Highly Stereoselective Total Synthesis of Multiply Protected 3-Amino-3,6-dideoxyaldohexoses (Mycosamine/Mycaminose) by Aldol Condensation Reaction, Mediated by Tin Triflate, of Tricarbonyliron/α-Aminodienone Complexes

Michel Franck-Neumann,*[a] Laurence Miesch-Gross,[a] and Christelle Gateau[a]

Keywords: Aldol reactions / Amino sugars / Enones / Mycosamine / Mycaminose / Tin / Total synthesis

The divalent tin enol ether of the racemic complex between *N*-BOC-α-aminoheptadienone and tricarbonyliron reacts with both enantiomers of protected lactaldehydes to yield predominantly one optically active, easily isolable ketol diastereoisomer (45%). From the enantiomerically pure (*S*)-(+) complex and (*R*)-(+)-*tert*-butyldimethylsilyloxylactaldehyde, the major ketol is obtained almost exclusively (isolated yield 86%). From there, the multiply protected 3-amino-3,6-dideoxy-D-aldohexose mycosamine is obtained in a few high-yield steps (decomplexation, stereospecific reduction to an *anti*-1,3-diol, transformation into a diacetate and ozonolysis; absolute configurations *S*,*S*,*S*,*R*). Reduction of the ketol before decomplexation completely reverses the stereochemistry of the reaction [control by the $Fe(CO)_3$ and not by the hydroxy group → *syn*-diol], also giving access to the (*R*,*S*,*S*,*R*) series (configuration of the *N*,*N*-dimethylated mycaminose). The key structures were determined by X-ray diffraction.

Introduction

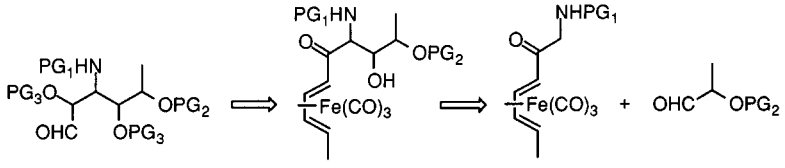
3-Amino-3,6-dideoxyaldohexoses constitute a widespread class of amino sugars. As constituents of polysaccharides or polyenic macrolides, these glucose, galactose, or mannose derivatives are important targets for synthetic investigations.[1] Among them, mycosamine (3-amino-3,6-dideoxymannose) has been obtained by hydrolysis of the polyene antifungal antibiotics amphotericin B, flavumycin A, nystatin, and pimaricin, and of several heptaene antifungal macrolides of unknown structure, such as levorin B, heptafungin A, and aureofuscin.

To the best of our knowledge, the synthesis of derivatives of mycosamine has been reported only once, by Nicolaou et al. in their total synthesis of amphotericin B.[3] Starting from a readily available glucose derivative[4] (3 steps from the commercial methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, 27%), the synthesis of a mycosamine equivalent was achieved in 14 steps in 29% overall yield.[5]

We report here a quite different and shorter approach to mycosamine. It does not use a natural sugar as starting material, but involves a highly diastereoselective crossed aldol condensation reaction between an α-aminodienone/tricarbonyliron complex (chiral equivalent of the synthon **A**) and (*R*)-(+)-*tert*-butyldimethylsilyloxylactaldehyde (Scheme 1):

After the crossed aldol condensation reaction, multiply protected 3-amino-3,6-dideoxy sugars should be accessible by reduction of the keto carbonyl group adjacent to the diene unit, protection of the alcohol functions, decomplexation and ozonolysis.

With an optically pure lactaldehyde, this aldol condensation reaction could lead to a maximum of eight diastereoisomers. If it is to be synthetically valuable, therefore, it must be highly stereoselective. For a time we have been interested in crossed aldol condensation reactions between aldehydes and dienone/tricarbonyliron complexes,[6] and we were able to verify that the trimethylsilyl enol ether of 3,5-heptadien-2-one/tricarbonyliron undergoes a highly stereoselective crossed aldol condensation reaction with $TiCl_4$-coordinated benzyloxylactaldehyde, yielding only two, separable diastereomeric ketols.[7] This, when using an optically active lactaldehyde, means a resolution of the complex.



Scheme 1. Retrosynthetic scheme for the synthesis of aminodideoxyaldohexoses using tricarbonyliron/dienone complexes

[a] Laboratoire de Chimie Organique Synthétique, associé au CNRS, Institut de Chimie, Université Louis Pasteur, 67000 Strasbourg, France
Fax: (internat.) + 33-3/88604248
E-mail: franckneu@chimie.u-strasbg.fr

  1434−193X/00/1122−3693 $ 17.50+.50/0

This was very useful for the synthesis, with high levels of *ee*, of chiral polyols such as deoxypentoses and dideoxyhexoses.[8] However, we observed that the crossed aldol condensation reactions of silyl enol ethers of α-aminodienone/tricarbonyliron complexes with α-hydroxy aldehydes were unsuccessful in the presence of $TiCl_4$. Therefore we investigated other reaction conditions, and rapidly found that divalent tin enolates of α-aminodienone/tricarbonyliron complexes were well suited for such aldol condensation reactions.

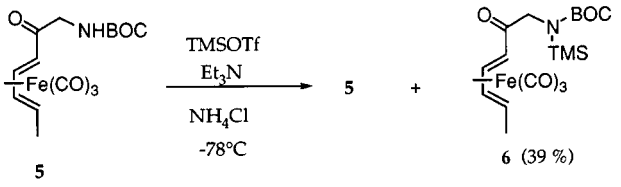
Results and Discussion

We first had to synthesize the protected α-amino ketone complex **5**, starting from the readily available dienone complex **1**.[9] However, the electrophilic amination of the lithium enolate or silyl enol ethers of this ketone, using lithium *tert*-butyl-*N*-tosyloxycarbamate (LiBTOC), according to Genet's procedure,[10,11] was unsuccessful.[12] The synthesis of an *N*-BOC-protected α-aminodienone by direct substitution of the bromine atom of the known bromodienone complex **2** by a *tert*-butylcarbamate group also failed. Therefore, we attempted the synthesis via an azide, but substitution of the bromodienone complex **2** with sodium azide in DMF led only to degradation products of the starting material. The required azide **3** was finally obtained only when the S_N2 displacement of the bromine atom with sodium azide was carried out in the presence of 15-crown-5 ether.[5] However, when the azide was subjected to catalytic hydrogenation with Pd/C, no reaction was observed. This was probably due to the presence of the tricarbonyliron group, with its well-known poisoning effect on catalytic hydrogenations.

Treatment of the azide **3** with conventional reducing agents such as $NaBH_4$, $LiAlH_4$, and DIBAL[13,14] did not yield the expected amine, but exclusively gave the secondary alcohol **4**. Conversion of the azide into an amine by using triphenylphosphane[15] was also tried, but even with the modified procedure of Carrié,[16] only the unsubstituted dienone complex was obtained, with no starting azide being recovered.[17]

The problem of the transformation of the azide into an amine could finally be overcome by following Saito's procedure,[18] using catalytic hydrogenation of the azide **3** under pressure (15 bar) in the presence of BOC_2O. Under these conditions, the desired BOC-protected aminodienone complex **5** was obtained in high yield (97%, Scheme 2).

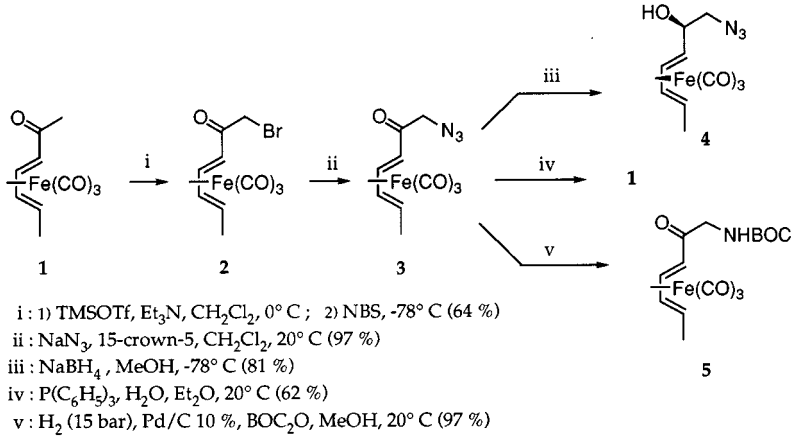
Initial attempts to achieve a $TiCl_4$-mediated aldol condensation reaction of silyl enol ethers of the α-aminodienone complex **5** failed, because of a critical degradation of the aminosilyl enol ether formed in situ. Moreover, treatment of the complex **5** with TMSOTf in the presence of NEt_3, followed by direct workup, produced only 22% of amino ketone **5** (hydrolysis), along with 39% of the *N*-silylated derivative **6** (Scheme 3).



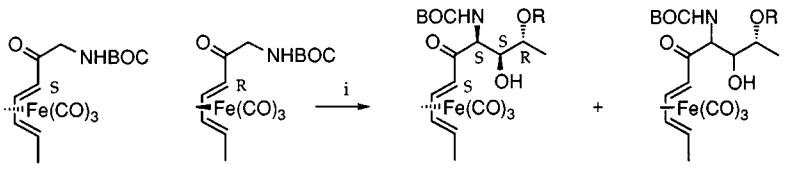
Scheme 3. Synthesis of the N-silylated derivative **6**

We then turned our attention to the procedure developed by Mukayiama et al.,[19] who showed that divalent tin enolates, in the presence of amines, display enhanced reactivity in aldol condensation reactions.[19] In particular, use of *N*-ethylpiperidine as a base led to highly diastereoselective crossed aldol condensation reactions.[20]

Indeed, the addition of protected (*R*)-lactaldehyde to the tin enolate of racemic amino ketone **5** in the presence of *N*-ethylpiperidine led in good yield to a mixture of four diastereomeric ketols. The major diastereomer (+)-**7** (45%) could easily be separated from the others (**8a**−**c**) by simple silica gel column chromatography (Scheme 4). Even if the yield of this product does seem rather low, one should bear in mind that the highest possible yield of a ketol as a resolved diene complex, starting from a racemic α-aminodienone, is 50%. Furthermore, out of eight possible ketols, only four were observed and, most importantly, this aldol condensation reaction mainly gave rise to one optically pure diastereomer which already included three of the four ste-



Scheme 2. Synthesis of azide **3** and amino ketone **5**



(*S*)-(+)-**5** (*R*)-(-)-**5** (+)-**7** **8a-c**

i : Sn $(OTf)_2$, N-ethylpiperidine, (R)-(+)-CH_3-CHOR-CHO

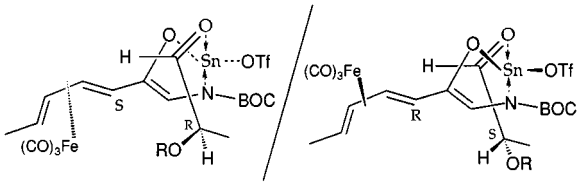
(±)-**5**	R = Me_2tBuSi	45 %	48 %
(±)-**5**	R = $C_6H_5CH_2$	46 %	47 %
(*S*)-(+)-**5**	R = Me_2tBuSi	86 %	< 1 %

Scheme 4. Crossed aldol condensation reaction between amino ketone **5** and protected (*R*)-lactaldehyde

reogenic centres present in the natural amino sugars. The structures of these complexes were determined by X-ray analysis of their corresponding acetates (vide infra).

When the aldol condensation was performed with the optically pure α-amino ketone (*S*)-(+)-**5**, the corresponding ketol (+)-**7** was obtained in 86% yield, along with less than 1% of a mixture of the other three diastereomers **8a**−**c**.

The good diastereoselectivity observed here probably results from favourable features in divalent tin(II) Lewis acids.[21] These, with their vacant d orbitals, are known to form complexes with amines,[22] and to have a good affinity towards oxygen atoms. Hence, the metal ion may be coordinated to the chiral aldehyde and to the nitrogen-containing moiety of the tin enolate. The enolate then attacks the aldehyde from the less hindered side (opposite to the iron centre), to produce mainly the aldol (+)-**7** (Scheme 5).



Scheme 5. Intermediates for the aldol reaction, mediated by tin triflate, with the protected (*R*)-(+)-lactaldehyde

To generate the last stereogenic centre present in the natural aminopolyols, the carbonyl group of the complexed dienone (+)-**7** has to be reduced. This reduction can be controlled stereochemically either by the tricarbonyliron unit or, after decomplexation, by the hydroxy group in the β-position.

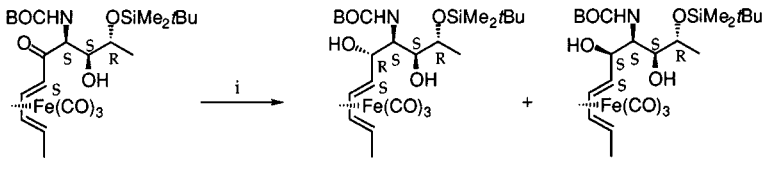
When the iron-complexed dienone (+)-**7** was treated with BH_3·SMe_2, the reduction proceeded from the side opposite to the metal centre, with the "enone" mainly in the *s-cis* conformation, affording the less polar ψ-*endo*-alcohol (−)-**9** in 70% yield, along with 17% of the easily separable ψ-*exo*-alcohol (−)-**10** (Scheme 6).[23]

Even with tetramethylammonium triacetoxyhydridoborate, known for converting β-hydroxy ketones into *anti*-1,3-diols,[24] we obtained nearly the same quantities of both isomers [39% ψ-*endo*-alcohol (−)-**9**; 35% ψ-*exo*-alcohol (−)-**10**] when the reaction was carried out in acetonitrile/acetic acid at −20° C. When it was carried out at room temperature, the yield of ψ-*exo*-alcohol (−)-**10** could be increased to 67%, but the ψ-*endo*-alcohol was still present.

Both diols (−)-**9** and (−)-**10** were protected as diacetates (Scheme 7). Single crystals of both diacetates (+)-**11** and (+)-**12** were obtained and their structures were determined by X-ray diffraction.

This allowed us to establish unambiguously that the absolute configurations of the compounds (+)-**11** and (+)-**12** were (*SRSSR*) and (*SSSSR*), respectively.

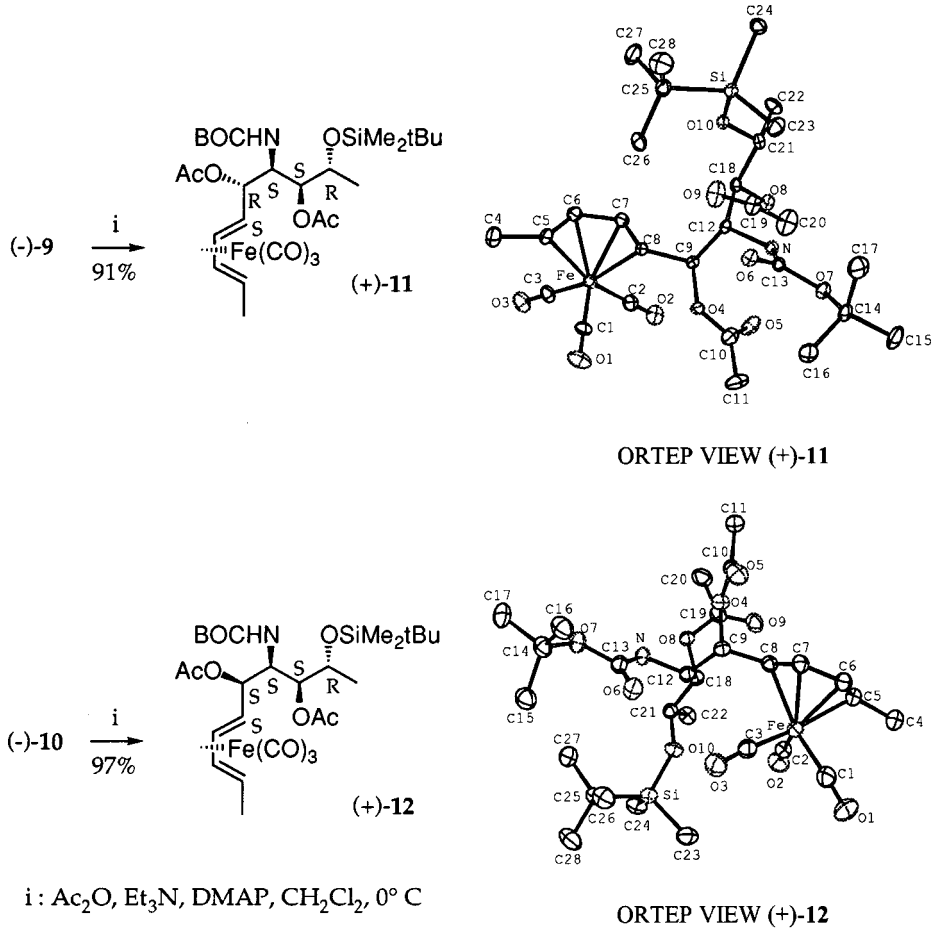
Cleavage of the diene moiety into a formyl group was achieved by decomplexation [→ dienes (+)-**13** and (+)-**14**] followed by ozonolysis (Scheme 8), finally giving the protected 3-amino-3,6-dideoxyglucose (−)-**15** and the multiply protected mycosamine (−)-**16**. Decomplexation was best per-



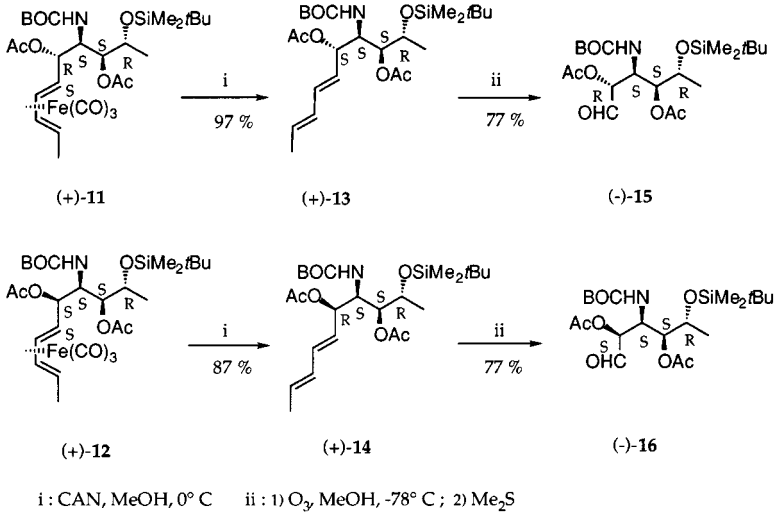
(+)-**7** (-)-**9** (-)-**10**

i : BH_3, Me_2S, THF, 20° C	70 %	17 %
i : $Me_4NBH(OAc)_3$, CH_3CN/AcOH, -20° C	39 %	30 %
i : $Me_4NBH(OAc)_3$, CH_3CN/AcOH, 20° C	18 %	67 %

Scheme 6. Reduction of the complexed dienone (+)-**7** with BH_3Me_2S and $Me_4NBH(OAc)_3$



Scheme 7. Diacetylation of (−)-**9** and (−)-**10** and X-ray structures of compounds (+)-**11** and (+)-**12**

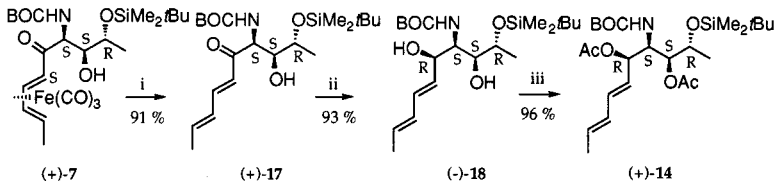


Scheme 8. Synthesis of 3-amino-3,6-dideoxyglucose (−)-**15** and multiply protected mycosamine (−)-**16**

formed using cerium(IV) ammonium nitrate (CAN)[25] in methanol at 0° C (yield 97%). The ozonolysis was performed in MeOH at −78° C, followed by reduction with Me_2S.

The diene (+)-**14** could be obtained exclusively if decomplexation was carried out before the reduction. Indeed, after decomplexation of the ketol (+)-**7**, the dienone (+)-**17** was reduced with $Me_4NBH(OAc)_3$ to give *anti*-diol-1,3 (−)-**18** as the sole product, in nearly quantitative manner (Scheme 9). Acetylation provided the diacetate (+)-**14**, already obtained from the complex (+)-**12**.

By using the same strategy and carrying out the cross aldol reaction with protected hydroxyaldehydes of (*S*) configuration, the enantiomers of each amino sugar were also obtained.



Scheme 9. High-yield synthesis of diene (+)-**14** by reduction of the dienone after decomplexation

In conclusion, we could show that tricarbonyliron/diene complexes are well suited for the synthesis of such optically active amino sugars, obtained with high enantiomeric purity. In this context, the possibility of completely reversing the stereochemistry of the reduction after the crossed aldol condensation, by performing this step either on the complex or only after decomplexation, is highly advantageous.

Experimental Section

All reactions with air- and moisture-sensitive compounds were performed under argon ain flame-dried glassware. All solvents were purified and dried prior to use. THF was distilled from sodium/benzophenone, dichloromethane from phosphorus pentoxide and methanol from magnesium. $Sn(OTf)_2$ was prepared according to a literature procedure.[26] − Thin layer chromatography for monitoring of the reactions was performed on Merck 60 F_{254} silica gel plates; compounds were visualized with UV light and vanillin/H_2SO_4 solution. Products were purified by chromatography on silica gel 60 (0.063−0.200 mm, E. Merck). − Melting points were measured with a Reichert hot stage microscope and are reported uncorrected. − Optical rotations were measured with a Perkin−Elmer 241 polarimeter. − IR spectra were determined in solution with a Perkin−Elmer 881 spectrometer in an NaCl cell. − NMR spectra were recorded in $CDCl_3$ with Bruker AC 200 or AM 400 spectrometers. Chemical shifts are reported in ppm on the δ scale with $CHCl_3$ as reference (δ = 7.26 for ^{1}H NMR spectra; δ = 77.0 for ^{13}C NMR spectra). ^{1}H NMR spectroscopic data are presented in the following manner: multiplicity (abbreviations: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; br., broad peak); coupling constant(s) in Hertz, number of protons. Assignment DEPT experiments served to determine the substitution pattern of ^{13}C NMR signals. − Mass spectra were measured with a VG analytical ZAB-HF apparatus in the FAB mode, using *m*-nitrobenzyl alcohol as matrix substance. − Elemental analyses were performed by the Service de Microanalyse du Centre de Recherche Chimie (ULP Strasbourg). − High pressure liquid chromatography was performed with the following set-up: Rheodyne injector 7125, Waters 600E multisolvent delivery system, Waters 486 tuneable absorbance detector, Waters 746 data module, Gibson FC203B fraction collector. The columns used were Zorbax ODX, size 6.5 × 280 mm, run at 3.5 mL/min for reversed phase (RP) HPLC, and Chiralcel OJ, size 4.6 × 250 mm, 10 mM, run 1.0 mL/min, detection DAD 250 mm.

Azide 3: α-Bromo ketone **2** (2.00 g, 6.1 mmol) in CH_2Cl_2 (30 mL) was added dropwise to a suspension of sodium azide (5.93 g, 91.2 mmol) and 15-crown-5 (1.34 g, 6.1 mmol) in CH_2Cl_2 (40 mL). After stirring for 3 h at room temperature, the mixture was filtered through a pad of Celite. The solvent was removed in vacuo and the residue (4.12 g) was purified by chromatography (40 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 88:12), yielding azide **3** (1.72 g, 97%). − IR (CCl_4): $\tilde{\nu}$ = 2108, 2063, 2004, 1989, 1679 cm^{-1}. − ^{1}H NMR (200 MHz): δ = 1.18 (dd, *J* = 8.0, 0.9 Hz, 1 H, H diene), 1.46 (d, *J* = 5.9 Hz, 3 H, CH_3), 1.45−1.70 (m, 1 H, H diene), AB signal (δ_A = 3.78, δ_B = 3.88, J_{AB} = 17.4, Δν = 7.5, 2 H, CH_2), 5.26 (dd, *J* = 8.5, 5.0 Hz, 1 H, H diene), 5.82 (ddd, *J* = 8.0, 5.0, 1.0 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 19.2, 49.1, 57.2, 60.1, 80.8, 89.5, 199.5.

Amino Ketone 5: A solution of azide **3** (0.150 g, 0.52 mmol) in MeOH (12 mL) was hydrogenated under reduced pressure (15 bar) for 24 h in the presence of 10% Pd/C (0.131 g) and BOC_2O (0.337 g, 1.55 mmol). After filtration to remove the catalyst and concentration in vacuo, the residue (0.342 g) was purified by chromatography (15 g, hexane/ethyl acetate gradient from 100:0 to 90:10), yielding protected amino ketone **5** (0.184 g, 97%) as a yellow solid; m.p. 90−91 °C. − IR (CCl_4): $\tilde{\nu}$ = 3432, 2063, 2003, 1988, 1721, 1687 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.12 (d, *J* = 7.9 Hz, 1 H, H diene), 1.35−1.65 (m, 1 H, H diene), 1.42 (s, 9 H, BOC), 1.46 (d, *J* = 5.9 Hz, 3 H, CH_3), 3.94 (d br., *J* = 4.7 Hz, 2 H, CH_2), 5.20−5.30 (m, 1 H, NH), 5.25 (dd, *J* = 8.1, 5.1 Hz, 1 H, H diene), 5.82 (dd, *J* = 8.0, 5.1 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 19.1, 28.3, 49.8, 50.0, 59.7, 79.9, 81.0, 89.0, 155.5, 200.4. − $C_{15}H_{19}FeNO_6$ (365.2): calcd. C 49.34, H 5.24, N 3.84; found C 49.62, H 5.48, N 3.82. − Similarly, the optically active complex (*S*)-(+)-**5** {$[\alpha]_D$ = +218 (*c* = 1; $CHCl_3$); *ee* = 98%; HPLC: Chiralcel OJ, isohexane/*i*PrOH} was obtained from the nearly enantiomerically pure dienone complex (*S*)-(+)-**1** {$[\alpha]_D$ = +395 (*c* = 1, $CHCl_3$)},[6] via the bromodienone complex (*S*)-(+)-**2** {$[\alpha]_D$ = +242 (*c* = 1.2, $CHCl_3$)}.

***N*-Silylated Derivative 6:** Triethylamine (0.09 mL, 0.066 g, 0.66 mmol) and trimethylsilyl trifluoromethanesulfonate (0.11 mL, 0.134 g, 0.60 mmol) were added to a solution of amino ketone **5** (0.100 g, 0.27 mmol) in CH_2Cl_2 (10 mL) at −78 °C. After stirring for 1 h at −78 °C, the reaction was quenched by adding saturated aqueous NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2, then with ether. The combined organic extracts were washed with brine, dried with $MgSO_4$, and the solvent was evaporated. The crude product (0.188 g) was purified by chromatography (15 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 80:20), yielding compound **6** (0.047 g, 39%) and amino ketone **5** (0.022 g, 22%). − IR (CCl_4): $\tilde{\nu}$ = 2065, 2005, 1987, 1724, 1687 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.23 [s, 9 H, $Si(CH_3)_3$], 1.15−1.30 (m, 1 H, H diene), 1.45−1.65 (m, 1 H, H diene), 1.45 (s, 9 H, BOC), 1.47 (d, *J* = 6.0 Hz, 3 H, CH_3), AB signal (δ_A = 3.79, δ_B = 4.09, J_{AB} = 17.9 Hz, Δν = 65.9, 2 H, CH_2), 5.24 (dd, *J* = 7.4, 5.0 Hz, 1 H, H diene), 5.80 (dd, *J* = 8.4, 5.0, 1 H, H diene).

Ketol (−)-7 (R = SiMe$_2$*t*Bu): A solution of the racemic amino ketone **5** (1.340 g, 3.7 mmol) in CH_2Cl_2 (20 mL) was added dropwise at −78 °C to a solution of $Sn(OTf)_2$ (3.370 g, 8.1 mmol) and *N*-ethylpiperidine (1.21 mL, 8.1 mmol) in CH_2Cl_2 (20 mL). After stir-

ring for 2 h at −78 °C, a solution of the protected (*S*)-(−)-lactaldehyde (1.04 g, 5.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The solution was stirred at −78 °C for 2 h, then for 3 h at −30 °C. The reaction was quenched by adding a saturated aqueous $NaHCO_3$ solution. After filtration through a pad of Celite, the aqueous layer was extracted with CH_2Cl_2 and Et_2O. The combined organic extracts were washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. The residue (3.500 g) was purified by chromatography (80 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 80:20) to afford aldol product (−)-**7** (R = SiMe_2tBu) (0.883 g, 43%) and a mixture of three diastereomers (0.953 g, 46%). − (−)-**7** (R = SiMe_2tBu): $[\alpha]_D$ = −41.9 (*c* = 0.8, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3428, 3380 (br.) 2062, 2000, 1986, 1718, 1670 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 6 H, $SiMe_2$), 0.89 (s, 9 H, Si*t*Bu), 1.15−1.35 (m, 1 H, H diene), 1.20 (d, *J* = 5.7 Hz, 3 H, CH_3), 1.40−1.55 (m, 4 H, H diene + CH_3), 1.44 (s, 9 H, BOC), 2.23 (s br., 1 H, OH), 3.75−3.90 (m, 2 H, CH × 2), 4.30 (d br., *J* = 7.4 Hz, 1 H, CH), 5.26 (dd, *J* = 8.2, 4.8 Hz, 1 H, H diene), 5.43 (d br., *J* = 8.6 Hz, 1 H, NH), 5.80 (dd, *J* = 8.1, 5.1 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.0, −4.1, 17.9, 19.1, 20.0, 25.9, 28.3, 50.5, 59.2, 59.9, 68.4, 74.4, 80.0, 81.6, 89.2, 156.2, 206.3. − $C_{24}H_{39}FeNO_8Si$ (553.5): calcd. C 52.08, H 7.10, N 2.53; found C 52.33, H 7.14, N 2.53.

Ketol (+)-7 (R = SiMe_2tBu): In analogy with the previous procedure, the aldol reaction of the racemic amino ketone **5** (0.200 g, 0.55 mmol) with the protected (*R*)-(+)-lactaldehyde (0.155 g, 0.82 mmol) yielded the aldol product (+)-**7** (R = SiMe_2tBu) (0.139 g, 45%) and a mixture of three diastereomers (0.148 g, 48%). (+)-**7** (R = SiMe_2tBu): $[\alpha]_D$ = +41.5 (*c* = 1.0, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3441, 3320 (br.) 2067, 2012, 1986, 1717, 1668 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 3 H, $SiCH_3$), 0.08 (s, 3 H, $SiCH_3$), 0.89 (s, 9 H, Si*t*Bu), 1.17−1.23 (m, 1 H, H diene), 1.20 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.41−1.51 (m, 1 H, H diene), 1.44 (s, 9 H, BOC), 1.47 (d, *J* = 6.2 Hz, 3 H, CH_3), 2.24 (s br., 1 H, OH), 3.81 (quint, *J* = 6.4 Hz, 1 H, CH), 3.76−3.90 (m, 1 H, CH), 4.25−4.35 (m, 1 H, CH), 5.26 (dd, *J* = 8.6, 4.8 Hz, 1 H, H diene), 5.39−5.49 (m, 1 H, NH), 5.80 (dd, *J* = 7.8, 4.8 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.2, 17.9, 19.1, 20.0, 25.9, 28.3, 50.5, 59.2, 59.9, 68.4, 74.4, 79.7, 81.6, 89.2, 155.9, 206.0. − $C_{24}H_{39}FeNO_8Si$ (553.5): calcd. C 52.08, H 7.10, N 2.53; found C 52.33, H 7.14, N 2.53.

Ketols 9 (3 Diastereomers): IR (CCl_4): $\tilde{\nu}$ = 3449, 3300 (br.) 2059, 2000, 1986, 1717, 1669 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$), 0.08 (s, 3 H, $SiCH_3$), 0.09 (s, 3 H, $SiCH_3$), 0.10 [s, 6 H, $Si(CH_3)_2$], 0.85 [s, 9 H, $SiC(CH_3)_3$], 0.89 [s, 9 H, $SiC(CH_3)_3$], 0.91 [s, 9 H, $SiC(CH_3)_3$], 1.15−1.30 (m, 5 H, CH_3, H diene), 1.20 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.40−1.65 (m, 5 H, CH_3, H diene), 1.41 (s, 9 H, BOC), 1.45 (s, 9 H, BOC), 1.46 (s, 9 H, BOC), 3.50−3.65 (m, 3 H, CH), 4.25−4.50 (m, 2 H, CH), 5.26 (dd, *J* = 8.8, 5.1 Hz, 1 H, H diene), 5.27 (dd, *J* = 8.6, 4.9 Hz, 1 H, H diene), 5.35−5.55 (m, 2 H, NH), 5.75−5.90 (m, 2 H, H diene). − $C_{24}H_{39}FeNO_8Si$ (553.5): calcd. C 52.08, H 7.10, N 2.53; found C 52.17, H 7.00, N 2.51.

Ketol (+)-7 (R = SiMe_2tBu): Analogously to the previous procedure, the aldol reaction of the nearly optically pure (*ee* = 98%) complex (*S*)-(+)-**5** (0.250 g, 0.68 mmol) with the protected (*R*)-(+)-lactaldehyde (0.193 g, 1.03 mmol) yielded the aldol product (+)-**7** (R = SiMe_2tBu) (0.326 g, 86%) and a mixture of three diastereomers (0.003 g, 0.9%). − $[\alpha]_D$ = +46.5 (*c* = 1.0, $CHCl_3$).

Ketol (−)-7 (R = Bn): Analogously to the previous procedure, the aldol reaction of the amino ketone **5** (0.090 g, 0.25 mmol) with the protected (*R*)-(+)-benzyloxypropanal (0.061 g, 0.37 mmol) yielded the aldol product (−)-**7** (R = Bn) (0.061 g, 46%) and a mixture of three diastereomers (0.062 g, 47%). − $[\alpha]_D$ = −17.9 (*c* = 1.1, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3420 (br.), 3419, 2060, 2000, 1986, 1716, 1668 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.20−1.35 (m, 1 H, H diene), 1.29 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.40−1.55 (m, 4 H, H diene + CH_3), 1.47 (s, 9 H, BOC), 2.48 (s br., 1 H, OH), 3.54 (dq, *J* = 7.8, 6.0 Hz, 1 H, CH), 3.90−4.05 (m, 1 H, CH), AB signal (δ_A = 4.42, δ_B = 4.56, J_{AB} = 10.7 Hz, Δν = 26.9, 2 H, CH_2), 4.50−4.70 (m, 1 H, CH), 5.26 (dd, *J* = 8.3, 5.2 Hz, 1 H, H diene), 5.46 (d br., *J* = 8.9 Hz, 1 H, NH), 5.78 (dd, *J* = 8.0, 5.1 Hz, 1 H, H diene), 7.25−7.40 (m, 5 H, C_6H_5). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = 16.2, 19.1, 28.3, 50.6, 59.6, 71.5, 73.4, 74.9, 79.9, 81.6, 89.3, 127.7, 128.2, 128.4, 156.0, 206.2. − $C_{25}H_{31}FeNO_8Si$ (529.4): calcd. C 56.72, H 5.90, N 2.65; found C 56.91, H 5.83, N 2.68.

Dienone (−)-17: A solution of CAN (0.990 g, 1.81 mmol) in MeOH (3 mL) was added at 0 °C to a solution of complex (−)-**7** (R = SiMe_2tBu) (0.200 g, 0.36 mmol) in MeOH (2 mL). After 1 h at 0 °C, the reaction was quenched by adding saturated aqueous $NaHCO_3$ solution. After filtration of the mixture through a pad of Celite, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water and brine and dried with $MgSO_4$, and the solvent was evaporated. The crude product (0.173 g) was purified by chromatography (15 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 92:8), yielding diene (−)-**17** (0.133 g, 89%) as a colourless oil. − $[\alpha]_D$ = −2.6 (*c* = 1.2, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3420, 3437, 1718, 1637 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.09 (s, 6 H, $SiMe_2$), 0.91 (s, 9 H, Si*t*Bu), 1.23 (d, *J* = 5.9 Hz, 3 H, CH_3), 1.42 (s, 9 H, BOC), 1.87 (d, *J* = 4.7 Hz, 3 H, CH_3), 2.62 (d br., *J* = 3.6 Hz, 1 H, OH), 3.60−3.80 (m, 1 H, CH), 3.81 (dq, *J* = 7.4, 6.0 Hz, 1 H, CH), 4.73 (d br., *J* = 7.9 Hz, 1 H, CH), 5.49 (d br., *J* = 7.1 Hz, 1 H, NH), 6.20−6.35 (m, 3 H, H diene × 3), 7.20−7.40 (m, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.0, −4.1, 17.9, 18.9, 20.3, 25.9, 28.3, 57.6, 68.5, 75.0, 79.7, 124.6, 130.5, 141.7, 145.1, 155.8, 199.9. − $C_{21}H_{39}NO_5Si$ (413.6): calcd. C 60.98, H 9.50, N 3.39; found C 60.95, H 9.52, N 3.16.

Dienone (+)-17: A solution of CAN (1.98 g, 3.6 mmol) in MeOH (10 mL) was added at 0 °C to a solution of complex (+)-**7** (R = SiMe_2tBu) (0.400 g, 0.72 mmol) in MeOH (10 mL). After 1 h at 0 °C, the reaction was quenched by adding saturated aqueous $NaHCO_3$ solution. After filtration of the mixture through a pad of Celite, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water and brine and dried with $MgSO_4$, and the solvent was evaporated. The crude product (0.417 g) was purified by chromatography (15 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 92:8), yielding diene (+)-**17** (0.273 g, 91%) as a colourless oil. − $[\alpha]_D$ = +3.0 (*c* = 0.8, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3437, 3420 (br.), 1718, 1637 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.09 (s, 6 H, $SiMe_2$), 0.91 (s, 9 H, Si*t*Bu), 1.23 (d, *J* = 5.9 Hz, 3 H, CH_3), 1.42 (s, 9 H, BOC), 1.87 (d, *J* = 4.8 Hz, 3 H, CH_3), 2.50 (s br., 1 H, OH), 3.60−3.80 (m, 1 H, CH), 3.82 (dq, *J* = 7.3, 5.9 Hz, 1 H, CH), 4.72 (d br., *J* = 8.0 Hz, 1 H, CH), 5.48 (d br., *J* = 7.1 Hz, 1 H, NH), 6.20−6.35 (m, 3 H, H diene × 3), 7.20−7.40 (m, 1 H, 1 diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.2, 17.9, 18.8, 20.4, 25.9, 28.3, 57.8, 68.5, 75.0, 79.5, 124.6, 130.5, 141.5, 145.0, 155.8, 200.0. − $C_{21}H_{39}NO_5Si$ (413.6): calcd. C 60.98, H 9.50, N 3.39; found C 61.07, H 9.55, N 3.20.

Diene (+)-18: A solution of dienone (−)-**17** (0.310 g, 0.75 mmol) in dry CH_3CN (5 mL) was added dropwise at −40 °C to a solution of $Me_4NBH(OAc)_3$ (0.986 g, 3.75 mmol) in dry CH_3CN (5 mL)

and AcOH (0.8 mL). The solution was stirred at −40 °C for 1 h, then for 5 h at −20 °C to −10 °C. The reaction was quenched by adding 0.25 M aqueous sodium tartrate solution. The aqueous phase was extracted with dichloromethane and diethyl ether. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ solution and brine, and dried with $MgSO_4$. The solvent was evaporated. After chromatography (15 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 90:10), diene (+)-**18** (0.300 g, 96%) was obtained. − $[\alpha]_D$ = +6.5 (*c* = 1.8, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3620, 3531, 3442, 1715 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, $SiMe_2$), 0.88 (s, 9 H, Si*t*Bu), 1.17 (d, *J* = 5.7 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 1.76 (d, *J* = 6.7 Hz, 3 H, CH_3), 2.70 (d br., *J* = 4.4 Hz, 1 H, OH), 2.97 (d, *J* = 1.8 Hz, 1 H, OH), 3.65−3.80 (m, 3 H, CH × 3), 4.45−4.60 (m, 1 H, CH), 5.39 (d br., *J* = 7.1 Hz, 1 H, NH), 5.59 (dd, *J* = 15.5, 5.8 Hz, 1 H, H diene), 5.70 (dq, *J* = 14.9, 6.7 Hz, 1 H, H diene), 6.06 (ddd, *J* = 14.9, 10.3, 1.5 Hz, 1 H, H diene), 6.30 (dd, *J* = 15.0, 10.5 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.1, 17.9, 18.1, 19.9, 25.9, 28.4, 53.6, 68.5, 73.9, 75.3, 79.3, 129.7, 129.9, 130.9, 131.8, 156.0. − $C_{21}H_{41}NO_5Si$ (415.6): calcd. C 60.63, H 9.94, N 3.37; found C 60.67, H 9.80, N 3.14.

Diene (−)-18: Following the same procedure as above, treatment of the dienone (+)-**17** (0.330 g, 0.80 mmol) with $Me_4NBH(OAc)_3$ (1.050 g, 4.0 mmol) provided compound (−)-**18** (0.309 g, 93%) as a colourless oil. − $[\alpha]_D$ = −6.9 (*c* = 1.0, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3620, 3520, 3441, 1715 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, $SiMe_2$), 0.88 (s, 9 H, Si*t*Bu), 1.17 (d, *J* = 5.7 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 1.76 (d, *J* = 6.6 Hz, 3 H, CH_3), 2.70 (d br., *J* = 4.4 Hz, 1 H, OH), 2.97 (d, *J* = 2.3 Hz, 1 H, OH), 3.65−3.80 (m, 3 H, CH × 3), 4.45−4.60 (m, 1 H, CH), 5.38 (d br., *J* = 7.4 Hz, 1 H, NH), 5.59 (dd, *J* = 15.3, 5.8 Hz, 1 H, H diene), 5.71 (dq, *J* = 14.8, 6.8 Hz, 1 H, H diene), 6.07 (ddd, *J* = 14.8, 10.5, 1.5 Hz, 1 H, H diene), 6.30 (dd, *J* = 15.7, 10.1 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.1, 17.9, 18.1, 19.8, 25.9, 28.4, 53.7, 68.6, 73.9, 75.3, 79.4, 129.6, 129.9, 130.9, 131.9, 156.1. − $C_{21}H_{41}NO_5Si$ (415.6): calcd. C 60.63, H 9.94, N 3.37; found C 60.74, H 9.73, N 3.23.

Diacetate (−)-14: To a mixture of the diene (+)-**18** (0.270 g, 0.65 mmol) in CH_2Cl_2 (10 mL) at 0 °C were added triethylamine (0.72 mL, 5.20 mmol), acetic anhydride (0.25 mL, 2.60 mmol) and DMAP (0.006 g). After stirring for 30 min, water was added and the aqueous phase was extracted with dichloromethane and diethyl ether. The combined organic extracts were washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. Flash chromatography (15 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 90:10) yielded the diacetylated product (−)-**14** (0.285 g, 87%). − $[\alpha]_D$ = −3.4 (*c* = 1.0, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3422, 1742, 1728 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.89 (s, 9 H, Si*t*Bu), 1.11 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.41 (s, 9 H, BOC), 1.72 (d, *J* = 6.4 Hz, 3 H, CH_3), 2.02 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 3.93 (quint, *J* = 6.4 Hz, 1 H, CH), 4.19 (ddd, *J* = 9.5, 7.5, 1.8 Hz, 1 H, CH), 4.80 (d br., *J* = 9.4 Hz, 1 H, CH), 4.95 (dd, *J* = 6.7, 1.8 Hz, 1 H, CH), 5.08 (t, *J* = 7.7 Hz, 1 H, NH), 5.48 (dd, *J* = 14.9, 8.2 Hz, 1 H, H diene), 5.70 (dq, *J* = 14.8, 6.7 Hz, 1 H, H diene), 5.99 (ddd, *J* = 14.9, 10.3, 1.3 Hz, 1 H, H diene), 6.23 (dd, *J* = 15.0, 10.3 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.2, 17.9, 18.1, 19.7, 21.0, 21.2, 25.9, 28.3, 51.6, 67.3, 73.8, 74.7, 79.5, 124.9, 130.5, 131.3, 135.4, 155.2, 169.7, 169.9 − $C_{25}H_{45}NO_7Si$ (499.7): calcd. C 60.09, H 9.08, N 2.80; found C 59.91, H 8.86, N 2.81.

Diacetate (+)-14: In the same way as above, the reaction of the diol (−)-**18** (0.230 g, 0.55 mmol) with triethylamine (0.62 mL, 4.43 mmol), acetic anhydride (0.21 mL, 2.21 mmol) and DMAP (0.008 g) yielded diacetylated product (+)-**14** (0.265 g, 96%). − $[\alpha]_D$ = +3.4 (*c* = 1.0, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3442, 1752, 1727 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.88 (s, 9 H, Si*t*Bu), 1.11 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.41 (s, 9 H, BOC), 1.72 (d, *J* = 6.4 Hz, 3 H, CH_3), 2.01 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 3.93 (quint, *J* = 6.4 Hz, 1 H, CH), 4.19 (ddd, *J* = 9.5, 7.5, 1.9 Hz, 1 H, CH), 4.79 (d br., *J* = 9.8 Hz, 1 H, CH), 4.95 (dd, *J* = 6.9, 1.9 Hz, 1 H, CH), 5.08 (t, *J* = 7.9 Hz, 1 H, NH), 5.48 (dd, *J* = 15.0, 8.3 Hz, 1 H, H diene), 5.70 (dq, *J* = 14.8, 6.4 Hz, 1 H, H diene), 5.99 (ddd, *J* = 14.9, 10.3, 1.3 Hz, 1 H, H diene), 6.23 (dd, *J* = 15.0, 10.1 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.3, 17.9, 18.1, 19.7, 20.9, 21.1, 25.9, 28.3, 51.5, 67.2, 73.8, 74.7, 79.5, 124.9, 130.5, 131.2, 135.4, 155.2, 169.6, 169.9. − $C_{25}H_{45}NO_7Si$ (499.7): calcd. C 60.09, H 9.08, N 2.80; found C 60.09, H 8.97, N 2.78.

Aldehyde (+)-16: Diene (−)-**14** (0.180 g, 0.36 mmol) in MeOH (15 mL) was treated at −78 °C with ozone, until the blue colour persisted. After removing excess ozone by passing a stream of argon through the solution, dimethyl sulfide (1.06 mL) was added at −78 °C and the mixture stirred at room temperature for 1 h. The solvent was removed in vacuo and the residue dissolved in ethyl acetate and washed with water and brine. The organic layer was dried with $MgSO_4$ and concentrated. Chromatography (15 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 80:20) provided the title aldehyde (+)-**16** (0.118 g, 71%). − $[\alpha]_D$ = +2.6 (*c* = 1.0, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3447, 1755, 1723 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, $SiMe_2$), 0.91 (s, 9 H, Si*t*Bu), 1.13 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 2.10 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 4.00 (quint, *J* = 6.3 Hz, 1 H, CH), 4.42 (t, *J* = 8.6 Hz, CH), 4.76 (d br., *J* = 8.8 Hz, 1 H, CH), 4.93 (d br., *J* = 6.8 Hz, 1 H, CH), 5.18 (d br., *J* = 8.2 Hz, 1 H, NH), 9.47 (s, 1 H, CHO). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.2, −4.2, 17.9, 19.9, 20.4, 20.8, 25.8, 28.2, 49.1, 67.0, 73.7, 77.1, 80.4, 155.3, 169.6, 169.9, 196.0. − $C_{21}H_{39}FeNO_8Si$ (461.6): calcd. C 54.64, H 8.52, N 3.03; found C 54.60, H 8.48, N 3.00.

Aldehyde (−)-16: Analogously to the previous procedure, treatment of diene (+)-**14** (0.232 g, 0.46 mmol) with ozone and dimethyl sulfide (1.36 mL) led to the aldehyde (−)-**16** (0.165 g, 77%). − $[\alpha]_D$ = −2.7 (*c* = 0.8, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3448, 1756, 1722 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, $SiMe_2$), 0.90 (s, 9 H, Si*t*Bu), 1.12 (d, *J* = 6.2 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 2.09 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 4.00 (quint, *J* = 7.8 Hz, 1 H, CH), 4.30−4.50 (m, 1 H, CH), 4.76 (d, *J* = 7.8 Hz, 1 H, CH), 4.93 (dd, *J* = 6.9, 1.6 Hz, 1 H, CH), 5.18 (d, *J* = 8.2 Hz, 1 H, NH), 9.46 (s, 1 H, CHO). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.2, 17.9, 19.9, 20.5, 20.98, 25.8, 28.3, 49.1, 67.1, 73.7, 77.1, 80.5, 155.2, 169.6, 169.9, 196.0. − $C_{21}H_{39}FeNO_8Si$ (461.6): calcd. C 54.64, H 8.52, N 3.03; found C 54.62, H 8.49, N 3.00.

ψ-*endo*-Alcohol (+)-9 and ψ-*exo*-Alcohol (+)-10: Dienone (−)-**7** (0.263 g, 0.47 mmol) in THF (12 mL) was treated at 0 °C with borane−dimethyl sulfide (2 M in THF, 0.26 mL, 0.52 mmol). Stirring was continued for 4 h at room temperature. The reaction was stopped by adding MeOH (10 mL) and water (20 mL). The aqueous layer was extracted with diethyl ether (4 × 25 mL). The organic layer was washed with water and brine, dried with $MgSO_4$ and concentrated in vacuo. Chromatography (15 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 90:10) yielded ψ-*endo*-alcohol (+)-**9** (0.182 g, 68%) and ψ-*exo*-alcohol (+)-**10** (0.033 g, 12%). − **ψ-*endo*-Alcohol (+)-9:** $[\alpha]_D$ = +46.3 (*c* = 0.7, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3520, 3439, 2047, 1976, 1717 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 3 H, $SiCH_3$), 0.08 (s, 3 H, $SiCH_3$), 0.90 (s, 9

H, Si*t*Bu), 1.02 (t, J = 8.4 Hz, 1 H, H diene), 1.10−1.30 (m, 1 H, H diene), 1.19 (d, J = 5.9, 3 H, CH_3), 1.40 (s, 9 H, BOC), 1.40 (d, J = 5.8 Hz, 3 H, CH_3), 2.37 (s br., 1 H, OH), 3.06 (d br., J = 5.5 Hz, 1 H, OH) 3.40−3.60 (m, 1 H, CH), 3.60−3.85 (m, 3 H, CH × 3), 5.09 (dd, J = 8.7, 5.0 Hz, 1 H, H diene), 5.15−5.25 (m, 2 H, H diene + NH). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −4.9, −4.1, 18.0, 19.11, 19.5, 26.0, 28.4, 55.4, 58.7, 63.6, 69.0, 76.7, 78.0, 79.6, 81.5, 86.3, 156.5. − $C_{24}H_{41}FeNO_8Si$ (555.5): calcd. C 51.89, H 7.44, N 2.52; found C 52.18, H 7.68, N 2.24. − **ψ-*exo*-Alcohol (+)-10:** $[\alpha]_D$ = +8.2 (c = 0.9, $CHCl_3$). − IR (CCl_4): ṽ = 3440, 3360 (br.), 2047, 1979, 1695 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 6 H, $SiMe_2$), 0.89 (s, 9 H, Si*t*Bu), 1.10−1.30 (m, 1 H, H diene), 1.19 (d, J = 5.6 Hz, 3 H, CH_3), 1.35−1.55 (m, 1 H, H diene), 1.42 (d, J = 6.1 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 3.10 (s br., 1 H, OH), 3.14 (s br., 1 H, OH), 3.60−3.75 (m, 1 H, CH), 3.75−3.90 (m, 1 H, CH), 3.83 (quint, J = 5.8 Hz, 1 H, CH), 3.90−4.05 (m, 1 H, CH), 5.12 (dd, J = 8.6, 4.9 Hz, 1 H, H diene), 5.30−5.45 (m, 2 H, H diene + NH). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −4.9, −4.2, 18.0, 19.1, 25.9, 28.4, 54.4, 57.9, 60.5, 73.6, 76.3, 79.4, 81.0, 86.0, 155.9. − $C_{24}H_{41}FeNO_8Si$ (555.5): calcd. C 51.89, H 7.44, N 2.52; found C 51.80, H 7.38, N 2.51.

ψ-*endo*-Alcohol (−)-9 and ψ-*exo*-Alcohol (−)-10: Following the same procedure as above, treatment of the dienone (+)-**7** (0.542 g, 0.98 mmol) with $BH_3{\cdot}SMe_2$ (2 M solution in THF, 0.50 mL, 1.08 mmol) led to the ψ-*endo*-alcohol (−)-**9** (0.383 g, 70%) and the ψ-*exo*-alcohol (−)-**10** (0.095 g, 17%). − **ψ-*endo*-Alcohol (−)-9:** $[\alpha]_D$ = −44.3 (c = 1.7, $CHCl_3$). − IR (CCl_4): ṽ = 3520, 3446, 2047, 1978, 1718 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 3 H, $SiCH_3$), 0.09 (s, 3 H, $SiCH_3$), 0.90 (s, 9 H, Si*t*Bu), 1.00 (t, J = 8.4 Hz, 1 H, H diene), 1.18−1.21 (m, 1 H, H diene), 1.20 (d, J = 6.2 Hz, 3 H, CH_3), 1.40 (s, 9 H, BOC), 1.38−1.42 (m, 3 H, CH_3), 2.39 (s br., 1 H, OH), 3.05 (s br., 1 H, OH), 3.49−3.57 (m, 1 H, CH), 3.62−3.69 (m, 1 H, OH), 3.77 (quint, J = 6.4 Hz, 1 H, CH), 3.77−3.84 (m, 1 H, CH), 5.09 (dd, J = 8.8, 5.1 Hz, 1 H, H diene), 5.16−5.27 (m, 2 H, H diene + NH). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −4.9, −4.1, 18.0, 19.1, 19.5, 26.0, 28.3, 55.4, 58.7, 63.6, 69.0, 76.6, 78.0, 79.5, 81.5, 86.3, 156.2. − $C_{24}H_{41}FeNO_8Si$ (555.5): calcd. C 51.89, H 7.44, N 2.52; found C 52.08, H 7.35, N 2.50. − **ψ-*exo*-Alcohol (−)-10:** $[\alpha]_D$ = −8.2 (c = 1.0, $CHCl_3$). − IR (CCl_4): ṽ = 3440, 3360 (br.), 2046, 1979, 1695 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.07 (s, 6 H, $SiMe_2$), 0.89 (s, 9 H, Si*t*Bu), 1.05−1.25 (m, 1 H, H diene), 1.19 (d, J = 5.7 Hz, 3 H, CH_3), 1.35−1.50 (m, 1 H, H diene), 1.42 (d, J = 6.0 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 3.13 (d, J = 2.7 Hz, 1 H, OH), 3.17 (d, J = 6.1 Hz, 1 H, OH), 3.65−3.75 (m, 1 H, CH), 3.83 (quint, J = 6.0 Hz, 1 H, CH), 3.75−3.90 (m, 1 H, CH), 3.90−4.05 (m, 1 H, CH), 5.10 (dd, J = 8.7, 4.9 Hz, 1 H, H diene), 5.30−5.45 (m, 2 H, H diene + NH). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.0, −4.3, 17.9, 19.0, 25.8, 28.3, 54.3, 57.8, 60.6, 73.6, 76.0, 78.4, 80.9, 85.7, 155.9, 210.8. − $C_{24}H_{41}FeNO_8Si$ (555.5): calcd. C 51.89, H 7.44, N 2.52; found C 52.05, H 7.29, N 2.48.

Diacetate (−)-11: To a mixture of the dienediol (+)-**9** (0.394 g, 0.71 mmol) in CH_2Cl_2 (10 mL) at 0 °C were added triethylamine (0.80 mL, 5.67 mmol), acetic anhydride (0.27 mL, 2.84 mmol) and DMAP (0.008 g). After stirring for 30 min, water was added, and the aqueous layer was extracted with dichloromethane and diethyl ether. The combined organic extracts were washed with brine, dried with $MgSO_4$ and concentrated under reduced pressure. Chromatography (40 g, SiO_2, hexane/ether gradient from 100:0 to 80:20) provided the diacetylated compound (−)-**11** (0.418 g, 92%) as a yellow solid. − M.p. 104−105 °C. − $[\alpha]_D$ = −14.5 (c = 1.1, $CHCl_3$). − IR (CCl_4): ṽ = 3451, 2051, 1986, 1974, 1747, 1720 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.80 (t, J = 9.1 Hz, 1 H, H diene), 0.86 (s, 9 H, Si*t*Bu), 1.05−1.25 (m, 1 H, H diene), 1.11 (d, J = 6.1 Hz, 3 H, CH_3), 1.40 (d, J = 7.4 Hz, 3 H, CH_3), 1.42 (s, 9 H, BOC), 2.09 (s, 3 H, Ac), 2.12 (s, 3 H, Ac), 3.89 (quint, J = 6.4 Hz, 1 H, CH), 4.05 (t br., J = 9.1 Hz, 1 H, CH), 4.50 (t, J = 8.3 Hz, 1 H, CH), 4.77 (d, J = 10.1 Hz, 1 H, NH), 4.97 (d, J = 9.1 Hz, 1 H, CH), 5.03 (dd, J = 8.9, 4.9 Hz, 1 H, H diene), 5.32 (dd, J = 8.7, 4.9 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.1, 17.9, 19.2, 19.6, 20.8, 21.0, 25.9, 28.3, 54.6, 58.2, 58.8, 67.1, 74.8, 75.1, 79.5, 81.6, 85.6, 155.3, 170.0, 170.4. − $C_{28}H_{45}FeNO_{10}Si$ (639.6): calcd. C 52.58, H 7.09, N 2.19; found C 52.74, H 7.02, N 2.16.

Diacetate (+)-11: Following the previous procedure, the reaction of diene diol (−)-**9** (0.312 g, 0.56 mmol) with triethylamine (0.63 mL, 4.49 mmol), acetic anhydride (0.21 mL, 2.25 mmol) and DMAP (0.008 g) yielded the diacetylated product (+)-**11** (0.328 g, 91%) as a yellow solid. − M.p.: 103−104 °C. − $[\alpha]_D$ = +13.6 (c = 1.2, $CHCl_3$). − IR (CCl_4): ṽ = 3448, 2051, 1985, 1970, 1746, 1723 cm^{-1}. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.79 (t br., J = 8.6 Hz, 1 H, H diene), 0.85 (s, 9 H, Si*t*Bu), 1.10 (d, J = 6.2 Hz, 3 H, CH_3), 1.05−1.19 (m, 1 H, H diene), 1.39 (d, J = 6.2 Hz, 3 H, CH_3), 1.42 (s, 9 H, BOC), 2.08 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 3.89 (quint, J = 6.4 Hz, 1 H, CH), 4.05 (t br., J = 8.8 Hz, 1 H, CH), 4.49 (t br., J = 8.3 Hz, 1 H, CH), 4.77 (d, J = 10.2 Hz, 1 H, NH), 4.96 (d br., J = 6.4 Hz, 1 H, CH), 5.02 (dd, J = 8.8, 4.8 Hz, 1 H, H diene), 5.31 (dd, J = 8.0, 4.8 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.2, 17.9, 19.1, 19.6, 20.7, 21.0, 25.9, 28.3, 54.6, 58.2, 58.8, 67.1, 74.8, 75.1, 79.5, 81.6, 85.6, 155.3, 170.0, 170.4. − $C_{28}H_{45}FeNO_{10}Si$ (639.6): calcd. C 52.58, H 7.09, N 2.19; found C 52.76, H 7.28, N 2.20.

Diacetate (+)-12: Analogously to the previous procedure, the reaction of diene diol (−)-**10** (0.100 g, 0.18 mmol) with triethylamine (0.20 mL, 1.44 mmol), acetic anhydride (0.07 mL, 0.72 mmol) and DMAP (0.004 g) gave the diacetylated product (+)-**12** (0.112 g, 97%). − M.p.: 120−121 °C. − $[\alpha]_D$ = +30.8 (c = 1.1, $CHCl_3$). − IR (CCl_4): ṽ = 3447, 2050, 1982, 1746, 1721 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, $SiMe_2$), 0.84 (t br., J = 7.5 Hz, 1 H, H diene), 0.90 (s, 9 H, Si*t*Bu), 1.12 (d, J = 6.1 Hz, 3 H, CH_3), 1.15−1.30 (m, 1 H, H diene), 1.39 (d, J = 5.9 Hz, 3 H, CH_3), 1.40 (s, 9 H, BOC), 1.97 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 3.89 (dq, J = 7.1, 6.1 Hz, 1 H, CH), 4.05−4.15 (m, 1 H, CH), 4.82 (d br., J = 9.3 Hz, 1 H, CH), 4.93 (dd, J = 6.5, 4.8 Hz, 1 H, CH), 5.03 (dd, J = 8.6, 4.9 Hz, 1 H, H diene), 5.11 (d br., J = 7.0 Hz, 1 H, NH), 5.33 (dd, J = 8.4, 4.9 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −4.9, −4.4, 17.9, 19.0, 19.7, 21.1, 25.9, 28.3, 52.2, 54.9, 58.5, 67.0, 73.8, 75.6, 79.5, 82.3, 86.3, 154.9, 169.7, 169.9, 211.1. − $C_{28}H_{45}FeNO_{10}Si$ (639.6): calcd. C 52.58, H 7.09, N 2.19; found C 52.60, H 7.15, N 2.21.

Diene (−)-13: A solution of CAN (0.540 g, 0.98 mmol) in MeOH (3 mL) was added at 0 °C to a solution of complex (−)-**11** (0.126 g, 0.20 mmol) in MeOH (2 mL). After 30 min at 0 °C, the reaction was quenched by adding saturated aqueous $NaHCO_3$ solution (10 mL). After filtration of the mixture through a pad of Celite, the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The organic layer was washed with water and brine, dried with $MgSO_4$ and concentrated. The crude product (0.115 g) was purified by chromatography (3 g SiO_2, hexane/ethyl acetate gradient from 100:0 to 90:10), yielding diene (−)-**13** (0.095 g, 96%) as a colourless oil. − $[\alpha]_D$ = −13.7 (c = 0.9, $CHCl_3$). − IR (CCl_4): ṽ = 3451, 1739, 1726 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.87 (s, 9 H, Si*t*Bu), 1.09 (d, J =

6.2 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 1.74 (d, J = 5.9 Hz, 3 H, CH_3), 2.04 (s, 3 H, Ac), 2.09 (s, 3 H, Ac), 3.91 (quint, J = 6.2 Hz, 1 H, CH), 4.12 (ddd, J = 9.7, 7.2, 2.5 Hz, 1 H, CH), 4.80 (d, J = 9.1 Hz, 1 H, NH), 4.84 (dd, J = 6.6, 2.5 Hz, 1 H, CH), 5.19 (t, J = 7.4 Hz, 1 H, CH), 5.43 (dd, J = 15.0, 7.4 Hz, 1 H, H diene), 5.74 (dq, J = 14.5, 6.6 Hz, 1 H, H diene), 6.00 (dd, J = 14.5, 10.6 Hz, 1 H, H diene), 6.21 (dd, J = 15.0, 10.1 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.0, −4.3, 18.0, 18.2, 19.5, 21.1, 25.9, 28.4, 52.6, 67.4, 74.3, 74.9, 79.4, 124.3, 130.4, 131.8, 135.3, 155.4, 169.9, 170.0. − $C_{25}H_{45}NO_7Si$ (499.7): calcd. C 60.09, H 9.08, N 2.80; found C 59.85, H 9.07, N 2.87.

Diene (+)-13: Analogously to the previous procedure, the decomplexation of the complex (+)-**11** (0.180 g, 0.28 mmol) with CAN (0.771 g, 1.41 mmol) in MeOH (7 mL) provided the diene (+)-**13** (0.136 g, 97%) as a colourless oil. − $[\alpha]_D$ = +10.8 (c = 0.9, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3452, 1739, 1728 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.03 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.87 (s, 9 H, Si*t*Bu), 1.09 (d, J = 6.2 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 1.74 (d, J = 6.6 Hz, 3 H, CH_3), 2.04 (s, 3 H, Ac), 2.09 (s, 3 H, Ac), 3.90 (quint, J = 6.2 Hz, 1 H, CH), 4.12 (ddd, J = 9.7, 7.2, 2.5 Hz, 1 H, CH), 4.80 (d, J = 9.2 Hz, 1 H, NH), 4.84 (dd, J = 6.6, 2.5 Hz, 1 H, CH), 5.19 (t, J = 7.2 Hz, 1 H, CH), 5.43 (dd, J = 15.0, 7.6 Hz, 1 H, H diene), 5.74 (dq, J = 14.8, 6.6 Hz, 1 H, H diene), 5.99 (dd, J = 14.5, 10.6 Hz, 1 H, H diene), 6.21 (dd, J = 15.0, 10.3 Hz, 1 H, H diene). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.0, −4.2, 17.9, 18.1, 19.5, 21.1, 25.9, 28.4, 52.6, 67.4, 74.3, 74.9, 79.4, 124.3, 130.4, 131.8, 135.3, 155.4, 169.9, 170.0 − $C_{25}H_{45}NO_7Si$ (499.7): calcd. C 60.09, H 9.08, N 2.80; found C 59.99, H 9.10, N 2.79.

Diene (+)-14: Following the previous procedure, the decomplexation of the complex (+)-**12** (0.080 g, 0.125 mmol) with CAN (0.343 g, 0.625 mmol) in MeOH (6 mL) led to the diene (+)-**14** (0.054 g, 87%) as a colourless oil. − $[\alpha]_D$ = +2.9 (c = 1.0, $CHCl_3$).

Aldehyde (+)-15: Diene (−)-**13** (0.070 g, 0.14 mmol) in MeOH (10 mL) was treated at −78 °C with ozone until the blue colour persisted. After removing excess ozone by passing a stream of argon through the solution, dimethyl sulfide (0.4 mL) was added at −78 °C and the mixture was stirred at room temperature for 1 h. After concentration, the residue (0.073 g) was dissolved in ethyl acetate and washed with water and brine. The organic layer was dried with $MgSO_4$. Chromatography (3 g, SiO_2, hexane/ethyl acetate gradient from 100:0 to 50:50) gave the aldehyde (+)-**15** (0.054 g, 84%). − $[\alpha]_D$ = +20.9 (c = 0.9, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3454, 1757, 1750, 1721 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, $SiMe_2$), 0.89 (s, 9 H, Si*t*Bu), 1.14 (d, J = 6.3 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 2.05 (s, 3 H, Ac), 2.15 (s, 3 H, Ac), 3.99 (quint, J = 6.2 Hz, 1 H, CH), 4.55 (quint, J = 3.9 Hz, 1 H, CH), 4.93 (dd, J = 5.8, 2.9 Hz,1 H, CH), 5.27 (d br., J = 4.1 Hz, 2 H, CH + NH), 9.54 (s, 1 H, CHO). − ^{13}C NMR (200 MHz, $CDCl_3$): δ = −5.1, −4.4, 17.9, 19.7, 20.4, 20.8, 25.8, 28.2, 49.6, 60.3, 67.6, 74.7, 80.3, 155.2, 169.4, 169.6, 194.9. − $C_{21}H_{39}NO_8Si$ (461.6): calcd. C 54.64, H 8.52, N 3.03; found C 54.53, H 8.50, N 3.07.

Aldehyde (−)-15: In the same way as above, treatment of diene (+)-**13** (0.090 g, 0.18 mmol) with ozone and dimethyl sulfide (0.55 mL) led to the aldehyde (−)-**15** (0.064 g, 77%). − $[\alpha]_D$ = −18.4 (c = 0.9, $CHCl_3$). − IR (CCl_4): $\tilde{\nu}$ = 3456, 1756, 1743, 1721 cm^{-1}. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.06 (s, 6 H, $SiMe_2$), 0.90 (s, 9 H, Si*t*Bu), 1.14 (d, J = 6.3 Hz, 3 H, CH_3), 1.43 (s, 9 H, BOC), 2.05 (s, 3 H, Ac), 2.15 (s, 3 H, Ac), 3.99 (quint, J = 6.2 Hz, 1 H, CH), 4.55 (quint, J = 3.9 Hz, 1 H, CH), 4.94 (dd, J = 5.8, 2.9 Hz,1 H, CH), 5.27 (d br., J = 4.1 Hz, 2 H, CH + NH), 9.54 (s, 1 H, CHO).

Table 1. X-ray experimental data

	(−)-**11**	(+)-**11**	(+)-**12**
Empirical formula	$C_{28}H_{45}FeNO_{10}Si$	$C_{28}H_{45}FeNO_{10}Si$	$C_{28}H_{45}FeNO_{10}Si$
Molecular mass	639.60	639.60	639.60
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P12_11$	$P12_11$	$P2_12_12_1$
a [Å]	11.962(2)	11.9531(9)	10.8410(1)
b [Å]	12.379(4)	12.2538(8)	12.9540(3)
c [Å]	12.812(2)	12.661(1)	23.8510(5)
β [°]	110.57(2)	110.81(1)	
V [Å^3]	1776(1)	1733.5(5)	3349.5(2)
Z	2	2	4
Colour	yellow	yellow	yellow
Crystal dim. [mm]	0.30 × 0.30 × 0.25	0.17 × 0.13 × 0.11	0.20 × 0.12 × 0.10
$D_{calcd.}$ [gcm^{-3}]	1.20	1.23	1.27
F(000)	680	680	1360
μ [mm^{-1}]	0.502	0.514	0.537
Trans. min/max	0.9328/1.0000		
Temperature [K]	294	173	173
Wavelength [Å]	0.71073	0.71073	0.71073
Radiation	Mo-K_α graphite-monochromated	Mo-K_α graphite-monochromated	Mo-K_α graphite-monochromated
Diffractometer	MACH3 Nonius	Kappa CCD	Kappa CCD
Scan mode	θ/2θ	scans	scans
hkl limits	0,14/0,15/−15,14	−16,16/−15,15/−16,16	−12,12/−15,15/−29,29
θ limits [°]	2.5/26.29	2.5/29.53	2.5/26.36
Number of data meas.	3960	14778	22751
Number of data with $I > 3\ \sigma(I)$	1693	2334	2807
Weighting scheme	$4F_o^2/[\sigma^2(F_o^2) + 0.0036\ F_o^4]$	$4F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$	$4F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$
Number of variables	369	369	370
R	0.036	0.047	0.039
Rw	0.043	0.067	0.053
GOF	1.025	1.203	1.138
Largest peak in final difference map [eÅ^{-3}]	0.199	0.398	0.505

– ^{13}C NMR (400 MHz, $CDCl_3$): δ = −5.1, −4.3, 17.9, 19.7, 20.4, 20.9, 25.8, 28.2, 49.7, 67.7, 74.7, 78.0, 80.3, 155.3, 169.5, 169.7, 195.0. – $C_{21}H_{39}NO_8Si$ (461.6): calcd. C 54.64, H 8.52, N 3.03; found C 54.70, H 8.58, N 3.06.

X-ray Crystal Structure Determination of Compounds (−)-11, (+)-11, and (+)-12: Crystal data, data collection parameters and results are summarized in Table 1. Data were collected at 173 K for (+)-**11** and (+)-**12** and at room temperature for (−)-**11**, corrected for Lorentz and polarisation factors. Absorption corrections are included in the scaling procedure for data collected using the Kappa CCD and derived from the ψ scans of 7 reflections for (−)-**11**. The structures were determined using direct methods and refined against |*F*| using the OpenMoleN package on a DEC Alpha workstation. The absolute configurations were determined by refining Flack's *x* parameter. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre [(−)-**11**: CCDC-127817; (+)-**11**: -127818; (+)-**12**: -127819]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, [Fax: (internat. + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to BASF for gifts of $Fe(CO)_5$ and to Chiral Technologies-Europe (Dr. Cristina Suten) for the *ee* determinations by HPLC.

[1] D. R. Walters, J. D. Dutcher, O. Wintersteiner, *J. Am. Chem. Soc.* **1957**, *79*, 5076; M. H. Von Saltza, J. Reid, J. D. Dutcher, O. Wintersteiner, *J. Am. Chem. Soc.* **1961**, *83*, 2785.
[2] E. Borowski, *Chemotherapy* **1965**, *10*, 176. Hungarian Pat. **1969**, 155813, *Chem. Abstr.* **1969**, *71*, 20924y; Shanghei Institute of Materia Medica, *Chem. Abstr.* **1976**, *84*, 87873f.
[3] K. C. Nicolaou, R. A. Daines, Y. Ogawa, T. K. Chakraborty, *J. Am. Chem. Soc.* **1988**, *100*, 4696−4705.
[4] R. Eby, K. T. Webster, C. Schuerch, *Carbohydr. Res.* **1984**, *129*, 111.
[5] K. C. Nicolaou, R. A. Daines, T. K. Chakraborty, Y. Ogawa, *J. Am. Chem. Soc.* **1987**, *109*, 2821.
[6] M. Franck-Neumann, P. Bissinger, P. Geoffroy, *Tetrahedron Lett.* **1997**, *38*, 4469.
[7] M. Franck-Neumann, P. Bissinger, P. Geoffroy, *Tetrahedron Lett.* **1997**, *38*, 4473.
[8] M. Franck-Neumann, P. Bissinger, P. Geoffroy, *Tetrahedron Lett.* **1997**, *38*, 4477.
[9] M. Franck-Neumann, A. Abdali, P. J. Colson, M. Sedrati, *Synlett* **1991**, 331.
[10] J. P. Genêt, S. Mallart, C. Greck, E. Piveteau, *Tetrahedron Lett.* **1991**, *32*, 2359.
[11] J. P. Genêt, C. Greck, *Synlett* **1997**, 741.
[12] A similar limitation had been observed by this author for amination at ester enolates: J. Rebeck, Jr., S. H. Shaber, Y. K. Shue, J. C. Gehret, S. Zimmermann, *J. Org. Chem.* **1984**, *49*, 5164−6174.
[13] A. K. Bose, J. F. Kistner, *J. Org. Chem.* **1962**, *27*, 2925−2927.
[14] J. H. Boyer, *J. Am. Chem. Soc.* **1951**, *73*, 5865; A. K. Bose, J. F. Kistner, L. Farber, *J. Org. Chem.* **1962**, *27*, 2925.
[15] H. Staudinger, E. Hauser, *Helv. Chim. Acta* **1920**, *3*, 861.
[16] N. Knouzi, M. Vaultier, R. Carrié, *Bull. Soc. Chim. Fr.* **1985**, 815.
[17] Similar debrominations have also been observed by Borowitz et al., when secondary and tertiary α-bromo ketones were treated with triphenylphosphane in a refluxing mixture of benzene and methanol: I. J. Borowitz, L. I. Grossman, *Tetrahedron Lett.* **1962**, 471.
[18] S. Saito, H. Nakajima, M. Inaba, T. Moriwake, *Tetrahedron Lett.* **1989**, *30*, 837.
[19] T. Mukayiama, N. Iwasawa, R. W. Stevens, T. Haga, *Tetrahedron* **1984**, *40*, 1381.
[20] T. Mukayiama, R. W. Stevens, N. Iwasawa, *Chem. Lett.* **1982**, 353.
[21] T. Mukayiama, *Aldrichim. Acta* **1996**, *29*, 59.
[22] J. D. Donaldson, in: *Progress in Inorganic Chemistry* (Ed.: F. A. Cotton), John Wiley & Sons, New York, **1967**, vol. 8, p. 287.
[23] N. A. Clinton, C. P. Lillya, *J. Am. Chem. Soc.* **1970**, *92*, 3058.
[24] D. A. Evans, K. T. Chapman, *Tetrahedron Lett.* **1986**, *27*, 5939.
[25] J. D. Holmes, R. Petit, *J. Am. Chem. Soc.* **1963**, *85*, 2531.
[26] R. J. Batchelor, J. N. R. Ruddick, J. R. Sams, F. Aubke, *Inorg. Chem.* **1977**, *16*, 1414.

Received March 20, 2000
[O00144]