alpha = 90 deg.

b = 9.7040 (18) Å beta = 102.60(3) deg.

c = 15.6420 (3) Å gamma = 90 deg.

Volume : 1262.3 (5) $Å^3$

Z : 2

Density (calculated) : 1.377 Mg/m^3

Absorption coefficient : 0.766 mm^{-1}

F(000) : 544

Crystal size : 0.57 x 0.53 x 0.20 mm

Theta range for data collection: 2.60 to 26.30

Index ranges : -11<=h<=11, -11<=k<=11, -19<=l<=19

Reflections collected : 5121

Independent reflections : 4649

Absorption correction : Semi-empirical by psi-scan

Max
no of parameters : 308

R_1 ($I>2\sigma(I)$) : 0.0363

wR_2 (all data) : 0.0975

goodness of fit : 1.099

14. ABBREVIATIONS

Ac	acetyl
Ar	aryl
Bn	benzyl
br.	Broad
brs	Broadsinglet
BARF	Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
calcd.	Calculated
CAN	Cerium Ammonium Nitrate
CH_2Cl_2	dichloromethane
COD	1,4-Cyclooctadiene
Conv.	Conversion
d	double
dec.	decomposition
DMF	*N*,*N*-dimethylformamide
ee	enantiomeric excess
equiv.	equivalent
EI	electron-impact
Et	ethyl
FAB	fast-atom bombardment
Fc	Ferrocenyl
Fur	2-furyl
GC	gas chromatography
h	hour
HRMS	high resolution mass spectroscopy
Hz	Hertz
n-Bu	*n*-butyl
i-Pr	isopropyl
IR	infra-red
J	coupling constant (NMR)
M	molarity

m	meta
m	multiplet
Me	methyl
min	minute
mol.	mole
mL	Millilitre
mp.	melting point
MS	mass spectroscopy
nbd	nonbornadiene
NMR	nuclear magnetic resonance
o	ortho
p	para
Pent	pentyl
Ph	phenyl
Pyr	Pyridyl
q	quartet
rt	room temperature
rac.	racemic
s	singlet
t	triplet
t-Bu	*tert*-butyl
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Tol	4-methylphenyl (tolyl)
TP	typical procedure
Xyl	3,5-Dimethylphenyl (xylyl)

Curriculum Vitae

Name: Murthy Narasimha Cheemala
Date of Birth: April, 27th 1981
Nationality: Indian
Place of birth: Eluru, India
Marital status: Single
Mother language: Telugu. Other language: English (Fluent written and spoken)

Education

08/2003-present:	**Ph.D.** student at the Ludwig-Maximilians-University, Muncih, Germany under the guidance of Prof. Dr. Paul Knochel **Thesis title:** "Synthesis of New Chiral Phosphine Ligands and Their Application in Asymmetric Catalysis"
2001-2003	**Master of Science**, Chemistry, University of Hyderabad, Hyderabad, India. **Master thesis title** "Synthesis of 1,1'-Binaphthyl Based Amines and Polyamines" Under the supervision of Prof. M. Periasamy, University of Hyderabad, India.
1998-2001	**Bachelor of Science** (Maths, Physics and Chemistry) at Sir. C. R. R. College, Eluru, Andhra Pradesh, India.
1996-1998	**Higher Secondary Education**, at Sir. C. R. R. College, Eluru, Andhra Pradesh, India

Publications

1.Korn, T. J.; Schade, M. A.; **Cheemala, M. N.**; Wirth, S.; Guevara, S. A.; Cahiez, G.; Knochel, P. "Cobalt-catalyzed cross-coupling reactions of heterocyclic chlorides with arylmagnesium halides and of polyfunctionalized arylcopper reagents with arylbromides, chlorides, fluorides and tosylates". *Synthesis* **2006**, *24*, 4270.

2. **Cheemala, M. N**.; Knochel, P. "New P,N-Ferrocenyl Ligands for the Asymmetric Ir-Catalyzed Hydrogenation of Imines" *Org. Lett.* **2007**, accepted.

3. **Cheemala, M. N.**; Gayral, M.; Brown, J. M.; Rossen, K.; Knochel, P. "New Paracyclophane Phosphine for Highly Enantioselective Ru-Catalyzed Hydrogenation of Prochiral Ketones." *Manuscript in preparation.*

4. **Cheemala, M. N.**; Knochel, P. "Synthesis of New Ferrocenyl P,N-ligands and their Applications in Asymmetric Catalysis" *Manuscript in Preparation.*

5. **Cheemala, M. N.;** Knochel, P. "Synthesis of New Planar Chiral Ferrocenyl Ligand through Selective Sulfoxide-Lithium Exchange" *Manuscript in Preparation.*

Conferences

1. Cheemala, M. N.; Knochel, P. “Chiral Ferrocenyl P,N-Ligands for Palladium-Catalyzed Allylic Substitution Reactions” Poster at OMCOS13, 17-21 July, 2005, Geneva, Switzerland
2. Cheemala, M. N.; Knochel, P. “A Chiral Ferrocenyl P,N-Ligand For Iridium-Catalyzed Asymmetric Imine Hydrogenation” Poster at 1st European Chemistry Congress, 27-31 August, 2006, Budapest, Hungary