Iron Catalyzed C-H Activation and Synthesis of Novel Ligands

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der
Rheinisch-Westfälischen Technischen Hochschule Aachen
zur Erlangung des akademischen Grades eines
Doktors der Naturwissenschaften genehmigte Dissertation

vorgelegt von

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Tag der mündlichen Prüfung: 8. Oktober 2007

The work reported in this thesis was carried out in the Institute für Organische Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen under the supervision of Universitätsprofessor Dr. Carsten Bolm from April 2004 until October 2007.

I would like to thank Prof. Bolm for giving me the great opportunity to work in his research group on this interesting topic and his support during my doctoral work.

Part of this work has already been published:

1) "*Palladium-Catalyzed N-Arylations of 1,4,7-Triazacyclononanes*" M. Nakanishi, C. Bolm, *Adv. Synth. Catal.* **2006**, *348*, 1823.

2) "*Iron-Catalyzed Benzylic Oxidation with Aqueous tert-Butyl Hydorperoxide*" M. Nakanishi, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 861.

3) "*Iron-Catalyzed Aziridination* " M. Nakanishi, C. Bolm, *Adv. Synth. Catal.*, in preparation.

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1 Introduction

Catalysis is the acceleration of a chemical reaction by means of a substance, called a catalyst, which is not consumed in the overall reaction. Also, catalysts can allow reactions to take place, which are conventionally unable to proceed, making innovative synthetic approaches possible. Therefore, metal-catalyzed reactions are used as key steps in organic synthesis especially for total syntheses of natural products.

Catalysts are classified as either homogeneous or heterogeneous. In heterogeneous catalysis, the catalyst provides a surface on which the reaction takes place. Heterogeneous catalyst is widely used for industrial processes. On the other hand, homogeneous catalysts are in the same phase as the reactants. An important example of homogeneous catalysis is ruthenium-BINAP-catalyzed asymmetric hydrogenation, which was developed by Noyori. This method was successfully applied on an industrial scale for the enantioselective synthesis of *L*-menthol by Takasago International Corporation in 1983. Nowadays, *L*-menthol is produced on a scale of more than 150 tons per year by Takasago. In 2001, Noyori, Knowles and Sharpless were jointly awarded the Nobel Prize for their contributions to the development of enantioselective hydrogenation and oxidation. Another award that emphasizes the value placed on catalysis by the scientific community was the 2005 Nobel Prize for chemistry, which was awarded to Chauvin, Grubbs and Schrock for the development of practical, catalytic olefin metathesis.

In the field of homogeneous catalysis, transition metal-catalyzed reactions have been extensively investigated. For instance, palladium-catalyzed reactions including the Heck,[1] Stille,[2] Hiyama[3] and Suzuki[4] reactions are often employed in organic synthesis.

Organocatalysis[5] has recently attracted attention as a means of applying small non-toxic organic molecules as catalysts as part of a more environmentally acceptable approach to synthesis. However, product purification can be problematic as high catalyst loadings are

[1] a) R. F. Heck, J. P. Nolley Jr., *J. Org. Chem.***1972**, *37*, 2320. b) R. F. Heck, *Org. React.* **1982**, *27*, 345.
[2] D. Milstein, J. K. Stille, *J. Am. Chem. Soc.* **1978**, *100*, 3636.
[3] Y. Okude, S. Hirano, T. Hiyama, H. Nozaki, *J. Am. Chem. Soc.* **1977**, *99*, 3179.
[4] a) N. Miyaura, A. Suzuki, *J. Chem. Soc., Chem. Commun.* **1979**, 866. b) N. Miyaura, K. Yamada, A. Suzuki, *Tetrahedron Lett.* **1979**, 3437. c) A. Suzuki, *Pure. Appl. Chem.* **1985**, *57*, 1749. d) N. Miyaura, A. Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
[5] P. I. Dalko, L. Moisan, *Angew. Chem.* **2004**, *116*, 5248, *Angew. Chem. Int, Ed.* **2004**, *43* 5138 and references therein.

required in many organocatalytic reactions. Thus, highly-active organocatalysts are desirable to make organocatalysis a more practical undertaking.

In contrast, transition metal and lanthanide catalysts have been developed that allow for the use of extremely low catalyst loadings. However, from the point of view of industrial application, most of these catalysts involve prohibitively high costs and utilize toxic metals. In this scenario, cheap and non-toxic iron may become the element of choice for catalyst development.

1.1 Iron-Catalyzed Reactions

Iron is the 4th most abundant element in the earth's crust. The common minerals, magnetite and hematite can be changed readily to metallic iron by reduction in a blast furnace. At last steel can be obtained by reducing the content of carbon. Thus, iron is available on a large scale as well as at low and stable cost. Conveniently, most iron salts and catalysts are commercially available.

Classically, an iron salt such as iron (III) trichloride was used in Friedel-Crafts reactions as a Lewis acid.[6] Additionally, iron-catalyzed cross-coupling has recently been reported.[7] These days, iron catalysts can be applied for many reactions.[8] In iron-oxidation chemistry, nitrogen containing ligands play a significant role to achieve efficient reactions.
Most transition metals fall into the category of soft metals. On the other hand, iron is considered a hard metal. In general, hard metals interact preferentially with hard elements. Therefore, soft elements such as phosphorus interact poorly with iron, whereas a hard element such as nitrogen can be useful as a ligating atom of a ligand. In this scenario, the design and development of convenient methods for the preparation of effective nitrogen containing ligands are absolutely imperative to achieve high reactivities.

1.2 Nitrogen Containing Ligands

[6] D. D. Diaz, P. O. Miranda, J. I. Padron, V. S. Martin, *Current Org.Chem.* **2006**, *10*, 457.
[7] a) M. Nakamura, K. Matsuo, S. Ito, E. Nakamura, *J. Am Chem. Soc.* **2004**, *126*, 3686. b) A. Fürstner, A. Leitner, M. Méndez, H. Krause, *J. Am. Chem. Soc.* **2002**, *124*, 13856.
[8] C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217 and references therein.

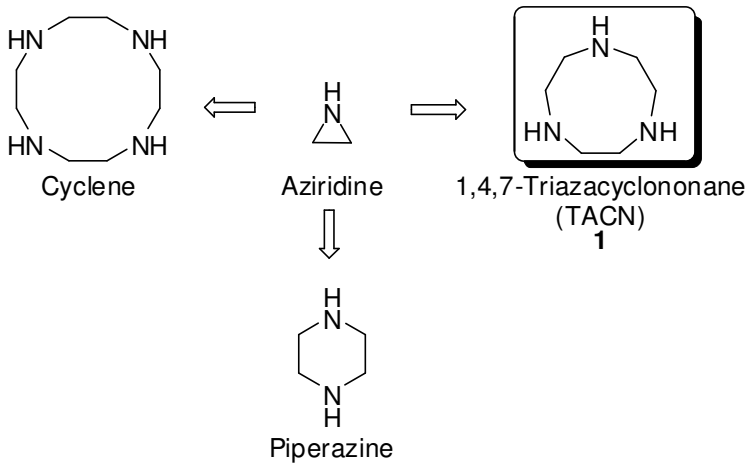
In catalysis, ligands play very important roles. Phosphine ligands have been especially well studied in transition metal-catalyzed processes. A typical, efficient phosphine ligand is BINAP. This ligand is applicable not only in transition metal-catalyzed asymmetric reactions but also in cross coupling reactions such as *N*-arylations. Most phosphine ligands are air sensitive because the phosphine can be easily oxidized to the corresponding phosphine oxide. Besides, organophosphorous compounds are often highly toxic and foul smelling. In general, re-utilization of phosphine ligands is very difficult due to their sensitivity towards oxidation and deactivation after reaction. For the development of a new generation of ligands, the use of non-toxic nitrogen containing compounds has attracted great attention. Nitrogen containing ligands can be manipulated and synthesized more easily than phosphines due to their higher air stability. Also, the ligand recycling problem can be avoided. Nowadays, the design of nitrogen containing catalysts and their synthesis are studied by many chemists.

1.2.1 1,4,7-Triazacyclononane (TACN) Derivatives

One of the nitrogen containing ligands, 1,4,7-Triazacyclononane (TACN) (**1**), which is called "tack-en" is one of the most famous and popular new classes of cyclic tridentate ligand in coordination chemistry. TACN is a tri-oligomer of aziridine. Other macrocyclic azacycloalkane ligands derived from aziridine, such as 1,4-diazacyclohexane (piperazine), 1,4,7,10-tetrazacyclodecane (cyclene) and ring expanded and contracted triazacycloalkanes like 1,5,9-triazacyclododecane [9] and 1,3,5-triazacyclohexane [10] have also been described (Figure 1). In addition, heterocyclononane, 1,4,7-triphosphacyclononane[11] and 12-crown-4 are included in this nitrogenated family of ligands.

Figure 1. Analogues of azacycloalkanes.

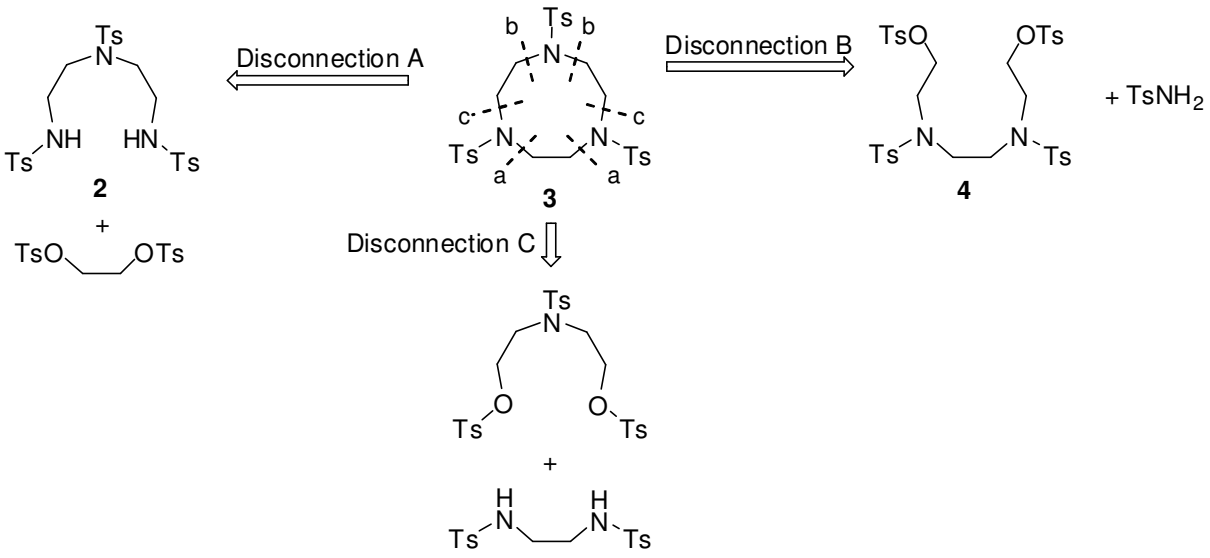
[9] a) R. W. Alder, R. W. Mowlam, D. J. Vachon, G. R. Weisman, *J. Chem. Soc., Chem. Commun.* **1987**, *12*, 886. b) N. G. Lukyanenko, S. S. Basok, L. K. Filonova, *J. Chem. Soc., Perkin Trans 1* **1998**, 3141. c) T. W. Bell, H-J. Choi, W. Harte, M. G. B. Drew, *J. Am. Chem. Soc*. **2003**, *125*, 12196. d) R. C. Hoye, J. E. Richman, G. A. Dantas, M. F. Lightbourne, L. S. Shinneman, *J. Org. Chem*. **2001**, *66*, 2722.
[10] V. Mévellec, A. Roucux, *Inorg. Chim. Acta* **2004**, *357*, 3099.
[11] P. G. Edwards, R. Haigh, D. Li, P. D. Newman, *J. Am.Chem. Soc*. **2006**, *128*, 3819.



Due to its specific macrocyclic skeleton and strong basicity,[12] TACN can behave as a tridentate ligand and thus methods for the synthesis of this class of compound are of interest. Actually, the history of TACN is still very short. TACN ligands have been prepared by syntheses involving one of three of the retrosynthetic disconnections A-C (Scheme 1). The first synthesis of TACN was described in 1972. This synthesis followed disconnection route A, and in a forward sense, involved condensation of ditosylethylene glycol and tritosyldiethylene triamine **2**[13] Afterwards, tritosyl-TACN **3** was synthesized by Watkinson using disconnection B.[14] In this case, the cyclization takes place between tetratosylated derivative **4** and $TsNH_2$. Disconnection C was used for the synthesis of chiral 1,4,7-trimethyl-2,3-cyclohexano-TACN ligand **23**. This last approach consists of the cyclization of 1,2-ditosylethylene-1,2-diamine with 2,2'-ditosyloxydiethyleneamine. In each route, the use of tosyl groups as leaving groups for cyclization is important. If ethylene dihalides are used the cyclization is less efficient.[15]

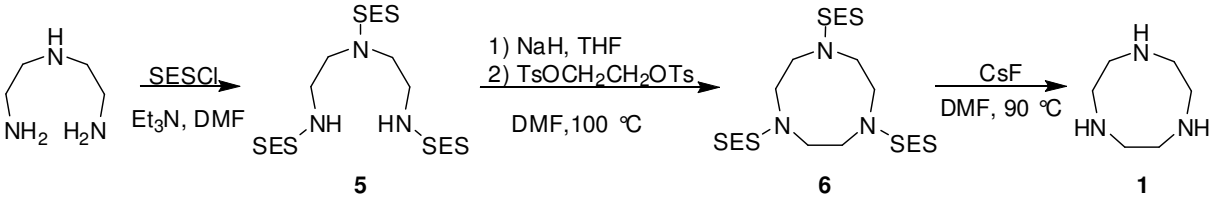
Scheme 1. Synthetic routes to the TACN framework.

[12] N. C. Meyer, C. Bolm, G. Raabe, U. Kölle, *Tetrahedron* **2005**, *61*, 12371.
[13] a) H. Koyama, T. Yoshino, *Bull. Chem. Soc. Jap*. **1972**, *45*, 481. b) J. E. Richman, T. J. Atkins, *J. Am Chem. Soc.* **1974**, *96*, 2268.
[14] S. Pulacchini, M. Watkinson, *Eur. J. Org. Chem*. **2001**, 4233.
[15] R. C. Hoye, J. E. Richman, G. A. Dantas, W. J. Lightbourne, L. S. Shinneman, *J. Org. Chem. Soc*. **2001**, *66*, 2722.



In these syntheses, the final detosylation requires harsh conditions. To overcome the deprotection difficulties, a synthesis of TACN with trimethylsilylethanesulfonyl (SES-) protecting groups was developed following disconnection route A (Scheme 2).

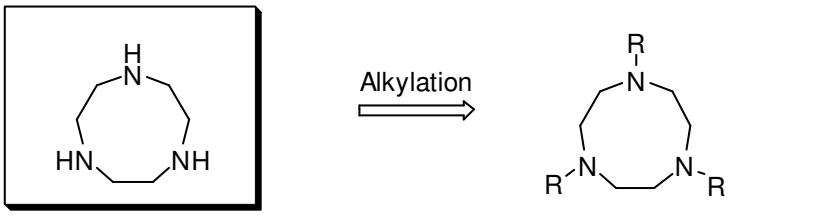
Scheme 2. Synthesis of TACN **1** using SES protecting groups.



In this procedure, all of the SES protecting groups on TACN **6** can be readily removed by treatment with cesium fluoride in DMF at 90 ˚C, affording TACN **1** in 68% yield.[16] The TACN skeleton has been modified on various positions such as the nitrogen atom and methylene groups to provide a diverse array of potential ligands. As a simple modification of the nitrogen atoms, trialkyl-TACN derivatives (Me and *i*-Pr) have been synthesized. Trimethyl-TACN **7** can be prepared by reductive alkylation of TACN with formaldehyde in formic acid. Also, 1,4,7-tri-(*i*-Pr)-TACN **8** can be prepared from TACN and isopropyl bromide (1:4) in toluene over KOH at 80-90 ˚C.

Figure 1. Modification of TACN by *N*-alkylation.

[16] S. M. Weinreb, D. M. Demko, T. A. Lessen, *Tetrahedron Lett.* **1986**, *27*, 2099.



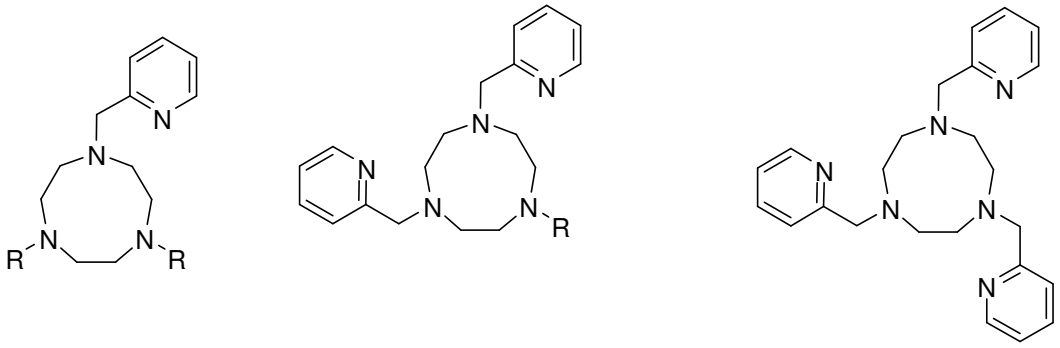
1,4,7-Triazacyclononane(TACN) 1,4,7-Trialkyl-triazacyclononane

7: R = Me
8: R = *i*-Pr

Several applications of trialkyl-TACN were subsequently reported. For example, remarkably efficient copper catalyzed aziridination with tri(*i*-Pr)-TACN **8** has been demonstrated.[17] Also, ruthenium-catalyzed dihydroxylation of alkenes with 1,4,7-tri(Me)-TACN (tmtacn) **9** has been reported.[18]

Modifications of TACN are facile and can provide various multidentate ligands. For example, by modification at the nitrogen atoms, 2-pyridylmethyl-pendant TACNs **10**, which can behave as tetradentate ligands, have been synthesized (Figure 2).

Figure 2. 2-Pyridylmethyl pendant TACN derivatives.



mptacn dmptacn tmptacn

10a: R = Me
10b: R = H

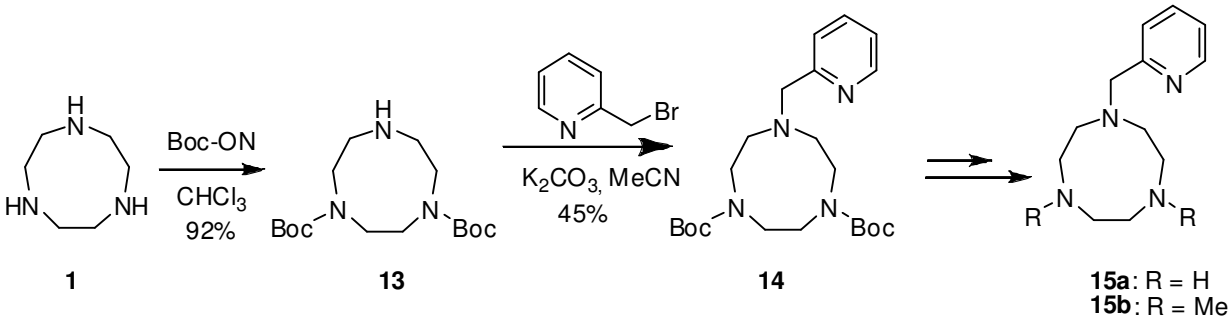
11a: R = Me
11b: R = H

12

In general, two routes provide access to mono 2-pyridylmethyl pendant mptacn. One route consists of the mono alkylation of di(Boc)-TACN (Scheme 3).[19] Following Boc protection, mono alkylation can be achieved. In the last step, the Boc groups can be removed by treatment with TFA in chloroform.

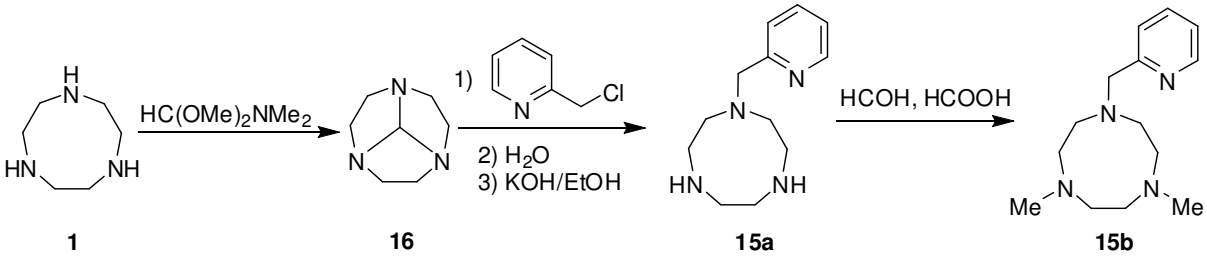
[17] J. A. Halfen, J. K. Hallman, J.A. Schulz, J. P. Emerson, *Organometallics* **1999**, *18*, 5435.
[18] W.-P. Yip, W.-Y, Yu, N. Zhu, C.-M. Che, *J. Am. Chem. Soc.* **2005**, *127*, 14239.
[19] a) G. L. Gillian, T. D. H. Bugg, *J. Am. Chem. Soc.* **2001**, *123*, 5030. b) A. J. Dickie, D. C. R. Hockless, A. C. Willis, J. A. Mckeon, W. G. Jackson, *Inorg. Chem.* **2003**, *42*, 3822. c) M. Tamura, Y. Urano, k. Kikuchi, T. Higuchi, M. hirobe, T. Nagano, *J. Organomet. Chem.* **2000**, *611*, 586.

Scheme 3. Synthesis of 2-pyridylmethyl pendant TACN **15** via Boc protected TACN.



The second route consists of elaboration of orthoamide **16** (Scheme 4). Orthoamide **16** can be prepared from TACN **1** by treatment with dimethylformamide dimethyl acetal or orthoformate.[20] Mono alkylation proceeds by reacting 2-chloromethylpyridine with the orthoamide in water at pH 9 for 7 days affording **15a** in good yield (91%).[21]

Scheme 4. Synthesis of 2-pyridylmethyl pendant TACN via orthoamide.



Dmptacn **10b**, which can act as a tetradentate ligand was synthesized by reductive alkylation of TACN with formaldehyde in formic acid.[22] Additionally, tmptacn **12**, which can be a hexadentate ligand, was synthesized by global alkylation of TACN **1**.[19, 23]

As described before, coordinating groups can be attached to the TACN framework by modification of its nitrogen atoms. A hexadentate ligand, 1,4,7-tris-*o*-aminobenzyl TACN and its metal complexes have been synthesized (Scheme 5).[24] However, its potential as a catalyst has not been investigated yet.

Scheme 5. Synthesis of 1,4,7-tris-*o*-aminobenzyl TACN **18**.

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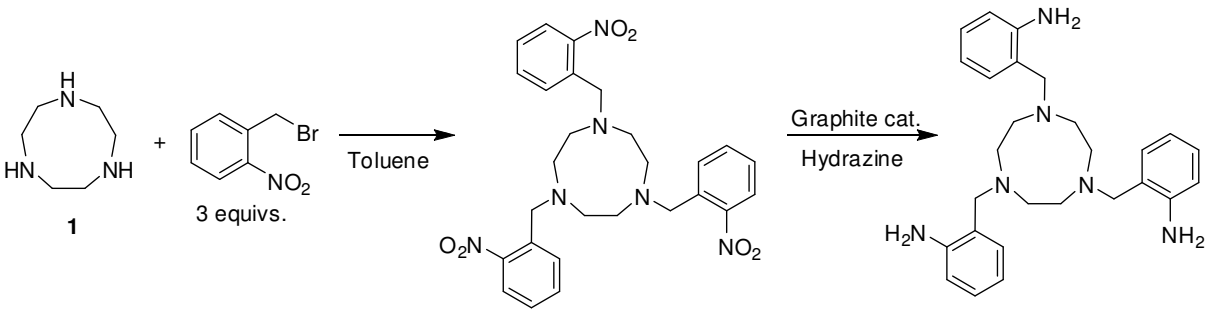
[20] a) J. M. Erhardt, J. D. Wuest, *J. Am. Chem. Soc*. **1980**, *102*, 6364. b) T. J. Atkins, U. S. Patents 4085106 and 4130715.

[21] P. C. McGowan, T. J. Podesta, M. Thornton-Pett, *Inorg. Chem*. **2001**, *40*, 1445.

[22] G. A. MacLachlan, G. D. Fallon, R. L. Martin, B. Moubaraki, K. S. Murray, L. Spiccia, *Inorg. Chem*. **1994**, *33*, 4663.

[23] H. Tsukube, K. Yamashita, T. Iwachido, M. Zenki, *J. Chem. Soc., Perkin Trans* **1991**, 1661.

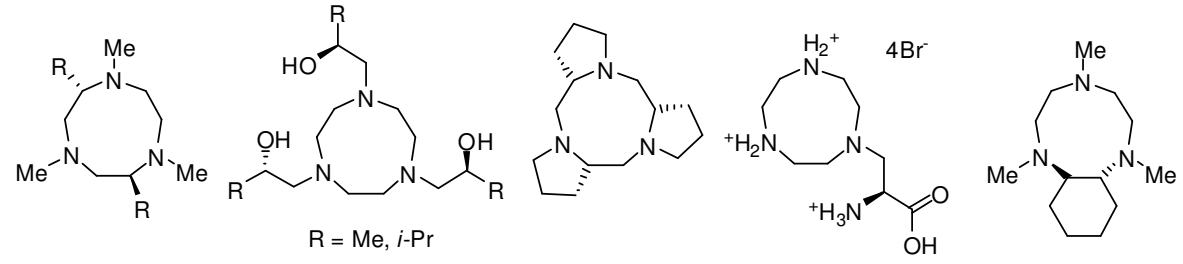
[24] a) O. Schlager, K. Wieghardt, H. Grondey, A. Rufińska, B. Nuber, *Inorg. Chem*. **1995**, *34*, 6440. b) O. Schlager, K. Wieghardt, B. Nuber, *Inorg. Chem*. **1995**, *34*, 6449. c) O. Schlager, K. Wieghardt, B. Nuber, *Inorg. Chem*. **1995**, *34*, 6456.



1 **17** **18**

For the use of the TACN skeleton in metal-catalyzed asymmetric reactions, several chiral ligands have been synthesized (Figure 3).

Figure 3. Chiral TACN ligands.



19a: $R^1 = R^2 = Me$
19b: $R^1 = R^2 = i\text{-Pr}$
19c: $R^1 = Me$, $R^2 = i\text{-Pr}$

R = Me, *i*-Pr

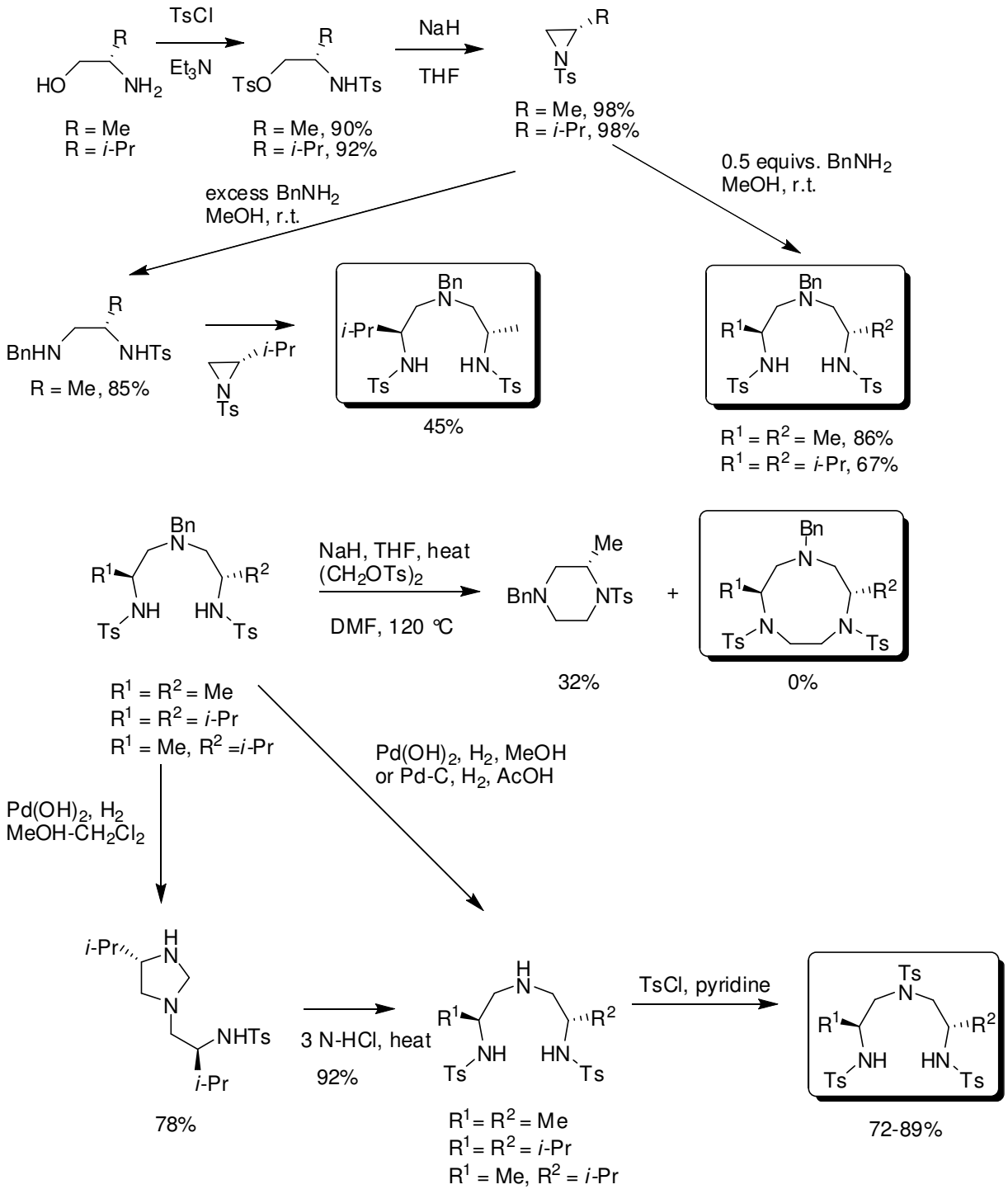
20a: R = Me
20b: R = *i*-Pr

21 **22** **23**

Each chiral ligand, which has chiral moieties located either pendant to the nitrogen or in the macrocyclic backbone, was synthesized by a different procedure. In the case of chiral ligand **19**, which has an achiral backbone, the chiral part has to be introduced before formulation of the TACN framework. For example, the first chiral TACN derivative was successfully synthesized by disconnection route A, whereas disconnection route B failed.[25] First, chiral aziridines were prepared from chiral amino alcohols in high yields, ring opening reactions with benzylamine then afforded acyclic triamines (Scheme 6). Unfortunately, the benzyl protected triamines could not be cyclized directly. Therefore, the benzyl group was removed by hydrogenolysis and replaced with a tosyl moiety.

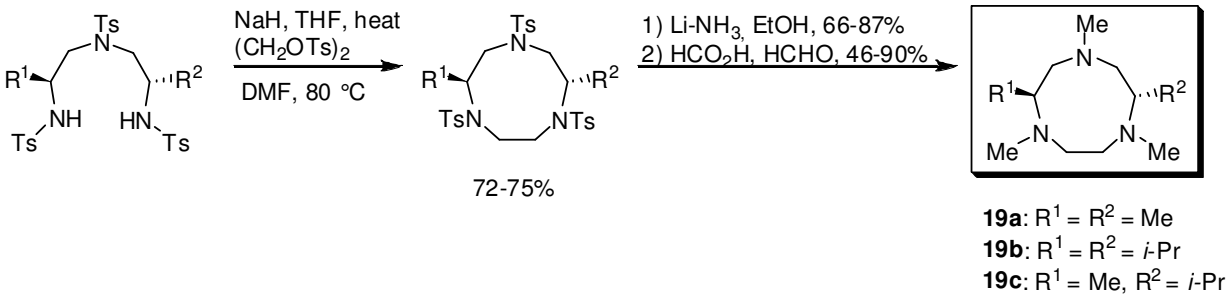
Scheme 6. Synthesis of intermediates for chiral TACN derivatives.

[25] G. Argouarch, C.L. Gibson, G. Stones, D. C. Sherrington, *Tetrahedron Lett*. **2002**, *43*, 3795.



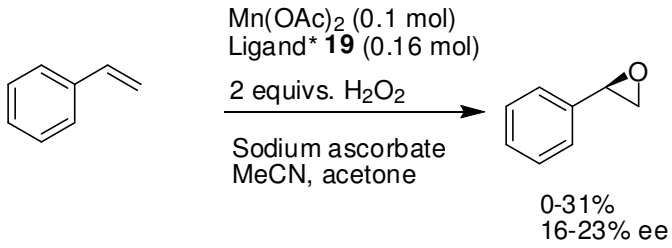
At last, desired products **19a-c** were obtained in good yields by Richmann-Atkins cyclization of the corresponding tritosyl triamines followed by deprotection of the *N*-tosyl groups by Li-NH_3 in EtOH (Scheme 7).

Scheme 7. Synthesis of chiral TACN derivatives.



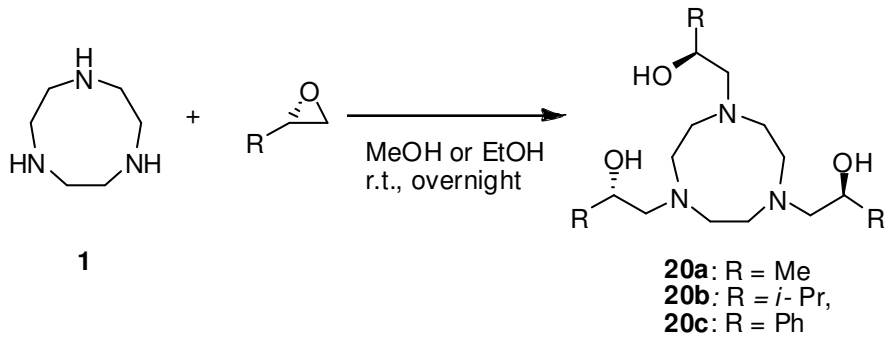
These chiral ligands were examined in manganese-catalyzed epoxidation of styrene. Unfortunately however, the epoxide was obtained in low yields with only 16-23% ee (Scheme 8).

Scheme 8. Mn-catalyzed epoxidation of styrene with chiral TACN ligands **19**.



A second type of chiral TACN ligand, which bears achiral side chains at the nitrogen atoms, can be easily prepared by using ring-opening reactions of chiral epoxides with TACN. [26] The application of this ligand class in manganese-catalyzed epoxidation of olefins was demonstrated by Bolm *et al*. (Scheme 9) [27].

Scheme 9. Synthesis of pendant chiral TACN derivatives.

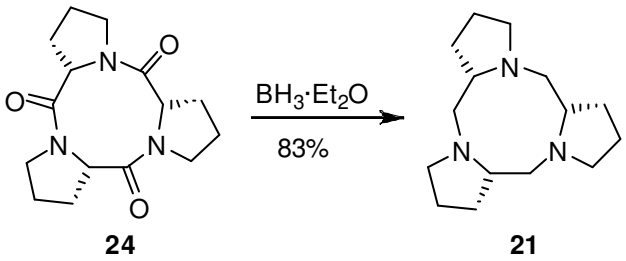


[26] a) I. A. Fallis, L. J. Farrugia, N. M. Macdonald, R. D. Peacock, *J. Chem. Soc., Dalton Trans* **1993**, 2759. b) J. M. Weeks, M. A. Buntine, S. F. Lincoln, E. R. T. Tiekink, K. P. Wainwright, *J. Chem. Soc. Dalton Trans* **2002**, 2157.

[27] C. Bolm, D. Kadereit, M. Valacchi, *Synlett* **1997**, 687.

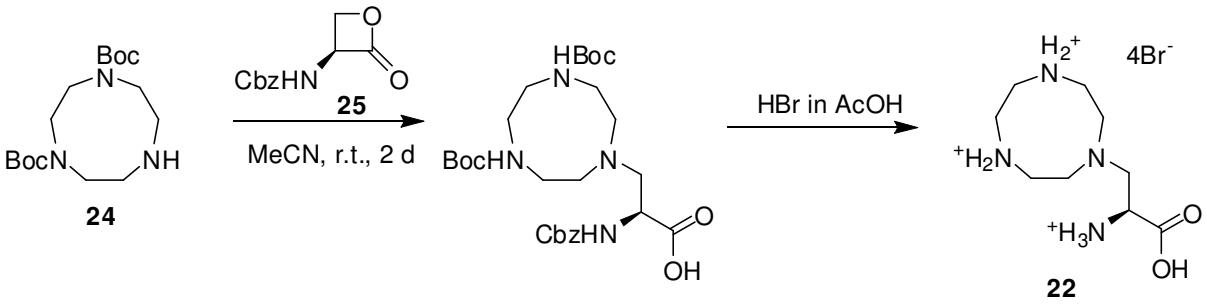
C_3-symmetric chiral ligand trispyrroridine-TACN (TP-TACN) **21** was prepared from *L*-proline derived cyclotripeptide **24** (Scheme 10).[28]

Scheme 10. Synthesis of chiral TP-TACN ligand.



A monofunctionalized Chiral TACN ligand **22** was synthesized by a ring opening reaction of lactone **25** with di-(Boc) TACN **24** followed by deprotection (Scheme 11).[29]

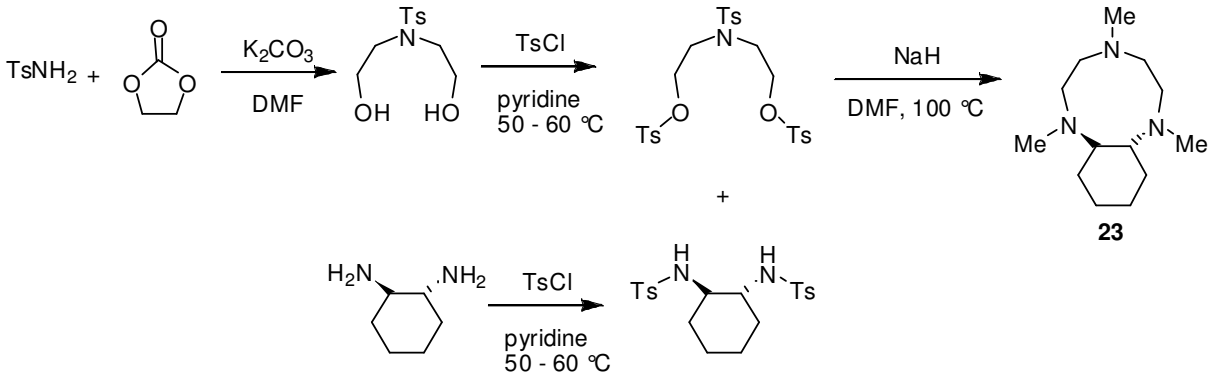
Scheme 11. Synthesis of chiral TACN ligand **22**.



A synthesis of novel chiral ligand **23** was developed by Watkinson *et al.*[30] In their study, disconnection route C successfully provided the desired product (Scheme 12).

Scheme 12. Synthesis of chiral TACN ligand **23**.

[28] C. Bolm, N. Meyer, G. Raabe, T. Weyhermüller, E. Bothe, *Chem. Commun*. **2000**, 2435.
[29] P. Rossi, F. Felluga, P. Scrimin, *Tetrahedron Lett*. **1998**, *39*, 7159.
[30] S. Pulacchini, K. F. Sibbons, K. Schastri, M. Motevalli, M. Watkinson, H. Wan, A. Whiting, A. P. Lightfoot, *J. Chem. Soc., Dalton Trans* **2003**, 2043.



In 1997, the synthesis of chiral TACN ligand **23** and its manganese complex was patented by Beller *et al.* [31] Some applications of this chiral ligand in the oxidations of olefins, alkanes and alcohols were recently reported.[32]

As mentioned previously, some TACN ligands have been successfully used in metal-catalyzed oxidation reactions.[33 , 34] Several metal complexes with TACN type ligands have been reported. [10, 13, 21, 22, 35, 36, 37,] Also, catechol oxygenase reactivity of an iron(III) complex with TACN ligands was demonstrated. As an application for these chiral ligands, manganese-catalyzed epoxidation of styrene has been described by Bolm[28] and Argouarch.[25]

To provide a means of separating the product and the catalyst to allow for catalyst recycling and easy product purification, the concepts of catalyst immobilization and perfluorination have been adopted. As an example of immobilization, polymer supported TACN was synthesized and its application in manganese-catalyzed oxidation was demonstrated (Scheme 13).[38]

Scheme 13. Synthesis of a polymer supported chiral TACN ligand.

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[31] M. Beller, T. Ahmed, F. R. Walter, S. Bernd, Patent DE 19523891.

[32] V. B. Romakh, B. Therrien, G. Süss-Fink, G. B. Shulpin, *Inorg. Chem*. **2007**, *46*, 1315.

[33] For Fe-catalyzed oxidations, see: a) E. Y. Tshuva, D. Lee, W. Bu, S. J. Lippard, *J. Am. Chem. Soc*. **2002**, *124*, 2416.

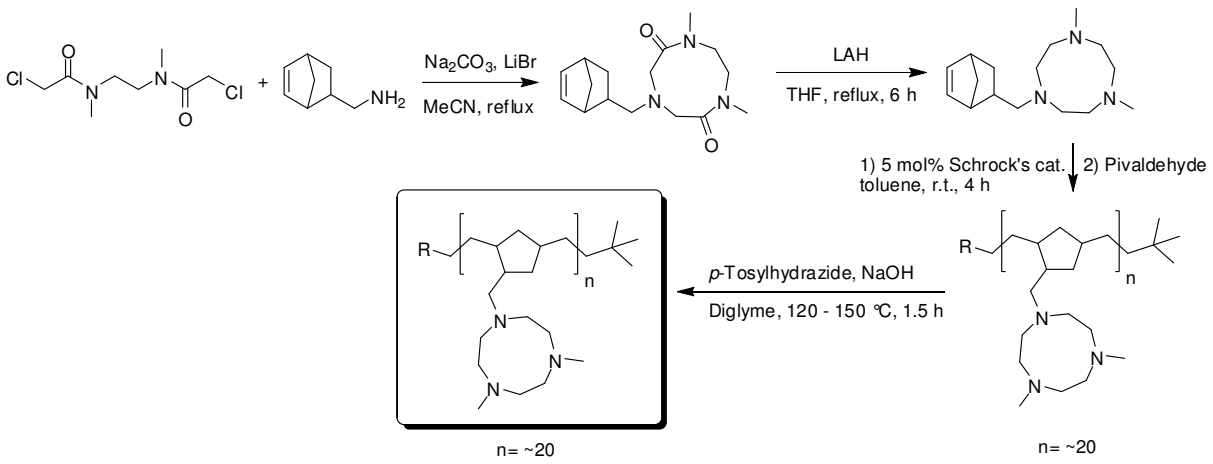
[34] For Mn-catalyzed epoxidations, see: a) A. Murphy, A. Pace, T. D. P. Stack, *Org. Lett.* **2004**, *6*, 3119. For Mn-catalyzed oxidation of sulfide, see: b) J. E. Barker, T. Ren, *Tetrahedron Lett*. **2004**, *45*, 4681.

[35] J. L. Sessler, J. W. Silbert, V. Lynch, *J. Am. Chem. Soc.* **1990**, *29*, 4143.

[36] For Fe-complexes, see: a) A. L. Gott, P. C. McGowan, T. J. Podesta, M. Thornton-Pett, *J. Chem. Soc., Dalton Trans* **2002**, 3619. b) L. Siccia, G. D. Fallon, M. J. Grannas, P. J. Nichols, E. R. T. Tiekink, *Inorg. Chim. Acta* **1998**, *279*, 192.

[37]For Co-complexes, see: a) A. R. Siedle, L. H. Pignolet, *Inorg. Chem*. **1982**, *21*, 3090. b) P. S. Roy, K. Wieghardt, *Inorg. Chem*. **1987**, *26*, 1885. c) K. Wieghardt, P. Chaudhuri, B. Nuber, J. Weiss, *Inorg. Chem*. **1982**, *21*, 3086.
For Mn-complexes, see: f) S. J. Brudenell, L. Spiccia, A. M. Bond, G. D. Fallon, D. C. R. Hockeless, G. Lazarev, P. J. Mahon, E. R. T. Tiekink, *Inorg. Chem.* **2000**, *39*, 881. g) G. D. Fallon, G. A. McLachlan, B. Moubaraki, K. S. Murray, L. O'Brien, L. Spiccia, *J. Chem. Soc., Dalton Trans* **1997**, 2765.

[38] a) A. Grenz, S. Ceccarelli, C. Bolm, *Chem. Commun*. **2001**, 1726. b) V. V. Subba Rao, D. E. De Vos, T. Bein, P. A. Jacobs, *Chem. Commun*. **1997**, 355. c) D. E. De Vos, S. de Wildeman, B. F. Sels, B. J. Grobet, P. A. Jacobsen, *Angew. Chem*. **1999**, *38*, 980, *Angew. Chem. Int. Ed*. **1999**, *38*, 937.



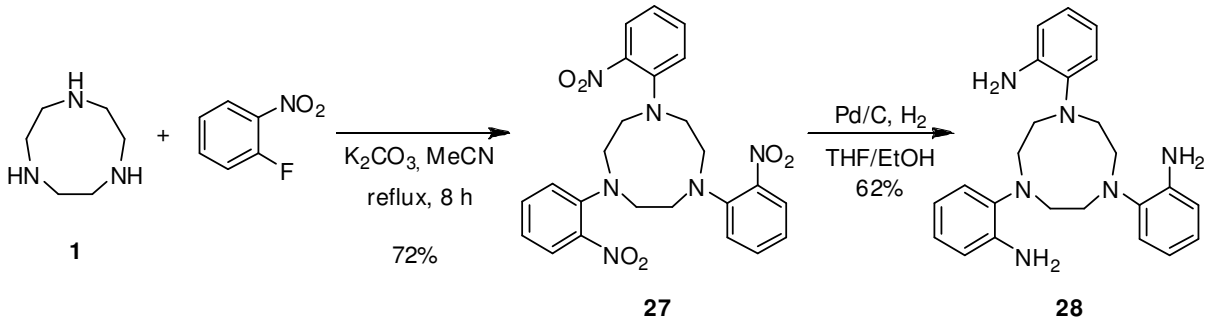
An example of fluorous biphasic catalysis (FBC), using a perfluoroponitailed TACN in a metal-catalyzed oxidation has been reported.[39]

Unfortunately, due to industrial interest in the ligand class, many kinds of TACN derivatives have been patented. Consequently, TACN chemistry has not been developed very extensively because patent protection limits the development of new industrial applications.

Although variations of the existing methods have been developed to overcome this problem, there are still only a few examples in which an aryl group is introduced at the nitrogen atoms of the TACN framework. In order to make a more rigid ligand and to increase the strength of metal-ligand interaction by reducing the chelate size from a 6 to a 5 membered ring, *tris*(*o*-aminophenyl)-TACN has been synthesized. As an example, the first *N*-aryl-TACN was obtained by arylation of TACN with *o*-nitro-phenyl fluoride **24** under basic conditions (Scheme 14).[40]

Scheme 14. Synthesis of a rigid hexadentate TACN ligand.

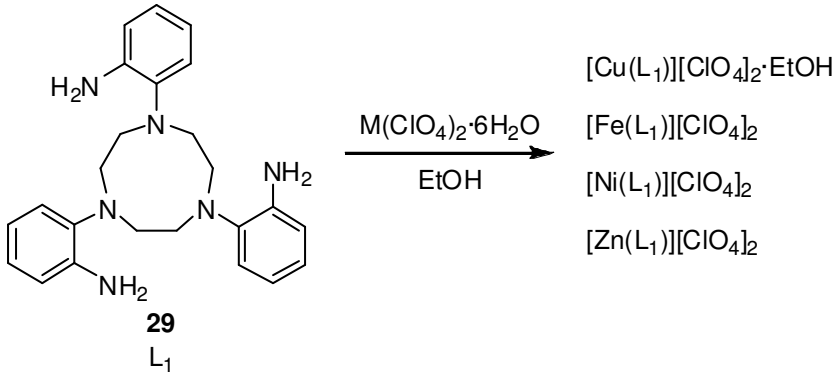
[39] J -M. Vincent, R. Rabion, V. K. La Yachandra, R. H. Fish, *Angew. Chem.* **1997**, *109*, 2438, *Angew. Chem.Int. Ed.* **1997**, *36*, 2346.
[40] I. A. Fallis, R. D. Farley, K. M. Abdul Malik, D. M. Murphy, H. J. Smith, *J. Chem. Soc., Dalton Trans* **2000**, 3632 and references therein.



1 27 28

The nitro groups in the ortho positions were reduced by hydrogenation with Pd/C to give a hexadentate TACN ligand **25**. Furthermore, complexation reactions with several metal(II) perchlorates such as zinc, nickel, copper and iron in degassed ethanol were successful and crystal structures were determined by X-ray analysis (Scheme 15). As expected, these complexes have extremely rigid structures.

Scheme 15. Complexation with several kinds of metal(II) perchlorates.



29
L_1

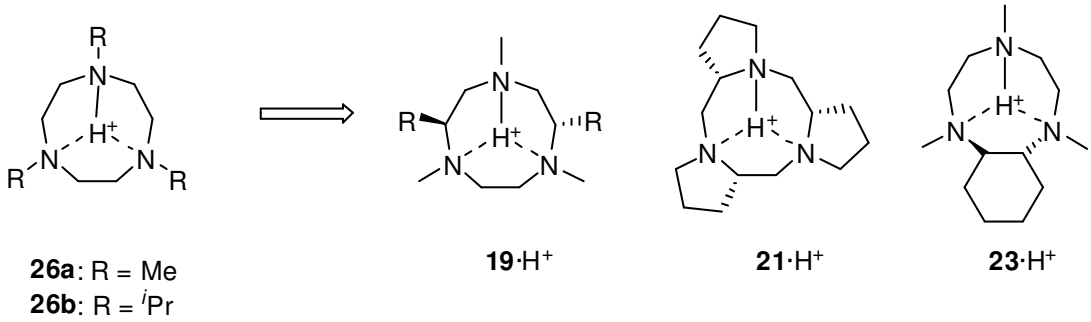
Unfortunately, 5 years after the first report, arylation of TACN with *p*-nitro-aryl fluoride was patented because of great interest from industry.[41] Another drawback is that the procedure probably proceeds by a S_NAr mechanism and would thus be limited to aryl halides bearing strongly electron withdrawing groups. Moreover, the claim in the patent includes only specific substrates so that other aryl-TACN derivatives are patent-free. In fact, this field is still relatively unexplored.

Another relatively new concept involves the synthesis of novel chiral, monoprotonated tmtacn **26** by treatment of tmtacn with perchloric acid. The structure of the salt was determined X-ray

[41] L. Vidal, S. Sabelle, T.-M. Ly-Carry, U.S. Patent 2005/0120494 A1.

crystallography.[42] If these monoprotonated derivatives are applicable as chiral TACN ligands, a new type of chiral proton source can be developed (Figure 4).

Figure 4. TACN derived chiral proton sources.



1.2.2 Dipyridylamine Type Ligands

A number of nitrogen containing bidentate ligands such as bipyridine and phenanthroline, which form five membered-ring chelates, have been reported. [43, 44] Also, applicability of these ligands in asymmetric metal-catalyzed synthesis has been demonstrated. [45] Terpyridine derivatives[46] can be used as tridentate ligands in metal-catalyzed reactions.

However, dipyridylamine type ligands, which give six membered-ring chelates have not been intensively studied. As representative analogues, bis(pyridyl)silane,[47] chiral dipyridylketone[48] and 2,2'-disubstituted dipyridylpropane[49] were introduced. Recently, non-heme iron catalysts with tris(2-pyridylmethyl)amine (tpa) type ligands[50] and their derivatives have been studied by Que, Jr. *et al*.[51]

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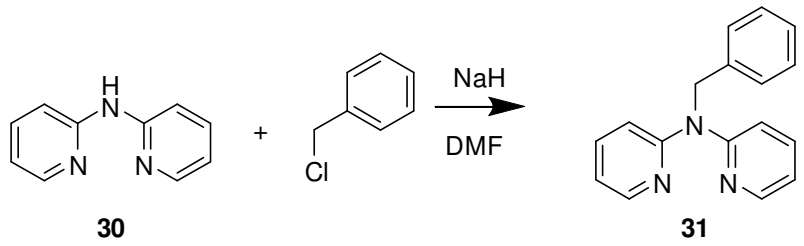
[42] K. Wieghardt, S. Brodka, E. M. Peters, K. Peters, A. Simon, *Z. Naturforsch., Teil B* **1987**, *42*, 279.
[43] a) C. Duboc-Toia, S. Ménage, C. Lambeaux, M. Fontecave, *Tetrahedron Lett*. **1997**, *38*, 3727. b) C. Duboc-Toia, S. Ménage, R. Y. N. Ho, L. Que, Jr., C. Lambeaux, M. Fontecave, *Eur. J. Inorg. Chem.* **2002**, 111. c) X. Liu, A. Qiu, D. T. Sawyer, *J. Am. Chem. Soc.* **1993**, *115*, 3239.
[44] a) C. Bolm, In *Advanced in Organic synthesis via Organometallics*, R. W. Hofffmann, K. H. Dötz, Eds.; Vieweg: Wiesbaden, 1991; p 223. b) A. V. Malkov, P. Kocovsky, *Curr. Org. Chem.* **2003**, *7*, 1737.
[45] a) G. Cheluchi, R. P. Thummel, *Chem. Rev*. **2002**, *102*, 3129. b) N. C. Fletcher, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1831. c) F. Fache, E. Schulz, M. L. Tommasino, M. Lemaire, *Chem. Rev*. **2000**, *100*, 2159.
[46] a) Y. Yamamoto, T. Tanaka, M. Yagi, M. Inamoto, *Heterocycles* **1996**, *42*, 189. b) S. Tu, T. Li, F. Shi, Q. Wang, J. Zhang, J. Xu, X. Zhu, X. Zhang, S. Zhu, D. Shi, *Synthesis* **2005**, 3045.
[47] M. E. Wright, S. A. Svejda, M. J. Jin, M. A. Peterson, *Organometallics* **1990**, *9*, 136.
[48] H.-L. Kwong, , L.-S. Cheng, W.-L. Wong, W.-T, Wing, *Eur. J. Inorg. Chem.* **2000**, 1997.
[49] G. Cheluchi, G. Loriga, G. Murineddu, G. A. Pinna, *Tetrahedron Lett*. **2002**, *43*, 8599.
[50] Z. Tyeklár, R. R. Jacobson, N. Wei, N. N. Murthy, J. Zubieta, K. D. Karlin, *J. Am. Chem. Soc*. **1993**, *115*, 2677.
[51] M. Costas, A. K. Tipton, K. Chen, D.-H. Jo, L. Que, Jr, *J. Am. Chem. Soc*. **2001**, *123*, 6722.

Dipyridylbenzylamine **31** can be prepared by alkylation of dipyridylamine with benzyl chloride and sodium hydride in refluxing DMF (Scheme 16). [52] Additionally, an X-ray structure of its copper complex was reported.

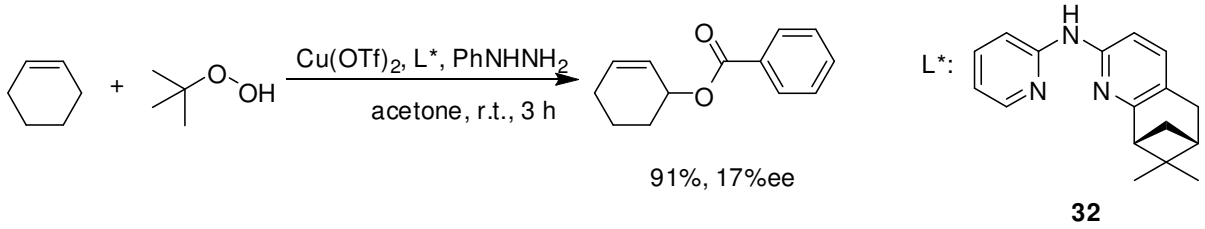
Scheme 16. Classical procedure for the synthesis of dipyridylbenzylamines.



30 **31**

As one application of chiral dipyridylamine ligands, the copper-catalyzed asymmetric allylic oxidation of cyclohexene based on the Kharasch-Sosnovski reaction has been reported by J. C. Frison (Scheme 17). [53]

Scheme 17. Copper-catalyzed allylic oxidation.



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First 2,2'-*N,N*-dipyridylamine ligand **34** was synthesized by Schindler *et al.* in 2002.[54a] In their paper, characterization of a copper(II) complex by X-ray analysis, UV/VIS spectroscopy and cyclic voltammetry was reported. Interestingly, the crystal structure of this copper complex indicates that one of the three pyridyl donors remains uncoordinated.

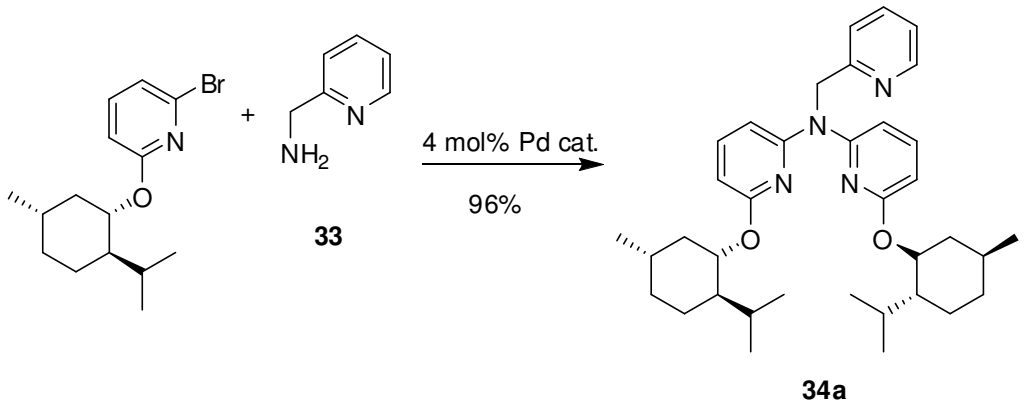
A few years later, catechol oxygenase reactivity of an iron(III) complex with this ligand was demonstrated.[53b] However, in their study, a sufficient amount of $[Fe(L)(dbc)]^+$ to characterize the catalytic species was not detectable by UV spectroscopy.

[52] Y. Oh, *J. Korean. Chem. Soc*. **2000**, *44*, 507.
[53] C. Bolm, J.-C. Frison, J. Le Paih, C. Moessner, *Tetrahedron Lett.* **2004**, *45*, 5019.
[54] a) S. P. Foxon, O. Walter, S. Schindler, *Eur. J. Inorg. Chem.* **2002**, 111. b) M.Merkel, M. Pascaly, B. Krebs, J. Astner, S. P. Foxon, S. Schindler, *Inorg. Chem.* **2005**, *44*, 7582.

As another example of metal complexation, molybdenum and ruthenium complexes of **31** have been reported for spectroscopic and electroscopic studies.[55]

In 2001, the synthesis of 2,2'-dipyridylbenzylamine type ligands and their complexes with palladium and nickel were reported by Kempe *et al*.[56] Moreover, in our group, synthesis of dipyridylamine type ligands using palladium-catalyzed *N*-arylation based on Buchwald-Hartwig amination[57] was developed by J. C. Frison. This method can be applied in the synthesis of chiral *N*,*N*'-2,2'-dipyridylamine **34a** (Scheme 18).

Scheme 18. Palladium-catalyzed *N*-arylation of 2-picolylamine.



This ligand was considered to hold undiscovered potential for catalysis. Due to the simplicity of its synthesis and structure, this ligand attracted attention as a new type of structure of unknown and potentially exciting reactivity.

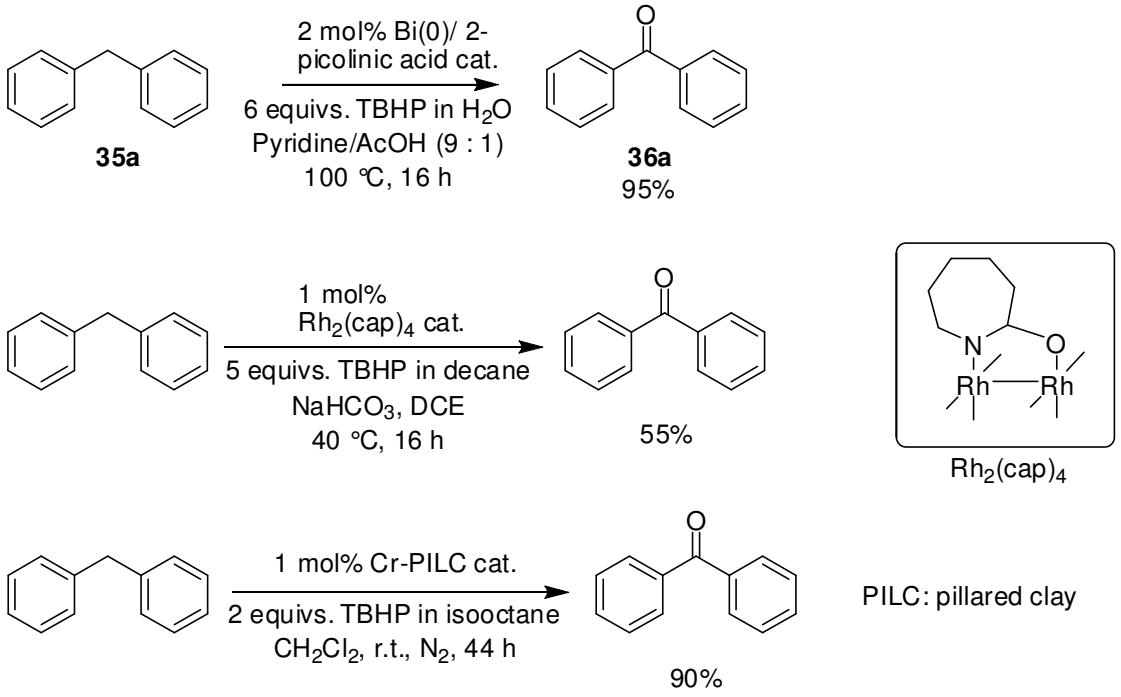
1.3 General Metal-Catalyzed Benzylic Oxidation Chemistry

Today, metal-catalyzed oxidation reactions are intensively studied in organic chemistry.[58] Among these reactions, metal-catalyzed oxidation of hydrocarbons is still a challenging transformation. Recently, metal-catalyzed benzylic oxidation reactions with *tert*-butyl hydroperoxide (TBHP) have been reported. Representative efficient benzylic oxidation

[55] R. M. Ramadan, M. S. A. Hamza, H. M. Mohamed, S. M. El-Medani, *Transit. Met. Chem. (Dordrecht, Netherlands)* **2006**, *31*, 107.
[56] T. Schareina, G. Hillebrand, H. Fuhrmann, R. Kempe, *Eur. J. Inorg. Chem.* **2001**, 2421.
[57] S. Wagaw, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 7240.
[58] For epoxidation, see: B. S. Lane, K. Burgess, *Chem. Rev*. **2003**, *103*, 2457.

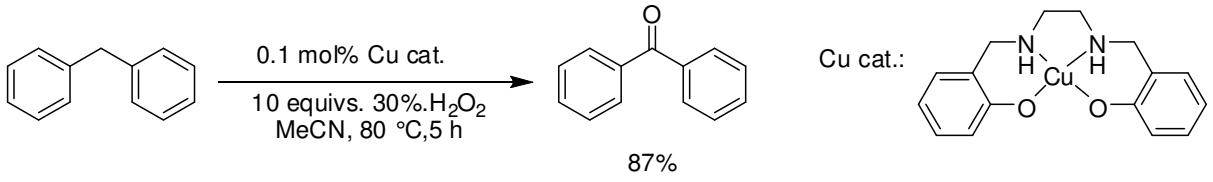
reactions of diphenylmethane with a metal catalyst such as Bi, Rh and Cr are shown in Scheme 19. [59]

Scheme 19. Metal-catalyzed benzylic oxidation with TBHP.



Hydrogen peroxide can be used in place of TBHP as a green oxidant. A representative copper-catalyzed benzylic oxidation reaction is shown in Scheme 20.[60] In this system, the salan ligand has been found to be an efficient in promoting this transformation Thus, a reaction using $Cu(OAc)_2$ without a ligand gave only 8% conversion.

Scheme 20. Copper-catalyzed benzylic oxidation with H_2O_2.



In the last decades, heme and non-heme iron-catalyzed oxidations such as Baeyer-Villiger type reactions, [61] epoxidation [62] and dihydroxylation of olefins, [63] and the oxidation of

[59] Bi-catalyzed oxidation, see: a) Y. Bonvin, E. Callens, I. Larrosa. A. Henderson, J. Oldham, A. J. Burton, A. G. M. Barette, *Org. Lett.* **2005**, *7*, 4549. Rh-catalyzed oxidation, see: b) A. J. Catino, J. M. Nichols, H. Choi, S. Gottipamula, M. P. Doyle, *Org. Lett.* **2005**, *7*, 5167. Cr-catalyzed oxidation, see: c) B. M. Choudary, A. D. Prasad, v. Bhuma, V. Swapna, *J. Org. Chem.* **1992**, *57*, 5841.
[60] S. Velusamy, T. Punniyamurthy, *Tetrahedron Lett.* **2003**, *44*, 8955.
[61] S. Murahashi, Y. Oda, T. Naota, *Tetrahedron Lett.* **1992**, *33*, 7557.

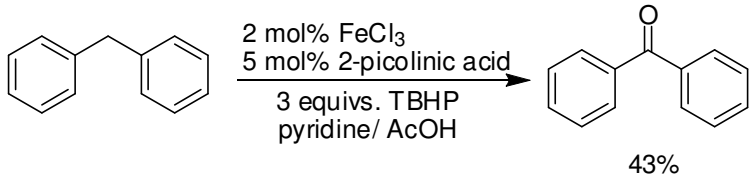
sulfides,[64] sulfoxides,[42a] alcohols[65] and hydrocarbons[66] have been studied by many chemists. On the other hand, iron-catalyzed C-H oxidation of hydrocarbons is one of the most difficult reactions in oxidation chemistry. Iron oxidation chemistry based on Gif chemistry, which was introduced by Sir Derek Barton in 1983, has been well studied. A summary of the Gif system is shown in Table 1.[67]

Table 1. Summary of the Gif oxidation system.

System	Precatalyst	Oxidant	Reductant	Solvent (r.t.)
Gif^{I}	X	O_2	$Fe^{II/III}$ / Na_2S	Py/ AcOH(10: 1)
Gif^{II}	X	O_2	Fe^{0} / H_2S	Py/ AcOH/H_2O(6.6 %)
Gif^{III}	X	O_2	Fe^{0}	Py/ AcOH/H_2O(6.6 %)
Gif^{IV}	$Fe^{II/III}$	O_2	Zn	Py/ AcOH/H_2O(6.6 %)
$GoAgg^{I}$	Fe^{II}	KO_2(under Ar or N_2)		Py/AcOH
$GoAgg^{II}$	Fe^{III}	H_2O_2(under Ar or O_2)		Py/AcOH
$GoAgg^{III}$	Fe^{III}/ PicH(1:3)	H_2O_2		Py/AcOH(or Py)
$GoAgg^{IV}$	$Fe(NO_3)_3$	TBHP		Py/AcOH(or Py)
$GoAgg^{V}$	$Fe(NO_3)_3$ / PicH(1:3)	TBHP		Py/AcOH Py/AcOH, 60 °C Py/AcOH, 60 °C

Untill now the best yields were obtained using the $GoAgg^{V}$ system (Scheme 21).[56b, 68]

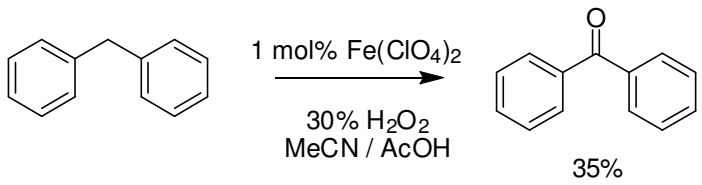
Scheme 21. Iron-catalyzed benzylic oxidation based on $GoAgg^{V}$.



[62] G. Dubois, A. Murphy, T. D. P. Stack, *Org. Lett*. **2003**, *5*, 2469.
[63] a) J. P. Collman, Z. Wang, A. Straumanis, M. Quelquejeu, E. Rose, *J. Am. Chem. Soc*. **1999**, *121*, 460. b) G. Dubois, A. Murphy, T. D. P. Stack, *Org. Lett.* **2003**, *5*, 2469. c) M. C. White, A. G. Doyle, E. N. Jacobsen, *J. Chem. Soc*. **2001**, *123*, 7194. d) M. B. Francis, E. N. Jacobsen, *Angew. Chem.* **1999**, *111*, 987, *Angew. Chem. Int. Ed.* **1999**, *38*, 937. e) P. D. Oldenburg, A. A. Shteinman, l. Que, Jr., *J. Am. Chem. Soc*. **2005**, *127*, 15672. f) Z. Gross, S. Ini, *J. Org. Chem*. **1997**, *62*, 5514. g) T. G. Trayler, S. Tsuchiya, Y. S. Byun, C. Kim, *J. Am. Chem. Soc*. **1993**, *115,* 2775. h) K. Chen, M. Costas, J. Kim, A. K. Tipton, L. Que. Jr., *J. Am. Chem. Soc*. **2002**, *124*, 3026. i) K. Chen, L. Que. Jr., *J. Am. Chem. Soc*. **2001**, *123*, 6327.
[64] a) H. Egami, T. Katsuki, *J. Am. Chem. Soc*. **2007**, *129*, 8940. b) J. Legros, C. Bolm, *Angew.Chem.* **2003**, *115*, 5645, *Angew.Chem. Int. Ed.* **2003**, *42* 5487. c) J. Legros, C. Bolm, *Angew.Chem.* **2004**, *116*, 4321, *Angew.Chem. Int. Ed.* **2004**, *43*, 4225. d) Y. Mekmouche, H. Hummel, R. Y. N. Ho, L. Que, Jr., V. Schünemann, F. Thomas, A. X. Trautwein, C. Lebrun, K. Gorgy, J.-C. Leprêtre, M-N. Collomb, A. Deronzier, M. Fontcave, S. Ménage, *Chem. Eur. J*. **2002**, *8*, 1196.
[65] S. E. Martin, D. F. Suárez, *Tetrahedron Lett*. **2002**, *43*, 4475.
[66] a) D. H. R. Barton, T. L. Wang, *Tetrahedron* **1994**, *54*, 1735. b) D. H. R. Barton, W. Chavasiri, *Tetrahedron* **1994**, *50*, 19. c) S. Murahashi, Y. Oda, T. Naota, *J. Am. Chem. Soc.* **1992**, *114*, 7913. d) J. T. Groves, P. Viski, *J. Am. Chem. Soc*. **1989**, *111*, 8537. e) J. T. Groves, P. Viski, *J. Org. Chem. Soc*. **1990**, 55, 3628. f) C. Sheu, S. A. Richert, P. Cofre, B. Ross, A. Sobkowiak, D. T. Sawyer, J. R. Konofsky, *J. Am. Chem. Soc*. **1990**, *112*, 1936.
[67] *Modern Oxidation Methods* (Ed.: J.-E. Bäckvall), Wiley-VCH, Weinheim, **2004**.
[68] D. H. R. Barton, T. L. Wang, *Tetrahedron* **1994**, *54*, 1735.

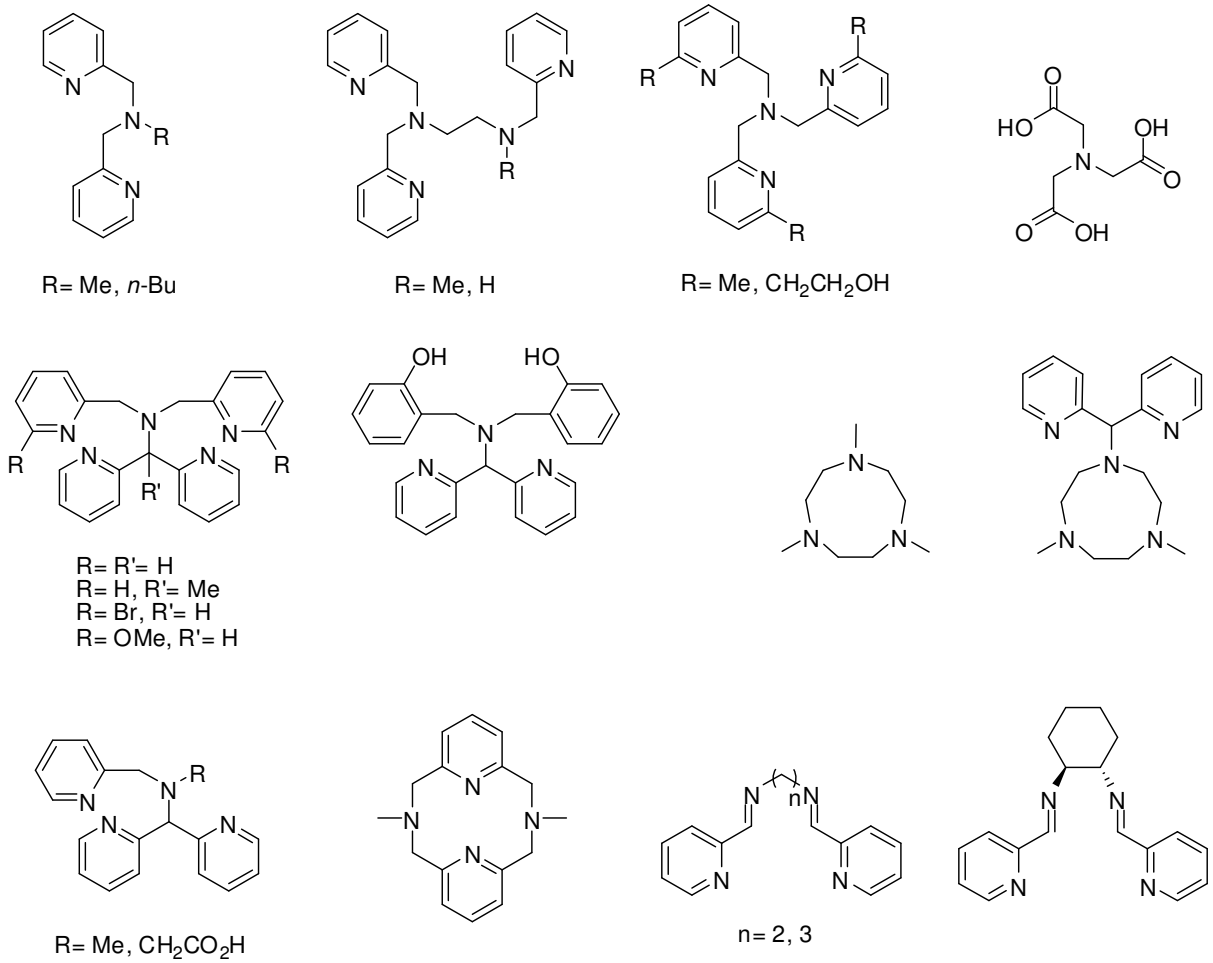
Recently, an iron-catalyzed benzylic oxidation with hydrogen peroxide as oxidant was reported by Bolm *et al*. (Scheme 22).[69] In this system, a slow addition of the oxidant is still necessary.

Scheme 22. Iron-catalyzed benzylic oxidation with H_2O_2.



Also, ligand screening for non-heme iron-catalyzed benzylic oxidation with hydrogen peroxide has been conducted.[70] However, for all of these types of ligands, benzylic oxidation did not work well. The ligands examined are shown in Figure 5.

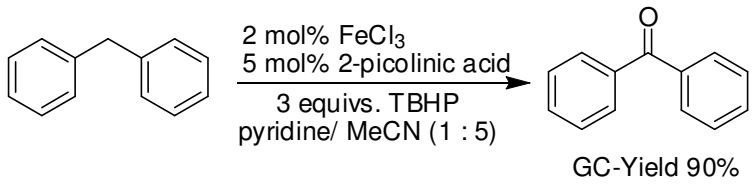
Figure 5. A variety of ligands used for benzylic oxidation.



[69] C. Pavan, J. Legros, C. Bolm, *Adv. Synth. Catal*. **2005**, *347*, 703.
[70] M. Klopstra, R. Hage, R. M. Kellogg, B. L. Feringa, *Tetrahedron Lett.* **2003**, *44*, 4581.

Recently, an iron-catalyzed benzylic oxidation with TBHP, which falls into the category of Gif chemistry, was reported by a Korean group (Scheme 23).[71] In their study, the best yield with most of the substrates was obtained using Gif type chemistry. However, changing the solvent system to pyridine/MeCN = 1/5 gave a dramatic improvement in yield.

Scheme 23. Iron-catalyzed benzylic oxidation with TBHP.

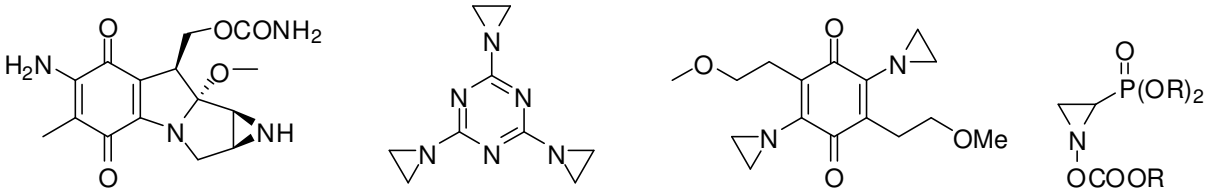


Superficially, their results seem to be excellent. However, there are several disadvantages. In their system, slow addition of the oxidant with a syringe pump is necessary. Furthermore, 2-picolinic acid was necessary as an additional ligand.

1.4 Aziridination Chemistry

Nitrogen transfer reactions are of great importance in organic synthesis. Among them, aziridination is studied intensively. Aziridines, which are the smallest saturated azaheterocyclic compounds, can be versatile synthetic intermediates. Also, the aziridine moiety itself is contained in the framework of drugs, natural products and ligands (Figure 6).[72]

Figure 6. Aziridine containing compounds.

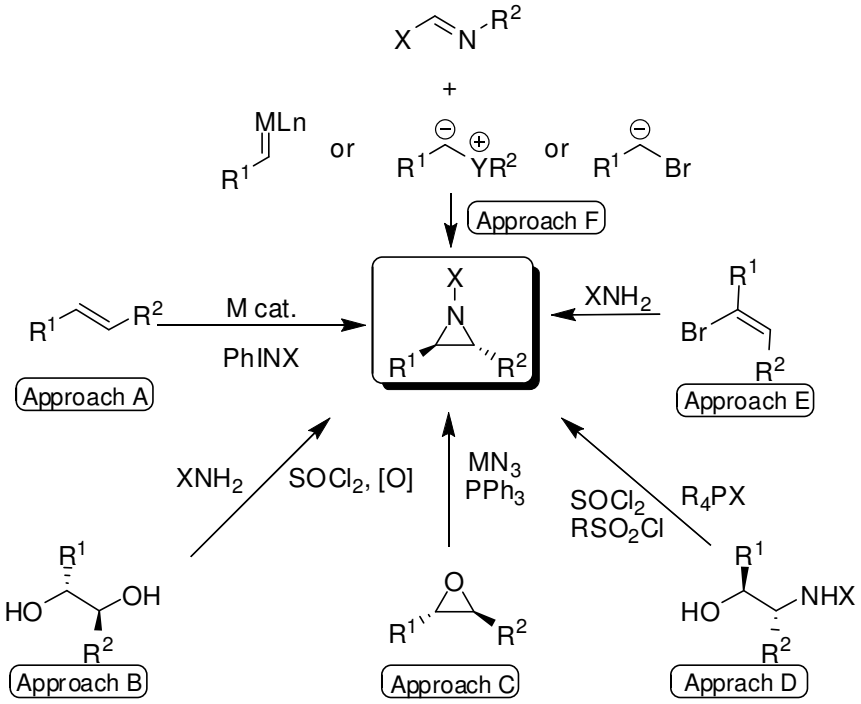


As already mentioned in chapter 1.2, aziridines are also important intermediates in the synthesis of chiral TACN ligands **19**.

[71] S. S. Kim, K. S. Sar, P. Tamrakar, *Bull. Korean Chem. Soc*. **2002**, *23*, 937.
[72] G. S. Singh, M. D'hooghe, N. D. Kimpe, *Chem. Rev*. **2007**, *107*, 2080.

The first aziridines were synthesized by Gabriel in 1888.[73] Classically, aziridines can be prepared from β-iodo azides,[74] haloamines,[75] amino alcohols (Wenker synthesis)[76] and epoxides.[77] Aziridination chemistry became of great interest due to its high utility in synthesis. In the past decades, metal-catalyzed aziridinations have been developed. By the same token, non-metal catalyzed [78] and organocatalyzed aziridinations[79] have been described. A summary of synthetic approaches to aziridines is shown in Scheme 24.[80]

Scheme 24. Synthetic approaches to aziridines.

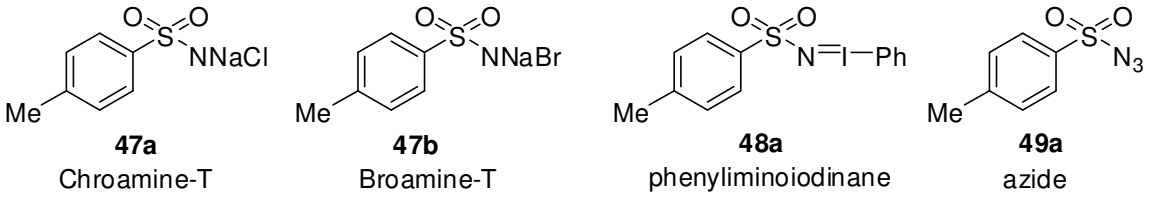


In these approaches, metal-catalyzed aziridination of olefins with a nitrene source (approach A) is one of the most challenging and potentially convenient methods. Typical nitrene sources

[73] S. Gabriel, *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 1049.
[74] A. Hassner, G. J. Matthew, F. W. Fowler, *J. Am. Chem. Soc.* **1969,** *91,* 5046.
[75] a) M. S. Kharasch, H. M. Priestley, *J. Am. Chem. Soc*. **1939**, *61*, 3435. b) A. Zwiezak, K. Osowka, *Angew. Chem.* **1976**, *88*, 302, *Angew. Chem. Int. Ed.* **1976**, *15*, 302,
[76] a) Y. Minoura, M. Takebayashi, C. C. Price, *J. Am. Chem. Soc*. **1959**, *81*, 4689. b) S. J. Brois, *J. Org. Chem.* **1962**, *27*, 3532. c) H. Wenker, *J. Am. Chem. Soc*. **1935**, *57*, 2328.
[77] a) J. Legters, L. Thijs, B. Zwanenburg, *Tetrahedron Lett*. **1989**, *30*, 4881. b) Y. Ittah, Y. Sasson, I. Shahak, F. Tsaroom, J. Blum, *J. Org. Chem*. **1978**, *43*, 4271.
[78] a) Y.-M. Chen, M. -X. Zhao, J. Xu, Y. Shi, *Angew. Chem.* **2006**, *118*, 8173, *Angew. Chem. Int. Ed.* **2006**, *45*, 8005. b) J. Vesely, I. Ibrahem, G.-L, Zhao, R. Rios, A. Córdova, *Angew. Chem*. **2007**, *119*, 792, *Angew. Chem. Int. Ed*. **2007**, *46*, 778. c) A. V. Gontcharov, H. Liu, B. Sharpless, *Org. Lett*. **1999**, *1*, 783.
[79] A. Armstrong, C. A. Baxter, S. G. Lamont, A. R. Pape, R. Wincewicz, *Org. Lett*. **2007**, *9*, 351.
[80] I. D. G. Watson, L. Yu, A. K. Yudin, *Acc. Chem. Res.* **2006**, *39*, 194 and references therein.

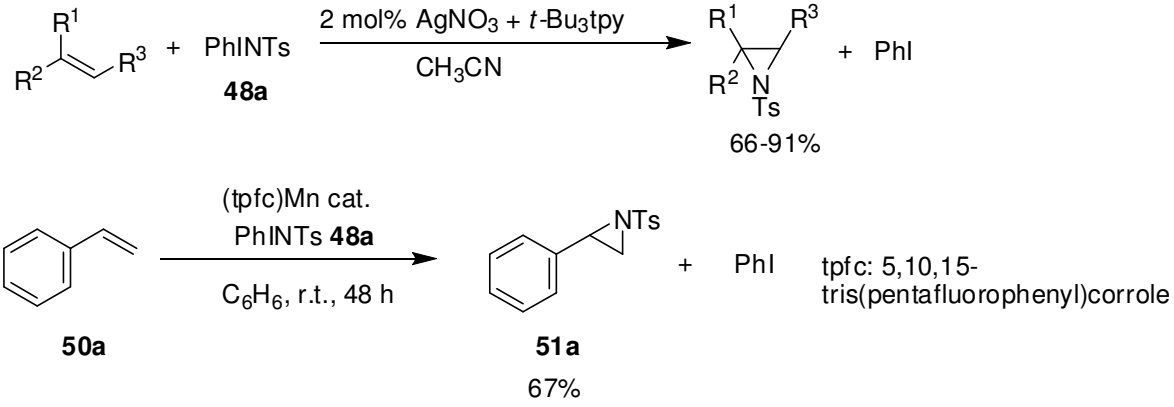
include chloramine-T (**47a**),[81] bromamine-T (**47b**),[82] *p*-tosyl-phenyliminoiodinane (**48a**)[83] and *p*-tosyl-azide **49**[84] (Figure 7).

Figure 7. Variety of *p*-tosyl nitrene sources.



Especially in metal-catalyzed aziridinations of olefins, iminophenyliodinane derivatives, which may be pre-formed or generated in situ, can be used as non-hazardous nitrene sources. Representative Ag and Mn-catalyzed aziridinations with iminophenyliodinane are shown in Scheme 25.[85]

Scheme 25. Metal-catalyzed aziridination of olefins with PhINTs **48a**.



Copper-catalyzed aziridination of olefins has been thoroughly studied by Evans *et al.* (Scheme 26).[86]

[81]Fe-catalyzed aziridination, see: a) L. Simkhovich, Z. Gross, *Tetrahedron Lett*. **2001**, *42*, 8089. Cu-catalyzed aziridination, see: b) D. P. Albonne, P. S. Aujla, P. C. Taylor, S. Challenger, A. M. Derrick, *J. Org. Chem*. **1998**, *63*, 9569.

[82] Pd-catalyzed aziridination, see: a) A. M. M. Atunes, S. J. L. Marto, P. S. Branco, S. Prabhaka, A. M. Lobo, *Chem. Commun*. **2001**, 405. Cu-catalyzed aziridination, see: b) R. V. Bahnu, M. Chanda, A. V. Bedekar, *Tetrahedron Lett*. **1998**, *39*, 4715. Transition metal-catalyzed aziridination, see: c) B. M. Chanda, R. Vyas, A. V. Bedekar, *J. Org. Chem*. **2001**, *66*, 30.

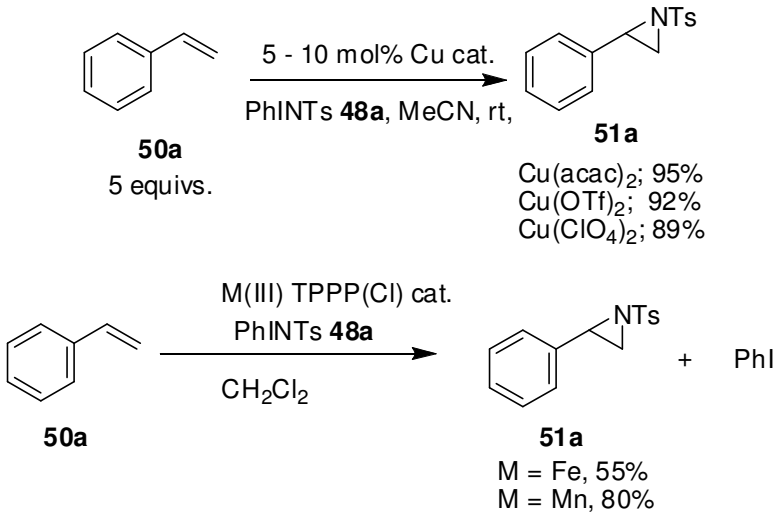
[83] P. Dauban, R. Dodd, *Synlett* **2003**, 157 and references therein.

[84]Ru-catalyzed aziridination, see: a) H. Kawabata, K. Omura, T. Katsuki, *Tetrahedron Lett.* **2006**, *47*, 1571. b) K. Omura, T. Uchida, R. Irie, T. Katsuki, *Chem. Commun*. **2004**, 2060.

[85] Ag-catalyzed aziridination, see: a) Y. Cui, C. He, *J. Am. Chem. Soc* **2003**, *125*, 16202. Mn-catalyzed aziridination, see: b) M. J. Zdilla, M. M. Abu-Omar, *J. Am. Chem. Soc*. **2006**, *128*, 16971.

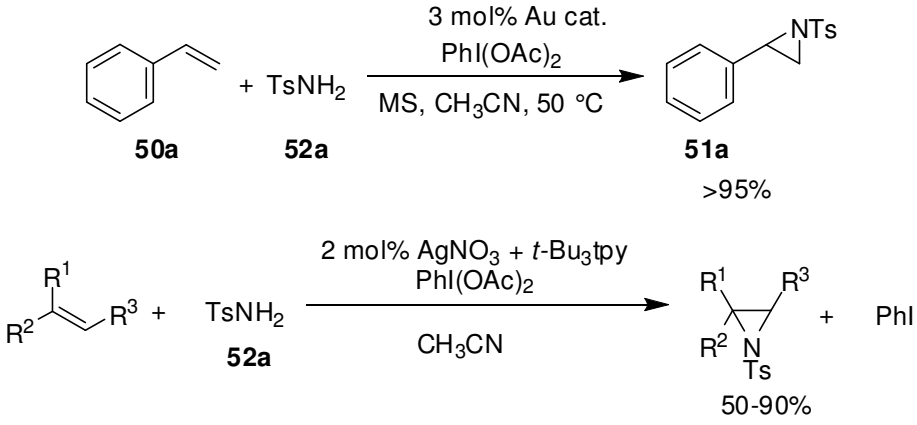
[86] D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Org. Chem. Soc*. **1991**, *56*, 6744.

Scheme 26. Metal-catalyzed aziridination of styrene with PhINTs **48a**.



Also, representative metal-catalyzed aziridinations in which the iminophenyliodinane is formed in situ are shown in Scheme 27. In general however, forming the iminophenyliodinane *in situ*, leads to diminished yields.[87]

Scheme 27. Metal-catalyzed aziridination of olefins with a combination of $PhI(OAc)_2$ and $TsNH_2$ **52a**.

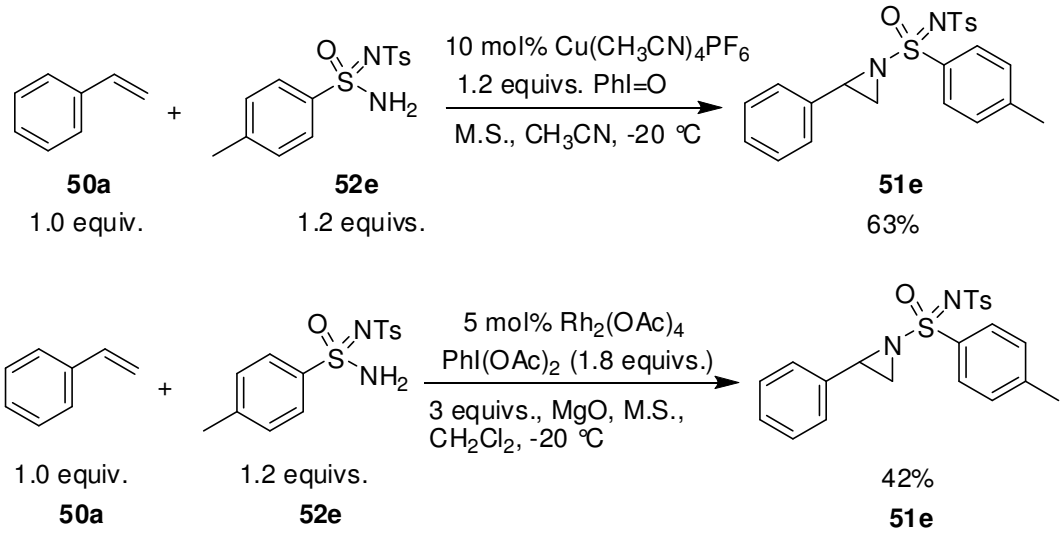


In situ iodinane synthesis is however advantageous for aziridination with sulfonamidamides, because iminophenyliodanes derived from sulfonamidamides could not be isolated. Representative metal-catalyzed reactions are shown in Scheme 28.[88]

[87] Au-catalyzed aziridination, see: a) Z. Li, X. Ding, C. He, *J. Org. Chem.* **2006**, *71*, 5876. Ag-catalyzed aziridination, see: b) Z. Li, C. He, *Eur. J. Org. Chem.* **2006**, 4313.

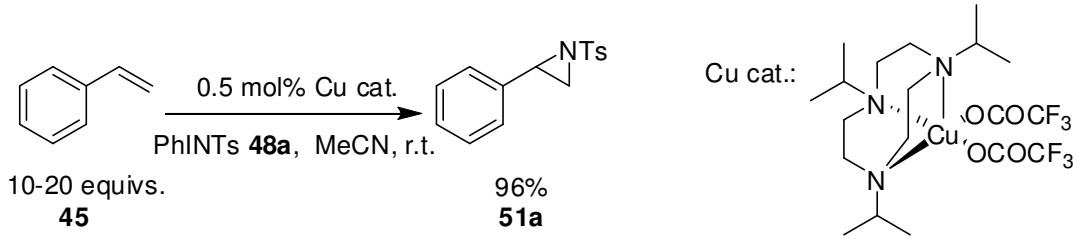
[88] Cu-catalyzed aziridination. See: a) P. H. Di Chenna, F. Robert-Peillard, P. Dauban, R. H. Dodd, *Org. Lett.* **2004**, *6*, 4503. Rh-catalyzed aziridination. See: b) C. Fruit, F. Robert-Peillard, G. Bernardinelli, P. Müller, R. H. Dodd, P. Dauban, *Tetrahedron: Asymmetry* **2005**, *16*, 3484.

Scheme 28. Metal-catalyzed aziridination of styrene with PhI=O or $PhI(OAc)_2$.



Additionally, tri(*i*-Pr)-TACN **8** was investigated for use in copper-catalyzed aziridination. Surprisingly, even 0.5 mol% of copper catalyst gave the aziridines in high yield (Scheme 29).

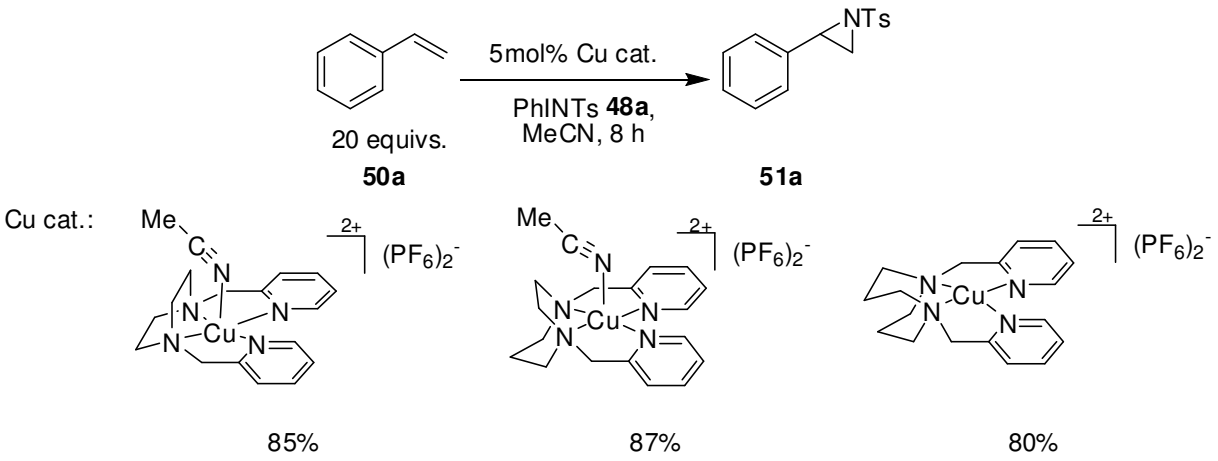
Scheme 29. Copper-catalyzed aziridination of styrene with PhINTs.



Two other efficient ligand classes for copper-catalyzed aziridination were the pyridyl-appended diazacycloalkanes and TACN derivatives (Scheme 30).[89]

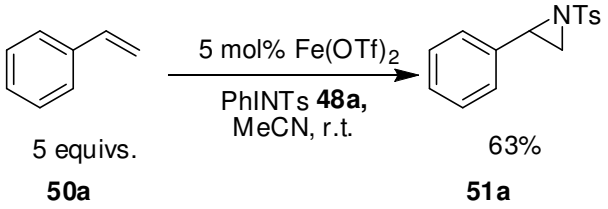
Scheme 30. Copper-catalyzed aziridination with pyridyl-appended diazacycloalkanes as ligands.

[89] J. A. Halfen, J. M. Uhan, D. C. Fox, M. P. Mehn, L. Que, Jr., *Inorg. Chem.* **2000**, *39*, 4913.



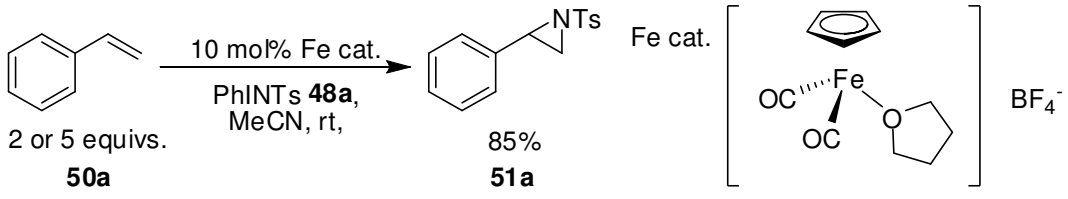
Despite the fact that many metal-catalyzed aziridinations have been developed, an efficient iron-catalyzed aziridination of olefins has not been developed yet. Only a few examples of olefin aziridination have been reported in the course of screening different metal salts in the course of catalyst development (Scheme 31).[90]

Scheme 31. Iron-catalyzed aziridination of styrene with PhINTs.



Aziridination of styrene using a different iron catalyst as a Lewis acid has been reported by Hossein *et al.* (Scheme 32).[91]

Scheme 32. Lewis acid iron-catalyzed aziridination of styrene with PhINTs.

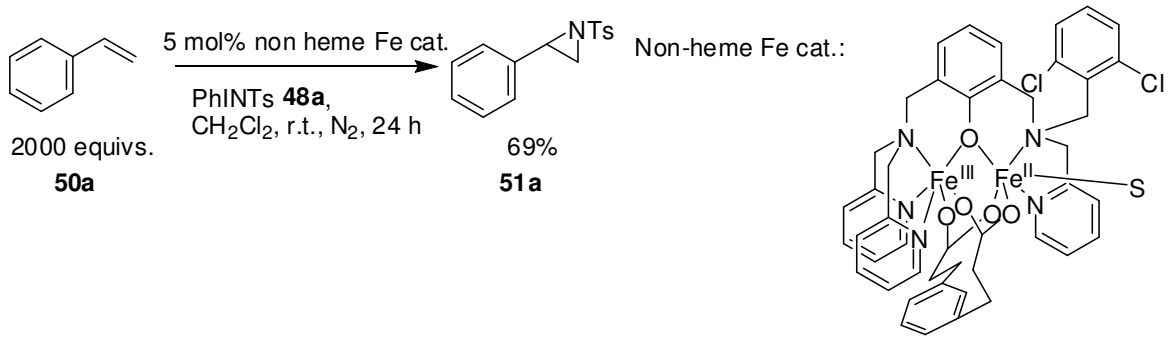


As an example of ligand effects in iron-catalyzed aziridination reactions, catalytic aziridination using a non-heme diiron complex has been studied (Scheme 33).[92]

[90] D. A. Evans, M. M. Faul, M. T. Bilodeau, *J. Am. Chem. Soc*. **1994**, *116*, 2742.
[91] B. D. Heuss, M. F. Mayer, S. Dennis, M. M. Hossain, *Inog. Chim. Acta* **2003**, *342*, 301.
[92] F. Avenier, J. M. Latour, *Chem. Commun*. **2004**, 1544.

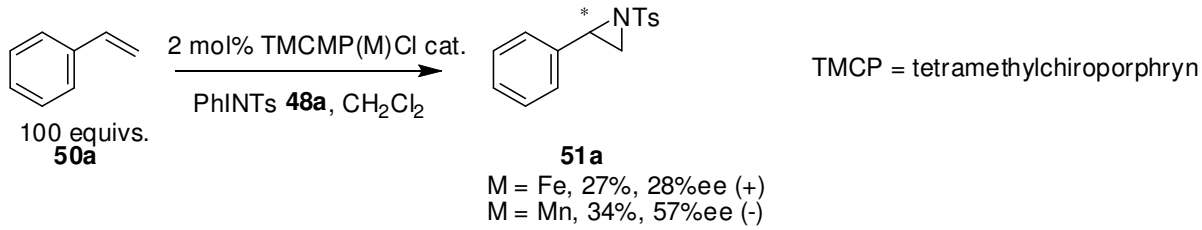
However in this system, a large excess of styrene is required.

Scheme 33. Non-heme iron-catalyzed aziridination of styrene with PhINTs.



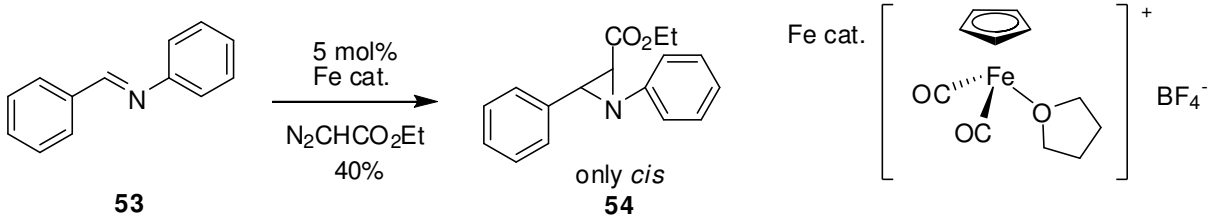
Chiral iron-porphyrin complex catalyzed asymmetric aziridination of styrene with PhINTs has been demonstrated (Scheme 34).[93] Interestingly, iron and manganese derived catalysts gave the oppposite stereoisomers of the product.

Scheme 34. Metal-catalyzed aziridination of styrene with PhINTs.



As another approach, aziridination of imines with diazoacetate[94] and its asymmetric version[95] have been reported (Scheme 35). However in this reaction, two kinds of ring opened side products were observed.

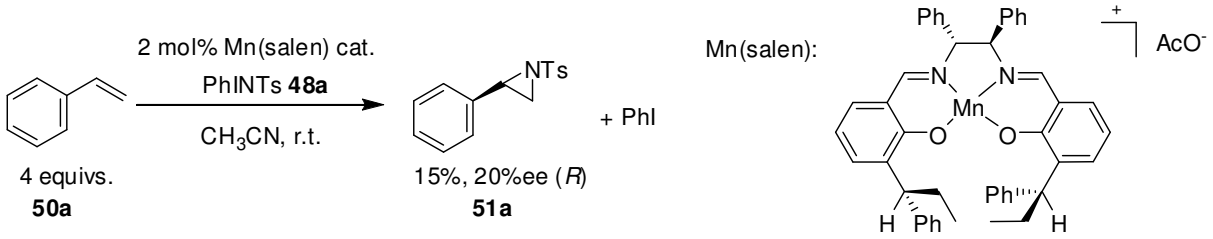
Scheme 35. Iron catalyzed aziridination of imine **53** with PhINTs.



[93] J.-P. Simonato, J. Pécaut, W. R. Scheidt, J -C. Marchon, *Chem. Commun*. **1999**, 989.
[94] M. F. Mayer, M. M. Hossein, *J. Org. Chem*. **1998**, *63*, 6839.
[95] M. Redlich, M. M. Hossein, *Tetrahedron Lett*. **2004**, *45*, 8987.

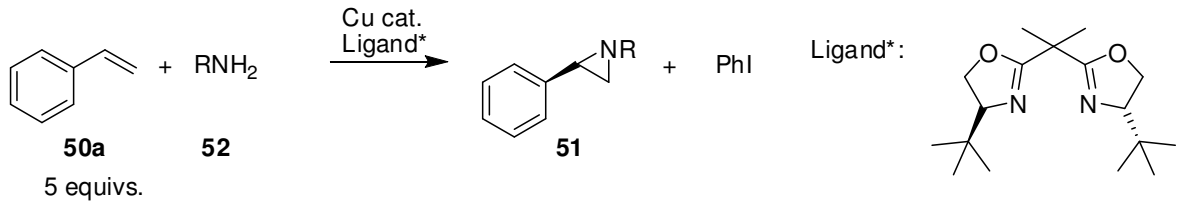
Recently, asymmetric, metal-catalyzed aziridinations have been developed. (salen)Mn(III) complexes-catalyzed asymmetric aziridination is shown in Scheme 36.[96] However, the reaction efficiency was quite low and only low enantiomeric excesses were observed.

Scheme 36. Mn-catalyzed asymmetric aziridination of styrene with PhINTs.



Copper-catalyzed asymmetric aziridination has been especially well studied. The first example used PhINTs (Scheme 37).[97, 98] Even using a combination of iodosylbenzene or iodobenzene diacetate with sulfonamide gave the aziridination product in good yield with moderate enantiomeric excess.

Scheme 37. Copper-catalyzed asymmetric aziridination with a Box type ligand.

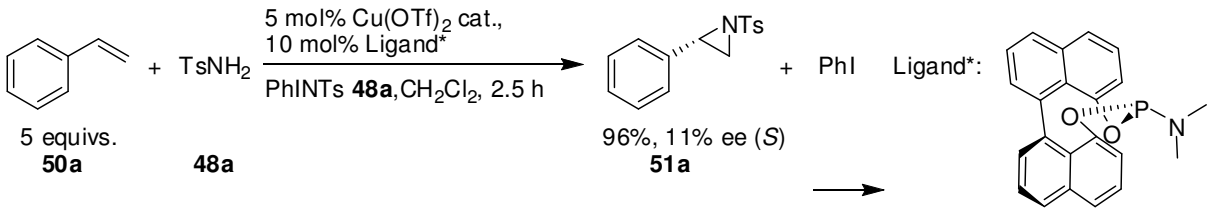


$Cu(OTf)_2$ (5 mol%), Ligand* (6 mol%), PhINR(R= Ts), 0 °C, 2.5 h; 89%, 63% ee (*R*)
$Cu(MeCN)ClO_4$ (5 mol%), Ligand* (6 mol%), RNH_2 (R= Ns), $PhI(OAc)_2$, C_6H_6, 0 °C, 2.5 h; 94%, 75% ee (*R*)
$Cu(OTf)_2$ (8 mol%), Ligand* (12 mol%), RNH_2 (R= Ts), PhI=O, MS 3Å, C_6H_6, 2.5 h; 86%, 59% ee (*R*)

Not only Box type ligands but also other kinds of ligand have been demonstated to promote asymmetric aziridination (Scheme 38).

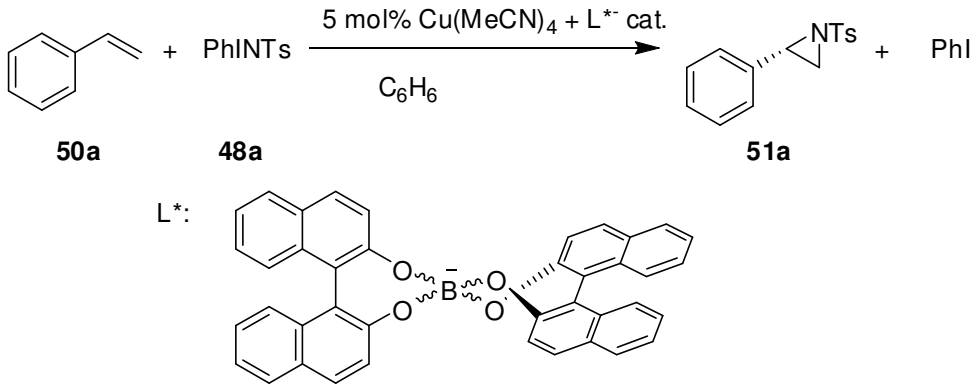
Scheme 38. Copper-catalyzed asymmetric aziridination with a chiral phosphine ligand.

[96] K. Noda, N. Hosoya, R. Irie, Y. Ito, T. Katsuki, *Synlett* **1993**, 469.
[97] a) D. A. Evans, M. M. Faul, T. Bilodeau, B. A. Anderson, D. A. Barnes, *J. Am. Chem. Soc*. **1993**, *115*, 5328. b) H.-L. Kwong, D. Liu, K.-Y. Chan, C.-S. Lee, K.-H. Huang, C-M. Che, *Tetrahedron Lett*. **2004**, *45*, 3965. c) M. J. Södergren, D. A. Alonso, P. G. Andersson, *Tetrahedorn: Asymmetry* **1997**, *8*, 3563.
[98] P. Müller, P. Nurry, G. Benardinelli, *Helv. Chim. Acta* **2000**, *83*, 843.



Asymmetric induction by use of a chiral counterion has been demonstrated in the copper-catalyzed aziridination of styrene (Scheme 39).[99]

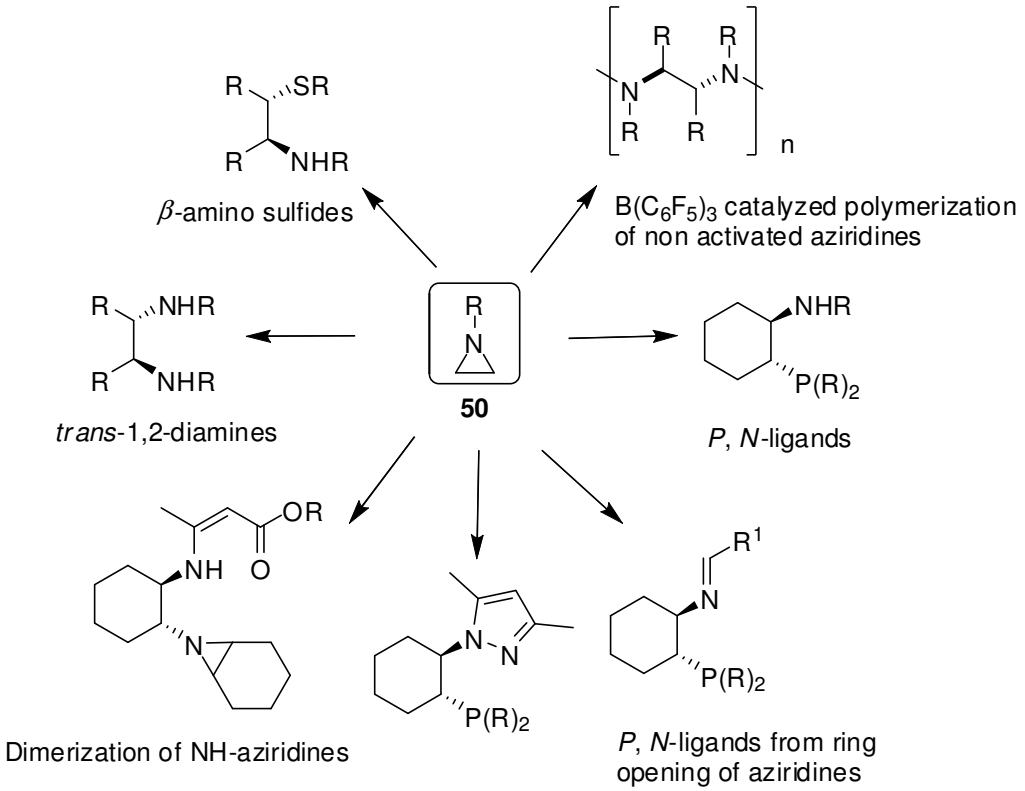
Scheme 39. Novel ion paring in copper-catalyzed asymmetric aziridination.



Aziridine ring opening reactions are useful tools for forming various kinds of nitrogen containing compounds. Methods for ring opening of aziridines are shown in Scheme 40.

Scheme 40. Methods for ring opening of aziridines.

[99] D. B. Llewellyn, D. Adamson, B. A. Arndtsen, *Org. Lett.* **2000**, *2*, 4165.



A recent practical application of an aziridine ring opening reaction is in the synthesis of the drug Tamiflu.[100]

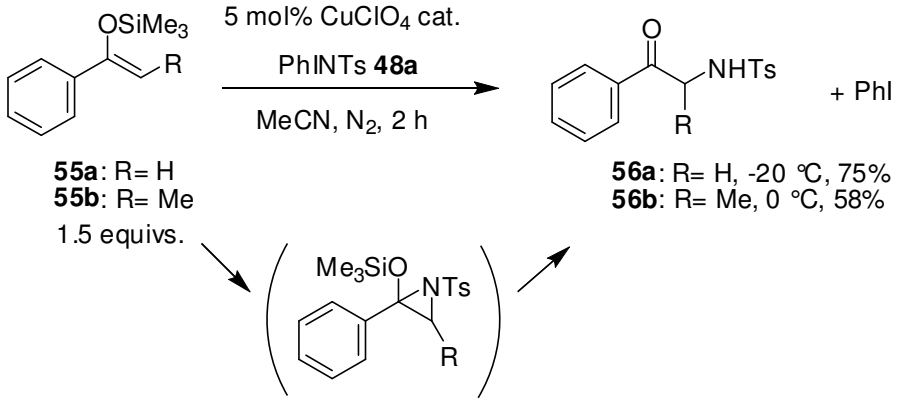
For efficient exploitation in synthesis, the development of aziridine deprotection methods, which nevertheless preserve the three membered ring, is important. Not only the tosyl group[101] but also several other protecting groups such as Cbz,[102] SES,[103] Ns,[104] Bus,[105] diphenylphosphonyl,[100] and 4-methyl-2-pyridinesulfonyl groups[106] have been introduced at the nitrogen atom, each requiring different conditions for deprotection.

1.4.1 Syntheisis of α-Aminoketones and -Esters

[100] Y. Fukuta, T. Mita, N. Fukuda, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc*. **2006**, *128*, 6312.
[101] T. W. Greene, P. G. M. Wuts, *Protecting group in Organic Synthesis, Ind. Ed.* ; John Wiely & Scns: New York, 1999, p 603.
[102] M. Pinesuchi, F. Bertolini, P. Crotti, F. Macchia, *Org. Lett*. **2006**, *8*, 2627.
[103] a) P. Dauban, R. H. Dodd, *J. Org, Chem.* **1999**, *64*, 5304. b) P. Ribière, V. Declerck, J. Martinez,F. Lamaty, *Chem. Rev*. **2006**, *106*, 2249.
[104] T. Fukuyama, C.-K. Jow, M. Cheung, *Tetrahedron Lett*. **1995**, *36*, 6373.
[105] P. Sun, S. M. Weinreb, *J. Org. Chem*. **1997**, *62*, 8604.
[106] H. Han, I. Bae, E. J. Yoo, J. Lee, Do, S. Chang, *Org. Lett.* **2004**, *6*, 4109.

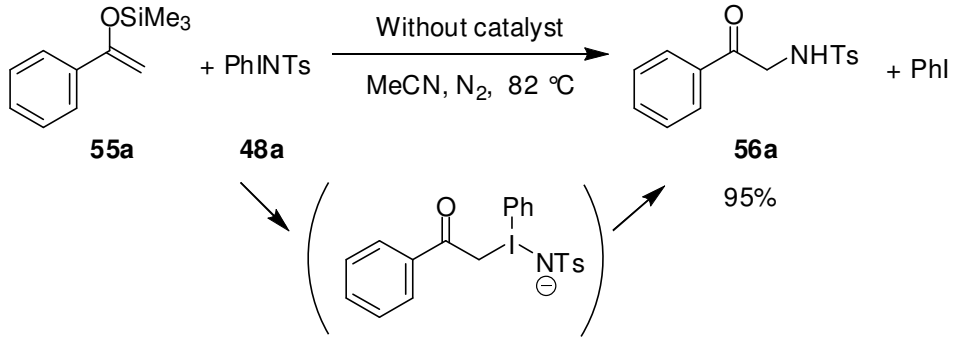
Aziridines can be transformed into useful α-amino ketones.[97a, 106, 107] In contrast, only a few examples of the direct synthesis of α-amino ketones from silyl enol ethers have been reported. The first example was the copper-catalyzed α-amination of silyl enol ethers, which was reported by Evans *et al*. in 1991 (Scheme 41).[90] According to their report, the synthesis of α-amino acid esters using copper-catalyzed nitrogen transfer is not reproducible.

Scheme 41. Copper-catalyzed asymmetric α-amination with PhINTs.



Five years later, a non-metal catalyzed α-amination was reported by a Korean group (Scheme 42).[108] Most of the aryl silyl enol ethers were transformed into α-amino ketones in good yields.

Scheme 42. Non-metal catalyzed aziridination of silyl enol ethers with PhINTs.



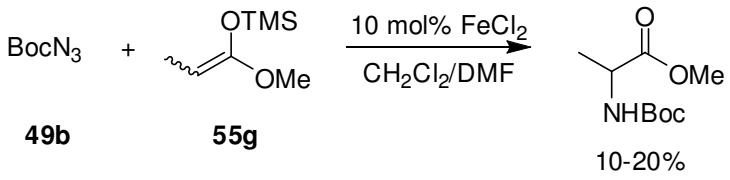
They mentioned that no copper-catalyst was required for *a*-amination. However, it was necessary to heat the solution in boiling acetonitrile to achieve nitrogen transfer. In Evans's system, α-amination occurred even at 0 °C. Thus, a metal-catalyst is still necessary to allow

[107] a) M. S. Reddy, M. Narender, K. Rama Rao, *Tetrahedron Lett.* **2005**, *46*, 1299. c) K. Srenda, N. S. Krishnaveni, K. Rama Rao, *Tetrahedron Lett*. **2005**, *46*, 4111. d) K. Srendra, N. S. Krishanveni, M. A. Reddy, Y. V. D. Nageswar, K. R. Rao, *J. Org. Chem*. **2003**, *68*, 9119.
[108] B.-W. Lim, K.-H. Ahn, *Synth. Comm*. **1996**, *26*, 3407.

the reaction to proceed at or below room temperature. Thus, there is scope for the development of an asymmetric reaction.

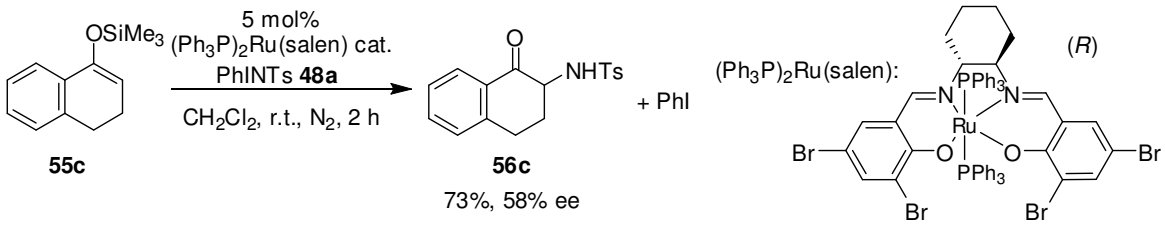
In 1998, the first iron-catalyzed α-amination of a ketene acetal was introduced using Boc-azide as nitrogen source. The reaction is still not effective and the α-amino acid ester was obtained in only 10-20 % yield (Scheme 43).[109]

Scheme 43. First approach to the synthesis of an α-amino acid ester from a ketene acetal catalyzed by iron(II) chloride.



Only two examples of asymmetric amination of enol silanes have been reported until now. The first example is the ruthenium complex catalyzed α-amination of silyl enol ethers with PhINTs using a Ru(salen) type as catalyst (Scheme 44).[110]

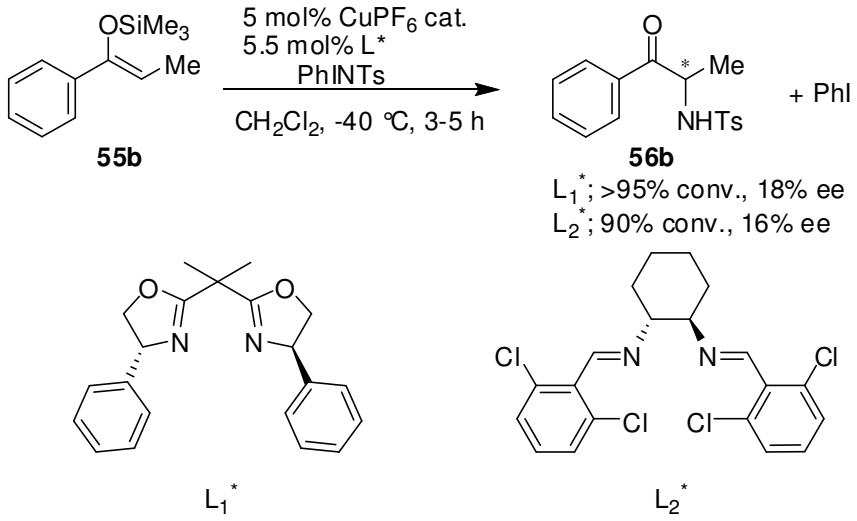
Scheme 44. Ruthenium-catalyzed asymmetric α-amination with PhINTs.



The second example involves copper-catalyzed α-amination (Scheme 45).[111] In this system, the asymmetric induction was very low.

Scheme 45. Copper-catalyzed asymmetric α-amination of silyl enol ether with PhINTs.

[109] T. Bach, C. Körber, *Tetrahedron Lett*. **1998**, *39*, 5015.
[110] J.-L. Liang, X.-Q. Yu, C.-M. Che, *Chem. Commun*. **2002**, 124.
[111] W. Adam, K. J. Roschmann, C. R. Saha-Möller, *Eur. J. Org. Chem.* **2000**, 557.

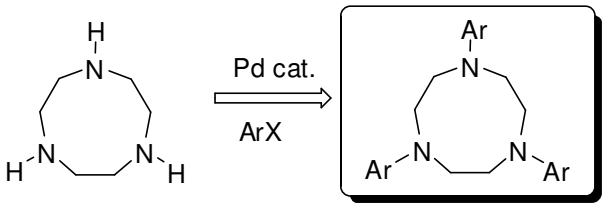


In the future, further development of this great new approach for the synthesis of α-amino ketones and esters is highly desireable.

2 Research Objectives

The first objective of the present work was to synthesize novel TACN ligands. Although a number of functionalizations have been developed, there are only a few examples of aryl substituted TACN derivatives.[40] As already mentioned in chapter 1.2.1, syntheses of aryl substituted TACNs are quite limited. Therefore, new, more efficient approaches to introduce aryl groups on nitrogen are desirable. One such approach, simple transition metal-catalyzed *N*-arylation, which has been extensively developed by Buchwald and Hartwig, was selected for *N*-arylation of TACN (Scheme 46).

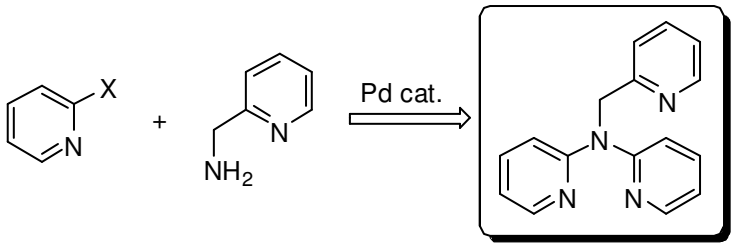
Scheme 46. Approach to triaryl-TACN by palladium-catalyzed *N*-arylation.



The development of nitrogen-based ligands such as dipyridylamines using Buchwald-Hartwig chemistry was also projected. More efficient synthetic methods for their preparation and the study of their ability as ligands were required (Scheme 47). Several complexes of these ligands with metals such as palladium and copper have been reported. In this work, iron and

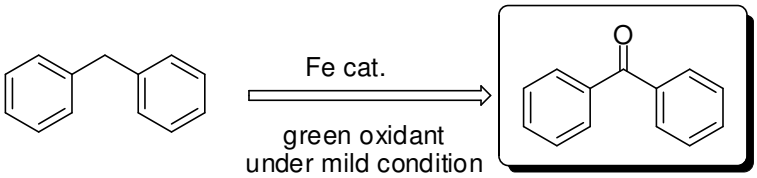
silver were chosen for complexation with this type of ligand. Furthermore, several kinds of reactions were examined using these metal complexes as catalysts.

Scheme 47. New methods for the synthesis of dipyridylamine ligands catalyzed by palladium complexes.



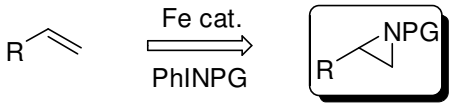
As a second part of the work, investigations of the iron catalyzed benzylic oxidation of bis(4-fluorophenyl)methane, which is of interest for the development of fragrances, were undertaken. Iron-catalyzed oxidation of diphenylmethane with hydrogen peroxide has been previously studied by Bolm *et al*. although their oxidation system gives very clean reactions, generating water as the side product from oxidation; a more efficient methodology was desireable. Therefore, the developement of a new iron-catalyzed oxidation system was required (Scheme 48).

Scheme 48. New methods catalyzed by iron with green oxidants.



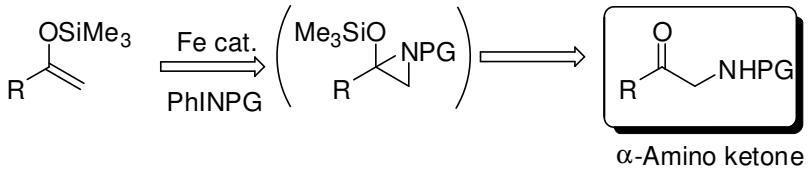
An iron-catalyzed aziridination reaction of olefins was also studied. As already mentioned in chapter 1.3, only a few example of iron-catalyzed aziridination have been reported until now. This is the most straightfoward strategy to access aziridines (Scheme 49).

Scheme 49. Iron-catalyzed synthesis of aziridines.



As an extension of the aziridination study, the synthesis of α-amino ketone derivatives by aziridination of silyl enol ethers was undertaken (Scheme 50).

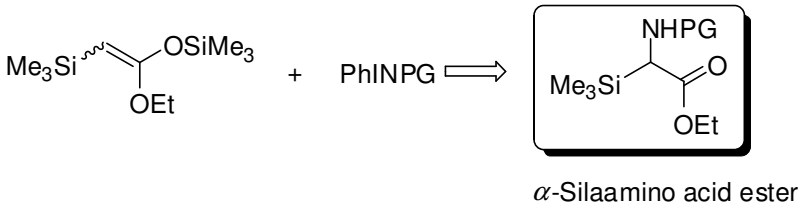
Scheme 50. New methods for the iron-catalyzed synthesis of α-amino acid esters.



This strategy has great potential for convenient synthesis of various α-amino acid esters from simple ketones.

In addition, the synthesis of α-silaamino acid esters [112] using this reaction system was considered (Scheme 51).

Scheme 51. Novel strategy for synthesis of α-silaamino acid esters.



As mentioned in chapter 1.4.1, a metal catalyst is necessary to afford amino ketones from enol silanes with PhINTs at ambient temperature or lower temperatures. Thus, if this innovative strategy could be realized, metal-catalyzed asymmetric α-amino acid synthesis could be applied in the furture.

[112] C. Bolm, A. Kasyan, K. Drauz, K. Günther, G. Raabe, *Angew. Chem.* **2000**, *39*, 2288, *Angew. Chem. Int. Ed.* **2000**, *112*, 2374.

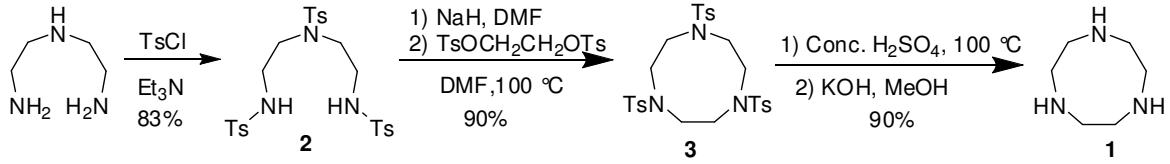
3 Synthesis of Aryl-TACN Derivatives

3.1 *N*-Arylation of TACN Derivatives

3.1.1 Synthesis of Precursors

TACN can be synthesized easily from 1,2-ditosylethylene glycol and diethylenetriamine which are commercially available (Scheme 52). Also, 1,2-ditosylethylene glycol can be prepared by ditosylation of ethylene glycol. At first, diethylene triamine was prepared by tosylation with tosyl chloride affording tritosyl diethylene triamine **2**. Subsequently, tri(Ts)-TACN **3** was prepared by cyclization of **2** with 1,2-ditosylethylene glycol in 90% yield. Finally, free TACN **1** was obtained by detosylation with conc. H_2SO_4 and neutralization with KOH.

Scheme 52. Synthesis of TACN **1**.

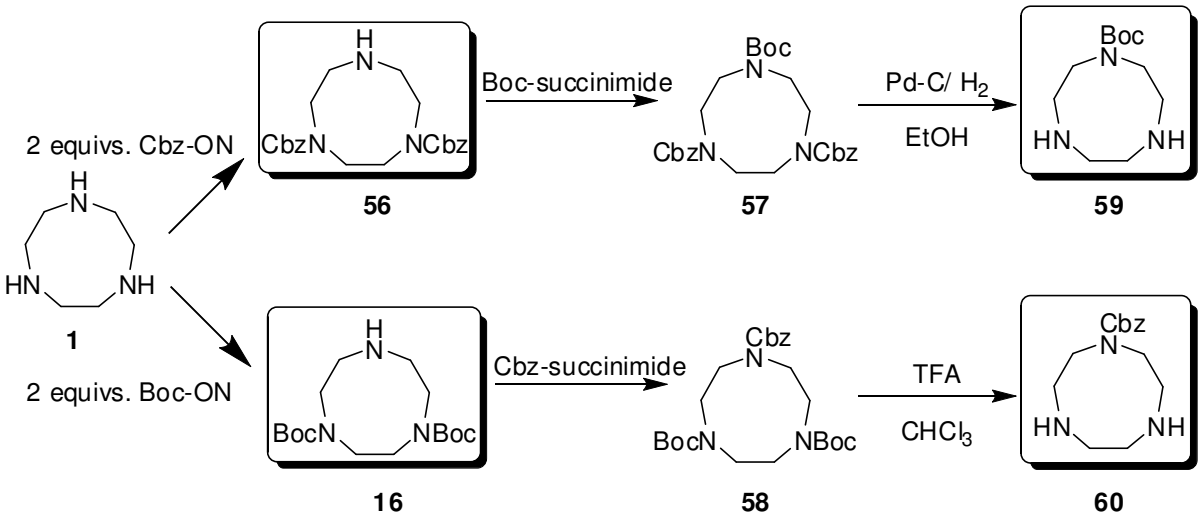


Notably ditosyl ethylene glycol is the best substrate for cyclization as alternatives such as dibromoethylene glycol do not cyclize as efficiently as mentioned by Richman *et al*.

TACN **1** can be protected easily and selectively with Cbz or Boc groups (Scheme 53). Di-protected TACN derivatives **56** and **16** were selectively synthesized using 2 equivs. of 2-(benzyloxycarbonyloxyimino)-2-phenylacetonitrile (Cbz-ON) or 2-(*t*-butoxycarbonyloxyimino)-2-phenylacetonitrile (Boc-ON) in chloroform under anhydrous conditions at ambient temperature. [113] Cbz-ON, which is not commercially available, was prepared without difficulty.[13b] Di-*N*-protection occurred smoothly when Boc-succinimide or Cbz-succinimide was used as electrophile. Mono-protected TACN derivatives **59** and **60** were obtained by standard double deprotection of di-Boc or di-Cbz protected TACN **57** or **58**.

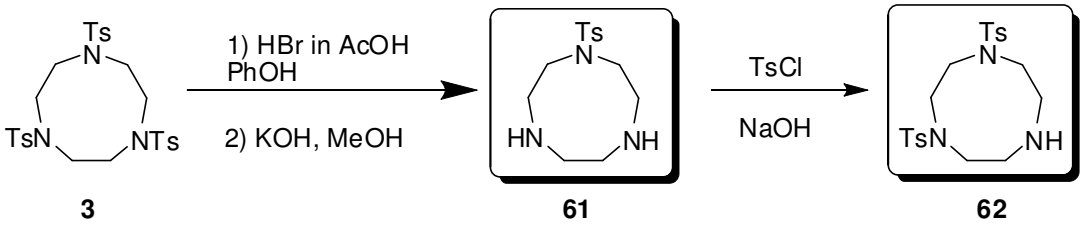
Scheme 53. Selective protection of TACN by Cbz and Boc groups.

[113] M. Itoh, D. Hagiwara, T. Kamiya, *Tetrahedron Lett*. **1975**, 4393.



Also, monotosyl-TACN **61** was synthesized selectively by double deprotection of tri(Ts)-TACN **3** (Scheme 54). Furthermore, di(Ts)-TACN **62** was prepared by selective mono-tosylation of monotosyl-TACN **61**.[114] These simple transformations afforded a library of TACN ligands bearing free NH groups, which were now suitable for use in arylation studies.

Scheme 54. Synthesis of mono- and di-tosyl protected TACN.

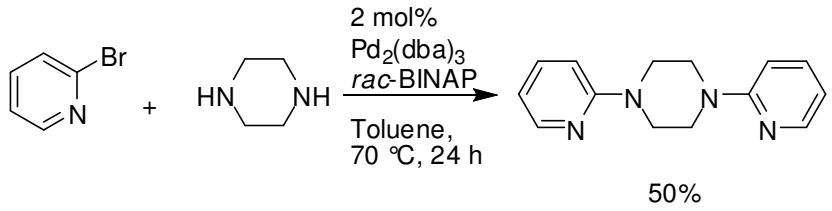


3.1.2 Palladium-catalyzed *N*-Arylations

Although many kinds of TACN derivatives have been synthesized, there are only few examples of aryl-TACN derivatives (Chapter 1.2.2). Due to the limitation of existing synthetic approaches, these kinds of ligands have not been developed until now (Scheme 11). As a first trial, palladium catalyzed *N*-arylation of piperazine with *rac*-BINAP[115] as ligand was tested. Encouragingly, diaryl-piperazine was obtained in 50% yield (Scheme 55).

Scheme 55. Palladium-catalyzed *N*-arylation of piperazine with 2-bromopyridine.

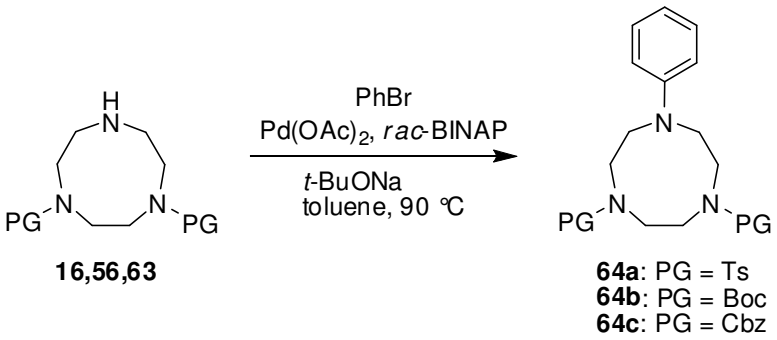
[114] J. L. Sessler. J. W. Silbert, V. Lynch, *Inorg. Chem.* **1990**, *29*, 4143.
[115] J. P. Wolf, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 1144.



Following this result, mono-*N*-arylation of diprotected TACN was tested using the same procedure as for the *N*-arylation of piperazine. Monoarylation of ditosylprotected TACN using 8 mol% of $Pd(OAc)_2$ proceeded to give monoaryldditosyl TACN in high yield (Scheme 56). A higher amount of catalyst (16 mol%) was required for mono-*N*-arylation of di-Cbz or di- Boc protected TACN.

Initial studies involved investigating the mono-arylation of ditosyl-protected TACN **63** with phenyl bromide. Following Buchwald's original protocol using a catalyst comprised of a mixture of $Pd(OAc)_2$ and racemic BINAP (8 mol%) in the presence of sodium *tert*-butoxide,[116] the arylation of **63** proceeded well leading to the quantitative formation of **64a** after 1 day. Analogously, di(Boc)-TACN **16** and di(Cbz)-TACN **56** coupled with phenyl bromide to give mono-arylated **64b** and **64c** in 85 and 70% yield, respectively.

Scheme 56. Arylation of di-protected TACN derivatives.



16,56,63

64a: PG = Ts
64b: PG = Boc
64c: PG = Cbz

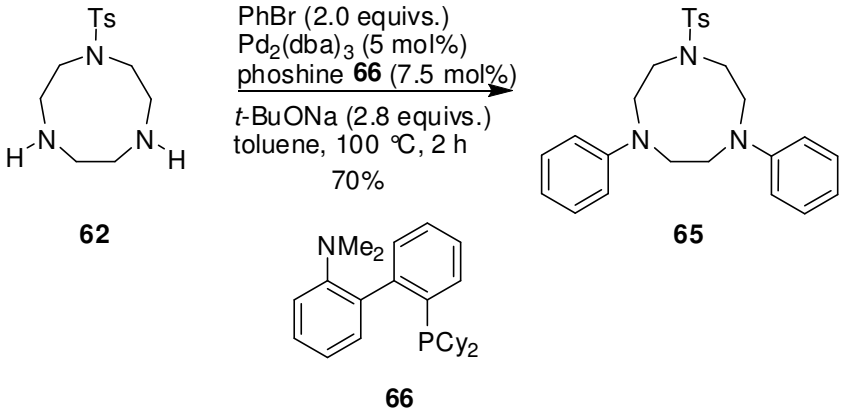
64a: **63** (1 equv.), PhBr (2.1 equivs.), $Pd(OAc)_2$ (8 mol%), *rac*-BINAP (8 mol%), *t*-BuONa (2.1 equivs.)
64b, 64c: **16** or **56** (1 equiv), PhBr (2.8 equivs.), $Pd(OAc)_2$ (16 mol%), *rac*-BINAP (16 mol%), *t*-BuONa (2.8 equivs.)

Surprisingly, mono-tosylated TACN **62** did not couple to give **65** under these conditions. Possibly, the two unprotected nitrogen atoms in the heterocycle coordinate too tightly to the metal catalyst leading to its deactivation. The palladium source was changed from $Pd(OAc)_2$

[116] For recent reviews on Pd-catalyzed N-arylations, see: a) A. R. Muci, S. L. Buchwald, *Top. Curr. Chem.* **2002**, *219*, 131; b) J. F. Hartwig, in: *Modern Amination Methods*, (Ed.: A. Ricci), Wiley-VCH, Weinheim, **2000**, pp. 195; c) J. F. Hartwig, in: *Handbook of Organopalladium Chemistry for Organic Synthesis*, (Ed.: E. Negishi), Wiley-Interscience, New York, **2002**, pp. 1051.

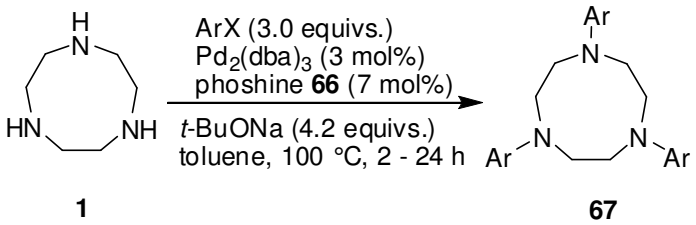
to $[Pd_2(dba)_3]$ and the effect of other phosphine ligands such as Ph_3P, DPPF,[117] and *n*-Bu_3P was studied in an effort to promote coupling. Finally, the best result was achieved by uising a Pd(0) catalyst bearing phosphine **66**[118] as ligand affording diaryl TACN **65** in 70% yield (Scheme 57).[119]

Scheme 57. Arylation of mono-tosylprotected TACN.

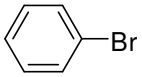
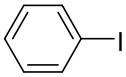
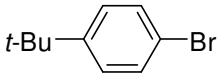
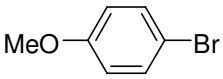
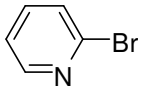


Gratifyingly, triple *N*-arylations of TACN **1** were also possible and various aryl bromides were tested (Table 1, entries 1-4). When a catalyst comprised of 3 mol % of $[Pd_2(dba)_3]$ and 7 mol% of phosphine **66** was employed in the presence of 4.2 equivs. of sodium *tert*-butoxide in toluene at 100 °C, triarylated TACNs **67** were obtained in up to 73% yield. Use of iodobenzene in the synthesis of **67a** gave a low yield (26%) of the triarylated product (Table 2, entry 2).

Table 2. Palladium-catalyzed *N*-Arylation of TACN **1**.[a]



[117] M. S. Driver, J. F. Hartwig, *J. Am. Chem. Soc*. **1996**, *118*, 7217.
[118] a) S. Kaye, J. M. Fox, F. A. Hicks, S. L. Buchwald, *Adv. Synth. Catal*. **2001**, *343*, 789. b) S. L. Buchwald, C. Mauger, G. Mignani, U. Sholz, *Adv. Synth. Catal*. **2006**, *348*, 23.
[119] a) For the early use of phosphine **66** in aryl aminations, see: D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 9722; b) for an advanced synthesis of the phosphine, see: H. Tomori, J. M. Fox, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 5334. c) for recent examples, see: M. D. Charles, P. Schultz, S. L. Buchwald, *Org. Lett.* **2005**, *7*, 3965 and references therein.

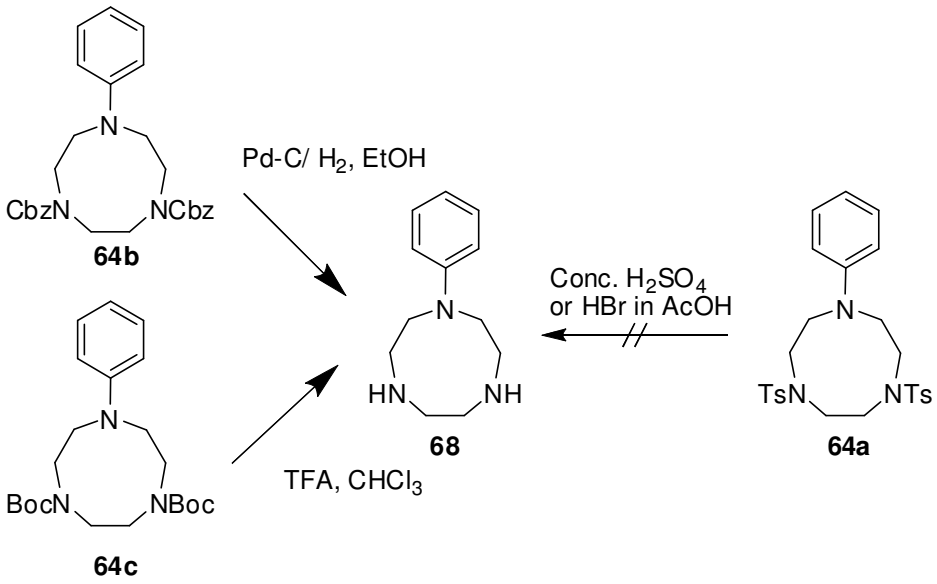
Entry	ArX	Product	Yield
1		**67a**	71%
2		**67a**	26%
3		**67b**	73%
4		**67c**	45%
5		**67d**	52%

3.1.3 Deprotection Methods

Deprotection of mono- and diprotected *N*-aryl-TACN ligands has been examined. At first, detosylation of monophenyl-ditosyl-TACN was studied. Several conditions such as HBr (33%) in acetic acid or concentrated H_2SO_4 were tested. In each case, the desired deprotected product was not obtained (Scheme 58).

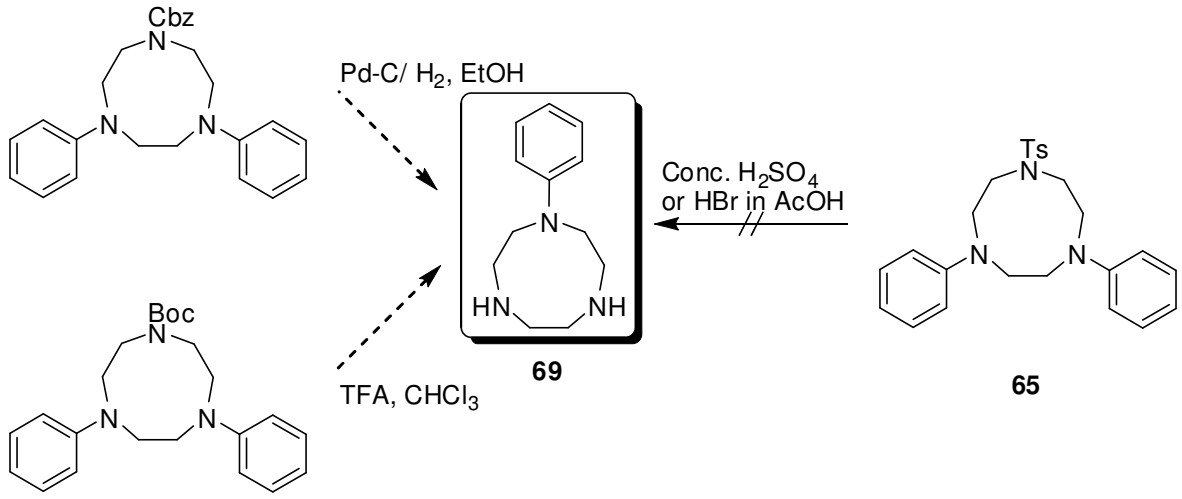
As an alternative approach, the deprotection of carbamate protected TACNs was examined. As expected, Cbz could be removed by hydrogenation with Pd/C. Also, the Boc group could be easily removed by TFA in chloroform.

Scheme 58. Deptotection reaction of Cbz and Boc groups.



Diphenyl-TACN derivatives could also be synthesized using the same deprodection method (Scheme 59).

Scheme 59. Deprotection methods for Boc and Cbz groups.

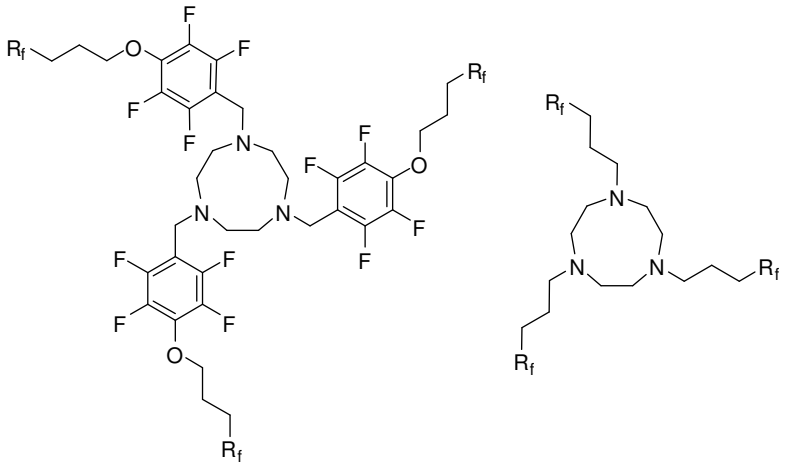


3.1.4 Synthesis of Perfluoroponytailed *N*-Aryl-TACN

Fluorous biphasic catalysis (FBC) has attracted attention as a new concept for facile catalyst separation. Recently, several perfluorinated TACN type ligands have been reported.[39, 120] All of them are shown in Figure 6.

Figure 6. A variety of perfluoroponitailed-TACNs.

[120] a) I. T. Horváth, J. Rábai, *Science* **1994**, *266*, 72, and references therein. b) M. Contel, C. Izuel, M. Laguna, P. R. Villuendas, P. J. Alonso, R. H. Fish, *Chem. Eur. J.* **2003**, *9*, 4168. c) R. H. Fish, *Chem. Eur. J.* **1999**, *5*, 1677. d) *Handbook of fluorous chemistry*, (Ed.: J. A. Gradysz), Wiley-VCH, Germany, **2004**, 395.



70 **71**

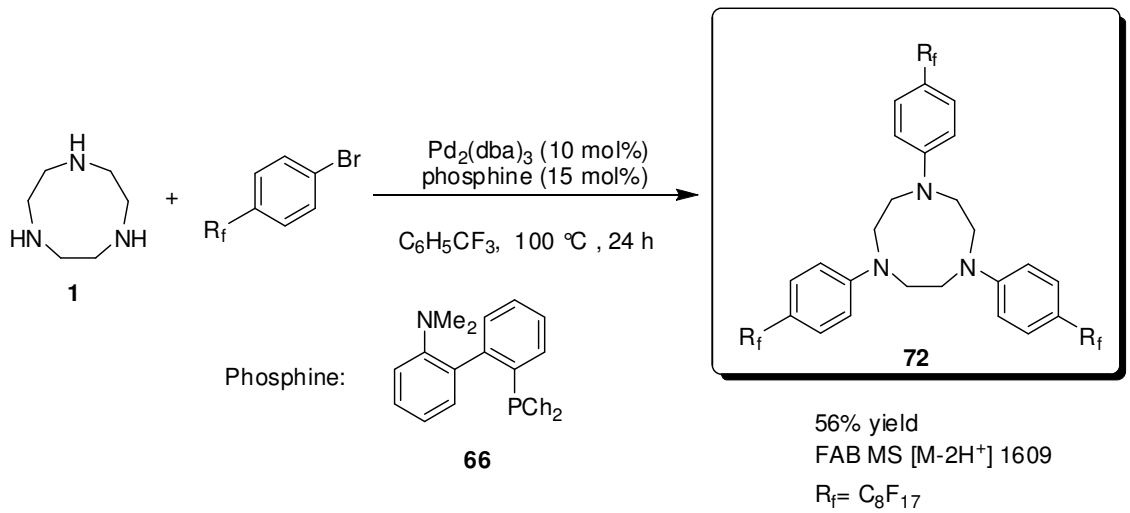
$R_f = C_8F_{17}$

The first perfluoroponitailed-TACN ligand **70**, which was synthesized by J.-M. Vincent, was not soluble in cold perfluoropentane and the content of fluorine was less than 60%.[39]

The second perfluoroponitailed-TACN ligand **71**, which has a fluorine content of more than 60%, has been reported in the literature. These perfluorinated TACN ligands have been applied in catalytic reactions. For example, various manganese and copper complexes of these ligands has been used in catalytic oxidations of olefins, alcohols and hydrocarbons.

Wherein, as a further development for potential use in FBC, *N*-arylation of TACN **1** with a *p*-perfluoroponytailed substituted bromobenzene was performed and led to the desired TACN ligand **72** in 55% (Scheme 60).

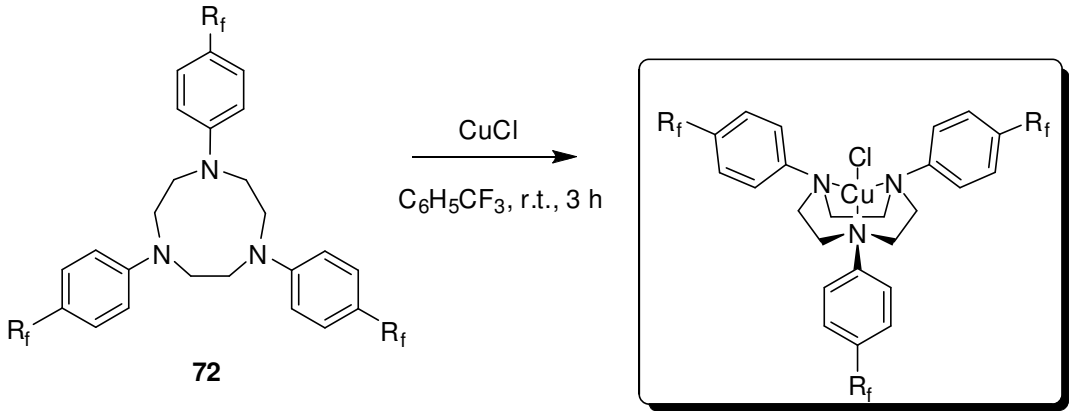
Scheme 60. Synthesis of novel perfluorinated TACN ligand.



1 **66** **72**

Finally, copper complexation with perfluoroponytailed-*N*-aryl-TACN **72** was examined. The value obtained from ESI-MS indicates the formation of a copper(I) chloride complex. (Scheme 61)

Scheme 61. Complexation of novel perfluorinated ligand **72** with copper(I) chloride.



73
LSI-MS: *m/z* 1693 [M-Cl]

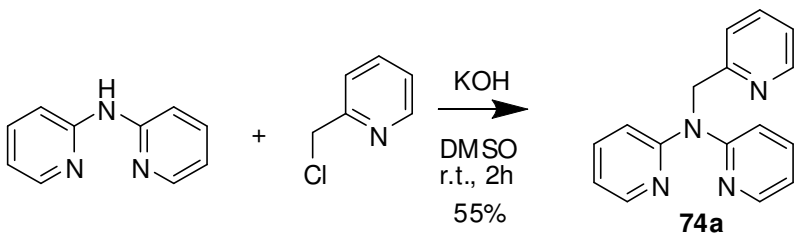
4 Synthesis of *N,N*-Dipyridylamino-2-picolylamines

4.1 Palladium-Catalyzed *N*-Arylation of Picolylamine Derivatives

4.1.1 Synthesis of *N*-(Pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine

The first *N,N*-dipyridylpicolylamine ligand **74a** was synthesized by Schindler *et al.* in 2002. [53a] Complexation of this ligand with copper has also been described. The X-ray crystal structure of this complex indicates that only two of three nitrogen atoms coordinate to copper. Classically, this ligand can be prepared by alkylation of dipyridylamine and chloromethylpyridine under basic condition in DMSO (Scheme 62). However, the yield obtained was low (55%), limiting the synthesis of more diverse derivatives.

Scheme 62. Classical alkylation of *N,N*-dipyridyl amine with 2-pyridyl methylchloride.



74a

Palladium-catalyzed *N*-arylation is a useful method in organic synthesis.[56, 121] Over the past dozen years or so, a large number of *N*-arylations have been developed. Palladium-catalyzed *N*-arylation of benzylamine derivatives and their applicability in the copper-catalyzed asymmetric allylic oxidation of cyclohexene has been demonstrated by Bolm *et al.* as mentioned in chapter 1.2.1.[52]

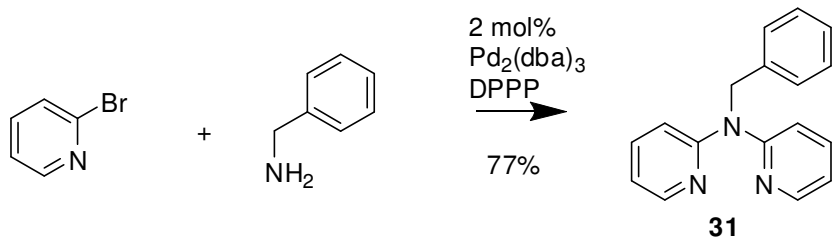
A chiral menthol-substituted dipyridyl amine ligand has been synthesized under the same conditions. In the synthesis of menthol derivatives, *rac*-BINAP promotes much faster reactions than DPPP.

A dipyridy picoline ligand has been previously synthesized by Bolm and coworkers. Due to structural similarities, these conditions were expected to be applicable for synthesis of *N,N*'-dipyridyl picolylamine ligands like **74a**.

4.1.1.1 Palladium-Catalyzed *N*-Arylation of Picolylamine Derivatives

Initially, the same conditions were examined for *N*-arylation of benzylamine. As mentioned in J. C. Frison's thesis, *N*-arylation of benzylamine using 1,3-bis(diphenylphosphino)propane (DPPP) as phosphine ligand proceeded well affording the corresponding dipyridylbenzylamine **31** in good yield (Scheme 63).

Scheme 63. *N*-Arylation of benzylamine

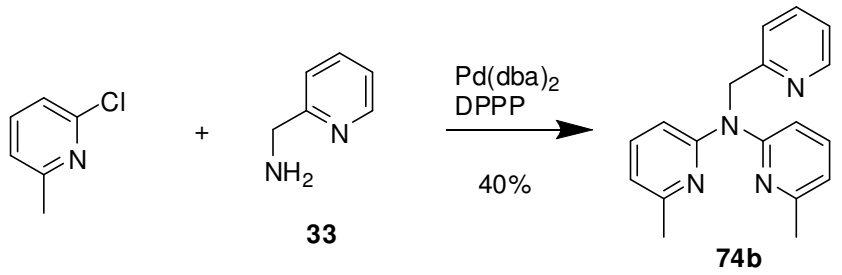


31

Attempted *N*-arylation of 2-picolylamine **33** using the same conditions gave dipyridyl picoline **74b** in low yield (Scheme 64).

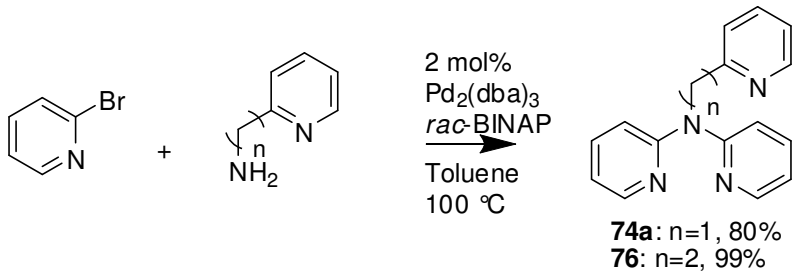
Scheme 64. Palladium-catalyzed *N*-arylation of benzylamine derivatives using DPPP as a phosphine ligand.

[121] S. Wagaw, S. L. Buchwald, *J. Org. Chem.* **1996**, *61*, 40.



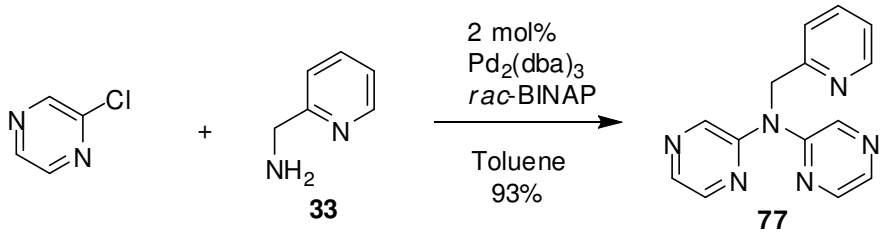
In J. C. Frison's thesis, it is described that *rac*-BINAP as a phosphine ligand is efficient for mono *N*-arylation of benzylamine derivatives. Thus, the *N*-arylation of *N*-2-(pyridyl)ethylamine using *rac*-BINAP as ligand looked promising. Although 2,2-dipyridylaminopicoline works as bidentate ligand, the new dipyridine is expected to be a tridentate ligand. Consequently, various phospine ligands were screened for optimization of the synthesis. Unexpectedly BINAP (*rac*) was discovered to be the most efficient phosphine ligand for di *N*-arylation although it is used for mono *N*-arylation reaction in general (Scheme 65).[122]

Scheme 65. Palladium-catalyzed *N*-arylation of benzylamine derivatives.



Also, this system is applicable for the functionalization of pyrazine rings as well as pyridine ring systems (Scheme 66). Under these conditions, the corresponding dipirazine ligand **77** was formed in an excellent 93% yield.

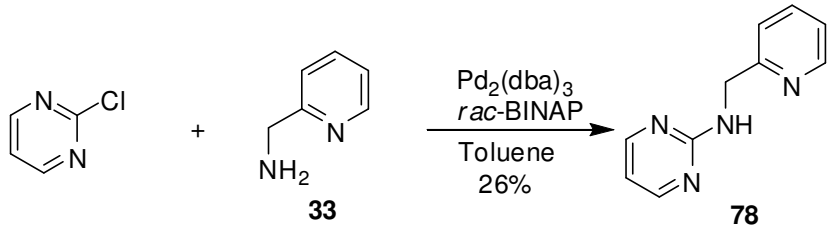
Scheme 66. Palladium-catalyzed *N*-arylation of 2-picolylamine with 2-chloropyrazine.



[122] C. Bolm, J.-C. Frison, J. L. Paih., C. Moessner, G. Raabe, *J. Organomet. Chem.* **2004**, *44*, 507.

As a final examination of the reactivity of various heteroaromatic halides, the arylation with chloropyrimidine was explored. Interestingly, only the mono coupling product was obtained in low yield when 2-chloropyrimidine was used as aryl source (Scheme 67).

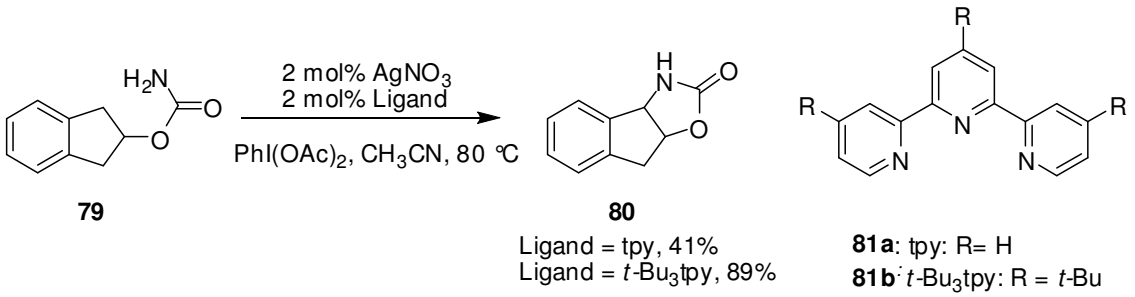
Scheme 67. Palladium-catalyzed *N*-arylation of 2-picolylamine with 2-chloropyrimidine.



4.1.1.2 Synthesis of *tert*-Butyl Substituted Dipyridylpicolylamine Derivatives in C-H Amidations

Silver-catalyzed C-H amidation has been reported by He *et al*. in 2004.[87b, 123] In this silver-catalyzed reaction, terpyridine **81a** was found to be an efficient ligand giving the desired product in 41% yield (Scheme 68). However, the use of **81b**, in which *tert*-butyl groups were introduced at the *para* positions in all of the pyridine moieties of the ligand led to a dramatically increased yield (89%).

Scheme 68. Silver-catalyzed benzylic C-H amidation.



In the same system, dipyridylaminopicoline ligand **74a** was examined in place of terpyridine. By GC-MS analysis, a trace of C-H-amidated product was detected. In silver-catalyzed amidation with terpyridine ligand **81a**, the yield was dramatically increased by introducing *tert*-butyl groups at the para positions.

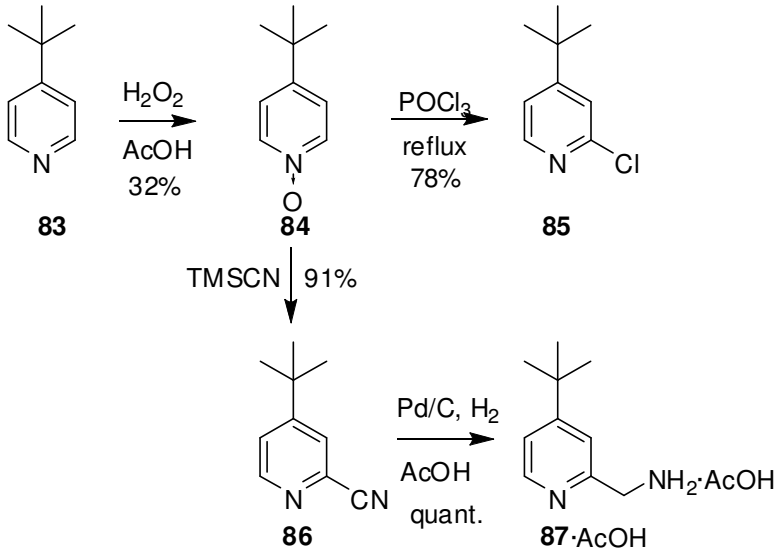
[123] a) Y. Cui, C. He, *J. Am. Chem. Soc.* **2006**, *125*, 16202. d) Y. Cui, C. He, *Angew. Chem.* **2004**, *116*, 4306, *Angew. Chem Int. Ed.* **2004**, *43*, 4210.

By following this scenario to improve the efficieny of this reaction, introduction of a *tert*-butyl group at the para position of the pyridine rings was attempted.

4.1.1.3 Synthesis of 4-*tert*-Butylpicolylamine and 2-Chloro-4-*tert*-butylpyridine

4-*tert*-Butylpicolylamine can be prepared easily from *tert*-butylpyridine. At first the *N*-oxide was synthesized following a known procedure by oxidation with H_2O_2 in acetic acid. Following the formation of *N*-oxide **84**, 2-chloride **85** was produced by refluxing with $POCl_3$ (Scheme 69). From *N*-oxide **84**, 4- *tert*-butyl-2-cyanopyridine **86** was produced by treatment with TMSCN. Finally, 4- *tert*-butyl-2-picolylamine **87** was obtained by hydrogenation with Pd/C.

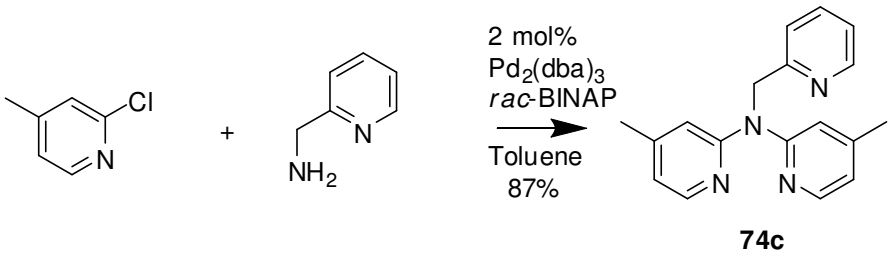
Scheme 69. Synthesis of 4-*tert*-butyl substituted pyridine derivatives.



4.1.1.4 Synthesis of 4-*tert*-Butyl substituted 2,2'-Pyridylaminopicoline Derivatives

As a first test, *N*-arylation of 2-picolylamine with 2-chloro-4-methyl pyridine was examined. The di-arylated product was obtained in 87% yield (Scheme 70).

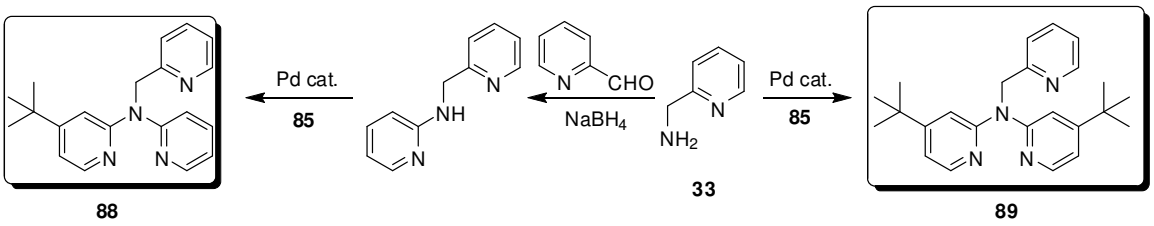
Scheme 70. *N*-Arylation of 2-picolylamine with 2-chloro-4-methyl-pyridine.



74c

By the same token, starting from 2-picolylamine, two kinds of 4-*tert*-butyl substituted 2,2'-pyridylaminopicoline derivatives **88** and **89** were synthesized using 2-chloropyridine **81** (Scheme 71).

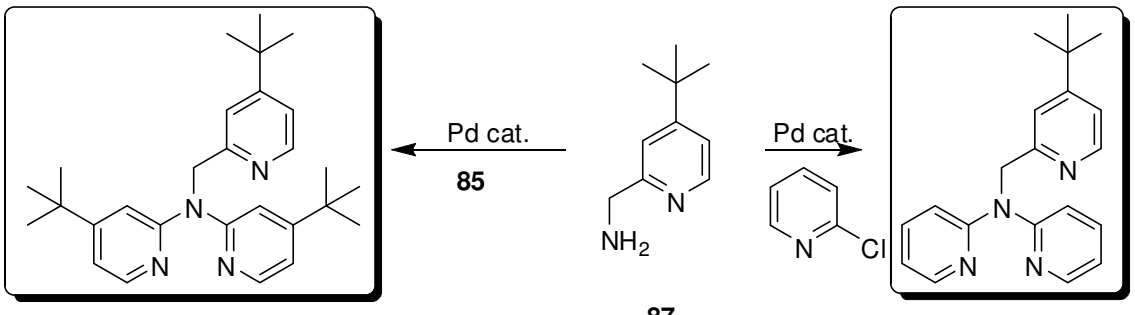
Scheme 71. Palladium-catalyzed *N*-arylation of picolylamine with 4-*tert*-butyl-2-chloropyridine.



88 **33** **89**

Following this success, another two kinds of 4-*tert*-butyl substituted 2,2'-*N*,*N*-pyridylaminopicoline derivatives **90** and **91** were synthesized from 4-*tert*-butyl-picolylamine **87** (Scheme 72).

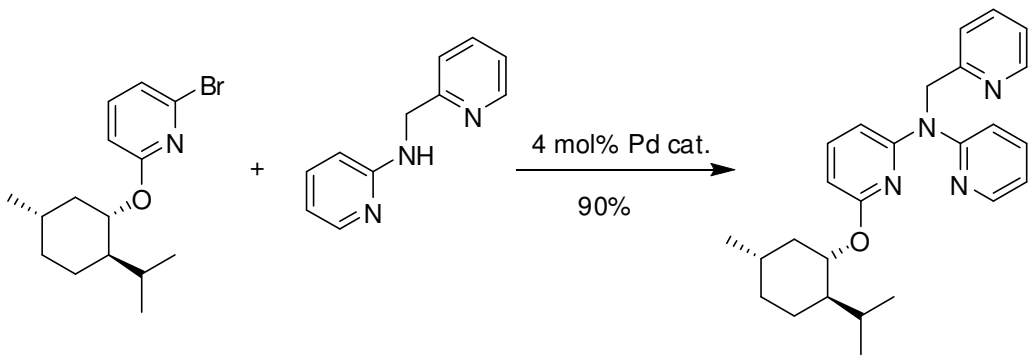
Scheme 72. *N*-arylation of 4- *tert*-butyl-2-picolylamine with chloropyridine derivatives.



90 **87** **91**

As part of studies toward the development of an asymmetric reaction, mono *L*-menthol substituted 2,2'-dimethyl-pyridyl-picolylamine ligand was prepared by using same procedure (Scheme 73). Complexation of this ligand **33b** with silver(I) nitrate is described in chapter 4.2.2.

Scheme 73. Synthesis of mono menthol-substituted 2,2'-dimethyl-pyridyl-pycolylamine **33b**.

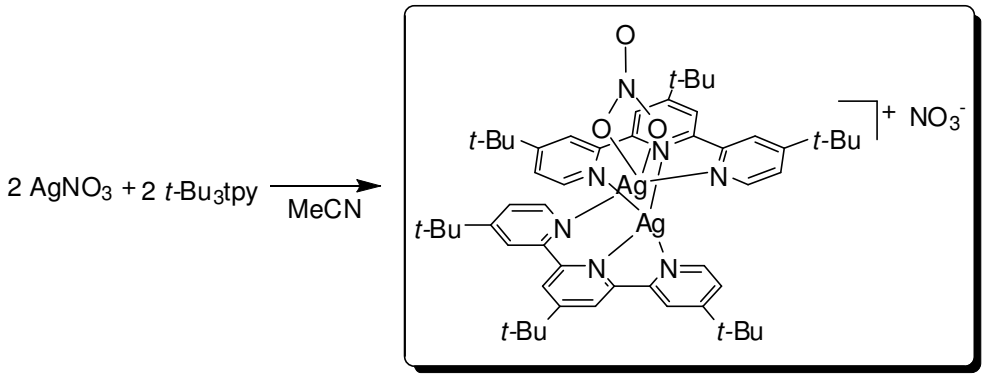


33b

4.2 Complexation of *N*-(Pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine with Silver(I) Nitrate

A silver complex of tri-*tert*-butylterpyridine[45a] has been reported by He (Scheme 74).[121b]

Scheme 74. Complexation of silver(I) nitrate with *t*-Bu_3tpy **81b**.



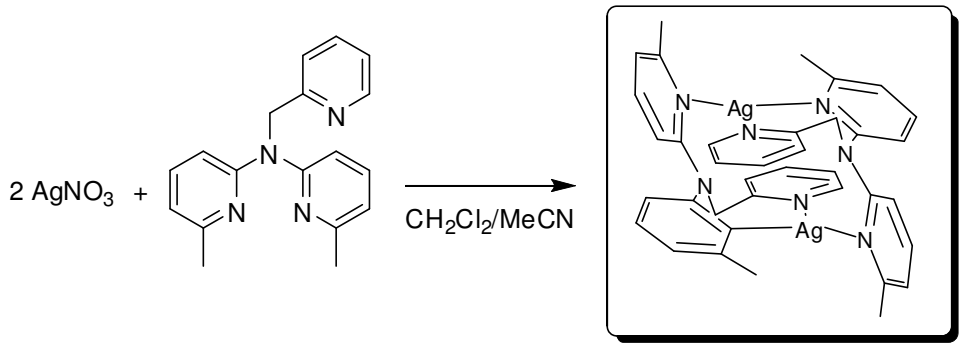
$[Ag_2(t\text{-}Bu_3tpy)_2(NO_3)]NO_3$

This silver complex can catalyze C-H amidation and aziridination reactions (Chapter 4.1.2). Thus, the synthesis of silver(I) complexes with dipyridylamine type ligands was examined, using the same condition described by He.[123]

When 6,6'-dimethyl-2,2'dipyridyl-2-picolylamine ligand **74b** was used, colorless, clear single crystals were obtained. The X-ray structure is shown in G. Y. Cho's thesis (Scheme 75).[124]

[124] G. Y. Cho, Ph.D Thesis, RWTH Aachen, **2006**.

Scheme 75. Complexation of dipyridylamine ligand **74b**.

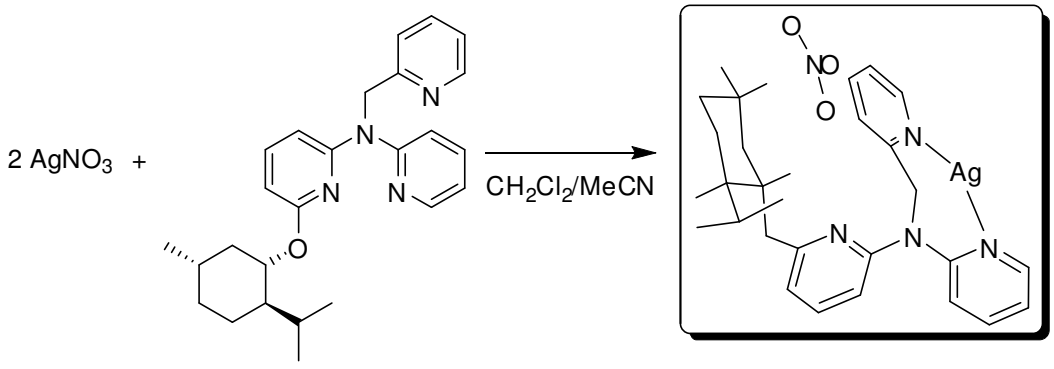


The coodination pattern is similar to the silver complex with *tert*-butylterpyridine reported by He and coworkers. Two of the nitrogen atoms of a ligand coordinate to a silver atom and the other nitrogen atom coordinate to second silver atom. However, the structures are different. Interestingly, one of the pyridine rings from a different ligand is located inside of the dimetal complex and seems to be parallel. On the other hand, all of pyridine rings are located outside of the silver complex with terpyridine.

Also, the complexation of 2,2'-dipyridyl-picolylamine was examined. Similary, a clear single crystal was obtained. However, the X-ray structure has not been determined yet.

Also, mono menthol substituted 2,2'-dimethyl-pyridyl-picolylamine **34b** was complexed with silver(I) nitrate (Scheme 76).

Scheme 76. Complexation of silver(I) nitrate and menthol substituted 2,2'-dimethyl-pyridyl-pycolylamine ligand **34b.**

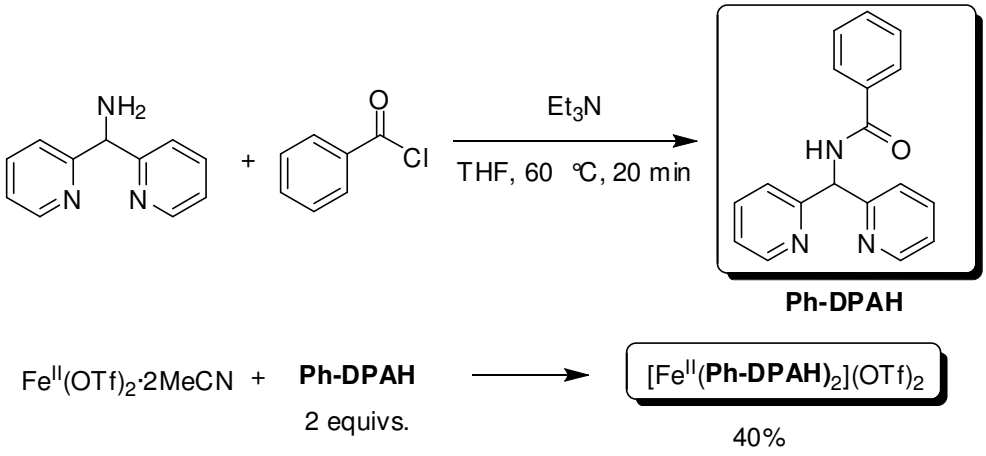


Contrary to expectations, a silver complex was obtained as a monomer (Chapter 8.1.4.). This ligand was not efficient for silver-catalyzed C-H amidation and no conversion was observed.

4.3 Complexation with Iron(II) Triflate

An iron complex with [di-(2-pyridyl)methyl]benzamide (Ph-DPAH) and its application for oxidation has been reported by Que, Jr.(Scheme 77).[63e]

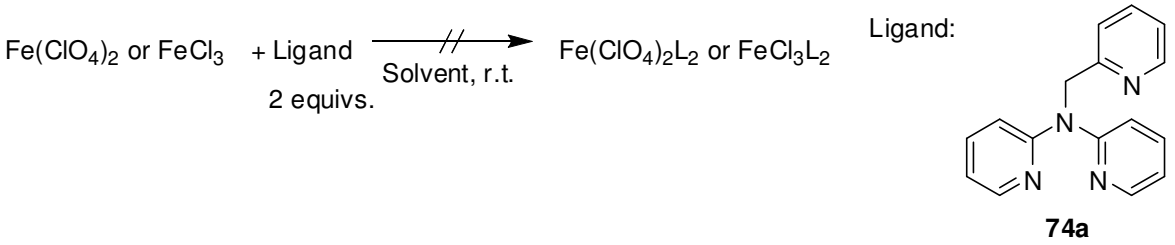
Scheme 77. Preparation of Ph-DPAH and its iron complex.



4.3.1 Complexation of Iron(II) Triflate with *N*-(Pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine

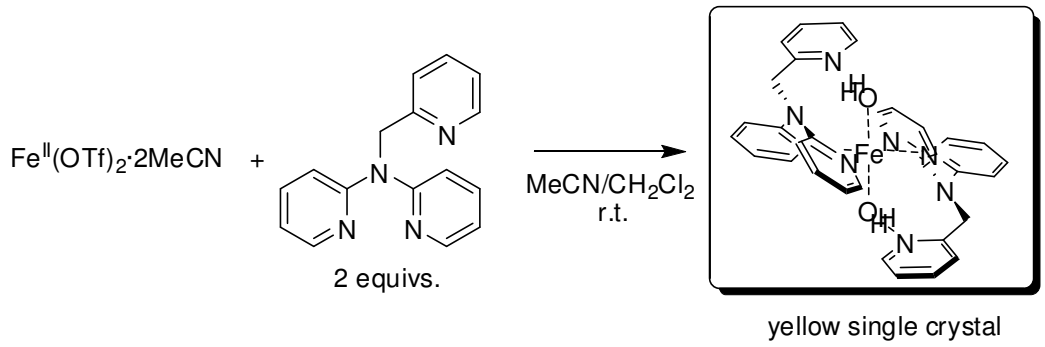
The first complexation was attempted by following the procedure developed by Schindler for copper complexation. Several iron salts such as iron(II) perchlorate and chloride have been tested. Unfortunately, complexation was not successful (Scheme 78).

Scheme 78. Complexation of iron salt and dipyridylamine ligand **74a**.



As a second trial, due to the similarity of the ligand structure, the complexation of iron(II) triflate and dipyridylpicoline ligand **74a** was tried using same procedure reported by Que.[112] Finally, clear yellow single crystals of the iron (II) triflate complex with dipyridylpicoline ligand **74a** were obtained from acetone (Scheme 79).

Scheme 79. Complexation of iron(II) triflate and dipyridylpicolylamine ligand **74a**



The X-ray structure shows a similar coordination system to that described for copper complexes, in which two of three nitrogen atoms coordinate to metal. The X-ray structure of this iron complex is shown in chapter 8.1.5.

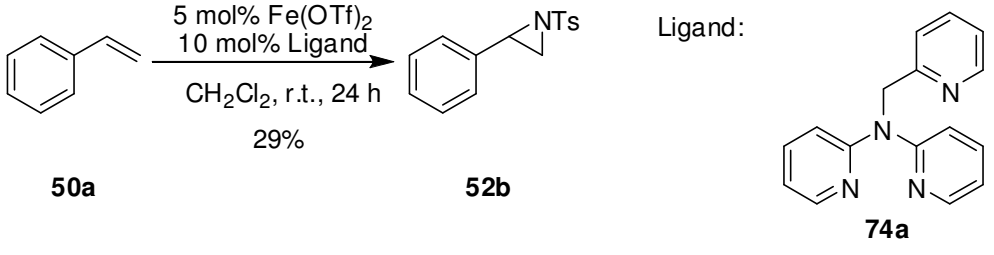
In addition, complexation of dipyridylbenzylamine with iron(II) triflate was also carried out for comparison. As a result, a pale yellow solid precipitated. However, it was not possible to obtain single crystals. Moreover, this complex seems to be unstable under air at room temperature, undergoing decomposition in a few hours.

4.3.2 Application in Iron-Catalyzed Oxidation Reactions

As a first application, iron-catalyzed benzylic oxidation of diphenylmethane with this ligand was tested and benzophenone was obtained in high yield (97%). It was observed later that pyridine was necessary for the benzylic oxidation to take place.

As another application, the iron-catalyzed aziridination of styrene has been examined (Scheme 80)

Scheme 80. Iron-catalyzed aziridination with *N,N*-dipyridylpicolylamine ligand **74a**.



The resulting aziridine product was obtained in only 29% yield. In a blank reaction, the aziridination without ligand gave only a trace of the product. Encouragingly, the yield was improved to 45% by using 6 equivs of ligand to iron(II) triflate.

5 Iron-Catalyzed Oxidation Reaction and Nitrogen Transfer Reaction

5.1 Iron-Catalyzed Benzylic Oxidation with TBHP

Benzylic oxidation is frequently used in organic synthesis for the construction of complex molecules. Classical oxidation protocols typically involved the use of stoichiometric quantities of oxidants such as potassium permanganate or potassium dichromate.[125] Recently, a number of oxidation catalysts have been reported.[57] Unfortunately, most existing procedures for benzylic functionalization are limited as they involve toxic metals[51] and the substrate scope is often narrow. Consequently, further developments in the metal-catalyzed oxidation area are desirable and the problem is especially acute on an industrial scale where environmentally benign oxidation catalysts and non-polluting stoichiometric oxidants are much sought after. Thus, low cost and non-toxic iron appears to be an optimal metal source for the construction of catalyst systems.[8] In 1983, Barton introduced a particular type of iron-catalyzed oxidation dubbed the "Gif" reaction,[126] a methodology which has evolved considerably in the meantime.[55b, 127] An exciting development in iron-catalyzed oxidation was recently reported by Kim *et al.* who demonstrated the applicabilty of their catalyst for the oxidation of activated methylene groups.[72] However, this system required the addition of an acid and slow addition of oxidants by using syringe pump. An alternative oxidation protocol, which allowed the oxidation of benzylic compounds efficiently under mild and convenient reaction conditions and which required no additional acid or ligand was desirable.

An oxidation methodology involving the use of iron(III) chloride as an inexpensive catalyst, low catalyst loadings (2 mol%), TBHP in water as stoichiometric oxidant and pyridine as

[125] M. Hudlicky, *Oxidations in Organic Chemistry*; ACS Monograph No. 186, American Chemical Society; Washington DC, **1990**.
[126] a) P. Stavropoulos, R. Çelenligil-Çetin, A. E. Tapper, *Acc. Chem. Res*. **2001**, *34*, 745. b) For a summery of Gif reactions, see: P. Stavropoulos, R. Çelenligil-Çetin, S. Kiani, A. Tapper, D. Pinnapareddy, P. Paraskevopoulou: *Handbook of C-H Transformations*, (Ed.: G. Dyker), Wiley-VCH, Weinheim, **2005**, pp. 497. c) D. H. R. Barton, D. Doller, *Acc. Chem. Res*. **1992**, *25*, 504.
[127] D. H. R. Barton, T. Li, *Tetrahedron* **1998**, *54*, 1735.

solvent and coordinating agent was developed.[128] This protocol presented the additional advantage that a solution of TBHP in water, instead of TBHP in hydrocarbons, can be applied as oxidant.

For initial catalyst optimization, diphenylmethane (**33a**) was chosen as a starting material. In the presence of 2 mol% of iron(III) trichloride, several oxidants such as TBHP, H_2O_2,[129] cumene peroxide, NaOCl and O_2[130] were examined in pyridine at 82 °C. Only cumene hydroperoxide and TBHP gave desired benzopheneone **36a** in 58% and 91% yield respectively whereas use of H_2O_2 led to substrate decomposition and the latter two gave no conversion at all. In the blank reaction, no reaction occurred without TBHP as an oxidant. Surprisingly, an aerobic atmosphere was beneficial, whereas under argon **36a** was obtained in only 13% yield as determined by GC analysis. Other iron salts also proved applicable, independent of their oxidation state (Table 3)

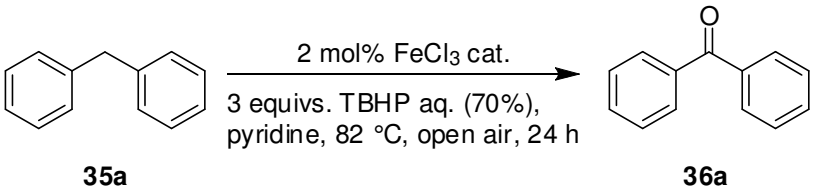
Table 3. Screening of iron salts.

Entry	Iron salt	Yield (%)
1	$Fe(ClO_4)_3$	94
2	$Fe(ClO_4)_2$:	70
3	$FeCl_3$	91
4	$FeCl_2$	87
5	$Fe(OTf)_2$	70
6	$Fe(acac)_3$	40

$FeCl_3$, which is easy to deal with and much cheaper and safer than $Fe(ClO_4)_3$, was chosen in subsequent studies in order to avoid the presence of the potentially explosive perchlorate ion, although the yield of **35a** was slightly higher by using $Fe(ClO_4)_3$ as catalyst,. After screening various solvents, pyridine appeared to be the optimal solvent when compared to MeCN, AcOH or *N*-methyl imidazole, which afforded **35a** in 73, 48, and 42% yield respectively. In conclusion, the best result was obtained using 2 mol% of $FeCl_3$•$6H_2O$ and 3 equivs. of TBHP aq. (70%) in pyridine at 82 °C under air for 24 hours affording the formation of

[128] a) W, Kissiling, *Z. Anorg. Allg. Chem.* **1922**, *120,* 209, 217, 229. b) M. Januszczyk, J. Janicki, H. Wojakowska, R. Krzyminiewski, J. Pietrzak, *Inorg. Chim. Acta* **1991**, *186*, 27. c) S. A. Cotton, V. Franckevicius, J. Fawcett, *Polyhedron* **2002**, *21*, 2055.
[129] C. Pavan, J. Legros, C. Bolm, *Adv. Synth. Catal.* **2005**, *347*, 703.
[130] T. Punniyamurthy, S. Velusamy, J. Iqbal, *Chem. Rev.* **2005**, *105*, 2329.

benzophenone **36a** in 91% yield (Eq. 1). Lower catalyst loading (0.5 mol) of $FeCl_3$ still gave benzophenone **36a** in 69% yield.

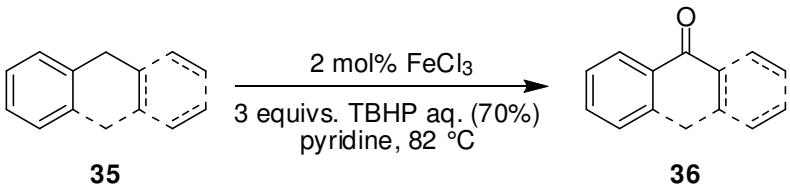


35a **36a** Eq. 1

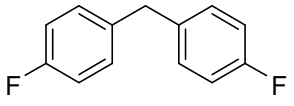
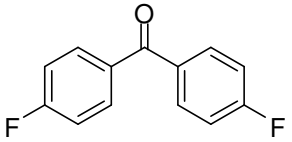
These conditions refer to a scale of up to 2 mmol. Using 5 mmol of **35a** under identical reaction conditions, benzophenone **36a** was obtained in 94% yield.

These optimized conditions were then applied for the oxidative conversion of other substrates (Table 4). Most diarylmethylene derivatives gave the corresponding products in excellent yields (up to >99%; Table 3, entries 1-6). Annulated compounds led to benzylic oxidation products in lower yields 30-74% yield (entries 7-13). Noncyclic compounds bearing one (hetero)aryl group could be oxidized in the benzylic position with moderate yields (entries 14-17). In these cases, no by-products were observed. The surprising reactivity difference between ethylbenzene (entry 16) and *p*-methoxy ethylbenzene (entry 17) is attributed to the presence of electron-donating substituents. The corresponding carboxylic acid was obtained in 53% yield by oxidation of *p*-methoxytoluene (entry 18). Benzylic alcohol such as diphenylmethanol gave diphenylketone (86% yield, entry 21). Interestingly, 1,4-dihydroxynaphthaline underwent oxidation to give binaphthoquinone in high yield (82%) under mild conditions (entry 20).[131] Interestingly, the oxidation of triphenylmethane **35v** gave *tert*-butyl triphenylmethyl peroxide in 91% yield instead of the corresponding alcohol (entry 21).

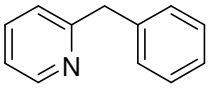
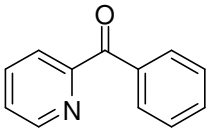
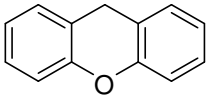
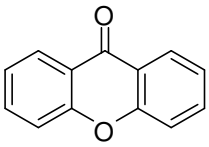
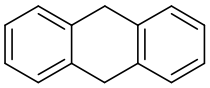
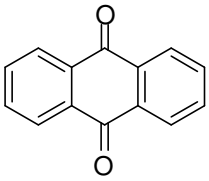
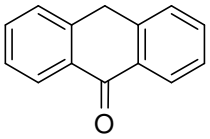
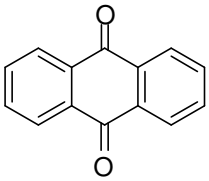
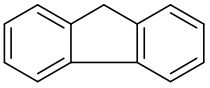
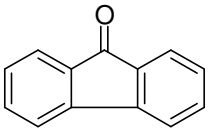
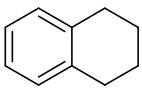
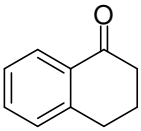
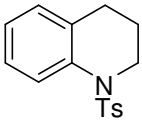
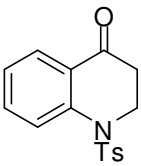
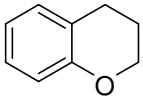
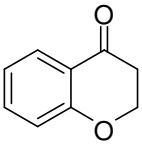
Table 4. Benzylic oxidation of various hydrocarbon derivatives.[a]

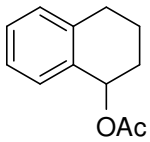
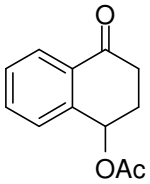
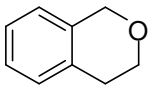
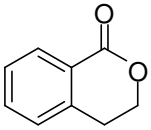
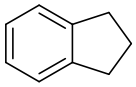
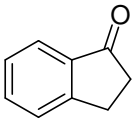
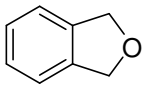
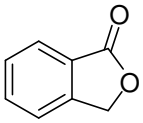
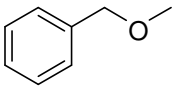
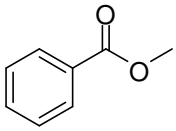
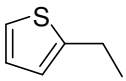
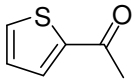
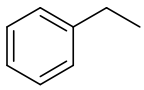
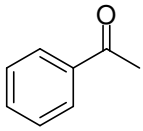
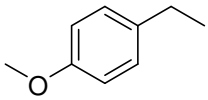
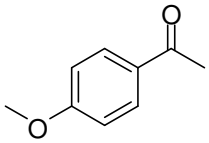
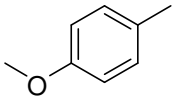
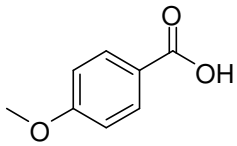


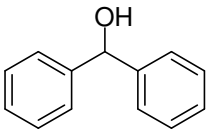
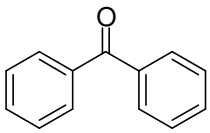
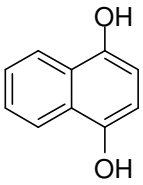
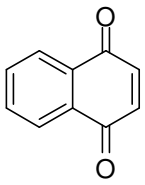
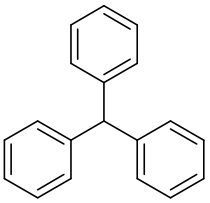
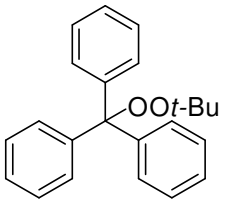
35 **36**

Entry	Substrate	Product	Yield (%)[b]
1	 **35b**		93

[131] This process may have application in the preparation of Vitamin K analogues J. Kowalski, J. Plonszyńska, A. Sobkowiak, *Catal. Commun.* **2003**, *4*, 603.

		36b	
2[c]	 **35c**	 **36c**	75
3	 **35d**	 **36d**	>99
4[d]	 **35e**	 **36e**	93
5	 **35f**	 **36e**	62
6	 **35g**	 **36f**	>99
7	 **35h**	 **36g**	41
8	 **35i**	 **36h**	60
9	 **35j**	 **36i**	54

10	 **35k**	 **36j**	66
11	 **35l**	 **36k**	74
12	 **35m**	 **36l**	61
13	 **35n**	 **36m**	45
14	 **35o**	 **36n**	48
15	 **35p**	 **36o**	15
16	 **35q**	 **36p**	17
17	 **35r**	 **36q**	84
18	 **35s**	 **36r**	53

19	 **35t**	 **36a**	86
20[e]	 **35u**	 **36s**	82
21	 **35v**	 **36t**	91

[a] Reaction conditions for a 2 mmol scale: 2 mol% of $FeCl_3$ •$6H_2O$, 3 equivs. of TBHP aq. (70%), pyridine, 82 °C, 24 h.

[b] Analytical data for all products were consistent with the literature or commercial materials.

[c] The reaction was carried out at 110 °C.

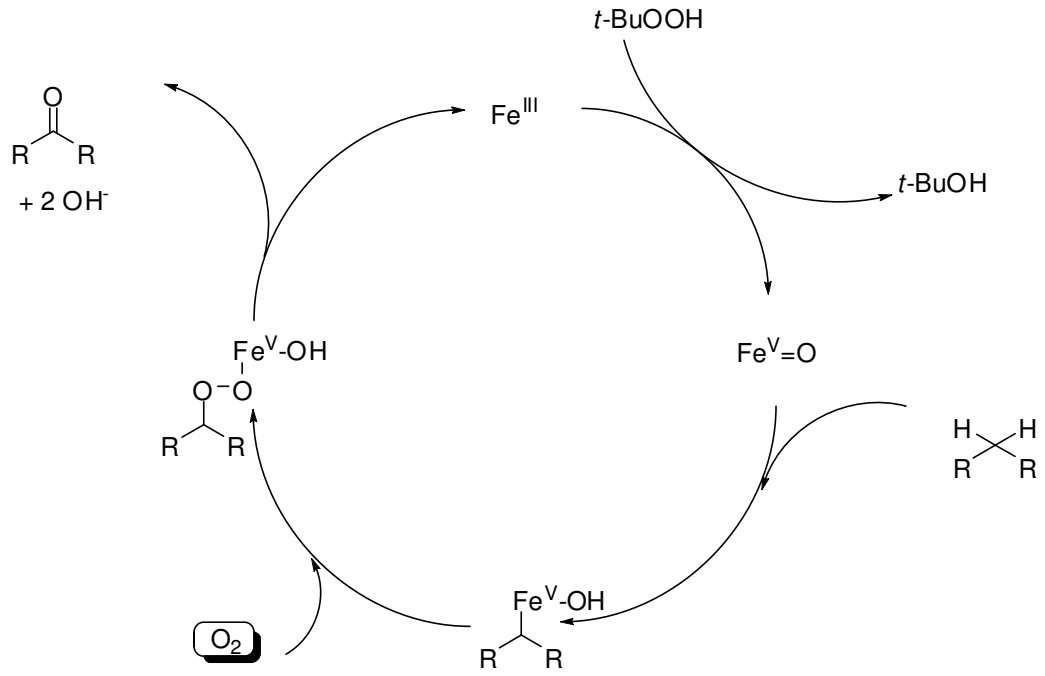
[d] 6 equivs. of aq. TBHP (70%) was used.

[e] The reaction was carried out at room temperature for 10 min in MeCN.

The dipyridylpicolylamine ligand **74a** was also examined for oxidation of diphenylmethane, resulting in the formation of benzophenone **35a** in 97% yield. But in the end it was found that only pyridine was necessary as ligand for this oxidation system.

A plausible mechanism is shown in Scheme 81. In the first step iron (III) is oxidized to generate a high valent iron oxo species, which can activate a C-H bond. After insertion of dioxygen, the ketone is formed and an iron(III) species can be regenarated.

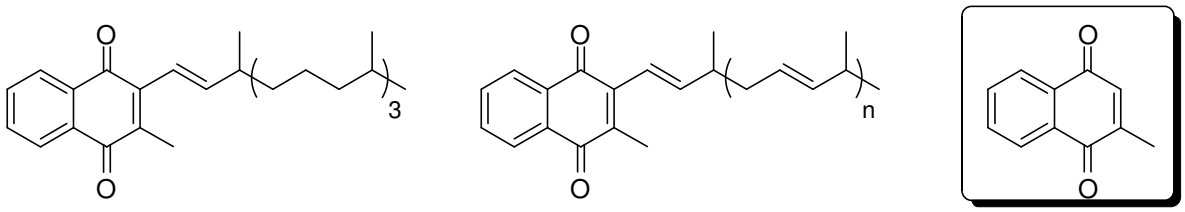
Scheme 81. Plausible catalytic cycle for benzylic oxidation.



5.2 Synthesis of Vitamin K_3

The series of Vitamin K compounds, which consist of a 1,4-naphthoquinone framework, are included in the lipophilic Vitamin K family (Figure 7). Vitamin K_3 (menadione) can be conveniently prepared synthetically.

Figure 7. Analogues of Vitamin K.

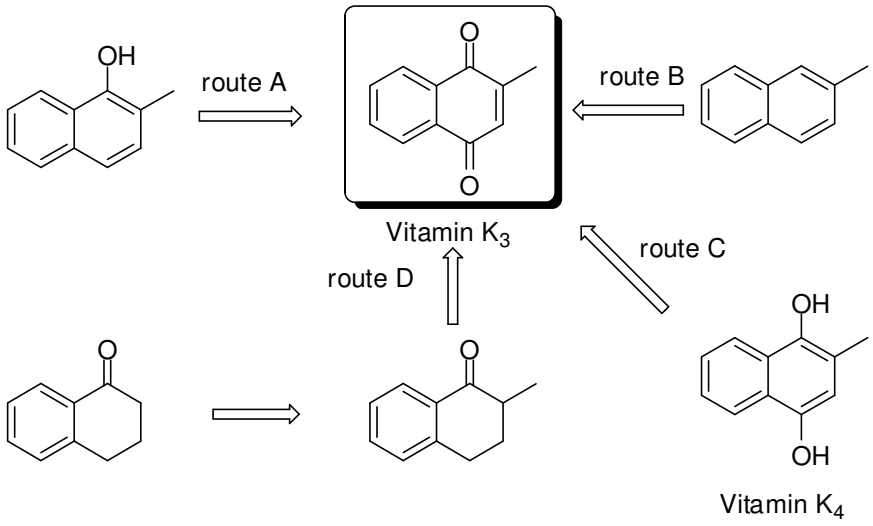


Vitamin K_1 Vitamin K_2 Vitamin K_3

Several procedures for the synthesis of Vitamin K_3 have been reported. The synthesis of Vitamin K_3 by applying this new iron-catalyzed oxidation methology can readily be envisaged. In principle, it can be accessed by several approaches from starting materials such

as 2-methylnaphthaline, [132] 1-hydroxy-2-methyl-naphthaline [133] and 1,4-dihydroxynaphthaline[134] (Scheme 82).

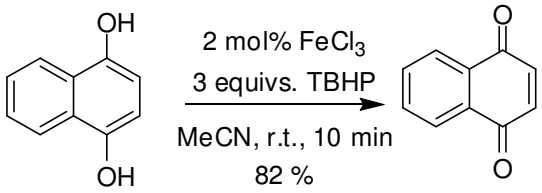
Scheme 82. Approaches to Vitamin K_3.



For example, from methylnaphthaline (route A), Vitamin K_3 can be synthesized by oxidation with PCC in 55% yield.[131] From methylnaphthaline (route B), Vitamin K_3 can be obtained in quantitative yield using hydrogen peroxide in acetic acid at 100 ℃ for 3 hours.

As described in chapter 5.2, 1,4-dihydroxynaphthaline was oxidized by an iron catalyst with TBHP affording naphthoquinone in good yield (Scheme 83).

Scheme 83. Transformation of 1,4-dihydroxynaphthaline by iron catalyisis.



Thus, by using the same oxidation conditions, Vitamin K_3 should be readily synthesized from 2-methyl-1,4-dihydroxynaphthaline (Vitamin K_4) (route C).

---

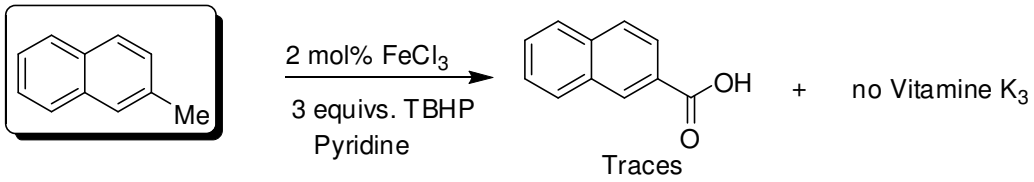
[132] a) S. Narayanan, K. V. V. S. B. S. R. Murthy, K. M. Reddy, N. Premchander, *Appl. Catal.* A: **2002**, *228*, 161. b) A. Bohle, A. Schubrert, Y. Sun, W. R. Thiel, *Adv. Synth. Catal*. **2006**, *348*, 1011. c) F. Shi, M. K. Tse, M. Beller, *Adv. Synth. Catal*. **2007**, *349*, 303. d) Patent, WO 02/079133 A1.

[133] E. Fillion, V. E. Trépanier, L. G. Mercier, A. A. Remorova, R. J. Carson, *Tetrahedron Lett*. **2005**, *46*, 1091.

[134] a) S. Shi, T. J. Katz, B. V. Yang, L. Liu, *J. Org. Chem*. **1995**, *60*, 1285. b) D. Villemin, M. Hammadi, M. Hachemi, *Synth. Commun*. **2002**, *32*, 1501. c) F. Minisci, A. Citterio, E. Vismara, F. Fontana, S. D. Bernardinis, *J. Org. Chem*. **1989**, *54*, 728.

These reaction conditions were applied to synthesize Vitamin K_3 from 2-methylnaphthaline. However, only traces of naphthaline-2-carboxylic acid were isolated and none of the desired product was observed (Scheme 84).

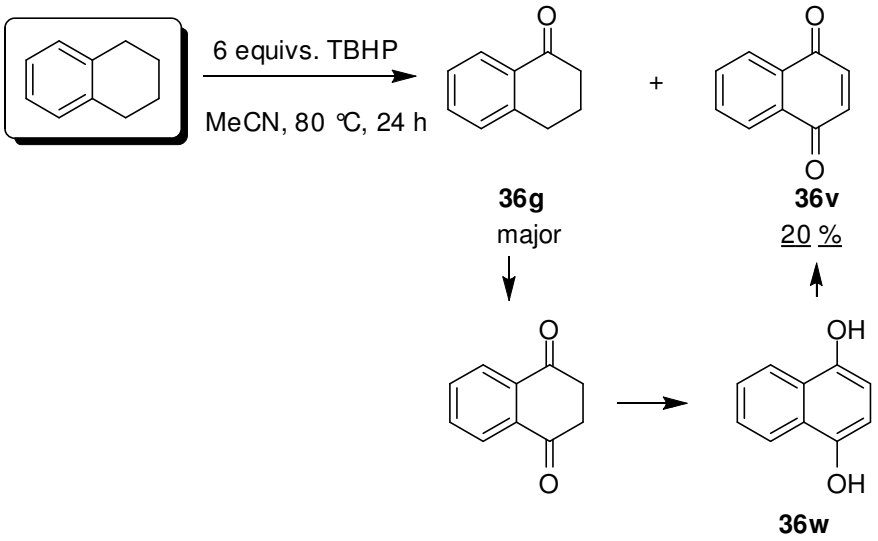
Scheme 84. Trial of Vitamin K_3 synthesis by iron-catalyzed oxidation with TBHP.



As a new approach, the synthesis of Vitamin K_3 from 1,2,3,4-tetrahydronaphthaline (route D) was attempted. Such a route has never been reported. α-Tetralone can be synthesized easily and even by iron-catalyzed benzylic oxidation as mentioned in chapter 5.2.

An interesting result was obtained when tetrahydronaphthaline was oxidized with TBHP in MeCN. Instead of α-tetralone and the related diketone, 1,4-naphthoquinone was obtained in low yield (Scheme 85).

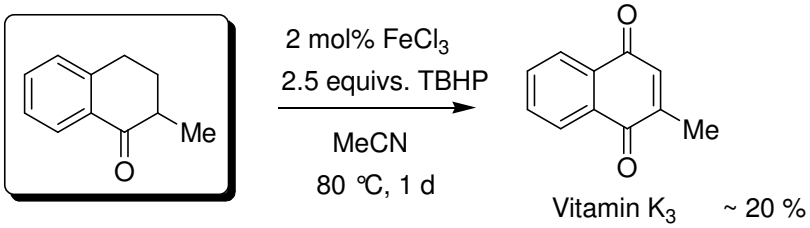
Scheme 85. Synthesis of 1,4-naphthoquinone from 1,2,3,4-tetrahydronaphthaline.



As a tentative reaction mechanism, α-tetralone can be considered to be formed first. Then, benzylic oxidation might occur to form the diketone, which can be coverted to 1,4-dihydroxynaphthaline under basic conditions. Immediately afterwards, the hydroxyl groups would be oxidized further to afford 1,4-naphthoquinone.

If this mechanism were right, Vitamin K_3 should be accessible from methyltetralone (Scheme 86).

Scheme 86. Synthesis of 1,4-naphtoquinone from 1,2,3,4-tetrahydronaphthaline.

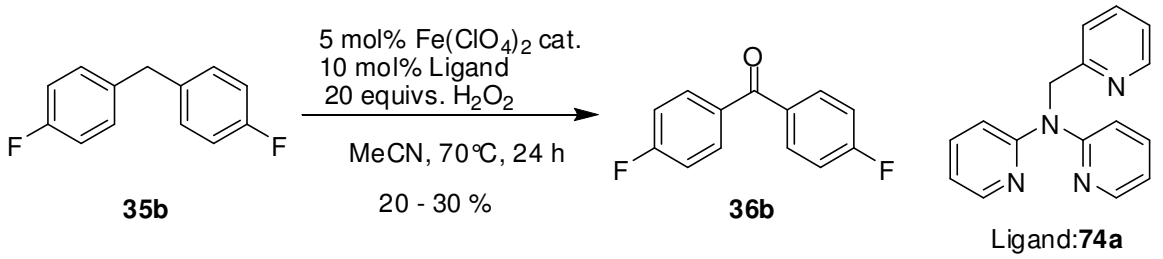


As expected, Vitamin K_3 could be obtained, although in low yield. Unfortunately, it was not possible to improve the yield with this catalytic system.

5.3 Iron-Catalyzed Benzylic Oxidation with Hydrogen peroxide

As described in chapter 1.3, the ligand plays an important role in benzylic oxidation reactions. *N*,*N*-dipyridylaminopicoline, which has been synthesized in this study, was examined as a new ligand for this transformation (Scheme 87).

Scheme 87. Iron-catalyzed benzylic oxidation with H_2O_2.

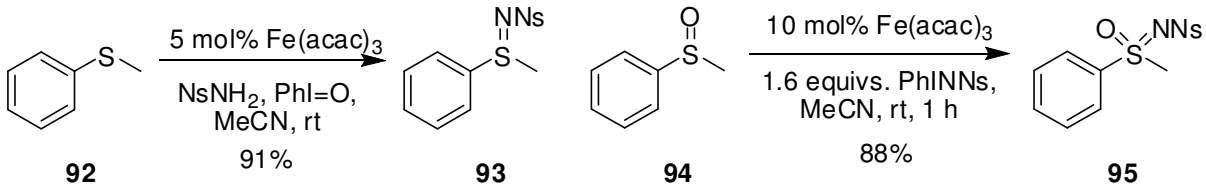


After optimization, use of 5 mol% iron(III) trichloride, ligand and hydrogen peroxide (20 equivs.) as oxidant in MeCN at 70 °C for 24 hours gave full conversion to diphenylketone. However, diarylketone **36b** was obtained only in 20% yield, probably due to decomposition of product. To avoid decomposition, the reaction was diluted. However, the conversion was lower and the isolated yield was still 30%.

5.4 Developement of Iron-Catalyzed Iminations of Sulfides and Sulfoxides

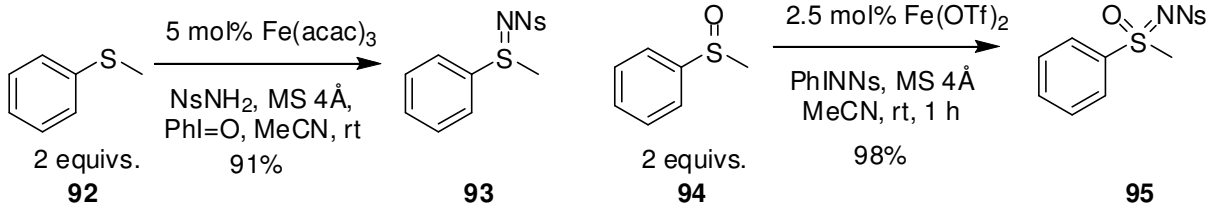
During recent years, iminations of sulfides and sulfoxides have generated great interest among chemists. Several metal-catalyzed iminations have been demonstrated.[135]. In our group, rhodium and silver-catalyzed iminations have been developed.[136] Even though they are efficient methods, most of them involve toxic metals. In 2006, an iron-catalyzed imination reaction of sulfides and sulfoxides was reported (Scheme 88).[137]

Scheme 88. Iron-catalyzed imination of sulfide and sulfoxide.



In the published screening of iron salts, iron(II) triflate was not examined and $Fe(acac)_3$ was found to be the optimal catalyst. Subsequent examination of $Fe(OTf)_2$ in imination of sulfoxide **92** using PhINNs as nitrene source revealed a slight improvement in conversion (Scheme 89).

Scheme 89. Imination of sulfide and sulfoxide with iron(II) triflate.



As an example, even only 2.5 mol% of iron(II) triflate was able to catalyze efficiently imination of thioanisole and its suloxide, affording the corresponding iminated products in

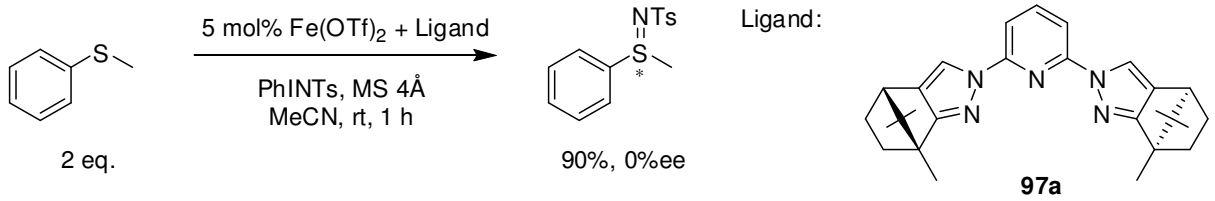
[135] Cu-catalyzed imination, see: a) J. F. K. Müller, P. Vogt, *Tetrahedron Lett*. **1998**, *39*, 4805. b) P. S. Aujla, C. P. Baird, P. C. Taylor, *Tetrahedron Lett*. **1997**, *38*, 7453. c) M. L. Kantam, B. Kavita, V. Neeraja, Y. Haritha, M. K. Chaudhuri, S. K. Dehury, *Adv. Synth. Catal*. **2005**, *347*, 641. d) H. Takada, Y. Nishibayashi, K. Ohe, S. Uemura, C. P. Baird, T. J. Sparey, P. C. Taylor, *J. Org.Chem*. **1997**, *62*, 6512. Ru-catalyzed imination, see: e) M. Murakami, T. Uchida, T. Katsuki, *Tetrahedron Lett*. **2001**, *42*, 7071.

[136] Rh-catalyzed imination, see: a) H. Okamura, C. Bolm, *Org. Lett.* **2004**, *6*, 1305. Ag-catalyzed imination, see: b) G. Y. Cho, C. Bolm, *Org. Lett.* **2005**, *7*, 4983.

[137] a) O. García Mancheño, C. Bolm, *Org. Lett.* **2006**, *8*, 2349. b) O. García Mancheño, C. Bolm, *Chem. Eur. J.* **2007**, *13*, 6674.

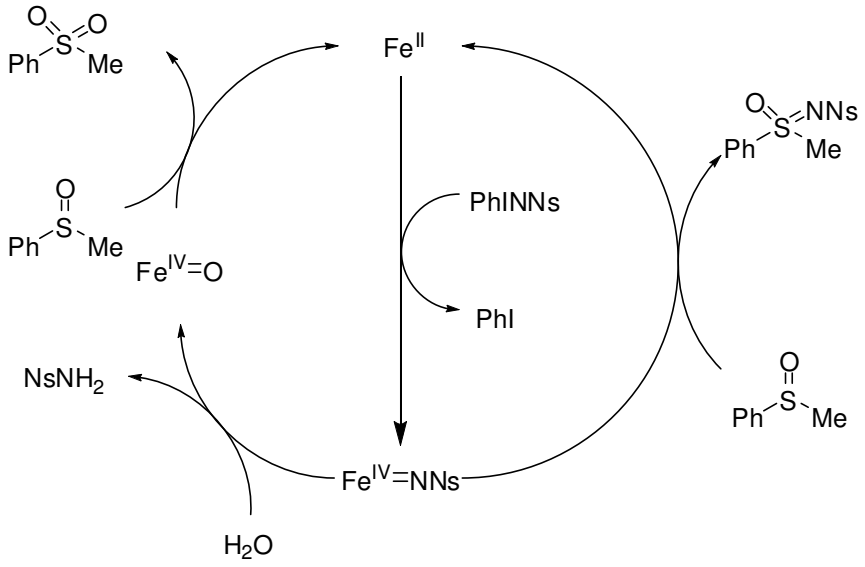
high yields (91% and 98% respectively). This system was applied for asymmetric iminations of sulfides using a chiral ligand **97a**. As a model reaction, the imination of thioanisole **92** with the combination of iron(II) triflate and chiral ligand **97a** was studied. Although no enantiomeric excess was observed, the yield was still satisfactory (Scheme 90)

Scheme 90. Iron-catalyzed asymmetric imination of sulfide.



A plausible mechanism for the imination of sulfoxides is depicted in Scheme 91 At the beginning iron(II) triflate reacts with PhINNs to generate an iron(IV)-nitrene intermediate. Afterwards, the iron-nitrene reacts with a sulfoxide to give a sulfoximine, regenerating the iron(II) catalyst. Molecular sieves play a very important role to eliminate undesired putative iron-oxo species, which can give sulfone as a side product. However, the iron-oxo species could not be detected by any analysis.

Scheme 91. Plausible catalytic cycle for imination of sulfoxide.



5.5 Iron-Catalyzed Aziridination of Olefins

During the last decades a number of metal-catalyzed aziridination processes have been developed due to the great utility of aziridine derivatives.[82c, 85, 138, 139, 140, 141, 142, , 143] However, most of them involve toxic metals as with sulfoxide iminations and benzylic oxidations. Consequently, further improvements in this area are still desirable. Paticulary, low cost and non-toxic iron would be of utility as a catalyst. Recently, several iron-catalyzed aziridinations have been developed. [81a, 91-93, 144]

Aziridination of styrene has been investigated using the same conditions as for the imination of sulfoxides (Scheme 75). Surprisingly, the use of 4Å molecular sieves was beneficial, whereas without molecular sieves the yield of aziridine **47** was only 63%.[90] Molecular sieves powder of 3 Å, 4 Å, 5 Å were tested to determine the effect of the cavity size. The aziridines **50a** was obtained in 60, 66, 63% yields, respectively, indicating that 4 Å sieves are optimal. The solvent effect is remarkable. When nitromethane was used, no aziridine product was obtained. Also, dichloromethane gave only traces of aziridine. Gratifying, several kinds of nitrene sources can be used affording aziridines in moderate yields (Table 5, entries 2-4).[78c]

Table 5. Aziridinations of styrene with various sulfonyliminophenyliodinanes **51**.[a]

[138] For Cu-catalyzed aziridinations, see: a) A. Pearson, G. R. Han, *J. Org. Chem*. **1985**, *50*, 2791. b) J. Muzart, *Tetrahedron Lett.* **1986**, *27*, 3139. c) R. Rahore, N. Saxena, S. Chandrasekaran, *Synth. Commun*. **1986**, *16*, 1493. d) J. Muzart, *Tetrahedron Lett*. **1987**, *28*, 2131. e) J. Muzart, A. N. A. Ajjou, *J. Mol. Catal*. **1991**, *66*, 155. f) T. K. Das, K. Chaudhari, E. Nandanan, A. J. Chandwadkar, A. Sudalai, T. Ravindranathan, S. Sivasanker, *Tetrahedron Lett.* **1997**, *38*, 3631. g) G. Rothenberg, H. Wiener, Y. Sasson, *J. Mol. Catal. A: Chem.* **1998**, *136*, 253. h) P. Dauban, R. H. Dodd, *Org. Chem*. **1999**, 64, 5304. i) S. L. Jain, B. Sain, *Tetrahedron Lett.* **2003**, *44*, 575. j) S. L. Jain, V. B. Sharma, B. Sain, *Synth. Commun.* **2005**, *35*, 9. k) P. Comba, M. Merz, H. Pritzkow, *Eur. J. Inorg. Chem.* **2003**, 1711. l) P. Dauban, L. Sanière, L. Tarrade, R. H. Dodd, *J. Am. Chem. Soc.* **2001**, *123*, 7707. m) H. L. Kwong, D. Liu, K.-Y. Chan, C.-S. Lee, K -H. Hung, C.-M. Che, *Tetrahedorn Lett*. **2004**, *45*, 3965.

[139] For Ag-catalyzed aziridinations, see: a) E. Modica, G. Bombieri, D. Colombo, N. Marchini, F. Ronchetti, A. Scala, L. Toma, *Eur. J. Org. Chem*. **2003**, 2964. b) M. Jurado-Gonzalez, A. C. Sullvian, J. R. H. Wilson, *Tetrahedron Lett.* **2003**, *44*, 4283. c) P. Lei, H. Alper, *J. Mol. Catal. A: Chem.* **1990**, *61*, 51..

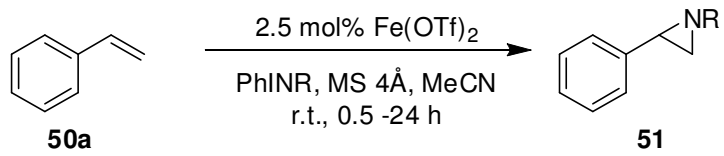
[140] For Au-catalyzed aziridinations, see: a) S. Murahashi, Y. Oda, T. Naota, T. Kuwabara, *Tetrahedron Lett.* **1993**, *34*, 1299. b) M. D. Nikalje, A. Sudaldai, *Tetrahedron* **1999**, *55*, 5903.

[141] For Rh-catalyzed aziridinations, see: a) G. Blay, I. Fernández, T. Gimenez, J. R. Pedro, R. Ruiz, E. Pardo, F. Lloret, M. Muoz, *Chem. Commun.* **2001**, 2102. b) J. F. Pan, K. M. Chen, *J. Mol. Catal. A: Chem.* **2001**, *176*, 19. c) N. H. Lee, C.-S. Lee, D. Jung, *Tetrahedron* **1998**, *39*, 1385. d) A. J. Catino, J. M. Nichols, R. E. Forslund, M. P. Doyle, *Org. Lett*. **2005**, *7*, 2787. e) M. P. Doyle, U.S. Pat. Appl. Publ., 2006211870.

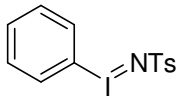
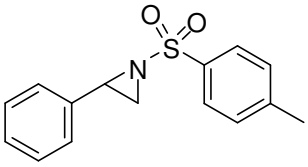
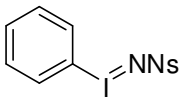
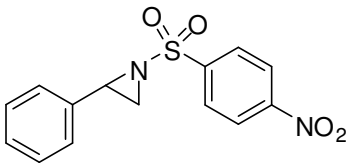
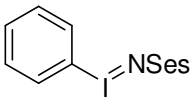
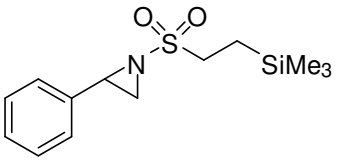
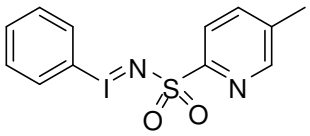
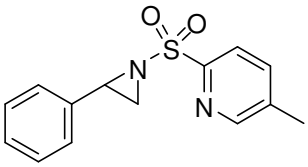
[142] For Mn-catalyzed aziridinations, see: a) D. Mansuy, J.-P. Mahy, A. Dureault, G. Bedi, P. Battioni, *J. Chem. Soc., Chem. Commun*. **1984**, 1161. b) T.-S. Lai, H.-L. Kwong, C.-M. Che, S.-M. Peng, *J. Chem. Soc., Chem. Commun*. **1997**, 2373. c) M. Nishimura, S. Minakata, T. Takahashi, Y. Oderaotoshi, M. Komatsu, *J. Org. Chem.* **2002**, *67*, 2101. d) H. Nishikori, T. Katsuki, *Tetrahedron Lett.* **1996**, *37*, 9245.

[143] For Co-catalyzed aziridinations, see: a) T. C. H. Lam, W.-L. Mak, W.-L. Wong, H.-L. Kwong, H. H. Y. Sung, S. M. F. Lo, I. D. Williams, W-H. Leung, *Organometallics* **2004**, *23*, 1247. b) G.-Y. Gao, J. E. Jones, J. D. Harden, X. P. Zhang, *J. Org. Chem.* **2006**, *71*, 6655.

[144] a) R. Vyas, G.-Yao. Gao, J. D. harden, X. P. Zhang, *Org. Lett*. **2004**, *6*, 1907. b) B. D. Heuss, M. F. Mayer, S. Dennis, M. M. Hossain, *Inog. Chem. Acta* **2003**, *342*, 301.



50a **51**

Entry [a]	Nitrene precursor	Product	Yield (%) [b]
1	 **48a**	 **51a**	66
2	 **48b**	 **51b**	88
3	 **48c**	 **51c**	65
4	 **48d**	 **51d**	87 [c]

[a] Reaction conditions for a 0.25 mmol scale: $Fe(OTf)_2$ (2.5 mol%), styrene (20 equivs.), MeCN, rt, 1 – 24 h.

[b] All products were identified by comparison of their analytical data with those of previous reports.

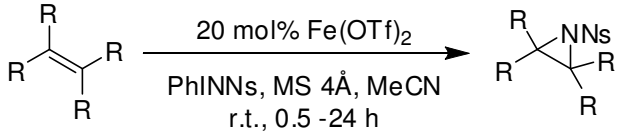
[c] $Fe(OTf)_2$ (5 mol%) was used.

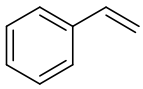
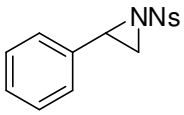
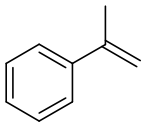
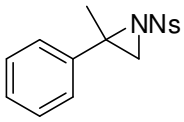
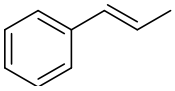
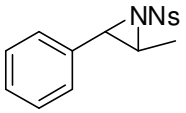
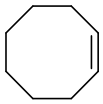
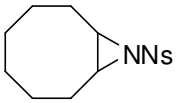
As alternative nitrene sources, chloramine-T **47a**, bromamine-T **47b** and tosylazide **49a** were tested for aziridination. However, no aziridine product was detected by GC-MS.

Next, using the best condition, the substrate scope of this reaction was explored. In the substrate screening, poorly reactive olefins such as α- or β-substituted styrene were

aziridinated (Table 6, entries 2-3). Cyclic olefins such as *cis*-cyclooctene can be aziridinated efficiently by increasing the amount of catalyst to 20 mol% (entry 4).

Table 6. Aziridinations of various olefins with PhINTs or PhINNs.[a]



Entry [a]	Substrate	Product	Yield (%) [b]
1	 **50a**	 **51a**	88 [c]
2	 **50b**	 **51e**	46
3	 **50c**	 **51f**	31 [d]
4	 **50d**	 **51g**	67

[a] Reaction conditions for a 0.25 mmol scale: $Fe(OTf)_2$ (20 mol%), olefins (20 equivs.), PhINNs (0.25 mmol), MeCN, r.t., 1–24 h.

[b] Analytical data for all products were consistent with the literature.

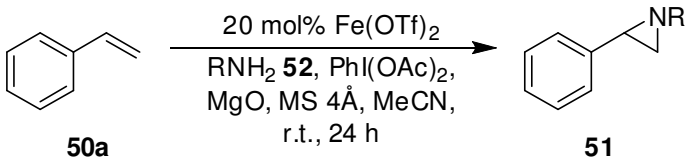
[c] $Fe(OTf)_2$ (10 mol%) was used.

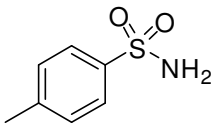
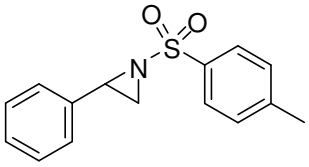
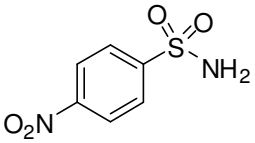
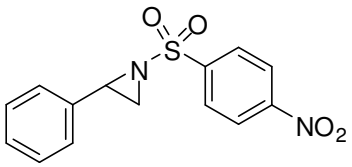
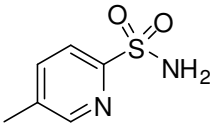
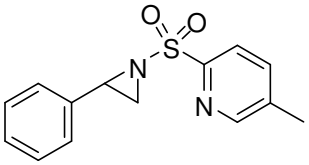
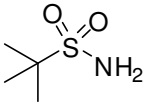
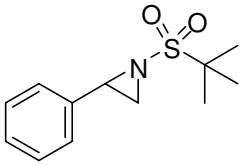
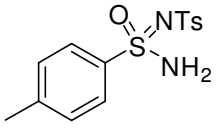
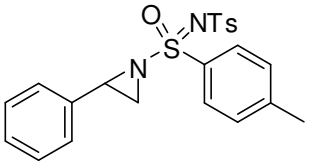
[d] Only trans product was obtained.

Aziridination using an in situ generated phenyliodinane was studied next. Thus, the reaction using 10-20 mol% of iron(II) triflate and a combination of the corresponding sulfonamide and iodobenzene diacetate with MgO as a base or iodosylbenzene proceeded well affording aziridines in high yields (Table 7, entries 1-4)[136l-m,] Significantly, *N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidophenylaziridine was obtained in good yield (58%, entry 5) even when it

was not possible to isolate the corresponding preformed iminoiodinane after reaction of sulfonimidamide **52e** with iodobenzene diacetate[96a].

Table 7. Aziridination of styrene **50a**.[a]



Entry[a]	Amide	Product	Yield (%)[b]
1	 **52a**	 **51a**	60
2	 **52b**	 **51b**	66
3	 **52d**	 **51d**	76[c]
4	 **52e**	 **52h**	50
5	 **52f**	 **51i**	58

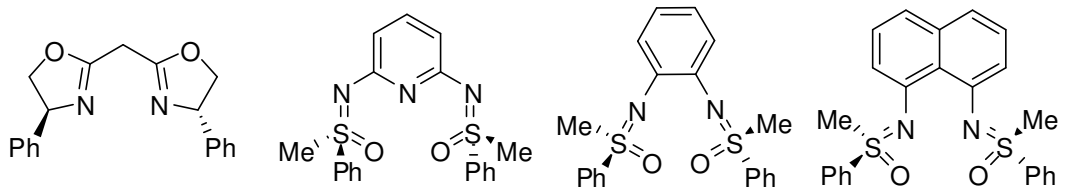
[a] Reaction conditions for a 0.25 mmol scale: $Fe(OTf)_2$ (20 mol%), styrene (10-20 equivs.), amide (0.25 mmol), $PhI(OAc)_2$ (0.5 mmol), MgO (1.5 mmol), MeCN, r.t., 24 h.

[b] Analytical data for all products were consistent with the literature..

[c] $Fe(OTf)_2$ (10 mol%) was used.

In addition, a screening of chiral ligands for asymmetric aziridination was carried out. Inefficient ligands which gave less than 5% ee are shown in Figure 8.

Figure 8. Variety of tested chiral ligands.



In copper-catalyzed asymmetric aziridination, bisoxazolines (Box)[145] are efficient ligands.[97a-b, 146] However, iron-catalyzed aziridination with a Box ligand gave a racemate. Also, salen type ligands which are efficient for Ru-catalyzed asymmetric reactions were examined, but yields and enantiomeric exesses were low. Probably, the imine part of the salen ligand reacted with the formed nitrene and the ligand itself decomposed.

During the optimizations, it was observed that the ratio of ligand to iron(II) triflate and the amount of catalyst were very important. When 2 equivs of ligand were used, higher enantiomeric excess were observed (30% ee). Also, 2.5 mol% of iron(II) triflate with 5 mol% of ligand gave lower enantiomeric excess (15% ee).

Finally, the best result was obtained with 5 mol% of iron(II) triflate and 30 mol% of (*S*, *S*)-*i*-Pr-pybox ligand giving the aziridine in 63% yield and 40% ee (Table 8, entry 1). Similar enantiomeric excess was observed using other pybox ligands (entries 2-4). Interestingly, chiral 2,6-bis(*N*-pyrazolyl)pyridines,[147] were efficient for this asymmetric reaction, even though the reaction took longer (entries 5-6).

Noteworthy results are that the (*S*, *S*)-Ph-pybox ligand and the pincer type disulfoximine ligand had similar efficiencies for this asymmetric reaction (entries 3 and 7).

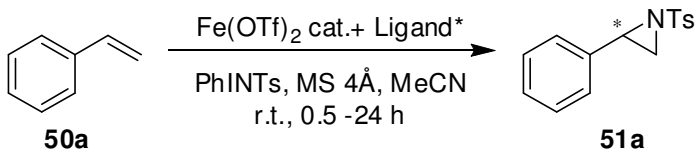
---

[145] G. Desimoni, G. Faita, K. A. Jørgensen, *Chem Rev*. **2006**, *106*, 3561.

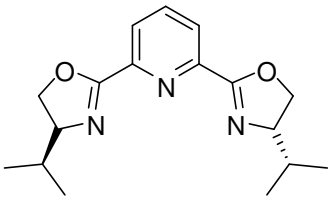
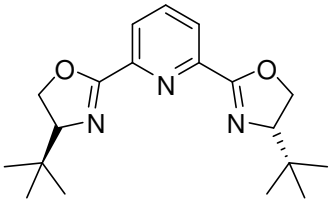
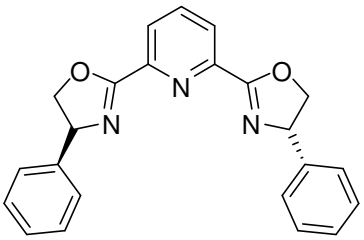
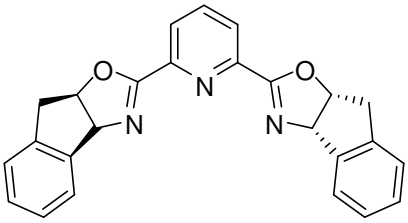
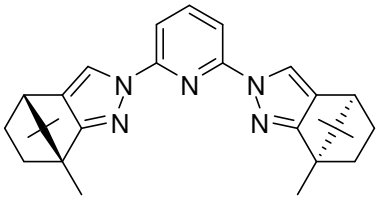
[146] a) S. Tylor, J. Gullick, P. McMorn, D. Bethell, P. C. Bullmann Page, F. E. Hancock, F. King, G. J. Hutchings, *J. Chem. Soc. Perkin Trans 2* **2001**, 1714. b) D. Ryan, P. McMorn, D. Bethell, G. J. Hutchings, *Org. Biomol. Chem.* **2004**, *2*, 3566. c) J. Gullick, S. Taylor, D. Ryan, P. McMorn, M. Coogan, D. Bethell, B. C. Bullmann Page, F. E. Hancock, F. King, G. J. Hutchings, *Chem. Commun*. **2003**, 2808. d) M. J. Södergren, D. A. Alonso, P. G. Andersson, *Tetrahedron: Asymmetry* **1997**, *8*, 3563.

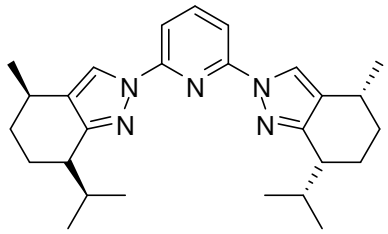
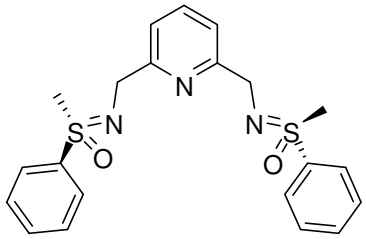
[147] a) M. Bovens, A. Togni, L. M. Venanzi, *J. Organomet. Chem*. **1993**, *451*, C28. b) A. A. Watson, D. A. House, P. J. Steel, *J. Org. Chem*. **1991**, *56*, 4072. c) D. D. LeCloux, W. B. Tolman, *J. Am. Chem. Soc*. **1993**, *115*, 1153. d) D. L. Christenson, C. J. Tokar, W. B. Tolman, *Organometallics* **1995**, *14*, 2148.

Table 8. Asymmetric aziridination of styrene.



50a **51a**

Entry [a]	Ligand	Yield (%)	E.e. (%)
1	 **96a**	67(72)	15(40) [b]
2	 **96b**	67	15
3	 **96c**	51	15
4	 **96d**	75	10
5	 **97a**	60	20

6	 **97b**	40	6
7	 **98**	67	15

[a] Reaction conditions for a 0.25 mmol scale: $Fe(OTf)_2$ (2.5 mol%), chiral ligand (5-10 mol%), styrene (20 equivs.), MeCN, r.t., 1–24 h.

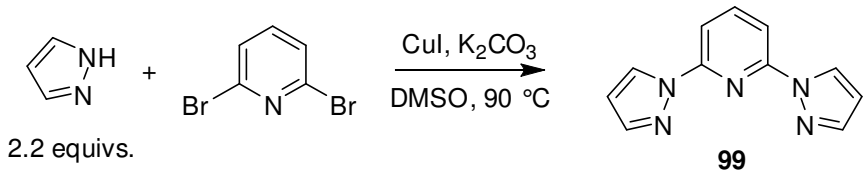
[b] $Fe(OTf)_2$ (5 mol%), chiral ligand (30 mol%) was used.

The effect of substitution at the sulfonamides employed as nitrogen sources was studied. Surprisingly, when nosyl amide was used, the aziridine was obtained as a racemate. Also, the Ses group was not efficient for asymmetric aziridination, giving **51a** in a low 20% ee. To improve the enantiomeric excess, some additives were examined. Addition of a radical scavenger such as 2,6-di-*tert*-butyl-4-methylphenol[148] gave lower enantomeric excess. Also, addition of a donor ligand such as pyridine-*N*-oxide[142c, 149] gave the product with lower yield and enantiomeric excess (20%, 10% ee).

Interestingly, aziridination of styrene works efficiently using *i*-Pr-Pybox ligand in dichloromethane giving the desired product in 92% yield, although only 3% enantiomeric excess was observed. Thus, 2,6-bis(*N*-pyrazolyl)pyridine (**99**),[150] which is a simple tridentate ligand and easy to prepare, was tested for aziridination reaction (Scheme 92).[151]

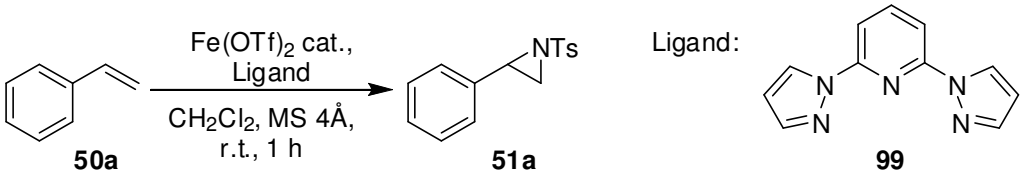
Scheme 92. Preparation of 2,6-bis(*N*-pyrazolyl)pyridine (**99**) catalyzed by copper(I) iodide.

[148] I. W. C. E. Arends, K. U. Ingold, D. D. M. Wayner, *J. Am. Chem. Soc*. **1995**, *117*, 4710.
[149] R. Irie, Y. Ito, T. Katsuki, *Synlett* **1991**, 265.
[150] a) D. L. Jameson, K. A. Goldsby, *J. Org. Chem.* **1990**, *55*, 4992. b) X. Sun, Z. Yu, S. Wu, W.-J. Xiao, *Organometallics* **2005**, *24*, 2959. c) G. Zoppellaro, M. Baumgarten, *Eur. J. Org. Chem.* **2005**, 2888.
[151] S. Özçubkuçu, E. Schmitt, A. Leifert, C. Bolm, *Synthesis* **2007**, 389.



As a result, the use of only 5 mol% of iron(II) triflate with 10 mol% of this ligand gave the aziridine product in 94% yield (Table 9, entry 1).

Table 9. Efficient aziridination catalyzed by iron(II) triflate with 2,6-bis(*N*-pyrazolyl)pyridine ligand **99**.



Entry [a]	$Fe(OTf)_2$ (mol%)	Ligand (mol%)	Yield (%)
1	5	10	94
2	2	4	78
3	1	2	50 [b]
4	5	0	trace

[a] Reaction conditions for a 0.25 mmol scale: $Fe(OTf)_2$ (1-5 mol%), ligand (0-10 mol%), styrene (20 equivs.), CH_2Cl_2, r.t., 1–24 h.

[b] Styrene (10 equivs.) was used.

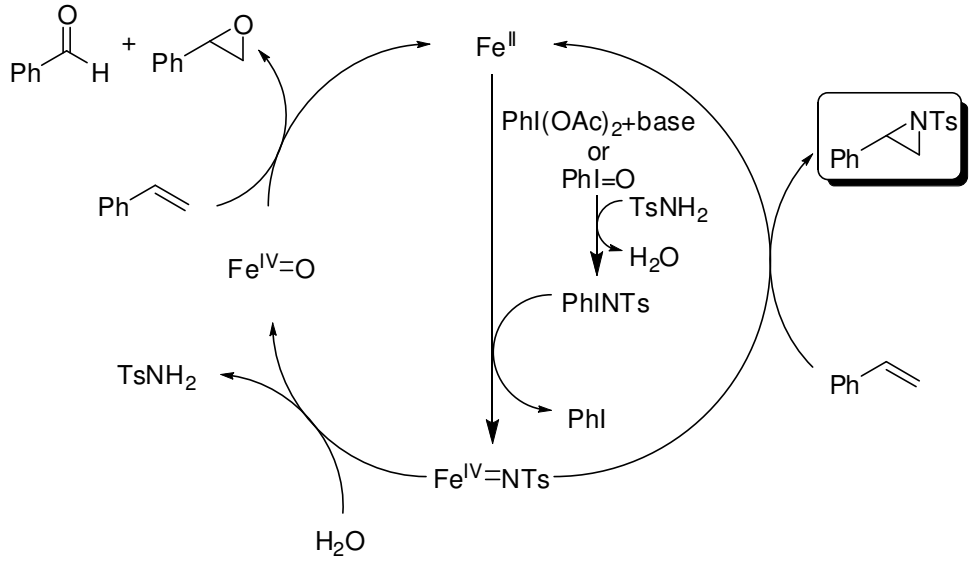
This combination of iron(II) triflate and 2,6-bis(*N*-pyrazolyl)pyridine **99** probably formed a mononuclear complex *in situ*.[152] Compared to the results obtained when the reaction was carried out in MeCN, this system is apparently more efficient in dichloromethane. By decreasing the amount of catalyst, the yields also tend to decrease. In a blank test without ligand, only traces of aziridine were detected by GC-MS and TLC, although PhINTs was consumed completely after 24 hours.

The proposed mechanism is shown in Scheme 93. As in the case of the imination reaction, iron(II) triflate forms an iron(IV)-nitrene intermediate with PhINTs. Then, the iron-nitrene reacts with styrene to give an aziridines product. At the same time, the iron(II) catalyst can be

[152] a) J. M. Holland, J. A. McAllister, C. A. Kilner, M. Thornton-Pett, A. J. Bridgeman, M. A. Halcrow, *J. Chem. Soc., Dalton Trans* **2002**, 548. b) J. Elhalïk, D. J. Evans, C. A. Kilner, M. L. Halcrow, *J. Chem. Soc. Dalton Trans* **2005**, 1693. c) J. Elhalïk, C. A. Kilner, M. L. Halcrow, *J. Chem. Soc., Dalton Trans* **2006**, 823. d) T. Ayer, S. Scott, J. Goins, N. Caylor, D. Hathcock, S. J. Slattery, D. J. Jameson, *Inorg. Chim. Acta* **2000**, *307*, 7.

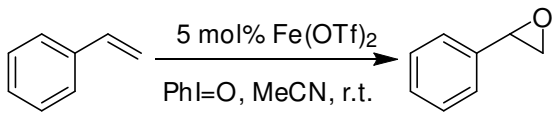
regenerated. Molecular sieves play a very important role to prevent the formation of an undesired iron-oxo species, which can give epoxide or aldehyde side products from styrene. Plausible side product such as epoxide were not detected by TLC, However, it was not able to isolated because of their trace amount and high volatility.[153]

Scheme 93. Plausible catalytic cycle for iron-catalyzed aziridinations of styrene.



As a mechanistic study, epoxidation with iodosylbenzene without sulfonamide, in which iron-oxo species will be formed, was examined. As expected, epoxidation product **100** was detected by TLC and characterized by NMR (Scheme 94).

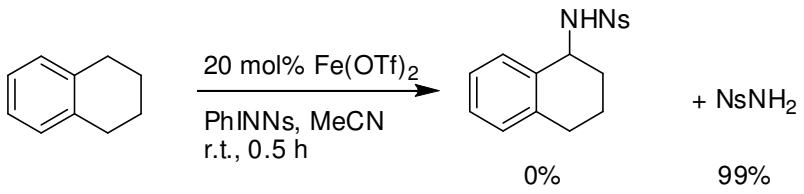
Scheme 94. Iron-catalyzed epoxidation of styrene.



As another application, C-H insertion of 1,2,3,4-tetrahydronaphthaline was examined. In this reaction, PhINNs was consumed completely. However, no amidation product was observed at all and ony $NsNH_2$ (99%) was recovered from PhINNs (Scheme 95).

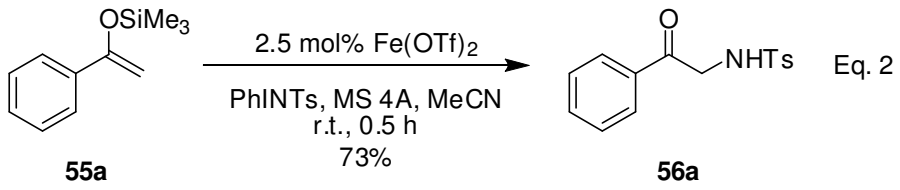
Scheme 95. Iron-catalyzed benzylic C-H insertion of 1,2,3,4-tetrahydronaphthaline.

[153] a) W. Nam, S. K. Choi, M. H. Lim, J-U. Rohde, I. Kim, J. Kim, C. Kim, L. Que, Jr. *Angew. Chem*. **2003**, *115*, 113. b) R. M. Moriarty, R. Penmasta, I. Prakash, *Tetrahedron Lett*. **1985**, *26*, 4699.



5.6 Iron-Catalyzed α-Amination of Silyl Enol Ethers Derivatives

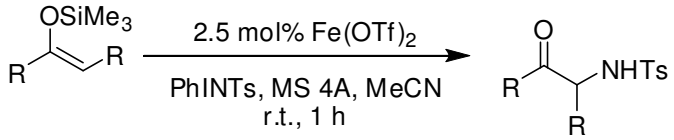
Metal-catalyzed α-amination of silyl enol ethers has been performed using several kinds of metal catalysts. For example, copper and ruthenium can be used (chapter 1.4).[88, 106] Also asymmetric α-aminations have been demonstrated.[110, 111] Actually, α-amination of silyl enol ethers proceeded by heating in boiling MeCN (82 °C) without metal catalysis as mentioned in chapter 1.4. However, the reaction works even at room temperature or lower temperature by using a metal catalyst. Further investigation of the iron(II) triflate catalyzed aziridination of styrene mentioned in chapter 5.5, has led to the discovery that attempted $Fe(OTf)_2$ catalyzed α-amination of silyl enol ethers using this system gave α-amino ketones (eq. 2). A typical α-amination (of enol silane (**55a**) to give α-amino ketone (**56a**)) is shown in equation 2.

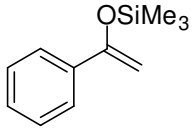
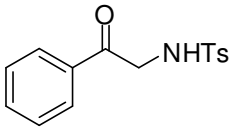
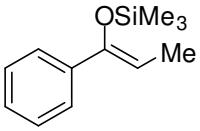
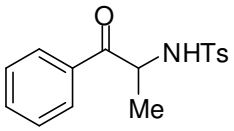
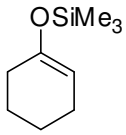
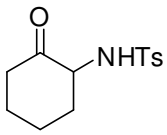
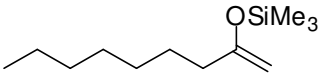
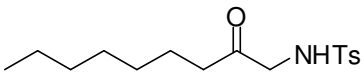
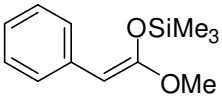
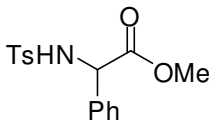


In the initial phase of the project, β-styryloxy trimethylsilane (**55a**) was chosen as substrate for the optimization of the catalysis protocol. The best result was achieved by using 2.5 mol% of $Fe(OTf)_2$•2MeCN, 20 mg of MS 4Å and 2 equivs. of silyl enol ether in acetonitrile at room temperature under argon, affording the formation of (**56a**) in 73% yield (eq. 2).

These optimized conditions were then applied to the conversion of several kinds of silyl enol ethers. Methyl substituted β-styryloxy trimethylsilane gave the corresponding α-amino ketone product in high yields(Table 10, entry 1). Use of a non-aromatic alkyl cyclic silyl enol ether led to the α-aminated product in 63% yield (entry 3). A linear aliphatic silyl enol ether was also able to be α-aminated with good yield (46%) (entry 4). Interestingly, reaction of a TMS protected ester enolate with PhINTs gave the α-amino acid ester in moderate yield (50%) (entry 5).

Table 10. α-Amination of various silyl enol ethers.[a]



Entry[a]	Substrate	Product	Yield (%)[b]
1	 **55a**	 **56a**	72
2	 **55b**	 **56b**	63
3	 **55c**	 **56c**	63
4	 **55d**	 **56d**	46
5	 **55e**	 **56e**	50

[a] Reaction conditions for a 0.25 mmol scale: $Fe(OTf)_2$ (2.5 mol%), silyl enol ethers (1-2 equivs.), MeCN, r.t., 1 h.

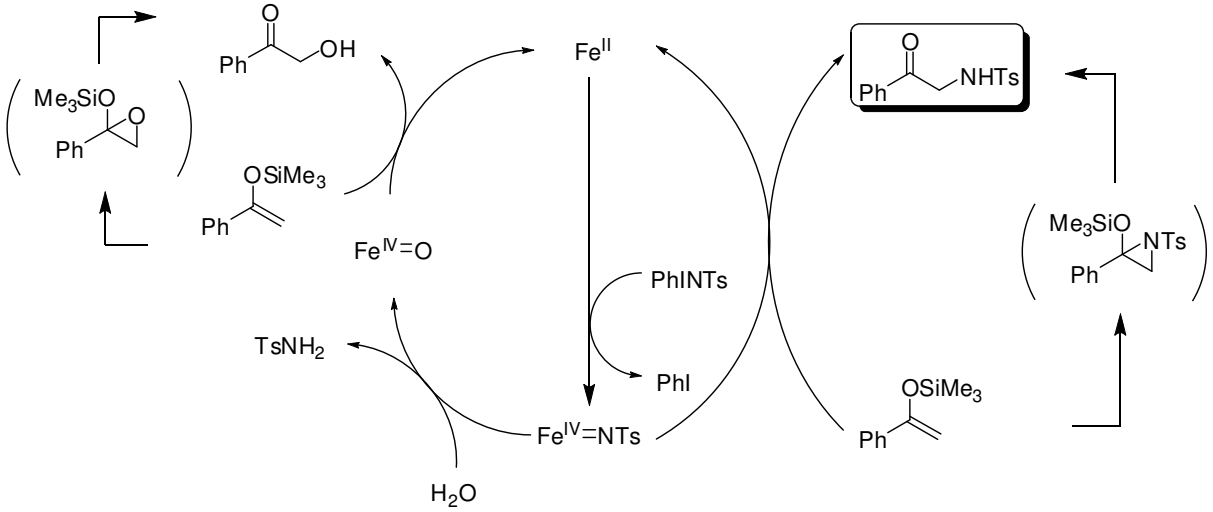
[b] Analytical data for all products were consistent with the literature.

To improve the yield a higher loading of catalyst was used. Conversely, 20 mol% of catalyst gave a lower yield (13%) in aziridination of cyclohexenyloxytrimethylsilane.

A proposed mechanism is given in Scheme 96. As in the case of imination reactions, iron(II) triflate generates an iron(IV)-nitrene intermediate with PhINTs. Then, the iron-nitrene reacts with silyl enol ethers to give α-amino ketones via aziridine intermediates and iron(II) is regenerated. Again molecular sieves are important to prevent side reaction due to iron-oxo

intervention. However, plausible side products from oxo intermediates such as α-hydroxy ketones were not observed by any analysis.

Scheme 96. Plausible catalytic cycle for iron-catalyzed α-amino ketonization of enol silane.



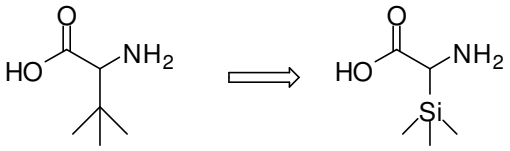
5.6.1 Synthesis of α-Silaamino Acid Derivatives

Application of the iron-catalyzed amination of silyl enol ethers to the synthesis of α-sila amino acid esters was studied next.

During recent years, α-silaamino acids have attracted biological interest. Characteristic differences in the chemical behavior of the compounds can be expected by displacement of *tert*-leucine by an α-silaamino acid. Especially, chemical properties such as biological activity and absorbability in to the human tumor cell lines can be modified by incorporation of α-silaamino acid into the peptide framework in the place of *tert*-leucine. For example, (-)-hemiasterin includes a *tert*-leucine residue. [154] The replacement of *tert*-leucine by α-sila amino acid in such a compound could be of great interest for the pharmaceutical industry (Figure 8).

Figure 8. Displacement of *tert*-leucine by α-silaamino acid.

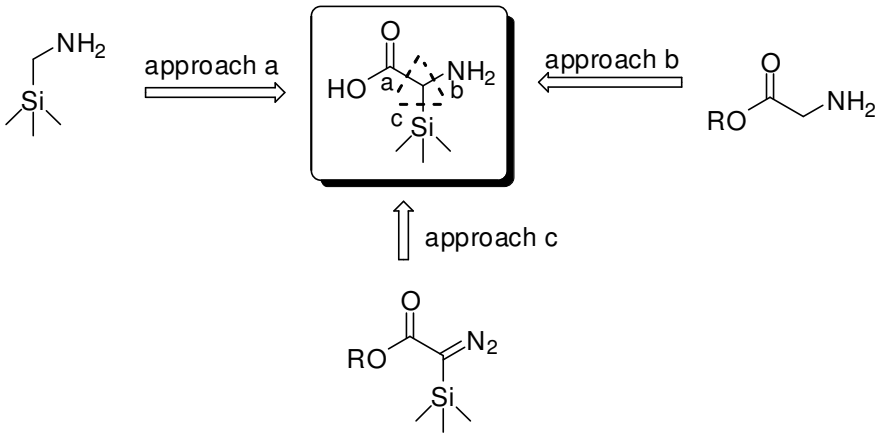
[154]R. Talpir, Y. Benayahu, Y. Kashman, L. Pannell, M. Schleyer, *Tetrahedron Lett*. **1994**, *35*, 4453.



tert-Leucine α-Silaamino acid

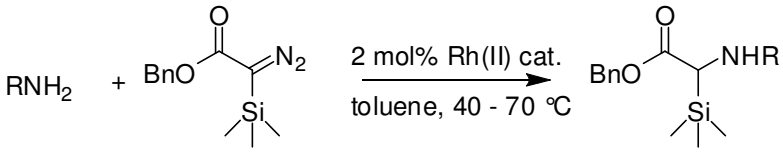
Conventionally, α-sila amino acid esters can be prepared by three approaches (Scheme 97).

Scheme 97. Synthetical approaches for α-silaamino acid.

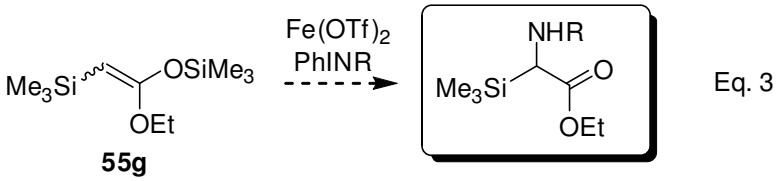


In our research group, rhodium-catalyzed C-H amination has suceeded using approach c (Scheme 98).

Scheme 98. Rhodium-catalyzed α-amination with diazocompounds.



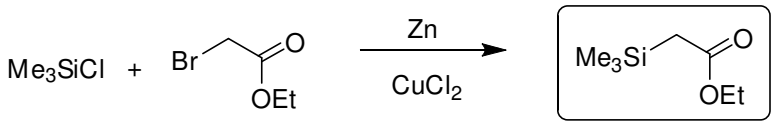
Finally, the applicability of this new strategy for the preparation of α-silaamino acid esters has been tested. As mentioned in chapter 5.7, silyl enol ethers could be converted to α-amino acid esters via iron-catalyzed α-amination. Thus, the synthesis of an α-silaamino acid ester may be achieved via amination of silyl ketene acetal **55g** (eq. 3).



55g Eq. 3

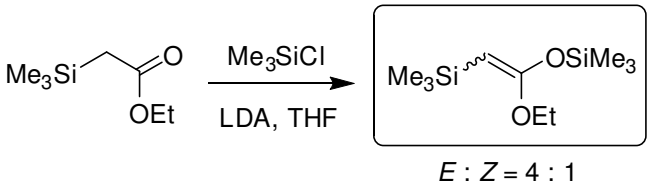
Actually, α-silylacetate, which is commercially available, can be easily synthesized from α-bromoacetate with TMSCl (Scheme 99).[155]

Scheme 99. Synthesis of trimethylsilyl acetic acid ethyl ester.



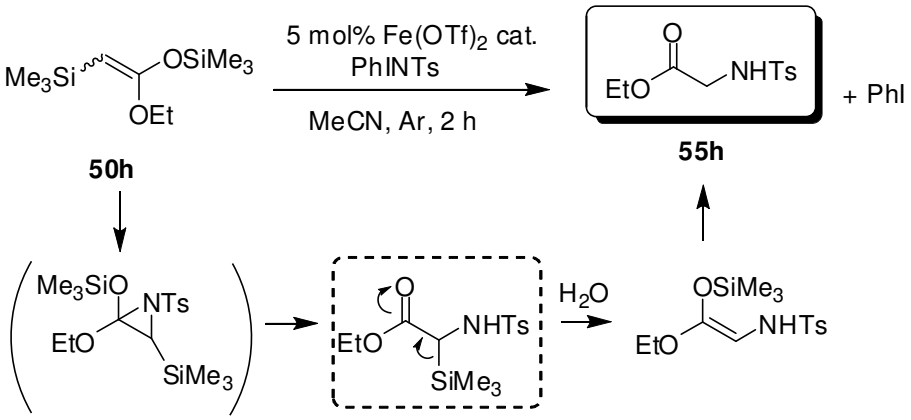
Furthermore, the silyl enol ether of α-silylacetate could be easily prepared in good yield (E : Z = 4 : 1) (Scheme 100).[156]

Scheme 100. Synthesis of trimethylsilyl acetic acid ethyl ester.



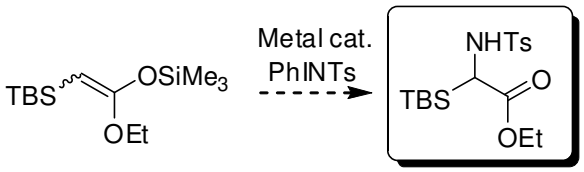
As a first trial, the synthesis of α-silaamino acid ester was examined by using the same reaction conditions as for the iron-catalyzed aziridination of silyl enol ethers. Unfortunately, instead of the α-sila amino acid ester, an α-amino acid ester was obtained in 13% yield. To explain this result, an elimination mechanism is proposed (Scheme 101).

Scheme 101. Plausible decomposition mechanism.



[155] G. Picotin, P. Miginiac, *J. Org. Chem.* **1987**, *52*, 4797.
[156] a) D. Hazelard, J. Ollivier, R. Paugam, J. Salaün, *Synlett* **2003**, 1155. b) I. Masuda, *J. Organomet. Chem.* **1987**, *321*, 307.

In another trial, a metal free reaction was tested at reflux in acetonitrile. However, α-amino acid ester **98** was obtained instead of an α-silaamino acid ester in this system as well. Probably, the desired α-trimethylsilyl amino acid ester is not stable. Only α-TBS substituted α-tosylamino acid esters have previously been prepared (Eq. 4).



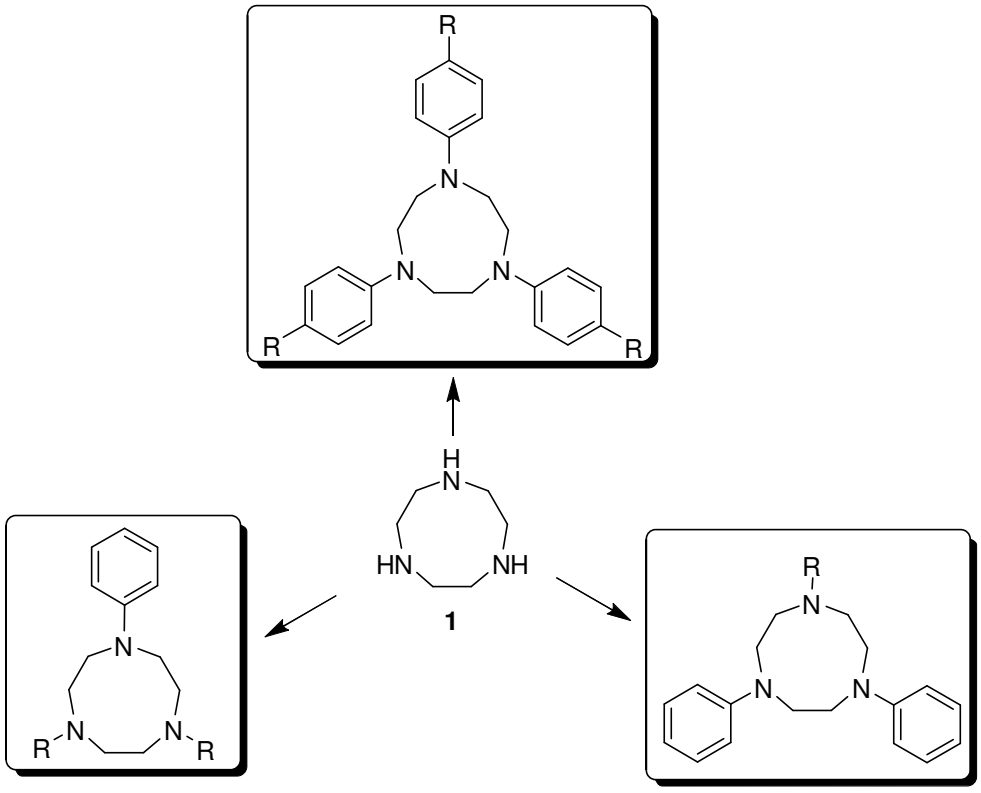
Eq. 4

Thus, the introduction of the more stable TBS group into the ketene acetal could be of interest for increasing the stability of the product.

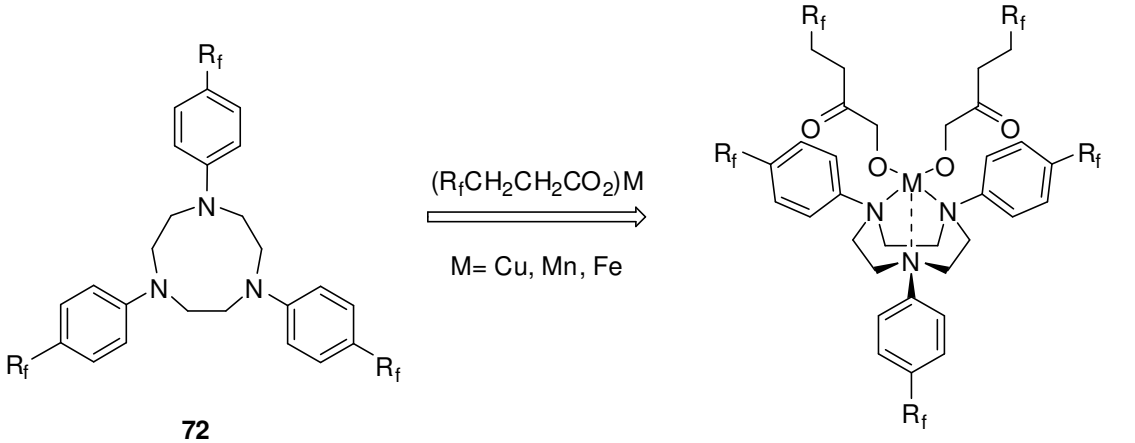
6 Summary and Outlook

In TACN chemistry, new modifications at the nitrogen atoms by palladium-catalyzed *N*-arylation have been developed. Also, deprotection of Cbz and Boc was succeefuly achieved. Thus a variety of aryl TACN derivatives can be synthesized by the developed procedure (Scheme 102).

Scheme 102. Summary of *N*-arylation of TACN **1**.

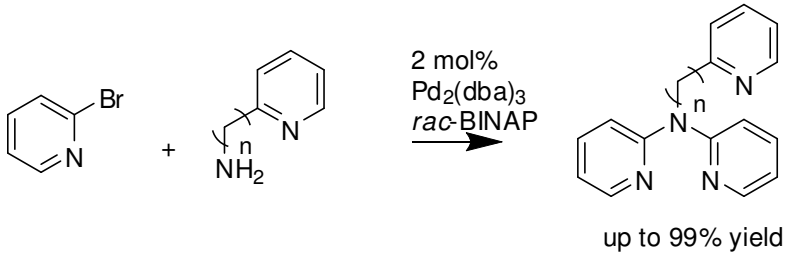


Furthermore, new chiral TACN ligands can be expected to be accessible using this protocol. Also, complexation of perfluorinated TACN ligand with copper(I) chloride was demonstrated and application of this complex in catalysis should be examined in the future.



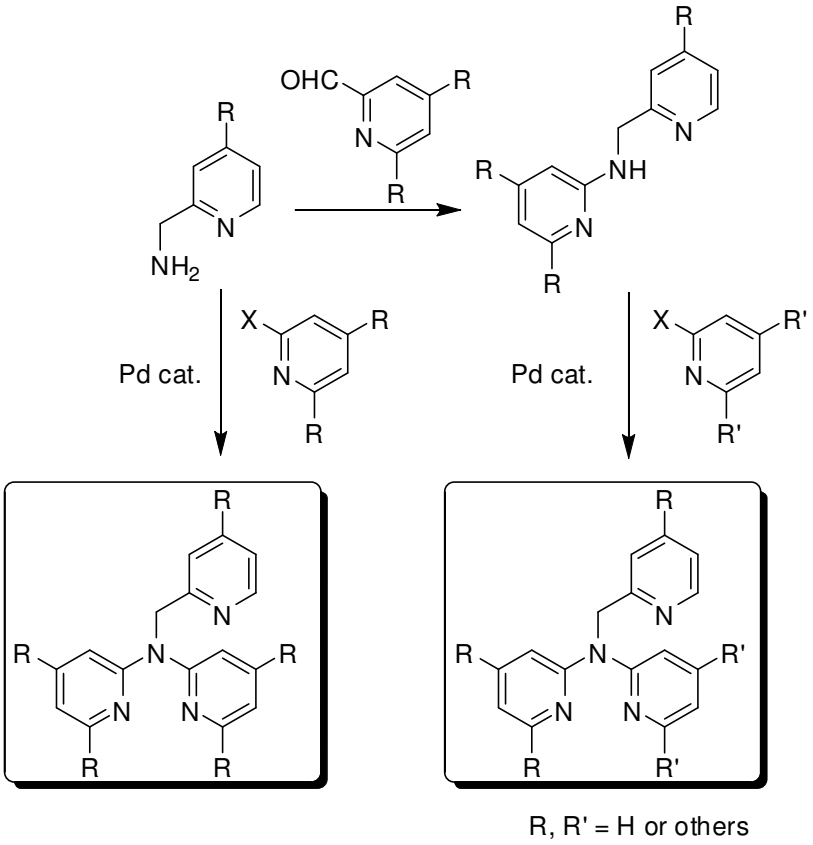
A synthesis of 2,2'-dipyridylamine type ligands has also been developed by using palladium catalysis (Scheme 103).

Scheme 103. Developed synthesis of dipyridylamine type ligands by palladium catalysis.



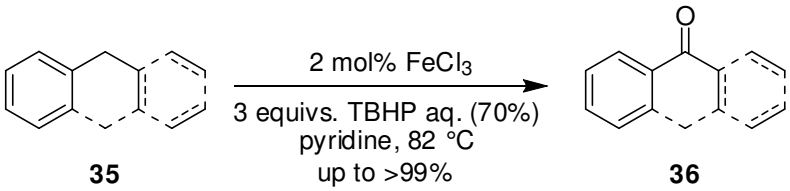
Also, the routes to access tertiary butyl substituted dipyridylamine type ligands are shown in Scheme 104. By using same conditions, dipyridylpicolylamines were obtained in high yield (up to 99% yield)

Scheme 104. Summary of synthetic approaches to dipyridylamine ligands.



In this thesis, the ability to coordinate dipyridylamines to iron and silver has been demonstrated. In the future applications for these ligands should be developed.
In this study, an iron-catalyzed benzylic oxidation was successfully developed (Scheme 105).

Scheme 105. Iron-catalyzed benzylic oxidation with TBHP.



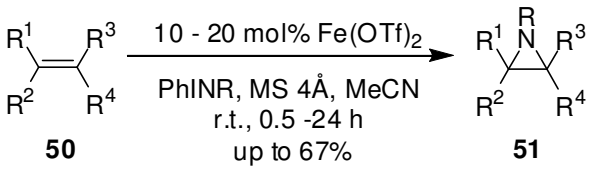
Most diarylmethylene derivatives gave the corresponding products in excellent yields (up to >99%). Also, one annelated aryl group in a cyclic system led to benzylic oxidation products in moderate to good yield. Noncyclic compounds bearing one (hetero)aryl group were oxidized in the benzylic position with moderate yields. Electron-donating substituents such as *p*-methoxy group on ethylbenzene and toluene are attributed to afford the corresponding ketone and carboxylic acid in 84% and 53% respectively. Even diphenylmethanol was oxidized to give benzophenone in 86% yield. 1,4-dihydroxynaphthaline underwent oxidation to give binaphthoquinone in high yield (82%) under mild conditions, which can be probably

applicable for the synthesis of Vitamin K analogues.[129] In this oxidation, triphenylmethane gave *tert*-butyl triphenyl peroxide in 91% yield instead of the corresponding alcohol.

Even though a cheap and low toxicity iron salt such as iron (III) trichloride was reactive enough to promote this benzylic oxidation, a better oxidant such a hydrogen peroxide is still required in place of TBHP. As a challenge that lies ahead, a much cleaner reaction which generates only water, for example, would be required for truly efficient iron-catalyzed oxidation chemistry.

In iron-catalyzed aziridination, the best result was obtained by using styrene as an olefin (up to 88% yield). However, the substrate scope is still limited. For example β-mono substituted styrene and cyclic aliphatic olefins gave aziridines in low yields, although yields were improved by increasing the amount of catalyst from 2.5 mol% to 10 mol% (31-67%) (Scheme 106.

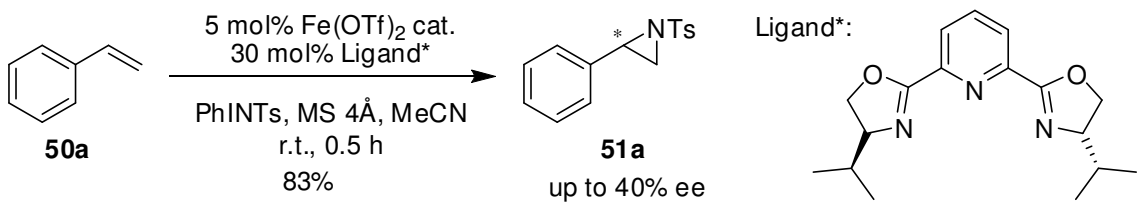
Scheme 106. Iron-catalyzed aziridination of olefins



Furthermore, in this system, an efficient ligand **99** was found which gave phenylaziridine **51a** in up to 94% yield.

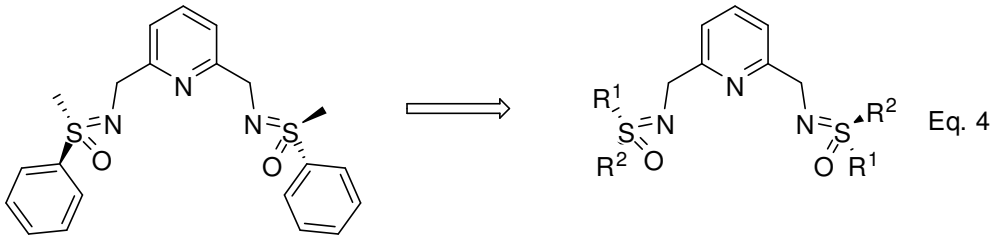
After testing a range of pybox type ligands, a chiral aziridine was obtained in low enantiomeric excess (up to 40% ee) although the yield was satisfactory (83%) (Scheme 107).

Scheme 107. Iron-catalyzed asymmetric aziridination of styrene.



In asymmetric aziridination, a further screening of ligands should be carried out in the furture. Also, to study the mechanism, the catalyst should be isolated and used in the reaction. The effect of substitution at the benzene ring has not been tested yet. Furthermore, the effect of counterions such as PF_6^-, BF_4^-, SbF_6^- and ClO_4^- should be studied in the future as they probably play a very important in the asymmetric induction.In general in iron chemistry, radical reactions are involved, therefore to obtain high chiral inductions in iron-catalyzed asymmetric reactions is challenging. However, the high potential and possibility of developing a selective process has been demonstrated in this thesis.

During the ligand screening, one tridentate pyridine sulfoximine pincer type ligand, which was synthesized by A. Correa, gave a chiral aziridine in 15% ee (Eq. 4).[157]



Eq. 4

As one candidate for an effective ligand, this type of ligand should be further studied. By modification of the functional groups on the sulfoximines, higher enantioselectivities can be expected. In conclusion, a more efficient iron-catalyzed aziridination of olefins has been developed in this study. Also, the most efficient iron-catalyzed asymmetric aziridination has been demonstrated. Firstly iron-catalyzed aziridination of styrene using iminophenyliodane, which was formed *in situ*, was successful. Additionally, using this system, aziridination of styrene with a sulfonimidamide gave the corresponding aziridine product. Finally, the application of these conditions for α-amination of silyl enol ethers was succesfull.

[157] Unpublished result.

7 Experimental Section

7.1 General Remarks

7.1.1 General Techniques

Air and moisture sensitive reactions were conducted under an inert atomosphere of argon using Schlenk techniques. All glass was flamed dried prior to use, then filled with argon.
The addition of liquid (reagents and solvents) was perfomed with a syringe through a septum or dropping funnel. Solids were added under gentle stream of argon. Solvents were removed under high vacuum for highly air sensitive compounds and on a rotary evaporator for air stable compounds at 30-40 ºC.

7.1.2 Solvents

Solvents for anhydrous reactions were dried and purified according to standard tequniques:

Chloroform:	Disstilled after reflux over phosphorus pentoxide under nitrogen
Dichlormethane:	Simple distillation, followed by reflux over calcium hydride under argon.
Diethylether:	Distilled after reflux over sodium under argon
Tetrahydrofuran:	Pre-drying over potassium hydroxide, passed through aluminium oxide, followed distillation after reflux over sodium under argon
Acetonitril	Purchased from Fluka or Acros ($H_2O \leq 0.001\%$)
Toluene:	Distilled after reflux over sodium under argon

7.1.3 Determination of the Physical Data

^{1}H-NMR-Spectroscopy:

Varian Gemini 300 (300 MHz), Varian Inova 400 (400 MHz), Varian Unity 500 (500 MHz) NMR Instruments were used. The chemical shift is given in ppm (parts per million) and is determined using tetramethylsilane (0.00 ppm) or the residual non-deutetrated solvent peaks

(chloroform 7.25 ppm; dimethylsulfoxide 2.50 ppm) as internal standard. The coupling constants are depicited in Hz and the multiplicity: s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet.

^{13}C-NMR-spectroscopy:

Varian Gemini 300 (75 MHz), Varian Inova 400 (100 MHz), Varian Unity 500 (125 MHz). The chemical shift is given in ppm (parts per million) and is determined using solvent ($CDCl_3$ 77.0 ppm; D_6-DMSO 39.5 ppm) as internal standard.

Melting Point

Melting points were measured in open glass cappilliaries with a Buechi B-540 apparatus and are uncorrected.

Infrared-Spectroscopy

IR spectra were measured on a Perkin-Elmer FT/IR 1760 FT spectrometer as KBr pellets or neat. Only characteristic absorption bands are reported. Absorptions are given in wave number (cm^{-1}).

Mass Spectroscopy:

Mass spectra were recorded on a Varian MAT 212 S and Finnigan MAT 95 Spectrometer with EI inonization at a 70eV ionization potential. Peaks are listed according to their elemental charge (*m*/*z*) value.

High Resolution Mass Spectroscopy (HRMS):

High resolution mass spectra were recorded on a *Finnigan* MAT 95 spectrometer

Elemental Analysis:

Elementat analyses were perfomed using a *Heraeus* CHNO-Rapid instrument.

7.1.4 Chromatographic Methods

Thin Layer Chromatography:

TLC-Plates Silica gel 60 F254 (Merck).

Detection:

1) UV-light (λ = 254nm).
2) color-producing reagent:
   a) treatment with acidic solution of molybdatophosphonic acid (6.25 g), cerium(IV)-sulfate tetrahydrate (2.50 g) and concentrated sulfric acid (15mL) in water (230 mL) followed by heating for a short time at ca. 200 °C.
   b) treatment with a basic solution of $KMnO_4$ (2 g) and K_2CO_3 (5 g) in Water (100 mL).
   c) treatment with a solution of ninhydrin in EtOH.
   d) I_2-SiO_2

Colum Chromatography:

Stationary Phase: Silica gel 60 (Merck), 43-60 μm diameter.
All column chromatography was performed under presure, using pentane / ethyl acetate or pentane / diethyl ether unless otherwise stated.

High Perfomance Liquid Chromatography (HPLC):

HPLC analysis was conducted using an Agilent 1100-series system (Degasser G13179A, UV-Detektor G1315B, Automatic sampler G1313A, Quanternary Pump G1311A, Column oven G1316A) with UV-Detecter, using chiral stationary phase columns from *Chiral Technologies Ltd.* (formerly *Daicel Chemical Industries Ltd*). (Length: 25 cm, ϕ: 0.46 cm).
All measurements were conducted at room temperature.

Gas Chromatography (GC):

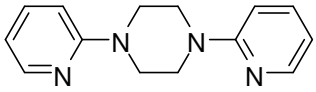
Hewlett Packard 5890 Series II-Gerät with Flame ionisation detector and HP-3396 integrator.

7.1.5 References for the Preparation of Known Compounds

terpyridine (**81a**),[46a] 4-*tert*-butypyridine-*N*-oxide, [158] (**83**), 2,6-bis(*N*-pyrazolyl)pyridine (**99**), [159] (*S*,*S*)-*i*-Pr-pybox (**96a**), [160] (*S*,*S*)-Ph-pybox (**96c**), [161] (*S*,*S*)-*t*-Bu-pybox (**96b**),[143] 2,3-dihydro-1H-inden-2-yl carbamate, [162] *N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide (**52e**),[88a] *N*-(pyridin-2-ylmethyl)pyridine-2-amine, [43b]

7.2 Synthesis of Aryl-TACN Derivatives by Palladium catalysis

7.2.1 *N*-Arylation of Piperazine:



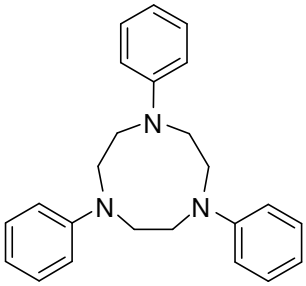
In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (18 mg, 0.02 mmol), *rac*-BINAP (26 mg, 0.04 mmol), 2-bromopyridine (4.2 mmol, 660 mg, 400 μL), piperazine (172.2 mg, 2 mmol) and sodium *tert*-butylate (424 mg, 4.4 mmol). After the addition of toluene (4 mL) the reaction mixture was heated at 70 ºC for 1 day. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : hexane = 1 : 1) affording 1,4-di(pyridin-2-yl)piperazine as a yellow solid in 50% yield (240 mg).

Analytical data for 1,4-di(pyridin-2-yl)piperazine: ^{1}H NMR (400 MHz): δ = 3.74 (s, 8H), 6.67-6.77 (m, 4H), 7.52-7.59 (m, 2H), 8.25-8.28 (m, 2H). ^{13}C NMR (75 MHz): δ = 159.5, 148.0, 137.6, 113.5, 107.2, 45.0.

Analytical data of 1,4-di(pyridin-2-yl)piperazine were consistent with that in the literature.[163]

[158] Z. R. Bell, G. R. Motson, J. C. Jeffery, J. A. McCleverty, M. D. Ward, **2001**, *20*, 2045.
[159] J. Houben, E. Schmidt, *Chem. Ber.* **1913**, *46*, 3616.
[160] J. H. Youn, R. Herrmann, *Tetrahedron Lett.* **1986**, *27*, 1493.
[161] Y. Tamura, K. Sumoto, J. Minamikawa, S. Fuji, M. Ikeda, *Tetrahedron Lett.* **1973**, *38*, 1239.
[162] A. R. A. S. Deshmukh, V. K. Gumaste, US Patent, 20050065361 A1.
[163] E. Brenner, R. Schneider, Y. Fort, *Tetrahedron* **2002**, *58*, 6913.

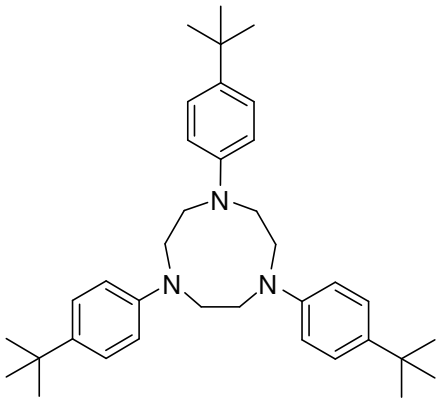
7.2.2 Representative Procedure (RP 1) for Synthesis of 1,4,7-Triphenyl TACN 58a:



In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (46 mg, 0.05 mmol), 2-dicyclohexylphosphino-2'-(*N*,*N*-dimethylamino)biphenyl (**66**, 60 mg, 0.15 mmol), bromobenzene (1.5 mmol, 239 mg, 150 μL), TACN **1** (65 mg, 0.5 mmol) and sodium *tert*-butylate (202 mg, 2.1 mmol). After the addition of toluene (4 mL) the reaction mixture was heated at 100 ºC for 1 day. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through Celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 10) affording triarylated TACN **63a** as a white solid in 71% yield (127 mg).

Analytical data for **63a**: m.p 199-201 ºC, ^{1}H NMR (400 MHz): δ = 3.59 (s, 12H), 6.57 (d, *J* = 8.4 Hz, 6H), 6.69 (t, *J* = 7.2 Hz, 3H), 7.20 (dd, *J* = 8.4, 7.2 Hz, 6H). ^{13}C NMR (75 MHz): δ = 147.8, 129.3, 116.4, 112.5, 51.2. MS (EI, 70 eV): *m/z* (%) = 425 (M^+); IR (KBr): υ = 2956, 2852, 1594, 1499, 1357, 1185, 745, 693 cm^{-1}; anal. calcd. for $C_{24}H_{27}N_3$ (357.49): C 80.63, H 7.61, N 11.75; found: C 80.33, H 7.47, N 11.57.

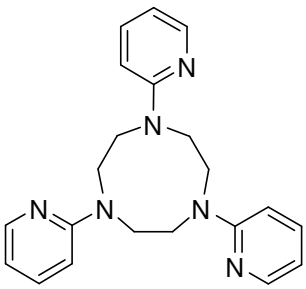
7.2.3 Synthesis of Triarylated TACN 63b:



Following RP1 using 4-*tert*-butyl-bromobenzene (1.5 mmol, 320 mg, 262 μL) instead of bromobenzene afforded [after 2 h at 100 °C; column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 10)] triarylated TACN **63b** as a white solid in 73% yield (191 mg).

Analytical data for **63b**: m.p 185-186 ºC, ^{1}H NMR (400 MHz): δ = 1.29 (s, 27H), 3.57 (s, 12H), 6.49 (d, *J* = 8.5 Hz, 6H), 7.16 (d, *J* = 8.5 Hz, 6H). ^{13}C NMR (75 MHz): δ = 145.4, 138.6, 125.7, 112.0, 51.4, 33.6, 31.5. MS (EI, 70 eV): *m/z* (%) = 525 (M^+); IR (KBr): υ = 2959, 2862, 1613, 1519, 814 cm^{-1}; anal. calcd. for $C_{36}H_{51}N_3$ (525.81): C 82.23, H 9.78, N 7.99; found: C 82.05, H 9.53, N 8.12.

7.2.4 Synthesis of Triarylated TACN 63d:

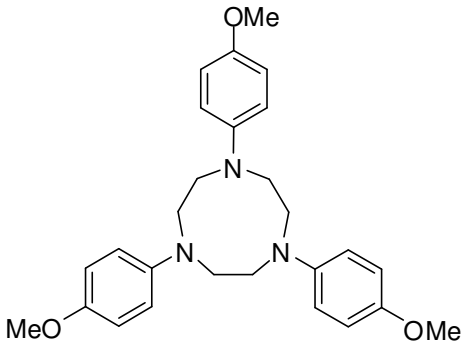


Following RP1 using 2-bromopyridine (1.5 mmol, 237 mg, 150 μL) instead of bromobenzene afforded [after 1 day at 100 °C; column chromatography (silica gel; eluent = ethyl acetate : pentane = 2 : 3)] triarylated TACN **63d** as a white solid in 52% yield (94 mg).

Analytical data for **63d**: m.p 144-145 ºC, ^{1}H NMR (400 MHz): δ = 3.77 (s, 12H), 6.32 (d, *J* = 8.8 Hz, 3H), 6.53 (dd, *J* = 6.9, 4.9 Hz, 3H), 7.32 (ddd, *J* = 8.8, 6.9, 2.2 Hz, 3H), 8.15 (ddd, *J* =

6.9, 4.9, 2.2 Hz, 3H). ^{13}C NMR (75 MHz): δ = 158.0, 147.4, 136.9, 111.6, 106.6, 50.4. MS (EI, 70 eV): *m/z* (%) = 361 (M^+); IR (KBr): υ = 2899, 2853, 1597, 1493, 1362, 766, 733 cm^{-1}; HRMS calcd. for $C_{21}H_{24}N_6$ 360.2063, found 360.2062.

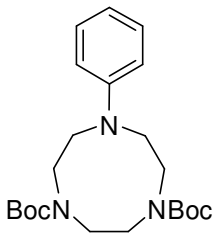
7.2.5 Synthesis of Triarylated TACN 63c:



Following RP1 using 4-bromoanisol (1.5 mmol, 280 mg, 192 μL) instead of bromobenzene afforded [after 1 day at 90 °C; column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 20)] triarylated TACN **63c** as a white solid in 45% yield (100 mg).

Analytical data for **63c**: m.p 180 ºC, ^{1}H NMR (400 MHz): δ = 3.52 (s, 12H), 3.76 (s, 9H), 6.53 (brd, 6H), 6.78 (d, *J* = 8.5 Hz, 6H). ^{13}C NMR (75 MHz): δ = 150.4, 142.4, 114.8, 113.3, 55.7, 51.6. MS (EI, 70 eV): *m/z* (%) = 447 (M^+); IR (KBr): υ = 2955, 2832, 1599, 1458, 1243, 1039, 813, 662 cm^{-1}; anal. calcd. for $C_{27}H_{33}N_3O_3$ (447.57): C 72.46, H 7.43, N 9.39; found: C 72.57, H 7.26, N 9.06.

7.2.6 Synthesis of mono-arylated di(Boc) TACN 60b:

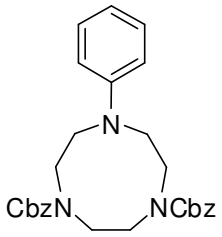


Following RP1 using $Pd(OAc)_2$ (9 mg, 0.04 mmol), *rac*-BINAP (25 mg, 0.04 mmol), bromobenzene (0.7 mmol, 110 mg, 74 μL), di(Boc) TACN **16** (82.5 mg, 0.25 mmol), sodium

tert-butylate (67 mg, 0.7 mmol) and toluene (5 mL). For the work-up the reaction mixture was diluted with ethyl acetate (5 mL), filtered through Celite, and the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 2 : 3) affording monoarylated di(Boc) TACN **60b** as an oil in 85% yield (86 mg).

Analytical data for **60b** (as a mixture of rotamers): Oil, ^{1}H NMR (400 MHz): δ = 1.34 (s, 4.5H), 1.38 (s, 4.5H), 1.48 (s, 4.5H), 1.49 (s, 4.5H), 3.42-3.69 (m, 12H), 6.64-6.76 (m, 3H), 7.15-7.24 (m, 2H). ^{13}C NMR (75 MHz): δ = 155.8, 155.7, 155.5, 148.4, 148.1, 147.9, 129.2, 116.6, 112.9, 112.5, 80.1, 80.0, 79.9, 79.8, 53.0, 52.7, 52.4, 51.5, 50.6, 49.8, 49.7, 49.6, 49.4, 48.5, 47.8, 28.6, 28.5, 28.4. MS (EI, 70 eV): *m/z* (%) = 405 (M^+); IR ($CHCl_3$): υ = 2976, 2927, 2358, 1687, 1599, 1503, 1467, 1409, 1364, 1243, 1169, 757 cm^{-1}; HRMS calcd. for $C_{22}H_{35}N_3O_4$ 405.2629, found 405.2628.

7.2.7 Synthesis of monoarylated di(Cbz) TACN 60c:

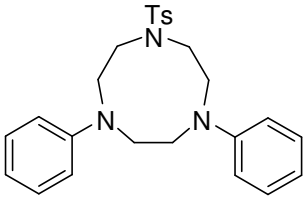


Following RP1 using $Pd(OAc)_2$ (9 mg, 0.04 mmol), *rac*-BINAP (25 mg, 0.04 mmol), bromobenzene (0.7 mmol, 110 mg, 74 μL), di(Cbz)TACN **56** (99.6 mg, 0.25 mmol), sodium *tert*-butylate (67 mg, 0.7 mmol) and toluene (5 mL). For the work-up the reaction mixture was diluted with ethyl acetate (5 mL), filtered through celite, and the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetete : pentane = 3 : 2) affording monoarylated di(Cbz) TACN **60c** in 70% yield (83 mg).

Analytical data for **60c** (as a mixture of rotamers): Oil, ^{1}H NMR (400 MHz): δ = 3.32-3.41 (m, 4H), 3.41-3.57 (m, 8H), 4.92 (s, 1H), 4.95 (s, 1H), 4.98 (s, 1H), 5.08 (s, 1H), 6.50-6.72 (m, 3H), 7.02-7.36 (m, 12H). ^{13}C NMR (75 MHz): δ = 156.9, 156.3, 136.6, 129.5, 129.4, 128.5, 128.1, 128.0, 117.3, 112.9, 112.6, 80.0, 67.4, 67.2, 53.4, 53.2, 52.9, 50.0, 49.5, 48.9, 48.5,

47.6; MS (EI, 70 eV): *m/z* (%) = 473 (M^+); IR ($CHCl_3$): υ = 2930, 2335, 1699, 1599, 1503, 1469, 1419, 1362, 1230, 1124, 991, 750, 697 cm^{-1}; HRMS calcd. for $C_{28}H_{31}N_3O_4$ 473.2316, found 473.2315.

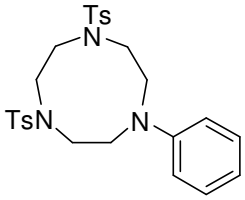
7.2.8 Synthesis of diarylated monotosyl TACN 61:



Following RP1 using bromobenzene (2.0 mmol, 313 mg, 210 μL), monotosyl TACN **56** (283 mg, 1.0 mmol) and sodium *tert*-butylate (269 mg, 2.8 mmol) afforded [after 2 h at 100 °C; column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 5)] diarylated TACN **6** in 70% yield (305 mg).

Analytical data for **6**: m.p 176-177 ºC, ^{1}H NMR (400 MHz): δ = 2.40 (s, 3H), 3.20-3.26 (m, 4H), 3.62-3.68 (m, 4H), 3.63 (s, 4H), 6.74 (t, *J* = 7.2 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 2H), 7.24 (dd, *J* = 8.7, 7.2 Hz, 4H), 7.28 (d, *J* = 8.7 Hz, 4H), 7.65 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (75 MHz): δ = 147.5, 143.5, 134.9, 129.8, 129.4, 127.4, 117.0, 112.6, 53.5, 51.7, 49.1, 21.5. MS (EI, 70 eV): *m/z* (%) = 435 (M^+); IR (KBr): υ = 2963, 2873, 1595, 1502, 1332, 1157, 745, 697 cm^{-1}; anal. calcd. for $C_{25}H_{29}N_3O_2S$ (438.58): C 68.93, H 6.71, N 9.65; found: C 69.09, H 6.76, N 9.66.

7.2.9 Synthesis of monoarylated di(Ts) TACN 61:

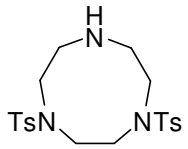


Following RP1 using $Pd(OAc)_2$ (1.8 mg, 0.008 mmol), *rac*-BINAP (5 mg, 0.008 mmol), bromobenzene (0.21 mmol, 33 mg, 20 μL), di(Ts) TACN **57** (44 mg, 0.1 mmol) and sodium *tert*-butylate (155 mg, 2.1 mmol). After the addition of toluene (2 mL) the reaction mixture

was heated at 90 ºC for 1 day. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (4 mL). After filtration through Celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 2 : 1) affording monoarylated ditosyl TACN **61** in quantitative yield (52 mg).

Analytical data for **61**: M.p 155-156 ºC, ^{1}H NMR (400 MHz): δ = 2.52 (s, 6H), 3.25 (s, 4H), 3.27 (t, *J* = 4.4 Hz, 4H), 3.63 (t, *J* = 4.4 Hz, 4H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 7.14 (dd, *J* = 8.0, 7.4 Hz 2H), 7.25 (d, *J* = 8.2 HZ, 4H), 7.63 (d, *J* = 8.2 Hz, 4H). ^{13}C NMR (75 MHz): δ = 147.2, 143.7, 134.7, 129.8, 129.4, 127.4, 117.3, 112.8, 53.8, 52.3, 49.3, 21.7. MS (EI, 70 eV): m/z (%) = 435 (M^+); IR (KBr): υ = 2925, 2868, 1599, 1507, 1337, 1157, 747, 692 cm^{-1}; HRMS calcd. for $C_{26}H_{31}N_3O_4S_2$ 513.1756, found 513.1756.

7.2.10 Synthesis of di(Ts) TACN 57:

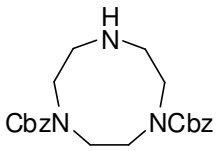


A solution of tosyl chloride (167 mg, 0.85 mmol) in diethyl ether (10 mL) was added into a suspension solution of 7.5 N-NaOH aq. (10 mL) and mono(Ts) TACN **56** (0.25 g, 0.85 mmol). After stirred at ambient temperature for 3 hours, the solvent was evaporated (rotary evaporator). The resulting white solid was taken up in chloroform and the organic phase was washed with water and dried over Na_2SO_4. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was recrystallized from ethanol (c.a. 20 mL) affording di(Ts) TACN **57** in 96% yield (360 mg).

Analytical data for **57**: ^{1}H NMR (400 MHz): δ = 2.44 (s, 6H), 3.20 (s, 8H), 3.27 (s, 4H), 7.33 (d, *J* = 8.5 HZ, 4H), 7.68 (d, *J* = 8.5 Hz, 4H). ^{13}C NMR (75 MHz): δ = 143.9, 135.1, 129.9, 127.2, 53.9, 53.1, 49.0, 21.5.

Analytical data of di(Ts) TACN **57** were consistent with that reported in the literature.[114]

7.2.11 Synthesis of di(Cbz) TACN 52:

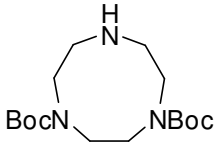


Cbz-ON (1.121 g, 4 mmol) was added to a solution of TACN **1** (258 mg, 2 mmol) in chloroform (20 mL). After stirring at ambient temperature overnight, the solvent was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate then $CHCl_3$: MeOH = 10 : 1) affording di(Cbz) TACN **52** in 78% yield (617 mg).

Analytical data for **52** (as a mixture of rotamers): ^{1}H NMR (400 MHz): δ = 2.80-2.94 (m, 4H), 3.24-3.31 (m, 4H), 3.51-3.60 (m, 4H), 5.10-5.17 (s, 1H), 7.28-7.37 (m, 10H). ^{13}C NMR (75 MHz): δ = 156.2, 136.7, 136.7, 128.4, 128.2, 67.0, 52.7, 52.4, 52.0, 51.0, 50.1, 49.8, 49.0, 48.2, 48.1, 47.6, 47.5.

Analytical data of di(Cbz) TACN **52** were consistent with that reported in the literature.[113]

7.2.12 Synthesis of di(Boc) TACN 16:



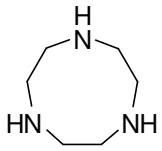
Boc-ON (986 mg, 4 mmol) was added to a solution of TACN **1** (334 mg, 1.7 mmol) in chloroform (20 mL). After stirring at ambient temperature for 3 hours, the solvent was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 10 then $CHCl_3$: MeOH = 9 : 1) affording di(Boc) TACN **16** in 76% yield (605 mg).

Analytical data for **16** (as a mixture of rotamers): ^{1}H NMR (400 MHz): δ = 1.34 (s, 4.5H), 1.38 (s, 4.5H), 1.48 (s, 4.5H), 1.49 (s, 4.5H), 3.42-3.69 (m, 12H), 6.64-6.76 (m, 3H), 7.15-7.24 (m, 2H). ^{13}C NMR (75 MHz): δ = 155.8, 155.7, 155.5, 148.4, 148.1, 147.9, 129.2, 116.6,

112.9, 112.5, 80.1, 80.0, 79.9, 79.8, 53.0, 52.7, 52.4, 51.5, 50.6, 49.8, 49.7, 49.6, 49.4, 48.5, 47.8, 28.6, 28.5, 28.4.

Analytical data of di(Boc) TACN **16** were consistent with that reported in the literature.[36]

7.2.13 Synthesis of TACN 1:

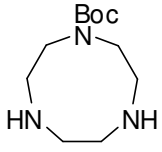


Tritosyl-TACN **3** (5.60 g, 9.8 mmol) was disolved in conc. H_2SO_4 (30 mL) at 90 ˚C and stirred for 3 days. The reaction mixture was cooled with an ice bath and EtOH/Et_2O (100 mL/100 mL) was added. A precipitate was collected by decantation and washed with EtOH/Et_2O (1 : 1). The resulting gray solid was dissolved in 5 N-NaOH aq. (20 mL) and stirred for 1 day. The reaction mixture was extracted with chloroform and dried over Na_2SO_4. The filtrate was evaporated and dried in vacuo affording TACN **1** in 90% yield (1.14 g).

Analytical data for TACN **1**: ^{1}H NMR (400 MHz): δ = 2.08 (brd, 3H), 2.84 (s, 12H). ^{13}C NMR (75 MHz): δ = 47.4.

Analytical data of TACN **1** were consistent with that reported in the literature.[12]

7.2.14 Synthesis of mono(Boc) TACN 55:



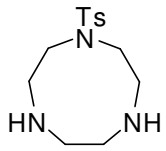
Prepared by analogy to **55**. Pd/C (300 mg) in EtOH (20 mL) was added to the di(Cbz)-mono(Boc)- TACN (0.5 g, 1.7 mmol) in EtOH. After stirring at ambient temperature under H_2

for 3 hours, the solvent was filtered and the filtrate was evaporated (rotary evaporator) affording mono(Boc) TACN **55** in 90% yield (680 mg).

Analytical data for mono(Boc) TACN **55**: ^{1}H NMR (400 MHz): δ = 1.49-1.51 (m, 9H), 2.70-3.81 (m, 12H). ^{13}C NMR (75 MHz): δ = 155.5, 79.2, 54.6, 54.3, 49.2, 48.2, 47.7, 47.3, 28.4.

Analytical data of mono(Boc) TACN **55** were consistent with that reported in the literature.[113]

7.2.15 Synthesis of mono(Ts) TACN 56:

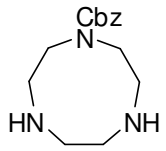


Phenol (23.16 g, 1.7 mmol) was added to a solution of HBr (33% in acetic acid) (300 mL) and tritosyl-TACN **3** (19.57 g, 3.28 mmol). After stirring at 90˚C for 36 hours a white solid precipitated. The White solid was isolated by filtration and washed with diethyl ether. The solid was dissolved in 1N-NaOH aq. to adjust pH to be >12. The mixture was extracted with chloroform and dried over $MgSO_4$ and the filtrate was evaporated affording mono(Ts) TACN **56** in 84% yield (7.9 g).

Analytical data for **56**: ^{1}H NMR (400 MHz): δ = 2.43 (s, 3H), 2.93 (s, 4H), 3.09-3.14 (m, 4H), 3.18-3.24 (m, 4H), 7.28-7.34 (m, 2H), 7.66-7.71 (m, 2H). ^{13}C NMR (75 MHz): δ = 143.4, 135.5, 129.7, 127.3, 54.0, 49.5, 49.4, 21.5,

Analytical data of mono(Ts) TACN **56** were consistent with that reported in the literature.[112]

7.2.16 Synthesis of mono(Cbz) TACN 54:

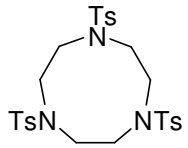


Prepared by analogy to **54** using a solution of TFA (112 μL, 1.7 mmol) which was added to a solution of mono(Cbz)-di(Boc)-TACN (315 mg, 0.68 mmol) in chloroform (10 mL). After stirring at ambient temperature for 3 hours, the solvent was evaporated (rotary evaporator) affording mono(Cbz) TACN **54** in 34% yield (60 mg).

Analytical data for **54**: ^{1}H NMR (400 MHz): δ = 2.52 (s, 6H), 3.25 (s, 4H), 3.27 (t, *J* = 4.4 Hz, 4H), 3.63 (t, *J* = 4.4 Hz, 4H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 2H), 7.14 (dd, *J* = 8.0, 7.4 Hz 2H), 7.25 (d, *J* = 8.2 HZ, 4H), 7.63 (d, *J* = 8.2 Hz, 4H). ^{13}C NMR (75 MHz): δ = 156.1, 136.84, 128.3, 127.8, 66.8, 54.9, 53.9, 49.3, 49.2, 48.3, 47.3.

Analytical data of mono(Cbz) TACN **54** were consistent with that reported in the literature.[122]

7.2.17 Synthesis of tri(Ts)-TACN 3:

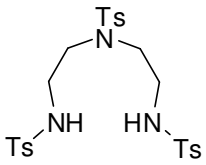


N,*N*,*N*-Tritosyldiethylene triamine **2** (6.5 g, 27.8 mmol) was dissolved in dry DMF and NaH (60%) (2.34 g, 58.4 mol). After stirring at 90 ˚C for 2 hours, 1,2-ditosylethyleneglycol (10.3 g, 27.8 mmol) was added at room temperature. After stirring at 100 ˚C for 2 hours, the reaction mixture was cooled down to room temperature and poured into the water (500 mL). The precipitate was collected and washed with water then diethyl ether affording tri(Ts) TACN **3** in 90% yield (15 g)

Analytical data for **3**: ^{1}H NMR (400 MHz): δ = 2.37 (s, 9H), 3.35 (s, 12H), 7.23 (d, *J* = 8.1 Hz, 6H), 7.63 (d, *J* = 8.1 Hz, 6H). ^{13}C NMR (75 MHz): δ = 143.9, 134.6, 130.0, 127.5, 117.3, 112.8, 52.0, 21.7.

Analytical data of tri-tosyl-TACN **3** were consistent with that reported in the literature.[12]

7.2.18 Synthesis of *N*, *N*, *N*-Tritosyl-diethylene triamine 2:

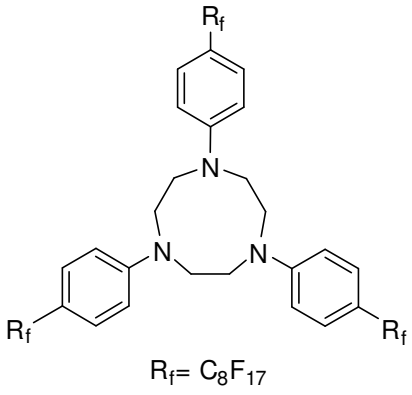


Diethylene triamine (5 mL, 46.5 mmol) was disolved in 300 mL of dichloromethane. After addition of triethylamine (40 mL, 213 mmol), *p*-toluenesulfonyl chloride was added slowly to the reaction mixture at room temperature over night. For the work-up the reaction mixture was poured into the water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and the filtrate was evaporated (rotary evaporator). The remaining mixture was triturated with diethyl ether affording *N*,*N*,*N*-tritosyldiethylene triamine **2** in 83% yield (22 g) as a white solid.

Analytical data for **2**: ^{1}H NMR (400 MHz): δ = 2.43 (s, 9H), 3.25 (s, 4H), 3.27 (t, *J* = 4.4 Hz, 4H), 3.63 (t, *J* = 4.4 Hz, 4H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.72 (d, J = 8.0 Hz, 2H), 7.14 (dd, *J* = 8.0, 7.4 Hz 2H), 7.25 (d, *J* = 8.2 HZ, 4H), 7.63 (d, *J* = 8.2 Hz, 4H). ^{13}C NMR (75 MHz): δ = 147.2, 143.7, 134.7, 129.8, 129.4, 127.4, 117.3, 112.8, 53.8, 52.3, 49.3, 21.7.

Analytical data of *N*,*N*,*N*-tritosyldiethylene triamine **2** were consistent with that reported in the literature.[164]

7.2.19 Synthesis of Perfluoroponytailed-triaryl-TACN 68:



Prepared in analogy to **68** using [$Pd_2(dba)_3$] (23 mg, 0.04 mmol), 2-dicyclohexylphosphino-2'-(*N*,*N*-dimethylamino)biphenyl (**66**, 30 mg, 0.76 mmol), *p*-perfluoroalkyl-bromobenzene

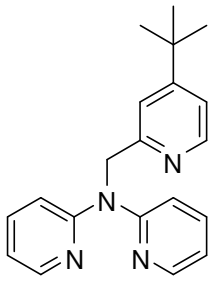
[164] G. R. Newkome, S. Pappalardo, V. K. Gupta, F. R. Fronczek, *J. Org. Chem*. **1983**, *48*, 4848.

(0.75 mmol, 431.3 mg), TACN **1** (32.5 mg, 0.25 mmol), sodium *tert*-butylate (101 mg, 1.05 mmol) and trifluoromethybenzene (10 mL). For the work-up the reaction mixture was diluted with ethyl acetate (10 mL), filtered through celite, and the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 10 : 1) affording perfluoroponytailed-triaryl-TACN **68** in 56% yield (227 mg) as a white solid.

Analytical data for **68**: m.p 80- 83 ºC, ^{1}H NMR (400 MHz): δ = 3.64 (s, 12H), 6.71-6.78 (m, 6H), 6.93 (d, *J* = 7.8 Hz, 3H), 7.29 (d, *J* = 7.8 Hz, 3H). FAB-MS (EI, 70 eV): *m/z* (%) = 1609 (M-2H$^+$). IR (KBr): υ = 2860, 2360, 1696, 1650, 1509, 1458, 1417, 1366, 1212, 1148, 667 cm^{-1}.

7.3 Synthesis of *N*-(pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine derivatives

7.3.1 Representative Procedure 2 for Synthesis of *N*-[(4-*tert*-Butylpyridin-2-yl)methyl]-*N*-(pyridin-2-yl)pyridin-2-amine (91):

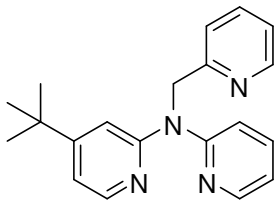


In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (9 mg, 0.01 mmol), *rac*-BINAP (13 mg, 0.02 mmol), 2-bromopyridine (2.2 mmol, 1.32 g, 215 μL), *N*-2-pyridyl-2-picolylamine (1 mmol, 224.3 mg) and sodium *tert*-butylate (318 mg, 3.3 mmol), tetrabutylammmonium bromide (644 mg, 2 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 100 ºC for 1 d. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate) affording *N*,*N*-

dipyridylaminopicoline **91** in 97% yield (310 mg). A single crystal for X-ray analysis was obtained from diethyl ether / pentane (chapter 8.1.2).

Analytical data for **91**: m.p 101-102 ºC, ^{1}H NMR (400 MHz): δ = 1.15 (s, 9H), 5.57 (s, 9H), 6.82-6.89 (m, 2H), 7.06-7.10 (m, 1H), 7.23-7.25 (m, 1H), 7.25-7.27 (m, 1H), 7.28-7.30 (m, 1H), 7.50-7.57 (m, 3H), 8.28-8.33 (m, 1H), 8.41-8.44 (m, 1H). ^{13}C NMR (75 MHz): δ = 160.1, 156.7, 156.9, 148.7, 148.0, 137.0, 118.6, 118.3, 117.0, 114.4, 53.6, 34.5, 30.4. MS (EI, 70 eV): *m/z* (%) = 318 (M^+); IR (KBr): υ = 2959, 1159, 1468, 1417, 976, 772 cm^{-1}.

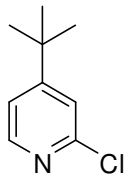
7.3.2 Synthesis of 4-*tert*-Butyl-*N*-(pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine (88):



In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (9.2 mg, 0.01 mmol), *rac*-BINAP (12.4 mg, 0.02 mmol), 4-*tert*-butyl-2-chloropyridine (1.1 mmol, 1.32 g, 800 μL), *N*-pyridyl-2-picolylamine (1 mmol, 185 mg) and sodium *tert*-butylate (144 mg, 1.5 mmol), tetrabutylammmonium bromide (322 mg, 1 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 100 ºC for 1 d. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through Celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 1) affording *N*,*N*-dipyridylaminopicoline **88** in 28% yield (89 mg). A single crystal for X-ray analysis was obtained from diethylether / pentane (chapter 8.1.3).

Analytical data for **88**: m.p 80 ºC, ^{1}H NMR (400 MHz): δ = 1.24 (s, 9H), 5.59 (s, 2H), 6.80-6.90 (m, 1H), 6.88-6.92 (m, 1H), 7.06-7.12 (m, 1H), 7.20-7.25 (m, 1H), 7.31-7.37 (m, 1H), 7.47-7.57 (m, 2H), 8.21-8.25 (m, 1H), 8.27-8.31 (m, 1H), 8.51-8.56 (m, 1H). ^{13}C NMR (75 MHz): δ = 161.5, 159.8, 157.2, 157.1, 156.5, 149.0, 148.2, 148.0, 137.1, 136.5, 121.6, 121.4, 116.8, 115.4, 114.0, 112.1, 53.8, 34.8, 30.5. MS (EI, 70 eV): *m/z* (%) = 318 (M^+); IR (KBr): υ = 2956, 2852, 1594, 1499, 1357, 1185, 745, 693 cm^{-1}.

7.3.3 Synthesis of 4-*tert*-Butyl-2-chloropyridine 81:

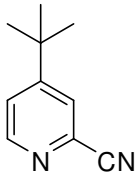


4-*tert*-Butylpyridine-1-oxide (**80**) (4.9 g, 32 mmol) was dissolved in $POCl_3$ (60 mL, 64 mmol) and refluxed under argon for 3 hours. The reaction mixture was allowed to cool down to room temperature and evaporated. The residure was then neutralized by 10% NaOH $_{(aq)}$. The mixture was then extracted with dichloromethane and dried over $MgSO_4$. After filtration, the remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 4) affording 4-*tert*-butyl-2-chloropyridine (**81**) in 78% yield (4.22 g).

Analytical data for **81**: ^{1}H NMR (400 MHz): δ = 1.31 (s, 9H), 7.29-7.31 (m, 1H), 7.21 (d, J = 5.3 Hz 1H), 8.28 (d, J = 5.3 Hz 1H). ^{13}C NMR (75 MHz): δ = 163.5, 151.7, 149.3, 121.3, 119.7, 34.8, 30.5.

Analytical data for 4-*tert*-butyl-2-chloropyridine (**81**) were consistent with that reported in the literature.[165]

7.3.4 Synthesis of 4-*tert*-butylpicolinonitrile 86:



4-*tert*-butylpyridine-1-oxide (**84**) (6.128 g, 40 mmol) was dissolved in dichloromethane (50 mL) and added to trimethylsilyl cyanide (6.23 g, 63 mmol) at room temperature. Dimethylcarbamoyl chloride (5.8 mL, 63 mmol) in dichloromethane (13 mL) was added dropwise with stirring to the reaction mixture over 30 minutes period. The reaction mixture

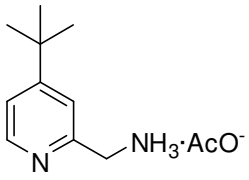
[165]a) C. Barolo, M. K. Nazeerruddin, S. Fantacci, D. D. Censo, P. Comte, P. Liska, G. Viscardi, P. Quagliotto, F. D. Angelis, S. Ito, M. Gräzel, *Inorg. Chem.* **2006**, *45*, 4642. b) C. X. Zhang, S. Kaderli, M. Costas, E.-I. Kim, Y.-M. Neuhold, K. D. Karlin, A. D. Zuberbuhler, *Inorg. Chem.* **2003**, *42*, 1807.

was stirred for 24 hours. A solution of 10% K_2CO_3 aq. (50 mL) was added dropwise, and stirred for 10 minutes. The organic layer was separated and aqueous layer was extracted two times with dichloromethane. The organic layer was dried over $MgSO_4$. After filtration, the remaining mixture evaporated *in vacuo* affording 4-*tert*-butylpicolino-2-nitrile (**86**) in 91% yield (5.83 g).

Analytical data for **86**: ^{1}H NMR (400 MHz): δ = 1.35 (s, 9H), 7.46-7.51 (m, 1H), 7.69-7.70 (m, 1H), 8.61-8.62 (m, 1H). ^{13}C NMR (75 MHz): δ = 161.5, 150.7 133.7, 125.8, 123.8, 117.4, 35.0, 30.2.

Analytical data for 4-*tert*-butylpicolino-2-nitrile (**86**) were consistent with that reported in the literature.[166]

7.3.5 Synthesis of (4-*tert*-Butylpyridin-2-yl)methanamine 87:



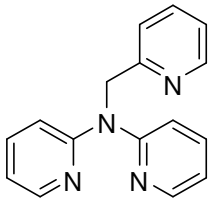
4-*tert*-butylpicolinonitrile (5.83 g, 26 mmol) was dissolved in acetic acid (300 mL) and stirred with Pd/C (1 g) under hydrogene at room temperature. The reaction mixture was filtrated and evaporated. After filtration, the remaining mixture was separated by column chromatography (almina (basic); eluent = ethyl acetate : pentane = 1 : 1) affording (4-*tert*-butylpyridin-2-yl)methanamine **87** acetic acid salt in quantitative yield.

Analytical data for **87**: ^{1}H NMR (400 MHz): δ=1.31 (s, 9H), 1.97 (s, 3H), 4.07 (s, 2H), 6.65 (s, 3H) 7.18-7.22 (m, 1H), 7.26 (s, 1H), 8.44-8.47 (m, 1H). ^{13}C NMR (75 MHz): δ = 176.1, 148.8, 115.4, 119.7, 118.8, 45.8, 34.9, 30.6, 22.3.

Analytical data of *N*-(pyridine-2-yl)-*N*-(pyridine-2-ylmethyl)pyridine-2-amine (**87**) were refered with that reported in the literature.[165b]

[166] R. T. Shuman, P. L. Ornstein, J. W. Paschal, P. D. Gesellchen, *J. Org. Chem.* **1990**, *55*, 738.

7.3.6 Synthesis of *N*-(Pyridin-2-yl)-*N*-(pyridine-2-ylmethyl)pyridin-2-amine (74a):

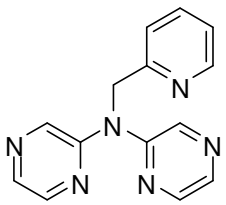


In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (36 mg, 0.04 mmol), *rac*-BINAP (52 mg, 0.08 mmol), 2-bromopyridine (8.2 mmol, 1.32 g, 800 μL), 2-picolylamine (4 mmol, 438.7 mg, 415 μL) and sodium *tert*-butylate (848 mg, 8.8 mmol). After the addition of toluene (20 mL) the reaction mixture was heated at 70 ºC for 20 h. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (20 mL). After filtration through Celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate) affording *N*,*N*-dipyridylaminopicoline **74a** in 80% yield (847 mg).

Analytical data for **74a**: m.p 102-103 ºC, ^{1}H NMR (400 MHz): δ = 5.59 (d, *J* = 8.4 Hz, 6H), 6.83-6.87 (m, 2H), 7.08-7.14 (m, 1H), 7.23-7.28 (m, 2H), 7.30-7.35 (m, 1H), 7.52-7.57 (m, 3H), 8.28-8.31 (m, 2H), 8.53-8.55 (m, 1H). ^{13}C NMR (75 MHz): δ = 159.4, 156.8, 148.8, 148.2, 137.3, 136.7, 121.7, 121.3, 117.3, 114.5, 53.6. MS (EI, 70 eV): *m/z* (%) = 262 (M^+); IR (KBr): υ = 2956, 2852, 1594, 1499, 1357, 1185, 745, 693 cm^{-1}.

Analytical data of *N*-(pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine (**74a**) were consistent with that reported in the literature.[54]

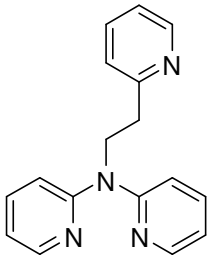
7.3.7 Synthesis of *N*-(Pyrazin-2-yl)-*N*-(pyridin-2-ylmethyl)pyrazin-2-amine (77):



In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (18 mg, 0.02 mmol), *rac*-BINAP (26 mg, 0.04 mmol), 2-chloropyrazine (4.2 mmol, 1.32 g, 800 μL), 2-picolylamine (2 mmol, 220 mg, 208 μL) and sodium *tert*-butylate (424 mg, 4.4 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 90 ºC for 18 h. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = chlorform : methaol = 15 : 1) affording *N*-(pyrazin-2-yl)-*N*-(pyridin-2-ylmethyl)pyrazin-2-amine **77** in 93% yield (491 mg).

Analytical data for **77**: M.p 97-98 ºC, ^{1}H NMR (400 MHz): δ = 5.59 (s, 2H), 6.83-6.88 (m, 2H), 7.08-7.13 (m, 1H), 7.23-7.25 (m, 1H), 7.25-7.27 (m, 1H), 7.30-7.34 (m, 1H), 7.50-7.57 (m, 3H), 8.28-8.30 (m, 2H), 8.52-8.54 (m, 1H). ^{13}C NMR (75 MHz): δ = 149.7, 149.6, 141.9, 141.8, 137.9, 137.5, 137.4, 136.8, 135.2, 130.8, 128.8, 122.4, 121.3, 52.8. MS (EI, 70 eV): *m/z* (%) = 264 (M^+).

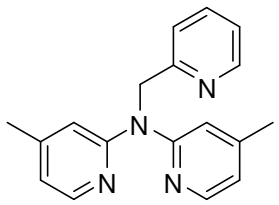
7.3.8 Synthesis of *N*-(Pyridin-2-yl)-*N*-(2-(pyridin-2-yl)ethyl)pyridin-2-amine (76):



In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (18 mg, 0.02 mmol), *rac*-BINAP (26 mg, 0.04 mmol), 2-bromopyridine (4.2 mmol, 660 mg, 400 μL), 2-(2-pyridyl)ethylamine (2 mmol, 246 mg, 240 μL) and sodium *tert*-butylate (424 mg, 4.4 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 70 ºC for 1d. The mixture was then allowed to cool to room temperature and diluted with ethylacetate (10 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate) affording *N*,*N* dipyridylaminoethylpyridine **76** in 99% yield (546 mg).

Analytical data for **76**: Oil, ^{1}H NMR (400 MHz): δ = 3.28 (dd, *J*= 7.7. 7.4 Hz, 2H), 4.60 (dd, *J*= 7.7. 7.4 Hz, 2H), 6.84-6.89 (m, 2H), 7.07-7.12 (m, 3H), 7.20-7.24 (m, 1H), 7.49-7.59 (m, 3H), 8.35-8.37 (m, 2H), 8.52-8.54 (m, 1H). ^{13}C NMR (75 MHz): δ = 159.9, 157.2, 149.1, 148.3, 136.2, 123.7, 121.2, 117.0, 114.8, 48.7, 37.2. IR (KBr): υ = 3058, 3008, 2955, 1587, 1499, 1471, 1428, 1322, 1273, 1184, 1152, 1078, 986, 773 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 276 (M^+).

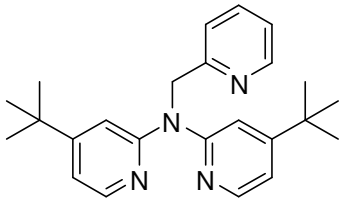
7.3.9 Synthesis of 4-Methyl-*N*-(4-methylpyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine (74c):



In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (36 mg, 0.04 mmol), *rac*-BINAP (52 mg, 0.08 mmol), 2-chloro-4-methylpyridine (4.2 mmol, 515.8mg, 751 μL), 2-picolylamine (4 mmol, 438.7 mg, 415 μL) and sodium *tert*-butylate (848 mg, 8.8 mmol). After the addition of toluene (20 mL) the reaction mixture was heated at 100 ºC for 22 h. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (20 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate) affording *N*,*N* dipyridylaminopicoline **74c** in 87% yield (1.015 g).

Analytical data for **74c**: m.p 84-85 ºC, ^{1}H NMR (400 MHz): δ = 2.26 (s, 6H), 5.54 (s, 2H), 6.68-6.72 (m, 2H), 7.01-7.06 (m, 2H), 7.06-7.14 (m, 1H), 7.30-7.36 (m, 1H), 7.50-7.58 (m, 1H), 8.16-8.18 (m, 2H), 8.53-8.57 (m, 1H). ^{13}C NMR (75 MHz): δ = 159.8, 157.3, 149.0, 148.5, 147.8, 136.6, 121.6, 121.3, 118.7, 115.0, 53.9, 21.3.

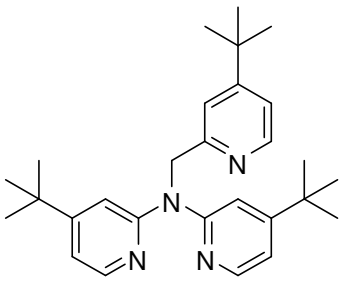
7.3.10 Synthesis of 4-*tert*-Butyl-*N*-(4-*tert*-butylpyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine (89):



In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (18 mg, 0.02 mmol), *rac*-BINAP (26 mg, 0.04 mmol), 2-chloro-4-*tert*-butylpyridine (4.2 mmol, 712.5 mg), 2-(2-pyridyl)ethylamine **89** (2 mmol, 246 mg, 207 μL) and sodium *tert*-butylate (424 mg, 4.4 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 100 ºC for 1 day. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 1) affording *N*,*N*-dipyridylaminopicoline **89** in 84% yield (626 mg).

Analytical data for **89**: m.p 127-129 ºC, ^{1}H NMR (400 MHz): δ = 1.24 (s, 9H), 5.62 (s, 2H), 6.85-6.88 (m, 2H), 7.05-7.10 (m, 1H), 7.22-7.24 (m, 2H), 7.33-7.77 (m, 1H), 7.50-7.56 (m, 1H), 8.21-8.24 (m, 2H), 8.51-8.54 (m, 1H). ^{13}C NMR (75 MHz): δ = 160.9, 159.8, 157.2, 148.6, 147.9, 136.3, 121.3, 121.2, 114.7, 111.2, 53.6, 34.7, 30.4.

7.3.11 Synthesis of 4-*tert*-Butyl-*N*-(4-*tert*-butylpyridin-2-yl)-*N*-[(4-*tert*-butylpyridin-2-yl)methyl]pyridin-2-amine (90):

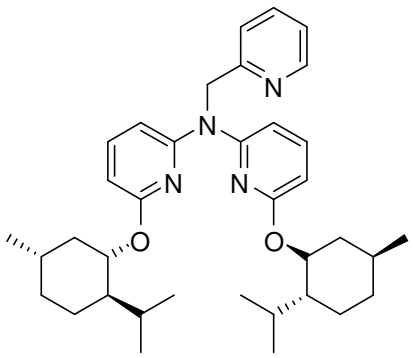


In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (9 mg, 0.01 mmol), *rac*-BINAP (13 mg, 0.02 mmol), 4-*tert*-butyl-2-chloropyridine (2.2 mmol, 373 mg, 800 μL), 4-*tert*-butyl-picolylamine (1 mmol, 224 mg) and sodium *tert*-butylate (318 mg, 3.3 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 100 ºC for 1 day. The

mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = MeOH : chloroform = 1 : 10) affording *N*,*N* dipyridylaminopicoline **90** in 66% yield (284 mg).

Analytical data for **90**: m.p 112 ºC, ^{1}H NMR (300 MHz): δ = 1.15 (s, 9H), 1.24 (s, 18H), 5.63 (s, 2H), 6.85-6.88 (m, 2H), 7.19-7.22 (m, 2H), 7.25-7.29 (m, 2H), 8.21-8.33 (m, 2H), 8.44 (m, 1H). ^{13}C NMR (75 MHz): δ = 161.1, 159.2, 157.6, 148.5, 148.1, 118.7, 114.8, 111.5, 53.5, 34.8, 30.5, 30.4. IR (KBr): υ = 2962, 2868, 1599, 1538, 1392, 1291, 1213, 984, 924, 829 cm^{-1}.

7.3.12 Synthesis of 6-[(1*R*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyloxy[-*N*-{6-[(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyloxy]pyridin-2-yl}-*N*-(pyridin-2-ylmethyl)pyridin-2-amine (34a):



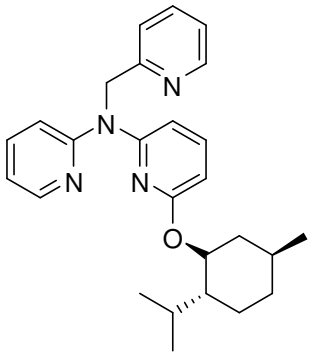
In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (11.5 mg, 0.02 mmol), DPPP (10.3 mg, 0.025 mmol), bromopyridine (1.1 mmol, 343 mg), picolylamine (0.5 mmol, 224 mg), TBAB (322 mg, 1 mmol) and sodium *tert*-butylate (318 mg, 3.3 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 100 ºC over night. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 10) affording *N*,*N*-dipyridylaminopicoline **34a** in 65% yield (186 mg) as oil.

Analytical data for **34a**: Oil, ^{1}H NMR (400 MHz): δ = 0.52 (td, *J* = 6.9 Hz, 6H), 0.98 (m, 18H), 1.00-1.19 (m, 2H), 1.59-1.49 (m, 6H), 1.78-1.98 (m, 4H), 4.60 (ddd, *J* = 10.7, 10.7, 4.4

Hz, 2H), 5.33 (d, *J* = 17.3 Hz, 1H), 5.53 (d, *J* = 17.3 Hz, 1H), 6.16 (d, *J* = 7.7 Hz, 2H), 6.82 (t, *J* = 7.7 Hz, 2H), 6.99 (m, 1H), 7.15 (td, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.41 (td, J = 4.0, 1.0 Hz, 1H), 8.45 (dq, *J* = 4.0, 1.0 Hz, 1H). ^{13}C NMR (75 MHz): δ = 162.8, 160.7, 154.7, 148.8, 139.6, 136.1, 121.1, 120.7, 105.0, 103.3, 74.5, 53.7, 47.4, 40.9, 34.5, 31.2, 26.3, 23.8, 22.2, 20.7, 16.6.

Analytical data of *N*,*N*-dipyridylaminopicoline **34a** were consistent with that reported in the literature.[167]

7.3.13 Synthesis of 6-[(1*R*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyloxy]-*N*-(pyridin-2-yl)-*N*-(pyridin-2-ylmethyl)pyridin-2-amine (34b):



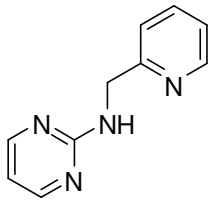
In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (27.6 mg, 0.03 mmol), *rac*-BINAP (37.2 mg, 0.02 mmol), bromopyridine (2.2 mmol, 373 mg, 800 μL), picolylamine (3 mmol, 555 mg), TBAB (322 mg, 1 mmol) and sodium *tert*-butylate (432 mg, 4.5 mmol). After the addition of toluene (20 mL) the reaction mixture was heated at 100 ºC for 7 hours. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through Celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 2 : 3) affording dipyridylaminopicoline **34b** in 90% yield (1.121 g) as yellow oil.

Analytical data for **34b**: Oil, ^{1}H NMR (400 MHz): δ = 0.63 (d, *J* = 7.2 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 3H), 1.08-1.35 (m, 1H), 1.57-1.65 (m, 2H), 1.86-1.92 (m,

[167] J.-C. Frison, Ph.D Thesis, RWTH Aachen, **2004**.

1H), 4.64 (td, *J* = 10.7, 4.4 Hz, 2H), 5.55 (q, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 7.0 Hz, 1H), 6.88 (ddd, *J* = 17.1, 5.0, 0.8 Hz, 1H), 6.99 (m, 1H), 7.11 (dd, *J* = 5.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.36 (td, *J* = 8.5, 0.8 Hz, 1H), 8.34 (dq, *J* = 5.0, 0.8 Hz, 1H), 8.54 (dq, *J* = 5.0, 0.8 Hz, 1H). ^{13}C NMR (75 MHz): δ = 162.5, 159.8, 156.9, 154.4, 148.4, 148.1, 139.6, 136.7, 135.6, 121.3, 120.8, 117.3, 115.2, 104.0, 103.1, 74.3, 53.5, 47.3, 40.8, 34.5, 31.2, 26.3, 22.2, 20.6, 16.6. IR (KBr): υ = 3056, 3009, 2951, 1949, 1592, 1472, 1392, 1151, 1213, 1041, 945, 920, 854, 780, 749, 612 cm^{-1}, MS (EI, 70 eV): *m/z* (%) = 416 (M^+), anal. calcd. for $C_{26}H_{32}N_4O$ (416.56): C 74.97, H 7.74, N 13.45; found: C 75.25, H 7.92, N 13.80.

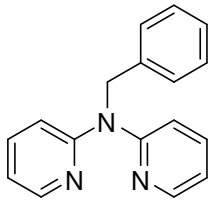
7.3.14 Synthesis of *N*-2-Pyrimidylpicolyllamine 78:



In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (18 mg, 0.02 mmol), DPPP (16 mg, 0.04 mmol), 2-chloropyrimidine (146 μL, 1.6 mmol), picolylamine (82 μL, 0.8 mmol), and sodium *tert*-butylate (134 mg, 1.4 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 100 ºC overnight. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate) affording *N*-pyrimidylpicolylamine **78** in 40% yield (60 mg) as a white solid.

Analytical data for **78**: ^{1}H NMR (400 MHz): δ = 4.67 (d, *J* = 5.0, 2H) 5.93 (brd, 1H), 7.18-7.22 (m, 1H), 7.63-7.69 (m, 1H), 7.79-7.80 (m, 1H), 7.98-8.00 (m, 2H), 8.55-8.58 (m, 1H).

7.3.15 Synthesis of 2,2'-*N*,*N*'-Dipyridylbenzylamine 31:



In a Schlenk tube flushed with argon were successively added [$Pd_2(dba)_3$] (9.2 mg, 0.01 mmol), DPPP (8.2 mg, 0.02 mmol), 2-bromopyridine (346.5 mg, 210 μL, 2.2 mmol), benzylamine (555 mg, 3 mmol), TBAB (644 mg, 2 mmol) and sodium *tert*-butylate (288 mg, 3 mmol). After the addition of toluene (10 mL) the reaction mixture was heated at 100 ºC overnight. The mixture was then allowed to cool to room temperature and diluted with ethyl acetate (10 mL). After filtration through Celite, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 3) affording *N*,*N*-dipyridylbenzylamine **31** in 77% yield (202 mg) as a pale yellow solid.

Analytical data for **31**: ^{1}H NMR (400 MHz): δ = 5.44 (s, 2H), 6.75-6.80 (m, 2H), 7.08-7.11 (m, 3H), 7.15-7.21 (m, 2H), 7.25-7.29 (m, 2H), 7.41-7.47 (m, 2H), 8.24-8.26 (m, 2H). ^{13}C NMR (75 MHz): δ = 157.0, 148.1 139.3, 137.2, 128.3, 127.0, 126.5, 117.2, 114.6, 51.4.

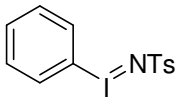
Analytical data of *N*,*N*-dipyridylbenzylamine **31** were consistent with that reported in the literature.[10]

7.4 Synthesis of Iminophenyliodinane Derivatives

7.4.1 Materials

Most starting materials were purchased from commercial suppliers and used without further purification. MeOH was used after distillation over KOH. Trimethylsilylethanesulfonamide was synthesized as described previously.[168]

7.4.2 Synthesis of [*N*-(*p*-Toluenenesulfonyl)imino]phenyliodinane (48a):



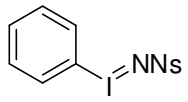
[168] V. Declerck, P. Ribière, J. Martinez, F. Lamaty, *J. Org. Chem*. **2004**, *69*, 8372.

KOH (1.4 g, 25 mmol) was added to a solution of *p*-toluenesulfonamide (1.71 g, 10 mmol) in 40 mL of methanol and then iodobenzene diacetate (3.22 g, 10 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The reaction mixture was poured in to water and left over night. Crystals were collected and washed with water and dichloromethane to afford [*N*-(*p*-toluenenesulfonyl)imino]phenyliodinane (**48a**) in 42% yield (1.56 g).

Analytical data for **48a**: ^{1}H NMR (400 MHz, d^6-DMSO): δ= 2.26 (s, 3H), 7.05-7.08 (m, 2H), 7.26-7.33 (m, 2H), 7.43-7.47 (m, 3H), 7.67-7.72 (m, 2H).

Analytical data of [*N*-(*p*-toluenenesulfonyl)imino]phenyliodinane (**48a**) were consistent with that reported in the literature.[169]

7.4.3 Synthesis of [*N*-(*p*-Nitrobenzenesulfonyl)imino]phenyliodinane (48b):



KOH (4.2 g, 8.3 mmol) was added to a solution of *p*-nitorobenzenesulfonamide (2.02 g, 10 mmol) in methanol (10 mL). And then iodobenzene diacetate (3.22 g, 10 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 3 hours. The reaction mixture was poured in to water and left over night. Crystals were collected and washed with water and dichloromethane to afford [*N*-(*p*-nitrobenzenesulfonyl)imino]phenyliodinane **48b**.

Analytical data for **48b**: ^{1}H NMR (400 MHz, d^6-DMSO): δ= 7.22 (m, 2H), 7.37-7.44 (m, 1H), 7.68-7.76 (m, 4H), 8.01-8.06 (m, 2H).

Analytical data of [*N*-(*p*-nitrobenzenesulfonyl)imino]phenyliodinane (**48b**) was consistent with the literature.[146b, 170]

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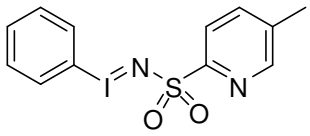
[169] Y. Yamada, T. Yamamoto, M. Okawara, *Chem. Lett*. **1975**, 361.
[170] a) J. Gullick, D. Ryan, P. McMorn, D. Bethell, F. King, F. Hancock, G. J. Hutchings, *New J. Chem.* **2004**, *28*, 1470. b) S. Taylor, J. Glullick, P. McMorn, D. Bethell, P. C. Bulman Page, F. E. Hancock, F. King, G. J. Hutchings, *Topics in Catalysis* **2003**, *24*, 43.

7.4.4 Synthesis of (5-methyl-2-pyridinesulfonyl)iminophenyliodinane (48d):

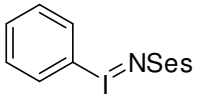


KOH (1.4 g, 25 mmol) was added to a solution of 5-methyl-2-pyridinesulfonamide (1.72 g, 10 mmol) in methanol (50 mL). And then iodobenzene diacetate (3.22 g, 10 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred for 3 hours. The reaction mixture was extracted with dichlromethane and the organic layers were dried over $MgSO_4$. Filtrate was evaporated and crystal was collected and washed with hot MeOH affording (5-methyl-2-pyridinesulfonyl)iminophenyliodinane (**48d**) in 59% yield (2.2 g) as a white solid.

Analytical data for **48d**: m.p 144 ºC (detonates), ^{1}H NMR (400 MHz, d^6-DMSO): δ = 2.28 (s, 3H), (m, 2H), 7.43-7.51 (m, 2H), 7.39-7.45 (m, 2H), 7.48-7.54 (m, 1H), 7.59-7.62 (m, 1H), 7.65-7.70 (m, 1H), 7.86-7.90 (m, 1H), 7.87-7.90 (m, 2H), 8.31-8.32 (m, 1H). ^{13}C NMR (75 MHz): δ = 159.6, 149.0, 138.7, 135.4, 133.1, 131.2, 131.0, 119.4, 119.3, 18.3. IR (KBr): υ = 1567, 1465, 1444, 1271, 1132, 1099, 922, 898, 825, 736, 673, 629 cm^{-1}. anal. calcd. for $C_{12}H_{11}IN_2O2S$ (357.49): C 38.52, H 2.96, N 7.49; found: C 38.42, H 3.18, N 7.43.

Analytical data for (5-methyl-2-pyridinesulfonyl)iminophenyliodinane (**48d**) were consistent with those in the literature.[171]

7.4.5 Synthesis of [*N*-(Trimethylsilylethanesulfonyl)imino]phenyliodinane 48e:



[171] B. V. Meprathu, S. Diltz, P. J. Walsh, J. D. Protasiewicz, *Tetrahedron Lett*. **1999**, *40*, 5459.

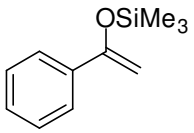
KOH (460 mg, 8.2 mmol) was added to a solution of trimethylsilylethanesulfonamide (595 mg, 3.28 mmol) in methanol (10 mL) and then iodobenzene diacetate (1.06 g, 3.28 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 3 hours. The reaction mixture was extracted with dichlromethane and the organic layer was dried over $MgSO_4$. The filtrate was evaporated and the crystals were collected and washed to afford [*N*-(trimethylsilylethanesulfonyl)imino]phenyliodinane in 75% yield (940 mg) as a white solid.

Analytical data for **48e**: ^{1}H NMR (400 MHz, d^6-DMSO): δ = 0.05 (s, 9H), 1.03-1.08 (m, 2H), 2.99-3.07 (m, 2H), 7.43-7.51 (m, 2H), 7.43-7.51 (m, 1H), 8.14-8.20 (m, 2H).

Analytical data of [*N*-(trimethylsilylethanesulfonyl)imino]phenyliodinane (**48e**) was consistent with that reported in the literature.[102]

7.5 Synthesis of Silyl Enol Ethers

7.5.1 Synthesis of Silyl Enol Ether 55a from Acetophenone:

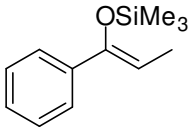


A solution of *n*-butyl lithium (11.6 mL) (1.6 M in hexane) was added slowly to a solution of diisopropylamine in 10 mL of THF at -78 °C. And then acetophenone (2 g, 1.95 mL, 16.6 mmol) in THF (10 mL) was added slowly at -78 °C. After stirring for 30 minutes, trimethylsilylchloride (2.4 mL, 18 8 mmol) was added slowly and the resulting solution was stirred for 3 hours. A solution of sat. $NH_4Cl_{(aq.)}$ was added at -78 °C and mixture was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and solvent was evaporated (rotary evaporator) after filtration. The remaining mixture was separated by column chromatography (silica gel; eluent = petroleum ether : diethyl ehter = 19 : 1) affording trimethyl(1-phenylvinyloxy)silane (**55a**) in 80% yield (2.56 g).

Analytical data for **55a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.25 (s, 9H), 4.17 (d, *J* = 1.7 Hz 1H), 4.90 (d, *J* =1.7 Hz, 1H), 7.26-7.34 (m, 3H), 7.55-7.60 (m, 2H). ^{13}C NMR (75 MHz): δ = 155.5, 135.6, 128.1, 128.0, 125.1, 91.0, 0.2.

Analytical data of the silyl enol ether **55a** were consistent with that reported in the literature.[172]

7.5.2 Synthesis of Silyl Enol Ether 55b from Propiophenone:



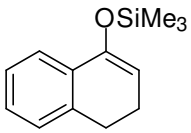
A solution of *n*-butyl lithium 11.6 mL (1.6 M in hexane) was added slowly into a solution of diisopropylamine in 10 mL of THF at -78 °C and then propiophenone (2.2 mL, 16.4 mmol) in THF (10 mL) was added slowly at -78 °C. After stirring for 30 minutes, trimethylsilylchloride (2.4 mL, 18 8 mmol) was added slowly and the resulting solution was stirred for 3 hours. A solution of sat. NH_4Cl aq. was added at -78 °C and the mixture was extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated (rotary evaporator) after filtration. The remaining mixture was separated by column chromatography (silica gel; eluent = petroleum ether : diethyl ehter = 19 : 1) affording (*Z*)-trimethyl(1-phenylprop-1-enyloxy)silane (**55b**).

Analytical data for **55b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.15 (s, 9H), 1.60 (d, *J* = 6.7 Hz, 3H), 5.21 (q, *J* = 6.7 Hz, 1H), 7.78-7.86 (m, 2H). ^{13}C NMR (75 MHz): δ = 149.0, 130.3, 127.9, 127.2, 125.1, 105.3, 11.8, 0.7.

Analytical data of silyl enol ether **55b** were consistent with that reported in the literature.[172]

7.5.3 Synthesis of Silyl Enol Ether 55c from *a*-Tetralone:

[172] J. Eames, G. S. Coumbarides, M. J. Sugatte, N. Weerasooriya, *Eur. J. Org. Chem*. **2003**, *4*, 634.

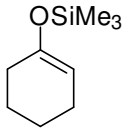


A solution of *n*-butyl lithium (11.6 mL) (1.6 M in hexane) was added slowly into a solution of diisopropylamine in 10 mL of THF at -78 °C and then α-tetralone (2.2 mL, 16.4 mmol) in THF (10 mL) was added slowly at -78 °C. After stirring for 30 minutes, trimethylsilylchloride (2.4 mL, 18 8 mmol) was added slowly and the resulting solution was stirred for 3 hours. The resulting slurry was allowed to warm to rom temperature and the volatiles were removed *in vacuo*. Pentane was added to the mixture which was filtered. The filtrate was evaporated and purified by distillation affording (3,4-dihydronaphthalen-1-yloxy)trimethylsilane (**55c**).

Analytical data for **55c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.24 (s, 9H), 2.31 (td, J = 8.0, 4.7 Hz, 2H), 2.75 (t, J = 8.0 Hz, 2H), 5.17 (t, J = 4.7 Hz, 1H), 7.06-7.21 (m, 3H), 7.15-7.17 (m, 1H).

Analytical data of (3,4-dihydronaphthalen-1-yloxy)trimethylsilane **55c** were consistent with that reported in the literature.[172]

7.5.4 Synthesis of Silyl Enol Ether 55d from Cyclohexanone:

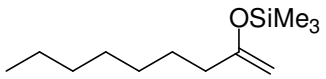


A solution of *n*-butyl lithium (11.6 mL) (1.6 M in hexane) was added slowly into the solution of diisopropylamine in 10 mL of THF at -78 °C and then cyclohexanone (1.7 mL, 16.4 mmol) in THF (10 mL) was added slowly at -78 °C. After stirring for 30 minutes, trimethylsilylchloride (2.4 mL, 18 8 mmol) was added slowly the resulting solution was stirred for 3 hours. The resulting slurry was allowed to warm to room temperature and the volatiles were removed *in vacuo*. Pentane was added to the mixture which was filtered. The filtrate was evaporated and purified by distillation affording cyclohexenyloxytrimethylsilane (**55d**).

Analytical data for **55d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 (s, 9H), 1.44-1.53 (m, 4H), 1.60-1.67 (m, 4H), 1.93-2.02 (m, 8H), 4.84-4.86 (m, 2H).

Analytical data of cyclohexenyloxytrimethylsilane **55d** were consistent with that reported in the literature.[173]

7.5.5 Synthesis of Silyl Enol Ether 55e from 2-Nonanone:

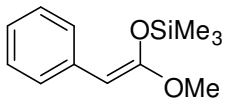


A solution of *n*-butyl lithium (11.6 mL) (1.6 M in hexane) was added slowly into the solution of diisopropylamine in 10 mL of THF at -78 °C and then 1-nonanone (2.8 mL, 16.4 mmol) in THF (10 mL) was added slowly at -78 °C. After stirring for 30 minutes, trimethylsilylchloride (2.4 mL, 18.8 mmol) was added slowly and stirred for 3 hours. The resulting slurry was allowed to warm to room temperature and volatiles were removed *in vacuo*. Pentane was added to the reaction mixture which was filtered. The filtrate was evaporated and purified by distillation affording trimethyl(non-1-en-2-yloxy)silane (**55e**).

Analytical data for **55e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 9H), 0.68-0.74 (m, 3H), 1.07-1.16 (m, 8H), 1.23-1.1.32 (m, 2H), 1.80-1.86 (m, 2H), 1.55 (s, 2H).

Analytical data of trimethyl(non-1-en-2-yloxy)silane **55e** were consistent with the literature.[174]

7.5.6 Synthesis of Synthesis of Silyl Enol Ether 55f from Methylphenylacetate:



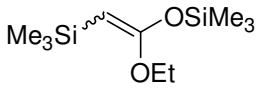
[173] H. W. Lee, J.-G. An, H. K. Yoon, H. Jang, N. G. Kim, Y. Do, *Bull. Korean Chem. Soc*. **2005**, *26*, 1569.
[174] J. P. McCormic, W. Tomasik, M. W. Johnson, *Tetrahedron Lett*. **1981**, *22*, 607.

A solution of *n*-butyl lithium (11.6 mL) (1.6 M in hexane) was added slowly into the solution of diisopropylamine in 10 mL of THF at -78 °C and then methylphenylacetate (2.36 mL, 16.4 mmol) in 10 mL of THF was added slowly at -78 °C. After stirring for 30 minutes, trimethylsilylchloride (2.4 mL, 18 8 mmol) was added slowly and the resulting solution was stirred for 3 hours. The resulting slurry was allowed to warm to room temperature and volatiles were removed in vacuo. Pentane was added to the mixture which was then filtered. The filtrate was evaporated and purified by distillation affording mixture of (*E*/*Z*)-(1-methoxy-2-phenylvinyloxy)trimethylsilane (**55f**).

Analytical data for **55f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 (s, 5.4H), 0.25 (s, 3.6H), 3.60 (s, 1.8H), 3.61 (s, 1.2H), 6.92-6.98 (m, 1H), 7.15-7.25 (m, 2H), 7.30-7.37 (m, 2H).

Analytical data for (*E*/*Z*)-(1-methoxy-2-phenylvinyloxy)trimethylsilane (**55f**) were consistent with the literature.[175]

7.5.7 Synthesis of Silyl Enol Ether 50h from Trimethylsilyl Acetic Acid Ethyl Ester:



A solution of *n*-butyl lithium (3.8 mL, 6.05 mmol) (1.6 M in hexane) was added slowly into the solution of diisopropylamine (0.85 mL, 6.05 mmol) in 10 mL of THF at -78 °C and then trimethylsilyl acetic acid ethyl ester (1 mL, 5.5 mmol) in THF (10 mL) was added slowly at -78 °C. After stirring for 30 minutes, trimethylsilylchloride (773 μL, 6.05 mmol) was added slowly and stirred for 3 hours. The resulting slurry was allowed to warm to room temperature and volatiles were removed in vacuo. Pentane was added to the mixture which was filtered. The filtrate was evaporated and purified by distillation affording mixture of (*E*/*Z*)-(1-ethoxy-2-(trimethylsilyl)vinyloxy)trimethylsilane (**55g**).

[175] a) N. Slougui, G. Rousseau, J.-M. Conia, *Synthesis* **1982**, 58. b) C. Ainworth, F. Chen, Y. N. Kuo, *J. Organomet. Chem.* **1972**, *46*, 59.

Analytical data for **55g**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.01 (s, 3H), 0.11 (s, 6H), 0.19 (s, 3H), 0.23 (s, 6H), 1.18 (t, *J* = 7.1 Hz, 1H), 1.126 (t, *J* = 7.1 Hz, 2H), 3.72 (q, *J* = 7.1 Hz, 0.67H), 3.82 (q, *J* = 7.1 Hz, 0.33H).

Analytical data of (*E*/*Z*)-(1-ethoxy-2-(trimethylsilyl)vinyloxy)trimethylsilane (**55g**) were consistent with that reported in the literature.[155b, 176]

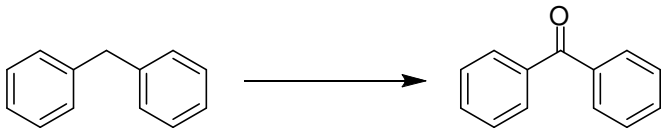
7.6 Catalytic Reaction with Iron catalyst

7.6.1 Iron-Catalyzed Benzylic Oxidation

7.6.1.1 Materials

Most starting materials were purchased from commercial suppliers and used without further purification. TBHP (70% in water) was obtained from Fluka. Tosyl-, acetyl- and butoxycarbonyl-protected substrates (Table 1, entries 8 and 10) were prepared by standard procedures. Chroman (Table 1, entry 9) was prepared by the previously reported protocol.[177] Pyridine was used after drying over KOH.

7.6.1.2 Representative Procedure (RP 3) for the Benzylic Oxidation: Conversion of Diphenylmethane 33a:



Diphenylmethane **35a** (84.1 mg, 83.3 μL, 0.5 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (2.7 mg, 0.01 mmol) in pyridine (0.5 mL). After the addition of TBHP (70% in H_2O; 206 μL, 1.5 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (10 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (40 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary

[176] G. Picotin, P. Miginiac, *J. Org. Chem.***1987**, *52*, 4796.
[177] W. E. Parham, L. D. Jones, Y. A. Sayed, *J. Org. Chem.* **1976**, *41*, 1184.

evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 20) affording benzphenone **36a** in 91% yield (83 mg).

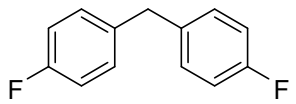
Analytical data for **36a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.53 (m, 4H), 7.56-7.64 (m, 2H), 7.80-7.84 (m, 4H).

Analytical data of benzophenone **36a** were consistent with that reported in the literature.[178]

7.6.1.3 Large scale for the benzylic oxidation: Conversion of Diphenylmethane 33a:

Diphenylmethane **35a** (841 mg, 833 μL, 5 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (27 mg, 0.1 mmol) in pyridine (5 mL). After the addition of TBHP (70% in H_2O; 2.06 mL, 15 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether: pentane = 1 : 20)affording benzophenone **36a** in 94% yield (853 mg).

7.6.1.4 Representative Procedure (RP 3) for the Benzylic Oxidation: Conversion of 4,4'-Difluorophenylmethane:



Prepared according to RP 2, 4,4'-difluorophenylmethane (**35b**) (204 mg, 1 mmol) was added to the solution of $FeCl_3 \cdot 6H_2O$ (5.4 mg, 0.02 mmol) in pyridine (1 mL). After the addition of TBHP (70% in H_2O; 412 μL, 3 mmol), the reaction mixture was heated at 80 ºC for 24 h. T The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (10 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (10 mL), washed with brine and dried over Na_2SO_4. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column

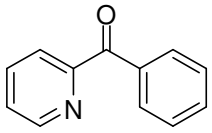
[178] A. J. Catino, J. M. Nichols, H. Choi, S. Gottipamula, M. P. Doyle, *Org. Lett.* **2005**, *23*, 5167.

chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 10) affording 4,4'-difluorobenzophenone **36b** in 94% yield (204 mg).

Analytical data for **36b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13-7.22 (s, 2H), 7.78-7.86 (m, 2H). ^{13}C NMR (75 MHz): δ = 194.0, 165.4 (d, J_{C-F} = 254 Hz), 132.5 (d, J_{C-F} = 9.6 Hz), 115.6 (d, J_{C-F} = 22 Hz).

Analytical data of 4,4'-difluorobenzophenone **36b** were consistent with the literature.[179]

7.6.1.5 Representative Procedure (RP 3) for the Benzylic Oxidation: Conversion of 2-Benzylpyridine:



Prepared according to RP 3, starting from benzylpyridine (**35c**) (338 mg, 321 μL, 2 mmol) was added to the solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 15 mmol), the reaction mixture was heated at 110 °C for 24 h. The mixture was then allowed to cool to room temperature and poured into water in order to remove the pyridine and *t*ert-BuOH. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over Na_2SO_4. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 2) affording 2-benzoylpyridine **36c** in 75% yield (260 mg).

Analytical data for **36c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.52, (m, 2H), 7.59-7.63 (m, 2H), 7.98-8.08 (m, 4H), 8.78-8.80 (m, 1H). ^{13}C NMR (75 MHz): δ = 153.7, 147.7, 138.3, 135.8, 133.3, 130.9, 128.3, 126.5, 125.0.

Analytical data of 2-benzoylpyridine **36c** were consistent with that reported in the literature.[180]

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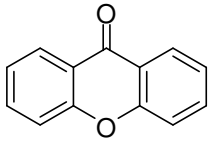
[179] P. Lucas, N. E. Mehdi, H. A. Ho, D. Bélanger, L. Breau, *Synthesis* **2000**, 1253.
[180] E. Maerten, M. Sauthier, A. Mortreux, Y. Castanet, *Tetrahedron* **2007**, *63*, 682.

7.6.1.6 Iron-Catalyzed Benzylic Oxidation: Conversion of Xanthene:

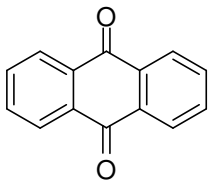


Xanthene (**35d**) (364.4 mg, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with ethyl acetate (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; diethyl acetate : pentane = 1 : 20 as eluent) affording xanthone **36d** in quantitative yield (398 mg).

Analytical data for **36d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.43 (m, 2H), 7.47-7.52 (m, 2H), 7.68-7.76 (m, 2H), 8.32-8.35 (m, 2H).

Analytical data of xanthone **36d** were consistent with that reported in the literature.[59]

7.6.1.7 Iron-Catalyzed the Benzylic Oxidation: Conversion of 9,10-Dihydroanthracene:



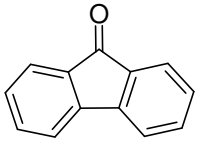
9,10-Dihydroanthracene (**35e**) (180.2 mg, 1 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (5.4 mg, 0.02 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with ethyl acetate (100 mL) and

chlorform, (100 mL) washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 20) affording anthroquinone **36e** in 93% yield (193 mg).

Analytical data for **36e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.25-7.32 (m, 2H), 7.46-7.54 (m, 4H), 7.65-7.67 (m, 2H). ^{13}C NMR (75 MHz): δ= 143.6, 129.3, 127.3, 127.0.

Analytical data of 9-fluorenone **36e** were consistent with the literature.[59]

7.6.1.8 Iron-Catalyzed Benzylic Oxidation: Conversion of Fluorene:

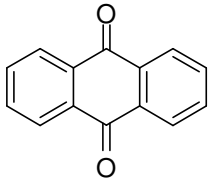


Fluorene (**35g**) (332 mg, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 15 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (50 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (50 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 20) affording 9-fluorenone **36f** in quantitative yield (359 mg).

Analytical data for **36f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.32 (m, 2H), 7.46-7.54 (m, 4H), 7.65-7.67 (m, 2H). ^{13}C NMR (75 MHz): δ= 144.2, 134.5, 134.0, 128.9, 124.1, 120.1.

Analytical data of 9-fluorenone **36f** were consistent with that reported in the literature.[59]

7.6.1.9 Iron-Catalyzed Benzylic Oxidation: Conversion of Anthrone:

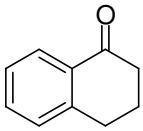


Anthrone (**35f**) (388.4 mg, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (4 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with ethyl acetate (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was washed MeOH affording anthroquinone **36e** in 62% yield (260 mg).

Analytical data for **36e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.25-7.32 (m, 2H), 7.46-7.54 (m, 4H), 7.65-7.67 (m, 2H). ^{13}C NMR (75 MHz): δ= 143.6, 129.3, 127.3, 127.0.

Analytical data of anthroquinone **36e** were consistent with the literature.[59]

7.6.1.10 Iron-Catalyzed Benzylic Oxidation: Conversion of Tetrahydronaphthalene:

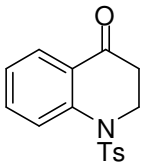


1,2,3,4-Tetrahydronaphthalene (**35h**) (265 mg, 271 μL, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 10) affording α-tetralone **36g** in 41% yield (120 mg).

Analytical data for **36g**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.67 (dd, *J* = 6.3, 6.0 Hz, 2H), 2.97 (d, *J* = 6.0 Hz, 2H), 2.15 (t, *J* = 6.3 Hz, 2H), 7.24-7.27 (m, 1H), 7.28-7.33 (m, 1H), 7.44-7.50 (m, 1H), 8.02-8.05 (m, 1H).

Analytical data of α-tetralone **36g** was consistent with that reported in the literature.[59]

7.6.1.11 Iron-Catalyzed Benzylic Oxidation: Conversion of *N*-Tosyl-1,2,3,4-tetrahydroquinoline:

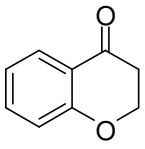


N-Tosyl-1,2,3,4-tetrahydroquinoline (**35i**) (306.8 mg, 1 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (5.4 mg, 0.02 mmol) in pyridine (1 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the filtrate was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 1) affording *N*-tosyl-2,3-dihydoro-1H-quinoline-4-one **36h** in 91% yield (60 mg).

Analytical data for **36h**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 2.37 (t, *J* = 6.3, 2H), 4.24 (t, *J* = 6.3, 2H), 7.18-7.29 (m, 5H), 7.51-7.60 (m, 3H), 7.83-7.96 (m, 2H).

Analytical data of *N*-tosyl-2,3-dihydoro-1H-quinoline-4-one **36h** were consistent with that reported in the literature.[59]

7.6.1.12 Iron-Catalyzed Benzylic Oxidation: Conversion of Chroman:

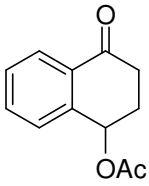


Chroman (**35j**) (268 mg, 2 mmol) was added to the solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 10) affording chromanone **36i** in 54% yield (160 mg).

Analytical data for **36i**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.81 (dd, J = 12.8, 6.4 Hz, 2H), 2.81 (dd, J = 12.8, 6.4 Hz, 2H), 6.95-7.04 (m, 2H), 7.44-7.50 (m, 1H), 7.88-7.91 (m, 1H). ^{13}C NMR (75 MHz): δ = 191.7, 161.8, 135.9, 127.1, 121.4, 117.9, 67.1, 37.9.

Analytical data of chromanone **36i** were consistent with that reported in the literature.[59]

7.6.1.13 Iron-Catalyzed Benzylic Oxidation: Conversion of 1-Acetyloxy-1,2,3,4-1-tetrahydro-1-naphthalene:

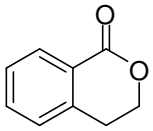


1-Acetyloxy-1,2,3,4-1-tetrahydro-1-naphthalene (**35k**) (380 mg, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 20) affording 4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate **36j** in 66% yield (268 mg).

Analytical data for **36j**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3H), 2.26-2.35 (m, 1H), 2.37-2.46 (m, 1H), 2.63-2.72 (m, 1H), 2.89-2.99 (m, 1H), 7.45-7.49 (m, 2H), 7.56-7.61 (m, 1H), 8.04-8.07 (m, 1H). ^{13}C NMR (75 MHz): δ = 196.7, 186.4, 140.6, 133.9, 133.9, 132.0, 129.0, 128.3, 127.2, 69.1, 34.5, 28.6, 21.4.

Analytical data of 4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate **36j** were consistent with that reported in the literature.[59]

7.6.1.14 Iron-Catalyzed Benzylic Oxidation: Conversion of Isochroman:

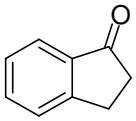


Isochroman (**35l**) (268 mg, 253 μL, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent: ethyl acetate : pentane = 1 : 5) affording 1-isochromanone **36k** in 74% yield (220 mg).

Analytical data for **36k**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.07 (t, J = 6.0 Hz, 2H), 4.55 (t, J = 6.0 Hz, 2H), 7.24-7.30 (m, 2H), 7.37-7.44 (m, 1H), 7.51-7.58 (m, 1H).

Analytical data of 1-isochromanone **36k** were consistent with that reported in the literature.[58]

7.6.1.15 Iron-Catalyzed Benzylic Oxidation: Conversion of Indane:

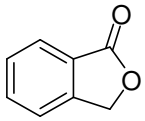


Indane (**35m**) (236 mg, 259 μL, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (50 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (50 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 5) affording 1-indanone **36l** in 61% yield (160 mg).

Analytical data for **36l**: ^{1}H NMR 400 MHz, $CDCl_3$): δ = 2.70 (t, J = 6.0 Hz, 2H), 3.16 (t, J = 6.0 Hz, 2H), 7.34-7.42 (m, 1H), 7.46-7.51 (m, 1H), 7.56-7.63 (m, 1H), 7.76-7.79 (m, 1H).

Analytical data of 1-indanone **36l** were consistent with that reported in the literature.[59]

7.6.1.16 Iron-Catalyzed Benzylic Oxidation: Conversion of Phthalan:

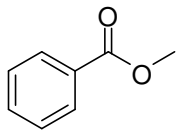


Phthalan (**35n**) (240 mg, 220 μL, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator) affording phthalide **36m** in 45% yield (120 mg).

Analytical data for **36m**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.34 (s, 2H), 7.48-7.57 (m, 2H), 7.67-7.72 (m, 1H), 7.93-7.95(m, 1H).

Analytical data of phthalide **36m** were consistent with that reported in the literature.[59]

7.6.1.17 Iron-Catalyzed Benzylic Oxidation: Conversion of Benzyl methyl ether:

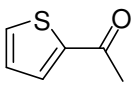


Benzyl methyl ether (**35o**) (247 mg, 263 μL, 5 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 10) affording benzoic acid methyl ester **36n** in 48% yield (131 mg).

Analytical data for **36n**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3H), 7.39-7.49 (m, 2H), 7.50-7.63 (m, 2H), 8.01-8.04 (m, 1H).

Analytical data of benzoic acid methyl ester **36n** were consistent with that reported in the literature.[58]

7.6.1.18 Iron-Catalyzed Benzylic Oxidation: Conversion of 2-Ethylthiophene:



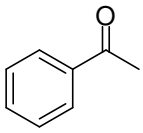
2-Ethylthiophene (**35p**) (225 mg, 227 μL, 5 mmol) was added to the solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (10 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (10 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel;

eluent = diethyl ether : pentane = 1 : 10 as eluent) affording 2-acetylthiophene **36o** in 25% yield (63 mg).

Analytical data for **36o**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.56 (s, 3H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.69 (dd, *J* = 3.8, 1.1 Hz, 1H).

Analytical data of 2-acetylthiophene **36o** were consistent with that reported in the literature.[59]

7.6.1.19 Iron-Catalyzed Benzylic Oxidation: Conversion of Acetophenone:

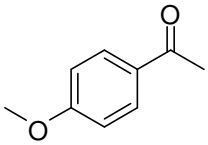


Ethylbenzene (**35q**) (212 mg, 247 μL, 5 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 20) affording acetophenone **36p** in 17% yield (41 mg).

Analytical data for **36p**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3H), 7.43 (m, 2H), 7.55(m, 2H), 7.95 (m, 2H).

Analytical data of acetophenone **36p** were consistent with the literature.[59]

7.6.1.20 Iron-Catalyzed Benzylic Oxidation: Conversion of 4-Methoxy-acetophenone:

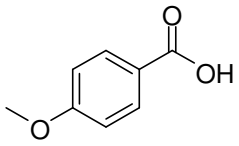


4-Ethylanisole (**33r**) (272 mg, 284 μL, 5 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with diethyl ether (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 5) affording 4-methoxyacetophenone **34q** in 84% yield (252 mg).

Analytical data for **34q**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.56 (s, 3H), 3.87 (s, 3H), 6.90-6.97 (m, 2H), 7.91-7.97 (m, 2H).

Analytical data of 4-methoxyacetophenone **34q** were consistent with that reported in the literature.[58]

7.6.1.21 Iron-Catalyzed Benzylic Oxidation: Conversion of 4-Methoxy-toluene:



4-Methylanisole (**35s**) (244.3 mg, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate) affording 4-methoxybenzoic acid **36r** in 53% yield (162 mg).

Analytical data for **36r**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 6.96 (d, J = 8.3 Hz, 2H), 8.08 (d, J = 8.3 Hz, 2H).

Analytical data of 4-methoxybenzoic acid **36r** was consistent with that reported in the literature.[59]

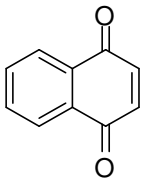
7.6.1.22 Iron-Catalyzed Benzylic Oxidation: Conversion of Diphenylcarbinol:

Diphenylcarbinol **35t** (368 mg, 2 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.04 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (50 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (50 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 10) affording benzophenone **36a** in 86% yield (314 mg).

Analytical data for **36a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.53 (m, 4H), 7.56-7.64 (m, 2H), 7.80-7.84 (m, 4H).

Analytical data of benzophenone **36a** were consistent with that reported in the literature.[177]

7.6.1.23 Iron-Catalyzed Benzylic Oxidation: Conversion of 1,4-Dihydroxynaphthalene (33w):



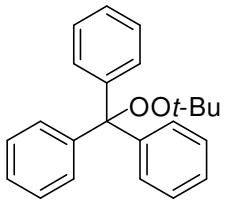
1,4-Dihydroxynaphthalene (**35u**) (160 mg, 1 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (10.5 mg, 0.02 mmol) in MeCN (1 mL). After the addition of TBHP (70% in H_2O; 412 μL, 3 mmol), the reaction mixture was heated at room temperature for 10 minutes. The mixture was

then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. Precipitate was collected and washed with water affording 1,4-naphthoquinone **36s** in 82% yield (130 mg).

Analytical data for **36s**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.01 (s, 2H), 7.77-7.80 (m, 2H), 8.10-8.13 (m, 2H).

Analytical data for 1,4-naphthoquinone **36s** were consistent with that reported in the literature.[181]

7.6.1.24 Iron-Catalyzed Benzylic Oxidation: Conversion of Triphenylmethane:



Triphenylmethane (**35v**) (488.6 mg, 2 mmol) was added to the solution of $FeCl_3 \cdot 6H_2O$ (10.8 mg, 0.1 mmol) in pyridine (2 mL). After the addition of TBHP (70% in H_2O; 824 μL, 6 mmol), the reaction mixture was heated at 82 ºC for 24 h. The mixture was then allowed to cool to room temperature and poured into a 1 N solution of aq. HCl (100 mL) in order to remove the pyridine. The organic phase was extracted with Et_2O (100 mL), washed with brine and dried over $MgSO_4$. After filtration, the solvents of the filtrate were evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = pentane) affording triphenylmethyl-*tert*-butylperoxide **36t** in 91% yield (606 mg).

Analytical data for **36t**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (s, 9H), 7.21-7.30 (m, 9H), 7.36-7.41 (m, 6H). ^{13}C NMR (75 MHz): δ = 143.6, 129.3, 127.3, 127.0, 79.7, 26.5. IR (KBr): υ = 2978, 2852, 1594, 1491, 1448, 1186, 1083, 745, 693 cm^{-1}.

Analytical data of triphenylmethyl-*tert*-butylperoxide **36t** were consistent with that reported in the literature.[182]

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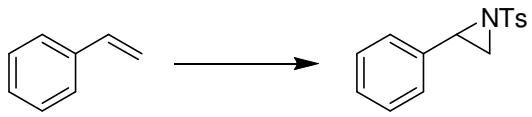
[181] M. H. Ali, M. Niedwalski, G. Bohnert, D. Bryant, *Synth. Commun.* **2006**, *36*, 1751.
[182] D. H. R. Barton, V. N. L. Gloahec, *Tetrahedron Lett.* **1998**, *54*, 15457.

7.6.2 Iron-Catalyzed Aziridination of Olefins:

7.6.2.1 Materials

Most starting materials were purchased from commercial suppliers and used without further purification. All of the silyl enol ethers were prepared according to the general procedure.[167] $Fe(OTf)_2$ and $Fe(OTf)_2$•2MeCN were prepared by the previously reported protocols respectively.[183] Dry acetonitrile was purchased from Fluka and Acros. Molecular sieves 3Å, 4Å, 5Å (powder) were purchased from Fluka and activated by the usual procedure.

7.6.2.2 Representative Procedure for the Aziridination with PhINTs: Conversion of Styrene:



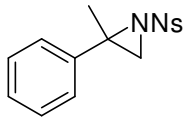
Styrene (997 mg, 1.1 mL, 10 mmol) was added to a solution of $Fe(OTf)_2$•2MeCN (21 mg, 0.01 mmol) and MS 4Å (10 mg) in MeCN (4 mL). After the addition of PhINTs (186.6 mg, 0.5 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ethyl acetate : pentane = 4 : 1) affording *N*-tosylphenyllaziridine **51a** in 90% yield (123 mg).

Analytical data for **51a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (d, J = 4.7 Hz, 1H), 2.43 (s, 1H), 2.98 (d, J = 7.1 Hz, 1H), 3.78 (dd, J = 7.1, 4.7 Hz, 2H), 7.20-7.23 (m, 2H), 7.26-7.30 (m, 3H), 7.31-7.35 (m, 2H), 7.85-7.89 (m, 2H). ^{13}C NMR (75 MHz): δ = 144.6, 129.7, 128.5, 128.3, 127.9, 126.5, 41.2, 36.1, 21.8.

Analytical data of *N*-tosyl-phenylaziridine **51a** were consistent with that reported in the literature.[85]

[183] a) J. S. Haynes, J. R. Sams, R. C. Thomson, *C. Can. J. Chem.* **1981**, *59*, 669. b) K. S. Hagen, *Inorg. Chem.* **2000**, *39*, 5867.

7.6.2.3 Iron-Catalyzed Aziridination with PhINNs: Conversion of α-Methylstyrene:

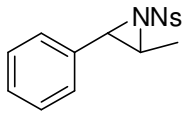


α-Methylstyrene (591mg, 650 μL, 5 mmol) was added to a solution of Fe(OTf)$_2$•2MeCN (2.6 mg, 0.00625 mmol) and MS 4Å (20 mg) in MeCN (2 mL). After the addition of PhINNs (101 mg, 0.25 mmol), the reaction mixture was stirred for 3 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; ethyl acetate : eluent = pentane = 5 : 1) affording *N*-nosyl-α-methylphenylaziridine **51e** in 46% yield (35 mg).

Analytical data for **51e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (d, *J* = 6.0 Hz, 3H), 3.06 (qd, *J* = 6.0, 4.4, Hz, 1H), 3.87 (d, *J* = 4.4 Hz, 1H), 7.10-7.17 (m, 2H), 7.22-7.30 (m, 3H), 8.11 (d, *J* = 8.9 Hz, 2H), 8.29 (d, *J* = 8.9 Hz, 2H).

Analytical data of *N*-nosyl-methylphenylaziridine **51e** were consistent with that reported in the literature.[97c]

7.6.2.4 Iron-Catalyzed Aziridination with PhINNs: Conversion of *trans*-β-Methylstyrene:

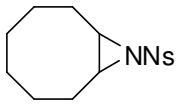


trans-β-Methylstyrene (593 mg, 652 μL, 5 mmol) was added to a solution of Fe(OTf)$_2$ (17.6 mg, 0.05 mmol) and MS 4Å (20 mg) in MeCN (4 mL). After the addition of PhINNs (101 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 5) affording *N*-nosyl-*trans*-methylphenylaziridine **51f** in 31% yield (25 mg).

Analytical data for **51f**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51 (d, J = 4.7 Hz, 1H), 3.11 (d, J = 7.1 Hz, 1H), 3.90 (dd, J = 7.1, 4.7 Hz, 2H), 7.20-7.23 (m, 2H), 7.29-7.34 (m, 3H), 7.31-7.35 (m, 2H), 8.16-8.21 (m, 2H), 8.35-8.40 (m, 2H).

Analytical data of *N*-nosyl-methylphenylaziridine **51f** were consistent with that reported in the literature.[97]

7.6.2.5 Iron-Catalyzed Aziridination with PhINTs: Conversion of *cis*-Octene:

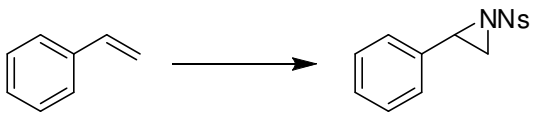


cis-Octene (553 mg, 650 μL, 5 mmol) was added to the solution of $Fe(OTf)_2$ (17.6 mg, 0.05 mmol) and MS 4Å (10 mg) in MeCN (4 mL). After the addition of PhINNs (101 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 6) affording *N*-nosylaziridine **51g** in 67% yield (52 mg).

Analytical data for **51g**: ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22-1.67 (m, 10H), 1.98-2.07 (m, 2H), 2.87-2.94 (m, J = 4.7 Hz, 2H), 8.14 (d, J= 4.7 Hz, 2H), 8.38 (d, J = 4.7 Hz, 2H).

Analytical data of *N*-nosyl-aziridine **51g** were consistent with that reported in the literature.[97]

7.6.2.6 Iron-Catalyzed Aziridination of Styrene with PhINNs:



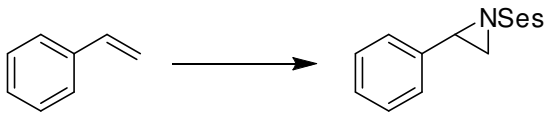
Styrene (432 mg, 0.55 mL, 5 mmol) was added to a solution of $Fe(OTf)_2 \cdot 2MeCN$ (2.6 mg, 0.01 mmol) and MS 4Å (10 mg) in MeCN (4 mL). After the addition of PhINNs (101 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary

evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 4 : 1) affording phenylaziridine **51b** in 88% yield (67 mg).

Analytical data for **51b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51 (d, *J* = 4.7 Hz, 1H), 3.11 (d, *J* = 7.1 Hz, 1H), 3.90 (dd, *J* = 7.1, 4.7 Hz, 2H), 7.20-7.23 (m, 2H), 7.29-7.34 (m, 3H), 7.31-7.35 (m, 2H), 8.16-8.21 (m, 2H), 8.35-8.40 (m, 2H).

Analytical data of *N*-nosyl-phenylaziridine **51b** were consistent with that reported in the literature.[94]

7.6.2.7 Iron-Catalyzed Aziridination of Styrene with PhINSes:

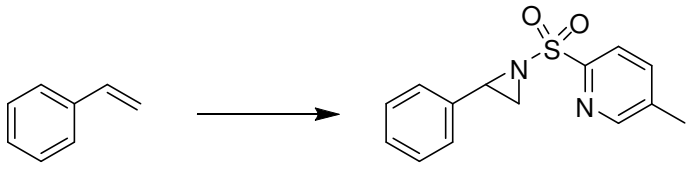


Styrene (432 mg, 0.55 mL, 2.5 mmol) was added to the solution of $Fe(OTf)_2$ (4.4 mg, 0.0125 mmol) and MS 4Å (10 mg) in MeCN (4 mL). After the addition of PhINSes (95.8 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 4 : 1) affording phenylaziridine **51c** in 65% yield (46 mg).

Analytical data for **51c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (s, 9H), 1.07-1.14 (m, 2H), 2.40 (d, *J* = 4.7 Hz, 1H), 2.96 (d, *J* = 7.2 Hz, 1H), 3.06 (m, 2H), 3.67 (dd, *J* = 7.2, 4.4 Hz, 1H), 7.25-7.38 (m, 5H).

Analytical data of *N*-trimethylethanesulfonyl-phenylaziridine **51c** were consistent with that reported in the literature.[84a]

7.6.2.8 Iron-Catalyzed Aziridination of Styrene with (5-Methyl-2-pyridinesulfonyl)iminophenyliodinane:

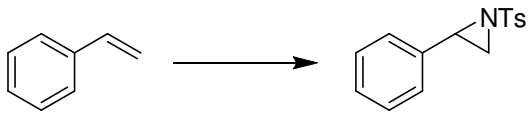


Styrene (432 mg, 0.55 mL, 5 mmol) was added to a solution of $Fe(OTf)_2$ (4.4 mg, 0.0125 mmol) and MS 4Å (20 mg) in MeCN (1 mL). After the addition of (5-methyl-2-pyridinesulfonyl)iminophenyliodinane (93.5 mg, 0.25 mmol), the reaction mixture was stirred for 0.5 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 2 : 3) affording *N*-5-methyl-2-pyridinesulfonyl-phenylaziridine **51d** in 87% yield (60 mg).

Analytical data for **51d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 2.49 (d, *J* = 4.7 Hz, 1H), 3.17 (d, *J* = 7.2 Hz, 1H), 3.24 (dd, *J* = 7.2, 4.7 Hz, 1H), 7.21-7.30 (m, 5H), 7.73-7.66 (m, 1H), 7.99-8.01 (m, 1H), 8.53-8.54 (m, 1H).

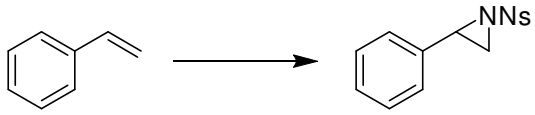
Analytical data for *N*-5-methyl-2-pyridinesulfonyl-phenylaziridine (**51d**) were consistent with the literature.[106]

7.6.2.9 Iron-Catalyzed Aziridination of Styrene with Iodobenzene diacetate and $TsNH_2$:



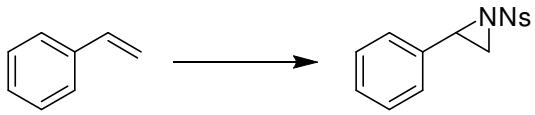
Iodobenzene diacetate (161 mg, 0.5 mmol) was added to a solution of $TsNH_2$ (43 mg, 0.25 mmol), MgO (50 mg, 1.25 mmol) and MS 4Å (400 mg) in MeCN (2 mL) and styrene (216 mg, 0.225 mL, 2.5 mmol). After the addition of $Fe(OTf)_2$ (17.6 mg, 0.1mmol) , the reaction mixture was stirred for 24 h. After filtration, the mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 5) affording *N*-tosylphenyaziridine **51a** in 60% yield (41 mg).

7.6.2.10 Iron-Catalyzed Aziridination of Styrene with Iodosylbenzene and $NsNH_2$:



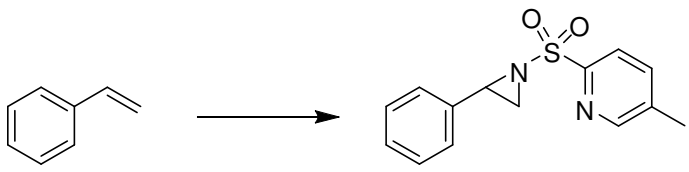
Iodosylbenzene (110 mg, 0.5 mmol) was added to the solution of $NsNH_2$ (50.5 mg, 0.25 mmol), MgO (50 mg, 1.25 mmol) and MS 4Å (300 mg) in MeCN (2 mL) and styrene (216 mg, 275 μL, 2.5 mmol). After the addition of $Fe(OTf)_2$ (17.6 mg, 0.05mmol) , the reaction mixture was stirred for 24 h. After filtration, the mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 4) affording *N*-nosylphenyaziridine **51b** in 60% yield (41 mg).

7.6.2.11 Iron-Catalyzed Aziridination of Styrene with Iodobenzene diacetate and $NsNH_2$:



Iodobenzene diacetate (161 mg, 0.5 mmol) was added to the solution of $NsNH_2$ (50.5 mg, 0.25 mmol), MgO (50 mg, 1.25 mmol) and MS 4Å (300 mg) in MeCN (2 mL) and styrene (216 mg, 225 μL, 5 mmol). After the addition of $Fe(OTf)_2$ (17.6 mg, 0.05 mmol) , the reaction mixture was stirred for 24 h. After filtration, the mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 4) affording *N*-nosylphenyaziridine **51b** in 80% yield (61 mg).

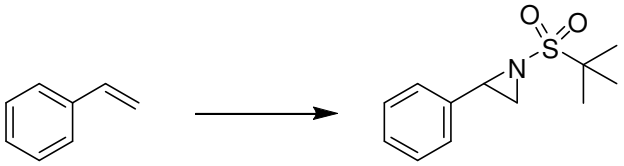
7.6.2.12 Iron-Catalyzed Aziridination of Styrene with Iodobenzene diacetate and 5-methyl-2-pyridinesulfonimide:



Iodobenzene diacetate (161 mg, 0.5 mmol) was added to a solution of 5-methyl-2-pyridinesulfonimide (43 mg, 0.25 mmol), MgO (60 mg, 1.5 mmol) and MS 4Å (400 mg) in MeCN (2 mL) and styrene (216 mg, 225 μL, 5 mmol). After the addition of $Fe(OTf)_2$ (8.8 mg, 0.025 mmol) , the reaction mixture was stirred for 24 h. After filtration, the mixture was

evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 2 : 3) affording *N*-5-methyl-2-pyridinesulfonyl-phenylaziridine (**51d**) in 76% yield (52 mg).

7.6.2.13 Iron-Catalyzed Aziridination of Styrene with Iodobenzene diacetate and sulfonimide 52e:

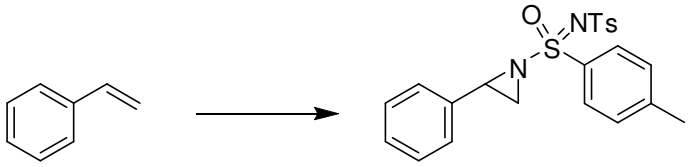


Iodobenzene diacetate (161 mg, 0.5 mmol) was added to a solution of *t*-butylsulfonamide **52e** (81 mg, 0.25 mmol), MgO (60 mg, 1.25 mmol) and MS 4Å (400 mg) in MeCN (2 mL) and styrene (520 mg, 550 μL, 5 mmol). After the addition of $Fe(OTf)_2$ (17.6 mg, 0.05 mmol), the reaction mixture was stirred for 24 h. After filtration, the mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 5 : 1) affording phenylaziridine **51h** in 50% yield (30 mg) as oil.

Analytical data for **51h**: Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.41 (s, 9H), 2.90 (d, *J* = 4.5 Hz, 1H), 2.18 (d, *J* = 4.5 Hz, 1H), 3.58 (dd, *J* = 7.2, 4.5 Hz, 1H), 7.18-7.38 (m, 5H). ^{13}C NMR (75 MHz): δ = 135.4, 128.7, 128.4, 126.4, 59.5, 41.6, 34.8, 24.2.

Analytical data of phenylaziridine **51h** were consistent with the literature.[184]

7.6.2.14 Iron-Catalyzed Aziridination of Styrene with Iodobenzene diacetate and sulfonimide 52f:



[184] A. V. Gontcharrov, H. Liu, K. B. Sharpless, *Org. Lett.* **1999**, *1*, 783.

Iodobenzene diacetate (161 mg, 0.5 mmol) was added to a solution of sulfonimide **52f** (81 mg, 0.25 mmol), MgO (60 mg, 1.25 mmol) and MS 4Å (400 mg) in MeCN (2 mL) and styrene (216 mg, 225 μL, 5 mmol). After the addition of $Fe(OTf)_2$ (17.6 mg, 0.05 mmol) , the reaction mixture was stirred for 24 h. After filtration, the mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 3 : 7) affording phenylaziridine **51i** in 58% yield (62 mg) as mixture of diastereomers (7 : 3).

Analytical data for **51i**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 2.39 (s, 3H), 2.44 (s, 6H), 2.58 (d, *J* = 4.8 Hz, 0.7H), 3.12 (d, *J* = 7.6 Hz, 0.3H), 3.24 (dd, *J* = 7.6 Hz, 0.3H), 3.84 (dd, *J* = 7.6, 4.8 Hz, 0.7H), 3.98 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.20 (m, 18H), 7.82 (m, 8H).

Analytical data of phenylaziridine **51i** were consistent with the literature.[88]

7.6.2.15 Iron-Catalyzed Asymmetric Aziridination of Styrene with PhINTs:

Styrene (528 mg, 550 μL, 5 mmol) was added to the solution of $Fe(OTf)_2 \cdot 2MeCN$ (21 mg, 0.01 mmol), (*S*,*S*)-2,6-bis(4-isopropyl-2-oxazolin-2-yl)pyridine (22.5 mg, 0.075 mmol) and MS 4Å (10 mg) in MeCN (1 mL). After the addition of PhINTs (93.3 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 4) affording *N*-tosylphenylaziridine (**51a**) in 72% yield (49 mg).

HPLC: (Chiralcel AS, heptane/*i*-propanol = 75:25, 0.55 mL/min, 254 nm): t_R = 18 [minor] and 20 [major] min (40% *ee*).

Analytical data of *N*-tosyl-phenyaziridine (**51a**) were consistent with the literature.[84a]

7.6.2.16 Iron-Catalyzed Asymmetric Aziridination of Styrene with PhINNs:

Styrene (498 mg, 0.5 mL, 5 mmol) was added to the solution of $Fe(OTf)_2 \cdot 2MeCN$ (21 mg, 0.01 mmol), (*S*,*S*)-2,6-bis(4-isopropyl-2-oxazolin-2-yl)pyridine (22.5 mg, 0.075 mmol) and MS 4Å (10 mg) in MeCN (4 mL). After the addition of PhINNs (101 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The

remaining mixture was separated by column chromatography (silica gel; diethyl ethyl acetate : pentane = 1 : 4 as eluent) affording **51b** in 74% yield (123 mg).

HPLC**:** (Chiralcel OJ, heptane/*i*-propanol = 1 : 1, 0.7 mL/min, 254 nm): t_R =53.5 [major] and 78.2 [minor] min (2% *ee*).

Analytical data of *N*-nosyl-phenyaziridine were consistent with the literature.[84a]

7.6.2.17 Iron-Catalyzed Asymmetric Aziridination of Styrene with PhINSes:

Stryrene (997 mg, 1.1 mL, 0.5 mmol) was added to a solution of Fe(OTf)·2MeCN (21 mg, 0.01 mmol), (*S*,*S*)-2,6-bis(4-isopropyl-2-oxazolin-2-yl)pyridine (22.5 mg, 0.075 mmol) and MS 4Å (20 mg) in MeCN (4 mL). After the addition of PhINSes (95.8 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 4) affording *N*-trimethylethanesulfonyl-phenyaziridine (**51c**) in 73% yield (52 mg).

HPLC: (Chiralcel OJ, heptane/*i*-propanol = 97:3, 1.0 mL/min, 254 nm): t_R = 18 [major] and 24 [minor] min (20% ee).[213]

Analytical data for **51c** were consistent with the literature.[84a]

7.6.2.18 Iron-Catalyzed Epoxidation of Styrene with Iodosylbenzene:

Iodosylbenzene (101 mg, 0.5 mmol) was added to a solution of MS 4Å (400 mg) and stryrene (498 mg, 0.55 mL, 5 mmol) in MeCN (2 mL). After the addition of $Fe(OTf)_2$ (8.8 mg, 0.025 mmol) , the reaction mixture was stirred for 24 h. After filtration, the mixture was evaporated (rotary evaporator). The remaining mixture was filtlated through silica gel affording crude phenyloxirane **97** (mixture with styrene).

Analytical data for **97**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.80 (dd, *J* = 5.4, 2.4 Hz, 1H), 3.06 (d, *J* = 5.4, 4.1 Hz, 1H), 3.84 (dd, *J* = 4.1, 2.4 Hz, 1H), 7.25-7.27.37 (m, 5H). ^{13}C NMR (75 MHz): δ = 137.4, 128.5, 128.2, 125.5, 52.5, 51.3.

7.6.2.19 Iron-Catalyzed Imination of Sulfide with PhINTs:

Thioanisole **92** (38.5 mg, 58.7 μL, 0.5 mmol) was added to the solution of Fe(OTf)$\cdot$2MeCN (2.6 mg, 0.00625 mmol) and MS 4Å (20 mg) in MeCN (4 mL). After the addition of PhINTs (93.3 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 3 : 1 then ethyl acetate) affording *N*-tosyl-methyl-phenyl-sulfilimine **93** in 98% yield (67 mg).

Analytical data for **93**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.81 (s, 3H), 7.14-7.24 (m, 2H), 7.45-7.54 (m, 3H), 7.64-7.69 (m, 2H), 7.65-7.53 (m, 2H). ^{13}C NMR (75 MHz): δ = 141.7, 132.4, 123.0, 129.2, 126.2, 125.8, 39.2, 21.5. MS (EI, 70 eV): *m/z* (%) = 293 (M^+).

Analytical data of *N*-tosyl-methyl-phenyl-sulfilimine **93** were consistent with the literature.[135d]

7.6.2.20 Iron-Catalyzed Asymmetric Imination of Sulfide with PhINTs:

Thioanisole **92** (38.5 mg, 58.7 μL, 0.5 mmol) was added to the solution of Fe(OTf)$\cdot$2MeCN (2.6 mg, 0.00625 mmol), chiral ligand (5.2 mg, 0.0125 mmol) and MS 4Å (20 mg) in MeCN (4 mL). After the addition of PhINTs (93.3 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 3 : 1 then ethyl acetate) affording *N*-tosyl-methyl-phenyl-sulfilimine **93** in 89% yield (65 mg).

HPLC: (Chiralcel OJ, heptane/*i*-propanol = 80:20, 1.0 mL/min, 254 nm): t_R = 37 and 56 min (0% ee).[133d]

7.6.2.21 Iron-Catalyzed Imination of Sulfoxide with PhINNs:

Methylphenylsulfoxide **94** (38.5 mg, 44.8 μL, 0.5 mmol) was added to the solution of Fe(OTf)$\cdot$2MeCN (2.6 mg, 0.00625 mmol) and MS 4Å (20 mg) in MeCN (4 mL). After the addition of PhINNs (101 mg, 0.25 mmol), the reaction mixture was stirred for 1 h. The

mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 1 then ethyl acetate) affording *N*-tosyl-methyl phenyl sulfoximine **95** in 98% yield (83 mg).

Analytical data for **95**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.45 (s, 3H), 7.60-7.66 (m, 2H), 7.70-7.76 (m, 1H), 7.97-7.8.03 (m, 2H), 8.11-8.16 (m, 2H), 8.26-8.32 (m, 2H).

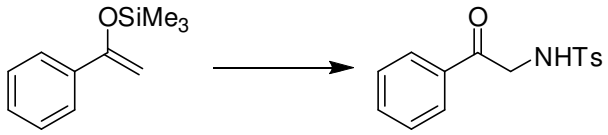
Analytical data of *N*-tosyl-methylphenylsulfoximine **95** were consistent with the literature.[137]

7.6.3 Iron-Catalyzed α-Amination of Silyl Enol Ethers:

7.6.3.1 Materials

Most starting materials were purchased from commercial suppliers and used without further purification. Enol silanes were prepared by general procedures (Chapter 7.5). Dry acetonitrile was purchased from Fluka or Acros.

7.6.3.2 Iron-Catalyzed α-Amination of Trimethyl(1-phenylvinyloxy)silane:

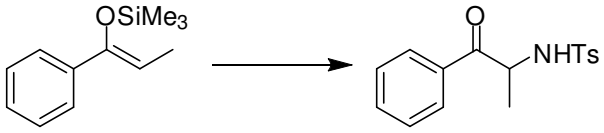


Silyl enol ether **55a** (96 mg, 101 mL, 0.5 mmol) was added to the solution of Fe(OTf)·2MeCN (2,6 mg, 0.006 mmol) and MS 4Å (10 mg) in MeCN (1 mL). After the addition of PhINTs (93.3 mg, 0.25 mmol) at room temperature, the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = diethyl ether : pentane = 1 : 5) affording *N*-tosyl-α-amino ketone **56a** in 72% yield (52 mg).

Analytical data for **56a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 4.30 (d, J = 4.4, 2H), 5.62 (brd, 1H), 7.25-7.32 (m, 2H), 7.42-7.48 (m, 2H), 7.56-7.62 (m, 1H), 7.74-7.85 (m, 4H). MS (EI, 70 eV): *m/z* (%) = 289 (M^+).

Analytical data of α-amino ketone **56a** were consistent with that reported in the literature.[90]

7.6.3.3 Iron-Catalyzed α-Amination of (*Z*)-Trimethyl(1-phenylprop-1-enyloxy)silane:

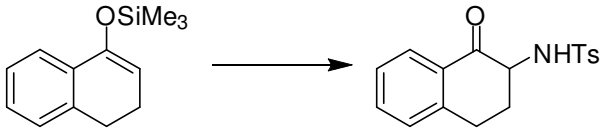


Silyl enol ether **55b** (51.5 mg, 56.7 µL, 0.25 mmol) was added to the solution of $Fe(OTf)_2 \cdot 2MeCN$ (2,6 mg, 0.006 mmol) and MS 4Å (10 mg) in MeCN (1 mL). After the addition of PhINTs (93.3 mg, 0.25 mmol) at room temperature, the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 5) affording *N*-tosyl-*α*-amino ketone **56b** in 65% yield (48 mg).

Analytical data for **56b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.40 (d, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 4.93 (dt, *J* = 8.2, 7.2 Hz, 1H), 5.80 (d, *J* = 8.2, 1H), 7.15-7.19 (m, 1H), 7.40-7.48 (m, 1H), 7.57-7.62 (m, 1H), 7.66-7.71 (m, 1H), 7.74-7.79 (m, 1H). ^{13}C NMR (75 MHz): δ = 198.1, 143.5, 137.0, 134.1, 133.4, 129.7, 128.9, 128.5, 127.1, 53.3, 21.4, 21.1.

Analytical data of *N*-tosyl-*α*-amino ketone **56b** was refered to literature.[90]

7.6.3.4 Iron-Catalyzed α-Amination of (3,4-Dihydronaphthalen-1-yloxy)trimethylsilane 50c:



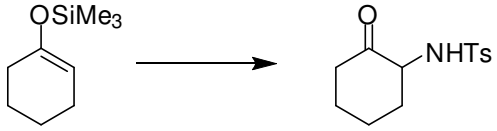
Silyl enol ether **55c** (60.9 mg, 0.275 mmol) was added to the solution of $Fe(OTf)_2$ (4.4 mg, 0.0125 mmol) and MS 4Å (20 mg) in MeCN (1 mL). After the addition of PhINTs (93.3 mg, 0.25 mmol) at room temperature, the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column

chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 5) affording *N*-tosyl-α-amino ketone **56c** in 65% yield (48 mg).

Analytical data for **56c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.67 (dd, *J* = 6.3, 6.0 Hz, 2H), 2.97 (d, *J* = 6.0 Hz, 2H), 2.15 (t, *J* = 6.3 Hz, 2H), 5.97 (s, 1H), 7.15-7.18 (m, 1H) 7.20-7.27 (m, 3H), 7.40-7.46 (m, 1H), 7.71-7.76 (m, 2H), 7.85-7.88 (m, 1H).

Analytical data for *N*-tosyl-α-amino ketone **56c** were consistent with the literature.[110]

7.6.3.5 Iron-Catalyzed α-Amination of Cyclohexenyloxytrimethylsilane:

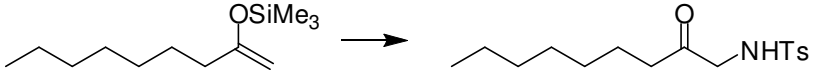


Silyl enol ether **55d** (63.9 mg, 0.375 mmol) was added to a solution of $Fe(OTf)_2$ (4.4 mg, 0.025 mmol) and MS 4Å (10 mg) in MeCN (1 mL) at 0 °C. After the addition of PhINTs (93.3 mg, 0.25 mmol), the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 5) affording *N*-tosyl-α-amino ketone **56d** in 63% yield (48 mg).

Analytical data for **56d**: ^{1}H NMR (400 MHz): δ = 1.30-2.70 (m, 8H), 2.42 (s, 3H), 3.65-3.73 (m, 1H), 5.82 (d, *J* = 4.4 Hz, 1H), 7.10- 7.90(m, 4H).

Analytical data of *N*-tosyl-α-amino ketone **56d** were consistent with that reported in the literature.[110]

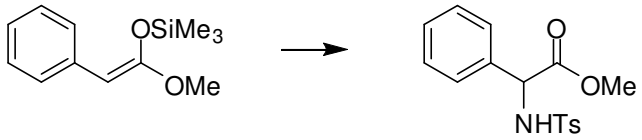
7.6.3.6 Iron-Catalyzed α-Amination of Trimethyl(non-1-en-2-yloxy)silane:



Silyl enol ether **55e** (80.4 mg, 0.375 mmol) was added to a solution of $Fe(OTf)_2$ (4.4 mg, 0.0125 mmol) and MS 4Å (10 mg) in MeCN (1 mL). After the addition of PhINTs (93.3 mg, 0.25 mmol) at room temperature, the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 5) affording α-amino ketone **56e** in 46% yield (36 mg).

Analytical data for **56e**: m.p 104-107 ºC, ^{1}H NMR (400 MHz): δ = 2.40 (t, J = 6.7 Hz 3H), 1.09-1.25 (m, 8H), 1.43 (quint, J = 7.4 Hz, 2H), 3.63 (t, J = 7.4 Hz, 2H), 2.35 (s, 3H), 3.75 (d, J = 4.7 Hz, 2H), 5.25 (t, J = 4.7 Hz, 1H), 7.20-7.26 (d, 2H), 7.62-7.69 (m, 2H). ^{13}C NMR (75 MHz): δ = 203.8, 143.8, 136.0, 129.8, 127.2, 51.3, 40.1, 31.5, 28.9, 23.6, 22.6, 21.5, 14.0. MS (EI, 70 eV): *m/z* (%) = 309 (M^{2+}); IR (KBr): υ = 3273, 2931, 2856, 1722, 1321, 1160, 691 cm^1; anal. calcd. for $C_{16}H_{25}NO_3S$ (311.44): C 61.70, H 8.09, N 4.50; found: C 61.94, H 8.19, N 4.44.

7.6.3.7 Iron-Catalyzed α-Amination of (*Z*)-(1-Methoxy-2-phenylvinyloxy)trimethylsilane:

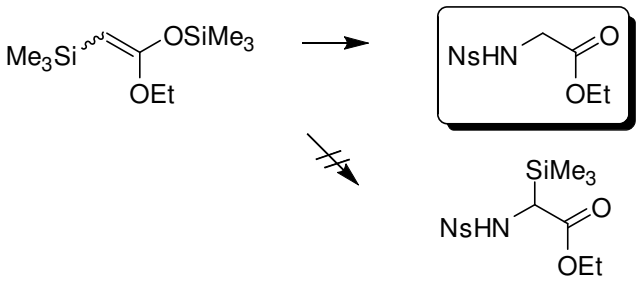


Silyl enol ether **55f** (61 mg, 0.275 mmol) was added to the solution of $Fe(OTf)_2$ (4.4 mg, 0.0125 mmol) and MS 4Å (20 mg) in MeCN (1 mL). After the addition of PhINTs (93.3 mg, 0.25 mmol) at room temperature, the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = ethyl acetate : pentane = 1 : 4) affording *N*-tosyl-α-amino acid methyl ester **56f** in 50% yield (40 mg).

Analytical data for **56f**: ^{1}H NMR (400 MHz): δ = 2.35 (s, 3H), 3.54 (s, 3H), 5.03 (d, J = 7.8 Hz, 1H), 5.64 (d, J = 7.8 Hz, 1H), 7.22 (m, 7H), 7.59 (d, J = 6.7Hz, 2H).

Analytical data of *N*-tosyl-α-amino acid methyl ester **56f** were consistent with that reported in the literature.[185]

7.6.3.8 Iron-Catalyzed Aziridination of (*E/Z*)-(1-ethoxy-2-(trimethylsilyl)vinyloxy)trimethylsilane:



Silyl enol ether **55h** (61 mg, 0.275 mmol) was added to a solution of $Fe(OTf)_2$ (4.4 mg, 0.0125 mmol) and MS 4Å (20 mg) in MeCN (1 mL). After the addition of PhINNs (101 mg, 0.25 mmol) at room temperature, the reaction mixture was stirred for 1 h. The mixture was evaporated (rotary evaporator). The remaining mixture was separated by column chromatography (silica gel; eluent = chloroform : MeOH = 50 : 1) affording *N*-nosyl-α-amino acid ethyl ester **56h** in 17% yield (40 mg) and nosylamide was recovered (83%).

Analytical data for **56h**: ^{1}H NMR (400 MHz): δ = 1.14 (t, *J*= 7.1 Hz, 3H), 3.79 (d, *J*= 7.1 Hz, 2H), 5.26 (t, *J* = 4.4 Hz, 1H) 7.78 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H).

Analytical data of *N*-nosyl-α-amino acid ethyl ester **56h** were consistent with that reported in the literature.[186]

[185] a) K. Kobayashi, T. Okamoto, T. Oida, S. Tanimoto, *Chem. Lett.* **1986**, *12*, 2031. b) D. J. Wallace, J. M. Goodman, D. J. Kennedy, A. J. Davies, C. J. Cowden, M. S. Ashwood, I. F. Cottrell, U.-H. Dolling, P. J. Reider, *Org. Lett*. **2001**, *3*, 671.
[186] T. Hoffmann, R. Waibel, P. Gmeiner, *J. Org. Chem*. **2003**. *68*, 62.

8 Additional Data

8.1 X-ray Structure of Metal Complexes

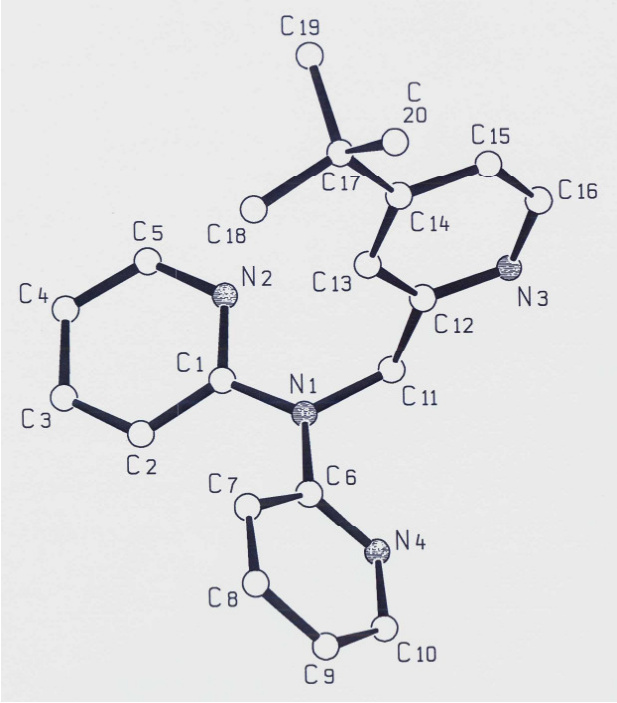
8.1.1 Definition [187]

$$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a_i}\,\boldsymbol{a_j}$$

The anisotropic displacement factor in the structure factor expression is:

$$t = \exp[-2\pi^2(\Sigma_i\Sigma_j U_{ij} h_i h_j a_i^* a_j^*)]$$

8.1.2 X-ray Structure of *N*,*N*- Dipyridyl-4-*tert*-butylpicolylamine 87:



Experimental Details

Crystal data:

Chemical formula : $C_{20}H_{22}N_4$

[187] Larson, A.C. In *Crystallographic Computing*, Ahmed, F. R.; Hall, S. R.; Huber, C. P., Hrsg.; Munksgaard, Copenhagen 1970, S. 291-294. (b) Zachariasen, W. H. *Acta Cryst*. **1967**, *23*, 558. (c) Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876. (d) *XTAL3.4 User's Manual*, Hall, S. R.; King, G. S. D.; Steward, J. M., Hrsg.; Lamb, Perth, 1995, Hall, S. R.; du Boulay, D. J. Olthof-Hazekamp, R., Hrsg.; *XTAL3.7 System*, University of Wesern Australia, Perth 2000.

formula weight	:	318.42
Crystal system	:	orthorhombic
Space group (No.)	:	$P2_12_12_1$ (19)
Z	:	4
a (Å)	:	8.2189(5)
b (Å)	:	12.566(5)
c (Å)	:	16.830(1)
α (°)	:	90.0
β (°)	:	90.0
γ (°)	:	90.0
cell volume	:	1738.2(7)Å^3
Density calc.	:	1.217g/cm^3
Radiation	:	CuKα (1.54179Å)
Range for lattice parameters	:	15.23E<Θ <18.67E
Absorption coefficient	:	0.576mm^{-1}
Temperature	:	298K
Crystal source	:	recrystallized from CH_2Cl_2 and Et_2O
Crystal colour	:	colourless
Crystal shape	:	irregular
Crystal size	:	ca. 0.3x0.3.x0.3mm

Data Collection

Diffractometer type	:	Enraf-Nonius CAD4
collection method	:	$\omega/2\vartheta$ scans
Absorption correction	:	none
No. of reflections measured	:	3638
No. of independent reflections:		3125
No. of observed reflections	:	2964
Θ_{max} (E)	:	67.87
h_{min} 6 h_{max}	:	- 9 6 9
k_{min} 6 k_{max}	:	- 13 6 15
l_{min} 6 l_{max}	:	- 20 6 20

Criterion for observed	:	$I > 2\sigma(I)$
R_{int}	:	0.048(46)
Standard reflections	:	2 1 5, -2 1 5, -2 -1 5
Variation	:	2661(96) 2970(107) 2826(124)
Refinement:		
On	:	*F*
Treatment of hydrogens	:	21 located. 1 calculated. 15 refined isotropically.
R	:	0.051
R_w	:	0.065
Weighting scheme	:	$w=1/\sigma^2(F)$
No. of parameters refined	:	286
No. of reflections in refmnt.	:	2953
Residual electron density	:	-0.23/0.28e/Å^3
r*[1]	:	not refined
XABS[2][a)]	:	-0.060(1.522) not significant!
Goodness of fit	:	2.326
Solution	:	XTAL3.7[3]
Remarks		[a)]From separate calculation

Atomic Positional and Isotropic Displacement Parameters

Atom	x/a	y/b	z/c	U_{eq}/Å^2
N1	0.3691(2)	0.4027(2)	0.5025(1)	* 0.048(1)
N2	0.4240(3)	0.5030(2)	0.3909(1)	* 0.055(1)
N3	0.7078(2)	0.5301(2)	0.6095(1)	* 0.054(1)
N4	0.3225(3)	0.2687(2)	0.5945(1)	* 0.051(1)
C1	0.3253(3)	0.4332(2)	0.4262(1)	* 0.044(1)
C2	0.1884(3)	0.3909(2)	0.3870(2)	* 0.048(1)
C3	0.1586(3)	0.4204(2)	0.3105(2)	* 0.056(2)
C4	0.2610(4)	0.4934(3)	0.2727(2)	* 0.064(2)
C5	0.3914(4)	0.5311(3)	0.3153(2)	* 0.063(2)
C6	0.2620(3)	0.3501(2)	0.5545(1)	* 0.043(1)
C7	0.1026(3)	0.3855(2)	0.5657(2)	* 0.050(1)
C8	0.0039(3)	0.3344(2)	0.6176(2)	* 0.055(2)
C9	0.0640(4)	0.2480(3)	0.6595(2)	* 0.058(2)
C10	0.2234(4)	0.2180(3)	0.6459(2)	* 0.060(2)
C11	0.5353(3)	0.4194(2)	0.5298(2)	* 0.048(1)
C12	0.5612(3)	0.5234(2)	0.5747(1)	* 0.042(1)
C13	0.4463(3)	0.6032(2)	0.5789(1)	* 0.042(1)
C14	0.4797(3)	0.6967(2)	0.6182(1)	* 0.043(1)
C15	0.6333(3)	0.7047(3)	0.6529(2)	* 0.054(2)
C17	0.3613(3)	0.7916(2)	0.6215(2)	* 0.054(1)
C16	0.7396(3)	0.6212(3)	0.6470(2)	* 0.059(2)
C18	0.1912(4)	0.7588(3)	0.5947(3)	* 0.087(3)
C19	0.4252(6)	0.8784(3)	0.5653(2)	* 0.079(2)
C20	0.3512(5)	0.8384(3)	0.7050(2)	* 0.069(2)
H4	0.239(4)	0.524(3)	0.214(2)	0.075(9)
H11a	0.600(4)	0.417(3)	0.485(2)	0.066(9)
H11b	0.578(3)	0.364(2)	0.567(2)	0.051(7)
H13	0.344(3)	0.591(2)	0.558(1)	0.040(6)
H16	0.852(4)	0.622(3)	0.669(2)	0.08(1)
H20c	0.265(4)	0.895(3)	0.717(2)	0.062(8)
H3	0.065(3)	0.381(2)	0.280(2)	0.059(8)
H7	0.070(3)	0.434(2)	0.538(2)	0.047(8)
H2	0.127(4)	0.354(3)	0.413(2)	0.062(9)
H15	0.667(4)	0.752(3)	0.686(2)	0.09(1)
H20b	0.459(5)	0.868(3)	0.734(2)	0.10(1)
H10	0.261(5)	0.146(3)	0.670(2)	0.10(1)
H19a	0.333(7)	0.913(5)	0.539(3)	0.17(2)
H5	0.474(4)	0.582(3)	0.287(2)	0.09(1)
H19b	0.527(5)	0.891(3)	0.585(2)	0.09(1)
H8	-0.110(4)	0.372(3)	0.626(2)	0.074(9)
H9	0.0000(-)	0.2097(-)	0.7106(-)	0.064(-)
H18a	0.1285(-)	0.6918(-)	0.6333(-)	0.120(-)
H18b	0.1214(-)	0.8203(-)	0.5954(-)	0.121(-)
H18c	0.1968(-)	0.7339(-)	0.5408(-)	0.121(-)
H19c	0.4066(-)	0.8440(-)	0.5133(-)	0.108(-)
H20a	0.3194(-)	0.7732(-)	0.7313(-)	0.103(-)

Atomic Displacement Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1	0.045(1)	0.045(1)	0.054(1)	−0.0013(9)	−0.0058(9)	−0.001(1)
N2	0.058(1)	0.049(1)	0.058(1)	−0.007(1)	−0.001(1)	0.002(1)
N3	0.042(1)	0.066(2)	0.055(1)	0.005(1)	−0.009(1)	−0.004(1)
N4	0.050(1)	0.052(1)	0.051(1)	0.006(1)	−0.0063(9)	0.004(1)
C1	0.049(1)	0.036(1)	0.048(1)	−0.000(1)	−0.002(1)	−0.006(1)
C2	0.048(1)	0.040(1)	0.056(1)	−0.005(1)	−0.000(1)	−0.006(1)
C3	0.057(2)	0.055(2)	0.056(1)	0.000(1)	−0.007(1)	−0.011(1)
C4	0.074(2)	0.066(2)	0.051(1)	−0.004(2)	−0.003(1)	0.001(1)
C5	0.070(2)	0.060(2)	0.059(2)	−0.009(2)	0.003(2)	0.005(1)
C6	0.050(1)	0.035(1)	0.042(1)	−0.001(1)	−0.007(1)	−0.005(1)
C7	0.053(1)	0.044(1)	0.055(1)	0.011(1)	−0.006(1)	−0.001(1)
C8	0.049(1)	0.058(2)	0.058(1)	0.003(1)	−0.003(1)	−0.003(1)
C9	0.060(2)	0.067(2)	0.048(1)	−0.003(1)	−0.001(1)	−0.003(1)
C10	0.068(2)	0.060(2)	0.054(1)	0.006(1)	−0.008(1)	0.006(1)
C11	0.042(1)	0.043(1)	0.061(1)	0.005(1)	−0.005(1)	−0.006(1)
C12	0.040(1)	0.045(1)	0.041(1)	−0.004(1)	−0.0020(9)	0.004(1)
C13	0.039(1)	0.045(1)	0.043(1)	−0.001(1)	−0.0041(9)	0.001(1)
C14	0.045(1)	0.047(1)	0.038(1)	−0.002(1)	−0.001(1)	0.001(1)
C15	0.051(1)	0.058(2)	0.053(1)	−0.006(1)	−0.007(1)	−0.011(1)
C16	0.045(1)	0.071(2)	0.061(1)	−0.000(1)	−0.014(1)	−0.016(2)
C17	0.057(1)	0.050(2)	0.056(1)	0.003(1)	−0.002(1)	−0.005(1)
C18	0.057(2)	0.069(2)	0.136(3)	0.016(2)	−0.020(2)	−0.027(2)
C19	0.104(3)	0.060(2)	0.072(2)	0.017(2)	0.002(2)	0.009(2)
C20	0.081(2)	0.056(2)	0.070(2)	0.012(2)	0.008(2)	−0.012(2)
H4	0.075(9)					
H11a	0.066(9)					
H11b	0.051(7)					
H13	0.040(6)					
H16	0.08(1)					

H20c	0.062(8)
H3	0.059(8)
H7	0.047(8)
H2	0.062(9)
H15	0.09(1)
H20b	0.10(1)
H10	0.10(1)
H19a	0.17(2)
H5	0.09(1)
H19b	0.09(1)
H8	0.074(9)
H9	0.064(-)
H18a	0.120(-)
H18b	0.121(-)
H18c	0.121(-)
H19c	0.108(-)
H20a	0.103(-)

Bond Distances	(Angstroms)
N1-C1	1.388(3)
N1-C6	1.406(3)
N1-C11	1.457(3)
N2-C1	1.334(3)
N2-C5	1.347(4)
C12-N3	1.342(3)
C12-C13	1.379(3)
C12-C11	1.526(4)
N4-C6	1.321(3)
N4-C10	1.349(4)
N3-C16	1.333(4)
C6-C7	1.396(4)
C13-H13	.93(2)
C13-C14	1.376(4)
C1-C2	1.409(4)
C14-C15	1.395(4)
C14-C17	1.540(4)
C11-H11a	.92(3)
C11-H11b	1.00(3)
C7-H7	.81(3)
C7-C8	1.354(4)
C2-H2	.81(3)
C2-C3	1.361(4)
C3-H3	1.05(3)
C3-C4	1.398(4)
C15-H15	.86(4)
C15-C16	1.368(4)
C8-H8	1.06(3)
C8-C9	1.385(4)
C9-H9	1.117(3)
C9-C10	1.383(4)
C10-H10	1.04(4)
C5-H5	1.05(4)
C5-C4	1.373(5)
C17-C20	1.525(4)
C17-C18	1.526(4)
C17-C19	1.537(5)
C16-H16	1.00(3)
C20-H20a	.966(3)
C20-H20c	1.02(3)
C20-H20b	1.07(4)
C4-H4	1.08(3)
C18-H18c	.960(4)
C18-H18b	.963(4)
C18-H18a	1.182(4)
C19-H19b	.91(4)
C19-H19a	.97(6)
C19-H19c	.987(4)

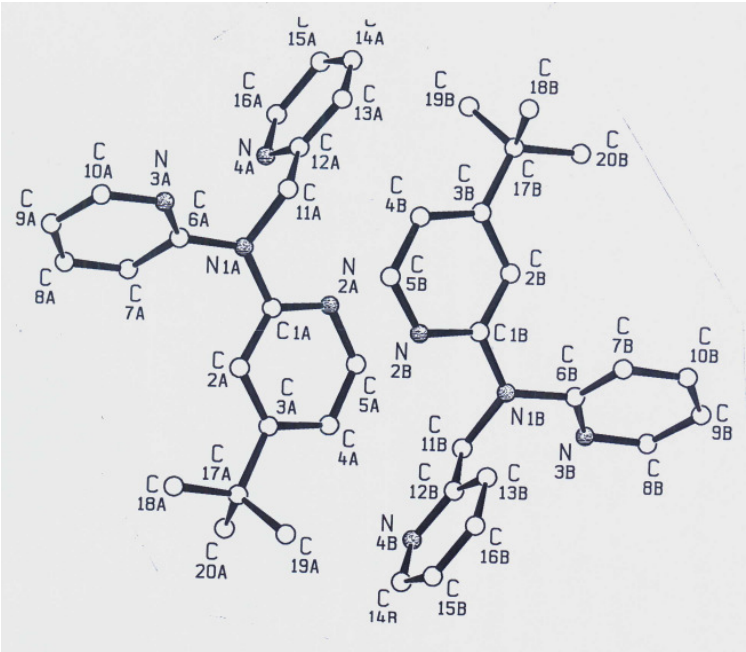
Bond Angles	(degrees)
C1-N1-C6	122.9(2)
C1-N1-C11	119.7(2)
C6-N1-C11	117.2(2)
C1-N2-C5	118.1(2)
N3-C12-C13	123.2(2)
N3-C12-C11	113.2(2)
C13-C12-C11	123.6(2)
C6-N4-C10	117.7(2)
C16-N3-C12	115.8(2)
N4-C6-C7	122.1(2)
N4-C6-N1	116.5(2)
C7-C6-N1	121.4(2)
H13-C13-C14	120(2)
H13-C13-C12	119(2)
C14-C13-C12	120.6(2)
N2-C1-N1	115.8(2)
N2-C1-C2	121.7(2)
N1-C1-C2	122.4(2)
C13-C14-C15	116.3(2)
C13-C14-C17	123.6(2)
C15-C14-C17	120.1(2)
H11a-C11-H11b	107(3)
H11a-C11-N1	106(2)
H11a-C11-C12	111(2)
H11b-C11-N1	115(2)
H11b-C11-C12	104(2)
N1-C11-C12	114.2(2)
H7-C7-C8	122(2)
H7-C7-C6	118(2)
C8-C7-C6	119.9(3)
H2-C2-C3	123(2)
H2-C2-C1	117(2)
C3-C2-C1	118.9(2)
H3-C3-C2	118(2)
H3-C3-C4	122(2)
C2-C3-C4	120.0(3)
H15-C15-C16	112(2)
H15-C15-C14	128(2)
C16-C15-C14	119.5(3)
H8-C8-C7	113(2)
H8-C8-C9	127(2)
C7-C8-C9	119.1(3)
H9-C9-C10	117.1(3)
H9-C9-C8	124.2(3)
C10-C9-C8	117.9(3)
H10-C10-N4	119(2)
H10-C10-C9	117(2)
N4-C10-C9	123.3(3)
H5-C5-N2	117(2)
H5-C5-C4	119(2)
N2-C5-C4	123.9(3)
C20-C17-C18	109.1(3)
C20-C17-C19	108.2(3)
C20-C17-C14	111.5(2)
C18-C17-C19	108.8(3)
C18-C17-C14	111.0(2)
C19-C17-C14	108.1(3)
H16-C16-N3	111(2)

H16–C16–C15	124(2)
N3–C16–C15	124.6(3)
H20a–C20–H20c	108(2)
H20a–C20–H20b	108(2)
H20a–C20–C17	96.3(3)
H20c–C20–H20b	104(3)
H20c–C20–C17	119(2)
H20b–C20–C17	121(2)
H4–C4–C5	119(2)
H4–C4–C3	123(2)
C5–C4–C3	117.3(3)
H18c–C18–H18b	107.6(4)
H18c–C18–H18a	108.0(3)
H18c–C18–C17	108.9(3)
H18b–C18–H18a	107.8(3)
H18b–C18–C17	109.0(3)
H18a–C18–C17	115.4(3)
H19b–C19–H19a	143(4)
H19b–C19–H19c	122(3)
H19b–C19–C17	102(3)
H19a–C19–H19c	71(3)
H19a–C19–C17	109(3)
H19c–C19–C17	100.5(3)

Dihedral Angles	(degrees)
C1-N1-C6-N4	136.0(2)
C1-N1-C6-C7	-46.9(3)
C11-N1-C6-N4	-40.4(3)
C11-N1-C6-C7	136.8(3)
C6-N1-C1-N2	165.0(2)
C6-N1-C1-C2	-17.0(4)
C11-N1-C1-N2	-18.7(3)
C11-N1-C1-C2	159.2(2)
C6-N1-C11-C12	-89.6(3)
C6-N1-C11-H11a	148(2)
C6-N1-C11-H11b	30(2)
C1-N1-C11-C12	94.0(3)
C1-N1-C11-H11a	-28(2)
C1-N1-C11-H11b	-146(2)
C5-N2-C1-N1	176.7(2)
C5-N2-C1-C2	-1.2(4)
C1-N2-C5-C4	1.0(5)
C1-N2-C5-H5	-176(2)
C13-C12-N3-C16	-2.2(4)
C11-C12-N3-C16	177.4(2)
N3-C12-C13-C14	1.8(4)
N3-C12-C13-H13	-174(2)
C11-C12-C13-C14	-177.7(2)
C11-C12-C13-H13	7(2)
N3-C12-C11-N1	170.6(2)
N3-C12-C11-H11a	-70(2)
N3-C12-C11-H11b	44(2)
C13-C12-C11-N1	-9.8(4)
C13-C12-C11-H11a	110(2)
C13-C12-C11-H11b	-136(2)
C10-N4-C6-N1	178.8(2)
C10-N4-C6-C7	1.7(4)
C6-N4-C10-C9	-1.1(4)
C6-N4-C10-H10	169(2)
C12-N3-C16-C15	1.3(4)
C12-N3-C16-H16	-178(2)
N1-C6-C7-C8	-178.5(2)
N1-C6-C7-H7	6(2)
N4-C6-C7-C8	-1.6(4)
N4-C6-C7-H7	-177(2)
C12-C13-C14-C15	-.3(4)
C12-C13-C14-C17	176.6(2)
H13-C13-C14-C15	175(2)
H13-C13-C14-C17	-8(2)
N1-C1-C2-C3	-176.4(2)
N1-C1-C2-H2	9(3)
N2-C1-C2-C3	1.4(4)
N2-C1-C2-H2	-173(3)
C13-C14-C15-C16	-.5(4)
C13-C14-C15-H15	-169(3)
C17-C14-C15-C16	-177.6(2)
C17-C14-C15-H15	14(3)
C13-C14-C17-C20	136.1(3)
C13-C14-C17-C18	14.2(4)
C13-C14-C17-C19	-105.1(3)
C15-C14-C17-C20	-47.1(3)
C15-C14-C17-C18	-169.0(3)
C15-C14-C17-C19	71.7(3)

C6-C7-C8-C9	.8(4)
C6-C7-C8-H8	174(2)
H7-C7-C8-C9	176(2)
H7-C7-C8-H8	-11(3)
C1-C2-C3-C4	-1.4(4)
C1-C2-C3-H3	173(2)
H2-C2-C3-C4	173(3)
H2-C2-C3-H3	-13(3)
C2-C3-C4-C5	1.2(5)
C2-C3-C4-H4	-176(2)
H3-C3-C4-C5	-173(2)
H3-C3-C4-H4	11(3)
C14-C15-C16-N3	.1(4)
C14-C15-C16-H16	179(2)
H15-C15-C16-N3	170(3)
H15-C15-C16-H16	-11(3)
C7-C8-C9-C10	-.2(4)
C7-C8-C9-H9	169.1(3)
H8-C8-C9-C10	-173(2)
H8-C8-C9-H9	-3(2)
C8-C9-C10-N4	.4(4)
C8-C9-C10-H10	-170(2)
H9-C9-C10-N4	-169.7(3)
H9-C9-C10-H10	20(2)
N2-C5-C4-C3	-1.0(5)
N2-C5-C4-H4	176(2)
H5-C5-C4-C3	176(2)
H5-C5-C4-H4	-7(3)
C14-C17-C20-H20c	-172(2)
C14-C17-C20-H20b	58(3)
C14-C17-C20-H20a	-56.6(3)
C18-C17-C20-H20c	-49(2)
C18-C17-C20-H20b	-179(3)
C18-C17-C20-H20a	66.3(3)
C19-C17-C20-H20c	70(2)
C19-C17-C20-H20b	-61(3)
C19-C17-C20-H20a	-175.4(3)
C14-C17-C18-H18a	60.9(4)
C14-C17-C18-H18b	-177.7(3)
C14-C17-C18-H18c	-60.7(4)
C20-C17-C18-H18a	-62.4(4)
C20-C17-C18-H18b	59.0(4)
C20-C17-C18-H18c	176.1(3)
C19-C17-C18-H18a	179.8(3)
C19-C17-C18-H18b	-58.8(4)
C19-C17-C18-H18c	58.2(4)
C14-C17-C19-H19a	143(3)
C14-C17-C19-H19b	-57(3)
C14-C17-C19-H19c	69.3(4)
C20-C17-C19-H19a	-96(3)
C20-C17-C19-H19b	64(3)
C20-C17-C19-H19c	-169.8(3)
C18-C17-C19-H19a	22(3)
C18-C17-C19-H19b	-178(3)
C18-C17-C19-H19c	-51.3(4)

8.1.3 X-ray Structure of *N*-4-*tert*-Butylpyridyl-*N*-pyridyl-picolylamine 84:



Experimental Details

Crystal data:

Chemical formula	:	$C_{40}H_{44}N_8$ (2· $C_{20}H_{22}N_4$)
formula weight	:	636.85
Crystal system	:	orthorhombic
Space group (No.)	:	$P2_12_12_1$ (19)
Z	:	4
a (Å)	:	11.818(1)
b (Å)	:	16.501(2)
c (Å)	:	18.379(1)
α (°)	:	90.0
β (°)	:	90.0
γ (°)	:	90.0
cell volume	:	3584.1(6)Å^3
Density calc.	:	1.180g/cm^3
Radiation	:	CuKα (1.54179Å)

Range for lattice parameters	:	15.08E<Θ <16.90E
Absorption coefficient	:	0.559mm^{-1}
Temperature	:	298K
Crystal source	:	recrystallized from CH_2Cl_2 and Et_2O
Crystal colour	:	colourless
Crystal shape	:	irregular
Crystal size	:	ca. 0.3x0.3.x0.3mm

Data Collection

Diffractometer type	:	Enraf-Nonius CAD4
collection method	:	$\omega/2\vartheta$ scans
Absorption correction	:	none
No. of reflections measured	:	7336
No. of independent reflections:		6507
No. of observed reflections	:	4756
Θ_{max} (E)	:	67.87
h_{min} 6 h_{max}	:	- 14 6 14
k_{min} 6 k_{max}	:	- 19 6 19
l_{min} 6 l_{max}	:	- 22 6 22

Criterion for observed	:	$I > 2\sigma(I)$
R_{int}	:	0.038(46)
Standard reflections	:	-2 -5 2, -2 4 4, -2 4 -4
Variation	:	4257(167) 2091(76) 2214(82)
Refinement:		
On	:	F
Treatment of hydrogens	:	Calculated in idealized positions. Us fixed at 1.5×U of the corresponding heavy atom. No refinement of hydrogen parameters
R	:	0.075
R_w	:	0.087
Weighting scheme	:	$w=1/\sigma^2(F)$
No. of parameters refined:		433
No. of reflections in refmnt.	:	4745
Residual electron density	:	-0.64/0.39e/Å^3
r*[1]	:	not refined
XABS[2][a)]	:	-0.16(1.62) not significant!
Goodness of fit	:	2.659
Solution	:	XTAL3.7[3]
Remarks	:	[a)]From separate calculation

Atomic Positional and Isotropic Displacement Parameters

Atom	x/a	y/b	z/c	U_{eq}/Å^2
N1a	0.4600(5)	0.7705(3)	0.0762(3)	* 0.048(4)
N2a	0.3602(5)	0.8027(3)	0.1791(3)	* 0.050(4)
N3a	0.5756(4)	0.7747(3)	-0.0258(3)	* 0.049(3)
N4a	0.4427(6)	0.6033(3)	0.1268(3)	* 0.065(4)
C1a	0.3747(6)	0.8171(4)	0.1098(4)	* 0.043(4)
C2a	0.3151(5)	0.8777(4)	0.0712(4)	* 0.039(4)
C3a	0.2327(6)	0.9200(3)	0.1062(3)	* 0.041(4)
C4a	0.2085(6)	0.9022(3)	0.1801(4)	* 0.049(4)
C5a	0.2772(7)	0.8457(4)	0.2113(4)	* 0.052(4)
C6a	0.4772(6)	0.7674(4)	0.0016(4)	* 0.047(4)
C7a	0.3801(6)	0.7527(5)	-0.0444(4)	* 0.052(5)
C8a	0.3967(8)	0.7518(4)	-0.1190(4)	* 0.062(5)
C9a	0.5026(7)	0.7610(5)	-0.1460(4)	* 0.063(5)
C10a	0.5905(7)	0.7723(5)	-0.1003(4)	* 0.062(5)
C11a	0.5483(6)	0.7339(4)	0.1223(4)	* 0.054(4)
C12a	0.5293(6)	0.6504(4)	0.1490(4)	* 0.053(4)
C13a	0.6109(7)	0.6239(4)	0.1928(4)	* 0.063(5)
C14a	0.6053(9)	0.5533(7)	0.2152(5)	* 0.105(7)
C15a	0.522(1)	0.4983(5)	0.1954(5)	* 0.091(7)
C16a	0.4285(9)	0.5223(5)	0.1515(4)	* 0.083(7)
C17a	0.1649(6)	0.9903(4)	0.0682(4)	* 0.049(4)
C18a	0.1998(7)	1.0004(4)	-0.0091(4)	* 0.067(5)
C19a	0.1790(7)	1.0681(4)	0.1097(4)	* 0.075(5)
C20a	0.0432(8)	0.9633(5)	0.0695(6)	* 0.099(7)
N1b	0.0391(5)	0.7292(3)	0.4225(3)	* 0.046(4)
N2b	0.1422(5)	0.6995(3)	0.3180(3)	* 0.045(3)
N3b	-0.0771(5)	0.7235(3)	0.5253(3)	* 0.055(4)
N4b	-0.1085(6)	0.8778(4)	0.3098(4)	* 0.072(5)
C1b	0.1241(5)	0.6843(4)	0.3892(4)	* 0.040(4)
C2b	0.1857(6)	0.6263(4)	0.4270(4)	* 0.045(4)
C3b	0.2698(6)	0.5807(4)	0.3919(4)	* 0.048(4)
C4b	0.2833(6)	0.5978(4)	0.3193(4)	* 0.051(4)
C5b	0.2218(7)	0.6560(4)	0.2834(4)	* 0.049(4)
C6b	0.0332(5)	0.7337(4)	0.5006(3)	* 0.038(3)
C7b	0.1236(7)	0.7483(5)	0.5442(4)	* 0.057(5)
C8b	-0.0878(6)	0.7290(4)	0.5952(4)	* 0.054(5)
C9b	-0.0030(7)	0.7403(4)	0.6463(4)	* 0.061(5)
C10b	0.1070(7)	0.7527(5)	0.6172(4)	* 0.063(5)
C11b	-0.0498(6)	0.7620(4)	0.3772(4)	* 0.050(4)
C12b	-0.0290(6)	0.8495(4)	0.3535(3)	* 0.051(4)
C13b	0.0705(8)	0.8943(5)	0.3744(5)	* 0.089(6)
C14b	-0.0976(8)	0.9568(4)	0.2857(4)	* 0.083(5)
C15b	-0.0119(9)	1.0078(4)	0.3046(5)	* 0.083(6)
C16b	0.0649(7)	0.9741(5)	0.3493(5)	* 0.074(6)
C17b	0.3391(6)	0.5194(4)	0.4308(4)	* 0.052(4)
C18b	0.4661(7)	0.5419(6)	0.4316(5)	* 0.084(6)
C19b	0.325(1)	0.4378(5)	0.3919(6)	* 0.139(9)
C20b	0.3050(9)	0.5072(6)	0.5124(6)	* 0.123(8)
H11aa	0.6187(-)	0.7337(-)	0.0916(-)	* 0.081(-)
H11ab	0.5646(-)	0.7687(-)	0.1617(-)	* 0.081(-)
H11ba	-0.0555(-)	0.7286(-)	0.3314(-)	* 0.075(-)
H11bb	-0.1231(-)	0.7580(-)	0.3988(-)	* 0.075(-)
H2b	0.1683(-)	0.6153(-)	0.4777(-)	* 0.066(-)
H2a	0.3296(-)	0.8865(-)	0.0193(-)	* 0.060(-)
H8b	-0.1673(-)	0.7207(-)	0.6169(-)	* 0.083(-)
H10a	0.6642(-)	0.7737(-)	-0.1165(-)	* 0.092(-)

H4a	0.1506(-)	0.9297(-)	0.2079(-)	* 0.075(-)
H4b	0.3459(-)	0.5709(-)	0.2932(-)	* 0.075(-)
H9b	-0.0188(-)	0.7360(-)	0.6968(-)	* 0.092(-)
H5b	0.2333(-)	0.6633(-)	0.2337(-)	* 0.075(-)
H5a	0.2644(-)	0.8352(-)	0.2657(-)	* 0.076(-)
H13a	0.6755(-)	0.6601(-)	0.2038(-)	* 0.093(-)
H10b	0.1625(-)	0.7694(-)	0.6509(-)	* 0.093(-)
H18ba	0.5084(-)	0.5062(-)	0.4595(-)	* 0.120(-)
H18bb	0.4933(-)	0.5541(-)	0.3876(-)	* 0.120(-)
H18bc	0.4699(-)	0.5960(-)	0.4616(-)	* 0.120(-)
H16b	0.1194(-)	1.0105(-)	0.3683(-)	* 0.110(-)
H14b	-0.1607(-)	0.9800(-)	0.2577(-)	* 0.122(-)
H19ba	0.3778(-)	0.3957(-)	0.4181(-)	* 0.210(-)
H19bb	0.2581(-)	0.4158(-)	0.3885(-)	* 0.210(-)
H19bc	0.3645(-)	0.4395(-)	0.3439(-)	* 0.210(-)
H14a	0.6580(-)	0.5404(-)	0.2510(-)	* 0.162(-)
H15b	0.0046(-)	1.0616(-)	0.2905(-)	* 0.126(-)
H15a	0.5448(-)	0.4445(-)	0.2139(-)	* 0.135(-)
H18aa	0.1699(-)	1.0436(-)	-0.0297(-)	* 0.105(-)
H18ab	0.2884(-)	1.0172(-)	-0.0021(-)	* 0.105(-)
H18ac	0.2048(-)	0.9530(-)	-0.0323(-)	* 0.105(-)
H19aa	0.1406(-)	1.1098(-)	0.0912(-)	* 0.113(-)
H19ab	0.1542(-)	1.0584(-)	0.1614(-)	* 0.113(-)
H19ac	0.2594(-)	1.0794(-)	0.1145(-)	* 0.113(-)
H20ba	0.3526(-)	0.4642(-)	0.5338(-)	* 0.183(-)
H20bb	0.3192(-)	0.5548(-)	0.5399(-)	* 0.183(-)
H20bc	0.2293(-)	0.4909(-)	0.5177(-)	* 0.183(-)
H8a	0.3268(-)	0.7530(-)	-0.1532(-)	* 0.095(-)
H9a	0.5209(-)	0.7584(-)	-0.2009(-)	* 0.095(-)
H20aa	-0.0064(-)	1.0019(-)	0.0466(-)	* 0.156(-)
H20ab	0.0328(-)	0.9122(-)	0.0445(-)	* 0.156(-)
H20ac	0.0145(-)	0.9552(-)	0.1186(-)	* 0.156(-)
H7a	0.2911(-)	0.7436(-)	-0.0196(-)	* 0.075(-)
H16a	0.3598(-)	0.4865(-)	0.1360(-)	* 0.125(-)
H7b	0.1998(-)	0.7555(-)	0.5240(-)	* 0.087(-)
H13b	0.1368(-)	0.8681(-)	0.4032(-)	* 0.126(-)

Atomic Displacement Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N1a	0.048(4)	0.046(4)	0.050(4)	0.015(3)	-0.007(3)	-0.003(3)
N2a	0.056(4)	0.046(3)	0.049(4)	0.000(3)	-0.002(3)	0.001(3)
N3a	0.030(3)	0.050(4)	0.067(4)	0.009(3)	0.000(3)	-0.004(3)
N4a	0.082(4)	0.059(3)	0.054(3)	0.027(3)	-0.009(3)	0.017(3)
C1a	0.045(4)	0.044(4)	0.040(4)	0.001(3)	0.002(3)	-0.001(3)
C2a	0.038(4)	0.037(3)	0.043(4)	0.002(3)	0.005(3)	0.008(3)
C3a	0.053(4)	0.023(3)	0.045(4)	-0.002(3)	-0.010(3)	-0.005(3)
C4a	0.050(4)	0.029(3)	0.068(5)	-0.002(3)	0.000(3)	-0.007(3)
C5a	0.064(5)	0.056(4)	0.037(4)	-0.001(4)	0.004(3)	0.005(3)
C6a	0.050(4)	0.040(4)	0.052(4)	0.009(3)	-0.000(3)	-0.002(3)
C7a	0.035(3)	0.060(5)	0.062(5)	-0.003(3)	-0.008(3)	0.002(4)
C8a	0.078(6)	0.054(4)	0.053(5)	0.005(4)	-0.017(4)	-0.006(3)
C9a	0.067(5)	0.071(6)	0.053(5)	0.012(4)	0.014(4)	0.007(4)
C10a	0.079(6)	0.061(5)	0.047(4)	0.013(4)	0.020(4)	0.002(3)
C11a	0.049(4)	0.060(5)	0.054(4)	0.004(3)	-0.016(3)	-0.007(3)
C12a	0.053(4)	0.046(4)	0.061(5)	0.014(3)	-0.006(4)	-0.013(3)
C13a	0.063(5)	0.051(5)	0.076(6)	0.016(4)	-0.009(4)	0.022(4)
C14a	0.105(7)	0.139(9)	0.071(6)	0.005(6)	-0.004(5)	0.003(6)
C15a	0.15(1)	0.051(4)	0.077(6)	0.038(6)	0.008(6)	0.023(4)
C16a	0.144(9)	0.050(5)	0.056(5)	-0.000(5)	0.011(5)	0.001(4)
C17a	0.050(4)	0.031(3)	0.066(4)	0.012(3)	-0.001(3)	0.004(3)
C18a	0.092(6)	0.052(3)	0.058(4)	0.013(3)	0.009(4)	0.018(3)
C19a	0.093(5)	0.046(4)	0.088(5)	0.011(3)	0.001(4)	-0.012(3)
C20a	0.069(6)	0.070(5)	0.158(9)	0.022(5)	-0.022(6)	0.030(5)
N1b	0.042(3)	0.049(4)	0.047(4)	0.004(3)	0.007(3)	0.014(3)
N2b	0.057(4)	0.037(3)	0.041(3)	0.004(3)	0.003(3)	0.006(2)

N3b	0.065(4)	0.050(4)	0.048(3)	−0.003(3)	0.014(3)	0.004(3)
N4b	0.075(5)	0.069(5)	0.072(5)	0.016(4)	−0.026(4)	0.018(4)
C1b	0.039(4)	0.029(3)	0.052(4)	−0.006(3)	−0.001(3)	0.004(3)
C2b	0.052(4)	0.034(3)	0.048(4)	−0.002(3)	−0.003(3)	0.002(3)
C3b	0.035(4)	0.045(4)	0.064(5)	−0.000(3)	0.009(3)	0.006(3)
C4b	0.052(4)	0.058(4)	0.044(4)	0.008(3)	0.012(3)	−0.007(3)
C5b	0.063(5)	0.037(3)	0.047(4)	0.001(3)	0.004(3)	−0.006(3)
C6b	0.035(3)	0.030(3)	0.051(4)	0.001(2)	0.004(3)	0.006(3)
C7b	0.064(5)	0.055(5)	0.051(5)	0.002(4)	0.009(4)	−0.001(4)
C8b	0.044(4)	0.053(5)	0.067(5)	0.001(3)	0.009(3)	0.003(4)
C9b	0.076(6)	0.053(5)	0.054(5)	0.006(4)	−0.001(4)	−0.009(4)
C10b	0.056(5)	0.073(5)	0.059(5)	−0.001(4)	0.003(4)	−0.001(4)
C11b	0.042(4)	0.050(4)	0.060(4)	0.010(3)	0.005(3)	0.024(3)
C12b	0.058(5)	0.059(4)	0.037(4)	0.015(4)	0.008(3)	0.012(3)
C13b	0.096(6)	0.068(5)	0.104(7)	−0.033(4)	0.032(5)	−0.025(4)
C14b	0.107(6)	0.042(3)	0.101(6)	0.036(4)	−0.023(5)	0.027(4)
C15b	0.119(8)	0.056(5)	0.075(6)	0.008(5)	0.015(5)	−0.001(4)
C16b	0.082(6)	0.056(5)	0.083(6)	−0.005(4)	0.005(5)	−0.001(4)
C17b	0.053(4)	0.038(3)	0.063(4)	0.005(3)	−0.006(3)	0.000(3)
C18b	0.043(4)	0.101(7)	0.107(7)	−0.004(4)	−0.010(4)	0.002(5)
C19b	0.23(1)	0.030(4)	0.162(9)	0.031(5)	−0.105(8)	−0.010(4)
C20b	0.125(9)	0.135(8)	0.107(8)	0.084(7)	−0.008(6)	0.037(6)
H11aa	0.081(−)	0.081(−)	0.081(−)	0.000(−)	0.000(−)	0.000(−)
H11ab	0.081(−)	0.081(−)	0.081(−)	0.000(−)	0.000(−)	0.000(−)
H11ba	0.075(−)	0.075(−)	0.075(−)	0.000(−)	0.000(−)	0.000(−)
H11bb	0.075(−)	0.075(−)	0.075(−)	0.000(−)	0.000(−)	0.000(−)
H2b	0.066(−)	0.066(−)	0.066(−)	0.000(−)	0.000(−)	0.000(−)
H2a	0.060(−)	0.060(−)	0.060(−)	0.000(−)	0.000(−)	0.000(−)
H8b	0.083(−)	0.083(−)	0.083(−)	0.000(−)	0.000(−)	0.000(−)
H10a	0.092(−)	0.092(−)	0.092(−)	0.000(−)	0.000(−)	0.000(−)

H4a	0.075(-)	0.075(-)	0.075(-)	0.000(-)	0.000(-)
0.000(-)					
H4b	0.075(-)	0.075(-)	0.075(-)	0.000(-)	0.000(-)
0.000(-)					
H9b	0.092(-)	0.092(-)	0.092(-)	0.000(-)	0.000(-)
0.000(-)					
H5b	0.075(-)	0.075(-)	0.075(-)	0.000(-)	0.000(-)
0.000(-)					
H5a	0.076(-)	0.076(-)	0.076(-)	0.000(-)	0.000(-)
0.000(-)					
H13a	0.093(-)	0.093(-)	0.093(-)	0.000(-)	0.000(-)
0.000(-)					
H10b	0.093(-)	0.093(-)	0.093(-)	0.000(-)	0.000(-)
0.000(-)					
H18ba	0.120(-)	0.120(-)	0.120(-)	0.000(-)	0.000(-)
0.000(-)					
H18bb	0.120(-)	0.120(-)	0.120(-)	0.000(-)	0.000(-)
0.000(-)					
H18bc	0.120(-)	0.120(-)	0.120(-)	0.000(-)	0.000(-)
0.000(-)					
H16b	0.110(-)	0.110(-)	0.110(-)	0.000(-)	0.000(-)
0.000(-)					
H14b	0.122(-)	0.122(-)	0.122(-)	0.000(-)	0.000(-)
0.000(-)					
H19ba	0.210(-)	0.210(-)	0.210(-)	0.000(-)	0.000(-)
0.000(-)					
H19bb	0.210(-)	0.210(-)	0.210(-)	0.000(-)	0.000(-)
0.000(-)					
H19bc	0.210(-)	0.210(-)	0.210(-)	0.000(-)	0.000(-)
0.000(-)					
H14a	0.162(-)	0.162(-)	0.162(-)	0.000(-)	0.000(-)
0.000(-)					
H15b	0.126(-)	0.126(-)	0.126(-)	0.000(-)	0.000(-)
0.000(-)					
H15a	0.135(-)	0.135(-)	0.135(-)	0.000(-)	0.000(-)
0.000(-)					
H18aa	0.105(-)	0.105(-)	0.105(-)	0.000(-)	0.000(-)
0.000(-)					
H18ab	0.105(-)	0.105(-)	0.105(-)	0.000(-)	0.000(-)
0.000(-)					
H18ac	0.105(-)	0.105(-)	0.105(-)	0.000(-)	0.000(-)
0.000(-)					
H19aa	0.113(-)	0.113(-)	0.113(-)	0.000(-)	0.000(-)
0.000(-)					
H19ab	0.113(-)	0.113(-)	0.113(-)	0.000(-)	0.000(-)
0.000(-)					
H19ac	0.113(-)	0.113(-)	0.113(-)	0.000(-)	0.000(-)
0.000(-)					
H20ba	0.183(-)	0.183(-)	0.183(-)	0.000(-)	0.000(-)
0.000(-)					
H20bb	0.183(-)	0.183(-)	0.183(-)	0.000(-)	0.000(-)
0.000(-)					
H20bc	0.183(-)	0.183(-)	0.183(-)	0.000(-)	0.000(-)
0.000(-)					
H8a	0.095(-)	0.095(-)	0.095(-)	0.000(-)	0.000(-)
0.000(-)					
H9a	0.095(-)	0.095(-)	0.095(-)	0.000(-)	0.000(-)
0.000(-)					
H20aa	0.156(-)	0.156(-)	0.156(-)	0.000(-)	0.000(-)
0.000(-)					

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 H20ab  0.156(-)    0.156(-)    0.156(-)    0.000(-)    0.000(-)
0.000(-)
 H20ac  0.156(-)    0.156(-)    0.156(-)    0.000(-)    0.000(-)
0.000(-)
 H7a    0.075(-)    0.075(-)    0.075(-)    0.000(-)    0.000(-)
0.000(-)
 H16a   0.125(-)    0.125(-)    0.125(-)    0.000(-)    0.000(-)
0.000(-)
 H7b    0.087(-)    0.087(-)    0.087(-)    0.000(-)    0.000(-)
0.000(-)
 H13b   0.126(-)    0.126(-)    0.126(-)    0.000(-)    0.000(-)
0.000(-)
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Bond Distances	(Angstroms)
N1b-C1b	1.391(9)
N1b-C6b	1.438(8)
N1b-C11b	1.446(9)
C6b-C7b	1.36(1)
C6b-N3b	1.390(9)
N2b-C5b	1.343(9)
N2b-C1b	1.350(9)
N3b-C8b	1.30(1)
C17b-C3b	1.49(1)
C17b-C19b	1.53(1)
C17b-C18b	1.55(1)
C17b-C20b	1.57(1)
C11b-H11bb	.955(7)
C11b-H11ba	1.007(7)
C11b-C12b	1.53(1)
C3b-C4b	1.37(1)
C3b-C2b	1.40(1)
C1b-C2b	1.388(9)
C2b-H2b	.972(7)
C8b-H8b	1.029(7)
C8b-C9b	1.39(1)
C4b-H4b	.987(7)
C4b-C5b	1.37(1)
C7b-H7b	.982(9)
C7b-C10b	1.36(1)
C9b-H9b	.948(8)
C9b-C10b	1.42(1)
C12b-N4b	1.32(1)
C12b-C13b	1.44(1)
C13b-H13b	1.040(9)
C13b-C16b	1.40(1)
C5b-H5b	.930(7)
N4b-C14b	1.382(9)
C10b-H10b	.943(8)
C18b-H18bb	.895(9)
C18b-H18ba	.927(9)
C18b-H18bc	1.05(1)
C16b-H16b	.946(9)
C16b-C15b	1.34(1)
C14b-H14b	.984(9)
C14b-C15b	1.36(1)
C19b-H19bb	.88(1)
C19b-H19bc	1.00(1)
C19b-H19ba	1.05(1)
C15b-H15b	.946(8)
C20b-H20bc	.94(1)
C20b-H20bb	.95(1)
C20b-H20ba	.99(1)
N1a-C6a	1.387(9)
N1a-C1a	1.409(9)
N1a-C11a	1.474(9)
N2a-C1a	1.306(9)
N2a-C5a	1.348(9)
C6a-N3a	1.273(9)
C6a-C7a	1.45(1)
N3a-C10a	1.38(1)
C17a-C18a	1.49(1)
C17a-C19a	1.50(1)

C17a-C20a	1.51(1)
C17a-C3a	1.574(9)
C11a-H11ab	.944(7)
C11a-H11aa	1.006(7)
C11a-C12a	1.48(1)
C3a-C2a	1.360(9)
C3a-C4a	1.418(9)
C1a-C2a	1.415(9)
C2a-H2a	.980(7)
C10a-H10a	.920(9)
C10a-C9a	1.35(1)
C4a-H4a	.967(7)
C4a-C5a	1.36(1)
C7a-H7a	1.156(7)
C7a-C8a	1.39(1)
C12a-C13a	1.33(1)
C12a-N4a	1.349(9)
C5a-H5a	1.027(7)
C13a-H13a	.990(8)
C13a-C14a	1.24(1)
N4a-C16a	1.42(1)
C14a-H14a	.93(1)
C14a-C15a	1.38(1)
C15a-H15a	.988(8)
C15a-C16a	1.43(1)
C18a-H18aa	.881(7)
C18a-H18ac	.892(7)
C18a-H18ab	1.091(9)
C19a-H19aa	.891(7)
C19a-H19ac	.972(8)
C19a-H19ab	1.008(8)
C16a-H16a	1.04(1)
C8a-H8a	1.038(8)
C8a-C9a	1.36(1)
C9a-H9a	1.033(8)
C20a-H20aa	.963(9)
C20a-H20ab	.968(9)
C20a-H20ac	.97(1)

Bond Angles	(degrees)
C1b-N1b-C6b	120.1(5)
C1b-N1b-C11b	118.2(5)
C6b-N1b-C11b	121.3(5)
C7b-C6b-N3b	124.4(6)
C7b-C6b-N1b	124.1(6)
N3b-C6b-N1b	111.4(5)
C5b-N2b-C1b	118.1(6)
C8b-N3b-C6b	114.1(6)
C3b-C17b-C19b	108.3(7)
C3b-C17b-C18b	112.1(6)
C3b-C17b-C20b	114.1(7)
C19b-C17b-C18b	108.5(7)
C19b-C17b-C20b	107.9(7)
C18b-C17b-C20b	105.8(7)
H11bb-C11b-H11ba	104.4(6)
H11bb-C11b-N1b	113.2(6)
H11bb-C11b-C12b	109.3(6)
H11ba-C11b-N1b	108.9(6)
H11ba-C11b-C12b	106.9(6)
N1b-C11b-C12b	113.6(5)
C4b-C3b-C2b	114.8(6)
C4b-C3b-C17b	123.0(6)
C2b-C3b-C17b	122.3(6)
N2b-C1b-C2b	122.0(6)
N2b-C1b-N1b	116.2(6)
C2b-C1b-N1b	121.8(6)
H2b-C2b-C1b	119.8(7)
H2b-C2b-C3b	119.4(6)
C1b-C2b-C3b	120.7(6)
H8b-C8b-N3b	117.6(7)
H8b-C8b-C9b	114.6(7)
N3b-C8b-C9b	127.6(7)
H4b-C4b-C3b	117.9(7)
H4b-C4b-C5b	118.5(7)
C3b-C4b-C5b	123.3(7)
H7b-C7b-C10b	120.0(8)
H7b-C7b-C6b	121.3(7)
C10b-C7b-C6b	118.7(8)
H9b-C9b-C8b	120.6(8)
H9b-C9b-C10b	124.1(8)
C8b-C9b-C10b	115.2(7)
N4b-C12b-C13b	124.1(7)
N4b-C12b-C11b	113.1(6)
C13b-C12b-C11b	122.7(6)
H13b-C13b-C16b	126.6(8)
H13b-C13b-C12b	122.5(7)
C16b-C13b-C12b	110.9(8)
H5b-C5b-N2b	119.9(7)
H5b-C5b-C4b	118.9(7)
N2b-C5b-C4b	121.1(6)
C12b-N4b-C14b	117.5(7)
H10b-C10b-C7b	124.4(8)
H10b-C10b-C9b	115.5(7)
C7b-C10b-C9b	119.8(7)
H18bb-C18b-H18ba	116.7(9)
H18bb-C18b-H18bc	105.5(9)
H18bb-C18b-C17b	113.2(8)
H18ba-C18b-H18bc	103.1(8)

H18ba-C18b-C17b	112.1(8)
H18bc-C18b-C17b	104.6(7)
H16b-C16b-C15b	115.0(8)
H16b-C16b-C13b	116.4(9)
C15b-C16b-C13b	128.6(8)
H14b-C14b-C15b	117.2(7)
H14b-C14b-N4b	117.6(8)
C15b-C14b-N4b	124.8(8)
H19bb-C19b-H19bc	112(1)
H19bb-C19b-H19ba	107.0(8)
H19bb-C19b-C17b	120(1)
H19bc-C19b-H19ba	99(1)
H19bc-C19b-C17b	109.9(8)
H19ba-C19b-C17b	107.8(9)
H15b-C15b-C16b	114.7(9)
H15b-C15b-C14b	131.5(9)
C16b-C15b-C14b	113.7(7)
H20bc-C20b-H20bb	110(1)
H20bc-C20b-H20ba	107.2(9)
H20bc-C20b-C17b	112.5(9)
H20bb-C20b-H20ba	106(1)
H20bb-C20b-C17b	110.9(9)
H20ba-C20b-C17b	109.1(9)
C6a-N1a-C1a	123.9(6)
C6a-N1a-C11a	116.7(6)
C1a-N1a-C11a	118.6(5)
C1a-N2a-C5a	115.3(6)
N3a-C6a-N1a	121.5(6)
N3a-C6a-C7a	120.6(6)
N1a-C6a-C7a	117.9(6)
C6a-N3a-C10a	120.4(6)
C18a-C17a-C19a	111.0(6)
C18a-C17a-C20a	108.3(7)
C18a-C17a-C3a	111.4(6)
C19a-C17a-C20a	110.5(7)
C19a-C17a-C3a	110.4(6)
C20a-C17a-C3a	105.1(6)
H11ab-C11a-H11aa	105.3(7)
H11ab-C11a-N1a	109.5(6)
H11ab-C11a-C12a	110.1(6)
H11aa-C11a-N1a	105.3(6)
H11aa-C11a-C12a	108.1(6)
N1a-C11a-C12a	117.7(6)
C2a-C3a-C4a	119.5(6)
C2a-C3a-C17a	122.2(6)
C4a-C3a-C17a	118.3(6)
N2a-C1a-N1a	114.9(6)
N2a-C1a-C2a	123.5(6)
N1a-C1a-C2a	121.5(6)
H2a-C2a-C3a	120.7(6)
H2a-C2a-C1a	120.4(6)
C3a-C2a-C1a	118.8(6)
H10a-C10a-C9a	122.0(8)
H10a-C10a-N3a	116.2(8)
C9a-C10a-N3a	121.5(8)
H4a-C4a-C5a	121.4(7)
H4a-C4a-C3a	123.5(6)
C5a-C4a-C3a	115.1(6)
H7a-C7a-C8a	121.1(7)
H7a-C7a-C6a	120.9(7)

C8a-C7a-C6a	118.0(7)
C13a-C12a-N4a	122.9(6)
C13a-C12a-C11a	113.5(6)
N4a-C12a-C11a	123.4(6)
H5a-C5a-N2a	116.5(7)
H5a-C5a-C4a	116.0(7)
N2a-C5a-C4a	127.5(7)
H13a-C13a-C14a	122.9(9)
H13a-C13a-C12a	118.8(7)
C14a-C13a-C12a	118.2(8)
C12a-N4a-C16a	122.3(7)
H14a-C14a-C13a	114(1)
H14a-C14a-C15a	121(1)
C13a-C14a-C15a	125(1)
H15a-C15a-C14a	108(1)
H15a-C15a-C16a	130.7(9)
C14a-C15a-C16a	121.1(8)
H18aa-C18a-H18ac	122.0(8)
H18aa-C18a-H18ab	103.2(7)
H18aa-C18a-C17a	112.9(7)
H18ac-C18a-H18ab	102.5(7)
H18ac-C18a-C17a	112.1(6)
H18ab-C18a-C17a	100.5(6)
H19aa-C19a-H19ac	112.7(8)
H19aa-C19a-H19ab	109.4(8)
H19aa-C19a-C17a	114.2(7)
H19ac-C19a-H19ab	103.2(7)
H19ac-C19a-C17a	108.6(7)
H19ab-C19a-C17a	108.1(6)
H16a-C16a-N4a	122.5(8)
H16a-C16a-C15a	127.0(7)
N4a-C16a-C15a	110.4(8)
H8a-C8a-C9a	120.8(7)
H8a-C8a-C7a	119.1(8)
C9a-C8a-C7a	119.4(7)
H9a-C9a-C10a	116.9(7)
H9a-C9a-C8a	123.1(7)
C10a-C9a-C8a	120.0(7)
H20aa-C20a-H20ab	107(1)
H20aa-C20a-H20ac	106.5(9)
H20aa-C20a-C17a	112.2(8)
H20ab-C20a-H20ac	106.1(9)
H20ab-C20a-C17a	111.8(8)
H20ac-C20a-C17a	112.9(9)

Dihedral Angles (degrees)	
C11b–N1b–C6b–N3b	36.7(8)
C11b–N1b–C6b–C7b	−141.6(7)
C1b–N1b–C6b–N3b	−135.4(6)
C1b–N1b–C6b–C7b	46.3(9)
C6b–N1b–C11b–C12b	92.6(7)
C6b–N1b–C11b–H11ba	−148.5(6)
C6b–N1b–C11b–H11bb	−32.8(9)
C1b–N1b–C11b–C12b	−95.2(7)
C1b–N1b–C11b–H11ba	23.8(8)
C1b–N1b–C11b–H11bb	139.4(6)
C6b–N1b–C1b–N2b	−163.4(6)
C6b–N1b–C1b–C2b	17.4(9)
C11b–N1b–C1b–N2b	24.3(8)
C11b–N1b–C1b–C2b	−154.9(6)
N1b–C6b–N3b–C8b	−178.4(6)
C7b–C6b–N3b–C8b	0(1)
N1b–C6b–C7b–C10b	178.7(7)
N1b–C6b–C7b–H7b	−1(1)
N3b–C6b–C7b–C10b	0(1)
N3b–C6b–C7b–H7b	−179.4(7)
C5b–N2b–C1b–N1b	−178.4(6)
C5b–N2b–C1b–C2b	.7(9)
C1b–N2b–C5b–C4b	0(1)
C1b–N2b–C5b–H5b	176.7(6)
C6b–N3b–C8b–C9b	−3(1)
C6b–N3b–C8b–H8b	−178.6(6)
C18b–C17b–C3b–C2b	−116.8(8)
C18b–C17b–C3b–C4b	62.6(9)
C19b–C17b–C3b–C2b	123.5(8)
C19b–C17b–C3b–C4b	−57(1)
C20b–C17b–C3b–C2b	3(1)
C20b–C17b–C3b–C4b	−177.2(7)
C3b–C17b–C18b–H18ba	174.8(8)
C3b–C17b–C18b–H18bb	−51(1)
C3b–C17b–C18b–H18bc	63.7(9)
C19b–C17b–C18b–H18ba	−66(1)
C19b–C17b–C18b–H18bb	69(1)
C19b–C17b–C18b–H18bc	−176.7(7)
C20b–C17b–C18b–H18ba	50(1)
C20b–C17b–C18b–H18bb	−175.5(9)
C20b–C17b–C18b–H18bc	−61.1(9)
C3b–C17b–C19b–H19ba	177.2(8)
C3b–C17b–C19b–H19bb	−61(1)
C3b–C17b–C19b–H19bc	71(1)
C18b–C17b–C19b–H19ba	55(1)
C18b–C17b–C19b–H19bb	178(1)
C18b–C17b–C19b–H19bc	−51(1)
C20b–C17b–C19b–H19ba	−59(1)
C20b–C17b–C19b–H19bb	63(1)
C20b–C17b–C19b–H19bc	−165.5(9)
C3b–C17b–C20b–H20ba	177.7(7)
C3b–C17b–C20b–H20bb	−65(1)
C3b–C17b–C20b–H20bc	59(1)
C18b–C17b–C20b–H20ba	−59(1)
C18b–C17b–C20b–H20bb	58(1)
C18b–C17b–C20b–H20bc	−177.5(8)
C19b–C17b–C20b–H20ba	57(1)
C19b–C17b–C20b–H20bb	174.3(9)

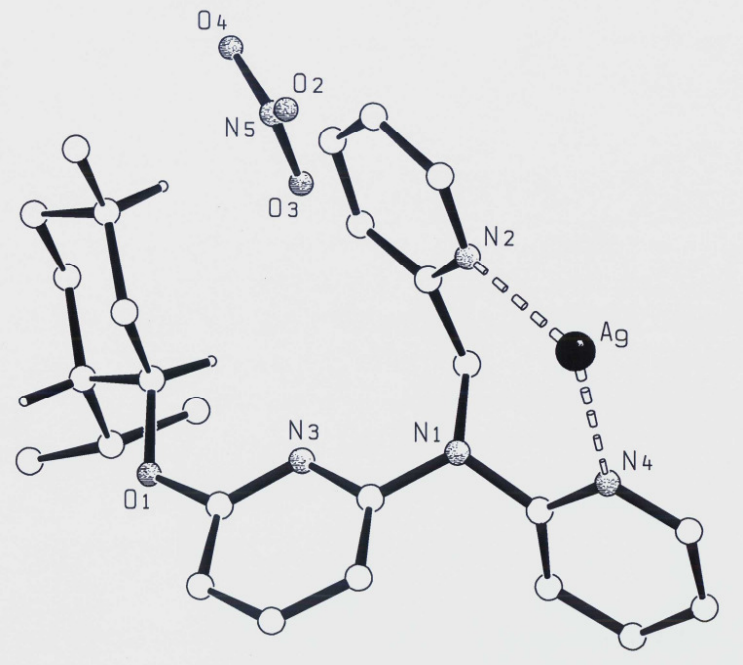
C19b-C17b-C20b-H20bc	-62(1)
N1b-C11b-C12b-C13b	.3(9)
N1b-C11b-C12b-N4b	177.5(6)
H11ba-C11b-C12b-C13b	-119.8(7)
H11ba-C11b-C12b-N4b	57.3(8)
H11bb-C11b-C12b-C13b	127.8(7)
H11bb-C11b-C12b-N4b	-55.1(8)
C17b-C3b-C2b-C1b	178.7(6)
C17b-C3b-C2b-H2b	-4(1)
C4b-C3b-C2b-C1b	0(1)
C4b-C3b-C2b-H2b	176.4(6)
C17b-C3b-C4b-C5b	-178.1(7)
C17b-C3b-C4b-H4b	-5(1)
C2b-C3b-C4b-C5b	1(1)
C2b-C3b-C4b-H4b	174.7(6)
N1b-C1b-C2b-C3b	178.9(6)
N1b-C1b-C2b-H2b	2(1)
N2b-C1b-C2b-C3b	0(1)
N2b-C1b-C2b-H2b	-177.5(6)
N3b-C8b-C9b-C10b	5(1)
N3b-C8b-C9b-H9b	-171.2(7)
H8b-C8b-C9b-C10b	-179.4(6)
H8b-C8b-C9b-H9b	5(1)
C3b-C4b-C5b-N2b	0(1)
C3b-C4b-C5b-H5b	-177.8(7)
H4b-C4b-C5b-N2b	-174.2(6)
H4b-C4b-C5b-H5b	9(1)
C6b-C7b-C10b-C9b	1(1)
C6b-C7b-C10b-H10b	-171.5(8)
H7b-C7b-C10b-C9b	-178.5(7)
H7b-C7b-C10b-H10b	9(1)
C8b-C9b-C10b-C7b	-4(1)
C8b-C9b-C10b-H10b	169.8(7)
H9b-C9b-C10b-C7b	171.9(7)
H9b-C9b-C10b-H10b	-14(1)
C11b-C12b-C13b-C16b	-176.3(7)
C11b-C12b-C13b-H13b	5(1)
N4b-C12b-C13b-C16b	7(1)
N4b-C12b-C13b-H13b	-171.6(8)
C11b-C12b-N4b-C14b	179.6(6)
C13b-C12b-N4b-C14b	-3(1)
C12b-C13b-C16b-C15b	-7(1)
C12b-C13b-C16b-H16b	168.3(8)
H13b-C13b-C16b-C15b	171.0(9)
H13b-C13b-C16b-H16b	-13(2)
C12b-N4b-C14b-C15b	-1(1)
C12b-N4b-C14b-H14b	-173.4(7)
C13b-C16b-C15b-C14b	4(1)
C13b-C16b-C15b-H15b	-173.7(9)
H16b-C16b-C15b-C14b	-171.9(8)
H16b-C16b-C15b-H15b	10(1)
N4b-C14b-C15b-C16b	0(1)
N4b-C14b-C15b-H15b	178.0(9)
H14b-C14b-C15b-C16b	173.2(8)
H14b-C14b-C15b-H15b	-10(2)
C11a-N1a-C6a-N3a	-36.3(9)
C11a-N1a-C6a-C7a	141.6(7)
C1a-N1a-C6a-N3a	133.1(7)
C1a-N1a-C6a-C7a	-49(1)
C6a-N1a-C11a-C12a	-97.7(7)

C6a-N1a-C11a-H11aa	22.7(8)
C6a-N1a-C11a-H11ab	135.5(7)
C1a-N1a-C11a-C12a	92.2(8)
C1a-N1a-C11a-H11aa	-147.3(6)
C1a-N1a-C11a-H11ab	-34.5(9)
C6a-N1a-C1a-N2a	169.8(6)
C6a-N1a-C1a-C2a	-14(1)
C11a-N1a-C1a-N2a	-21.0(9)
C11a-N1a-C1a-C2a	155.5(6)
C5a-N2a-C1a-N1a	-178.6(6)
C5a-N2a-C1a-C2a	5(1)
C1a-N2a-C5a-C4a	0(1)
C1a-N2a-C5a-H5a	179.9(6)
N1a-C6a-N3a-C10a	-179.3(6)
C7a-C6a-N3a-C10a	3(1)
N1a-C6a-C7a-C8a	178.2(6)
N1a-C6a-C7a-H7a	0(1)
N3a-C6a-C7a-C8a	-4(1)
N3a-C6a-C7a-H7a	177.8(6)
C6a-N3a-C10a-C9a	0(1)
C6a-N3a-C10a-H10a	-175.1(7)
C18a-C17a-C3a-C2a	2.3(9)
C18a-C17a-C3a-C4a	-179.4(6)
C19a-C17a-C3a-C2a	-121.4(7)
C19a-C17a-C3a-C4a	56.8(8)
C20a-C17a-C3a-C2a	119.4(8)
C20a-C17a-C3a-C4a	-62.4(8)
C3a-C17a-C18a-H18aa	-172.1(7)
C3a-C17a-C18a-H18ab	-62.7(7)
C3a-C17a-C18a-H18ac	46(1)
C19a-C17a-C18a-H18aa	-49(1)
C19a-C17a-C18a-H18ab	60.7(7)
C19a-C17a-C18a-H18ac	168.9(7)
C20a-C17a-C18a-H18aa	72.8(9)
C20a-C17a-C18a-H18ab	-177.9(6)
C20a-C17a-C18a-H18ac	-69.6(9)
C3a-C17a-C19a-H19aa	-178.2(7)
C3a-C17a-C19a-H19ab	-56.2(8)
C3a-C17a-C19a-H19ac	55.1(8)
C18a-C17a-C19a-H19aa	58(1)
C18a-C17a-C19a-H19ab	179.8(7)
C18a-C17a-C19a-H19ac	-68.9(8)
C20a-C17a-C19a-H19aa	-62(1)
C20a-C17a-C19a-H19ab	59.7(9)
C20a-C17a-C19a-H19ac	171.0(7)
C3a-C17a-C20a-H20aa	-179.0(8)
C3a-C17a-C20a-H20ab	-59(1)
C3a-C17a-C20a-H20ac	60.6(9)
C18a-C17a-C20a-H20aa	-60(1)
C18a-C17a-C20a-H20ab	60(1)
C18a-C17a-C20a-H20ac	179.7(7)
C19a-C17a-C20a-H20aa	62(1)
C19a-C17a-C20a-H20ab	-178.0(8)
C19a-C17a-C20a-H20ac	-59(1)
N1a-C11a-C12a-C13a	-177.1(6)
N1a-C11a-C12a-N4a	8(1)
H11aa-C11a-C12a-C13a	63.9(8)
H11aa-C11a-C12a-N4a	-111.0(8)
H11ab-C11a-C12a-C13a	-50.6(9)
H11ab-C11a-C12a-N4a	134.4(7)

C17a-C3a-C2a-C1a	178.0(6)
C17a-C3a-C2a-H2a	-6(1)
C4a-C3a-C2a-C1a	-.2(9)
C4a-C3a-C2a-H2a	175.8(6)
C17a-C3a-C4a-C5a	-174.4(6)
C17a-C3a-C4a-H4a	2(1)
C2a-C3a-C4a-C5a	3.9(9)
C2a-C3a-C4a-H4a	-179.5(6)
N1a-C1a-C2a-C3a	179.2(6)
N1a-C1a-C2a-H2a	3(1)
N2a-C1a-C2a-C3a	-5(1)
N2a-C1a-C2a-H2a	179.3(6)
N3a-C10a-C9a-C8a	.0(9)
N3a-C10a-C9a-H9a	-178.4(7)
H10a-C10a-C9a-C8a	173.8(8)
H10a-C10a-C9a-H9a	-5(1)
C3a-C4a-C5a-N2a	-4(1)
C3a-C4a-C5a-H5a	175.7(6)
H4a-C4a-C5a-N2a	179.7(7)
H4a-C4a-C5a-H5a	0(1)
C6a-C7a-C8a-C9a	3(1)
C6a-C7a-C8a-H8a	-167.8(7)
H7a-C7a-C8a-C9a	-178.7(7)
H7a-C7a-C8a-H8a	11(1)
C11a-C12a-C13a-C14a	-176.6(8)
C11a-C12a-C13a-H13a	0(1)
N4a-C12a-C13a-C14a	-2(1)
N4a-C12a-C13a-H13a	174.9(7)
C11a-C12a-N4a-C16a	177.8(7)
C13a-C12a-N4a-C16a	3(1)
C12a-C13a-C14a-C15a	3(1)
C12a-C13a-C14a-H14a	-171.0(9)
H13a-C13a-C14a-C15a	-173.4(9)
H13a-C13a-C14a-H14a	13(2)
C12a-N4a-C16a-C15a	-6(1)
C12a-N4a-C16a-H16a	177.4(7)
C13a-C14a-C15a-C16a	-6(2)
C13a-C14a-C15a-H15a	170.3(9)
H14a-C14a-C15a-C16a	168(1)
H14a-C14a-C15a-H15a	-16(1)
C14a-C15a-C16a-N4a	7(1)
C14a-C15a-C16a-H16a	-176.5(9)
H15a-C15a-C16a-N4a	-169(1)
H15a-C15a-C16a-H16a	8(2)
C7a-C8a-C9a-C10a	-1(1)
C7a-C8a-C9a-H9a	177.2(7)
H8a-C8a-C9a-C10a	169.4(7)
H8a-C8a-C9a-H9a	-12(1)

8.1.4 X-ray Structure of Menthol Substituted *N*,*N*-Dipyridylaminopicoline-silver(I) Nitrate:

Measured by Herrn Dr. Ch. Lehmann, MPI für Kohlenforschung (coal research) Mülheim/Ruhr



Experimental Details

Crystal data:

Chemical formula	:	$C_{26}H_{32}N_5O_4Ag$
formula weight	:	586.44
Crystal system	:	monoclinic
Space group (No.)	:	$P2_1$ (4)
Z	:	2
a (Å)	:	10.9377(1)
b (Å)	:	8.0289(1)
c (Å)	:	15.1207(1)
α (°)	:	90.0
β (°)	:	106.529(1)
γ (°)	:	90.0

cell volume	:	1272.99(2)Å^3
Density calc.	:	1.53g/cm^3
Radiation	:	MoKα (0.71073Å)
Range for lattice parameters	:	
Absorption coefficient	:	0.834mm^{-1}
Temperature	:	120K
Crystal source	:	recrystallized from CH_2Cl_2 and MeCN
Crystal colour	:	colourless/grey
Crystal shape	:	irregular
Crystal size	:	ca. 0.20x0.53.x0.27mm

Data Collection

Diffractometer type	:	Bruker AXS KappaCCD with FR591 rotating anode
collection method	:	φ and ω scans
Absorption correction	:	Scalepack
No. of reflections measured	:	135480
No. of independent reflections:	12500	
No. of observed reflections	:	12422
Θ_{max} (E)	:	37.01
h_{min} 6 h_{max}	:	- 18 6 18
k_{min} 6 k_{max}	:	- 13 6 13
l_{min} 6 l_{max}	:	- 25 6 25

Criterion for observed	:	$I > 2\sigma(I)$
R_{int}	:	0.017(13)
Standard reflections	:	
Variation	:	
Refinement:		
On	:	F
Treatment of hydrogens	:	Hydrogen positions calculated in idealized positions. All Us fixed at 1.5×U of the corresponding heavy atom prior to final refinement. No refinement of hydrogen parameters.
R	:	0.018
R_w	:	0.023
Weighting scheme	:	$w=1/\sigma^2(F)$
No. of parameters refined:		324
No. of reflections in refmnt.	:	12422
Residual electron density	:	-0.42/0.38e/Å^3
r*[1]	:	not refined
XABS[2][a)]	:	0.020(9)
Goodness of fit	:	2.319
Solution	:	XTAL3.7[3]
Remarks	:	[a)]From separate calculation

Atomic Positional and Isotropic Displacement Parameters

Atom	x/a	y/b	z/c	U_{eq}/Å^2
Ag1	0.43322(-)	0.36541(-)	0.08582(-)	* 0.01693(3)
O1	0.09827(6)	0.56449(9)	0.42890(4)	* 0.0172(3)
O2	-0.24692(6)	0.64467(9)	0.05756(5)	* 0.0218(3)
O3	-0.34964(7)	0.44643(9)	0.10319(5)	* 0.0220(3)
O4	-0.45083(6)	0.66749(9)	0.03818(5)	* 0.0214(3)
N1	0.29218(6)	0.28999(9)	0.23215(4)	* 0.0123(3)
N2	0.26321(7)	0.53486(9)	0.07345(5)	* 0.0138(3)
N3	0.19563(6)	0.43324(9)	0.32954(4)	* 0.0123(3)
N4	0.42071(7)	0.12262(9)	0.16836(5)	* 0.0149(3)
N5	-0.34804(7)	0.58711(9)	0.06626(5)	* 0.0148(3)
C1	0.35223(7)	0.1336(1)	0.22880(5)	* 0.0125(3)
C2	0.33389(8)	-0.0007(1)	0.28199(6)	* 0.0155(3)
C3	0.38786(8)	-0.1538(1)	0.27139(5)	* 0.0176(4)
C4	0.45783(8)	-0.1670(1)	0.20759(6)	* 0.0173(4)
C5	0.47145(8)	-0.0266(1)	0.15797(6)	* 0.0171(4)
C6	0.17733(7)	0.32211(9)	0.15510(5)	* 0.0121(3)
C7	0.17114(7)	0.4938(1)	0.11283(5)	* 0.0119(3)
C8	0.06780(7)	0.5974(1)	0.10867(5)	* 0.0139(3)
C9	0.05766(8)	0.7478(1)	0.06109(6)	* 0.0163(3)
C10	0.15190(8)	0.7900(1)	0.02000(6)	* 0.0174(4)
C11	0.25297(8)	0.6805(1)	0.02831(6)	* 0.0167(4)
C12	0.29963(6)	0.3559(1)	0.31939(4)	* 0.0118(3)
C13	0.41356(7)	0.3407(1)	0.39044(5)	* 0.0152(3)
C14	0.41683(7)	0.4054(1)	0.47623(5)	* 0.0167(3)
C15	0.30979(8)	0.4820(1)	0.48940(5)	* 0.0156(3)
C16	0.20183(7)	0.4924(1)	0.41302(5)	* 0.0130(3)
C17	-0.00610(7)	0.6219(1)	0.35156(5)	* 0.0136(3)
C18	0.03446(8)	0.7851(1)	0.31688(6)	* 0.0156(3)
C19	-0.07471(7)	0.8762(1)	0.24822(5)	* 0.0158(3)
C20	-0.18434(8)	0.9003(1)	0.29109(6)	* 0.0176(4)
C21	-0.22820(7)	0.7329(1)	0.31872(6)	* 0.0154(3)
C22	-0.12028(7)	0.6429(1)	0.39009(5)	* 0.0134(3)
C24	-0.16342(9)	0.4774(1)	0.42335(6)	* 0.0184(4)
C25	-0.25289(9)	0.5084(1)	0.48309(6)	* 0.0203(4)
C26	-0.2280(1)	0.3572(2)	0.34433(8)	* 0.0333(6)
C27	-0.0285(1)	1.0415(1)	0.21980(7)	* 0.0238(5)
H13	0.4863(-)	0.2888(-)	0.3799(-)	* 0.017(-)
H24	-0.0870(-)	0.4266(-)	0.4594(-)	* 0.014(-)
H3	0.3762(-)	-0.2477(-)	0.3069(-)	* 0.015(-)
H22	-0.0952(-)	0.7108(-)	0.4436(-)	* 0.007(-)
H17	-0.0274(-)	0.5476(-)	0.3011(-)	* 0.007(-)
H5	0.5187(-)	-0.0354(-)	0.1149(-)	* 0.019(-)
H2	0.2857(-)	0.0119(-)	0.3248(-)	* 0.016(-)
H26a	-0.2528(-)	0.2589(-)	0.3690(-)	* 0.052(-)
H26b	-0.1712(-)	0.3316(-)	0.3095(-)	* 0.052(-)
H26c	-0.3025(-)	0.4100(-)	0.3049(-)	* 0.052(-)
H8	0.0045(-)	0.5663(-)	0.1377(-)	* 0.021(-)
H9	-0.0123(-)	0.8221(-)	0.0572(-)	* 0.017(-)
H6a	0.1050(-)	0.3091(-)	0.1769(-)	* 0.007(-)
H6b	0.1753(-)	0.2430(-)	0.1082(-)	* 0.007(-)
H11	0.3172(-)	0.7107(-)	0.0002(-)	* 0.016(-)
H15	0.3100(-)	0.5274(-)	0.5475(-)	* 0.007(-)
H10	0.1474(-)	0.8919(-)	-0.0131(-)	* 0.007(-)
H14	0.4919(-)	0.3962(-)	0.5263(-)	* 0.007(-)

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H4     0.4968(-)  -0.2690(-)   0.1979(-)  * 0.007(-)
H19   -0.1048(-)   0.8101(-)   0.1939(-)  * 0.007(-)
H21a  -0.2971(-)   0.7515(-)   0.3447(-)  * 0.007(-)
H21b  -0.2571(-)   0.6651(-)   0.2655(-)  * 0.007(-)
H25a  -0.2779(-)   0.4057(-)   0.5028(-)  * 0.024(-)
H25b  -0.3265(-)   0.5671(-)   0.4475(-)  * 0.024(-)
H25c  -0.2106(-)   0.5743(-)   0.5350(-)  * 0.024(-)
H18a   0.0984(-)   0.7626(-)   0.2875(-)  * 0.007(-)
H18b   0.0675(-)   0.8573(-)   0.3680(-)  * 0.007(-)
H20a  -0.2535(-)   0.9536(-)   0.2473(-)  * 0.007(-)
H20b  -0.1560(-)   0.9696(-)   0.3441(-)  * 0.007(-)
H27a  -0.0969(-)   1.0971(-)   0.1766(-)  * 0.007(-)
H27b   0.0383(-)   1.0222(-)   0.1916(-)  * 0.007(-)
H27c   0.0033(-)   1.1106(-)   0.2724(-)  * 0.007(-)
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Atomic Displacement Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag1	0.01712(3)	0.01642(3)	0.02117(3)	0.00130(2)	0.01176(2)	0.00178(2)
O1	0.0143(2)	0.0260(3)	0.0119(2)	0.0092(2)	0.0050(2)	0.0009(2)
O2	0.0145(3)	0.0238(3)	0.0282(3)	-0.0059(2)	0.0080(2)	-0.0032(3)
O3	0.0211(3)	0.0186(3)	0.0273(3)	0.0003(2)	0.0085(2)	0.0044(2)
O4	0.0171(3)	0.0266(3)	0.0242(3)	0.0070(2)	0.0117(2)	0.0052(3)
N1	0.0133(3)	0.0140(3)	0.0100(2)	0.0033(2)	0.0041(2)	-0.0002(2)
N2	0.0130(3)	0.0146(3)	0.0148(3)	-0.0004(2)	0.0053(2)	0.0012(2)
N3	0.0114(2)	0.0147(3)	0.0121(2)	0.0016(2)	0.0053(2)	0.0001(2)
N4	0.0151(3)	0.0171(3)	0.0144(3)	0.0029(2)	0.0073(2)	0.0001(2)
N5	0.0153(3)	0.0169(3)	0.0135(3)	-0.0008(2)	0.0060(2)	-0.0039(2)
C1	0.0122(3)	0.0142(3)	0.0113(3)	0.0016(2)	0.0035(2)	-0.0006(2)
C2	0.0164(3)	0.0162(3)	0.0153(3)	0.0023(3)	0.0069(3)	0.0021(3)
C3	0.0209(3)	0.0147(4)	0.0165(3)	0.0036(3)	0.0040(2)	0.0007(3)
C4	0.0169(3)	0.0164(4)	0.0171(3)	0.0050(2)	0.0023(3)	-0.0008(2)
C5	0.0165(3)	0.0193(3)	0.0163(3)	0.0058(3)	0.0063(3)	-0.0017(3)
C6	0.0115(3)	0.0122(3)	0.0123(3)	-0.0003(2)	0.0028(2)	0.0008(2)
C7	0.0115(3)	0.0133(3)	0.0108(3)	-0.0006(2)	0.0030(2)	-0.0005(2)
C8	0.0123(3)	0.0163(3)	0.0128(3)	0.0010(2)	0.0033(2)	0.0014(2)
C9	0.0156(3)	0.0168(3)	0.0150(3)	0.0027(3)	0.0019(2)	0.0027(3)
C10	0.0176(3)	0.0166(3)	0.0165(3)	0.0008(3)	0.0025(3)	0.0046(3)
C11	0.0151(3)	0.0182(3)	0.0172(3)	-0.0011(3)	0.0050(3)	0.0045(3)
C12	0.0111(2)	0.0134(3)	0.0116(2)	0.0009(3)	0.0046(2)	-0.0005(3)
C13	0.0105(3)	0.0203(4)	0.0148(3)	0.0028(2)	0.0034(2)	-0.0022(2)
C14	0.0112(3)	0.0240(4)	0.0138(3)	0.0020(2)	0.0016(2)	-0.0031(2)
C15	0.0143(3)	0.0207(3)	0.0117(3)	0.0020(3)	0.0035(2)	-0.0025(3)

C16	0.0126(3)	0.0151(3)	0.0129(3)	0.0024(2)	0.0060(2)	0.0006(2)
C17	0.0117(3)	0.0179(3)	0.0117(3)	0.0036(2)	0.0045(2)	0.0010(2)
C18	0.0132(3)	0.0184(3)	0.0157(3)	-0.0012(3)	0.0051(2)	-0.0004(3)
C19	0.0162(3)	0.0146(3)	0.0170(3)	-0.0014(3)	0.0053(2)	0.0019(3)
C20	0.0158(3)	0.0140(4)	0.0234(3)	0.0025(2)	0.0061(3)	0.0046(2)
C21	0.0120(3)	0.0156(3)	0.0188(3)	0.0018(2)	0.0049(2)	0.0033(3)
C22	0.0131(3)	0.0150(3)	0.0136(3)	0.0036(2)	0.0061(2)	0.0013(2)
C24	0.0210(4)	0.0178(3)	0.0207(3)	0.0059(3)	0.0128(3)	0.0060(3)
C26	0.0572(6)	0.0152(4)	0.0378(5)	-0.0071(5)	0.0304(5)	-0.0041(5)
C25	0.0185(3)	0.0253(4)	0.0207(3)	0.0034(3)	0.0113(3)	0.0052(3)
C27	0.0262(4)	0.0184(4)	0.0284(4)	-0.0043(3)	0.0102(3)	0.0048(3)
H13	0.017(-)	0.017(-)	0.017(-)	0.000(-)	0.005(-)	0.000(-)
H24	0.014(-)	0.014(-)	0.014(-)	0.000(-)	0.004(-)	0.000(-)
H3	0.015(-)	0.015(-)	0.015(-)	0.000(-)	0.004(-)	0.000(-)
H22	0.007(-)	0.007(-)	0.007(-)	0.000(-)	0.002(-)	0.000(-)
H17	0.007(-)	0.007(-)	0.007(-)	0.000(-)	0.002(-)	0.000(-)
H5	0.019(-)	0.019(-)	0.019(-)	0.000(-)	0.005(-)	0.000(-)
H2	0.016(-)	0.016(-)	0.016(-)	0.000(-)	0.005(-)	0.000(-)
H26a	0.052(-)	0.052(-)	0.052(-)	0.000(-)	0.015(-)	0.000(-)
H26b	0.052(-)	0.052(-)	0.052(-)	0.000(-)	0.015(-)	0.000(-)
H26c	0.052(-)	0.052(-)	0.052(-)	0.000(-)	0.015(-)	0.000(-)
H8	0.021(-)	0.021(-)	0.021(-)	0.000(-)	0.006(-)	0.000(-)
H9	0.017(-)	0.017(-)	0.017(-)	0.000(-)	0.005(-)	0.000(-)
H6a	0.007(-)	0.007(-)	0.007(-)	0.000(-)	0.002(-)	0.000(-)
H6b	0.007(-)	0.007(-)	0.007(-)	0.000(-)	0.002(-)	0.000(-)
H11	0.016(-)	0.016(-)	0.016(-)	0.000(-)	0.005(-)	0.000(-)
H15	0.007(-)	0.007(-)	0.007(-)	0.000(-)	0.002(-)	0.000(-)
H10	0.007(-)	0.007(-)	0.007(-)	0.000(-)	0.002(-)	0.000(-)
H14	0.007(-)	0.007(-)	0.007(-)	0.000(-)	0.002(-)	0.000(-)
H4	0.007(-)	0.007(-)	0.007(-)	0.000(-)	0.002(-)	0.000(-)

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 H19   0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H21a  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H21b  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H25a  0.024(-)    0.024(-)    0.024(-)    0.000(-)    0.007(-)
0.000(-)
 H25b  0.024(-)    0.024(-)    0.024(-)    0.000(-)    0.007(-)
0.000(-)
 H25c  0.024(-)    0.024(-)    0.024(-)    0.000(-)    0.007(-)
0.000(-)
 H18a  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H18b  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H20a  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H20b  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H27a  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H27b  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
 H27c  0.007(-)    0.007(-)    0.007(-)    0.000(-)    0.002(-)
0.000(-)
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Bond Distances (Angstroms)

Ag1-N2	2.2685(8)
C16-N3	1.332(1)
C16-O1	1.353(1)
C16-C15	1.3998(9)
C12-N3	1.342(1)
C12-C13	1.4001(8)
C12-N1	1.4021(9)
C13-H13	.9509(8)
C13-C14	1.388(1)
C24-H24	.9500(9)
C24-C25	1.529(2)
C24-C22	1.542(1)
C24-C26	1.542(1)
C3-H3	.9548(9)
C3-C2	1.392(1)
C3-C4	1.396(1)
C22-H22	.9483(7)
C22-C17	1.530(1)
C22-C21	1.535(1)
C1-N4	1.339(1)
C1-C2	1.393(1)
C1-N1	1.425(1)
N1-C6	1.4728(8)
C17-H17	.9446(8)
C17-O1	1.4573(9)
C17-C18	1.523(1)
C5-H5	.943(1)
C5-N4	1.348(1)
C5-C4	1.386(1)
N2-C11	1.343(1)
N2-C7	1.349(1)
C7-C8	1.390(1)
C7-C6	1.513(1)
C2-H2	.950(1)
C26-H26b	.945(1)
C26-H26a	.945(1)
C26-H26c	.960(1)
C8-H8	.9521(9)
C8-C9	1.394(1)
C9-H9	.9583(9)
C9-C10	1.388(1)
C6-H6a	.9456(8)
C6-H6b	.9477(8)
C11-H11	.950(1)
C11-C10	1.390(1)
C15-H15	.9509(8)
C15-C14	1.386(1)
C10-H10	.9525(9)
C14-H14	.9478(6)
C4-H4	.9534(9)
C19-H19	.9541(8)
C19-C27	1.525(1)
C19-C18	1.528(1)
C19-C20	1.529(1)
C21-H21b	.9481(8)
C21-H21a	.9555(9)
C21-C20	1.524(1)
C25-H25a	.942(1)

C25–H25c	.9510(9)
C25–H25b	.9561(9)
C18–H18a	.946(1)
C18–H18b	.9513(8)
C20–H20b	.9524(8)
C20–H20a	.9527(8)
C27–H27c	.950(1)
C27–H27a	.9528(9)
C27–H27b	.957(1)
N5–O2	1.240(1)
N5–O4	1.261(1)
N5–O3	1.262(1)

Bond Angles	(degrees)
N3–C16–O1	120.08(6)
N3–C16–C15	124.34(8)
O1–C16–C15	115.55(7)
N3–C12–C13	123.41(7)
N3–C12–N1	117.25(5)
C13–C12–N1	119.34(7)
H13–C13–C14	121.34(6)
H13–C13–C12	120.93(7)
C14–C13–C12	117.73(7)
H24–C24–C25	109.73(8)
H24–C24–C22	104.81(8)
H24–C24–C26	108.08(9)
C25–C24–C22	111.04(7)
C25–C24–C26	109.30(9)
C22–C24–C26	113.71(8)
H3–C3–C2	120.23(9)
H3–C3–C4	121.07(9)
C2–C3–C4	118.70(8)
H22–C22–C17	108.59(7)
H22–C22–C21	107.87(7)
H22–C22–C24	104.95(7)
C17–C22–C21	109.39(7)
C17–C22–C24	112.82(7)
C21–C22–C24	112.93(6)
N4–C1–C2	122.92(8)
N4–C1–N1	115.79(7)
C2–C1–N1	121.20(8)
C12–N1–C1	117.53(6)
C12–N1–C6	119.10(7)
C1–N1–C6	115.10(6)
H17–C17–O1	113.95(7)
H17–C17–C18	107.08(7)
H17–C17–C22	109.69(7)
O1–C17–C18	108.05(6)
O1–C17–C22	105.50(6)
C18–C17–C22	112.67(7)
H5–C5–N4	118.18(9)
H5–C5–C4	118.55(9)
N4–C5–C4	123.27(9)
C1–N4–C5	117.82(8)
C11–N2–C7	118.21(8)
C11–N2–Ag1	120.81(7)
C7–N2–Ag1	120.97(5)
N2–C7–C8	122.24(7)
N2–C7–C6	117.39(7)
C8–C7–C6	120.15(7)
H2–C2–C3	120.57(9)
H2–C2–C1	120.65(9)
C3–C2–C1	118.77(9)
H26b–C26–H26a	110.3(1)
H26b–C26–H26c	109.0(1)
H26b–C26–C24	109.8(1)
H26a–C26–H26c	109.0(1)
H26a–C26–C24	109.7(1)
H26c–C26–C24	109.0(1)
H8–C8–C7	120.71(8)
H8–C8–C9	120.22(8)
C7–C8–C9	119.07(8)

H9-C9-C10	120.11(9)
H9-C9-C8	121.08(9)
C10-C9-C8	118.81(8)
C16-O1-C17	119.81(6)
H6a-C6-H6b	110.03(7)
H6a-C6-N1	108.37(7)
H6a-C6-C7	107.86(7)
H6b-C6-N1	107.93(7)
H6b-C6-C7	107.82(7)
N1-C6-C7	114.79(6)
H11-C11-N2	118.97(9)
H11-C11-C10	117.93(9)
N2-C11-C10	123.10(9)
H15-C15-C14	121.51(7)
H15-C15-C16	121.32(9)
C14-C15-C16	117.16(7)
H10-C10-C9	120.64(9)
H10-C10-C11	120.8(1)
C9-C10-C11	118.57(8)
H14-C14-C15	119.63(8)
H14-C14-C13	120.23(8)
C15-C14-C13	120.13(6)
H4-C4-C5	119.7(1)
H4-C4-C3	121.83(9)
C5-C4-C3	118.51(8)
H19-C19-C27	107.64(8)
H19-C19-C18	109.25(9)
H19-C19-C20	108.33(7)
C27-C19-C18	110.53(7)
C27-C19-C20	111.88(8)
C18-C19-C20	109.15(7)
C16-N3-C12	117.18(6)
H21b-C21-H21a	109.16(7)
H21b-C21-C20	109.16(8)
H21b-C21-C22	109.28(7)
H21a-C21-C20	108.77(7)
H21a-C21-C22	108.81(8)
C20-C21-C22	111.63(6)
H25a-C25-H25c	110.04(9)
H25a-C25-H25b	109.60(9)
H25a-C25-C24	109.61(9)
H25c-C25-H25b	108.9(1)
H25c-C25-C24	109.65(9)
H25b-C25-C24	109.06(8)
H18a-C18-H18b	109.68(8)
H18a-C18-C17	108.91(8)
H18a-C18-C19	108.16(8)
H18b-C18-C17	108.97(8)
H18b-C18-C19	107.62(8)
C17-C18-C19	113.46(7)
H20b-C20-H20a	109.03(8)
H20b-C20-C21	109.68(8)
H20b-C20-C19	108.89(8)
H20a-C20-C21	109.69(7)
H20a-C20-C19	108.98(8)
C21-C20-C19	110.54(7)
H27c-C27-H27a	109.2(1)
H27c-C27-H27b	108.9(1)
H27c-C27-C19	110.10(9)
H27a-C27-H27b	108.7(1)

H27a-C27-C19	110.02(9)
H27b-C27-C19	109.92(9)
O2-N5-O4	120.70(7)
O2-N5-O3	120.37(7)
O4-N5-O3	118.93(8)

Dihedral Angles (degrees)

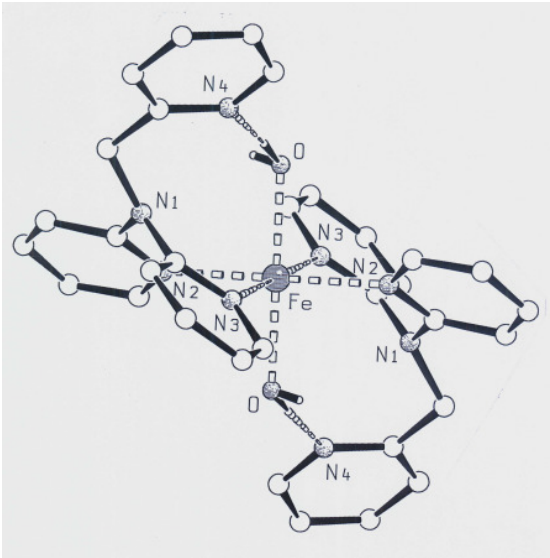
C15-C16-O1-C17	163.59(7)
N3-C16-O1-C17	-18.1(1)
O1-C16-C15-C14	178.53(8)
O1-C16-C15-H15	-2.6(1)
N3-C16-C15-C14	.3(1)
N3-C16-C15-H15	179.18(8)
O1-C16-N3-C12	-176.81(8)
C15-C16-N3-C12	1.4(1)
N1-C12-C13-C14	-179.10(8)
N1-C12-C13-H13	1.5(1)
N3-C12-C13-C14	1.9(1)
N3-C12-C13-H13	-177.51(8)
C13-C12-N1-C1	39.7(1)
C13-C12-N1-C6	-173.37(8)
N3-C12-N1-C1	-141.18(8)
N3-C12-N1-C6	5.7(1)
C13-C12-N3-C16	-2.5(1)
N1-C12-N3-C16	178.48(8)
C12-C13-C14-C15	-.1(1)
C12-C13-C14-H14	179.16(9)
H13-C13-C14-C15	179.29(8)
H13-C13-C14-H14	-1.5(1)
C26-C24-C22-C17	-70.9(1)
C26-C24-C22-C21	53.8(1)
C26-C24-C22-H22	171.06(8)
C25-C24-C22-C17	165.36(6)
C25-C24-C22-C21	-69.96(9)
C25-C24-C22-H22	47.29(8)
H24-C24-C22-C17	46.94(9)
H24-C24-C22-C21	171.62(8)
H24-C24-C22-H22	-71.1(1)
C22-C24-C26-H26a	-179.5(1)
C22-C24-C26-H26b	59.1(1)
C22-C24-C26-H26c	-60.2(1)
C25-C24-C26-H26a	-54.8(1)
C25-C24-C26-H26b	-176.17(9)
C25-C24-C26-H26c	64.5(1)
H24-C24-C26-H26a	64.6(1)
H24-C24-C26-H26b	-56.8(1)
H24-C24-C26-H26c	-176.2(1)
C22-C24-C25-H25a	-179.86(7)
C22-C24-C25-H25b	60.16(9)
C22-C24-C25-H25c	-58.96(9)
C26-C24-C25-H25a	53.9(1)
C26-C24-C25-H25b	-66.1(1)
C26-C24-C25-H25c	174.80(8)
H24-C24-C25-H25a	-64.5(1)
H24-C24-C25-H25b	175.56(8)
H24-C24-C25-H25c	56.4(1)
C4-C3-C2-C1	-.3(1)
C4-C3-C2-H2	179.88(7)

H3-C3-C2-C1	-179.71(7)
H3-C3-C2-H2	.4(1)
C2-C3-C4-C5	.5(1)
C2-C3-C4-H4	179.87(7)
H3-C3-C4-C5	179.94(7)
H3-C3-C4-H4	-.7(1)
C24-C22-C17-O1	-63.56(8)
C24-C22-C17-C18	178.77(6)
C24-C22-C17-H17	59.58(8)
C21-C22-C17-O1	169.84(6)
C21-C22-C17-C18	52.17(8)
C21-C22-C17-H17	-67.02(9)
H22-C22-C17-O1	52.34(9)
H22-C22-C17-C18	-65.33(8)
H22-C22-C17-H17	175.48(7)
C24-C22-C21-C20	176.97(8)
C24-C22-C21-H21a	56.93(9)
C24-C22-C21-H21b	-62.2(1)
C17-C22-C21-C20	-56.49(9)
C17-C22-C21-H21a	-176.54(7)
C17-C22-C21-H21b	64.35(9)
H22-C22-C21-C20	61.5(1)
H22-C22-C21-H21a	-58.6(1)
H22-C22-C21-H21b	-177.70(8)
N4-C1-N1-C12	-135.73(7)
N4-C1-N1-C6	76.08(9)
C2-C1-N1-C12	47.6(1)
C2-C1-N1-C6	-100.55(8)
N1-C1-N4-C5	-175.23(6)
C2-C1-N4-C5	1.3(1)
N1-C1-C2-C3	175.70(6)
N1-C1-C2-H2	-4.4(1)
N4-C1-C2-C3	-.7(1)
N4-C1-C2-H2	179.17(7)
C12-N1-C6-C7	77.9(1)
C12-N1-C6-H6a	-42.8(1)
C12-N1-C6-H6b	-161.88(8)
C1-N1-C6-C7	-134.47(8)
C1-N1-C6-H6a	104.91(8)
C1-N1-C6-H6b	-14.2(1)
C22-C17-O1-C16	162.43(7)
C18-C17-O1-C16	-76.83(9)
H17-C17-O1-C16	42.0(1)
C22-C17-C18-C19	-52.75(9)
C22-C17-C18-H18a	-173.27(6)
C22-C17-C18-H18b	67.12(9)
O1-C17-C18-C19	-168.90(7)
O1-C17-C18-H18a	70.58(9)
O1-C17-C18-H18b	-49.0(1)
H17-C17-C18-C19	67.9(1)
H17-C17-C18-H18a	-52.58(9)
H17-C17-C18-H18b	-172.19(7)
C4-C5-N4-C1	-1.1(1)
H5-C5-N4-C1	179.10(7)
N4-C5-C4-C3	.2(1)
N4-C5-C4-H4	-179.21(7)
H5-C5-C4-C3	179.99(7)
H5-C5-C4-H4	.6(1)
Ag1-N2-C7-C8	178.10(5)
Ag1-N2-C7-C6	-7.32(9)

C11–N2–C7–C8	-.5(1)
C11–N2–C7–C6	174.07(7)
Ag1–N2–C11–C10	-178.95(6)
Ag1–N2–C11–H11	1.5(1)
C7–N2–C11–C10	-.3(1)
C7–N2–C11–H11	-179.87(7)
N2–C7–C8–C9	1.0(1)
N2–C7–C8–H8	-179.23(7)
C6–C7–C8–C9	-173.49(7)
C6–C7–C8–H8	6.3(1)
N2–C7–C6–N1	62.13(9)
N2–C7–C6–H6a	-176.97(6)
N2–C7–C6–H6b	-58.18(9)
C8–C7–C6–N1	-123.17(8)
C8–C7–C6–H6a	-2.27(9)
C8–C7–C6–H6b	116.52(8)
C7–C8–C9–C10	-.5(1)
C7–C8–C9–H9	-179.78(7)
H8–C8–C9–C10	179.65(7)
H8–C8–C9–H9	.4(1)
C8–C9–C10–C11	-.3(1)
C8–C9–C10–H10	179.89(8)
H9–C9–C10–C11	179.00(8)
H9–C9–C10–H10	-.9(1)
N2–C11–C10–C9	.7(1)
N2–C11–C10–H10	-179.42(8)
H11–C11–C10–C9	-179.74(8)
H11–C11–C10–H10	.1(1)
C16–C15–C14–C13	-.9(1)
C16–C15–C14–H14	179.85(8)
H15–C15–C14–C13	-179.81(9)
H15–C15–C14–H14	.9(1)
C20–C19–C18–C17	54.1(1)
C20–C19–C18–H18a	175.02(7)
C20–C19–C18–H18b	-66.6(1)
C27–C19–C18–C17	177.53(8)
C27–C19–C18–H18a	-61.5(1)
C27–C19–C18–H18b	56.9(1)
H19–C19–C18–C17	-64.2(1)
H19–C19–C18–H18a	56.7(1)
H19–C19–C18–H18b	175.16(9)
C18–C19–C20–C21	-57.33(9)
C18–C19–C20–H20a	-177.95(7)
C18–C19–C20–H20b	63.2(1)
C27–C19–C20–C21	-179.98(6)
C27–C19–C20–H20a	59.40(9)
C27–C19–C20–H20b	-59.42(9)
H19–C19–C20–C21	61.53(9)
H19–C19–C20–H20a	-59.1(1)
H19–C19–C20–H20b	-177.91(8)
C18–C19–C27–H27a	179.48(9)
C18–C19–C27–H27b	59.9(1)
C18–C19–C27–H27c	-60.1(1)
C20–C19–C27–H27a	-58.7(1)
C20–C19–C27–H27b	-178.28(7)
C20–C19–C27–H27c	61.8(1)
H19–C19–C27–H27a	60.2(1)
H19–C19–C27–H27b	-59.4(1)
H19–C19–C27–H27c	-179.35(9)
C22–C21–C20–C19	60.42(9)

C22–C21–C20–H20a	–179.39(8)
C22–C21–C20–H20b	–59.7(1)
H21a–C21–C20–C19	–179.51(6)
H21a–C21–C20–H20a	–59.3(1)
H21a–C21–C20–H20b	60.41(9)
H21b–C21–C20–C19	–60.49(8)
H21b–C21–C20–H20a	59.7(1)
H21b–C21–C20–H20b	179.42(7)

8.1.5 X-ray Structure of *N*,*N*-Dipyridylaminopicoline-iron(II) Triflate:



Experimental Details

Crystal data:

Chemical formula	:	$C_{17}H_{16}F_3Fe_{0.5}N_4O_4S$
formula weight	:	457.32
Crystal system	:	monoclinic
Space group (No.)	:	$P2_1/n$ (14)
Z	:	4
a (Å)	:	9.0516(9)
b (Å)	:	16.2770(15)
c (Å)	:	13.7375(13)
α (°)	:	90.0
β (°)	:	105.225(2)
γ (°)	:	90.0
cell volume	:	1952.9(3)Å^3
Density calc.	:	1.555g/cm^3
Radiation	:	MoKα (1.54179Å)
Range for lattice parameters	:	E<Θ <E

Absorption coefficient	:	$0.583mm^{-1}$
Temperature	:	130K
Crystal source	:	recrystallized from acetone and Et_2O
Crystal colour	:	yellow
Crystal shape	:	irregular
Crystal size	:	ca. 0.10x0.13x0.32mm

Data Collection

Diffractometer type	:	Bruker Smart CCD area detector
collection method	:	ω scans
Absorption correction	:	none
No. of reflections measured	:	46610
No. of independent reflections:		4009
No. of observed reflections	:	3441
Θ_{max} (E)	:	26.42
h_{min} 6 h_{max}	:	- 11 6 11
k_{min} 6 k_{max}	:	- 20 6 20
l_{min} 6 l_{max}	:	- 17 6 17

Criterion for observed	:	$I > 2\sigma(I)$
R_{int}	:	0.079(65)
Standard reflections	:	
Variation	:	
Refinement:		
On	:	*F*
Treatment of hydrogens	:	Calculated in idealized positions. No refinement of hydrogen parameters
R	:	0.098
R_w	:	**0.104**[a)]
Weighting scheme	:	$w=1/\sigma^2(F)$
No. of parameters refined	:	304
No. of reflections in refmnt.	:	3441
Residual electron density	:	-2.44/1.97e/Å^3
r*[1]	:	not refined
XABS[2]	:	
Goodness of fit	:	3.31
Solution	:	XTAL3.7[3]
Remarks	:	[a)]Cell contains disordered $CF_3SO_3^-$,

Atomic Positional, Isotropic Displacement and Site Occupation Parameters

Atom	x/a	y/b	z/c	U_{eq}/Å^2	PP
Fe	1/2	1/2	0	* 0.0230(6)	
S	0.1559(2)	0.3114(1)	0.4698(1)	* 0.047(1)	
O	0.3471(5)	0.5907(2)	0.0260(3)	* 0.037(3)	
O1	0.058(1)	0.3695(5)	0.427(1)	* 0.28(1)	
O2	0.239(2)	0.2858(5)	0.411(1)	* 0.26(2)	
O3	0.0936(6)	0.2519(3)	0.5207(4)	* 0.065(4)	
N1	0.2627(5)	0.4369(3)	0.1176(4)	* 0.037(3)	
N2	0.3175(6)	0.4101(3)	-0.0366(3)	* 0.031(3)	
N3	0.5298(5)	0.4456(3)	0.1479(3)	* 0.028(3)	
N4	0.2594(6)	0.5906(4)	0.2045(4)	* 0.046(4)	
C1	0.2244(7)	0.3992(4)	0.0220(4)	* 0.038(4)	
C2	0.0912(8)	0.3514(4)	-0.0094(5)	* 0.052(5)	
C3	0.0591(9)	0.3142(4)	-0.1014(6)	* 0.064(5)	
C4	0.159(1)	0.3221(4)	-0.1602(5)	* 0.056(5)	
C5	0.2866(8)	0.3707(3)	-0.1263(4)	* 0.042(4)	
C6	0.4089(7)	0.4271(3)	0.1836(4)	* 0.033(4)	
C7	0.4282(8)	0.4008(4)	0.2830(5)	* 0.043(4)	
C8	0.5727(8)	0.3927(4)	0.3441(5)	* 0.048(4)	
C9	0.6987(7)	0.4081(4)	0.3073(5)	* 0.041(4)	
C10	0.6713(7)	0.4342(4)	0.2088(4)	* 0.034(4)	
C11	0.1374(7)	0.4583(5)	0.1639(5)	* 0.050(5)	
C12	0.1761(7)	0.5316(5)	0.2328(5)	* 0.048(4)	
C13	0.1208(8)	0.5372(6)	0.3169(5)	* 0.063(6)	
C14	0.155(1)	0.6074(8)	0.3746(6)	* 0.083(7)	
C15	0.238(1)	0.6677(6)	0.3469(6)	* 0.076(7)	
C16	0.2913(8)	0.6569(5)	0.2629(5)	* 0.060(5)	
C18b	0.306(2)	0.348(1)	0.562(1)	* 0.05(1)	0.5000(-)
C18a	0.258(2)	0.395(1)	0.553(1)	* 0.05(1)	0.5000(-)
F1a	0.136(1)	0.4470(6)	0.5564(9)	* 0.095(9)	0.5000(-)
F1b	0.407(1)	0.2901(7)	0.5907(8)	* 0.104(8)	0.5000(-)
F2a	0.344(2)	0.4446(8)	0.514(1)	* 0.054(8)	0.5000(-)
F2b	0.375(2)	0.4067(9)	0.529(2)	* 0.08(1)	0.5000(-)
F3a	0.285(4)	0.374(2)	0.638(2)	* 0.15(2)	0.5000(-)
F3b	0.299(3)	0.380(1)	0.647(2)	* 0.08(1)	0.5000(-)
H10	0.7577(-)	0.4465(-)	0.1825(-)	0.044(-)	
H9	0.8014(-)	0.4002(-)	0.3486(-)	0.052(-)	
H7	0.3397(-)	0.3886(-)	0.3081(-)	0.055(-)	
H5	0.3574(-)	0.3770(-)	-0.1681(-)	0.054(-)	
H8	0.5887(-)	0.3753(-)	0.4133(-)	0.059(-)	
H2	0.0229(-)	0.3451(-)	0.0345(-)	0.064(-)	
H4	0.1389(-)	0.2933(-)	-0.2244(-)	0.071(-)	
H11a	0.1181(-)	0.4106(-)	0.2016(-)	0.062(-)	
H11b	0.0458(-)	0.4680(-)	0.1115(-)	0.062(-)	
H16	0.3532(-)	0.7010(-)	0.2433(-)	0.079(-)	
H3	-0.0331(-)	0.2831(-)	-0.1251(-)	0.073(-)	
H13	0.0608(-)	0.4920(-)	0.3351(-)	0.082(-)	
H14	0.1224(-)	0.6136(-)	0.4348(-)	0.105(-)	
H15	0.2611(-)	0.7196(-)	0.3853(-)	0.094(-)	
H_b	0.2916(-)	0.5752(-)	0.0183(-)	0.056(-)	
H_a	0.3169(-)	0.5928(-)	0.0889(-)	0.056(-)	

Atomic Displacement Parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.0319(6)	0.0191(6)	0.0193(6)	-0.0001(5)	0.0088(5)	0.0006(5)
S	0.077(1)	0.0309(9)	0.0294(9)	0.0054(9)	0.0075(9)	-0.0037(7)
O	0.047(3)	0.036(2)	0.033(2)	0.007(2)	0.019(2)	-0.003(2)
O1	0.153(8)	0.120(7)	0.41(2)	-0.081(6)	-0.19(1)	0.17(1)
O2	0.51(2)	0.094(6)	0.35(1)	-0.132(9)	0.40(2)	-0.112(8)
O3	0.077(4)	0.067(3)	0.062(3)	-0.001(3)	0.038(3)	0.002(3)
N1	0.029(3)	0.049(3)	0.031(3)	-0.009(2)	0.007(2)	0.005(2)
N2	0.043(3)	0.022(2)	0.023(3)	-0.005(2)	0.000(2)	0.001(2)
N3	0.027(3)	0.032(3)	0.023(2)	-0.003(2)	0.004(2)	0.003(2)
N4	0.037(3)	0.072(4)	0.033(3)	-0.002(3)	0.017(3)	-0.011(3)
C1	0.046(4)	0.029(3)	0.032(3)	-0.010(3)	-0.002(3)	0.010(3)
C2	0.045(4)	0.051(4)	0.051(4)	-0.019(4)	-0.003(4)	0.014(4)
C4	0.080(6)	0.027(4)	0.041(4)	-0.006(4)	-0.021(4)	-0.000(3)
C3	0.061(5)	0.043(4)	0.063(5)	-0.022(4)	-0.025(4)	0.011(4)
C5	0.064(5)	0.023(3)	0.030(3)	-0.003(3)	-0.005(3)	-0.000(3)
C6	0.037(4)	0.032(3)	0.027(3)	-0.005(3)	0.005(3)	0.005(3)
C7	0.046(4)	0.054(4)	0.031(3)	-0.012(3)	0.013(3)	0.011(3)
C8	0.060(5)	0.055(4)	0.025(3)	-0.012(4)	0.004(3)	0.018(3)
C9	0.039(4)	0.045(4)	0.033(3)	-0.009(3)	-0.002(3)	0.011(3)
C10	0.033(3)	0.036(3)	0.032(3)	-0.007(3)	0.004(3)	0.006(3)
C11	0.033(4)	0.075(5)	0.045(4)	-0.007(4)	0.014(3)	0.015(4)
C12	0.030(4)	0.083(5)	0.035(4)	0.003(4)	0.016(3)	0.004(4)
C13	0.036(4)	0.117(7)	0.037(4)	0.012(4)	0.015(3)	0.011(5)
C14	0.057(5)	0.16(1)	0.033(4)	0.031(6)	0.014(4)	-0.005(5)
C15	0.060(5)	0.122(8)	0.047(5)	0.013(5)	0.018(4)	-0.029(5)
C16	0.045(4)	0.093(6)	0.041(4)	0.004(4)	0.010(3)	-0.026(4)
C18a	0.04(1)	0.06(1)	0.05(1)	-0.010(9)	0.026(8)	-0.029(9)
C18b	0.05(1)	0.049(9)	0.05(1)	0.008(8)	0.026(8)	-0.013(8)
F1a	0.072(7)	0.072(7)	0.15(1)	-0.008(6)	0.053(7)	-0.052(7)
F1b	0.054(6)	0.122(9)	0.104(8)	0.044(6)	-0.035(6)	-0.023(7)
F2a	0.060(8)	0.060(9)	0.047(6)	-0.024(8)	0.021(5)	-0.010(7)
F2b	0.06(1)	0.08(1)	0.09(1)	-0.05(1)	0.038(9)	-0.03(1)
F3a	0.26(3)	0.15(2)	0.005(8)	-0.12(2)	0.00(1)	-0.019(9)
F3b	0.14(2)	0.056(9)	0.03(1)	0.02(1)	0.00(1)	-0.008(7)
H10	0.044(-)					
H9	0.052(-)					
H7	0.055(-)					
H5	0.054(-)					
H8	0.059(-)					
H2	0.064(-)					
H4	0.071(-)					
H11a	0.062(-)					
H11b	0.062(-)					
H16	0.079(-)					
H3	0.073(-)					
H13	0.082(-)					
H14	0.105(-)					
H15	0.094(-)					
H_b	0.056(-)					
H_a	0.056(-)					

Bond Distances (Angstroms)

S-O2	1.31(2)
S-O1	1.322(9)
S-O3	1.397(6)
S-C18b	1.70(2)
S-C18a	1.85(2)
C18b-C18a	.88(2)
C18b-F3a	1.19(4)
C18b-F2b	1.29(3)
C18b-F1b	1.29(2)
C18b-F3b	1.30(3)
C18a-F3a	1.18(3)
C18a-F2b	1.20(3)
C18a-F3b	1.28(3)
C18a-F2a	1.33(3)
C18a-F1a	1.41(2)
F3b-F3a	.17(4)
F2a-F2b	.69(2)
N2-C1	1.322(9)
N2-C5	1.351(7)
N3-C6	1.346(8)
N3-C10	1.346(7)
N1-C6	1.403(7)
N1-C1	1.409(8)
N1-C11	1.480(9)
N4-C16	1.33(1)
N4-C12	1.34(1)
C6-C7	1.398(9)
C10-H10	.965(7)
C10-C9	1.377(8)
C1-C2	1.404(9)
C9-H9	.962(6)
C9-C8	1.39(1)
C7-H7	.971(7)
C7-C8	1.363(9)
C5-H5	.973(7)
C5-C4	1.38(1)
C8-H8	.966(6)
C2-H2	.975(8)
C2-C3	1.36(1)
C12-C13	1.38(1)
C12-C11	1.51(1)
C4-H4	.973(7)
C4-C3	1.37(1)
C11-H11b	.958(6)
C11-H11a	.973(8)
C16-H16	.991(8)
C16-C15	1.37(1)
C3-H3	.958(7)
C13-H13	.985(9)
C13-C14	1.38(1)
C14-H14	.954(9)
C14-C15	1.35(2)
C15-H15	.99(1)
O-H_b	.547(4)
O-H_a	.972(4)

Bond Angles	(degrees)
O2-S-O1	112.4(8)
O2-S-O3	117.5(5)
O2-S-C18b	95.1(8)
O2-S-C18a	109.6(8)
O1-S-O3	114.1(6)
O1-S-C18b	113.2(7)
O1-S-C18a	85.2(7)
O3-S-C18b	102.5(6)
O3-S-C18a	113.7(6)
C18b-S-C18a	28.2(8)
C18a-C18b-F3a	68(2)
C18a-C18b-F2b	64(2)
C18a-C18b-F1b	165(2)
C18a-C18b-F3b	69(2)
C18a-C18b-S	85(1)
F3a-C18b-F2b	104(2)
F3a-C18b-F1b	105(2)
F3a-C18b-F3b	6(2)
F3a-C18b-S	120(2)
F2b-C18b-F1b	107(2)
F2b-C18b-F3b	99(2)
F2b-C18b-S	111(1)
F1b-C18b-F3b	103(2)
F1b-C18b-S	110(1)
F3b-C18b-S	126(2)
C18b-C18a-F3a	69(2)
C18b-C18a-F2b	75(2)
C18b-C18a-F3b	71(2)
C18b-C18a-F2a	106(2)
C18b-C18a-F1a	153(2)
C18b-C18a-S	66(1)
F3a-C18a-F2b	110(2)
F3a-C18a-F3b	7(2)
F3a-C18a-F2a	125(2)
F3a-C18a-F1a	95(2)
F3a-C18a-S	110(2)
F2b-C18a-F3b	105(2)
F2b-C18a-F2a	31(1)
F2b-C18a-F1a	132(2)
F2b-C18a-S	107(1)
F3b-C18a-F2a	118(2)
F3b-C18a-F1a	96(2)
F3b-C18a-S	117(2)
F2a-C18a-F1a	101(1)
F2a-C18a-S	117(1)
F1a-C18a-S	101.3(9)
F3a-F3b-C18a	54(*)
F3a-F3b-C18b	49(*)
C18a-F3b-C18b	40(1)
F2b-F2a-C18a	64(2)
F2a-F2b-C18a	85(3)
F2a-F2b-C18b	126(3)
C18a-F2b-C18b	41(1)
F3b-F3a-C18a	119(*)
F3b-F3a-C18b	124(*)
C18a-F3a-C18b	43(2)
C1-N2-C5	118.6(5)
C6-N3-C10	118.3(5)
C6-N1-C1	120.8(5)
C6-N1-C11	116.6(5)

C1-N1-C11	118.3(5)
C16-N4-C12	117.1(6)
N3-C6-C7	121.3(5)
N3-C6-N1	117.3(5)
C7-C6-N1	121.3(6)
H10-C10-N3	118.1(5)
H10-C10-C9	118.6(5)
N3-C10-C9	123.3(6)
N2-C1-C2	121.4(6)
N2-C1-N1	118.0(5)
C2-C1-N1	120.6(6)
H9-C9-C10	121.1(7)
H9-C9-C8	121.4(6)
C10-C9-C8	117.5(5)
H7-C7-C8	120.6(6)
H7-C7-C6	120.4(6)
C8-C7-C6	119.0(7)
H5-C5-N2	118.5(6)
H5-C5-C4	119.1(6)
N2-C5-C4	122.4(7)
H8-C8-C7	120.4(8)
H8-C8-C9	119.2(6)
C7-C8-C9	120.4(6)
H2-C2-C3	120.8(7)
H2-C2-C1	120.1(6)
C3-C2-C1	119.1(7)
N4-C12-C13	123.5(7)
N4-C12-C11	116.2(6)
C13-C12-C11	120.2(7)
H4-C4-C3	119.8(7)
H4-C4-C5	121.5(8)
C3-C4-C5	118.7(6)
H11b-C11-H11a	106.9(7)
H11b-C11-N1	108.9(6)
H11b-C11-C12	110.8(7)
H11a-C11-N1	107.8(6)
H11a-C11-C12	110.0(6)
N1-C11-C12	112.2(5)
H16-C16-N4	118.2(7)
H16-C16-C15	118.8(8)
N4-C16-C15	122.9(8)
H3-C3-C2	120.3(9)
H3-C3-C4	120.1(8)
C2-C3-C4	119.6(7)
H13-C13-C12	120.6(8)
H13-C13-C14	122.0(8)
C12-C13-C14	117.4(8)
H14-C14-C15	119(1)
H14-C14-C13	121(1)
C15-C14-C13	119.9(8)
H15-C15-C14	121.5(9)
H15-C15-C16	119.4(9)
C14-C15-C16	119.2(9)
H_b-O-H_a	74.3(5)

Dihedral Angles (degrees)

O3-S-C18b-C18a	-117(2)
O3-S-C18b-F3b	-58(2)
O3-S-C18b-F2b	-177(1)
O3-S-C18b-F1b	65(1)
O3-S-C18b-F3a	-56(2)
O2-S-C18b-C18a	123(2)
O2-S-C18b-F3b	-177(2)
O2-S-C18b-F2b	63(2)
O2-S-C18b-F1b	-54(1)
O2-S-C18b-F3a	-176(2)
O1-S-C18b-C18a	6(2)
O1-S-C18b-F3b	66(2)
O1-S-C18b-F2b	-54(2)
O1-S-C18b-F1b	-171(1)
O1-S-C18b-F3a	67(2)
C18a-S-C18b-C18a	0(2)
C18a-S-C18b-F3b	60(2)
C18a-S-C18b-F2b	-60(2)
C18a-S-C18b-F1b	-177(3)
C18a-S-C18b-F3a	61(2)
O3-S-C18a-C18b	71(2)
O3-S-C18a-F3b	19(2)
O3-S-C18a-F2a	168(1)
O3-S-C18a-F1a	-83(1)
O3-S-C18a-F2b	136(1)
O3-S-C18a-F3a	17(2)
O2-S-C18a-C18b	-62(2)
O2-S-C18a-F3b	-115(2)
O2-S-C18a-F2a	34(2)
O2-S-C18a-F1a	143(1)
O2-S-C18a-F2b	2(2)
O2-S-C18a-F3a	-117(2)
O1-S-C18a-C18b	-174(2)
O1-S-C18a-F3b	133(2)
O1-S-C18a-F2a	-78(1)
O1-S-C18a-F1a	31(1)
O1-S-C18a-F2b	-110(1)
O1-S-C18a-F3a	131(2)
C18b-S-C18a-C18b	0(2)
C18b-S-C18a-F3b	-52(2)
C18b-S-C18a-F2a	96(2)
C18b-S-C18a-F1a	-155(2)
C18b-S-C18a-F2b	65(2)
C18b-S-C18a-F3a	-55(3)
S-C18b-C18a-S	-.0(1)
S-C18b-C18a-F3b	132(2)
S-C18b-C18a-F2a	-113(1)
S-C18b-C18a-F1a	67(4)
S-C18b-C18a-F2b	-116(1)
S-C18b-C18a-F3a	125(2)
F3b-C18b-C18a-S	-132(2)
F3b-C18b-C18a-F3b	0(2)
F3b-C18b-C18a-F2a	115(2)
F3b-C18b-C18a-F1a	-64(4)
F3b-C18b-C18a-F2b	112(2)
F3b-C18b-C18a-F3a	-7(2)
F2b-C18b-C18a-S	116(1)
F2b-C18b-C18a-F3b	-112(2)
F2b-C18b-C18a-F2a	3(1)
F2b-C18b-C18a-F1a	-176(4)
F2b-C18b-C18a-F2b	0(1)

F2b-C18b-C18a-F3a	-119(2)
F1b-C18b-C18a-S	171(9)
F1b-C18b-C18a-F3b	-58(9)
F1b-C18b-C18a-F2a	58(9)
F1b-C18b-C18a-F1a	-122(8)
F1b-C18b-C18a-F2b	54(9)
F1b-C18b-C18a-F3a	-64(9)
F3a-C18b-C18a-S	-125(2)
F3a-C18b-C18a-F3b	7(2)
F3a-C18b-C18a-F2a	122(2)
F3a-C18b-C18a-F1a	-58(4)
F3a-C18b-C18a-F2b	119(2)
F3a-C18b-C18a-F3a	0(3)
S-C18b-F3b-C18a	-67(2)
S-C18b-F3b-F3a	13(*)
C18a-C18b-F3b-C18a	0(2)
C18a-C18b-F3b-F3a	80(*)
F2b-C18b-F3b-C18a	57(2)
F2b-C18b-F3b-F3a	137(*)
F1b-C18b-F3b-C18a	167(2)
F1b-C18b-F3b-F3a	-113(*)
F3a-C18b-F3b-C18a	-80(*)
F3a-C18b-F3b-F3a	0(*)
S-C18b-F2b-C18a	73(2)
S-C18b-F2b-F2a	66(4)
C18a-C18b-F2b-C18a	0(2)
C18a-C18b-F2b-F2a	-7(3)
F3b-C18b-F2b-C18a	-61(2)
F3b-C18b-F2b-F2a	-68(4)
F1b-C18b-F2b-C18a	-167(2)
F1b-C18b-F2b-F2a	-174(3)
F3a-C18b-F2b-C18a	-57(2)
F3a-C18b-F2b-F2a	-64(4)
S-C18b-F3a-C18a	-71(2)
S-C18b-F3a-F3b	-168(*)
C18a-C18b-F3a-C18a	0(2)
C18a-C18b-F3a-F3b	-97(*)
F3b-C18b-F3a-C18a	97(*)
F3b-C18b-F3a-F3b	0(*)
F2b-C18b-F3a-C18a	54(2)
F2b-C18b-F3a-F3b	-43(*)
F1b-C18b-F3a-C18a	166(2)
F1b-C18b-F3a-F3b	68(*)
S-C18a-F3b-C18b	50(2)
S-C18a-F3b-F3a	-17(*)
C18b-C18a-F3b-C18b	0(2)
C18b-C18a-F3b-F3a	-67(*)
F2a-C18a-F3b-C18b	-98(2)
F2a-C18a-F3b-F3a	-165(*)
F1a-C18a-F3b-C18b	156(2)
F1a-C18a-F3b-F3a	89(*)
F2b-C18a-F3b-C18b	-68(2)
F2b-C18a-F3b-F3a	-135(*)
F3a-C18a-F3b-C18b	67(*)
F3a-C18a-F3b-F3a	0(*)
S-C18a-F2a-F2b	-77(2)
C18b-C18a-F2a-F2b	-6(3)
F3b-C18a-F2a-F2b	71(3)
F1a-C18a-F2a-F2b	174(2)
F2b-C18a-F2a-F2b	0(3)
F3a-C18a-F2a-F2b	69(3)
S-C18a-F2b-C18b	-59(1)
S-C18a-F2b-F2a	115(2)

C18b-C18a-F2b-C18b	0(2)
C18b-C18a-F2b-F2a	174(3)
F3b-C18a-F2b-C18b	65(2)
F3b-C18a-F2b-F2a	-121(3)
F2a-C18a-F2b-C18b	-174(3)
F2a-C18a-F2b-F2a	0(2)
F1a-C18a-F2b-C18b	178(3)
F1a-C18a-F2b-F2a	-8(3)
F3a-C18a-F2b-C18b	60(2)
F3a-C18a-F2b-F2a	-126(3)
S-C18a-F3a-C18b	53(2)
S-C18a-F3a-F3b	164(*)
C18b-C18a-F3a-C18b	0(2)
C18b-C18a-F3a-F3b	111(*)
F3b-C18a-F3a-C18b	-111(*)
F3b-C18a-F3a-F3b	0(*)
F2a-C18a-F3a-C18b	-95(3)
F2a-C18a-F3a-F3b	16(*)
F1a-C18a-F3a-C18b	157(2)
F1a-C18a-F3a-F3b	-92(*)
F2b-C18a-F3a-C18b	-64(2)
F2b-C18a-F3a-F3b	47(*)
C18b-F3b-F3a-C18b	0(1)
C18b-F3b-F3a-C18a	-51(9)
C18a-F3b-F3a-C18b	51(9)
C18a-F3b-F3a-C18a	0(1)
C18a-F2a-F2b-C18b	5(2)
C18a-F2a-F2b-C18a	0(1)
C5-N2-C1-N1	176.5(5)
C5-N2-C1-C2	-3.5(8)
C1-N2-C5-C4	2.5(8)
C1-N2-C5-H5	-177.5(5)
C10-N3-C6-N1	-177.9(5)
C10-N3-C6-C7	3.3(8)
C6-N3-C10-C9	-3.0(9)
C6-N3-C10-H10	178.7(5)
C1-N1-C6-N3	53.6(8)
C1-N1-C6-C7	-127.7(6)
C11-N1-C6-N3	-149.8(6)
C11-N1-C6-C7	28.9(8)
C6-N1-C1-N2	-51.1(8)
C6-N1-C1-C2	128.8(6)
C11-N1-C1-N2	152.6(6)
C11-N1-C1-C2	-27.4(8)
C6-N1-C11-C12	52.0(7)
C6-N1-C11-H11a	-69.4(7)
C6-N1-C11-H11b	175.0(6)
C1-N1-C11-C12	-150.8(5)
C1-N1-C11-H11a	87.8(6)
C1-N1-C11-H11b	-27.8(9)
C16-N4-C12-C11	178.3(6)
C16-N4-C12-C13	1.3(9)
C12-N4-C16-C15	-2(1)
C12-N4-C16-H16	179.8(6)
N3-C6-C7-C8	-1.0(9)
N3-C6-C7-H7	179.0(6)
N1-C6-C7-C8	-179.7(6)
N1-C6-C7-H7	0(1)
N3-C10-C9-C8	.3(9)
N3-C10-C9-H9	179.5(6)
H10-C10-C9-C8	178.6(6)
H10-C10-C9-H9	-2(1)
N2-C1-C2-C3	1.4(9)

N2-C1-C2-H2	-178.6(6)
N1-C1-C2-C3	-178.6(6)
N1-C1-C2-H2	1(1)
C10-C9-C8-C7	2(1)
C10-C9-C8-H8	-178.9(6)
H9-C9-C8-C7	-177.1(6)
H9-C9-C8-H8	2(1)
C6-C7-C8-C9	-2(1)
C6-C7-C8-H8	179.2(6)
H7-C7-C8-C9	178.2(6)
H7-C7-C8-H8	0(1)
N2-C5-C4-C3	.7(9)
N2-C5-C4-H4	-179.0(6)
H5-C5-C4-C3	-179.3(6)
H5-C5-C4-H4	0(1)
C1-C2-C3-C4	2(1)
C1-C2-C3-H3	-177.7(6)
H2-C2-C3-C4	-178.1(6)
H2-C2-C3-H3	2(1)
N4-C12-C11-N1	35.5(8)
N4-C12-C11-H11a	155.5(6)
N4-C12-C11-H11b	-86.5(8)
C13-C12-C11-N1	-147.4(6)
C13-C12-C11-H11a	-27.3(9)
C13-C12-C11-H11b	90.6(8)
N4-C12-C13-C14	0(1)
N4-C12-C13-H13	-179.5(6)
C11-C12-C13-C14	-177.4(7)
C11-C12-C13-H13	4(1)
C5-C4-C3-C2	-3(1)
C5-C4-C3-H3	176.7(6)
H4-C4-C3-C2	176.9(6)
H4-C4-C3-H3	-3(1)
N4-C16-C15-C14	3(1)
N4-C16-C15-H15	-176.7(7)
H16-C16-C15-C14	-179.4(7)
H16-C16-C15-H15	1(1)
C12-C13-C14-C15	0(1)
C12-C13-C14-H14	-178.0(8)
H13-C13-C14-C15	179.8(8)
H13-C13-C14-H14	0(1)
C13-C14-C15-C16	-2(1)
C13-C14-C15-H15	177.6(8)
H14-C14-C15-C16	176.9(8)
H14-C14-C15-H15	-4(1)

8.2 Appendix

Å	Ångstrom
abs.	absolute
Ac	acetyl
acac	acetylacetonato
aq.	aqueous
eq.	equivalent
Ar	aryl, argon
RP	representative procedure
Calc.	calculated
B.p.	boiling point
BINAP	2,2´-bis-(diphenylphosphino)-1,1´-binaphthyl
Boc	*tert*-butyloxycarbonyl
Box	bis(oxazoline)
Bn	benzyl
Bz	benzoyl
br.	broad
BuLi	butyllithium
Bus	*tert*-butylsulfonyl
Cbz	benzyloxycarbonyl
Cy	cyclohexyl
CHP	cumene hydroperoxide
conc.	concentrated
Cy	cyclohexyl
d	day, doublett
dba	dibenzylidenacetone
DMAP	dimethylaminopyridine
DME	dimethoxyethane
DMF	dimethyl formamide
DMSO	dimethylsulfoxide
dppp	1,3-bis(diphenylphosphino)propane
dppf	1,1'-bis(diphenylphosphino)ferocene
ee	enantiomeric excess

EA	ethyl acetate
EI	elecronic Ionisation
Et	ethyl
eV	electronvolt
g	gram
GC	gaschromatography
h	hours, heptet
HMDS	1,1,1,3,3,3-hexamethyldisilazane
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectroscopy
HV	high vacuum
i-Pr	isopropyl
IR	Infrared spectroscopy
cat.	catalyst
L	ligand
LDA	lithiumdiisopropylamine
Solv.	solvent
M	molar
m	multiplet
m/*z*	mass/ charge
Me	methyl
mg	milligram
min	minute
mL	milliliter
mmol	millimol
MS	mass spektroscopy, molecularsiebs
MTBE	methyl-*tert*-butylether
NMR	nuclear magnetic resonance
NBS	*N*-bromosuccimide
n	normal
Ns	*p*-nitrobenzenesulfonyl
PCC	pyridinium chlorochromate
PE	petroleumether (boiling point 40-80°C)
PG	protecting group

Ph	pheny
PMB	*p*-methoxybenzyl
ppm	parts per million
^{i}Pr	isopropyl
Py	pyridine, pyridyl
Pybox	2,6-bis(2-oxazoline-2-yl) pyridine
PTC	phase transfer catalyst
p-Tol	*para*-tolyl
q	quartet
R	organischer Rest
rac	racemic
R_f	ratio of fronts
r.t.	room temperature
s	singlet
SES	trimethylethanesulfonyl
Sat.	saturated
t	triplet
t_R	Retention time
tert	tertiary
t-Bu	*tert*-butyl
TBAB	tetrabutylammonium bromide
TBAF	tetrabutylammonium fluoride
TBHP	*tert*-butylhydroperoxide
TBS	*t*-butyldimethysilyl
Temp.	temperature
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Tf	trifluormethansulfonyl
tpy	terpyridine
Ts	*para*-toluenesulfonyl
υ	wave length
Z	benzyloxycarbonyl

8.3 Acknowledgments

An dieser Stelle möchte ich meine tiefste Dankbarkeit dem ganzen Leute des OC-Institutes ausdrücken und zwar allen Freunden, Kollegen und Mitarbeitern, die mich mit ihrer Hilfe auf dem ganzen Weg bis zu meiner Promotion begleitet haben. Diese Arbeit wäre ohne ihre Mitwirkung nicht geschafft.

Danke sehr Ingrid Voss für die viele nette Hilfe von der Anfang bis Ende meiner Doktorarbeit.

Ein besonderer Dank geht zuallererst an meinen ehemaligen Laborkollegen für die vielen schönen gemeinsamen Stunden inner- und ausserhalb des Labors, die aufregenden Diskussionen, Ratschläge und Unterstützung.

Herzlichen Dank an frühren Laborkollegen Elisabetta Veri, Daniel Whelligan und Iuliana Atodiresei für die Zusammenarbeit, die vielen Beratungen und die Hilfsbereitschaft.

Vielen Dank für Toni Rantanen, Joerg Sedelmeier und Ellen Schmitt für ihre Hilfe bei der HPLC-Analytik.

Danke Marcus Frings für die technische Beratung und die Hilfe bei häutigen Computer-Probleme.

Einen ganz besonders herzlichen Dank dem hoch motivierten “Super Korrekturen-Gruppe”, der mit großem Engagement, Kompetenz, Geduld, diese Arbeit sorgfältig und schnell gelesen und verbessert hat: Matthew McGrath, Olga Garcia und Juta Kobayashi sei hier für die hilfreichen Diskussionen gedankt.

Vielen Dank an Nicole Brendgen und Susi Grünebaum für ihre tatkräftige präparative Unterstützung, Zuneigung und ständige große Hilfsbereitschaft besonderes GC analyse in den drei Jahren.

Herzlichen Dank Herrn Prof. Gerhard Raabe für die Durchführung der X-ray Strukturanalyse.

Danke allen alten Mitarbeitern des Labors 5.06 für die gemeinsam verbrachten Tage, die gegenseitige Hilfe und die freundliche Stimmung, besonderes die Arbeitsstunden so angenehm gemacht haben: Iuliana Atodiresei, Elisabetta Veri und Daniel Whelligan.

Danke der “Japanese Connection” Juta Kobayashi für die nette Aufnahme und Hilfe.

Extra herzlichen Dank an der Familie Atodiresei für viele sorte Hilfe und angenahme Zeit nach der Arbeit und am Feiertag und Wochenende.

Vielen Dank “Latin Mafia”: Olivia Bistri, Arkaitz Correa und Miguel Pena für Diskussionen und schöne Zeit während meiner Doktorarbeit.

Einen großen Dank an der “jungen Generation des AK-Bolm” Angelika Bruckmann, Ralph Husmann und Anne Nijs für die angenehme Zeit be meiner Doktorarbeit. Danke Marinella Verrucci, Sandra Saladin, Martin Langner, Iuliana Atodiresei, Gae Young Cho, Jean Cedric Frison, Lorenzo Zani, Julien Legros, Chiara Pavan, Salih Özcubukcu, Frank Schmidt, Toni Rantanen, Elisabetta Veri, Rene Stemmler, Jenny Jansson, Yu Yuan, Pauline Remy, Helene Villar, Arno Claßen, Lukas Hintermann, Daniel Whelligan, Juan Dehli, und ganz besonders Christian Mößner für die Vitalität, die Unternehmungslust und große Hilfe.

Einen ganz besonderes Dank an Salih Özcubukcu am Anfang meiner Arbeit. Ohne deine Hilfe konnte ich meine Doktorarbeit im Labor nicht anfangen.

Einen großen Dank an der 3. Etage, Ingo Schiffers, Aurélie Labonne, Marco Schmitz und Bernhard Füger für die Einarbeitung in Chemie, Sprache und viele deutsche Kulturen.

Vorletzt, Dank an der “Rest des AK-Bolm”.

Zuletzt, vielen Dank an allen Leuten, die aus der Ferne dieser Arbeit in Deutschland verfolgt haben und immer mit Beistand, Gedanken und Aufmunterung präsent waren: vor allem meine Familie, besoderes meine Eltern und Großeltern sowie meine Geschwister Mitsuko und Hiroko.

8.4 Curriculum Vitae

Personal Data

Name:	Masafumi Nakanishi
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School Education

1984-1990	Ōharano-elementary school
1990-1993	Rakusai-junior high school
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Educational Qualifications:

2004-2006 Ph.D. work from the Institute of Organic Chemistry, RWTH Aachen university, thesis topic, "Iron catalyzed C-H activation and novel ligand synthesis"**,** supervisor: Prof. Dr. Carsten Bolm.

2002 Completed an MSc at Hokkaido University, thesis topic: "Palladium complex catalyzed acylation of allylic esters with acylstannanes", supervisor: Prof. Dr. Yasushi Tsuji.

2000 Completed a BSc at the Himeji Institute of Technology; thesis topic "Stereochemical study on cyclic acetal formation during anodic oxidation of napthalene derivatives by Transformation of chiral alcohols into achiral acetals", supervisor: Prof. Dr. Takashi Okuyama.

Relevant Work Experience:

2002-2004 Research Worker, Discovery Research, Central Research Laboratories, ZERIA Pharmaceutical Co., Ltd.