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Reactions of (η^5-C_5H_5)(CO)$_2$Fe-Substituted *N*-Sulfonyl Azadienes with C-Nucleophiles. A Route to 5-Substituted Dihydropyrrolones

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A variety of cyclic β-[(η^5-C_5H_5)(CO)$_2$Fe]-substituted *N*-sulfonyl azadienes **4** were prepared: e.g., from the corresponding iron-substituted (*Z*)-enals and benzenesulfonamide. Reactions of these iron compounds with Grignard reagents or organolithiums gave 5-substituted α,β-unsaturated *N*-sulfonyl γ-lactams **5**. In some cases the corresponding non-N-protected 5-substituted γ-lactams **6** were isolated as well. Key steps of these reaction cascades are the initial 1,2-addition to the imine moiety and the subsequent carbonylation step. The reaction of the chromene−iron complex **4e** with (allyl)MgCl gave the (η^3-allyl)-iron−γ-lactam complex **8a** with a ring-opened chromene framework. This complex was structurally characterized by X-ray analysis.

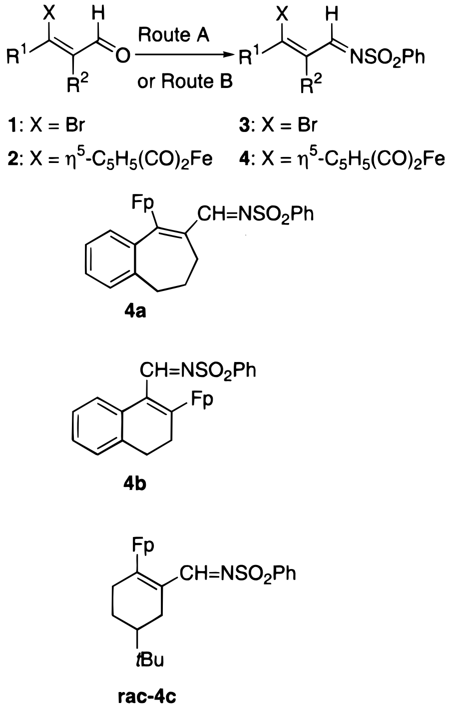
Introduction

Transition-metal-mediated cyclocarbonylations have attracted a great deal of interest in recent years in catalytic as well as stoichiometric processes.[1−3] Recently, we reported on novel cyclocarbonylations of β-[(η^5-C_5H_5)(CO)$_2$Fe]-substituted (*Z*)-enals leading to γ-lactones and γ-lactams in one-pot procedures.[4−6] These reaction cascades involve the addition of an organometallic reagent (e.g., K-Selectride,[5] RMgCl, or RLi[6]) or the $TiCl_4$-mediated addition of electron-rich primary amines[4] to the aldehyde functionality as the initial key step. In this paper reactions of β-[(η^5-C_5H_5)(CO)$_2$Fe]-substituted *N*-sulfonyl azadienes with organolithiums and Grignard reagents furnishing 5-substituted dihydropyrrolones are presented.

Results and Discussion

There are two synthetic routes to [(η^5-C_5H_5)(CO)$_2$Fe]-substituted *N*-sulfonyl azadienes **4**; both start from β-bromo enals **1** as shown in Scheme 1. The cyclic *N*-sulfonyl imines **4** are accessible from the (η^5-C_5H_5)-(CO)$_2$Fe-substituted enals **2** and benzenesulfonamide by the use of titanium tetrachloride and triethylamine in almost quantitative yield (route A).[4,7] The iron compounds **2** were synthesized from β-bromo enals **1** and the sodium ferrate [(η^5-C_5H_5)(CO)$_2$Fe]Na as previously described.[4,5] Alternatively, compound **4a** (Scheme 1, Table 1) was synthesized from the sodium ferrate [(η^5-C_5H_5)(CO)$_2$Fe]Na and the corresponding β-bromo-substituted azadiene **3a** in 67% yield (route B). Compound **3a** was quantitatively obtained from the corresponding β-bromo enal **1a** and benzenesulfonamide (see the Experimental Section). Purification of the *N*-sulfonyl

Scheme 1[a]



[a] Route A: (a) **1**, [Cp(CO)$_2$Fe]Na, THF; (b) **2**, benzenesulfonamide, $TiCl_4$, NEt_3, CH_2Cl_2, **4**, quantitative yield. Route B: (a) **1a**, benzenesulfonamide, $TiCl_4$, NEt_3, CH_2Cl_2, **3a**, quantitative yield; (b) **3a**, [Cp(CO)$_2$Fe]Na, THF, **4a**, 67% yield.

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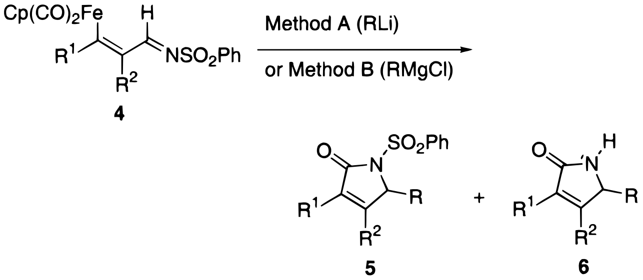
Table 1. Reactions of β-[(η^5-C_5H_5)(CO)$_2$Fe]-substituted *N*-sulfonyl Azadienes 4 with Grignard Reagents and Organolithiums

				product (yield, %)	
entry	reactant	method	RM	5	6
1	**4a**	A	*n*BuLi	**5a** (43)	**6a**
2	**4a**	A	MeLi	**5b** (54)	**6b**
3	**4a**	B	(allyl)MgCl	**5c** (42)	**6c**
4	**4b**	B	(allyl)MgCl	**5d** (37)	**6d** (41)
5	**4b**	B	*n*PrMgCl	**5e** (25)	**6e** (25)
6	**4b**	A	MeLi	**5f** (44)	**6f** (56)
7	***rac*-4c**	A	*n*BuLi	**5g** (36)	**6g** (traces)
8	***rac*-4c**	B	(allyl)MgCl	**5h** (19)	**6h**
9	***rac*-4c**	C	(allyl)MgCl	**5h** (76)	**6h**

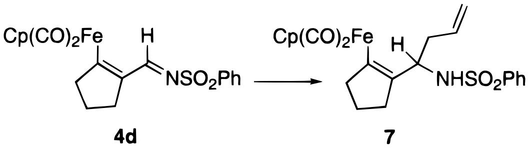
Scheme 2



imines **4** was generally accomplished by crystallization rather than chromatography, because slow decomposition was observed during silica gel chromatography. The IR spectra (CH_2Cl_2) of the iron complexes **4** show two characteristic ν(C≡O) absorptions in the ranges 2020−2030 and 1970−1980 cm^{-1}. The ν(C═N) stretching frequencies are generally observed at about 1525−1550 cm^{-1}. The ^{1}H NMR chemical shifts of CH═N range from δ 8.90 to δ 9.35 in $CDCl_3$.

N-Arenesulfonyl imines are known to undergo 1,2-addition reactions with various Grignard and organolithium reagents.[8,9] In fact, the *N*-sulfonyl imines **4a**−**c** reacted with organolithium compounds (method A: MeLi, *n*BuLi, THF, 1−1.3 equiv, −78 or 0 °C and then room temperature) as well as Grignard reagents (method B: (allyl)MgCl, *n*PrMgCl, CH_2Cl_2, room temperature), furnishing 5-substituted *N*-sulfonyl dihydropyrrolones **5** and in a few cases 5-substituted *N*-unprotected dihydropyrrolones **6** in 40%-quantitative overall yield (Scheme 2, Table 1). The five-membered annulated lactam moieties are formed by reaction cascades starting with the initial 1,2-addition of the C-nucleophile to the imine functionality followed by a carbonylation and a subsequent reductive elimination step. The results of our studies are shown in Table 1. Treatment of compound **4a** with either Grignard reagents or organolithiums afforded the γ-lactams **5a**−**c** in 42−54% unoptimized yield, in addition to ferrocene, (η^5-C_5H_5)(CO)$_2$Fe dimer, and undefined byproducts, as indicated by IR and ^{1}H NMR spectroscopy of the crude reaction mixtures. The characteristic ν(CO) absorption of the γ-lactams **5** is detected at ~1720−1730 cm^{-1} in dichloromethane or THF. Reactions with Grignard reagents carried out at −78 °C proceeded sluggishly. Generally, in reactions with organolithiums more byproducts were observed. After complete consumption of the starting materials (IR and TLC monitoring) the reaction mixtures were hydrolyzed with NH_4Cl solution or citrate buffer (pH 6) and the crude products purified by flash chromatography.

Scheme 3



Surprisingly, treatment of **4b** with either organolithiums or Grignard reagents gave unprotected dihydropyrrolones **6d**−**f** (ν(C═O) ~ 1690 cm^{-1}) together with the expected *N*-sulfonyl compounds **5d**−**f** as ~1:1 mixtures in 50%-quantitative overall yield. Treatment of ***rac*-4c** with *n*BuLi in CH_2Cl_2 or toluene furnished traces of impure **6g** in addition to **5g** according to IR and NMR spectroscopy (Table 1, entry 7). In all other cases examined (Table 1, entries 1−3, 8, and 9) products of type **6** were not isolated or detected by ^{1}H NMR spectroscopy of the crude product mixtures. The addition of (allyl)MgCl to the cyclohexene derivative ***rac*-4c** at room temperature gave the *N*-sulfonyl γ-lactam **5h** in only 19% yield after flash chromatography. For this case the influence of higher temperature on the course of the reaction cascade was studied in more detail. In 1,2-dichloroethane as solvent, raising the reaction temperature to 50 °C led to complete turnover to the γ-lactam **5h**, and the latter was isolated in 76% yield (Table 1, method C). All attempts to run reactions shown in Table 1 with an excess of organometallic reagents as well as prolongation of the reaction time led to no significant increase in yield but gave more impurities.

From the reactions of the iron compounds **4a**−**c**,**e** with organometallic reagents 1,2-addition products were not isolated or identified as byproducts. Only from the cyclopentene derivative **4d** were 1,2-addition products obtained exclusively, possibly due to steric reasons.[5] From (allyl)MgCl and **4d** the adduct **7** was isolated in 63% yield after chromatography (Scheme 3). For compound **7** characteristic ν(C═O) stretching frequencies are observed at 2013 and 1953 cm^{-1}.

The reaction of compound **4e** with (allyl)MgCl was found to yield the (η^3-allyl)iron complex **8a** as product in 84% yield after flash chromatography (Scheme 4). For the reaction of **4e** with *n*PrMgCl in 1,2-dichloroethane at room temperature incomplete turnover was observed after prolonged time (3 days), and **8b** was obtained in only 24% yield. The structure of complex **8a** was elucidated by spectroscopic methods and by X-ray analysis. In the solid state the intramolecular hydrogen bond −OH···(O═C)− is observed for **8a**, as shown by the structure in Figure 1. Bond lengths and angles are as expected. Selected data are presented in Figure 1; the crystallographic data are given in Table 2. An *anti* orientation of the metal fragment and the allyl residue at carbon 5 of the lactam moiety can be concluded from the single-crystal structure analysis.

Similarly, the chiral β-[(η^5-C_5H_5)(CO)$_2$Fe]-substituted *N*-sulfonyl azadiene **4f**, synthesized from 2-sulfamylbenzoic acid (−)-menthyl ester and iron compound **2e**

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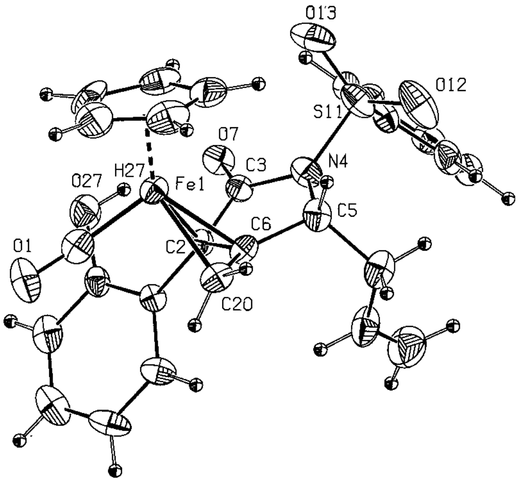


Figure 1. Structure of **8a** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Fe−C2 = 2.124(2), Fe−C6 = 2.030(2), Fe−C20 = 2.113(3), H27−O7 = 1.814, C2−C6 = 1.435(3), C2−C3 = 1.471(3), C6−C20 = 1.408(3), C3−O7 = 1.225(2); C2−C6−C20 = 124.7(2), O7−C3−C2−C6 = 175.4(2).

Scheme 4

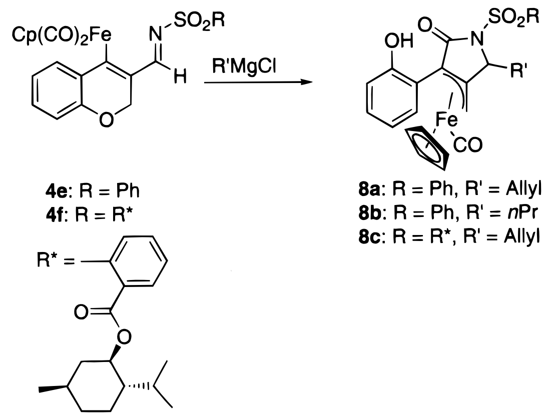
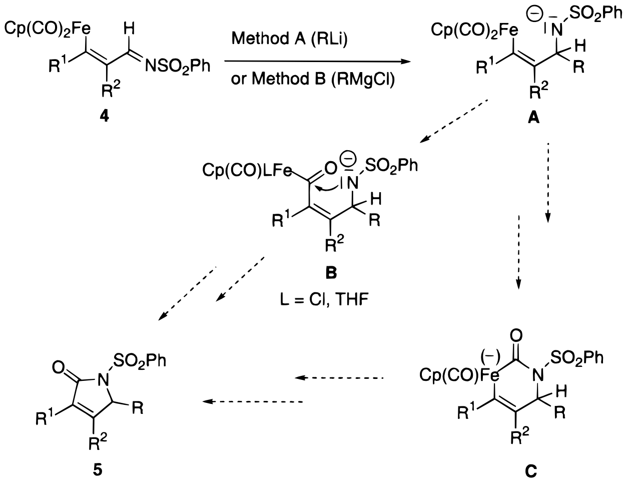


Table 2. Crystallographic Data for 8a

chem formula	$C_{26}H_{23}FeNO_5S$
fw	517.36
cryst syst	orthorhombic
space group	$P2_12_12_1$
Z	4
T, K	298
a (Å)	7.920(2)
b (Å)	20.418(1)
c (Å)	14.807(2)
V (Å^3)	2394.3(7)
D_{calcd}, g cm^{-3}	1.4351
μ(Mo Kα), mm^{-1}	0.75
2θ range, deg	1.5−27.0
no. of indep rflns	5189
no. of rflns obsd	4648
no. of refined params	328
S	1.037
R1 (for reflections obsd)	0.0297
wR2	0.0789
$(\Delta/\rho)_{max}$	0.26
$(\Delta/\rho)_{min}$, e Å^{-3}	−0.39

Scheme 5



in 53% yield, gave an isomeric mixture (see the Experimental Section) of chromene-ring-opened (η^3-allyl)iron complex **8c** upon treatment with (allyl)MgCl (−78 °C, then room temperature) in 56% overall yield. The IR spectra of the (η^3-allyl)iron complexes **8** in dichloromethane display absorptions at about 1975−1990 cm^{-1} for the carbon monoxide ligand and in the range of 1660−1680 cm^{-1} for the lactam C=O bond.

The formation of the 5-substituted γ-lactams **5** is in agreement with the mechanistic considerations shown in Scheme 5. After 1,2-addition of the organometallic reagent to the imine functionality, leading to intermediate **A**, the carbonylation step may proceed either by a CO insertion followed by a subsequent aminolysis of the acyl iron intermediate **B** or by direct attack of the metalated amide at the carbon monoxide ligand, leading to the ferrilactam species **C** prior to reductive elimination.[4,5] By IR monitoring at first the formation of the metalated amides by 1,2-addition is indicated by the disappearance of the educt absorptions and by the appearance of two new ν(C≡O) absorptions at lower wavelength around 2005 and 1955 cm^{-1}. Only for the reaction of **4c** with *n*BuLi was the appearance and disappearance of a new absorption at 1853 cm^{-1} observed subsequently (Table 1, entry 7). For the anionic ferrilactam **C** one might expect an absorption for the carbonyl ligand in this region.[10] In all other examples examined with either Grignard reagents or organolithiums new absorptions at 1950−1990 cm^{-1} and at 1640−1660 cm^{-1} appeared and disappeared, which we attribute to intermediate acyliron complexes **B**.[11]

At the current stage of research the formation of the N-unsubstituted γ-lactams **6** is not completely conclusive. However, during IR monitoring the characteristic absorptions of the N-unsubstituted γ-lactams **6** at about 1680−1690 cm^{-1} were not observed. Moreover, rather harsh acid-catalyzed reductive or electrochemical cleavage conditions generally have to be employed to remove *N*-arenesulfonyl groups from *N*-arenesulfonyl carboxamides.[12] Iron-mediated redox processes may be involved in the formation of the unprotected γ-lactams **6**.

The formation of the complexes **8a**−**c** can be rationalized according to Scheme 6. Since the formation of the (η^3-allyl)iron−γ-lactam skeletons (ν(C≡O) ≈ 1975−1990 cm^{-1}, ν(C=O) ≈ 1660−1680 cm^{-1}) was observed during

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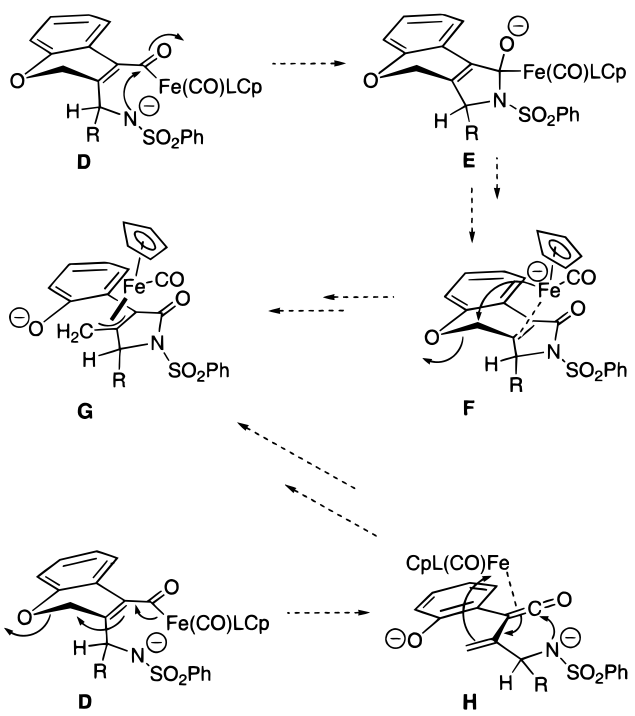
Scheme 6



IR monitoring, it seems reasonable to propose the anionic (π-alkene)iron complex **F** as an intermediate being formed from **D** via **E** during the reductive elimination step. Subsequently, an intramolecular nucleophilic substitution reaction would give phenolate intermediate **G** prior to hydrolytic workup by attack of the iron moiety at the neighboring methylene group. Alternatively, the iron–carbon bond in intermediate **D** could break to furnish the iron ketene complex **H** with phenoxide anion as the leaving group. Attack of the metalated amide on the complexed ketene would lead to intermediate **G** and, thereby, to the allyl complexes isolated.[13]

In conclusion, the 1,2-addition of Grignard reagents and organolithiums to the imine functionality of β-[(η^5-C_5H_5)(CO)$_2$Fe]-substituted *N*-sulfonyl azadienes **4** generally evolves into reaction cascades leading to 5-substituted dihydropyrrolones **5**, **6**, and **8** in 40%-quantitative overall yield.

Experimental Section

All reactions were carried out under an atmosphere of argon in oven-dried glassware by standard needle/syringe techniques. THF was dried and distilled from potassium/benzophenone under argon. CH_2Cl_2 and 1,2-dichloroethane were distilled from CaH_2 under argon. Solvents were degassed (ultrasound) before use. CCl_4 was distilled over P_4O_{10}. Triethylamine was distilled and stored over KOH. Solvents for chromatography were of technical quality and were purified as follows: petroleum ether (40–60 °C) was distilled from P_4O_{10} and ethyl acetate from K_2CO_3. Acetone (p.a., supplied by Riedel-de-Haen) was used without further purification. Allylmagnesium chloride (2 M in THF), propylmagnesium chloride (2 M in Et_2O), *n*-butyllithium (1.6 M in hexane), and $TiCl_4$ (1 M solution in CH_2Cl_2) were purchased from Aldrich, sodium amalgam (2%) was obtained from Lancaster, and $\{\eta^5$-$C_5H_5(CO)_2Fe\}_2$ and methyllithium (1.6 M in Et_2O) were purchased from Fluka. Buffer solution was used as indicated (pH 6: 7.86 g of citric acid monohydrate + 22.28 g of Na_2HPO_4·$2H_2O$ in 1.0 L of water). Melting points were determined with a Büchi melting-point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker AC200 or a Bruker AM400 spectrometer in $CDCl_3$, unless otherwise stated. Carbon multiplicities were determined by GASPE or DEPT135; residual protons were used as the internal standard ($CDCl_3$, δ(^{1}H) 7.24, δ(^{13}C) 77.0; [D$_6$]DMSO, δ(^{1}H) 2.49, δ(^{13}C) 39.7). Chemical shifts are given in ppm relative to tetramethylsilane (TMS), and coupling constants are in Hz. FD, FAB, and HRMS (EI) mass spectra were recorded on a Finnigan MAT95. IR spectra were recorded with a Perkin-Elmer 1760X FTIR spectrometer; NaCl cells were used for IR monitoring. Thin-layer chromatography (TLC) was performed on Merck plates (silica gel 60 F_{254}); detection was by UV light (λ = 254 nm) or by treatment with either a $KMnO_4$ solution ($KMnO_4$ (1.25 g) and Na_2CO_3 (6.25 g) in water (250 mL)) or a solution of phosphomolybdic acid (2.5 g), cerium(IV) sulfate (1 g), and H_2SO_4 in water (96 mL). R_f values are given for 2:1 petroleum ether/ethyl acetate. The products were purified by column chromatography (using the technique developed by Helquist et al.,[14] but without inert gas atmosphere) on Baker silica gel 60 (230–400 mesh) or Florisil (140–200 mesh, supplied by Aldrich or Fluka). Elemental analyses were carried out by the Microanalytical Division of the Institute of Organic Chemistry at the University of Mainz (Mainz, Germany).

General Procedures for the Synthesis of β-[η^5-C_5H_5-(CO)$_2$Fe]-Substituted *N*-Sulfonyl Imines 4. Route A. The β-[(η^5-C_5H_5)(CO)$_2$Fe]-substituted (*Z*)-enals **2** were prepared from the β-bromovinyl aldehydes **1** and [(η^5-C_5H_5)(CO)$_2$Fe]Na as previously described.[4,5] Method A (1.5–8 mmol scale): to a solution of the (*Z*)-enal **2** and benzenesulfonamide (1.1 equiv) in 25 mL of CH_2Cl_2 was added triethylamine (2.33 equiv) and $TiCl_4$ (0.6 equiv) at 0 °C. The light-protected mixture was stirred for 5 min; then the cold bath was removed and stirring was continued at room temperature. After complete turnover (IR monitoring) the mixture was added to saturated aqueous NH_4Cl solution. The organic layer was washed with 2 N HCl (3 × 40 mL). The combined aqueous layer was extracted with ethyl acetate (3 × 40 mL). The combined organic layer was washed with brine (50 mL) and dried ($MgSO_4$) and the solvent removed in vacuo.

Route B. According to route A, β-bromo-substituted *N*-sulfonyl imines can be prepared from β-bromovinyl aldehydes **1** and benzenesulfonamide as described for the synthesis of compound **3a**. Method B: to a solution of the β-bromo-substituted *N*-sulfonyl imine **3** (2.6 mmol) in THF (100 mL) was added [(η^5-C_5H_5)(CO)$_2$Fe]Na, prepared from [(η^5-C_5H_5)(CO)$_2$Fe]$_2$ and sodium amalgam in THF (65 mL) at −78 °C. The light-protected solution was stirred at −78 °C for 40 min, and then it was warmed to room temperature over a period of 145 min. The solvent was evaporated and the crude product purified by column chromatography on Florisil (6:1 to 2:1 petroleum ether/ethyl acetate).

9-Bromo-8-[{(phenylsulfonyl)imino}methyl]-6,7-dihydro-5*H*-benzo[*a*]cycloheptene (3a). According to the general procedure (method A) 2 g (7.96 mmol) of the β-bromo enal **1a** and 1.25 g (1 equiv) of benzenesulfonamide gave 3.28 g (quantitative) of crude **3a** as a yellow wax. After 2.5 h of stirring at room temperature workup was carried out by following the general procedure, except for washing with 2 N HCl. The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL); R_f = 0.65. ^{1}H NMR (200 MHz): δ 9.30 (s, 1H), 8.00–7.96 (dd, *J* = 7.3 Hz, *J* = 2.0 Hz, 2H), 7.67–7.50 (m, 4H), 7.38–7.28 (m, 2H), 7.21–7.17 (m, 1H), 2.62–2.55 (t, *J* = 7.3 Hz, 2H), 2.39–2.32 (t, *J* = 7.3 Hz, 2H), 2.18–2.04 (quintet, *J* = 6.9 Hz,

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[13] We thank one of the reviewers for the suggestions made, especially regarding the formation of the allyl complexes via a complexed ketene intermediate.

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2H). ^{13}C NMR (50.3 MHz): δ 170.4 (CH), 142.4 (C_{quat}), 140.6 (C_{quat}), 139.3 (C_{quat}), 136.7 (C_{quat}), 133.5 (CH), 130.8 (CH), 130.1 (CH), 129.2 (CH), 128.9 (CH), 128.1 (CH), 126.7 (CH), 33.4 (CH_2), 31.9 (CH_2), 25.4 (CH_2); IR (CH_2Cl_2): $\tilde{\nu}$ 1621, 1559 cm^{-1}. MS (FD): *m/z* (%) 394.4 (1.2), 393.4 (6.6), 392.4 (23.3), 391.4 (M^+, 100), 389.4 (M^+, 98.2). Anal. Calcd for $C_{18}H_{16}NO_2S \cdot {}^1/_8CH_2Cl_2$ (390.1): C, 54.35; H, 4.06; N, 3.50. Found: C, 54.76; H, 4.42; N, 3.68.

9-[(η^5-Cyclopentadienyl)dicarbonyliron]-8-{[(phenylsulfonyl)imino]methyl}-6,7-dihydro-5*H*-benzo[*a*]cycloheptene (4a). According to method A treatment of the enal **2a**[4] (850 mg, 2.44 mmol) gave 1.19 g (quantitative) of **4a** as a golden yellow foam. Complete turnover was detected after 50 min (IR monitoring). The combined aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL).

By following method B, treatment of the β-bromo-substituted *N*-sulfonyl imine **3a** (1 g, 2.56 mmol) with [(η^5-C_5H_5)(CO)$_2$Fe]Na, prepared from [{η^5-C_5H_5(CO)$_2$Fe}$_2$] (476 mg, 1.35 mmol) and sodium amalgam (4.12 g), afforded 832 mg (67%) of **4a** as a yellow solid.

Mp: 93−94 °C (dec). $R_f = 0.52$. ^{1}H NMR (200 MHz): δ 9.19 (s, 1H), 7.99−7.96 (d, J = 6.3 Hz, 2H), 7.59−7.49 (m, 3H), 7.24−7.21 (m, 1H), 7.12−6.98 (m, 3H), 5.09 (s, 5H), 2.92−2.86 (m, 1H), 2.41−2.32 (m, 1H), 2.16−2.06 (m, 1H), 1.85−1.64 (m, 3H). ^{13}C NMR (50.3 MHz): δ 214.6 (C_{quat}, CO), 212.5 (C_{quat}, CO), 200.3 (C_{quat}), 175.6 (CH), 155.7 (C_{quat}), 149.2 (C_{quat}), 139.7 (C_{quat}), 133.6 (C_{quat}), 132.8 (CH), 129.1 (CH), 128.6 (CH), 128.1 (CH), 127.7 (CH), 127.6 (CH), 126.9 (CH), 126.4 (CH), 126.1 (CH), 86.2 (CH), 31.9 (CH_2), 31.7 (CH_2), 26.6 (CH_2). IR (CH_2Cl_2): $\tilde{\nu}$ 2027, 1977, 1529 cm^{-1}. MS (FD): *m/z* (%) 459.2 (27.9, $M^+ -$ CO), 339.0 (46.7), 156.7 (100, $PhSO_2NH_2$). Anal. Calcd for $C_{25}H_{21}FeNO_4S$ (486.85)$\cdot$0.5CH_2Cl_2: C, 57.81; H, 4.16; N, 2.64. Found: C, 57.46; H, 4.06; N, 2.65.

2-[(η^5-Cyclopentadienyl)dicarbonyliron]-1-{[(phenylsulfonyl)imino]methyl}-3,4-dihydronaphthalene (4b). According to method A 1.385 g (4.15 mmol) of the enal **2b**[4] gave 1.96 g (quantitative) of **4b** as a yellow-brown amorphous solid. The reaction mixture was stirred for 16.5 h at room temperature before workup. $R_f = 0.42$. ^{1}H NMR (200 MHz): δ 9.34 (s, 1H), 8.01−7.97 (d, J = 8.3 Hz, 2H), 7.87−7.84 (d, J = 7.8 Hz, 1H), 7.58−7.46 (m, 3H), 7.19−7.04 (m, 3H), 5.05 (s, 5H), 3.06−2.99 (t, J = 6.8 Hz, 2H), 2.57−2.50 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100.6 MHz): δ 215.3 (C_{quat}), 213.5 (C_{quat}, CO), 175.9 (CH), 144.0 (C_{quat}), 139.9 (C_{quat}), 135.9 (C_{quat}), 132.8 (CH), 132.1 (C_{quat}), 129.0 (CH), 127.6 (CH), 126.4 (CH), 126.4 (CH), 126.2 (CH), 125.0, (CH), 86.5 (CH), 51.4 (CH_2), 29.4 (CH_2). IR (CH_2Cl_2): $\tilde{\nu}$ 2027, 1977, 1548 cm^{-1}. IR (KBr): $\tilde{\nu}$ 3054, 2986, 2019, 1968, 1535, 1446, 1422, 1346, 1164, 1088, 813, 800 cm^{-1}. MS (FD): *m/z* (%) 473.0 (M^+, 2.0), 447 (8.5), 446.0 (19.9), 445.0 ($M^+ -$ CO, 100), 443.0 (2.7), 389.0 (3.6), 324.9 (9.1).

2-[(η^5-Cyclopentadienyl)dicarbonyliron]-5-*tert*-butyl-1-[(phenylsulfonyl)iminomethyl]-1-cyclohexene (*rac*-4c). According to method A 1.93 g (5.65 mmol) of the enal **2c**[5] in 50 mL of CH_2Cl_2 gave 2.63 g (97%) of **4c** as a yellow amorphous solid. Complete turnover was detected after 5 h (IR monitoring). The combined aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). Mp: 105 °C dec. $R_f = 0.55$. ^{1}H NMR (400 MHz): δ 9.00 (s, 1H), 7.95−7.93 (d, J = 7.33 Hz, 2H), 7.57−7.54 (m, 1H), 7.51−7.47 (m, 2H), 4.88 (s, 5H), 3.07−3.02 (d, J = 19.6 Hz, 1H), 2.83−2.74 (m, 1H), 2.53−2.49 (d, J = 15.8 Hz, 1H), 2.03−1.97 (m, 1H), 1.63−1.59 (m, 1H), 1.23−1.11 (m, 2H), 0.82 (s, 9H). ^{13}C NMR (50.3 MHz, mixture of isomers or conformers, ratio: ~6:1, the asterisk denotes minor): δ 214.6, 214.4, 204.4, 177.7, 144.5, 139.8, 132.8*, 132.7, 129.2*, 129.0, 127.7, 126.5*, 86.4, 54.4, 44.0, 32.4, 30.5, 27.7, 27.2. IR (CH_2Cl_2): $\tilde{\nu}$ 2022, 1969, 1525 cm^{-1}. IR (KBr): $\tilde{\nu}$ 2961, 2868, 2017, 1964, 1755, 1720, 1636, 1525, 1478, 1448, 1365, 1331, 1307, 1237, 1155, 1089, 811, 593 cm^{-1}. MS (FD): *m/z* (%) 937.6 (1.7), 936.9 (3.9), 935.7 (25.7), 934.7 (2 $M^+ -$ CO, 59.9), 455.1 (1.8), 454.1 (28.5), 453.1 ($M^+ -$ CO, 100), 451.1 (1.5). Anal. Calcd for $C_{24}H_{27}FeNO_4S$ (480.85): C, 59.89; H, 5.62; N, 2.91. Found: C, 59.73; H, 5.74; N, 2.83.

2-[(η^5-Cyclopentadienyl)dicarbonyliron]-1-{[(phenylsulfonyl)imino]methyl}cyclopentene (4d). According to method A 1.23 g (4.52 mmol) of the enal **2d**[5] in 50 mL of CH_2Cl_2 gave 1.86 g (quantitative) of **4d** as a yellow foam. The reaction mixture was stirred for 200 min at room temperature. The combined aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). Mp: 161 °C dec. ^{1}H NMR ([D_6]-DMSO, 200 MHz): δ 8.71 (s, 1H), 7.85−7.82 (d, J = 7.8 Hz, 2H), 7.71−7.58 (m, 3H), 5.13 (s, 5H), 2.89−2.82 (t, J = 7.3 Hz, 2H), 2.43−2.35 (t, J = 7.3 Hz, 2H), 1.81−1.66 (quintet, J = 7.3 Hz, 2H). ^{1}H NMR (200 MHz): δ 8.93 (s, 1H), 7.94−7.90 (d, J = 7.8 Hz, 2H), 7.55−7.44 (m, J = 7.8 Hz, 3H), 4.88 (s, 5H), 2.88−2.81 (t, J = 7.3 Hz, 2H), 2.57−2.50 (t, J = 7.3 Hz, 2H), 1.87−1.72 (quintet, J = 7.3 Hz, 2H). ^{13}C NMR (50.3 MHz): δ 214.0, 210.5, 170.9, 139.9, 132.6, 129.1, 128.9, 127.6, 126.4, 85.7, 56.4, 32.0, 24.2. IR (CH_2Cl_2): $\tilde{\nu}$ 2027, 1976, 1536 cm^{-1}. IR (KBr): $\tilde{\nu}$ 3117, 2967, 2021, 1969, 1529, 1447, 1347, 1318, 1304, 1290, 1156, 1088, 813, 743, 589, 555 cm^{-1}. MS (FD): *m/z* (%) 411 (M^+, 2.33%), 382.9 ($M^+ -$ CO, 100%). Anal. Calcd for $C_{19}H_{17}FeNO_4S \cdot {}^1/_8CH_2Cl_2$ (410.85): C, 54.04; H, 4.27; N, 3.32. Found: C, 53.93; H, 4.26; N 3.29. Recrystallization from CH_2Cl_2/petroleum ether furnished brown-yellow crystals.

4-[(η^5-Cyclopentadienyl)dicarbonyliron]-3-{[(phenylsulfonyl)imino]methyl}-(2*H*)-chromene (4e). According to method A 500 mg (1.49 mmol) of the enal **2e**[4] gave 708 mg (quantitative) of **4e** as a yellow amorphous solid. Complete turnover was detected after 100 min (IR monitoring). The combined aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). Mp: 167 °C (dec). $R_f = 0.39$. ^{1}H NMR (400 MHz): δ 9.19 (s, 1H), 7.96−7.94 (dd, J = 7.6 Hz, J = 1.2 Hz, 2H), 7.64−7.62 (dd, J = 7.9 Hz, J = 1.2 Hz, 1H), 7.58−7.56 (d, J = 7.3 Hz, 1H), 7.53−7.49 (t, J = 7.5 Hz, 2H), 7.22−7.18 (m, 1H), 7.05−6.95 (m, 1H), 6.86−6.84 (d, J = 7.9 Hz, 1H), 5.11 (s, 5H), 4.75−4.3 (br s, 2H). ^{1}H NMR ([D_6]-DMSO, 200 MHz): δ 8.90 (s, 1H), 7.93−7.89 (d, J = 6.8 Hz, 2H), 7.83−7.71 (m, J = 6.8 Hz, 3H), 7.35−7.23 (m, J = 7.3 Hz, 2H), 7.10−7.03 (m, 1H), 6.87−6.83 (d, J = 7.8 Hz, 1H), 5.33 (s, 5H), 5.0−4.65 (br s, 1H), 4.5−4.2 (br s, 1H). ^{13}C NMR (100.6 MHz): δ 213.6, 189.3, 173.0, 153.8, 141.7, 139.5, 136.1, 135.0, 132.9, 131.6, 129.0, 127.7, 121.2, 116.5, 86.6, 65.8. ^{13}C NMR ([D_6]-DMSO, 50.3 MHz): δ 213.6, 189.7, 173.0, 153.7, 141.7, 139.4, 136.1, 135.0, 133.0, 131.6, 129.1, 127.6, 121.2, 116.5, 86.6, 65.7. IR (KBr): $\tilde{\nu}$ 3112, 3070, 2854, 2030, 2021, 1970, 1521, 1494, 1322, 1302, 1285, 1158, 1085, 816, 734, 607, 585, 560 cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ 2030, 1980, 1526 cm^{-1}. MS (FAB): *m/z* (%) 476.0 ($M^+ + H^+$, 19.4), 418.9 ($M^+ -$ 2CO, 11.4), 306.9 (31.9), 153.6 (100, $PhSO_2N$). Anal. Calcd for $C_{23}H_{17}FeNO_5S \cdot 0.25\ CH_2Cl_2$ (475.02): C, 56.27; H, 3.38; N, 2.75. Calcd: C, 56.25; H, 3.53; N, 2.82. Recrystallization from $CHCl_3$/petroleum ether furnished yellow crystals.

4-[(η^5-Cyclopentadienyl)dicarbonyliron]-3-{[(*o*-benzoic acid (−)-menthyl ester)sulfonyl]iminomethyl}-(2*H*)-chromene (4f). According to method A 638 mg (1.90 mmol) of the enal **2e**[4] and 627 mg (1.86 mmol) of 2-sulfamylbenzoic acid (−)-menthyl ester gave 789 mg (65%) of crude **4f** as a golden yellow foam. After 5 h of stirring at room temperature another 0.4 equiv of $TiCl_4$ and then 0.21 mL (1.86 mmol, 2 equiv) of orthoformic acid trimethyl ester were added to the reaction mixture (IR monitoring) to complete turnover. The product was purified by flash chromatography with petroleum ether/ethyl acetate (4:1 to ethyl acetate) to yield 644 mg (53%) of **4f**. Mp: 175 °C dec. Recrystallization from CH_2Cl_2/petroleum ether furnished brown-yellow crystals. $\alpha_D^{20} = -38.9°$ (c = 0.1; CH_2Cl_2). $R_f = 0.5$. ^{1}H NMR (400 MHz): δ 9.02 (s, 1H), 8.26−8.24 (m, 1H), 7.64−7.62 (m, 3H), 7.59−7.58 (m, 1H), 7.21−7.17 (dt, J = 7.3 Hz, J = 1.2 Hz, 1H), 7.01−6.97 (t, J = 7.3 Hz, 1H), 6.86−6.84 (d, J = 8.2 Hz, 1H), 5.15 (s, 5H), 4.89−4.83 (dt, J = 11.2 Hz, J = 4.1 Hz, 1H), 4.70−4.30 (br s, 2H), 2.30−2.20 (m, 1H), 2.08−2.04 (m, 1H), 1.72−1.65 (m, 1H), 1.54−1.48 (m, 1H), 1.46−1.38 (m, 1H), 1.19−1.00 (m, 2H), 0.95−0.88 (m, 8H), 0.82−0.80 (d, J = 7.0 Hz, 3H). ^{13}C NMR (50.3 MHz): δ 213.4 ($\mathrm{C_{quat}}$, CO), 188.6 ($\mathrm{C_{quat}}$), 173.2 (CH), 166.6 ($\mathrm{C_{quat}}$), 153.8 ($\mathrm{C_{quat}}$), 142.1 ($\mathrm{C_{quat}}$), 137.5 ($\mathrm{C_{quat}}$), 136.3 ($\mathrm{C_{quat}}$), 135.0 (CH), 133.4 ($\mathrm{C_{quat}}$), 132.8 (CH), 131.3 (CH), 130.9 (CH), 128.9 (CH), 122.0 (CH), 116.5 (CH), 86.6 (CH), 76.2 (CH), 65.9 ($\mathrm{CH_2}$), 47.0 (CH), 40.5 ($\mathrm{CH_2}$), 34.2 ($\mathrm{CH_2}$), 31.6 (CH), 26.2 (CH), 23.3 ($\mathrm{CH_2}$), 22.0 ($\mathrm{CH_3}$), 20.9 ($\mathrm{CH_3}$), 16.1 ($\mathrm{CH_3}$). IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ 2030, 1980, 1723, 1524 cm^{-1}. IR (KBr): $\tilde{\nu}$ 2956, 2928, 2869, 2025, 1975, 1723, 1523 cm^{-1}. MS (FAB): m/z (%) 658.6 ($\mathrm{M^+ + H^+}$, 77.3), 601.5 ($\mathrm{M^+ - 2CO}$, 55.9), 277.8 (100). Anal. Calcd for $\mathrm{C_{34}H_{35}FeNO_7S}$ (656.85): C, 62.11; H, 5.33; N, 2.13; S, 4.87; Found: C, 61.84; H, 5.79; N, 1.86; S, 4.85.

2-Sulfamylbenzoic acid (−)-menthyl ester was prepared according to the following procedure: a solution of 15.16 g (76 mmol) *o*-sulfamidobenzoic acid, 17.9 g (1.5 equiv, 114 mmol) of (−)-menthol and 2 g (11 mmol) of *p*-toluenesulfonic acid in 400 mL of tetrachloromethane was refluxed (Dean and Stark separator) for 84 h.[15] The collected water was removed occasionally. After this time 5 drops of $\mathrm{H_2SO_4}$ was added to the suspension and the mixture was refluxed for another 24 h. The solvent was removed and the product mixture separated by flash chromatography (silica gel, 6:1 to 2:1 petroleum ether/ethyl acetate) to yield 2.37 g (9.5%) of a colorless solid. Mp: 89−90 °C. R_f = 0.56. $\alpha_D^{20} = -47.3°$ (c = 0.1; $\mathrm{CH_2Cl_2}$). ^{1}H NMR (200 MHz): δ 8.13−8.07 (m, 1H), 7.79−7.73 (m, 1H), 7.65−7.56 (m, 2H), 5.74 (br s, 2H, $\mathrm{NH_2}$), 5.04−4.91 (dt, J = 10.7 Hz, J = 4.4 Hz, 1H), 2.19−2.11 (m, 1H), 2.07−1.91 (m, 1H), 1.76−1.69 (m, 2H), 1.60−1.47 (m, 2H), 1.18−1.00 (m, 2H), 0.94−0.89 (m, 7H), 0.83−0.79 (d, J = 6.9 Hz, 3H). ^{13}C NMR (50.3 MHz): δ 167.4 ($\mathrm{C_{quat}}$, C=O), 141.4 ($\mathrm{C_{quat}}$), 132.3 (CH), 131.7 (CH), 131.0 ($\mathrm{C_{quat}}$), 130.3 (CH), 128.3 (CH), 77.0 (CH), 47.1 (CH), 40.5 ($\mathrm{CH_2}$), 34.2 ($\mathrm{CH_2}$), 31.5 (CH), 26.3 (CH), 23.3 ($\mathrm{CH_2}$), 22.0 ($\mathrm{CH_3}$), 20.8 ($\mathrm{CH_3}$), 16.1 ($\mathrm{CH_3}$). IR (KBr): $\tilde{\nu}$ 3365, 3256, 3087, 2959, 2946, 2925, 1718, 1458, 1356, 1299, 1273, 1151, 1140, 1121, 1063, 1056, 952, 758, 732, 717 cm^{-1}. Anal. Calcd for $\mathrm{C_{17}H_{25}NO_4S}$ (337.9): C, 60.37; H, 7.40; N, 4.14. Found: C, 60.19; H, 7.30; N, 4.09.

General Procedure for the Synthesis of the α,*β*-Unsaturated *γ*-Lactams 5, 6, and 8. Method A: Addition of Organolithium Reagents. To a light-protected solution of the *N*-sulfonyl imine **4** in 15−20 mL of THF was added 1.1 equiv of the organolithium reagent at −78 or 0 °C. After removal of the cold bath the reaction mixture was stirred at room temperature. After complete turnover (IR monitoring), the reaction mixture was worked up according to method B unless otherwise noted.

Method B: Addition of Grignard Reagents. To a light-protected solution of the *N*-sulfonyl imine **4** in 10−25 mL of $\mathrm{CH_2Cl_2}$ was added 2.05 equiv of the Grignard reagent at room temperature. After complete turnover (IR monitoring), the mixture was added to an aqueous saturated $\mathrm{NH_4Cl}$ solution with stirring. After phase separation, the aqueous layer was extracted with ethyl acetate (3 × 40 mL). The combined organic layer was dried ($\mathrm{MgSO_4}$) and the solvent evaporated. The crude product was purified by flash chromatography (silica gel, 15:1 to 2:1 petroleum ether/ethyl acetate, then ethyl acetate unless otherwise noted).

5′-*n*-Butyl-*N*-(phenylsulfonyl)-4,5,6-trihydro-3*H*-benzo[3,4]cyclohepta[1,2-*c*]pyrrol-1′-one (5a). According to method A treatment of the imine **4a** (500 mg, 1.03 mmol) with *n*BuLi gave 173 mg (43%) of **5a** as a yellow oil. The addition of *n*BuLi was carried out at −78 °C. Stirring was continued at −78 °C for 20 h and at room temperature for 23 h. R_f = 0.76. ^{1}H NMR (200 MHz): δ 8.17−8.12 (dd, J = 7.6 Hz, J = 1.5 Hz, 2H), 7.97−7.93 (dd, J = 7.3 Hz, J = 2.0 Hz, 1H), 7.65−7.46 (m, 3H), 7.28−7.08 (m, 3H), 4.82−4.79 (dd, J = 7.3 Hz, J = 2.9 Hz, 1H), 2.68−2.60 (q, J = 4.9 Hz, 2H), 2.52−2.35 (t, J = 7.3 Hz, 3H), 2.15−2.06 (m, 2H), 1.99−1.77 (m, 2H), 1.23−1.07 (m, 2H), 0.87−0.77 (m, 1H), 0.75−0.68 (t, J = 7.3 Hz, 3H). ^{13}C NMR (50.3 MHz): δ 168.5 ($\mathrm{C_{quat}}$, C=O), 160.6 ($\mathrm{C_{quat}}$), 142.5 ($\mathrm{C_{quat}}$), 139.2 ($\mathrm{C_{quat}}$), 133.7 (CH), 129.2 ($\mathrm{C_{quat}}$), 129.2 ($\mathrm{C_{quat}}$), 129.1 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.0 (CH), 126.2 (CH), 63.9 (CH), 33.9 ($\mathrm{CH_2}$), 30.0 ($\mathrm{CH_2}$), 28.9 ($\mathrm{CH_2}$), 28.7 ($\mathrm{CH_2}$), 23.4 ($\mathrm{CH_2}$), 22.4 ($\mathrm{CH_2}$), 13.9 ($\mathrm{CH_3}$). IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ 1718 cm^{-1}. MS (FD): m/z (%) 396.1 (17), 395.1 ($\mathrm{M^+}$, 100); $\mathrm{C_{23}H_{25}NO_3S}$. HR-MS (EI): m/z found 395.1541, calcd 395.1549.

5′-Methyl-*N*-(phenylsulfonyl)-4,5,6-trihydro-3*H*-benzo[3,4]cyclohepta[1,2-*c*]pyrrol-1′-one (5b). According to method A treatment of the imine **4a** (564 mg, 1.16 mmol) with MeLi gave 222 mg (54%) of **5b** as a light yellow solid. The reaction mixture was stirred for 23 h at room temperature before workup. Mp: 127−129 °C. R_f = 0.58. ^{1}H NMR (400 MHz): δ 8.13−8.11 (dd, J = 7.3 Hz J = 1.5 Hz, 2H), 7.89−7.87 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H), 7.61−7.57 (t, J = 7.3 Hz, 1H), 7.53−7.49 (t, J = 7.3 Hz, 2H), 7.24−7.16 (m, 2H), 7.11−7.10 (d, J = 7.1 Hz, 1H), 4.72−4.67 (q, J = 6.8 Hz, 1H), 2.67−2.53 (m, 3H), 2.50−2.42 (m, 1H), 2.19−2.02 (m, 2H), 1.67−1.65 (d, J = 6.5 Hz, 3H). ^{13}C NMR (50.3 MHz): δ 167.9 ($\mathrm{C_{quat}}$, CO), 162.7 ($\mathrm{C_{quat}}$), 142.3 ($\mathrm{C_{quat}}$), 139.2 ($\mathrm{C_{quat}}$), 133.7 (CH), 129.1 ($\mathrm{C_{quat}}$), 128.9 (CH), 128.8 (CH), 128.3 (CH), 128.1 (CH), 126.1 (CH), 60.1(CH), 33.7 ($\mathrm{CH_2}$), 29.1 ($\mathrm{CH_2}$), 28.5 ($\mathrm{CH_2}$), 19.5 ($\mathrm{CH_3}$); one quaternary signal and one tertiary signal in the aromatic region are overlapped by the adjacent tertiary signals. IR (KBr): $\tilde{\nu}$ 3018, 2999, 2943, 2869, 1707, 1664, 1449, 1356, 1340, 1330, 1184, 1169, 1157, 1091 cm^{-1}. IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ 1721 cm^{-1}. MS (FD): m/z (%) 356.3 (0.7), 355.3 (3.2), 354.3 (14), 353.2 ($\mathrm{M^+}$, 100); $\mathrm{C_{20}H_{19}NO_3S}$ (353.0). HR-MS (EI): m/z found 353.1099, calcd 353.1086.

5′-Allyl-*N*-(phenylsulfonyl)-4,5,6-trihydro-3*H*-benzo[3,4]cyclohepta[1,2-*c*]pyrrol-1′-one (5c). According to method B treatment of the imine **4a** (256 mg, 0.53 mmol) with allylmagnesium chloride gave 83 mg (42%) of **5c** as a yellow oil. The solution was stirred for 22.5 h at room temperature before workup. R_f = 0.64. ^{1}H NMR (400 MHz): δ 8.16−8.14 (d, J = 7.4 Hz, 2H), 7.91−7.89 (dd, J = 7.3 Hz, J = 1.5 Hz, 1H), 7.62−7.59 (t, J = 7.3 Hz, 1H), 7.54−7.50 (t, J = 7.3 Hz, 2H), 7.23−7.16 (m, 2H), 7.12−7.10 (d, J = 7.0 Hz, 1H), 5.34−5.24 (m, J = 15.8 Hz, J = 9.1 Hz, J = 7.6 Hz, 1H, C*H*=CH$_2$), 5.05−5.01 (dd, J = 15.8 Hz, J = 1.2 Hz, 1H), 4.98−4.95 (d, J = 10.3 Hz, 1H), 4.83−4.81 (dd, J = 7.3 Hz, J = 0.9 Hz, 1H), 3.30−3.23 (m, 1H), 2.68−2.42 (m, 5H), 2.12−2.06 (quintet, J = 7.0 Hz, 2H). ^{13}C NMR (50.3 MHz): δ 168.4 ($\mathrm{C_{quat}}$, CO), 160.3 ($\mathrm{C_{quat}}$), 142.6 ($\mathrm{C_{quat}}$), 139.1 ($\mathrm{C_{quat}}$), 133.8 (CH), 129.6 (CH), 129.2 ($\mathrm{C_{quat}}$), 129.0 (CH), 129.0 (CH), 128.8 (CH), 128.4 (CH), 128.2 (CH), 126.2 (CH), 120.0 ($\mathrm{CH_2}$), 63.3 (CH), 34.9 ($\mathrm{CH_2}$), 33.8 ($\mathrm{CH_2}$), 28.9 ($\mathrm{CH_2}$), 28.8 ($\mathrm{CH_2}$); one quaternary signal of the aromatic region is overlapped by the adjacent tertiary signal. IR (KBr): $\tilde{\nu}$ 3067, 2961, 2932, 1718 cm^{-1}. IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ 1721 cm^{-1}. MS (FD): m/z (%) 381.0 (6.3), 379.9 (22.8), 378.9 ($\mathrm{M^+}$, 100); $\mathrm{C_{22}H_{21}NO_3S}$ (379.1). HR-MS (EI): m/z found 379.1242, found 379.1242.

Reaction of 4b with (allyl)MgCl. According to method B 561 mg (1.19 mmol) of the imine **4b** gave 161 mg (37%) of **5d** and 111 mg (41%) of **6d** as yellow oils. The solution was stirred for 22 h at room temperature before workup.

1-Allyl-1,2,3,4,5-pentahydro-*N*-(phenylsulfonyl)benzo[*e*]isoindol-3-one (5d). R_f = 0.74. ^{1}H NMR (200 MHz): δ 8.16−8.13 (d, J = 6.8 Hz, 2H), 7.65−7.46 (m, 3H), 7.33−7.14 (m, 4H), 5.35−5.30 (dd, J = 6.4 Hz, J = 2.9 Hz, 1H), 5.23−5.06 (m, J = 7.3 Hz, J = 9.8 Hz, J = 14.4 Hz, 1H, C*H*=CH$_2$), 4.84−4.79 (dd, J = 10.3 Hz, J = 1.2 Hz, 1H), 4.70−4.61 (dd, J = 6.6 Hz, J = 1.2 Hz, 1H), 3.30−3.17 (m, 1H), 2.87−2.51 (m, 4H), 2.37−2.21 (m, 1H). ^{13}C NMR (50.3 MHz): δ 168.5, 153.5, 139.9, 138.2, 133.8, 130.8, 130.2, 129.2, 129.0, 129.0, 128.8, 128.1, 127.1, 124.2, 120.2, 61.0, 35.4, 27.9, 18.0. IR ($\mathrm{CH_2Cl_2}$): $\tilde{\nu}$ 1719 cm^{-1}. MS (FD): m/z (%) 368.0 (1.2), 367.0 (7.0), 366.0 (24.2), 365.0 ($\mathrm{M^+}$, 100), 269.9 (2.4); $\mathrm{C_{21}H_{19}NO_3S}$ (365.0). HR-MS (EI): m/z found 365.1070, calcd 365.1081.

1-Allyl-1,2,3,4,5-pentahydrobenzo[*e*]isoindol-3-one (6d). R_f = 0.1. ^{1}H NMR (200 MHz): δ 7.26−7.21 (m, 3H), 7.18−7.13 (m, 1H), 6.48 (br s, 1H, NH), 5.88−5.67 (m, J = 7.4 Hz, J =

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10.2 Hz, J = 15.1 Hz, 1H, CH=CH_2), 5.15 (s, 1H), 5.10−5.07 (d, J = 5.9 Hz, 1H), 4.57−4.53 (m, 1H), 2.95−2.88 (m, 2H), 2.78−2.72 (m, 1H), 2.69−2.61 (m, 1H), 2.43−2.33 (m, 1H), 2.29−2.10 (m, 1H). ^{13}C NMR (50.3 MHz): δ 173.0 (C_{quat}, C=O), 152.0 (C_{quat}), 137.6 (C_{quat}), 133.0 (CH), 132.0 (C_{quat}), 129.4 (CH), 129.3 (C_{quat}), 128.6 (CH), 126.8 (CH), 123.4 (CH), 119.0 (CH_2), 55.6 (CH), 38.0 (CH_2), 28.3 (CH_2), 18.3 (CH_2). IR (CH_2Cl_2): $\tilde{\nu}$ 1690 cm^{-1}. MS (FD): m/z (%) 226.9 (0.5), 225.9 (16.1), 224.8 (M^+, 100), 223.8 (1.0), 222.8 (2.9); $C_{15}H_{15}NO$ (225.0). HR-MS (EI): m/z found 225.1142, calcd 225.1150.

Reaction of 4b with *n*PrMgCl. According to method B 560 mg (1.18 mmol) of the imine **4b** gave 108 mg (25%) of **5e** and 66 mg (25%) of **6e** as yellow oils. After having been stirred for 20 h 40 min at room temperature another 0.6 equiv of the Grignard reagent was added due to incomplete turnover (IR monitoring). Stirring was continued, and after 8.5 h the reaction mixture was added to a buffer solution (pH 6, 60 mL) with stirring. The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL).

1,2,3,4,5-Pentahydro-*N*-(phenylsulfonyl)-1-*n*-propylbenzo[*e*]isoindol-3-one (5e). R_f = 0.67. ^{1}H NMR (400 MHz): δ 8.15−8.11 (dd, J = 7.8 Hz, J = 2.0 Hz, 2H), 7.61−7.48 (m, 3H), 7.32−7.20 (m, 4H), 5.34−5.32 (dd, J = 3.9 Hz, J = 1.0 Hz, 1H), 2.90−2.80 (m, 2H), 2.67−2.56 (m, 1H), 2.49−2.23 (m, 2H), 2.03−1.84 (m, 1H), 0.85−0.81 (m, 1H), 0.78−0.68 (m, 1H), 0.65−0.60 (m, 3H). ^{13}C NMR (50.3 MHz): δ 168.6 (C_{quat}, C=O), 153.9 (C_{quat}), 139.4 (C_{quat}), 138.1 (C_{quat}), 133.7 (CH), 130.7 (CH), 129.8 (C_{quat}), 129.0 (CH), 128.8 (CH), 128.1 (C_{quat}), 127.9 (CH), 127.1 (CH), 124.2 (CH), 61.7 (CH), 33.0 (CH_2), 27.9 (CH_2), 18.0 (CH_2), 14.7 (CH_2), 13.5 (CH_3). IR (CH_2Cl_2): $\tilde{\nu}$ 1718 cm^{-1}. MS (FD): m/z (%) 370.1 (1.0), 369.1 (13.6), 368.1 (18.5), 367.1 (M^+, 100), 366.1 (0.8); $C_{21}H_{21}NSO_3$ (367).

1,2,3,4,5-Pentahydro-1-*n*-propylbenzo[*e*]isoindol-3-one (6e). R_f = 0.11. ^{1}H NMR (200 MHz): δ 7.25−7.11 (m, 4H), 6.47 (br s, 1H), 4.56 (m, 1H), 2.92−2.87 (m, 2H) 2.71−2.62 (m, 1H), 2.47−2.34 (m, 1H), 1.93−1.88 (m, 1H), 1.55−1.29 (m, 3H), 0.94−0.82 (m, 3H). ^{13}C NMR (50.3 MHz): δ 173.3, 152.7, 137.6, 131.5, 129.6, 129.3, 128.5, 126.7, 123.5, 56.2, 35.7, 28.3, 18.7, 18.3, 13.9. IR (CH_2Cl_2): $\tilde{\nu}$ 1687 cm^{-1}. MS (FD): m/z (%) 228.0 (21.1), 227.0 (M^+, 100); $C_{15}H_{17}NO$ (227.0). HR-MS (EI): m/z found 227.1306, calcd 227.1310.

Reaction of 4b with MeLi. According to method A 500 mg (1.057 mmol) of the imine **4b** gave 159 mg (44%) of **5f** and 119 mg (56%) of **6f** as yellow oils. The mixture was stirred for 19.5 h at room temperature before the reaction mixture was added to a buffer solution (pH 6, 60 mL) and worked up as described before for **5d** and **6d**. The crude product was purified by flash chromatography on Florisil (20:1 petroleum ether/ethyl acetate (1% NEt_3) to ethyl acetate and then acetone).

1-Methyl-1,2,3,4,5-pentahydro-*N*-(phenylsulfonyl)benzo[*e*]isoindol-3-one (5f). R_f = 0.52. ^{1}H NMR (200 MHz): δ 8.14−8.10 (dd, J = 7.8 Hz, J = 1.5 Hz, 2H), 7.61−7.48 (m, 3H), 7.35−7.15 (m, 4H), 5.22−5.16 (m, 1H), 2.91−2.83 (dd, J = 5.9 Hz, J = 4.9 Hz, 2H), 2.65−2.51 (m, 1H), 2.40−2.26 (m, 1H), 1.71−1.68 (d, J = 6.3 Hz, 3H). ^{13}C NMR (50.3 MHz): δ 168.2 (C_{quat}, CO), 155.9 (C_{quat}), 139.5 (C_{quat}), 138.2 (C_{quat}), 133.7 (CH), 130.7 (CH), 129.0 (CH), 128.9 (CH), 128.7 (C_{quat}), 128.1 (CH), 128.0 (C_{quat}), 127.1 (CH), 124.3 (CH), 57.9 (CH), 27.8 (CH_2), 20.4 (CH_2), 17.9 (CH_3). IR (CH_2Cl_2): $\tilde{\nu}$ 1718 cm^{-1}. MS (FD): m/z (%) 342.0 (0.9), 341.0 (6.2), 340.0 (20.0), 339.0 (M^+, 100), 337.0 (3.0); $C_{19}H_{17}NO_3S$ (339.0). HR-MS (EI): m/z found 339.0916, calcd 339.0929.

1-Methyl-1,2,3,4,5-pentahydrobenzo[*e*]isoindol-3-one (6f). R_f = 0.05. ^{1}H NMR (400 MHz): δ 7.27−7.21 (m, 3H), 7.14−7.12 (m, 1H), 7.09 (br s, 1H), 4.57 (m, 1H), 2.94−2.86 (m, 2H), 2.69−2.63 (m, 1H), 2.45−2.35 (m, 1H), 1.46−1.44 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100.6 MHz): δ 173.1 (C_{quat}, C=O), 154.1 (C_{quat}), 137.7 (C_{quat}), 131.0 (C_{quat}), 129.4 (CH), 129.1 (C_{quat}), 128.6 (CH), 126.7 (CH), 123.6 (CH), 52.2 (CH), 28.2 (CH_2), 19.8 (CH_2), 18.2 (CH_3). IR (CH_2Cl_2): $\tilde{\nu}$ 1691 cm^{-1}. MS (FD): m/z (%) 198.9 (M^+, 100), 196.9 (11.4); $C_{13}H_{13}NO$ (199.0). HR-MS (EI): m/z found 199.0999, calcd 199.0997.

3-*n*-Butyl-5-*tert*-butyl-*N*-(phenylsulfonyl)-4,5,6,7-tetrahydro-1(3*H*)-isobenzopyrrolone (5g). According to method A treatment of the imine ***rac*-4c** (880 mg, 1.83 mmol) with *n*BuLi gave 252 mg (35.5%, isomeric mixture ~2.5:1 (^{13}C NMR)) of **5g** as a yellow oil. The reaction mixture was stirred at 0 °C (90 min) and at room temperature (2 h). The reaction mixture was added to a buffer solution (pH 6, 80 mL), and the aqueous layer was extracted with ethyl acetate (3 × 40 mL). R_f = 0.78. ^{1}H NMR (200 MHz): δ 8.09−8.05 (dd, J = 8.3 Hz, J = 1.5 Hz, 2H), 7.62−7.44 (m, 3H), 4.70 (m, 1H), 2.37−2.11 (m, 3H), 1.96−1.71 (m, 4H), 1.69−1.67 (d, J = 2.9 Hz, 1H), 1.16−0.94 (m, 3H), 0.88 (s, 9H), 0.77−0.56 (m, 5H). ^{13}C NMR (50.3 MHz, the asterisk denotes minor): δ 169.3 (C_{quat}, C=O), 159.6*, 159.4 (C_{quat}), 139.5 (C_{quat}), 133.6 (CH), 130.9, 130.7* (C_{quat}), 128.9 (CH), 127.8 (CH), 64.6*, 64.1 (CH), 44.3, 43.9* (CH), 32.3 (C_{quat}), 29.7, 29.2* (CH_2), 27.2 (CH_3), 25.7*, 24.9 (CH_2), 23.5 (CH_2), 23.2 (CH_2), 22.3 (CH_2), 20.9 (CH_2), 13.8 (CH_3). IR (CH_2Cl_2): $\tilde{\nu}$ 1720 cm^{-1}. MS (FD): m/z (%) 392.1 (3.1), 391.1 (8.0), 390.1 ($M^+ + H^+$, 41), 389.1 (M^+, 3.9), 388.1 (3.8), 335.0 (0.8), 334.0 (5.4), 333.0 (23.4), 332.0 ($M^+ - C_4H_9$, 100); $C_{22}H_{31}NO_3S$ (389).

3-Allyl-5-*tert*-butyl-*N*-(phenylsulfonyl)-4,5,6,7-tetrahydro-1(3*H*)isobenzopyrrolone (5h). According to method C treatment of the imine ***rac*-4c** (500 mg, 1.04 mmol) gave 295 mg (76%, isomeric mixture ~2:1 (^{13}C NMR)) of **5h** as a yellow oil. The reaction was carried out in 1,2-dichloroethane (13 mL), and the reaction mixture was heated to 50 °C for 6 h before stirring was continued for 17 h at room temperature. R_f = 0.66. ^{1}H NMR (200 MHz): δ 8.09−8.04 (m, 2H), 7.63−7.45 (m, 3H), 5.36−5.09 (m, J = 7.3 Hz, J = 10.3 Hz, J = 14.2 Hz, 1H, CH=CH_2), 5.03−4.88 (m, 2H), 4.67−4.65 (m, 1H), 3.17−3.00 (m, 1H), 2.59−2.49 (m, 1H), 2.34−2.13 (m, 2H), 2.01−1.83 (m, 2H), 1.38−0.94 (m, 3H), 0.86 (s, 9H). ^{13}C NMR (50.3 MHz, the asterisk denotes minor): δ 169.2 (C_{quat}, C=O), 159.3, 159.1* (C_{quat}), 139.3 (C_{quat}), 133.7 (CH), 131.3*, 131.0 (C_{quat}), 129.9 (CH), 128.9 (CH), 128.0 (CH), 119.6, 119.5* (CH_2), 63.8, 63.3* (CH), 44.1*, 44.0 (CH), 34.7*, 34.3 (CH_2), 27.2 (CH_3), 26.0 (CH_2), 25.2 (CH_2), 23.1 (CH_2), 20.9 (CH_2). IR (CH_2Cl_2): $\tilde{\nu}$ 1723 cm^{-1}. MS (FD): m/z (%) 377.2 (1.3), 375.1 (8.9), 374.1 (M^+, 54.2), 373.1 (25.1), 372.1 (0.8), 319.0 (1.0), 318.0 (2.7), 317.0 (22.0), 316.0 ($M^+ - C_4H_9$, 100), 314.9 (1.3); $C_{21}H_{27}NO_3S$ (374.0). HR-MS (EI): m/z found 374.1774, calcd 374.1783.

1-Allyl-1-(aminomethyl)-2-[cyclopentadienyldicarbonyliron]-*N*-phenylsulfonylcyclopentene 7. According to method B treatment of the imine **4d** (280 mg, 0.68 mmol) with 1.5 equiv of (allyl)MgCl gave 194 mg (63%) of **7** as a yellow oil, which solidified on standing at 4 °C. The reaction mixture was stirred for 1 h (IR monitoring). The combined aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). Purification of the crude product was performed by column chromatography. R_f = 0.61. ^{1}H NMR (200 MHz): δ 7.87−7.84 (d, J = 6.3 Hz, 2H), 7.54−7.47 (m, 3H), 5.75−5.54 (m, J = 6.8 Hz, J = 9.8 Hz, 1H, CH=CH_2), 5.02−5.01 (d, J = 2.9 Hz, 1H), 4.95 (s, 1H), 4.81 (s, 5H), 4.51−4.48 (d, J = 6.3 Hz, 1H), 4.39−4.29 (m, 1H), 2.28−2.13 (m, 6H), 1.73−1.67 (m, 1H), 1.48−1.38 (m, 1H). ^{13}C NMR (50.3 MHz): δ 216.4, 215.4, 145.4, 142.0, 140.1, 134.7, 132.3, 128.8, 126.9, 117.8, 85.5, 57.4, 51.6, 39.9, 31.8, 24.4. IR (CH_2Cl_2): $\tilde{\nu}$ 2010, 1953, 1536 cm^{-1}. Anal. Calcd for $C_{22}H_{23}FeNO_4S$ (452.85): C, 58.30; H, 5.08; N, 3.09; Found: C, 58.30; H, 5.42; N, 2.91.

{(1−3-η^3)-[2,3:3′,4′]-([3:3′]-*o*-Hydroxyphenyl)-5′-(prop-2′′-en-1′′yl)(1′-phenylsulfonyl)-1′,5′-dihydro-2′*H*-pyrrol-2′-one}-carbonylcyclopentadienyliron (8a). According to method B treatment of the imine **4e** (540 mg, 1.137 mmol) with 1.6 equiv of (allyl)MgCl gave 494 mg (84%) of **8a** as an orange-red solid. Recrystallization of **8a** in CH_2Cl_2/petroleum ether gave deep red crystals. After addition of the Grignard reagent to the reaction mixture at room temperature an immediate change in color and a temperature increase was observed. The reaction mixture was stirred for another 60 min at room temperature before it was added to brine (100 mL). Mp: 160 °C dec. $R_f = 0.71$. ^{1}H NMR (400 MHz): δ 9.04 (s, 1H), 8.18−8.14 (dd, J = 8.3 Hz, J = 1.5 Hz, 2H), 7.67−7.49 (m, 3H), 7.01−6.93 (dt, J = 6.8 Hz, J = 1.0 Hz, 1H), 6.88−6.84 (dd, J = 6.8 Hz, J = 1.0 Hz, 1H), 6.45−6.37 (dt, J = 6.8 Hz, J = 1.0 Hz, 1H), 6.04−6.00 (d, J = 7.8 Hz, 1H), 5.69−5.52 (m, J = 14.1 Hz, J = 9.3 Hz, J = 7.3 Hz, 1H, $\mathrm{C}\mathit{H}{=}\mathrm{CH_2}$), 5.09 (br s, 1H), 5.03−5.01 (d, J = 3.9 Hz, 1H), 4.83−4.79 (dd, J = 6.3 Hz, J = 3.4 Hz, 1H), 4.67 (s, 5H), 3.78−3.76 (d, J = 3.4 Hz, 1H), 2.99−2.96 (ddd, J = 14.1 Hz, J = 7.3 Hz, J = 3.4 Hz, 1H), 2.90−2.79 (m, 1H), 2.19−2.17 (d, J = 3.4 Hz, 1H). ^{13}C NMR (50.3 MHz): δ 216.0 (C_{quat}, CO), 179.6 (C_{quat}, CO), 155.2 (C_{quat}), 138.9 (C_{quat}), 134.2 (CH), 130.7 (CH), 129.1 (CH), 128.6 (CH), 128.3 (CH), 125.9 (C_{quat}), 122.7 (CH), 120.6 (CH_2), 119.8 (CH), 119.1 (CH), 98.2 (C_{quat}), 81.5 (CH), 68.0 (CH), 58.9 (C_{quat}), 42.0 (CH_2), 34.7 (CH_2). IR (CH_2Cl_2): $\tilde{\nu}$ 1979, 1669 cm^{-1}. IR (KBr): $\tilde{\nu}$ 3430, 3108, 3084, 3016, 2928, 1957, 1914, 1669, 1493, 1485, 1449, 1362, 1348, 1318, 1170, 1153, 1138, 1084, 1058, 993 cm^{-1}. MS (FD): m/z (%) 517.4 (M$^+$, 100%). Anal. Calcd for $C_{26}H_{23}FeNO_5S$ (517.4): C, 60.36; H, 4.45; N, 2.71; Found: C, 60.05; H, 4.42; N, 2.66.

{(1−3-η^3)-[2,3:3′,4′]([3:3′]-*o*-Hydroxyphenyl)-5′-*n*-propyl-(1′-phenylsulfonyl)-1′,5′-dihydro-2′*H*-pyrrol-2′-one}-carbonylcyclopentadienyliron (8b). According to method B treatment of the imine **4e** (301 mg, 0.63 mmol) with *n*PrMgCl in 1,2-dichloroethane (10 mL) gave 80 mg (24%) of **8b** as an orange oil. After addition of *n*PrMgCl to the reaction mixture an immediate change in color and a temperature increase was observed. After it was stirred for 72 h at room temperature, the reaction mixture was added to brine (80 mL) with stirring and worked up by following the general procedure. $R_f = 0.67$. ^{1}H NMR (400 MHz): δ 9.15 (s, 1H), 8.15−8.12 (dd, J = 7.9 Hz, J = 1.5 Hz, 2H), 7.64−7.60 (dt, J = 7.3 Hz, J = 2.0 Hz, 1H), 7.55−7.51 (t, J = 7.3 Hz, 2H), 6.99−6.95 (dt, J = 7.3 Hz, J = 1.5 Hz, 1H), 6.88−6.86 (dd, J = 7.0 Hz, J = 1.2 Hz, 1H), 6.45−6.41 (dt, J = 7.3 Hz, J = 1.2 Hz, 1H), 6.01−5.99 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H), 4.78−4.75 (dd, J = 6.7 Hz, J = 2.9 Hz, 1H), 4.67 (s, 5H), 3.80−3.79 (d, J = 3.3 Hz, 1H), 2.21−2.17 (d, J = 3.2 Hz, 1H), 2.22−2.14 (m, 1H), 2.07−1.98 (m, 1H), 1.51−1.44 (m, 1H), 1.17−1.12 (m, 1H), 0.88−0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100.6 MHz): δ 214.9, 178.6, 154.2, 138.0, 132.9, 127.9, 127.5, 127.1, 124.9, 121.2, 118.7, 118.1, 97.7, 80.5, 67.4, 38.5, 33.2, 15.6, 12.6. IR (CH_2Cl_2): $\tilde{\nu}$ 1978, 1674 cm^{-1}. IR (KBr): $\tilde{\nu}$ 3436, 2966, 2932, 2874, 1970, 1729, 1663, 1449, 1364, 1339, 1186, 1174, 1152, 1089, 1062, 732, 592 cm^{-1}. MS (FD): m/z (%) 519.3 (M$^+$, 100), 369.1 (79.3). Anal. Calcd for $C_{26}H_{25}FeNO_5$ (518.85): C, 60.13; H, 4.82; N, 2.70. Found: C, 60.19; H, 4.79; N, 2.69.

{(1−3-η^3)-[2,3:3′,4′]-([3:3′]-*o*-Hydroxyphenyl)-5′-(prop-2″-en-1″yl)(1′-(*o*-benzoic acid (−)-menthyl ester)sulfonyl)-1′,5′-dihydro-2′*H*-pyrrol-2′-one}carbonylcyclopentadienyliron (8c). According to method B treatment of the imine **4f** (230 mg, 0.35 mmol) with (allyl)MgCl gave 137 mg (56% as a mixture of diastereomers; by ^{1}H and ^{13}C NMR spectroscopy four isomers were detectable; ratio 3:3:1:1) of **8c** as a red amorphous solid. The Grignard reagent was added at −80 °C, and stirring was continued for 15 min at that temperature and 6 h 45 min at room temperature. The reaction mixture was added to brine (90 mL) with stirring and was worked up by following the general procedure. $R_f = 0.69$. $\alpha_D^{20} = +72.2°$ (c = 0.2; CH_2Cl_2). ^{1}H NMR (400 MHz, major:minor 55:45, the asterisk denotes minor): δ 9.08, 9.07* (s, 1H), 8.54−8.52 (m, 1H), 7.67−7.63 (m, 2H), 7.42−7.40 (m, 1H), 7.16−7.14 (m, 1H), 7.01−6.97 (t, J = 7.3 Hz, 1H), 6.89−6.87 (m, 1H), 6.47−6.43 (dt, J = 7.3 Hz, J = 1.2 Hz, 1H), 6.10−6.08 (d, J = 7.6 Hz, 1H), 5.92−5.81, 5.80−5.66* (m, J = 14.1 Hz, J = 10.0 Hz, J = 7.3 Hz, 1H, $\mathrm{C}\mathit{H}{=}\mathrm{CH_2}$), 5.21−5.10 (m, 2H), 4.95−4.92 (m, 1H), 4.49, 4.47* (s, 5H), 3.74−3.73 (d, J = 1.8 Hz, 1H), 3.11−3.04, 2.85−2.72* (m, 2H), 2.17−2.16 (d, J = 1.8 Hz, 1H), 2.08−2.04 (m, 1H), 1.75−1.70 (m, 2H), 1.55−1.42 (m, 1H), 1.20−1.09 (m, 2H), 0.99−0.82 (m, 12H). ^{13}C NMR (50.3 MHz, the asterisk denotes minor): δ 216.0, 180.5, 167.4, 155.2, 136.6, 133.9, 133.6, 131.1*, 131.0, 130.8*, 130.6, 129.1*, 128.5, 128.3, 128.1*, 126.1, 125.3, 122.6, 120.8, 120.6, 119.8, 119.0, 98.9, 80.9, 76.8, 68.3, 47.1, 46.9*, 43.0*, 42.8, 40.5, 40.1*, 34.2, 34.0, 33.9*, 31.6, 26.2*, 25.9, 23.3*, 23.2, 22.1, 20.9, 16.1*, 16.0. IR (CH_2Cl_2): $\tilde{\nu}$ 1989, 1696, 1669 cm^{-1}. MS (FD): m/z (%) 701.4 (17.5), 700.3 (40.2), 699.4 (M$^+$, 100), 671.3 (M$^+$ − CO, 14.8); $C_{37}H_{41}FeNO_7S$ (699).

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Supporting Information Available: Tables giving atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and experimental details of X-ray study for **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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