denitrobenzoate was isolated as yellow crystals (17 mg, 51%): mp 165–166 °C; ^{1}H NMR ($CDCl_3$) δ 9.21 (t, J = 2.1 Hz, 1 H), 9.1 (d, J = 2.1 Hz, 2 H), 5.67 (dd, J = 10.9, 4.9 Hz, 1 H), 4.08 (m, 2 H), 3.89 (m, 2 H), 2.36 (m, 2 H), 2.17–1.58 (series of m, 15 H), 1.40 (m, 1 H).

(1*R*,3*R*,5*S*)-2-(4,5-Dihydro-2-furyl)dihydro-1,4,4-trimethylspiro[bicyclo[3.2.1]octane-3,2′(3′*H*)-furan]-2-ol (27). Alcohol **27** was produced as a single diastereomer according to the general procedure (3.14 g, 46%) from 5.22 g of **7** after flash chromatography (silica gel, elution with 12% ethyl acetate in petroleum ether): colorless oil; IR (neat, cm^{-1}) 3500; ^{1}H NMR ($CDCl_3$) δ 4.93 (t, J = 2.5 Hz, 1 H), 4.30 (m, 2 H), 3.79 (s, 1 H), 3.72 (m, 2 H), 2.47 (m, 5 H), 2.03 (m, 1 H), 1.85 (m, 2 H), 1.60 (m, 3 H), 1.20 (m, 2 H), 1.17 (s, 3 H), 1.02 (s, 3 H), 0.84 (s, 3 H); ^{13}C NMR ($CDCl_3$) ppm 163.0, 99.7, 90.1, 81.5, 70.5, 68.5, 48.1, 46.7, 42.6, 38.1, 32.9, 29.33, 29.30, 27.7, 27.0, 26.3, 25.8, 22.8; MS m/z (M^+) calcd 292.2038, obsd 292.2046; $[\alpha]^{20}_D$ +3.4° (c 2.5, $CHCl_3$).

Acid-Catalyzed Rearrangement of 27. Isomerization of **27** (3.38 g, 15.2 mmol) according to the general procedure gave 325 mg (31%) of **28** and 136 mg (12%) of **29** after MPLC (silica gel, elution with 10% ethyl acetate in petroleum ether).

For **28**: colorless crystals, mp 67.5–68.5 °C; IR ($CHCl_3$, cm^{-1}) 1700; ^{1}H NMR ($CDCl_3$) δ 4.04 (dt, J = 4.6, 7.8 Hz, 1 H), 3.94 (dt, J = 4.0, 8.0 Hz, 1 H), 3.70 (dq, J = 6.0, 7.4 Hz, 2 H), 2.46 (d, J = 14.1 Hz, 1 H), 2.35 (m, 1 H), 2.25 (m, 1 H), 2.14–1.80 (series of m, 7 H), 1.75–1.55 (m, 3 H), 1.50–1.35 (m, 2 H), 1.23 (s, 3 H), 1.12 (s, 3 H), 0.96 (s, 3 H); ^{13}C NMR ($CDCl_3$) pm 214.7, 99.4, 95.4, 71.2, 66.6, 53.4, 51.7, 43.9, 40.9, 39.0, 32.8, 31.8, 27.5, 26.69, 26.67, 26.3, 25.8, 25.5; MS m/z (M^+) calcd 292.2038, obsd 292.2020; $[\alpha]^{27}_D$ −89.8° (c 2.2, $CHCl_3$).

Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.92; H, 9.66. Found: C, 73.94; H, 9.63.

For **29**: colorless crystals, mp 40–41 °C; IR ($CHCl_3$, cm^{-1}) 1690; ^{1}H NMR ($CDCl_3$) δ 3.89–3.70 (m, 3 H), 3.58 (dt, J = 9.5, 6.7 Hz, 1 H), 2.55 (d, J = 1.37 Hz, 1 H), 2.50 (m, 1 H), 2.11–1.41 (series of m, 13 H), 1.21 (s, 3 H), 1.20 (s, 3 H), 0.91 (s, 3 H); ^{13}C NMR ($CDCl_3$) ppm 215.9, 100.2, 91.0, 69.3, 66.2, 53.3, 50.6, 44.0, 49.8, 39.8, 38.8, 32.0, 31.4, 27.9, 27.3, 26.6, 26.5, 26.3, 25.5; MS m/z (M^+) calcd 292.2038, obsd 292.2063; $[\alpha]^{23}_D$ −54.7° (c 1.2, $CHCl_3$).

Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.92; H, 9.66. Found: C, 73.90; H, 9.70.

Prototypical Control Experiment. Pure **32** (93 mg, 0.44 mmol) in $CHCl_3$ (45 mL) containing 8 mg of p-toluenesulfonic acid was heated at reflux under nitrogen for 19 h. After cooling, the solvent was carefully evaporated and the residue chromatographed (silica gel, elution with 15–30% ether in petroleum ether) to give 48.8 mg (54%) of **33** and return 24.2 mg (26%) of **32**.

Acknowledgment. We thank the National Science Foundation for financial support, Eugene Hickey for the molecular mechanics calculations, and Dr. Richard T. Taylor for his initial observation of the acid-catalyzed isomerization of **11**.

Supplementary Material Available: ^{1}H NMR spectra of **2**, **4**, **6**, **14**, **17b**, **17c**, **19**, **20**, **25**, **26**, and **27** as well as ORTEP diagrams of all 11 compounds studied, figure of the second molecule of **25**, figure of the unit cell of **25**, crystallographic experimental and tables of X-ray crystal data, bond lengths and angles, final fractional parameters, thermal parameters **4**, **7**, **8**, **13**, **14**, **17c**, **22**, **25**, **26**, **28**, and **29**, and final computed atomic coordinates for **21**, **22**, **23**, **24**, **28**, **29**, **30**, and **31** (85 pages); observed and calculated structure factors (28 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Approaches to the Synthesis of Heptitol Derivatives via Iron-Mediated Stereocontrolled Functionalization of Cycloheptatrienone

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Stereocontrolled reduction of tropone–$Fe(CO)_3$ (**9**) followed by alcohol protection gives the [(trialkylsilyl)oxy]cycloheptatriene complex **11**. Osmylation of **11** proceeds with complete stereoselectivity to give the protected trihydroxycycloheptadiene complex **12**, treatment of which with acid in the presence of methanol (generated in situ) gives the symmetrically trioxygenated diene complex **15**. Decomplexation of these complexes, followed by stereocontrolled diene oxygenation and ring cleavage, provides methodology for the construction of heptitol derivatives. Conversion of complex **15** to ether-substituted dienyl–$Fe(CO)_3$ cationic complexes was studied. These complexes react with nucleophiles to give diene-, dienyl-, or enediyl–$Fe(CO)_2L$ complexes, depending on the nature of the nucleophile and the spectator ligand.

Introduction

Previous studies in our laboratories have led to the development of methods for the stereocontrolled functionalization of cycloheptadienes via nucleophile additions to the derived diene–$Mo(CO)_2Cp$[1] and dienyl–$Fe(CO)_2L$[2] cationic complexes (L = CO, triphenylphosphine, or triphenyl phosphite). This methodology has led to efficient synthetic routes to the (+)-Prelog–Djerassi lactone[3] and subunits of the macrolide antibiotics carbomycin[4] and tylosin.[5] Recent work has also indicated potential approaches to building blocks for FK-506 and the macbecins.[6] The latter studies have revealed that the introduction of one alkyl group and one heteroatom substituent onto the cycloheptadiene ring with complete stereocontrol, as shown for the conversion of **1** to **5** or **6**, is very straightforward, but the introduction of *two* heteroatom substituents is not possible using this chemistry. This is due to the fact that

(1) Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276. See also: Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.
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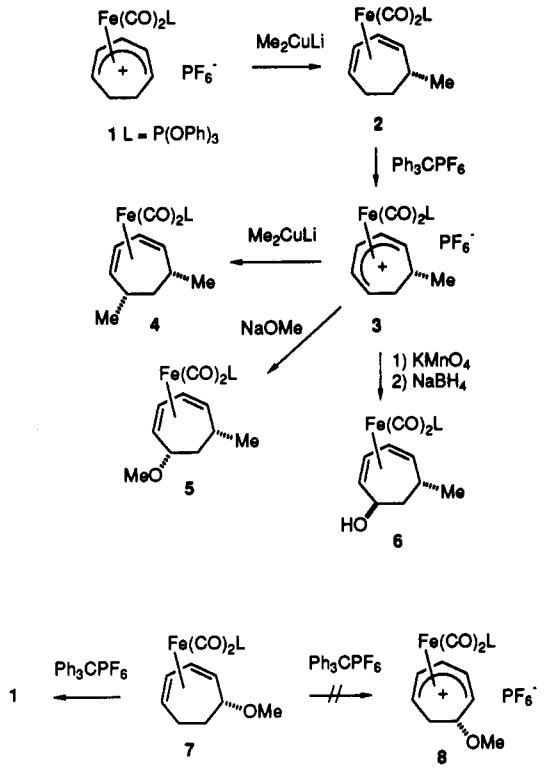
treatment of a complex such as 7 with triphenylmethyl (trityl) hexafluorophosphate, the usual reagent for hydride abstraction, results only in demethoxylation to give 1 and gives none of the substituted complex 8. This is not an unexpected result.

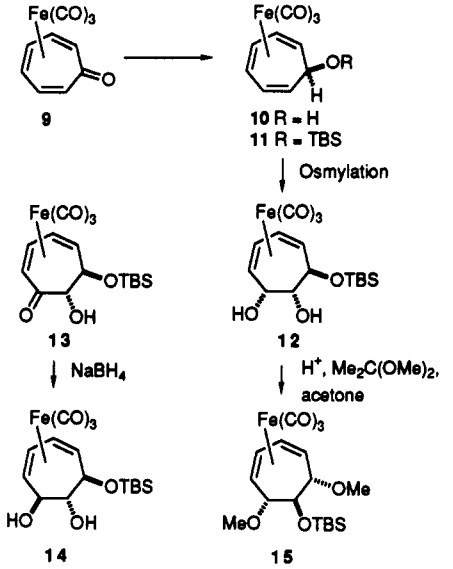


The controlled synthesis of polyhydroxylated heptanes and aminoheptanes (heptitols and aminoheptitols) is a very desirable goal, owing to their potential application as, or in the synthesis of, glycosidase inhibitors[7] and in the synthesis of compounds related to antitumor substances such as swainsonine[8] and castanospermine.[8] Functionalization of a cycloheptane ring system, followed by ring opening, would provide an alternative route to such compounds. It has been previously established that a variety of reactions, such as hydroboration[9] and osmylation,[10] can be performed on an uncomplexed carbon–carbon double bond in the presence of a diene–$Fe(CO)_2L$ moiety. The $Fe(CO)_2L$ group acts as an efficient protecting group for the diene. Combining this capability with its powerful stereochemical directing effect as well as its ability to stabilize carbocations (as in complex 1) would allow the development of powerful methodology for the construction of polyhydroxylated cycloheptenes that can be opened to give heptitol derivatives with defined relative stereochemistry.

Tropone–$Fe(CO)_3$ (9) has been prepared in optically pure form by resolution, and has reasonable configurational stability,[11a] so that any syntheses of heptitols starting from this complex can in principle lead to enantiomerically pure materials, provided racemization does not occur during reactions of 9 and that the products of such reactions are configurationally stable.[11b] Therefore, we decided to examine methods for conversion of racemic 9 to polyhydroxylated derivatives, with special emphasis on developing new approaches to functionalized dienyliron cations related to 8 and assessing the reactivity of these systems.[12]

Results and Discussion

(1) Osmylation Studies Leading to Heptitols. Reduction of tropone–$Fe(CO)_3$ (9) with $NaBH_4$–$CeCl_3$ gave the crystalline alcohol complex 10 as a single diastereomer



in yields of up to 98%, the stereochemical assignment of which was based on our earlier observation[6] that reduction of a ketone α to a diene–$Fe(CO)_2L$ is sterically controlled and occurs by anti addition of hydride. Protection of the alcohol gave 11 quantitatively, osmylation of which, under stoichiometric conditions, gave a single triol derivative (12) in 99% yield. For larger scale preparation of 12 we investigated the catalytic osmylation procedure described by Sharpless and co-workers[13] (cat. OsO_4, *t*-BuOOH, Et_4NOAc, acetone). This gave mixtures of the desired complex 12 and the ketol derivative 13, the ratio of which

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(10) Grée, R. *Synthesis* **1989**, 341. Pearson, A. J.; Chen, Y. S. *J. Org. Chem.* **1986**, *51*, 1939. See also ref 9.

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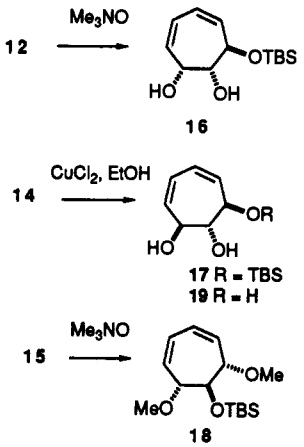
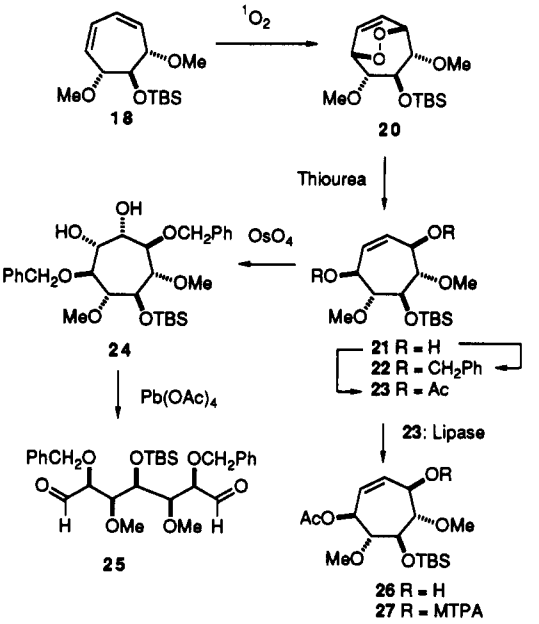
was critically dependent on reaction conditions. An equimolar mixture of 12 and 13 was obtained under standard conditions after a 12-h reaction time, but the use of higher reactant concentration and short reaction time (2–3 h) gave a 9:1 mixture in favor of 12. This reaction is especially noteworthy in that no decomposition of the complex was observed.[14] Also, none of the isomeric ketol was produced, presumably reflecting the more facile in situ oxidation of the pseudoallylic alcohol of 12. Reduction of complex 13 with sodium borohydride gave a single stereoisomer 14, again due to steric control by the metal moiety. In addition to providing access to a different stereoisomeric triol series, the conversion of 13 to 14 provides a convenient method of purification of these compounds, since 12 and 13 were only partially separable by flash chromatography, while 12 and 14 are easily separated.

An interesting conversion of 12 occurred on treatment with catalytic amounts of acid in the presence of 2,2-dimethoxypropane in acetone solution, which led to the formation of a single, symmetrically substituted dimethyl ether 15, the structure of which was readily assigned form its NMR spectrum. A plausible mechanism for this transformation is given elsewhere.[12] Not only does this chemistry allow access to differentially protected *trans,trans*-cycloheptatrienetriols, but it also indicates that alkoxy-substituted cationic dienyl complexes can be prepared, as discussed later. Since 15 is a meso compound it does not, of course, allow access to enantiomerically enriched materials through the use of optically pure complex 9.



In order to utilize this methodology for the construction of differentially protected heptitols, decomplexation followed by selective diene functionalization is necessary. Each of the complexes 12, 14, and 15 was subjected to known decomplexation procedures. Treatment of 12 and 15 with trimethylamine *N*-oxide[15] gave 16 and 18, in 50% and 91% yields, respectively, while treatment of 14 with $CuCl_2$ in ethanol[16] gave 17 in 60% yield. Prolonged treatment of 14 with $CuCl_2$/EtOH led to desilylation and formation of the triol 19. It should be noted that complexes 12 and 15, in which one or more allylic OR groups are anti to the metal, are very acid sensitive, owing to their facile conversion to dienyl–$Fe(CO)_3$ cations, so that the acidic conditions of the $CuCl_2$/EtOH system are not tolerated. On the other hand, the syn arrangement of pseudo allylic OR groups in complex 14 leads to greater acid stability.



Singlet oxygen addition[17] to the symmetrical diene 18 proceeded with complete stereoselectivity to give the endoperoxide 20, which was converted by reduction with thiourea[18] to the diol 21, and this compound was protected as the dibenzyl ether 22, obtained in ca. 62% overall yield from 17, or as the diacetate 23. The relative stereochemistry of these compounds was readily assigned from proton NMR coupling constants, which we have previously shown to be diagnostic for these types of molecule.[5] Attempted direct alkene cleavage of 22 or 23 via ozonolysis or treatment with ruthenium tetraoxide[19] failed to give single characterizable products. Accordingly, 22 was converted to the diol 24, obtained as a single stereoisomer, by catalytic osmylation, and this diol was converted to the acyclic dialdehyde 25 by cleavage with freshly recrystallized lead tetraacetate (78% overall yield from 22).

Hydrolysis of the meso diacetate 23 with lipase enzyme[20] gave enantiomerically pure hydroxy acetate 26. The enantiomeric purity was determined by ^{19}F NMR spectroscopy of the MTPA ester 27, and the absolute stereochemistry was determined using Mosher's method[21] and comparison with closely related compounds previously prepared in our laboratories[3,5] and by Johnson's group.[22] That polyoxygenated molecules such as 23 are suitable substrates for enzyme hydrolysis is of considerable interest, since it allows the construction of heptitol derivatives in optically pure form.

Osmylation of the diene 18 under stoichiometric conditions gave an 84% yield of a single diol 28, the stereochemical assignment of which was based on our own observations of anti stereoselectivity during singlet oxygen addition to these dienes as well as the known anti directing effect of allylic ethers during osmylation of monoalkenes.[23] Proton NMR coupling constants were not conclusive for

(14) Treatment with alkaline hydrogen peroxide is known to cause decomplexation of diene–$Fe(CO)_3$ complexes: Franck-Neumann, M.; Heitz, M. D.; Martina, D. *Tetrahedron Lett.* **1983**, *24*, 1615.
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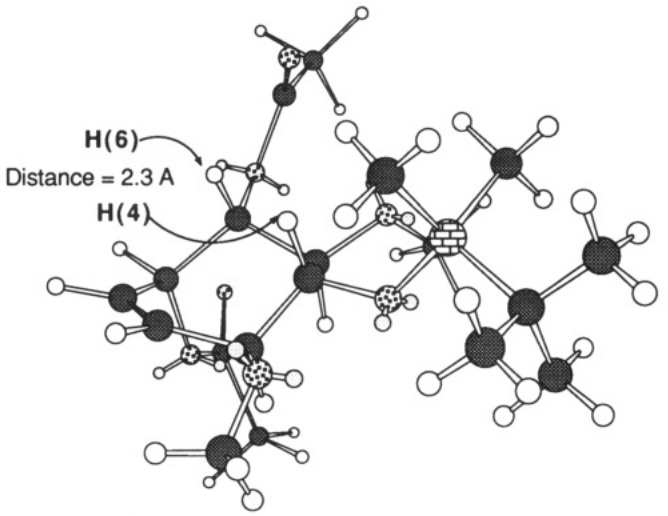
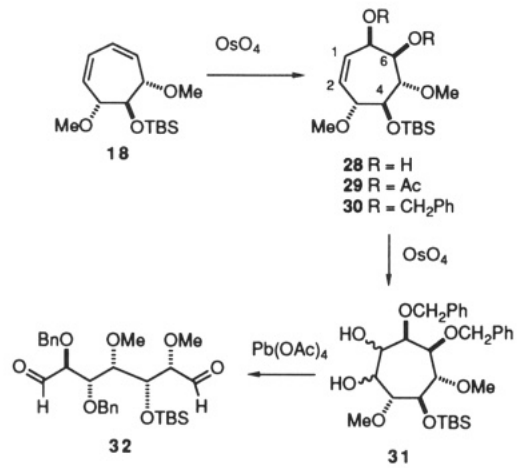
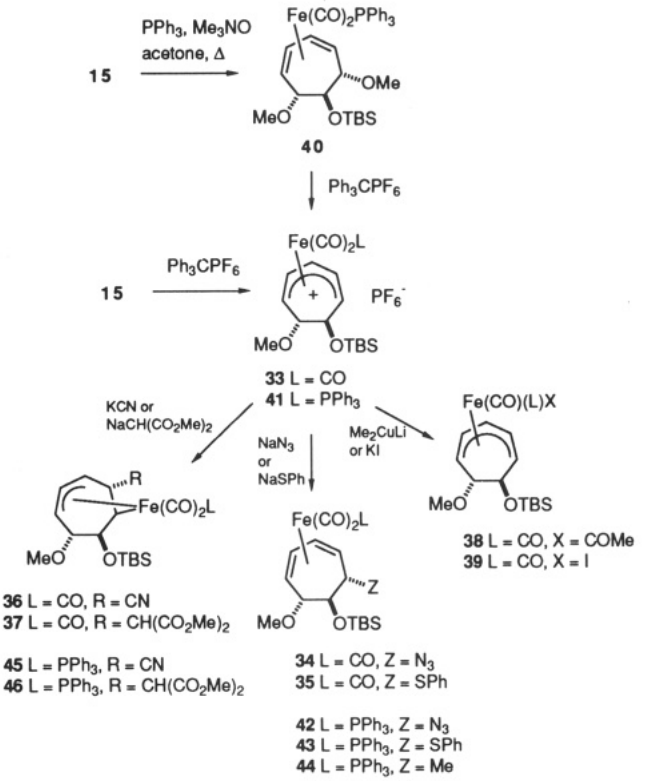


Figure 1. Conformation of cycloheptene derivative **29**, showing proximity of H(4) and H(6) for observed NOE. (Lone pairs are included on O atoms. The drawing is an energy-minimized CHEM 3D diagram for the enantiomer of structure **29**.)

assignment of stereochemistry, owing to their sensitivity to electron-withdrawing substituents (OR and OAc for **29**), generally leading to a smaller value than anticipated for a diaxial coupling (only 3.4 Hz for H-6). Consequently, after establishing the proton connectivity by a 2D COSY NMR spectrum, the stereochemistry of **29** was confirmed by a NOESY experiment, which showed NOE between H-6 and H-4, as well as between 5-OMe and the TBS ether methyl and *tert*-butyl groups, as expected for the conformation shown in Figure 1. Interestingly, treatment of **18** with 1 equiv of *N*-methylmorpholine *N*-oxide in the presence of a catalytic amount of osmium tetraoxide gave the diol **28**, together with small amounts of unreacted **18**. When 2 equiv of oxidant were used, a stereoisomeric mixture of tetrols was obtained.[24] Protection of the diol **28** as its dibenzyl ether **30**, followed by osmylation gave **31** as a 1:1 mixture of stereoisomers, cleavage of which with $Pb(OAc)_4$ afforded the stereochemically homogeneous dialdehyde **32**. These experiments demonstrate that stereodefined heptulose derivatives such as **25** and **32** are readily prepared via organometal-mediated stereocontrolled functionalization of cycloheptatriene derivatives.



(2) Preparation and Reactions of Alkoxy-Substituted Cycloheptadienyl–Fe(CO)$_2$L Complexes. The availability of complex **15** allows access to dienyliron cationic systems with hitherto unexplored substitution patterns. Treatment of **15** with Ph_3CPF_6 in methylene chloride at 0 °C gave the dienyl complex **33** in 96% yield. The reactions of this complex with simple nucleophiles were studied. Thus, reaction with azide and thiophenoxide gave products of C(1) addition **34** and **35**, respectively, the structures of which were readily assigned from their NMR spectra by comparison with complex **15**. The pronounced



(a) NaN_3; (b) NaSPh; (c) KCN; (d) $NaCH(CO_2Me)_2$; (e) Me_2CuLi; (f) KI

regioselectivity during these reactions is accounted for by the greater steric hindrance at the C(5) position, caused by the methoxy group (the nucleophile always adds anti to the metal and therefore would be forced to add syn to MeO). Cyanide gave exclusively **36**, the product of C(2) addition, presumed to be via attack at the sterically more accessible position. (The structural assignments of these C(2) adducts is tentative at this time, since rigorous assignments of proton NMR spectra are not possible for this series of complexes, owing to the uncertainty in the chemical shifts of C*H*OMe vs C*H*OTBS protons. Attempts to resolve this problem via deprotection of the OTBS group were unsuccessful, resulting only in decomposition of the complex.) Neither of these results is surprising in view of the known behavior of the parent cycloheptadienyl–Fe(CO)$_3$ complex.[25] Reaction of **33** with dimethyl sodiomalonate gave **37**, again the product of C(2) attack. This is unusual because the parent complex gives the product of C(1) addition of malonate.[26] It appears that regioselectivity during these reactions is very sensitive to elec-

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tronic effects on the dienyl, and that *inductive* electron withdrawal (by the ether substituents) is sufficient to perturb the dienyl system significantly. We[27] and others[28] have observed related effects on regioselectivity due to an ester substituent directly attached to the pentadienyl moiety, but in those cases there is a direct resonance interaction that removes electron density from the dienyl. As far as we are aware, the inductive effects recorded here are unprecedented.

Reaction of **33** with Me_2CuLi gave **38**, the product of methyl addition to CO ligand, but in modest yield, while reaction with iodide gave **39**, the product of attack at CO followed by migratory deinsertion. Neither of these results are surprising, since iodide is known to exhibit this behavior on reaction with the parent complex,[25] while low yields during the reaction of cycloheptadienyl–$Fe(CO)_3$ have been attributed to competing attack on CO ligands.[2] The latter problem was solved earlier in our laboratory by replacing one CO ligand by triphenylphosphine or triphenyl phosphite, both of which are poorer π-acceptors. This leads to increased electron density at the metal and a moderation of reactivity of the CO ligands. We considered that such a ligand substitution in the present series would give similar changes in reactivity and might also lead to a tempering of the electron-withdrawing effects from the ether substituents.

The desired phosphine complex **40** was prepared in 91% yield by treatment of **15** with 2-equiv of Me_3NO and 1.1 equiv of PPh_3 in refluxing acetone.[29] Methoxy abstraction, using Ph_3CPF_6, proceeded much more rapidly than with the tricarbonyliron complex **15**, requiring only 15 min at −100 to −78 °C to give the dienyl salt **41**. Treatment of **41** with azide and thiophenoxide gave good yields of complexes **42** and **43**, respectively, while reaction with cyanide gave **45**, as expected. While the introduction of the triphenylphosphine led to a significant change in the outcome of dimethyl cuprate addition, leading to the desired C(1) adduct **44** in modest yield (37%), the perturbation was insufficient to affect the regiochemistry of malonate addition, and this gave exclusively the C(2) adduct **46**. Thus, the reactivity of the carbonyl ligands may be altered significantly by appropriate ligand substitution, but this change is insufficient to override the effects of (inductively) electron-withdrawing substituents attached to the dienyl ligand. We have noted the same resistance to ligand substitution effects when the electron-withdrawing group is methoxycarbonyl, which transmits its effect by resonance interaction with the dienyl.[27]

Conclusions

Metal-mediated stereocontrolled functionalization of cycloheptatrienes, coupled with standard organic transformations on the diene products resulting from such manipulations, provides suitable methodology for the construction of stereochemically homogeneous heptitol derivatives. Coupled with enzymatic hydrolysis of symmetrical diacetates, this can provide access to optically pure materials in certain cases. While the full scope of this approach has not been explored, it is of interest to note that the acyclic polyhydroxylated molecules so produced are differentially protected and are stereochemically related to some of the rarer hexoses (e.g., **25** relates to idose and **32** relates to gulose or idose).

Experimental Section

For general procedures and methods of characterization see earlier publications.[2,5]

Tricarbonyl[(1–4-η)-7-*endo*-hydroxycyclohepta-1,3,5-triene]iron (10). To a solution of 11.4 g (46.3 mmol) of tropone complex **9**, prepared according to the literature procedure,[30] in 200 mL of methanol was added to 20.7 g (55.47 mmol) of $CeCl_3{\cdot}7H_2O$. The red solution was stirred for 10 min at rt and cooled to 0 °C, and 2.63 g (69.52 mmol) of $NaBH_4$ was added in small portions (ca. 15 min). The reaction was complete in 30 min. The reaction mixture was poured into 300 mL of saturated brine, and the aqueous solution was extracted with 5 × 200 mL of ether in the usual way to give 11.02 g of yellow solid which was purified by flash chromatography (20% EtOAc–hexanes) to give 10.13 g of pure product as a bright yellow crystalline solid (88% yield). An analytical sample was obtained by recrystallization from EtOAc–hexanes. Mp: 102 °C. IR: 3598, 2053, 1982, 1684, 1210 cm^{-1}. ^1H NMR (200 MHz): δ 5.90 (ddd, J = 9.4, 9.4, 2.0 Hz, 1 H, C_5-H), 5.40 (ddd, J = 7.2, 4.7, 1.2 Hz, 1 H, C_3-H or C_2-H), 5.31–5.22 (m, 1 H, C_2-H or C_3-H), 5.19 (broad d, J = 10.0 Hz, 1 H, C_6-H), 3.73 (broad d, J = 6.4 Hz, 1 H, C_7-H), 3.51 (broad d, J = 7.9 Hz 1 H, C_1-H), 3.0 (t, J = 7.8 Hz, 1 H, C_4-H), 1.57 (d, J = 9 Hz, 1 H, –OH). ^{13}C NMR (75 MHz): δ 200.6, 130.0, 127.7, 94.4, 83.6, 66.8, 63.6, 53.9. HRMS calcd for (M^+ – 3CO): 191.9874. Found: 191.9870.

Tricarbonyl[(1–4-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]cyclohepta-1,3,5-triene]iron (11). To a stirred solution of 9.016 g (36.35 mmol) of **10** in 200 mL of CH_2Cl_2 at 0 °C was added 23.5 mL (276.9 mmol) of pyridine followed by dropwise addition of 35.3 mL (145.4 mmol) of TBDMSOTf. The reaction mixture was stirred at 0 °C for 1 h and at rt for 1 h and poured into 500 mL of satd $NaHCO_3$ solution, and the organic layer was separated and successively washed with 100 mL satd $NaHCO_3$, 2 × 100 mL of water, and 3 × 100 mL of brine. The CH_2Cl_2 solution was then dried over $MgSO_4$, filtered, and solvent evaporated under reduced pressure to give crude product which was then passed through a short column of silica gel with hexanes as eluent to give 12.20 g of pure **11** (92.6% yield) as a yellow crystalline solid. Mp: 59–60 °C (hexanes). R_f: 0.73 (5% EtOAc–hexanes); IR 2055, 1955, 1648, 1062 cm^{-1}. ^1H NMR (200 MHz): δ 5.79 (ddd, J = 9.3, 9.3, 2 Hz, 1 H, C_5-H), 5.39 (ddd, J = 7.3, 4.7, 1.1 Hz, 1 H, C_2-H or C_3-H) 5.26–5.20 (m, 1 H, C_3-H or C_2-H), 5.04 (dt, J = 10.8, 2.3 Hz, 1 H, C_6-H), 3.77–3.75 (m, 1 H, C_7-H), 3.36–3.29 (broad d, J = 8.0 Hz, 1 H, C_1-H), 2.94 (t, J = 8.0 Hz, C_4-H), 0.88 (s, 9 H, ^{t}BuSi), 0.08 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz): δ 210.3, 128.7, 128.0, 94.0, 83.5, 68.1, 63.6, 53.6, 25.7, 18.0, –4.6, –4.9. HRMS calcd for (M^+ – 3CO): 278.0789. Found: 278.0769.

Tricarbonyl[(1–4-η)-5,6-*exo*-dihydroxy-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]cyclohepta-1,3-diene]iron (12). To a stirred solution of 175 mg (0.48 mmol) of triene complex **11** in 1.7 mL of pyridine was added 6.76 mL of 0.0786 M OsO_4 solution in THF (1 g of OsO_4/50 mL of THF). The reaction mixture was stirred at rt for 10 h, after which 10 mL of saturated sodium bisulfite was added. After being stirred for another 10 h, the reaction mixture was poured into 100 mL of EtOAc and filtered through Celite, the celite pad was washed thoroughly with EtOAc, and the aqueous layer was separated from the combined filtrate and washings. The organic layer was subjected to standard workup to give 195 mg of **12** as pale yellow crystals (98% yield). An analytical sample was prepared by recrystallization from CH_2Cl_2–hexanes. Mp: 115–116 °C. R_f: 0.37 (40% EtOAc–hexanes). IR 3601, 3505, 2054, 1970, 1090, 1061 cm^{-1}. ^1H NMR (200 MHz) δ 5.54 (ddd, J = 7.4, 4.8, 1.0 Hz, 1 H, C_2-H or C_3-H) 5.37 (dd, J = 7.7, 4.8 Hz, 1 H, C_3-H or C_2-H), 4.35 (br, 1 H, C_5-H), 4.25 (dd, J = 6.02, 3.7 Hz, 1 H, C_7-H), 3.4 (br, 1 H, C_6-H), 2.69 (dd, J = 7.3, 6.1 Hz, 1 H, C_4-H or C_1-H) 2.55 (dd, J = 7.4, 1.0 Hz, 1 H, C_1-H or C_4-H). 2.34 (br, 1 H, –OH), 1.8 (br, 1 H, OH), 0.90 (s, 9 H, Si^{t}Bu), 0.04 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz): δ 210.2, 90.5, 87.3, 74.9, 72.4, 69.4, 60.5, 55.8, 25.9, 18.3, –4.5, –5.0. HRMS calcd for $C_{14}H_{24}O_4FeSi$ (M^+ – 2CO): 340.0793. Found:

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340.0748. Anal. Calcd for $C_{16}H_{24}O_6FeSi$: C, 48.49, H, 6.10. Found: C, 47.99, H, 5.77.

Catalytic Osmylation of 11. To a solution of 7.0 g (19.32 mmol) of 11 in 25 mL of acetone was added 1.21 g (4.82 mmol) of Et_4NOAc. The mixture was stirred for 5 min at rt, cooled to 0 °C, and 3.1 mL (31 mmol) of *t*-BuOOH (90%) was added, followed by 12.3 mL of 0.0786 M OsO_4 solution (1 g of OSO_4 in 50 mL of THF). The reaction mixture was stirred at 0 °C for 30 min and then allowed to warm to room temperature and stirred for 1 h. Saturated sodium bisulfite solution (25 mL) was then added, the mixture was stirred for 2 h, diluted with 300 mL of EtOAc, and filtered through Celite, and the Celite pad was washed with 50 mL of EtOAc. The combined filtrate and washings were then subjected to standard workup conditions to give 5.67 g (74% yield) of diol 12 and ketol 13 mixture in 9:1 ratio (by ^1H NMR). Data for 13. Mp: 140–142 °C (CH_2Cl_2–hexane). R_f: 0.22 (30% EtOAc–hexanes). IR: 2070, 2013, 1934, 1653 cm^{-1}. ^1H NMR (200 MHz): δ 5.92 (t, *J* = 5.8 Hz, 1 H, C_2-H), 5.66–5.60 (m, 1 H, C_3-H), 4.62 (dd, *J* = 4.5 Hz, 3.1 Hz, 1 H, C_6-H), 3.50 (m, 1 H, C_7-H), 2.94–2.85 (m, 2 H, C_1-H, C_4-H), 2.77 (br doublet, *J* = 3.5 Hz, –OH) 0.92 (s, 9 H, ^{t}BuSi), 0.11, 0.09 (s, 3 H, 3 H, $Si(CH_3)_2$). ^{13}C NMR (75 MHz): δ 209.4, 209.2, 92.8, 90.2, 80.5, 64.3, 54.2, 26.7, 19.2, –3.9, –4.0). HRMS calcd for $C_{14}H_{22}O_4FeSi$ (M^+ – 2CO): 338.0637. Found: 338.0639. Anal. Calcd for $C_{16}H_{22}O_6FeSi$: C, 48.74; H, 5.62. Found: C, 48.55; H, 5.33.

Tricarbonyl[(1–4-η)-5-*endo*-[(*tert*-butyldimethylsilyl)oxy]-5-*endo*,6-*exo*-dihydroxycyclohepta-1,3-diene]iron (14). To an ice-cooled solution of 100 mg ketol 13 in 3 mL of methanol was added 24 mg (0.63 mmol) of $NaBH_4$. After being stirred at 0 °C for 1 h, the reaction mixture was diluted with 100 mL of ether, washed with 2 × 50 mL of brine and 2 × 50 water, dried over $MgSO_4$, and filtered, the solvent was removed under reduced pressure, and the crude product thus obtained was purified by flash chromatography (30% EtOAc–hexanes) to give of 90 mg of trans diol (89.6% yield). R_f: 0.17 (30% EtOAc–hexanes). An analytical sample was prepared by recrystallizing from CH_2Cl_2–hexanes. Mp: 87–88 °C. IR: 3601, 3505, 2054, 1970, 1099 cm^{-1}. ^1H NMR (200 MHz): δ 5.32–5.26 (m, 2 H, C_2-H and C_3-H), 3.56 (dd, *J* = 5.9, 4.1 Hz, 2 H, C_5-H and C_7-H), 3.16 (dd quartet, *J* = 5.9 Hz, 1 H, C_6-H), 3.06–2.90 (m, 2 H, C_4-H, OH), 2.79–2.60 (m, 1 H, C_1-H), 1.98 (d, *J* = 8.6 Hz, 1 H, OH), 0.91 (s, 9 H), 0.13 (s, 3 H), 0.08 (s, 3 H). ^{13}C NMR (75 MHz): δ 210.2, 87.7, 87.6, 78.4, 70.7, 69.6, 61.4, 61.3, 25.9, 18.2, –4.5, –4.8. HRMS calcd for $C_{14}H_{24}O_4FeSi$ (M^+ – 2CO): 340.0793. Found: 340.0795. Anal. Calcd for $C_{16}H_{24}O_6FeSi$: C, 48.49, H, 6.10. Found: C, 48.46; H, 6.18.

Tricarbonyl[(1–4-η)-6-*exo*-[(*tert*-butyldimethylsilyl)oxy]-5,7-*endo*-dimethoxycyclohepta-1,3-diene]iron (15). To a stirred solution of 207 mg (0.52 mmol) of diol 12 in 18 mL of 1:1 acetone–2,2-dimethoxypropane was added 63 mg (0.27 mmol) of camphorsulfonic acid. The reaction mixture was stirred at rt for 15 min and diluted with 100 mL of ether, and the ether solution was subjected to standard workup conditions to give 220 mg (98%) of 15 as a pale yellow solid, which was recrystallized from boiling hexanes. Mp: 125–126 °C. R_f 0.46 (10% EtOAc–hexanes). IR: 3044, 3035, 3032, 2048, 1966, 1173, 1125 cm^{-1}. ^1H NMR (200 MHz): δ 5.35 (dd, *J* = 5.7, 2.7 Hz, 2 H, C_2-H, C_3-H), 3.37 (s, 6 H, C_5-OCH_3, C_7-OCH_3), 3.24 (dd, *J* = 8.7, 1.6 Hz, C_5-H, C_7-H), 2.90–2.78 (dd overlapping t, 3 H, C_5-H, C_9-H, C_6-H). 0.85 (s, 9 H, ^{t}BuSi), 0.01 (s, 6 H $(CH_3)_2Si$). ^{13}C NMR (75 MHz) δ 210.2, 88.7, 85.1, 74.4, 57.6, 54.6, 26.0, 18.3, –4.5. HRMS calcd for $C_{15}H_{28}O_3FeSi$ (M^+ – 3CO): 340.1156. Found: 340.1154.

7β-[(*tert*-Butyldimethylsilyl)oxy]-5α,6α-dihydroxycyclohepta-1,3-diene (16). To an ice-cooled solution of 200 mg (0.51 mmol) of diol complex 12 in 5 mL of anhydrous *N,N*-dimethylacetamide was added 200 mg (2.65 mmol) of Me_3NO. The reaction mixture was stirred at 0 °C for 6 h, diluted with 100 mL of ether, and filtered through Celite, and the Celite pad was washed with 25 mL of ether. The combined ether solution was subjected to standard workup conditions to give 110 mg of crude product which was purified by flash chromatography to give 66 mg of 16 as a colorless oil (52% yield). R_f: 0.35 (30% EtOAc–hexane). ^1H NMR (200 MHz): δ 5.97–5.73 (m, 4 H, C_1-H, C_4-H), 4.40 (m, 1 H, C_5-H), 4.28 (broad s, *J* = 8.8 Hz, C_7-H), 3.65 (ddd, *J* = 8.7, 3.4, 1.8 Hz, 1 H, C_6-H), 2.93 (s, broad, 2 H, O-H), 0.89 (s, 9 H, –Si^{t}Bu), 0.11 (s, 6 H, $Si(CH_3)_2$. HRMS calcd for $C_{13}H_{24}O_3Si$ (M^+): 256.1495. Found: 256.1499.

7β-[(*tert*-Butyldimethylsilyl)oxy]-5β,6α-dihydroxycyclohepta-1,3-diene (17). To an ice-cooled solution of 500 mg (1.26 mmol) of diol 14 in 10 mL of ethanol was added 1.05 g (7.53 mmol) of anhydrous $CuCl_2$ in small portions. The reaction mixture was stirred at 0 °C for 4 h, diluted with 200 mL of ether, and filtered through Celite, and the Celite pad was washed with 50 mL of ether. The combined ether solution was subjected to standard workup, and the crude product thus obtained was purified by flash chromatography (20% EtOAc–hexane) to give 165 mg of diol as a white crystalline solid (51% yield), which was recrystallized from hexanes. Mp: 52–53 °C. R_f: 0.52 (30% EtOAc–hexanes). IR: 3576, 1471, 1464. ^1H NMR (200 MHz): δ 5.72–5.59 (m, 4 C_1-H–C_4-H), C_4-H), 4.33 (m, 2 H, C_5-H, C_7-H), 3.75 (t, *J* = 8.7 Hz, C_6-H), 2.93 (d, *J* = 1.4 Hz, –OH), 2.85 (d, *J* = 2.0 Hz, 1 H, –OH), 0.89 (s, 9 H, Si^{t}Bu), 0.10 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz) δ 134.4, 132.0, 123.2, 122.9, 73.5, 73.2, 72.5, 25.8, 18.2, –4.3, –4.7. HRMS calcd for $C_7H_{15}O_3Si$ (M^+): 256.1495. Found: 256.1498.

6β-[(*tert*-Butyldimethylsilyl)oxy]-5α,7α-dimethoxycyclohepta-1,3-diene (18). To a stirred solution of 1.155 g (2.72 mmol) of 15 in 20 mL of acetone was added 2.35 g (31.3 mmol) of anhydrous Me_3NO. After being stirred at rt for 2 h, the mixture was poured into 200 mL of ether filtered through Celite, worked up in the usual way, and purified by flash chromatography (5% EtOAc–hexanes) to give 706 mg of 17 as a colorless oil (91% yield). R_f: 0.54 (10% EtOAc–hexanes). IR: 3032, 2956, 1521, 1141 cm^{-1}. ^1H NMR (200 MHz): δ 5.96–5.79 (m, 4 H, C_1-H–C_4-H), 3.88 (t, *J* = 7.4 Hz, 1 H, C_6-H), 3.74 (dd, *J* = 7.0, 3.8 Hz, 2 H, C_5-H, C_7-H), 3.34 (s, 6 H, C_5-OMe, C_7-OMe), 0.89 (s, 9 H, ^{t}BuSi), 0.07 (s, 6 H, $(CH_3)_2$-Si). ^{13}C NMR (75 MHz): δ 132.3, 126.7, 82.7, 80.1, 57.6, 26.0, 18.4, –4.6. HRMS calcd for $C_{15}H_{24}O_7Si$ (M^+): 284.1808. Found: 284.1806.

5β-[(*tert*-Butyldimethylsilyl)oxy]-3β,7β-endoperoxy-4α,6α-dimethoxycyclohept-1-ene (20). To a solution of 104 mg (0.39 mmol) of diene 18 in 20 mL of CH_2Cl_2 was added 4 mg (0.007 mmol) of tetraphenylporphin. The deep purple solution was stirred while irradiated with a 100-W tungsten lamp under a steady stream of O_2 bubbled through the solution. After 3 h the solvent was removed under reduced pressure and the crude product was chromatographed (7% EtOAc–hexanes) to give 92 mg (76%) of pure 20 as a pale yellow solid. R_f: 0.3 (10% EtOAc–hexanes). IR: 3070, 2931, 1472 cm^{-1}. ^1H NMR (200 MHz): δ 6.49 (dd, *J* = 5.07, 3.4 Hz, 2 Hz, C_1-H, C_2-H), 4.66 (t, *J* = 3.4 Hz, 2 H, C_3-H, C_7-H), 3.44 (s, 6 *H*, C_4-OMe, C_6-OMe), 3.29 (multiplet, 3 H, C_4-H, C_5-H, C_6-H), 0.90 (s, 9 H, Si^{t}Bu), 0.07 (s, 6 H, $Si(CH_3)_2$). ^{13}C NMR (75 MHz): δ 128.0, 84.7, 75.3, 73.4, 58.4, 25.9, 18.2, –4.5. HRMS calcd for $C_{15}H_{28}O_5Si$: 316.1706. Found: 316.1672.

3β,7β-Dihydroxy-5β-[(*tert*-butyldimethylsilyl)oxy]-4α,6α-dimethoxycyclohept-1-ene (21). To a stirred solution of 92 mg (0.29 mmol) of endoperoxide 20 in 4 mL of MeOH was added 23 mg (0.3 mmol) of thiourea. The solution was stirred at rt for 36 h and filtered through Celite, and the pad was washed with 50 mL of ether. The combined MeOH and ether fractions were concentrated under reduced pressure, and the crude product was subjected to flash chromatography (30% EtOAc–petroleum ether) to give 83 mg of diol as a white crystalline solid, which was recrystallized from EtOAc–hexanes. Mp: 115–116 °C. R_f: 0.27 (30% EtOAc–hexanes). IR: 3566, 3050, 2956, 1472 cm^{-1}. ^1H NMR (200 MHz): δ 5.69 (d, *J* = 1.5 Hz, 2 H, C_1-H, C_2-H), 4.13 (dd, *J* = 7.8, 1.5 Hz, 2 H, C_3-H, C_7-H), 3.66 (t, *J* = 7.8 Hz, 1 H, C_5-H), 3.55 (s, 6 H, C_4-OMe, C_6-OMe), 2.92 (t, *J* = 7.8 Hz, 2 H, C_4-H, C_6-H), 2.83 (broad multiplet, 2 H, –OH), 0.94 (s, 9 H, Si^{t}Bu), 0.14 (s, 6 H, $Si(CH_3)_2$). ^{13}C NMR (75 MHz): δ 130.8, 86.2, 78.6, 69.6, 62.1, 26.3, 18.6, –4.0. Anal. Calcd for $C_{15}H_{30}O_5Si.^1/_2H_2O$: C, 55.10, H, 9.41. Found: C, 55.22, H, 9.08.

5β-[(*tert*-Butyldimethylsilyl)oxy]-3β,7β-bis(benzyloxy)-4α,6α-dimethoxycyclohept-1-ene (22). To a stirred solution of 30 mg (0.094 mmol) of diol 21 in 2 mL of THF was added 7 mg (0.29 mmol) of NaH. To this was added 88 μL (0.75 mmol) of benzyl bromide and 4 mg (0.01 mmol) of $Bu_4N^+I^-$. The reaction mixture was stirred at rt for 12 h, diluted with 20 mL of CH_2Cl_2 and subjected to standard workup conditions and flash chromatography (3% EtOAc–hexanes) to give 43 mg of 22 as a colorless oil (91.6% yield). R_f: 0.77 (10% EtOAc–hexanes). IR: 3013, 1684, 1653, 1521, 1476 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 7.39–7.29 (m, 10 H aromatic H), 5.74 (d, *J* = 2.2 Hz, 2 H, C_1-H, C_2-H), 4.65

(s, 4 H, benzylic-CH_2), 4.13 (dd, J = 7.7, 2.2 Hz, 2 H, C_3-H, C_7-H), 3.77 (t, J = 5.7 Hz, 1 H, C_5-H), 3.51 (s, 6 H, $-OCH_3$), 3.29 (dd, 2 H, J = 7.4, 5.7 Hz, 2 H, C_4-H, C_6-H), 0.90 (s, 9 H, Si^{t}Bu), 0.11 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz): δ 138.7, 131.1, 128.4, 127.6, 121.5, 85.8, 78.5, 75.5, 72.1, 60.3, 26.0, 18.1, -4.4. HRMS calcd for $C_{22}H_{35}O_5Si$ ($M^+ - C_7H_7$): 407.2254. Found: 407.2249.

3β,7β-Diacetoxy-5β-[(*tert*-butyldimethylsilyl)oxy]-4α,6α-dimethoxycycloheptene (23). To a stirred solution of 185 mg of diol **21** in 1 mL of CH_2Cl_2 was added 463 μL (5.6 mmol) of pyridine, 264 μL (2.8 mmol) of Ac_2O, and 4 mg (0.03 mmol) of 4-(*N*,*N*-dimethylamino)pyridine. The mixture was stirred at rt for 24 h, diluted with 50 mL of ether, and subjected to standard workup conditions and chromatography to give 55 mg of diacetate **23** as a coloroless oil (99% yield). R_f: 0.5 (20% EtOAc–hexanes). IR: 2952, 2931, 1736, 1442, 1238 cm^{-1}. ^1H NMR (300 MHz): δ 5.57 (d, J = 2.0 Hz, 2 H, C_1-H, C_2-H), 5.44 (d, J = 7.8 Hz, 2 H, C_3-H, C_7-H), 3.75 (t, J = 5.3 Hz 1 H, C_5-H), 3.39–3.35 (s, overlapping m, 8 H, C_4-OMe, C_6-OMe, C_4-H, C_6-H), 1.99 (s, 6 H, C_3-OAc, C_7-OAc), 0.79 (s, 9 H, Si^{t}Bu), 0.00 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz): δ 170.0, 129.5, 83.6, 76.1, 70.3, 60.2, 25.9, 21.3, 18.0, -4.6. HRMS calcd for $C_{15}H_{25}O_2Si$ ($M^+ - C_4H_9$): 345.1369. Found: 345.1370.

1β,5β-Bis(benzyloxy)-3β-[(*tert*-butyldimethylsilyl)oxy]-6α,7α-dihydroxy-2α,4α-dimethoxycycloheptane (24). To a stirred solution of 21.7 mg (0.043 mmol) of cycloheptene derivative **22** in 1 mL of acetone–water (8:1) was added 29 mg (0.215 mmol) of *N*-methylmorpholine *N*-oxide and 100 μL of 0.078 M OsO_4 solution in THF. The reaction mixture was stirred at rt for 5 h, and 1 mL of saturated sodium metabisulfite solution was added. After being stirred for 1 h, the mixture was filtered through Celite and subjected to standard workup and flash chromatography (30% EtOAc–hexanes) to give 20.2 mg of **24** as a colorless oil (87% yield). R_f: 0.32 (30% EtOAc–hexanes). IR: 3677, 3058, 2361, 1539, 1445, 1271, 1214, 1260 cm^{-1}. ^1H NMR (300 MHz): δ 7.34–7.24 (m, 10 H, aromatic H), 4.83 (d, J = 11.5 Hz, benzylic H), 4.05 (dd, J = 8.7, 2.5 Hz, 2 H, C_2-H, C_7-H), 3.72 (t, J = 6.7 Hz, 1 H, C_3-H) 3.69 (5, J = 6.8 Hz, 2 H, C_1-H, C_5-H), 3.47 (s, 6 H, C_2-OMe, C_4-OMe), 3.31 (t, J = 6.7 Hz, 2 H, C_2-H, C_4-H), 2.81 (d, J = 2.3 Hz, 2 H, -OH), 0.90 (s, 9 H ^{t}BuSi), 0.12 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz): δ 138.3, 128.5, 127.9, 127.9, 85.7, 80.0, 75.4, 74.1, 71.8, 60.3, 26.0, 18.3, -4.3. HRMS calcd for $C_{25}H_{35}O_7Si$ ($M^+ - C_4H_9$): 475.2152. Found: 475.2147.

Cleavage of Diol 24. To an ice-cooled solution of 12.8 mg (0.024 mmol) of diol **24** in 0.5 mL of benzene was added 14.5 mg (0.029 mmol) of freshly recrystallized $Pb(OAc)_4$. The reaction mixture was stirred at 0 °C for 15 min, diluted with 10 mL of EtOAc, and filtered through Celite, and the filtrate was subjected to standard workup to give 12.9 mg of crude dialdehyde **25** which was purified by flash chromatography (10% EtOAc–hexanes). IR: 3020, 3010, 2930, 1729, 1472 cm^{-1}. ^1H NMR (200 MHz) δ 9.15 (d, J = 0.5 Hz, 2 H, CHO), 7.45–7.17 (m, 10 H, aromatic), 4.73 (d, J = 11.8 Hz, 2 H, PhCH), 4.60 (d, J = 11.8 Hz, 2 H, PhCH), 4.30–4.25 (m, 3 H) 3.63 (dd, J = 6.6, 2.4 Hz, 2 H), 3.25 (s, 6 H) 0.86 (s, 9 H, ^{t}BuSi) 0.10 (s, 6 H, $Si(CH_3)_2$. ^{13}C NMR (75 MHz): δ 204.2, 136.9, 128.7, 128.6, 128.3, 83.1, 82.8, 73.2, 70.1, 60.7, 25.9, 17.9, -4.7. HRMS calcd for ($M^+ - C_4H_9$): 441.2097. Found: 441.2084.

Enzymatic Hydrolysis of Diactate 23. To a stirred solution of 63 mg (0.16 mmol) of diacetate **23** in 5 mL of aqueous phosphate buffer (0.2 m, pH 7.5) was added 58 mg of lipase (from *Candida cylindracea*) in one portion. The reaction mixture was stirred at rt for 44 h at which time traces of diol **21** were detected on TLC. The aqueous solution was extracted with 4 × 10 mL of EtOAc. The combined EtOAc extract was then subjected to standard workup conditions to give a mixture of diacetate **23** and monoacetate **26** which were separated by flash chromatography to give 22.2 mg of diacetate **23** and 34 mg of monoacetate **26** as colorless oil (61% yield, 93% based on recovery of **23**). R_f: 0.56 (30% EtOAc–hexane). $[\alpha]^{23}_D$ +2.7 (c 1.155, CH_2Cl_2). IR: 3012, 1522, 1476 cm^{-1}. ^1H NMR (200 MHz): δ 5.66 (dd, J = 10.5, 3.3 Hz, 1 H, C_2-H), 5.57–5.48 (m, 2 H, C_1-H, C_3-H), 4.25 (d, J = 8.8 Hz, 1 H, C_7-H), 3.81 (dd, J = 8.3, 5.1 Hz 1 H, C_6-H), 3.56 (s, 3 H, C_4-OCH_3, or C_6-OCH_3), 3.44 (s, 3 H, C_6-OCH_3, C_4-OCH_3), 3.32 (dd, J = 7.9, 5.1 Hz, 1 H, C_4-H), 3.19, (dd, J = 8.8, 7.2 Hz, C_6-H), 2.86 (d, J = 2.4 Hz, 1 H, -OH), 0.91 (s, 9 H, Si^{t}Bu), 0.13 (s, 3 H, $SiCH_3$), 0.12 (s, 3 H, $SiCH_3$). ^{13}C NMR (75 MHz): δ 170.1, 134.1, 126.1, 86.2, 83.7, 76.3, 70.4, 69.1, 61.6, 60.2, 26.0, 21.3, 18.0, -4.4, -4.45. HRMS calcd for $C_{13}H_{26}O_6Si$ ($M^+ - C_4H_9$) 303.1264. Found: 303.1263.

(3*S*,4*R*,5*S*,6*S*,7*R*)-3-Acetoxy-5-[(*tert*-butyldimethylsilyl)oxy]-4,5-dimethoxy-7-[(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetoxy]cycloheptene (27). To a stirred solution of 33.6 mg of (0.14 mmol) (*R*)-MTPA chloride, 29.0 mg of (0.14 mmol) DCC, and 17.1 mg of DMAP in 1 mL of CH_2Cl_2 was added a solution of 24.5 mg (0.07 mmol) of **26** in one portion. The reaction mixture was stirred at room temperature for 60 h at which time no starting material was detected by TLC. The reaction mixture was then diluted with 50 mL of CH_2Cl_2 and washed successively with 4 × 30 mL of cold 10% HCl, 30 mL of water, 4 × 30 mL of cold aqueous Na_2CO_3, and 30 mL of water. The product **27** obtained after drying and evaporation of the CH_2Cl_2 solution (38.1 mg 97% yield) was sufficiently pure for NMR analysis. ^1H NMR (200 MHz): δ 7.58–7.54 (m, 2 H, aromatic), 7.44–7.38 (m, 3 H, aromatic), 5.72–5.66 (m, 3 H, C_1-H, C_2-H, and C_7-H), 5.47 (dd, J = 5.9, 4.7 Hz, 1 H, C_3-H), 3.48 (dd, J = 8.8, 6.5 Hz, 1 H, C_5-H), 3.56 (unresolved quartet, 3 H, $-OCH_3$), 3.49, (dd, J = 8.8, 6.5 Hz, 1 H, C_6-H), 3.43–3.33 (dd overlaps two singlets, 1 H, C_4-H), 3.41 (s, 3 H, OCH_3), 3.37 (s, 3 H, OCH_3), 2.03 (s, 3 H, OAc), 0.89 (s, 9 H, Si^{t}Bu), 0.11 (s, 3 H, CH_3Si), 0.10 (s, 3 H, CH_3Si). ^{19}F NMR ($CDCl_3/CFCl_3$, 282.3 Mhz): δ -71.8. No other peak was observed.

The racemic alcohol (16.9 mg) obtained from K_2CO_3 partial hydrolysis of **23** was converted to the Mosher ester using the same procedure. The crude product obtained in this case was purified by preparative TLC. ^{19}F NMR (282.3 MHz, $CDCl_3/CFCl_3$): δ -71.8, -71.9. The configuration was assigned by comparing ^1H NMR chemical shifts of the C_6-methoxy group in the carbocyclic ring.

4β-[(*tert*-Butyldimethylsilyl)oxy]-6β,7β-dihydroxy-3α,5α-dimethoxycycloheptene (28). To a stirred solution of 63 mg (0.22 mmol) of cycloheptadiene derivative **17** in 0.7 mL of pyridine was added 2.8 μL of 0.0786 M OsO_4 in THF. The reaction mixture was stirred at rt for 14 h, 2 mL of saturated sodium metabisulfite solution was added, and stirring was continued for 8 h. After diluting with 100 mL of ether and separating the aqueous layer, the ether solution was subjected to standard workup and flash chromatography (50% EtOAc–hexanes) to give 60 mg of **28** as a colorless oil (84% yield). R_f: 0.33 (50% EtOAc–hexanes). IR: 3579, 3476, 1471, 1463 cm^{-1}. ^1H NMR (200 MHz): δ 5.99 (dd, J = 11.6, 5.6 Hz, 1 H, C_1-H), 5.80 (dd, J = 11.6, 5.6 Hz, 1 H, C_2-H), 4.38 (dd, J = 5.6, 1.9 Hz, 1 H, C_7-H), 4.03–3.98 (dd, overlapping m, J = 6.5, 4.0 Hz, 2 H, C_3-H, C_6-H), 3.83 (t, J = 5.8 Hz, 1 H, C_4-H), 3.55 (s, 3 H, C_5-OMe), 3.44 (dd, J = 7.7, 4.3 Hz, 1 H, C_5-H), 3.37 (s, 3 H, C_3-OMe), 0.89 (s, 9 H, ^{t}BuSi), 0.13 (s, 3 H, $SiCH_3$), 0.10 (s, 3 H, $SiCH_3$). ^{13}C NMR (75 MHz): δ 132.8, 129.3, 86.9, 79.2, 73.5, 72.1, 69.8, 60.1, 57.7, 25.8, 19.1, -4.7, -4.8. HRMS calcd for $C_{15}H_{24}O_4$ ($M^+ - H_2O$): 300.1757. Found: 300.1752.

4β-[(*tert*-Butyldimethylsilyl)oxy]-6β,7β-diacetoxy-3α,5α-dimethoxycycloheptene (29). To a stirred solution of 32 mg (0.1 mmol) of diol **28** in 1 mL of CH_2Cl_2 was added 323 μL (4 mmol) of pyridine, 0.86 mL (2 mmol) of Ac_2O, and 3 mg (0.025 mmol) of DMAP. The reaction mixture was stirred at rt for 24 h, diluted with 30 mL of ether, and subjected to standard workup to give the crude product which was passed through a short column (2 in.) of silica gel (10% EtOAc–hexanes) to give 38 mg of diacetate **29** as a colorless oil (94% yield). R_f: 0.22 (10% EtOAc–hexanes). IR: 3154, 2982, 2954, 1793, 1741 cm^{-1}. ^1H NMR (200 MHz): δ 5.80 (dd, J = 10.6, 2.2 Hz, 1 H, C_1-H), 5.54–5.47 (m, 2 H, C_2-H, C_7-H), 5.26 (dd, J = 3.4, 1.4 Hz, 1 H, C_6-H), 3.73 (dd, J = 9.6, 2.0 Hz, 1 H, C_3-H), 3.59 (dd, J = 9.6, 6.8 Hz, 1 H C_4-H), 3.49 (s, 3 H, C_3-OMe or C_5OMe), 3.39 (3 H, C_5-OMe or C_7-OMe), 3.32 (dd, J = 6.8 Hz, 2.1 Hz, 1 H, C_5-H), 2.09 (s, 3 H, C_6-OAc or C_5-OAc), 2.07 (s, 3 H, C_5-OAc or C_6-OAc), 0.90 (9 H, ^{t}BuSi), 0.07 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz): δ 170.0, 133.9, 125.3, 84.8, 78.8, 76.7, 71.6, 69.3, 59.4, 58.5, 26.0, 21.2, 21.1, 18.4, -4.3, -4.8. HRMS calcd for $C_{15}H_{25}O_7Si$ ($M^+ - C_4H_9$): 345.1369. Found: 345.1366.

6β,7β-Bis(benzyloxy)-4β-[(*tert*-butyldimethylsilyl)oxy]-3α,5α-dimethoxycycloheptene (30). To a stirred solution of 43.3 mg (0.14 mmol) of diol **28** in 1.5 mL of THF was added 8 mg (0.33 mmol) of NaH. After 5 min, 4 mg (0.011 mmol) of $Bu_4N^+I^-$ and 164 μL (1.4 mmol) of BnBr were added, and the

reaction mixture was stirred for 15 h. Dilution with 50 mL of ether, followed by standard workup and flash chromatography (5% EtOAc–hexanes) gave 48.7 mg of **30** as a colorless oil (62% yield). R_f: 0.55 (10% EtOAc–hexanes). IR ($CDCl_3$): 3030, 3011, 2930, 1521, 1496, 1473, 1423 cm^{-1}. ^1H NMR (400 MHz): δ 7.38–7.26 (m, 10 H, aromatic), 5.80 (dd, J = 12.3, 1.3 Hz, 1 H), 5.67 (d, J = 12.3 Hz, 1 H), 4.95 (d, J = 12.2 Hz, 1 H, PhCH), 4.63 (d, J = 12.3 Hz, 1 H, PhCH), 4.59 (d, J = 12.1 Hz, 1 H, PhCH), 4.50 (d, J = 12.0 Hz, 1 H, PhCH), 4.18 (br, 1 H), 3.88 (dd, J = 9.9, 2.1 Hz, 1 H), 3.84 (d, J = 3.8 Hz, 1 H), 3.51 (dd, J = 9.8, 7.2 Hz, 1 H), 3.33 (s, 3 H), 3.31 (s, 3 H), 3.30 (m, 1 H), 0.96 (s, 9 H, ^{t}BuSi), 0.13, (s, 3 H, $SiCH_3$), 0.01 (s, 3 H, $SiCH_3$). ^{13}C NMR (75 MHz): δ 138.4, 132.4, 128.4, 128.3, 127.8, 127.6, 127.5, 127.1, 86.2, 79.4, 78.0, 78.0, 76.2, 72.4, 71.4, 59.1, 58.6, 26.1, 18.5, –4.1, –4.7. HRMS calcd for $C_{22}H_{37}O_7Si$ ($M^+ - C_4H_9$): 441.2097. Found: 441.2082.

Preparation of Heptanedial Derivative 32. To a solution of 41.7 mg (0.02 mmol) of cycloheptene derivative **30** in 1 mL of acetone–water (8:1) mixture was added 56 mg (0.9 mmol) of NMO and 200 μL of 0.08 M OsO_4 in THF. The reaction mixture was stirred at rt for 12 h, 1 mL of saturated sodium metabisulfite solution was added, and stirring was continued for 1 h. Dilution with 20 mL of EtOAc, followed by separation of the layers and standard workup, gave 41.6 mg (95% yield) of diol product **31** as a 1:1 mixture of diastereomers (by ^1H NMR), which was used in the next step without further characterization. To an ice-cooled solution of 43 mg (0.08 mmol) of diols **31** in 1 mL of PhH was added 49 mg (0.11 mmol) of $Pb(OAc)_4$. The solution was stirred for 30 min, diluted with 30 mL of ether, and filtered through a Celite pad in the usual way. Standard workup gave 42 mg of crude product which was purified by flash chromatography (20% EtOAc–hexanes) to give 32.4 mg of **32** as a colorless oil (76% yield). IR: 3068, 3036, 3032, 3020, 1729, 1257, 1234, 1217 cm^{-1}. ^1H NMR (200 MHz): δ 9.72 (d, J = 2.1 Hz, 1 H, CHO), 9.62 (s, 1 H, CHO), 7.40–7.31 (m, 10 H, ArH) 4.73 (d, J = 11.2 Hz, 1 H, PhCH), 4.71 (d, J = 11.5 Hz, 1 H, PhCH), 4.66 (d, J = 11.2 Hz, 1 H, PhCH), 4.50 (d, J = 11.5 Hz, 1 H, PhCH), 4.24 (t, J = 5.1 Hz 1 H), 4.11 (dd, J = 5.6, 4.1 Hz, 1 H), 4.01 (dd, J = 4.0, 2.0 Hz, 1 H), 3.72 (d, J = 5.3 Hz, 1 H), 3.46 (t, J = 5.3 Hz, 1 H), 3.32 (s, 3 H, –OMe), 3.21 (s, 3 H, –OMe), 0.89 (s, 9 H, ^{t}BuSi), 0.07 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz): δ 201.5, 199.9, 137.7, 137.1, 128.6, 128.5, 128.2, 128.1, 127.9, 86.5, 84.3, 81.6, 78.9, 74.4, 72.9, 59.5, 58.6, 25.9, 18.2, –4.4, –4.6. HRMS calcd for ($M^+ - C_4H_9$): 473.1995. Found: 473.1957.

Tricarbonyl[(1–5-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]-6-*exo*-methoxycycloheptadienyl]iron Hexafluorophosphate (33). To an ice-cooled solution of 380 mg (0.89 mmol) of **15** in 8 mL of CH_2Cl_2 was added 388 mg (1 mmol) of acid-free triphenylmethyl hexafluorophosphate. The reaction mixture was stirred for 20 min, poured into wet ether, and filtered, and the residue was dried in vacuo to give 462 mg of **33** as a pale yellow powder (96% yield). Mp: 190–200 °C dec. IR: 2118, 2075 cm^{-1}. ^1H NMR (200 MHz): δ 6.99 (t, J = 6.6 Hz, 1 H, C_3-H), 6.01 (dd, J = 9.7, 6.8 Hz, 2 H, C_2-H, C_4-H), 4.62 (dd, J = 4.9, 4.1 Hz, 1 H), 4.33 (dt, J = 9.2, 1.7 Hz, 1 H), 4.05 (t, J = 4.7 Hz, 1 H), 3.36 (m, 1 H), 3.31 (s, 3 H, $-OCH_3$), 0.90 (s, 9 H, Si^{t}Bu), 0.06 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$). ^{13}C NMR (75 MHz): δ 109.4, 106.7, 102.8, 96.1, 92.5, 85.2, 77.3, 62.7, 30.3, 22.9, –0.4. Anal. Calcd for $C_{17}H_{25}O_5F_6FePSi$: C, 37.72; H, 4.42. Found: C, 37.72, H, 4.68.

Tricarbonyl[(1–4-η)-5-*exo*-azido-6-*endo*-[(*tert*-butyldimethylsilyl)oxy]-6-*exo*-methoxycyclohepta-1,3-diene]iron (34). To an ice-cooled solution of 50 mg (0.095 mmol) of dienyl salt **33** in 2 mL of CH_3CN was added 16.5 mg (0.255 mmol) of NaN_3. The reaction mixture was stirred at 0 °C for 30 min and at rt for 30 min., diluted with 30 mL of ether, and the ether solution was subjected to standard work up to give 40 mg of **34** as a pale yellow solid (98% yield). R_f: 0.74 (20% EtOAc–hexanes). IR: 2097, 2054, 1976 cm^{-1}. ^1H NMR (200 MHz) δ 5.39 (dd, J = 4.5, 3.8 Hz, 2 H, C_2-H, C_3-H), 3.57 (dd, J = 9.2, 1.6 Hz, 1 H, C_5-H), 3.37 (s, 3 H, $-OCH_3$), 3.31 (dd, J = 8.7, 1.5 Hz, 1 H, C_7-H), 2.91 (d with fine splitting, J = 7 Hz, 1 H, C_4-H), 2.82–2.72 (t overlaps m, J = 9.0 Hz, 2 H, C_6-H, C_1-H), 0.67 (s, 9 H, Si^{t}Bu), 0.06 (s, 3 H, $SiCH_3$), 0.02 (s, 3 H, $SiCH_3$). ^{13}C NMR (75 MHz): δ 210.4, 90.2, 88.8, 85.7, 74.5, 70.5, 70.4, 58.5, 55.4, 54.7, 26.6, 19.2, –3.3, –4.0. HRMS calcd for $C_{13}H_{16}O_5FeSiN_3$ ($M^+ - C_4H_9$): 378.0208. Found: 378.0201.

Tricarbonyl[(1–4-η)-6-*endo*-[(*tert*-butyldimethylsilyl)oxy]-5-*exo*-methoxy-7-*endo*-(phenylthio)cyclohepta-1,3-diene]iron (35). To a stirred suspension of 2.5 mg (0.104 mmol) of NaH in 2.5 mL of THF was added 10 μL (0.097 mmol) of thiophenol. The mixture was stirred at room temperature for 30 min and cooled to –75 °C, and 30 mg of (0.056 mmol) of dienyl salt **33** was added in one portion. Stirring was continued at –75 °C for 30 min, and the mixture was diluted with 20 mL of ether. Standard workup followed by flash chromatography (10% EtOAc–hexanes) gave 10.5 mg of **35** as a pale yellow oil (68% yield). IR: 3154, 2983, 2955, 2052, 1906, 1471, 1302 cm^{-1}. ^1H NMR (300 MHz): δ 7.31–7.12 (m, 5 H, ArH), 5.21 (dd, J = 7.1, 5.5 Hz, 1 H, C_3-H), 5.01 (dd, J = 7.1, 5.0 Hz, 1 H, C_2-H), 3.50 (dd, J = 10.0, 1.8 Hz, 1 H, C_5-H), 3.28 (dd overlaps s, 4 H, J = 8.5, 1.7 Hz, 1 H, C_7-H, $-OCH_3$), 2.98–2.89 (m, 2 H, C_4-H, C_6-H) 2.84 (d, J = 7.3 Hz, 1 H, C_1-H), 0.80 (s, 9 H, ^{t}BuSi), –0.03 (s, 3 H, $SiCH_3$), –0.09 (s, 3 H, $SiCH_3$). HRMS calcd for $C_{21}H_{30}O2FeSSi$ (M^+ – 2CO): 446.1034. Found: 446.1078.

Tricarbonyl[(3–5-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]-2-*exo*-cyano-6-*exo*-methoxycycloheptenediyl]iron (36). To an ice-cooled solution of 30 mg of (0.056 mmol) of dienyl salt **33** in 2.5 mL of CH_3CN was added 5.5 mg (0.084 mmol) of KCN. After being stirred at 0 °C for 1 h, the mixture was diluted with 30 mL of ether and subjected to standard workup and flash chromatography (15% EtOAc–hexanes) to give 17.9 mg of **36** as a pale yellow oil. R_f: 0.35 (20% EtOAc–hexanes). IR: 2221, 2066, 1989 cm^{-1}. ^1H NMR (200 MHz): δ 4.74 (t, J = 7.7 Hz, 1 H), 4.55–4.38 (m, 2 H), 4.10 (d, J = 1.6 Hz, 1 H), 4.02 (dd, J = 6.8, 2.0 Hz, 1 H), 3.86 (dd, J = 9.7, 6.7 Hz, 1 H), 0.94 (broad d, J = 8.6 Hz, 1 H), 0.87 (s, 9 H, Si^{t}Bu), 0.06 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz) δ 211.9, 210.9, 201.4, 117.0, 98.6, 91.3, 82.0, 73.8, 59.0, 58.7, 32.5, 25.8, 20.4, 18.1, –4.5, –4.8. HRMS calcd for $C_{15}H_{25}O_2FeNSi$ (M^+ – 3CO): 335.1003. Found 335.1105.

Tricarbonyl[(3–5-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]-2-*exo*-(dicarbomethoxymethyl)-6-*exo*-methoxycycloheptenediyl]iron (37). To a stirred solution of 30 mg (0.22 mmol) of dimethyl malonate in 10 mL of THF was added 6 mg (0.25 mmol) of NaH. The solution was stirred at rt for 15 min, and cooled to 0 °C, and 100 mg (0.19 mmol) of dienyl salt **33** was added in one portion. The reaction mixture was stirred at 0 °C until the reaction was complete (ca. 25 min), diluted with 20 mL of water, and extracted with 3 × 10 mL of ether. Standard workup followed by flash chromatography (20% EtOAc–hexane) gave **37** as a pale yellow oil. R_f: 0.46 (20% EtOAc–hexane). IR: 3035, 3025, 3005, 2930, 2058, 1991, 1729 cm^{-1}. ^1H NMR (200 MHz): δ 4.29 (t, J = 7.4 Hz, 1 H), 4.18–4.03 (m, 3 H), 3.73 (s, 3 H), 3.62 (s, 3 H), 3.38–3.32 (m 1 H), 3.26–3.23 (m, 1 H), 3.15 (t, J = 5.1 Hz), 2.99 (s, 3 H), 0.90 (s overlaps m, 9 H, 1 H), 0.10 (s, 3 H), 0.05 (s, 3 H). ^{13}C NMR (75 MHz): δ 212.9, 168.2, 167.1, 97.6, 94.8, 75.0, 74.5, 63.8, 59.5, 57.2, 52.6, 52.1, 42.3, 25.8, 18.1, 15.6, –4.6, –4.8. HRMS calcd for $C_{19}H_{31}O_6FeSi$ (M^+ – 3CO): 440.1317. Found: 440.1325.

Dicarbonyl[(1–5-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]-6-*exo*-methoxycycloheptadienyl]acetyliron (38). A stirred suspension of 22.8 mg (0.12 mmol) of CuI in 0.5 mL of ether was cooled to 0 °C and added to 170 mL (0.24 mmol) of a 1.38 M solution of MeLi. The mixture was stirred at 0 °C for few minutes, cooled to –78 °C, and transferred by a canula to a suspension of 30 mg (0.56 mmol) of the dienyl salt **33** in ether. After the mixture was stirred at –78 °C for 1 h, the temperature was gradually raised to 0 °C, the mixture was quenched with 0.5 mL of water and diluted with 5 mL of ether, and the ether layer was separated and subjected to standard workup followed by preparative TLC to give 16 mg of **38** as pale yellow oil (80% pure by NMR). Further purification was not attempted. IR: 2018, 1968, 1649 cm^{-1}. ^1H NMR (200 MHz): δ 6.13 (t, J = 6.3 Hz, 1 H), 5.01 (dd, J = 8.7, 5.2 Hz, 1 H), 4.81 (dd, J = 9.9, 6.6 Hz, 1 H) 3.98–3.89 (m, 2 H), 3.60–3.50 (m, 1 H) 3.4 (s, 3 H, OCH_3), 2.76–2.71 (m, 1 H), 2.43 (s, 3 H, $COCH_3$) 0.87 (s, 9 H, ^{t}BuSi), –0.01 (s, 3 H, $SiCH_3$), –0.02 (s, 3 H, $SiCH_3$). This compound was not further characterized.

Dicarbonyl[(1–5-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]-6-*exo*-methoxycycloheptadienyl]iodoiron (39). To a solution of 100 mg (0.181 mmol) of dienyl salt **33** in 2 mL of acetone was added 33 mg (0.199 mmol) of KI. The reaction mixture was stirred at rt for 3 h and evaporated to dryness under

reduced pressure, the residue was redissolved in benzene and filtered through neutral alumina, and solvent was removed under reduced pressure to give 67 mg of **39** as a maroon-colored solid (82% yield). R_f: 0.55 (20% EtOAc–hexanes). IR: 3024, 3021, 2046, 2009. ^{1}H NMR (200 MHz): δ 6.75 (t, J = 6.8 Hz, 1 H), 5.63 (t, J = 6.8 Hz, 1 H), 5.53 (t, J = 8.2 Hz, 1 H), 4.04 (t, J = 4.7 Hz, 1 H), 3.79 (m, 1 H,), 3.35 (s, 3 H, $-OCH_3$), 3.14 (broad d, 1 H, J = 8.2 Hz), 2.76 (m, 1 H), 0.87 (s, 9 H, Si^{t}Bu), 0.02 (s, 6 H, $(CH_3)_2Si$). HRMS calcd for $C_{14}H_{25}O_2FeISi$ ($M^+ - 2CO$) 436.0020. Found: 436.0060.

Dicarbonyl[6-*endo*-[(*tert*-butyldimethylsilyl)oxy]-5,7-*exo*-dimethoxycyclohepta-1,3-diene](triphenylphosphine)iron (40). To a stirred solution of 160 mg (0.38 mmol) of tricarbonyl complex **15** in 5 mL of acetone was added 159 mg (0.605 mmol) of PPh_3 followed by 57 mg (0.76 mmol) of anhydrous Me_3NO. The mixture was stirred at rt under a vigorous stream of N_2 for 15 min and then refluxed for 2 h, diluted with 50 mL of ether, and filtered through Celite, and the Celite pad was washed with 20 mL of ether. The solvent was then removed under reduced pressure, and the crude mixture was subjected to flash chromatography (7% EtOAc–hexane) to give 227 mg of crystalline **40** (91% yield). Mp: 163–164 °C (hexanes). R_f: 0.57 (20% EtOAc–hexanes). IR: 3023, 3018, 1981, 1922 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.53–7.29 (m, 15 H), 4.81–4.78 (m, 2 H, C_2H, C_3-H), 3.43 (d, J = 8.6 Hz, 2 H, C_2-H, C_7-H), 3.25 (s, 6 H, 2-OCH_3), 2.80 (t, J = 8.7 Hz, 1 H, C_6-H), 2.36–2.30 (m, 2 H, C_1-H, C_4-H), 0.88 (s, 9 H, Si^{t}Bu), 0.07 (s, 6 H, $(CH_3)_2Si$). ^{13}C NMR (75 MHz): δ 217.6, 217.5, 134.9 (d, J_{CP} = 155 Hz), 133.2 (d, J_{CP} = 34.8 Hz), 130.0, 128.4 (d, J_{CP} = 37.5 Hz), 88.3, 86.0, 74.5, 57.1, 53.1, 26.0, 18.4, –4.5.

Dicarbonyl[(1–5-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]-6-*exo*-methoxycycloheptadienyl](triphenylphosphine)iron Hexafluorophosphate (41). To a stirred solution of 20 mg of complex **40** (0.08 mmol) in 1.5 mL of CH_2Cl_2 at –78 °C was added 20 mg (0.05 mmol) of trityl hexafluorophosphate. The reaction mixture was stirred at –78 °C for 15 min and then poured into 10 mL of hexane. The precipitate formed was separated by centrifugation to give 19 mg of dienyl salt **41** (81% yield). IR: 2052, 2013 cm^{-1}. ^{1}H NMR (200 MHz, CD_3CN): δ 7.76–7.53 (m, 15 H, ArH), 6.91 (t, J = 6.4 Hz 1 H, C_3-H), 5.63–5.62 (m, 1 H, C_2-H or C_4-H), 5.43–5.40 (m, 1 H, C_4-H or C_2-H), 4.50–4.20 (broad m, 1 H), 4.13 (t, J = 5.0 Hz, 1 H), 3.34 (s, 3 H, OCH_3), 3.05–2.99 (broad m, 2 H), 0.88 (s, 9 H, ^{t}BuSi), 0.07 (s, 3 H, $SiCH_3$), –0.54 (s, 3 H, $SiCH_3$).

Dicarbonyl[(1–4-η)-5-*exo*-azido-6-*endo*-[(*tert*-butyldimethylsilyl)oxy]-7-*exo*-methoxycyclohepta-1,3-diene](triphenylphosphine)iron (42). To a stirred solution of 40 mg (0.052 mmol) of dienyl salt **41** in 2.5 mL of CH_3CN at 0 °C was added 5 mg (0.77 mmol) of NaN_3. The reaction mixture was stirred at 0 °C for 1 h and diluted with 20 mL of ether, and the ether solution was subjected to standard workup to give 30.4 mg of crude product (decomposes on TLC, 90% purity by ^{1}H NMR). IR: 2093, 1985, 1927 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.60–7.32 (m, 15 H, ArH) 4.87 (m, 1 H), 4.67 (m, 1 H), 3.67 (broad d, J = 9.2 Hz, 1 H), 3.35 (dd, J = 8.5, 1.4 Hz, 1 H), 3.14 (s, 3 H, $-OCH_3$), 2.72 (t, J = 8.9 Hz, 1 H), 2.31–2.32 (m, 2 H), 0.89 (s, 9 H, ^{t}BuSi), 0.00 (s, 3 H, $SiCH_3$), –0.02 (s, 3 H, $SiCH_3$). This compound was not further characterized.

Dicarbonyl[(1–4-η)-6-*endo*-[(*tert*-butyldimethylsilyl)oxy]-5-*exo*-methoxy-7-*exo*-(phenylthio)cyclohepta-1,3-diene](triphenylphosphine)iron (43). To a suspension of 2.5 mg (0.10 mmol) of NaH in 2.5 mL of dry THF was added 8 μL of PhSH. The mixture was stirred at rt for 10 min and cooled to 0 °C, and 40 mg of dienyl salt **41** was added in one portion. The reaction mixture was stirred at 0 °C for 90 min and diluted with 30 mL of ether, and the ether solution was subjected to standard workup and flash chromatography to give 39 mg of **43** (99% yield). R_f: 0.35 (10% EtOAc–hexanes). IR: 1980, 1922, 1479, 1436 cm^{-1}. ^{1}H NMR (200 MHz) δ 7.65–7.14 (m, 20 H, ArH), 4.57–4.56 (m, 2 H, C_2-H, C_3-H), 3.73 (dt, J = 9.9, 1.5 Hz, 1 H, C_5-H), 3.46 (dt, J = 8.4, 1.1 Hz, 1 H, C_7-H), 3.13 (s, 3 H, $-OCH_3$), 2.94 (dd, J = 9.8, 8.5 Hz, 1 H, C_6-H), 2.66 (m, 1 H, C_1-H), 2.22 (m, 1 H, C_4-H), 0.85 (s, 9 H, ^{t}BuSi), 0.05 (s, 3 H, $-SiCH_3$), –0.01 (s, 3 H, $-SiCH_3$).

Dicarbonyl[(1–4-η)-6-*endo*-[(*tert*-butyldimethylsilyl)oxy]-6-*exo*-methoxy-7-*exo*-methylcyclohepta-1,3-diene](triphenylphosphine)iron (44). To a stirred suspension of 423 mg of CuI (0.22 mmol) in 2 mL of CH_2Cl_2 was added 130 mL (3.0 M) of MeMgCl at 0 °C. The mixture was stirred for 45 min at –10 °C and cooled to –100 °C, and 77 mg (0.1 mmol) of dienyl salt **41** was added in one portion. Stirring was continued at –100 to –80 °C for 30 min, 0.5 mL of water was added, the temperature was raised to rt, and the crude reaction mixture was filtered through a pad of Celite, worked up in the usual way, and chromatographed (basic alumina, 10% EtOAc–hexanes) to give 21 mg of **45** as an oil (37% yield, approximately 90% pure by NMR. This could not be purified further). IR: 1985, 1914 cm^{-1}. ^{1}H NMR (200 MHz): δ 7.49–7.36 (m, 15 H, Ar-H), 4.83–4.77 (m, 1 H, C_3-H), 4.59 (m, 1 H, C_4-H), 3.28–3.23 (m, 1 H, C_5-H), 3.09 (s, 3 H, $-OCH_3$), 2.94 (dd, J = 9.2 Hz, 5.9 Hz, 1 H, C_6-H) 2.49 (t, J = 6.5 Hz, 1 H, C_6-H), 2.43–2.40 m, (1 H, C_7-H), 1.92 (t, J = 7.4 Hz, 1 H, C_1-H), 0.80 (s, 9 H, ^{t}BuSi), –0.08 (s, 3 H, $SiCH_3$), –0.10 (s, 3 H, $SiCH_3$).

Dicarbonyl[(3–5-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]-6-*exo*-methoxy-2-cyanoheptenediyl](triphenylphosphine)iron (45). To an ice-cooled solution of 5 mg (0.077 mmol) of KCN in 2.5 mL of CH_3CN was added 40 mg (0.052 mmol) of dienyl salt **41** in one portion. After being stirred at 0 °C for 1 h, the mixture was diluted with 50 mL of ether and subjected to standard workup and flash chromatography (15% EtOAc–hexanes) to give 29 mg of **45** as an oil (85% yield). R_f: 0.27, 15% EtOAc–hexanes). IR: 2223, 1999, 1941 cm^{-1}. ^{1}H NMR (400 MHz): δ 7.27–7.19 m (15 H, ArH), 4.08 (d, J = 7 Hz, 1 H), 4.03 (dd, J = 6.7, 2.0 Hz, 1 H), 3.99 (dd, J = 9.8, 6.2 Hz, 1 H), 3.92–3.83 (m, 2 H), 3.76 (dt, J = 9.4, 6.7 Hz, 1 H) 3.32 (s, 3 H, $-OCH_3$), 0.95–0.89 (m, 1 H), 0.88 (s, 9 H, ^{t}BuSi), 0.06 (s, 6 H, $(CH_3)_2Si$).

Dicarbonyl[(3–5-η)-7-*endo*-[(*tert*-butyldimethylsilyl)oxy]-2-*exo*-(dicarbomethoxymethyl)-6-*exo*-methoxycycloheptenediyl](triphenylphosphine)iron (46). To a stirred solution of 71 mg (0.054 mmol) of dimethyl malonate in 0.5 mL of THF was added 2.2 mg (0.09 mmol) of NaH. The mixture was stirred at rt for 15 min and cooled to 0 °C, and 30 mg (0.039 mmol) of dienyl salt **41** was added in one portion. The mixture was stirred at 0 °C for 1 h, and the usual workup followed by partial purification by preparative TLC gave 22 mg of product as yellow oil (51%). ^{1}H NMR (200 MHz): δ 7.39–7.28 (m, 15 H, Ar-H), 3.97 (d, J = 1.7 Hz, 1 H), 3.92–3.77 (m, 1 H), 3.71 (s, 3 H), 3.65 (s, 3 H), 3.62–3.42 (m, 2 H), 3.35–3.20 (m, 2 H), 3.04 (s overlaps m, 4 H), 1.27–1.25 (m, 1 H), 0.86 (s, 9 H), 0.00, (s, 3 H), –0.05 (s, 3 H). This compound was not further characterized.

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Supplementary Material Available: ^{1}H and/or ^{13}C NMR spectra for compounds **10, 11, 16–18, 20–30, 32, 34–39,** and **42–46** and ^{19}F NMR spectra for **27** (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.