

**1,3-Dipolar Cycloaddition to the Fe–N=C Fragment. 17.¹
Diastereoselectivity with C₂- and non-C₂-Symmetric
Chirally N-Substituted α -Diimine Ligands,
R*–N=C(H)–C(R')=N–R* and C₅H₄N-2-C(R')=N–R*, with
Dimethyl Acetylenedicarboxylate (DMAD) and Methyl
Propiolate (MP). Decomplexation of the Pyrrolinone
Ligand of Fe(CO)₃(pyrrolinone) Complexes**

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The 1,3-dipolar cycloaddition reaction of Fe[R*–DAB(H;H)](CO)₃ (**6k**; R*–DAB(H;H) = R*–N=C(H)–C(H)=N–R*) with dimethyl acetylenedicarboxylate (DMAD), in which the R*–DAB(H;H) ligand is C₂-symmetric and is chirally N-substituted, gives the two expected diastereomers with low diastereoselectivity, due to a small difference in the rate constants of the two reactive C=N groups in **6k** exposing their *re* and *si* faces, respectively. The 1,3-dipolar cycloaddition reaction of Fe(α -diimine)(CO)₃ (**1**, **6m**) with DMAD and methyl propiolate (MP), in which a non-C₂-symmetric α -diimine ligand (R*–DAB(H;Me) and Py-2-C(R')=N–R* (R*, R'–PyCa) is chirally N-substituted, gives the two expected diastereomers with medium to high diastereoselectivity. The diastereoselectivity with the non-C₂-symmetric α -diimine ligands, which have only one reactive imino group, depends on the size of the chiral group R*, the distance of the chiral group to the reacting centers, and the type of dipolarophile. The two starting complexes (**1** and **6m**) exist in solution in the form of two rapidly interconverting diastereomeric conformers I and II. In contrast to the C₂-symmetric case, the free energies of activation for the two different conformers and their respective concentrations may be quite different here. The diastereoselectivities could not be influenced by variation of temperature, solvent, or the additional ligand. Kinetic resolution by a cycloreversion reaction could be excluded by the use of a chiral additional ligand and an achiral α -diimine ligand (*i*-Pr, H-PyCa, or *i*-Pr–DAB(H; H)). X-ray crystal structures have been determined from the respective diastereomeric mixtures of the pyrrolinone complex **5cks** and the [2.2.2] bicyclic product **7aks**. The structures of the [2.2.2] bicyclic product **4aks** and of the free pyrrolinone ligand **8als** have been determined using diastereomerically pure products. The 5-(2-pyridyl)pyrrolin-2-one ligands **8** are decomplexed from their precursors **5** by Me₃NO, air oxidation, exchange by CO, and oxidative reactions with dihalogens or H₂O₂.

Introduction

The development of highly efficient and diastereoselective asymmetric cycloaddition reactions, e.g. Diels–Alder reactions, for the construction of chiral intermediates in synthetic organic chemistry has attracted

considerable synthetic effort in the last decades.² Organotransition-metal complexes tuned with the right ligand system are very useful, because of their significant impact on synthetic organic chemistry and their applications in the area of asymmetric induction. In the production of chiral products, e.g., in the synthesis of natural products as alkaloids, the Fe(CO)₃ group has

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(1) Part 16: Feiken, N.; Frühauf, H.-W.; Vrieze, K.; Veldman, N.; Spek, A. L. *J. Organomet. Chem.*, in press.

(2) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876.

been shown to be very useful in controlling the regio- and stereochemistry of, e.g., nucleophilic addition.³

The 1,4-diaza 1,3-diene ligand system, represented by R*-DAB(H;R'),⁴ R*,R'-PyCa,⁴ bipyridine, and 1,10-phenanthroline, with its good σ -donor and π -acceptor properties and its versatile coordination behavior, has long been known to stabilize a wide variety of transition metals in low oxidation states.⁵ In catalytic systems it is particularly useful for the ease with which it can be tailored with respect to its electronic and steric properties and the rigidity^{5d,e} or flexibility of its N=C–C=N backbone.⁵ In addition, the ready availability of the diaza dienes makes them attractive as reactive building blocks for organic syntheses, e.g., for the formation of nitrogen heterocycles in the coordination sphere of the metal.

Over the last decade much research has been carried out in our laboratory on the 1,3-dipolar cycloaddition reactions of mononuclear M(R-DAB)(CO)_{3-n}(R'-NC)_n (M = Fe, Ru, Mn; n = 0, 1, 3) complexes with unsaturated substrates.⁶

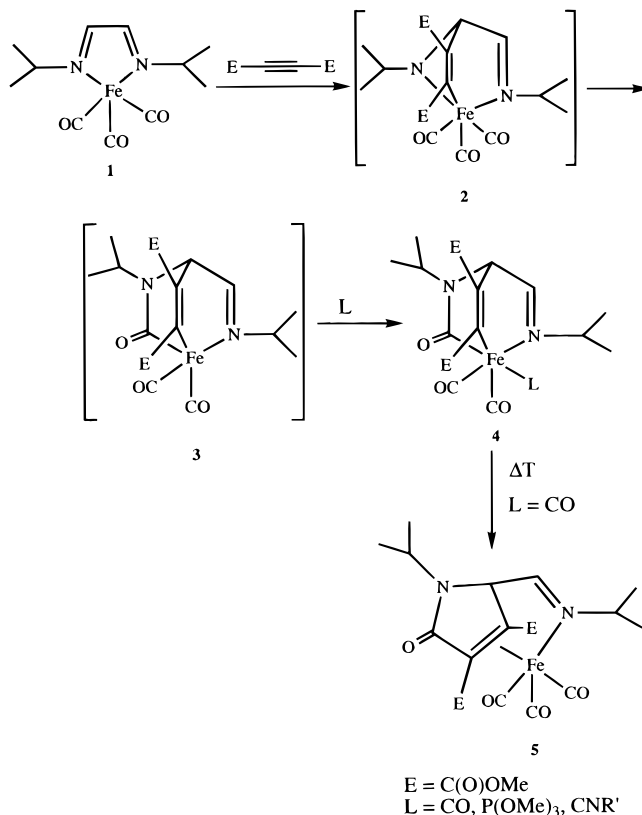
As was demonstrated in previous parts of this series of articles,^{1,6} the product formation, for the type of reactions shown in Scheme 1, is dependent on the coligands, additional ligands (L), the metal, and the substitutional pattern of both the DAB ligand and the dipolarophile.

In the first step of this reaction sequence, a prochiral sp²-hybridized imine carbon atom is converted in an oxidative 1,3-dipolar cycloaddition reaction to a chiral sp³-hybridized amino carbon atom. Under achiral reaction conditions, the two expected enantiomers are formed with equal probability. The isomer ratio may differ from 1:1 if the conversion of the prochiral carbon atom is done under chiral conditions. In the present paper we report on the diastereoselectivity with C₂- and non-C₂-symmetric chirally N-substituted α -diimine ligands.

Results and Discussion

General Considerations. The employed ligands and complexes are shown in Scheme 2. The type of complex is identified by Arabic numbers. The different

Scheme 1. Reaction Steps in the Cycloaddition of DMAD to the Fe–N=C Fragment in Complexes Fe(CO)₃(iPr-DAB)



chiral N-substituents in the α -diimine ligands are differentiated by the letters **a–d**, and the R' groups are denoted by the letters **k–m**, whereas the complexes formed in the reaction with MP or DMAD bear the letters **r** and **s**, respectively. The combination **ik** stands for (S)-phenylethyl isocyanide as the additional ligand and *i*-Pr, H-PyCa, or *i*-Pr-DAB(H; H) as the (achiral) α -diimine ligand.

If, in the text, one or more letters are omitted in a compound number, e.g., **4ks** or **5r** (vide infra), we refer to that compound type with all combinations of the omitted letter; i.e., **4ks** denotes the respective [2.2.2] bicyclic complexes with all four different chiral groups **a–d**, and **5r** refers to all the pyrrolinone complexes **5** derived from methyl propiolate (**r**) as dipolarophile.

Reactivity, Regioselectivity, and Chemoselectivity. The 1,3-dipolar cycloaddition reactions of the present chiral Fe(α -diimine)(CO)₃ complexes with DMAD or MP under an atmosphere of CO, or in the presence of another additional ligand L, lead in a HOMO-controlled (type I)⁷ oxidative cycloaddition reaction to the [2.2.1] bicyclic intermediate **2**. From this intermediate the [2.2.2] bicyclic compounds of type **4** or **7** are formed via insertion of one of the coordinated CO ligands and an uptake of 1 equiv of L.

Depending on the dipolarophile used and the substituent on the imine carbon atom (R') of the R*,R'-PyCa ligands, the [2.2.2] bicyclic complexes **4** may or may not be isolable. In the latter case the first observable products are the pyrrolinone complexes **5**. With MP as

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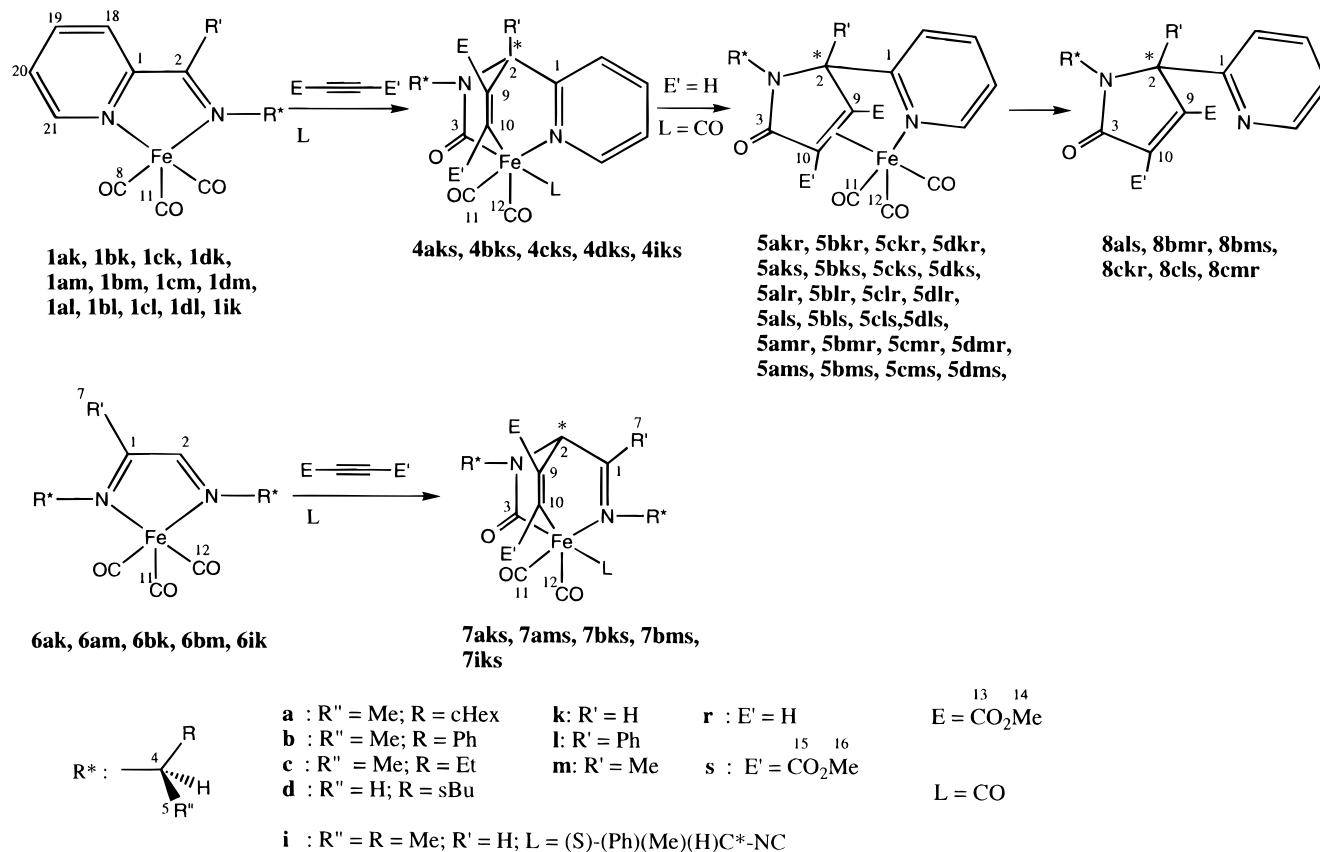
(3) (a) Pearson, A. J. *Pure Appl. Chem.* **1983**, *55*, 1767. (b) Pearson, A. J.; Ray, T. *Tetrahedron* **1985**, *41*, 5765.

(4) The 1,4-diaza-1,3-butadienes of formula R*-N=C(H)-C-(R')=N-R* are abbreviated as R*-DAB(H;R'). R*,R'-PyCa stands for Py-2-C(R')=N-R* (Py = C₅H₄N); DMAD and MP stand for dimethyl acetylenedicarboxylate and methyl propiolate, respectively.

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Scheme 2. 1,3-Cycloaddition Reactions of DMAD and MP to Chiral (α -diimine)Fe(CO)₃ Complexes and Atom Numbering for NMR Assignments^a



^a The numbers of all compounds are given that appear in the text or in tables.

dipolarophile the first observed products, in a slow reaction, are the Fe(pyrrolinone)(CO)₃ complexes **5r**. However, with R' = H and DMAD as dipolarophile, the first stable products are the Fe(CO)₃[[2.2.2]bic] complexes **4ks**. The cycloaddition reaction with MP has a higher energy barrier for the formation of the initial [2.2.1] bicyclic complex **2**. The reductive elimination from the [2.2.2] bicyclic compounds **4** to the Fe(pyrrolinone)(CO)₃ complexes **5** probably has a lower activation barrier for the MP reactions than for the DMAD reactions (with R' = H). With R' = Ph or Me, independent of the dipolarophile, the first observed and isolable products are the Fe(pyrrolinone)(CO)₃ complexes **5l,m**, respectively.

The isolated [2.2.2] bicyclic complexes **4ks** can be converted to the corresponding Fe(pyrrolinone)(CO)₃ complexes **5ks** after several hours under 50 bar of CO pressure at elevated temperatures. However, attempts to convert the [2.2.2] bicyclic compounds **7s** with L = CO to the corresponding pyrrolinone complexes of type **5** by stirring a solution of **7s** in a suitable solvent were not successful. Even under high CO pressure and at high temperatures, no conversion to complexes of type **5** could be observed. In earlier papers we reported^{6a} that the pyrrolinone complexes are easily obtained by stirring the [2.2.2] bicyclic compounds in e.g. chloroform or benzene with some silica gel. It appears that the steric bulk of the chiral R* groups of the DAB ligands somehow impedes the rearrangement of **7s** into complexes of type **5**.

As has been described earlier, cycloaddition reactions with MP as dipolarophile show complete regio-

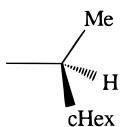
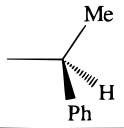
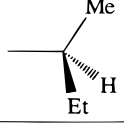
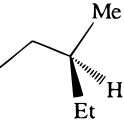
selectivity;^{6b} i.e., the unsubstituted acetylenic carbon atom of MP becomes exclusively bonded to the iron atom, and in the present case a single set of two diastereomers is formed. The cycloaddition reaction of DMAD and **6m** shows a complete chemoselectivity^{6b} for the unsubstituted C=N group of the R*-DAB(H;Me) ligand in **6m**. The reactions were carried out at a temperature range of -40 to +20 °C in different solvents, but a dependence of the diastereomeric ratio on the temperature or the solvent could not be observed.

In view of the Sustmann classification⁷ it is expected that, for type I cycloaddition reactions, electron-donating substituents on the 1,3-dipole will increase its reactivity. However, with the Me group on the imine carbon atom of the R*,R'-PyCa ligand (R' = Me) no acceleration of the cycloaddition reaction was observed. This lack of acceleration can be explained by steric hindrance for the incoming dipolarophile, reducing the reaction rate. The reaction rate in the case of R' = Ph is lowered as expected, because the HOMO level of the 1,3-dipole is lowered. Also, the reactions with MP are slower than with DMAD, because there is only one electron-withdrawing group present, and therefore the LUMO level of the dipolarophile is at higher energy.

Decomplexation of the Pyrrolinone Ligand. Several methods are available to liberate organic ligands from their (transition) metal complexes.⁸ We tested

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Table 1. Diastereomeric Ratios Obtained with DMAD and MP as Dipolarophiles in Cycloaddition Reactions with Fe(CO)₃(R*,R'-PyCa)

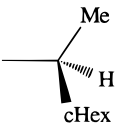
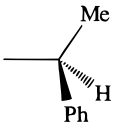
R*	R'	diastereomeric ratios			
		compd. nr.	DMAD	compd. nr.	MP
	H	4aks	100:0	5akr	75:25
	Me	5ams	88:12	5amr	91:9
	Ph	5als	98:2	5alr	---
	H	4bks	93:7	5bkr	66:34
	Me	5bms	60:40	5bmr	74:26
	Ph	5bls	88:12	5blr	75:25
	H	4cks	62:38	5ckr	65:35
	Me	5cms	58:42	5cmr	61:39
	Ph	5cls	72:28	5clr	63:37
	H	4dks	51:49	5dkr	50:50
	Me	5dms	50:50	5dmr	50:50
	Ph	5dls	50:50	5dlr	51:49

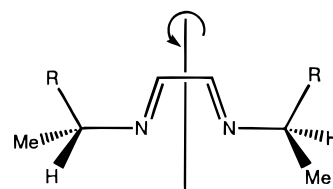
some oxidative methods and one ligand exchange method. In the oxidative methods, complexes **5l,m** were treated with I₂, Cl₂, H₂O₂, or air; also, the reaction with Me₃NO was successful. Oxidative degradation when solutions of **5** were stirred in air (with formation of iron oxides) gave the best results, and for complexes with R' = H it was the only useful method. Displacement of the pyrrolinone ligand by CO with formation of Fe(CO)₅ was successful for complexes **5l** and **5m**, with only moderate yields, however.

Diastereoselectivity. The introduction of a chiral N-substituent in the α-diimine ligand in the starting compounds **1** and **6** induces diastereoselectivity in our organometal cycloaddition reactions. The chiral α-diimine ligands are derived from chiral amines and 2-pyridinecarbaldehyde or (methyl) glyoxal. Some of these Schiff base ligands have been used earlier⁹ in order to study the optically active transition-metal compounds after complexation of these ligands. The R*,R'-PyCa ligands have been used in rhodium catalysts in the enantioselective hydrosilylation of acetophenone to give 1-phenylethanol in high optical yields.^{9b} The diastereoselectivities obtained with these ligands in the present cycloaddition reactions with DMAD and MP are summarized in Tables 1 and 2.

From Tables 1 and 2 it appears that the diastereoselectivity depends on the following: (1) the size of the chiral group R*, (cHex)(Me)(H)C* > (Ph)(Me)(H)C* > (Et)(Me)(H)C*; (2) the distance of the chiral center to the reacting centers, (Et)(Me)(H)C* > (Et)(Me)(H)C*CH₂; (3) the type of dipolarophile, DMAD > MP; (4)

Table 2. Diastereomeric Ratios Obtained with DMAD as Dipolarophile in the Cycloaddition Reactions with Fe(CO)₃[R*-DAB(H, R')]

R*	R'	diastereomeric ratios	
		compd. nr.	DMAD
	H	7aks	64:36
	Me	7ams	95:5
	H	7bks	62:38
	Me	7bms	90:10

**Figure 1.** C₂-Symmetric R*-DAB ligand.

the R' group (for the chiral R*,R'-PyCa ligand and DMAD, H > Ph > Me; for R*-DAB(H;R'), Me > H).

During the reductive elimination of the [2.2.2] bicyclic complexes **4ks** to the pyrrolinone complexes **5ks** the diastereomeric ratio remains unchanged. This means that the diastereomeric ratios in the different isolated products can be directly compared with each other. In the case of **4bks**, the two diastereomers have sufficiently different *R_f* values, and it was possible to separate the two diastereomers by column chromatography on a small column, by an appropriate selection of eluents.

The diastereoselectivity of the described cycloaddition reactions was found to be independent of the temperature and of the polarity of the solvent (CH₃CN, toluene, THF, hexane). The diastereoselectivities with complexes **1** and **6m** are much higher than those with complexes **6k**. In **1** and **6m** the α-diimine ligand is non-C₂-symmetric, whereas in **6k** it is C₂-symmetric. In the following the differences between these two types with respect to the diastereoselectivity will be discussed.

(a) The C₂-Symmetric Case. The R*-DAB(H;H) ligands are C₂-symmetric (see Figure 1), because the same chiral group is bonded to both nitrogen atoms of the symmetrical DAB skeleton. In a square-pyramidal coordination geometry, as depicted in Figure 2 for the complex Fe[R*-DAB(H;H)](CO)₃ (**6k**), a rotation of the R*-DAB ligand through 180° around its C₂ axis (see Figure 1) delivers an identical situation; i.e., there is only one stereochemical form possible, and the iron atom is not a chiral center.

When a dipolarophile approaches the square pyramid in the C₂-symmetric case (see Figure 2) from below, it encounters the *re* face of one and the *si* face of the other imino group in **6k**. Attack of the *re* face of **6k** gives a different diastereomer (**7k** or **7k'**) than attack of the *si* face of **6k**, which gives the other diastereomer (**7k'** or **7k**). The *si* and *re* face of **6k** have very similar reactivities, and the diastereomeric ratio is therefore caused by a small difference of the rate constants of attack at the *re* and *si* faces. We found that the

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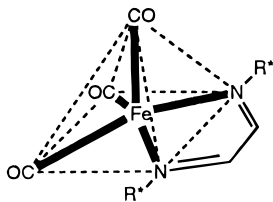


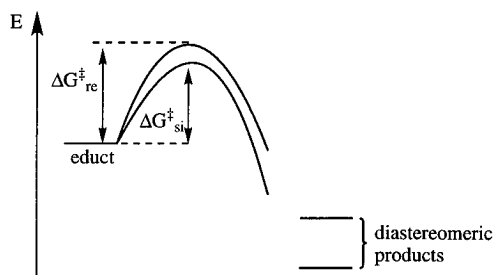
Figure 2. Square-pyramidal intermediate in the Berry pseudorotation process with a C_2 -symmetric α -diimine ligand. Of the two reactive imine groups, one exposes its *re* face and the other its *si* face toward an incoming dipolarophile.

diastereoselectivities in these cases are rather low (cf. Table 2). Possible reaction profiles are shown in Figure

3, where the free energy of the system (vertical axis) is set out against the reaction coordinate.

From the low observed diastereoselectivity with the C_2 -symmetric diaza dienes, we have to conclude that the free energies of activation ΔG^\ddagger are of comparable size for an attack of the dipolarophile on one or the other C=N group, which exposes the *re* and *si* faces, respectively; i.e., $\Delta G^\ddagger_{re} \approx \Delta G^\ddagger_{si}$. We have to emphasize that there is only one 1,3-dipolar species present which at the same time exposes reactive *re* and *si* faces. The rates at which the two diastereomeric products are formed depend only on the concentrations of the two transition states (proportional to ΔG^\ddagger_{re} and ΔG^\ddagger_{si}), since the concentrations of the two reactive sites are inher-

a) C_2 -symmetric α -diimine ligands



b) non- C_2 -symmetric α -diimine ligands

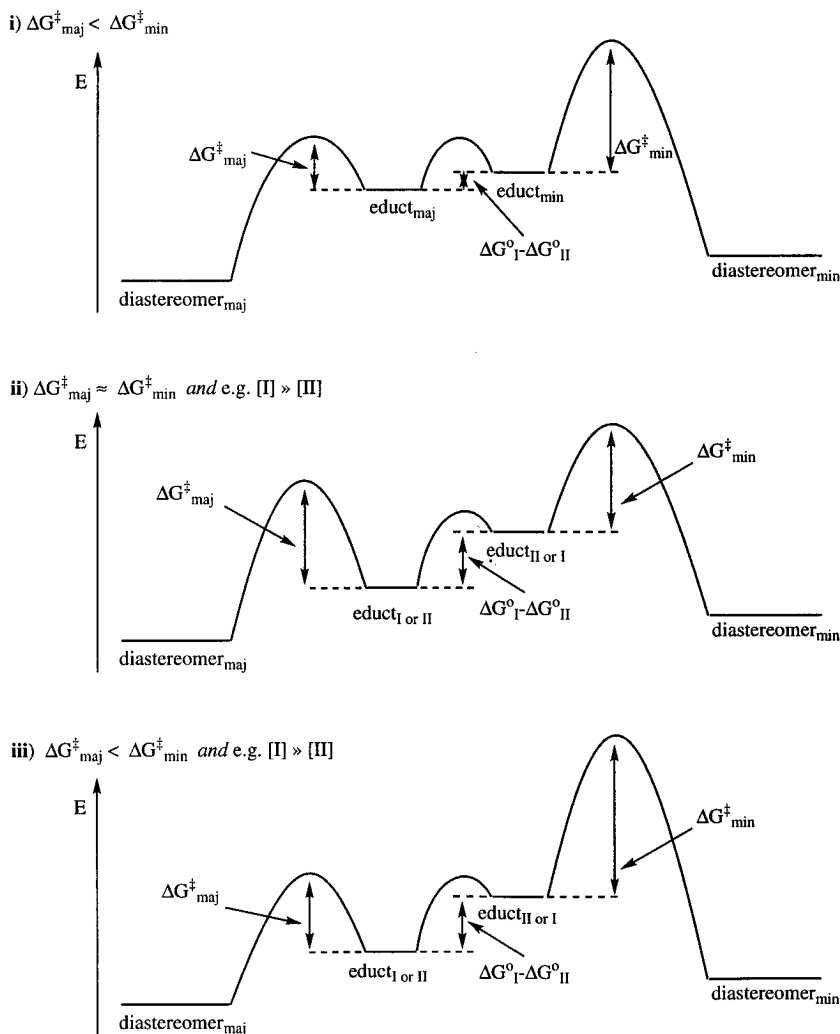


Figure 3. Reaction profiles for the reactions with the C_2 and the non- C_2 α -diimine ligands.

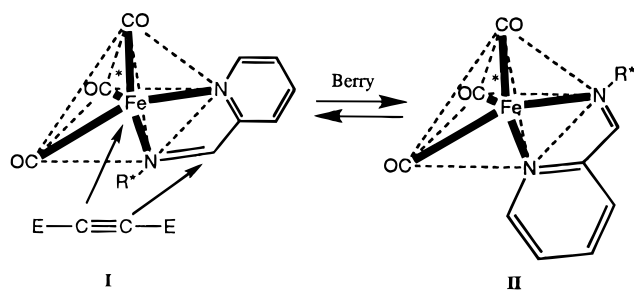


Figure 4. The starting diastereomeric conformers in complexes **1** and **6m** with non- C_2 -symmetric α -diimine ligands. Of the two rapidly interconverting conformers, one exposes the *re* face of the reactive imine group and the other the *si* face toward an incoming dipolarophile.

ently equal. The bulkiness of the R^* group influences the accessibility of the dipolarophile to the dipole. This implies that one of the stereofaces reacts faster than the other.

(b) The Non- C_2 -Symmetric Case. There is an obvious difference in the diastereoselectivity with the C_2 - and non- C_2 -symmetric diaza diene ligand systems. The achievable diastereoselectivities in the cycloaddition reactions of complexes **1** and **6m** are much higher than those with the chiral C_2 -symmetric α -diimines. With the non- C_2 -symmetric α -diimine ligands in **1** and **6m**, which have only one reactive imino group in each starting epimer, the central iron atom is also chiral, and the starting complexes **1** and **6m** exist in the form of two (via Berry pseudorotation¹⁰) very rapidly equilibrating epimers (with opposite configurations at the iron atom) and are present in different stationary concentrations according to their difference in free energy $\Delta G^\circ_{\text{I}} - \Delta G^\circ_{\text{II}}$. In Figure 4 the epimers **I** and **II** are drawn in the square-pyramidal conformation, which we think is attacked by the dipolarophile from below.

One of the epimers exposes the *re* face of the reactive imine-carbon atom, while the other exposes its *si* face. In such chiral complexes with unsymmetrical diaza diene skeletons the two Fe–N=C fragments are inherently chemically different and the attacking dipolarophile in a 1,3-dipolar cycloaddition reaction has a strong chemoselectivity;^{6b} i.e., only the unsubstituted α -diimine group is reactive. Unfortunately, we cannot conclusively explain the high diastereoselectivities in this case. As opposed to the C_2 -symmetric case, the free energies of activation and the concentrations of the two different diastereomeric 1,3-dipolar species **I** and **II** may be quite different here. Any of three cases may prevail. (i) The major (or only) diastereomer of the product is produced at a (much) faster rate because the activation energy $\Delta G^\ddagger_{\text{maj}}$ is much lower than $\Delta G^\ddagger_{\text{min}}$. Then any stationary concentration difference is overruled and rendered unimportant. (ii) $\Delta G^\ddagger_{\text{maj}}$ and $\Delta G^\ddagger_{\text{min}}$ are of comparable size, but **I** and **II** are present in very different stationary concentrations. This would mean that the diastereoselectivity is governed by thermodynamics, namely $\Delta G^\circ_{\text{I}} - \Delta G^\circ_{\text{II}}$. (iii) Both a low activation energy and a high stationary concentration work together, e.g. $\Delta G^\ddagger_{\text{maj}} < \Delta G^\ddagger_{\text{min}}$ and $[\text{I}] \gg [\text{II}]$ (cf. Figure 3).

The Berry pseudorotation in **1** and **6** is too fast to observe the two diastereomers separately on the NMR time scale, even at the lowest possible temperatures.

Table 1 shows different diastereoselectivities for the reaction of specific PyCa complexes (combinations of R^* and R') with the two dipolarophiles DMAD and MP. If the diastereomer ratio (dr) in the products only depends on the equilibrium position of the epimers **I** and **II** in the starting complexes (case ii, vide supra), then we should observe the same dr's independent of the dipolarophile. From the different dr's with the two dipolarophiles we can conclude that they react at different rates with **I** and **II**; i.e., there is definitely a (small) kinetic bias between the *re* and *si* faces, and the observed dr's are not a measure for the equilibrium position $\text{I} \rightleftharpoons \text{II}$.

There are strong steric interactions between the syn-positioned C- and N-substituents of an imine group (R^* and R');¹¹ i.e., R' influences the conformation of R^* , which in turn is reflected by differing dr's for $R' = \text{H}, \text{Me}, \text{Ph}$. In the cycloaddition reactions with DMAD, the lowest diastereoselectivities are observed for $R' = \text{Me}$.

The reaction of achiral Fe(α -diimine)(CO)₃ (**1k** and **6ik**) with DMAD in the presence of a chiral additional ligand L gives the two expected diastereomers (**4iks** and **7iks**, respectively) in a ratio of 1:1. Thus, at least under the employed reaction conditions, the reversibility of the cycloaddition reaction and consequent kinetic resolution can be excluded. Obviously the activation barrier for the retro-cycloaddition reaction is too high. This activation barrier may vary when other dipolarophiles and ligands other than CO are employed in the starting compound **6k**, which we have described earlier.^{6e,g} Variation of the additional ligands L has no effect on the diastereoselectivity of the cycloaddition reactions, which is shown for the reaction of **1k** and **6** with DMAD in the presence of P(OMe)₃ and *t*-Bu-NC instead of CO. This is not surprising, because the additional ligand reacts after the cycloaddition step with the unsaturated [2.2.2] bicyclic intermediate **3** to give **4**.

In all the cycloaddition reactions described in this paper, we find no solvent or temperature effects on the diastereoselectivity of the reaction. It is not very surprising that the solvent polarity does not influence the diastereoselectivity of the cycloaddition reaction, because the two transition states resulting from attack of either the *re* or *si* face cannot possess very different polarities. In the non- C_2 -symmetric case the temperature should influence the equilibrium between **I** and **II**, and thus, if case ii applies, also the diastereoselectivity. However, in the relatively small temperature range in which the reaction can be run ($238 \text{ K} \leq T \leq 298 \text{ K}$), we did not find such an effect.

Crystal Structure of the Complex 4aks. The molecular structure of complex **4aks** together with the atomic numbering is shown in Figure 5. Bond lengths and bond angles are given in Tables 3 and 4, respectively.

The reaction leading to **4aks** is highly diastereoselective (100:0), giving only one diastereomer (cf. Table 1). The configuration of the former prochiral imine carbon atoms C(14) and C(7) of the R^* group is *S*. The configuration of the chiral iron atom is OC-6-24-C, according to the Baird–Cook–Sloan modification of the

(10) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

(11) Frühauf, H.-W.; Breuer, J. *J. Organomet. Chem.* **1986**, *301*, 183.

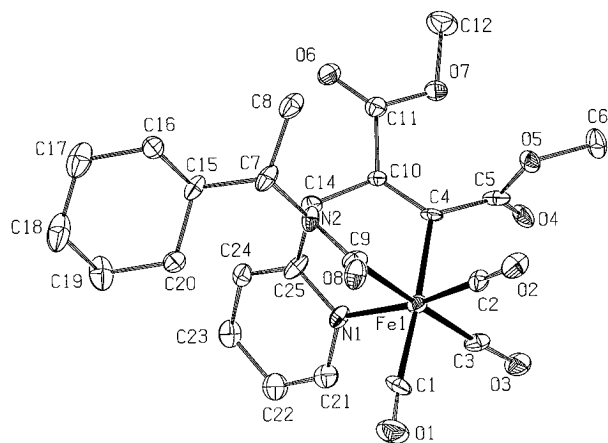


Figure 5. ORTEP plot of **4aks** at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 3. Bond Distances (Å) of the Non-Hydrogen Atoms of Complex 4aks (Esd's in Parentheses)

Fe(1)–N(1)	2.023(12)	N(2)–C(9)	1.338(18)
Fe(1)–C(1)	1.870(15)	N(2)–C(14)	1.464(17)
Fe(1)–C(2)	1.792(15)	C(4)–C(5)	1.409(18)
Fe(1)–C(3)	1.851(13)	C(4)–C(10)	1.348(18)
Fe(1)–C(4)	2.001(13)	C(7)–C(8)	1.53(2)
Fe(1)–C(9)	2.028(13)	C(7)–C(15)	1.51(2)
O(1)–C(1)	1.108(19)	C(10)–C(11)	1.551(19)
O(2)–C(2)	1.120(19)	C(10)–C(14)	1.500(18)
O(3)–C(3)	1.142(16)	C(14)–C(25)	1.501(19)
O(4)–C(5)	1.233(15)	C(15)–C(16)	1.52(2)
O(5)–C(5)	1.365(17)	C(15)–C(20)	1.53(2)
O(6)–C(11)	1.172(17)	C(16)–C(17)	1.53(3)
O(7)–C(11)	1.322(17)	C(17)–C(18)	1.50(3)
O(8)–C(9)	1.244(18)	C(18)–C(19)	1.53(2)
N(1)–C(21)	1.354(18)	C(19)–C(20)	1.53(3)
N(1)–C(25)	1.356(17)	C(21)–C(22)	1.33(2)
N(2)–C(7)	1.485(15)	C(22)–C(23)	1.39(2)
		C(23)–C(24)	1.38(2)
		C(24)–C(25)	1.35(2)

CIP rules.¹² The total configuration of **4aks** as shown in Figure 5 is *OC*-6-24-*C*-(*S*),(*S*).

The molecular structure of complex **4aks** has the familiar [2.2.2] bicyclic skeleton that has been found earlier.^{6e–g} The geometry around the metal atom is slightly distorted octahedral. The mean angles around the chiral atom C(14) (110°) are characteristic for sp^3 hybridization.

Crystal Structure of the Complex 5cks. The molecular structure of the complex **5cks** together with the atomic numbering is shown in Figure 6. Bond lengths and bond angles are given in Tables 5 and 6, respectively.

From the data set it is not clear if the given structure, shown in Figure 6, represents the major diastereomer. The diastereomeric ratio (62:38) found in the bulk of the crystals by ¹H NMR is the same as in the crude reaction mixture of **5cks**. This means that no fractional crystallization of one of the diastereomers had occurred. Molecules of **5cks** contain two rings, which coordinate to the iron atom via the nitrogen atom (N(1)) of the pyridine ring and via the C(7)–C(8) double bond of the pyrrolinone ring. The two rings are connected by the chiral former imine carbon atom C(6). The configuration of both chiral carbon atoms C(6) and C(14) is *S*.

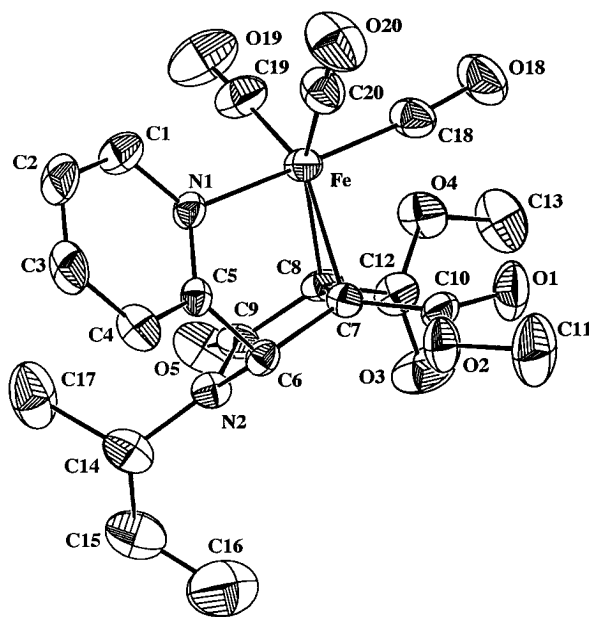


Figure 6. ORTEP plot of **5cks** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 4. Bond Angles (deg) of the Non-Hydrogen Atoms of Complex 4aks (Esd's in Parentheses)

N(1)–Fe(1)–C(1)	91.2(6)	O(4)–C(5)–O(5)	121.2(12)
N(1)–Fe(1)–C(2)	169.9(5)	O(4)–C(5)–C(4)	126.8(13)
N(1)–Fe(1)–C(3)	93.7(5)	O(5)–C(5)–C(4)	111.8(10)
N(1)–Fe(1)–C(4)	88.5(5)	N(2)–C(7)–C(8)	108.4(13)
N(1)–Fe(1)–C(9)	88.1(5)	N(2)–C(7)–C(15)	114.2(11)
C(1)–Fe(1)–C(2)	92.7(7)	C(8)–C(7)–C(15)	115.7(12)
C(1)–Fe(1)–C(3)	94.7(6)	Fe(1)–C(9)–O(8)	122.3(10)
C(1)–Fe(1)–C(4)	174.6(5)	Fe(1)–C(9)–N(2)	116.7(9)
C(1)–Fe(1)–C(9)	86.2(6)	O(8)–C(9)–N(2)	120.9(12)
C(2)–Fe(1)–C(3)	95.2(6)	C(4)–C(10)–C(11)	125.6(12)
C(2)–Fe(1)–C(4)	86.7(6)	C(4)–C(10)–C(14)	119.1(11)
C(2)–Fe(1)–C(9)	82.9(6)	C(11)–C(10)–C(14)	115.3(11)
C(3)–Fe(1)–C(4)	90.8(5)	O(6)–C(11)–O(7)	125.5(14)
C(3)–Fe(1)–C(9)	178.0(6)	O(6)–C(11)–C(10)	124.6(13)
C(4)–Fe(1)–C(9)	88.3(5)	O(7)–C(11)–C(10)	109.9(11)
C(5)–O(5)–C(6)	116.4(11)	N(2)–C(14)–C(10)	111.7(12)
C(11)–O(7)–C(12)	114.5(12)	N(2)–C(14)–C(25)	110.2(11)
Fe(1)–N(1)–C(21)	123.6(10)	C(10)–C(14)–C(25)	109.2(10)
Fe(1)–N(1)–C(25)	119.2(9)	C(7)–C(15)–C(16)	110.1(12)
C(21)–N(1)–C(25)	117.1(12)	C(7)–C(15)–C(20)	112.1(13)
C(7)–N(2)–C(9)	123.0(11)	C(16)–C(15)–C(20)	110.2(13)
C(7)–N(2)–C(14)	117.5(11)	C(15)–C(16)–C(17)	110.9(13)
C(9)–N(2)–C(14)	118.8(10)	C(16)–C(17)–C(18)	114.7(15)
Fe(1)–C(1)–O(1)	172.1(15)	C(17)–C(18)–C(19)	111.3(16)
Fe(1)–C(2)–O(2)	177.3(13)	C(18)–C(19)–C(20)	110.2(14)
Fe(1)–C(3)–O(3)	174.3(13)	C(15)–C(20)–C(19)	112.7(13)
Fe(1)–C(4)–C(5)	118.2(9)	N(1)–C(21)–C(22)	124.7(15)
Fe(1)–C(4)–C(10)	116.2(9)	C(21)–C(22)–C(23)	118.6(15)
C(5)–C(4)–C(10)	125.2(12)	C(22)–C(23)–C(24)	117.4(14)
C(23)–C(24)–C(25)	121.4(13)	N(1)–C(25)–C(24)	120.8(13)
N(1)–C(25)–C(14)	114.9(12)	C(14)–C(25)–C(24)	124.2(12)

The configuration of the chiral iron atom is *TB*-5-12-*A*, according to the Baird–Cook–Sloan modification of the CIP rules.¹² The total configuration of the diastereomer given in Figure 6 is *TB*-5-12-*A*-(*S*),(*S*). The long bond distance of the olefinic carbon atoms C(7)–C(8) of 1.444(8) Å is caused by the coordination to $Fe(CO)_3$ and indicates partial rehybridization $sp^2 \rightarrow sp^3$ of the atoms.

Crystal Structure of the Complex 7aks. The crystal structure of complex **7aks** together with the atomic numbering is shown in Figure 7. Bond lengths and angles are given in Tables 7 and 8, respectively.

Molecules of **7aks** have a [2.2.2] bicyclic structure in which the bridgehead positions are occupied by the iron atom and the chiral former imine carbon atom (C(14)).

(12) (a) Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1975**, *14*, 1273. (b) Brown, M. F.; Cook, B. R.; Sloan, T. E. *Inorg. Chem.* **1975**, *14*, 1563. (c) *IUPAC Nomenclature of Inorganic Chemistry Recommendations 1990*; Blackwell Scientific Publications: Oxford, 1990.

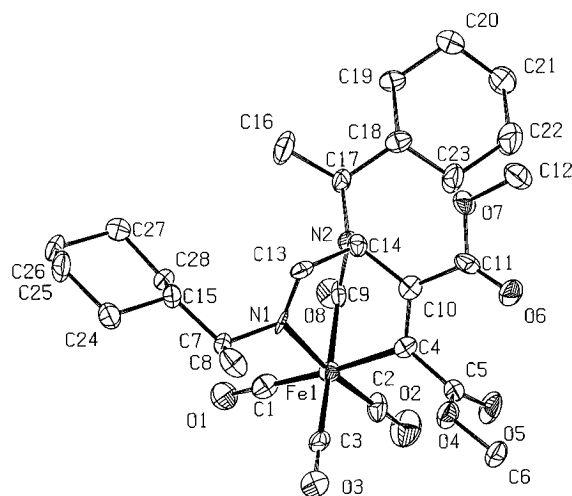


Figure 7. Molecular structure of complex 7aks.

Table 5. Bond Distances of the Non-Hydrogen Atoms (Å) of Complex 5cks (Esd's in Parentheses)

Fe–C(7)	2.033(6)	C(8)–C(12)	1.512(9)
Fe–C(8)	2.068(6)	C(9)–N(2)	1.367(8)
Fe–C(18)	1.778(7)	C(9)–O(5)	1.231(8)
Fe–C(19)	1.812(8)	C(10)–O(1)	1.209(9)
Fe–C(20)	1.808(8)	C(10)–O(2)	1.342(8)
Fe–N(1)	2.040(5)	C(11)–O(2)	1.451(1)
C(1)–C(2)	1.38(1)	C(12)–O(3)	1.214(9)
C(1)–N(1)	1.352(9)	C(12)–O(4)	1.312(8)
C(2)–C(3)	1.38(1)	C(13)–O(4)	1.46(1)
C(3)–C(4)	1.39(1)	C(14)–C(15)	1.51(1)
C(4)–C(5)	1.383(9)	C(14)–C(17)	1.60(1)
C(5)–C(6)	1.488(8)	C(14)–N(2)	1.455(9)
C(5)–N(1)	1.350(8)	C(15)–C(16)	1.46(2)
C(6)–C(7)	1.547(8)	C(18)–O(18)	1.140(9)
C(6)–N(2)	1.476(8)	C(19)–O(19)	1.15(1)
C(7)–C(8)	1.444(8)	C(20)–O(20)	1.13(1)
C(7)–C(10)	1.457(9)	C(1s)–Cl(1s)	1.73(2)
C(8)–C(9)	1.485(9)	C(1s)–Cl(2s)	1.65(2)

Table 6. Bond Angles (deg) of the Non-Hydrogen Atoms of Complex 5cks (Esd's in Parentheses)

C(7)–Fe–C(8)	41.2(2)	Fe–C(8)–C(7)	68.1(3)
C(7)–Fe–C(18)	98.0(3)	Fe–C(8)–C(9)	117.7(4)
C(7)–Fe–C(19)	137.8(3)	Fe–C(8)–C(12)	123.3(5)
C(7)–Fe–C(20)	114.1(3)	C(7)–C(8)–C(9)	108.9(5)
C(7)–Fe–N(1)	82.4(2)	C(7)–C(8)–C(12)	120.8(5)
C(8)–Fe–C(18)	91.6(3)	C(9)–C(8)–C(12)	111.1(5)
C(8)–Fe–C(19)	97.8(3)	C(8)–C(9)–N(2)	108.0(5)
C(8)–Fe–C(20)	154.2(3)	C(8)–C(9)–O(5)	25.5(6)
C(8)–Fe–N(1)	97.1(2)	N(2)–C(9)–O(5)	126.3(6)
C(18)–Fe–C(19)	91.2(4)	C(7)–C(10)–O(1)	124.7(6)
C(18)–Fe–C(20)	84.0(3)	C(7)–C(10)–O(2)	112.6(5)

The bond angles around C(14) are indicative of sp^3 hybridization. The coordination geometry around the iron atom is slightly distorted octahedral. Interesting to note is the extremely short intramolecular contact (3.080(11) Å) for C(13) to O(8), possibly indicating a weak $N=C-H\cdots O=C$ interaction. Similar examples of such short intramolecular contacts have been found in the literature.^{12,13}

The diastereomeric ratio found in the crude product mixture of 7aks is the same as that found in the bulk of the crystals, as was shown with 1H NMR, which means that no fractional crystallization of one of the diastereomers had occurred during the crystallization.

(13) Kulpe, S.; Seidel, I.; Geissler, G.; Tomaschewski, G. *Cryst. Res. Technol.* **1982**, *17*, 91.

(14) Miller, R. D.; Theis, W.; Heilig, G.; Kirchmeyer, S. *J. Org. Chem.* **1991**, *56*, 1453.

Table 7. Bond Distances (Å) for Compound 7aks

Fe(1)–N(1)	2.011(7)	C(4)–C(5)	1.454(11)
Fe(1)–C(1)	1.779(11)	C(4)–C(10)	1.344(12)
Fe(1)–C(2)	1.792(10)	C(7)–C(8)	1.544(13)
Fe(1)–C(3)	1.826(8)	C(7)–C(15)	1.525(11)
Fe(1)–C(4)	2.014(9)	C(10)–C(11)	1.496(12)
Fe(1)–C(9)	2.002(8)	C(10)–C(14)	1.531(13)
O(1)–C(1)	1.167(13)	C(13)–C(14)	1.483(12)
O(2)–C(2)	1.128(12)	C(15)–C(24)	1.539(12)
O(3)–C(3)	1.139(11)	C(15)–C(28)	1.524(13)
O(4)–C(5)	1.355(11)	C(16)–C(17)	1.557(14)
O(4)–C(6)	1.433(10)	C(17)–C(18)	1.500(13)
O(5)–C(5)	1.196(11)	C(18)–C(19)	1.552(12)
O(6)–C(11)	1.199(10)	C(18)–C(23)	1.500(13)
O(7)–C(11)	1.352(11)	C(19)–C(20)	1.518(13)
O(7)–C(12)	1.423(12)	C(20)–C(21)	1.504(16)
O(8)–C(9)	1.258(11)	C(21)–C(22)	1.547(14)
N(1)–C(7)	1.493(11)	C(22)–C(23)	1.511(13)
N(1)–C(13)	1.268(11)	C(24)–C(25)	1.524(14)
N(2)–C(9)	1.348(12)	C(25)–C(26)	1.531(15)
N(2)–C(14)	1.459(12)	C(26)–C(27)	1.547(13)
N(2)–C(17)	1.476(10)	C(27)–C(28)	1.517(13)

Table 8. Bond Angles (deg) for Compound 7aks

N(1)–Fe(1)–C(1)	92.7(4)	C(24)–C(25)–C(26)	112.1(9)
N(1)–Fe(1)–C(2)	172.6(4)	C(25)–C(26)–C(27)	110.9(8)
N(1)–Fe(1)–C(3)	90.7(4)	C(26)–C(27)–C(28)	110.4(8)
N(1)–Fe(1)–C(4)	88.9(3)	C(15)–C(28)–C(27)	112.7(8)
N(1)–Fe(1)–C(9)	87.4(3)	O(4)–C(5)–O(5)	124.0(7)
C(1)–Fe(1)–C(2)	90.4(5)	O(4)–C(5)–C(4)	110.7(7)
C(1)–Fe(1)–C(3)	94.5(4)	O(5)–C(5)–C(4)	124.8(8)
C(1)–Fe(1)–C(4)	173.0(4)	N(1)–C(7)–C(8)	108.7(7)
C(1)–Fe(1)–C(9)	85.5(4)	N(1)–C(7)–C(15)	110.8(7)
C(2)–Fe(1)–C(3)	95.8(4)	C(8)–C(7)–C(15)	114.3(7)
C(2)–Fe(1)–C(4)	87.3(4)	Fe(1)–C(9)–O(8)	122.3(6)
C(2)–Fe(1)–C(9)	86.2(4)	Fe(1)–C(9)–N(2)	117.5(6)
C(3)–Fe(1)–C(4)	92.4(4)	O(8)–C(9)–N(2)	120.0(7)
C(3)–Fe(1)–C(9)	178.0(4)	C(4)–C(10)–C(11)	120.8(8)
C(4)–Fe(1)–C(9)	87.7(3)	C(4)–C(10)–C(14)	117.9(8)
C(5)–O(4)–C(6)	114.3(7)	C(11)–C(10)–C(14)	121.2(7)
C(11)–O(7)–C(12)	113.9(7)	O(6)–C(11)–O(7)	122.8(8)
Fe(1)–N(1)–C(7)	122.5(5)	O(6)–C(11)–C(10)	125.8(8)
Fe(1)–N(1)–C(13)	118.9(6)	O(7)–C(11)–C(10)	111.4(7)
C(7)–N(1)–C(13)	118.5(7)	N(1)–C(13)–C(14)	118.9(8)
C(9)–N(2)–C(14)	117.8(7)	N(2)–C(14)–C(10)	110.0(7)
C(9)–N(2)–C(17)	122.9(8)	N(2)–C(14)–C(13)	110.1(7)
C(14)–N(2)–C(17)	118.6(7)	C(10)–C(14)–C(13)	108.6(7)
Fe(1)–C(1)–O(1)	176.0(10)	C(7)–C(15)–C(24)	113.7(7)
Fe(1)–C(2)–O(2)	176.9(9)	C(7)–C(15)–C(28)	111.4(7)
Fe(1)–C(3)–O(3)	177.9(8)	C(24)–C(15)–C(28)	108.9(7)
Fe(1)–C(4)–C(5)	122.3(6)	N(2)–C(17)–C(16)	110.1(7)
Fe(1)–C(4)–C(10)	116.6(6)	N(2)–C(17)–C(18)	112.4(7)
C(5)–C(4)–C(10)	121.1(8)	C(16)–C(17)–C(18)	114.7(8)
C(19)–C(20)–C(21)	110.3(8)	C(17)–C(18)–C(19)	110.8(7)
C(20)–C(21)–C(22)	110.5(10)	C(17)–C(18)–C(23)	111.3(8)
C(21)–C(22)–C(23)	110.8(8)	C(19)–C(18)–C(23)	109.7(8)
C(18)–C(23)–C(22)	112.8(9)	C(18)–C(19)–C(20)	113.6(7)
C(15)–C(24)–C(25)	111.7(8)		

In the molecular structure shown in Figure 7, the configuration of the chiral carbon atom C(14) is *R*, and the configuration of the iron atom is *OC-6-24-A*, according to the Baird–Cook–Sloan modification of the CIP rules.¹² The total configuration of this diastereomer is *OC-6-24-A-(R),(S),(S)*, in which the last two chirality symbols stand for the configuration of the chiral *R** groups of the *R**-DAB ligand.

Crystal Structure of the Compound 8als. A crystal structure determination was carried out for the organic compound 8als. Figure 8 gives the ORTEP representation and the atomic numbering. Bond lengths and angles are given in Tables 9 and 10, respectively.

A 1H NMR spectrum of the crystal batch, which was used for the structure determination, showed that this batch contained only one diastereomer! The diastereoselectivity of the cycloaddition reaction was 98:2. After

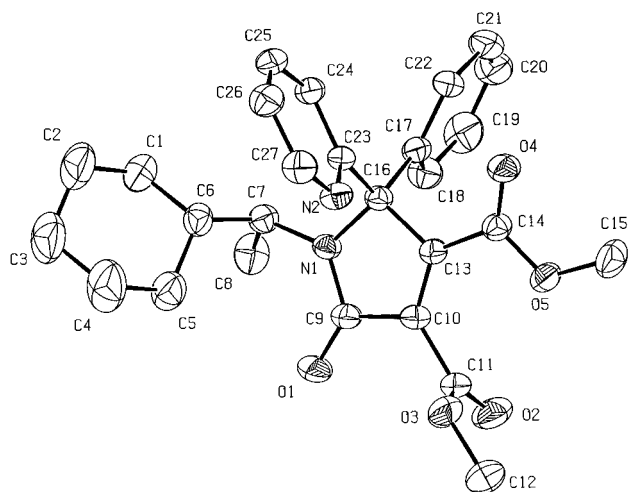


Figure 8. ORTEP plot of **8als** at the 30% probability level. Hydrogen atoms are omitted for clarity

Table 9. Bond Distances of the Non-Hydrogen Atoms (Å) of Complex **8als** (Esd's in Parentheses)

O(1)–C(9)	1.218(2)	C(7)–C(8)	1.532(3)
O(2)–C(11)	1.197(2)	C(9)–C(10)	1.484(2)
O(3)–C(11)	1.320(2)	C(10)–C(11)	1.492(2)
O(3)–C(12)	1.455(3)	C(10)–C(13)	1.328(2)
O(4)–C(14)	1.205(2)	C(13)–C(14)	1.482(2)
O(5)–C(14)	1.327(2)	C(13)–C(16)	1.524(2)
O(5)–C(15)	1.442(3)	C(16)–C(17)	1.534(2)
N(1)–C(7)	1.473(2)	C(16)–C(23)	1.5315(19)
N(1)–C(9)	1.368(2)	C(17)–C(18)	1.384(2)
N(1)–C(16)	1.4821(18)	C(17)–C(22)	1.394(2)
N(2)–C(23)	1.3387(18)	C(18)–C(19)	1.378(3)
N(2)–C(27)	1.338(2)	C(19)–C(20)	1.372(4)
C(1)–C(2)	1.516(4)	C(20)–C(21)	1.370(3)
C(1)–C(6)	1.530(3)	C(21)–C(22)	1.384(3)
C(2)–C(3)	1.483(5)	C(23)–C(24)	1.381(2)
C(3)–C(4)	1.537(5)	C(24)–C(25)	1.387(2)
C(4)–C(5)	1.518(4)	C(25)–C(26)	1.368(3)
C(5)–C(6)	1.485(3)	C(26)–C(27)	1.378(3)
C(6)–C(7)	1.532(2)		

Table 10. Bond Angles (deg) of the Non-Hydrogen Atoms of Complex **8als** (Esd's in Parentheses)

C(11)–O(3)–C(12)	115.77(16)	C(18)–C(17)–C(22)	117.86(14)
C(10)–C(13)–C(16)	110.54(13)	N(1)–C(7)–C(6)	112.83(13)
C(14)–O(5)–C(15)	116.57(15)	C(17)–C(18)–C(19)	121.43(18)
C(14)–C(13)–C(16)	121.07(12)	N(1)–C(7)–C(8)	112.25(15)
C(7)–N(1)–C(9)	126.50(13)	C(18)–C(19)–C(20)	120.2(2)
O(4)–C(14)–O(5)	124.18(15)	C(6)–C(7)–C(8)	113.60(15)
C(7)–N(1)–C(16)	121.36(11)	C(19)–C(20)–C(21)	119.3(2)
O(4)–C(14)–C(13)	124.46(15)	O(1)–C(9)–N(1)	127.53(15)
C(9)–N(1)–C(16)	112.12(12)	C(20)–C(21)–C(22)	121.04(19)
O(5)–C(14)–C(13)	111.36(14)	O(1)–C(9)–C(10)	126.06(15)
C(23)–N(2)–C(27)	117.51(13)	C(17)–C(22)–C(21)	120.15(16)
N(1)–C(16)–C(13)	101.09(10)	N(1)–C(9)–C(10)	106.41(13)
C(2)–C(1)–C(6)	111.5(3)	N(2)–C(23)–C(16)	114.15(11)
N(1)–C(16)–C(17)	111.54(11)	C(9)–C(10)–C(11)	121.49(14)
C(1)–C(2)–C(3)	111.0(3)	N(2)–C(23)–C(24)	122.34(13)
N(1)–C(16)–C(23)	108.05(10)	C(9)–C(10)–C(13)	109.77(13)
C(2)–C(3)–C(4)	111.2(3)	C(16)–C(23)–C(24)	123.27(12)
C(13)–C(16)–C(17)	107.64(11)	C(11)–C(10)–C(13)	128.69(15)
C(3)–C(4)–C(5)	110.8(3)	C(23)–C(24)–C(25)	119.45(15)
C(13)–C(16)–C(23)	111.82(11)	O(2)–C(11)–O(3)	124.91(17)
C(4)–C(5)–C(6)	111.7(2)	C(24)–C(25)–C(26)	118.25(17)
C(17)–C(16)–C(23)	115.74(11)	O(2)–C(11)–C(10)	123.86(17)
C(1)–C(6)–C(5)	109.35(18)	C(25)–C(26)–C(27)	119.13(17)
C(16)–C(17)–C(18)	120.75(13)	O(3)–C(11)–C(10)	111.22(15)
C(1)–C(6)–C(7)	110.97(16)	N(2)–C(27)–C(26)	123.31(16)
C(16)–C(17)–C(22)	121.19(13)	C(10)–C(13)–C(14)	128.34(14)
C(5)–C(6)–C(7)	116.14(17)		

crystallization only one was present. However, it was not possible to distinguish which diastereomer (*SR* or *RS*) was present in the single-crystal X-ray determina-

tion, due to the absence of heavy atoms and the presence of a solvent area for which no discrete model could be refined. The known configuration of C(7) of the R* group, however, is *S*. The configuration of the new chiral carbon atom (C(16)) is thus *R*.

The unit cell in the crystal contains four voids with a volume and electron count one would expect for an ether molecule of solvation. The correct elemental analysis of **8als** (without solvent; cf. Table 16) has been done of a sample from the same batch as the structure determination; however, for homogeneity, it had been ground, which has obviously led to the evaporation of all solvent ether present in the crystals. Obviously the ether molecules sit very loosely in the lattice (disorder, easy evaporation) and therefore could not be refined.

The C(10)–C(13) distance of 1.328(2) Å is now in the normal range of free alkenes (ca. 1.34 Å). The crystal structure shows that H(6) of the cyclohexyl group is pointed toward the π -electron cloud of the pyridine ring. The anisotropy effect of the pyridine ring is reflected in the ^1H NMR spectrum of **8als** (vide infra).

NMR Spectroscopy. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR data for the complexes **1** and **6** are listed in Tables 11 and 12, respectively; those for complexes **4**, **5**, and **7** and for compound **8** are listed in Tables 13 and 14, respectively; the atom numbering for all complexes is given in Scheme 2.

^1H and ^{13}C NMR of **1 and **6**.** The spectra of complexes **1** and **6** show great resemblance to the spectra of the corresponding free ligands and to the earlier reported Fe(α -diimine)(CO) $_3$ complexes.^{6,15} For the diastereomeric mixtures of complexes **1** and **6m** only one set of ^1H resonances is observed. The ^{13}C NMR spectra show only one resonance for the CO ligands, indicative of scrambling of these ligands¹⁵ via a fast Berry pseudorotation process.¹⁰

^1H NMR of **4, **5**, **7**, and **8**.** Enantiomers under achiral conditions have identical NMR spectra. However, mixtures of two diastereomers as well as the two diastereomeric pairs of enantiomers do not give the same ^1H NMR spectra as, e.g., was observed for R* = (\pm)-*sec*-Bu. In that case four stereoisomers were formed in the cycloaddition reaction, i.e., two diastereomers and the two enantiomers of these diastereomers. Accordingly, ^1H and ^{13}NMR showed only two sets of signals, one set for *S,S* and *R,R* and the other set for *S,R* and *R,S*. For all compounds a sufficient separation of the resonances of the two diastereomers is found, which allows for an easy and reliable determination of the diastereomeric ratio.

The spectra of the complexes **4k** and **7** show the familiar pattern of a [2.2.2] bicyclic complex, which has also been observed for analogous compounds reported earlier.⁶ The spectra of compounds **5** and **8** very closely resemble those of the corresponding complexes **4**.

Figure 9 shows a part of the ^1H NMR spectrum of the crude reaction mixture of the reaction of **6b** and DMAD leading to **7bks** and **7'bk**s. The appearance of the crude spectrum in Figure 9 shows not only that the formation of **7** and **7'** is a very clean reaction but also that the two diastereomers, unprimed and primed assignments in Figure 9, show appreciable shift differences. This allows for an easy and reliable determina-

(15) Leibfritz, D.; tom Dieck, H. *J. Organomet. Chem.* **1976**, *105*, 255.

Table 11. ¹H NMR Data of Complexes 1 and 6 (Atomic Numbering as in Scheme 2)

compd	¹ H NMR data
1ak	9.23, 1H, d, 6.1 Hz [H(21)]; 8.08, 1H, s [H(2)]; 7.62, 1H, d, 8.1 Hz [H(18)]; 7.31, 1H, t, 7.4 Hz and 6.83, 1H, t, 6.5 Hz [H(19, 20)]; 4.17, 1H, m [H(4)]; 1.57, 3H, d, 6.5 Hz [R'']; 1.95–0.85, 11H, m [R]
1al	9.35, 1H, d, 5.3 Hz [H(21)]; 8.73–6.83, 8H, m [R' and H(18–20)]; 3.94–3.85, 1H, m [H(4)]; 1.78–0.79, 11H, m [R]; 1.55, d, 3H, 6.5 Hz [R'']
1am	8.56, 1H, d, 5.0 Hz [H(21)]; 8.12, 1H, d, 8.0 Hz [H(18)]; 7.69–7.26, 2H, m [H(19, 20)]; 3.51, 1H, m [H(4)]; 2.33, 3H, s [R']; 1.74–0.72, 11H, m [R]; 1.12, 3H, d, 6.0 Hz [R'']
1bk	9.22, 1H, d, 6.2 Hz [H(21)]; 8.10, 1H, s [H(2)]; 7.60–6.77, 8H, m [R and H(18–20)]; 5.94, 1H, q, 6.9 Hz [H(4)]; 1.99, 3H, d, 6.9 Hz [R'']
1bl	9.31, 1H, d, 6.2 Hz [H(21)]; 7.50–6.84, 13H, m [H(18–20); R and R']; 5.55, 1H, q, 6.7 Hz [H(4)]; 1.97, 3H, d, 6.7 Hz [R'']
1bm	9.32, 1H, d, 6.0 Hz [H(21)]; 8.22, 1H, d, 7.7 Hz [H(18)]; 7.75–6.89, 7H, m [H(19, 20) and R]; 6.01, 1H, q, 6.8 Hz [H(4)]; 2.30, 3H, s [R']; 2.05, 3H, d, 6.9 Hz [R'']
1ck	9.23, 1H, d, 6.1 Hz [H(21)]; 8.12, 1H, s [H(2)]; 7.63, 1H, d, 8.2 Hz [H(18)]; 7.31, 1H, t, 7.9 Hz and 6.84, 1H, t, 6.6 Hz [H(19, 20)]; 4.50–4.40, 1H, m [H(4)]; 2.20–1.80, 2H, m and 0.95, 3H, t, 7.3 Hz [R]; 1.59, 3H, d, 6.7 Hz [R'']
1cl	9.35, 1H, d, 6.0 Hz [H(21)]; 7.02, 1H, d, 8.3 Hz [H(18)]; 7.52–7.18, 6H, m and 6.88, 1H, t, 6.8 Hz [R' and H(19, 20)]; 4.25–4.13, 1H, m [H(4)]; 2.13–1.73, 2H, m and 0.74, 3H, t, 7.4 Hz [R]; 1.54, 3H, d, 6.5 Hz [R'']
1cm	7.72, 1H, d, 6.0 Hz [H(18)]; 7.42–6.91, 2H, m [H(19, 20)]; 9.36, 1H, d, 5.1 Hz [H(21)]; 4.50, 1H, m [H(4)]; 2.09–1.98, 2H, m and 0.94, 3H, d, 6.1 Hz [R]; 2.44, 3H, s [R']; 1.64, 3H, d, 6.3 Hz [R'']
1dk	9.25, 1H, d, 5.6 Hz [H(21)]; 7.97, 1H, s [H(2)]; 7.68, 1H, d, 6.1 Hz [H(18)]; 7.35–6.77, 2H, m [H(19, 20)]; 4.19, 2H, ddd [H(4, 5)]; 2.30–2.15, 3H, m and 1.01, 3H, t, 7.4 Hz and 0.91, 3H, d, 6.7 Hz [R]
1dl	9.32, 1H, d, 5.0 Hz [H(21)]; 7.50–6.84, 8H, m [H(18–20) and R']; 4.30–4.05, 2H, m [H(4, 5)]; 2.25–0.70, 9H, m [R]
1dm	9.32, 1H, d, 5.9 Hz [H(21)]; 7.68, 1H, d, 8.3 Hz [H(18)]; 7.37, 1H, t, 7.8 Hz and 6.87, 1H, t, 6.5 Hz [H(19, 20)]; 4.40, 1H, dd, 12.0/6.7 Hz and 4.25, 1H, dd, 12.0/7.0 Hz [H(4, 5)]; 2.40, 3H, s [R']; 2.34–1.25, 9H, m [R]
6ak	7.56, 2H, s [H(1, 2)]; 4.17–4.07, 2H, m [H(4)]; 2.00–0.89, 22H, m [R]; 1.51, 6H, d, 6.7 Hz [H(5)]
6am	7.39, 1H, s [H(2)]; 4.12, 1H, m and 3.88, 1H, m [2xH(4)]; 2.10, 3H, s [R']; 2.05–1.02, 22H, m [R]; 1.52, 3H, d, 6.5 Hz and 1.51, 3H, d, 6.6 Hz [R'']
6bk	7.59, 2H, s [H(1, 2)]; 7.40–7.05, 10H, m [R]; 5.79, 2H, quart, 6.9 Hz [H(4)]; 1.89, 6H, d, 6.9 Hz [H(5)]
6bm	7.45–7.20, 10H, m [R]; 7.41, 1H, s [H(2)]; 5.77, 1H, q, 6.8 Hz and 5.63, 1H, q, 6.8 Hz [2xH(4)]; 1.99, 3H, d, 7.1 Hz and 1.78, 3H, d, 7.0 Hz [R'']; 1.98, 3H, s [R']

^a Chemical shifts are in ppm relative to Me₄Si and measured in CD₂Cl₂ at 263 K and 300.13 MHz.

Table 12. ¹³C NMR Data of Complexes 1 and 6 (Atomic Numbering as in Scheme 2)^a

compd	¹³ C NMR data
1ak	218.5 [C(8, 11, 12)]; 154.2 [C(2)]; 151.6 [C(1)]; 145.4, 129.2, 126.2, 118.2 [C(18–21)]; 75.5 [C(4)]; 22.6 [C(5, 7)]; 31.3, 30.5, 27.1, 46.3 [R]
1al	218.9 [C(8, 11, 12)]; 156.9 [C(2)]; 154.8 [C(21)]; 152.6 [C(1)]; 130.4–128.8 [C(19) and R']; 127.9 [C(18)]; 118.5 [C(20)]; 69.4 [C(4)]; 48.0, 31.9–26.9 [R]; 23.9 [R'']
1am	119.0 [C(8, 11, 12)]; 164.0 [C(2)]; 159.2 [C(1)]; 148.8 [C(21)]; 136.7 [C(19)]; 124.5 [C(18)]; 118.9 [C(20)]; 61.9 [C(4)]; 45.5, 31.6–27.2 [R]; 18.9 and 13.9 [R' and R'']
1bk	217.4 [C(8, 11, 12)]; 154.1 [C(2)]; 151.3 [C(1)]; 145.1, 129.3–126.4, 117.9 [[C(18–21)]; 143.9, 129.3–126.4 [R]; 71.4 [C(4)]; 24.6 [R' and R'']
1bl	217.4 [C(8, 11, 12)]; 156.6 [C(2)]; 154.8 [C(21)]; 151.9 [C(1)]; 146.1, 136.4, 129.6–127.3 [C(18, 19) and R and R']; 118.2 [C(20)]; 65.3 [C(4)]; 25.2 [R'']
1bm	218.0 [C(8, 11, 12)]; 154.8 [C(2)]; 154.3 [C(21)]; 151.9 [C(1)]; 144.8, 129.4–127.4 [C(18, 19) and R]; 119.5 [C(20)]; 66.6 [C(4)]; 17.4 [R']; 23.2 [R'']
1ck	218.8 [C(8, 11, 12)]; 154.0 [C(2)]; 151.8 [C(1)]; 145.4, 129.2, 126.3, 118.4 [C(18–21)]; 71.7 [C(4)]; 33.3, 11.7 [R]; 24.8 [R' and R'']
1cl	219.0 [C(8, 11, 12)]; 157.0 [C(2)]; 154.7 [C(21)]; 152.6 [C(1)]; 137.1, 129.9–129.5 [C(19) and R']; 127.9 [C(18)]; 118.6 [C(20)]; 65.9 [C(4)]; 34.7, 12.2 [R]; 26.1 [R'']
1cm	219.9 [C(8, 11, 12)]; 164.4 [C(2)]; 159.1 [C(1)]; 148.9 [C(21)]; 136.7 [C(19)]; 126.0 [C(18)]; 121.5 [C(20)]; 58.4 [C(4)]; 31.9, 12.3 [R]; 21.6 and 14.0 [R' and R']
1dk	218.1 [C(8, 11, 12)]; 154.6 [C(2)]; 151.2 [C(1)]; 148.1, 129.3, 125.9, 117.8 [C(18–21)]; 73.4 [C(4)]; 40.5, 27.9, 17.5, 11.9 [R]
1dl	218.5 [C(8, 11, 12)]; 157.4 [C(2)]; 154.6 [C(21)]; 152.2 [C(1)]; 130.7–127.4 [C(18, 19) and R']; 118.3 [C(20)]; 67.3 [C(4)]; 41.8, 27.9, 17.5, 12.0 [R]
1dm	219.4 [C(8, 11, 12)]; 155.0 [C(21)]; 154.4 [C(2)]; 151.7 [C(1)]; 129.7 [C(19)]; 125.7 [C(18)]; 118.8 [C(20)]; 66.7 [C(4)]; 41.3, 28.2, 17.5, 15.9, 12.3 [R and R']
6ak	216.8 [C(8, 11, 12)]; 143.2 [C(1, 2)]; 74.7 [C(4)]; 46.3, 31.3, 30.8, 27.2, 27.1 [R]; 22.8 [C(5)]
6am	217.3 [C(8, 11, 12)]; 153.8 [C(1)]; 145.7 [C(2)]; 74.6 [2xC(4)]; 31.7–26.8 [R]; 23.3 and 22.8 and 17.9 [R' and R'']
6bk	215.3 [C(8, 11, 12)]; 143.5 [C(1, 2)]; 129.1, 128.0, 127.7 [R]; 71.0 [C(4)]; 24.6 [C(5)]
6bm	216.2 [C(8, 11, 12)]; 154.9 [C(1)]; 146.4 [C(2)]; 145.5, 144.9, 129.3–127.5 [R]; 71.4 and 65.4 [2xC(4)]; 24.6 and 23.8 and 17.8 [R' and R'']

^a Chemical shifts are in ppm relative to Me₄Si and measured in CD₂Cl₂ at 263 K and 75.47 MHz.

Table 13. ¹H NMR Data of Compounds 4, 5, 7, and 8

compd	¹ H NMR data
4aks	
major	8.56, 1H, d, 5.2 Hz [H(21)]; 7.81, 1H, t, 7.5 Hz [H(19)]; 7.53, 1H, d, 7.5 Hz [H(18)]; 7.18, 1H, t, 6.8 Hz [H(20)]; 5.95, 1H, s [H(2)]; 4.42–4.35, 1H, m [H(4)]; 3.82, 3.73, 2 × 3H, 2 s [H(14, 16)]; 1.80–0.55, 11H, m [R]; 1.16, 3H, d, 6.8 Hz [R'']
minor	8.56, 1H, d, 5.2 Hz [H(21)]; 7.81, 1H, t, 7.5 Hz [H(19)]; 7.53, 1H, d, 7.5 Hz [H(18)]; 7.18, 1H, t, 6.8 Hz [H(20)]; 5.97, 1H, s [H(2)]; 4.42–4.35, 1H, m [H(4)]; 3.83, 3.75, 2 × 3H, 2 s [H(14, 16)]; 1.80–0.55, 11H, m [R]; 1.04, 3H, d, 6.8 Hz [R'']
4bks	
major	8.45, 1H, d, 5.5 Hz [H(21)]; 7.44–6.34, 8H, m [R and H(18–20)]; 5.96, 1H, q, 6.9 Hz [H(4)]; 5.70, 1H, s [H(2)]; 3.83, 3.74, 2 × 3H, 2 s [H(14, 16)]; 1.55, 3H, d, 7.0 Hz [R'']
minor	8.55, 1H, d, 5.5 Hz [H(21)]; 7.44–6.34, 8H, m [R and H(18–20)]; 6.03, 1H, q, 7.0 Hz [H(4)]; 5.56, 1H, s [H(2)]; 3.81, 3.34, 2 × 3H, 2 s [H(14, 16)]; 1.42, 3H, d, 7.1 Hz [R'']
4cks	
major	8.55, 1H, d, 5.5 Hz [H(21)]; 7.85–7.79, 1H, m [H(19)]; 7.53, 1H, d, 7.5 Hz [H(18)]; 7.73–7.13, 1H, m [H(20)]; 5.97, 1H, s [H(2)]; 4.66–4.52, 1H, m [H(4)]; 3.82, 3.74, 2 × 3H, 2 s [H(14, 16)]; 1.90–1.40, 2H, m and 0.50, 3H, t, 3.7 Hz [R]; 1.15, 3H, d, 6.8 Hz [R'']
minor	8.55, 1H, d, 5.5 Hz [H(21)]; 7.85–7.79, 1H, m [H(19)]; 7.53, 1H, d, 7.5 Hz [H(18)]; 7.73–7.13, 1H, m [H(20)]; 5.97, 1H, s [H(2)]; 4.66–4.52, 1H, m [H(4)]; 3.82, 3.74, 2 × 3H, 2 s [H(14, 16)]; 1.90–1.40, 2H, m and 0.80, 3H, t, 3.7 Hz [R]; 1.06, 3H, d, 6.8 Hz [R'']
4cks^b	
major	8.59, 1H, d, 5.5 Hz [H(21)]; 7.76–7.70, 1H, m [H(19)]; 7.44, 1H, d [H(18)]; 7.09–7.00, 1H, m [H(20)]; 5.88, 1H, s [H(2)]; 4.59–4.47, 1H, m [H(4)]; 3.68, 3.66, 2 × 3H, 2 s [H(14, 16)]; 3.41, 9H, d, 10.7 Hz [P(OCH ₃) ₃]; 1.45–1.12, 2H, m and 0.37, 3H, t, 7.3 Hz [R]; 1.01, 3H, d, 6.8 Hz [R'']
minor	8.59, 1H, d, 5.5 Hz [H(21)]; 7.76–7.70, 1H, m [H(19)]; 7.44, 1H, d [H(18)]; 7.09–7.00, 1H, m [H(20)]; 5.88, 1H, s [H(2)]; 4.59–4.47, 1H, m [H(4)]; 3.68, 3.67, 2 × 3H, 2 s [H(14, 16)]; 3.41, 9H, d, 10.7 Hz [P(OCH ₃) ₃]; 1.45–1.12, 2H, m and 0.71, 3H, t, 7.3 Hz [R]; 0.92, 3H, d, 6.8 Hz [R'']
4dks	
major	8.55, 1H, d, 5.5 Hz [H(21)]; 7.82, 1H, t, 7.6 Hz [H(19)]; 7.54, 1H, d, 7.6 Hz [H(18)]; 7.21, 1H, t, 6.1 Hz [H(20)]; 5.86, 1H, s [H(2)]; 3.83, 3.74, 2 × 3H, 2 s [H(14, 16)]; 3.42–3.24, 2H, m [H(4, 5)]; 1.80–0.64, 9H, m [R]
minor	8.55, 1H, d, 5.5 Hz [H(21)]; 7.82, 1H, t, 7.6 Hz [H(19)]; 7.54, 1H, d, 7.6 Hz [H(18)]; 7.21, 1H, t, 6.1 Hz [H(20)]; 5.87, 1H, s [H(2)]; 3.83, 3.74, 2 × 3H, 2 s [H(14, 16)]; 3.42–3.24, 2H, m [H(4, 5)]; 1.80–0.64, 9H, m [R]
4iks	
major	8.40, 1H, d, 4.2 Hz [H(21)]; 7.84–6.93, 8H, m [H(18–20) and Ph (L)]; 6.02, 1H, s [H(2)]; 5.09, 1H, q, 7.3 Hz [HC* of L]; 5.89, 1H, sept, 6.9 Hz [H(4)]; 3.78, 3.73, 2 × 3H, 2 s [H(14, 16)]; 1.76, 3H, d, 6.9 Hz [Me (L)]; 1.10, 3H, d, 6.3 Hz and 1.02, 3H, d, 6.6 Hz [R and R'']
minor	8.40, 1H, d, 4.2 Hz [H(21)]; 7.84–6.93, 8H, m [H(18–20) and Ph (L)]; 6.02, 1H, s [H(2)]; 5.04, 1H, q, 6.8 Hz [HC* of L]; 5.89, 1H, sept, 6.9 Hz [H(4)]; 3.78, 3.73, 2 × 3H, 2 s [H(14, 16)]; 1.76, 3H, d, 6.9 Hz [Me (L)]; 1.10, 3H, d, 6.3 Hz and 1.02, 3H, d, 6.6 Hz [R and R'']
5akr	
major	8.40, 1H, d, 5.3 Hz [H(21)]; 7.75–7.13, 3H, m [H(18–20)]; 5.03, 1H, s [H(2)]; 4.20, 1H, s [E']; 3.88, 3H, s [H(14)]; 2.90–2.70, 1H, m [H(4)]; 1.80–0.78, 11H, m [R]; 0.60, 3H, d, 6.9 Hz [H(5)]
minor	8.40, 1H, d, 5.3 Hz [H(21)]; 7.75–7.13, 3H, m [H(18–20)]; 5.06, 1H, s [H(2)]; 4.20, 1H, s [E']; 3.70, 3H, s [H(14)]; 3.31–3.10, 1H, m [H(4)]; 1.80–0.78, 11H, m [R]; 0.50, 3H, d, 6.9 Hz [H(5)]
5aks	
major	8.40, 1H, d, 5.3 Hz [H(21)]; 7.75–7.15, 3H, m [H(18–20)]; 5.09, 1H, s [H(2)]; 3.82, 3.71, 2 × 3H, 2 s [H(14, 16)]; 2.64–2.54, 1H, m [H(4)]; 1.65–0.64, 11H, m [R]; 0.48, 3H, d, 6.8 Hz [H(5)]
minor	8.40, 1H, d, 5.3 Hz [H(21)]; 7.75–7.15, 3H, m [H(18–20)]; 5.18, 1H, s [H(2)]; 3.82, 3.71, 2 × 3H, 2 s [H(14, 16)]; 2.64–2.54, 1H, m [H(4)]; 1.65–0.64, 11H, m [R]; 0.48, 3H, d, 6.8 Hz [H(5)]
5als	
major	8.59, 1H, m/d, 4.8 Hz [H(21)]; 7.79–7.26, 8H, m [R' and H(18–20)]; 3.81, 3.18, 2 × 3H, 2 s [H(14, 16)]; 2.28–2.20, 1H, m [H(4)]; 1.79 to –0.40, 11H, m [R]; 1.38, 3H, d, 6.9 Hz [R'']
5amr	
major	8.44, 1H, d, 5.4 Hz [H(21)]; 7.71, 1H, t, 7.5 Hz [H(19)]; 7.25, 1H, d, 7.8 Hz [H(18)]; 7.13, 1H, t, 7.8 Hz [H(20)]; 4.19, 1H, s [E']; 3.64, 3H, s [H(14)]; 2.16–0.85, 11H, m [R and H(4)]; 1.95, 3H, s [R']; 1.64, 3H, d, 6.1 Hz [R'']; –1.73, 1H, dq, 3.6 Hz/12.3 Hz [R]
minor	8.44, 1H, d, 5.4 Hz [H(21)]; 7.71, 1H, t, 7.5 Hz [H(19)]; 7.25, 1H, d, 7.8 Hz [H(18)]; 7.13, 1H, t, 7.8 Hz [H(20)]; 4.43, 1H, s [E']; 3.73, 3H, s [H(14)]; 2.16–0.85, 11H, m [R and H(4)]; 1.95, 3H, s [R']; 1.64, 3H, d, 6.1 Hz [R'']; –1.73, 1H, dq, 3.6 Hz/12.3 Hz [R]
5ams	
major	8.41, 1H, d, 5.4 Hz [H(21)]; 7.75, 1H, t, 7.8 Hz [H(19)]; 7.27–7.15, 2H, m [H(18, 20)]; 3.81, 3.63, 2 × 3H, 2 s [H(14, 16)]; 1.40, 3H, s [R']; 2.15 to –0.07, 10H, m [R]; 1.31, 3H, d, 6.6 Hz [R'']; –1.67, 1H, dq, 3.3 Hz/12.3 Hz [R]
minor	8.41, 1H, d, 5.4 Hz [H(21)]; 7.75, 1H, t, 7.8 Hz [H(19)]; 7.27–7.15, 2H, m [H(18, 20)]; 3.81, 3.63, 2 × 3H, 2 s [H(14, 16)]; 2.01, 3H, s [R']; 2.15 to –0.07, 10H, m [R]; 0.94, 3H, d, 6.6 Hz [R'']; –1.67, 1H, dq, 3.3 Hz/12.3 Hz [R]
5bkr	
major	8.13, 1H, d, 5.3 Hz [H(21)]; 7.55–6.67, 8H, m [R and H(18–20)]; 5.37, 1H, q, 7.2 Hz [H(4)]; 5.28, 1H, s [H(2)]; 4.29, 1H, s [E']; 3.66, 3H, s [H(14)]; 1.63, 3H, d, 7.2 Hz [R'']
minor	8.34, 1H, d, 5.4 Hz [H(21)]; 7.55–6.67, 8H, m [R and H(18–20)]; 5.12, 1H, q, 7.0 Hz [H(4)]; 4.91, 1H, s [H(2)]; 4.32, 1H, s [E']; 3.66, 3H, s [H(14)]; 1.63, 3H, d, 7.2 Hz [R'']

Table 13 (Continued)

compd	¹ H NMR data
5bks	
major	8.13, 1H, d, 4.8 Hz [H(21)]; 7.50–6.68, 8H, m [H(18–20) and R]; 5.38, 1H, s [H(2)]; 5.29, 1H, q, 7.2 Hz [H(4)]; 3.87, 3.71, 2 × 3H, 2 s [H(14, 16)]; 1.63, d, 3H, 7.2 Hz [R'']
minor	8.31, 1H, d, 5.1 Hz [H(21)]; 7.50–6.68, 8H, m [H(18–20) and R]; 5.03, 1H, s [H(2)]; 5.01, 1H, q, 7.0 Hz [H(4)]; 3.87, 3.71, 2 × 3H, 2 s [H(14, 16)]; 0.76, 3H, d, 7.1 Hz [R'']
5blr	
major	8.28, 1H, d, 5.6 Hz [H(21)]; 7.90–6.51, 13H, m [R; R' and H(18–20)]; 4.40, 1H, s [E']; 3.84, 1H, q, 6.5 Hz [H(4)]; 3.30, 3H, s [H(14)]; 1.89, 3H, d, 7.2 Hz [R'']
minor	8.55, 1H, d, 5.2 Hz [H(21)]; 7.90–6.51, 13H, m [R; R' and H(18–20)]; 4.40, 1H, s [E']; 5.20, 1H, q, 6.6 Hz [H(4)]; 3.24, 3H, s [H(14)]; 0.55, 3H, d, 7.1 Hz [R'']
5bls	
major	8.25, 1H, d, 5.4 Hz [H(21)]; 7.81–6.54, 14H, m [R; R' and H(4, 18–20)]; 3.88, 3.23, 2 × 3H, 2 s [H(14, 16)]; 1.86, 3H, d, 7.2 Hz [R'']
minor	8.60, 1H, d, 5.4 Hz [H(21)]; 7.81–6.54, 14H, m [R; R' and H(4, 18–20)]; 3.84, 3.12, 2 × 3H, 2 s [H(14, 16)]; 0.45, 3H, d, 7.2 Hz [R'']
5bmr	
major	8.10, 1H, d, 5.6 Hz [H(21)]; 7.80–6.60, 8H, m [R and H(18–20)]; 4.37, 1H, s [E']; 3.99, 1H, q, 7.3 Hz [H(4)]; 3.66, 3H, s [H(14)]; 2.04, 3H, s [R']; 1.76, 3H, d, 7.3 Hz [R'']
minor	8.48, 1H, d, 5.4 Hz [H(21)]; 7.77–6.60, 8H, m [R and H(18–20)]; 4.36, 1H, s [E']; 3.82, 1H, q, 7.1 Hz [H(4)]; 3.65, 3H, s [H(14)]; 1.95, 1H, s [R']; 0.74, 3H, d, 7.0 Hz [R'']
5bms	
major	8.03, 1H, d, 5.3 Hz [H(21)]; 7.83–6.64, 8H, m [R and H(18–20)]; 3.87, 3.66, 2 × 3H, 2 s [H(14, 16)]; 3.97, 1H, q, 6.4 Hz [H(4)]; 2.11, 3H, s [R']; 1.74, 3H, d, 7.2 Hz [R'']
minor	8.46, 1H, d, 5.3 Hz [H(21)]; 7.83–6.64, 8H, m [R and H(18–20)]; 3.86, 3.66, 2 × 3H, 2 s [H(14, 16)]; 3.80, 1H, q, 6.6 Hz [H(4)]; 1.98, 3H, s [R']; 0.71, 3H, d, 7.0 Hz [R'']
5ckr	
major	8.40, 1H, d, 5.5 Hz [H(21)]; 7.67, 1H, t, 7.6 Hz [H(19)]; 7.38, 1H, d, 7.7 Hz [H(18)]; 7.17, 1H, t, 5.9 Hz [H(20)]; 5.10, 1H, s [H(2)]; 4.22, 1H, s [E']; 3.68, 3H, s [H(14)]; 3.28–3.14, 1H, m [H(4)]; 1.46–0.97, 2H, m and 0.64, 3H, t, 7.1 Hz [R]; 0.71, 3H, d, 6.4 Hz [R'']
minor	8.40, 1H, d, 5.5 Hz [H(21)]; 7.67, 1H, t, 7.6 Hz [H(19)]; 7.38, 1H, d, 7.7 Hz [H(18)]; 7.17, 1H, t, 5.9 Hz [H(20)]; 5.11, 1H, s [H(2)]; 4.21, 1H, s [E']; 3.67, 3H, s [H(14)]; 3.43–3.31, 1H, m [H(4)]; 1.46–0.97, 2H, m and 0.47, 3H, t, 7.4 Hz [R]; 0.60, 3H, d, 6.6 Hz [R'']
5cks	
major	8.37, 1H, d, 5.5 Hz [H(21)]; 7.77–7.69, 1H, m [H(19)]; 7.40, 1H, d, 7.6 Hz [H(18)]; 7.25–7.19, 1H, m [H(20)]; 5.14, 1H, s [H(2)]; 3.77, 3.66, 2 × 3H, 2 s [H(14, 16)]; 3.08–2.96, 1H, m [H(4)]; 1.50–0.91, 2H, m and 0.67, 3H, t, 7.3 Hz [R]; 0.53, 3H, d, 6.8 Hz [R'']
minor	8.37, 1H, d, 5.5 Hz [H(21)]; 7.77–7.69, 1H, m [H(19)]; 7.40, 1H, d, 7.6 Hz [H(18)]; 7.25–7.19, 1H, m [H(20)]; 5.18, 1H, s [H(2)]; 3.77, 3.66, 2 × 3H, 2 s [H(14, 16)]; 3.29–3.17, 1H, m [H(4)]; 1.50–0.91, 2H, m and 0.43, 3H, t, 7.3 Hz [R]; 0.57, 3H, d, 6.8 Hz [R'']
5clr	
major	8.59, 1H, d, 4.5 Hz [H(21)]; 7.74–7.19, 8H, m [R and H(18–20)]; 4.29, 1H, s [E']; 3.25, 3H, s [H(14)]; 2.26, 1H, m [H(4)]; 1.42, 3H, d, 6.9 Hz [R'']; 0.25, 3H, t, 7.5 Hz and 1.85, 1H, m and –1.23, 1H, m [R]
minor	8.59, 1H, d, 4.5 Hz [H(21)]; 7.74–7.19, 8H, m [R and H(18–20)]; 4.30, 1H, s [E']; 3.25, 3H, s [H(14)]; 2.26, 1H, m [H(4)]; 0.64, 3H, t, 7.5 Hz and 1.85, 1H, m and –1.23, 1H, m [R]; –0.05, 3H, d, 6.0 Hz [R'']
5cls	
major	8.56, 1H, d, 5.1 Hz [H(21)]; 7.99–7.01, 8H, m [R' and H(18–20)]; 3.80, 3.15, 2 × 3H, 2 s [H(14, 16)]; 2.24, 1H, m [H(4)]; 1.41, 3H, d, 6.6 Hz [R'']; 0.24, 3H, t, 7.5 Hz and –1.41, 2H, m [R]
minor	7.97, 1H, d, 5.1 Hz [H(21)]; 7.99–7.01, 8H, m [R' and H(18–20)]; 3.77, 3.22, 2 × 3H, 2 s [H(14, 16)]; 2.24, 1H, m [H(4)]; –0.28, 3H, d, 6.0 Hz [R'']; 0.66, 3H, t, 6.9 Hz and –1.41, 2H, m [R]
5cmr	
major	8.43, 1H, d, 5.4 Hz [H(21)]; 7.74–7.11, 3H, m [H(18–20)]; 4.24, 1H, s [E']; 3.64, 3H, s [H(14)]; 2.44, 1H, m, 6.9 Hz [H(4)]; 1.93, 3H, s [R']; 1.43, 0.55, 2 × 1H, m and –0.10, 3H, t, 7.5 Hz [R]; 1.32, 3H, d, 6.9 Hz [R'']
minor	8.43, 1H, d, 5.4 Hz [H(21)]; 7.74–7.11, 3H, m [H(18–20)]; 4.31, 1H, s [E']; 3.64, 3H, s [H(14)]; 2.44, 1H, m, 6.9 Hz [H(4)]; 1.90, 3H, s [R']; 1.43, 0.55, 2 × 1H, m and 0.85, 3H, t, 7.5 Hz [R]; 0.05, d, 3H, 6.8 Hz [R'']
5cms	
major	8.41, 1H, d, 5.7 Hz [H(21)]; 7.77–7.13, 3H, m [H(18–20)]; 3.84, 3.65, 2 × 3H, 2 s [H(14, 16)]; 2.42, 1H, m [H(4)]; 2.01, 3H, s [R']; 1.54, 2H, m and 0.87, 3H, t, 7.5 Hz [R]; 1.32, 3H, d, 6.9 Hz [R'']
minor	8.41, 1H, d, 5.7 Hz [H(21)]; 7.77–7.13, 3H, m [H(18–20)]; 3.84, 3.65, 2 × 3H, 2 s [H(14, 16)]; 2.42, 1H, m [H(4)]; 1.98, 3H, s [R']; 0.15, 2H, m and 0.00, 3H, t, 5.7 Hz [R]; 0.03, 3H, d, 6.6 Hz [R'']
5dlr	
major	8.50, 1H, d, 5.7 Hz [H(21)]; 8.08–7.13, 8H, m [R' and H(18–20)]; 4.31, 1H, s [E']; 3.29, 3H, s [H(14)]; 2.81–2.22, 2H, 8 d, 8 × 7.3 Hz [H(4, 5)]; 1.30–0.55, 6H, m and 0.27, 3H, d, 6.6 Hz [R]
minor	8.50, 1H, d, 5.7 Hz [H(21)]; 8.08–7.13, 8H, m [R' and H(18–20)]; 4.33, 1H, s [E']; 3.28, 3H, s [H(14)]; 2.81–2.22, 2H, 8 d, 8 × 7.3 Hz [H(4, 5)]; 1.30–0.55, 6H, m and 0.41, 3H, d, 6.6 Hz [R]

Table 13 (Continued)

compd	¹ H NMR data
5dls	
major	8.54, 1H, d, 5.5 Hz [H(21)]; 7.79–7.17, 8H, m [R' and H(18–20)]; 3.87, 3.18, 2 × 3H, 2 s [H(14, 16)]; 2.30–2.01, 2H, m [H(4, 5)]; 1.68–0.56, 9H, m [R]
minor	8.54, 1H, d, 5.5 Hz [H(21)]; 7.79–7.17, 8H, m [R' and H(18–20)]; 3.86, 3.17, 2 × 3H, 2 s [H(14, 16)]; 2.30–2.01, 2H, m [H(4, 5)]; 1.68–0.56, 9H, m [R]
5dmr	
major	8.39, 1H, d, 5.3 Hz [H(21)]; 7.73, 1H, t, 7.5 Hz [H(19)]; 7.23, 1H, d, 6.9 Hz [H(18)]; 7.12, 1H, t, 6.4 Hz [H(20)]; 4.40, 1H, s [E']; 3.65, 3H, s [H(14)]; 2.59–1.87, 2H, m [H(4, 5)]; 1.95, 3H, s [R']; 1.68–1.15, 3H, m and 0.78, 3H, t, 6.9 Hz and 0.70, 3H, d, 5.8 Hz [R]
minor	8.39, 1H, d, 5.3 Hz [H(21)]; 7.73, 1H, t, 7.5 Hz [H(19)]; 7.23, 1H, d, 6.9 Hz [H(18)]; 7.12, 1H, t, 6.4 Hz [H(20)]; 4.40, 1H, s [E']; 3.65, 3H, s [H(14)]; 2.59–1.87, 2H, m [H(4, 5)]; 1.95, 3H, s [R']; 1.68–0.85, 3H, m and 0.78, 3H, t, 6.9 Hz and 0.70, 3H, d, 5.8 Hz [R]
5dms	
major	8.54, 1H, d, 5.9 Hz [H(21)]; 7.76, 1H, t, 7.6 Hz [H(19)]; 7.29–7.10, 2H, m [H(18, 20)]; 3.85, 3.66, 2 × 3H, 2 s [H(14, 16)]; 2.01, 3H, s [R']; 2.90–1.20, 10H, m [R and H(4)]
minor	8.53, 1H, t, 5.9 Hz [H(21)]; 7.92, 1H, t, 5.9 Hz [H(19)]; 7.54, 1H, d, 8.3 Hz [H(18)]; 7.29–7.10, 1H, m [H(20)]; 3.79, 3.32, 2 × 3H, 2 s [H(14, 16)]; 2.00, 3H, s [R']; 2.90–1.20, 10H, m [R and H(4)]
5dkr	
major	8.39, 1H, d, 5.1 Hz [H(21)]; 7.71, 1H, t, 7.3 Hz [H(19)]; 7.21, 1H, d [H(18)]; 7.11, 1H, t, 6.0 Hz [H(20)]; 5.14, 1H, s [H(2)]; 4.30, 1H, s [E']; 3.72, 3H, s [H(14)]; 3.30–3.11, 2H, m [H(4, 5)]; 1.85–0.60, 9H, m [R]
5dks	
major	8.36, 1H, d, 5.3 Hz [H(21)]; 7.74, 1H, t, 7.5 Hz [H(19)]; 7.27–7.10, 2H, m [H(18, 20)]; 5.21, 1H, s [H(2)]; 3.80, 3.73, 2 × 3H, 2 s [H(14, 16)]; 3.21–3.00, 2H, m [H(4, 5)]; 1.74–0.82, 9H, m [R]
minor	8.36, d, 1H, 5.3 Hz [H(21)]; 7.74, t, 1H, 7.5 Hz [H(19)]; 7.27–7.10, 2H, m [H(18, 20)]; 5.22, 1H, s [H(2)]; 3.80, 3.73, 2 × 3H, 2 s [H(14, 16)]; 3.21–3.00, 2H, m [H(4, 5)]; 1.74–0.82, 9H, m [R]
7aks	
major	8.36, 1H, d, 5.2 Hz [H(1)]; 5.77, 1H, d, 5.1 Hz [H(2)]; 4.31–4.21, 1H, m [H(4)]; 3.45–3.35, 1H, m [H(4)]; 3.80, 3H, s and 3.75, 3H, s [H(14, 16)]; 1.23, 3H, d, 6.6 Hz and 1.07, 3H, d, 6.8 Hz [H(5)]; 1.80–0.82, 22H, m [R]
minor	8.36, 1H, d, 5.2 Hz [H(1)]; 5.76, 1H, d, 5.1 Hz [H(2)]; 4.31–4.21, 1H, m [H(4)]; 3.81, 3H, s and 3.74, 3H, s [H(14, 16)]; 3.45–3.35, 1H, m [H(4)]; 1.23, 3H, d, 6.6 Hz and 1.07, 3H, d, 6.8 Hz [H(5)]; 1.80–0.82, 22H, m [R]
7aks^b	
major	8.42, 1H, dd, 5.0/2.7 Hz [H(1)]; 5.67, 1H, d, 5.3 Hz [H(2)]; 4.34–4.24, 1H, m [H(4)]; 4.02–3.61, 1H, m [H(4)]; 3.75, 3.73, 6H, 2 s [H(14, 16)]; 3.73, 9H, d, 10.1 Hz [L']; 1.21, 3H, d, 6.9 Hz and 1.12, 3H, d, 6.9 Hz [H(5)]; 1.80–0.85, 22H, m [R]
minor	8.35, 1H, dd, 5.1/2.8 Hz [H(1)]; 5.71, 1H, d, 5.2 Hz [H(2)]; 4.34–4.24, 1H, m [H(4)]; 4.02–3.61, 1H, m [H(4)]; 3.74, 3.66, 6H, 2 s [H(14, 16)]; 3.71, 9H, d, 10.5 Hz [L']; 0.98, 6H, pst, 6.7 Hz [H(5)]; 1.80–0.85, 22H, m [R]
7iks	
major	8.38, 1H, d, 5.1 Hz [H(1)]; 5.78, 1H, d, 5.1 Hz [H(2)]; 4.78, 1H, sept, 6.8 Hz [H(4)]; 3.39, 1H, sept, 6.8 Hz [H(4)]; 3.74, 3H, s and 3.71, 3H, s [H(14, 16)]; 1.22, 6H, d, 6.7 Hz and 1.05, 6H, d, 6.8 Hz and 1.01, 6H, d, 6.8 Hz and 0.97, 3H, d, 6.7 Hz and 0.96, 3H, d, 6.7 Hz [H(5) of major and minor compd]; 1.76, 3H, d, 6.8 Hz and 5.09, 1H, quart, 6.8 Hz and 7.5–7.4, 5H, m [L]
minor	8.38, 1H, d, 5.1 Hz [H(1)]; 5.78, 1H, d, 5.1 Hz [H(2)]; 4.78, 1H, sept, 6.8 Hz [H(4)]; 3.76, 3H, s and 3.73, 3H, s [H(14, 16)]; 3.39, 1H, sept, 6.8 Hz [H(4)]; 1.22, 6H, d, 6.7 Hz and 1.05, 6H, d, 6.8 Hz and 1.01, 6H, d, 6.8 Hz and 0.97, 3H, d, 6.7 Hz and 0.96, 3H, d, 6.7 Hz [H(5) of major and minor compd]; 1.77, 3H, d, 6.8 Hz and 5.08, 1H, quart, 6.8 Hz and 7.5–7.4, 5H, m [L]
7ams	
major	5.30, 1H, s [H(2)]; 4.37–4.30, 1H, m [H(4)]; 3.79, 3.73, 2 × 3H, 2 s [H(14, 16)]; 3.57–3.51, 1H, m [H(4)]; 2.35, 3H, s [H(7)]; 1.80–0.81, 44H, m [R]; 1.29, 3H, d, 6.8 Hz and 0.95, 3H, d, 6.9 Hz [H(5)]
7ams^b	
major	5.31, 1H, s [H(2)]; 4.39–4.28, 1H, m [H(4)]; 3.75, 9H, d, 10.0 Hz [P(OCH ₃) ₃]; 3.81–3.67, 1H, m [H(4)]; 3.72, 3.71, 2 × 3H, 2 s [H(14, 16)]; 2.37, 3H, s [H(7)]; 1.75–0.77, 44H, m [R]; 1.27, 3H, d, 6.6 Hz and 0.93, 3H, d, 6.7 Hz [H(5)]
minor	5.39, 1H, s [H(2)]; 4.39–4.28, 1H, m [H(4)]; 3.53, 9H, d, 10.6 Hz [P(OCH ₃) ₃]; 3.81–3.67, 1H, m [H(4)]; 3.72, 3.71, 2 × 3H, 2 s [H(14, 16)]; 2.39, 3H, s [H(7)]; 1.75–0.77, 44H, m [R]; 1.20, 3H, d, 6.6 Hz and 1.15, 3H, d, 6.7 Hz [H(5)]
7bks	
major	7.74, 1H, d, 5.1 Hz [H(1)]; 7.49–6.86, 20H, m [R]; 5.90, 1H, quart, 6.8 Hz [H(4)]; 5.57, 1H, d, 5.1 Hz [H(2)]; 4.85, 1H, quart, 6.6 Hz [H(4)]; 3.77, 3H, s and 3.76, 3H, s [H(14, 16)]; 1.43, 6H, pst, 6.7 Hz [H(5)]
minor	8.42, 1H, d, 5.1 Hz [H(1)]; 7.49–6.86, 20H, m [R]; 5.90, 1H, quart, 6.8 Hz [H(4)]; 5.39, 1H, d, 5.2 Hz [H(2)]; 4.91, 1H, quart, 6.6 Hz [H(4)]; 3.82, 3H, s and 3.35, 3H, s [H(14, 16)]; 1.57, 3H, d, 6.6 Hz and 1.52, 3H, d, 6.6 Hz [H(5)]
7bks^b	
major	7.63, 1H, dd, 5.1/2.9 Hz [H(1)]; 7.40–6.97, 20H, m [R]; 5.89, 1H, quart, 6.6 Hz [H(4)]; 5.43, 1H, d, 5.2 Hz [H(2)]; 4.97, 1H, quart, 6.7 Hz [H(4)]; 3.73, 3H, s and 3.68, 3H, s [H(14, 16)]; 3.60, 9H, d, 10.4 Hz [L']; 1.49, 3H, d, 6.7 Hz and 1.39, 3H, d, 6.7 Hz [H(5)]
minor	8.67, 1H, dd, 5.2/3.0 Hz [H(1)]; 7.40–6.97, 20H, m [R]; 5.98, 1H, quart, 6.7 Hz [H(4)]; 5.43, 1H, d, 5.2 Hz [H(2)]; 5.07, 1H, quart, 6.7 Hz [H(4)]; 3.72, 3H, s and 3.25, 3H, s [H(14, 16)]; 3.67, 9H, d, 10.6 Hz [L']; 1.49, 3H, d, 6.7 Hz and 0.83, 3H, d, 6.8 Hz [H(5)]

Table 13 (Continued)

compd	¹ H NMR data
7bks^c	
major	8.29, 1H, d, 5.2 Hz [H(1)]; 7.41–7.10, 20H, m [R]; 5.95, 1H, quart, 6.6 Hz [H(4)]; 5.30, 1H, d, 5.1 Hz [H(2)]; 5.94, 1H, sept, 6.6 Hz [H(4)]; 3.81, 3H, s and 3.30, 3H, s [H(14, 16)]; 1.56, 9H, s [L]; 1.45, 3H, d, 7.1 Hz and 1.30, 3H, d, 6.7 Hz [H(5)]
minor	7.59, 1H, d, 5.0 Hz [H(1)]; 7.41–7.10, 20H, m [R]; 5.93, 1H, quart, 6.6 Hz [H(4)]; 5.94, 1H, sept, 6.6 Hz [H(4)]; 5.46, 1H, d, 5.0 Hz [H(2)]; 3.83, 3H, s and 3.73, 3H, s [H(14, 16)]; 1.50, 6H, pst, 6.9/7.1 Hz [H(5)]; 1.29, 9H, s [L]
7bms	
major	7.55–7.12, 8H, m [R]; 6.92, 6.89, 2 × 1H, s [R]; 6.00, 1H, q, 6.9 Hz [H(4)]; 5.22, 1H, s [H(2)]; 5.10, 1H, q, 7.1 Hz [H(4)]; 3.87, 3.78, 2 × 3H, 2 s [H(14, 16)]; 1.57, 3H, d, 7.0 Hz [H(5)]; 1.49, 3H, d, 7.0 Hz [H(5)]; 0.98, 3H, s [R']
minor	7.55–7.12, 8H, m [R]; 6.92, 6.89, 2 × 1H, s [R]; 6.00, 1H, q, 6.9 Hz [H(4)]; 5.02, 1H, s [H(2)]; 5.10, 1H, q, 7.1 Hz [H(4)]; 3.85, 3.36, 2 × 3H, 2 s [H(14, 16)]; 1.22, 3H, d, 6.8 Hz [H(5)]; 1.19, 3H, d, 7.5 Hz [H(5)]; 0.97, 3H, s [R']
8als	
major	8.66, 1H, m/d, 4.8 Hz [H(21)]; 7.80–7.33, 8H, m [R' and H(18–20)]; 3.93, 3.59, 2 × 3H, 2 s [H(14, 16)]; 3.34, 1H, sept, 5.9 Hz [H(4)]; 1.42, 3H, d, 6.9 Hz [R'']; 1.77–0.62, 10H, m and –0.30 to –0.40, 1H, m [R]
8bmr	
major	8.52, 1H, d, 3.0 Hz [H(21)]; 7.70–6.92, 8H, m [R and H(18–20)]; 6.84, 1H, s [E']; 4.55, 1H, q, 7.2 Hz [H(4)]; 3.69, 3H, s [H(14)]; 2.01, 3H, s [R']; 1.74, 3H, d, 7.2 Hz [R'']
minor	8.62, 1H, d, 3.0 Hz [H(21)]; 7.67, 1H, t, 7.6 Hz [H(19)]; 7.70–6.92, 8H, m [R and H(18, 19, 20)]; 6.84, 1H, s [E']; 4.25, 1H, q, 7.1 Hz [H(4)]; 3.69, 3H, s [H(14)]; 1.87, 3H, s [R']; 1.52, 3H, d, 7.1 Hz [R'']
8bms	
major	8.56, 1H, d, 4.7 Hz [H(21)]; 8.13–6.86, 8H, m [R and H(18–20)]; 4.54, 1H, q, 7.1 Hz [H(4)]; 3.85, 3.67, 2 × 3H, 2 s [H(14, 16)]; 2.01, 3H, s [R']; 1.73, 3H, d, 7.0 Hz [R'']
minor	8.64, 1H, d, 4.6 Hz [H(21)]; 8.13–6.86, 8H, m [R and H(18–20)]; 4.54, 1H, q, 7.1 Hz [H(4)]; 3.85, 3.67, 2 × 3H, 2 s [H(14, 16)]; 1.94, 3H, s [R']; 1.56, 3H, d, 6.8 Hz [R'']
8ckr	
major	8.58, 1H, d, 5.4 Hz [H(21)]; 7.67, 1H, t, 7.4 Hz [H(19)]; 7.35–7.20, 2H, m [H(18, 20)]; 6.93, 1H, s [E']; 5.49, 1H, s [H(2)]; 4.05, 1H, m, 7.0 Hz [H(4)]; 3.68, 3H, s [H(14)]; 1.83–1.07, 2H, m and 0.72, 3H, t, 6.7 Hz [R]; 1.24, 3H, d, 6.7 Hz [R'']
minor	8.58, 1H, d, 5.4 Hz [H(21)]; 7.67, 1H, t, 7.4 Hz [H(19)]; 7.35–7.20, 2H, m [H(18, 20)]; 6.93, 1H, s [E']; 5.46, 1H, s [H(2)]; 3.90, 1H, m, 7.0 Hz [H(4)]; 3.68, 3H, s [H(14)]; 1.83–1.07, 2H, m and 0.75, 3H, t, 6.7 Hz [R]; 1.63, 3H, d, 7.2 Hz [R'']
8cls	
major	8.61, 1H, d, 4.6 Hz [H(21)]; 7.72, 1H, t, 7.8 Hz [H(19)]; 7.43–7.26, 7H, m [R' and H(18, 20)]; 3.89, 3.66, 2 × 3H, 2 s [H(14, 16)]; 3.34–0.66, 3H, m [H(4) and R]; 1.30, 3H, d, 6.8 Hz [R'']; 0.43, 3H, t, 7.4 Hz [R]
minor	8.61, 1H, d, 4.6 Hz [H(21)]; 7.72, 1H, t, 7.8 Hz [H(19)]; 7.43–7.26, 7H, m [R' and H(18, 20)]; 3.89, 3.66, 2 × 3H, 2 s [H(14, 16)]; 3.34–0.66, 3H, m [H(4) and R]; 0.84, 3H, d, 6.6 Hz [R'']; 0.61, 3H, t, 7.4 Hz [R]
8cmr	
major	8.52, 1H, d, 5.2 Hz [H(21)]; 7.59, 1H, t, 7.8 Hz [H(19)]; 7.20–7.11, 2H, m [H(18, 20)]; 6.85, 1H, s [E']; 3.66, 3H, s [H(14)]; 3.08, 1H, m, 7.1 Hz [H(4)]; 1.92, 3H, s [R']; 1.87–1.40, 2H, m and 0.25, 3H, t, 7.6 Hz [R]; 1.30, 3H, d, 6.8 Hz [R'']
minor	8.52, 1H, d, 5.2 Hz [H(21)]; 7.59, 1H, t, 7.8 Hz [H(19)]; 7.20–7.11, 2H, m [H(18, 20)]; 6.85, 1H, s [E']; 3.65, 3H, s [H(14)]; 3.00, 1H, m, 7.1 Hz [H(4)]; 1.90, 3H, s [R']; 1.87–1.40, 2H, m and 0.81, 3H, t, 7.5 Hz [R]; 0.81, 3H, d, 6.8 Hz [R'']

^a “Major” and “minor” identify the values for the major and minor diastereomers of the respective compound. The resonances are characterized in consecutive order by chemical shift (ppm), integral, multiplicity, coupling constant, and (in brackets) the assignment according to Scheme 2. Chemical shifts are in ppm relative to Me₄Si and measured in CDCl₃ at 293 K and 300.13 MHz. ^b With L = P(OMe)₃. ^c With L = tBu-NC.

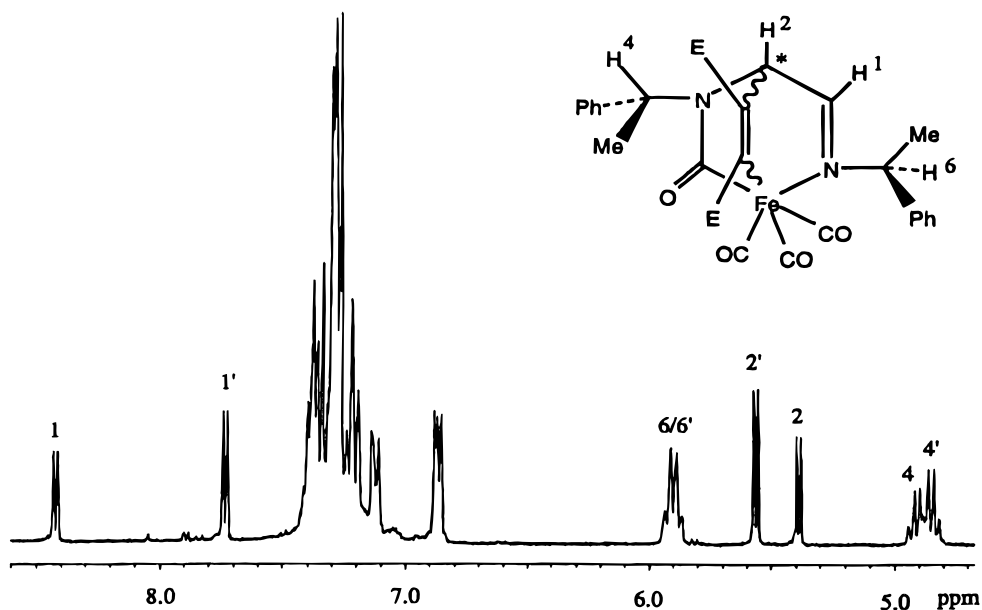


Figure 9. ¹H NMR spectrum of the crude reaction mixture 7/7'bks (in CDCl₃ at 300.13 MHz).

Table 14. ^{13}C NMR Data of Compounds 4, 5, 7, and 8

compd	^{13}C NMR data
4aks	
major	206.4, 204.7, 202.4 [L and C(3, 11, 12)]; 190.8 [C(10)]; 178.2 [C(15)]; 161.7, 161.2 [C(1, 13)]; 156.0 [C(21)]; 139.8 [C(19)]; 130.3 [C(9)]; 124.7 [C(18)]; 123.3 [C(20)]; 60.3 [C(2)]; 54.8 [C(4)]; 52.8, 52.0 [C(14, 16)]; 42.6, 30.4, 26.6, 26.5, 26.2 [R]; 17.2 [C(5)]
4bks	
major	206.0, 202.8, 204.5, 201.4 [L and C(3, 11, 12)]; 190.5 [C(10)]; 178.0 [C(15)]; 161.2, 161.1 [C(1, 13)]; 155.3 [C(21)]; 139.2 [C(19)]; 130.0 [C(19)]; 141.6, 128.8, 128.3, 127.8 [R]; 124.7 [C(18)]; 123.0 [C(20)]; 60.5 [C(2)]; 52.8, 52.1, 51.5 [C(4, 14, 16)]; 16.8 [C(5)]
4cks	
major	205.5, 204.6, 203.7, 201.4 [L and C(3, 11, 12)]; 190.9 [C(10)]; 178.5 [C(15)]; 161.5, 161.1 [C(1, 13)]; 156.0 [C(21)]; 140.2 [C(19)]; 130.2 [C(9)]; 124.9 [C(18)]; 123.5 [C(20)]; 59.6 [C(2)]; 53.1, 52.3, 51.4 [C(4, 14, 16)]; 28.8, 11.6 [R]; 18.3 [C(5)]
minor	206.6, 204.5, 203.7, 201.3 [L and C(3, 11, 12)]; 190.7 [C(10)]; 178.5 [C(15)]; 161.6, 161.2 [C(1, 13)]; 156.0 [C(21)]; 140.2 [C(19)]; 130.0 [C(9)]; 124.9 [C(18)]; 123.5 [C(20)]; 59.6 [C(2)]; 53.1, 52.3, 51.4 [C(4, 14, 16)]; 28.8, 11.7 [R]; 19.7 [C(5)]
4cks^b	
major	212–209.3, m [C(3, 11, 12)]; 197.1 [C(10)]; 179.0 [C(15)]; 162.0 161.8 [C(1, 13)]; 156.2 [C(21)]; 139.5 [C(19)]; 130.8, 7.5Hz [C(9)]; 124.0 [C(18)]; 122.4 [C(20)]; 59.6 [C(2)]; 53.2–52.9 [P(OCH ₃) ₃]; 52.6, 2.3Hz [C(4)]; 51.8, 50.1 [C(14, 16)]; 28.7 [R]; 11.5, 18.3Hz [R]; 19.4, 20.8Hz [C(5)]
minor	212–209.3, m [C(3, 11, 12)]; 197.1 [C(10)]; 179.0 [C(15)]; 162.0 161.8 [C(1, 13)]; 156.2 [C(21)]; 139.3 [C(19)]; 130.9, 7.5Hz [C(9)]; 123.9 [C(18)]; 122.2 [C(20)]; 59.8 [C(2)]; 53.2–52.9 [P(OCH ₃) ₃]; 13.1Hz [C(4)]; 51.3, 50.2 [C(14, 16)]; 28.9 [R]; 11.4, 17.3Hz [R]; 19.3, 22.3Hz [C(5)]
4dks	
major	206.5, 204.3, 203.9, 201.1 [L and C(3, 11, 12)]; 189.9 [C(10)]; 178.3 [C(15)]; 161.1, 160.4 [C(1, 13)]; 156.0 [C(21)]; 140.1 [C(19)]; 129.7 [C(9)]; 124.9 [C(18)]; 123.6 [C(20)]; 65.2 [C(2)]; 53.5 [C(4)]; 52.9, 52.2 [C(14, 16)]; 34.7, 26.9, 17.2, 11.8 [R'']; 11.8 [R'']
minor	206.5, 204.3, 203.9, 201.1 [L and C(3, 11, 12)]; 189.9 [C(10)]; 178.3 [C(15)]; 161.1, 160.4 [C(1, 13)]; 156.0 [C(21)]; 140.1 [C(19)]; 129.7 [C(9)]; 124.9 [C(18)]; 123.6 [C(20)]; 65.2 [C(2)]; 53.7 [C(4)]; 52.9, 52.2 [C(14, 16)]; 34.7, 26.9, 16.8, 11.6 [R'']; 11.6 [R'']
4iks	
major	210.8, 209.4, 208.1 [L and C(3, 11, 12)]; 198.7 [C(10)]; 179.4 [C(15)]; 162.2, 161.4 [C(1, 13)]; 157.0 [(Ph)(Me)(H)C*–NC]; 155.6 [C(21)]; 139.1 [C(19)]; 138.9, 129.7, 126.1, 122.3 [(Ph)(Me)(H)C*–NC]; 129.7 [C(9)]; 129.3 [C(18)]; 124.0 [C(20)]; 59.2, 57.2 [C(2) and (Ph)(Me)(H)C*–NC]; 52.8, 51.9 [C(14, 16)]; 44.1 [C(4)]; 25.1 [(Ph)(Me)(H)C*–NC]; 21.7 [C(5)]
minor	210.9, 209.4, 208.2 [L and C(3, 11, 12)]; 198.9 [C(10)]; 179.1 [C(15)]; 162.3, 161.3 [C(1, 13)]; 157.0 [(Ph)(Me)(H)C*–NC]; 155.6 [C(21)]; 139.1 [C(19)]; 138.9, 129.8, 126.0, 122.4 [(Ph)(Me)(H)C*–NC]; 129.7 [C(9)]; 129.3 [C(18)]; 124.0 [C(20)]; 59.2, 57.1 [C(2) and (Ph)(Me)(H)C*–NC]; 52.8, 51.8 [C(14, 16)]; 44.1 [C(4)]; 25.4 [(Ph)(Me)(H)C*–NC]; 21.5 [C(5)]
5akr	
major	212.0, 210.1, 209.7 [L and C(11, 12)]; 175.8, 170.7 [C(1, 3, 13, 15)]; 155.6 [C(21)]; 138.3 [C(19)]; 124.4 [C(18)]; 123.1 [C(20)]; 70.5 [C(9)]; 70.0 [C(2)]; 56.9, 52.2 [C(4, 10, 14)]; 41.8, 31.2, 26.7, 26.4 [R]; 16.2 [C(5)]
minor	212.1, 210.1, 209.8 [L and C(11, 12)]; 174.1, 171.4 [C(1, 3, 13, 15)]; 155.6 [C(21)]; 138.1 [C(19)]; 124.4 [C(18)]; 123.1 [C(20)]; 71.0 [C(9)]; 67.3 [C(2)]; 55.5, 54.7, 52.2 [C(4, 10, 14)]; 39.8, 30.9, 30.5, 26.6 [R]; 17.5 [C(5)]
5aks	
major	210.1, 209.6, 207.6 [L and C(11, 12)]; 174.9 [C(15)]; 170.8, 170.7, 170.3 [C(1, 3, 13)]; 155.9 [C(21)]; 138.9 [C(19)]; 124.7 [C(18)]; 122.6 [C(20)]; 71.0 [C(2)]; 70.0 [C(10)]; 67.2 [C(9)]; 58.2 [C(4)]; 53.8, 52.6 [C(14, 16)]; 41.3, 31.2, 31.1, 26.8, 26.3 [R]; 15.9 [C(5)]
minor	210.1, 209.6, 207.6 [L and C(11, 12)]; 174.9 [C(15)]; 170.8, 170.7, 170.3 [C(1, 3, 13)]; 155.9 [C(21)]; 138.9 [C(19)]; 124.7 [C(18)]; 122.6 [C(20)]; 67.7 [C(2)]; 70.0 [C(10)]; 67.2 [C(9)]; 55.0 [C(4)]; 53.8, 52.6 [C(14, 16)]; 41.3, 31.2, 31.1, 26.8, 26.3 [R]; 15.9 [C(5)]
5als	
major	210.2, 209.7, 207.0 [L and C(11, 12)]; 171.6, 170.7, 170.3, 169.5 [C(1, 3, 13, 15)]; 156.3 [C(21)]; 138.1 [C(19)]; 134.7 [R']; 130.9–124.6 [R'; C(18, 20)]; 82.3 [C(2)]; 77.8 [C(9)]; 69.6 [C(10)]; 56.3 [C(4)]; 53.2, 50.8 [C(14, 16)]; 43.2, 30.7, 29.8, 26.6, 26.1 [R]; 15.2 [R'']
5amr	
major	212.6, 210.7, 210.4 [L and C(11, 12)]; 173.2, 172.2 [C(1, 3, 13)]; 152.1 [C(21)]; 138.0 [C(19)]; 124.1 [C(18)]; 121.7 [C(20)]; 78.0 [C(2)]; 73.6 [C(9)]; 57.2, 55.1, 51.6 [C(4, 10, 14)]; 40.0, 32.4, 29.2, 26.7, 26.6, 26.3 [R]; 19.2, 19.1 [R' and R'']
5ams	
major	210.8, 209.3, 207.4 [L and C(11, 12)]; 172.4, 171.7, 170.6, 170.4 [C(1, 3, 13, 15)]; 155.8 [C(21)]; 138.5 [C(19)]; 124.4 [C(18)]; 121.4 [C(20)]; 73.9, 73.1, 71.7 [C(2, 9, 10)]; 55.4, 53.9, 51.8 [C(4, 14, 16)]; 39.7, 35.1–25.7 [R]; 19.2, 18.5 [R' and R'']
5bkr	
major	211.9, 209.5, 209.4 [L and C(11, 12)]; 175.1 [C(3, 13)]; 169.3 [C(1)]; 154.4 [C(21)]; 141.3, 128.8–123.4 [R and C(18, 20)]; 137.9 [C(19)]; 70.8 [C(9)]; 65.8 [C(2)]; 54.0 [C(4)]; 51.7, 48.6 [C(10, 14)]; 16.5 [C(5)]
minor	211.8, 209.6, 209.4 [L and C(11, 12)]; 174.8 [C(3, 13)]; 170.4 [C(1)]; 155.2 [C(21)]; 139.3, 128.8–123.4 [R and C(18, 20)]; 137.8 [C(19)]; 70.6 [C(9)]; 65.8 [C(2)]; 54.8 [C(4)]; 52.0, 51.7 [C(10, 14)]; 17.1 [C(5)]
5bks	
major	210.3, 209.2, 207.5 [L and C(11, 12)]; 174.8, 172.3, 170.7, 169.2 [C(1, 3, 13, 15)]; 154.9 [C(21)]; 141.2 [R]; 137.4 [C(19)]; 129.3–123.4 [C(18, 20) and R]; 68.6, 67.9, 66.3 [C(2, 9, 10)]; 53.9, 52.6, 49.4 [C(4, 14, 16)]; 16.9 [C(5)]
minor	210.2, 209.1, 207.5 [L and C(11, 12)]; 174.6, 171.8, 170.5, 170.4 [C(1, 3, 13, 15)]; 155.5 [C(21)]; 139.1 [R]; 138.4 [C(19)]; 129.3–123.4 [C(18, 20) and R]; 69.5, 67.8, 67.6 [C(2, 9, 10)]; 52.9, 52.5, 49.4 [C(4, 14, 16)]; 17.0 [C(5)]

Table 14 (Continued)

compd	¹³ C NMR data
5blr	
major	212.0, 210.5, 210.1 [L and C(11, 12)]; 175.4, 171.5, 168.5 [C(1, 3, 13)]; 155.6 [C(21)]; 143.6, 135.1, 130.9–123.8 [R and R' and C(18–20)]; 82.6, 79.7 [C(2, 9)]; 56.1, 55.0, 51.1 [C(4, 10, 14)]; 23.4 [R'']
minor	212.0, 210.5, 210.1 [L and C(11, 12)]; 175.4, 174.4, 168.5 [C(1, 3, 13)]; 155.5 [C(21)]; 142.5, 134.0, 130.9–123.8 [R and R' and C(18–20)]; 82.6, 79.7 [C(2, 9)]; 56.0, 53.9, 51.0 [C(4, 10, 14)]; 19.1 [R'']
5bls	
major	210.3, 210.2, 207.1 [L and C(11, 12)]; 172.8, 171.1, 170.8, 168.7 [C(1, 3, 13, 15)]; 155.7 [C(21)]; 143.6, 135.1, 129.2–124.0 [R and R'; C(18, 20)]; 137.2 [C(19)]; 83.1, 66.3 [C(2, 9, 10)]; 56.7, 53.5, 51.4 [C(4, 14, 16)]; 23.6 [R'']
minor	210.3, 210.2, 207.1 [L and C(11, 12)]; 172.8, 171.1, 170.8, 168.7 [C(1, 3, 13, 15)]; 155.7 [C(21)]; 143.6, 135.1, 129.2–124.0 [R and R'; C(18, 20)]; 137.2 [C(19)]; 78.3, 68.7 [C(2, 9, 10)]; 55.4, 53.5, 51.6 [C(4, 14, 16)]; 15.8 [R'']
5bmr	
major	212.5, 210.5, 210.0 [L and C(11, 12)]; 174.5, 172.7, 171.1 [C(1, 3, 13)]; 155.4 [C(21)]; 142.4, 128.9–126.6 [R]; 138.0 [C(19)]; 123.8 [C(18)]; 121.9 [C(20)]; 76.5, 73.8 [C(2, 9)]; 57.4 [C(4)]; 53.3, 51.8 [C(10,14)]; 22.8, 18.6 [R' and R'']
minor	212.0, 210.3, 209.9 [L and C(11, 12)]; 173.4, 172.9, 171.3 [C(1, 3, 13)]; 155.7 [C(21)]; 142.2, 128.9–126.6 [R]; 138.5 [C(19)]; 124.3 [C(18)]; 121.5 [C(20)]; 75.5, 73.6 [C(2, 9)]; 56.0 [C(4)]; 52.1, 51.7 [C(10, 14)]; 19.2, 18.2 [R' and R'']
5bms	
major	211.0, 209.2, 207.6 [L and C(11, 12)]; 172.3, 172.1, 171.2, 170.6 [C(1, 3, 13, 15)]; 156.6 [C(21)]; 142.5 [R]; 138.4 [C(19)]; 129.8–121.0 [R and C(18, 20)]; 74.2, 66.3 [C(2, 9, 10)]; 53.9, 53.7, 51.6 [C(4, 14, 16)]; 22.7, 18.0 [R' and R'']
minor	210.4, 209.2, 207.5 [L and C(11, 12)]; 172.4, 172.0, 171.1, 170.2 [C(1, 3, 13, 15)]; 155.9 [C(21)]; 142.2 [R]; 139.0 [C(19)]; 129.8–121.0 [R and C(18, 20)]; 74.2, 72.6, 72.4 [C(2, 9, 10)]; 53.9, 53.7, 51.6 [C(4, 14, 16)]; 18.6, 18.4 [R' and R'']
5ckr	
major	211.9, 210.0, 209.7 [L and C(11, 12)]; 175.8, 174.1, 171.0 [C(1, 3, 13)]; 155.8 [C(21)]; 138.4 [C(19)]; 124.5 [C(18)]; 123.2 [C(20)]; 70.4 [C(9)]; 68.8 [C(2)]; 55.4 [C(4)]; 52.7, 51.7 [C(10, 14)]; 28.3, 17.2, 12.1 [R and R'']
minor	212.0, 209.8, 209.7 [L and C(11, 12)]; 175.8, 174.4, 171.3 [C(1, 3, 13)]; 155.8 [C(21)]; 138.2 [C(19)]; 124.5 [C(18)]; 123.5 [C(20)]; 70.6 [C(9)]; 67.5 [C(2)]; 55.2 [C(4)]; 52.3 [C(10, 14)]; 26.7, 19.0, 11.7 [R and R'']
5cks	
major	210.1, 209.4, 207.6 [L and C(11, 12)]; 174.8, 171.0, 170.7, 170.5 [C(1, 3, 13, 15)]; 156.0 [C(21)]; 139.0 [C(19)]; 124.8 [C(18)]; 122.8 [C(20)]; 70.3 [C(10)]; 69.8 [C(2)]; 67.2 [C(9)]; 53.8, 53.7, 52.5 [C(4, 14, 16)]; 27.9, 12.1 [R]; 17.5 [R'']
minor	210.2, 209.3, 207.7 [L and C(11, 12)]; 174.8, 171.3, 171.0, 170.7 [C(1, 3, 13, 15)]; 156.0 [C(21)]; 138.8 [C(19)]; 124.8 [C(18)]; 123.1 [C(20)]; 70.3 [C(10)]; 69.8 [C(2)]; 67.5 [C(9)]; 53.8, 53.7, 52.5 [C(4, 14, 16)]; 26.5, 11.6 [R]; 18.6 [R'']
5clr	
major	211.5, 210.5, 210.0 [L and C(11, 12)]; 173.6, 171.8, 170.4 [C(1, 3, 13)]; 156.2 [C(21)]; 137.4 [C(19)]; 135.0, 129.1–124.4 [R' and C(18, 20)]; 82.2 [C(2)]; 78.9 [C(9)]; 54.5, 53.1, 51.2 [C(4, 10, 14)]; 26.3, 17.2, 12.2 [R and R'']
minor	211.6, 210.4, 210.0 [L and C(11, 12)]; 173.9, 171.7, 170.3 [C(1, 3, 13)]; 156.2 [C(21)]; 137.8 [C(19)]; 135.0, 129.1–124.4 [R' and C(18, 20)]; 82.3 [C(2)]; 78.9 [C(9)]; 54.6, 52.9, 51.2 [C(4, 10, 14)]; 26.1, 15.0, 12.7 [R and R'']
5cls	
major	210.3, 209.7, 207.1 [L and C(11, 12)]; 171.1, 170.9 [C(1, 3, 13, 15)]; 166.2 [C(21)]; 137.8 [C(19)]; 135.3, 129.0–124.4 [R' and C(18, 20)]; 82.9, 78.1, 68.1 [C(2, 9, 10)]; 53.6, 53.4, 51.4 [C(4, 14, 16)]; 26.3, 17.4, 12.3 [R and R'']
minor	210.3, 209.7, 207.1 [C(8, 11, 12)]; 171.1, 170.9 [C(1, 3, 13, 15)]; 166.2 [C(21)]; 138.2 [C(19)]; 135.3, 129.0–124.4 [R' and C(18, 20)]; 82.9, 78.1, 68.1 [C(2, 9, 10)]; 53.6, 53.4, 51.3 [C(4, 14, 16)]; 28.8, 19.9, 13.0 [R and R'']
5cmr	
major	212.0, 210.3, 209.8 [L and C(11, 12)]; 172.6, 172.2, 171.7 [C(1, 3, 13)]; 155.4 [C(21)]; 138.0 [C(19)]; 124.0 [C(18)]; 121.2 [C(20)]; 76.3, 73.0 [C(2, 9)]; 56.5 [C(4)]; 51.1, 50.7 [C(10, 14)]; 25.8, 19.3, 16.1, 12.1, 10.1 [R and R' and R'']
minor	211.9, 210.3, 209.7 [L and C(11, 12)]; 172.6, 172.2, 171.9 [C(1, 3, 13)]; 155.3 [C(21)]; 138.3 [C(19)]; 124.0 [C(18)]; 121.3 [C(20)]; 76.3, 73.0 [C(2, 9)]; 56.6 [C(4)]; 51.1, 50.9 [C(10, 14)]; 27.5, 18.7, 18.2, 16.1, 10.7 [R and R' and R'']
5cms	
major	210.6, 209.6, 207.9 [L and C(11, 12)]; 172.8, 172.6, 170.7 [C(1, 3, 13, 15)]; 156.0 [C(21)]; 138.4 [C(19)]; 124.3 [C(18)]; 121.0 [C(20)]; 73.7, 72.7, 68.4 [C(2, 9, 10)]; 53.8, 51.8, 51.7 [C(4, 14, 16)]; 26.4, 19.4, 16.8, 11.7 [R and R' and R'']
minor	210.7, 209.5, 207.9 [L and C(11, 12)]; 172.6, 172.5, 170.6, 170.5 [C(1, 3, 13, 15)]; 156.0 [C(21)]; 138.8 [C(19)]; 124.3 [C(18)]; 121.1 [C(20)]; 73.7, 72.7, 68.4 [C(2, 9, 10)]; 53.8, 51.8, 51.7 [C(4, 14, 16)]; 27.9, 18.6, 18.3, 12.5 [R and R' and R'']
5dkr	
major	211.2, 209.6, 209.1 [L and C(11, 12)]; 175.2 [C(3)]; 168.4 [C(1, 13)]; 155.6 [C(21)]; 137.9 [C(19)]; 124.1 [C(18)]; 122.5 [C(20)]; 69.0 [C(9)]; 67.7 [C(2)]; 53.6, 45.1 [C(4, 10, 14)]; 33.0, 26.5, 17.1, 11.1 [R]
minor	211.2, 209.6, 209.1 [L and C(11, 12)]; 175.2 [C(3)]; 168.4 [C(1, 13)]; 155.6 [C(21)]; 137.9 [C(19)]; 124.1 [C(18)]; 122.5 [C(20)]; 69.0 [C(9)]; 67.3 [C(2)]; 53.6, 44.7 [C(4, 10, 14)]; 33.0, 27.6, 17.2, 11.6 [R]
5dks	
major	209.8, 209.5, 207.2 [L and C(11, 12)]; 174.9, 171.9, 170.8, 168.2 [C(1, 3, 13, 15)]; 156.1 [C(21)]; 138.6 [C(19)]; 124.5 [C(18)]; 122.4 [C(20)]; 69.6 [C(10)]; 67.7 [C(2)]; 66.4 [C(9)]; 53.8, 52.8 [C(14, 16)]; 45.3 [C(4)]; 33.0, 27.8, 17.4, 12.0 [R]
minor	209.8, 209.5, 207.2 [L and C(11, 12)]; 174.9, 171.5, 170.8, 168.2 [C(1, 3, 13, 15)]; 156.1 [C(21)]; 138.6 [C(19)]; 124.5 [C(18)]; 122.4 [C(20)]; 69.5 [C(10)]; 67.7 [C(2)]; 66.4 [C(9)]; 53.8, 52.8 [C(14, 16)]; 45.8 [C(4)]; 33.0, 26.7, 17.5, 11.5 [R'']
5dlr	
major	211.4, 210.3, 209.9 [L and C(11, 12)]; 171.3, 169.9 [C(1, 3, 13)]; 156.3 [C(21)]; 137.2 [C(19)]; 134.5, 128.9–124.1 [R' and C(18, 20)]; 81.4, 79.8 [C(2, 9)]; 53.7, 51.0 [C(4, 10, 14)]; 33.5, 27.7, 16.7, 11.7 [R]
minor	211.4, 210.3, 209.9 [L and C(11, 12)]; 171.3, 169.9 [C(1, 3, 13)]; 156.3 [C(21)]; 137.2 [C(19)]; 134.6, 128.9–124.1 [R' and C(18, 20)]; 81.4, 79.5 [C(2, 9)]; 53.7, 51.0 [C(4, 10, 14)]; 30.0, 27.5, 17.7, 11.7 [R]

Table 14 (Continued)

compd	¹³ C NMR data
8cls	
major	162.0, 156.6, 153.1 [C(1, 3, 13, 15)]; 165.6, 163.1 [C(9, 10)]; 149.7 [C(21)]; 137.3 [C(19)]; 135.1–128.7 [R']; 124.3, 124.2 [C(18, 20)]; 69.1 [C(2)]; 53.3, 53.1 [C(4, 14, 16)]; 27.3, 11.6 [R]; 16.3 [R'']
8cmr	
major	162.5, 157.1, 152.6 [C(1, 3, 13)]; 168.6, 137.2 [C(9, 10)]; 149.5 [C(21)]; 135.9 [C(19)]; 123.7 [C(18)]; 121.5 [C(20)]; 71.8 [C(2)]; 52.6, 51.6 [C(4, 14)]; 27.0, 11.7 [R]; 20.9, 18.5 [R' and R'']

^a "Major" and "minor" identify the values for the major and minor diastereomers of the respective compound. Chemical shifts are in ppm relative to Me₄Si and measured in CDCl₃ at 263 K and 75.47 MHz. Assignments use the atom numbering according to Scheme 2. ^b With L = P(OMe)₃. ^c With L = tBu-NC.

tion of the diastereomer ratio by the integration of corresponding signals. Protons H(1) and H(1') in the complexes with phenylethylimines show the largest shift difference, which we ascribe to the anisotropy effect of the phenyl rings of the R* group in 7/7**bks**.

In all cases the chemical shifts of H(2) for the MP-derived complexes **5kr** have lower ppm values than those of the DMAD-derived complexes **5ks**, because the DMAD-derived complexes **5ks** have two electron-withdrawing ester groups, which deshield the H(2) nuclei.

In the compounds **8kr** and **8mr** the alkene proton H(10) is shifted ca. 2.6 ppm downfield in comparison to the corresponding complexes **5r**. This proton has now a chemical shift that is normally found for olefinic protons. This confirms the liberation of the pyrrolinone ligand from its iron complex.

In some compounds **8** the ³J coupling between H(20) and H(21) is significantly smaller than in the corresponding complexes **5**, indicating a larger dihedral angle between the C–H bonds as a consequence of the distorted geometry of the pyridine ring. For compounds **8**, the resonance of H(4) is shifted downfield in comparison with complexes **5**.

Compounds **5als**, **5am**, **5cl**, **5cmr**, and also **8als** with R* = (±)-*sec*-Bu (**c**) or (cHex)(Me)(H)C (**a**) and R' = Me (**m**) or Ph (**l**) show resonances at negative ppm values. These resonances belong to the protons at the carbon atoms at the 1-position of the R group of the chiral nitrogen substituent, i.e., the 1-ethyl or 1-cyclohexyl protons. Such negative ppm values can only be explained by the anisotropy effect of an aromatic ring current; i.e., a position above the plane of an aromatic ring that gives the extra diamagnetic shielding. Since the negative values are observed not only for the compounds with R' = Ph but also for those with R' = Me, the anisotropy effect of the pyridine ring must be responsible. A phenyl or methyl group at C(2), but not a proton as in compounds **5k**, enforce a conformation of the R* substituent that brings the protons at the 1-position of R in a position above the plane of the pyridine ring.

In the compounds **5ak** and **5ck** the Me groups (R'') of the R* substituent are positioned above the plane of the pyridine ring. The protons of these Me groups resonate, therefore, at lower ppm values, namely in the region of 0.48–0.71 ppm. This is in contrast to the chemical shifts found in **5al** and **5am**, which resonate in the region 1.64–0.94 ppm. In compounds **5b** (except for **5bkr**) these protons resonate in the region 1.89–1.63 ppm for the major diastereomer, whereas in the minor diastereomer these resonances are found in the region +0.45 to –0.76 ppm. The same trend is found for **5cl** and **5cm**.

¹³C NMR of Complexes 4, 5, 7, and 8. Just like the ¹H NMR spectra, the ¹³C NMR spectra show sufficient shift differences for the two diastereomers in **4**, **5**, **7** and **8** to make them easily distinguishable. The most remarkable change in the chemical shifts of the complexes **4**, **5**, **7** and **8**, as compared to those of **1** and **6** results from rehybridization of the former imine carbon atom (C(2)) from sp² to sp³.

After the cycloaddition reaction, the two diastereomers of **4** and **7** show different chemical shifts for most of their corresponding carbon nuclei. However, the general appearance of the partial spectra of each diastereomer resembles the general pattern of the bicyclo [2.2.2] complexes that have been described in previous parts of this series of articles. The resonance of the intact imine carbon atom C(1) is shifted downfield from ca. 143 ppm in **6k** to ca. 170 ppm in **7**, while the former imine carbon atom C(2) is shifted upfield to ca. 56 ppm as a consequence of its rehybridization from sp² to sp³. The resonances of the former acetylene sp-hybridized carbon atoms are different as a consequence of the cycloaddition reaction. The CO ligands in the complexes **4**, **5**, and **7** give three separate resonances, which indicates rigidity around the iron atom on the NMR time scale. The chemical shift of the terminal CO ligands depends on the choice of the additional ligand. The stronger σ-donation of (*S*)-α-methylbenzyl isocyanide, *t*-Bu-NC, and P(OMe)₃ as opposed to CO causes a downfield shift with respect to the tricarbonyl complexes.

The reductive elimination of **4k** to **5k** has the following spectroscopic consequences. Complexes **5** have ppm values for their carbonyl resonances higher than those of complexes **4**. The reason is the change in oxidation state from Fe(II) (**4**) to Fe(0) (**5**). This causes a decrease in σ-donation/increase of π-acceptance from the CO ligands to the metal in **5**. The former acetylenic carbon nuclei (C(10)) resonate around 190.5 ppm in complexes **4k**, while in complexes **5** they are found at 54–74 ppm, because only in **4k** is C(10) is σ-bonded to the iron atom. Also, the chemical shift of the bridgehead carbon nuclei C(2) is influenced by this reductive elimination, by an upfield shift of approximately 10 ppm in **5ks**.

As in the ¹H NMR spectra, comparison of the ¹³C NMR spectra of compounds **5** and **8** very clearly shows the loss of the metal fragment in **8**. Not only are the Fe(CO)₃ carbonyl resonances absent in **8** but also the olefinic carbon atoms C(9) and C(10) are shifted to lower field by circa 70 ppm, indicating that the olefinic π-bond in the pyrrolinone ring is no longer coordinated.

IR Spectroscopy. The IR data of complexes **1** and **4–8** together with the elemental analyses and FAB mass spectral data are collected in Tables 15 and 16.

X-ray Structure Determination of 5cks. A yellow crystal with approximate dimensions $0.03 \times 0.70 \times 0.80 \text{ mm}^3$ was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu K α radiation and ω - 2θ scan. A total of 5036 unique reflections was measured within the ranges $0 \leq h \leq 9$, $0 \leq k \leq 14$, $-30 \leq l \leq 30$. Of these, 3546 were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin \theta)/\lambda$ used was 0.61 \AA^{-1} . Two reference reflections (032, 1,1,-5) were measured hourly and showed no decrease during the 60 h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $80 \leq 2\theta \leq 86^\circ$. Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods. After isotropic refinement a ΔF synthesis revealed three peaks, which could be interpreted as dichloromethane, one of the solvents used in the crystallization of the compound. The hydrogen atoms were calculated. Full-matrix least-squares refinement on F , anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, with the latter restrained in such a way that the distance to their carrier atoms remained constant at approximately 1.09 \AA , converged to $R = 0.087$, $R_w = 0.113$, and $(\Delta/\sigma)_{\text{max}} = 0.69$. An empirical absorption correction (DIFABS)¹⁹ was applied, with coefficients in the range of 0.71–1.64. The secondary isotropic extinction coefficient²⁴ was refined to $E_{\text{ct}} = 0.07(2)$. A final difference Fourier map revealed a residual electron density between -0.9 and 1.1 e \AA^{-3} in the vicinity of the heavy atom. Scattering factors were from Cromer and Mann.²⁵ The anomalous scattering of Fe was taken into account. All calculations were performed with XTAL,²⁶ unless stated otherwise. Crystal data and numerical details of the structure determination are given in Table 17.

X-ray Structure Determination of 7aks. Crystals were grown from a saturated $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (3:1) solution at -20°C . A crystal with approximate dimensions $0.20 \times 0.25 \times 0.75 \text{ mm}^3$ was mounted on a Lindemann-glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Crystals were found to reflect poorly, with broad, structured reflection profiles. Accurate unit-cell parameters and an orientation matrix were determined from the setting angles of 25 well-centered reflections (SET4) in the range $9.8^\circ < \theta < 13.8^\circ$. The unit-cell parameters were checked for the presence of higher lattice symmetry.¹⁸ Crystal data and details on data collection and refinement are shown in Table 17. Data were corrected for Lp effects. An empirical absorption/extinction correction was applied (DIFABS¹⁹ as implemented in PLATON²⁰). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).²¹ Re-

finement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93²²); no observance criterion was applied during refinement. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter amounting to 1.5 and 1.2 times the value of the equivalent isotropic thermal parameter of their carrier atoms, for the methyl hydrogen atoms and all other hydrogen atoms, respectively. Weights were optimized in the final refinement cycles. The structure contains a small void of 31 \AA^3 at 0.146, 0.727, 0.328. However, no significant residual density was found in that area (PLATON/SQUEEZE²³). Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 28.

X-ray Structure Determination of 8als. A colourless crystal ($0.20 \times 0.40 \times 0.80 \text{ mm}^3$, cut to size) was mounted on a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD-4F diffractometer. Accurate unit cell parameters and an orientation matrix were determined from the setting angles of 25 reflections (SET4)¹⁷ in the range $17.8^\circ < \theta < 23.5^\circ$. Reduced-cell calculations did not indicate higher lattice symmetry.¹⁸ In Table 17 crystal data and details on data collection and refinement are shown. Data were corrected for Lp effects and for a linear decay of 1% of the periodically measured reference reflections. The structure was solved by automated direct methods (SHELXS86).²⁷ Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93);²² no observance criterion was applied during refinement. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and a factor of 1.2 for the other hydrogen atoms. It was not possible to determine the correct enantiomer through the final Flack absolute structure parameter (0.47(18)). In four voids in the unit cell of an area of 179 \AA^3 an electron count was encountered (PLATON/SQUEEZE),^{20,21} probably diethyl ether. Weights were optimized in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 28. Geometrical calculations and illustrations were performed with PLATON;¹⁹ all calculations were performed on a DEC5000/125.

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Supporting Information Available: Tables giving full details of crystallographic parameters, final coordinates, thermal parameters, bond distances, bond angles, and torsion angles (except for 5cks) for 4aks, 5cks, 7aks, and 8als (32 pages). Ordering information is given on any current masthead page.

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