149. Synthesis of Enantiomerically Pure Ferrocenes from Glycofuranosyl-cyclopentadienes, Synthetic Equivalents of (Alkoxyalkyl)fulvenes

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Cyclopentadienyl *C*-glycosides (= glycosyl-cyclopentadienes) have been prepared as latent fulvenes. Their reaction with nucleophiles leads to cyclopentadienes substituted with (protected) alditol moieties and, hence, to enantiomerically pure metallocenes. Treatment of **1** with cyclopentadienyl anion gave the epimeric glycosyl-cyclopentadienes **6**/**7** (*Scheme 1*). Each epimer consisted of a *ca.* 1:1 mixture of the 1,3- and 1,4-cyclopentadienes **a** and **b**, respectively, which were separated by prep. HPLC. Slow regioisomerisation occurred at room temperature. *Diels-Alder* addition of *N*-phenylmaleimide to **6a**/**b** *ca.* 3:7 at room temperature yielded three '*endo*'-adducts, *i.e.*, a disubstituted alkene (**8** or **9**, 25%) and the trisubstituted alkenes **10** (45%) and **11** (13%). The structure of **10** was established by X-ray analysis. Reduction of **6**/**7** (after isolation or *in situ*) with $LiAlH_4$ gave the cyclopentadienyl-mannitols **12a**/**b** (80%) which were converted to the silyl ethers **13a**/**b** (*Scheme 2*). Lithiation of **13a**/**b** and reaction with $FeCl_2$ or $TiCl_4$ led to the symmetric ferrocene **14** (76%) and the titanocene **15** (34%), respectively. The mixed ferrocene **16** (63%) was prepared from **13a**/**b** and pentamethylcyclopentadiene. Treatment of **6**/**7** with PhLi at −78° gave a 5:3 mixture of the 1-*C*-phenylated alcohols **17a**/**b** and **18a**/**b** (71%) which were silylated to **19a**/**b** and **20a**/**b**, respectively. Lithiation of **19**/**20** and reaction with $FeCl_2$ afforded the symmetric ferrocenes **21** and **22** and the mixed ferrocene **23** (54:15:31, 79%) which were partially separated by MPLC. The configuration at C(1) of **17**–**22** was assigned on the basis of a conformational analysis. The reaction of the ribofuranose **24** with cyclopentadienyl-sodium led to the epimeric *C*-glycosides **27a**/**b** and **28a**/**b** (57%, *ca.* 1:1, *Scheme 3*). The *in-situ* reduction of **27**/**28** with $LiAlH_4$ followed by isopropylidenation gave **25a**/**b** (65%) which were transformed into the ferrocene **26** (79%) using the standard method. Phenylation of **27**/**28**, desilylation, and isopropylidenation gave a 20:1 mixture of **33a**/**b** and **34a**/**b** (86%) which was separated by prep. HPLC. The same mixture was obtained upon phenylation of the fulvene **32** which was obtained in 36% yield from the reaction of the *aldehydo*-ribose **30** with cyclopentadienylsodium at −100°. Lithiation of **33**/**34** and reaction with $FeCl_2$ gave the symmetric ferrocene **35** (88%). Similarly, the *aldehydo*-arabinose **36** was transformed *via* the fulvene **37** (32%) into a 18:1 mixture of **38a**/**b** and **39a**/**b** (78%) and, hence, into the ferrocene **40** (83%). Conformational analysis allowed to assign the configuration of **33**–**35**, whereas an X-ray analysis of **40** established the (1*S*)-configuration of **38a**/**b** and **40**. The opposite configuration at C(1) of **38a**/**b** and **33a**/**b** was established by chemical degradation (*Scheme 4*). Hydrogenation (→ **41** and **44**, resp.), deprotection (→ **42** and **45**, resp.), $NaIO_4$ oxidation, and $NaBH_4$ reduction yielded (+)-(*S*)-**43** and (−)-(*R*)-**43**, respectively.

Introduction. – There is considerable interest in chiral cyclopentadienyl ligands [1], as enantiomerically pure organometallic complexes are useful in a wide range of catalytic or stoichiometric asymmetric reactions, including hydrogenation [2–7], epoxidation [8], alkene isomerisation [9] [10], reduction of ketones [1] [11], aldol reactions [12], *Diels-Alder* reactions [13], hydroamination [14], and alkene polymerisation [15–18].

Monocyclopentadienyl titanium [19], zirconium [20], and hafnium [20] complexes possessing carbohydrate-derived alkoxy ligands have been used in stoichiometric amounts for the highly enantioselective addition of alkyl [20] [21] and allyl groups [20–23] and of ester enolates [20–22] [24] to aldehydes. Zirconocenes have been used for the ring

contraction of carbohydrate derivatives [25], and metallocenes have been connected to nucleoside bases [26–28].

Ferrocenes, containing carbohydrate substituents connected to the cyclopentadienyl ligand by a heteroatom, have been well investigated, such as ferrocenes bound to cyclodextrins [29–32], to anomeric O- [33], S- [34] [35], or Se-atoms [36], and to non-anomeric O- and N-atoms [34] [37]. To the best of our knowledge, there is only one example of a metallocene (a perbenzylated glucopyranosyl-ferrocene, [38]) where the carbohydrate moiety is connected by a C–C bond to the cyclopentadienyl group.

Glycosyl-cyclopentadienes (= cyclopentadienyl *C*-glycosides) should be available from hemiacetals. Base-catalyzed condensation with cyclopentadiene is expected to yield (alkoxyalkyl)fulvenes which should react by reversible intramolecular addition of the alkoxy group to the fulvene moiety, and lead to *C*-glycosides; these can be viewed as latent fulvenes[1]). Metallocenes may be available either from the glycosyl-cyclopentadienes, or *via* the corresponding (alkoxyalkyl)fulvenes after irreversible, diastereoselective addition of external nucleophiles. These Cp ligands possess several alkoxy groups which may interact with the metal center and modify the catalytic properties of the complexes.

We report here the preparation of a number of enantiomerically pure cyclopentadienes derived from carbohydrates and their transformation into ferrocenes and into a titanocene.

Results and Discussion. – 1. *1-C-(Cyclopentadienyl)-mannitol Derivatives.* The *Thiele* synthesis of fulvenes [41] has been considerably improved by using pyrrolidine as a base [42], but reaction of **1** with cyclopentadiene and pyrrolidine gave only the mannofuranosyl-pyrrolidines **2** (*Scheme 1*). Apparently, the equilibrium between the iminium intermediate and **2** is too strongly biased to allow a reaction with the cyclopentadienyl anion. The glycosyl-cyclopentadienes **6** and **7** were, however, obtained from **1** and excess cyclopentadienylsodium (67%, 49:51). Both anomers were 1:1 mixtures of the regioisomers **6a**/**b** and **7a**/**b**, respectively. The low diastereoselectivity is presumably the result of a thermodynamic control; treatment of pure **6a**/**b** or **7a**/**b** with NaH or BuLi led quickly to epimerization. Chromatography gave pure samples (^{1}H-NMR) of **6a**, **6b**, **7a**, and **7b**. Neither the fulvene **3** nor the regioisomers **6c** or **7c** could be detected [43] [44], and attempts to intercept the intermediate fulvene **4** by *O*-silylation failed.

To confirm the structure of the glycosyl-cyclopentadienes, we treated **6** and **7** with *N*-phenylmaleimide. *Diels-Alder* addition of a *ca.* 3:7 mixture **6a**/**6b** occurred at room temperature. Only three of the four possible '*endo*'-adducts[2]) were detected in the ^{1}H-NMR spectrum of the crude product: a disubstituted alkene (**8** or **9**) derived from **6a**, and two trisubstituted alkenes (**10** and **11**) derived from **6b** (*Scheme 1*). This interpretation was corroborated by the cycloaddition of *N*-phenylmaleimide to the pure dienes **6a** and **6b**. The ratio of (**8** or **9**)/**10**/**11** was independent of the temperature within 0–80°, in keeping with kinetic control [46–48]. A *ca.* 4:1 ratio of **10** and **11** was deduced from integration of the vinylic H signals in the ^{1}H-NMR spectrum of the crude product. The *Diels-Alder*-addition of *N*-phenylmaleimide to the epimeric regioisomers **7a**/**b** also proceeded highly

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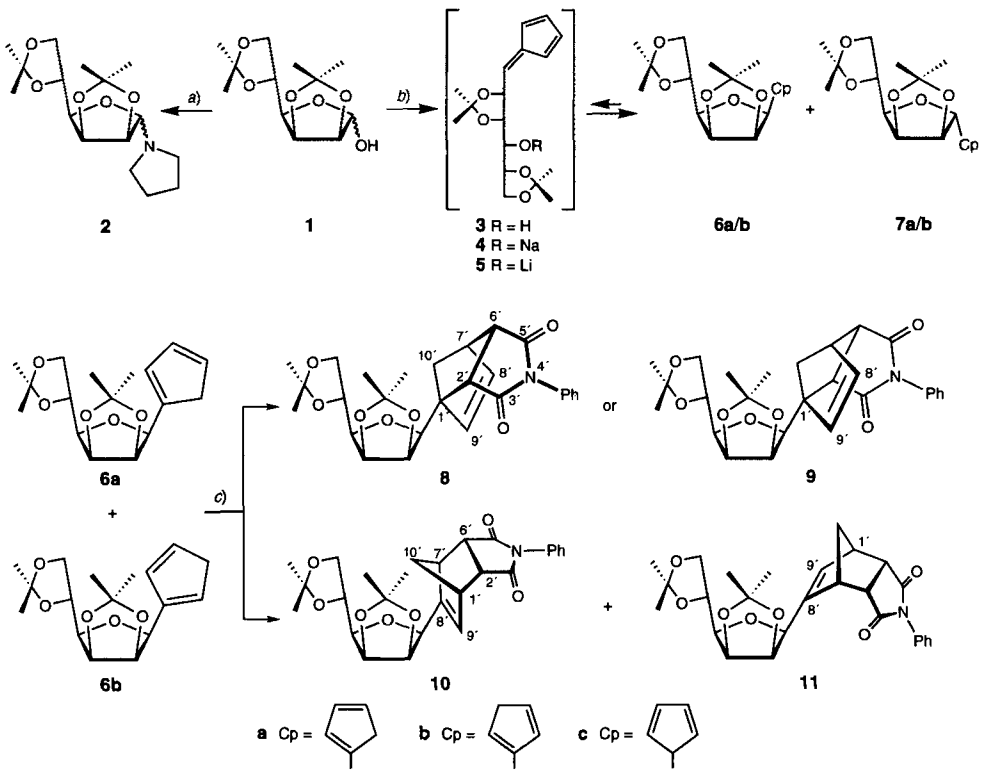
[1]) For the preparation of cyclopentadienyl (Cp) ligands by the addition of nucleophiles to fulvenes, see [39]. For the synthesis of ferrocenyl ligands from enantiomerically pure 6-aminofulvenes, see *Togni* and *Albenhuis* [40]. We thank Prof. *A. Togni* for a copy of the manuscript.

[2]) As a rule '*exo*'-adducts are only observed at temperatures higher than 200° [45].

Scheme 1



a) C_5H_6, pyrrolidine, MeOH, r.t. *b*) CpNa, THF, r.t., 67% of **6**/**7** 49:51. *c*) *N*-Phenylmaleimide, CH_2Cl_2, r.t., 83% of (**8** or **9**)/**10**/**11** 30:56:14.

diastereoselectively, yielding two disubstituted alkenes in a ratio of *ca.* 4:1 and two trisubstituted alkenes in a ratio of *ca.* 7:3.

The structure of '*endo*'-adducts was evidenced by the $J(1',2')$ and $J(6',7')$ values of 3–4.6 Hz (*cf.* [49–51]) and the absence of long-range couplings between the more deshielded H–C(10') and H–C(2')/H–C(6') [49] [52]. The absolute configuration of the *Diels-Alder* adducts derived from **6a**, **7a**, and **7b** was not determined. X-Ray analysis of **10** (*Fig. 1*) established the structure and confirmed the '*endo*'-addition and the β-D-configuration of **10** and its precursor **6b**. It also reveals the (1'*S*)-configuration of **10** and, hence, the (1'*R*)-configuration of **11**. In the solid state, **10** shows dihedral angles H–C(4)–C(5)–H of +184.3° and H–C(1)–C(8')–C(9') of –22.8°. The orientation of the C(4) substituent is similar in the solid state and in solution ($J(4,5)$ = 8.3 Hz), while the orientation of the C(1) substituent is different. This is evidenced by the chemical shift of H–C(2), which is shielded by *ca.* 0.3 ppm as compared to the other two adducts. In the solid state of **10**, H–C(2) is located in the deshielding zone of the olefinic C=C bond, while, in solution, it is presumably shielded by a C=O group (dihedral angle H–C(1)–C(8')–C(9') of *ca.* –90°).

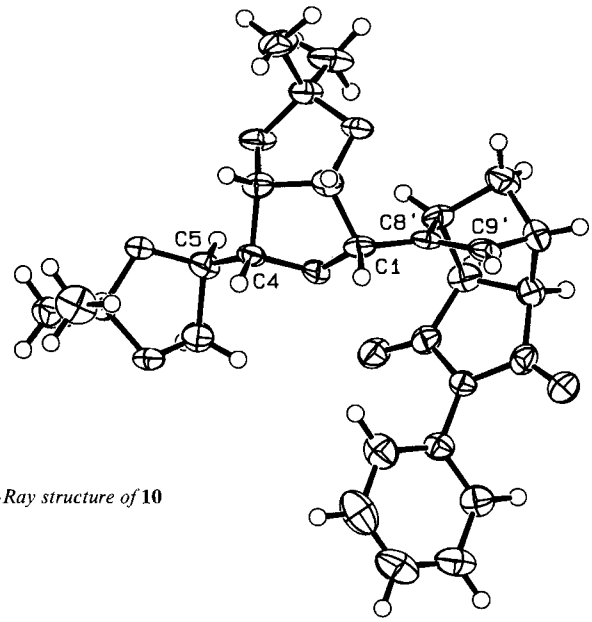


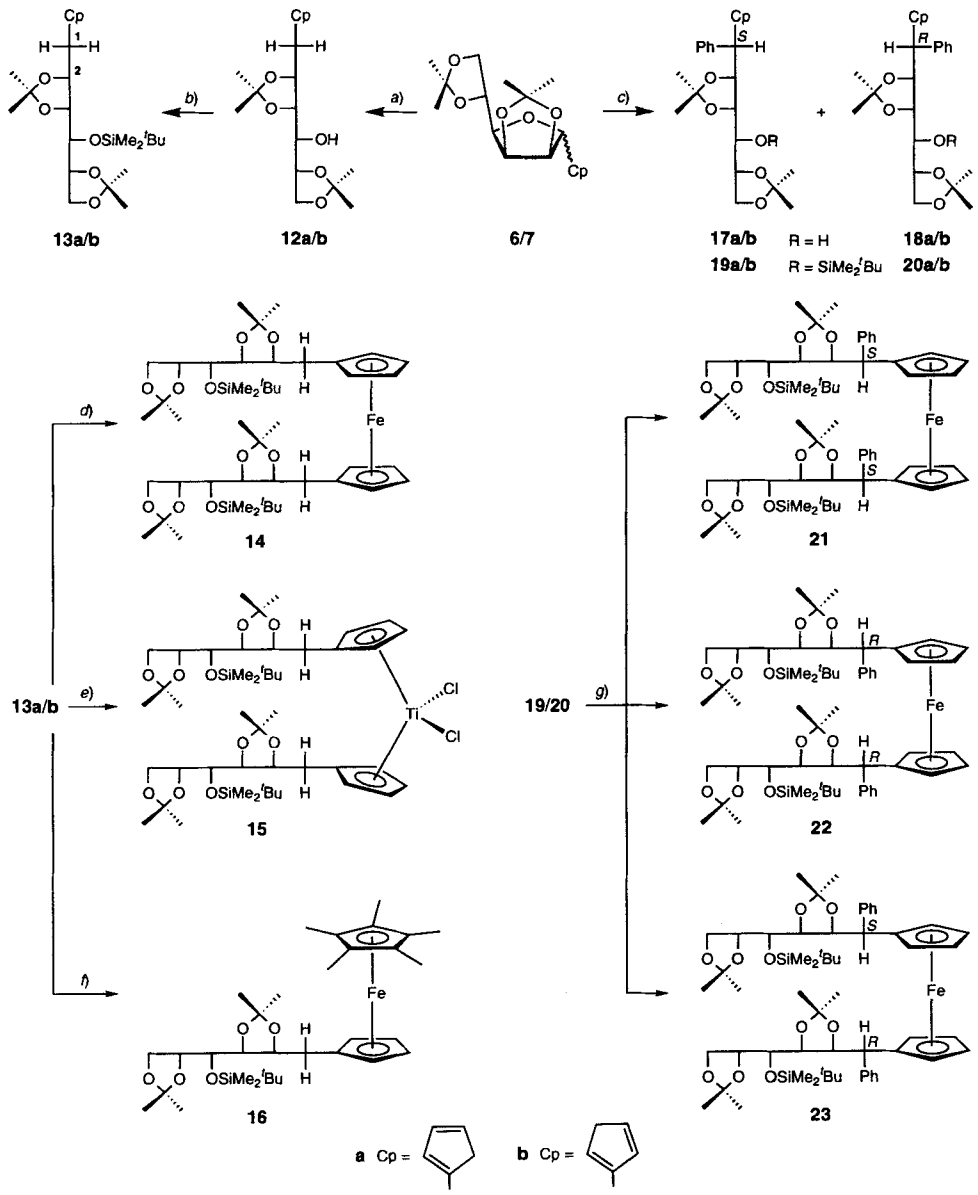
Fig. 1. *X-Ray structure of* **10**

Attempts to prepare ferrocenes by metallation of **6**/**7** with NaH or BuLi followed by treatment with $FeCl_2$ or $TiCl_4$ failed, possibly due to formation of the fulvenyl alkoxides **4** and **5** and their reaction with the metal halide. The *bona fide* fulvene was intercepted by reduction [53–56] of **6**/**7** with excess NaH and $LiAlH_4$, yielding the alkoxyalkylated cyclopentadienes **12a**/**b** (*Scheme 2*) in 73% (80%, if the product derived from **1** and cyclopentadienylsodium was directly reduced). Silylation gave the fully protected cyclopentadienes **13a**/**b** (71%). Pure samples of **13a** and **13b** were obtained by preparative HPLC. Lithiation of **13a**/**b** (BuLi) followed by treatment with $FeCl_2$ or $TiCl_4$ yielded 76% of the ferrocene **14** as yellow, air-stable crystals, and 34% of the titanocene **15** as purple, air-sensitive crystals, respectively. By applying *Manriquez'* method for the preparation of mixed ferrocenes ([57], *cf.* [58]), we obtained **16** (63%)[3]).

The fulvenyl alkoxide **5** derived from the *C*-glycosides **6**/**7** was also intercepted with PhLi in THF. The resulting phenylalkyl-cyclopentadienes **17a**/**b** and **18a**/**b** (5:3 by ^{1}H-NMR; 71%) were silylated, yielding a 5:3 mixture of **19a**/**b** and **20a**/**b** (86%, d.e. 25%), which were separated by preparative HPLC. The ratio **19**/**20** was determined by integration of the ^{1}H-NMR signals for three of the four Me groups. Pure samples of **19a** or **19b** in $CDCl_3$ solution slowly isomerized to mixtures **19a**/**b**; similarly, pure **20a** or **20b** gave **20a**/**b**. This isomerization allowed to distinguish between the constitutional and configurational isomers. Lithiation of **19**/**20** and treatment with $FeCl_2$ yielded a mixture of the ferrocenes **21**/**22**/**23** (54:15:31, 79%). The statistical ratio, based on the relative amounts of the cyclopentadienes **19**/**20**, is 36:16:48; formation of **21** containing two identical cyclopentadienyl ligands is, thus, somewhat preferred. The ratio was determined by integration of the Me_2Si signals at 0.31 ppm (**21**), −0.01 ppm (2 $SiMe_2$, **22**), and

[3]) We thank Prof. *A. Togni* and Dr. *H.C.L. Abbenhuis* for a sample of 1,2,3,4,5-pentamethylcyclopentadiene and for experimental details.

Scheme 2



a) $LiAlH_4$, NaH, THF, r.t.→60°, 73%. *b*) *t*-$BuMe_2SiOTf$, Et_3N, CH_2Cl_2, −60°→0°, 71%. *c*) PhLi, THF, −78°→0°, 71% of **17**/**18** 5:3; *t*-$BuMe_2SiOTf$, Et_3N, CH_2Cl_2, −60°→r.t., 86% of **19**/**20** 5:3. *d*) BuLi, THF, −60°→0°; $FeCl_2$, 0°→r.t., 76%. *e*) BuLi, THF, −60°→r.t.; $TiCl_4$, −78°→r.t., 34%. *f*) $(Me_5Cp)Li$, THF, $[Fe(acac)_2]$, −78°→r.t.; lithium salt of **13**, r.t., 63%: *g*) BuLi, THF, −50°→0°; $FeCl_2$, r.t., 79% of **21**/**22**/**23** 54:15:31.

−0.03 ppm (**23**) in the ^{1}H-NMR spectrum of the crude product; pure samples were obtained by preparative HPLC. The configuration of **17–23** was deduced from the ^{1}H-NMR data (see below, *Conformational Analysis*).

The EI-mass spectra of **7a/b**, **12a/b**, **13a/b**, **14**, and **17–23** show peaks for $M^{+\cdot}$ ($[M+1]^+$ for **13a/b**) and $[M-Me]^+$ typical for isopropylidene acetals. The EI-MS of **13a/b**, **14**, **16**, and **19–23** show characteristic $[M-{}^t\text{Bu}]^+$ and $[M-{}^t\text{BuMe}_2\text{Si}]^+$ peaks. In addition, the MS of **7a/b** exhibits a peak for a dimer ($[2M]^{+\cdot}$ at m/z 616), presumably due to the product of an intermolecular *Diels-Alder* reaction. The IR spectra of **6a/b**, **7a/b**, and **13–23** show the characteristic isopropylidene bands at 1371–1384 cm^{-1}. The 1,3-dioxolane rings in **13a**, **13b**, **14–16**, and **21–23** are evidenced by the ^{13}C-NMR, *s*'s at 109.8–107.5 ppm (*Table 2*) [59–62].

The ratio of the epimers **6a/b** and **7a/b** was determined by integration of the H–C(4) signals (for **6a/b**, 3.60; for **7a/b**, 3.71 and 3.75 ppm) in the ^{1}H-NMR spectrum of crude **6/7**. The allylic CH_2 group of the cyclopentadiene moiety of **6a** and **7a** resonates as a characteristic ABX_3 system (J_{gem} = 24 Hz, *cf.* [63]) at 3.27 and 3.11 (**6a**) and 3.03 and 2.94 ppm (**7a**), whereas the one of the regioisomers **6b** and **7b** appears as unresolved *m*'s at 3.03 and 3.00 ppm, respectively. The J(1,2) values (*Table 1* and *Exper. Part*) are typical for 1,2-*cis*- (**6a** and **6b**) and 1,2-*trans*-configurated (**7a** and **7b**) 2,3-*O*-isopropylidene-furanosides. The allylic CH_2 groups of the cyclopentadienyl ring of **13a/b** and **14a/b** show a similar signal pattern as **6a/b** and **7a/b**.

The formation of metallocenes is best evidenced by the characteristic ^{1}H- and ^{13}C-NMR chemical shifts of the cyclopentadienyl moieties (**14**: 4.37–4.08, 86.4, and 70.8–68.4 ppm (*cf.* [36] [64]); **15**: 6.46–6.36, 134.6, and 128.8–112.4 ppm (*cf.* [65–67], *Exper. Part*, *Table 2*). The four ferrocene H-atoms of **16** are shifted upfield by *ca.* 0.5 ppm, as compared to **14**, due to the electron-donating effect of the pentamethylcyclopentadienyl ligand. The ^{1}H- and ^{13}C-NMR spectra of **21** and **22** show only one set of signals, while **23** shows two sets, with chemical-shift and J(H,H) values closely resembling a combination of those of the symmetric ferrocenes **21** and **22**. As compared to **14**, the ferrocene H-signals of **21–23** are shifted upfield by *ca.* 0.1 to 0.3 ppm (see *Exper. Part*). The four *d* of the ferrocene C-atoms appear in the same range, whereas the Ph group in β-position induces a downfield shift (*ca.* 5–7 ppm) for the *s* (*Table 2*).

Conformational Analysis. An antiperiplanar arrangement of the C(1′)–C(1) and the C(2)–C(3) bonds of **13–16** is evidenced by the coupling constants for H_A–C(1) and H_B–C(1) which resonate as *ddd*'s with J_{gem} = 13.6–14.3, $J(1A,2)$ = 2.6–3.2, and $J(1B,2)$ = 10.6–11.4 Hz (*Table 1*). A different conformation of the alcohols **12a** and **12b**, on the one hand, and the silyl ethers **14** and **16**, on the other hand, is apparent from J(3,4), which is small for **12a** and **12b**, but large for **14** and **16**. Signal overlapping prevents the determination of J(3,4) of **13a**, **13b**, and **15**. Macromodel calculations (MM3 force field) of the conformation of the Me-ether analogue of **13a** led to the global minimum **B** (*Fig. 2*) which corresponds well to the coupling constants of **14** and **16**.

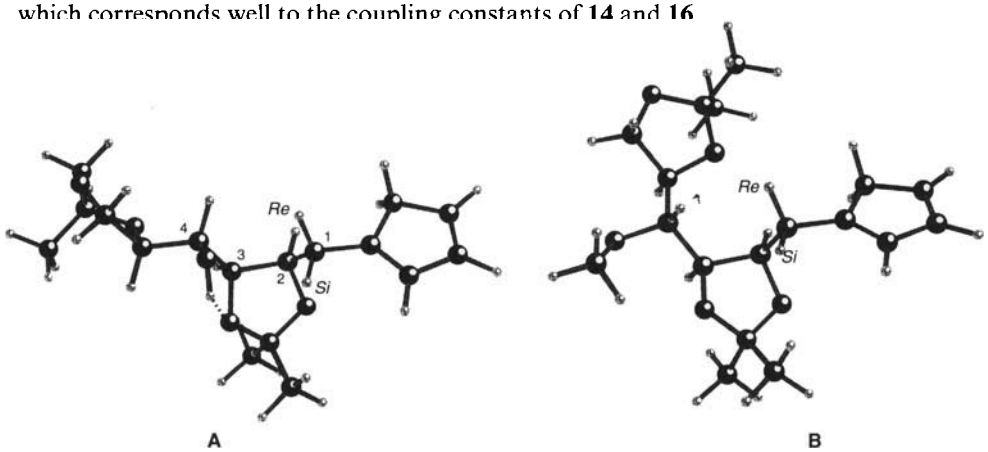


Fig. 2. *Calculated conformations* (Macromodel program, MM3 force field) *of* **12a** (**A**) *and of the 4-MeO analogue* **13a** (**B**)

The synclinal arrangement of H–C(3) and H–C(4) and the antiperiplanar arrangement of H–C(4) and H–O(4) (J(H,OH) = 8.1 Hz) of the alcohols **12a/b** evidence an intramolecular H-bond to O(3). Indeed, calculation resulted in conformer **A** as a minimum for **12a** (distances O(4)···O(3) of 2.64 and H···O(3) of 2.09 Å), in keeping with the observed coupling constants[4]). The central dioxolane ring adopts a different conformation in **A** (E_4) and **B** ($^2H_3$), although in both conformers C(1) is in a pseudoaxial and C(4) in a pseudoequatorial position. The difference implies that J(2,3) of **B** (dihedral angle of 44°) should be smaller than J(2,3) of **A** (dihedral angle of 36°). Indeed, J(2,3) of **13–16** are smaller than J(2,3) of **12a/b**, indicating that **13a/b** and **15** also possess conformation **B**.

Substitution of H_{Re} in conformer **B** (*Fig. 2*) by a Ph group leads to an unfavorable steric interaction with the terminal dioxolane moiety which is avoided by rotation to generate a conformation of type **A**, where H–C(1) and H–C(2) remain in an antiperiplanar relation. The substitution of H_{Si} in conformer **B** by the Ph group results in a severe steric interaction with the 2,3-*O*-isopropylidene group. A compound possessing two substituents of similar bulk at C(1), as it is the case for a Ph and a cyclopentadienyl group, can adopt a favorable conformation by counter clockwise rotation of the CpPhC(1)H group around C(1)–C(2) by 60°, again leading to an antiperiplanar orientation of H–C(1) and H–C(2). This means that the diastereoisomers **19a/20a** and **19b/20b** should possess similar and large couplings constants. This is the case (*Table 1*); J(1,2) of 9.7–10.3 and J(3,4) of 2.7–4.0 Hz agree well with a conformation similar to **A**. The ferrocenyl group is sterically more demanding than the Ph group and should, therefore, adopt the antiperiplanar orientation to the C(2)–C(3) bond; H_{Re} or H_{Si} will then be substituted by a Ph group. No unfavorable steric interactions are involved, if H_{Re} of a conformer of the type **A** is substituted by Ph, and the corresponding ferrocene should then exhibit a large J(1,2) value, similar to those of **19** and **20**. Substitution of H_{Si} by Ph, however, leads to an unfavorable interaction with the 2,3-*O*-isopropylidene group, which can be avoided by rotation around C(1)–C(2). In the ensuing conformer, H–C(1) and H–C(2) are no longer antiperiplanar. Indeed, J(1,2) of **21** (10.0 Hz) and of one ligand of **23** (9.4 Hz) reflect the antiperiplanar arrangement of H–C(1) and H–C(2), whereas J(1,2) of **22** (5.6 Hz) and of the other ligand of **23** (5.3 Hz) suggest a dihedral angle of 130–145°. Thus, the (1*S*)-configuration is assigned to the major isomers **21**, **17a/b**, and **19a/b** and the (1*R*)-configuration to the minor isomers **22**, **18a/b**, and **20a/b**. A striking property of the (1*S*)-isomers is the upfield shift of one Me signal in the $CDCl_3$ spectra (**19a**: 1.07, **19b**: 1.02, **21**: 0.99, **23**: 1.01 ppm). Since such an upfield shift is not observed for **12a/b** and **13a/b**, and the Ph group of the (*S*)-configurated compounds is far removed from the 3,4-*O*-isopropylidene group, these signals must belong to the *cis*-Me group (relative to C(4)) of the 5,6-*O*-isopropylidene moiety which is located in the shielding zone of the Ph group. A similar upfield shift of a Me group is also observed in ribitol derivatives, where the assignment is established by NOE experiments (see below). The shielding effect of the cyclopentadienyl moieties is weak, as evidenced by the absence of similar upfield shifts in the spectra of **20a** and **20b**.

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[4]) Similar conformations were observed for the 1-*C*-(4-oxo-4*H*-thiopyran-2-yl) and the 1-*C*-(1,2,3-thiadiazol-5-yl) analogues of **12** in $CDCl_3$ solution [68]. In the solid state of the thiadiazole, however, O(5) and not O(3) is the intramolecular H-bond acceptor.

2. *1-C-(Cyclopentadienyl)-ribitol and -arabinitol Derivatives.* Similarly to the D-mannofuranose **1**, treatment of the D-ribofuranose **24** [69] (*Scheme 3*) with excess cyclopentadienylsodium yielded the epimeric glycosyl-cyclopentadienes **27** and **28** (47:53; 57%). Again, each epimer was a *ca.* 1:1 mixture of two regioisomers (**27a/b** and **28a/b**) which were separated by chromatography. The ratio of **27a/b** and **28a/b** was determined by integration of the H–C(1) signals of **27a/b** and of the H–C(2) signals of **28a/b** in the ^{1}H-NMR spectrum of the crude product. The one-pot reaction of **24** with cyclopentadienylsodium and then with $LiAlH_4$ [70] entailed loss of the silyl group; isopropylidenation of the crude product gave 65% of the cyclopentadienes **25a/b**. The ferrocene **26** was obtained in 79% yield upon lithiation of **25a/b** and treatment with anhydrous $FeCl_2$.

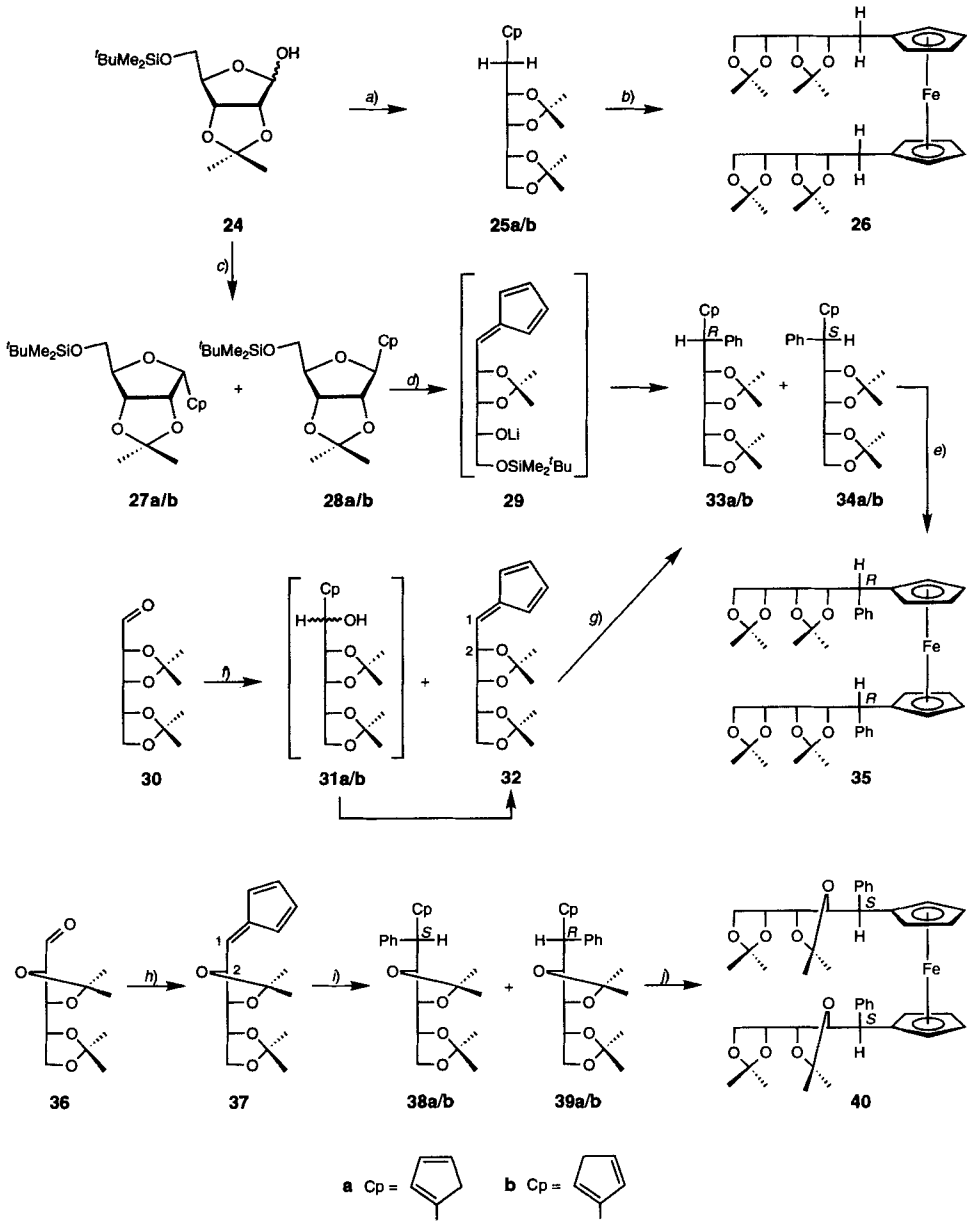
Reaction of **27/28** with excess PhLi in THF, followed by desilylation ($Bu_4NF \cdot 3\ H_2O$ in THF) and isopropylidenation yielded 86% of a 20:1 mixture of the epimeric cyclopentadienes **33a/b** and **34a/b** (*Scheme 3*). The ratio of **33a/b** and **34a/b** was determined by integration of the Me signals. The high diastereoselectivity in the addition of PhLi to the intermediary lithoxy-fulvene **29** contrasts with the low d.e. for the addition to the *manno*-analogue **5**. The influence of the lithoxy group of **29** upon the diastereoselectivity may be clarified by comparing the addition of PhLi to **29** and to the fully protected fulvenes **32** and **37**. Treatment of the *aldehydo*-D-ribose **30** [71] with cyclopentadienylsodium in THF at −100° for 30 min, followed by aqueous workup, gave a crude mixture (*ca.* 1:3) of the fulvene **32** and presumably the intermediate hydroxycyclopentadienes **31**. The best yield of **32** (36%) was obtained upon treatment of the crude product with Ac_2O and Et_3N. No epimerization at C(2) was observed under these conditions, while *Little* and *Stone* [42] [72] noticed partial epimerization in α-position of an aldehyde during condensation with cyclopentadiene and pyrrolidine in MeOH. Higher reaction temperatures (−90 or −78°) or prolonged reaction times at −100° decreased the yields of **32**. Attempts to prepare **32** by the method of *Schaltegger* and *Neuenschwander* [73], *i.e.*, by treating **30** with AcCl in presence of $ZnCl_2$ and addition of cyclopentadienylsodium in the presence of Et_3N, led only to very small amounts of **32**. Similarly to **32**, the D-*arabino*-fulvene **37** was prepared from the *aldehydo*-D-arabinose **36** [74] in 32% yield.

Addition of excess PhLi to **32** gave a 20:1 mixture of the cyclopentadiene **33a/b** and **34a/b** (71%). This shows that the lithoxy group of **29** has at best a weak influence upon the steric course of the addition. Similarly, addition to the *arabino*-fulvene **37** in THF led to an 18:1 mixture of **38a/b** and **39a/b** (ratio by integration of the H–C(2) and Me signals). In Et_2O, however, the ratio **38/39** dropped to *ca.* 4:1. The ferrocenes **35** and **40** were obtained in 88 and 83% yield, respectively, by lithiation of **33/34** or **38/39**, followed by treatment with $FeCl_2$.

H–C(1) of **27a** and **27b** resonates at 5.09 and 5.05 ppm ($J(1,2) = 4.0$ and 4.1 Hz), respectively, whereas H–C(1) of **28a** (4.74 ppm, $J(1,2) = 5.2$ Hz) and **28b** (4.72 ppm, 5.3 Hz) resonates at higher fields. $J(3,4)$ is small (1.0 Hz) for **27a/b**, and somewhat larger for **28a/b** (3.6 and 3.3 Hz). The assignment of the configuration is based upon comparison of the chemical shift of H–C(1), $J(1,2)$, and especially $J(3,4)$ with data of related compounds [75]. These coupling constants suggest a $^2T_3$ (southern) conformation for **27a/b** and a ^0E conformation for **28a/b**. Both epimers possess a pseudoequatorial cyclopentadienyl group and similar $\Delta\delta$ values for the 2,3-*O*-isopropylidene Me signals (**27**: 0.17 ppm, **28**: 0.21 ppm, see [75] and refs. cit. therein).

The configuration at C(1) of **33–35** is again deduced from a conformational analysis. The 2,3-*cis*-configuration of *manno*- and *ribo*-configurated products is reflected in the similar $J(1A,2)$ and $J(1B,2)$ values of **25a/b**, **26** and **13a/b** (2.6–3.6 and 9.4–10.9 Hz, see

Scheme 3



a) CpNa, THF, r.t., $LiAlH_4$, −60°→r.t.; 2,2-dimethoxypropane, $TsOH \cdot H_2O$, acetone, 0°, 65%. *b*) BuLi, THF, −60°→r.t.; $FeCl_2$, r.t., 79%. *c*) CpNa, THF, r.t., 57% of **27/28** 47:53. *d*) PhLi, THF, −78°→0°; $Bu_4NF \cdot 3\ H_2O$, THF, r.t.; 2,2-dimethoxypropane, $TsOH \cdot H_2O$, acetone, 0°, 86% of **33/34** 20:1. *e*) BuLi, THF, −60°→r.t.; $FeCl_2$, r.t., 88%. *f*) CpNa, THF, −100°; Ac_2O, NEt_3, DMAP, THF, r.t., 36%. *g*) PhLi, Et_2O, −78°, 71% of **33/34** 20:1. *h*) CpNa, THF, −100°; Ac_2O, NEt_3, DMAP, THF, r.t., 32%. *i*) PhLi, THF, −78°, 78% of **38/39** 18:1. *j*) BuLi, THF, −20°→r.t.; $FeCl_2$, r.t., 83%.

Tables 1 and *3* in the *Exper. Part*), evidencing a similar distribution of rotamers. The phenylated cyclopentadienes **33a/b** and **34a/b**, and the ferrocene **35** are characterized by large $J(1,2)$ values (9.3–10.2 Hz) which show the antiperiplanar arrangement of H–C(1) and H–C(2). For the same reasons as discussed for the mannitol derivatives, these values allow to assign the (1*R*)-configuration to **33a/b** and **35**. The assignment is corroborated by NOE's for **35** (see *Exper. Part*), indicating the proximity of H–C(4) and H–C(1) and of H–C(4) and one *ortho*-H of the Ph group.

In the 2,3-*trans*-configurated di-*O*-isopropylidene-arabinitols, however, H–C(1) and H–C(2) are no longer antiperiplanar. The $J(1,2)$ values for **38a/b**, **39a/b**, and **40** drop to 4.2–6.5 Hz (*Table 3*) and do not allow to assign the configuration at C(1). X-Ray analysis established the (1*S*)-configuration of **40** (*Fig. 3*) and, hence, of its precursors **38a/b**. The values for $J(1,2)$ of 4.7 ($CDCl_3$) and 6.6 Hz (C_6D_6) of **40** suggest an equilibrium of conformers, one with H–C(1) and H–C(2) antiperiplanar, and the other, as in the solid state, with H–C(1) and H–C(2) synclinal.

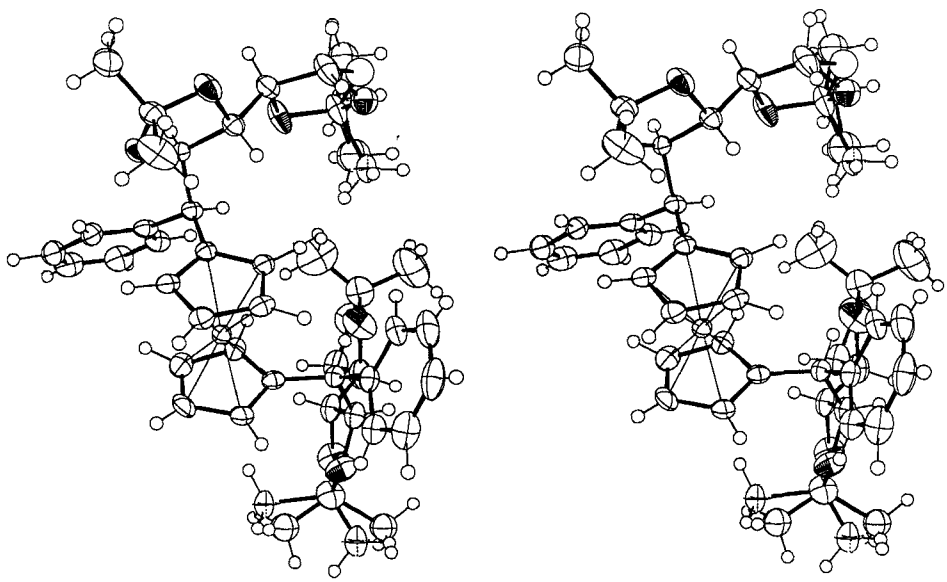
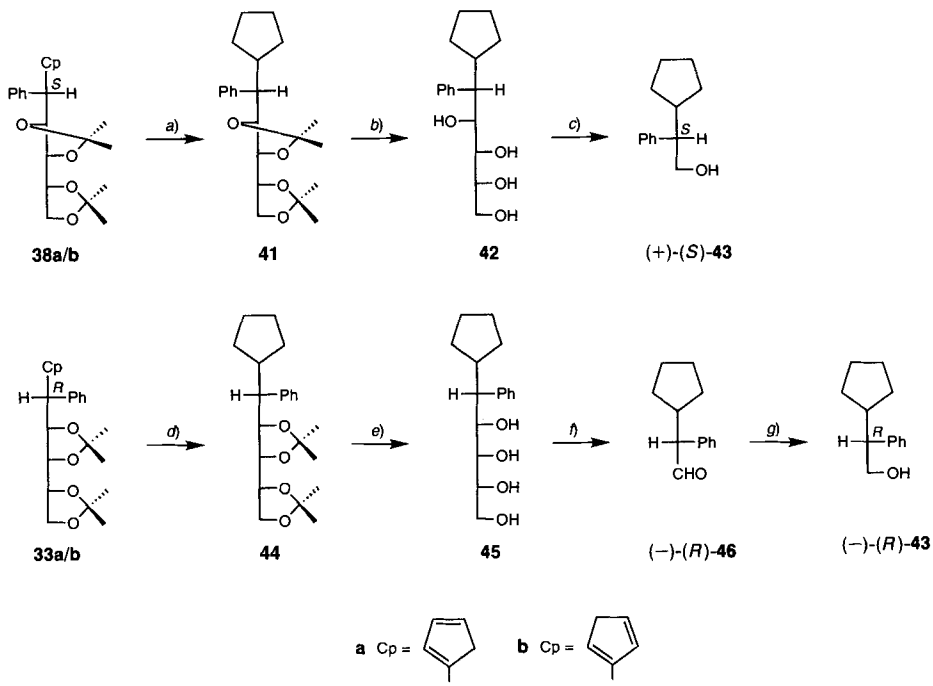


Fig. 3. *X-Ray structure of* **40**

The configuration at C(1) of the arabinitols **38a/b** and the ribitols **33a/b** was determined by degrading both products to **43** (*Scheme 4*). Catalytic hydrogenation of the (1*S*)-configurated **38a/b** (see above) gave the cyclopentane **41** (95%) which was deprotected to the crystalline (1*S*)-tetrol **42** (82%). Periodate oxidation of **42** and immediate reduction of the crude aldehyde led to the phenethyl alcohol (*S*)-**43** (74%; 57.5% overall; $[\alpha]_D^{20} = +18.1$; for racemic **43**, see [76]). The analogous degradation of the ribitols **33a/b** gave **43** *via* **44**–**46** in 51% overall yield. Its specific rotation ($[\alpha]_D^{20} = -17.4$) establishes the (1*R*)-configuration of **33a/b**. The intermediate phenylacetaldehyde (*R*)-**46** racemized slowly, even when pure, and decomposed partially upon storage at 5°. The absence of any

Scheme 4



a) H_2, Pd/C, hexane, r.t., 95%. *b*) 37% aq. HCl, MeOH, r.t., 82%. *c*) $NaIO_4$, $MeCN/H_2O$ 5:1, r.t.; $NaBH_4$, EtOH, r.t., 74%. *d*) As *a*), 95%. *e*) As *b*), 84%. *f*) $NaIO_4$, $MeCN/H_2O$ 1:1, r.t., 76%. *g*) $NaBH_4$, EtOH, r.t., 84%.

signals of the enantiomer in the ^{1}H-NMR spectra of (*S*)- or (*R*)-**43** measured in the presence of the chiral shift reagent [Eu(tfc)$_3$] indicated an e.e. of $\geq 95\%$ for both samples.

The cyclopentyl moiety in **41**–**46** is evidenced by the NMR spectra (see *Exper. Part* and *Table 4*, *cf.* [77] [78]). A large $\Delta\delta$ value is observed for C(1) of **44** and **45** (8.4 ppm), but a small one for C(1) of **41** and **42** (−0.8 ppm), reflecting a shielding of C(1) of **44** (γ-effect), as it is the case for C(4) of **44** and its precursors (*Table 4*). The formyl group of **46** resonates at 9.68 ($J = 3$ Hz) and 200.8 ppm. The ^{1}H-NMR spectra of (*R*)- and (*S*)-**43** show the characteristic *ABX* system for the two H–C(1). No coupling with HO–C(1) is visible in the $CDCl_3$ spectra. As observed for the (1*S*)-configurated mannitols, one Me signal of **33a/b**, **35**, and **44** is shifted upfield (1.02, 1.08, 1.01, and 0.96 ppm, resp.) due to the anisotropy of the Ph group. That this Me group is Me_{Re} (*cis* to C(3)) of the 4,5-*O*-isopropylidene moiety was evidenced by NOE experiments. Irradiation at the H–C(4) resonances of **35** leads to medium NOE's for the H–C(1) and H_A–C(5) signals and to weak NOE's for the signals of the *ortho*-H of the Ph group and for the two Me signals resonating at 1.32 and 1.30 ppm, indicating that these H are located on one side of the molecule, while H–C(2), H–C(3), and H_B–C(5) are located on the other side, as evidenced by NOE's between Me_{Re} of the 2,3-*O*-isopropylidene moiety resonating at 1.21 ppm and H–C(2) and H–C(3), and between Me_{Re} of the 4,5-*O*-isopropylidene moiety resonating at 1.01 ppm and H–C(3) and H_B–C(5). These NOE's allow an unambiguous assignment of the Me groups. Weak NOE's between Me_{Re} resonating at 1.01 ppm and the Ph resonances at 7.28 and 7.10 ppm evidence the location of this Me group in the shielding zone of the Ph group. Similarly, irradiation of the Me signal of **44** at 0.96 ppm leads to weak NOE's for the signals of H–C(3)/H_B–C(5) and the Ph group.

The diastereoselectivity of the addition of PhLi to the 2,3-*O*-isopropylidenated glycosylidene-cyclopentadienes is governed by the configuration of C(2). The main products

are 1,2-*erythro*-configurated. The $J(1,2)$ values of the fulvenes **32** and **37** (8.3 and 7.9 Hz) correspond to dihedral angles of *ca.* 30 or 150°. A H–C(1)–C(2)–H dihedral angle of 30° implies severe A(1,3)-strains [79–84], which should also operate in the transition state. Two conformations are characterized by a dihedral angle of 150°: one with the C(2)–C(3), the other with the C(2)–O(2) bond in the π-plane of the fulvene. The second conformation is favored considering the smaller size of the O-substituent and the interaction of σ^*(C(2)–O) with the fulvenyl LUMO, lowering the LUMO energy [85] and increasing the electrophilic character of the fulvene[5]). Attack of the Ph anion on the double bond '*syn*' to the C(2)–O bond appears to be sterically disfavored, but may become important in the PhLi addition to the 2,3:5,6-di-*O*-isopropylidene mannose derived fulvene **5** which proceeds with a lower degree of diastereoselectivity, conceivably due to the direct or indirect (*via* the orientation of the lithoxy group) influence of the 5,6-*O*-isopropylidene group. The solvent effect on the diastereoselectivity of the addition to **37** shows that additional factors such as aggregation and pre-complexation must be taken into account for a comprehensive analysis.

We thank Dr. *A. Linden* and Dr. *B. Schweizer* for performing the X-ray analyses, the *Danish Technical Research Council* for a grant to *P. V.* and *F. Hoffmann-La Roche AG*, Basle, for their generous support.

Experimental Part

General. Solvents were freshly distilled. Reagents were from *Fluka* or *Aldrich*, and used as received. All reactions were performed under N_2. Normal workup means distribution of the crude product between CH_2Cl_2 and sat. $NaHCO_3$ soln., drying of the org. layer ($MgSO_4$), and evaporation *i.v.* at or below 40° in a *Büchi* rotary evaporator. Anal. TLC: *Merck* precoated silica gel *60 F-254* plates; detection by treatment with a soln. of $(NH_4)_6Mo_7O_{26}\cdot 4\,H_2O$ (5%) and $Ce(SO_4)_2\cdot 4\,H_2O$ (0.1%). Flash chromatography (FC): silica gel *Merck 60* (40–63 μm). High-performance liquid chromatography (HPLC): anal. *Spherisorb* silica (5 μm, 250 × 4.6 mm column), UV detection (254 nm), 2 ml/min; prep. *Spherisorb* silica (5 μm, 250 × 20 mm column), 16 ml/min. M.p.'s: uncorrected. Optical rotations: 1-dm cell at 25° at 589 nm. UV: λ_{max} (ε) in nm. IR spectra: 0.025M solns. in $CHCl_3$. ^{1}H- and ^{13}C-NMR Spectra: at 200, 300, and 500 (^{1}H) and at 50 and 75 MHz (^{13}C); chemical shifts in ppm relative to TMS, coupling constants J in Hz. Mass spectra: EI at 70 eV.

(1S/1R)-1,4-Anhydro-1-C-(cyclopenta-1',3'-dienyl)-2,3:5,6-di-O-isopropylidene-D-mannitol (**6a**/**7a**) *and (1S/1R)-1,4-Anhydro-1-C-(cyclopenta-1',4'-dienyl)-2,3:5,6-di-O-isopropylidene-D-mannitol* (**6b**/**7b**). At 0°, a soln. of cyclopentadienylsodium (CpNa; 2M in THF, 16 ml, 32 mmol) was added to a stirred soln. of **1** (2.11 g, 8.1 mmol) in dry THF (8 ml). The dark purple soln. was stirred at r.t. for 6 h. Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:10) afforded 1.68 g (67%) of **6**/**7** 49:51 as a yellow oil which slowly decomposed at r.t. A second FC afforded NMR-pure samples of **6a** and **6b**, and prep. HPLC (hexane/Et_2O 90:10) pure ones of **7a** and **7b**. A $CDCl_3$ soln. of pure **6a**, **6b**, **7a**, or **7b** isomerized over several days to a mixtures **6a**/**b** and **7a**/**b**, respectively.

Data of **6a**/**b** *1:1*: R_f (CH_2Cl_2/Et_2O/pentane 1:1:6) 0.48 and 0.43. $[\alpha]_D^{25} = +18.6$ (c = 2.04, CH_2Cl_2). IR: 2992*s*, 2940*m*, 2883*w*, 1382*s*, 1372*s*, 1225*m* (br.), 1155*m*, 1105*m*, 1068*s*, 993*w*, 973*w*, 951*w*, 899*m*, 841*m*.

Data of **6a**: ^{1}H-NMR (300 MHz, $CDCl_3$): 6.51 (*m*, 1 olef. H); 6.48 (*m*, 1 olef. H); 6.44 (*m*, 1 olef. H); 4.81 (*dd*, J = 3.7, 6.1, irrad. at 3.60→*d*, J = 6, irrad. at 4.69→*d*, J = 3.5, H–C(3)); 4.69 (*dd*, J = 3.8, 6.1, H–C(2)); 4.48 (*d*, J = 3.8, irrad. at 4.69→*s*, H–C(1)); 4.43 (*dt*, J = 7.2, 5.7, irrad. at 3.60→*t*, $J \approx 5.5$, irrad. at 4.11→*d*, J = 7, H–C(5)); 4.11 (*d*, J = 5.8, 2 H–C(6)); 3.60 (*dd*, J = 3.8, 7.2, H–C(4)); 3.27 (*dq*, $J \approx 24$, 1, H_A–C(5')); 3.11 (*dq*, $J \approx 24$, 1, H_B–C(5')); 1.49 (*s*, Me); 1.46 (*s*, Me); 1.40 (*s*, Me); 1.31 (*s*, Me).

Data of **6b**: ^{1}H-NMR (300 MHz, $CDCl_3$): 6.66 (*m*, 1 olef. H); 6.48 (*m*, 1 olef. H); 6.40 (*m*, 1 olef. H); 4.83 (*dd*, J = 3.7, 6.8, H–C(3)); 4.76 (*dd*, J = 3.6, 6.8, H–C(2)); 4.46 (*d*, J = 3.6, H–C(1)); 4.43 (*m*, H–C(5)); 4.10 (*d*,

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[5]) The same factors – *mutatis mutandis* – are operative in the diastereoselectivity of the addition of nucleophiles to 2-alkoxynitrones [86].

J = 5.5, 2 H–C(6)); 3.60 (*dd*, J = 3.7, 7.6, H–C(4)); 3.05–3.01 (*m*, 2 H–C(5′)); 1.51 (*s*, Me); 1.47 (*s*, Me); 1.40 (*s*, Me); 1.33 (*s*, Me).

Data of **7a**/**b** *1:1*: R_f(CH_2Cl_2/Et_2O/pentane 1:1:6) 0.59. $[\alpha]_D^{25}$ = +18.8 (c = 0.49, CH_2Cl_2). IR: 2992*s*, 2940*m*, 2882*w*, 1382*s*, 1372*s*, 1225*m* (br.), 1149*m*, 1115*m*, 1067*s*, 976*w*, 950*w*, 895*m*, 843*m*. EI-MS: 616 (3, $[2M]^+$), 601 (4, $[2M - Me]^+$), 308 (23, $M^{+\cdot}$), 293 (32, $[M - Me]^+$), 250 (231), 192 (16), 175 (20), 150 (22), 141 (18), 101 (100), 43 (60).

Data of **7a**: t_R (hexane/Et_2O 90:10) 28.3 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.43 (*m*, 2 olef. H); 6.37 (*m*, 1 olef. H); 4.94 (*s*, H–C(1)); 4.93 (*d*, J = 5.6, irrad. at 4.78→*s*, H–C(2)); 4.78 (*dd*, J = 3.7, 5.6, irrad. at 3.71→*d*, J = 5.5, H–C(3)); 4.44 (*ddd*, J = 4.6, 6.2, 7.7, irrad. at 3.71→*dd*, J = 4.5, 6, H–C(5)); 4.13 (*dd*, J = 6.2, 8.7, H_A–C(6)); 4.04 (*dd*, J = 4.6, 8.7, H_B–C(6)); 3.71 (*dd*, J = 3.7, 7.6, irrad. at 4.78→*d*, J = 7.5, H–C(4)); 3.03 (*dq*, $J \approx 24$, 1, H_A–C(5′)); 2.94 (*dq*, $J \approx 24$, 1, H_B–C(5′)); 1.54 (*s*, Me); 1.43 (*s*, Me); 1.38 (*s*, 2 Me).

Data of **7b**: t_R (hexane/Et_2O 90:10) 24.5 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.50 (*m*, 2 olef. H); 6.23 (*m*, 1 olef. H); 4.92 (*d*, J < 1, H–C(1)); 4.91 (*d*, J = 5.6, irrad. at 4.78→*s*, H–C(2)); 4.78 (*dd*, J = 3.8, 5.6, irrad. at 3.75→*d*, J = 5.5, H–C(3)); 4.45 (*ddd*, J = 4.6, 6.2, 7.8, irrad. at 3.75→*dd*, J = 4.5, 6, H–C(5)); 4.15 (*dd*, J = 6.2, 8.7, H_A–C(6)); 4.09 (*dd*, J = 4.6, 8.7, H_B–C(6)); 3.75 (*dd*, J = 3.9, 7.8, irrad. at 4.78→*d*, J = 7.5, H–C(4)); 3.02–2.98 (*m*, 2 H–C(5′)); 1.55 (*s*, Me); 1.43 (*s*, Me); 1.382 (*s*, Me); 1.376 (*s*, Me).

Treatment of **6a**/**b** *with* N-*Phenylmaleimide*. At 20°, a soln. of *N*-phenylmaleimide (194 mg, 1.12 mmol) in CH_2Cl_2 (2.5 ml) was added to a freshly prepared soln. of **6a**/**b** *ca.* 3:7 (345 mg, 1.12 mmol) in CH_2Cl_2 (2.5 ml). After stirring for 3 h, the solvent was evaporated giving (**8** or **9**)/**10**/**11** *ca.* 30:56:14 (^{1}H-NMR) as a pale yellow foam. FC (AcOEt/hexane 1:1→2:1) afforded **8** (135 mg, 25%, white solid), **10** (242 mg, 45%, white needles from hexane/Et_2O), and **11** (70 mg, 13%, white crystals from hexane/Et_2O).

(1S,1′R,2′S*,6′S*,7′R*)-1,4-Anhydro-1-*C*-(3,5-dioxo-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-1-yl)-2,3:5,6-di-*O*-isopropylidene-*D*-mannitol* (**8** or **9**): R_f(AcOEt/hexane 2:1) 0.50. $[\alpha]_D^{25}$ = −48.1 (c = 0.55, $CHCl_3$). UV (EtOH): 202. IR: 2995*m*, 2933*m*, 2880*w*, 1710*s*, 1500*w*, 1380*s*, 1112*s*, 1070*s*, 910*m*, 842*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.46–7.36 (*m*, 3 arom. H); 7.16–7.13 (*m*, 2 arom. H); 6.32 (*dd*, J = 2.8, 5.7, H–C(8′)); 6.19 (br. *d*, J = 5.7, irrad. at 6.32→br. *s*, H–C(9′)); 4.85 (*dd*, J = 3.3, 6.2, H–C(2)); 4.82 (*dd*, J = 3.6, 6.1, H–C(3)); 4.43 (*q*, $J \approx 6$, H–C(5)); 4.39 (*d*, J = 3.2, irrad. at 4.85→*s*, H–C(1)); 4.11 (*d*, J = 5.5, 2 H–C(6)); 3.70 (*dd*, J = 3.6, 6.9, irrad. at 4.82→*d*, J = 6.9, H–C(4)); 3.58 (*d*, J = 7.5, H–C(2′)); 3.47 (br. *t*, $J \approx 3.5$, H–C(7′)); 3.44 (*dd*, J = 4.6, 7.5, irrad. at 3.58→*d*, J = 4.5, H–C(6′)); 2.27 (*dd*, J = 1.5, 9.0, H_A–C(10′)); 1.78 (br. *d*, J = 8.9, irrad. at 2.27→*s*, H_B–C(10′)); 1.47 (*s*, Me); 1.43 (*s*, Me); 1.40 (*s*, Me); 1.31 (*s*, Me).

*(1S,1′S,2′R,6′S,7′S)-1,4-Anhydro-1-*C*-(3,5-dioxo-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-8-yl)-2,3:5,6-di-*O*-isopropylidene-*D*-mannitol* (**10**): R_f(AcOEt/hexane 2:1) 0.34. M.p. 164–166°. $[\alpha]_D^{25}$ = −36.8 (c = 0.14, $CHCl_3$). UV (EtOH): 206. IR: 2990*m*, 2941*w*, 2878*w*, 1710*s*, 1602*w*, 1495*w*, 1378*s*, 1111*s*, 1069*s*, 868*m*, 842*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.46–7.34 (*m*, 3 arom. H); 7.20–7.17 (*m*, 2 arom. H); 6.36 (br. *s*, H–C(9′)); 4.73 (*dd*, J = 3.8, 6.2, H–C(3)); 4.56 (*dd*, J = 3.6, 6.3, irrad. at 4.73→*d*, J = 3.6, H–C(2)); 4.41 (*ddd*, J = 4.2, 6.1, 8.3, H–C(5)); 4.05 (*dd*, J = 6.1, 8.9, H_A–C(6)); 3.97 (*dd*, J = 0.5, 3.6, H–C(1)); 3.92 (*dd*, J = 4.2, 8.9, H_B–C(6)); 3.68 (br. *d*, $J \approx 4.5$, irrad. at 3.44→br. *s*, H–C(7′)); 3.52–3.48 (*m*, H–C(1′), H–C(2′)); 3.44 (*dd*, J = 3.8, 8.0, irrad. at 4.73→*d*, J = 8.0, H–C(4)); 3.44–3.41 (*m*, irrad. at 3.68→change, H–C(6′)); 1.97 (br. *dt*, J = 8.8, 1.8, H_A–C(10′)); 1.63 (br. *d*, J = 8.8, H_B–C(10′)); 1.51 (*s*, Me); 1.43 (*s*, Me); 1.36 (*s*, Me); 1.30 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 176.71 (*s*); 176.65 (*s*); 143.65 (*s*); 132.65 (*s*); 129.03 (*d*); 128.94 (2*d*); 126.49 (2*d*); 126.31 (*d*); 112.45 (*s*); 109.17 (*s*); 82.58 (*d*); 81.73 (*d*); 80.72 (*d*); 78.70 (*d*); 72.87 (*d*); 67.10 (*t*); 52.66 (*t*); 48.24 (*d*); 46.84 (*d*); 45.91 (*d*); 45.58 (*d*); 27.00 (*q*); 25.72 (*q*); 25.31 (*q*); 25.21 (*q*).

*(1S,1′R,2′S,6′R,7′R)-1,4-Anhydro-1-*C*-(3,5-dioxo-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-8-yl)-2,3:5,6-di-*O*-isopropylidene-*D*-mannitol* (**11**): R_f(AcOEt/hexane 2:1) 0.28. M.p. 146–147°. $[\alpha]_D^{25}$ = +54.7 (c = 0.32, $CHCl_3$). UV (EtOH): 201. IR: 2980*s*, 2937*w*, 2875*s*, 1709*s*, 1602*w*, 1448*w*, 1382*s*, 1110*s*, 1071*s*, 863*w*, 843*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.47–7.36 (*m*, 3 arom. H); 7.13–7.10 (*m*, 2 arom. H); 6.12 (br. *t*, $J \approx 2.0$, irrad. at 3.40→*t*, J = 2.0, H–C(9′)); 4.84 (*dd*, J = 4.2, 6.1, H–C(2)); 4.77 (*dd*, J = 3.2, 6.1, irrad. at 4.84→*d*, J = 3.2, H–C(3)); 4.40 (*ddd*, J = 4.6, 6.2, 7.8, H–C(5)); 4.10 (*dd*, J = 6.2, 8.7, H_A–C(6)); 4.07 (*dd*, J = 2.0, 4.2, irrad. at 6.12→*d*, J = 4.2, irrad. at 4.84→*d*, J = 2.0, H–C(1)); 4.01 (*dd*, J = 4.6, 8.7, H_B–C(6)); 3.54 (*dd*, J = 3.3, 7.7, H–C(4)); 3.52–3.46 (*m*, 3 H); 3.40 (*m*, $J \approx 3$, irrad. at 6.12→weak change, H–C(7′)); 1.93 (*dt*, J = 9.0, 1.5, H_A–C(10′)); 1.63 (br. *d*, J = 9.0, H_B–C(10′)); 1.57 (*s*, Me); 1.43 (*s*, Me); 1.39 (*s*, Me); 1.33 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 177.05 (*s*); 176.99 (*s*); 143.7 (*s*); 131.98 (*s*); 129.21 (2*d*); 128.89 (*d*); 127.67 (*d*); 127.11 (2*d*); 112.96 (*s*); 109.16 (*s*); 81.30 (*d*); 81.09 (*d*); 80.94 (2*d*); 73.02 (*d*); 66.99 (*t*); 51.52 (*t*); 47.08 (*d*); 46.94 (*d*); 45.82 (*d*); 45.74 (*d*); 26.89 (*q*); 25.82 (*q*); 25.31 (*q*); 25.18 (*q*).

*1-*C*-(Cyclopenta-1′,3′-dienyl)- and 1-*C*-(Cyclopenta-1′,4′-dienyl)-1-deoxy-2,3:5,6-di-*O*-isopropylidene-*D*-mannitol* (**12a**/**b**). *a*) At 0°, a soln. of CpNa (2M in THF, 33 ml, 66 mmol) was added to a stirred soln. of **1** (4.22 g,

16.2 mmol) in dry THF (10 ml). The soln. was stirred at r.t. for 11 h, cooled to −70°, and treated with small portions of $LiAlH_4$ (625 mg, 16.5 mmol). The mixture was allowed to warm to r.t. over 2 h, stirred for 30 min at r.t., cooled to −70°, and treated with AcOEt (10 ml). The mixture was allowed to warm to r.t. over 1 h, cooled to −70°, treated with sat. $NaHCO_3$ soln. (10 ml), and allowed to warm to r.t. over 1 h. Addition of H_2O (100 ml), filtration through *Celite*, extraction of the aq. phase with CH_2Cl_2, drying of the org. layer ($MgSO_4$), evaporation, and FC (AcOEt/hexane 1:3) afforded 4.04 g (80%, yellow oil) of slightly impure **12a/b**. Prep. HPLC (hexane/Et_2O 85:15) gave pure samples of **12a** and **12b**. A $CDCl_3$ soln. of pure **12a** or **12b** isomerized over several days to mixtures **12a/b**.

b) The reaction of a soln. of **6/7** (156 mg, 0.51 mmol) in THF (2.5 ml) with $LiAlH_4$ (31 mg, 0.82 mmol) and NaH (55% suspension; 38 mg, 0.87 mmol) for 2 h at r.t. and 2 h at 60° and FC (AcOEt/hexane 1:3) gave 115 mg (73%) of **12a/b**.

Data of **12a/b** *1:1*: R_f(CH_2Cl_2/Et_2O/pentane 1:1:2) 0.55. ^{13}C-NMR (75 MHz, $CDCl_3$): 145.09; 143.05; 134.50; 134.14; 132.32; 131.32; 128.09; 127.59; 109.26; 107.86; 76.75; 76.24; 76.18; 75.95; 70.42; 70.35; 67.06; 44.02; 41.49; 31.21; 30.42; 26.89; 26.79; 25.31; 24.57. EI-MS: 310 (1, $M^{+\cdot}$), 295 (13, $[M - Me]^+$), 253 (8), 234 (5), 194 (8), 173 (21), 131 (26), 121 (50), 101 (53), 93 (28), 79 (35), 59 (100), 43 (96).

Data of **12a**: t_R(hexane/Et_2O 85:15) 38 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.43 (*m*, 1 olef. H); 6.29 (*m*, 1 olef. H); 6.26 (br. *s*, 1 olef. H); 4.53 (*q*, $J \approx 6.9$, irrad. at 2.93→*d*, $J \approx 5$, H–C(2)); 4.37 (*dd*, $J = 1.3$, 6.9, irrad. at 4.53→br. *s*, H–C(3)); 4.10–3.97 (*m*, H–C(5), 2 H–C(6)); 3.53 (*dt*, $J \approx 1.3$, 7.9, H–C(4)); 3.05–2.89 (*m*, 2 H–C(5′)); 2.96 (*ddd*, $J = 1.5$, 7.8, 15.8, irrad. at 4.53→*dd*, $J \approx 1$, 14, H_A–C(1)); 2.87 (*ddd*, $J = 1.3$, 6.0, 15.8, irrad. at 4.53→*dd*, $J \approx 1$, 14, H_B–C(1)); 2.22 (*d*, $J = 8.1$, OH); 1.52 (*s*, Me); 1.40 (*s*, Me); 1.36 (*s*, Me); 1.35 (*s*, Me).

Data of **12b**: t_R(hexane/Et_2O 85:15) 31 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.49 (*m*, 1 olef. H); 6.45 (*m*, 1 olef. H); 6.12 (br. *s*, 1 olef. H); 4.59 (*q*, $J \approx 6.9$, irrad. at 2.90→*d*, $J \approx 5$, H–C(2)); 4.37 (*dd*, $J = 1.3$, 6.9, H–C(3)); 4.10–3.99 (*m*, H–C(5), 2 H–C(6)); 3.56 (*dt*, $J \approx 1.3$, 8.0, irrad. at 2.22→*dd*, $J \approx 1$, 7, H–C(4)); 2.98–2.95 (*m*, 2 H–C(5′)); 2.97–2.80 (*m*, 2 H–C(1)); 2.22 (*d*, $J = 8.2$, OH); 1.53 (*s*, Me); 1.41 (*s*, Me); 1.34 (*s*, 2 Me).

*4-O-[(*tert*-Butyl)dimethylsilyl]-1-C-(cyclopenta-1′,3′-dienyl)- and -1-C-(cyclopenta-1′,4′-dienyl)-1-deoxy-2,3:5,6-di-O-isopropylidene-*D*-mannitol* (**13a/b**). At −60°, (*tert*-butyl)dimethylsilyl trifluoromethanesulfonate (*t*-$BuMe_2SiOTf$; 1.5 ml, 6.5 mmol) was added dropwise to a soln. of **12** (1.67 g, 5.4 mmol) and (Et_2(i-Pr)N (1.9 ml, 11 mmol) in dry CH_2Cl_2 (5 ml). The mixture was allowed to warm to 0° over 1 h and stirred for 3 h. Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:16→1:1:10) afforded 1.63 g (71%; yellow oil) of **13a/b**. An anal. sample of **13a/b** was obtained after a second FC. Crystallization from MeOH/H_2O gave a white powder of **13a/b**. Prep. HPLC (hexane/Et_2O 95:5) afforded pure sample of **13a** and **13b**. A $CDCl_3$ soln. of pure **13a** or **13b** isomerized over several days to mixtures **13a/b**.

Data of **13a/b** *1:1*: R_f(CH_2Cl_2/Et_2O/pentane 1:1:2) 0.57, 0.51. M.p. 35°. $[\alpha]_D^{25} = +83.3$ ($c = 1.05$, $CHCl_3$). IR: 2988*s*, 2956*s*, 2931*s*, 2886*s*, 2858*s*, 1472*m*, 1463*m*, 1381*s*, 1371*s*, 1297*w*, 1255*s*, 1153*s*, 1105*s*, 1076*s*, 1053*s*, 1006*m*, 966*w*, 950*w*, 838*w*, 900*m*, 882*s*, 839*s*, 592*w*. EI-MS: 425 (0.5, $[M + 1]^+$), 409 (3, $[M - Me]^+$), 367 (1, $[M - {}^tBu]^+$), 309 (8, $[M - {}^tBuMe_2Si]^+$), 251 (18), 187 (28), 171 (17), 159 (23), 131 (28), 129 (32), 121 (23), 117 (31), 115 (16), 101 (100), 73 (73), 59 (27), 43 (55). Anal. calc. for $C_{23}H_{40}O_5Si$ (424.65): C 65.05, H 9.49; found C 65.00, H 9.26.

Data of **13a**: t_R(hexane/Et_2O 95:5) 16.6 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.46–6.42 (*m*, 1 olef. H); 6.30–6.27 (*m*, 1 olef. H); 6.25 (br. *s*, 1 olef. H); 4.23 (*ddd*, $J = 2.7$, 4.4, 10.9, H–C(2)); 4.12 (*dd*, $J = 5.7$, 7.4, H_A–C(6)); 4.01–3.87 (*m*, H–C(3), H–C(4), H–C(5)); 3.87 (*t*, $J = 7.3$, H_B–C(6)); 3.02 (*dq*, $J \approx 24$, 1.3, H_A–C(5′)); 2.93 (*dq*, $J \approx 24$, 1.3, H_B–C(5′)); 2.74 (*ddd*, $J = 1.3$, 2.5, 14.3, irrad. at.→*dd*, $J \approx 1$, 14, H_A–C(1)); 2.53 (*ddd*, $J = 1.0$, 10.9, 14.3, irrad. at 4.23→br. *d*, $J \approx 14$, H_B–C(1)); 1.50 (*s*, Me); 1.42 (*s*, Me); 1.34 (*s*, Me); 1.32 (*s*, Me); 0.89 (*s*, ^{t}BuSi); 0.15 (*s*, MeSi); 0.13 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.98 (*s*); 132.45 (*d*); 131.24 (*d*); 128.47 (*d*); 109.42 (*s*); 107.50 (*s*); 80.42 (*d*); 77.88 (*d*); 77.25 (*d*); 72.10 (*d*); 67.85 (*t*); 44.02 (*t*); 32.12 (*t*); 28.63 (*q*); 26.37 (*q*); 26.15 (*q*); 26.01 (3*q*); 25.18 (*q*); 18.51 (*s*); −3.74 (*q*); −4.52 (*q*).

Data of **13b**: t_R(hexane/Et_2O 95:5) 20.3 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.52–6.49 (*m*, 1 olef. H); 6.44–6.41 (*m*, 1 olef. H); 6.11 (br. *s*, 1 olef. H); 4.30 (br. *d*, $J \approx 10.6$, 3.5, H–C(2)); 4.11 (*dd*, $J = 5.5$, 7.4, H_A–C(6)); 3.99–3.91 (*m*, H–C(3), H–C(4), H–C(5)); 3.88 (*t*, $J = 7.3$, H_B–C(6)); 3.07–2.89 (*m*, 2 H–C(5′)); 2.70 (br. *dd*, $J \approx 1.3$, 14, irrad. at 4.30→br. *d*, $J \approx 14$, H_A–C(1)); 2.50 (*ddd*, $J \approx 1$, 10.5, 14, irrad. at 4.30→br. *d*, $J \approx 14$, H_B–C(1)); 1.52 (*s*, Me); 1.42 (*s*, Me); 1.34 (*s*, Me); 1.33 (*s*, Me); 0.90 (*s*, ^{t}BuSi); 0.15 (*s*, MeSi); 0.14 (*s*, MeSi). ^{13}C-NMR (75 MHz, $CDCl_3$): 143.59 (*s*); 134.63 (*d*); 133.93 (*d*); 128.30 (*d*); 109.39 (*s*); 107.57 (*s*); 80.36 (*d*); 77.29 (*d*); 77.23 (*d*); 72.04 (*d*); 67.71 (*t*); 41.40 (*t*); 31.44 (*t*); 28.59 (*q*); 26.36 (*q*); 26.01 (4*q*); 25.23 (*q*); 18.51 (*s*); −3.74 (*q*); −4.51 (*q*).

*1,1′-Bis{4-O-[(*tert*-butyl)dimethylsilyl]-1-deoxy-2,3:5,6-di-O-isopropylidene-*D*-mannitol-1-yl}ferrocene* (**14**). At −60°, a soln. of BuLi (1.6M in hexane, 0.70 ml, 1.1 mmol) was added dropwise to a stirred soln. of **13** (396 mg, 0.93 mmol) in dry THF (2 ml). The mixture was allowed to warm to 0° over 1 h and stirred for 45 min. The clear soln. was treated with anh. $FeCl_2$ (66 mg, 0.52 mmol) and stirred for 1 h at 0° and 2 h at r.t. Normal workup and FC

(CH_2Cl_2/Et_2O/pentane 1:1:10) afforded 320 mg (76%, yellow oil) of **14**. Crystallization from $MeNO_2$ gave yellow crystals which contained *ca.* 65 mol-% of $MeNO_2$ (m.p. 81–85°). An anal. sample was obtained by dissolving these crystals in MeOH and evaporating the soln. to dryness, leading to a yellow solid. R_f(CH_2Cl_2/Et_2O/pentane 1:1:10) 0.34. M.p. 44–46°. $[\alpha]_D^{25} = +65.9$ ($c = 0.54$, $CHCl_3$). IR: 3091*w*, 2988*s*, 2956*s*, 2931*s*, 2897*m*, 2858*s*, 1472*m*, 1464*m*, 1437*m*, 1381*s*, 1371*s*, 1295*w*, 1256*s*, 1155*s*, 1104*s*, 1075*s*, 1053*s*, 1040*s*, 1006*m*, 965*w*, 931*w*, 884*s*, 871*s*, 838*s*. ^{1}H-NMR (500 MHz, C_6D_6): 4.38 (*ddd*, $J = 2.6$, 5.0, 10.5, H–C(2)); 4.37 (*dt*, $J = 1.4$, 2.1, 1 arom. H); 4.23 (*dt*, $J = 1.3$, 2.1, 1 arom. H); 4.10 (*dd*, $J = 5.9$, 7.5, H_A–C(6)); 4.10–4.08 (*m*, 2 arom. H); 4.06 (*dd*, $J = 6.5$, 8.9, H–C(4)); 3.98 (*t*, $J = 7.7$, H_B–C(6)); 3.95 (*dd*, $J \approx 5.0$, 8.9, irrad. at 4.38→change, H–C(3)); 3.935 (br. *dt*, $J = 7.5$, 6.6, H–C(5)); 2.83 (*dd*, $J = 2.6$, 14.2, irrad. at 4.38→*d*, $J \approx 14$, H_A–C(1)); 2.66 (*dd*, $J = 10.6$, 14.2, irrad. at 4.38→*d*, $J \approx 14$, H_B–C(1)); 1.54 (*s*, Me); 1.52 (*s*, Me); 1.31 (*s*, 2 Me); 1.02 (*s*, ^{t}Bu); 0.30 (*s*, MeSi); 0.21 (*s*, MeSi). ^{13}C-NMR (75 MHz, C_6D_6): 109.75 (*s*); 107.54 (*s*); 86.40 (*s*); 81.15 (*d*); 79.51 (*d*); 77.84 (*d*); 72.81 (*d*); 70.76 (*d*); 69.71 (*d*); 68.59 (*d*); 68.45 (*d*); 68.39 (*t*); 31.42 (*t*); 28.97 (*q*); 26.85 (*q*); 26.50 (*q*); 26.37 (3*q*); 25.56 (*q*); 18.85 (*s*); −3.27 (*q*); −4.17 (*q*). EI-MS: 902 (100, $M^{+\cdot}$), 887 (8, $[M - Me]^+$), 845 (15, $[M - {}^tBu]^+$), 787 (7, $[M - Si^tBuMe_2]^+$), 614 (6), 213 (7), 187 (5), 131 (6), 129 (6), 119 (7), 115 (8), 101 (31), 75 (34), 73 (45), 43 (38). Anal. calc. for $C_{46}H_{78}FeO_{10}Si_2$ (903.14): C 61.18, H 8.71; found: C 61.25, H 8.54.

*1,1′-Bis{4-O-[(*tert*-butyl)dimethylsilyl]-1-deoxy-2,3:5,6-di-*O*-isopropylidene-*D*-mannitol-1-yl}titanocene Dichloride* (**15**). At −60°, a soln. of BuLi (1.6M in hexane, 0.52 ml, 0.83 mmol) was added dropwise to a stirred soln. of **13** (312 mg, 0.73 mmol) in dry degassed THF (1.2 ml). The mixture was allowed to warm to r.t. over 1 h and stirred for 1 h. The clear soln. was cooled to −78° and treated with $TiCl_4$ (40 µl, 0.36 mmol). Stirring of the brown suspension for 1 h at −78°, 2 h at 0° and 22 h at r.t. gave a dark red soln. Solvents were evaporated at 0.01 Torr, and the resulting brown residue was extracted with warm (30°) degassed pentane (30 ml) and cooled to −78°, whereupon purple crystals separated out. *Schlenk* filtration and washing of the filter cake with cold pentane (2 × 5 ml) afforded 121 mg (34%; air-sensitive purple powder) of **15**. M.p. 170–176°. $[\alpha]_D^{25} = 9.3$ ($c = 0.205$, $CHCl_3$). IR: 2989*s*, 2956*m*, 2931*s*, 2887*m*, 2857*m*, 2361*w*, 2333*w*, 1472*m*, 1457*m*, 1382*s*, 1372*s*, 1295*w*, 1254*s*, 1154*s*, 1102*s*, 1075*s*, 1052*s*, 1006*w*, 963*w*, 938*w*, 881*m*, 838*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.46–6.44 (*m*, 1 arom. H); 6.38–6.36 (*m*, 3 arom. H); 4.19 (br. *d*, $J \approx 11.5$, irrad. at 2.85→br. *s*, H–C(2)); 4.11 (*dd*, $J = 5.7$, 7.4, H_A–C(6)); 4.02–3.95 (*m*, H–C(3), H–C(4), H–C(5)); 3.85 (*t*, $J = 7.4$, irrad. at 4.11→*d*, $J \approx 7$, H_B–C(6)); 3.14 (*dd*, $J = 1.9$, 14.0, irrad. at 4.19→*d*, $J \approx 14$, H_A–C(1)); 2.85 (*dd*, $J = 11.4$, 14.1, irrad. at 4.19→*d*, $J \approx 14$, H_B–C(1)); 1.47 (*s*, Me); 1.35 (*s*, Me); 1.32 (*s*, Me); 1.26 (*s*, Me); 0.88 (*s*, ^{t}BuSi); 0.13 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, C_6D_6): 134.67 (*s*); 124.81 (*d*); 123.93 (*d*); 113.82 (*d*); 112.14 (*d*); 109.48 (*s*); 107.61 (*s*); 80.98 (*d*); 77.65 (*d*); 77.26 (*d*); 72.14 (*d*); 67.65 (*t*); 32.70 (*t*); 28.62 (*q*); 26.65 (*q*); 26.03 (3*q*); 25.65 (*q*); 25.37 (*q*); 18.48 (*s*); −3.79 (*q*); −4.63 (*q*). Anal. calc. for $C_{46}H_{78}Cl_2O_{10}Si_2Ti$ (966.08): C 57.19, H 8.14; found: C 57.47, H 8.09.

*1-{4-O-[(*tert*-Butyl)dimethylsilyl]-1-deoxy-2,3:5,6-di-*O*-isopropylidene-*D*-mannitol-1-yl}-1′,2′,3′,4′,5′-pentamethylferrocene* (**16**). At 20°, 1.6M MeLi in Et_2O (0.60 ml, 0.96 mmol) was added dropwise to a stirred soln. of 1,2,3,4,5-pentamethylcyclopentadiene (0.15 ml, 0.93 mmol) in dry THF (5 ml), followed by stirring for 0.5 h at r.t. The resulting white suspension was added to a cooled (−78°) slurry of freshly prepared iron(II) acetylacetonate (229 mg, 0.90 mmol) [57] in dry THF (7 ml). The purple soln. was allowed to warm to r.t. over 10 min and stirred for further 5 min, leading to a dark red soln. A clear soln. of the lithium salt of **13** (0.98 mmol) in dry THF (1 ml)[6]) was added *via* a cannula leading to a dark yellow soln. Stirring was continued for 1 h at r.t. Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:16) afforded 417 mg (yellow oil) of **16** containing *ca.* 7% of **13**. Crystallization from MeOH/H_2O gave 350 mg (63%; air-sensitive yellow powder) of pure **16**. An anal. sample was obtained by recrystallization in pentane. R_f(CH_2Cl_2/Et_2O/pentane 1:1:10) 0.61. M.p. 144°. $[\alpha]_D^{25} = 33.5$ ($c = 1.06$, $CHCl_3$). IR: 3083*w*, 2988*s*, 2952*s*, 2931*s*, 2904*s*, 2858*s*, 1472*m*, 1463*m*, 1454*m*, 1432*w*, 1381*s*, 1372*s*, 1296*w*, 1256*s*, 1157*s*, 1102*s*, 1074*s*, 1052*s*, 1036*s*, 1006*m*, 965*w*, 928*w*, 885*m*, 872*m*, 839*s*. ^{1}H-NMR (500 MHz, C_6D_6): 4.22 (*dd*, $J = 6.1$, 9.0, H–C(4)); 4.11 (*ddd*, $J = 3.2$, 5.0, 10.1, H–C(2)); 4.06 (*dd*, $J = 6.4$, 7.8, H_A–C(6)); 4.01 (*t*, $J = 7.7$, H_B–C(6)); 3.93 (*dd*, $J = 5.0$, 8.9, irrad. at 4.11→change, irrad. at 4.22→change, H–C(3)); 3.925 (*dt*, $J = 7.5$, 6.3, irrad. at 4.22→change, H–C(5)); 3.83 (*dt*, $J = 1.2$, 2.3, 1 arom. H); 3.63 (*dt*, $J = 2.4$, 1.3, 1 arom. H); 3.57 (*m*, 2 arom. H); 2.66 (*dd*, $J = 3.2$, 13.6, irrad. at 4.11→*d*, $J = 13.5$, H_A–C(1)); 2.57 (*dd*, $J = 10.2$, 13.6, irrad. at 4.11→*d*, $J = 13.5$, H_B–C(1)); 1.86 (*s*, 5 Me); 1.58 (*s*, Me); 1.53 (*s*, Me); 1.28 (*s*, Me); 1.27 (*s*, Me); 1.04 (*s*, ^{t}Bu); 0.34 (*s*, MeSi); 0.28 (*s*, MeSi). ^{13}C-NMR (75 MHz, C_6D_6): 109.44 (*s*); 107.54 (*s*); 84.00 (*s*); 80.75 (*d*); 79.88 (5*s*); 79.34 (*d*); 77.76 (*d*); 73.19 (*d*); 72.63 (*d*); 72.53 (*d*); 71.83 (*d*); 71.73 (*d*); 67.94 (*t*); 30.82 (*t*); 29.00 (*q*); 27.00 (*q*); 26.42 (4*q*); 25.42 (*q*); 18.91 (*s*); 11.44 (5*q*); −3.35 (*q*); −4.21 (*q*). EI-MS: 614 (100, $M^{+\cdot}$), 599 (2, $[M - Me]^+$), 557 (5, $[M - {}^tBu]^+$), 499 (5,

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[6]) Prepared by stirring **13a/b** (417 mg, 0.98 mmol) in THF (1 ml) with BuLi (1.6M in hexane, 0.75 ml, 1.2 mmol) for 1 h at r.t.

Table 1. *Selected ^{1}H-NMR* ($CDCl_3$) *Chemical Shifts* [Hz] *and Coupling Constants* [Hz] *of the Mannitol Moieties of* **6**–**16** *and* **19**–**23**

	H_A–C(1)	H_B–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	$J(1A,1B)$	$J(1A,2)$	$J(1B,2)$	$J(2,3)$	$J(3,4)$	$J(4,5)$
7a	4.94	–	4.93	4.78	3.71	4.44	–	0	–	5.6	3.7	7.7
7b	4.92	–	4.91	4.78	3.75	4.45	–	1	–	5.6	3.8	7.8
6a	4.48	–	4.69	4.81	3.60	4.43	–	3.8	–	6.1	3.8	7.2
6b	4.46	–	4.76	4.83	3.60	4.43	–	3.6	–	6.8	3.7	7.6
8 or **9**	4.39	–	4.85	4.82	3.70	4.43	–	3.2	–	6.2	3.6	6.9
10	3.97	–	4.56	4.73	3.46–3.42	4.41	–	3.6	–	6.2	3.8	8.3
11	4.07	–	4.84	4.77	3.54	4.40	–	4.2	–	6.1	3.2	7.7
12a	2.96	2.87	4.53	4.37	3.53	4.10–3.97	15.8	7.8	6.0	6.9	1.3	7.9
12b	2.97–2.80	2.97–2.80	4.59	4.37	3.56	4.10–3.97	a)	6.9	6.9	6.9	1.3	8.0
13a	2.74	2.53	4.23	4.01–3.83	4.01–3.83	4.01–3.83	14.3	2.6	10.9	4.4	[a]	[a]
13b	2.70	2.50	4.30	3.93–3.91	3.93–3.91	3.93–3.91	14	3	10.6	*ca.* 4	[a]	[a]
14[b]	2.83	2.66	4.38	3.95	4.06	3.95–3.92	14.2	2.6	10.5	5.0	8.9	6.5
15	3.14	2.85	4.19[c]	4.02–3.95	4.02–3.95	4.02–3.95	14.1	1.9	11.4	[a]	[a]	[a]
16[b]	2.66	2.57	4.11	3.93	4.22	3.94–3.91	13.6	3.2	10.2	5.0	9.0	6.1
19a	4.23	–	4.85	4.10	3.90–3.78	3.90–3.78	–	9.7	–	6.0	3.3	[a]
19b	4.25	–	4.84	4.13	3.72	3.93–3.77	–	10.3	–	5.9	3.7	5.4
20a	4.23	–	4.84	4.25	4.07–3.88	4.07–3.88	–	10.2	–	5.9	4.0	[a]
20b	4.24	–	4.85	4.34	4.02–3.86	4.02–3.86	–	10.1	–	6.1	2.7	[a]
21	3.88	–	4.44	3.94	3.675	3.70	–	10.0	–	5.9	3.0	5.8
22[b]	4.14	–	4.74	4.06	4.45	3.88	–	5.6	–	6.4	8.0	4.8
23[b]	4.07	–	4.64	[a]	4.46	[a]	–	5.3	–	6.3	8.2	4.5
	4.14	–	4.52	[a]	[a]	[a]	–	9.4	–	6.0	[a]	[a]

[a]) Not determined. [b]) In C_6D_6. [c]) In C_6D_6 at 4.41 ppm with $J(1A,2) = 1.7$, $J(1B,2) = 11.4$, and $J(2,3) = 5.0$ Hz.

Table 2. *Selected* ^{13}C*-NMR* ($CDCl_3$) *Chemical Shifts* [Hz] *of the Mannitol Derivatives* **10–16** *and* **21–23**[a])

	C(1)	C(2), C(3), C(4)	C(5)	C(6)	R–C(1): $C_{15}H_{12}NO_2$, C_5H_5, C_5H_4, or C_5Me_4[b])	Me_2C
10	82.58[d])	81.73[d]), 80.72, 78.70	72.87	67.10	$C_{15}H_{12}NO_2$: 176.71, 176.65, 143.65 (3*s*), 126.31 (*d*), 52.66 (*t*), 48.24, 46.84, 45.91, 45.58 (4*d*)	112.45, 109.17
11	81.30[d])	81.09[d]), 80.94 (2×)	73.02	66.99	$C_{15}H_{12}NO_2$: 177.05, 176.99, 143.71 (3*s*), 127.67 (*d*), 51.52 (*t*), 47.08, 46.94, 45.82, 45.74 (4*d*)	112.96, 109.16
12a/b	31.21 30.42	76.75, 76.24, 76.18, 75.95	70.42 70.35	67.06	C_5H_5: 145.09, 143.05, 134.50, 134.14, 132.32, 131.32, 128.09, 127.59, 44.02, 41.49	109.26, 107.86
13a	32.12	80.42, 77.88, 77.25	72.10	67.85	C_5H_5: 145.98, 132.45, 131.24, 128.47, 44.02	109.42, 107.50
13b	31.44	80.36, 77.29, 77.23	72.04	67.71	C_5H_5: 143.59, 134.63, 133.93, 128.30, 41.40	109.39, 107.57
14[c])	31.42	81.15, 79.51, 77.84	72.81	68.39	C_5H_4: 86.40, 70.76, 69.71, 68.59, 68.45	109.75, 107.54
15[c])	32.70	80.98, 77.65, 77.26	72.14	67.65	C_5H_4: 134.67, 128.81, 123.93, 113.82, 112.14	109.84, 107.61
16[c])	30.82	80.75, 77.34, 77.76	72.53[d])	67.94	C_5H_4: 84.00, 73.19, 72.63[d]), 71.83, 71.73; C_5Me_4: 79.88, 11.44	109.44, 107.54
21[c])	45.47	81.19, 78.85, 77.59	71.55	66.05	C_5H_4: 91.50, 71.07, 69.11, 68.87, 68.68	108.48, 108.41
22[c])	45.98	81.31, 80.28, 77.93	70.79	66.69	C_5H_4: 93.74, 70.01, 69.44, 68.50, 68.32	109.21, 107.74
23[c])	46.00, 45.26	81.12 (2×), 80.27, 78.86, 77.79, 77.65	71.63, 70.77	66.47, 66.15	C_5H_4: 93.52, 92.00, 70.66, 69.99, 69.26, 69.19, 68.94, 68.61, 68.28 (2×)	109.19, 108.46, 108.39, 107.69

[a]) Assignment based upon comparison with related compounds [68]. [b]) Signals of Ph, see *Exper. Part.* [c]) In C_6D_6. [d]) Assignment may be interchanged.

$[M - Si^tBuMe_2]^+$), 282 (6), 269 (19), 73 (5). Anal. calc. for $C_{33}H_{54}FeO_5Si$ (614.72): C 64.48, H 8.85; found: C 64.52, H 8.84.

*(1S/1R)-1-C-(Cyclopenta-1',3'-dienyl)- and (1S/1R)-1-C-(cyclopenta-1',4'-dienyl)-1-deoxy-2,3:5,6-di-O-isopropylidene-1-C-phenyl-*D*-mannitol* (**17a/18a** and **17b/18b**). At −78°, 2M PhLi in cyclohexane/Et_2O (13.5 ml, 27 mmol) was added to a stirred soln. of **6/7** (2.66 g, 8.66 mmol) in dry THF (15 ml). The mixture was allowed to warm to 0° over 1.5 h. Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:6→1:1:2) afforded 2.36 g (71%, light brown oil) of **17/18** 5:3 (^{1}H-NMR). R_f(CH_2Cl_2/Et_2O/pentane 1:1:2) 0.64, 0.59. $[\alpha]_D^{25} = +0.9$ ($c = 0.99$, $CHCl_3$). IR: 3560*w* (br.), 3065*w*, 3007*s*, 2990*s*, 2938*m*, 2887*m*, 1712*w*, 1677*w*, 1599*w*, 1497*w*, 1482*w*, 1454*m*, 1384*s*, 1373*s*, 1302*w*, 1253*s*, 1157*s*, 1111*m*, 1057*s*, 1031*s*, 968*m*, 898*m*, 845*m*, 639*w*, 616*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.38–7.18 (*m*, 5 arom. H); 6.52–6.12 (*m*, 3 olef. H); 5.07–4.97 (*m*, 0.6 H); 4.93–4.85 (*m*, 0.4 H); 4.54 (br. *t*, $J \approx 6.6$, 0.4 H); 4.35–4.23 (*m*, 1.6 H); 4.06–3.85 (*m*, 3 H); 3.57–3.45 (*m*, 0.4 H); 3.35–3.26 (*m*, 0.6 H); 3.04–2.73 (*m*, 2 H); 2.27–2.15 (*m*, 1 H); 1.55–0.88 (*m*, 12 H). EI-MS: 386 (1, M^+), 371 (7, $[M - Me]^+$), 328 (3), 231 (55), 197 (19), 173 (87), 169 (21), 155 (36), 129 (16), 115 (60), 101 (38), 91 (22), 71 (26), 59 (100), 43 (58).

*(1S/1R)-4-O-[(*tert*-Butyl)dimethylsilyl]-1-C-(cyclopenta-1',3'-dienyl)- and -1-C-(cyclopenta-1',4'-dienyl)-1-deoxy-2,3:5,6-di-O-isopropylidene-1-C-phenyl-*D*-mannitol* (**19a/20a** and **20b/20b**). At −60°, *t*-$BuMe_2SiTf$ (0.29 ml, 1.3 mmol) was added dropwise to a soln. of **17/18** 5:3 (385 mg, 1.0 mmol) and Et_2(i-Pr)N (0.35 ml, 2.0 mmol) in dry CH_2Cl_2 (1.1 ml). The mixture was allowed to warm to r.t. over 1 h and stirred for 3 h. Normal workup and FC (CH_2Cl_2/Et_2O/hexane 1:1:10) gave 430 mg (86%, light brown oil) of **19/20** 5:3 (^{1}H-NMR). An anal. sample of **19/20** was obtained after a second FC. Prep. HPLC (hexane/Et_2O 97:3) gave pure samples of **19a**, **19b**, **20a**, and **20b**. A $CDCl_3$ soln. of pure **19a**, **19b**, **20a**, or **20b** isomerized over several days to mixtures of **19a/b** and **20a/b**, respectively.

Data of **19/20**: R_f(CH_2Cl_2/Et_2O/hexane 1:1:10) 0.42. $[\alpha]_D^{25} = +4.2$ ($c = 1.25$, $CHCl_3$). IR: 3066*m*, 2987*s*, 2959*s*, 2933*s*, 2886*s*, 2859*s*, 1720*m*, 1600*w*, 1496*w*, 1472*m*, 1463*m*, 1381*s*, 1371*s*, 1256*s*, 1140*s*, 1074*s*, 1055*s*, 1005*m*, 953*w*, 933*w*, 898*s*, 836*s*, 642*w*. EI-MS: 500 (0.4, M^+), 485 (2, $[M - Me]^+$), 443 (0.3, $[M - {}^tBu]^+$), 385 (5, $[M - {}^tBuMe_2Si]^+$), 345 (25), 327 (11), 287 (11), 229 (40), 217 (22), 197 (21), 187 (38), 171 (32), 159 (20), 155 (47), 129 (27), 115 (19), 101 (100), 73 (67), 43 (31). Anal. calc. for $C_{29}H_{44}O_5Si$ (500.75): C 69.56, H 8.86; found: C 69.56, H 8.72.

Data of **19a**: t_R(hexane/Et_2O 97:3) 17.8 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.28 (*m*, 4 arom. H); 7.23–7.14 (*m*, 1 arom. H); 6.57 (*m*, 1 olef. H); 6.36 (*m*, 1 olef. H); 6.12 (br. *s*, 1 olef. H); 4.85 (*dd*, $J = 6.0$, 9.7, H–C(2)); 4.23 (*d*, $J = 9.6$, H–C(1)); 4.10 (*dd*, $J = 3.3$, 5.9, H–C(3)); 3.90–3.78 (*m*, 4 H); 2.95–2.91 (*m*, 2 H–C(5')); 1.51 (*s*, Me); 1.40 (*s*, Me); 1.16 (*s*, Me); 1.07 (*s*, Me); 0.93 (*s*, ^{t}BuSi); 0.24 (*s*, MeSi); 0.20 (*s*, MeSi).

Data of **19b**: t_R(hexane/Et_2O 97:3) 18.4 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37–7.28 (*m*, 4 arom. H); 7.23–7.15 (*m*, 1 arom. H); 6.59 (*m*, 1 olef. H); 6.26 (*m*, 2 olef. H); 4.84 (*dd*, $J = 5.9$, 10.3, H–C(2)); 4.25 (*d*, $J = 10.3$, H–C(1)); 4.13 (*dd*, $J = 3.7$, 5.9, H–C(3)); 3.93–3.77 (*m*, 3 H); 3.72 (*dd*, $J = 3.7$, 5.4, H–C(4)); 2.99–2.97 (*m*, 2 H–C(5')); 1.51 (*s*, Me); 1.41 (*s*, Me); 1.16 (*s*, Me); 1.02 (*s*, Me); 0.94 (*s*, ^{t}BuSi); 0.27 (*s*, MeSi); 0.21 (*s*, MeSi).

Data of **20a**: t_R(hexane/Et_2O 97:3) 23.7 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.27 (*m*, 4 arom. H); 7.22–7.16 (*m*, 1 arom. H); 6.48 (*m*, 1 olef. H); 6.42 (*m*, 1 olef. H); 6.27 (br. *s*, 1 olef. H); 4.84 (*dd*, $J = 5.8$, 10.2, H–C(2)); 4.25 (*dd*, $J = 4.0$, 5.9, H–C(3)); 4.23 (*d*, $J \approx 10.2$, H–C(1)); 4.07–3.88 (*m*, 4 H); 3.01 (br. *d*, $J \approx 24$, H_A–C(5')); 2.92 (br. *d*, $J \approx 24$, H_B–C(5')); 1.40 (*s*, Me); 1.33 (*s*, Me); 1.30 (*s*, Me); 1.26 (*s*, Me); 0.94 (*s*, ^{t}BuSi); 0.22 (*s*, MeSi); 0.19 (*s*, MeSi).

Data of **20b**: t_R(hexane/Et_2O 97:3) 20.3 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31–7.27 (*m*, 4 arom. H); 7.22–7.16 (*m*, 1 arom. H); 6.42 (br. *s*, 1 olef. H); 6.39 (*m*, 1 olef. H); 6.24 (*m*, 1 olef. H); 4.85 (*dd*, $J = 6.1$, 10.1, H–C(2)); 4.34 (*dd*, $J = 2.7$, 6.1, H–C(3)); 4.24 (*d*, $J = 10.1$, H–C(1)); 4.02–3.86 (*m*, 4 H); 2.83 (*m*, 2 H–C(5')); 1.41 (*s*, Me); 1.34 (*s*, Me); 1.30 (*s*, Me); 1.28 (*s*, Me); 0.93 (*s*, ^{t}BuSi); 0.21 (*s*, MeSi); 0.20 (*s*, MeSi).

*(1''S,1'''S)-, (1''R,1'''R)-, and (1''R,1'''S)-1,1'-Bis{4-O-[(*tert*-butyl)dimethylsilyl]-1-deoxy-2,3:5,6-di-O-isopropylidene-1-C-phenyl-*D*-mannitol-1-yl}ferrocene* (**21**, **22**, and **23**). At −50°, 1.6M BuLi in hexane (1.45 ml, 2.3 mmol) was added dropwise to a stirred soln. of **19/20** 5:3 (950 mg, 1.9 mmol) in dry THF (4.5 ml). The mixture was allowed to warm to 0° over 1 h and stirred for 2.5 h. The clear soln. was treated with $FeCl_2$ (138 mg, 1.09 mmol) and stirred for 16 h at r.t. Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:10→1:1:4) afforded 795 mg (79%, yellow foam) of **21/22/23** 54:15:31 (^{1}H-NMR). The products were partially separated by MPLC (CH_2Cl_2/Et_2O/pentane 1:1:10). Prep. HPLC (CH_2Cl_2/Et_2O/pentane 1:1:10) gave pure samples of **21**, **22**, and **23**. Isomer **21** crystallized from $MeNO_2$ giving yellow crystals containing $MeNO_2$ (m.p. 86–89°). An anal. sample of **21** was obtained by recrystallization in MeOH/H_2O. Yellow powders of **22** and **23** were obtained from MeOH/H_2O.

Data of **21**: R_f(CH_2Cl_2/Et_2O/pentane 1:1:10) 0.14. t_R(hexane/Et_2O 85:15) 28.8 min. M.p. 166–175°. $[\alpha]_D^{25} = 23.1$ ($c = 0.55$, $CHCl_3$). IR: 3089*w*, 3068*w*, 3043*w*, 2988*s*, 2957*m*, 2933*s*, 2887*m*, 2858*m*, 1564*w*, 1472*w*, 1462*w*, 1452*w*, 1381*s*, 1372*s*, 1256*s*, 1140*s*, 1075*s*, 1054*s*, 967*w*, 933*w*, 897*m*, 836*s*. ^{1}H-NMR (500 MHz, $CDCl_3$):

7.34–7.23 (*m*, 5 arom. H); 4.44 (*dd*, *J* = 5.9, 10.0, irrad. at 3.94→*d*, *J* = 10, H–C(2)); 4.04 (br. *quint.*, *J* ≈ 1, 1 arom. H); 3.94 (*dd*, *J* = 3.0, 5.9, irrad. at 4.44→*d*, *J* ≈ 3, H–C(3)); 3.88 (*d*, *J* = 10.0, irrad. at 4.44→*s*, H–C(1)); 3.83 (*dd*, *J* = 5.9, 7.9, H_A–C(6)); 3.79–3.78 (*m*, 1 arom. H); 3.75 (*dd*, *J* = 5.6, 8.2, H_B–C(6)); 3.70 (*q*, *J* = 5.7, H–C(5)); 3.69–3.67 (*m*, 1 arom. H); 3.675 (*dd*, *J* = 2.8, 5.8, H–C(4)); 3.47 (br. *quint.*, *J* ≈ 1, 1 arom. H); 1.44 (*s*, Me); 1.26 (*s*, Me); 1.14 (*s*, Me); 0.99 (*s*, Me); 0.95 (*s*, ^{t}BuSi); 0.31 (*s*, MeSi); 0.23 (*s*, MeSi). ^{13}C-NMR (75 MHz, C_6D_6): 142.11 (*s*); 129.11 (2*d*); 128.68 (2*d*); 127.16 (*d*); 108.48 (*s*); 108.41 (*s*); 91.50 (*s*); 81.19 (*d*); 78.85 (*d*); 77.59 (*d*); 71.55 (*d*); 71.07 (*d*); 69.11 (*d*); 68.87 (*d*); 68.68 (*d*); 66.05 (*t*); 45.47 (*d*); 27.01 (*q*); 26.92 (3*q*); 26.62 (*q*); 25.82 (*q*); 25.21 (*q*); 19.32 (*s*); −2.52 (*q*); −2.98 (*q*). EI-MS: 1054.5 (100, $M^{+\cdot}$), 1039 (7, $[M - Me]^+$), 997 (6, $[M - {}^t\text{Bu}]^+$), 939 (2, $[M - Si^t\text{BuMe}_2]^+$), 709 (7), 377 (11), 223 (29), 187 (12), 115 (11), 101 (48), 73 (52). Anal. calc. for $C_{58}H_{86}FeO_{10}Si_2$ (1055.33): C 66.01, H 8.21; found: C 66.01, H 8.19.

Data of **22**: R_f(CH_2Cl_2/Et_2O/pentane 1:1:10) 0.14. t_R(hexane/Et_2O 85:15) 23.2 min. M.p. 67–73°. $[\alpha]_D^{25} = -29.5$ (*c* = 0.42, $CHCl_3$). IR: 3089*w*, 3064*w*, 2988*s*, 2932*s*, 2887*m*, 2858*m*, 1493*w*, 1472*m*, 1462*m*, 1454*m*, 1381*s*, 1371*s*, 1253*s*, 1157*s*, 1095*s*, 1075*s*, 1052*s*, 1005*m*, 938*w*, 896*m*, 836*s*. ^{1}H-NMR (500 MHz, C_6D_6): 7.50–7.48 (*m*, 2 arom. H); 7.23–7.19 (*m*, 2 arom. H); 7.10–7.06 (*m*, 1 arom. H); 4.74 (*dd*, *J* = 5.6, 6.3, H–C(2)); 4.45 (*dd*, *J* = 4.8, 8.0, irrad. at 3.88→*d*, *J* = 8, H–C(4)); 4.29 (*dt*, *J* = 2.4, 1.3, 1 arom. H); 4.14 (*d*, *J* = 5.5, irrad. at 4.74→*s*, H–C(1)); 4.07 (*t*, *J* = 7.8, irrad. at 3.88→*d*, *J* ≈ 8, H_A–C(6)); 4.06 (*dd*, *J* = 6.4, 8.0, irrad. at 4.74→*d*, *J* ≈ 8, H–C(3)); 4.00 (*dd*, *J* = 6.3, 7.7, irrad. at 3.88→*d*, *J* ≈ 8, H_B–C(6)); 3.88 (*ddd*, *J* = 4.8, 6.3, 7.8, H–C(5)); 3.84 (*dt*, *J* = 1.3, 2.4, 1 arom. H); 3.73 (*dt*, *J* = 1.3, 2.4, 1 arom. H); 3.70 (*dt*, *J* = 2.4, 1.3, 1 arom. H); 1.58 (*s*, Me); 1.34 (*s*, Me); 1.33 (*s*, Me); 1.23 (*s*, Me); 1.02 (*s*, ^{t}BuSi); 0.15 (*s*, MeSi); 0.11 (*s*, MeSi). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34–7.30 (*m*, 4 arom. H); 7.27–7.21 (*m*, 1 arom. H); 4.52 (br. *t*, *J* ≈ 6.5, H–C(2)); 4.11 (*dd*, *J* = 4.9, 7.0, H–C(4)); 3.98–3.83 (*m*, 5 H); 3.72–3.66 (*m*, 2 H); 3.57 (*m*, 1 arom. H); 3.46 (*m*, 1 arom. H); 1.42 (*s*, Me); 1.30 (*s*, Me); 1.29 (*s*, Me); 1.26 (*s*, Me); 0.85 (*s*, ^{t}BuSi); −0.01 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, C_6D_6): 144.00 (*s*); 130.67 (2*d*); 128.07 (2*d*); 126.69 (*d*); 109.21 (*s*); 107.74 (*s*); 93.74 (*s*); 81.31 (*d*); 80.28 (*d*); 77.93 (*d*); 70.79 (*d*); 70.01 (*d*); 69.44 (*d*); 68.50 (*d*); 68.32 (*d*); 66.69 (*t*); 45.98 (*d*); 27.00 (*q*); 26.47 (4*q*); 25.66 (*q*); 24.95 (*q*); 18.90 (*s*); −3.35 (*q*); −3.89 (*q*). EI-MS: 1054.6 (52, $M^{+\cdot}$), 1039 (3, $[M - Me]^+$), 997 (4, $[M - {}^t\text{Bu}]^+$), 939 (5, $[M - Si^t\text{BuMe}_2]^+$), 562 (6), 377 (16), 223 (36), 195 (10), 187 (17), 129 (22), 117 (20), 115 (20), 101 (100), 91 (16), 73 (84), 43 (89).

Data of **23**: R_f(CH_2Cl_2/Et_2O/pentane 1:1:10) 0.14. t_R(hexane/Et_2O 85:15) 25.8 min. M.p. 71–74°. $[\alpha]_D^{25} = -18.7$ (*c* = 0.45, $CHCl_3$). IR: 3090*w*, 2988*s*, 2932*s*, 2887*m*, 2858*s*, 1493*w*, 1472*m*, 1462*m*, 1453*m*, 1432*w*, 1408*w*, 1381*s*, 1371*s*, 1225*s*, 1155*s*, 1075*s*, 1053*s*, 1005*m*, 968*w*, 937*w*, 896*m*, 836*s*. ^{1}H-NMR (500 MHz, C_6D_6): 7.43–7.36 (*m*, 4 arom. H); 7.22–7.18 (*m*, 4 arom. H); 7.09–7.06 (*m*, 2 arom. H); 4.64 (*dd*, *J* = 5.3, 6.3, H–C(2′)); 4.52 (*dd*, *J* = 6.0, 9.4, H–C(2)); 4.46 (*dd*, *J* = 4.5, 8.2, H–C(4′)); 4.20 (*dt*, *J* = 2.4, 1.2, 1 arom. H); 4.14 (*d*, *J* = 9.4, irrad. at 4.52→*s*, H–C(1)); 4.11 (*dt*, *J* = 2.4, 1.3, 1 arom. H); 4.08 (*t*, *J* ≈ 7.7, 1 H); 4.07 (*d*, *J* ≈ 5.6, irrad. at 4.64→*s*, H–C(1′)); 4.02–3.93 (*m*, 7 H); 3.89–3.80 (*m*, 7 H); 1.57 (*s*, Me); 1.53 (*s*, Me); 1.35 (*s*, Me); 1.29 (*s*, Me); 1.28 (*s*, Me); 1.22 (*s*, Me); 1.20 (*s*, Me); 1.13 (*s*, Me); 1.09 (*s*, ^{t}BuSi); 1.03 (*s*, ^{t}BuSi); 0.44 (*s*, MeSi); 0.34 (*s*, MeSi); 0.14 (*s*, MeSi); 0.11 (*s*, MeSi). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.45–7.17 (*m*, 10 arom. H); 4.50 (br. *t*, *J* ≈ 6.5, H–C(2′)); 4.47 (*dd*, *J* = 6.0, 10.0, H–C(2)); 4.14 (*dd*, *J* = 4.9, 7.1, 1 H); 3.96–3.59 (*m*, 19 H); 1.44 (*s*, Me); 1.43 (*s*, Me); 1.31 (*s*, Me); 1.28 (*s*, Me); 1.254 (*s*, Me); 1.247 (*s*, Me); 1.15 (*s*, Me); 1.01 (*s*, Me); 0.95 (*s*, ^{t}BuSi); 0.85 (*s*, ^{t}BuSi); 0.29 (*s*, MeSi); 0.23 (*s*, MeSi); −0.03 (*s*, Me_2Si). ^{13}C-NMR (75 MHz, C_6D_6): 144.04 (*s*); 142.12 (*s*); 130.73 (2*d*); 129.24 (2*d*); 128.77 (2*d*); 128.07 (2*d*); 127.35 (*d*); 126.64 (*d*); 109.19 (*s*); 108.46 (*s*); 108.39 (*s*); 107.69 (*s*); 93.52 (*s*); 92.00 (*s*); 81.12 (2*d*); 80.27 (*d*); 78.86 (*d*); 77.79 (*d*); 77.65 (*d*); 71.63 (*d*); 70.77 (*d*); 70.66 (*d*); 69.99 (*d*); 69.26 (*d*); 69.19 (*d*); 68.94 (*d*); 68.61 (*d*); 68.28 (2*d*); 66.47 (*t*); 66.15 (*t*); 46.00 (*d*); 45.26 (*d*); 26.92 (4*q*); 26.61 (2*q*); 26.46 (4*q*); 25.84 (*q*); 25.69 (*q*); 25.19 (*q*); 25.00 (*q*); 19.30 (*s*); 18.89 (*s*); −2.58 (*q*); −2.95 (*q*); −3.40 (*q*); −3.87 (*q*). EI-MS: 1054.4 (100, $M^{+\cdot}$), 1039 (7, $[M - Me]^+$), 997 (7, $[M - {}^t\text{Bu}]^+$), 939 (6, $[M - Si^t\text{BuMe}_2]^+$), 709 (7), 377 (13), 223 (27), 187 (13), 115 (11), 101 (55), 73 (46). Anal. calc. for $C_{58}H_{86}FeO_{10}Si_2$ (1055.33): C 66.01, H 8.21; found: C 65.76, H 7.83.

*1-C-(Cyclopenta-1′,3′-dienyl)- and 1-C-(Cyclopenta-1′,4′-dienyl)-1-deoxy-2,3:4,5-di-O-isopropylidene-*D*-ribitol* (**25a**/**b**). At 0°, 2M CpNa in THF (15 ml, 30 mmol) was added to a stirred soln. of **24** (2.22 g, 7.3 mmol) [69] in dry THF (5 ml). The soln. was stirred at r.t. for 2 h, cooled to −60°, and treated with small portions of $LiAlH_4$ (630 mg, 16.5 mmol). The mixture was warmed to r.t. over 10 min, stirred for 5 h, cooled to −60°, and treated with AcOEt (5 ml). The mixture was allowed to warm to r.t. over 1 h, cooled to −70°, treated with sat. $NaHCO_3$ soln. (5 ml), and warmed to r.t. over 1 h. Addition of H_2O (100 ml), filtration through *Celite*, extraction of the aq. phase with CH_2Cl_2, drying of the org. layer ($MgSO_4$), and evaporation gave a brown oil, which was dissolved in acetone (25 ml) and treated with 2,2-dimethoxypropane (4.5 ml, 37 mmol) and $TsOH \cdot H_2O$ (100 mg) at 0° for 30 min. Addition of Et_3N (2 ml), evaporation, and FC (Et_2O/pentane 1:13) afforded **25** (1.37 g, 65%, oil). Crystallization from MeOH/H_2O gave white needles of **25a**/**b** 1:1. Attempts to separate **25a** and **25b** by prep. HPLC (hexane/Et_2O 95:5) failed. R_f(Et_2O/pentane 1:8) 0.55. t_R(hexane/Et_2O 95:5) 24.5 min. M.p. 41°. $[\alpha]_D^{25} = -18.6$

Table 3. *Selected ^{1}H-NMR* ($CDCl_3$) *Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *of the Ribitol and Arabinitol Moieties of* **25**–**28**, **32**–**35**, **37**–**42**, **44**, *and* **45**

	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H_A–C(5)	H_B–C(5)	*J*(1,2)	*J*(2,3)	*J*(3,4)	*J*(4,5*A*)	*J*(4,5*B*)	*J*(5*A*,5*B*)
27a	5.09	4.70	4.90	4.12	3.80	3.74	4.0	5.9	1.0	4	3.5	11
27b	5.05	4.78	4.92	4.19	3.81	3.76	4.1	6.0	1.0	4	3.5	11
28a	4.74	4.52	4.70	4.07	3.80–3.70	3.80–3.70	5.2	6.6	3.6	4.1	4.2	[a])
28b	4.72	4.56	4.72	4.10	3.78	3.76	5.3	6.6	3.3	4.1	4.4	11.1
32	6.33	5.23	4.24	4.09	4.03	3.93	8.3	6.3	7.6	6.0	5.6	8.2
25a/b	2.91–2.59	4.42, 4.39	[a])	[a])	[a])	[a])	3.5, 10.0	5.5	[a])	[a])	[a])	[a])
26[b])	2.79, 2.58	4.29	[a])	[a])	[a])	[a])	3.6, 9.4	5.6	[a])	[a])	[a])	[a])
33a	4.17	4.84	3.96	4.12	4.04	3.86	9.5	5.2	8.2	6.3	6.2	8.3
33b	4.14	4.87	3.97	4.15	4.04	3.86	9.3	5.2	8.3	6.5	6.3	8.4
34a	4.04	4.79	4.12–4.18	4.12–4.18	4.07	3.93	10.5	4.5	[a])	6.0	5.7	8.6
34b	4.02	4.82	4.12–4.21	4.12–4.21	4.03–4.09	3.85	10.2	4.7	[a])	[a])	5.7	8.4
35[b])	4.10	4.56	3.81	4.24	4.05	4.00	10.2	4.9	8.7	6.4	6.2	8.6
44	3.02	4.66	3.89–3.79	4.07–3.96	4.07–3.96	3.89–3.79	11.1	5.0	[a])	[a])	[a])	[a])
45[c])	2.84	3.98	3.60–3.48	3.60–3.48	3.79–3.68	3.79–3.68	6.2	6.3	[a])	[a])	[a])	[a])
37	6.28	4.92	3.89	4.18	4.09	3.93	7.9	7.3	6.8	6.2	4.8	8.3
38a	4.14	4.42	3.78–3.91	3.78–3.91	4.04	3.78–3.91	5.3	5.9	[a])	5.7	[a])	8.3
38b	4.11	4.45	3.81–3.92	3.81–3.92	4.04	3.81–3.92	5.1	6.5	[a])	6.0	[a])	8.0
39a	4.05	4.57	3.61	4.07	4.13	3.86	4.2	7.2	7.5	6.5	5.4	7.7
39b	4.07	4.58	3.57	4.12	4.06	3.86	4.7	6.7	8.1	6.0	6.8	8.1
40	3.66	4.04	3.70	3.63	3.92	3.76	6.5	6.6	6.6	6.4	6.2	8.3
40[b])	3.93	4.22	3.89	3.74	3.88	3.86	4.7	7.1	7.3	6.6	5.9	8.4
41	2.79	4.18	3.95	3.67	3.84–3.79	3.84–3.79	7.1	6.2	8.3	6	6	[a])
42[c])	2.92	4.21	3.10	3.43	3.69–3.60	3.69–3.60	10.6	0.6	8.2	[a])	[a])	[a])

[a]) Not determined. [b]) In C_6D_6. [c]) In CD_3OD.

Table 4. *Selected* ^{13}C*-NMR* ($CDCl_3$) *Chemical Shifts* [Hz] *of the Ribitol and Arabinitol Derivatives* **25**, **26**, **32**, **35**, **37**, **40–42**, **44**, *and* **45**

	C(1)	C(2), C(3)	C(4)	C(5)	R–C(1): C_5H_5, C_5H_4, or C_5H_9[a])	Me_2C
25a/b	30.67,	78.85 (2×),	73.53,	67.95	C_5H_5: 145.92, 143.69, 134.90, 133.61, 132.28,	109.66 (2×)
	29.92	77.77, 77.15	73.47	(2×)	131.17, 128.07, 127.79, 44.03, 41.38	108.30, 108.24
26	29.44	78.82, 78.78	73.54	68.01	C_5H_4: 85.59, 70.15, 69.14, 68.35, 68.17	109.73, 108.19
32	120.32	79.75, 76.10	74.08	67.31	C_5H_4: 148.09, 134.76, 133.91, 132.47, 126.24	109.92, 109.83
35[b])	44.85	81.36, 79.32	73.69	67.86	C_5H_4: 92.04, 71.02, 69.05, 68.81, 68.51	109.70, 107.71
44	44.69	79.61, 78.25	73.37	66.82	C_5H_9: 43.49, 30.46, 27.54, 24.27, 23.90	109.04, 107.46
45[c])	55.10	78.06, 74.30[d])	74.01[d])	63.76	C_5H_9: 43.33, 32.93, 32.26, 26.07, 25.16	–
37	120.10	81.18, 77.37[d])	76.15[d])	66.54	C_5H_4: 147.09, 135.38, 134.03, 131.93, 125.49	110.15, 109.43
40[b])	49.41	84.08, 79.76[d])	77.36[d])	67.46	C_5H_4: 88.54, 71.45, 70.21, 69.60, 68.17	109.69, 109.54
41	53.94	83.14, 79.66[d])	76.50[d])	66.26	C_5H_9: 42.54, 32.12, 31.22, 25.07, 24.03	109.27, 109.21
42[c])	53.15	73.69, 73.20[d])	72.32[d])	65.13	C_5H_9: 44.08, 32.69, 30.35, 25.76, 25.25	–

[a]) Signals of Ph, see *Exper. Part.* [b]) In C_6D_6. [c]) In CD_3OD. [d]) Assignment may be interchanged.

($c = 0.93$, $CHCl_3$). IR: 3062*w*, 2990*s*, 2937*m*, 2884*m*, 1604*w*, 1455*m*, 1420*w*, 1382*s*, 1372*s*, 1253*s*, 1158*s*, 1103*m*, 1062*s*, 984*w*, 966*m*, 900*m*, 846*s*, 590*w*, 566*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.54 (*m*, 0.5 olef. H); 6.44 (*m*, 1 olef. H); 6.29 (*m*, 1 olef. H); 6.18 (*m*, 0.5 olef. H); 4.42 (*ddd*, $J = 3.5, 5.5, 10.0, 0.5$ H); 4.39 (*ddd*, $J = 3.5, 5.5, 10.0, 0.5$ H, H–C(2)); 4.20–4.10 (*m*, 2 H); 4.04–3.87 (*m*, 2 H); 3.02–2.96 (*m*, 2 H–C(5′)); 2.91–2.59 (*m*, 2 H–C(1)); 1.44–1.33 (*m*, 4 Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 145.92 (*s*); 143.69 (*s*); 134.90 (*d*); 133.61 (*d*); 132.38 (*d*); 131.17 (*d*); 128.07 (*d*); 127.79 (*d*); 109.66 (2*s*); 108.30 (*s*); 108.24 (*s*); 78.85 (2*d*); 77.55 (*d*); 77.15 (*d*); 73.53 (*d*); 73.47 (*d*); 67.95 (2*t*), 44.03 (*t*); 41.38 (*t*); 30.67 (*t*); 29.92 (*t*); 28.26 (2*q*); 26.77 (2*q*); 25.58 (4*q*). EI-MS: 560 (0.2, $2M^+$), 545 (0.1, $[2M - Me]^+$), 281 (5, $[M + 1]^+$), 280 (5, M^+), 265 (11, $[M - Me]^+$), 222 (14), 147 (16), 143 (100), 137 (13), 121 (21), 101 (68), 91 (20), 85 (32), 59 (42), 43 (97), 28 (21). Anal. calc. for $C_{16}H_{24}O_4$ (280.36): C 68.55, H 8.63; found: C 68.73, H 8.41.

*1,1′-Bis(1-deoxy-2,3:4,5-di-*O*-isopropylidene-*D*-ribitol-1-yl)ferrocene* (**26**). At –60°, 1.6M BuLi in hexane (1.9 ml, 3.0 mmol) was added dropwise to a stirred soln. of **25a/b** (710 mg, 2.5 mmol) in dry THF (3.5 ml). The mixture was allowed to warm to r.t. over 10 min and stirred for further 0.5 h. The clear soln. was treated with $FeCl_2$ (171 mg, 1.35 mmol) and stirred for 2.5 h at r.t. Normal workup and FC (Et_2O/pentane 1:8→1:4) afforded 611 mg (79%) of **26** as a yellow oil. Crystallization from MeOH/H_2O gave a yellow powder. R_f(Et_2O/pentane 1:8) 0.11. M.p. 64°. $[\alpha]_D^{25} = -23.1$ ($c = 0.925$, $CHCl_3$). IR: 3090*w*, 2990*s*, 2937*m*, 2885*m*, 1454*w*, 1382*s*, 1372*s*, 1334*w*, 1253*s*, 1158*s*, 1062*s*, 964*w*, 920*w*, 881*w*, 842*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.29 (*ddd*, $J = 3.6, 5.6, 9.4$, H–C(2)); 4.19 (*m*, 1 arom. H); 4.17–4.12 (*m*, 2 H); 4.11 (*m*, 1 arom. H); 4.04 (*dt*, $J \approx 1, 2, 1$ arom. H); 4.01 (*dt*, $J \approx 1, 2, 1$ arom. H); 3.99–3.91 (*m*, 2 H); 2.79 (*dd*, $J = 3.6, 14.8$, H_A–C(1)); 2.58 (*dd*, $J = 9.4, 14.8$, H_B–C(1)); 1.44 (*s*, Me); 1.42 (*s*, Me); 1.40 (*s*, Me); 1.32 (*s*, Me). ^{13}C-NMR (75 MHz, $CDCl_3$): 109.73 (*s*); 108.19 (*s*); 85.59 (*s*); 78.82 (*d*); 78.78 (*d*); 73.54 (*d*); 70.15 (*d*); 69.14 (*d*); 68.35 (*d*); 68.17 (*d*); 68.01 (*t*); 29.44 (*t*); 28.29 (*q*); 26.89 (*q*); 25.69 (2*q*). EI-MS: 614 (100, M^+), 599 (4, $[M - Me]^+$), 542 (1), 335 (2), 219 (3), 163 (4), 141 (4), 135 (4), 43 (4). Anal. calc. for $C_{32}H_{46}FeO_8$ (614.56): C 62.54, H 7.54; found: C 62.56, H 7.60.

*(1*R*/1*S*)-1,4-Anhydro-4-*O*-[(*tert*-butyl)dimethylsilyl]-1-*C*-(cyclopenta-1′,3′-dienyl)-2,3-*O*-isopropylidene-*D*-ribitol* (**27a/28a**) *and (1*R*/1*S*)-1,4-Anhydro-4-*O*-[(*tert*-butyl)dimethylsilyl]-1-*C*-(cyclopenta-1′,4′-dienyl)-2,3-*O*-isopropylidene-*D*-ribitol* (**27b/28b**). At 0°, 2M CpNa in THF (20 ml, 40 mmol) was added to a stirred soln. of **24** [69] (3.01 g, 9.9 mmol) in dry THF (7 ml). Stirring was continued at r.t. for 1.3 h. Normal workup and FC (Et_2O/pentane 1:20) afforded 1.99 g (57%; yellow oil) of **27/28** 47:53 (^{1}H-NMR). The products slowly decomposed at r.t. A second FC afforded pure samples of **27a** and **27b** and prep. HPLC (hexane/Et_2O 90:10) pure samples of **28a** and **28b**. A $CDCl_3$ soln. of pure **27a**, **27b**, **28a**, and **28b** isomerized over several days to a mixtures of **27a/b** and **28a/b**, respectively.

Data of **27a/b** *1:1*: $[\alpha]_D^{25} = -58.5$ ($c = 0.90$, $CHCl_3$). IR: 3073*w*, 2955*s*, 2931*s*, 2900*m*, 2858*s*, 1472*m*, 1462*m*, 1383*s*, 1374*s*, 1257*s*, 1162*m*, 1125*s*, 1106*s*, 1073*s*, 1040*m*, 1005*m*, 990*m*, 974*m*, 938*m*, 898*m*, 840*s*. EI-MS: 352 (2, M^+), 337 (2, $[M - Me]^+$), 295 (9, $[M - {}^tBu]^+$), 237 (35, $[M - {}^tBuMe_2Si]^+$), 207 (10), 162 (19), 149 (25), 143 (15), 129 (16), 121 (15), 117 (64), 91 (26), 89 (26), 79 (66), 75 (100), 50 (23), 28 (26).

Data of **27a**: R_f(Et_2O/pentane 1:20) 0.16. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.49–6.42 (*m*, 3 olef. H); 5.09 (*d*, $J = 4.1$, H–C(1)); 4.90 (*dd*, $J = 1.1, 5.9$, H–C(3)); 4.70 (*dd*, $J = 3.9, 5.9$, H–C(2)); 4.12 (*dt*, $J \approx 1, 3.7$, H–C(4)); 3.80 (*dd*, $J \approx 4, 11$, H_A–C(5)); 3.74 (*dd*, $J \approx 3.5, 11$, H_B–C(5)); 3.26 (*dq*, $J \approx 24, 1.5$, H_A–C(5′)); 3.13 (*dq*, $J \approx 24, 1.3$, H_B–C(5′)); 1.50 (*s*, Me); 1.33 (*s*, Me); 0.90 (*s*, ^{t}BuSi); 0.07 (*s*, Me_2Si).

Data of **27b**: R_f(Et_2O/pentane 1:20) 0.13. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.68 (*m*, 1 olef. H); 6.44 (*m*, 1 olef. H); 6.36 (br. *s*, 1 olef. H); 5.05 (*d*, $J = 4.0$, H–C(1)); 4.92 (*dd*, $J = 1.0, 6.0$, H–C(3)); 4.78 (*dd*, $J = 4.1, 6.0$, H–C(2)); 4.19 (*dt*, $J \approx 1, 3.5$, H–C(4)); 3.81 (*dd*, $J \approx 4, 11$, H_A–C(5)); 3.76 (*dd*, $J \approx 3.5, 11$, H_B–C(5)); 3.03–3.00 (*m*, 2 H–C(5′)); 1.50 (*s*, Me); 1.33 (*s*, Me); 0.90 (*s*, ^{t}BuSi); 0.07 (*s*, Me_2Si).

Data of **28a/b** *1:1*: R_f(Et_2O/pentane 1:20) 0.28. $[\alpha]_D^{25} = -38.2$ ($c = 1.33$, $CHCl_3$). IR: 2993*m*, 2955*s*, 2931*s*, 2885*m*, 2858*s*, 1384*s*, 1374*s*, 1256*s*, 1155*s*, 1139*s*, 1077*s*, 1006*m*, 976*m*, 950*w*, 926*w*, 899*m*, 860*s*, 838*s*.

Data of **28a**: t_R (hexane/Et_2O 97:3) 28 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.50–6.39 (*m*, 3 olef. H); 4.74 (*dd*, $J = 1.1, 5.2$, H–C(1)); 4.70 (*dd*, $J = 3.6, 6.7$, irrad. at 4.07→*d*, $J = 6.6$, H–C(3)); 4.52 (*dd*, $J = 5.3, 6.6$, H–C(2)); 4.07 (*q*, $J = 3.9$, H–C(4)); 3.80–3.70 (*m*, 2 H–C(5)); 3.07 (*dq*, $J \approx 24, 1.5$, H_A–C(5′)); 2.97 (*dq*, $J \approx 24, 1.3$, H_B–C(5′)); 1.58 (*s*, Me); 1.37 (*s*, Me); 0.90 (*s*, ^{t}BuSi); 0.07 (*s*, MeSi); 0.06 (*s*, MeSi).

Data of **28b**: t_R (hexane/Et_2O 97:3) 26.2 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.57 (*m*, 1 olef. H); 6.47 (*m*, 1 olef. H); 6.34 (br. *s*, 1 olef. H); 4.72 (*d*, $J \approx 4.8$, irrad. at 4.56→*s*, H–C(1)); 4.72 (*dd*, $J = 3.3, 6.6$, irrad. at 4.56→change, irrad. at 4.07→*d*, $J = 6.5$, H–C(3)); 4.56 (*dd*, $J = 5.3, 6.6$, H–C(2)); 4.07 (*q*, $J = 4.0$, irrad. at 3.77→*d*, $J = 3.5$, H–C(4)); 3.78 (*dd*, $J = 4.1, 11.1$, irrad. at 4.07→*d*, $J \approx 10$, H_A–C(5)); 3.76 (*dd*, $J = 4.4, 11.1$, irrad. at 4.07→*d*, $J \approx 10$, H_B–C(5)); 3.02–3.00 (*m*, 2 H–C(5′)); 1.58 (*s*, Me); 1.37 (*s*, Me); 0.90 (*s*, ^{t}BuSi); 0.07 (*s*, MeSi); 0.06 (*s*, MeSi).

1-C-(Cyclopenta-2,4-dienylidene)-1-deoxy-2,3:4,5-di-O-isopropylidene-D-ribitol (**32**). At −110°, 2M CpNa in THF (4.4 ml, 8.8 mmol) was added over 5 min to a stirred soln. of **30** [71] (1.30 g, 5.6 mmol) in dry THF (19 ml). The soln. was stirred at −100° for 0.5 h, and treated dropwise with sat. $NaHCO_3$ (5 ml). The mixture was then allowed to warm to r.t. over 0.5 h. Normal workup gave a light brown oil which was dissolved in THF (15 ml), treated with Et_3N (2.6 ml, 19 mmol), Ac_2O (0.85 ml, 9 mmol), and 4-(dimethylamino)pyridine (DMAP; 50 mg), and stirred at r.t. for 1.5 h. Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:16) afforded **32** (562 mg, 36%, yellow oil) which decomposed at r.t. Even storage of a CH_2Cl_2 soln. of **32** for 2 days at −25° led to significant decomposition. R_f(CH_2Cl_2/Et_2O/pentane 1:1:10) 0.43. $[\alpha]_D^{25} = 11.8$ ($c = 1.01$, $CHCl_3$). UV ($CHCl_3$): 257 (14400), 371 (160). IR: 3681*w*, 3493*w* (br.), 3043*w*, 2990*s*, 2937*m*, 2891*m*, 1709*w*, 1651*w*, 1602, 1479*w*, 1455*w*, 1382*s*, 1373*s*, 1347*w*, 1253*s*, 1157*s*, 1060*s*, 963*w*, 948*w*, 886*m*, 846*m*, 619*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.56 (*t*, $J = 1.7$, 2 olef. H); 6.48 (*dt*, $J = 5.3$, 1.6, 1 olef. H); 6.33 (br. *d*, $J = 8.3$, irrad. at 5.23→br. *s*, H–C(1)); 6.31 (*dt*, $J = 5.6$, 1.7, 1 olef. H); 5.23 (*dd*, $J = 6.3$, 8.3, irrad. 4.24→*d*, $J = 8.2$, H–C(2)); 4.24 (*dd*, $J = 6.3$, 7.6, irrad. at 5.23→*d*, $J = 7.5$, H–C(3)); 4.09 (*dt*, $J = 7.7$, 5.8, irrad. at 4.24→br. *t*, $J \approx 6.5$, H–C(4)); 4.03 (*dd*, $J = 6.0$, 8.2, H_A–C(5)); 3.93 (*dd*, $J \approx 5.6$, 8.1, H_B–C(5)); 1.52 (*s*, Me); 1.42 (*s*, Me); 1.36 (*s*, Me); 1.26 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 148.09 (*s*); 134.76 (*d*); 133.91 (*d*); 132.47 (*d*); 126.24 (*d*); 120.32 (*d*); 109.92 (*s*); 109.83 (*s*); 79.75 (*d*); 76.10 (*d*); 74.08 (*d*); 67.31 (*t*); 28.06 (*q*); 26.89 (*q*); 25.58 (2*q*). EI-MS: 278 (2, M^+), 263 (17, $[M - Me]^+$), 220 (24), 171 (39), 133 (100), 119 (26), 101 (37), 91 (34), 78 (37), 43 (71), 28 (26). Anal. calc. for $C_{16}H_{22}O_4$ (278.35): C 69.04, H 7.97; found: C 69.27, H 7.97.

(1R/1S)-1-C-(Cyclopenta-1′,3′-dienyl)- and (1R/1S)-1-C-(Cyclopenta-1′,4′-dienyl)-1-deoxy-2,3:4,5-di-O-isopropylidene-1-C-phenyl-D-ribitol (**33a**/**34a** and **33b**/**34b**, resp.). a) *From* **27**/**28**. At −78°, 2M PhLi in cylcohexane/Et_2O (1.45 ml, 2.9 mmol) was added to a stirred soln. of **27**/**28** (249 mg, 0.71 mmol) in dry THF (7.2 ml). The mixture was stirred at −78° for 15 min, allowed to warm to 0° over 10 min, and stirred for 1 h at 0°. Normal workup afforded a yellow oil which was dissolved in THF (1 ml). Addition of $Bu_4NF \cdot 3\ H_2O$ (450 mg, 1.43 mmol) in THF (3 ml) and stirring at r.t. for 30 min, followed by normal workup, gave a brown oil which was dissolved in acetone (4 ml) and treated with 2,2-dimethoxypropane (0.9 ml, 7 mmol) and $TsOH \cdot H_2O$ (20 mg) at 0° for 30 min. Addition of Et_3N (0.5 ml), evaporation and FC (CH_2Cl_2/Et_2O/pentane 1:1:16→1:1.10) afforded 216 mg (86%) of **33**/**34** 20:1 (^{1}H-NMR) as an oil.

b) *From* **32**. At −78°, 2M PhLi in cyclohexane/Et_2O (0.32 ml, 0.64 mmol) was added to a stirred soln. of **32** (87 mg, 0.31 mmol) in dry Et_2O (3.2 ml). The mixture was stirred at −78° for 0.5 h and quenched with sat. $NaHCO_3$ soln. (5 ml). Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:16) afforded 79 mg (71%) of **33**/**34** 20:1. Crystallization from $MeOH/H_2O$ gave white crystals of **33**/**34**. Prep. HPLC (hexane/Et_2O 95:5) afforded pure samples of **33a**, **33b**, **34a**, and **34b**. A $CDCl_3$ soln. of pure **33a**, **33b**, **34a**, or **34b** isomerized over several days to mixtures of **33a**/**b** and **34a**/**b**, respectively.

Data of **33**/**34**: R_f(CH_2Cl_2/Et_2O/pentane 1:1:10) 0.39. M.p. 67–71°. IR: 3065*w*, 3043*w*, 2990*s*, 2940*m*, 2885*m*, 1600*w*, 1497*m*, 1454*m*, 1382*s*, 1372*s*, 1253*s*, 1157*s*, 1063*s*, 1001*w*, 953*w*, 899*m*, 851*m*, 638*w*, 617*w*. EI-MS: 356 (4, M^+), 341 (2, $[M - Me]^+$), 298 (4), 155 (11), 143 (100), 101 (15), 85 (13), 57 (13), 43 (13). Anal. calc. for $C_{22}H_{28}O_4$ (356.46): C 74.13, H 7.92; found: C 74.18, H 7.89.

Data of **33a**/**b**: $[\alpha]_D^{20} = +3.6$ ($c = 0.95$, $CHCl_3$).

Data of **33a**: t_R (hexane/Et_2O 95:5) 28.7 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31–7.24 (*m*, 4 arom. H); 7.19–7.13 (*m*, 1 arom. H); 6.41–6.35 (*m*, 2 olef. H); 6.25 (*m*, 1 olef. H); 4.84 (*dd*, $J = 5.2$, 9.5, H–C(2)); 4.17 (*d*, $J = 9.3$, irrad. at 4.84→*s*, H–C(1)); 4.16–4.08 (*m*, H–C(4)); 4.04 (*dd*, $J = 6.3$, 8.3, H_A–C(5)); 3.96 (*dd*, $J = 5.2$, 8.2, irrad. at 4.84→*d*, $J = 8$, H–C(3)); 3.86 (*dd*, $J = 6.2$, 8.3, H_B–C(5)); 2.96–2.94 (*m*, 2 H–C(5′)); 1.45 (*s*, Me); 1.41 (*s*, Me); 1.23 (*s*, Me); 1.02 (*s*, Me).

Data of **33b**: t_R (hexane/Et_2O 95:5) 31 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.24 (*m*, 4 arom. H); 7.20–7.16 (*m*, 1 arom. H); 6.55 (*m*, 1 olef. H); 6.35 (*m*, 1 olef. H); 6.19 (br. *s*, 1 olef. H); 4.87 (*dd*, $J = 5.2$, 9.3, H–C(2)); 4.19–4.11 (*m*, H–C(4)); 4.14 (*d*, $J \approx 9$, irrad. at 4.87→*s*, H–C(1)); 4.04 (*dd*, $J = 6.3$, 8.4, H_A–C(5)); 3.97 (*dd*, $J = 5.2$, 8.3, irrad. at 4.87→8, H–C(3)); 3.86 (*dd*, $J = 6.5$, 8.4, H_B–C(5)); 2.96–2.93 (*m*, 2 H–C(5′)); 1.46 (*s*, Me); 1.41 (*s*, Me); 1.25 (*s*, Me); 1.08 (*s*, Me).

Data of **34a**: t_R (hexane/Et_2O 95:5) *ca.* 29 min. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.28–7.26 (*m*, 4 arom. H); 7.20–7.16 (*m*, 1 arom. H); 6.39 (*dq*, $J = 5.3$, 1.7, 1 olef. H); 6.37 (*m*, 1 olef. H); 6.21 (*dq*, $J = 5.3$, 1.3, 1 olef. H); 4.79 (*dd*, $J = 4.5$, 10.5, H–C(2)); 4.18–4.12 (*m*, irrad. at 4.79→change, H–C(3), H–C(4)); 4.07 (*dd*, $J = 6.0$, 8.6, H_A–C(5)); 4.04 (*dd*, $J = 1.0$, 10.6, irrad. at 4.79→br. *s*, H–C(1)); 3.93 (*dd*, $J = 5.7$, 8.6, H_B–C(5)); 2.87 (*dq*, $J = 23.4$, 1.4, H_A–C(5′)); 2.77 (*dq*, $J = 23.4$, 1.4, H_B–C(5′)); 1.34 (*s*, Me); 1.283 (*s*, Me); 1.278 (*s*, Me); 1.16 (*s*, Me).

Data of **34b**: t_R (hexane/Et_2O 95:5) 36 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.25 (*m*, 4 arom. H); 7.22–7.17 (*m*, 1 arom. H); 6.38–6.31 (*m*, 2 olef. H); 6.21 (br. *s*, 1 olef. H); 4.82 (*dd*, $J = 4.7$, 10.2, H–C(2)); 4.21–4.12 (*m*, irrad.

at 4.82→change, H–C(3), H–C(4)); 4.09–4.03 (*m*, H_A–C(5)); 4.02 (*d*, *J* = 10.3, irrad. at 4.82→*s*, H–C(1)); 3.85 (*dd*, *J* = 5.7, 8.4, H_B–C(5)); 3.05–2.87 (*m*, 2 H–C(5')); 1.36 (*s*, Me); 1.31 (*s*, Me); 1.28 (*s*, Me); 1.20 (*s*, Me).

1,1'-Bis[(1R)-1-deoxy-2,3:4,5-di-O-isopropylidene-1-C-phenyl-D-ribitol-1-yl]ferrocene (**35**). At −60°, 1.6M BuLi in hexane (0.36 ml, 0.58 mmol) was added dropwise to a stirred soln. of **33**/**34** 20:1 (172 mg, 0.48 mmol) in dry THF (2 ml). The mixture was allowed to warm to r.t. over 5 min and stirred for further 0.5 h. The clear soln. was treated with $FeCl_2$ (59 mg, 0.46 mmol) and stirred for 1.2 h at r.t. Normal workup and FC (CH_2Cl_2/Et_2O/pentane (1:1:10→1:1:4) afforded **35** (163 mg, 88%, yellow oil). Crystallization from EtOH/H_2O gave a yellow powder. R_f(CH_2Cl_2/Et_2O/pentane 1:1:4) 0.48. M.p. 54–57. $[\alpha]_D^{25} = -46.1$ (*c* = 0.41, $CHCl_3$). IR: 3090*w*, 3065*w*, 2990*s*, 2937*m*, 2885*w*, 1499*w*, 1453*m*, 1382*s*, 1372*s*, 1322*w*, 1258*m*, 1162*m*, 1119*w*, 1063*s*, 1032*m*, 1001*w*, 963*w*, 930*w*, 877*m*, 849*m*, 834*m*. ^{1}H-NMR (500 MHz, C_6D_6): 7.28 (*d*, *J* ≈ 8, 2 arom. H); 7.15 (*t*, *J* ≈ 8, 2 arom. H); 7.13–7.07 (*m*, 1 arom. H); 4.56 (*dd*, *J* = 4.9, 10.2, irrad. at 3.81→*d*, *J* = 10, H–C(2)); 4.35 (*dt*, *J* = 2.4, 1.3, 1 arom. H); 4.24 (*dt*, *J* = 8.7, 6.3, irrad. at 3.81→*t*, *J* ≈ 6, H–C(4)); 4.10 (*d*, *J* = 10.1, irrad. at 4.56→*s*, H–C(1)); 4.05 (*dd*, *J* = 6.4, 8.5, H_A–C(5)); 4.00 (*dd*, *J* = 6.2, 8.6, H_B–C(5)); 3.91 (*dt*, *J* = 1.3, 2.4, 1 arom. H); 3.84 (*dt*, *J* = 1.3, 2.4, 1 arom. H); 3.81 (*dd*, *J* = 4.9, 8.7, irrad. at 4.56→*d*, *J* = 8.5, irrad. at 4.24→*d*, *J* ≈ 4.5, H–C(3)); 3.77 (*dt*, *J* = 2.4, 1.3, 1 arom. H); 1.32 (*s*, Me_{Si} of 2,3-*O*-CMe_2); 1.30 (*s*, Me_{Si} of 4,5-*O*-CMe_2); 1.21 (*s*, Me_{Re} of 2,3-*O*-CMe); 1.01 (*s*, Me_{Re} of 4,5-*O*-CMe_2). NOE: irrad. at 4.24 (H–C(4))→1% at 7.28 (H_o of Ph), 10% at 4.05 (H–C(1), H_A–C(5)), 2% at 1.32 (Me_{Si} of 2,3-*O*-CMe_2), 1% at 1.30 (Me_{Si} of 4,5-*O*-CMe_2); irrad. at 1.21 (Me_{Re} of 2,3-*O*-CMe)→3% at 4.56 (H–C(2)), 1% at 3.81 (H–C(3)); irrad. at 1.01 (Me_{Re} of 4,5-*O*-CMe_2)→0.5% at 7.28 (H_o of Ph), 0.5% at 7.10 (H_m, H_p of Ph), 0.5% at 4.00 (H_B–C(5)), 1% at 3.81 (H–C(3)), 2% at 1.30 (Me_{Si} of 4,5-*O*-CMe_2). ^{13}C-NMR (75 MHz, C_6D_6): 142.70 (*s*); 129.63 (2*d*); 127.84 (2*d*); 126.54 (*d*); 109.70 (*s*); 107.71 (*s*); 92.04 (*s*); 81.36 (*d*); 79.32 (*d*); 73.69 (*d*); 71.02 (*d*); 69.05 (*d*); 68.81 (*d*); 68.51 (*d*); 67.86 (*t*); 44.85 (*d*); 28.41 (*q*); 26.29 (*q*); 26.17 (*q*); 25.75 (*q*). EI-MS: 766 (100, M^+), 751 (4, $[M - Me]^+$), 565 (13), 377 (8), 295 (8), 223 (30), 211 (19), 101 (8), 43 (25), 28 (22). Anal. calc. for $C_{44}H_{54}FeO_8$ (766.75): C 68.92, H 7.10; found: C 69.09, H 7.38.

1-C-(Cyclopenta-2,4-dienylidene)-1-deoxy-2,3:4,5-di-O-isopropylidene-D-arabinitol (**37**). At −110°, 2M CpNa in THF (11 ml, 22 mmol) was added over 10 min to a stirred soln. of **36** (3.36 g, 14.6 mmol) [74] in dry THF (48 ml). The soln. was stirred at −100° for 0.5 h, and treated dropwise with sat. $NaHCO_3$ soln. (10 ml). The mixture was then allowed to warm to r.t. over 0.5 h. Normal workup gave a brown oil which was dissolved in THF (38 ml), treated with Et_3N (6.1 ml, 44 mmol), Ac_2O (2.1 ml, 22 mmol), and DMAP (100 mg), and stirred at r.t. for 2 h. Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:16) afforded **37** (1.31 g, 32%, yellow oil) which decomposed at r.t. Even storage of a CH_2Cl_2 soln. of **37** for 2 days at −25° resulted in significant decomposition. R_f (CH_2Cl_2/Et_2O/pentane 1:1:10) 0.33. $[\alpha]_D^{25} = -12.3$ (*c* = 1.18, $CHCl_3$). UV ($CHCl_3$): 255 (11700), 373 (130). IR: 3043*w*, 2990*s*, 2936*m*, 2890*m*, 1653*w*, 1559*w*, 1540*w*, 1506*w*, 1481*w*, 1456*m*, 1383*s*, 1373*s*, 1344*m*, 1253*s*, 1156*s*, 1064*s*, 976*w*, 959*w*, 920*w*, 885*m*, 843*m*, 618*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.62–6.51 (*m*, 2 olef. H); 6.46 (*dt*, *J* = 5.2, 1.4, 1 olef. H); 6.28 (br. *d*, *J* = 7.9, H–C(1)); 6.18 (*dt*, *J* = 5.2, 1.7, 1 olef. H); 4.92 (*t*, *J* = 7.6, H–C(2)); 4.18 (*dt*, *J* = 4.8, 6.4, H–C(4)); 4.09 (*dd*, *J* = 6.2, 8.3, H_A–C(5)); 3.93 (*dd*, *J* = 4.8, 8.3, H_B–C(5)); 3.89 (*t*, *J* ≈ 6.8, H–C(3)); 1.47 (*s*, Me); 1.46 (*s*, Me); 1.32 (*s*, Me); 1.31 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 147.09 (*s*); 135.38 (*d*); 134.03 (*d*); 131.93 (*d*); 125.49 (*d*); 120.10 (*d*); 110.15 (*s*); 109.43 (*s*); 81.18 (*d*); 77.37 (*d*); 76.15 (*d*); 66.54 (*t*); 26.88 (*q*); 26.78 (*q*); 26.26 (*q*); 24.92 (*q*). EI-MS: 278 (2, M^+), 263 (21, $[M - Me]^+$), 220 (66), 205 (10), 162 (15), 145 (12), 133 (100), 119 (37), 101 (68), 91 (39), 78 (42), 59 (15), 43 (77). Anal. calc. for $C_{16}H_{22}O_4$ (278.35): C 69.04, H 7.97; found: C 69.24, H 8.01.

(1S/1R)-1-C-(Cyclopenta-1',3'-dienyl)- and (1S/1R)-1-C-(Cyclopenta-1',4'-dienyl)-1-deoxy-2,3:4,5-di-O-isopropylidene-1-C-phenyl-D-arabinitol (**38a**/**39a** and **38b**/**39b**, resp.). At −78°, a soln. of **37** (61 mg, 0.22 mmol) in dry THF (2.5 ml) was added to a stirred soln. of PhLi (1.3 mmol) in THF (1 ml)[7]. The mixture was stirred at −78° for 0.5 h and quenched with sat. $NaHCO_3$ soln. (5 ml). Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:10) afforded 61 mg (78%; oil) of **38**/**39** 18:1 (^{1}H-NMR)[8]. Crystallization from MeOH/H_2O gave a white microcrystalline powder of **38**/**39**. Prep. HPLC (hexane/Et_2O 95:5) afforded pure samples of **38a**, **38b**, **39a**, and **39b**. A $CDCl_3$ soln. of pure **38a**, **38b**, **39a**, or **39b** isomerized over several days to **38a**/**b** or **39a**/**b**, respectively.

Data of **38**/**39**: R_f(CH_2Cl_2/Et_2O/pentane 1:1:10) 0.34. M.p. 41–45°. $[\alpha]_D^{25} = +47.5$ (*c* = 1.07, $CHCl_3$). IR: 3064*w*, 2990*s*, 2936*m*, 2887*m*, 1601*w*, 1496*w*, 1454*m*, 1382*s*, 1373*s*, 1253*s*, 1155*s*, 1070*s*, 1002*w*, 976*w*, 954*w*, 921*w*, 900*m*, 848*m*, 644*w*. EI-MS: 356 (3, M^+), 341 (5, $[M - Me]^+$), 298 (2), 200 (9), 181 (3), 167 (4), 155 (10), 143 (100), 128 (3), 115 (5), 101 (18), 85 (20), 59 (15), 57 (22), 43 (20). Anal. calc. for $C_{22}H_{28}O_4$ (356.46): C 74.13, H 7.92; found: C 73.97, H 7.91.

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[7]) Prepared by evaporating 2M PhLi in cyclohexane/Et_2O (0.65 ml) and THF (2 ml) to a volume of *ca.* 0.5 ml at 0.01 Torr, repeated addition of THF (2 ml) and evaporation to *ca.* 1 ml.

[8]) With Et_2O as solvent, a 79:21 mixture of **38**/**39** (43% yield) was obtained.

Data of **38a**: t_R(hexane/Et_2O 95:5) 24.8 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.37–7.27 (*m*, 4 arom. H); 7.23–7.19 (*m*, 1 arom. H); 6.45–6.43 (*m*, 2 olef. H); 6.30–6.28 (*m*, 1 olef. H); 4.42 (*dd*, *J* = 5.5, 5.9, H–C(2)); 4.14 (*d*, *J* = 5.3, H–C(1)); 4.04 (*dd*, *J* = 5.7, 8.3, H_A–C(5)); 3.91–3.78 (*m*, H–C(3), H–C(4), H_B–C(5)); 3.07 (*dq*, *J* ≈ 24, 1.4, H_A–C(5′)); 2.81 (*dq*, *J* ≈ 24, 1.4, H_B–C(5′)); 1.40 (*s*, Me); 1.39 (*s*, Me); 1.30 (*s*, Me); 1.29 (*s*, Me).

Data of **38b**: t_R(hexane/Et_2O 95:5) 27.2 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.40–7.27 (*m*, 4 arom. H); 7.24–7.19 (*m*, 1 arom. H); 6.54–6.51 (*m*, 1 olef. H); 6.36–6.34 (*m*, 1 olef. H); 6.29 (br. *s*, 1 olef. H); 4.45 (*dd*, *J* = 5.1, 6.5, H–C(2)); 4.11 (br. *d*, *J* = 5.0, H–C(1)); 4.04 (*dd*, *J* = 6.0, 8.0, H_A–C(5)); 3.92–3.81 (*m*, H–C(3), H–C(4), H_B–C(5)); 3.01–2.98 (*m*, 2 H–C(5′)); 1.39 (*s*, Me); 1.38 (*s*, Me); 1.31 (*s*, Me); 1.29 (*s*, Me).

Data of **39a**: t_R(hexane/Et_2O 95:5) 22.2 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.20 (*m*, 5 arom. H); 6.39 (*m*, 2 olef. H); 6.35–6.33 (*m*, 1 olef. H); 4.57 (*dd*, *J* = 4.1, 7.2, H–C(2)); 4.13 (*dd*, *J* = 6.5, 7.8, H_A–C(5)); 4.07 (*dt*, *J* ≈ 5.2, 7.3, H–C(4)); 4.05 (br. *d*, *J* = 4.3, H–C(1)); 3.86 (*dd*, *J* = 5.4, 7.7, H_B–C(5)); 3.61 (br. *t*, *J* ≈ 7.5, H–C(3)); 3.03–3.00 (*m*, 2 H–C(5′)); 1.45 (*s*, Me); 1.38 (*s*, 2 Me); 1.15 (*s*, Me).

Data of **39b**: t_R(hexane/Et_2O 95:5) 22.9 min. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.34–7.20 (*m*, 5 arom. H); 6.46–6.41 (*m*, 2 olef. H); 6.29–6.26 (*m*, 1 olef. H); 4.58 (*dd*, *J* = 4.7, 6.7, H–C(2)); 4.09 (*dt*, *J* = 6.3, 8.0, H–C(4)); 4.07 (*d*, *J* ≈ 4.9, H–C(1)); 4.06 (*dd*, *J* ≈ 6.0, 7.5, H_A–C(5)); 3.86 (*dd*, *J* = 5.1, 7.8, H_B–C(5)); 3.57 (*dd*, *J* = 6.8, 8.1, H–C(3)); 2.89 (*m*, 2 H–C(5′)); 1.41 (*s*, Me); 1.37 (*s*, 2 Me); 1.19 (*s*, Me).

*1,1′-Bis[(1S)-1-deoxy-2,3:4,5-di-*O*-isopropylidene-1-*C*-phenyl-*D*-arabinitol-1-yl]ferrocene* (**40**). At −20°, 1.6M BuLi in hexane (0.78 ml, 1.2 mmol) was added dropwise to a stirred soln. of **38**/**39** 18:1 (367 mg, 1.03 mmol) in dry THF (4.3 ml). The mixture was allowed to warm to r.t. over 5 min and stirred for further 0.5 h. The clear soln. was treated with $FeCl_2$ (131 mg, 1.03 mmol) and stirred for 3 h at r.t. Normal workup and FC (CH_2Cl_2/Et_2O/pentane 1:1:10→1:1:6) afforded slightly impure **40** (327 mg, 83%, yellow crystals, M.p. 164–177°). Slow recrystallization in AcOEt gave well formed yellow orthorhombic crystals suited for X-ray analysis. R_f(CH_2Cl_2/Et_2O/pentane 1:1:4) 0.44. M.p. 185°. $[\alpha]_D^{25}$ = 126.1 (*c* = 0.955, $CHCl_3$). IR: 3089*w*, 3065*w*, 2990*s*, 2936*m*, 2893*m*, 1494*w*, 1453*m*, 1382*s*, 1372*s*, 1344*w*, 1253*s*, 1156*s*, 1070*s*, 978*w*, 931*w*, 918*w*, 886*m*, 847*s*, 825*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.47–7.25 (*m*, 5 arom. H); 4.04 (*t*, *J* = 6.4, H–C(2)); 3.97 (*dt*, *J* = 2.3, 1.3, 1 arom. H); 3.92 (*dd*, *J* = 6.4, 8.3, H_A–C(5)); 3.76 (*dd*, *J* = 6.2, 8.3, H_B–C(5)); 3.70 (*t*, *J* = 6.7, H–C(3)); 3.69–3.67 (*m*, 2 arom. H); 3.66 (br. *d*, *J* = 6.5, H–C(1)); 3.64 (*dt*, *J* = 2.4, 1.2, 1 arom. H); 3.63 (*q*, *J* = 6.4, H–C(4)); 1.30 (*s*, Me); 1.28 (*s*, Me); 1.25 (*s*, Me); 1.247 (*s*, Me). ^{1}H-NMR (500 MHz, C_6D_6): 7.48–7.46 (*m*, 2 arom. H); 7.21–7.19 (*m*, 2 arom. H); 7.12–7.09 (*m*, 1 arom. H); 4.22 (*dd*, *J* = 4.6, 7.1, H–C(2)); 4.20 (*dt*, *J* = 2.4, 1.4, 1 arom. H); 3.93 (br. *d*, *J* = 4.8, irrad. at 4.22→*s*, H–C(1)); 3.92 (*dt*, *J* = 2.5, 1.3, 1 arom. H); 3.89 (*t*, *J* = 7.3, H–C(3)); 3.88 (*dd*, *J* = 6.6, 8.4, H_A–C(5)); 3.86 (*dd*, *J* = 5.9, 8.4, H_B–C(5)); 3.79 (*dt*, *J* = 1.3, 2.4, 1 arom. H); 3.74 (*dt*, *J* = 6.0, 7.0, H–C(4)); 3.737 (*dt*, *J* = 1.4, 2.4, 1 arom. H); 1.41 (*s*, Me); 1.26 (*s*, Me); 1.233 (*s*, Me); 1.226 (*s*, Me). ^{13}C-NMR (75 MHz, C_6D_6): 143.83 (*s*); 129.77 (2*d*); 128.40 (2*d*); 126.95 (*d*); 109.69 (*s*); 109.54 (*s*); 88.54 (*s*); 84.08 (*d*); 79.76 (*d*); 77.36 (*d*); 71.45 (*d*); 70.21 (*d*); 69.60 (*d*); 68.17 (*d*); 67.46 (*t*); 49.41 (*d*); 27.85 (*q*); 27.81 (*q*); 26.87 (*q*); 25.61 (*q*). EI-MS: 766 (100, M^+), 751 (2, $[M - Me]^+$), 565 (11), 377 (4), 295 (6), 253 (8), 223 (17), 211 (18), 143 (9), 101 (6), 43 (31), 28 (22). Anal. calc. for $C_{44}H_{54}FeO_8$ (766.75): C 68.92, H 7.10; found: C 69.05, H 7.28.

*(1S)-1-C-Cyclopentyl-1-deoxy-2,3:4,5-di-*O*-isopropylidene-1-*C*-phenyl-*D*-arabinitol* (**41**). A soln. of **38a**/**b** (217 mg, 0.61 mmol) in hexane (40 ml) was treated with 10% Pd/C (197 mg), degassed, and stirred under H_2 at r.t. for 17 h. Filtration through *Celite* and evaporation gave **41** (208 mg, 95%, white powder). Recrystallization in MeOH/H_2O afforded white crystals of **41**. M.p. 59–60°. $[\alpha]_D^{20}$ = +34.9 (*c* = 1.025, $CHCl_3$). IR ($CHCl_3$): 2990*s*, 2954*s*, 2871*m*, 1734*w*, 1717*w*, 1602*w*, 1496*w*, 1454*m*, 1382*s*, 1372*s*, 1248*m* (br.), 1156*m*, 1066*s*, 1010*w*, 910*w*, 888*w*, 847*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.31–7.17 (*m*, 5 arom. H); 4.18 (*dd*, *J* = 6.1, 7.1, H–C(2)); 3.95 (*dd*, *J* = 6.4, 8.3, H–C(3)); 3.84–3.79 (*m*, 2 H–C(5)); 3.67 (br. *q*, *J* ≈ 6.4, H–C(4)); 2.79 (*dd*, *J* = 7.1, 8.6, H–C(1)); 2.41–2.27 (*m*, 1 H); 2.06–1.97 (*m*, 1 H); 1.61–1.41 (*m*, 5 H); 1.37 (*s*, Me); 1.31 (*s*, Me); 1.25 (*s*, Me); 1.24 (*s*, Me); 1.29–1.18 (*m*, 1 H); 1.06–0.93 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 141.15 (*s*); 129.52 (2*d*); 128.02 (2*d*); 126.48 (*d*); 109.27 (*s*); 109.21 (*s*); 83.14 (*d*); 79.66 (*d*); 76.50 (*d*); 66.26 (*t*); 53.94 (*d*); 42.54 (*d*); 32.12 (*t*); 31.22 (*t*); 27.87 (*q*); 27.75 (*q*); 26.24 (*q*); 25.32 (*q*); 25.07 (*t*); 24.03 (*t*). EI-MS: 360 (0.4, M^+); 345 (2.5, $[M - Me]^+$), 302 (0.4), 227 (0.6), 209 (1.2), 201 (10), 183 (3), 157 (3), 143 (100), 129 (5), 115 (5), 101 (18), 91 (24), 85 (15), 59 (18), 57 (21), 43 (31), 28 (8). Anal. calc. for $C_{22}H_{32}O_4$ (360.49): C 73.30, H 8.95; found: C 73.50, H 8.76.

*(1S)-1-C-Cyclopentyl-1-deoxy-1-*C*-phenyl-*D*-arabinitol* (**42**). A soln. of **41** (195 mg, 0.541 mmol) in MeOH (15 ml) was treated with 37% aq. HCl (0.6 ml) and stirred at r.t. for 3.5 h. After evaporation, the residue was dissolved in MeOH (2 × 20 ml) and evaporated. Crystallization from MeOH/pentane gave **42** (125 mg, 82%, white crystals). M.p. 175–176.5°. $[\alpha]_D^{20}$ = +11.6 (*c* = 0.76, MeOH). IR (KBr): 3333*s*, 2956*m*, 2933*m*, 2905*w*, 2855*m*, 1458*w*, 1406*w*, 1381*w*, 1274*w*, 1256*w*, 1214*w*, 1089*m*, 1042*w*, 1028*w*, 1022*m*, 887*w*, 762*w*, 694*m*. ^{1}H-NMR (300 MHz, CD_3OD): 7.28–7.21 (*m*, 2 arom. H); 7.19–7.12 (*m*, 3 arom. H); 4.21 (*dd*, *J* = 0.6, 10.6, H–C(2)); 3.69–3.60 (*m*, 2 H–C(5)); 3.43 (*m*, H–C(4)); 3.10 (*dd*, *J* = 0.6, 8.2, H–C(3)); 2.92 (*dd*, *J* = 6.6, 10.5, H–C(1)); 2.47–2.34 (*m*,

1 H); 1.94–1.84 (*m*, 1 H); 1.57–1.34 (*m*, 5 H); 1.23–1.04 (*m*, 2 H). ^{13}C-NMR (75 MHz, CD_3OD): 142.93 (*s*); 130.81 (2*d*); 129.01 (2*d*); 127.10 (*d*); 73.69 (*d*); 73.20 (*d*); 72.32 (*d*); 65.13 (*t*); 53.15 (*d*); 44.08 (*d*); 32.69 (*t*); 30.35 (*t*); 25.76 (*t*); 25.25 (*t*). CI-MS (NH_3): 298 (0.2, $[M + NH_4]^+$), 281 (0.2, $[M + 1]^+$), 263 (1), 245 (2), 201 (2), 189 (3), 171 (6), 160 (57), 143 (9), 120 (11), 117 (15), 103 (18), 91 (100), 81 (9), 67 (11), 41 (10), 28 (28). Anal. calc. for $C_{16}H_{24}O_4$ (280.36): C 68.55, H 8.63; found: C 68.44, H 8.48.

(+)-(S)-2-Cyclopentyl-2-phenylethanol ((+)-(*S*)-**43**). A suspension of **42** (102 mg, 0.36 mmol) in MeCN (35 ml) was treated with a soln. of $NaIO_4$ (363 mg, 1.70 mmol) in H_2O (7 ml), stirred at r.t. for 3 h, and neutralized by adding aq. sat. $NaHCO_3$ soln. Extraction with CH_2Cl_2, drying ($MgSO_4$), and evaporation afforded an oil (62 mg) which was immediately dissolved in EtOH (8 ml), treated with $NaBH_4$ (30 mg, 0.793 mmol), and stirred at r.t. for 14 h. After addn. of MeOH (15 ml) and stirring for 1 h, evaporation and FC (pentane/Et_2O 10:3) gave crude **43**. Dissolution of the residue in Et_2O, filtration, evaporation and drying the residue in high vacuum gave (+)-(*S*)-**43** (51 mg, 74%; colorless oil). R_f(pentane/Et_2O 10:3) 0.19. $[\alpha]_D^{20} = +18.1$ ($c = 0.93$, $CHCl_3$). IR ($CHCl_3$): 3590*m*, 3084*w*, 3064*w*, 3008*s*, 2956*s*, 2871*s*, 1602*w*, 1494*m*, 1468*w*, 1452*m*, 1388*w*, 1340*w*, 1310*w*, 1178*w*, 1075*w*, 1051*m*, 1015*m*, 971*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.37–7.20 (*m*, 5 arom. H); 3.89 (*dd*, $J = 4.3, 10.8$, H_A–C(1)); 3.75 (*dd*, $J = 8.9, 10.8$, H_B–C(1)); 2.56 (*dt*, $J = 4.5, 9.3$, H–C(2)); 2.17–1.85 (*m*, 2 H); 1.80–1.17 (*m*, 7 H); 1.11–0.92 (*m*, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 142.71 (*s*); 128.59 (2*d*); 128.45 (2*d*); 126.64 (*d*); 66.60 (*t*); 54.82 (*d*); 42.31 (*d*); 31.59 (*t*); 31.26 (*t*); 25.24 (*t*); 24.41 (*t*). EI-MS: 190 (22, $M^{+\cdot}$), 159 (100, $[M - CH_2OH]^+$), 129 (9), 117 (19), 115 (19), 104 (26), 91 (94), 81 (14), 77 (11), 67 (7), 65 (7), 41 (9), 39 (9).

(1R)-1-C-Cyclopentyl-1-deoxy-2,3:4,5-di-O-isopropylidene-1-C-phenyl-D-ribitol (**44**). A soln. of **33a**/**b** (446 mg, 1.251 mmol) in hexane (50 ml) was treated with 10% Pd/C (220 mg), degassed, and stirred under H_2 for 14 h. Filtration through *Celite* and evaporation afforded **44** (430 mg, 95%, white microcrystalline powder). M.p. 51.5–52.5°. $[\alpha]_D^{20} = +21.2$ ($c = 0.89$, $CHCl_3$). IR ($CHCl_3$): 3088*w*, 3063*w*, 2990*s*, 2953*s*, 2871*m*, 1730*w*, 1602*w*, 1498*w*, 1453*m*, 1382*s*, 1372*s*, 1248*m* (br.), 1158*m*, 1132*s*, 1059*s*, 1033*m*, 963*w*, 909*w*, 851*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.29–7.11 (*m*, irrad. at 0.96→weak NOE, 5 arom. H); 4.66 (*dd*, $J = 5.0, 11.1$, H–C(2)); 4.07–3.96 (*m*, H–C(4), H_A–C(5)); 3.89–3.79 (*m*, irrad. at 0.96→weak, NOE, H–C(3), H_B–C(5)); 3.02 (*dd*, $J = 5.6, 11.1$, H–C(1)); 2.43–2.23 (*m*, 1 H); 1.85–1.72 (*m*, 1 H); 1.61–0.86 (*m*, 7 H); 1.45 (*s*, Me); 1.41 (*s*, Me); 1.21 (*s*, Me); 0.96 (*s*, Me). ^{13}C-NMR (50 MHz, $CDCl_3$): 140.10 (*s*); 129.59 (2*d*); 127.49 (2*d*); 126.18 (*d*); 109.04 (*s*); 107.46 (*s*); 79.61 (*d*); 78.25 (*d*); 73.37 (*d*); 66.82 (*t*); 46.69 (*d*); 43.49 (*d*); 30.46 (*t*); 27.91 (*q*); 27.54 (*t*); 25.72 (*q*); 25.51 (*q*); 25.36 (*q*); 24.27 (*t*); 23.90 (*t*). EI-MS: 360 (0.5, $M^{+\cdot}$), 345 (1.8, $[M - Me]^+$), 302 (0.4), 287 (1), 259 (1), 201 (27), 183 (11), 143 (100), 101 (33), 91 (29), 59 (13), 57 (12), 43 (22). Anal. calc. for $C_{22}H_{32}O_4$ (360.49): C 73.30, H 8.95; found: C 73.16, H 8.73.

(1R)-1-C-Cyclopentyl-1-deoxy-1-C-phenyl-D-ribitol (**45**). A soln. of **44** (340 mg, 0.943 mmol) in MeOH (20 ml) was treated with 37% HCl (0.8 ml), stirred at r.t. for 5 h, and evaporated. The residue was dissolved in MeOH (3 × 20 ml) and evaporated. Crystallization from Et_2O/hexane afforded **45** (221 mg, 84%, white microcrystalline powder). M.p. 113–114.5°. $[\alpha]_D^{20} = -20.2$ ($c = 0.45$, MeOH). IR (KBr): 3267*s*, 2956*m*, 2933*m*, 2856*w*, 1450*w*, 1430*w*, 1292*w*, 1250*w*, 1083*m*, 1067*m*, 1028*m*, 1010*w*, 961*w*, 905*w*, 770*w*, 700*m*, 622*w*. ^{1}H-NMR (200 MHz, CD_3OD): 7.26–7.11 (*m*, 5 arom. H); 3.98 (*t*, $J = 6.3$, H–C(2)); 3.79–3.68 (*m*, 2 H–C(5)); 3.60–3.48 (*m*, H–C(3), H–C(4)); 2.84 (*dd*, $J = 6.2, 8.7$, H–C(1)); 2.60–2.38 (*m*, 1 H); 2.08–1.93 (*m*, 1 H); 1.64–1.37 (*m*, 5 H); 1.34–1.14 (*m*, 1 H); 1.08–0.88 (*m*, 1 H). ^{13}C-NMR (50 MHz, CD_3OD): 144.16 (*s*); 130.44 (2*d*); 128.96 (2*d*); 127.07 (*d*); 78.06 (*d*); 74.30 (*d*); 74.01 (*d*); 63.76 (*t*); 55.10 (*d*); 43.33 (*d*); 32.93 (*t*); 32.26 (*t*); 26.07 (*t*); 25.16 (*t*). CI-MS (NH_3): 298 (5, $[M + NH_4]^+$), 281 (3, $[M + 1]^+$), 263 (4), 245 (10), 185 (25), 171 (16), 160 (99), 147 (13), 117 (18), 91 (100). Anal. calc. for $C_{16}H_{24}O_4$ (280.36): C 68.55, H 8.63; found: C 68.32, H 8.61.

(–)-(R)-2-Cyclopentyl-2-phenylacetaldehyde ((–)-(*R*)-**46**). A soln. of **45** (182 mg, 0.649 mmol) in MeCN/H_2O 2:1 (30 ml) was treated with a soln. of $NaIO_4$ (527 mg, 2.464 mmol) in H_2O (14 ml), stirred at r.t. for 3 h, and neutralized by the addition of aq. sat. $NaHCO_3$ soln. Extraction with CH_2Cl_2, drying ($MgSO_4$), evaporation, and FC (hexane/Et_2O 10:2) afforded (–)-(*R*)-**46** (93 mg, 76%; colorless oil). R_f(hexane/Et_2O 10:2) 0.58. $[\alpha]_D^{20} = -61.5$ ($c = 1.33$, $CHCl_3$). (–)-(*R*)-**46** decomposed and racemized slowly at r.t. IR ($CHCl_3$): 3065*w*, 3038*w*, 2957*s*, 2870*m*, 2821*w*, 2720*w*, 1950*w*, 1721*s*, 1601*m*, 1494*m*, 1453*m*, 1355*w*, 1155*w*, 1099*w*, 1077*w*, 1002*w*, 558*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.68 (*d*, $J = 3.0$, H–C(1)); 7.41–7.22 (*m*, 5 arom. H); 3.31 (*dd*, $J = 3.0, 10.6$, H–C(2)); 2.61–2.47 (*m*, 1 H); 2.03–1.93 (*m*, 1 H); 1.76–1.40 (*m*, 5 H); 1.33–1.20 (*m*, 1 H); 1.15–1.03 (*m*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 200.77 (*d*); 136.19 (*s*); 129.04 (2*d*); 128.88 (2*d*); 127.40 (*d*); 65.26 (*d*); 40.25 (*d*); 31.04 (*t*); 30.71 (*t*); 25.20 (*t*); 24.46 (*t*). EI-MS: 188 (2, $M^{+\cdot}$), 159 (66, $[M - CHO]^+$), 129 (6), 128 (6), 120 (25), 117 (15), 115 (15), 91 (100), 81 (13), 77 (9), 67 (7), 65 (9), 41 (7), 39 (8).

(–)-(R)-2-Cyclopentyl-2-phenylethanol ((–)-(*R*)-**43**). A soln. of freshly prepared (–)-(*R*)-**46** (44 mg, 0.234 mmol) in EtOH (4 ml) was treated with $NaBH_4$ (20 mg, 0.53 mmol), stirred at r.t. for 4 h, treated with MeOH (7 ml) and stirred for 1 h. Evaporation and FC (pentane/Et_2O 10:3) gave a residue which was treated with Et_2O.

Filtration, evaporation of the filtrate, and drying in high vacuum afforded (–)-(*R*)-**43** (37 mg, 84%; colorless oil). R_f(pentane/Et_2O 10:3) 0.19. $[\alpha]_D^{20} = -17.4$ ($c = 0.985$, $CHCl_3$).

X-Ray Analysis of **10**. $C_{27}H_{31}NO_7$ (481.54); monoclinic; $a = 10.948$ (2), $b = 9.561$ (2), $c = 12.518$ (2), Å, $\beta = 109.34$ (1)°; $V = 1236.3$ (3) $Å^3$; $D_x = 1.293$ Mg/m^3; $Z = 2$. Intensities were measured in the ω-scan mode on a *Nicolet R3* diffractometer (graphite monochromator, MoK_α, $\lambda = 0.71069$ Å) at 203 K, $2\Theta_{(max)} = 57°$, variable scan speed of 2.5 to 19.3°/min in ω. Of the 3033 total collected reflections, 2318 independent reflections were observed. $R = 0.0473$, $R_w = 0.0397$.

X-Ray Analysis of **40**: $C_{44}H_{54}FeO_8$ (766.72); orthorhombic $P2_12_12_1$; $a = 9.9747$ (10), $b = 15.676$ (3), $c = 25.753$ (6) Å; $V = 4027.0$ (13) Å^3; $D_x = 1.265$ Mg/m^3; $Z = 4$. Intensities were measured in the ω-scan mode on a *CAD4* diffractometer (graphite monochromator, MoK_α, $\lambda = 0.71073$ Å) at 173 K. Of the 3626 total collected reflections, 3621 independent reflections were observed. $R = 0.0325$, $R_w = 0.0954$.

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