Applications of Planar-Chiral Heterocycles in Asymmetric Catalysis

by

Beata Tao

B.Sc., Honors, Chemistry
University of Toronto, 1996

Submitted to the Department of
Chemistry in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY
IN ORGANIC CHEMISTRY

at the

Massachusetts Institute of Technology

June 2002

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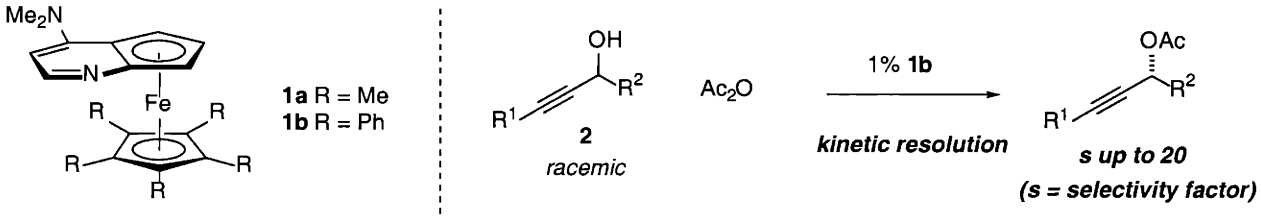
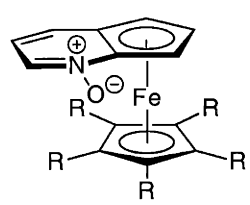
ABSTRACT

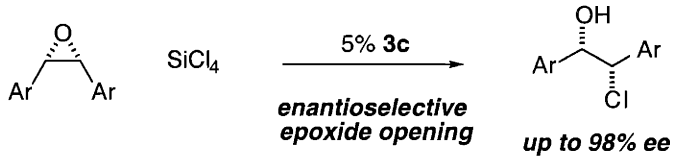
The development of planar-chiral heterocycles for asymmetric catalysis and their applications to enantioselective processes were investigated. Reactions including the kinetic resolution of propargylic alcohols, the enantioselective ring opening of meso epoxides, and the asymmetric hydrosilylation of ketones were studied.



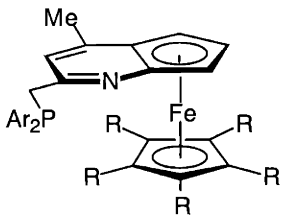
During the past few years, our group has developed **1b** as one of the most effective and versatile nonenzymatic acylation catalysts for the kinetic resolution of arylalkylcarbinols. Surprisingly, however, when the optimized reaction conditions were applied to the kinetic resolution of secondary propargylic alcohols, only low to moderate selectivity factors were obtained. Detailed investigations revealed that triethylamine serves as a competitive general base catalyst in the acylation reaction of propargylic alcohols, thereby suppressing the intrinsic selectivity factor. When base is omitted, the selectivity factor for propargylic alcohol **2** (R^1 = Ph, R^2 = Me) increases from 6 to 20. Using this new protocol, we can effect the kinetic resolution of a number of propargylic alcohols with selectivity factors of 10 or above.



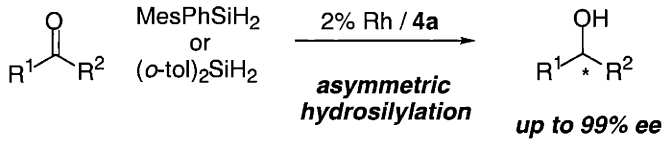
3a R = Me
3b R = Ph
3c R = 3,5-$Me_2C_6H_3$



Catalysts in which oxygen is the nucleophilic site effect a number of useful transformations. In view of the utility of planar-chiral pyridine derivatives such as **1**, it occurred to us that pyridine *N*-oxides **3** might also prove to be effective asymmetric catalysts. We synthesized complexes **3a-c** and were gratified to discover that **3a** efficiently catalyzes the ring opening of *cis*-stilbene oxide by $SiCl_4$, albeit in modest enantiomeric excess. By increasing the steric demand of the bottom ring, we found that the selectivity increases significantly. Thus, bulky derivative **3c** affords 92% ee in the ring opening of *cis*-stilbene oxide at –85 °C. A number of epoxides can be desymmetrized in very good yield and high stereoselectivity under these conditions (up to 98% ee).



4a R = Me, Ar = Ph
4b R = Me, Ar = *o*-tol
4c R = *p*-tol, Ar = Ph



In addition, we have also synthesized a new family of planar-chiral *N,P*-ligands (**4**). The ligand design allows incorporation of different substituents on the phosphorus atom and on the C_5R_5 bottom ring, thereby providing a means for tuning catalyst enantioselectivity. We chose the asymmetric hydrosilylation of ketones to test the effectiveness of our ligand design. In general, sterically demanding silanes such as $MesPhSiH_2$ and $(o\text{-tol})_2SiH_2$ furnish better enantioselectivities than simple silanes like Ph_2SiH_2. Among the planar-chiral ligands tested, we found that ligand **4a** gives the best yields and enantioselectivities for a wide array of substrates (arylalkyl ketones: up to 99% ee; dialkyl ketones: up to 96% ee). Deuterated benzaldehyde-1-*d* can also be reduced with excellent enantioselectivity (95% ee). Access to chiral silanes is also possible using the same ligand.

Thesis Supervisor: Gregory C. Fu

Title: Professor of Chemistry

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Tao, B.; Lo, M. M.-C.; Fu, G. C. "Planar-Chiral Pyridine *N*-Oxides, a New Family of Asymmetric Catalysts: Exploiting an η^5-C_5R_5 Ligand to Achieve High Enantioselectivity," *J. Am. Chem. Soc.* **2001**, *123*, 353-354.

Tao, B.; Ruble, J. C.; Hoic, D. A.; Fu, G. C. "Non-Enzymatic Kinetic Resolution of Propargylic Alcohols by a Planar-Chiral DMAP Derivative; Crystallographic Characterization of the Acylated Catalyst," *J. Am. Chem. Soc.* **1999**, *121*, 5091-5092.

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I have become who I am today because of my parents, and I am eternally grateful to the countless sacrifices that they have made for my siblings and me throughout their lives. Although they never had the chance to pursue their dreams, they have provided us with opportunities that a humble family, such as ours, would never have dared dream of. I would also like to express my deepest thanks to my siblings: Rolita, Anita and Edwin. Thank you all for taking care of Mum and Dad while I have been away from home and for being wonderful friends with whom I have shared my ups and downs.

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It has been a great pleasure to work with many intelligent and talented chemists in the Fu group. Special thanks goes to Michael Lo for many insightful discussions and suggestions. I would also like to thank Shuang Qiao for her friendship, support and encouragement throughout my Ph. D. career. I am grateful to Jack Liang for all of the pioneering work that he did; if it were not for him, I may still be struggling in my thesis research. Thanks to Ken Tanaka, the MVP (most valuable postdoc) in our laboratory for showing me how to finish a Ph. D. thesis in two years' time, Jens Hildebrand, for providing the "Jenstein" service (the most powerful human search engine that I have ever met) when I was too lazy to go to the library, and Matthew Netherton (also known

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I thank God for my husband, Desmond Lim, whose love for me is boundless. I am very fortunate to be able to spend the rest of my life with this intelligent young man. I have also been blessed with a wonderful family of in-laws, and I thank them for all their love and support that they have poured out to me.

Last but not least, I would like to thank God for granting me the wisdom, courage and perseverance to follow my dreams.

Ad Maiorem Dei Gloriam.

To my husband and my parents

TABLE OF CONTENTS

ABBREVIATIONS

Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
d	doublet
DMAP	4-(dimethylamino)pyridine
eq	equation
equiv	equivalent(s)
GC	gas chromatography
h	hour(s)
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectroscopy
IR	infrared
LDA	lithium diisopropylamide
min	minute(s)
MTO	methyltrioxorhenium
NMR	nuclear magnetic resonance
ppm	parts per million
PPY	4-(pyrrolidino)pyridine
q	quartet
r.t.	room temperature
s	singlet
t	triplet
THF	tetrahydrofuran
TLC	thin-layer chromatography

Chapter 1:

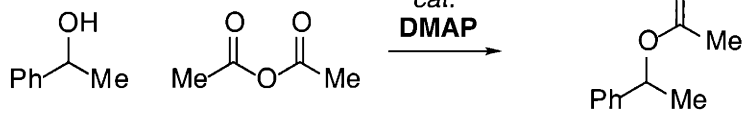
Introduction to Planar-Chiral Heterocycles

Introduction to Planar-Chiral Heterocycles

Nucleophilic catalysts have been demonstrated to accelerate a wide spectrum of reactions. One of the most well-known nucleophilic catalysts in organic synthesis is 4-(dimethylamino)pyridine (DMAP).[1] For example, the acylation of alcohols is catalyzed by DMAP (Scheme 1.1),[2] the rearrangement of *O*-acylated azlactones to their *C*-acylated isomers proceeds in the presence of a catalytic amount of DMAP,[3] and the ring opening of azlactones with alcohols to give protected amino acids[4] is also facilitated by DMAP (Scheme 1.1).

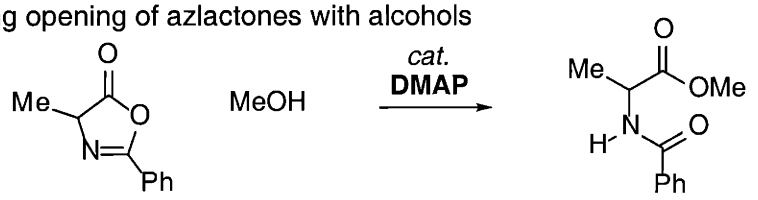
Scheme 1.1 Reactions Subject to Pyridine-Based Nucleophilic Catalysis

- Acylation of alcohols



- Rearrangement of *O*-acylated azlactones

- Ring opening of azlactones with alcohols



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1 For reviews, see: (a) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 569-583. (b) Hassner, A.; Krepski, L. R.; Alexanian, V. *Tetrahedron* **1978**, *34*, 2069-2076. (c) Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *12*, 129-161.

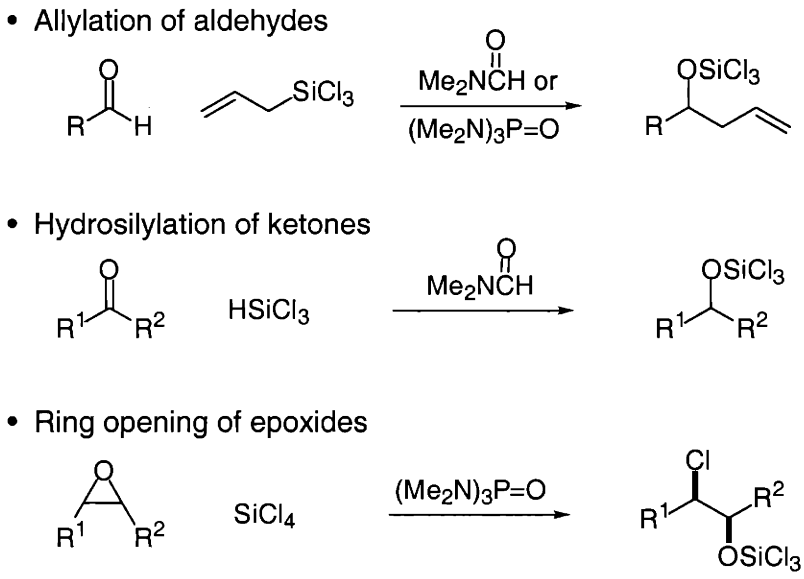
2 Steglich, W.; Höfle, G. *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 981.

3 Steglich, W.; Höfle, G. *Tetrahedron Lett.* **1970**, 4727-4730.

4 Liang, J.; Ruble, J. C.; Fu, G. C. unpublished results.

In addition to pyridine-based nucleophiles, there are a number of reactions that are catalyzed by oxygen-based nucleophiles. For example, the allylation of aldehydes with allyltrichlorosilane is promoted in the presence of *N,N*-dimethylformamide[5] (DMF) or hexamethylphosphoramide (HMPA).[6] Hydrosilylation of ketones[7] and the ring opening of epoxides[8] can also be mediated by DMF and HMPA (Scheme 1.2).

Scheme 1.2 Reactions Subject to Oxygen-Based Nucleophilic Catalysis



Despite the usefulness of these reactions, not many asymmetric versions of these processes had been developed at the time we initiated our studies in this field. As depicted in Scheme 1.3, while there were a number of examples of chiral

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5 (a) Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453-3456. (b) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620-6628.

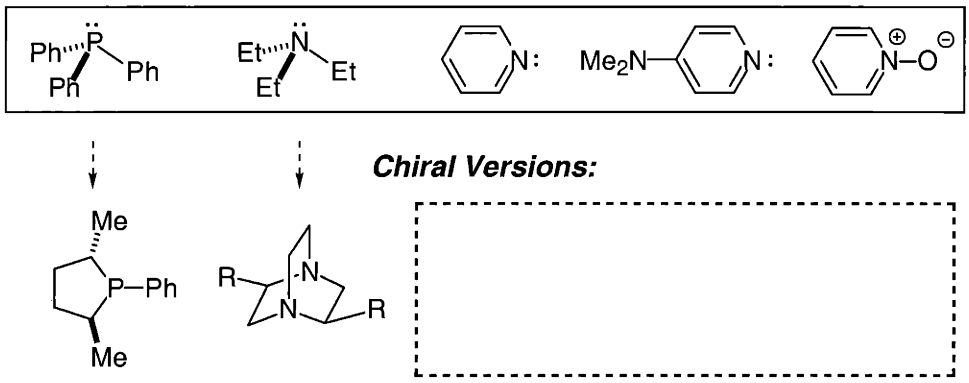
6 Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161-6163.

7 Kobayashi, S.; Yasuda, M.; Hachiya, I. *Chem. Lett.* **1996**, 407-408.

8 Denmark, S. E.; Barsanti, P. A.; Wong, K.-T.; Stavenger, R. A. *J. Org. Chem.* **1998**, *63*, 2428-2429.

phosphines and chiral tertiary amines reported in the literature, chiral variants of pyridine, DMAP, and pyridine *N*-oxide were scarce prior to 1995. Therefore, we hoped to develop new chiral nucleophiles as selective and versatile catalysts for asymmetric versions of the above processes.

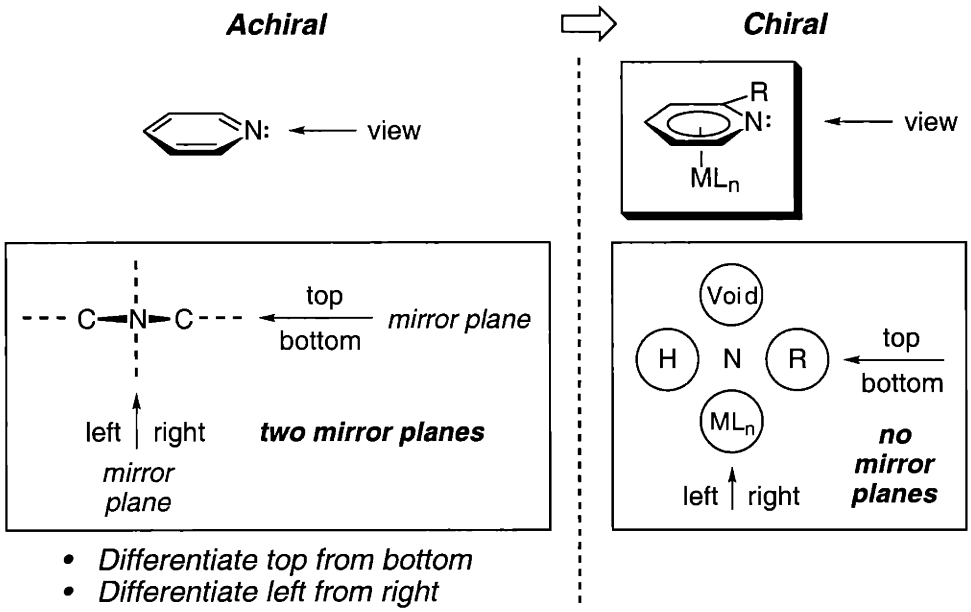
Scheme 1.3 Commonly Used Nucleophiles and Their Chiral Variants



Our approach to create a chiral version of pyridine, DMAP, and pyridine *N*-oxide is as follows (Scheme 1.4).[9] Pyridine is achiral because it contains two mirror planes, one in the plane of the molecule (horizontal mirror plane) and the other perpendicular to the plane of the molecule and passing through the nitrogen atom (vertical mirror plane). Therefore, to develop a chiral version of pyridine, we need to destroy the two mirror planes. To remove the horizontal mirror plane, a metal fragment is π-complexed to the heterocycle, and to eliminate the vertical mirror plane, a substituent is incorporated at the 2-position of the molecule. Hence, the resulting complex is chiral with a well-defined asymmetric environment around the nucleophilic nitrogen atom.

9 Fu, G. C. *Acc. Chem. Res.* **2000**, *33*, 412-420.

Scheme 1.4 Design of a Planar-Chiral Heterocycle

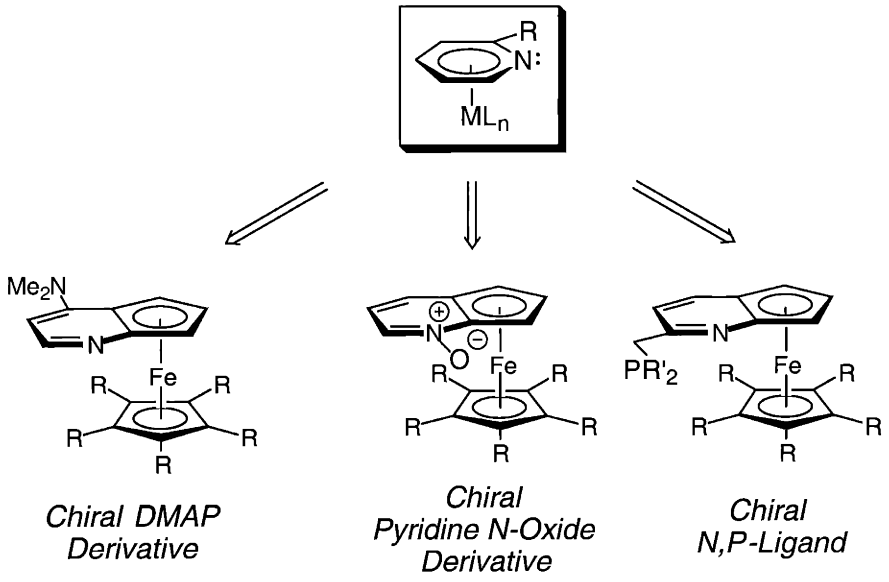


Because pyridine π-complexes are difficult to synthesize due to the ease of σ-donation of pyridine to metals, we chose to complex a pyrindinyl ring, in which the metal would π-complex to a carbocylic ring rather than the heterocycle. Using this design, we were able to synthesize a chiral DMAP derivative, a chiral pyridine *N*-oxide derivative, and a chiral *N,P*-ligand (Scheme 1.5). The planar-chiral design offers us several advantages over other systems (e.g., central chirality). First, we can avoid placing a bulky stereogenic center at the 2-substituent, which can lower the catalytic activity of the nucleophiles. This is especially crucial in the case of chiral DMAP, as it has been demonstrated by Vedejs that the steric bulk of the stereogenic carbon in the 2-position of pyridine greatly reduces the nucleophilicity of the nitrogen.[10] Second, we can choose to functionalize the top pyrindinyl ring and incorporate different heteroatoms (e.g., nitrogen, oxygen, sulfur, and phosphorus) into the molecule, giving rise to new families of chiral bidentate ligands for

10 Vedejs, E.; Chen, X. *J. Am. Chem. Soc.* **1996**, *118*. 1809-1810.

asymmetric catalysis, using one general design. Third, the choice of "FeC_5R_5" as our metal fragment allows us to tune the steric and electronic properties of the metal fragment. This enables us to readily adapt the chiral environment for different asymmetric processes.

Scheme 1.5 Planar-Chiral Heterocycles



In this thesis, the development of planar-chiral heterocycles as chiral catalysts and ligands in asymmetric catalysis will be presented. In Chapter 2, the application of the planar-chiral DMAP analogue in the kinetic resolution of propargylic alcohols will be discussed. Presented in Chapter 3 is the synthesis of the planar-chiral pyridine *N*-oxides, followed by their application in the enantioselective ring opening of meso epoxides. In Chapter 4, the synthesis of a new family of chiral *N,P*-ligands, and their applications in asymmetric hydrosilylation will be described.

Chapter 2:

Kinetic Resolution of Propargylic Alcohols Using Planar-Chiral DMAP Derivatives

Introduction to Kinetic Resolution

Kinetic resolution[1] is a process used to separate enantiomers by selectively reacting one enantiomer with a chiral reagent. Unlike most asymmetric reactions, the observed enantiomeric excess in a kinetic resolution depends on the intrinsic selectivity of the reaction as well as the conversion. Also, it is usually the unreacted starting material rather than the reaction product that is of interest.

Because the enantiomeric excess of the reaction is dependent on the conversion, it is useful to quantify the effectiveness of a resolution process without mentioning both the ee and the conversion. Therefore, the term selectivity factor (s) was introduced, which is the ratio of the first-order rate constants for the conversion of the enantiomers to give their respective products.

$$s = \frac{k_R}{k_S} \qquad 2.1.1$$

The selectivity factor (s) can be expressed in terms of the conversion (C) and the ee of the unreacted starting material (ee):

$$s = \frac{\ln[(1-C)(1-ee)]}{\ln[(1-C)(1+ee)]} \qquad 2.1.2$$

The selectivity factor (s) can also be expressed in terms of the conversion (C) and the ee of the product (ee') if the products are chiral and there exists a one to one relationship between the starting material and the product:

$$s = \frac{\ln[1-C(1+ee')]}{\ln[1-C(1-ee')]} \qquad 2.1.3$$

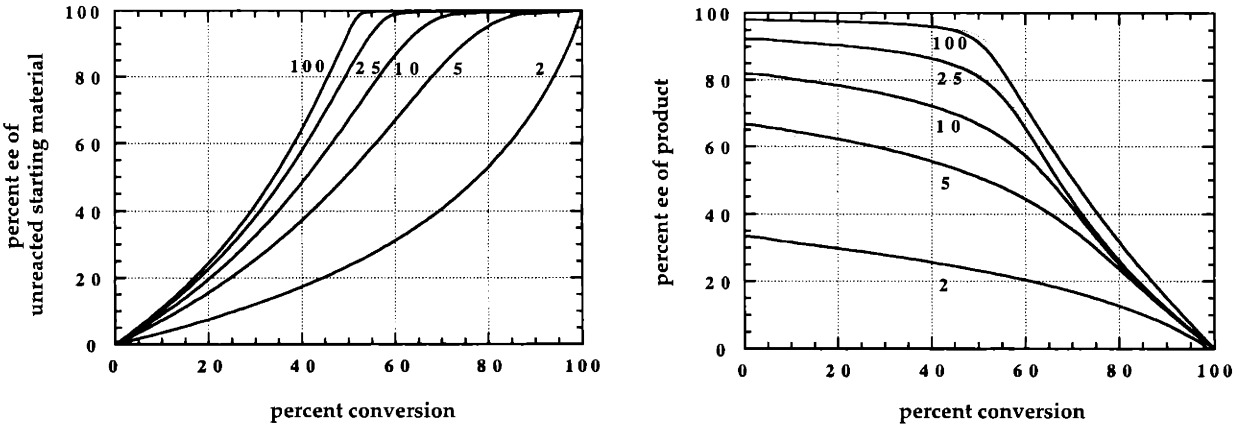
---

1 For reviews of kinetic resolution, see: (a) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1988**, *18*, 249-331. (b) Hoveyda, A. H.; Didiuk, M. T. *Curr. Org. Chem.* **1998**, 2, 537-574. (c) Keith, J. M.; Larrow, J. F.; Jacobsen, E. N. *Adv. Synth. Catal.* **2001**, *343*, 5-26.

Using the above two equations, one can easily express ee/ee' in terms of conversion (eq. 2.1.4). Hence, if the enantiomeric excess of the unreacted starting material (ee) and the product (ee') can be easily measured, one can determine the selectivity factor as well as the conversion of the reaction.

$$\frac{ee}{ee'} = \frac{C}{1-C} \qquad 2.1.4$$

Figure 2.1 Graph of ee Versus Percent Conversion at Different Selectivity Factors



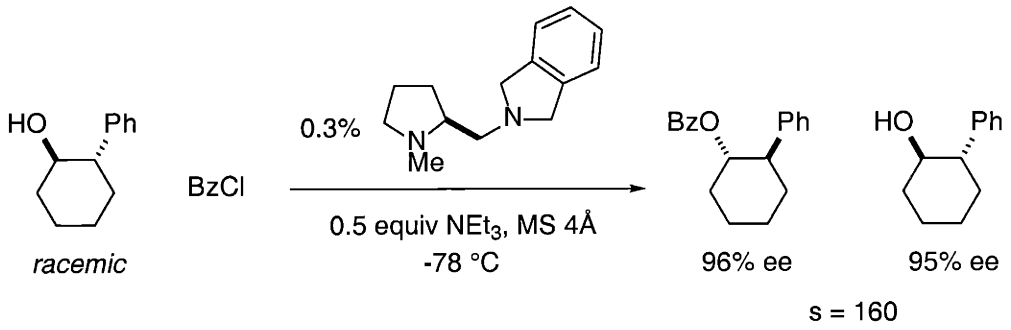
The compound of interest in a simple kinetic resolution is usually the unreacted starting material because the ee of the starting material increases as the reaction proceeds whereas the product enantiopurity decreases as the reaction approaches higher conversion (Figure 2.1). Hence, even with a selectivity factor of 2, one can still obtain highly enantiomerically enriched unreacted starting material (>80% ee) at the expense of yield (>94% conversion). As the selectivity factor reaches double digits, enantiomeric excess of 90% or greater of the unreacted starting material can be obtained at around 62% conversion. When a system approaches a perfect kinetic resolution, the selectivity factor approaches infinity, and both the unreacted starting material and the product can be obtained in high enantiomeric purity at 50% conversion. Note that in a simple kinetic resolution, the maximum yield of the

enantiomerically pure unreacted starting material is 50%.

Kinetic resolution is therefore a very powerful technique with which to obtain compounds of high optical purity, especially for oily and non-crystalline compounds for which it is not possible to crystallize to high enantiomeric excess. Below are some of the recent advances in non-enzymatic catalytic kinetic resolution of secondary alcohols by asymmetric acylation.

Oriyama et al. reported the use of a chiral proline-derived diamine in the kinetic resolution of certain classes of secondary alcohols. Their initial study required the presence of $SnBr_2$ as an additive and a 30% catalyst loading.[2] More recently, improved selectivities were obtained with the use of 0.3% catalyst loading of the chiral diamine in the presence of NEt_3; e.g., *trans*-2-phenyl-1-cyclohexanol and 1-(2-methylphenyl)ethanol were kinetically resolved with s values of 160 and 20, respectively.[3] In addition, highly efficient asymmetric acylation of meso diols could be achieved using a similar catalytic system.[4]

Scheme 2.1 Kinetic Resolution of Secondary Alcohols by Oriyama



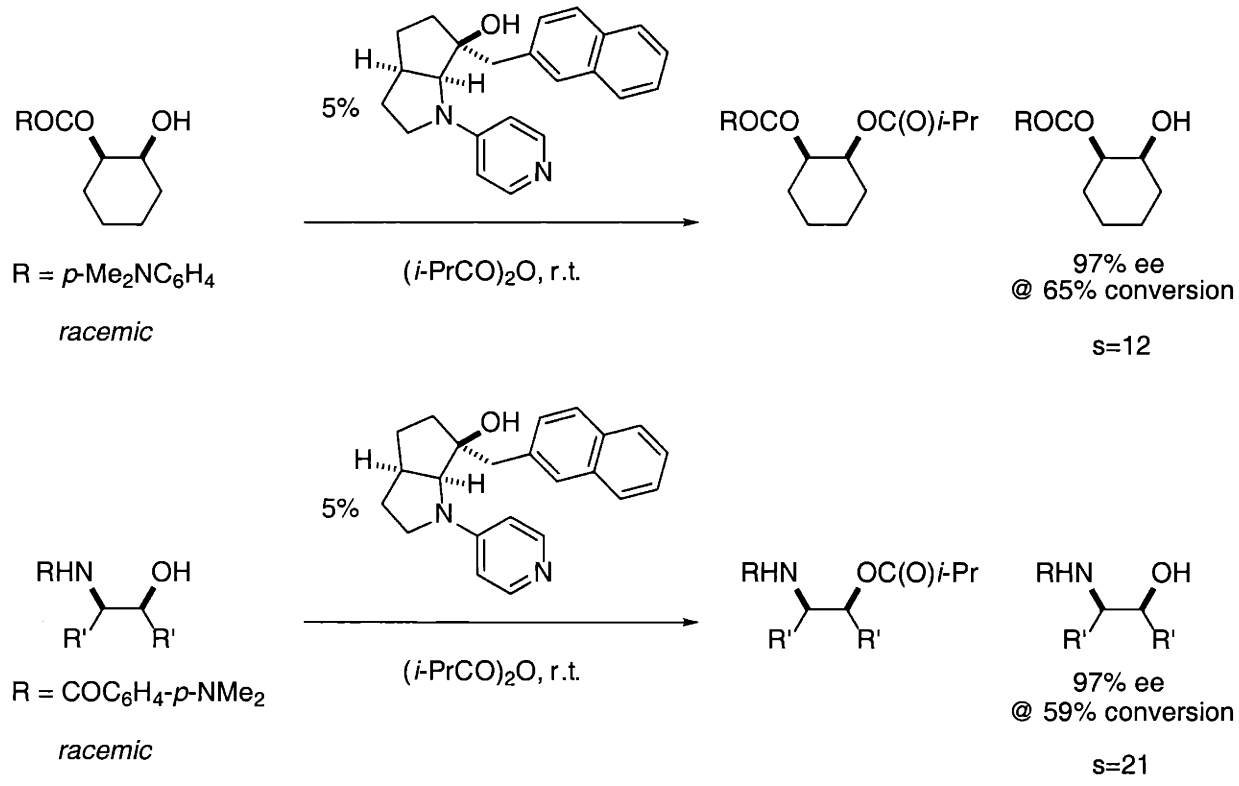
2 Oriyama, T.; Hori, Y.; Imai, K.; Sasaki, R. *Tetrahedron Lett.* **1996**, *37*, 8543-8546.

3 Sano, T.; Imai, K.; Ohashi, K.; Oriyama, T. *Chem. Lett.* **1999**, 265-266.

4 Oriyama, T.; Imai, K.; Sano, T.; Hosoya, T. *Tetrahedron Lett.* **1998**, *39*, 3529-3532.

Fuji and co-workers used a chiral pyrrolidinopyridine derivative for the asymmetric acylation of monobenzyolated *cis*-1,2-cyclohexanediol.[5] Employing isobutyric anhydride as the acylating agent, a selectivity factor of 12 was obtained. Kinetic resolution of cyclic cis amino alcohol derivatives could also be carried out using the same catalyst with selectivity factors up to 21.[6] Acyclic amino alcohol derivatives, however, gave poor to low selectivities under the same reaction conditions.

Scheme 2.2 Kinetic Resolution of Secondary Alcohols by Fuji



In utilizing small-molecule catalysts that mimic the functions of peptides, Miller

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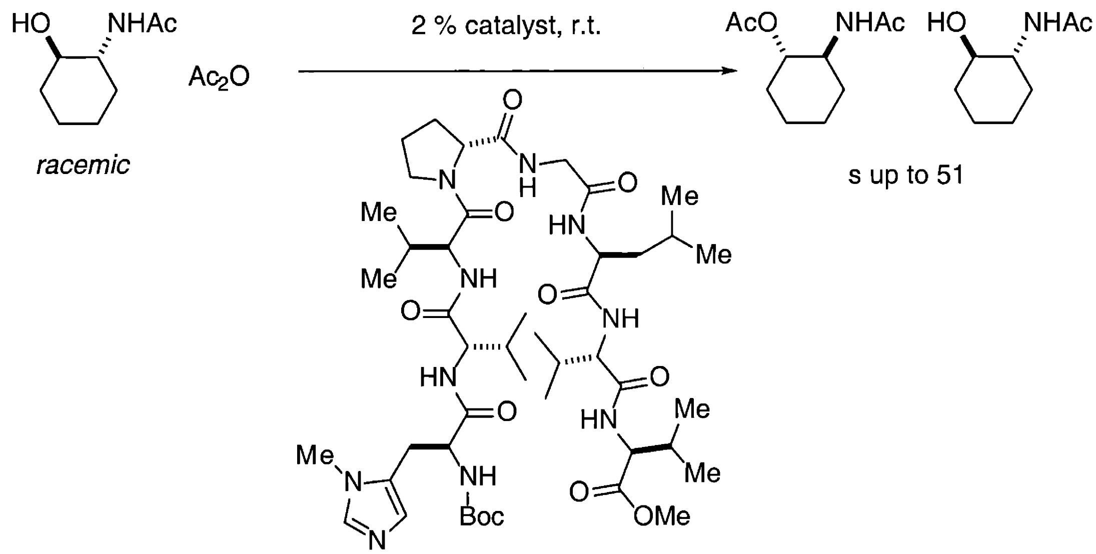
5 Kawabata, T.; Nagato, M.; Takasu, K.; Fuji, K. *J. Am. Chem. Soc.* **1997**, *119*, 3169-3170.

6 Kawabata, T.; Yamamoto, K.; Momose, Y.; Yoshida, H.; Nagaoka, Y.; Fuji, K. *Chem. Commun.* **2001**, 2700-2701.

et al. reported the use of a short peptide (tetrapeptide), into which an alkylimidazole was incorporated, for the kinetic resolution of racemic alcohols bearing an amide functionality.[7] It is believed that these substrates participate in hydrogen bonding with the peptide catalyst in the transition state, and hence provide enantio-differentiation.[8]

Scheme 2.3 Kinetic Resolution of Secondary Alcohols by Miller



The kinetic resolution of *trans*-1,2-hydroxyacetamides could be further optimized using an octapeptide catalyst to obtain selectivity factors up to 51.[9] To accelerate catalyst identification, Miller and co-workers developed a high-throughput

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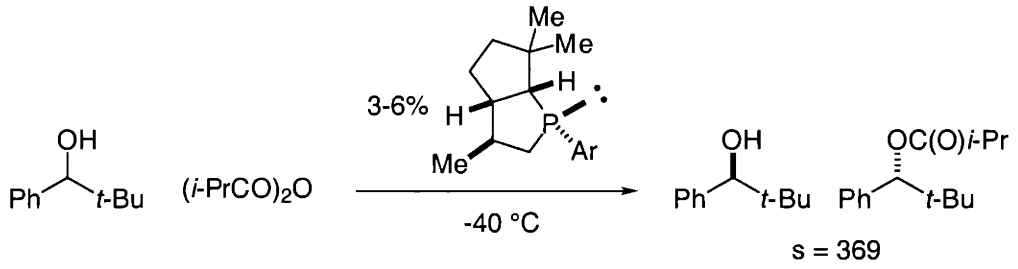
7 (a) Miller, S. J.; Copeland, G. T.; Papaioannou, N.; Horstmann, T. E.; Ruel, E. M. *J. Am. Chem. Soc.* **1998**, *120*, 1629-1630. (b) Copeland, G. T.; Jarvo, E. R.; Miller, S. J. *J. Org. Chem.* **1998**, *63*, 6784-6785.

8 Vasbinder, M. M.; Jarvo, E. R.; Miller, S. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 2824-2827.

9 (a) Jarvo, E. R.; Copeland, G. T.; Papaioannou, N.; Bonitatebus, Jr., P. J.; Miller, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 11638-11643. (b) Jarvo, E. R.; Vasbinder, M. M.; Miller, S. J. *Tetrahedron* **2000**, *56*, 9773-9779.

fluorescent-based assay for screening catalyst activities.[10] By attaching a pH-fluorescent sensor and catalyst onto a unique bead, the acylation activity of each catalyst could be monitored through a fluorescence response, which is triggered by acetic acid generated in the reaction. Using this method, a pentapeptide catalyst for the kinetic resolution of tertiary alcohols[11] and a new class of octapeptide catalysts for the kinetic resolution of secondary alcohols of a broad substrate scope were rapidly identified.[12]

Scheme 2.4 Kinetic Resolution of Secondary Alcohols by Vedejs



Vedejs' continuous effort on the kinetic resolution of secondary alcohols has led to the development of a very effective chiral phosphine. Following their initial work reported in 1996,[13] the Vedejs group has developed a new generation of chiral phosphine catalysts based on the 2-phosphabicyclo[3.3.0]octane skeleton for enantioselective acylation.[14] Selectivity factors of 369 and 49 were reported for mesityl methyl carbinol and 1-cyclohexyl methyl carbinol, respectively, using isobutyric anhydride as the acylating agent. In general, aryl alkyl carbinols could be effectively resolved with s values greater than 30. Allylic alcohols could also be

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10 Harris, R. F.; Nation, A. J.; Copeland, G. T.; Miller, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 11270-11271.

11 Jarvo, E. R.; Evans, C. A.; Copeland, G. T.; Miller, S. J. *J. Org. Chem.* **2001**, *66*, 5522-5527.

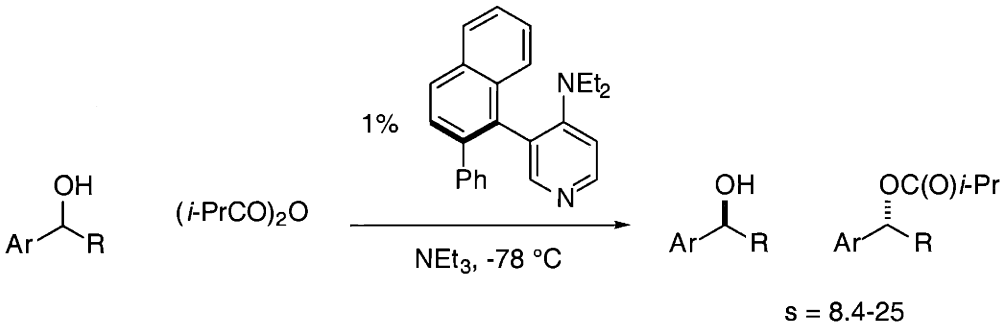
12 Copeland, G. T.; Miller, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 6496-6502.

13 Vedejs, E.; Daugulis, O.; Diver, S. T. *J. Org. Chem.* **1996**, *61*, 430-431.

14 Vedejs, E.; Daugulis, O. *J. Am. Chem. Soc.* **1999**, *121*, 5813-5814.

kinetically resolved with selectivity factors of 32-82.[15]

Scheme 2.5 Kinetic Resolution of Secondary Alcohols by Spivey



In 2000, Spivey developed a chiral analogue of DMAP derived from 4-pyridone. His group demonstrated that this DMAP derivative could serve as an efficient catalyst in the kinetic resolution of secondary alcohols using isobutyric anhydride.[16] Good levels of selectivity (s = 8.4 to 25) were obtained for aryl alkyl carbinols (Scheme 2.5).

In our group, we had already demonstrated that aryl alkyl carbinols[17] and allylic alcohols[18] could be kinetically resolved with good to outstanding stereoselectivities using one of our planar-chiral DMAP nucleophilic catalysts (Scheme 2.6). We were interested in extending the scope of the reaction to include another class of

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15 Vedejs, E.; MacKay, J. A. *Org. Lett.* **2001**, *3*, 535-536.

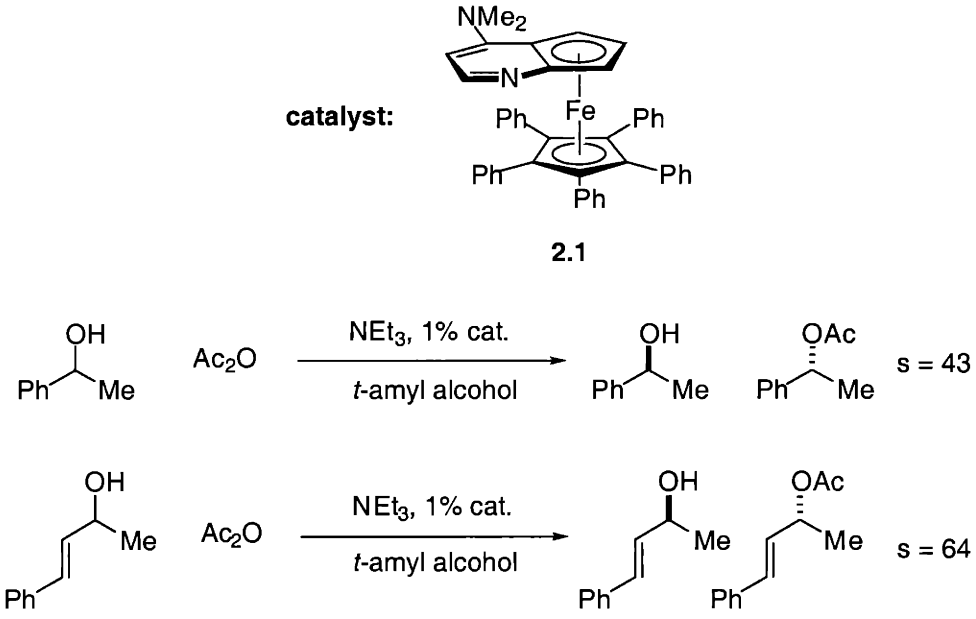
16 (a) Spivey, A. C.; Fekner, T.; Spey, S. E. *J. Org. Chem.* **2000**, *65*, 3154-3159. (b) Spivey, A. C.; Fekner, T.; Spey, S. E.; Adams, H. *J. Org. Chem.* **1999**, *64*, 9430-9443.

17 (a) Ruble, J. C.; Latham, H. A.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 1492-1493. (b) Ruble, J. C.; Tweddell, J.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 2794-2795.

18 Bellemin-Laponnaz, S.; Tweddell, J.; Ruble, J. C.; Breitling, F. M.; Fu, G. C. *Chem. Commun.* **2000**, 1009-1010.

secondary alcohols — propargylic alcohols.[19] At the time that we initiated the study, there were no reports of non-enzymatic kinetic resolutions of propargylic alcohols.

Scheme 2.6 Kinetic Resolution of Secondary Alcohols Using Planar-Chiral DMAP Catalyst

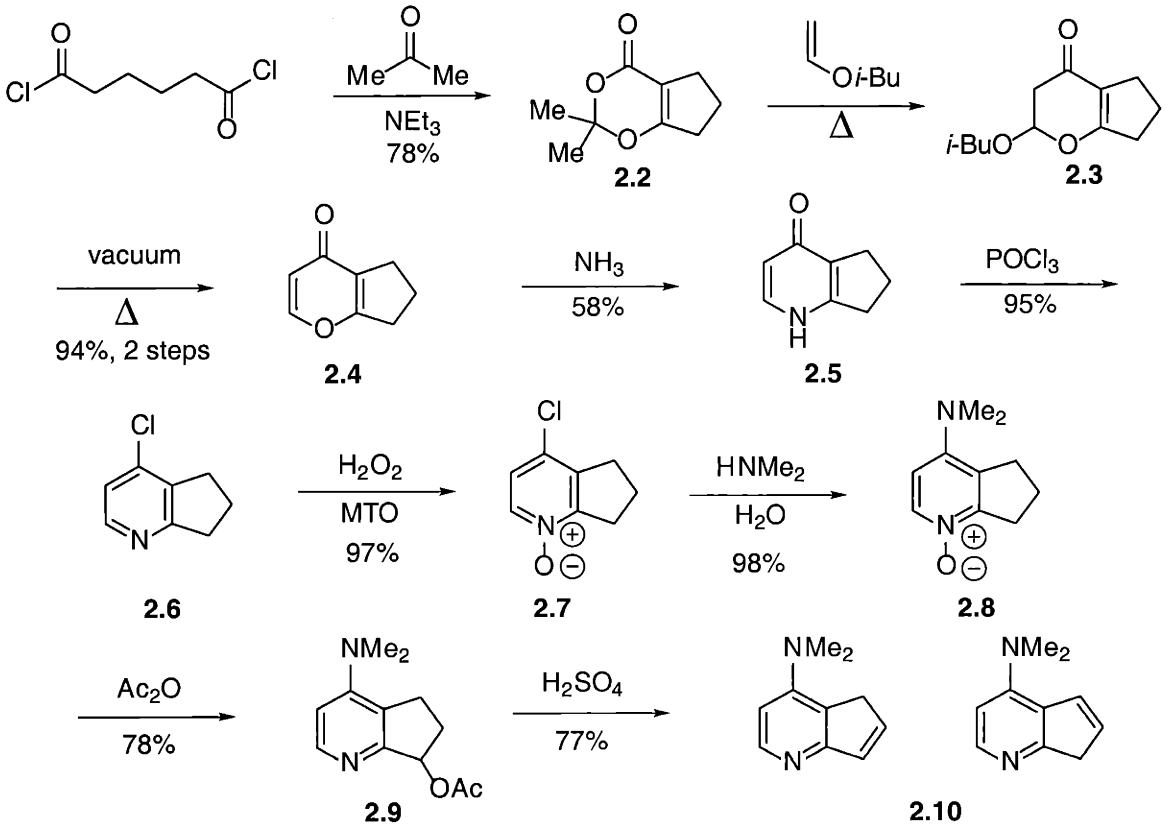


19 For leading references to methods for preparing optically pure propargylic alcohols, see: (a) Matsumura, K.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 8738-8739. (b) Frantz, D. E.; Fässler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 1806-1807.

Results and Discussion

The synthetic route to the planar-chiral DMAP catalyst was developed by Dr. J. Craig Ruble in our group.[20] First, the cyclized product **2.2** can be obtained upon treatment of a solution of adipoyl chloride and acetone with triethylamine.[21] Heating **2.2** with an excess of isobutyl vinyl ether in xylenes followed by further heating under vacuum results in elimination of *i*-BuOH from **2.3**, affording pyrone **2.4** in high yield.[22]

Scheme 2.7 Synthesis of 4-Dimethylaminopyrindine 2.10



20 Ruble, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

21 Jäger, G. *Chem. Ber.* **1972**, *105*, 137-149.

22 Jäger, G.; Wenzelburger, J. *Liebigs Ann. Chem.* **1976**, 1689-1712.

The conversion of pyrone into pyridone was then carried out by heating **2.4** in aqueous ammonia.[23] Reacting **2.5** with $POCl_3$ afforded 4-chloropyrindine derivative **2.6**, which was oxidized to its corresponding *N*-oxide **2.7** by hydrogen peroxide in the presence of a catalytic amount of methyltrioxorhenium (MTO).[24]

Heating **2.7** with aqueous dimethylamine afforded the 4-dimethylamino derivative **2.8** in high yield. Further heating of **2.8** with acetic anhydride resulted in the 4-dimethylamino-7-acetoxy compound, **2.9**, which was warmed with concentrated sulfuric acid to afford **2.10** as a mixture of isomers.

Treatment of iron(II) chloride with $(C_5Ph_5)Li$ and the lithium salt of **2.10** resulted in the formation of the planar-chiral DMAP derivative. The enantiomers of **2.1** can be separated either by classical resolution with dibenzoyl tartaric acid or by semi-preparative chiral HPLC on a Regis Whelk-O2 (*R,R*) column. The absolute configuration of **2.1** was assigned by X-ray crystallography (anomalous dispersion).

The synthesis of the planar-chiral PPY (pyrrolidinopyridine) derivative is analogous to the planar-chiral DMAP derivative and can be obtained by reacting **2.7** with pyrrolidine in place of dimethylamine and performing the subsequent reactions in Scheme 2.7 and 2.8. The enantiomers of **2.11** can also be separated by classical resolution with dibenzoyl tartaric acid or by semi-preparative chiral HPLC on a Regis Whelk-O2 (*R,R*) column.

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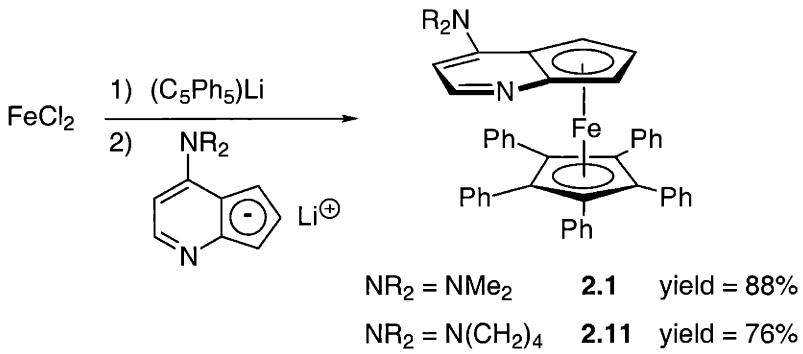
23 Katano, K.; Ogino, H.; Iwamatsu, K.; Nakabayashi, S.; Yoshida, T.; Komiya, I.; Tsuruoka, T.; Inouye, S.; Kondo, S. *J. Antibiot.* **1990**, *43*, 1150-1159.

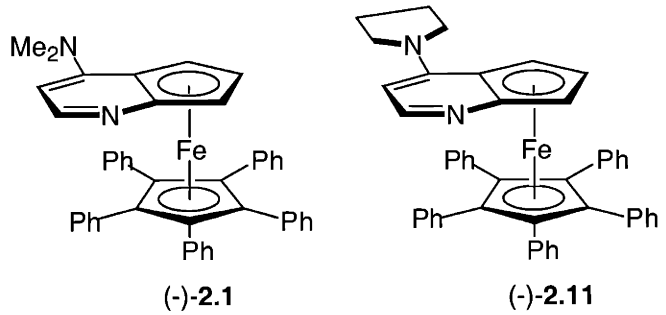
24 Copéret, C.; Adolfsson, H.; Khuong, T.-A. V.; Yudin, A. K.; Sharpless, K. B. *J. Org. Chem.* **1998**, *63*, 1740-1741.

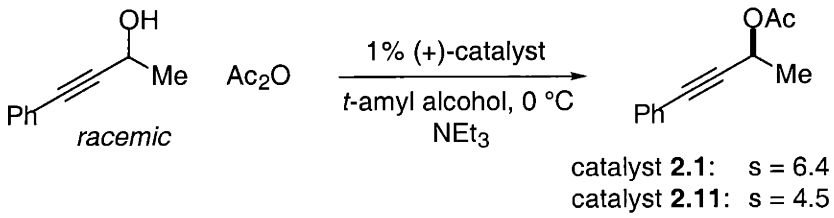
Scheme 2.8 Synthesis of Planar-Chiral DMAP and PPY Derivative



With the enantiomeric pure catalysts in hand, we then tried to study and extend the scope of substrates in the kinetic resolution of secondary alcohols. We attempted to resolve 4-phenyl-3-butyn-2-ol utilizing catalytic amounts of these chiral DMAP and PPY derivatives. We first found that planar-chiral DMAP derivative **2.1** was superior to PPY derivative **2.11**, giving a higher s (selectivity) factor.

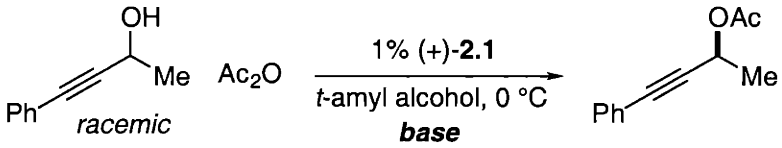
Scheme 2.9 Kinetic Resolution of 4-Phenyl-3-butyn-2-ol with Planar-Chiral DMAP and PPY Catalysts





catalyst **2.1**: s = 6.4
catalyst **2.11**: s = 4.5

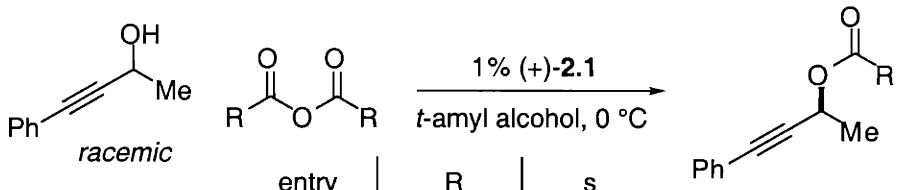
Table 2.1 Selectivity Factor as a Function of Base



entry	***base***	s
1	NEt_3	6.4
2	$N(i\text{-}Pr)_2Et$	12
3	2,6-lutidine	13
4	$NaHCO_3$	13
5	***none***	***17***

When employing the optimized reaction conditions obtained in our previous work with aryl alkyl carbinols to the propargylic alcohols, we found that NEt_3 itself acted as a competitive general base catalyst in the acylation process, thereby suppressing the intrinsic selectivity factor. To minimize this non-selective background reaction, we replaced NEt_3 with a variety of other Brønsted bases, both organic and inorganic. Ultimately, we discovered that the highest enantioselection was obtained when no base was added (Table 2.1).[25]

Table 2.2 Selectivity Factor as a Function of Anhydride



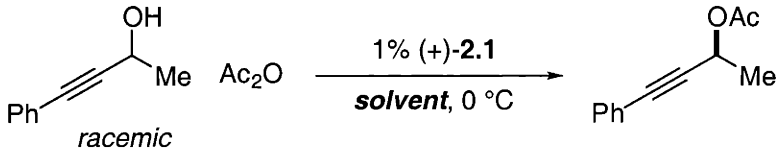
entry	R	s
1	***Me***	***17***
2	*n*-Pr	14
3	*i*-Pr	7.0
4	Ph	2.0

25 In the absence of NEt_3, the rate of acylation decreases, due to protonation of the catalyst by acetic acid.

When examining the selectivity factor as a function of acylating agents, we discovered that the best selectivity was achieved when acetic anhydride was used (Table 2.2, entry 1). In the presence of more bulky alkyl anhydrides (entries 2 and 3) or an aromatic anhydride (entry 4), lower s values were obtained.

Consistent with what was observed in the case of aryl alkyl carbinols, it was found that *t*-butanol and *t*-amyl alcohol gave high selectivity factors and accelerated the acylation reaction relative to other solvents. To take advantage of the increased rate of reaction, we decided to use *t*-amyl alcohol due to its lower melting point (*t*-butanol m.p. = 25 °C; *t*-amyl alcohol m.p. = -12 °C). Interestingly, the solvent, a tertiary alcohol, was not acylated during the course of the reaction.

Table 2.3 Selectivity Factor as a Function of Solvent



entry	***solvent***	s
1	CH_3CN	3.4
2	CH_2Cl_2	6.1
3	acetone	7.3
4	toluene	7.4
5	THF	8.5
6	EtOAc	9.4
7	Et_2O	12
8	*t*-butanol	13
9	*t*-amyl alcohol	***17***

Hence, using the modified protocol without added base, an array of propargylic

alcohols could be resolved with useful levels of stereoselection using this acylation system (Table 2.4).[26] In contrast to aryl alkyl carbinols, for which the selectivity factor *increases* as the steric demand of the alkyl group increases, for propargylic alcohols the selectivity factor *decreases* as the steric demand increases (entries 1-4). Interestingly, substitutions at positions far removed from the hydroxyl group can affect enantioselection (entry 1 vs. entries 5-7). Kinetic resolutions of propargylic alcohols by catalyst **2.1** are more effective and efficient when the remote position of the alkyne is substituted with an unsaturated group (e.g., aryl, carbonyl, alkynyl, alkenyl; entries 8-11), rather than with an alkyl group (entry 15). When the alkyne and phenyl moieties are both present in the molecule but not in conjugation with each other (entries 12-14), only moderate selectivities are observed. All the reactions were carried out at 1 M concentration, and the catalyst could be recovered and recycled at the end of the reaction, giving essentially the same rate and selectivity.

We believe that π-stacking interactions between the substrate and the active intermediate (*vide infra*) are crucial to obtain high selectivity. Hence, the presence of an unsaturated group is required for a fast, selective reaction. When both substituents of the carbinol are unsaturated (entries 12-14), the acylation reaction is only moderately selective. This is attributed to a competitive π-stacking interaction between the phenyl and the alkyne group, and the interaction between the catalyst and the phenyl group is stronger than that of the alkyne moiety, leading to the absolute stereochemical outcome of the products.

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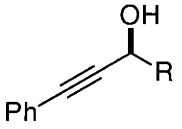
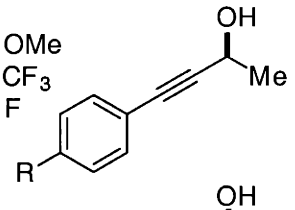
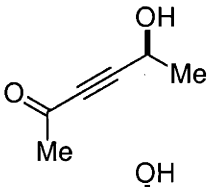
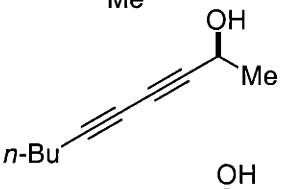
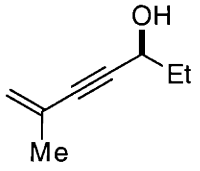
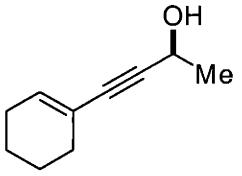
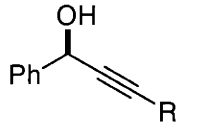
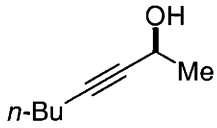
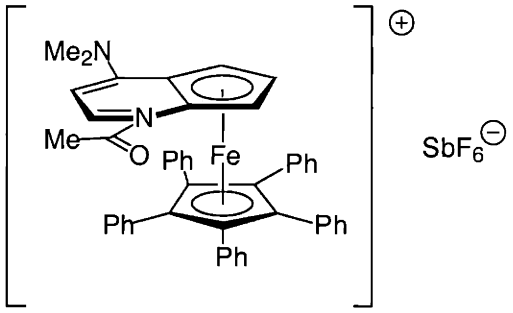
[26] Note: The difference in selectivity factors that we report for the kinetic resolution of 4-phenyl-3-butyn-2-ol (Table 2.1, entry 5; Table 2.2, entry 1, and Table 2.3, entry 9: s = 17; Table 2.4, entry 1: s = 20) is due to a difference in the concentrations at which the reactions were run (1.0 M vs. 0.5 M in 4-phenyl-3-butyn-2-ol).

Table 2.4 Kinetic Resolutions of Propargylic Alcohols by 1% (–)-2.1

entry	unreacted alcohol, major enantiomer	selectivity factor [a] (ee of unreacted alcohol)
1 R = Me		***20*** *(96% ee @ 58% conv.)*
2 Et		***18*** *(94% ee @ 58% conv.)*
3 *i*-Pr		***11*** *(93% ee @ 63% conv.)*
4 *t*-Bu		***3.8*** *(95% ee @ 86% conv.)*
5 R = OMe		***14*** *(94% ee @ 60% conv.)*
6 CF_3		***10*** *(99% ee @ 71% conv.)*
7 F		***13*** *(97% ee @ 65% conv.)*
8		***12*** *(95% ee @ 64% conv.)*
9		***10*** *(95% ee @ 66% conv.)*
10		***7.9*** *(94% ee @ 69% conv.)*
11		***6.1*** *(93% ee @73% conv.)*
12 R = H		***5.7*** *(88% ee @ 71% conv.)*
13 *i*-Pr		***6.3*** *(95% ee @ 74% conv.)*
14 *t*-Bu		***6.1*** *(95% ee @ 76% conv.)*
15		***3.9*** *(91% ee @ 82% conv.)*

[a] The selectivity factors are averages of two runs.

Next, we began to conduct experiments to study the mechanism of acylations catalyzed by the planar-chiral DMAP derivative. It is believed that for reactions catalyzed by DMAP, an acylpyridium salt is the active acylating agent.[27] In order to determine whether the same pathway holds in the case of the planar-chiral catalyst **2.1**, attempts were made to prepare acylpyridium salts. Dr. J. Craig Ruble in the group showed that when catalyst **2.1** and Ac_2O were mixed in a 1:1 ratio, the equilibrium strongly favored the non-acylated catalyst **2.1**.[28] On the other hand, he demonstrated that a 1:1 mixture of the catalyst and AcCl led to quantitative formation of the acylpyridium salt; exchange of chloride for SbF_6 yielded another acylpyridium salt, and its X-ray structure was determined as shown in Figure 2.2.



2.12

As depicted in the ORTEP diagram, the dimethylamino group, pyrindine ring, and acetyl group adopt a nearly coplanar geometry, which is consistent with extended conjugation. Upon acylation, the changes in bond lengths of the (dimethylamino)pyrindine are consistent with the significant contribution of resonance structure **B** (Figure 2.3). This is further supported by the increased

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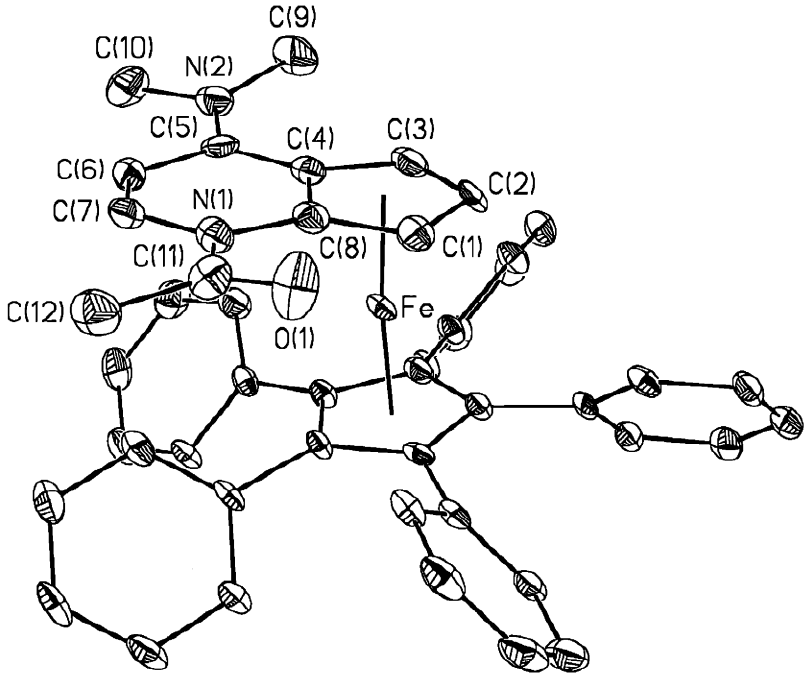
27 (a) Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *12*, 129-161. (b) Hassner, A.; Krepski, L. R.; Alexanian, V. *Tetrahedron* **1978**, *34*, 2069-2076. (c) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 569-583.

28 The same was observed for DMAP.

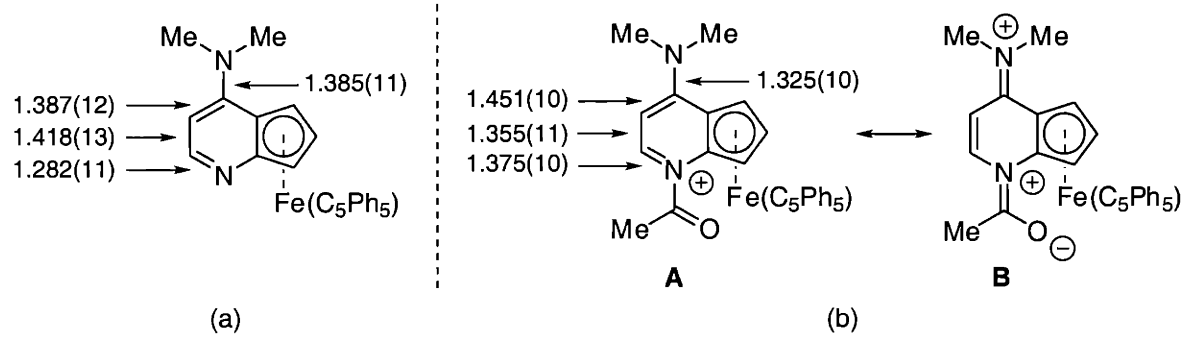
rotational energy barrier about the Me_2N—C bond upon acylation ($\Delta G^{\ddagger}$ ~ 10 kcal/mol for **2.1**; $\Delta G^{\ddagger}$ > 21 kcal/mol for **2.12**).

Figure 2.2 ORTEP Representation of Salt 2.12 (With thermal ellipsoids drawn at the 35% probability level; the SbF_6 counterion and two THF molecules have been omitted for clarity)



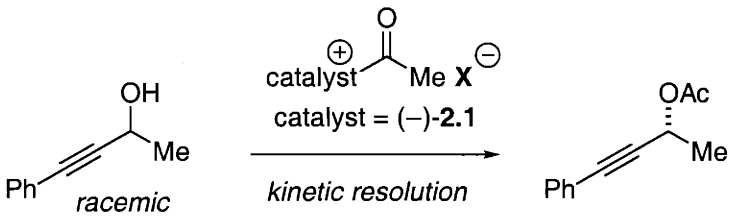
There are two possible rotamers of the acetyl group around N(1)—C(11). However, in the crystal structure, we observe that the acetyl group only adopts a configuration such that the oxygen is closer to the fused five-membered ring, consistent with minimization of steric interactions with the fused five-membered ring. The acetyl group's orientation is further supported by NMR studies (presaturation difference NOE experiments in CD_2Cl_2), indicating that this rotamer is the predominant species in solution.

Figure 2.3 Bond Distances (Å) for the (Dimethylamino)pyrindine Fragment of: (a) Complex 2.1; (b) Acetylated Complex 2.12.



To support the idea that the acetylated complexes (counterion: Cl, SbF_6) are indeed the active intermediates in our system, the acetylated complexes were used to kinetically resolve 4-phenyl-3-butyn-2-ol. Both salts preferentially acylated the same enantiomer of 4-phenyl-3-butyn-2-ol (Scheme 2.10). However, diminished reaction rates and selectivity factors were observed as compared with the catalytic version (**X** = OAc in *t*-amyl alcohol: s = 17), probably due to the differences in the counterion[29] and the reaction conditions.[30]

Scheme 2.10 Acylation of 4-Phenyl-3-butyn-2-ol by Acylpyridium Salt of 2.1



X	solvent	s
Cl	*t*-amyl alcohol	6.0
SbF_6	CH_2Cl_2	2.5

29 In contrast to Cl or SbF_6, it is believed that acetate anions assist in the deprotonation of alcohols in the transition state of the DMAP-catalyzed acylation, leading to a faster rate of reaction.

30 The reaction using the SbF_6 acylpyridium salt (CH_2Cl_2, NEt_3, r.t.) could not be conducted in *t*-amyl alcohol due to the poor solubility of the salt.

Conclusions

Using the planar-chiral DMAP derivative developed in our laboratory, we have described the first effective non-enzymatic acylation for the kinetic resolution of propargylic alcohols.

In this reaction, 4-(dimethylamino)pyrindinyl complex **2.1** is a more effective catalyst when compared to the corresponding 4-(pyrrolidino)pyrindinyl derivative. Acetic anhydride was found to be the acylating agent of choice, and *t*-amyl alcohol is the optimal solvent. In contrast to our previous work on aryl alkyl carbinols, the kinetic resolution of propargylic alcohols is recommended to be carried out in the absence of base in order to minimize the background reaction. The catalyst loading of this system is low, and reactions can be carried out at 1 M concentration. Moreover, the catalyst can be recovered almost quantitatively and recycled at the end of the reaction. Using this new protocol, a number of propargylic alcohols were kinetically resolved with selectivity factors up to 20.

We believe that π-stacking interactions between the substrate and the active catalytic intermediate play an important role in achieving high selectivities because kinetic resolutions of propargylic alcohols by catalyst **2.1** are more effective and efficient when the alkyne is substituted with an unsaturated group.

In order to understand the mechanism of the asymmetric acylation using planar-chiral DMAP derivative, we obtained X-ray structural data of the acylpyridium salt. The coplanarity of the acetyl group, pyrindine ring, and the dimethylamino group, together with the changes in bond lengths of the catalyst upon acylation, are all consistent with the extended conjugation of the system. The acylpyridium salt

preferentially acylates the same enantiomer of 4-phenyl-3-butyn-2-ol as in the catalytic version with **2.1**/Ac_2O, although with lower selectivity.

Experimental

I. General

Analytical thin layer chromatography was performed using EM Reagents 0.25 mm silica gel 60 plates, and visualization was accomplished with potassium permanganate or with ethanolic phosphomolybdic acid. Flash chromatography was performed on EM Reagents silica gel 60 (230-400 mesh).

Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer. High resolution mass spectra were recorded on a Finnegan MAT System 8200 spectrometer. Melting points (uncorrected) were obtained on a Thomas Hoover Unimelt capillary melting point apparatus.

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian XL-300 or XL-500 NMR spectrometer at ambient temperature. ^{1}H data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (δ scale), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C spectra were determined with complete proton decoupling.

Analytical chiral HPLC was performed on a Daicel CHIRALCEL OD column (4.6 mm x 25 cm). Analytical chiral GC was performed on a Chiraldex G-TA column (20 m x 0.25 mm).

Catalyst **2.1** was prepared and resolved as previously reported.[31]

Ac_2O (Mallinckrodt) was distilled from quinoline prior to use. $FeCl_2$ (Strem), *n*-BuLi (Strem), and 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (Aldrich) were used without further purification. Solvents were distilled from the indicated drying agents: benzene (sodium/benzophenone); THF (sodium/benzophenone); CH_2Cl_2 (calcium hydride); Et_2O (sodium/benzophenone); toluene (molten sodium); *t*-amyl alcohol (calcium hydride).

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated.

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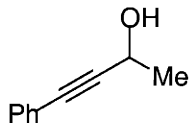
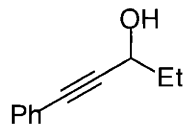
31 Ruble, J. C.; Latham, H. A.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 1492-1493.

II. Preparation of Racemic Propargylic Alcohols

General procedure. *n*-BuLi (0.020 mol; 1.45 M in hexanes) was added to a stirred, -78 °C solution of the terminal alkyne (0.020 mol) in THF (40 mL). The reaction mixture was slowly warmed to 0 °C, stirred for 2 h, and then cooled to -78 °C. The aldehyde (0.020 mol) was added, and the reaction mixture was stirred for 1 h at -78 °C. It was then warmed to room temperature, Et_2O was added, and the resulting organic layer was washed with saturated aq $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted twice with Et_2O. The organic extracts were combined, washed with saturated aq NaCl, dried over $MgSO_4$, and concentrated. The resulting residue was purified by flash chromatography.



This was prepared as described in general procedure. The ^1H NMR spectrum of the product was identical to that reported in the literature.[32]



This was prepared as described in general procedure. The ^1H NMR spectrum of

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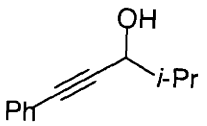
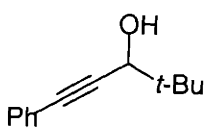
32 Shokat, K.; Uno, T.; Schultz, P. G. *J. Am. Chem. Soc.* **1994**, *116*, 2261-2270.

the product was identical to that reported in the literature.[33]



This was prepared as described in general procedure. The ^1H NMR spectrum of the product was identical to that reported in the literature.[34] ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9, 23.2, 65.0, 79.3, 93.2, 126.8, 128.3, 128.6, 141.3. IR (neat): 3344, 3063, 3031, 2970, 2932, 2871, 2252, 1054 cm^{-1}. HRMS (EI, *m/z*): Calcd for $C_{12}H_{14}O$: 174.1045 (M^+). Found: 174.1041.



This was prepared as described in general procedure. The ^1H NMR spectrum of the product was identical to that reported in the literature.[35]

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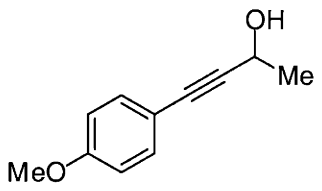
33 Brown, H. C.; Molander, G. A.; Singh, S. M.; Racherla, U. S. *J. Org. Chem.* **1985**, *50*, 1577-1582.

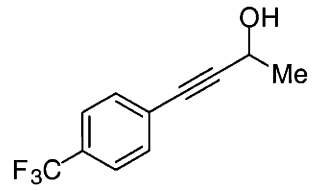
34 Creary, X. *J. Am. Chem. Soc.* **1977**, *99*, 7632-7639.

35 Borden, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 4898-4901.



A mixture of but-3-yn-2-ol (1.40 mL, 17.8 mmol), $Pd(PPh_3)_2Cl_2$ (350 mg, 0.50 mmol), CuI (65 mg, 0.34 mmol), and *p*-iodoanisole (8.00 g, 34.2 mmol) in NEt_3 (80 mL) was sonicated for 2 h at 40 °C. The mixture was then diluted with Et_2O and filtered through a Celite pad. The filtrate was evaporated, and the residue was purified by flash chromatography (10% EtOAc/hexanes → 25% EtOAc/hexanes), which afforded a yellow solid.

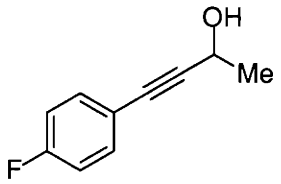
^1H NMR (300 MHz, $CDCl_3$): δ 1.55 (d, 3H, J = 6.5), 1.86 (d, 1H, J = 5.3), 3.81 (s, 3H), 4.75 (dq, 1H, J = 6.5, 5.3), 6.83 (d, 2H, J = 9.0), 7.36 (d, 2H, J = 9.0). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.8, 55.5, 59.1, 84.1, 89.8, 114.0, 114.7, 133.2, 159.6. IR (KBr): 3378, 2987, 1607, 1509, 1248, 837 cm^{-1}. mp 47-48 °C. HRMS (EI, *m/z*): Calcd for $C_{11}H_{12}O_2$: 176.0837 (M^+). Found: 176.0833.



A mixture of but-3-yn-2-ol (1.40 mL, 17.8 mmol), $Pd(PPh_3)_2Cl_2$ (387 mg, 0.55 mmol), CuI (70 mg, 0.37 mmol), and *p*-(trifluoromethyl)iodobenzene (4.00 g, 14.7 mmol) in NEt_3 (80 mL) was sonicated for 2 h at 40 °C. The mixture was then diluted with Et_2O and filtered through a Celite pad. The filtrate was evaporated, and the residue was purified by flash chromatography (10% EtOAc/hexanes → 25%

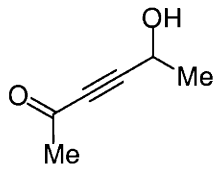
EtOAc/hexanes), which provided a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (d, 3H, J = 6.5), 2.43 (d, 1H, J = 5.3), 7.50 (dq, 1H, J = 5.3, 6.5), 7.50 (d, 2H, J = 8.7), 7.54 (d, 2H, J = 8.7). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.5, 59.0, 82.9, 93.6, 124.0 (q, $^1J_{C-F}$ = 271), 125.3 (q, $^3J_{C-F}$ = 3.8), 126.6 (d, $^4J_{C-F}$ = 1.4), 130.2 (q, $^2J_{C-F}$ = 130), 132.0. IR (neat): 3322, 2985, 1615, 1324, 842 cm^{-1}. HRMS (EI, *m/z*): Calcd for $C_{11}H_9F_3O$: 214.0606 (M^+). Found: 214.0604.



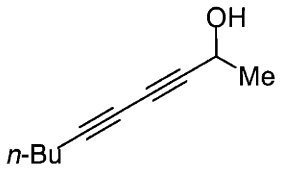
This was prepared as described in general procedure.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (d, 3H, J = 6.5), 2.08 (d, 1H, J = 5.3), 4.74 (dq, 1H, J = 5.3, 6.5), 6.9-7.0 (m, 2H), 7.3-7.4 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.7, 59.1, 83.2, 90.8, 115.7 (d, $^2J_{C-F}$ = 22.0), 118.8 (d, $^4J_{C-F}$ = 3.5), 133.7 (d, $^3J_{C-F}$ = 8.3), 162.6 (d, $^1J_{C-F}$ = 249). IR (KBr): 3376, 2985, 2230, 1604, 1507, 1237, 834 cm^{-1}. mp 40-41 °C. HRMS (EI, *m/z*): Calcd for $C_{10}H_9FO$: 164.0637 (M^+). Found: 164.0639.



This was prepared according to the literature procedure.[36] The ^{1}H NMR spectrum of the product was identical to that reported in the literature.

^{13}C NMR (75 MHz, $CDCl_3$): δ 23.5, 32.8, 57.9, 83.0, 93.4, 185.0. IR (neat): 3417, 2982, 2937, 2217, 1681, 1216, 1111 cm^{-1}. HRMS (EI, *m/z*): Calcd for $C_6H_8O_2$: 112.0524 (M^+). Found: 112.0526.



CuI (190 mg, 1.00 mmol) was added to a stirred solution of 1-iodohex-1-yne (2.8 g, 10 mmol) and but-3-yn-2-ol (1.6 mL, 20 mmol) in pyrrolidine (15 mL). After stirring at room temperature for 30 min, the reaction mixture was hydrolyzed with saturated aq NH_4Cl and extracted with EtOAc. The organic extracts were dried over $MgSO_4$ and concentrated. The product was then purified by flash chromotography (10% EtOAc/hexanes → 25% EtOAc/hexanes), which afforded a yellow oil.

The ^{1}H NMR of the product was identical to that reported in the literature.[37] ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 19.2, 22.2, 24.3, 30.4, 58.9, 64.5, 69.4, 77.3, 82.1. HRMS

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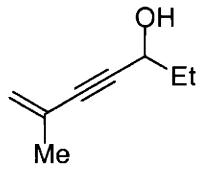
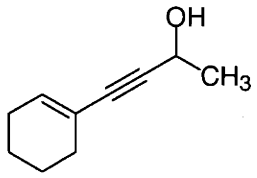
36 Dunn, P. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1579-1584.

37 Doolittle, R. E. *Synthesis* **1984**, *9*, 730-732.

(EI, *m/z*): Calcd for $C_{10}H_{14}O$: 150.1045 (M^+). Found: 150.1046.



This was prepared as described in general procedure. The ^1H NMR spectrum of the product was identical to that reported in the literature.[38] HRMS (EI, *m/z*): Calcd for $C_8H_{12}O$: 124.0888 (M^+). Found: 124.0887.



This was prepared as described in general procedure. ^1H NMR (300 MHz, $CDCl_3$): δ 1.45 (d, 3H, J = 6.5), 1.5-1.6 (m, 4H), 2.0-2.1 (m, 5H), 4.62 (q, 1H, J = 6.5), 6.1 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7, 22.5, 24.8, 25.9, 29.4, 59.0, 85.9, 88.5, 120.2, 135.3. IR (neat): 3342, 3027, 2982, 2937, 2862, 2217, 1096 cm^{-1}. HRMS (EI, *m/z*): Calcd for $C_{10}H_{14}O$: 150.1045 (M^+). Found: 150.1046.

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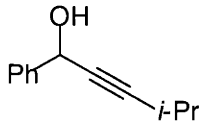
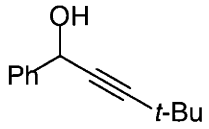
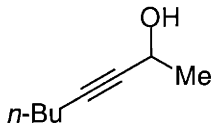
38 Brown, H. C.; Molander, G. A.; Singh, S. M.; Racherla, U. S. *J. Org. Chem.* **1985**, *50*, 1577-1582.



This was prepared as described in general procedure. The ^{1}H NMR spectrum of the product was identical to that reported in the literature.[39] ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9, 23.2, 65.0, 79.3, 93.2, 126.8, 128.3, 128.6, 141.3. IR (neat): 3344, 3063, 3031, 2970, 2932, 2871, 2252, 1054 cm^{-1}. HRMS (EI, *m/z*): Calcd for $C_{12}H_{14}O$: 174.1045 (M^+). Found: 174.1041.



This was prepared as described in general procedure. The ^{1}H NMR spectrum of the product was identical to that reported in the literature.[40] HRMS (EI, *m/z*): Calcd for $C_{13}H_{16}O$: 188.1201 (M^+). Found: 188.1200.



This was prepared as described in general procedure. The ^{1}H NMR spectrum of the product was identical to that reported in the literature.[41]

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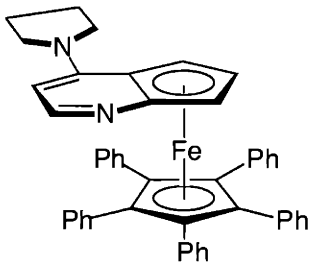
39 Borden, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 4898-4901.

40 Brown, H. C.; Molander, G. A.; Singh, S. M.; Racherla, U.S. *J. Org. Chem.* **1985**, *50*, 1577.

41 Marshall. J. A.; Wang, X.-j. *J. Org. Chem.* **1991**, *56*, 960-969.

III. Preparation of Catalyst 2.11



Compound 2.11. *n*-BuLi (2.62 M in hexane; 4.77 mL, 12.5 mmol) was added by syringe over ~2 minutes to a slurry of pentaphenylcyclopentadiene (5.59 g, 12.5 mmol) in THF (120 mL). The mixture was stirred for 3 hours, after which the resulting dark-orange solution was added by cannula over 5 minutes to a slurry of $FeCl_2$ (1.53 g, 12.1 mmol) in THF (50 mL). The first few drops resulted in the formation of a purple color, but the color changed to green-brown as the addition progressed. After 3 hours, a solution of the lithium salt of 4-pyrrolidinopyrindine [made 1 hour prior to use by the reaction of *n*-BuLi (2.62 M in hexane; 3.69 mL, 9.67 mmol) and 4-pyrrolidinopyrindine[42] (1.80 g, 9.66 mmol) in 50 mL of THF at room temperature] was added by cannula, resulting in a dark-purple solution. This solution was stirred in a 60 °C oil bath for 2.5 hours, after which it was filtered through a 1" plug of silica gel using aspirator vacuum. The silica gel was washed with 10% NEt_3/45% EtOAc/45% hexanes until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was dissolved in CH_2Cl_2 and loaded onto a silica gel column. The column was eluted with CH_2Cl_2 until all of the solids on the top of the column (Ph_5C_5H) had dissolved, and then all of the Ph_5C_5H was eluted by the addition of two column volumes of CH_2Cl_2. The eluant was then changed to 10% NEt_3/90% CH_2Cl_2, and the product

42 Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 11532-11533.

was collected as a tight purple band at the solvent front. Removal of the solvent yielded 5.02 g (75.8%) of pure **2.11**, a purple solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, 1H, J = 5.1), 7.14 (t, 5H, J = 7.2), 7.06 (t, 10H, J = 7.2), 6.95 (d, 10H, J = 7.2), 5.72 (d, 1H, J = 5.1), 5.01 (d, 1H, J = 2.7), 4.92 (d, 1H, J = 2.7), 4.24 (t, 1H, J = 2.7), 3.47 (br, 4H), 2.10 (br, 2H), 1.94 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9 (br), 153.8 (br), 135.3, 132.5, 127.1, 126.2, 113.5 (br), 96.9, 86.0, 78.0, 77.4, 69.3, 66.0, 50.0 (br), 25.8 (br). FTIR (KBr) 3052, 2974, 2857, 1600, 1539, 1500, 1403, 1338, 1025, 743 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{47}H_{38}FeN_2$ (M^+) 686.2384, found 686.2391. mp 261-265 °C (significant darkening above 150 °C).

The enantiomers of the product were separated using semi-preparative HPLC (Daicel CHIRALCEL OD, 1 cm x 25 cm, chloroform/hexanes/diethylamine 25:75:0.4, 3.0 mL/min, 10 mg per injection). Enantiomer (–)-**2.11** ($[\alpha]^{20}_D$ = -1800° (c = 0.0069, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 10.67 minutes to 13.50 minutes, and enantiomer (+)-**2.11** ($[\alpha]^{20}_D$ = +1700° (c = 0.10, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 18.00 minutes to 23.50 minutes.

The absolute configuration of (–)-**2.11** has been tentatively assigned by analogy to (–)-**2.1** (sign of optical rotation, elution order on chiral HPLC, and sense of selectivity in the kinetic resolution of 1-phenylethanol).

IV. Comparison of the Enantioselectivity of Catalysts 2.1 and 2.11 (Scheme 2.9)

A vial containing 4-phenyl-3-butyn-2-ol (73.0 mg, 0.500 mmol), NEt_3 (49 μL, 0.35 mmol), and catalyst (0.0050 mmol) in *t*-amyl alcohol (1.0 mL) was capped with a septum and sonicated to help dissolve the catalyst. The resulting purple solution was cooled to 0 °C, and Ac_2O (28.0 μL, 0.300 mmol) was added by syringe. After 16 hours, an aliquot of the reaction was quenched by the addition of a large excess of MeOH. The resulting solution was concentrated, and the catalyst was removed by passing the mixture through a 2" plug of silica gel with 50% EtOAc/hexanes as the eluant (the catalyst can be recovered by adding NEt_3 to the eluant). The catalyst-free filtrate was concentrated and analyzed by GC to determine the percent conversion.[43] The acetate product was then separated from the alcohol by flash chromatography (10% EtOAc/hexanes → 50% EtOAc/hexanes), and each was analyzed by chiral GC to determine the s value.

Catalyst	Product ee	Alcohol ee	% Convers.	S
(+)-2.1	54.2	65.4	54.7	6.4
(+)-2.11	39.7	69.2	63.6	4.5

43 This value for the percent conversion is used as a check against the value for the percent conversion that is calculated from the product ee and the alcohol ee.

V. Selectivity Factor as a Function of Base (Table 2.1)

General procedure. 4-Phenyl-3-butyn-2-ol (73.0 mg, 0.500 mmol) was added to a vial containing catalyst (+)-**2.1** (3.3 mg, 0.0050 mmol). The base (0.350 mmol) and *t*-amyl alcohol (0.50 mL) were then added. The vial was capped with a rubber septum and then sonicated to help dissolve the catalyst. The reaction mixture was cooled to 0 °C, and then Ac_2O (28.0 μL, 0.300 mmol) was added. After an appropriate amount of time, an aliquot of the reaction was quenched by the addition of a large excess of MeOH. The resulting solution was concentrated, and the catalyst was removed by passing the mixture through a short (2″) plug of silica gel with 50% EtOAc/hexanes as the eluant (the catalyst can be recovered by adding NEt_3 to the solvent). The catalyst-free filtrate was concentrated and analyzed by GC to determine the percent conversion.[43] The acetate product was then separated from the alcohol by flash chromatography (10% EtOAc/hexanes → 50% EtOAc/hexanes), and each was analyzed by chiral GC to determine the s value.

Table 2.1. Selectivity Factor as a Function of Base

Base	Acetate ee	Alcohol ee	% Convers.	S
NEt_3	54.2	65.4	54.7	6.4
$N(i\text{-}Pr)_2Et$	63.0	87.3	58.1	12
2,6-lutidine	69.7	76.2	52.2	13
$NaHCO_3$	72.1	69.2	49.0	13

None	**79.9**	**65.4**	**45.0**	**17**

VI. Selectivity Factor as a Function of Anhydride (Table 2.2)

General procedure. 4-Phenyl-3-butyn-2-ol (73.0 mg, 0.500 mmol) was added to a vial containing catalyst (+)-**2.1** (3.3 mg, 0.0050 mmol). *t*-Amyl alcohol (0.50 mL) was added, and the vial was then capped with a rubber septum and sonicated to help dissolve the catalyst. The reaction mixture was cooled to 0 °C, and then the anhydride (0.300 mmol) was added. After 17 hours, an aliquot of the reaction was quenched by the addition of a large excess of MeOH. The resulting solution was concentrated, and the catalyst was removed by passing the mixture through a short (2″) plug of silica gel with 50% EtOAc/hexanes as the eluant (the catalyst can be recovered by adding NEt_3 to the solvent). The catalyst-free filtrate was concentrated and analyzed by GC to determine the percent conversion.[43] The acetate product was then separated from the alcohol by flash chromatography (10% EtOAc/hexanes → 50% EtOAc/hexanes), and each was analyzed by chiral GC or chiral HPLC to determine the s value.

Table 2.2. Selectivity Factor as a Function of Anhydride

Anhydride	Product ee	Alcohol ee	% Convers.	S
acetic anhydride	79.9	65.4	45.0	17
butyric anhydride	80.4	44.8	35.8	14
isobutyric anhydride	74.3	3.6	4.6	7.0
Benzoic anhydride	31.8	0.4	1.3	2.0

VII. Selectivity Factor as a Function of Solvent (Table 2.3)

General procedure. 4-Phenyl-3-butyn-2-ol (73.0 mg, 0.500 mmol) was added to a vial containing catalyst (+)-**2.1** (3.3 mg, 0.0050 mmol). Solvent (0.50 mL) was then added. The vial was capped with a rubber septum and then sonicated to help dissolve the catalyst. The reaction mixture was cooled to 0 °C, and then Ac_2O (28.0 μL, 0.300 mmol) was added. After an appropriate amount of time, an aliquot of the reaction was quenched by the addition of a large excess of MeOH. The resulting solution was concentrated, and the catalyst was removed by passing the mixture through a short (2″) plug of silica gel with 50% EtOAc/hexanes as the eluant (the catalyst can be recovered by adding NEt_3 to the solvent). The catalyst-free filtrate was concentrated and analyzed by GC to determine the percent conversion.[43] The acetate product was then separated from the alcohol by flash chromatography (10% EtOAc/hexanes → 50% EtOAc/hexanes), and each was analyzed by chiral GC to determine the s value.

Table 2.3. Selectivity Factor as a Function of Solvent

Solvent	Acetate ee	Alcohol ee	% Convers.	S
CH_3CN	49.0	14.4	22.7	3.4
CH_2Cl_2	65.8	23.8	26.5	6.1
Acetone	65.9	41.7	38.8	7.3
Toluene	71.7	20.7	22.4	7.4

THF	71.2	36.7	34.0	8.5
EtOAc	71.1	47.6	40.1	9.4
Et_2O	78.7	32.6	29.3	11.5
t-butanol*	64.7	86.9	57.3	12.8
t-amyl alcohol	60.8	97.3	61.5	16.5

* reaction was carried out at room temperature

VIII. Kinetic Resolution of Propargylic Alcohols (Table 2.4)

For Methods Used to Assay Enantiomeric Excess, see Section IX. For Assignment of Absolute Stereochemistry, see Section X.

General procedure (Table 2.4, entry 1). A vial containing 4-phenyl-3-butyn-2-ol (73.0 mg, 0.500 mmol) and catalyst (–)-**2.1** (3.3 mg, 0.0050 mmol) in *t*-amyl alcohol (1.0 mL) was capped with a septum and sonicated to help dissolve the catalyst. The resulting purple solution was cooled to 0 °C, and Ac_2O (35.4 μL, 0.375 mmol) was added by syringe. After 49 hours, the reaction was quenched by the addition of a large excess of MeOH. The acetate was then separated from the alcohol by flash chromatography (10% → 50% EtOAc/hexanes; the catalyst can be recovered by adding NEt_3 to the eluant). Analysis of the acetate by chiral GC revealed a 68.6% ee of the *R* enantiomer. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 96.0% ee of the *S* enantiomer. These ee values correspond to a selectivity factor of 20.2 at 58.3% conversion.

A second run provided a 78.9% ee of the acetate and a 79.1% ee of alcohol (s = 20.3 at 50.1% conversion).

Table 2.4, entry 2. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 80.0 mg (0.500 mmol) of alcohol, and 35.4 μL (0.375 mmol) of Ac_2O. Reaction time: 39 hours. Analysis of the acetate by chiral GC revealed a 67.5% ee of the *R* acetate. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 94.5% ee of the *S* enantiomer. These ee values correspond to a selectivity factor of 18.0 at 58.3% conversion.

A second run provided a 71.0% ee of acetate and a 90.2% ee of alcohol (s = 17.7 at 55.9% conversion).

Table 2.4, entry 3. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 87.0 mg (0.500 mmol) of alcohol, and 35.4 μL (0.375 mmol) of Ac_2O. Reaction time: 86 hours. Analysis of the acetate by chiral GC revealed a 55.1% ee of the *R* acetate. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 92.9% ee of the *S* enantiomer. These ee values correspond to a selectivity factor of 11.0 at 62.8% conversion.

A second run provided a 54.8% ee of acetate and a 93.3% ee of alcohol (s = 11.0 at 63.0% conversion).

Table 2.4, entry 4. The general procedure was followed using 3.0 mg (0.0045 mmol) of catalyst (–)-**2.1**, 85.0 mg (0.450 mmol) of alcohol, and 42.0 μL (0.450 mmol) of Ac_2O. Reaction time: 479 hours. Analysis of the acetate by chiral GC revealed an 18.2% ee of the *R* acetate. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 92.0% ee of the *S* enantiomer. These ee values correspond to a selectivity factor of 3.8 at 83.5% conversion.

A second run provided a 15.0% ee of acetate and a 95.1% ee of alcohol (s = 3.8 at 86.4% conversion).

Table 2.4, entry 5. The general procedure was followed using 3.1 mg (0.0047 mmol) of catalyst (–)-**2.1**, 84.0 mg (0.470 mmol) of alcohol, and 44.0 μL (0.470 mmol) of Ac_2O. Reaction time: 92 hours. Analysis of the acetate by chiral GC revealed an 62.7% ee of the *R* acetate. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 94.0% ee of the *S* enantiomer. These ee

values correspond to a selectivity factor of 14.7 at 60.0% conversion.

A second run provided a 59.9% ee of acetate and a 94.1% ee of alcohol (s = 13.4 at 61.1% conversion. Alcohol: $[\alpha]^{20}_D$ = -25.3° (c = 1.00, $CHCl_3$, 94% ee).

Table 2.4, entry 6. The general procedure was followed using 2.3 mg (0.0035 mmol) of catalyst (–)-**2.1**, 76.1 mg (0.350 mmol) of alcohol, and 33.0 μL (0.350 mmol) of Ac_2O. Reaction time: 47 hours. Analysis of the acetate by chiral GC revealed an 40.2% ee of the *R* acetate. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 99.0% ee of the *S* enantiomer. These ee values correspond to a selectivity factor of 10.6 at 71.1% conversion.

A second run provided a 38.2% ee of acetate and a 99.2% ee of alcohol (s = 10.4 at 72.2% conversion). Alcohol: $[\alpha]^{20}_D$ = -21.4° (c = 0.80, $CHCl_3$, 99% ee).

Table 2.4, entry 7. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 82.0 mg (0.500 mmol) of alcohol, and 47.0 μL (0.500 mmol) of Ac_2O. Reaction time: 84 hours. Analysis of the acetate by chiral GC revealed a 53.4% ee of the *R* acetate. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 97.0% ee of the *S* enantiomer. These ee values correspond to a selectivity factor of 12.7 at 64.5% conversion.

A second run provided a 52.0% ee of acetate and a 97.5% ee of alcohol (s = 12.6 at 65.2% conversion). Alcohol: $[\alpha]^{20}_D$ = -32.0° (c = 0.91, $CHCl_3$, 97% ee).

Table 2.4, entry 8. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 56.0 mg (0.500 mmol) of alcohol, and 47.0 μL (0.500 mmol) of Ac_2O. Reaction time: 17 hours. Analysis by chiral GC revealed a 55.8% ee of the *R*

acetate and a 92.5% ee of the *S* alcohol. These ee values correspond to a selectivity factor of 11.1 at 62.4% conversion.

A second run provided a 54.5% ee of acetate and a 95.3% ee of alcohol (s = 11.9 at 63.6% conversion).

A third run provided a 50.3% ee of acetate and a 97.1% ee of alcohol (s = 11.6 at 65.9% conversion). Alcohol: $[\alpha]^{20}_D$ = +3.4° (c = 0.25, $CHCl_3$, 97% ee).

Table 2.4, entry 9. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 75.0 mg (0.500 mmol) of alcohol, and 47.0 μL (0.500 mmol) of Ac_2O. Reaction time: 41 hours. Analysis of the acetate by chiral GC revealed a 53.3% ee of the *R* acetate. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 92.7% ee of the *S* enantiomer. These ee values correspond to a selectivity factor of 10.3 at 63.5% conversion.

A second run provided a 49.5% ee of acetate and a 94.8% ee of alcohol (s = 10.0 at 65.7% conversion).

A third run provided a 41.6% ee of acetate and a 98.7% ee of alcohol (s = 10.5 at 70.4% conversion). Alcohol: $[\alpha]^{20}_D$ = -32.4° (c = 1.00, $CHCl_3$, 99% ee).

Table 2.4, entry 10. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 63.0 mg (0.500 mmol) of alcohol, and 47.0 μL (0.500 mmol) of Ac_2O. Reaction time: 130 hours. Analysis of the acetate by chiral GC revealed a 43.3% ee of the *R* acetate. The alcohol was converted into the acetate and then analyzed by chiral GC, which revealed a 93.2% ee of the *S* enantiomer. These ee values correspond to a selectivity factor of 7.8 at 68.3% conversion.

A second run provided a 41.6% ee of acetate and a 94.5% ee of alcohol (s = 7.9 at 69.4% conversion). Alcohol: $[\alpha]^{20}_D$ = -6.6° (c = 0.28, $CHCl_3$, 95% ee).

Table 2.4, entry 11. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 75.0 mg (0.50 mmol) of alcohol and 47.0 μL (0.50 mmol) of acetic anhydride. Reaction time: 214 hours. Analysis by chiral GC revealed a 33.8% ee of *R* acetate. The alcohol was converted into the acetate derivative and GC analysis revealed a 93.3% ee of the *S* enantiomer. These ee values correspond to a selectivity factor (s) of 6.0 at 73.4% conversion.

A second run provided a 33.8% ee of acetate and a 93.6% ee of alcohol (s = 6.1 at 73.4% conversion). Alcohol: $[\alpha]^{20}_D$ = -28.1° (c = 1.00, $CHCl_3$, 95% ee).

Table 2.4, entry 12. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 66.0 mg (0.50 mmol) of alcohol and 47.0 μL (0.50 mmol) of acetic anhydride. Reaction time: 43 hours. Analysis by chiral GC revealed a 36.8% ee of *R* acetate. The alcohol was converted into the acetate derivative and GC analysis revealed a 88.1% ee of the *S* enantiomer. These ee values correspond to a selectivity factor (s) of 5.7 at 70.6% conversion.

A second run provided a 25.7% ee of acetate and a 96.6% ee of alcohol (s = 5.6 at 79.0% conversion).

Table 2.4, entry 13. The general procedure was followed using 3.3 mg (0.0050 mmol) of cata,yst (–)-**2.1**, 87.0 mg (0.50 mmol) of alcohol and 47.0 μL (0.50 mmol) of acetic anhydride. Reaction time: 53 hours. Analysis by chiral GC revealed a 32.7% ee of *R* acetate. The alcohol was converted into the acetate derivative and GC analysis revealed a 95.5% ee of the *S* enantiomer. These ee values correspond to a selectivity

factor (s) of 6.4 at 74.5% conversion.

A second run provided a 33.1% ee of acetate and a 94.6% ee of alcohol (s = 6.2 at 74.1% conversion). Alcohol: $[\alpha]^{20}_D$ = +14.5° (c = 0.70, $CHCl_3$, 99% ee).

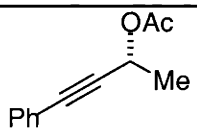
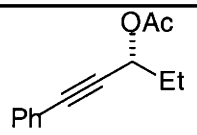
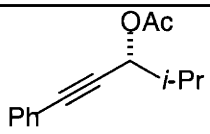
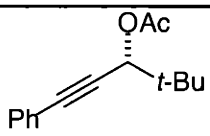
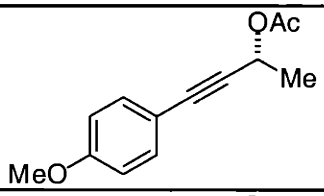
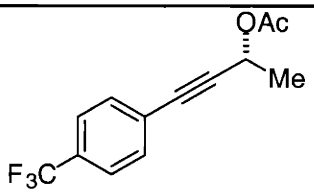
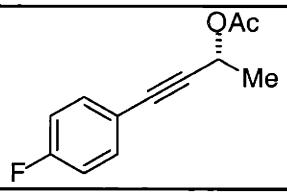
Table 2.4, entry 14. The general procedure was followed using 3.0 mg (0.0045 mmol) of catalyst (–)-**2.1**, 85.0 mg (0.45 mmol) of alcohol and 43.0 μL (0.45 mmol) of acetic anhydride. Reaction time: 46 hours. Analysis by chiral GC revealed a 30.0% ee of *R* acetate. The alcohol was converted into the acetate derivative and GC analysis revealed a 96.4% ee of the *S* enantiomer. These ee values correspond to a selectivity factor (s) of 6.3 at 76.2% conversion.

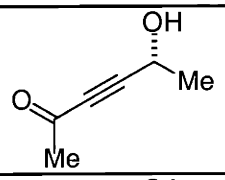
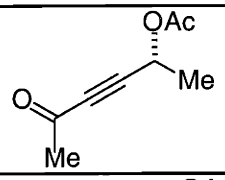
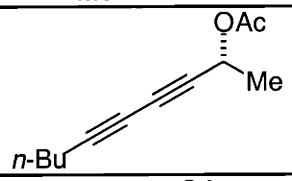
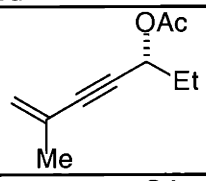
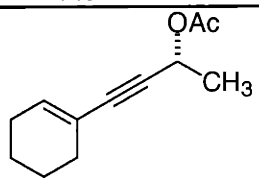
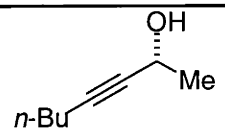
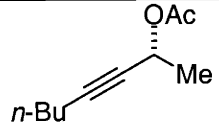
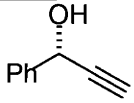
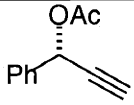
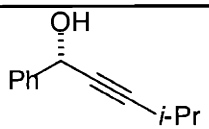
A second run provided a 30.9% ee of acetate and a 94.8% ee of alcohol (s = 5.9 at 75.5% conversion). Alcohol: $[\alpha]^{20}_D$ = +26.1° (c = 1.00, $CHCl_3$, 94% ee)

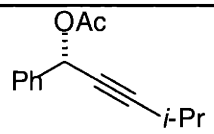
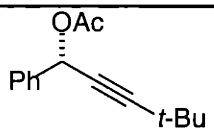
Table 2.4, entry 15. The general procedure was followed using 3.3 mg (0.0050 mmol) of catalyst (–)-**2.1**, 63.0 mg (0.500 mmol) of alcohol, and 47.0 μL (0.500 mmol) of Ac_2O. Reaction time: 336 hours. Analysis by chiral GC revealed a 20.4% ee of the *R* acetate and a 90.9% ee of the *S* alcohol. These ee values correspond to a selectivity factor of 3.9 at 81.6% conversion.

A second run provided a 22.5% ee of acetate and a 88.3% ee of alcohol (s = 3.9 at 79.7% conversion).

IX. Methods Used to Assay Enantiomeric Excess

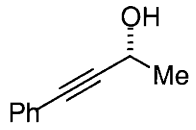
Substrate	ee Assay	Conditions	Retention Time of Isomer with Indicated Configuration (min)	Retention Time of Isomer with Opposite Configuration (min)
	GC Chiraldex G-TA	120 °C; 1.63 mL/min carrier gas flow	8.19	9.57
	GC Chiraldex G-TA	120 °C; 1.63 mL/min carrier gas flow	12.38	15.42
	GC Chiraldex G-TA	120 °C; 1.63 mL/min carrier gas flow	15.06	17.51
	GC Chiraldex G-TA	110 °C; 1.70 mL/min carrier gas flow	28.60	31.21
	GC Chiraldex G-TA	130 °C; 1.37 mL/min carrier gas flow	31.26	35.50
	GC Chiraldex G-TA	130 °C; 1.37 mL/min carrier gas flow	5.64	5.97
	GC Chiraldex G-TA	110 °C; 1.50 mL/min carrier gas flow	14.11	16.18

	GC Chiraldex G-TA	110 °C; 1.50 mL/min carrier gas flow	10.18	10.41
	GC Chiraldex G-TA	90 °C; 1.85 mL/min carrier gas flow	7.67	10.78
	GC Chiraldex G-TA	130 °C; 1.37 mL/min carrier gas flow	8.54	11.65
	GC Chiraldex G-TA	75 °C; 1.98 mL/min carrier gas flow	7.57	11.84
	GC Chiraldex G-TA	110 °C; 1.70 mL/min carrier gas flow	12.58	14.54
	GC Chiraldex G-TA	60 °C; 2.13 mL/min carrier gas flow	17.24	15.39
	GC Chiraldex G-TA	60 °C; 2.13 mL/min carrier gas flow	28.20	33.13
	GC Chiraldex G-TA	90 °C; 1.85 mL/min carrier gas flow	25.88	27.35
	GC Chiraldex G-TA	90 °C; 1.85 mL/min carrier gas flow	20.25	24.65
	GC Chiraldex G-TA	90 °C; 1.64 mL/min carrier gas flow	75.53	70.56

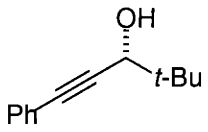
	GC Chiraldex G-TA	90 °C; 1.64 mL/min carrier gas flow	62.95	64.67
	GC Chiraldex G-TA	90 °C; 1.64 mL/min carrier gas flow	61.02	59.17

X. Assignment of Absolute Stereochemistry

Assignment of Absolute Configuration. The absolute configurations were established through comparison of the sign of the optical rotation of our alcohols with rotations reported in the literature. For those alcohols not listed below, the assignment of absolute configuration was based on analogy.



The sign of the optical rotation of the kinetically resolved alcohol produced in the presence of (+)-**2.1** is positive; therefore, its absolute stereochemistry is *R*.[44]



The sign of the optical rotation of the kinetically resolved alcohol produced in the presence of (+)-**2.1** is positive; therefore, its absolute stereochemistry is *R*.[45]

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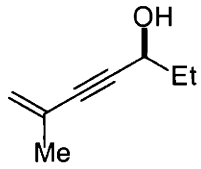
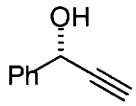
44 Ishihara, K.; Mori, A.; Arai, I.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 983-986.

45 Ramachandran, P. V.; Teodorovic, A. V.; Rangaishenvi, M. V.; Brown, H. C. *J. Org. Chem.* **1992**, *57*, 2379-2386.



The sign of the optical rotation of the kinetically resolved alcohol produced in the presence of (–)-**2.1** is negative; therefore, its absolute stereochemistry is *S*.[46]



The sign of the optical rotation of the kinetically resolved alcohol produced in the presence of (+)-**2.1** is negative; therefore, its absolute stereochemistry is *R*.

46 Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1991**, *113*, 6129-6139.

Chapter 3:

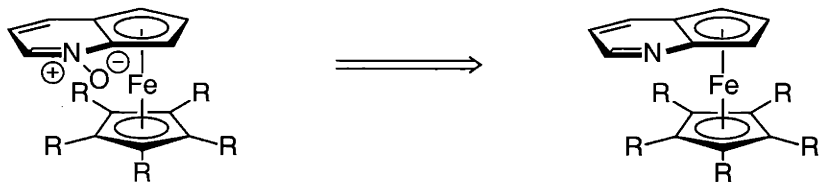
Desymmetrization of Meso Epoxides Using Planar-Chiral Pyridine *N*-Oxide Derivatives

Introduction to Oxygen Nucleophiles

In our laboratory, we have developed planar-chiral DMAP derivatives, in which nitrogen is the nucleophilic site. These catalysts were shown to effect a number of transformations, including the kinetic resolution of secondary alcohols,[1] the ring opening of azlactones,[2] and the rearrangement of *O*-acylated azlactones.[3]

Catalysts in which oxygen is the nucleophilic site, though not as well-known, can also effect a number of transformations. Hence, consistent with our goals of developing new planar-chiral nucleophilic catalysts, we planned to incorporate oxygen functionality into complex **3.2** by a simple oxidation reaction of the planar-chiral pyridine derivative (Scheme 3.1).

Scheme 3.1 Retrosynthesis of Planar-Chiral Pyridine *N*-Oxide



3.1 **3.2**

There are a number of reactions reported in the literature that are catalyzed by oxygen nucleophiles. For example, it has been independently reported by Kobayashi and Denmark that DMF or HMPA coordinates to the silicon in allyltrichlorosilane

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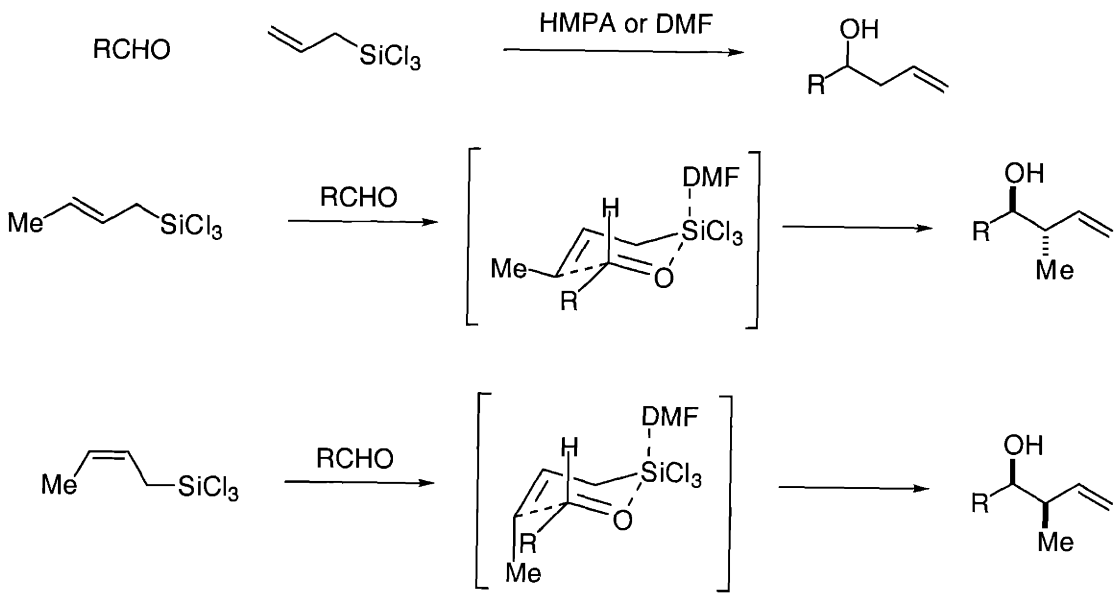
1 (a) Bellemin-Laponnaz, S.; Tweddell, J.; Ruble, J. C.; Breitling, F. M.; Fu, G. C. *Chem. Commun.* **2000**, 1009-1010. (b) Ruble, J. C.; Tweddell, J.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2794-2795. (c) Ruble, J. C.; Latham, H. A.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 1492-1493.

2 Liang, J.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 3154-3155.

3 Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 11532-11533.

to form a hypervalent silicate, which in turn reacts with aldehydes to give the corresponding homoallylic alcohols (Scheme 3.2).[4] This hypothesis is supported by ^{29}Si NMR, which indicates that DMF or HMPA is coordinated to the silicon atom of crotyltrichlorosilane to form the corresponding five or six coordinated organosilicate.[5] In this stereospecific reaction, syn homoallylic alcohols are obtained when (*Z*)-2-propenyltrichlorosilane is used, while anti products resulted with (*E*)-2-propenyltrichlorosilane. This sense of internal stereoinduction strongly indicates that the reaction proceeds via a cyclic six-membered transition state. When triethylamine or triphenylphosphine is used in place of DMF or HMPA, no reactivity is observed, suggesting the importance of the oxygen moiety in DMF and HMPA as the nucleophilic site.

Scheme 3.2 Allylation of Aldehydes Catalyzed by DMF or HMPA



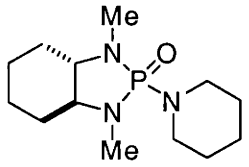
In 1994 Denmark reported that asymmetric allylation of aldehydes can be

4 Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620-6628.

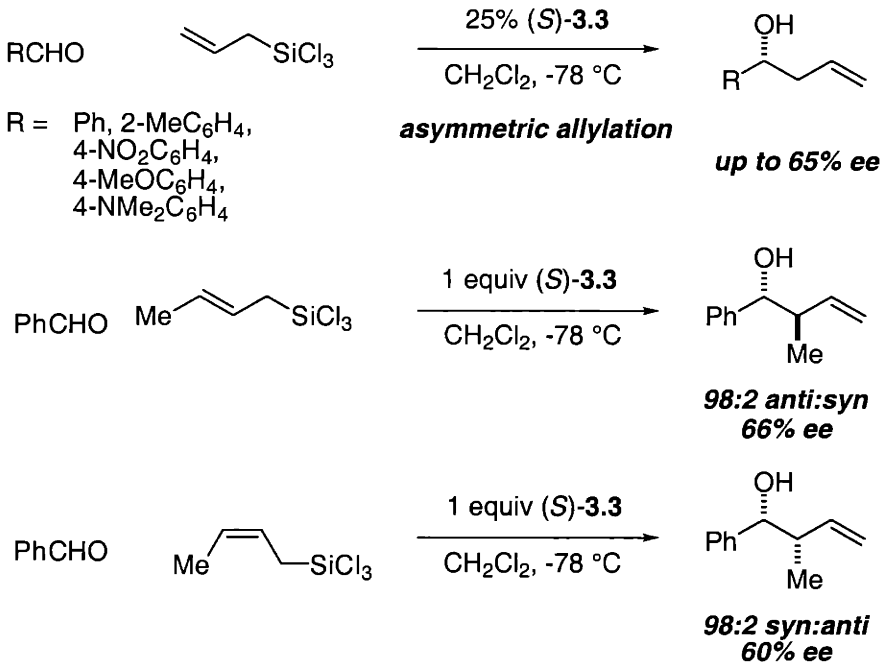
5 Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453-3456.

promoted by chiral phosphoramides in high yields and modest enantiomeric excess (Scheme 3.3).[6] However, the scope of the reaction is limited to aromatic aldehydes.

Scheme 3.3 Asymmetric Allylation of Aldehydes by a Chiral Phosphoramide



3.3



Two years later, Iseki reported the same transformation using substoichiometric amounts of chiral phosphoramides with satisfactory yields and enantioselectivities (Scheme 3.4).[7] However, the scope of the reaction is again limited to aromatic aldehydes and the reaction proceeds well only with high catalyst loading.

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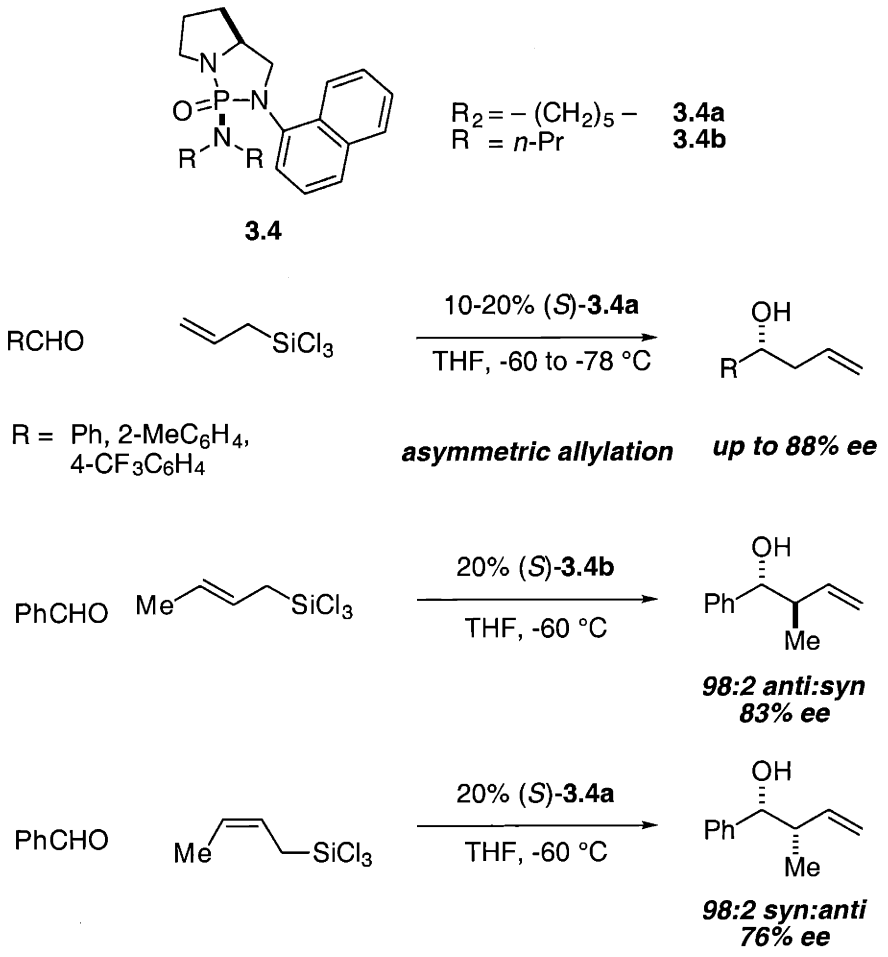
6 Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994,** *59,* 6161-6163.

7 Iseki, K.; Kuroki, Y.; Takahashi, M.; Kobayashi, Y. *Tetrahedron Lett.* **1996,** *37,* 5149-5150.

Scheme 3.4 Asymmetric Allylation of Aldehydes by a Chiral Phosphoramide



The scope of the reaction was later expanded by utilizing a chiral formamide catalyst **3.5** (Scheme 3.5).[8,9] Using HMPA as an additive, allylation of aliphatic aldehydes with allyltrichlorosilane was carried out affording enantioselectivities up to 98%. Allenylation of aliphatic aldehydes can also be carried out, although the reaction time is typically 14 days.[10] With 1.5 equiv of a mixture of propargyl- and allenyl-trichlorosilanes (75:25), a number of aliphatic aldehydes were allenylated,

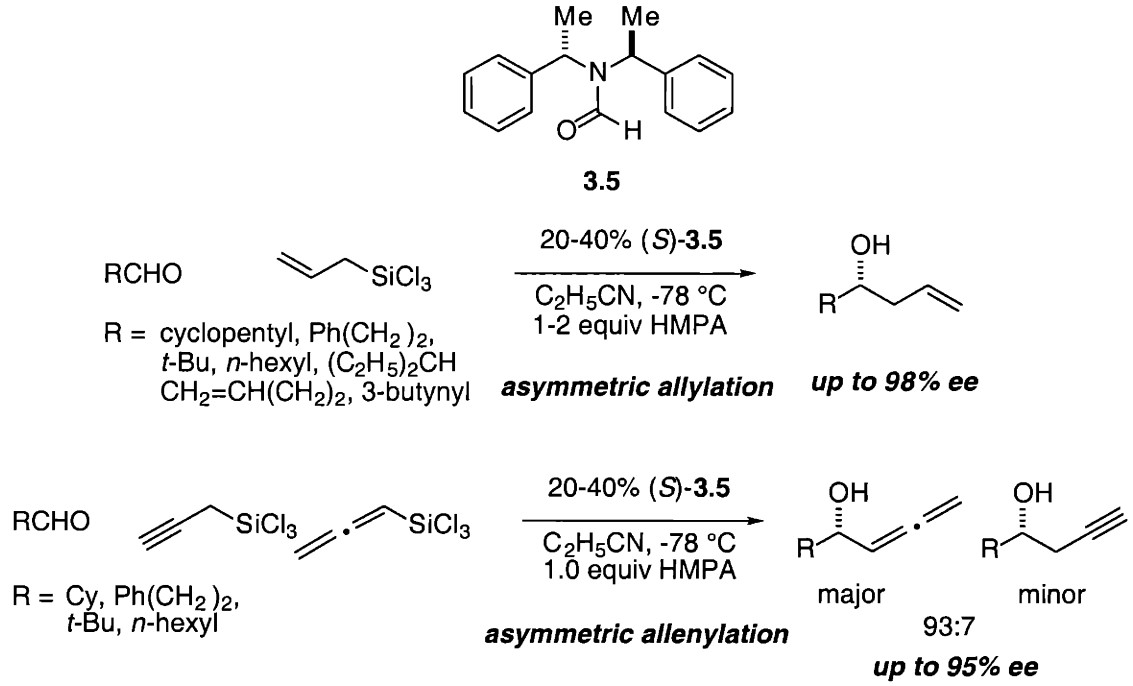
8 Iseki, K.; Mizuno, S.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron Lett.* **1998**, *39*, 2767-2770.

9 Iseki, K.; Mizuno, S.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron* **1999**, *55*, 977-988.

10 Iseki, K.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron: Asymmetry* **1998**, *9*, 2889-2894.

giving the allenic alcohols as the major products. This suggests that the formamide catalyzes the reaction of aldehydes with allenylsilane very slowly. Interestingly, benzaldehyde gave essentially racemic product in this reaction.

Scheme 3.5 Allylation and Allenylation of Aldehydes by a Chiral Formamide

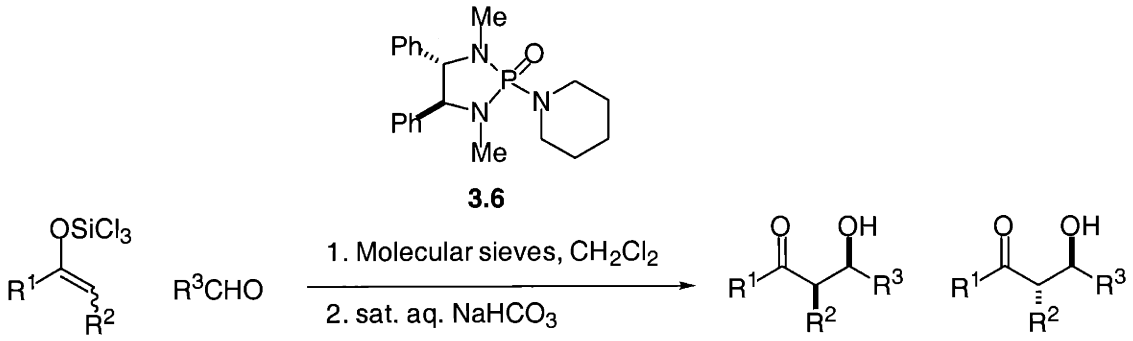


Chiral analogues of HMPA have also been demonstrated to catalyze the aldol reaction in good stereoselectivity as shown by Denmark and coworkers (Scheme 3.6).[11] In the presence of catalytic amounts of chiral phosphoramide, the aldol reaction of the trichlorosilyl enolates of ketones with aldehydes can proceed rapidly. A number of structurally diverse chiral phosphoramides were surveyed, and the best selectivities were obtained with the *N,N*-dimethylphospholidine derived from stilbene diamine in which the phosphorus contains a piperidino group. Extremely high diastereoselectivity (E enoxytrichlorosilane to anti product; Z

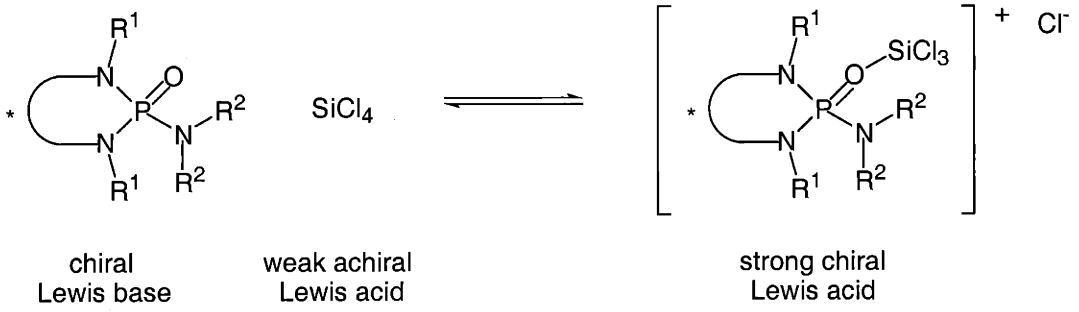
11 Denmark, S. E.; Stavenger, R. A. *Acc. Chem. Res.* **2000**, *33*, 432-440 and references therein.

enoxytrichlorosilane to syn product) and excellent enantioselectivity can be achieved in this reaction. The authors believe that the reaction proceeds via a closed transition state with a phosphoramide in a hexacoordinated silicon species.

Scheme 3.6 Asymmetric Aldol Reaction Catalyzed by a Chiral Phosphoramide



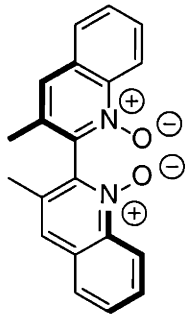
Scheme 3.7 Coordination of a Lewis Base to a Weak Lewis Acid Resulting in a Strong Lewis Acid



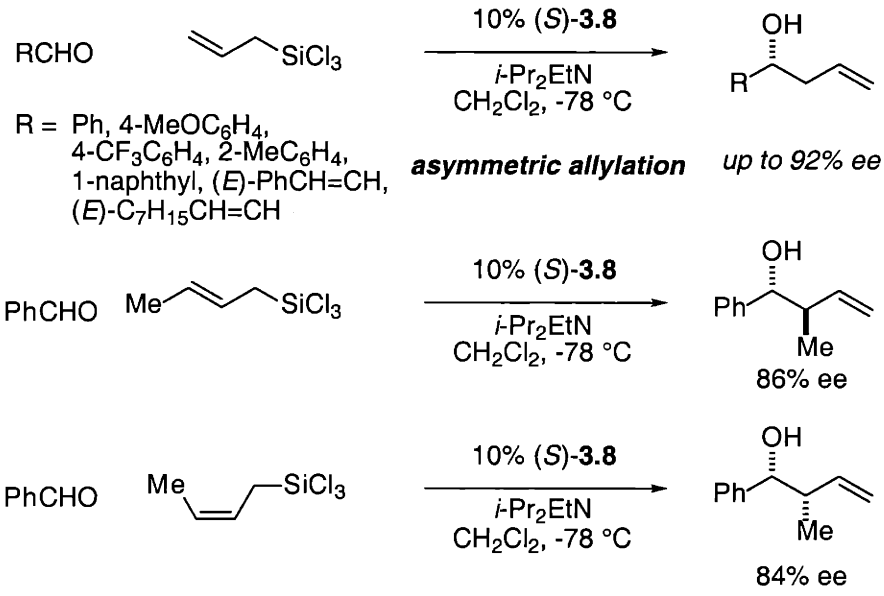
Although this sounds counter-intuitive, a Lewis basic donor ligand can enhance the activity of a Lewis acidic acceptor. According to Gutmann, upon coordination of a polyatomic donor to a polyatomic acceptor, a net increase in electron density on the donor and a net decrease in electron density on the acceptor atom can result

(Scheme 3.7).[12] Hence, coordination of a Lewis base can make the central atom of a Lewis acid more electrophilic with the excess charge residing on the peripheral ligands.

Scheme 3.8 Enantioselective Allylation of Aldehydes Catalyzed by a Chiral Biquinoline *N,N*-Dioxide



(*S*)-**3.8**



Other than DMF and HMPA, amine *N*-oxides are also known to exhibit a strong affinity for the silicon atom. Effective enantioselective allylation of aldehydes with allyltrichlorosilane can be carried out in the presence of (*S*)-3,3'-dimethyl-2,2'-biquinoline *N,N'*-dioxide **3.8** as a catalyst (Scheme 3.8).[13] In this reaction, diisopropylethylamine was added to increase the rate of the reaction, although the role of diisopropylethylamine remains unclear. While aromatic and α,β-unsaturated aldehydes were allylated in high yields and good enantiomeric excess,

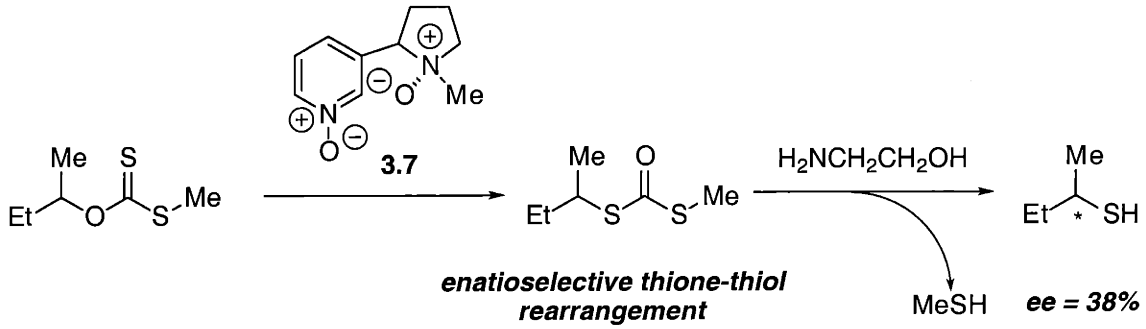
12 (a) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions;* Plenum Press: New York, 1978. (b) Jensen, W. B. *The Lewis Acid-Base Concepts;* Wiley-Interscience: New York, 1980; Chapter 4.

13 Nakajima, M.; Saito, M.; Shiro, M.; Hashimoto, S.-i. *J. Am. Chem. Soc.* **1998**, *120*, 6419-6420.

aliphatic aldehydes were poor substrates in terms of yield and enantioselectivity. Again, anti homoallylic alcohols were obtained from (*E*)-crotyltrichlorosilane while syn homoallylic alcohols resulted from (*Z*)-crotyltrichlorosilane, consistent with a cyclic six-membered chair transition state.

Pyridine *N*-oxide can also catalyze the rearrangement of thiones to thiols.[14] To obtain enantiomerically enriched thiols, (*S*)-(–)-3-(1-methyl-2-pyrrolidino)pyridine (nicotine) was oxidized to give a mixture of two diastereomeric (1'*R*, 2'*S*)- and (1'*S*, 2'*S*)-3-(1-methyl-2-pyrrolidino)pyridine *N,N'*-dioxides in a ratio of 0.8:1, and the mixture was used as a catalyst for the rearrangement reaction (Scheme 3.9).[15] A relatively high catalyst loading (50%) was employed to give a modest 38% ee of the thiol.

Scheme 3.9 Rearrangement of Thiones to Thiols by an Amine *N*-Oxide



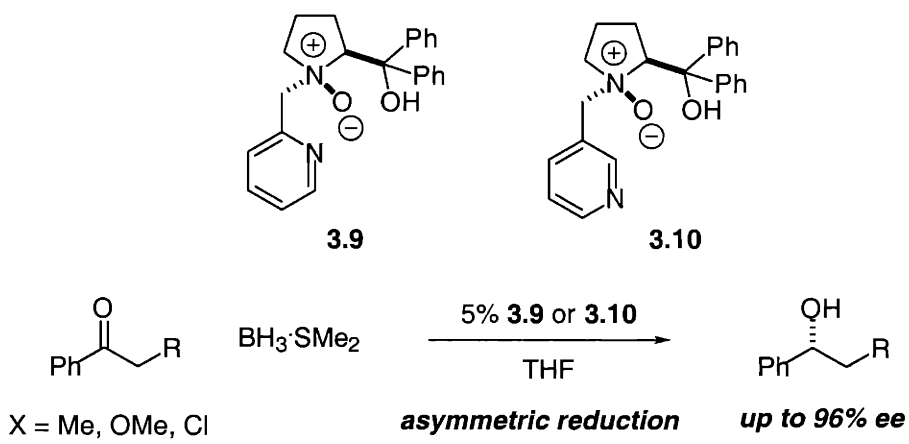
In addition to nucleophilic catalysis, amine *N*-oxides can also serve as ligands in catalytic asymmetric reactions. For example, catalytic reduction of ketones can be

14 (a) Harano, K.; Shinihara, I.; Murase, M.; Hisano, T. *Heterocycles* **1987**, *26*, 2583. (b) Harano, K.; Kiyonaga, H.; Sugimoto, S.-I.; Matsuka, T.; Hisano, T. *Heterocycles* **1988**, *27*, 2327. (c) Harano, K.; Shinohara, I.; Sugimoto, S.-I.; Matsuoka, T. *Chem. Pharm. Bull.* **1989**, *37*, 576.

15 Diana, M. B.; Marchetti, M.; Melloni, G. *Tetrahedron: Asymmetry* **1995**, *6*, 1175-1179.

carried out with chiral prolinol *N*-oxide derivatives (Scheme 3.10).[16] The presence of a tertiary alcohol on the ligand is crucial. When the pyridinyl group in the ligand was replaced by a phenyl group, the enantioselectivity of acetophenone reduction drops tremendously from 79% to 12%. The amine *N*-oxide ligand could be recovered from the reaction mixture, and no reduction of the *N*-oxides to the parent tertiary amine was observed. Although enantiomeric excess of up to 96% could be obtained, only three substrates were reported.

Scheme 3.10 Asymmetric Reduction of Ketones Catalyzed by a Chiral Prolinol *N*-Oxide



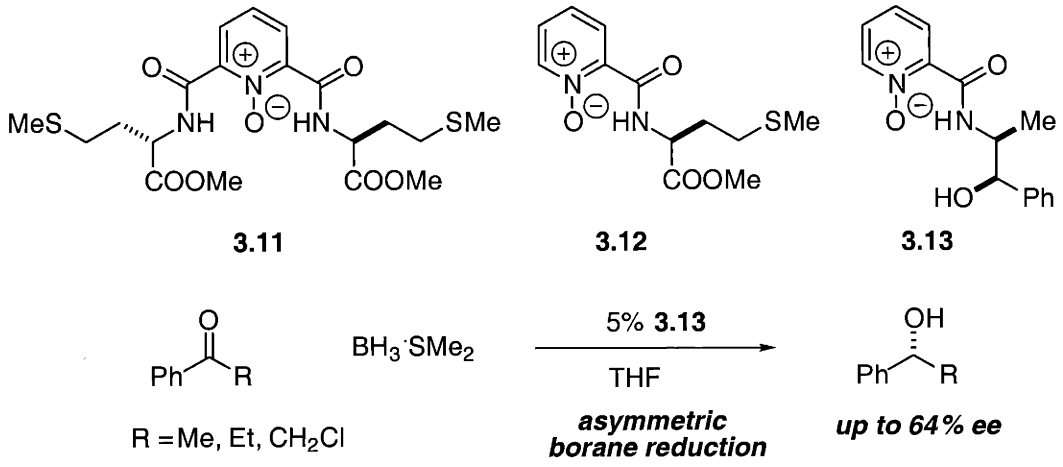
Catalytic asymmetric reduction can also be carried out using chiral pyridine *N*-oxides (Scheme 3.11).[17] The ligand design allows different chiral amines to be incorporated onto either 2-acylpyridine or 2,6-diacylpyridine moieties to tune the stereochemical environment of the ligand. To enhance the chelating ability of the ligands, chiral amines bearing additional donor groups (e.g., OH, SMe) were used. In general, ligands derived from methionine or norephedrine are superior to those

16 O'Neil, I. A.; Turner, C. D.; Kalindjian, S. B. *Synlett* **1997**, 777-780.

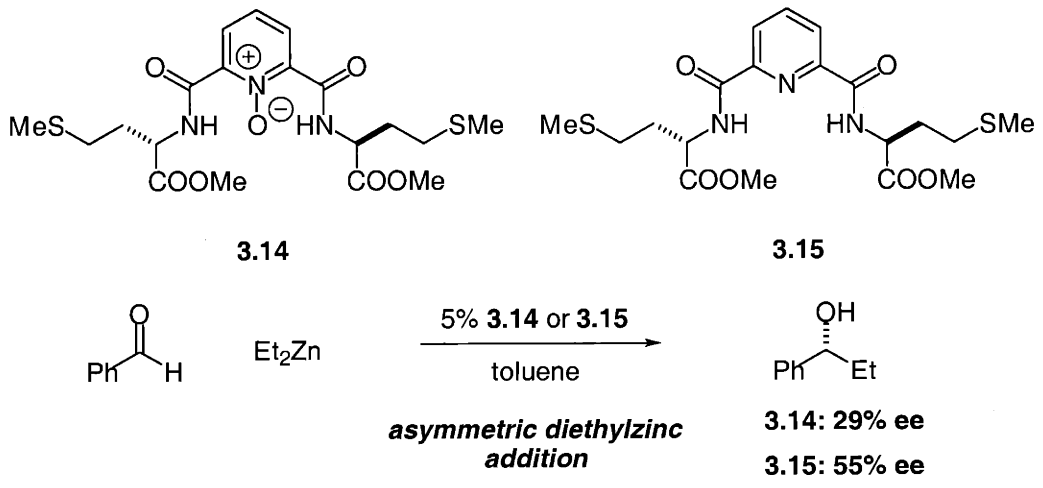
17 Derdau, V.; Laschat, S.; Hupe, E.; König, W. A.; Dix, I.; Jones, P. G. *Eur. J. Inorg. Chem.* **1999**, 2, 1001-1007.

derived from alanine, leucine, or valine. An increase in selectivity was observed for bis-methionine ligands relative to the mono-methionine ligands. However, mono-norephedrine ligand **3.13** displays the highest enantioselectivity in the asymmetric reduction, and the *N*-oxide moiety is crucial for this chemistry.

Scheme 3.11 Asymmetric Reduction of Ketones Catalyzed by a Chiral Pyridine *N*-Oxide



Scheme 3.12 Asymmetric Diethylzinc Addition to Aldehydes Catalyzed by a Chiral Pyridine *N*-Oxide



Asymmetric addition of diethylzinc to benzaldehyde can be carried out with catalytic amounts of a pyridine *N*-oxides (Scheme 3.12).[17] Ligands derived from methionine gave better enantioselectivity. However, higher enantioselectivities (55% ee) of 1-phenylpropanol can be achieved by using **3.15**. Hence, the *N*-oxide functionality is not essential in this asymmetric diethylzinc addition.

To test our catalyst design, we chose to examine the effectiveness of the planar-chiral pyridine *N*-oxide catalysts in the desymmetrization of meso epoxides with chlorosilanes.[18] This reaction was first studied by Denmark with a chiral phosphoramide catalyst (Scheme 3.13).[19,20] The authors believe a complex is first formed between $SiCl_4$ and the phosphoramide, which undergoes ionization to produce a highly reactive silicon cation and a chloride ion. The epoxide is then activated through the phosphorous/silicon cation, which then undergoes nucleophilic attack by the chloride ion.

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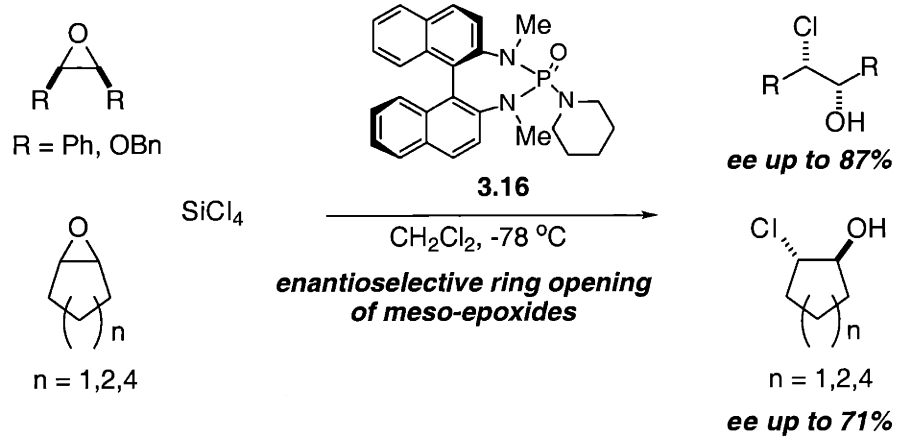
18 For a review of catalytic asymmetric ring openings of epoxides, see: Jacobsen, E. N.; Wu, M. H. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Chapter 35.

19 Denmark, S. E.; Barsanti, P. A.; Wong, K.-T.; Stavenger, R. A. *J. Org. Chem.* **1998**, *63*, 2428-2429.

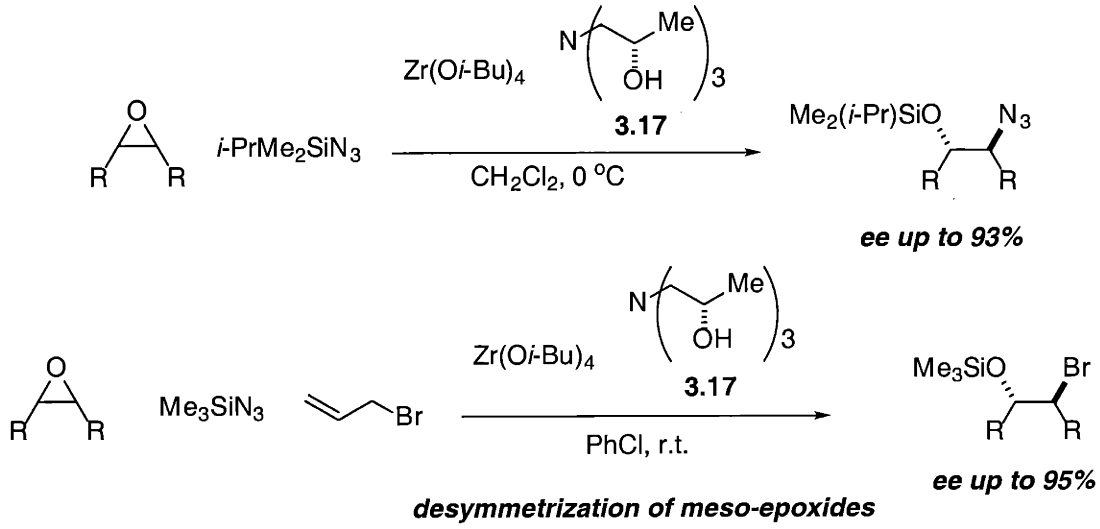
20 After the completion of our work, Buono reported the asymmetric ring opening of meso epoxides using a chiral *ortho*-methoxyphenyl diazaphosphonamide Lewis base: (a) Brunel, J. M.; Legrannd, O.; Reymond, S.; Buono, G. *Angew. Chem. Int. Ed.* **2000**, *39*, 2554-2557. (b) Reymond, S.; Brunel, J. M.; Buono, G. *Tetrahedron: Asymmetry* **2000**, *11*, 4441-4445. (c) Reymond, S.; Legrand, O.; Brunel, J. M.; Buono, G. *Eur. J. Org. Chem.* **2001**, 2819-2823. However, Denmark et al. did not succeed in reproducing the results. Under the described conditions, we obtained results consistent with Denmark's finding for ring opening of cyclooctene oxide: Denmark, S. E.; Wynn, T.; Jellerichs, B. G. *Angew. Chem. Int. Ed.* **2001**, *40*, 2255-2256. The above-mentioned manuscripts (a)-(c) were later withdrawn: Buono, G. *Angew. Chem. Int. Ed.* **2001**, *40*, 4536. Buono, G. *Eur. J. Org. Chem.* **2002**, 218.

Scheme 3.13 Desymmetrization of Meso Epoxides by a Chiral Phosphoramide



Nugent has demonstrated that a zirconium complex bearing homochiral tri-2-propanol amine ligands can also serve as an effective catalyst in the ring opening of meso epoxides (Scheme 3.14).[21]

Scheme 3.14 Desymmetrization of Meso Epoxides Using a C_3-Symmetric Ligand



21 (a) Nugent, W. *J. Am. Chem. Soc.* **1992**, *114*, 2768-2769. (b) McCleland, B. W.; Nugent, W.; Finn, M. G. *J. Org. Chem.* **1998**, *63*, 6656-6666.

High enantioselectivities were realized with the bulky azide reagent *i*-$PrMe_2SiN_3$. When excess allyl bromide is added, a high yield of the protected β-bromohydrin is obtained.[22] This is because the azide, situated on the zirconium, is replaced by the bromide and this rate of replacement is fast relative to azide transfer.

Jacobsen's chromium salen complex is a highly effectively catalyst for the enantioselective ring opening of epoxides with $TMSN_3$ to give azido silyl ethers (Scheme 3.15).[23] Epoxides fused to five-membered rings undergo ring opening with high enantioselectivity (>94% ee), while six-membered ring and acyclic epoxides are slightly less effective (81-88% ee). Reactions can be carried out under solvent-free conditions, and the catalyst can be recovered and recycled without loss of reactivity or enantioselectivity. The asymmetric ring opening technology can be extended to include alkanethiols as nucleophiles (Scheme 3.15).[24] Benzyl mercaptan was identified as the best nucleophile, affording the ring-opened product in 59% ee. Therefore, the use of a dithiol with 2 equiv of epoxide would result in mixtures of chiral and meso bis-adducts with improved enantioselectivities, assuming that no diasteroselection occurs in the second ring-opening step. The chiral bis-adduct can be transformed into the free thiol by dissolving metal reduction (Na/NH_3) of the protected silyl ether.

In addition to $TMSN_3$ and thiols, Jacobsen and co-workers also reported ring opening of meso epoxides using benzoic acid.[25] Co(II) salen complex **3.19** is the

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22 Nugent, W. *J. Am. Chem. Soc.* **1998**, *120*, 7139-7140.

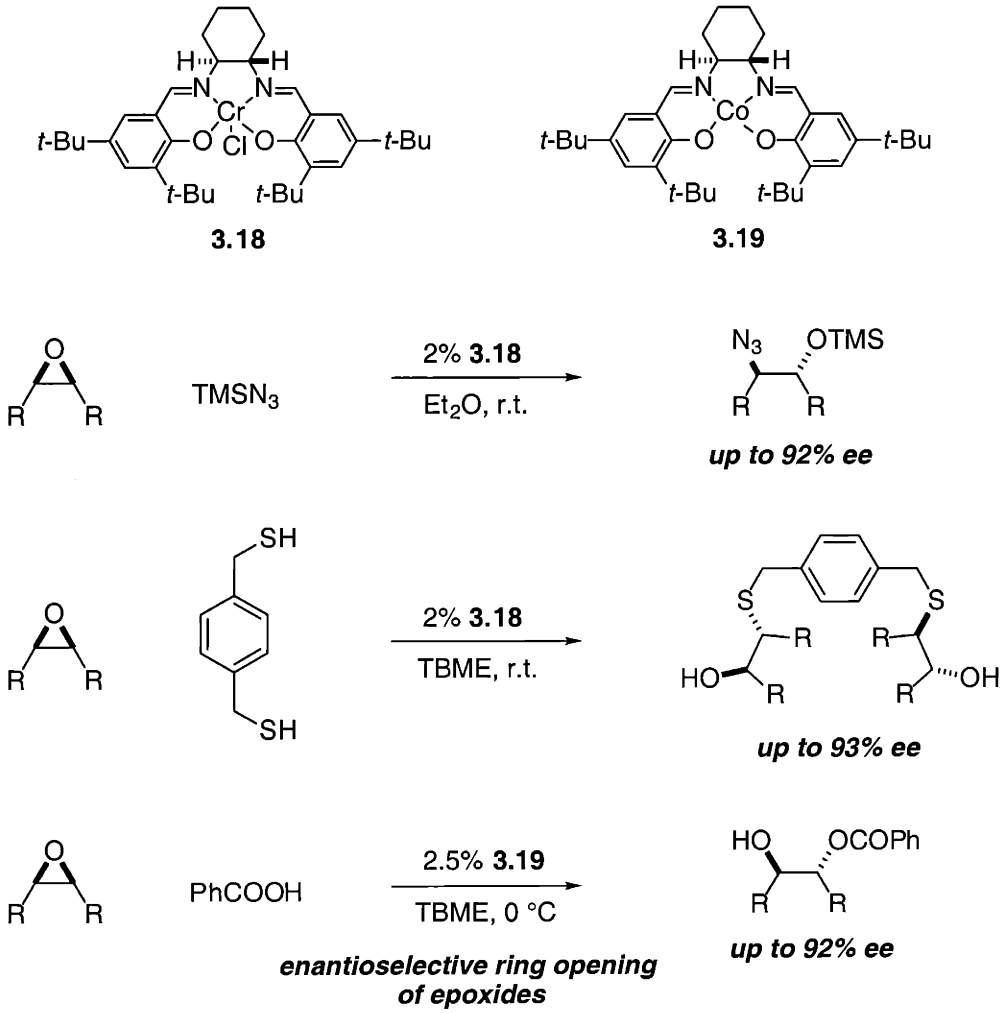
23 (a) Martínez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5897-5898. (b) Jacobsen, E. N. *J. Am. Chem. Soc.* **2000**, *33*, 421-431.

24 Jacobsen, E. N.; Wu, M. H. *J. Org. Chem.* **1998**, *63*, 5252-5254.

25 Jacobsen, E. N.; Kakiuchi, F.; Konsler, R. G.; Larrow, J. F.; Tokunaga, M. *Tetrahedron Lett.* **1997**, *38*, 773-776.

catalyst of choice, giving the highest enantioselectivity. The reaction can be carried out in the absence of solvent and on multi-gram scale. The reactive species is believed to be the Co(III) salen complex because, under anaerobic conditions, the reaction proceeds at a slower rate and with lower enantioselectivity with the Co(II) salen complex.

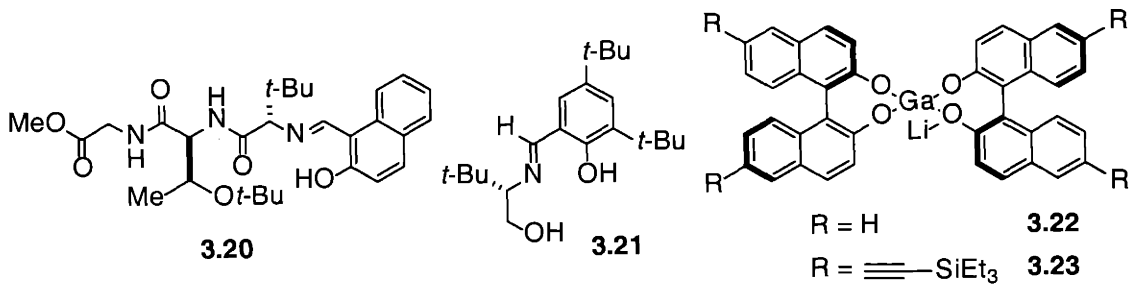
Scheme 3.15 Enantioselective Ring Opening of Meso Epoxides Using Metal Salen Complexes



Snapper and Hoveyda et al. reported a titanium-catalyzed enantioselective

addition of TMSCN to meso epoxides using chiral Schiff base **3.20** (Scheme 3.16).[26] Enantioselective ring opening of meso epoxides can also be carried out using PhLi and a catalytic amount of chiral Schiff base **3.21** to give up to 86% ee.[27] Shibasaki and co-workers have also reported a highly enantioselective ring opening of epoxides with *t*-BuSH catalyzed by a gallium-lithium bis(binaphthoxide) complex **3.22** (R = H).[28] 4-Methoxyphenol, an oxygen nucleophile, can be introduced as well using gallium heterobimetallic complex **3.23** in the presence of molecular sieves.[29] More recently, a novel BINOL with an oxygen-containing linker was developed by the same group in order to increase the stability of the gallium complex. This affords 1,2 diol monoethers in up to 96% ee.[30]

Scheme 3.16 Other Literature Examples of Chiral Ligands and Catalysts in the Enantioselective Ring Opening of Meso Epoxides



26 (a) Shimizu, K. D.; Cole, B. M.; Krueger, C. A.; Kuntz, K. W.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1704-1707. (b) Cole, B. M.; Shimizu, K. D.; Krueger, C. A.; Harrity, J. P. A.; Snapper, M. L.; Hoveyda, A. H. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1668-1671.

27 Oguni, N.; Miyagi, Y.; Itoh, K. *Tetrahedron Lett.* **1998**, *39*, 9023-9026.

28 Iida, T.; Yamamoto, N.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1997**, *119*, 4783-4784.

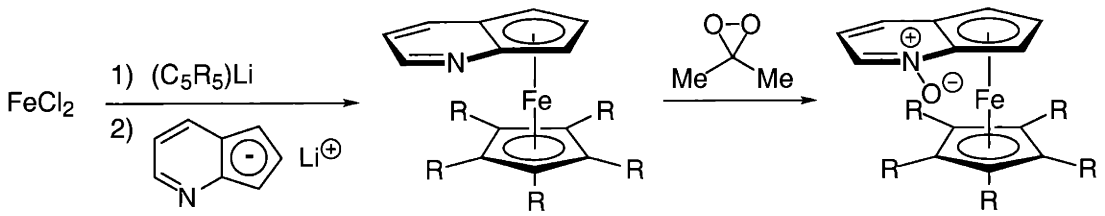
29 Iida, T.; Yamamoto, N.; Matsunaga, S.; Woo, H.-G.; Shibasaki, M. *Angew. Chem. Int. Ed.* **1998**, *37*, 2223-2226.

30 Matsunaga, S.; Das, J.; Roels, J.; Vogl, E. M.; Yamamoto, N.; Iida, T.; Yamaguchi, K.; Shibasaki, M. *J. Am. Chem. Soc.* **2000**, *122*, 2252-2260.

Results and Discussion

In addition to π-bound nitrogen heterocycles, we have expanded our scope of investigation to π-bound nitrogen-oxide heterocycles. Applying our catalyst design, we decided to synthesize complexes **3.1**. Since the nucleophilic site is the oxygen atom, we speculated that the electron-donating 4-dialkylamino substituent could be left out without affecting the reactivity of these complexes. We were glad to learn that this family of compounds can be easily obtained by treatment of $FeCl_2$ with $(C_5R_5)Li$ and the lithio salt of pyrindine, followed by oxidation of **3.2** with dimethyldioxirane (DMDO) (Scheme 3.17). The resulting planar-chiral *N*-oxide compounds can be readily separated by chiral HPLC into their enantiomers.

Scheme 3.17 Synthesis of Planar-Chiral Pyridine *N*-Oxide Catalyst



3.2a (R = Me) (50%)
3.2b (R = Ph) (52%)

3.1a (R = Me) (79%)
3.1b (R = Ph) (45%)

In order to determine the effectiveness of this new family of planar-chiral heterocycles as nucleophilic catalysts, we decided to investigate the ring opening of meso epoxides.[31] Recent findings by Denmark showed that these substrate can be

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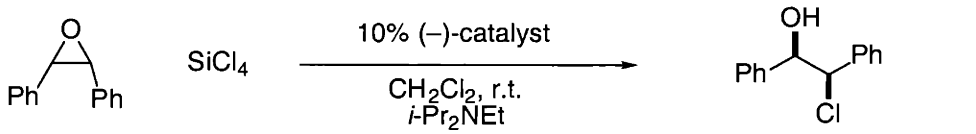
[31] For leading references of catalytic enantioselective ring opening of meso epoxides, see: (a) Nugent, W. A. *J. Am. Chem. Soc.* **1998**, *120*, 7139-7140. (b) Martínez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am Chem. Soc.* **1995**, *117*, 5897-5898. (c) Jacobsen, E. N.; Kakiuchi, F.; Konsler, R. G.; Larrow, J. F.; Tokunaga, M. *Tetrahedron Lett.* **1997**, *38*, 773-776. (d) Iida, T.; Yamamoto, N.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1997**, *119*, 4783-4784. (e) Iida, T.; Yamamoto, N.

enantioselectively opened in the presence of a chiral phosphoramide. Since it is known that, in addition to phosphoramides, amine *N*-oxides also exhibit significant nucleophilicity toward silicon,[32] silicon tetrachloride was chosen as the chloride source for the opening of meso epoxides. An initial study showed that an appreciable amount of a non-selective background reaction was observed in the ring opening of *cis*-stilbene oxide, due to the presence of adventitious HCl in the $SiCl_4$. However, when diisopropylethylamine was added to the reaction mixture, this background reaction was suppressed.

After establishing that $SiCl_4$ does not effect the ring opening in the presence of diisopropylethylamine alone, *cis*-stilbene oxide was treated with silicon tetrachloride in the presence of 10% (–)-**3.1a** or (–)-**3.1b** and diisopropylethylamine (Scheme 3.18). Both reactions proceeded smoothly to give the corresponding chlorohydrin; however, the enantioselectivities were unsatisfactory. Nonetheless, an increase in the bulk of the remote cyclopentadienyl ring does lead to a slight improvement in enantioselectivity (11% ee vs. 25% ee).

Scheme 3.18 Effect of the Bottom Ring of the Catalyst on Enantioselectivity



catalyst **3.1a** ee = 11%
catalyst **3.1b** ee = 25%

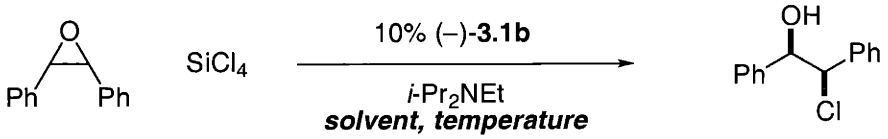
The ring-opening reaction proceeded very efficiently at room temperature (less

Matsunaga, S.; Woo, H.-G.; Shibasaki, M. *Angew. Chem. Int. Ed.* **1998**, *37*, 2223-2226. (f) Denmark, S. E.; Barsanti, P. A.; Wong, K.-T.; Stavenger, R. A. *J. Org. Chem.* **1998**, *63*, 2428-2429.

32 Sato, K.; Kira, M.; Sakurai, H. *Tetrahedron Lett.* **1989**, *30*, 4375-4378.

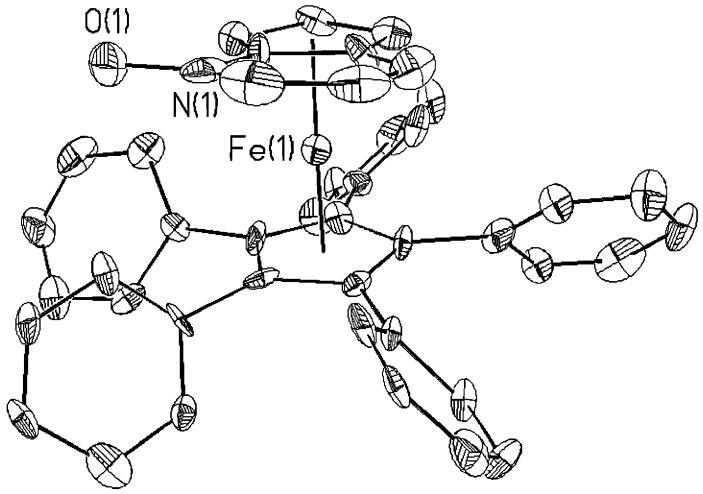
than 10 min as monitored by ^{1}H NMR). This allowed us to carry out the reaction at lower temperature. We were glad to see that the enantioselectivity does improve at -78 °C (Table 3.1, entry 2). Dichloromethane is the solvent of choice (Table 3.1), giving the best enantioselectivity for the corresponding chlorohydrin.

Table 3.1 Enantioselectivity as a Function of Solvent and Temperature

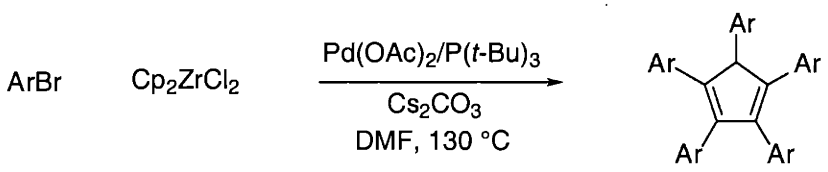


entry	*solvent*	*temperature*	ee (%)
1	CH_2Cl_2	r.t.	25
2	CH_2Cl_2	-78 °C	60
3	toluene	-78 °C	45
4	toluene	-90 °C	48
5	$CHCl_3$	-40 °C	43
6	Et_2O/CH_2Cl_2	-78 °C	40

Figure 3.1 ORTEP Representation of (–)-3.1b (With thermal ellipsoids drawn at the 35% probability level)



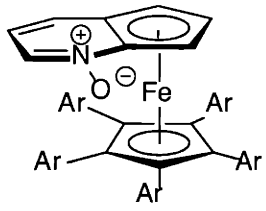
Examination of the X-ray structure of **3.1b** provided us with an explanation for the modest stereoselectivity. Because it is oxygen rather than nitrogen that is the nucleophilic atom, η^5-C_5Ph_5 may not be bulky enough to shield the bottom part of the catalyst, thereby providing poor top-from-bottom differentiation. Hence, to provide a more effective chiral environment around the catalyst, incorporation of a meta substituent on each of the phenyl ring on η^5-C_5Ph_5 might be necessary. Fortunately, it has been recently reported by Miura and Dyker that such cyclopentadiene derivatives can be easily accessed as shown in eq 3.1.[33]



eq 3.1

Therefore, a series of catalysts (**3.1b-3.1i**) was synthesized and resolved according to Scheme **3.17**, and their effectiveness as chiral catalysts in the ring opening of *cis*-stilbene oxide was examined (Table 3.2).

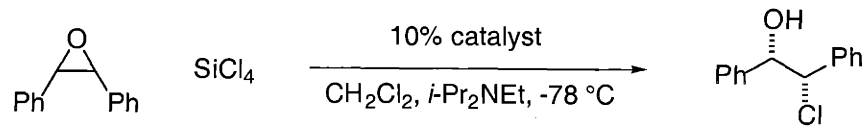
Scheme 3.19 A Family of Planar-Chiral Pyridine *N*-Oxides with Different Cyclopentadienyl Bottom Rings



Ar =	Ph	**3.1b**
	4-Me-C_6H_4	**3.1c**
	4-(*t*-Bu)-C_6H_4	**3.1d**
	4-MeO-C_6H_4	**3.1e**
	4-(*i*-PrO)-C_6H_4	**3.1f**
	3,5-$Me_2C_6H_3$	**3.1g**
	3,5-$Et_2C_6H_3$	**3.1h**
	3,5-(*i*-Pr)$_2$-C_6H_3	**3.1i**

33 Miura, M.; Pivsa-Art, S.; Dyker, G.; Heiermann, J.; Satoh, T.; Nomura, M. *Chem. Commun.* **1998**, 1889-1890.

Table 3.2 Enantioselectivity as a Function of the Catalyst



entry	***catalyst***	ee (%)
1	**3.1b**	60
2[a]	**3.1c**	6
3	**3.1d**	50
4[a]	**3.1e**	4
5[a]	**3.1f**	41
6	**3.1g**	96
7	**3.1h**	97
8	**3.1i**	19

[a] Reaction was carried out at r.t.

Introducing para substituents on the phenyl group of the cyclopentadienyl ring does not improve the enantioselectivity of the ring opening of *cis*-stilbene oxide (Table 2, entries 2-5). However, when both meta positions of the phenyl group are replaced by Me or Et (Table 3.2, entry 6, 7), the enantioselectivity of the resulting chlorohydrin increases from 60% to 96% and 97%, respectively. Further increasing the steric demand of the cyclopentadienyl ring results in a drastic decrease in ee (Table 3.2, entry 8).

The effective chiral environments generated by catalysts **3.1b** and **3.1g** can be easily compared by their X-ray crystal structures. The improved enantioselectivity displayed by **3.1g** is attributable to the presence of the meta substituents in the η^5-C_5Ar_5 group, which helps to block the bottom face of the catalyst more effectively, thus leading to better stereodifferentiation.

Figure 3.2 ORTEP Representation of (+)-3.1g (With thermal ellipsoids drawn at the 35% probability level)

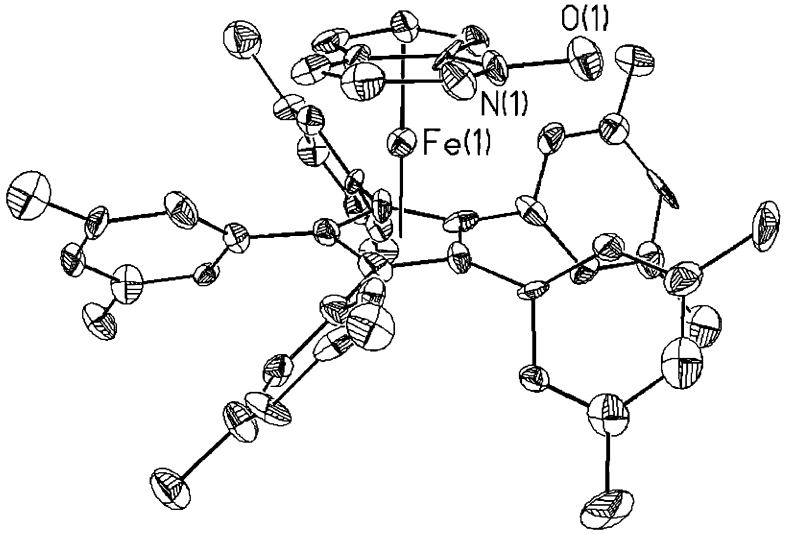
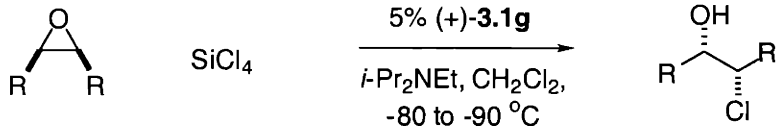


Table 3.3 Catalytic Enantioselective Ring-Opening of Meso Epoxides



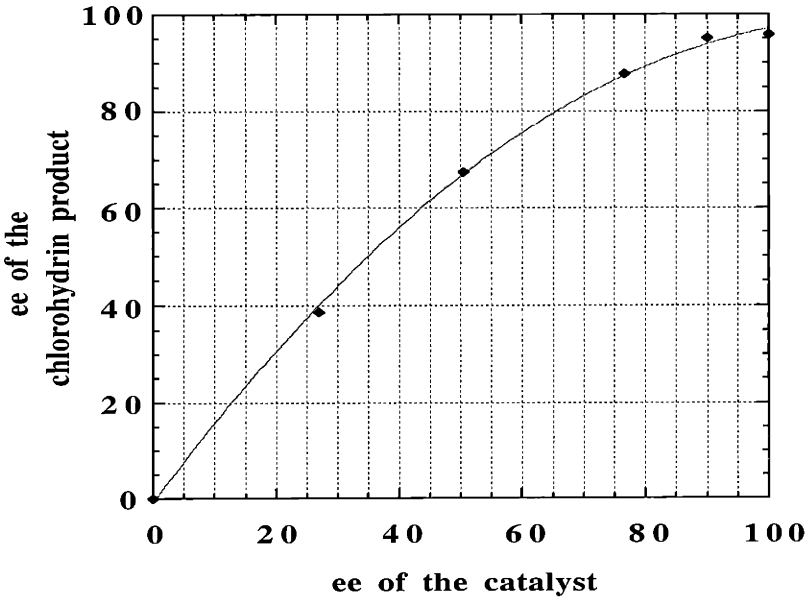
entry	R	Yield	ee (%)
1	Ph	88	94
2	4-FC_6H_4	97	91
3	4-$CF_3C_6H_4$	93	98
4	4-$CH_3C_6H_4$	94	93
5	2-naphthyl	84	94
6	CH_2OBn	91	50

With the improved protocol in hand, we investigated the ring opening of an array of meso epoxides (Table 3.3). The catalyst loading can be reduced to 5% without compromising the enantioselectivity. For *cis*-stilbene oxide and its derivatives, catalyst **3.1g** provided the corresponding chlorohydrin with excellent

enantioselectivity (Table 3.3, entries 1-5). However, only modest enantioselectivity was observed for *cis*-1,4-benzyloxy-2,3-epoxybutane (entry 6).

The high enantiopurity of the products generated by this reaction prompted us to try to understand the mechanism of the reaction. Interestingly, the reaction system displayed a positive non-linear correlation between the enantiomeric excess of the reaction product and the chiral catalyst.[34]

Figure 3.3 (+)-NLEs in the Opening of *cis*-Stilbene Oxide with $SiCl_4$ Using 5% 3.1g



Kinetics data showed that the initial rate of the reaction was 2-3 times faster using enantiomerically pure catalyst than racemic catalyst. Preliminary kinetics data also showed that the initial rate of the reaction is between first and second order with respect to the catalyst, and zeroth order with respect to $SiCl_4$ and *i*-Pr_2NEt. This

34 For reviews of non-linear effects, see: (a) Avalos, M.; Babiano, R.; Cintas, P.; Jiménez, J. L.; Palacios, J. C. *Tetrahedron: Asymmetry*, **1997**, *8*, 2997-3017. (b) Girard, C.; Kagan, H. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 2922-2969. (c) Blackmond, D. *Acc. Chem. Res.* **2000**, *33*, 402-411.

is consistent with a catalyst-bound silicon species as the resting state of the system.

We therefore attempted to observe the interaction between the catalyst and $SiCl_4$ using ^1H and ^{29}Si NMR at -70 °C. A 1:1 mixture of $SiCl_4$ and *i*-Pr_2NEt gave one signal at -19.1 ppm in the ^{29}Si NMR, corresponding to free $SiCl_4$. This suggests that there is no interaction between $SiCl_4$, and *i*-Pr_2NEt and that the role of the base in the reaction is to neutralize the residual HCl contaminant in $SiCl_4$, thus suppressing the background reaction. When 1:10:10 of (+)-**3.1g**, $SiCl_4$, and *i*-Pr_2NEt were mixed at -70 °C, two new peaks were observed in the ^{29}Si NMR: -42.0, -166.6[35] ppm, in the ratio of 3:1. However, when 1:10:10 of racemic catalyst (±)-**3.1g**, $SiCl_4$, and *i*-Pr_2NEt was used, three peaks were observed: -166.0, -166.6, -174.0 ppm, in the ratio of 1:1:2. Due to the lack of literature ^{29}Si NMR data for *N*-oxide complexes, it is very difficult to assign structures to each of the signals observed. It is possible that there are homo and hetero 2:1 catalyst-bound silicon adducts or higher aggregates present when racemic catalyst was used. We speculate that these aggregates are not the reactive species in the catalytic cycle, and have to dissociate into 1:1 catalyst-bound silicon species for the reaction to take place. The hetero adducts are most likely more stable than the homo ones, resulting in a reduction of reaction rate when racemic catalyst is used. Therefore, when enantiomerically enriched catalyst was used, the hetero 2:1 catalyst-bound silicon adducts retain the minor enantiomer of the catalyst. This accounts for the observation of a positive non-linear effect.

After analyzing the above information, a possible mechanism for the desymmetrization of meso epoxides catalyzed by planar-chiral pyridine *N*-oxides is proposed (Scheme 3.20).

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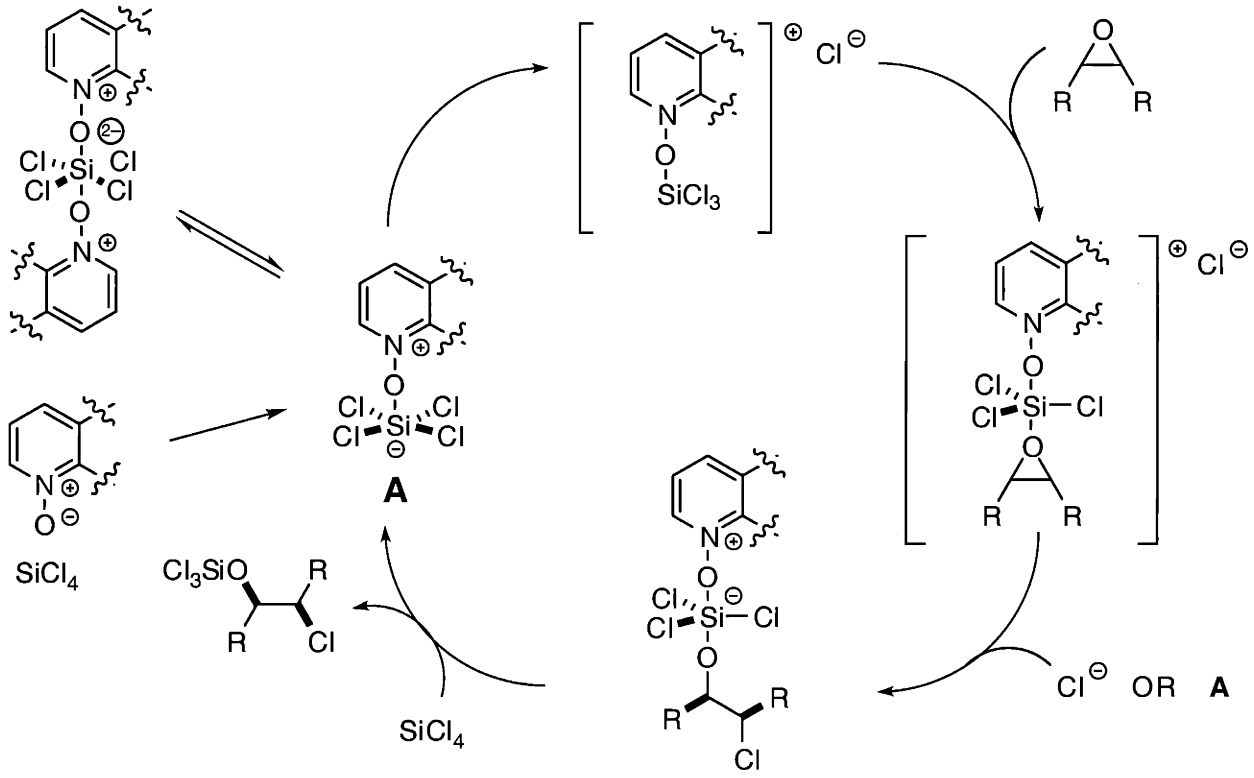
35 The peak at –166.6 ppm is consistent with the presence of a hypervalent silicon species.

Scheme 3.20 A Possible Mechanism for the Desymmetrization of Meso Epoxides Catalyzed by Planar-Chiral Pyridine *N*-Oxide



First, a hypervalent species (**A**) is formed when the pyridine *N*-oxide catalyst coordinates to silicon tetrachloride. Upon coordination of a Lewis base, the silicon atom becomes more electrophilic. Ionization of a chloride ligand gives rise to a strong Lewis acid, which then coordinates to an epoxide molecule. The epoxide can then be opened by a source of chloride, giving the catalyst-bound silyl ether species. The chloride can come from either the free chloride ion or from intermediate **A**. The order with respect to the catalyst should be one if the free chloride ion is the sole chloride source; on the other hand, the catalyst order should be two if **A** is providing the chloride source. However, if both pathways are operating, the catalyst order would be between first and second, which is consistent with what was observed in our kinetic studies. Also, if the reaction mechanism involves two

molecules of the catalyst, matched and mis-matched pairs of the two molecules can result, which can explain the observed positive non-linear effect.[36] To complete the catalytic cycle, another molecule of $SiCl_4$ will displace the trichlorosilyl ether, regenerating the active intermediate **A**.

36 Positive non-linear effect has been observed in Jacobsen's Cr-salen catalyst and Yb-pybox catalyst where the catalyst order is 2: (a) Konsler, R. G; Karl, J.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 10780-10781. (b) Schaus, S. E.; Jacobsen, E. N. *Org. Lett.* **2000**, *2*, 1001-1004.

Conclusions

In summary, we have developed a simple synthetic route to afford a novel family of planar-chiral heterocycles bearing the *N*-oxide moiety. We have demonstrated that this class of compounds can serve as effective catalysts in the ring opening of meso epoxides, affording chlorohydrins in high enantioselectivities using silicon tetrachloride.

The X-ray crystal structure of (+)-**3.1b** suggests that η^5-C_5Ph_5 may not be bulky enough to shield the bottom part of the catalyst, thus giving poor top-from-bottom differentiation. Incorporation of meta substituents on each of the phenyl rings on η^5-C_5Ph_5 should improve the top-from-bottom differentiation of the catalyst. The merit of our catalyst design allows us to fine-tune the steric and electronic properties of the catalysts, leading to enhancement in enantioselectivity. By increasing the bulk of the bottom ring to η^5-C_5Ar_5 (Ar = 3,5-$Me_2C_6H_3$), up to 98% ee for the ring opening of meso epoxides was realized.

Preliminary NMR data suggest that higher aggregates of silicon-catalyst adducts are present in the reaction. Since the rate of reaction is reduced when racemic catalyst is used, we speculate that the hetero 2:1 catalyst-bound silicon adduct partly retains the minor enantiomer of the catalyst. This is consistent with the observed non-linear effect.

The order of the catalyst, which is between first and second, suggests that there is more than one reaction pathway. This can be explained by the chloride source coming from either the free chloride ion or the silicon-bound catalyst intermediate **A**. The observed non-linear effect of catalyst enantiomeric composition on reaction

enantioselectivity can also be explained when the reaction mechanism involves two molecules of the catalyst.

Experimental

I. General

Analytical thin layer chromatography was performed using EM Reagents 0.25 mm silica gel 60 plates, and visualization was accomplished with potassium permanganate or with ethanolic phosphomolybdic acid. Flash chromatography was performed on EM Reagents silica gel 60 (230-400 mesh).

Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer. High resolution mass spectra were recorded on a Finnegan MAT System 8200 spectrometer. Melting points (uncorrected) were measured on a Thomas Hoover Unimelt capillary melting point apparatus.

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian XL-300 or XL-500 NMR spectrometer at ambient temperature. ^{1}H data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (δ scale), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C spectra were determined with complete proton decoupling.

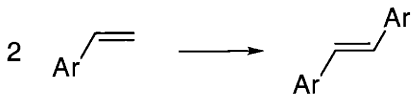
Analytical chiral HPLC was performed on a Daicel CHIRALCEL OD column (4.6 mm x 25 cm). Analytical chiral GC was performed on a Chiraldex G-TA column (20 m x 0.25 mm).

(*i*-Pr)$_2$NEt (Mallinckrodt) was distilled from CaH_2 prior to use. $FeCl_2$ (Strem), *n*-BuLi (Strem), *cis*-stilbene oxide (Aldrich), and $SiCl_4$ (1.0 M; Aldrich) were used without further purification. Solvents were distilled from the indicated drying agents: benzene (sodium/benzophenone); THF (sodium/benzophenone); CH_2Cl_2 (CaH_2); Et_2O (sodium/benzophenone); toluene (molten sodium). Pyrindine was prepared according to the method of Robison.[37]

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware, unless otherwise indicated.

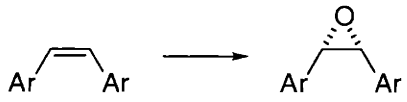
37 Robison, M. M. *J. Am. Chem. Soc.* **1958**, *80*, 6254-6257.

II. Preparation of Epoxides

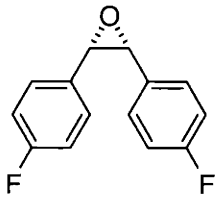


General procedure for the preparation of 1,2-disubstituted olefins. $Cl_2(PCy_3)_2Ru{=}CHPh$ (0.50 g; 0.61 mmol) was added to a solution of the starting olefin (30 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was placed in a 55 °C oil bath overnight. It was then quenched by passing it through a plug of silica, which was washed with Et_2O. The CH_2Cl_2 and Et_2O solutions were combined and concentrated, and the disubstituted olefin (predominantly trans) was purified by column chromatography (hexanes → 10% Et_2O/hexanes). The ^1H NMR spectrum of each reaction product was identical to that reported in the literature.

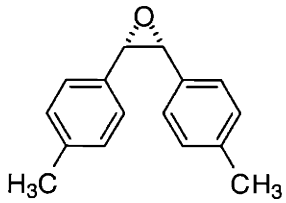
General procedure for the preparation of *cis*-1,2-disubstituted olefins. The trans olefin (100 mg) was dissolved in benzene (20 mL), and the solution was irradiated at 300 nm. After 4 hours, the reaction mixture was concentrated and purified by column chromatography (aluminium oxide; 1:10 benzene/hexanes → 1:1:9 Et_2O/benzene/hexanes). The ^1H NMR spectrum of each reaction product was identical to that reported in the literature.



General procedure for the preparation of epoxides. A solution of the cis olefin (1.6 mmol) in CH_2Cl_2 (4 mL) was placed in an ice bath, and CH_3ReO_3 (10 mg, 0.04 mmol) was added, followed by pyridine (17 μL, 0.21 mmol) and H_2O_2 (30% w/w; 0.27 mL, 2.4 mmol). After 20-24 hours, the reaction mixture was quenched with a catalytic amount of MnO_2 (1-2 mg), and then extracted with CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated. The epoxide was then purified by column chromatography (15% Et_2O/hexanes).

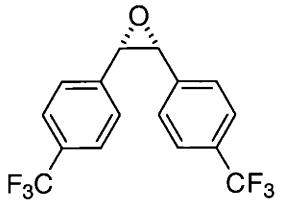


This was prepared as described in the general procedure. ^1H NMR (300 MHz, $CDCl_3$): δ 4.32 (s, 2H), 6.88 (m, 4H), 7.11 (m, 4H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 59.6, 115.3 (d, $^2J_{C-F}$ = 21.9), 129.1 (d, $^3J_{C-F}$ = 8.1), 130.9 (d, $^4J_{C-F}$ = 3.5), 162.7 (d, $^1J_{C-F}$ = 245). IR (neat): 3072, 2981, 1606, 1513, 1223, 1156, 878, 784 cm^{-1}.

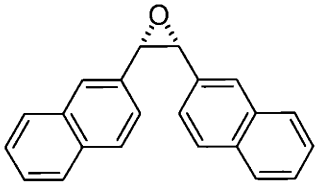


This was prepared as described in the general procedure. ^1H NMR (500 MHz,

$CDCl_3$): δ 2.26 (s, 6H), 4.31 (s, 2H), 7.00 (d, 4H, J = 7.7), 7.07 (d, 4H, J = 8.2). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 21.4, 60.3, 127.2, 129.0, 132.2, 137.8. IR (neat): 3025, 2969, 2920, 1517, 1175, 900, 875, 803 cm^{-1}.



This was prepared as described in the general procedure. ^1H NMR (500 MHz, CD_2Cl_2): δ 4.48 (s, 2H), 7.36 (d, 4H, J = 7.9), 7.49 (d, 4H, J = 8.2). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 59.9, 124.6 (q, $^1J_{C-F}$ = 272), 125.5 (q, $^3J_{C-F}$ = 4.0), 127.8, 130.3 (q, $^2J_{C-F}$ = 32.2), 138.9. IR (neat): 3074, 2977, 1621, 1321, 1107, 1064, 1017 cm^{-1}.

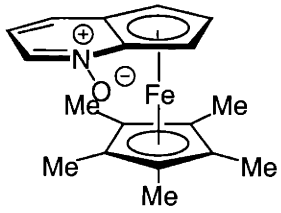


This can be prepared by a literature procedure.[38] ^1H NMR (500 MHz, CD_2Cl_2): δ 4.68 (s, 2H), 7.44 (m, 6H), 7.71 (d, 2H, J = 8.5), 7.77 (d, 2H, J = 7.6), 7.84 (d, 2H, J = 7.9), 7.92 (s, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 60.7, 125.0, 126.4, 126.6, 126.7, 128.0, 128.1, 128.2, 132.7, 133.3. IR (neat): 3053, 2973, 1602, 1509, 1271, 1126, 953, 816 cm^{-1}.

38 Wong, J. P. K.; Fahmi, A. A.; Griffin, G. W.; Bhacca, N. S. *Tetrahedron*,**1981**, *37*, 3345-3355.

III. Preparation of Catalysts

These reactions have not been optimized.



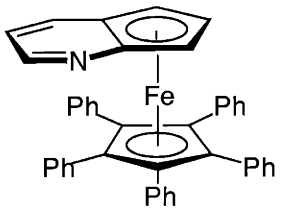
Compound 3.1a. Dimethyldioxirane (0.08 M in acetone; 55 mL, 4.4 mmol) was added dropwise to a –10 °C solution of **3.2a**[39] (1.02 g, 3.3 mmol) in CH_2Cl_2 (11 mL). The reaction mixture was stirred for 3.5 h, and then it was concentrated and purified by column chromatography (acetone → 10% NEt_3/acetone), which furnished 0.85 g (79%) of a purple solid.

^1H NMR (300 MHz, CD_2Cl_2) δ 8.02 (d, 1H, J = 5.5), 7.38 (d, 1H, J = 8.6), 6.77 (dd, 1H, J = 8.6, 5.5), 4.95 (s, 1H), 4.37 (dd, 1H, J = 2.6, 1.3), 3.95 (t, 1H, J = 2.6), 1.67 (s, 15H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 132.0, 128.3, 117.1, 103.9, 85.5, 79.9, 76.5, 65.6, 42.5, 9.9. FTIR (neat) 3060, 2902, 1458, 1334, 1262, 1241, 1034, 764 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{18}H_{21}FeNO$ (M^+) 323.0973, found 323.0966.

The enantiomers of the catalyst were separated by semi-preparative HPLC (Daicel CHIRALCEL OD, 1 cm x 25 cm, chloroform/hexanes/diethylamine/ethanol 25:75:0.4:1.0, 2.5 mL/min). Enantiomer (–)-**3.1a** ($[\alpha]^{20}_D$ = –407° (c = 0.014, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 16.5 minutes to

39 Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 7230-7231.

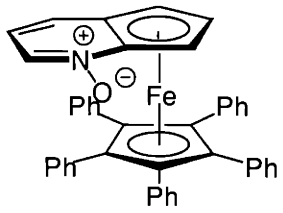
19.0 minutes, and enantiomer (+)-**3.1a** ($[\alpha]^{20}_D$ = +392° (c = 0.012, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 20.0 minutes to 25.8 minutes.



Compound 3.2b. In a glove box, *n*-BuLi (1.71 M in hexanes; 2.73 mL, 4.67 mmol) was added by syringe over ~2 minutes to a slurry of pentaphenylcyclopentadiene (2.09 g, 4.67 mmol) in THF (20 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (0.59 g, 4.7 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.71 M in hexanes; 2.73 mL, 4.67 mmol) and pyrindine (0.43 g, 4.7 mmol) in THF (20 mL) at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing 1.2 g (52%) of a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (dd, 1H, J = 4.0, 1.5), 7.84 (dd, 1H, J = 9.0, 1.5), 7.15 (t, 5H, J = 7.5), 7.08 (t, 10H, J = 7.5), 6.96 (dd, 1H, J = 9.0, 4.0), 6.91 (d, 10H, J = 7.5), 5.20 (dd, 1H, J = 3.0, 1.0), 4.84 (dd, 1H, J = 3.0, 1.0), 4.36 (t, 1H, J = 3.0). ^{13}C NMR (126 MHz,

$CDCl_3$) δ 153.8, 138.3, 135.0, 132.3, 127.3, 126.5, 120.5, 110.3, 86.1, 83.6, 79.6, 70.0, 66.3. FTIR (neat) 3049, 1600, 1502, 1443, 1315, 1071, 1028, 742, 702 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{43}H_{31}FeN$ (M^+) 617.1806, found 617.1806.

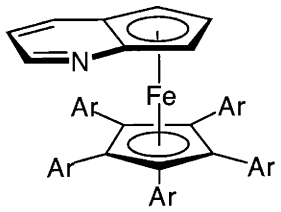


Compound 3.1b. Dimethyldioxirane (0.08 M in acetone; 30 mL, 2.4 mmol) was added dropwise to a –10 °C solution of **3.2b** (0.58 g, 0.94 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 4 h, and then it was concentrated and purified by column chromatography (50% EtOAc/hexanes → NEt_3), which furnished 0.26 g (45%) of a purple solid.

^1H NMR (500 MHz, CD_2Cl_2) δ 7.94 (d, 1H, J = 5.5), 7.42 (d, 1H, J = 8.5), 7.18 (m, 5H), 7.09 (m, 10H), 6.95 (d, 10H, J = 7.9), 6.86 (dd, 1H, J = 8.5, 5.5), 5.32 (m, 1H), 4.95 (m, 1H), 4.38 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 134.8, 134.5, 132.8, 127.8, 127.2, 126.7, 120.5, 105.4, 87.8, 87.4, 79.1, 68.6, 64.3. FTIR (neat) 3049, 2921, 2851, 1738, 1503, 1462, 1271, 1244 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{43}H_{31}FeNO$ (M^+) 633.1755, found 633.1751.

The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine 25:75:0.4, 2.5 mL/min). Enantiomer (–)-**3.1b** ($[\alpha]^{20}_D$ = –660° (c = 0.030, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 19.0 minutes to 22.5 minutes, and enantiomer (+)-**3.1b** ($[\alpha]^{20}_D$ = +682° (c = 0.034, $CHCl_3$); enantiomerically pure by

analytical chiral HPLC) was collected from 26.0 minutes to 31.5 minutes.

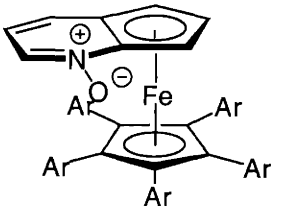


Ar = 4-Me-C_6H_3

Compound 3.2c. In a glove box, *n*-BuLi (1.61 M in hexanes; 1.30 mL, 2.09 mmol) was added by syringe over ~2 minutes to a slurry of penta(4-methylphenyl)cyclopentadiene (1.10 g, 2.13 mmol) in THF (20 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (0.265 g, 2.09 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 1.30 mL, 2.09 mmol) and pyrindine (0.245 g, 2.09 mmol) in 20 mL of THF at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing 1.30 g (89%) of a purple solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.46 (dd, 1H, J = 3.8, 1.4), 7.85 (dd, 1H, J = 8.8, 0.8), 6.94 (dd, 1H, J = 8.8, 3.8), 6.89 (d, 10H, J = 8.5), 6.76 (d, 10H, J = 8.2), 5.13 (m, 1H), 4.82 (m, 1H), 4.31 (m, 1H), 2.29 (s, 15H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 153.9, 138.6, 136.4, 132.7, 132.4, 128.3, 120.7, 110.7, 86.2, 84.0, 79.6, 70.0, 66.4, 21.5. FTIR (neat) 3013, 2919, 1590, 1519, 1314, 1185, 803 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{48}H_{41}FeN$ (M^+) 687,2583,

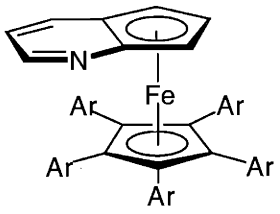
found 687.2560.



Compound 3.1c. Dimethyldioxirane (0.08 M in acetone; 25 mL, 2.0 mmol) was added dropwise to a –10 °C solution of **3.2c** (0.80 g, 1.16 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 1.5 h, and then it was concentrated and purified by column choromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), which furnished a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.38 (d, 1H, J = 6.7), 6.88 (d, 10H, J = 7.6), 6.82 (d, 10H, J = 7.9), 7.79 (m, 1H), 5.50 (s, 1H), 4.82 (s, 1H), 4.31 (s, 1H), 2.28 (s, 15H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 136.5, 134.2, 132.5, 131.8, 128.3, 126.8, 120.1, 105.3, 87.5, 87.0, 79.1, 68.4, 64.1, 21.6. FTIR (neat) 3034, 2922, 1520, 1462, 1267, 730 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{48}H_{41}FeNO$ (M^+) 703.2538, found 703.2543.

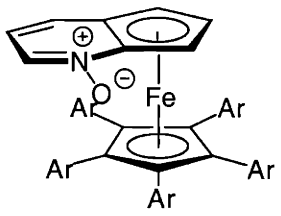
The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine 50:50:0.5, 2.5 mL/min). Enantiomer (–)-**3.1c** ($[\alpha]^{20}_D$ = –450° (c = 0.020, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 14.3 minutes to 18.0 minutes, and enantiomer (+)-**3.1c** ($[\alpha]^{20}_D$ = +441° (c = 0.022, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 19.5 minutes to 26.0 minutes.



Ar = 4-(*t*-Bu)-C_6H_3

Compound 3.2d. In a glove box, *n*-BuLi (1.61 M in hexanes; 0.85 mL, 1.37 mmol) was added by syringe over ~2 minutes to a slurry of penta(4-*t*-butylphenyl)cyclopentadiene (1.00 g, 1.37 mmol) in THF (20 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (0.174 g, 1.37 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 0.85 mL, 1.37 mmol) and pyrindine (0.161 g, 1.37 mmol) in 20 mL of THF at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing of a purple solid.

^1H NMR (500 MHz, CD_2Cl_2) δ 8.51 (dd, 1H, J = 5.3, 1.5), 7.94 (dd, 1H, J = 8.9, 0.9), 7.12 (d, 10H, J = 8.6), 6.98 (dd, 1H, J = 8.9, 4.0), 6.87 (d, 10H, J = 8.2), 5.24 (d, 1H, J = 2.4), 4.92 (dd, 1H, J = 2.4, 0.9), 4.41 (t, 1H, J = 2.4), 1,36 (s, 45H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 154.0, 149.6, 138.8, 133.8, 132.2, 124.4, 120.6, 110.8, 86.4, 84.1, 79.6, 70.0, 66.3, 35.00, 31.8. FTIR (neat) 2963, 1515, 1362, 1269, 837 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{63}H_{71}FeN$ (M^+) 897.4936, found 897.4958.

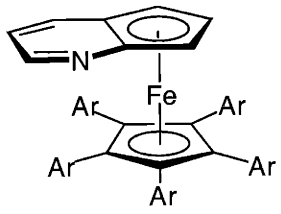


Ar = 4-(*t*-Bu)-C_6H_3

Compound 3.1d. Dimethyldioxirane (0.08 M in acetone; 9.4 mL, 0.75 mmol) was added dropwise to a –10 °C solution of **3.2d** (0.54 g, 0.60 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 1.5 h, and then it was concentrated and purified by column choromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), which furnished a purple solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.93 (d, 1H, J = 5.2), 7.46 (d, 1H, J = 8.5), 7.13 (m, 1H), 7.09 (d, 10H, J = 8.2), 6.85 (d, 10H, J = 8.2), 5.51 (s, 1H), 4.94 (d, 1H, J = 1.5), 4.38 (t, 1H, J = 2.4), 1.30 (s, 45H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 149.9, 134.3, 132.3, 132.0, 127.3, 124.5, 120.1, 105.5, 87.5, 87.2, 79.1, 68.3, 64.0, 34.9, 31.6. FTIR (neat) 3050, 2963, 2904, 1517, 1463, 1270 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{63}H_{71}FeNO$ (M^+) 913.4885, found 913.4866.

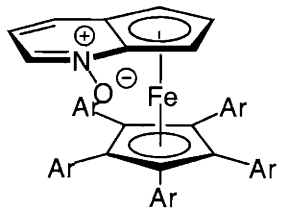
The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine 25:75:0.4, 2.5 mL/min). Enantiomer (–)-**3.1d** ($[\alpha]^{20}_D$ = –195° (c = 0.020, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 26.0 minutes to 32.5 minutes, and enantiomer (+)-**3.1d** ($[\alpha]^{20}_D$ = +205° (c = 0.021, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 33.5 minutes to 43.0 minutes.



Ar = 4-(MeO)-C_6H_3

Compound 3.2e. In a glove box, *n*-BuLi (1.61 M in hexanes; 0.20 mL, 0.32 mmol) was added by syringe over ~2 minutes to a slurry of penta(4-methoxyphenyl)cyclopentadiene (179 mg, 0.300 mmol) in THF (20 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (40 mg, 0.32 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 0.20 mL, 0.32 mmol) and pyrindine (35 mg, 0.30 mmol) in 20 mL of THF at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing 218 mg (95%) of a purple solid.

^{1}H NMR (300 MHz, C_6D_6) δ 8.44 (dd, 1H, J = 3.9, 1.4), 7.58 (d, 1H, J = 7.1), 7.16 (d, 10H, J = 8.5), 6.58 (d, 10H, J = 8.8), 6.47 (dd, 1H, J = 8.8, 3.9), 5.43 (d, 1H, J = 2.5), 4.68 (dd, 1H, J = 2.8, 0.8), 4.34 (t, 1H, J = 2.8), 3.22 (s, 15H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 158.6, 154.0, 138.7, 133.6, 127.7, 120.6, 113.1, 110.6, 85.6, 84.0, 79.5, 69.9, 66.2, 55.5. FTIR (neat) 3012, 2955, 2834, 1609, 1517, 1289, 1245, 1177, 1032, 809 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{48}H_{41}FeNO_5$ (M^+) 767.2329, found 767.2361.

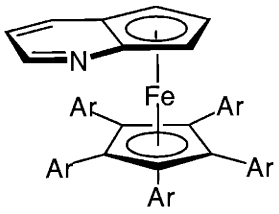


Ar = 4-(MeO)-C_6H_3

Compound 3.1e. Dimethyldioxirane (0.08 M in acetone; 3.5 mL, 0.28 mmol) was added dropwise to a –10 °C solution of **3.2e** (0.18 g, 0.23 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 1.5 h, and then it was concentrated and purified by column choromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), which furnished a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.0 (s, 1H), 7.38 (d, 1H, J = 8.2), 6.88 (d, 10H, J = 8.2), 6.81 (d, 10H, J = 7.3), 6.64 (m, 1H), 5.47 (s, 1H), 4.78 (s, 1H), 4.27 (s, 1H), 3.77 (s, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 134.3, 133.5, 127.6, 126.5, 119.5, 112.9, 104.9, 87.0, 86.0, 79.2, 68.0, 64.0, 55.2. FTIR (neat) 2918, 2849, 1607, 1516, 1245 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{48}H_{41}FeNO_6$ (M^+) 783.2283, found 783.2293.

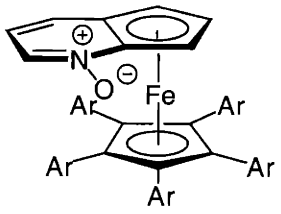
The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine 75:25:0.5, 2.5 mL/min). Enantiomer (–)-**3.1e** ($[\alpha]^{20}_D$ = –390° (c = 0.020, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 11.0 minutes to 12.5 minutes, and enantiomer (+)-**3.1e** ($[\alpha]^{20}_D$ = +409° (c = 0.022, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 14.0 minutes to 18.0 minutes.



Ar = 4-(*i*-PrO)-C_6H_3

Compound 3.2f. In a glove box, *n*-BuLi (1.61 M in hexanes; 0.20 mL, 0.32 mmol) was added by syringe over ~2 minutes to a slurry of penta(4-isopropoxyphenyl)cyclopentadiene (0.24 g, 0.33 mmol) in THF (20 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (40 mg, 0.32 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 0.19 mL, 0.31 mmol) and pyrindine (35 mg, 0.30 mmol) in 20 mL of THF at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing 0.20 g (75%) of a purple solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.44 (dd, 1H, J = 3.9, 1.7), 7.85 (dd, 1H, J = 8.8, 0.8), 6.93 (dd, 1H, J = 8.8, 3.8), 6.81 (d, 10H, J = 8.8), 6.60 (d, 10H, J = 8.8), 5.09 (d, 1H, J = 2.5), 4.77 (dd, 1H, J = 2.8, 1.1), 4.50 (sept, 5H, J = 6.0), 4.28 (t, 1H, J = 2.8), 1.32 (d, 15H, J = 5.5), 1.31 (d, 15H, J = 5.8). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 156.9, 153.8, 138.8, 133.6, 127.6, 120.5, 114.8, 110.6, 85.6, 84.0, 79.6, 70.2, 69.9, 66.2, 22.5, 22.4. FTIR (neat) 3060, 2975, 1608, 1514, 1242, 1120, 955, 835 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{58}H_{61}FeNO_5$ (M^+) 907.3894, found 907.3865.

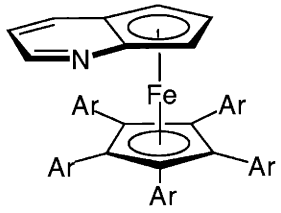


Ar = 4-(*i*-PrO)-C_6H_3

Compound 3.1f. Dimethyldioxirane (0.08 M in acetone; 3.0 mL, 0.24 mmol) was added dropwise to a –10 °C solution of **3.2f** (60 mg, 0.066 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 1.5 h, and then it was concentrated and purified by column choromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), which furnished a purple solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.36 (s, 1H), 6.86 (d, 10H, J = 7.7), 6.80 (m, 1H), 6.60 (d, 10H, J = 7.7), 5.46 (s, 1H), 4.77 (s, 1H), 4.49 (m, 5H), 4.27 (s, 1H), 1.34 (d, 15H, J = 5.8), 1.32 (d, 15 H, J = 5.8). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 134.0, 133.4, 127.5, 126.2, 119.1, 114.5, 104.9, 86.8, 85.8, 79.1, 69.6, 67.8, 63.8, 22.3, 22.1. FTIR (neat) 3050, 2922, 1608, 1514, 1244, 1183, 1120, 955 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{58}H_{61}FeNO_6$ (M^+) 923.3848, found 923.3863.

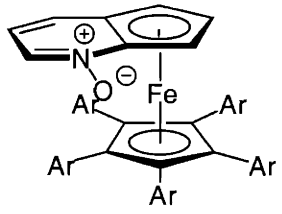
The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine 50:50:0.5, 2.5 mL/min). Enantiomer (–)-**3.1f** ($[\alpha]^{20}_D$ = –409° (c = 0.022, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 13.5 minutes to 17.0 minutes, and enantiomer (+)-**3.1f** ($[\alpha]^{20}_D$ = +392° (c = 0.024, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 19.0 minutes to 25.5 minutes.



Ar = 3,5-$Me_2C_6H_3$

Compound 3.2g. In a glove box, *n*-BuLi (1.61 M in hexanes; 1.25 mL, 2.01 mmol) was added by syringe over ~2 minutes to a slurry of penta(3,5-dimethylphenyl)cyclopentadiene (1.18 g, 2.01 mmol) in THF (20 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (0.25 g, 2.0 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 1.25 mL, 2.01 mmol) and pyrindine (0.235 g, 2.01 mmol) in 20 mL of THF at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing 1.02 g (67%) of a purple solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.47 (dd, 1H, J = 3.7, 1.2), 7.78 (d, 1H, J = 8.0), 6.92 (dd, 1H, J = 8.6, 3.7), 6.79 (s, 5H), 6.52 (s, 10H), 5.10 (d, 1H, J = 1.5), 4.80 (d, 1H, J = 1.8), 4.31 (t, 1H, J = 2.7), 2.11 (s, 30H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 153.3, 138.3, 136.3, 135.4, 130.6, 128.1, 120.3, 110.9, 86.3, 84.0, 79.9, 70.2, 66.6, 21.4. FTIR (neat) 3008, 2917, 1600, 1482, 1315, 848 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{53}H_{51}FeN$ (M^+) 757.3371, found 757.3396.

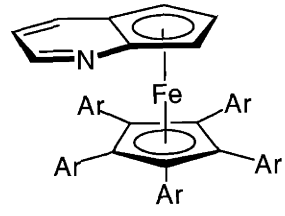


Ar = 3,5-$Me_2C_6H_3$

Compound 3.1g. Dimethyldioxirane (0.08 M in acetone; 20 mL, 1.6 mmol) was added dropwise to a –10 °C solution of **3.2g** (0.82 g, 1.1 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 1.5 h, and then it was concentrated and purified by column choromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), which furnished 0.77 g (92%) of a purple solid.

^{1}H NMR (500 MHz, C_6D_6) δ 7.83 (d, 1H, J = 5.8), 7.05 (d, 1H, J = 8.5), 6.94 (s, 10H), 6.71 (s, 5H), 6.25 (dd, 1H, J = 8.5, 5.8), 5.90 (s, 1H), 4.76 (dd, 1H, J = 2.8, 1.2), 4.35 (dd, 1H, J = 2.8, 1.2), 2.03 (s, 30H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 136.5, 134.7, 133.8, 130.8, 128.4, 126.9, 119.7, 105.5, 87.5, 87.2, 79.6, 68.8, 64.6, 21.4. FTIR (neat) 3037, 2918, 1600, 1462, 1269 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{53}H_{51}FeNO$ (M^+) 773.3320, found 773.3302.

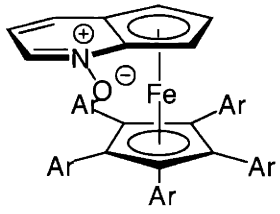
The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine 50:50:0.5, 2.5 mL/min). Enantiomer (–)-**3.1g** ($[\alpha]^{20}_D$ = –368° (c = 0.025, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 9.0 minutes to 11.0 minutes, and enantiomer (+)-**3.1g** ($[\alpha]^{20}_D$ = +376° (c = 0.025, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 12.0 minutes to 14.5 minutes.



Ar = 3,5-$Et_2C_6H_3$

Compound 3.2h. In a glove box, *n*-BuLi (1.61 M in hexanes; 1.81 mL, 2.91 mmol) was added by syringe over ~2 minutes to a slurry of penta(3,5-diethylphenyl)cyclopentadiene (2.12 g, 2.92 mmol) in THF (20 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (0.370 g, 2.92 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 1.81 mL, 2.91 mmol) and pyrindine (0.342 g, 2.92 mmol) in 20 mL of THF at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing 1.80 g (69%) of a purple solid.

^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (dd, 1H, J = 3.7, 1.5), 7.77 (dd, 1H, J = 8.5, 0.9), 6.87 (dd, 1H, J = 8.9, 4.0), 6.72 (s, 5H), 6.57 (d, 10H, J = 1.5), 5.11 (dd, 1H, J = 1.5, 0.9), 4.74 (dd, 1H, J = 2.8, 1.2), 4.28 (t, 1H, J = 2.8), 2.40 (m, 20H), 0.93 (t, 30H, J = 7.3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 142.5, 138.2, 135.1, 129.3, 125.4, 119.7, 110.6, 86.1, 83.2, 79.8, 70.0, 66.3, 28.8, 15.7. FTIR (neat) 2963, 2931, 1598, 1462, 872 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{63}H_{71}FeN$ (M^+) 897.4930, found 897.4905.

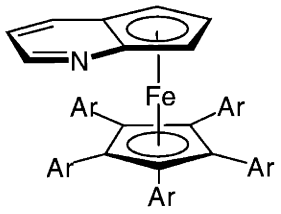


Ar = 3,5-$Et_2C_6H_3$

Compound 3.1h. Dimethyldioxirane (0.08 M in acetone; 2.0 mL, 0.16 mmol) was added dropwise to a –10 °C solution of **3.2h** (90 mg, 0.10 mmol) in CH_2Cl_2 (2.5 mL). The reaction mixture was stirred for 1.5 h, and then it was concentrated and purified by column choromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), which furnished 55 mg (60%) of a purple solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.93 (d, 1H, J = 5.8), 7.39 (d, 1H, J = 8.9), 6.81 (s, 5H), 6.78 (m, 1H), 6.64 (s, 10H), 5.47 (d, 1H, J = 1.2), 4.88 (dd, 1H, J = 2.8, 1.2), 4.33 (d, 1H, J = 2.8), 2.44 (q, 20H, J = 7.3), 0.96 (t, 30H, J = 7.6). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 143.3, 134.8, 133.6, 129.8, 126.6, 126.0, 119.7, 105.5, 87.5, 87.3, 79.5, 68.7, 64.5, 29.1, 15.9. FTIR (neat) 3037, 2918, 1600, 1462, 1269 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{63}H_{71}FeNO$ [(M+H)$^+$] 914.4958, found 914.4989.

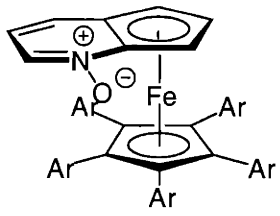
The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine 50:50:0.5, 2.5 mL/min). Enantiomer (–)-**3.1h** ($[\alpha]^{20}_D$ = –427° (c = 0.030, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 7.0 minutes to 8.5 minutes, and enantiomer (+)-**3.1h** ($[\alpha]^{20}_D$ = +444° (c = 0.036, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 9.7 minutes to 12.5 minutes.



Ar = 3,5-(*i*-Pr)$_2$-C$_6$H$_3$

Compound 3.2i. In a glove box, *n*-BuLi (1.61 M in hexanes; 0.88 mL, 1.4 mmol) was added by syringe over ~2 minutes to a slurry of penta(3,5-diisopropylphenyl)cyclopentadiene (1.23 g, 1.42 mmol) in THF (20 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (0.18 g, 1.4 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 0.88 mL, 1.4 mmol) and pyrindine (0.166 g, 1.42 mmol) in 20 mL of THF at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, 1H, J = 4.0, 1.5), 7.86 (dd, 1H, J = 8.5, 0.9), 6.89 (dd, 1H, J = 8.5, 4.0), 6.74 (t, 5H, J = 1.5), 6.64 (d, 10H, J = 1.5), 5.17 (d, 1H, J = 2.8), 4.80 (dd, 1H, J = 2.8, 1.2), 4.28 (t, 1H, J = 2.8), 2.64 (sept, 10H, J = 6.7), 1.01 (d, 30H, J = 7.0), 0.95 (d, 30H, J = 7.0). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 153.4, 147.7, 138.5, 135.5, 128.0, 123.2, 120.4, 111.1, 87.2, 83.7, 79.5, 70.0, 66.0, 34.4, 24.5, 24.1. FTIR (neat) 3049, 2956, 2867, 1597, 1463, 876 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{73}H_{91}FeN$ (M^+) 1037.6469, found 1037.6474.



Ar = 3,5-(*i*-Pr)$_2$-C$_6$H$_3$

Compound 3.1i. Dimethyldioxirane (0.08 M in acetone; 2.0 mL, 0.16 mmol) was added dropwise to a –10 °C solution of **3.2i** (0.103 g, 0.100 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 1.5 h, and then it was concentrated and purified by column choromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), which furnished 67 mg (64%) of a purple solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, 1H, J = 5.5), 7.47 (d, 1H, J = 8.8), 6.78 (m, 1H), 6.76 (s, 5H), 6.66 (d, 10H, J = 1.4), 5.57 (m, 1H), 4.86 (m, 1H), 4.30 (t, 1H, J = 2.8), 2.65 (sept, 10H, J = 6.9), 1.02 (d, 30H, J = 6.9), 0.94 (d, 30H, J = 6.9). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.9, 134.8, 133.7, 128.2, 126.7, 123.4, 119.8, 105.5, 88.0, 87.2, 79.0, 68.2, 68.1, 34.3, 24.5, 23.9. FTIR (neat) 2957, 2926, 1597, 1464, 1274 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{73}H_{91}FeNO$ [(M+H)$^+$] 1054.6523, found 1054.6497.

The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine 20:80:0.2, 2.5 mL/min). Enantiomer (–)-**3.1i** ($[\alpha]^{20}_D$ = –383° (c = 0.030, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 16.5 minutes to 23.5 minutes, and enantiomer (+)-**3.1i** ($[\alpha]^{20}_D$ = +367° (c = 0.030, $CHCl_3$); enantiomerically pure by analytical chiral HPLC) was collected from 26.8 minutes to 35.0 minutes.

IV. Effect of the Bottom Ring of the Catalyst on Enantioselectivity (Scheme 3.18)

General procedure. *cis*-Stilbene oxide (25.0 mg, 0.127 mmol), catalyst (–)-**3.1a** (4.0 mg, 0.013 mmol) in CH_2Cl_2 (1.0 mL), $(i\text{-Pr})_2NEt$ (24 μL, 0.14 mmol), and $SiCl_4$ (16 μL, 0.14 mmol) were added in turn to a vial. After 2.5 hour, the reaction was quenched by the addition of saturated KF/1 M KH_2PO_4 (1:1). The resulting mixture was extracted with EtOAc, and the organic layer was dried over Na_2SO_4, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 11% ee in favor of (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol.

The general procedure was followed using (–)-**3.1b**, which afforded (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol with 25% ee (Reaction time: 15 minutes).

V. Enantioselectivity as a Function of Solvent and Temperature (Table 3.1)

General procedure (Table 3.1, entry 1). *cis*-Stilbene oxide (25.0 mg, 0.127 mmol), catalyst (–)-**3.1b** (4.0 mg, 0.013 mmol) in CH_2Cl_2 (1.0 mL), (*i*-Pr)$_2$NEt (24 μL, 0.14 mmol), and $SiCl_4$ (16 μL, 0.14 mmol) were added in turn to a vial. After 15 minutes, the reaction was quenched by the addition of saturated KF/1 M KH_2PO_4 (1:1). The resulting mixture was extracted with EtOAc, and the organic layer was dried over Na_2SO_4, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 25% ee in favor of (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol.

Table 3.1, entry 2. The general procedure was followed and the temperature of the reaction mixture was lowered to –78 °C before the addition of $SiCl_4$. Reaction time: 3 h. The (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol was obtained with 60% ee.

Table 3.1, entry 3. The general procedure was followed using toluene as solvent, and the temperature of the reaction mixture was lowered to –78 °C before the addition of $SiCl_4$. Reaction time: 4 h. The (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol with 45% ee.

Table 3.1, entry 4. The general procedure was followed using toluene as solvent, and the temperature of the reaction mixture was lowered to –90 °C before the addition of $SiCl_4$. Reaction time: 2.5 h. The (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol with 48% ee.

Table 3.1, entry 5. The general procedure was followed using $CHCl_3$ as solvent, and the temperature of the reaction mixture was lowered to –40 °C before the

addition of $SiCl_4$. Reaction time: 3 h. The (*R,R*)-2-chloro-1,2-diphenylethan-1-ol with 43% ee.

Table 3.1, entry 6. The general procedure was followed using Et_2O (1 mL) and CH_2Cl_2 (0.5 mL) as solvent, and the temperature of the reaction mixture was lowered to –78 °C before the addition of $SiCl_4$. Reaction time: 3 h. The (*R,R*)-2-chloro-1,2-diphenylethan-1-ol with 40% ee.

VI. Enantioselectivity as a Function of Catalyst (Table 3.2)

General procedure (Table 3.2, entry 1). *cis*-Stilbene oxide (25.0 mg, 0.127 mmol), catalyst (–)-**3.1b** (4.0 mg, 0.013 mmol) in CH_2Cl_2 (1.0 mL), and $(i\text{-Pr})_2NEt$ (24 μL, 0.14 mmol) were added to a vial in the glovebox. The reaction vial was then cooled to -78 °C followed by addition of $SiCl_4$ (16 μL, 0.14 mmol). After 4 h at –78 °C, the reaction was quenched by the addition of saturated KF/1 M KH_2PO_4 (1:1). The resulting mixture was extracted with EtOAc, and the organic layer was dried over Na_2SO_4, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 60% ee in favor of (*R,R*)-2-chloro-1,2-diphenylethan-1-ol.

Table 3.2, entry 2. The general procedure was followed with catalyst **3.1c**. The reaction was carried out at room temperature, affording (*R,R*)-2-chloro-1,2-diphenylethan-1-ol in 6% ee.

Table 3.2, entry 3. The general procedure was followed with catalyst **3.1d**, affording (*R,R*)-2-chloro-1,2-diphenylethan-1-ol in 50% ee.

Table 3.2, entry 4. The general procedure was followed with catalyst **3.1e**. The reaction was carried out at room temperature, affording (*R,R*)-2-chloro-1,2-diphenylethan-1-ol in 4% ee.

Table 3.2, entry 5. The general procedure was followed with catalyst **3.1f**. The reaction was carried out at room temperature, affording (*R,R*)-2-chloro-1,2-diphenylethan-1-ol in 41% ee.

Table 3.2, entry 6. The general procedure was followed with catalyst **3.1g**,

affording (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol in 96% ee.

Table 3.2, entry 7. The general procedure was followed with catalyst **3.1h**, affording (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol in 97% ee.

Table 3.2, entry 8. The general procedure was followed with catalyst **3.1i**, affording (*R*,*R*)-2-chloro-1,2-diphenylethan-1-ol in 19% ee.

VII. Catalytic Enantioselective Desymmetrization of Meso Epoxides (Table 3.3)

For Methods Used to Assay Enantiomeric Excess, see Section IX.

Assignment of Absolute Configuration. The absolute configuration of the chlorohydrin formed upon ring opening of *cis*-stilbene oxide was established through comparison of the sign of its optical rotation with a rotation reported in the literature: the chlorohydrin produced in the presence of (+)-**3.1g** has a positive rotation; therefore, its absolute stereochemistry is *S,S*.[40]

The absolute configuration of the other chlorohydrins was assigned by analogy.

General procedure (Table 3.3, entry 1). A solution of catalyst (+)-**3.1g** (11.6 mg, 0.0150 mmol) in CH_2Cl_2 (1.0 mL), *cis*-stilbene oxide (58.9 mg, 0.30 mmol) in CH_2Cl_2 (1.0 mL), $(i\text{-Pr})_2NEt$ (60 μL, 0.34 mmol), and CH_2Cl_2 (4.0 mL) were added in turn to a Schlenk tube. The Schlenk tube was closed and then cooled to –80 °C. $SiCl_4$ (1.0 M solution in CH_2Cl_2; 0.36 mL, 0.36 mmol) was added by syringe to the reaction mixture over 5-10 minutes. After 24 hours at ~–85 °C, the reaction was quenched by the addition of a solution of saturated KF/1 M KH_2PO_4 (1:1). The resulting mixture was extracted with EtOAc, and the organic layer was dried (Na_2SO_4), filtered, and concentrated. Purification by silica gel chromatography (10% Et_2O in hexanes) afforded 60.8 mg (87%) of (*S,S*)-2-chloro-1,2-diphenylethan-1-ol. GC analysis showed 94% ee. $[\alpha]^{20}_D$ = +21.6°, c = 0.97, EtOH.

The general procedure was repeated with catalyst (–)-**3.1g**, affording 61.3 mg (88%) of (*R,R*)-2-chloro-1,2-diphenylethan-1-ol with 93% ee. $[\alpha]^{20}_D$ = –20.5°, c = 0.57, EtOH.

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40 Denmark, S. E.; Barsanti, P. A.; Wong, K.-T.; Stavenger, R. A. *J. Org. Chem.* **1998**, *63*, 2428-2429.

Table 3.3, entry 2. The general procedure was followed with catalyst (+)-**3.1g** (11.6 mg, 0.0150 mmol) and the epoxide (70.0 mg, 0.300 mmol) to give 76.3 mg (95%) of the (*S,S*) chlorohydrin with 91% ee. $[\alpha]^{20}_D = -1.6°$, c = 1.01, $CHCl_3$.

When catalyst (–)-**3.1g** was used, 78.8 mg (98%) of the (*R,R*) chlorohydrin was obtained with 90% ee. $[\alpha]^{20}_D = +1.5°$, c = 1.15, $CHCl_3$.

^1H NMR (500 MHz, $CDCl_3$): δ 3.08 (s, 1H), 4.89 (d, 1H, J = 8.5), 4.92 (d, 1H, J = 8.5), 6.90 (m, 4H), 7.05 (m, 2H), 7.11 (m, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 70.0, 78.6, 115.5 (d, $^2J_{C-F}$ = 21.9), 115.8 (d, $^2J_{C-F}$ = 21.9), 129.3 (d, $^3J_{C-F}$ = 8.1), 130.4 (d, $^3J_{C-F}$ = 8.6), 134.3 (d, $^4J_{C-F}$ = 2.9), 135.3 (d, $^4J_{C-F}$ = 3.5), 163.0 (d, $^1J_{C-F}$ = 246), 163.1 (d, $^1J_{C-F}$ = 246). IR (neat): 3428, 3047, 2894, 1894, 1605, 1514 cm^{-1}.

Table 3.3, entry 3. The general procedure was followed with catalyst (+)-**3.1g** (11.6 mg, 0.0150 mmol) and the epoxide (100 mg, 0.300 mmol) to give 99.0 mg (90%) of the (*S,S*) chlorohydrin with 98% ee. $[\alpha]^{20}_D = -14.2°$, c = 1.04, $CHCl_3$.

When catalyst (–)-**3.1g** was used, 105 mg (95%) of the (*R,R*) chlorohydrin was obtained with 97% ee. $[\alpha]^{20}_D = +14.0°$, c = 1.23, $CHCl_3$.

^1H NMR (300 MHz, $CDCl_3$): δ 3.09 (s, 1H), 5.02 (s, 2H), 7.23 (d, 2H, J = 8.2), 7.31 (d, 2H, J = 8.2), 7.51 (dd, 4H, J = 8.2, 10.2). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 69.2, 78.3, 125.7 (q, $^3J_{C-F}$ = 3.5), 126.0, (q, $^3J_{C-F}$ = 3.5), 124.5 (q, $^1J_{C-F}$ = 272), 124.6 (q, $^1J_{C-F}$ = 272), 128.0, 129.1, 130.8 (q, $^2J_{C-F}$ = 32.2), 131.2, (q, $^2J_{C-F}$ = 32.2), 142.0, 143.3. IR (neat): 3422, 2916, 1925, 1621, 1419, 1327, 1127 cm^{-1}.

Table 3.3, entry 4. The general procedure was followed with catalyst (+)-**3.1g** (11.6 mg, 0.0150 mmol) and the epoxide (67.3 mg, 0.3 mmol) to give 74.1 mg (95%) of the

(*S,S*) chlorohydrin with 93% ee. $[\alpha]^{20}_D$ = –43.3°, c = 0.52, $CHCl_3$.

When catalyst (–)-**3.1g** was used, 72.0 mg (92%) of the (*R,R*) chlorohydrin was obtained with 93% ee. $[\alpha]^{20}_D$ = +38.4°, c = 0.56, $CHCl_3$.

^1H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H), 2.30 (s, 3H), 3.02 (s, 1H), 4.93 (d, 1H, J = 8.2), 5.00 (d, 1H, J = 8.2), 7.07 (m, 8H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 21.36, 21.39, 71.2, 78.6, 127.5, 128.4, 129.3, 129.5, 135.7, 136.7, 138.4, 139.0. IR (neat): 3432, 3027, 2921, 1904, 1611, 1514, 1180, 1056 cm^{-1}.

Table 3.3, entry 5. The general procedure was followed with (+)-**3.1g** (11.6 mg, 0.0150 mmol) and the epoxide (88.9 mg, 0.300 mmol) to give 83.2 mg (83%) of the (*S,S*) chlorohydrin with 95% ee. $[\alpha]^{20}_D$ = –38.9°, c = 0.35, $CHCl_3$.

When catalyst (–)-**3.1g** was used, 84.9 mg (85%) of the (*R,R*) chlorohydrin was obtained with 93% ee. $[\alpha]^{20}_D$ = +36.6°, c = 0.71, $CHCl_3$.

^1H NMR (500 MHz, $CDCl_3$): δ 3.18 (d, 1H, J = 2.8), 5.28 (dd, 1H, J = 2.4, 7.9), 5.32 (d, 1H, J = 7.9), 7.19 (dd, 1H, J = 1.5, 8.5), 7.43 (m, 5H), 7.62 (d, 1H, J = 8.5), 7.72 (m, 7H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 71.3, 78.9, 125.1, 125.7, 126.65, 126.69, 126.85, 126.95, 127.1, 128.0, 128.06, 128.11, 128.3, 128.44, 128.48, 128.8, 133.3, 133.5, 133.61, 133.66, 135.8, 137.16. IR (neat): 3518, 3049, 1597, 1362, 1074, 825 cm^{-1}.

Table 3.3, entry 6. The general procedure was followed with (+)-**3.1g** (11.6 mg, 0.0150 mmol) and the epoxide (85.3 mg, 0.300 mmol) to give 87.8 mg (91%) of the (–)-chlorohydrin with 52% ee. $[\alpha]^{20}_D$ = –2.21°, c = 1.04, EtOH.

When catalyst (–)-**3.1g** was used, 86.6 mg (90%) of the (+)-chlorohydrin was

obtained with 48% ee. $[\alpha]^{20}_{D}$ = +2.29°, c = 1.05, EtOH.

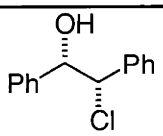
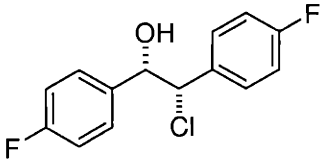
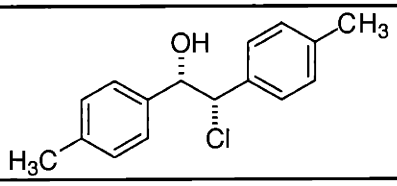
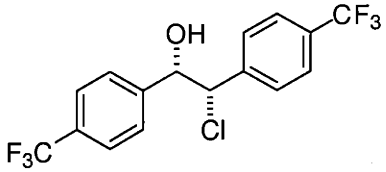
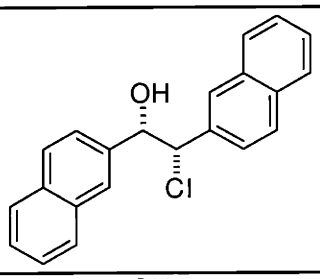
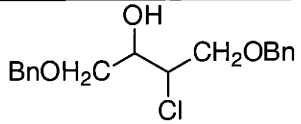
VIII. Non-linear Effects Experiments (Figure 3.3)

General procedure. In the glove box, to a vial was added 90.0% ee of catalyst **3.1g** (2 mg, 0.0026 mmol), *cis*-stilbene oxide (9.6 mg, 0.049 mmol) in 1.0 mL CH_2Cl_2, followed by *i*-Pr_2NEt (10μL, 0.057 mmol). The vial was capped, brought outside the glove box, and cooled to -80 °C. $SiCl_4$ (0.055 mmol, 0.10 mL, 0.55 M solution) was then added to the reaction mixture. After 24 hours, the reaction was quenched by the addition of sat. KF/1 M KH_2PO_4 (1:1). The resulting solution was extracted with EtOAc. The catalyst was removed by passing the organic extracts through a short plug of silica. The ee of the product 2-chloro-1,2-diphenylethan-1-ol was analyzed by GC.

The above procedure was repeated with different ee of catalyst **3.1g** and the results are tabulated below:

ee of catalyst	ee of product
0	0
27.0	38.7
50.4	67.4
76.7	87.8
90.0	95.2
100	96.0

IX. Methods Used to Assay Enantiomeric Excess

Substrate	ee Assay	Conditions	Retention Time of Isomer with Indicated Configuration (min)	Retention Time of Isomer with Opposite Configuration (min)
	GC Chiraldex G-TA	130 °C; 1.63 mL/min carrier gas flow	51.38	56.02
	GC Chiraldex G-TA	140 °C; 1.63 mL/min carrier gas flow	35.10	37.37
	Mosher Ester	$CDCl_3$	δ 6.31 (d)	δ 6.19 (d)
	GC Chiraldex G-TA	150 °C; 1.63 mL/min carrier gas flow	40.71	43.78
	HPLC Chiralcel OD	10% isopropanol, 90% hexanes	23.05	21.18
 *syn isomers*	HPLC Chiralcel OD	10% isopropanol, 4% ethanol, 86% hexanes	10.28; (+) enantiomer	12.46; (–) enantiomer

X. X-ray Crystal Structure of (–)-3.1b•MeOH

A few drops of methanol were added to a purple toluene solution of (–)-**3.1b**, resulting in a green solution. Crystals suitable for X-ray structural analysis were obtained by diffusing pentane into this solution at room temperature.

A green block of dimensions 0.18 x 0.10 x 0.04 mm^3 was mounted under STP and transferred to a Bruker AXS/CCD three circle diffractometer (χ fixed at 54.78°) equipped with a cold stream of N_2 gas. An initial unit cell was determined by harvesting reflections $I > 20\ \sigma(I)$ from 45 x 10-s frames of 0.30° ω scan data with monochromated Mo K_α radiation (λ = 0.71073 Å). The cell thus determined was triclinic.

A hemisphere of data was then collected using ω scans of 0.30° and 20-s frames. The raw data frames were integrated using the Bruker program SAINT+ for NT version 6.01. An initial background was determined from the first 12° of data. Actual integration was performed with constant spot sizes of 1.6° in the detector plane and 0.6° in ω. Backgrounds were then calculated as a continuing average over 8 frames of data. The data that were collected (6709 total reflections, 5505 unique, R_{int} = 0.0493) had the following Miller index ranges: -11 to 13 in h, -13 to 6 in k, and -14 to 14 in l. The data were corrected for Lorentz and polarization effects. A semi-empirical absorption correction from ψ-scans was also applied, maximum and minimum transmission: 0.9840 and 0.8329, respectively.

All aspects of the solution and refinement were handled by SHELXTL NT version 5.10.[41] The structure was solved by direct methods in the chiral monoclinic

41 SHELXTL: Bruker AXS, Inc., SHELTXL™ Reference Manual Version 5.1, 1997.

space group P1, a = 11.9079(19) Å; b = 12.472(2) Å; c = 13.071(2) Å; α = 91.335(3)°; β = 108.005(3)°; γ = 114.111(3)°, and refined using standard difference Fourier techniques. Final, full-matrix least-squares refinement (5505 data for 846 parameters) on F^2 yielded residuals of R_1 and wR_2[42] of 0.0523 and 0.1106, respectively, for data $I > 2\sigma(I)$, and 0.0925 and 0.1318, respectively, for all data. During the final refinement all nonhydrogen atoms were treated anisotropically. Hydrogen atoms were included in calculated positions and refined isotropically on a riding model except for those on the methanol molecule. A secondary extinction coefficient of 0.0129(16) was also included in the refinement. Residual electron density amounted to a maximum of 0.331 e/Å^3 and a minimum of -0.325 e/Å^3.

The absolute structure (Flack) parameter for the correct enantiomer is -0.05(4). The structure was also inverted and refined in order to confirm the initial assignment of absolute stereochemistry.

The full crystallographic data for the X-ray structure is provided in Appendix III.

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42 Equations:

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

$w = 1/[\sigma^2(F_o)^2 + (0.0647 * P)^2 + 0.0934 * P]$

where $P = [Max(F_o^2, 0) + 2 * F_c^2]/3$

XI. X-ray Crystal Structure of (+)-3.1g•TsOH

A blue benzene solution of (+)-**3.1g** was added to a few crystals of *p*-TsOH, resulting in a green solution. Crystals suitable for X-ray structural analysis were obtained by diffusing pentane into this solution at room temperature.

A green plate of dimensions 0.24 x 0.08 x 0.04 mm^3 was mounted under STP and transferred to a Bruker AXS/CCD three circle diffractometer (χ fixed at 54.78°) equipped with a cold stream of N_2 gas. An initial unit cell was determined by harvesting reflections $I > 20\ \sigma(I)$ from 45 x 10-s frames of 0.30° ω scan data with monochromated Mo K_α radiation (λ = 0.71073 Å). The cell thus determined was monoclinic.

A hemisphere of data was then collected using ω scans of 0.30° and 30-s frames. The raw data frames were integrated using the Bruker program SAINT+ for NT version 6.01. An initial background was determined from the first 12° of data. Actual integration was performed with constant spot sizes of 1.6° in the detector plane and 0.6° in ω. Backgrounds were then calculated as a continuing average over 8 frames of data. The data that were collected (20253 total reflections, 13106 unique, R_{int} = 0.1341) had the following Miller index ranges: -14 to 20 in h, -16 to 16 in k, and -21 to 21 in l. The data were corrected for Lorentz and polarization effects. A semi-empirical absorption correction from ψ-scans was also applied, maximum and minimum transmission: 0.9980 and 0.8295, respectively.

All aspects of the solution and refinement were handled by SHELXTL NT version 5.10. The structure was solved by direct methods in the chiral monoclinic space group $P2_1$, a = 18.271(2) Å; b = 14.6869(18) Å; c = 19.379(2) Å; β = 102.568(2)°, and

refined using standard difference Fourier techniques. Final, full-matrix least-squares refinement (13106 data for 1232 parameters) on F^2 yielded residuals of R_1 and wR_2[43] of 0.0880 and 0.1435, respectively, for data $I > 2\sigma(I)$, and 0.2139 and 0.1924, respectively, for all data. During the final refinement all nonhydrogen atoms were treated anisotropically. Hydrogen atoms were included in calculated positions and refined isotropically on a riding model, except for the one residing on the oxygen of the N-O moiety. A secondary extinction coefficient of 0.0054(4) was also included in the refinement. Residual electron density amounted to a maximum of 0.278 e/Å^3 and a minimum of -0.300 e/Å^3.

The absolute structure (Flack) parameter for the correct enantiomer is -0.05(4). The structure was also inverted and refined in order to confirm the initial assignment of absolute stereochemistry.

The full crystallographic data for the X-ray structure is provided in Appendix III.

---

43 Equations:

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$

$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

$w = 1/[\sigma^2(F_o)^2 + (0.0537 * P)^2]$

where $P = [Max(F_o^2, 0) + 2 * F_c^2]/3$

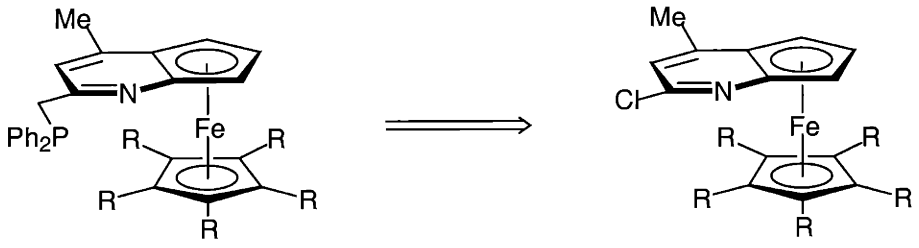
Chapter 4:

Asymmetric Hydrosilylation of Ketones Using Planar-Chiral *N,P*-Ligands

Introduction to Hydrosilylation of Simple Ketones

In our continuing interest in the design and development of planar-chiral heterocycles for asymmetric catalysis, we have expanded the scope of our investigation to a new family of compounds — complexes bearing both nitrogen and phosphorus functionalities. It is conceivable that planar-chiral *N,P*-ligands could be easily synthesized by functional group manipulations from 2-chloro-4-methylpyrindine derivative **4.2**, a compound which had been developed in our laboratory. We hoped that the planar-chiral *N,P*-ligand design, which allows for steric and electronic tuning of the bottom ring and the phosphorus group, could outperform existing *N,P* ligands in asymmetric catalysis. Since the asymmetric reduction of ketones has been recognized as a versatile method for providing enantiomerically enriched secondary alcohols, we chose to study the asymmetric catalytic hydrosilylation of ketones to test the effectiveness of our ligand design.[1]

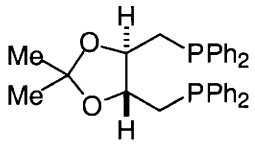
Scheme 4.1 Retrosynthesis of Planar-Chiral *N,P*-Ligand



4.1 **4.2**

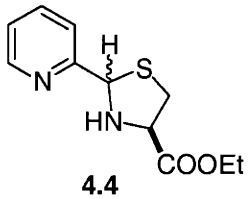
1 For a review of catalytic asymmetric hydrosilylation, see: (a) Nishiyama, H. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Chapter 6.3. (b) Nishiyama, H.; Itoh, K. In *Catalytic Asymmetric Synthesis 2nd Edition*, Ojima, I. Ed.; Wiley-VCH: New York, 2000; Chapter 2.

In the early 1970s, Wilkinson's complex ($RhCl(PPh_3)_3$) was shown to be an effective catalyst for hydrosilylation. Since then, there have been many reports of asymmetric hydrosilylation using optically active phosphorus ligands that were developed mainly for the asymmetric hydrogenation of olefins. For example, when DIOP (**4.3**) was used as a ligand with $[Rh(COD)Cl]_2$, 58% ee was achieved in the reduction of acetophenone.[2] It was also noted that α-$NpPhSiH_2$ gave higher enantioselectivity than Ph_2SiH_2.



4.3

A breakthrough in this field occurred in 1983, when very high enantioselectivity in the asymmetric hydrosilylation of ketones was achieved using a chiral nitrogen ligand, pyridine thiazolidine (Pythia, **4.4**)[3] in the presence of $[Rh(COD)Cl]_2$. Acetophenone can be hydrosilylated in 97.6% ee using Ph_2SiH_2. Dialkyl ketones, such as *n*-butyl methyl ketone and 2-methylpropyl methyl ketone were reduced in 52% ee and 56% ee, respectively.[4]



4.4

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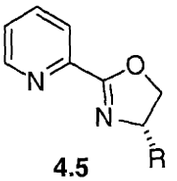
2 Dumont, W.; Poulin, J. C.; Dang, T.-P.; Kagan, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8295-8299.

3 (a) Brunner, H.; Riepl, G.; Weitzer, H. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 331-332. (b) Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1984**, *3*, 1354-1359.

4 Brunner, H.; Kürzinger, A. *J. Organomet. Chem.* **1988**, *346*, 413-424.

Pyridine-oxazolines (Pymox, **4.5**), which were first introduced in 1986 for the copper-catalyzed asymmetric monophenylation of diols with bismuth reagents,[5] were found to serve as effective ligands in the rhodium-catalyzed asymmetric hydrosilylation.[6] The chiral center on the oxazoline (at the 4'-position) is derived from readily available amino acids. Using this class of ligand, the best enantioselectivity for the hydrosilylation of acetophenone (91% ee) was achieved with Pymox-*t*-Bu (**4.5**, R = *t*-Bu). In spite of the structural similarity between Pythia and Pymox, the alcohol products obtained were of opposite absolute configuration.



4.5

In 1989, Pybox (2,6-bis(oxazolinyl)pyridine, **4.6**), a C_2-symmetric ligand, was introduced. It was found that Pybox-*i*-Pr, when complexed with $[Rh(COD)Cl]_2$, reduced acetophenone with an enantiomeric excess of 76% in the presence of Ph_2SiH_2.[6b] The rate of the reaction is increased using $RhCl_3$(Pybox-*i*-Pr) in the presence of $AgBF_4$, and the enantioselectivity of the reaction is also improved to 94-95% ee.[7] This system provides high enantioselectivities for the reduction of aryl methyl ketones (90-99% ee). The reduction of 2-octanone can be carried out in an enantiomeric excess of 63%.

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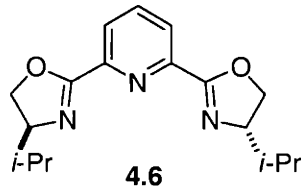
5 Brunner, H.; Obermann, U.; Wimmer, P. *J. Organomet. Chem.* **1986**, *316*, C1-C3.

6 (a) Brunner, H.; Obermann, U. *Chem. Ber.* **1989**, *122*, 499. (b) Nishiyama, H.; Sakaguchi, H.; Nakamura, T.; Horihata, M.; Kondo, M.; Itoh, K. *Organometallics* **1989**, *8*, 846-848. (c) Brunner, H.; Brandl, P. *J. Organomet. Chem.* **1990**, *390*, C81. (d) Brunner, H.; Brandl, P. *Tetrahedron: Asymmetry*, **1991**, *2*, 919-930.

7 Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991**, *10*, 500-508.



4.6

In 1994, a trans-chelating bis-phosphinoferrocene derivative, TRAP (**4.7**), having a wide bite angle of 164° (P-Rh-P), was found to be the first chiral diphosphine ligand for asymmetric hydrosilylation to achieve enantiomeric excesses greater than 90%.[8] The substituents on the phosphine can be varied to increase the enantioselectivity. Using $Rh(COD)_2BF_4$ and BuTRAP (**4.7**; R = *n*-Bu), acetophenone and 1-cyclohexenyl methyl ketone were reduced in 92% ee and 95% ee, respectively.[9] Ketoesters, diketones, and dialkyl ketones can also be reduced by Rh-TRAP (**4.7**; R = Me, Et, *n*-Bu) in good to excellent enantioselectivity. Another trans-chelating chiral diphosphine complex, EtTRAP-H (**4.8**), was also developed for the rhodium-catalyzed asymmetric hydrosilylation of ketones.[10] The reaction of acetophenone with Ph_2SiH_2 using EtTRAP-H yields *sec*-phenethyl alcohol in 94% ee. The EtTRAP-H ligand was also very effective in the hydrosilylation of 2-octanone to give the corresponding alcohol in 77% ee, which is the highest enantioselectivity reported to date for the catalytic asymmetric reduction of linear 2-alkanones.

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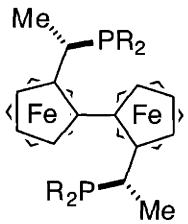
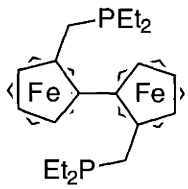
8 (a) Sawamura, M.; Kuwano, R.; Ito, Y. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 111-113. (b) Sawamura, M.; Kuwano, R.; Shirai, J.; Ito, Y. *Synlett* **1995**, 347-348. (c) Kuwano, R.; Sawamura, M.; Shirai, J.; Takahashi, M.; Ito, Y. *Tetrahedron Lett.* **1995**, *36*, 5239-5242.

9 Kuwano, R.; Sawamura, M.; Shirai, J.; Takahashi, M.; Ito, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 485-496.

10 Kuwano, R.; Uemura, T.; Saitoh, M.; Ito, Y. *Tetrahedron Lett.* **1999**, *40*, 1327-1330.

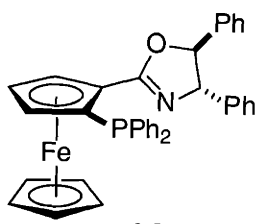


4.7



4.8

Other than dinitrogen and diphosphorus-type ligands, a few *N,P*-ligands have also been investigated in the asymmetric hydrosilylation reaction. For example, ferrocenylphosphino oxazoline **4.9** can give high catalytic activity in the reduction of acetophenone, providing *sec*-phenethyl alcohol in 91% ee in the presence of $[Rh(COD)Cl]_2$.[11] Linear 2-nonanone can also be hydrosilylated in 60% ee. Interestingly, in substituting $[Ir(COD)Cl]_2$ for $[Rh(COD)Cl]_2$, the opposite enantiomer of *sec*-phenethyl alcohol[12] was obtained in 96% ee using the same ligand.[13]



4.9

The phosphino oxazoline ligands developed for palladium-catalyzed asymmetric allylic substitution[14] were also applied to asymmetric hydrosilylation.[15]

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11 Nishibayashi, Y.; Segawa, K.; Ohe, K.; Uemura, S. *Organometallics* **1995**, *14*, 5486-5487.

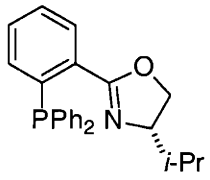
12 Similar phenomena were observed in the literature: (a) Faller, J. W.; Chase, K. J. *Organometallics* **1994**, *13*, 989-992. (b) Kinting, A.; Kreuzfeld, H.-J.; Abicht, H.-P. *J. Organomet. Chem.* **1989**, *370*, 343-349.

13 Nishibayashi, Y.; Segawa, K.; Takada, H.; Ohe, K.; Uemura, S. *Chem. Commun.* **1996**, 847-848.

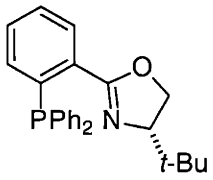
14 von Matt, P.; Pfaltz, A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 566-568.

15 (a) Newman, L. M.; Williams, J. M. J.; McCague, R.; Potter, G. A. *Tetrahedron: Asymmetry* **1996**, *7*, 1597-1598. (b) Langer, T.; Janssen, J.; Helmchen G. *Tetrahedron: Asymmetry* **1996**, *7*, 1599-1602.

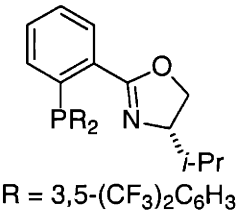
Acetophenone can be hydrosilylated in 82% ee using isopropyl ligand **4.10** and $[Rh(COD)Cl]_2$. However, the *tert*-butyl derivative **4.11** leads to a decrease in enantioselectivity. Increasing the bulk of the phosphine substituents to 3,5-$(CF_3)_2C_6H_3$ (**4.12**) increases the enantioselectivity slightly to 86%; the indane derivative[16] **4.13** gave 94% ee for the same reaction. The rhodium-catalyzed hydrosilylation of dialkyl ketones can also be carried out using ligand **4.13**. Cyclohexyl methyl ketone and 2-octanone were reduced to their corresponding alcohols in 87% ee and 52% ee, respectively.



4.10

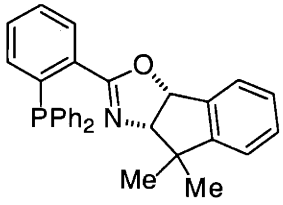


4.11



R = 3,5-$(CF_3)_2C_6H_3$

4.12



4.13

The use of ruthenium complexes in place of rhodium complexes as catalysts in the hydrosilylation of ketones was first investigated using chiral tridentate ligand **4.14**.[17] Under the optimized conditions, hydrosilylation of aryl alkyl ketones could be carried out in the presence of AgOTf, giving products with enantioselectivities ranging from 47 to 66%. Ruthenium-catalyzed hydrosilylation of ketones can also be carried out using an (oxazolinylferrocenyl)phosphine ligand (**4.15**; R = Ph).[18] Using $Cu(OTf)_2$ as an additive, propiophenone can be reduced to give 1-phenyl-1-propanol in 97% ee. The Ru-**4.15** complex can also serve as an effective catalyst in the hydrosilylation of an imine.

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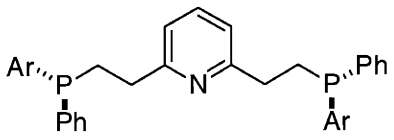
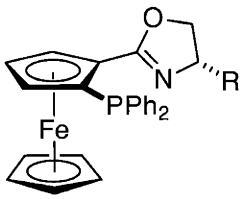
16 Sudo, A.; Yoshida, H.; Saigo, K. *Tetrahedron: Asymmetry* **1997**, *8*, 3205-3208.

17 Zhu, G.; Terry, M.; Zhang, X. *J. Organomet. Chem.* **1997**, *547*, 97-101.

18 Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1998**, *17*, 3420-3422.



4.14 (Ar = 2-MeO-C_6H_4)



4.15

In addition to rhodium and ruthenium complexes, hydrosilylation can also be carried out using titanium complexes. One of the representative examples is the chiral ethylenebis(tetrahydroindenyl)titanium(IV)-binaphthdiolate (**4.16**), reported by Yun and Buchwald.[19] Using polymethylhydrosiloxane (PMHS) as the reducing agent, aryl alkyl ketones were reduced to the corresponding alcohols with high enantioselectivities (up to 97%). Dialkyl ketones, however, gave less satisfactory results. Addition of an alkyllithium, such *n*-BuLi, was necessary to generate the active low-valent Ti hydride species.

The asymmetric hydrosilylation of ketones using a titanium complex was further improved using chiral ethylenebis(tetrahydroindenyl)titanium(IV) difluoride (**4.17**).[20] In the presence of $PhSiH_3$ and MeOH, more efficient asymmetric hydrosilylation of aryl alkyl ketones can be carried out, giving the corresponding alcohols with a high level of enantioselectivity (up to 99%). The improved protocol avoided the need to use alkyllithium reagents for catalyst activation, which broadened the choice of solvent and the substrate scope.

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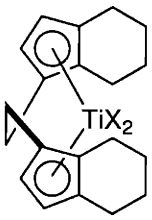
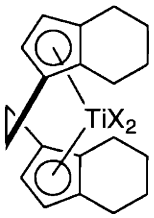
19 Carter, M. B.; Schiøtt, B.; Gutiérrez, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11667-11670.

20 Yun, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5640-5644.



4.16 X_2 = 1,1'-binaphth-2,2'-diolate



4.17 X_2 = F
4.18 X_2 = Cl

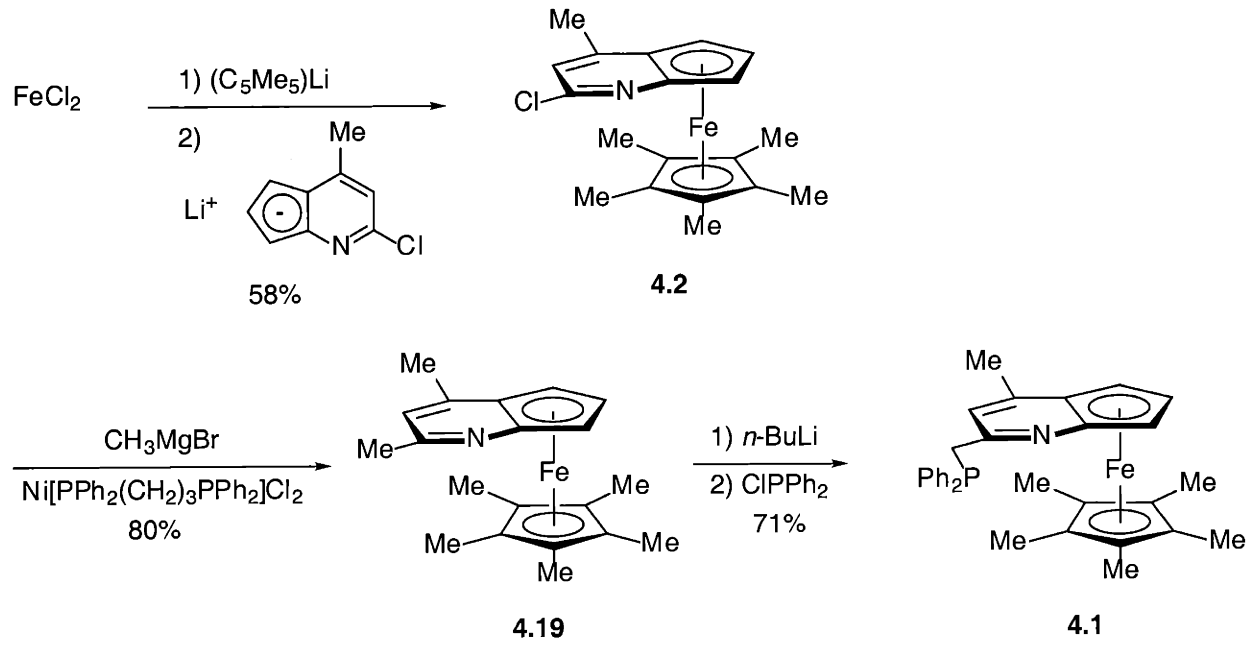
The ethylenebis(tetrahydroindenyl)titanium(IV) dichloride (**4.18**) also displayed good catalytic activity in the reduction of ketones with Ph_2SiH_2 and $PhMeSiH_2$.[21] Methyllithium was added to the titanium complex to generate the active catalytic species. Although the reduction of acetophenone resulted in only 12% ee, dialkyl ketones, such as isopropyl ethyl ketone and cyclopentyl ethyl ketone, were converted to the corresponding alcohols in 65% ee and 70% ee, respectively.

21 Xin, S.; Harrod, J. F. *Can. J. Chem.* **1995**, *73*, 999-1002.

Results and Discussion

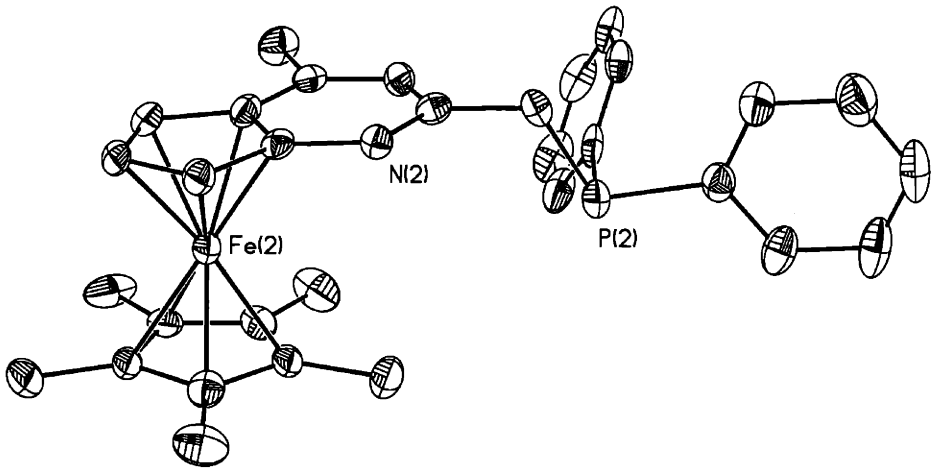
The synthesis of planar-chiral heterocycles bearing both nitrogen and phosphorus functionalities is depicted in Scheme 4.2. First, treatment of $FeCl_2$ with C_5R_5Li and 2-chloro-4-methyl-5H-[1]pyrindine anion[22] afforded ferrocene **4.2**. Methylation with MeMgBr followed by lithiation and nucleophilic attack on $ClPPh_2$ furnished the desired compound **4.1**, the enantiomers of which were readily resolved by chiral HPLC. We have determined the absolute configuration of (–)-**4.1** by X-ray crystallography (Figure 4.1).

Scheme 4.2 Synthesis of Planar-Chiral *N,P*-Ligand



22 For the synthesis of 2-chloro-4-methyl-5H-[1]pyrindine, see Liang, J. S. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

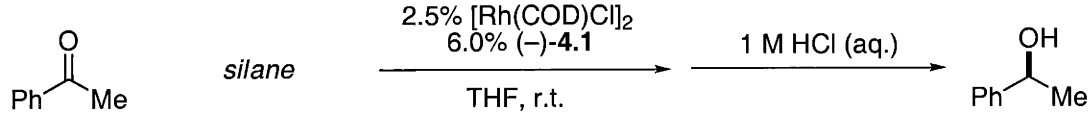
Figure 4.1 ORTEP Representation of (–)-4.1 (With thermal ellipsoids drawn at the 35% probability level)



Since the asymmetric reduction of ketones has been recognized as a versatile method for providing enantiomerically enriched secondary alcohols, we chose to study the asymmetric catalytic hydrosilylation of ketones to test the effectiveness of our ligand design. When applying ligand (–)-**4.1** to the catalytic asymmetric hydrosilylation of acetophenone, we discovered that the enantioselectivity is highly dependent on the size of silane employed (Table 4.1). In general, dihydrosilanes gave better enantioselectivities than trihydrosilanes (entries 1-2 vs entries 4-10). As the bulk of the silane increased from Et_2SiH_2 to $MesPhSiH_2$, the enantiomeric excess increased from 1% to 98%. However, further increase of the bulk of the silane to (*o*-tol)$_2SiH_2$ and Mes_2SiH_2 led to decrease in reactivity or in the enantioselectivity of the reaction (entries 9, 10).

The design of our planar-chiral *N,P*-ligands allows us to incorporate different bottom rings and different phosphino groups into the molecule. This modular design enables us to tune the electronic and steric properties of the ligands to improve enantioselectivities.

Table 4.1 Hydrosilylation of Acetophenone with Different Silanes



entry	*silane*	ee (%)
1	*n*-octylSiH_3	3
2	$PhSiH_3$	8
3	Et_2SiH_2	1
4	$PhMeSiH_2$	66
5	Ph_2SiH_2	80
6	(α-Np)$PhSiH_2$	90
7	(*o*-tol)$PhSiH_2$	95
8	$MesPhSiH_2$	98
9	(*o*-tol)$_2SiH_2$	92
10	Mes_2SiH_2	NR

A number of planar-chiral *N,P*-ligands were synthesized and their selectivities in the hydrosilylation of acetophenone were assessed. Out of all of the *N,P*-ligands that could be resolved by chiral HPLC, we discovered that ligand **4.21** was the most effective for the asymmetric hydrosilylation of acetophenone when Ph_2SiH_2 was used. However, when we tried to optimize the enantioselectivity with respect to both the ligand and the silane reagent, we found that *N,P*-ligand **4.1** and $MesPhSiH_2$ was the best combination.

Scheme 4.3 Family of Planar-Chiral *N,P*-Ligands

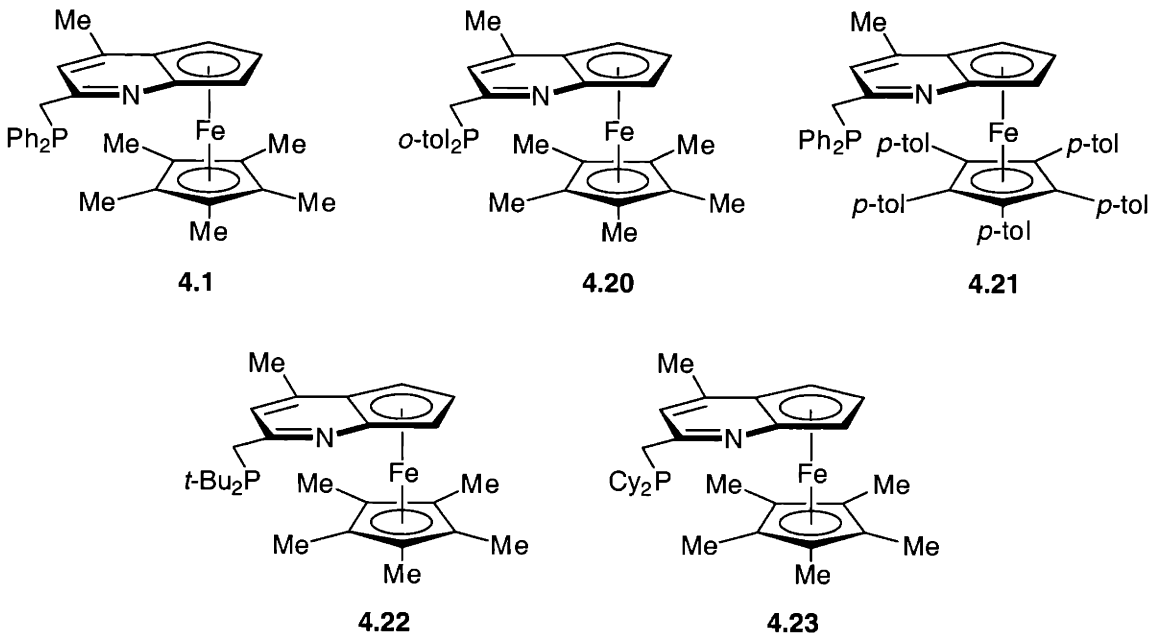
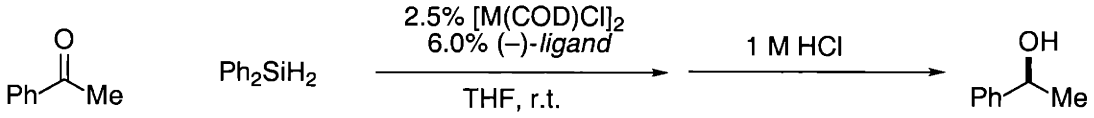


Table 4.2 Hydrosilylation of Acetophenone as a Function of Catalyst

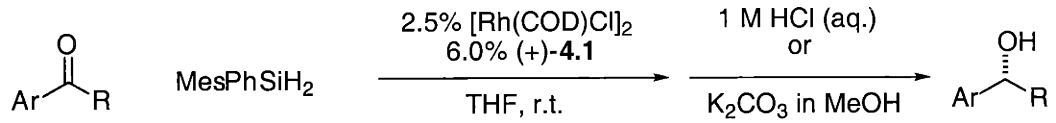


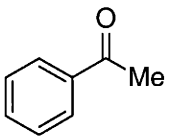
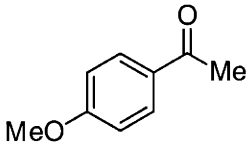
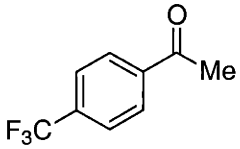
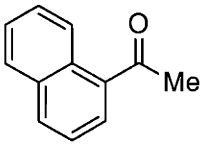
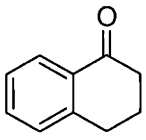
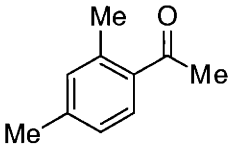
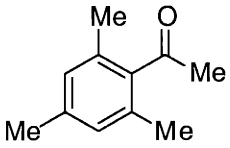
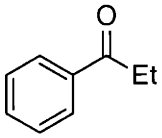
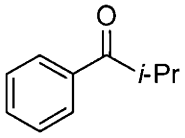
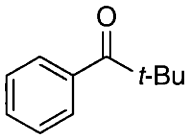
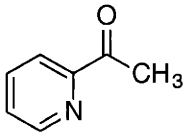
entry	*Metal*	*ligand*	ee (%)
1	Rh	**4.1**	80
2	Rh	**4.20**	64
3	Rh	**4.21**	84
4	Ir	**4.1**	51

Interestingly, when the metal was switched from rhodium to iridium in the asymmetric hydrosilylation, the sense of the chiral induction was reversed using the same enantiomer of the ligand. This is consistent with Uemura's observation in

asymmetric hydrosilylations using a chiral oxazolinylferrocene as the ligand.[23]

Table 4.3 Scope of Substrates for Asymmetric Hydrosilylation of Aryl Alkyl Ketones



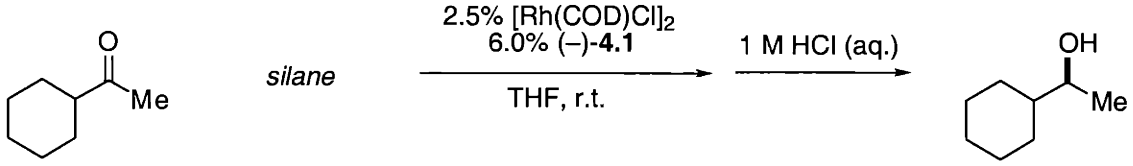
entry	ketone	ee (%)
1		98
2		94
3		94
4		96
5		93
6		92
7		96
8		95
9		86
10		NR
11		79

23 Nishibayashi, Y.; Segawa, K.; Takada, H.; Ohe, K.; Uemura, S. *Chem. Commun.* **1996**, 847-848.

Using heterocycle (+)-**4.1** as the ligand and $MesPhSiH_2$ as the silane reagent, a series of aryl alkyl ketones can be hydrosilylated with very good enantioselectivities as shown in Table 4.3.

Electron-withdrawing and electron-donating groups on the aryl group are tolerated, giving high enantioselectivities (entries 2, 3). Sterically demanding substrates like mesityl methyl ketone (entry 7) can also be hydrosilylated in excellent enantioselectivity, although at a slower rate. As the bulk of the alkyl moiety of aryl alkyl ketone increases from methyl to ethyl, high enantioselectivity is still maintained (entry 8). A further increase in the size of the alkyl group leads to a decrease in enantioselectivity (entry 9) or no reaction (entry 10). 2-Pyridyl methyl ketone can also be hydrosilylated in moderate enantioselectivity (entry 11).

Table 4.4 Hydrosilylation of Cyclohexyl Methyl Ketone as a Function of Silane

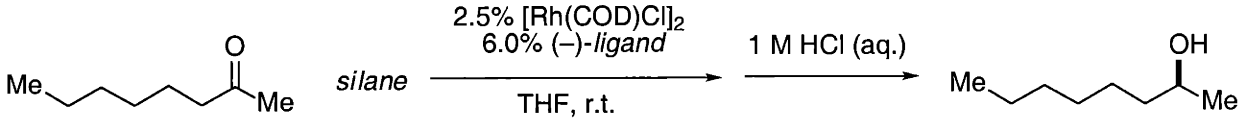


entry	*silane*	ee (%)
1	Ph_2SiH_2	75
2	(α-Np)$PhSiH_2$	86
3	(*o*-tol)$PhSiH_2$	90
4	(*o*-tol)$_2SiH_2$	92
5	$MesPhSiH_2$	86

In addition to aryl alkyl ketones, we were gratified to learn that our planar-chiral

N,P-complex can also serve as an effective ligand for the hydrosilylation of dialkyl ketones such as cyclohexyl methyl ketone. We also discovered that the enantiomeric excess of the alcohol product was dependent on the size of the silane reagent, with (*o*-tol)$_2$SiH$_2$ giving the highest enantiomeric excess (Table 4.4).

Table 4.5 Hydrosilylation of *n*-Hexyl Methyl Ketone as a Function of Silane and Ligand



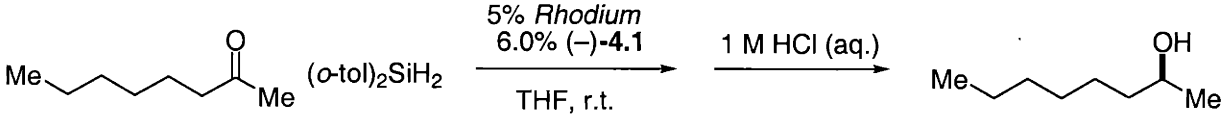
entry	*ligand*	*silane*	ee (%)
1	**4.1**	(α-Np)PhSiH$_2$	54
2	**4.1**	(*o*-tol)PhSiH$_2$	60
3	**4.1**	(*o*-tol)$_2$SiH$_2$	64
4	**4.1**	MesPhSiH$_2$	38
5	**4.21**	Ph$_2$SiH$_2$	62
6	**4.21**	(α-Np)PhSiH$_2$	43
7	**4.21**	MesPhSiH$_2$	17

Linear 2-alkanones have been viewed as challenging substrates for asymmetric reductions. With our system, *n*-hexyl methyl ketone can be hydrosilylated in modest enantioselectivity (Table 4.5). Again, the enantioselectivity is dependent on the size of the silane reagent, with (*o*-tol)$_2$SiH$_2$ being the optimal silane (entry 3) giving an enantiomeric excess of 64%. The enantioselectivity of the reaction is not

only dependent on the silane reagent but also on the ligand used. When the bulkier ligand **4.21** was used, a less sterically demanding silane, Ph_2SiH_2, gave the best enantioselectivity (entry 5).

Next, we chose to investigate the effect of the rhodium source on the rate and the selectivity of the asymmetric hydrosilylation. As shown in Table 4.6, similar enantioselectivities were obtained using either cationic or neutral rhodium(I) sources. Interestingly, among all the rhodium sources surveyed, $[Rh(COD)Cl]_2$ and $[Rh(NBD)Cl]_2$ provided the highest reactivity.

Table 4.6 Hydrosilylation of *n*-Hexyl Methyl Ketone as a Function of Rhodium Source



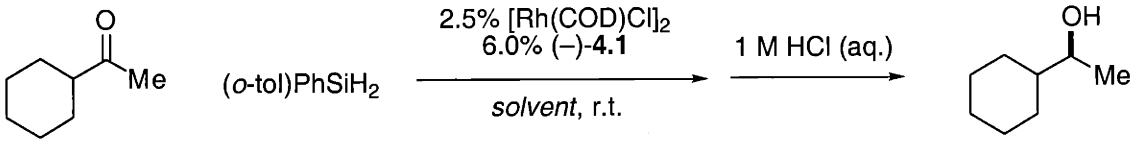
entry	*Rhodium Source*	ee (%)
1	$[RhCl(COD)]_2$	64
2	$[RhCl(NBD)]_2$	64
3	$Rh(COD)_2BF_4$	62
4	$Rh(COD)_2PF_6$	63
5	$Rh(COD)_2ClO_4$	64
6*	$Rh(COD)_2SbF_6$	ND

* Enantiomeric excess was not determined due to polymerization of the solvent.

The asymmetric hydrosilylation has also been optimized with respect to solvent

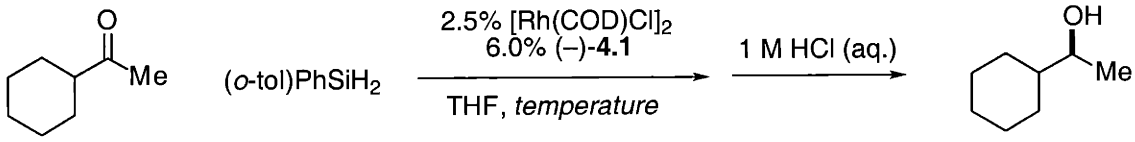
(Table 4.7). It was found that CCl_4 gave the highest enantioselectivity in the hydrosilylation of cyclohexyl methyl ketone (entry 5). However, CCl_4 is not the solvent of choice due to its toxicity. Ethereal solvents, such as THF and Et_2O, also gave excellent enantioselectivities. Therefore, THF was determined to be the solvent of choice (entries 1, 2).

Table 4.7 Hydrosilylation of Cyclohexyl Methyl Ketone as a Function of Solvent



entry	*solvent*	ee (%)
1	THF	90
2	Et_2O	90
3	toluene	88
4	CH_2Cl_2	79
5	CCl_4	94

Table 4.8 Hydrosilylation of Cyclohexyl Methyl Ketone as a Function of Temperature



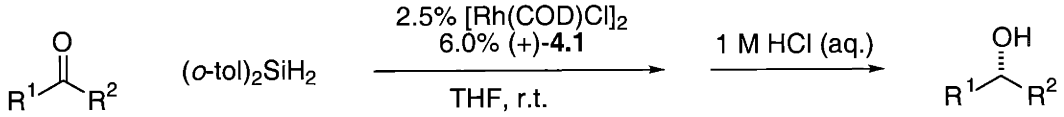
entry	*temperature*	ee (%)
1	r.t.	90
2	0 °C	92
3	-40 °C	94

The reaction was also found to be slightly dependent on temperature (Table 4.8). Higher enantioselectivity was observed with lower temperature, though a decrease in the rate of the reaction was also observed.

Using heterocycle (+)-**4.1** as the ligand and (o-tol)$_2$SiH$_2$ as the silane reagent, a series of dialkyl ketones can be effectively hydrosilylated as shown in Table 4.9. Changing the alkyl group from methyl to ethyl in the cyclohexyl alkyl ketone series led to a significant decrease in enantioselectivity (entries 1, 2). α,β-Unsaturated ketones gave low to modest enantiomeric excess in the hydrosilylation reaction (entries 3, 5). Adamantyl methyl ketone gave 92% ee, although 2,2-dimethylcyclohexanone showed only modest ee (entry 4, 6). Challenging substrates like benzylacetone and n-hexyl methyl ketone can be hydrosilylated with respectable enantioselectivities of 76% and 64%, respectively (entries 7, 8).

A faster reaction rate was observed when the reaction was run at higher concentration. This was particularly beneficial to substrates like mesityl methyl ketone and propiophenone where the reactions were sluggish. By increasing the concentration of the reaction to 1 M, we were able to increase the rate of the reaction. As a result, the catalyst loading could be decreased to 2% and essentially the same enantioselectivity was obtained. Hence, under the optimized conditions (2% catalyst loading, (+)-**4.1** as the ligand, MesPhSiH$_2$ as the silane reagent, at 1 M concentration), a number of aryl alkyl ketones were hydrosilylated in excellent yields and enantioselectivities (Table 4.10).

Table 4.9 Scope of Substrates for Asymmetric Hydrosilylation of Dialkyl Ketones



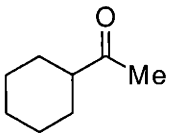
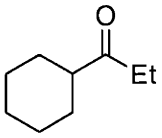
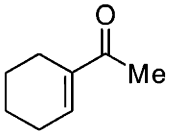
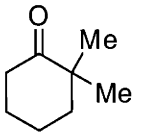
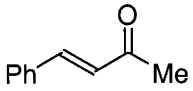
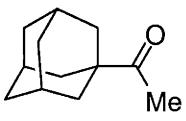
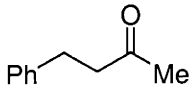
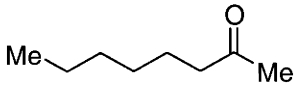
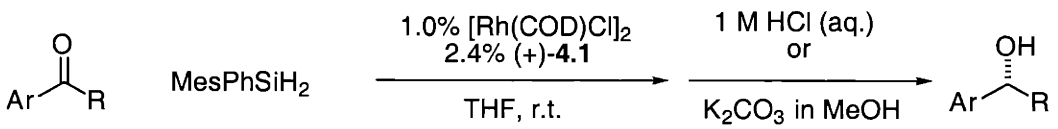
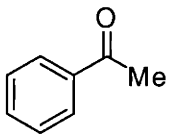
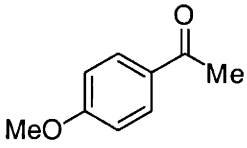
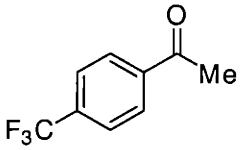
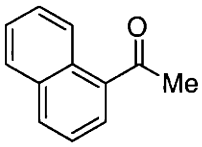
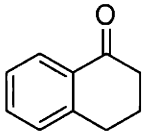
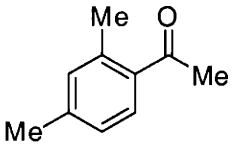
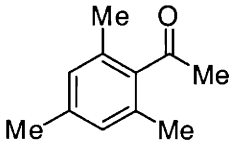
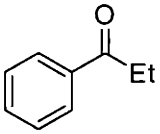
entry	ketone	ee (%)
1		92
2		62
3		51
4		50
5		0
6		92
7		76
8		64

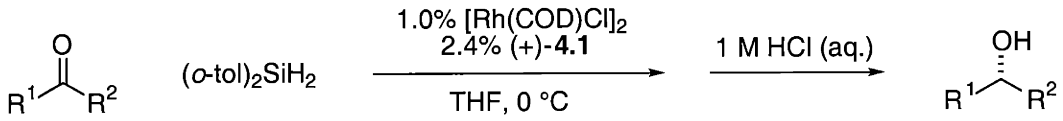
Table 4.10 Catalytic Asymmetric Hydrosilylation of Aryl Alkyl Ketones

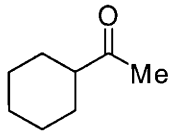
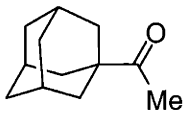
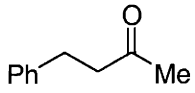
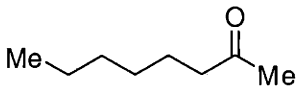


entry	ketone	yield (%)	ee (%)
1		94	98
2		97	97
3		88	96
4		97	99
5		95	98
6		97	95
7		99	98
8		96	98

For dialkyl ketones, utilizing $(o\text{-tol})_2SiH_2$ as the silane reagent at 0 °C, both cyclohexyl methyl ketone and adamantyl methyl ketone afforded good yields and high enantiomeric excesses (Table 4.11, entries 1 and 2). Even benzylacetone and *n*-hexyl methyl ketone could be hydrosilylated in good enantioselectivities (entries 3 and 4).

Table 4.11 Catalytic Asymmetric Hydrosilylation of Dialkyl Ketones

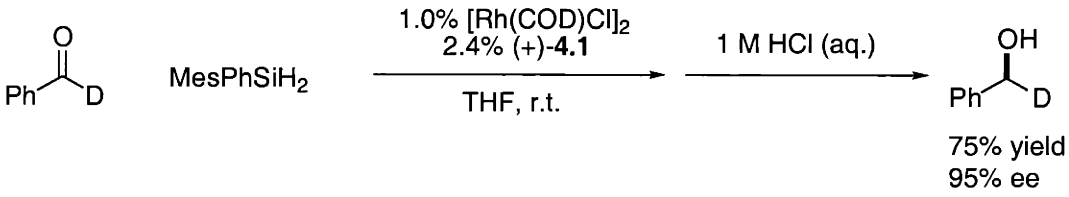


entry	ketone	yield (%)	ee (%)
1		91	94
2		92	96
3		98	82
4[a]		81	71

[a] Reaction was carried out at –20 °C.

Since chiral monodeuterated benzyl alcohol and its derivatives are useful in probing the mechanism of organic reactions,[24] it is worthwhile to develop asymmetric reduction methods for the synthesis of these compounds.[25,26] Using the reaction conditions for asymmetric hydrosilylation of ketones, benzaldehyde-1-*d* could be converted to benzyl-1-*d* alcohol in excellent enantioselectivity (Scheme 4.4).

Scheme 4.4 Asymmetric Hydrosilylation of Benzaldehyde-1-*d*



In the asymmetric hydrosilylation of ketones, construction of a stereogenic center at silicon[27,28] is also possible since $MesPhSiH_2$ is prochiral.[29] Reaction of

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24 (a) Arigoni, D.; Eliel, E. L. *Top. Stereochem.* **1969**, *4*, 127-244. (b) Floss, H. G.; Lee, S. *Acc. Chem. Res.* **1993**, *26*, 116-122. (c) Parry, R. J.; Trainor, D. A. *J. Am. Chem. Soc.* **1978**, *100*, 5243-5244. (d) Mu, Y.; Omer, C. A.; Gibbs, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 1817-1823.

25 (a) Corey, E. J.; Link, J. O. *Tetrahedron Lett.* **1989**, *30*, 6275-6278. (b) Keck, G. E.; Krishnamurthy, D. *J. Org. Chem.* **1996**, *61*, 7638-7639.

26 (a) Ohta, T.; Tsutsumi, T.; Takaya, H. *J. Organomet. Chem.* **1994**, *484*, 191-193. (b) Yamada, I.; Noyori, R. *Org. Lett.* **2000**, *2*, 3425-3427 and references therein.

27 (a) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1974**, *64*, C51-C54. (b) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1975**, *85*, 19-33. (c) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *120*, 337-346. (d) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1975**, *91*, C27-C30. (e) Corriu, R. J. P.; Moreau, J. J. E. *Nouv. J. Chim.* **1977**, *1*, 71-76.

28 Rh-catalyzed reduction of aliphatic ketones with α-$NpPhSiH_2$ gave the corresponding (*R*)-(alkoxy)(α-naphthyl)phenylsilane in >99% ee: Ohta, T.; Ito, M.; Tsuneto, A.; Takaya, H. *Chem. Commun.* **1994**, 2525-2526.

acetophenone with $MesPhSiH_2$ in the presence of $[Rh(NBD)Cl]_2$ and (+)-**4.1** afforded an alkoxysilane, to which was added EtMgCl to give MesPhSiEtH in 72% ee. Since the asymmetric induction at carbon and silicon are not necessarily correlated, ketones that display poor enantioselectivity on carbon may give excellent selectivity on silicon. Therefore, the enantioselectivity as a function of carbonyl compounds was surveyed (Table 4.12).

It was found that both benzaldehyde and cyclohexyl methyl ketone (entries 3, 4) provided MesPhSiEtH in similar ee as acetophenone. Decreasing the steric demand of the ketone to *n*-hexyl methyl ketone or acetone increased the enantioselectivity to 84% and 93%, respectively (entries 5, 6). However, further decrease in the steric environment around the carbonyl group to acetaldehyde resulted in an enantiomeric excess of 38% (entry 7).

The addition of Grignard reagents to silyl ethers is known to proceed with retention of configuration at silicon, with only slight loss of optical purity.[30] Hence, to determine the intrinsic selectivity of the chiral induction at silicon, the alkoxysilane product was isolated.[31] We found that (+)-**4.1** served as an excellent ligand for the stereoselective hydrosilylation of acetone with $MesPhSiH_2$, giving the alkoxysilane in 97% ee.

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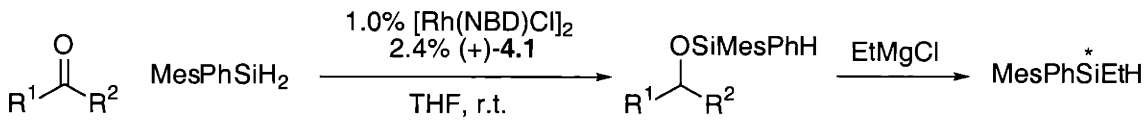
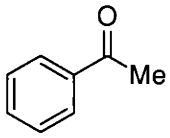
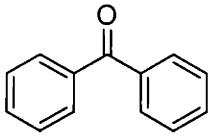
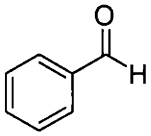
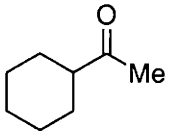
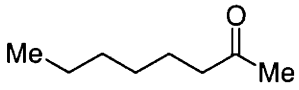
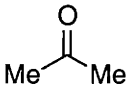
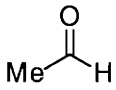
29 Methods to construct sterogenic centers at silicon are limited because sp^2 hybridized silicon is too unstable for synthetic use. Hence, replacement of one of the two enantiotopic X groups in $R^1R^2SiX_2$ has been commonly employed to obtain silanes chiral at silicon.

30 Patai, S.; Rappoport, Z. *The Chemistry of Organic Silicon Compounds* **1989**, Wiley, Chichester.

31 The silyl ether was purified by column chromatography on Florisil inside a glovebox using pentane as eluent.

Table 4.12 Enantioselectivities of Silanes as a Function of Carbonyl Compounds



entry	ketone / aldehyde	ee of silane (%)
1		72
2		2
3		76
4		69
5		84
6		93
7		38

Conclusions

A novel family of planar-chiral heterocycles bearing nitrogen and phosphorus functionalities has been synthesized. We have successfully demonstrated that this family of compounds can serve as effective ligands in the rhodium-catalyzed hydrosilylation of ketones affording alcohols in high enantioselectivities. At 2% catalyst loading, aryl alkyl ketones can be hydrosilylated with excellent enantioselectivities using $MesPhSiH_2$ as the silane reagent. Dialkyl ketones, which are in general more challenging substrates in asymmetric reduction, can also be reduced with very good enantioselection to the corresponding alcohols using $(o\text{-tol})_2SiH_2$. This represents one of the best systems for asymmetric reduction of simple ketones reported to date.

The rhodium-catalyzed hydrosilylation also serves as an efficient method for converting deuterated benzaldehyde to chiral deuterated benzyl alcohol in excellent enantioselectivity. Using (+)-**4.1** as the ligand and $MesPhSiH_2$ as the silane reagent, we can also access chiral silicon compounds with up to 97% ee.

In addition, the modular design of the ligand should allow us to tune the electronic and steric properties of the bottom ring and the phosphorus group to improve enantioselectivity for other asymmetric reactions.

Experimental

I. General

Analytical thin layer chromatography was performed using EM Reagents 0.25 mm silica gel 60 plates, and visualization was accomplished with potassium permanganate or with ethanolic phosphomolybdic acid. Flash chromatography was performed on EM Reagents silica gel 60 (230-400 mesh).

Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer. High resolution mass spectra were recorded on a Finnegan MAT System 8200 spectrometer. Melting points (uncorrected) were measured on a Thomas Hoover Unimelt capillary melting point apparatus.

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian XL-300 or XL-500 NMR spectrometer at ambient temperature. ^{1}H data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (δ scale), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C spectra were determined with complete proton decoupling.

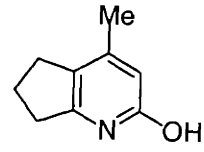
Analytical chiral HPLC was performed on a Daicel CHIRALCEL OD column (4.6 mm x 25 cm). Analytical chiral GC was performed on a Chiraldex G-TA column (20 m x 0.25 mm).

$FeCl_2$ (Strem), *n*-BuLi (Strem), 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (Aldrich), methyl magnesium bromide (Aldrich) and chlorodiphenylphosphine (Alfa Aesar) were used without further purification. The ketone substrates were purified by distillation or column chromatography. $MesPhSiH_2$ and $(o\text{-tol})_2SiH_2$ are prepared according to the literature procedure.[32] Solvents were distilled from the indicated drying agents: benzene (sodium/benzophenone); THF (sodium/benzophenone); CH_2Cl_2 (CaH_2); Et_2O (sodium/benzophenone); toluene (molten sodium).

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware, unless otherwise indicated.

32 Braddock-Wilking, J.; Schieser, M.; Brammer, L.; Huhmann, J.; Shaltout, R. *J. Organomet. Chem.* **1995**, *499*, 89-98.

II. Preparation of Ligands



4-Methyl-6,7-dihydro-5H-[1]pyrindin-2-ol.[33] To a flask fitted with a reflux condenser under argon was added cyclopentanone (323 g, 3840 mmol), ethyl acetoacetate (500 g, 3850 mmol) and ammonium acetate (297 g, 3850 mmol) to give a pale yellow slurry. The reaction mixture was heated at reflux in a heating mantle (a homogeneous brown solution was obtained after 1 hour). After 8 hours, the reaction was cooled to room temperature overnight to allow for the precipitation of an orange solid. The liquid was decanted and the orange solid was rinsed with Et_2O until the color of the Et_2O wash is a consistent pale yellow. After the residual solid was air dried, 121 g (21%) of pyridone was obtained as a pale yellow solid. This material was used as is for the next step. ^1H NMR (250 MHz, $CDCl_3$) δ 6.20 (s, 1H), 2.90 (t, 2H, J = 8.0), 2.66 (t, 2H, J = 8.0), 2.13 (s, 3H), 2.12 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 151.0, 148.5, 120.7, 114.9, 30.9, 28.2, 22.2, 19.7.

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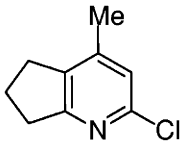
33 Sakurai, A.; Midorikawa, H. *Bull. Chem. Soc. Jpn.* **1968,** *41,* 165.



2-Chloro-4-methyl-6,7-dihydro-5H-[1]pyrindine. To an oven-dried Schlenk tube under argon was added 4-methyl-6,7-dihydro-5H-[1]pyrindin-2-ol (14.9 g, 100 mmol) and $POCl_3$ (30 mL, 320 mmol) to give a brown slurry after a slight exotherm. The Schlenk tube was sealed under an argon atmosphere and immersed in an oil bath at 140 °C. A homogeneous black solution resulted after ~ 30 minutes. After 3 hours, the Schlenk tube was cooled to room temperature and placed under vacuum for 1 hour to remove the excess $POCl_3$. The resulting black tar was rinsed out of the Schlenk tube with cold (~ 0 °C) 1 N HCl.[34] The acidic solution was washed with Et_2O (3 x 100 mL). The Et_2O wash was extracted with 2 N HCl (3 x 100 mL) and the acidic phases were combined and neutralized by K_2CO_3 to give a thick brown slurry (pH ~ 10). The neutralized aqueous phase was extracted with $CHCl_3$ (5 x 200 mL) followed by EtOAc (200 mL). The organic phases were combined, dried with $MgSO_4$, filtered and stripped of solvent to give a brown tar. The crude was dissolved inEt_2O (~ 100 mL) and filtered through silica gel (rinsed with 5 x 100 mL of Et_2O). After solvent removal, 12.3 g (74%) of product was obtained as an orange solid. ^1H NMR (250 MHz, $CDCl_3$) δ 6.91 (s, 1H), 2.99 (t, 2H, J = 8.0), 2.83 (t, 2H, J = 8.0), 2.23 (s, 3H), 2.13 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 148.6, 145.5, 134.7, 121.2, 33.6, 28.2, 21.9, 18.3. IR (thin film) 3055, 2970, 2918, 1735, 1587, 1440, 1376, 1308, 1098, 878 cm^{-1}. HRMS calcd for $C_9H_{10}ClN$ 167.0502, found 167.0498. mp 51-53 °C.

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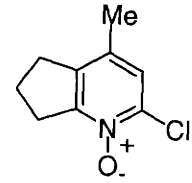
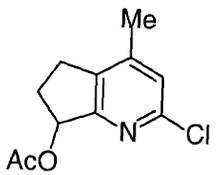
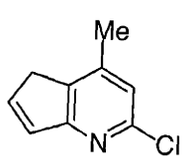
34 It is important to keep the temperature of the quenching operation around ca. 0 °C. 2-Halopyridines are known to revert to 2-hydroxypyridine when heated in aqueous acid.



2-Chloro-4-methyl-6,7-dihydro-5H-[1]pyrindine-1-oxide. To a flask fitted with a reflux condenser was added 2-chloro-4-methyl-6,7-dihydro-5H-[1]pyrindine (4.3 g, 146 mmol), acetic acid (90 mL, 1600 mmol) and H_2O_2 (30%, 20 mL, 180 mmol) to give an orange solution. After heating at 80 °C for 5 hours, more H_2O_2 (30%, 15 mL, 130 mmol) was added to the hot reaction mixture and the resulting yellow solution was heated at 80 °C overnight. After cooling to room temperature, the reaction was placed under vacuum for 1 hour to remove the excess peracetic acid generated in situ. The reaction was quenched by pouring into K_2CO_3 (~ 250 g) in water (~ 400 mL). The resulting slurry (pH ~ 11) was extracted with $CHCl_3$ followed by EtOAc. The organic layers were combined, dried with $MgSO_4$ and filtered. After removal of solvent, 24.7 g (93%) of the product was obtained along with ~ 5% of the unreacted starting material. The product was used in the next step without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, 1H), 3.22 (t, 2H, J = 8.0), 2.92 (t, 2H, J = 8.0), 2.22 (s, 3H), 2.21 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 138.8, 138.7, 133.6, 125.1, 30.4, 30.1, 21.7, 17.8. IR (thin film) 3040, 2976, 2925, 1439, 1382, 1271, 1181, 1077, 1022, 906, 841 cm^{-1}. HRMS calcd for $C_9H_{10}ClNO$ 183.0451, found 183.0449. mp 176-179 °C.

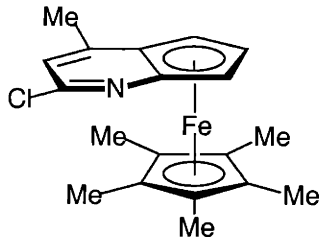


1-(2-Chloro-4-methyl-6,7-dihydro-5H-[1]pyrindin-7-yl)-ethanone. To a flask fitted with a reflux condenser was added 2-chloro-4-methyl-6,7-dihydro-5H-[1]pyrindine-1-oxide (24.7 g, 135 mmol) and Ac_2O (200 mL, 2120 mmol) to give a white slurry. After heating in an oil bath at 100 °C for 30 minutes, a brown homogeneous solution resulted. After an additional 2.5 hours at 100 °C, the excess Ac_2O was removed at reduced pressure. Distillation (bp 145-155 °C at 600 mtorr) gave 17.6 g (58%) of the desired product contaminated with unknown impurities. The impure product solidified upon standing. The product was used in the next step without further purification. ^1H NMR (250 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.03 (m, 1H), 2.61-2.99 (m, 3H), 2.37 (s, 3H), 2.14 (s, 3H), 2.05-2.17 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 159.2, 149.7, 146.7, 135.7, 123.7, 76.3, 27.7, 25.5, 20.7, 18.2. IR (thin film) 2953, 1735, 1589, 1435, 1368, 1228, 1103, 1047, 936, 888 cm^{-1}. HRMS calcd for $C_{11}H_{12}ClNO_2$ 225.0557, found 225.0555. mp 38-40 °C.



2-Chloro-4-methyl-5H-[1]pyrindine. To a flask fitted with a reflux condenser under argon was added crude 1-(2-chloro-4-methyl-6,7-dihydro-5H-[1]pyrindin-7-yl)-ethanone (17.6 g, 78.2 mmol) and concentrated H_2SO_4 (30 mL, 560 mmol) to give a yellow solution. The flask was immersed in an oil bath at 90 °C. After 1 hour, the

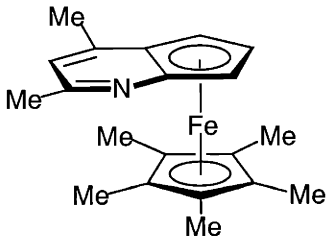
resulting orange solution was cooled to room temperature and poured into ice followed by 80 mL of 50% NaOH solution. Precipitates formed during the quench and an exotherm was observed. After cooling this mixture in an ice bath, K_2CO_3 was added portionwise until pH ~ 10. The aqueous phase was extracted with $CHCl_3$ followed by EtOAc. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated to give a brown oil. Distillation (bp 85-90 °C at 200 mtorr; no cooling water was used due to the low melting point of the product) gave 10.2 g (79%) of the desired product as a ~ 3:1 mixture of isomers contaminated with trace amount of 2-chloro-4-methyl-6,7-dihydro-5H-[1]pyrindine. The oily product solidified upon standing and was used without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ 6.91-7.04 (m, 3H, major and minor isomer), 6.63 (m, 1H, minor isomer), 3.48 (t, 2H, J = 3.0, minor isomer), 3.32 (t, 2H, J = 3.0, major isomer), 2.42 (s, 3H, minor isomer), 2.37 (s, 3H, major isomer). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 149.4, 131.3, 130.0, 114.5, 113.3, 113.1, 108.5, 83.0, 78.7, 76.5, 67.2, 62.1, 19.6, 10.1. IR (thin film) 3067, 2917, 1741, 1593, 1549, 1430, 1260, 1178, 1116, 892 cm^{-1}. HRMS calcd for C_9H_8ClN 165.0345, found 165.0343. mp 38-40 °C.



Compound 4.2. In a glove box, *n*-BuLi (1.71 M in hexanes; 6.40 mL, 11.0 mmol) was added by syringe over ~2 minutes to a solution of pentamethylcyclopentadiene (1.70 mL, 11.0 mmol) in THF (30.0 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (1.35 g,

10.6 mmol) in THF (10.0 mL). After 10 minutes, a solution of the lithium salt of 2-chloro-4-methyl-pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.71 M in hexanes; 5.80 mL, 9.90 mmol) and 2-chloro-4-methyl-5H-[1]pyrindine (1.65 g, 10.0 mmol) in THF (15.0 mL) at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 6 h at room temperature, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (EtOAc:hexanes 1:9), furnishing 2.08 g (58%) of a purple solid.

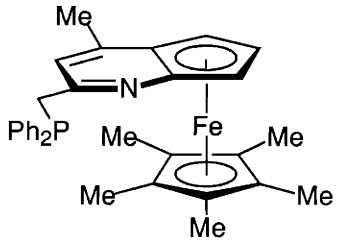
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (s, 1H), 4.70 (dd, 1H, J = 2.0), 4.24 (dd, 1H, J = 2.0), 3.88 (t, 1H, J = 2.0), 2.39 (s, 3H), 1.67 (s, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 9.74, 19.0, 61.7, 66.9, 76.2, 78.6, 80.3, 107.9, 116.0, 148.7, 154.4. FTIR (neat) 2969, 2904, 1572, 1526, 1379, 1246, 1098, 1029, 893, 803 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{19}H_{22}ClFeN$ (M^+) 355.0790, found 355.0792. mp 115-118 °C.



Compound 4.19. In a glove box, complex **4.2** (1.52 g, 4.27 mmol) was dissolved in Et_2O (80 mL) followed by addition of $Ni[PPh_2(CH_2)_3PPh_2]Cl_2$ (252 mg, 0.46 mmol). The mixture was cooled to –30 °C and MeMgBr (1.96 mL, 3.0 M in Et_2O, 5.88 mmol) was added. The reaction mixture was allowed to stir at room temperature. After 20

h, NEt_3 was added, and the reaction was removed from the glove box and the mixture was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (EtOAc:hexanes 1:19), furnishing 1.15 g (80%) of a purple solid.

^1H NMR (500 MHz, C_6D_6) δ 6.31 (s, 1H), 4.71 (dd, 1H, J = 2.4, 0.6), 4.00 (d, 1H, J = 2.75), 3.63 (t, 1H, J = 2.4), 2.45 (s, 3H), 2.05, (s, 3H), 1.56 (s, 15H). ^{13}C NMR (126 MHz, C_6D_6) δ 159.8., 149.5, 114.9, 110.0, 81.5, 78.6, 75.7, 67.7, 61.8, 26.2, 19.5, 10.5. FTIR (neat) 2966, 2900, 2849, 1595, 1373, 1028 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{20}H_{25}FeN$ (M^+) 335.1331, found 335.1349.

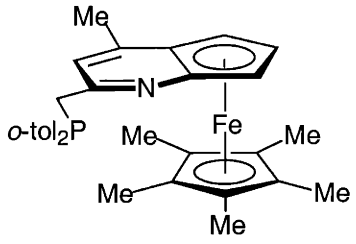


Compound 4.1. In a glove box, *n*-BuLi (1.61 M in hexanes; 2.13 mL, 3.43 mmol) was added by syringe over ~2 minutes to a solution of complex **4.19** (1.15 g, 3.43 mmol) in Et_2O (100 mL) cooled to –30 °C. The mixture was stirred for 10 minutes at room temperature, after which the reaction was cooled to –30 °C followed by addition of $ClPPh_2$. The resulting solution was stirred at room temperature. After 3 h, the reaction mixture was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was

purified by column chromatography (Et_2O : pentane 1: 5), furnishing 1.27 g (71%) of a purple solid.

^1H NMR (500 MHz, C_6D_6) δ 7.61-7.66 (m, 4H), 7.00-7.12 (m, 6H), 6.64 (s, 1H), 4.75, (s, 1H), 3.99 (s, 1H), 3.62-3.99 (m, 3H), 2.00 (s, 3H), 1.57 (s, 15H). ^{13}C NMR (126 MHz, C_6D_6) δ 160.4, 158.3, 149.9, 140.5, 140.3, 133.8, 133.7, 129.1, 129.0, 128.7, 118.1, 110.0, 81.8, 78.7, 76.0, 67.8, 61.8, 41.4, 19.5, 10.6. FTIR (neat) 3072, 2903, 1584, 1433, 740, 696 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{32}H_{34}FeNP$ (M^+) 519.1773, found 519.1761.

The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine/ethanol 50:50:0.4:1, 3.0 mL/min). Enantiomer (+)-**4.1** ($[\alpha]^{20}_D$ = +680° (c = 0.1, THF); enantiomerically pure by analytical chiral HPLC) was collected from 4.8 minutes to 5.6 minutes, and enantiomer (–)-**4.1** ($[\alpha]^{20}_D$ = -690° (c = 0.1, THF); enantiomerically pure by analytical chiral HPLC) was collected from 6.3 minutes to 7.4 minutes.

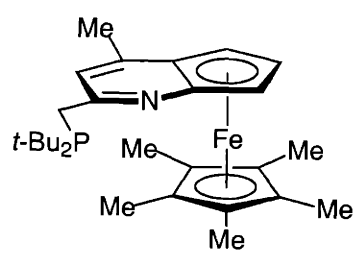


Compound 4.20. In a glove box, *n*-BuLi (1.61 M in hexanes; 70 μL, 0.11 mmol) was added by syringe over ~2 minutes to a solution of complex **4.19** (34 mg, 0.1 mmol) in Et_2O (2.0 mL) cooled to –30 °C. The mixture was stirred for 10 minutes at room temperature, after which the reaction was cooled to –30 °C followed by addition of $ClP(o\text{-tol})_2$ (37 mg, 0.15 mmol). The resulting solution was stirred at

room temperature. After 3 h, the reaction mixture was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (Et_2O : pentane 1: 5), furnishing 56 mg (99%) of a purple solid.

^1H NMR (500 MHz, C_6D_6) δ 7.70 (m, 1H), 7.64 (m, 1H), 6.94-7.07 (m, 6H), 6.67 (s, 1H), 4.73, (s, 1H), 3.99 (s, 1H), 3.67 (d, 1H, J = 4.0), 3.61 (s, 1H), 3.54 (d, 1H, J = 4.0) 2.44 (s, 3H), 2.40 (s, 3H), 2.01 (s, 3H), 1.55 (s, 15H). ^{13}C NMR (126 MHz, C_6D_6) δ 160.4, 160.3, 149.8, 142.8, 142.5, 138.3, 138.1, 132.8, 132.5, 130.7, 130.6, 129.1, 128.7, 126.9, 117.9, 110.0, 81.7, 78.7, 76.0, 67.8, 61.8, 39.7, 21.8, 21.6, 19.5, 10.6. FTIR (neat) 2920, 2851, 1587, 1451, 747 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{34}H_{38}FeNP$ (M^+) 547.2086, found 547.2064.

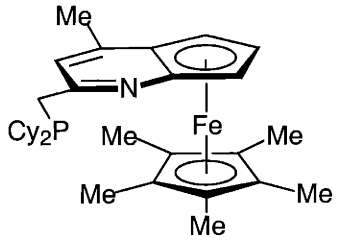
The enantiomers of the catalyst were separated by semi-preparative HPLC (Regis (*R,R*)-Whelk-O 2, 1 cm x 25 cm, chloroform/hexanes/diethylamine/ethanol 25:75:0.2:0.5, 3.0 mL/min). The first enantiomer was collected from 8.2 minutes to 9.7 minutes, and the second was collected from 10.8 minutes to 12.5 minutes.



Compound 4.22. In a glove box, *n*-BuLi (1.61 M in hexanes; 70 μL, 0.11 mmol) was added by syringe over ~2 minutes to a solution of complex **4.19** (34 mg, 0.1 mmol) in Et_2O (2.0 mL) cooled to –30 °C. The mixture was stirred for 10 minutes at

room temperature, after which the reaction was cooled to –30 °C followed by addition of ClP(*t*-Bu)$_2$ (28 mg, 0.15 mmol). The resulting solution was stirred at room temperature. After 3 h, the reaction mixture was filtered through a 1" plug of silica gel. The silica gel was washed with NEt$_3$/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (Et$_2$O : pentane 1: 5), furnishing 43mg (88%) of a purple solid.

^{1}H NMR (500 MHz, C_6D_6) δ 7.12 (s, 1H), 4.75 (dd, 1H, J = 2.8, 1.2), 4.01 (dd, 1H, J = 2.8, 1.2), 3.62 (t, 1H, J = 2.8), 3.44 (dd, 1H, 13.7, 4.6), 3.01 (dd, 1H, J = 14.0, 1.2), 2.08 (d, 3H, J = 0.9), 1.62 (s, 15H), 1.19 (d, 9H, J = 10.7), 1.14 (d, 9H, J = 11.0). ^{13}C NMR (126 MHz, C_6D_6) δ 163.7, 149.3, 118.4, 109.8, 81.6, 78.7, 75.7, 67.8, 61.9, 34.5, 32.9, 31.8, 30.4, 30.3, 19.6, 10.7. FTIR (neat) 2940, 2899, 2860, 1590, 1471, 1297, 1029, 810 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{28}H_{42}FeNP$ (M^+) 479.2399, found 479.2406.



Compound 4.23. In a glove box, *n*-BuLi (1.61 M in hexanes; 70 μL, 0.11 mmol) was added by syringe over ~2 minutes to a solution of complex **4.19** (37 mg, 0.1 mmol) in Et$_2$O (2.0 mL) cooled to –30 °C. The mixture was stirred for 10 minutes at room temperature, after which the reaction was cooled to –30 °C followed by addition of ClPCy$_2$ (35 mg, 0.15 mmol). The resulting solution was stirred at room temperature. After 3 h, the reaction mixture was filtered through a 1" plug of silica

gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (Et_2O : pentane 1: 5), furnishing 55 mg (94%) of a purple solid.

^1H NMR (500 MHz, C_6D_6) δ 6.93 (d, 1H, J = 1.2), 4.76 (dd, 1H, J = 2.4, 0.9), 4.01 (dd, 1H, J = 2.8, 1.2), 3.63 (t, 1H, J = 2.4), 3.24 (dd, 1H, 13.1, 4.0), 3.02 (d, 1H, J = 13.4), 2.08 (d, 3H, J = 0.9), 1.88-1.95 (m, 4H), 1.65-1.80 (m, 7H), 1.63 (s, 15H), 1.07-1.61 (m, 11H). ^{13}C NMR (126 MHz, C_6D_6) δ 162.9, 149.4, 118.3, 110.0, 81.6, 78.7, 75.7, 67.7, 61.9, 34.8, 34.7, 34.5, 30.8, 30.5, 30.1, 29.9, 28.2, 28.02, 28.01, 28.0, 27.3, 27.2, 19.6, 10.7. FTIR (neat) 2922, 2849, 1590, 1446, 1298, 1029 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{32}H_{46}FeNP$ (M^+) 531.2712, found 531.2700.

III. Catalytic Enantioselective Hydrosilylation of Acetophenone as a Function of Silane

General procedure (Table 4.1, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added acetophenone (12 mg, 0.1 mmol) in 1.5 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of *n*-octylSiH$_3$ (29 mg, 39μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 1% ee in favor of (*R*)-*sec*-phenethyl alcohol.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 5% ee.

Table 4.1, entry 2. The general procedure was followed using ligand (+)-**4.1** and PhSiH$_3$, which afforded (*R*)-*sec*-phenethyl alcohol with 6% ee.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 10% ee.

Table 4.1, entry 3. The general procedure was followed using ligand (+)-**4.1** and Et_2SiH_2, which afforded (*R*)-*sec*-phenethyl alcohol with 2% ee.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 0% ee.

Table 4.1, entry 4. The general procedure was followed using ligand (+)-**4.1** and $PhMeSiH_2$, which afforded (*R*)-*sec*-phenethyl alcohol with 64% ee.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 67% ee.

Table 4.1, entry 5. The general procedure was followed using ligand (+)-**4.1** and Ph_2SiH_2, which afforded (*R*)-*sec*-phenethyl alcohol with 79% ee.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 80% ee.

Table 4.1, entry 6. The general procedure was followed using ligand (+)-**4.1** and (α-Np)$PhSiH_2$, which afforded (*R*)-*sec*-phenethyl alcohol with 88% ee.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 91% ee.

Table 4.1, entry 7. The general procedure was followed using ligand (+)-**4.1** and (*o*-tol)$PhSiH_2$, which afforded (*R*)-*sec*-phenethyl alcohol with 94% ee.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 95% ee.

Table 4.1, entry 8. The general procedure was followed using ligand (+)-**4.1** and $MesPhSiH_2$, which afforded (*R*)-*sec*-phenethyl alcohol with 98% ee.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 98% ee.

Table 4.1, entry 9. The general procedure was followed using ligand (+)-**4.1** and $(o\text{-tol})_2SiH_2$, which afforded (*R*)-*sec*-phenethyl alcohol with 91% ee.

When ligand (–)-**4.1** was used, (*S*)-*sec*-phenethyl alcohol was obtained with 93% ee.

Table 4.1, entry 10. The general procedure was followed using ligand (+)-**4.1** and Mes_2SiH_2. The reaction results in no apparent conversion.

When ligand (–)-**4.1** was used, the reaction results in no apparent conversion.

IV. Catalytic Enantioselective Hydrosilylation of Acetophenone as a Function of Metal and Ligand

For Methods Used to Assay Enantiomeric Excess, see Section XVI.

General procedure (Table 4.2, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added acetophenone (12 mg, 0.10 mmol) in 1.5 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of Ph_2SiH_2 (36 mg, 40μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 80% ee in favor of (*R*)-*sec*-phenethyl alcohol.

Table 4.2, entry 2. The general procedure was followed using ligand (–)-**4.20**, which afforded *sec*-phenethyl alcohol with 64% ee.

Table 4.2, entry 3. The general procedure was followed using ligand (–)-**4.21**, which afforded *sec*-phenethyl alcohol with 84% ee.

Table 4.2, entry 4. The general procedure was followed using $[IrCl(COD)]_2$ and ligand (+)-**4.1**, which afforded (*S*)-*sec*-phenethyl alcohol with 51% ee.

V. Scope of Catalytic Enantioselective Hydrosilylation

General procedure (Table 3, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added acetophenone (12 mg, 0.10 mmol) in 1.5 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of $MesPhSiH_2$ (45 mg, 50μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 98% ee in favor of (*R*)-*sec*-phenethyl alcohol.

Table 4.3, entry 2. The general procedure was followed using ligand (+)-**4.1** and 4'-methoxyacetophenone. The reaction mixture is quenched with 1% K_2CO_3 in MeOH in place of HCl/acetone, affording (*R*)-4-methoxy-α-methylbenzyl alcohol with 94% ee.

Table 4.3, entry 3. The general procedure was followed using ligand (+)-**4.1** and 4'-(trifluoromethyl)acetophenone, affording (*R*)-α-methyl-4-(trifluoromethyl)benzyl alcohol with 94% ee.

Table 4.3, entry 4. The general procedure was followed using ligand (+)-**4.1** and 1-acetonaphthone, affording (*R*)-α-methyl-1-naphthalenemethanol with 96% ee.

Table 4.3, entry 5. The general procedure was followed using ligand (–)-**4.1** and α-tetralone, affording (*S*)-1,2,3,4-tetrahydro-1-naphthol with 93% ee.

Table 4.3, entry 6. The general procedure was followed using ligand (+)-**4.1** and 2',4'-dimethylacetophenone, affording (*R*)-2,4-dimethyl-α-methylbenzyl alcohol with 92% ee.

Table 4.3, entry 7. The general procedure was followed using ligand (+)-**4.1** and 2',4',6'-trimethylacetophenone. The reaction mixture is quenched with 1% K_2CO_3 in MeOH in place of HCl/acetone, affording (*R*)-α-methyl-2,4,6-(trimethyl)benzyl alcohol with 96% ee.

Table 4.3, entry 8. The general procedure was followed using ligand (–)-**4.1** and propiophenone, affording (*S*)-1-phenyl-1-propanol with 95% ee.

Table 4.3, entry 9. The general procedure was followed using ligand (+)-**4.1** and isobutyrophenone, affording (*S*)-2-methyl-1-phenyl-1-propanol with 86% ee. (very low conversion).

Table 4.3, entry 10. The general procedure was followed using ligand (+)-**4.1** and 2,2-diemthylpropiophenone ketone resulting in a very low conversion.

Table 4.3, entry 11. The general procedure was followed using ligand (+)-**4.1** and 2-acetylpyridine, affording (*R*)-methyl-2-pyridinemethanol with 79% ee.

VI. Catalytic Enantioselective Hydrosilylation of Cyclohexylmethyl Ketone as a Function of Silane

General procedure (Table 4, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added cyclohexylmethyl ketone (12.6 mg, 0.10 mmol) in 1.5 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of Ph_2SiH_2 (36 mg, 40μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC of the acetate of the product showed 75% ee in favor of (*R*)-1-cyclohexylethanol.

Table 4.4, entry 2. The general procedure was followed using ligand (–)-**4.1** and α-$NpPhSiH_2$, which afforded (*R*)-1-cyclohexylethanol with 86% ee.

Table 4.4, entry 3. The general procedure was followed using ligand (–)-**4.1** and (*o*-tol)$PhSiH_2$, which afforded (*S*)-1-cyclohexylethanol with 90% ee.

Table 4.4, entry 4. The general procedure was followed using ligand (–)-**4.1** and (*o*-tol)$_2SiH_2$, which afforded (*S*)-1-cyclohexylethanol with 92% ee.

Table 4.4, entry 5. The general procedure was followed using ligand (–)-**4.1** and using $MesPhSiH_2$, which afforded (*S*)-1-cyclohexylethanol with 86% ee.

VII. Catalytic Enantioselective Hydrosilylation of as a Function of Silane and Ligand

General procedure (Table 5, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (–)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added *n*-hexylmethyl ketone (12.8 mg, 0.10 mmol) in 1.5 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of α-$NpPhSiH_2$ (47 mg, 50μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC of the acetate of the product showed 54% ee in favor of (*S*)-*n*-hexylethanol.

Table 4.5, entry 2. The general procedure was followed using ligand (–)-**4.1** and (*o*-tol)$PhSiH_2$, which afforded (*S*)-*n*-hexylethanol with 60% ee.

Table 4.5, entry 3. The general procedure was followed using ligand (–)-**4.1** and $(o\text{-tol})_2SiH_2$, which afforded (*S*)-*n*-hexylethanol with 64% ee.

Table 4.5, entry 4. The general procedure was followed using ligand (–)-**4.1** and $MesPhSiH_2$, which afforded (*S*)-*n*-hexylethanol with 38% ee.

Table 4.5, entry 5. The general procedure was followed using ligand **4.21** and Ph_2SiH_2, which afforded *n*-hexylethanol with 62% ee.

Table 4.5, entry 6. The general procedure was followed using ligand **4.21** and α-$NpPhSiH_2$, which afforded *n*-hexylethanol with 43% ee.

Table 4.5, entry 7. The general procedure was followed using acetophenone, ligand (–)-**4.21** and $MesPhSiH_2$, which afforded *sec*-phenethyl alcohol with 17% ee.

VIII. Catalytic Enantioselective Hydrosilylation of *n*-Hexylmethyl Ketone as a Function of Rhodium Source

General procedure (Table 4.6, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added *n*-hexylmethyl ketone (12.8 mg, 0.1 mmol) in 1.5 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of $(o\text{-tol})_2SiH_2$ (42 mg, 40μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 64% ee in favor of (*R*)-*n*-hexylethanol.

Table 4.6, entry 2. The general procedure was followed using $[RhCl(NBD)]_2$, which afforded (*R*)-*n*-hexylethanol with 64% ee.

Table 4.6, entry 3. The general procedure was followed using $Rh(COD)_2BF_4$, which afforded (*R*)-*n*-hexylethanol with 62% ee.

Table 4.6, entry 4. The general procedure was followed using $Rh(COD)_2PF_6$, which afforded (*R*)-*n*-hexylethanol with 63% ee.

Table 4.6, entry 5. The general procedure was followed using $Rh(COD)_2ClO_4$, which afforded (*R*)-*n*-hexylethanol with 64% ee.

Table 4.6, entry 6. The general procedure was followed using $Rh(COD)_2SbF_6$, which result in polymerization of the reaction mixture.

IX. Catalytic Enantioselective Hydrosilylation of Cyclohexylmethyl Ketone as a Function of Solvent

General procedure (Table 4.7, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (–)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added cyclohexylmethyl ketone (12.6 mg, 0.10 mmol) in 1.5 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of (*o*-tol)$PhSiH_2$ (40 mg, 50μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC of the acetate of the product showed 90% ee in favor of (*S*)-1-cyclohexylethanol.

Table 4.7, entry 2. The general procedure was followed using Et_2O as solvent, which afforded (*S*)-1-cyclohexylethanol with 90% ee.

Table 4.7, entry 3. The general procedure was followed using toluene as solvent, which afforded (*S*)-1-cyclohexylethanol with 88% ee.

Table 4.7, entry 4. The general procedure was followed using CH_2Cl_2 as solvent, which afforded (*S*)-1-cyclohexylethanol with 79% ee.

Table 4.7, entry 5. The general procedure was followed using CCl_4 as solvent, which afforded (*S*)-1-cyclohexylethanol with 94% ee.

X. Catalytic Enantioselective Hydrosilylation of Cyclohexylmethyl Ketone as a Function of Temperature

General procedure (Table 4.8, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (–)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added cyclohexylmethyl ketone (12.6 mg, 0.10 mmol) in 1.5 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of (*o*-tol)$PhSiH_2$ (40 mg, 50μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC of the acetate of the product showed 90% ee in favor of (*S*)-1-cyclohexylethanol.

Table 4.8, entry 2. The general procedure was followed at 0 °C, which afforded (*S*)-1-cyclohexylethanol with 92% ee.

Table 4.8, entry 3. The general procedure was followed at -40 °C, which afforded (*S*)-1-cyclohexylethanol with 94% ee.

XI. Scope of Dialkyl Ketones

General procedure for dialkyl ketones (Table 4.9, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (4.9 mg, 0.01 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (12.5 mg, 0.024 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added cyclohexylmethyl ketone (126 mg, 1.0 mmol) and 1 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of $(o\text{-tol})_2SiH_2$ (424 mg, 2.0 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 92% ee in favor of (*R*)-1-cyclohexylethanol.

Table 4.9, entry 2. The general procedure was followed using ligand (+)-**4.1** and cyclohexylethyl ketone, affording 1-cyclohexylpropanol with 62% ee.

Table 4.9, entry 3. The general procedure was followed using ligand (+)-**4.1** and 1-acetyl-1-cyclohexene, affording 1-cyclohexenylethanol with 51% ee.

Table 4.9, entry 4. The general procedure was followed using ligand (+)-**4.1** and 2,2-dimethylcyclohexanone, affording 2,2-dimethylcyclohexanol with 50% ee.

Table 4.9, entry 5. The general procedure was followed using ligand (+)-**4.1** and *trans*-4-phenyl-3-buten-2-one, affording *trans*-4-phenyl-3-buten-2-ol with 0% ee.

Table 4.9, entry 6. The general procedure was followed using ligand (+)-**4.1** and 1-adamantyl methyl ketone, affording (*R*)-(1-adamantanyl)ethanol with 92% ee.

Table 4.9, entry 7. The general procedure was followed using ligand (+)-**4.1** and benzylacetone, affording (*R*)-4-phenyl-2-butanol with 76% ee.

Table 4.9, entry 8. The general procedure was followed using ligand (–)-**4.1** and 2-octanone, affording (*S*)-2-octanol with 64% ee.

XII. Catalytic Enantioselective Hydrosilylation of Aryl Alkyl Ketones

General procedure for aryl alkyl ketones (Table 4.10, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (4.9 mg, 0.01 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (12.5 mg, 0.024 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added acetophenone (120 mg, 1.0 mmol) and 1 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of $MesPhSiH_2$ (453 mg, 2.0 mmol). The reaction mixture was then kept at room temperature. After 24-72 h, the reaction mixture was cooled to 0 °C and 10 mL of 1N HCl was added slowly followed by 10 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. Purification by silica gel chromatography (5-10% Et_2O in pentane) afforded 114 mg (93%) of (*R*)-*sec*-phenethyl alcohol. GC analysis showed 98% ee.

The general procedure was repeated with ligand (–)-**4.1** affording 115 mg (94%) of (*S*)-*sec*-phenethyl alcohol with 98% ee.

Table 4.10, entry 2. The general procedure was followed using ligand (+)-**4.1** and 4'-methoxyacetophenone. After 24 h, the reaction mixture is quenched with 1% K_2CO_3 in MeOH in place of HCl/acetone, affording 144 mg (95%) of (*R*)-4-methoxy-α-methylbenzyl alcohol with 97% ee ($[\alpha]^{20}_D$ = +42.3°, c = 1.06, toluene).

When ligand (–)-**4.1** was used, 150 mg (99%) of (*S*)-4-methoxy-α-methylbenzyl alcohol was obtained with 97% ee.

Table 4.10, entry 3. The general procedure was followed with ligand (+)-**4.1** and 4'-(trifluoromethyl)acetophenone, affording 174 mg (92%) of (*R*)-α-methyl-4-(trifluoromethyl)benzyl alcohol with 96% ee after 24 h of reaction time ($[\alpha]^{20}_D$ = +29.5°, c = 1.05, MeOH).

When ligand (–)-**4.1** was used, 160 mg (84%) of (*S*)-α-methyl-4-(trifluoromethyl)benzyl alcohol was obtained with 96% ee.

Table 4.10, entry 4. The general procedure was followed with ligand (+)-**4.1** and 1-acetonaphthone, affording 168 mg (98%) of (*R*)-α-methyl-1-naphthalenemethanol with 99% ee after 24 h of reaction time.

When ligand (–)-**4.1** was used, 165 mg (96%) of (*S*)-α-methyl-1-naphthalenemethanol was obtained with 99% ee.

Table 4.10, entry 5. The general procedure was followed with ligand (+)-**4.1** and α-tetralone, affording 140 mg (95%) of (*R*)-1,2,3,4-tetrahydro-1-naphthol with 98% ee after 72 h of reaction time ($[\alpha]^{20}_D$ = -32.5°, c = 2.51, $CHCl_3$).

When ligand (–)-**4.1** was used, 140 mg (95%) of (*S*)-1,2,3,4-tetrahydro-1-naphthol was obtained with 97% ee.

Table 4.10, entry 6. The general procedure was followed with ligand (+)-**4.1** and 2',4'-dimethylacetophenone, affording 143 mg (95%) of (*R*)-2,4-dimethyl-α-methylbenzyl alcohol with 97% ee after 24 h of reaction time ($[\alpha]^{20}_D$ = +59.0°, c = 1.05, EtOH).

When ligand (–)-**4.1** was used, 148 mg (99%) of (*S*)-2,4-dimethyl-α-methylbenzyl alcohol was obtained with 92% ee.

Table 4.10, entry 7. The general procedure was followed using ligand (+)-**4.1** and 2',4',6'-trimethylacetophenone. After 72 h, the reaction mixture is quenched with 1% K_2CO_3 in MeOH in place of Cl/acetone, affording 162 mg (99%) of (*R*)-α-methyl-2,4,6-(trimethyl)benzyl alcohol with 97% ee ($[\alpha]^{20}_D$ = +47.7°, c = 1.10, $CHCl_3$).

When ligand (–)-**4.1** was used, 162 mg (99%) of (*S*)-α-methyl-2,4,6-(trimethyl)benzyl alcohol was obtained with 99% ee.

Table 4.10, entry 8. The general procedure was followed with ligand (+)-**4.1** and propiophenone, affording 135 mg (98%) of (*R*)-1-phenyl-1-propanol with 98% ee after 72 h of reaction time ($[\alpha]^{20}_D$ = +47.2°, c = 5.02, $CHCl_3$).

When ligand (–)-**4.1** was used, 128 mg (94%) of (*S*)-1-phenyl-1-propanol was obtained with 98% ee.

XIII. Catalytic Enantioselective Hydrosilylation of Dialkyl Ketones

General procedure for dialkyl ketones (Table 4.11, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (4.9 mg, 0.01 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (12.5 mg, 0.024 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added cyclohexyl methyl ketone (126 mg, 1.0 mmol) and 1 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of $(o\text{-tol})_2SiH_2$ (424 mg, 2.0 mmol). The reaction mixture was then kept at 0 °C. After 48 h, the reaction mixture was added 10 mL of 1N HCl followed by 10 mL of acetone at 0 °C. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. Purification by silica gel chromatography (5-10% Et_2O in pentane) afforded 111 mg (87%) of (*R*)-1-cyclohexylethanol. GC analysis showed 94% ee ($[\alpha]^{20}_D$ = -6.69°, c = 3.05, Et_2O).

The general procedure was repeated with ligand (–)-**4.1**, affording 122 mg (95%) of (*S*)-1-cyclohexylethanol with 94% ee.

Table 4.11, entry 2. The general procedure was followed with ligand (+)-**4.1** and 1-adamantyl methyl ketone, affording 160 mg (89%) (*R*)-(1-adamantanyl)ethanol with 94% ee ($[\alpha]^{20}_D$ = +18.9°, c = 0.54, CCl_4).

When ligand (–)-**4.1** was used, 175 mg (95%) of (*S*)-1-(adamantanyl)ethanol was obtained with 97% ee.

Table 4.11, entry 3. The general procedure was followed with ligand (+)-**4.1** and benzylacetone, affording 147 mg (98%) of (*R*)-4-phenyl-2-butanol with 83% ee ($[\alpha]^{20}_D$ = -14.3°, c = 6.57, $CHCl_3$).

When ligand (–)-**4.1** was used, 146 mg (97%) of (*S*)-4-phenyl-2-butanol was obtained with 80% ee.

Table 4.11, entry 4. The general procedure was followed with ligand (+)-**4.1** and 2-octanone, affording 108 mg (83%) of (*R*)-2-octanol with 69% ee ($[\alpha]^{20}_D$ = -6.98°, c = 4.84, EtOH). When the reaction was carried out at –20 °C, 105 mg (81%) of (*R*)-2-octanol was obtained with 71% ee.

When ligand (–)-**4.1** was used, 115 mg (88%) of (*S*)-2-octanol was obtained with 68% ee. When the reaction was carried out at –20 °C, 106 mg (81%) of (*S*)-2-octanol was obtained with 72% ee.

XIV. Hydrosilylation of Benzaldehyde-1-*d*

Procedure for Hydrosilylation of Benzaldehyde-1-*d*. In a glove box, to a stirring solution of $[RhCl(NBD)]_2$ (4.6 mg, 0.01 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (12.5 mg, 0.024 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added benzaldehyde-1-*d* (107 mg, 1.0 mmol) and 1 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of $MesPhSiH_2$ (424 mg, 2.0 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature. Sodium bicarbonate solution was added and the reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. Purification by silica gel chromatography (5-10% Et_2O in pentane) afforded 82 mg (75%) of (*S*)-benzyl-1-*d* alcohol. The product was converted to its corresponding Mosher ester (derived from (*R*)-Mosher acid chloride). ^1H nmr revealed the product with 95% ee (δ 5.31 ppm).

When ligand (–)-**4.1** was used, 80 mg (73%) of (*R*)-benzyl-1-*d* alcohol was obtained. The product was converted to its corresponding Mosher ester (derived from (*R*)-Mosher acid chloride). ^1H nmr revealed the product with 94% ee (δ 5.36 ppm).

XV. Enantioselectivities of Silanes as a Function of Carbonyl Compounds

General procedure (Table 4.12, entry 1). In a glove box, to a stirring solution of $[RhCl(NBD)]_2$ (1.15 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added $MesPhSiH_2$ (56 mg, 0.25 mmol) in 0.25 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of acetophenone (89 mg, 0.75 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was added EtMgCl (0.75 mL, 2.0 M in THF). The reaction was allowed to stand for 18-24h. The reaction mixture was cooled to 0 °C and 2 mL of 1N HCl was added slowly followed by 2 mL of acetone. The reaction mixture was then extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was purified by column chromatography (100% pentane) and HPLC showed 72% ee of ethylmesitylphenylsilane.

When ligand (–)-**4.1** was used, the chiral silane product was obtained with 72% ee.

Table 4.12, entry 2. The general procedure was followed using ligand (+)-**4.1** and benzophenone, and 3% ee of ethylmesitylphenylsilane was obtained.

When ligand (–)-**4.1** was used, the chiral silane product was obtained with 1% ee.

Table 4.12, entry 3. The general procedure was followed using ligand (+)-**4.1** and benzaldehyde, and 76% ee of ethylmesitylphenylsilane was obtained.

When ligand (–)-**4.1** was used, the chiral silane product was obtained with 75% ee.

Table 4.12, entry 4. The general procedure was followed using ligand (+)-**4.1** and cyclohexyl methyl ketone, and 69% ee of ethylmesitylphenylsilane was obtained.

When ligand (–)-**4.1** was used, the chiral silane product was obtained with 69% ee.

Table 4.12, entry 5. The general procedure was followed using ligand (+)-**4.1** and *n*-hexyl methyl ketone, and 83% ee of ethylmesitylphenylsilane was obtained.

When ligand (–)-**4.1** was used, the chiral silane product was obtained with 84% ee.

Table 4.12, entry 6. The general procedure was followed using ligand (+)-**4.1** and acetone, and 53 mg (84%) of ethylmesitylphenylsilane was obtained with 93% ee. $[\alpha]^{20}_{D}$ = +29.8°, c = 1.00, hexanes.

^{1}H NMR (500 MHz, C_6D_6) δ 7.54 (m, 2H), 7.16 (m, 3H), 6.77 (s, 2H), 5.37 (m, 1H), 2.37, (s, 6H), 2.13 (s, 3H), 1.22 (m, 1H), 1.14 (m, 4H). ^{13}C NMR (126 MHz, C_6D_6) δ 145.6, 139.9, 136.5, 135.4, 129.8, 129.5, 128.7, 128.3, 24.8, 21.5, 9.6, 5.7. FTIR (neat) 2955, 2138, 1604, 1428, 1108, 847, 804 cm^{-1}. HRMS (ES, *m/e*) calcd for $C_{17}H_{22}Si$ [(M+Na)$^{+}$] 277.1383, found 277.1393.

When ligand (–)-**4.1** was used, 49 mg (79%) ethylmesitylphenylsilane was obtained with 92% ee. $[\alpha]^{20}_{D}$ = -31.2°, c = 1.02, hexanes.

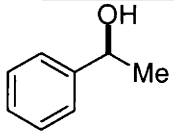
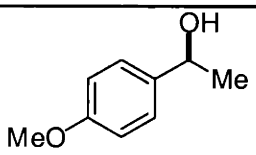
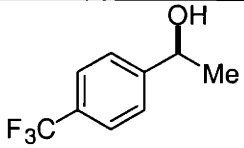
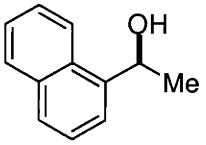
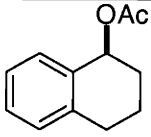
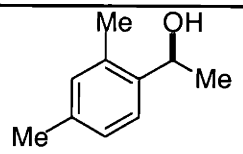
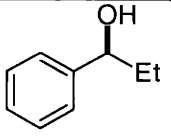
When the general procedure was followed using ligand (+)-**4.1** and acetone, but without the addition of EtMgCl, the corresponding silylether product was obtained with 97% ee. $[\alpha]^{20}_D$ = +53.7°, c = 1.00, hexanes. This was repeated using ligand (–)-**4.1**, giving the opposite enantiomer in 97% ee. $[\alpha]^{20}_D$ = -54.7°, c = 1.02, hexanes.

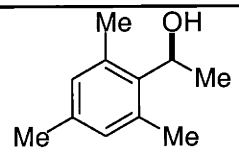
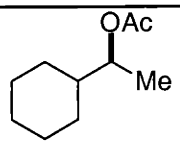
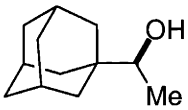
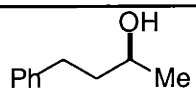
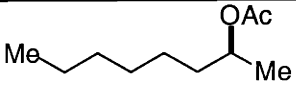
^{1}H NMR (300 MHz, C_6D_6) δ 7.68 (m, 2H), 7.13 (m, 3H), 6.71 (s, 2H), 6.01 (s, 1H), 4.06, (sept, 1H, J = 6.0), 2.44 (s, 6H), 2.07 (s, 3H), 1.16 (d, 3H, J = 6.0), 1.10 (d, 3H, J = 6.0). ^{13}C NMR (126 MHz, C_6D_6) δ 145.7, 140.6, 136.8, 135.0, 130.4, 129.6, 128.9, 128.7, 68.3, 25.72, 25.68, 23.9, 21.6. FTIR (neat) 2970, 2141, 1604, 1429, 1381, 1116, 1017, 881 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{18}H_{24}OSi$ [(M+Na)$^+$] 307.1486, found 307. 1486.

Table 4.12, entry 7. The general procedure was followed using ligand (+)-**4.1** and acetaldehyde, and 37% ee of ethylmesitylphenylsilane was obtained.

When ligand (–)-**4.1** was used, the chiral silane product was obtained with 38% ee.

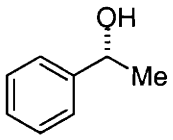
XVI. Methods Used to Assay Enantiomeric Excess

Substrate or its derivative	ee Assay	Conditions	Retention Time of Isomer with Indicated Configuration (min)	Retention Time of Isomer with Opposite Configuration (min)
	GC Chiraldex BPH	70 °C; 1.0 mL/min Carrier gas flow	35.79	34.97
	GC Chiraldex G-TA	100 °C; 1.0 mL/min Carrier gas flow	26.18	24.58
	GC Chiraldex G-TA	100 °C; 1.0 mL/min Carrier gas flow	7.66	6.91
	Chiralcel Analytical OD Column	10:90 isopropanol : hexanes	10.01	15.50
	GC Chiraldex GTA	110 °C; 1.0 mL/min Carrier gas flow	20.00	19.45
	GC Chiraldex G-TA	105 °C; 1.0 mL/min Carrier gas flow	14.85	12.53
	GC Chiraldex GTA	90 °C; 1.0 mL/min Carrier gas flow	15.64	13.95

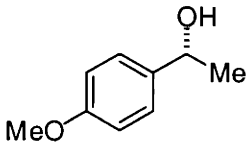
	GC Chiraldex BPH	120 °C; 1.0 mL/min Carrier gas flow	13.62	13.16
	GC Chiraldex GTA	70 °C; 1.0 mL/min Carrier gas flow	17.64	19.90
	GC Chiraldex BPH	110 °C; 1.0 mL/min Carrier gas flow	40.05	38.94
	GC Chiraldex G-TA	90 °C; 1.0 mL/min carrier gas flow	21.45	22.29
	GC Chiraldex G-TA	70 °C; 1.0 mL/min carrier gas flow	11.36	12.80

XVII. Assignment of Absolute Stereochemistry

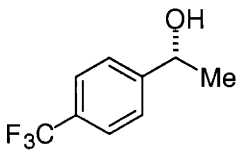
Assignment of Absolute Configuration. The absolute configurations were established through comparison of the retention time on the chiral GC/HPLC columns or the sign of the optical rotation of our alcohols with rotations reported in the literature. For those alcohols not listed below, the assignment of absolute configuration was based on analogy.



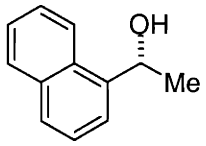
The absolute configuration of the alcohol produced in the presence of (+)-**4.1** is assigned based on the comparing the retention time on chiral GC with (*R*)-*sec*-phenethyl ethanol.



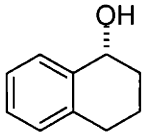
The sign of the optical rotation of the alcohol produced in the presence of (+)-**4.1** is positive; therefore, its absolute stereochemistry is *R*.[9]



The sign of the optical rotation of the alcohol produced in the presence of (+)-**4.1** is positive; therefore, its absolute stereochemistry is *R*.[35]

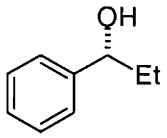


The absolute configuration of the alcohol produced in the presence of (+)-**4.1** is assigned based on the comparing the retention time on chiral HPLC with (*R*)-α-methyl-1-naphthalenemethanol.

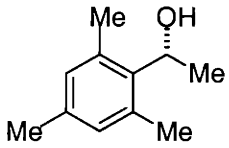


The sign of the optical rotation of the alcohol produced in the presence of (+)-**4.1** is negative; therefore, its absolute stereochemistry is *R*.[9]

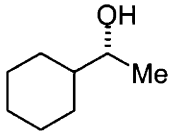
35 Nakamura, K.; Matsuda, T. *J. Org. Chem.* **1998**, *63*, 8957-8964.



The sign of the optical rotation of the alcohol produced in the presence of (+)-**4.1** is positive; therefore, its absolute stereochemistry is *R*.[36]

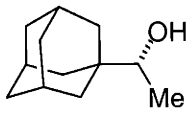


The sign of the optical rotation of the alcohol produced in the presence of (+)-**4.1** is positive; therefore, its absolute stereochemistry is *R*.[35]

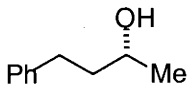


The sign of the optical rotation of the alcohol produced in the presence of (+)-**4.1** is negative; therefore, its absolute stereochemistry is *R*.[9]

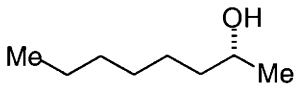
36 Kasai, M.; Froussios, C.; Ziffer, H. *J. Org. Chem.* **1983**, *48*, 459-464.



The sign of the optical rotation of the corresponding acetate produced in the presence of (+)-**4.1** is positive; therefore, its absolute stereochemistry is *R*.[9]



The sign of the optical rotation of the alcohol produced in the presence of (+)-**4.1** is negative; therefore, its absolute stereochemistry is *R*.[9]



The sign of the optical rotation of the alcohol produced in the presence of (+)-**4.1** is negative; therefore, its absolute stereochemistry is *R*.[9]

Appendix I:

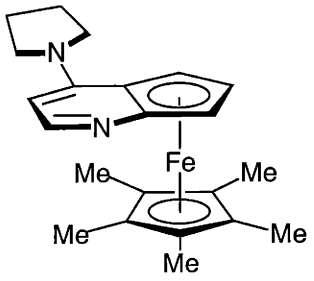
Miscellaneous Planar-Chiral Heterocycles and Their Applications in Asymmetric Catalysis

In this chapter, the synthesis of some planar-chiral heterocycles and attempts to apply them in asymmetric catalysis will be presented. Also, preliminary results in applying planar-chiral pyridine *N*-oxides and *N,P*-ligands in other asymmetric processes will be discussed.

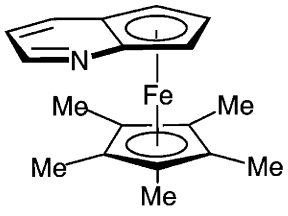
Section I. Substitution of a 2-Amino Group in a Planar-Chiral Pyridine

It has been shown in our group that planar-chiral 4-(pyrrolidino)pyrindine **5.1** can serve as an effective nucleophilic catalyst for the rearrangement of *O*-acylated enolates to β-dicarbonyls,[1] and the addition of imines to ketenes to give β-lactams.[2] However, the parent compound **5.2**, which lacks the 4-amino group, displayed poor catalytic reactivity in the acylation of *sec*-phenethyl alcohol with acetic anhydride or diketene and in the cyanosilylation of dodecanal.[3]

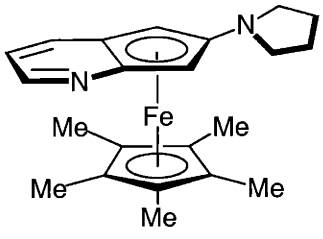
Scheme 5.1 Planar-Chiral Pyridine Derivatives



5.1



5.2



5.3

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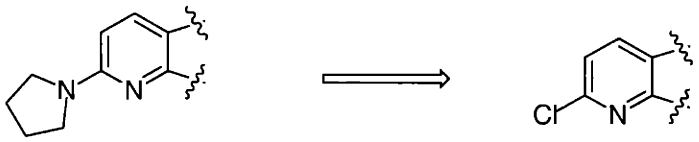
1 Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 11532-11533.

2 Hodous, B. L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 1578-1579.

3 (a) Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 7230-7231. (b) Ruble, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

In order to evaluate the importance of the position of the pyrrolidino group in catalysis, our group has synthesized 6-(pyrrolidino)pyrindine **5.3**.[4] Compared with the parent compound **5.2**, increased nucleophilicity was observed by installing a pyrrolidino group at the 6-position of the pyrindine ring. However, the effect is relatively small compared with that of the 4-(pyrrolidino)pyrindine derivative **5.1**.

Scheme 5.2 Retrosynthesis of a 2-Amino Pyridine Derivative



5.4 **5.5**

Inspired by the recent developments in the synthesis of 2-substituted planar-chiral heterocycles in our group,[4] we anticipated that compound **5.4** could be easily accessed by a coupling reaction between 2-chloropyrindine derivative **5.5** and pyrrolidine. The synthetic route is depicted in Scheme 5.3. Cyclization of **5.6** was carried out in concentrated H_2SO_4 and Ac_2O to give 2-hydroxypyrindine **5.7**, which was reacted with $POCl_3$ to give 2-chloropyrindine **5.8**. Oxidation with peracetic acid furnished the 2-chloropyrindine *N*-oxide **5.9**, which, when reacted with Ac_2O, gave the rearranged acetate **5.10**. Palladium-catalyzed amination of 2-chloropyrindine derivative **5.11** with pyrrolidine gave the corresponding 2-(pyrrolidino)pyrindine. However, decomposition was observed in attempting to eliminate AcOH to give the corresponding olefins **5.12** and **5.13**. Interestingly, when piperidine was used in place of pyrrolidine, we were able to obtain the olefinic top ring, which was then complexed to (FeClCp*) to give heterocycle **5.14**.

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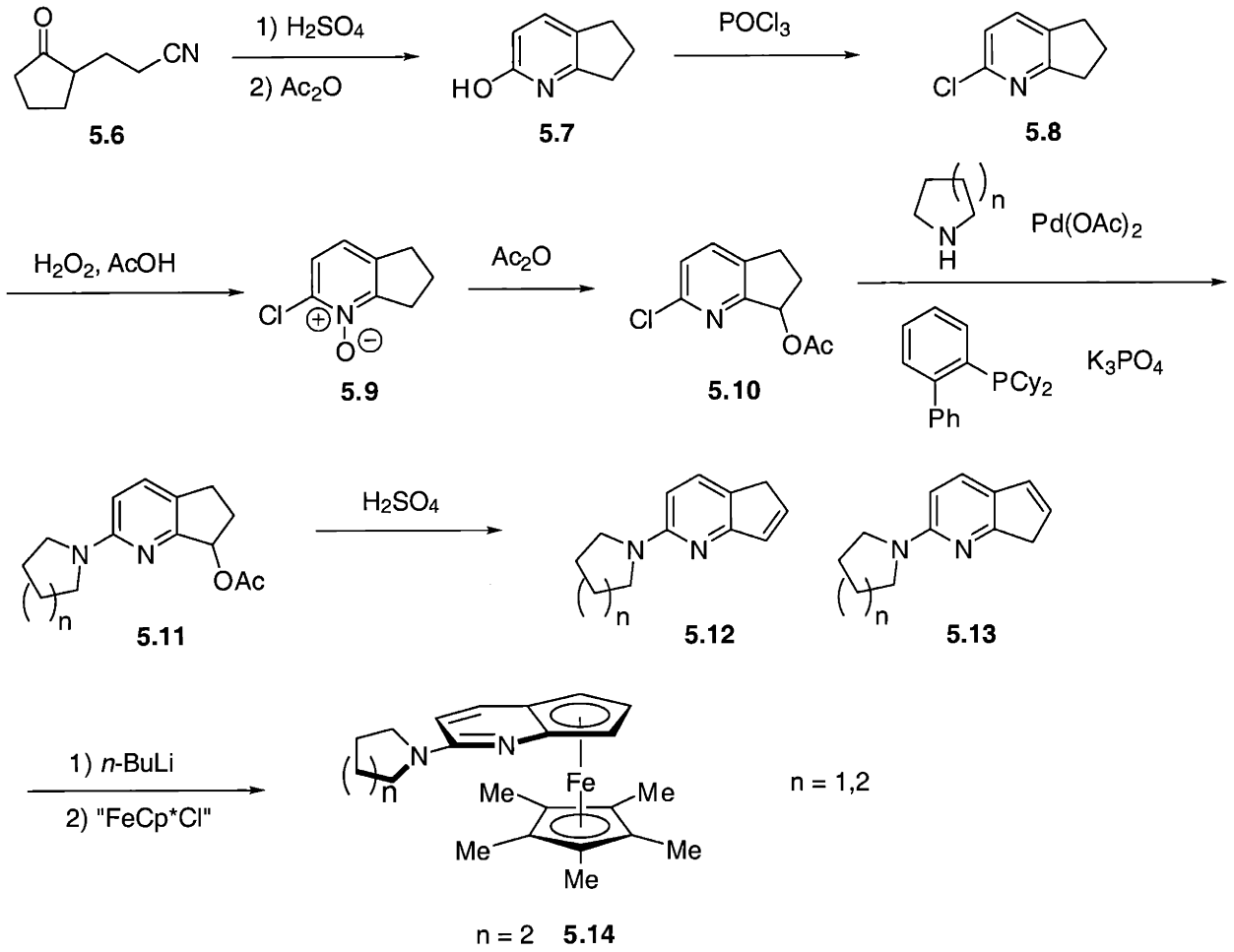
4 Liang, J. S. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

Scheme 5.3 Synthetic Route to the Planar-Chiral 2-Amino Pyrindine



To evaluate the nucleophilicity of **5.14**, the half-life of the acylation reaction of *sec*-phenethyl alcohol with acetic anhydride was compared to other planar-chiral ferrocene complexes, as shown in Table 5.1.

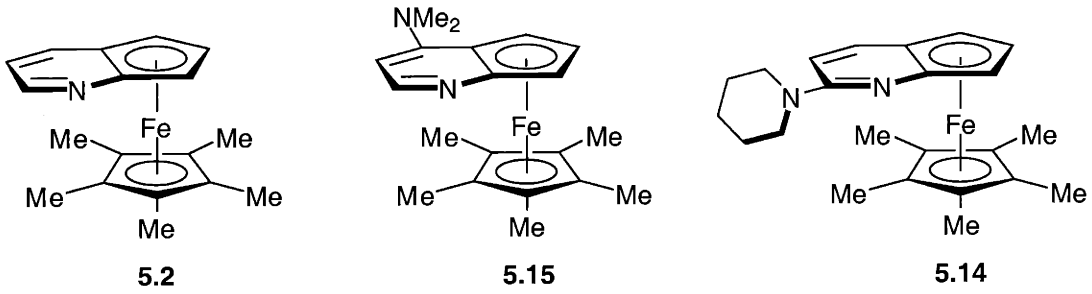
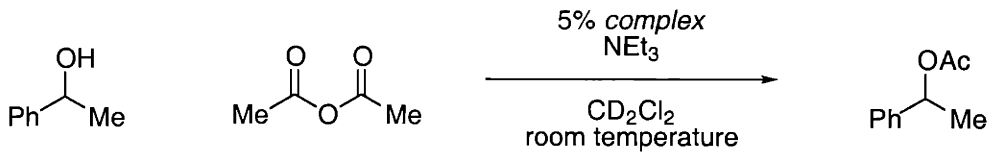


Table 5.1 Determination of Half-life in the Acylation of *sec*-Phenethyl Alcohol[5]



complex	half-life (min)
none	2600
5.2	no catalysis
5.15	20
5.14	>1200

Previous studies in our group revealed that there was a background reaction in the absence of a catalyst. In the presence of the pyrindinyl complex **5.2**, the rate of the reaction was not significantly different from that of the background reaction. While the presence of a 4-dialkylamino group on the pyridinyl iron complex enhanced the activity of the reaction as shown in complex **5.15**, incorporation of a 2-piperidino group on the pyrindine ring completely shut down the nucleophilicity of the pyrindine nitrogen (**5.14**).

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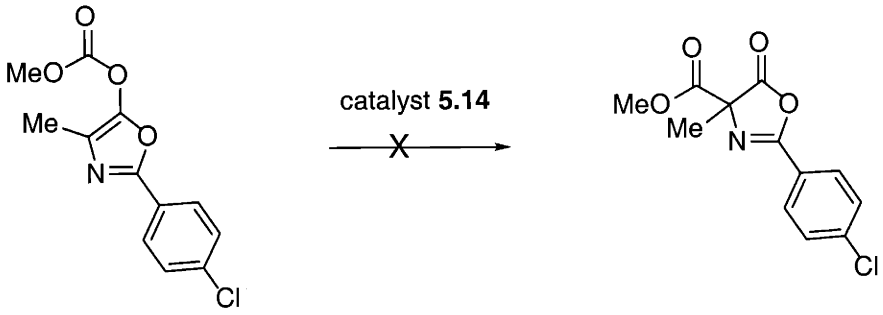
5 The half-life data for complexes **5.2** and **5.15** are extracted from: Ruble, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

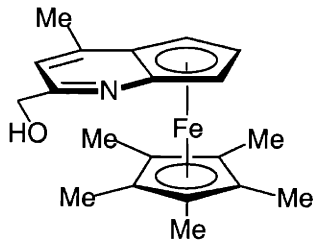
Scheme 5.4 Rearrangement of an *O*-Acylated Azlactone



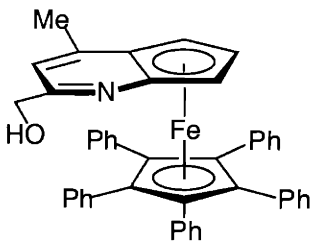
It was reported in our group that **5.1** also served as an effective catalyst for the rearrangement of *O*-acylated enolates to β-dicarbonyls. However, no reactivity was observed when 2-(piperidino)pyrindine derivative **5.14** was used instead. This is probably because the substituent on the 2-position of the pyridinyl ring exerts a steric interaction with the nucleophilic heterocyclic nitrogen, which in turn shuts down the nucleophilicity of the molecule.

Section II. Synthesis of Planar-Chiral *N,O*-Ligands and Their Application to Asymmetric Catalysis

Scheme 5.5 Planar-Chiral *N,O*-Ligand



5.16

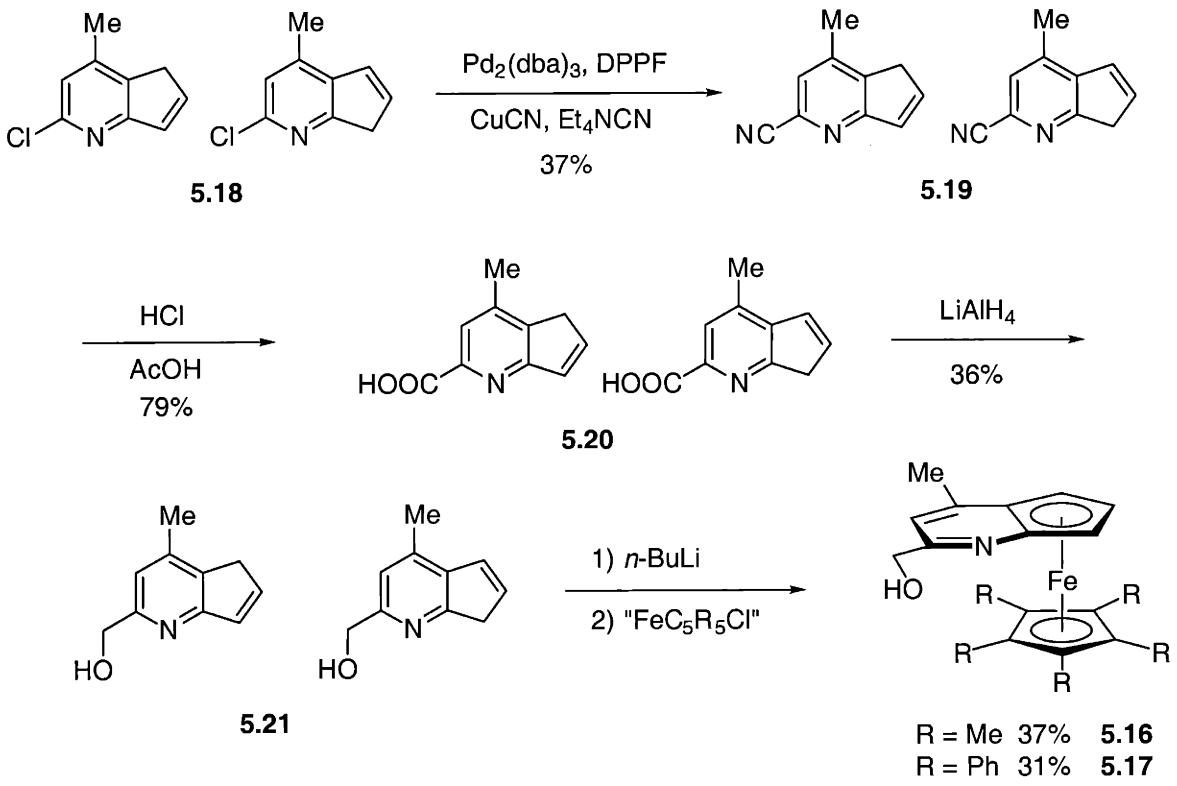


5.17

As an extension of our development of planar-chiral ligands, it occurred to us that complexes **5.16** and **5.17** could serve as bidentate ligands in asymmetric catalysis. We were pleased to discover that *N,O*-complexes could be prepared as shown in Scheme 5.6. First, 2-chloro-4-methylpyridinyl derivative **5.18** was converted to 2-cyano-4-methylpyrindine **5.19** as a mixture of isomers. The cyano group could be hydrolyzed in the presence of strong acid, then reduced with $LiAlH_4$ to give **5.21**. The deprotonated top ring was then complexed with "$FeClC_5R_5$" (R = Me, Ph) to give the corresponding *N,O*-ligand. These complexes could be resolved by chiral HPLC into their enantiomers, and they were examined in the asymmetric reduction

of acetophenone to *sec*-phenethyl alcohol[6] as well as the asymmetric addition of diethylzinc to benzaldehyde.[7]

Scheme 5.6 Synthesis of Planar-Chiral *N,O*-Complexes



As shown in Scheme 5.7, complexes **5.16** and **5.17** were not effective ligands in the asymmetric reduction of acetophenone, leading to racemic product.

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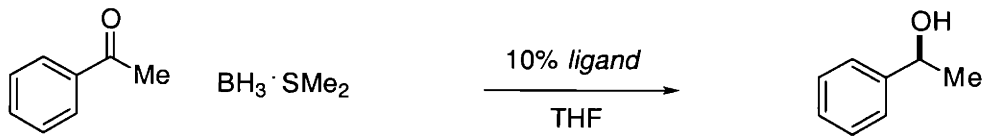
6 For a review of asymmetric hydroboration of carbonyl groups, see: (a) Itsuno, S. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Chapter 6.4. (b) Corey, E. J.; Helal, C. J. *Angew. Chem. Int. Ed.* **1998**, *37*, 1986-2012.

7 For a review of asymmetric alkylation of carbonyl groups, see: Soai, K.; Shibata, T. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Chapter 26.1.

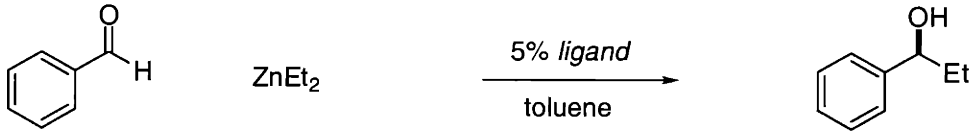
Scheme 5.7 Asymmetric Reduction of Acetophenone Using 5.16 and 5.17 as Ligands



ligand **5.16**: ee = 0%
ligand **5.17**: ee = 0%

Attempts to apply these new planar-chiral *N,O*-complexes to the enantioselective addition of diethylzinc to benzaldehyde resulted in low enantiomeric excess of *sec*-phenylpropanol when **5.16** was used as the ligand. Increasing the steric demand of the bottom ring of the ligand from η^5-Cp* (**5.16**) to η^5-C_5Ph_5 (**5.17**) improved the enantioselectivity slightly from 17% to 26%.

Scheme 5.8 Asymmetric Diethylzinc Addition



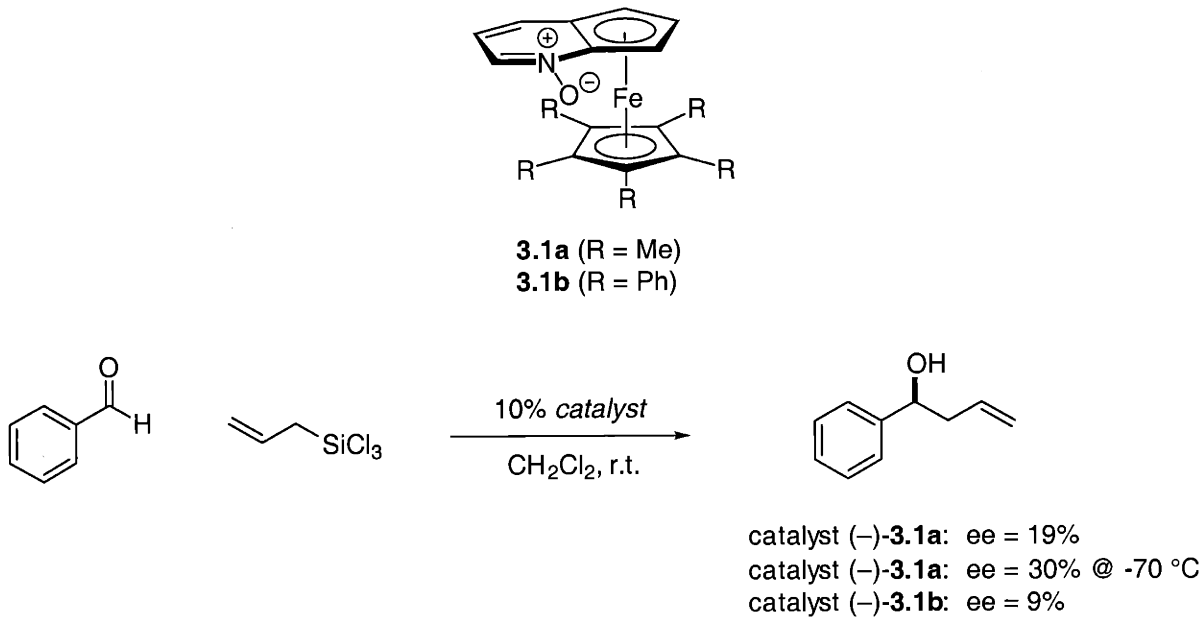
ligand **5.16**: ee = 17%
ligand **5.17**: ee = 26%

Since there are many systems and methods in the literature that can mediate the enantioselective reduction of ketones and the asymmetric addition of diethylzinc to aldehydes with excellent stereoselectivities, we decided to terminate our studies of planar-chiral *N,O*-complexes in these applications.

Section III. Enantioselective Allylation of Benzaldehyde using Planar-Chiral Pyridine *N*-Oxides

Pyridine *N*-oxides are known to catalyze the allylation of aldehydes with allyltrichlorosilane.[8] In searching for applications of our planar-chiral pyridine *N*-oxide complexes, the allylation of benzaldehyde was examined.[9]

Scheme 5.9 Enantioselective Allylation of Benzaldehyde



Preliminary results showed that when 10% of (–)-**3.1a** was used, the reaction proceeded to give the corresponding homoallylic alcohol in 19% ee. Improved stereoselectivity was observed when the temperature of the reaction was decreased

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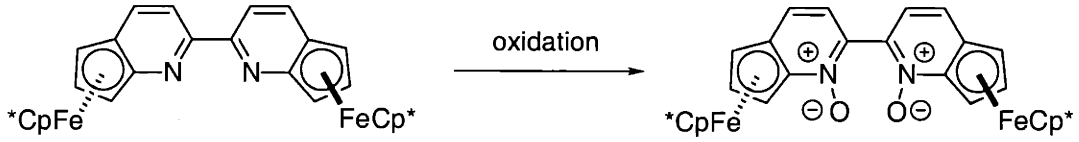
8 Nakajima, M.; Saito, M.; Shiro, M.; Hashimoto, S.-i. *J. Am. Chem. Soc.* **1998**, *120*, 6419-6420.

9 For a review of asymmetric allylation of carbonyl groups, see: Yanagisawa, A. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Chapter 27.

to –70 °C. Increasing the steric of the bottom ring from η^5-Cp* (**3.1a**) to η^5-C_5Ph_5 (**3.1b**) reduced the stereoselectivity to 9%. Furthermore, changing the bottom ring to η^5-C_5Ar_5 (Ar = 4-MeC_6H_4, 4-(*t*-Bu)C_6H_4, 4-MeO-C_6H_4, 4-(*i*-PrO)C_6H_4, 3,5-$Me_2C_6H_3$, 3,5-$Et_2C_6H_3$, 3,5-(*i*-Pr)$_2C_6H_3$) resulted in poor enantioselectivities, or, in some cases, a marked decrease in reaction rate. Other allysilanes (CH_2=$CHCH_2SiRCl_2$: R = Me, Ph, $CH_2CH_2CH_2Cl$) were surveyed, and the rate of the reactions with these reagents was low.

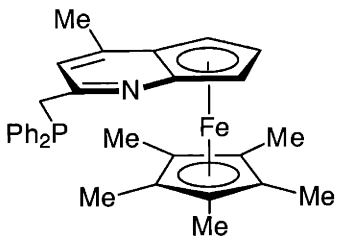
Efforts were made to synthesize a C_2-symmetric planar-chiral pyridine *N*-oxide (**5.23**). Unfortunately, attempts to synthesize **5.23** by oxidation of **5.22** resulted in decomposition.



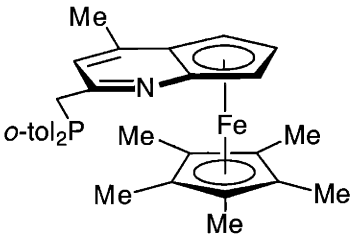
5.22 **5.23**

Section IV. Asymmetric Catalysis Using Planar-Chiral *N,P*-Ligands

The rhodium-catalyzed hydrosilylation of ketones can be carried out effectively using ligand **4.1** as described in Chapter 4 of this thesis. To extend the utility of this new family of *N,P*-ligands, the hydrosilylation of imines[10] was carried out, and preliminary results are shown in Scheme 5.10 and Table 5.2.

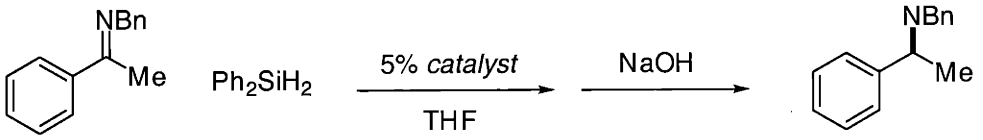


4.1



4.20

Scheme 5.10 Asymmetric Hydrosilylation of an *N*-Benzyl Imine



[Rh(COD)Cl]$_2$, (+)-**4.1**: ee = 0%
[Ir(COD)Cl]$_2$ (+)-**4.1**: ee = 20%

A racemic mixture of the product was obtained in the rhodium-catalyzed hydrosilylation of an *N*-benzyl imine (Scheme 5.10). Changing the metal from Rh to Ir increased the enantioselectivity to 20%, although the rate of the reaction decreased significantly. The rhodium-catalyzed hydrosilylation of an *N*-phenyl

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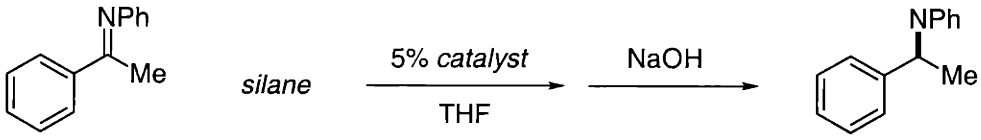
10 For reviews of asymmetric hydrosilylation of imines, see: (a) Nishiyama, H. In *Comprehensive Asymmetric Catalysis;* Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Chapter 6.3. (b) Nishiyama, H.; Itoh, K. In *Catalytic Asymmetric Synthesis 2nd Edition,* Ojima, I. Ed.; Wiley-VCH: New York, 2000; Chapter 2.

imine resulted in 10% ee of the corresponding amine product when (+)-**4.1** was used (Table 5.2, entry 1). Replacing the ligand from (+)-**4.1** to (+)-**4.20** gave essentially the same enantioselectivity. Attempts to improve the reaction by changing the silane and metal source all resulted in a racemic mixture of products.

Table 5.2 Asymmetric Hydrosilylation of *N*-Phenyl Imine



entry	*Metal Source*	*ligand*	*silane*	ee (%)
1	$[Rh(COD)Cl]_2$	(+)-**4.1**	Ph_2SiH_2	10
2	$[Rh(COD)Cl]_2$	(+)-**4.20**	Ph_2SiH_2	9
3	$[Rh(COD)Cl]_2$	(+)-**4.1**	$PhMeSiH_2$	0
4	$[Rh(COD)Cl]_2$	(+)-**4.1**	α-NpPhSiH$_2$	0
5	$[Ir(COD)Cl]_2$	(+)-**4.1**	Ph_2SiH_2	0

Efforts were made in applying *N,P*-ligand (–)-**4.1** to the asymmetric hydroboration of styrene using catecholborane.[11] Unfortunately, only racemic *sec*-phenethyl alcohol was afforded at the end of the reaction, together with the regioisomer phenethyl alcohol as a side product.

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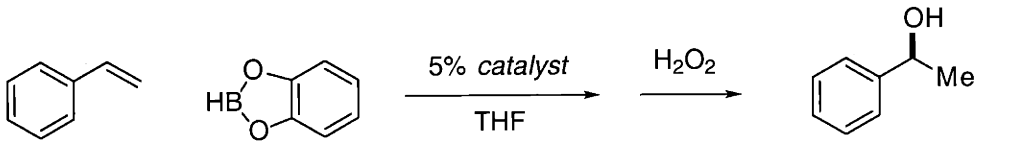
11 For reviews of asymmetric hydroboration of carbon-carbon double bonds with transition-metal catalysts, see: (a) Hayashi, T. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Chapter 9. (b) Nishiyama, H.; Itoh, K. In *Catalytic Asymmetric Synthesis 2nd Edition*, Ojima, I. Ed.; Wiley-VCH: New York, 2000; Chapter 2.

Scheme 5.11 Asymmetric Hydroboration of Styrene



$[Rh(COD)Cl]_2$, (–)-**4.1**: ee = 0%
$Rh(COD)_2BF_4$, (–)-**4.1**: ee = 0%

In conclusion, a number of planar-chiral heterocycles have been successfully synthesized, and the attempts to utilize them in asymmetric catalysis have been discussed. The planar-chiral design may offer some advantages over existing systems for certain transformations. However, there is no general solution to asymmetric transformations in terms of efficiency and enantioselectivity, hence, the search for new chiral ligands and catalysts is still in demand.

Experimental

I. General

Analytical thin layer chromatography was performed using EM Reagents 0.25 mm silica gel 60 plates, and visualization was accomplished with potassium permanganate or with ethanolic phosphomolybdic acid. Flash chromatography was performed on EM Reagents silica gel 60 (230-400 mesh).

Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer. High resolution mass spectra were recorded on a Finnegan MAT System 8200 spectrometer. Melting points (uncorrected) were measured on a Thomas Hoover Unimelt capillary melting point apparatus.

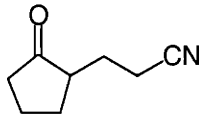
^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian XL-300 or XL-500 NMR spectrometer at ambient temperature. ^{1}H data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (δ scale), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C spectra were determined with complete proton decoupling.

Analytical chiral HPLC was performed on a Daicel CHIRALCEL OD column (4.6 mm x 25 cm). Analytical chiral GC was performed on a Chiraldex G-TA column (20 m x 0.25 mm).

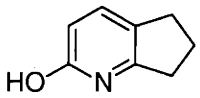
$FeCl_2$ (Strem), *n*-BuLi (Strem), 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (Aldrich) were used without further purification. All substrates and reagents were purified by distillation or column chromatography. Solvents were distilled from the indicated drying agents: benzene (sodium/benzophenone); THF (sodium/benzophenone); CH_2Cl_2 (CaH_2); Et_2O (sodium/benzophenone); toluene (molten sodium).

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware, unless otherwise indicated.

II. Preparation of Planar-Chiral Heterocycles



Compound 5.6 (3-(2-oxo-cyclopentyl)-propionitrile). This was prepared according to a literature procedure.[12]



Compound 5.7 (6,7-dihydro-5H-[1]pyrindin-2-ol). 3-(2-oxo-cyclopentyl)-propionitrile (11.5 g, 83.8 mmol) was added dropwise to conc. H_2SO_4 (50 mL) with stirring at room temperature. Ac_2O (20 mL) was then added slowly and the reaction mixture was then heated at 50 °C in a water bath for 1 h. The reaction mixture was then cooled to room temperature and added to cold distilled water (600 mL). The resulting solution was then extracted with $CHCl_3$. The organic layer was discarded and the aqueous layer was then neutralized with $NaHCO_3$ followed by extraction with $CHCl_3$. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated to give 6.6 g (58%) of the desired product.

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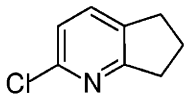
12 Clive, D. L. J.; Beaulieu, P. L.; Set, L. *J. Org. Chem.* **1984**, *49*, 1313-1314.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, 1H, J = 9.1), 7.38 (d, 1H, J = 9.1), 2.92 (t, 2H, J = 7.7), 2.72 (t, 2H, J = 7.3), 2.13 (tt, 2H, J = 7.4, 7.4). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 149.7, 139.3, 119.9, 116.3, 31.1, 29.6, 23.2.



Compound 5.8 (2-chloro-6,7-dihydro-5H-[1]pyrindine). To an oven-dried Schlenk tube under argon was added 6,7-dihydro-5H-[1]pyrindin-2-ol (5 g, 37 mmol) and $POCl_3$ (13 mL, 139 mmol) to give a brown slurry after a slight exotherm. The Schlenk tube was sealed under an argon atmosphere and immersed in an oil bath at 140 °C. A homogeneous black solution resulted after ~ 30 minutes. After 3 hours, the Schlenk tube was cooled to room temperature and placed under vacuum for 1 hour to remove the excess $POCl_3$. The resulting black tar was rinsed out of the Schlenk tube with cold (~ 0 °C) 1 N HCl.[13] The acidic solution was washed with Et_2O (3 x 100 mL). The Et_2O wash was extracted with 2 N HCl (3 x 100 mL) and the acidic phases were combined and neutralized by K_2CO_3 to give a thick brown slurry (pH ~ 10). The neutralized aqueous phase was extracted with $CHCl_3$ (5 x 200 mL) followed by EtOAc (200 mL). The organic phases were combined, dried with $MgSO_4$, filtered and stripped of solvent to give a brown tar. The crude was dissolved in Et_2O (100 mL) and filtered through silica gel (rinsed with 5 x 100 mL of Et_2O). After solvent removal, 3.9 g (69%) of product was obtained as an orange solid.

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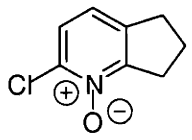
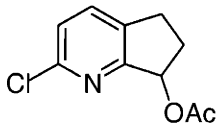
13 It is important to keep the temperature of the quenching operation around ca. 0 °C. 2-Halopyridines are known to revert to 2-hydroxypyridine when heated in aqueous acid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 1H, J = 8.2), 7.05 (d, 1H, J = 8.0), 3.00, (t, 2H, J = 7.7), 2.91 (t, 2H, J = 7.6), 2.15 (tt, 2H, J = 7.6, 7.6). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 148.9, 135.6, 134.4, 121.0, 34.1, 30.1, 23.3.



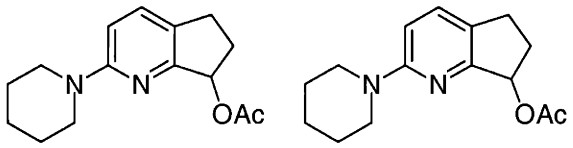
Compound 5.9 (2-chloro-6,7-dihydro-5H-[1]pyrindine-1-oxide). To a flask fitted with a reflux condenser was added 2-chloro-6,7-dihydro-5H-[1]pyrindine (3.9 g, 25 mmol), acetic acid (16 mL, 284 mmol) and H_2O_2 (30%, 3.5 mL, 32 mmol) to give an orange solution. After heating at 80 °C for 5 hours, more H_2O_2 (30%, 5 mL, 43 mmol) was added to the hot reaction mixture and the resulting yellow solution was heated at 80 °C overnight. After cooling to room temperature, the reaction was placed under vacuum for 1 hour to remove the excess peracetic acid generated in situ. The reaction was quenched by pouring into K_2CO_3 in water. The resulting slurry (pH ~ 11) was extracted with $CHCl_3$ followed by EtOAc. The organic layers were combined, dried with $MgSO_4$ and filtered. After removal of solvent, 3.9 g (91%) of the product was obtained. The product was used in the next step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, 1H, J = 8.3), 7.03 (d, 1H, J = 8.1), 3.19, (t, 2H, J = 7.6), 3.01 (t, 2H, J = 7.7), 2.20 (tt, 2H, J = 7.7, 7.7). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 139.8, 139.5, 124.5, 122.1, 31.5, 30.4, 22.4.



Compound 5.10 (1-(2-chloro-6,7-dihydro-5H-[1]pyrindin-7-yl)-ethanone). To a flask fitted with a reflux condenser was added 2-chloro-6,7-dihydro-5H-[1]pyrindine-1-oxide (3.8 g, 22 mmol) and Ac_2O (34 mL, 360 mmol) to give a yellow solution. After heating in an oil bath at 100 °C for 30 minutes, a brown homogeneous solution resulted. After an additional 2.5 hours at 100 °C, the excess Ac_2O was removed at reduced pressure. The mixture was purified by column chromatography to give 4.8 g (81%) of the desired product.

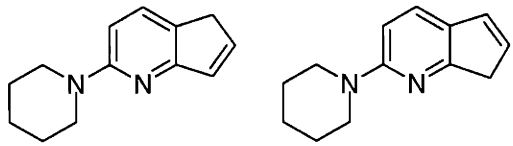
^1H NMR (300 MHz, $CDCl_3$) δ 7.53-7.56 (m, 1H), 7.22 (d, 1H, J = 8.0), 6.02 (dd, 1H, J = 7.4, 4.4), 3.04 (ddd, 1H, J = 16.6, 9.0, 5.4), 2.85 (dddd, 1H, J = 16.5, 8.8, 5.5, 0.8), 2.59-2.71 (m, 1H), 2.07-2.14 (m, 1H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 160.7, 150.3, 136.3, 135.5, 123.9, 76.6, 31.0, 27.3, 21.2.



Compound 5.11 (1-(2-piperidino-6,7-dihydro-5H-[1]pyrindin-7-yl)-ethanone). In a glove box, 1-(2-chloro-6,7-dihydro-5H-[1]pyrindin-7-yl)-ethanone (53 mg, 0.25 mmol), piperidine (30 μL), $Pd(OAc)_2$ (4.5 mg, 0.020 mmol), 2-(dicyclohexylphosphino)biphenyl, and K_3PO_4 (106 mg, 0.500 mmol) were dissolved in toluene (10 mL) in Schlenk tube. The tube was sealed and brought out of the box and heated in an oil bath at 100 °C. The reaction mixture was filtered through a plug

of silica, the filtrated was concentrated, and purified by column chromatography to give the desired product.

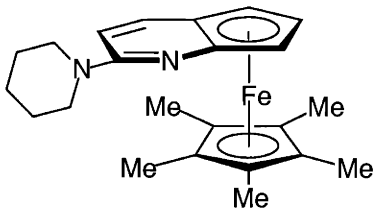
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, 1H, J = 8.5), 6.57 (d, 1H, J = 8.5), 5.97 (dd, 1H, J = 7.5, 4.5), 3.50 (m, 4H), 2.90 (m, 1H), 2.71 (m, 1H), 2.54 (m, 1H), 2.10 (s, 3H), 2.00 (m, 1H), 1.62 (m, 6H).



Compounds 5.12 & 5.13 (2-piperidino-5H-[1]pyrindine). To a flask fitted with a reflux condenser under argon was added, 1-(2-piperidino-6,7-dihydro-5H-[1]pyrindin-7-yl)-ethanone (80 mg, 0.31 mmol) and concentrated H_2SO_4 (0.6 mL, 11 mmol) to give a yellow solution. The flask was immersed in an oil bath at 90 °C. After 1 hour, the resulting orange solution was cooled to room temperature and poured into ice followed by 50% NaOH solution (80 mL). Precipitates formed during the quench and an exotherm was observed. After cooling this mixture in an ice bath, K_2CO_3 was added portionwise until pH ~ 10. The aqueous phase was extracted with $CHCl_3$ followed by EtOAc. The organic layers were combined, dried over $MgSO_4$, filtered and concentrated to give a brown oil. The mixture was purified by column chromatography to give the desired products.

Major Isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, 1H, J = 8.0), 6.89 (m, 1H), 6.80 (m, 1H), 6.46 (d, 1H, J = 8.0), 3.52 (m, 4H), 3.29 (t, 2H, J = 2.0), 1.65 (m, 6H).

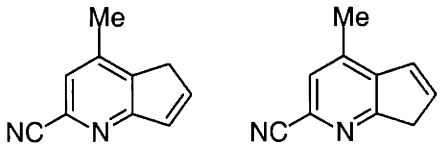
Minor Isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, 1H, J = 8.5), 6.74 (dt, 1H, J = 6.0, 1.5), 6.53 (d, 1H, J = 8.5), 6.30 (dt, 1H, J = 6.5, 1.5), 3.52 (m, 4H), 3.36 (t, 2H, J = 2.0), 1.65 (m, 6H).



Compound 5.14. In a glove box, *n*-BuLi (1.61 M in hexanes; 170 μL, 0.27 mmol) was added by syringe over ~2 minutes to a slurry of pentamethylcyclopentadiene (39 mg, 0.27 mmol) in THF (5 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (35 mg, 0.27 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 170 μL, 0.27 mmol) and 2-piperidino-5H-[1]pyrindine (55 mg, 0.27 mmol) in THF (5 mL) at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), affording a purple solid.

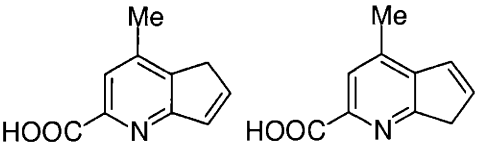
^{1}H NMR (500 MHz, C_6D_6) δ 7.31 (d, 1H, J = 9.5), 6.50 (d, 1H, J = 9.5), 4.84 (t, 1H, J = 0.9), 3.94 (dd, 1H, J = 2.4, 0.9), 3.62 (t, 1H, J = 2.4), 3.48 (t, 4H, J = 5.5), 1.70 (s, 15H), 1.40 (m, 6H). ^{13}C NMR (126 MHz, C_6D_6) δ 159.4, 140.3, 110.8, 110.1, 78.7, 75.3, 74.3, 66.1, 63.0,

47.7, 26.4, 25.7, 10.9. FTIR (neat) 2932, 2852, 1599, 1424, 1254 cm^{-1}. HRMS (EI, m/e) calcd for $C_{23}H_{30}FeN_2$ (M^+) 390.1753, found 390.1744.



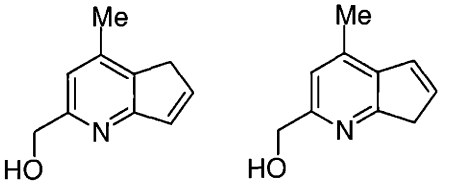
Compound 5.19 (4-methyl-5H-[1]pyrindine-2-carbonitrile). In a glove box, $Pd_2(dba)_3$ (0.44 g, 0.48 mmol) and DPPF (1.07 g, 1.9 mmol) were dissolved in dioxane (10 mL) and stirred in a Schlenk tube for 30 min. Afterwards, 4-methyl-5H-[1]pyrindine-2-chloride (2.0 g, 12 mmol), CuCN (4.3 g, 48 mmol), and Et_4NCN (3.8 g, 22 mmol) in 50 mL of dioxane was added to the Schlenk tube which was sealed and heated in an oil bath at 100 °C for 12 h. The reaction mixture was then cooled and filtered through a plug of celite. Saturated $NaHCO_3$ solution was added and the reaction mixture was extracted with EtOAc. The organic layers were combined and dried over $MgSO_4$, filtered, and concentrated and purified by column chromatography (EtOAc/hexanes 1:9), furnishing 0.7 g (37%) of the desired product.

Major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.03 (dt, 1H, J = 5.7, 2.0), 7.00 (m, 1H), 3.40 (dd, 2H, J = 1.8, 1.8), 2.41 (s, 3H). Minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 6.98 (dt, 1H, J = 5.8, 1.8), 6.86 (dt, 1H, J = 6.1, 2.0), 3.52 (dd, 2H, J = 1.8, 1.8), 2.46 (s, 3H).



Compound 5.20 (4-methyl-5H-[1]pyrindine-2-carboxylic acid). 4-methyl-5H-[1]pyrindine-2-carbonitrile (800 mg, 5.1 mmol) was added to conc. acetic acid (7 mL) and conc. hydrogen chloride (14 mL). The reaction mixture was heated in an oil bath at 100 °C for 2.5 h. Afterwards, the reaction mixture was cooled to room temperature and placed in the fridge for 12 h. White crystals were afforded upon cooling, which were filtered, washed with Et_2O, dried under vacuum to give 710 mg (79%) of white solid. The product was used in the next step without further purification.

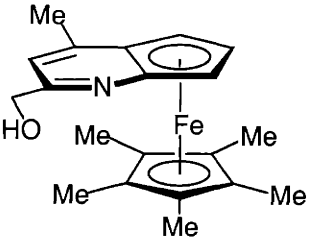
Major isomer: ^{1}H NMR (400 MHz, DMSO d-6) δ 11.60 (br, 1H), 7.88 (s, 1H), 7.34 (d, 1H, J = 5.5), 7.06 (d, 1H, J = 5.6), 3.61 (s, 2H), 2.43 (s, 3H). Minor isomer: ^{1}H NMR (400 MHz, DMSO d-6) δ 11.60 (br, 1H), 7.80 (s, 1H), 7.22 (s, 1H), 6.82 (d, 1H, J = 5.0), 3.52 (s, 2H), 2.38 (s, 3H).



Compound 5.21 (4-methyl-5H-[1]pyrindinyl-2-methanol). In a glove box, $LiAlH_4$ (70 mg) was suspended in THF (1 mL) in a round-bottom flask. 4-methyl-5H-[1]pyrindine-2-carboxylic acid (88 mg, 0.5 mmol) in THF (1 mL) was added to the reaction flask. The flask was equipped with a condenser and was brought outside

the box. The reaction mixture was then refluxed for 24 h. After which, the reaction mixture was cooled and added distilled water (0.9 mL), 1 M NaOH solution (2 mL), and distilled water (0.9 mL). The solid was filtered and washed with Et_2O, and the filtrate was extracted with Et_2O, dried over $MgSO_4$, filtered, concentrated, and purified by column chromatography (EtOAc ——> EtOAc/MeOH 10:1) to give 29 mg (36%) of the desired products.

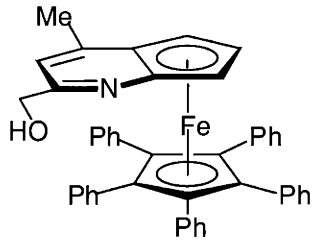
Major isomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.01 (dt, 1H, J = 5.5, 2.0), 7.01 (dt, 1H, J = 6.0, 2.0), 6.88 (s, 1H), 4.76 (s, 2H), 3.80 (br, 1H), 3.32 (s, 2H, J = 1.5), 2.37 (s, 3H). Minor isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (m, 2H), 6.60 (dt, 1H, J = 6.0, 2.0), 4.76 (s, 2H), 3.80 (br, 1H), 3.47 (t, 2H, J = 2.0), 2.43 (s, 3H).



Compound 5.16. In a glove box, *n*-BuLi (1.61 M in hexanes; 390 μL, 1.24 mmol) was added by syringe over ~2 minutes to a slurry of pentamethylcyclopentadiene (89 mg, 0.62 mmol) in THF (5 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (79 mg, 0.62 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 390 μL, 0.62 mmol) and 4-methyl-5H-[1]pyrindinyl-2-methanol (100 mg, 0.62 mmol) in THF (5 mL) at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of

silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (CH_2Cl_2/EtOAc/hexanes 1:1:8), furnishing 80 mg (37%) of a purple solid.

^1H NMR (500 MHz, C_6D_6) δ 6.05 (s, 1H), 4.93 (br, s, 1H), 4.67 (d, 2H), 4.00 (s, 1H), 3.64 (s, 1H), 1.99 (s, 3H), 1.50 (s, 15H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 161.4, 151.2, 114.0, 108.1, 82.5, 78.8, 76.1, 67.6, 65.0, 62.2, 19.5, 10.4. FTIR (neat) 3198, 2903, 1590, 1532, 1091, 1028, 853, 792 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{20}H_{25}FeNO$ (M^+) 351.1280, found 351.1285.



Compound 5.17. In a glove box, *n*-BuLi (1.61 M in hexanes; 110 μL, 0.35 mmol) was added by syringe over ~2 minutes to a slurry of pentaphenylcyclopentadiene (80 mg, 0.18 mmol) in THF (5 mL). The mixture was stirred for 10 minutes, after which the resulting solution was added dropwise to a slurry of $FeCl_2$ (23 mg, 0.18 mmol) in THF (5 mL). After 10 minutes, a solution of the lithium salt of pyrindine [made 10 minutes prior to use by the reaction of *n*-BuLi (1.61 M in hexanes; 110 μL, 0.18 mmol) and 4-methyl-5H-[1]pyrindinyl-2-methanol (29 mg, 0.18 mmol) in THF (5 mL) at room temperature] was added dropwise, resulting in a dark-purple solution. This solution was stirred for 24 h, after which it was filtered through a 1" plug of silica gel. The silica gel was washed with NEt_3/EtOAc/hexanes (1:9:9) until all of the

purple compound had been collected. The resulting solution was concentrated to give a purple solid, which was purified by column chromatography (EtOAc/hexanes 3:1), furnishing 37 mg (31%) of a purple solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.91-7.18 (m, 25H), 6.68 (d, 1H, J = 1.2), 5.17 (dd, 1H, J = 2.8, 1.2), 4.99 (dd, 1H, J = 1.2), 4.23-4.44 (m, 3H), 3.83 (br, s, 1H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 163.1, 151.0, 135.5, 132.7, 127.6, 126.9, 117.9, 109.8, 86.6, 86.0, 78.5, 69.6, 64.8, 64.1, 20.6. FTIR (neat) 3058, 2922, 1600, 1502, 1443, 741, 700 cm^{-1}. HRMS (EI, *m/e*) calcd for $C_{45}H_{35}FeNO$ (M^+) 661.2063, found 661.2031.

III. Determination of Half-life in the Acylation of *sec*-Phenethyl Alcohol (Table 5.1)

To 0.5 mL of CD_2Cl_2 in an NMR tube was added 21 μL of *sec*-phenethyl alcohol, 25 μL of acetic anhydride, 29 μL of triethylamine under inert atmosphere. Complex **5.14** in 0.1 mL of CD_2Cl_2 was then added to the NMR tube and the reaction was monitored by ^1H NMR. The percent conversion was determined by comparing the signal of the methyl protons of *sec*-phenethyl alcohol with that of the corresponding acetate. After 20h, the conversion of the acylation reaction was 30%.

IV. Rearrangement of *O*-Acylated Azlactone (Scheme 5.4)

To a small vial was added complex **5.14** (1.0 mg, 0.0025 mmol) followed by 0.5 mL *t*-amyl alcohol containing 5-methoxycarbonyloxy-4-methyl-2-(4-chlorophenyl)-oxazole (34 mg, 0.125 mmol). Aliquots were removed by syringe and filtered through a plug of silica. Solvent was removed and the percent conversion of the reaction was monitored by ^{1}H NMR. No conversion of the rearrangement product was observed after 24 h.

V. Asymmetric Reduction of Acetophenone (Scheme 5.7)

In a glove box, to a solution of **5.16** (3.5 mg, 0.01 mmol) in 1.0 mL of THF was added neat BH_3 (9.6 μL). After 5 minutes, acetophenone (12 mg, 0.10 mmol) in 0.5 mL of THF was added. The reaction was allowed to stir for 13 h, after which, water was added and the reaction mixture was extracted with CH_2Cl_2. The organic phase was collected, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 0% ee of the desired product.

The above procedure was repeated using complex **5.17**, which afforded 0% ee of the desired product.

VI. Asymmetric Diethyl Zinc Addition (Scheme 5.8)

In a glove box, to a solution of **5.16** (1.7 mg, 0.0047 mmol) in 0.5 mL of toluene was added benzaldehyde (10 mg, 0.094 mmol) followed by dropwise addition of diethylzinc (0.1 mL, 1.1 M). The reaction was allowed to stir for 2 d, after which, 2N HCl was added to the reaction mixture followed by extraction with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated to give the desired alcohol. The alcohol was then converted to its corresponding acetate and it ee was determined by chiral GC, which showed 17% ee of the desired product.

The above procedure was repeated using complex **5.17**, which afforded 26% ee of the desired product.

VII. Enantioselective Allylation of Benzaldehyde (Scheme 5.9)

In a glove box, to a solution of (–)-**3.1a** (8.0 mg, 0.025 mmol) in 0.5 mL of THF was added benzaldehyde (26 mg, 0.25 mmol) followed by allyltrichlorosilane (50 μL, 0.34 mmol). The reaction was allowed to stir for 16-20 h, after which, the product was separated from the catalyst by passing the residue through a plug of silica. GC showed 19% ee of the desired product.

The above procedure was repeated at –70 °C, which afforded 30% ee of the desired product.

The above procedure was repeated using complex (–)-**3.1b**, which afforded 9% ee of the desired product.

VIII. Asymmetric Hydrosilylation of *N*-Benzyl Imine (Scheme 5.10)

In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added the *N*-benzyl imine (20 mg, 0.10 mmol) in 1.0 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of Ph_2SiH_2 (36 mg, 40μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N NaOH. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature followed by extraction with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 0% ee of the desired product.

The above procedure was repeated using $[IrCl(COD)]_2$, which afforded 20% ee of the desired product.

IX. Asymmetric Hydrosilylation of N-Phenyl Imine (Table 5.2)

General procedure (Table 5.2, entry 1). In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (+)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added the *N*-phenyl imine (19 mg, 0.10 mmol) in 1.0 mL THF. The resulting reaction mixture was cooled to -30 °C followed by the addition of Ph_2SiH_2 (36 mg, 40μL, 0.20 mmol). The reaction mixture was then kept at room temperature. After 16-18 h, the reaction mixture was cooled to 0 °C and 2 mL of 1N NaOH. The mixture was allowed to stir for 2 h at 0 °C and 0.5 h at room temperature followed by extraction with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 10% ee of the desired product.

Table 5.2, entry 2. The general procedure was followed using ligand (+)-**4.20**, which afforded 9% ee of the desired product.

Table 5.2, entry 3. The general procedure was followed using ligand (+)-**4.1** and $PhMeSiH_2$, which afforded 0% ee of the desired product.

Table 5.2, entry 4. The general procedure was followed using ligand (+)-**4.1** and α-$NpPhSiH_2$, which afforded 0% ee of the desired product.

Table 5.2, entry 5. The general procedure was followed using ligand (+)-**4.1** and $[IrCl(COD)]_2$, which afforded 0% ee of the desired product.

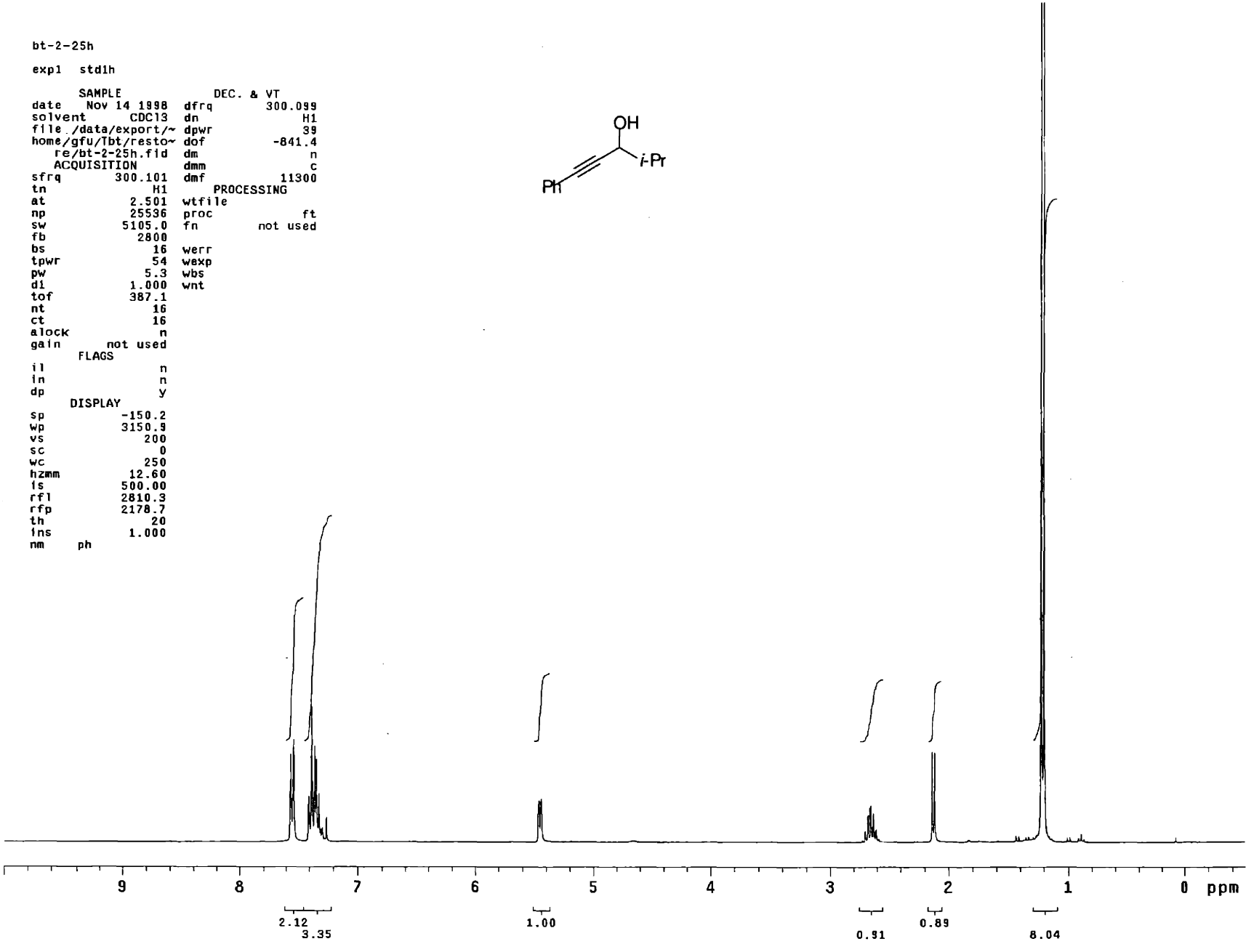
X. Asymmetric Hydroboration of Styrene (Scheme 5.11)

In a glove box, to a stirring solution of $[RhCl(COD)]_2$ (1.22 mg, 0.0025 mmol) in 2 mL CH_2Cl_2 in a vial was added slowly ligand (–)-**4.1** (3.11 mg, 0.0060 mmol) in 2 mL CH_2Cl_2 and the mixture was stirred for 30-45 min. The resulting catalyst was then concentrated. Under inert atmosphere, this solid was added styrene (10 mg, 0.10 mmol), followed by catecholborane (13 mg, 0.11 mmol). The reaction mixture was then kept at room temperature. After 19 h, the reaction mixture was added MeOH and was cooled to 0 °C. 1 M NaOH solution (0.5 mL) was then added followed by H_2O_2 solution (30%, 0.2 mL). The mixture was allowed to stir for 3 h and was allowed to warm slowly to room temperature. The reaction mixture was extracted with excess Et_2O. The organic phase was collected, combined, dried over $MgSO_4$, filtered, and concentrated. The product was separated from the catalyst by passing the residue through a plug of silica. GC showed 0% ee of the *sec*-phenethyl alcohol.

The above procedure was repeated using $Rh(COD)_2BF_4$, which again afforded 0% ee of the *sec*-phenethyl alcohol.

Appendix II:

NMR Spectra for Selected Compounds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ins 1.000
nm ph
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dmm c
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proc ft
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wexp
wbs
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Ph
9
8
7
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8.04

bt-3-89

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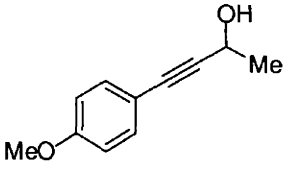

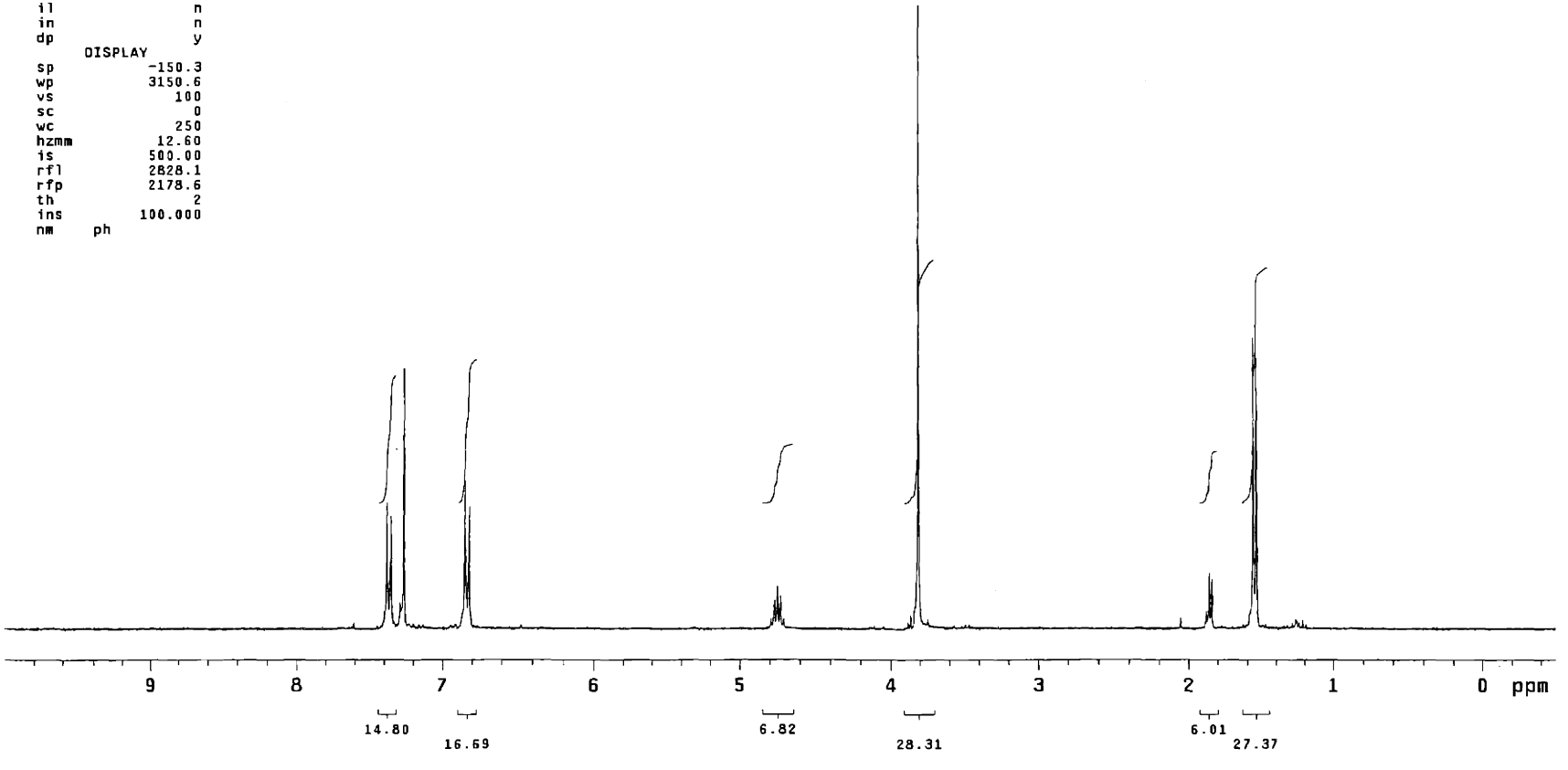

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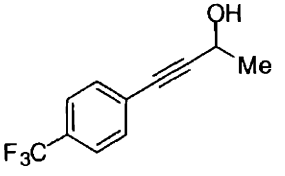

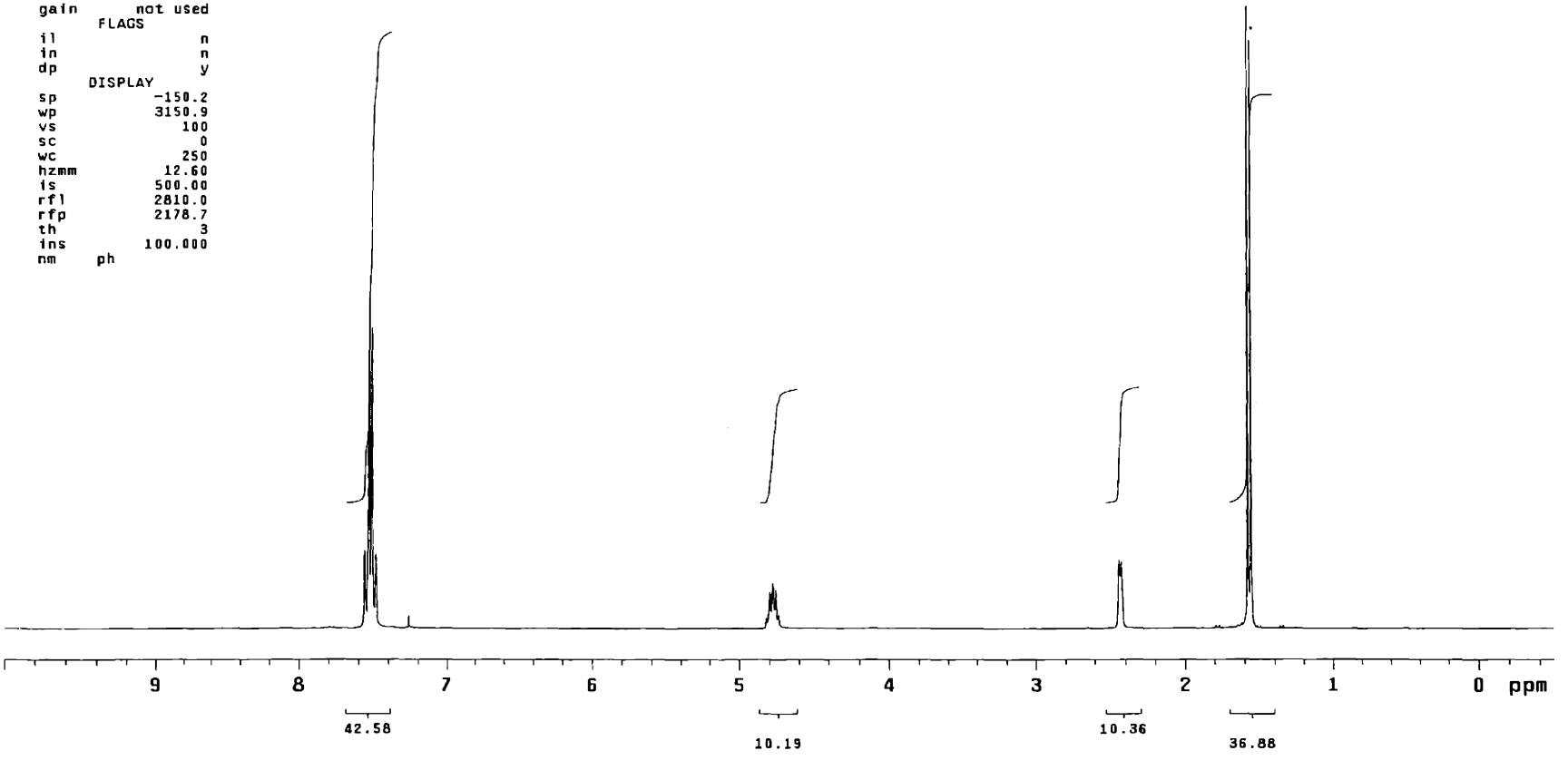

bt-3-87

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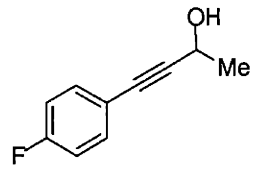

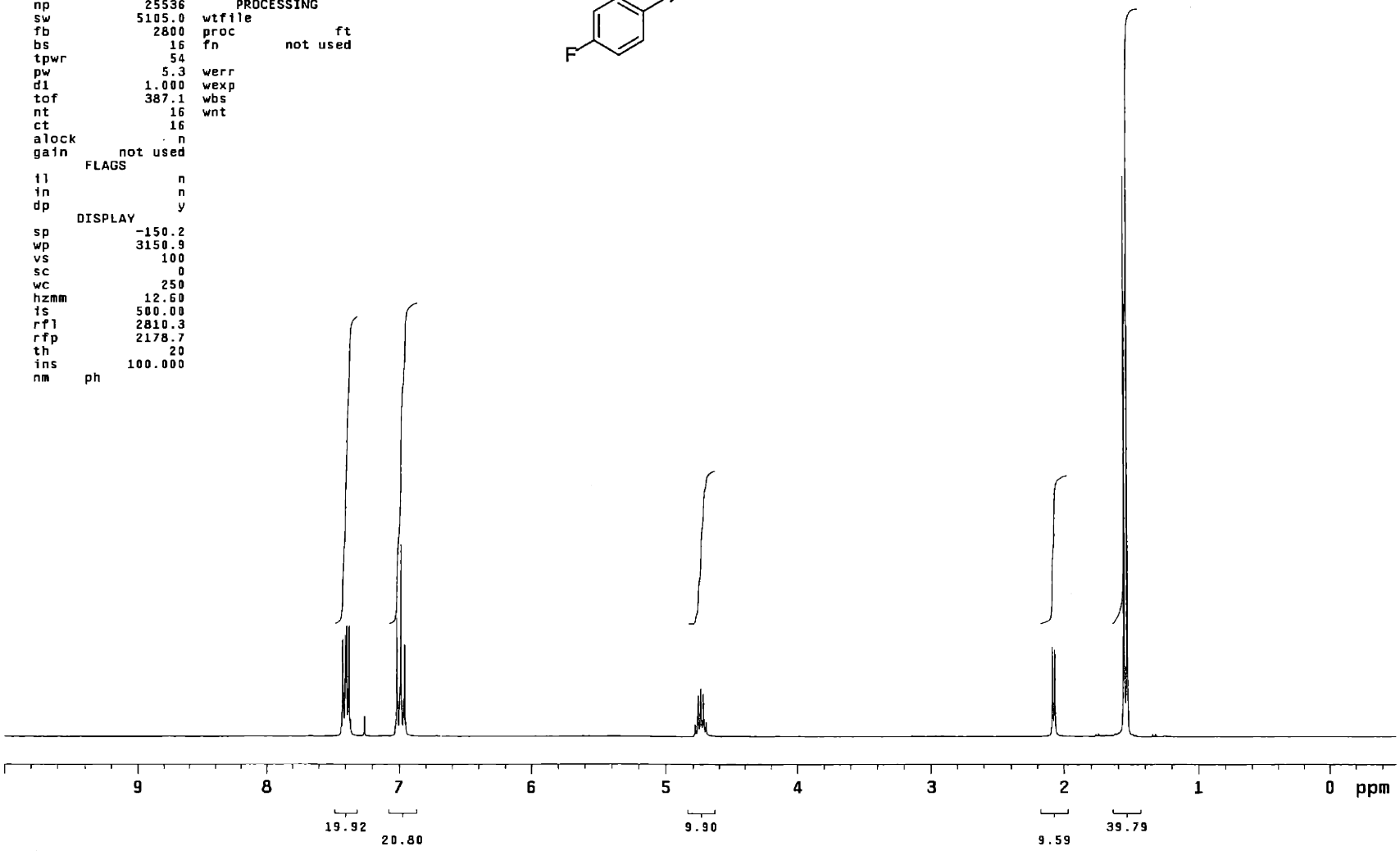

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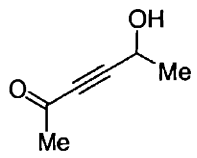

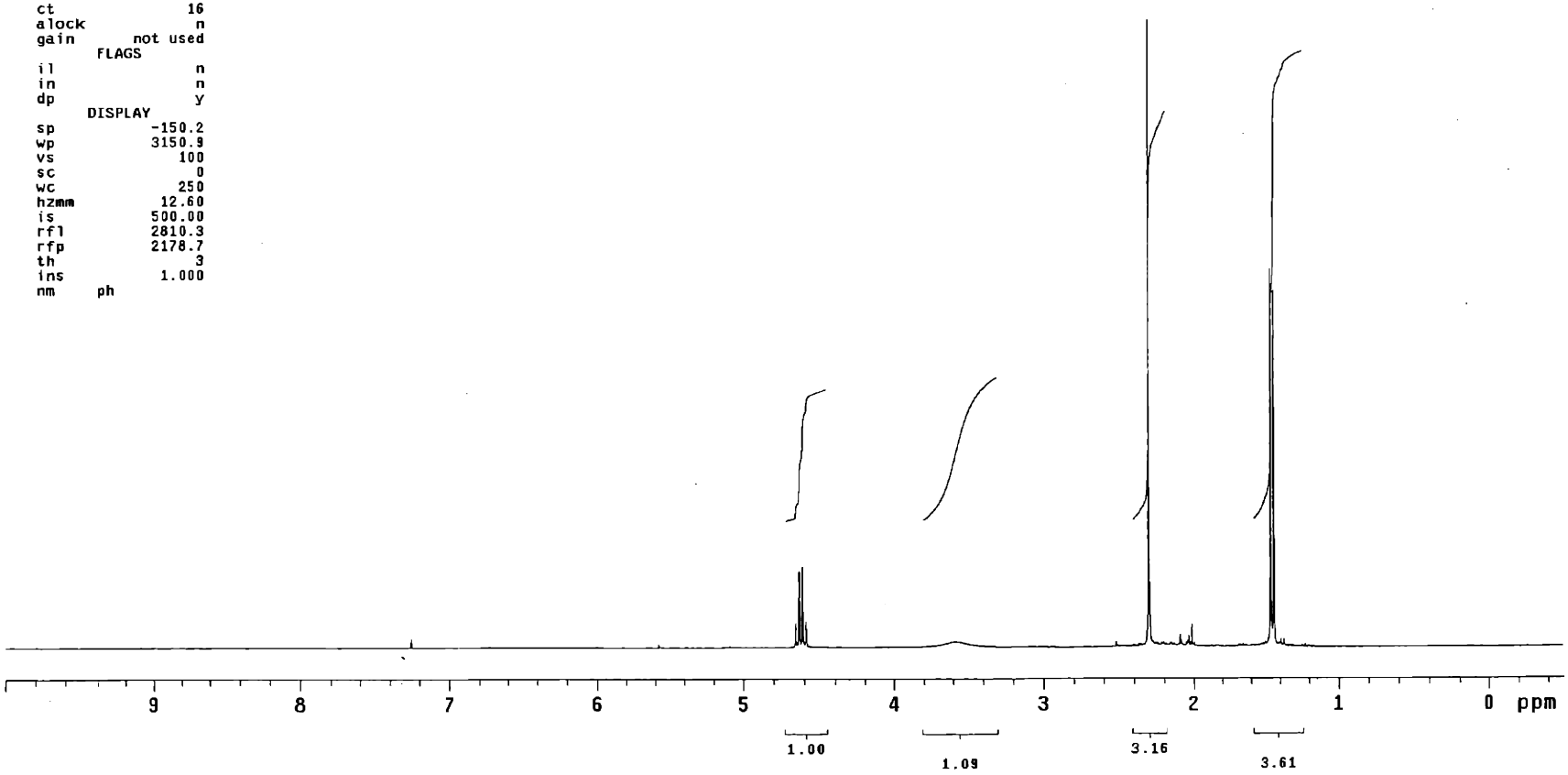

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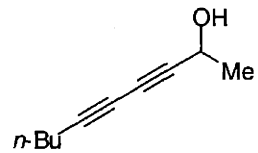

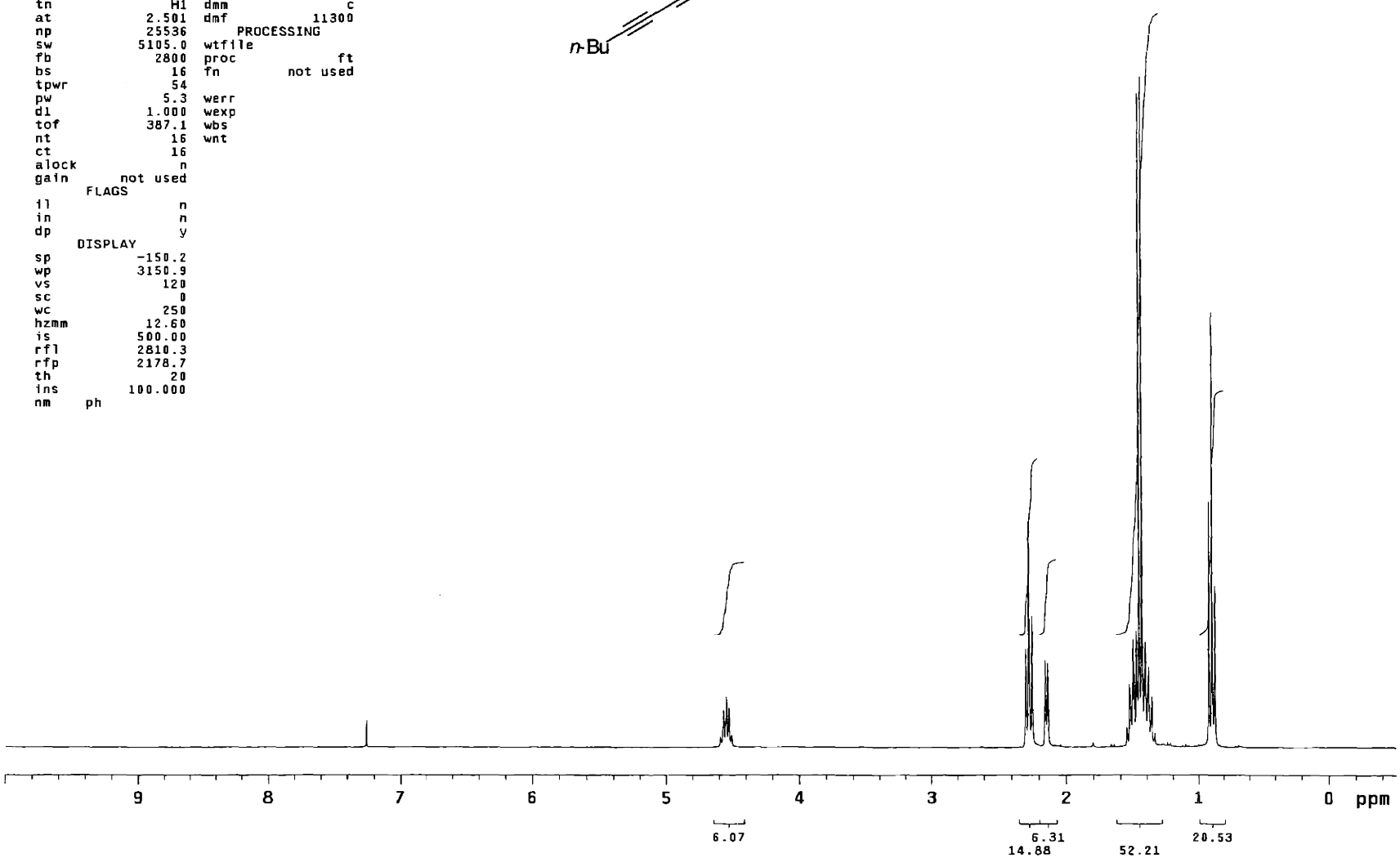

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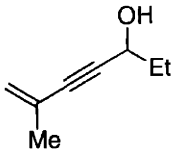

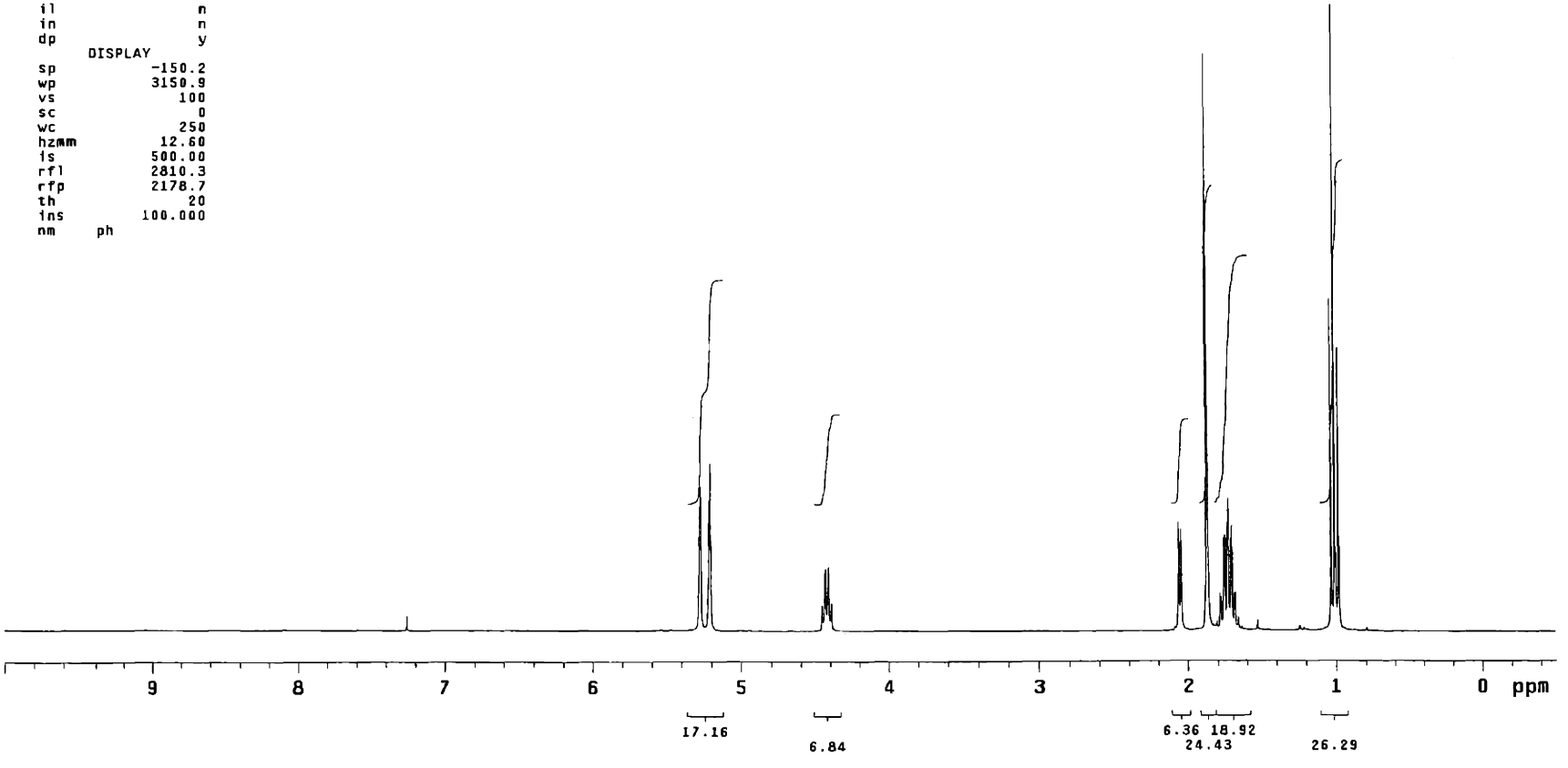

bt-2-3

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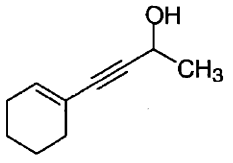

STANDARD 1H OBSERVE

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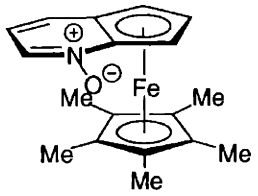
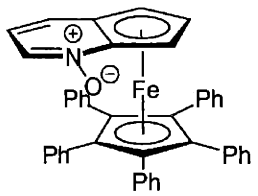
		rfl	2197.4
		rfp	1595.3
		th	20
		ins	100.000
		nm	ph

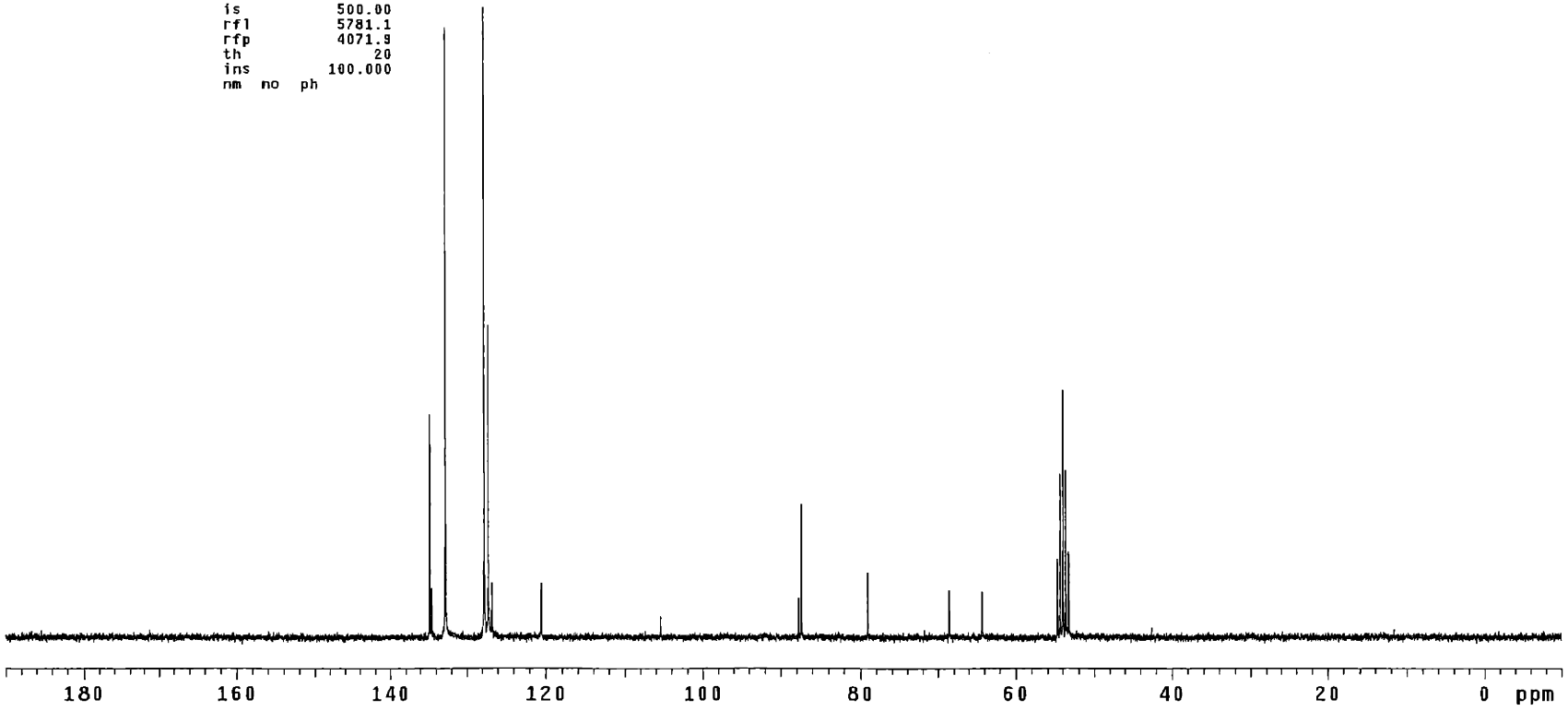


13C OBSERVE

exp1 std13c

SAMPLE		DEC. & VT	
date	May 10 1999	dn	H1
solvent	cd2cl2	dof	0
file	exp	dm	y
ACQUISITION		dmm	w
sfrq	75.410	dmf	9900
tn	C13	dpwr	49
at	2.500	PROCESSING	
np	98048	lb	1.00
sw	19607.8	wtfile	
fb	10800	proc	ft
bs	16	fn	not used
tpwr	60	math	f
pw	6.0		
d1	3.000	werr	
tof	618.6	wexp	
nt	10000	wbs	
ct	464	wnt	
alock	n	DISPLAY	
gain	not used	sp	-754.1
FLAGS		wp	15081.0
il	n	vs	100
in	n	sc	0
dp	y	wc	250
hs	nn	hzmm	60.32
		is	500.00
		rfl	5781.1
		rfp	4071.9
		th	20
		ins	100.000
		nm no ph	

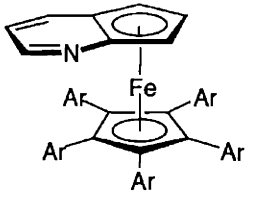




STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Jan 17 2000	dn	H1
solvent	cd2cl2	dof	0
file	exp	dm	nnn
ACQUISITION		dmm	c
sfrq	299.865	dmf	200
tn	H1	dpwr	15
at	3.500	PROCESSING	
np	37376	wtfile	
sw	5339.7	proc	ft
fb	3000	fn	not used
bs	4	math	f
tpwr	60	werr	
pw	12.0	wexp	
d1	4.000	wbs	
tof	995.5	wnt	
nt	16	DISPLAY	
ct	16	sp	-150.0
alock	n	wp	3148.4
gain	not used	vs	150
FLAGS		sc	0
il	n	wc	250
in	n	hzmm	12.59
dp	y	is	10000.00
hs	nn	rfl	2197.9
		rfp	1595.3
		th	20
		ins	1.000
		nm	ph

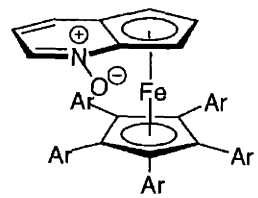


Ar = 4-Me-C_6H_3

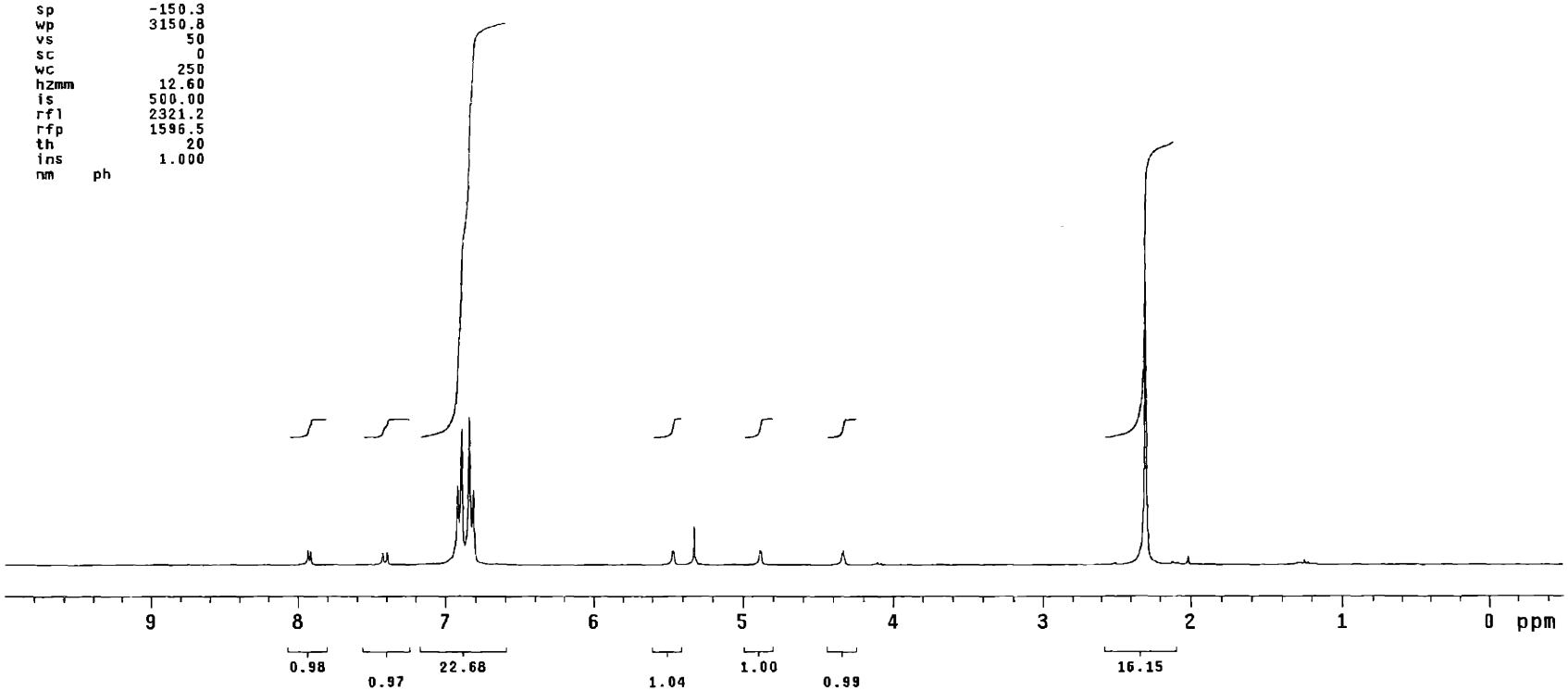
STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Jan 26 2000	dfrq	300.101
solvent	cd2cl2	dn	H1
file	exp	dpwr	40
ACQUISITION		dof	0
sfrq	300.101	dm	nnn
tn	H1	dmm	c
at	1.998	dmf	11300
np	17984	PROCESSING	
sw	4500.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	54		
pw	7.0	werr	
d1	4.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-150.3		
wp	3150.8		
vs	50		
sc	0		
wc	250		
hzmm	12.60		
is	500.00		
rfl	2321.2		
rfp	1596.5		
th	20		
ins	1.000		
nm	ph		



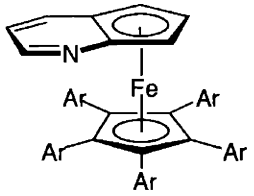
Ar = 4-Me-C_6H_3



STANDARD PROTON PARAMETERS

expl s2pul

SAMPLE		DEC. & VT	
date	Jan 22 2000	dfrq	125.675
solvent	cd2cl2	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.759	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	56	dfrq2	0
pw	8.5	dn2	
d1	4.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.0	dof3	0
wp	5247.3	dm3	n
vs	200	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	500.00	homo3	n
rfl	3678.9	PROCESSING	
rfp	2658.7	wtfile	
th	7	proc	ft
ins	1.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	

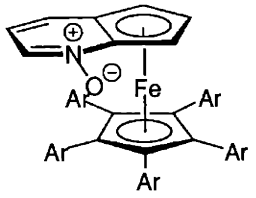


Ar = 4-(*t*-Bu)-C_6H_3

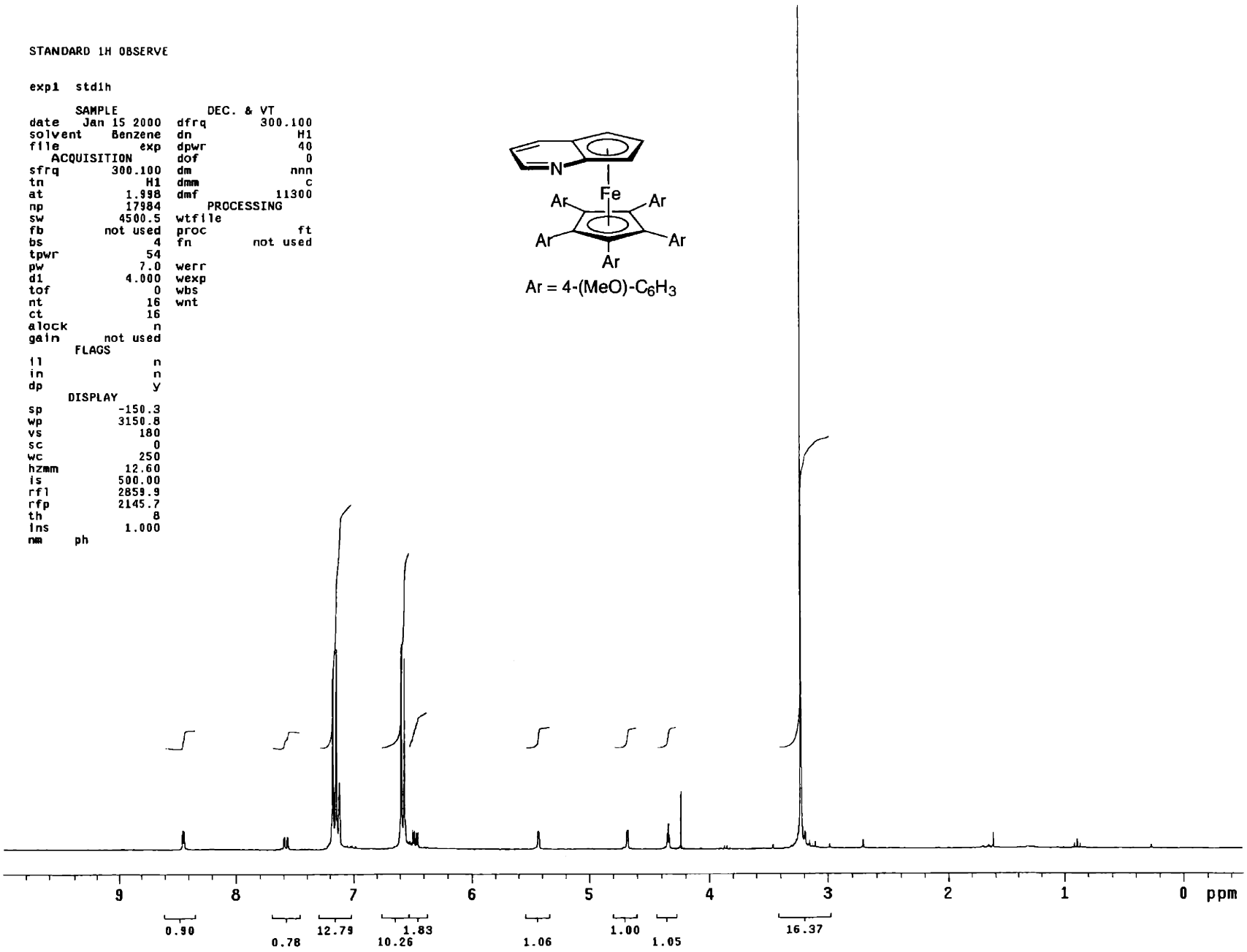
STANDARD PROTON PARAMETERS

expl s2pul

SAMPLE		DEC. & VT	
date	Jan 18 2000	dfrq	500.248
solvent	cd2cl2	dn	H1
file	exp	dpwr	37
ACQUISITION		dof	0
sfrq	500.249	dm	nnn
tn	H1	dmm	c
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	y
bs	4	PROCESSING	
tpwr	58	wtfile	
pw	8.1	proc	ft
d1	4.000	fn	not used
tof	1498.2	math	f
nt	16		
ct	16	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.4		
wp	5252.5		
vs	500		
sc	0		
wc	250		
hzmm	21.01		
is	1000.00		
rfl	3670.9		
rfp	2661.3		
th	7		
ins	1.000		
nm	ph		



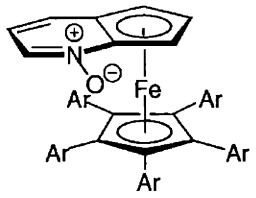
Ar = 4-(*t*-Bu)-C_6H_3


STANDARD 1H OBSERVE
exp1 stdih
SAMPLE
date Jan 15 2000
solvent Benzene
file exp
ACQUISITION
sfrq 300.100
tn H1
at 1.998
np 17984
sw 4500.5
fb not used
bs 4
tpwr 54
pw 7.0
d1 4.000
tof 0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -150.3
wp 3150.8
vs 180
sc 0
wc 250
hzmm 12.60
is 500.00
rfl 2859.9
rfp 2145.7
th 8
lns 1.000
nm ph
DEC. & VT
dfrq 300.100
dn H1
dpwr 40
dof 0
dm nnn
dmm c
dmf 11300
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
N
Fe
Ar
Ar = 4-(MeO)-C6H3
9
8
7
6
5
4
3
2
1
0 ppm
0.90
0.78
12.79
1.83
10.26
1.06
1.00
1.05
16.37

STANDARD PROTON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Jan 27 2000	dfrq	125.675
solvent	CDCl3	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.758	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	56	dfrq2	0
pw	8.5	dn2	
d1	4.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-249.9	dof3	0
wp	5247.3	dm3	n
vs	100	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	1000.00	homo3	n
rfl	4636.4	PROCESSING	
rfp	3628.2	wtfile	
th	7	proc	ft
ins	1.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	

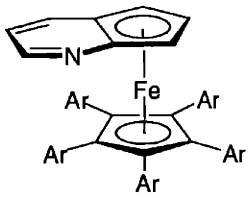


Ar = 4-(MeO)-C_6H_3

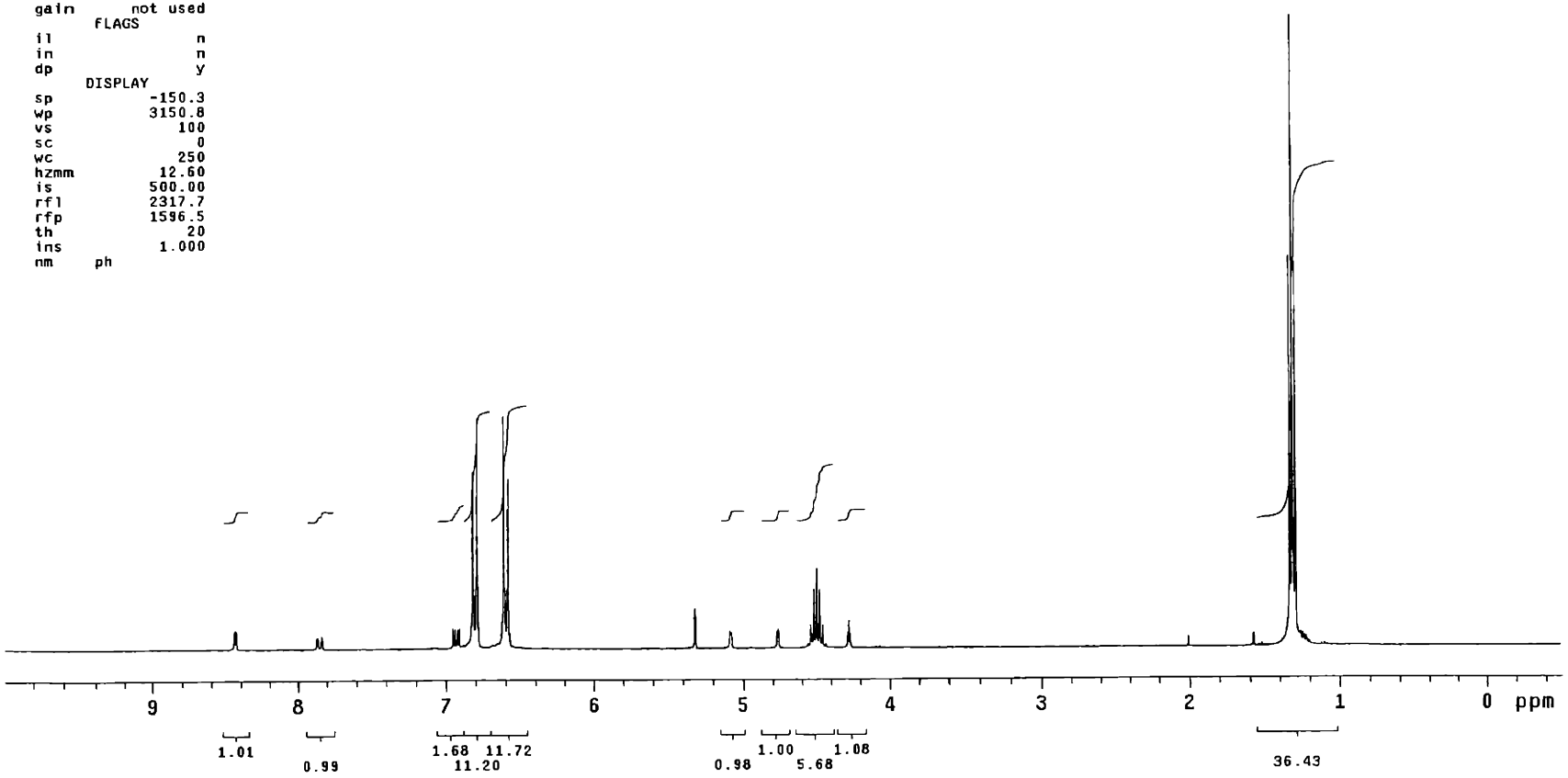
STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Jan 18 2000	dfrq	300.101
solvent	cd2cl2	dn	H1
file	exp	dpwr	40
ACQUISITION		dof	0
sfrq	300.101	dm	nnn
tn	H1	dmm	c
at	1.998	dmf	11300
np	17984	PROCESSING	
sw	4500.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	54		
pw	7.0	werr	
d1	4.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-150.3		
wp	3150.8		
vs	100		
sc	0		
wc	250		
hzmm	12.60		
is	500.00		
rfl	2317.7		
rfp	1596.5		
th	20		
ins	1.000		
nm	ph		



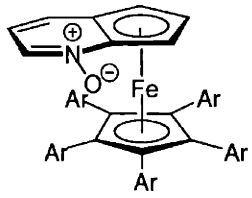
Ar = 4-(*i*-PrO)-C_6H_3



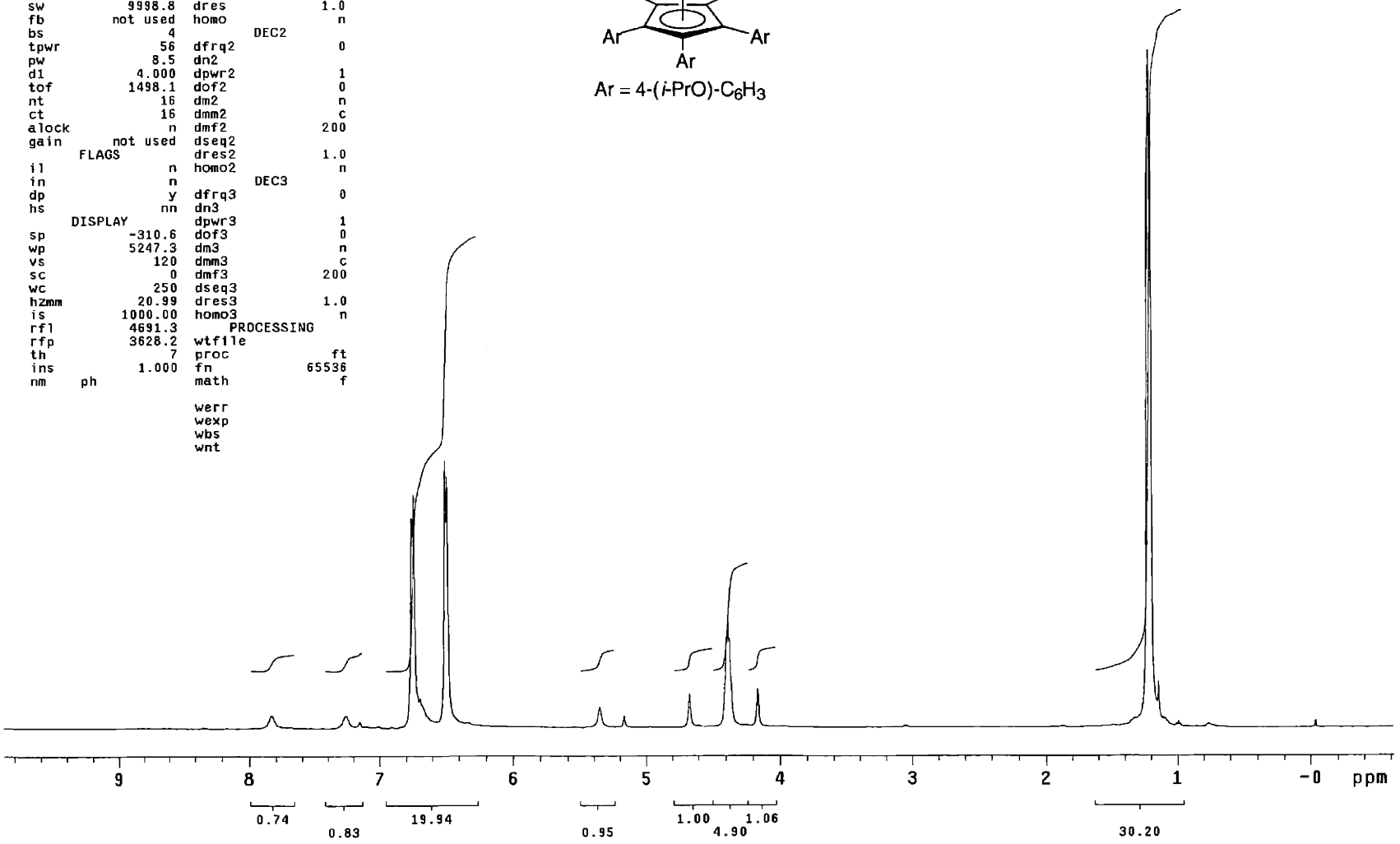
STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jan 27 2000	dfrq	125.675
solvent	CDCl3	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.758	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	56	dfrq2	0
pw	8.5	dn2	
d1	4.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-310.6	dof3	0
wp	5247.3	dm3	n
vs	120	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	1000.00	homo3	n
rfl	4691.3	PROCESSING	
rfp	3628.2	wtfile	
th	7	proc	ft
ins	1.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	



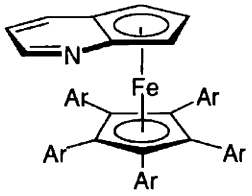
Ar = 4-(*i*-PrO)-C_6H_3



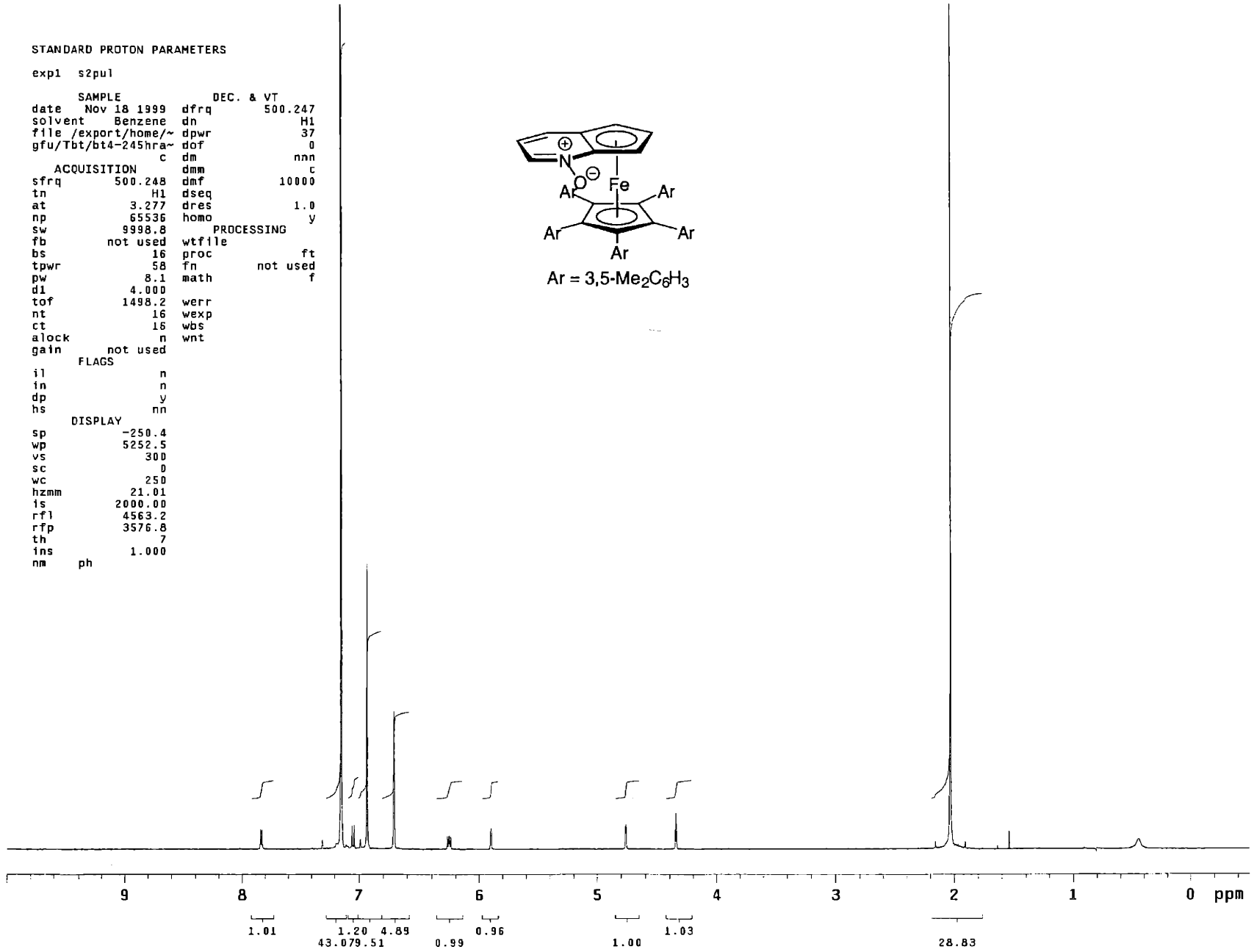
STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jan 17 2000	dfrq	125.675
solvent	cd2cl2	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.759	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	56	dfrq2	0
pw	8.5	dn2	
d1	2.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.0	dof3	0
wp	5247.3	dm3	n
vs	224	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	500.00	homo3	n
rfl	3672.7	PROCESSING	
rfp	2658.7	wtfile	
th	7	proc	ft
ins	1.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	



Ar = 3,5-$Me_2C_6H_3$


STANDARD PROTON PARAMETERS
exp1 s2pul
SAMPLE
date Nov 18 1999
solvent Benzene
file /export/home/~
gfu/Tbt/bt4-245hra~
c
ACQUISITION
sfrq 500.248
tn H1
at 3.277
np 65536
sw 9998.8
fb not used
bs 16
tpwr 58
pw 8.1
d1 4.000
tof 1498.2
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.4
wp 5252.5
vs 300
sc 0
wc 250
hzmm 21.01
is 2000.00
rfl 4563.2
rfp 3576.8
th 7
ins 1.000
nm ph
DEC. & VT
dfrq 500.247
dn H1
dpwr 37
dof 0
dm nnn
dmm c
dmf 10000
dseq
dres 1.0
homo y
PROCESSING
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
Ar = 3,5-Me2C6H3
9
8
7
6
5
4
3
2
1
0 ppm
1.01
1.20 4.89
43.079.51
0.99
0.96
1.00
1.03
28.83

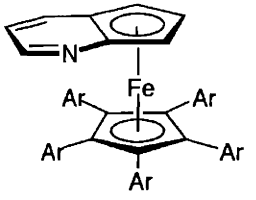
STANDARD PROTON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Aug 17 1999	dfrq	500.247
solvent	CDCl3	dn	H1
file	/export/home/~gfu/Tbt/bt5-79h	dpwr	37
		dof	0
ACQUISITION		dm	nnn
sfrq	500.248	dmm	c
tn	H1	dmf	10000
at	3.277	dseq	
np	65536	dres	1.0
sw	9998.8	homo	y
fb	not used	PROCESSING	
bs	8	wtfile	
tpwr	58	proc	ft
pw	8.1	fn	not used
dl	4.000	math	f
tof	1498.2		
nt	16	werr	
ct	16	wexp	
alock	n	wbs	
gain	not used	wnt	

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-250.3
wp	5252.5
vs	200
sc	0
wc	250
hzmm	21.01
is	1000.00
rfl	4634.9
rfp	3631.8
th	7
ins	1.000
nm	ph

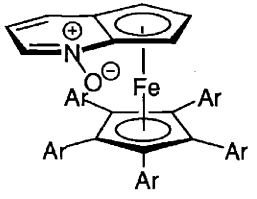


Ar = 3,5-$Et_2C_6H_3$

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jan 13 2000	dfrq	125.675
solvent	cd2cl2	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
$frq	499.759	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	56	dfrq2	0
pw	8.5	dn2	
d1	4.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.0	dof3	0
wp	5247.3	dm3	n
vs	150	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	1000.00	homo3	n
rfl	3674.0	PROCESSING	
rfp	2658.7	wtfile	
th	7	proc	ft
ins	1.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	



Ar = 3,5-$Et_2C_6H_3$

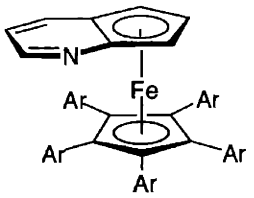
STANDARD PROTON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Aug 17 1999	dfrq	500.247
solvent	CDCl3	dn	H1
file	/export/home/~gfu/Tbt/bt5-73h	dpwr	37
ACQUISITION		dof	0
sfrq	500.248	dm	nnn
tn	H1	dmm	c
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	y
bs	16	PROCESSING	
tpwr	58	wtfile	
pw	8.1	proc	ft
d1	4.000	fn	not used
tof	1498.2	math	f
nt	16	werr	
ct	16	wexp	
alock	n	wbs	
gain	not used	wnt	

FLAGS	
il	n
in	n
dp	y
hs	nn

DISPLAY	
sp	-250.3
wp	5252.5
vs	200
sc	0
wc	250
hzmm	21.01
is	1000.00
rfl	4634.3
rfp	3631.8
th	4
ins	1.000
nm	ph

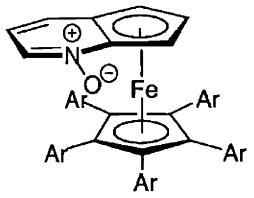


Ar = 3,5-(i-Pr)$_2$-C$_6$H$_3$

STANDARD PROTON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Jan 18 2000	dfrq	500.248
solvent	cd2cl2	dn	H1
file	exp	dpwr	37
ACQUISITION		dof	0
sfrq	500.249	dm	nnn
tn	H1	dmm	c
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	y
bs	4	temp	23.0
tpwr	58	PROCESSING	
pw	8.1	wtfile	
d1	4.000	proc	ft
tof	1498.2	fn	not used
nt	16	math	f
ct	16		
alock	n	werr	
gain	not used	wexp	
FLAGS		wbs	
il	n	wnt	
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.4		
wp	5252.5		
vs	130		
sc	0		
wc	250		
hzmm	21.01		
is	1000.00		
rfl	3671.2		
rfp	2661.3		
th	7		
ins	1.000		
nm	ph		

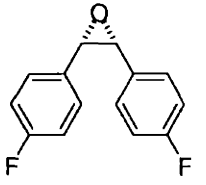


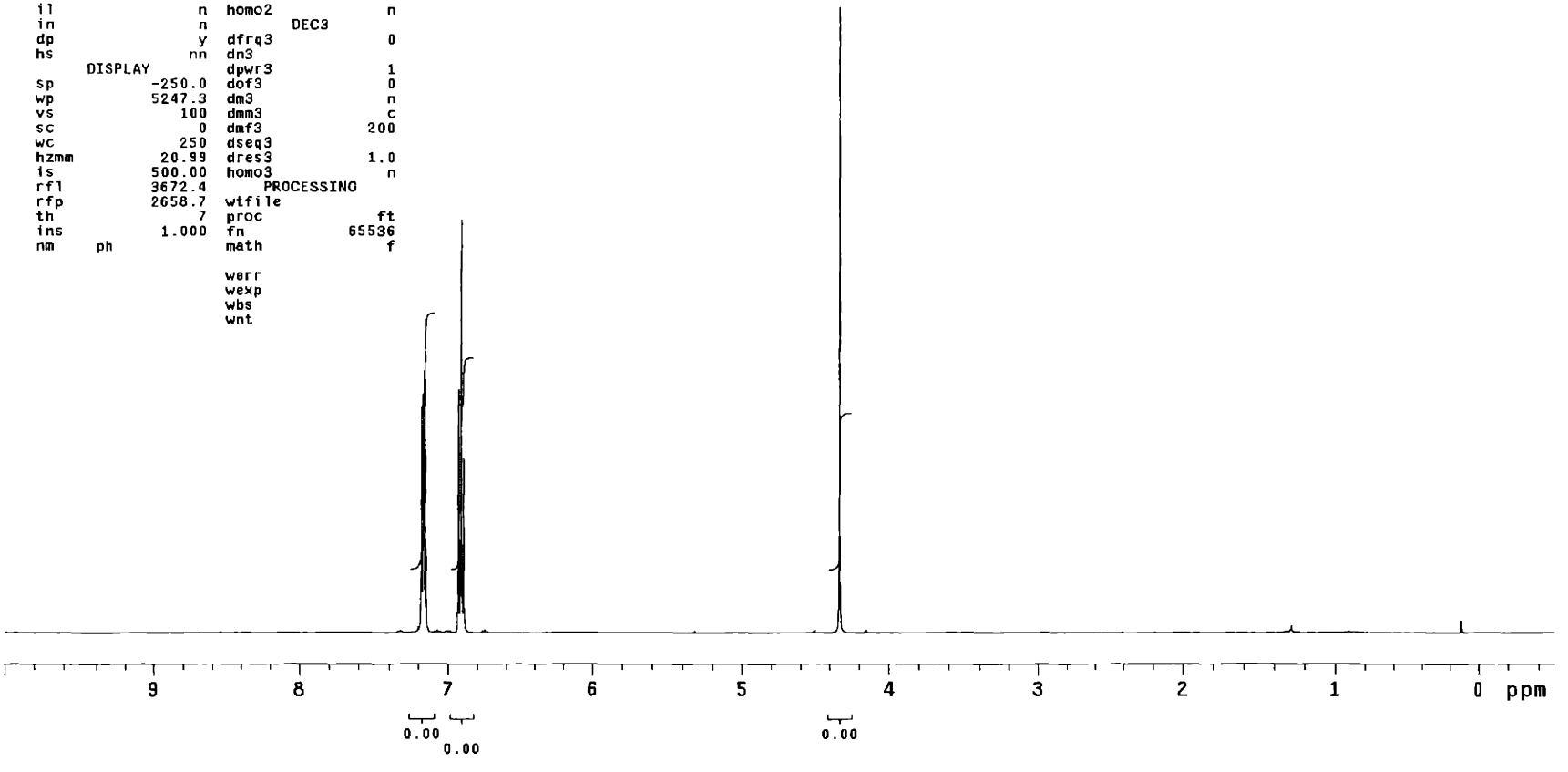
Ar = 3,5-(*i*-Pr)$_2$-C$_6$H$_3$

STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 14 2000	dfrq	125.675
solvent	cd2cl2	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.759	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10400
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	16	DEC2	
tpwr	55	dfrq2	0
pw	8.5	dn2	
d1	0	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.0	dof3	0
wp	5247.3	dm3	n
vs	100	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	500.00	homo3	n
rfl	3672.4	PROCESSING	
rfp	2658.7	wtfile	
th	7	proc	ft
ins	1.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	

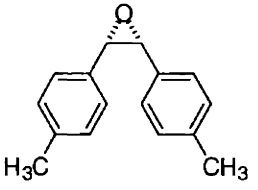


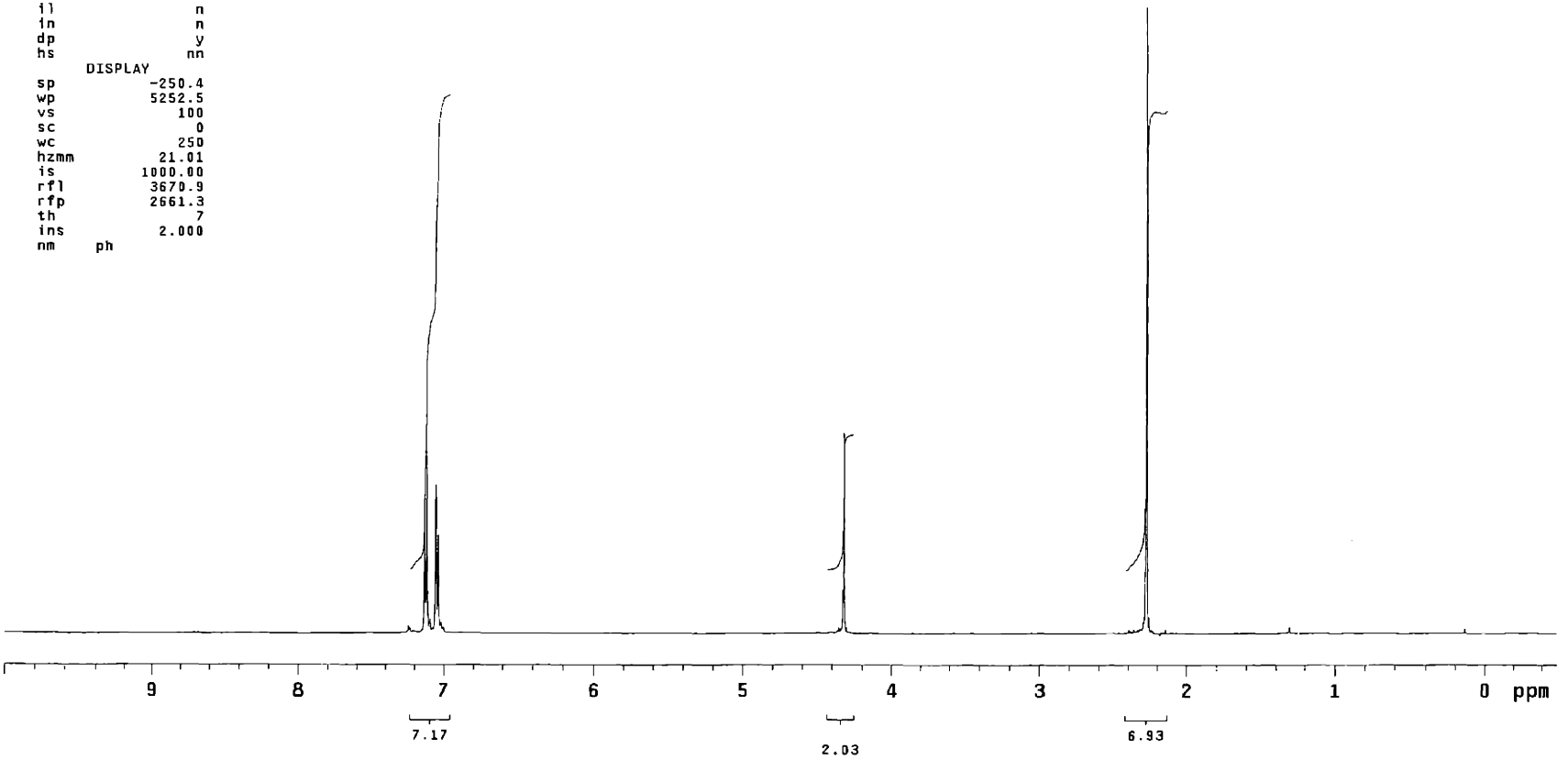


STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 14 2000	dfrq	500.248
solvent	cd2cl2	dn	H1
file	exp	dpwr	37
ACQUISITION		dof	0
sfrq	500.249	dm	nnn
tn	H1	dmm	c
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	y
bs	4	PROCESSING	
tpwr	58	wtfile	
pw	8.1	proc	ft
d1	4.000	fn	not used
tof	1498.2	math	f
nt	16		
ct	16	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.4		
wp	5252.5		
vs	100		
sc	0		
wc	250		
hzmm	21.01		
is	1000.00		
rfl	3670.9		
rfp	2661.3		
th	7		
ins	2.000		
nm	ph		

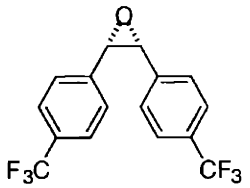


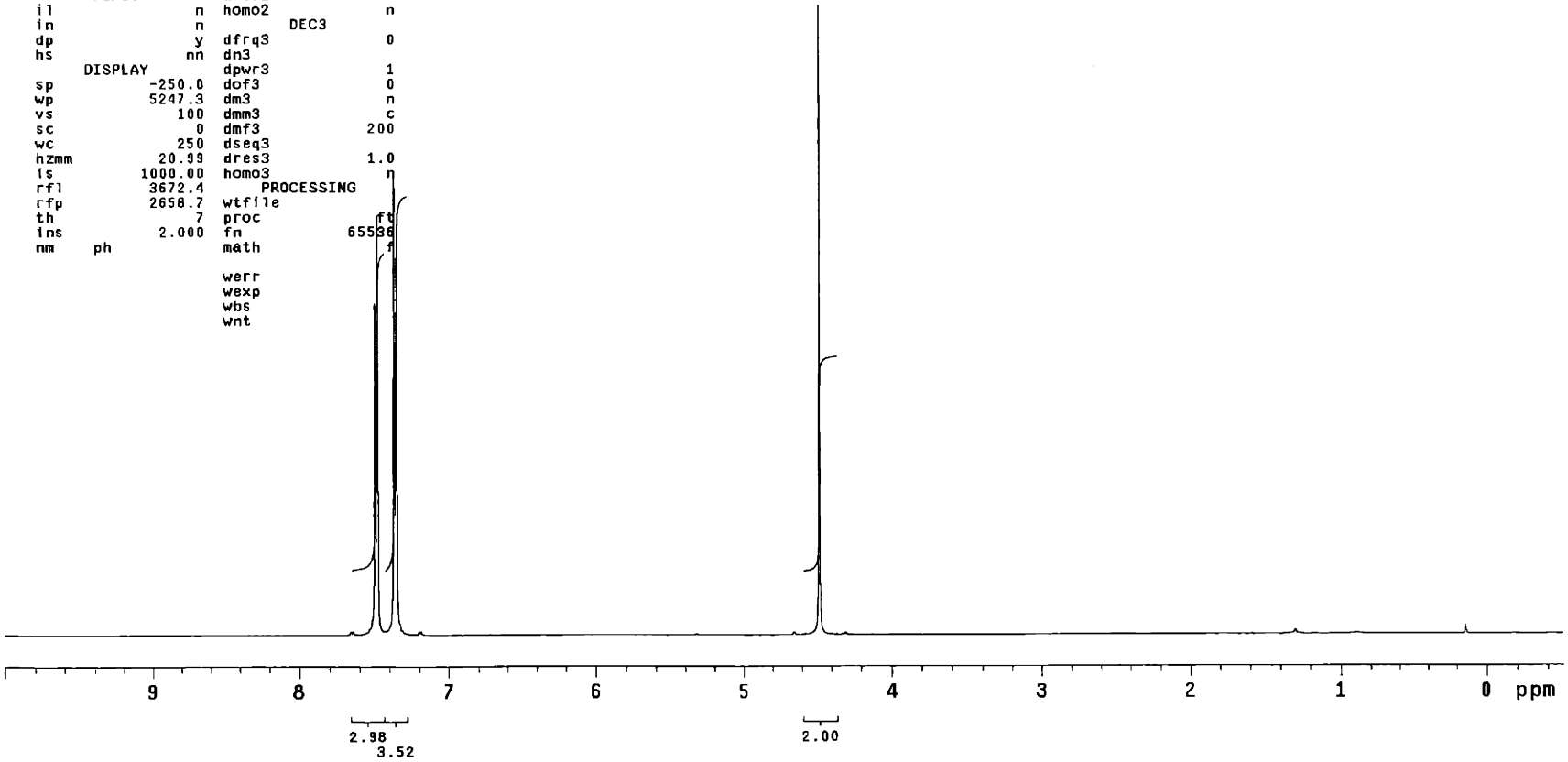


STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 14 2000	dfrq	125.675
solvent	cd2cl2	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.759	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10400
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	16	DEC2	
tpwr	55	dfrq2	0
pw	8.5	dn2	
d1	0	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.0	dof3	0
wp	5247.3	dm3	n
vs	100	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	1000.00	homo3	n
rfl	3672.4	PROCESSING	
rfp	2658.7	wtfile	
th	7	proc	ft
ins	2.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	

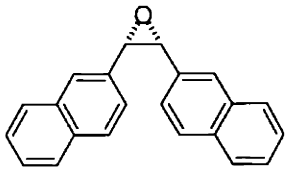


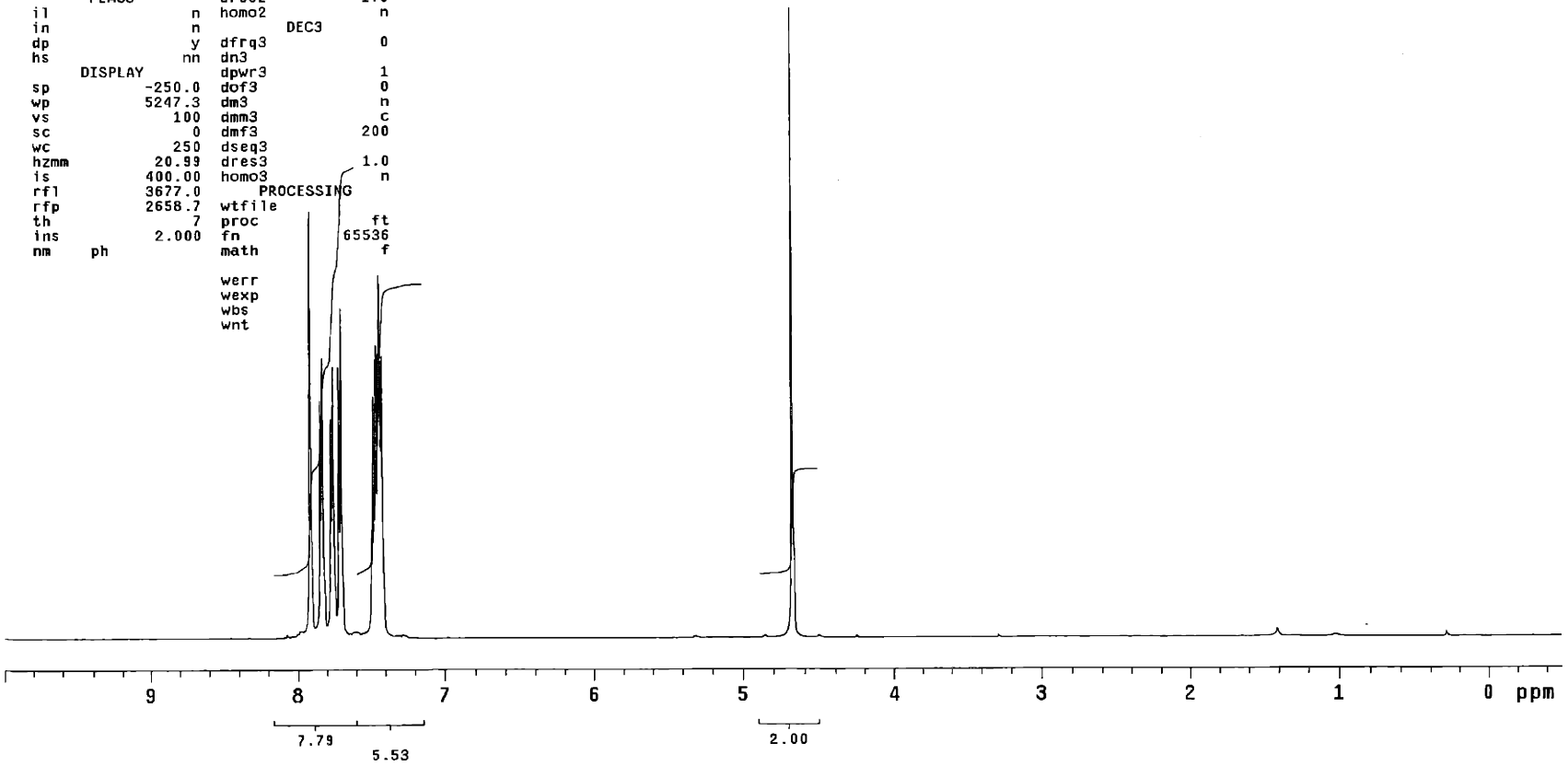


STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 14 2000	dfrq	125.675
solvent	cd2cl2	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.759	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10400
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	55	dfrq2	0
pw	8.5	dn2	
d1	4.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-250.0	dof3	0
wp	5247.3	dm3	n
vs	100	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	400.00	homo3	n
rfl	3677.0	PROCESSING	
rfp	2658.7	wtfile	
th	7	proc	ft
ins	2.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	

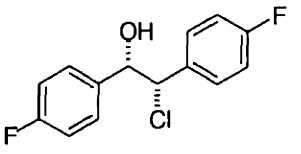


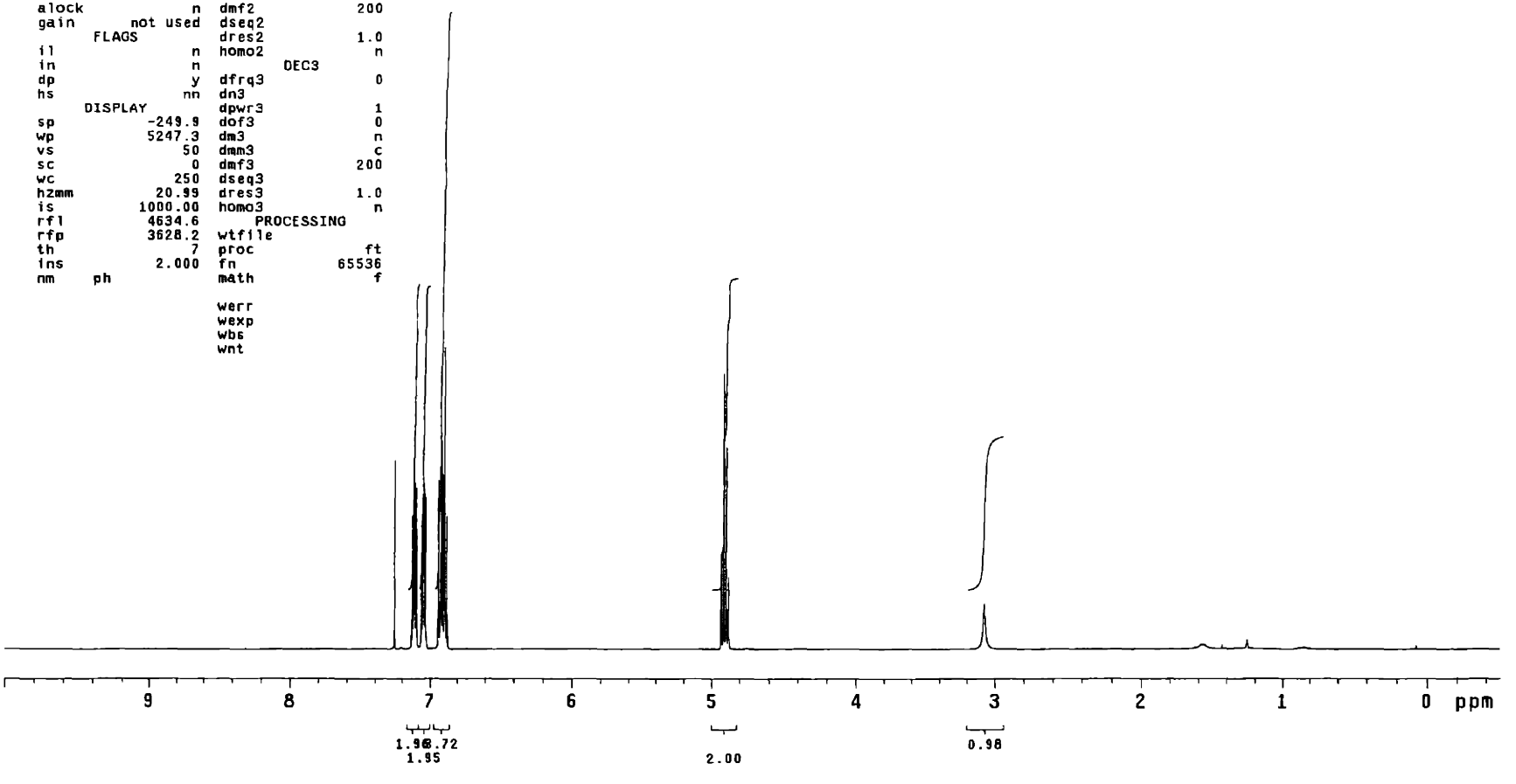


STANDARD PROTON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Feb 11 2000	dfrq	125.675
solvent	CDCl3	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.758	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	56	dfrq2	0
pw	8.5	dn2	
d1	4.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-249.9	dof3	0
wp	5247.3	dm3	n
vs	50	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	1000.00	homo3	n
rfl	4634.6	PROCESSING	
rfp	3628.2	wtfile	
th	7	proc	ft
ins	2.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	

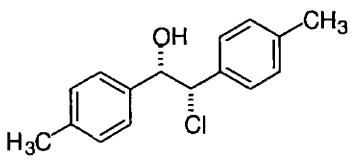


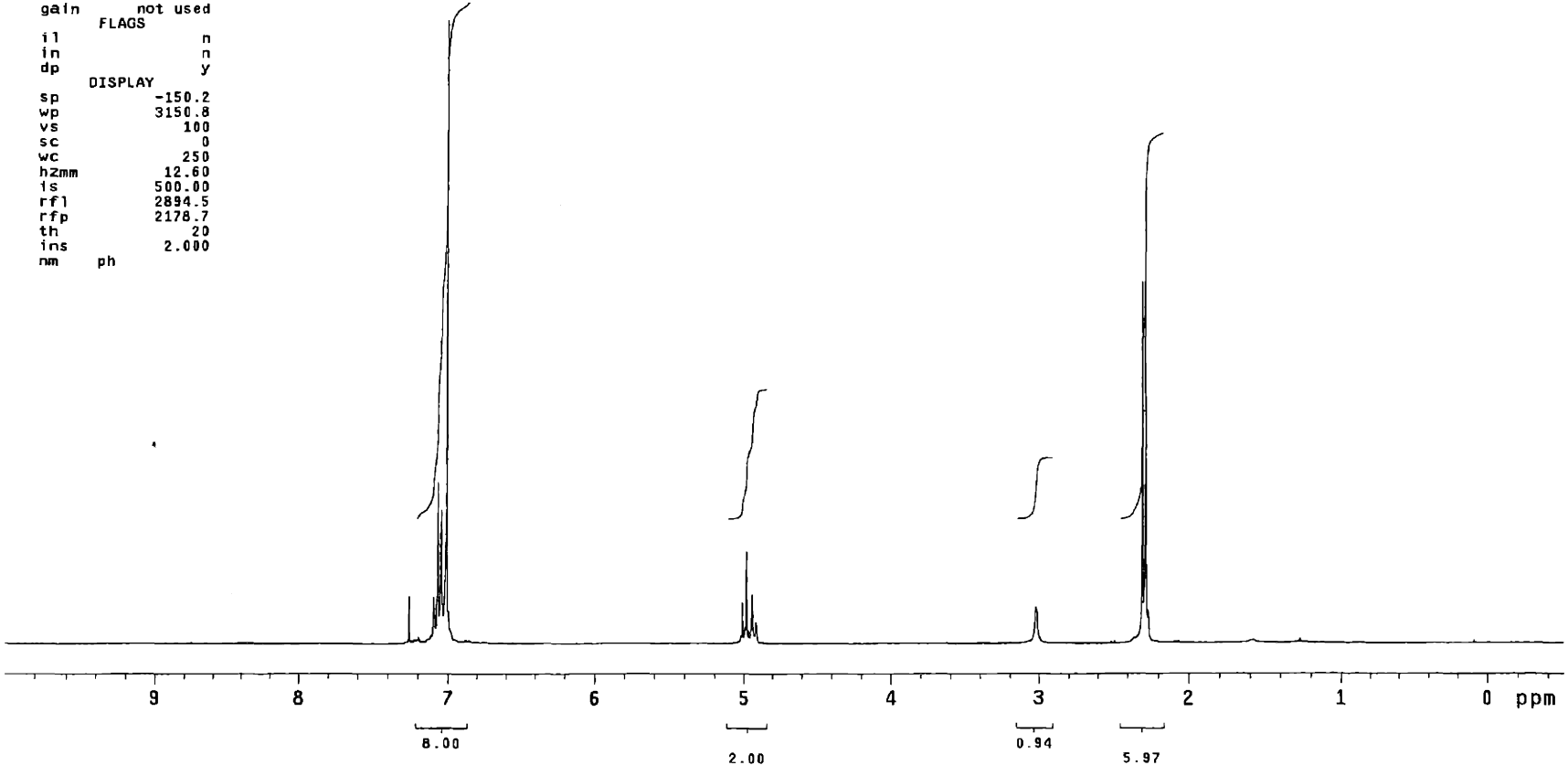


STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Feb 11 2000	dfrq	300.100
solvent	CDCl3	dn	H1
file	exp	dpwr	40
ACQUISITION		dof	0
sfrq	300.100	dm	nnn
tn	H1	dmm	c
at	1.998	dmf	11300
np	17984	PROCESSING	
sw	4500.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	54		
pw	7.0	werr	
d1	4.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-150.2		
wp	3150.8		
vs	100		
sc	0		
wc	250		
hzmm	12.60		
is	500.00		
rfl	2894.5		
rfp	2178.7		
th	20		
ins	2.000		
nm	ph		

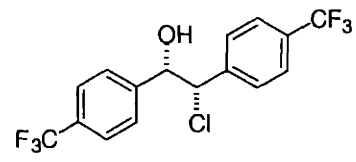


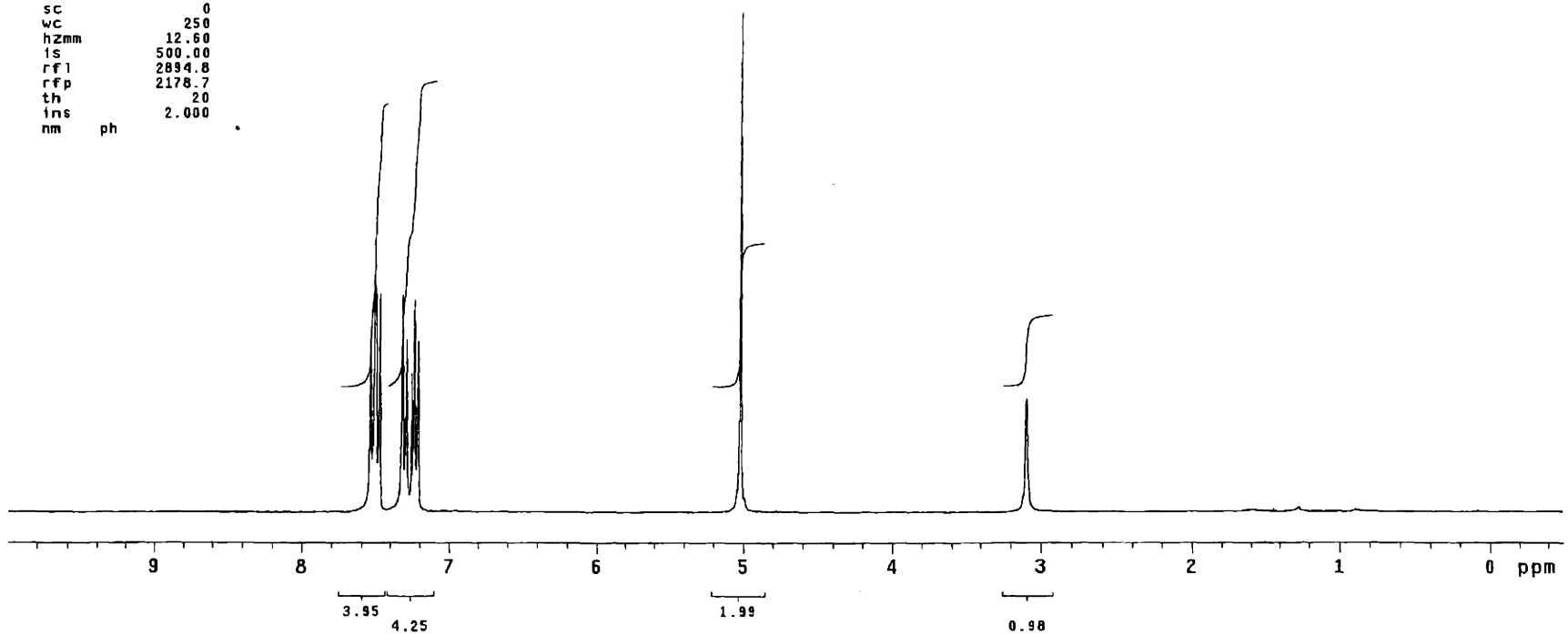


STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Feb 12 2000	dfrq	300.100
solvent	CDCl3	dn	H1
file	exp	dpwr	40
ACQUISITION		dof	0
sfrq	300.100	dm	nnn
tn	H1	dmm	c
at	1.998	dmf	11300
np	17984	PROCESSING	
sw	4500.5	wtfile	
fb	not used	proc	ft
bs	4	fn	not used
tpwr	54		
pw	7.0	werr	
d1	4.000	wexp	
tof	0	wbs	
nt	16	wnt	
ct	16		
alock	n		
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-150.2		
wp	3150.8		
vs	80		
sc	0		
wc	250		
hzmm	12.60		
is	500.00		
rfl	2894.8		
rfp	2178.7		
th	20		
ins	2.000		
nm	ph		

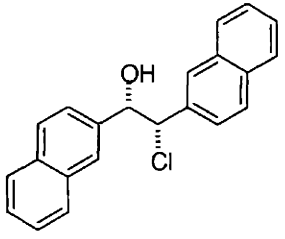


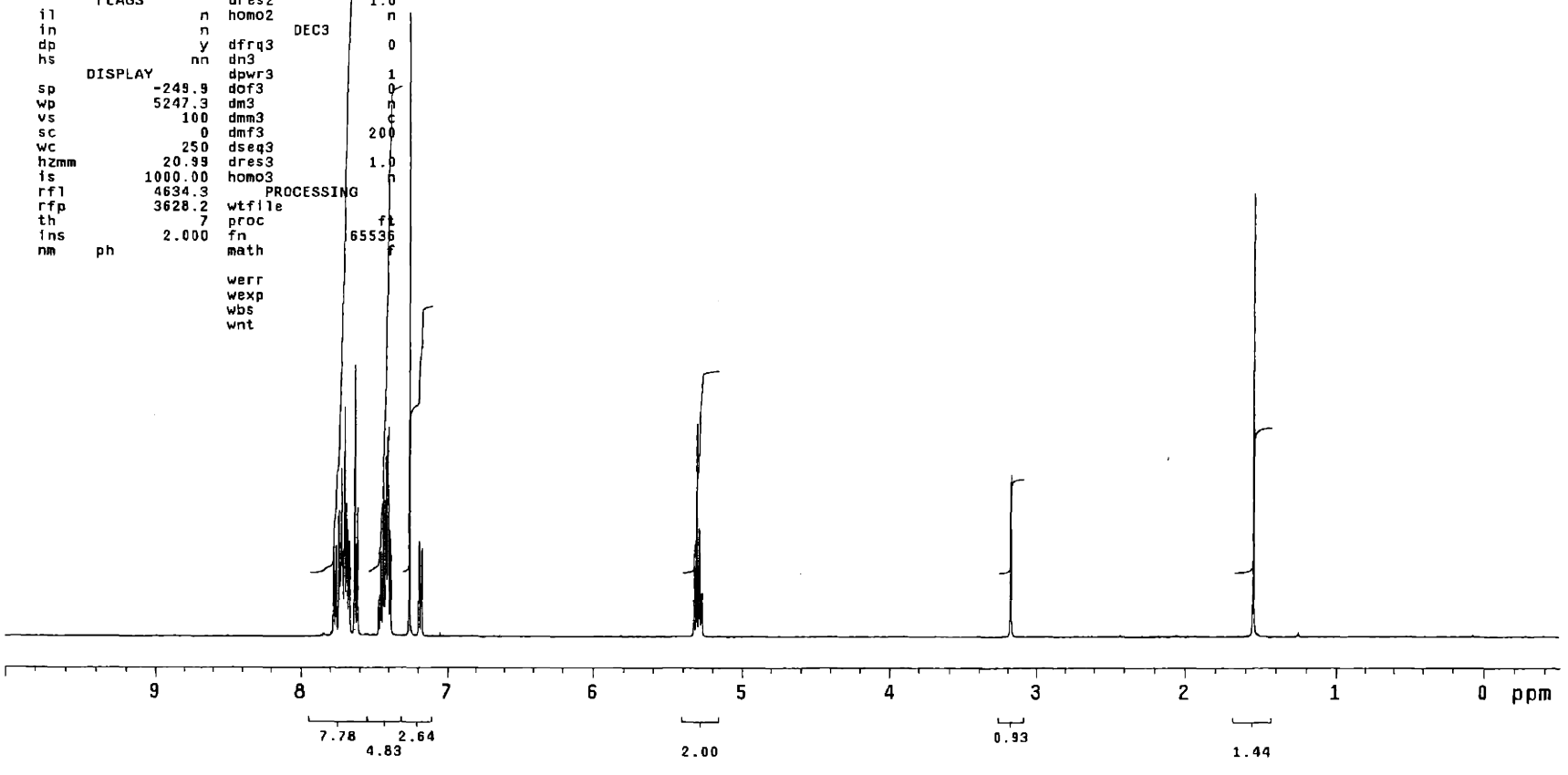


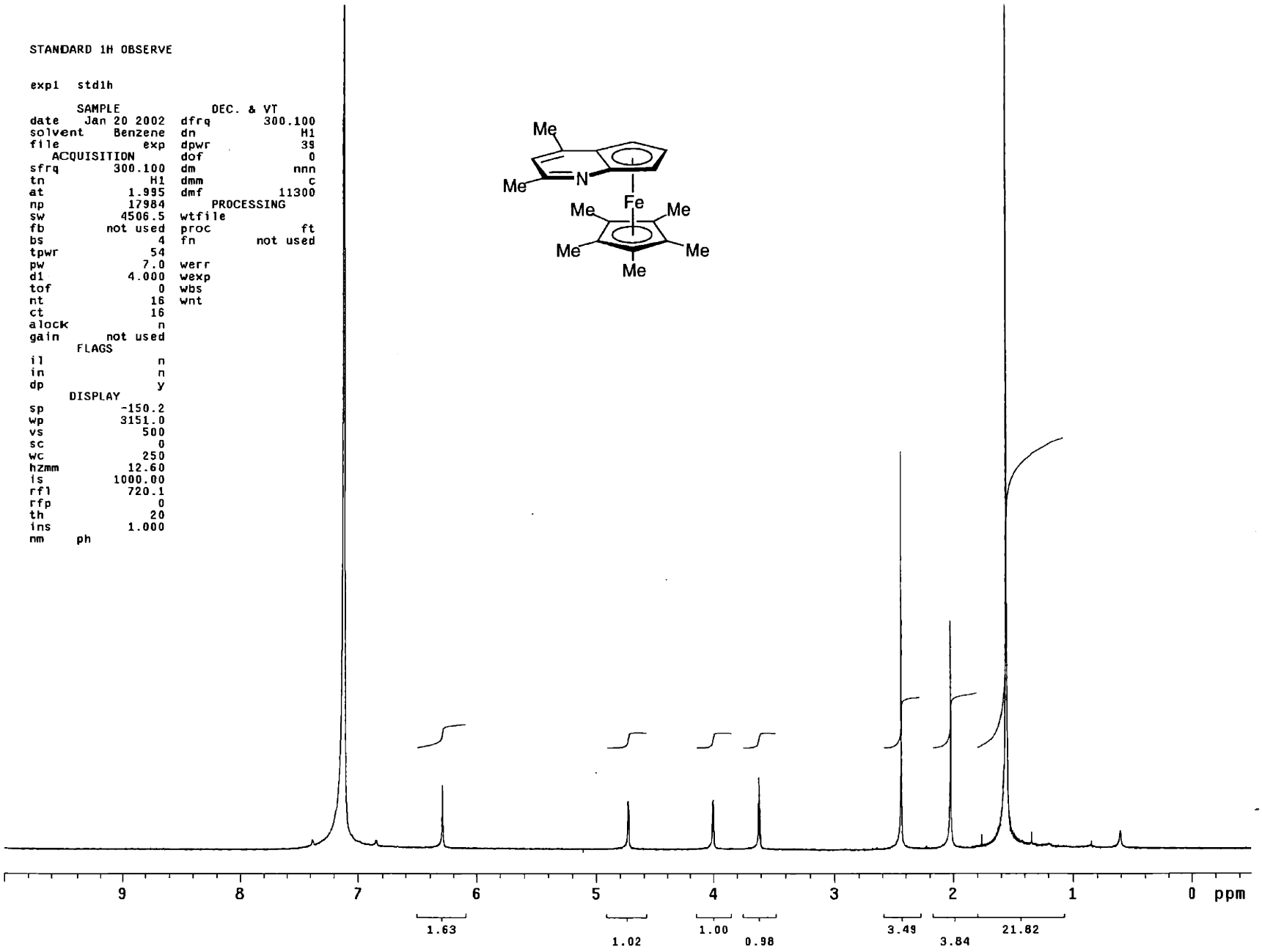
STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Feb 10 2000	dfrq	125.675
solvent	CDCl3	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.758	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	56	dfrq2	0
pw	8.5	dn2	
d1	4.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-249.9	dof3	0
wp	5247.3	dm3	n
vs	100	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	1000.00	homo3	n
rfl	4634.3	PROCESSING	
rfp	3628.2	wtfile	
th	7	proc	ft
ins	2.000	fn	65536
nm ph		math	
		werr	
		wexp	
		wbs	
		wnt	



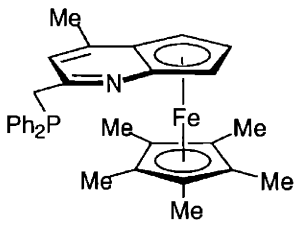



STANDARD 1H OBSERVE
expl std1h
SAMPLE
date Jan 20 2002
solvent Benzene
file exp
ACQUISITION
sfrq 300.100
tn H1
at 1.995
np 17984
sw 4506.5
fb not used
bs 4
tpwr 54
pw 7.0
d1 4.000
tof 0
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -150.2
wp 3151.0
vs 500
sc 0
wc 250
hzmm 12.60
is 1000.00
rfl 720.1
rfp 0
th 20
ins 1.000
nm ph
DEC. & VT
dfrq 300.100
dn H1
dpwr 39
dof 0
dm nnn
dmm c
dmf 11300
PROCESSING
wtfile
proc ft
fn not used
werr
wexp
wbs
wnt
Me
Me
N
Fe
Me
Me
Me
Me
Me
9
8
7
6
5
4
3
2
1
0 ppm
1.63
1.02
1.00
0.98
3.49
3.84
21.82

STANDARD PROTON PARAMETERS

exp1 s2pul

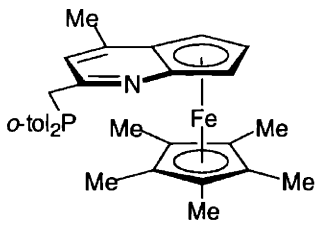
SAMPLE		DEC. & VT	
date	Feb 8 2002	dfrq	125.795
solvent	Benzene	dn	C13
file	exp	dpwr	37
ACQUISITION		dof	0
sfrq	500.235	dm	nnn
tn	H1	dmm	c
at	3.200	dmf	10000
np	64000	dseq	
sw	10000.0	dres	1.0
fb	not used	homo	n
bs	4	PROCESSING	
ss	1	wtfile	
tpwr	59	proc	ft
pw	9.8	fn	131072
d1	4.000	math	f
tof	1498.2		
nt	16	werr	
ct	16	wexp	
alock	n	wbs	
gain	not used	wnt	
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.1		
wp	5252.5		
vs	300		
sc	0		
wc	250		
hzmm	21.01		
is	1000.00		
rfl	4562.0		
rfp	3576.7		
th	7		
ins	1.000		
nm	ph		



STANDARD PROTON PARAMETERS

exp2 s2pul

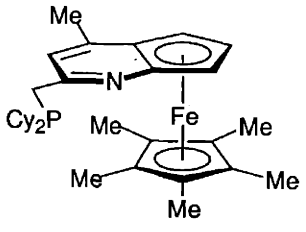
SAMPLE		DEC. & VT	
date	Dec 2 2000	dfrq	125.675
solvent	Benzene	dn	C13
file	exp	dpwr	34
ACQUISITION		dof	0
sfrq	499.758	dm	nnn
tn	H1	dmm	w
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	n
bs	4	DEC2	
tpwr	56	dfrq2	0
pw	8.5	dn2	
d1	4.000	dpwr2	1
tof	1498.1	dof2	0
nt	16	dm2	n
ct	16	dmm2	c
alock	n	dmf2	200
gain	not used	dseq2	
FLAGS		dres2	1.0
il	n	homo2	n
in	n	DEC3	
dp	y	dfrq3	0
hs	nn	dn3	
DISPLAY		dpwr3	1
sp	-249.9	dof3	0
wp	5247.3	dm3	n
vs	224	dmm3	c
sc	0	dmf3	200
wc	250	dseq3	
hzmm	20.99	dres3	1.0
is	1000.00	homo3	n
rfl	4562.9	PROCESSING	
rfp	3573.2	wtfile	
th	7	proc	ft
ins	1.000	fn	65536
nm ph		math	f
		werr	
		wexp	
		wbs	
		wnt	



STANDARD PROTON PARAMETERS

exp1 s2pul

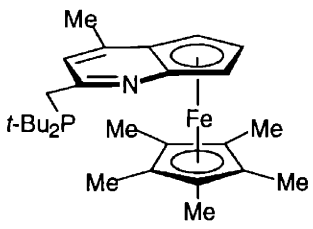
SAMPLE		DEC. & VT	
date	Dec 26 2000	dfrq	125.675
solvent	Benzene	dn	C13
file	/data/export/~	dpwr	34
home/gfu/Tbt/resto~		dof	0
re/bt9-27hh.fid		dm	nnn
ACQUISITION		dmm	w
sfrq	499.758	dmf	10000
tn	H1	dseq	
at	3.277	dres	1.0
np	65536	homo	n
sw	9998.8	PROCESSING	
fb	not used	wtfile	
bs	4	proc	ft
tpwr	56	fn	65536
pw	8.5	math	f
d1	4.000		
tof	1498.1	werr	
nt	16	wexp	
ct	16	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-249.9		
wp	5247.3		
vs	1000		
sc	0		
wc	250		
hzmm	20.99		
is	1000.00		
rfl	4563.5		
rfp	3573.2		
th	7		
ins	1.000		
nm	ph		



STANDARD PROTON PARAMETERS

exp1 s2pul

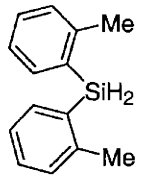
SAMPLE		DEC. & VT	
date	Dec 23 2000	dfrq	500.247
solvent	Benzene	dn	H1
file	/data/export/~	dpwr	37
home/gfu/Tbt/resto~		dof	0
re/bt9-21h.fid		dm	nnn
ACQUISITION		dmm	c
sfrq	500.248	dmf	10000
tn	H1	dseq	
at	3.277	dres	1.0
np	65536	homo	y
sw	9998.8	PROCESSING	
fb	not used	wtfile	
bs	4	proc	ft
tpwr	58	fn	not used
pw	8.1	math	f
d1	4.000		
tof	1498.2	werr	
nt	16	wexp	
ct	16	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.4		
wp	5252.5		
vs	150		
sc	0		
wc	250		
hzmm	21.01		
is	2000.00		
rfl	4563.5		
rfp	3576.8		
th	7		
ins	1.000		
nm	ph		

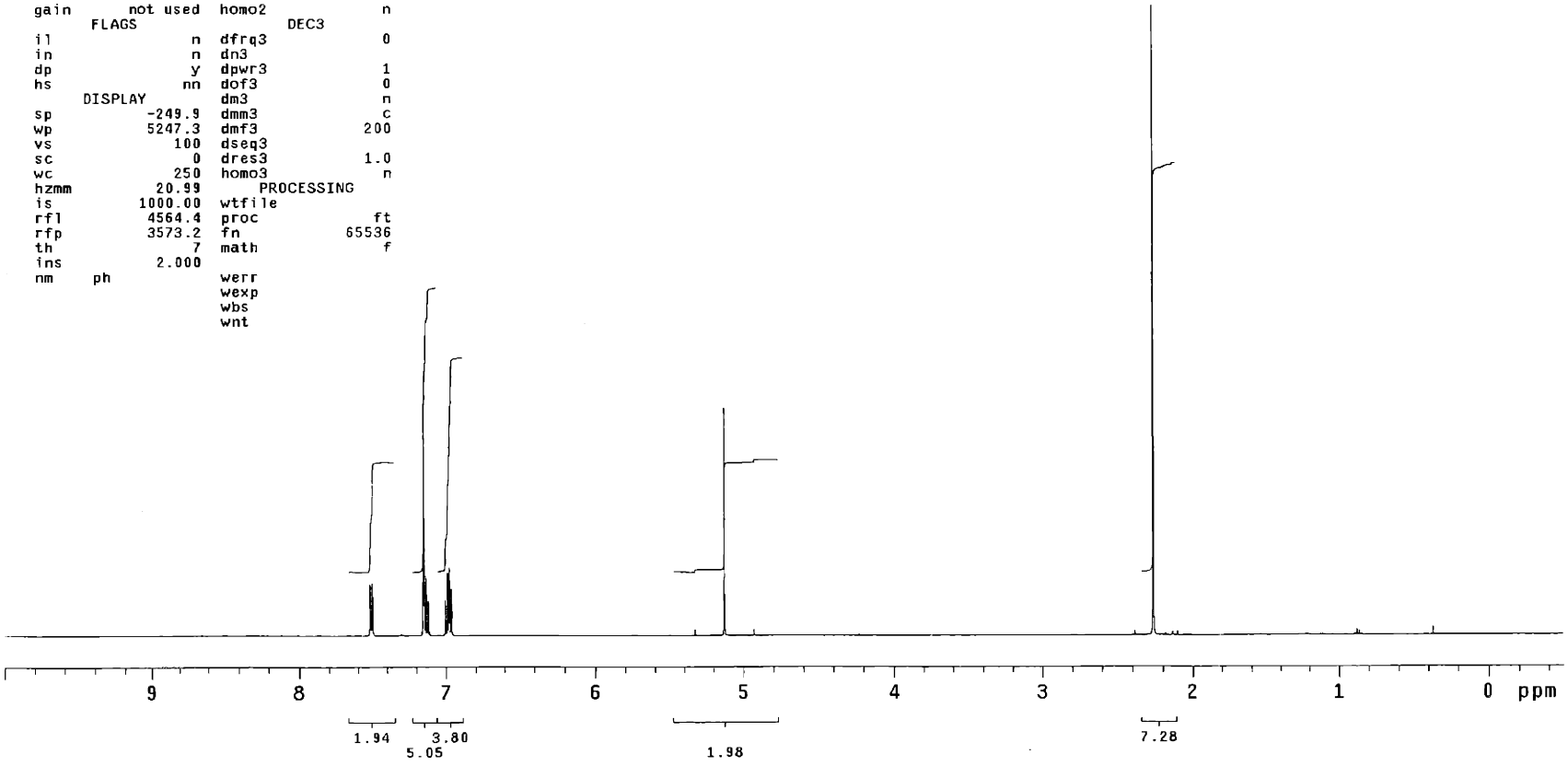


STANDARD PROTON PARAMETERS

exp4 s2pul

SAMPLE		DEC. & VT	
date	Feb 17 2001	dfrq	125.675
solvent	Benzene	dn	C13
file	/export/home/~	dpwr	34
gfu/Tbt/bt9-101h.f~		dof	0
	id	dm	nnn
ACQUISITION		dmm	w
sfrq	499.758	dmf	10400
tn	H1	dseq	
at	3.277	dres	1.0
np	65536	homo	n
sw	9998.8	DEC2	
fb	not used	dfrq2	0
bs	4	dn2	
tpwr	56	dpwr2	1
pw	8.2	dof2	0
d1	4.000	dm2	n
tof	1498.1	dmm2	c
nt	16	dmf2	200
ct	16	dseq2	
alock	n	dres2	1.0
gain	not used	homo2	n
FLAGS		DEC3	
il	n	dfrq3	0
in	n	dn3	
dp	y	dpwr3	1
hs	nn	dof3	0
DISPLAY		dm3	n
sp	-249.9	dmm3	c
wp	5247.3	dmf3	200
vs	100	dseq3	
sc	0	dres3	1.0
wc	250	homo3	n
hzmm	20.99	PROCESSING	
is	1000.00	wtfile	
rfl	4564.4	proc	ft
rfp	3573.2	fn	65536
th	7	math	f
ins	2.000		
nm ph		werr	
		wexp	
		wbs	
		wnt	



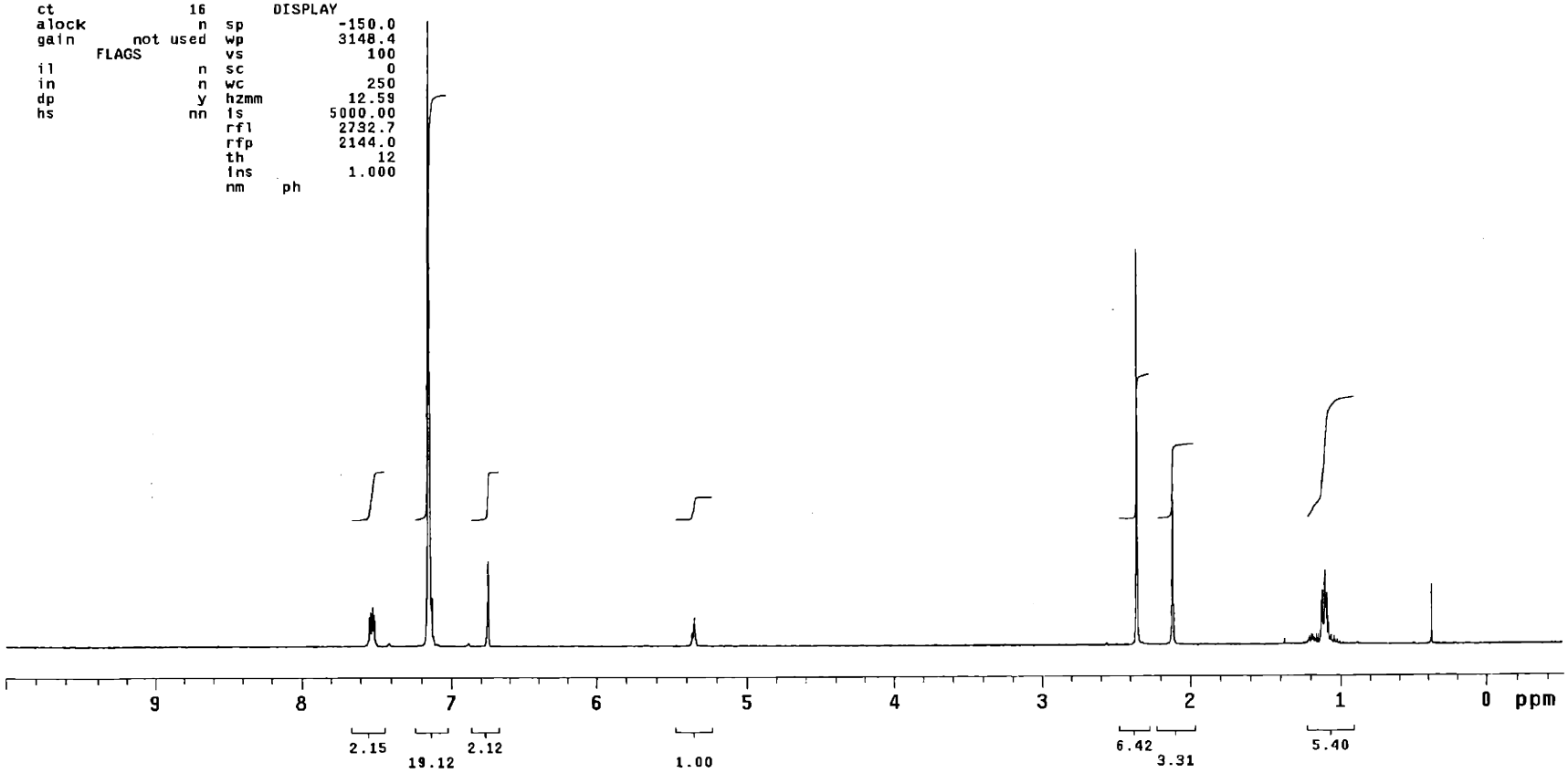


STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Feb 4 2002	dn	H1
solvent	Benzene	dof	0
file	/data/export/~	dm	nnn
home/gfu/Tbt/boris~		dmm	c
	/bt11-21h.fid	dmf	3000
ACQUISITION		dpwr	46
sfrq	299.858	PROCESSING	
tn	H1	wtfile	
at	3.500	proc	ft
np	37376	fn	not used
sw	5339.7	math	f
fb	3000		
bs	4	werr	
tpwr	60	wexp	wft f full ap~
pw	9.2	h vsadj update ds ~	
d1	4.000		dscale
tof	995.5	wbs	update
nt	16	wnt	
ct	16	DISPLAY	
alock	n	sp	-150.0
gain	not used	wp	3148.4
FLAGS		vs	100
il	n	sc	0
in	n	wc	250
dp	y	hzmm	12.59
hs	nn	is	5000.00
		rfl	2732.7
		rfp	2144.0
		th	12
		ins	1.000
		nm	ph

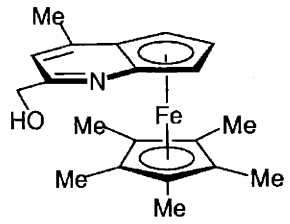
MesPhEtSiH

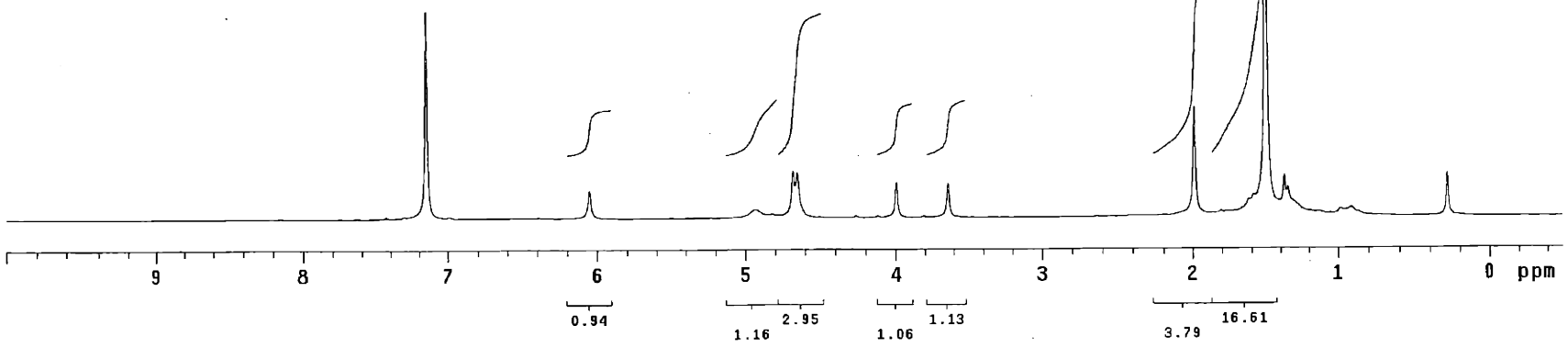


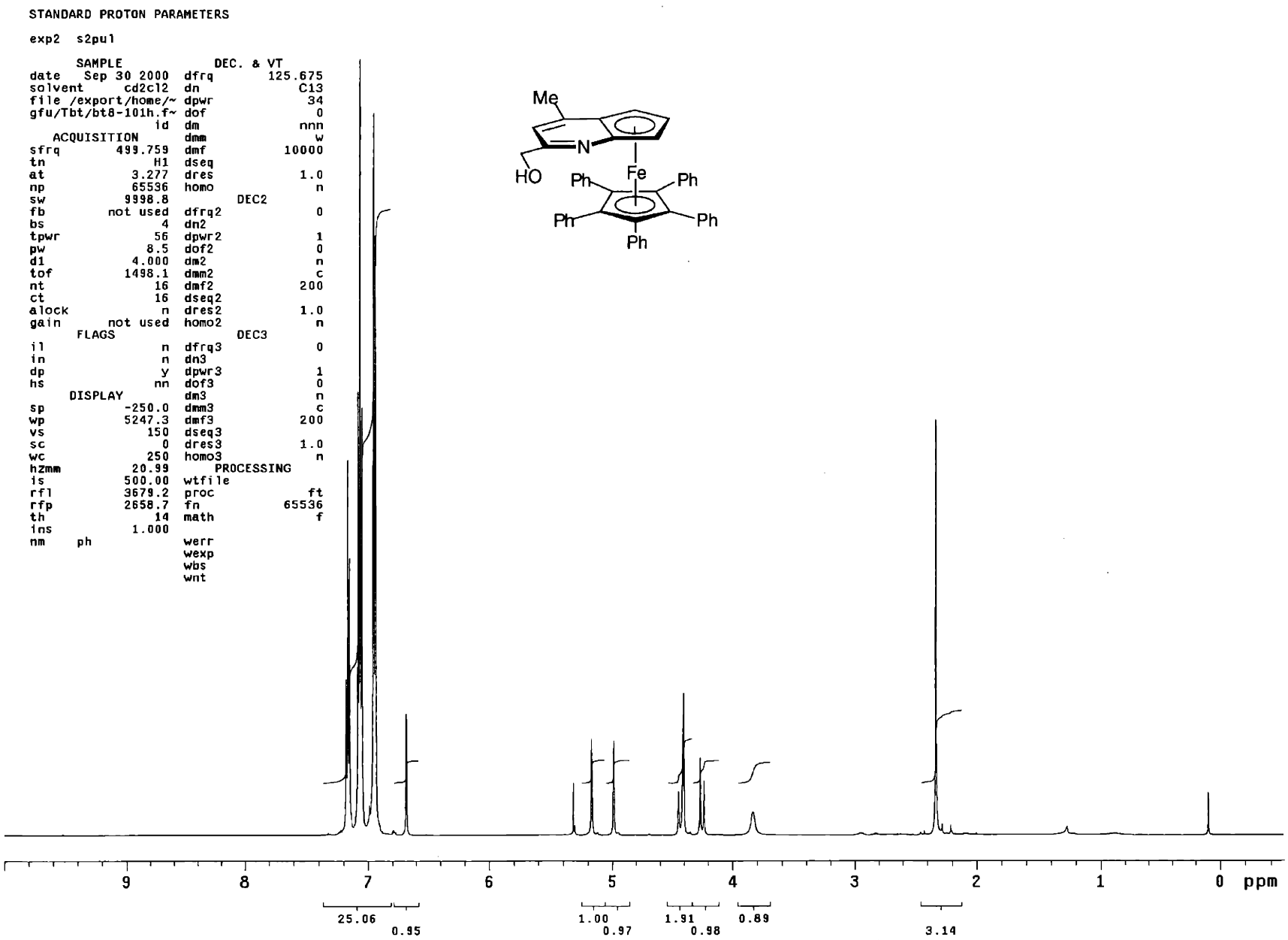
STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Sep 29 2000	dfrq	125.675
solvent	Benzene	dn	C13
file	/data/export/~	dpwr	34
home/gfu/Tbt/resto~		dof	0
re/bt8-105h.fid		dm	nnn
ACQUISITION		dmm	w
sfrq	499.758	dmf	10000
tn	H1	dseq	
at	3.277	dres	1.0
np	65536	homo	n
sw	9998.8	PROCESSING	
fb	not used	wtfile	
bs	4	proc	ft
tpwr	56	fn	65536
pw	8.5	math	f
d1	4.000		
tof	1498.1	werr	
nt	16	wexp	
ct	16	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-249.9		
wp	5247.3		
vs	100		
sc	0		
wc	250		
hzmm	20.99		
is	1000.00		
rfl	4564.1		
rfp	3573.2		
th	7		
ins	1.000		
nm	ph		



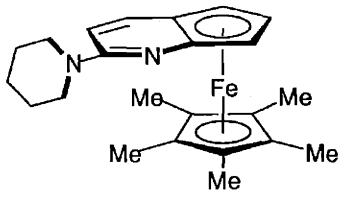



STANDARD PROTON PARAMETERS
exp2 s2pul
SAMPLE
date Sep 30 2000
solvent cd2cl2
file /export/home/~
gfu/Tbt/bt8-101h.f~
id
ACQUISITION
sfrq 499.759
tn H1
at 3.277
np 65536
sw 9998.8
fb not used
bs 4
tpwr 56
pw 8.5
d1 4.000
tof 1498.1
nt 16
ct 16
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -250.0
wp 5247.3
vs 150
sc 0
wc 250
hzmm 20.99
is 500.00
rfl 3679.2
rfp 2658.7
th 14
ins 1.000
nm ph
DEC. & VT
dfrq 125.675
dn C13
dpwr 34
dof 0
dm nnn
dmm w
dmf 10000
dseq
dres 1.0
homo n
DEC2
dfrq2 0
dn2
dpwr2 1
dof2 0
dm2 n
dmm2 c
dmf2 200
dseq2
dres2 1.0
homo2 n
DEC3
dfrq3 0
dn3
dpwr3 1
dof3 0
dm3 n
dmm3 c
dmf3 200
dseq3
dres3 1.0
homo3 n
PROCESSING
wtfile
proc ft
fn 65536
math f
werr
wexp
wbs
wnt
Me
N
HO
Fe
Ph
Ph
Ph
Ph
Ph
9
8
7
6
5
4
3
2
1
0 ppm
25.06
0.95
1.00
0.97
1.91
0.98
0.89
3.14

STANDARD PROTON PARAMETERS

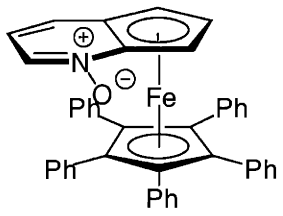
exp1 s2pul

SAMPLE		DEC. & VT	
date	Jul 6 2000	dfrq	125.675
solvent	Benzene	dn	C13
file	/data/export/~	dpwr	34
home/gfu/Tbt/resto~		dof	0
re/bt8-41h.fid		dm	nnn
ACQUISITION		dmm	w
sfrq	499.758	dmf	10000
tn	H1	dseq	
at	3.277	dres	1.0
np	65536	homo	n
sw	9998.8	PROCESSING	
fb	not used	wtfile	
bs	4	proc	ft
tpwr	56	fn	65536
pw	8.5	math	f
d1	4.000		
tof	1498.1	werr	
nt	16	wexp	
ct	16	wbs	
alock	n	wnt	
gain	not used		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-249.9		
wp	5247.3		
vs	150		
sc	0		
wc	250		
hzmm	20.99		
is	1000.00		
rfl	4563.2		
rfp	3573.2		
th	7		
ins	1.000		
nm	ph		



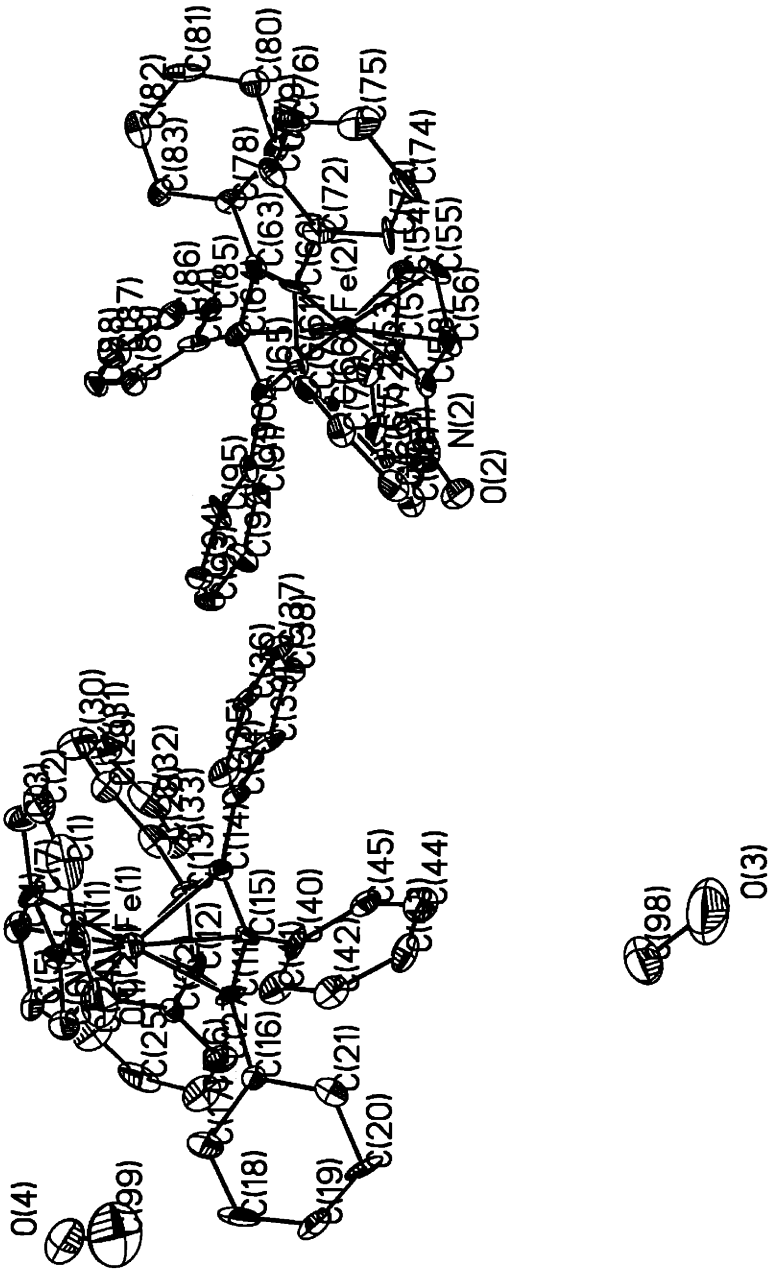
Appendix III:

X-Ray Crystal Structure Data for Selected Compounds



(–)-3.1b

Structure solved by Michael M.-C. Lo


C(81)
C(82)
C(80)
C(83)
C(78)
C(75)
C(74)
C(72)
C(55)
C(56)
Fe(2)
N(2)
O(2)
Fe(1)
C(45)
C(44)
C(40)
C(42)
C(16)
C(21)
C(20)
C(18)
C(19)
O(4)
O(3)

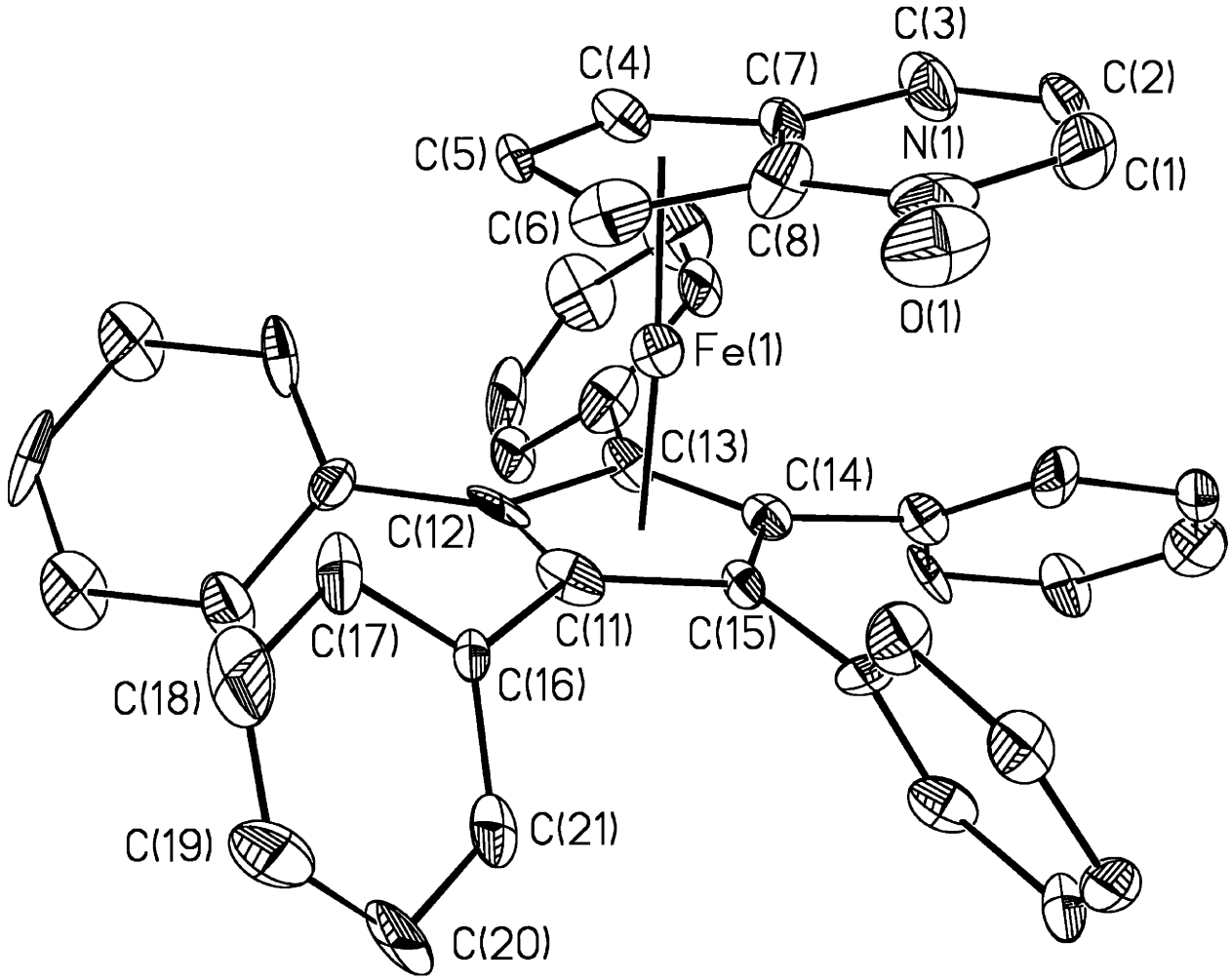

C(3)
C(4)
C(7)
C(2)
C(5)
N(1)
C(1)
C(6)
C(8)
O(1)
Fe(1)
C(13)
C(14)
C(12)
C(17)
C(11)
C(15)
C(18)
C(16)
C(19)
C(21)
C(20)

Table 1. Crystal data and structure refinement for 99305.

Identification code	99305	
Empirical formula	C44 H35 Fe N O2	
Formula weight	665.58	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 11.9070(19) Å	α= 91.335(3)°.
	b = 12.472(2) Å	β= 108.005(3)°.
	c = 13.071(2) Å	γ = 114.111(3)°.
Volume	1659.9(5) $Å^3$	
Z	2	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.494 mm^{-1}	
F(000)	696	
Crystal size	0.18 x 0.10 x 0.04 mm^3	
Theta range for data collection	2.24 to 23.27°.	
Index ranges	-11<=h<=13, -13<=k<=6, -14<=l<=14	
Reflections collected	6709	
Independent reflections	5505 [R(int) = 0.0493]	
Completeness to theta = 23.27°	98.1 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9840 and 0.8329	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5505 / 3 / 846	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1106	
R indices (all data)	R1 = 0.0925, wR2 = 0.1318	
Absolute structure parameter	-0.05(4)	
Extinction coefficient	0.0129(16)	
Largest diff. peak and hole	0.331 and -0.325 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 99305. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	4604(1)	3874(1)	1294(1)	29(1)
Fe(2)	583(1)	9192(1)	7052(1)	29(1)
O(1)	3672(8)	454(7)	1171(6)	66(2)
O(2)	4294(7)	10032(7)	7830(6)	55(2)
O(3)	8762(16)	2330(30)	9153(13)	212(12)
O(4)	6484(12)	1330(10)	-568(11)	78(3)
N(1)	3014(16)	1090(14)	1057(11)	51(4)
N(2)	3649(13)	10679(15)	7620(11)	42(4)
C(1)	1860(20)	741(18)	1311(16)	69(7)
C(2)	1180(18)	1439(18)	1124(15)	52(6)
C(3)	1478(17)	2366(19)	661(15)	47(5)
C(4)	3185(15)	3636(15)	-173(13)	38(5)
C(5)	4247(13)	3520(14)	-327(12)	33(4)
C(6)	4434(18)	2575(18)	198(14)	45(5)
C(7)	2604(13)	2716(15)	361(13)	32(4)
C(8)	3376(16)	2047(15)	564(13)	37(4)
C(11)	6496(15)	4672(15)	2311(13)	32(4)
C(12)	6173(13)	5566(13)	1810(13)	31(4)
C(13)	5058(14)	5511(14)	2104(13)	26(4)
C(14)	4841(14)	4674(14)	2815(12)	25(4)
C(15)	5688(14)	4102(13)	2932(11)	25(4)
C(16)	7641(14)	4456(14)	2273(12)	25(4)
C(17)	7878(16)	4162(16)	1303(15)	42(4)
C(18)	9029(19)	4062(18)	1443(17)	58(6)
C(19)	9911(16)	4246(18)	2429(16)	53(5)
C(20)	9784(14)	4474(16)	3362(17)	47(5)
C(21)	8623(15)	4627(12)	3267(14)	32(3)
C(22)	6804(16)	6391(15)	1151(12)	31(4)
C(23)	6111(15)	6668(14)	241(14)	39(4)
C(24)	6722(18)	7464(14)	-341(15)	50(4)
C(25)	8050(20)	8089(18)	21(15)	62(6)

C(26)	8782(18)	7802(14)	938(15)	50(4)
C(27)	8167(16)	6973(17)	1523(15)	50(5)
C(28)	4410(18)	6299(15)	1790(14)	41(5)
C(29)	3044(15)	5817(13)	1438(13)	34(3)
C(30)	2430(20)	6570(20)	1117(17)	64(5)
C(31)	3160(20)	7834(18)	1248(16)	59(6)
C(32)	4480(20)	8240(16)	1658(16)	63(5)
C(33)	5102(16)	7560(13)	1923(13)	34(3)
C(34)	3946(15)	4353(14)	3439(13)	25(4)
C(35)	3176(15)	3290(15)	3510(13)	36(4)
C(36)	2430(13)	3053(16)	4197(13)	31(4)
C(37)	2416(17)	3940(20)	4761(16)	52(6)
C(38)	3173(15)	5099(12)	4709(13)	36(4)
C(39)	3955(12)	5336(12)	4050(12)	30(4)
C(40)	5884(14)	3224(15)	3659(12)	30(4)
C(41)	5788(15)	2188(16)	3314(15)	40(4)
C(42)	6049(15)	1513(14)	4088(14)	36(4)
C(43)	6365(15)	1785(15)	5186(14)	37(4)
C(44)	6433(16)	2895(17)	5532(15)	47(5)
C(45)	6202(15)	3598(16)	4753(14)	34(4)
C(51)	3990(20)	11679(19)	7133(17)	63(6)
C(52)	3192(17)	12290(18)	6881(15)	48(5)
C(53)	2163(18)	11997(14)	7147(14)	46(5)
C(54)	806(16)	10514(16)	8190(14)	39(5)
C(55)	916(18)	9572(16)	8688(14)	47(5)
C(56)	1990(17)	9434(15)	8546(11)	37(5)
C(57)	1788(15)	10969(14)	7706(13)	40(5)
C(58)	2529(17)	10320(15)	7949(13)	38(5)
C(61)	85(16)	7550(14)	6245(12)	31(4)
C(62)	-917(15)	7566(15)	6597(12)	35(4)
C(63)	-1416(15)	8385(14)	6104(12)	29(4)
C(64)	-609(14)	8888(14)	5443(13)	30(4)
C(65)	340(15)	8437(15)	5551(13)	32(4)
C(66)	774(13)	6776(15)	6519(11)	26(4)
C(67)	2152(15)	7211(16)	6973(12)	39(4)
C(68)	2754(18)	6481(16)	7200(13)	41(3)

C(69)	2019(19)	5318(18)	7068(13)	45(5)
C(70)	646(16)	4763(16)	6647(12)	41(3)
C(71)	26(19)	5593(17)	6343(12)	44(4)
C(72)	-1572(16)	6712(13)	7274(14)	32(4)
C(73)	-844(16)	6454(16)	8223(11)	41(4)
C(74)	-1488(19)	5561(17)	8742(12)	56(5)
C(75)	-2867(17)	5017(16)	8392(17)	60(6)
C(76)	-3568(18)	5225(17)	7478(15)	60(5)
C(77)	-2952(17)	6093(14)	6930(13)	33(4)
C(78)	-2541(16)	8581(15)	6076(15)	37(5)
C(79)	-2657(15)	8886(17)	7015(14)	40(3)
C(80)	-3768(17)	9039(16)	7040(15)	42(4)
C(81)	-4758(17)	8866(14)	6044(16)	45(5)
C(82)	-4583(17)	8506(14)	5073(14)	40(4)
C(83)	-3496(15)	8416(16)	5081(14)	40(3)
C(84)	-786(14)	9711(14)	4664(14)	32(4)
C(85)	-813(14)	10810(15)	5033(13)	30(4)
C(86)	-1028(16)	11588(17)	4326(16)	45(5)
C(87)	-1266(19)	11180(20)	3234(17)	57(6)
C(88)	-1270(17)	10174(18)	2871(13)	42(5)
C(89)	-1021(16)	9415(17)	3557(14)	38(5)
C(90)	1246(16)	8593(16)	4909(12)	33(4)
C(91)	2005(14)	9860(13)	4809(12)	29(4)
C(92)	2803(18)	10091(17)	4200(14)	48(5)
C(93)	2718(16)	9098(16)	3554(14)	37(5)
C(94)	1968(16)	7935(17)	3635(12)	47(5)
C(95)	1245(16)	7715(16)	4324(11)	44(5)
C(98)	8840(30)	2470(30)	8135(18)	123(11)
C(99)	6530(30)	630(20)	270(20)	125(10)

Table 3. Bond lengths [Å] and angles [°] for 99305.

Fe(1)-C(11)	2.022(15)
Fe(1)-C(5)	2.027(15)
Fe(1)-C(6)	2.041(18)
Fe(1)-C(4)	2.045(16)
Fe(1)-C(13)	2.056(16)
Fe(1)-C(15)	2.073(15)
Fe(1)-C(12)	2.082(14)
Fe(1)-C(14)	2.087(15)
Fe(1)-C(8)	2.134(18)
Fe(1)-C(7)	2.134(15)
Fe(2)-C(62)	1.996(17)
Fe(2)-C(65)	2.040(16)
Fe(2)-C(61)	2.044(16)
Fe(2)-C(55)	2.057(16)
Fe(2)-C(56)	2.061(15)
Fe(2)-C(57)	2.063(15)
Fe(2)-C(64)	2.064(16)
Fe(2)-C(54)	2.070(17)
Fe(2)-C(58)	2.074(17)
Fe(2)-C(63)	2.092(16)
O(1)-N(1)	1.306(16)
O(2)-N(2)	1.306(16)
O(3)-C(98)	1.37(2)
O(4)-C(99)	1.42(2)
N(1)-C(8)	1.35(2)
N(1)-C(1)	1.41(2)
N(2)-C(51)	1.38(2)
N(2)-C(58)	1.43(2)
C(1)-C(2)	1.39(3)
C(2)-C(3)	1.29(3)
C(3)-C(7)	1.41(2)
C(4)-C(5)	1.40(2)
C(4)-C(7)	1.40(2)
C(5)-C(6)	1.44(2)

C(6)-C(8)	1.40(2)
C(7)-C(8)	1.45(2)
C(11)-C(15)	1.43(2)
C(11)-C(12)	1.43(2)
C(11)-C(16)	1.51(2)
C(12)-C(13)	1.47(2)
C(12)-C(22)	1.48(2)
C(13)-C(14)	1.41(2)
C(13)-C(28)	1.47(2)
C(14)-C(15)	1.43(2)
C(14)-C(34)	1.47(2)
C(15)-C(40)	1.51(2)
C(16)-C(21)	1.40(2)
C(16)-C(17)	1.45(2)
C(17)-C(18)	1.38(2)
C(18)-C(19)	1.33(2)
C(19)-C(20)	1.31(2)
C(20)-C(21)	1.44(2)
C(22)-C(23)	1.36(2)
C(22)-C(27)	1.39(2)
C(23)-C(24)	1.37(2)
C(24)-C(25)	1.36(3)
C(25)-C(26)	1.40(2)
C(26)-C(27)	1.40(2)
C(28)-C(29)	1.39(2)
C(28)-C(33)	1.42(2)
C(29)-C(30)	1.40(2)
C(30)-C(31)	1.43(3)
C(31)-C(32)	1.35(3)
C(32)-C(33)	1.32(2)
C(34)-C(35)	1.29(2)
C(34)-C(39)	1.44(2)
C(35)-C(36)	1.40(2)
C(36)-C(37)	1.33(2)
C(37)-C(38)	1.37(2)
C(38)-C(39)	1.41(2)

C(40)-C(41)	1.31(2)
C(40)-C(45)	1.38(2)
C(41)-C(42)	1.37(2)
C(42)-C(43)	1.36(2)
C(43)-C(44)	1.41(2)
C(44)-C(45)	1.39(2)
C(51)-C(52)	1.41(3)
C(52)-C(53)	1.29(2)
C(53)-C(57)	1.47(2)
C(54)-C(55)	1.39(3)
C(54)-C(57)	1.42(2)
C(55)-C(56)	1.42(2)
C(56)-C(58)	1.42(2)
C(57)-C(58)	1.40(2)
C(61)-C(62)	1.41(2)
C(61)-C(65)	1.44(2)
C(61)-C(66)	1.49(2)
C(62)-C(63)	1.45(2)
C(62)-C(72)	1.52(2)
C(63)-C(78)	1.45(2)
C(63)-C(64)	1.45(2)
C(64)-C(65)	1.43(2)
C(64)-C(84)	1.49(2)
C(65)-C(90)	1.52(2)
C(66)-C(71)	1.34(2)
C(66)-C(67)	1.412(19)
C(67)-C(68)	1.36(2)
C(68)-C(69)	1.33(2)
C(69)-C(70)	1.40(2)
C(70)-C(71)	1.50(2)
C(72)-C(73)	1.41(2)
C(72)-C(77)	1.41(2)
C(73)-C(74)	1.40(2)
C(74)-C(75)	1.41(2)
C(75)-C(76)	1.33(3)
C(76)-C(77)	1.39(2)

C(78)-C(79)	1.34(2)
C(78)-C(83)	1.38(2)
C(79)-C(80)	1.42(2)
C(80)-C(81)	1.40(2)
C(81)-C(82)	1.44(2)
C(82)-C(83)	1.34(2)
C(84)-C(89)	1.40(2)
C(84)-C(85)	1.46(2)
C(85)-C(86)	1.40(2)
C(86)-C(87)	1.40(3)
C(87)-C(88)	1.33(3)
C(88)-C(89)	1.38(2)
C(90)-C(95)	1.32(2)
C(90)-C(91)	1.50(2)
C(91)-C(92)	1.37(2)
C(92)-C(93)	1.43(2)
C(93)-C(94)	1.39(2)
C(94)-C(95)	1.39(2)

C(11)-Fe(1)-C(5)	118.0(6)
C(11)-Fe(1)-C(6)	107.4(7)
C(5)-Fe(1)-C(6)	41.4(7)
C(11)-Fe(1)-C(4)	150.8(6)
C(5)-Fe(1)-C(4)	40.3(6)
C(6)-Fe(1)-C(4)	69.3(7)
C(11)-Fe(1)-C(13)	68.7(6)
C(5)-Fe(1)-C(13)	123.8(6)
C(6)-Fe(1)-C(13)	162.2(7)
C(4)-Fe(1)-C(13)	105.2(7)
C(11)-Fe(1)-C(15)	40.8(6)
C(5)-Fe(1)-C(15)	153.7(6)
C(6)-Fe(1)-C(15)	120.1(7)
C(4)-Fe(1)-C(15)	165.8(6)
C(13)-Fe(1)-C(15)	69.1(6)
C(11)-Fe(1)-C(12)	40.8(6)
C(5)-Fe(1)-C(12)	104.1(6)

C(6)-Fe(1)-C(12)	124.2(7)
C(4)-Fe(1)-C(12)	115.5(6)
C(13)-Fe(1)-C(12)	41.6(6)
C(15)-Fe(1)-C(12)	69.5(6)
C(11)-Fe(1)-C(14)	66.8(6)
C(5)-Fe(1)-C(14)	162.3(6)
C(6)-Fe(1)-C(14)	156.1(7)
C(4)-Fe(1)-C(14)	127.5(6)
C(13)-Fe(1)-C(14)	39.8(6)
C(15)-Fe(1)-C(14)	40.2(6)
C(12)-Fe(1)-C(14)	67.7(6)
C(11)-Fe(1)-C(8)	130.1(6)
C(5)-Fe(1)-C(8)	65.6(6)
C(6)-Fe(1)-C(8)	39.1(6)
C(4)-Fe(1)-C(8)	66.3(6)
C(13)-Fe(1)-C(8)	155.5(6)
C(15)-Fe(1)-C(8)	113.2(6)
C(12)-Fe(1)-C(8)	162.9(6)
C(14)-Fe(1)-C(8)	126.0(6)
C(11)-Fe(1)-C(7)	168.2(7)
C(5)-Fe(1)-C(7)	66.1(6)
C(6)-Fe(1)-C(7)	67.8(7)
C(4)-Fe(1)-C(7)	39.2(6)
C(13)-Fe(1)-C(7)	119.3(6)
C(15)-Fe(1)-C(7)	131.2(6)
C(12)-Fe(1)-C(7)	150.8(6)
C(14)-Fe(1)-C(7)	112.9(6)
C(8)-Fe(1)-C(7)	39.7(6)
C(62)-Fe(2)-C(65)	69.5(6)
C(62)-Fe(2)-C(61)	40.9(6)
C(65)-Fe(2)-C(61)	41.4(6)
C(62)-Fe(2)-C(55)	102.7(7)
C(65)-Fe(2)-C(55)	164.8(7)
C(61)-Fe(2)-C(55)	124.5(7)
C(62)-Fe(2)-C(56)	114.0(7)
C(65)-Fe(2)-C(56)	129.5(6)

C(61)-Fe(2)-C(56)	106.4(6)
C(55)-Fe(2)-C(56)	40.5(6)
C(62)-Fe(2)-C(57)	163.8(6)
C(65)-Fe(2)-C(57)	123.1(7)
C(61)-Fe(2)-C(57)	155.4(7)
C(55)-Fe(2)-C(57)	67.3(7)
C(56)-Fe(2)-C(57)	67.4(7)
C(62)-Fe(2)-C(64)	67.5(6)
C(65)-Fe(2)-C(64)	40.7(6)
C(61)-Fe(2)-C(64)	67.7(6)
C(55)-Fe(2)-C(64)	149.7(7)
C(56)-Fe(2)-C(64)	169.8(7)
C(57)-Fe(2)-C(64)	114.2(6)
C(62)-Fe(2)-C(54)	124.1(6)
C(65)-Fe(2)-C(54)	155.7(7)
C(61)-Fe(2)-C(54)	161.4(7)
C(55)-Fe(2)-C(54)	39.3(7)
C(56)-Fe(2)-C(54)	67.0(7)
C(57)-Fe(2)-C(54)	40.3(6)
C(64)-Fe(2)-C(54)	121.2(7)
C(62)-Fe(2)-C(58)	150.2(7)
C(65)-Fe(2)-C(58)	112.8(6)
C(61)-Fe(2)-C(58)	120.5(7)
C(55)-Fe(2)-C(58)	67.1(7)
C(56)-Fe(2)-C(58)	40.1(7)
C(57)-Fe(2)-C(58)	39.5(6)
C(64)-Fe(2)-C(58)	134.7(7)
C(54)-Fe(2)-C(58)	66.6(6)
C(62)-Fe(2)-C(63)	41.5(6)
C(65)-Fe(2)-C(63)	70.8(6)
C(61)-Fe(2)-C(63)	70.0(6)
C(55)-Fe(2)-C(63)	112.7(6)
C(56)-Fe(2)-C(63)	146.5(6)
C(57)-Fe(2)-C(63)	128.7(7)
C(64)-Fe(2)-C(63)	40.9(6)
C(54)-Fe(2)-C(63)	105.3(7)

C(58)-Fe(2)-C(63)	168.1(7)
O(1)-N(1)-C(8)	118.0(14)
O(1)-N(1)-C(1)	122.8(17)
C(8)-N(1)-C(1)	118.7(17)
O(2)-N(2)-C(51)	124.9(15)
O(2)-N(2)-C(58)	116.2(14)
C(51)-N(2)-C(58)	118.9(17)
C(2)-C(1)-N(1)	119.5(18)
C(3)-C(2)-C(1)	124.7(19)
C(2)-C(3)-C(7)	117.2(19)
C(5)-C(4)-C(7)	108.2(15)
C(5)-C(4)-Fe(1)	69.2(9)
C(7)-C(4)-Fe(1)	73.8(9)
C(4)-C(5)-C(6)	109.7(14)
C(4)-C(5)-Fe(1)	70.5(9)
C(6)-C(5)-Fe(1)	69.8(9)
C(8)-C(6)-C(5)	105.4(14)
C(8)-C(6)-Fe(1)	74.1(10)
C(5)-C(6)-Fe(1)	68.8(10)
C(4)-C(7)-C(3)	132.5(16)
C(4)-C(7)-C(8)	106.6(13)
C(3)-C(7)-C(8)	120.8(16)
C(4)-C(7)-Fe(1)	67.0(8)
C(3)-C(7)-Fe(1)	129.4(13)
C(8)-C(7)-Fe(1)	70.2(9)
N(1)-C(8)-C(6)	131.4(16)
N(1)-C(8)-C(7)	118.9(15)
C(6)-C(8)-C(7)	109.7(15)
N(1)-C(8)-Fe(1)	128.6(12)
C(6)-C(8)-Fe(1)	66.9(11)
C(7)-C(8)-Fe(1)	70.2(9)
C(15)-C(11)-C(12)	111.8(13)
C(15)-C(11)-C(16)	124.6(14)
C(12)-C(11)-C(16)	123.3(15)
C(15)-C(11)-Fe(1)	71.5(9)
C(12)-C(11)-Fe(1)	71.8(8)

C(16)-C(11)-Fe(1)	128.9(12)
C(11)-C(12)-C(13)	104.9(13)
C(11)-C(12)-C(22)	129.1(14)
C(13)-C(12)-C(22)	126.0(13)
C(11)-C(12)-Fe(1)	67.4(9)
C(13)-C(12)-Fe(1)	68.3(8)
C(22)-C(12)-Fe(1)	128.9(11)
C(14)-C(13)-C(12)	107.4(13)
C(14)-C(13)-C(28)	127.8(14)
C(12)-C(13)-C(28)	124.4(14)
C(14)-C(13)-Fe(1)	71.3(9)
C(12)-C(13)-Fe(1)	70.2(8)
C(28)-C(13)-Fe(1)	128.8(12)
C(13)-C(14)-C(15)	111.0(13)
C(13)-C(14)-C(34)	130.7(14)
C(15)-C(14)-C(34)	118.3(14)
C(13)-C(14)-Fe(1)	68.9(9)
C(15)-C(14)-Fe(1)	69.3(8)
C(34)-C(14)-Fe(1)	130.2(11)
C(11)-C(15)-C(14)	104.6(14)
C(11)-C(15)-C(40)	124.5(14)
C(14)-C(15)-C(40)	130.3(13)
C(11)-C(15)-Fe(1)	67.7(8)
C(14)-C(15)-Fe(1)	70.5(9)
C(40)-C(15)-Fe(1)	131.9(11)
C(21)-C(16)-C(17)	115.8(13)
C(21)-C(16)-C(11)	117.2(13)
C(17)-C(16)-C(11)	126.9(14)
C(18)-C(17)-C(16)	117.9(17)
C(19)-C(18)-C(17)	121.8(17)
C(20)-C(19)-C(18)	125.7(17)
C(19)-C(20)-C(21)	114.9(17)
C(16)-C(21)-C(20)	123.7(15)
C(23)-C(22)-C(27)	118.9(15)
C(23)-C(22)-C(12)	122.9(14)
C(27)-C(22)-C(12)	118.0(14)

C(22)-C(23)-C(24)	121.9(15)
C(25)-C(24)-C(23)	120.9(16)
C(24)-C(25)-C(26)	118.0(16)
C(25)-C(26)-C(27)	121.1(17)
C(22)-C(27)-C(26)	118.9(17)
C(29)-C(28)-C(33)	116.8(15)
C(29)-C(28)-C(13)	119.3(15)
C(33)-C(28)-C(13)	123.6(16)
C(28)-C(29)-C(30)	119.0(15)
C(29)-C(30)-C(31)	122.4(18)
C(32)-C(31)-C(30)	114.7(18)
C(33)-C(32)-C(31)	125.0(18)
C(32)-C(33)-C(28)	121.8(17)
C(35)-C(34)-C(39)	117.1(14)
C(35)-C(34)-C(14)	127.0(15)
C(39)-C(34)-C(14)	115.9(13)
C(34)-C(35)-C(36)	123.7(17)
C(37)-C(36)-C(35)	120.1(17)
C(36)-C(37)-C(38)	120.0(16)
C(37)-C(38)-C(39)	119.7(14)
C(38)-C(39)-C(34)	119.3(13)
C(41)-C(40)-C(45)	120.6(15)
C(41)-C(40)-C(15)	124.5(15)
C(45)-C(40)-C(15)	114.9(15)
C(40)-C(41)-C(42)	117.3(17)
C(43)-C(42)-C(41)	127.3(17)
C(42)-C(43)-C(44)	114.3(15)
C(45)-C(44)-C(43)	118.7(17)
C(40)-C(45)-C(44)	121.8(17)
N(2)-C(51)-C(52)	121.2(18)
C(53)-C(52)-C(51)	122.4(19)
C(52)-C(53)-C(57)	118.5(18)
C(55)-C(54)-C(57)	108.6(16)
C(55)-C(54)-Fe(2)	69.8(10)
C(57)-C(54)-Fe(2)	69.6(9)
C(54)-C(55)-C(56)	108.2(16)

C(54)-C(55)-Fe(2)	70.8(10)
C(56)-C(55)-Fe(2)	69.9(8)
C(58)-C(56)-C(55)	107.1(15)
C(58)-C(56)-Fe(2)	70.5(9)
C(55)-C(56)-Fe(2)	69.7(10)
C(58)-C(57)-C(54)	107.4(16)
C(58)-C(57)-C(53)	121.1(16)
C(54)-C(57)-C(53)	131.2(18)
C(58)-C(57)-Fe(2)	70.7(10)
C(54)-C(57)-Fe(2)	70.1(9)
C(53)-C(57)-Fe(2)	129.4(12)
C(57)-C(58)-C(56)	108.7(15)
C(57)-C(58)-N(2)	117.8(17)
C(56)-C(58)-N(2)	133.5(16)
C(57)-C(58)-Fe(2)	69.8(9)
C(56)-C(58)-Fe(2)	69.4(9)
N(2)-C(58)-Fe(2)	128.7(11)
C(62)-C(61)-C(65)	107.5(14)
C(62)-C(61)-C(66)	127.7(13)
C(65)-C(61)-C(66)	124.8(14)
C(62)-C(61)-Fe(2)	67.8(10)
C(65)-C(61)-Fe(2)	69.2(10)
C(66)-C(61)-Fe(2)	128.4(11)
C(61)-C(62)-C(63)	112.1(12)
C(61)-C(62)-C(72)	125.7(14)
C(63)-C(62)-C(72)	121.6(13)
C(61)-C(62)-Fe(2)	71.4(10)
C(63)-C(62)-Fe(2)	72.8(9)
C(72)-C(62)-Fe(2)	130.6(11)
C(78)-C(63)-C(64)	124.7(14)
C(78)-C(63)-C(62)	132.5(14)
C(64)-C(63)-C(62)	102.1(13)
C(78)-C(63)-Fe(2)	135.0(12)
C(64)-C(63)-Fe(2)	68.5(8)
C(62)-C(63)-Fe(2)	65.7(9)
C(65)-C(64)-C(63)	112.4(14)

C(65)-C(64)-C(84)	122.1(14)
C(63)-C(64)-C(84)	125.3(13)
C(65)-C(64)-Fe(2)	68.8(9)
C(63)-C(64)-Fe(2)	70.6(9)
C(84)-C(64)-Fe(2)	132.3(12)
C(64)-C(65)-C(61)	105.7(14)
C(64)-C(65)-C(90)	129.7(14)
C(61)-C(65)-C(90)	123.3(14)
C(64)-C(65)-Fe(2)	70.5(10)
C(61)-C(65)-Fe(2)	69.4(9)
C(90)-C(65)-Fe(2)	134.2(11)
C(71)-C(66)-C(67)	118.7(16)
C(71)-C(66)-C(61)	117.3(13)
C(67)-C(66)-C(61)	124.0(16)
C(68)-C(67)-C(66)	122.6(17)
C(69)-C(68)-C(67)	118.8(17)
C(68)-C(69)-C(70)	124.7(17)
C(69)-C(70)-C(71)	114.6(17)
C(66)-C(71)-C(70)	120.4(16)
C(73)-C(72)-C(77)	117.2(14)
C(73)-C(72)-C(62)	122.2(15)
C(77)-C(72)-C(62)	120.5(15)
C(74)-C(73)-C(72)	120.0(15)
C(73)-C(74)-C(75)	119.9(16)
C(76)-C(75)-C(74)	120.4(17)
C(75)-C(76)-C(77)	120.4(18)
C(76)-C(77)-C(72)	121.5(16)
C(79)-C(78)-C(83)	121.2(14)
C(79)-C(78)-C(63)	119.5(16)
C(83)-C(78)-C(63)	119.3(15)
C(78)-C(79)-C(80)	122.0(16)
C(81)-C(80)-C(79)	118.1(16)
C(80)-C(81)-C(82)	116.8(15)
C(83)-C(82)-C(81)	123.2(17)
C(82)-C(83)-C(78)	118.5(16)
C(89)-C(84)-C(85)	118.3(15)

C(89)-C(84)-C(64)	121.3(15)
C(85)-C(84)-C(64)	120.2(14)
C(86)-C(85)-C(84)	122.5(16)
C(85)-C(86)-C(87)	113.7(18)
C(88)-C(87)-C(86)	125.0(18)
C(87)-C(88)-C(89)	122.2(17)
C(88)-C(89)-C(84)	118.3(18)
C(95)-C(90)-C(91)	120.0(15)
C(95)-C(90)-C(65)	124.9(17)
C(91)-C(90)-C(65)	114.2(14)
C(92)-C(91)-C(90)	118.8(14)
C(91)-C(92)-C(93)	117.9(17)
C(94)-C(93)-C(92)	121.3(15)
C(93)-C(94)-C(95)	119.9(16)
C(90)-C(95)-C(94)	121.5(18)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 99305. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	29(1)	28(2)	31(1)	5(1)	11(1)	12(1)
Fe(2)	29(1)	32(2)	30(1)	8(1)	11(1)	16(1)
O(1)	91(6)	48(5)	57(5)	9(4)	5(4)	42(5)
O(2)	41(4)	59(5)	63(5)	6(4)	14(4)	23(4)
O(3)	113(12)	430(40)	88(11)	99(17)	30(9)	109(18)
O(4)	59(6)	79(7)	82(8)	10(6)	5(6)	32(6)
N(1)	57(10)	42(10)	29(7)	-17(7)	-3(6)	13(9)
N(2)	32(8)	54(11)	28(7)	-4(7)	0(6)	15(8)
C(1)	88(15)	30(11)	50(11)	16(9)	15(10)	-6(11)
C(2)	37(11)	44(12)	41(10)	-4(9)	17(9)	-17(10)
C(3)	30(10)	50(13)	57(12)	2(10)	25(9)	8(10)
C(4)	26(9)	32(11)	41(11)	1(8)	7(8)	1(8)
C(5)	17(8)	38(10)	27(9)	12(7)	7(7)	-4(8)
C(6)	50(12)	56(14)	39(11)	2(10)	12(9)	35(11)
C(7)	13(8)	46(11)	34(9)	19(8)	7(7)	10(8)
C(8)	53(10)	46(11)	41(9)	24(8)	26(8)	42(9)
C(11)	19(8)	37(10)	47(10)	-2(8)	9(7)	21(8)
C(12)	12(7)	10(7)	45(9)	-3(7)	-7(6)	-6(6)
C(13)	18(8)	21(9)	45(10)	5(8)	13(7)	13(8)
C(14)	21(8)	23(9)	26(9)	-5(7)	8(7)	7(8)
C(15)	20(8)	28(9)	20(8)	-8(7)	13(7)	1(7)
C(16)	20(8)	30(9)	25(9)	13(7)	12(7)	7(7)
C(17)	43(9)	40(9)	50(9)	14(7)	34(7)	12(7)
C(18)	55(12)	72(14)	72(14)	4(10)	48(11)	31(11)
C(19)	27(9)	74(13)	61(12)	12(10)	8(9)	29(9)
C(20)	13(8)	57(12)	78(13)	19(10)	20(8)	19(8)
C(21)	39(8)	10(6)	42(8)	-1(6)	24(7)	-2(6)
C(22)	33(9)	42(11)	22(8)	10(7)	14(7)	18(9)
C(23)	38(9)	33(9)	70(12)	22(8)	44(8)	20(8)
C(24)	54(8)	21(6)	81(9)	34(6)	26(7)	19(6)
C(25)	110(16)	70(14)	55(12)	43(10)	69(12)	53(13)

C(26)	54(8)	21(6)	81(9)	34(6)	26(7)	19(6)
C(27)	32(10)	57(13)	61(12)	11(10)	25(9)	11(10)
C(28)	71(13)	20(9)	42(10)	12(8)	25(10)	25(10)
C(29)	36(7)	16(6)	47(7)	17(5)	16(5)	7(5)
C(30)	55(11)	62(12)	88(13)	16(10)	29(10)	33(10)
C(31)	67(14)	38(11)	90(15)	4(10)	37(12)	33(11)
C(32)	97(14)	26(9)	73(12)	26(9)	60(11)	10(10)
C(33)	36(7)	16(6)	47(7)	17(5)	16(5)	7(5)
C(34)	20(8)	23(8)	37(9)	6(7)	11(7)	14(7)
C(35)	35(9)	41(11)	44(9)	32(8)	16(8)	25(9)
C(36)	15(7)	41(11)	42(10)	26(8)	10(7)	17(8)
C(37)	34(11)	90(18)	51(12)	27(12)	20(10)	39(12)
C(38)	40(10)	11(7)	52(10)	-7(7)	23(8)	3(7)
C(39)	13(7)	12(8)	63(11)	10(7)	15(7)	2(7)
C(40)	22(8)	37(10)	27(9)	19(8)	-2(6)	17(8)
C(41)	40(9)	36(10)	53(10)	24(8)	16(7)	24(8)
C(42)	39(8)	19(8)	53(10)	13(7)	14(7)	16(7)
C(43)	32(9)	30(9)	40(10)	21(8)	2(7)	13(8)
C(44)	33(10)	52(12)	52(12)	28(10)	22(9)	7(9)
C(45)	25(9)	30(10)	47(11)	0(9)	6(8)	17(8)
C(51)	59(13)	52(13)	62(12)	19(11)	24(11)	9(11)
C(52)	33(9)	51(12)	38(9)	10(8)	-2(7)	7(9)
C(53)	47(11)	16(9)	56(10)	21(8)	2(8)	7(8)
C(54)	29(10)	37(11)	47(11)	-11(9)	11(9)	12(9)
C(55)	67(13)	47(12)	35(10)	-15(9)	30(9)	24(10)
C(56)	60(12)	47(12)	18(9)	19(8)	14(9)	37(10)
C(57)	22(8)	27(9)	29(9)	-9(7)	-5(7)	-17(7)
C(58)	46(11)	41(12)	20(9)	-17(8)	0(8)	23(10)
C(61)	47(11)	25(10)	18(8)	12(8)	12(8)	12(9)
C(62)	41(9)	57(12)	32(9)	21(8)	33(8)	31(9)
C(63)	30(9)	25(9)	19(7)	5(7)	10(7)	0(7)
C(64)	22(8)	28(9)	41(10)	15(8)	8(7)	13(8)
C(65)	29(9)	33(10)	32(10)	16(8)	10(8)	12(9)
C(66)	15(7)	43(11)	18(8)	11(7)	9(6)	9(8)
C(67)	31(7)	60(10)	37(8)	9(7)	14(6)	29(7)
C(68)	57(8)	45(8)	34(6)	6(6)	9(6)	40(7)

C(69)	71(13)	61(13)	36(9)	29(9)	25(9)	54(12)
C(70)	57(8)	45(8)	34(6)	6(6)	9(6)	40(7)
C(71)	61(10)	71(12)	26(7)	11(7)	19(7)	49(9)
C(72)	38(10)	8(8)	55(11)	8(7)	26(9)	8(7)
C(73)	47(9)	45(10)	7(6)	2(6)	-7(6)	9(8)
C(74)	80(11)	83(12)	13(7)	11(7)	24(7)	38(10)
C(75)	41(10)	31(10)	89(15)	9(10)	32(10)	-7(8)
C(76)	40(9)	74(12)	57(10)	-5(9)	37(9)	3(9)
C(77)	54(11)	25(9)	27(8)	3(7)	17(8)	20(9)
C(78)	40(11)	37(11)	53(12)	3(9)	19(9)	33(9)
C(79)	36(7)	59(9)	37(7)	15(6)	6(6)	37(7)
C(80)	46(10)	45(11)	46(10)	23(8)	22(8)	26(9)
C(81)	48(10)	30(9)	89(14)	31(9)	53(10)	25(8)
C(82)	68(12)	22(8)	31(8)	12(7)	9(8)	27(8)
C(83)	36(7)	59(9)	37(7)	15(6)	6(6)	37(7)
C(84)	24(8)	18(8)	59(11)	4(8)	27(8)	6(7)
C(85)	14(6)	34(9)	33(8)	-5(7)	6(6)	5(6)
C(86)	35(8)	42(10)	61(11)	10(8)	10(8)	25(8)
C(87)	60(12)	65(14)	56(13)	45(11)	32(10)	28(11)
C(88)	51(11)	72(14)	21(9)	14(9)	13(8)	42(11)
C(89)	38(10)	47(12)	32(10)	23(9)	15(9)	17(10)
C(90)	37(10)	45(10)	15(8)	8(8)	5(7)	19(9)
C(91)	28(8)	18(8)	31(8)	-13(6)	10(7)	3(7)
C(92)	69(12)	40(11)	42(10)	7(8)	32(10)	22(10)
C(93)	45(11)	44(12)	43(11)	25(9)	31(9)	27(10)
C(94)	54(11)	96(15)	30(9)	34(9)	22(8)	64(11)
C(95)	68(12)	60(13)	9(7)	4(8)	14(8)	33(11)
C(98)	160(20)	220(30)	49(13)	21(15)	25(13)	140(20)
C(99)	170(20)	120(20)	100(19)	72(17)	39(17)	80(20)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 99305.

	x	y	z	U(eq)
H(3)	9387	2202	9536	318
H(4)	7230	1663	-624	117
H(1A)	1544	34	1608	83
H(2A)	445	1217	1354	63
H(3A)	962	2796	526	56
H(4A)	2860	4237	-443	46
H(5A)	4802	4029	-727	40
H(6A)	5112	2291	215	54
H(17A)	7262	4041	594	50
H(18A)	9193	3856	818	70
H(19A)	10703	4210	2460	64
H(20A)	10410	4534	4047	57
H(21A)	8520	4857	3918	39
H(23A)	5179	6298	4	46
H(24A)	6208	7581	-1007	60
H(25A)	8468	8702	-338	75
H(26A)	9713	8177	1167	60
H(27A)	8672	6810	2165	61
H(29A)	2536	4993	1415	41
H(30A)	1501	6224	803	77
H(31A)	2748	8349	1061	71
H(32A)	5003	9075	1763	76
H(33A)	6035	7924	2210	41
H(35A)	3111	2633	3074	43
H(36A)	1935	2253	4259	37
H(37A)	1880	3781	5199	63
H(38A)	3170	5739	5116	43
H(39A)	4483	6134	4008	36
H(41A)	5549	1913	2559	48
H(42A)	6004	773	3829	43

H(43A)	6525	1271	5676	45
H(44A)	6632	3160	6282	57
H(45A)	6265	4355	4984	41
H(51A)	4770	11960	6965	75
H(52A)	3424	12942	6502	58
H(53A)	1657	12436	6986	55
H(54A)	138	10813	8165	47
H(55A)	349	9086	9091	57
H(56A)	2320	8842	8833	44
H(67A)	2679	8049	7125	47
H(68A)	3684	6798	7450	50
H(69A)	2456	4826	7272	54
H(70A)	147	3926	6562	50
H(71A)	-902	5283	6024	53
H(73A)	85	6887	8511	50
H(74A)	-995	5320	9331	67
H(75A)	-3299	4499	8811	72
H(76A)	-4496	4778	7198	72
H(77A)	-3473	6274	6311	40
H(79A)	-1976	9004	7684	48
H(80A)	-3837	9253	7712	50
H(81A)	-5509	8980	6012	54
H(82A)	-5272	8323	4392	48
H(83A)	-3385	8243	4417	48
H(85A)	-679	11005	5781	36
H(86A)	-1014	12320	4563	54
H(87A)	-1437	11669	2713	68
H(88A)	-1451	9971	2114	51
H(89A)	-1010	8708	3285	46
H(91A)	1933	10492	5161	34
H(92A)	3395	10884	4205	57
H(93A)	3185	9240	3061	45
H(94A)	1950	7289	3220	56
H(95A)	737	6914	4375	52
H(98A)	8554	3072	7867	185
H(98B)	8269	1704	7634	185

H(98C)	9748	2712	8175	185
H(99A)	7350	1066	894	188
H(99B)	6497	-124	-4	188
H(99C)	5782	466	510	188

Table 6. Torsion angles [°] for 99305.

O(1)-N(1)-C(1)-C(2)	-177.2(15)
C(8)-N(1)-C(1)-C(2)	-5(3)
N(1)-C(1)-C(2)-C(3)	5(3)
C(1)-C(2)-C(3)-C(7)	-2(3)
C(11)-Fe(1)-C(4)-C(5)	51.4(17)
C(6)-Fe(1)-C(4)-C(5)	-37.4(10)
C(13)-Fe(1)-C(4)-C(5)	124.8(10)
C(15)-Fe(1)-C(4)-C(5)	-171(2)
C(12)-Fe(1)-C(4)-C(5)	81.6(10)
C(14)-Fe(1)-C(4)-C(5)	162.2(9)
C(8)-Fe(1)-C(4)-C(5)	-79.7(10)
C(7)-Fe(1)-C(4)-C(5)	-117.3(14)
C(11)-Fe(1)-C(4)-C(7)	168.7(12)
C(5)-Fe(1)-C(4)-C(7)	117.3(14)
C(6)-Fe(1)-C(4)-C(7)	79.9(11)
C(13)-Fe(1)-C(4)-C(7)	-118.0(10)
C(15)-Fe(1)-C(4)-C(7)	-53(3)
C(12)-Fe(1)-C(4)-C(7)	-161.1(9)
C(14)-Fe(1)-C(4)-C(7)	-80.6(12)
C(8)-Fe(1)-C(4)-C(7)	37.6(10)
C(7)-C(4)-C(5)-C(6)	-5.0(19)
Fe(1)-C(4)-C(5)-C(6)	59.0(12)
C(7)-C(4)-C(5)-Fe(1)	-64.0(11)
C(11)-Fe(1)-C(5)-C(4)	-154.4(9)
C(6)-Fe(1)-C(5)-C(4)	120.8(14)
C(13)-Fe(1)-C(5)-C(4)	-72.5(11)
C(15)-Fe(1)-C(5)-C(4)	174.9(13)
C(12)-Fe(1)-C(5)-C(4)	-113.0(10)
C(14)-Fe(1)-C(5)-C(4)	-53(2)
C(8)-Fe(1)-C(5)-C(4)	81.5(10)
C(7)-Fe(1)-C(5)-C(4)	37.9(9)
C(11)-Fe(1)-C(5)-C(6)	84.9(11)
C(4)-Fe(1)-C(5)-C(6)	-120.8(14)
C(13)-Fe(1)-C(5)-C(6)	166.8(10)

C(15)-Fe(1)-C(5)-C(6)	54.1(17)
C(12)-Fe(1)-C(5)-C(6)	126.3(10)
C(14)-Fe(1)-C(5)-C(6)	-173.8(18)
C(8)-Fe(1)-C(5)-C(6)	-39.2(9)
C(7)-Fe(1)-C(5)-C(6)	-82.9(11)
C(4)-C(5)-C(6)-C(8)	6.2(19)
Fe(1)-C(5)-C(6)-C(8)	65.6(12)
C(4)-C(5)-C(6)-Fe(1)	-59.4(11)
C(11)-Fe(1)-C(6)-C(8)	133.2(10)
C(5)-Fe(1)-C(6)-C(8)	-114.0(13)
C(4)-Fe(1)-C(6)-C(8)	-77.6(10)
C(13)-Fe(1)-C(6)-C(8)	-152.4(19)
C(15)-Fe(1)-C(6)-C(8)	90.5(10)
C(12)-Fe(1)-C(6)-C(8)	175.0(9)
C(14)-Fe(1)-C(6)-C(8)	61(2)
C(7)-Fe(1)-C(6)-C(8)	-35.4(9)
C(11)-Fe(1)-C(6)-C(5)	-112.8(10)
C(4)-Fe(1)-C(6)-C(5)	36.4(9)
C(13)-Fe(1)-C(6)-C(5)	-38(3)
C(15)-Fe(1)-C(6)-C(5)	-155.5(8)
C(12)-Fe(1)-C(6)-C(5)	-71.0(11)
C(14)-Fe(1)-C(6)-C(5)	175.3(13)
C(8)-Fe(1)-C(6)-C(5)	114.0(13)
C(7)-Fe(1)-C(6)-C(5)	78.6(10)
C(5)-C(4)-C(7)-C(3)	-175.9(18)
Fe(1)-C(4)-C(7)-C(3)	123(2)
C(5)-C(4)-C(7)-C(8)	1.8(18)
Fe(1)-C(4)-C(7)-C(8)	-59.2(11)
C(5)-C(4)-C(7)-Fe(1)	61.0(11)
C(2)-C(3)-C(7)-C(4)	177.9(18)
C(2)-C(3)-C(7)-C(8)	0(3)
C(2)-C(3)-C(7)-Fe(1)	-88(2)
C(11)-Fe(1)-C(7)-C(4)	-152(3)
C(5)-Fe(1)-C(7)-C(4)	-38.9(10)
C(6)-Fe(1)-C(7)-C(4)	-84.1(11)
C(13)-Fe(1)-C(7)-C(4)	77.8(11)

C(15)-Fe(1)-C(7)-C(4)	164.8(10)
C(12)-Fe(1)-C(7)-C(4)	36.8(17)
C(14)-Fe(1)-C(7)-C(4)	121.8(10)
C(8)-Fe(1)-C(7)-C(4)	-118.9(14)
C(11)-Fe(1)-C(7)-C(3)	81(4)
C(5)-Fe(1)-C(7)-C(3)	-165.9(19)
C(6)-Fe(1)-C(7)-C(3)	149.0(19)
C(4)-Fe(1)-C(7)-C(3)	-127(2)
C(13)-Fe(1)-C(7)-C(3)	-49(2)
C(15)-Fe(1)-C(7)-C(3)	38(2)
C(12)-Fe(1)-C(7)-C(3)	-90(2)
C(14)-Fe(1)-C(7)-C(3)	-5.2(19)
C(8)-Fe(1)-C(7)-C(3)	114(2)
C(11)-Fe(1)-C(7)-C(8)	-33(4)
C(5)-Fe(1)-C(7)-C(8)	80.0(10)
C(6)-Fe(1)-C(7)-C(8)	34.9(9)
C(4)-Fe(1)-C(7)-C(8)	118.9(14)
C(13)-Fe(1)-C(7)-C(8)	-163.3(9)
C(15)-Fe(1)-C(7)-C(8)	-76.3(11)
C(12)-Fe(1)-C(7)-C(8)	155.7(12)
C(14)-Fe(1)-C(7)-C(8)	-119.3(10)
O(1)-N(1)-C(8)-C(6)	-6(3)
C(1)-N(1)-C(8)-C(6)	-178.3(19)
O(1)-N(1)-C(8)-C(7)	175.8(13)
C(1)-N(1)-C(8)-C(7)	3(3)
O(1)-N(1)-C(8)-Fe(1)	-97.4(15)
C(1)-N(1)-C(8)-Fe(1)	89.8(19)
C(5)-C(6)-C(8)-N(1)	176.1(17)
Fe(1)-C(6)-C(8)-N(1)	-122(2)
C(5)-C(6)-C(8)-C(7)	-5.1(19)
Fe(1)-C(6)-C(8)-C(7)	57.0(12)
C(5)-C(6)-C(8)-Fe(1)	-62.1(11)
C(4)-C(7)-C(8)-N(1)	-178.9(15)
C(3)-C(7)-C(8)-N(1)	-1(3)
Fe(1)-C(7)-C(8)-N(1)	123.9(15)
C(4)-C(7)-C(8)-C(6)	2.2(19)

C(3)-C(7)-C(8)-C(6)	-179.8(16)
Fe(1)-C(7)-C(8)-C(6)	-55.0(13)
C(4)-C(7)-C(8)-Fe(1)	57.2(11)
C(3)-C(7)-C(8)-Fe(1)	-124.8(16)
C(11)-Fe(1)-C(8)-N(1)	59.9(18)
C(5)-Fe(1)-C(8)-N(1)	166.9(17)
C(6)-Fe(1)-C(8)-N(1)	125.3(19)
C(4)-Fe(1)-C(8)-N(1)	-148.9(17)
C(13)-Fe(1)-C(8)-N(1)	-75(2)
C(15)-Fe(1)-C(8)-N(1)	15.6(17)
C(12)-Fe(1)-C(8)-N(1)	111(2)
C(14)-Fe(1)-C(8)-N(1)	-28.7(18)
C(7)-Fe(1)-C(8)-N(1)	-111.7(18)
C(11)-Fe(1)-C(8)-C(6)	-65.4(13)
C(5)-Fe(1)-C(8)-C(6)	41.5(10)
C(4)-Fe(1)-C(8)-C(6)	85.8(11)
C(13)-Fe(1)-C(8)-C(6)	160.0(14)
C(15)-Fe(1)-C(8)-C(6)	-109.7(10)
C(12)-Fe(1)-C(8)-C(6)	-14(3)
C(14)-Fe(1)-C(8)-C(6)	-154.0(10)
C(7)-Fe(1)-C(8)-C(6)	122.9(14)
C(11)-Fe(1)-C(8)-C(7)	171.6(9)
C(5)-Fe(1)-C(8)-C(7)	-81.4(10)
C(6)-Fe(1)-C(8)-C(7)	-122.9(14)
C(4)-Fe(1)-C(8)-C(7)	-37.1(9)
C(13)-Fe(1)-C(8)-C(7)	37.1(19)
C(15)-Fe(1)-C(8)-C(7)	127.3(9)
C(12)-Fe(1)-C(8)-C(7)	-137.1(19)
C(14)-Fe(1)-C(8)-C(7)	83.1(11)
C(5)-Fe(1)-C(11)-C(15)	-159.7(9)
C(6)-Fe(1)-C(11)-C(15)	-116.1(10)
C(4)-Fe(1)-C(11)-C(15)	165.4(13)
C(13)-Fe(1)-C(11)-C(15)	82.4(10)
C(12)-Fe(1)-C(11)-C(15)	121.4(13)
C(14)-Fe(1)-C(11)-C(15)	39.2(9)
C(8)-Fe(1)-C(11)-C(15)	-79.1(11)

C(7)-Fe(1)-C(11)-C(15)	-52(3)
C(5)-Fe(1)-C(11)-C(12)	78.9(10)
C(6)-Fe(1)-C(11)-C(12)	122.5(10)
C(4)-Fe(1)-C(11)-C(12)	43.9(17)
C(13)-Fe(1)-C(11)-C(12)	-39.1(9)
C(15)-Fe(1)-C(11)-C(12)	-121.4(13)
C(14)-Fe(1)-C(11)-C(12)	-82.2(10)
C(8)-Fe(1)-C(11)-C(12)	159.4(9)
C(7)-Fe(1)-C(11)-C(12)	-173(3)
C(5)-Fe(1)-C(11)-C(16)	-39.7(17)
C(6)-Fe(1)-C(11)-C(16)	3.9(17)
C(4)-Fe(1)-C(11)-C(16)	-75(2)
C(13)-Fe(1)-C(11)-C(16)	-157.6(17)
C(15)-Fe(1)-C(11)-C(16)	120.0(19)
C(12)-Fe(1)-C(11)-C(16)	-118.6(19)
C(14)-Fe(1)-C(11)-C(16)	159.2(17)
C(8)-Fe(1)-C(11)-C(16)	40.9(18)
C(7)-Fe(1)-C(11)-C(16)	68(4)
C(15)-C(11)-C(12)-C(13)	-2.4(18)
C(16)-C(11)-C(12)-C(13)	-176.7(15)
Fe(1)-C(11)-C(12)-C(13)	58.2(10)
C(15)-C(11)-C(12)-C(22)	176.8(15)
C(16)-C(11)-C(12)-C(22)	3(3)
Fe(1)-C(11)-C(12)-C(22)	-122.6(17)
C(15)-C(11)-C(12)-Fe(1)	-60.6(11)
C(16)-C(11)-C(12)-Fe(1)	125.1(16)
C(5)-Fe(1)-C(12)-C(11)	-116.7(9)
C(6)-Fe(1)-C(12)-C(11)	-76.6(11)
C(4)-Fe(1)-C(12)-C(11)	-157.9(9)
C(13)-Fe(1)-C(12)-C(11)	117.8(13)
C(15)-Fe(1)-C(12)-C(11)	36.5(9)
C(14)-Fe(1)-C(12)-C(11)	79.8(10)
C(8)-Fe(1)-C(12)-C(11)	-66(2)
C(7)-Fe(1)-C(12)-C(11)	177.3(12)
C(11)-Fe(1)-C(12)-C(13)	-117.8(13)
C(5)-Fe(1)-C(12)-C(13)	125.5(9)

C(6)-Fe(1)-C(12)-C(13)	165.6(9)
C(4)-Fe(1)-C(12)-C(13)	84.3(10)
C(15)-Fe(1)-C(12)-C(13)	-81.3(9)
C(14)-Fe(1)-C(12)-C(13)	-38.0(9)
C(8)-Fe(1)-C(12)-C(13)	176.4(19)
C(7)-Fe(1)-C(12)-C(13)	59.4(16)
C(11)-Fe(1)-C(12)-C(22)	122.7(18)
C(5)-Fe(1)-C(12)-C(22)	6.0(15)
C(6)-Fe(1)-C(12)-C(22)	46.2(16)
C(4)-Fe(1)-C(12)-C(22)	-35.2(16)
C(13)-Fe(1)-C(12)-C(22)	-119.5(17)
C(15)-Fe(1)-C(12)-C(22)	159.3(15)
C(14)-Fe(1)-C(12)-C(22)	-157.4(15)
C(8)-Fe(1)-C(12)-C(22)	57(3)
C(7)-Fe(1)-C(12)-C(22)	-60(2)
C(11)-C(12)-C(13)-C(14)	4.3(17)
C(22)-C(12)-C(13)-C(14)	-174.9(15)
Fe(1)-C(12)-C(13)-C(14)	61.9(11)
C(11)-C(12)-C(13)-C(28)	178.3(16)
C(22)-C(12)-C(13)-C(28)	-1(3)
Fe(1)-C(12)-C(13)-C(28)	-124.1(16)
C(11)-C(12)-C(13)-Fe(1)	-57.7(10)
C(22)-C(12)-C(13)-Fe(1)	123.1(15)
C(11)-Fe(1)-C(13)-C(14)	-78.9(10)
C(5)-Fe(1)-C(13)-C(14)	170.9(9)
C(6)-Fe(1)-C(13)-C(14)	-159(2)
C(4)-Fe(1)-C(13)-C(14)	131.2(9)
C(15)-Fe(1)-C(13)-C(14)	-35.0(8)
C(12)-Fe(1)-C(13)-C(14)	-117.3(12)
C(8)-Fe(1)-C(13)-C(14)	65.3(18)
C(7)-Fe(1)-C(13)-C(14)	91.5(10)
C(11)-Fe(1)-C(13)-C(12)	38.4(9)
C(5)-Fe(1)-C(13)-C(12)	-71.8(10)
C(6)-Fe(1)-C(13)-C(12)	-42(2)
C(4)-Fe(1)-C(13)-C(12)	-111.5(9)
C(15)-Fe(1)-C(13)-C(12)	82.3(9)

C(14)-Fe(1)-C(13)-C(12)	117.3(12)
C(8)-Fe(1)-C(13)-C(12)	-177.4(13)
C(7)-Fe(1)-C(13)-C(12)	-151.2(8)
C(11)-Fe(1)-C(13)-C(28)	157.2(17)
C(5)-Fe(1)-C(13)-C(28)	47.0(16)
C(6)-Fe(1)-C(13)-C(28)	77(3)
C(4)-Fe(1)-C(13)-C(28)	7.3(16)
C(15)-Fe(1)-C(13)-C(28)	-158.9(16)
C(12)-Fe(1)-C(13)-C(28)	118.8(18)
C(14)-Fe(1)-C(13)-C(28)	-123.9(18)
C(8)-Fe(1)-C(13)-C(28)	-59(2)
C(7)-Fe(1)-C(13)-C(28)	-32.5(17)
C(12)-C(13)-C(14)-C(15)	-4.8(18)
C(28)-C(13)-C(14)-C(15)	-178.5(15)
Fe(1)-C(13)-C(14)-C(15)	56.4(11)
C(12)-C(13)-C(14)-C(34)	173.3(15)
C(28)-C(13)-C(14)-C(34)	0(3)
Fe(1)-C(13)-C(14)-C(34)	-125.5(17)
C(12)-C(13)-C(14)-Fe(1)	-61.2(10)
C(28)-C(13)-C(14)-Fe(1)	125.1(18)
C(11)-Fe(1)-C(14)-C(13)	84.0(10)
C(5)-Fe(1)-C(14)-C(13)	-26(2)
C(6)-Fe(1)-C(14)-C(13)	164.6(15)
C(4)-Fe(1)-C(14)-C(13)	-66.2(11)
C(15)-Fe(1)-C(14)-C(13)	123.8(12)
C(12)-Fe(1)-C(14)-C(13)	39.6(8)
C(8)-Fe(1)-C(14)-C(13)	-152.2(9)
C(7)-Fe(1)-C(14)-C(13)	-108.8(9)
C(11)-Fe(1)-C(14)-C(15)	-39.8(9)
C(5)-Fe(1)-C(14)-C(15)	-149.4(17)
C(6)-Fe(1)-C(14)-C(15)	40.8(19)
C(4)-Fe(1)-C(14)-C(15)	170.0(9)
C(13)-Fe(1)-C(14)-C(15)	-123.8(12)
C(12)-Fe(1)-C(14)-C(15)	-84.2(9)
C(8)-Fe(1)-C(14)-C(15)	83.9(10)
C(7)-Fe(1)-C(14)-C(15)	127.4(9)

C(11)-Fe(1)-C(14)-C(34)	-149.9(16)
C(5)-Fe(1)-C(14)-C(34)	101(2)
C(6)-Fe(1)-C(14)-C(34)	-69(2)
C(4)-Fe(1)-C(14)-C(34)	59.9(17)
C(13)-Fe(1)-C(14)-C(34)	126.1(18)
C(15)-Fe(1)-C(14)-C(34)	-110.1(17)
C(12)-Fe(1)-C(14)-C(34)	165.7(16)
C(8)-Fe(1)-C(14)-C(34)	-26.2(17)
C(7)-Fe(1)-C(14)-C(34)	17.3(16)
C(12)-C(11)-C(15)-C(14)	-0.4(18)
C(16)-C(11)-C(15)-C(14)	173.8(15)
Fe(1)-C(11)-C(15)-C(14)	-61.2(10)
C(12)-C(11)-C(15)-C(40)	-172.8(14)
C(16)-C(11)-C(15)-C(40)	1(3)
Fe(1)-C(11)-C(15)-C(40)	126.4(15)
C(12)-C(11)-C(15)-Fe(1)	60.8(11)
C(16)-C(11)-C(15)-Fe(1)	-125.0(16)
C(13)-C(14)-C(15)-C(11)	3.3(18)
C(34)-C(14)-C(15)-C(11)	-175.1(13)
Fe(1)-C(14)-C(15)-C(11)	59.4(10)
C(13)-C(14)-C(15)-C(40)	175.0(15)
C(34)-C(14)-C(15)-C(40)	-3(2)
Fe(1)-C(14)-C(15)-C(40)	-128.9(17)
C(13)-C(14)-C(15)-Fe(1)	-56.1(11)
C(34)-C(14)-C(15)-Fe(1)	125.5(13)
C(5)-Fe(1)-C(15)-C(11)	43.7(18)
C(6)-Fe(1)-C(15)-C(11)	81.9(11)
C(4)-Fe(1)-C(15)-C(11)	-150(2)
C(13)-Fe(1)-C(15)-C(11)	-81.1(10)
C(12)-Fe(1)-C(15)-C(11)	-36.5(9)
C(14)-Fe(1)-C(15)-C(11)	-115.8(13)
C(8)-Fe(1)-C(15)-C(11)	125.2(9)
C(7)-Fe(1)-C(15)-C(11)	167.7(10)
C(11)-Fe(1)-C(15)-C(14)	115.8(13)
C(5)-Fe(1)-C(15)-C(14)	159.5(13)
C(6)-Fe(1)-C(15)-C(14)	-162.2(9)

C(4)-Fe(1)-C(15)-C(14)	-34(3)
C(13)-Fe(1)-C(15)-C(14)	34.7(8)
C(12)-Fe(1)-C(15)-C(14)	79.3(9)
C(8)-Fe(1)-C(15)-C(14)	-118.9(9)
C(7)-Fe(1)-C(15)-C(14)	-76.5(11)
C(11)-Fe(1)-C(15)-C(40)	-117.1(17)
C(5)-Fe(1)-C(15)-C(40)	-73(2)
C(6)-Fe(1)-C(15)-C(40)	-35.1(16)
C(4)-Fe(1)-C(15)-C(40)	93(3)
C(13)-Fe(1)-C(15)-C(40)	161.8(15)
C(12)-Fe(1)-C(15)-C(40)	-153.6(15)
C(14)-Fe(1)-C(15)-C(40)	127.1(17)
C(8)-Fe(1)-C(15)-C(40)	8.2(16)
C(7)-Fe(1)-C(15)-C(40)	50.6(17)
C(15)-C(11)-C(16)-C(21)	-55(2)
C(12)-C(11)-C(16)-C(21)	118.2(17)
Fe(1)-C(11)-C(16)-C(21)	-148.9(13)
C(15)-C(11)-C(16)-C(17)	128.9(17)
C(12)-C(11)-C(16)-C(17)	-58(2)
Fe(1)-C(11)-C(16)-C(17)	35(2)
C(21)-C(16)-C(17)-C(18)	1(2)
C(11)-C(16)-C(17)-C(18)	176.6(17)
C(16)-C(17)-C(18)-C(19)	-1(3)
C(17)-C(18)-C(19)-C(20)	4(3)
C(18)-C(19)-C(20)-C(21)	-5(3)
C(17)-C(16)-C(21)-C(20)	-3(2)
C(11)-C(16)-C(21)-C(20)	-179.0(14)
C(19)-C(20)-C(21)-C(16)	5(2)
C(11)-C(12)-C(22)-C(23)	139.7(18)
C(13)-C(12)-C(22)-C(23)	-41(3)
Fe(1)-C(12)-C(22)-C(23)	49(2)
C(11)-C(12)-C(22)-C(27)	-45(2)
C(13)-C(12)-C(22)-C(27)	134.0(17)
Fe(1)-C(12)-C(22)-C(27)	-136.0(15)
C(27)-C(22)-C(23)-C(24)	3(3)
C(12)-C(22)-C(23)-C(24)	178.1(16)

C(22)-C(23)-C(24)-C(25)	-6(3)
C(23)-C(24)-C(25)-C(26)	7(3)
C(24)-C(25)-C(26)-C(27)	-6(3)
C(23)-C(22)-C(27)-C(26)	-1(3)
C(12)-C(22)-C(27)-C(26)	-176.9(16)
C(25)-C(26)-C(27)-C(22)	3(3)
C(14)-C(13)-C(28)-C(29)	-49(3)
C(12)-C(13)-C(28)-C(29)	138.0(17)
Fe(1)-C(13)-C(28)-C(29)	47(2)
C(14)-C(13)-C(28)-C(33)	124.4(19)
C(12)-C(13)-C(28)-C(33)	-48(2)
Fe(1)-C(13)-C(28)-C(33)	-139.7(14)
C(33)-C(28)-C(29)-C(30)	7(2)
C(13)-C(28)-C(29)-C(30)	-178.6(16)
C(28)-C(29)-C(30)-C(31)	-7(3)
C(29)-C(30)-C(31)-C(32)	3(3)
C(30)-C(31)-C(32)-C(33)	0(3)
C(31)-C(32)-C(33)-C(28)	0(3)
C(29)-C(28)-C(33)-C(32)	-4(3)
C(13)-C(28)-C(33)-C(32)	-178.2(16)
C(13)-C(14)-C(34)-C(35)	133.6(19)
C(15)-C(14)-C(34)-C(35)	-48(2)
Fe(1)-C(14)-C(34)-C(35)	38(2)
C(13)-C(14)-C(34)-C(39)	-48(2)
C(15)-C(14)-C(34)-C(39)	130.3(15)
Fe(1)-C(14)-C(34)-C(39)	-143.7(13)
C(39)-C(34)-C(35)-C(36)	-4(2)
C(14)-C(34)-C(35)-C(36)	174.4(14)
C(34)-C(35)-C(36)-C(37)	5(2)
C(35)-C(36)-C(37)-C(38)	-3(2)
C(36)-C(37)-C(38)-C(39)	1(3)
C(37)-C(38)-C(39)-C(34)	0(2)
C(35)-C(34)-C(39)-C(38)	2(2)
C(14)-C(34)-C(39)-C(38)	-176.9(13)
C(11)-C(15)-C(40)-C(41)	-63(2)
C(14)-C(15)-C(40)-C(41)	126.3(19)

Fe(1)-C(15)-C(40)-C(41)	26(2)
C(11)-C(15)-C(40)-C(45)	115.6(17)
C(14)-C(15)-C(40)-C(45)	-55(2)
Fe(1)-C(15)-C(40)-C(45)	-154.5(11)
C(45)-C(40)-C(41)-C(42)	-2(3)
C(15)-C(40)-C(41)-C(42)	177.4(15)
C(40)-C(41)-C(42)-C(43)	2(3)
C(41)-C(42)-C(43)-C(44)	-1(3)
C(42)-C(43)-C(44)-C(45)	-1(2)
C(41)-C(40)-C(45)-C(44)	0(3)
C(15)-C(40)-C(45)-C(44)	-179.1(15)
C(43)-C(44)-C(45)-C(40)	1(2)
O(2)-N(2)-C(51)-C(52)	176.5(16)
C(58)-N(2)-C(51)-C(52)	-5(3)
N(2)-C(51)-C(52)-C(53)	4(3)
C(51)-C(52)-C(53)-C(57)	-2(3)
C(62)-Fe(2)-C(54)-C(55)	66.0(13)
C(65)-Fe(2)-C(54)-C(55)	-175.7(15)
C(61)-Fe(2)-C(54)-C(55)	34(3)
C(56)-Fe(2)-C(54)-C(55)	-38.2(11)
C(57)-Fe(2)-C(54)-C(55)	-119.9(15)
C(64)-Fe(2)-C(54)-C(55)	148.6(11)
C(58)-Fe(2)-C(54)-C(55)	-82.0(12)
C(63)-Fe(2)-C(54)-C(55)	107.2(11)
C(62)-Fe(2)-C(54)-C(57)	-174.0(10)
C(65)-Fe(2)-C(54)-C(57)	-56(2)
C(61)-Fe(2)-C(54)-C(57)	154(2)
C(55)-Fe(2)-C(54)-C(57)	119.9(15)
C(56)-Fe(2)-C(54)-C(57)	81.7(11)
C(64)-Fe(2)-C(54)-C(57)	-91.5(11)
C(58)-Fe(2)-C(54)-C(57)	37.9(10)
C(63)-Fe(2)-C(54)-C(57)	-132.8(10)
C(57)-C(54)-C(55)-C(56)	1(2)
Fe(2)-C(54)-C(55)-C(56)	60.2(11)
C(57)-C(54)-C(55)-Fe(2)	-59.0(12)
C(62)-Fe(2)-C(55)-C(54)	-129.1(11)

C(65)-Fe(2)-C(55)-C(54)	173(2)
C(61)-Fe(2)-C(55)-C(54)	-167.4(10)
C(56)-Fe(2)-C(55)-C(54)	118.7(16)
C(57)-Fe(2)-C(55)-C(54)	37.4(10)
C(64)-Fe(2)-C(55)-C(54)	-62.1(18)
C(58)-Fe(2)-C(55)-C(54)	80.4(12)
C(63)-Fe(2)-C(55)-C(54)	-86.7(12)
C(62)-Fe(2)-C(55)-C(56)	112.2(11)
C(65)-Fe(2)-C(55)-C(56)	55(3)
C(61)-Fe(2)-C(55)-C(56)	74.0(12)
C(57)-Fe(2)-C(55)-C(56)	-81.3(11)
C(64)-Fe(2)-C(55)-C(56)	179.2(12)
C(54)-Fe(2)-C(55)-C(56)	-118.7(16)
C(58)-Fe(2)-C(55)-C(56)	-38.3(10)
C(63)-Fe(2)-C(55)-C(56)	154.7(10)
C(54)-C(55)-C(56)-C(58)	0.1(19)
Fe(2)-C(55)-C(56)-C(58)	60.9(11)
C(54)-C(55)-C(56)-Fe(2)	-60.7(12)
C(62)-Fe(2)-C(56)-C(58)	161.0(9)
C(65)-Fe(2)-C(56)-C(58)	78.5(11)
C(61)-Fe(2)-C(56)-C(58)	118.1(10)
C(55)-Fe(2)-C(56)-C(58)	-117.6(14)
C(57)-Fe(2)-C(56)-C(58)	-36.6(9)
C(64)-Fe(2)-C(56)-C(58)	65(4)
C(54)-Fe(2)-C(56)-C(58)	-80.4(10)
C(63)-Fe(2)-C(56)-C(58)	-163.4(11)
C(62)-Fe(2)-C(56)-C(55)	-81.3(11)
C(65)-Fe(2)-C(56)-C(55)	-163.9(11)
C(61)-Fe(2)-C(56)-C(55)	-124.3(11)
C(57)-Fe(2)-C(56)-C(55)	81.0(11)
C(64)-Fe(2)-C(56)-C(55)	-178(4)
C(54)-Fe(2)-C(56)-C(55)	37.2(11)
C(58)-Fe(2)-C(56)-C(55)	117.6(14)
C(63)-Fe(2)-C(56)-C(55)	-45.8(17)
C(55)-C(54)-C(57)-C(58)	-2.1(19)
Fe(2)-C(54)-C(57)-C(58)	-61.2(11)

C(55)-C(54)-C(57)-C(53)	-175.4(16)
Fe(2)-C(54)-C(57)-C(53)	125.5(18)
C(55)-C(54)-C(57)-Fe(2)	59.1(12)
C(52)-C(53)-C(57)-C(58)	0(3)
C(52)-C(53)-C(57)-C(54)	172.8(18)
C(52)-C(53)-C(57)-Fe(2)	-90(2)
C(62)-Fe(2)-C(57)-C(58)	136(2)
C(65)-Fe(2)-C(57)-C(58)	-86.3(12)
C(61)-Fe(2)-C(57)-C(58)	-43(2)
C(55)-Fe(2)-C(57)-C(58)	81.1(12)
C(56)-Fe(2)-C(57)-C(58)	37.1(10)
C(64)-Fe(2)-C(57)-C(58)	-131.9(10)
C(54)-Fe(2)-C(57)-C(58)	117.6(15)
C(63)-Fe(2)-C(57)-C(58)	-177.4(10)
C(62)-Fe(2)-C(57)-C(54)	18(3)
C(65)-Fe(2)-C(57)-C(54)	156.1(10)
C(61)-Fe(2)-C(57)-C(54)	-160.6(14)
C(55)-Fe(2)-C(57)-C(54)	-36.5(10)
C(56)-Fe(2)-C(57)-C(54)	-80.5(11)
C(64)-Fe(2)-C(57)-C(54)	110.4(11)
C(58)-Fe(2)-C(57)-C(54)	-117.6(15)
C(63)-Fe(2)-C(57)-C(54)	65.0(12)
C(62)-Fe(2)-C(57)-C(53)	-110(2)
C(65)-Fe(2)-C(57)-C(53)	28.6(19)
C(61)-Fe(2)-C(57)-C(53)	72(2)
C(55)-Fe(2)-C(57)-C(53)	-164.1(19)
C(56)-Fe(2)-C(57)-C(53)	152.0(18)
C(64)-Fe(2)-C(57)-C(53)	-17.1(19)
C(54)-Fe(2)-C(57)-C(53)	-128(2)
C(58)-Fe(2)-C(57)-C(53)	115(2)
C(63)-Fe(2)-C(57)-C(53)	-62.5(19)
C(54)-C(57)-C(58)-C(56)	2.1(17)
C(53)-C(57)-C(58)-C(56)	176.3(14)
Fe(2)-C(57)-C(58)-C(56)	-58.7(11)
C(54)-C(57)-C(58)-N(2)	-175.1(14)
C(53)-C(57)-C(58)-N(2)	-1(2)

Fe(2)-C(57)-C(58)-N(2)	124.0(13)
C(54)-C(57)-C(58)-Fe(2)	60.8(11)
C(53)-C(57)-C(58)-Fe(2)	-125.0(15)
C(55)-C(56)-C(58)-C(57)	-1.4(18)
Fe(2)-C(56)-C(58)-C(57)	58.9(11)
C(55)-C(56)-C(58)-N(2)	175.3(16)
Fe(2)-C(56)-C(58)-N(2)	-124.4(18)
C(55)-C(56)-C(58)-Fe(2)	-60.3(11)
O(2)-N(2)-C(58)-C(57)	-178.0(13)
C(51)-N(2)-C(58)-C(57)	3(2)
O(2)-N(2)-C(58)-C(56)	6(2)
C(51)-N(2)-C(58)-C(56)	-173.1(17)
O(2)-N(2)-C(58)-Fe(2)	-92.4(16)
C(51)-N(2)-C(58)-Fe(2)	89(2)
C(62)-Fe(2)-C(58)-C(57)	-156.8(11)
C(65)-Fe(2)-C(58)-C(57)	115.0(10)
C(61)-Fe(2)-C(58)-C(57)	160.8(9)
C(55)-Fe(2)-C(58)-C(57)	-81.6(11)
C(56)-Fe(2)-C(58)-C(57)	-120.2(14)
C(64)-Fe(2)-C(58)-C(57)	72.9(12)
C(54)-Fe(2)-C(58)-C(57)	-38.6(10)
C(63)-Fe(2)-C(58)-C(57)	10(4)
C(62)-Fe(2)-C(58)-C(56)	-36.7(16)
C(65)-Fe(2)-C(58)-C(56)	-124.9(9)
C(61)-Fe(2)-C(58)-C(56)	-79.1(10)
C(55)-Fe(2)-C(58)-C(56)	38.6(10)
C(57)-Fe(2)-C(58)-C(56)	120.2(14)
C(64)-Fe(2)-C(58)-C(56)	-167.0(10)
C(54)-Fe(2)-C(58)-C(56)	81.5(10)
C(63)-Fe(2)-C(58)-C(56)	130(3)
C(62)-Fe(2)-C(58)-N(2)	93(2)
C(65)-Fe(2)-C(58)-N(2)	5.0(19)
C(61)-Fe(2)-C(58)-N(2)	50.8(19)
C(55)-Fe(2)-C(58)-N(2)	168.5(19)
C(56)-Fe(2)-C(58)-N(2)	130(2)
C(57)-Fe(2)-C(58)-N(2)	-110(2)

C(64)-Fe(2)-C(58)-N(2)	-37(2)
C(54)-Fe(2)-C(58)-N(2)	-148.6(19)
C(63)-Fe(2)-C(58)-N(2)	-100(3)
C(65)-Fe(2)-C(61)-C(62)	-120.2(13)
C(55)-Fe(2)-C(61)-C(62)	67.3(11)
C(56)-Fe(2)-C(61)-C(62)	107.9(9)
C(57)-Fe(2)-C(61)-C(62)	179.4(15)
C(64)-Fe(2)-C(61)-C(62)	-81.0(9)
C(54)-Fe(2)-C(61)-C(62)	42(2)
C(58)-Fe(2)-C(61)-C(62)	149.2(9)
C(63)-Fe(2)-C(61)-C(62)	-37.0(8)
C(62)-Fe(2)-C(61)-C(65)	120.2(13)
C(55)-Fe(2)-C(61)-C(65)	-172.4(10)
C(56)-Fe(2)-C(61)-C(65)	-131.9(9)
C(57)-Fe(2)-C(61)-C(65)	-60.4(19)
C(64)-Fe(2)-C(61)-C(65)	39.3(9)
C(54)-Fe(2)-C(61)-C(65)	161.8(19)
C(58)-Fe(2)-C(61)-C(65)	-90.6(10)
C(63)-Fe(2)-C(61)-C(65)	83.2(10)
C(62)-Fe(2)-C(61)-C(66)	-121.2(16)
C(65)-Fe(2)-C(61)-C(66)	118.6(18)
C(55)-Fe(2)-C(61)-C(66)	-53.9(16)
C(56)-Fe(2)-C(61)-C(66)	-13.3(15)
C(57)-Fe(2)-C(61)-C(66)	58(2)
C(64)-Fe(2)-C(61)-C(66)	157.9(15)
C(54)-Fe(2)-C(61)-C(66)	-80(3)
C(58)-Fe(2)-C(61)-C(66)	28.0(16)
C(63)-Fe(2)-C(61)-C(66)	-158.2(15)
C(65)-C(61)-C(62)-C(63)	4(2)
C(66)-C(61)-C(62)-C(63)	-176.1(15)
Fe(2)-C(61)-C(62)-C(63)	61.7(12)
C(65)-C(61)-C(62)-C(72)	175.0(15)
C(66)-C(61)-C(62)-C(72)	-5(3)
Fe(2)-C(61)-C(62)-C(72)	-127.1(17)
C(65)-C(61)-C(62)-Fe(2)	-57.9(12)
C(66)-C(61)-C(62)-Fe(2)	122.2(17)

C(65)-Fe(2)-C(62)-C(61)	37.6(8)
C(55)-Fe(2)-C(62)-C(61)	-128.8(9)
C(56)-Fe(2)-C(62)-C(61)	-87.6(9)
C(57)-Fe(2)-C(62)-C(61)	-179(2)
C(64)-Fe(2)-C(62)-C(61)	81.4(9)
C(54)-Fe(2)-C(62)-C(61)	-165.2(9)
C(58)-Fe(2)-C(62)-C(61)	-62.7(14)
C(63)-Fe(2)-C(62)-C(61)	121.3(12)
C(65)-Fe(2)-C(62)-C(63)	-83.8(9)
C(61)-Fe(2)-C(62)-C(63)	-121.3(12)
C(55)-Fe(2)-C(62)-C(63)	109.9(9)
C(56)-Fe(2)-C(62)-C(63)	151.0(8)
C(57)-Fe(2)-C(62)-C(63)	60(3)
C(64)-Fe(2)-C(62)-C(63)	-39.9(8)
C(54)-Fe(2)-C(62)-C(63)	73.5(11)
C(58)-Fe(2)-C(62)-C(63)	175.9(11)
C(65)-Fe(2)-C(62)-C(72)	159.0(16)
C(61)-Fe(2)-C(62)-C(72)	121.4(18)
C(55)-Fe(2)-C(62)-C(72)	-7.3(15)
C(56)-Fe(2)-C(62)-C(72)	33.8(15)
C(57)-Fe(2)-C(62)-C(72)	-58(3)
C(64)-Fe(2)-C(62)-C(72)	-157.2(15)
C(54)-Fe(2)-C(62)-C(72)	-43.7(17)
C(58)-Fe(2)-C(62)-C(72)	58.7(19)
C(63)-Fe(2)-C(62)-C(72)	-117.2(17)
C(61)-C(62)-C(63)-C(78)	169.4(17)
C(72)-C(62)-C(63)-C(78)	-2(3)
Fe(2)-C(62)-C(63)-C(78)	-129.7(19)
C(61)-C(62)-C(63)-C(64)	-1.4(19)
C(72)-C(62)-C(63)-C(64)	-173.0(14)
Fe(2)-C(62)-C(63)-C(64)	59.5(10)
C(61)-C(62)-C(63)-Fe(2)	-60.9(12)
C(72)-C(62)-C(63)-Fe(2)	127.5(15)
C(62)-Fe(2)-C(63)-C(78)	126.7(19)
C(65)-Fe(2)-C(63)-C(78)	-152.8(17)
C(61)-Fe(2)-C(63)-C(78)	163.2(17)

C(55)-Fe(2)-C(63)-C(78)	43.1(18)
C(56)-Fe(2)-C(63)-C(78)	73(2)
C(57)-Fe(2)-C(63)-C(78)	-35.3(19)
C(64)-Fe(2)-C(63)-C(78)	-118(2)
C(54)-Fe(2)-C(63)-C(78)	2.1(17)
C(58)-Fe(2)-C(63)-C(78)	-43(4)
C(62)-Fe(2)-C(63)-C(64)	-115.1(12)
C(65)-Fe(2)-C(63)-C(64)	-34.6(9)
C(61)-Fe(2)-C(63)-C(64)	-78.6(9)
C(55)-Fe(2)-C(63)-C(64)	161.3(10)
C(56)-Fe(2)-C(63)-C(64)	-168.4(11)
C(57)-Fe(2)-C(63)-C(64)	82.9(11)
C(54)-Fe(2)-C(63)-C(64)	120.3(10)
C(58)-Fe(2)-C(63)-C(64)	75(3)
C(65)-Fe(2)-C(63)-C(62)	80.5(9)
C(61)-Fe(2)-C(63)-C(62)	36.5(8)
C(55)-Fe(2)-C(63)-C(62)	-83.6(10)
C(56)-Fe(2)-C(63)-C(62)	-53.3(15)
C(57)-Fe(2)-C(63)-C(62)	-162.0(8)
C(64)-Fe(2)-C(63)-C(62)	115.1(12)
C(54)-Fe(2)-C(63)-C(62)	-124.6(9)
C(58)-Fe(2)-C(63)-C(62)	-170(3)
C(78)-C(63)-C(64)-C(65)	-173.4(16)
C(62)-C(63)-C(64)-C(65)	-1.7(19)
Fe(2)-C(63)-C(64)-C(65)	55.9(13)
C(78)-C(63)-C(64)-C(84)	2(3)
C(62)-C(63)-C(64)-C(84)	173.8(16)
Fe(2)-C(63)-C(64)-C(84)	-128.6(17)
C(78)-C(63)-C(64)-Fe(2)	130.7(17)
C(62)-C(63)-C(64)-Fe(2)	-57.6(10)
C(62)-Fe(2)-C(64)-C(65)	-84.3(10)
C(61)-Fe(2)-C(64)-C(65)	-39.9(9)
C(55)-Fe(2)-C(64)-C(65)	-160.7(13)
C(56)-Fe(2)-C(64)-C(65)	17(4)
C(57)-Fe(2)-C(64)-C(65)	113.3(10)
C(54)-Fe(2)-C(64)-C(65)	158.4(9)

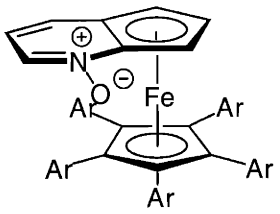
C(58)-Fe(2)-C(64)-C(65)	71.5(12)
C(63)-Fe(2)-C(64)-C(65)	-124.8(13)
C(62)-Fe(2)-C(64)-C(63)	40.5(9)
C(65)-Fe(2)-C(64)-C(63)	124.8(13)
C(61)-Fe(2)-C(64)-C(63)	84.9(10)
C(55)-Fe(2)-C(64)-C(63)	-35.9(18)
C(56)-Fe(2)-C(64)-C(63)	141(4)
C(57)-Fe(2)-C(64)-C(63)	-121.9(10)
C(54)-Fe(2)-C(64)-C(63)	-76.8(11)
C(58)-Fe(2)-C(64)-C(63)	-163.7(10)
C(62)-Fe(2)-C(64)-C(84)	161.0(16)
C(65)-Fe(2)-C(64)-C(84)	-114.7(18)
C(61)-Fe(2)-C(64)-C(84)	-154.6(16)
C(55)-Fe(2)-C(64)-C(84)	85(2)
C(56)-Fe(2)-C(64)-C(84)	-98(4)
C(57)-Fe(2)-C(64)-C(84)	-1.4(17)
C(54)-Fe(2)-C(64)-C(84)	43.7(17)
C(58)-Fe(2)-C(64)-C(84)	-43.2(18)
C(63)-Fe(2)-C(64)-C(84)	120.5(18)
C(63)-C(64)-C(65)-C(61)	4(2)
C(84)-C(64)-C(65)-C(61)	-171.7(15)
Fe(2)-C(64)-C(65)-C(61)	60.9(11)
C(63)-C(64)-C(65)-C(90)	171.1(15)
C(84)-C(64)-C(65)-C(90)	-4(3)
Fe(2)-C(64)-C(65)-C(90)	-131.9(18)
C(63)-C(64)-C(65)-Fe(2)	-56.9(12)
C(84)-C(64)-C(65)-Fe(2)	127.4(16)
C(62)-C(61)-C(65)-C(64)	-4.6(19)
C(66)-C(61)-C(65)-C(64)	175.3(15)
Fe(2)-C(61)-C(65)-C(64)	-61.6(12)
C(62)-C(61)-C(65)-C(90)	-172.8(15)
C(66)-C(61)-C(65)-C(90)	7(3)
Fe(2)-C(61)-C(65)-C(90)	130.2(15)
C(62)-C(61)-C(65)-Fe(2)	57.0(11)
C(66)-C(61)-C(65)-Fe(2)	-123.1(16)
C(62)-Fe(2)-C(65)-C(64)	79.0(10)

C(61)-Fe(2)-C(65)-C(64)	116.1(13)
C(55)-Fe(2)-C(65)-C(64)	141(3)
C(56)-Fe(2)-C(65)-C(64)	-176.3(10)
C(57)-Fe(2)-C(65)-C(64)	-89.6(11)
C(54)-Fe(2)-C(65)-C(64)	-49.9(19)
C(58)-Fe(2)-C(65)-C(64)	-133.1(10)
C(63)-Fe(2)-C(65)-C(64)	34.7(9)
C(62)-Fe(2)-C(65)-C(61)	-37.1(9)
C(55)-Fe(2)-C(65)-C(61)	24(3)
C(56)-Fe(2)-C(65)-C(61)	67.7(12)
C(57)-Fe(2)-C(65)-C(61)	154.4(10)
C(64)-Fe(2)-C(65)-C(61)	-116.1(13)
C(54)-Fe(2)-C(65)-C(61)	-166.0(14)
C(58)-Fe(2)-C(65)-C(61)	110.9(10)
C(63)-Fe(2)-C(65)-C(61)	-81.3(10)
C(62)-Fe(2)-C(65)-C(90)	-154.1(17)
C(61)-Fe(2)-C(65)-C(90)	-117.0(19)
C(55)-Fe(2)-C(65)-C(90)	-93(3)
C(56)-Fe(2)-C(65)-C(90)	-49.3(18)
C(57)-Fe(2)-C(65)-C(90)	37.4(18)
C(64)-Fe(2)-C(65)-C(90)	127(2)
C(54)-Fe(2)-C(65)-C(90)	77(2)
C(58)-Fe(2)-C(65)-C(90)	-6.1(18)
C(63)-Fe(2)-C(65)-C(90)	161.7(17)
C(62)-C(61)-C(66)-C(71)	53(2)
C(65)-C(61)-C(66)-C(71)	-127.1(17)
Fe(2)-C(61)-C(66)-C(71)	142.9(13)
C(62)-C(61)-C(66)-C(67)	-125.6(19)
C(65)-C(61)-C(66)-C(67)	54(2)
Fe(2)-C(61)-C(66)-C(67)	-35(2)
C(71)-C(66)-C(67)-C(68)	3(2)
C(61)-C(66)-C(67)-C(68)	-179.1(15)
C(66)-C(67)-C(68)-C(69)	-5(2)
C(67)-C(68)-C(69)-C(70)	4(3)
C(68)-C(69)-C(70)-C(71)	0(2)
C(67)-C(66)-C(71)-C(70)	1(2)

C(61)-C(66)-C(71)-C(70)	-177.1(13)
C(69)-C(70)-C(71)-C(66)	-3(2)
C(61)-C(62)-C(72)-C(73)	48(2)
C(63)-C(62)-C(72)-C(73)	-141.4(17)
Fe(2)-C(62)-C(72)-C(73)	-47(2)
C(61)-C(62)-C(72)-C(77)	-128.2(17)
C(63)-C(62)-C(72)-C(77)	42(2)
Fe(2)-C(62)-C(72)-C(77)	136.2(14)
C(77)-C(72)-C(73)-C(74)	4(2)
C(62)-C(72)-C(73)-C(74)	-172.3(15)
C(72)-C(73)-C(74)-C(75)	-7(3)
C(73)-C(74)-C(75)-C(76)	9(3)
C(74)-C(75)-C(76)-C(77)	-8(3)
C(75)-C(76)-C(77)-C(72)	5(3)
C(73)-C(72)-C(77)-C(76)	-3(2)
C(62)-C(72)-C(77)-C(76)	173.7(15)
C(64)-C(63)-C(78)-C(79)	-132.1(18)
C(62)-C(63)-C(78)-C(79)	59(3)
Fe(2)-C(63)-C(78)-C(79)	-38(3)
C(64)-C(63)-C(78)-C(83)	50(2)
C(62)-C(63)-C(78)-C(83)	-119(2)
Fe(2)-C(63)-C(78)-C(83)	143.3(14)
C(83)-C(78)-C(79)-C(80)	1(3)
C(63)-C(78)-C(79)-C(80)	-177.2(16)
C(78)-C(79)-C(80)-C(81)	0(3)
C(79)-C(80)-C(81)-C(82)	2(2)
C(80)-C(81)-C(82)-C(83)	-5(2)
C(81)-C(82)-C(83)-C(78)	6(3)
C(79)-C(78)-C(83)-C(82)	-3(3)
C(63)-C(78)-C(83)-C(82)	174.6(15)
C(65)-C(64)-C(84)-C(89)	54(2)
C(63)-C(64)-C(84)-C(89)	-120.9(18)
Fe(2)-C(64)-C(84)-C(89)	143.8(14)
C(65)-C(64)-C(84)-C(85)	-130.4(17)
C(63)-C(64)-C(84)-C(85)	55(2)
Fe(2)-C(64)-C(84)-C(85)	-41(2)

C(89)-C(84)-C(85)-C(86)	-2(2)
C(64)-C(84)-C(85)-C(86)	-177.4(15)
C(84)-C(85)-C(86)-C(87)	2(2)
C(85)-C(86)-C(87)-C(88)	-1(3)
C(86)-C(87)-C(88)-C(89)	-1(3)
C(87)-C(88)-C(89)-C(84)	1(3)
C(85)-C(84)-C(89)-C(88)	0(2)
C(64)-C(84)-C(89)-C(88)	175.3(15)
C(64)-C(65)-C(90)-C(95)	-119(2)
C(61)-C(65)-C(90)-C(95)	46(2)
Fe(2)-C(65)-C(90)-C(95)	138.8(16)
C(64)-C(65)-C(90)-C(91)	50(2)
C(61)-C(65)-C(90)-C(91)	-145.1(15)
Fe(2)-C(65)-C(90)-C(91)	-52(2)
C(95)-C(90)-C(91)-C(92)	-7(2)
C(65)-C(90)-C(91)-C(92)	-176.9(15)
C(90)-C(91)-C(92)-C(93)	9(2)
C(91)-C(92)-C(93)-C(94)	-7(3)
C(92)-C(93)-C(94)-C(95)	2(2)
C(91)-C(90)-C(95)-C(94)	2(2)
C(65)-C(90)-C(95)-C(94)	170.7(14)
C(93)-C(94)-C(95)-C(90)	0(2)

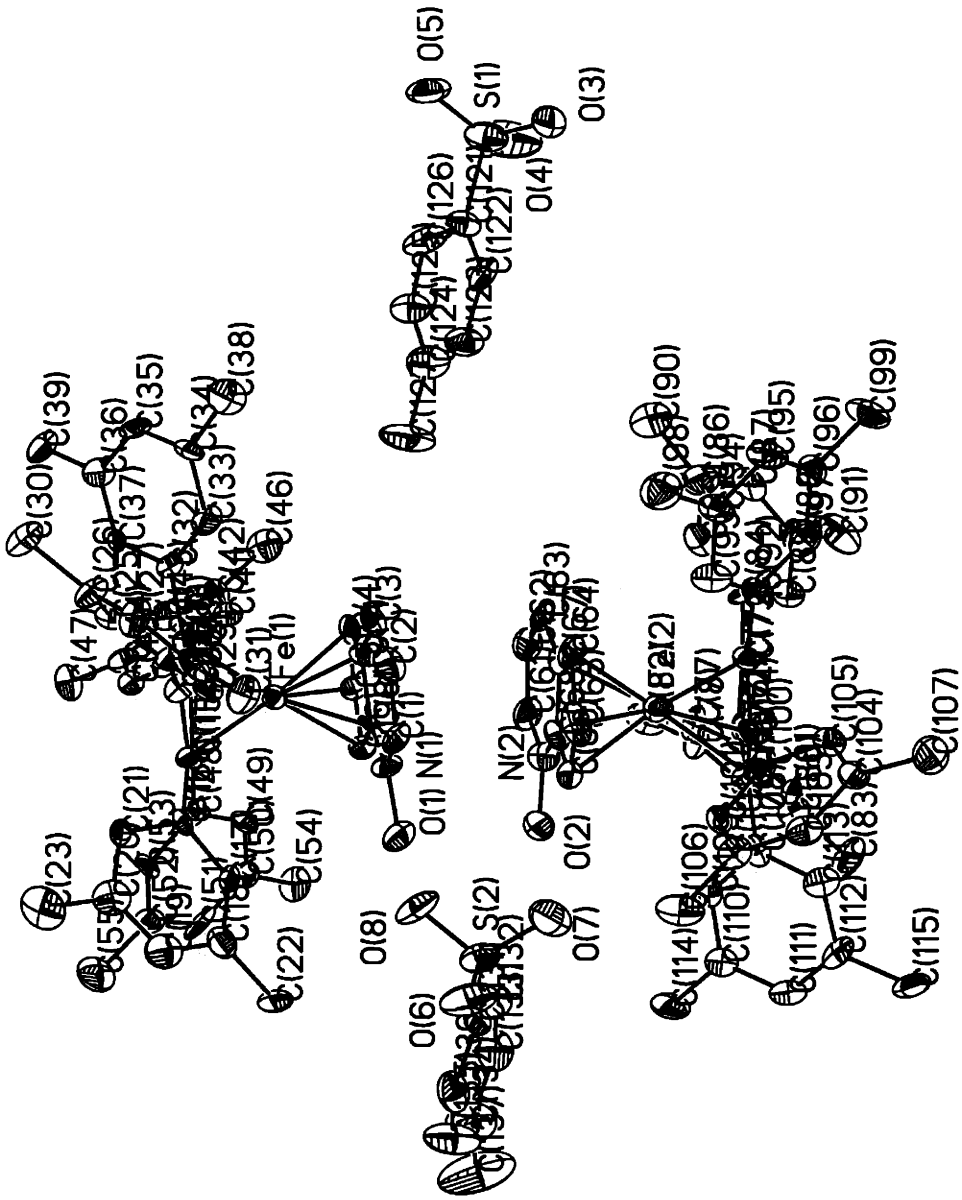
Symmetry transformations used to generate equivalent atoms:



Ar = 3,5-$Me_2C_6H_3$

(–)-3.1g

Structure solved by Michael M.-C. Lo



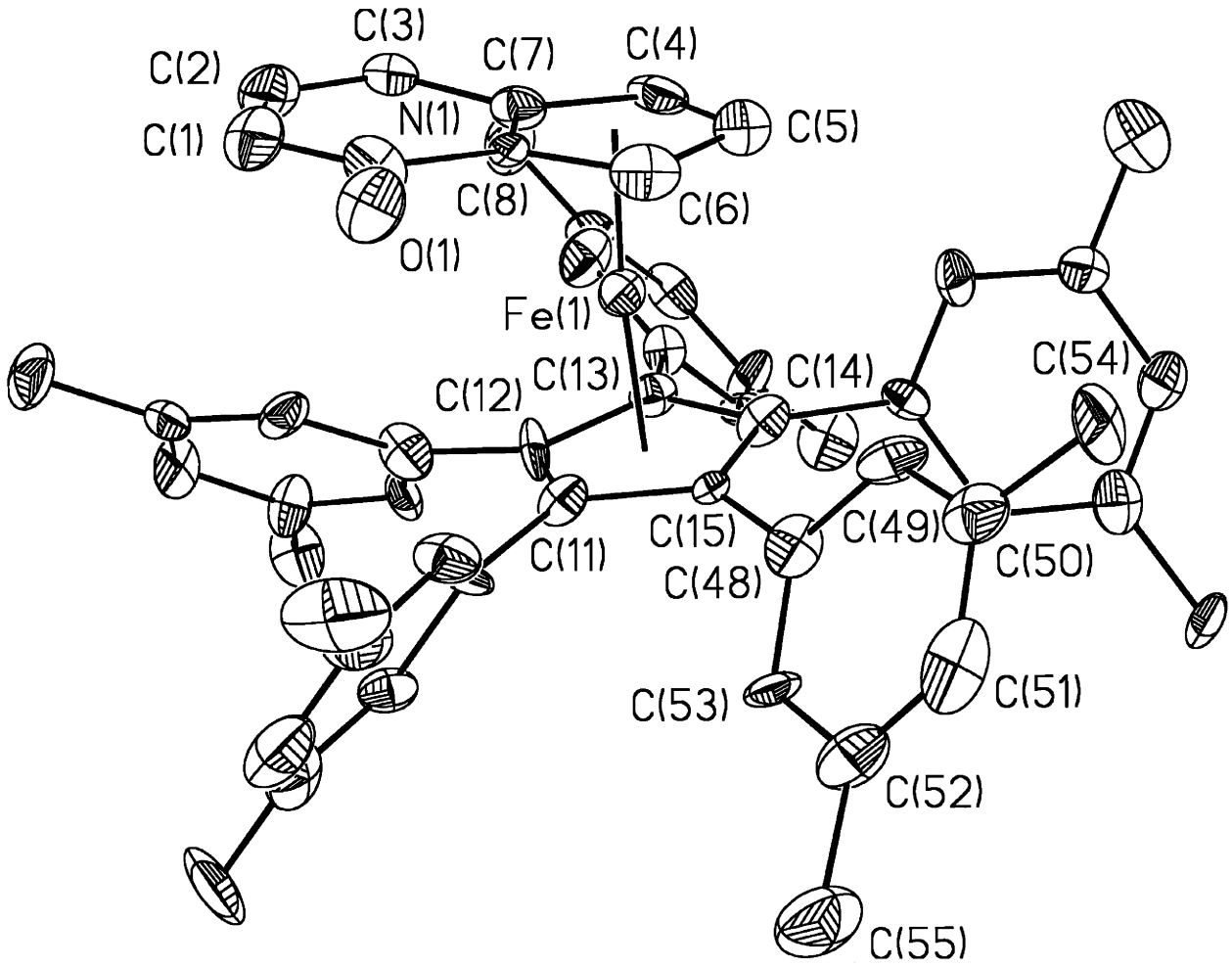

C(3)
C(2)
C(7)
C(4)
N(1)
C(1)
C(5)
C(8)
C(6)
O(1)
Fe(1)
C(12)
C(13)
C(14)
C(54)
C(11)
C(15)
C(49)
C(50)
C(48)
C(53)
C(51)
C(52)
C(55)

Table 1. Crystal data and structure refinement for 99323.

Identification code	99323	
Empirical formula	C60 H59 Fe N O4 S	
Formula weight	945.99	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 18.271(2) Å	α= 90°.
	b = 14.6869(18) Å	β= 102.568(2)°.
	c = 19.379(2) Å	γ = 90°.
Volume	5075.5(11) $Å^3$	
Z	4	
Density (calculated)	1.238 Mg/m^3	
Absorption coefficient	0.386 mm^{-1}	
F(000)	2000	
Crystal size	0.04 x 0.10 x 0.24 mm^3	
Theta range for data collection	2.56 to 23.16°.	
Index ranges	-14<=h<=20, -16<=k<=16, -21<=l<=21	
Reflections collected	20253	
Independent reflections	13106 [R(int) = 0.1341]	
Completeness to theta = 23.16°	99.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9980 and 0.8295	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13106 / 1 / 1232	
Goodness-of-fit on F^2	0.964	
Final R indices [I>2sigma(I)]	R1 = 0.0880, wR2 = 0.1435	
R indices (all data)	R1 = 0.2139, wR2 = 0.1924	
Absolute structure parameter	-0.05(4)	
Extinction coefficient	0.0054(4)	
Largest diff. peak and hole	0.278 and -0.300 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 99323. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	2951(1)	4499(1)	1601(1)	33(1)
Fe(2)	7042(1)	4706(1)	3341(1)	37(1)
S(1)	5243(3)	11709(3)	602(2)	71(2)
S(2)	5185(3)	2164(3)	4708(2)	59(1)
O(1)	4335(5)	3075(6)	3034(5)	54(3)
O(2)	5845(5)	2746(7)	2248(6)	70(3)
O(3)	5910(6)	11956(6)	1164(6)	84(3)
O(4)	5475(11)	11591(8)	-63(7)	150(7)
O(5)	4615(7)	12325(6)	636(6)	85(4)
O(6)	5074(8)	1995(8)	5406(5)	91(5)
O(7)	5897(6)	2596(7)	4656(5)	81(4)
O(8)	4548(5)	2683(6)	4287(5)	69(3)
N(1)	4207(7)	3986(7)	2927(6)	39(3)
N(2)	5892(8)	3666(9)	2149(8)	57(4)
C(1)	4322(7)	4563(11)	3468(7)	46(4)
C(2)	4248(9)	5485(11)	3326(9)	52(5)
C(3)	4065(8)	5842(11)	2667(7)	43(4)
C(4)	3762(8)	5282(11)	1330(8)	44(5)
C(5)	3789(8)	4359(9)	1042(8)	39(4)
C(6)	3904(8)	3740(10)	1630(8)	43(5)
C(7)	3916(8)	5191(9)	2074(8)	34(4)
C(8)	4021(8)	4262(9)	2236(7)	28(4)
C(11)	2068(8)	3891(9)	1962(7)	31(4)
C(12)	1995(8)	4844(10)	1985(7)	36(4)
C(13)	1982(8)	5221(9)	1294(7)	31(4)
C(14)	1992(8)	4448(9)	824(7)	34(4)
C(15)	2039(8)	3635(10)	1235(7)	31(4)
C(16)	2052(8)	3242(10)	2530(7)	32(4)
C(17)	2543(8)	2510(10)	2715(8)	42(4)
C(18)	2498(10)	1881(12)	3205(9)	52(5)
C(19)	1942(11)	1993(12)	3558(9)	64(6)

C(20)	1425(11)	2696(12)	3440(9)	55(5)
C(21)	1462(8)	3320(10)	2911(8)	34(4)
C(22)	3048(10)	1110(11)	3370(10)	83(7)
C(23)	805(11)	2806(13)	3828(8)	82(6)
C(24)	1930(9)	5419(11)	2611(8)	45(5)
C(25)	1378(9)	6027(9)	2554(7)	34(4)
C(26)	1273(9)	6543(10)	3147(8)	43(5)
C(27)	1767(9)	6418(11)	3786(8)	48(5)
C(28)	2343(9)	5789(12)	3862(8)	45(5)
C(29)	2410(8)	5273(9)	3277(7)	36(4)
C(30)	628(10)	7233(11)	3055(8)	58(5)
C(31)	2870(8)	5662(12)	4584(7)	53(5)
C(32)	1824(9)	6200(10)	1078(7)	32(4)
C(33)	2260(9)	6904(10)	1442(8)	47(5)
C(34)	2074(9)	7804(10)	1285(8)	37(4)
C(35)	1460(9)	7986(10)	751(8)	43(5)
C(36)	1012(9)	7314(11)	368(7)	48(5)
C(37)	1207(7)	6421(10)	555(7)	31(4)
C(38)	2508(9)	8579(11)	1675(8)	66(5)
C(39)	341(8)	7548(10)	-187(8)	61(5)
C(40)	1851(8)	4556(10)	34(6)	27(3)
C(41)	2313(9)	5043(9)	-296(7)	37(4)
C(42)	2126(9)	5126(10)	-1031(8)	43(4)
C(43)	1494(8)	4692(11)	-1423(7)	48(4)
C(44)	1040(9)	4174(10)	-1095(8)	45(4)
C(45)	1209(8)	4094(9)	-367(7)	34(4)
C(46)	2658(10)	5667(12)	-1403(8)	74(6)
C(47)	348(8)	3723(11)	-1542(7)	55(5)
C(48)	2013(9)	2691(11)	973(8)	42(4)
C(49)	2535(9)	2352(10)	584(8)	45(5)
C(50)	2531(10)	1478(12)	360(8)	45(5)
C(51)	2013(10)	887(11)	543(9)	56(6)
C(52)	1498(11)	1160(11)	933(9)	51(5)
C(53)	1519(8)	2064(10)	1160(7)	35(4)
C(54)	3047(9)	1083(11)	-77(8)	56(5)
C(55)	935(10)	559(12)	1171(9)	78(6)

C(61)	5729(9)	4027(12)	1506(9)	57(5)
C(62)	5722(9)	4975(12)	1403(9)	55(5)
C(63)	5865(8)	5541(11)	1980(8)	51(5)
C(64)	6131(8)	5540(12)	3381(8)	49(5)
C(65)	6175(8)	4758(13)	3853(8)	58(5)
C(66)	6128(9)	3944(11)	3475(9)	50(5)
C(67)	6041(8)	5181(9)	2682(8)	35(4)
C(68)	6010(8)	4196(10)	2762(8)	37(4)
C(71)	7966(7)	4264(10)	2991(7)	29(4)
C(72)	7980(8)	5231(10)	3046(8)	36(4)
C(73)	7944(9)	5467(9)	3765(8)	33(4)
C(74)	7971(7)	4631(11)	4151(7)	36(4)
C(75)	7995(9)	3903(10)	3683(8)	40(5)
C(76)	8068(8)	3740(9)	2366(7)	24(4)
C(77)	7589(8)	3835(11)	1702(7)	45(5)
C(78)	7679(9)	3318(11)	1134(8)	44(5)
C(79)	8253(10)	2686(11)	1238(8)	45(5)
C(80)	8746(10)	2545(11)	1877(8)	45(5)
C(81)	8640(8)	3075(9)	2435(8)	36(4)
C(82)	7150(10)	3436(12)	436(8)	76(6)
C(83)	9382(10)	1871(12)	2000(8)	75(6)
C(84)	8026(10)	5880(9)	2467(8)	41(5)
C(85)	7544(9)	6603(12)	2316(7)	52(5)
C(86)	7599(12)	7250(12)	1767(10)	72(6)
C(87)	8180(11)	7068(13)	1416(8)	60(6)
C(88)	8683(10)	6354(13)	1556(8)	51(5)
C(89)	8576(10)	5731(11)	2087(7)	46(5)
C(90)	7048(12)	8047(13)	1615(11)	108(8)
C(91)	9268(11)	6229(13)	1135(9)	87(7)
C(92)	7977(9)	6437(10)	4025(7)	28(4)
C(93)	7494(10)	6763(11)	4435(7)	46(5)
C(94)	7506(10)	7688(12)	4622(9)	51(5)
C(95)	8025(10)	8257(11)	4419(8)	52(5)
C(96)	8533(10)	7941(11)	4032(8)	45(5)
C(97)	8513(10)	7015(12)	3866(8)	52(5)
C(98)	6922(10)	8038(11)	4993(9)	72(6)

C(99)	9123(10)	8584(11)	3843(10)	84(7)
C(100)	8024(8)	4539(11)	4958(7)	38(4)
C(101)	7557(9)	3984(10)	5227(8)	42(4)
C(102)	7647(9)	3879(10)	5946(7)	39(4)
C(103)	8271(9)	4286(9)	6368(8)	43(4)
C(104)	8775(9)	4818(10)	6106(8)	42(4)
C(105)	8624(8)	4952(9)	5384(8)	40(4)
C(106)	7096(10)	3349(10)	6240(7)	60(5)
C(107)	9439(9)	5215(10)	6608(8)	64(5)
C(108)	8101(9)	2935(11)	3887(7)	40(4)
C(109)	7650(9)	2252(11)	3553(7)	35(4)
C(110)	7778(10)	1340(11)	3699(8)	43(4)
C(111)	8449(10)	1103(11)	4194(8)	47(5)
C(112)	8920(9)	1781(12)	4540(8)	45(5)
C(113)	8736(9)	2683(11)	4392(7)	41(4)
C(114)	7267(9)	588(10)	3336(9)	72(6)
C(115)	9633(8)	1536(10)	5061(8)	62(5)
C(121)	5001(8)	10606(9)	849(6)	45(4)
C(122)	5221(9)	9864(11)	506(8)	56(5)
C(123)	5007(11)	8985(12)	689(10)	72(6)
C(124)	4619(10)	8836(12)	1205(8)	66(5)
C(125)	4434(8)	9630(12)	1544(7)	57(4)
C(126)	4589(10)	10482(11)	1374(7)	60(5)
C(127)	4397(12)	7878(12)	1387(11)	123(9)
C(131)	5168(7)	1103(9)	4287(7)	45(4)
C(132)	5357(9)	1019(12)	3636(8)	54(5)
C(133)	5369(9)	161(12)	3345(9)	66(5)
C(134)	5109(12)	-631(14)	3687(11)	99(7)
C(135)	4909(12)	-487(14)	4265(9)	96(8)
C(136)	4922(9)	345(13)	4593(8)	66(5)
C(137)	5173(16)	-1570(13)	3315(10)	171(13)

Table 3. Bond lengths [Å] and angles [°] for 99323.

Fe(1)-C(4)	2.033(15)
Fe(1)-C(13)	2.039(14)
Fe(1)-C(14)	2.049(13)
Fe(1)-C(6)	2.058(15)
Fe(1)-C(7)	2.067(15)
Fe(1)-C(5)	2.070(15)
Fe(1)-C(11)	2.092(15)
Fe(1)-C(15)	2.094(14)
Fe(1)-C(8)	2.100(14)
Fe(1)-C(12)	2.103(14)
Fe(2)-C(73)	2.013(15)
Fe(2)-C(65)	2.046(15)
Fe(2)-C(74)	2.049(13)
Fe(2)-C(71)	2.057(14)
Fe(2)-C(72)	2.069(15)
Fe(2)-C(66)	2.075(16)
Fe(2)-C(64)	2.081(16)
Fe(2)-C(75)	2.088(15)
Fe(2)-C(67)	2.109(15)
Fe(2)-C(68)	2.111(14)
S(1)-O(4)	1.452(13)
S(1)-O(5)	1.475(11)
S(1)-O(3)	1.492(11)
S(1)-C(121)	1.771(13)
S(2)-O(6)	1.433(9)
S(2)-O(7)	1.470(11)
S(2)-O(8)	1.480(9)
S(2)-C(131)	1.755(14)
O(1)-N(1)	1.366(12)
O(2)-N(2)	1.370(14)
N(1)-C(1)	1.329(17)
N(1)-C(8)	1.368(16)
N(2)-C(61)	1.327(19)
N(2)-C(68)	1.398(18)

C(1)-C(2)	1.38(2)
C(2)-C(3)	1.352(18)
C(3)-C(7)	1.474(18)
C(4)-C(7)	1.414(18)
C(4)-C(5)	1.47(2)
C(5)-C(6)	1.437(19)
C(6)-C(8)	1.380(18)
C(7)-C(8)	1.405(17)
C(11)-C(12)	1.406(19)
C(11)-C(15)	1.449(18)
C(11)-C(16)	1.463(18)
C(12)-C(13)	1.445(18)
C(12)-C(24)	1.503(19)
C(13)-C(14)	1.458(18)
C(13)-C(32)	1.509(18)
C(14)-C(15)	1.428(18)
C(14)-C(40)	1.504(17)
C(15)-C(48)	1.47(2)
C(16)-C(17)	1.395(18)
C(16)-C(21)	1.438(18)
C(17)-C(18)	1.341(19)
C(18)-C(19)	1.35(2)
C(18)-C(22)	1.50(2)
C(19)-C(20)	1.38(2)
C(20)-C(21)	1.39(2)
C(20)-C(23)	1.50(2)
C(24)-C(25)	1.334(19)
C(24)-C(29)	1.410(18)
C(25)-C(26)	1.424(19)
C(26)-C(27)	1.378(18)
C(26)-C(30)	1.54(2)
C(27)-C(28)	1.38(2)
C(28)-C(29)	1.391(19)
C(28)-C(31)	1.527(18)
C(32)-C(37)	1.380(18)
C(32)-C(33)	1.399(18)

C(33)-C(34)	1.382(19)
C(34)-C(35)	1.377(19)
C(34)-C(38)	1.496(19)
C(35)-C(36)	1.388(19)
C(36)-C(37)	1.387(18)
C(36)-C(39)	1.484(18)
C(40)-C(41)	1.367(17)
C(40)-C(45)	1.429(17)
C(41)-C(42)	1.395(18)
C(42)-C(43)	1.392(17)
C(42)-C(46)	1.55(2)
C(43)-C(44)	1.378(19)
C(44)-C(45)	1.383(18)
C(44)-C(47)	1.520(18)
C(48)-C(53)	1.39(2)
C(48)-C(49)	1.43(2)
C(49)-C(50)	1.35(2)
C(50)-C(51)	1.39(2)
C(50)-C(54)	1.51(2)
C(51)-C(52)	1.39(2)
C(52)-C(53)	1.40(2)
C(52)-C(55)	1.50(2)
C(61)-C(62)	1.407(19)
C(62)-C(63)	1.37(2)
C(63)-C(67)	1.429(19)
C(64)-C(67)	1.429(19)
C(64)-C(65)	1.46(2)
C(65)-C(66)	1.39(2)
C(66)-C(68)	1.40(2)
C(67)-C(68)	1.458(17)
C(71)-C(72)	1.425(18)
C(71)-C(75)	1.432(19)
C(71)-C(76)	1.480(18)
C(72)-C(73)	1.45(2)
C(72)-C(84)	1.489(19)
C(73)-C(74)	1.433(19)

C(73)-C(92)	1.508(19)
C(74)-C(75)	1.410(19)
C(74)-C(100)	1.552(17)
C(75)-C(108)	1.48(2)
C(76)-C(77)	1.397(18)
C(76)-C(81)	1.414(18)
C(77)-C(78)	1.375(19)
C(78)-C(79)	1.38(2)
C(78)-C(82)	1.492(19)
C(79)-C(80)	1.380(19)
C(80)-C(81)	1.381(19)
C(80)-C(83)	1.50(2)
C(84)-C(85)	1.37(2)
C(84)-C(89)	1.386(19)
C(85)-C(86)	1.45(2)
C(86)-C(87)	1.41(2)
C(86)-C(90)	1.53(2)
C(87)-C(88)	1.38(2)
C(88)-C(89)	1.42(2)
C(88)-C(91)	1.49(2)
C(92)-C(97)	1.38(2)
C(92)-C(93)	1.394(19)
C(93)-C(94)	1.40(2)
C(94)-C(95)	1.38(2)
C(94)-C(98)	1.50(2)
C(95)-C(96)	1.39(2)
C(96)-C(97)	1.40(2)
C(96)-C(99)	1.54(2)
C(100)-C(101)	1.363(19)
C(100)-C(105)	1.363(18)
C(101)-C(102)	1.376(19)
C(102)-C(103)	1.387(18)
C(102)-C(106)	1.480(19)
C(103)-C(104)	1.385(18)
C(104)-C(105)	1.380(18)
C(104)-C(107)	1.499(18)

C(108)-C(109)	1.368(19)
C(108)-C(113)	1.40(2)
C(109)-C(110)	1.379(19)
C(110)-C(111)	1.43(2)
C(110)-C(114)	1.517(19)
C(111)-C(112)	1.39(2)
C(112)-C(113)	1.381(19)
C(112)-C(115)	1.509(19)
C(121)-C(122)	1.382(18)
C(121)-C(126)	1.403(19)
C(122)-C(123)	1.42(2)
C(123)-C(124)	1.36(2)
C(124)-C(125)	1.41(2)
C(124)-C(127)	1.53(2)
C(125)-C(126)	1.34(2)
C(131)-C(136)	1.383(19)
C(131)-C(132)	1.385(17)
C(132)-C(133)	1.38(2)
C(133)-C(134)	1.47(2)
C(134)-C(135)	1.27(2)
C(134)-C(137)	1.57(2)
C(135)-C(136)	1.37(2)

C(4)-Fe(1)-C(13)	105.4(6)
C(4)-Fe(1)-C(14)	112.7(6)
C(13)-Fe(1)-C(14)	41.8(5)
C(4)-Fe(1)-C(6)	69.7(6)
C(13)-Fe(1)-C(6)	164.9(6)
C(14)-Fe(1)-C(6)	125.7(6)
C(4)-Fe(1)-C(7)	40.3(5)
C(13)-Fe(1)-C(7)	118.5(6)
C(14)-Fe(1)-C(7)	148.6(5)
C(6)-Fe(1)-C(7)	67.7(6)
C(4)-Fe(1)-C(5)	42.0(6)
C(13)-Fe(1)-C(5)	126.4(6)
C(14)-Fe(1)-C(5)	102.9(6)

C(6)-Fe(1)-C(5)	40.8(5)
C(7)-Fe(1)-C(5)	68.0(6)
C(4)-Fe(1)-C(11)	170.4(6)
C(13)-Fe(1)-C(11)	68.6(6)
C(14)-Fe(1)-C(11)	68.4(5)
C(6)-Fe(1)-C(11)	118.0(6)
C(7)-Fe(1)-C(11)	135.0(5)
C(5)-Fe(1)-C(11)	147.6(6)
C(4)-Fe(1)-C(15)	145.8(6)
C(13)-Fe(1)-C(15)	68.8(6)
C(14)-Fe(1)-C(15)	40.3(5)
C(6)-Fe(1)-C(15)	106.7(6)
C(7)-Fe(1)-C(15)	171.0(6)
C(5)-Fe(1)-C(15)	112.8(6)
C(11)-Fe(1)-C(15)	40.5(5)
C(4)-Fe(1)-C(8)	66.9(5)
C(13)-Fe(1)-C(8)	153.7(6)
C(14)-Fe(1)-C(8)	164.4(6)
C(6)-Fe(1)-C(8)	38.8(5)
C(7)-Fe(1)-C(8)	39.4(5)
C(5)-Fe(1)-C(8)	65.8(5)
C(11)-Fe(1)-C(8)	114.9(5)
C(15)-Fe(1)-C(8)	132.0(5)
C(4)-Fe(1)-C(12)	131.6(6)
C(13)-Fe(1)-C(12)	40.8(5)
C(14)-Fe(1)-C(12)	68.0(5)
C(6)-Fe(1)-C(12)	152.1(6)
C(7)-Fe(1)-C(12)	114.7(6)
C(5)-Fe(1)-C(12)	167.1(6)
C(11)-Fe(1)-C(12)	39.2(5)
C(15)-Fe(1)-C(12)	66.7(6)
C(8)-Fe(1)-C(12)	124.8(5)
C(73)-Fe(2)-C(65)	115.7(6)
C(73)-Fe(2)-C(74)	41.3(5)
C(65)-Fe(2)-C(74)	103.3(6)
C(73)-Fe(2)-C(71)	69.6(6)

C(65)-Fe(2)-C(71)	161.7(7)
C(74)-Fe(2)-C(71)	68.5(5)
C(73)-Fe(2)-C(72)	41.6(6)
C(65)-Fe(2)-C(72)	153.5(7)
C(74)-Fe(2)-C(72)	68.5(6)
C(71)-Fe(2)-C(72)	40.4(5)
C(73)-Fe(2)-C(66)	149.2(6)
C(65)-Fe(2)-C(66)	39.6(6)
C(74)-Fe(2)-C(66)	115.5(6)
C(71)-Fe(2)-C(66)	127.7(6)
C(72)-Fe(2)-C(66)	166.8(7)
C(73)-Fe(2)-C(64)	104.4(6)
C(65)-Fe(2)-C(64)	41.4(6)
C(74)-Fe(2)-C(64)	122.6(6)
C(71)-Fe(2)-C(64)	156.8(6)
C(72)-Fe(2)-C(64)	120.5(6)
C(66)-Fe(2)-C(64)	68.9(6)
C(73)-Fe(2)-C(75)	68.4(6)
C(65)-Fe(2)-C(75)	123.2(7)
C(74)-Fe(2)-C(75)	39.8(5)
C(71)-Fe(2)-C(75)	40.4(5)
C(72)-Fe(2)-C(75)	67.4(6)
C(66)-Fe(2)-C(75)	107.1(6)
C(64)-Fe(2)-C(75)	159.8(6)
C(73)-Fe(2)-C(67)	126.1(6)
C(65)-Fe(2)-C(67)	67.7(6)
C(74)-Fe(2)-C(67)	161.2(6)
C(71)-Fe(2)-C(67)	124.8(5)
C(72)-Fe(2)-C(67)	111.8(6)
C(66)-Fe(2)-C(67)	68.8(6)
C(64)-Fe(2)-C(67)	39.9(5)
C(75)-Fe(2)-C(67)	158.8(6)
C(73)-Fe(2)-C(68)	166.3(6)
C(65)-Fe(2)-C(68)	64.8(6)
C(74)-Fe(2)-C(68)	152.0(6)
C(71)-Fe(2)-C(68)	114.5(6)

C(72)-Fe(2)-C(68)	133.1(6)
C(66)-Fe(2)-C(68)	39.1(5)
C(64)-Fe(2)-C(68)	66.4(6)
C(75)-Fe(2)-C(68)	123.7(6)
C(67)-Fe(2)-C(68)	40.4(5)
O(4)-S(1)-O(5)	119.6(9)
O(4)-S(1)-O(3)	109.1(10)
O(5)-S(1)-O(3)	109.7(6)
O(4)-S(1)-C(121)	105.6(7)
O(5)-S(1)-C(121)	107.9(7)
O(3)-S(1)-C(121)	103.7(6)
O(6)-S(2)-O(7)	116.7(7)
O(6)-S(2)-O(8)	110.7(7)
O(7)-S(2)-O(8)	110.0(6)
O(6)-S(2)-C(131)	107.0(7)
O(7)-S(2)-C(131)	106.1(7)
O(8)-S(2)-C(131)	105.6(6)
C(1)-N(1)-O(1)	120.8(12)
C(1)-N(1)-C(8)	123.1(12)
O(1)-N(1)-C(8)	115.8(11)
C(61)-N(2)-O(2)	121.2(14)
C(61)-N(2)-C(68)	122.5(14)
O(2)-N(2)-C(68)	115.6(13)
N(1)-C(1)-C(2)	118.3(14)
C(3)-C(2)-C(1)	124.1(15)
C(2)-C(3)-C(7)	116.8(14)
C(7)-C(4)-C(5)	106.5(13)
C(7)-C(4)-Fe(1)	71.1(8)
C(5)-C(4)-Fe(1)	70.3(9)
C(6)-C(5)-C(4)	107.1(13)
C(6)-C(5)-Fe(1)	69.2(9)
C(4)-C(5)-Fe(1)	67.7(9)
C(8)-C(6)-C(5)	107.0(13)
C(8)-C(6)-Fe(1)	72.3(9)
C(5)-C(6)-Fe(1)	70.1(9)
C(8)-C(7)-C(4)	107.9(13)

C(8)-C(7)-C(3)	117.5(13)
C(4)-C(7)-C(3)	134.2(14)
C(8)-C(7)-Fe(1)	71.6(8)
C(4)-C(7)-Fe(1)	68.5(8)
C(3)-C(7)-Fe(1)	131.2(11)
N(1)-C(8)-C(6)	128.9(13)
N(1)-C(8)-C(7)	120.0(13)
C(6)-C(8)-C(7)	111.1(13)
N(1)-C(8)-Fe(1)	128.6(10)
C(6)-C(8)-Fe(1)	69.0(9)
C(7)-C(8)-Fe(1)	69.0(9)
C(12)-C(11)-C(15)	107.8(13)
C(12)-C(11)-C(16)	127.4(14)
C(15)-C(11)-C(16)	124.1(13)
C(12)-C(11)-Fe(1)	70.8(9)
C(15)-C(11)-Fe(1)	69.8(8)
C(16)-C(11)-Fe(1)	132.4(11)
C(11)-C(12)-C(13)	109.5(12)
C(11)-C(12)-C(24)	127.5(13)
C(13)-C(12)-C(24)	122.9(13)
C(11)-C(12)-Fe(1)	70.0(9)
C(13)-C(12)-Fe(1)	67.2(8)
C(24)-C(12)-Fe(1)	129.6(11)
C(12)-C(13)-C(14)	106.3(12)
C(12)-C(13)-C(32)	125.9(13)
C(14)-C(13)-C(32)	126.6(12)
C(12)-C(13)-Fe(1)	72.0(8)
C(14)-C(13)-Fe(1)	69.5(8)
C(32)-C(13)-Fe(1)	132.7(11)
C(15)-C(14)-C(13)	108.1(11)
C(15)-C(14)-C(40)	129.2(13)
C(13)-C(14)-C(40)	122.1(12)
C(15)-C(14)-Fe(1)	71.5(8)
C(13)-C(14)-Fe(1)	68.7(8)
C(40)-C(14)-Fe(1)	132.4(10)
C(14)-C(15)-C(11)	108.0(13)

C(14)-C(15)-C(48)	127.0(13)
C(11)-C(15)-C(48)	124.8(13)
C(14)-C(15)-Fe(1)	68.2(8)
C(11)-C(15)-Fe(1)	69.7(8)
C(48)-C(15)-Fe(1)	130.6(11)
C(17)-C(16)-C(21)	116.2(13)
C(17)-C(16)-C(11)	125.3(14)
C(21)-C(16)-C(11)	118.4(14)
C(18)-C(17)-C(16)	125.3(16)
C(17)-C(18)-C(19)	116.3(18)
C(17)-C(18)-C(22)	122.0(18)
C(19)-C(18)-C(22)	121.7(17)
C(18)-C(19)-C(20)	124.6(19)
C(19)-C(20)-C(21)	118.3(19)
C(19)-C(20)-C(23)	124.1(19)
C(21)-C(20)-C(23)	117.5(17)
C(20)-C(21)-C(16)	119.3(15)
C(25)-C(24)-C(29)	119.0(15)
C(25)-C(24)-C(12)	120.1(14)
C(29)-C(24)-C(12)	120.7(14)
C(24)-C(25)-C(26)	121.5(15)
C(27)-C(26)-C(25)	118.5(14)
C(27)-C(26)-C(30)	121.9(14)
C(25)-C(26)-C(30)	119.5(14)
C(26)-C(27)-C(28)	121.3(14)
C(27)-C(28)-C(29)	118.5(15)
C(27)-C(28)-C(31)	119.4(14)
C(29)-C(28)-C(31)	122.1(16)
C(28)-C(29)-C(24)	121.1(15)
C(37)-C(32)-C(33)	118.8(13)
C(37)-C(32)-C(13)	120.3(13)
C(33)-C(32)-C(13)	120.7(13)
C(34)-C(33)-C(32)	120.6(15)
C(35)-C(34)-C(33)	118.2(14)
C(35)-C(34)-C(38)	119.2(14)
C(33)-C(34)-C(38)	122.6(14)

C(34)-C(35)-C(36)	123.5(14)
C(37)-C(36)-C(35)	116.4(13)
C(37)-C(36)-C(39)	122.2(14)
C(35)-C(36)-C(39)	121.3(14)
C(32)-C(37)-C(36)	122.4(14)
C(41)-C(40)-C(45)	120.7(12)
C(41)-C(40)-C(14)	123.0(13)
C(45)-C(40)-C(14)	116.3(12)
C(40)-C(41)-C(42)	119.1(14)
C(43)-C(42)-C(41)	120.4(14)
C(43)-C(42)-C(46)	120.7(14)
C(41)-C(42)-C(46)	118.8(14)
C(44)-C(43)-C(42)	120.9(14)
C(43)-C(44)-C(45)	119.6(14)
C(43)-C(44)-C(47)	119.2(13)
C(45)-C(44)-C(47)	121.2(15)
C(44)-C(45)-C(40)	119.3(14)
C(53)-C(48)-C(49)	116.8(15)
C(53)-C(48)-C(15)	120.4(15)
C(49)-C(48)-C(15)	122.4(15)
C(50)-C(49)-C(48)	122.9(16)
C(49)-C(50)-C(51)	117.9(17)
C(49)-C(50)-C(54)	125.6(17)
C(51)-C(50)-C(54)	116.5(16)
C(50)-C(51)-C(52)	122.6(16)
C(51)-C(52)-C(53)	118.1(17)
C(51)-C(52)-C(55)	126.1(16)
C(53)-C(52)-C(55)	115.7(17)
C(48)-C(53)-C(52)	121.4(16)
N(2)-C(61)-C(62)	121.5(17)
C(63)-C(62)-C(61)	119.3(17)
C(62)-C(63)-C(67)	121.1(15)
C(67)-C(64)-C(65)	106.4(14)
C(67)-C(64)-Fe(2)	71.1(9)
C(65)-C(64)-Fe(2)	68.0(9)
C(66)-C(65)-C(64)	110.9(14)

C(66)-C(65)-Fe(2)	71.3(9)
C(64)-C(65)-Fe(2)	70.6(9)
C(65)-C(66)-C(68)	105.6(14)
C(65)-C(66)-Fe(2)	69.1(9)
C(68)-C(66)-Fe(2)	71.8(9)
C(64)-C(67)-C(63)	136.2(15)
C(64)-C(67)-C(68)	105.3(14)
C(63)-C(67)-C(68)	117.5(14)
C(64)-C(67)-Fe(2)	69.0(9)
C(63)-C(67)-Fe(2)	133.2(11)
C(68)-C(67)-Fe(2)	69.9(9)
N(2)-C(68)-C(66)	130.8(15)
N(2)-C(68)-C(67)	117.7(15)
C(66)-C(68)-C(67)	111.5(14)
N(2)-C(68)-Fe(2)	127.2(11)
C(66)-C(68)-Fe(2)	69.1(9)
C(67)-C(68)-Fe(2)	69.7(9)
C(72)-C(71)-C(75)	107.6(14)
C(72)-C(71)-C(76)	125.2(14)
C(75)-C(71)-C(76)	126.0(13)
C(72)-C(71)-Fe(2)	70.3(9)
C(75)-C(71)-Fe(2)	71.0(9)
C(76)-C(71)-Fe(2)	133.8(10)
C(71)-C(72)-C(73)	107.9(13)
C(71)-C(72)-C(84)	125.8(15)
C(73)-C(72)-C(84)	126.4(13)
C(71)-C(72)-Fe(2)	69.3(9)
C(73)-C(72)-Fe(2)	67.1(9)
C(84)-C(72)-Fe(2)	129.2(12)
C(74)-C(73)-C(72)	107.1(12)
C(74)-C(73)-C(92)	129.7(13)
C(72)-C(73)-C(92)	122.7(13)
C(74)-C(73)-Fe(2)	70.7(8)
C(72)-C(73)-Fe(2)	71.3(9)
C(92)-C(73)-Fe(2)	129.1(11)
C(75)-C(74)-C(73)	108.4(11)

C(75)-C(74)-C(100)	125.3(14)
C(73)-C(74)-C(100)	126.1(14)
C(75)-C(74)-Fe(2)	71.6(8)
C(73)-C(74)-Fe(2)	68.0(8)
C(100)-C(74)-Fe(2)	129.6(10)
C(74)-C(75)-C(71)	108.8(13)
C(74)-C(75)-C(108)	125.3(13)
C(71)-C(75)-C(108)	125.7(14)
C(74)-C(75)-Fe(2)	68.6(8)
C(71)-C(75)-Fe(2)	68.6(8)
C(108)-C(75)-Fe(2)	133.0(13)
C(77)-C(76)-C(81)	117.3(12)
C(77)-C(76)-C(71)	122.5(13)
C(81)-C(76)-C(71)	120.2(13)
C(78)-C(77)-C(76)	121.4(14)
C(77)-C(78)-C(79)	118.3(15)
C(77)-C(78)-C(82)	119.7(15)
C(79)-C(78)-C(82)	122.1(15)
C(80)-C(79)-C(78)	124.0(16)
C(79)-C(80)-C(81)	116.2(15)
C(79)-C(80)-C(83)	124.9(15)
C(81)-C(80)-C(83)	118.9(15)
C(80)-C(81)-C(76)	122.8(14)
C(85)-C(84)-C(89)	121.0(15)
C(85)-C(84)-C(72)	121.2(16)
C(89)-C(84)-C(72)	117.8(13)
C(84)-C(85)-C(86)	121.5(17)
C(87)-C(86)-C(85)	114.3(17)
C(87)-C(86)-C(90)	125.9(19)
C(85)-C(86)-C(90)	120(2)
C(88)-C(87)-C(86)	126.1(17)
C(87)-C(88)-C(89)	116.1(18)
C(87)-C(88)-C(91)	120.8(17)
C(89)-C(88)-C(91)	123.0(18)
C(84)-C(89)-C(88)	120.8(17)
C(97)-C(92)-C(93)	118.8(14)

C(97)-C(92)-C(73)	119.0(15)
C(93)-C(92)-C(73)	122.1(14)
C(92)-C(93)-C(94)	120.3(15)
C(95)-C(94)-C(93)	118.9(17)
C(95)-C(94)-C(98)	122.1(16)
C(93)-C(94)-C(98)	118.8(16)
C(94)-C(95)-C(96)	122.0(16)
C(95)-C(96)-C(97)	117.5(16)
C(95)-C(96)-C(99)	120.6(15)
C(97)-C(96)-C(99)	121.8(16)
C(92)-C(97)-C(96)	122.1(16)
C(101)-C(100)-C(105)	121.6(14)
C(101)-C(100)-C(74)	122.1(13)
C(105)-C(100)-C(74)	115.9(14)
C(100)-C(101)-C(102)	120.5(14)
C(101)-C(102)-C(103)	116.8(15)
C(101)-C(102)-C(106)	120.5(14)
C(103)-C(102)-C(106)	122.7(13)
C(104)-C(103)-C(102)	123.7(14)
C(105)-C(104)-C(103)	116.8(14)
C(105)-C(104)-C(107)	123.8(15)
C(103)-C(104)-C(107)	119.4(14)
C(100)-C(105)-C(104)	120.4(14)
C(109)-C(108)-C(113)	117.5(15)
C(109)-C(108)-C(75)	123.2(15)
C(113)-C(108)-C(75)	118.9(14)
C(108)-C(109)-C(110)	123.9(15)
C(109)-C(110)-C(111)	117.2(15)
C(109)-C(110)-C(114)	123.6(15)
C(111)-C(110)-C(114)	119.1(15)
C(112)-C(111)-C(110)	120.1(15)
C(113)-C(112)-C(111)	119.4(15)
C(113)-C(112)-C(115)	120.2(16)
C(111)-C(112)-C(115)	120.4(15)
C(112)-C(113)-C(108)	121.7(15)
C(122)-C(121)-C(126)	120.3(14)

C(122)-C(121)-S(1)	118.4(13)
C(126)-C(121)-S(1)	121.3(11)
C(121)-C(122)-C(123)	118.3(16)
C(124)-C(123)-C(122)	123.0(17)
C(123)-C(124)-C(125)	115.0(16)
C(123)-C(124)-C(127)	121.5(17)
C(125)-C(124)-C(127)	123.4(17)
C(126)-C(125)-C(124)	124.8(15)
C(125)-C(126)-C(121)	118.4(14)
C(136)-C(131)-C(132)	119.2(15)
C(136)-C(131)-S(2)	119.4(12)
C(132)-C(131)-S(2)	121.3(12)
C(133)-C(132)-C(131)	118.8(15)
C(132)-C(133)-C(134)	120.3(16)
C(135)-C(134)-C(133)	116.7(18)
C(135)-C(134)-C(137)	128(2)
C(133)-C(134)-C(137)	115(2)
C(134)-C(135)-C(136)	125.2(19)
C(135)-C(136)-C(131)	119.5(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 99323. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	33(1)	34(1)	31(1)	0(1)	5(1)	-4(1)
Fe(2)	35(2)	40(2)	36(1)	1(1)	7(1)	1(1)
S(1)	106(4)	46(3)	66(3)	-12(2)	30(3)	-9(3)
S(2)	76(3)	53(3)	48(3)	18(2)	14(2)	10(2)
O(1)	55(7)	49(7)	53(6)	7(5)	-2(6)	13(5)
O(2)	54(7)	48(7)	96(8)	6(6)	-11(7)	-13(6)
O(3)	61(7)	51(7)	141(10)	-14(7)	25(7)	-4(6)
O(4)	290(20)	74(10)	121(12)	-32(9)	127(14)	-21(12)
O(5)	108(10)	31(6)	107(9)	-7(6)	2(8)	11(6)
O(6)	157(13)	78(9)	41(7)	37(6)	27(8)	26(9)
O(7)	87(9)	69(8)	87(8)	6(7)	19(7)	-19(7)
O(8)	89(8)	63(7)	62(6)	22(5)	30(6)	50(6)
N(1)	50(8)	23(7)	51(8)	1(6)	23(7)	14(6)
N(2)	57(10)	49(9)	64(10)	9(8)	6(9)	-3(7)
C(1)	38(9)	51(11)	44(9)	11(10)	-5(7)	14(9)
C(2)	52(11)	51(12)	57(12)	-26(9)	18(10)	-14(9)
C(3)	34(9)	52(11)	44(9)	-1(9)	14(7)	-12(8)
C(4)	25(10)	66(12)	42(9)	27(8)	9(7)	-5(8)
C(5)	41(10)	32(10)	45(9)	-1(8)	10(8)	4(8)
C(6)	42(11)	20(9)	71(12)	-12(9)	23(10)	6(8)
C(7)	31(9)	31(9)	40(9)	12(7)	8(8)	-3(7)
C(8)	32(9)	34(9)	18(7)	12(7)	1(6)	-23(7)
C(11)	32(10)	23(9)	33(9)	2(7)	-4(8)	3(7)
C(12)	50(11)	47(11)	14(7)	-5(7)	11(7)	14(9)
C(13)	29(10)	27(9)	38(9)	-6(7)	8(8)	0(7)
C(14)	37(10)	20(8)	37(8)	8(7)	-6(8)	1(7)
C(15)	20(10)	51(11)	22(8)	-9(8)	4(7)	-16(8)
C(16)	23(9)	41(10)	39(9)	6(8)	18(8)	-6(8)
C(17)	22(9)	51(11)	51(10)	19(9)	5(8)	6(8)
C(18)	42(12)	55(13)	58(11)	7(10)	7(10)	-12(9)
C(19)	64(15)	54(13)	61(12)	-6(10)	-14(11)	-14(11)

C(20)	72(15)	47(12)	46(11)	-24(10)	12(11)	-3(10)
C(21)	23(9)	31(9)	50(10)	-3(8)	9(8)	1(7)
C(22)	63(14)	62(14)	114(16)	63(12)	-5(12)	0(11)
C(23)	101(17)	115(17)	44(11)	19(11)	48(12)	-3(14)
C(24)	39(12)	55(12)	42(10)	15(9)	11(9)	18(9)
C(25)	51(12)	34(10)	22(8)	4(7)	16(8)	-4(9)
C(26)	49(12)	40(10)	34(10)	-4(8)	-5(9)	18(8)
C(27)	48(13)	59(12)	40(10)	-31(9)	18(10)	15(10)
C(28)	49(12)	56(12)	33(9)	-5(9)	18(9)	-27(10)
C(29)	40(11)	26(9)	38(9)	-1(7)	-3(8)	-13(7)
C(30)	65(13)	58(12)	52(10)	9(9)	15(9)	30(10)
C(31)	46(11)	71(12)	34(9)	4(9)	-11(9)	7(10)
C(32)	38(11)	29(9)	30(9)	1(7)	7(8)	7(8)
C(33)	48(12)	39(11)	53(10)	-20(9)	4(9)	9(9)
C(34)	47(11)	20(9)	47(10)	-3(7)	15(8)	-12(8)
C(35)	59(13)	29(10)	43(10)	25(8)	18(9)	17(9)
C(36)	52(12)	44(11)	36(9)	-4(8)	-16(8)	-5(9)
C(37)	17(9)	33(9)	40(9)	15(7)	1(7)	-1(7)
C(38)	77(13)	71(13)	44(10)	7(9)	-2(9)	-7(10)
C(39)	52(13)	55(11)	70(11)	1(9)	4(10)	25(9)
C(40)	33(9)	20(8)	30(7)	11(7)	13(7)	-1(7)
C(41)	53(11)	32(9)	28(8)	-8(7)	15(8)	3(8)
C(42)	39(11)	50(10)	39(10)	1(8)	10(8)	-9(8)
C(43)	47(10)	56(11)	34(8)	-1(9)	-4(8)	0(9)
C(44)	61(12)	35(9)	40(9)	-1(7)	11(9)	12(8)
C(45)	39(9)	28(8)	29(8)	-14(6)	-4(7)	-4(7)
C(46)	85(14)	74(13)	70(12)	3(10)	30(11)	12(11)
C(47)	45(10)	75(11)	40(9)	-33(8)	1(8)	-18(9)
C(48)	36(12)	40(11)	48(10)	-9(9)	5(9)	14(9)
C(49)	42(12)	27(10)	63(11)	-1(9)	6(9)	-16(8)
C(50)	37(12)	50(13)	41(10)	11(9)	-7(9)	-1(10)
C(51)	57(14)	39(11)	64(12)	-23(9)	-5(11)	42(10)
C(52)	53(14)	30(11)	64(12)	-2(9)	-3(10)	-5(9)
C(53)	28(10)	33(9)	42(9)	-2(8)	2(8)	-20(8)
C(54)	64(13)	62(12)	50(10)	-27(9)	33(10)	13(10)
C(55)	80(15)	54(13)	100(15)	-22(11)	18(13)	-22(12)

C(61)	48(12)	61(13)	51(11)	-2(10)	-12(9)	3(10)
C(62)	50(11)	63(13)	49(10)	-5(9)	3(8)	3(9)
C(63)	31(10)	59(12)	54(11)	25(10)	-13(8)	10(8)
C(64)	35(11)	61(12)	43(10)	2(9)	-8(9)	12(9)
C(65)	44(11)	86(15)	55(10)	-32(12)	31(9)	-12(11)
C(66)	33(10)	47(11)	70(13)	16(9)	12(10)	3(8)
C(67)	28(9)	36(9)	46(10)	-18(8)	15(8)	1(7)
C(68)	33(10)	40(10)	37(9)	-17(8)	6(7)	-14(7)
C(71)	10(9)	42(10)	32(9)	8(7)	0(7)	3(7)
C(72)	30(10)	31(10)	52(11)	17(8)	20(9)	-2(7)
C(73)	36(11)	25(9)	40(10)	-5(7)	13(9)	-3(8)
C(74)	31(9)	40(9)	34(8)	7(9)	3(7)	-17(8)
C(75)	51(12)	35(10)	28(9)	-2(8)	-2(9)	18(8)
C(76)	41(11)	18(8)	21(8)	-3(6)	19(8)	-9(7)
C(77)	31(11)	73(12)	31(9)	3(9)	6(8)	20(9)
C(78)	39(11)	64(12)	27(9)	-3(9)	3(9)	9(9)
C(79)	54(13)	58(12)	29(9)	12(8)	21(9)	-11(10)
C(80)	57(13)	50(11)	36(10)	6(8)	25(10)	13(9)
C(81)	25(10)	36(10)	41(9)	5(8)	-8(8)	2(8)
C(82)	114(18)	72(14)	45(11)	1(10)	27(12)	-17(12)
C(83)	65(14)	75(14)	77(13)	-32(11)	-2(11)	40(11)
C(84)	47(12)	19(9)	47(10)	3(8)	-12(9)	10(8)
C(85)	50(12)	70(13)	32(9)	17(9)	-2(9)	-20(10)
C(86)	84(17)	47(13)	68(13)	-6(11)	-18(12)	-5(12)
C(87)	62(14)	81(14)	46(11)	30(10)	34(10)	-22(12)
C(88)	34(11)	74(13)	35(10)	5(9)	-15(9)	-8(9)
C(89)	57(12)	54(11)	33(9)	18(8)	21(9)	-5(9)
C(90)	99(18)	77(17)	140(20)	30(15)	8(15)	6(14)
C(91)	105(18)	98(16)	65(13)	-15(12)	31(13)	-45(14)
C(92)	30(11)	36(10)	16(8)	-1(7)	1(8)	-7(8)
C(93)	79(14)	37(11)	26(8)	-2(8)	22(9)	1(9)
C(94)	61(14)	35(11)	61(12)	-2(9)	20(10)	-9(10)
C(95)	76(15)	34(10)	57(11)	1(9)	37(11)	-6(10)
C(96)	39(12)	44(11)	55(11)	-8(9)	14(9)	-1(9)
C(97)	49(13)	58(13)	54(11)	-2(9)	19(10)	21(10)
C(98)	75(16)	60(13)	86(14)	-1(11)	28(12)	11(11)

C(99)	79(15)	38(11)	160(20)	-3(12)	77(14)	-14(11)
C(100)	30(9)	45(10)	34(8)	-21(9)	-5(7)	3(8)
C(101)	30(10)	34(9)	60(11)	0(8)	6(8)	-6(7)
C(102)	49(11)	49(10)	22(8)	1(7)	15(8)	8(8)
C(103)	59(12)	35(10)	36(9)	-4(7)	10(9)	4(8)
C(104)	46(10)	27(9)	49(10)	-10(8)	-1(8)	-5(8)
C(105)	44(10)	39(10)	44(9)	2(8)	25(8)	0(8)
C(106)	101(14)	56(11)	31(8)	14(8)	34(9)	-4(10)
C(107)	61(12)	74(12)	51(10)	16(9)	-2(9)	-8(9)
C(108)	40(11)	54(12)	23(9)	-5(8)	6(8)	-10(9)
C(109)	30(10)	56(12)	20(8)	6(8)	9(7)	-2(8)
C(110)	57(12)	41(11)	34(9)	-6(8)	15(9)	-1(9)
C(111)	72(14)	33(10)	38(10)	3(8)	17(10)	4(9)
C(112)	42(11)	61(13)	39(9)	14(9)	28(8)	31(10)
C(113)	70(13)	42(10)	11(7)	-11(7)	6(8)	4(9)
C(114)	88(14)	24(9)	97(14)	-6(9)	4(11)	-15(9)
C(115)	64(14)	45(11)	86(13)	34(9)	36(11)	25(9)
C(121)	64(11)	36(9)	30(8)	-4(7)	1(8)	-11(8)
C(122)	47(10)	63(12)	54(10)	5(9)	4(8)	27(9)
C(123)	88(15)	42(12)	71(14)	-10(10)	-11(12)	-8(10)
C(124)	105(16)	65(13)	28(9)	11(9)	17(10)	2(11)
C(125)	88(12)	45(10)	46(9)	-5(9)	28(8)	3(10)
C(126)	108(15)	45(11)	32(9)	5(8)	24(10)	32(10)
C(127)	180(20)	50(13)	135(18)	32(12)	21(16)	-27(13)
C(131)	37(9)	48(10)	52(9)	13(8)	10(7)	-6(7)
C(132)	62(12)	64(13)	42(9)	5(9)	24(9)	2(9)
C(133)	68(12)	72(13)	58(11)	-32(10)	14(10)	2(10)
C(134)	140(20)	71(17)	78(14)	-24(13)	4(14)	-7(14)
C(135)	170(20)	53(13)	46(11)	-2(11)	-16(12)	-41(14)
C(136)	50(12)	98(15)	47(10)	2(10)	5(9)	-14(10)
C(137)	340(40)	65(15)	84(16)	-31(13)	-17(19)	42(18)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 99323.

	x	y	z	U(eq)
H(11)	4470	2971	3469	81
H(12)	6278	2528	2380	105
H(1)	4451	4347	3941	56
H(2)	4331	5894	3715	63
H(3)	4034	6481	2591	51
H(4)	3662	5832	1067	53
H(5)	3740	4202	558	47
H(6)	3900	3094	1606	52
H(17)	2941	2454	2474	50
H(19)	1904	1560	3913	77
H(21)	1101	3793	2801	41
H(22A)	3015	835	3823	125
H(22B)	3557	1341	3400	125
H(22C)	2931	650	2996	125
H(23A)	939	3284	4186	123
H(23B)	728	2230	4057	123
H(23C)	342	2977	3492	123
H(25)	1047	6118	2108	41
H(27)	1712	6770	4183	57
H(29)	2784	4814	3327	44
H(30A)	788	7763	3358	87
H(30B)	193	6949	3188	87
H(30C)	491	7429	2560	87
H(31A)	3268	5232	4541	80
H(31B)	2587	5424	4919	80
H(31C)	3093	6250	4753	80
H(33)	2689	6762	1801	57
H(35)	1335	8605	638	51
H(37)	904	5944	316	37
H(38A)	2668	8990	1337	100

H(38B)	2951	8342	2007	100
H(38C)	2191	8912	1937	100
H(39A)	-113	7377	-26	91
H(39B)	358	7216	-622	91
H(39C)	335	8204	-279	91
H(41)	2754	5320	-29	44
H(43)	1373	4754	-1923	57
H(45)	902	3736	-136	41
H(46A)	3016	5247	-1545	111
H(46B)	2931	6124	-1078	111
H(46C)	2364	5970	-1823	111
H(47A)	0	3563	-1242	82
H(47B)	497	3170	-1759	82
H(47C)	103	4144	-1913	82
H(49)	2900	2756	478	54
H(51)	2010	270	394	68
H(53)	1188	2255	1449	42
H(54A)	2758	947	-554	84
H(54B)	3275	522	145	84
H(54C)	3442	1524	-105	84
H(55A)	702	154	784	118
H(55B)	548	938	1308	118
H(55C)	1187	194	1577	118
H(61)	5615	3636	1106	68
H(62)	5619	5222	938	66
H(63)	5847	6182	1912	62
H(64)	6158	6164	3513	58
H(65)	6228	4798	4350	70
H(66)	6167	3343	3662	60
H(77)	7192	4265	1641	54
H(79)	8311	2328	845	54
H(81)	8964	2991	2885	44
H(82A)	6754	2976	382	113
H(82B)	7424	3366	56	113
H(82C)	6927	4045	410	113
H(83A)	9402	1569	1553	112

H(83B)	9302	1415	2345	112
H(83C)	9856	2191	2181	112
H(85)	7165	6681	2577	63
H(87)	8231	7474	1048	71
H(89)	8885	5205	2182	55
H(90A)	7319	8603	1544	162
H(90B)	6808	8132	2016	162
H(90C)	6664	7918	1188	162
H(91A)	9106	6526	674	131
H(91B)	9343	5577	1066	131
H(91C)	9740	6502	1389	131
H(93)	7156	6359	4588	55
H(95)	8035	8882	4547	62
H(97)	8879	6776	3635	63
H(98A)	7165	8388	5411	108
H(98B)	6650	7523	5139	108
H(98C)	6570	8430	4671	108
H(99A)	8896	9181	3709	126
H(99B)	9308	8329	3445	126
H(99C)	9542	8652	4252	126
H(101)	7166	3668	4916	50
H(103)	8359	4195	6865	52
H(105)	8941	5334	5182	48
H(10A)	6754	3031	5856	89
H(10B)	6808	3763	6477	89
H(10C)	7360	2904	6582	89
H(10D)	9805	5430	6342	97
H(10E)	9671	4748	6947	97
H(10F)	9277	5727	6862	97
H(109)	7224	2417	3200	42
H(111)	8575	481	4288	57
H(113)	9051	3145	4642	50
H(11A)	7011	305	3677	108
H(11B)	7565	128	3155	108
H(11C)	6894	845	2944	108
H(11D)	9512	1168	5443	93

H(11E)	9891	2093	5259	93
H(11F)	9960	1186	4820	93
H(122)	5509	9941	156	67
H(123)	5141	8475	440	86
H(125)	4181	9554	1920	69
H(126)	4425	10989	1604	72
H(27D)	4813	7458	1383	184
H(27E)	3954	7680	1036	184
H(27F)	4281	7880	1857	184
H(132)	5477	1541	3393	65
H(133)	5545	84	2923	79
H(135)	4736	-994	4489	115
H(136)	4763	398	5027	79
H(37D)	4948	-2049	3554	256
H(37E)	5703	-1712	3342	256
H(37F)	4909	-1534	2819	256

Table 6. Torsion angles [°] for 99323.

O(1)-N(1)-C(1)-C(2)	174.4(13)
C(8)-N(1)-C(1)-C(2)	0(2)
N(1)-C(1)-C(2)-C(3)	0(2)
C(1)-C(2)-C(3)-C(7)	2(2)
C(13)-Fe(1)-C(4)-C(7)	116.0(9)
C(14)-Fe(1)-C(4)-C(7)	159.7(9)
C(6)-Fe(1)-C(4)-C(7)	-79.0(10)
C(5)-Fe(1)-C(4)-C(7)	-116.2(13)
C(11)-Fe(1)-C(4)-C(7)	65(4)
C(15)-Fe(1)-C(4)-C(7)	-169.1(10)
C(8)-Fe(1)-C(4)-C(7)	-37.3(8)
C(12)-Fe(1)-C(4)-C(7)	79.6(11)
C(13)-Fe(1)-C(4)-C(5)	-127.8(8)
C(14)-Fe(1)-C(4)-C(5)	-84.1(9)
C(6)-Fe(1)-C(4)-C(5)	37.2(8)
C(7)-Fe(1)-C(4)-C(5)	116.2(13)
C(11)-Fe(1)-C(4)-C(5)	-178(3)
C(15)-Fe(1)-C(4)-C(5)	-52.9(14)
C(8)-Fe(1)-C(4)-C(5)	78.9(9)
C(12)-Fe(1)-C(4)-C(5)	-164.2(8)
C(7)-C(4)-C(5)-C(6)	4.2(17)
Fe(1)-C(4)-C(5)-C(6)	-58.1(11)
C(7)-C(4)-C(5)-Fe(1)	62.3(11)
C(4)-Fe(1)-C(5)-C(6)	119.7(12)
C(13)-Fe(1)-C(5)-C(6)	-169.2(9)
C(14)-Fe(1)-C(5)-C(6)	-130.6(9)
C(7)-Fe(1)-C(5)-C(6)	80.9(9)
C(11)-Fe(1)-C(5)-C(6)	-60.8(13)
C(15)-Fe(1)-C(5)-C(6)	-89.4(10)
C(8)-Fe(1)-C(5)-C(6)	38.0(8)
C(12)-Fe(1)-C(5)-C(6)	-174(2)
C(13)-Fe(1)-C(5)-C(4)	71.1(10)
C(14)-Fe(1)-C(5)-C(4)	109.7(9)
C(6)-Fe(1)-C(5)-C(4)	-119.7(12)

C(7)-Fe(1)-C(5)-C(4)	-38.8(8)
C(11)-Fe(1)-C(5)-C(4)	179.5(10)
C(15)-Fe(1)-C(5)-C(4)	150.9(8)
C(8)-Fe(1)-C(5)-C(4)	-81.7(9)
C(12)-Fe(1)-C(5)-C(4)	66(3)
C(4)-C(5)-C(6)-C(8)	-6.1(17)
Fe(1)-C(5)-C(6)-C(8)	-63.3(11)
C(4)-C(5)-C(6)-Fe(1)	57.2(10)
C(4)-Fe(1)-C(6)-C(8)	78.0(9)
C(13)-Fe(1)-C(6)-C(8)	152(2)
C(14)-Fe(1)-C(6)-C(8)	-178.1(8)
C(7)-Fe(1)-C(6)-C(8)	34.6(8)
C(5)-Fe(1)-C(6)-C(8)	116.3(12)
C(11)-Fe(1)-C(6)-C(8)	-95.7(9)
C(15)-Fe(1)-C(6)-C(8)	-138.0(8)
C(12)-Fe(1)-C(6)-C(8)	-66.4(15)
C(4)-Fe(1)-C(6)-C(5)	-38.3(9)
C(13)-Fe(1)-C(6)-C(5)	35(3)
C(14)-Fe(1)-C(6)-C(5)	65.6(10)
C(7)-Fe(1)-C(6)-C(5)	-81.7(9)
C(11)-Fe(1)-C(6)-C(5)	148.0(8)
C(15)-Fe(1)-C(6)-C(5)	105.7(9)
C(8)-Fe(1)-C(6)-C(5)	-116.3(12)
C(12)-Fe(1)-C(6)-C(5)	177.3(11)
C(5)-C(4)-C(7)-C(8)	-0.8(18)
Fe(1)-C(4)-C(7)-C(8)	61.0(11)
C(5)-C(4)-C(7)-C(3)	170.9(16)
Fe(1)-C(4)-C(7)-C(3)	-127.3(18)
C(5)-C(4)-C(7)-Fe(1)	-61.8(10)
C(2)-C(3)-C(7)-C(8)	-4(2)
C(2)-C(3)-C(7)-C(4)	-175.0(17)
C(2)-C(3)-C(7)-Fe(1)	85.0(18)
C(4)-Fe(1)-C(7)-C(8)	-118.7(13)
C(13)-Fe(1)-C(7)-C(8)	161.2(8)
C(14)-Fe(1)-C(7)-C(8)	-156.6(10)
C(6)-Fe(1)-C(7)-C(8)	-34.1(9)

C(5)-Fe(1)-C(7)-C(8)	-78.3(9)
C(11)-Fe(1)-C(7)-C(8)	73.7(11)
C(15)-Fe(1)-C(7)-C(8)	18(4)
C(12)-Fe(1)-C(7)-C(8)	115.5(9)
C(13)-Fe(1)-C(7)-C(4)	-80.2(10)
C(14)-Fe(1)-C(7)-C(4)	-38.0(16)
C(6)-Fe(1)-C(7)-C(4)	84.6(10)
C(5)-Fe(1)-C(7)-C(4)	40.4(9)
C(11)-Fe(1)-C(7)-C(4)	-167.6(9)
C(15)-Fe(1)-C(7)-C(4)	137(4)
C(8)-Fe(1)-C(7)-C(4)	118.7(13)
C(12)-Fe(1)-C(7)-C(4)	-125.9(10)
C(4)-Fe(1)-C(7)-C(3)	130.6(18)
C(13)-Fe(1)-C(7)-C(3)	50.4(15)
C(14)-Fe(1)-C(7)-C(3)	92.7(17)
C(6)-Fe(1)-C(7)-C(3)	-144.8(15)
C(5)-Fe(1)-C(7)-C(3)	171.0(15)
C(11)-Fe(1)-C(7)-C(3)	-37.0(17)
C(15)-Fe(1)-C(7)-C(3)	-92(4)
C(8)-Fe(1)-C(7)-C(3)	-110.7(17)
C(12)-Fe(1)-C(7)-C(3)	4.7(15)
C(1)-N(1)-C(8)-C(6)	178.5(15)
O(1)-N(1)-C(8)-C(6)	4(2)
C(1)-N(1)-C(8)-C(7)	-2(2)
O(1)-N(1)-C(8)-C(7)	-176.9(12)
C(1)-N(1)-C(8)-Fe(1)	-88.5(16)
O(1)-N(1)-C(8)-Fe(1)	97.0(14)
C(5)-C(6)-C(8)-N(1)	-174.9(14)
Fe(1)-C(6)-C(8)-N(1)	123.2(16)
C(5)-C(6)-C(8)-C(7)	5.8(18)
Fe(1)-C(6)-C(8)-C(7)	-56.0(12)
C(5)-C(6)-C(8)-Fe(1)	61.8(10)
C(4)-C(7)-C(8)-N(1)	177.5(12)
C(3)-C(7)-C(8)-N(1)	4(2)
Fe(1)-C(7)-C(8)-N(1)	-123.4(14)
C(4)-C(7)-C(8)-C(6)	-3.2(19)

C(3)-C(7)-C(8)-C(6)	-176.5(13)
Fe(1)-C(7)-C(8)-C(6)	55.9(11)
C(4)-C(7)-C(8)-Fe(1)	-59.1(11)
C(3)-C(7)-C(8)-Fe(1)	127.6(13)
C(4)-Fe(1)-C(8)-N(1)	150.4(14)
C(13)-Fe(1)-C(8)-N(1)	72.5(17)
C(14)-Fe(1)-C(8)-N(1)	-118(2)
C(6)-Fe(1)-C(8)-N(1)	-123.6(16)
C(7)-Fe(1)-C(8)-N(1)	112.3(16)
C(5)-Fe(1)-C(8)-N(1)	-163.5(14)
C(11)-Fe(1)-C(8)-N(1)	-19.2(14)
C(15)-Fe(1)-C(8)-N(1)	-63.9(14)
C(12)-Fe(1)-C(8)-N(1)	24.8(14)
C(4)-Fe(1)-C(8)-C(6)	-86.0(10)
C(13)-Fe(1)-C(8)-C(6)	-163.9(12)
C(14)-Fe(1)-C(8)-C(6)	6(2)
C(7)-Fe(1)-C(8)-C(6)	-124.1(13)
C(5)-Fe(1)-C(8)-C(6)	-39.9(9)
C(11)-Fe(1)-C(8)-C(6)	104.4(9)
C(15)-Fe(1)-C(8)-C(6)	59.7(11)
C(12)-Fe(1)-C(8)-C(6)	148.4(9)
C(4)-Fe(1)-C(8)-C(7)	38.1(9)
C(13)-Fe(1)-C(8)-C(7)	-39.8(16)
C(14)-Fe(1)-C(8)-C(7)	129.9(19)
C(6)-Fe(1)-C(8)-C(7)	124.1(13)
C(5)-Fe(1)-C(8)-C(7)	84.2(9)
C(11)-Fe(1)-C(8)-C(7)	-131.5(9)
C(15)-Fe(1)-C(8)-C(7)	-176.2(9)
C(12)-Fe(1)-C(8)-C(7)	-87.5(10)
C(4)-Fe(1)-C(11)-C(12)	17(4)
C(13)-Fe(1)-C(11)-C(12)	-36.2(8)
C(14)-Fe(1)-C(11)-C(12)	-81.3(9)
C(6)-Fe(1)-C(11)-C(12)	158.7(8)
C(7)-Fe(1)-C(11)-C(12)	73.2(11)
C(5)-Fe(1)-C(11)-C(12)	-161.1(9)
C(15)-Fe(1)-C(11)-C(12)	-118.2(12)

C(8)-Fe(1)-C(11)-C(12)	115.4(9)
C(4)-Fe(1)-C(11)-C(15)	135(3)
C(13)-Fe(1)-C(11)-C(15)	82.0(9)
C(14)-Fe(1)-C(11)-C(15)	36.9(8)
C(6)-Fe(1)-C(11)-C(15)	-83.0(10)
C(7)-Fe(1)-C(11)-C(15)	-168.6(9)
C(5)-Fe(1)-C(11)-C(15)	-42.9(14)
C(8)-Fe(1)-C(11)-C(15)	-126.4(9)
C(12)-Fe(1)-C(11)-C(15)	118.2(12)
C(4)-Fe(1)-C(11)-C(16)	-107(3)
C(13)-Fe(1)-C(11)-C(16)	-159.8(15)
C(14)-Fe(1)-C(11)-C(16)	155.1(15)
C(6)-Fe(1)-C(11)-C(16)	35.1(16)
C(7)-Fe(1)-C(11)-C(16)	-50.4(17)
C(5)-Fe(1)-C(11)-C(16)	75.3(17)
C(15)-Fe(1)-C(11)-C(16)	118.2(17)
C(8)-Fe(1)-C(11)-C(16)	-8.2(15)
C(12)-Fe(1)-C(11)-C(16)	-123.6(18)
C(15)-C(11)-C(12)-C(13)	-4.8(19)
C(16)-C(11)-C(12)-C(13)	-175.3(14)
Fe(1)-C(11)-C(12)-C(13)	55.5(11)
C(15)-C(11)-C(12)-C(24)	174.5(15)
C(16)-C(11)-C(12)-C(24)	4(3)
Fe(1)-C(11)-C(12)-C(24)	-125.2(17)
C(15)-C(11)-C(12)-Fe(1)	-60.3(11)
C(16)-C(11)-C(12)-Fe(1)	129.2(16)
C(4)-Fe(1)-C(12)-C(11)	-176.3(9)
C(13)-Fe(1)-C(12)-C(11)	122.6(12)
C(14)-Fe(1)-C(12)-C(11)	82.3(9)
C(6)-Fe(1)-C(12)-C(11)	-43.1(16)
C(7)-Fe(1)-C(12)-C(11)	-131.8(9)
C(5)-Fe(1)-C(12)-C(11)	129(2)
C(15)-Fe(1)-C(12)-C(11)	38.5(8)
C(8)-Fe(1)-C(12)-C(11)	-87.5(9)
C(4)-Fe(1)-C(12)-C(13)	61.1(10)
C(14)-Fe(1)-C(12)-C(13)	-40.3(8)

C(6)-Fe(1)-C(12)-C(13)	-165.8(11)
C(7)-Fe(1)-C(12)-C(13)	105.6(8)
C(5)-Fe(1)-C(12)-C(13)	6(3)
C(11)-Fe(1)-C(12)-C(13)	-122.6(12)
C(15)-Fe(1)-C(12)-C(13)	-84.1(8)
C(8)-Fe(1)-C(12)-C(13)	149.9(8)
C(4)-Fe(1)-C(12)-C(24)	-53.6(15)
C(13)-Fe(1)-C(12)-C(24)	-114.7(17)
C(14)-Fe(1)-C(12)-C(24)	-155.0(15)
C(6)-Fe(1)-C(12)-C(24)	79.5(19)
C(7)-Fe(1)-C(12)-C(24)	-9.1(15)
C(5)-Fe(1)-C(12)-C(24)	-108(3)
C(11)-Fe(1)-C(12)-C(24)	122.7(17)
C(15)-Fe(1)-C(12)-C(24)	161.2(15)
C(8)-Fe(1)-C(12)-C(24)	35.2(16)
C(11)-C(12)-C(13)-C(14)	4.3(18)
C(24)-C(12)-C(13)-C(14)	-175.1(14)
Fe(1)-C(12)-C(13)-C(14)	61.4(10)
C(11)-C(12)-C(13)-C(32)	172.7(14)
C(24)-C(12)-C(13)-C(32)	-7(2)
Fe(1)-C(12)-C(13)-C(32)	-130.2(15)
C(11)-C(12)-C(13)-Fe(1)	-57.1(11)
C(24)-C(12)-C(13)-Fe(1)	123.5(15)
C(4)-Fe(1)-C(13)-C(12)	-137.2(9)
C(14)-Fe(1)-C(13)-C(12)	115.9(12)
C(6)-Fe(1)-C(13)-C(12)	154(2)
C(7)-Fe(1)-C(13)-C(12)	-95.8(9)
C(5)-Fe(1)-C(13)-C(12)	-178.2(8)
C(11)-Fe(1)-C(13)-C(12)	34.8(8)
C(15)-Fe(1)-C(13)-C(12)	78.4(9)
C(8)-Fe(1)-C(13)-C(12)	-68.3(15)
C(4)-Fe(1)-C(13)-C(14)	106.9(9)
C(6)-Fe(1)-C(13)-C(14)	38(3)
C(7)-Fe(1)-C(13)-C(14)	148.3(8)
C(5)-Fe(1)-C(13)-C(14)	65.9(10)
C(11)-Fe(1)-C(13)-C(14)	-81.0(9)

C(15)-Fe(1)-C(13)-C(14)	-37.4(8)
C(8)-Fe(1)-C(13)-C(14)	175.8(11)
C(12)-Fe(1)-C(13)-C(14)	-115.9(12)
C(4)-Fe(1)-C(13)-C(32)	-14.5(15)
C(14)-Fe(1)-C(13)-C(32)	-121.4(17)
C(6)-Fe(1)-C(13)-C(32)	-84(3)
C(7)-Fe(1)-C(13)-C(32)	26.9(16)
C(5)-Fe(1)-C(13)-C(32)	-55.6(16)
C(11)-Fe(1)-C(13)-C(32)	157.5(15)
C(15)-Fe(1)-C(13)-C(32)	-158.9(16)
C(8)-Fe(1)-C(13)-C(32)	54(2)
C(12)-Fe(1)-C(13)-C(32)	122.7(17)
C(12)-C(13)-C(14)-C(15)	-2.1(16)
C(32)-C(13)-C(14)-C(15)	-170.4(15)
Fe(1)-C(13)-C(14)-C(15)	61.0(10)
C(12)-C(13)-C(14)-C(40)	169.3(13)
C(32)-C(13)-C(14)-C(40)	1(2)
Fe(1)-C(13)-C(14)-C(40)	-127.6(13)
C(12)-C(13)-C(14)-Fe(1)	-63.1(10)
C(32)-C(13)-C(14)-Fe(1)	128.6(16)
C(4)-Fe(1)-C(14)-C(15)	153.2(9)
C(13)-Fe(1)-C(14)-C(15)	-118.8(12)
C(6)-Fe(1)-C(14)-C(15)	72.5(10)
C(7)-Fe(1)-C(14)-C(15)	178.8(11)
C(5)-Fe(1)-C(14)-C(15)	110.1(9)
C(11)-Fe(1)-C(14)-C(15)	-37.1(8)
C(8)-Fe(1)-C(14)-C(15)	68(2)
C(12)-Fe(1)-C(14)-C(15)	-79.4(9)
C(4)-Fe(1)-C(14)-C(13)	-88.0(9)
C(6)-Fe(1)-C(14)-C(13)	-168.7(9)
C(7)-Fe(1)-C(14)-C(13)	-62.5(14)
C(5)-Fe(1)-C(14)-C(13)	-131.1(8)
C(11)-Fe(1)-C(14)-C(13)	81.7(9)
C(15)-Fe(1)-C(14)-C(13)	118.8(12)
C(8)-Fe(1)-C(14)-C(13)	-173.1(17)
C(12)-Fe(1)-C(14)-C(13)	39.3(8)

C(4)-Fe(1)-C(14)-C(40)	26.6(15)
C(13)-Fe(1)-C(14)-C(40)	114.6(17)
C(6)-Fe(1)-C(14)-C(40)	-54.1(16)
C(7)-Fe(1)-C(14)-C(40)	52.1(19)
C(5)-Fe(1)-C(14)-C(40)	-16.5(15)
C(11)-Fe(1)-C(14)-C(40)	-163.8(15)
C(15)-Fe(1)-C(14)-C(40)	-126.6(17)
C(8)-Fe(1)-C(14)-C(40)	-59(3)
C(12)-Fe(1)-C(14)-C(40)	153.9(15)
C(13)-C(14)-C(15)-C(11)	-0.8(16)
C(40)-C(14)-C(15)-C(11)	-171.4(14)
Fe(1)-C(14)-C(15)-C(11)	58.4(10)
C(13)-C(14)-C(15)-C(48)	175.6(15)
C(40)-C(14)-C(15)-C(48)	5(3)
Fe(1)-C(14)-C(15)-C(48)	-125.1(16)
C(13)-C(14)-C(15)-Fe(1)	-59.2(10)
C(40)-C(14)-C(15)-Fe(1)	130.2(16)
C(12)-C(11)-C(15)-C(14)	3.5(18)
C(16)-C(11)-C(15)-C(14)	174.3(14)
Fe(1)-C(11)-C(15)-C(14)	-57.5(10)
C(12)-C(11)-C(15)-C(48)	-173.1(14)
C(16)-C(11)-C(15)-C(48)	-2(2)
Fe(1)-C(11)-C(15)-C(48)	126.0(16)
C(12)-C(11)-C(15)-Fe(1)	61.0(11)
C(16)-C(11)-C(15)-Fe(1)	-128.2(15)
C(4)-Fe(1)-C(15)-C(14)	-47.7(15)
C(13)-Fe(1)-C(15)-C(14)	38.8(8)
C(6)-Fe(1)-C(15)-C(14)	-126.0(9)
C(7)-Fe(1)-C(15)-C(14)	-176(4)
C(5)-Fe(1)-C(15)-C(14)	-83.1(10)
C(11)-Fe(1)-C(15)-C(14)	120.2(13)
C(8)-Fe(1)-C(15)-C(14)	-160.3(9)
C(12)-Fe(1)-C(15)-C(14)	82.9(9)
C(4)-Fe(1)-C(15)-C(11)	-167.9(10)
C(13)-Fe(1)-C(15)-C(11)	-81.5(9)
C(14)-Fe(1)-C(15)-C(11)	-120.2(13)

C(6)-Fe(1)-C(15)-C(11)	113.8(9)
C(7)-Fe(1)-C(15)-C(11)	64(4)
C(5)-Fe(1)-C(15)-C(11)	156.7(8)
C(8)-Fe(1)-C(15)-C(11)	79.4(10)
C(12)-Fe(1)-C(15)-C(11)	-37.3(8)
C(4)-Fe(1)-C(15)-C(48)	73.1(18)
C(13)-Fe(1)-C(15)-C(48)	159.5(16)
C(14)-Fe(1)-C(15)-C(48)	120.7(17)
C(6)-Fe(1)-C(15)-C(48)	-5.3(15)
C(7)-Fe(1)-C(15)-C(48)	-55(4)
C(5)-Fe(1)-C(15)-C(48)	37.7(15)
C(11)-Fe(1)-C(15)-C(48)	-119.0(17)
C(8)-Fe(1)-C(15)-C(48)	-39.6(16)
C(12)-Fe(1)-C(15)-C(48)	-156.3(15)
C(12)-C(11)-C(16)-C(17)	-136.0(17)
C(15)-C(11)-C(16)-C(17)	55(2)
Fe(1)-C(11)-C(16)-C(17)	-38(2)
C(12)-C(11)-C(16)-C(21)	48(2)
C(15)-C(11)-C(16)-C(21)	-121.4(16)
Fe(1)-C(11)-C(16)-C(21)	145.6(12)
C(21)-C(16)-C(17)-C(18)	1(2)
C(11)-C(16)-C(17)-C(18)	-175.4(15)
C(16)-C(17)-C(18)-C(19)	-2(3)
C(16)-C(17)-C(18)-C(22)	179.7(14)
C(17)-C(18)-C(19)-C(20)	1(3)
C(22)-C(18)-C(19)-C(20)	178.9(15)
C(18)-C(19)-C(20)-C(21)	2(3)
C(18)-C(19)-C(20)-C(23)	179.1(16)
C(19)-C(20)-C(21)-C(16)	-3(2)
C(23)-C(20)-C(21)-C(16)	179.5(13)
C(17)-C(16)-C(21)-C(20)	2(2)
C(11)-C(16)-C(21)-C(20)	178.4(14)
C(11)-C(12)-C(24)-C(25)	-129.2(18)
C(13)-C(12)-C(24)-C(25)	50(2)
Fe(1)-C(12)-C(24)-C(25)	136.5(14)
C(11)-C(12)-C(24)-C(29)	46(3)

C(13)-C(12)-C(24)-C(29)	-135.1(15)
Fe(1)-C(12)-C(24)-C(29)	-49(2)
C(29)-C(24)-C(25)-C(26)	1(2)
C(12)-C(24)-C(25)-C(26)	176.2(15)
C(24)-C(25)-C(26)-C(27)	1(3)
C(24)-C(25)-C(26)-C(30)	-179.9(15)
C(25)-C(26)-C(27)-C(28)	-2(3)
C(30)-C(26)-C(27)-C(28)	179.6(15)
C(26)-C(27)-C(28)-C(29)	-1(3)
C(26)-C(27)-C(28)-C(31)	-179.0(15)
C(27)-C(28)-C(29)-C(24)	3(2)
C(31)-C(28)-C(29)-C(24)	-178.2(13)
C(25)-C(24)-C(29)-C(28)	-4(2)
C(12)-C(24)-C(29)-C(28)	-178.6(14)
C(12)-C(13)-C(32)-C(37)	-117.3(17)
C(14)-C(13)-C(32)-C(37)	49(2)
Fe(1)-C(13)-C(32)-C(37)	144.1(13)
C(12)-C(13)-C(32)-C(33)	57(2)
C(14)-C(13)-C(32)-C(33)	-136.7(16)
Fe(1)-C(13)-C(32)-C(33)	-41(2)
C(37)-C(32)-C(33)-C(34)	0(2)
C(13)-C(32)-C(33)-C(34)	-174.1(14)
C(32)-C(33)-C(34)-C(35)	-1(2)
C(32)-C(33)-C(34)-C(38)	178.0(14)
C(33)-C(34)-C(35)-C(36)	1(2)
C(38)-C(34)-C(35)-C(36)	-178.6(15)
C(34)-C(35)-C(36)-C(37)	1(2)
C(34)-C(35)-C(36)-C(39)	178.0(14)
C(33)-C(32)-C(37)-C(36)	1(2)
C(13)-C(32)-C(37)-C(36)	176.0(14)
C(35)-C(36)-C(37)-C(32)	-2(2)
C(39)-C(36)-C(37)-C(32)	-179.1(14)
C(15)-C(14)-C(40)-C(41)	-126.5(17)
C(13)-C(14)-C(40)-C(41)	64(2)
Fe(1)-C(14)-C(40)-C(41)	-26(2)
C(15)-C(14)-C(40)-C(45)	52(2)

C(13)-C(14)-C(40)-C(45)	-117.8(15)
Fe(1)-C(14)-C(40)-C(45)	152.7(11)
C(45)-C(40)-C(41)-C(42)	4(2)
C(14)-C(40)-C(41)-C(42)	-178.3(13)
C(40)-C(41)-C(42)-C(43)	-2(2)
C(40)-C(41)-C(42)-C(46)	-179.1(14)
C(41)-C(42)-C(43)-C(44)	0(2)
C(46)-C(42)-C(43)-C(44)	176.8(15)
C(42)-C(43)-C(44)-C(45)	1(2)
C(42)-C(43)-C(44)-C(47)	179.2(14)
C(43)-C(44)-C(45)-C(40)	0(2)
C(47)-C(44)-C(45)-C(40)	-177.9(12)
C(41)-C(40)-C(45)-C(44)	-3(2)
C(14)-C(40)-C(45)-C(44)	179.1(13)
C(14)-C(15)-C(48)-C(53)	-128.7(16)
C(11)-C(15)-C(48)-C(53)	47(2)
Fe(1)-C(15)-C(48)-C(53)	139.4(13)
C(14)-C(15)-C(48)-C(49)	58(2)
C(11)-C(15)-C(48)-C(49)	-126.3(17)
Fe(1)-C(15)-C(48)-C(49)	-34(2)
C(53)-C(48)-C(49)-C(50)	4(2)
C(15)-C(48)-C(49)-C(50)	177.9(15)
C(48)-C(49)-C(50)-C(51)	-2(2)
C(48)-C(49)-C(50)-C(54)	177.5(14)
C(49)-C(50)-C(51)-C(52)	1(2)
C(54)-C(50)-C(51)-C(52)	-179.0(14)
C(50)-C(51)-C(52)-C(53)	-1(2)
C(50)-C(51)-C(52)-C(55)	-178.1(16)
C(49)-C(48)-C(53)-C(52)	-5(2)
C(15)-C(48)-C(53)-C(52)	-178.4(14)
C(51)-C(52)-C(53)-C(48)	3(2)
C(55)-C(52)-C(53)-C(48)	-179.7(14)
O(2)-N(2)-C(61)-C(62)	175.1(15)
C(68)-N(2)-C(61)-C(62)	5(3)
N(2)-C(61)-C(62)-C(63)	-2(3)
C(61)-C(62)-C(63)-C(67)	2(3)

C(73)-Fe(2)-C(64)-C(67)	129.9(9)
C(65)-Fe(2)-C(64)-C(67)	-117.4(13)
C(74)-Fe(2)-C(64)-C(67)	170.7(8)
C(71)-Fe(2)-C(64)-C(67)	58.1(19)
C(72)-Fe(2)-C(64)-C(67)	88.1(10)
C(66)-Fe(2)-C(64)-C(67)	-81.8(10)
C(75)-Fe(2)-C(64)-C(67)	-163.9(17)
C(68)-Fe(2)-C(64)-C(67)	-39.4(9)
C(73)-Fe(2)-C(64)-C(65)	-112.7(10)
C(74)-Fe(2)-C(64)-C(65)	-71.8(11)
C(71)-Fe(2)-C(64)-C(65)	175.5(13)
C(72)-Fe(2)-C(64)-C(65)	-154.5(9)
C(66)-Fe(2)-C(64)-C(65)	35.7(9)
C(75)-Fe(2)-C(64)-C(65)	-46(2)
C(67)-Fe(2)-C(64)-C(65)	117.4(13)
C(68)-Fe(2)-C(64)-C(65)	78.0(10)
C(67)-C(64)-C(65)-C(66)	1.0(18)
Fe(2)-C(64)-C(65)-C(66)	-60.1(11)
C(67)-C(64)-C(65)-Fe(2)	61.1(11)
C(73)-Fe(2)-C(65)-C(66)	-156.1(9)
C(74)-Fe(2)-C(65)-C(66)	-114.1(10)
C(71)-Fe(2)-C(65)-C(66)	-53(2)
C(72)-Fe(2)-C(65)-C(66)	177.6(12)
C(64)-Fe(2)-C(65)-C(66)	121.3(13)
C(75)-Fe(2)-C(65)-C(66)	-76.1(11)
C(67)-Fe(2)-C(65)-C(66)	83.3(10)
C(68)-Fe(2)-C(65)-C(66)	39.0(9)
C(73)-Fe(2)-C(65)-C(64)	82.6(10)
C(74)-Fe(2)-C(65)-C(64)	124.7(9)
C(71)-Fe(2)-C(65)-C(64)	-174.4(17)
C(72)-Fe(2)-C(65)-C(64)	56.3(17)
C(66)-Fe(2)-C(65)-C(64)	-121.3(13)
C(75)-Fe(2)-C(65)-C(64)	162.7(9)
C(67)-Fe(2)-C(65)-C(64)	-38.0(8)
C(68)-Fe(2)-C(65)-C(64)	-82.2(10)
C(64)-C(65)-C(66)-C(68)	-3.4(18)

Fe(2)-C(65)-C(66)-C(68)	-63.0(12)
C(64)-C(65)-C(66)-Fe(2)	59.7(11)
C(73)-Fe(2)-C(66)-C(65)	45.5(17)
C(74)-Fe(2)-C(66)-C(65)	79.8(11)
C(71)-Fe(2)-C(66)-C(65)	161.5(10)
C(72)-Fe(2)-C(66)-C(65)	-175(2)
C(64)-Fe(2)-C(66)-C(65)	-37.3(9)
C(75)-Fe(2)-C(66)-C(65)	121.8(10)
C(67)-Fe(2)-C(66)-C(65)	-80.2(10)
C(68)-Fe(2)-C(66)-C(65)	-115.4(14)
C(73)-Fe(2)-C(66)-C(68)	160.9(11)
C(65)-Fe(2)-C(66)-C(68)	115.4(14)
C(74)-Fe(2)-C(66)-C(68)	-164.8(9)
C(71)-Fe(2)-C(66)-C(68)	-83.1(11)
C(72)-Fe(2)-C(66)-C(68)	-60(3)
C(64)-Fe(2)-C(66)-C(68)	78.1(10)
C(75)-Fe(2)-C(66)-C(68)	-122.8(9)
C(67)-Fe(2)-C(66)-C(68)	35.2(8)
C(65)-C(64)-C(67)-C(63)	169.7(17)
Fe(2)-C(64)-C(67)-C(63)	-131.2(19)
C(65)-C(64)-C(67)-C(68)	1.7(18)
Fe(2)-C(64)-C(67)-C(68)	60.8(11)
C(65)-C(64)-C(67)-Fe(2)	-59.1(10)
C(62)-C(63)-C(67)-C(64)	-171.1(18)
C(62)-C(63)-C(67)-C(68)	-4(2)
C(62)-C(63)-C(67)-Fe(2)	83.3(19)
C(73)-Fe(2)-C(67)-C(64)	-66.9(11)
C(65)-Fe(2)-C(67)-C(64)	39.4(10)
C(74)-Fe(2)-C(67)-C(64)	-25(2)
C(71)-Fe(2)-C(67)-C(64)	-155.9(10)
C(72)-Fe(2)-C(67)-C(64)	-112.0(10)
C(66)-Fe(2)-C(67)-C(64)	82.1(10)
C(75)-Fe(2)-C(67)-C(64)	164.6(16)
C(68)-Fe(2)-C(67)-C(64)	116.2(13)
C(73)-Fe(2)-C(67)-C(63)	67.5(17)
C(65)-Fe(2)-C(67)-C(63)	173.9(17)

C(74)-Fe(2)-C(67)-C(63)	110(2)
C(71)-Fe(2)-C(67)-C(63)	-21.5(17)
C(72)-Fe(2)-C(67)-C(63)	22.4(17)
C(66)-Fe(2)-C(67)-C(63)	-143.4(17)
C(64)-Fe(2)-C(67)-C(63)	134.5(19)
C(75)-Fe(2)-C(67)-C(63)	-61(2)
C(68)-Fe(2)-C(67)-C(63)	-109.3(18)
C(73)-Fe(2)-C(67)-C(68)	176.8(9)
C(65)-Fe(2)-C(67)-C(68)	-76.8(10)
C(74)-Fe(2)-C(67)-C(68)	-141.1(16)
C(71)-Fe(2)-C(67)-C(68)	87.9(10)
C(72)-Fe(2)-C(67)-C(68)	131.7(9)
C(66)-Fe(2)-C(67)-C(68)	-34.1(9)
C(64)-Fe(2)-C(67)-C(68)	-116.2(13)
C(75)-Fe(2)-C(67)-C(68)	48(2)
C(61)-N(2)-C(68)-C(66)	174.4(17)
O(2)-N(2)-C(68)-C(66)	4(2)
C(61)-N(2)-C(68)-C(67)	-7(2)
O(2)-N(2)-C(68)-C(67)	-178.1(13)
C(61)-N(2)-C(68)-Fe(2)	-92.1(18)
O(2)-N(2)-C(68)-Fe(2)	97.3(15)
C(65)-C(66)-C(68)-N(2)	-177.2(16)
Fe(2)-C(66)-C(68)-N(2)	121.6(18)
C(65)-C(66)-C(68)-C(67)	5(2)
Fe(2)-C(66)-C(68)-C(67)	-56.7(12)
C(65)-C(66)-C(68)-Fe(2)	61.2(11)
C(64)-C(67)-C(68)-N(2)	177.5(13)
C(63)-C(67)-C(68)-N(2)	7(2)
Fe(2)-C(67)-C(68)-N(2)	-122.2(14)
C(64)-C(67)-C(68)-C(66)	-4(2)
C(63)-C(67)-C(68)-C(66)	-174.6(13)
Fe(2)-C(67)-C(68)-C(66)	56.3(12)
C(64)-C(67)-C(68)-Fe(2)	-60.3(11)
C(63)-C(67)-C(68)-Fe(2)	129.1(13)
C(73)-Fe(2)-C(68)-N(2)	99(3)
C(65)-Fe(2)-C(68)-N(2)	-165.5(16)

C(74)-Fe(2)-C(68)-N(2)	-95.6(18)
C(71)-Fe(2)-C(68)-N(2)	-5.7(16)
C(72)-Fe(2)-C(68)-N(2)	38.3(17)
C(66)-Fe(2)-C(68)-N(2)	-126.0(19)
C(64)-Fe(2)-C(68)-N(2)	148.9(16)
C(75)-Fe(2)-C(68)-N(2)	-51.1(16)
C(67)-Fe(2)-C(68)-N(2)	110.0(18)
C(73)-Fe(2)-C(68)-C(66)	-135(2)
C(65)-Fe(2)-C(68)-C(66)	-39.5(10)
C(74)-Fe(2)-C(68)-C(66)	30.4(17)
C(71)-Fe(2)-C(68)-C(66)	120.3(10)
C(72)-Fe(2)-C(68)-C(66)	164.3(10)
C(64)-Fe(2)-C(68)-C(66)	-85.1(10)
C(75)-Fe(2)-C(68)-C(66)	74.9(11)
C(67)-Fe(2)-C(68)-C(66)	-124.0(13)
C(73)-Fe(2)-C(68)-C(67)	-11(3)
C(65)-Fe(2)-C(68)-C(67)	84.5(10)
C(74)-Fe(2)-C(68)-C(67)	154.4(11)
C(71)-Fe(2)-C(68)-C(67)	-115.7(9)
C(72)-Fe(2)-C(68)-C(67)	-71.7(11)
C(66)-Fe(2)-C(68)-C(67)	124.0(13)
C(64)-Fe(2)-C(68)-C(67)	38.9(9)
C(75)-Fe(2)-C(68)-C(67)	-161.1(8)
C(73)-Fe(2)-C(71)-C(72)	-37.4(9)
C(65)-Fe(2)-C(71)-C(72)	-147.9(18)
C(74)-Fe(2)-C(71)-C(72)	-81.7(10)
C(66)-Fe(2)-C(71)-C(72)	172.1(9)
C(64)-Fe(2)-C(71)-C(72)	41.6(19)
C(75)-Fe(2)-C(71)-C(72)	-117.6(13)
C(67)-Fe(2)-C(71)-C(72)	83.1(11)
C(68)-Fe(2)-C(71)-C(72)	128.6(9)
C(73)-Fe(2)-C(71)-C(75)	80.3(9)
C(65)-Fe(2)-C(71)-C(75)	-30(2)
C(74)-Fe(2)-C(71)-C(75)	35.9(9)
C(72)-Fe(2)-C(71)-C(75)	117.6(13)
C(66)-Fe(2)-C(71)-C(75)	-70.3(11)

C(64)-Fe(2)-C(71)-C(75)	159.2(14)
C(67)-Fe(2)-C(71)-C(75)	-159.3(9)
C(68)-Fe(2)-C(71)-C(75)	-113.8(9)
C(73)-Fe(2)-C(71)-C(76)	-157.6(15)
C(65)-Fe(2)-C(71)-C(76)	92(2)
C(74)-Fe(2)-C(71)-C(76)	158.0(15)
C(72)-Fe(2)-C(71)-C(76)	-120.3(18)
C(66)-Fe(2)-C(71)-C(76)	51.8(16)
C(64)-Fe(2)-C(71)-C(76)	-79(2)
C(75)-Fe(2)-C(71)-C(76)	122.1(18)
C(67)-Fe(2)-C(71)-C(76)	-37.2(16)
C(68)-Fe(2)-C(71)-C(76)	8.3(16)
C(75)-C(71)-C(72)-C(73)	-5.4(19)
C(76)-C(71)-C(72)-C(73)	-173.6(13)
Fe(2)-C(71)-C(72)-C(73)	56.1(11)
C(75)-C(71)-C(72)-C(84)	174.4(15)
C(76)-C(71)-C(72)-C(84)	6(3)
Fe(2)-C(71)-C(72)-C(84)	-124.2(17)
C(75)-C(71)-C(72)-Fe(2)	-61.5(11)
C(76)-C(71)-C(72)-Fe(2)	130.3(15)
C(73)-Fe(2)-C(72)-C(71)	121.0(13)
C(65)-Fe(2)-C(72)-C(71)	158.0(13)
C(74)-Fe(2)-C(72)-C(71)	81.6(10)
C(66)-Fe(2)-C(72)-C(71)	-29(3)
C(64)-Fe(2)-C(72)-C(71)	-162.3(8)
C(75)-Fe(2)-C(72)-C(71)	38.5(9)
C(67)-Fe(2)-C(72)-C(71)	-118.7(9)
C(68)-Fe(2)-C(72)-C(71)	-77.1(11)
C(65)-Fe(2)-C(72)-C(73)	37.0(18)
C(74)-Fe(2)-C(72)-C(73)	-39.4(8)
C(71)-Fe(2)-C(72)-C(73)	-121.0(13)
C(66)-Fe(2)-C(72)-C(73)	-150(3)
C(64)-Fe(2)-C(72)-C(73)	76.7(10)
C(75)-Fe(2)-C(72)-C(73)	-82.5(9)
C(67)-Fe(2)-C(72)-C(73)	120.4(9)
C(68)-Fe(2)-C(72)-C(73)	161.9(9)

C(73)-Fe(2)-C(72)-C(84)	-119.1(18)
C(65)-Fe(2)-C(72)-C(84)	-82(2)
C(74)-Fe(2)-C(72)-C(84)	-158.5(16)
C(71)-Fe(2)-C(72)-C(84)	119.9(19)
C(66)-Fe(2)-C(72)-C(84)	91(3)
C(64)-Fe(2)-C(72)-C(84)	-42.4(17)
C(75)-Fe(2)-C(72)-C(84)	158.4(16)
C(67)-Fe(2)-C(72)-C(84)	1.3(16)
C(68)-Fe(2)-C(72)-C(84)	42.8(18)
C(71)-C(72)-C(73)-C(74)	4.6(18)
C(84)-C(72)-C(73)-C(74)	-175.2(15)
Fe(2)-C(72)-C(73)-C(74)	62.0(10)
C(71)-C(72)-C(73)-C(92)	177.6(14)
C(84)-C(72)-C(73)-C(92)	-2(3)
Fe(2)-C(72)-C(73)-C(92)	-125.0(15)
C(71)-C(72)-C(73)-Fe(2)	-57.4(11)
C(84)-C(72)-C(73)-Fe(2)	122.8(16)
C(65)-Fe(2)-C(73)-C(74)	80.7(10)
C(71)-Fe(2)-C(73)-C(74)	-80.2(9)
C(72)-Fe(2)-C(73)-C(74)	-116.6(12)
C(66)-Fe(2)-C(73)-C(74)	50.4(15)
C(64)-Fe(2)-C(73)-C(74)	123.4(9)
C(75)-Fe(2)-C(73)-C(74)	-36.8(8)
C(67)-Fe(2)-C(73)-C(74)	160.9(8)
C(68)-Fe(2)-C(73)-C(74)	170(2)
C(65)-Fe(2)-C(73)-C(72)	-162.7(9)
C(74)-Fe(2)-C(73)-C(72)	116.6(12)
C(71)-Fe(2)-C(73)-C(72)	36.4(8)
C(66)-Fe(2)-C(73)-C(72)	167.0(11)
C(64)-Fe(2)-C(73)-C(72)	-120.1(9)
C(75)-Fe(2)-C(73)-C(72)	79.8(9)
C(67)-Fe(2)-C(73)-C(72)	-82.5(10)
C(68)-Fe(2)-C(73)-C(72)	-74(3)
C(65)-Fe(2)-C(73)-C(92)	-45.3(15)
C(74)-Fe(2)-C(73)-C(92)	-126.0(17)
C(71)-Fe(2)-C(73)-C(92)	153.8(15)

C(72)-Fe(2)-C(73)-C(92)	117.4(17)
C(66)-Fe(2)-C(73)-C(92)	-75.6(18)
C(64)-Fe(2)-C(73)-C(92)	-2.7(15)
C(75)-Fe(2)-C(73)-C(92)	-162.8(16)
C(67)-Fe(2)-C(73)-C(92)	34.9(16)
C(68)-Fe(2)-C(73)-C(92)	44(3)
C(72)-C(73)-C(74)-C(75)	-2.0(17)
C(92)-C(73)-C(74)-C(75)	-174.3(17)
Fe(2)-C(73)-C(74)-C(75)	60.4(10)
C(72)-C(73)-C(74)-C(100)	173.8(13)
C(92)-C(73)-C(74)-C(100)	1(3)
Fe(2)-C(73)-C(74)-C(100)	-123.7(14)
C(72)-C(73)-C(74)-Fe(2)	-62.4(11)
C(92)-C(73)-C(74)-Fe(2)	125.2(17)
C(73)-Fe(2)-C(74)-C(75)	-119.6(12)
C(65)-Fe(2)-C(74)-C(75)	126.4(10)
C(71)-Fe(2)-C(74)-C(75)	-36.4(9)
C(72)-Fe(2)-C(74)-C(75)	-80.0(10)
C(66)-Fe(2)-C(74)-C(75)	86.4(10)
C(64)-Fe(2)-C(74)-C(75)	166.7(10)
C(67)-Fe(2)-C(74)-C(75)	-174.7(16)
C(68)-Fe(2)-C(74)-C(75)	65.7(15)
C(65)-Fe(2)-C(74)-C(73)	-114.0(10)
C(71)-Fe(2)-C(74)-C(73)	83.2(9)
C(72)-Fe(2)-C(74)-C(73)	39.6(8)
C(66)-Fe(2)-C(74)-C(73)	-154.1(9)
C(64)-Fe(2)-C(74)-C(73)	-73.8(10)
C(75)-Fe(2)-C(74)-C(73)	119.6(12)
C(67)-Fe(2)-C(74)-C(73)	-55(2)
C(68)-Fe(2)-C(74)-C(73)	-174.8(12)
C(73)-Fe(2)-C(74)-C(100)	119.4(18)
C(65)-Fe(2)-C(74)-C(100)	5.4(16)
C(71)-Fe(2)-C(74)-C(100)	-157.4(16)
C(72)-Fe(2)-C(74)-C(100)	159.0(16)
C(66)-Fe(2)-C(74)-C(100)	-34.7(17)
C(64)-Fe(2)-C(74)-C(100)	45.6(17)

C(75)-Fe(2)-C(74)-C(100)	-121.0(18)
C(67)-Fe(2)-C(74)-C(100)	64(2)
C(68)-Fe(2)-C(74)-C(100)	-55(2)
C(73)-C(74)-C(75)-C(71)	-1.3(17)
C(100)-C(74)-C(75)-C(71)	-177.2(13)
Fe(2)-C(74)-C(75)-C(71)	56.9(11)
C(73)-C(74)-C(75)-C(108)	173.6(16)
C(100)-C(74)-C(75)-C(108)	-2(3)
Fe(2)-C(74)-C(75)-C(108)	-128.3(17)
C(73)-C(74)-C(75)-Fe(2)	-58.2(10)
C(100)-C(74)-C(75)-Fe(2)	125.9(14)
C(72)-C(71)-C(75)-C(74)	4.2(19)
C(76)-C(71)-C(75)-C(74)	172.3(14)
Fe(2)-C(71)-C(75)-C(74)	-56.8(11)
C(72)-C(71)-C(75)-C(108)	-170.7(16)
C(76)-C(71)-C(75)-C(108)	-3(3)
Fe(2)-C(71)-C(75)-C(108)	128.3(17)
C(72)-C(71)-C(75)-Fe(2)	61.0(11)
C(76)-C(71)-C(75)-Fe(2)	-130.9(15)
C(73)-Fe(2)-C(75)-C(74)	38.1(8)
C(65)-Fe(2)-C(75)-C(74)	-69.3(11)
C(71)-Fe(2)-C(75)-C(74)	121.7(13)
C(72)-Fe(2)-C(75)-C(74)	83.2(10)
C(66)-Fe(2)-C(75)-C(74)	-109.5(9)
C(64)-Fe(2)-C(75)-C(74)	-34(2)
C(67)-Fe(2)-C(75)-C(74)	175.3(14)
C(68)-Fe(2)-C(75)-C(74)	-149.1(9)
C(73)-Fe(2)-C(75)-C(71)	-83.5(9)
C(65)-Fe(2)-C(75)-C(71)	169.1(9)
C(74)-Fe(2)-C(75)-C(71)	-121.7(13)
C(72)-Fe(2)-C(75)-C(71)	-38.5(9)
C(66)-Fe(2)-C(75)-C(71)	128.8(9)
C(64)-Fe(2)-C(75)-C(71)	-156.0(18)
C(67)-Fe(2)-C(75)-C(71)	54(2)
C(68)-Fe(2)-C(75)-C(71)	89.2(10)
C(73)-Fe(2)-C(75)-C(108)	157.1(17)

C(65)-Fe(2)-C(75)-C(108)	49.7(17)
C(74)-Fe(2)-C(75)-C(108)	118.9(18)
C(71)-Fe(2)-C(75)-C(108)	-119.4(18)
C(72)-Fe(2)-C(75)-C(108)	-157.9(16)
C(66)-Fe(2)-C(75)-C(108)	9.4(16)
C(64)-Fe(2)-C(75)-C(108)	85(2)
C(67)-Fe(2)-C(75)-C(108)	-66(2)
C(68)-Fe(2)-C(75)-C(108)	-30.2(17)
C(72)-C(71)-C(76)-C(77)	-60(2)
C(75)-C(71)-C(76)-C(77)	133.7(16)
Fe(2)-C(71)-C(76)-C(77)	36(2)
C(72)-C(71)-C(76)-C(81)	123.6(16)
C(75)-C(71)-C(76)-C(81)	-42(2)
Fe(2)-C(71)-C(76)-C(81)	-140.5(13)
C(81)-C(76)-C(77)-C(78)	-1(2)
C(71)-C(76)-C(77)-C(78)	-177.7(14)
C(76)-C(77)-C(78)-C(79)	1(3)
C(76)-C(77)-C(78)-C(82)	179.6(14)
C(77)-C(78)-C(79)-C(80)	0(3)
C(82)-C(78)-C(79)-C(80)	-178.9(15)
C(78)-C(79)-C(80)-C(81)	0(3)
C(78)-C(79)-C(80)-C(83)	-179.0(16)
C(79)-C(80)-C(81)-C(76)	-1(2)
C(83)-C(80)-C(81)-C(76)	178.5(15)
C(77)-C(76)-C(81)-C(80)	1(2)
C(71)-C(76)-C(81)-C(80)	177.8(14)
C(71)-C(72)-C(84)-C(85)	130.8(17)
C(73)-C(72)-C(84)-C(85)	-49(2)
Fe(2)-C(72)-C(84)-C(85)	39(2)
C(71)-C(72)-C(84)-C(89)	-49(2)
C(73)-C(72)-C(84)-C(89)	130.3(17)
Fe(2)-C(72)-C(84)-C(89)	-140.9(13)
C(89)-C(84)-C(85)-C(86)	-2(2)
C(72)-C(84)-C(85)-C(86)	178.3(14)
C(84)-C(85)-C(86)-C(87)	0(2)
C(84)-C(85)-C(86)-C(90)	180.0(15)

C(85)-C(86)-C(87)-C(88)	-1(3)
C(90)-C(86)-C(87)-C(88)	179.3(17)
C(86)-C(87)-C(88)-C(89)	3(3)
C(86)-C(87)-C(88)-C(91)	179.1(16)
C(85)-C(84)-C(89)-C(88)	4(2)
C(72)-C(84)-C(89)-C(88)	-176.1(14)
C(87)-C(88)-C(89)-C(84)	-4(2)
C(91)-C(88)-C(89)-C(84)	179.6(14)
C(74)-C(73)-C(92)-C(97)	125.4(17)
C(72)-C(73)-C(92)-C(97)	-46(2)
Fe(2)-C(73)-C(92)-C(97)	-137.7(13)
C(74)-C(73)-C(92)-C(93)	-53(2)
C(72)-C(73)-C(92)-C(93)	135.5(16)
Fe(2)-C(73)-C(92)-C(93)	44(2)
C(97)-C(92)-C(93)-C(94)	6(2)
C(73)-C(92)-C(93)-C(94)	-175.2(15)
C(92)-C(93)-C(94)-C(95)	-3(2)
C(92)-C(93)-C(94)-C(98)	173.2(14)
C(93)-C(94)-C(95)-C(96)	0(3)
C(98)-C(94)-C(95)-C(96)	-175.5(16)
C(94)-C(95)-C(96)-C(97)	-1(2)
C(94)-C(95)-C(96)-C(99)	-177.4(16)
C(93)-C(92)-C(97)-C(96)	-7(2)
C(73)-C(92)-C(97)-C(96)	173.9(15)
C(95)-C(96)-C(97)-C(92)	5(2)
C(99)-C(96)-C(97)-C(92)	-179.0(15)
C(75)-C(74)-C(100)-C(101)	-54(2)
C(73)-C(74)-C(100)-C(101)	130.7(17)
Fe(2)-C(74)-C(100)-C(101)	41(2)
C(75)-C(74)-C(100)-C(105)	117.7(17)
C(73)-C(74)-C(100)-C(105)	-57(2)
Fe(2)-C(74)-C(100)-C(105)	-147.5(12)
C(105)-C(100)-C(101)-C(102)	5(2)
C(74)-C(100)-C(101)-C(102)	176.3(14)
C(100)-C(101)-C(102)-C(103)	-6(2)
C(100)-C(101)-C(102)-C(106)	174.0(14)

C(101)-C(102)-C(103)-C(104)	3(2)
C(106)-C(102)-C(103)-C(104)	-176.9(14)
C(102)-C(103)-C(104)-C(105)	1(2)
C(102)-C(103)-C(104)-C(107)	-179.0(14)
C(101)-C(100)-C(105)-C(104)	0(2)
C(74)-C(100)-C(105)-C(104)	-172.1(14)
C(103)-C(104)-C(105)-C(100)	-3(2)
C(107)-C(104)-C(105)-C(100)	177.4(14)
C(74)-C(75)-C(108)-C(109)	130.6(17)
C(71)-C(75)-C(108)-C(109)	-55(2)
Fe(2)-C(75)-C(108)-C(109)	38(2)
C(74)-C(75)-C(108)-C(113)	-57(2)
C(71)-C(75)-C(108)-C(113)	117.5(17)
Fe(2)-C(75)-C(108)-C(113)	-149.3(12)
C(113)-C(108)-C(109)-C(110)	2(2)
C(75)-C(108)-C(109)-C(110)	174.5(15)
C(108)-C(109)-C(110)-C(111)	-4(2)
C(108)-C(109)-C(110)-C(114)	178.7(15)
C(109)-C(110)-C(111)-C(112)	4(2)
C(114)-C(110)-C(111)-C(112)	-179.0(14)
C(110)-C(111)-C(112)-C(113)	-1(2)
C(110)-C(111)-C(112)-C(115)	-179.6(13)
C(111)-C(112)-C(113)-C(108)	-2(2)
C(115)-C(112)-C(113)-C(108)	176.7(13)
C(109)-C(108)-C(113)-C(112)	2(2)
C(75)-C(108)-C(113)-C(112)	-171.5(14)
O(4)-S(1)-C(121)-C(122)	14.3(15)
O(5)-S(1)-C(121)-C(122)	143.3(11)
O(3)-S(1)-C(121)-C(122)	-100.4(11)
O(4)-S(1)-C(121)-C(126)	-165.0(14)
O(5)-S(1)-C(121)-C(126)	-36.0(13)
O(3)-S(1)-C(121)-C(126)	80.2(13)
C(126)-C(121)-C(122)-C(123)	1(2)
S(1)-C(121)-C(122)-C(123)	-178.1(13)
C(121)-C(122)-C(123)-C(124)	-2(3)
C(122)-C(123)-C(124)-C(125)	1(3)

C(122)-C(123)-C(124)-C(127)	179.9(17)
C(123)-C(124)-C(125)-C(126)	3(2)
C(127)-C(124)-C(125)-C(126)	-176.7(17)
C(124)-C(125)-C(126)-C(121)	-4(2)
C(122)-C(121)-C(126)-C(125)	2(2)
S(1)-C(121)-C(126)-C(125)	-179.0(11)
O(6)-S(2)-C(131)-C(136)	12.1(14)
O(7)-S(2)-C(131)-C(136)	137.4(12)
O(8)-S(2)-C(131)-C(136)	-105.9(12)
O(6)-S(2)-C(131)-C(132)	-171.4(12)
O(7)-S(2)-C(131)-C(132)	-46.2(13)
O(8)-S(2)-C(131)-C(132)	70.6(13)
C(136)-C(131)-C(132)-C(133)	-7(2)
S(2)-C(131)-C(132)-C(133)	176.9(12)
C(131)-C(132)-C(133)-C(134)	6(2)
C(132)-C(133)-C(134)-C(135)	-3(3)
C(132)-C(133)-C(134)-C(137)	-178.3(17)
C(133)-C(134)-C(135)-C(136)	-1(3)
C(137)-C(134)-C(135)-C(136)	174(2)
C(134)-C(135)-C(136)-C(131)	0(3)
C(132)-C(131)-C(136)-C(135)	4(2)
S(2)-C(131)-C(136)-C(135)	-179.9(14)

Symmetry transformations used to generate equivalent atoms:

Least-squares planes (x,y,z in crystal coordinates) and deviations from them

(* indicates atom used to define plane)

18.2042 (0.0125) x + 1.1209 (0.1165) y - 3.4820 (0.1362) z = 6.9934 (0.0540)

* -0.0155 (0.0100) C4

* 0.0302 (0.0097) C5

* -0.0349 (0.0098) C6

* -0.0056 (0.0102) C7

* 0.0258 (0.0101) C8

-1.6741 (0.0056) Fe1

Rms deviation of fitted atoms = 0.0248

17.9068 (0.0261) x + 0.8532 (0.1162) y - 0.5408 (0.1362) z = 3.9057 (0.0523)

Angle to previous plane (with approximate esd) = 8.82 (0.30)

* 0.0242 (0.0102) C11

* -0.0268 (0.0105) C12

* 0.0185 (0.0095) C13

* -0.0039 (0.0089) C14

* -0.0121 (0.0093) C15

1.6765 (0.0057) Fe1

Rms deviation of fitted atoms = 0.0190

18.1873 (0.0126) x - 0.3469 (0.1217) y - 2.4482 (0.1373) z = 10.1337 (0.0718)

Angle to previous plane (with approximate esd) = 7.34 (0.31)

* -0.0027 (0.0099) C64

* -0.0122 (0.0099) C65

* 0.0230 (0.0105) C66

* 0.0166 (0.0105) C67

* -0.0246 (0.0110) C68

1.6927 (0.0056) Fe2

Rms deviation of fitted atoms = 0.0177

17.8099 (0.0275) x + 0.3400 (0.1267) y + 0.0881 (0.1297) z = 14.3875 (0.0619)

Angle to previous plane (with approximate esd) = 7.98 (0.32)

* -0.0283 (0.0108) C71

* 0.0295 (0.0108) C72

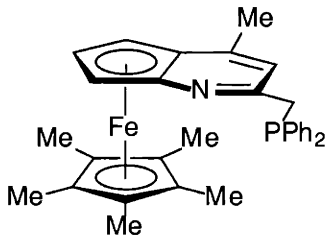
* -0.0196 (0.0098) C73

* 0.0023 (0.0092) C74

* 0.0161 (0.0099) C75

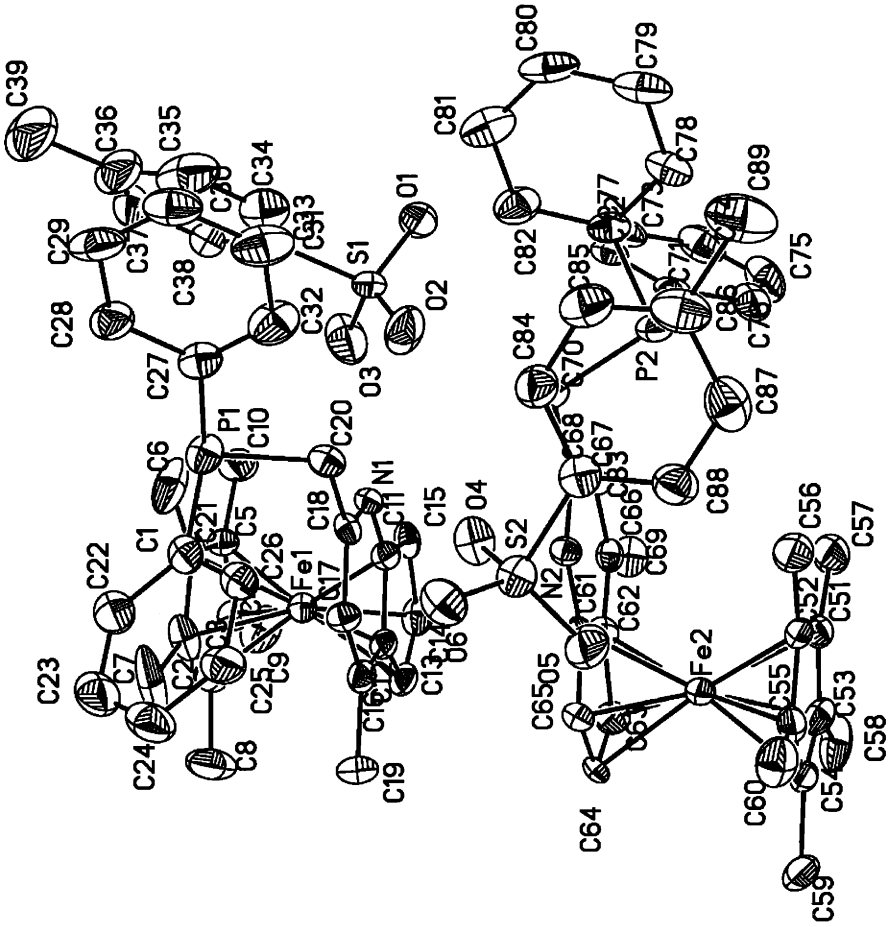
-1.6562 (0.0056) Fe2

Rms deviation of fitted atoms = 0.0216



(–)-4.1

Structure solved by Ivory D. Hills


C39
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C35
C34
C33
C29
C37
C38
C28
C27
C32
O1
S1
O2
O3
P1
C10
C20
C6
C1
C21
C5
C18
N1
C11
C15
O4
S2
C22
C26
Fe1
C17
N2
C61
C62
C69
C23
C7
C2
C8
C25
C9
C16
C13
C14
O6
C65
O5
C64
C24
C8
C19
C80
C79
C81
C78
C89
C82
C77
C73
C85
C71
C75
C84
C70
P2
C86
C87
C68
C67
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C66
C88
C56
C57
C52
C51
Fe2
C55
C53
C58
C60
C54
C59

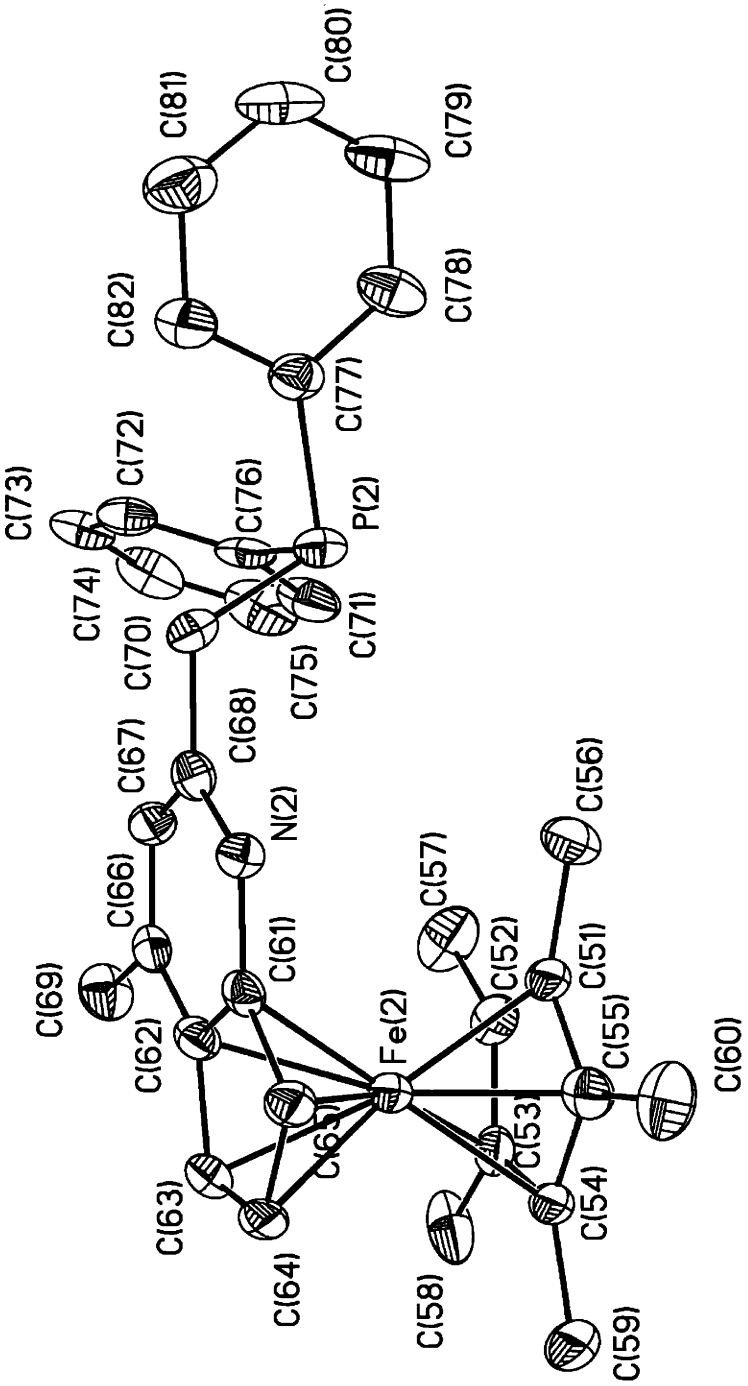
C(80)
C(81)
C(79)
C(82)
C(78)
C(77)
C(72)
C(73)
C(76)
P(2)
C(74)
C(71)
C(70)
C(75)
C(68)
C(67)
N(2)
C(66)
C(57)
C(56)
C(52)
C(51)
C(69)
C(61)
Fe(2)
C(62)
C(55)
C(60)
C(53)
C(63)
C(54)
C(64)
C(58)
C(59)

Table 1. Crystal data and structure refinement for 011781s.

Identification code	011781s	
Empirical formula	C39 H42 Fe N O3 P S	
Formula weight	691.62	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 11.3695(10) Å	a= 78.384(2)°.
	b = 11.3787(10) Å	b= 86.377(2)°.
	c = 14.1642(12) Å	g = 86.2590(10)°.
Volume	1788.7(3) $Å^3$	
Z	2	
Density (calculated)	1.284 Mg/m^3	
Absorption coefficient	0.562 mm^{-1}	
F(000)	728	
Crystal size	0.4 x 0.2 x 0.09 mm^3	
Theta range for data collection	2.63 to 23.29°.	
Index ranges	-12<=h<=12, -12<=k<=12, -15<=l<=8	
Reflections collected	7202	
Independent reflections	5915 [R(int) = 0.0263]	
Completeness to theta = 23.29∞	97.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5915 / 3 / 843	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1116	
R indices (all data)	R1 = 0.0524, wR2 = 0.1157	

Absolute structure parameter 0.047(19)

Largest diff. peak and hole 0.535 and -0.285 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)

for 011781s. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	10055(1)	10732(1)	2354(1)	33(1)
Fe(2)	9963(1)	9252(1)	7639(1)	33(1)
S(1)	5350(2)	9721(2)	2969(2)	51(1)
S(2)	9114(2)	4790(2)	7031(1)	45(1)
P(1)	8387(2)	6054(2)	2983(1)	45(1)
P(2)	5392(1)	7826(2)	6998(1)	43(1)
O(1)	4238(4)	10221(5)	3228(4)	60(1)
O(2)	5958(6)	9021(7)	3757(5)	91(2)
O(3)	6086(7)	10636(7)	2411(6)	117(3)
O(4)	8758(5)	5710(4)	6196(4)	53(1)
O(5)	9770(5)	5281(5)	7681(4)	68(2)
O(6)	9649(4)	3751(4)	6725(4)	55(1)
N(1)	8400(4)	8984(4)	3669(3)	31(1)
N(2)	8540(4)	8019(4)	6343(4)	31(1)
C(1)	9655(7)	9975(6)	1237(5)	48(2)
C(2)	10867(8)	9798(6)	1388(5)	52(2)

C(3)	11353(6)	10936(7)	1277(5)	48(2)
C(4)	10387(6)	11834(6)	1055(5)	42(2)
C(5)	9368(6)	11213(6)	1039(5)	40(2)
C(6)	8792(10)	9027(8)	1276(6)	82(3)
C(7)	11563(11)	8622(8)	1612(6)	100(4)
C(8)	12614(7)	11226(11)	1323(7)	92(4)
C(9)	10509(9)	13181(7)	836(7)	75(3)
C(10)	8165(7)	11803(9)	808(6)	68(2)
C(11)	9069(5)	9980(5)	3565(5)	32(2)
C(12)	10311(6)	9818(6)	3769(5)	35(2)
C(13)	10743(6)	11004(6)	3600(5)	41(2)
C(14)	9786(7)	11826(6)	3334(6)	50(2)
C(15)	8741(6)	11221(5)	3299(5)	38(2)
C(16)	10814(6)	8648(5)	4044(5)	36(2)
C(17)	10076(5)	7714(5)	4112(5)	34(1)
C(18)	8880(5)	7888(5)	3926(4)	30(1)
C(19)	12069(6)	8448(7)	4242(6)	50(2)
C(20)	8096(6)	6856(5)	4002(5)	37(2)
C(21)	9759(6)	5182(6)	3346(6)	43(2)
C(22)	10698(8)	5226(7)	2651(7)	60(2)
C(23)	11759(8)	4635(9)	2890(8)	73(3)
C(24)	11920(7)	4001(8)	3801(9)	71(3)
C(25)	11016(6)	3932(6)	4497(7)	54(2)
C(26)	9947(6)	4520(5)	4264(6)	42(2)
C(27)	7283(6)	4908(6)	3295(6)	45(2)
C(28)	7058(7)	4324(7)	2550(7)	57(2)
C(29)	6234(7)	3440(7)	2691(9)	72(3)

C(30)	5627(8)	3150(7)	3565(9)	66(3)
C(31)	5815(8)	3746(8)	4296(8)	75(3)
C(32)	6647(8)	4621(7)	4152(7)	67(3)
C(33)	5146(6)	8734(6)	2187(5)	41(2)
C(34)	4863(7)	7556(7)	2539(8)	69(2)
C(35)	4691(10)	6805(9)	1945(13)	101(4)
C(36)	4778(10)	7168(14)	957(13)	108(5)
C(37)	5058(8)	8362(12)	587(8)	88(3)
C(38)	5244(6)	9123(8)	1208(6)	56(2)
C(39)	4597(12)	6343(15)	286(14)	174(8)
C(51)	8922(6)	8560(6)	8810(5)	38(2)
C(52)	8801(6)	9840(6)	8643(5)	40(2)
C(53)	9922(7)	10274(6)	8676(5)	42(2)
C(54)	10763(6)	9282(6)	8890(5)	39(2)
C(55)	10119(6)	8216(6)	8980(5)	40(2)
C(56)	7934(7)	7718(8)	8867(6)	63(2)
C(57)	7679(7)	10573(8)	8446(6)	69(2)
C(58)	10235(9)	11576(7)	8541(6)	69(3)
C(59)	12035(7)	9351(9)	8997(6)	66(2)
C(60)	10640(8)	6952(7)	9253(6)	63(2)
C(61)	9535(5)	8642(5)	6434(5)	30(1)
C(62)	9455(6)	9910(5)	6242(5)	35(2)
C(63)	10588(6)	10300(7)	6369(5)	45(2)
C(64)	11322(6)	9243(7)	6630(5)	44(2)
C(65)	10670(5)	8207(6)	6695(5)	38(2)
C(66)	8355(5)	10535(5)	5970(4)	34(1)
C(67)	7428(5)	9838(5)	5903(5)	35(2)

C(68)	7536(5)	8598(5)	6077(4)	33(1)
C(69)	8253(7)	11877(6)	5741(6)	52(2)
C(70)	6530(5)	7849(6)	5989(5)	36(2)
C(71)	4649(5)	9309(6)	6622(6)	43(2)
C(72)	4253(5)	9737(5)	5703(6)	41(2)
C(73)	3758(6)	10894(6)	5448(6)	51(2)
C(74)	3619(8)	11629(8)	6106(8)	69(3)
C(75)	4003(8)	11221(8)	7027(8)	74(3)
C(76)	4513(7)	10088(7)	7269(7)	60(2)
C(77)	4335(6)	6828(6)	6687(6)	42(2)
C(78)	3511(6)	6360(6)	7385(7)	52(2)
C(79)	2690(6)	5588(7)	7247(8)	63(3)
C(80)	2704(7)	5247(7)	6370(8)	63(3)
C(81)	3516(8)	5665(7)	5668(8)	68(3)
C(82)	4330(7)	6467(7)	5800(6)	59(2)
C(83)	7758(6)	4365(6)	7662(6)	45(2)
C(84)	6809(7)	4157(6)	7164(6)	54(2)
C(85)	5763(8)	3843(7)	7647(7)	66(2)
C(86)	5624(7)	3708(7)	8623(8)	68(3)
C(87)	6576(8)	3943(7)	9137(7)	67(2)
C(88)	7624(7)	4290(7)	8640(6)	57(2)
C(89)	4455(9)	3366(10)	9174(10)	100(4)

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Table 3. Bond lengths [Å] and angles [°] for 011781s.

Fe(1)-C(5)	2.025(7)

Fe(1)-C(1)	2.036(7)
Fe(1)-C(4)	2.036(7)
Fe(1)-C(2)	2.038(7)
Fe(1)-C(14)	2.040(7)
Fe(1)-C(3)	2.044(7)
Fe(1)-C(11)	2.055(7)
Fe(1)-C(13)	2.060(7)
Fe(1)-C(15)	2.066(7)
Fe(1)-C(12)	2.092(7)
Fe(2)-C(51)	2.030(7)
Fe(2)-C(55)	2.035(7)
Fe(2)-C(64)	2.038(6)
Fe(2)-C(53)	2.045(7)
Fe(2)-C(54)	2.050(6)
Fe(2)-C(65)	2.056(7)
Fe(2)-C(52)	2.061(7)
Fe(2)-C(63)	2.061(7)
Fe(2)-C(61)	2.064(6)
Fe(2)-C(62)	2.073(7)
S(1)-O(1)	1.410(5)
S(1)-O(2)	1.423(6)
S(1)-O(3)	1.452(7)
S(1)-C(33)	1.762(7)
S(2)-O(6)	1.426(5)
S(2)-O(5)	1.438(6)
S(2)-O(4)	1.471(5)
S(2)-C(83)	1.778(7)

P(1)-C(21)	1.838(8)
P(1)-C(27)	1.838(7)
P(1)-C(20)	1.860(7)
P(2)-C(71)	1.831(7)
P(2)-C(77)	1.837(7)
P(2)-C(70)	1.864(7)
N(1)-C(18)	1.320(7)
N(1)-C(11)	1.383(7)
N(2)-C(68)	1.317(8)
N(2)-C(61)	1.399(8)
C(1)-C(5)	1.400(10)
C(1)-C(2)	1.403(11)
C(1)-C(6)	1.495(10)
C(2)-C(3)	1.417(11)
C(2)-C(7)	1.497(11)
C(3)-C(4)	1.455(10)
C(3)-C(8)	1.500(11)
C(4)-C(5)	1.400(9)
C(4)-C(9)	1.515(10)
C(5)-C(10)	1.510(10)
C(11)-C(15)	1.417(9)
C(11)-C(12)	1.452(9)
C(12)-C(16)	1.403(9)
C(12)-C(13)	1.436(9)
C(13)-C(14)	1.406(10)
C(14)-C(15)	1.420(10)
C(16)-C(17)	1.381(8)

C(16)-C(19)	1.467(9)
C(17)-C(18)	1.395(8)
C(18)-C(20)	1.503(8)
C(21)-C(26)	1.387(10)
C(21)-C(22)	1.402(11)
C(22)-C(23)	1.370(13)
C(23)-C(24)	1.363(13)
C(24)-C(25)	1.374(12)
C(25)-C(26)	1.374(10)
C(27)-C(32)	1.365(12)
C(27)-C(28)	1.400(11)
C(28)-C(29)	1.396(11)
C(29)-C(30)	1.369(14)
C(30)-C(31)	1.381(14)
C(31)-C(32)	1.394(11)
C(33)-C(38)	1.369(10)
C(33)-C(34)	1.384(10)
C(34)-C(35)	1.345(15)
C(35)-C(36)	1.376(19)
C(36)-C(37)	1.403(17)
C(36)-C(39)	1.496(15)
C(37)-C(38)	1.386(13)
C(51)-C(55)	1.414(10)
C(51)-C(52)	1.426(10)
C(51)-C(56)	1.511(9)
C(52)-C(53)	1.404(10)
C(52)-C(57)	1.488(10)

C(53)-C(54)	1.427(10)
C(53)-C(58)	1.518(9)
C(54)-C(55)	1.437(9)
C(54)-C(59)	1.472(10)
C(55)-C(60)	1.504(10)
C(61)-C(65)	1.397(9)
C(61)-C(62)	1.412(9)
C(62)-C(63)	1.423(9)
C(62)-C(66)	1.433(9)
C(63)-C(64)	1.417(11)
C(64)-C(65)	1.418(10)
C(66)-C(67)	1.378(8)
C(66)-C(69)	1.494(9)
C(67)-C(68)	1.382(8)
C(68)-C(70)	1.496(8)
C(71)-C(72)	1.388(10)
C(71)-C(76)	1.393(11)
C(72)-C(73)	1.385(9)
C(73)-C(74)	1.367(12)
C(74)-C(75)	1.383(14)
C(75)-C(76)	1.365(12)
C(77)-C(78)	1.369(11)
C(77)-C(82)	1.397(12)
C(78)-C(79)	1.371(10)
C(79)-C(80)	1.373(14)
C(80)-C(81)	1.348(13)
C(81)-C(82)	1.388(11)

C(83)-C(88)	1.371(11)
C(83)-C(84)	1.384(10)
C(84)-C(85)	1.365(12)
C(85)-C(86)	1.360(13)
C(86)-C(87)	1.411(12)
C(86)-C(89)	1.530(13)
C(87)-C(88)	1.383(11)
C(5)-Fe(1)-C(1)	40.3(3)
C(5)-Fe(1)-C(4)	40.3(3)
C(1)-Fe(1)-C(4)	68.2(3)
C(5)-Fe(1)-C(2)	68.0(3)
C(1)-Fe(1)-C(2)	40.3(3)
C(4)-Fe(1)-C(2)	68.9(3)
C(5)-Fe(1)-C(14)	120.3(3)
C(1)-Fe(1)-C(14)	156.0(3)
C(4)-Fe(1)-C(14)	106.0(3)
C(2)-Fe(1)-C(14)	161.5(3)
C(5)-Fe(1)-C(3)	68.7(3)
C(1)-Fe(1)-C(3)	68.3(3)
C(4)-Fe(1)-C(3)	41.8(3)
C(2)-Fe(1)-C(3)	40.6(3)
C(14)-Fe(1)-C(3)	123.9(3)
C(5)-Fe(1)-C(11)	122.4(3)
C(1)-Fe(1)-C(11)	108.7(3)
C(4)-Fe(1)-C(11)	156.7(3)
C(2)-Fe(1)-C(11)	124.6(3)
C(14)-Fe(1)-C(11)	66.9(3)

C(3)-Fe(1)-C(11)	160.5(3)
C(5)-Fe(1)-C(13)	156.2(3)
C(1)-Fe(1)-C(13)	162.5(3)
C(4)-Fe(1)-C(13)	121.8(3)
C(2)-Fe(1)-C(13)	126.3(3)
C(14)-Fe(1)-C(13)	40.1(3)
C(3)-Fe(1)-C(13)	108.7(3)
C(11)-Fe(1)-C(13)	68.1(3)
C(5)-Fe(1)-C(15)	104.6(3)
C(1)-Fe(1)-C(15)	120.7(3)
C(4)-Fe(1)-C(15)	119.9(3)
C(2)-Fe(1)-C(15)	157.7(3)
C(14)-Fe(1)-C(15)	40.5(3)
C(3)-Fe(1)-C(15)	158.4(3)
C(11)-Fe(1)-C(15)	40.2(2)
C(13)-Fe(1)-C(15)	68.8(3)
C(5)-Fe(1)-C(12)	160.4(2)
C(1)-Fe(1)-C(12)	125.9(3)
C(4)-Fe(1)-C(12)	159.1(2)
C(2)-Fe(1)-C(12)	110.6(3)
C(14)-Fe(1)-C(12)	67.4(3)
C(3)-Fe(1)-C(12)	124.0(3)
C(11)-Fe(1)-C(12)	41.0(2)
C(13)-Fe(1)-C(12)	40.5(2)
C(15)-Fe(1)-C(12)	68.9(3)
C(51)-Fe(2)-C(55)	40.7(3)
C(51)-Fe(2)-C(64)	155.9(3)

C(55)-Fe(2)-C(64)	119.5(3)
C(51)-Fe(2)-C(53)	68.4(3)
C(55)-Fe(2)-C(53)	68.3(3)
C(64)-Fe(2)-C(53)	122.7(3)
C(51)-Fe(2)-C(54)	69.2(3)
C(55)-Fe(2)-C(54)	41.2(3)
C(64)-Fe(2)-C(54)	104.5(3)
C(53)-Fe(2)-C(54)	40.8(3)
C(51)-Fe(2)-C(65)	121.6(3)
C(55)-Fe(2)-C(65)	105.6(3)
C(64)-Fe(2)-C(65)	40.5(3)
C(53)-Fe(2)-C(65)	158.2(3)
C(54)-Fe(2)-C(65)	120.9(3)
C(51)-Fe(2)-C(52)	40.8(3)
C(55)-Fe(2)-C(52)	68.1(3)
C(64)-Fe(2)-C(52)	160.1(3)
C(53)-Fe(2)-C(52)	40.0(3)
C(54)-Fe(2)-C(52)	68.3(3)
C(65)-Fe(2)-C(52)	159.1(3)
C(51)-Fe(2)-C(63)	163.0(3)
C(55)-Fe(2)-C(63)	154.6(3)
C(64)-Fe(2)-C(63)	40.5(3)
C(53)-Fe(2)-C(63)	107.0(3)
C(54)-Fe(2)-C(63)	118.9(3)
C(65)-Fe(2)-C(63)	68.9(3)
C(52)-Fe(2)-C(63)	125.4(3)
C(51)-Fe(2)-C(61)	111.2(2)

C(55)-Fe(2)-C(61)	125.2(3)
C(64)-Fe(2)-C(61)	66.1(3)
C(53)-Fe(2)-C(61)	160.2(3)
C(54)-Fe(2)-C(61)	158.9(3)
C(65)-Fe(2)-C(61)	39.7(2)
C(52)-Fe(2)-C(61)	126.7(3)
C(63)-Fe(2)-C(61)	67.2(3)
C(51)-Fe(2)-C(62)	127.5(3)
C(55)-Fe(2)-C(62)	162.5(2)
C(64)-Fe(2)-C(62)	67.0(3)
C(53)-Fe(2)-C(62)	123.6(3)
C(54)-Fe(2)-C(62)	156.2(2)
C(65)-Fe(2)-C(62)	68.1(3)
C(52)-Fe(2)-C(62)	111.7(3)
C(63)-Fe(2)-C(62)	40.3(3)
C(61)-Fe(2)-C(62)	39.9(2)
O(1)-S(1)-O(2)	114.4(4)
O(1)-S(1)-O(3)	111.2(4)
O(2)-S(1)-O(3)	111.1(5)
O(1)-S(1)-C(33)	108.7(3)
O(2)-S(1)-C(33)	105.7(4)
O(3)-S(1)-C(33)	105.1(4)
O(6)-S(2)-O(5)	115.8(3)
O(6)-S(2)-O(4)	110.8(3)
O(5)-S(2)-O(4)	111.9(3)
O(6)-S(2)-C(83)	107.1(3)
O(5)-S(2)-C(83)	106.2(3)

O(4)-S(2)-C(83)	104.1(3)
C(21)-P(1)-C(27)	102.1(3)
C(21)-P(1)-C(20)	100.5(3)
C(27)-P(1)-C(20)	100.2(3)
C(71)-P(2)-C(77)	102.0(3)
C(71)-P(2)-C(70)	100.2(3)
C(77)-P(2)-C(70)	101.1(3)
C(18)-N(1)-C(11)	121.1(5)
C(68)-N(2)-C(61)	121.0(5)
C(5)-C(1)-C(2)	108.4(6)
C(5)-C(1)-C(6)	124.6(8)
C(2)-C(1)-C(6)	127.0(8)
C(5)-C(1)-Fe(1)	69.4(4)
C(2)-C(1)-Fe(1)	69.9(4)
C(6)-C(1)-Fe(1)	126.4(5)
C(1)-C(2)-C(3)	108.5(6)
C(1)-C(2)-C(7)	127.1(8)
C(3)-C(2)-C(7)	124.4(9)
C(1)-C(2)-Fe(1)	69.8(4)
C(3)-C(2)-Fe(1)	69.9(4)
C(7)-C(2)-Fe(1)	127.0(6)
C(2)-C(3)-C(4)	106.8(6)
C(2)-C(3)-C(8)	129.0(8)
C(4)-C(3)-C(8)	124.2(8)
C(2)-C(3)-Fe(1)	69.5(4)
C(4)-C(3)-Fe(1)	68.8(4)
C(8)-C(3)-Fe(1)	128.7(6)

C(5)-C(4)-C(3)	107.0(6)
C(5)-C(4)-C(9)	127.8(7)
C(3)-C(4)-C(9)	125.1(7)
C(5)-C(4)-Fe(1)	69.4(4)
C(3)-C(4)-Fe(1)	69.4(4)
C(9)-C(4)-Fe(1)	128.6(6)
C(4)-C(5)-C(1)	109.3(6)
C(4)-C(5)-C(10)	124.6(7)
C(1)-C(5)-C(10)	126.0(7)
C(4)-C(5)-Fe(1)	70.3(4)
C(1)-C(5)-Fe(1)	70.3(4)
C(10)-C(5)-Fe(1)	127.3(5)
N(1)-C(11)-C(15)	130.4(6)
N(1)-C(11)-C(12)	119.5(5)
C(15)-C(11)-C(12)	110.0(5)
N(1)-C(11)-Fe(1)	126.5(5)
C(15)-C(11)-Fe(1)	70.3(4)
C(12)-C(11)-Fe(1)	70.8(4)
C(16)-C(12)-C(13)	135.2(6)
C(16)-C(12)-C(11)	119.0(5)
C(13)-C(12)-C(11)	105.8(6)
C(16)-C(12)-Fe(1)	126.1(5)
C(13)-C(12)-Fe(1)	68.6(4)
C(11)-C(12)-Fe(1)	68.2(4)
C(14)-C(13)-C(12)	107.6(6)
C(14)-C(13)-Fe(1)	69.2(4)
C(12)-C(13)-Fe(1)	70.9(4)

C(13)-C(14)-C(15)	111.1(6)
C(13)-C(14)-Fe(1)	70.7(4)
C(15)-C(14)-Fe(1)	70.8(4)
C(11)-C(15)-C(14)	105.4(6)
C(11)-C(15)-Fe(1)	69.5(4)
C(14)-C(15)-Fe(1)	68.8(4)
C(17)-C(16)-C(12)	117.0(6)
C(17)-C(16)-C(19)	122.4(6)
C(12)-C(16)-C(19)	120.6(6)
C(16)-C(17)-C(18)	123.2(5)
N(1)-C(18)-C(17)	120.2(5)
N(1)-C(18)-C(20)	117.6(5)
C(17)-C(18)-C(20)	122.2(5)
C(18)-C(20)-P(1)	112.2(4)
C(26)-C(21)-C(22)	117.7(7)
C(26)-C(21)-P(1)	124.9(5)
C(22)-C(21)-P(1)	117.3(6)
C(23)-C(22)-C(21)	120.1(9)
C(24)-C(23)-C(22)	120.8(9)
C(23)-C(24)-C(25)	120.6(9)
C(24)-C(25)-C(26)	119.0(9)
C(25)-C(26)-C(21)	121.7(7)
C(32)-C(27)-C(28)	118.3(7)
C(32)-C(27)-P(1)	126.6(6)
C(28)-C(27)-P(1)	115.1(6)
C(29)-C(28)-C(27)	120.8(9)
C(30)-C(29)-C(28)	119.6(9)

C(29)-C(30)-C(31)	120.1(8)
C(30)-C(31)-C(32)	119.9(10)
C(27)-C(32)-C(31)	121.2(9)
C(38)-C(33)-C(34)	118.0(7)
C(38)-C(33)-S(1)	120.6(5)
C(34)-C(33)-S(1)	121.4(6)
C(35)-C(34)-C(33)	121.6(10)
C(34)-C(35)-C(36)	121.9(11)
C(35)-C(36)-C(37)	117.3(10)
C(35)-C(36)-C(39)	122.6(16)
C(37)-C(36)-C(39)	120.1(16)
C(38)-C(37)-C(36)	120.2(11)
C(33)-C(38)-C(37)	121.0(9)
C(55)-C(51)-C(52)	107.7(6)
C(55)-C(51)-C(56)	125.9(7)
C(52)-C(51)-C(56)	126.2(7)
C(55)-C(51)-Fe(2)	69.9(4)
C(52)-C(51)-Fe(2)	70.8(4)
C(56)-C(51)-Fe(2)	128.1(5)
C(53)-C(52)-C(51)	108.0(6)
C(53)-C(52)-C(57)	126.6(7)
C(51)-C(52)-C(57)	125.3(7)
C(53)-C(52)-Fe(2)	69.4(4)
C(51)-C(52)-Fe(2)	68.4(4)
C(57)-C(52)-Fe(2)	126.6(5)
C(52)-C(53)-C(54)	109.2(6)
C(52)-C(53)-C(58)	127.3(7)

C(54)-C(53)-C(58)	123.5(7)
C(52)-C(53)-Fe(2)	70.6(4)
C(54)-C(53)-Fe(2)	69.8(4)
C(58)-C(53)-Fe(2)	127.1(5)
C(53)-C(54)-C(55)	106.3(6)
C(53)-C(54)-C(59)	126.3(7)
C(55)-C(54)-C(59)	127.4(7)
C(53)-C(54)-Fe(2)	69.4(4)
C(55)-C(54)-Fe(2)	68.9(4)
C(59)-C(54)-Fe(2)	126.5(5)
C(51)-C(55)-C(54)	108.6(6)
C(51)-C(55)-C(60)	126.4(7)
C(54)-C(55)-C(60)	124.9(6)
C(51)-C(55)-Fe(2)	69.4(4)
C(54)-C(55)-Fe(2)	70.0(4)
C(60)-C(55)-Fe(2)	128.5(5)
C(65)-C(61)-N(2)	130.0(6)
C(65)-C(61)-C(62)	110.7(6)
N(2)-C(61)-C(62)	119.3(5)
C(65)-C(61)-Fe(2)	69.9(4)
N(2)-C(61)-Fe(2)	126.6(4)
C(62)-C(61)-Fe(2)	70.4(4)
C(61)-C(62)-C(63)	107.3(6)
C(61)-C(62)-C(66)	119.5(5)
C(63)-C(62)-C(66)	133.2(6)
C(61)-C(62)-Fe(2)	69.7(4)
C(63)-C(62)-Fe(2)	69.4(4)

C(66)-C(62)-Fe(2)	126.3(5)
C(64)-C(63)-C(62)	106.1(6)
C(64)-C(63)-Fe(2)	68.9(4)
C(62)-C(63)-Fe(2)	70.3(4)
C(63)-C(64)-C(65)	110.5(6)
C(63)-C(64)-Fe(2)	70.7(4)
C(65)-C(64)-Fe(2)	70.4(4)
C(61)-C(65)-C(64)	105.3(6)
C(61)-C(65)-Fe(2)	70.5(4)
C(64)-C(65)-Fe(2)	69.0(4)
C(67)-C(66)-C(62)	116.7(5)
C(67)-C(66)-C(69)	122.6(6)
C(62)-C(66)-C(69)	120.6(6)
C(66)-C(67)-C(68)	122.6(5)
N(2)-C(68)-C(67)	120.9(6)
N(2)-C(68)-C(70)	116.8(5)
C(67)-C(68)-C(70)	122.3(5)
C(68)-C(70)-P(2)	112.4(4)
C(72)-C(71)-C(76)	117.0(7)
C(72)-C(71)-P(2)	123.6(5)
C(76)-C(71)-P(2)	119.2(7)
C(73)-C(72)-C(71)	120.8(7)
C(74)-C(73)-C(72)	120.7(8)
C(73)-C(74)-C(75)	119.5(8)
C(76)-C(75)-C(74)	119.6(8)
C(75)-C(76)-C(71)	122.4(9)
C(78)-C(77)-C(82)	116.9(7)

C(78)-C(77)-P(2)	117.9(6)
C(82)-C(77)-P(2)	125.1(6)
C(77)-C(78)-C(79)	123.4(9)
C(78)-C(79)-C(80)	118.6(9)
C(81)-C(80)-C(79)	120.1(8)
C(80)-C(81)-C(82)	121.4(9)
C(81)-C(82)-C(77)	119.6(8)
C(88)-C(83)-C(84)	119.2(7)
C(88)-C(83)-S(2)	120.5(6)
C(84)-C(83)-S(2)	120.2(6)
C(85)-C(84)-C(83)	120.3(8)
C(86)-C(85)-C(84)	121.6(8)
C(85)-C(86)-C(87)	118.6(8)
C(85)-C(86)-C(89)	122.3(9)
C(87)-C(86)-C(89)	119.0(10)
C(88)-C(87)-C(86)	119.5(9)
C(83)-C(88)-C(87)	120.6(8)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 011781s. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	36(1)	30(1)	33(1)	-6(1)	0(1)	-4(1)
Fe(2)	26(1)	43(1)	32(1)	-8(1)	0(1)	-7(1)

S(1)	27(1)	74(1)	59(1)	-29(1)	-5(1)	-2(1)
S(2)	52(1)	33(1)	49(1)	-8(1)	-3(1)	-4(1)
P(1)	58(1)	32(1)	46(1)	-7(1)	-3(1)	-13(1)
P(2)	30(1)	54(1)	47(1)	-10(1)	-4(1)	-12(1)
O(1)	46(3)	69(3)	69(4)	-26(3)	-10(3)	14(2)
O(2)	85(4)	125(5)	71(4)	-46(4)	-38(4)	44(4)
O(3)	109(6)	128(6)	140(7)	-87(5)	67(5)	-81(5)
O(4)	69(3)	36(2)	51(3)	-3(2)	3(3)	6(2)
O(5)	63(4)	84(4)	65(4)	-30(3)	1(3)	-29(3)
O(6)	58(3)	38(2)	67(4)	-8(2)	4(3)	7(2)
N(1)	24(2)	36(3)	32(3)	-7(2)	0(2)	1(2)
N(2)	28(3)	28(2)	35(3)	-5(2)	-2(2)	1(2)
C(1)	72(6)	42(4)	32(4)	-11(3)	16(4)	-20(4)
C(2)	76(6)	35(4)	37(4)	2(3)	12(4)	17(4)
C(3)	37(4)	68(5)	33(4)	1(4)	-3(3)	4(4)
C(4)	44(4)	41(4)	35(4)	8(3)	-3(3)	-12(3)
C(5)	31(3)	46(4)	43(4)	-11(3)	-1(3)	-10(3)
C(6)	138(9)	74(6)	44(5)	-20(5)	10(6)	-59(6)
C(7)	177(11)	68(6)	36(5)	2(4)	33(6)	59(7)
C(8)	37(5)	158(10)	69(6)	6(7)	-1(4)	-7(5)
C(9)	113(8)	43(4)	68(6)	0(4)	-13(6)	-23(5)
C(10)	46(5)	104(7)	53(5)	-12(5)	-15(4)	6(4)
C(11)	32(3)	32(3)	33(4)	-7(3)	-3(3)	-2(3)
C(12)	35(4)	39(4)	36(4)	-17(3)	2(3)	-12(3)
C(13)	45(4)	44(4)	40(4)	-19(3)	-1(3)	-14(3)
C(14)	70(5)	32(4)	51(5)	-16(3)	2(4)	-15(4)
C(15)	50(4)	28(3)	35(4)	-10(3)	3(3)	11(3)

C(16)	40(4)	40(4)	26(3)	-6(3)	-3(3)	1(3)
C(17)	33(3)	28(3)	40(4)	-4(3)	-7(3)	2(3)
C(18)	33(3)	25(3)	32(4)	-8(3)	8(3)	-2(3)
C(19)	29(3)	59(4)	61(5)	-11(4)	-11(3)	-5(3)
C(20)	34(3)	30(3)	46(4)	-2(3)	3(3)	-5(3)
C(21)	47(4)	30(3)	56(5)	-21(3)	8(4)	-13(3)
C(22)	60(5)	53(5)	71(6)	-24(4)	12(5)	-23(4)
C(23)	54(5)	80(6)	93(8)	-39(6)	22(5)	-27(5)
C(24)	42(5)	66(5)	115(9)	-43(6)	11(5)	-12(4)
C(25)	42(4)	43(4)	81(6)	-25(4)	-4(4)	-6(3)
C(26)	42(4)	30(3)	58(5)	-17(3)	4(3)	-6(3)
C(27)	47(4)	28(3)	60(5)	-4(4)	-8(4)	-8(3)
C(28)	49(5)	50(4)	80(6)	-27(4)	-10(4)	-4(4)
C(29)	41(5)	52(5)	133(10)	-36(6)	-22(6)	-5(4)
C(30)	45(5)	44(5)	107(8)	-7(5)	-10(5)	-8(4)
C(31)	65(6)	61(5)	94(8)	11(6)	-12(5)	-32(5)
C(32)	72(6)	57(5)	71(6)	-3(5)	-6(5)	-32(4)
C(33)	30(3)	45(4)	49(5)	-9(3)	-7(3)	-3(3)
C(34)	63(5)	55(5)	86(7)	-5(5)	-14(5)	5(4)
C(35)	74(7)	58(6)	183(15)	-45(8)	-39(9)	5(5)
C(36)	73(7)	123(11)	157(14)	-98(11)	-33(8)	20(7)
C(37)	63(6)	147(11)	65(6)	-53(7)	-9(5)	14(6)
C(38)	44(4)	72(5)	56(5)	-22(4)	2(4)	-6(4)
C(39)	110(10)	212(16)	260(20)	-196(16)	-37(12)	22(11)
C(51)	34(4)	57(4)	27(4)	-13(3)	-1(3)	-12(3)
C(52)	36(4)	50(4)	36(4)	-14(4)	-3(3)	8(3)
C(53)	54(4)	45(4)	28(4)	-2(3)	-7(3)	-14(3)

C(54)	34(4)	60(4)	27(4)	-12(3)	1(3)	-16(3)
C(55)	41(4)	47(4)	35(4)	-17(3)	5(3)	-4(3)
C(56)	56(5)	87(6)	49(5)	-13(4)	7(4)	-38(4)
C(57)	55(5)	96(6)	60(6)	-33(5)	-8(4)	25(5)
C(58)	123(8)	48(4)	37(5)	-9(4)	6(5)	-30(5)
C(59)	50(5)	114(7)	37(4)	-15(5)	-9(4)	-25(5)
C(60)	81(6)	54(5)	51(5)	-7(4)	-11(4)	12(4)
C(61)	28(3)	36(3)	26(4)	-8(3)	7(3)	0(3)
C(62)	35(4)	33(4)	35(4)	-5(3)	4(3)	-9(3)
C(63)	40(4)	55(4)	37(4)	0(3)	4(3)	-21(4)
C(64)	19(3)	85(5)	30(4)	-21(4)	10(3)	-8(3)
C(65)	26(3)	51(4)	37(4)	-11(3)	2(3)	-1(3)
C(66)	41(4)	34(3)	25(3)	-3(3)	2(3)	-4(3)
C(67)	24(3)	41(3)	39(4)	-3(3)	-4(3)	3(3)
C(68)	36(3)	32(3)	30(3)	-7(3)	4(3)	1(3)
C(69)	68(5)	30(3)	56(5)	-2(3)	-1(4)	-8(3)
C(70)	34(3)	37(3)	40(4)	-11(3)	-11(3)	-4(3)
C(71)	23(3)	50(4)	64(5)	-25(4)	9(3)	-17(3)
C(72)	21(3)	38(4)	65(5)	-18(3)	2(3)	-1(3)
C(73)	32(4)	42(4)	82(6)	-21(4)	14(4)	-13(3)
C(74)	54(5)	51(5)	97(8)	-11(5)	18(5)	-11(4)
C(75)	78(6)	56(5)	100(8)	-49(6)	37(6)	-20(5)
C(76)	57(5)	60(5)	71(6)	-30(5)	20(4)	-29(4)
C(77)	34(4)	38(4)	53(5)	0(3)	-10(3)	-3(3)
C(78)	34(4)	44(4)	77(6)	-11(4)	8(4)	-4(3)
C(79)	30(4)	40(4)	118(9)	-15(5)	-1(5)	-6(3)
C(80)	36(4)	36(4)	122(9)	-19(5)	-23(5)	-5(3)

C(81)	65(6)	56(5)	84(7)	-3(5)	-30(5)	-9(5)
C(82)	57(5)	59(5)	60(6)	-3(4)	-8(4)	-24(4)
C(83)	53(4)	28(3)	53(5)	-7(3)	-3(4)	-3(3)
C(84)	56(5)	56(4)	52(5)	-13(4)	-1(4)	-12(4)
C(85)	60(5)	58(5)	83(7)	-16(5)	-15(5)	-8(4)
C(86)	53(5)	50(5)	95(8)	0(5)	-1(5)	-8(4)
C(87)	77(6)	65(5)	51(5)	2(4)	5(5)	8(5)
C(88)	46(4)	67(5)	52(5)	-3(4)	0(4)	-5(4)
C(89)	67(6)	98(7)	128(10)	0(7)	6(6)	-26(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 011781s.

	x	y	z	U(eq)
H(1)	7643	9084	3563	37
H(2)	8585	7228	6466	37
H(6A)	8022	9299	1527	124
H(6B)	9072	8285	1700	124
H(6C)	8719	8876	626	124
H(7A)	11074	8021	2020	150
H(7B)	12263	8719	1953	150
H(7C)	11809	8356	1010	150

H(8A)	13010	10596	1790	138
H(8B)	12640	12000	1523	138
H(8C)	13016	11273	684	138
H(9A)	10571	13470	135	113
H(9B)	11221	13368	1120	113
H(9C)	9816	13577	1110	113
H(10A)	8068	11924	112	102
H(10B)	8090	12582	1009	102
H(10C)	7555	11287	1155	102
H(13)	11570	11210	3671	49
H(14)	9839	12719	3175	60
H(15)	7938	11592	3138	45
H(17)	10399	6915	4295	41
H(19A)	12204	8691	4851	74
H(19B)	12539	8925	3716	74
H(19C)	12303	7594	4293	74
H(20A)	7261	7162	4012	45
H(20B)	8222	6283	4617	45
H(22)	10597	5665	2013	71
H(23)	12390	4667	2414	87
H(24)	12664	3603	3955	85
H(25)	11128	3485	5131	64
H(26)	9321	4472	4745	50
H(28)	7472	4532	1941	69
H(29)	6094	3042	2184	86
H(30)	5076	2539	3669	79
H(31)	5379	3560	4896	90

H(32)	6773	5025	4659	80
H(34)	4789	7271	3217	83
H(35)	4504	6001	2215	121
H(37)	5122	8649	-91	105
H(38)	5441	9926	949	67
H(39A)	5280	5771	287	262
H(39B)	4510	6813	-369	262
H(39C)	3883	5904	499	262
H(56A)	8208	7040	8565	94
H(56B)	7260	8150	8529	94
H(56C)	7694	7419	9545	94
H(57A)	7169	10485	9037	103
H(57B)	7276	10298	7944	103
H(57C)	7851	11420	8225	103
H(58A)	9708	12081	8085	103
H(58B)	11054	11655	8288	103
H(58C)	10144	11831	9163	103
H(59A)	12341	10010	8505	99
H(59B)	12449	8592	8917	99
H(59C)	12162	9499	9640	99
H(60A)	10506	6661	9949	94
H(60B)	11490	6940	9086	94
H(60C)	10263	6432	8902	94
H(63)	10825	11149	6271	54
H(64)	12176	9230	6765	52
H(65)	10971	7348	6856	45
H(67)	6685	10227	5730	42

H(69A)	7456	12147	5536	78
H(69B)	8832	12176	5220	78
H(69C)	8403	12187	6317	78
H(70A)	6837	7017	5980	43
H(70B)	6159	8171	5369	43
H(72)	4323	9230	5243	49
H(73)	3512	11180	4810	62
H(74)	3261	12415	5931	82
H(75)	3913	11725	7489	89
H(76)	4785	9822	7901	72
H(78)	3509	6581	7997	62
H(79)	2124	5296	7747	75
H(80)	2141	4716	6257	76
H(81)	3532	5405	5071	82
H(82)	4881	6770	5291	70
H(84)	6885	4232	6483	65
H(85)	5116	3717	7293	79
H(87)	6498	3865	9818	80
H(88)	8257	4478	8981	68
H(89A)	3806	3869	8854	150
H(89B)	4479	3491	9837	150
H(89C)	4331	2519	9185	150

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Table 6. Selected torsion angles [°] for 011781s.

Symmetry transformations used to generate equivalent atoms:

Table 7. Torsion angles [°] for 011781s.

C(4)-Fe(1)-C(1)-C(5)	-37.0(4)
C(2)-Fe(1)-C(1)-C(5)	-119.7(6)
C(14)-Fe(1)-C(1)-C(5)	43.3(9)
C(3)-Fe(1)-C(1)-C(5)	-82.2(4)
C(11)-Fe(1)-C(1)-C(5)	118.3(4)
C(13)-Fe(1)-C(1)-C(5)	-165.4(8)
C(15)-Fe(1)-C(1)-C(5)	75.8(5)
C(12)-Fe(1)-C(1)-C(5)	160.7(4)
C(5)-Fe(1)-C(1)-C(2)	119.7(6)
C(4)-Fe(1)-C(1)-C(2)	82.7(4)
C(14)-Fe(1)-C(1)-C(2)	163.0(6)
C(3)-Fe(1)-C(1)-C(2)	37.5(4)
C(11)-Fe(1)-C(1)-C(2)	-121.9(4)
C(13)-Fe(1)-C(1)-C(2)	-45.7(11)
C(15)-Fe(1)-C(1)-C(2)	-164.5(4)
C(12)-Fe(1)-C(1)-C(2)	-79.6(5)
C(5)-Fe(1)-C(1)-C(6)	-118.5(10)
C(4)-Fe(1)-C(1)-C(6)	-155.5(9)
C(2)-Fe(1)-C(1)-C(6)	121.8(10)
C(14)-Fe(1)-C(1)-C(6)	-75.2(11)
C(3)-Fe(1)-C(1)-C(6)	159.3(9)
C(11)-Fe(1)-C(1)-C(6)	-0.1(9)
C(13)-Fe(1)-C(1)-C(6)	76.1(14)

C(15)-Fe(1)-C(1)-C(6)	-42.7(9)
C(12)-Fe(1)-C(1)-C(6)	42.3(10)
C(5)-C(1)-C(2)-C(3)	-0.5(9)
C(6)-C(1)-C(2)-C(3)	179.6(7)
Fe(1)-C(1)-C(2)-C(3)	-59.4(5)
C(5)-C(1)-C(2)-C(7)	-179.4(7)
C(6)-C(1)-C(2)-C(7)	0.7(13)
Fe(1)-C(1)-C(2)-C(7)	121.7(8)
C(5)-C(1)-C(2)-Fe(1)	58.9(5)
C(6)-C(1)-C(2)-Fe(1)	-121.0(8)
C(5)-Fe(1)-C(2)-C(1)	-37.3(4)
C(4)-Fe(1)-C(2)-C(1)	-80.8(4)
C(14)-Fe(1)-C(2)-C(1)	-158.1(9)
C(3)-Fe(1)-C(2)-C(1)	-119.7(6)
C(11)-Fe(1)-C(2)-C(1)	77.7(5)
C(13)-Fe(1)-C(2)-C(1)	164.5(4)
C(15)-Fe(1)-C(2)-C(1)	37.2(9)
C(12)-Fe(1)-C(2)-C(1)	121.6(4)
C(5)-Fe(1)-C(2)-C(3)	82.4(4)
C(1)-Fe(1)-C(2)-C(3)	119.7(6)
C(4)-Fe(1)-C(2)-C(3)	38.9(4)
C(14)-Fe(1)-C(2)-C(3)	-38.4(11)
C(11)-Fe(1)-C(2)-C(3)	-162.6(4)
C(13)-Fe(1)-C(2)-C(3)	-75.8(5)
C(15)-Fe(1)-C(2)-C(3)	156.9(6)
C(12)-Fe(1)-C(2)-C(3)	-118.7(4)
C(5)-Fe(1)-C(2)-C(7)	-159.1(10)

C(1)-Fe(1)-C(2)-C(7)	-121.8(11)
C(4)-Fe(1)-C(2)-C(7)	157.4(10)
C(14)-Fe(1)-C(2)-C(7)	80.1(13)
C(3)-Fe(1)-C(2)-C(7)	118.5(11)
C(11)-Fe(1)-C(2)-C(7)	-44.1(10)
C(13)-Fe(1)-C(2)-C(7)	42.7(10)
C(15)-Fe(1)-C(2)-C(7)	-84.6(12)
C(12)-Fe(1)-C(2)-C(7)	-0.2(10)
C(1)-C(2)-C(3)-C(4)	0.4(9)
C(7)-C(2)-C(3)-C(4)	179.4(7)
Fe(1)-C(2)-C(3)-C(4)	-58.9(5)
C(1)-C(2)-C(3)-C(8)	-177.0(8)
C(7)-C(2)-C(3)-C(8)	2.0(14)
Fe(1)-C(2)-C(3)-C(8)	123.7(9)
C(1)-C(2)-C(3)-Fe(1)	59.3(5)
C(7)-C(2)-C(3)-Fe(1)	-121.7(8)
C(5)-Fe(1)-C(3)-C(2)	-80.7(5)
C(1)-Fe(1)-C(3)-C(2)	-37.2(4)
C(4)-Fe(1)-C(3)-C(2)	-118.4(6)
C(14)-Fe(1)-C(3)-C(2)	166.3(5)
C(11)-Fe(1)-C(3)-C(2)	47.5(10)
C(13)-Fe(1)-C(3)-C(2)	124.5(5)
C(15)-Fe(1)-C(3)-C(2)	-156.2(7)
C(12)-Fe(1)-C(3)-C(2)	82.3(5)
C(5)-Fe(1)-C(3)-C(4)	37.7(4)
C(1)-Fe(1)-C(3)-C(4)	81.2(5)
C(2)-Fe(1)-C(3)-C(4)	118.4(6)

C(14)-Fe(1)-C(3)-C(4)	-75.3(5)
C(11)-Fe(1)-C(3)-C(4)	165.9(7)
C(13)-Fe(1)-C(3)-C(4)	-117.1(4)
C(15)-Fe(1)-C(3)-C(4)	-37.8(10)
C(12)-Fe(1)-C(3)-C(4)	-159.3(4)
C(5)-Fe(1)-C(3)-C(8)	155.2(9)
C(1)-Fe(1)-C(3)-C(8)	-161.3(9)
C(4)-Fe(1)-C(3)-C(8)	117.5(10)
C(2)-Fe(1)-C(3)-C(8)	-124.1(10)
C(14)-Fe(1)-C(3)-C(8)	42.2(9)
C(11)-Fe(1)-C(3)-C(8)	-76.6(13)
C(13)-Fe(1)-C(3)-C(8)	0.4(9)
C(15)-Fe(1)-C(3)-C(8)	79.7(11)
C(12)-Fe(1)-C(3)-C(8)	-41.8(9)
C(2)-C(3)-C(4)-C(5)	-0.1(8)
C(8)-C(3)-C(4)-C(5)	177.3(8)
Fe(1)-C(3)-C(4)-C(5)	-59.5(5)
C(2)-C(3)-C(4)-C(9)	-177.2(8)
C(8)-C(3)-C(4)-C(9)	0.3(13)
Fe(1)-C(3)-C(4)-C(9)	123.4(8)
C(2)-C(3)-C(4)-Fe(1)	59.3(5)
C(8)-C(3)-C(4)-Fe(1)	-123.2(8)
C(1)-Fe(1)-C(4)-C(5)	37.1(4)
C(2)-Fe(1)-C(4)-C(5)	80.5(5)
C(14)-Fe(1)-C(4)-C(5)	-118.3(4)
C(3)-Fe(1)-C(4)-C(5)	118.3(6)
C(11)-Fe(1)-C(4)-C(5)	-49.8(9)

C(13)-Fe(1)-C(4)-C(5)	-159.0(4)
C(15)-Fe(1)-C(4)-C(5)	-76.8(5)
C(12)-Fe(1)-C(4)-C(5)	173.3(7)
C(5)-Fe(1)-C(4)-C(3)	-118.3(6)
C(1)-Fe(1)-C(4)-C(3)	-81.3(5)
C(2)-Fe(1)-C(4)-C(3)	-37.9(5)
C(14)-Fe(1)-C(4)-C(3)	123.3(5)
C(11)-Fe(1)-C(4)-C(3)	-168.1(6)
C(13)-Fe(1)-C(4)-C(3)	82.7(5)
C(15)-Fe(1)-C(4)-C(3)	164.9(4)
C(12)-Fe(1)-C(4)-C(3)	55.0(9)
C(5)-Fe(1)-C(4)-C(9)	122.6(9)
C(1)-Fe(1)-C(4)-C(9)	159.6(8)
C(2)-Fe(1)-C(4)-C(9)	-157.0(8)
C(14)-Fe(1)-C(4)-C(9)	4.2(8)
C(3)-Fe(1)-C(4)-C(9)	-119.1(9)
C(11)-Fe(1)-C(4)-C(9)	72.8(10)
C(13)-Fe(1)-C(4)-C(9)	-36.4(8)
C(15)-Fe(1)-C(4)-C(9)	45.8(8)
C(12)-Fe(1)-C(4)-C(9)	-64.1(12)
C(3)-C(4)-C(5)-C(1)	-0.1(9)
C(9)-C(4)-C(5)-C(1)	176.8(8)
Fe(1)-C(4)-C(5)-C(1)	-59.6(5)
C(3)-C(4)-C(5)-C(10)	-178.2(7)
C(9)-C(4)-C(5)-C(10)	-1.3(13)
Fe(1)-C(4)-C(5)-C(10)	122.3(8)
C(3)-C(4)-C(5)-Fe(1)	59.5(5)

C(9)-C(4)-C(5)-Fe(1)	-123.6(8)
C(2)-C(1)-C(5)-C(4)	0.4(9)
C(6)-C(1)-C(5)-C(4)	-179.7(7)
Fe(1)-C(1)-C(5)-C(4)	59.6(5)
C(2)-C(1)-C(5)-C(10)	178.4(7)
C(6)-C(1)-C(5)-C(10)	-1.6(12)
Fe(1)-C(1)-C(5)-C(10)	-122.3(8)
C(2)-C(1)-C(5)-Fe(1)	-59.3(5)
C(6)-C(1)-C(5)-Fe(1)	120.7(7)
C(1)-Fe(1)-C(5)-C(4)	-120.2(6)
C(2)-Fe(1)-C(5)-C(4)	-82.9(5)
C(14)-Fe(1)-C(5)-C(4)	78.7(5)
C(3)-Fe(1)-C(5)-C(4)	-39.0(4)
C(11)-Fe(1)-C(5)-C(4)	159.1(4)
C(13)-Fe(1)-C(5)-C(4)	49.0(9)
C(15)-Fe(1)-C(5)-C(4)	119.3(4)
C(12)-Fe(1)-C(5)-C(4)	-172.9(7)
C(4)-Fe(1)-C(5)-C(1)	120.2(6)
C(2)-Fe(1)-C(5)-C(1)	37.3(4)
C(14)-Fe(1)-C(5)-C(1)	-161.2(4)
C(3)-Fe(1)-C(5)-C(1)	81.1(5)
C(11)-Fe(1)-C(5)-C(1)	-80.8(5)
C(13)-Fe(1)-C(5)-C(1)	169.2(7)
C(15)-Fe(1)-C(5)-C(1)	-120.5(4)
C(12)-Fe(1)-C(5)-C(1)	-52.7(10)
C(1)-Fe(1)-C(5)-C(10)	120.8(8)
C(4)-Fe(1)-C(5)-C(10)	-119.0(8)

C(2)-Fe(1)-C(5)-C(10)	158.1(7)
C(14)-Fe(1)-C(5)-C(10)	-40.4(7)
C(3)-Fe(1)-C(5)-C(10)	-158.0(7)
C(11)-Fe(1)-C(5)-C(10)	40.0(7)
C(13)-Fe(1)-C(5)-C(10)	-70.0(10)
C(15)-Fe(1)-C(5)-C(10)	0.3(7)
C(12)-Fe(1)-C(5)-C(10)	68.1(11)
C(18)-N(1)-C(11)-C(15)	179.9(7)
C(18)-N(1)-C(11)-C(12)	-1.8(9)
C(18)-N(1)-C(11)-Fe(1)	85.3(7)
C(5)-Fe(1)-C(11)-N(1)	53.0(6)
C(1)-Fe(1)-C(11)-N(1)	10.6(6)
C(4)-Fe(1)-C(11)-N(1)	88.8(8)
C(2)-Fe(1)-C(11)-N(1)	-31.3(7)
C(14)-Fe(1)-C(11)-N(1)	165.3(6)
C(3)-Fe(1)-C(11)-N(1)	-67.0(11)
C(13)-Fe(1)-C(11)-N(1)	-151.1(6)
C(15)-Fe(1)-C(11)-N(1)	126.3(7)
C(12)-Fe(1)-C(11)-N(1)	-113.0(7)
C(5)-Fe(1)-C(11)-C(15)	-73.3(5)
C(1)-Fe(1)-C(11)-C(15)	-115.7(4)
C(4)-Fe(1)-C(11)-C(15)	-37.5(8)
C(2)-Fe(1)-C(11)-C(15)	-157.6(4)
C(14)-Fe(1)-C(11)-C(15)	39.0(4)
C(3)-Fe(1)-C(11)-C(15)	166.7(8)
C(13)-Fe(1)-C(11)-C(15)	82.6(4)
C(12)-Fe(1)-C(11)-C(15)	120.6(5)

C(5)-Fe(1)-C(11)-C(12)	166.1(4)
C(1)-Fe(1)-C(11)-C(12)	123.6(4)
C(4)-Fe(1)-C(11)-C(12)	-158.1(6)
C(2)-Fe(1)-C(11)-C(12)	81.8(5)
C(14)-Fe(1)-C(11)-C(12)	-81.6(4)
C(3)-Fe(1)-C(11)-C(12)	46.1(10)
C(13)-Fe(1)-C(11)-C(12)	-38.1(4)
C(15)-Fe(1)-C(11)-C(12)	-120.6(5)
N(1)-C(11)-C(12)-C(16)	1.6(9)
C(15)-C(11)-C(12)-C(16)	-179.8(6)
Fe(1)-C(11)-C(12)-C(16)	-120.2(6)
N(1)-C(11)-C(12)-C(13)	-179.7(6)
C(15)-C(11)-C(12)-C(13)	-1.0(8)
Fe(1)-C(11)-C(12)-C(13)	58.5(5)
N(1)-C(11)-C(12)-Fe(1)	121.8(6)
C(15)-C(11)-C(12)-Fe(1)	-59.6(5)
C(5)-Fe(1)-C(12)-C(16)	73.5(10)
C(1)-Fe(1)-C(12)-C(16)	34.0(7)
C(4)-Fe(1)-C(12)-C(16)	-93.6(9)
C(2)-Fe(1)-C(12)-C(16)	-8.8(6)
C(14)-Fe(1)-C(12)-C(16)	-169.0(6)
C(3)-Fe(1)-C(12)-C(16)	-52.4(7)
C(11)-Fe(1)-C(12)-C(16)	110.8(7)
C(13)-Fe(1)-C(12)-C(16)	-131.1(8)
C(15)-Fe(1)-C(12)-C(16)	147.3(6)
C(5)-Fe(1)-C(12)-C(13)	-155.5(8)
C(1)-Fe(1)-C(12)-C(13)	165.1(4)

C(4)-Fe(1)-C(12)-C(13)	37.5(10)
C(2)-Fe(1)-C(12)-C(13)	122.3(5)
C(14)-Fe(1)-C(12)-C(13)	-37.9(4)
C(3)-Fe(1)-C(12)-C(13)	78.7(5)
C(11)-Fe(1)-C(12)-C(13)	-118.2(6)
C(15)-Fe(1)-C(12)-C(13)	-81.6(4)
C(5)-Fe(1)-C(12)-C(11)	-37.3(10)
C(1)-Fe(1)-C(12)-C(11)	-76.8(5)
C(4)-Fe(1)-C(12)-C(11)	155.7(7)
C(2)-Fe(1)-C(12)-C(11)	-119.5(4)
C(14)-Fe(1)-C(12)-C(11)	80.3(4)
C(3)-Fe(1)-C(12)-C(11)	-163.1(4)
C(13)-Fe(1)-C(12)-C(11)	118.2(6)
C(15)-Fe(1)-C(12)-C(11)	36.6(4)
C(16)-C(12)-C(13)-C(14)	179.9(8)
C(11)-C(12)-C(13)-C(14)	1.5(8)
Fe(1)-C(12)-C(13)-C(14)	59.7(5)
C(16)-C(12)-C(13)-Fe(1)	120.2(8)
C(11)-C(12)-C(13)-Fe(1)	-58.2(5)
C(5)-Fe(1)-C(13)-C(14)	41.5(9)
C(1)-Fe(1)-C(13)-C(14)	-162.4(9)
C(4)-Fe(1)-C(13)-C(14)	76.6(5)
C(2)-Fe(1)-C(13)-C(14)	162.6(4)
C(3)-Fe(1)-C(13)-C(14)	120.8(5)
C(11)-Fe(1)-C(13)-C(14)	-79.7(4)
C(15)-Fe(1)-C(13)-C(14)	-36.3(4)
C(12)-Fe(1)-C(13)-C(14)	-118.3(6)

C(5)-Fe(1)-C(13)-C(12)	159.8(6)
C(1)-Fe(1)-C(13)-C(12)	-44.1(11)
C(4)-Fe(1)-C(13)-C(12)	-165.2(4)
C(2)-Fe(1)-C(13)-C(12)	-79.1(5)
C(14)-Fe(1)-C(13)-C(12)	118.3(6)
C(3)-Fe(1)-C(13)-C(12)	-120.9(4)
C(11)-Fe(1)-C(13)-C(12)	38.6(4)
C(15)-Fe(1)-C(13)-C(12)	82.0(4)
C(12)-C(13)-C(14)-C(15)	-1.4(9)
Fe(1)-C(13)-C(14)-C(15)	59.4(5)
C(12)-C(13)-C(14)-Fe(1)	-60.8(5)
C(5)-Fe(1)-C(14)-C(13)	-162.0(4)
C(1)-Fe(1)-C(14)-C(13)	167.1(6)
C(4)-Fe(1)-C(14)-C(13)	-120.7(4)
C(2)-Fe(1)-C(14)-C(13)	-49.4(11)
C(3)-Fe(1)-C(14)-C(13)	-78.6(5)
C(11)-Fe(1)-C(14)-C(13)	82.9(4)
C(15)-Fe(1)-C(14)-C(13)	121.7(6)
C(12)-Fe(1)-C(14)-C(13)	38.2(4)
C(5)-Fe(1)-C(14)-C(15)	76.3(5)
C(1)-Fe(1)-C(14)-C(15)	45.4(9)
C(4)-Fe(1)-C(14)-C(15)	117.6(4)
C(2)-Fe(1)-C(14)-C(15)	-171.1(8)
C(3)-Fe(1)-C(14)-C(15)	159.7(4)
C(11)-Fe(1)-C(14)-C(15)	-38.8(4)
C(13)-Fe(1)-C(14)-C(15)	-121.7(6)
C(12)-Fe(1)-C(14)-C(15)	-83.5(4)

N(1)-C(11)-C(15)-C(14)	178.6(7)
C(12)-C(11)-C(15)-C(14)	0.2(8)
Fe(1)-C(11)-C(15)-C(14)	-59.7(5)
N(1)-C(11)-C(15)-Fe(1)	-121.7(7)
C(12)-C(11)-C(15)-Fe(1)	59.9(5)
C(13)-C(14)-C(15)-C(11)	0.8(8)
Fe(1)-C(14)-C(15)-C(11)	60.1(5)
C(13)-C(14)-C(15)-Fe(1)	-59.4(6)
C(5)-Fe(1)-C(15)-C(11)	123.3(4)
C(1)-Fe(1)-C(15)-C(11)	82.9(4)
C(4)-Fe(1)-C(15)-C(11)	163.9(4)
C(2)-Fe(1)-C(15)-C(11)	55.8(9)
C(14)-Fe(1)-C(15)-C(11)	-116.8(6)
C(3)-Fe(1)-C(15)-C(11)	-168.0(7)
C(13)-Fe(1)-C(15)-C(11)	-80.8(4)
C(12)-Fe(1)-C(15)-C(11)	-37.2(4)
C(5)-Fe(1)-C(15)-C(14)	-119.9(4)
C(1)-Fe(1)-C(15)-C(14)	-160.4(4)
C(4)-Fe(1)-C(15)-C(14)	-79.3(5)
C(2)-Fe(1)-C(15)-C(14)	172.6(7)
C(3)-Fe(1)-C(15)-C(14)	-51.2(9)
C(11)-Fe(1)-C(15)-C(14)	116.8(6)
C(13)-Fe(1)-C(15)-C(14)	36.0(4)
C(12)-Fe(1)-C(15)-C(14)	79.5(4)
C(13)-C(12)-C(16)-C(17)	-178.9(7)
C(11)-C(12)-C(16)-C(17)	-0.6(9)
Fe(1)-C(12)-C(16)-C(17)	-83.6(7)

C(13)-C(12)-C(16)-C(19)	0.9(12)
C(11)-C(12)-C(16)-C(19)	179.2(6)
Fe(1)-C(12)-C(16)-C(19)	96.2(7)
C(12)-C(16)-C(17)-C(18)	-0.2(10)
C(19)-C(16)-C(17)-C(18)	180.0(7)
C(11)-N(1)-C(18)-C(17)	1.0(9)
C(11)-N(1)-C(18)-C(20)	-178.7(6)
C(16)-C(17)-C(18)-N(1)	0.1(10)
C(16)-C(17)-C(18)-C(20)	179.8(6)
N(1)-C(18)-C(20)-P(1)	106.2(5)
C(17)-C(18)-C(20)-P(1)	-73.5(7)
C(21)-P(1)-C(20)-C(18)	76.5(5)
C(27)-P(1)-C(20)-C(18)	-179.0(5)
C(27)-P(1)-C(21)-C(26)	-56.4(6)
C(20)-P(1)-C(21)-C(26)	46.5(6)
C(27)-P(1)-C(21)-C(22)	126.0(6)
C(20)-P(1)-C(21)-C(22)	-131.1(5)
C(26)-C(21)-C(22)-C(23)	-0.5(10)
P(1)-C(21)-C(22)-C(23)	177.3(6)
C(21)-C(22)-C(23)-C(24)	-0.1(12)
C(22)-C(23)-C(24)-C(25)	0.6(12)
C(23)-C(24)-C(25)-C(26)	-0.5(11)
C(24)-C(25)-C(26)-C(21)	-0.1(10)
C(22)-C(21)-C(26)-C(25)	0.6(9)
P(1)-C(21)-C(26)-C(25)	-177.0(5)
C(21)-P(1)-C(27)-C(32)	90.9(8)
C(20)-P(1)-C(27)-C(32)	-12.3(8)

C(21)-P(1)-C(27)-C(28)	-91.9(6)
C(20)-P(1)-C(27)-C(28)	164.9(6)
C(32)-C(27)-C(28)-C(29)	-2.2(11)
P(1)-C(27)-C(28)-C(29)	-179.6(6)
C(27)-C(28)-C(29)-C(30)	0.8(12)
C(28)-C(29)-C(30)-C(31)	1.2(13)
C(29)-C(30)-C(31)-C(32)	-1.7(13)
C(28)-C(27)-C(32)-C(31)	1.7(13)
P(1)-C(27)-C(32)-C(31)	178.8(7)
C(30)-C(31)-C(32)-C(27)	0.2(14)
O(1)-S(1)-C(33)-C(38)	94.7(6)
O(2)-S(1)-C(33)-C(38)	-142.1(6)
O(3)-S(1)-C(33)-C(38)	-24.5(7)
O(1)-S(1)-C(33)-C(34)	-84.1(7)
O(2)-S(1)-C(33)-C(34)	39.2(7)
O(3)-S(1)-C(33)-C(34)	156.8(7)
C(38)-C(33)-C(34)-C(35)	0.3(12)
S(1)-C(33)-C(34)-C(35)	179.1(7)
C(33)-C(34)-C(35)-C(36)	-0.5(16)
C(34)-C(35)-C(36)-C(37)	0.2(17)
C(34)-C(35)-C(36)-C(39)	179.6(10)
C(35)-C(36)-C(37)-C(38)	0.4(15)
C(39)-C(36)-C(37)-C(38)	-179.0(10)
C(34)-C(33)-C(38)-C(37)	0.3(11)
S(1)-C(33)-C(38)-C(37)	-178.5(6)
C(36)-C(37)-C(38)-C(33)	-0.6(13)
C(64)-Fe(2)-C(51)-C(55)	41.1(8)

C(53)-Fe(2)-C(51)-C(55)	-81.5(4)
C(54)-Fe(2)-C(51)-C(55)	-37.6(4)
C(65)-Fe(2)-C(51)-C(55)	76.7(4)
C(52)-Fe(2)-C(51)-C(55)	-118.1(5)
C(63)-Fe(2)-C(51)-C(55)	-158.9(9)
C(61)-Fe(2)-C(51)-C(55)	119.8(4)
C(62)-Fe(2)-C(51)-C(55)	162.1(4)
C(55)-Fe(2)-C(51)-C(52)	118.1(5)
C(64)-Fe(2)-C(51)-C(52)	159.2(6)
C(53)-Fe(2)-C(51)-C(52)	36.6(4)
C(54)-Fe(2)-C(51)-C(52)	80.5(4)
C(65)-Fe(2)-C(51)-C(52)	-165.1(4)
C(63)-Fe(2)-C(51)-C(52)	-40.8(11)
C(61)-Fe(2)-C(51)-C(52)	-122.1(4)
C(62)-Fe(2)-C(51)-C(52)	-79.8(5)
C(55)-Fe(2)-C(51)-C(56)	-120.4(8)
C(64)-Fe(2)-C(51)-C(56)	-79.3(10)
C(53)-Fe(2)-C(51)-C(56)	158.1(8)
C(54)-Fe(2)-C(51)-C(56)	-158.0(8)
C(65)-Fe(2)-C(51)-C(56)	-43.7(8)
C(52)-Fe(2)-C(51)-C(56)	121.4(8)
C(63)-Fe(2)-C(51)-C(56)	80.6(12)
C(61)-Fe(2)-C(51)-C(56)	-0.7(8)
C(62)-Fe(2)-C(51)-C(56)	41.6(8)
C(55)-C(51)-C(52)-C(53)	2.2(8)
C(56)-C(51)-C(52)-C(53)	178.0(7)
Fe(2)-C(51)-C(52)-C(53)	-58.2(5)

C(55)-C(51)-C(52)-C(57)	-179.3(7)
C(56)-C(51)-C(52)-C(57)	-3.4(12)
Fe(2)-C(51)-C(52)-C(57)	120.3(7)
C(55)-C(51)-C(52)-Fe(2)	60.4(5)
C(56)-C(51)-C(52)-Fe(2)	-123.7(7)
C(51)-Fe(2)-C(52)-C(53)	120.3(6)
C(55)-Fe(2)-C(52)-C(53)	82.0(4)
C(64)-Fe(2)-C(52)-C(53)	-34.6(10)
C(54)-Fe(2)-C(52)-C(53)	37.5(4)
C(65)-Fe(2)-C(52)-C(53)	158.1(7)
C(63)-Fe(2)-C(52)-C(53)	-73.3(5)
C(61)-Fe(2)-C(52)-C(53)	-159.7(4)
C(62)-Fe(2)-C(52)-C(53)	-116.9(4)
C(55)-Fe(2)-C(52)-C(51)	-38.3(4)
C(64)-Fe(2)-C(52)-C(51)	-154.9(8)
C(53)-Fe(2)-C(52)-C(51)	-120.3(6)
C(54)-Fe(2)-C(52)-C(51)	-82.8(4)
C(65)-Fe(2)-C(52)-C(51)	37.8(9)
C(63)-Fe(2)-C(52)-C(51)	166.4(4)
C(61)-Fe(2)-C(52)-C(51)	80.0(4)
C(62)-Fe(2)-C(52)-C(51)	122.9(4)
C(51)-Fe(2)-C(52)-C(57)	-118.7(8)
C(55)-Fe(2)-C(52)-C(57)	-157.0(8)
C(64)-Fe(2)-C(52)-C(57)	86.4(11)
C(53)-Fe(2)-C(52)-C(57)	121.0(9)
C(54)-Fe(2)-C(52)-C(57)	158.5(8)
C(65)-Fe(2)-C(52)-C(57)	-80.9(11)

C(63)-Fe(2)-C(52)-C(57)	47.7(8)
C(61)-Fe(2)-C(52)-C(57)	-38.7(8)
C(62)-Fe(2)-C(52)-C(57)	4.1(8)
C(51)-C(52)-C(53)-C(54)	-1.7(8)
C(57)-C(52)-C(53)-C(54)	179.8(7)
Fe(2)-C(52)-C(53)-C(54)	-59.3(5)
C(51)-C(52)-C(53)-C(58)	-179.9(7)
C(57)-C(52)-C(53)-C(58)	1.5(12)
Fe(2)-C(52)-C(53)-C(58)	122.5(7)
C(51)-C(52)-C(53)-Fe(2)	57.6(5)
C(57)-C(52)-C(53)-Fe(2)	-120.9(8)
C(51)-Fe(2)-C(53)-C(52)	-37.4(4)
C(55)-Fe(2)-C(53)-C(52)	-81.3(4)
C(64)-Fe(2)-C(53)-C(52)	166.7(4)
C(54)-Fe(2)-C(53)-C(52)	-120.1(6)
C(65)-Fe(2)-C(53)-C(52)	-159.0(7)
C(63)-Fe(2)-C(53)-C(52)	125.2(4)
C(61)-Fe(2)-C(53)-C(52)	55.3(9)
C(62)-Fe(2)-C(53)-C(52)	84.2(5)
C(51)-Fe(2)-C(53)-C(54)	82.7(4)
C(55)-Fe(2)-C(53)-C(54)	38.8(4)
C(64)-Fe(2)-C(53)-C(54)	-73.2(5)
C(65)-Fe(2)-C(53)-C(54)	-38.9(9)
C(52)-Fe(2)-C(53)-C(54)	120.1(6)
C(63)-Fe(2)-C(53)-C(54)	-114.7(4)
C(61)-Fe(2)-C(53)-C(54)	175.4(7)
C(62)-Fe(2)-C(53)-C(54)	-155.7(4)

C(51)-Fe(2)-C(53)-C(58)	-160.0(8)
C(55)-Fe(2)-C(53)-C(58)	156.1(8)
C(64)-Fe(2)-C(53)-C(58)	44.1(8)
C(54)-Fe(2)-C(53)-C(58)	117.3(9)
C(65)-Fe(2)-C(53)-C(58)	78.4(11)
C(52)-Fe(2)-C(53)-C(58)	-122.6(9)
C(63)-Fe(2)-C(53)-C(58)	2.6(8)
C(61)-Fe(2)-C(53)-C(58)	-67.3(12)
C(62)-Fe(2)-C(53)-C(58)	-38.4(8)
C(52)-C(53)-C(54)-C(55)	0.5(8)
C(58)-C(53)-C(54)-C(55)	178.9(6)
Fe(2)-C(53)-C(54)-C(55)	-59.2(5)
C(52)-C(53)-C(54)-C(59)	-179.4(7)
C(58)-C(53)-C(54)-C(59)	-1.1(12)
Fe(2)-C(53)-C(54)-C(59)	120.8(7)
C(52)-C(53)-C(54)-Fe(2)	59.8(5)
C(58)-C(53)-C(54)-Fe(2)	-121.9(7)
C(51)-Fe(2)-C(54)-C(53)	-80.7(4)
C(55)-Fe(2)-C(54)-C(53)	-117.8(5)
C(64)-Fe(2)-C(54)-C(53)	123.7(4)
C(65)-Fe(2)-C(54)-C(53)	164.2(4)
C(52)-Fe(2)-C(54)-C(53)	-36.7(4)
C(63)-Fe(2)-C(54)-C(53)	82.7(5)
C(61)-Fe(2)-C(54)-C(53)	-175.7(6)
C(62)-Fe(2)-C(54)-C(53)	58.1(8)
C(51)-Fe(2)-C(54)-C(55)	37.2(4)
C(64)-Fe(2)-C(54)-C(55)	-118.5(4)

C(53)-Fe(2)-C(54)-C(55)	117.8(5)
C(65)-Fe(2)-C(54)-C(55)	-78.0(4)
C(52)-Fe(2)-C(54)-C(55)	81.1(4)
C(63)-Fe(2)-C(54)-C(55)	-159.4(4)
C(61)-Fe(2)-C(54)-C(55)	-57.9(8)
C(62)-Fe(2)-C(54)-C(55)	175.9(6)
C(51)-Fe(2)-C(54)-C(59)	158.7(8)
C(55)-Fe(2)-C(54)-C(59)	121.6(9)
C(64)-Fe(2)-C(54)-C(59)	3.1(8)
C(53)-Fe(2)-C(54)-C(59)	-120.6(8)
C(65)-Fe(2)-C(54)-C(59)	43.6(8)
C(52)-Fe(2)-C(54)-C(59)	-157.4(8)
C(63)-Fe(2)-C(54)-C(59)	-37.9(8)
C(61)-Fe(2)-C(54)-C(59)	63.7(11)
C(62)-Fe(2)-C(54)-C(59)	-62.6(11)
C(52)-C(51)-C(55)-C(54)	-1.8(8)
C(56)-C(51)-C(55)-C(54)	-177.7(7)
Fe(2)-C(51)-C(55)-C(54)	59.1(5)
C(52)-C(51)-C(55)-C(60)	175.7(7)
C(56)-C(51)-C(55)-C(60)	-0.2(12)
Fe(2)-C(51)-C(55)-C(60)	-123.4(7)
C(52)-C(51)-C(55)-Fe(2)	-61.0(5)
C(56)-C(51)-C(55)-Fe(2)	123.1(7)
C(53)-C(54)-C(55)-C(51)	0.8(8)
C(59)-C(54)-C(55)-C(51)	-179.3(7)
Fe(2)-C(54)-C(55)-C(51)	-58.8(5)
C(53)-C(54)-C(55)-C(60)	-176.7(7)

C(59)-C(54)-C(55)-C(60)	3.2(12)
Fe(2)-C(54)-C(55)-C(60)	123.6(7)
C(53)-C(54)-C(55)-Fe(2)	59.6(5)
C(59)-C(54)-C(55)-Fe(2)	-120.5(7)
C(64)-Fe(2)-C(55)-C(51)	-162.1(4)
C(53)-Fe(2)-C(55)-C(51)	81.6(4)
C(54)-Fe(2)-C(55)-C(51)	120.0(6)
C(65)-Fe(2)-C(55)-C(51)	-120.6(4)
C(52)-Fe(2)-C(55)-C(51)	38.4(4)
C(63)-Fe(2)-C(55)-C(51)	165.8(6)
C(61)-Fe(2)-C(55)-C(51)	-81.9(5)
C(62)-Fe(2)-C(55)-C(51)	-54.4(10)
C(51)-Fe(2)-C(55)-C(54)	-120.0(6)
C(64)-Fe(2)-C(55)-C(54)	77.9(5)
C(53)-Fe(2)-C(55)-C(54)	-38.4(4)
C(65)-Fe(2)-C(55)-C(54)	119.4(4)
C(52)-Fe(2)-C(55)-C(54)	-81.6(4)
C(63)-Fe(2)-C(55)-C(54)	45.8(8)
C(61)-Fe(2)-C(55)-C(54)	158.1(4)
C(62)-Fe(2)-C(55)-C(54)	-174.5(8)
C(51)-Fe(2)-C(55)-C(60)	120.8(8)
C(64)-Fe(2)-C(55)-C(60)	-41.3(8)
C(53)-Fe(2)-C(55)-C(60)	-157.7(8)
C(54)-Fe(2)-C(55)-C(60)	-119.2(8)
C(65)-Fe(2)-C(55)-C(60)	0.2(7)
C(52)-Fe(2)-C(55)-C(60)	159.1(7)
C(63)-Fe(2)-C(55)-C(60)	-73.4(10)

C(61)-Fe(2)-C(55)-C(60)	38.8(8)
C(62)-Fe(2)-C(55)-C(60)	66.3(12)
C(68)-N(2)-C(61)-C(65)	-179.4(7)
C(68)-N(2)-C(61)-C(62)	0.5(9)
C(68)-N(2)-C(61)-Fe(2)	86.9(7)
C(51)-Fe(2)-C(61)-C(65)	-114.3(4)
C(55)-Fe(2)-C(61)-C(65)	-70.5(5)
C(64)-Fe(2)-C(61)-C(65)	39.8(4)
C(53)-Fe(2)-C(61)-C(65)	160.8(7)
C(54)-Fe(2)-C(61)-C(65)	-27.5(9)
C(52)-Fe(2)-C(61)-C(65)	-158.0(4)
C(63)-Fe(2)-C(61)-C(65)	84.0(4)
C(62)-Fe(2)-C(61)-C(65)	122.0(5)
C(51)-Fe(2)-C(61)-N(2)	11.2(6)
C(55)-Fe(2)-C(61)-N(2)	55.0(6)
C(64)-Fe(2)-C(61)-N(2)	165.3(6)
C(53)-Fe(2)-C(61)-N(2)	-73.6(10)
C(54)-Fe(2)-C(61)-N(2)	98.1(8)
C(65)-Fe(2)-C(61)-N(2)	125.5(7)
C(52)-Fe(2)-C(61)-N(2)	-32.4(6)
C(63)-Fe(2)-C(61)-N(2)	-150.5(6)
C(62)-Fe(2)-C(61)-N(2)	-112.5(7)
C(51)-Fe(2)-C(61)-C(62)	123.7(4)
C(55)-Fe(2)-C(61)-C(62)	167.5(4)
C(64)-Fe(2)-C(61)-C(62)	-82.2(4)
C(53)-Fe(2)-C(61)-C(62)	38.8(9)
C(54)-Fe(2)-C(61)-C(62)	-149.5(6)

C(65)-Fe(2)-C(61)-C(62)	-122.0(5)
C(52)-Fe(2)-C(61)-C(62)	80.0(5)
C(63)-Fe(2)-C(61)-C(62)	-38.0(4)
C(65)-C(61)-C(62)-C(63)	1.1(8)
N(2)-C(61)-C(62)-C(63)	-178.8(6)
Fe(2)-C(61)-C(62)-C(63)	59.5(5)
C(65)-C(61)-C(62)-C(66)	-179.5(6)
N(2)-C(61)-C(62)-C(66)	0.6(9)
Fe(2)-C(61)-C(62)-C(66)	-121.1(6)
C(65)-C(61)-C(62)-Fe(2)	-58.3(5)
N(2)-C(61)-C(62)-Fe(2)	121.8(6)
C(51)-Fe(2)-C(62)-C(61)	-78.0(5)
C(55)-Fe(2)-C(62)-C(61)	-36.0(11)
C(64)-Fe(2)-C(62)-C(61)	79.7(4)
C(53)-Fe(2)-C(62)-C(61)	-165.2(4)
C(54)-Fe(2)-C(62)-C(61)	153.0(6)
C(65)-Fe(2)-C(62)-C(61)	35.7(4)
C(52)-Fe(2)-C(62)-C(61)	-121.8(4)
C(63)-Fe(2)-C(62)-C(61)	118.6(6)
C(51)-Fe(2)-C(62)-C(63)	163.4(4)
C(55)-Fe(2)-C(62)-C(63)	-154.6(8)
C(64)-Fe(2)-C(62)-C(63)	-38.9(4)
C(53)-Fe(2)-C(62)-C(63)	76.2(5)
C(54)-Fe(2)-C(62)-C(63)	34.5(9)
C(65)-Fe(2)-C(62)-C(63)	-82.9(5)
C(52)-Fe(2)-C(62)-C(63)	119.6(5)
C(61)-Fe(2)-C(62)-C(63)	-118.6(6)

C(51)-Fe(2)-C(62)-C(66)	34.3(7)
C(55)-Fe(2)-C(62)-C(66)	76.2(11)
C(64)-Fe(2)-C(62)-C(66)	-168.0(6)
C(53)-Fe(2)-C(62)-C(66)	-53.0(6)
C(54)-Fe(2)-C(62)-C(66)	-94.7(8)
C(65)-Fe(2)-C(62)-C(66)	148.0(6)
C(52)-Fe(2)-C(62)-C(66)	-9.5(6)
C(63)-Fe(2)-C(62)-C(66)	-129.2(7)
C(61)-Fe(2)-C(62)-C(66)	112.3(7)
C(61)-C(62)-C(63)-C(64)	0.2(8)
C(66)-C(62)-C(63)-C(64)	-179.1(7)
Fe(2)-C(62)-C(63)-C(64)	59.9(5)
C(61)-C(62)-C(63)-Fe(2)	-59.6(5)
C(66)-C(62)-C(63)-Fe(2)	121.1(8)
C(51)-Fe(2)-C(63)-C(64)	-167.6(9)
C(55)-Fe(2)-C(63)-C(64)	45.5(8)
C(53)-Fe(2)-C(63)-C(64)	120.8(4)
C(54)-Fe(2)-C(63)-C(64)	78.1(5)
C(65)-Fe(2)-C(63)-C(64)	-36.5(4)
C(52)-Fe(2)-C(63)-C(64)	160.8(4)
C(61)-Fe(2)-C(63)-C(64)	-79.4(4)
C(62)-Fe(2)-C(63)-C(64)	-117.0(6)
C(51)-Fe(2)-C(63)-C(62)	-50.5(11)
C(55)-Fe(2)-C(63)-C(62)	162.5(6)
C(64)-Fe(2)-C(63)-C(62)	117.0(6)
C(53)-Fe(2)-C(63)-C(62)	-122.2(4)
C(54)-Fe(2)-C(63)-C(62)	-164.9(4)

C(63)-C(64)-C(65)-C(61)	2.2(8)
Fe(2)-C(64)-C(65)-C(61)	61.6(5)
C(63)-C(64)-C(65)-Fe(2)	-59.4(5)
C(51)-Fe(2)-C(65)-C(61)	85.6(4)
C(55)-Fe(2)-C(65)-C(61)	126.8(4)
C(64)-Fe(2)-C(65)-C(61)	-115.8(6)
C(53)-Fe(2)-C(65)-C(61)	-162.6(6)
C(54)-Fe(2)-C(65)-C(61)	168.8(4)
C(52)-Fe(2)-C(65)-C(61)	57.6(9)
C(63)-Fe(2)-C(65)-C(61)	-79.3(4)
C(62)-Fe(2)-C(65)-C(61)	-35.9(4)
C(51)-Fe(2)-C(65)-C(64)	-158.6(4)
C(55)-Fe(2)-C(65)-C(64)	-117.3(4)
C(53)-Fe(2)-C(65)-C(64)	-46.8(9)
C(54)-Fe(2)-C(65)-C(64)	-75.4(5)
C(52)-Fe(2)-C(65)-C(64)	173.4(7)
C(63)-Fe(2)-C(65)-C(64)	36.5(4)
C(61)-Fe(2)-C(65)-C(64)	115.8(6)
C(62)-Fe(2)-C(65)-C(64)	79.9(4)
C(61)-C(62)-C(66)-C(67)	-0.5(9)
C(63)-C(62)-C(66)-C(67)	178.7(7)
Fe(2)-C(62)-C(66)-C(67)	-86.0(7)
C(61)-C(62)-C(66)-C(69)	-178.6(6)
C(63)-C(62)-C(66)-C(69)	0.6(12)
Fe(2)-C(62)-C(66)-C(69)	96.0(7)
C(62)-C(66)-C(67)-C(68)	-0.7(10)
C(69)-C(66)-C(67)-C(68)	177.3(6)

C(65)-Fe(2)-C(63)-C(62)	80.5(4)
C(52)-Fe(2)-C(63)-C(62)	-82.1(5)
C(61)-Fe(2)-C(63)-C(62)	37.7(4)
C(62)-C(63)-C(64)-C(65)	-1.5(8)
Fe(2)-C(63)-C(64)-C(65)	59.3(5)
C(62)-C(63)-C(64)-Fe(2)	-60.8(5)
C(51)-Fe(2)-C(64)-C(63)	171.1(6)
C(55)-Fe(2)-C(64)-C(63)	-159.4(4)
C(53)-Fe(2)-C(64)-C(63)	-77.5(5)
C(54)-Fe(2)-C(64)-C(63)	-117.7(4)
C(65)-Fe(2)-C(64)-C(63)	121.3(6)
C(52)-Fe(2)-C(64)-C(63)	-51.8(10)
C(61)-Fe(2)-C(64)-C(63)	82.4(4)
C(62)-Fe(2)-C(64)-C(63)	38.7(4)
C(51)-Fe(2)-C(64)-C(65)	49.8(8)
C(55)-Fe(2)-C(64)-C(65)	79.3(4)
C(53)-Fe(2)-C(64)-C(65)	161.2(4)
C(54)-Fe(2)-C(64)-C(65)	121.0(4)
C(52)-Fe(2)-C(64)-C(65)	-173.1(7)
C(63)-Fe(2)-C(64)-C(65)	-121.3(6)
C(61)-Fe(2)-C(64)-C(65)	-38.9(4)
C(62)-Fe(2)-C(64)-C(65)	-82.6(4)
N(2)-C(61)-C(65)-C(64)	177.9(6)
C(62)-C(61)-C(65)-C(64)	-2.0(8)
Fe(2)-C(61)-C(65)-C(64)	-60.6(5)
N(2)-C(61)-C(65)-Fe(2)	-121.5(7)
C(62)-C(61)-C(65)-Fe(2)	58.6(5)

C(61)-N(2)-C(68)-C(67)	-1.7(9)
C(61)-N(2)-C(68)-C(70)	179.2(5)
C(66)-C(67)-C(68)-N(2)	1.8(10)
C(66)-C(67)-C(68)-C(70)	-179.1(6)
N(2)-C(68)-C(70)-P(2)	106.2(6)
C(67)-C(68)-C(70)-P(2)	-72.9(7)
C(71)-P(2)-C(70)-C(68)	76.7(5)
C(77)-P(2)-C(70)-C(68)	-178.8(4)
C(77)-P(2)-C(71)-C(72)	-54.1(6)
C(70)-P(2)-C(71)-C(72)	49.6(6)
C(77)-P(2)-C(71)-C(76)	129.1(5)
C(70)-P(2)-C(71)-C(76)	-127.2(5)
C(76)-C(71)-C(72)-C(73)	0.6(9)
P(2)-C(71)-C(72)-C(73)	-176.3(5)
C(71)-C(72)-C(73)-C(74)	-1.7(10)
C(72)-C(73)-C(74)-C(75)	1.5(11)
C(73)-C(74)-C(75)-C(76)	-0.2(13)
C(74)-C(75)-C(76)-C(71)	-1.0(12)
C(72)-C(71)-C(76)-C(75)	0.8(10)
P(2)-C(71)-C(76)-C(75)	177.8(6)
C(71)-P(2)-C(77)-C(78)	-92.4(6)
C(70)-P(2)-C(77)-C(78)	164.6(5)
C(71)-P(2)-C(77)-C(82)	90.2(7)
C(70)-P(2)-C(77)-C(82)	-12.9(7)
C(82)-C(77)-C(78)-C(79)	-1.1(11)
P(2)-C(77)-C(78)-C(79)	-178.8(6)
C(77)-C(78)-C(79)-C(80)	1.2(12)

C(78)-C(79)-C(80)-C(81)	0.3(12)
C(79)-C(80)-C(81)-C(82)	-1.8(12)
C(80)-C(81)-C(82)-C(77)	1.8(12)
C(78)-C(77)-C(82)-C(81)	-0.4(11)
P(2)-C(77)-C(82)-C(81)	177.1(6)
O(6)-S(2)-C(83)-C(88)	110.2(6)
O(5)-S(2)-C(83)-C(88)	-14.2(7)
O(4)-S(2)-C(83)-C(88)	-132.4(6)
O(6)-S(2)-C(83)-C(84)	-72.6(6)
O(5)-S(2)-C(83)-C(84)	163.0(6)
O(4)-S(2)-C(83)-C(84)	44.8(6)
C(88)-C(83)-C(84)-C(85)	-2.0(11)
S(2)-C(83)-C(84)-C(85)	-179.3(6)
C(83)-C(84)-C(85)-C(86)	-1.1(12)
C(84)-C(85)-C(86)-C(87)	2.5(13)
C(84)-C(85)-C(86)-C(89)	179.5(8)
C(85)-C(86)-C(87)-C(88)	-0.8(13)
C(89)-C(86)-C(87)-C(88)	-177.9(8)
C(84)-C(83)-C(88)-C(87)	3.7(11)
S(2)-C(83)-C(88)-C(87)	-179.1(6)
C(86)-C(87)-C(88)-C(83)	-2.3(12)

Symmetry transformations used to generate equivalent atoms:

Beata Tao

Education

1998-2002 **Massachusetts Institute of Technology, Massachusetts, USA**
- Ph.D. in Organic Chemistry
- Thesis Title: "Applications of Planar-Chiral Heterocycles in Asymmetric Catalysis"
  Advisor: Professor Gregory C. Fu
- GPA 5.0 out of 5.0

1996-1997 **The Scripps Research Institute, California, USA**
- Candidate for Ph.D. in Organic Chemistry
  Advisor: Professor K. Barry Sharpless
- GPA 5.0 out of 5.0

1992-1996 **University of Toronto, Toronto, Ontario, Canada**
- Bachelor of Science, Specializing in Chemistry
- Thesis Title: "Hydrostannylation of Allenic Alcohols"
  Advisor: Professor Mark Lautens
- GPA 4.23 out of 4.30

Awards and Scholarships

• Sept. 2000-Aug. 2001	Pharmacia Graduate Fellowship
• Sept. 1996-May 1997	The Andrew D. Baines Graduation Award in Life Sciences
• Sept. 1994-Apr. 1997	University of Toronto Scholar
• Sept. 1993-Apr. 1997	Faculty Scholar
• Sept. 1995-Apr. 1997	The Ivan Szak Prize in Chemistry
• Sept. 1996-Apr. 1997	The Society of Chemical Industry Merit Award in Chemistry
• Sept. 1996-Apr. 1997	The University of Toronto Chemistry Club Prize
• May 1995-Aug. 1995	Industrial NSERC Undergraduate Research Scholarship
• Sept. 1995-Apr. 1996	The Canadian Society for Chemistry Silver Medal
• Sept. 1995-Apr. 1996	The David McLaren Scholarship
• Sept. 1995-Apr. 1996	The F. E. Beamish Scholarship in Chemistry
• Sept. 1995-Apr. 1996	University Lodge 496 Masonic Scholarship
• Sept. 1993-Apr. 1995	Gollop Memorial Scholarship
• Sept. 1994-Apr. 1995	Rhea V. Scott In-Course Scholarship
• May 1993-Aug. 1993	NSERC Undergraduate Summer Research Scholarship
• Sept. 1993-Apr. 1994	Wetmore In-Course Scholarship
• Sept. 1993-Apr. 1994	CRC Press Freshman Chemistry Achievement Award

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- Tao, B.; Ruble, J. C.; Hoic, D.A.; Fu, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 5091-5092.
- Jeong, J. U.; Tao, B.; Sagasser, I.; Sharpless, K. B. *J. Am. Chem. Soc.* **1998**, *120*, 6844-6845.
- Tao, B.; Schlingloff, G.; Sharpless, K. B. *Tetrahedron Lett.* **1998**, *39*, 2507-2510.
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Patent

- Sharpless, K. B.; Tao, B.; Schlingloff, G.
  "Preparation of Aryl Serines by Catalytic Asymmetric Aminohydroxylation of Cinnamates" U.S. Patent 5767304, 1998.