Development and Applications of Enantioselective Organometallic Catalysts:
I. Organotin Catalysts
II. Planar-Chiral Nitrogen Heterocyclic Catalysts

by

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Submitted to the Department of
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ABSTRACT

One of the major focuses in organic chemistry today is the development of novel enantioselective organic transformations. Indeed, significant progress has been made in this area using organometallic compounds ranging from boranes to lanthanides and actinides. Upon casual perusal, however, one cannot help but notice the conspicuous absence of organotin compounds in this mix. Organotin reagents are one of few classes of organometallics for which there have been no reports of enantioselective catalysis. Much of the work in asymmetric catalysis has been aimed at chiral Lewis acids with very little attention paid to Lewis basic/nucleophilic catalysts. Pioneering work in our laboratory has resulted in the application of planar-chiral ferrocenyl derivatives of DMAP as effective enantioselective nucleophilic catalysts. We have applied one such compound to the dynamic kinetic resolution/ring-opening of azlactones. Following the lead of our first-generation planar-chiral *N*-heterocycles, we have synthesized a series of second-generation derivatives and investigated their structure-activity relationships. Of course, organometallic chemistry has two components, the ligand and the metal. Examining the literature in regard to the ligands, one would find that although there has been a plethora of optically pure axial-chiral and planar-chiral phosphines, there has been a dearth of planar-chiral nitrogen ligands. It is thus our mission to fill these voids.

We believe the rather limited examples (none when we first started; only two in the past three years) of enantioselective organotin catalysts is due to the intrinsic chemical properties of organotin compounds, as opposed to cost and/or toxicity issues. More specifically, the rapid racemization of an optically pure tin stereocenter along with the lability of tin-heteroatom bonds have been the two major obstacles in the development of enantioselective organotin catalysts. To circumnavigate these roadblocks, we initially

turned to the C_2-symmetric 1,1′-binaphthyl scaffold. Investigations in this domain revealed the possibility that pentacoordinate organotin compounds might be a more viable system. We therefore prepared a family of pentacoordinate organotin compounds using planar-chiral ferrocenes as the ultimate source of stereochemical information. Taking the leads from these two classes of organotin catalysts, we synthesized a planar-chiral C_2-symmetric organotin catalyst based on the arene chromiumtricarbonyl moiety. For all three families of catalysts, we achieved only modest levels of asymmetric induction.

Following our foray into the realm of enantioselective organotin catalysis, we turned our attention to planar-chiral *N*-heteroaromatic compounds developed in our laboratory. We have applied one member of this family, a planar-chiral derivative of DMAP, as an enantioselective nucleophilic catalyst for the dynamic kinetic resolution/ring-opening of racemic azlactones to give protected α-amino acid derivatives. This study furnished a new benchmark for non-enzymatic enantioselective catalysis of this interesting process.

Interesting results, both in terms of reactivity and enantioselectivity, were obtained when we made modifications to both the organic and the organometallic halves of this novel class of nucleophilic catalyst. We have demonstrated that electron donation to the reactive nitrogen atom from remote sites is possible. Although the reactivity and enantioselectivity profile of these structural analogues do not represent a significant improvement over the first-generation catalysts, we nevertheless obtained valuable information in regard to structure-activity relationships of this new class of catalysts.

Lastly, we have synthesized and resolved a planar-chiral C_2-symmetric derivative of 2,2′-bipyridine. Preliminary results with this new ligand show significant promise. As a proof-of-principle, we have used this new ligand for the Cu(I)-catalyzed asymmetric cyclopropanation of olefins. The result we obtained using this new planar-chiral derivative of 2,2′-bipyridine ligand is comparable to the earlier results in our group using another C_2-symmetric bidentate-nitrogen ligand.

Thesis Supervisor: Gregory C. Fu

Title: Professor of Chemistry

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Liang, J.; Ruble, J. C.; Fu, G. C. "Dynamic Kinetic Resolutions Catalyzed by a Planar-Chiral Derivative of DMAP: Enantioselective Synthesis of protected α-Amino Acids from Racemic Azlactones," *J. Org. Chem.* **1998**, *63*, 3154.

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A long long time ago, during the Reagan administration, Mr. Saks, my 10th grade chemistry teacher, added a few drops of phenolphthalein to a tub full of water with a paper boat floating on top. A chunk of sodium was added to the boat. The boat burst in flames and sank as the water turned pink. And now here I am. Along the way, I was fortunate to have wonderful high school science teachers along the way. Thank you Mr. Saks, Mrs Mueller, Mr. Weston and last but not least Doc Kimmel, who showed me how to make sodium chloride from sodium and chlorine. It is the best testing salt I have had.

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DEDICATED TO

MY PARENTS AND MY BROTHER

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ABBREVIATIONS

AIBN	2,2'-Azobisisobutyronitrile
BHT	2,6-di-*tert*-butyl-4-methylphenol
COD	1,5-cyclooctadiene
Cp	cyclopentadiene
Cp*	1,2,3,4,5-pentamethylcyclopentadienyl
d	doublet
dba	*trans, trans*-dibenzylideneacetone
DCC	1,3-dicyclohexylcarbodiimide
DMAP	4-(dimethylamino)pyridine
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
ee	enantiomeric excess
eq	equation
equiv	equivalent(s)
GC	gas chromatography
h	hour(s)
HMPA	hexamethylphosphoramide
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectroscopy
IR	infrared
LAH	lithium aluminum hydride
min	minute(s)
m-CPBA	3-chloroperoxylbenzoic acid
MTO	methyltrioxorhenium
MTPA	α-methoxy-α-(trifluoromethyl)phenylacetic acid (Mosher's acid)
NMO	4-methylmorpholine *N*-oxide
NMR	nuclear magnetic resonance
OTf	trifluoromethanesulfonate (triflate)
PMHS	polymethylhydrosiloxane

ppm	parts per million
q	quartet
r.t.	room temperature
s	singlet
t	triplet
TBACN	tetra-*n*-butyl ammonium cyanide
TBAF	tetra-*n*-butyl ammonium fluoride
TBDMS	*tert*-butyldimethylsilyl
TES	triethylsilyl
TFAA	trifluoroacetic anhydride
THF	tetrahydrofuran
TLC	thin-layer chromatography
TsOH	*p*-toluenesulfonic acid monohyrdate
TMS	trimethylsilyl

Chapter 1

Development and Applications of Enantioselective Organotin Catalysts

I. Introduction and Background

In recent years, a wealth of metal-catalyzed asymmetric organic transformations have been reported.[1] Concurrently, investigators in our research group have developed applications of organotin compounds as efficient catalysts for a wide variety of organic reactions, such as the cyanosilylation[2] and cyanoacylation[3] of aldehydes, reductive cyclization of enals and enones,[4] conjugate reduction of α,β-unsaturated ketones,[5] reduction of azides,[6] reduction of imines,[7] Barton-McCombie deoxygenation of alcohols,[8] and reduction of aliphatic nitro compounds to alkanes.[9] Of particular interest among these reactions are the cyanosilylation/cyanoacylation of aldehydes and the reductive cyclization of enals and enones, where new carbon-carbon bond and new stereogenic center(s) are formed. The advent of these novel organotin-catalyzed reactions, along with the well-established tin hydride-catalyzed reduction of carbonyl compounds,[10] has motivated us to develop optically pure organotin compounds for the *enantioselective* catalysis of these transformations (Scheme 1).

---

1 (a) *Catalytic Asymmetric Synthesis;* Ojima, I. Ed.; VCH: New York, 1993. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis;* Wiley: New York, 1994.

2 Scholl, M.; Fu, G. C. *J. Org. Chem.* **1994**, *59*, 7178.

3 Scholl, M.; Lim, C.-K.; Fu, G. C. *J. Org. Chem.* **1995**, *60*, 6229.

4 Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 4.

5 Hays, D. S.; Scholl, M.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 6751.

6 Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 7070.

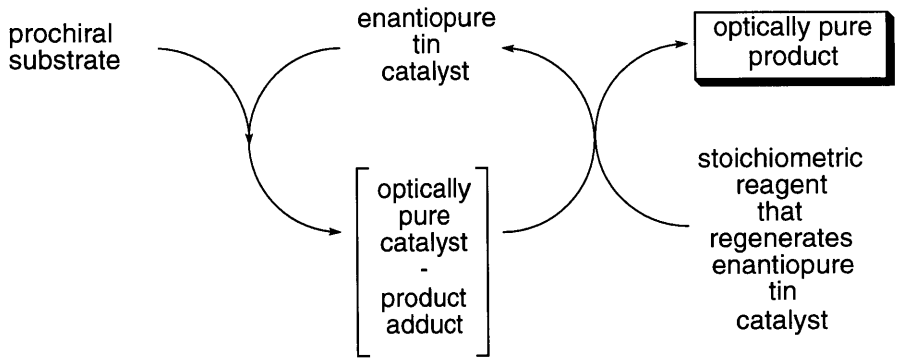
7 Lopez, R. M.; Fu, G. C. *Tetrahedron* **1997**, *53*, 16349.

8 Lopez, R. M.; Hays, D. S.; Fu. G.C. *J. Am. Chem. Soc.* **1997**, *119*, 6949.

9 Tormo, J.; Hays, D. S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2797.

10 (a) Nitzsche, S.; Wick, M. *Angew. Chem.* **1957**, *69*, 96. (b) Itoi, K. Fr. Paten. 1,368,522, 1964. Itoi, K.; Kumano, S. *Kogyo Kagaku Zasshi* **1967**, *70*, 82. (c) Hayashi, K.; Iyoda, J.; Shiihara, I. *J. Organomet. Chem.* **1967**, *10*, 81. (d) Bellegarde, B.; Pereyre, M. *Bull. Soc. Chim. Fr.* **1967**, 3082. (e) Lipowitz, J.; Bowman, S. A. *Aldrichimica Acta* **1973**, *6*, 1.

Scheme 1. Enantioselective organotin catalysis



The two key features of the cycle are: (1) the optically pure organotin catalyst reacts with the prochiral substrate to generate an optically pure intermediate, and (2) under the reaction conditions, the stoichiometric reagent reacts only with the said intermediate to release the optically pure product and regenerates the organotin catalyst without any loss of chemical and optical activity.

Thus far, the world of enantioselective organotin catalysis can be perhaps best characterized as that of an uncharted wilderness. When we first embarked upon this expedition, there were no reports of enantioselective reactions involving organotin compounds, be they *catalytic or stoichiometric*. At the present time, to the best of our knowledge, there have been only two published examples of organotin-catalyzed enantioselective reactions.[11] In either case, the enantioselectivity was modest at best (<42% ee). More surprisingly, perhaps, there have been only two reported cases of asymmetric reactions involving *stoichiometric*

---

[11] (a) Blumestein, M.; Schwarzkopf, K.; Metzer, J. O. *Angew. Chem., Int. Ed. Engl.* **1997,** *36,* 235. (b) Otera, A.; Sakamoto, K.; Tuskamoto, T.; Orita, A. *Tetrahedron Lett.* **1998**, *39*, 3201.

enantiopure organotin compounds, again with modest asymmetric induction (<41% ee).[12]

The two chief culprits for this dramatic lack of success in the domain of enantioselective organotin catalysis are the lability of the tin-heteroatom bonds under the reaction conditions[13] and the inherent optical instability of tetravalent stereogenic tin atom.[14] It is known that Sn-O and Sn-N bonds are cleaved by Si-CN and Si-H via metathesis. Indeed, it is this chemical property of organotin compounds that allowed for the new organotin-catalyzed reactions mentioned previously.[2-10] However, what was an advantageous chemical property of organotin compounds for achiral catalysis proves to be a deleterious one for enantioselective catalysis. The lability of the tin-oxygen and tin-nitrogen bonds under the reaction conditions precludes the use of the vast number of optically pure diols and diamines as ligands (and hence as a source of stereochemical information) on tin. Moreover, our hands are further tied by the inherent optical instability of tetravalent organotin compounds. In enantioselective organometallic catalysis, it is often preferable to employ catalysts in which the reactive metal center is stereogenic (i.e., $R_SR_MR_L$Sn-X; **1**). However, the optical instability of **1** (Scheme 2) makes this approach difficult if not impossible: even if enantiopure **1** can be synthesized, it will readily racemize under the reaction conditions via **2**/***ent*-2** and/or **3**/***ent*-3**.

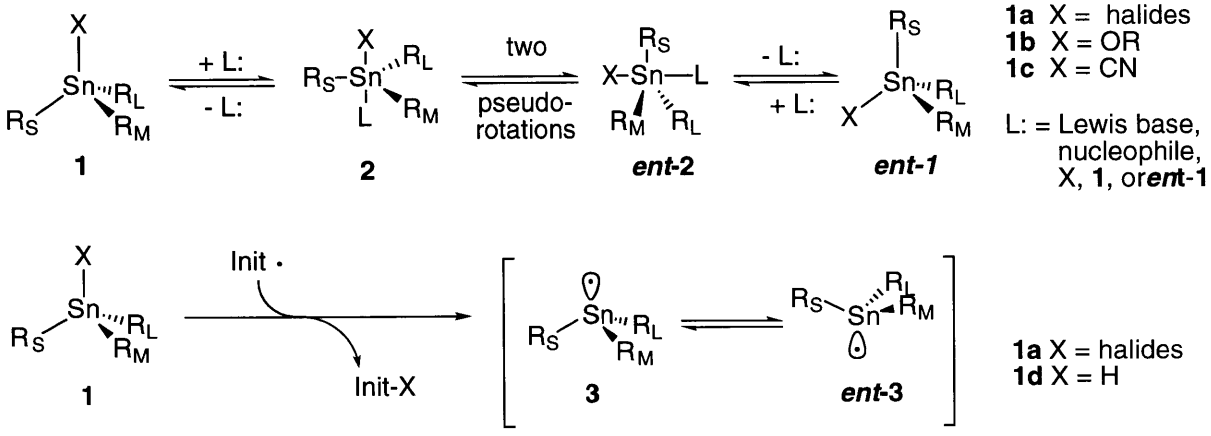
---

12 (a) Podesta, J. C.; Chipa, A.B.; Radivoy, G. E.; Vitale, C. A. *J. Organomet. Chem.* **1995**, *494*, 11. (b) Nanni, D.; Curran, D. P. *Tetrahedron: Asymmetry* **1996**, *7*, 2417.

13 For a general review, see: (a) Gielen, M. *Organotin Compounds;* Springer-Verlag: New York, 1982. (b) Pereyre, M.; Quintard, J.-P.; Rahm A. *Tin in Organic Synthesis;* Butterworths: Boston, 1987. (c) *Chemistry of Tin;* Harrison, P. G., Ed.: Chapman and Hall: New York, 1989. (d) Omae, I. *Organotin Chemistry;* Elsevier: New York, 1989. For specific studies on the lability of Sn-N bonds, see: (e) Hays, D. S.; Fu. G. C. *J. Org. Chem.* **1997**, *62*, 7070.

14 For a general review, see: ref. 13a-d. For specific studies on the optical stability of chiral triorganotin alkoxides, see: Folli, U.; Iarossi, D.; Taddei, F. *J. Chem. Soc., Perkins Trans. II* **1973**, 1284.

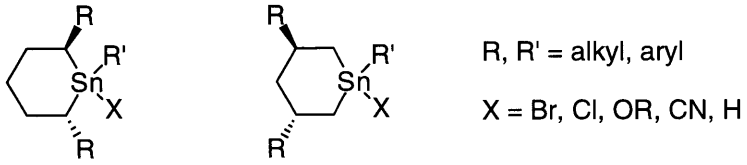
Scheme 2. Optical instability of tetravalent organotin compounds



To overcome these obstacles, we have synthesized C_2-symmetric and pentacoordinate organotin compounds.

II.A. C_2–Symmetric Organotin Catalysts: Introduction

Of all C_2-symmetric systems,[15] organotin compounds in the family of **4** and **5** are the easiest to envision.[16]



4 **5**

Unfortunately, there are two fundamental difficulties in obtaining **4** in optically pure form. The first problem lies with the synthesis of any organostannacycles: even under high dilution conditions, oligomerization routinely competes with cyclization. The second and more daunting obstacle lies with the stereogenic α-carbons (i.e., C-2 and C-6 of **4**). It has been shown that nucleophilic displacement of enantiopure secondary tosylates or halides with an organotin anion is either sluggish or leads to loss of optical integrity.[17] Repeated attempts by our group at the asymmetric synthesis of derivatives of **4** have not been successful. The 3,5 di-substituted analog **5** has been prepared in optically pure form in our group.[18] Unfortunately, although **5** is a chemically active catalyst, it does not impart any enantioselectivity.[18]

---

15 For a review, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.

16 Stannacyclo*pentanes* have been shown to be highly unstable due to the ring strain incurred by the large tin atom. See: (a) Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1976**, *110*, 167. (b) Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1977**, *137*, 165. (c) Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1978**, *153*, 305. (d) Bulten, E. J.; Budding, H. A. *J. Organomet. Chem.* **1979**, *166*, 339.

17 (a) SanFilippo, J.; Sibermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978,** *100*, 4834. (b) SanFilippo, J.; Silbermann, J. *J. Am. Chem. Soc.* **1982,** *104*, 2831.

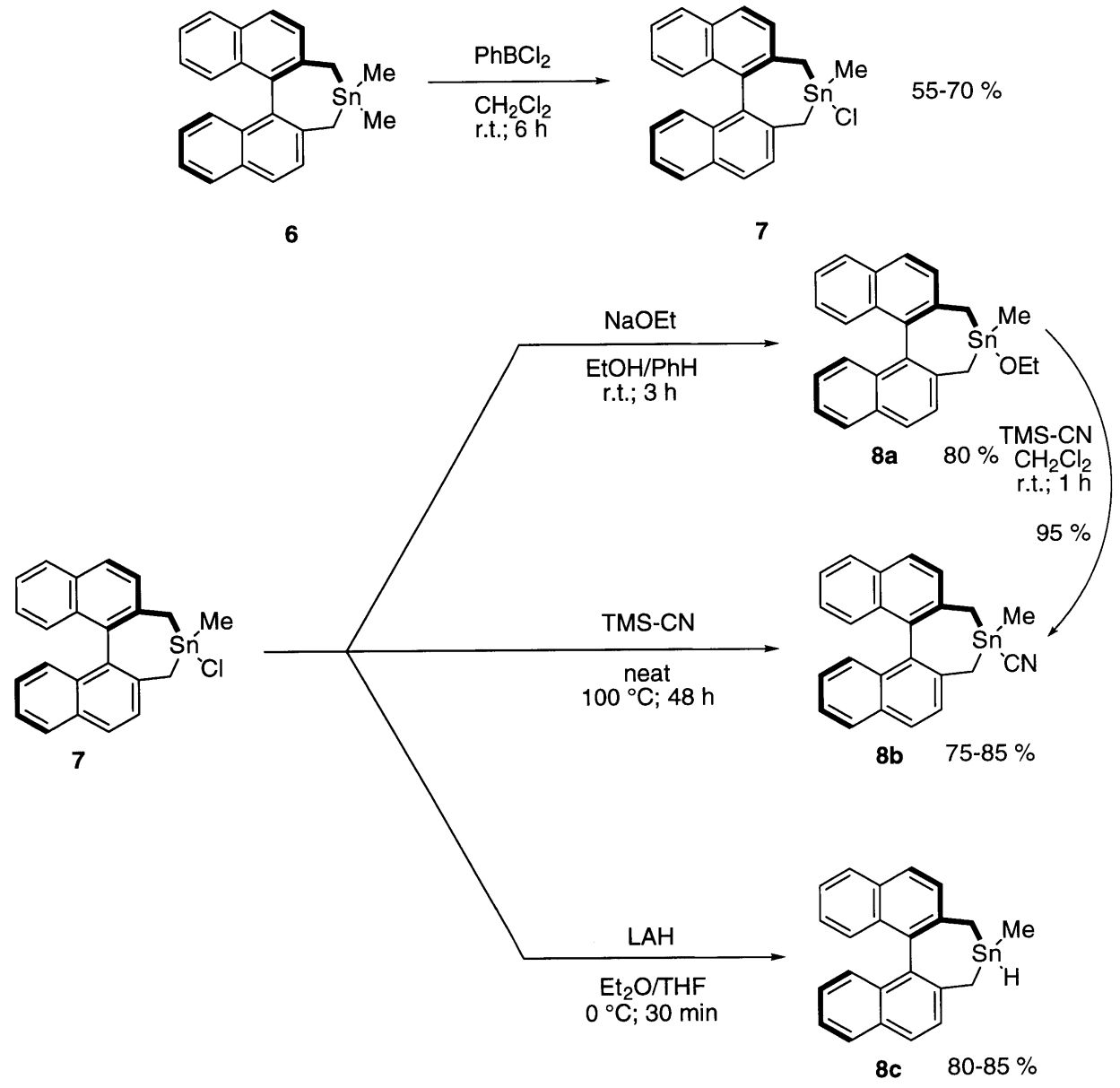
18 Lim, C.-K. S.M. Thesis. Massachusetts Institute of Technology, 1995.

Because of the difficulties in achieving cyclization *and* absolute stereochemical control, it would be prudent of us to resolve each issue separately. Of the two challenges, cyclization is more easily tackled. Provided that the reaction can be conducted on a sufficiently large scale, we could in principle afford to have a low chemical yield for the cyclization step. This is especially true in the early stages of catalyst development, when all we need is a small amount of optically pure material to test its effectiveness as an enantioselective catalyst. Stereochemical control, on the other hand, must be absolute and uncompromising. Our experiences with **5** along with the dearth of reports of enantioselective organotin catalysis have led us to believe tin is a rather unforgiving metal to work with. Thus, we felt that in order for an optically pure organotin compound to be a viable enantioselective catalyst, the stereogenic element(s) should be as proximal to the tin atom as possible. Owing to the inherent uncertainty in controlling stereochemical integrity of an sp^3 carbon (central chirality) α to tin, we decided to use axial and/or planar chirality as the source of stereochemical information.

II.B. 1,1′-Binaphthyl-Derived C_2-symmetric Organotin Catalysts

Motivated by the success enjoyed by BINAP-type systems,[19] we have synthesized the stannepins **8a**, **8b**, and **8c** (Scheme 3).

Scheme 3. Synthesis of 1,1'-binaphthyl-derived C_2-symmetric organotin catalysts



19 For reviews, see Ref. 1.

The synthesis starts from the known enantiopure dimethyl stannepin **6**.[20',21] Selective electrophilic cleavage of only one of the exocyclic methyl groups by phenyldichloroborane gives the chloride **7**.[22] Treatment of **7** with the appropriate nucleophile gives the corresponding enantiomerically pure catalyst **8a**, **8b**, or **8c**.[23] The ethoxide **8a** was not sufficiently stable for further purification (e.g., recrystallization) from the crude mixture (>90% yield; >90% purity) and was therefore not investigated as a catalyst.

As an initial trial, we attempted to use hydride **8c** to effect the tin radical-catalyzed reduction of aldehydes, with the ultimate goal of achieving catalytic enantioselective reductive cyclization of enals. Unfortunately, under either thermal (AIBN/C_6D_6/80 °C) or photochemical (AIBN/C_6D_6/$h\nu$/r.t.) radical initiation conditions, the tin-hydride **8c** decomposed within ten minutes with concomitant gas evolution (assumed to be N_2 from AIBN). Since **8c** did not decompose when either heated alone in C_6D_6 at 80 °C for six hours or left standing in C_6D_6 at ambient conditions in the presence of AIBN for three hours, it can be inferred that the decomposition of **8c** occurred only in the presence of radicals. The product(s) of the decomposition cannot be identified. The transient nature of hydride **8c** under the reaction conditions makes it unsuitable as an enantioselective catalyst. Subsequent to this work, Curran and co-workers published a paper in which they used *2.2*

---

20 Optically pure 1,1'-binaphthyl-2,2'dimethyl scaffold could be assembled via either asymmetric coupling (a) Hayashi, T.; Hayashizake, K.; Kiyai, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153 or by classical resolution (b) Margiot, N.; Mazaleyrat, J. -P. *Synthesis.* **1985**, 317. For throughput reasons, we eventually choose the classical resolution route.

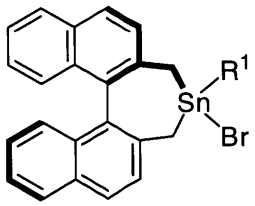
21 For the stannacycle formation, see: Gross, U. -M.; Bartel, M.; Kaufmann, D. *J. Organomet. Chem.* **1988**, *344*, 277.

22 The authors in Ref. 21 used the non-commercially available $EtBCl_2$ as the electrophile. Fortunately, we have found the commercially available $PhBCl_2$ is a viable substitute.

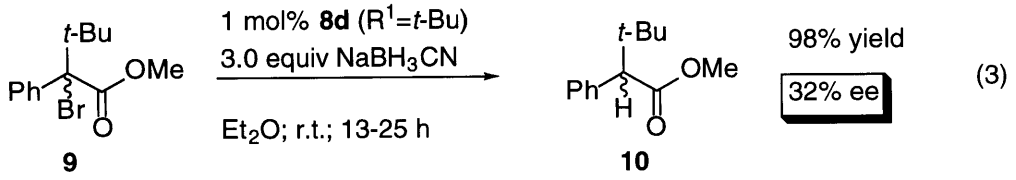
23 Each enantiomer of **8a**, **8b** or **8c** can be obtained in optically pure form in ten steps (including purification of the starting material) from commercially available 1-bromo-2-methyl naphthalene with an overall yield of ~ 0.5%. Starting from 100 g of 1-bromo-2-methyl naphthalene, ~ 500-600 mg (~ 1.1-1.2 mmol) of each enantiomer of **8a**, **8b**, or **8c** can be obtained.

equivalents of **8c** to effect the hydro-debromination of an α-bromoketone. Not surprisingly, both the chemical (30 %) and optical (41% ee) yields were poor.[12b] Thus, it appears that tin-hydride **8c** may have of limited utility as an enantioselective catalyst.

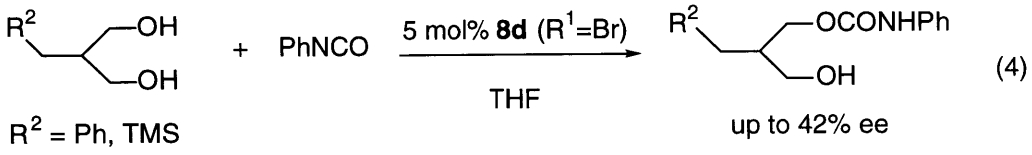
Subsequent to our work in this area, there have been two reports of enantioselective organotin catalysis, both of which, not surprisingly, utilize the 1,1'-binaphthyl scaffold (eq 3 and eq 4).[11]



8d



9 **10**



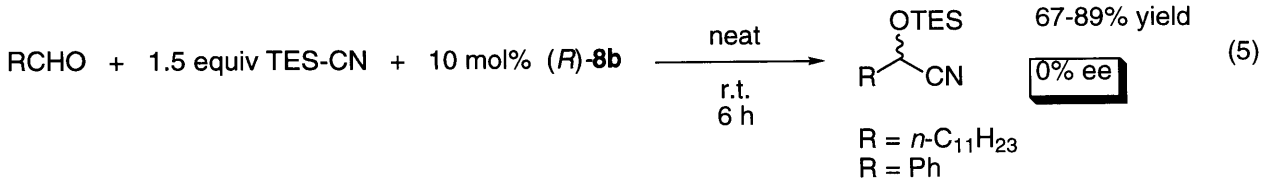
R^2 = Ph, TMS

11 **12**

up to 42% ee

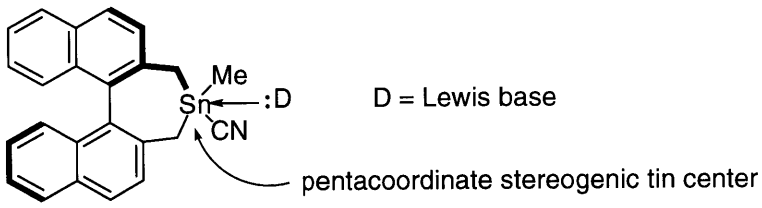
In light of the tremendous success enjoyed by 1,1'-binaphthyl-transition metal systems, it is perhaps interesting to note that the 1,1'-binaphthyl-tin systems only give modest enantioselectivity (<50% ee).

Not deterred by our initial setback in the realm of radical chemistry, we turned our attention to polar reactions, more specifically, the cyanosilylation of aldehydes.[2] Our initial attempts, however, met with failure (eq 5).



(5)

We surmised, in retrospect, that the axial chirality of **8b** is too distant to transmit stereochemical information from the catalyst to the substrate. This shortcoming could be remedied if there were a mechanism to bring the chirality "closer" to the reactive metal center of **8b**. One plausible solution would be to have stereogenic center on the benzylic carbons. However, this runs into the problem of absolute stereochemical control mentioned previously.[17] Since it is well known that Lewis bases readily coordinate to triorganotin halides and pseudohalides to form hypervalent complexes,[13b] an alternative solution would be the coordination of a Lewis base to **8b**, giving rise to a pentacoordinate moiety **13b**, in which the *tin itself is stereogenic.*



13b

Increasing the coordination number of tin from four to five typically leads to an upfield shift of about 50-60 ppm in the ^{119}Sn NMR chemical shift.[24] A similar

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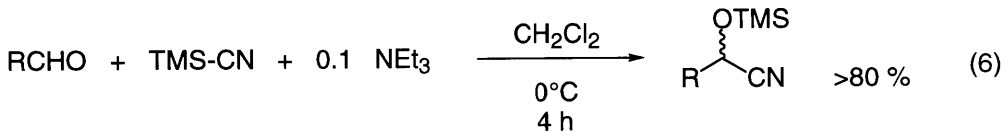
24 Wrackmeyer, B. *Annual Reports on NMR Spectroscopy* **1985,** *16,* 73.

change, albeit to a lesser extent, was observed for **8b** when the solvent was changed from $CDCl_3$ to d_5-pyridine, d_6-DMSO, or d_7-DMF (Table 1).

Table 1. Evidence of pentacoordinate **13b** seen in ^{119}Sn NMR (ppm from Me_4Sn):

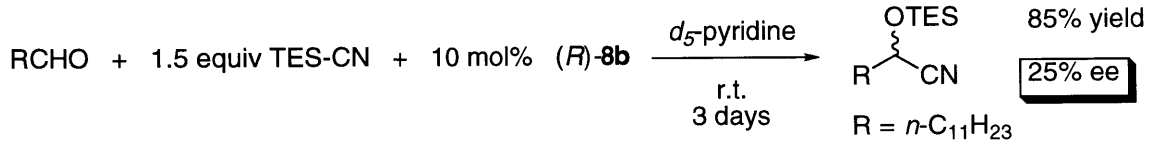
13b	$CDCl_3$	-27 ppm	Bu_3Sn-CN	$CDCl_3$	-33 ppm
	d_5 - pyridine	-63 ppm		d_5 - pyridine	-83 ppm
	d_6 - DMSO	-89 ppm		d_6 - DMSO	-97 ppm
	d_7 - DMF	-72 ppm		d_7 - DMF	-83 ppm

We thus have spectroscopic evidence that the tin atom of **8b** is indeed pentacoordinate as depicted in **13b**. Analogous to organotin compounds, organosilicon compounds such as TES-CN (which is present in 15-fold excess relative to catalyst **13b**) can adopt pentacoordination as well.[25] More importantly, it is known that hypervalent *silyl*cyanides react with aldehydes to give the corresponding *racemic* silylated cyanohydrins (eq 6).[26]



(6)

This of course would be a *non-enantioselective* background reaction and thus have an eroding effect on the observed enantioselectivity of the tin-catalyzed reaction. These complications notwithstanding, we were able to achieve an enantioselective organotin-catalyzed cyanosilylation of aldehyde (eq 7).



(7)

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25 Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, 1371.

26 Kobayashi, S.; Tsuchiya, Y.; Mukaiyama, T. *Chem. Lett.* **1991**, 537.

A more detailed study is shown in Table 2.

Table 2. Effect of Lewis bases on enantioselectivity.[a]

	n-$C_{11}H_{23}$-CHO			*o*-tol-CHO		
	% yield[b]	% ee[c]	% bkg.[d]	% yield[b]	% ee[c]	% bkg.[d]
d_5-pyridine	85	25	100	79	34	40
d_6-DMSO	50	8	40	78	17	50
d_7-DMF	77	35	45	61	22	30
HMPA	72	34	100	72	24	100
10 equiv TBAF[e]	decomp.	---	100	decomp.	---	100
10 equiv TBA-CN[f]	decomp.	---	100	decomp.	---	100
10 equiv Me_3N-O[f]	57	7	100	66	4	100
10 equiv Ph_3P-O[f]	61	30	20	0	0	0

[a] 1.0 M in RCHO; r.t.; 3 days. [b] Isolated yield. [c] ee assayed by hydrolysis of the silyl ether to the corresponding cyanohydrin followed by treatment of the resulting alcohol with Mosher's acid chloride.[27] [d] Same conditions as catalyzed reaction; no **8b**; % conversion determined by ^{1}H NMR. [e] In THF. [f] In $CDCl_3$.

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27 The enantiomeric excess of the silylated cyanohydrins was analyzed by hydrolysis of the silyl ether to the corresponding cyanohydrin followed by treatment with Mosher's acid chloride. No lost of optical purity during hydrolysis was observed. (a) Hayashi, M.; Matsude, T.; Oguni, Y. *J. Chem. Soc., Perkins Trans. I* **1992,** 3135. (b) Hayashi, M.; Miyamoto, Y.; Inoue, Y.; Oguni, N. *J. Org. Chem.* **1993,** *58,* 1515.

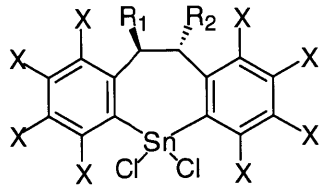
The results in Table 2 showed low to modest enantioselectivity along with a significant *non-stereoselective* background reaction. The data presented in Table 2 is not sufficient to determine the relative rate of the tin-catalyzed reaction versus the silicon-mediated background reaction. However, it is obvious that the non-stereoselective background reaction is operating at a competitive rate and therefore has partially masked the intrinsic enantioselectivity of **8b**. In order to obtain this intrinsic selectivity, it is necessary to use **8b** stoichiometrically. However, due to the tedious synthesis of **8b**,[23] this option was not explored, especially given that the objective of the project is asymmetric *catalysis*. The dilemma we faced here is as follows: we need the donor ligand to generate the stereogenic tin center that is essential for asymmetric induction; however, the same donor ligand is also responsible for the non-stereoselective background reaction. For a discussion pertaining to how this issue is addressed, see Section III.

In conclusion, we have achieved, for the first time, the enantioselective organotin-catalyzed cyanosilylation of aldehydes, albeit with modest optical yield. Due to the apparent instability of the 1,1'-binaphthyl scaffold, presumably due to the endocyclic benzylic carbon-tin bond, and the tedious synthesis of the catalysts **8b** and **8c**, we decided not to pursue this area further. Our attention shifted to other C_2-symmetric systems as well as pentacoordinate organotin catalysts.

II.C. Arene Chromiumtricarbonyl-Based Systems

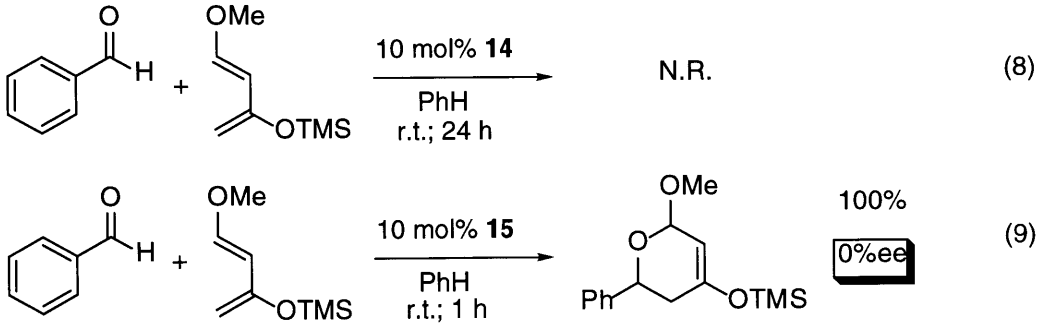
Due to the difficulties in the asymmetric synthesis of enantiopure organotin compounds, it would be desirable to have a versatile catalyst that can effect a wide range of organic transformations. Tin compounds are widely used as Lewis acids. Thus, we would like to have an organotin catalyst that, with minimal modifications, can catalyze Lewis acid promoted reactions in addition to cyanosilylation and enal cyclization.

The work of Vedejs et al. has demonstrated that organotin compounds can serve as efficient Lewis acid catalysts for hetero-Diels-Alder reactions, provided that the organic substituent is sufficiently electron-withdrawing (eq 8 and 9).[28]



14 R^1 = Me; R^2 = Me; X = H

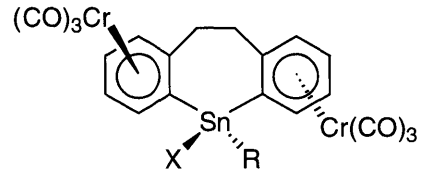
15 R^1 = H; R^2 = Me; X = F



28 Vedejs, E.; Erdman, D. E.; Powell, D. R. *J. Org. Chem.* **1993**, *58*, 2840.

Perhaps not surprisingly, due to the distant location of the stereogenic center of **15**, no enantioselectivity was observed with enantiopure **15**. Nonetheless, this provides us with precedent that a diorganotin dichloride can in fact serve as an efficient Lewis acid catalyst. The crucial feature of **15** is the electron-withdrawing fluorides, since simple cyclic diorganotin dichlorides (e.g., **14**) are not sufficiently Lewis acidic to promote the desired reaction. In summary, the Vedejs system demonstrated the viability of organotin compounds as Lewis acids and emphasized the necessity of having stereochemical elements in close proximity to tin for asymmetric induction.

Thus, in order to maximize the potential versatility of our enantiopure organotin catalyst, we are faced with a task of more than just the design and synthesis of C_2-symmetric organotin compounds whose source of stereoinduction is in close proximity to the tin atom. We also need to have an enantiopure organotin compound whose optically pure organic scaffold is sufficiently electron-deficient to allow for Lewis acid catalysis. To this end, we proposed to synthesize compounds of the general type **16**.



16

X = OR, CN, H; R = alkyl

X = R = H

X = R = Cl, Br, OTf

X = $(SbF_6)^-$; R = alkyl

The organic scaffold of **16** is based on that of Vedejs. However, the crucial element of our design lies with the metal fragment. The $Cr(CO)_3$ moiety is designed to play two roles. First, the powerful electron-withdrawing $Cr(CO)_3$[29] units are to serve the same electronic purpose as the fluorides in **15**: to allow for Lewis acid catalysis. Second, the planar-chiral arene chromiumtricarbonyl is to act as the source of stereochemical information. We reasoned that the close proximity of the electron-withdrawing planar-chiral arene chromiumtricarbonyl fragments to the reactive tin center would allow us to use **16** as a highly versatile and enantioselective organotin catalyst.

The synthesis starts from the known enantiomerically pure bisbromide **17** (Scheme 4).[30]

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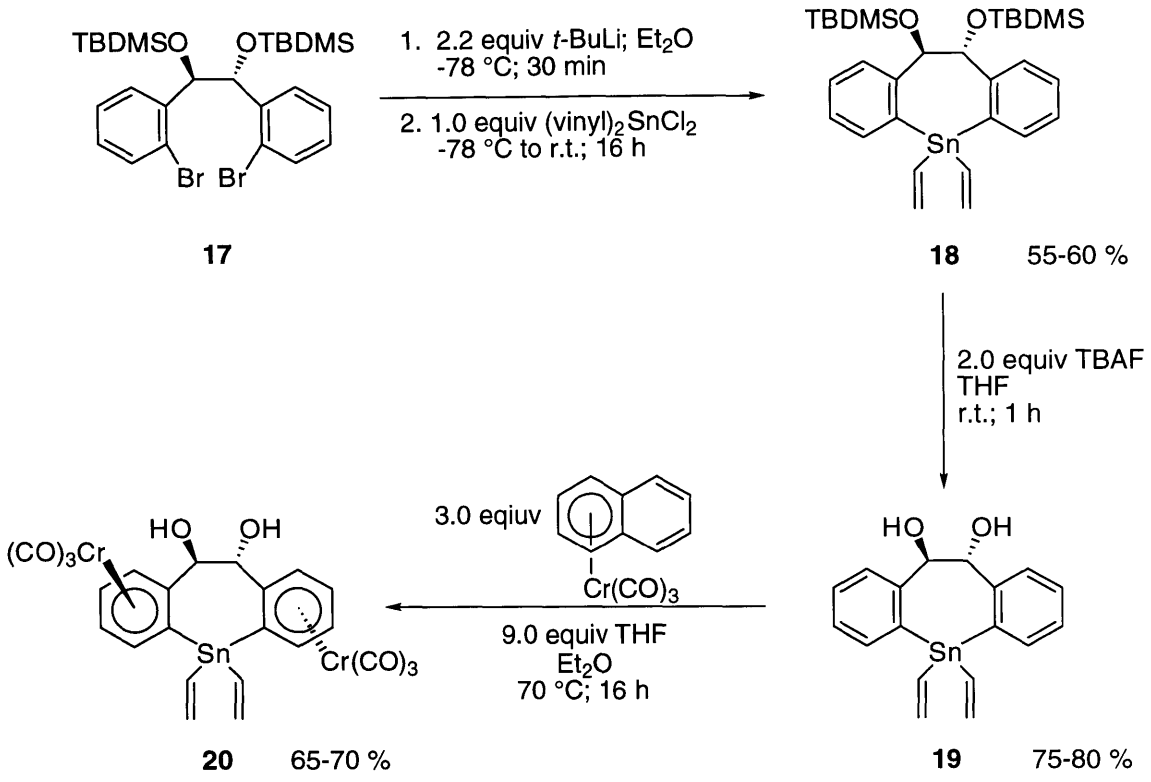
29 For reviews, see: (a) Morris, M. J. In *Compreshensive Organometallic Chemistry II* Labinger, J. A., Winter, M. J., Ed.; Pergamon: Oxford, 1995, Vol. 5; Chapter 8, pp. 472-549. (b) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebraranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957. (c) Solladie-Cavallo, A. *Polyhedron* **1985**, *4*, 901.

30 Compound **17** can be synthesized in optically pure form from commercially available 2-bromobenzaldehyde in three steps with an overall yield of 60-70% on a 20 g scale. For the McMurry coupling of 2-bromobenzaldehyde, see: (a) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepsik, L. *J. Org. Chem.* **1978**, *43*, 3255. (b) Warren, S.; Wyatt, P. *Tetrahedron. Lett.* **1996**, *37*, 5609. The original procedure calls for a $TiCl_3$/Li coupling system. However, $TiCl_3$ is no longer commercially available. We have found the $TiCl_4$/Zn coupling system to work equally well. See: (c) Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973,** 1041. (d) Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 817. (e) Coe, P. L.; Scriven, C. E. *J. Chem. Soc., Perkin Trans. I* **1986**, 475. (f) McMurry, J. E.; *Chem. Rev.* **1989**, *89*, 1513. (g) Furstner, A.; Bogdanovic, B. *Angew. Chem., Int. Ed.* **1996**, *35*, 2442. For AD, see: (h) Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K. -S.; Kwong, H. -L.; Morikawa, K.; Wang, Z. -M.; Xu, D.; Zhang, X. -L. *J. Org. Chem.* **1992**, *57*, 2768. (i) Zhang, S. Y.; Girard, C.; Kagan, H. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2637. For the protection of the diol as the TBDMS ether, see: (j) Corey, E. J.; Cho. H.; Rucker, C.; Hua, D. H. *Tetrahedron Lett.* **1981**, *22*, 3455.

Scheme 4. Synthesis of arene chromiumtricarbonyl-based C_2-symmetric organotin catalysts



The organotin partner (i.e., the eventual exocyclic substituents of the stannacycle) in the cyclization step[31] (**17** → **18**) must be chosen with foresight for two reasons: (1) the exocyclic substituents must be compatible with the subsequent diastereoselective complexation of the $Cr(CO)_3$ fragment, and (2) the exocyclic substituents must be amenable to selective removal later on in the synthesis. To satisfy both criteria, we choose to install sp^2-carbons in the exocyclic positions. In general, tin-sp^2 carbon bonds are more robust than tin-sp carbon bonds (enhanced stability to the chromiumtricarbonyl complexation conditions) and tin-sp^2 carbon bonds are more susceptible to electrophilic cleavage than tin-sp^3 carbon bonds (better chance of selective cleavage).[13] At a first glance, a reasonable choice for the tin partner amongst commercially available compounds would be either diphenyltin dichloride

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[31] Warren, S.; Wyatt, P.; McPartlin, M.; Woodroffe, T. *Tetrahedron Lett.* **1996**, *37*, 5609.

or divinyltin dichloride. Upon further examination, divinyltin dichloride is in fact the *only* choice. We do not expect the incoming $Cr(CO)_3$ moiety to discriminate between the targeted endocyclic arenes from the exocyclic ones (i.e., those that would have been introduced by diphenyltin dichloride). Thus, we decided to use vinyl group as potential precursors to halides. Once the organic scaffold of the catalyst is completed, we come to the crucial stage of the synthesis: setting the absolute stereochemistry at the arene chromiumtricarbonyl. The absolute stereochemistry of the organic backbone was set via Sharpless AD.[30h-i] Thus, the obvious choice would be to use the optically pure ether functionality (or the corresponding alcohol) to control the diastereoselective complexation of $Cr(CO)_3$.

Halogen-metal exchange of the bis-bromide **17** followed by the addition of divinyltin dichloride gives the stannacycle **18**. Removal of the silyl protecting group reveals the free hydroxyls which we used to direct the complexation of $Cr(CO)_3$, using naphthalene chromiumtricarbonyl as the $Cr(CO)_3$ source.[32] The completely diastereoselective hydroxyl-directed complexation of $Cr(CO)_3$ is confirmed as shown in Scheme 5.

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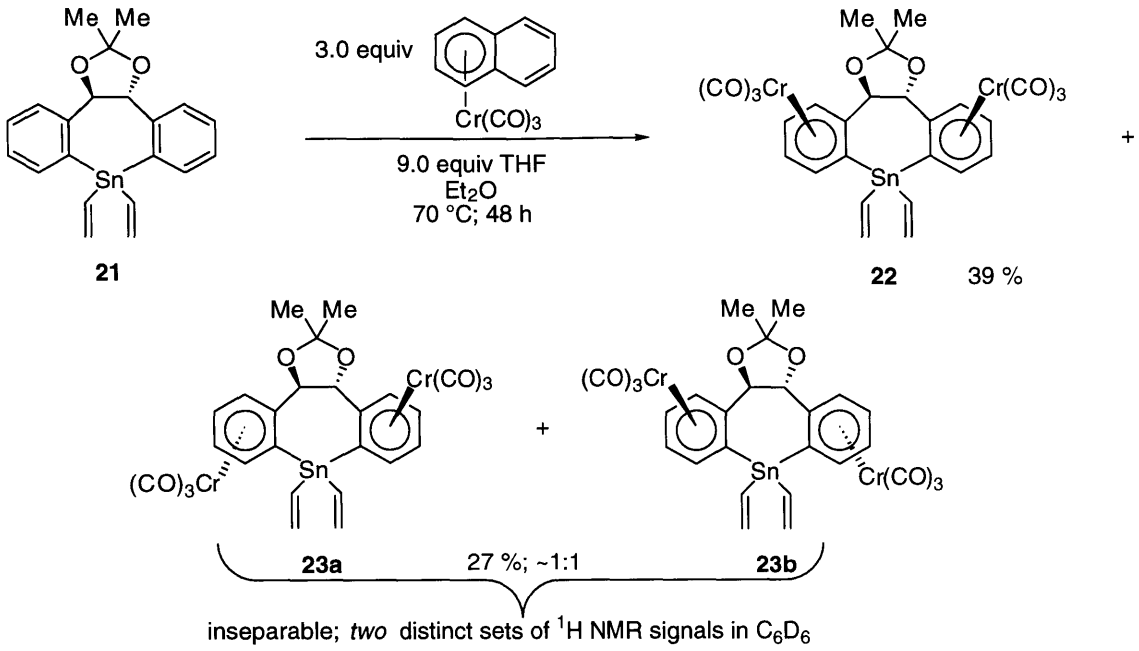
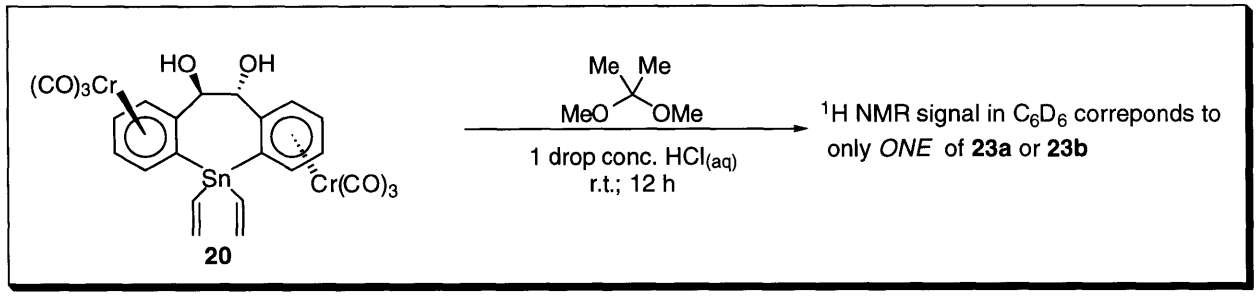
[32] For directed complexation of $Cr(CO)_3$, see: (a) Uemura, M.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 2859. (b) Brocard, J.; Lebibi, J.; Pelinksi, L; Mahmoudi, M. *Tetrahedron Lett.* **1986**, *27*, 6325. (c) Davies, S. G.; Goodfellow, C. L. *J. Organomet. Chem.* **1988**, *340*, 195. (d) Brocard, L.; Pelinski, L.; Lebibi, J.; Mahmoudi, M.; Maciejewski, L. *Tetrahedron* **1989**, *45*, 709. (e) Schmalz, H. -G.; Millies, B.; Bats, J. W.; Durner, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 631.

Scheme 5. Confirmation of diastereoselective hydroxyl-directed complexation of $Cr(CO)_3$





When we attempted to effect the diastereoselective complexation via **21** using the acetal oxygens as the directing group,[33] we obtained an almost statistical mixture of the *syn*-$Cr(CO)_3$ diastereomer **22** and the *anti*-$Cr(CO)_3$ diastereomers **23a** and **23b**. Using silica gel column chromatography, we were able to separate the *syn*-diastereomer **22** from the *anti*-diastereomers **23a** and **23b**.[34] We were unable to separate **23a** and **23b** from each other. Fortunately, **23a** and **23b** have distinct ^1H

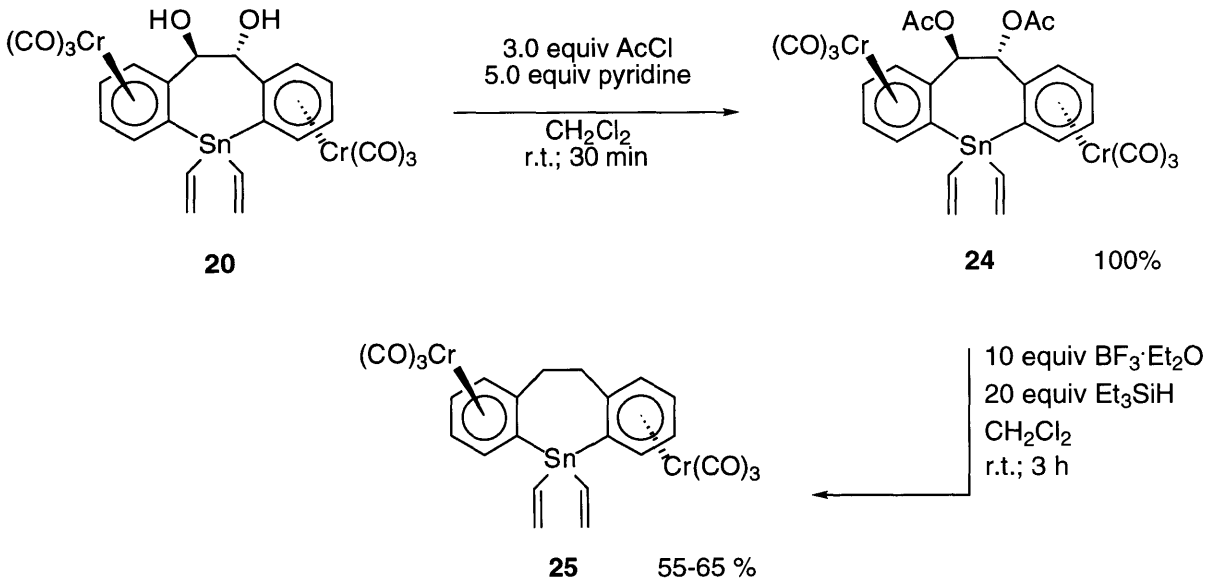
---

[33] Compound **21** was synthesized analogously to the synthesis of **18**. See Ref. 31 and 32. We had attempted to conduct the complexation using **18**; however, the reaction was sluggish.

[34] The *syn*-$Cr(CO)_3$ diastereomer **22** showed two distinct sets of vinyl protons (*syn* or *anti* to both $Cr(CO)_3$). Furthermore, the *syn*-diastereomer **22**, as expected, is more polar (lower R_f) than **23**: the dipole moment in the *anti*- $Cr(CO)_3$ compound **23** cancels out and is therefore less polar.

NMR signals in C_6D_6. We took advantage of this spectroscopic property to ascertain the complete diastereoselectivity of the *hydroxyl*-directed complexation (**19** to **20**; see Scheme 4). The crude ^1H NMR spectra after the conversion of **20** to the corresponding acetonide revealed only one set of peaks (no starting material was observed). Since this set of ^1H NMR peaks correlates to only ONE of the *anti*-$Cr(CO)_3$ diastereomers (i.e., **23a** *or* **23b**), we can conclude that the complexation is in fact completely diastereoselective (within the limit of ^1H NMR detection). Thus, the absolute stereochemistry at the arene chromiumtricarbonyl is now set. At this point, we have an enantiopure C_2-symmetric organotin catalyst precursor. It must be cautioned, however, that the stereochemical assignment at the arenes is based on the *assumed* hydroxyl-directed complexation. The hydroxyl groups are removed as shown in Scheme 6.

Scheme 6. Removal of the hydroxyl groups

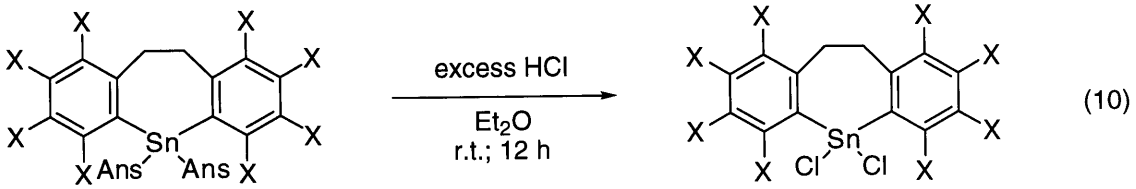


20 **24** 100%

25 55-65 %

At this stage, we are ready to remove one or both of the vinyl groups to give the tin-monohalide catalyst precursors or the tin-dihalide catalysts. Of the potpourri of

methods available for cleaving tin-sp^2 carbon bonds to give the corresponding halides, we had initially chosen to use ethereal HCl. Vedejs and others have demonstrated that ethereal HCl preferentially cleaves the more electron-rich tin-sp^2 carbon bond (eq 10).

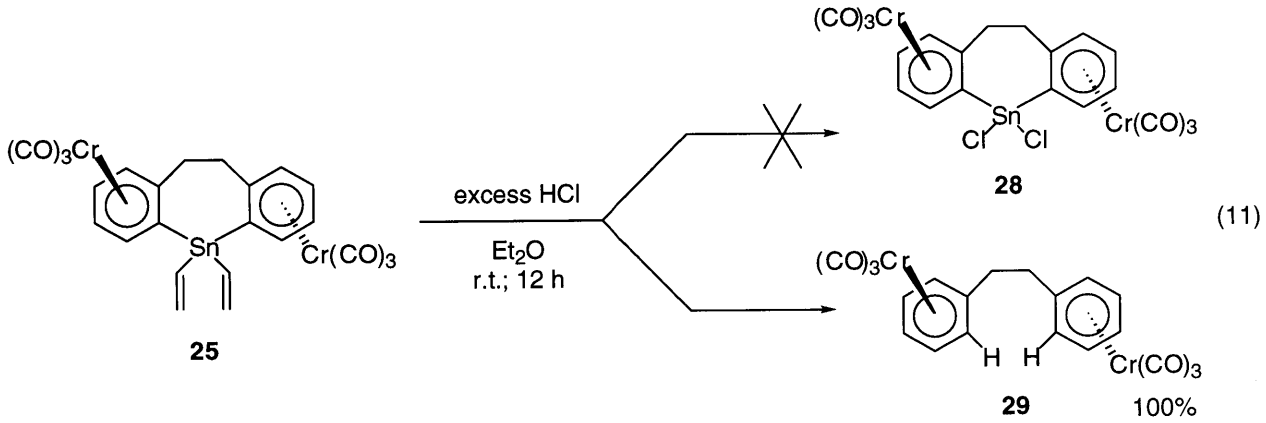


(10)

26 X = H or F
Ans = 4-MeO-C_6H_4

27 100 %

We reasoned that we can take advantage of this selectivity as well, since we also have an electron-poor arene (complexed to $Cr(CO)_3$). Much to our surprise and dismay, under conditions identical to that reported by Vedejs, we obtained exclusively *endocyclic* cleavage: only **29** was obtained (eq 11).



(11)

We screened a wide ensemble of electrophiles in an attempt to achieve selective exocyclic cleavage. Of the reagents tested, only BCl_3, BBr_3 and $SnCl_4$ showed some promise. When these reagents were used, the desired mono exocyclic cleavage

product could be observed in the crude ^{1}H NMR spectra. However, all attempts at purifying the tin mono-halides via recrystallization failed, as the corresponding tin halides do not appear to be crystalline. Furthermore, we were unable to achieve double exocyclic cleavage (i.e., obtaining the dihalide of the type **28**) regardless of the electrophiles and/or conditions used. Subsequent model studies have shown that the tin-arene chromiumtricarbonyl bond is extremely labile under protic conditions.[35]

In addition to screening electrophiles, we also varied the nature of the exocyclic substituents.[36] During our attempts to unearth a suitable exocyclic substituent, we noticed that the methyl-tin[37] compounds are typically more crystalline than their higher homologues. Thus, we set out to synthesize the methyl-vinyl analogs as shown in Scheme 7. Methylvinyltin dichloride is not commercially available. However, it can be easily obtained by treating methyltin trichloride with excess vinylmagnesium bromide to give methyltrivinyltin, which is converted to the desired dichloride upon treatment with excess ethereal HCl.

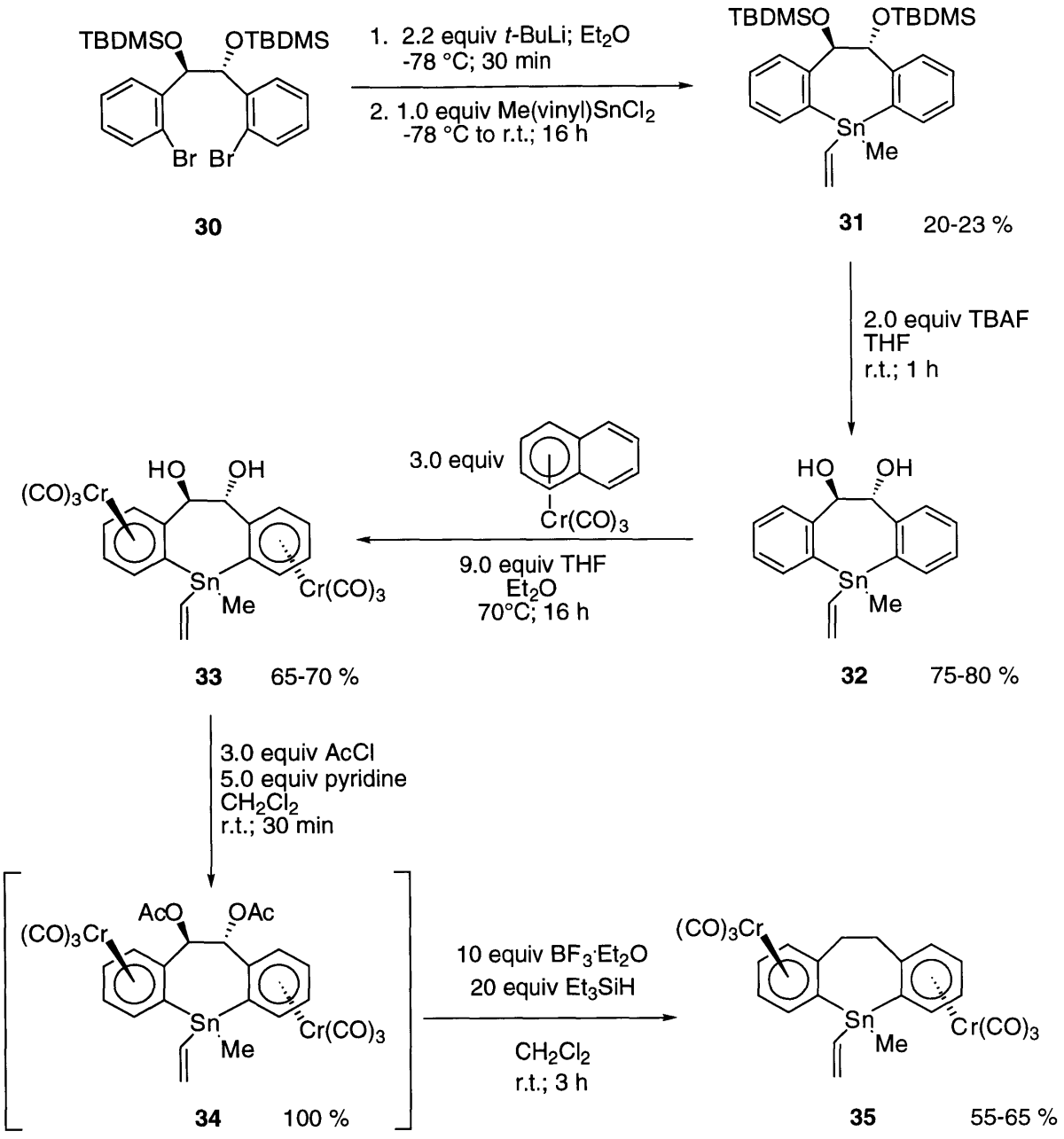
---

[35] For example, the reaction of ethereal HCl between bis-(3-furyl)-diphenyltin gave exclusively furan and diphenyltin dichloride: the more electron-rich furan was cleaved as expected. However, under identical conditions, treatment of bis-(3-furyl)-bis-(benzene chromiumtricarbonyl)tin with ethereal HCl gave bis-(3-furyl)tin dichloride and benzene chromiumtricarbonyl: the presumably more electron-deficient arene chromiumtricarbonyl was cleaved instead.

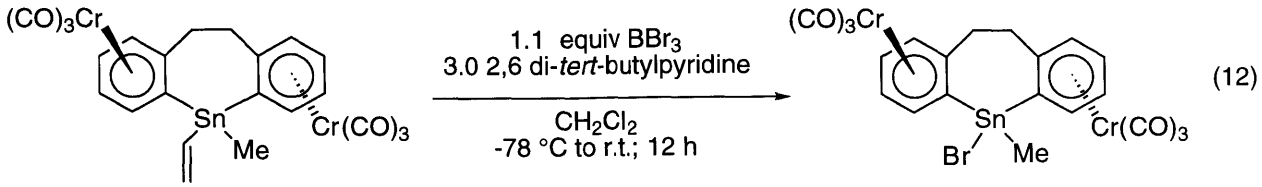
[36] We have synthesized the bis-(3-furyl) analog of **20**; however, the furans are apparently incompatible with the conditions used in the ionic hydrogenation of the diols (~ 10% yield). Regardless, treatment of the bis-(3-furyl) analog of **25** with $SnCl_4$ gives only the mono exocyclic cleavage product (i.e., we were not able to remove both furans) and thus the bis-(3-furyl) derivative has no advantage over other systems.

[37] We have synthesized the dimethyl analog of **25**. Attempts at cleaving the exocyclic methyl(s) using $HgCl_2$, BBr_3, $SnCl_4$, or $PhBCl_2$ (analogous to **6** → **7**) failed.

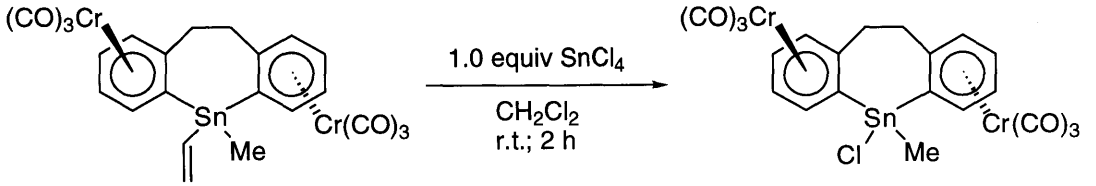
Scheme 7 Synthesis of the methyl analogue



The significantly inferior yield of the stannacycle formation step (**30** → **31**) is puzzling and all attempts at improvement were not fruitful. Fortunately, either the mono-bromide **36** or the mono-chloride **37** can be obtained as outlined in eq 12 and eq. 13, respectively. The dihalides, however, still eluded us.

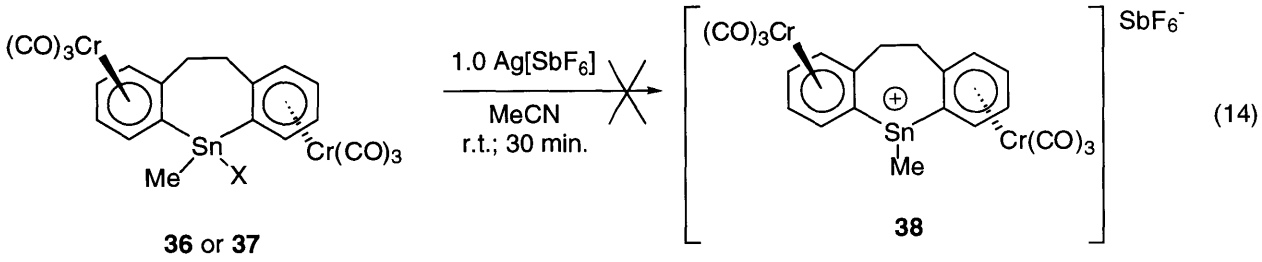


35 **36** 55-65 %



35 **37** 70-75 %

Note that in eq 12, excess 2,6 di-*tert*-butylpyridine is used to scavenge adventitious HBr. In the absence of the proton scavenger, the reaction is irreproducible due to the undesired endocyclic cleavage. This further emphasizes the acid sensitivity of the tin-arene chromiumtricarbonyl bond. As an interesting aside, under identical conditions, BCl_3 and $SnBr_4$ do not give the corresponding product **37** and **36**, respectively. With the mono-halides in hand, we attempted to synthesize the cationic organotin Lewis acid **38** (eq 14).[38]



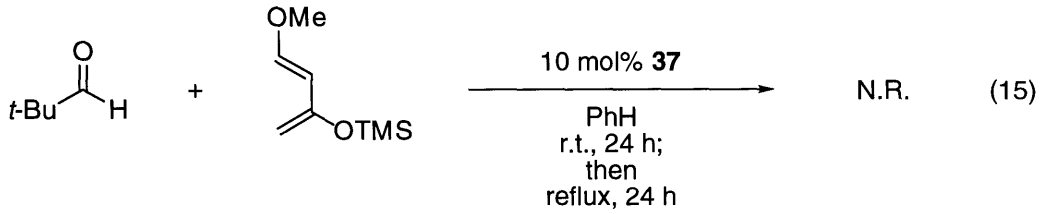
36 or **37** **38**

Unfortunately, we were unable to obtain the desired product **38**. Although the diagnostic precipitation of silver halide was observed, we were unable to isolate any

38 Nugent, W. A.; McKinney, R. J.; Harlow, R. L. *Organometallics* **1984**, *3*, 1315.

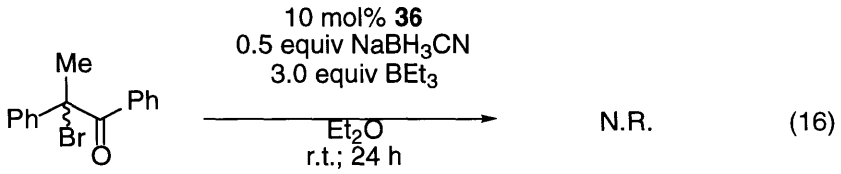
identifiable product other than the double endocyclic cleavage product **29**. Addition of 2,6-di-*tert*-butylpyridine had no effect in this case.

We hypothesized that perhaps the tin monochloride **37** with two electron-withdrawing arene chromiumtricarbonyl groups might be sufficiently Lewis acidic to catalyze hetero-Diels-Alder reactions. Unfortunately, this is not the case (eq 15).



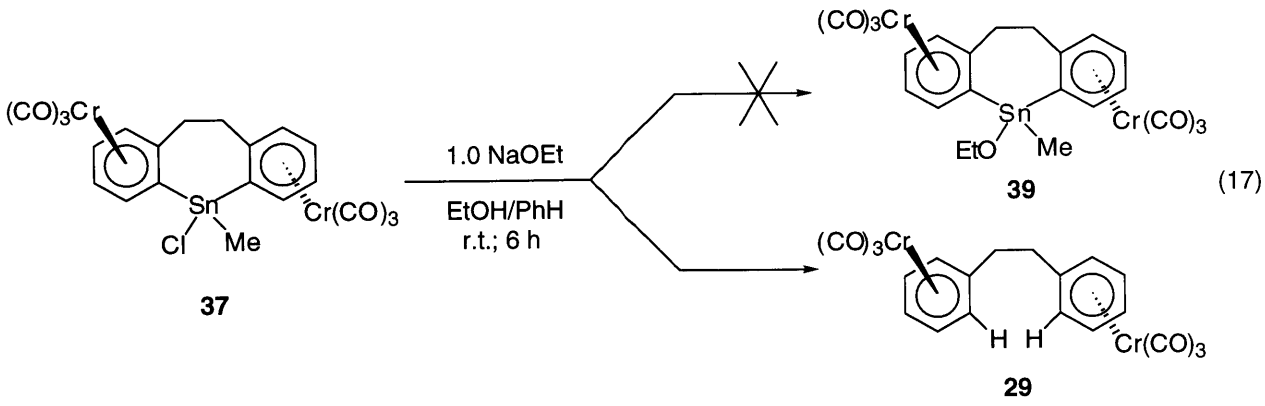
(15)

At this point, we abandoned the plan to use catalyst of the type **16** as a Lewis acid and shifted our focus to using **16** to catalyze polar and/or radical-mediated reactions. We attempted to use the monobromide **36** as a catalyst for the dehalohydrogenation of an α-bromoketone. Unfortunately, **36** is not an active catalyst for such reaction (eq 16).



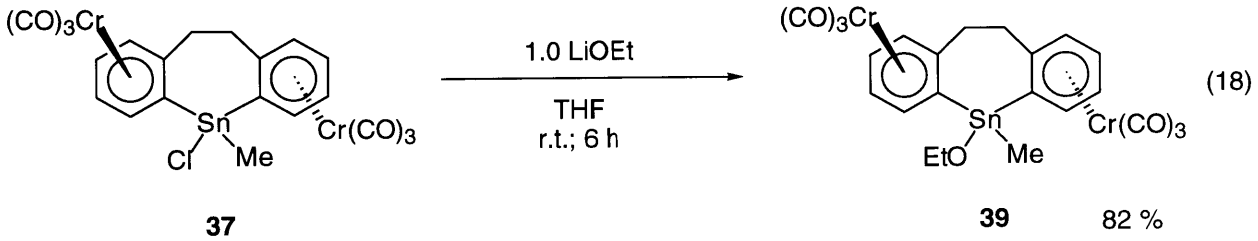
(16)

We attempted to synthesize the ethoxide **38** via the conventional route of sodium ethoxide in an ethanol/benzene co-solvent system. Once again, endocyclic cleavage product **29** was formed instead (eq 17).



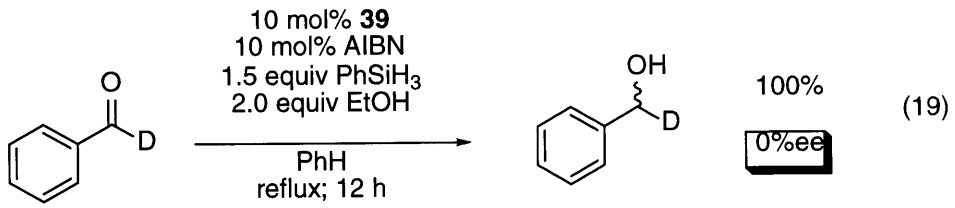
(17)

It would thus appear that the tin-arene chromiumtricarbonyl bound is far more sensitive to protic medium than we had anticipated. To circumvent this problem, we used the commercially available LiOEt in 1.0 M THF solution (eq 18).



(18)

All attempts at synthesizing the corresponding tin-cyanide and tin-hydride were unsuccessful. Attempts to use **39** as a catalyst for the asymmetric reduction of deutro-benzaldehyde met with failure (eq. 19).



(19)

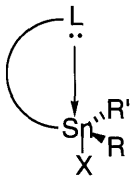
In eq. 19, ethanol was added in an attempt to enhance catalyst turn-over.[4] However, in the presence of ethanol, the catalyst decomposed, and the endocyclic

cleavage product **28** was observed in the reaction mixture. The same result was obtained when ethanol was omitted from the reaction mixture.

In conclusion, for reasons of poor chemical stability and lack of enantioselectivity, we decided not to pursue catalysts of the type **16** any further.

III.A. Pentacoordinate Catalyst: Introduction

The dilemma presented in Table 2 (see page 24) is as follows: a Lewis base is needed to form the pentacoordinate stereogenic-at-tin catalyst. However, the same Lewis base inevitably also activates the stoichiometric TES-CN to give racemic products via a competitive background reaction. Thus, the challenge is to design a catalyst system in which the Lewis base selectively coordinates to an optically pure organotin catalyst without activating the stoichiometric silicon reagent. This may be accomplished via a chelation system as shown in **40**.



L = Lewis base

X = halides, OR, CN, H

40

Studies on the silicon analogs of **40** have shown that the metal adapts a trigonal bipyramidal geometry with the Lewis base (L:) and the most electronegative group (X) occupying the apical positions.[39] The strength of the dative (L: → M) interaction is directly proportional to the polarizability of the M-X bond (OAc, Br, Cl > F, SR > H > OR > R). It has been shown that chelated pentacoordinate tin moieties behave similarly.[40]

Since the Lewis base chelates the tin *intra*molecularly, *inter*molecular activation of the silicon reagent should be eliminated. The structure depicted in **40** could also

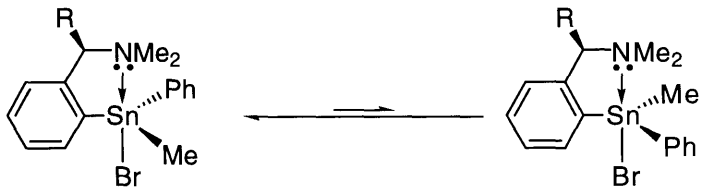
---

[39] For a general review on hypervalent silicon species, see Ref. 25 and references therein.

[40] For a recent review, see: Jastrzebski, J. T. B. H.; van Koten, G. *Advances in Organometallic Chemistry* **1993**, *35*, 241. For ^{119}Sn NMR data on intramolecularly coordinated hypervalent organotin compounds, see: Jastrzebski, J. T. B. H.; Grove, D. M.; Boersma, J.; van Koten, J.; Ernsting, J. -M. *Magnetic Resonance in Chemistry* **1991**, *29*, S23.

lead to configurationally stable triorganotin-X species since the rigid structure of the chelation ring should prevent racemization via the Barry pseudorotation pathway (Scheme 1). Thus, the internal chelating Lewis base serves two purposes: (1) eliminates the Lewis base activation of the silicon reagent and thus curbs the background reaction, and (2) enhances the configurational stability of the stereogenic tin center. Work by van Koten and Metzger has shown that pentacoordination of tin via chelation is indeed possible. Furthermore, the distribution of configurations at tin is a function of the steric bulk of the chelating arm (Scheme 8).[41]

Scheme 8. Diastereomeric ratio at tin as a function of sterics of the chelating arm



	41a	41b
R = Me	60 %	40 %
Et	60 %	40 %
i-Pr	80 %	20 %
t-Bu	>98 %	< 2 %

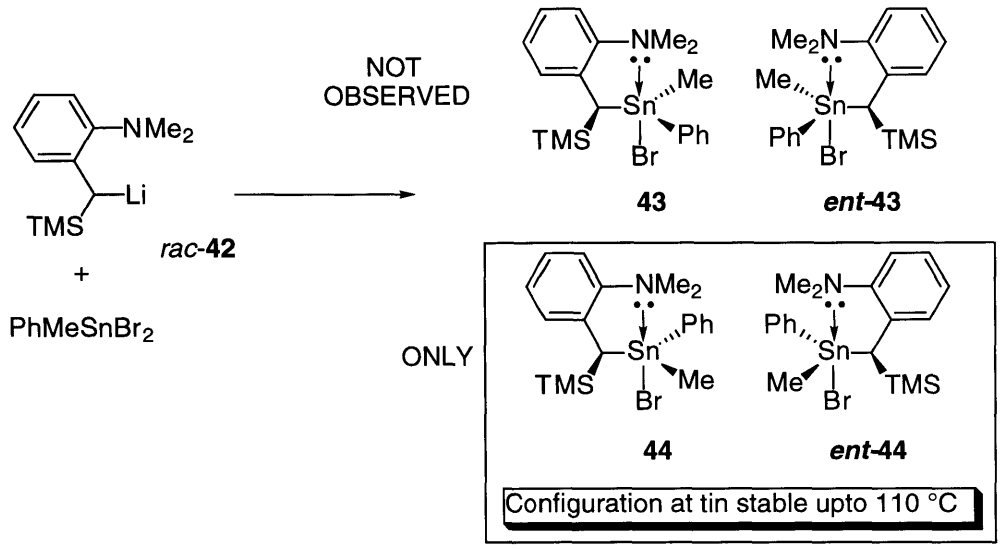
More importantly, van Koten has shown that, unlike tetracoordinate organotin compounds, pentacoordinate organotin compounds can be configurationally stable (Scheme 9).[42]

---

41 (a) Jastrzebski, J. T. B. H.; van Koten, G.; Knapp, C. T. *Organometallics* **1986**, 1551. (b) Schwarzkopf, K; Metzger, J. O.; Saak, W.; Pohl, S. *Chem. Ber.* **1997**, *130*, 1539.

42 Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1991**, *413*, 43.

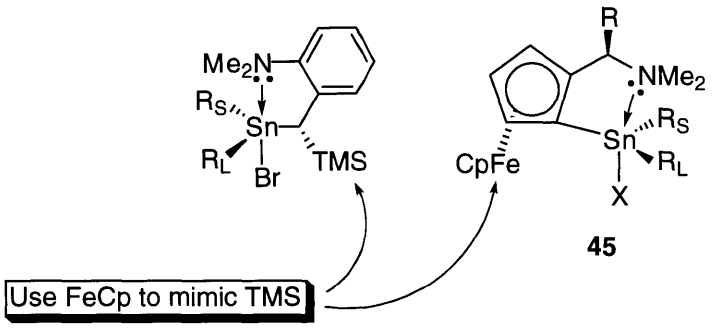
Scheme 9. Pentacoordinate organotin compounds CAN be configurationally stable



The result depicted in Scheme 9 illustrates that the bulky groups (TMS and phenyl) prefer to be *trans* in the ring. Pentacoordination of **44** and ***ent*-44** in non-Lewis basic solvents has been confirmed by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy. In addition, variable temperature ^{1}H and ^{13}C NMR spectra of **44** and ***ent*-44** revealed only one resonance pattern over a wide temperature range (-50 °C to +110 °C), indicating that only one diastereomer is present. This implies that epimerization at tin (i.e., **44** → **43** and/or ***ent*-44** → ***ent*-43**) does not occur. Thus, if **42** could be prepared as a single enantiomer, then we would obtain a pentacoordinate triorganotin bromide as a single stereoisomer. As stated previously, controlling the stereochemistry of a sp^3-carbon (central chirality) α to tin is difficult. Concurrent work in our laboratory has shown that *planar*-chirality is much more easily controlled. We thus began to design and synthesize a pentacoordinate enantiopure-at-tin catalyst using a planar-chiral scaffold.

III.B. Pentacoordinate Ferrocenyl Systems

Due to the difficulty of synthesizing enantiopure **42** (requires enantioselective lithiation at a highly hindered secondary benzylic position), we chose to synthesize compounds of the type **45** instead.



We are still depending on the structural rigidity of chelation to prevent intermolecular activation of the silicon reagent and to maintain the optical integrity of the tin center. We propose that the FeCp fragment of **45** will serve the same steric purpose as the TMS group in the van Koten system: to force the larger substituent on tin to be on the opposite side of the chelating ring. Furthermore, rather than attempting to control the absolute stereochemistry at a stereogenic carbon atom, we will instead rely on the much more manageable and well-studied planar-chirality of the ferrocenyl system. The catalyst was synthesized as shown in Scheme 10.[43,44]

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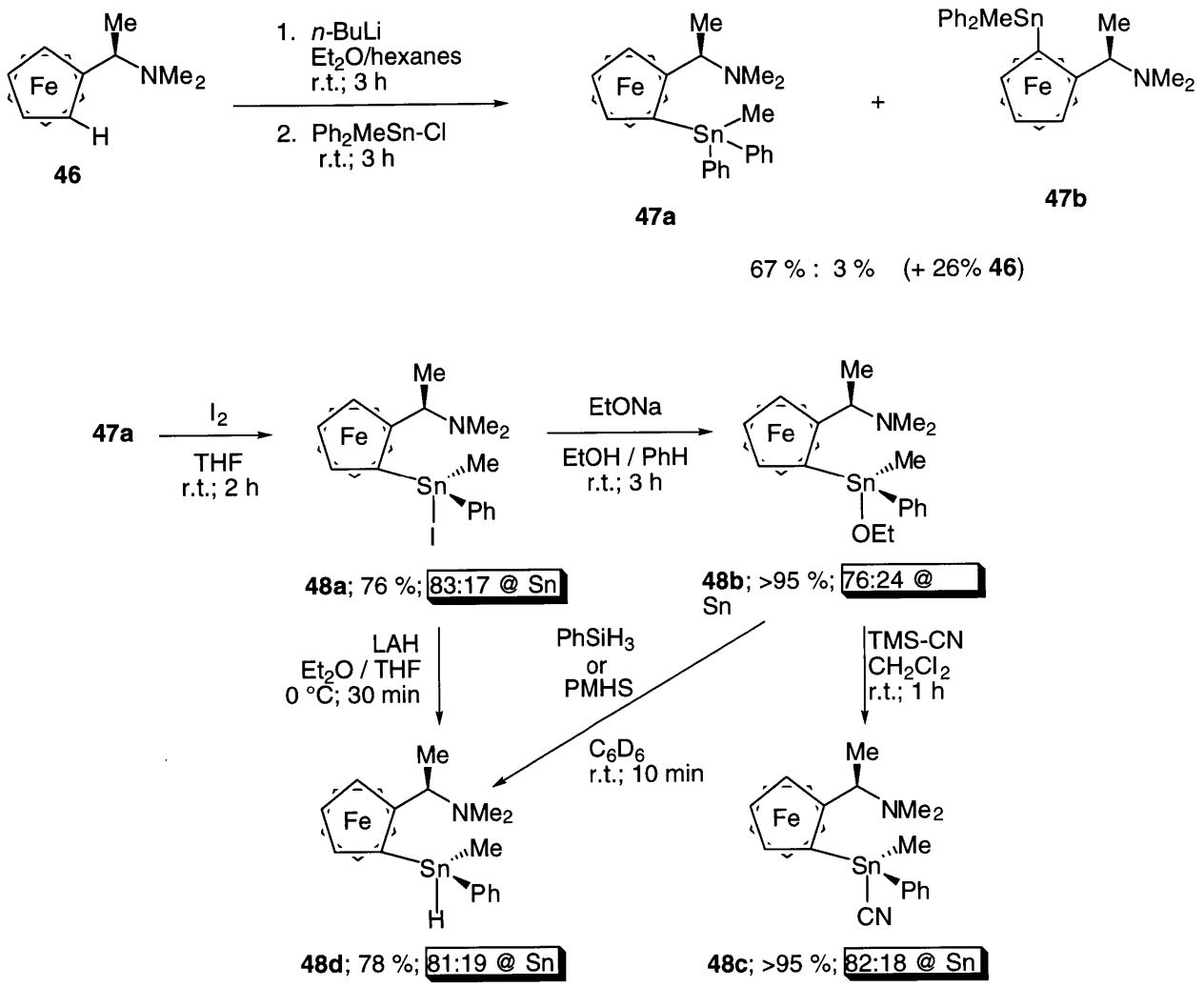
[43] (a) Slocum, D. W.; Rockett, B. W.; Hauser, C. R. *J. Am. Chem. Soc.* **1965**, *87*, 1241. (b) Gielen, M.; Eynde, I. V.; *J. Organomet. Chem.* **1981**, *217*, 205. (c) Roberts, R. M. G.; Silvers, J. *J. Organomet. Chem.* **1986**, *303*, 387. (d) Vedejs, E.; Duncan, S. M.; Haight, A. R. *J. Org. Chem.* **1993**, *58*, 3046.

[44] Prepared in 50% yield from the amine **46** (Fluka at $191/mL). For every 1 mL (1.222 g) of **46**, ~1 g (~2 mmol) of either **48b**, **48c**, or **48d** can be obtained.

Scheme 10. Synthesis of ferrocenyl-derived pentacoordinate organotin catalysts



The key step is the directed-lithiation of the optically pure ferrocenyl amine **46**[45] to give the enantiopure product **47a**. Selective electrophilic cleavage of one phenyl group by iodine (**47a** → **48a**) is believed to be assisted by a pentacoordinate transition state in which the axial phenyl group is cleaved preferentially (for steric reasons, the ferrocenyl group cannot be axial).[39, 40a, 41a]

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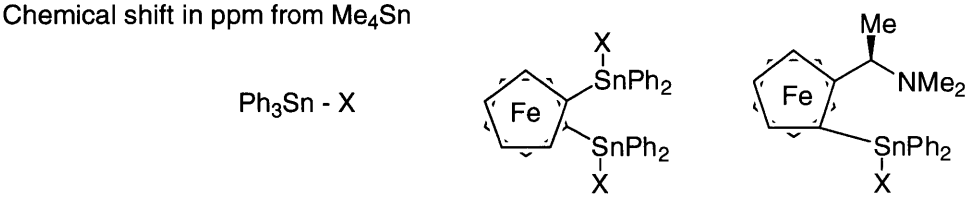
45 Racemic **46** can be obtained on a 30 g scale in 4 steps from ferrocene. Resolution of *rac*-**46** using L-tartaric acid gives each enantiomer of **46** on a 10 g scale. See: Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389.

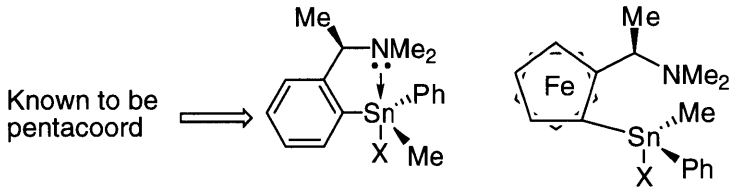
To study the solution state conformation of **48a-d**, we have prepared **51** and **52** (along with the known compounds **49**[46] and **50**[47]) and compared their ^{119}Sn NMR chemical shifts (Scheme 11).

Scheme 11. ^{119}Sn NMR evidence for pentacoordination

Chemical shift in ppm from Me_4Sn



	49	**50**	**51**
a; X = Ph	-128	-116	-113
b; I	-115	-91	-170



		52	**48**
X =	Ph	-118	-84.9
a:	I	-131	-116, -118
b:	OEt	-116, -118	-47.8, -49.6
c:	CN	-198	-167, -171
d:	H	-158, -160	-133, -135

Examination of the ^{119}Sn NMR data of ferrocenyltin compounds revealed that the ^{119}Sn chemical shift of the ferrocenyltin compounds is in general downfield shifted by ~ 20 ppm relative to the corresponding phenyltin compounds (e.g., **50a** vs. **49a; 50b** vs. **49b**).[46, 47] Also, recall that increasing the coordination number of tin from four to five typically leads to an upfield shift of about 50-60 ppm in ^{119}Sn

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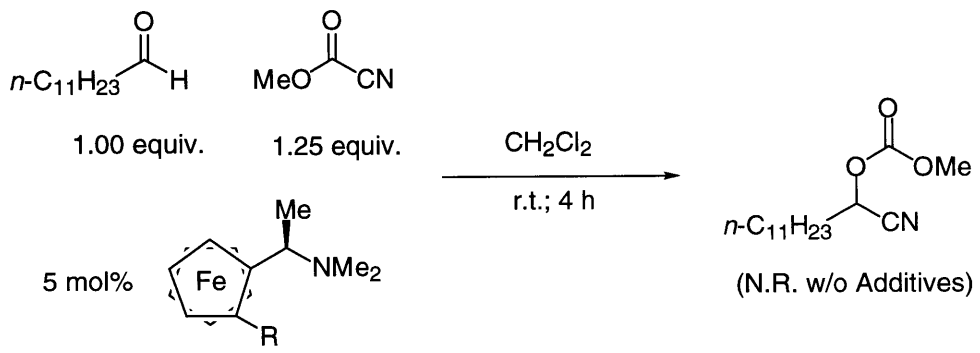
[46] (a) Roberts, R. M. G.; Silver, J. *J. Organomet. Chem.* **1986**, *303*, 387. (b) Kohler, F. H.; Geike, W. A.; Hertkorn, N. *J. Organomet. Chem.* **1987**, *334*, 359. (c) Kruger, C.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1989**, *569*, 97.

[47] Roberts, R. M. G.; Silver, J. *J. Organomet. Chem.* **1986**, *303*, 387.

NMR.[48] Since the ^{119}Sn NMR chemical shift of **51b** (-170 ppm) is significantly upfield compared to **50b** (-91 ppm), it can be inferred that **51b** is pentacoordinate. Also, by comparing the ^{119}Sn chemical shift of **48** with the corresponding known pentacoordinate family **52**, taking into account the difference between ferrocenyl and phenyl groups,[41] we have additional spectroscopic evidence that **48** is in fact pentacoordinate.

More importantly, we have established the pentacoordinate nature of **48** from a *reactivity* standpoint (Scheme 12).

Scheme 12. Evidence of pentacoordination from reactivity



	Additives R =	Conversion
1	H (**46**)	100 %
2	**46** + 5 mol% Bu_3Sn - Cl	100 %
3	MePhSn - *t*-Bu (**48e**)	100 %
4	MePhSn - I (**48a**)	0 %
5	MePhSn - CN (**48c**)	10 %

It is widely known that amines can catalyze the cyanoacylation of aldehydes, and indeed this is observed for the ferrocenyl amine **46** (entry 1; 100% conversion after 4

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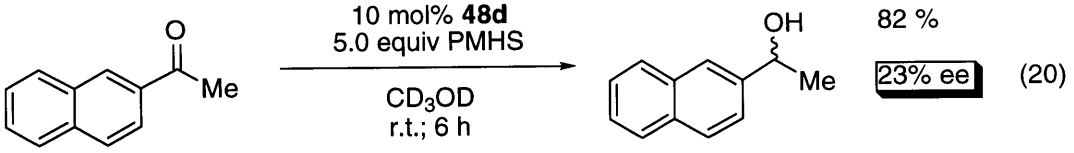
[48] For example, ^{119}Sn NMR chemical shift of Ph_3SnI is –113 ppm in $CDCl_3$ but is shifted to -229 ppm in d_6-DMSO. Holecek, J.; Nadrornik, K. *J. Organomet. Chem.* **1983**, *241*, 177. See also ref. 24 and 40b.

hours). Neither an external Lewis acid (entry 2) nor an internal bulky *ortho* substituent (entry 3) has any adverse effect on *nucleophilic* catalysis. Most interestingly however, nucleophilic catalysis is completely shut down when there is an internal Lewis acid (Sn-I) available for chelation (entry 4). This implies that the nucleophilic amine is bound to the internal Lewis acid. In other words, the tin atom is *pentacoordinate*. In the same time frame, *organotin* catalysis proceeded in 10% conversion (entry 5). We have thus established the pentacoordinate nature of the tin center in catalysts of the type **48a-d**.

With hypervalent organotin compounds in hand, we proceeded to use them as enantioselective catalysts. With the tin-hydride **48d**, we obtained modest enantioselectivity in the *polar* reduction of ketones (eq 20).



(20)

The reason why we describe the reaction in eq 20 as "polar" is because it has been established that hypervalent Sn-H acts as a hydride donor instead of a hydrogen atom donor.[49] Indeed, when CD_3OD was added to the presumed hypervalent catalyst **48d**, gas evolution was observed along with HD in ^1H NMR spectra and Sn-OR in ^{119}Sn NMR spectra.[50] Thus, not surprisingly, when we attempted to effect

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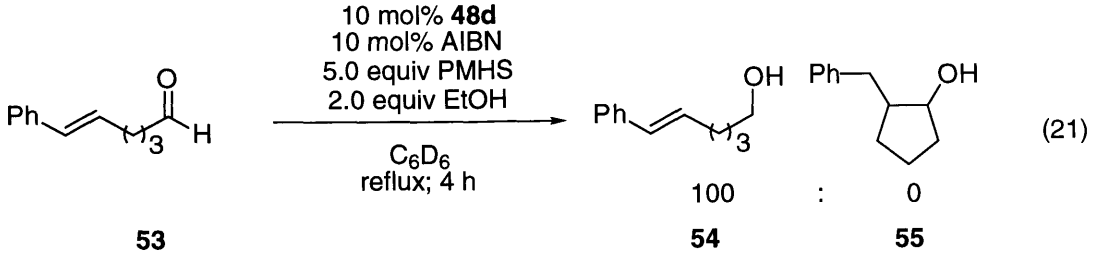
49 For a general review on the chemistry of tin hydrides, see Ref. 13(b). For selected examples of the reactivity of *hypervalent* organotin hydrides, see (and references therein): (a) Shibata, I.; Suzuki, T.; Baba, A.; Matsuda, H. *J. Chem. Soc., Chem. Commun.* **1988**, 882. (b) Shibata, I.; Yoshida, T.; Baba, A.; Matsuda, H. *Chem. Lett* **1989**, 619. (c) Shibata, I.; Yoshida, T.; Baba, A.; Matsuda, H. *Chem. Lett.* **1991**, 307. (d) Vedejs, E.; Duncan, S. M.; Haight, A. R. *J. Org. Chem.* **1993**, *58*, 3046. (e) Kawakami, T.; Sugimoto, T.; Shibata, I.; Baba, A.; Matsuda, H.; Sonoda, H. *J. Org. Chem.* **1995**, *60*, 2677.

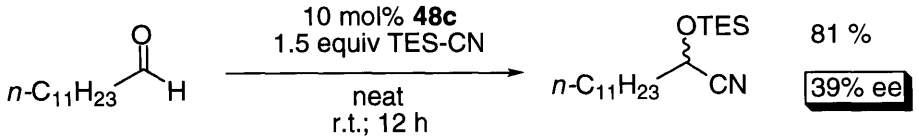
50 Bu_3Sn-H, on the other hand, displayed no such gas evolution in CD_3OD.

the radical-mediated enal cyclization of **53**, only the 1,2-reduced product **54** was observed (eq 21).

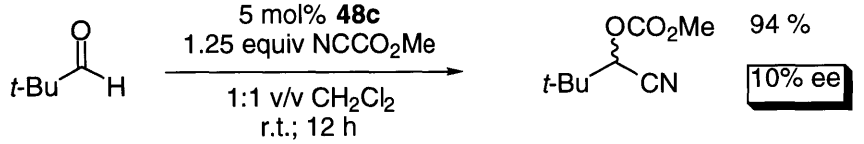


(21)

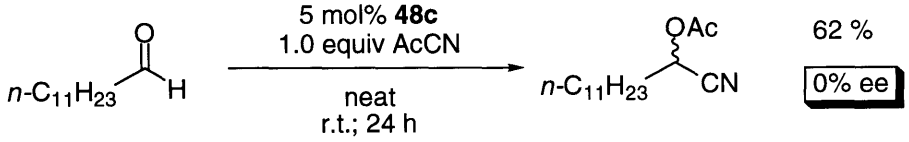
From these observations, it is obvious that we have to turn our attention to the polar aspect of organotin chemistry. Thus, we focused on the cyanosilylation and cyanoacylation of aldehydes (eqs 22, 23 and 24):



(22)



(23)



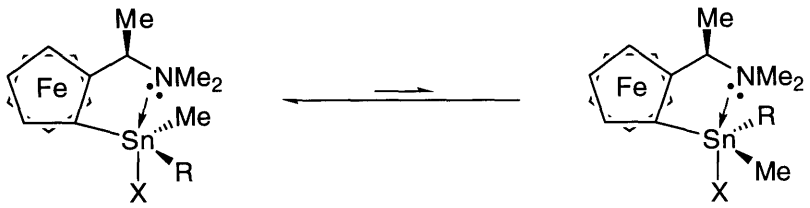
(24)

Although the results are somewhat disappointing in the sense that the enantioselectivity is modest, these nevertheless represent the highest values known. Furthermore, it should be noted that the observed enantioselectivity is

obtained with a catalyst (i.e., **48c**) that has a diastereomeric ratio of ~4:1 at tin. In other words, the "optical purity" of the catalyst at tin is in effect ~ 60% ee. We proposed that analogous to the work of van Koten and Metzger,[41] increasing the steric bulk of the tin substituent should increase the diastereomeric ratio (i.e., "optical purity") at tin. With an enhanced diastereomeric purity (i.e., more "enantiomerically pure" at the tin atom), we may observe higher enantioselectivity.

Using a more bulky organotin substituent, we were able to achieve the first part of our goal, the synthesis of diastereomerically pure pentacoordinate organotin compounds (Table 3).[51]

Table 3. Ratio of diastereomers as a function of the steric bulk of the tin substituent:



		Ratio of Configuration at Tin			
R =		Ph	4-*t*-Bu-C_6H_5	*o*-tol	*t*-Bu
		48	**56**	**57**	**58**
X =	**a:** I	86 : 14	86 : 14	> 95 : 5	> 95 : 5 (X = Cl)
	b: OEt	77 : 23	73 : 27	> 95 : 5	90 : 10
	c: CN	82 : 18	87 : 13	> 95 : 5	> 95 : 5
	d: H	82 : 18	---	---	---

When R=*o*-tol or *t*-Bu, we have, to the limit of ^{1}H NMR detection, diastereomerically pure pentacoordinate organotin compounds. Note that in all cases, we are *assuming* the diastereomer with bulky R and FeCp *trans* to each other in the chelation ring is preferred. The true test, of course, is to use these compounds as enantioselective catalysts (Table 4).

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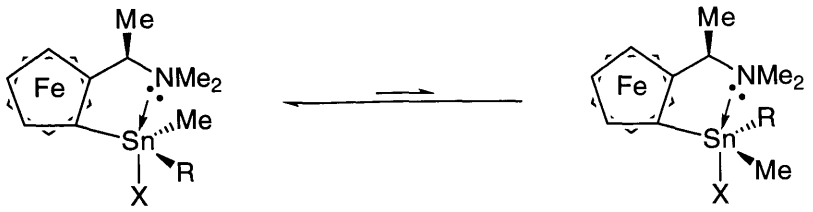
[51] The synthesis of **56**, **57** and **58** is analogous to that outlined for **48** in Scheme 10.

Table 4. Enantioselectivity as a function of the steric bulk on the tin substituent:

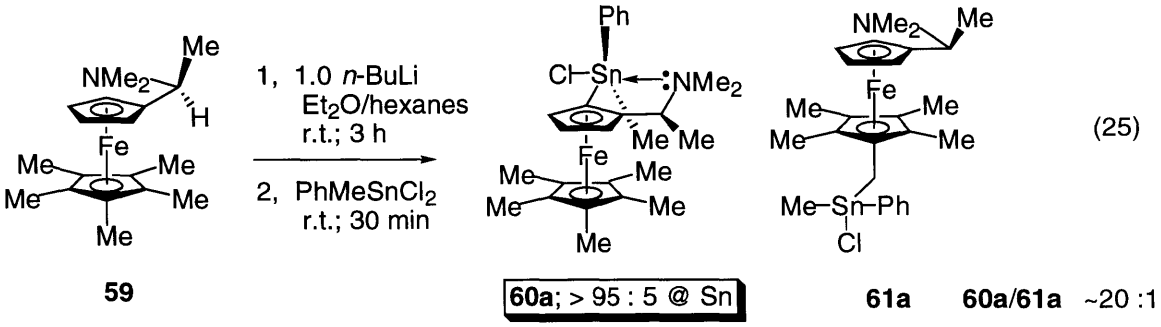


R =	Ph	4-*t*-Bu-C_6H_5	*o*-tol	*t*-Bu
	48	**56**	**57**	**58**
c: X = CN %ee of cyanosilylation	39	15	0	0
b: X = OEt %ee of reduction	23	13	10	0

Much to our dismay, the enantioselectivity dropped monotonically with an *increase* in the diastereomeric purity of the catalysts. Our tentative explanation is that as the steric bulk of "R" is increased, the catalyst became more and more *sterically symmetrical.* That is, from the substrate's standpoint, *o*-tol or *t*-Bu is sufficiently bulky such that they are *sterically identical* to the ferrocenyl group. As an illustration, if we were to assign a "steric factor" of "10" for the ferrocenyl group, and we arbitrarily assign a steric factor of "5" to the phenyl group of **48**, the more bulky *o*-tol and the *t*-Bu can be thought of as having a steric factor of "9". Thus, based on steric arguments, with **57** and **58**, we have in essence an achiral catalyst of the type R_2MeSn-X.[52]

[52] The *diphenyl* analogue **51c** (X=CN) displayed no asymmetric induction in the cyanosilylation of aldehydes.

Since modifying the organic substituent did not bear fruit (and we cannot make the methyl group any smaller), we attempted to increase the size of the metal fragment instead (eq 25).[53]



59 **60a**; > 95 : 5 @ Sn **61a** **60a/61a** ~20 :1

It is interesting to note that by changing the metal fragment from FeCp to FeCp*, we can increase the diastereomeric ratio from ~80:20 to >95:5 (**48a** vs. **60a**). Unfortunately, we were unable to purify/isolate **60a** from the trace amount of Cp*-lithiated product **61a** at any stages (e.g., as the Sn-OEt or the Sn-CN). Attempts at enantioselective catalysis (polar reduction, cyanosilylation and cyanoacylation) using the impure catalyst gave only racemic products. This is perhaps not surprising considering that the tin of the Cp*-lithiated product is not only racemic but is also in a much less sterically hindered environment. Furthermore, and perhaps far more damaging, *the amine of the Cp*-lithiated catalysts is no longer occupied by the tin atom.* A control reaction using the optically pure ferrocenyl amine **46** has shown that the amine itself is an efficient catalyst for the *non-stereoselective* cyanosilylation of aldehydes. Thus, it is conceivable that it is the "free" amine of **61** that is responsible for the observed racemic product.

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53 Schwink, L.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 25.

In conclusion, we have accomplished the synthesis of enantiopure hypervalent planar-chiral organotin catalyst and obtained modest enantioselectivity (39% ee; eq 22) in the cyanosilylation of aldehyde.

IV. Experimental

General

Benzene, C_6D_6, Et_2O, THF, d_8-THF, and pentane were distilled from sodium. Methylene chloride was distilled from calcium hydride. Ethanol was distilled from Mg/I_2. Pyridine (Mallinkrodt), 2,6-di-*t*-butylpyridine (Aldrich) were distilled from calcium hydride. TMS-CN (Aldrich), *n*-dodecyl aldehyde (Aldrich), *o*-tolylbenzaldehyde (Aldrich), trimethylacetaldehyde, benzaldehyde, d_5-pyridine (CIL), d_6-DMSO (CIL), d_7-DMF (CIL), HMPA (Aldrich), acetylcyanide (Aldrich), methylcyanoformate (Aldrich), phenylsilane (Fluka), triethylsilane (Aldrich), 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene (Danishefsky's diene; Fluka) were distilled prior to use. AIBN (Aldrich), 2-nitrobenzaldehyde (Aldrich), trimethylamine oxide (Aldrich), triphenylphosphine oxide (Aldrich) and sodium cyanoborohydride (Aldrich) were recrystallized prior to use. LAH (Aldrich) was washed with Et_2O (white powder obtained from the commercial gray powder). *t*-BuLi in pentane (Aldrich) was titrated prior to use.[54] PMHS (Fluka) and 2'-acetonaphthone (Aldrich) were purified by chromatography prior to use. Phenyldichloroborane (Aldrich), EtONa (Aldrich), 1.0 M TBAF in THF (Aldrich), Bu_4NCN (Aldrich), divinyltin dichloride (Strem), 2,2-dimethoxypropane (Aldrich), acetyl chloride (Aldrich), $BF_3 \bullet Et_2O$ (Aldrich), $SnCl_4$ (Aldrich), 1.0 M BBr_3 in CH_2Cl_2 (Aldrich), 1.0 M LiOEt in THF (Aldrich), iodine (Mallinkrodt), *(R)-N,N*-dimethyl-*sec*-phenylethylamine (Aldrich), (*R*)-(+)-*N,N*-dimethyl-1-ferrocenyl-ethylamine **46** (Aldrich or Fluka),[55] triphenyltin chloride (Aldrich), 1.6 M *n*-BuLi in hexanes

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[54] The halogen-metal exchange reactions are extremely sensitive to the amount of *t*-BuLi present: a deviation of ~ 10% will lead to a dramatic decrease in yield.

[55] The *(S)*-enantiomer of **46** was obtained via classical resolution of the synthetic *rac*-**46** following Ugi's procedure, see: Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970,** *92*, 5389.

(Strem), methyltin trichloride (Aldrich or Strem), 1.0 M HCl in Et_2O (Aldrich), 3.0 M methylmagnesium bromide in Et_2O (Aldrich), 1.0 M *t*-butylmagnesium chloride in THF (Aldrich), 2.0 M 4-*t*-butylphenylmagnesium bromide in Et_2O (Aldrich), 1.0 M *o*-tolylmagnesium bromide in THF (Aldrich) and 1.0 M vinylmagnesium bromide in THF (Aldrich) were used as received. *(R)*-α-methoxy-α-(trifluoromethyl)phenylacetic acid chloride (MTPA-Cl/Mosher's acid chloride; Aldrich) were used as received or prepared according to literature procedure.[56] The stannepin**6**,[20,21,22] TES-CN,[57] the bis-bromide **17** and its acetonide derivative,[30] the *(S)*-Cp*-ferrocenylamine **59**,[53] naphthalene chromiumtricarbonyl,[58] and the organotin compounds[59] were synthesized according to literature procedures.

Analytical thin layer chromatography was performed using EM Reagents 0.25 mm silica gel 60 plates, and visualization was accomplished with UV. Flash chromatography was performed on TCI silica gel 60 (230-400 mesh).[60]

^1H nuclear magnetic resonance spectra were recorded on a Bruker AC-250 or a Varian XL-300 NMR spectrometer. ^{13}C and ^{119}Sn nuclear magnetic resonance spectra were recorded on a Varian XL-300 NMR spectrometer. ^1H 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). ^{119}Sn chemical shifts are

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56 Ward, D. E.; Rhee, C. K. *Tetrahedron Lett.* **1991**, *32*, 7165.

57 Becu, C.; Anteunis, M. J. O. *Bull. Soc. Chim. Belg.* **1987**, *96*, 115.

58 Bland, M. J.; Davis, R.; Durrant, J. L. A. *J. Organomet. Chem.* **1985**, *280*, 95. Although naphthalene chromiumtricarbonyl is available from Aldrich, we have found the quality of the purchased reagent to be inferior to that of the freshly prepared reagent.

59 See Experimental Section on Preparation of Organotin Electrophiles.

60 Whenever arene chromiumtricarbonyl compounds are subjected to column chromatography, the chromatography is conducted under a nitrogen pressure and the overhead light is turned off in order to minimize decomposition.

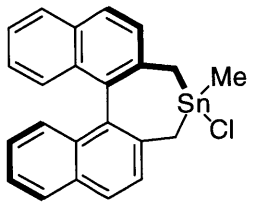
reported in ppm downfield from tetramethylstannane (δ scale). All ^{13}C and ^{119}Sn spectra were determined with complete proton decoupling.
Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer. Melting points (uncorrected) were obtained on a Thomas Hoover Unimelt capillary melting point apparatus.

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

Structural assignments are tentative for compounds that are not fully characterized. However, we are extremely confident of the structures as shown.

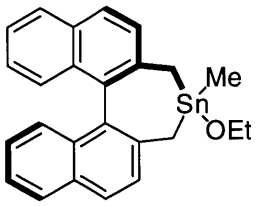
Synthesis of 1,1′-Binaphthyl-derived C_2-Symmetric Organotin Catalysts

(Scheme 3)



7

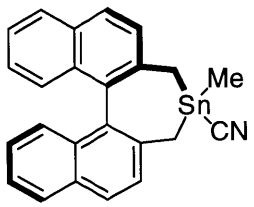
7: To an oven-dried vial in a glove box was added 438 mg (1.02 mmol) of **6** in 10 mL of CH_2Cl_2 and 133 μL (1.02 mmol; 1.00 equiv) of $PhBCl_2$. The resulting pale yellow solution was stirred at room temperature for 24 hours, after which solvent was removed *in vacuo* to give a pale yellow solid. Recrystallization of the crude from 5:1 pentane/CH_2Cl_2 at –30 °C gave 329 mg (72% yield) of Sn-Cl **7** as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.96 (m, 4H), 7.00-7.57 (m, 6H), 2.74-2.86 (m, 2H), 2.36-2.52 (m, 2H), 0.702 (s, 3H, $^2J_{H\text{-}Sn}$=52); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.2, 134.4, 133.2, 132.8, 132.3, 131.9, 131.8, 128.8, 128.4, 128.1, 128.0, 127.7, 126.6, 126.3, 126.1, 126.0, 125.8, 125.0, 124.7, 24.6, 23.5, -1.21; ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -146.



8a

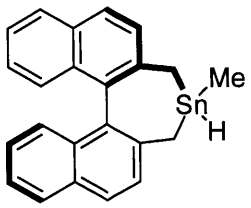
8a: To an oven-dried vial in a glove box was added 6.2 mg (0.092 mmol; 1.0 equiv) of EtONa in 250 μL of EtOH and 41 mg (0.092 mmol) of Sn-Cl **7** in 750 μL of benzene. The resulting pale yellow solution was stirred at room temperature for 3 hours, after

which the solvent was removed *in vacuo* to give 40 mg (98% yield) of crude **8a**. ^{1}H NMR (300 MHz $CDCl_3$) δ 7.89-7.96 (m, 4H), 7.00-7.57 (m, 6H), 3.74 (q, 2H, J=7), 2.18-2.76 (4d, 4H), 1.15 (t, 3H, J=7), 0.550 (s, 3H); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ 116.



8b

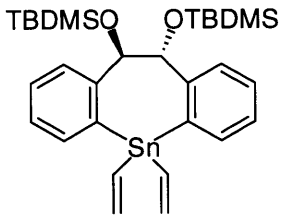
8b: To an oven-dried Schlenk tube in a glove box was added 249 mg (0.556 mmol) of Sn-Cl **7** and 7.4 mL (56 mmol, 100 equiv) of TMS-CN. The resulting pale yellow solution was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 75 °C. After 96 hours, the Schlenk tube was cooled to room temperature and moved back into a glove box. The excess TMS-CN was removed *in vacuo* and the resulting black solid was recrystallized from pentane/CH_2Cl_2 at –30 °C to give 222 mg (92% yield) of Sn-CN **8b** as a brown solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87-7.97 (m, 4H), 6.96-7.60 (m, 6H), 2.63-2.74 (m, 2H), 2.25-2.57 (m, 2H), 0.658 (s, 3H, $^{2}J_{H-Sn}$=58); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.8, 134.3, 133.1, 132.8, 132.2, 132.1, 131.9, 131.6, 128.9, 128.8, 128.2, 127.9, 126.9, 126.5, 126.3, 126.2, 125.8, 125.6, 125.1, 124.9, 124.3 ($^{2}J_{C-Sn}$ = 39.5), 19.7 ($^{1}J_{C-Sn}$=357, 339), 18.2 ($^{1}J_{C-Sn}$=356, 340), -6.41 ($^{1}J_{C-Sn}$=316, 301); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -27.0.



8c

8c: To an oven-dried vial in a glove box was added 42 mg (0.094 mmol) of Sn-Cl **7** and 3.7 mg (0.097 mmol; 1.0 equiv) of LAH in 1 mL of THF.[61] After 30 minutes at room temperature, the reaction was removed from the glove box and quenched with distilled water. The crude mixture was extracted with 3 x 10 mL of Et_2O. Drying the organic layer with $MgSO_4$ followed by filtration and solvent removal gave crude Sn-H **8c** as a clear oil. ^1H NMR (300 MHz, C_6D_6) δ 7.74-7.67 (m, 4H), 6.93-7.34 (m, 6H), 5.77 (m, 1H), 1.81-2.09 (m, 2H), 2.36-2.52 (m, 2H), 0.710 (s, 3H, ^4J=3); ^{119}Sn NMR (111 MHz, C_6D_6) δ -28.3.

Synthesis of Arene Chromiumtricarbonyl-based C_2-Symmetric Organotin Catalysts (Scheme 4)



18

18: To an oven-dried flask fitted with an addition funnel under argon was added 1.80 g (3.00 mmol) of **17** and 100 mL of Et_2O. The resulting clear colorless solution

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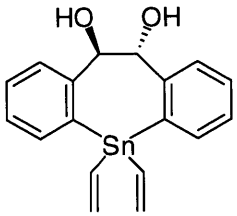
61 As close to exactly 1.00 equiv of LAH should be used. When we monitored the reaction by ^1H NMR, we observed that the reaction is effectively instantaneous and only one hydride of $LiAlH_4$ is transferred. However, **8c** decomposed in the presence of slight excess (~ 10 mol%) of LAH within 30 minutes at room temperature.

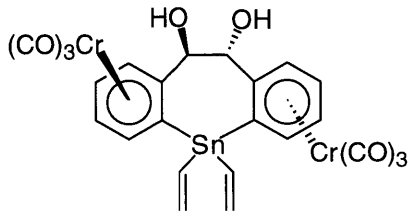
was immersed in a dry ice/acetone bath at –78 °C. To the cold reaction mixture was added 4.0 mL (6.8 mmol; 2.3 equiv) of 1.7 M *t*-BuLi in pentane dropwise over 5 minutes. After stirring at –78 °C for 1 hour, 750 mg (3.07 mmol; 1.02 equiv) of divinyltin dichloride in 50 mL of Et_2O was added to the addition funnel. The tin halide solution was added dropwise to the reaction mixture over 30 minutes. After the addition was completed, the reaction was allowed to warm to room temperature overnight. The reaction was quenched by water, and the organic and aqueous layers were separated. The organic layer was washed with 1 x 50 mL of sat. NaCl and dried with Na_2SO_4. After filtration and solvent removal, silica gel column chromatography (pentane; R_f ~ 0.5; UV) gave 984 mg (53% yield) of the stannacycle **18** as a clear colorless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, 2H, J=6), 7.16-7.26 (m, 6H), 6.56 (dd, 2H, J=14, 20), 6.27 (dd, 2H, J=14, 3), 5.86 (dd, 2H, J=3,2 0), 5.19 (s, 2H), 0.492 (s, 18H), -0.25 (s, 6H), -0.33 (s, 6H). ^{1}H NMR (300 MHz, C_6D_6) δ 7.67 (d, 2H, J= 6), 7.07 - 7.16 (m, 6H), 6.77 (dd, 2H, J=14,20), 6.35 (dd, 2H, J=3, 14), 6.05 (dd, 2H, J=3, 20), 5.29 (s, 2H), 0.73 (s, 18H), -0.15 (s, 6H), -0.24 (s, 6H).



19

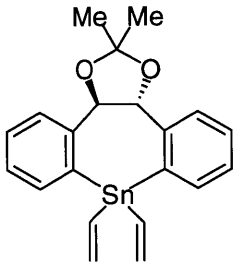
19: To an oven-dried flask under argon was added 984 mg (1.61 mmol) of TBDMS ether **18** in 15 mL of THF and 3.6 mL (3.6 mmol; 2.2 equiv) of 1.0 M TBAF in THF. The resulting clear, colorless solution was stirred at room temperature. After 1 hour, the reaction was quenched with 2 N HCl and extracted with 3 x 30 mL of EtOAc. The organic layer was washed with 2 x 20 mL of sat. $NaHCO_3$ followed by 1 x 20 mL of sat. NaCl. The organic phase was dried over Na_2SO_4, filtered and stripped

of solvent. Silica gel column chromatography (25% EtOAc/75% hexanes; R_f ~ 0.3; UV) gave 488 mg (79% yield) of diol **19** as a clear colorless, viscous oil. ^{1}H NMR (300 MHz, C_6D_6) δ 7.57 (t, 2H, J= 6), 7.06-7.20 (m, 6H), 6.55 (dd, 2H, J=14, 20), 6.24 (dd, 2H, J=3, 14), 5.97 (dd, 2H, J=3, 20), 4.83 (d, 2H, J=5), 2.09 (d, 2H).



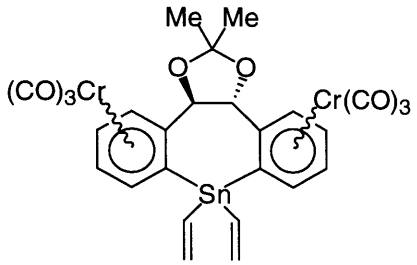
20

20: To an oven-dried Schlenk tube in a glove box was added 155 mg (0.587 mmol; 3.01 equiv) of naphthalene chromiumtricarbonyl, 75 mg (0.20 mmol) of diol **19** in 1.5 mL of Et_2O and 140 μL (1.73 mmol; 8.87 equiv) of THF to give a red slurry. The Schlenk tube was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 70 °C. After 18 hours, the orange reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. The excess naphthalene chromiumtricarbonyl was eluted as a red band on silica gel column chromatography (25% EtOAc/75% hexanes). After the elution of the red band, the solvent system was switched to 50% EtOAc/50% hexanes. The subsequently eluted yellow band, after solvent removal, gave 66 mg (52% yield) of **20** as a pale yellow solid. ^{1}H NMR (300 MHz, C_6D_6) δ 6.50 (dd, 2H, J=14, 20), 6.18 (dd, 2H, J=3, 14), 5.81 (dd, 2H, J=3, 20), 5.08 (d, 2H, J=6), 4.87 (d, 2H, J=7), 4.61 (d, 2H, J=7), 4.24-4.28 (m, 4H), 2.47 (br, 2H).

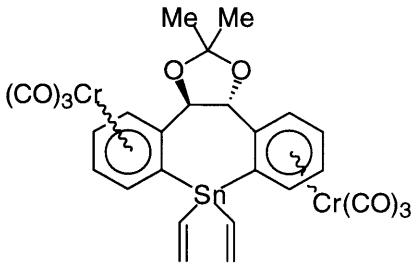


21

21: To an oven-dried flask fitted with an addition funnel under argon was added 436 mg (1.06 mmol) of the acetonide derivative of **17** and 15 mL of THF. The resulting clear, colorless solution was immersed in a dry ice/acetone bath at –78 °C. To the cold reaction mixture was added 1.5 mL (2.6 mmol; 2.4 equiv) of 1.7 M *t*-BuLi in pentane dropwise over 5 minutes. After stirring at –78 °C for 1 hour, 258 mg (1.06 mmol; 1.00 equiv) of divinyltin dichloride in 35 mL of THF was added to the addition funnel. The tin halide solution was added dropwise to the reaction mixture over 1 hour. After the addition was completed, the reaction was allowed to warm to room temperature overnight. The reaction was quenched by water and extracted with EtOAc. The organic layer was washed with 1 x 50 mL of sat. NaCl and dried with Na_2SO_4. After filtration and solvent removal, silica gel column chromatography (5% EtOAc/95% hexanes; R_f ~ 0.5; UV) gave 267 mg (59% yield) of **21** as a clear colorless, viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, 2H, J=8), 7.53 (d, 2H, J=7), 7.41 (dd, 2H, J=7, 8), 7.29 (dd, 2H, J=7, 8), 6.56 (dd, 2H, J=13, 20), 6.33 (dd, 2H, J=3, 13), 5.82 (dd, 2H, J=3, 20), 5.22 (s, 2H), 1.57 (s, 6H).



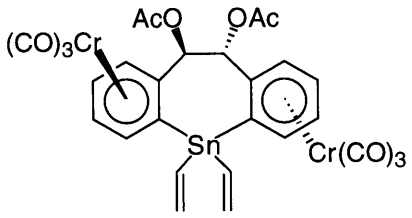
22



23

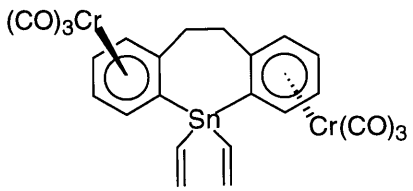
22 and **23**: To an oven-dried Schlenk tube in a glove box was added 415 mg (1.57 mmol; 2.50 equiv) of naphthalene chromiumtricarbonyl, 267 mg (0.628 mmol) of stannacycle **21** in 5.6 mL of Et_2O and 400 μL (4.94 mmol; 7.87 equiv) of THF to give a red slurry. The Schlenk tube was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 70 °C. After 57 hours, the orange reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. Silica gel column chromatography (25% EtOAc/75% hexanes) eluted the excess naphthalene chromiumtricarbonyl along with the *anti* $-Cr(CO)_3$ stannacycle **23** as a red band followed by a yellow band which was identified as of the *syn* $-Cr(CO)_3$ stannacycle **22** as a yellow solid (120 mg; 27% yield). **22**: ^1H NMR (300 MHz, C_6D_6) δ 6.86 (dd, 1H, J=13, 20), 6.22 (d, 1H, J=8), 5.97-6.13 (m, 3H), 5.66 (dd, 1H, J=3, 20), 5.25 (m, 1H), 5.18 (d, 2H, J=6), 4.96 (d, 1H, J=6), 4.88 (t, 1H, J=6), 4.67 (d, 1H, J=6), 4.63 (t, 1H, J=6), 4.24 (m, 2H), 1.63 (s, 3H), 1.56 (s, 3H). The products from the first red band was re-subjected to silica gel column chromatography (10% EtOAc/90% hexanes, R_f ~ 0.1; yellow) to give 53 mg (12% yield) of *anti* $-Cr(CO)_3$ **23** as an orange solid. Major Diastereomer of **23**: ^1H NMR (300 MHz, C_6D_6) δ 6.51 (dd, 2H, J=14, 20), 6.17 (dd, 2H, J=3, 14), 5.79 (dd, 2H, J=3, 20), 5.28 (d, 2H, J=6), 4.90 (s, 2H), 4.86 (d, 2H, J=6), 4.73 (t, 2H, J=6), 4.21 (t, 2H, J=6), 1.21 (s, 6H). Minor Diastereomer of **23**: ^1H NMR (300 MHz, C_6D_6) δ 6.43 (dd, 2H, J=14, 20), 6.09 (dd, 2H, J=3, 14), 5.68 (dd, 2H, J=3, 20), 5.58 (d, 2H, J=6), 5.13 (s, 2H), 4.63 (d, 2H, J=6), 4.47 (t, 2H, J=6), 4.18 (t, 2H, J=6), 1.56 (s, 6H).

Scheme 5. Confirmation of diastereoselective hydroxyl-directed complexation of $Cr(CO)_3$ to (20): To an oven-dried vial in a glove box was added 66 mg (0.010 mmol) of **20**, 1 ml (8 mmol) of 2,2-dimethoxypropane and 1 drop (~ 20 µl) of aqueous HCl. After stirring at room temperature for 24 hours, the solvent was evaporated *in vacuo*. To the crude reaction mixture was added ~ 1 ml of CH_2Cl_2 and ~ 5 drops of NEt_3. The resulting black solution was filtered through basic alumina. After solvent was removed *in vacuo*, crude ^1H NMR showed only the major diastereomer of **23** (along with some impurity, most likely the endocyclic cleavage product **29**). ^1H NMR (300 MHz, C_6D_6) δ 6.51 (dd, 2H, J=14, 20), 6.17 (dd, 2H, J=3, 14), 5.79 (dd, 2H, J=3, 20), 5.28 (d, 2H, J=6), 4.90 (s, 2H), 4.86 (d, 2H, J=6), 4.73 (t, 2H, J=6), 4.21 (t, 2H, J=6), 1.21 (s, 6H).



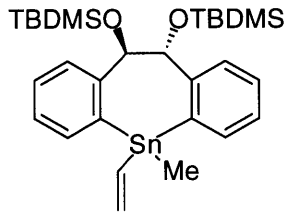
24

24: To an oven-dried vial in a glove box was added 120 mg (0.183 mmol) of diol **21**, 2.5 mL of CH_2Cl_2, 50 µL (0.62 mmol; 3.4 equiv) of pyridine and 55 µL (0.77 mmol; 4.2 equiv) of acetyl chloride to give a yellow solution. After stirring at room temperature for 1 hour, the solvent was removed *in vacuo*. The residual solid was taken up in ~ 5 mL of benzene and filtered through an 0.45 µm Acrodisc. Removal of the solvent *in vacuo* gave 120 mg (89% yield) of bis-acetate **24** as a yellow solid. ^1H NMR (300 MHz, C_6D_6) δ 6.53 (dd, 2H, J=14, 20), 6.18 (dd, 2H, J=3, 14), 5.88 (d, 2H, J=6), 5.81 (dd, 2H, J=3, 20), 5.19 (d, 2H, J=7), 4.83 (d, 2H, J=7), 4.73 (d, 2H, J=7), 4.27 (d, 2H, J=7), 1.63 (s, 6H).



25

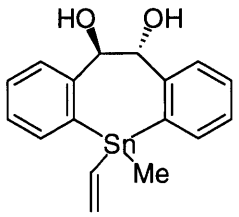
25: To an oven-dried vial in a glove box was added 110 mg (0.148 mmol) of bis-acetate **24** and 3 mL of CH_2Cl_2. To the resulting orange solution was added 190 μL (1.50 mmol; 10.1 equiv) of BF_3•Et_2O to give a dark green solution within 5 minutes. To this dark green solution was added 480 μL (3.01 mmol; 20.3 equiv) of Et_3SiH. The reaction was stirred at room temperature as the color of the reaction gradually returned to the original orange. After the 3 hours, the vial was removed from the glove box and the reaction was quenched with 2 N HCl and extracted with Et_2O. The organic layer was washed with 1 x 10 mL of sat. $NaHCO_3$ and 1 x 10 mL of sat. NaCl. The organic layer was dried with Na_2SO_4, filtered and stripped of solvent. Silica gel column chromatography (25% EtOAc/75% hexanes; R_f ~ 0.4; orange) gave 54 mg (58% yield) of stannacycle **25** as an orange solid. ^1H NMR (300 MHz, C_6D_6) δ 6.57 (dd, 2H, J=14, 20), 6.22 (dd, 2H, J=3, 14), 5.84 (dd, 2H, J=3, 20), 4.92 (d, 2H, J=6), 4.87 (d, 2H, J=7), 4.67 (dd, 2H, J=7), 4.18-4.27 (m, 4H), 2.41 (d, 2H, J=14), 2.11 (d, 2H, J=14).



31

31: To an oven-dried flask fitted with an addition funnel under argon was added 3.60 g (6.00 mmol) of **17** and 200 mL of Et_2O. The resulting clear colorless solution was immersed in a dry ice/acetone bath at –78 °C. To this cold reaction mixture was added 9.2 mL (14 mmol; 2.3 equiv) of 1.5 M *t*-BuLi in pentane dropwise over 10

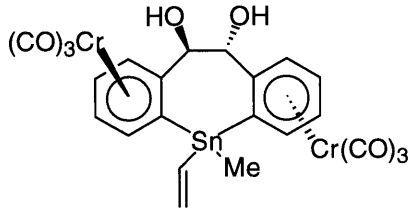
minutes. After stirring at –78 °C for an additional 1 hour, 1.60 g (6.90 mmol; 1.15 equiv) of methylvinyltin dichloride in 100 mL of Et_2O was added to the addition funnel. The tin halide solution was added dropwise to the reaction mixture over 30 minutes. After the addition was completed, the reaction was allowed to warm to room temperature overnight. The reaction was quenched by water and the organic and aqueous layers were separated. The organic layer was washed with 1 x 50 mL of sat. NaCl and dried with Na_2SO_4. After filtration and solvent removal, silica gel column chromatography (hexane; R_f ~ 0.6; UV) gave 1.04 g (29% yield) of stannacycle **31** as a clear colorless, viscous oil. ^{1}H NMR (250 MHz, C_6D_6) δ 7.55-7.64 (m, 2H), 7.00-7.20 (m, 6H), 6.83 (dd, 1H, J=14, 20), 6.34 (dd, 1H, J=3, 14), 5.99 (dd, 1H, J=3, 20), 5.26 (s, 2H), 0.64 (s, 9H), 0.63 (s, 9H), 0.59 (s, 2H, $^2J_{H\text{-}Sn}$=54), -0.12 (s, 3H), -0.16 (s, 3H), -0.24 (s, 3H), -0.26 (s, 3H).



32

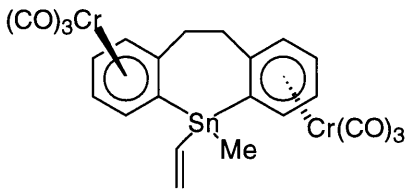
32: To an oven-dried flask under argon was added 2.17 g (3.61 mmol) of TBDMS ether **31** in 40 mL of THF and 7.2 mL (7.2 mmol; 2.0 equiv) of 1.0 M TBAF in THF. The resulting clear colorless solution was stirred at room temperature for 1 hour. The reaction was quenched with sat. $NaHCO_3$ and extracted with 3 x 50 mL of EtOAc. The organic layer was washed with 1 x 50 mL of sat. NaCl and dried over $MgSO_4$. Filtration of the organic phase followed by solvent removal and silica gel column chromatography (25% EtOAc/75% hexanes; R_f ~ 0.4; UV) gave 1.14 g (84% yield) of diol **32** as a clear colorless, viscous oil. ^{1}H NMR (300 MHz, C_6D_6) δ 7.36-7.64 (m, 4H), 7.00-7.20 (m, 4H), 6.56 (dd, 1H, J=14, 20), 6.21 (dd, 1H, J=3, 14), 5.81 (dd, 1H, J=3, 20),

4.83 (s, 2H), 2.20 (br, 1H), 2.09 (br, 1H), 0.34 (s, 3H, $^2J_{H\text{-}Sn}$=56).



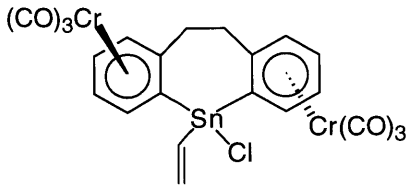
33

33: To an oven-dried Schlenk tube in a glove box was added 2.42 g (9.17 mmol; 3.00 equiv) of naphthalene chromiumtricarbonyl, 1.14 g (3.06 mmol) of diol **32** in 22 mL of Et_2O and 2.2 mL (27 mmol; 8.9 equiv) of THF to give a red slurry. The Schlenk tube was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 70 °C. After 18 hours, the orange reaction mixture was cooled to room temperature and the solvent removed *in vacuo*. Silica gel column chromatography (25% EtOAc/75% hexanes) eluted the excess naphthalene chromiumtricarbonyl as a red band. A yellow band was collected after the solvent system was switched to 50% EtOAc/50% hexanes. After solvent removal, the crude yellow solid was moved into a glove box and recrystallized from 40 mL of CH_2Cl_2 at –30 °C to give 875 mg (44% yield) of the desired compound **33** as a pale yellow solid. ^{1}H NMR (300 MHz, C_6D_6) δ 6.53 (dd, 1H, J=14, 20), 6.14 (dd, 2H, J=3, 14), 5.67 (dd, 1H, J=3, 20), 5.08 (dd, 1H, J=2, 6), 4.67-4.82 (m, 4H), 4.19-4.29 (m, 4H), 2.49 (br, 1H), 2.39 (br, 1H), 0.519 (s, 2H, $^2J_{H\text{-}Sn}$=59).



35

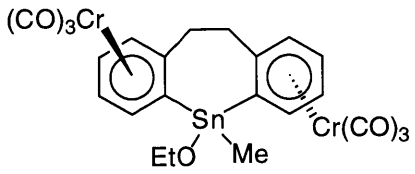
35: To an oven-dried vial in a glove box was added 875 mg (1.36 mmol) of diol **33**, 30



37

mL of CH_2Cl_2 and 350 μL (4.33 mmol; 3.18 equiv) of pyridine. To the resulting orange solution was added 400 μL (5.65 mmol; 4.15 equiv) of acetyl chloride. After stirring at room temperature for 1 hour, the solvent was removed *in vacuo* and the residual solid was taken up in benzene and filtered through an 0.45 μm Acrodisc. Removal of the solvent *in vacuo* gave a yellow solid, which was the dissolved in 20 mL of CH_2Cl_2 to give an orange solution. To this orange solution was added 1.7 mL (13 mmol; 9.9 equiv) of $BF_3 \bullet Et_2O$ to give a dark green solution within 5 minutes. To this dark green solution was added 4.3 mL (27 mmol; 20 equiv) of Et_3SiH. The reaction was stirred at room temperature as the color of the reaction gradually returned to the original orange. After 4 hours, the vial was removed from the glove box and the reaction was quenched with sat. $NaHCO_3$ and extracted with 2 x 20 mL of Et_2O. The organic layer was washed with 1 x 20 mL of sat. NaCl and dried with $MgSO_4$. Filtration followed by solvent removal and silica gel column chromatography (25% EtOAc/75% hexanes; $R_f \sim 0.5$; yellow) gave 397 mg (48% yield) of stannacycle **35** as a yellow solid. ^1H NMR (250 MHz, C_6D_6) δ 6.55 (dd, 2H, J=14, 20), 6.18 (dd, 2H, J=3, 14), 5.81 (dd, 2H, J=3, 20), 4.67-4.86 (m, 4H), 4.18-4.25 (m, 6H), 2.31-2.42 (m, 2H), 2.05-2.10 (m, 2H), 0.54 (s, 3H, $^2J_{H\text{-}Sn}$=59).

37: To an oven-dried vial in a glove box was added 50 mg (0.082 mmol) of the stannacycle **35** in 1 mL of CH_2Cl_2 to give a yellow solution. The addition of 10 μL (0.085 mmol; 1.1 equiv) of $SnCl_4$ resulted in a yellow cloudy slurry. After stirring at room temperature for 1 hour, the solvent was removed *in vacuo* and the residual solid was taken up by benzene. After filtration through an 0.45 μm Acrodisc, the



39

solvent was removed *in vacuo*. Recrystallization from 2 mL of ~ 1:1 pentane/CH_2Cl_2 at –30 °C gave 25 mg (49% yield) of Sn-Cl **37** as a yellow solid. ^{1}H NMR (300 MHz, C_6D_6) δ 4.91 (d, 1H, J=6), 4.81 (d, 1H, J=6), 4.66 (dd, 1H, J=6), 4.58 (dd, 1H, J=6), 4.17 (dd, 2H, J=6), 4.04-4.08 (m, 2H), 2.58-2.65 (m, 1H), 1.98-2.08 (m, 3H), 0.76 (s, 3H, $^2J_{H\text{-}Sn}$ =65).

39: To an oven-dried vial in a glove box was added 25 mg (0.040 mmol) of Sn-Cl **37** in 1 mL of THF and 40 μL (0.040 mmol; 1.0 equiv) of 1.0 M LiOEt in THF from a previously unopened bottle.[62] The resulting yellow solution was stirred at room temperature. After 8 hours, the solvent was removed *in vacuo* and the residual solid was taken up by benzene. After filtration through an 0.45 μm Acrodisc, the solvent was removed *in vacuo*. Recrystallization from 2 mL of ~ 1:1 pentane/Et_2O at –30 °C gave 20 mg (80% yield) of Sn-OEt **39** as a yellow solid. ^{1}H NMR (300 MHz, C_6D_6) δ 5.30 (d, 1H, J=6), 5.10 (d, 1H, J=6), 4.80 (t, 1H, J=7), 4.70 (t, 1H, J=7), 4.40 (m, 2H), 4.35 (d, 1H, J=6), 4.17 (d, 1H, J=6), 3.50 (m, 2H), 2.00-2.50 (m, 4H), 0.90 (s, 3H), OCH_2CH_3 obscured.

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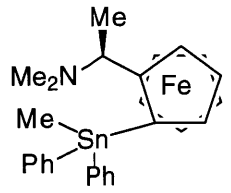
62 We have found the reaction to be much more reproducible if a new bottle of 1.0 M LiOEt in THF is used each time.



47a

Synthesis of Pentacoordinate Organotin Catalysts

47a:[63] To an oven-dried flask under argon was added 1.10 g (4.28 mmol) of the (*S*)-ferrocenylamine **46** and 5 mL of Et_2O to give an orange solution. To this solution was added dropwise 3.4 mL (5.4 mmol; 1.3 equiv) of 1.6 M *n*-BuLi in hexanes. After stirring at room temperature for 2 hours, to the resulting slightly cloudy orange solution was added dropwise 2.10 g (6.50 mmol; 1.52 equiv) of $Ph_2MeSnCl$ in 5 mL of Et_2O. Gentle reflux was observed during the addition and an orange cloudy slurry resulted immediately. After stirring at room temperature for an additional 16 hours, the reaction was quenched with water and extracted with 3 x 100 mL of EtOAc. The orange organic layer was dried with $MgSO_4$, filtered and stripped of solvent. Silica gel column chromatography (25% EtOAc/75% hexanes; $R_f \sim 0.3$; orange) gave 1.55 g (67% yield) of the directed-lithiation product **47a** as an orange solid. After the first orange band (i.e., **47a**) had eluted, the chromatography solvent system was switched to 100% EtOAc and a second orange band was collected and identified as **47b** (67 mg; 3% yield). The starting material **46** (285 mg; 26% recovery) was recovered by further eluting the column with 10%NEt3/90%EtOAc after **47b** had eluted. **47a**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.60-7.90 (m, 4H), 7.37-7.53 (m, 6H), 4.43

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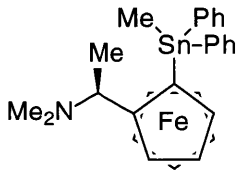
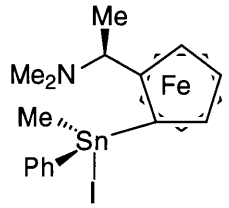
63 Initial syntheses and studies were carried out using (*R*)-**46** from Fluka because it is the cheaper of the two enantiomers. However, for the large scale reactions shown here, we used the our "home-made" resolved (*S*)-**46** because its L-tartarate salt is the one that is preferentially crystallized during resolution. Thus, compounds **47a**, **47b**, **48a**, **48b**,**48c** and **48e** shown here are the corresponding enantiomer of the compounds shown in the text. Spectroscopic data are identical. The Sn-H **48d** was prepared from an earlier batch using (*R*)-**46**.

(dd, 1H, J=1, 2), 4.40 (dd, 1H, J=1, 2), 4.24 (dd, 1H, J=1, 2), 4.19 (s, 5H), 4.02 (q, 1H, J=7), 1.84 (s, 6H), 1.23 (d, 3H, J=7), 0.86 (s, 3H, 2JH-Sn=57); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0 ($^1J_{C-Sn}$=458, 480), 142.3 ($^1J_{C-Sn}$ =453, 469), 137.0 ($^2J_{C-Sn}$ =35), 136.6 ($^2J_{C-Sn}$ =37), 128.5, 128.3, 128.2 ($^3J_{C-Sn}$ =50), 96.8 ($^2J_{C-Sn}$ =45), 75.9 ($^3J_{C-Sn}$ =55), 70.2 ($^1J_{C-Sn}$ =571, 595), 69.7, 69.6, 69.3, 59.0, 39.4, 8.27, -9.22 ($^1J_{C-Sn}$ =399, 418); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -86.5; IR (neat) 3062, 2970, 2819, 2776, 1428, 1075, 726, 700, 497, 488 cm^{-1}; HRMS calcd for $C_{27}H_{31}FeNSn$ 545.0828, found 545.0830; $[\alpha]^{20}_D$ = +74.3 (c=0.9 in $CHCl_3$).



47b

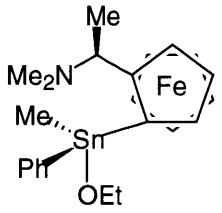
47b:[63] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.71 (m, 4H), 7.33-7.40 (m, 6H), 4.35 (dd, 1H, J=2), 4.36 (s, 1H), 4.16 (s, 5H), 4.08 (s, 1H), 3.15 (q, 1H, J=7), 1.99 (s, 6H), 1.29 (d, 3H, J=7), 0.81 (s, 3H, $^2J_{H-Sn}$=56, 60); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 141.9, 136.3, 128.3, 128.1, 127.7, 99.1, 75.0, 70.0, 69.8, 68.6, 66.3, 58.6, 42.3, 16.1, -8.07 ($^1J_{C-Sn}$=406, 425); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -80.9; IR (neat) 3061, 2976, 2819, 2774, 1428, 1074, 727, 700, 490, 468 cm^{-1}; HRMS calcd for $C_{27}H_{31}FeNSn$ 545.0828, found 545.0830; $[\alpha]_D$ = -159 (c=1.2 in $CHCl_3$).



48a

48a (86:14 @ Sn):[63] To an oven-dried flask under argon was added 1.38 g (2.54 mmol) of Sn-Ph **47a** and 30 mL of THF. Dropwise, to the initial orange solution, was added 644 mg (2.54 mmol; 1.00 equiv) of I_2 in 20 mL of THF to give a black solution. After 1

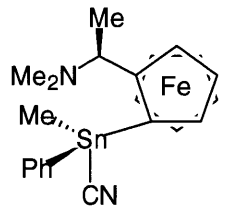
hour, the original orange color was restored. After an additional 1 hour, the solvent was removed *in vacuo* to give an orange soli. In a glove box, the orange solid was dissolved in 20 mL of 1:1 pentane/CH_2Cl_2 and the resulting orange solution was evaporated slowly *in vacuo* until slight cloudiness was observed. Recrystallization at –30 °C gave yellow solids. The solvent was removed by pipet and the residual solid was dried *in vacuo* to give 1.15 g (76% yield) of Sn-I **48a** as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.82 (m, 2H), 7.27-7.40 (m, 3H), 4.63 (dd, 1H, J=4), 4.57 (s, 1H), 4.30-4.44 (m, 2H), 4.28 (s, 5H), 4.18 (q, 1H, J=6), 4.06 (q, 1H, J=6), 1.79 (s, 6H), 1.76 (br, 6H), 1.39 (s, 3H, $^2J_{H\text{-}Sn}$=62, 65), 1.11 (d, 3H, J=7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2 ($^1J_{C\text{-}Sn}$=482), 141.0, 134.6, 134.3, 134.0, 133.7, 128.9, 128.6, 128.4, 128.2, 128.0, 127.5, 94.5 ($^2J_{C\text{-}Sn}$=63), 95.0, 74.8 ($^3J_{C\text{-}Sn}$=67), 74.2, 69.2, 69.0, 68.8, 68.2, 59.8, 59.2, 38.0-44.0 (broad), 7.53, 7.18, -1.34 ($^1J_{C\text{-}Sn}$=492, 515), -0.24; ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -115 (major diastereomer), -117 (minor diastereomer); IR (neat) 3096, 2970, 2890, 1459, 1430, 1161, 996, 922, 812, 729, 699 cm^{-1}; HRMS calcd for $C_{21}H_{26}FeINSn$ 594.9481, found 594.9483; $[\alpha]^{20}_D$ = +192 (c=1.0 in $CHCl_3$).



48b

48b (76:24 @ Sn):[63] To an oven-dried vial in a glove box was added 675 mg (1.14 mmol) of Sn-I **48a** in 5 mL of benzene and 80 mg (1.2 mmol; 1.0 equiv) of EtONa in 5 mL of EtOH. The resulting orange solution was stirred at room temperature for 1 hour after which the solvent was removed *in vacuo* to give an orange solid. To the orange solid was added 10 mL of pentane and the resulting cloudy orange slurry was filtered through an 0.45 μm Acrodisc. Removal of solvent *in vacuo* gave 572 mg

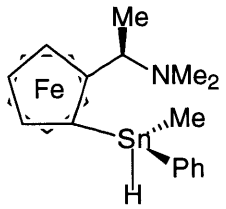
(98% yield) of Sn-OEt **48b** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.80 (m, 2H), 7.30-7.40 (m, 3H), 4.31-4.50 (m, 3H), 4.19 (s, 5H), 4.17 (s, 5H), 4.05 (q, 1H, J=7), 3.91 (m, 2H), 1.70 (s, 6H), 1.62 (s, 6H), 1.18-1.19 (m, 3H), 1.07 (d, 3H, J=7), 0.841 (s, 3H, $^{2}J_{H-Sn}$=64), 0.55 (s, 3H, ^{2}JSn-CH_3=63, 66); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 142.0, 135.9, 135.3, 128.9, 128.6, 128.2, 128.0, 96.4, 96.2, 74.3, 74.2, 72.8, 71.9, 69.5, 69.3, 69.2, 68.5, 68.1, 60.8, 60.7, 38.9, 21.2, 21.0, 7.65, 7.41, -5.59, -6.65 ($^{1}J_{C-Sn}$=515, 539); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -50.9 (major diastereomer), -48.5 (minor diastereomer); IR (neat) 2968, 2828, 1429, 1367, 1104, 1059, 728, 700, 522, 484 cm^{-1}; HRMS calcd for $C_{23}H_{31}FeNOSn$ 513.0777, found 513.0770; $[\alpha]^{20}_{D}$ = -28.1 (c=1.0 $CHCl_3$).



48c

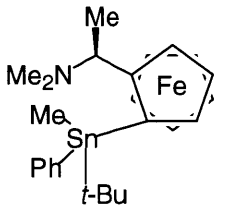
48c (82:18 @ Sn):[63] To an oven-dried vial in a glove box was added 256 mg (0.500 mmol) of Sn-OEt **48b** in 2.5 mL of pentane and 300 μL (2.13 mmol; 4.26 equiv) of TMS-CN to give an orange solution. Precipitation (orange needles) was observed after 15 minutes. After an additional 4 hours, the resulting clear colorless liquid was removed by pipet and the remaining orange needle was washed with 3 x 5 mL of pentane. Drying the solid *in vacuo* overnight gave 208 mg (84% yield) of Sn-CN **48c** as orange needles. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.80 (m, 2H), 7.30-7.40 (m, 3H), 4.60 (t, 1H, J=2), 4.49 (t, 1H, J=2), 4.33-4.41 (m, 2H), 4.22 (s, 5H), 4.21 (s, 5H), 4.10 (q, 1H, J=6), 3.97 (q, 1H, J=6), 1.81 (s, 6H), 1.74 (s, 6H), 1.09 (d, 3H, J=7), 0.99 (s, 3H, $^{2}J_{H-Sn}$=65, 68), 0.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 137.7, 135.9, 135.2, 131.9 ($^{1}J_{C-Sn}$=101, 117), 128.3, 128.7, 128.6, 95.7, 95.4, 74.0, 73.7, 70.2, 69.4, 68.8, 59.7, 59.2, 39.2, 7.80, 7.52, -6.32, -7.36 ($^{1}J_{C-Sn}$=533, 557); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -178.1 (major

diastereomer), -172.9 (minor diastereomer); IR (neat) 2990, 2874, 2143 (Sn-CN), 1430, 1070, 926, 813, 759, 703, 480 cm^{-1}; HRMS calcd for $C_{22}H_{26}FeN_2Sn$ 494.0467, found 494.0468; $[\alpha]^{20}_D$ = +90.8 (c=1.0 in $CHCl_3$).



48d

48d (82:18 @ Sn):[64] To an oven-dried vial in a glove box was added 180 mg (0.303 mmol) of Sn-I **48a** and 2 mL of Et_2O. To the resulting yellow solution was added 23 mg (0.61 mmol; 2.0 equiv) of LAH in 2 mL of THF. After 30 minutes, the vial was removed from glove box and the reaction was quenched with ice. The quenched reaction mixture was extracted with 5 mL of Et_2O which was washed with ice-cold water. The organic layer was dried with $MgSO_4$, filtered through glass wool/Na_2SO_4. After solvent removal, 111 mg (78% yield) of Sn-H **48d** was obtained as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.68 (m, 2H), 7.18-7.25 (m, 3H), 6.08-6.12 (q, ^{4}J=2, $^1J_{H\text{-}Sn}$=1944, 1947), 3.95-4.21 (m, 3H), 3.93 (s, 5H), 3.90 (s, 5H), 3.83 (q, 1H, J=6), 1.81 (s, 6H), 1.79 (s, 6H), 0.92 (d, 3H, J=7), 0.85 (s, 3H, ^{4}J=2, $^2J_{H\text{-}Sn}$=41, 46).

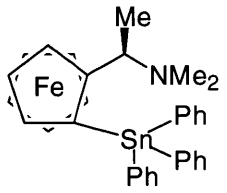


48e

48e (~ 1:1 @ Sn):[63] To an oven-dried flask under argon was added 500 μL (2.38

64 This compound was prepared from an earlier batch of **48a** which originated from the commercial (*R*)-**46**.

mmol) of (*S*)-ferrocenylamine **46** and 1 mL of Et_2O to give an orange solution. To this solution was added dropwise 1.5 mL (2.4 mmol; 1.0 equiv) of 1.6 M *n*-BuLi in hexanes and stirred at room temperature for 16 hours. To the resulting slightly cloudy orange solution was added dropwise 879 mg (2.90 mmol; 1.22 equiv) of *t*-Bu(Me)PhSnCl in 3 mL of Et_2O. Gentle reflux was observed during the addition and an orange cloudy slurry resulted immediately. After stirring at room temperature for an additional 4 hours, the reaction was quenched with water and extracted with 2 x 30 mL of EtOAc. The orange organic layer was dried with $MgSO_4$, filtered and stripped of solvent. Silica gel column chromatography (50% EtOAc/50% hexanes; orange) gave 437 mg (35% yield) of **48e** as a thick orange oil.[65] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.82 (m, 10H, both diastereomers), 4.16-4.45 (m, 6H, both diastereomers), 4.20 (s, 5H), 4.01 (s, 5H), 3.90 (m, 2H), 2.10 (s, 6H), 1.90 (s, 6H), 1.40 (s, 9H), 1.32 (s, 9H), 1.29 (d, 3H, J=7), 1.21 (d, 3H, J=7), 0.66 (s, 3H), 0.64 (s, 3H); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -41.9, -46.5.



51a

51a: To an oven-dried flask under argon was added 600 mg (2.38 mmol) of the (*R*)-ferrocenylamine **46** and 10 mL of Et_2O to give an orange solution. To this solution was added dropwise 1.5 mL (2.4 mmol; 1.0 equiv) of 1.6 M *n*-BuLi in hexanes and stirred at room temperature for 2 hours. To the resulting slightly cloudy orange solution was added dropwise 1.37 g (3.57 mmol; 1.50 equiv) of Ph_3SnCl in 20 mL of Et_2O. Gentle reflux was observed during the addition and an orange cloudy slurry

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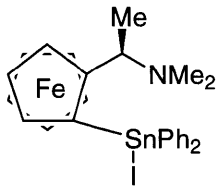
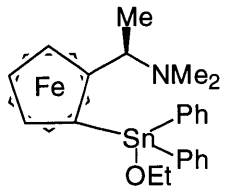
[65] It is interesting to note that when **48e** was treated with I_2, the expected phenyl-cleavage product (i.e., the iodide analog of **58a**) was not obtained. Instead, we obtained exclusively the *t*-Bu-cleavage product **48a**.

resulted immediately. After stirring at room temperature for an additional 16 hours, the reaction was quenched with water and extracted with 3 x 50 mL of EtOAc. The orange organic layer was dried with $MgSO_4$, filtered and stripped of solvent. Silica gel column chromatography (50% EtOAc/50% hexanes; R_f ~ 0.5; orange) gave 967 mg (67% yield) of Sn-Ph **51a** as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.68 (m, 6H, $^4J_{C\text{-}Sn}$=50), 7.30-7.38 (m, 9H), 4.32-4.34 (m, 2H), 4.21 (m, 1H), 4.06 (s, 5H), 3.79 (q, 1H, J=7), 1.59 (s, 6H), 1.07 (d, 3H, J=7); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -117.8.



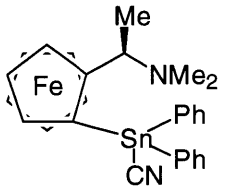
51b

51b: To an oven-dried flask under argon was added 400 mg (0.662 mmol) of Sn-Ph **51a** and 10 mL of THF. Dropwise, to the initial orange solution, was added 168 mg (0.662 mmol; 1.00 equiv) of I_2 in 10 mL of THF to give a black solution. After 1 hour, the original orange color was restored. After an additional 1 hour, the solvent was removed *in vacuo* to give an orange solid which was moved into a glove box. The orange solid was dissolved in 15 mL of 2:1 pentane/CH_2Cl_2 and the resulting orange solution was concentrated slowly *in vacuo* until slight cloudiness was observed. Recrystallization in a –30 °C freezer gave yellow solids. The solvent was removed by pipet and the residual solid was dried *in vacuo* to give 368 mg (85% yield) of Sn-I **51b** as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, 2H, J=8, $^4J_{H\text{-}Sn}$=64), 7.61 (d, 2H, J=8, $^4J_{H\text{-}Sn}$=64), 7.26-7.52 (m, 6H), 4.68 (m, 1H), 4.39-4.41 (m, 2H), 4.26 (s, 5H), 4.24 (q, 1H, J=7), 1.55 (s, 6H), 1.06 (d, 3H, J=7); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -165.9.



51c

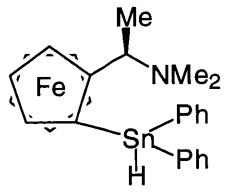
51c: To an oven-dried vial in a glove box was added 88 mg (0.14 mmol) of Sn-I **51b** in 1 mL of benzene and 9.0 mg (0.14 mmol; 1.0 equiv) of EtONa in 1 mL of EtOH. The resulting orange solution was stirred at room temperature for 1 hour after which the solvent was removed *in vacuo* to give an orange solid. To the orange solid was added 5 mL of benzene. The resulting cloudy orange slurry was filtered through an 0.45 μm Acrodisc to give an orange solution. Removal of solvent *in vacuo* gave 57 mg (74% yield) of Sn-OEt **51c** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 2H, J=8, $^{4}J_{H\text{-}Sn}$=64), 7.56 (d, 2H, J=8, $^{4}J_{H\text{-}Sn}$=64), 7.27-7.48 (m, 6H), 4.49 (m, 1H), 4.33-4.38 (m, 2H), 4.18 (s, 5H), 4.05 (q, 1H, J=7), 3.87 (m, 2H), 1.46 (s, 6H), 1.08 (t, 3H, J=6), 1.02 (d, 3H, J=7); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -108.6.



51d

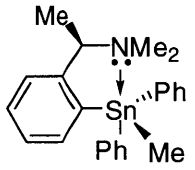
51d: To an oven-dried vial in a glove box was added 57 mg (0.098 mmol) of Sn-OEt **51c** and 2.0 mL (15 mmol; 150 equiv) of TMS-CN to give an orange solution. Precipitation (orange needles) was observed after 15 minutes. After an additional 4 hours, the resulting clear colorless liquid was removed by pipet and the residual orange needle was washed with 3 x 5 mL of pentane. Drying the solid *in vacuo* overnight gave 48 mg (87% yield) of Sn-CN **51d** as orange needles. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H, J=8, $^{4}J_{H\text{-}Sn}$=66), 7.61 (d, 2H, J=8, $^{4}J_{H\text{-}Sn}$=66), 7.35-7.56 (m, 6H),

4.64 (m, 1H), 4.41-4.46 (m, 2H), 4.25 (s, 5H), 4.18 (q, 1H, J=7), 1.66 (s, 6H), 1.09 (d, 3H, J=7); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -209.8.



51e

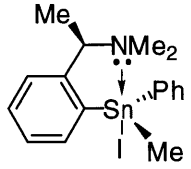
51e: To an oven-dried vial in a glove box was added 47 mg (0.072 mmol) of Sn-I **51b** and 1 mL of Et_2O. To the resulting yellow solution was added 5.5 mg (0.14 mmol; 2.0 equiv) of LAH in 1 mL of THF. After 30 minutes, the vial was removed from the glove box and the reaction was quenched with ice. The quenched reaction mixture was extracted with 5 mL of Et_2O and the organic phase was washed with ice-cold water. The organic layer was dried with $MgSO_4$, filtered through glass wool/Na_2SO_4. After solvent removal, 29 mg (76% yield) of Sn-H **51e** was obtained as a yellow oil. ^{1}H NMR (300 MHz, C_6D_6) δ 7.94 (d, 2H, J=8, $^4J_{H\text{-}Sn}$= 46, 49), 7.62 (d, 2H, J=8, $^4J_{H\text{-}Sn}$= 52), 7.13-7.29 (m, 6H), 6.82 (s, 1H, $^1J_{H\text{-}Sn}$= 1974, 2088), 4.14-4.19 (m, 3H), 3.95 (s, 5H), 3.93 (q, 1H, J= 7), 1.73 (s, 6H), 0.935 (d, 3H, J= 7); ^{119}Sn NMR (111 MHz, C_6D_6) δ -165.9.



52

52: To an oven-dried flask under argon was added 600 mg (4.03 mmol) of *(R)-N,N*-dimethyl-*sec*-phenylethyl amine and 10 mL of Et_2O to give a clear colorless solution. To this solution was added dropwise 2.5 mL (4.0 mmol; 0.99 equiv) of 1.6 M *n*-BuLi in hexanes. After stirring at room temperature for 3 hours, to the resulting slightly

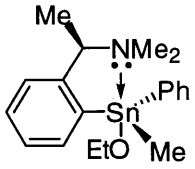
cloudy solution was added dropwise 1.86 g (4.80 mmol; 1.19 equiv) of $Ph_2MeSnCl$ in 5 mL of Et_2O. Gentle reflux was observed during the addition and a white cloudy slurry resulted immediately. After stirring at room temperature for an additional 4 hours, the reaction was quenched with water and extracted with 3 x 100 mL of EtOAc. The organic layer was dried with $MgSO_4$, filtered and stripped of solvent. Silica gel column chromatography (10% EtOAc/90% hexanes; R_f ~ 0.6; UV) gave 546 mg (31% yield) of Sn-Ph **52** as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.12-7.52 (m, 14H), 3.50 (q, 1H, J=6), 1.80 (s, 6H), 1.22 (d, 3H, J=6), 0.73 (s, 3H, $^2J_{H-Sn}$=48); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 144.5, 142.9, 138.5, 138.4, 136.4, 136.3, 128.7, 127.9, 127.8, 127.7, 126.6, 126.4, 64.4, 41.6, 14.3, -8.00 ($^1J_{C-Sn}$=424, 445); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -110.



52a

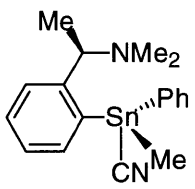
52a (65:35 @ Sn): To an oven-dried flask under argon was added 260 mg (0.596 mmol) of Sn-Ph **52** and 30 mL of THF. Dropwise, to the initial clear colorless solution, was added 151 mg (0.596 mmol; 1.00 equiv) of I_2 in 20 mL of THF to give a black solution. After 1 hour, the original clear colorless appearance was restored. After an additional 1 hour, the solvent was removed *in vacuo* to give a clear colorless oil which was moved into a glove box and washed with pentane (the product is not soluble in pentane). The solvent was removed by pipet and the residual oil was dried *in vacuo* to give 283 mg (98% yield) of Sn-I **52a** as a clear, colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 8.47-8.51 (m, 1H), 7.16-7.53 (m, 8H), 3.74 (q, 1H, J=7), 3.59 (q, 1H, J=7), 2.35 (s, 3H), 2.09 (s, 3H), 1.88 (s, 3H), 1.66 (s, 3H), 1.26-1.33 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.2, 146.9, 144.1, 142.5, 140.1, 139.8, 135.0, 134.4,

130.1, 129.0, 128.9, 128.7, 128.5, 127.7, 125.9, 64.3, 64.1, 45.1, 44.8, 38.6, 14.0, 12.8, 4.11 ($^1J_{C-Sn}$=518, 538), 1.45 ($^1J_{C-Sn}$=498, 512); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -131.



52b

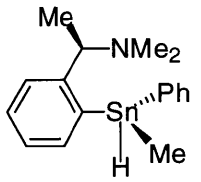
52b (65:35 @ Sn): To an oven-dried vial in a glove box was added 123 mg (0.256 mmol) of Sn-I **52a** in 1 mL of benzene and 18 mg (0.26 mmol; 1.0 equiv) of EtONa in 1 mL of EtOH. The resulting white cloudy solution was stirred at room temperature for 1 hour after which the solvent was removed *in vacuo* to give a viscous oil. To this residue was added 10 mL of benzene and the resulting slurry was filtered through an 0.45 μm Acrodisc to give an clear colorless solution. Removal of solvent *in vacuo* gave 72 mg (71% yield) of Sn-OEt **52b** as a clear colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10-8.13 (m, 1H), 7.15-7.52 (m, 8H), 3.45 - 3.62 (m, 3H), 1.80 (br, 6H), 1.23 (d, 3H, J=7), 1.15 (d, 3H, J=7), 0.99-1.07 (m, 3H), 0.71 (s, 3H, $^2J_{H-Sn}$=63, 66), 0.65 (s, 3H, $^2J_{H-Sn}$=62, 64); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 148.9, 142.4, 141.3, 138.8, 138.4, 137.9, 137.6, 135.6, 129.2, 129.1, 128.7, 128.6, 128.2, 128.1, 127.0, 126.9, 126.0, 64.3, 63.8, 59.9, 38 - 44 (broad), 20.9, 20.8, 13.9, 13.6, -5.63 ($^1J_{C-Sn}$=574, 548), -7.18 ($^1J_{C-Sn}$=540, 514); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -116 (major diastereomer), -119 (minor diastereomer).



52c

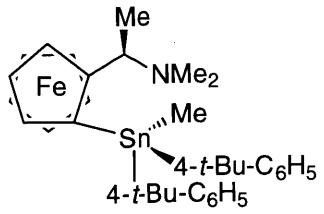
52c (65:35 @ Sn): To an oven-dried vial in a glove box was added 19 mg (0.047 mmol) of Sn-OEt **52b** and 1.0 mL (7.5 mmol; 160 equiv) of TMS-CN to give a clear

colorless solution. After stirring at room temperature for 12 hours, the excess TMS-CN was removed *in vacuo* to give 18 mg (100% yield) of Sn-CN **52c** as a clear colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05-8.25 (m, 1H), 7.20-7.75 (m, 8H), 3.74 (q, 1H, J=7), 3.55 (q, 1H, J=7), 1.80-2.20 (m, 6H), 1.40 (d, 3H, J=7), 1.20 (d, 3H, J=7), 0.921 (s, 3H), 0.863 (s, 3H); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -198.1 (major diastereomer), -198.3 (minor diastereomer).



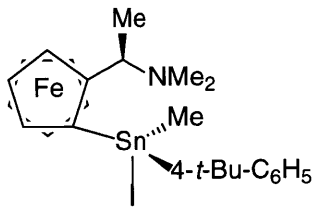
52d

52d (54:46 @ Sn): To an oven-dried screw-cap NMR tube in a glove box was added 20 mg (0.041 mmol) of Sn-I **52a** in 300 μL of d_8-THF and 1.6 mg (0.041 mmol; 1.0 equiv) of LAH in 200 μL of d_8-THF. After 5 minutes, the NMR tube was sealed under a nitrogen atmosphere and removed from the glove box. ^{1}H NMR (300 MHz, d_8-THF) δ 6.95-7.80 (m, 9H), 6.16 (q, 1H, J=2), 6.04 (q, 1H, J=2), 3.74 (m, 1H), 2.05 (s, 6H), 1.15 (m, 3H), 0.450 (m, 3H); ^{119}Sn NMR (111 MHz, d_8-THF) δ -158, -160.



56

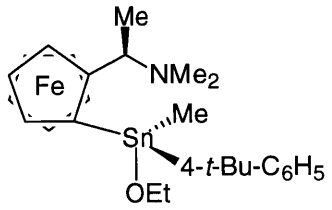
56: To an oven-dried flask under argon was added 432 mg (1.68 mmol) of (*R*)-ferrocenylamine **46** and 2 mL of Et_2O to give an orange solution. To this solution was added dropwise 1.1 mL (1.8 mmol; 1.1 equiv) of 1.6 M *n*-BuLi in hexanes. After stirring at room temperature for 2 hours, to the resulting slightly cloudy orange solution was added dropwise 1.06 g (2.44 mmol; 1.45 equiv) of (4-*t*-Bu-C_6H_4)$_2$MeSnCl in 10 mL of Et_2O. Gentle reflux was observed during the addition and an orange cloudy slurry resulted immediately. After stirring at room temperature for an additional 16 hours, the reaction was quenched with water and extracted with 3 x 50 mL of EtOAc. The orange organic layer was dried with $MgSO_4$, filtered and stripped of solvent. Silica gel column chromatography (50% EtOAc/50% hexanes; R_f ~ 0.5; orange) gave 372 mg (34 %yield) of **56** as an orange solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.86 (m, 8H), 4.24-4.33 (m, 3H), 4.20 (s, 5H), 4.01 (q, 1H, J=7), 1.88 (s, 6H), 1.47 (s, 9H), 1.44 (s, 9H), 1.26 (d, 3H, J=7), 0.83 (s, 3H, $^2J_{H\text{-}Sn}$=56); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -86.1.



56a

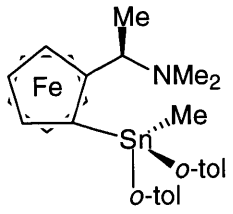
56a (86:14 @ Sn): To an oven-dried flask under argon was added 165 mg (0.252 mmol) of **56** and 10 mL of THF. Dropwise, to the initial orange solution, was added 64 mg (0.25 mmol; 1.0 equiv) of I_2 in 10 mL of THF to give a black solution. After 1

hour, the original orange color was restored. After an additional 1 hour, the solvent was removed *in vacuo* to give an orange solid which was moved into the glove box. The orange solid was dissolved in 1 mL of CH_2Cl_2 and pentane (~ 10 mL) was added slowly until slight cloudiness was observed. Recrystallization at –30 °C gave yellow solids. The solvent was removed by pipet and the residual solid was dried *in vacuo* to give 109 mg (67% yield) of Sn-I **56a** as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.48 (m, 4H), 4.61-4.62 (2s, 1H), 4.30-4.38 (m, 2H), 4.23 (s, 5H), 4.18 (q, 1H, J=7), 4.07 (q, 1H, J=7), 1.79 (s, 6H), 1.38 (s, 3H, $^2J_{H\text{-}Sn}$=66), 1.34 (s, 9H), 1.28 (s, 9H), 1.12 (d, 3H, J=7); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -117.6 (major diastereomer), -119.8 (minor diastereomer).



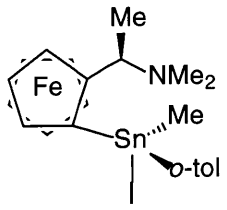
56b

56b (73:27 @ Sn): To an oven-dried vial in a glove box was added 78 mg (0.12 mmol) of Sn-I **56a** in 1 mL of benzene and 8 mg (0.12 mmol; 1.0 equiv) of EtONa in 1 mL of EtOH. The resulting orange solution was stirred at room temperature. After 1 hour, the solvent was removed *in vacuo* to give an orange solid. To the orange solid was added 5 mL of benzene and the resulting cloudy orange slurry was filtered through an 0.45 μm Acrodisc to give an orange solution. Removal of solvent *in vacuo* gave 57 mg (85% yield) of Sn-OEt **56b** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16-7.35 (m, 4H), 4.21-4.26 (m, 3H), 4.09 (s, 5H), 4.07 (s, 5H), 3.83-4.06 (m, 3H), 1.61 (s, 6H), 1.54 (s, 6H), 1.25 (s, 9H), 1.20 (s, 9H), 1.18 (t, 3H, J=7), 1.10 (d, 3H, J=7), 0.72 (s, 3H), 0.58 (s, 3H); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -46.8 (major diastereomer), -44.1 (minor diastereomer).



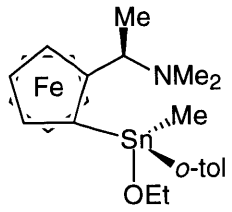
57

57: To an oven-dried flask under argon was added 257 mg (1.00 mmol) of (*R*)-ferrocenylamine **46** and 2 mL of Et_2O to give an orange solution. To this solution was added dropwise 630 μL (1.0 mmol; 1.0 equiv) of 1.6 M *n*-BuLi in hexanes. After stirring at room temperature for 2 hours, to the resulting slightly cloudy orange solution was added dropwise 509 mg (1.50 mmol; 1.50 equiv) of $(o\text{-tol})_2MeSnCl$ in 10 mL of Et_2O. Gentle reflux was observed during the addition and an orange cloudy slurry resulted immediately. After stirring at room temperature for an additional 16 hours, the reaction was quenched with water and extracted with 3 x 10 mL of EtOAc. The orange organic layer was dried with $MgSO_4$, filtered and stripped of solvent. Silica gel column chromatography (50% EtOAc/50% hexanes; R_f ~ 0.5; orange) gave 263 mg (44 %yield) of **57** as an orange solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, 1H, J=7, $^4J_{H\text{-}Sn}$=47), 7.47 (d, 1H, J=7, $^4J_{H\text{-}Sn}$=53), 7.16-7.35 (m, 6H), 4.29-4.34 (m, 2H), 4.18 (m, 1H), 4.08 (s, 5H), 3.85 (q, 1H, J=7), 2.36 (s, 3H), 2.24 (s, 3H), 1.63 (s, 6H), 1.13 (d, 3H, J=7), 0.79 (s, 3H, $^2J_{H\text{-}Sn}$=56); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -91.4.



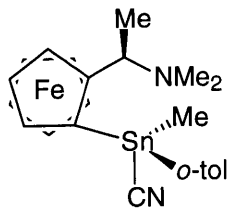
57a (>95:5 @ Sn): To an oven-dried flask under argon was added 120 mg (0.210 mmol) of **57** and 10 mL of THF. Dropwise, to the initial orange solution, was added 53 mg (0.21 mmol; 1.0 equiv) of I_2 in 10 mL of THF to give a black solution. After 1

hour, the original orange color was restored. After an additional 1 hour, the solvent was removed *in vacuo* to give an orange solid which was moved into a glove box. The orange solid was dissolved in 15 mL of 4:1 pentane/CH_2Cl_2 and the resulting orange solution was concentrated slowly *in vacuo* until slight cloudiness was observed. Recrystallization at –30 °C overnight gave yellow solids. The solvent was removed by pipet and the residual solid was dried *in vacuo* to give 96 mg (75% yield) of Sn-I **57a** as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11-7.38 (m, 4H), 4.56 (d, 1H, J=2), 4.30-4.33 (m, 2H), 4.20 (s, 5H), 4.13 (q, 1H, J=7), 2.42 (s, 3H), 1.68 (s, 6H), 1.34 (s, 3H, $^2J_{H\text{-}Sn}$= 62), 1.06 (d, 3H, J=7); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -132.0.



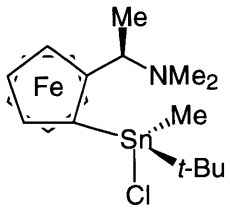
57b

57b (>95:5 @ Sn): To an oven-dried vial in a glove box was added 48 mg (0.079 mmol) of Sn-I **57a** in 1 mL of benzene and 5.4 mg (0.079 mmol; 1.0 equiv) of EtONa in 1 mL of EtOH. The resulting orange solution was stirred at room temperature for 1 hour after which the solvent was removed *in vacuo* to give an orange solid. To the orange solid was added 2 mL of benzene and the resulting cloudy orange slurry was filtered through an 0.45 μm Acrodisc to give an orange solution. Removal of solvent *in vacuo* gave 38 mg (90% yield) of Sn-OEt **57b** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98-7.33 (m, 4H), 4.36 (d, 1H, J=1), 4.20-4.26 (m, 2H), 4.09 (s, 5H), 3.96 (q, 1H, J=6), 3.79 (m, 2H), 2.33 (s, 3H), 1.49 (s, 6H), 1.08 (t, 3H, J=7), 0.96 (d, 3H, J=6), 0.75 (s, 3H, $^2J_{H\text{-}Sn}$=59, 63), 0.96 (d, 3H, J=6); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -51.1.



57c

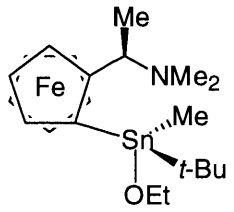
57c (>95:5 @ Sn): To an oven-dried vial in a glove box was added 19 mg (0.036 mmol) of Sn-OEt **57b** and 1.0 mL of (7.5 mmol; 210 equiv) of TMS-CN resulting in an orange solution. Precipitation (orange needles) was observed after 15 minutes. After an additional 4 hours, the resulting clear colorless liquid was removed by pipet and the remaining orange needle was rinsed with 3 x 5 mL of pentane. Drying the solid *in vacuo* overnight gave 10 mg (56% yield) of Sn-CN **57c** as orange needles. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14-7.41 (m, 4H), 4.62 (dd, 1H, J=3), 4.36-4.39 (m, 2H), 4.23 (s, 5H), 4.10 (q, 1H, J=7), 2.47 (s, 3H), 1.70 (s, 6H), 1.10 (d, 3H, J=7), 0.99 (s, 3H, $^{2}J_{H\text{-}Sn}$=63); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -195.



58a

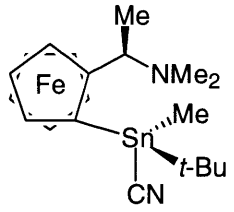
58a (>95:5 @ Sn): To an oven-dried vial in a glove box was added 130 mg (0.505 mmol) of (*R*)-ferrocenylamine **46** and 10 mL of Et_2O to give an orange solution. To this solution was added dropwise 320 μL (0.51 mmol; 1.0 equiv) of 1.6 M *n*-BuLi in hexanes. After stirring at room temperature for 2 hours, the resulting slightly cloudy orange solution was added dropwise to 133 mg (0.506 mmol; 1.00 equiv) of Me(*t*-Bu)$SnCl_2$ in 1 mL of Et_2O. Gentle reflux was observed during the addition and an orange cloudy slurry resulted immediately. After stirring at room temperature for 3 hours, the reaction mixture was filtered through an 0.45 μm Acrodisc to give

an orange solution. Removal of solvent and recrystallization from pentane at –30 °C gave 114 mg (47% yield) of Sn-Cl **58a** as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27-4.32 (m, 3H), 4.13 (s, 5H), 3.96 (q, 1H, J=7), 2.02 (s, 6H), 1.23 (s, 6H), 1.23 (s, 9H), 1.14 (d, 3H, J=7), 0.81 (s, 3H, $^{2}J_{H\text{-}Sn}$=52, 54); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -64.8.



58b

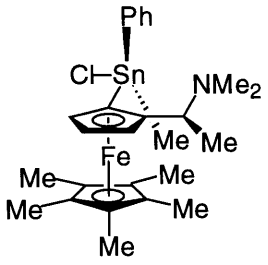
58b (>95:5 @ Sn): To an oven-dried vial in a glove box was added 57 mg (0.12 mmol) of Sn-Cl **58a** in 1 mL of benzene and 8.0 mg (0.12 mmol; 1.0 equiv) of EtONa in 1 mL of EtOH. After stirring at room temperature for 1 hour, the solvent was removed *in vacuo*. To the residual orange solid was added 2 mL of benzene and the resulting cloudy orange slurry was filtered through an 0.45 μm Acrodisc to give an orange solution. Evaporation of solvent *in vacuo* gave 52 mg (90% yield) of Sn-OEt **58b** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.14-4.29 (m, 3H), 4.13 (s, 5H), 3.96 (q, 1H, J=7), 3.84 (m, 2H), 1.98 (s, 6H), 1.29 (t, 3H, J=7), 1.19 (s, 6H), 1.23 (s, 9H), 1.14 (d, 3H, J=7), 0.54 (s, 3H, $^{2}J_{H\text{-}Sn}$=53, 59); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -35.7.



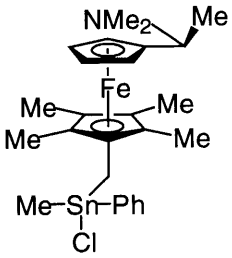
58c

58c (>95:5 @ Sn): To an oven-dried vial in a glove box was added 26 mg (0.053 mmol) of Sn-OEt **58b** and 1.0 mL of (7.5 mmol; 140 equiv) of TMS-CN resulting in an orange solution. After 4 hours, the solvent was removed *in vacuo* to give 25 mg (100%

yield) of Sn-CN **58c** as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33-4.35 (m, 3H), 4.17 (s, 5H), 3.90 (q, 1H, J=7), 2.00 (s, 6H), 1.23 (s, 6H), 1.29 (s, 9H), 1.14 (d, 3H, J=7), 0.70 (s, 3H, $^2J_{H\text{-}Sn}$=56, 59); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -71.5.



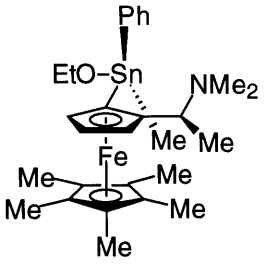
60a



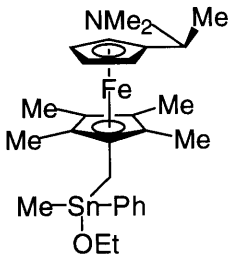
61a

60a: To an oven-dried vial in a glove box was added 117 mg (0.358 mmol) of the (*S*)-Cp*-ferrocenylamine **59** in 1 mL of Et_2O and 225 μL (0.36 mmol; 1.0 equiv) of 1.6 M *n*-BuLi in hexanes. After the resulting reddish orange solution was stirred at room temperature for 12 hours, it was added dropwise to 105 mg (0.372 mmol; 1.04 equiv) of $MePhSnCl_2$ in 1 mL of Et_2O to give a cloudy mixture. After an additional 3 hours at room temperature, the solvent was removed *in vacuo*. The residual orange solid was taken up in benzene and filtered through an 0.45 μm Acrodisc. Removal of solvent followed by recrystallization from 4 mL of 3:1 pentane/CH_2Cl_2 at –30 °C gave 53 mg (26% yield) of the Sn-Cl **60a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.55 (m, 5H), 4.14 (d, 1H, J=2), 3.85 (d, 1H, J=2), 3.72 (q, 1H, J=7), 3.66 (d, 1H, J=2), 2.09-2.32 (br, 6H), 1.89 (s, 15H), 1.08 (s, 3H, $^2J_{H\text{-}Sn}$=64, 66), 1.00 (d, 3H, J= 7); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -65.5.

61a: From the recrystallized product above was also observed ~ 5% of the Cp*-lithiated product **61a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (Cp* protons, the only observable protons of **61a** in the mixture); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -173.

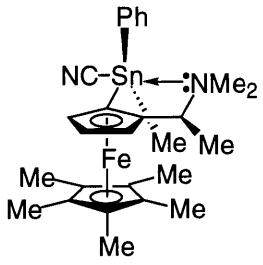


60b

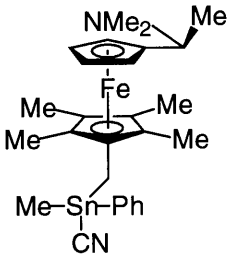


61b

60b/61b: To an oven-dried vial in a glove box was added 53 mg (0.093 mmol) of the impure Sn-Cl **60a** and 61a in 1 mL of benzene and 6.3 mg (0.093 mmol; 1.0 equiv) of EtONa in 1 mL of EtOH. The resulting orange cloudy solution was stirred at room temperature for 12 hours. After the removal of solvent, the resulting orange solid was taken up in 1 mL of pentane and filtered through an 0.45 mm Acrodisc. After solvent removal, 52 mg (96% yield) of Sn-OEt **60b** and **61b** was obtained as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.55 (m, 5H), 4.03 (d, 1H, J=2), 3.89 (dd, 1H, J=2), 3.65-3.83 (m, 5H), 1.93 (s, 15H), 1.82-1.84 (2s, Cp* of **61b**), 1.50-1.60 (br, 6H), 1.15 (t, 3H, J=7), 1.00 (d, 3H, J=7), 0.82 (s, 3H, $^{2}J_{H\text{-}Sn}$=60, 65); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -53.7 (**60b**).



60c



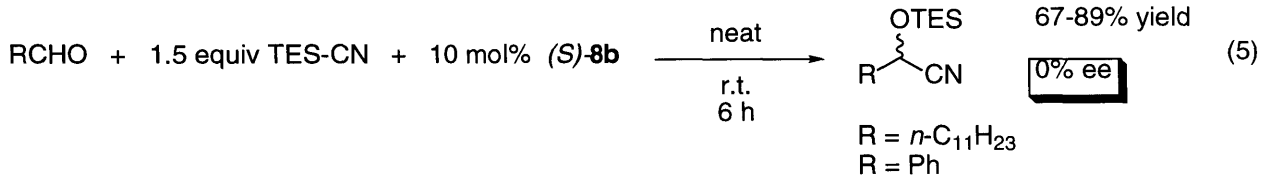
61c

60c/61c ~20 :1

60c/61c: To an oven-dried vial in a glove box was added 50 mg (0.086 mmol) of the Sn-OEt **60b** and **61b** in 1 mL of pentane and 250 μL (1.77 mmol; 20.6 equiv.) of TMS-CN to give a yellow solution. After stirring at room temperature for 2 hours, the solvent and excess TMS-CN were removed *in vacuo*. Recrystallization from ~ 2 mL

of 2:1 pentane/CH_2Cl_2 at –30 °C gave 10 mg (21% yield) of the Sn-CN as a ~ 95:5 mixture of **60c/61c**. Repeated recrystallization attempts did not improve this ratio. The mother liquor after each recrystallization showed approximately the same ratio of **60c**:**61c** as the precipitate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.44 (m, 2H), 7.27-7.31 (m, 3H), 4.16 (t, 1H, J=2), 3.91 (t, 1H, J=2), 7.61 (m, 2H), 1.98 (s, 15H, Cp* of **60c**), 1.86 (s, Cp* of **61c**), 1.02 (t, 3H, J=7), 0.96 (s, 3H, $^2J_{H\text{-}Sn}$=66, 68), the NMe_2 protons are not seen; ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -177 (**60c**).

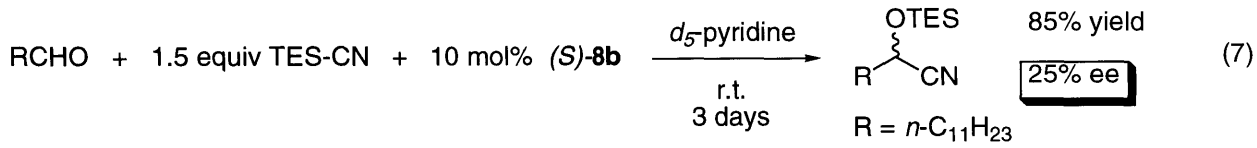
Asymmetric Catalysis Using Optically Pure Organotin Catalysts



(5)

Eq 5: To an oven-dried vial in a glove box was added 17 mg (0.039 mmol; 10 mol%) of the catalyst *(S)*-**8b**, 88 μL (0.39 mmol) of *n*-$C_{11}H_{23}CHO$, and 115 mg (0.580 mmol; 1.50 equiv) of TES-CN. The resulting solution was stirred at room temperature for 12 hours. Column chromatography of the reaction mixture (10% EtOAc/90% hexanes; R_f ~ 0.7; PMA) gave 115 mg (91% yield) of the corresponding silylated cyanohydrin. The product was dissolved in ~ 1 mL of Et_2O and stirred with ~ 5 mL of 6 N HCl at room temperature under air for 6 hours. After extraction with Et_2O and evaporation of solvent, the cyanohydrin was obtained. The cyanohydrin was treated with a slight excess of *(R)*-MTPA-Cl in 1 mL of CH_2Cl_2 with ~ 2 drops of pyridine for 12 hours. The reaction was quenched with 2 N HCl and extracted with EtOAc. The organic phase was washed with sat. NaCl and dried with Na_2SO_4. Filtration and solvent removal gave the MTPA ester. ^{1}H NMR (300 MHz, $CDCl_3$)

analysis of the crude revealed a product mixture of 0% de (methine proton, δ=5.50, 5.46). Analogous reactions were carried out for benzaldehyde and 2-nitrobenzaldehyde. ^{1}H NMR (300 MHz, $CDCl_3$) of the MTPA ester of the cyanohydrin derived from benzaldehyde (methine proton δ=6.60, 6.58) revealed a product of 0% de. ^{1}H NMR (300 MHz, $CDCl_3$) of the MTPA ester of the cyanohydrin derived from 2-nitrobenzaldehyde (methoxy protons δ=3.59, 3.48) revealed a product of 0% de.

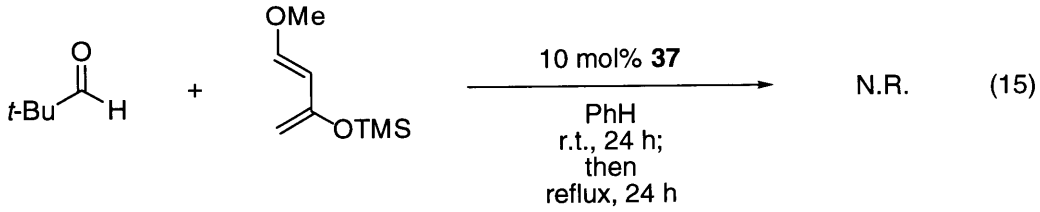


(7)

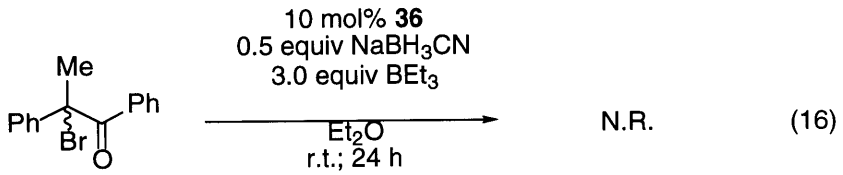
Eq 7: To an oven-dried vial in a glove box was added 35 mg (0.080 mmol; 10 mol%) of *(S)*-**8b**, 750 μL of d_5-pyridine, 180 μL (0.795 mmol) of *n*-$C_{11}H_{23}CHO$ and 170 mg (1.21 mmol; 1.52 equiv) of TES-CN. The resulting solution was transferred to an oven-dried screw-cap NMR tube and sealed under a nitrogen atmosphere. The progress of the reaction was monitored by ^{1}H NMR for 3 days (until the aldehyde has been completely consumed). Column chromatography of the reaction mixture (10% EtOAc/90% hexanes; R_f ~ 0.7; PMA) gave 219 mg (85% yield) of the corresponding silylated cyanohydrin. The product was hydrolyzed and the enantiomeric excess was assayed as in eq 5. ^{1}H NMR (300 MHz, $CDCl_3$) analysis revealed a product mixture of 25% de. The enantiomeric excess as determined by ^{1}H NMR integration does not vary with the length of the hydrolysis reaction, the extent of MTPA-ester formation reaction, or the relaxation delay of the NMR spectrometer.

Table 2. Effect of Lewis bases on enantioselectivity: An analogous procedure to that described in eq 7 was carried out on a 0.23 mmol scale (50 μl) of *n*-$C_{11}H_{23}CHO$, 10 mg (0.023 mmol, 10 mol%) of *(S)*-**8b**, 48 mg (0.34 mmol, 1.5 equiv) of TES-CN and one of

the following additives: 230 μL of d_6-DMSO, 230 μL of d_7-DMF, 230 μL of HMPA , 230 μL of 1.0 M TBAF in THF, 10 equiv TBAF in 200 μl $CDCl_3$,10 equiv of TBA-CN in 200 μl $CDCl_3$, 10 equiv of trimethylamine oxide in 200 μl $CDCl_3$, 10 equiv of triphenylphosphine oxide in 250 μl $CDCl_3$. The enantiomeric excess of the product was assayed as the MTPA-ester following the protocol used in eq 5. Reactions with *o*-tolylbenzaldehyde were carried out under identical conditions. The enantiomeric excess of the product is assayed as the MTPA-ester (methyl protons, δ=2.39, 2.28) following the protocol used in eq 5.

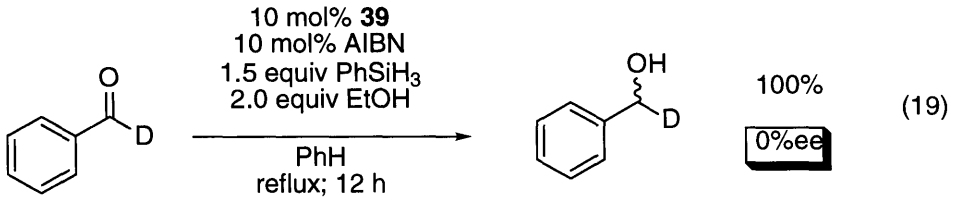


Eq 15: To an oven-dried screw-cap NMR tube in a glove box was added 6 mg (0.01 mmol; 10 mol%) of Sn-Cl **37**, 500 μL of C_6D_6, 21 μL (0.19 mmol) of *t*-BuCHO and 37 μL (0.19 mmol) of Danishefsky's diene. The resulting yellow solution was sealed under a nitrogen atmosphere and removed from the glove box. The progress of the reaction was monitored by ^{1}H NMR. No reaction was observed after 24 hours at room temperature. No reaction was observed after an additional 24 hours at 80 °C, at which point the reaction was aborted.



Eq 16: To an oven-dried vial in a glove box was added 7.0 mg (0.10 mmol; 0.50 equiv) $NaBH_3CN$, 61 mg (0.21 mmol) of the α-bromoketone, and 7.0 mg (0.010 mmol; 5 mol%) of Sn-Br **36** in 2.5 mL of THF. The reaction was monitored by TLC.

No reaction was observed after 40 hours at room temperature. Addition of 1.0 equiv of BEt_3 under a nitrogen atmosphere had no effect. Addition of dry air to the reaction mixture containing BEt_3 led to the decomposition of **36**.

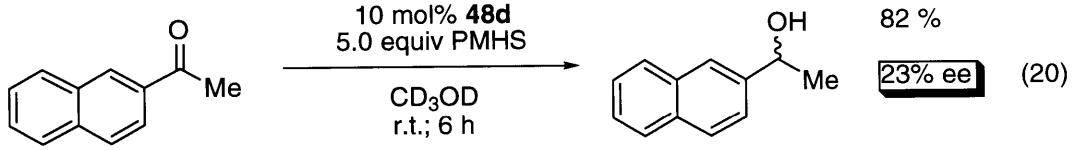


(19)

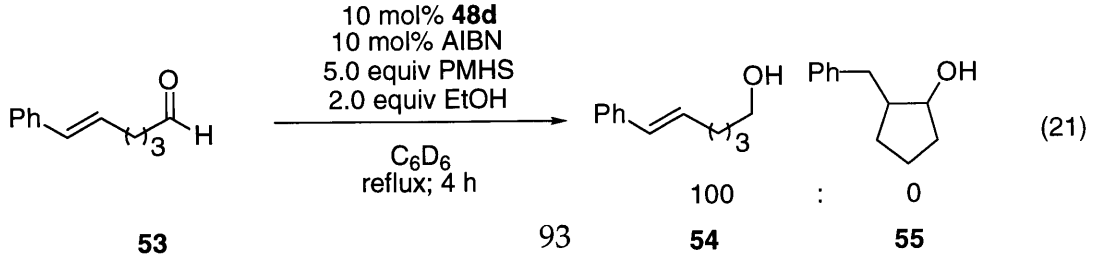
Eq 19: To an oven-dried screw-cap NMR tube in a glove box was added 5.0 mg (0.030 mmol; 10 mol%) of AIBN, 10 mg (0.016 mmol; 5 mol%) of Sn-OEt **39** in 600 μL of C_6D_6, 34 mg (0.32 mmol) of PhCDO, and 39 μL (0.32 mmol; 1.0 equiv) of $PhSiH_3$. The resulting yellow solution was sealed under a nitrogen atmosphere, wrapped in aluminum foil and removed from the glove box. After heating at 80 °C for 12 hours, ^1H NMR and TLC (1:1 Et_2O/pentane) showed no PhCDO remained. The reaction was quenched with ~ 1 mL of 1.0 M TBAF in THF and stirred at room temperature for 1 hour. After the addition of 2 N HCl, the reaction mixture was extracted with Et_2O. The organic phase was dried with Na_2SO_4, filtered and stripped of solvent. Column chromatography (1:1 Et_2O/pentane; R_f ~ 0.5; UV) gave 30 mg (88% yield) of PhCHDOH as a clear colorless oil. The product was dissolved in 600 μL of CD_2Cl_2 and treated with 50 μL of pyridine and 70 mg of *(R)*-MTPA-Cl at room temperature for 16 hours. The reaction was quenched with 2 N HCl and extracted with EtOAc. The organic layer was dried with Na_2SO_4, filtered and stripped of solvent. ^1H NMR (300 MHz, $CDCl_3$) revealed a product mixture of 0% de (methine proton, δ=4.97, 4.87). An otherwise identical reaction conducted in the presence of 2.00 equiv EtOH gave racemic product as well.

Scheme 12. Evidence of pentacoordination from reactivity: To oven-dried vials in a

glove box was added 115 μL of CH_2Cl_2, 17 μL (0.17 mmol) of *n*-$C_{11}H_{23}CHO$, 40 μL (0.22 mmol; 1.25 equiv) methylcyanoformate and one of the following additives (5 mol% each): 1.8 μL of **46** (entry 1), 1.4 μl Bu_3SnCl and 1.8 μL of **46** (entry 2), 4.4 mg of **48e** (entry 3), 5 mg of **48a** (entry 4) or 4.2 mg of **48c** (entry 5). The reaction was stirred at room temperature for 4 hours. After dilution with $CDCl_3$, the progress of the reactions was monitored by ^1H NMR.



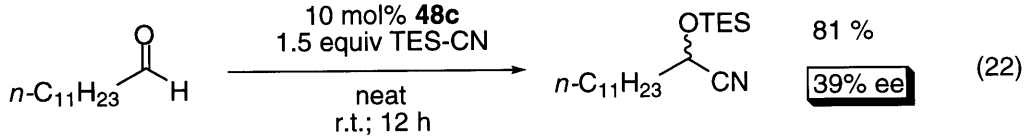
Eq 20: To an oven-dried screw-cap NMR tube in a glove box was added 73 mg (0.43 mmol) of 2'-acetonaphthone, 20 mg (0.043 mmol; 10 mol%) of Sn-OEt **48d** in 500 μL of CD_3OD and 16 μL (0.13 mmol; 3.00 equiv) of $PhSiH_3$. The screw-cap NMR tube was sealed under a nitrogen atmosphere. Gas evolution was observed in the resulting yellow solution. ^1H NMR revealed the presence of H-D. After 12 hours at room temperature, ^1H NMR indicated the complete consumption of $PhSiH_3$. Column chromatography (5:1 hexanes/EtOAc; UV) gave 38 mg (52% recovery) of the d_3-starting material (R_f ~ 0.5) and 29 mg (40% yield) of the desired alcohol (R_f ~ 0.3). The product was treated with a slight excess of *(R)*-MTPA-Cl in 1 mL of CH_2Cl_2 with ~ 2 drops of pyridine for 12 hours. The reaction was quenched with 2 N HCl and extracted with EtOAc. The organic phase was washed with sat. NaCl and dried with Na_2SO_4. Filtration and solvent removal gave the MTPA ester. ^1H NMR (300 MHz, $CDCl_3$) analysis revealed a product mixture of 23% de (methyl protons, δ=1.71, 1.65).



53 93 **54** **55**

Eq 21: To an oven-dried vial in a glove box was added 85 mg (0.49 mmol) of the enal **53**, 8 mg (0.05 mmol; 10 mol%) of AIBN, 25 mg (0.049 mmol; 10 mol%) of Sn-OEt **48d** in 1 mL of C_6D_6, 57 μL (1.0 mmol; 2.0 equiv) of EtOH and 30 μL (0.24 mmol; 0.50 equiv) of $PhSiH_3$. The resulting yellow solution was added to an oven-dried screw-cap NMR tube that was sealed under a nitrogen atmosphere and then removed from the glove box. No reaction was observed by ^1H NMR after 1 hour at room temperature. After heating at 80 °C for 5 hours, a black solution resulted. ^1H NMR revealed the presence of only the 1,2-reduction product **54** and none of the cyclized product **55**. An identical result was obtained when PMHS was used as the stoichiometric reagent. Leaving out EtOH had no effect on the product distribution.

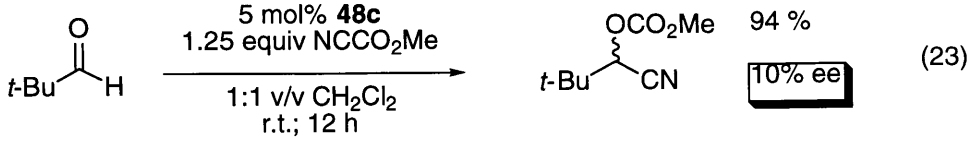
Eq 22: To an oven-dried vial in a glove box was added 7.0 mg (0.014 mmol; 10 mol%) of Sn-CN **48c**, 33 μL (0.15 mmol) of *n*-$C_{11}H_{23}CHO$ and 30 mg (0.21 mmol; 1.4 equiv) of TES-CN to give an orange solution, in which some of the catalyst remained insoluble. A homogeneous solution was obtained upon the addition of 100 μL of CD_2Cl_2. After 16 hours at room temperature, column chromatography of



(22)

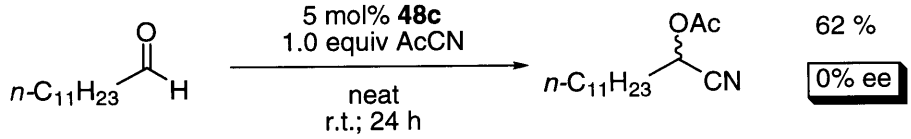
the reaction mixture (10% EtOAc/90% hexanes; R_f ~ 0.7; PMA) gave 41 mg (87% yield) of the corresponding silylated cyanohydrin. The product was hydrolyzed and the ee was assayed as the MTPA-ester as in eq 5. ^1H NMR (300 MHz, $CDCl_3$) analysis revealed a product mixture of 38% de. Reaction using the catalyst precursor Sn-OEt **48b** gave 81% yield and 40% ee. The enantiomeric excess as determined by ^1H NMR integration does not vary with the length of hydrolysis reaction, the extent of MTPA-ester formation reaction or the relaxation delay of the NMR spectrometer. An analogous reaction with 4-*t*-Bu-C_6H_4CHO gave 20% ee (^1H NMR of *(R)*-MPTA-

ester, methine proton, δ=6.56, 6.55).



(23)

Eq 23: To an oven-dried vial in a glove box was added 10 mg (0.020 mmol; 5 mol%) of the catalyst **48c**, 44 μL (0.41 mmol) of *t*-BuCHO, 80 μL of CH_2Cl_2 and 40 μL (0.51 mmol; 1.3 equiv) of methylcyanoformate. The resulting orange solution was stirred at room temperature for 12 hours. Column chromatography of the reaction mixture (25% EtOAc/75% hexanes; R_f ~ 0.5; PMA) gave 66 mg (94 % yield) of the product. Chiral GC assay revealed a product of 10% ee. Analogous reaction using *n*-$C_6H_{13}CHO$ gave a racemic product.



(24)

Eq 24: To an oven-dried vial in a glove box was added 9 mg (0.02 mmol; 5 mol%), 84 μL (0.37 mmol) of *n*-$C_{11}H_{23}CHO$ and 26 μL (0.37 mmol; 1.0 equiv) of acetylcyanide. The resulting orange solution was stirred at room temperature for 24 hours. Column chromatography (10% EtOAc/90% hexanes; R_f ~ 0.5; PMA) gave 35 mg (36% yield) of the product. Hydrolysis with *p*-toluenesulfonic acid in refluxing EtOH for 12 hours gave the cyanohydrin which was treated with excess *(R)*-MTPA-Cl in 1 mL of CH_2Cl_2 with ~ 2 drops of pyridine for 12 hours. The reaction was quenched with 2 N HCl and extracted with EtOAc. The organic phase was washed with sat. NaCl, dried with Na_2SO_4, filtered and stripped of solvent to give the crude MTPA ester. ^1H NMR (300 MHz, $CDCl_3$) analysis revealed a product mixture of 0% de.

Table 4. Enantioselectivity as a function of the steric bulk on the tin substituent:

The cyanosilylation reactions were conducted analogously to eq 20. The polar reduction reactions were conducted analogously to eq 22.

Using the Cp*-based catalysts 60b and 60c: The cyanosilylation reactions were conducted analogously to eq 20. The polar reduction reactions were conducted analogously to eq 22. The cyanoacylation reaction was conducted analogously to eq 23.

Preparation of Organotin Electrophiles

Methyltriphenyltin: To an oven-dried flask fitted with a reflux condenser under argon was added 50.0 g (130 mmol) of triphenyltin chloride and 500 mL of Et_2O to give a white slurry. Dropwise, 60 mL (180 mmol; 1.4 equiv) of 3.0 M methylmagnesium bromide in Et_2O was added (gentle reflux was observed during the addition). The resulting white cloudy solution was immersed in an oil bath at 40 °C. After 3 hours, the flask was cooled to room temperature. While immersed in an ice bath, the reaction was quenched via dropwise addition of water until bubbling stopped. The organic and aqueous phases were separated. The aqueous phase was extracted with 3 x 30 mL of Et_2O and the organic phases were combined and washed with 3 x 50 mL of sat. NaCl. The organic layer was dried with Na_2SO_4, filtered and stripped of solvent. The crude product was recrystallized from ~300 mL of EtOH (80 °C cooled to 0 °C) to give 42.9 g (90% yield) of methyltriphenyltin as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.63 (m, 15H), 0.71 (s, 3H, $^2J_{H-Sn}$=55); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1 ($^1J_{C-Sn}$=500), 136.7($^2J_{C-Sn}$=37), 128.8 , 128.5 ($^3J_{C-Sn}$=49), -10.5 ($^1J_{C-Sn}$=367); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -91.1.

Methyldiphenyltin chloride: To an oven-dried flask under argon was added 10.0 g

(27.4 mmol) of methyltriphenyltin, 120 mL of Et_2O and 24 mL (27 mmol; 1.0 equiv) of 1.15 M HCl in Et_2O. The resulting clear colorless solution was stirred at room temperature for 5 hours after which the solvent was removed *in vacuo*. ^1H NMR showed ~80 % of the desired methyldiphenyltin chloride along with ~ 10% of starting material and ~ 10% of the corresponding dichloride. The impure mixture was used as is. ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.66 (m, 15H), 1.04 (s, 3H, $^2J_{H\text{-}Sn}$=56).

Methylphenyltin dichloride: To an oven-dried flask under argon was added 5.00 g (13.7 mmol) of methyltriphenyltin, 100 mL of Et_2O and 137 mL (137 mmol; 10 equiv) of 1.0 M HCl in Et_2O. The resulting clear colorless solution was stirred at room temperature for 5 hours after which the solvent was removed *in vacuo* to give 3.87 g (100% yield) of methylphenyltin dichloride as a brown solid. Care must be taken when stripping the reaction mixture of solvent *in vacuo* as the product sublimes at room temperature under full vacuum (~ 200 mtorr). ^1H NMR (300 MHz, $CDCl_3$) δ 7.49-7.75 (m, 5H), 1.31 (s, 3H, $^2J_{H\text{-}Sn}$=69); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1 ($^1J_{C\text{-}Sn}$=727), 134.2($^2J_{C\text{-}Sn}$=66), 131.3 ($^4J_{C\text{-}Sn}$=17), 129.2 ($^3J_{C\text{-}Sn}$=81), 4.58 ($^1J_{C\text{-}Sn}$=500); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ 55.1.

Methyl-tri-(4-*t*-butylphenyl)tin: To an oven-dried flask fitted with a reflux condenser under argon was added 2.50 g (10.4 mmol) of methyltin trichloride, 20 mL of Et_2O and 20 mL (40 mmol; 3.9 equiv) of 2.0 M 4-*t*-butylphenylmagnesium bromide in Et_2O (gentle reflux was observed during the addition). The resulting white cloudy solution was immersed in an oil bath at 45 °C. After 5 hours, the flask was cooled to room and the reaction was quenched via dropwise addition of water until bubbling stopped. The organic and aqueous phases were separated. The aqueous phase was extracted with EtOAc and the organic phases were combined and washed with sat. NaCl. The organic layer was dried with Na_2SO_4 and filtered. After

solvent removal, the crude product was recrystallized from ~ 400 mL of EtOH (80 °C cooled to 0 °C) to give 2.07 g (37% yield) of methyl-tri-(4-*t*-butyl-phenyl)tin as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.52 (m, 12H), 1.31 (s, 27H), 0.66 (s, 3H, $^{2}J_{H-Sn}$=55); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 136.6 ($^{2}J_{C-Sn}$=38), 135.7, 125.3 ($^{3}J_{C-Sn}$=50), 34.6, 31.3, -10.4 ($^{1}J_{C-Sn}$=358, 375).

Methyl-di-(4-*t*-butylphenyl)tin chloride: To an oven-dried flask under argon was added 1.30 g (2.44 mmol) of methyl-tri-(4-*t*-butylphenyl)tin, 40 mL of Et_2O and 2.2 mL (2.5 mmol; 1.0 equiv) of 1.15 M HCl in Et_2O to give a white cloudy solution. After the reaction was stirred at room temperature for 5 hours, a clear colorless solution resulted. The solvent was removed *in vacuo* to give 1.06 g of methyl-di-(4-*t*-butylphenyl)tin chloride (along with some contaminants) as a white solid. The crude product mixture was used as is. ^{1}H NMR showed ~80 % of the Methyl-di-(4-*t*-butylphenyl)tin chloride along with ~ 10 % of starting material and ~ 10% of the corresponding dichloride. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.70 (m, 8H), 0.91 (s, 18H), 0.59 (s, 3H); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ 28.1.

Methyl-tri-(*o*-tolyl)tin: To an oven-dried flask fitted with a reflux condenser under argon was added 2.50 g (10.4 mmol) of methyltin trichloride, 10 mL of THF and 50 mL (50 mmol; 4.8 equiv) of 1.0 M *o*-tolylmagnesium bromide in THF (gentle reflux was observed during the addition). The resulting clear yellow solution was immersed in an oil bath at 80 °C. After 18 hours, the flask was cooled to room and the reaction was quenched via dropwise addition of water until bubbling stopped. The organic and aqueous phases were separated. The aqueous phase was extracted with of 2 x 20 mL of Et_2O. The organic phases were combined and washed with sat. NaCl. The organic layer was dried with Na_2SO_4 and filtered. After solvent removal, the crude product was recrystallized from ~40 mL of EtOH (80 °C cooled to

0 °C) to give 1.86 g (44% yield) of methyl-tri-(*o*-tolyl)tin as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04-7.41 (m, 12H), 2.34 (s, 9H), 0.81 (s, 3H, $^{2}J_{H\text{-}Sn}$=53); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 139.8, 137.1, 129.3, 129.0, 125.5, 25.0 ($^{4}J_{C\text{-}Sn}$=29), -6.32 ($^{1}J_{C\text{-}Sn}$=347, 362); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -88.6.

Methyl-di-(*o*-tolyl)tin chloride: To an oven-dried flask under argon was added 610 mg (1.50 mmol) of methyl-tri-(*o*-tolyl)tin, 10 mL of Et_2O and 1.5 mL (1.5 mmol; 1.0 equiv) of 1.0 M HCl in Et_2O to give a clear colorless solution. After the reaction was stirred at room temperature for 5 hours, the solvent was removed *in vacuo* to give 600 mg of methyl-di-(*o*-tolyl)tin chloride (contaminated with toluene) as a viscous oil. The crude was used as is. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.12-7.59 (m, 8H), 2.43 (s, 6H), 1.08 (s, 3H, $^{2}J_{H\text{-}Sn}$=58).

***tert*-Butyl-triphenyltin:** To an oven-dried flask fitted with a reflux condenser under argon was added 16.5 g (42.9 mmol) of triphenyltin chloride, 80 mL of THF and 64 mL (64 mmol; 1.5 equiv) of 1.0 M *t*-butylmagnesium chloride in THF (gentle reflux was observed during the addition). The resulting brown solution was immersed in an oil bath at 80 °C. After 24 hours, the flask was cooled to room temperature. While immersed in an ice bath, the reaction was quenched via dropwise addition of water until bubbling stopped. After the addition of 100 mL of Et_2O, the organic and aqueous phases were separated. The aqueous phase was extracted with 3 x 50 mL of Et_2O and the organic phases were combined and washed with 1 x 100 mL of sat. NaCl. The organic layer was dried with Na_2SO_4 and filtered. After solvent removal, the crude product was recrystallized from ~ 1500 mL of EtOH (80 °C cooled to 0 °C). The first recrystallization gave mostly the unreacted triphenyltin chloride. The mother liquor was concentrated to ~500 mL on a hot plate and placed in freezer at 0 °C. The second recrystallization gave mostly the desired product which was

further purified by silica gel column chromatography (2% EtOAc/98% hexanes) to give 3.22 g (19% yield) of *tert*-butyl-triphenyltin as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32-7.56 (m, 15H), 1.39 (s, 9H, $^{4}J_{H\text{-}Sn}$=38); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 137.5, 128.7, 128.4, 31.0, 28.8; ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -106.

***tert*-Butyl-diphenyltin iodide:** To an oven-dried flask under argon was added 3.22g (7.92 mmol) of *t*-butyl-triphenyltin and 20 mL of THF. To the resulting clear colorless solution was added 2.01 g (7.92 mmol; 1.00 equiv) of iodine in 10 mL of THF to give a black solution. Over the course of 3 hours, the black color gradually disappeared. After an additional 2 hours, the solvent was removed *in vacuo* to give the crude *tert*-butyl-diphenyltin iodide as a gray oil which was used as is for the next step. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.90 (m, 10H), 1.50 (s, 9H); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -35.1.

***tert*-Butyl-methyl-diphenyltin:** To an oven-dried flask fitted with a reflux condenser under argon was added the crude *tert*-butyl-diphenyltin iodide (7.92 mmol) in 20 mL of Et_2O and 4.0 mL (12 mmol; 1.5 equiv) of 3.0 M methylmagnesium bromide in Et_2O (gentle reflux was observed during the addition). The resulting white cloudy solution was immersed in an oil bath at 40 °C. After 24 hours, the flask was cooled to room temperature. While immersed in an ice bath, the reaction was quenched via dropwise addition of water until bubbling stopped. The organic and aqueous phases were separated. The organic phases was washed with 3 x 30 mL of sat. NaCl and organic layer was dried with Na_2SO_4, filtered and stripped of solvent. Silica gel column chromatography (2% EtOAc/98% hexane; R_f ~ 0.7, 0.5; UV) gave the desired product along with some impurities. The impure product was re-subjected to silica gel column chromatography (hexane; R_f ~ 0.3; UV) to give 1.60 g (59% overall yield from *t*-butyl triphenyltin) of *tert*-butyl-methyl-diphenyltin as a white solid. ^{1}H

NMR (300 MHz, $CDCl_3$) δ 7.42-7.65 (m, 10H), 1.36 (s, 9H, $^4J_{H-Sn}$=71, 68), 0.55 (s, 3H, $^2J_{H-Sn}$ =49); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1 ($^1J_{C-Sn}$=404, 430), 136.9($^2J_{C-Sn}$=30), 128.5, 128.3 ($^3J_{C-Sn}$=44), 30.5, 26.3 ($^1J_{C-Sn}$=451, 433), -12.8 ($^1J_{C-Sn}$=311, 301); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ -65.9.

***tert*-Butyl-methyl-phenyltin chloride:** To an oven-dried flask under argon was added 1.00 g (2.90 mmol) of *tert*-butyl-methyl-diphenyltin, 10 mL of Et_2O and 2.9 mL (2.9 mmol; 1.0 equiv) of 1.0 M HCl in Et_2O to give a clear colorless solution. After the reaction was stirred at room temperature for 5 hours the solvent was removed *in vacuo* to give 900 mg of the desired product *tert*-butyl-methyl-phenyltin chloride (along with some contaminant) as a white solid which was used as is. ^1H NMR (300 MHz, $CDCl_3$) δ 7.44-7.58 (m, 5H), 1.37 (s, 9H, 68), 0.76 (s, 3H); ^{119}Sn NMR (111 MHz, $CDCl_3$) δ 74.7.

***tert*-Butyl-methyltin dichloride:** To an oven-dried flask under argon was added 500 mg (1.45 mmol) of *tert*-butyl-methyl-diphenyltin and 14.5 mL (14.5 mmol; 10 equiv) of 1.0 M HCl in Et_2O to give a clear colorless solution. After the reaction was stirred at room temperature for 5 hours, the solvent was removed *in vacuo* to give 283 mg of the desired product *tert*-butyl-methyltin dichloride (along with some contaminant) as a white solid. The crude was used as is. Care must be taken when stripping the reaction mixture of solvent *in vacuo* as the product sublimes at room temperature under full vacuum (~ 200 mtorr). ^1H NMR (250 MHz, $CDCl_3$) δ 1.42 (s, 9H, $^2J_{H-Sn}$ =30), 1.08 (s, 3H, $^4J_{H-Sn}$=55).

Methyltrivinyltin: To an oven-dried flask fitted with a reflux condenser under argon was added 100 mL (100 mmol; 4.8 equiv) of 1.0 M vinylmagnesium bromide in THF and 5.00 g (20.8 mmol) of methyltin trichloride in 10 mL of THF (gentle

reflux was observed during the addition). The resulting orange solution was immersed in oil bath at 80 °C. After refluxing overnight, the flask was cooled to room temperature. While immersed in an ice bath, the reaction was quenched via dropwise addition of water till bubbling stopped. The crude mixture was extracted with 3 x 100 mL of Et_2O. The organic phase was washed with sat. NaCl 2 x 50 mL, was with Na_2SO_4 and filtered. After solvent removal, 3.72 g (83% yield) of the desired product methyltrivinyltin was obtained as a yellow oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.55 (dd, 3H, J=14, 20), 6.21 (dd, 3H, J=4, 14), 5.74 (dd, 3H, J=4, 21), 0.20 (s, 3H, $^2J_{H\text{-}Sn}$=55, 58).

Methylvinyltin dichloride: To an oven-dried flask under argon was added 3.15 g (14.7 mmol) of methyltrivinyltin and 100 mL (100 mmol; 6.8 equiv) of 1.0 M HCl in Et_2O. The resulting clear colorless solution was stirred at room temperature for 5 hours (gas evolution was observed) after which the solvent was removed *in vacuo* to give 2.83 g (83% yield) of the desired product methylvinyltin dichloride as an orange oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.11-6.66 (m, 3H), 1.23 (s, 3H).

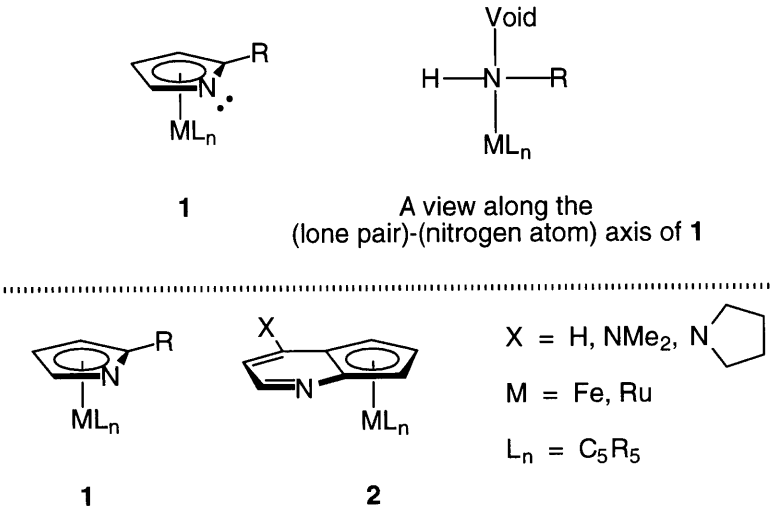
Chapter 2

Development and Applications of Planar-Chiral Nitrogen Heterocyclic Catalysts

I. Introduction

Nitrogen-based compounds such as imidazole, pyridine, and 4-(dimethylamino)pyridine (DMAP) are versatile catalysts for a large array of organic transformations. Like their cousin triphenylphosphine, significant efforts have been made to develop chiral versions of these nitrogen heterocycles for the purpose of asymmetric catalysis. Recently, efforts in this laboratory have resulted in the synthesis, resolution, and application of planar-chiral derivatives (**1** and **2**) of *N*-heteroaromatic compounds (Figure 1).[1] Initial investigations focused on the ferrocene derivatives have been since extended to the ruthenium analog as well.[2]

Figure 1. Planar-chiral *N*-heteroaromatic organometallic complexes



The asymmetry at the reactive nitrogen atom of these π-bound heterocycles is illustrated in Figure 1. The organic substituents on the heterocycle allow for

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[1] (a) Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1996**, *61*, 7230. For a more detailed discussion, see: (b) Ruble, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

[2] (a) Garrett, C. E.; Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 7479. (b) Garrett, C. E. Ph.D. Thesis, Massachusetts Institute of Technology, 1998.

differentiation between the left and right sides (H vs. R) and the π-bound metal fragment allows for the discrimination between the top and bottom faces ("void" vs. ML_n) of heterocycle **1**. These substituents desymmetrize both the vertical and the horizontal planes of the heterocycle, thereby providing an asymmetric environment for the reactive nitrogen atom.[1b]

Members of our laboratory have employed planar-chiral azaferrocenes **1** as a ligand for the enantioselective addition of organozinc reagents to carbonyls[3] and Cu(I)-catalyzed asymmetric cyclopropanation of olefins,[4] as well as to ketene solvolysis.[5] The planar-chiral derivatives of DMAP (**2**, X = amine) have been applied to the kinetic resolution of secondary alcohols[6] and the rearrangement of *O*-acylated azlactones.[7] The focus of this section will be on the application of a planar-chiral derivative of DMAP (**2**; X=NMe_2, M=Fe, R=Me) to the dynamic kinetic resolution/ring opening of racemic azlactones. Furthermore, a family of structural analogs of **2** was prepared and the structure-activity relationship of these sister compounds was investigated in an attempt to better understand this new class of nucleophilic catalysts.

In addition, we have very recently completed the synthesis and resolution of a planar-chiral C_2-symmetric derivative of 2,2'-bipyridine. We are currently probing

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3 For the addition of Et_2Zn to aldehydes, see: (a) Dosa, P. I.; Ruble, J. C.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 444. For the addition of Ph_2Zn to ketones, see: (b) Dosa, P. I.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 445.

4 Lo, M. M. -C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270.

5 Hodous, B. L.; Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1999**,*121*, 2637.

6 (a) Ruble, J. C.; Latham, H. A.; Fu, G.C. *J. Am. Chem. Soc.* **1997**, *119*, 1492. (b) Ruble, J. C.; Tweddell, J.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2794. (c) Tao, B.; Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1999**, In Press.

7 Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 11532.

the utility of this new class of compound as ligands for metal-catalyzed asymmetric organic transformations. Preliminary results in the area of asymmetric Heck reactions and the Cu(I)-catalyzed asymmetric cyclopropanation of olefins, as well as possible future (and more ambitious) applications of this latest addition to our collection of planar-chiral *N*-heteroaromatic compounds, will be discussed.

II. Dynamic Kinetic Resolution/Ring-Opening of Racemic Azlactones

Suffice it to say, the enantioselective synthesis of α-amino acids is of considerable importance.[8] To date, approaches that employ stoichiometric chiral auxiliaries have been the primary focus of attention, although several effective catalytic methods have also been reported, perhaps most notably the metal-catalyzed asymmetric hydrogenation of dehydroamino acids.[9]

One straightforward route to the synthesis of protected α-amino acids involves the ring opening of azlactones by alcohols or by water. Because of the propensity of azlactones to racemize ($pK_a \sim 9$),[10] this process is especially interesting from the standpoint of asymmetric catalysis, since a *dynamic* kinetic resolution[11] should be possible.[12] Starting from racemic azlactones, we could, in principle, obtain products in 100% optical *and* chemical yield. This is in sharp contrast with the "classical" kinetic resolution where the chemical yield of the optically pure product has a theoretical ceiling of 50%.

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8 (a) Duthaler, R. O. *Tetrahedron* **1994**,*50*, 1539. (b) Williams, R. M. *Synthesis of Optically Active α–Amino Acids*; Pergamon: New York, 1989.

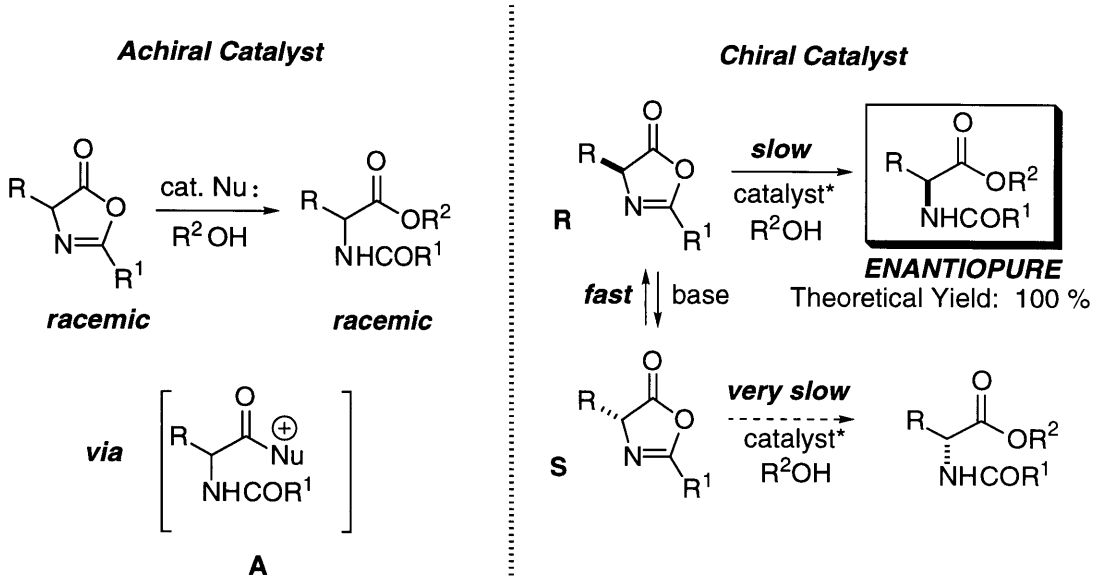
9 (a) Qiao, S.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 4168. (b) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (c) Takaya, H.; Ohta, T.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 1. (d) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994; Chapter 2.

10 (a) de Jersey, J.; Zerner, B. *Biochemistry* **1969**, *8*, 1967. (b) Goodman, M.; Levine, L. *J. Am. Chem. Soc.* **1964**, *86*, 2918. (c) Benoiton, N. L. *The Peptides*; Academic: New York, 1983; Volume 5, Chapter 4.

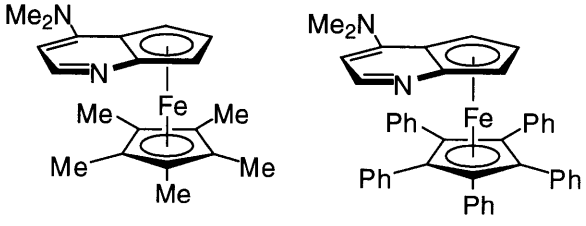
11 (a) Stecher, H.; Faber, K. *Synthesis* **1997**, 1. (b) Caddick, S.; Jenkins, K. *Chem. Soc. Rev.* **1996**, *25*, 447. (c) Ward, R. S. *Tetrahedron: Asymmetry* **1995**, *6*, 1475. (d) Noyori, R.; Tokunaga, M.; Kitamura, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 36.

12 For enzymatic protocols, see: (a) Pugniere, M.; Kraicsovits, F.; Coletti-Previero, M.-A.; Previero, A. *Biotech. Lett.* **1985**, *7*, 641. (b) Bevinakatti, H. S.; Newadkar, R. V.; Banerji, A. A. *J. Chem. Soc., Chem. Commun.* **1990**, 1091. (c) Crich, J. Z.; Brieva, R.; Marquart, P.; Gu, R.-L.; Flemming, S.; Sih, C. J. *J. Org. Chem.* **1993**, *58*, 3252. (d) Turner, N. J.; Winterman, J. R.; McCague, R.; Parratt, J. S.; Taylor, S. J. C. *Tetrahedron Lett.* **1995**, *36*, 1113.

Scheme 1. Principle behind dynamic kinetic resolution/ring-opening of racemic azlactones



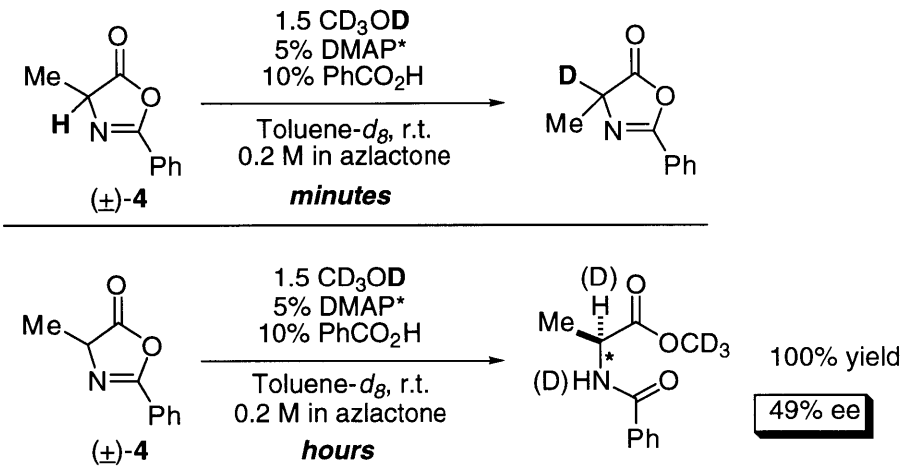
The protocol for the chemically mediated deracemization and ring-opening of azlactones outlined in Scheme 1 calls for both a base to effect the epimerization (interconversion of **R** and **S**) of the azlactones and a nucleophile to generate the acyl intermediate **A** (ring opening). The key to this dynamic kinetic resolution is that the rate of epimerization must be significantly greater than the rate of ring-opening of the disfavored enantiomer (e.g., **S**). 4-(Dimethylamino)pyridine (DMAP), an efficient basic *and* nucleophilic catalyst, effectively catalyzes the ring opening of azlactones by alcohols. We thus hypothesized that we could achieve an asymmetric variant of this reaction using our new planar-chiral derivatives of DMAP **3a** and/or **3b**.



3a; "DMAP*" **3b**

Preliminary studies in our laboratory have demonstrated the feasibility of a dynamic kinetic resolution of azlactones using **3a** ("**DMAP***")[13] as the catalyst (Scheme 2).

Scheme 2. Demonstration of the feasibility of dynamic kinetic resolution of azlactone



Based on Scheme 2, we learned that like DMAP itself, planar-chiral DMAP analogue **3a** catalyzes the addition of alcohols to azlactones. Most importantly, we have established that deuterium incorporation (i.e., racemization) occurs rapidly relative to ring-opening.[14] With regard to the central issue of stereoselectivity, we investigated the methanolysis of (±)-**4** and learned that enantiopure (-)-**3a** catalyzes the dynamic kinetic resolution of this alanine-derived azlactone to preferentially give the L-alanine derivative as shown (Scheme 2). Although this is an

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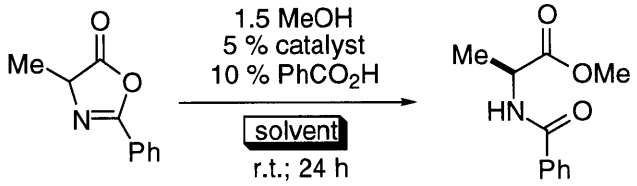
[13] The pentaphenyl derivative **3b** is an efficient catalyst in term of chemical yield; however, its enantioselectivity is significantly lower than **3a**. This is in direct contrast to the results we obtained for the kinetic resolution of secondary alcohols (Ref. 6).

[14] We inadvertently discovered the presence of benzoic acid leads to ring opening of the azlactone at a faster rate and with higher enantioselectivity than in the absence of benzoic acid (with no benzoic acid: <2% ee for the ring opening of (±)-**4** with MeOH catalyzed by (-)-**3a**). Since this discovery, we have screened a number of Lewis and protic (achiral and optically pure) acids. However, none of these additives gave better enantioselectivity than benzoic acid.

encouraging result,[15] we nevertheless would like to obtain a higher level of asymmetric induction. This is crucial since the ring-opened product is an amino acid derivative. It should be noted that the azlactone precursor itself is also an amino acid derivative, typically optically pure.

Earlier studies by Dr. J. Craig Ruble in our group have already established the optimal benzoic acid loading (10 mol% relative to substrate) as well as the optimal acyl substituent (i.e., phenyl) on the azlactone. Of the remaining variables, the simplest to change are the solvent and the concentration. A selected list of solvents is shown in Table 1.

Table 1. Solvent studies



Solvent	%ee @ 0.4 M	%ee @ 0.2 M	%ee @ 0.1 M	%ee @ 0.05 M
CH_3CN	---	11	---	---
$PhNO_2$	---	17	---	---
acetone	---	20	---	---
THF	---	31	---	---
CH_2Cl_2	---	33	---	---
EtOAc	---	40	---	---
CCl_4	38	40	47	53
PhBr	---	42	---	45
PhOMe	---	46	---	53
$PhCH_3$	46	49	54	59

We screened a diverse array of solvents without achieving any breakthrough. Toluene remains the best solvent. Somewhat disappointingly, the

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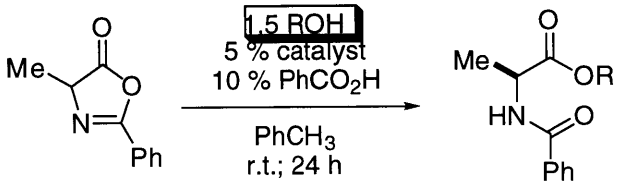
[15] We are aware of only one example of catalytic, enantioselective deracemization/ring-opening of azlactones with a non-enzymatic catalyst (copper complex, <15% ee): Belokon, Y. N.; Bachurina, I. B.; Tararov, V. I.; Saporovskaya, M. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1992**, *41*, 422.

enantioselectivity increases upon dilution. Although the enantioselectivity is higher when the concentration of the substrate is 0.05 M in toluene, the reaction is prohibitively slow (34% yield after 24 h). The next logical variable to explore was the nature of the alcohol nucleophile (Table 2).

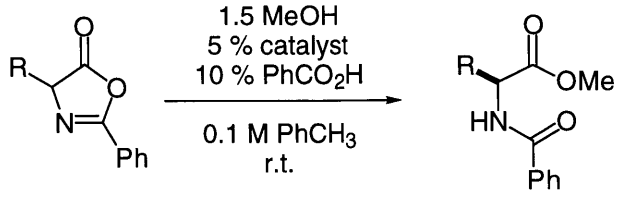
Table 2. Alcohol studies



R =	Conc. $PhCH_3$	Temp.	t [h]	% yield	% ee
Me	0.1 M	r.t.	24	81	54
Et	0.1 M	r.t.	24	46	62
Et	0.2 M	r.t.	24	61	53
i-Pr	0.2 M	r.t.	96	29	78
i-Pr	0.4 M	r.t.	96	40	73
i-Pr	0.4 M	80 °C	24	44	42

As shown in Table 2, the stereoselectivity increases as the steric bulk of the incoming alcohol increases, reaching 78% ee with *i*-PrOH. Unfortunately, ring opening under these conditions is extremely slow ($t_{1/2}$ ~ 1 week). From these studies, it can be seen that although higher levels of asymmetric induction is possible (e.g., 0.05 M of substrate in toluene or using *i*-PrOH as the nucleophile), the reaction is unacceptably sluggish under these conditions. Thus, in a compromise between optical and chemical yield (e.g., 0.05 M vs. 0.1 M; *i*-PrOH vs. MeOH), we choose to conduct the reaction at 0.1 M in toluene as the solvent with methanol as the nucleophile. We have synthesized azlactones derived from a number of natural and unnatural amino acids, and we have subjected them to DMAP* (**3a**)-catalyzed dynamic kinetic resolution/ring-opening under these conditions (Table 3).

Table 3. Substrate scope



R =	t [h]	% yield	% ee	R =	t [h]	% yield	% ee
Me	48	98	55	CH_2*c*-Hex	96	93	54
Et	72	95	45	CH_2Ph	48	94	56
Allyl	48	95	61	Ph	72	84	25
i-Pr	120	41	13	CH_2CH_2SMe	48	95	50
i-Bu	48	95	55	CH_2SMe	48	83	48

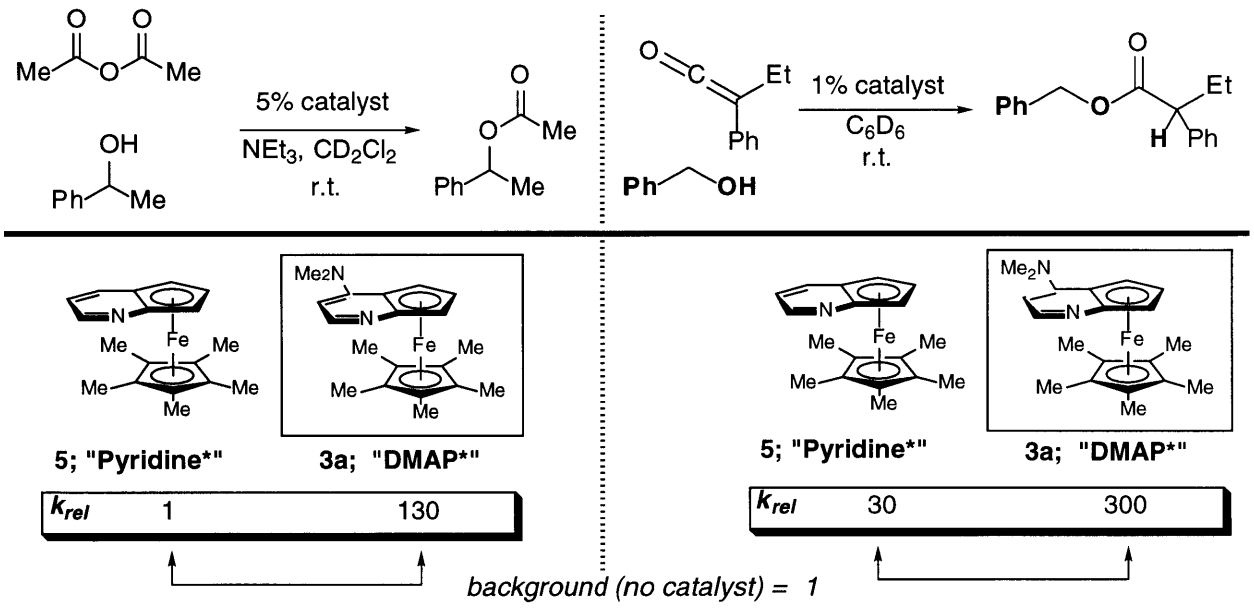
As illustrated in Table 3, our planar-chiral DMAP derivative **3a** catalyzes the dynamic kinetic resolution of a range of azlactones with fair enantioselectivity and good yield. While the observed enantiomeric excesses are modest compared with the ultimate goal of 100% ee, it is worthwhile to note that these values represent the best selectivities reported to date for the deracemization/ring-opening of azlactones with non-enzymatic catalysts.[8]

In conclusion, we have established that chiral DMAP derivative **3a** catalyzes the deracemization/ring-opening of azlactones, thereby affording protected α-amino acids. This study furnishes a new benchmark for non-enzymatic enantioselective catalysis of this interesting process.

III.A. "Second-Generation" Catalysts: Introduction

In the azlactone chemistry, it is clear that we sacrificed optical yield for chemical yield. That is, our "optimized" reaction conditions are NOT the ones that give the best enantioselectivity. We chose not to conduct the reaction at a lower concentration (Table 1) or use a bulkier nucleophile (Table 2) because of the resulting sluggish reaction. This shortcoming, however, could be surmounted if we can obtain a more reactive catalyst. Earlier investigations have shown that the 4-amino group greatly enhances the reactivity of these complexes (Scheme 3).[1b]

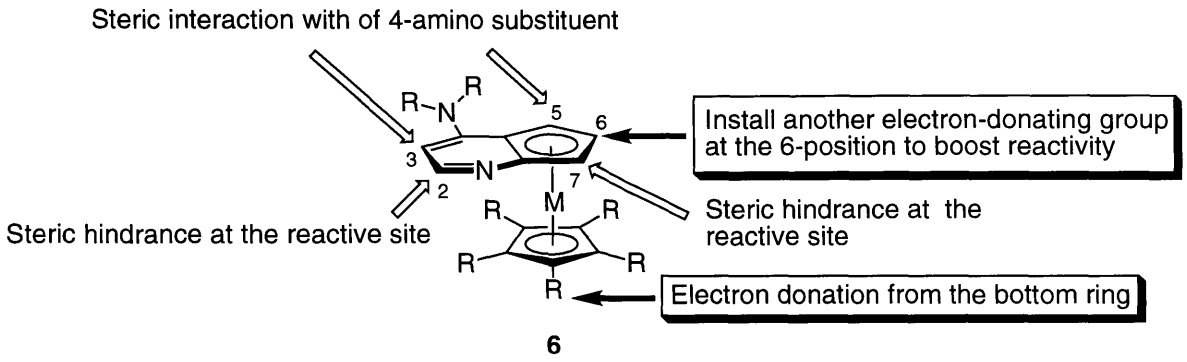
Scheme 3. Effect of the 4-amino substituent on reactivity



From the data in Scheme 3, it is apparent that the catalyst owes its reactivity to electron donation from the 4-amino substituent. Armed with this information, it thus follows that increasing the electron density at the pyridine nitrogen of **3a** should further boost its reactivity. Our strategy for obtaining a more reactive catalyst

by modifying the electronics of both the "top" (pyridine) ring and the "bottom" Cp-ring is shown in Figure 2.

Figure 2. Design of a more reactive catalyst



Working with assumption that "more is better", we would like to add a second amino group to the top ring. The question now lies with the placement of the second amino group. As is shown in Figure 2, because of steric considerations, the only logical position is the 6-position.[16]

Furthermore, for the pentaphenyl derivative **3b**, we could, in principle, replace the electron-withdrawing phenyls with sterically similar but electronically more favorable substituents. We hypothesize that with appropriate modifications of both the organic and organometallic halves of **3a**, we can arrive at more efficient and more potent second-generation catalysts.

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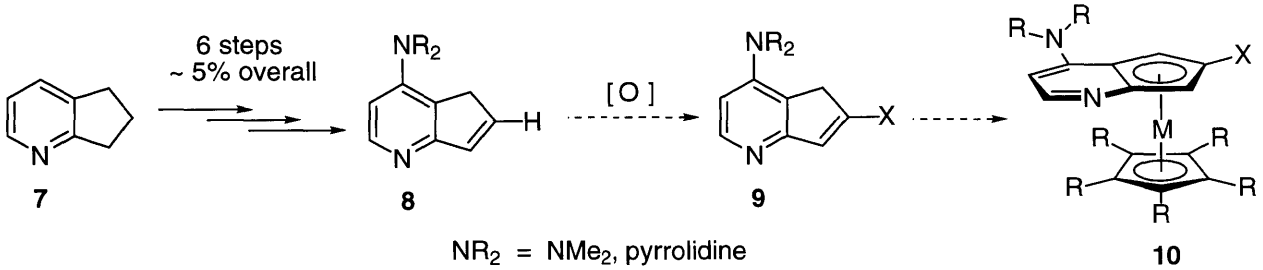
16 Of course, we do not expect the electronic boost from either the 6-position or the Cp-ring to be as significant as that from the 4-position, due to the cross-conjugated nature of the 6-amino group relative to the reactive site and the attenuation by the aromatic ring and/or the metal.

III.B. Modification of the Pyridine Ring

In principle, the synthesis of the 4,6-diamino derivative **10** can be achieved as shown in Scheme 4.

Scheme 4. General strategy for the synthesis of the 4,6-diamino catalyst



However, due to the tedious nature in the synthesis of the "top ring" olefin 8[17] and the generally capricious nature of *N*-heteroaromatic compounds, we decided to conduct a model study first and synthesize the 4-H, 6-amino derivative. Not only is it easier to synthesize this simpler derivative, it also allows us to quantify the effects of the 6-amino substituent alone on reactivity and enantioselectivity. The synthesis is shown in Scheme 5. The key steps are the Jacobsen epoxidation[18] of the regioisomeric olefins **13** to the corresponding epoxides **14**, followed by a palladium-catalyzed rearrangement[19] to give the desired 6-ketone **15**, which was converted in situ to the corresponding enamine **16**. Complexation of **16** gave the racemic 6-amino derivative **17**, which was resolved via semi-preparative chiral HPLC.

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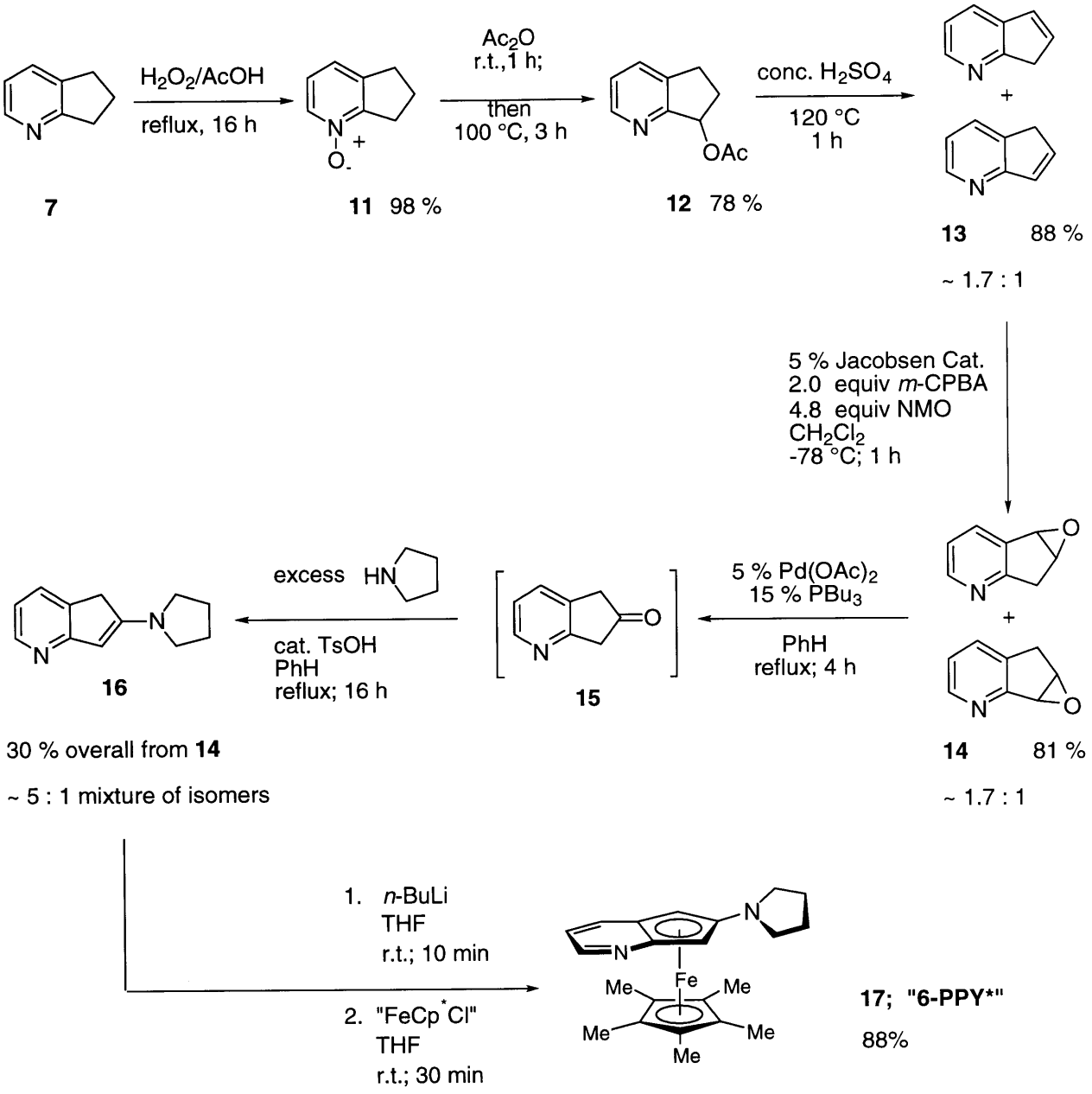
17 Since the completion of this work, compound **7** is no longer commercially available. Fortunately, an alternative and more facile synthesis of **8** starting from adipoyl chloride has been developed. See: Ruble, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

18 Palucki, M.; Pospisil, P. J.; Zhang, W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 9333.

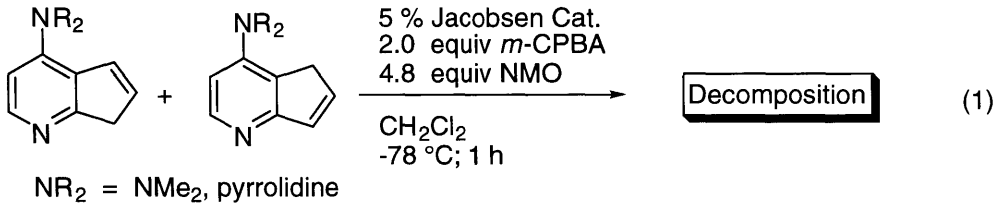
19 (a) Kulasegaram, S.; Kulawiec, R. J. *J. Org. Chem.* **1997**, *62*, 6547. (b) Kulasegaram, S.; Kulawiec, R. J. *Tetrahedron* **1998**, *54*, 1361.

Scheme 5. Model study: synthesis of the 4-H, 6-amino derivative



Because of the susceptibility of the pyridine nitrogen to undergo oxidation to the corresponding *N*-oxide, chemoselective oxidation of the olefin **13** was problematic. In the end, only the Jacobsen system (Mn-Salen/*m*-CPBA/NMO) proved to be

fruitful.[20] Furthermore, due to the Lewis-basic nature of the pyridine nitrogen of **14**, standard Lewis acid-catalyzed rearrangement of epoxides could not be employed.[21] Lastly, although we could observe the clean formation of **15** by conducting and monitoring the rearrangement reaction (**14** → **15**) in C_6D_6, we were unable to isolate the desired product, which appeared to decompose upon silica gel column chromatography. Attempts at isolating **15** by solvent removal, followed by filtration to remove the palladium, were also unsuccessful.[22] Fortunately, we were able to convert the ketone **15** to the corresponding enamine **16** in situ. Standard complexation conditions gave the desired 6-amino derivative *rac*-**17**, which was resolved via chiral HPLC. These difficulties notwithstanding, we hypothesized that if we subject the 4-amino olefin **8** to the epoxidation-rearrangement process, we could obtain the desired 4,6-diamino compound **9**. Unfortunately, this was not the case (eq 1).



8 (1)

Presumably due to the ease of oxidative decomposition of electron-rich pyridine compounds, we were unable to effect the desired selective oxidation despite

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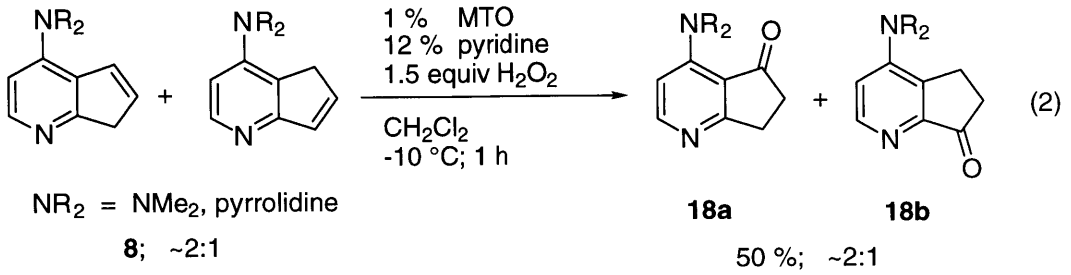
[20] An earlier protocol that used commercial bleach as the oxidant gave lower yield (~ 50%). See: Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991,** *56,* 2296.

[21] For reviews on epoxide to carbonyl rearrangement reactions, see: Rickborn, B. In *Comprehensive Organic Chemistry;* Trost, B. M., Ed.; Pergamon: Oxford, 1991, Vol. 3; Chapter 3.3, pp. 733-85.

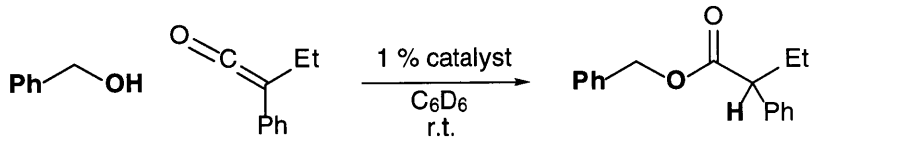
[22] We believe the instability of the 6-ketone **15** is due to the acidity of the α-hydrogens. The pK_a of acetone is ~ 20, phenylacetone is ~17, and 2-indanone is ~ 12. This indicates that perhaps there is some anomalous effect in a 6-5 fused aromatic-cyclopentenone system. See: Keeffe, J. R.; Kresge, A. J.; Yin, Y. *J. Am. Chem. Soc.* **1988,** *110,* 8201. Due to the electron-deficient nature of pyridine, we expect this effect to be even more pronounced in **15**. Furthermore, the basic pyridine nitrogen in **15** probably facilitates the decomposition via self-condensation (aldol).

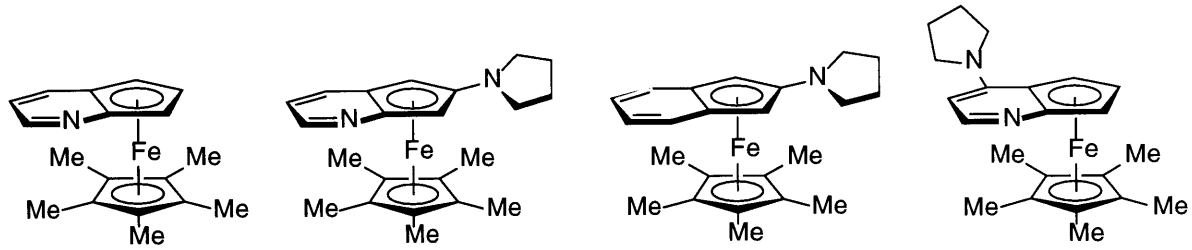
repeated attempts with a number of oxidants. As an interesting aside, during our oxidant screening process, we unearthed a reaction that gave us access to the 5- and 7-ketone **18a** and **18b** (eq 2).[23]



Despite repeated efforts via a number of alternative routes, we were not able to synthesize the desired 4,6-diamino compound **10**. However, since we have the 6-amino compound **17** ("6-PPY*") in hand, we decided to investigate the effect of the lone 6-amino group on reactivity (Table 4).

Table 5. Effect of the top-ring substituent on reactivity: *addition of benzyl alcohol to phenylethyl ketene*





	5	**17**	**19**	**20**
	"Py*"	**"6-PPY*"**	**"2-PInd*"**	**"4-PPY-Cp*"**
k_{rel}	30	120	1	840

background (no catalyst) = 1 $k_{rel,\ DMAP^*}$ = 300

23 For the use of MTO in epoxidation of olefins, see: (a) Herrmann, W.A.; Fischer, R. W.; Marz, D. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1638. (b) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189.

We chose to use ketene solvolysis (eq 3) as our benchmark reaction because of the convenient of rate of reaction ($t_{1/2}$ ~ 15 minutes) and ease of data acquisition (^{1}H NMR). As shown in Table 4, we observed a four-fold reactivity boost from the 6-position relative to the "parent" compound (**17** vs. **5**). In order to ensure that the reactivity boost observed for the 6-amino compound **17** was not an artifact of the exocyclic amine in the 6-position, we have synthesized the 2-aminoindenyl compound **19** as a control.[24] Since **19** is not a viable catalyst (**19** vs. background), we can conclude that the exocyclic amine of **17** is not nucleophilic. Thus, the observed reactivity boost of **17** can be attributed exclusively to electron donation from the 6-amino group to the pyridine nitrogen, and it is the resulting more electron-rich pyridine nitrogen that is responsible for the enhanced reactivity. Lastly, as expected,[16] the rate enhancement due to the amine from the 6-position is inferior to that from the 4-position (**17** vs. **20**).

In conclusion, we have demonstrated the capability of an amine at a remote position to donate electron density to the pyridine nitrogen and thereby elevating the reactivity of a planar-chiral nucleophilic catalyst. However, the effect of the 6-amino group is relatively small when compared with that of the 4-amino group (**17** vs. **20**). We do not expect the hypothetical 4,6-diamino compound (**10**) to be more than four times more reactive than the parent 4-amino compound (**20**). Thus, although we think it may be possible to synthesize the desired 4,6-diamino catalyst, we do not think the benefit gained justifies the added costs both in terms of time and money.

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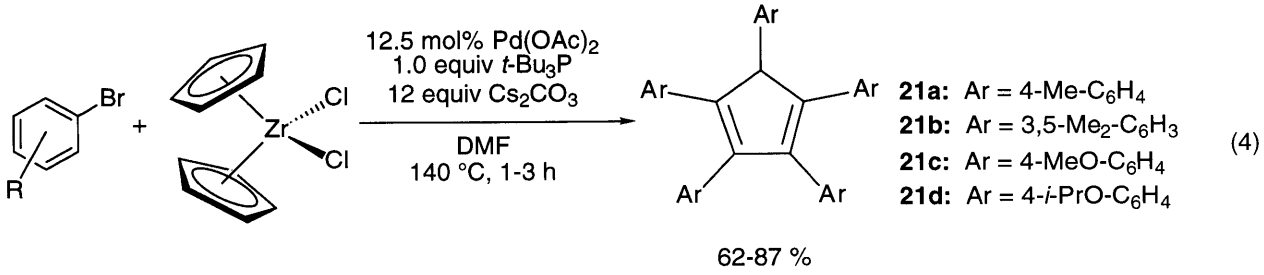
[24] Compound **19** was prepared by the complexation of 1-indene-2-yl-pyrrolidine. 1-Indene-2-yl-pyrrolidine was prepared from the condensation of pyrrolidine with 2-indano ne. See: Blomquist, A. T.; Moriconi, E. J. *J. Org. Chem.* **1961**, *26*, 3761.

III.C. Modification of the Cp-Ring

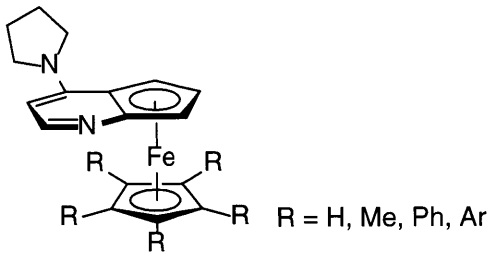
As we were in the process of wrapping up our structure-activity study of the pyridine ring, a paper appeared that reported an easy entry into various penta-aryl cyclopentadienes (eq 4).[25]



(4)

This gives us an opportunity to study the effects of changes in Cp-ring substituents on the reactivity and enantioselectivity. A previous investigation by Dr. Christine E. Garrett on azaferrocenes (**1**) illustrated that the substituents on the Cp-ring can effect the reactivity of the catalyst.[26] To this end, we have synthesized a family of compounds in order to study the structure-activity relationships of the planar-chiral DMAP derivative **3b** (**22-27**; Figure 3).

Figure 3. Structural analogs of 4-PPY-Cp*



22-27

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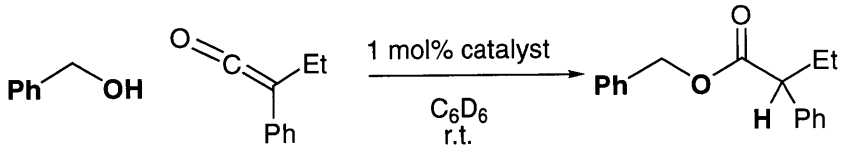
25 Miura, M.; Pivsa-Art, S.; Dyker, G.; Heiermann, J.; Satoh, T.; Nomura, M. *J. Chem. Soc., Chem. Commun.* **1998**, 1889.

26 Garrett, C. E. Ph.D. Thesis, Massachusetts Institute of Technology, 1998.

Based on our experience with the parent penta-*phenyl* compound **3b**, we learned that solubility can be a major obstacle in the resolution of the racemic catalyst by chiral HPLC. We thus hypothesized that a more "greasy" alkyl- or alkoxy-substituted derivative of **3b** could alleviate this problem. That is, in addition to the possibility of obtaining better reactivity and/or enantioselectivity profiles, there might be a practical advantage to preparing derivatives of **3b** as well. Furthermore, since phenyls are more electron-withdrawing than methyls, the pentaphenyl catalyst is less reactive than the pentamethyl catalyst. We theorized that the electron-donating 4-alkoxy substituted penta-aryl derivatives might partly compensate for the rate retardation.

To investigate the effect of the Cp-ring substituent on reactivity, we once again turned to ketene solvolysis (Table 5).

Table 5. Effect of the Cp-ring substituent on reactivity: *addition of benzyl alcohol to phenylethyl ketene*



(5)

Catalyst:	**22**	**20**	**23**	**24**	**25**	**26**	**27**
R =	H	Me	Ph	4-Me-C_6H_4	3,5-Me_2-C_6H_3	4-MeO-C_6H_4	4-*i*-PrO-C_6H_4
k_{rel}	400	800	200	200	50	220	220

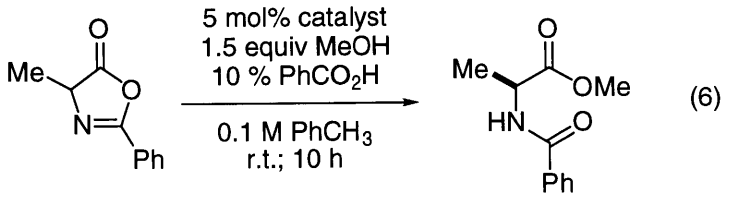
background (no catalyst) = 1

On the basis of steric reasons, one would expect **20** (R=Me) to be less reactive than **22** (R=H). In fact, it is the more sterically hindered Cp* catalyst **20** that is more reactive than the Cp catalyst **20**. The most logical explanation that can account for this apparent paradox is that electronic effects outweigh steric effects and the more electron-rich Cp* of **20** leads to a more electron rich and hence more reactive

pyridine nitrogen atom.[27] Thus, we have an indication that there is in fact electronic information being transferred from the Cp-ring to the reactive nitrogen center. Not surprisingly, the pentaphenyl compound **23** is less reactive than the pentamethyl compound **20** due to both steric and electronic reasons. The 4-alkoxy and the 4-alkyl substituted penta-aryl derivatives (**24**, **26**, and **27**) showed little or no rate acceleration relative to the parent compound **23**. Interestingly, the 3,5-dimethyl substituted derivative **25** showed a significant rate *decrease*. This could imply that the 3,5-dimethyl substituents are interacting with the reactive center and perhaps creating a more bulky and "more chiral" catalyst.

The easiest way of test this hypothesis is to conduct asymmetric transformations. We initially choose to use the dynamic kinetic resolution/ring-opening of racemic azlactones as the testing ground (Table 6).

Table 6. Effect of Cp-ring substituent on enantioselectivity:
dynamic kinetic resolution/ring-opening of azlactone



(6)

Catalyst:	**22**	**20**	**23**	**24**	**25**	**27**
R =	H	Me	Ph	4-Me-C_6H_4	3,5-Me_2-C_6H_3	4-*i*-PrO-C_6H_4
% *ee*	16	54	26	28	38	24
% conv.	54	56	21	32	20	34

As expected, the less sterically demanding Cp derivative **22** is inferior to the Cp* catalyst **20** with regard to asymmetric induction. Surprisingly, the more sterically

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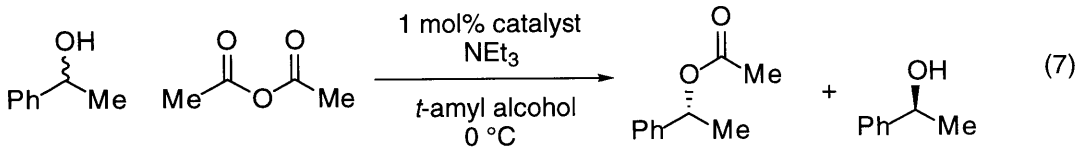
27 Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882.

demanding pentaphenyl and penta-aryl[28] derivatives **23, 24, 25,** and **27** all displayed a lower level of enantioselectivity than pentamethyl compound **20**.[13] Regardless, our previous suspicion that the 3,5-dimethyl derivative **25** is "more chiral" than its sister compounds **23, 24,** and **27** seems to hold true: **25** does show a higher degree of asymmetric induction than **23, 24,** and **27**, albeit the difference is modest.

We next turned our attention to the kinetic resolution of secondary alcohols (Table 7).

Table 7. Effect of Cp-ring substituent on enantioselectivity: *kinetic resolution of alcohols*



(7)

Catalyst:	**22**	**20**	**23**	**24**	**25**	**27**
R =	H	Me	Ph	4-Me-C_6H_4	3,5-Me_2-C_6H_3	4-*i*-PrO-C_6H_4
S	1.5	1.5	36	31	17	32
in Et_2O at r.t.: ***S***			15	15	19	15

The results are puzzling to say the least. In *t*-amyl alcohol at 0 °C, the 3,5-dimethyl derivative **25** is significant *less* selective than the pentaphenyl and the other penta-aryl catalysts (**23, 24,** and **27**). On the other hand, in Et_2O at room temperature, **25** is now *more* selective than **23, 24,** and **27**. The most puzzling result is, to the limit of experimental error, **25** is more selective in Et_2O at *room temperature* than it is in *t*-

[28] The 4-MeO-C_6H_4 derivative **26** could not be resolved via chiral HPLC and was therefore not used in studies involving asymmetric transformations.

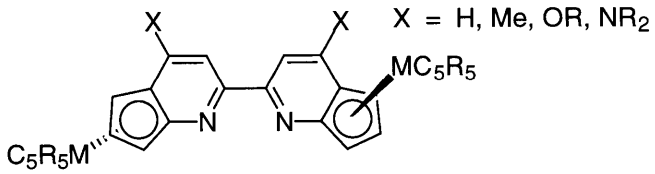
amyl alcohol at *0* °C. This is in direct contrast to the results we obtained for the parent pentaphenyl catalyst **23**.[6]

In conclusion, we have synthesized a series of structural analogs of our planar-chiral DMAP catalyst. The structure-activity relationship studies of these compounds revealed interesting reactivity and enantioselectivity profiles. However, although the results are interesting, there was no significant breakthrough--the pentaphenyl derivative **23** is still the best catalyst.

IV.A. Planar-Chiral C_2-Symmetric Derivatives of 2,2′-Bipyridine: Introduction

Following our work in the area of planar-chiral derivatives of "monomeric" nitrogen heterocycles, it was only natural that we extend the concept of planar-chirality to the "dimeric" equivalents. More specifically, we decided to pursue the syntheses and applications of planar-chiral derivatives of 2,2′-bipyridine (Figure 4).

Figure 4. Planar-chiral derivatives of 2,2'-bipyridine



M = Fe, Ru

R = H, Me, Ph, Ar

2,2′-Bipyridine and its derivatives have long attracted the attention of chemists because of the propensity of these bidentate nitrogen heterocyles to form interesting adducts with inorganic as well as organometallic compounds. The ease with which 2,2′-bipyridines form complexes with copper, nickel, and palladium, coupled with recent interest in the area of transition metal-catalyzed asymmetric organic transformations, have inevitably sparked the development of optically pure 2,2′-bipyridines.[29] In general, optically pure transition metal-bidentate nitrogen ligand systems have not been as thoroughly studied as their phosphine counterparts. Thus, it is very likely that the efforts in developing chiral bidentate nitrogen ligands

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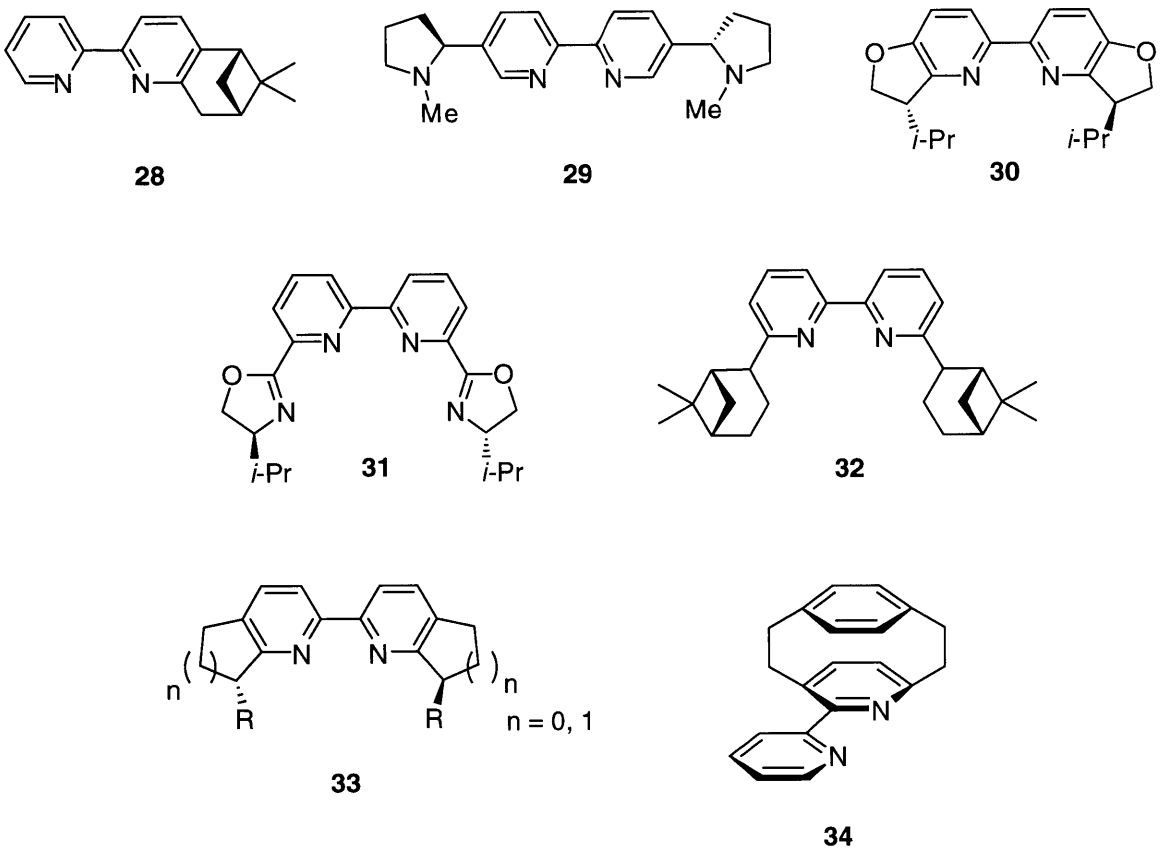
[29] For reviews, see: (a) Chelucci, G. *Gazz. Chim. Ital.* **1992**, *122*, 89. (b) Bolm, C. "Optically Active Bipyridines in Enantioselective Catalysis", in *Organic Synthesis via Organometallics*, Hoffmann, R. W.; Dotz, K. H. Eds., Vieweg: Braunschweig, 1990.

will result in reactions complementary to those using the well-known chiral bidentate phosphine ligands.

Some of the more recently developed optically pure derivatives of 2,2′-bipyridine are shown in Figure 5.[30]

Figure 5. Selected examples of chiral derivatives 2,2'-bipyridine



Notice that most of these species (e.g., **28–32**) procure their chiral scaffold from the chiral pool. Some of the asymmetric transformations utilizing these ligands

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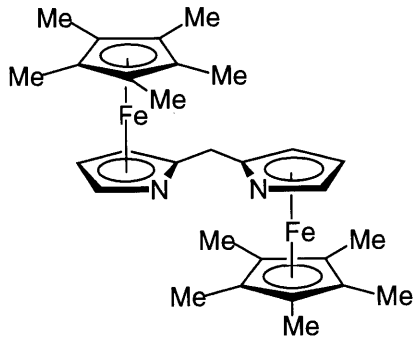
[30] For **28-32**, respectively, see: (a) Chen, C. *Synlett* **1998**, 1311. (b) Schmidt, B.; Neitemeier, V. *Synthesis* **1998**, 42. (c) Bolm, C.; Ewald, M.; Zehnder, M.; Neuburger, M. A. *Chem. Ber.* **1992**,*125*, 453. (d) Nishiyama, H.; Yamaguchi, S.; Park, S.-B.; Itoh, K. *Tetrahedron: Asymmetry* **1993**, *4*, 143. (e) Chelucci, G.; Pinna, G. A.; Saba, A. *Tetrahedron: Asymmetry* **1998**, *9*, 531.

include $NiCl_2/CrCl_2$-mediated coupling reaction of ketones with alkenyl halides (**28**),[29a] rhodium-catalyzed hydrosilylation of ketones (**31**),[29d] and palladium-catalyzed allylic substitution (**32**).[29e]

Of particular interest among the compounds shown in Figure 5 are **33**[31] and **34**.[32] Katsuki and co-workers have synthesized and applied derivatives of **33** to the Cu(I)-catalyzed asymmetric cyclopropanation of olefins and the Cu(I)-catalyzed enantioselective ring expansion of oxetanes to tetrahydrofurans. The Katuski system gave excellent level of asymmetric induction for the former reaction (> 90% ee) and good enantioselectivity for the latter (> 80% ee). Very recently, Vogtle and co-workers reported the synthesis of planar-chiral **34** using the [2.2] paracyclophane skeleton as the chiral scaffold. The preliminary results, however, were somewhat disappointing (< 25% ee for cyclopropanation; < 35% ee for transfer hydrogenation).

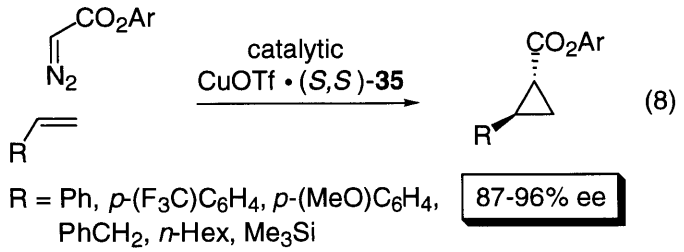
Thus far, there has yet to be a report of a planar-chiral C_2-symmetric derivative of 2,2'-bipyridine. The closest relative of this hitherto unknown ligand is the bisazaferrocene **35** developed in our laboratory.[4]



(-)-(*S*,*S*)-**35**

31 (a) Ito, K.; Yoshitake, M.; Katsuki, T. *Heterocycles* **1996**, *42*, 305. (b) Ito, K.; Katuski, T. *Chem. Lett.*, **1994**, 1857. (c) Ito, K.; Katsuki, T. *Tetrahedron Lett.*, **1993**, *34*, 2661. (d) Ito, K.; Katsuki, T. *Synlett* **1993**, 638. (e) Ito, K.; Tabuchi, S.; Katsuki, T. *Synlett* **1992**, 575.

Michael M.-C. Lo has utilized this bidentate C_2-symmetric moiety as a ligand for the Cu(I)-catalyzed asymmetric cyclopropanation of olefins with excellent enantioselectivity (eq 8).



Our objective is to synthesize planar-chiral C_2-symmetric derivatives of 2,2′-bipyridine and to investigate their application as ligands for transition metal-catalyzed asymmetric organic transformations.

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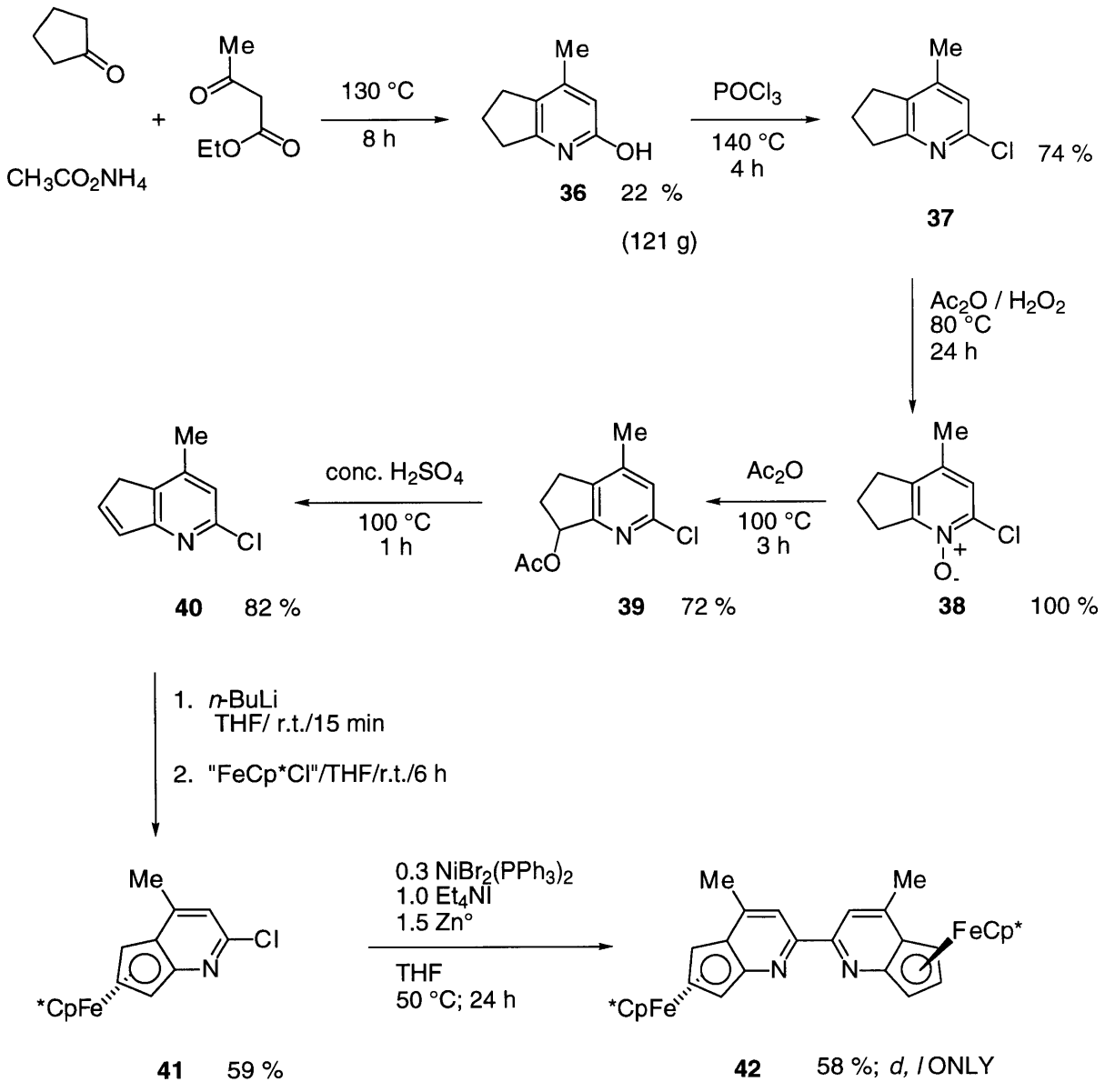
32 Worsdorfer, U.; Vogtle, F.; Nieger, M.; Waletzke, M.; Grimme, S.; Glorius, F.; Pfaltz, A. *Synthesis* **1999**, 597.

IV.B. Planar-Chiral Derivatives of 2,2′-Bipyridine: Synthesis and Applications

Inspired by our success with planar-chiral derivatives of imidazole and DMAP, we set out to extend this concept to 2,2′-bipyridine (Scheme 6).

Scheme 6. Synthesis of planar-chiral derivative of 2,2'-bipyridine



Of the possible routes to planar-chiral C_2-symmetric 2,2'-bipyridines, we eventually settled on the one shown in Scheme 6. Although the preparation of hydroxypyridine/pyridone **36** via three-component coupling is inefficient (22% yield),[33] the low yield of the reaction is readily compensated by the high throughput (121 g) that is possible.[34] After the reaction is cooled to room temperature, the desired product **36** simply precipitated from the crude mixture, and it is pure according to ^{1}H NMR after filtration and an ether rinse. Although the 4-position is substituted with a methyl group,[35] we do not expect the remote 4-alkyl substituent to have any significant effect on either the reactivity or the enantioselectivity of the enantiopure ligand. Although it is possible to synthesize the "parent" unsubstituted compound, that route is rather tedious.[36]

Standard organic reactions gave the chloro olefin **40** (Scheme 6). It should be noted that up to this point, no chromatographic purification is necessary, and the reactions are typically carried out on a 100 mmol scale.[37] Complexation with the metal fragment afforded the racemic planar-chiral 2-chloropyridine **41**. We have attempted to resolve *rac* **41** via chiral HPLC; however, we were unable to do so using the available columns.[38] Fortunately, nickel-mediated homo-coupling[39] of **41** gave

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33 (a) Sakurai, A.; Midorikawa, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 165. For a protocol that gives a higher chemical yield (> 60% yield) but requires an aqueous work-up, see: (b) Kato, T.; Sato, M.; Noda, M.; Itoh, T. *Chem. Pharm. Bull.* **1980**, *28*, 2244.

34 We have obtained 197 g of **36** from an even larger scale reaction; however, the yield was low (10 %).

35 The 4-methyl group comes from ethyl acetoacetate.

36 Meyer, A. I.; Garcia-Munoz, G. *J. Org. Chem.* **1964**, *29*, 1435 (4 steps; not all yields were given)

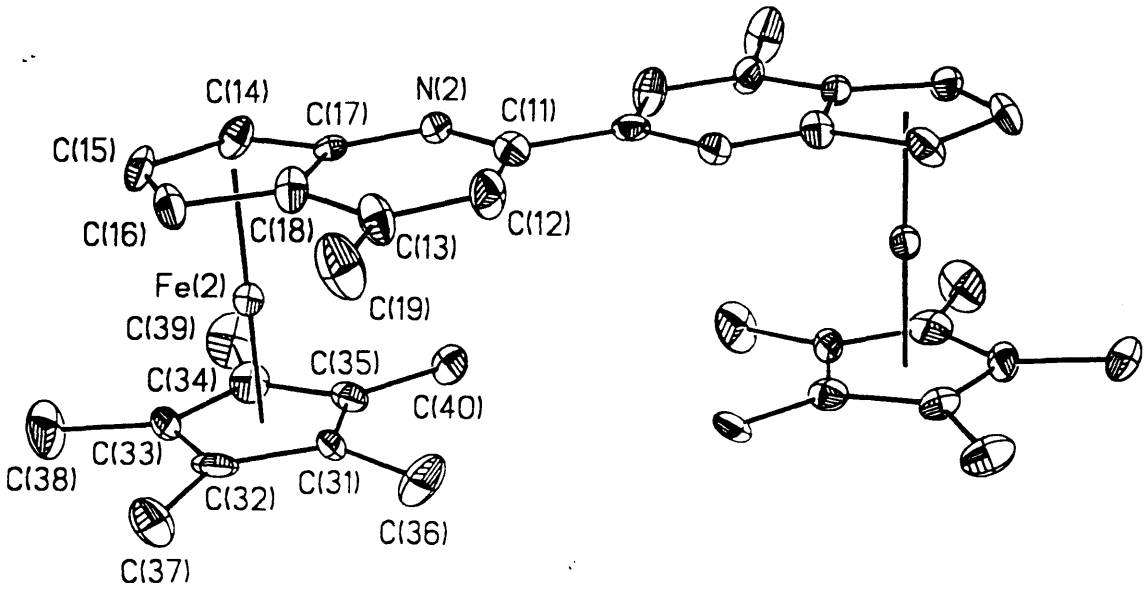
37 The scale of the reaction is limited by the size of the Schlenk tube available for the sealed-tube reaction to prepare chloropyridine **37**.

38 We have tried Daicel CHIRALCEL OD, Daicel CHIRALCEL AD, and Regis *R,R* Whelk columns. The major obstacle seems to be the solubility, or more precisely the lack thereof, of the complex.

39 Iyoda, M.; Otsuka, H.; Sato, K.; Nisato, N.; Oda, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80.

exclusively the desired *d,l* dimer **42**, which can be resolved via chiral HPLC. An x-ray structure of (+)-(*S,S*)-**42** is shown in Figure 6.[40]

Figure 6. X-ray structure of (+)-(*S,S*)-**42**



Although we have synthesized penta-aryl derivatives of **41** as well as the corresponding deca-aryl derivatives of **42**, we were not able to resolve any of these planar-chiral complexes via chiral HPLC.[38] Fortunately, closer inspection of the synthetic route in Scheme 6 reveals a possible alternative. We could, in principle, employ an enantiomerically pure phosphine such as (*R*)-BINAP or (*R*)-MOP to effect a homo-coupling, kinetic resolution of *rac* **41**. The process should give enantio-enriched coupled product **42**[41] along with unreacted but now enantiopure starting material **41**. Subjecting the hypothetically enantiopure **41** to the standard

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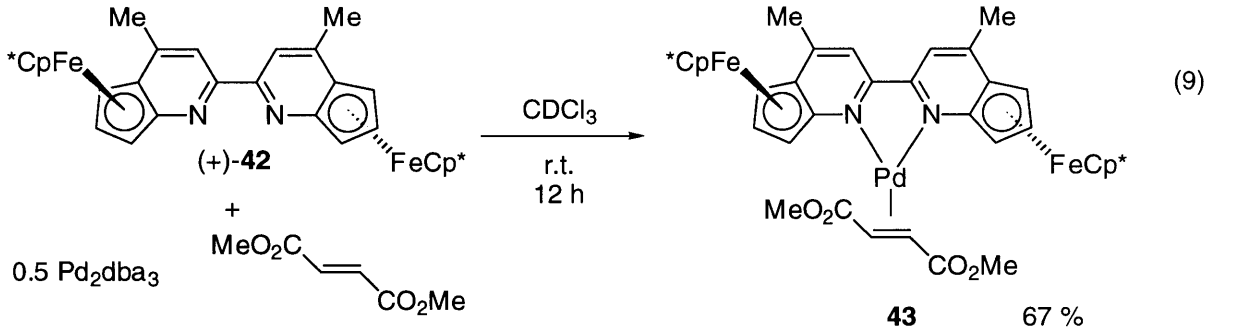
[40] The structure was solved by Michael M.-C. Lo.

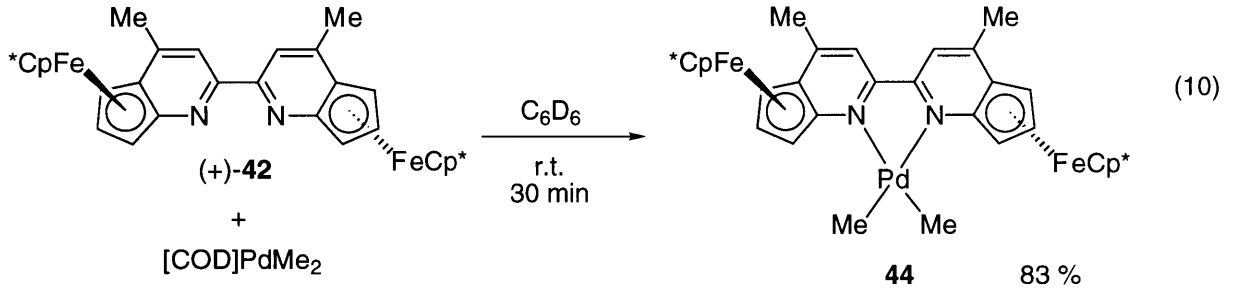
[41] Based on our experience with planar-chiral derivatives bearing a pentaphenyl Cp-ring (e.g. **3b** and **23**), we know that the optically-enriched **3b** and **23** are far more soluble than the corresponding racemic compound. Thus, the optically-enriched penta-aryl derivatives of **41** and/or deca-aryl derivatives of **42** may be more amenable to resolution via chiral HPLC (Ref. 38).

coupling conditions would give the desired optically pure dimer **42**. This option may be explored in the future.

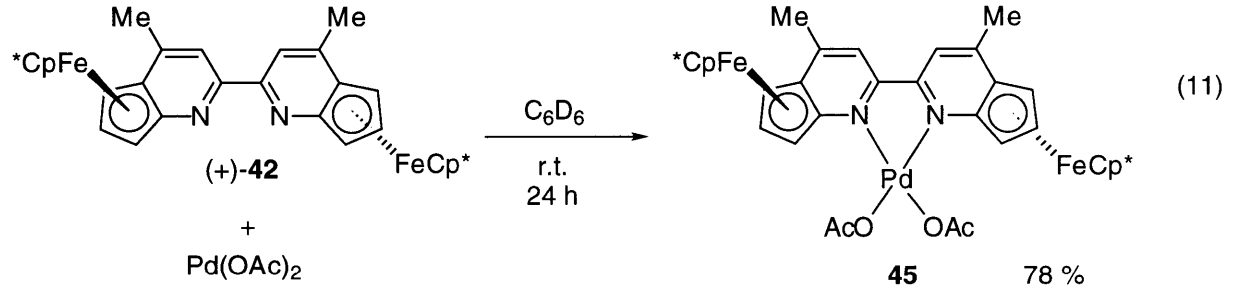
With an optically pure diamine in hand, the Pavlovian response would be to use it as a ligand on Cu(I). However tempting, the diamine-copper system is in fact well-established. To not re-invent the wheel too quickly, we initially turned our attention to the path less traveled: the diamine-palladium systems. To this end, we have prepared, in optically pure form, the Pd(0) (eq 9) and the Pd(II) complexes (eq 10 and eq 11).



(9)

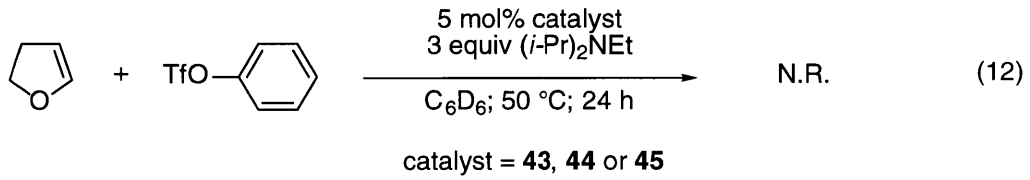


(10)



(11)

The palladium/tertiary phosphine system is one of the most commonly used and thoroughly investigated catalyst systems in organometallic chemistry.[42] On the other hand, the use of nitrogen ligands in organopalladium chemistry has been more limited, perhaps because palladium is often regarded as a soft metal that prefers soft ligands such as phosphines. It is not until recent years that there has been significant interest in the development of bidentate nitrogen ligands for palladium-catalyzed reaction.[43] One of the newly developed palladium-bidentate nitrogen catalyst systems that caught our attention is the use of 1,10-phenanthroline derivatives as ligands for the Heck reaction.[44] We postulated that we could use our enantiopure palladium complexes **43**, **44** and/or **45** to effect the asymmetric Heck reaction between 2,3-dihydrofuran and phenyl triflate.[45] Unfortunately, we observed only catalyst decomposition (deposition of Pd°; eq 12).



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42 (a) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vol. 2. (b) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669. (c) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Berlag: Berlin, 1980. (d) Negishi, E.-I. *Acc. Chem. Res.* **1982**, *15*, 340. (e) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A., Abel, E. W. Eds.; Pergamon: New York, 1982; Vol. 8, p 799. (f) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: London, 1985.

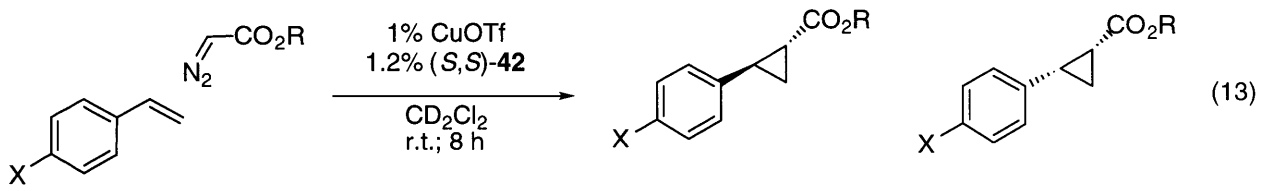
43 For selected examples, see (and references there in): (a) Groen, J. H.; deJong, B. J.; Ernsting, J.-M.; vanLeeuwen, P. W. N. M.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1999**, *573*, 3. (b) Widenhoefer, R. A.; Stengone, C. N. *Tetrahedron Lett.* **1999**, *40*, 1451 (c) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (d) vanAsselt, R.; Elsevier, C. J. *Organometallics* **1994**, *13*, 1972.

44 (a) Cabri, W.; Candiani, I.; Bedeschi, A. *J. Org. Chem.* **1993**, *58*, 7421. (b) Cabri, W.; Candiani, I.; Bedeshi, A.; Santi, R. *Synlett* **1992**, 871.

45 For a review, see: Shibasaki, M.; Boden, C. D. J.; Kojima, A. *Tetrahedron* **1997**, *53*, 7371. For the first reports of asymmetric Heck reaction using these two substrates, see: (b) Ozawa, F.; Kubo, A.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 1417. (c) Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T. *Organometallics* **1993**, *12*, 4188, and references therein.

We next turned our attention to the Cu(I)-catalyzed asymmetric cyclopropanation of olefins (eq 13), the standard testing ground for all new enantiomerically pure bidentate nitrogen ligands. Following the protocol developed in our group,[4] we were gratified to find that (*S,S*)-**42** is in fact an efficient ligand for this reaction (Table 8).

Table 8. Cu(I)-catalyzed cyclopropanation of olefins



(13)

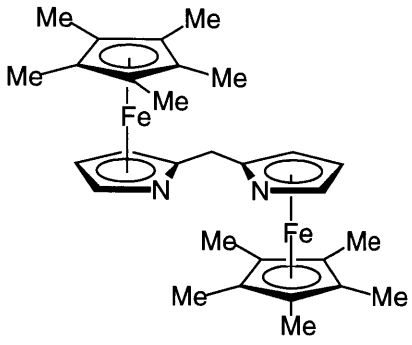
(1*R*,2*R*) (1*R*,2*S*)

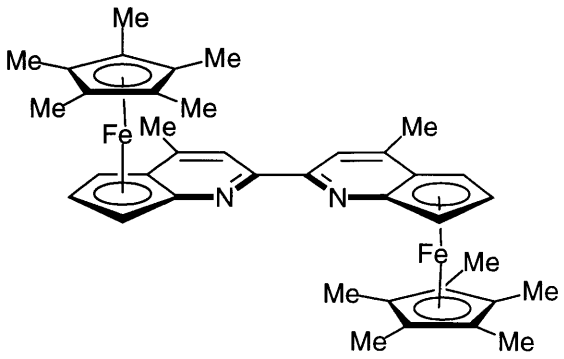
Entry	X	R	trans : cis	% ee, trans	% ee, cis	% yield
1	H	Et	75 : 25	73	65	75[a] (34)[b]
2	H	*t*-Bu	87 : 13	82	79	63[c]
3	H	BHT	97 : 3	86	-	67[c]
4	MeO	BHT	96 : 4	70	-	54[c]
5	CF_3	BHT	93 : 7	92	-	60[c]

[a] Isolated yield of a mixture of trans and cis. [b] Isolated yield of the trans (1*R*, 2*R*).
[c] Isolated yield of the corresponding alcohol after treating the ester with LAH.

The absolute configuration of the products was determined by comparing the chiral GC retention time of our products with those obtained using (*S,S*)-**35**.[4] Not surprisingly, in all cases, the absolute configuration of the major enantiomer obtained from using (*S,S*)-**42** is the same as that obtained from using (*S,S*)-**35**. It is perhaps worthwhile to make a more in-depth comparison between the two planar-chiral C_2-symmetric bidentate nitrogen ligands developed in our group (Table 9).

Table 9. Comparing the diastereoselectivity and enantioselectivity of **35** and **42**





			(-)-(*S,S*)-**35**			(+)-(*S,S*)-**42**		
Entry	X	R	trans : cis	% ee, trans	% ee, cis	trans : cis	% ee, trans	% ee, cis
1	H	Et	75 : 25	73	43	75 : 25	73	65
2	H	*t*-Bu	86 : 14	87	81	87 : 13	82	79
3	H	BHT	96 : 4	95	-	97 : 3	86	-
4	MeO	BHT	94 : 6	89	-	96 : 4	70	-
5	CF_3	BHT	94 : 6	94	-	93 : 7	92	-

It can be seen that (*S,S*)-**35** and (*S,S*)-**42** displayed almost identical levels of diastereoselectivity (trans to cis product ratio). Not surprisingly, **42**, with its reactive center further removed from the planar-chiral stereogenic elements, gave a slightly lower level of asymmetric induction. Nonetheless, we have illustrated the capability of our planar-chiral derivative of 2,2′-bipyridine **42** to serve as a ligand for an asymmetric organometallic reaction.

V. Experimental

General

Benzene, toluene, d_8-toluene, THF and pentane were distilled from sodium. Methylene chloride and CD_2Cl_2 were distilled from calcium hydride. Methanol, ethanol, and isopropanol were distilled from Mg/I_2. CH_3CN and $CHCl_3$ were distilled from P_2O_5. Acetone was distilled from K_2CO_3. Nitrobenzene and anisole were distilled from calcium hydride. Distilled water was from an MIT tap (pH ~ 6). DMF (anhydrous from Aldrich) was used as received. Benzoic acid (Aldrich) was recrystallized from benzene. (±)-*sec*-Phenylethyl alcohol (Aldrich) and ethyl diazoacetate (Aldrich) were purified by chromatography prior to use. 3,5-Dimethylbromobenzene (Aldrich), benzyl alcohol (Aldrich), NEt_3 (Mallinkrodt), 2,3-dihydrofuran (Aldrich), *N,N*-diisopropylethylamine (Aldrich), styrene (Aldrich), 4-vinylanisole (Aldrich) and 4-(trifluoromethyl)styrene (Aldrich) were distilled from calcium hydride. Pyrrolidine (Aldrich) was distilled from sodium. Phenyl triflate (Aldrich) was distilled prior to use. $FeCl_2$ (Strem or Alfa) and Cs_2CO_3 (Strem) were grounded into fine powder in a glove box prior to use. Powdered 4Å molecular sieve (Aldrich) was dried in a vacuum oven for 24 hours prior to use. Dimethylfumarate (Aldrich) was recrystallized from CH_2Cl_2. Et_4NI (Alfa) was dried under vacuum at 80 °C for 3 hours. *n*-BuLi (Strem) was titrated prior to use. L-Alanine (Aldrich), (±) 2-aminobutryic acid (Aldrich), (±) 2-amino-4-pentenoic acid (Aldrich), L-valine (Aldrich), L-leucine (Aldrich), *(S)*-α-aminocyclohexanepropionic acid (Aldrich), L-phenylalanine (Aldrich), (±) phenylglycine (Aldrich), L-methionine (Aldrich), benzoyl chloride (Aldrich), sodium hydroxide (Fisher), concentrated aqueous hydrochloric acid (Fisher), and 1,3-dicyclohexylcarbodiimide

(Aldrich), 2,3-cyclopentenopyridine **7** (Acros),[46] acetic acid (Mallinkrodt), 30 % H_2O_2 (EM Science), acetic anhydride (Mallinkrodt), concentrated H_2SO_4 (EM Science), *R,R* Jacobsen's catalyst (Strem), *m*-CPBA (Aldrich),[47] NMO (Aldrich), $Pd(OAc)_2$ (Strem), *n*-Bu_3P (Lancaster), $TsOH \bullet H_2O$ (Aldrich, Alfa, or Fluka), Cp*-H (Strem) and 2-indanone (Aldrich), 4-bromophenol (Aldrich), isopropylbromide (Alfa), sodium ethoxide (Alfa), Cp_2ZrCl_2 (Strem), *t*-Bu_3P (Strem), $[CpFe(cumene)]PF_6$ (Aldrich), cyclopentanone (Alfa), ammonium acetate (Alfa), ethyl acetoacetate (Alfa), phosphorus oxychloride (Alfa), acetic acid (Mallinkrodt), $NiBr_2(PPh_3)_2$ (Alfa), Zn° (Alfa), $[COD]PdCl_2$ (Alfa), 1.6 M MeLi in Et_2O (Alfa), Pd_2dba_3 (Strem), $(CuOTf)_2 \bullet$benzene (Aldrich), 1.0 M LAH in Et_2O (Aldrich) and trifluoroacetic anhydride (Aldrich) were used as received. The olefin **8**,[48] $(p\text{-tol})_5C_5$-H **21a**,[49] $(4\text{-MeO-}C_6H_4)_5C_5$-H **21c**,[50] the catalysts **3a**, **5, 20** and **23**,[51] phenylethyl ketene,[52] and *t*-butyl diazoacetate and BHT diazoacetate[53] were prepared according to literature procedures.

Analytical thin layer chromatography was performed using EM Reagents 0.25 mm silica gel 60 plates, and visualization was accomplished with UV. Flash chromatography was performed on TCI silica gel 60 (230-400 mesh).

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46 2,3-Cyclopentenopyridine **7** is no longer commercially available. For an alternative synthesis, see Ruble, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

47 Aldrich has since replaced the 80-85% *m*-CPBA used in our procedure with a 57-86% variant.

48 Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 11532. For an improved route to **8**, see Ruble, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

49 Miura, M.; Pivsa-Art, S.; Dyker, G.; Heiermann, J.; Satoh, T.; Nomura, M. *J. Chem. Soc., Chem. Commun.* **1998**, 1889. The product is isolated *without* column chromatography. See the purification procedures used for **21b** or **21d**.

50 The reaction is conducted as described in Ref. 3. The product is soluble in 10% EtOAc/90% hexanes and is isolated via silica gel column chromatography (10% EtOAc/90% hexanes).

51 Ruble, J. C.; Latham, H. A.; Fu, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 1492. For an improved route to **20** and **23**, see Ruble, J. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1999.

52 Hodous, B. L.; Ruble, J. C.; Fu, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 2637.

53 Lo, M. M. -C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270.

Semi-preparative chiral HPLC was performed on a Daicel CHIRALCEL OD column (1.0 cm x 25 cm), a Daicel CHIRALCEL AD column (1.0 cm x 25 cm), or a Regis *R,R* Whelk column (1.0 cm x 25 cm). Analytical chiral HPLC was performed on a Daicel CHIRALCEL OD column (4.6 mm x 25 cm). Analytical chiral GC was performed on either a Chiraldex G-TA column (0.25 mm x 20 m), a Chiraldex V-AL column (0.25 mm x 20 m) or a Chiraldex B-PH column (0.25mm x 20 m). Analytical achiral GC was performed on a J & W Scientific DB-1701 column (0.25mm x 30 m).

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker AC-250, Varian XL-300 NMR, Varian Unity 300, Varian Mercury 300 or Varian Innova 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.

Infrared spectra were obtained on a Perkin-Elmer Series 1600 FT-IR spectrophotometer. Melting points (uncorrected) were obtained on a Thomas Hoover Unimelt capillary melting point apparatus. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

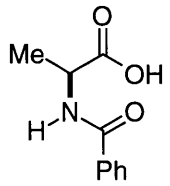
All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated.

Synthesis of *N*-Benzoyl Amino Acids

General procedure.[54] Benzoyl chloride (26.0 mL, 223 mmol) and NaOH (8.80 g, 220 mmol; in 40 mL of distilled water) were added alternately in 4 portions over 30 minutes to a 0 °C solution of the amino acid (200 mmol) and NaOH (8.00 g, 200 mmol) in 80 mL of distilled water (in air). After the addition was complete, the ice bath was removed, and the reaction was stirred at room temperature for an additional 2 hours. The reaction was quenched by the dropwise addition of concentrated aqueous hydrochloric acid until pH ~ 1, which resulted in the formation of a white precipitate. The solid was isolated by filtration and then recrystallized from water. The resulting crystals were air dried to give the desired *N*-benzoyl amino acid, which showed no trace of benzoic acid by ^{1}H NMR.

Because it makes no difference for our purposes, we have not assayed the enantiomeric excess of the product *N*-benzoyl amino acids (some are derived from enantiomerically pure starting materials).

All yields are unoptimized.



***N*-Benzoylalanine:**[55] 47% yield of clear, colorless crystals. ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.67 (d, ^{1}H, J=8), 7.88 (d, 2H, J=7), 7.58-7.44 (m, 3H), 4.40 (dq, ^{1}H, J_1=J_2=8), 1.39 (d, 3H, J=8). ^{13}C NMR (75 MHz, d_6-DMSO) δ 164.3, 166.2, 133.9, 131.4, 128.2, 127.5, 48.2, 16.9. IR (thin film) 3418, 2588, 1724, 1653 cm^{-1}. Lit. mp: 150 °C.[55]

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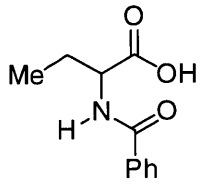
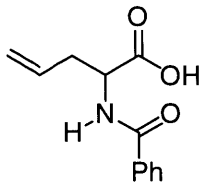
54 Furniess, B. S.; Hannaford, A .J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's New Edition Textbook of Practical Organic Chemistry, 5th Ed.* John Wiley & Sons Inc.: New York, 1989.

55 Fischer, E. *Chem. Ber.* **1899**, *32*, 2458.



***N*-Benzoyl-2-aminobutyric acid:**[56] 28% yield of clear, colorless crystals. ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.56 (d, ^{1}H, J=8), 7.88 (d, 2H, J=8), 7.54-7.44 (m, 3H), 4.27 (m, ^{1}H), 1.86 (m, 2H), 0.95 (t, 3H, J=8). ^{13}C NMR (75 MHz, d_6-DMSO) δ 173.5, 166.4, 133.9, 131.2, 128.1, 127.3, 54.2, 24.1, 11.0. IR (thin film) 3287, 2593, 1719, 1644 cm^{-1}. mp: 143-144 °C.[57]



***N*-Benzoyl-2-amino-4-pentenoic acid:**[58] 66% yield of clear, colorless crystals. ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.54 (d, 1H, J=8), 7.79 (d, 2H, J=8), 7.49-7.35 (m, 3H), 5.78 (m, ^{1}H), 4.98 (m, 2H), 4.37 (m, 1H), 2.44 (m, 2H). ^{13}C NMR (75 MHz, d_6-DMSO) δ 173.2, 166.4, 134.6, 133.9, 131.4, 128.3, 127.4, 117.5, 52.3, 35.0. IR (thin film) 3313, 2532, 1725, 1653 cm^{-1}. mp: 110-111 °C.[59]

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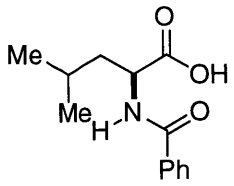
56 Fischer, E. *Chem. Ber.* **1900,** *33,* 2390.

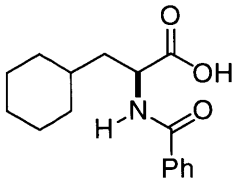
57 Fischer, E. *Chem. Ber.* **1900,** *33,* 2388.

58 Soerensen, S. P. L. *Chem. Ber.* **1908,** *41,* 3388.

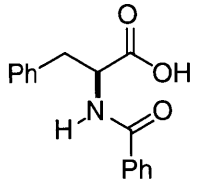
59 Miyake, A. *Chem. Pharm. Bull.* **1960,** *8,* 1079.



***N*-Benzoylleucine:**[60] 18% yield of white crystals. ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.60 (d, 1H, J=8), 7.88 (d, 2H, J=7), 7.55-7.44 (m, 3H), 4.44 (m, 1H), 1.70 (m, 3H), 0.91 (d, 3H, J=8), 0.89 (d, 3H, J=8). ^{13}C NMR (75 MHz, d_6-DMSO) δ 174.1, 166.3, 133.9, 131.2, 128.1, 127.4, 50.9, 24.6, 23.1, 21.2. IR (thin film) 3284, 2588, 1722, 1652 cm^{-1}. Lit. mp: 105-107 °C.



***N*-Benzoyl-α-amino-3-cyclohexanepropionic acid:**[61] 66% yield of white crystals. ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.58 (d, 1H, J=8), 7.88 (d, 2H, J=7), 7.55-7.45 (m, 3H), 4.45 (m, 1H), 1.76-0.78 (m, 13H). ^{13}C NMR (75 MHz, d_6-DMSO) δ 174.4, 166.4, 134.0, 131.4, 128.3, 127.5, 50.2, 37.9, 33.8, 33.2, 31.4, 26.1, 25.8, 25.6. IR (thin film) 3426, 2585, 1722, 1651 cm^{-1}. Lit. mp: 186 °C.



***N*-Benzoylphenylalanine:**[62] 23% yield of clear, colorless crystals. ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.71 (d, 1H, J=8), 7.78 (d, 2H, J=7), 7.52-7.17 (m, 8H), 4.61 (m, 1H), 3.15 (m,

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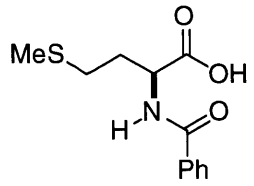
60 Fischer, E. *Chem. Ber.* **1900,** *33,* 2375.

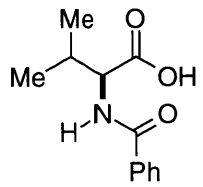
61 Waser, E.; Brauchli, E. *Helv. Chim. Acta.* **1923,** *6,* 199.

62 Schulle, W. H.; Niemann, C. *J. Am. Chem. Soc.* **1951,** *73,* 1644.

2H). ^{13}C NMR (75 MHz, d_6-DMSO) δ 173.3, 166.4, 138.2, 133.9, 131.4, 129.1, 128.3, 128.2, 127.4, 126.4, 54.3, 36.3. IR (thin film) 3312, 2508, 1715, 1642 cm^{-1}. Lit. mp: 142-143 °C.



***N*-Benzoylmethionine:**[63] 17% yield of white flakes. ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.63 (d, 1H, J=8), 7.88 (d, 2H, J=7), 7.55-7.45 (m, 3H), 4.51 (dt, 1H, J_1=J_2=8), 2.55 (ddd, 2H, J_1=J_2=J_3=8), 2.10-2.01 (m, 5H). ^{13}C NMR (75 MHz, d_6-DMSO) δ 173.5, 166.7, 133.9, 131.4, 128.3, 127.4, 51.6, 30.2, 30.1, 14.6. IR (thin film) 3438, 2555, 1721, 1654 cm^{-1}. Lit. mp: 145-147 °C.



***N*-Benzoylvaline:**[64] 52% yield of clear, colorless crystals. ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.43 (d, 1H, J=9), 7.87 (d, 2H, J=8), 7.55-7.44 (m, 3H), 4.28 (dd, 1H, J_1=J_2=8), 2.17 (m, 1H), 0.98 (d, 3H, J=8), 0.96 (d, 3H, J=8). ^{13}C NMR (75 MHz, d_6-DMSO) δ 173.2, 166.9, 134.2, 131.3, 128.2, 127.6, 58.4, 29.5, 19.4, 18.9. IR (thin film) 3278, 2582, 1721, 1653 cm^{-1}. Lit. mp: 132.5 °C.

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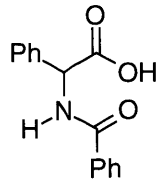
63 Uchio, H. *Nippon, Kagaku Zasshi.* **1960,** *81,* 316.

64 Slimmer, M. D. *Chem. Ber.* **1902,** *32,* 402.



***N*-Benzoylphenylglycine:**[65] 44% yield of white crystals. ^{1}H NMR (250 MHz, d_6-DMSO) δ 9.04 (d, 1H, J=8), 7.92 (d, 2H, J=7), 7.54-7.33 (m, 8H), 5.59 (d, 1H, J=8). ^{13}C NMR (75 MHz, d_6-DMSO) δ 172.0, 166.3, 137.1, 133.8, 131.5, 128.4, 128.2, 127.9, 127.7, 56.9. IR (thin film) 3431, 2580, 1724, 1653 cm^{-1}. mp: 177-178 °C.

Synthesis of Azlactones

General procedure.[66] A solution of 1,3-dicyclohexylcarbodiimide (4.12 g, 20 mmol) in 40 mL of CH_2Cl_2 was added by cannula to a white slurry of the *N*-benzoyl amino acid (20 mmol) in 40 mL of CH_2Cl_2 (0 °C). After the addition was complete, the ice bath was removed, and the reaction was stirred at room temperature for an additional 2 hours. The mixture was then filtered to remove the white 1,3-dicyclohexylurea, and the filtrate was concentrated to a viscous, pale-yellow oil. As a precaution, purification of the azlactone was performed in a glove box. CH_2Cl_2 (~ 10 mL) was added to the oil, and the resulting cloudy solution was filtered through an Acrodisc (0.45 μm), which provided a clear, pale-yellow solution. This solution was diluted with ~ 50 mL of pentane and placed in a -30 °C freezer for 12 hours. The

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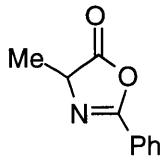
65 Kossel, A. *Chem. Ber.* **1891,** *24,* 4145.

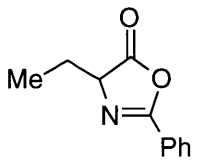
66 Chen, F. M. F.; Kuroda, K.; Bentoiton, N. L. *Synthesis.* **1979,** 230. Although the azlactones are fairly air and moisture stable, the purification (recrystallization) was conducted in a glove box to avoid any chances of hydrolysis. The hydrolyzed product is a carboxylic acid (insoluble in the solvents used), which may affect the rate and the enantioselectivity of the dynamic kinetic resolution reaction (benzoic acid enhances both).

mother liquor was removed from the resulting crystals by pipet, and the desired azlactone (free of benzoic acid, according to ^{1}H NMR) was dried under vacuum.

All yields are unoptimized.



2-Phenyl-4-methyloxazalone:[67] 23% yield of a white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.00 (d, 2H, J=7), 7.58-7.46 (m, 3H), 4.45 (q, 1H, J=8), 1.60 (d, 3H, J=8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.9, 161.4, 132.6, 128.7, 127.7, 125.7, 60.9, 16.8. IR (thin film) 1825, 1654 cm^{-1}. mp: 37-38 °C.[68]



2-Phenyl-4-ethyloxazalone:[69] 42% yield of a white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.01 (d, 2H, J=7), 7.62-7.45 (m, 3H), 4.40 (dd, 1H, J_1=J_2=8), 2.15-1.90 (m, 2H, J=8), 1.05 (t, 3H, J=8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 161.5, 132.6, 128.6, 127.7, 125.8, 66.3, 24.9, 9.6. IR (thin film) 1821, 1654 cm^{-1}. mp: 49-50 °C.

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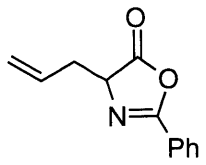
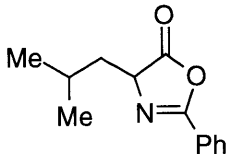
67 Mohr, F.; Stroschein, F. *Chem. Ber.* **1909,** *42,* 2521.

68 Chen, F. M. F.; Kuroda, K.; Bentoiton, N. L. *Synthesis.* **1979,** 230.

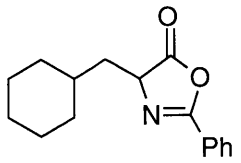
69 Tschaman, E. C.; Schemjakin, M. M. *Zh. Obshch. Khim.* **1955,** *25,* 1360.



2-Phenyl-4-allyloxazalone: 33% yield of a white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.00 (d, 2H, J=8), 7.62-7.45 (m, 3H), 5.81 (m, 1H), 5.25 (m, 2H), 4.50 (m, 1H), 2.88-2.59 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 161.6, 132.6, 131.3, 128.7, 127.8, 125.7, 119.6, 65.4, 35.4. IR (thin film) 1821, 1653 cm^{-1}. mp: 40-41 °C.



2-Phenyl-4-isobutyloxazalone:[70] 32% yield of a white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.00 (d, 2H, J=7), 7.58-7.46 (m, 3H), 4.42 (dd, 1H, J=5, 8), 2.06 (m, 1H), 1.90-1.62 (m, 2H), 1.03 (d, 3H, J=8), 1.01 (d, 3H, J=8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.8, 161.2, 132.5, 128.6, 127.7, 125.9, 64.0, 40.8, 25.3, 22.8, 22.1. IR (thin film) 1818, 1652 cm^{-1}. mp: 55-56 °C.



2-Phenyl-4-cyclohexylmethyloxazalone: 53% yield of a white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.01 (d, 2H, J=7), 7.58-7.46 (m, 3H), 4.44 (m, 1H), 1.88-0.88 (m, 13H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.9, 161.2, 132.5, 128.6, 127.7, 125.9, 63.4, 39.6, 34.4, 33.5, 32.7, 26.4, 26.1. IR (thin film) 1825, 1649 cm^{-1}. mp: 57-58 °C.

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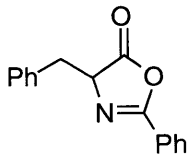
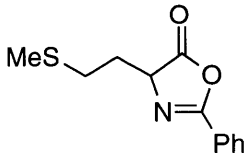
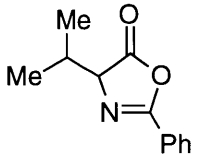
70 DiBello, C.; Felira, F.; D'Angel I. F. *J. Org. Chem.* **1971,** *36,* 1818.



2-Phenyl-4-benzyloxazalone:[71] 7% yield of a white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.92 (d, 2H, J=7), 7.57-7.21 (m, 8H), 4.70 (dd, 1H, J_1=J_2=6), 3.38 (dd, 1H, J=15, 6), 3.19 (dd, 1H, J=15, 6). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 161.5, 135.1, 132.6, 129.4, 128.3, 128.2, 127.7, 127.1, 125.2, 66.4, 37.2. IR (thin film) 1820, 1654 cm^{-1}. mp: 69-70 °C.



2-Phenyl-4-(2-methylthio)ethyloxazalone:[72] 31% yield of a clear, colorless oil (a white solid at -30 °C). ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.01 (d, 2H, J=7), 7.59-7.46 (m, 3H), 4.61 (dd, 1H, J_1=J_2=8), 2.74 (ddd, 2H, J_1=J_2=J_3=8), 2.36-2.12 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.3, 161.8, 132.6, 128.7, 127.7, 125.7, 63.6, 30.3, 29.9, 15.0. IR (neat) 1822, 1650 cm^{-1}.



2-Phenyl-4-isopropyloxazalone:[73] 7% yield of a white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.02 (d, 2H, J=8), 7.58-7.46 (m, 3H), 4.29 (d, 1H, J=5), 2.39 (m, 1H), 1.15 (d, 3H,

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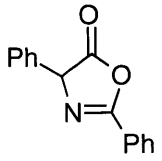
71 Carter, H. E.; Handler, P.; Stevens, C. M. *J. Biol. Chem.* **1941,** *138,* 619.

72 Schultz, G. *Chem. Ber.* **1979,** *112,* 3221.

73 Chemiakine, M. M.; Tchaman, E. S.; Deneiova, C. I.; Randel, G. A.; Rodionov, W. J. *Bull. Soc. Chim. Fr.* **1959,** 530.

J=6), 1.02 (d, 3H, J=6). ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 161.5, 132.5, 128.6, 127.7, 125.8, 70.5, 31.1, 18.6, 17.4. IR (thin film) 1821, 1654 cm^{-1}. mp: 49-51 °C.



2, 4-Diphenyloxazalone:[74] 49% yield of a yellow solid. ^1H NMR (250 MHz, $CDCl_3$) δ 8.11 (d, 2H, J=7), 7.66-7.36 (m, 8H), 5.33 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2, 162.6, 133.4, 133.1, 129.0, 128.9, 128.7, 128.3, 127.2, 126.8, 68.1. IR (thin film) 1828, 1659 cm^{-1}. mp: 86-87 °C.

Rate of Racemization Versus Ring Opening of Azlactone with MeOD (Scheme 2)

A purple solution of (-)-**3a** (3.5 mg, 0.010 mmol), 2-phenyl-4-methyl-oxazalone (35.0 mg, 0.200 mmol), and benzoic acid (2.4 mg, 0.020 mmol) in 1.0 mL of d_8-toluene was prepared in a glove box and transferred to an NMR tube. An initial ^1H NMR spectrum revealed that the ratio of the methyl:methine resonances for the azlactone was 3.1 to 1. CD_3OD (12.2 μL, 0.300 mmol) was added by syringe. An NMR spectrum taken 2 minutes after the addition showed a methyl:methine ratio of 7.4 to 1, indicating significant deuterium incorporation at the methine position (statistical: ~ 8 to 1). After 16 minutes, the methyl:methine ratio was 7.8 to 1, and 7% of the azlactone had ring opened to the α-amino acid derivative. After 12 hours, 84% of

74 Hoefle, G. *Chem. Ber.* **1976,** *109,* 2648.

the azlactone had ring opened; the methyl:methine ratio in the starting material was 8.4 to 1, and the methyl:methine ratio in the product was 8.2 to 1.

V.B.iv. Dynamic Kinetic Resolution: Solvent Effect on Enantioselectivity (Table 1)

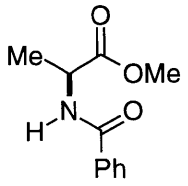
General procedure. In a glove box, a solution of benzoic acid (2.4 mg, 0.020 mmol) and methanol (12 μL; 0.30 mmol) in 0.4 mL of solvent was added to a solution of catalyst (-)-**3a** (3.5 mg, 0.010 mmol) and azlactone (35 mg, 0.20 mmol) in 0.6 mL of solvent. The resulting reaction mixture was stirred at room temperature for 24 hours. The solution was then poured directly onto a column of silica gel, and the product was purified by flash chromatography. GC analysis (Chiralcel G-TA) provided the data illustrated in Table 10.

Dynamic Kinetic Resolution: Nucleophile Effect on Enantioselectivity (Table 2)

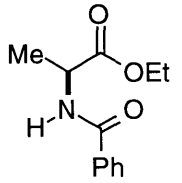
General Procedure. In a glove box, a solution of benzoic acid (6.1 mg, 0.050 mmol) and alcohol (0.75 mmol) in 1 mL of toluene was added to a solution of catalyst (-)-**3a** (8.8 mg, 0.025 mmol) and azlactone (88 mg, 0.50 mmol) in 1.5 mL of toluene. The resulting purple reaction mixture was stirred at room temperature for 24 hours. The solution was then poured directly onto a column of silica gel, and the product was purified by flash chromatography. GC analysis provided the data illustrated in Table 2.

In the case of isopropanol, the reaction was run in d_8-toluene (to determine an approximate half-life by ^{1}H NMR) and worked up after 4 days (~ 34% conversion).

Absolute configurations were determined by comparison with authentic samples[75] (chiral GC).



***N*-Benzoylalanine, methyl ester:**[76] 98% yield, 49% ee; white solid. For characterization, see section on Dynamic Kinetic Resolution of Azlactones.

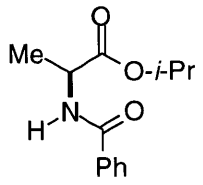


N-Benzoylalanine, ethyl ester: 61% yield, 53% ee; white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.81 (d, 2H, J=7), 7.51-7.40 (m, 3H), 6.81 (br d, 1H, J=8), 4.79 (dq, 1H, $J_1=J_2=8$), 3.24 (q, 2H, J=8), 1.55 (d, 3H, J=8), 1.31 (t, 3H, J=8). ^{13}C NMR (75 MHz, CDCl3) δ 73.3, 166.8, 133.9, 131.7, 128.4, 127.0, 61.6, 48.5, 18.7, 14.1. IR (thin film) 3347, 1743, 1640 cm^{-1}. mp: 77-78 °C. $[\alpha]^{20}_D$ = +19.9 (53% ee S; c=1.0, $CHCl_3$).

---

75 The enantiomerically pure methyl and ethyl esters of alanine were purchased as the hydrochloride salts (Aldrich) and then benzoylated (benzoyl chloride, NEt_3, CH_2Cl_2). The isopropyl ester was prepared through acid-catalyzed transesterification of the methyl ester.

76 vonMax, J. *Justus Liebigs Ann. Chem.* **1909,** *369,* 277.



***N*-Benzoylalanine, isopropyl ester:** 29% yield (34% conversion by ^{1}H NMR), 78% ee; white solid. 1H NMR (250 MHz, $CDCl_3$) δ 7.80 (d, 2H, J=7), 7.54-7.41 (m, 3H), 6.84 (br d, 1H, J=8), 5.09 (m, 1H), 4.75 (dq, 1H, J_1=J_2=8), 1.51 (d, 3H, J=8), 1.29 (d, 3H, J=8), 1.28 (d, 3H, J=8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.1, 167.1, 134.4, 132.0, 128.9, 127.3, 69.8, 49.1, 22.2, 19.3. IR (thin film) 3337, 1744, 1639 cm-1. mp: 82-83 °C. $[\alpha]^{20}_{D}$ = +30.5 (78% ee *S*; c=0.25, $CHCl_3$).

Dynamic Kinetic Resolution of Azlactones

(Table 3)

General procedure. A solution of benzoic acid (6.1 mg, 0.050 mmol) and methanoL (30 μL, 0.74 mmol) in 2 mL of toluene was added to a pink solution of catalyst (-)-**3a** (8.8 mg, 0.025 mmol) and azlactone (0.50 mmol) in 3 mL of toluene (in a glove box[77]). The resulting purple reaction mixture was stirred at room temperature until TLC showed the reaction to be complete. The solution was then poured directly onto a column of silica gel, and the product was purified by flash chromatography and analyzed by GC or HPLC.

Each azlactone was ring-opened by methanol with (-)-**3a** and with (+)-**3a** as the catalyst. The yields and ee's reported in Table 3 are the average of these two runs.

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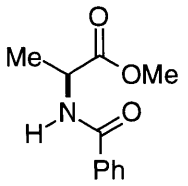
[77] The reactions were set up in a glove box, as a precaution, due to the moisture sensitivity of the azlactone. In the case of 2-phenyl-4-methyloxazalone, a reaction set up in a glove box with purified reagents and solvent proceeded to 81% conversion, 54% ee after 24 hours at room temperature. When an otherwise identical reaction was run with unpurified reagents and solvent, exposed to air and moisture, the reaction proceeded to 51% conversion, 44% ee after 24 hours at room temperature.

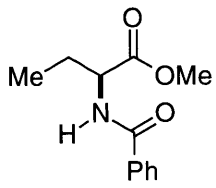
Enantiomeric excesses were determined as tabulated in Table 10 (two injections per data point). Absolute configurations were determined by comparison with authentic samples[78] (chiral GC or HPLC).

Note: If the flash chromatography is performed on the benchtop with N_2 as the source of pressure, catalyst **3a** can be recovered pure in ~ 85% yield (catalyst **3a** is slightly air-sensitive in solution).



***N*-Benzoylalanine, methyl ester:** reaction time: 48 h; 100% yield, 54% ee; white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.81 (d, 2H, J=7), 7.53-7.42 (m, 3H), 6.72 (br d, 1H, J=8), 4.82 (dq, 1H, J_1=J_2=8), 3.80 (s, 3H), 1.53 (d, 3H, J=8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 166.7, 133.7, 131.5, 128.4, 127.0, 52.5, 48.5, 18.5. IR (thin film) 3308, 1747, 1633 cm^{-1}. mp: 79-80 °C. $[\alpha]^{20}_D$ = +20.9 (54% ee *S*; c=1.0, $CHCl_3$).

With (+)-**3a** as the catalyst, the product was obtained in 96% yield and 55% ee.



***N*-Benzoyl-2-aminobutyric acid, methyl ester:**[79] reaction time: 72 h; 96% yield, 44% ee; white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.82 (d, 2H, J=7), 7.53-7.42 (m, 3H), 6.67

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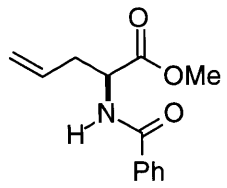
78 In most cases, the enantiomerically pure methyl esters of the α-amino acids were purchased as the hydrochloride salts (Aldrich or Advanced ChemTech) and then benzoylated (benzoyl chloride, NEt_3, CH_2Cl_2). For cases in which the methyl esters were not commercially available, the enantiomerically pure benzoylated amino acids were esterified (K_2CO_3, MeI, acetone).

79 Urabe, Y.; Miyoshi, M.; Matsumoto, K. *Agric. Biol. Chem.* **1975,** *39,* 1085.

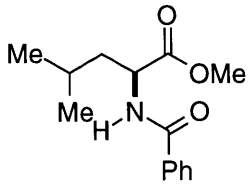
(br, 1H), 4.80 (dd, 1H, J_1=J_2=8), 3.80 (s, 3H), 2.10-1.80 (m, 2H), 0.98 (t, 3H, J=8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 166.8, 133.9, 131.6, 128.4, 126.9, 53.6, 52.4, 25.8, 9.6. IR (thin film) 3317, 1744, 1643 cm^{-1}. mp: 80-82 °C. $[\alpha]^{20}_D$ = +15.2 (44% ee *S*; c=1.0, $CHCl_3$).

With (+)-**3a** as the catalyst, the product was obtained in 93% yield and 45% ee.



***N*-Benzoyl-2-amino-4-pentenoic acid, methyl ester:**[80] reaction time: 48 h; 94% yield, 60% ee; white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.79 (d, 2H, J=8), 7.53-7.45 (m, 3H), 6.65 (br d, 1H), 5.70 (m, 1H), 5.14 (m, 2H), 4.90 (m, 1H), 3.80 (s, 3H), 2.67 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2, 166.8, 133.7, 132.1, 131.6, 128.4, 126.9, 119.2, 52.3, 51.9, 36.4. IR (thin film) 3324, 1746, 1650 cm^{-1}. mp: 73-74 °C. $[\alpha]^{20}_D$ = +30.5 (60% ee *S*; c=1.0, $CHCl_3$).

With (+)-**3a** as the catalyst, the product was obtained in 95% yield and 62% ee.



***N*-Benzoylleucine, methyl ester:**[81] reaction time: 48 h; 93% yield, 56% ee; white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.80 (d, 2H, J=7), 7.53-7.45 (m, 3H), 6.50 (br, 1H), 4.88 (m, 1H), 3.76 (s, 3H), 1.84 (m, 3H), 1.00 (d, 3H, J=8), 0.98 (d, 3H, J=8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 166.9, 133.7, 131.5, 128.4, 127.0, 52.3, 51.1, 41.7, 25.0, 22.9, 22.0. IR

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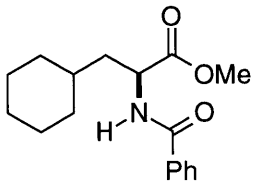
80 Easton, C. J.; Scharfbillig, I. M.; Tan, W. E. *Tetrahedron Lett.* **1988,** *29,* 1565.

81 Karrer, K. *Helv. Chim. Acta.* **1930,** *13,* 50.

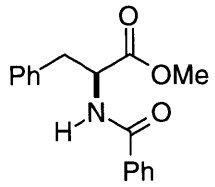
(thin film) 3320, 1745, 1638 cm^{-1}. mp: 94-95 °C. $[\alpha]^{20}_D$ = +24.8 (56% ee *S*; c=1.0, $CHCl_3$).

With (+)-**3a** as the catalyst, the product was obtained in 97% yield and 54% ee.



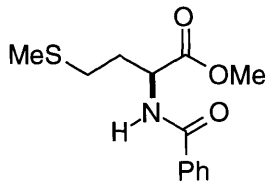
***N*-Benzoyl-α-amino-3-cyclohexanepropionic acid, methyl ester:** reaction time: 96 h; 94% yield, 54% ee; white solid. ^1H NMR (250 MHz, $CDCl_3$ $CDCl_3$) δ 7.81 (d, 2H, J=7), 7.53-7.46 (m, 3H), 6.47 (br d, 1H, J=8), 4.88 (m, 1H), 3.77 (s, 3H), 1.88-0.88 (m, 13H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 167.0, 133.8, 131.5, 128.4, 127.0, 52.2, 50.4, 40.0, 34.1, 33.3, 32.4, 26.2, 26.0, 25.9. IR (thin film) 3321, 1746, 1641 cm^{-1}. mp: 78-79 °C. $[\alpha]^{20}_D$ = +9.4 (54% ee *S*; c=1.0, $CHCl_3$).

With (+)-**3a** as the catalyst, the product was obtained in 92% yield and 54% ee.



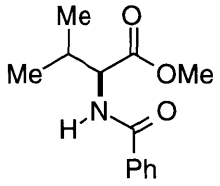
***N*-Benzoylphenylalanine, methyl ester:** reaction time: 48 h; 92% yield, 57% ee; white solid. ^1H NMR (250 MHz, $CDCl_3$) δ 7.73 (d, 2H, J=7), 7.52-7.12 (m, 8H), 6.56 (br d, 1H, J=8), 5.10 (m, 1H), 3.77 (s, 3H), 3.26 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 166.7, 135.8, 133.8, 131.6, 129.2, 128.5, 127.1, 126.9, 53.6, 52.4, 37.9. IR (thin film) 3321, 1744, 1643 cm^{-1}. mp: 75-76 °C. $[\alpha]^{20}_D$ = +63.4 (57% ee *S*; c=1.0, $CHCl_3$).

With (+)-**3a** as the catalyst, the product was obtained in 95% yield and 55% ee.



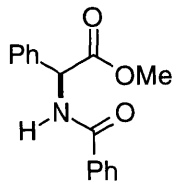
***N*-Benzoylmethionine, methyl ester:**[82] reaction time: 48 h; 96% yield, 50% ee; white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.82 (d, 2H, J=7), 7.54-7.46 (m, 3H), 6.95 (br, 1H), 4.94 (m, 1H), 3.80 (s, 3H), 2.60 (m, 2H), 2.29-2.04 (ddd and s, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 167.0, 133.5, 131.7, 128.4, 127.0, 52.6, 52.0, 31.5, 30.2, 15.6. IR (thin film) 3322, 1744, 1643 cm^{-1}. mp: 79-80 °C. $[\alpha]^{20}_D$ = +20.9 (50% ee *S*; c=1.0, $CHCl_3$).

With (+)-**3a** as the catalyst, the product was obtained in 93% yield and 50% ee.



***N*-Benzoylvaline, methyl ester:**[83] reaction time: 120 h; 43% yield, 14% ee; white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.81 (d, 2H, J=8), 7.53-7.46 (m, 3H), 6.75 (br d, 1H, J=8), 4.79 (dd, 1H, J=8, 5), 3.79 (s, 3H), 2.30 (m, 1H), 1.01 (d, 3H, J=8), 0.98 (d, 3H, J=8). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 167.1, 134.0, 131.6, 128.5, 126.9, 57.3, 52.1, 31.5, 18.9, 17.8. IR (thin film) 3346, 1738, 1641 cm^{-1}. mp: 90-91 °C. $[\alpha]^{20}_D$ = +6.4 (14% ee *S*; c=1.0, $CHCl_3$).

With (+)-**3a** as the catalyst, the product was obtained in 38% yield and 12% ee.



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82 Nakagawa, M.; Suzuki, T.; Kawashima, T.; Hino, T. *Chem. Pharm. Bull.* **1972,** *20,* 2413.

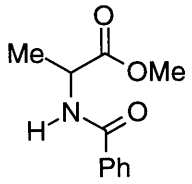
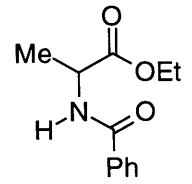
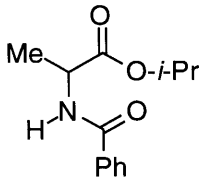
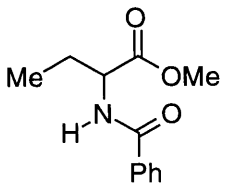
83 Hinmann, J. W.; Caron, E. L.; Christensen, H. N. *J. Am. Chem. Soc.* **1950,** *72,* 1620.

***N*-Benzoylphenylglycine, methyl ester:**[84] reaction time: 72 h; 87% yield, 23% ee; white solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.83 (d, 2H, J=7), 7.53-7.36 (m, 8H), 7.14 (d, 1H, J=6), 5.78 (d, 1H, J=6), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 166.4, 136.4, 133.4, 131.7, 128.9, 128.4, 127.2, 127.1, 56.7, 52.8. IR (thin film) 3314, 1745, 1643 cm^{-1}. mp: 102-103 °C. $[\alpha]^{20}_D$ = +26.6 (23% ee *S*; c=1.0, $CHCl_3$).

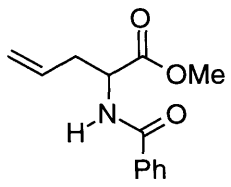
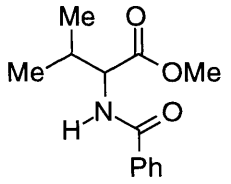
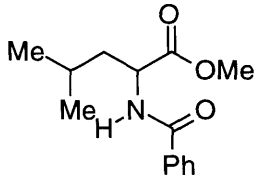
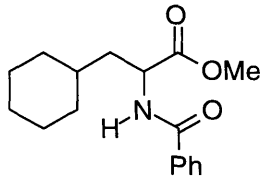
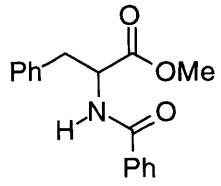
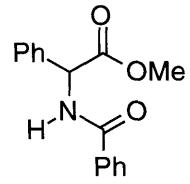
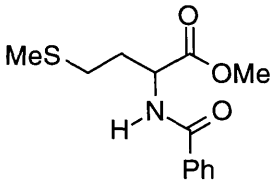
With (+)-**3a** as the catalyst, the product was obtained in 80% yield and 26% ee.

Methods Used to Assay Enantiomeric Excess

Table 10.

Substrate	ee Assay	Conditions	Retention Time of *R* Isomer [min]	Retention Time of *S* Isomer [min]*
	GC Chiraldex G-TA	150 °C 2.0 mL/min carrier gas flow	10.5	11.5
	GC Chiraldex G-TA	150 °C 2.0 mL/min carrier gas flow	13.5	14.6
	GC Chiraldex V-AL	150 °C 1.0 mL/min carrier gas flow	20.1	21.6
	GC Chiraldex G-TA	150 °C 2.0 mL/min carrier gas flow	13.9	15.7

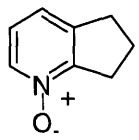
84 Zoller, U.; Ben-Ishai, D. *Tetrahedron* **1975,** *31,* 863.

	GC Chiraldex G-TA	150 °C 2.0 mL/min carrier gas flow	18.1	19.2
	GC Chiraldex G-TA	150 °C 2.0 mL/min carrier gas flow	15.5	16.4
	GC Chiraldex G-TA	150 °C 2.0 mL/min carrier gas flow	22.4	23.8
	GC Chiraldex V-AL	190 °C 1.0 mL/min carrier gas flow	28.2	29.0
	GC Chiraldex V-AL	190 °C 1.0 mL/min carrier gas flow	30.0	30.6
	HPLC Chiralcel OD	10% *i*PrOH/hexane 1.0 mL/min	13.8	17.6
	GC Chiraldex V-AL	190 °C 1.0 mL/min carrier gas flow	22.1	22.8

*The *S* enantiomer is the enantiomer that is derived from the natural L-amino acid.

Synthesis of the 6-Amino Analog "6-PPY*"

(Scheme 5)



11

11:[85] To a flask fitted with a condenser was added 500 mL of acetic acid, 100 g (840 mmol) of 2,3-cyclopentenopyridine **7** and 88 mL of 30 % H_2O_2 from a previously unopened bottle.[86] The resulting yellow solution was immersed in an oil bath at 80 °C.[87] After 3 hours, an additional 72 mL of 30 % H_2O_2 was added to the hot reaction mixture. Heating (80 °C) was continued for an additional 21 hours. After heating for the prescribed length of time, the reaction was cooled to room temperature and placed under vacuum to remove the excess peracetic acid generated during the reaction. After 2 hours under vacuum, the reaction mixture was slowly poured into a slurry of ~ 800 g of K_2CO_3 in ~ 1200 mL of water. After the vigorous exothermic gas evolution had subsided and the resulting slurry cooled to room temperature, the solid precipitate was filtered off and the mother liquor was extracted with 20 x 200 mL of $CHCl_3$ followed by 4 x 250 mL of EtOAc. The organic phases were combined, dried with $MgSO_4$, filtered and stripped of solvent to give 98.4 g (87% yield) of *N*-oxide **11** as a white solid which darkened upon standing. This material was used as is for the next step. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.04 (d, 1H, J=8), 7.05-7.14 (m, 2H), 3.18 (t, 2H, J=8), 3.03 (t, 2H, J=8), 2.19 (m, 2H).

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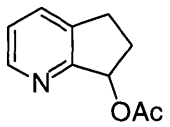
85 Robison, M. M. *J. Am. Chem. Soc.* **1958,** *80,* 6254.

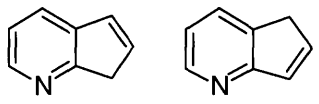
86 We have found it is best to use a new bottle of H_2O_2 for each reaction due to the tendency of H_2O_2 to decompose during prolonged storage.

87 Care must be taken to ensure that the reaction temperature stays below ca. 100 °C, the explosive decomposition temperature of the peracetic acid that is generated in situ.



12

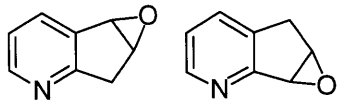
12:[85] To a flask fitted with a condenser was added 27.0 g (200 mmol) of *N*-oxide **11**, 190 mL (2010 mmol; 10.1 equiv) of acetic anhydride and 1.6 mL (89 mmol; 0.44 equiv) of distilled water. The initial clear colorless solution turned red within 10 minutes. After standing at room temperature for 1 hour, the reaction mixture was immersed in an oil bath at 100 °C. After an additional 3 hours, the resulting black solution was placed under reduced pressure to remove the volatile (acetic anhydride and acetic acid). The acetate **12** was isolated via distillation under vacuum (bp 95 °C at 250 mtorr). The yellow distillate (24.4 g) was contaminated with unknown impurities. This material was used as is for the next step. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.52 (d, 1H, J=5), 7.61 (d, 1H, J=8), 7.08 (dd, 1H, J=5, 8), 5.14 (dd, J=5, 8), 2.70-3.08 (m, 3H), 2.64 (m, 1H), 2.16 (s, 3H).



13

13: [85] To a flask fitted with a condenser was added 24.4 g of the impure acetate **12** and 45 mL (810 mmol) of concentrated H_2SO_4. The homogeneous pale yellow solution was heated at 120 °C for 1 hour to give a brown solution. After cooling in an ice bath, the reaction mixture was poured into a slurry of ~ 1.5 g of Ph_2NH in ~ 200 g of ice. An additional ~ 100 g of 50% NaOH solution was added to this mixture to give a black slurry with a pH of ~ 12. After extraction with 6 x 80 mL of EtOAc, 10 mL of NEt_3 was added to the organic layer. The organic phase was dried with $MgSO_4$,

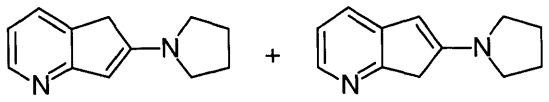
filtered and stripped of solvent. Vacuum distillation (bp 35 °C at 500 mtorr) gave 13.3 g (84% yield) of an ~ 1.7:1 mixture of olefins **13** as an orange oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.46 (d, 1H, J=5, *major*), 8.37 (d, 1H, J=5, *minor*), 7.71 (d, 1H, J=5, *major*), 7.61 (d, 1H, J=5, *minor*), 7.12-7.17 (m, 1H, *minor*), 7.06-7.09 (m, 3H, *major* and *minor*), 6.87-6.92 (m, 2H, *major* and *minor*), 6.62-6.64 (m, 1H, *minor*), 3.44 (s, 2H, *minor*), 3.41 (s, 2H, *major*).



14

14: To a flask under argon was added 1.59 g (2.50 mmol; 5 mol%) of *R,R*-Jacobsen's catalyst, 28.1 g (240 mmol; 4.80 equiv) of NMO, 400 mL of CH_2Cl_2 and 5.85 g (50.0 mmol) of olefin **13**. The resulting black solution was immersed in a dry ice/acetone bath at –78 °C. To this chilled solution was added 17.3 g (80–85 mmol; 1.6–1.7 equiv) of 80-85 wt% *m*-CPBA in 20 portions over 10 minutes under a positive flow of argon. After the addition was complete, the resulting black solution was stirred at –78 °C for an additional 1 hour. The reaction was quenched by pouring into 500 mL of 1 N NaOH. The organic and aqueous phases were separated. The organic phase was extracted with 300 mL of sat. NaCl. The aqueous phases were combined and extracted with 4 x 100 mL of CH_2Cl_2 followed by 1 x 100 mL of EtOAc. All organic portions were combined, dried with $MgSO_4$, filtered and stripped of solvent. Column chromatography (1:50:50 NEt_3/EtOAc/hexanes; R_f ~ 0.3 and 0.25; UV) gave an ~ 1.8:1 mixture of regioisomeric epoxide **14** as a black oil (5.36 g; 81% yield). Although it is possible to separate the regioisomers via repeated column chromatography, this proved to be unnecessary as far as the next step is concerned. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.44 (d, 1H, J=5, *minor*), 8.38 (d, 1H, J=5, *major*), 7.28 (d,

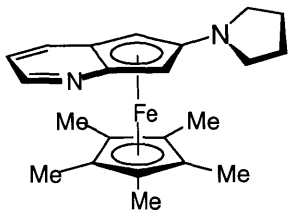
1H, J=7, *minor*), 7.55 (d, 1H, J=7, *major*), 7.07 (m, 1H, *major* and *minor*), 4.14-4.34 (m, 2H, *major* and *minor*), 2.93-3.34 (m, 2H, *major* and *minor*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 160.6, 148.2, 146.2, 135.7, 134.0, 133.1, 131.7, 122.1, 120.1, 57.7, 56.0, 55.0, 54.8, 35.8, 32.0; IR (neat) 3065, 2916, 2816, 1732, 1597, 1575, 1468, 1416, 1370, 1293, 1207, 1167, 1105 cm^{-1}; HRMS calcd for C_8H_7NO 133.05275, found 133.0529.



16

16: To an oven-dried Schlenk tube in a glove box was added 113 mg (0.502 mmol; 5 mol%) of $Pd(OAc)_2$, 10 mL of benzene, 1.33 g (10.0 mmol) of epoxide **14** in 15 mL of benzene and 375 μL (1.51 mmol; 15 mol%) of *n*-Bu_3P to give a brown solution. The Schlenk tube was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 80 °C. After 3 hours, the resulting black solution along with an orange precipitate was cooled to room temperature and moved into a glove box. After filtration through an 0.45 μm Acrodisc, the resulting homogeneous solution was transferred to another over-dried Schlenk tube. To this crude reaction mixture was added ~ 1 g of powdered 4Å molecular sieve, 95 mg (0.50 mmol; 5 mol%) of $TsOH \bullet H_2O$ and 4.2 mL (50 mmol; 5.0 equiv) of pyrrolidine to give a dark orange solution. The Schlenk tube was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 80 °C. After an additional 22 hours, the reaction was cooled to room temperature and concentrated to ~ 1/2 of the original volume via a rotatory evaporator. Column chromatography (5% NEt_3/95% EtOAc; R_f ~ 0.5; UV/orange) gave 426 mg (23% yield) of an ~ 5:1 mixture of enamine **16** as a black solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.12 (d, 1H, J=5, *major*), 8.00 (d, 1H, J=5, *minor*), 7.30 (d, 1H, J=5, *major*), 7.12 (d, 1H, J=5, *minor*), 6.96 (m, 1H, *minor*), 6.61 (m, 1H, *major*), 5.35 (s, 2H, *major*), 5.12 (s, 2H, *minor*), 3.45 (s,

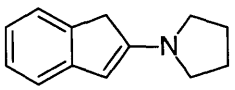
1H, *minor*), 3.31 (m, 9H, *major* and *minor*), 2.00 (m, 8H, *major* and *minor*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 158.5, 158.3, 153.7, 146.3, 145.4, 141.7, 138.4, 129.4, 127.6, 127.3, 121.1, 120.9, 113.2, 95.6, 91.7, 47.8, 39.0, 35.1, 25.0, 23.3; IR (thin film) 2955, 2844, 1601, 1552, 1458, 1420, 1371, 1349, 1215, 1153 cm^{-1}; HRMS calcd for $C_{12}H_{14}NO$ 186.1157, found 186.1155. mp 143-146 °C.



17; "6-PPY*"

17 ("6-PPY*"): To an oven-dried vial in a glove box was added 10 mL of THF and 400 μL (2.56 mmol; 1.12 equiv) of Cp*-H to give a clear colorless solution. Upon dropwise addition of 1.7 mL (2.5 mmol; 1.1 equiv) of 1.45 M *n*-BuLi in hexanes, a thick white slurry was formed. After stirring at room temperature for 10 minutes, this thick white slurry was added to a suspension of 320 mg (2.51 mmol; 1.10 equiv) of $FeCl_2$ in 5 mL of THF to give a dark green slurry ("FeCp*Cl") which was stirred at room temperature for an additional 30 minutes. To another oven-dried vial in a glove box was added 426 mg (2.29 mmol) of enamine **16** in 10 mL of THF and 1.6 mL (2.3 mmol; 1.0 equiv) of 1.45 M *n*-BuLi in hexanes to give an orange solution. After stirring at room temperature for 30 minutes, the orange solution was added to the dark green slurry of "FeCp*Cl" to give a black solution. The reaction was sealed under a nitrogen atmosphere and removed from the glove box. After stirring at room temperature for an additional 1 hour, the reaction mixture was subjected to silica gel column chromatography (2% NEt_3/98% EtOAc; R_f ~ 0.5; black) to give 712 mg (83% yield) of **6-PPY*** as a black solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.57 (d, 1H, J=5), 7.82 (d, 1H, J=7), 6.79 (dd, 1H, J=5, 7), 4.31 (s, 1H), 3.76 (s, 1H), 3.13 (m, 4H), 1.95,

(m, 4H), 1.62 (s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 141.2, 115.9, 115.7, 106.6, 78.7, 76.3, 52.8, 48.4, 47.7, 25.2, 9.91; IR (thin film) 2960, 2898, 2850, 1581, 1537, 1503, 1378, 1380, 1332, 1289, 1148, 1031 cm^{-1}; HRMS calcd for $C_{22}H_{28}FeN_2$ 376.1602, found 376.1605. mp 134-136 °C. The enantiomers were resolved via a Daicel CHIRALCEL OD column (1 cm x 25 cm; 50:50:0.3 hexanes/isopropanol/diethylamine; 2.5 mL/min; 25 mg of *rac* **17** per mL per injection). The retention time were 8.0–9.5 minutes for the first enantiomer ($[\alpha]^{20}_D$ = -450; c=0.019 in $CHCl_3$) and 16-21 minutes for the second enantiomer ($[\alpha]^{20}_D$ = +430; c=0.019 in $CHCl_3$). The stock solution of racemic **17** was prepared in a glove box. Both the stock solution of racemic **17** and the HPLC eluant containing the resolved enantiomers of **17** were kept under a nitrogen atmosphere to minimize decomposition. The resolved enantiomers of **17** were further purified via column chromatography (2% NEt_3/98% EtOAc; R_f ~ 0.5; black) under a nitrogen atmosphere to give 279 mg of (-)-**17** and 296 mg of (+)-**17**. Enantiopure **17** is stored in a –30 °C freezer in a glove box.



1-Indene-2-yl-pyrrolidine:[88] To an oven-dried Schlenk tube in a glove box was added 190 mg (1.00 mmol; 5 mol%) of $TsOH \bullet H_2O$, ~ 1 g of powdered 4Å MS, 2.64 g (20.0 mmol) of 2-indanone, 20 mL of benzene and 2.5 mL (30 mmol, 1.5 equiv) of pyrrolidine. The resulting black slurry was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 80 °C. After 16 hours, the reaction was cooled to room temperature. The crude reaction mixture was filtered through celite (rinsed with 3 x 10 mL of 10% NEt_3/90% EtOAc) to give a black solution. After solvent removal, 3.14 g (85% yield) of 1-indene-2-yl-pyrrolidine was

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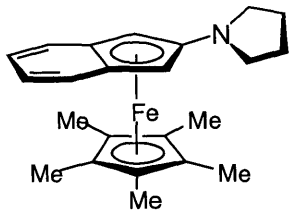
[88] Blomquist, A. T.; Moriconi, E. J. *J. Org. Chem.* **1961**, *26*, 3761.

obtained as a black solid. This material was used as is for the next step. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, 1H, J=7), 7.15 (dd, 1H, J=7), 7.00 (d, 1H, J=7), 6.80 (dd, 1H, J=7), 3.50 (s, 2H), 3.30 (m, 4H), 2.00 (m, 4H).

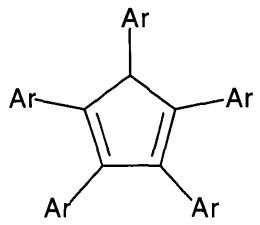


19

19: To an oven-dried vial in a glove box was added 5 mL of THF, 170 μL (1.09 mmol; 1.09 equiv) of Cp*-H to give a clear colorless solution. Upon dropwise addition of 770 μL (1.12 mmol; 1.12 equiv) of 1.45 M *n*-BuLi in hexanes, a thick white slurry formed. After stirring at room temperature for 10 minutes, this thick white slurry was added to a suspension of 141 mg (1.11 mmol; 1.11 equiv) of $FeCl_2$ in 2 mL of THF to give a dark green slurry ("FeCp*Cl") which was stirred at room temperature for an additional 30 minutes. To another oven-dried vial in a glove box was added 185 mg (1.00 mmol) of 1-indene-2-yl-pyrrolidine in 5 mL of THF and 700 μL (1.02 mmol; 1.02 equiv) of 1.45 M *n*-BuLi in hexanes to give an black solution. After stirring at room temperature for 30 minutes, this black solution was added to the dark green slurry of "FeCp*Cl". A purple solution formed immediately. The reaction was sealed under a nitrogen atmosphere and removed from the glove box. After stirring at room temperature for an additional 1 hour, the reaction mixture was subjected to silica gel column chromatography (5% EtOAc/95% hexanes) under a nitrogen atmosphere. The initial purple band was collected and the residual purple streak was left behind on the column. The collected eluant was quickly stripped of solvent

and moved into a glove box.[89] The crude was taken up in ~ 10 mL of pentane and filtered through a 0.45 μm Acrodisc. The resulting purple homogeneous solution was concentrated to ~ 1/2 of original volume and placed in freezer at –30 °C. After the formation of purple needle-like crystals, the mother liquor was removed by pipet and the residual solid was dried *in vacuo* to give 46 mg (39% yield) of **19** as a purple solid. The product is stored in a –30 °C freezer in a glove box. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, 2H, J=3, 7), 6.93 (dd, 2H, J=3, 7), 3.91 (s, 2H), 3.14 (m, 4H), 1.96 (m, 4H), 1.62 (s, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.5, 121.4, 116.0, 85.2, 77.3, 51.2, 48.9, 25.5, 10.2; IR (thin film) 3039, 2969, 2895, 1529, 1486, 1365, 1141, 1070, 1030 cm^{-1}; HRMS calcd for $C_{23}H_{29}FeN$ 375.1649, found 375.1645. mp 134-136 °C.

Synthesis of Second-Generation Catalysts: Derivatization of the Cp-ring (Figure 3)

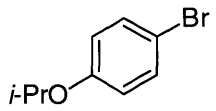


21b: Ar = 3,5-Me_2-C_6H_3

21b: To an oven-dried Schlenk tube in a glove box was added 15.6 g (47.9 mmol; 12.0 equiv) of Cs_2CO_3, 225 mg (1.00 mmol; 12.5 mol%) of $Pd(OAc)_2$ in 20 mL of DMF, 808 mg (4.00 mmol; 1.00 equiv) of *t*-Bu_3P in 20 mL of DMF, 1.17 g (4.01 mmol) of Cp_2ZrCl_2 in 20 mL of DMF, an additional 20 mL of DMF followed by 6.6 mL (48

89 Bisindenyliron and bisindenylruthenium is extremely air sensitive, see: Osiecki, J. H.; Hoffman, C. J.; Hollis, D. P. *J. Organomet. Chem.* **1965,** *3*, 107.

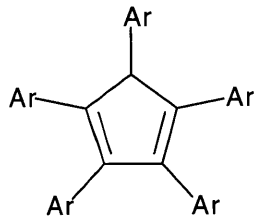
mmol; 12 equiv) of 3,5-dimethylbromobenzene. The resulting brown slurry was sealed under a nitrogen atmosphere, removed from the gloved box and immersed in an oil bath at 130 °C. After 3 hours, the resulting dark green slurry was allowed to cool to room temperature. The reaction was quenched with 18.2 g (95.8 mmol; 23.9 equiv) of TsOH•H_2O to give, after bubbling, a brown slurry. Filtration through a plug of silica gel (rinsed with 3 x 30 mL of DMF and 2 x 50 mL of CH_2Cl_2) gave a brown solution. Evaporation of solvent at reduced pressure in an 80 °C water bath gave a black slurry which was dissolved in ~ 100 mL of $CHCl_3$. After washing with 5 x 50 mL of sat. $NaHCO_3$ and 2 x 100 mL of sat. NaCl, the organic layer was dried with $MgSO_4$ and filtered through a plug of silica gel (rinsed with 5 x 50 mL of $CHCl_3$). After the removal of solvent, the resulting orange solid was placed on a filter paper and rinsed with hexane until the hexane wash is colorless. The tan solid obtained after air drying is identified as the desired product **21b** (3.09 g, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.82 (s, 2H), 6.74 (s, 2H), 6.66 (s, 9H), 6.62 (s, 2H), 4.99 (s, 1H), 2.19 (s, 6H), 2.13 (s, 12H), 2.05 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 144.2, 138.6, 137.2, 136.6, 136.4, 136.3, 135.6, 127.9, 127.6, 126.9, 126.3, 61.4, 21.3, 21.2, 21.1; IR (thin film) 3015, 2916, 2861, 2731, 1598, 1470, 1256, 1036, 855, 694 cm^{-1}; HRMS calcd for $C_{45}H_{46}$ 586.3600, found 586.3604. mp 208-210 °C.



4-Isopropoxy-bromobenzene:[90] To an oven-dried flask in a glove box was added 82.0 g (1200 mmol; 4.00 equiv) of EtONa. The flask was sealed under a nitrogen atmosphere, removed from the glove box and fitted with a condenser under argon. To EtONa was added 500 mL of EtOH to give an orange solution. To this solution was added 52.0 g (301 mmol) of 4-bromophenol resulting in a slurry. After stirring

90 LaJis, N. H.; Khan, M. N.; Hassan, L. A. *Tetrahedron* **1993**, *49*, 3405.

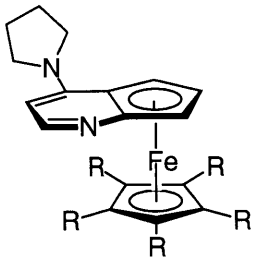
at room temperature for 30 minutes, a homogeneous solution resulted and 165 mL (1760 mmol; 5.84 equiv) of 2-bromopropane was added. The reaction was heated at reflux for 6 hours (cloudy after 15 minutes) and then cool to room temperature overnight. After filtration through filter paper (rinsed with 2 x 100 mL of EtOH), the solvent was removed via a rotatory evaporator to give a yellow/orange slurry. To this slurry was added CaH_2 until there is no further gas evolution. This slurry was allowed to stirred at room temperature for an additional 1 hour. Distillation (bp 68-70°C at full vacuum) of the crude mixture gave 49.7 g (77% yield) of 4-isopropoxy-bromobenzene as a pale yellow oil. ^1H NMR (250 MHz, $CDCl_3$) δ 7.35 (d, 2H, J=8), 6.77 (d, 2H, J=8), 4.49 (m, 1H), 1.33 (d, 5H, J=8)



21d: Ar = 4-*i*-PrO-C_6H_4

21d: To an oven-dried Schlenk tube in a glove box was added 15.6 g (47.9 mmol; 12.0 equiv) of Cs_2CO_3, 225 mg (1.00 mmol; 12.5 mol%) of $Pd(OAc)_2$ in 20 mL of DMF, 808 mg (4.00 mmol; 1.00 equiv) of *t*-Bu_3P in 20 mL of DMF, 1.17 g (4.01 mmol) of Cp_2ZrCl_2 in 20 mL of DMF, an additional 20 mL of DMF followed by 10.3 g (47.9 mmol; 12.0 equiv) of 4-isoproproxybromobenzene. The resulting brown slurry was sealed under a nitrogen atmosphere, removed from the glovedbox and immersed in an oil bath at 130 °C. After 3 hours, the resulting dark green slurry was allowed to cool to room temperature. The reaction was quenched with 18.2 g (95.8 mmol; 23.9 equiv) of TsOH•H_2O to give, after bubbling, a brown slurry. Filtration through a plug of silica gel (rinsed with 2 x 30 mL of DMF and 2 x 30 mL of EtOAc) gave a brown solution. Evaporation of solvent at reduced pressure in an 80 °C water bath

gave a black slurry which was dissolved in ~ 100 mL of $CHCl_3$. After washing with 4 x 50 mL of sat. $NaHCO_3$ and 1 x 100 mL of sat. NaCl, the organic layer was dried with $MgSO_4$ and filtered through a plug of silica gel (rinsed with 4 x 50 mL of $CHCl_3$). After the removal of solvent, the resulting orange solid was placed on a filter paper and rinsed with hexane until the hexane wash is colorless. After air drying, the tan solid is identified as the desired product **21d** (3.64 g; 62% yield). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.06 (d, 2H, J=8), 6.89 (d, 8H, J=8), 6.65 (d, 6H, J=8), 6.53 (d, 4H, J=8), 4.86 (s, 1H), 4.38-4.86 (m, 5H), 1.23-1.31 (m, 30H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 156.1, 156.0, 144.8, 142.1, 131.3, 130.7, 130.0, 129.3, 128.9, 128.6, 115.6, 115.2, 114.7, 69.6, 69.4, 61.4, 32.1, 22.0; IR (thin film) 3034, 2973, 2932, 1609, 1503, 1383, 1281, 1243, 1182 cm^{-1}; HRMS calcd for $C_{50}H_{46}O_5$ 736.4127, found 736.4120. mp 180-182 °C.



22 R = H

22: To an oven-dried vial in a glove box was added 114 mg (0.295 mmol; 1.00 equiv) of [CpFe(cumene)]PF_6[91] and 3 mL of THF. The resulting orange solution was placed in a freezer at –30 °C. To a separate oven-dried vial in a glove box was added 55 mg (0.30 mmol) of olefin **8** and 2 mL of THF to give a yellow solution. A brown solution formed upon the addition of 200 μL (0.290 mmol; 0.981 equiv) of 1.45 M *n*-BuLi in hexanes. After stirring at room temperature for 10 minutes, this solution was added to the cold [CpFe(cumene)]PF_6 solution. The resulting black solution was allowed to warm to room temperature for 3 hours. The reaction mixture was

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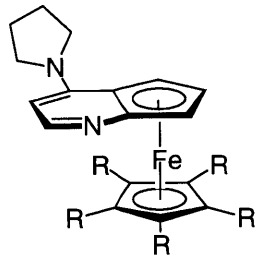
91 Roberts, R. M. G.; Wells, A. S. *Inorg. Chim. Acta.* **1986**, *112*, 171.

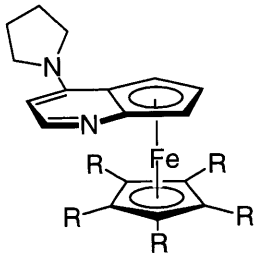
removed from the glove box and subjected to silica gel column chromatography under a nitrogen atmosphere (10% NEt_3/90% EtOAc; R_f ~ 0.3; purple) to give 27 mg (30% yield) of **22** as a red oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.14 (d, 1H, J=5), 5.58 (d, 1H, J=5), 5.18 (m, 1H), 4.91 (m, 1H), 4.10 (m, 1H), 3.87 (s, 5H), 3.69 (m, 4H), 2.13 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 153.9, 111.9, 94.0, 71.8, 68.8, 68.7, 62.7, 60.3, 49.3, 25.6; IR (thin film) 2970, 2869, 1532, 1484, 1395, 1336, 1248, 1155, 1102, 1021 cm^{-1}; HRMS calcd for $C_{17}H_{18}FeN_2$ 306.0819, found 306.0822. mp (decomp) 144-146 °C. The enantiomers were resolved via a Daicel CHIRALCEL OD column (1 cm x 25 cm; 50:50:0.4 hexanes/isopropanol /diethylamine; 2.5 mL/min; 15 mg of *rac* **22** per mL per injection). The retention times were 9.5–11 minutes for the first enantiomer ($[\alpha]^{20}_D$ = +2300; c = 0.031 in $CHCl_3$) and 14-17 minutes for the second enantiomer ($[\alpha]^{20}_D$ = -2100; c = 0.031 in $CHCl_3$). The stock solution of racemic **22** was prepared in a glove box. Both the stock solution of racemic **22** and the HPLC eluant containing resolved enantiomers of **22** were kept under a nitrogen atmosphere to minimize decomposition. The resolved enantiomers of **22** were further purified via column chromatography (10% NEt_3/90% EtOAc; R_f ~ 0.3; purple) under a nitrogen atmosphere to give 11 mg of (+)-**22** and 12 mg of (-)-**22**. Enantiopure **22** is stored in a –30 °C freezer in a glove box.



24 R = 4-Me-C_6H_4

24: To an oven-dried vial in a glove box was added 153 mg (0.297 mmol; 1.00 equiv) of (4-Me-C_6H_4)$_5C_5$-H **21a** and 2 mL of THF to give a brown solution. To this solution was added dropwise 200 μL (0.290 mmol; 0.981 equiv) of 1.45 M *n*-BuLi in hexanes to

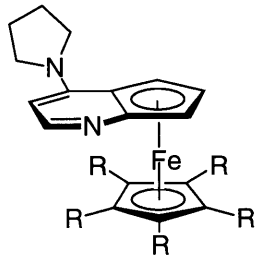
give a black solution. After stirring at room temperature for 10 minutes, this black solution was added to a suspension of 38 mg (0.30 mmol; 1.0 equiv) of $FeCl_2$ in 2 mL of THF. The insoluble $FeCl_2$ disappeared after ~ 30 minutes. To a separate oven-dried vial in a glove box was added 55 mg (0.30 mmol) of olefin **8** in 2 mL of THF to give a yellow solution. To this solution was added dropwise 200 μL (0.290 mmol, 0.981 equiv) of 1.45 M *n*-BuLi in hexanes to give an orange solution. After stirring at room temperature for 10 minutes, this solution was added to the (4-Me-$C_6H_4)_5C_5$-Li/$FeCl_2$ reaction mixture to give a black solution. After stirring at room temperature for an additional 1 hour, the vial was removed from the glove box and subjected to silica gel column chromatography (2% NEt_3/98% EtOAc; R_f ~ 0.3; purple) to give 126 mg (56% yield) of **24** as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, 1H, J=5), 6.78-6.86 (m, 20H), 5.67 (d, 1H, J=5), 4.95 (s, 1H), 4.83 (s, 1H), 4.17 (s, 1H), 3.20-3.60 (br, 4H), 2.27 (s, 15H), 1.94-2.03 (br, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 153.4, 135.2, 132.3, 132.1, 127.5, 113.2, 96.4, 85.3, 77.9, 69.0, 65.7, 49.7, 25.5, 21.2; IR (thin film) 2920.3, 1537.3, 1485.7, 1454.4, 1402.8, 1338.0, 1182.7, 1021.5 cm^{-1}; HRMS calcd for $C_{52}H_{45}FeN_2$ 756.3167, found 756.3183. mp (decomp) 190-192 °C. The enantiomers were resolved via a Daicel CHIRALCEL OD column (1 cm x 25 cm; 75:25:0.4 hexanes/$CHCl_3$/diethylamine; 2.5 mL/min; 20 mg of *rac* **24** per mL per injection). The retention times were 9.5–12.5 minutes for the first enantiomer ($[\alpha]^{20}_D$ = -1100; c = 0.019 in $CHCl_3$) and 15.5-24.0 minutes for the second enantiomer ($[\alpha]^{20}_D$ = +1200; c = 0.019 in $CHCl_3$). The stock solution of racemic **24** was prepared in a glove box. Both the stock solution of racemic **24** and the HPLC eluant containing resolved enantiomers of **24** were kept under a nitrogen atmosphere to minimize decomposition. The resolved enantiomers of **24** were further purified via column chromatography (2% NEt_3/98% EtOAc; R_f ~ 0.3; purple) under a nitrogen atmosphere to give 50 mg of (-)-**24** and 52 mg of (+)-**24**. Enantiopure **24** is stored in a –30 °C freezer in a glove box.



25 R = 3,5-Me_2-C_6H_3

25: To an oven-dried vial in a glove box was added 194 mg (0.297 mmol; 1.00 equiv) of (3,5-Me_2-C_6H_3)$_5C_5$-H **21b** and 2 mL of THF to give a brown solution. To this solution was added dropwise 220 μL (0.319 mmol; 1.08 equiv) of 1.45 M *n*-BuLi in hexanes. After stirring at room temperature for 5 minutes, the homogeneous solution turned into a brown slurry. After an additional 10 minutes, the brown slurry was added to a suspension of 40 mg (0.32 mmol; 1.1 equiv) of $FeCl_2$ in 1 mL of THF. The insoluble $FeCl_2$ disappeared after ~ 20 minutes. To a separate oven-dried vial in a glove box was added 55 mg (0.30 mmol) of olefin **8** in 2 mL of THF to give a yellow solution. To this solution was added dropwise 210 μL (0.305 mmol; 1.03 equiv) of 1.45 M *n*-BuLi in hexanes to give an orange solution. After stirring at room temperature for 10 minutes, this solution was added to the (3,5-Me_2-C_6H_3)$_5C_5$-Li/$FeCl_2$ reaction mixture to give a black solution. After stirring at room temperature for an additional 2 hours, the reaction was removed from the glove box and subjected to silica gel column chromatography (5% NEt_3/95% EtOAc; purple) to give 142 mg (58% yield) of **25** as a purple solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.11 (d, 1H, J=5), 6.72 (s, 5H), 6.58 (s, 10H), 5.72 (d, 1H, J=5), 4.97 (d, 1H, J=3), 4.91 (d, 1H, J=3), 4.15 (dd, 1H, J=3), 3.30-3.60 (br, 4H), 2.08 (s, 30H), 1.80-2.03 (br, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1, 153.0, 135.3, 135.2, 130.3, 127.1, 113.6, 96.6, 85.2, 77.7, 69.3, 64.9, 49.6, 25.3, 21.2; IR (thin film) 2917, 2860, 1599, 1535, 1399, 1264, 1154, 904, 848 cm^{-1}; HRMS calcd for $C_{57}H_{58}FeN_2$ 826.3949, found 826.3945. mp 198-200 °C. The enantiomers were

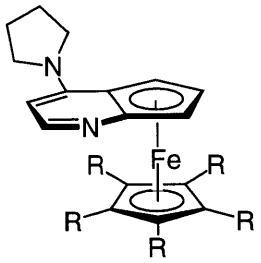
resolved via a Daicel CHIRALCEL OD column (1 cm x 25 cm; 80:20:0.4 hexanes/$CHCl_3$/diethylamine; 2.5 mL/min; 15 mg of *rac* **25** per mL per injection). The retention times were 8.0–9.5 minutes for the first enantiomer ($[\alpha]^{20}_D$ = +1600; c=0.01 in $CHCl_3$) and 12-17 minutes for the second enantiomer ($[\alpha]^{20}_D$ = -1400; c=0.01 in $CHCl_3$). The stock solution of racemic **25** was prepared in a glove box. Both the stock solution of racemic **25** and the HPLC eluant containing resolved enantiomers of **25** were kept under a nitrogen atmosphere to minimize decomposition. The resolved enantiomers of **25** were further purified via column chromatography (5% NEt_3/95% EtOAc; R_f ~ 0.3; purple) under a nitrogen atmosphere to give 75 mg of (+)-**25** and 72 mg of (-)-**25**. Enantiopure **25** is stored in a –30 °C freezer in a glove box.



26 R = 4-MeO-C_6H_4

26: To an oven-dried vial in a glove box was added 176 mg (0.295 mmol) of (4-MeO-C_6H_4)$_5C_5$-H **21c** and 2 mL of THF to give an orange solution. To this solution was added dropwise 200 μL (0.290 mmol, 0.981 equiv) of 1.45 M *n*-BuLi in hexanes to give a black solution. After stirring at room temperature for 10 minutes, this black solution was added to a suspension of 38 mg (0.30 mmol, 1.0 equiv) of $FeCl_2$ in 2 mL of THF. The insoluble $FeCl_2$ disappeared after ~ 30 minutes. To a separate oven-dried vial in a glove box was added 55 mg (0.30 mmol) of olefin **8** in 2 mL of THF to give a yellow solution. To this solution was added dropwise 200 μL (0.290 mmol, 0.981 equiv) of 1.45 M *n*-BuLi in hexanes to give an orange solution. After stirring at room temperature for 10 minutes, this solution was added to the (4-MeO-C_6H_4)$_5C_5$-Li/$FeCl_2$ reaction mixture to give a black solution. After stirring at room

temperature for an additional 1 hour, the reaction was removed from the glove box and subjected to silica gel column chromatography (5% NEt_3/95% EtOAc; R_f ~ 0.4; purple) to give 106 mg (43% yield) of **26** as a purple solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.07 (d, 1H, J=5), 6.84 (d, 10H, J=10), 6.60 (d, 10H, J=10), 5.68 (d, 1H, J=5), 4.89 (s, 1H), 4.79 (s, 1H), 4.12 (s, 1H), 3.78 (s, 15H), 3.30-3.60 (br, 4H), 1.80-2.20 (br, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 155.9, 153.5, 133.2, 131.3, 130.0, 127.5, 113.0, 112.3, 96.3, 84.7, 77.7, 68.9, 65.4, 55.0, 49.7, 25.6; IR (thin film) 2920, 2833, 1609, 1535, 1516, 1461, 1288, 1245, 1176, 1032 cm^{-1}; HRMS calcd for $C_{52}H_{48}FeN_2O_5$ 836.2912, found 836.2917. mp 246-249 °C. The enantiomers cannot be resolved via chiral HPLC (Daicel CHIRALCEL AD and Daicel CHIRALCEL OD columns).



27; R=4-*i*-PrO-C_6H_4

27: To an oven-dried vial in a glove box was added 220 mg (0.297 mmol) of (4-*i*-PrO-C_6H_4)$_5$$C_5$-H **22d** and 2 mL of THF to give a brown solution. To this solution was added dropwise 210 μL (0.305 mmol, 1.03 equiv) of 1.45 M *n*-BuLi in hexanes to give a black solution. After stirring at room temperature for 10 minutes, the black solution was added to a suspension of 40 mg (0.32 mmol, 1.1 equiv) of $FeCl_2$ in 1 mL of THF. The insoluble $FeCl_2$ disappeared after ~ 20 minutes. To a separate oven-dried vial in a glove box was added 55 mg (0.30 mmol) of olefin **8** in 2 mL of THF to give a yellow solution. To this solution was added dropwise 200 μL (0.290 mmol, 0.981 equiv) of 1.45 M *n*-BuLi in hexanes to give an orange solution. After stirring at room temperature for 10 minutes, this solution was added to the (4-*i*-PrO-C_6H_4)$_5$$C_5$-

Li/$FeCl_2$ reaction mixture to give a black solution. After stirring at room temperature for an additional 1 hour, the reaction was removed from the glove box and subjected to silica gel column chromatography (2% NEt_3/98% EtOAc; purple) to give 198 mg (67% yield) of **27** as a purple solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.05 (d, 1H, J=5), 6.83 (d, 10H, J=8), 6.57 (d, 10H, J=8), 5.66 (d, 1H, J=5), 4.91 (s, 1H), 4.77 (s, 1H), 4.49 (m, 5H), 4.13 (s, 1H), 3.43 (br, 4H), 1.94-2.06 (br, 4H) 1.28-1.33 (m, 30H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 153.5, 133.3, 132.9, 127.4, 113.1, 114.2, 96.4, 84.6, 77.2, 69.6, 68.0, 65.6, 49.7, 25.6, 22.1, 22.0; IR (thin film) 3059, 2974, 2931, 1608, 1535, 1513, 1383, 1241, 1182, 1119 cm^{-1}; HRMS calcd for $C_{62}H_{68}FeN_2O_5$ 976.4477, found 976.4488. mp 130-132 °C. The enantiomers were resolved via a Daicel CHIRALCEL AD column (1 cm x 25 cm; 80:20:0.4 hexanes/isopropanol/diethylamine; 2.5 mL/min; 15 mg of *rac* **27** per mL per injection). The retention times were 7.5–9.0 minutes for the first enantiomer ($[\alpha]^{20}_D$ = -1100; c=0.024 in $CHCl_3$) and 14.5-16.5 minutes for the second enantiomer ($[\alpha]^{20}_D$ = +960; c=0.024 in $CHCl_3$). The stock solution of racemic **27** was prepared in a glove box. Both the stock solution of racemic **27** and the resolved enantiomers of **27** were kept under a nitrogen atmosphere to minimize decomposition. The resolved enantiomers of **27** were further purified via column chromatography (2% NEt_3/98% EtOAc; purple) under a nitrogen atmosphere to give 79 mg of (-)-**27** and 80 mg of (+)-**27**. Enantiopure **27** is stored in a –30 °C freezer in a glove box.

Structure-Activity Relationship of the Second-Generation Catalysts

Table 4. Effect of the top-ring substituent on reactivity, addition of benzyl alcohol to phenylethyl ketene: In oven-dried vials in a glove box were prepared catalyst stock solutions of 0.01 mmol in 2 mL of C_6D_6, the alcohol stock solution of 27 μL (0.26

mmol) of benzyl alcohol in 3.75 mL of C_6D_6 and the ketene stock solution of 185 mg (1.27 mmol) of phenylethyl ketene in 10 mL of C_6D_6. To oven-dried screw-cap NMR tubes in the glove box were added 100 μL of the catalyst stock solution (100 μL of C_6D_6 for the background reaction) and 750 μL of the benzyl alcohol stock solution. The NMR tubes were sealed under a nitrogen atmosphere. The ketene stock solution was sealed under a nitrogen atmosphere with a teflon-lined septum cap. The NMR tubes and the ketene stock solution were removed from the glove box and transported to a Bruker 250 MHz NMR spectrometer. After the addition of 400 μL of the ketene solution to the NMR tubes via a gas-tight syringe (0.04 M in ketene; 1 mol% catalyst), the progress of the reaction was monitored by ^1H NMR until ca. 90% conversion.

Table 5. Effect of the Cp-ring substituent on reactivity, addition of benzyl alcohol to phenylethyl ketene: In oven-dried vials in a glove box were prepared catalyst stock solutions of 0.01 mmol in 4 mL of C_6D_6, the alcohol stock solution of 43 μL (0.42 mmol) of benzyl alcohol in 12 mL of C_6D_6 and the ketene stock solution of 58 mg (0.40 mmol) of phenylethyl ketene in 8 mL of C_6D_6. To oven-dried vials were added 100 μL of the catalyst stock solution. The vials were placed under vacuum for 1 hour to remove the solvent. Following solvent removal, 750 μL of the benzyl alcohol stock solution was added to each vial. The resulting solution was transferred to oven-dried screw-cap NMR tubes. The NMR tubes were sealed under a nitrogen atmosphere. The ketene stock solution was sealed under a nitrogen atmosphere with a teflon-lined septum cap. The NMR tubes and the ketene stock solution were removed from the glove box and transported to a Bruker 250 MHz NMR spectrometer. After the addition of 500 μL of the ketene solution to the NMR tubes via a gas-tight syringe (0.02 M in ketene; 1 mol% catalyst), the progress of the reaction was monitored by ^1H NMR until ca. 90% conversion.

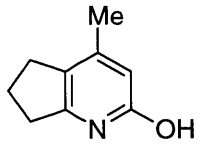
Table 6. Effect of the Cp-ring substituent on enantioselectivity, dynamic kinetic resolution/ring-opening of racemic azlactones: To oven-dried vials in a glove box were added 0.005 mmol of catalysts via stock solutions in CH_2Cl_2. The solvent was removed *in vacuo*. To the dry catalysts were added 1.0 mL of a stock solution consists of 175 mg (1.00 mmol) of the azlactone, 12 mg of benzoic acid (0.098 mmol) and 60 μL (1.5 mmol) of MeOH in 10 mL of d_8-toluene. The reaction mixture (5 mol% catalyst; 10 mol% benzoic acid; 1.5 equiv MeOH; 0.1 M in azlactone) was added to oven-dried screw-cap NMR tube. The screw-cap NMR tubes were sealed under a nitrogen atmosphere and removed from the glove box. The progress of the reactions was monitored by ^1H NMR. After 10 hours, the product was isolated via column chromatography (25% EtOAc/75% hexanes). The enantiomeric excess of the ring-opened product was assayed via chiral GC (G-TA column; 150 °C; t = 14.0, 15.6 min).

Table 7. Effect of the Cp-ring substitutent on enantioselectivity, kinetic resolution of alcohol: To oven-dried vials in a glove box were added 0.01 mmol of catalysts via stock solutions in CH_2Cl_2. The solvent was removed *in vacuo*. To the dry catalysts were added 2 mL of *t*-amyl alcohol, 104 μL (0.748 mmol) of NEt_3 and 122 mg (1.00 mmol) of racemic *sec*-phenylethanol. The resulting solutions were sealed under a nitrogen atmosphere via a septum. After removal from the glove box, the vials were immersed in ice bath and 71 μL (0.75 mmol) of Ac_2O was added to each vial (1 mol% catalyst). The ice bath with the vials was moved into a refrigerator. After 24 hours, the reactions were quenched with ~ 2 mL of MeOH and filtered through a plug of silica gel (50% EtOAc/50% hexanes). The eluant was collected as one fraction and was concentrated to ~ 10 mL via a rotatory evaporator at room temperature. Both the starting material as well as the product are somewhat volatile. The

enantiomeric excess of the starting material and product as well as the extent of the reaction were determined by chiral GC (G-TA column; 80 °C; $t_{alcohol}$ = 18.0, 19.6 min; $t_{acetate}$ = 14.1, 15.6 min). Analogous reactions were conducted in Et_2O at room temperature.

Synthesis of Planar-Chiral Derivatives of 2,2′-Bipyridine

(Scheme 6)



36

36:[92] To a flask fitted with a reflux condenser under argon was added 323 g (3840 mmol) of cyclopentanone, 500 g (3850 mmol) of ethyl acetoacetate and 297 g (3850 mmol) of ammonium acetate 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% yield) of pyridone **36** was obtained as a pale yellow solid. This material was used as is for the next step. ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.20 (s, 1H), 2.90 (t, 2H, J=8), 2.66 (t, 2H, J=8), 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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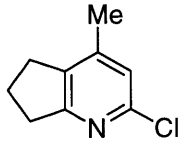
92 Sakurai, A.; Midorikawa, H. *Bull. Chem. Soc. Jpn.* **1968,** *41,* 165.



37

37: To an oven-dried Schlenk tube under argon was added 14.9 g (100 mmol) of pyridone **36** and 30 mL (320 mmol; 3.20 equiv) of $POCl_3$ 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 cool 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.[93] The acidic solution was washed with 3 x 100 mL of Et_2O. The Et_2O wash was extracted with 3 x 100 mL of 2 N HCl 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 5 x 200 mL of $CHCl_3$ followed by 1 x 200 mL of EtOAc. The organic phases were combined, dried with $MgSO_4$, filtered and stripped of solvent to give a brown tar. The crude was dissolved in ~ 100 mL of Et_2O and filtered through silica gel (rinsed with 5 x 100 mL of Et_2O). After solvent removal, 12.3 g (74% yield) of chloropyridine **37** was obtained as an orange solid. ^1H NMR (250 MHz, $CDCl_3$) δ 6.91 (s, 1H), 2.99 (t, 2H, J=8), 2.83 (t, 2H, J=8), 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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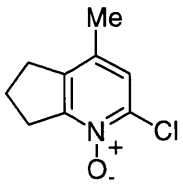
[93] It is important to keep the temperature of the quenching operation around ca. 0 °C. 2-Halopyridines are known to revert to 2-hydroxypyridine when heated in aqueous acid.



38

38: To a flask fitted with a reflux condenser was added 24.3 g (146 mmol) of chloropyridine **37**, 90 mL (1600 mmol; 11 equiv) of acetic acid and 20 mL (180 mmol; 1.2 equiv) of 30 % H_2O_2 from a previously unopened bottle[94] to give an orange solution. After heating at 80 °C[95] for 5 hours, an additional 15 mL (130 mmol; 0.90 equiv) of 30 % H_2O_2 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 ~ 250 g of K_2CO_3 in ~ 400 mL of water. The resulting slurry (pH ~ 11) was extracted with 5 x 400 mL of $CHCl_3$ followed by 2 x 200 mL of EtOAc. The organic layers were combined, dried with $MgSO_4$ and filtered. After removal of solvent, 24.7 g (93% crude yield) of *N*-oxide **38** was obtained along with ~ 5 % of the unreacted starting material **37**. This material was used as is for the next step. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, 1H), 3.22 (t, 2H, J=8), 2.92 (t, 2H, J=8), 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.

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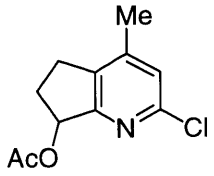
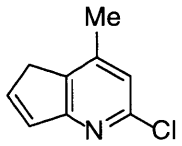
94 We have found it is best to use a new bottle for H_2O_2 each time.

95 Care must be taken to ensure that the reaction temperature stays below ca. 100 °C, the explosive decomposition temperature of the peracetic acid that is generated in situ.



39

39: To a flask fitted with a reflux condenser was added 24.7 g (135 mmol) of the crude *N*-oxide **38** and 200 mL (2120 mmol; 15.7 equiv) of Ac_2O 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[96] (bp 145-155 °C at 600 mtorr) gave 17.6 g (58% crude yield) of acetate **39** contaminated with unknown impurities. The impure product solidified upon standing. This material was used as is for the next step. ^{1}H 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.



40

40: To a flask fitted with a reflux condenser under argon was added 17.6 g (78.2 mmol) of the crude acetate **31** and 30 mL (560 mmol; 7.2 equiv) of concentrated

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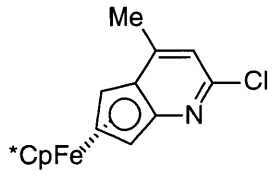
[96] No cooling water was used in the condenser during the initial stage of distillation due to a lower boiling fraction (most likely **37**) that has a freezing point above room temperature.

H_2SO_4 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 ~ 200 g of ice followed by ~ 80 g 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.[97] The aqueous phase was extracted with 5 x 200 mL of $CHCl_3$ followed by 1 x 200 mL of EtOAc. The organic layers were combined, dried with $MgSO_4$, filtered and stripped of solvent 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% crude yield) of **40** as a ~ 3:1 mixture of isomers contaminated with trace amount of **37**. The oily product solidified upon standing. This material was used as is for the next step. ^{1}H 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, minor isomer), 3.32 (t, 2H, J=3, 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.



41

41: To an oven-dried flask in a glove box was added 1.7 mL (11 mmol; 1.1 equiv) of

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97 We have found that the elimination reaction is much more reproducible if a sub-stoichiometric amount (relative to H_2SO_4 used) of 50% NaOH is used in the initial quench (i.e., after the addition of 50% NaOH, the aqueous phase is still acidic). This is to be followed by just enough K_2CO_3 to bring the pH of the solution to ~ 10.

Cp*-H and 30 mL of THF. The this clear colorless solution was added dropwise 6.4 mL (11 mmol; 1.1 equiv) of 1.71 M *n*-BuLi in hexanes to give a thick white slurry. An additional 5 mL of THF was added to facilitate stirring. After 15 minutes at room temperature, the white slurry was added to a suspension of 1.35 g (10.6 mmol; 1.06 equiv) of $FeCl_2$ in 10 mL of THF to give a dark green slurry ("FeCp*Cl"). To a separate oven-dried flask in a glove box was added 1.65 g (10.0 mmol) of olefin **40** and 15 mL of THF. To this clear colorless solution was added dropwise 5.8 mL (9.9 mmol; 0.99 equiv) of 1.71 M *n*-BuLi in hexanes to give an orange/brown solution. Gentle reflux occurred during the addition. After stirring at room temperature for 15 minutes, this solution was added to the dark green "FeCp*Cl" slurry to give a purple solution. After an additional 6 hours at room temperature, the reaction was removed from the glove box and concentrated to ~ 1/2 of the original volume via a rotatory evaporator.[98] Column chromatography (10% EtOAc/90% hexanes; R_f ~ 0.3; purple) gave 2.08 g (58% yield) of **41** as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.71 (s, 1H), 4.70 (dd, 1H, J=2), 4.24 (dd, 1H, J=2), 3.88 (t, 1H, J=2), 2.39 (s, 3H), 1.67 (s, 15H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 148.7, 116.0, 107.9, 80.3, 78.6, 76.2, 66.9, 61.7, 19.0, 9.74; IR (thin film) 2969, 2904, 1572, 1526, 1379, 1246, 1098, 1029, 893, 803 cm^{-1}; HRMS calcd for $C_{19}H_{22}ClFeN$ 335.0790, found 335.0792. mp 115-118°C. The enantiomers cannot be resolved via chiral HPLC (Daicel CHIRALCEL AD, Daicel CHIRALCEL OD, or Regis *R,R* Whelk column).

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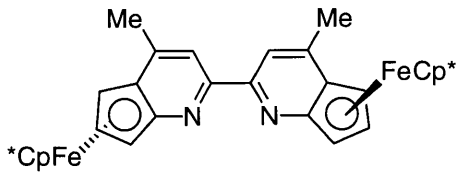
98 The product is only sparingly soluble in the column chromatography solvent system (10% EtOAc/90% hexanes). It is necessary to load the crude reaction mixture (THF solution) onto the column. Although it is possible to conduct the reaction on a larger scale, the limiting factor is the size of the column (to allow THF to elute at solvent front while leaving the product behind.)



42

42: To an oven-dried Schlenk tube in a glove box was added 551 mg (8.43 mmol; 1.50 equiv) of Zn°, 1.25 g (1.68 mmol; 0.299 equiv) of $NiBr_2(PPh_3)_2$, 1.44 g (5.60 mmol; 0.997 equiv) of Et_4NI and 12 mL of THF. The initial green slurry turned reddish/brown in ~ 10 minutes. After stirring at room temperature for an additional 20 minutes, 2.00 g (5.62 mmol) of the "monomer" **41** in 8 mL of THF was added to the reaction mixture. The Schlenk tube was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 50 °C. After 24 hours, the reaction was cooled to room temperature and quenched with ~ 150 mL of 10% NH_3. The pale blue aqueous layer was extracted with 3 x 150 mL of $CHCl_3$ followed by 1 x 100 mL of EtOAc. The organic layers were combined, dried with $MgSO_4$, filtered and stripped of solvent. Silica gel column chromatography (10% EtOAc/90% hexanes; loaded as a $CHCl_3$ solution;[99] R_f ~ 0.1; green) gave 1.05 g (58% yield) of **42** (*d,l* only) as a green solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 2H), 4.86 (dd, 2H, J=3), 4.38 (dd, 2H, J=3), 3.98 (t, 2H, J=3), 2.51 (s, 6H), 1.69 (s, 30H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 149.6, 114.4, 108.5, 83.0, 78.4, 76.6, 67.3, 62.0, 19.5, 9.96; IR (thin film) 2920, 1537, 1485, 1454, 1402, 1338, 1182, 1021 cm^{-1}; HRMS calcd for $C_{38}H_{44}Fe_2N_2$ 640.2203, found 640.2195. mp (decomp) 220 °C. The enantiomers were resolved via a Regis *R,R* Whelk column (1 cm x 25 cm; 66:33:0.4 hexanes/$CHCl_3$/diethylamine;

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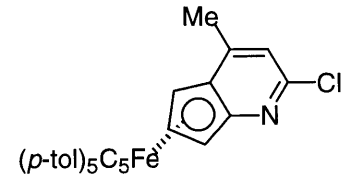
99 The product is only sparingly soluble in the column chromatography solvent system (10% EtOAc/90% hexanes). It is necessary to load the crude reaction mixture as a $CHCl_3$ solution onto the column. Although it is theoretically possible to conduct the reaction on a larger scale, the limiting factor is the size of the column (to allow for $CHCl_3$ to elute at solvent front while leaving the product behind.)

2.5 mL/min; 12 mg of *rac* **42** per mL per injection[100]). The retention times were 7.5–9.0 minutes for the first enantiomer ($[\alpha]^{20}_D$ = +2000; c=0.001 in $CHCl_3$) and 10.0-13.0 minutes for the second enantiomer ($[\alpha]^{20}_D$ = -2000; c=0.001 in $CHCl_3$). The stock solution of *rac* **42** was prepared in a glove box. Both the stock solution and the resolved solutions of enantiopure **42** were kept under nitrogen. X-ray quality crystals were obtained via the slow evaporation of the HPLC eluant of the (+)-enantiomer under a flow of nitrogen. The absolute configuration of the (+)-enantiomer was determined to be (*S,S*) via x-ray crystallography.[101] The resolved enantiopure **42** was further purified via column chromatography (10% EtOAc/90% hexanes) under a nitrogen atmosphere to give 351 mg of (+)-**42** and 419 mg of (-)-**42**. Enantiopure **42** is stored in a –30 °C freezer in a glove box.



To an oven-dried vial flask in a glove box was added 179 mg (0.347 mmol) of C_5(*p*-tol)$_5$-H, 5 mL of THF and 210 µL (0.359 mmol; 1.03 equiv) of 1.71 M *n*-BuLi in hexanes to give a black solution. After 15 minutes at room temperature, this solution was added to a suspension of 46 mg (0.36 mmol; 1.0 equiv) of $FeCl_2$ in 1 mL of THF. The insoluble $FeCl_2$ disappeared after 15 minutes and the resulting black solution was stirred at room temperature for an additional 15 minutes. To a separate oven-dried vial in a glove box was added 62 mg (0.38 mmol; 1.1 equiv) of olefin **40** and 2 mL of THF. To this clear colorless solution was added 220 µL (0.376 mmol; 1.08 equiv) of 1.71 M *n*-BuLi in hexanes to give an orange/brown solution.

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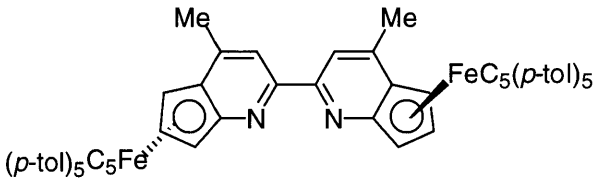
100 This is approximately the solubility limit of the *rac* **42** at room temperature. The solubility in a glove box is ~ 20 mg/mL.

101 The x-ray structure of (+)-(*S,S*)-**42** was solved by Michael M.-C. Lo.

After stirring at room temperature for 15 minutes, this solution was added to the black $C_5(p\text{-tol})_5$-Li/$FeCl_2$ reaction mixture to give a purple solution. After an additional 6 hours at room temperature, the reaction was removed from the glove box and concentrated to ~ 1/2 of the original volume via a rotatory evaporator.[102] Column chromatography (10% EtOAc/90% hexanes; R_f ~ 0.3; purple) gave 174 mg (68% yield) of the complex as a purple solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (d, 10H, J=8), 6.80 (d, 10H, J=8), 6.72 (s, 1H), 5.12 (s, 1H), 4,88 (s, 1H), 4.31 (s, 1H), 2.87 (s, 20H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 151.2, 135.6, 131.8, 131.7, 127.8, 120.1, 110.4, 85.5, 83.9, 79.1, 69.5, 63.6, 21.2, 20.1; IR (thin film) 3131, 2919, 2862, 1573, 1519, 1251, 1102, 908, 820, 730 cm^{-1}; HRMS calcd for $C_{49}H_{42}ClFeN$ 735.235518, found 735.2367. mp 150-160 °C. The enantiomers cannot be resolved via chiral HPLC (Daicel CHIRALCEL AD, Daicel CHIRALCEL OD, or Regis *R,R* Whelk column).



To an oven-dried Schlenk tube in a glove box was added 23 mg (0.35 mmol; 1.5 equiv) of Zn°, 53 mg (0.071 mmol; 0.30 equiv) of $NiBr_2(PPh_3)_2$, 61 mg (0.24 mmol; 1.0 equiv) of Et_4NI and 1 mL of THF. The initial green slurry turned reddish/brown in ~ 10 minutes. After stirring at room temperature for an additional 20 minutes, 174 mg (0.236 mmol) of the complexed monomer in 1 mL of THF was added to the reaction mixture. The Schlenk tube was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 50 °C. After 24 hours,

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102 The product is only sparingly soluble in the column chromatography solvent system (10% EtOAc/90% hexanes). It is necessary to load the crude reaction mixture (THF solution) onto the column.

the reaction was cooled to room temperature and quenched with ~ 20 mL of 10% NH_3. The pale blue aqueous layer was extracted with 3 x 30 mL of $CHCl_3$ followed by 1 x 50 mL of EtOAc. The organic layer was dried with $MgSO_4$, filtered and stripped of solvent. Column chromatography (10% EtOAc/90% hexanes; loaded as a $CHCl_3$ solution;[103] R_f ~ 0.1; green). The green band was collected, concentrated and re-flashed using a 25% EtOAc/75% hexanes system to remove the trace impurity. After solvent evaporation, 42 mg (25% yield) of the *d,l* dimer was obtained as a green solid along with trace amount of trapped solvents. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 2H), 6.85 (d, 20H, J=8), 6.77 (d, 20H, J=8), 5.23 (s, 2H), 4.98 (s, 2H), 4.26 (s, 2H), 2.36 (s, 6H), 2.19 (s, 30H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 150.2, 135.3, 132.3, 132.1, 127.8, 119.4, 110.9, 85.6, 85.3, 79.7, 70.9, 64.3, 21.1, 19.7; IR (thin film) 2920, 1580, 1519, 1445, 1328, 1247, 1184, 1112, 1020, 909 cm^{-1}; HRMS calcd for $C_{98}H_{84}Fe_2N_2$ 1400.5333, found 1400.5325. mp (decomp) 185 °C. The enantiomers cannot be resolved via chiral HPLC (Daicel CHIRALCEL AD, Daicel CHIRALCEL OD, or Regis *R,R* Whelk column).

[COD]PdMe$_2$:[104] To an oven-dried flask under argon was added 1.00 g (3.51 mmol) of [COD]$PdCl_2$ and 30 mL of Et_2O to give a yellow slurry which was immersed in a dry ice/CH_3CN bath at –45 °C. To this slurry was added dropwise 8.8 mL (14 mmol; 4.0 equiv) of 1.6 M MeLi in Et_2O to give a black slurry. After 2 hours at –45 °C, the flask was immersed in an ice bath. The reaction was *quench under argon* with ~ 10 mL of ice cold water. After the gas evolution had stopped, the flask was re-immersed in

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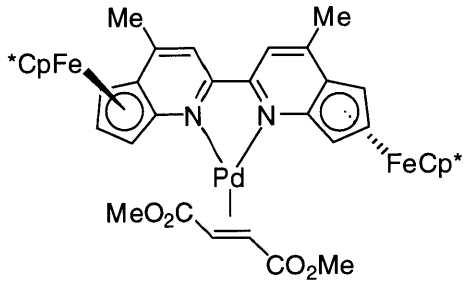
103 The product is only sparingly soluble in the column chromatography solvent system (10% EtOAc/90% hexanes). It is necessary to load the crude reaction mixture as a $CHCl_3$ solution onto the column. The lower yield of this reaction relative to that for **42** is probably due to both the steric bulk of this substrate and the fact that this reaction was conducted at ~ 1/2 of the original concentration.

104 (a) Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960,** 2008. (b) Rudler-Chauvier, M.; Rudler, H. *J. Organomet. Chem.* **1977,** *134,* 115.

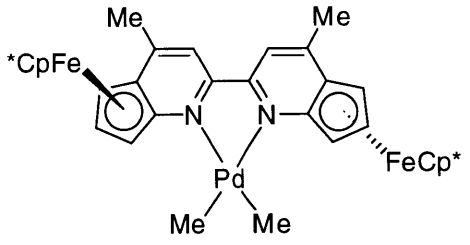
the –45 °C bath and the aqueous phase was allowed to freeze. After the complete solidification of the aqueous phase (~ 5 minutes), the pale yellow organic phase was cannula under argon into an oven-dried flask under argon immersed in an ice bath. The solvent was removed *in vacuo* during which the initial pale yellow solution darkened. After complete solvent removal, a gray solid was left behind and the flask was quickly moved into a glove box. The gray solid was rinsed out with chilled (~ -30 °C) Et_2O and filtered through an 0.45 μm Acrodisc. The rinse and filter operation has to be carried out as quickly as possible to minimize product decomposition. The initial color of the filtrate was pale yellow but quickly darkened upon standing at room temperature. Recrystallization from Et_2O at –30 °C gave 474 mg (55% yield) of [COD]$PdMe_2$ as a off-white/gray solid which decomposes in solution at room temperature. The isolated product is stored in a –30 °C freezer in a glove box and is apparently indefinitely stable under these conditions. ^1H NMR (300 MHz, CD_2Cl_2) δ 5.40 (m, 4H), 2.42 (m, 8H), 0.253 (s, 6H).



43

43: To an oven-dried vial in a glove box was added 23 mg (0.025 mmol; 0.50 equiv) of Pd_2dba_3, 7.2 mg (0.050 mmol; 1.0 equiv) of dimethylfumarate in 1 mL of $CDCl_3$ and 32 mg (0.050 mmol) of (+)-**42** in 1 mL of $CDCl_3$. The initial purple solution turned dark green after stirring at room temperature for 12 hours. After filtration through an 0.45 μm Acrodisc, the solvent was removed *in vacuo* to give a dark green solid. The solid was rinsed with 3 x 2 mL of pentane to remove the liberated dba.

Recrystallization from 3 mL of CH_2Cl_2 layered with 9 mL of pentane at –30 °C gave 30 mg (67% yield) of the dimethylfumarate complex **43** (trapped ~ 25 mol% CH_2Cl_2) as a dark green solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (s, 2H), 5.80 (d, 2H, J=2), 4.47 (d, 2H, J=2), 4.25 (s, 2H), 4.20 (t, 2H, J=2), 3.59 (s, 3H), 2.52 (s, 6H), 1.71 (s, 30H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 155.5, 154.0, 112.3, 110.2, 84.1, 79.3, 79.2, 70.1, 63.4, 50.5, 40.2,[105] 20.2, 10.2; IR (thin film) 2944, 2902, 1681, 1573 (C=O), 1432, 1314, 1251, 1141, 1029, 910 cm^{-1};[106] HRMS calcd for $C_{98}H_{84}Fe_2N_2$ 890.1661, found 890.1721.



44

44: To an oven-dried vial in a glove box was added 10 mg (0.041 mmol; 1.4 equiv) of [COD]$PdMe_2$ and 19 mg (0.030 mmol) of (+)-**42** in 2 mL of C_6D_6. The initial black solution turned dark green after ~ 5 minutes. After 30 minutes, the solvent was removed *in vacuo* and ~ 2 mL of Et_2O was added and evaporated *in vacuo* (repeated twice to decompose the excess [COD]$PdMe_2$). Recrystallization from ~ 2 mL of CH_2Cl_2 layered with ~ 12 mL of pentane at –30 °C gave 18 mg (78% yield) of the $PdMe_2$ adduct **44** as a dark green solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.41 (s, 2H), 5.65 (d, 2H, J=2), 4.44 (d, 2H, J=2), 4.11 (t, 2H, J=2), 2.50 (s, 6H), 1.64 (s, 30H), 0.680 (s, 6H). The product is not sufficiently stable as a solution in CD_2Cl_2 for a ^{13}C NMR (decomposition was observed after 10 hours at room temperature). HRMS (FAB) revealed M^{-30} (MW=746; lose of ethane) along with the signature Pd isotope

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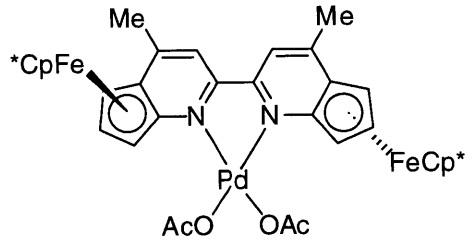
105 We believe this peak correlates to the *vinyl* carbon of the complexed dimethylfumarate.

106 Spectral data for the free dimethylfumarate: ^{1}H (300 MHz, $CDCl_3$) δ 4.21 (s, 2H), 3.81 (s, 6H). ^{13}C (126 MHz, $CDCl_3$) δ 165.0, 133.1, 52.0. IR (thin film) 1681.7 (C=O) cm^{-1}.

envelope.[107]



45

45: To an oven-dried vial in a glove box was added 12 mg (0.053 mmol) of $Pd(OAc)_2$ and 1 mL of C_6D_6. The mixture was stirred at room temperature until all of the $Pd(OAc)_2$ dissolved to give a homogeneous orange solution. This solution was added to 35 mg (0.55 mmol; 1.0 equiv) of (+)-**42** in an oven-dried vial in a glove box. The resulting black solution was allowed to sit *without stirring* in the glove box. After 24 hours, formation of black precipitates was observed. The mother liquor was removed via pipet and the residual solid was dried *in vacuo* to give 36 mg (78% yield) of the $Pd(OAc)_2$ complex **45** as a dark green solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (s, 2H), 6.00 (dd, 2H, J=3, 2), 4.41 (dd, 2H, J=3, 2), 4.22 (t, 2H, J=3), 2.53 (s, 6H), 2.20 (s, 6H), 1.80 (s, 30H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.1, 157.8, 157.5, 111.3, 109.8, 85.6, 81.5, 79.8, 66.7, 62.9, 23.9, 20.2, 10.0; IR (thin film) 2903, 1627 (C=O), 1563, 1359, 1296, 1028, 726 cm^{-1};[108] HRMS (FAB) showed MW=746 which corresponds to (+)-**42** plus Pd° (640 + 106) along with the signature Pd isotope envelope.[107]

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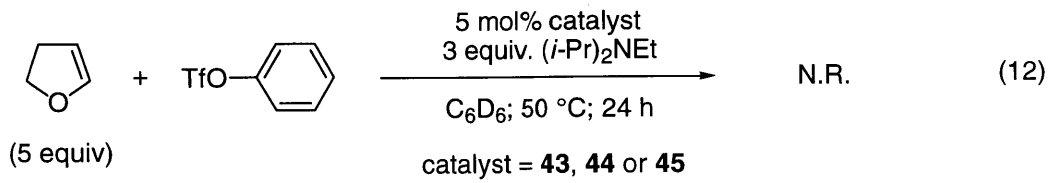
107 Isotopic abundance of palladium: ^{102}Pd, 1.0%; ^{104}Pd, 11.0%; ^{105}Pd, 22.2%; ^{106}Pd, 27.3%, ^{108}Pd, 26.7%; ^{110}Pd, 11.8%. Relative abundance (^{106}Pd = 1.00): ^{102}Pd, 0.04; ^{104}Pd, 0.40; ^{105}Pd, 0.81; ^{106}Pd, 1.00; ^{108}Pd, 0.98; ^{110}Pd, 0.43.

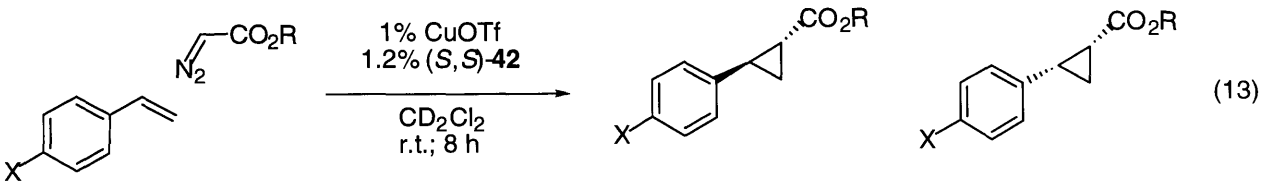
108 Spectral data for the free $Pd(OAc)_2$: ^{1}H (300 MHz, $CDCl_3$) δ 4.21 (s, 2H), 2.00 (s, 6H). ^{13}C (126 MHz, $CDCl_3$) δ 188.3, 22.8. IR (thin film) 1605.1 (C=O) cm^{-1}.

Applications of Planar-Chiral Derivative of 2,2′-Bipyridine in Asymmetric Catalysis



N.R. (12)

Eq 12. Asymmetric Heck reactions: To an oven-dried Schlenk tube in a glove box was added 5 mol% of the (+)-**42**/Pd complex **43**, **44** or **45** in 2 mL of C_6D_6, 5 equiv of 2,3-dihydrofuran, 1 equiv of phenyl triflate and 3 equiv of *N,N*-diisopropylethylamine. An aliquot was taken from this initial reaction mixture and diluted with C_6D_6 for the t=0 ^{1}H NMR spectra. The dark green solution was sealed under a nitrogen atmosphere, removed from the glove box and immersed in an oil bath at 50 °C. Metallic coating (Pd°) was observed after 16 hours for the reactions using **44** and **45**. The ^{1}H NMR spectra of the aliquot taken in the glove box of these two reactions after 16 hours at 50 °C showed there was no reaction. The reaction using **43** showed no Pd° deposit after heating at 50 °C for 16 hours; however, ^{1}H NMR spectra of the reaction mixture showed no reaction at that time. Metallic coating was observed after heating the reaction using **43** for an additional 24 hours at 80 °C. ^{1}H NMR spectra of the reaction at this time again showed no reaction.



(13)

Preparation of the Catalyst for Cu(I)-Catalyzed Asymmetric Cyclopropanation of Olefins (eq. 13):[4] To an oven-dried vial in a glove box was added 55 mg (0.086 mmol; 2.4 equiv) of (+)-(*S,S*)-**42** and 7 mL of CD_2Cl_2. The resulting black solution was added to 18 mg (0.036 mmol) of $(CuOTf)_2 \bullet C_6H_6$. The insoluble $(CuOTf)_2 \bullet C_6H_6$ gradually disappeared and the appearance of the reaction mixture gradually turned to a dark green homogeneous solution. After stirring at room temperature for 30 minutes, the dark green solution was filtered through an 0.45 μm Acrodisc to give a catalyst stock solution of 0.010 mM.

The trans to cis ratio of the products as well as the absolute configuration of the major enantiomer of the products were determined by comparing the GC retention time with those reported in the literature.[4]

Table 8, entry 1: To an oven-dried 20 mL vial in a glove box was added 700 μL of the catalyst stock solution (0.0070 mmol; 1 mol%) and 83 μL (0.73 mmol) of styrene. The resulting dark green solution was stirred at room temperature. After 5 minutes, 240 μL (2.24 mmol; 3.10 equiv) of ethyl diazoacetate in 800 μL of CD_2Cl_2 was added dropwise over 5 minutes with concomitant gas evolution. The rate of addition was such that the rate of gas evolution was consistent and under control. The color of the reaction remained dark green during the addition and gas evolution. The gas evolution stopped upon the completion of addition. After 1 hour, an aliquot was taken and diluted with $CDCl_3$. ^1H NMR showed complete consumption of the

olefin. The vial was sealed under a nitrogen atmosphere, removed from the glove box and placed under an argon atmosphere. After an additional 7 hours, the reaction was filtered through a plug of silica gel (rinsed with 15% EtOAc). Achiral GC (DB-1701 column; 140 °C) analysis of the crude reaction mixture showed a 75:25 trans/cis product ratio (t_{trans} = 7.29 min; t_{cis} = 7.12 min). Chiral GC (BPH column; 85 °C) analysis of the crude showed a 65% ee for the cis product (t = 39.2, 40.2 min). An aliquot of the crude reaction mixture was taken, stripped of solvent and treated with excess LAH in Et_2O at room temperature for 15 minutes. Following aqueous workup, the crude alcohol was treated with excess TFAA in CH_2Cl_2 for 30 minutes. After the solvent and the excess TFAA were removed *in vacuo*, chiral GC (G-TA column; 90 °C) analysis revealed a 65% ee for the cis product (t = 16.3, 19.4 min) and a 73% ee for the trans product (t = 23.1, 25.2 min). The crude reaction mixture was stripped of solvent and subjected to silica gel column chromatography (50% $CHCl_3$/50% hexanes; R_f ~ 0.3; PMA) to give 103 mg (75% yield) a mixture of cis and trans product as a pale yellow oil. The trans product (47 mg; 34% yield) was obtained after a second column chromatography using a 15% EtOAc/85% hexanes solvent system. The cis product was not recovered after this chromatography.

Table 8, entry 2: To an oven-dried 20 mL vial in a glove box was added 700 μL of the catalyst stock solution (0.0070 mmol; 1 mol%) and 83 μL (0.73 mmol) of styrene. The resulting dark green solution was stirred at room temperature. After 5 minutes, 322 mg (2.27 mmol; 3.13 equiv) of *t*-butyl diazoacetate in 800 μL of CD_2Cl_2 was added dropwise over 5 minutes with concomitant gas evolution. The rate of addition was such that the rate of gas evolution was consistent and under control. The color of the reaction remained dark green during the addition and gas evolution. The gas evolution stopped upon the completion of addition. After 1 hour, an aliquot was taken and diluted with $CDCl_3$. ^1H NMR showed complete consumption of the

olefin. The vial was sealed under a nitrogen atmosphere, removed from the glove box and placed under an argon atmosphere. After an additional 7 hours, the reaction was filtered through a plug of silica gel (rinsed with 15% EtOAc). Achiral GC (DB-1701 column; 150 °C) analysis of the crude reaction mixture showed a 87:13 trans/cis product ratio (t_{trans} = 7.09 min; t_{cis} = 6.20 min). Chiral GC (G-TA column; 100 °C) analysis of the crude showed a 79% ee for the cis product (t = 28.8, 32.5 min). The crude reaction mixture was stripped of solvent and moved into a glove box. To this neat crude mixture was added 15 mL of 1.0 M LAH in Et_2O. After the initial vigorous exotherm, the reaction was stirred at room temperature for 1 hour. The reaction was quenched under an argon atmosphere at 0 °C via the sequential addition of 1 mL of water, 1 mL of 6 N NaOH, and 3 mL of water. The resulting white slurry was filtered, rinsed with EtOAc and stripped of solvent. Silica gel column chromatography (30% EtOAc/70% hexanes; R_f ~ 0.3; PMA) gave 67 mg (63% yield) of a mixture of the trans and cis alcohol as a clear colorless oil. The alcohol was treated with excess TFAA in CH_2Cl_2 at room temperature for 30 minutes. After the solvent and the excess TFAA were removed *in vacuo*, chiral GC (G-TA column; 90 °C) analysis revealed an 82% ee for the trans product (t = 23.2, 25.3 min). There was insufficient material to determine the ee of the cis product (minor enantiomer not seen on Chiral GC).

Table 8, entry 4: To an oven-dried 20 mL vial in a glove box was added 700 μL of the catalyst stock solution (0.0070 mmol; 1 mol%) and 96 μL (0.72 mmol) of 4-vinylanisole. The resulting dark green solution was stirred at room temperature. After 5 minutes, 650 mg (2.26 mmol; 3.11 equiv) of BHT diazoacetate in 800 μL of CD_2Cl_2 was added dropwise over 5 minutes. No gas evolution was observed. The color of the reaction remained dark green during the addition. After 1 hour, an aliquot was taken and diluted with $CDCl_3$. ^1H NMR showed complete consumption

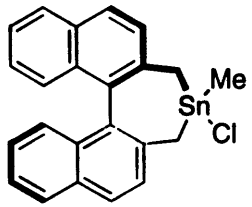
of the olefin. The vial was sealed under a nitrogen atmosphere, removed from the glove box and placed under an argon atmosphere. After an additional 7 hours, the reaction was filtered through a plug of silica gel (rinsed with 15% EtOAc). Achiral GC (DB-1701 column; 240 °C) analysis of the crude reaction mixture showed a 96:4 trans/cis product ratio (t_{trans} = 14.5 min; t_{cis} = 13.8 min). The crude reaction mixture was stripped of solvent and moved into a glove box. To this neat crude mixture was added 15 mL of 1.0 M LAH in Et_2O. After the initial vigorous exotherm, the reaction was stirred at room temperature for 12 hours. The reaction was quenched under an argon atmosphere at 0 °C via the sequential addition of 1 mL of water, 1 mL of 6 N NaOH, and 3 mL of water. The resulting white slurry was filtered, rinsed with EtOAc and stripped of solvent. Silica gel column chromatography (30% EtOAc/70% hexanes; R_f ~ 0.2; PMA) gave 69 mg (54% yield) of the corresponding alcohol (trans only) as a white solid. The alcohol was treated with excess TFAA in CH_2Cl_2 at room temperature for 30 minutes. After the solvent and the excess TFAA were removed *in vacuo*, chiral GC (G-TA column; 100 °C) analysis revealed a 70% ee for the trans product (t = 62.9, 63.7 min).

Table 8, entry 5: To an oven-dried 20 mL vial in a glove box was added 700 μL of the catalyst stock solution (0.0070 mmol; 1 mol%) and 84 μL (0.73 mmol) of 4-(trifluoromethyl)styrene. The resulting dark green solution was stirred at room temperature. After 5 minutes, 650 mg (2.26 mmol; 3.09 equiv) of BHT diazoacetate in 800 μL of CD_2Cl_2 was added dropwise over 5 minutes. There was a gentle gas evolution which lasted for ~ 10 minutes. The color of the reaction remained dark green during the addition and gas evolution. After 1 hour, an aliquot was taken and diluted with $CDCl_3$. ^1H NMR showed complete consumption of the olefin. The vial was sealed under an nitrogen atmosphere, removed from the glove box and placed under an argon atmosphere. After an additional 7 hours, the reaction was filtered

through a plug of silica gel (rinsed with 15% EtOAc). Achiral GC (DB-1701 column; 220 °C) analysis of the crude reaction mixture showed a 93:7 trans/cis product ratio (t_{trans} = 12.9 min; t_{cis} = 13.2 min). The crude reaction mixture was stripped of solvent and moved into a glove box. To this neat crude mixture was added 15 mL of 1.0 M LAH in Et_2O. After the initial vigorous exotherm, the reaction was stirred at room temperature for 12 hours. The reaction was quenched under an argon atmosphere at 0 °C via the sequential addition of 1 mL of water, 1 mL of 6 N NaOH, and 3 mL of water. The resulting white slurry was filtered, rinsed with EtOAc and stripped of solvent. Silica gel column chromatography (30% EtOAc/70% hexanes; R_f ~ 0.2; PMA) gave 93 mg (60% yield) of the corresponding alcohol (trans only) as a clear colorless oil. The alcohol was treated with excess TFAA in CH_2Cl_2 at room temperature for 30 minutes. After the solvent and the excess TFAA were removed *in vacuo*, chiral GC (G-TA column; 100 °C) analysis revealed an ca. 92% ee for the trans product (t = 30.7, 33.0 min; non-baseline resolution).

Appendix A

^{1}H NMR Spectra of Selected Compounds in Chapter 1



7

^{1}H NMR
300 MHz, $CDCl_3$

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RFL= 2303.5 RFP= 2177.5

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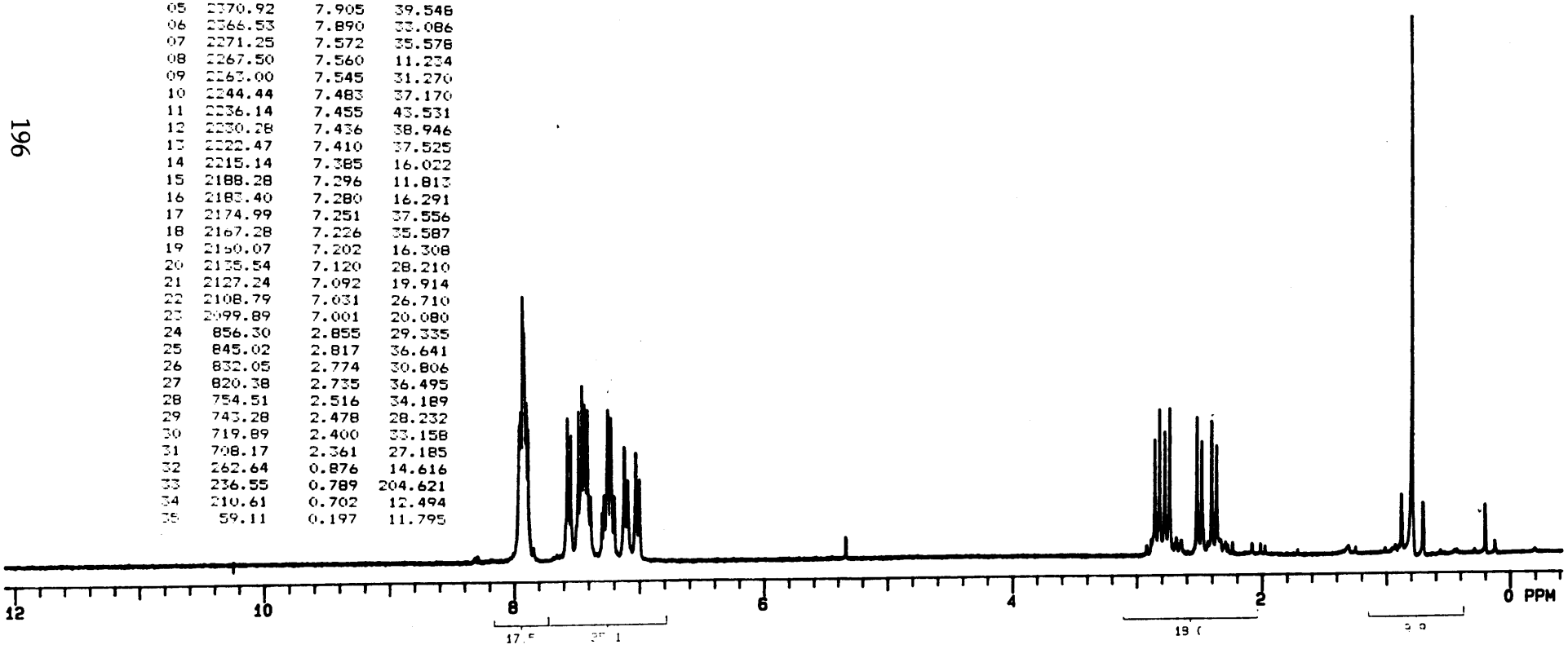
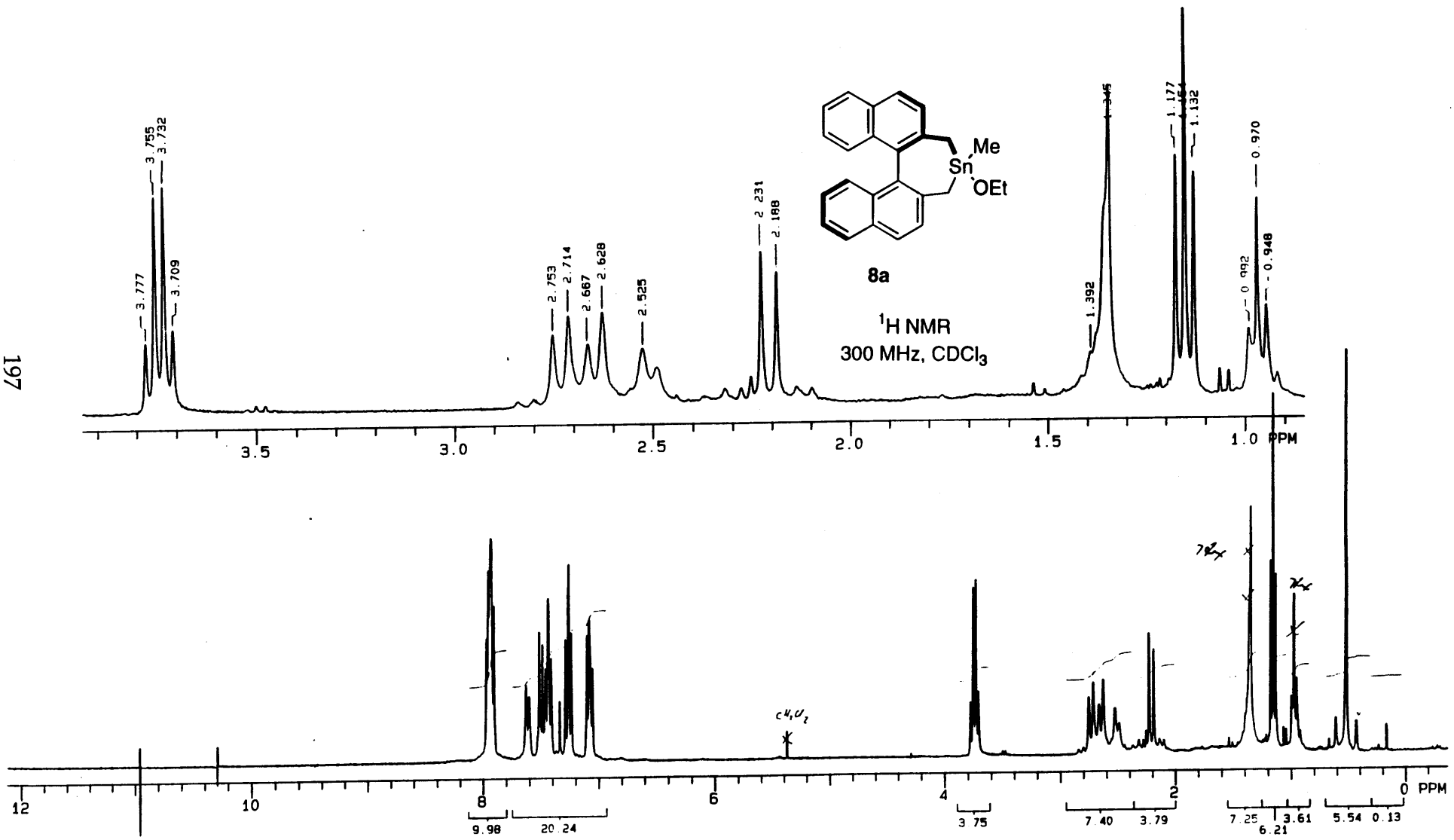
02	2384.60	7.950	37.273
03	2379.12	7.932	66.350
04	2375.81	7.921	57.001
05	2370.92	7.905	39.548
06	2366.53	7.890	33.086
07	2271.25	7.572	35.578
08	2267.50	7.560	11.234
09	2263.00	7.545	31.270
10	2244.44	7.483	37.170
11	2236.14	7.455	43.531
12	2230.28	7.436	38.946
13	2222.47	7.410	37.525
14	2215.14	7.385	16.022
15	2188.28	7.296	11.813
16	2183.40	7.280	16.291
17	2174.99	7.251	37.556
18	2167.28	7.226	35.587
19	2160.07	7.202	16.308
20	2135.54	7.120	28.210
21	2127.24	7.092	19.914
22	2108.79	7.031	26.710
23	2099.89	7.001	20.080
24	856.30	2.855	29.335
25	845.02	2.817	36.641
26	832.05	2.774	30.806
27	820.38	2.735	36.495
28	754.51	2.516	34.189
29	743.28	2.478	28.232
30	719.89	2.400	33.158
31	708.17	2.361	27.185
32	262.64	0.876	14.616
33	236.55	0.789	204.621
34	210.61	0.702	12.494
35	59.11	0.197	11.795

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3.732
3.709
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2.714
2.667
2.628
2.525
2.231
2.188
1.392
1.345
1.177
1.164
1.132
0.992
0.970
0.948
3.5
3.0
2.5
2.0
1.5
1.0 PPM
12
10
8
6
4
2
0 PPM
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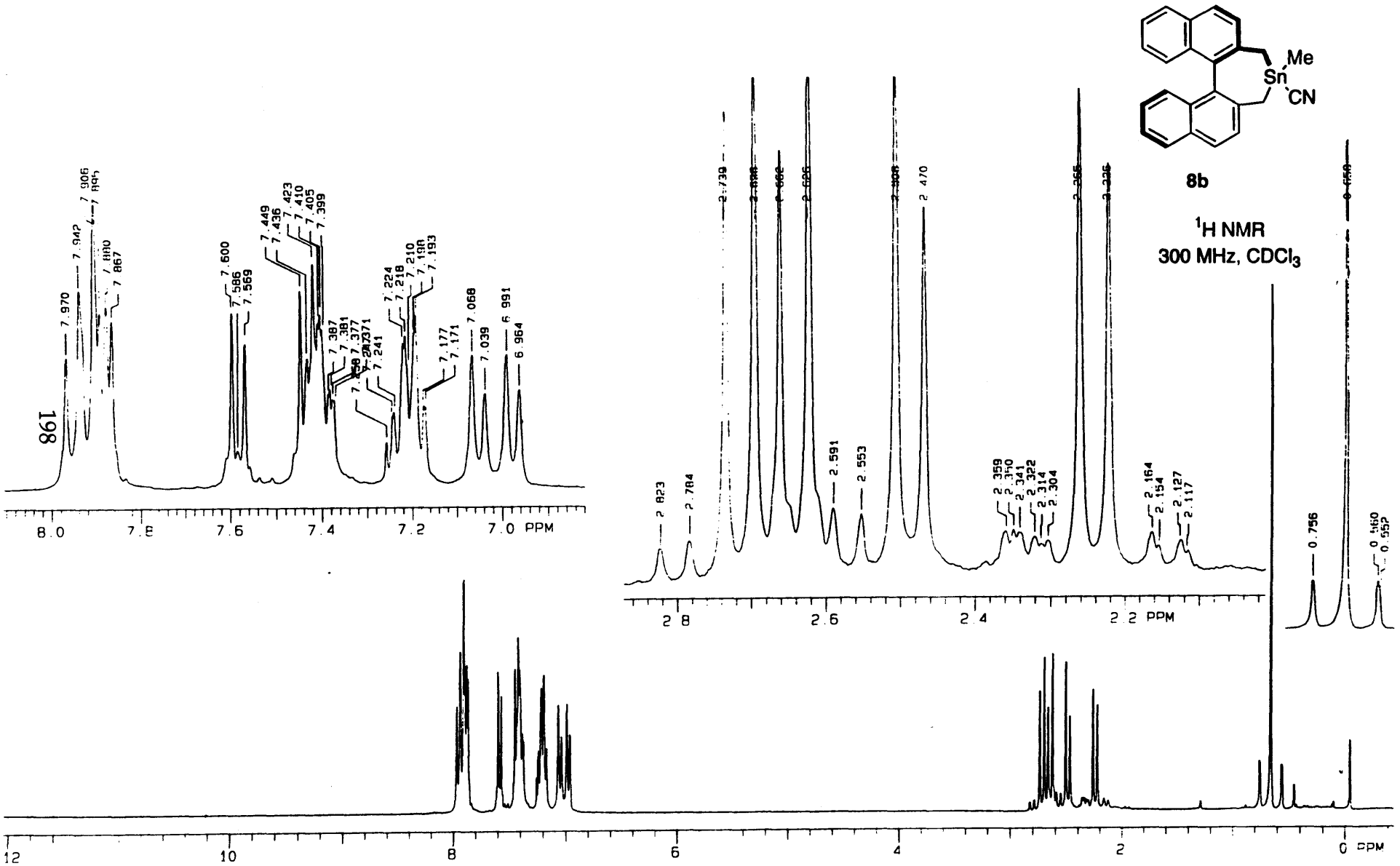
7.25
3.61
6.21
5.54
0.13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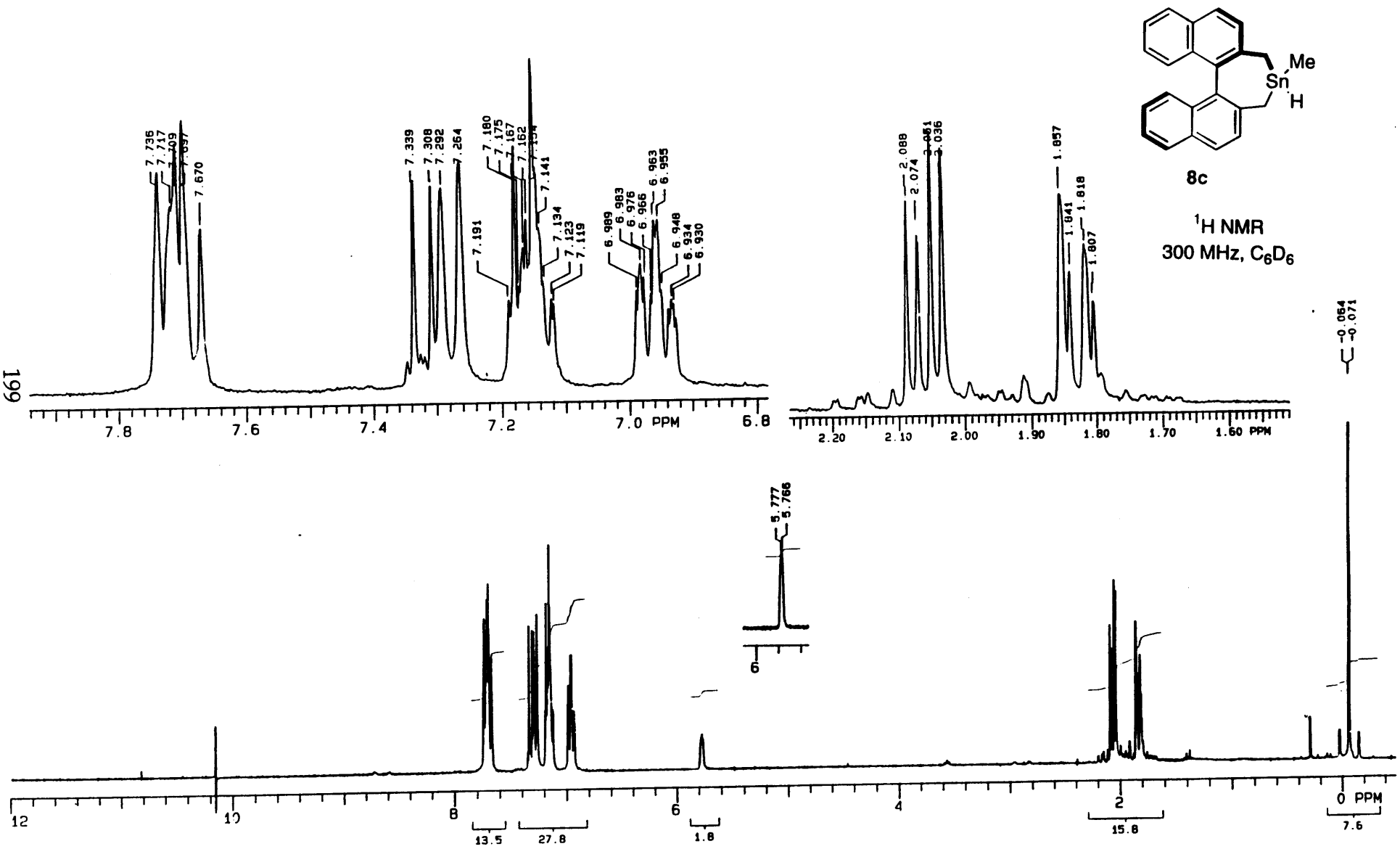
Sn
CN
8b
^{1}H NMR
300 MHz, CDCl$_3$
198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Sn
H
8c
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7.339
7.308
7.292
7.264
7.191
7.180
7.175
7.167
7.162
7.141
7.134
7.123
7.119
6.989
6.983
6.976
6.966
6.963
6.955
6.948
6.934
6.930
2.088
2.074
2.051
2.036
1.857
1.841
1.818
1.807
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-0.071
5.777
5.766
7.8
7.6
7.4
7.2
7.0 PPM
6.8
2.20
2.10
2.00
1.90
1.80
1.70
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2
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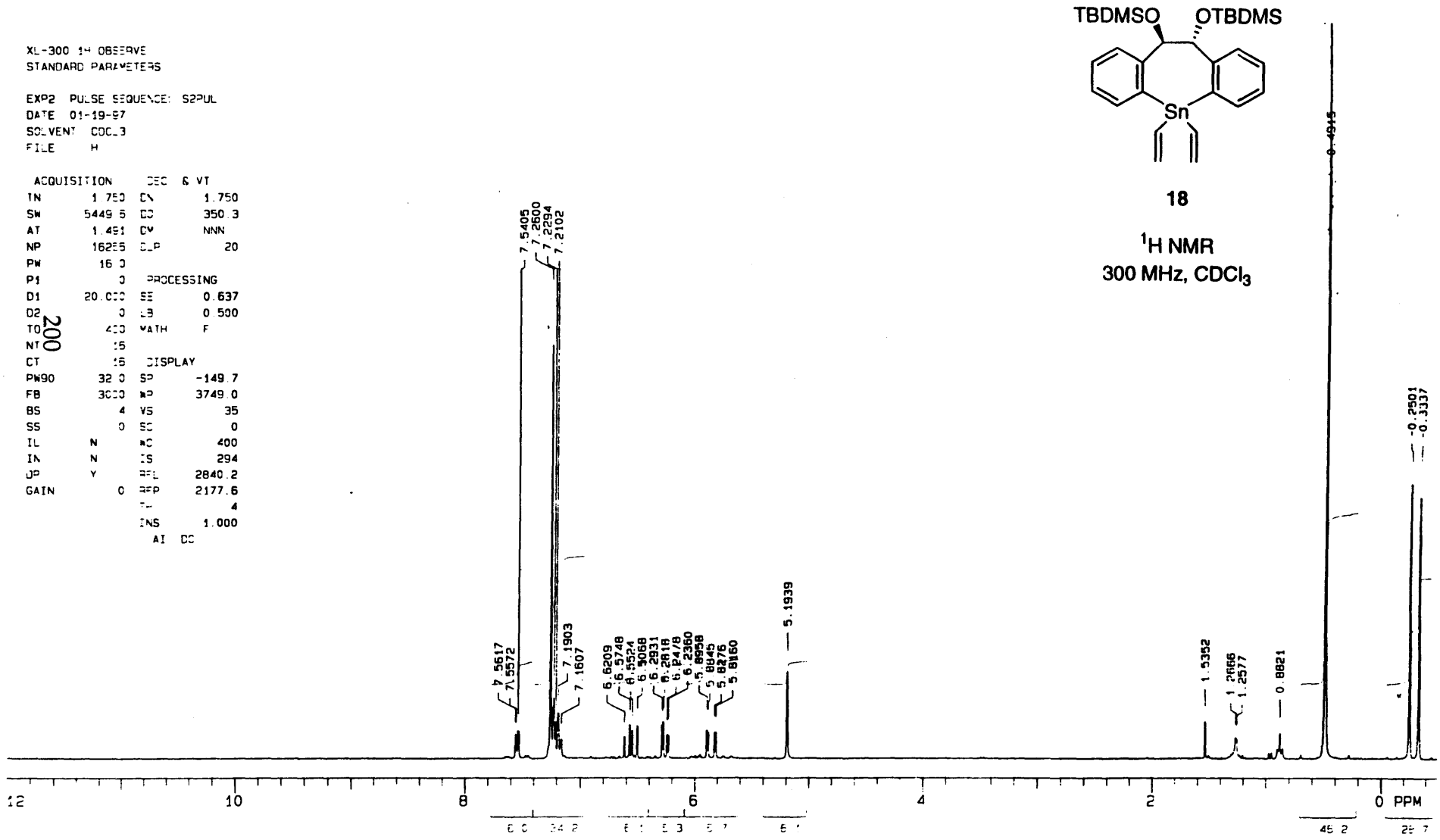
27.8
1.8
15.8
7.6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Sn
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7.1903
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6.5748
6.5524
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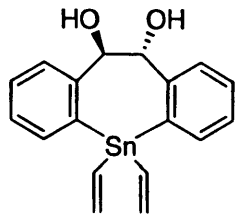

19

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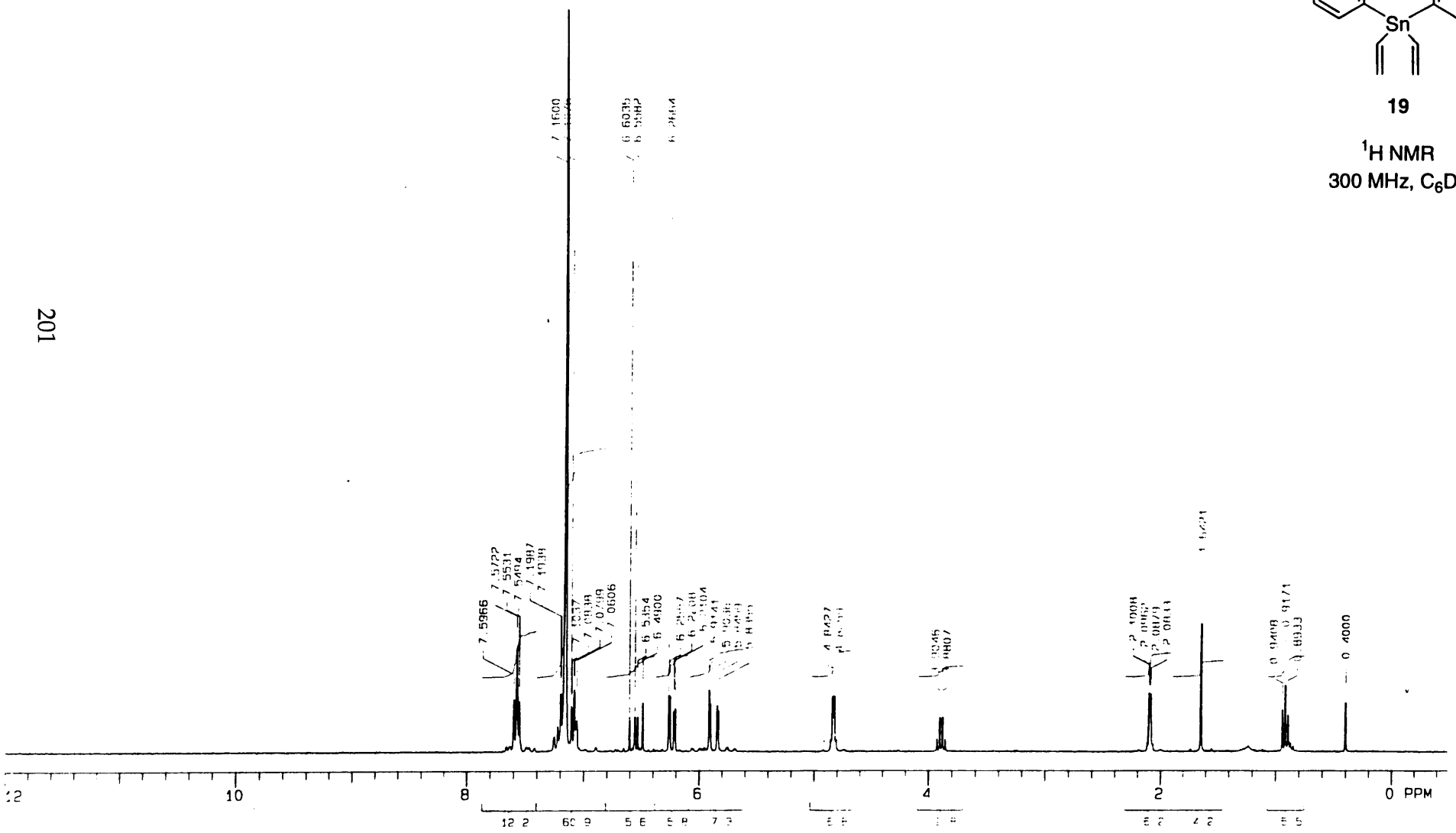

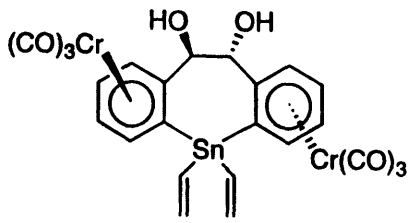

20

^{1}H NMR
300 MHz, C_6D_6

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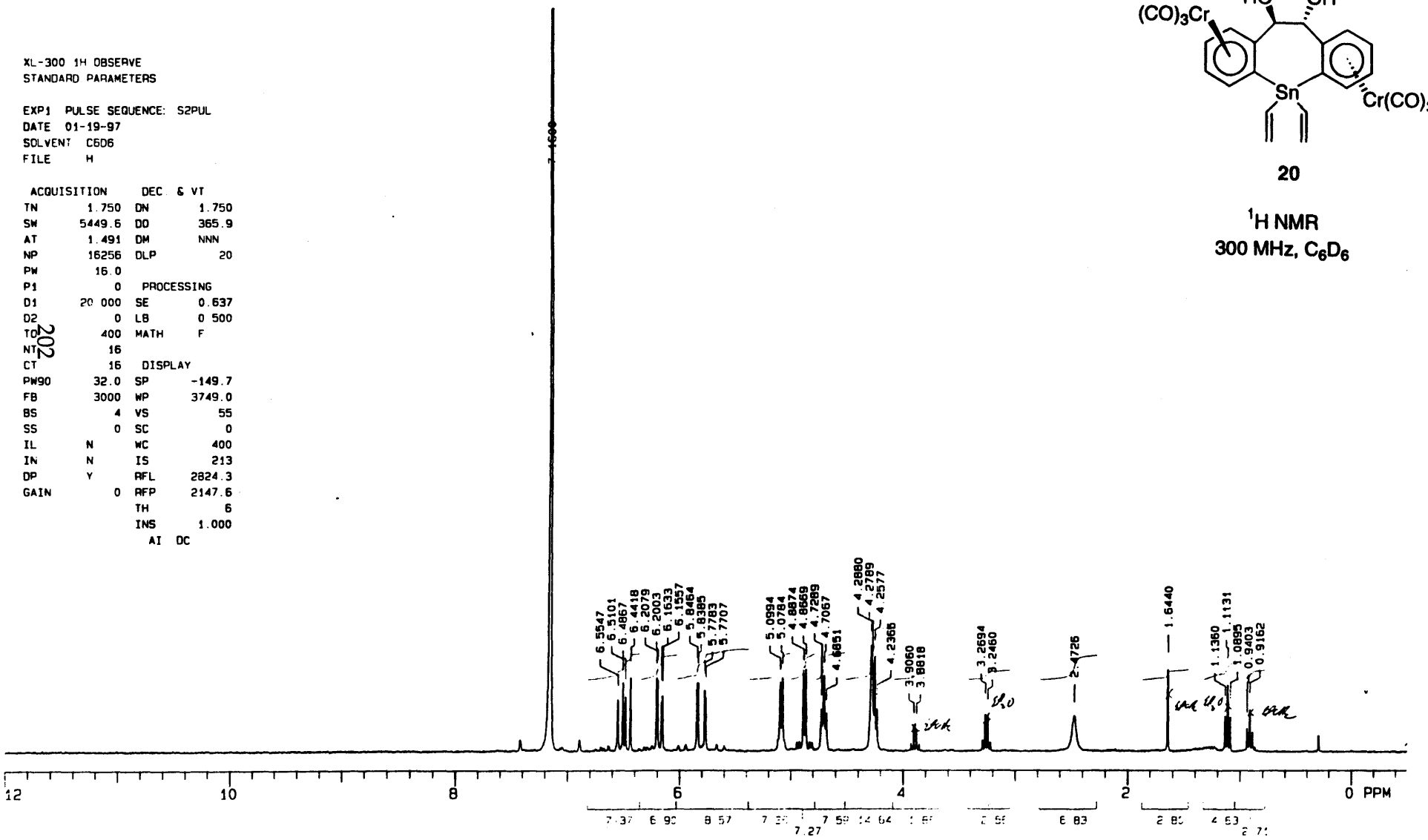

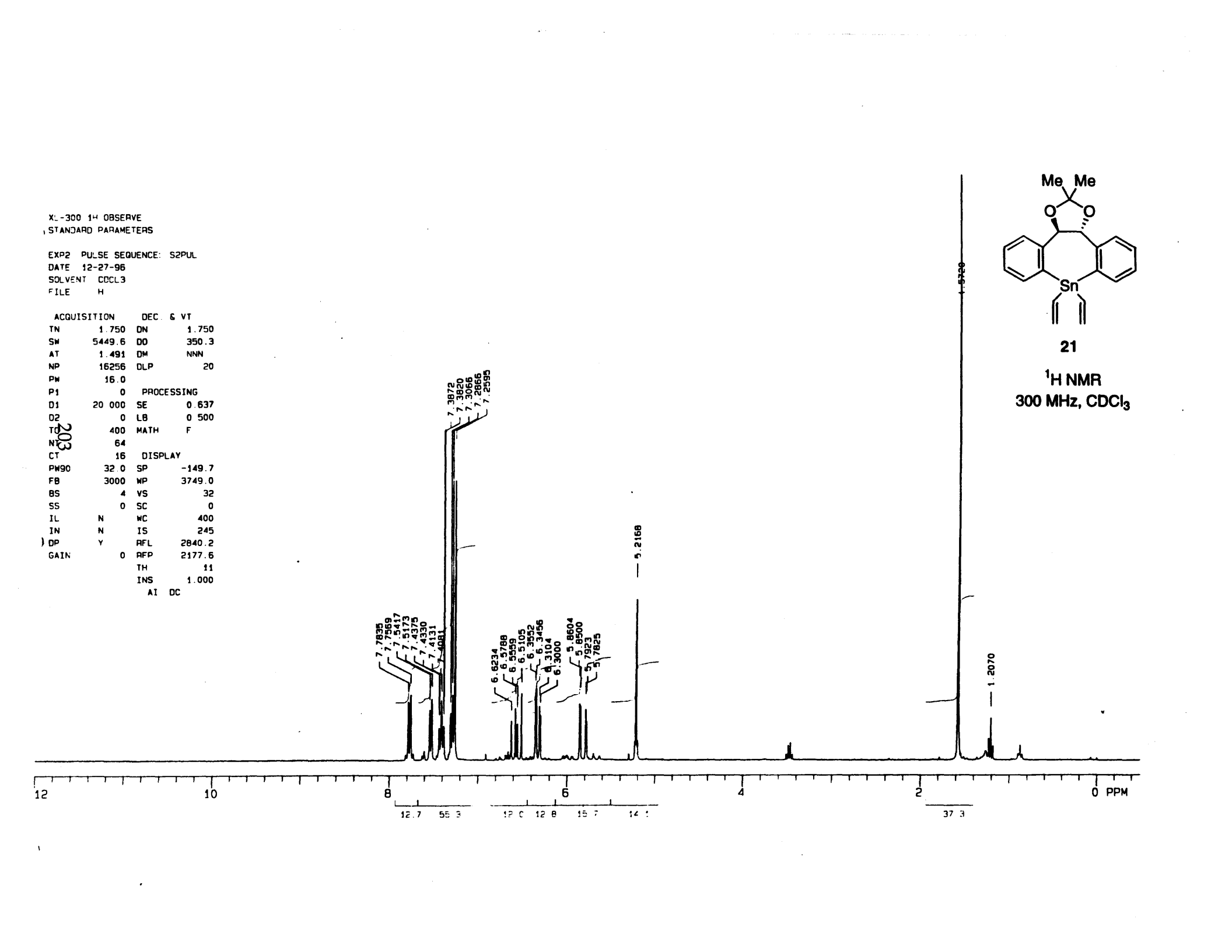
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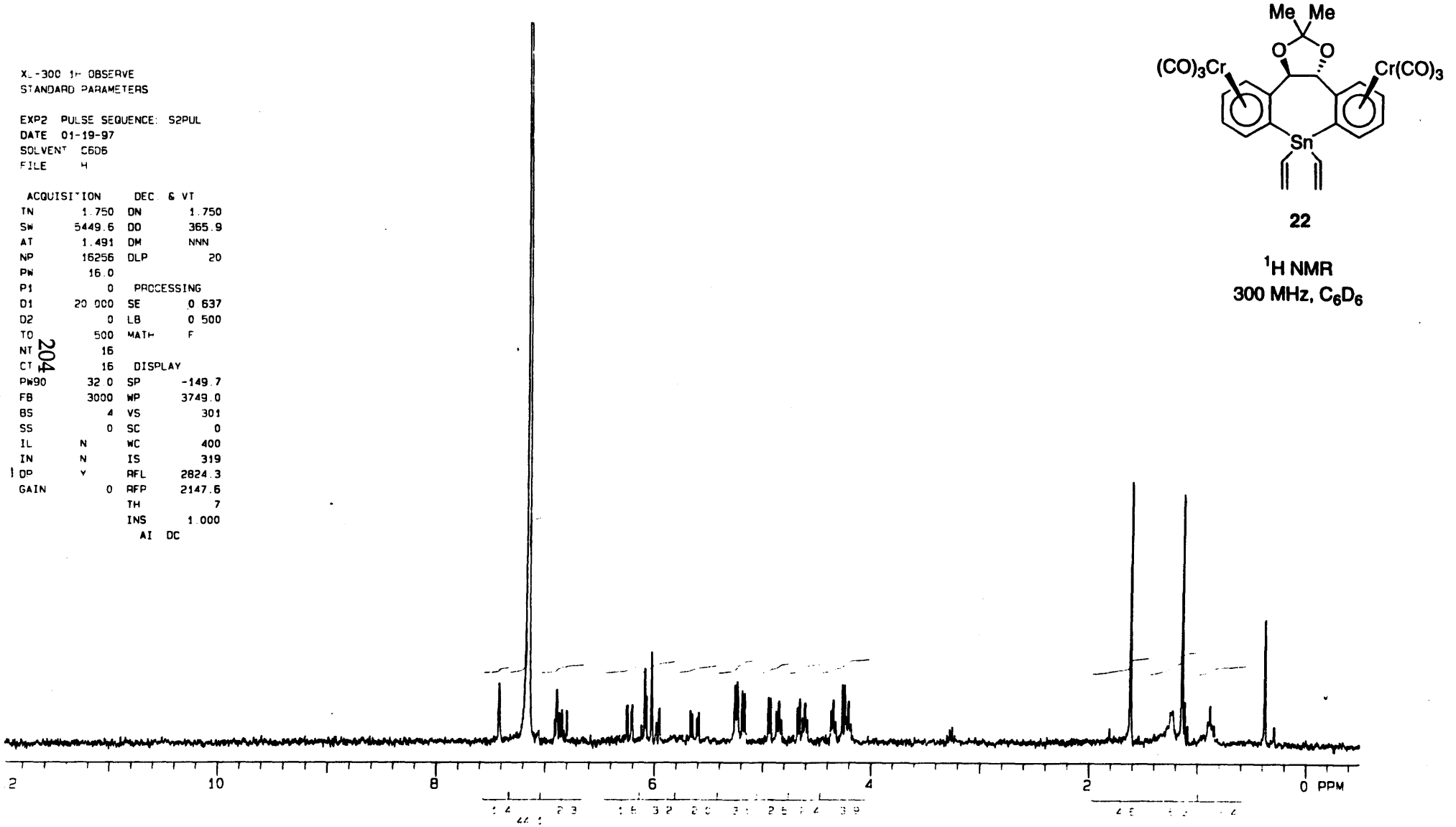

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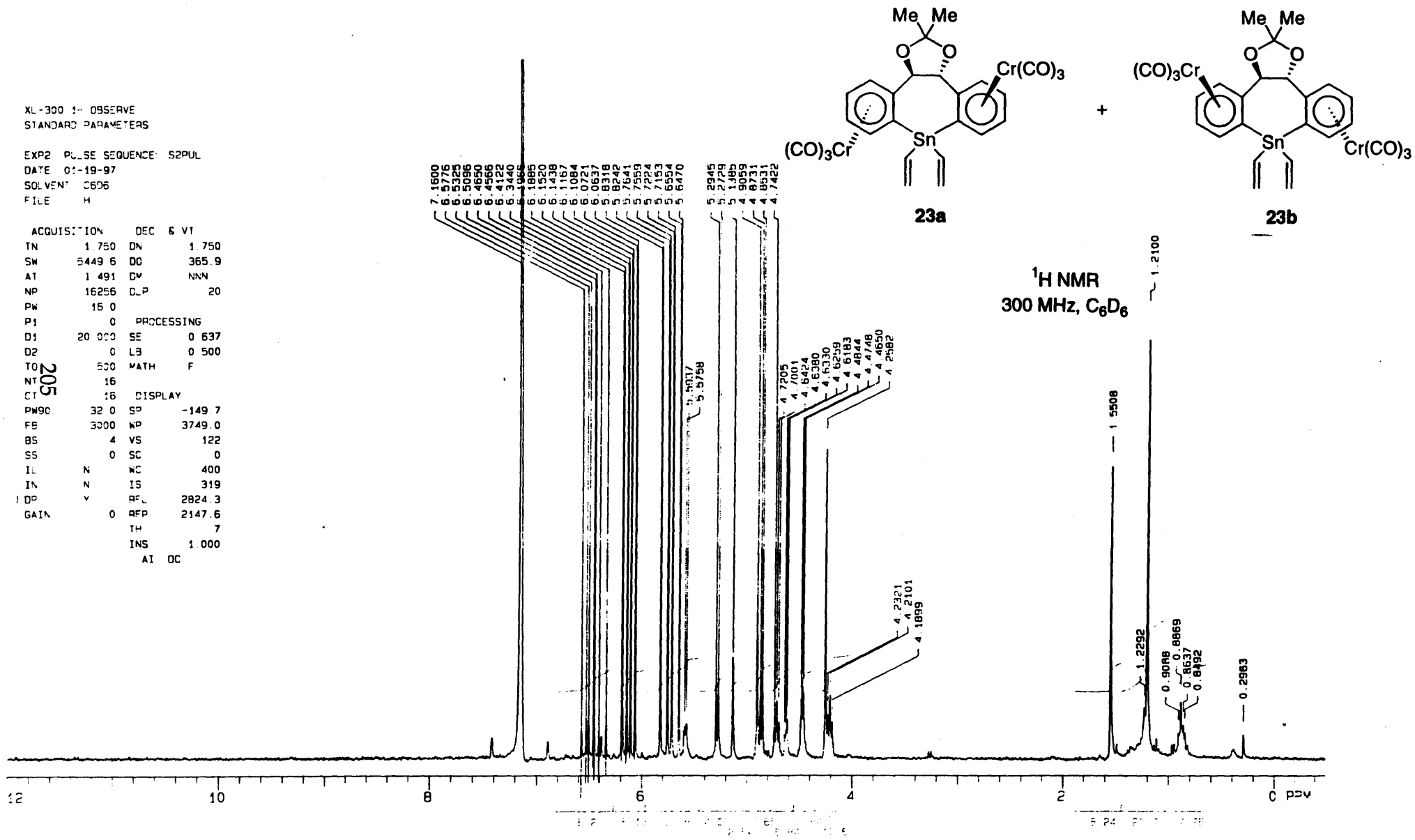
^{1}H NMR
300 MHz, C_6D_6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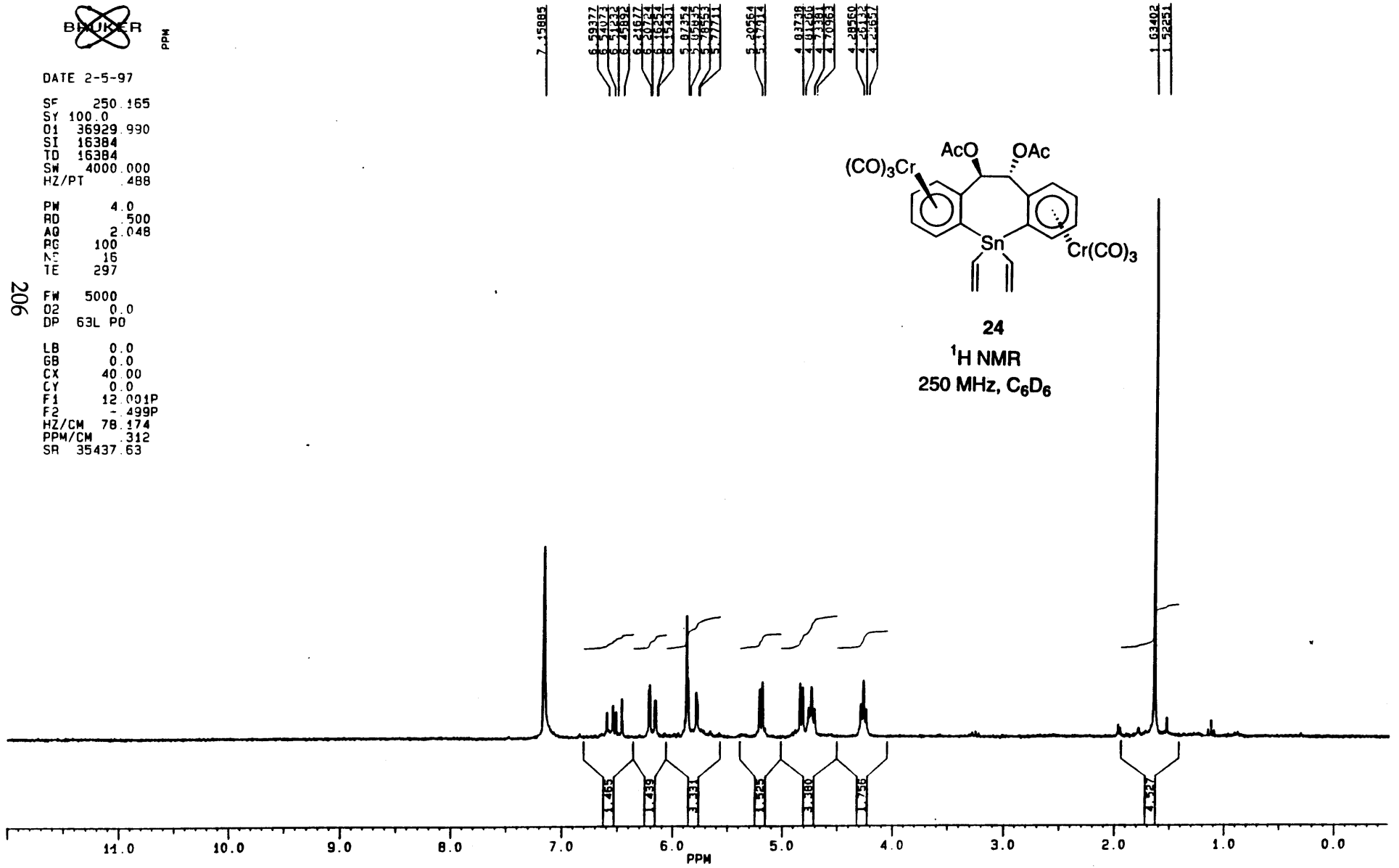
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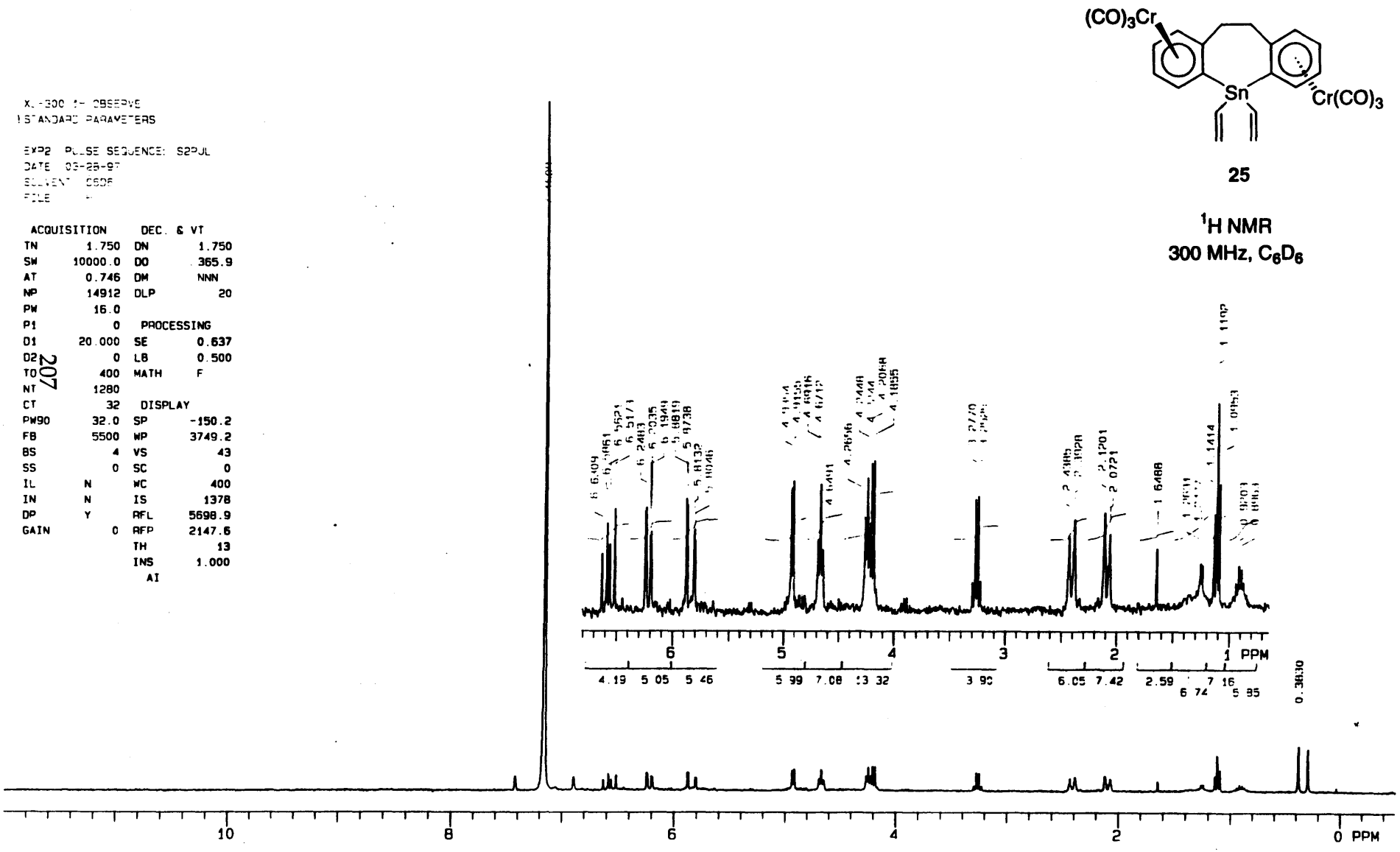
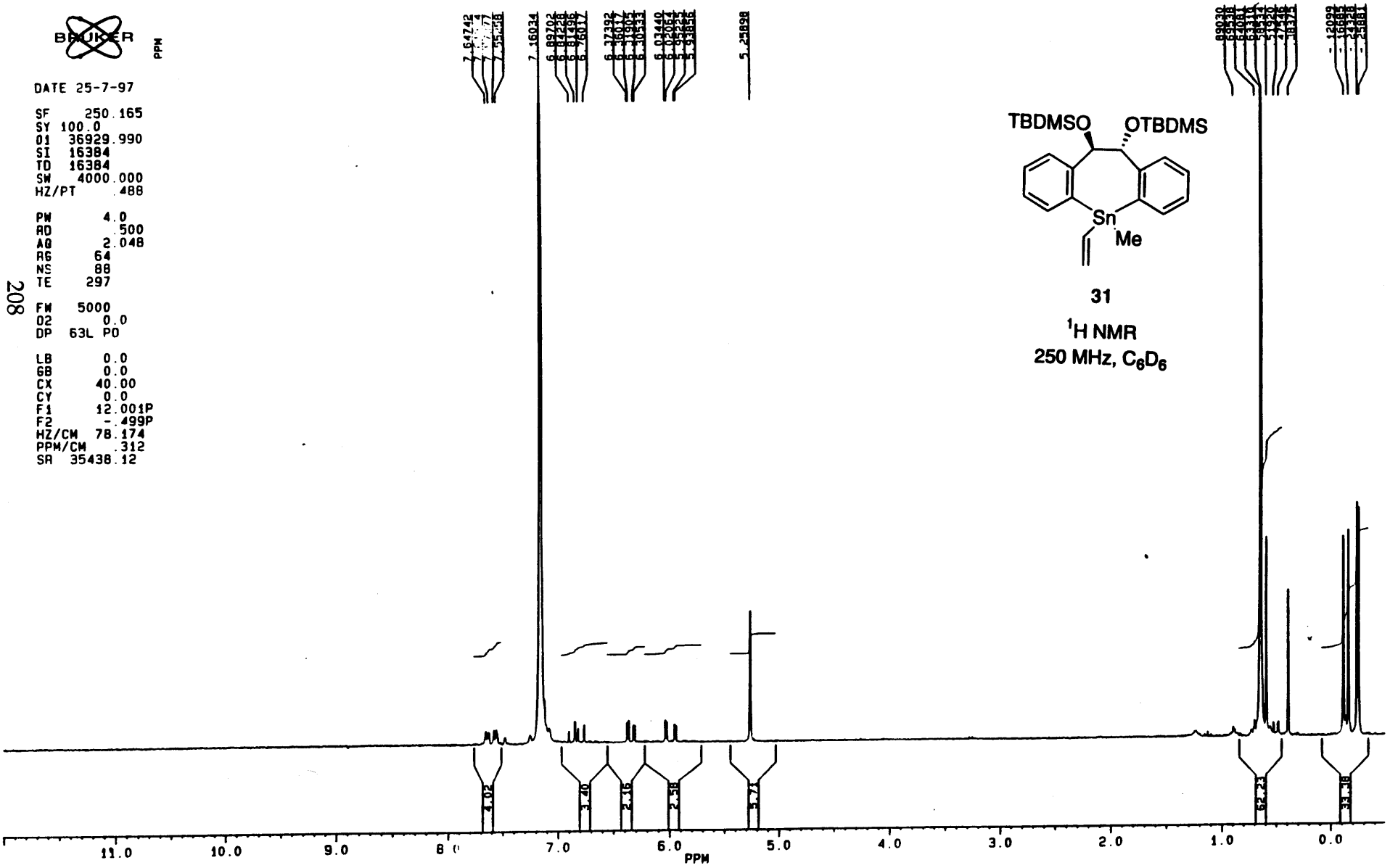
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35437.63
7.15885
6.59377
6.54073
6.51232
6.45892
6.21677
6.20724
6.16254
6.15431
5.87354
5.85835
5.78553
5.77711
5.20564
5.17914
4.83738
4.81466
4.71381
4.70963
4.28560
4.26132
4.25657
1.63402
1.52251
AcO
OAc
(CO)3Cr
Sn
Cr(CO)3
24
1H NMR
250 MHz, C6D6
1.465
1.439
3.331
1.525
3.380
1.756
4.527
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

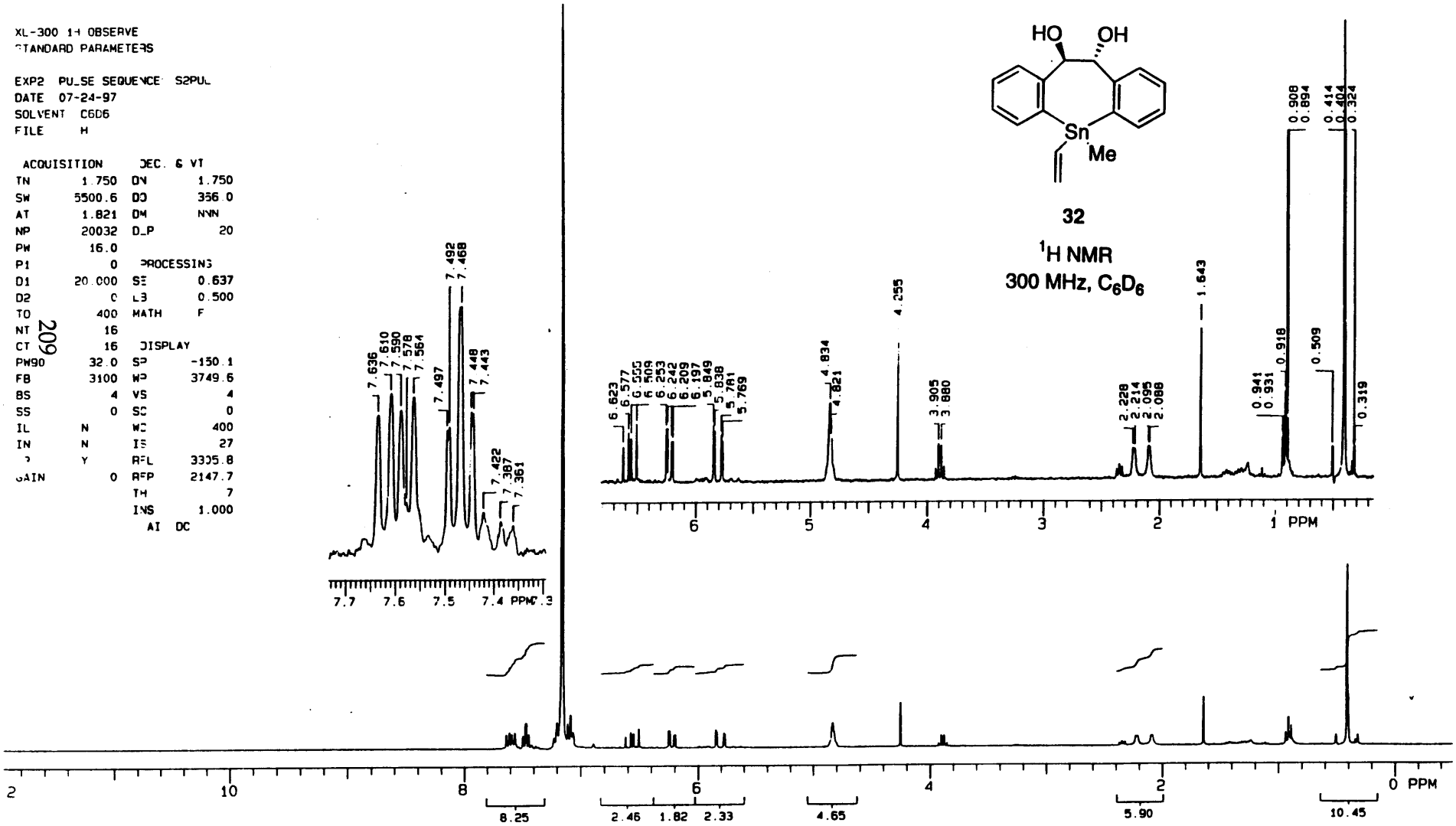

(CO)3Cr
Sn
Cr(CO)3
25
1H NMR
300 MHz, C6D6
X-300 1H OBSERVE
STANDARD PARAMETERS
EXP2 PULSE SEQUENCE: S2PUL
DATE 08-28-97
SOLVENT C6D6
FILE
ACQUISITION
TN 1.750
SW 10000.0
AT 0.746
NP 14912
PW 16.0
P1 0
D1 20.000
D2 0
TO 400
NT 1280
CT 32
PW90 32.0
FB 5500
BS 4
SS 0
IL N
IN N
DP Y
GAIN 0
DEC. & VT
DN 1.750
DO 365.9
DM NNN
DLP 20
PROCESSING
SE 0.637
LB 0.500
MATH F
DISPLAY
SP -150.2
WP 3749.2
VS 43
SC 0
WC 400
IS 1378
RFL 5698.9
RFP 2147.6
TH 13
INS 1.000
AI
207
PPM
4.19 5.05 5.46
5.99 7.08 13.32
3.90
6.05 7.42
2.59 7.16
6.74 5.85
0.3830

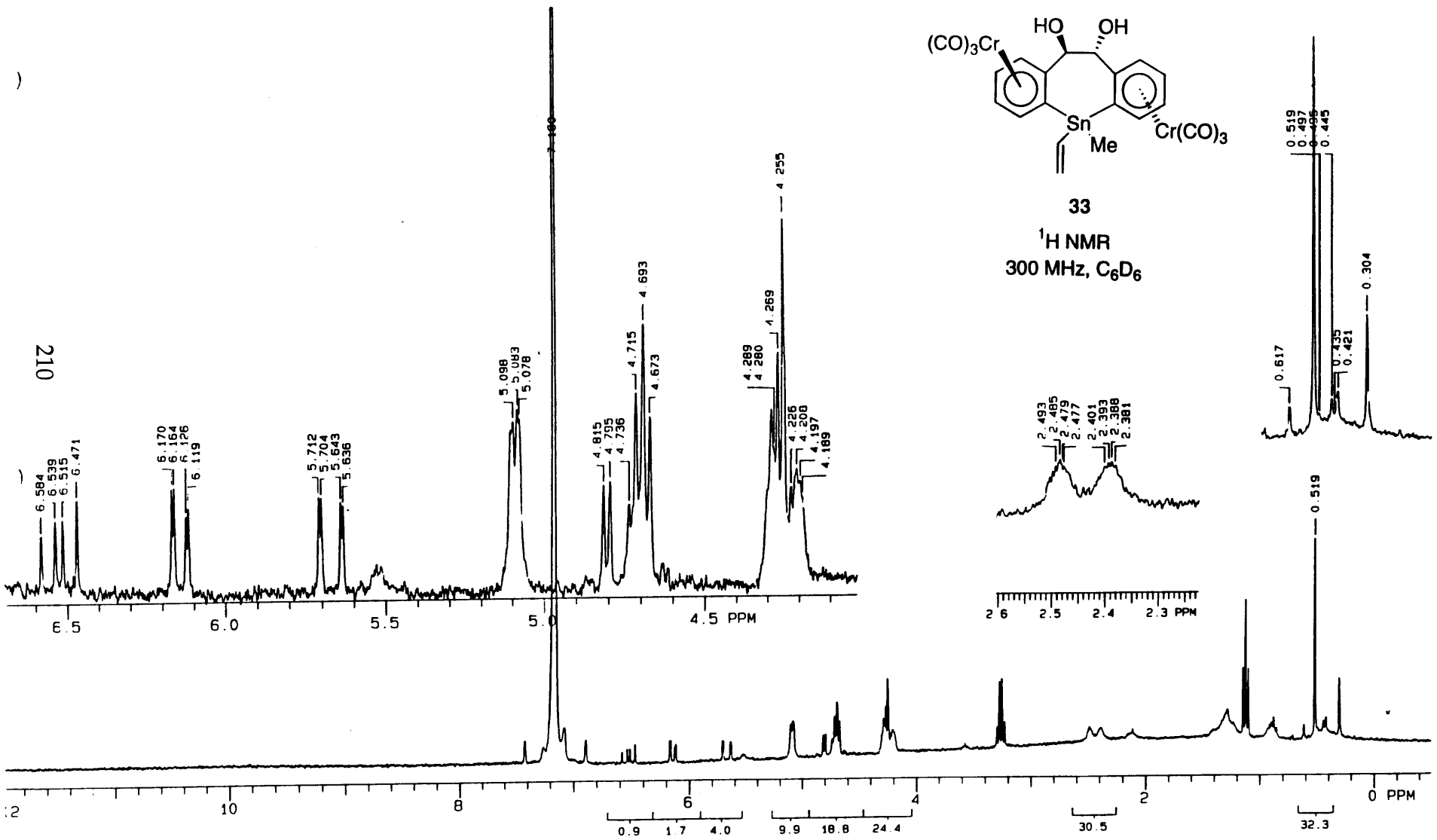


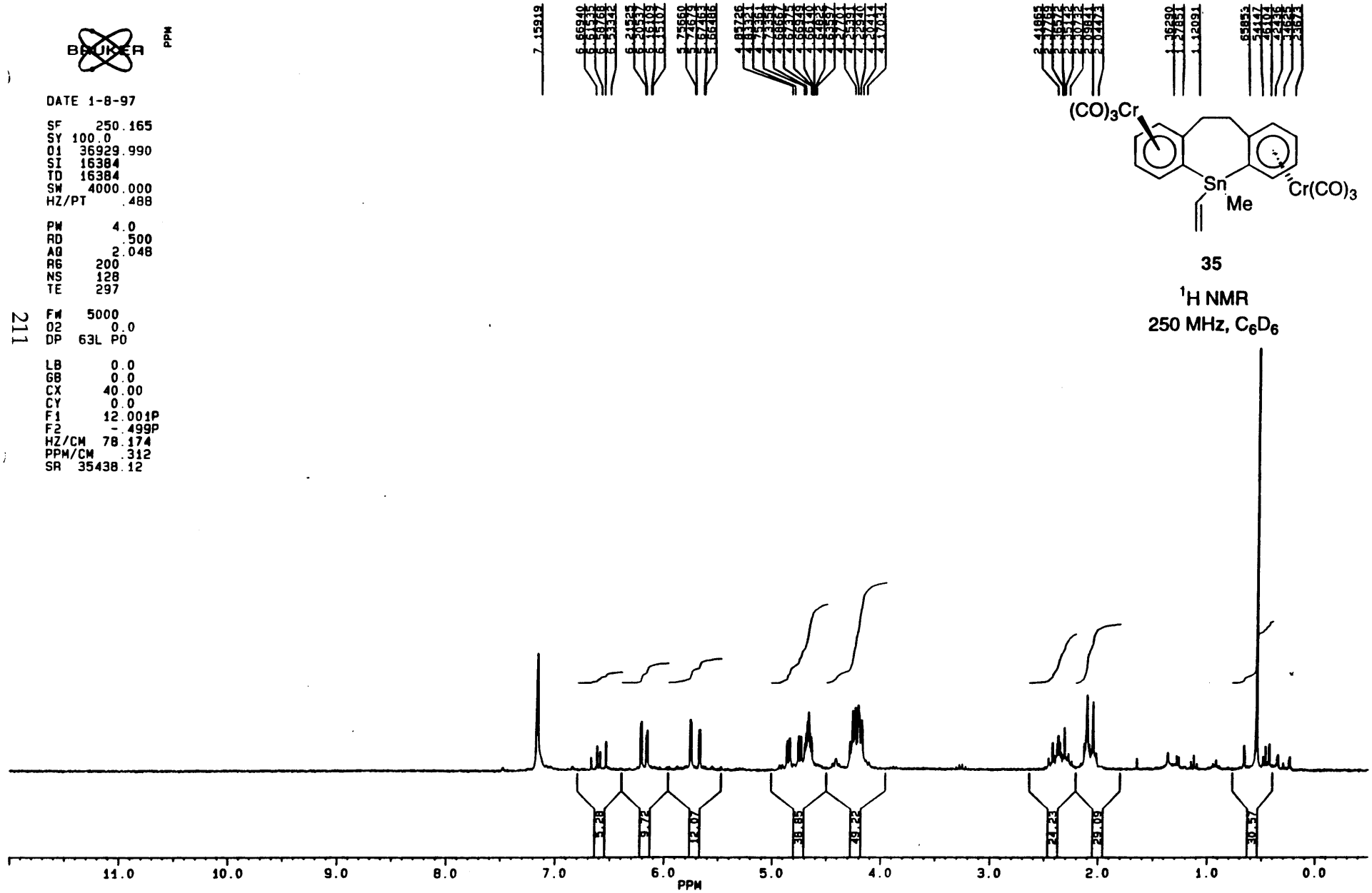
31

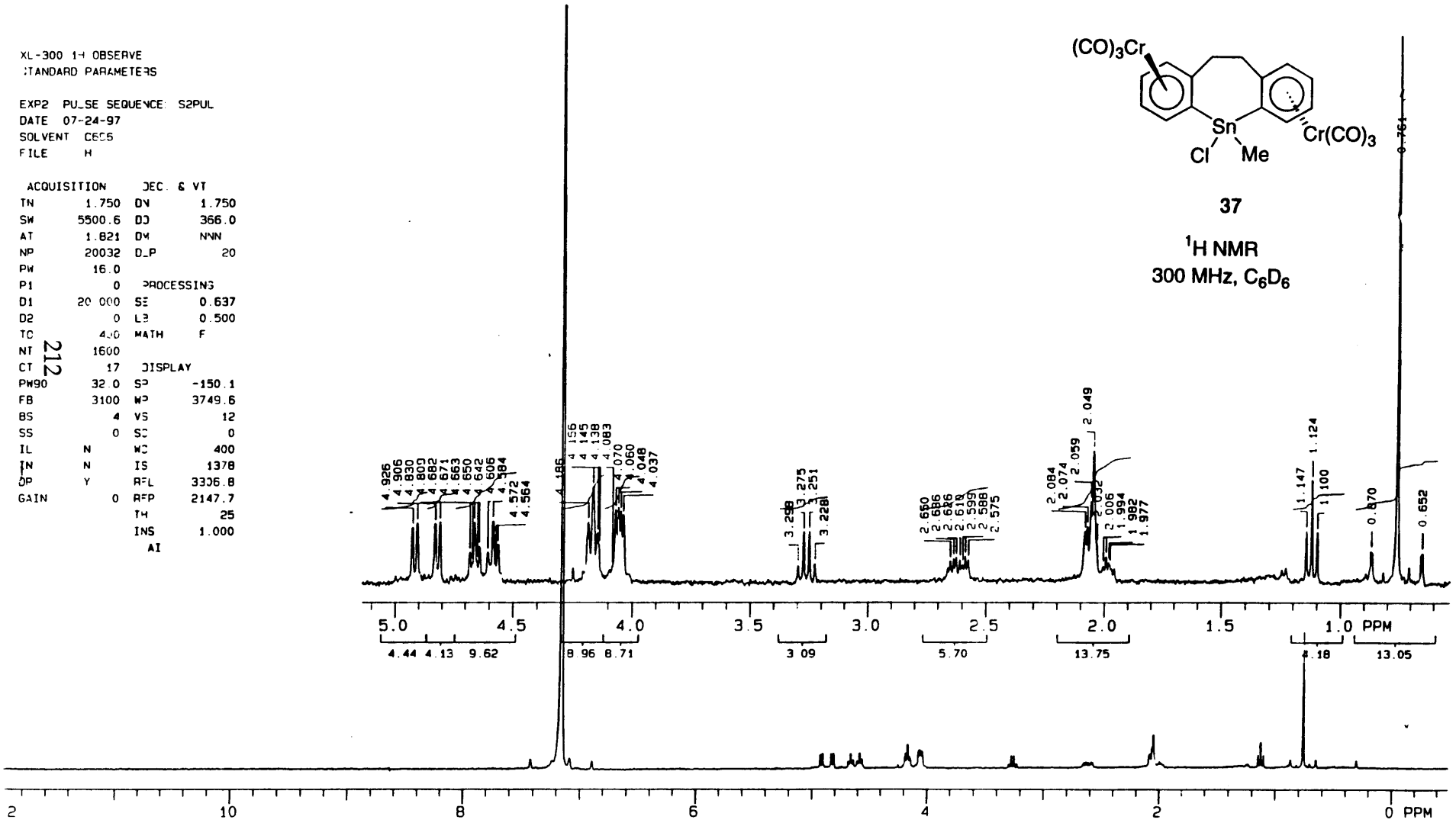
^{1}H NMR

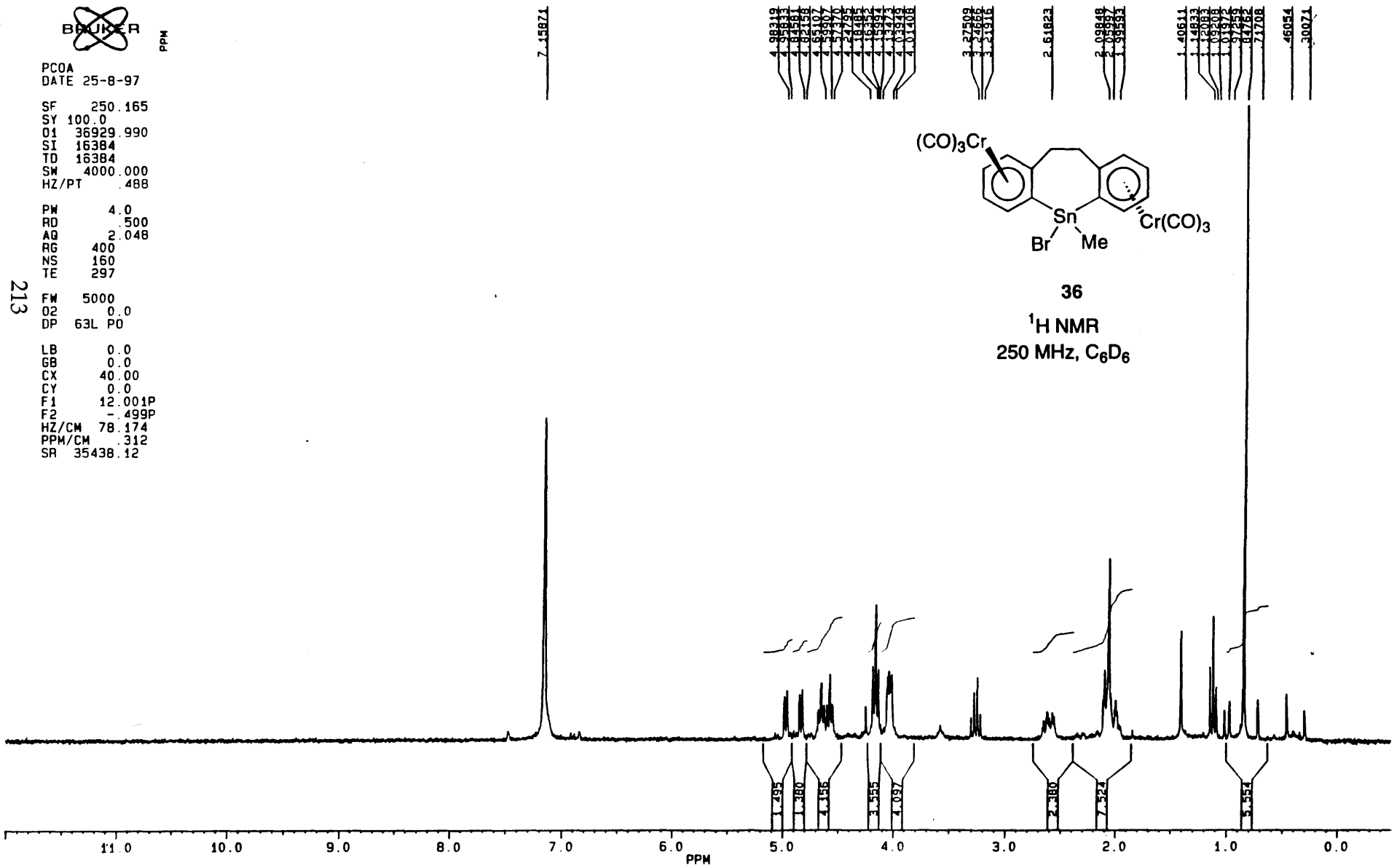
250 MHz, C_6D_6

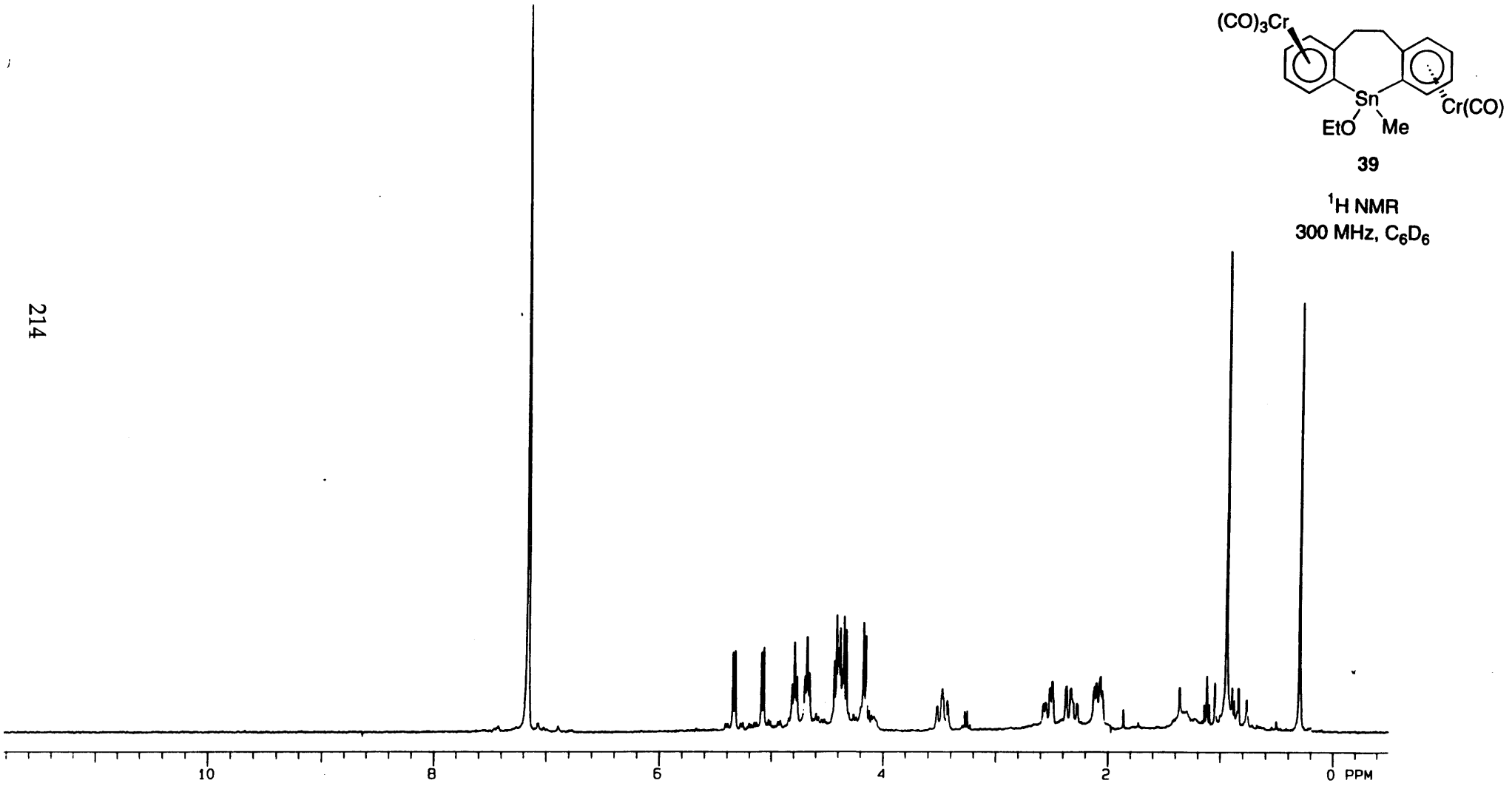

XL-300 1H OBSERVE
STANDARD PARAMETERS
EXP2 PULSE SEQUENCE S2PUL
DATE 07-24-97
SOLVENT C6D6
FILE H
ACQUISITION
TN 1.750
SW 5500.6
AT 1.821
NP 20032
PW 16.0
P1 0
D1 20.000
D2 0
TO 400
NT 16
CT 16
PW90 32.0
FB 3100
BS 4
SS 0
IL N
IN N
GAIN 0
DEC. & VT
DN 1.750
DO 356.0
DM NNN
D_P 20
PROCESSING
SF 0.637
LB 0.500
MATH F
DISPLAY
SP -150.1
WP 3749.6
VS 4
SC 0
WC 400
IS 27
RFL 3335.8
RFP 2147.7
TH 7
INS 1.000
AI DC
209
HO
OH
Sn
Me
32
1H NMR
300 MHz, C6D6
7.636
7.610
7.590
7.578
7.564
7.497
7.492
7.468
7.448
7.443
7.422
7.387
7.361
6.623
6.577
6.555
6.509
6.253
6.242
6.209
6.197
5.849
5.838
5.781
5.769
4.834
4.821
4.255
3.905
3.880
2.228
2.214
2.095
2.088
1.643
0.941
0.931
0.918
0.908
0.894
0.509
0.414
0.404
0.324
0.319
PPM
8.25
2.46
1.82
2.33
4.65
5.90
10.45

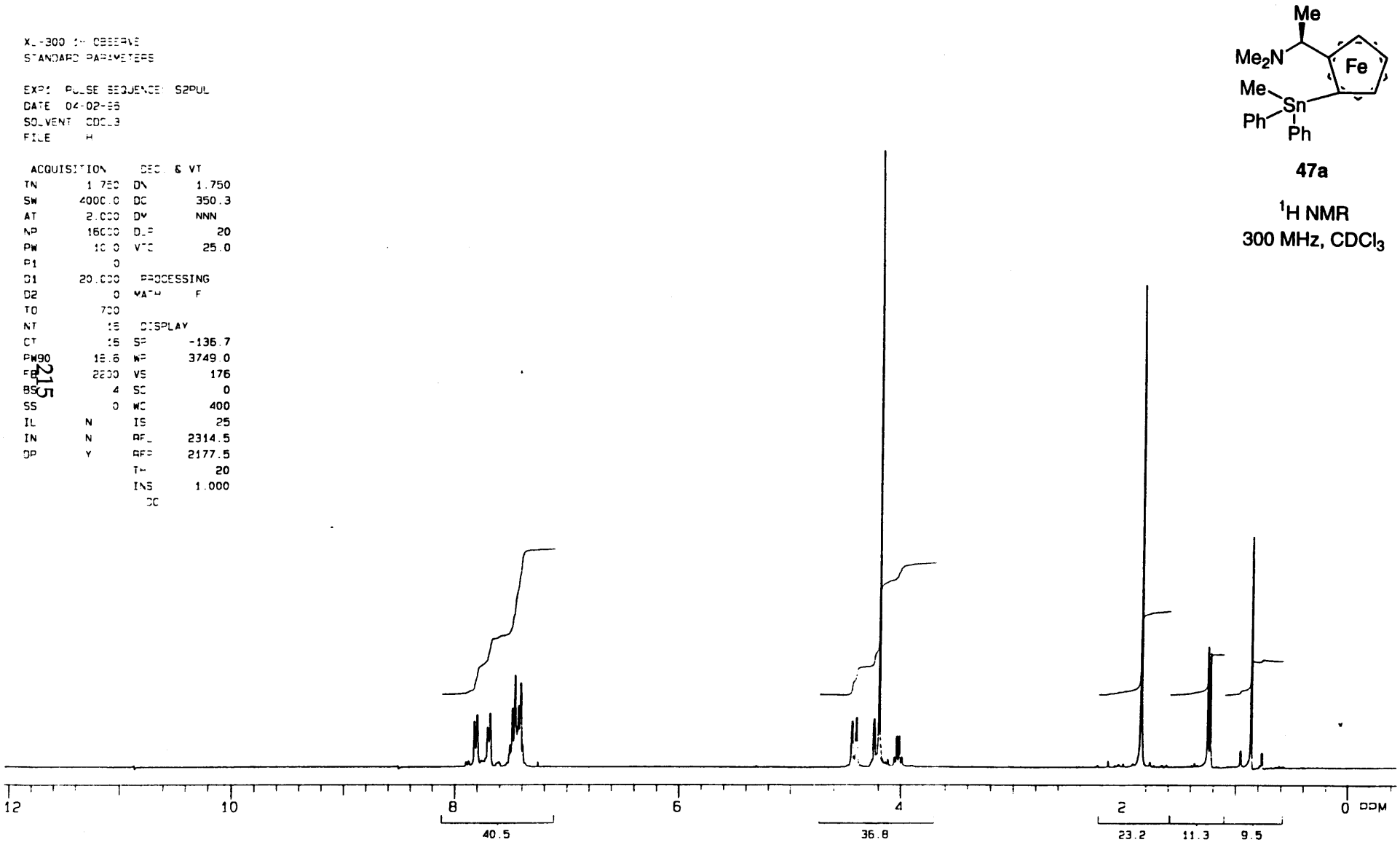

HO
OH
(CO)3Cr
Sn
Me
Cr(CO)3
33
1H NMR
300 MHz, C6D6
6.584
6.539
6.515
6.471
6.170
6.164
6.126
6.119
5.712
5.704
5.643
5.636
5.098
5.083
5.078
4.815
4.795
4.736
4.715
4.693
4.673
4.289
4.280
4.269
4.255
4.226
4.208
4.197
4.189
2.493
2.485
2.479
2.477
2.401
2.393
2.388
2.381
0.617
0.519
0.497
0.435
0.421
0.304
6.5
6.0
5.5
5.0
4.5 PPM
2.6
2.5
2.4
2.3 PPM
12
10
8
6
4
2
0 PPM
0.9
1.7
4.0
9.9
18.8
24.4
30.5
32.3

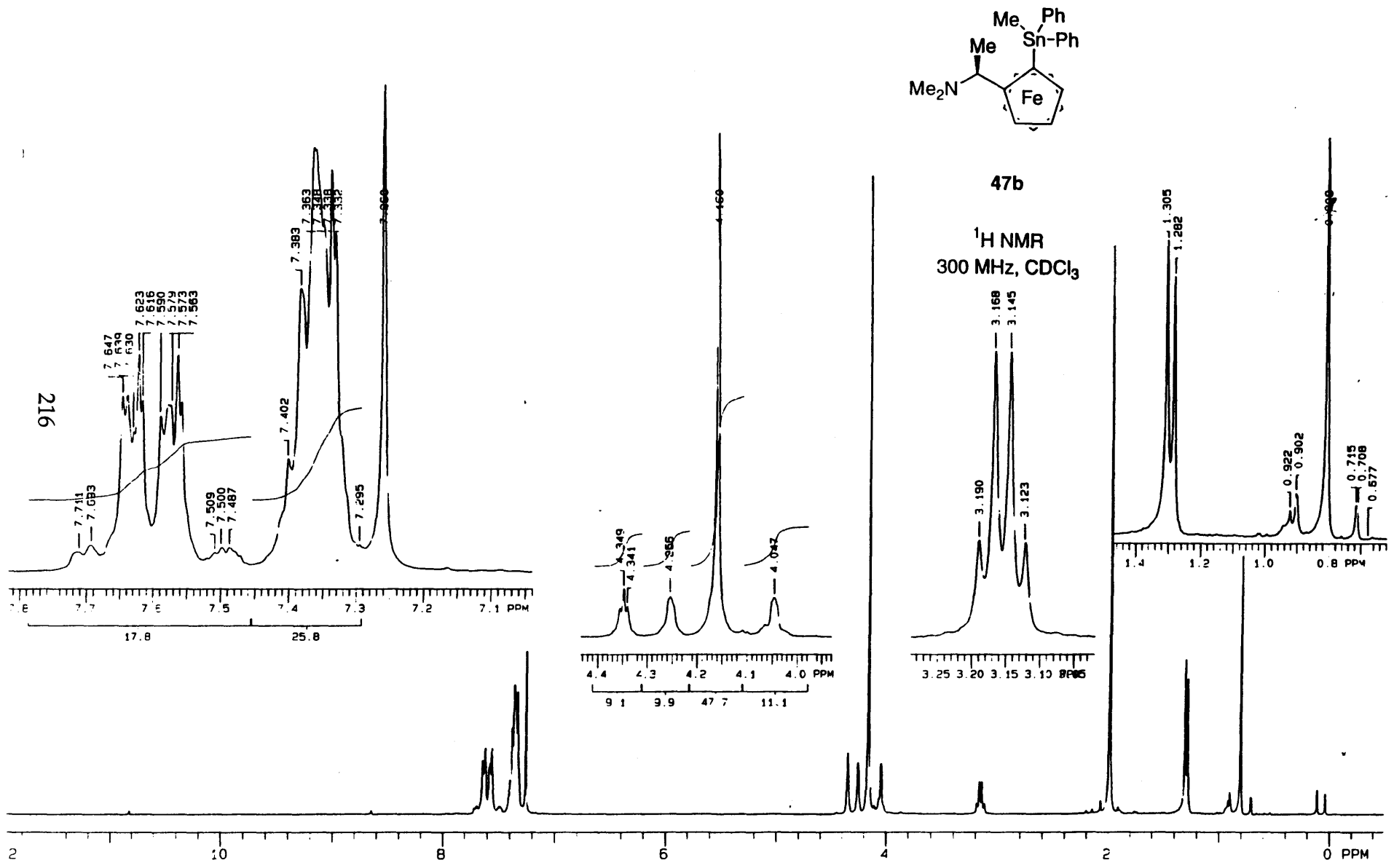

BRUKER
PPM
DATE 1-8-97
SF 250.165
SY 100.0
O1 36929.990
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 200
NS 128
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35438.12
(CO)3Cr
Sn
Me
Cr(CO)3
35
1H NMR
250 MHz, C6D6
5.28
9.72
12.07
38.85
49.22
24.23
29.09
30.57
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


XL-300 1H OBSERVE
STANDARD PARAMETERS
EXP2 PULSE SEQUENCE: S2PUL
DATE 07-24-97
SOLVENT C6D6
FILE H
ACQUISITION
TN 1.750
SW 5500.6
AT 1.821
NP 20032
PW 16.0
P1 0
D1 20.000
D2 0
TC 400
NT 1600
CT 17
PW90 32.0
FB 3100
BS 4
SS 0
IL N
IN N
DP Y
GAIN 0
DEC. & VT
DN 1.750
DO 366.0
DM NNN
DP 20
PROCESSING
SF 0.637
LB 0.500
MATH F
DISPLAY
SP -150.1
WP 3749.6
VS 12
SC 0
WC 400
IS 1378
RFL 3306.8
RFP 2147.7
TH 25
INS 1.000
AI
212
(CO)3Cr
Sn
Cl
Me
Cr(CO)3
37
1H NMR
300 MHz, C6D6
4.926
4.906
4.830
4.809
4.682
4.671
4.663
4.650
4.642
4.606
4.584
4.572
4.564
4.186
4.156
4.145
4.138
4.083
4.070
4.060
4.048
4.037
3.258
3.275
3.251
3.228
2.650
2.636
2.626
2.619
2.599
2.588
2.575
2.084
2.074
2.059
2.049
2.032
2.006
1.994
1.982
1.977
1.147
1.124
1.100
0.870
0.764
0.652
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0 PPM
4.44 4.13 9.62
8.96 8.71
3.09
5.70
13.75
4.18
13.05
2
10
8
6
4
2
0 PPM


BRUKER
PPM
PCOA
DATE 25-8-97
SF 250.165
SY 100.0
O1 36929.990
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 400
NS 160
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35438.12
7.15871
2.61823
1.40611
1.14833
1.12083
1.09208
1.01972
.97259
.84782
.21708
.46054
.30021
(CO)3Cr
Sn
Br
Me
Cr(CO)3
36
1H NMR
250 MHz, C6D6
1.495
1.380
4.156
3.555
4.097
2.380
7.524
3.554
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


(CO)3Cr
Sn
EtO
Me
Cr(CO)
39
1H NMR
300 MHz, C6D6
10
8
6
4
2
0 PPM


XL-300 1H OBSERVE
STANDARD PARAMETERS
EXP1 PULSE SEQUENCE: S2PUL
DATE 04-02-96
SOLVENT CDCL3
FILE H
ACQUISITION
TN 1.750
SW 4000.0
AT 2.000
NP 16000
PW 10.0
P1 0
D1 20.000
D2 0
TO 700
NT 16
CT 16
PW90 18.6
FB 2200
BS 4
SS 0
IL N
IN N
DP Y
DEC & VT
DN 1.750
DC 350.3
DM NNN
DLP 20
VTC 25.0
PROCESSING
MATH F
DISPLAY
SP -136.7
WP 3749.0
VS 176
SC 0
WC 400
IS 25
RFL 2314.5
RFP 2177.5
TH 20
INS 1.000
DC
215
Me
Me2N
Fe
Me
Sn
Ph
Ph
47a
1H NMR
300 MHz, CDCl3
12
10
8
6
4
2
0 PPM
40.5
36.8
23.2
11.3
9.5


Me
Ph
Sn-Ph
Me
Me_2N
Fe
47b
^{1}H NMR
300 MHz, $CDCl_3$
7.711
7.693
7.647
7.639
7.630
7.623
7.616
7.590
7.579
7.573
7.563
7.509
7.500
7.487
7.402
7.383
7.363
7.348
7.338
7.332
7.295
7.860
4.349
4.341
4.160
4.047
3.190
3.168
3.145
3.123
1.305
1.282
0.922
0.902
0.715
0.708
0.577
17.8
25.8
9.1
9.9
47.7
11.1
PPM

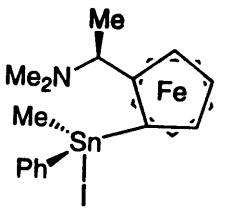
STANDARD PARAMETERS

EXP1 PULSE SEQUENCE: S2PUL
DATE 09-11-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-149.9
PW90	18.6	WP	3749.0
EB	2200	VS	200
GS	32	SC	0
SS	0	WC	400
IL	N	IS	14
IN	N	RFL	2332.3
DP	Y	RFP	2177.5
		TH	20
		INS	1.000
		DC	

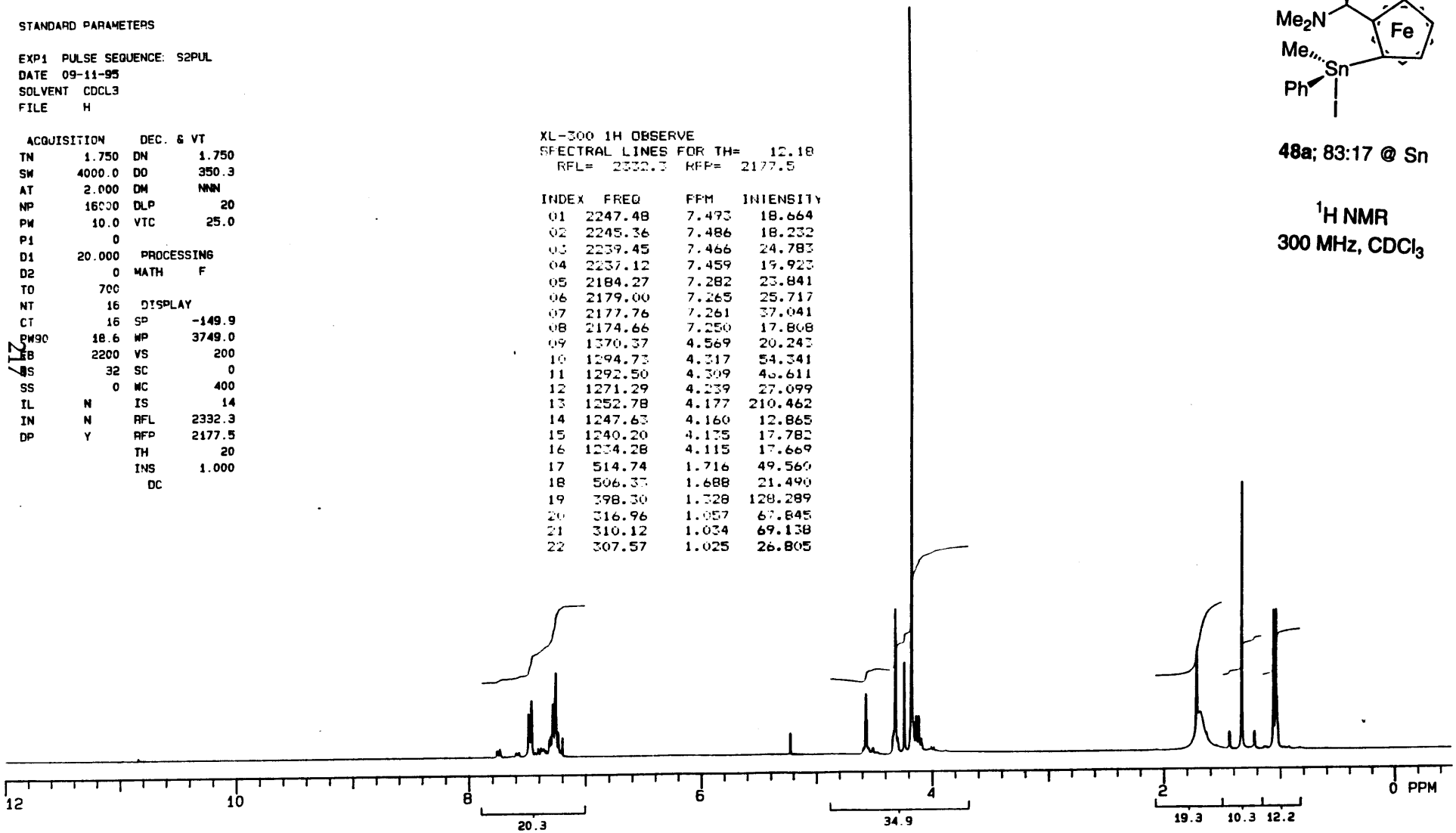
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 12.18
RFL= 2332.3 RFP= 2177.5

INDEX	FREQ	PPM	INTENSITY
01	2247.48	7.493	18.664
02	2245.36	7.486	18.232
03	2239.45	7.466	24.783
04	2237.12	7.459	19.923
05	2184.27	7.282	23.841
06	2179.00	7.265	25.717
07	2177.76	7.261	37.041
08	2174.66	7.250	17.808
09	1370.37	4.569	20.243
10	1294.73	4.317	54.341
11	1292.50	4.309	46.611
12	1271.29	4.239	27.099
13	1252.78	4.177	210.462
14	1247.63	4.160	12.865
15	1240.20	4.135	17.782
16	1234.28	4.115	17.669
17	514.74	1.716	49.560
18	506.33	1.688	21.490
19	398.30	1.328	128.289
20	316.96	1.057	67.845
21	310.12	1.034	69.138
22	307.57	1.025	26.805



48a; 83:17 @ Sn

^{1}H NMR
300 MHz, $CDCl_3$

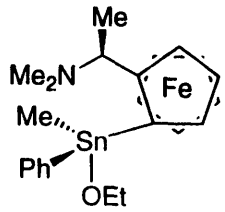


XL-300 1H OBSERVE
STANDARD PARAMETERS

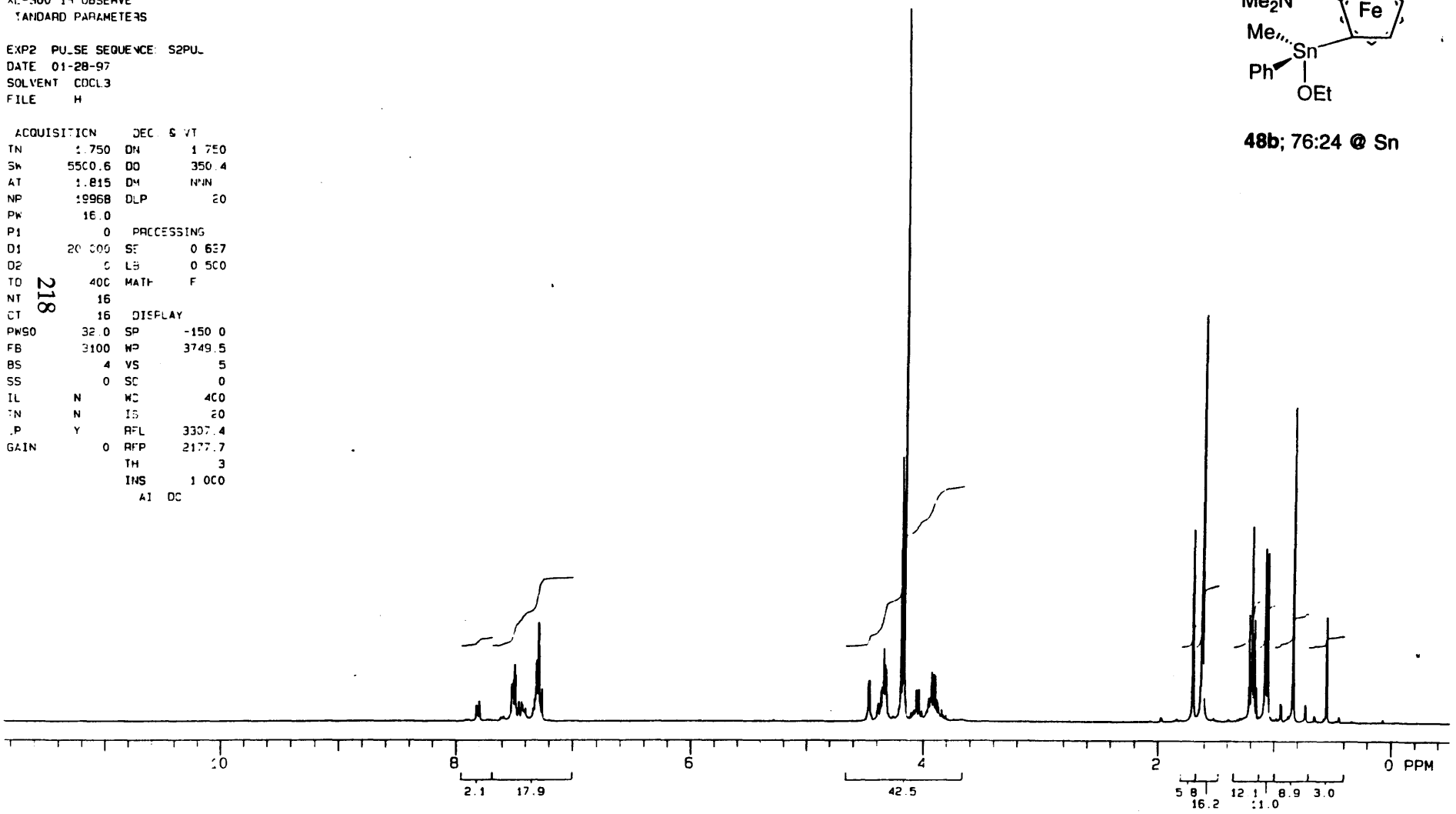
EXP2 PULSE SEQUENCE: S2PUL
DATE 01-28-97
SOLVENT CDCL3
FILE H

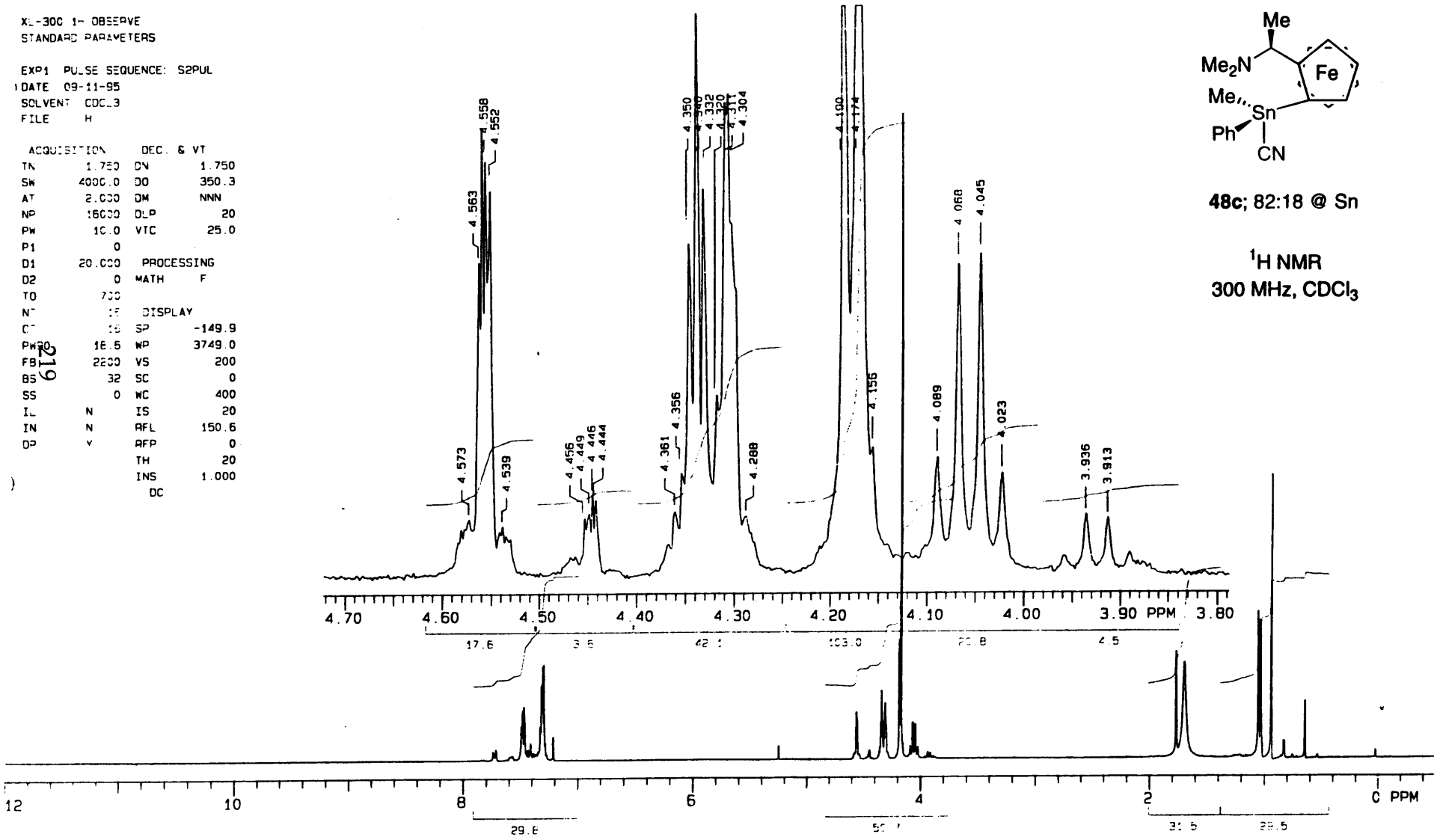
ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	5500.6	DO	350.4
AT	1.815	DM	NNN
NP	19968	DLP	20
PW	16.0		
P1	0	PROCESSING	
D1	20.000	SF	0.637
D2	0	LB	0.500
TD	400	MATH	F
NT	16		
CT	16	DISPLAY	
PWS0	32.0	SP	-150.0
FB	3100	WP	3749.5
BS	4	VS	5
SS	0	SC	0
IL	N	WC	400
IN	N	IS	20
LP	Y	RFL	3307.4
GAIN	0	RFP	2177.7
		TH	3
		INS	1.000
		AI DC	

218



48b; 76:24 @ Sn




XL-300 1H OBSERVE
STANDARD PARAMETERS
EXP1 PULSE SEQUENCE: S2PUL
DATE 09-11-95
SOLVENT CDCL3
FILE H
ACQUISITION
SW 4000.0
AT 2.000
NP 16000
PW 10.0
P1 0
D1 20.000
D2 0
TO 700
PW90 16.6
FB 2200
BS 32
SS 0
IN N
DP Y
DEC. & VT
DN 1.750
DO 350.3
DM NNN
DLP 20
VTC 25.0
PROCESSING
MATH F
DISPLAY
SP -149.9
WP 3749.0
VS 200
SC 0
WC 400
IS 20
RFL 150.6
RFP 0
TH 20
INS 1.000
DC
4.573
4.563
4.558
4.552
4.539
4.456
4.449
4.446
4.444
4.361
4.356
4.350
4.332
4.320
4.311
4.304
4.288
4.100
4.174
4.156
4.089
4.068
4.045
4.023
3.936
3.913
4.70
4.60
4.50
4.40
4.30
4.20
4.10
4.00
3.90 PPM
3.80
12
10
8
6
4
2
0 PPM
Me
Me2N
Fe
Me
Sn
Ph
CN
48c; 82:18 @ Sn
1H NMR
300 MHz, CDCl3

219

XL-300 1H OBSERVE
STANDARD PARAMETERS
EXP2 PULSE SEQUENCE: S2PUL
DATE 09-11-95
SOLVENT C6D6
FILE H
ACQUISITION
SW 4000.0
AT 2.000
NP 16000
PW 10.0
P1 0
D1 20.000
D2 0
TO 700
NT 16
CT 16
FB 2200
BS 32
SS 0
IL N
IN N
DP Y
DEC. & VT
DO 365.9
DM NNN
DLP 20
VTC 25.0
PROCESSING
MATH F
DISPLAY
SP -149.9
WP 3749.0
VS 200
SC 0
WC 400
IS 19
RFL 166.2
RFP 0
TH 20
INS 1.000
DC
220
Me
Fe
NMe2
Me
Sn
Ph
H
48d; 81:19 @ Sn
1H NMR
300 MHz, CDCl3
2.955
2.948
2.937
2.906
2.810
2.787
3.00
2.90
2.80 PPM
9.441
9.435
9.430
9.423
9.295
9.290
9.280
9.45
9.40
9.35
9.30
9.25 PPM
0.924
0.883
0.880
0.98
0.96
0.94
0.92
0.90
0.88
0.86
0.84 PPM
12
10
8
6
4
2
0 PPM

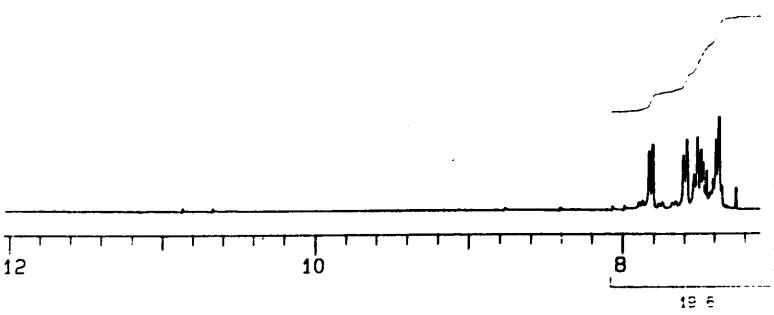
XL-300 1H OBSERVE
STANDARD PARAMETERS

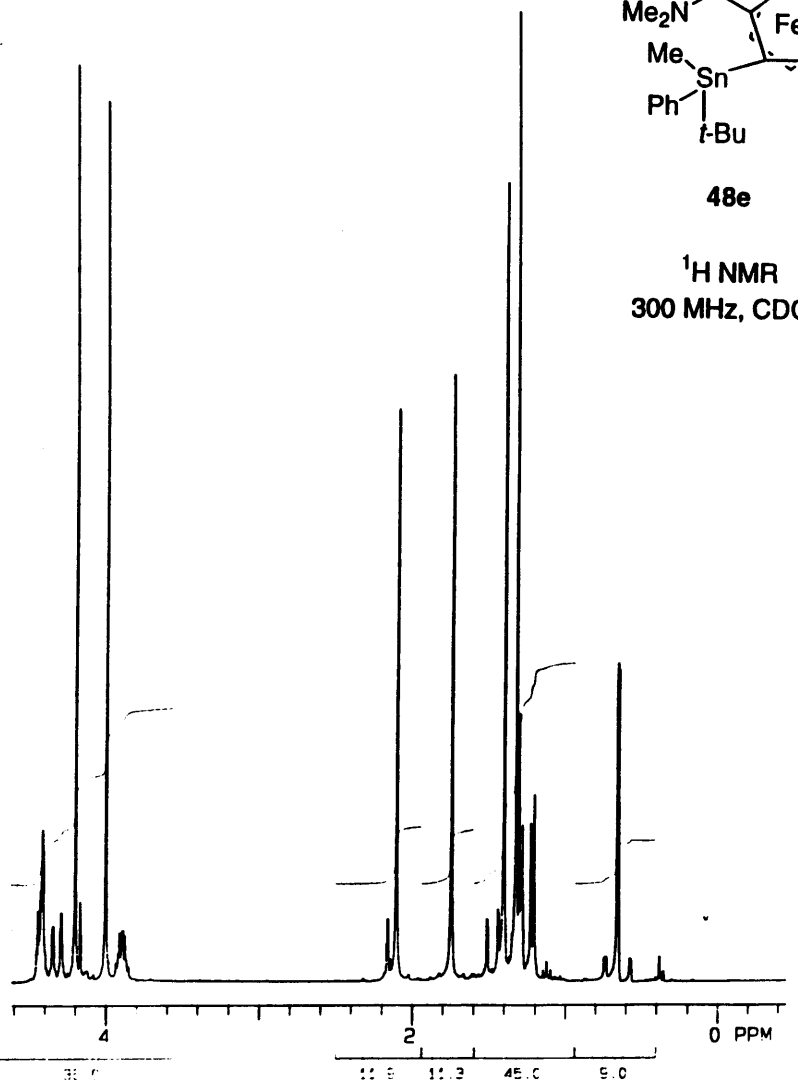
EXP2 PULSE SEQUENCE: S2PUL
DATE 11-08-95
SOLVENT CDCL3
FILE H

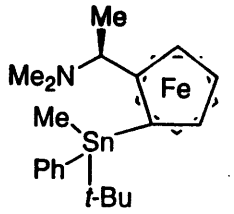
ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TC	700		
NT	15	DISPLAY	
CT	16	SP	-136.7
PA	18.6	WP	3749.0
FB	2200	VS	203
BS	32	SC	0
SS	0	WC	400
IL	N	IS	16
IN	N	RFL	2314.5
DP	Y	RFP	2177.5
		TH	10
		INS	1.000
		DC	

221

01	2409.09	7.813	12.851
02	2348.93	7.813	12.215
03	2342.48	7.814	15.913
04	2341.12	7.805	10.783
05	2282.74	7.611	11.289
06	2281.00	7.605	10.027
07	2275.62	7.587	15.786
08	2267.30	7.559	11.221
09	2259.06	7.531	15.859
10	2251.79	7.494	11.793
11	2245.45	7.480	10.191
12	2210.48	7.364	13.454
13	2211.49	7.370	20.051
14	1338.62	4.446	15.743
15	1331.01	4.438	15.215
16	1327.59	4.426	19.041
17	1324.94	4.417	27.636
18	1322.7	4.410	20.688
19	1305.73	4.353	10.891
20	1302.44	4.343	11.847
21	1288.80	4.297	11.196
22	1287.66	4.293	14.715
23	1259.50	4.199	214.891
24	1250.22	4.168	19.009
25	1249.86	4.164	11.618
26	1199.92	4.001	212.674
27	1173.93	3.914	10.188
28	1170.08	3.901	12.625
29	1166.93	3.891	10.608
30	1161.34	3.873	9.185
31	648.04	2.161	13.631
32	630.14	2.101	140.264
33	522.19	1.741	136.744
34	458.36	1.512	13.905
35	451.84	1.506	11.962
36	432.35	1.441	16.180
37	430.78	1.436	15.004
38	420.26	1.401	202.620
39	404.14	1.347	9.849
40	396.60	1.322	221.506
41	390.90	1.303	57.866
42	388.73	1.296	19.817
43	386.34	1.288	29.061
44	384.72	1.283	34.517
45	368.49	1.229	34.788
46	361.66	1.206	41.336
47	196.92	0.657	74.917
48	194.16	0.647	69.610

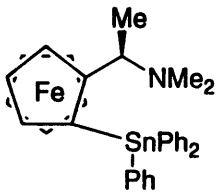






48e

^{1}H NMR
300 MHz, $CDCl_3$



51a

^{1}H NMR
300 MHz, $CDCl_3$

XL-300 1H OBSERVE
STANDARD PARAMETERS

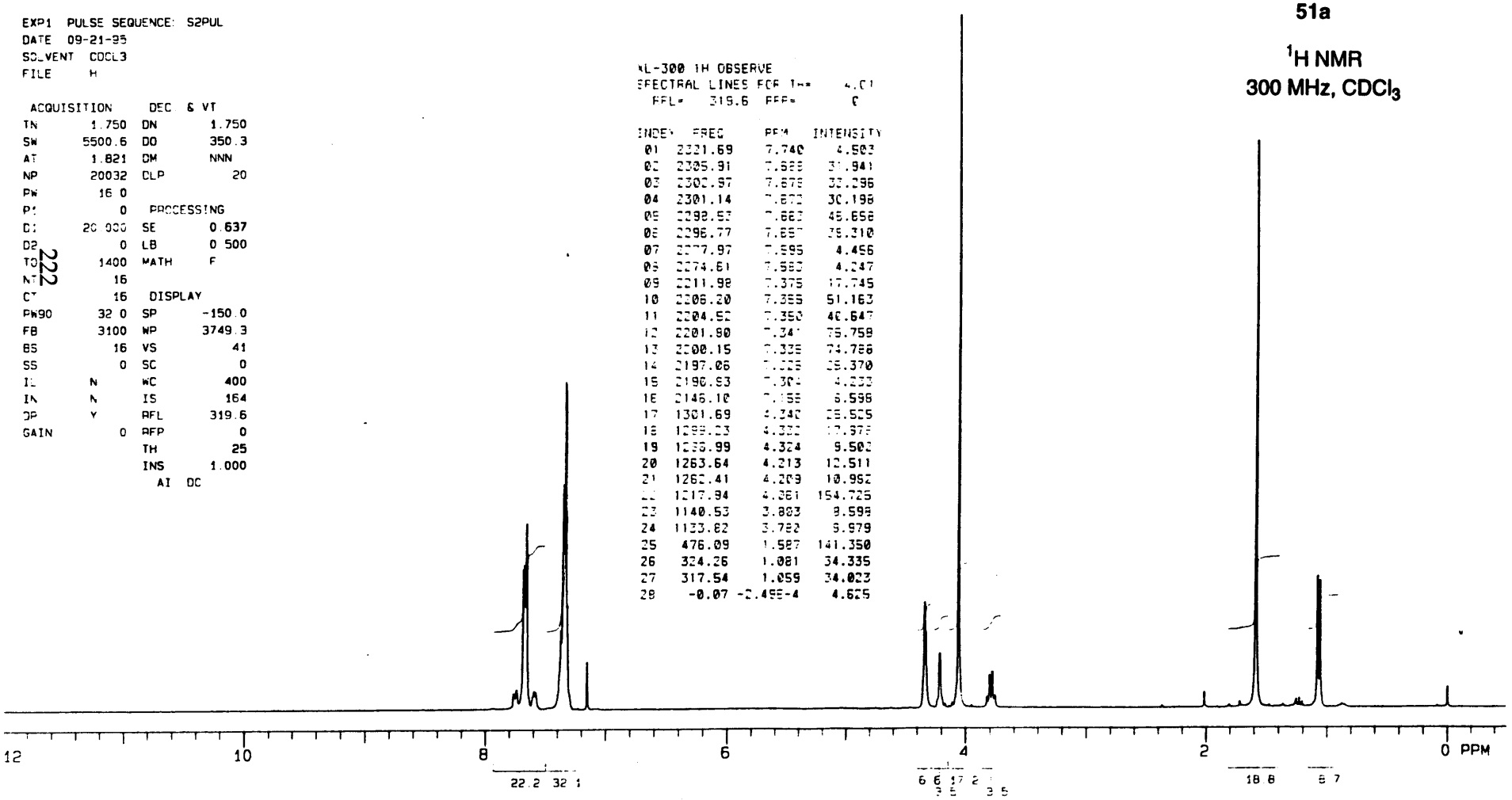
EXP1 PULSE SEQUENCE: S2PUL
DATE 09-21-95
SOLVENT CDCL3
FILE H

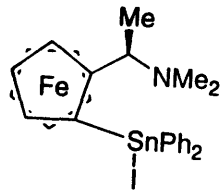
ACQUISITION		DEC & VT	
TN	1.750	DN	1.750
SW	5500.6	DO	350.3
AT	1.821	DM	NNN
NP	20032	DLP	20
PW	16.0		
P1	0	PROCESSING	
D1	20.000	SE	0.637
D2	0	LB	0.500
TO	1400	MATH	F
NT	16		
CT	16	DISPLAY	
PW90	32.0	SP	-150.0
FB	3100	WP	3749.3
BS	16	VS	41
SS	0	SC	0
IL	N	WC	400
IN	N	IS	164
DP	Y	RFL	319.6
GAIN	0	RFP	0
		TH	25
		INS	1.000
		AI DC	

222

XL-300 1H OBSERVE
SPECTRAL LINES FOR THE 4.01
RFL= 319.6 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2321.69	7.740	4.503
02	2305.91	7.688	31.941
03	2302.97	7.678	33.296
04	2301.14	7.672	30.198
05	2298.53	7.663	45.658
06	2296.77	7.657	38.310
07	2277.97	7.595	4.496
08	2274.61	7.583	4.247
09	2211.98	7.375	17.745
10	2206.20	7.355	51.163
11	2204.52	7.350	40.647
12	2201.80	7.341	75.758
13	2200.15	7.335	74.786
14	2197.06	7.325	25.370
15	2190.83	7.304	4.223
16	2146.10	7.155	6.598
17	1301.69	4.340	28.525
18	1299.23	4.332	17.979
19	1298.99	4.324	9.502
20	1263.64	4.213	12.511
21	1262.41	4.209	10.952
22	1217.94	4.061	154.725
23	1140.53	3.803	8.598
24	1133.82	3.782	8.979
25	476.09	1.587	141.350
26	324.26	1.081	34.335
27	317.54	1.059	34.023
28	-0.07	-2.49E-4	4.625





51b

^{1}H NMR
300 MHz, $CDCl_3$

XL-300 1H OBSERVE
STANDARD PARAMETERS

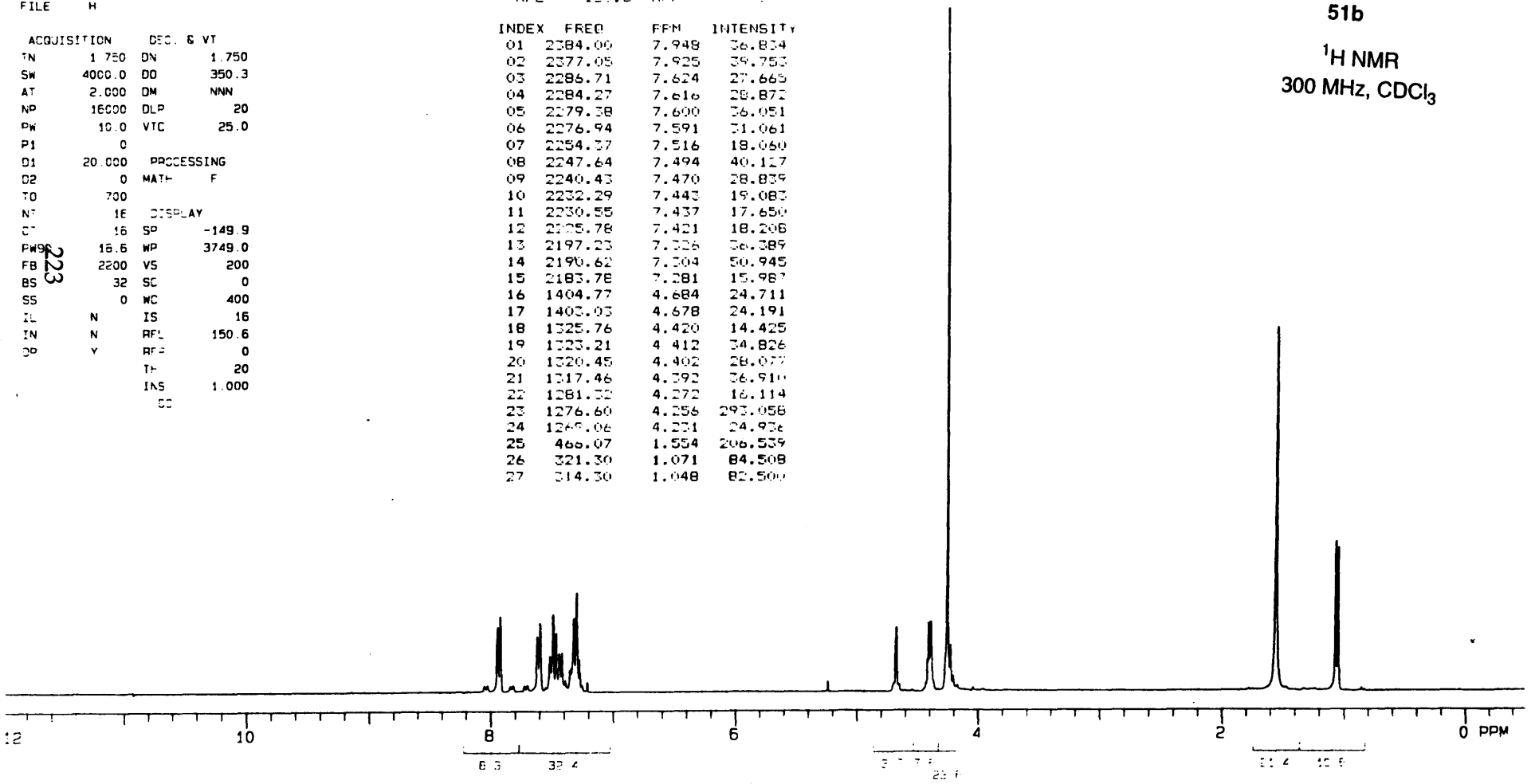
EXP2 PULSE SEQUENCE: S2PUL
DATE 09-20-95
SOLVENT CDCL3
FILE H

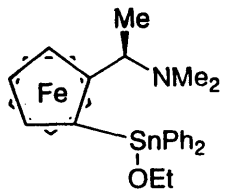
ACQUISITION		DEC. & VT	
TN	1 750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-149.9
PW90	16.6	WP	3749.0
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	16
IN	N	RFL	150.6
DP	Y	RFP	0
		TH	20
		INS	1.000
		DS	

223

XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 12.6
RFL= 150.6 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2384.00	7.948	36.834
02	2377.05	7.925	39.753
03	2286.71	7.624	27.665
04	2284.27	7.616	28.872
05	2279.38	7.600	36.051
06	2276.94	7.591	31.061
07	2254.37	7.516	18.060
08	2247.64	7.494	40.127
09	2240.43	7.470	28.839
10	2232.29	7.443	19.083
11	2230.55	7.437	17.650
12	2225.78	7.421	18.206
13	2197.23	7.326	36.389
14	2190.62	7.304	50.945
15	2183.78	7.281	15.987
16	1404.77	4.684	24.711
17	1403.03	4.678	24.191
18	1325.76	4.420	14.425
19	1323.21	4.412	34.826
20	1320.45	4.402	28.077
21	1317.46	4.392	36.910
22	1281.32	4.272	16.114
23	1276.60	4.256	293.058
24	1269.06	4.231	24.936
25	466.07	1.554	206.539
26	321.30	1.071	84.508
27	314.30	1.048	82.500





51c

^{1}H NMR
300 MHz, $CDCl_3$

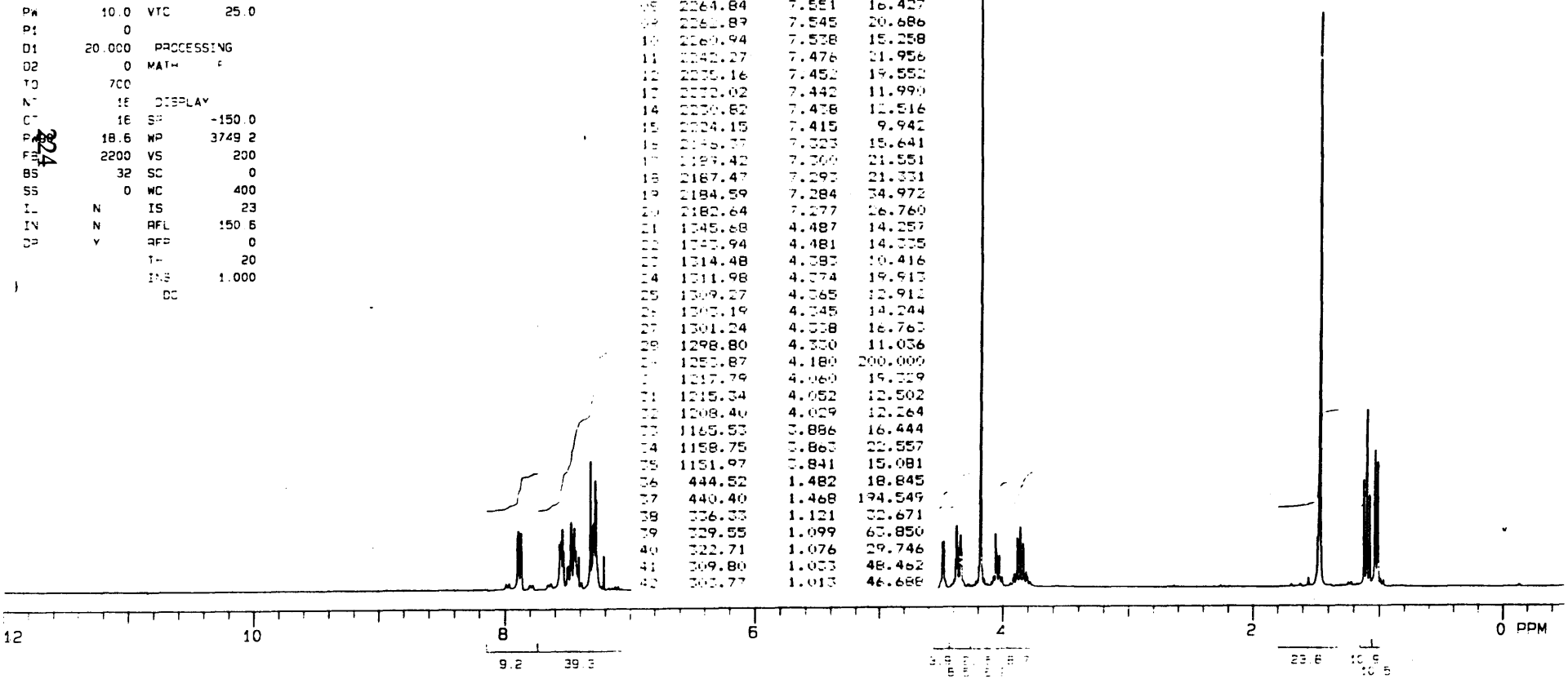
XL-300 1H OBSERVE
STANDARD PARAMETERS

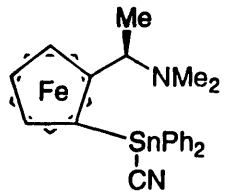
EXP2 PULSE SEQUENCE: S2PUL
DATE 09-20-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TD	700		
NT	16	DISPLAY	
CT	16	SP	-150.0
PW	18.6	WP	3749.2
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	23
IN	N	RFL	150.6
DP	Y	RFP	0
		TH	20
		INS	1.000
		DC	

300 1H OBSERVE
SPECTRAL LINES FOR TH= 9.49
RFL= 150.6 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2369.84	7.901	18.176
02	2367.29	7.893	19.796
03	2361.91	7.875	24.192
04	2359.47	7.867	17.937
05	2270.11	7.569	15.226
06	2268.37	7.563	11.147
07	2266.69	7.557	14.894
08	2264.84	7.551	16.427
09	2262.89	7.545	20.686
10	2260.94	7.538	15.258
11	2242.27	7.476	21.956
12	2235.16	7.452	19.552
13	2232.02	7.442	11.990
14	2230.82	7.438	12.516
15	2224.15	7.415	9.942
16	2196.37	7.323	15.641
17	2189.42	7.300	21.551
18	2187.47	7.293	21.331
19	2184.59	7.284	34.972
20	2182.64	7.277	26.760
21	1345.68	4.487	14.257
22	1343.94	4.481	14.335
23	1314.48	4.383	10.416
24	1311.98	4.374	19.913
25	1309.27	4.365	12.912
26	1303.19	4.345	14.244
27	1301.24	4.338	16.763
28	1298.80	4.330	11.036
29	1253.87	4.180	200.000
30	1217.79	4.060	19.329
31	1215.34	4.052	12.502
32	1208.40	4.029	12.264
33	1165.53	3.886	16.444
34	1158.75	3.863	22.557
35	1151.97	3.841	15.081
36	444.52	1.482	18.845
37	440.40	1.468	194.549
38	336.33	1.121	32.671
39	329.55	1.099	63.850
40	322.71	1.076	29.746
41	309.80	1.033	48.462
42	303.77	1.013	46.688





51d

^{1}H NMR

300 MHz, $CDCl_3$

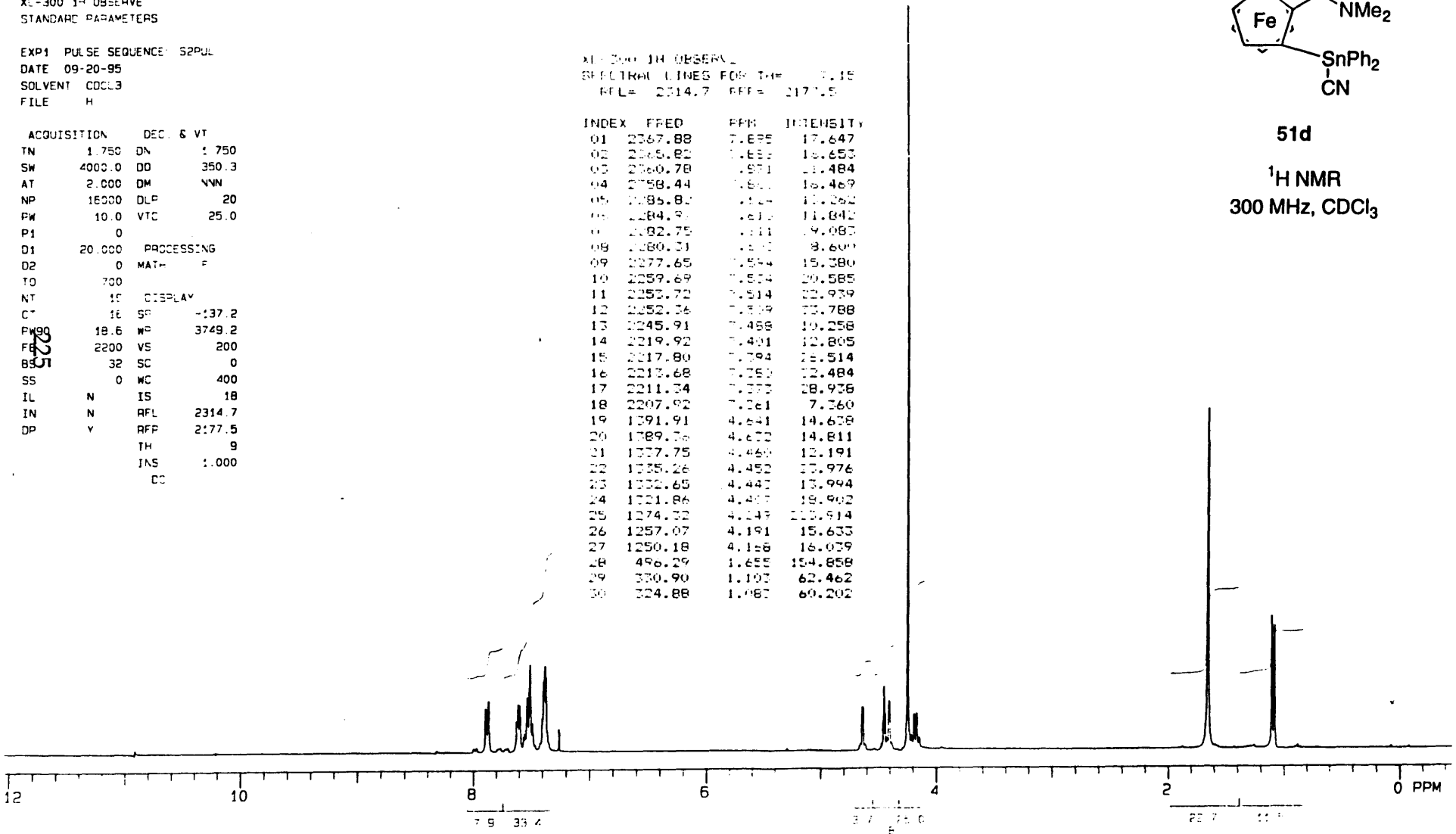
XL-300 1H OBSERVE
STANDARD PARAMETERS

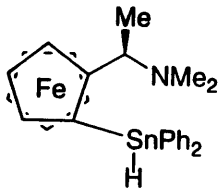
EXP1 PULSE SEQUENCE: S2PUL
DATE 09-20-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SR	-137.2
PW90	18.6	WP	3749.2
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	18
IN	N	RFL	2314.7
DP	Y	RFP	2177.5
		TH	9
		INS	1.000
		DC	

XL-300 1H OBSERVE
SPECTRAL LINES FOR THE [illegible] 7.15
RFL= 2314.7 RFP= 2177.5

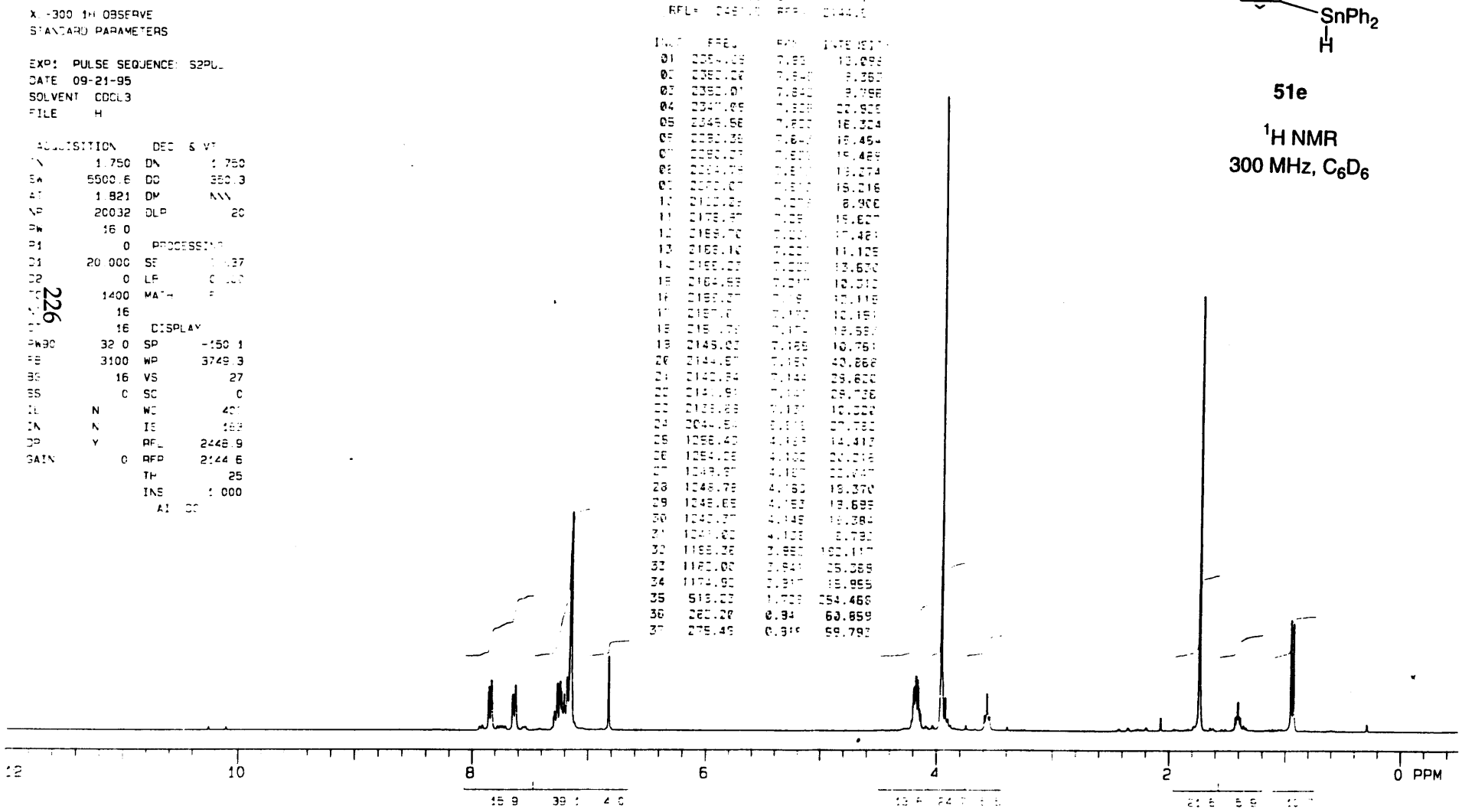
INDEX	FREQ	PPM	INTENSITY
01	2367.88	7.895	17.647
02	2365.82	7.888	16.653
03	2360.78	7.871	11.484
04	2358.44	7.863	16.469
05	2285.80	7.621	10.262
06	2284.91	7.618	11.842
07	2282.75	7.611	9.085
08	2280.31	7.603	8.607
09	2277.65	7.594	15.380
10	2259.69	7.534	20.585
11	2253.72	7.514	22.939
12	2252.36	7.509	23.788
13	2245.91	7.488	19.258
14	2219.92	7.401	12.805
15	2217.80	7.394	25.514
16	2213.68	7.380	22.484
17	2211.34	7.372	28.936
18	2207.92	7.361	7.360
19	1391.91	4.641	14.638
20	1389.36	4.632	14.811
21	1377.75	4.469	12.191
22	1355.26	4.452	13.976
23	1332.65	4.442	13.994
24	1321.86	4.407	18.902
25	1274.32	4.249	213.914
26	1257.07	4.191	15.633
27	1250.18	4.168	16.029
28	496.29	1.655	154.858
29	330.90	1.103	62.462
30	324.88	1.083	60.202

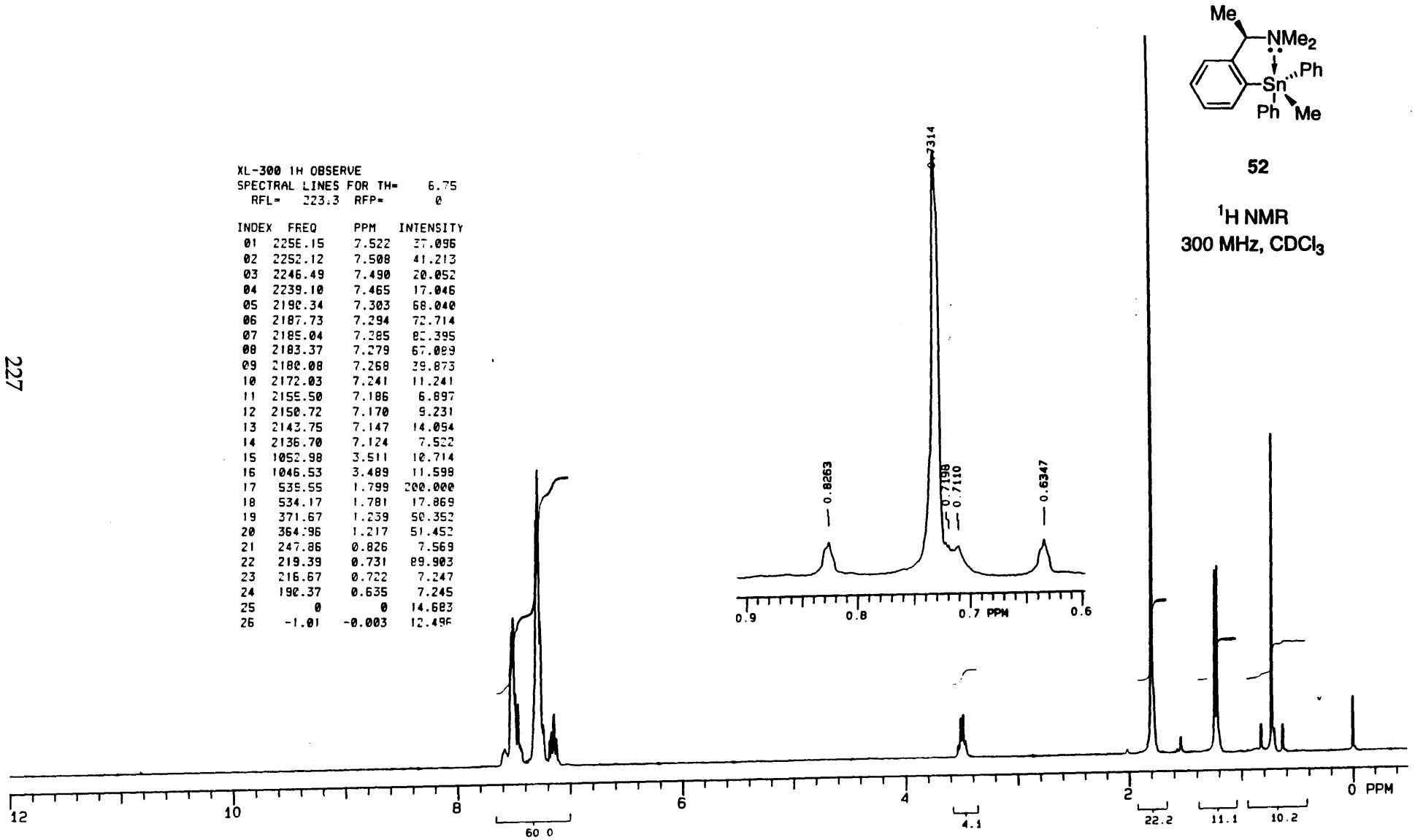




51e

^{1}H NMR
300 MHz, C_6D_6




Me
NMe2
Ph
Sn
Ph
Me
52
1H NMR
300 MHz, CDCl3
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 6.75
RFL= 223.3 RFP= 0
INDEX FREQ PPM INTENSITY
01 2256.15 7.522 37.096
02 2252.12 7.508 41.213
03 2246.49 7.490 20.052
04 2239.10 7.465 17.046
05 2190.34 7.303 68.040
06 2187.73 7.294 72.714
07 2185.04 7.285 82.395
08 2183.37 7.279 67.089
09 2180.08 7.268 39.873
10 2172.03 7.241 11.241
11 2155.50 7.186 6.897
12 2150.72 7.170 9.231
13 2143.75 7.147 14.054
14 2136.70 7.124 7.522
15 1052.98 3.511 10.714
16 1046.53 3.489 11.598
17 535.55 1.799 200.000
18 534.17 1.781 17.869
19 371.67 1.239 50.352
20 364.96 1.217 51.452
21 247.86 0.826 7.569
22 219.39 0.731 89.903
23 216.67 0.722 7.247
24 190.37 0.635 7.245
25 0 0 14.683
26 -1.01 -0.003 12.496
0.8263
0.7314
0.7198
0.7110
0.6347
0.9
0.8
0.7 PPM
0.6
12
10
8
6
4
2
0 PPM
60.0
4.1
22.2
11.1
10.2

STANDARD PARAMETERS

EXP1 PULSE SEQUENCE: S2PUL
DATE 07-24-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-149.9
PW90	18.6	WP	3749.0
SF	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	14
IN	N	RFL	150.6
DP	Y	RFP	0
		TH	9
		INS	1.000
		DC	

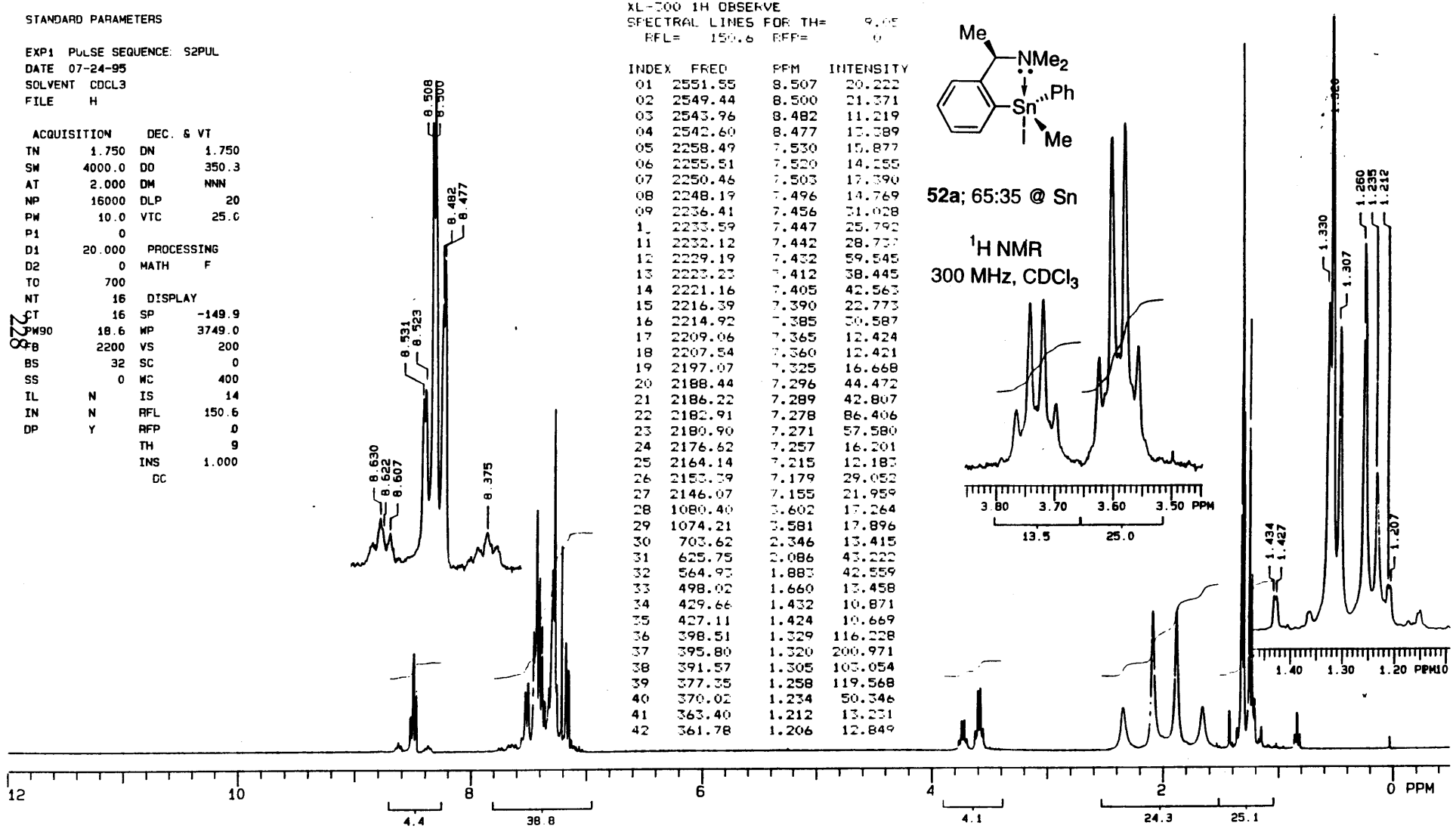
228

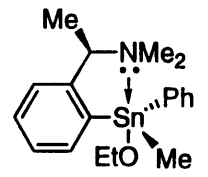
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 9.05
RFL= 150.6 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	2551.55	8.507	20.222
02	2549.44	8.500	21.371
03	2543.96	8.482	11.219
04	2542.60	8.477	13.389
05	2258.49	7.530	15.877
06	2255.51	7.520	14.255
07	2250.46	7.503	17.390
08	2248.19	7.496	14.769
09	2236.41	7.456	31.028
10	2233.59	7.447	25.792
11	2232.12	7.442	28.737
12	2229.19	7.432	59.545
13	2223.23	7.412	38.445
14	2221.16	7.405	42.563
15	2216.39	7.390	22.773
16	2214.92	7.385	30.587
17	2209.06	7.365	12.424
18	2207.54	7.360	12.421
19	2197.07	7.325	16.668
20	2188.44	7.296	44.472
21	2186.22	7.289	42.807
22	2182.91	7.278	86.406
23	2180.90	7.271	57.580
24	2176.62	7.257	16.201
25	2164.14	7.215	12.183
26	2153.39	7.179	29.052
27	2146.07	7.155	21.959
28	1080.40	3.602	17.264
29	1074.21	3.581	17.896
30	703.62	2.346	13.415
31	625.75	2.086	43.222
32	564.93	1.883	42.559
33	498.02	1.660	13.458
34	429.66	1.432	10.871
35	427.11	1.424	10.669
36	398.51	1.329	116.228
37	395.80	1.320	200.971
38	391.57	1.305	103.054
39	377.35	1.258	119.568
40	370.02	1.234	50.346
41	363.40	1.212	13.231
42	361.78	1.206	12.849

52a; 65:35 @ Sn

^{1}H NMR
300 MHz, $CDCl_3$

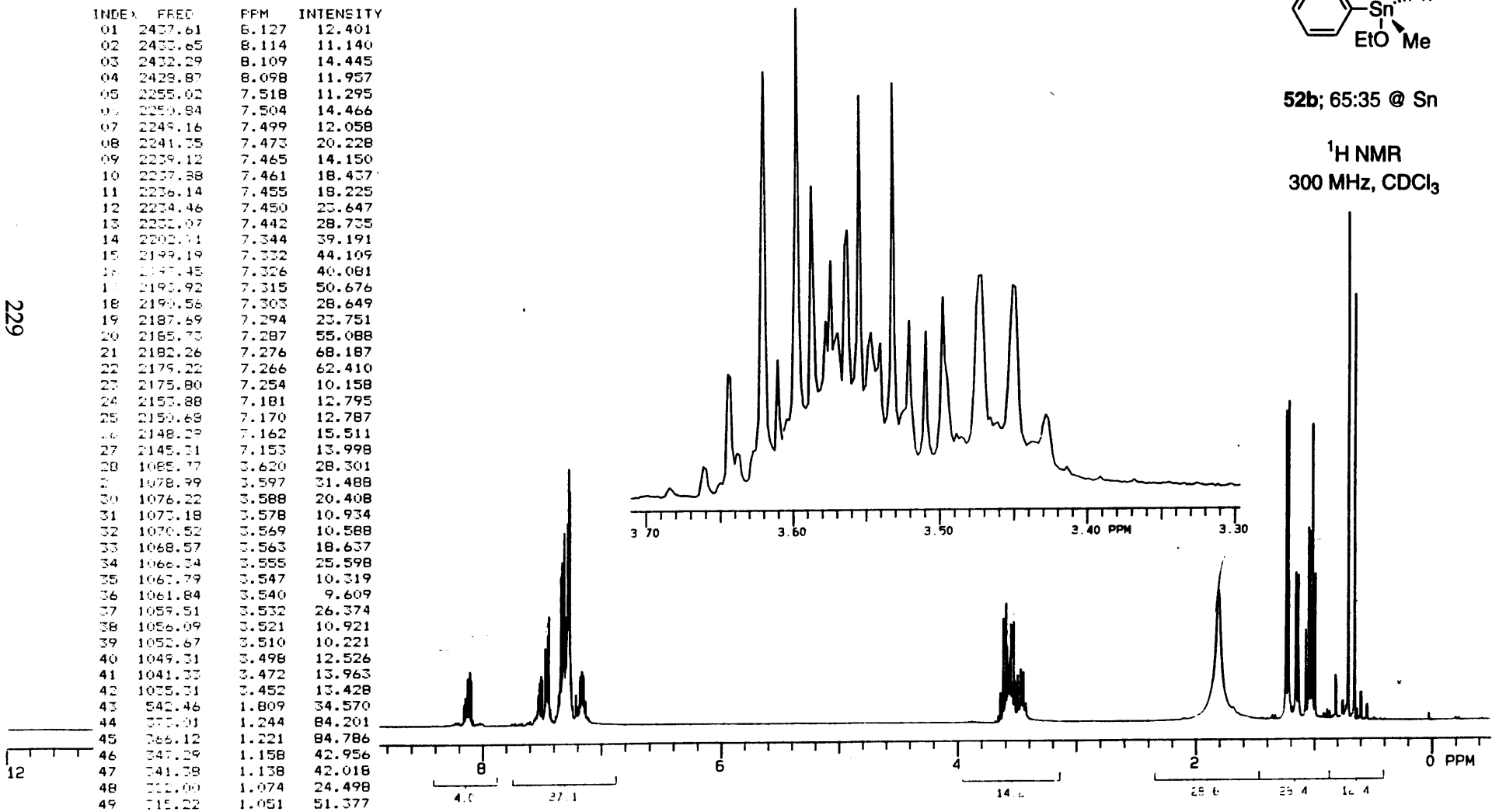




52b; 65:35 @ Sn

^{1}H NMR

300 MHz, $CDCl_3$



SPECTRAL LINES FOR TH= 8.80

REF= 1500.0 REF= 0

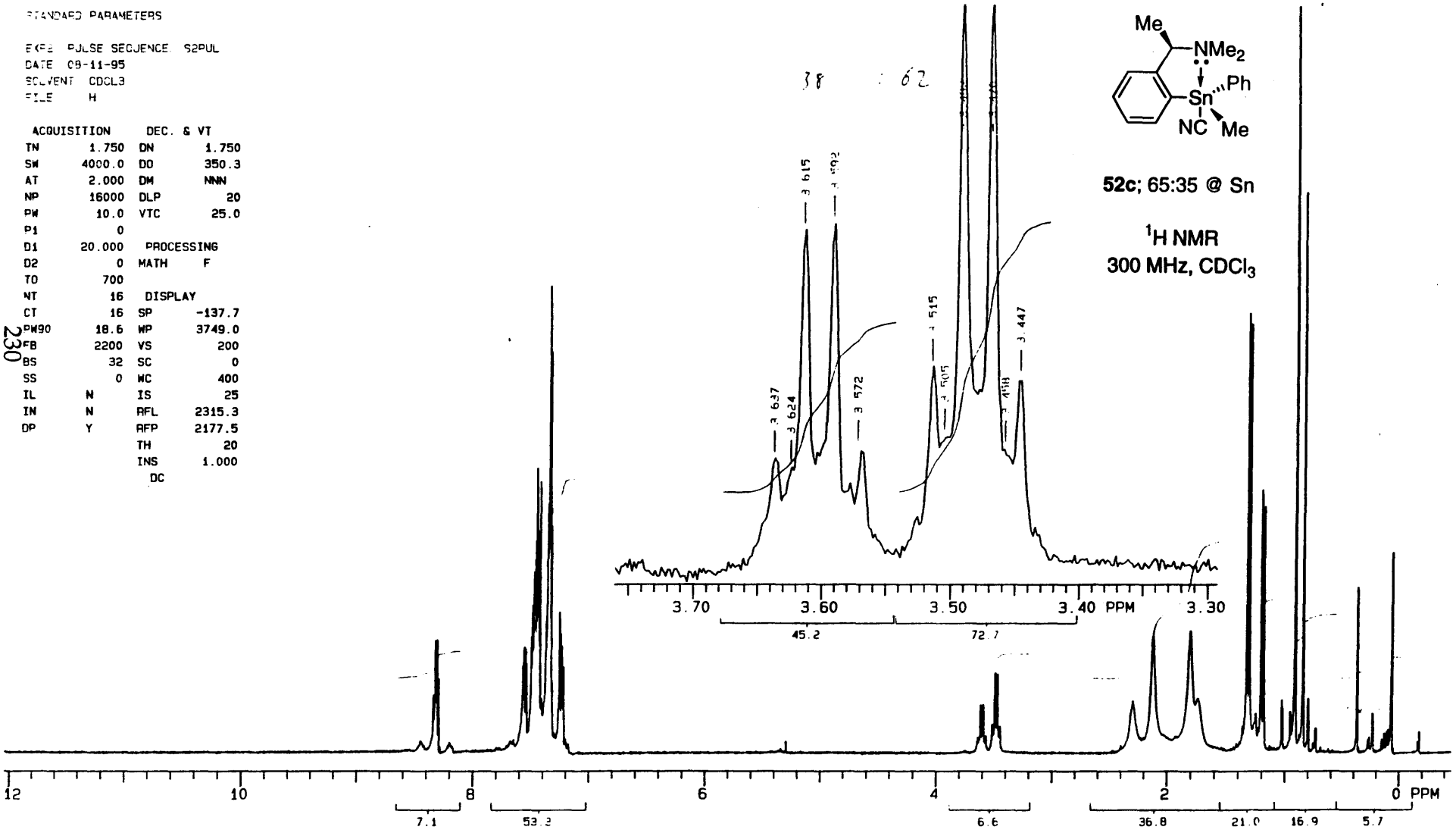
INDEX	FREQ	PPM	INTENSITY
01	2437.61	8.127	12.401
02	2433.65	8.114	11.140
03	2432.29	8.109	14.445
04	2428.87	8.098	11.957
05	2255.02	7.518	11.295
06	2250.84	7.504	14.466
07	2248.16	7.499	12.058
08	2241.35	7.473	20.228
09	2239.12	7.465	14.150
10	2237.38	7.461	18.437
11	2236.14	7.455	18.225
12	2234.46	7.450	23.647
13	2232.07	7.442	28.735
14	2202.71	7.344	39.191
15	2199.19	7.332	44.109
16	2197.45	7.326	40.081
17	2193.92	7.315	50.676
18	2190.56	7.303	28.649
19	2187.69	7.294	23.751
20	2185.73	7.287	55.088
21	2182.26	7.276	68.187
22	2179.22	7.266	62.410
23	2175.80	7.254	10.158
24	2153.88	7.181	12.795
25	2150.68	7.170	12.787
26	2148.29	7.162	15.511
27	2145.31	7.153	13.998
28	1088.77	3.630	28.301
29	1078.99	3.597	31.488
30	1076.22	3.588	20.408
31	1073.18	3.578	10.934
32	1070.52	3.569	10.588
33	1068.57	3.563	18.637
34	1066.34	3.555	25.598
35	1061.79	3.547	10.319
36	1061.84	3.540	9.609
37	1059.51	3.532	26.374
38	1056.09	3.521	10.921
39	1052.67	3.510	10.221
40	1049.31	3.498	12.526
41	1041.33	3.472	13.963
42	1035.31	3.452	13.428
43	542.46	1.809	34.570
44	373.01	1.244	84.201
45	366.12	1.221	84.786
46	347.29	1.158	42.956
47	341.38	1.138	42.018
48	322.00	1.074	24.498
49	315.22	1.051	51.377
50	311.91	1.040	51.002
51	308.38	1.028	28.321
52	305.18	1.017	84.453
53	297.53	0.992	41.402
54	245.01	0.817	12.001
55	243.49	0.812	10.602
56	211.80	0.706	200.137
57	195.14	0.651	111.528

STANDARD PARAMETERS

EXPT PULSE SEQUENCE S2PUL
DATE 08-11-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-137.7
PW90	18.6	WP	3749.0
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	25
IN	N	RFL	2315.3
DP	Y	RFP	2177.5
		TH	20
		INS	1.000
		DC	

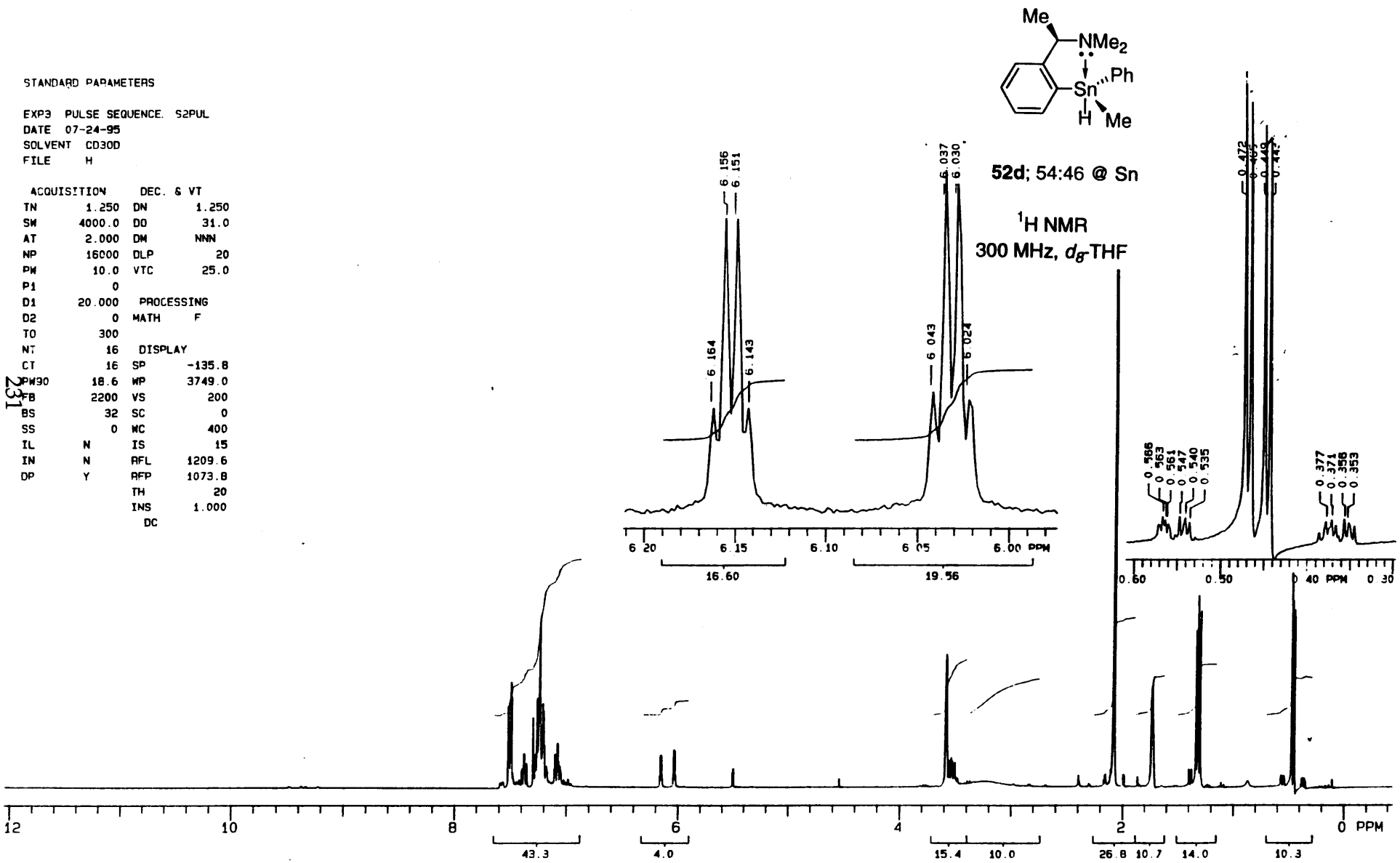
230

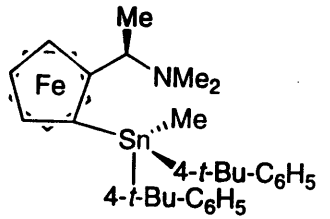


STANDARD PARAMETERS

EXP3 PULSE SEQUENCE. S2PUL
DATE 07-24-95
SOLVENT CD3OD
FILE H

ACQUISITION		DEC. & VT	
TN	1.250	DN	1.250
SW	4000.0	DO	31.0
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	300		
NT	16	DISPLAY	
CT	16	SP	-135.8
PW90	18.6	WP	3749.0
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	15
IN	N	RFL	1209.6
DP	Y	RFP	1073.8
		TH	20
		INS	1.000
		DC	





56

^{1}H NMR
300 MHz, $CDCl_3$

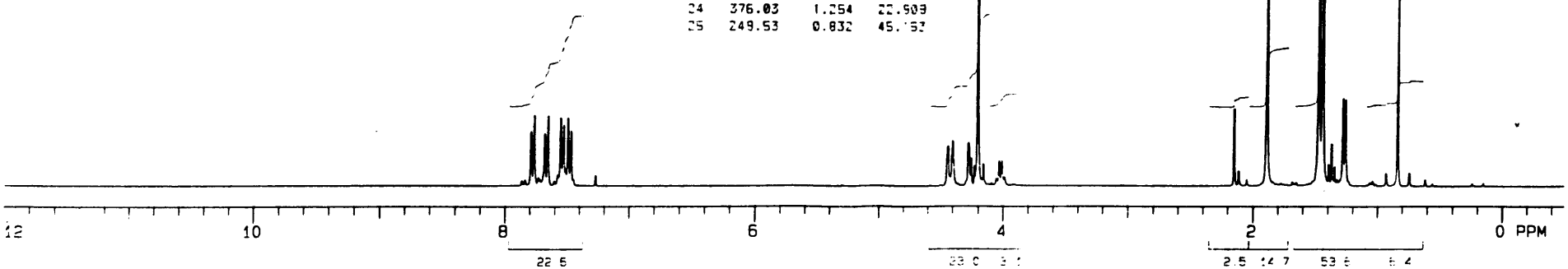
XL-300 1H OBSERVE
STANDARD PARAMETERS

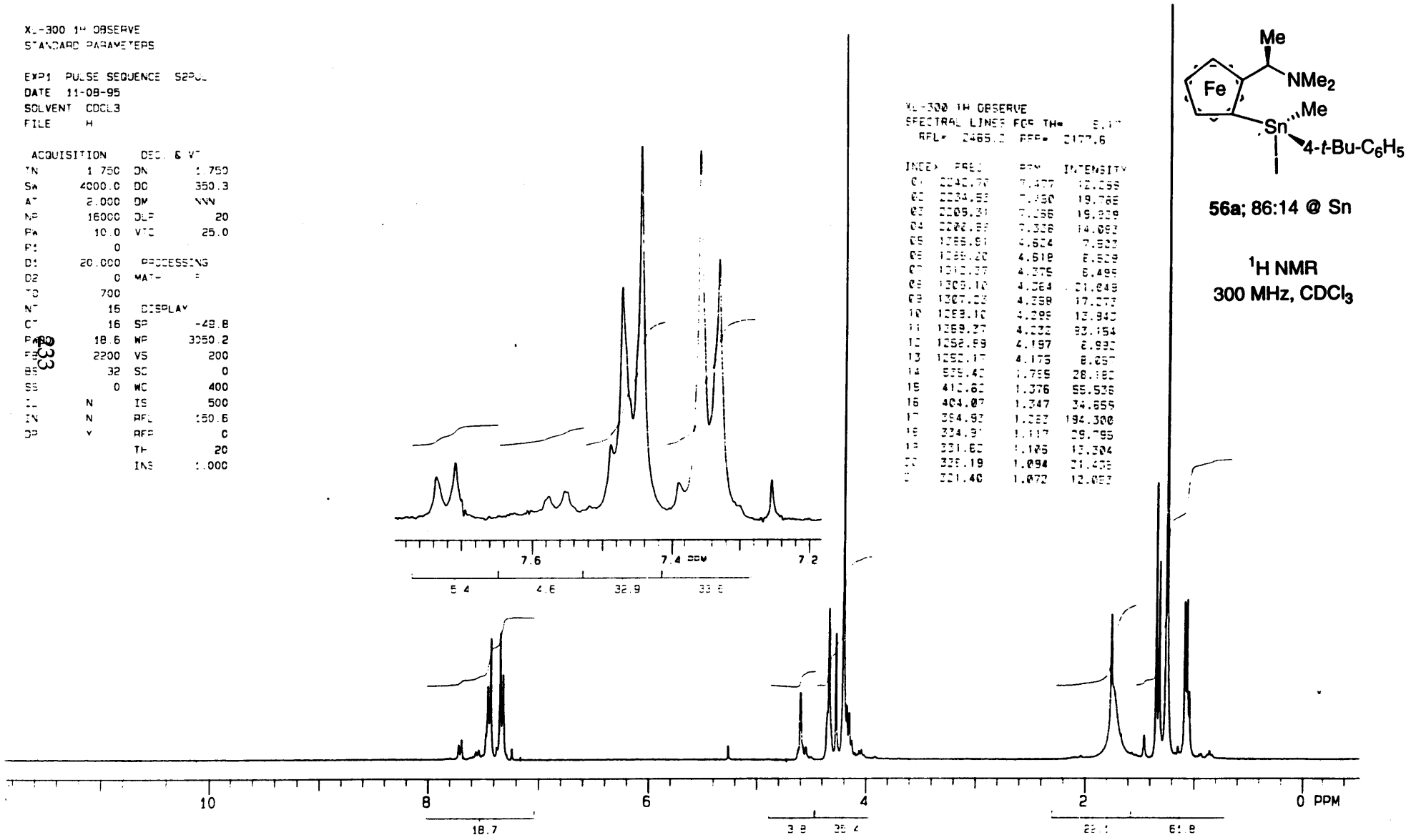
EXP2 PULSE SEQUENCE: S2PUL
DATE 10-11-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC & VT	
TN	1.750	DN	1.750
SW	5500.6	DO	350.3
AT	1.821	DM	NNN
NP	20032	DLP	20
PW	15.0		
P1	0	PROCESSING	
D1	2[illegible].000	SE	0.637
D2	0	LB	0.500
TO	1400	MATH	F
NT	16		
CT	16	DISPLAY	
PW90	32.0	SP	-150.1
FB	3100	WP	3749.3
BS	16	VS	48
SS	0	SC	0
IF	N	WC	400
IN	N	IC	229
DP	Y	RFL	2461.6
GAIN	0	RFP	2177.6
		TH	25
		INS	1.000
		AI	

XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 4.55
RFL= 2463.6 RFP= 2177.6

INDEX	FREQ	PPM	INTENSITY
01	2335.86	7.788	12.170
02	2327.99	7.761	18.625
03	2302.88	7.678	12.065
04	2294.71	7.651	16.762
05	2284.35	7.648	15.705
06	2258.36	7.523	14.311
07	2246.22	7.489	16.344
08	2238.20	7.462	13.715
09	1328.55	4.433	9.440
10	1320.90	4.404	6.755
11	1318.55	4.398	10.279
12	1316.38	4.389	6.142
13	1281.61	4.273	9.379
14	1280.61	4.269	8.828
15	1260.22	4.201	102.[illegible]
16	1207.75	4.027	5.920
17	1201.03	4.004	6.246
18	643.54	2.145	[illegible]
19	565.13	1.884	94.920
20	441.09	1.471	183.306
21	431.84	1.440	176.071
22	410.16	1.367	7.243
23	362.56	1.275	22.854
24	376.03	1.254	22.909
25	249.53	0.832	45.[illegible]




XL-300 1H OBSERVE
STANDARD PARAMETERS
EXP1 PULSE SEQUENCE S2PUL
DATE 11-08-95
SOLVENT CDCL3
FILE H
ACQUISITION
DEC. & VT
TN 1.750 DN 1.750
SW 4000.0 DO 350.3
AT 2.000 DM NNN
NP 16000 DLP 20
PW 10.0 VTC 25.0
P1 0
D1 20.000 PROCESSING
D2 0 MATH F
TD 700
NT 16 DISPLAY
CT 16 SP -48.8
PW 18.6 WP 3050.2
FB 2200 VS 200
BS 32 SC 0
SS 0 WC 400
IL N IS 500
IN N RFL 150.6
DP Y RFP 0
TH 20
INS 1.000
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 5.17
RFL= 2465.2 RFP= 2177.6
INDEX FREQ PPM INTENSITY
01 2242.70 7.477 12.266
02 2234.53 7.450 19.765
03 2205.31 7.356 19.939
04 2202.99 7.338 14.093
05 1285.91 4.624 7.523
06 1285.20 4.618 8.529
07 1312.37 4.375 6.499
08 1309.10 4.364 21.049
09 1307.23 4.358 17.273
10 1289.10 4.299 13.943
11 1269.37 4.232 93.154
12 1252.99 4.197 8.992
13 1252.17 4.175 8.057
14 535.42 1.785 28.182
15 412.62 1.376 55.536
16 404.07 1.347 34.659
17 394.93 1.283 194.300
18 334.91 1.117 29.795
19 331.62 1.105 13.304
20 325.19 1.094 21.435
21 321.40 1.072 12.053
Me
NMe2
Fe
Me
Sn
4-t-Bu-C6H5
56a; 86:14 @ Sn
1H NMR
300 MHz, CDCl3
7.6
7.4 PPM
7.2
5.4
4.6
32.9
33.6
10
8
6
4
2
0 PPM
18.7
3.8
35.4
22.1
61.8

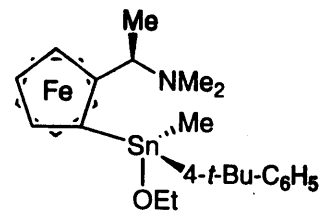
XL-300 1H OBSERVE
STANDARD PARAMETERS

EXP1 PULSE SEQUENCE: S2PUL
DATE 10-24-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-149.9
PW90	16.6	WP	3749.0
FB	2200	VS	184
BS	4	SC	0
SS	0	WC	400
IL	N	IS	22
IN	N	RFL	2344.5
DP	Y	RFP	2177.5
		TH	8
		INS	1.000
		DC	

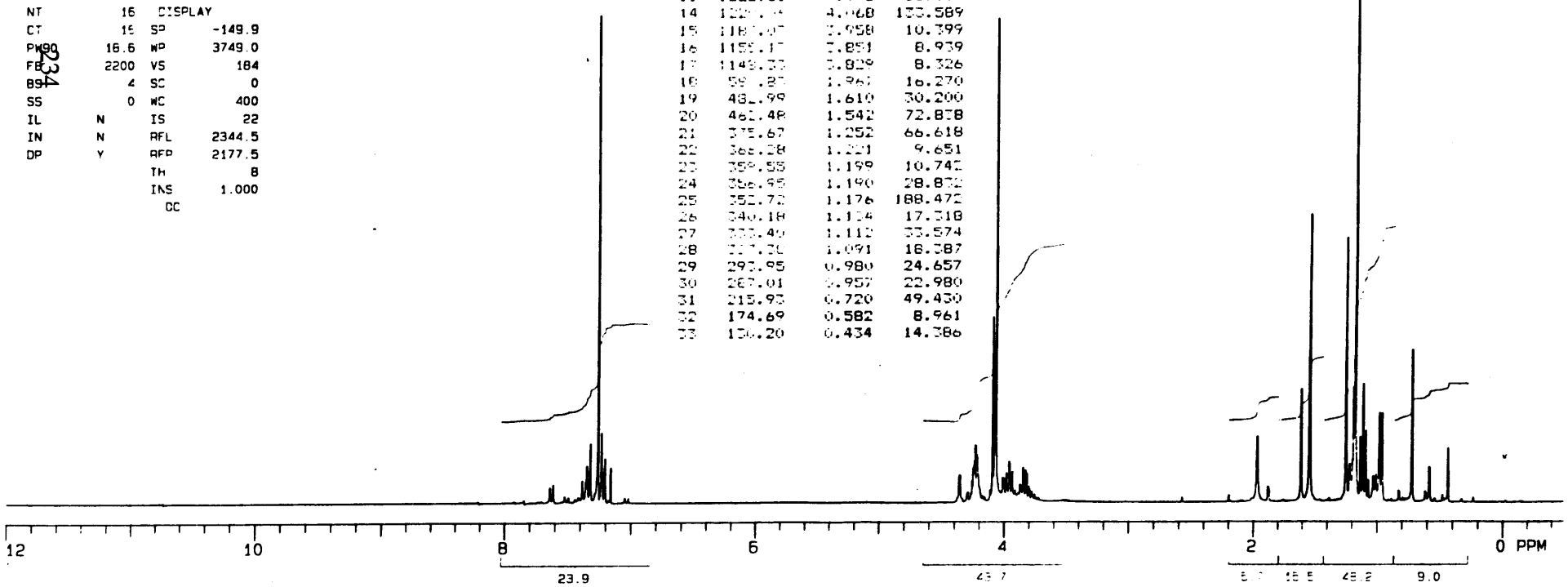
XL-300 1H OBSERVE
[illegible] LINES FOR TH= [illegible]
RFL= 2344.5 RFP= 2177.5

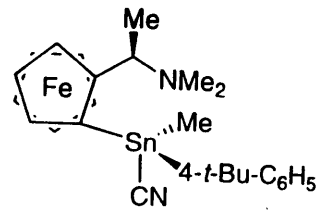
INDEX	RFEL	PPM	INTENSITY
01	2202.96	7.348	10.962
02	2192.50	7.320	16.500
03	2177.59	7.260	179.491
04	2169.73	[illegible]	18.137
05	2161.32	[illegible]	11.841
06	214[illegible].86	[illegible].161	12.130
07	1274.70	4.250	8.665
08	1271.1[illegible]	4.238	10.296
09	1269.39	4.232	14.606
10	1266.08	4.22[illegible]	12.029
11	1261.96	4.214	11.140
12	1227.72	4.095	48.206
13	1222.61	4.076	33.117
14	122[illegible]	4.068	133.589
15	1187.07	3.958	10.399
16	1155.17	3.851	8.939
17	1149.33	3.829	8.326
18	59[illegible].87	1.967	16.270
19	482.99	1.610	30.200
20	462.48	1.542	72.838
21	375.67	1.252	66.618
22	366.28	1.221	9.651
23	359.55	1.199	10.742
24	356.95	1.190	28.832
25	352.72	1.176	188.472
26	340.18	1.134	17.318
27	333.40	1.112	33.574
28	327.30	1.091	18.387
29	293.95	0.980	24.657
30	287.01	0.957	22.980
31	215.93	0.720	49.430
32	174.69	0.582	8.961
33	130.20	0.434	14.386



56b; 73:27 @ Sn

^{1}H NMR
300 MHz, $CDCl_3$





56c; 87:13 @ Sn

^{1}H NMR
300 MHz, $CDCl_3$

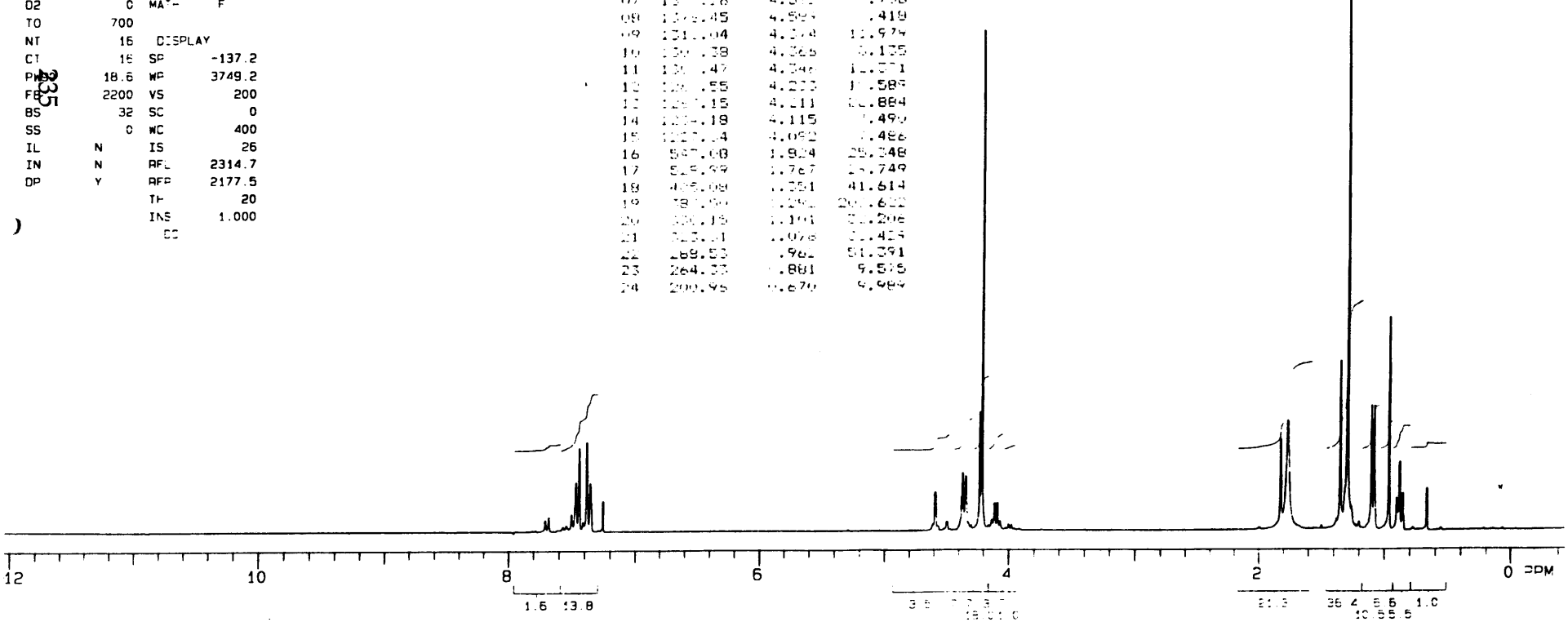
XL-300 1H OBSERVE
STANDARD PARAMETERS

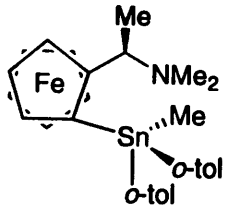
EXP1 PULSE SEQUENCE S2PUL
DATE 11-08-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-137.2
PW	18.6	WP	3749.2
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	26
IN	N	RFL	2314.7
DP	Y	RFP	2177.5
		TH	20
		INS	1.000
		DC	

XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 7.15
RFL= 2314.1 RFP= 2177.5

INDEX	FREQ	PPM	INTENSITY
01	2241.14	7.472	11.570
02	2233.32	7.446	20.509
03	2211.10	7.386	21.187
04	2200.44	7.350	11.617
05	2205.05	7.352	7.538
06	1771.24	4.595	7.486
07	1370.26	4.592	7.708
08	1376.45	4.589	7.419
09	1311.04	4.374	11.979
10	1300.38	4.366	6.135
11	1300.47	4.346	11.371
12	1260.55	4.233	10.589
13	1257.15	4.211	22.884
14	1234.18	4.115	7.490
15	1227.34	4.092	7.486
16	597.08	1.924	25.348
17	529.99	1.767	29.749
18	405.08	1.351	41.614
19	387.50	1.292	200.622
20	330.15	1.101	32.206
21	323.31	1.078	31.429
22	288.53	.962	51.391
23	264.33	.881	9.575
24	200.95	0.670	9.989





57

^{1}H NMR
300 MHz, $CDCl_3$

XL-300 1H OBSERVE
STANDARD PARAMETERS

EXP2 PULSE SEQUENCE: S2PUL
DATE 01-12-96
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-149.9
PW90	18.6	WP	3749.0
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	19
IN	N	RFL	167.0
DP	Y	RFP	0
		TH	20
		INS	1.000
		DC	

SPECIFIED LINES FOR THE

INDEX	FREQ	PPM	INTENSITY
01	2342.56	7.490	8.771
02	2338.11	7.476	9.191
03	2309.70	7.385	8.693
04	2262.92	7.211	13.011
05	2260.91	7.205	14.025
06	2257.98	7.195	14.592
07	2251.14	7.173	14.467
08	2246.46	7.160	10.134
09	2245.28	7.152	15.014
10	2243.71	7.147	15.592
11	2238.61	7.130	11.771
12	2236.44	7.123	12.224
13	2231.72	7.107	11.526
14	2224.19	7.082	12.707
15	2222.32	7.076	13.518
16	1300.94	4.227	14.559
17	1298.04	4.221	15.411
18	1294.21	4.210	12.987
19	1291.71	4.202	17.758
20	1284.17	4.181	14.488
21	1282.22	4.175	15.625
22	1280.64	4.170	15.099
23	1275.74	4.154	16.008
24	1271.94	4.142	209.745
25	1263.81	4.115	19.338
26	1257.07	4.093	19.471
27	709.28	2.309	15.412
28	698.89	2.275	15.447
29	691.99	2.253	7.211
30	669.79	2.180	14.959
31	667.18	2.172	75.447
32	664.09	2.162	23.351
33	484.91	1.579	174.969
34	370.35	1.205	11.264
35	343.47	1.118	44.93
36	336.47	1.095	42.396
37	287.39	0.936	94.621

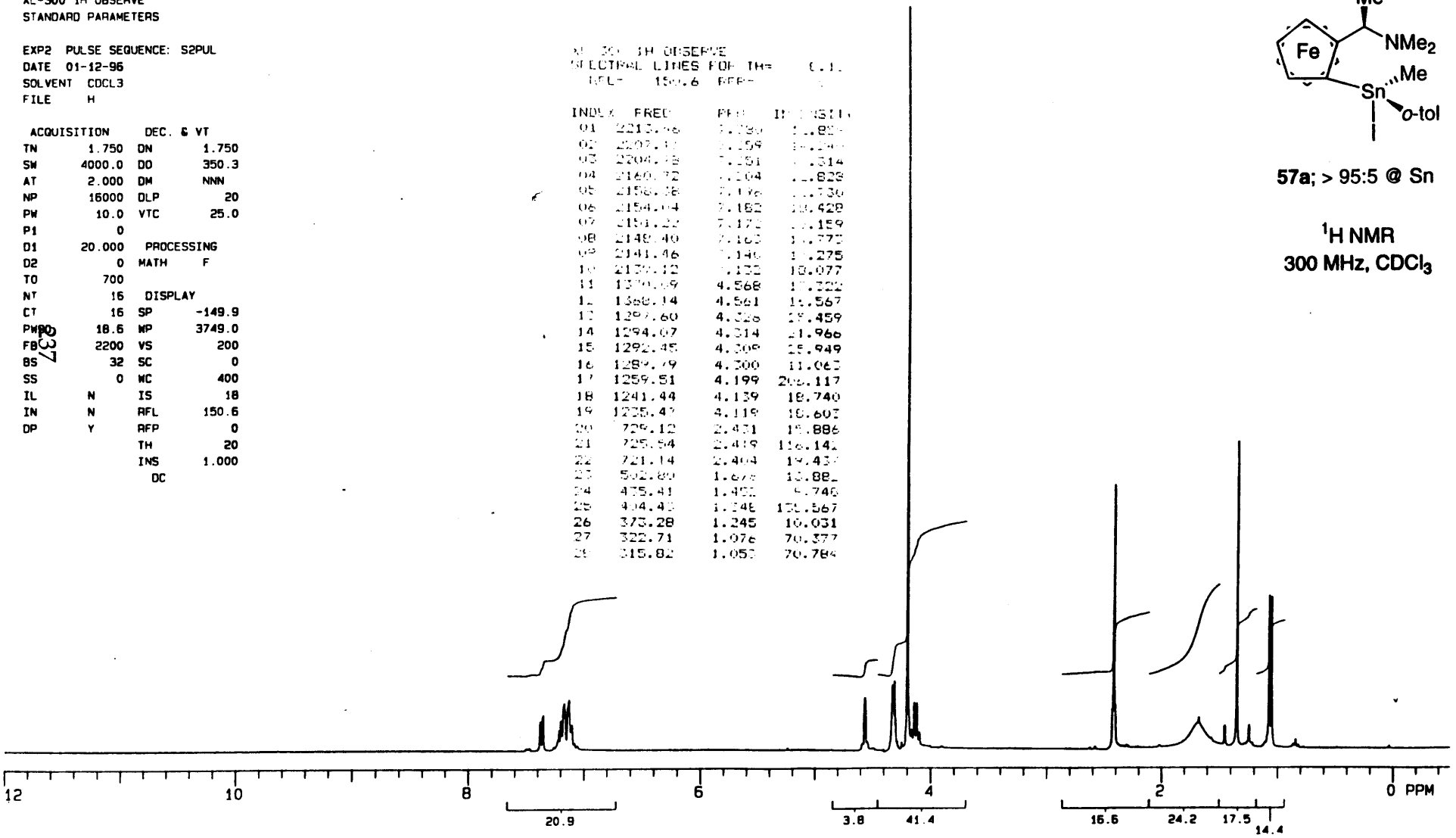
XL-300 1H OBSERVE
STANDARD PARAMETERS

EXP2 PULSE SEQUENCE: S2PUL
DATE 01-12-96
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-149.9
PWRD	18.6	WP	3749.0
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	18
IN	N	RFL	150.6
DP	Y	RFP	0
		TH	20
		INS	1.000
		DC	

XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= [illegible]
RFL= 150.6 RFP= [illegible]

INDEX	FREQ	PPM	INTENSITY
01	2213.46	[illegible]	[illegible]
02	2207.[illegible]	[illegible]	[illegible]
03	2204.78	[illegible]	[illegible].314
04	2160.72	[illegible]	[illegible].829
05	2158.38	[illegible]	[illegible].730
06	2154.04	7.182	[illegible].428
07	2151.22	7.172	[illegible].159
08	2148.40	7.163	[illegible].773
09	2141.46	7.140	[illegible].275
10	2139.12	7.132	18.077
11	1370.09	4.568	[illegible].322
12	1368.14	4.561	[illegible].567
13	1297.60	4.326	[illegible].459
14	1294.07	4.314	21.966
15	1292.45	4.309	25.949
16	1289.79	4.300	11.063
17	1259.51	4.199	206.117
18	1241.44	4.139	18.740
19	1235.47	4.119	18.603
20	729.12	2.431	15.886
21	725.54	2.419	116.142
22	721.14	2.404	19.437
23	502.80	1.676	13.882
24	435.41	1.452	[illegible].746
25	404.43	1.348	135.567
26	373.28	1.245	10.031
27	322.71	1.076	70.377
28	315.82	1.053	70.784



57a; > 95:5 @ Sn

^{1}H NMR
300 MHz, $CDCl_3$

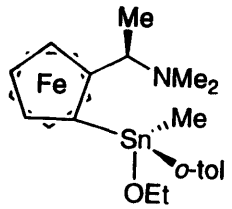
XL-300 1- OBSERVE
STANDARD PARAMETERS

EXP2 PULSE SEQUENCE: S2PUL
DATE 01-12-96
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-150.0
PW90	18.6	WP	3749.2
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	23
IN	N	RFL	2345.5
DP	Y	RFP	2177.5
		TH	20
		INS	1.000
		DC	

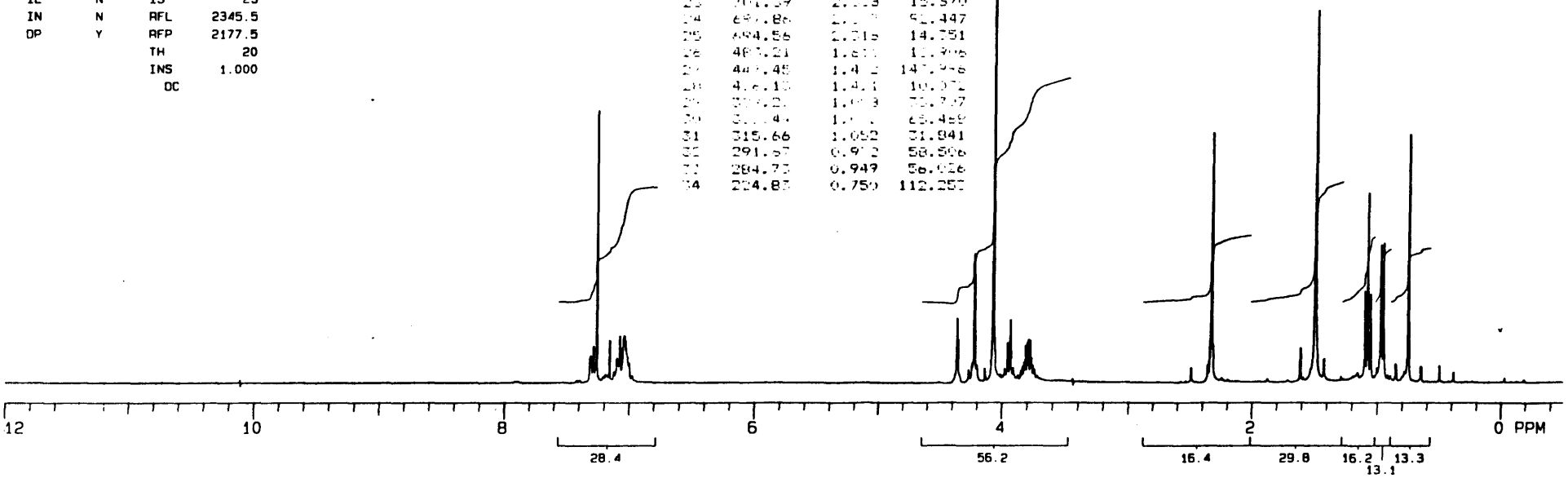
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= [illegible]
RFL= 2345.5 RFP= 2177.5

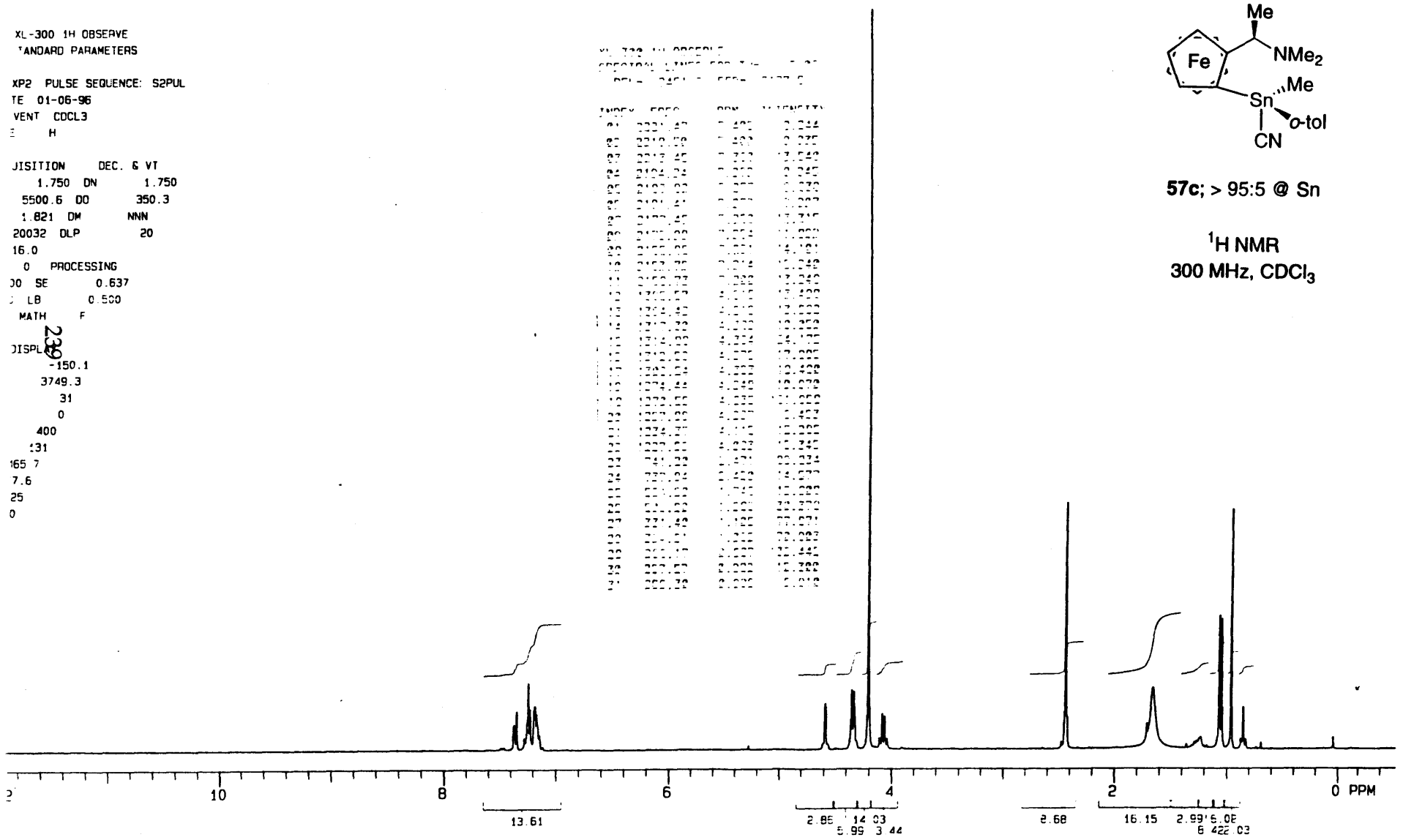
INDEX	FREQ	PP	INTENSITY
*01	[illegible]	[illegible]	[illegible]
02	[illegible]	[illegible]	[illegible]
03	2191.92	[illegible]	[illegible]
04	2185.[illegible]	[illegible]	[illegible]
05	2177.76	[illegible]	[illegible]
06	2122.[illegible]	[illegible]	[illegible]
07	2120.13	[illegible]	[illegible]
08	2114.16	[illegible]	15.121
09	2111.61	[illegible]	15.869
10	2108.[illegible]	[illegible]	14.311
11	1308.78	4.364	12.366
12	1307.53	4.359	21.683
13	1305.25	4.352	13.745
14	1266.08	4.2[illegible]	45.974
15	1264.94	4.217	45.139
16	1219.68	4.0[illegible]	219.976
17	1185.61	[illegible]	15.195
18	1178.39	[illegible]	19.70[illegible]
19	1147.23	3.8[illegible]	14.414
20	1139.49	[illegible]	15.268
21	1136.45	[illegible]	15.64[illegible]
22	1132.71	[illegible]	15.100
23	701.39	2.[illegible]	15.570
24	697.86	[illegible]	92.447
25	694.56	2.315	14.751
26	483.21	1.6[illegible]	1[illegible]
27	44[illegible].45	1.4[illegible]	147.[illegible]
28	4[illegible].1[illegible]	1.4[illegible]	10.[illegible]
29	[illegible]	1.[illegible]	[illegible]
30	[illegible]	1.[illegible]	65.469
31	315.66	1.052	31.841
32	291.67	0.972	58.506
33	284.73	0.949	56.026
34	224.83	0.750	112.25[illegible]



57b; > 95:5 @ Sn

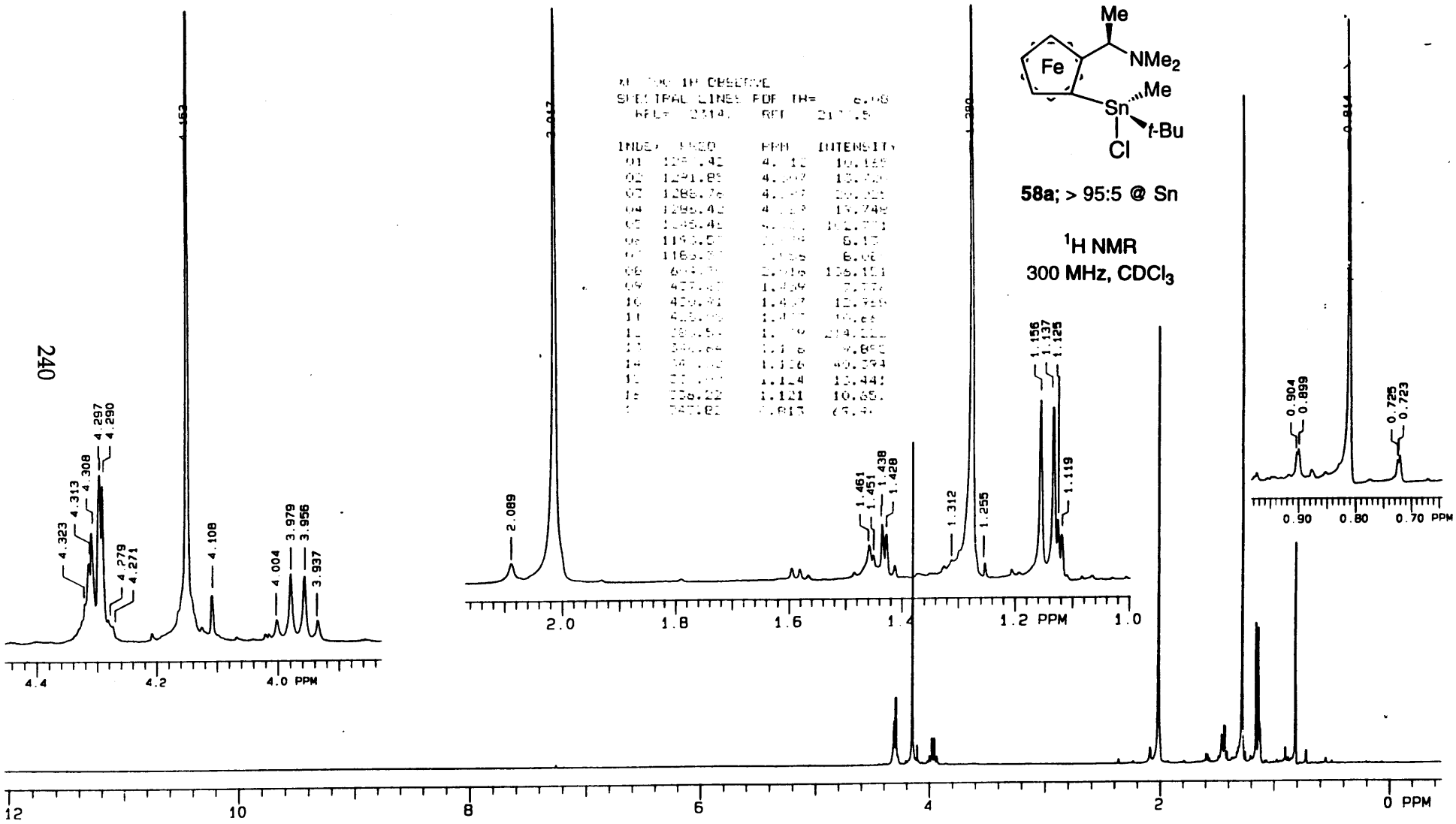
^{1}H NMR
300 MHz, $CDCl_3$

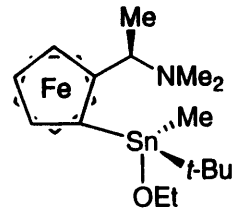




57c; > 95:5 @ Sn

^{1}H NMR
300 MHz, $CDCl_3$


Me
Fe
NMe2
Me
Sn
t-Bu
Cl
58a; > 95:5 @ Sn
1H NMR
300 MHz, CDCl3
4.323
4.313
4.308
4.297
4.290
4.279
4.271
4.162
4.108
4.004
3.979
3.956
3.937
2.089
2.017
1.461
1.451
1.438
1.428
1.312
1.280
1.255
1.156
1.137
1.125
1.119
0.904
0.899
0.814
0.725
0.723
4.4
4.2
4.0 PPM
2.0
1.8
1.6
1.4
1.2 PPM
1.0
0.90
0.80
0.70 PPM
12
10
8
6
4
2
0 PPM



58b; 90:10 @ Sn

^{1}H NMR
300 MHz, $CDCl_3$

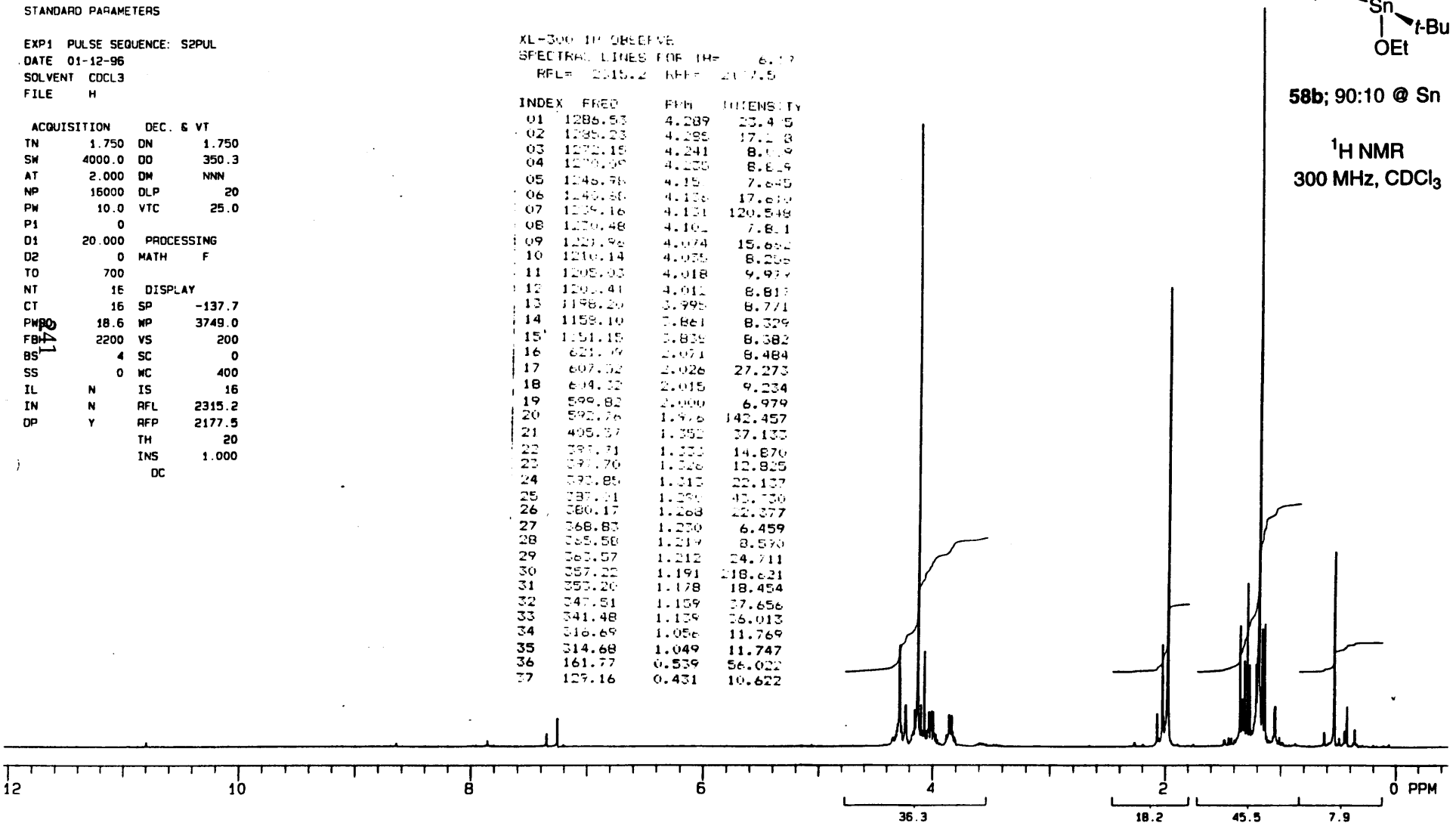
XL-300 1H OBSERVE
STANDARD PARAMETERS

EXP1 PULSE SEQUENCE: S2PUL
DATE 01-12-96
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-137.7
PWR	18.6	WP	3749.0
FB	2200	VS	200
BS	4	SC	0
SS	0	WC	400
IL	N	IS	16
IN	N	RFL	2315.2
DP	Y	RFP	2177.5
		TH	20
		INS	1.000
		DC	

XL-300 1H OBSERVE
SPECTRAL LINES FOR 1H= 6.17
RFL= 2315.2 RFP= 2177.5

INDEX	FREQ	PPM	INTENSITY
01	1286.53	4.289	23.415
02	1285.23	4.285	17.128
03	1272.15	4.241	8.159
04	1270.98	4.235	8.814
05	1246.98	4.15	7.645
06	1240.86	4.136	17.610
07	1239.16	4.131	120.548
08	1230.48	4.102	7.851
09	1221.96	4.074	15.692
10	1210.14	4.035	8.256
11	1205.93	4.018	9.977
12	1204.41	4.012	8.813
13	1198.20	3.995	8.771
14	1158.10	3.861	8.329
15	1151.15	3.838	8.382
16	621.49	2.071	8.484
17	607.52	2.026	27.273
18	604.32	2.015	9.234
19	599.82	2.000	6.979
20	592.76	1.976	142.457
21	495.37	1.652	37.133
22	489.71	1.633	14.870
23	487.70	1.626	12.825
24	482.86	1.610	22.137
25	480.41	1.602	40.730
26	480.17	1.601	42.377
27	468.83	1.563	6.459
28	465.58	1.552	8.590
29	463.57	1.546	24.711
30	457.22	1.525	218.621
31	453.20	1.511	18.454
32	447.51	1.492	37.656
33	441.48	1.472	26.013
34	416.69	1.389	11.769
35	414.68	1.382	11.747
36	161.77	0.539	56.022
37	159.16	0.531	10.622



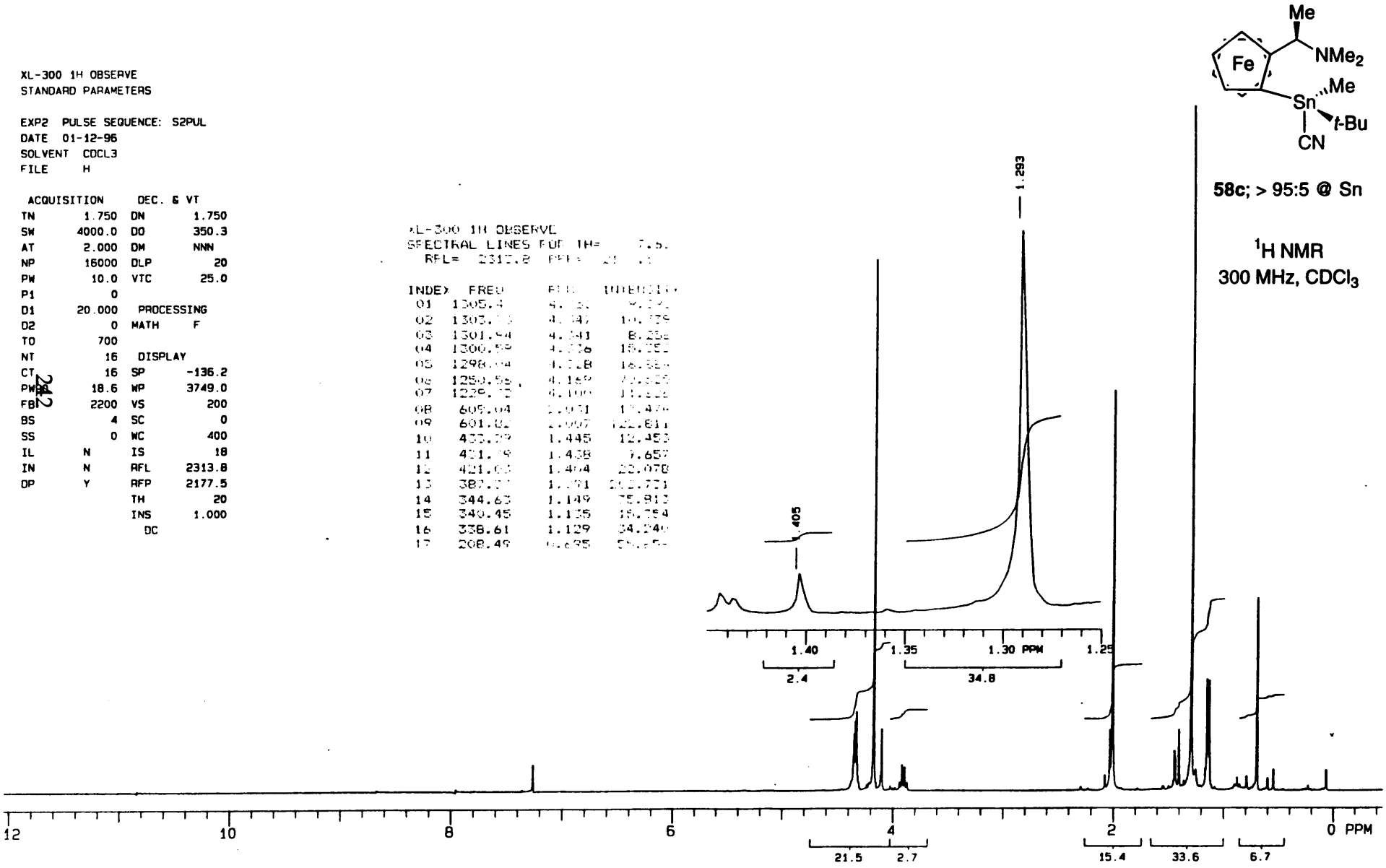
XL-300 1H OBSERVE
STANDARD PARAMETERS

EXP2 PULSE SEQUENCE: S2PUL
DATE 01-12-96
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-136.2
PW	18.6	WP	3749.0
FB	2200	VS	200
BS	4	SC	0
SS	0	WC	400
IL	N	IS	18
IN	N	RFL	2313.8
DP	Y	RFP	2177.5
		TH	20
		INS	1.000
		DC	

XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 7.5
RFL= 2313.8 RFP= 21[illegible]

INDEX	FREQ	[illegible]	INTENSITY
01	1305.4[illegible]	[illegible]	[illegible]
02	1303.[illegible]	4.[illegible]	10.[illegible]
03	1301.94	4.341	8.2[illegible]
04	1300.59	4.336	15.[illegible]
05	1298.[illegible]	4.328	16.[illegible]
06	1250.56	4.169	[illegible]
07	1229.[illegible]	4.100	[illegible]
08	609.04	2.031	[illegible]
09	601.[illegible]	2.007	122.811
10	433.[illegible]	1.445	12.453
11	431.[illegible]	1.438	7.657
12	421.[illegible]	1.404	22.078
13	387.[illegible]	1.[illegible]91	[illegible]
14	344.63	1.149	75.813
15	340.45	1.135	15.754
16	338.61	1.129	34.240
17	208.49	0.695	[illegible]



XL-300 1H OBSERVE
STANDARD PARAMETERS

EXP2 PULSE SEQUENCE: S2PUL
DATE 04-03-96
SOLVENT CDCL3
FILE H

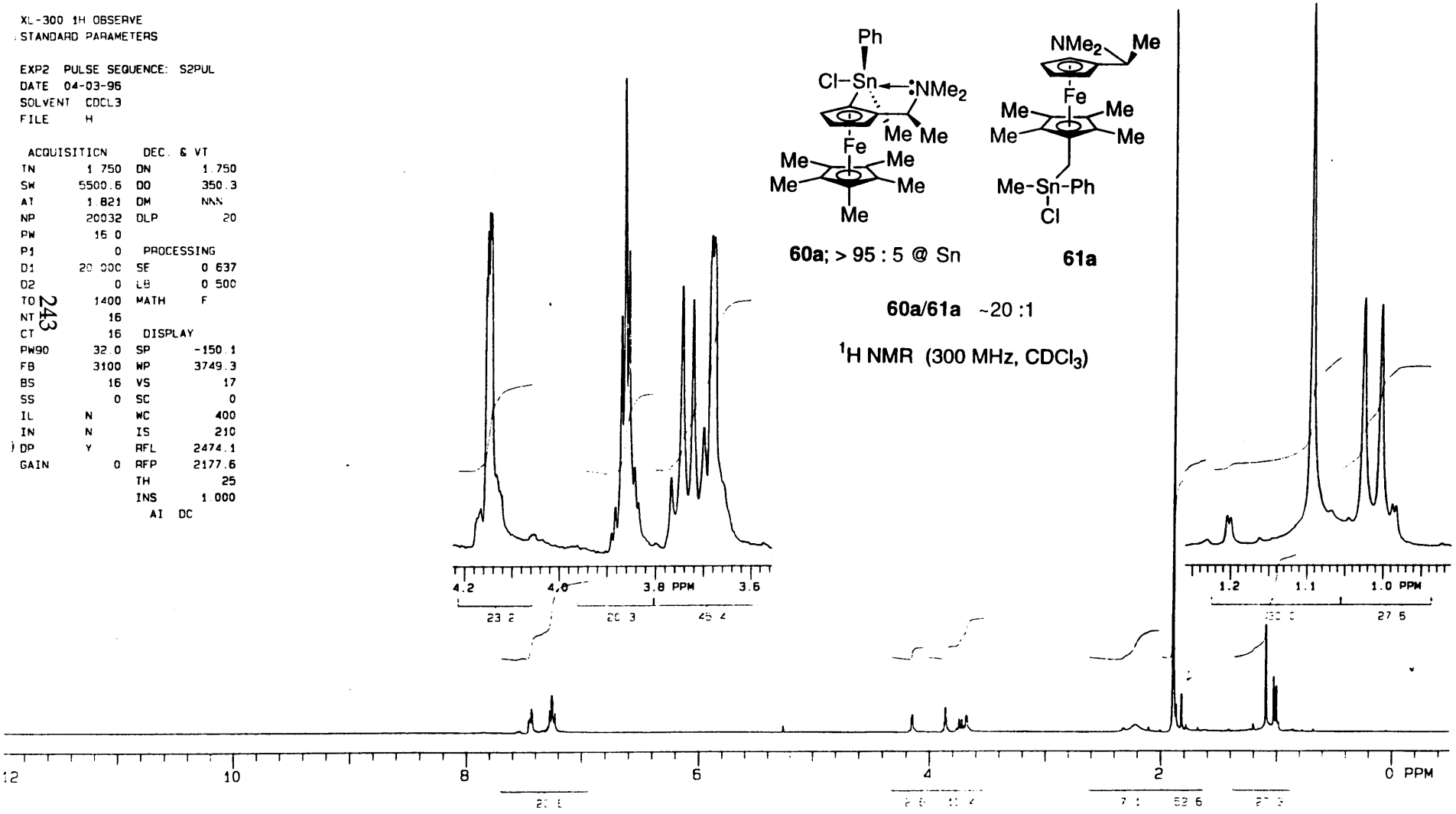
ACQUISITION		DEC. & VT	
TN	1 750	DN	1 750
SW	5500.6	DO	350.3
AT	1 821	DM	NNN
NP	20032	DLP	20
PW	16 0		
P1	0	PROCESSING	
D1	20 000	SE	0 637
D2	0	LB	0 500
TO	1400	MATH	F
NT	16		
CT	16	DISPLAY	
PW90	32.0	SP	-150 1
FB	3100	WP	3749.3
BS	16	VS	17
SS	0	SC	0
IL	N	WC	400
IN	N	IS	210
DP	Y	RFL	2474.1
GAIN	0	RFP	2177.6
		TH	25
		INS	1.000
		AI DC	

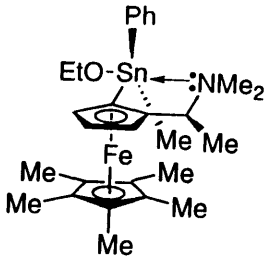
243

60a; > 95 : 5 @ Sn **61a**

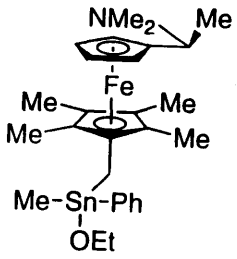
60a/61a ~20 :1

^{1}H NMR (300 MHz, $CDCl_3$)





60b; > 95 : 5 @ Sn



61b

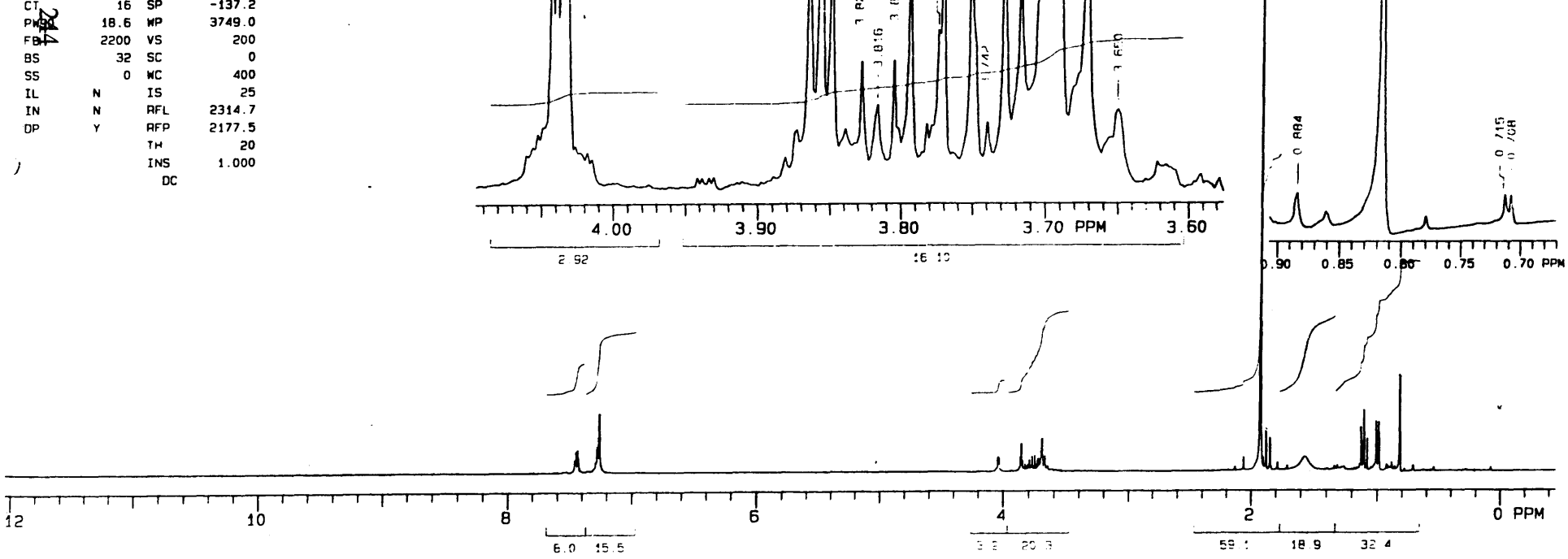
60b/61b ~20 :1

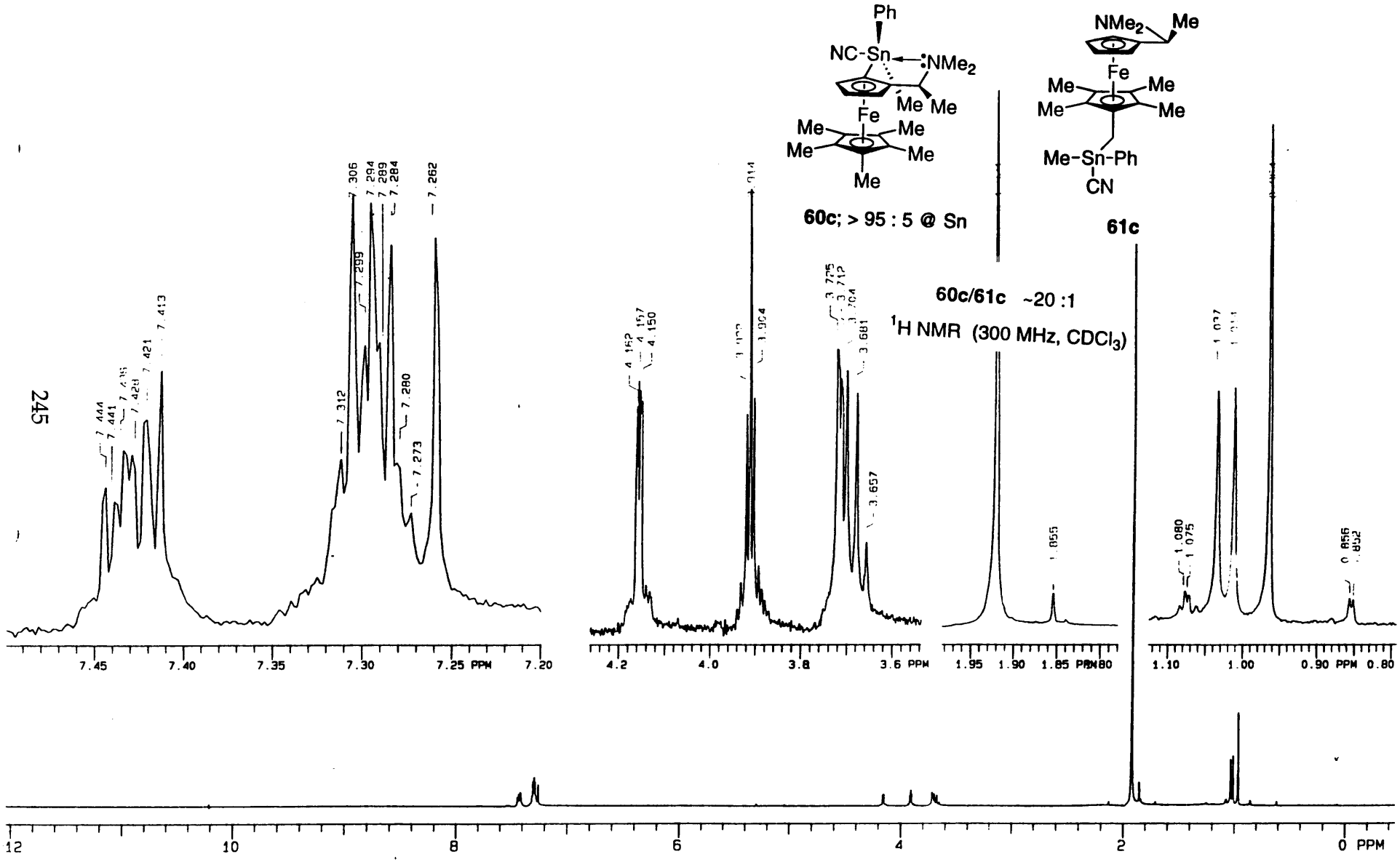
^{1}H NMR (300 MHz, $CDCl_3$)

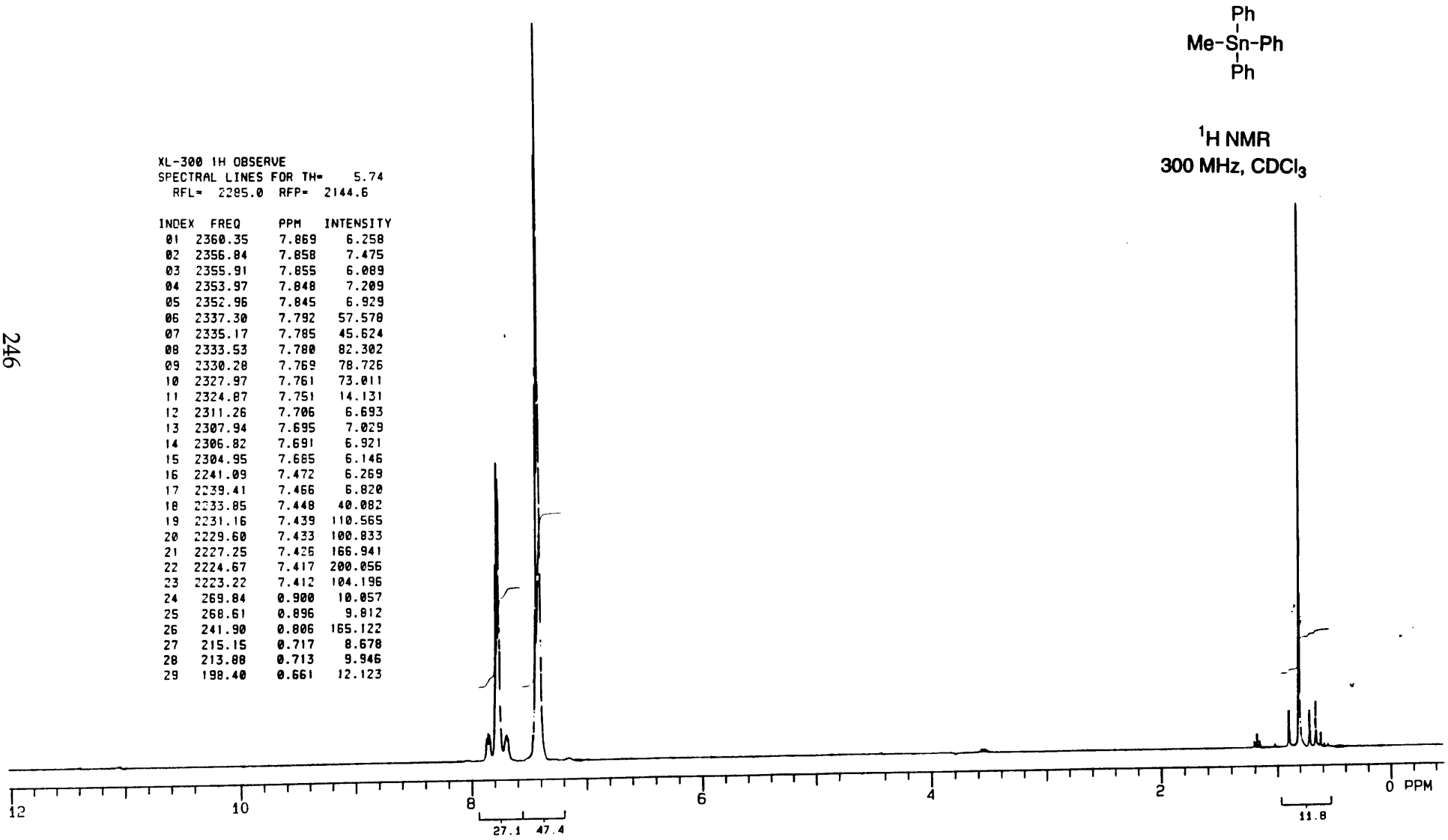
XL-300 1H OBSERVE
STANDARD PARAMETERS

EXP3 PULSE SEQUENCE: S2PUL
DATE 04-02-96
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1 750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-137.2
PW	18.6	WP	3749.0
FB	2200	VS	200
BS	32	SC	0
SS	0	WC	400
IL	N	IS	25
IN	N	RFL	2314.7
DP	Y	RFP	2177.5
		TH	20
		INS	1.000
		DC	

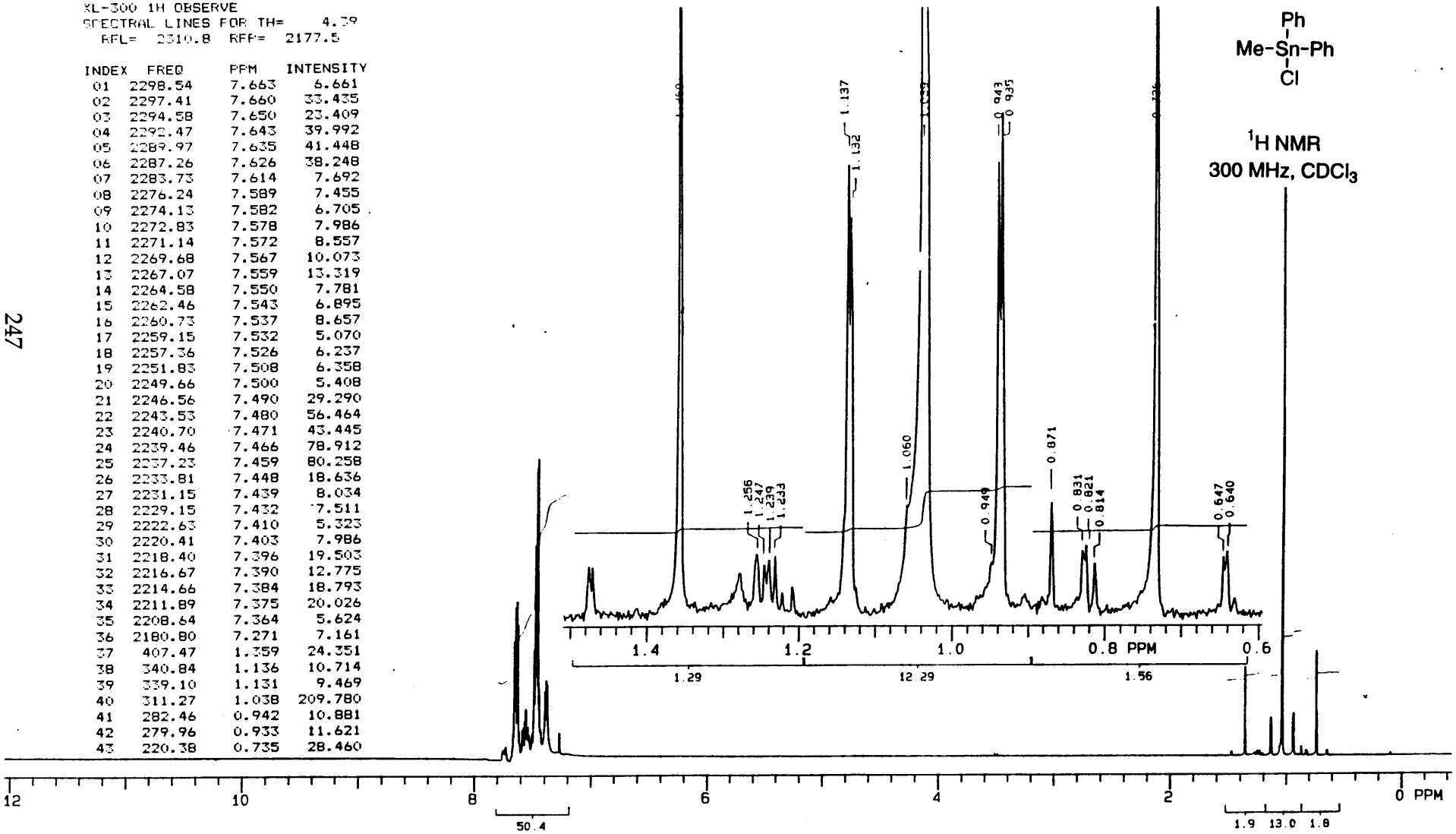


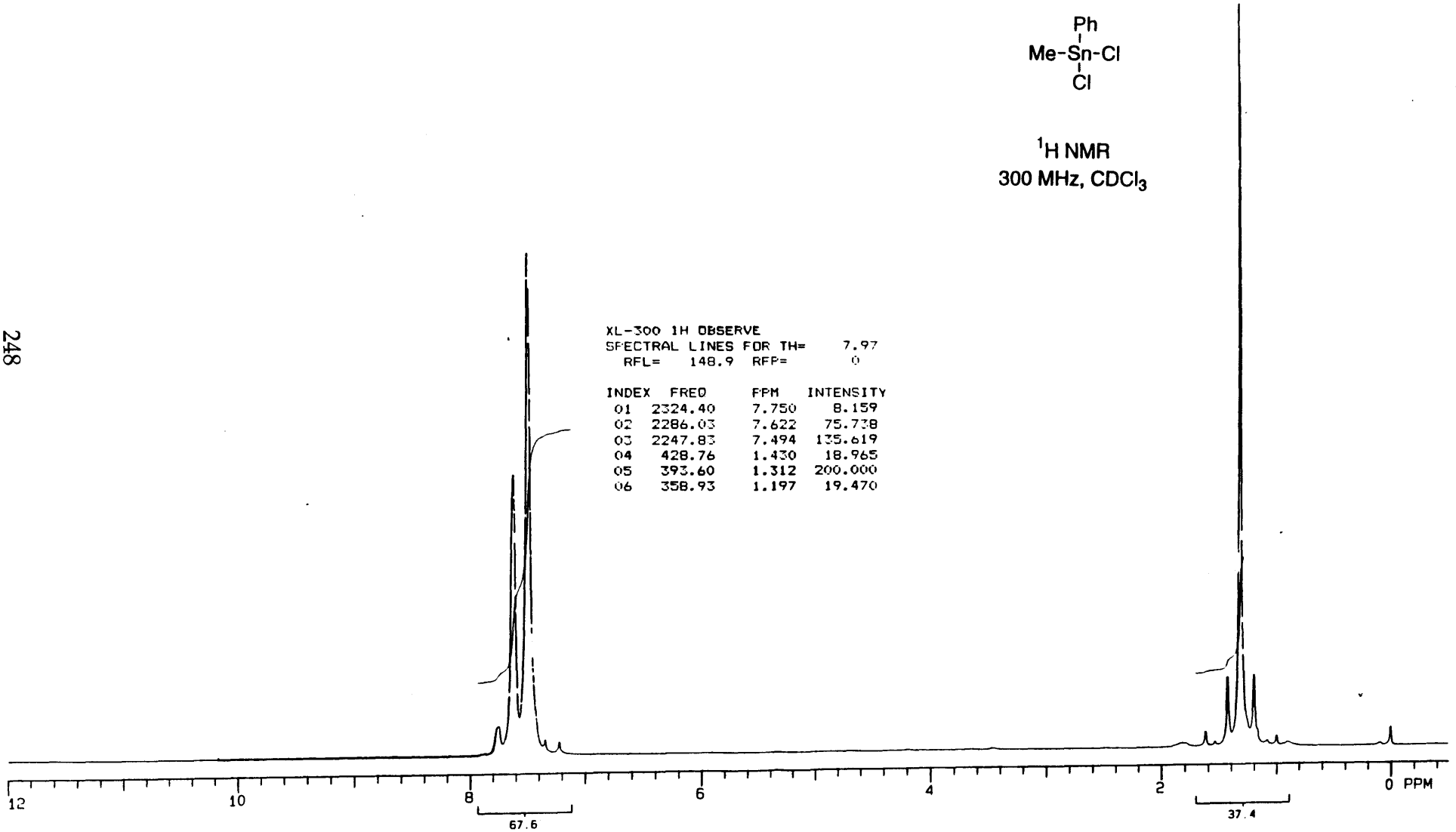

Ph
NC-Sn
NMe2
Me Me
Fe
Me
Me
Me
Me
Me
60c; > 95 : 5 @ Sn
NMe2
Me
Fe
Me
Me
Me
Me
Me-Sn-Ph
CN
61c
60c/61c ~20 :1
1H NMR (300 MHz, CDCl3)
7.444
7.441
7.421
7.413
7.312
7.306
7.299
7.294
7.289
7.284
7.280
7.273
7.262
4.162
4.157
4.150
3.964
3.725
3.712
3.681
3.657
1.855
1.080
1.075
1.037
1.011
0.856
0.852
7.45
7.40
7.35
7.30
7.25 PPM
7.20
4.2
4.0
3.8
3.6 PPM
1.95
1.90
1.85 PPM
1.80
1.10
1.00
0.90 PPM
0.80
12
10
8
6
4
2
0 PPM

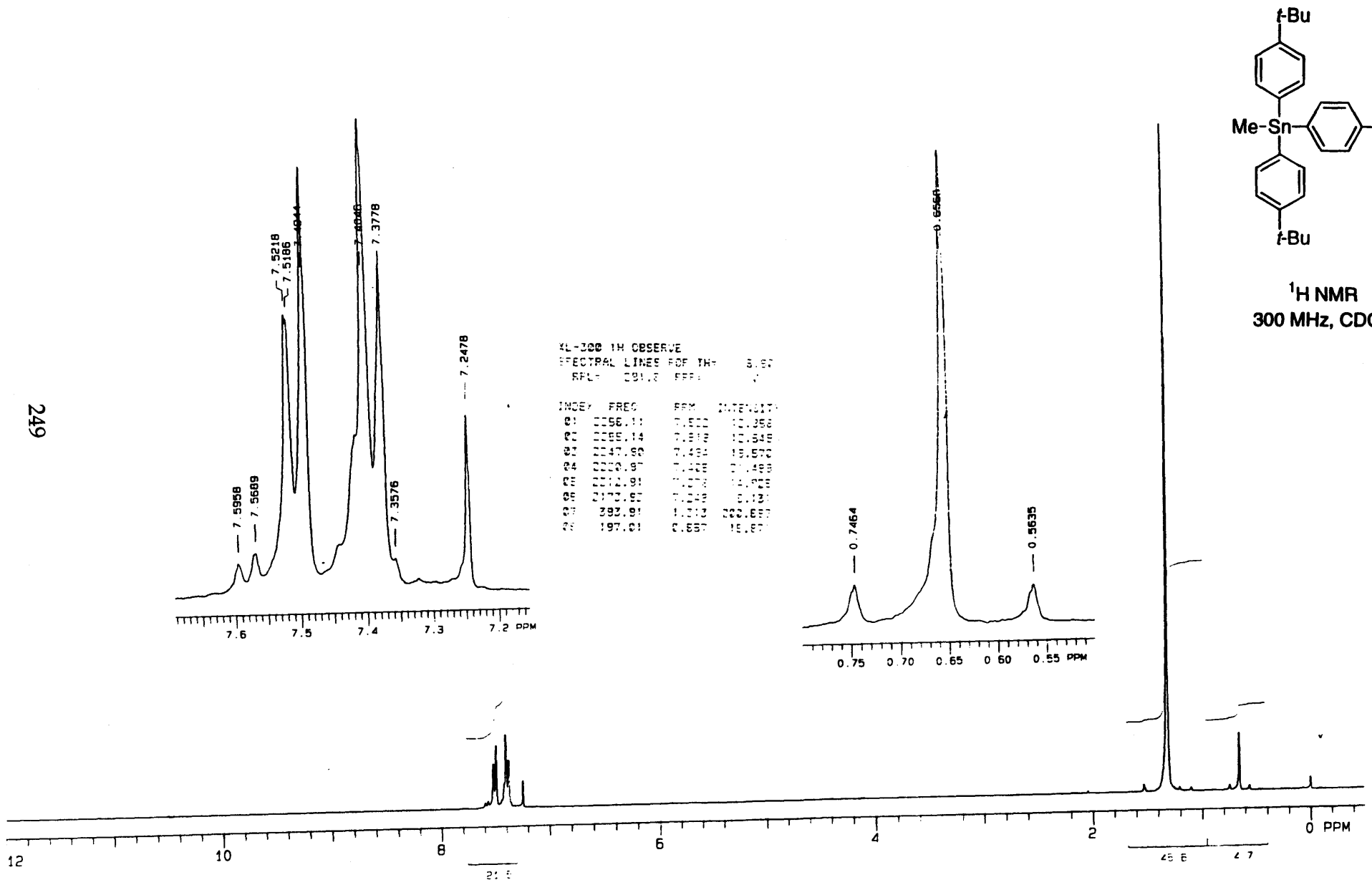

Ph
Me-Sn-Ph
Ph
Ph
^{1}H NMR
300 MHz, $CDCl_3$
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 5.74
RFL= 2285.0 RFP= 2144.6
INDEX FREQ PPM INTENSITY
01 2360.35 7.869 6.258
02 2356.84 7.858 7.475
03 2355.91 7.855 6.089
04 2353.97 7.848 7.209
05 2352.96 7.845 6.929
06 2337.30 7.792 57.578
07 2335.17 7.785 45.624
08 2333.53 7.780 82.302
09 2330.28 7.769 78.726
10 2327.97 7.761 73.011
11 2324.87 7.751 14.131
12 2311.26 7.706 6.693
13 2307.94 7.695 7.029
14 2306.82 7.691 6.921
15 2304.95 7.685 6.146
16 2241.09 7.472 6.269
17 2239.41 7.466 6.820
18 2233.85 7.448 40.082
19 2231.16 7.439 110.565
20 2229.60 7.433 100.833
21 2227.25 7.426 166.941
22 2224.67 7.417 200.056
23 2223.22 7.412 104.196
24 269.84 0.900 10.057
25 268.61 0.896 9.812
26 241.90 0.806 165.122
27 215.15 0.717 8.678
28 213.88 0.713 9.946
29 198.40 0.661 12.123
12
10
8
6
4
2
0 PPM
27.1 47.4
11.8

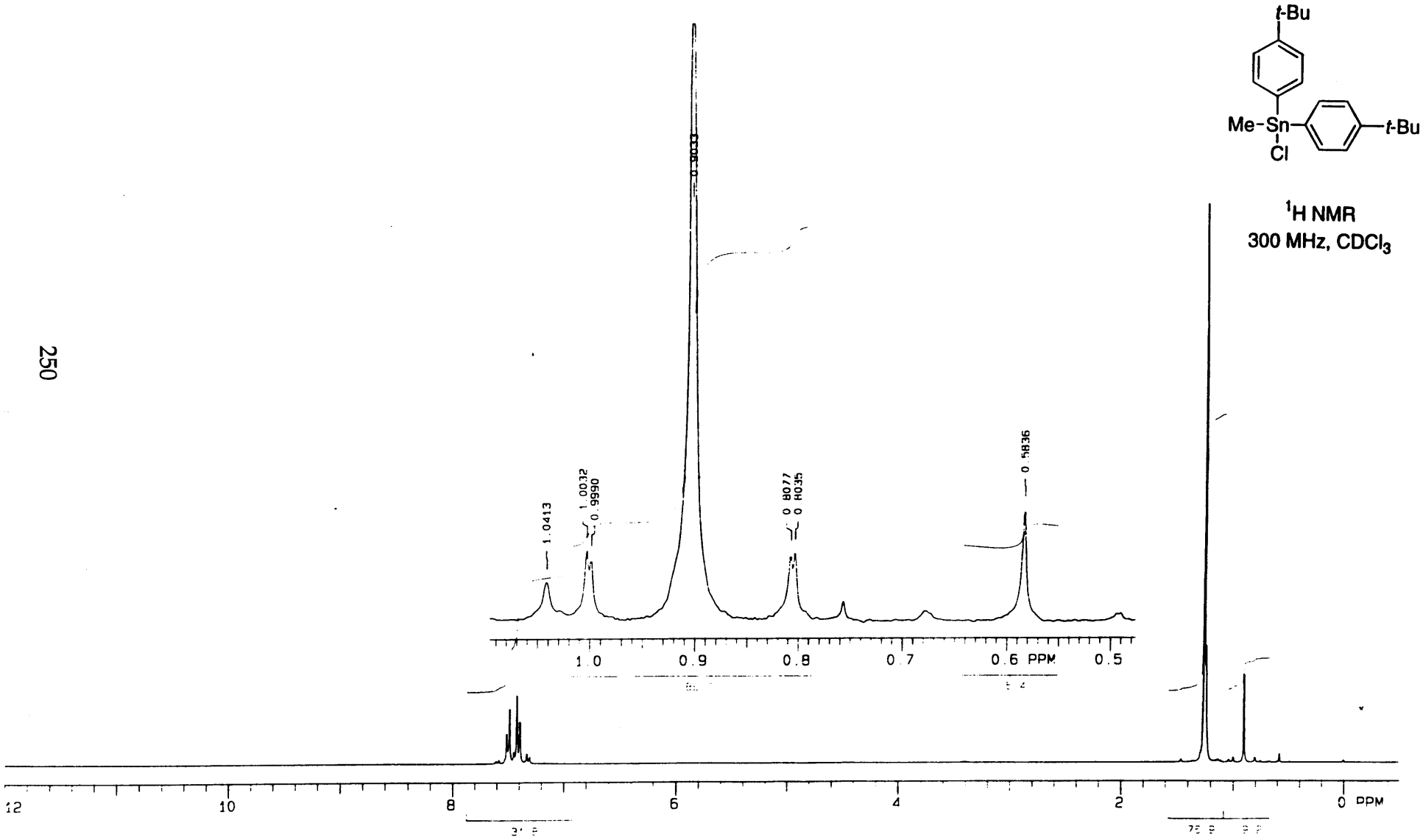
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 4.39
REL= 2310.8 REF= 2177.5

INDEX	FREQ	PPM	INTENSITY
01	2298.54	7.663	6.661
02	2297.41	7.660	33.435
03	2294.58	7.650	23.409
04	2292.47	7.643	39.992
05	2289.97	7.635	41.448
06	2287.26	7.626	38.248
07	2283.73	7.614	7.692
08	2276.24	7.589	7.455
09	2274.13	7.582	6.705
10	2272.83	7.578	7.986
11	2271.14	7.572	8.557
12	2269.68	7.567	10.073
13	2267.07	7.559	13.319
14	2264.58	7.550	7.781
15	2262.46	7.543	6.895
16	2260.73	7.537	8.657
17	2259.15	7.532	5.070
18	2257.36	7.526	6.237
19	2251.83	7.508	6.358
20	2249.66	7.500	5.408
21	2246.56	7.490	29.290
22	2243.53	7.480	56.464
23	2240.70	7.471	43.445
24	2239.46	7.466	78.912
25	2237.23	7.459	80.258
26	2233.81	7.448	18.636
27	2231.15	7.439	8.034
28	2229.15	7.432	7.511
29	2222.63	7.410	5.323
30	2220.41	7.403	7.986
31	2218.40	7.396	19.503
32	2216.67	7.390	12.775
33	2214.66	7.384	18.793
34	2211.89	7.375	20.026
35	2208.64	7.364	5.624
36	2180.80	7.271	7.161
37	407.47	1.359	24.351
38	340.84	1.136	10.714
39	339.10	1.131	9.469
40	311.27	1.038	209.780
41	282.46	0.942	10.881
42	279.96	0.933	11.621
43	220.38	0.735	28.460




Ph
Me-Sn-Cl
Cl
1H NMR
300 MHz, CDCl3
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH= 7.97
RFL= 148.9 RFP= 0
INDEX FREQ PPM INTENSITY
01 2324.40 7.750 8.159
02 2286.03 7.622 75.738
03 2247.83 7.494 135.619
04 428.76 1.430 18.965
05 393.60 1.312 200.000
06 358.93 1.197 19.470
12
10
8
6
4
2
0 PPM
67.6
37.4


t-Bu
Me-Sn
t-Bu
t-Bu
t-Bu
1H NMR
300 MHz, CDCl3
7.5958
7.5689
7.5218
7.5186
7.3778
7.3576
7.2478
0.7464
0.6558
0.5635
7.6
7.5
7.4
7.3
7.2 PPM
0.75
0.70
0.65
0.60
0.55 PPM
12
10
8
6
4
2
0 PPM

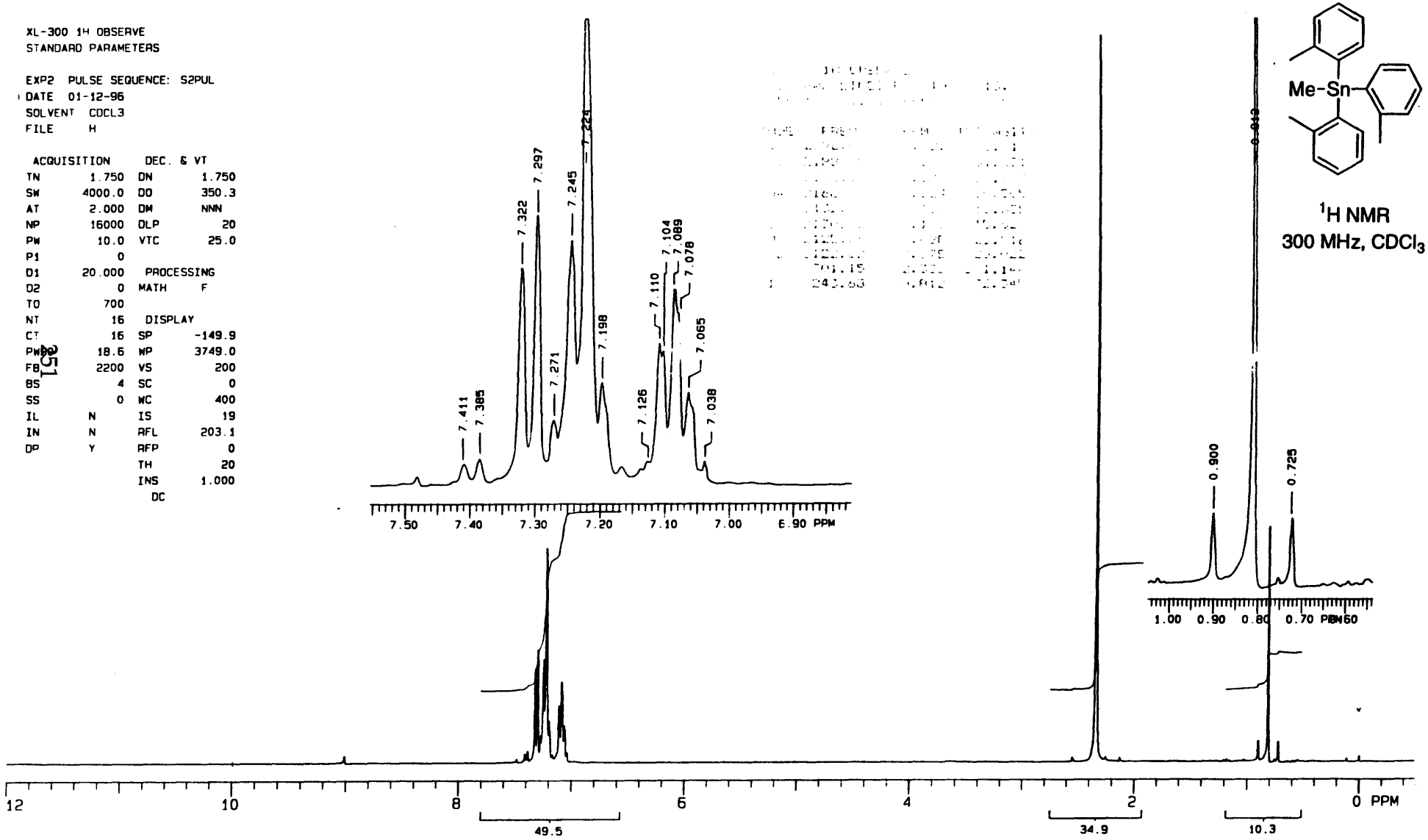

t-Bu
Me-Sn
Cl
t-Bu
1H NMR
300 MHz, CDCl3
1.0413
1.0032
0.9990
0.8077
0.8035
0.5836
1.0
0.9
0.8
0.7
0.6 PPM
0.5
12
10
8
6
4
2
0 PPM

XL-300 1H OBSERVE
STANDARD PARAMETERS

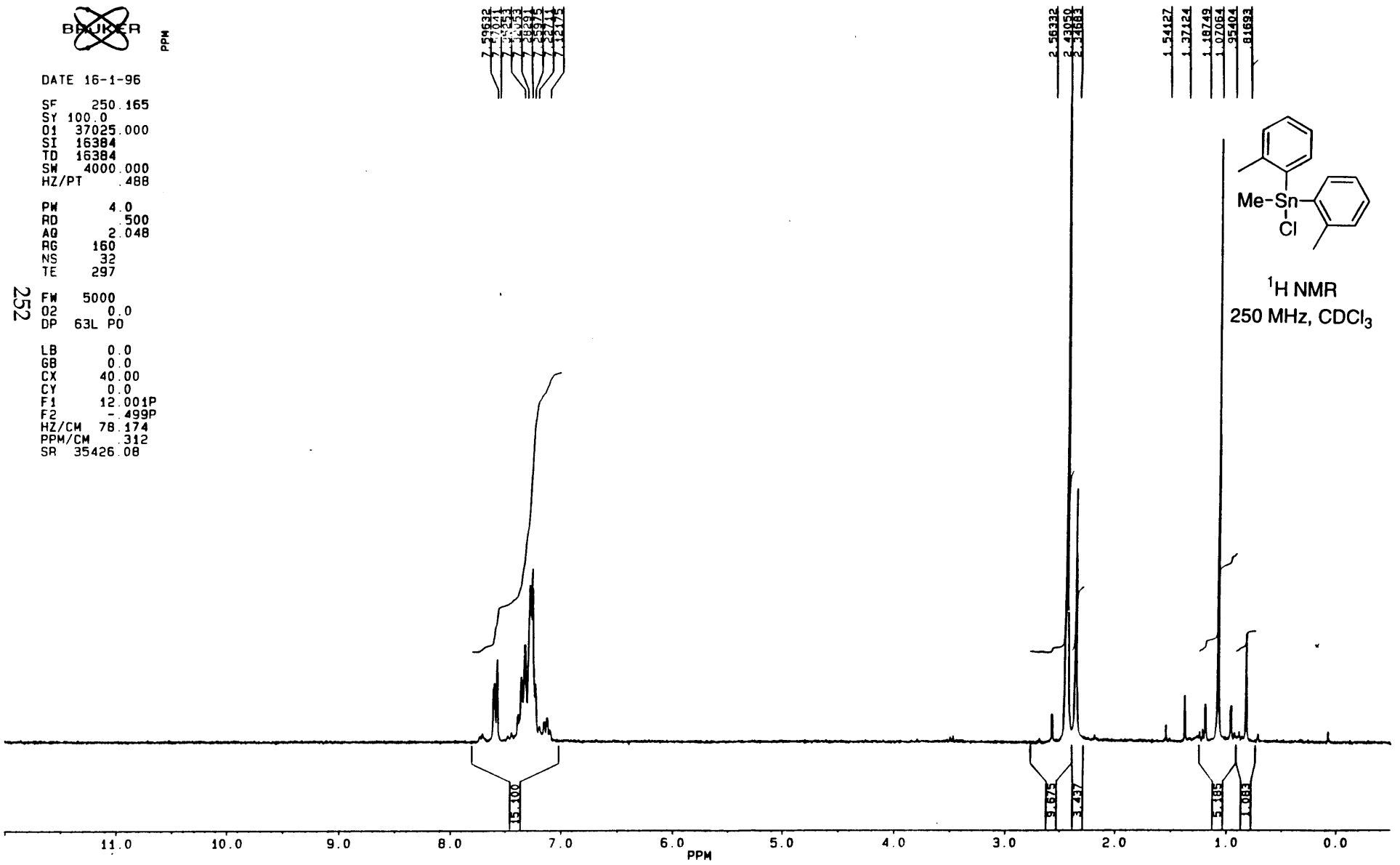
EXP2 PULSE SEQUENCE: S2PUL
DATE 01-12-96
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-149.9
PW90	18.6	WP	3749.0
FB	2200	VS	200
BS	4	SC	0
SS	0	WC	400
IL	N	IS	19
IN	N	RFL	203.1
DP	Y	RFP	0
		TH	20
		INS	1.000
		DC	

151



^{1}H NMR
300 MHz, $CDCl_3$


BRUKER
PPM
DATE 16-1-96
SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 160
NS 32
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35426.08
7.59632
7.12175
2.56332
2.43050
2.34683
1.54127
1.37124
1.18749
1.07064
.95404
.81693
Me-Sn-
Cl
^{1}H NMR
250 MHz, $CDCl_3$
15.100
9.675
3.437
5.185
1.083
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

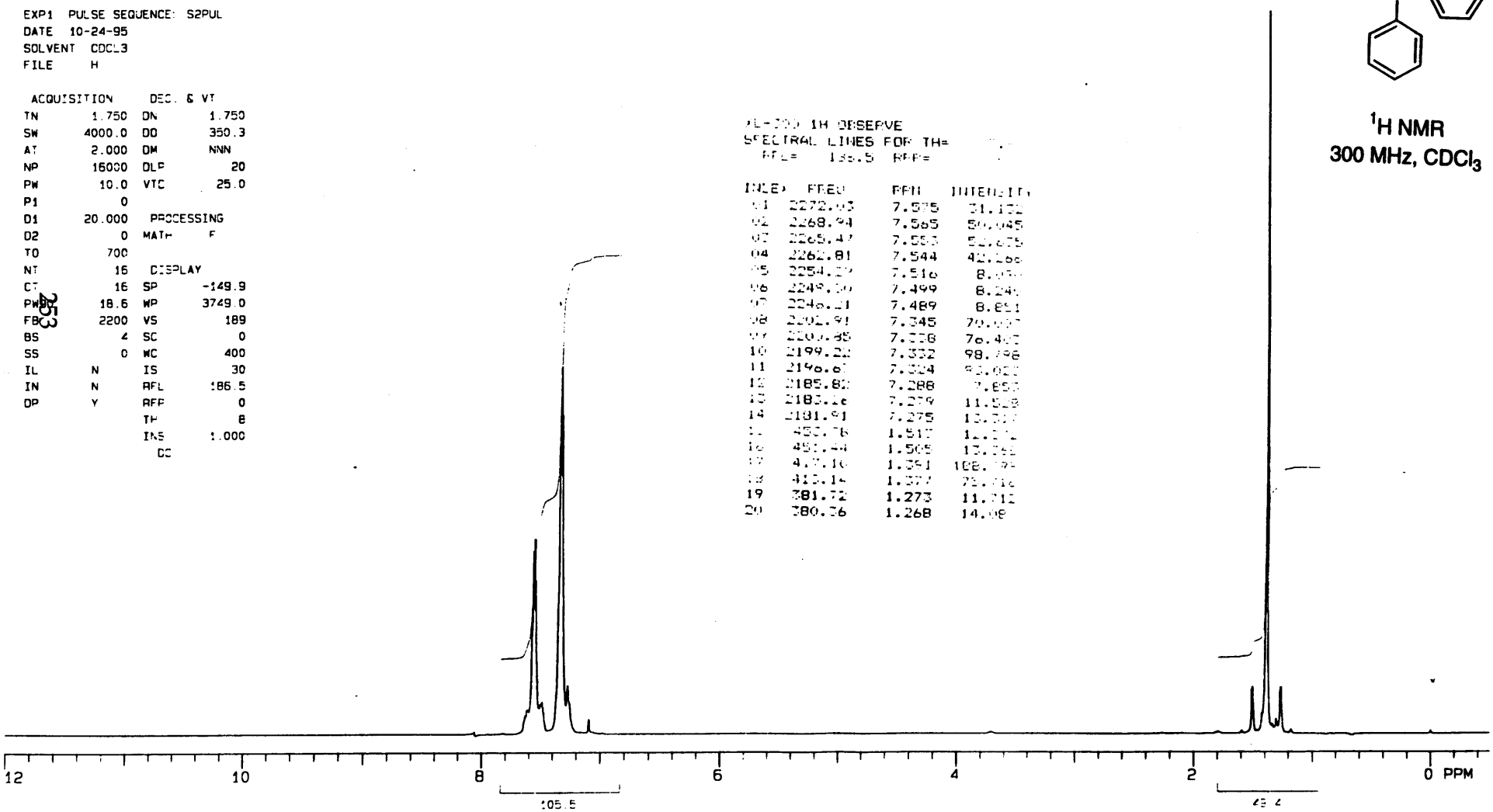
XL-300 1H OBSERVE
STANDARD PARAMETERS

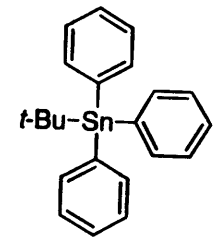
EXP1 PULSE SEQUENCE: S2PUL
DATE 10-24-95
SOLVENT CDCL3
FILE H

ACQUISITION		DEC. & VT	
TN	1.750	DN	1.750
SW	4000.0	DO	350.3
AT	2.000	DM	NNN
NP	16000	DLP	20
PW	10.0	VTC	25.0
P1	0		
D1	20.000	PROCESSING	
D2	0	MATH	F
TO	700		
NT	16	DISPLAY	
CT	16	SP	-149.9
PW	18.6	WP	3749.0
FB	2200	VS	189
BS	4	SC	0
SS	0	WC	400
IL	N	IS	30
IN	N	RFL	186.5
DP	Y	RFP	0
		TH	8
		INS	1.000
		DC	

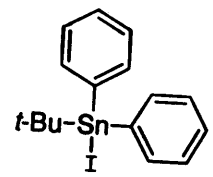
XL-300 1H OBSERVE
SPECTRAL LINES FOR TH=
RFL= 186.5 RFP=

INDEX	FREQ	PPM	INTENSITY
01	2272.03	7.575	31.132
02	2268.94	7.565	50.045
03	2265.47	7.553	52.675
04	2262.81	7.544	42.266
05	2254.29	7.516	8.[illegible]
06	2249.30	7.499	8.24[illegible]
07	2246.21	7.489	8.851
08	2202.91	7.345	70.[illegible]
09	2200.85	7.338	76.40[illegible]
10	2199.22	7.332	98.798
11	2196.67	7.324	93.022
12	2185.82	7.288	7.85[illegible]
13	2183.26	7.279	11.528
14	2181.91	7.275	13.[illegible]
15	453.76	1.517	1.[illegible]
16	451.44	1.505	13.[illegible]
17	417.10	1.391	188.[illegible]
18	413.14	1.377	75.716
19	381.72	1.273	11.712
20	380.36	1.268	14.08

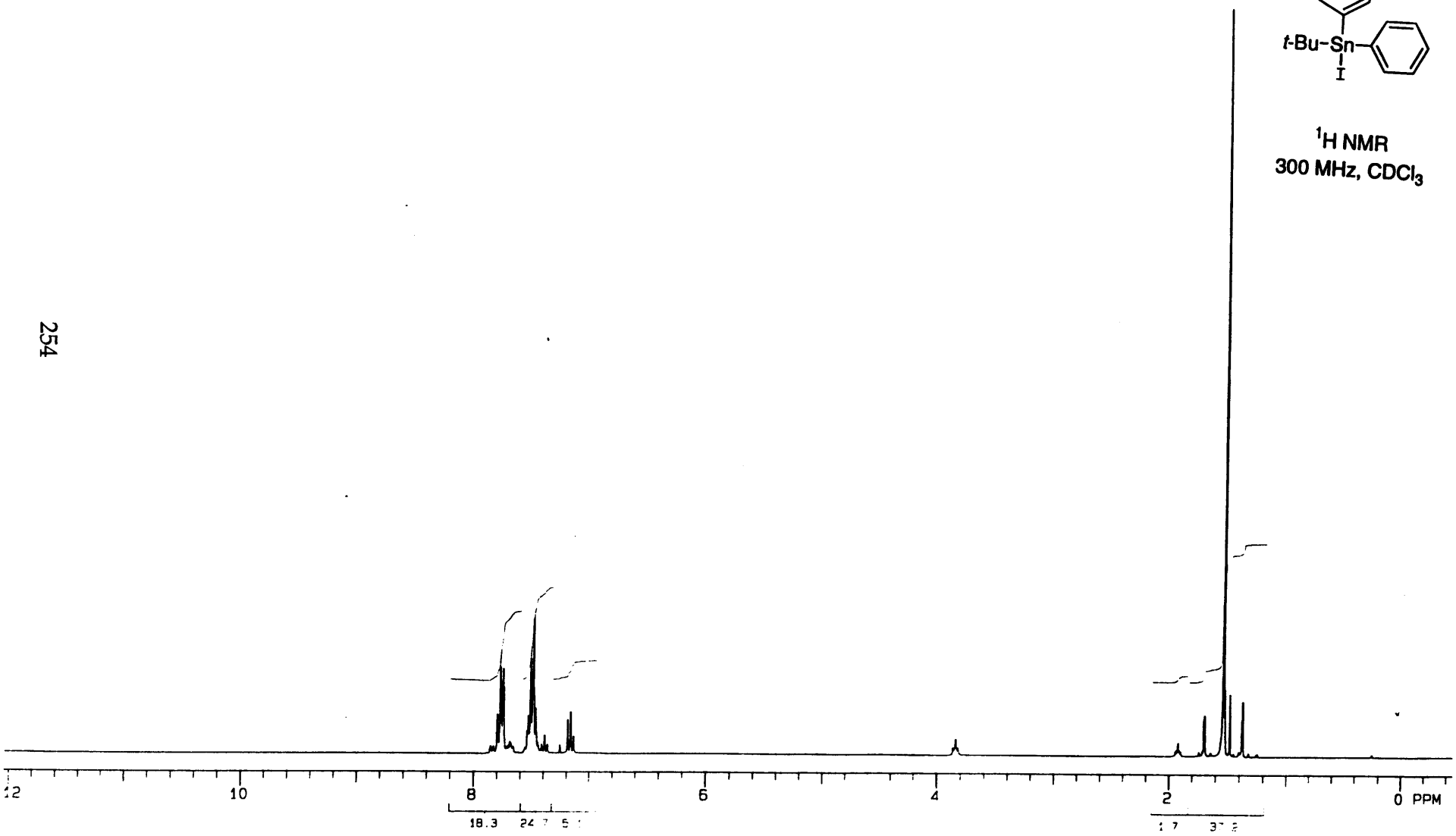


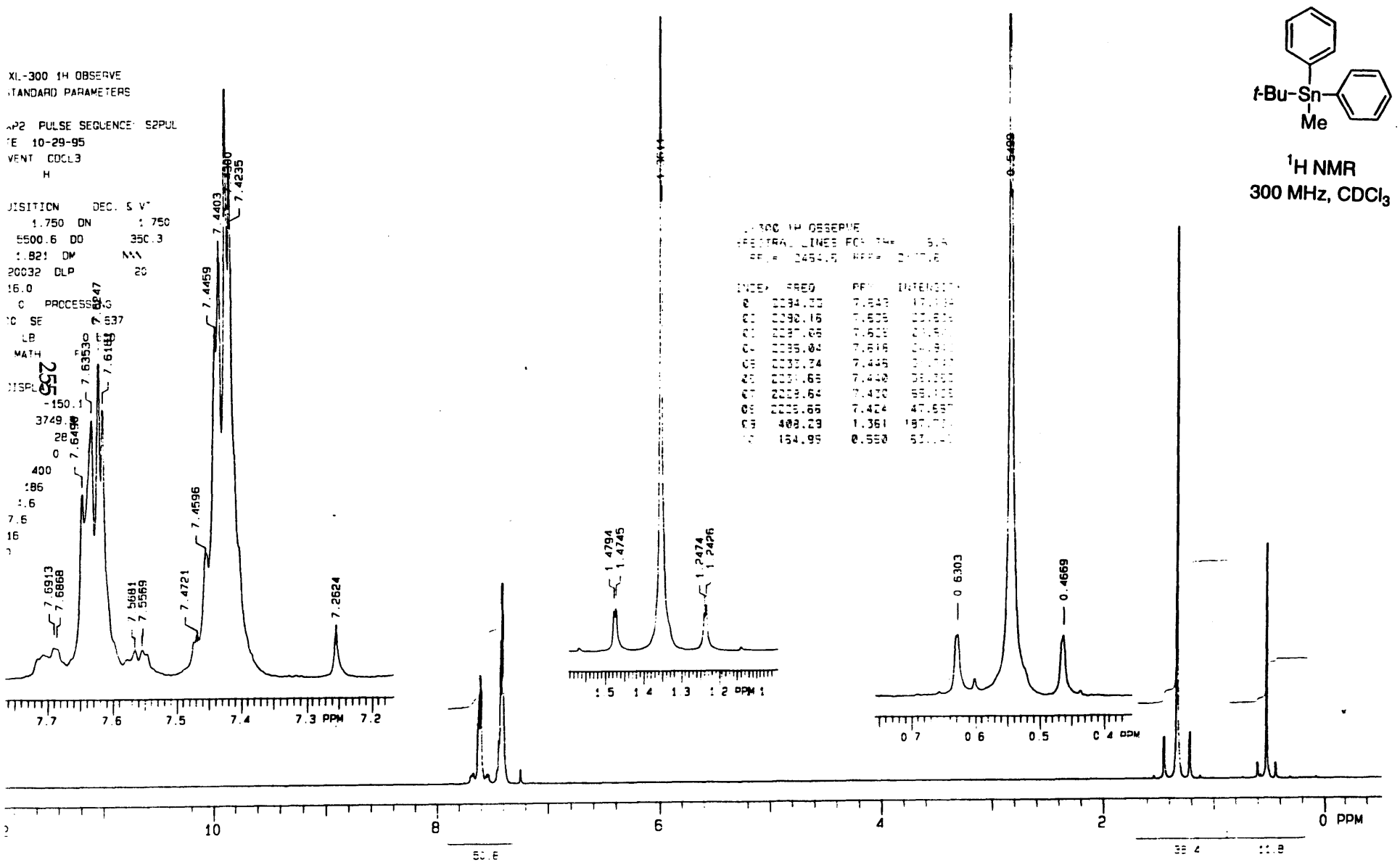


^{1}H NMR
300 MHz, $CDCl_3$

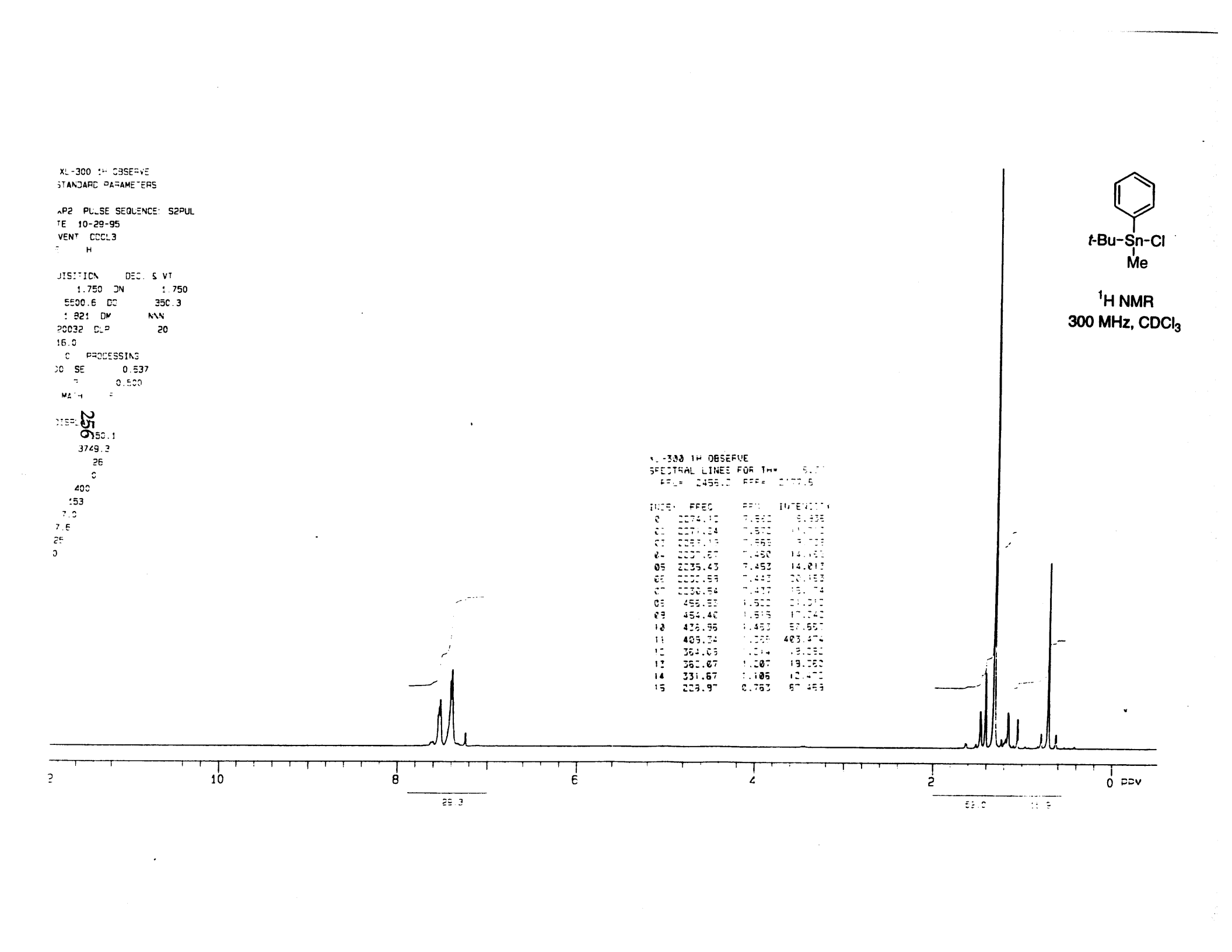


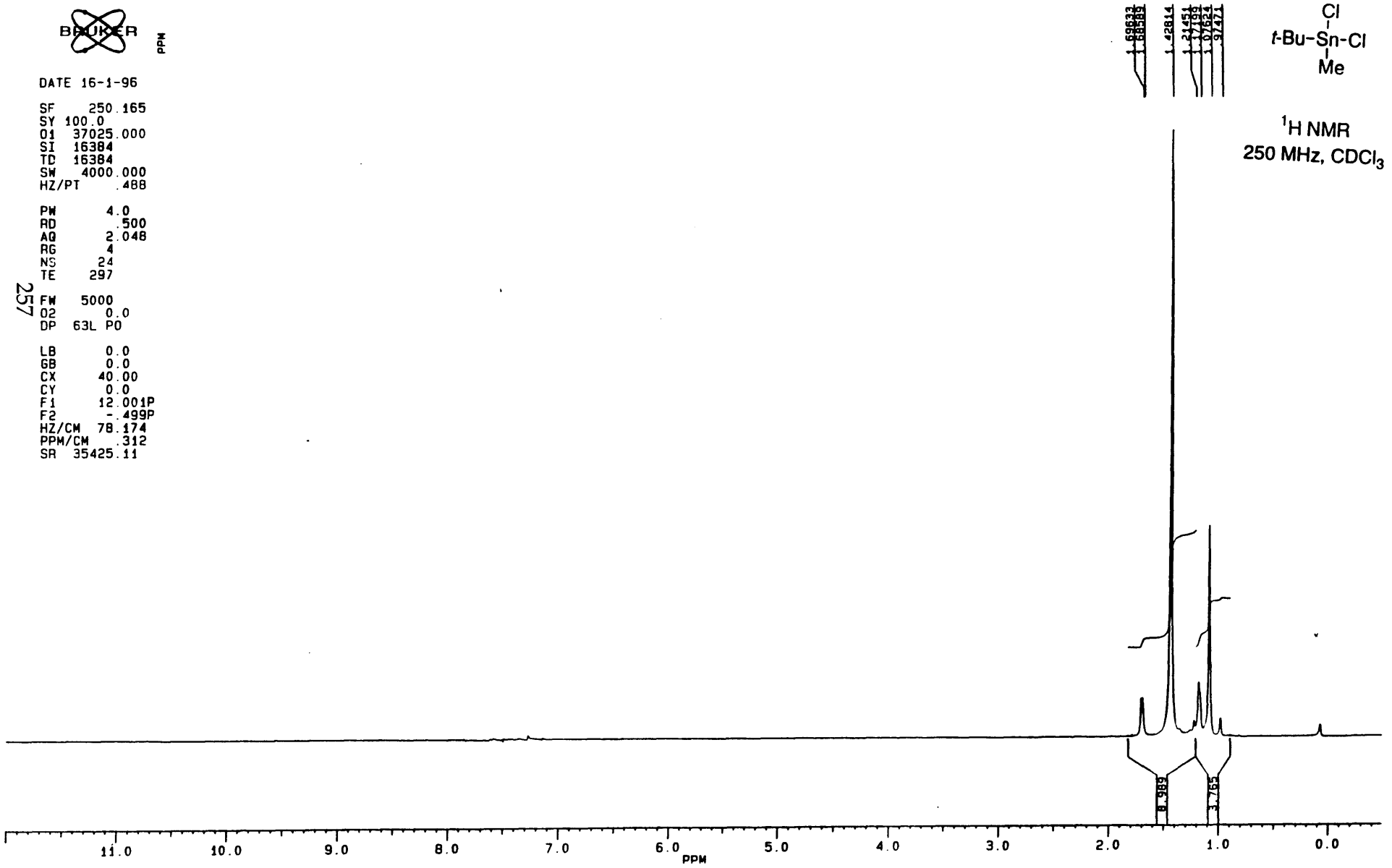
^{1}H NMR
300 MHz, $CDCl_3$





^{1}H NMR
300 MHz, $CDCl_3$


t-Bu-Sn-Cl
Me
1H NMR
300 MHz, CDCl3
ppm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DATE 16-1-96
SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
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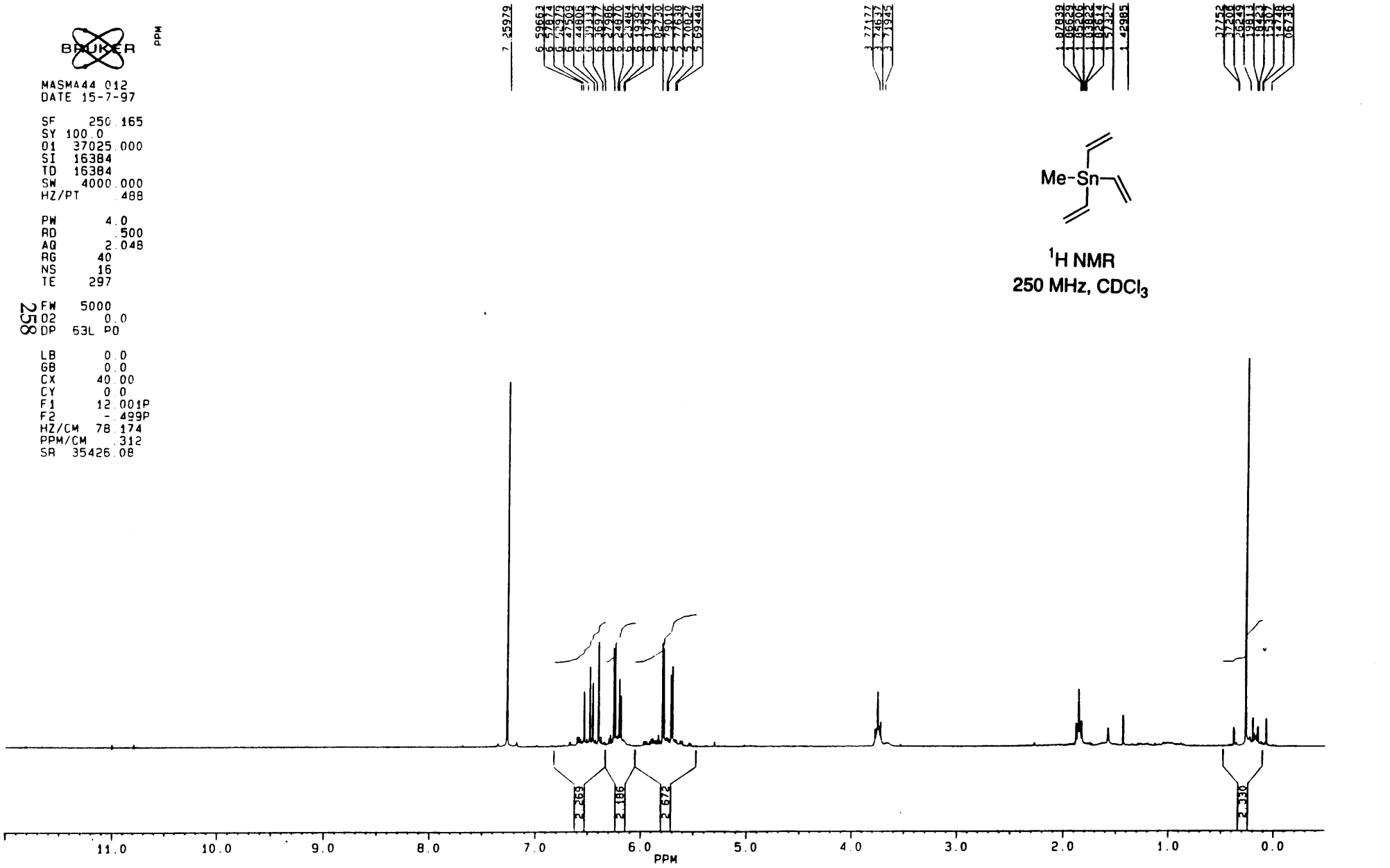
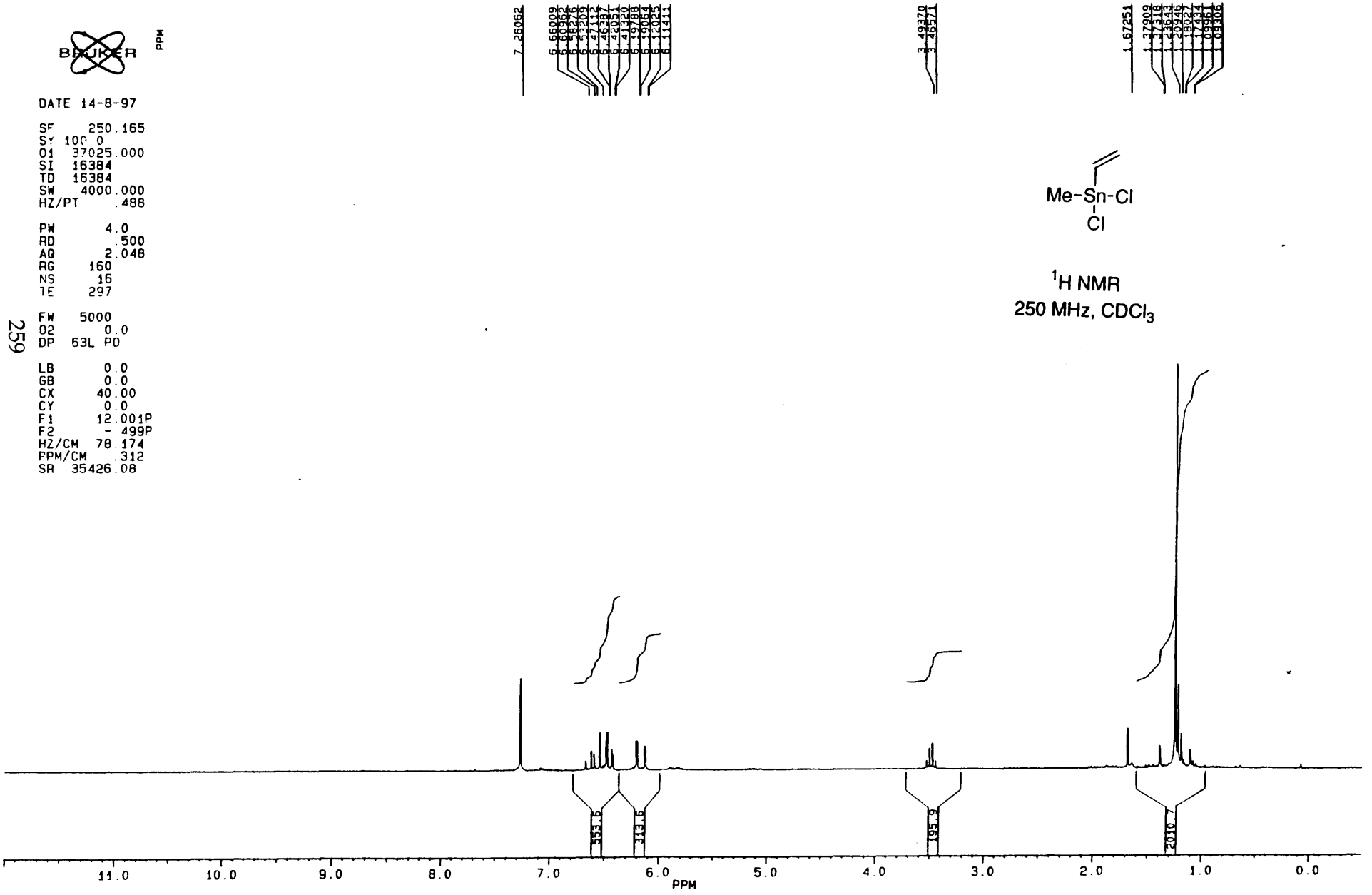
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 4
NS 24
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35425.11
257
1.69633
1.68589
1.42814
1.21451
1.17193
1.07624
.97471
Cl
t-Bu-Sn-Cl
Me
1H NMR
250 MHz, CDCl3
8.989
3.765
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


BRUKER
MASMA44 012
DATE 15-7-97
SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 40
NS 16
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35426.08
PPM
Me-Sn
^{1}H NMR
250 MHz, $CDCl_3$
2.269
2.186
2.672
2.330
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


BRUKER
PPM
DATE 14-8-97
SF 250.165
SY 100 0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 160
NS 16
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35426.08
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6.66009
6.60962
6.58276
6.53209
6.47112
6.46387
6.42051
6.41320
6.19788
6.19064
6.12025
6.11411
3.49370
3.46571
1.67251
1.37909
1.37318
1.23643
1.20946
1.19027
1.17434
1.09961
1.09306
Me-Sn-Cl
Cl
^{1}H NMR
250 MHz, $CDCl_3$
553.6
313.6
195.9
2010.7
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

Appendix B

^{1}H NMR Spectra of Selected Compounds in Chapter 2

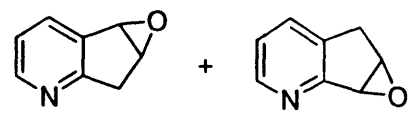
DATE 9-5-98

SF 250.165
SY 100.0
01 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488

PW 4.0
RD .500
AQ 2.048
RG 10
NS 16
TE 297

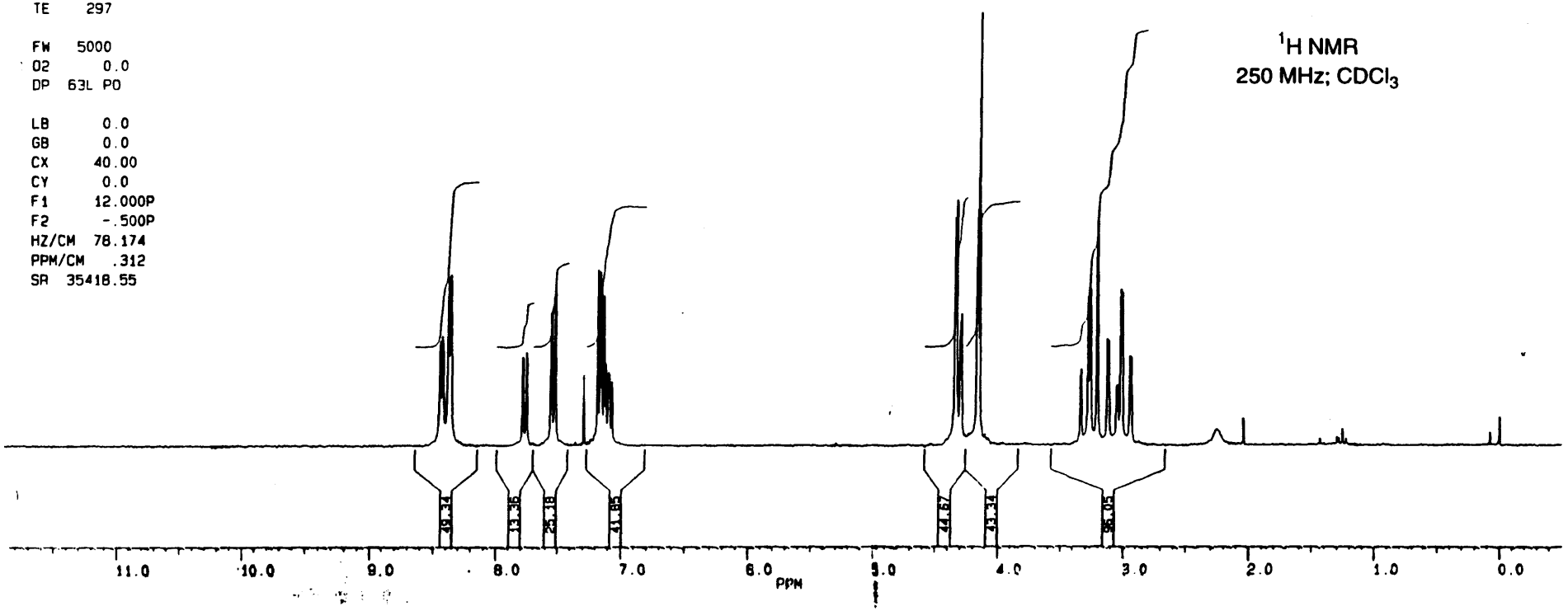
FW 5000
02 0.0
DP 63L PD

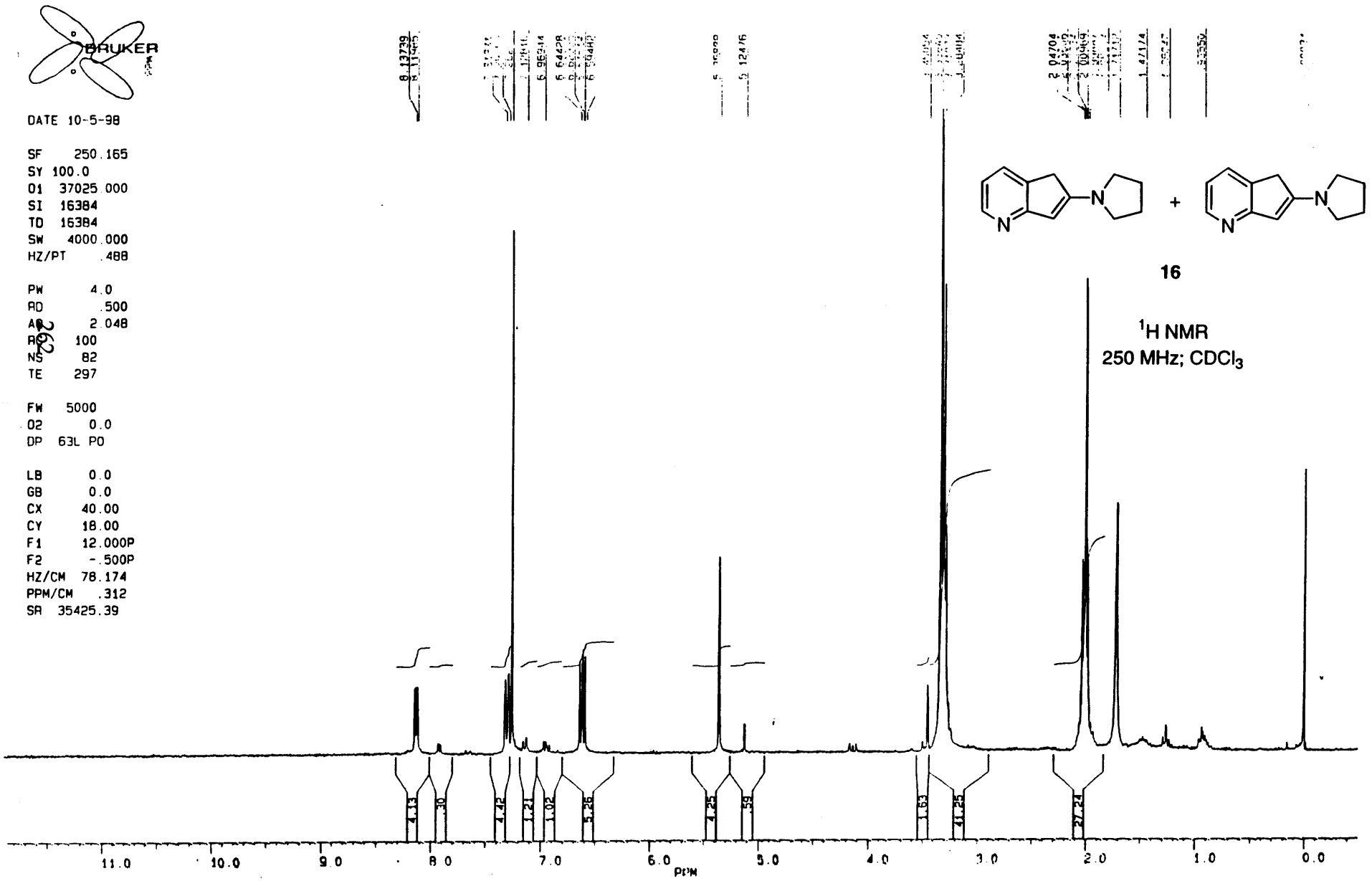
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.000P
F2 -.500P
HZ/CM 78.174
PPM/CM .312
SR 35418.55

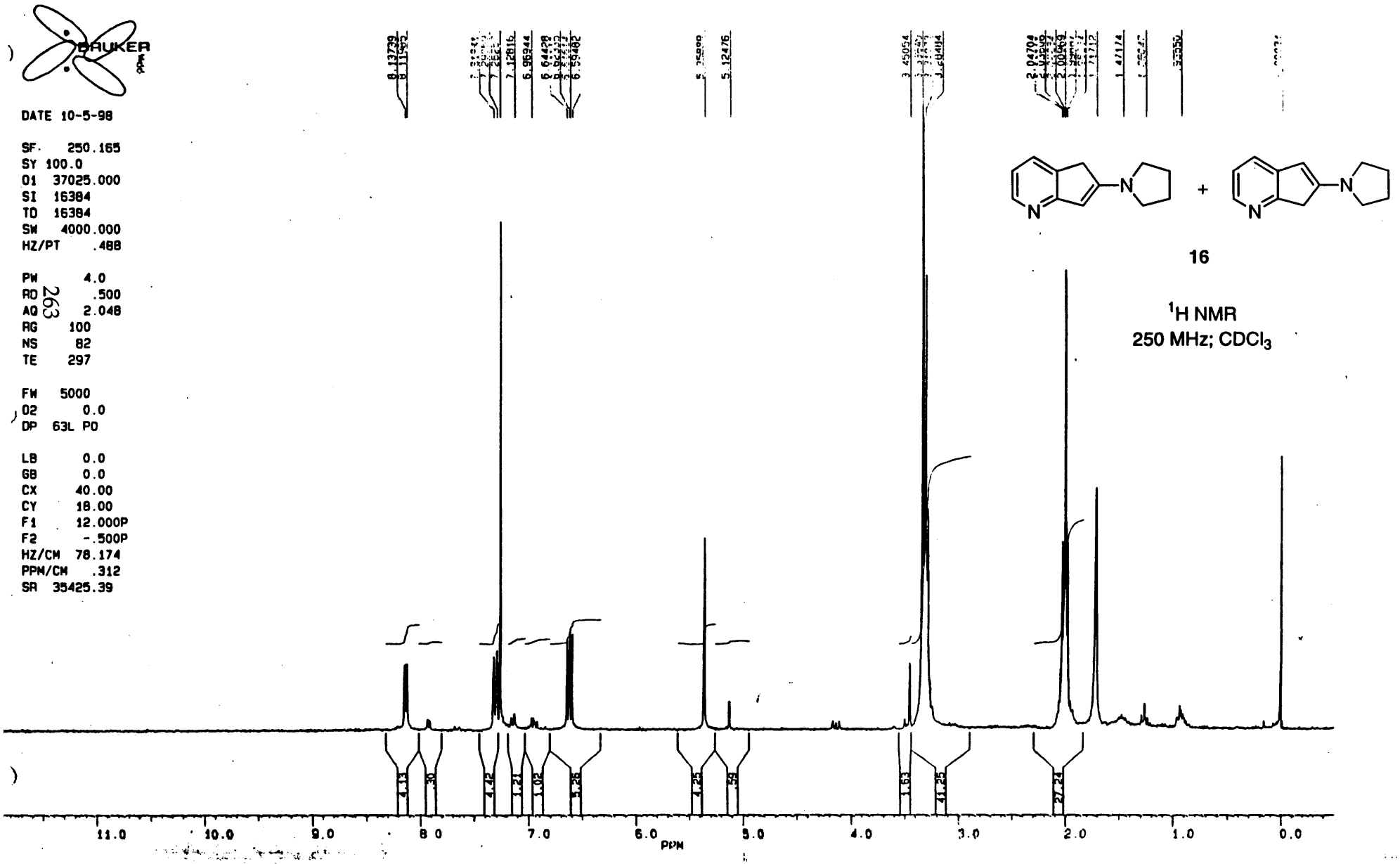


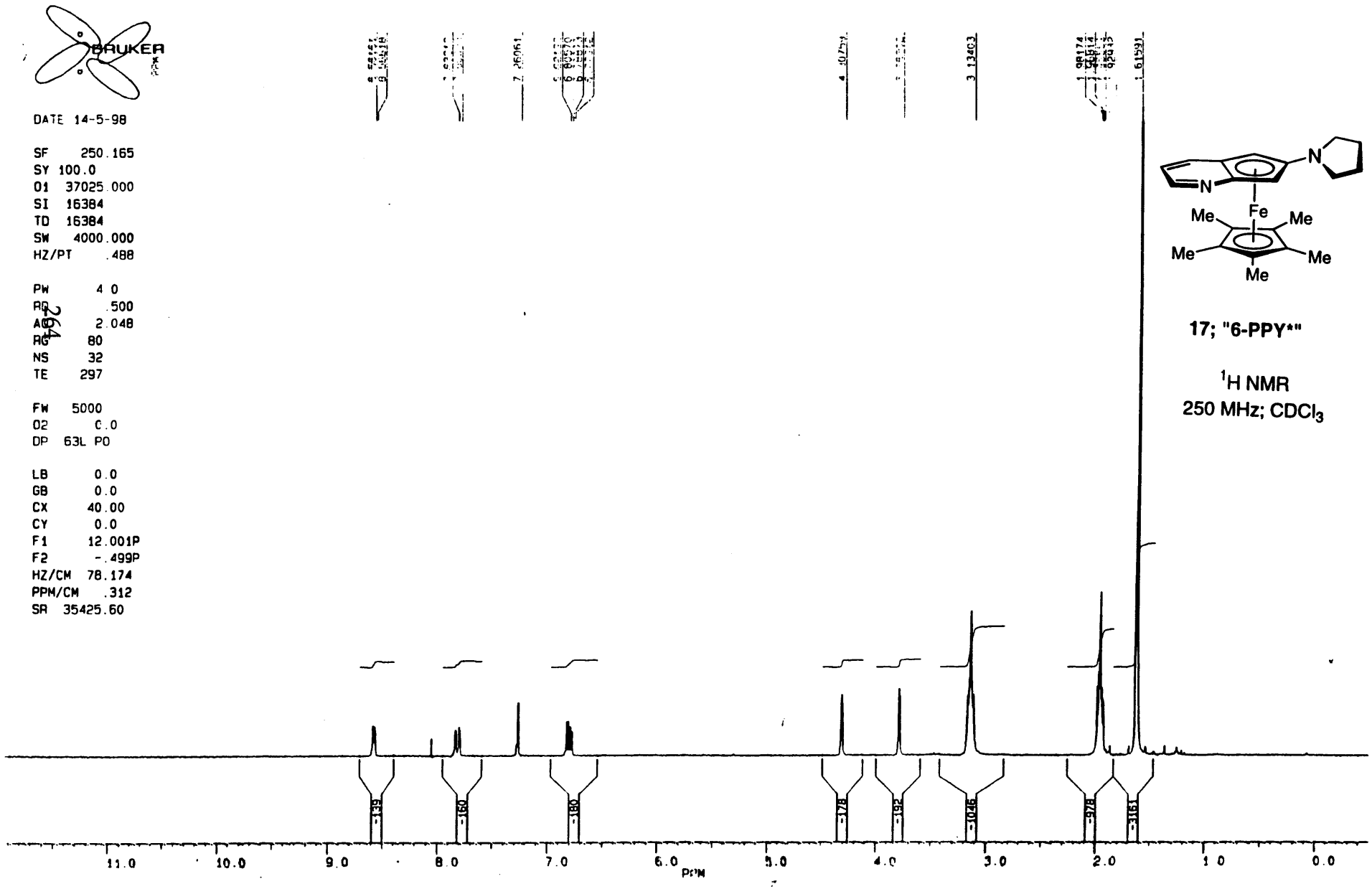
14; ~ 1.7 : 1

^{1}H NMR
250 MHz; $CDCl_3$




DATE 10-5-98
SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 100
NS 82
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 18.00
F1 12.000P
F2 -.500P
HZ/CM 78.174
PPM/CM .312
SR 35425.39
16
^{1}H NMR
250 MHz; $CDCl_3$
4.13
3.30
4.42
1.21
1.02
5.26
4.25
3.59
1.63
11.35
27.24
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


DATE 10-5-98
SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 100
NS 82
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 18.00
F1 12.000P
F2 -.500P
HZ/CM 78.174
PPM/CM .312
SR 35425.39
263
16
^{1}H NMR
250 MHz; $CDCl_3$
PPM


BRUKER
DATE 14-5-98
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SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4 0
RD .500
AQ 2.048
RG 80
NS 32
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35425.60
N
N
Fe
Me
Me
Me
Me
Me
17; "6-PPY*"
1H NMR
250 MHz; CDCl3
-139
-160
-180
-178
-192
-1046
-978
-3161
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

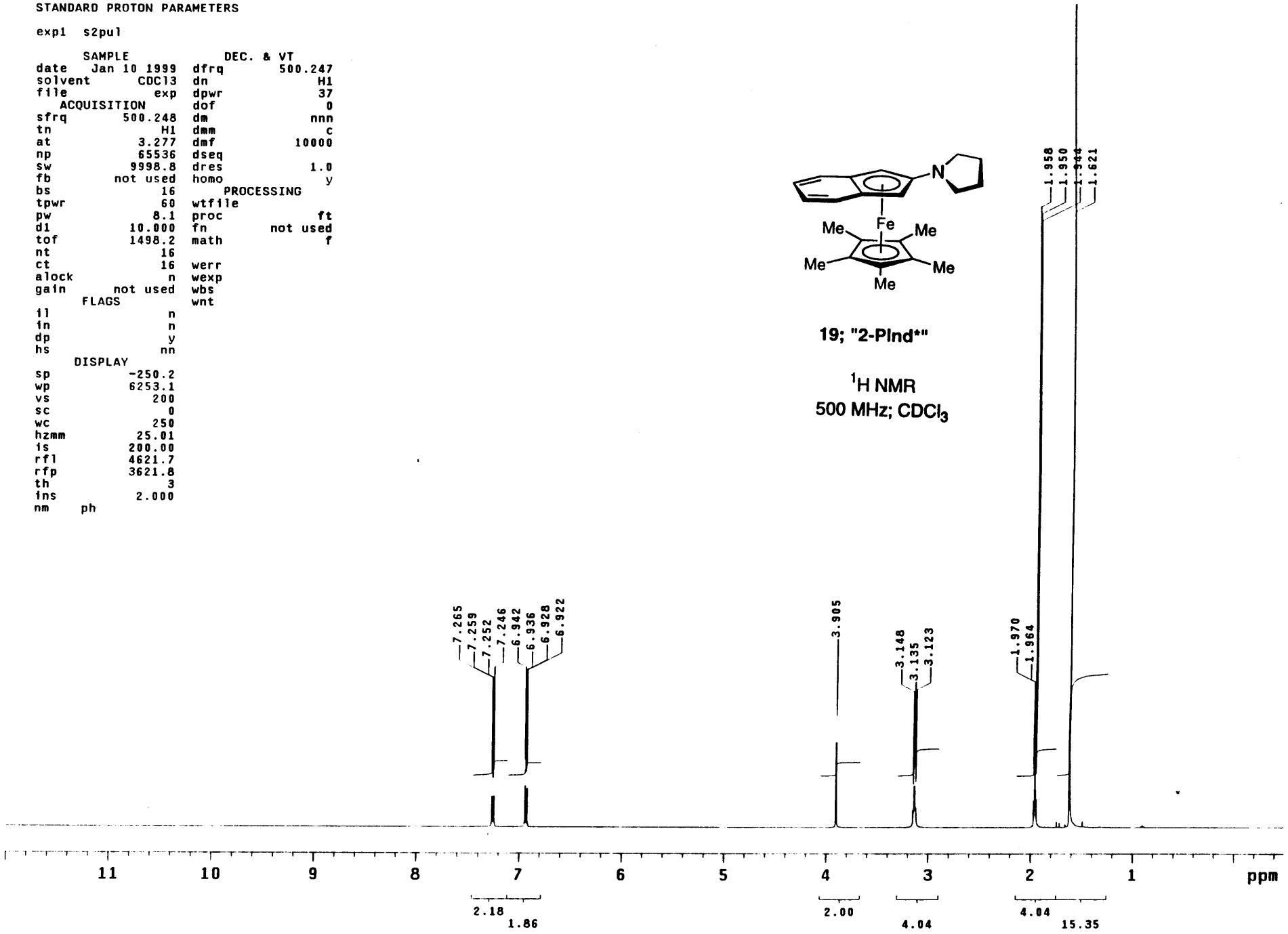
STANDARD PROTON PARAMETERS

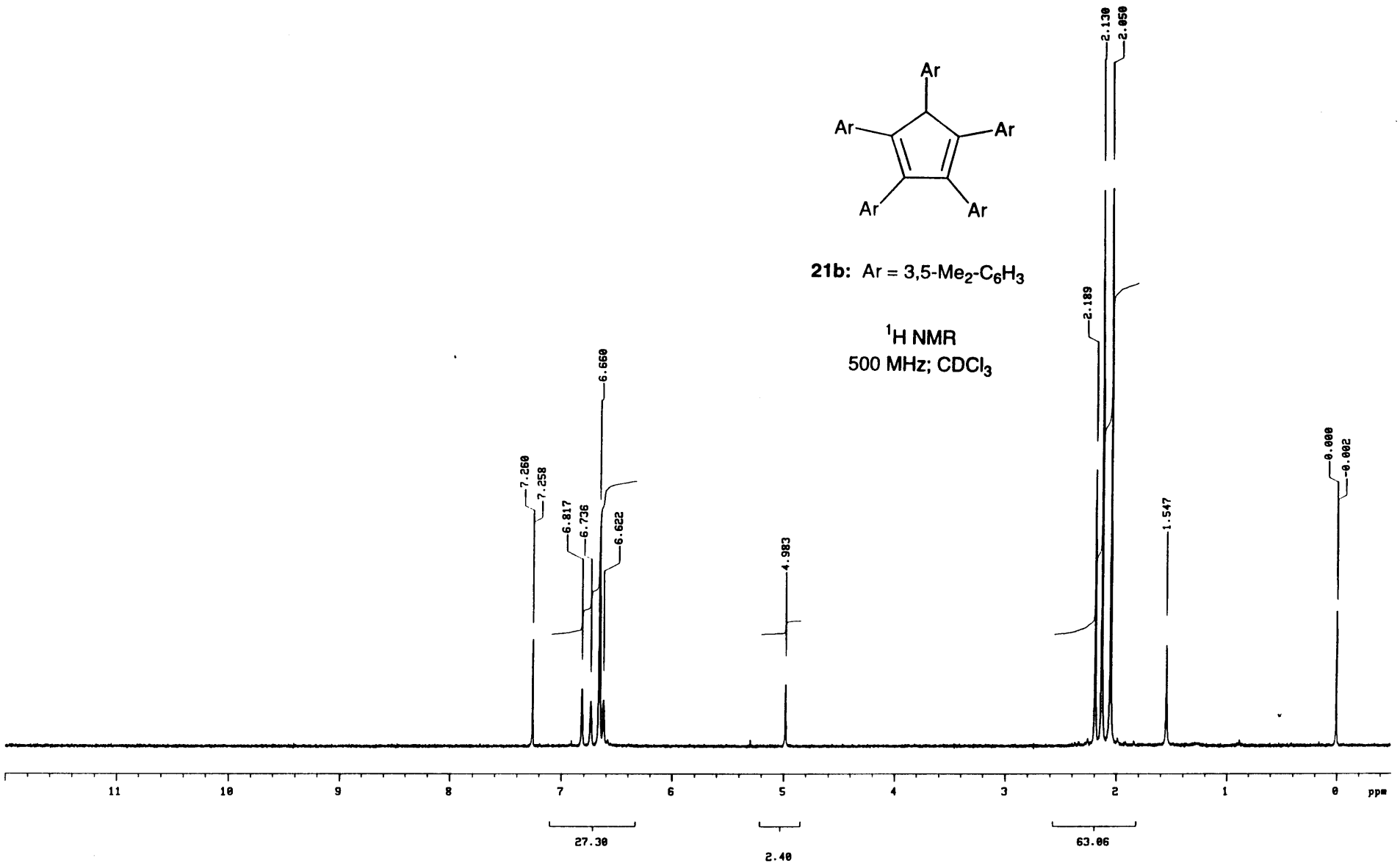
exp1 s2pul

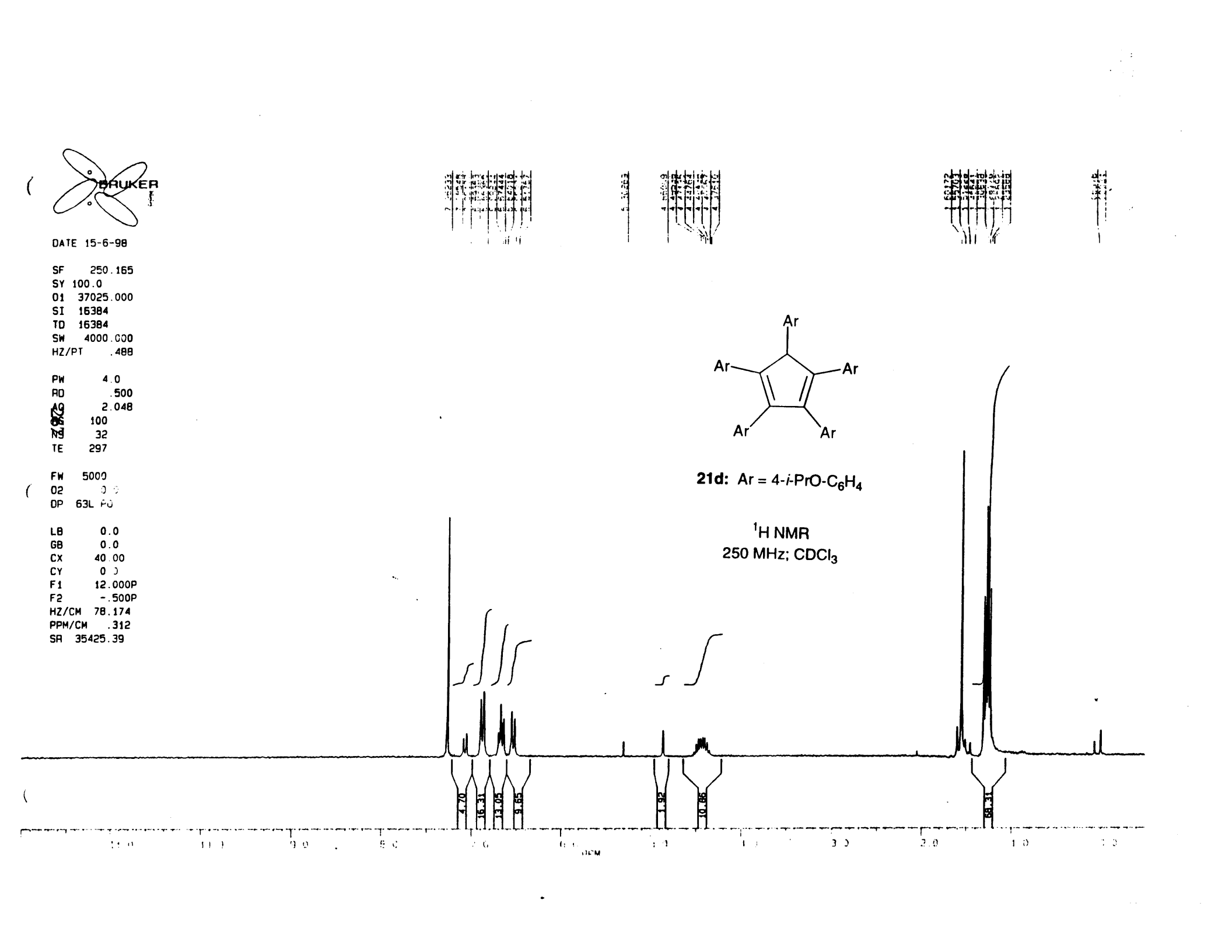
SAMPLE		DEC. & VT	
date	Jan 10 1999	dfrq	500.247
solvent	CDCl3	dn	H1
file	exp	dpwr	37
ACQUISITION		dof	0
sfrq	500.248	dm	nnn
tn	H1	dmm	c
at	3.277	dmf	10000
np	65536	dseq	
sw	9998.8	dres	1.0
fb	not used	homo	y
bs	16	PROCESSING	
tpwr	60	wtfile	
pw	8.1	proc	ft
d1	10.000	fn	not used
tof	1498.2	math	f
nt	16		
ct	16	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.2		
wp	6253.1		
vs	200		
sc	0		
wc	250		
hzmm	25.01		
is	200.00		
rfl	4621.7		
rfp	3621.8		
th	3		
ins	2.000		
nm	ph		

19; "2-PInd*"

^{1}H NMR
500 MHz; $CDCl_3$




Ar
Ar
Ar
Ar
Ar
21b: Ar = 3,5-Me2-C6H3
1H NMR
500 MHz; CDCl3
2.130
2.050
2.189
6.660
7.260
7.258
6.817
6.736
6.622
4.983
1.547
0.000
-0.002
11
10
9
8
7
6
5
4
3
2
1
0
ppm
27.30
2.40
63.06


DATE 15-6-98
SF 250.165
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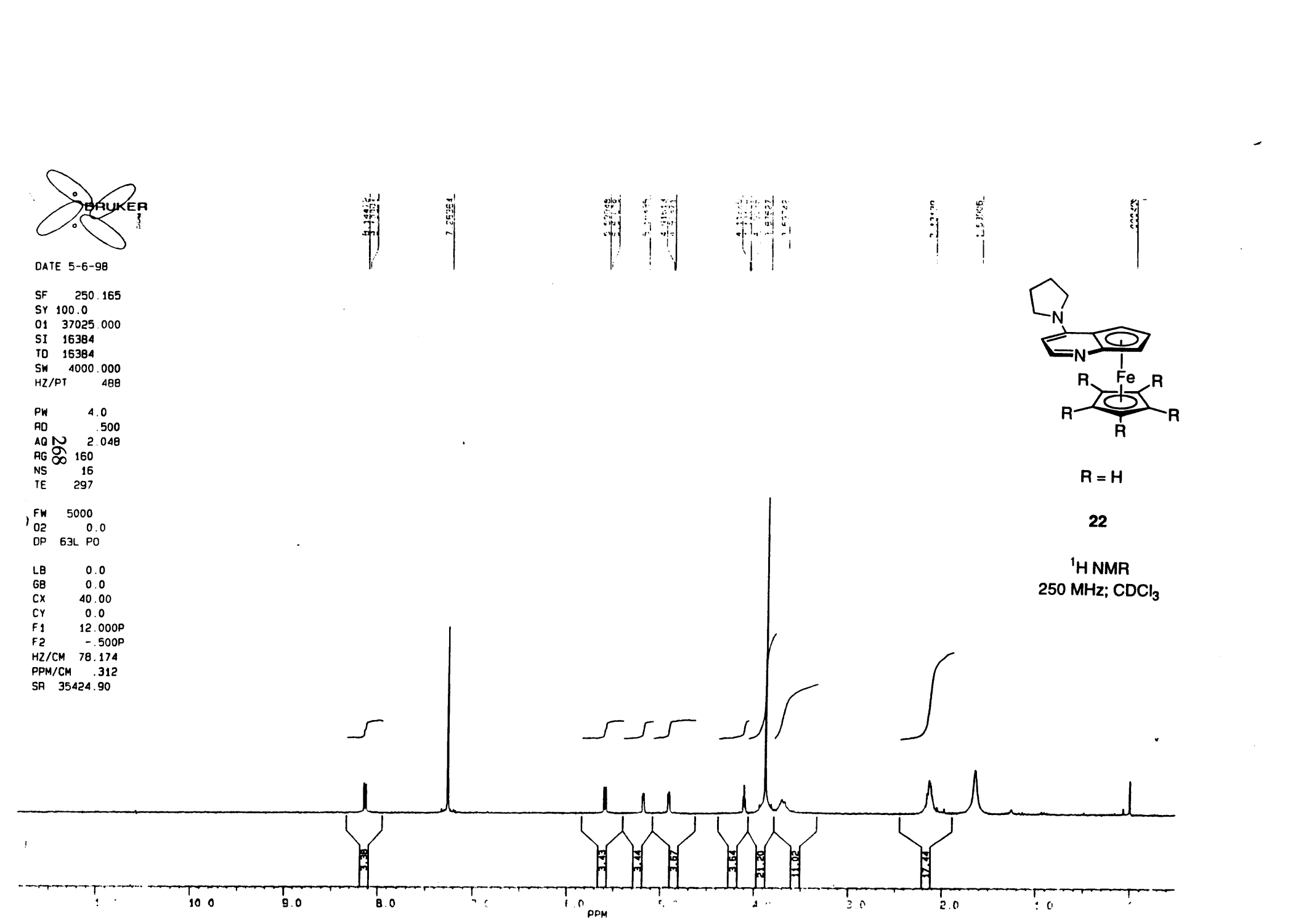
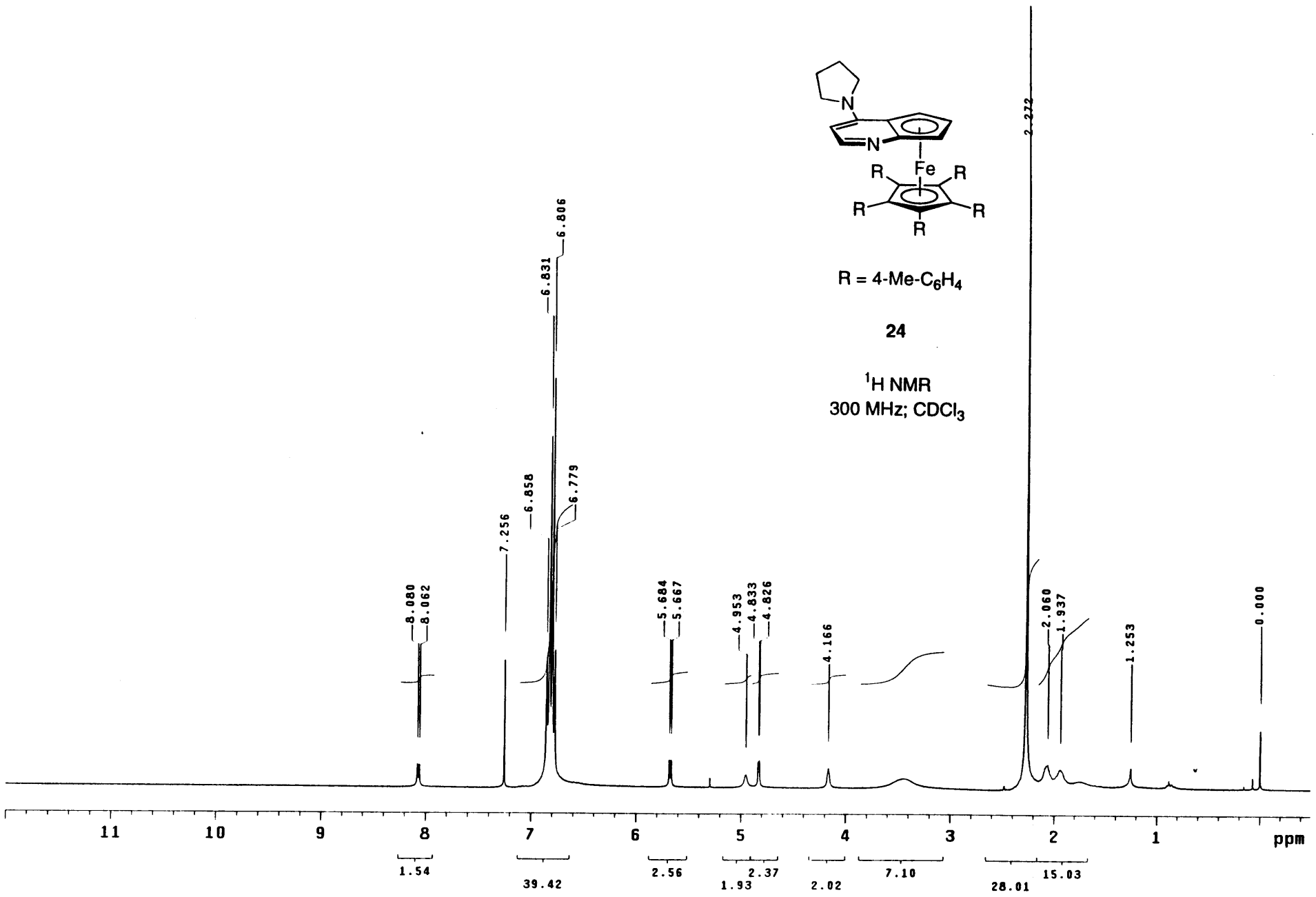
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
NS 100
TE 297
FW 5000
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
F1 12.000P
F2 -.500P
HZ/CM 78.174
PPM/CM .312
SR 35425.39
Ar
Ar
Ar
Ar
Ar
21d: Ar = 4-i-PrO-C6H4
1H NMR
250 MHz; CDCl3
4.70
16.31
13.05
9.65
1.92
10.86
38.31


BRUKER
DATE 5-6-98
SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT 488
PW 4.0
RD .500
AQ 2.048
RG 160
NS 16
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.000P
F2 -.500P
HZ/CM 78.174
PPM/CM .312
SR 35424.90
268
N
N
Fe
R
R
R
R
R
R = H
22
^{1}H NMR
250 MHz; $CDCl_3$
3.38
3.43
3.44
3.67
3.64
21.20
11.02
37.44
10.0
9.0
8.0
PPM
3.0
2.0
1.0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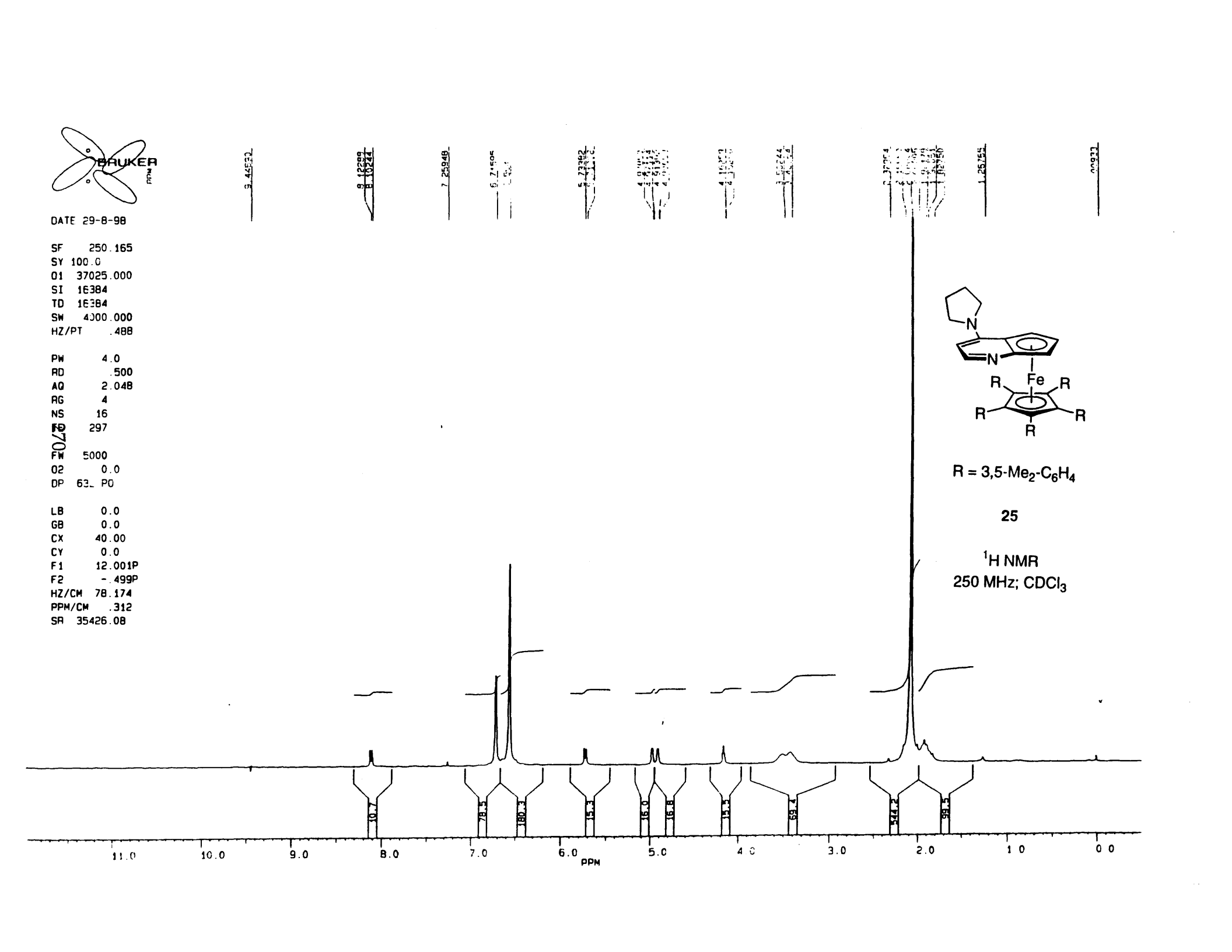
24
1H NMR
300 MHz; CDCl3
8.080
8.062
7.256
6.858
6.831
6.806
6.779
5.684
5.667
4.953
4.833
4.826
4.166
2.222
2.060
1.937
1.253
0.000
ppm
1.54
39.42
2.56
1.93
2.37
2.02
7.10
28.01
15.03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TD 16384
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HZ/PT .488
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RD .500
AQ 2.048
RG 4
NS 16
FW 5000
O2 0.0
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35426.08
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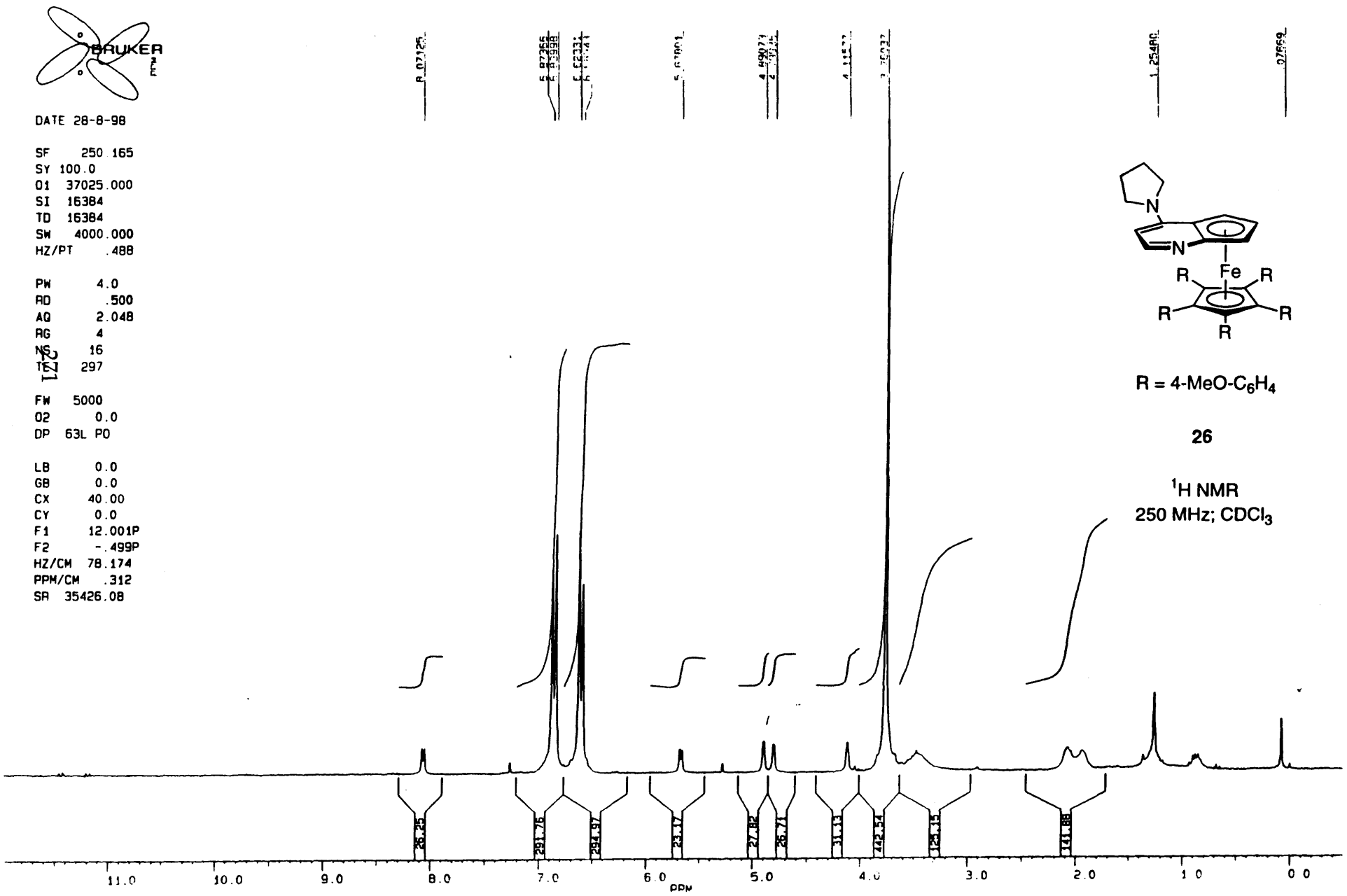
25
1H NMR
250 MHz; CDCl3
PPM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SY 100.0
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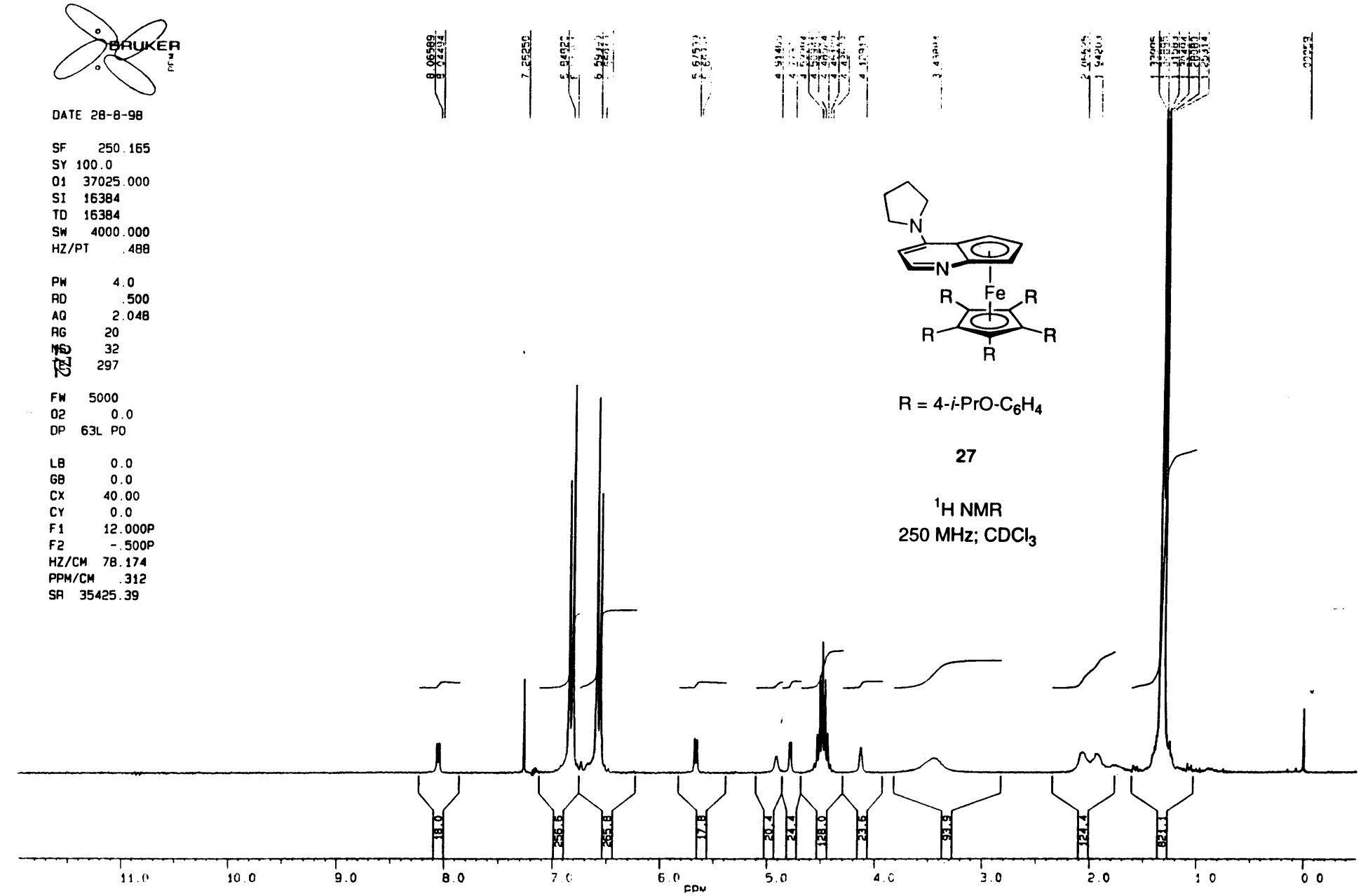
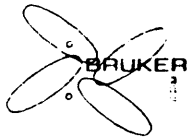
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 4
NS 16
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.001P
F2 -.499P
HZ/CM 78.174
PPM/CM .312
SR 35426.08
N
N
Fe
R
R = 4-MeO-C6H4
26
1H NMR
250 MHz; CDCl3
26.25
291.76
294.97
23.07
27.82
26.71
31.13
42.34
25.15
141.88
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


DATE 28-8-98
SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 20
NS 32
DS 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.000P
F2 -.500P
HZ/CM 78.174
PPM/CM .312
SR 35425.39
N
N
Fe
R
R
R
R
R
R = 4-i-PrO-C6H4
27
1H NMR
250 MHz; CDCl3
18.0
256.6
265.8
17.8
20.4
24.4
128.0
23.6
93.9
124.4
821.1
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM



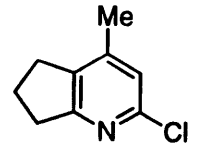
DATE 30-7-98

SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488

PW 4.0
RD .500
AQ 2.048
RG 80
NS 16
TE 297

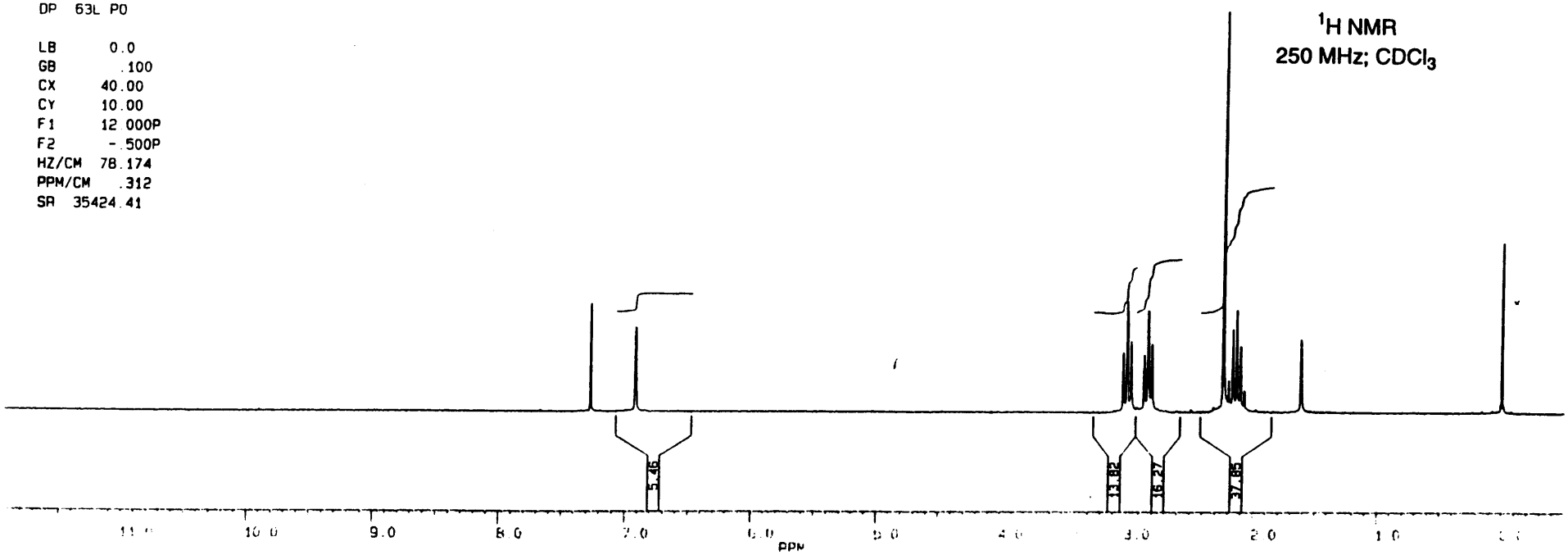
FW 5000
O2 0.0
DP 63L PO

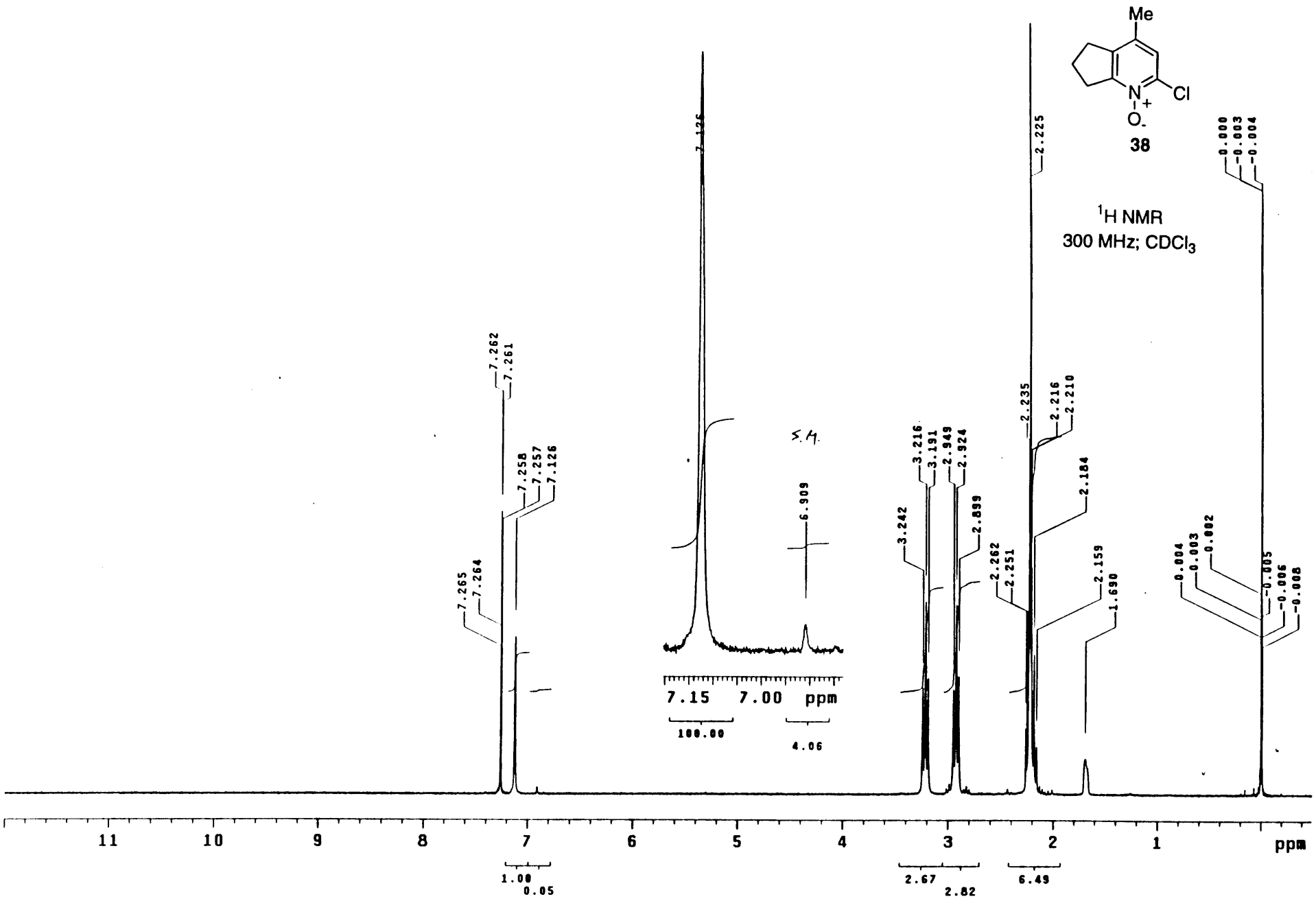
LB 0.0
GB .100
CX 40.00
CY 10.00
F1 12.000P
F2 -.500P
HZ/CM 78.174
PPM/CM .312
SR 35424.41

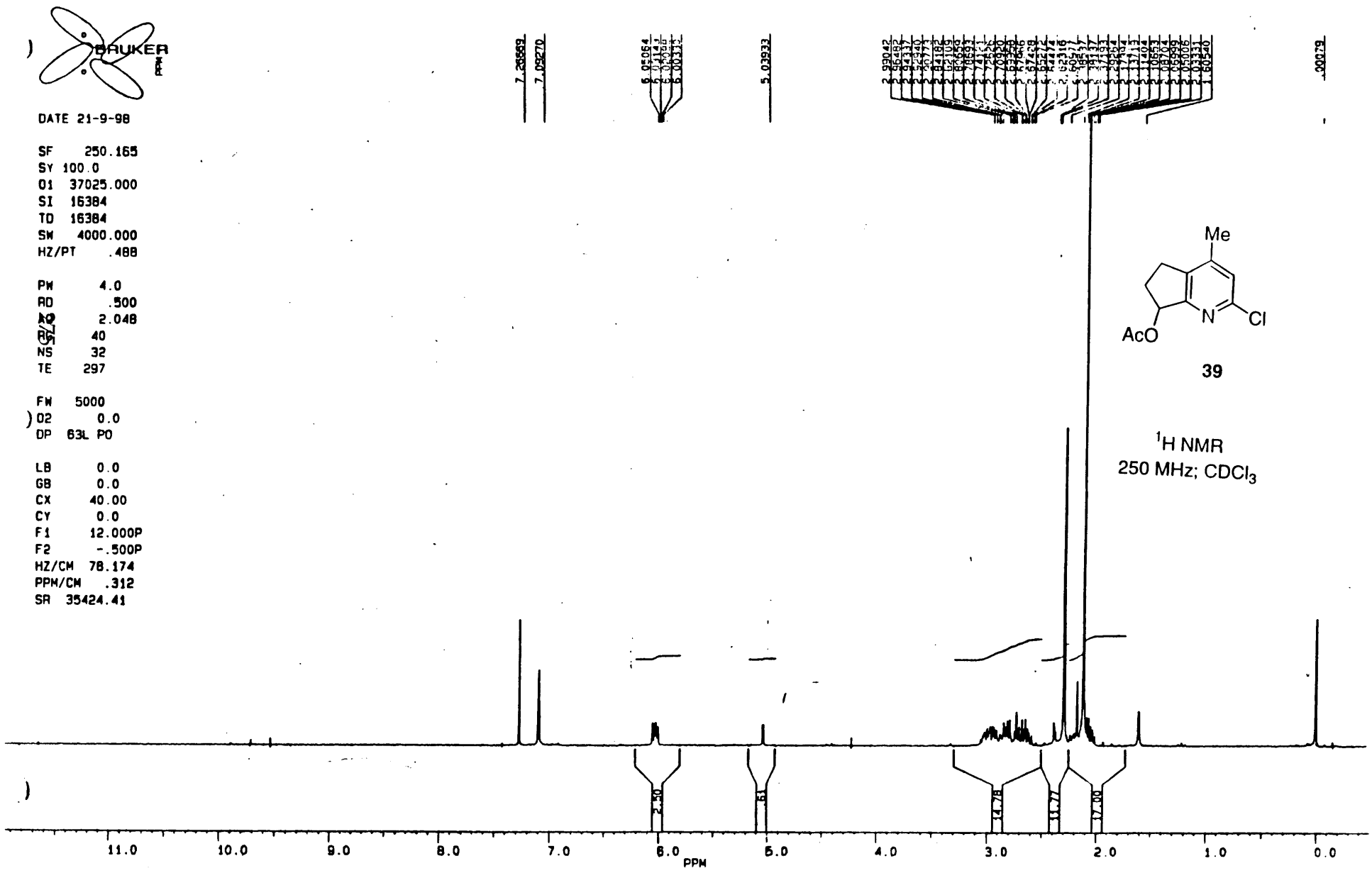


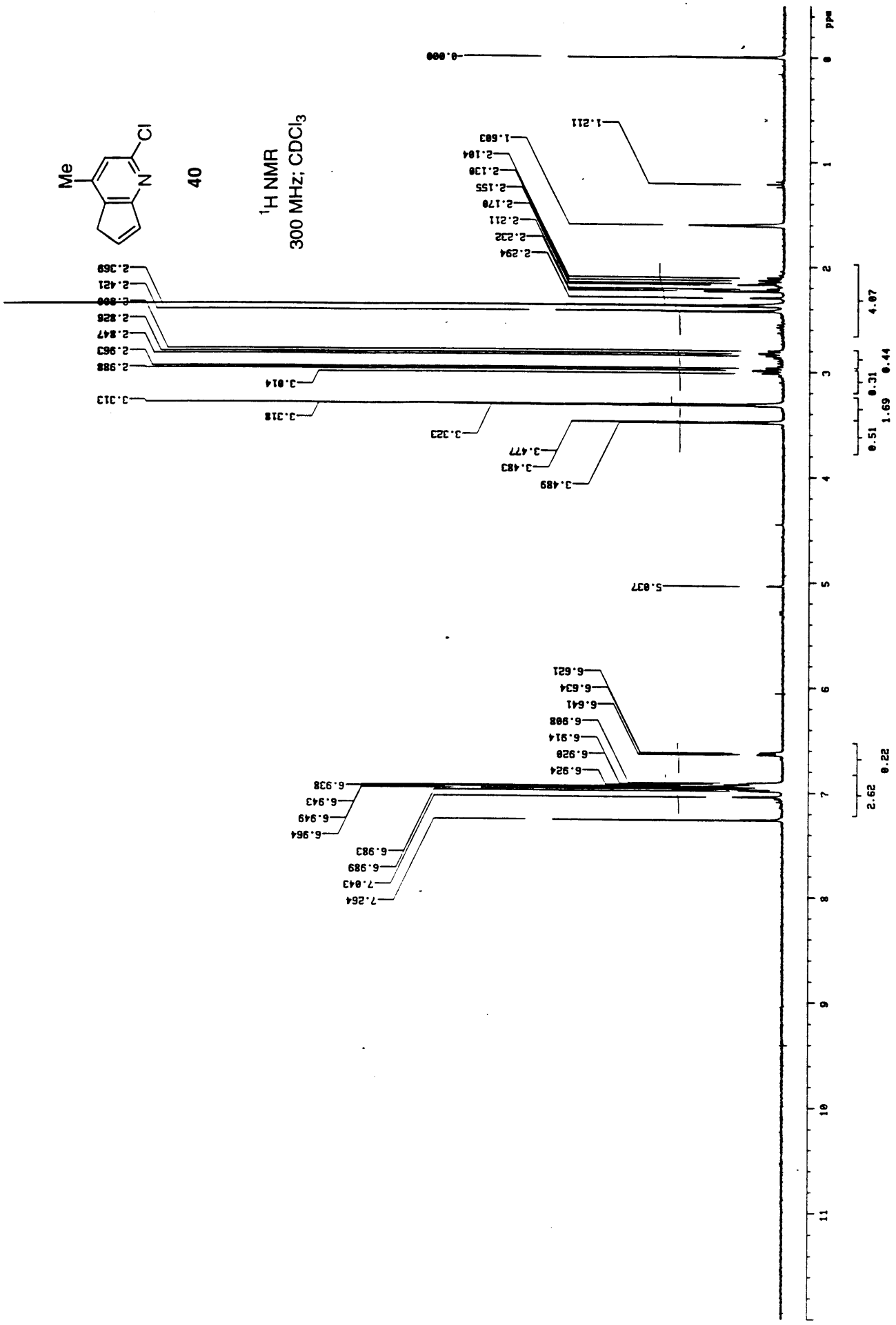
37

^{1}H NMR
250 MHz; $CDCl_3$




Me
Cl
N+
O-
38
1H NMR
300 MHz; CDCl3
7.265
7.264
7.262
7.261
7.258
7.257
7.126
7.126
6.909
S.M.
7.15
7.00
ppm
100.00
4.06
3.242
3.216
3.191
2.949
2.924
2.899
2.262
2.251
2.235
2.225
2.216
2.210
2.184
2.159
1.690
0.004
0.003
0.002
0.000
-0.003
-0.004
-0.005
-0.006
-0.008
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.05
2.67
2.82
6.49


DATE 21-9-98
SF 250.165
SY 100.0
O1 37025.000
SI 16384
TD 16384
SW 4000.000
HZ/PT .488
PW 4.0
RD .500
AQ 2.048
RG 40
NS 32
TE 297
FW 5000
O2 0.0
DP 63L PO
LB 0.0
GB 0.0
CX 40.00
CY 0.0
F1 12.000P
F2 -.500P
HZ/CM 78.174
PPM/CM .312
SR 35424.41
7.26569
7.09270
6.05064
5.03933
.00079
2.50
.61
14.78
11.77
17.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
Me
N
Cl
AcO
39
1H NMR
250 MHz; CDCl3


Me
Cl
N
40
^{1}H NMR
300 MHz; $CDCl_3$

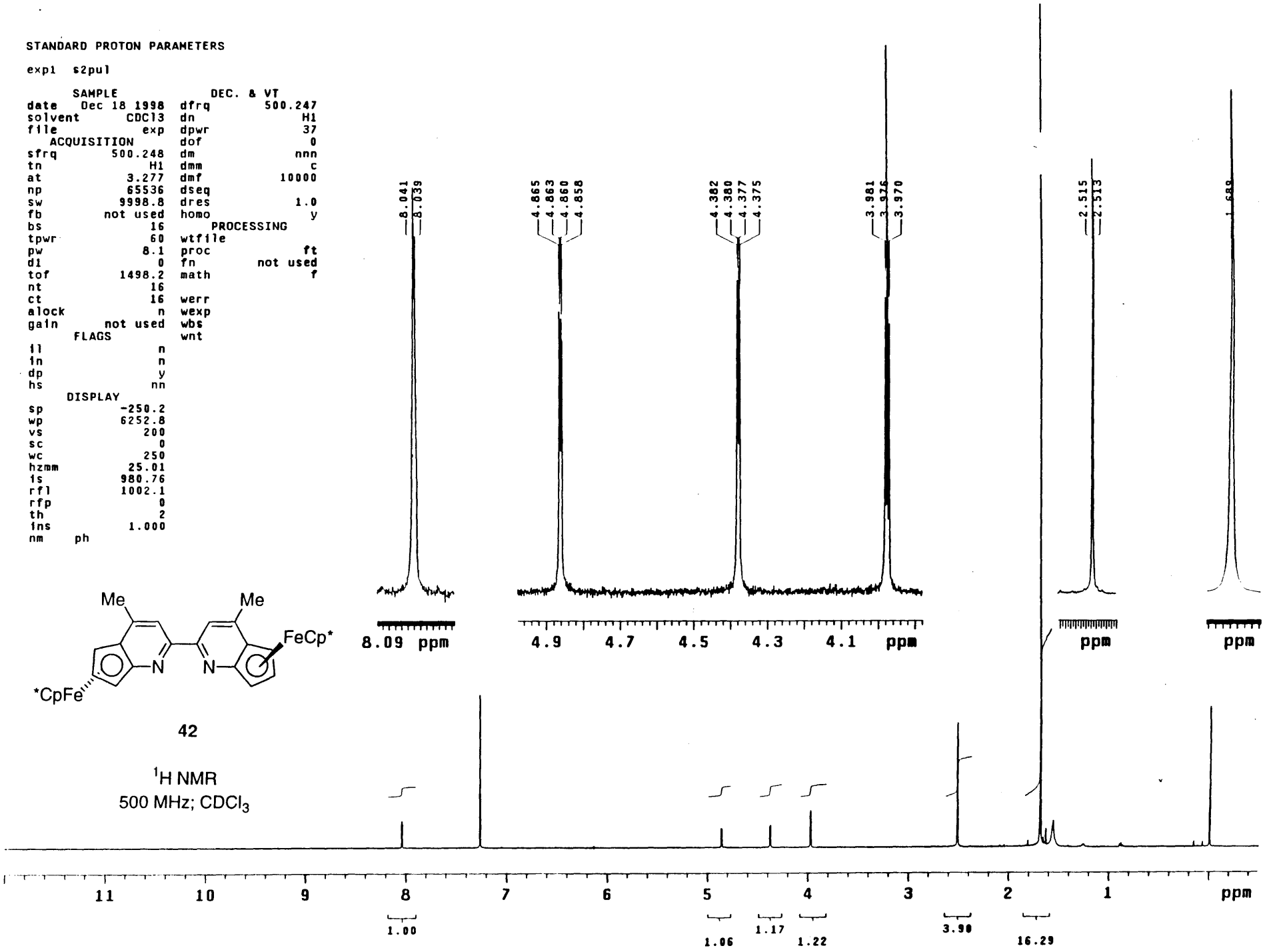
STANDARD PROTON PARAMETERS

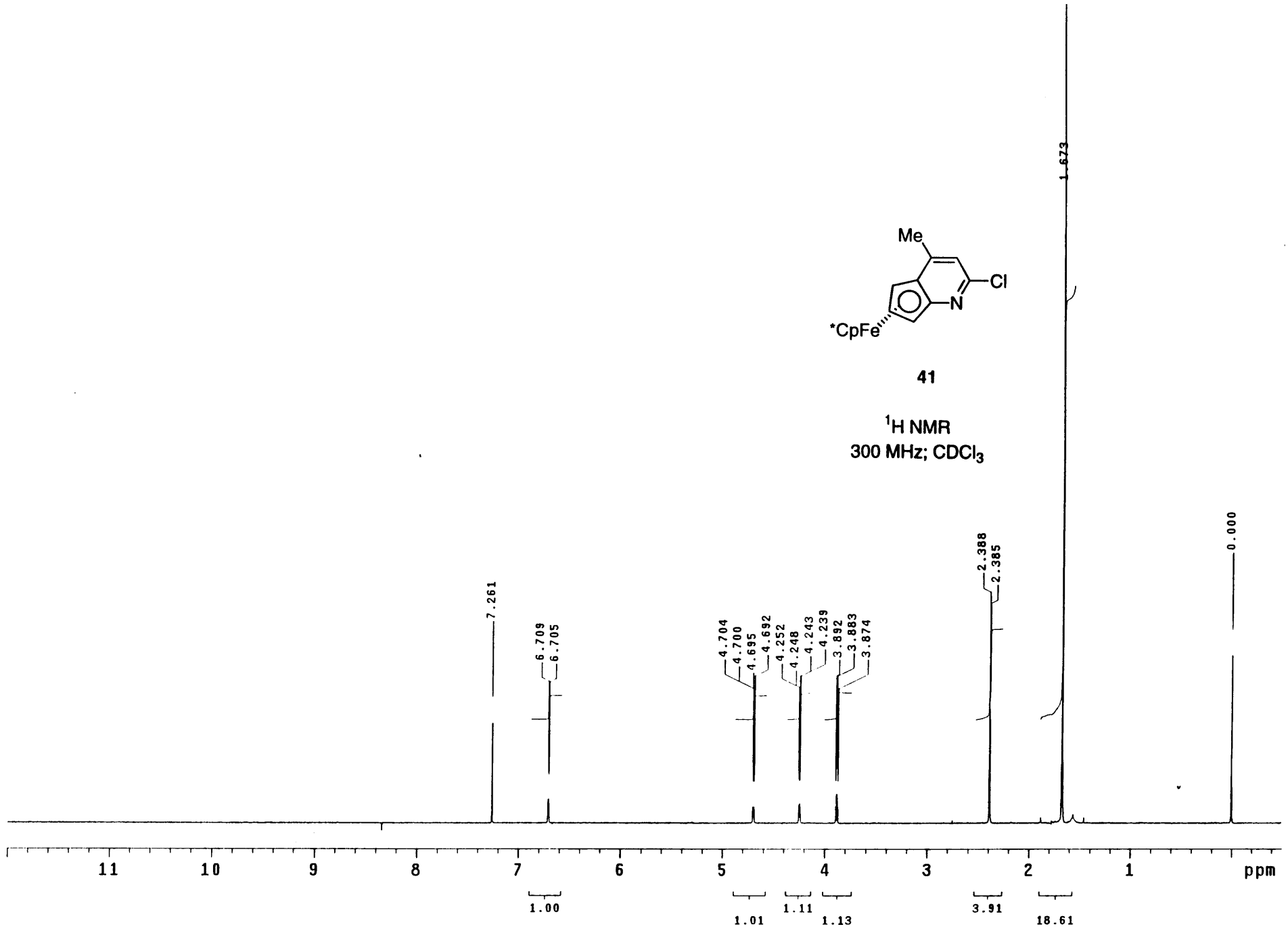
exp1 s2pul

SAMPLE		DEC. & VT	
date	Dec 18 1998	dfrq	500.247
solvent	CDCl3	dn	H1
file	exp	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	60	wtfile	
pw	8.1	proc	ft
d1	0	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	-250.2		
wp	6252.8		
vs	200		
sc	0		
wc	250		
hzmm	25.01		
is	980.76		
rfl	1002.1		
rfp	0		
th	2		
ins	1.000		
nm	ph		

42

^{1}H NMR
500 MHz; $CDCl_3$




Me
Cl
N
*CpFe
41
1H NMR
300 MHz; CDCl3
7.261
6.709
6.705
4.704
4.700
4.695
4.692
4.252
4.248
4.243
4.239
3.892
3.883
3.874
2.388
2.385
1.673
0.000
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.11
1.13
3.91
18.61

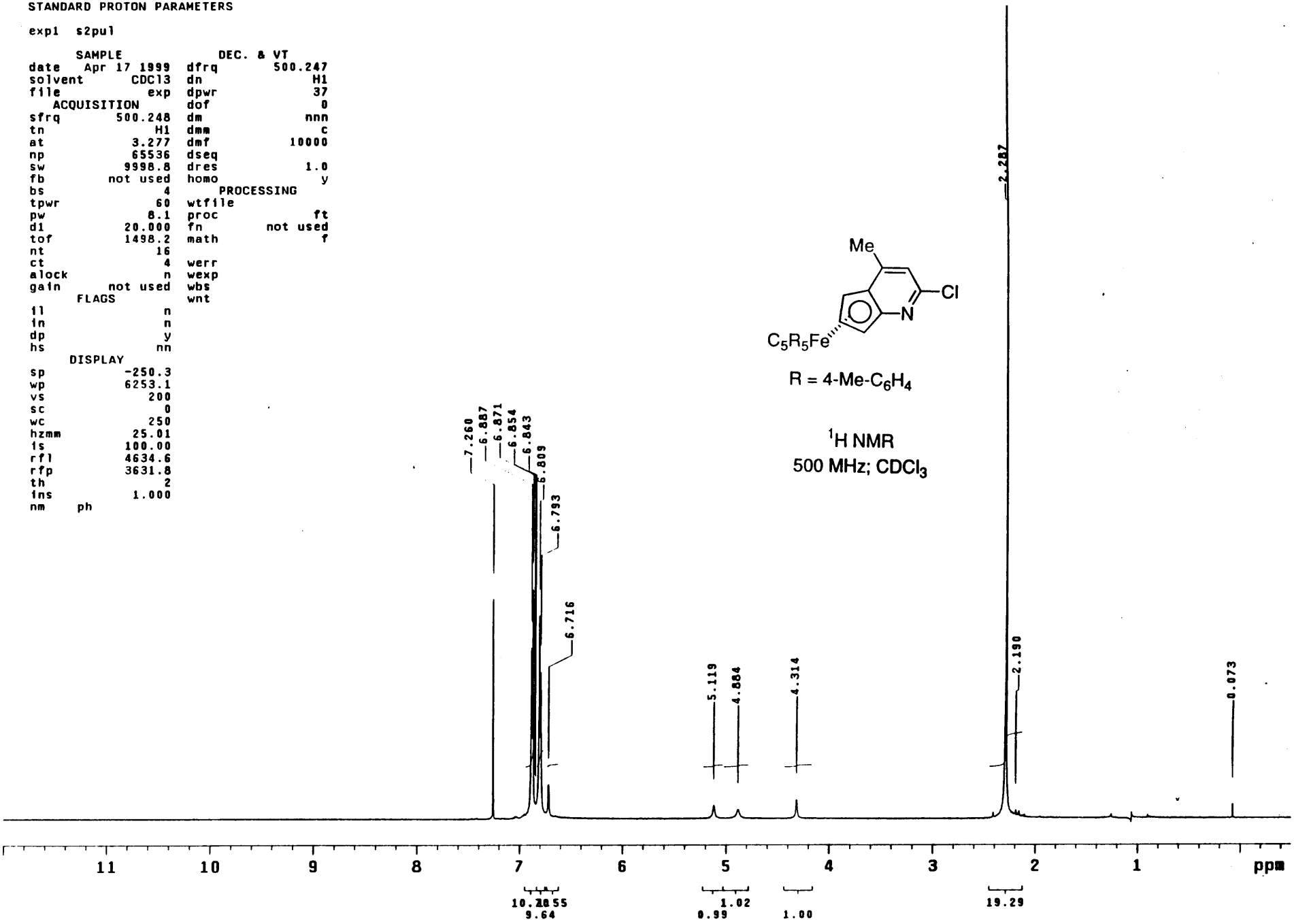
STANDARD PROTON PARAMETERS

expl s2pul

SAMPLE		DEC. & VT	
date	Apr 17 1999	dfrq	500.247
solvent	CDCl3	dn	H1
file	exp	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	4	PROCESSING	
tpwr	60	wtfile	
pw	8.1	proc	ft
d1	20.000	fn	not used
tof	1498.2	math	f
nt	16		
ct	4	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.3		
wp	6253.1		
vs	200		
sc	0		
wc	250		
hzmm	25.01		
is	100.00		
rfl	4634.6		
rfp	3631.8		
th	2		
ins	1.000		
nm	ph		

R = 4-Me-C_6H_4

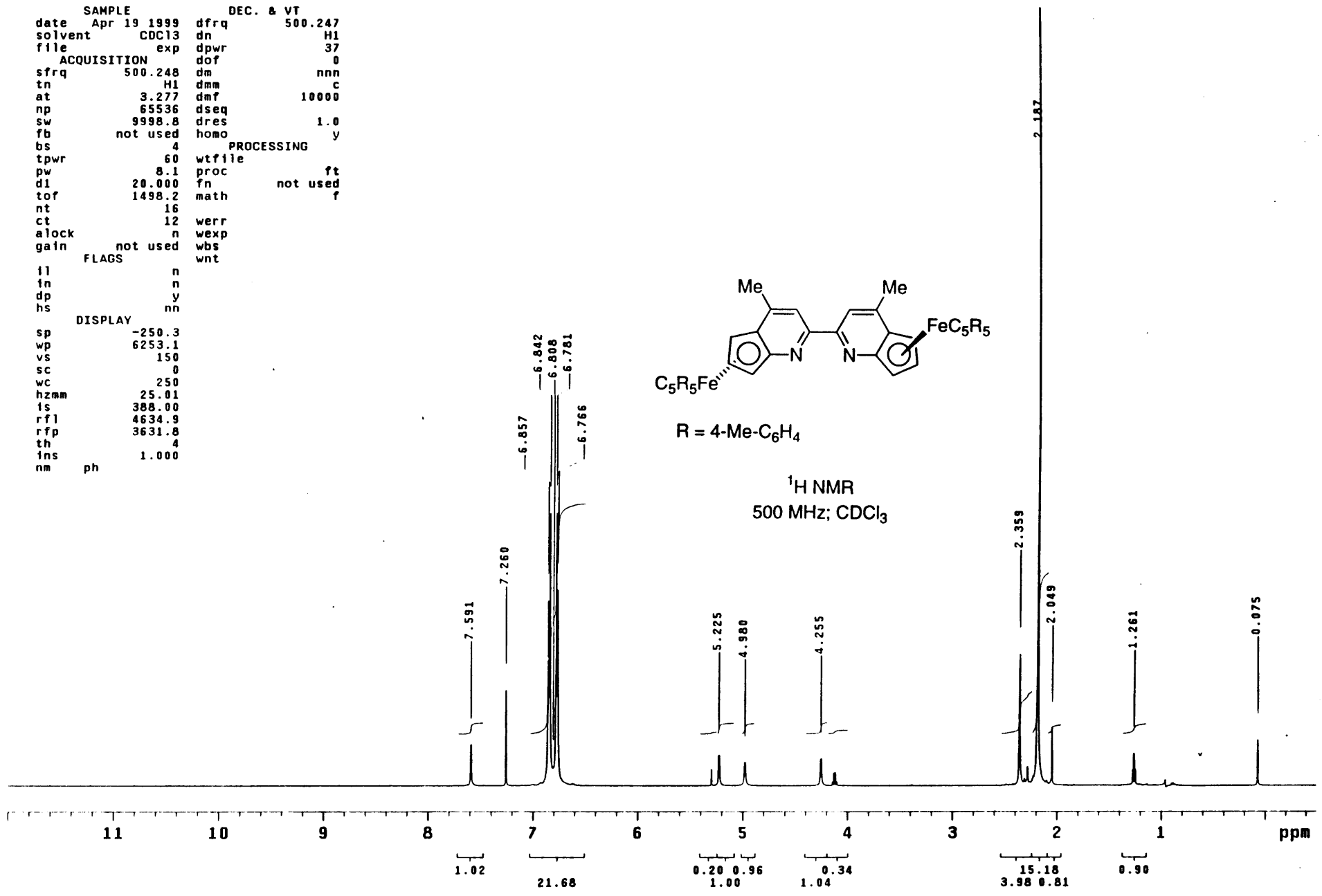
^{1}H NMR
500 MHz; $CDCl_3$



STANDARD PROTON PARAMETERS

expl s2pul

SAMPLE		DEC. & VT	
date	Apr 19 1999	dfrq	500.247
solvent	CDCl3	dn	H1
file	exp	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	4	PROCESSING	
tpwr	60	wtfile	
pw	8.1	proc	ft
d1	20.000	fn	not used
tof	1498.2	math	f
nt	16		
ct	12	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-250.3		
wp	6253.1		
vs	150		
sc	0		
wc	250		
hzmm	25.01		
is	388.00		
rfl	4634.9		
rfp	3631.8		
th	4		
ins	1.000		
nm	ph		



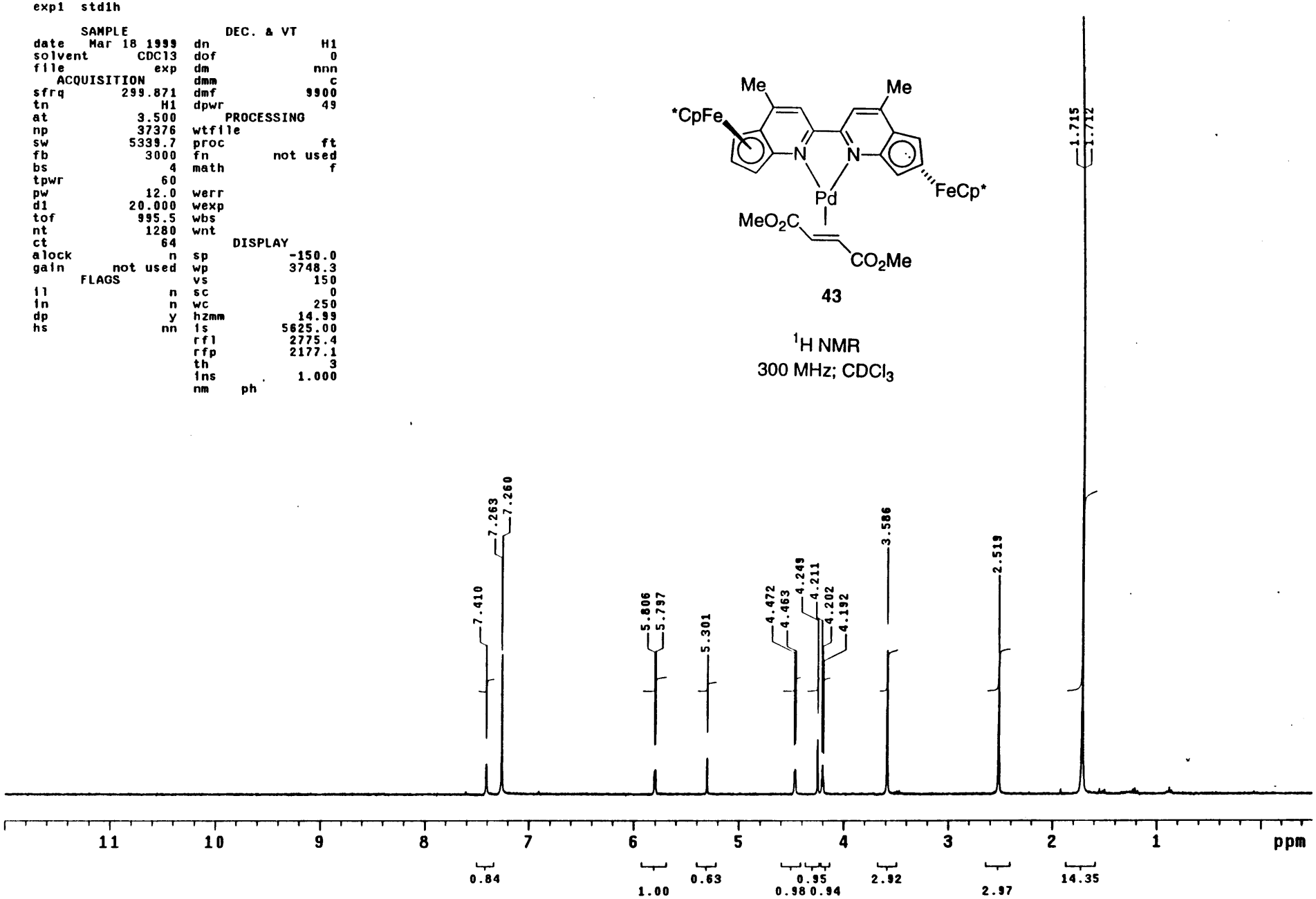
STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Mar 18 1999	dn	H1
solvent	CDCl3	dof	0
file	exp	dm	nnn
ACQUISITION		dmm	c
sfrq	299.871	dmf	9900
tn	H1	dpwr	49
at	3.500	PROCESSING	
np	37376	wtfile	
sw	5339.7	proc	ft
fb	3000	fn	not used
bs	4	math	f
tpwr	60		
pw	12.0	werr	
d1	20.000	wexp	
tof	995.5	wbs	
nt	1280	wnt	
ct	64	DISPLAY	
alock	n	sp	-150.0
gain	not used	wp	3748.3
FLAGS		vs	150
il	n	sc	0
in	n	wc	250
dp	y	hzmm	14.99
hs	nn	is	5625.00
		rfl	2775.4
		rfp	2177.1
		th	3
		ins	1.000
		nm	ph

43

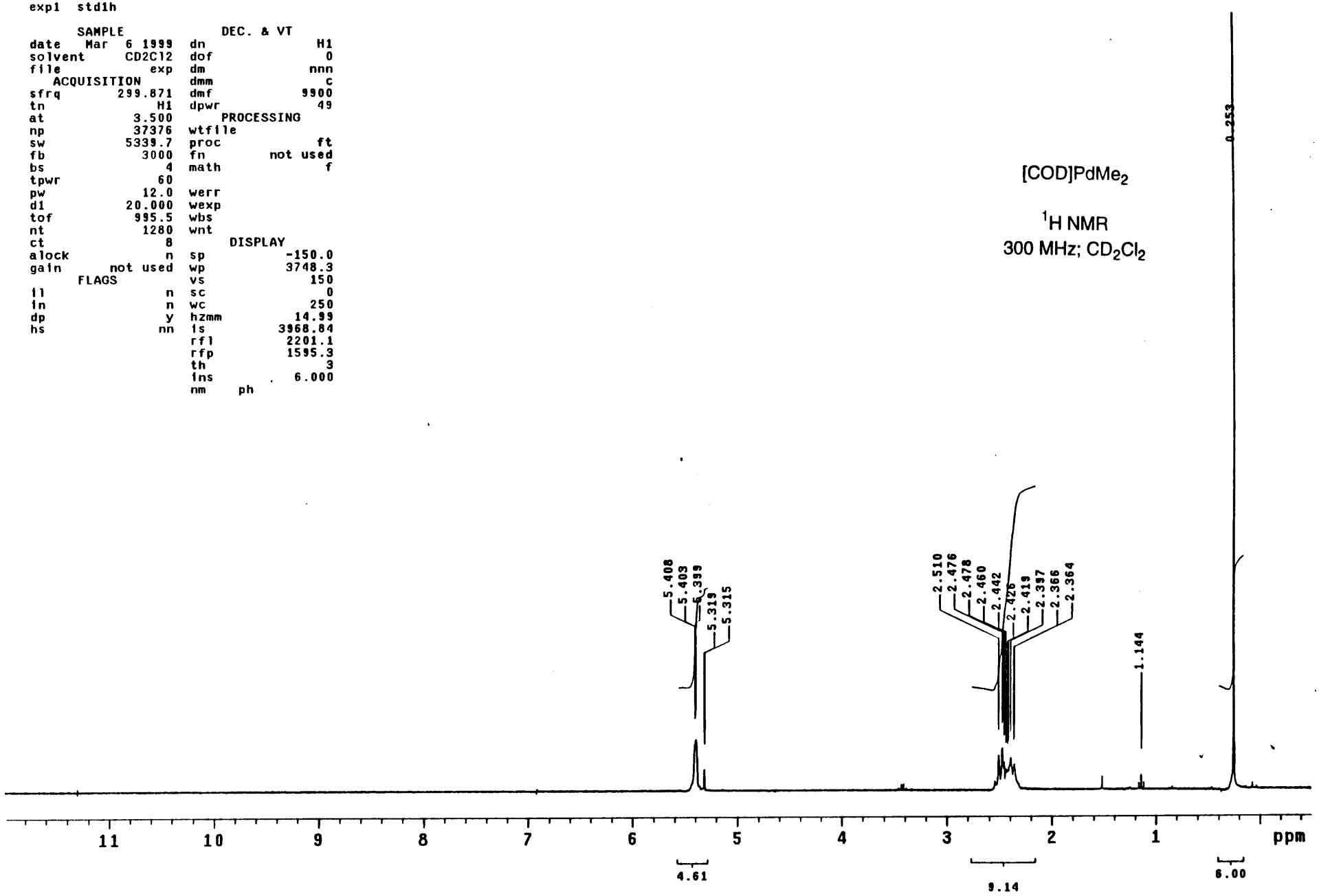
^{1}H NMR
300 MHz; $CDCl_3$



STANDARD 1H OBSERVE

exp1 std1h

SAMPLE		DEC. & VT	
date	Mar 6 1999	dn	H1
solvent	CD2C12	dof	0
file	exp	dm	nnn
ACQUISITION		dmm	c
sfrq	299.871	dmf	9900
tn	H1	dpwr	49
at	3.500	PROCESSING	
np	37376	wtfile	
sw	5339.7	proc	ft
fb	3000	fn	not used
bs	4	math	f
tpwr	60		
pw	12.0	werr	
d1	20.000	wexp	
tof	995.5	wbs	
nt	1280	wnt	
ct	8	DISPLAY	
alock	n	sp	-150.0
gain	not used	wp	3748.3
FLAGS		vs	150
il	n	sc	0
in	n	wc	250
dp	y	hzmm	14.99
hs	nn	is	3968.84
		rfl	2201.1
		rfp	1595.3
		th	3
		ins	6.000
		nm	ph



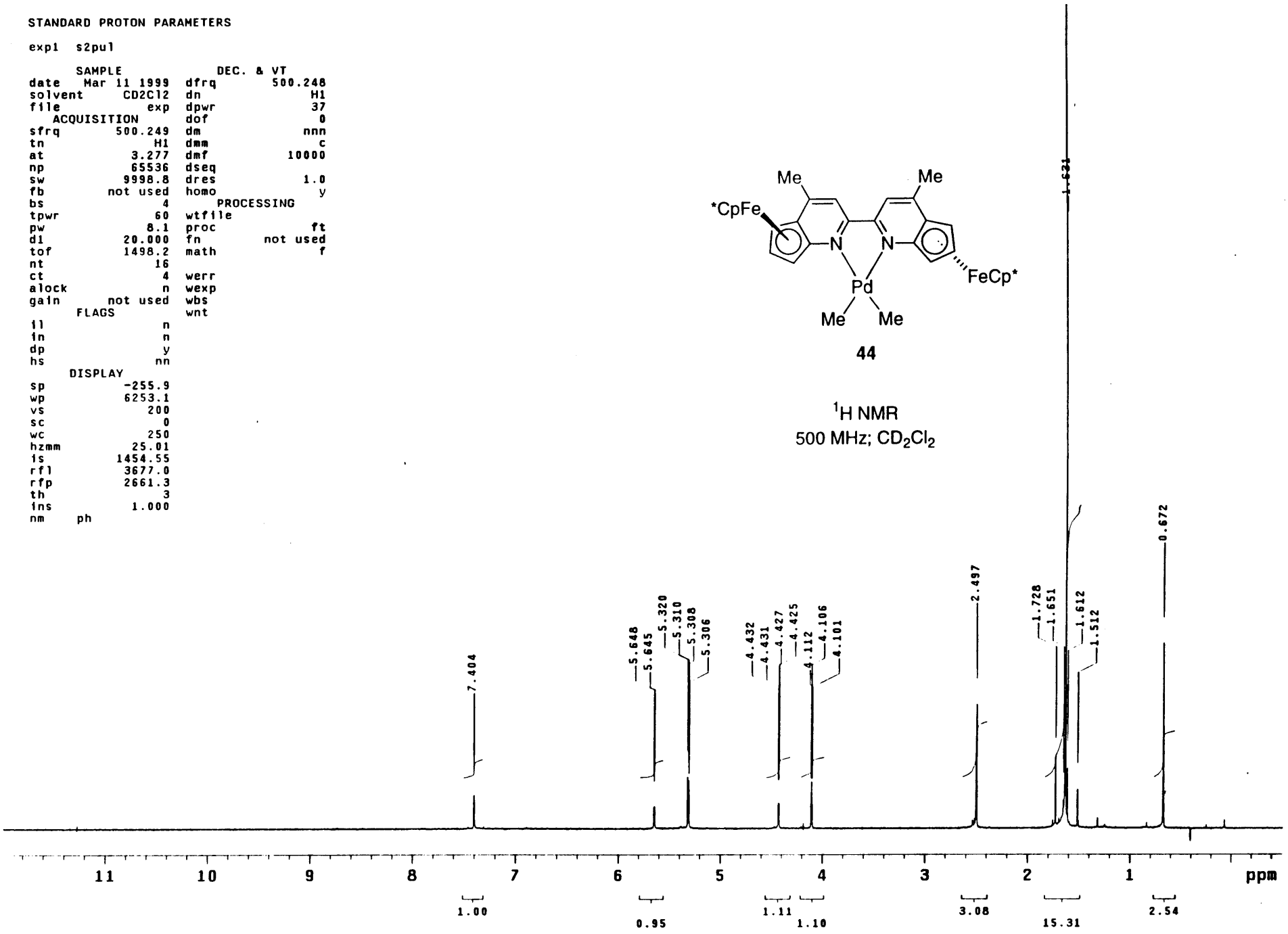
STANDARD PROTON PARAMETERS

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 11 1999	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	60	wtfile	
pw	8.1	proc	ft
d1	20.000	fn	not used
tof	1498.2	math	f
nt	16		
ct	4	werr	
alock	n	wexp	
gain	not used	wbs	
FLAGS		wnt	
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	-255.9		
wp	6253.1		
vs	200		
sc	0		
wc	250		
hzmm	25.01		
is	1454.55		
rfl	3677.0		
rfp	2661.3		
th	3		
ins	1.000		
nm	ph		

44

^{1}H NMR
500 MHz; CD_2Cl_2



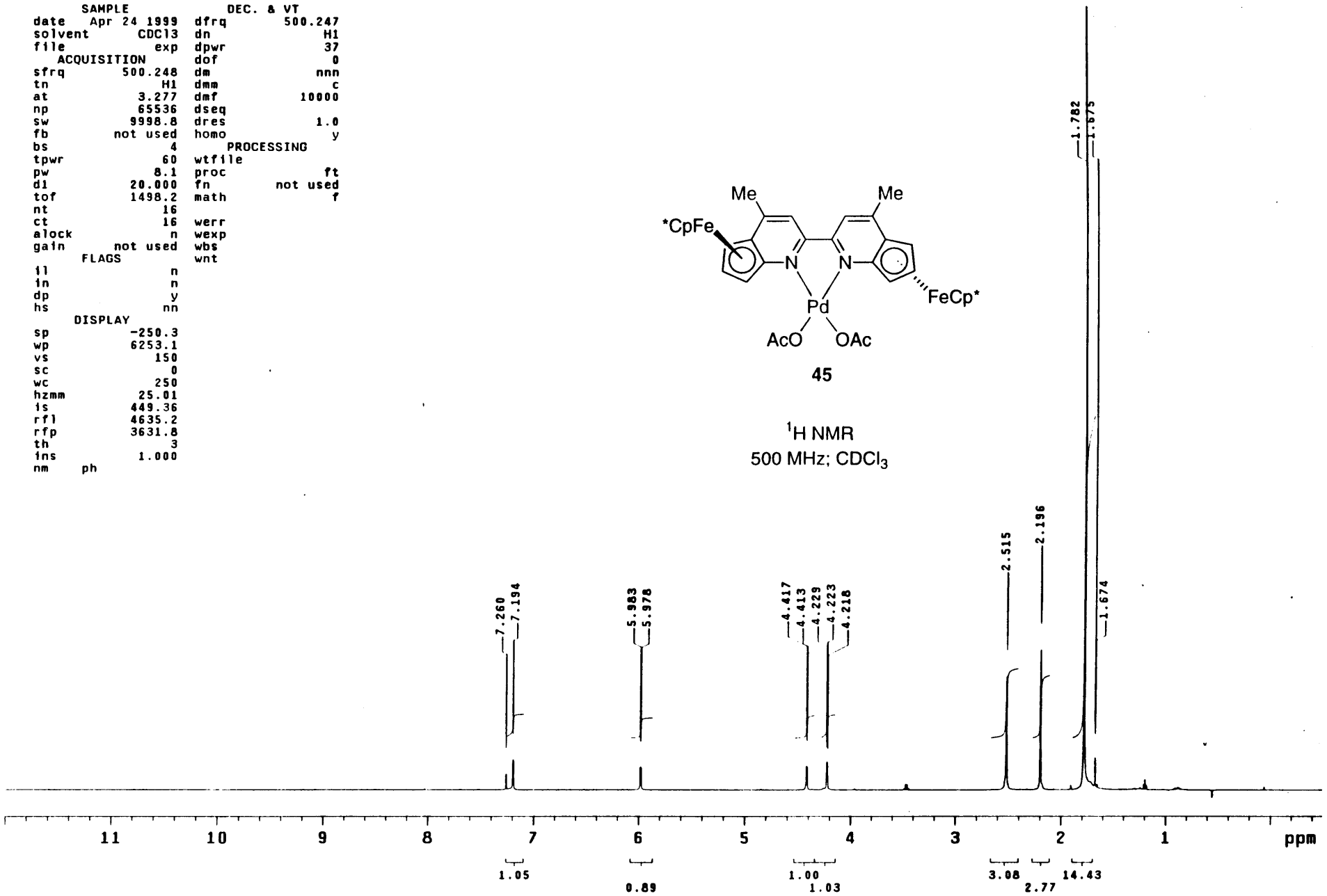
STANDARD PROTON PARAMETERS

exp2 s2pul

SAMPLE		DEC. & VT	
date	Apr 24 1999	dfrq	500.247
solvent	CDCl3	dn	H1
file	exp	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	4	PROCESSING	
tpwr	60	wtfile	
pw	8.1	proc	ft
d1	20.000	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	-250.3		
wp	6253.1		
vs	150		
sc	0		
wc	250		
hzmm	25.01		
is	449.36		
rfl	4635.2		
rfp	3631.8		
th	3		
ins	1.000		
nm	ph		

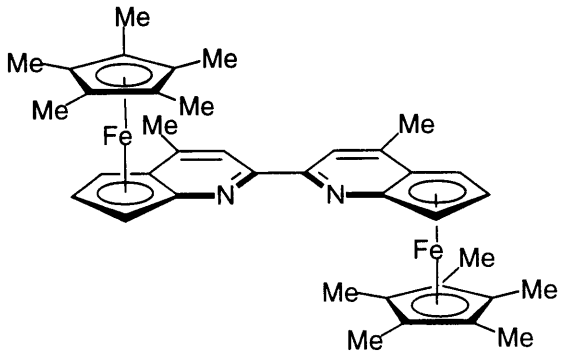
45

^{1}H NMR
500 MHz; $CDCl_3$



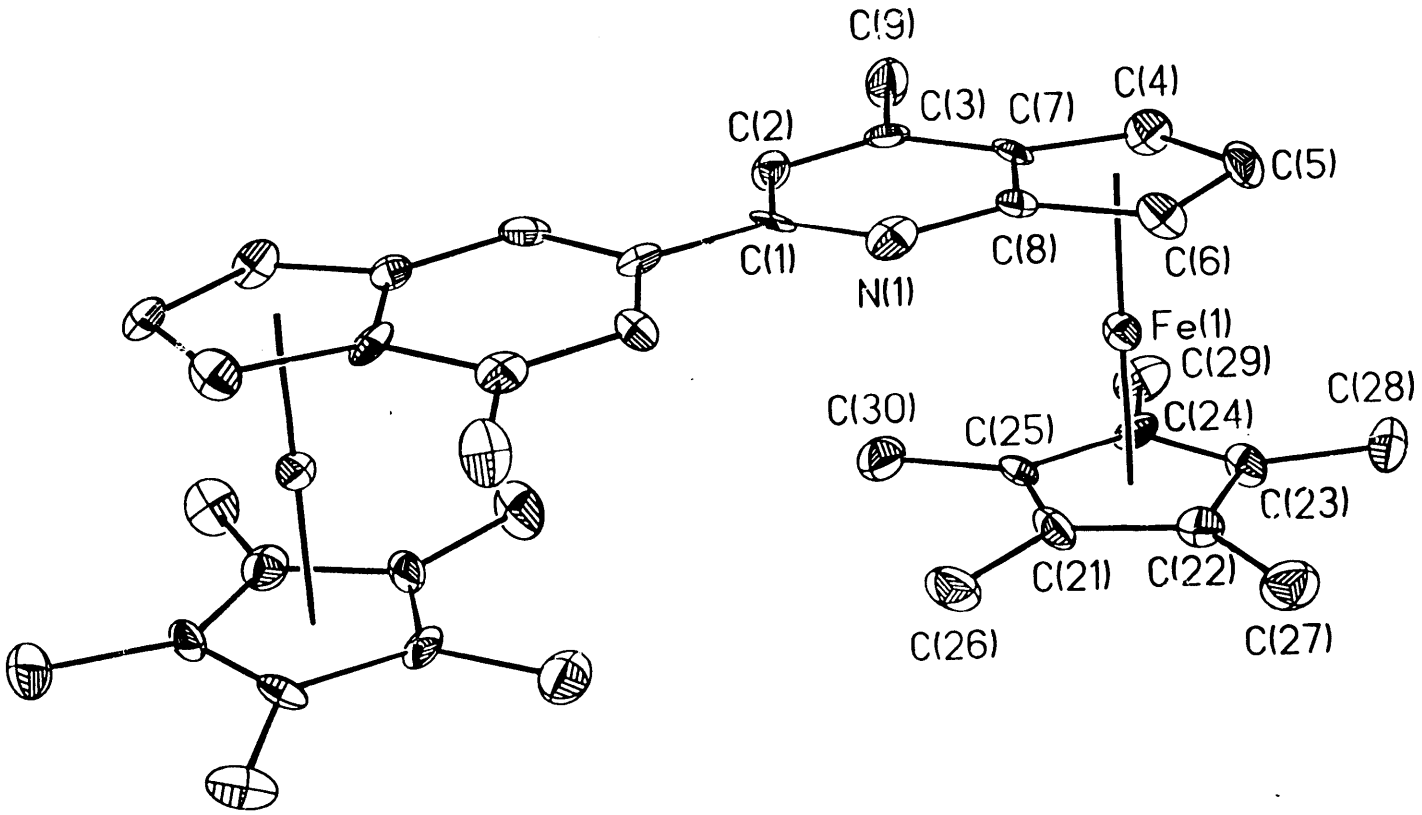
Appendix C

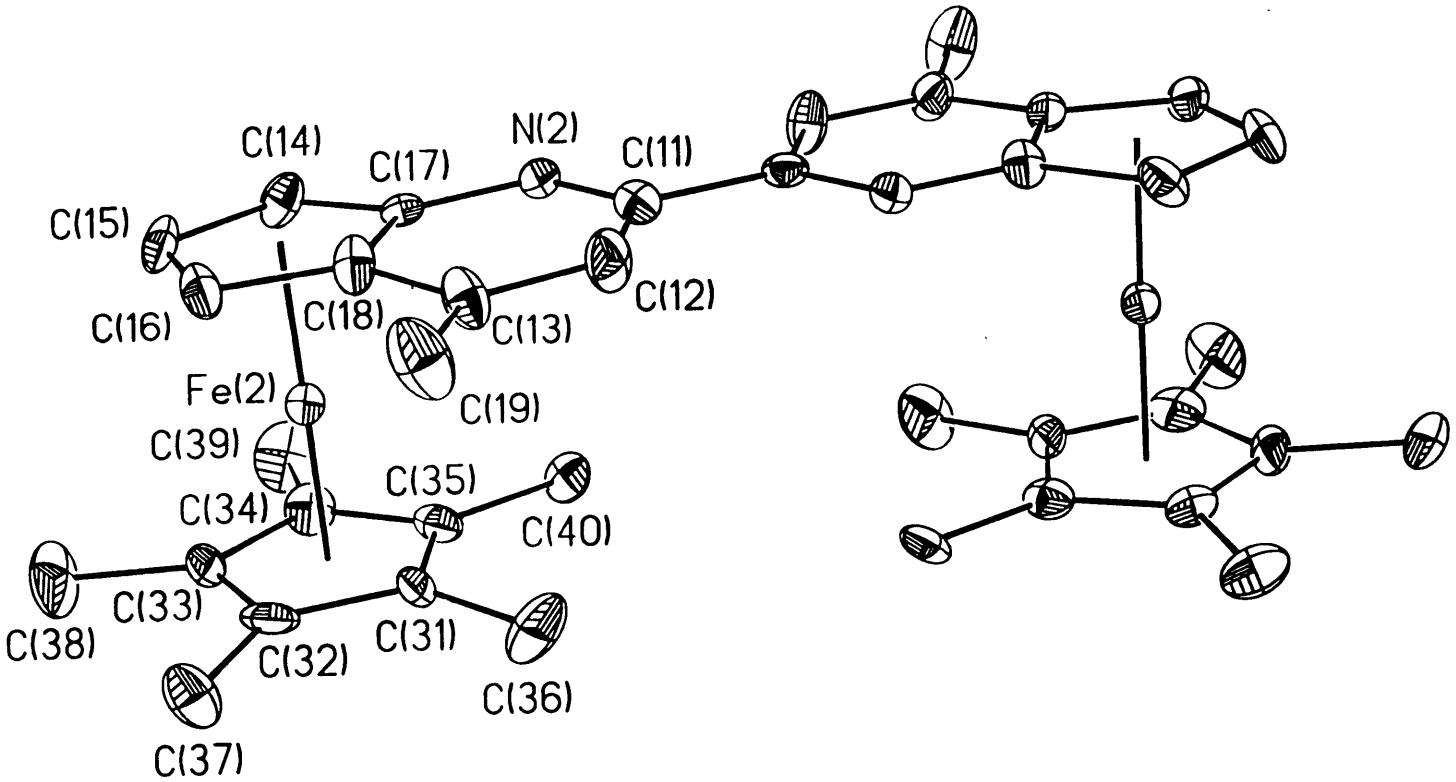
X-ray Crystal Structure Data for (+)-(*S,S*)-42



(+)-(*S,S*)-**42**

Structure Solved by Michael M.-C. Lo


C(9)
C(3)
C(7)
C(4)
C(2)
C(5)
C(1)
N(1)
C(8)
C(6)
Fe(1)
C(29)
C(28)
C(30)
C(25)
C(24)
C(23)
C(21)
C(22)
C(26)
C(27)


C(14)
C(17)
N(2)
C(11)
C(15)
C(16)
C(18)
C(13)
C(12)
C(19)
Fe(2)
C(39)
C(35)
C(34)
C(40)
C(33)
C(38)
C(32)
C(31)
C(36)
C(37)

Cl(3)
Cl(11)
Cl(12)
C(101)
Cl(2)

N(2A)
N(2)
Fe(2A)
Fe(2)
N(1)
N(1A)
Fe(1)
Fe(1A)

Table 1. Crystal data and structure refinement for 99019.

CA. Crystal Data

Identification code	99019
Empirical formula	$C_{39}H_{45}Cl_3Fe_2N_2$
Formula weight	759.82
Temperature	142(2) K
Wavelength	0.71073 Å
Crystal size	0.06 x 0.12 x 0.24 mm
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	a = 28.796(10) Å alpha = 90° b = 6.917(4) Å beta = 112.41(3)° c = 19.075(5) Å gamma = 90°
Volume, Z	3512(3) $Å^3$, 4
Density (calculated)	1.437 Mg/m^3
Absorption coefficient	1.085 mm^{-1}
F(000)	1584

CB. Data Collection and Reduction

Diffractometer	Siemens SMART/CCD
Scan Type	ω Scans
Scan angle	0.30°
θ range for data collection	1.53 to 23.27°
Limiting indices	$-31 \le h \le 28$, $-7 \le k \le 7$, $-18 \le l \le 21$
Reflections collected	7301
Independent reflections	4533 (R_{int} = 0.0589)
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.9483 and 0.7319

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4530 / 1 / 425
Goodness-of-fit on F^2	1.110
Final R indices [$I>2\sigma(I)$]	R1 = 0.0682, wR2 = 0.1406
R indices (all data)	R1 = 0.1068, wR2 = 0.1697
Absolute structure parameter	-0.04(5)
Extinction coefficient	0.0003(2)
Largest diff. peak and hole	0.479 and -0.420 $e\text{Å}^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 99019. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe(1)	-1533(1)	-7384(3)	-706(1)	22(1)
Fe(2)	1144(1)	-12208(3)	4238(1)	24(1)
N(1)	-627(3)	-4889(15)	-687(4)	27(2)
N(2)	650(3)	-9749(15)	5116(5)	24(2)
C(1)	-257(3)	-4968(14)	-13(6)	26(2)
C(2)	-334(4)	-5060(15)	690(5)	22(2)
C(3)	-812(4)	-5064(16)	696(6)	24(3)
C(4)	-1749(4)	-5054(22)	-247(7)	29(3)
C(5)	-1976(4)	-4944(22)	-1049(6)	30(3)
C(6)	-1584(4)	-4952(23)	-1327(6)	26(3)
C(7)	-1222(4)	-5013(19)	-13(6)	22(3)
C(8)	-1117(4)	-4926(20)	-697(6)	22(3)
C(9)	-918(4)	-5101(19)	1413(6)	35(3)
C(11)	152(3)	-9758(17)	4757(5)	25(2)
C(12)	-92(4)	-9790(20)	3957(6)	38(3)
C(13)	166(4)	-9841(23)	3480(6)	35(3)
C(14)	1458(4)	-9828(24)	4874(7)	33(3)
C(15)	1560(5)	-9812(27)	4197(7)	36(3)
C(16)	1094(4)	-9839(23)	3562(7)	32(3)
C(17)	924(4)	-9775(22)	4660(6)	26(3)
C(18)	707(4)	-9758(25)	3851(6)	29(3)
C(19)	-80(4)	-9774(25)	2639(6)	56(4)
C(21)	-1181(4)	-9737(21)	-930(7)	30(3)
C(22)	-1697(4)	-9689(22)	-1452(7)	30(3)
C(23)	-1992(4)	-9733(23)	-998(7)	26(3)
C(24)	-1676(4)	-9812(22)	-207(6)	25(3)
C(25)	-1166(4)	-9843(22)	-179(6)	26(3)
C(26)	-733(4)	-9712(21)	-1152(7)	42(3)
C(27)	-1882(4)	-9637(20)	-2290(6)	41(3)
C(28)	-2559(3)	-9788(21)	-1280(6)	39(3)
C(29)	-1838(4)	-9986(18)	442(6)	40(3)
C(30)	-693(4)	-9944(20)	523(6)	42(3)
C(31)	691(4)	-14590(22)	3958(7)	30(3)
C(32)	1013(5)	-14590(22)	3552(7)	36(3)
C(33)	1527(5)	-14559(25)	4118(8)	39(4)
C(34)	1503(4)	-14566(23)	4855(7)	35(3)
C(35)	984(5)	-14624(23)	4755(6)	30(3)
C(36)	122(4)	-14696(28)	3613(8)	56(4)
C(37)	874(5)	-14623(23)	2721(6)	56(4)
C(38)	1993(4)	-14587(23)	3927(8)	62(4)
C(39)	1950(4)	-14598(24)	5585(7)	59(4)
C(40)	788(4)	-14598(20)	5374(6)	35(3)
C(101)	-3494(4)	5421(25)	-3134(6)	49(4)
Cl(2)	-3593(2)	3376(6)	-2653(2)	79(1)
Cl(3)	-3641(1)	-2503(7)	-2736(2)	69(1)
Cl(11)	-2871(8)	5010(32)	-3024(13)	84(7)
Cl(12)	-2864(10)	6009(33)	-3042(16)	88(7)

Table 3. Bond lengths [Å] and angles [°] for 99019.

Fe(1)-C(21)	2.046(13)	Fe(1)-C(23)	2.034(14)
Fe(1)-C(24)	2.047(14)	Fe(1)-C(6)	2.03(2)
Fe(1)-C(25)	2.053(14)	Fe(1)-C(4)	2.041(14)
Fe(1)-C(5)	2.065(14)	Fe(1)-C(22)	2.067(14)
Fe(1)-C(8)	2.077(13)	Fe(1)-C(7)	2.083(13)
Fe(2)-C(14)	2.04(2)	Fe(2)-C(33)	2.03(2)
Fe(2)-C(31)	2.04(2)	Fe(2)-C(32)	2.048(14)
Fe(2)-C(34)	2.047(14)	Fe(2)-C(16)	2.056(14)
Fe(2)-C(15)	2.06(2)	Fe(2)-C(35)	2.08(2)
Fe(2)-C(18)	2.07(2)	Fe(2)-C(17)	2.066(14)
N(1)-C(1)	1.321(12)	N(1)-C(8)	1.405(13)
N(2)-C(11)	1.333(12)	N(2)-C(17)	1.379(13)
C(1)-C(2)	1.440(13)	C(1)-C(1)#1	1.47(2)
C(2)-C(3)	1.382(13)	C(3)-C(7)	1.416(14)
C(3)-C(9)	1.511(14)	C(4)-C(5)	1.42(2)
C(4)-C(7)	1.41(2)	C(5)-C(6)	1.42(2)
C(6)-C(8)	1.42(2)	C(7)-C(8)	1.45(2)
C(11)-C(12)	1.416(13)	C(11)-C(11)#2	1.50(2)
C(12)-C(13)	1.378(13)	C(13)-C(18)	1.45(2)
C(13)-C(19)	1.49(2)	C(14)-C(15)	1.43(2)
C(14)-C(17)	1.43(2)	C(15)-C(16)	1.42(2)
C(16)-C(18)	1.42(2)	C(17)-C(18)	1.43(2)
C(21)-C(25)	1.42(2)	C(21)-C(22)	1.44(2)
C(21)-C(26)	1.505(14)	C(22)-C(23)	1.43(2)
C(22)-C(27)	1.48(2)	C(23)-C(24)	1.44(2)
C(23)-C(28)	1.511(14)	C(24)-C(25)	1.45(2)
C(24)-C(29)	1.483(14)	C(25)-C(30)	1.50(2)
C(31)-C(32)	1.42(2)	C(31)-C(35)	1.43(2)
C(31)-C(36)	1.52(2)	C(32)-C(33)	1.46(2)
C(32)-C(37)	1.48(2)	C(33)-C(34)	1.43(2)
C(33)-C(38)	1.52(2)	C(34)-C(35)	1.43(2)
C(34)-C(39)	1.49(2)	C(35)-C(40)	1.49(2)
C(101)-Cl(2)	1.77(2)	C(101)-Cl(11)	1.75(2)
C(101)-Cl(3)#3	1.75(2)	C(101)-Cl(12)	1.80(3)
Cl(3)-C(101)#4	1.75(2)	Cl(11)-Cl(12)	0.69(4)

C(21)-Fe(1)-C(23)	68.3(5)	C(21)-Fe(1)-C(24)	69.4(5)
C(23)-Fe(1)-C(24)	41.2(4)	C(21)-Fe(1)-C(6)	117.9(5)
C(23)-Fe(1)-C(6)	127.5(5)	C(24)-Fe(1)-C(6)	165.6(4)
C(21)-Fe(1)-C(25)	40.5(5)	C(23)-Fe(1)-C(25)	68.4(5)
C(24)-Fe(1)-C(25)	41.4(5)	C(6)-Fe(1)-C(25)	151.8(4)
C(21)-Fe(1)-C(4)	166.8(5)	C(23)-Fe(1)-C(4)	118.4(5)
C(24)-Fe(1)-C(4)	107.5(4)	C(6)-Fe(1)-C(4)	68.3(5)
C(25)-Fe(1)-C(4)	128.9(5)	C(21)-Fe(1)-C(5)	151.5(5)
C(23)-Fe(1)-C(5)	107.9(4)	C(24)-Fe(1)-C(5)	127.5(5)
C(6)-Fe(1)-C(5)	40.5(4)	C(25)-Fe(1)-C(5)	166.7(5)
C(4)-Fe(1)-C(5)	40.4(5)	C(21)-Fe(1)-C(22)	40.9(5)
C(23)-Fe(1)-C(22)	40.7(5)	C(24)-Fe(1)-C(22)	69.8(5)
C(6)-Fe(1)-C(22)	106.9(4)	C(25)-Fe(1)-C(22)	68.8(5)
C(4)-Fe(1)-C(22)	151.4(4)	C(5)-Fe(1)-C(22)	117.5(5)
C(21)-Fe(1)-C(8)	108.8(4)	C(23)-Fe(1)-C(8)	165.8(4)
C(24)-Fe(1)-C(8)	152.2(4)	C(6)-Fe(1)-C(8)	40.4(4)
C(25)-Fe(1)-C(8)	119.1(5)	C(4)-Fe(1)-C(8)	67.6(5)
C(5)-Fe(1)-C(8)	67.5(5)	C(22)-Fe(1)-C(8)	128.0(5)
C(21)-Fe(1)-C(7)	129.2(4)	C(23)-Fe(1)-C(7)	151.7(4)

C(24)-Fe(1)-C(7)	117.7(5)	C(6)-Fe(1)-C(7)	68.6(5)
C(25)-Fe(1)-C(7)	108.9(4)	C(4)-Fe(1)-C(7)	39.9(4)
C(5)-Fe(1)-C(7)	67.8(5)	C(22)-Fe(1)-C(7)	166.8(4)
C(8)-Fe(1)-C(7)	40.7(4)	C(14)-Fe(2)-C(33)	125.3(6)
C(14)-Fe(2)-C(31)	154.3(4)	C(33)-Fe(2)-C(31)	69.1(6)
C(14)-Fe(2)-C(32)	163.9(5)	C(33)-Fe(2)-C(32)	42.0(5)
C(31)-Fe(2)-C(32)	40.5(5)	C(14)-Fe(2)-C(34)	106.8(4)
C(33)-Fe(2)-C(34)	41.3(5)	C(31)-Fe(2)-C(34)	68.9(6)
C(32)-Fe(2)-C(34)	69.9(6)	C(14)-Fe(2)-C(16)	68.8(5)
C(33)-Fe(2)-C(16)	118.6(6)	C(31)-Fe(2)-C(16)	126.4(5)
C(32)-Fe(2)-C(16)	106.7(4)	C(34)-Fe(2)-C(16)	153.5(5)
C(14)-Fe(2)-C(15)	40.7(5)	C(33)-Fe(2)-C(15)	107.0(4)
C(31)-Fe(2)-C(15)	163.7(5)	C(32)-Fe(2)-C(15)	126.1(5)
C(34)-Fe(2)-C(15)	119.3(6)	C(16)-Fe(2)-C(15)	40.4(5)
C(14)-Fe(2)-C(35)	119.7(5)	C(33)-Fe(2)-C(35)	68.8(6)
C(31)-Fe(2)-C(35)	40.6(5)	C(32)-Fe(2)-C(35)	68.7(5)
C(34)-Fe(2)-C(35)	40.7(5)	C(16)-Fe(2)-C(35)	164.3(5)
C(15)-Fe(2)-C(35)	154.2(5)	C(14)-Fe(2)-C(18)	67.9(6)
C(33)-Fe(2)-C(18)	154.0(5)	C(31)-Fe(2)-C(18)	109.1(4)
C(32)-Fe(2)-C(18)	119.4(5)	C(34)-Fe(2)-C(18)	164.2(5)
C(16)-Fe(2)-C(18)	40.2(4)	C(15)-Fe(2)-C(18)	67.1(6)
C(35)-Fe(2)-C(18)	127.7(5)	C(14)-Fe(2)-C(17)	40.9(5)
C(33)-Fe(2)-C(17)	163.5(5)	C(31)-Fe(2)-C(17)	120.0(5)
C(32)-Fe(2)-C(17)	153.6(4)	C(34)-Fe(2)-C(17)	126.0(5)
C(16)-Fe(2)-C(17)	68.7(5)	C(15)-Fe(2)-C(17)	68.2(6)
C(35)-Fe(2)-C(17)	108.3(4)	C(18)-Fe(2)-C(17)	40.4(5)
C(1)-N(1)-C(8)	116.3(8)	C(11)-N(2)-C(17)	115.9(8)
N(1)-C(1)-C(2)	123.8(9)	N(1)-C(1)-C(1)#1	117.4(12)
C(2)-C(1)-C(1)#1	118.8(11)	C(3)-C(2)-C(1)	121.0(9)
C(2)-C(3)-C(7)	117.5(9)	C(2)-C(3)-C(9)	123.6(9)
C(7)-C(3)-C(9)	118.9(9)	C(5)-C(4)-C(7)	109.8(11)
C(5)-C(4)-Fe(1)	70.7(8)	C(7)-C(4)-Fe(1)	71.6(8)
C(4)-C(5)-C(6)	107.3(10)	C(4)-C(5)-Fe(1)	68.9(8)
C(6)-C(5)-Fe(1)	68.4(8)	C(5)-C(6)-C(8)	108.4(10)
C(5)-C(6)-Fe(1)	71.0(8)	C(8)-C(6)-Fe(1)	71.5(7)
C(3)-C(7)-C(4)	134.9(11)	C(3)-C(7)-C(8)	118.5(9)
C(4)-C(7)-C(8)	106.5(9)	C(3)-C(7)-Fe(1)	125.9(9)
C(4)-C(7)-Fe(1)	68.4(8)	C(8)-C(7)-Fe(1)	69.4(7)
N(1)-C(8)-C(6)	129.3(10)	N(1)-C(8)-C(7)	122.9(9)
C(6)-C(8)-C(7)	107.9(9)	N(1)-C(8)-Fe(1)	126.1(9)
C(6)-C(8)-Fe(1)	68.0(8)	C(7)-C(8)-Fe(1)	69.9(7)
N(2)-C(11)-C(12)	123.4(8)	N(2)-C(11)-C(11)#2	116.7(10)
C(12)-C(11)-C(11)#2	119.9(10)	C(13)-C(12)-C(11)	122.7(9)
C(12)-C(13)-C(18)	115.4(10)	C(12)-C(13)-C(19)	123.8(10)
C(18)-C(13)-C(19)	120.5(9)	C(15)-C(14)-C(17)	108.1(11)
C(15)-C(14)-Fe(2)	70.5(9)	C(17)-C(14)-Fe(2)	70.6(8)
C(16)-C(15)-C(14)	108.6(10)	C(16)-C(15)-Fe(2)	69.5(9)
C(14)-C(15)-Fe(2)	68.8(8)	C(18)-C(16)-C(15)	107.0(10)
C(18)-C(16)-Fe(2)	70.5(8)	C(15)-C(16)-Fe(2)	70.0(8)
N(2)-C(17)-C(18)	124.2(10)	N(2)-C(17)-C(14)	129.1(10)
C(18)-C(17)-C(14)	106.7(10)	N(2)-C(17)-Fe(2)	126.2(10)
C(18)-C(17)-Fe(2)	70.0(8)	C(14)-C(17)-Fe(2)	68.6(8)
C(16)-C(18)-C(17)	109.6(10)	C(16)-C(18)-C(13)	131.8(11)
C(17)-C(18)-C(13)	118.3(10)	C(16)-C(18)-Fe(2)	69.3(8)
C(17)-C(18)-Fe(2)	69.6(8)	C(13)-C(18)-Fe(2)	122.5(12)
C(25)-C(21)-C(22)	109.1(10)	C(25)-C(21)-C(26)	125.8(11)
C(22)-C(21)-C(26)	125.2(11)	C(25)-C(21)-Fe(1)	70.0(8)
C(22)-C(21)-Fe(1)	70.3(8)	C(26)-C(21)-Fe(1)	126.6(10)
C(21)-C(22)-C(23)	106.1(10)	C(21)-C(22)-C(27)	126.8(11)

C(23)-C(22)-C(27)	127.1(10)	C(21)-C(22)-Fe(1)	68.8(8)
C(23)-C(22)-Fe(1)	68.4(8)	C(27)-C(22)-Fe(1)	128.2(11)
C(22)-C(23)-C(24)	110.6(9)	C(22)-C(23)-C(28)	126.7(10)
C(24)-C(23)-C(28)	122.7(9)	C(22)-C(23)-Fe(1)	70.9(8)
C(24)-C(23)-Fe(1)	69.9(8)	C(28)-C(23)-Fe(1)	128.2(11)
C(25)-C(24)-C(23)	105.6(9)	C(25)-C(24)-C(29)	127.2(10)
C(23)-C(24)-C(29)	127.1(10)	C(25)-C(24)-Fe(1)	69.5(7)
C(23)-C(24)-Fe(1)	68.9(8)	C(29)-C(24)-Fe(1)	129.6(10)
C(21)-C(25)-C(24)	108.7(10)	C(21)-C(25)-C(30)	124.8(10)

C(24)-C(25)-C(30)	126.5(10)	C(21)-C(25)-Fe(1)	69.5(8)
C(24)-C(25)-Fe(1)	69.1(8)	C(30)-C(25)-Fe(1)	126.7(10)
C(32)-C(31)-C(35)	109.8(11)	C(32)-C(31)-C(36)	126.0(11)
C(35)-C(31)-C(36)	124.1(11)	C(32)-C(31)-Fe(2)	70.0(8)
C(35)-C(31)-Fe(2)	71.1(8)	C(36)-C(31)-Fe(2)	129.0(12)
C(31)-C(32)-C(33)	106.6(11)	C(31)-C(32)-C(37)	128.2(12)
C(33)-C(32)-C(37)	125.2(11)	C(31)-C(32)-Fe(2)	69.5(8)
C(33)-C(32)-Fe(2)	68.2(8)	C(37)-C(32)-Fe(2)	127.3(11)
C(34)-C(33)-C(32)	108.2(10)	C(34)-C(33)-C(38)	127.7(13)
C(32)-C(33)-C(38)	124.1(12)	C(34)-C(33)-Fe(2)	70.1(8)
C(32)-C(33)-Fe(2)	69.8(8)	C(38)-C(33)-Fe(2)	127.3(12)
C(33)-C(34)-C(35)	107.9(11)	C(33)-C(34)-C(39)	124.6(11)
C(35)-C(34)-C(39)	127.5(11)	C(33)-C(34)-Fe(2)	68.6(8)
C(35)-C(34)-Fe(2)	70.9(8)	C(39)-C(34)-Fe(2)	127.9(12)
C(31)-C(35)-C(34)	107.6(10)	C(31)-C(35)-C(40)	126.6(11)
C(34)-C(35)-C(40)	125.8(11)	C(31)-C(35)-Fe(2)	68.3(8)
C(34)-C(35)-Fe(2)	68.4(8)	C(40)-C(35)-Fe(2)	125.9(10)
Cl(2)-C(101)-Cl(11)	99.7(10)	Cl(2)-C(101)-Cl(3)#3	108.6(6)
Cl(11)-C(101)-Cl(3)#3	119.2(11)	Cl(2)-C(101)-Cl(12)	119.0(11)
Cl(11)-C(101)-Cl(12)	22.4(12)	Cl(3)#3-C(101)-Cl(12)	100.0(12)
Cl(12)-Cl(11)-C(101)	83(4)	Cl(11)-Cl(12)-C(101)	75(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z #2 -x,y,-z+1 #3 x,y+1,z #4 x,y-1,z

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for 99019.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2$ [$(ha^*)^2 U_{11}$ + ... + $2hka^*b^*U_{12}$]

	U11	U22	U33	U23	U13	U12
Fe(1)	21(1)	20(1)	25(1)	3(1)	10(1)	2(1)
Fe(2)	23(1)	24(1)	25(1)	-1(1)	11(1)	-1(1)
N(1)	37(5)	16(5)	25(5)	5(5)	9(5)	-6(5)
N(2)	25(5)	21(5)	27(5)	0(5)	12(4)	-1(5)
C(1)	27(5)	4(5)	45(7)	1(5)	12(5)	9(5)
C(2)	20(6)	22(6)	26(6)	-3(5)	11(5)	-5(5)
C(3)	32(6)	11(6)	27(6)	-7(5)	10(5)	1(5)
C(4)	31(7)	32(8)	29(7)	-3(7)	17(6)	-2(6)
C(5)	24(7)	24(8)	35(7)	9(7)	4(6)	8(7)
C(6)	31(7)	34(8)	17(6)	5(6)	15(5)	11(7)
C(7)	27(6)	13(7)	24(6)	0(5)	6(5)	13(5)
C(8)	23(6)	10(6)	31(7)	-2(6)	9(5)	3(6)
C(9)	28(6)	46(8)	29(6)	-10(6)	10(5)	-1(6)
C(11)	33(7)	20(6)	22(6)	7(5)	11(5)	6(5)
C(12)	19(6)	55(8)	39(7)	-6(7)	9(5)	0(6)
C(13)	38(7)	42(8)	30(6)	11(7)	20(6)	14(7)
C(14)	34(7)	38(8)	30(7)	9(8)	13(6)	-7(8)
C(15)	34(7)	40(8)	44(8)	6(8)	25(6)	-9(8)
C(16)	39(7)	32(8)	36(7)	9(7)	26(6)	11(7)
C(17)	26(7)	21(7)	30(7)	-13(7)	11(5)	-11(7)
C(18)	27(7)	31(8)	33(7)	18(7)	16(6)	11(7)
C(19)	43(7)	90(11)	31(7)	-8(8)	11(6)	13(9)
C(21)	18(6)	19(6)	56(8)	2(7)	19(6)	3(6)
C(22)	32(7)	21(7)	34(7)	-3(7)	9(6)	2(7)
C(23)	18(6)	27(7)	41(7)	3(8)	19(6)	-1(7)
C(24)	30(6)	17(6)	30(7)	-5(7)	15(5)	-14(6)
C(25)	24(6)	13(6)	35(7)	0(7)	4(5)	10(6)
C(26)	33(7)	36(8)	68(9)	-13(8)	31(7)	1(7)
C(27)	45(7)	43(8)	37(7)	-11(7)	20(6)	-1(7)
C(28)	25(6)	46(8)	37(7)	-1(7)	2(5)	-5(6)
C(29)	58(8)	30(7)	35(7)	0(6)	23(6)	-14(6)
C(30)	40(7)	27(7)	45(7)	-3(7)	1(6)	0(6)
C(31)	39(7)	20(7)	43(8)	-6(7)	29(6)	0(7)
C(32)	53(8)	18(7)	38(7)	-12(7)	18(7)	-5(7)
C(33)	43(8)	22(8)	69(10)	-8(8)	41(8)	1(8)
C(34)	34(7)	32(8)	36(8)	11(8)	10(6)	10(7)
C(35)	46(8)	20(7)	29(7)	-2(7)	19(6)	2(8)
C(36)	33(7)	66(10)	60(9)	-3(10)	8(7)	-23(9)
C(37)	79(9)	63(10)	39(7)	-14(8)	39(7)	-8(9)
C(38)	53(8)	55(9)	97(11)	21(9)	52(8)	27(8)
C(39)	48(8)	60(10)	59(8)	29(8)	10(7)	22(8)
C(40)	48(7)	27(7)	37(7)	14(7)	25(6)	0(7)
C(101)	40(7)	90(11)	18(6)	1(8)	13(5)	5(8)
Cl(2)	100(3)	56(3)	63(2)	12(2)	10(2)	20(2)
Cl(3)	79(2)	58(3)	56(2)	-15(3)	11(2)	-23(3)
Cl(11)	21(6)	189(22)	35(6)	-3(12)	3(5)	13(11)
Cl(12)	47(8)	157(18)	59(8)	3(12)	20(6)	-25(12)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 99019.

	x	y	z	U(eq)
H(2B)	-52(4)	-5118(15)	1156(5)	27
H(4A)	-1935(4)	-5121(22)	101(7)	35
H(5A)	-2345(4)	-4914(22)	-1362(6)	36
H(6A)	-1628(4)	-4908(23)	-1873(6)	31
H(9A)	-1282(4)	-5109(19)	1282(6)	52
H(9B)	-771(4)	-3952(19)	1718(6)	52
H(9C)	-769(4)	-6265(19)	1705(6)	52
H(12A)	-449(4)	-9776(20)	3740(6)	46
H(14A)	1715(4)	-9834(24)	5404(7)	40
H(15A)	1901(5)	-9834(27)	4174(7)	43
H(16A)	1049(4)	-9857(23)	3016(7)	39
H(19A)	177(4)	-9838(25)	2419(6)	83
H(19B)	-269(4)	-8567(25)	2484(6)	83
H(19C)	-309(4)	-10875(25)	2460(6)	83
H(26A)	-846(4)	-9615(21)	-1705(7)	63
H(26B)	-540(4)	-10907(21)	-979(7)	63
H(26C)	-520(4)	-8599(21)	-916(7)	63
H(27A)	-2250(4)	-9612(20)	-2502(6)	61
H(27B)	-1764(4)	-10790(20)	-2472(6)	61
H(27C)	-1753(4)	-8477(20)	-2450(6)	61
H(28A)	-2662(3)	-9843(21)	-846(6)	58
H(28B)	-2684(3)	-10933(21)	-1598(6)	58
H(28C)	-2698(3)	-8622(21)	-1578(6)	58
H(29A)	-2205(4)	-9915(18)	256(6)	60
H(29B)	-1691(4)	-8930(18)	801(6)	60
H(29C)	-1724(4)	-11228(18)	697(6)	60
H(30A)	-780(4)	-10020(20)	971(6)	62
H(30B)	-491(4)	-8784(20)	555(6)	62
H(30C)	-501(4)	-11094(20)	500(6)	62
H(36A)	-9(4)	-14683(28)	4018(8)	84
H(36B)	18(4)	-15892(28)	3319(8)	84
H(36C)	-11(4)	-13582(28)	3279(8)	84
H(37A)	1179(5)	-14601(23)	2609(6)	83
H(37B)	668(5)	-13488(23)	2493(6)	83
H(37C)	683(5)	-15801(23)	2510(6)	83
H(38A)	1893(4)	-14572(23)	3375(8)	92
H(38B)	2187(4)	-15760(23)	4136(8)	92
H(38C)	2199(4)	-13447(23)	4147(8)	92
H(39A)	1838(4)	-14604(24)	6010(7)	88
H(39B)	2156(4)	-13448(24)	5617(7)	88
H(39C)	2149(4)	-15761(24)	5606(7)	88
H(40A)	1070(4)	-14606(20)	5866(6)	52
H(40B)	579(4)	-15743(20)	5332(6)	52
H(40C)	587(4)	-13429(20)	5331(6)	52

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5	1	15	224	248	66	-11	-3	16	0	157	1	-20	2	16	53	106	52	-7	-1	17	581	546	34	-1	-3	18	506	468	52
3	1	15	278	214	51	-9	-3	16	378	263	46	-18	2	16	517	472	38	-5	-1	17	190	198	111	-22	-2	18	379	335	54
1	1	15	787	757	27	-7	-3	16	366	328	48	-16	2	16	294	288	57	-3	-1	17	254	210	74	-20	-2	18	0	231	1
9	1	15	249	209	58	-5	-3	16	134	196	133	-14	2	16	596	557	29	-1	-1	17	166	225	166	-18	-2	18	566	489	41
7	1	15	1109	1101	23	-3	-3	16	356	213	58	-12	2	16	257	202	57	1	-1	17	0	125	1	-16	-2	18	0	69	1
5	1	15	320	155	48	-1	-3	16	370	267	52	-10	2	16	79	87	78	3	-1	17	110	69	109	-14	-2	18	545	468	41
3	1	15	812	822	16	1	-3	16	525	536	43	-8	2	16	429	458	39	5	-1	17	384	323	38	-12	-2	18	413	275	47
1	1	15	305	271	45	3	-3	16	475	368	46	-6	2	16	432	460	40	7	-1	17	298	289	69	-10	-2	18	245	222	85
1	1	15	772	756	17	5	-3	16	457	346	52	-4	2	16	385	400	42	-26	0	17	126	84	126	-8	-2	18	461	486	46
3	1	15	275	291	39	-26	-2	16	395	308	45	-2	2	16	358	297	28	-24	0	17	674	600	34	-6	-2	18	253	202	88
5	1	15	410	436	30	-24	-2	16	134	70	134	0	2	16	64	157	63	-22	0	17	154	53	153	-4	-2	18	411	333	50
7	1	15	75	207	75	-22	-2	16	439	470	55	2	2	16	230	237	37	-20	0	17	705	651	31	-2	-2	18	0	96	1
9	1	15	177	123	125	-20	-2	16	208	113	56	4	2	16	0	30	1	-18	0	17	29	63	29	0	-2	18	291	73	81
1	1	15	283	164	70	-18	-2	16	465	472	44	6	2	16	223	82	91	-16	0	17	699	693	29	2	-2	18	63	144	62
8	2	15	0	113	1	-16	-2	16	345	296	50	8	2	16	275	301	70	-14	0	17	0	61	1	-25	-1	18	341	285	42
6	2	15	0	85	1	-14	-2	16	567	560	31	-23	3	16	363	392	58	-12	0	17	0	142	1	-23	-1	18	285	280	47
4	2	15	682	645	32	-12	-2	16	65	206	64	-21	3	16	413	435	48	-10	0	17	325	443	56	-21	-1	18	287	271	50
0	2	15	613	592	31	-10	-2	16	155	15	154	-19	3	16	391	241	53	-8	0	17	693	693	30	-19	-1	18	352	267	57
8	2	15	0	138	1	-8	-2	16	346	450	58	-17	3	16	418	358	44	-6	0	17	1076	1090	26	-17	-1	18	301	245	60
6	2	15	425	457	38	-6	-2	16	514	466	39	-15	3	16	0	175	1	-4	0	17	0	173	1	-15	-1	18	0	130	1
4	2	15	97	178	96	-4	-2	16	412	390	45	-13	3	16	279	361	57	-2	0	17	917	899	29	-13	-1	18	384	410	51
2	2	15	114	211	114	-2	-2	16	364	301	51	-11	3	16	0	143	1	0	0	17	316	282	63	-11	-1	18	272	157	70
0	2	15	514	539	33	0	-2	16	206	150	127	-9	3	16	269	267	60	2	0	17	646	580	24	-9	-1	18	510	520	40
8	2	15	509	510	33	2	-2	16	186	239	139	-7	3	16	373	328	51	4	0	17	252	190	49	-7	-1	18	0	25	1
6	2	15	638	660	30	4	-2	16	220	30	58	-5	3	16	184	223	126	6	0	17	476	505	61	-5	-1	18	738	628	33
4	2	15	153	127	63	6	-2	16	142	77	141	-3	3	16	198	219	72	-27	1	17	251	60	90	-3	-1	18	387	272	52
2	2	15	752	785	19	8	-2	16	270	297	55	-1	3	16	376	265	44	-25	1	17	0	125	1	-1	-1	18	582	507	38
0	2	15	124	95	58	-27	-1	16	396	385	37	1	3	16	563	559	20	-23	1	17	197	161	96	1	-1	18	332	224	57
2	2	15	538	486	17	-25	-1	16	390	322	33	3	3	16	422	387	23	-21	1	17	117	207	116	3	-1	18	295	310	72
4	2	15	377	370	43	-23	-1	16	516	461	26	5	3	16	349	336	29	-19	1	17	436	419	41	-24	0	18	0	49	1
6	2	15	589	634	34	-21	-1	16	532	525	25	-20	4	16	0	147	1	-17	1	17	180	230	107	-22	0	18	758	687	35
8	2	15	0	63	1	-19	-1	16	464	430	65	-18	4	16	0	15	1	-15	1	17	662	645	31	-20	0	18	130	40	129
0	2	15	265	329	74	-17	-1	16	705	723	19	-16	4	16	300	183	68	-13	1	17	212	199	84	-18	0	18	817	784	29
5	3	15	0	190	1	-15	-1	16	0	233	1	-14	4	16	276	317	75	-11	1	17	736	751	28	-16	0	18	710	640	33
3	3	15	386	330	51	-13	-1	16	386	461	46	-12	4	16	459	523	43	-9	1	17	278	176	57	-14	0	18	639	635	32
1	3	15	205	136	96	-11	-1	16	72	119	72	-10	4	16	889	898	26	-7	1	17	587	568	35	-12	0	18	497	538	41
9	3	15	101	137	100	-9	-1	16	481	421	36	-8	4	16	360	357	46	-5	1	17	0	209	1	-10	0	18	521	485	38
7	3	15	204	246	86	-7	-1	16	312	287	49	-2	4	16	225	243	85	-3	1	17	96	211	96	-8	0	18	250	277	67
5	3	15	266	349	56	-5	-1	16	259	341	62	0	4	16	0	149	1	-1	1	17	277	232	65	-6	0	18	98	119	97
3	3	15	238	233	66	-3	-1	16	179	255	125	2	4	16	121	107	120	1	1	17	0	118	1	-4	0	18	0	18	1
1	3	15	717	698	27	-1	-1	16	536	516	36	-16	-4	17	365	447	63	3	1	17	185	62	63	-2	0	18	371	421	64
9	3	15	143	297	143	1	-1	16	507	485	25	-14	-4	17	0	121	1	5	1	17	254	316	68	0	0	18	395	387	53
7	3	15	704	722	28	3	-1	16	419	421	56	-12	-4	17	27	205	27	7	1	17	290	270	65	2	0	18	254	168	91
5	3	15	144	120	144	5	-1	16	539	490	28	-10	-4	17	387	336	53	-24	2	17	376	389	53	4	0	18	345	373	104
3	3	15	691	677	38	7	-1	16	260	263	81	-8	-4	17	545	543	41	-22	2	17	163	72	163	-25	1	18	287	275	69
1	3	15	419	396	26	9	-1	16	328	370	117	-6	-4	17	715	667	36	-20	2	17	311	192	58	-23	1	18	282	284	66
1	3	15	517	537	21	-28	0	16	307	116	66	-4	-4	17	391	344	61	-18	2	17	0	50	1	-21	1	18	91	270	91
3	3	15	512	521	20	-26	0	16	379	299	49	-2	-4	17	840	758	36	-16	2	17	0	211	1	-19	1	18	287	277	63
5	3	15	354	334	30	-24	0	16	0	3	1	-23	-3	17	0	119	1	-14	2	17	0	213	1	-17	1	18	180	249	180
7	3	15	183	137	67	-22	0	16	654	712	31	-21	-3	17	98	146	98	-10	2	17	0	158	1	-15	1	18	181	127	151
2	4	15	205	202	102	-20	0	16	157	272	157	-19	-3	17	312	338	64	-8	2	17	212	246	83	-13	1	18	399	436	46
0	4	15	547	559	43	-18	0	16	0	66	1	-17	-3	17	0	167	1	-6	2	17	0	89	1	-11	1	18	361	164	52
8	4	15	368	342	50	-16	0	16	259	224	62	-15	-3	17	596	523	34	-4	2	17	113	135	113	-9	1	18	571	544	37
6	4	15	762	770	29	-14	0	16	554	494	31	-13	-3	17	217	224	92	-2	2	17	508	419	38	-7	1	18	0	29	1
4	4	15	637	632	33	-12	0	16	772	769	26	-11	-3	17	530	509	39	0	2	17	239	164	70	-5	1	18	743	623	31
2	4	15	858	814	28	-10	0	16	1259	1228	24	-9	-3	17	171	18	171	2	2	17	601	629	48	-3	1	18	257	256	79
0	4	15	261	260	61	-8	0	16	315	236	51	-7	-3	17	423	433	50	4	2	17	0	34	1	-1	1	18	554	499	42
8	4	15	235	255	62	-6	0	16	669	635	29	-5	-3	17	153	231	153	6	2	17	330	294	55	1	1	18	290	209	73
4	4	15	281	290	49	-4	0	16	413	366	40	-3	-3	17	191	211	161	-23	3	17	245	121	91	3	1	18	365	311	55
2	4	15	742	749	26	-2	0	16	394	390	44	-1	-3	17	215	203	104	-21	3	17	128	145	128	-22	2	18	344	333	59
0	4	15	434	444	29	0	0	16	357	301	65	1	-3	17	19	127	18	-19	3	17	342	356	57	-20	2	18	338	227	52
2	4	15	339	361	121	2	0	16	281	142	51	3	-3	17	0	28	1	-17	3	17	386	174	54	-18	2	18	442	483	46
4	4	15	0	59	1	4	0	16	192	120	111	-24	-2	17	362	394	76	-15	3	17	449	524	40	-16	2	18	0	50	1
5	5	15	220	90	103	6	0	16	348	359	39	-22	-2	17	170	71	170	-13	3	17	88	234	87	-14	2	18	467	472	42
3	5	15	217	278	89	8	0	16	0	107	1	-20	-2	17	191	172	55	-11	3	17	476	497	39	-12	2	18	335	285	54
1	5	15	471	499	44	10	0	16	0	113	1	-18	-2	17	182	63	156	-9	3	17	0	16	1	-10	2	18	147	217	147

Table 6. Observed and calculated structure factors for****

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
-8	2	18	440	492	45	-8	-2	19	381	349	60	-4	0	19	464	468	47	-15	3	19	333	326	63	-6	0	20	94	201	93
-6	2	18	141	196	140	-6	-2	19	342	333	59	-2	0	19	544	462	48	-13	3	19	226	203	112	-4	0	20	631	655	37
-4	2	18	306	336	68	-4	-2	19	146	179	146	0	0	19	309	236	69	-11	3	19	184	209	184	-2	0	20	0	58	1
-2	2	18	160	87	160	-2	-2	19	0	89	1	2	0	19	23	186	22	-9	3	19	213	137	113	-19	1	20	288	191	82
2	2	18	265	148	66	-23	-1	19	378	348	57	-23	1	19	428	370	50	-7	3	19	0	24	1	-17	1	20	279	368	77
19	3	18	0	45	1	-21	-1	19	367	382	54	-21	1	19	258	390	78	-16	-2	20	222	99	112	-15	1	20	128	205	127
17	3	18	0	142	1	-19	-1	19	462	419	46	-19	1	19	465	419	51	-14	-2	20	0	104	1	-13	1	20	507	542	43
15	3	18	201	85	106	-17	-1	19	431	303	54	-17	1	19	428	302	50	-12	-2	20	222	135	115	-11	1	20	283	94	83
3	3	18	285	353	69	-15	-1	19	513	469	42	-15	1	19	516	455	39	-10	-2	20	146	73	146	-9	1	20	555	557	42
1	3	18	283	199	81	-13	-1	19	191	130	148	-13	1	19	0	118	1	-8	-2	20	0	66	1	-7	1	20	136	174	136
-9	3	18	508	482	43	-11	-1	19	243	224	81	-11	1	19	131	226	130	-6	-2	20	331	185	74	-5	1	20	228	378	105
-7	3	18	187	118	107	-9	-1	19	0	100	1	-9	1	19	0	96	1	-19	-1	20	0	175	1	-3	1	20	197	138	144
12	4	18	353	422	61	-7	-1	19	142	156	142	-7	1	19	261	161	78	-17	-1	20	363	363	59	-16	2	20	0	102	1
10	4	18	377	341	56	-5	-1	19	0	97	1	-5	1	19	240	94	82	-15	-1	20	273	189	79	-14	2	20	0	97	1
17	-3	19	0	202	1	-3	-1	19	419	395	51	-3	1	19	417	422	49	-13	-1	20	569	530	43	-12	2	20	0	128	1
15	-3	19	386	321	55	-1	-1	19	269	268	93	-1	1	19	265	278	95	-11	-1	20	0	102	1	-10	2	20	136	63	135
13	-3	19	108	200	107	1	-1	19	316	354	64	1	1	19	386	360	64	-9	-1	20	595	549	43	-8	2	20	159	72	159
11	-3	19	273	214	80	-24	0	19	262	232	101	-20	2	19	0	76	1	-7	-1	20	163	176	163	-6	2	20	30	183	30
9	-3	19	344	143	67	-22	0	19	150	24	150	-18	2	19	0	66	1	-5	-1	20	351	368	68	-13	-1	21	179	84	178
7	-3	19	30	27	30	-20	0	19	373	199	58	-16	2	19	259	209	76	-3	-1	20	304	139	76	-16	0	21	622	619	42
5	-3	19	0	90	1	-18	0	19	0	156	1	-14	2	19	175	141	174	-20	0	20	138	6	137	-14	0	21	510	409	47
20	-2	19	262	74	101	-16	0	19	342	245	59	-12	2	19	246	154	74	-18	0	20	295	248	74	-12	0	21	245	460	111
18	-2	19	0	73	1	-14	0	19	39	21	39	-10	2	19	308	197	70	-16	0	20	0	67	1	-10	0	21	382	370	58
16	-2	19	185	206	185	-12	0	19	667	641	35	-8	2	19	330	348	54	-14	0	20	0	166	1	-13	1	21	306	90	74
14	-2	19	168	141	167	-10	0	19	391	275	55	-6	2	19	225	337	98	-12	0	20	293	34	72	-11	1	21	301	216	80
12	-2	19	234	155	94	-8	0	19	431	419	47	-4	2	19	0	187	1	-10	0	20	353	245	65						
10	-2	19	207	202	103	-6	0	19	325	239	69	-17	3	19	169	192	168	-8	0	20	496	435	50						

Identification code: **99019**
Empirical Formula: **$C_{39}H_{45}Cl_3Fe_2N_2$**

Selected torsion angles

-0.92 (1.58) C8 - N1 - C1 - C2
178.89 (0.77) C8 - N1 - C1 - C1_$1
-0.19 (1.61) N1 - C1 - C2 - C3
180.00 (0.75) C1_$1 - C1 - C2 - C3
1.21 (1.58) C1 - C2 - C3 - C7
-178.22 (0.96) C1 - C2 - C3 - C9
157.82 (2.12) C21 - Fe1 - C4 - C5
-84.51 (0.79) C23 - Fe1 - C4 - C5
-127.94 (0.76) C24 - Fe1 - C4 - C5
37.42 (0.73) C6 - Fe1 - C4 - C5
-168.74 (0.74) C25 - Fe1 - C4 - C5
0.00 (0.00) C5 - Fe1 - C4 - C5
-48.23 (1.41) C22 - Fe1 - C4 - C5
81.22 (0.77) C8 - Fe1 - C4 - C5
119.61 (1.09) C7 - Fe1 - C4 - C5
38.22 (2.66) C21 - Fe1 - C4 - C7
155.88 (0.69) C23 - Fe1 - C4 - C7
112.45 (0.75) C24 - Fe1 - C4 - C7
-82.19 (0.76) C6 - Fe1 - C4 - C7
71.65 (0.88) C25 - Fe1 - C4 - C7
-119.61 (1.09) C5 - Fe1 - C4 - C7
-167.84 (0.97) C22 - Fe1 - C4 - C7
-38.39 (0.68) C8 - Fe1 - C4 - C7
0.00 C7 - Fe1 - C4 - C7
3.50 (1.72) C7 - C4 - C5 - C6
-57.79 (1.04) Fe1 - C4 - C5 - C6
61.28 (1.04) C7 - C4 - C5 - Fe1
0.00 (0.00) Fe1 - C4 - C5 - Fe1
-169.59 (0.96) C21 - Fe1 - C5 - C4
113.07 (0.78) C23 - Fe1 - C5 - C4
71.51 (0.87) C24 - Fe1 - C5 - C4
-119.69 (1.09) C6 - Fe1 - C5 - C4
41.18 (2.55) C25 - Fe1 - C5 - C4
0.00 (0.00) C4 - Fe1 - C5 - C4
156.24 (0.72) C22 - Fe1 - C5 - C4
-81.30 (0.78) C8 - Fe1 - C5 - C4
-37.09 (0.73) C7 - Fe1 - C5 - C4
-49.90 (1.35) C21 - Fe1 - C5 - C6
-127.24 (0.75) C23 - Fe1 - C5 - C6
-168.80 (0.71) C24 - Fe1 - C5 - C6
0.00 (0.00) C6 - Fe1 - C5 - C6
160.87 (2.04) C25 - Fe1 - C5 - C6
119.69 (1.09) C4 - Fe1 - C5 - C6
-84.07 (0.76) C22 - Fe1 - C5 - C6
38.39 (0.72) C8 - Fe1 - C5 - C6
82.60 (0.77) C7 - Fe1 - C5 - C6
-4.10 (1.73) C4 - C5 - C6 - C8
-62.16 (1.04) Fe1 - C5 - C6 - C8
58.06 (1.04) C4 - C5 - C6 - Fe1
0.00 Fe1 - C5 - C6 - Fe1
155.58 (0.71) C21 - Fe1 - C6 - C5
72.60 (0.84) C23 - Fe1 - C6 - C5
38.22 (2.35) C24 - Fe1 - C6 - C5
-170.80 (0.96) C25 - Fe1 - C6 - C5
-37.32 (0.72) C4 - Fe1 - C6 - C5
0.00 (0.00) C5 - Fe1 - C6 - C5
112.71 (0.75) C22 - Fe1 - C6 - C5
-117.79 (1.06) C8 - Fe1 - C6 - C5
-80.42 (0.75) C7 - Fe1 - C6 - C5
-86.64 (0.74) C21 - Fe1 - C6 - C8
-169.61 (0.70) C23 - Fe1 - C6 - C8
156.00 (1.84) C24 - Fe1 - C6 - C8
-53.02 (1.31) C25 - Fe1 - C6 - C8
80.47 (0.75) C4 - Fe1 - C6 - C8
117.79 (1.06) C5 - Fe1 - C6 - C8
-129.51 (0.72) C22 - Fe1 - C6 - C8
0.00 C8 - Fe1 - C6 - C8
37.37 (0.67) C7 - Fe1 - C6 - C8
177.83 (1.47) C2 - C3 - C7 - C4
-2.72 (2.21) C9 - C3 - C7 - C4
-1.07 (1.69) C2 - C3 - C7 - C8
178.39 (1.11) C9 - C3 - C7 - C8
83.16 (1.26) C2 - C3 - C7 - Fe1
-97.38 (1.16) C9 - C3 - C7 - Fe1
179.49 (1.46) C5 - C4 - C7 - C3
-119.80 (1.59) Fe1 - C4 - C7 - C3
-1.52 (1.63) C5 - C4 - C7 - C8
59.19 (0.91) Fe1 - C4 - C7 - C8
-60.71 (1.06) C5 - C4 - C7 - Fe1
0.00 Fe1 - C4 - C7 - Fe1
-38.85 (1.22) C21 - Fe1 - C7 - C3
81.37 (1.34) C23 - Fe1 - C7 - C3
46.22 (1.10) C24 - Fe1 - C7 - C3
-148.06 (1.05) C6 - Fe1 - C7 - C3
1.96 (1.05) C25 - Fe1 - C7 - C3
130.64 (1.33) C4 - Fe1 - C7 - C3
168.15 (1.07) C5 - Fe1 - C7 - C3

-75.67 (2.49) C22 - Fe1 - C7 - C3
-110.95 (1.15) C8 - Fe1 - C7 - C3
-169.49 (0.78) C21 - Fe1 - C7 - C4
-49.27 (1.29) C23 - Fe1 - C7 - C4
-84.41 (0.78) C24 - Fe1 - C7 - C4
81.30 (0.76) C6 - Fe1 - C7 - C4
-128.68 (0.74) C25 - Fe1 - C7 - C4
0.00 C4 - Fe1 - C7 - C4
37.51 (0.74) C5 - Fe1 - C7 - C4
153.69 (2.06) C22 - Fe1 - C7 - C4
118.41 (0.99) C8 - Fe1 - C7 - C4
72.10 (0.79) C21 - Fe1 - C7 - C8
-167.68 (0.95) C23 - Fe1 - C7 - C8
157.17 (0.62) C24 - Fe1 - C7 - C8
-37.11 (0.63) C6 - Fe1 - C7 - C8
112.91 (0.68) C25 - Fe1 - C7 - C8
-118.41 (0.99) C4 - Fe1 - C7 - C8
-80.90 (0.69) C5 - Fe1 - C7 - C8
35.28 (2.44) C22 - Fe1 - C7 - C8
0.00 (0.00) C8 - Fe1 - C7 - C8
-176.74 (1.35) C1 - N1 - C8 - C6
1.02 (1.76) C1 - N1 - C8 - C7
-86.89 (1.15) C1 - N1 - C8 - Fe1
-178.78 (1.30) C5 - C6 - C8 - N1
119.37 (1.44) Fe1 - C6 - C8 - N1
3.20 (1.69) C5 - C6 - C8 - C7
-58.65 (0.93) Fe1 - C6 - C8 - C7
61.85 (1.06) C5 - C6 - C8 - Fe1
0.00 Fe1 - C6 - C8 - Fe1
-0.03 (1.88) C3 - C7 - C8 - N1
-179.22 (1.24) C4 - C7 - C8 - N1
-120.67 (1.24) Fe1 - C7 - C8 - N1
178.15 (1.18) C3 - C7 - C8 - C6
-1.04 (1.61) C4 - C7 - C8 - C6
57.52 (0.99) Fe1 - C7 - C8 - C6
120.63 (1.12) C3 - C7 - C8 - Fe1
-58.55 (0.97) C4 - C7 - C8 - Fe1
0.00 (0.00) Fe1 - C7 - C8 - Fe1
-12.14 (0.95) C21 - Fe1 - C8 - N1
-87.72 (2.14) C23 - Fe1 - C8 - N1
69.16 (1.41) C24 - Fe1 - C8 - N1
-123.38 (1.20) C6 - Fe1 - C8 - N1
31.02 (1.06) C25 - Fe1 - C8 - N1
154.27 (0.97) C4 - Fe1 - C8 - N1
-161.84 (0.98) C5 - Fe1 - C8 - N1
-53.77 (1.06) C22 - Fe1 - C8 - N1
116.61 (1.10) C7 - Fe1 - C8 - N1
111.24 (0.75) C21 - Fe1 - C8 - C6
35.65 (2.32) C23 - Fe1 - C8 - C6
-167.46 (0.97) C24 - Fe1 - C8 - C6
0.00 C6 - Fe1 - C8 - C6
154.40 (0.66) C25 - Fe1 - C8 - C6
-82.36 (0.74) C4 - Fe1 - C8 - C6
-38.46 (0.69) C5 - Fe1 - C8 - C6
69.61 (0.82) C22 - Fe1 - C8 - C6
-120.01 (0.96) C7 - Fe1 - C8 - C6
-128.75 (0.66) C21 - Fe1 - C8 - C7
155.67 (1.86) C23 - Fe1 - C8 - C7
-47.45 (1.25) C24 - Fe1 - C8 - C7
120.01 (0.96) C6 - Fe1 - C8 - C7
-85.59 (0.70) C25 - Fe1 - C8 - C7
37.66 (0.65) C4 - Fe1 - C8 - C7
81.55 (0.67) C5 - Fe1 - C8 - C7
-170.38 (0.67) C22 - Fe1 - C8 - C7
0.00 C7 - Fe1 - C8 - C7
-0.07 (1.82) C17 - N2 - C11 - C12
179.17 (0.85) C17 - N2 - C11 - C11_$2
0.89 (2.08) N2 - C11 - C12 - C13
-178.32 (1.06) C11_$2 - C11 - C12 - C13
-3.08 (2.16) C11 - C12 - C13 - C18
-176.76 (1.40) C11 - C12 - C13 - C19
74.07 (0.96) C33 - Fe2 - C14 - C15
-168.35 (1.18) C31 - Fe2 - C14 - C15
40.13 (2.37) C32 - Fe2 - C14 - C15
115.61 (0.84) C34 - Fe2 - C14 - C15
-36.75 (0.77) C16 - Fe2 - C14 - C15
0.00 (0.00) C15 - Fe2 - C14 - C15
157.89 (0.78) C35 - Fe2 - C14 - C15
-80.19 (0.84) C18 - Fe2 - C14 - C15
-118.28 (1.13) C17 - Fe2 - C14 - C15
-167.65 (0.77) C33 - Fe2 - C14 - C17
-50.08 (1.55) C31 - Fe2 - C14 - C17
158.41 (1.81) C32 - Fe2 - C14 - C17
-126.11 (0.77) C34 - Fe2 - C14 - C17
81.53 (0.78) C16 - Fe2 - C14 - C17
118.28 (1.13) C15 - Fe2 - C14 - C17
-83.83 (0.79) C35 - Fe2 - C14 - C17
38.09 (0.71) C18 - Fe2 - C14 - C17
0.00 (0.00) C17 - Fe2 - C14 - C17
-2.63 (1.96) C17 - C14 - C15 - C16
58.23 (1.21) Fe2 - C14 - C15 - C16
-60.86 (1.12) C17 - C14 - C15 - Fe2

0.00 Fe2 - C14 - C15 - Fe2
-120.66 (1.17) C14 - Fe2 - C15 - C16
114.47 (0.88) C33 - Fe2 - C15 - C16
41.15 (2.44) C31 - Fe2 - C15 - C16
72.13 (0.94) C32 - Fe2 - C15 - C16
157.58 (0.74) C34 - Fe2 - C15 - C16
0.00 (0.00) C16 - Fe2 - C15 - C16
-169.36 (1.10) C35 - Fe2 - C15 - C16
-38.52 (0.76) C18 - Fe2 - C15 - C16
-82.31 (0.83) C17 - Fe2 - C15 - C16
0.00 C14 - Fe2 - C15 - C14
-124.87 (0.87) C33 - Fe2 - C15 - C14
161.81 (1.83) C31 - Fe2 - C15 - C14
-167.21 (0.79) C32 - Fe2 - C15 - C14
-81.76 (0.85) C34 - Fe2 - C15 - C14
120.66 (1.17) C16 - Fe2 - C15 - C14
-48.70 (1.61) C35 - Fe2 - C15 - C14
82.14 (0.85) C18 - Fe2 - C15 - C14
38.35 (0.76) C17 - Fe2 - C15 - C14
3.32 (1.93) C14 - C15 - C16 - C18
61.10 (1.14) Fe2 - C15 - C16 - C18
-57.78 (1.19) C14 - C15 - C16 - Fe2
0.00 (0.00) Fe2 - C15 - C16 - Fe2
-80.35 (0.86) C14 - Fe2 - C16 - C18
159.99 (0.82) C33 - Fe2 - C16 - C18
75.91 (0.88) C31 - Fe2 - C16 - C18
116.05 (0.84) C32 - Fe2 - C16 - C18
-165.64 (1.17) C34 - Fe2 - C16 - C18
-117.34 (1.19) C15 - Fe2 - C16 - C18
45.38 (2.31) C35 - Fe2 - C16 - C18
0.00 (0.00) C18 - Fe2 - C16 - C18
-36.36 (0.77) C17 - Fe2 - C16 - C18
36.99 (0.80) C14 - Fe2 - C16 - C15
-82.67 (0.91) C33 - Fe2 - C16 - C15
-166.75 (0.81) C31 - Fe2 - C16 - C15
-126.61 (0.86) C32 - Fe2 - C16 - C15
-48.30 (1.58) C34 - Fe2 - C16 - C15
0.00 (0.00) C15 - Fe2 - C16 - C15
162.71 (1.77) C35 - Fe2 - C16 - C15
117.34 (1.19) C18 - Fe2 - C16 - C15
80.98 (0.86) C17 - Fe2 - C16 - C15
1.74 (2.10) C11 - N2 - C17 - C18
-178.05 (1.46) C11 - N2 - C17 - C14
-87.40 (1.24) C11 - N2 - C17 - Fe2
-179.29 (1.51) C15 - C14 - C17 - N2
119.88 (1.62) Fe2 - C14 - C17 - N2
0.89 (1.93) C15 - C14 - C17 - C18
-59.94 (1.12) Fe2 - C14 - C17 - C18
60.83 (1.19) C15 - C14 - C17 - Fe2
0.00 Fe2 - C14 - C17 - Fe2
-123.54 (1.25) C14 - Fe2 - C17 - N2
-85.71 (2.09) C33 - Fe2 - C17 - N2
33.90 (1.09) C31 - Fe2 - C17 - N2
69.72 (1.55) C32 - Fe2 - C17 - N2
-50.62 (1.09) C34 - Fe2 - C17 - N2
154.62 (1.00) C16 - Fe2 - C17 - N2
-161.76 (1.03) C15 - Fe2 - C17 - N2
-9.00 (0.91) C35 - Fe2 - C17 - N2
118.37 (1.20) C18 - Fe2 - C17 - N2
118.09 (1.07) C14 - Fe2 - C17 - C18
155.92 (1.80) C33 - Fe2 - C17 - C18
-84.47 (0.79) C31 - Fe2 - C17 - C18
-48.65 (1.43) C32 - Fe2 - C17 - C18
-168.99 (0.76) C34 - Fe2 - C17 - C18
36.25 (0.74) C16 - Fe2 - C17 - C18
79.87 (0.80) C15 - Fe2 - C17 - C18
-127.37 (0.79) C35 - Fe2 - C17 - C18
0.00 (0.00) C18 - Fe2 - C17 - C18
0.00 (0.00) C14 - Fe2 - C17 - C14
37.83 (2.22) C33 - Fe2 - C17 - C14
157.44 (0.71) C31 - Fe2 - C17 - C14
-166.74 (1.10) C32 - Fe2 - C17 - C14
72.92 (0.85) C34 - Fe2 - C17 - C14
-81.84 (0.78) C16 - Fe2 - C17 - C14
-38.22 (0.74) C15 - Fe2 - C17 - C14
114.54 (0.75) C35 - Fe2 - C17 - C14
-118.09 (1.07) C18 - Fe2 - C17 - C14
-2.78 (1.95) C15 - C16 - C18 - C17
58.04 (1.16) Fe2 - C16 - C18 - C17
-176.40 (1.82) C15 - C16 - C18 - C13
-115.57 (1.97) Fe2 - C16 - C18 - C13
-60.83 (1.17) C15 - C16 - C18 - Fe2
0.00 (0.00) Fe2 - C16 - C18 - Fe2
-178.65 (1.37) N2 - C17 - C18 - C16
1.18 (1.96) C14 - C17 - C18 - C16
-57.85 (1.16) Fe2 - C17 - C18 - C16
-4.05 (2.46) N2 - C17 - C18 - C13
175.78 (1.43) C14 - C17 - C18 - C13
116.75 (1.55) Fe2 - C17 - C18 - C13
-120.80 (1.46) N2 - C17 - C18 - Fe2
59.03 (1.11) C14 - C17 - C18 - Fe2
0.00 (0.00) Fe2 - C17 - C18 - Fe2

177.61 (1.66) C12 - C13 - C18 - C16
-8.48 (2.87) C19 - C13 - C18 - C16
4.45 (2.29) C12 - C13 - C18 - C17
178.36 (1.45) C19 - C13 - C18 - C17
87.22 (1.52) C12 - C13 - C18 - Fe2
-98.87 (1.48) C19 - C13 - C18 - Fe2
82.94 (0.83) C14 - Fe2 - C18 - C16
-43.18 (1.66) C33 - Fe2 - C18 - C16
-124.34 (0.81) C31 - Fe2 - C18 - C16
-81.10 (0.87) C32 - Fe2 - C18 - C16
156.05 (1.92) C34 - Fe2 - C18 - C16
0.00 (0.00) C16 - Fe2 - C18 - C16
38.70 (0.80) C15 - Fe2 - C18 - C16
-165.91 (0.76) C35 - Fe2 - C18 - C16
121.48 (1.15) C17 - Fe2 - C18 - C16
-38.54 (0.70) C14 - Fe2 - C18 - C17
-164.66 (1.17) C33 - Fe2 - C18 - C17
114.19 (0.76) C31 - Fe2 - C18 - C17
157.43 (0.69) C32 - Fe2 - C18 - C17
34.57 (2.47) C34 - Fe2 - C18 - C17
-121.48 (1.14) C16 - Fe2 - C18 - C17
-82.77 (0.81) C15 - Fe2 - C18 - C17
72.61 (0.89) C35 - Fe2 - C18 - C17
0.00 (0.00) C17 - Fe2 - C18 - C17
-149.87 (1.00) C14 - Fe2 - C18 - C13
84.01 (1.49) C33 - Fe2 - C18 - C13
2.85 (0.96) C31 - Fe2 - C18 - C13
46.09 (1.07) C32 - Fe2 - C18 - C13
-76.76 (2.49) C34 - Fe2 - C18 - C13
127.19 (1.33) C16 - Fe2 - C18 - C13
165.89 (1.07) C15 - Fe2 - C18 - C13
-38.72 (1.17) C35 - Fe2 - C18 - C13
-111.33 (1.15) C17 - Fe2 - C18 - C13
-81.76 (0.78) C23 - Fe1 - C21 - C25
-37.42 (0.71) C24 - Fe1 - C21 - C25
156.24 (0.68) C6 - Fe1 - C21 - C25
0.00 (0.00) C25 - Fe1 - C21 - C25
41.28 (2.59) C4 - Fe1 - C21 - C25
-169.54 (0.99) C5 - Fe1 - C21 - C25
-119.97 (1.05) C22 - Fe1 - C21 - C25
113.07 (0.72) C8 - Fe1 - C21 - C25
72.07 (0.85) C7 - Fe1 - C21 - C25
38.21 (0.73) C23 - Fe1 - C21 - C22
82.55 (0.78) C24 - Fe1 - C21 - C22
-83.79 (0.77) C6 - Fe1 - C21 - C22
119.97 (1.05) C25 - Fe1 - C21 - C22
161.24 (2.13) C4 - Fe1 - C21 - C22
-49.57 (1.34) C5 - Fe1 - C21 - C22
0.00 (0.00) C22 - Fe1 - C21 - C22
-126.96 (0.74) C8 - Fe1 - C21 - C22
-167.96 (0.71) C7 - Fe1 - C21 - C22
157.95 (1.18) C23 - Fe1 - C21 - C26
-157.71 (1.16) C24 - Fe1 - C21 - C26
35.95 (1.25) C6 - Fe1 - C21 - C26
-120.29 (1.38) C25 - Fe1 - C21 - C26
-79.02 (2.71) C4 - Fe1 - C21 - C26
70.17 (1.54) C5 - Fe1 - C21 - C26
119.74 (1.40) C22 - Fe1 - C21 - C26
-7.22 (1.14) C8 - Fe1 - C21 - C26
-48.22 (1.31) C7 - Fe1 - C21 - C26
1.03 (1.73) C25 - C21 - C22 - C23
-179.96 (1.37) C26 - C21 - C22 - C23
-58.42 (1.03) Fe1 - C21 - C22 - C23
-178.02 (1.39) C25 - C21 - C22 - C27
0.99 (2.44) C26 - C21 - C22 - C27
122.52 (1.54) Fe1 - C21 - C22 - C27
59.46 (1.04) C25 - C21 - C22 - Fe1
-121.53 (1.44) C26 - C21 - C22 - Fe1
0.00 (0.00) Fe1 - C21 - C22 - Fe1
0.00 (0.00) C21 - Fe1 - C22 - C21
-118.29 (1.08) C23 - Fe1 - C22 - C21
-81.50 (0.80) C24 - Fe1 - C22 - C21
113.31 (0.77) C6 - Fe1 - C22 - C21
-37.15 (0.72) C25 - Fe1 - C22 - C21
-171.17 (1.04) C4 - Fe1 - C22 - C21
155.80 (0.71) C5 - Fe1 - C22 - C21
73.84 (0.86) C8 - Fe1 - C22 - C21
45.24 (2.50) C7 - Fe1 - C22 - C21
118.29 (1.08) C21 - Fe1 - C22 - C23
0.00 (0.00) C23 - Fe1 - C22 - C23
36.78 (0.73) C24 - Fe1 - C22 - C23
-128.40 (0.73) C6 - Fe1 - C22 - C23
81.14 (0.79) C25 - Fe1 - C22 - C23
-52.89 (1.38) C4 - Fe1 - C22 - C23
-85.91 (0.76) C5 - Fe1 - C22 - C23
-167.87 (0.70) C8 - Fe1 - C22 - C23
163.53 (1.97) C7 - Fe1 - C22 - C23
-120.81 (1.35) C21 - Fe1 - C22 - C27
120.90 (1.31) C23 - Fe1 - C22 - C27
157.69 (1.10) C24 - Fe1 - C22 - C27
-7.50 (1.04) C6 - Fe1 - C22 - C27
-157.96 (1.12) C25 - Fe1 - C22 - C27

68.02 (1.56) C4 - Fe1 - C22 - C27
35.00 (1.17) C5 - Fe1 - C22 - C27
-46.97 (1.20) C8 - Fe1 - C22 - C27
-75.56 (2.50) C7 - Fe1 - C22 - C27
-0.12 (1.76) C21 - C22 - C23 - C24
178.94 (1.47) C27 - C22 - C23 - C24
-58.80 (1.10) Fe1 - C22 - C23 - C24
-177.42 (1.45) C21 - C22 - C23 - C28
1.64 (2.57) C27 - C22 - C23 - C28
123.90 (1.58) Fe1 - C22 - C23 - C28
58.68 (1.01) C21 - C22 - C23 - Fe1
-122.27 (1.54) C27 - C22 - C23 - Fe1
0.00 Fe1 - C22 - C23 - Fe1
-38.37 (0.73) C21 - Fe1 - C23 - C22
-121.48 (1.07) C24 - Fe1 - C23 - C22
70.84 (0.83) C6 - Fe1 - C23 - C22
-82.12 (0.77) C25 - Fe1 - C23 - C22
154.23 (0.70) C4 - Fe1 - C23 - C22
111.51 (0.76) C5 - Fe1 - C23 - C22
0.00 (0.00) C22 - Fe1 - C23 - C22
42.38 (2.33) C8 - Fe1 - C23 - C22
-172.17 (0.92) C7 - Fe1 - C23 - C22
83.12 (0.81) C21 - Fe1 - C23 - C24
0.00 (0.00) C24 - Fe1 - C23 - C24
-167.68 (0.71) C6 - Fe1 - C23 - C24
39.36 (0.72) C25 - Fe1 - C23 - C24
-84.29 (0.78) C4 - Fe1 - C23 - C24
-127.00 (0.75) C5 - Fe1 - C23 - C24
121.48 (1.07) C22 - Fe1 - C23 - C24
163.87 (1.81) C8 - Fe1 - C23 - C24
-50.69 (1.28) C7 - Fe1 - C23 - C24
-160.51 (1.12) C21 - Fe1 - C23 - C28
116.37 (1.28) C24 - Fe1 - C23 - C28
-51.31 (1.15) C6 - Fe1 - C23 - C28
155.73 (1.09) C25 - Fe1 - C23 - C28
32.08 (1.16) C4 - Fe1 - C23 - C28
-10.64 (0.98) C5 - Fe1 - C23 - C28
-122.15 (1.32) C22 - Fe1 - C23 - C28
-79.76 (2.25) C8 - Fe1 - C23 - C28
65.68 (1.51) C7 - Fe1 - C23 - C28
-0.81 (1.75) C22 - C23 - C24 - C25
176.61 (1.37) C28 - C23 - C24 - C25
-60.20 (0.99) Fe1 - C23 - C24 - C25
-176.30 (1.40) C22 - C23 - C24 - C29
1.12 (2.49) C28 - C23 - C24 - C29
124.31 (1.52) Fe1 - C23 - C24 - C29
59.39 (1.10) C22 - C23 - C24 - Fe1
-123.18 (1.47) C28 - C23 - C24 - Fe1
0.00 (0.00) Fe1 - C23 - C24 - Fe1
36.69 (0.69) C21 - Fe1 - C24 - C25
116.83 (1.02) C23 - Fe1 - C24 - C25
159.70 (1.86) C6 - Fe1 - C24 - C25
0.00 C25 - Fe1 - C24 - C25
-129.71 (0.72) C4 - Fe1 - C24 - C25
-169.85 (0.69) C5 - Fe1 - C24 - C25
80.46 (0.74) C22 - Fe1 - C24 - C25
-54.76 (1.28) C8 - Fe1 - C24 - C25
-87.64 (0.71) C7 - Fe1 - C24 - C25
-80.14 (0.78) C21 - Fe1 - C24 - C23
0.00 (0.00) C23 - Fe1 - C24 - C23
42.86 (2.34) C6 - Fe1 - C24 - C23
-116.83 (1.02) C25 - Fe1 - C24 - C23
113.46 (0.75) C4 - Fe1 - C24 - C23
73.32 (0.84) C5 - Fe1 - C24 - C23
-36.37 (0.70) C22 - Fe1 - C24 - C23
-171.59 (0.95) C8 - Fe1 - C24 - C23
155.53 (0.65) C7 - Fe1 - C24 - C23
158.56 (1.12) C21 - Fe1 - C24 - C29
-121.30 (1.34) C23 - Fe1 - C24 - C29
-78.43 (2.29) C6 - Fe1 - C24 - C29
121.87 (1.29) C25 - Fe1 - C24 - C29
-7.84 (1.03) C4 - Fe1 - C24 - C29
-47.98 (1.21) C5 - Fe1 - C24 - C29
-157.66 (1.11) C22 - Fe1 - C24 - C29
67.11 (1.54) C8 - Fe1 - C24 - C29
34.24 (1.18) C7 - Fe1 - C24 - C29
-1.57 (1.75) C22 - C21 - C25 - C24
179.43 (1.40) C26 - C21 - C25 - C24
58.10 (1.02) Fe1 - C21 - C25 - C24
179.20 (1.35) C22 - C21 - C25 - C30
0.20 (2.34) C26 - C21 - C25 - C30
-121.13 (1.43) Fe1 - C21 - C25 - C30
-59.67 (1.05) C22 - C21 - C25 - Fe1
121.33 (1.45) C26 - C21 - C25 - Fe1
0.00 (0.00) Fe1 - C21 - C25 - Fe1
1.44 (1.70) C23 - C24 - C25 - C21
176.93 (1.36) C29 - C24 - C25 - C21
-58.33 (1.02) Fe1 - C24 - C25 - C21
-179.34 (1.40) C23 - C24 - C25 - C30
-3.86 (2.47) C29 - C24 - C25 - C30
120.88 (1.47) Fe1 - C24 - C25 - C30
59.78 (1.04) C23 - C24 - C25 - Fe1

-124.74 (1.48) C29 - C24 - C25 - Fe1
0.00 Fe1 - C24 - C25 - Fe1
0.00 (0.00) C21 - Fe1 - C25 - C21
81.38 (0.77) C23 - Fe1 - C25 - C21
120.60 (1.03) C24 - Fe1 - C25 - C21
-48.87 (1.34) C6 - Fe1 - C25 - C21
-168.82 (0.70) C4 - Fe1 - C25 - C21
157.90 (2.06) C5 - Fe1 - C25 - C21
37.48 (0.70) C22 - Fe1 - C25 - C21
-85.24 (0.75) C8 - Fe1 - C25 - C21
-128.70 (0.72) C7 - Fe1 - C25 - C21
-120.60 (1.03) C21 - Fe1 - C25 - C24
-39.23 (0.68) C23 - Fe1 - C25 - C24
0.00 C24 - Fe1 - C25 - C24
-169.47 (0.97) C6 - Fe1 - C25 - C24
70.58 (0.85) C4 - Fe1 - C25 - C24
37.30 (2.52) C5 - Fe1 - C25 - C24
-83.12 (0.75) C22 - Fe1 - C25 - C24
154.16 (0.64) C8 - Fe1 - C25 - C24
110.69 (0.69) C7 - Fe1 - C25 - C24
118.78 (1.34) C21 - Fe1 - C25 - C30
-159.84 (1.14) C23 - Fe1 - C25 - C30
-120.62 (1.28) C24 - Fe1 - C25 - C30
69.91 (1.51) C6 - Fe1 - C25 - C30
-50.04 (1.27) C4 - Fe1 - C25 - C30
-83.32 (2.54) C5 - Fe1 - C25 - C30
156.26 (1.13) C22 - Fe1 - C25 - C30
33.54 (1.21) C8 - Fe1 - C25 - C30
-9.92 (1.12) C7 - Fe1 - C25 - C30
-168.25 (1.17) C14 - Fe2 - C31 - C32
-39.00 (0.82) C33 - Fe2 - C31 - C32
0.00 (0.00) C32 - Fe2 - C31 - C32
-83.35 (0.84) C34 - Fe2 - C31 - C32
71.81 (0.89) C16 - Fe2 - C31 - C32
39.78 (2.39) C15 - Fe2 - C31 - C32
-120.37 (1.14) C35 - Fe2 - C31 - C32
113.34 (0.81) C18 - Fe2 - C31 - C32
156.36 (0.73) C17 - Fe2 - C31 - C32
-47.87 (1.57) C14 - Fe2 - C31 - C35
81.37 (0.84) C33 - Fe2 - C31 - C35
120.37 (1.14) C32 - Fe2 - C31 - C35
37.03 (0.75) C34 - Fe2 - C31 - C35
-167.81 (0.74) C16 - Fe2 - C31 - C35
160.15 (1.88) C15 - Fe2 - C31 - C35
0.00 (0.00) C35 - Fe2 - C31 - C35
-126.28 (0.76) C18 - Fe2 - C31 - C35
-83.27 (0.82) C17 - Fe2 - C31 - C35
71.15 (1.80) C14 - Fe2 - C31 - C36
-159.60 (1.26) C33 - Fe2 - C31 - C36
-120.60 (1.46) C32 - Fe2 - C31 - C36
156.05 (1.22) C34 - Fe2 - C31 - C36
-48.79 (1.27) C16 - Fe2 - C31 - C36
-80.82 (2.31) C15 - Fe2 - C31 - C36
119.02 (1.39) C35 - Fe2 - C31 - C36
-7.26 (1.14) C18 - Fe2 - C31 - C36
35.75 (1.28) C17 - Fe2 - C31 - C36
-1.84 (1.83) C35 - C31 - C32 - C33
-177.44 (1.55) C36 - C31 - C32 - C33
58.34 (1.09) Fe2 - C31 - C32 - C33
177.87 (1.56) C35 - C31 - C32 - C37
2.28 (2.57) C36 - C31 - C32 - C37
-121.95 (1.61) Fe2 - C31 - C32 - C37
-60.18 (1.13) C35 - C31 - C32 - Fe2
124.22 (1.65) C36 - C31 - C32 - Fe2
0.00 Fe2 - C31 - C32 - Fe2
161.45 (1.82) C14 - Fe2 - C32 - C31
118.54 (1.17) C33 - Fe2 - C32 - C31
0.00 (0.00) C31 - Fe2 - C32 - C31
80.67 (0.82) C34 - Fe2 - C32 - C31
-127.03 (0.79) C16 - Fe2 - C32 - C31
-167.17 (0.79) C15 - Fe2 - C32 - C31
37.07 (0.77) C35 - Fe2 - C32 - C31
-85.23 (0.82) C18 - Fe2 - C32 - C31
-51.28 (1.47) C17 - Fe2 - C32 - C31
42.92 (2.33) C14 - Fe2 - C32 - C33
0.00 (0.00) C33 - Fe2 - C32 - C33
-118.54 (1.17) C31 - Fe2 - C32 - C33
-37.87 (0.79) C34 - Fe2 - C32 - C33
114.43 (0.82) C16 - Fe2 - C32 - C33
74.29 (0.93) C15 - Fe2 - C32 - C33
-81.47 (0.85) C35 - Fe2 - C32 - C33
156.24 (0.76) C18 - Fe2 - C32 - C33
-169.82 (1.08) C17 - Fe2 - C32 - C33
-75.47 (2.42) C14 - Fe2 - C32 - C37
-118.39 (1.46) C33 - Fe2 - C32 - C37
123.07 (1.49) C31 - Fe2 - C32 - C37
-156.26 (1.24) C34 - Fe2 - C32 - C37
-3.96 (1.15) C16 - Fe2 - C32 - C37
-44.10 (1.36) C15 - Fe2 - C32 - C37
160.14 (1.24) C35 - Fe2 - C32 - C37
37.84 (1.31) C18 - Fe2 - C32 - C37
71.79 (1.67) C17 - Fe2 - C32 - C37

0.71 (1.83) C31 - C32 - C33 - C34
-179.01 (1.43) C37 - C32 - C33 - C34
59.88 (1.11) Fe2 - C32 - C33 - C34
178.81 (1.41) C31 - C32 - C33 - C38
-0.92 (2.53) C37 - C32 - C33 - C38
-122.03 (1.61) Fe2 - C32 - C33 - C38
-59.17 (1.06) C31 - C32 - C33 - Fe2
121.11 (1.53) C37 - C32 - C33 - Fe2
0.00 Fe2 - C32 - C33 - Fe2
74.32 (0.89) C14 - Fe2 - C33 - C34
-81.40 (0.83) C31 - Fe2 - C33 - C34
-119.07 (1.15) C32 - Fe2 - C33 - C34
0.00 (0.00) C34 - Fe2 - C33 - C34
157.57 (0.76) C16 - Fe2 - C33 - C34
115.30 (0.84) C15 - Fe2 - C33 - C34
-37.73 (0.77) C35 - Fe2 - C33 - C34
-172.18 (1.17) C18 - Fe2 - C33 - C34
44.86 (2.25) C17 - Fe2 - C33 - C34
-166.61 (0.74) C14 - Fe2 - C33 - C32
37.67 (0.76) C31 - Fe2 - C33 - C32
0.00 C32 - Fe2 - C33 - C32
119.07 (1.15) C34 - Fe2 - C33 - C32
-83.35 (0.82) C16 - Fe2 - C33 - C32
-125.63 (0.81) C15 - Fe2 - C33 - C32
81.35 (0.82) C35 - Fe2 - C33 - C32
-53.11 (1.57) C18 - Fe2 - C33 - C32
163.93 (1.68) C17 - Fe2 - C33 - C32
-48.50 (1.50) C14 - Fe2 - C33 - C38
155.78 (1.42) C31 - Fe2 - C33 - C38
118.11 (1.62) C32 - Fe2 - C33 - C38
-122.82 (1.66) C34 - Fe2 - C33 - C38
34.75 (1.49) C16 - Fe2 - C33 - C38
-7.52 (1.27) C15 - Fe2 - C33 - C38
-160.55 (1.43) C35 - Fe2 - C33 - C38
65.00 (1.96) C18 - Fe2 - C33 - C38
-77.96 (2.40) C17 - Fe2 - C33 - C38
0.66 (1.86) C32 - C33 - C34 - C35
-177.34 (1.58) C38 - C33 - C34 - C35
60.34 (1.11) Fe2 - C33 - C34 - C35
178.19 (1.50) C32 - C33 - C34 - C39
0.19 (2.66) C38 - C33 - C34 - C39
-122.14 (1.58) Fe2 - C33 - C34 - C39
-59.67 (1.10) C32 - C33 - C34 - Fe2
122.32 (1.71) C38 - C33 - C34 - Fe2
0.00 (0.00) Fe2 - C33 - C34 - Fe2
-124.85 (0.83) C14 - Fe2 - C34 - C33
0.00 (0.00) C33 - Fe2 - C34 - C33
81.95 (0.86) C31 - Fe2 - C34 - C33
38.53 (0.81) C32 - Fe2 - C34 - C33
-48.72 (1.58) C16 - Fe2 - C34 - C33
-82.44 (0.89) C15 - Fe2 - C34 - C33
118.93 (1.17) C35 - Fe2 - C34 - C33
167.34 (1.96) C18 - Fe2 - C34 - C33
-165.64 (0.78) C17 - Fe2 - C34 - C33
116.22 (0.78) C14 - Fe2 - C34 - C35
-118.93 (1.17) C33 - Fe2 - C34 - C35
-36.98 (0.74) C31 - Fe2 - C34 - C35
-80.41 (0.81) C32 - Fe2 - C34 - C35
-167.65 (1.10) C16 - Fe2 - C34 - C35
158.63 (0.73) C15 - Fe2 - C34 - C35
0.00 (0.01) C35 - Fe2 - C34 - C35
48.40 (2.46) C18 - Fe2 - C34 - C35
75.43 (0.87) C17 - Fe2 - C34 - C35
-6.95 (1.11) C14 - Fe2 - C34 - C39
117.90 (1.44) C33 - Fe2 - C34 - C39
-160.15 (1.21) C31 - Fe2 - C34 - C39
156.42 (1.22) C32 - Fe2 - C34 - C39
69.18 (1.75) C16 - Fe2 - C34 - C39
35.46 (1.28) C15 - Fe2 - C34 - C39
-123.17 (1.46) C35 - Fe2 - C34 - C39
-74.77 (2.48) C18 - Fe2 - C34 - C39
-47.74 (1.29) C17 - Fe2 - C34 - C39
2.28 (1.86) C32 - C31 - C35 - C34
177.97 (1.48) C36 - C31 - C35 - C34
-57.20 (1.14) Fe2 - C31 - C35 - C34
178.79 (1.40) C32 - C31 - C35 - C40
-5.52 (2.65) C36 - C31 - C35 - C40
119.31 (1.57) Fe2 - C31 - C35 - C40
59.48 (1.08) C32 - C31 - C35 - Fe2
-124.82 (1.62) C36 - C31 - C35 - Fe2
0.00 (0.00) Fe2 - C31 - C35 - Fe2
-1.78 (1.85) C33 - C34 - C35 - C31
-179.21 (1.53) C39 - C34 - C35 - C31
57.11 (1.14) Fe2 - C34 - C35 - C31
-178.33 (1.46) C33 - C34 - C35 - C40
4.24 (2.65) C39 - C34 - C35 - C40
-119.43 (1.53) Fe2 - C34 - C35 - C40
-58.89 (1.10) C33 - C34 - C35 - Fe2
123.68 (1.70) C39 - C34 - C35 - Fe2
0.00 (0.00) Fe2 - C34 - C35 - Fe2
158.29 (0.72) C14 - Fe2 - C35 - C31
-82.22 (0.85) C33 - Fe2 - C35 - C31

0.00 (0.00) C31 - Fe2 - C35 - C31
-36.99 (0.75) C32 - Fe2 - C35 - C31
-120.47 (1.13) C34 - Fe2 - C35 - C31
38.90 (2.31) C16 - Fe2 - C35 - C31
-167.38 (1.18) C15 - Fe2 - C35 - C31
74.45 (0.87) C18 - Fe2 - C35 - C31
115.06 (0.77) C17 - Fe2 - C35 - C31
-81.24 (0.82) C14 - Fe2 - C35 - C34
38.25 (0.82) C33 - Fe2 - C35 - C34
120.47 (1.13) C31 - Fe2 - C35 - C34
83.48 (0.84) C32 - Fe2 - C35 - C34
0.00 (0.01) C34 - Fe2 - C35 - C34
159.37 (1.80) C16 - Fe2 - C35 - C34
-46.91 (1.57) C15 - Fe2 - C35 - C34
-165.08 (0.81) C18 - Fe2 - C35 - C34
-124.47 (0.78) C17 - Fe2 - C35 - C34
38.09 (1.20) C14 - Fe2 - C35 - C40
157.58 (1.18) C33 - Fe2 - C35 - C40
-120.20 (1.36) C31 - Fe2 - C35 - C40
-157.19 (1.14) C32 - Fe2 - C35 - C40
119.33 (1.37) C34 - Fe2 - C35 - C40
-81.30 (2.21) C16 - Fe2 - C35 - C40
72.42 (1.70) C15 - Fe2 - C35 - C40
-45.75 (1.25) C18 - Fe2 - C35 - C40
-5.14 (1.02) C17 - Fe2 - C35 - C40
-151.22 (4.16) Cl2 - C101 - Cl11 - Cl12
-33.50 (4.63) Cl3_$4 - C101 - Cl11 - Cl12
0.00 (0.00) Cl12 - C101 - Cl11 - Cl12
0.00 (0.00) C101 - Cl11 - Cl12 - C101
32.86 (4.72) Cl2 - C101 - Cl12 - Cl11
0.00 (0.00) Cl11 - C101 - Cl12 - Cl11
150.71 (4.10) Cl3_$4 - C101 - Cl12 - Cl11

Least-squares planes (x,y,z in crystal coordinates) and deviations from them
(* indicates atom used to define plane)

0.522 (0.215) x + 6.913 (0.004) y + 0.637 (0.149) z = 3.404 (0.031)

* 0.014 (0.009) C4
* -0.022 (0.010) C5
* 0.021 (0.010) C6
* -0.001 (0.009) C7
* -0.012 (0.009) C8
1.666 (0.007) Fe1

Rms deviation of fitted atoms = 0.016

- 0.084 (0.228) x + 6.910 (0.005) y + 0.761 (0.150) z = 6.816 (0.033)

Angle to previous plane (with approximate esd) = 1.51 (0.10)

* -0.008 (0.010) C21
* 0.003 (0.010) C22
* 0.002 (0.010) C23
* -0.007 (0.010) C24
* 0.009 (0.010) C25
-1.647 (0.007) Fe1

Rms deviation of fitted atoms = 0.006

- 0.576 (0.253) x + 6.916 (0.004) y - 0.162 (0.161) z = 6.781 (0.065)

Angle to previous plane (with approximate esd) = 2.78 (0.09)

* 0.010 (0.011) C14
* -0.017 (0.011) C15
* 0.018 (0.011) C16
* 0.001 (0.011) C17
* -0.012 (0.011) C18
1.664 (0.008) Fe2

Rms deviation of fitted atoms = 0.013

0.427 (0.232) x + 6.916 (0.004) y + 0.149 (0.157) z = 10.073 (0.063)

Angle to previous plane (with approximate esd) = 2.00 (0.05)

* -0.012 (0.010) C31
* 0.007 (0.010) C32
* 0.000 (0.010) C33
* -0.007 (0.010) C34
* 0.012 (0.010) C35
-1.645 (0.008) Fe2

Rms deviation of fitted atoms = 0.009