# Intramolecular Coupling Reactions of Allylic Thioesters with Diene Iron Tricarbonyl Systems

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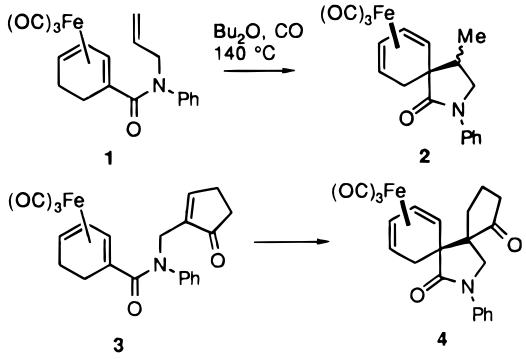
Cyclization reactions are reported for a series of allylic thioester derivatives of cyclohexadiene iron tricarbonyl systems, leading to the formation of spiro thialactone derivatives. The overall reaction process is equivalent to a [6$\pi$ + 2$\pi$] ene reaction in which the pendant alkene, derived from the allyl thioester, is coupled with the diene of the diene−$Fe(CO)_3$ moiety. While simple substrates were found to undergo this cyclization readily, increased substitution on the pendant double bond led to lower, or zero, yields. Methodology for ring opening of the product thialactones, with or without reductive extrusion of sulfur, is described. The X-ray structure of one of the products (**21b**) is reported: $C_{15}H_{14}FeO_4$, $M_r$ = 346.17. Crystal dimensions: 0.20 × 0.20 × 0.10 mm. Yelow, clear prism. Mo Kα radiation ($\lambda$ = 0.71073 Å). Monoclinic space group *P*2(1)/n; $a$ = 11.355(2) Å, $b$ = 6.4943(13) Å, $c$ = 20.060(4) Å, $\beta$ = 103.30(3)°, $V$ = 1439.6 (5) Å$^3$. $Z$ = 4. $\Theta$ = 2.35−27.06°. $T$ = 150 (2) K.

## Introduction

Some years ago we introduced a novel intramolecular coupling between a diene−$Fe(CO)_3$ complex and a pendant alkene that results in the efficient construction of quaternary carbon centers.[1] The reaction is related to intermolecular processes that had previously been discovered by Green.[2] The most efficient reactions were found to occur with allylic amide derivatives, such as **1** and **3**, which produced high yields of **2** and **4**, respectively, under thermal conditions. Allylic esters gave poorer yields and were limited to substrates having low substitution levels on the olefinic double bond.




One of the problems that we have identified with this reaction, as a general method for the construction of quaternary carbon centers, is the relative difficulty of opening a lactam ring to generate nonspirocyclic structures, a process that would be necessary for application of this chemistry to the synthesis of a broad range of natural product structures. In this paper we describe some attempts to effect ring opening of the lactam system, and then we discuss the use of thioesters in the cyclization reaction and their subsequent ring opening and sulfur extrusion.

## Results and Discussion

Amides are usually quite resistant toward reduction to the corresponding alcohols or aldehydes.[3] Lactams are even less susceptible to conversion to alcohols, and reduction in this case usually results in the formation of cyclic amines. It was anticipated that lactam complexes, formed as a result of thermal spirocyclization, having a quaternary center in the position α- to the carbonyl group and, therefore, being sterically crowded, may be highly resistant toward reduction to alcohols or hydrolysis. However, we decided to study the possibility of such conversion on lactams related to **2**. The complex **7** (Scheme 2) was chosen as a model to study the reduction.

*N*-Benzyl-*N*-allylamine was prepared from benzylamine by protection with diphenylphosphinic chloride,[4,5] phase-transfer-catalyzed alkylation, and acidic deprotection (Scheme 1).[6,7] The only modification of the deprotection procedure employed (reported for similar substrates) was the use of $CH_2Cl_2$ as a solvent instead of THF, to avoid formation of chlorobutanol as a side product. This method provides a convenient route to secondary amines with high yields and excellent purity, and it was found superior to direct Pd-catalyzed alkyla-

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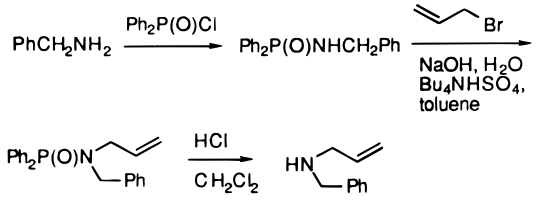
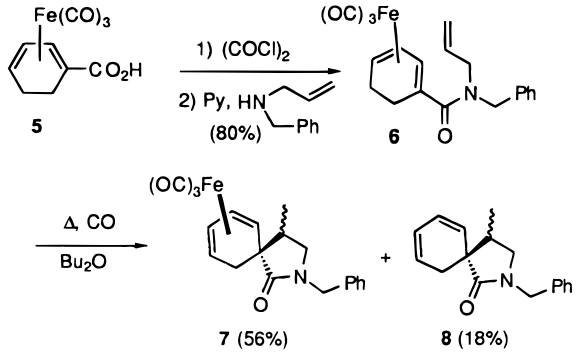
**Scheme 1**




**Scheme 2**

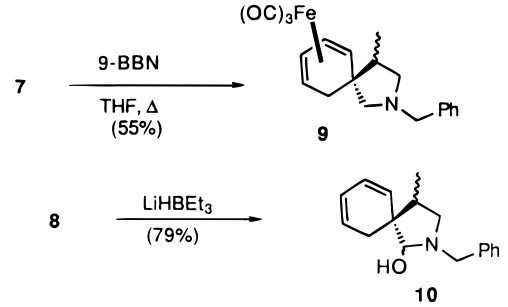



tion of benzylamine with allyl acetate,[8,9] which yields a mixture of products.

Coupling of the resulting amine with tricarbonyl(cyclohexadienoic acid)iron (**5**)[10] yielded amide **6**, which was subjected to standard thermal cyclization conditions (n-$Bu_2O$, 142 °C, CO atmosphere, 7 h) to form the desired bicyclic complex **7** (56%), together with demetalated ligand **8** (18%) (Scheme 2). Both lactams **7** and **8** were produced as a 1:1 mixture of epimers.

Complex **7** proved to be resistant to solvolysis under the usual conditions[11] (MeONa/MeOH, 65 °C, 24 h). 9-BBN and lithium triethylborohydride (Superhydride) are among the reagents that have been reported to reduce dimethylamides to alcohols under mild conditions.[12−14] However, 9-BBN did not affect complex **7** at room temperature, and at elevated temperature (THF, 67 °C, 5 h), lactam **7** was reduced to amine **9**. Treatment with Superhydride caused partial demetalation of complex **7**, presumably via an attack of hydride on the iron tricarbonyl moiety. Lithium triethylborohydride reduction of lactam **8** (THF, rt, 48 h) yielded only cyclic hemiaminal **10** as a mixture of four epimers (79% yield).

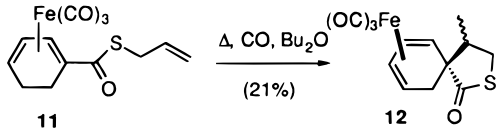
Reduction of complex **7** with in situ generated lithium *N*-pyrrolidinium borohydride[15] (pyrrolidine, $BH_3$−THF, THF, 0 °C−rt, 1 h; n-BuLi, 0 °C, 30 min; and then complex **7**, rt, 24 h) caused demetalation with the formation of cyclic hemiaminal **10**. The same product was formed when reduction with methanol-activated lithium borohydride[16] was attempted (3 equiv of $LiBH_4$, THF, 67 °C; 11 equiv of MeOH added over 4 h). Attempts




to reduce **10** to the corresponding amino alcohol by treatment with $NaBH_4$ in basic ethanolic solution resulted only in the recovery of starting material.

Our investigation of the reduction of lactam complex **7** indicated that this route is troublesome even in the case of a relatively simple substrate. Moreover, removal or modification of the amine nitrogen would be necessary for broad-ranging applications of this chemistry in organic synthesis. In an effort to overcome these difficulties, cyclization of thiol ester complexes and the possibility of desulfurization were studied.

**Cyclizations of Tricarbonyl(cyclohexadienethioate)iron Complexes with Pendant Alkenes.** The simplest derivative in a series of allyl thiol ester complexes, tricarbonyl(allyl 1-4-$\eta^4$-1,3-cyclohexadiene-1-carbothioate)iron (**11**), was prepared from acid complex **5** and allyl thiol. Heating complex **11** in butyl ether (142 °C) in a CO atmosphere for 9 h yielded the desired spirobicyclic complex **12** as a 1:1 mixture of epimers, but in only 21% yield. Longer reaction times resulted in extensive decomposition of the product and no improvement in yield.




According to the proposed mechanism of metal-assisted cyclization,[1] dissociation of a carbon monoxide ligand is the first step of the reaction. It is well-documented that CO dissociation from iron carbonyl complexes can be induced not only thermally, but also photochemically.[17] Therefore, the behavior of thiol ester **11** under photochemical conditions was evaluated. After considerable experimentation, using a variety of light sources and reaction conditions, the optimum protocol for effecting the conversion of **11** to **12** was found to be in a Rayonet photochemical reactor, using a 350 nm light source, and in benzene at 80 °C as solvent, whereupon 95−100% yield of cyclized material was obtained as a 1:1 epimeric mixture (ca. 10% decomplexed spirocycle **13** is formed under these conditions). It may be noted that the optimum photochemical conditions do vary according to the structure of the substrate (see later). Thialactone **13** was obtained from bicyclic complex **12** by treatment with trimethylamine *N*-oxide (benzene, rt, 1.2 h, 92% yield), thus demonstrating the possibility of demetalation in this series.

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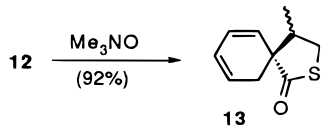



The photothermal cyclization conditions developed in the present work are superior to the thermal method also in the case of amides. For comparison, cyclization of amide complex **6** was performed under the above optimized conditions, and lactam **7** was formed in 83% yield (1:1 mixture of epimers; demetalation under the reaction conditions was not observed; compare with Scheme 2).

Having demonstrated the possibility of cyclization and demetalation, the scope and limitations of the reaction were studied. Thiol esters **14**, **16**, **18**, and **20** were prepared from the corresponding thiols, which were themselves prepared from the corresponding alcohols or chlorides via thiauronium salts.[18] Selected results of cyclizations of these thiol ester complexes are summarized in Table 1.

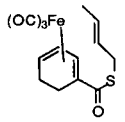
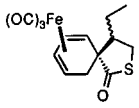
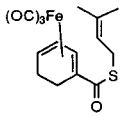
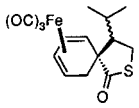
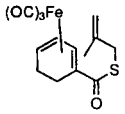
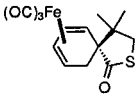
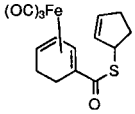
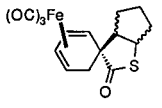
Complex **14**, with a disubstituted C=C bond, was found to be much less reactive than the simpler analogue **11** with a monosubstituted C=C bond. When a Rayonet reactor with a 350 nm light source was used, cyclization product **15** was formed in only 12% yield as a 1.5:1 mixture of epimers (formation of ca. 2% of demetalated cyclization product was also observed). Use of higher temperatures ($Bu_2O$, 142 °C, or toluene, 111 °C) did not favorably affect the reaction. A Q-beam Spotlight was found to be the optimal light source in this particular case, yielding **15** in 45% yield (based on the amount of consumed starting material) as a 1:1 mixture of epimers after irradiation for 22 h in benzene.

The relative unreactivity of more highly substituted allyl thiol esters under the cyclization conditions can be attributed to steric hindrance during coordination of olefin to the metal atom in the putative intermediate 16-electron complex.[1] The lower reactivity of thiol esters in comparison with amides can also be explained in terms of stereoelectronic effects. It is well-known that esters and thiol esters can exist in two conformations, *Z* and *E*. In both conformations, the carbonyl oxygen has an electron pair oriented antiperiplanar to the C−SR bond, and an n−$\sigma$* interaction between a lone pair orbital of the former with the antibonding orbital of the C−SR bond exists (secondary electronic effect).[19] Only in the *Z* form, however, is there the possibility for another secondary electronic effect, since only in that case does the thiol sulfur have an electron pair oriented antiperiplanar to the C−O $\sigma$-bond of the carbonyl group, allowing overlap with the corresponding antibonding orbital (n−$\sigma$* interaction). As a result, thiol esters and esters exist preferentially in a *Z* conformation (for esters, the difference in stability of the two conformations is ca. 3 kcal/mol[20]).

In the case of amides, the nitrogen lone pair cannot be oriented antiperiplanar to the carbonyl C−O bond (because of amide resonance); consequently, there is no stereoelectronic preference, and amides exist preferentially in the less sterically hindered conformation. In the case of *N*-benzyl-*N*-allyl amide complex **6**, the conformation favorable for cyclization would be the major one, so with amides in general the steric bulk of the allyl substituent is less problematic, and cyclization proceeds even with highly substituted compounds. The energy required to force thiol esters to adopt the conformation necessary for cyclization is higher than that for amides, and so the activation energy for the reaction is higher. Since substitution in the alkyl chain imposes additional steric restrictions, functionalized thiol ester complexes are even less susceptible to cyclization. As a result of these effects, tricarbonyliron complex **16**, with a trisubstituted double bond, did not cyclize under any conditions. Substitution at the $\beta$-position of the allyl thiol (complex **18**) was also found to completely block the cyclization.

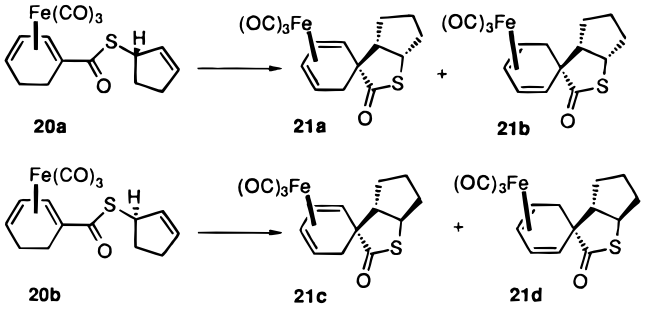
Complex **20** was obtained as an inseparable mixture of diastereomers and therefore was subjected to irradiation as such. Generally, four isomers from this reaction are possible (Scheme 3), but only two compounds were produced in a 4:1 ratio (by integration of $^1$H NMR spectrum).

**Table 1. Photothermal Cyclizations of Allylic Thiol Ester Complexes**[a]

| substrate | light source (rxn time, h) | temp., °C (solvent) | product | yield, % |
|---|---|---|---|---|
|  **14** | A (7.5) | 111 (toluene) |  **15** | 12 |
| | B (4) | 142 (n-$Bu_2O$) | | 10 |
| | B (22) | 80 (benzene) | | 45 |
|  **16** | A (19) | 80 (benzene) |  **17** | 0 |
| | B (5) | 142 (n-$Bu_2O$) | | 0 |
|  **18** | A (4) | 80 (benzene) |  **19** | 0 |
| | B (4.5) | 80 (benzene) | | 0 |
|  **20** | A (5) | 80 (benzene) |  **21** | 11 |
| | A (7) | 111 (toluene) | | 15 |
| | B (22) | 80 (benzene) | | 30 |

[a] A: Rayonet, 350 nm; B: Q-beam Spotlight. Yields are based on the amount of consumed starting material.

**Scheme 3**

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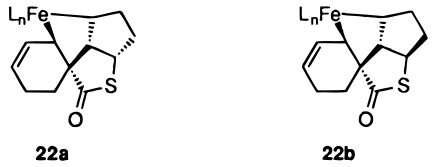



**22a** **22b**

**Figure 1.** Strained and unstrained intermediates for cyclization of **20**.

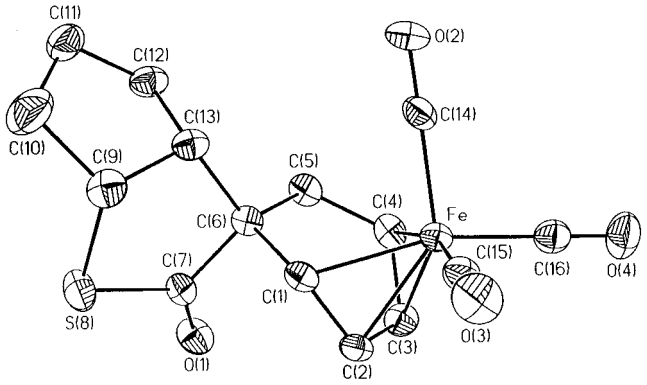
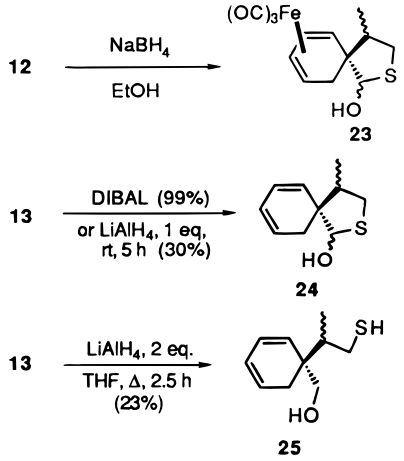



**Figure 2.** Crystal structure of **21b**.

Since the cyclization is a metal-assisted process, complex **20a** should react through intermediate **22a**, while **20b** would cyclize through **22b** (Figure 1). Intermediate **22b** has a thiabicyclooctanone fragment with a more strained *trans*-ring junction, and so formation of **21a** and **21b** is preferred. The major epimer of complex **21** was obtained pure by multiple recrystallization (ether/hexane, 1:5, −78 °C). Crystals were then grown by slow evaporation (24 h) of solvent from an ether solution, and X-ray crystallographic analysis gave the molecular structure shown in Figure 2.

As expected, the thialactone carbonyl is located at the face opposite to the iron tricarbonyl unit, and the thiabicyclooctanone fragment has a *cis*-ring junction. According to the proposed mechanism of epimerization,[1] complex **21b** is produced from its epimer **21a** (actually, the enantiomer of the structure shown), and therefore the minor product was assigned the latter structure**.** These two epimers exist in equilibrium under the reaction conditions (80 °C), and the observed preferential formation of **21b** is probably the result of its greater thermodynamic stability. To estimate the difference in stability of the two epimeric complexes, semiempirical calculations were performed using Spartan molecular modeling software. Structures **21a** and **21b** were subjected to semiempirical minimization using PM3(tm) method, and **21b** was found to be the more stable by 0.6 kcal/mol. Given that a 4:1 ratio of products under the reaction conditions (80 °C) corresponds to ca. 0.9 kcal/mol difference in heats of formation, the results of these calculations are in accordance with the observed ones. However, there are notable differences in bond lengths of the minimized structure and the ones from X-ray analysis. According to X-ray data, the Fe−C1 and Fe−C4 bond lengths in complex **21b** are 0.04−0.05 Å longer than the Fe−C2 and Fe−C3 ones. The bond lengths of the structure minimized using the Spartan semiempirical module have an opposite relation. Therefore, care must be exercised in interpretation of the results of calculations using the present level of molecular modeling.

**Desulfurization of Thialactone Complexes.** A number of Pd-catalyzed methods[21] were examined for the reduction of thialactone **12**. Both heterogeneous and homogeneous reductions with triethylsilane ($Et_3SiH$, 10% Pd/C or $Pd(OAc)_2$ at room temperature or 56 °C), as well as treatment with $Bu_3SnH$ in the presence of $Pd(PPh_3)_4$ and hydrogenolysis with hydrogen on 10% Pd/C, did not affect complex **12**. Triethyl phosphite[22] or $Bu_3SnH$/AIBN[23] also did not react with this compound. Reduction of **12** with $NaBH_4$ yielded cyclic hemithioacetal **23** as a mixture of epimers, while reduction of the free ligand **13** with DIBAL (−78 °C) or $LiAlH_4$ (rt) afforded hemithioacetal **24** (it may be noted that diene−$Fe(CO)_3$ complexes are generally unstable to $LiAlH_4$, so the use of this reagent is limited the free ligand). Treatment of **13** with $LiAlH_4$ at 67 °C yielded alcohol **25**, but in only 23% yield.




Reduction of complex **12** with 9-BBN in THF at reflux afforded, after acidic work up in methanol, thioacetal **26** (quantitative yield at 66% conversion) as a mixture of four isomers. The latter was separated chromatographically into two fractions, each containing two isomers in 3.8:1 and 2.4:1 ratio, respectively (ratio determined from $^1H$ NMR spectra). Ring opening of **26** (used as a mixture of four isomers) with MeI in wet acetone at reflux in the presence of $Na_2CO_3$ for 48 h yielded aldehyde **27** (1.4:1 mixture of epimers; 68% yield at 24% conversion).[24]

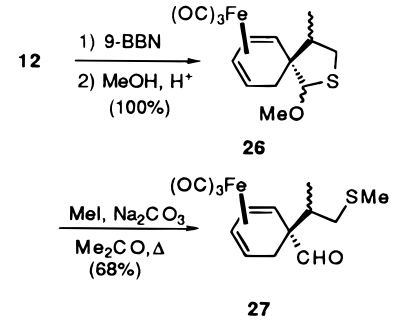



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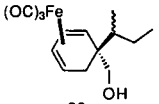
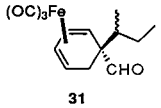
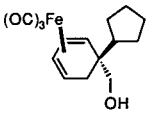
**Table 2. Reductions of Complex 12 with Commercial Raney Ni**

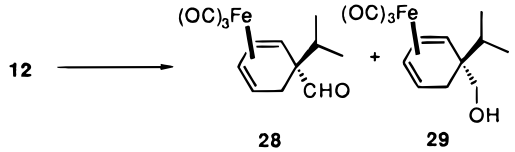
| entry | solvent | Ra-Ni, g/mmol of substrate | rxn time, h | % **28** | % **29** |
|---|---|---|---|---|---|
| 1 | ethanol/$H_2O$ | 2.8 | 24 | 6 | 6 |
| 2 | ethanol | 4 | 0.6 | 0 | 28 |
| 3 | ethanol | 2.3 | 3 | 24 | 8 |
| 4 | acetone | 7.7 | 0.4 | 6 | 16 |
| 5 | ether | 4.8 | 5 | 21 | 8 |

**Table 3. Desulfurizations of Thialactone Complexes**[a]

| Substrate | Ra Ni, g/mmol | Product | Yield (%) | Product | Yield (%) |
|---|---|---|---|---|---|
| **12** | 2.3 | **29** | 12 | **28** | 36 |
| | 4.2 | | 59 | | 2 |
| **15** | 4.6 |  **30** | 12* |  **31** | 29* |
| | 7.8 | | 40 | | 0 |
| **21** | 8.12 |  **32** | 16 | | |

[a] Asterisk denote that yield is based on the amount of consumed starting material (94% conversion).

Reduction of complex **12** with *commercial* Raney Ni (W2 activity) in ethanol solution at room temperature was found to give aldehyde **28** as a major product or alcohol **29** as the only product, depending on the amount of reagent used. However, yields of the reduction were disappointingly low, and change of solvent or the use of lower (0 °C) or higher (80 °C) temperatures did not improve the yields. The use of W2 Raney nickel, prepared by the method described by Augustine,[25] led to a significant improvement for this conversion. For example, complex **12** was reduced to alcohol **30** in 59% yield (accompanied by the formation of 2% of aldehyde **31**). Results of the reductions of thialactones **12**, **15**, and **21** are summarized in Table 3.




**28** **29**

## Conclusions

Overall, the cyclization of allylic thiol ester complexes and subsequent desulfurization of the spirocyclic products is a promising result as far as organic synthesis application is concerned. Summarizing the results of studies on the behavior of thiol ester complexes under thermal or photothermal conditions, one should note that these complexes were found to be generally less reactive toward the metal-assisted cyclization than were the corresponding amide analogues. The range of substrates that undergo the cyclization is limited to simpler, less-substituted derivatives, and the low reactivity can be attributed to a combination of stereoelectronic and steric restrictions. To capitalize on the ability of amide to ameliorate these effects and produce efficient cyclization, as well as the capabilities of sulfur to allow ring opening of the product, trivalent acylsulfonium derivatives, related to complexes such as **6**, would be useful candidates for future study. This effort will form the basis for the next generation of studies from our laboratory on this reaction.

## Experimental Section

General experimental and spectroscopic methods are as described elsewhere.[26]

**General Procedure for the Preparation of Allylic Esters, Thiol Esters, and Amides.** The appropriate carboxylic acid was dissolved in freshly distilled $CH_2Cl_2$ in a single neck round-bottom flask under argon. Two equivalents of oxalyl chloride were added via a syringe at room temperature. The reaction mixture was stirred at room temperature for 3 h under argon. The solvent was then evaporated in a vacuum. The resulting viscous oil was kept under high vacuum (0.5 mmHg) for 10 min and then dissolved in freshly distilled benzene. Pyridine (2 equiv) was added via a syringe, followed by 2 equiv of the appropriate thiol or amine. The reaction mixture was stirred under argon for 16−24 h (reaction can be monitored by TLC). The product mixture was diluted with diethyl ether, washed with 2 N HCl and water, dried over $MgSO_4$, and concentrated in a vacuum. Flash chromatography on silica gel or preparative TLC separation (EtOAc/hexane, 3:7) afforded the desired racemic allyl ester, thiol ester, or amide, usually as a yellow viscous oil. Deviations from this procedure are noted in the experimental data for the specific compound.

**General Procedure for the Photothermally Induced Cyclization.** The appropriate ester, thiol ester, or amide was dissolved in freshly distilled benzene in a quartz tube equipped with a reflux condenser under argon. The solution was purged with CO for 1 min. The reaction mixture was irradiated in a Rayonet reactor with 350 nm light source at 80 °C with magnetic stirring for 2.5 h (unless otherwise noted). The product mixture was diluted with ether, filtered through Celite, and concentrated. Flash chromatography or preparative TLC separation ($CH_2Cl_2$/hexane, 1:1, unless otherwise noted) yielded the desired product. Deviations from this procedure are noted in the experimental data for the specific compound.

**General Procedure for the Thermally Induced Cyclization.** The appropriate ester, thiol ester, or amide was dissolved in freshly distilled *n*-butyl ether under argon. The solution was purged with CO for 1 min and then refluxed under a balloon of CO for 6−8 h. The product mixture was diluted with ether, filtered through Celite, and concentrated. Flash chromatography or preparative TLC separation ($CH_2Cl_2$/hexane, 1:1, unless otherwise noted) yielded the desired product. Deviations from this procedure are noted in the experimental data for the specific compound.

**Tricarbonyl[*N*-allyl,*N*-Benzyl(1−4-$\eta^4$-cyclohexa-1,3-diene)carboxamide]iron (6).** Acid **5** (241 mg) was treated with oxalyl chloride (0.16 mL), pyridine (0.15 mL), and *N*-benzyl-*N*-allylamine (0.268 g) according to the general procedure. A 283 mg amount of complex **6** was isolated by chromatography (80% yield). IR ($cm^{-1}$, $CHCl_3$): 2992, 2050, 1986, 1613. $^1H$ NMR ($\delta$, ppm, $CDCl_3$): 7.4−7.2 (m, 5H), 6.17 (d, 1H, $J$ = 4.4 Hz), 5.8 (ddt, 1H, $J$ = 11.4, 10.8, 6 Hz), 5.29 (dd, 1H, $J$ = 6.5, 4.4 Hz), 5.21−5.15 (m, 2H), 4.47 (d, 1H, $J$ = 5.4 Hz), 4.33 (d, 1H, $J$ = 5.4 Hz), 4.0−3.6 (m, 2H), 3.45−3.41 (m, 1H), 1.95−1.40 (m, 4H). $^{13}C$ NMR ($\delta$, ppm, $CDCl_3$): 173.5, 137.0, 136.9, 133.0, 128.2, 127.4, 118.3, 85.7, 85.3, 70.7, 64.3,

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49.3, 49.0, 26.4, 24.2. HRMS for $M^+ - CO$ ($C_{19}H_{19}FeNO_3$): calcd: 365.0714; found: 365.0722.

**Tricarbonyl(6−9-$\eta^4$-1-oxo-2-benzyl-4-methyl-2-azaspiro-[4.5]deca-6,8-diene)iron (7). A. Thermal Cyclization Method.** Amide **6** (37 mg) was dissolved in freshly distilled *n*-butyl ether (5 mL) under Ar. The solution was purged with CO for 1 min and then refluxed under a balloon of CO for 7 h. The product mixture was diluted with ether, filtered through Celite, and concentrated. Preparative TLC separation (EtOAc/hexane, 3:7) yielded complex **7** (15 mg, 54% corrected yield, 1:1 mixture of epimers), lactam **8** (3 mg, 19%), and starting complex **6** (6 mg). **B. Photothermal Cyclization Method.** Amide **6** (42 mg) was irradiated according to the procedure described above to yield, after chromatographic separation (EtOAc/hexane, 3:7), 35 mg of complex **7** (83%) as a yellow viscous oil (1:1 mixture of epimers). IR ($cm^{-1}$, $CHCl_3$): 2053, 1984, 1689. $^1H$ NMR ($\delta$, ppm, $CDCl_3$), first epimer: 7.39−7.16 (m, 5H), 5.54 (ddd, 1H, $J$ = 6.6, 4, 1.4 Hz), 5.35 (ddd, 1H, $J$ = 6.6, 4, 1.6), 4.4 (s, 2H), 3.54 (br dd, 1H, $J$ = 10, 6.4 Hz), 3.39 (dddd, $J$ = 6.6, 3, 3, 1.4 Hz), 2.87 (dd, 1H, $J$ = 6.6, 1.6 Hz), 2.7 (dd, 1H, $J$ = 10, 0.8 Hz), 2.2−2.18 (m, 1H), 1.96 (apparent d, 2H, $J$ = 3 Hz), 0.89 (d, 3H, $J$ = 7 Hz); second epimer: 7.38−7.16 (m, 5H), 5.59−5.46 (m, 2H), 4.38 (s, 2H), 3.25−3.17 (m, 2H), 2.76 (dd, 1H, $J$ = 10, 4 Hz), 2.73 (dd, 1H, $J$ = 6.4, 1.4 Hz), 2.05−1.97 (m, 1H), 1.53 (apparent d, 2H, $J$ = 6.4 Hz), 1.09 (d, 3H, $J$ = 7 Hz). $^{13}C$ NMR ($\delta$, ppm, $CDCl_3$, mixture of epimers): 211.9, 211.7, 136.6, 129.3, 128.7, 128.1, 127.6, 91.9, 89.7, 88.4, 87.0, 84.1, 82.3, 64.0, 63.5, 61.6, 60.0, 51.5, 50.5, 47.2, 40.0, 39.5, 37.3, 32.0, 27.0, 21.4, 20.3, 15.8, 14.5. HRMS (for $M^+ - CO$, $C_{19}H_{19}FeNO_3$): calcd: 365.0714; found: 365.0710.

**6−9-$\eta^4$-1-Oxo-2-benzyl-4-methyl-2-azaspiro[4.5]deca-6,8-diene (8).** Complex **7** (36 mg) was dissolved in dry benzene (5 mL) under Ar. $Me_3NO$ (237 mg, 35 equiv) was added. The reactiom mixture was stirred at room temperature under Ar for 4 h, and then diluted with ether and filtered through Celite. The solution was washed with water, dried over $MgSO_4$, and concentrated. Preparative TLC purification (EtOAc/hexane, 3:7, multiple development) afforded lactam **8** (16 mg, 70% yield). IR ($cm^{-1}$, $CHCl_3$): 2993, 2969, 1686. $^1H$ NMR ($\delta$, ppm, $CDCl_3$, two epimers): 7.33−7.20 (m, 5H), 6.15−6.05 (m, 1H), 5.9−5.71 (m, 2H), 5.57 and 5.59 (2 × d, 1H, $J$ = 9.9 Hz), 4.51 (AB, 1H, $\nu_A$ = 4.39, $\nu_B$ = 4.62 ppm, $J_{AB}$ = 14.7 Hz), 4.44 (AB, 1H, $\nu_A$ = 4.36, $\nu_B$ = 4.52 ppm, $J_{AB}$ = 14.7 Hz), 3.16 and 2.78 (2 apparent dd, 1H, $J$ = 10, 7.5 Hz), 3.04 and 2.64 (2 apparent d, 1H, $J$ = 14 Hz), 2.33 and 2.27 (2 d, 1H, $J$ = 6 Hz), 2.18−2.13 (m, 1H), 2.12 (dd, 1H, $J_{vic}$= 14 Hz, $J_{gem}$= 6 Hz), 1.00, 0.98 (2 d, 3H, $J$ = 4.4 Hz). $^{13}C$ NMR ($\delta$, ppm, $CDCl_3$, mixture of epimers): 178.8, 178.1, 136.7, 128.7, 128.2, 127.6, 127.2, 126.6, 125.4, 125.3, 124.3, 123.4, 123.1, 122.8, 50.4, 49.9, 48.4, 48.3, 47.0, 46.8, 39.8, 39.4, 31.4, 25.3, 14.4, 13.7. HRMS for $M^+$ ($C_{17}H_{19}NO$): calcd: 253.1466; found: 253.1464.

**Tricarbonyl(6−9-$\eta^4$-2-benzyl-4-methyl-2-azaspiro[4.5]-deca-6,8-diene)iron (9).** Lactam **7** (12 mg) was dissolved in 0.5 mL of dry THF under Ar. A solution of 19 mg of 9-BBN (5 equiv) in 1.5 mL of dry THF was added. The reaction mixture was refluxed for 5 h and then cooled to room temperature and quenched by addition of 0.1 mL of methanol. THF and excess of methanol were evaporated in a vacuum. The crude product mixture was dissolved in dry ether, and ethanolamine (10 $\mu$L, 5 equiv) was added. The precipitate was filtered off and washed with ether, the filtrate was concentrated in a vacuum, and the products were separated by preparative TLC ($CH_2Cl_2$). Amine **9** (5 mg) was obtained as a 1:1 mixture of epimers (55%). IR ($cm^{-1}$, $CHCl_3$): 2943, 2044, 1980. $^1H$ NMR ($\delta$, ppm, $CDCl_3$, for two epimers): 7.3−1.8 (m, 5H), 5.3−5.24 (m, 2H), 3.8−3.3 (m, 2H), 3.2−2.9 (m, 2H), 2.3−1.3 (m, 5H), 1.05 and 0.89 (2 d, 3H, $J$ = 7 Hz). HRMS for $M^+ - 2CO$ ($C_{18}H_{21}FeNO_2$): calcd: 323.0972; found: 323.0957.

**2-Benzyl-4-methyl-2-azaspiro[4.5]deca-6,8-dien-1-ol (10).** Lactam **8** (10 mg) was dissolved in THF. Superhydride (2.2 equiv, 79 $\mu$L of 1 M solution in THF) was added. The reaction mixture was stirred at room temperature for 48 h and then cooled to 0 °C. Water (10 $\mu$L) and 3 N HCl (30 $\mu$L) were added under Ar (to avoid oxidation by air). THF and $Et_3B$ were removed under reduced pressure, and the crude reaction mixture was diluted with 1 N HCl solution and then extracted with ether. The water layer was basified with NaOH solution and extracted with ether, and the extracts were dried over $MgSO_4$ and concentrated to yield 8 mg of **10** (79% yield) as a mixture of four epimers. IR ($cm^{-1}$, $CHCl_3$): 3693, 2943, 1611. $^1H$ NMR ($\delta$, ppm, $CDCl_3$): 7.37−7.17 (m, 5H), 6.06−6.0 (m, 1H), 5.8−5.65 (m, 2H), 5.43−5.38 (m, 1H), 4.66−4.37 (m, 2H), 3.32−3.13 (m, 2H), 2.86−2.67 (m, 1H), 1.0, 0.97, 0.96, 0.95 (4 d, 3H, $J$ = 7 Hz). HRMS for $M^+$ ($C_{17}H_{21}NO$): calcd: 255.1623; found: 255.1635.

**Tricarbonyl(1−4-$\eta^4$-allyl-1,3-cyclohexadiene-1-carbothioate)iron (11).** Acid **5** (200 mg) was treated with oxalyl chloride (0.13 mL), pyridine (0.122 mL), and allylthiol (0.15 mL) according to the general procedure. Complex **11** (145 mg) was isolated after chromatographic purification (70% corrected yield). IR ($CHCl_3$ solution, $cm^{-1}$): 2062, 1998, 1645. $^1H$ NMR ($CDCl_3$, $\delta$, ppm): 6.07 (d, 1H, $J$ = 4.6 Hz), 5.83 (ddt, 1H, $J$ =17, 10, 7 Hz), 5.37 (dd, 1H, $J$ = 5.1, 4.6 Hz), 5.26 (dd, 1H, $J$ = 17, 1 Hz), 5.11 (d, 1H, $J$ = 10 Hz), 3.57 (ddd, 2H, $J$ = 7, 1, 1 Hz), 3.43−3.38 (m, 1H), 2.28−1.5 (m, 4H). $^{13}C$ NMR ($CDCl_3$, $\delta$, ppm): 209.9, 195.9, 133.3, 117.8, 86.7, 85.2, 73.2, 62.8, 31.8, 25.6, 23.2. HRMS for $M^+$ ($C_{13}H_{12}FeO_4S$): calcd: 319.9806; found: 319.9819.

**Tricarbonyl[1−4-$\eta^4$-(2-butenyl)-1,3-cyclohexadiene-1-carbothioate)iron (14).** Acid **5** (500 mg) was treated with oxalyl chloride (0.33 mL), pyridine (0.31 mL), and 2-butene-1-thiol (0.377 mL) according to the general procedure. Complex **14** (324 mg) was isolated after chromatographic purification (204 mg of starting acid recovered; 87% yield based on consumed starting material). IR ($CHCl_3$ solution, $cm^{-1}$): 2940, 2058, 1999, 1646. $^1H$ NMR ($CDCl_3$, $\delta$, ppm): 6.06 (d, 1H, $J$ = 4.4 Hz,), 5.7 (ddq, 1H, $J$ = 15, 6.3, 1 Hz), 5.52−5.4 (m, 1H), 5.36 (ddd, 1H, $J$ = 6.4, 4.4, 1 Hz), 3.52 (ddd, 2H, $J$ = 7, 1, 1 Hz), 3.42−3.35 (m, 1H), 1.67 (ddd, 3H, $J$ = 6.3, 2.5, 1 Hz), 2.29−1.47 (m, 4H). $^{13}C$ NMR ($CDCl_3$, $\delta$, ppm): 210.0, 196.2, 129.2, 125.8, 86.6, 85.1, 73.2, 62.7, 31.2, 25.6, 23.2, 17.7. HRMS for $M^+ - CO$ ($C_{13}H_{14}FeO_3S$): calcd: 306.0013 found: 306.0016.

**Tricarbonyl[1−4-$\eta^4$-(3-methyl-2-butenyl)-1,3-cyclohexadiene-1-carbothioate]iron (16).** Acid **5** (136 mg) was treated with oxalyl chloride (0.09 mL), pyridine (0.08 mL), and 3-methyl-2-butene-1-thiol (0.116 mL) according to the general procedure. Complex **16** (60 mg) was isolated after chromatography (75 mg of the starting acid recovered; 60% yield based on consumed starting material). IR ($CHCl_3$ solution, $cm^{-1}$): 2931, 2060, 1996, 1638. $^1H$ NMR ($CDCl_3$, $\delta$, ppm): 6.06 (d, 1H, $J$ = 5 Hz), 5.36 (dd, 1H, $J$ = 5, 5 Hz), 5.23 (t, 1H, $J$ = 7.7 Hz), 3.29 (d, 2H, $J$ = 7.7 Hz), 3.4−3.36 (m, 1H), 1.72 (s, 3H), 1.7 (s, 3H), 2.23−1.65 (m, 4H). HRMS for $M^+ - 2CO$ ($C_{13}H_{16}FeO_2S$): calcd: 292.0220; found: 292.0233.

**Tricarbonyl[1−4-$\eta^4$-(2-methallyl)-1,3-cyclohexadiene-1-carbothioate]iron (18).** Acid **5** (113 mg) was treated with oxalyl chloride (75$\mu$L), pyridine (69 $\mu$L), and 2-methallylthiol (82 $\mu$L) according to the general procedure. Complex **18** (57 mg) was isolated after chromatographic purification (52% corrected yield; 26 mg of starting acid recovered). IR ($CHCl_3$ solution; $cm^{-1}$): 2062, 1998, 1645. $^1H$ NMR ($CDCl_3$; $\delta$, ppm): 6.08 (d, 1H, $J$ = 5 Hz), 5.36 (t, 1H, $J$ = 5 Hz), 4.97 (m, 1H), 4.84 (m, 1H), 3.62 and 3.56 (AB, 2H, $J_{AB}$=13.5 Hz), 3.43−3.36 (m, 1H), 1.78 (dd, 3H, $J$ = 4.5, 0.85 Hz), 2.35−1.47 (m, 4H). $^{13}C$ NMR ($CDCl_3$; $\delta$, ppm): 210.0, 196.0, 141.1, 113.9, 86.8, 85.2, 73.0, 62.8, 35.7, 25.6, 23.2, 21.2. HRMS for $M^+$ ($C_{14}H_{14}FeO_4S$): calcd: 333.9962; found: 333.9964.

**Tricarbonyl[1−4-$\eta^4$-(2-cyclopentenyl)-1,3-cyclohexadiene-1-carbothioate]iron (20).** 2-Cyclopenten-1-thiol was prepared as follows: Cyclopentadiene (23.2 g) was distilled from dicyclopentadiene into a three-necked round-bottom flask (equipped with a condenser and a drying tube) cooled to −78 °C. HCl gas (12.8 g, 1 equiv) was admitted at such a rate that the temperature remained at −40 to −20 °C. The product chlorocyclopentene (18 mL, cooled to −45 °C, $D^{-45}$: 1.120) was added to a warm solution (90 °C) of thiourea (16.72 g) in water (10 mL, deoxygenated) in 0.5−1 mL aliquots. The reaction

mixture was refluxed for 1 h and then cooled to room temperature, and 20 mL of 10 N NaOH solution (deoxygenated) was added. After stirring for 5 min at room temperature, the mixture was distilled to produce a biphasic mixture with water. The water layer was removed, and the organic fraction was washed with water, dried over $MgSO_4$, and filtered. The thiol (10.283 g, 51% yield) was obtained as a colorless liquid. (This compound slowly polymerizes and should be purified prior to use by distillation.) Bp 127 °C. $^1$H NMR ($\delta$, ppm, $CDCl_3$): 5.8−5.75 (m, 2H, H2, H3), 3.96−3.89 (m, 1H, H1), 2.6−2.29 (m, 3H), 1.94−1.72 (m, 1H), 1.66 (d, 1H, SH). $^{13}$C NMR ($\delta$, ppm, $CDCl_3$): 134.8, 131.36, 43.81, 35.27, 31.29. Acid **5** (509 mg) was treated with oxalyl chloride (0.34 mL), pyridine (0.32 mL), and 2-cyclopenten-1-thiol (396 mg) according to the general procedure. Complex **20** (362 mg) was obtained after chromatography as a 1:1 mixture of diastereomers (236 mg of the starting acid recovered; 92% yield based on consumed starting material). IR ($CHCl_3$ solution, cm$^{-1}$): 2953, 2058, 1995, 1638. $^1$H NMR ($CDCl_3$, $\delta$, ppm, for two epimers): 6.05 (d, 1H, $J$ = 5 Hz), 5.93 and 5.91 (2 dd, 1H, $J$ = 4, 2 Hz), 5.76−5.71 (m, 1H), 5.36 (dd, 1H, $J$ = 5, 5 Hz), 4.56−4.53 (m, 1H), 3.41−3.37 (m, 1H), 2.51−1.5 (m, 8H). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm): 210.1, 197.3, 134.3, 134.2, 130.4, 130.3, 86.6, 86.5, 85.2, 85.2, 73.4, 62.8, 48.8, 31.6, 31.5, 31.3, 25.6, 25.6, 23.3, 23.2. HRMS for $M^+$ ($C_{15}H_{14}FeO_4S$): calcd: 345.9962 found: 345.9956.

**Tricarbonyl(6−9-$\eta^4$-1-oxo-4-methyl-2-thiaspiro[4.5]deca-6,8-diene)iron (12).** Complex **11** (48 mg) was irradiated according to the general procedure for 2.5 h. Purification by preparative TLC yielded complex **12** (46 mg; a 10:1 mixture with demetalated ligand **13**; 100% combined yield, 91% yield of **12**). IR ($CHCl_3$ solution, cm$^{-1}$): 2063, 1987, 1688. $^1$H NMR ($CDCl_3$, $\delta$, ppm), first epimer: 5.55−5.31 (m, 2H), 3.34 (dd, 1H, $J$ = 11.5, 5.7 Hz), 3.26−3.19 (m, 1H), 3.06−2.99 (m, 2H), 2.34−2.24 (m, 1H), 1.95−1.8 (AB part of pseudo-ABX system, 2H, $J_{AB}$ = 15.5 Hz), 1.24 (d, 3H, $J$ = 7 Hz). Second epimer: 5.55−5.31 (m, 2H), 3.71 (dd, 1H, $J$ = 11.6, 5.3 Hz), 3.4−3.37 (m, 1H), 3.06−2.99 (m, 1H), 2.66 (dd, $J$ = 5.5, 1.4 Hz), 2.48−2.39 (m, 1H), 2.0−1.86 (AB part of pseudo-ABX system, 2H, $J_{AB}$ = 15.5 Hz), 1.03 (d, 3H, $J$ = 7 Hz). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm, mixture of epimers): 211.4, 211.2, 89.2, 87.2, 83.6, 81.4, 63.1, 61.8, 61.0, 59.4, 59.2, 58.2, 44.2, 41.5, 38.6, 36.0, 34.8, 33.7, 15.4, 14.7. HRMS for $M^+$ ($C_{13}H_{12}FeO_4S$): calc: 319.9606, found: 319.9844; for $M^+ - CO$: calculated: 291.9856, found: 291.9843.

**Tricarbonyl(6−9-$\eta^4$-1-oxo-4-ethyl-2-thiaspiro[4.5]deca-6,8-diene)iron (15).** Complex **14** (196 mg) was irradiated for 22 h according to the general procedure with Q-Beam Spotlight as light source. Chromatographic separation yielded 35 mg of product **15** (118 mg of starting complex **14** recovered; 45% yield at 40% conversion). IR ($CHCl_3$ solution, cm$^{-1}$): 2052, 1990, 1692. $^1$H NMR ($CDCl_3$, $\delta$, ppm, for two epimers): 5.52−5.32 (m, 4H), 3.59 (dd, 1H, $J$ = 11.6, 5.4 Hz), 3.39−3.56 (m, 1H), 3.31 (dd, 1H, $J$ = 11.6, 5.6 Hz), 3.26−3.22 (m, 1H), 3.21−3.01 (m, 3H), 2.69 (d, 1H, $J$ = 5.3 Hz), 2.18−1.77 (m, 6H), 1.5−1.2 (m, 4H), 1.03 (t, 3H, $J$ = 7.3 Hz), 0.98 (t, 3H, $J$ = 7.3 Hz). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm, mixture of epimers): 211.4, 211.2, 89.4, 87.4, 83.3, 81.3, 63.2, 62.2, 61.3, 59.2, 59.1, 58.4, 50.9, 48.7, 38.7, 33.7, 32.0, 31.2, 21.1, 19.8, 12.6, 11.9. HRMS for $M^+ - 2CO$ ($C_{12}H_{14}FeO_2S$): calcd: 278.0064; found: 278.0063.

**Tricarbonyl(1−4-$\eta^4$-7-oxo-8-thiaspiro[5.7.0$^{9,13}$]trideca-1,3-diene)iron (21b).** Thiol ester **20** (280 mg) was irradiated for 22 h according to the general procedure with Q-Beam Spotlight as light source. Chromatographic separation yielded **21** as 4:1 mixture of epimers (179 mg of starting complex **20** recovered; 30% yield at 36% conversion). Double recrystallization from ether/hexane (1:5, −78 °C) afforded the major epimer **21b** as a yellow crystalline product. Mp 155 °C. IR ($CHCl_3$ solution, cm$^{-1}$): 2941, 2057, 1987, 1691. $^1$H NMR ($CDCl_3$, $\delta$, ppm): 5.47 (dddd, 1H, $J$ = 6.5, 4.1, 1.3, 1.3 Hz), 5.31 (ddd, 1H, $J$ = 6.1, 4.1, 1.5 Hz), 4.27 (ddd, 1H, $J$ = 6, 6, 1.7 Hz), 3.35 (dddd, 1H, $J$ = 6.5, 3, 3, 1.5 Hz), 2.99 (dd, 1H, $J$ = 6.1, 1.3 Hz), 2.7 (ddd, 1H, $J$ = 9, 9, 6 Hz), 2.2−1.7 (m, 7H), 1.42−1.34 (m, 1H). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm): 211.3, 210.0, 89.0, 81.6, 64.6, 63.0, 62.3, 55.1, 49.2, 35.3, 32.6, 25.7, 23.3. HRMS for $M^+$ ($C_{15}H_{14}FeO_4S$): calcd: 345.9962, found: 345.9956.

X-ray data for **21b**: Crystals were grown by slow evaporation (24 h) of solvent from an ether solution of **21b**. Crystal data: $C_{15}H_{14}FeO_4$, $M_r$ = 346.17. Crystal dimensions: 0.20 × 0.20 × 0.10 mm. Yelow, clear prism. Mo Kα radiation ($\lambda$ = 0.71073 Å). Monoclinic space group $P2(1)/n$; $a$ = 11.355(2) Å, $b$ = 6.4943(13) Å, $c$ = 20.060(4) Å, $\beta$ = 103.30(3)°, $V$ = 1439.6 (5) Å$^3$. $Z$ = 4. $\Theta$ = 2.35−27.06°. $T$ = 150(2) K. Measured reflections: 9425; independent reflections: 3534. Tables of fractional atomic coordinates, bond lengths, and bond angles are included in the Supporting Information.

**Tricarbonyl(1−4-$\eta^4$-7-oxo-8-thiaspiro[5.7.0$^{9,13}$]trideca-1,3-diene)iron (21a).** Spectral assignments for the minor epimer **21a** are deduced from spectra of **21b** and the mixture of **21a** and **21b**. $^1$H NMR ($CDCl_3$, $\delta$, ppm): 5.7 (dd, $J$ = 5 Hz), 5.38 (dd, 1H, $J$ = 5 Hz), 4.05 (dd, 1H, $J$ = 6 Hz), 3.07−3.04 (m, 1H), 2.99 (d, 1H, $J$ = 6 Hz), 2.55−2.47 (m, 1H), 2.11−1.8 (m, remaining protons, overlapping with signals from major epimer **21b**). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm): 211.3, 210.0, 86.2, 85.8, 60.89 60.5, 59.0, 58.3, 48.0, 40.3, 31.5, 26.7, 23.7.

**1-Oxo-4-methyl-2-thiaspiro[4.5]deca-6,8-diene (13).** Complex **12** (101 mg, containing 9% of **13**) was dissolved in dry benzene (5 mL) under Ar. $Me_3NO$ (227 mg, 10 equiv) was added. The reaction mixture was stirred at room temperature under Ar for 1 h 10 min (the reaction can be monitored by IR) and then diluted with ether and filtered through Celite. The solution was washed with water, dried over $MgSO_4$, and concentrated. Flash chromatography purification (silica gel, $CH_2Cl_2$/hexane, 3:7) afforded compound **13** (54 mg; 92% yield of demetalation). IR ($CHCl_3$ solution, cm$^{-1}$): 2941, 1713, 1690. $^1$H NMR ($CDCl_3$, $\delta$, ppm): first epimer: 6.18−6.13 (m, 1H), 5.86−5.83 (m, 2H), 5.7 (d, 1H, $J$ = 9.6 Hz), 3.15 (dd, 1H, $J$ = 11.2, 6.3 Hz), 3.02 (dd, 1H, $J$ = 11.2, 10 Hz), 2.21−2.12 (m, 3H), 1 17 (d, 3H, $J$ = 6.8 Hz); second epimer: 6.16 (dd, 1H, $J$ = 9.5, 5.2 Hz), 5.93−5.67 (m, 2H), 5.45 (d, 1H, $J$ = 9.5 Hz), 3.27 (dd, 1H, $J$ = 11.4, 6 Hz), 3.03 (dd, 1H, $J$ = 11.4, 9 Hz), 2.53−2.31 (m, 3H), 1.12 (d, 3H, $J$ = 6.8 Hz). $^{13}$C NMR ($CDCl_3$, $\delta$, ppm, mixture of epimers): 211.6, 210.4, 127.6, 126.7, 125.9, 125.8, 124.0, 123.3, 122.0, 120.2, 56.2, 55.8, 45.5, 43.8, 34.8, 34.3, 30.4, 25.4, 15.5, 14.7. HRMS for $M^+$ ($C_{10}H_{12}OS$): calcd: 180.0609, found: 180.0608.

**Tricarbonyl(6−9-$\eta^4$-1-hydroxy-4-methyl-2-thiaspiro-[4.5]deca-6,8-diene)iron (23).** To a solution of complex **12** (19 mg) in anhydrous ethanol (2 mL) at 0 °C was added $NaBH_4$ (10 mg, 4.5 equiv) via a solids addition tube. The reaction mixture was stirred at room temperature for 24 h and then quenched by the addition of 1 mL of saturated $NH_4Cl$ solution at 0 °C. The mixture was poured into 1 N HCl at 0 °C and extracted with $CH_2Cl_2$. The organic fraction was dried over $MgSO_4$ and concentrated in a vacuum. Preparative TLC separation ($CH_2Cl_2$/hexane, 1:1) afforded complex **23** (2 mg, 10% yield; a mixture of epimers) and starting complex **12** (7 mg). IR ($CHCl_3$ solution, cm$^{-1}$): 2052, 1977, 1420. $^1$H NMR ($CDCl_3$, $\delta$, ppm, for two epimers): 5.38−5.32 (m, 2H), 4.56 (s, 1H), 3.61−3.55 (m, 1H), 3.34−3.22 (m, 1H), 3.09 (dd, $J$ = 10.7, 6.3 Hz), 2.81−2.77 (m, 1H), 2.5 and 2.47 (ds, 1H, $J$ = 5 Hz), 2.35 (dd, 1H, $J$ = 15.8, 3.2 Hz), 2.2−2.13 (m, 1H), 1.19 and 1.13 (d, 3H, $J$ = 7 Hz). HRMS for $M^+$ ($C_{13}H_{14}FeO_3S$): calcd: 321.9962; found: 321.9948.

**1-Hydroxy-4-methyl-2-thiaspiro[4.5]deca-6,8-diene (24).** Compound **13** (10 mg) was dissolved in freshly distilled $CH_2Cl_2$ (1.5 mL) under Ar. The solution was cooled to −78 °C. DIBAL (0.12 mL of 1 M THF solution, 2.1 equiv) was added. The solution was stirred at −78 °C for 3 h, quenched with saturated $NH_4Cl$ solution, and warmed to room temperature. 1 N HCl was added, the organic layer was separated, and the water layer was extracted with $CH_2Cl_2$. Combined organic fractions were dried over $MgSO_4$, and solvent was evaporated in a vacuum. Preparative TLC separation ($CH_2Cl_2$/hexane, 1:1, multiple development) yielded 6 mg of starting material **13** and 4 mg of hemithioacetal **24** as a 1:1 mixture of epimers (99% yield at 40% conversion). IR ($CHCl_3$ solution, cm$^{-1}$): 3595, 2970, 1463, 1006. $^1$H NMR ($CDCl_3$, $\delta$, ppm, for two epimers): 6.13 (dd, 1H, $J$ = 10, 5 Hz), 6.05 (dd, 1H, $J$ = 10, 5 Hz), 5.96−5.76 (m, 4H), 5.56 (d, 1H, $J$ = 10 Hz), 5.47 (d, 1H, $J$ = 10 Hz), 5.25 (d, 1H, $J$ = 4.5 Hz), 4.95 (d, 1H, $J$ = 5.2 Hz),

3.15−3.03 (m, 2H), 2.83−2.4 (m, 4H), 2.36−2.16 (m, 2H), 2.06 (d, 1H, $J$ = 6 Hz), 2.0 (d, 1H, $J$ = 6 Hz), 1.87 (d, 1H, $J$ = 4.5 Hz, OH), 1.79 (d, 1H, $J$ = 5.2 Hz, OH), 1.06 (d, 3H, $J$ = 6.7 Hz), 1.04 (d, 3H, $J$ = 6.7 Hz). HRMS for $M^+ - H$ ($C_{10}H_{13}OS$): calcd: 181.0687; found: 181.0685.

**Reduction of 13 with $LiAlH_4$ at Room Temperature.** Compound **13** (10 mg) was dissolved in anhydrous ether (1 mL). $LiAlH_4$ (1 equiv, 42 $\mu$L of 1.3 M THF solution) was added. The reaction mixture was stirred at room temperature for 5 h and then quenched by sequential addition of wet ether, water, and 40% NaOH solution at 0 °C. The organic layer was separated, the water layer was extracted with ether, and the combined organic fraction was dried over $MgSO_4$ and concentrated. Preparative TLC separation ($CH_2Cl_2$) afforded 3 mg (30%) of hemithioacetal **24** as a 1:1 mixture of epimers.

**1-(1-Methyl-2-sulfanylethyl)-2,4-cyclohexadienylmethanol (25).** Thialactone **13** (8.5 mg) was dissolved in anhydrous THF (1.5 mL), and $LiAlH_4$ (2 equiv, 73 $\mu$L of 1.3 M THF solution) was added via a syringe under Ar. The solution was refluxed in an inert atmosphere for 2.5 h and then cooled to room temperature and quenched by sequential addition of wet ether, water, and 15% NaOH solution. The organic layer was separated, the water layer was extracted with ether, and the combined organic fraction was dried over $MgSO_4$. Solvent was removed in a vacuum. Preparative TLC separation (EtOAc/hexane, 3:7) afforded 2 mg (23%) of alcohol **25** as a 1:1 mixture of epimers. IR ($CHCl_3$ solution, $cm^{-1}$): 3670, 2967, 2929, 1462. $^1H$ NMR ($CDCl_3$, $\delta$, ppm, for two epimers): 6.02−5.97 (m, 2H), 5.82−5.72 (m, 4H), 5.41 (d, 2H, $J$ = 10.2 Hz), 3.67−3.44 (m, 4H), 3.1−2.9 (m, 2H), 2.35−2.15 (m, 4H), 2.1−1.9 (m, 4H),1.4−1.3 (m, 2H), 1.05 (d, 3H, $J$ = 7 Hz), 1.02 (d, 3H, $J$ = 7 Hz). HRMS for $M^+ - 2H$ ($C_{10}H_{14}OS$): calcd: 182.0765; found: 182.0769.

**Tricarbonyl(6−9-$\eta^4$-1-methoxy-4-methyl-2-thiaspiro-[4.5]deca-6,8-diene)iron (26).** Complex **12** (18 mg) was dissolved in anhydrous THF (0.5 mL). A solution of 9-BBN (35 mg, 5 equiv) in 0.5 mL of anhydrous THF was added under Ar via a syringe, and the reaction mixture was refluxed under Ar for 10 h and then cooled to room temperature. Methanol (0.1 mL) was added, and then solvent was evaporated in a vacuum. The product mixture was dissolved in dry ether, and 30 $\mu$L of ethanolamine was added. The precipitate that formed was filtered off, and the solution was washed with 2 N HCl, water, dried over $MgSO_4$, and concentrated. Preparative TLC separation (EtOAc/hexane, 3:7) yielded 6 mg of starting complex and 9-BBN-protected hemithioacetal. The acetal was stirred in a 4:1 mixture of methanol and concentrated HCl for 5 h at room temperature, and then the solution was diluted with water and extracted with ether. The combined ether extracts were dried over $MgSO_4$, and concentrated in a vacuum. Preparative TLC separation ($CH_2Cl_2$/hexane, 1:2) yielded two fractions (6 and 7 mg), each of which consisted of two epimers of **26**. First fraction ($R_f$ 0.52 in $CH_2Cl_2$/hexane, 1:1; 3.8:1 mixture of epimers): IR ($CHCl_3$ solution, $cm^{-1}$): 2057, 1979, 1471, 1451, 1107, 1088. $^1H$ NMR ($CDCl_3$, $\delta$, ppm), major epimer: 5.5−5.31 (m, 2H), 3.95 (s, 1H), 3.24 (s, 3H), 3.22−3.08 (m, 3H), 2.58 (d, 1H, $J$ = 13.6 Hz), 2.3−2.21 (m, 1H), 1.79−1.64 (AB part of pseudo-ABX, 2H, $J_{AB}$ = 11.6 Hz, $\nu_A{}^{*1}$ = 1.68, $\nu_B{}^{*1}$ = 1.75, $\nu_A{}^{*2}$ = 1.67, $\nu_B{}^{*2}$ = 1.74,), 1.21 (d, 3H, $J$ = 7.2 Hz, H11); minor epimer: 5.4−5.3 (m, 2H), 4.2 (s, 1H), 3.19 (s, 3H), 3.22−3.08 (m, 3H), 2.65 (dd, 10.7, 1.9 Hz), 2.36−2.25 (m, 1H), 1.98−1.9 (m, 2H), 1.01 (d, 3H, $J$ = 7.2 Hz). $^{13}C$ NMR ($CDCl_3$, $\delta$, ppm): 211.8, 102.3, 88.2, 86.6, 83.1, 62.9, 62.4, 60.1, 57.1, 56.6, 47.0, 45.2, 42.0, 36.7, 31.6, 16.7. HRMS for $M^+$ ($C_{14}H_{16}FeO_4S$): calcd: 336.0119 found: 336.0105. Second fraction ($R_f$ 0.45 in $CH_2Cl_2$/hexane, 1:1; 2.4:1 mixture of epimers): IR ($CHCl_3$ solution, $cm^{-1}$): 2944, 2048, 1981, 1469, 1090. $^1H$ NMR ($CDCl_3$, $\delta$, ppm, for two epimers): 5.52−5.26 (m, 2H), 4.43 and 3.97 (2 s, 1H, minor and major epimers, respectively), 3.28 and 3.27 (2 s, 3H, major and minor epimers, respectively), 3.24−3.22 and 3.05 (m, and dd, $J$ = 10.7, 6.5 Hz), 2.83−2.76 (m, 2H), 2.38−2.31 (m, 1H), 1.92 (dd, $J$ = 16, 2.4 Hz), 1.65 (dd, $J$ = 16, 3 Hz), 1.14 and 1.12 (d, $J$ = 7 Hz, and d, $J$ = 6 Hz, 3H). $^{13}C$ NMR ($CDCl_3$, $\delta$, ppm): 212.0, 211.8, 102.8, 99.1, 87.3, 87.1, 81.9, 64.8, 63.1, 62.2, 57.7, 56.4, 44.3, 41.8, 35.6, 35.2, 34.3, 14.8, 13.9. HRMS for $M^+$ ($C_{14}H_{16}FeO_4S$): calcd: 336.0119 found: 336.0075; for $M^+$ - CO ($C_{13}H_{16}FeO_3S$): calcd: 308.0169, found: 308.0163.

**Tricarbonyl[2−5-$\eta^4$-1-(1-(methylthio)-2-propyl)-2,4-cyclohexadien-1-carboxaldehyde]iron (27).** Complex **26** (8 mg, mixture of 4 epimers) was dissolved in acetone (2 mL) containing 0.02 mL of water. $Na_2CO_3$ (10 mg) and MeI (6 $\mu$L, 16 equiv) were added, and the mixture was refluxed for 48 h and then cooled to room temperature and concentrated. The crude product mixture was dissolved in EtOAc, washed with water, and dried with $MgSO_4$. Solvent was evaporated in a vacuum, and the products were separated by preparative TLC ($CH_2Cl_2$/hexane, 1:2, multiple development). Aldehyde **27** (1.3 mg) was obtained as a 1.4:1 mixture of epimers (6.1 mg of starting complex **26** were recovered, 68% yield at 24% conversion). IR ($CHCl_3$ solution, $cm^{-1}$): 2069, 1988, 1719, 912. $^1H$ NMR ($CDCl_3$, $\delta$, ppm), major epimer: 9.2 (s, 1H,), 5.46−5.33 (m, 2H), 3.35−3.29 (m, 1H), 2.94 (dd, $J$ = 6.4, 1.5 Hz), 2.65 (dd, 1H, $J$ = 13, 3.8 Hz), 2.39−2.11 (m, 2H), 2.08 (s, 3H), 2.06−1.84 (m, 1H), 1.62 (dd, 1H, 15.7, 2.8 Hz), 1.17 (d, 3H, $J$ = 7 Hz); minor epimer: 9.15 (s, 1H), 5.46−5.33 (m, 2H), 3.35−3.29 (m, 1H), 2.83 (dd, $J$ = 6, 1.4 Hz), 2.62 (dd, 1H, $J$ = 13, 2.7 Hz), 2.39−2.11 (m, 2H), 2.1 (s, 3H), 2.06−1.84 (m, 1H), 1.71 (dd, 1H, 15.7, 2.8 Hz), 1.05 (d, 3H, $J$ = 7 Hz). HRMS for $M^+ - CO$ ($C_{13}H_{16}FeO_3S$): calcd: 308.0169, found: 308.0151.

**General Procedure for Raney Ni Reduction of Thialactones.** The appropriate amount of Raney Ni as a slurry in ethanol was placed in a flask, and 1 mL of ethanol was added. After stirring for 0.5 min, the ethanol was carefully removed with a pipet. Ethanol (1 mL) was added, followed by a solution of the appropriate thialactone complex in 0.5−5 mL of ethanol. The reaction mixture was stirred at room temperature for 15 min (unless otherwise indicated; the reaction can be monitored by TLC) and then filtered through Celite; the remaining Ni was washed with ethanol and then acetone. Solvent was evaporated in a vacuum, and preparative TLC separation ($CH_2Cl_2$/hexane, 1:1) yielded corresponding alcohol or aldehyde.

**Tricarbonyl(2−5-$\eta^4$-1-isopropyl-2,4-cyclohexadienylmethanol)iron (29).** Complex **12** (80 mg) in 5 mL of ethanol was treated with Raney Ni (2 g) according to the general procedure. Preparative TLC separation yielded alcohol **29** (41 mg, 59% yield) as a yellow crystalline compound, and aldehyde **28** (1.3 mg, 2% yield). Mp 70−71 °C. IR ($CHCl_3$ solution; $cm^{-1}$): 2967, 2052, 1976, 1470. $^1H$ NMR ($CDCl_3$; $\delta$, ppm): 5.43 (ddd, 1H, $J$ = 6.5, 4, 2 Hz), 5.36 (dd, 1H, $J$ = 6.3, 4 Hz), 3.4 (dd, 1H, $J$ = 10.7, 5 Hz), 3.25 (dd, 1H, $J$ = 10.7, 5 Hz), 3.15 (m, 1H), 3.04 (dd, 1 H, $J$ = 6.5, 1 Hz), 1.75 (septet, 1 H, $J$ = 7 Hz), 1.67 (dd, 1H, $J$ = 15, 3 Hz), 1.63 (dd, 1H, $J$ = 10, 3 Hz), 0.98 (d, 3 H, $J$ = 7 Hz), 1.23 (m, 1H, OH), 0.93 (d, 3 H, $J$ = 7 Hz). $^{13}C$ NMR ($CDCl_3$; $\delta$, ppm): 212.2, 86.8, 82.4, 68.7, 67.3, 62.6, 44.5, 37.3, 36.3, 17.6, 17.5. HRMS for $M^+ - CO$ ($C_{12}H_{16}FeO_3$): calcd: 264.0448; found: 264.0436.

**Tricarbonyl(2−5-$\eta^4$-1-isopropyl-2,4-cyclohexadiene-1-carboxaldehyde)iron (28).** Thialactone complex **12** (20 mg in 1 mL of ethanol) was treated with Raney Ni (0.28 g) according to the general procedure (reaction time = 3 h). Preparative TLC separation yielded aldehyde **28** (3 mg, 36% yield at 50% conversion), alcohol **29** (1 mg, 12% yield at 50% conversion), and starting complex **12** (10 mg). For **28**: IR ($CHCl_3$ solution; $cm^{-1}$): 2053, 1990, 1717. $^1H$ NMR ($CDCl_3$; $\delta$, ppm): 9.25 (s, 1H), 5.42 (ddd, 1H, $J$ = 5.5, 4, 1.5 Hz), 5.31 (ddd, 1H, $J$ = 5.5, 4, 1.1 Hz), 3.29 (m, 1H), 2.91 (dd, 1H, $J$ = 5.5, 1.3 Hz), 2.27 (dd, 1H, $J$ =15.5, 2.8 Hz), 1.83 (septet, 1H), 1.62 (dd, 1H, $J$ = 15.5, 2.8 Hz), 1.01 (d, 3H, $J$ = 7 Hz), 0.91 (d, 3 H, $J$ = 7 Hz). $^{13}C$ NMR ($CDCl_3$; $\delta$, ppm): 211.3, 200.7, 88.2, 82.0, 63.2, 60.7, 54.8, 34.8, 34.1, 17.5, 17.3. HRMS for $M^+$ ($C_{13}H_{14}FeO_4$): calcd: 290.0241; found: 290.0245.

**Tricarbonyl[2−5-$\eta^4$-1(*sec*-butyl)-2,4-cyclohexadiene-1-carboxaldehyde]iron (31).** Complex **15** (10 mg) in 0.5 mL of ethanol was treated with Raney Ni (0.275 mg) according to the general procedure (reaction time = 40 min). Preparative TLC separation afforded aldehyde **31** (2.5 mg, 29% yield at 94% conversion, 1:1 mixture of epimers), alcohol **30** (1 mg, 12% yield at 94% conversion), and starting complex **15** (0.6 mg).

IR ($CHCl_3$ solution; $cm^{-1}$): 2054, 1981, 1720. $^1H$ NMR ($CDCl_3$; $\delta$, ppm, for two epimers): 9.24 (s, 1H), 9.21 (s, 1H), 5.43 (m, 4H), 3.3−3.27 (m, 2H), 2.93 (dd, 1H, $J$ = 6.3, 1.6 Hz), 2.88 (dd, 1H, $J$ = 6.3, 1.6 Hz, epimer), 2.32 (dd, 1H, $J$ = 9, 2.6 Hz), 2.26 (dd, 1H, $J$ = 9, 2.6 Hz, epimer), 1.67−1.41 (m, 8H), 1.0 (d, 3H, $J$ = 7 Hz), 0.93 (t, 3H, $J$ = 7 Hz), 0.92 (t, obscure, epimer), 0.89 (d, 3H, $J$ = 7 Hz). $^{13}C$ NMR ($CDCl_3$; $\delta$, ppm, mixture of epimers): 211.3, 200.6, 200.6, 88.3, 88.2, 82.1, 81.9, 63.4, 63.1, 60.5, 55.4, 42.3, 41.6, 34.6, 34.1, 24.3, 23.9, 13.7, 13.5, 13.0, 12.8. HRMS for $M^+ - CO$ ($C_{13}H_{16}FeO_3$): calcd: 276.0448; found: 276.0440.

**Tricarbonyl(2−5-$\eta^4$-1-(*sec*-butyl)-2,4-cyclohexadienylmethanol)iron (30).** Thialactone **15** (22 mg in 0.5 mL of ethanol) was treated with Raney Ni (1 g) according to the general procedure (reaction time = 10 min). Preparative TLC purification yielded alcohol **30** (8 mg, 40% yield). IR ($CHCl_3$ solution; $cm^{-1}$): 2051, 1970, 1652. $^1H$ NMR ($CDCl_3$; $\delta$, ppm, for two epimers): 5.45−5.35 (m, 4H), 3.37 (t, 2H, $J$ = 10.7 Hz), 3.25 (t, $J$ = 10.7 Hz), 3.16−3.13 (m, 2H), 3.09 (dd, 1H, $J$ = 6.5, 1.6 Hz), 3.03 (dd, 1H, $J$ = 6.5, 1.6 Hz), 1.8−1.2 (m, 10H), 0.97 (d, 3H, $J$ = 7 Hz), 0.94 (t, obscured, 6H), 0.85 (d, 3H, $J$ = 7 Hz). $^{13}C$ NMR ($CDCl_3$; $\delta$, ppm; mixture of epimers): 212.2, 86.8, 86.8, 82.5, 82.4, 68.8, 68.7, 67.2, 67.0, 62.5, 62.5, 45.4, 45.2, 44.4, 43.7, 37.7, 37.5, 24.4, 24.2, 13.89, 13.8, 13.6, 13.4. HRMS for $M^+$ ($C_{14}H_{18}FeO_4$): calcd: 306.0554; found: 306.0549; for $M^+ - CO$ ($C_{13}H_{18}FeO_3$): calcd: 278.0605; found: 278.0595.

**Tricarbonyl(2−5-$\eta^4$-1-cyclopentyl-2,4-cyclohexadienylmethanol)iron (32).** Complex **21** (14 mg in1.5 mL of ethanol) was treated with Raney Ni (0.65 g) according to the general procedure (reaction time = 10 min). Preparative TLC separation yielded alcohol **32** (2 mg, 16% yield). IR ($CHCl_3$ solution; $cm^{-1}$): 2048, 1980, 1558. $^1H$ NMR ($CDCl_3$; $\delta$, ppm): 5.41 (ddd, 1H, $J$ = 6.4, 4, 1.6 Hz), 5.37−5.32 (m, 1H), 3.41−3.28 ($AB_q$, 2H, $\nu^A$ = 3.37, $\nu^B$ = 3.31, $J_{AB}$ = 10.7 Hz), 3.17−3.32 (m, 1H), 2.94 (dd, 1H, $J$ = 6.4, 1.6 Hz), 2.4−2.3 (m, 1H), 2.06−1.97 (m, 1H), 1.76−1.58 (m, 5H), 1.37−1.26 (m, 4H). $^{13}C$ NMR ($CDCl_3$; $\delta$, ppm): 212.3, 86.9, 81.9, 69.4, 68.7, 62.7, 49.0, 43.4, 37.5, 27.0, 26.7, 25.5, 25.2. HRMS for $M^+$ ($C_{15}H_{18}FeO_4$): calcd: 318.0554; found: 318.0549.

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**Supporting Information Available:** $^1H$ and $^{13}C$ NMR spectra for new compounds, and a structure report for complex **21b** (47 pages). This material is contained in 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.

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