Synthesis of Five-Membered Nitrogen Heterocycles from Iron-Substituted Enals: Novel Insight into the η^5-Cyclopentadienyl(dicarbonyl)iron Residue as a Versatile Functional Group

Karola Rück-Braun,* Til Martin, and Mark Mikulás[a]

Abstract: Dihydropyrrolones have been synthesized from β-cyclopentadienyl(dicarbonyl)iron-substituted enals and primary amines in a novel titanium-mediated intramolecular reaction cascade. The iron compounds were readily prepared from the corresponding β-halogeno-substituted enals. Experimental studies, carried out to provide mechanistic details, support the key role of the titanium hemiaminal functionality in the reaction cascade and are in agreement with a carbonylation–reductive elimination sequence prior to the reduction of the hemiaminal, which involves a π-alkene-hydridoiron intermediate.

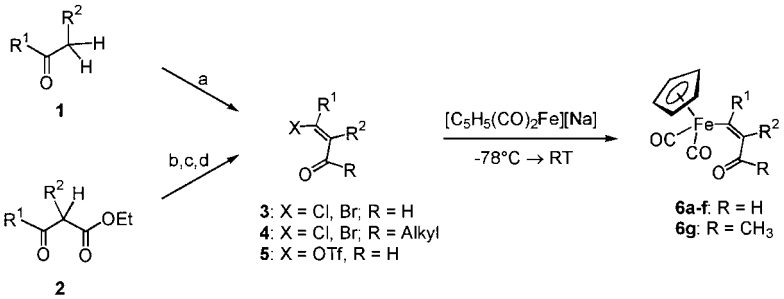
Keywords: beta-halogeno enals · carbonylations · domino reactions · iron · lactams

Introduction

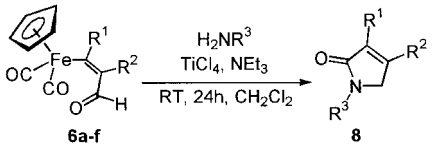
Transformations in which several bonds are formed in a single reaction sequence are of current interest.[1, 2] Thus, stoichiometric as well as catalytic transition-metal-mediated reaction cascades have received considerable attention in the last decades, for example, in the construction of annulated ring systems by well-defined carbonylation reactions.[2, 3]

The synthesis of γ-lactams has been achieved by a variety of strategies.[2–4] The majority of the synthetic methodologies involve palladium-mediated carbonylations of allylamines or appropriately substituted benzylamines.[2–5] In these processes higher temperatures and pressures of carbon monoxide are usually required.[4b, 5]

During our studies on the synthesis of azadienes from (*Z*)-configurated β-cyclopentadienyl(dicarbonyl)iron-substituted enals **6** with the Weingarten procedure,[6, 7] surprisingly the formation of α,β-unsaturated γ-lactams **8** from electron-rich primary amines was discovered (Scheme 1 and Scheme 2).[7] Thus, the titanium-mediated attack of an appropriate primary amine at the aldehyde group of the iron complexes **6** in the presence of triethylamine initiates a multistep reaction cascade. The key steps involve the generation of a titanium hemiaminal followed by carbonylation and reductive elimination to furnish the five-membered ring skeleton. With the support of mechanistic studies, a π-alkene-hydridoiron complex is suggested to be the key intermediate in the subsequent reduction of the hemiaminal functionality. The iron compounds **6** were synthesized from α-methylene ketones **1** or β-keto esters **2** in a few steps (Scheme 1). In this paper the scope and limitations of this new approach to α,β-unsaturated γ-lactams is presented.



Scheme 1. Synthetic routes to iron-substituted (*Z*)-enals **6**. Reagents and conditions: R^1, R^2 = alkyl, aryl; a) DMF, $POCl_3$ or PBr_3; b) $(i\mathrm{Pr})_2\mathrm{NEt}$, Tf_2O, $-78\,^\circ C$; c) DIBALH, $-78\,^\circ C$; d) TPAP (cat.), NMO, CH_2Cl_2, RT.



Scheme 2. $TiCl_4$-mediated synthesis of dihydropyrrolones **8**.

Results and Discussion

The iron compounds **6** are available from the corresponding enals that have an appropriate leaving group in the β-position,

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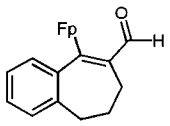
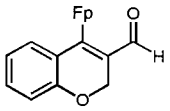
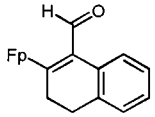
for example, triflate or halide. The synthetic strategies are shown in Scheme 1. In general, β-halogeno-substituted enals **3** were chosen as the starting materials. These compounds are readily accessible by treatment of the enolizable α-methylene ketone precursors **1** with Vilsmeier–Haack reagents, following the procedure of Arnold and Zemlicka.[8, 9] While this method has proven useful for cyclic ketones, difficulties arise for open-chain compounds due to the formation of (*Z*)/(*E*)-isomeric mixtures. However, the (*Z*)-configurated isomers (*Z*)-**3a** and (*Z*)-**4** (Table 1, entries 1 and 8), employed in this study as model compounds, could be separated by flash chromatography.

The addition of the sodium ferrate complex ([$\eta^5C_5H_5(CO)_2$-Fe]Na;[10, 11] Scheme 1) to a solution of the (*Z*)-configurated β-halovinyl aldehydes **3** (Scheme 1) in THF at −78 °C gave the iron compounds **6** within one hour. When the crude products were purified by column chromatography immediately after workup, the iron-substituted enals **6** were obtained in yields of 44–89% (Scheme 1 and Table 1, Experimental Section). The cyclic vinyl triflate **5a** (Table 1, entry 4), which was readily prepared by a three-step sequence starting from the corresponding β-keto ester (Scheme 1, Experimental Section),[12] gave the iron compound **6c** in 41% yield. Usually, the fairly air-stable products were obtained as yellow-brown amorphous solids. Reaction of the (*Z*)-β-halogeno vinyl carbonyl compounds (*Z*)-**3a** and (*Z*)-**4** with the sodium ferrate complex preferentially afforded the corresponding (*Z*)-configurated iron derivatives (*Z*)-**6a**[7] and (*Z*)-**6g** (75%, (*Z*)/(*E*) = 10:1; Table 1, entries 1 and 8). Obviously, these reactions proceed by the 1,4-addition of the sodium ferrate complex to the (*Z*)-β-halogeno-substituted vinyl carbonyl compounds to generate the aldehyde or ketone enolate intermediates of apparently short lifetime. These intermediates subsequently undergo the elimination of the halide to furnish the iron compounds **6** with a (*Z*)-configuration.

Table 1. Synthesis of the iron compounds **6** from β-halogeno-substituted enals **3** according to Scheme 1.

	Starting material	R^1, R^2	**6**[a]	Yield [%]
1	(*Z*)-**3a**	Ph, H	**a**	63[b]
2	**3b**	—$(CH_2)_3$—	**b**	76
3	**3c**	—$(CH_2)_4$—	**c**	52
4	**5a**	—$(CH_2)_4$—	**c**	41
5	**3d**		**d**	56
6	**3e**		**e**	89
7	**3f**		**f**	44
8	(*Z*)-**4**	CH_3, H	**g**	75[c]

Abstract in German: *Dihydropyrrolone können in Titantetrachlorid-katalysierten intramolekularen Reaktionskaskaden aus primären Aminen und β-Cyclopentadienyl(dicarbonyl)eisen-substituierten (Z)-Enalen, die aus β-Halogenvinylaldehyden leicht zugänglich sind, hergestellt werden. Eine Reaktionssequenz aus Carbonylierung, reduktiver Eliminierung und Reduktion der Titanhalbaminalfunktion unter Beteiligung eines intermediär gebildeten π-Olefinhydridoeisenkomplexes ist im Einklang mit den experimentellen Ergebnissen, und erklärt plausibel die Bildung der α,β-ungesättigten γ-Lactame.*

At first $TiCl_4$-mediated reactions of the iron compound (*Z*)-**6a** with primary amino compounds in the presence of triethylamine (2.3 equiv) were examined. The imines [$Cp(CO)_2Fe$\{CPh=CH–CH=NPh\}] [(*Z*)-**7a**] and [$Cp(CO)_2$-Fe\{CPh=CH–CH=NSO_2Ph\}] [(*Z*)-**7b**] were formed smoothly in 55% and 74% yield from aniline and benzenesulfonamide.[7] However, when (*S*)-phenylethylamine was employed, surprisingly it was found that the α,β-unsaturated γ-lactam **8c** was formed; it was isolated in 61% yield by flash chromatography (Scheme 2 and Table 2, entry 3).

Table 2. Reactions of $[C_5H_5(CO)_2Fe]$-substituted enals **6** with the appropriate primary amines to give the dihydropyrrolones **8** according to Scheme 2.

	6	R^3	Product	Yield [%][a]
1	**6a**	tC_4H_9	**8a**	49
2	**6a**	C_6H_{11}	**8b**	56
3	**6a**	(*S*)-CH(CH_3)Ph	**8c**	61
4	**6a**	(*R*)-CH[$CH(CH_3)_2$]CO_2Me	**8d**	41
5	**6c**	(*S*)-CH(CH_3)Ph	**8e**	63
6	**6d**	(*S*)-CH(CH_3)Ph	**8f**	42[b]
7	**6f**	(*S*)-CH(CH_3)Ph	**8g**	37[b]

[a] Isolated yield. [b] Yield on 1 mmol scale after flash chromatography: **8f:** 68%, **8g**: 51%.

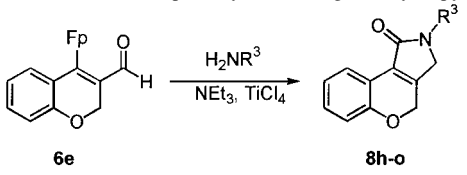
The key steps in the reaction cascade seem to be carbonylation and reductive elimination, in addition to a rather unusual reduction step. To the best of our knowledge this is the first example of an intramolecular multistep domino process mediated by iron that includes a reduction step in the absence of a reducing agent.[13]

Attempts to run the reaction in the absence of the Lewis acid $TiCl_4$ proved to be in vain. Variation of the amount of $TiCl_4$, from 0.5 to 1.0 equivalents, did not influence the reaction outcome. However, in the absence of a tertiary amine, such as triethylamine or *N*-methylmorpholine, the Lewis acid alone failed to promote the reaction cascade (IR monitoring). For the purpose of mechanistic considerations, the imine [$Cp(CO)_2Fe$\{CPh=CH–CH=N\{(*S*)–CH(CH_3)Ph\}\}] [(*Z*)-**7c**] was synthesized from the iron compound (*Z*)-**6a** and (*S*)-phenylethylamine in ether in the presence of $MgSO_4$,

whereby **8c** already was found to be formed as an impurity, although nonreproducibly and in low amounts (e.g., (*Z*)-**7c**:**8c** ≥ 9:1, Experimental Section).[7] Treatment of the crude aldimine with $TiCl_4$ and Et_3N in CH_2Cl_2 did not produce a considerable improvement in the yield of **8c** (yield: 0–30%) and thus proved to be inferior to the one-pot procedure.

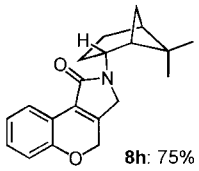
In order to test the scope of the standard reaction conditions outlined above, (*Z*)-**6a** and the chromanone complex **6e** were chosen as candidates to investigate primary amines of different nucleophilicity. These iron compounds were treated with a variety of primary amines to furnish the α,β-unsaturated γ-lactams **8** listed in Table 2 and Table 3.

Table 3. Reactions of **6e** with primary amines to give dihydropyrrolones **8**.

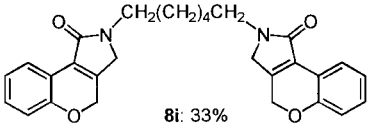


6e **8h-o**

	8	R^3	Yield [%]
1	**8j**	(*S*)-$CH(CH_3)$Ph	64
2	**8k**	*n*Prop	66
3	**8l**	*t*Bu	56
4	**8m**	C_6H_{11}	68
5	**8n**	CH_2–CH=CH_2	67
6	**8o**	$CH_2CH_2OCH_3$	41

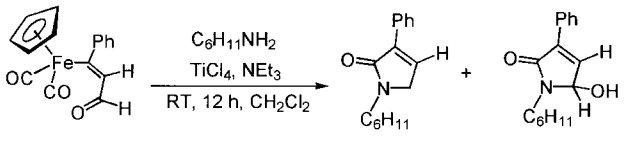


8h: 75%



8i: 33%

Among the primary amino compounds tested only benzylamine ($pK_a = 9.3$)[14] along with benzenesulfonamide and aniline did not afford any lactam under standard reaction conditions. Imine formation was observed instead. In general, within 18–24 h complete reaction to the products prior to aqueous workup was determined by IR monitoring (**8**: $\tilde{\nu}(CO) \approx 1660-1680\ cm^{-1}$).[7] Ferrocene, which stemmed from the iron moiety, was unambiguously identified as the byproduct by ^1H NMR spectroscopy of the crude reaction mixture. On a 1 mmol scale, the products **8f** and **8g** were obtained in 68% and 51% yield after purification by flash chromatography. On larger scale (> 3 mmol, Table 2, entries 6 and 7), the precipitation of iron oxide and hydroxide residues prior to purification by flash chromatography or recrystallization is recommended in order to obtain pure products, although lower yields are observed. The reaction of (*Z*)-**6a** with cyclohexylamine furnished the product **8b** exclusively within 18 h (Table 2, entry 2). However, the 5-hydroxy-substituted γ-lactam **9** (Scheme 3) was isolated as a byproduct

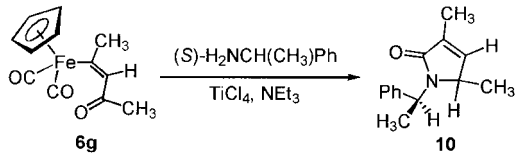


6a **8b** **9**

Scheme 3. Incomplete reaction of **6a** to **8b** and γ-lactam **9**.

in 16% yield in addition to **8b** (34%), if the reaction mixture was worked up after 12 h, when the reaction was still incomplete. This is supporting evidence for a fundamental role of the titanium hemiaminal functionality in the reaction cascade.

Iron compounds with aliphatic and aromatic substituents at the alkene moiety were successfully employed as starting materials (Table 2). Only treatment of the cyclopentene compound **6b** with primary amines, such as (*S*)-phenylethylamine or cyclohexylamine, did not result in the formation of the desired γ-lactams under standard conditions, possibly for steric reasons. In the case of the iron acyl compound (*Z*)-**6g** (Scheme 4), the attack of the primary amine (*S*)-phenylethylamine at the ketone functionality was found to be the limiting



6g **10**

Scheme 4. Reaction scheme for the formation of **10**.

step, evidenced by the incomplete reaction, even after 23 h (IR monitoring). Compound **10** was isolated in 28% yield by flash chromatography (isomer ratio: 50:50).

A variety of Lewis acids were tested for the reaction of iron compound **6e** with *n*-propyl amine.[15] $SnCl_4$ gave unsatisfactory results, mainly due to decomposition of the starting material. With $AlCl_3$ and BCl_3 problems were encountered, especially during workup and purification, that lead to lower yields of **8k** (38%, Experimental Section).

Carbonylation reactions can also be induced oxidatively.[16] Thus, ferrocenium hexafluorophosphate was investigated as a catalyst in its ability to promote the reaction of (*Z*)-**6a** with (*S*)-phenylethylamine in the presence of triethylamine. However, the lactam formation proceeded sluggishly and, after 48 h, **8c** was isolated in only 23% yield.

According to the results summarized above, γ-lactam formation is obviously determined by the nucleophilicity of the primary amine employed. The experiments described are consistent with the reaction mechanism envisioned in Scheme 5.

After $TiCl_4$-promoted attack of the primary amines at the aldehyde group of the iron compounds to produce a titanium hemiaminal **A**, two routes for the carbonylation step appear reasonable. Appropriate substituents at the nitrogen atom promote both reaction paths outlined in Scheme 5 by increasing the nucleophilicity of the nitrogen atom (pathway A) as well as the migratory tendency of the vinyl side chain (pathway B).[7] Thus, nucleophilic attack of the hemiaminal nitrogen on one of the carbonyl ligands to furnish a carbamoyl species, such as **B** and **B′**, and the formation of an iron acyl intermediate **C** (pathway B) is feasible.[17] The participation of the tertiary amine base might be possible in both steps.[7] Subsequent to reductive elimination and the accompanying intramolecular electron transfer to the remaining iron fragment, η^2-coordination of the latter to the alkene moiety is proposed. Protonation of the iron residue would furnish a hydrido complex **D**, which would undergo hydride

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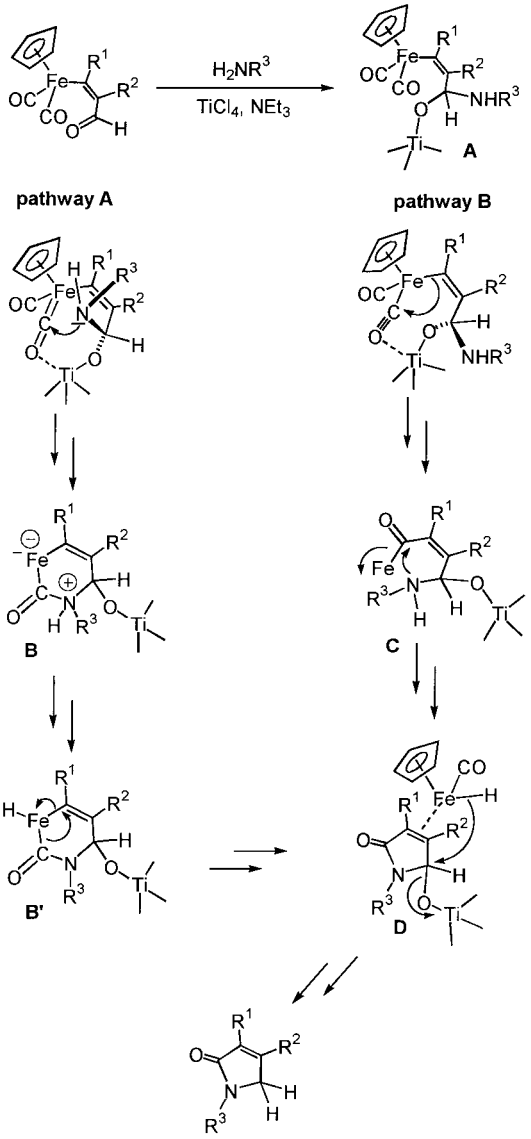
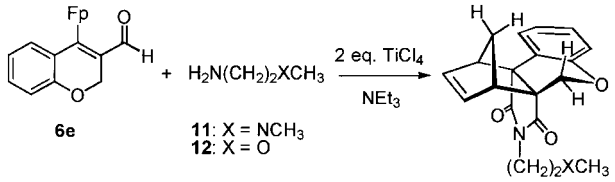


Scheme 5. Proposed mechanism for γ-lactam formation which involves a π-alkene-hydridoiron intermediate **D**.

transfer to the titanium hemiaminal carbon atom replacing the titanium alkoxide group.[17] The proton could stem from the amine addition reaction (Scheme 5). In the case of reaction cascades of iron-substituted enals **6** that lead to γ-lactones, labeling experiments did provide strong arguments for a π-alkene-hydridoiron intermediate formed after reductive elimination.[19] Even though positive evidence for the formation of a π-alkene-hydridoiron intermediate during lactam formation is not provided, the mechanistic considerations outlined in Scheme 5 provide the best explanation of the experimental findings.

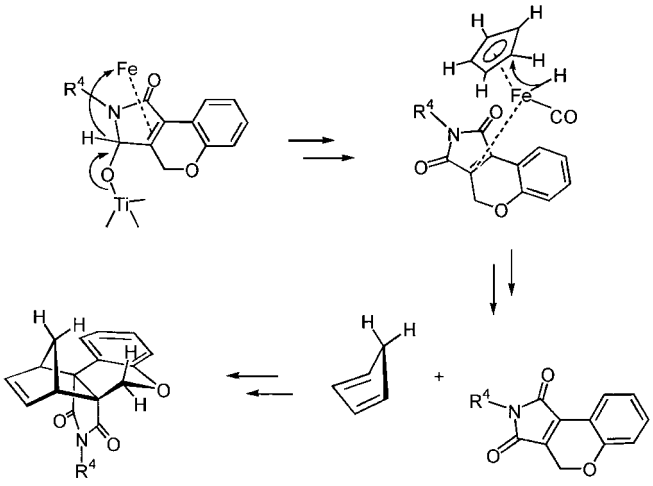
When the iron compound **6e** was treated with the primary amine **11** (Scheme 6) which bears a dimethylamine group in the 2 position, the imide-derived Diels–Alder cycloadduct **13** was isolated by flash chromatography in low yield (Scheme 6). The formation of **13** is assumed to be the result of the oxidation of the titanium–hemiaminal functionality to a carbonyl group with participation of the cyclopentadienyl ligand in the reaction cascade. Similarly, upon treatment of



Scheme 6. Cycloadducts from multistep reaction cascades of **6** (Fp = $[C_5H_5(CO)_2Fe]$) and primary amines **11** and **12** that involve the cyclopentadienyl ligand.

the iron compound **6e** with 2-methoxyethylamine **12** and two equivalents of $TiCl_4$, the cycloadduct **14** was isolated reproducibly (13% yield) in addition to **8o** (see, Table 3 and Experimental Section). IR monitoring shows the $\tilde{\nu}$(CO) stretching mode for the imide **14** at about 1704 cm^{-1}.

The electronic properties of the titanium hemiaminal may be influenced by chelation by the donor functionalities present in β-position of the primary amines **11** and **12** employed in the reaction. It is therefore possible that the oxidation of the hemiaminal to an imide takes place (Scheme 7).



Scheme 7. Proposed key steps and selected intermediates in the reaction cascades which furnish the cycloadducts **13** and **14**.

Although the circumstances and, thus, the mechanism of this alternative pathway that leads to Diels–Alder adducts have not yet been established, a reasonable sequence of reaction steps that furnishes the products obtained is disclosed in Scheme 7.

The mechanistic origin of cyclopentadiene from the cyclopentadienyl ligand of the remaining iron fragment after reductive elimination is not clear at present. However, it should be considered that hydride transfer from the iron fragment to the cyclopentadienyl ligand to furnish a η^4-cyclopentadiene iron complex[20] might be the crucial reaction step prior the cycloaddition reaction.[21] These findings provide further evidence of the fundamental role of the titanium hemiaminal in the reaction cascade which leads to α,β-unsaturated γ-lactams.

Conclusion

The two-step reaction sequence described provides a novel and preparatively useful route to α,β-unsaturated γ-lactams that starts, for example, from β-halogeno-substituted enals. Mechanistic studies provide strong evidence for the crucial role of the titanium hemiaminal functionality in this process. It seems reasonable to suggest that a π-alkene-hydridoiron intermediate complex participates in the reduction step of the reaction cascade. The application of the iron-substituted enals **6** in the synthesis of 5-substituted dihydropyrrolones is currently under investigation.

Experimental Section

General methods: Solvents were purified according to standard procedures.[22] Melting points were determined with a Büchi melting-point apparatus and are uncorrected. 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; 2D NMR spectra were recorded on a Bruker ARX400; residual solvent protons were used as the internal standard {$CDCl_3$: $\delta(^1H) = 7.24$, $\delta(^{13}C) = 77.0$; $[D_6]$DMSO: $\delta(^1H) = 2.49$, $\delta(^{13}C) = 39.7$}. Chemical shifts are given in ppm relative to tetramethylsilane (TMS) and coupling constants in Hz. For some signal assignments, standard techniques, such as homo- and heteronuclear decoupling, 2D FT COSY or HETCOR, were employed. Low-resolution electron-impact mass spectra (EIMS, 70 eV) were recorded with a Varian MAT CH7a. FD and FAB mass spectra were recorded on a Finnigan MAT95. IR spectra were recorded with a Perkin–Elmer FTIR spectrometer 1760X; NaCl cells were used for IR monitoring.

Thin-layer chromatography (TLC) was performed on Merck plates, silica gel $60\,F_{254}$; detection by UV light ($\lambda = 254$ nm) or by treatment with either a solution of $KMnO_4$ (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 (6 mL) in water (96 mL). Elemental analyses were carried out by the Microanalytical Division of the Institute of Organic Chemistry at the University of Mainz (Germany).

Compounds **3b**,[23] **3c**,[24] and **3f**[25] were prepared according to literature procedures. Sodium amalgam (2%) was purchased from Lancaster, [{$Cp(CO)_2Fe$}$_2$] from Fluka, and $TiCl_4$ (1M solution in CH_2Cl_2) from Aldrich.

(*Z*)-β-Chlorocinnamaldehyde ((*Z*)-**3a**): To a suspension of 3-chloro-3-phenyl-1-prop-2-en-1-yliden-dimethyliminium perchlorate[26] (15 g, 51 mmol) in chloroform (90 mL) was added a solution of NaOAc (12.6 g, 153 mmol) in water (60 mL) at room temperature. The mixture was stirred vigorously until TLC monitoring indicated the complete disappearance of the starting material (3 h). The clear orange organic layer was separated and washed with water (2×80 mL) and brine (80 mL), dried ($MgSO_4$), and concentrated in vacuo. The yellow-red concentrate was suspended in ether (200 mL) and filtered through a pad of Celite. The residue was washed with ether (50 mL) and the combined filtrate was evaporated to dryness to yield (*Z*)-**3a** (5.45 g, 64%) as a yellow-brown oil, sufficiently pure for further transformations. ^{1}H NMR (200 MHz): $\delta = 10.18$ (d, $J = 6.9$ Hz, 1H, CHO), 7.73–7.68 (m, 2H, arom CH), 7.48–7.36 (m, 3H, arom CH), 6.63 (d, $J =$ 6.9 Hz, 1H, alkene CH); IR (film): $\tilde{\nu} = 3055$, 2986, 2929, 2862, 1671, 1602, 1575, 1513, 1491, 1448, 1422, 1389, 1263, 1230, 1128, 890, 841 cm^{-1}; C_9H_7ClO (166.6): calcd C 64.88, H 4.23; found C 64.97, H 4.43.

9-Bromo-6,7-dihydro-5*H*-benzocyclohepten-8-carbaldehyde (**3d**): To a solution of DMF (36 mL, 455 mmol) in chloroform (225 mL) was added PBr_3 (35.6 mL, 375 mmol) dropwise at 0°C, and the mixture was stirred for 1 h at room temperature. A solution of benzosuberone (15.3 g, 95.5 mmol) in chloroform (15 mL) was added, and the reaction mixture was refluxed for 135 min (TLC monitoring). The mixture was cooled to 0°C and then hydrolyzed by the careful addition of saturated aqueous $NaHCO_3$ solution, water, and solid $NaHCO_3$. The aqueous layer was separated and extracted with CH_2Cl_2 (3×100 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Column chromatography (silica gel, CH_2Cl_2) gave **3d** (16 g, 67%) as a yellow, viscous liquid, which solidified on standing at −22°C. M.p. 47°C; $R_f = 0.8$ (petroleum ether/ethyl acetate 4:1); ^{1}H NMR (400 MHz): $\delta = 10.18$ (s, 1H, CHO), 7.64 (dd, $J = 1.8$, 7.9 Hz, 1H, arom H1), 7.37–7.28 (m, $J = 1.5$, 7.3 and 5.9 Hz, 2H, arom H2 and H3), 7.20 (dd, $J = 1.8$, 7.0 Hz, 1H, arom H4), 2.57 (t, $J = 7$ Hz, 2H, H5a/b), 2.21 (dt, $J = 1.2$, 6.8 Hz, 2H, H7a/b), 2.10 (m, 2H, H6a/b); ^{13}C{^{1}H} GASPE NMR (100.6 MHz): $\delta = 192.3$ (CHO), 140.3 (s), 139.1 (s), 139.0 (s), 138.5 (s), 130.4 (d), 129.6 (d), 128.8 (d), 126.6 (d), 33.7 (t), 31.9 (t), 23.6 (t); IR (CH_2Cl_2): $\tilde{\nu} = 1670$, 1602, 1580, 1565 cm^{-1}; $C_{12}H_{11}BrO$ (251.1): calcd C 57.39, H 4.42; found C 57.32, H 4.58.

4-Bromo-2*H*-chromen-3-carbaldehyde (**3e**): To a solution of DMF (13 mL, 169 mmol) in chloroform (70 mL) was added PBr_3 (12.8 mL, 135 mmol) dropwise at 0°C. The mixture was stirred for 1 h at room temperature then a solution of 4-chromanone (5.0 g, 33.7 mmol) in chloroform (50 mL) was added, and the reaction mixture was heated to 50–55°C for 1 h (TLC monitoring). The workup procedure was performed under the same conditions as described above for **3d**. Column chromatography (silica gel, CH_2Cl_2) gave **3e** (6.73 g, 83%) as a yellow, viscous liquid, which solidified on standing at −22°C. M.p. 74°C; $R_f = 0.77$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $[D_6]$DMSO): $\delta = 9.86$ (s, 1H, CHO), 7.63 (dd, $J =$ 1.5, 7.9 Hz, 1H, arom CH), 7.44–7.39 (m, $J = 0.8$, 8.0 Hz, 1H, arom CH), 7.11 (dt, $J = 0.8$, 8.0 Hz, 1H, arom CH), 6.92 (d, $J = 8.1$ Hz, 1H, arom CH), 4.87 (s, 2H, CH_2); ^{1}H NMR (400 MHz): $\delta = 9.98$ (s, 1H, CHO), 7.66 (dd, $J = 1.5$, 7.8 Hz, 1H, arom H5), 7.34 (dt, $J = 1.5$, 7.8 Hz, 1H, arom H7), 7.02 (dt, $J = 1.0$, 7.8 Hz, 1H, arom H6), 6.85 (d, $J = 8.3$ Hz, 1H, arom H8), 4.93 (s, 2H, CH_2); ^{13}C NMR (100.6 MHz) $\delta = 190.0$ (CHO), 156.4 (C9), 135.4 (C4), 134.0 (C7), 128.9 (C5), 127.3 (C3), 122.3 (C6), 121.6 (C10), 116.6 (C8), 65.0 (C2); IR (CH_2Cl_2): $\tilde{\nu} = 1664$, 1601, 1567, 1476 cm^{-1}; IR (KBr): $\tilde{\nu} = 3060$, 3001, 2975, 2905, 2882, 2866, 1665, 1602, 1569, 1474, 1458, 1384, 1369, 1288, 1273, 1232, 1182, 1153, 1116, 1044 cm^{-1}; $C_{10}H_7BrO_2$ (239.0): calcd C 50.24, H 2.95; found C 50.20, H 2.94.

4-Chloro-3-penten-2-one (**4**):[27] Following the general procedure of Mewshaw,[28] a stirred solution of pentan-2,4-dione (9.2 mL, 89 mmol) and DMF (9.0 mL, 117 mmol) in CH_2Cl_2 (120 mL) was cooled to 0°C and oxalyl chloride (9.2 mL, 107 mmol) was added dropwise. The yellow solution was stirred for 15 min at 0°C and was then allowed to warm to room temperature over a period of 90 min. The mixture was hydrolyzed by the addition of water (150 mL). The separated aqueous layer was extracted with CH_2Cl_2 (4×50 mL), the combined organic phases were dried ($MgSO_4$), and the solvent was evaporated. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 3:1) gave **4** as a mixture of the (*E*)- and the (*Z*)-isomers [8.2 g, 78%, ratio (*E*)/(*Z*) = 77:23 (^{1}H NMR)]. Flash chromatography on silica gel with petroleum ether/ethyl acetate (40:1) gave i) (*E*)-**4** (6.0 g, 57%) and ii) (*Z*)-**4** (1.84 g, 17%).

*Compound (E)-**4***:[27] A pale yellow liquid; $R_f = 0.85$ (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (200 MHz): $\delta = 6.43$ (s, 1H), 2.50 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (50.3 MHz): $\delta = 195.5$, 151.5, 125.7, 31.6, 23.8.

*Compound (Z)-**4***:[27] A pale yellow liquid; 0.68 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (200 MHz): $\delta = 6.22$ (s, 1H), 2.32 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (50.3 MHz): $\delta = 196.1$, 142.8, 125.5, 31.2, 28.2.

2-[(Trifluoromethanesulfonyl)oxy]-1-cyclohexen-1-carbaldehyde (**5a**): To a colorless suspension of 1-hydroxymethyl-2-[(trifluoromethanesulfonyl)oxy]-1-cyclohexene[12] (2.08 g, 8 mmol), *N*-methylmorpholine-*N*-oxide (1.41 g, 12 mmol), and molecular sieves (4 g) in CH_2Cl_2 (100 mL) was added TPAP (141 mg, 5 mol%) at room temperature.[29] The green solution was stirred for 3 h (TLC monitoring) and then filtered through a plug of silica gel. The residue was washed with CH_2Cl_2 and the filtrate concentrated in vacuo. Purification by flash chromatography on silica gel with petroleum ether/ethyl acetate (5:1) gave **4a** (1.68 g, 82%) as a colorless oil. $R_f = 0.89$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz): $\delta = 10.06$ (s, 1H, CHO), 2.60–2.52 (m, 2H), 2.37–2.29 (m, 2H), 1.87–1.76 (m, 2H), 1.70–1.57 (m, 2H); ^{13}C{^{1}H} GASPE NMR (50.3 MHz): $\delta = 187.6$, 160.6, 129.9, 118.3 (s, $J = 319.6$ Hz, CF_3), 28.9, 22.3, 21.9, 20.4; IR (film): $\tilde{\nu} = 2950$, 2872, 2765, 1691, 1662, 1453, 1421, 1359, 1273, 1248, 1224, 1179, 1139, 1102 cm^{-1}; MS (EI): *m*/*z* (%) = 258.2 (9), 125.2 (100), 108.2 (34), 99.1 (7), 97.1 (11), 86.1 (31), 84.1 (50) 79.1 (65); $C_8H_9F_3O_4S$ (258.2).

(*Z*)-β-[Cyclopentadienyl(dicarbonyl)iron]-cinnamaldehyde ((*Z*)-**6a**): A solution of $[Cp(CO)_2Fe]Na$,[10] prepared from [{$Cp(CO)_2Fe$}$_2$] (3.88 g,

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11 mmol) and sodium amalgam (36 g) in THF (50 mL), was added slowly at −78 °C by means of a cannula to a solution of (*Z*)-**3a** (3.7 g, 22 mmol) in THF (20 mL). The reaction mixture was stirred at −78 °C for 1 h and then allowed to warm to room temperature over a period of 1 h. The solvent was evaporated in vacuo and the residue dissolved in ether/acetone (1:1) and subsequently purified by column chromatography[30] on silica gel. With petroleum ether/ether (2:1) [{Cp(CO)$_2$Fe}$_2$] was separated, whereas with ether/acetone (1:1) the iron complex **6a** was obtained. The solvent was evaporated and the yellow-brown solid was dissolved in CH_2Cl_2 (200 mL), dried ($MgSO_4$), and the solution concentrated in vacuo to yield **6a** as a mixture of the (*Z*)- and the (*E*)-isomers [4.24 g, 63 %, ratio (*Z*)/(*E*) = 83:17 (^{1}H NMR)]. Flash chromatography on silica gel with petroleum ether/ether (5:1 to 2:1) afforded 2.7 g of (*Z*)-**6a** (40 %) as a yellow-brown, amorphous solid; ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 9.79 (d, *J* = 7.7 Hz, 1H, CHO), 7.26 (t, *J* = 7.3 Hz, 2H, arom CH), 7.16–7.12 (m, 1H, arom CH), 6.96 (dd, *J* = 1.3, 8.5 Hz, 2H, arom CH), 6.45 (d, *J* = 7.8 Hz, 1H, alkene CH), 5.33 (s, 5H, C_5H_5); ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 214.4, 195.9, 195.3, 157.6, 143.3, 127.4, 125.3, 123.4, 86.0; IR (CH_2Cl_2): $\tilde{\nu}$ = 2028, 1977, 1648 cm^{-1}; $C_{16}H_{12}FeO_3$ (307.8): calcd C 62.37, H 3.93; found C 62.32 H 3.88.

2-[Cyclopentadienyl(dicarbonyl)iron]-cyclopenten-1-carbaldehyde (**6b**): A solution of the aldehyde **3b** (0.7 g, 4 mmol) in THF (20 mL) was treated with [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (0.71 g, 2 mmol) and sodium amalgam (5.8 g) in THF (30 mL), at −78 °C. The workup procedure was performed as described for **6a** to yield **6b** (0.83 g, 76 %) as a yellow-brown, crystalline solid. M.p. 83–84 °C; R_f = 0.44 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): δ = 9.84 (s, 1H, CHO), 4.87 (s, 5H, C_5H_5), 2.77 (t, *J* = 7.1 Hz, 2H, CH_2), 2.49 (t, *J* = 7.3 Hz, 2H, CH_2), 1.77 (q, *J* = 7.4 Hz, 2H, CH_2); ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 9.78 (s, 1H, CHO), 5.21 (s, 5H, C_5H_5), 2.76 (t, *J* = 7.4 Hz, 2H, CH_2), 2.35 (t, *J* = 7.3 Hz, 2H, CH_2), 1.78–1.63 (m, *J* = 7.4 Hz, 2H, CH_2); ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 218.2, 196.8, 194.8, 154.5, 89.2, 57.0, 33.6, 25.9; IR (CH_2Cl_2): $\tilde{\nu}$ = 2024, 1971, 1637, 1534 cm^{-1}; $C_{13}H_{12}FeO_3$ (272.1): calcd C 57.39, H 4.45; found C 57.25, H 4.39.

2-[Cyclopentadienyl(dicarbonyl)iron]-cyclohexen-1-carbaldehyde (**6c**): A solution of the aldehyde **3c** (0.87 g, 6 mmol) in THF (30 mL) was treated with [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (1.06 g, 3 mmol) and sodium amalgam (8.7 g) in THF (30 mL), at −78 °C. The workup procedure was accomplished as described for **6a** to yield **6f** (0.88 g, 52 %) as a yellow-brown, highly viscous oil. Alternatively, a solution of **5a** (1.03 g, 4 mmol) in THF (15 mL) was treated with [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (0.71 g, 2 mmol) and sodium amalgam (8.7 g) in THF (50 mL), at −78 °C and worked up. Purification by column chromatography on silica gel with CH_2Cl_2 gave firstly [{Cp(CO)$_2$Fe}$_2$]. With ether as the eluent **6c** (0.47 g, 41 %) was obtained. R_f = 0.46 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 9.68 (br s, 1H, CHO), 5.16 (s, 5H, C_5H_5), 2.74 (br s, 2H, CH_2), 2.15 (br m, 2H, CH_2), 1.51 (br m, 4H, CH_2); ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 215.9, 196.7, 189.0, 146.0, 87.0, 50.6, 27.3, 26.0, 22.2; IR (CH_2Cl_2): $\tilde{\nu}$ = 2016, 1963, 1642 cm^{-1}; MS (FD): *m*/*z* (%) = 286.9 (17), 286.0 (100).

9-[Cyclopentadienyl(dicarbonyl)iron]-6,7-dihydro-5*H*-benzocyclohepten-8-carbaldehyde (**6d**): The aldehyde **3d** (2.9 g, 11.3 mmol) dissolved in THF (60 mL) was treated with [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (2 g, 5.7 mmol) and sodium amalgam (17.2 g) in THF (60 mL) at −78 °C, as described above for **6a**. After purification by column chromatography, **6d** (2.2 g) was isolated in 56 % yield as a yellow-brown, amorphous solid, sufficiently pure for further transformations. R_f = 0.46 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 9.87 (s, 1H, CHO), 7.25–7.14 (m, 3H, arom CH), 7.07–7.01 (m, 1H, arom CH), 5.36 (s, 5H, C_5H_5), 2.77–2.32 [m, CH_2 (2H) overlayed by the adjacent DMSO signal], 2.09–1.85 (m, 2H, CH_2), 1.66–1.32 (m, 2H, CH_2); ^{13}C NMR (100.6 MHz, [D$_6$]DMSO): δ = 215.9, 213.6, 194.8, 184.8, 155.2, 150.4, 132.5, 128.7, 127.0, 126.0, 125.7, 86.8, 32.0, 30.8, 24.7; IR (CH_2Cl_2): $\tilde{\nu}$ = 2023.5, 1973, 1641 cm^{-1}; MS (FD): *m*/*z* (%) = 320.2 (44); $C_{19}H_{16}FeO_3$ (348.2): calcd C 65.54, H 4.63; found C 63.96, H 4.89.

4-[Cyclopentadienyl(dicarbonyl)iron]-2*H*-chromen-3-carbaldehyde (**6e**): The aldehyde **3e** (5.5 g, 23 mmol) dissolved in THF (70 mL) was treated with [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (4.1 g, 11.6 mmol) and sodium amalgam (35.3 g) in THF (80 mL) at −78 °C and purified as described above for **6a** to yield **6e** (6.9 g, 89 %) as a yellow-brown, amorphous solid. M.p. 62 °C; R_f = 0.3 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 9.93 (s, 1H, CHO), 7.76 (d, *J* = 7.1 Hz, 1H, arom CH), 7.20 (t, *J* = 6.8 Hz, 1H, arom CH), 7.05 (t, *J* = 7.3 Hz, 1H, arom CH), 6.81 (d, *J* = 7.7 Hz, 1H, arom CH), 5.42 (s, 5H, C_5H_5), 4.78 (br s, 1H, CH_2O), 4.27 (br s, 1H, CH_2O); ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 215.1, 194.0, 177.0, 152.8, 144.0, 135.5, 135.4, 130.3, 121.2, 115.4, 87.5, 64.4; IR (CH_2Cl_2): $\tilde{\nu}$ = 2028, 1977, 1634 cm^{-1}; MS (FD): *m*/*z* (%) = 307.9 (100); $C_{17}H_{12}FeO_4$ (336.1): calcd C 60.74, H 3.60; found C 60.67, H 3.55.

2-[Cyclopentadienyl(dicarbonyl)iron]-3,4-dihydronaphthalen-1-carbaldehyde (**6f**): The aldehyde **3f** (1.4 g, 4.8 mmol) dissolved in THF (40 mL) was treated with [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (0.85 g, 2.4 mmol) and sodium amalgam (7 g) in THF (30 mL), at −78 °C. The reaction mixture was purified as described above for **6a** to yield **6f** (0.7 g, 44 %) as a yellow-brown foam. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 10.04 (s, 1H, CHO), 7.77 (d, *J* = 7.4 Hz, 1H, arom CH), 7.31–7.02 (m, 3H, arom CH), 5.32 (s, 5H, C_5H_5), 2.87 (t, 2H, CH_2), 2.55–2.49 (m, CH_2 overlayed by the adjacent DMSO signal); ^{1}H NMR (200 MHz): δ = 10.19 (br s, 1H, CHO), 7.83–7.80 (br d, *J* = 6.7 Hz, 1H, arom CH), 7.27–7.07 (m, 3H, arom CH), 4.98 (s, 5H, C_5H_5), 2.93–2.90 (m, 2H, CH_2), 2.78–2.71 (m, 2H, CH_2); IR (CH_2Cl_2): $\tilde{\nu}$ = 2024, 1972, 1652 cm^{-1}; MS (FD): *m*/*z* (%) = 362.1 (100), 306.1 (24), 250.2 (19), 212.0 (12), 200.1 (17), 186.2 (75), 184.1 (19).

(*Z*)-4-[Cyclopentadienyl(dicarbonyl)iron]-3-penten-2-one (**6g**): A solution of [Cp(CO)$_2$Fe]Na, prepared from [{Cp(CO)$_2$Fe}$_2$] (3.54 g, 10 mmol) and sodium amalgam (28.7 g) in THF (70 mL), was added slowly at −78 °C to a solution of the ketone (*Z*)-**4** (2.37 g, 20 mmol) in THF (25 mL). The reaction mixture was stirred at −78 °C for 30 min and then allowed to warm to room temperature over a period of 90 min (TLC and IR monitoring). The solvent was evaporated in vacuo, and the residue purified by column chromatography (silica gel, CH_2Cl_2) to yield **6g** as a mixture of isomers, which was separated by column chromatography on silica gel with petroleum ether/ether (2:1) to give firstly 3.55g (*Z*)-**6g** (68 %) and secondly 0.34 g (*E*)-**6g** (7 %).

*Compound (Z)-**6g***: Yellow oil; R_f = 0.52 (petroleum ether/ether 2:1); ^{1}H NMR (400 MHz,): δ = 7.07 (s, 1H), 4.81 (s, 5H), 2.47 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100.6 MHz): δ = 214.7, 197.4, 191.0, 139.0, 86.2, 43.7, 32.3; IR (CH_2Cl_2): $\tilde{\nu}$ = 2021, 1964, 1666, 1532 cm^{-1}; $C_{12}H_{12}FeO_3$ (260.1): calcd C 55.42, H 4.65; found C 55.08; H 4.69.

*Compound (E)-**6g***: Amber crystals (petroleum ether/ether) for crystal structure analysis, see ref. [31]. M.p. 58–59 °C; R_f = 0.20 (petroleum ether/ether 2:1), ^{1}H NMR (200 MHz): δ = 6.76 (s, 1H), 4.82 (s, 5H), 2.71 (d, *J* = 1.0 Hz, 3H), 2.07 (s, 3H); ^{13}C NMR (50.3 MHz): δ = 214.8, 193.6, 190.1, 141.1, 85.8, 37.6, 30.8; IR (CH_2Cl_2): $\tilde{\nu}$ = 2018, 1963, 1663, 1529 cm^{-1}; IR (KBr): $\tilde{\nu}$ = 3108, 3101, 2988, 2932, 2893, 2010, 1951, 1662, 1521, 1426, 1416, 1362, 1342, 1177, 1115, 1075 cm^{-1}.

(*Z*)-*N*-Phenyl-3-[cyclopentadienyl(dicarbonyl)iron]-3-phenyl-2-propen-1-imine ((*Z*)-**7a**): To the iron complex (*Z*)-**6a** (910 mg, 3 mmol) dissolved in CH_2Cl_2 (35 mL) was added aniline (0.5 mL, 1.8 equiv) at 0 °C in the dark followed by triethylamine (0.5 mL, 1.2 equiv). After 40 min the reaction mixture was treated with $TiCl_4$ (1.8 mL, 1 M solution in CH_2Cl_2). The solution was stirred for 1 h at 0 °C and then at room temperature for 2 h until IR monitoring indicated that the reaction was complete. The reaction mixture was hydrolyzed with saturated aqueous NH_4Cl solution (100 mL), and the aqueous layer was extracted twice with CH_2Cl_2 (200 mL). The combined organic phases were washed with 2 N HCl (150 mL) and water (150 mL) and dried ($MgSO_4$), and the solvent evaporated. The brown oil obtained was treated with CH_2Cl_2/petroleum ether/ether (1:1:1) and stored at −22 °C overnight. The mother liquor was removed by means of a cannula, and the precipitate was dried in vacuo to yield (*Z*)-**7a** (626 mg, 55 %) as a yellow-brown, amorphous foam. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 7.43 (d, *J* = 9.2 Hz, 1H, CH=N), 7.28–7.18 (m, 4H, arom CH), 7.11–7.03 (m, 2H, arom CH), 6.95 (d, *J* = 7.2 Hz, 2H, arom CH), 6.82 (d, *J* = 9.5 Hz, 1H, alkene CH), 6.76 (d, *J* = 7.7 Hz, 2H, arom CH), 5.15 (s, 5H, C_5H_5); ^{13}C NMR (50.3 MHz, [D$_6$]DMSO): δ = 215.4, 181.5, 155.3, 154.0, 152.6, 142.0, 128.9, 127.8, 124.8, 124.6, 124.5, 120.3, 86.9; IR (CH_2Cl_2): $\tilde{\nu}$ = 2030, 1972, 1601, 1579, 1551 cm^{-1}; MS (FD): *m*/*z* (%) = 384.4 (30), 383.4 (100); $C_{22}H_{17}FeNO_2$ (383.2): calcd C 68.92, H 4.47, N 3.66; found C 68.33, H 4.64, N 3.06.

(*Z*)-*N*-Benzenesulfonyl-3-[cyclopentadienyl(dicarbonyl)iron]-3-phenyl-2-propen-1-imine [(*Z*)-**7b**]: To the iron complex (*Z*)-**6a** (437 mg, 1.4 mmol) dissolved in CH_2Cl_2 (35 mL) was added benzenesulfonamide (290 mg, 1.3 equiv, 1.9 mmol). The suspension was cooled to 0 °C and then treated

with triethylamine (0.47 mL, 2.3 equiv) followed by $TiCl_4$ (0.85 mL, 1M solution in CH_2Cl_2). The reaction mixture was warmed to room temperature and stirred in the dark until IR monitoring indicated that the reaction was complete (24 h). The reaction mixture was hydrolyzed and worked up as described for (*Z*)-**7a**. The brown oil obtained was dissolved in CH_2Cl_2 and diluted with petroleum ether to precipitate a dark brown solid. The solution was removed by means of a cannula, and the solvent was evaporated to yield (*Z*)-**7b** (472 mg, 74%) as a yellow-brown oil. ^{1}H NMR (200 MHz): $\delta = 7.93$ (d, $J = 9.7$ Hz, 1H, CH=N), 7.79 (d, $J = 10$ Hz, 2H, arom CH), 7.70–7.42 (m, 3H, arom CH), 7.32–6.97 (br d, 2H, arom CH), 7.01 (d, $J = 9.7$ Hz, 1H, alkene CH), 6.81 (d, $J = 6.7$ Hz, 2H, arom CH), 4.80 (s, 5H, C_5H_5); ^{13}C NMR (50.3 MHz): $\delta = 213.1$, 211.3, 161.1, 153.0, 140.5, 138.9, 132.6, 128.7, 127.9, 127.3, 126.1, 123.8, 86.4; IR (CH_2Cl_2): $\tilde{\nu} = 2030$, 1981 cm^{-1}; MS (FD): *m*/*z* (%) = 447.5 (20), 419.4 (100).

***N*-*tert*-Butyl-2,5-dihydro-3-phenyl-1*H*-pyrrol-2-one** (**8a**): To a solution of (*Z*)-**6a** (1.26 g, 4.1 mmol) in CH_2Cl_2 (40 mL) was added *tert*-butylamine (0.45 mL, 1.05 equiv) and triethylamine (1.3 mL, 2.3 equiv) at 0 °C in the dark. The reaction mixture was stirred for 1 h before $TiCl_4$ (4.1 mL, 1M solution in CH_2Cl_2) was added dropwise. The reaction mixture was then stirred at 0 °C for 1 h and at room temperature for 48 h. IR monitoring and TLC indicated that the reaction was complete after 24 h. The solution was hydrolyzed by the addition of saturated aqueous NH_4Cl solution (100 mL), diluted with CH_2Cl_2 (150 mL) and 2N HCl (150 mL). This two-layer mixture was vigorously stirred for 5 min. The separated aqueous layer was extracted with CH_2Cl_2 (100 mL). The combined organic phases were washed with 2N HCl (2 × 120 mL), water (120 mL), and brine (120 mL), dried ($MgSO_4$), and then concentrated in vacuo. Flash chromatography (Florisil, petroleum ether/ethyl acetate 16:1 to 4:1) gave 430 mg **8a** (49%) as a pale yellow, amorphous solid. M.p. 81–83 °C; $R_f = 0.43$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz): $\delta = 7.83$ (dd, $J = 1.8$, 7.9 Hz, 2H, arom CH), 7.39–7.25 (m, 3H, arom CH), 7.09 (t, $J = 2$ Hz, 1H, alkene CH), 4.04 (d, $J = 2$ Hz, 2H, CH_2N), 1.49 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (^{13}C{^{1}H} DEPT 135 NMR, 100.6 MHz): $\delta = 170.1$ (CO), 138.4 (s), 134.3 (d), 132.0 (s), 128.7 (d), 128.2 (d), 127.1 (d), 54.1 (s), 48.5 (s), 27.9 (q); IR (CH_2Cl_2): $\tilde{\nu} = 1677$ cm^{-1}; IR (KBr): $\tilde{\nu} = 3391$, 3053, 3034, 2979, 2955, 2921, 2851, 1701 (sh), 1667, 1635 (sh), 1493, 1457, 1448, 1440, 1393, 1381, 1365, 1307, 1275, 1232, 1204 cm^{-1}; MS (EI): *m*/*z* (%) = 216.2 (2), 215.2 (54); $C_{14}H_{17}NO$ (215.3) · 0.25 H_2O: calcd C 76.50, H 8.02, N 6.27; found C 76.89, H 7.96, N 6.21.

***N*-Cyclohexyl-2,5-dihydro-3-phenyl-1*H*-pyrrol-2-one** (**8b**): The iron complex (*Z*)-**6a** (330 mg, 1.1 mmol) dissolved in CH_2Cl_2 (20 mL) was treated with cyclohexylamine (0.13 mL, 1.2 mmol), triethylamine (0.35 mL, 2.5 mmol), and $TiCl_4$ (1.1 mL, 1M solution in CH_2Cl_2) as described above for **8a** until IR monitoring indicated that the reaction was complete (24 h). Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate (6:1) to ethyl acetate) gave **8b** (145 mg, 56%) as a brown-yellow foam. $R_f = 0.64$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): $\delta = 7.86$ (dd, $J = 1.5$, 7.1 Hz, 2H, arom CH), 7.37–7.27 (m, 3H, arom CH), 7.13 (t, $J = 2$ Hz, 1H, alkene CH), 4.11–4.05 (m, 1H, CHN), 3.92 (d, $J =$ 2 Hz, 2H, CH_2N), 1.84–1.79 (m, 4H, CH_2), 1.69–1.66 (m, 1H, CH_2), 1.46–1.35 (m, 4H, CH_2), 1.33–1.15 (m, 1H, CH_2); ^{13}C NMR (^{13}C{^{1}H} DEPT 135 NMR, 100.6 MHz): $\delta = 169.3$ (s), 137.4 (s), 135.0 (d), 134.9 (s), 128.3 (d), 127.1 (d), 127.0 (d), 50.8 (d), 46.5 (t), 31.5 (t), 25.6 (t), 25.5 (t); IR (CH_2Cl_2): $\tilde{\nu} = 1674$ cm^{-1}; MS (FD): *m*/*z* (%) = 241.2 (24), 240.2 (100); $C_{16}H_{19}NO$ (241.1): calcd C 79.62, H 7.94, N 5.91; found C 78.91, H 7.89, N 5.52.

***N*-Cyclohexyl-2,5-dihydro-5-hydroxy-3-phenyl-1*H*-pyrrol-2-one** (**9**): Under the same conditions as described above (*Z*)-**6a** (310 mg, 1 mmol) dissolved in CH_2Cl_2 (20 mL) was treated with cyclohexylamine (0.12 mL), triethylamine (0.34 mL), and $TiCl_4$ (1 mL, 1M solution in CH_2Cl_2), except that the reaction mixture was worked up after 12 h. The crude, solid product obtained was separated by flash chromatography (Florisil, petroleum ether/ethyl acetate 9:1, 0.1% triethylamine) to yield firstly **8b** (83 mg, 34%) and secondly **9** (40 mg, 16%) as a pale yellow foam. $R_f = 0.61$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): $\delta = 7.68$ (dd, $J =$ 2.4, 8 Hz, 2H, arom CH), 7.36–7.26 (m, 3H, arom CH), 6.90 (s, 1H, alkene CH), 4.74 (s, 1H, CHN), 4.06–3.99 (m, 1H, CH_2CHN), 2.09–2.07 (m, 1H, CH_2), 1.96–1.66 (m, 6H, CH_2), 1.53–1.40 (m, 2H, CH_2), 1.27–1.17 (m, 1H, CH_2); ^{13}C NMR (^{13}C{^{1}H} DEPT 135 NMR, 100.6 MHz): $\delta = 170.3$ (s), 138.7 (s), 136.1 (d), 131.0 (s), 128.8 (d), 128.4 (d), 127.2 (d), 58.8 (d), 53.7 (d), 32.6 (t), 31.4 (t), 26.2 (t), 25.9 (t), 25.5 (t); IR (CH_2Cl_2): $\tilde{\nu} = 1680$ cm^{-1}; MS (FD): *m*/*z* (%) = 257.2 (1); MS (FAB): *m*/*z* (%) = 241.2 (100).

***N*-[(*S*)-Methylbenzyl]-2,5-dihydro-3-phenyl-1*H*-pyrrol-2-one** (**8c**): The iron complex (*Z*)-**6a** (234 mg, 0.76 mmol) dissolved in CH_2Cl_2 (25 mL) was treated with (*S*)-phenylethylamine (0.1 mL, 0.80 mmol), triethylamine (0.25 mL, 1.8 mmol), and $TiCl_4$ (0.8 mL, 1M solution in CH_2Cl_2) as described above for **8a**, except that ether was used for extraction after hydrolysis of the blue-black reaction mixture with saturated aqueous NH_4Cl solution. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 6:1) gave **8c** (121 mg, 61%) as pale, yellow crystals (ether).

Under the same conditions as described above (*Z*)-**6a** (438 mg, 1.4 mmol) dissolved in CH_2Cl_2 (20 mL) was treated with (*S*)-phenylethylamine (0.2 mL, 1.5 mmol) and triethylamine (0.45 mL, 3.3 mmol). The reaction mixture was stirred for 2 h at 0 °C. Then ferrocenium hexafluorophosphate (235 mg, 0.5 equiv) dissolved in 40 mL CH_2Cl_2 was added. The reaction mixture was stirred for 49 h at room temperature (IR monitoring) and worked up as described above. The concentrate was purified by flash chromatography (Florisil, petroleum ether/ethyl acetate 12:1) to yield **8c** (83 mg, 23%).

Compound ***8c***: M.p. 106–108 °C (ether); $R_f = 0.68$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz): $\delta = 7.88$ (dd, $J = 1.8$, 8 Hz, 2H, arom CH), 7.42–7.25 (m, 8H, arom CH), 7.12 (t, $J = 2$ Hz, 1H, alkene CH), 5.66 (q, $J = 7.2$ Hz, 1H, $CH(CH_3)$), 3.95 (dd, $J = 2.0$, 20.7 Hz, 1H, CH_2N), 3.62 (dd, $J = 2.0$, 20.7 Hz, 1H, CH_2N), 1.62 (d, $J = 7.2$ Hz, 3H, CH_3); ^{13}C NMR (100.6 MHz): $\delta = 169.5$, 141.1, 137.1, 135.3, 131.9, 128.6, 128.4, 128.3, 127.5, 127.0 (2 signals), 49.4, 46.2, 17.6; IR (CH_2Cl_2): $\tilde{\nu} = 1678$ cm^{-1}; MS (FAB): *m*/*z* (%) = 264.2 (30), 263.2 (100); $C_{18}H_{17}NO$ (263.3) · 0.5 H_2O: calcd C 79.38, H 6.66, N 5.14; found C 79.12, H 6.63, N 4.94.

Alternatively, a solution of the iron complex (*Z*)-**6a** (260 mg, 0.9 mmol) in ether (20 mL) was treated with (*S*)-phenylethylamine (0.12 mL, 1.05 equiv) at 0 °C, and the mixture was then stirred for 90 min. $MgSO_4$ was added, and the mixture stirred for a further 30 min. The reaction mixture was filtered through a plug of Celite, washed with ether, and the filtrate concentrated in vacuo. ^{1}H NMR spectroscopy of the crude product indicated the formation of **8c** and (*Z*)-**7c** (ratio (*Z*)-**7c**:**8c** = 9:1). Selected data for (*Z*)-*N*-[(*S*)-methylbenzyl]-3-[cyclopentadienyl(dicarbonyl)iron]-3-phenyl-2-propen-1-imine (*Z*)-**7c**: ^{1}H NMR (200 MHz): $\delta = 8.11$ (d, $J = 8.8$ Hz, 1H, CH=N), 7.46–7.05 (m, 8H, arom CH), 6.92 (d, 2H, arom CH), 6.83 (d, $J = 8.8$ Hz, 1H, alkene CH), 4.79 (s, 5H, C_5H_5), 4.53 (q, 1H, $J = 6.4$ Hz, $CH(CH_3)$), 1.60 (d, $J = 6.6$ Hz, 3H, CH_3); IR (CH_2Cl_2): $\tilde{\nu} = 2021$, 1969, 1608 cm^{-1}.

***N*-[(*R*)-2-Methyl-1-methyloxycarbonyl-propyl]-2,5-dihydro-3-phenyl-1*H*-pyrrol-2-one** (**8d**): To a solution of the iron complex (**Z**)-**6a** (310 mg, 1 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added neat (D)-valine methylester hydrochloride (176 mg, 1.05 mmol). Triethylamine (0.5 mL, 3.4 mmol) was added to give a homogenous solution which was treated with $TiCl_4$ (1.0 mL, 1M solution in CH_2Cl_2) and worked up as described for compound **8a** after complete consumption of the starting material. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 2:1) gave **8d** (110 mg, 41%) as a pale yellow, viscous oil. $R_f = 0.48$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz): $\delta = 7.87$ (dd, $J = 1.7$, 8.0 Hz, 2H, arom CH), 7.40–7.26 (m, 3H, arom CH), 7.25 (t, $J = 1.9$ Hz, 1H, alkene CH), 4.69 (d, $J = 10.2$ Hz, 1H, CH), 4.36 (dd, $J = 1.7$, 20.7 Hz, 1H, CH_2N), 4.02 (dd, $J = 1.9$, 20.7 Hz, 1H, CH_2N), 3.70 (s, 3H, OCH_3), 2.31–2.16 (m, 1H, CH), 1.00 (d, $J = 6.6$ Hz, 3H, CH_3), 0.89 (d, $J = 6.7$ Hz, 3H, CH_3); ^{13}C NMR (100.6 MHz): $\delta = 171.7$, 170.3, 136.3, 136.2, 131.6, 128.5, 128.4, 127.0, 59.9, 51.8, 47.8, 29.3, 19.4, 19.2; IR (CH_2Cl_2): $\tilde{\nu} = 1684$ cm^{-1}; MS (FD): *m*/*z* (%) = 274.2 (17), 273.1 (100); $C_{16}H_{19}NO_3$ (273.3): calcd C 70.31, H 7.01, N 5.12; found C 69.61, H 6.94, N 5.22.

***N*-[(*S*)-Methylbenzyl]-4,5,6,7-tetrahydro-3*H*-isoindol-1-one** (**8e**): A solution of the iron complex **6c** (428 mg, 1.5 mmol) in CH_2Cl_2 (15 mL) was treated with (*S*)-phenylethylamine (0.2 mL, 1.55 mmol), triethylamine (0.48 mL, 3.45 mmol), and $TiCl_4$ (1.5 mL, 1M solution in CH_2Cl_2), as described above for **8a**. Purification by flash chromatography {Florisil, petroleum ether/ethyl acetate [20:1 (300 mL) to 10:1 (300 mL) to 2:1 (300 mL)]} gave **8e** (230 mg, 63%) as a yellow-brown oil, which solidified on standing. $R_f = 0.33$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): $\delta = 7.29$ (br m, 5H, arom CH), 5.54 (br q, $J = 5.5$ Hz, 1H, $CH(CH_3)$), 3.68 (d, $J = 18.2$ Hz, 1H, CH_2), 3.36 (d, $J = 18.5$ Hz, 1H, CH_2), 2.19 (m, 4H, CH_2), 1.66 (m, 4H, CH_2), 1.55 (br d, $J = 5.8$ Hz, 3H, CH_3); ^{13}C NMR (100.6 MHz) $\delta = 171.4$, 149.8, 141.5, 131.9, 128.4, 127.2, 127.0, 48.9, 48.8, 24.3, 22.2, 21.9, 20.4, 17.6; IR (CH_2Cl_2): $\tilde{\nu} = 1674$ cm^{-1}; MS (FD): *m*/*z*

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(%) = 242.1 (27), 241.1 (100); $C_{16}H_{19}NO$ (241.3): calcd C 79.63, H 7.94, N 5.80; found C 79.63, H 7.84, N 5.80.

***N*-[(*S*)-Methylbenzyl]-4,5,6-trihydro-3*H*-benzo[3,4]cyclohepta[1,2-c]pyrrol-1-one** (**8f**): A solution of the iron complex **6d** (1.22 g, 3.5 mmol) in CH_2Cl_2 (80 mL) was treated with (*S*)-phenylethylamine (0.55 mL, 3.7 mmol), triethylamine (1.25 mL, 9 mmol), and $TiCl_4$ (3.8 mL, 1M solution in CH_2Cl_2), as described above for **8a**. The crude, solid product was purified initially by flash chromatography (Florisil, petroleum ether/ethyl acetate 15:1 to 10:1 to 5:1). After evaporation of the solvents, the residue was dissolved in CH_2Cl_2/petroleum ether and stored overnight at room temperature. The precipitate (iron oxide and iron hydroxide) was removed by filtration through a PTFE syringe filter (0.45 mm). The filtrate was concentrated in vacuo and then recrystallized from ether/CH_2Cl_2/petroleum ether (1:1:4) to yield **8f** (449 mg, 42%) as a pale yellow foam. Under the same conditions as described above, 1 mmol **6d** gave **8f** in 68% yield after flash chromatography. $R_f = 0.65$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (200 MHz): $\delta = 8.31$ (dd, 1H, $J = 1.0$, 8.4 Hz, arom CH), 7.35–7.08 (m, 8H, arom CH), 5.66 (q, $J = 7.1$ Hz, 1H, C*H*(CH_3)), 3.83 (d, $J = 19.1$ Hz, 1H, CH_2N), 3.50 (d, $J = 19$ Hz, 1H, CH_2N), 2.74–2.68 (m, 2H, CH_2), 2.56 (dt, $J = 7.3$ Hz, 2H, CH_2), 2.15–1.95 (m, 2H, CH_2), 1.62 (d, $J = 7.1$ Hz, 3H, CH(CH_3)); ^{13}C NMR (100.6 MHz): $\delta = 170.6$, 152.4, 142.6, 141.2, 130.8, 129.7, 129.1, 128.5, 128.4, 127.5, 127.3, 127.1, 125.9, 49.6, 49.1, 34.6, 30.5, 27.7, 17.5; IR (CH_2Cl_2): $\tilde{\nu} = 1672$ cm^{-1}; IR (KBr): $\tilde{\nu} = 3436$, 3280 (sh), 3060, 3028, 2935, 1671, 1493, 1450, 1401, 1356, 1236 cm^{-1}; $C_{21}H_{21}NO$ (303.4)·H_2O: calcd C 78.47, H 7.21, N 4.36; found C 78.18, H 6.73, N 3.93.

***N*-[(*S*)-Methylbenzyl]-1,2,3,4,5-pentahydro-benz[e]isoindol-3-one** (**8g**): A solution of the iron complex **6f** (1.0 g, 3.2 mmol) in CH_2Cl_2 (80 mL) was treated with (*S*)-phenylethylamine (0.4 mL, 3.2 mmol), triethylamine (1.0 mL, 7.2 mmol), and $TiCl_4$ (3.0 mL, 1M solution in CH_2Cl_2), as described above for **8a**. The crude solid product was initially purified by flash chromatography (Florisil, petroleum ether/ethyl acetate 12:1 to 5:1). After evaporation of the solvents, the residue was dissolved in ether/petroleum ether (40 mL, 1:1) and stored at room temperature overnight. The precipitate was removed by filtration through a PTFE syringe filter (0.45 mm). The filtrate was concentrated in vacuo and then recrystallized from ether (−22 °C) to yield **8g** (320 mg, 37%) as a beige, amorphous solid. Under the same conditions as described above, 1 mmol **6f** gave **8g** in 51% yield after flash chromatography. M.p. 62 °C; $R_f = 0.5$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): $\delta = 7.38–7.11$ (m, 8H, arom CH), 7.01 (d, $J = 7.5$ Hz, 1H, arom CH), 5.65 (q, $J = 7.1$ Hz, 1H, C*H*(CH_3)), 4.15 (dt, $J = 2.0$, 18.6 Hz, 1H, CH_2N), 3.83 (dt, $J = 2.0$, 18.6 Hz, 1H, CH_2N), 2.93 (t, $J = 8.2$ Hz, 2H, CH_2), 2.60–2.56 (m, $J = 8.2$ Hz, 2H, CH_2), 1.65 (d, $J = 7.1$ Hz, 3H, CH_3); ^{13}C NMR (100.6 MHz): $\delta = 170.6$, 146.3, 142.2, 136.7, 131.8, 129.7, 129.1, 128.5, 128.2, 127.3, 126.9, 126.5, 122.4, 48.9, 45.1, 27.9, 18.5, 17.6; IR (CH_2Cl_2): $\tilde{\nu} = 1672$ cm^{-1}; MS (FD): *m*/*z* (%) = 290.2 (29), 289.2 (100); $C_{20}H_{19}NO$ (284.4)·H_2O: calcd C 78.15, H 6.89, N 4.56; found C 77.95, H 6.81, N 4.31.

***N*-(6′,6′-Dimethylbicyclo[3.1.1]hept-2′-yl)-1,2,3,4-tetrahydro[1]benzopyrano[3,4-c]pyrrol-1-one** (**8h**): The iron complex **6e** (672 mg, 2 mmol) dissolved in CH_2Cl_2 (30 mL) was treated with (*R*)-(−)-nopinylamine (322 mg), triethylamine (0.64 mL), and $TiCl_4$ (2.0 mL, 1M solution in CH_2Cl_2), as described for **8a**. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 15:1) gave **8h** (464 mg, 75%) as a yellow foam. $R_f = 0.68$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): $\delta = 8.06$ (dd, $J = 1.8$, 7.3 Hz, 1H, H9), 7.13 (dt, $J = 1.8$, 7.6 Hz, 1H, H7), 6.92 (dt, $J = 1.2$, 7.3 Hz, 1H, H8), 6.80 (dd, $J = 1.2$, 7.9 Hz, 1H, H6), 5.12 (s, 2H, OCH_2), 4.66 (ddd, $J = 1.8$, 7.9, 10.0 Hz, 1H, H2′), 4.03 (d, $J = 19.7$ Hz, 1H, NCH_2), 3.89 (d, $J = 19.9$ Hz, 1H, NCH_2), 2.53–2.47 (m, $J = 10.0$ Hz, 1H, H7′-*exo*), 2.28–2.23 (m, 1H, H3′), 2.15 (ddd, $J = 1.8$, 5.0, 6.8 Hz, 1H, H1′), 2.01–1.94 (m, 2H, H4′ and H5′), 1.93–1.83 (m, 2H, H3′ and H4′), 1.24 (s, 3H, CH_3-*exo*), 1.13 (s, 3H, CH_3-*endo*), 1.03 (d, $J = 10.0$ Hz, 1H, H7′-*endo*); The assignments of the *exo* and *endo* protons and methyl groups were made on the basis of NOE measurements. For instance, irradiation of the proton at $\delta = 1.03$ showed NOE enhancement to that at $\delta = 4.66$ and vice versa. In addition, the observed NOEs at $\delta = 2.01–1.94$ (H5′), 2.53–2.47 (H7′-*exo*), and 2.15 (H1′) by irradiation of the methyl group at $\delta = 1.24$ (CH_3-*exo*), as well as the NOE enhancements ($\delta = 4.03$, 3.89, 2.01–1.94, and 1.93–1.83), obtained upon irradiation of the methyl group at $\delta = 1.13$ (CH_3-*endo*), confirm the assignment. ^{13}C NMR (100.6 MHz): $\delta = 168.4$ (CO), 152.6 (C5a), 141.5 (C3a), 129.6 (C7), 126.2 (C9a), 123.9 (C9), 121.7 (C8), 117.4 (C9b), 115.5 (C6), 65.1 (C4), 54.2 (C2′), 48.2 (NCH_2), 46.5 (C1′), 41.2 (C5′), 37.7 (C6′), 33.8 (C7′), 28.0 (CH_3-*exo*), 25.4 (C4′), 24.2 (CH_3-*endo*), 21.9 (C3′); IR (CH_2Cl_2): $\tilde{\nu} = 1685$ cm^{-1}; IR (KBr): $\tilde{\nu} = 3286$, 3066, 3041, 2988, 2919, 2868, 1679, 1654, 1607, 1575, 1495, 1471, 1457, 1406, 1386, 1366, 1320, 1302, 1281, 1254, 1233, 1207, 1165, 1128, 1077, 1052, 1036, 1003 cm^{-1}; MS (EI): *m*/*z* (%) = 323.1 (59), 309.2 (37), 279.9 (8), 267.9 (45), 253.9 (16), 239.8 (37), 226.9 (22), 203.9 (44), 187.0 (27), 159.9 (14), 147.0 (32), 130.9 (32), 123.0 (100); $C_{20}H_{23}NO_2$ (309.4)·1.5H_2O: calcd C 71.40, H 7.79, N 4.16; found C 71.49, H 7.46, N 3.79.

Dimer 8i: The iron complex **6e** (672 mg, 2 mmol) dissolved in CH_2Cl_2 (30 mL) was treated with hexamethylendiamine (122 mg), triethylamine (0.64 mL), and $TiCl_4$ (2.0 mL, 1M solution in CH_2Cl_2), as described above for **8a**. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 2:1) gave **8i** (150 mg, 33%) as a brown, amorphous solid. Side products could not be determined nor isolated. M.p. 191 °C; $R_f = 0.31$ (CH_2Cl_2/ethyl acetate 2:1); ^{1}H NMR (200 MHz): $\delta = 8.05$ (d, $J = 6.8$ Hz, 1H, arom CH), 7.14 (t, $J = 7.3$ Hz, 1H, arom CH), 6.92 (t, $J = 7.8$ Hz, 1H, arom CH), 6.81 (d, $J = 7.8$ Hz, 1H, arom CH), 5.12 (s, 2H, OCH_2), 3.91 (s, 2H, NCH_2), 3.47 (t, $J = 6.3$ Hz, 2H, NCH_2), 1.58 (br s, 2H, CH_2), 1.35 (br s, 2H, CH_2); ^{13}C NMR (50.3 MHz): $\delta = 168.1$ (s), 152.5 (s), 141.6 (s), 129.7 (d), 126.4 (s), 123.8 (d), 121.7 (d), 117.3 (s), 115.6 (d), 65.1 (t), 49.6 (t), 41.8 (t), 28.5 (t), 26.3 (t); IR (CH_2Cl_2): $\tilde{\nu} = 1685$ cm^{-1}; IR (KBr): $\tilde{\nu} = 3446$, 2933, 2863, 2849, 1678, 1659, 1495, 1460, 1446, 1410, 1399, 1382, 1369, 1309, 1297, 1282, 1215, 1139, 1125, 1035, 1001 cm^{-1}; MS (FD): *m*/*z* (%) = 456.5 (100); $C_{28}H_{28}N_2O_4$ (457.3)·1.5H_2O: calcd C 69.50, H 6.46, N 5.79; found C 69.69, H 6.16, N 5.28.

***N*-[(*S*)-Methylbenzyl]-1,2,3,4-tetrahydro[1]benzopyrano[3,4-c]pyrrol-1-one** (**8j**): The iron complex **6e** (1.2 g, 3.6 mmol) dissolved in CH_2Cl_2 (80 mL) was treated with (*S*)-phenylethylamine (0.48 mL, 3.7 mmol), triethylamine (1.2 mL, 8.3 mmol), and $TiCl_4$ (3.6 mL, 1M solution in CH_2Cl_2), as described above for **8a**. The crude, solid product was purified initially by flash chromatography (Florisil, petroleum ether/ethyl acetate 15:1 to 8:1). The solvent was evaporated and the residue, dissolved in ether/petroleum ether, was stored overnight at room temperature. The fluffy precipitate was removed by filtration through a PTFE syringe filter (0.45 mm). The filtrate was concentrated in vacuo and then recrystallized from ether/petroleum ether to yield **8j** (667 mg, 64%) as a beige, amorphous solid. M.p. 48–50 °C; $R_f = 0.5$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): $\delta = 8.10$ (dd, $J = 1.7$, 7.6 Hz, 1H, arom CH), 7.35–7.29 (m, 4H, arom CH), 7.28–7.24 (m, 1H, arom CH), 7.14 (dt, $J = 1.8$, 8 Hz, 1H, arom CH), 6.94 (dt, $J = 1.2$, 7.7 Hz, 1H, arom CH), 6.80 (dd, $J = 0.9$, 8.2 Hz, 1H, arom CH), 5.63 (q, $J = 7$ Hz, 1H, C*H*(CH_3)) 5.07 (d, $J = 15.9$ Hz, 2H, CH_2O), 5.01 (d, $J = 15.9$ Hz, 2H, CH_2O), 3.87 (d, $J = 19.6$ Hz, 1H, CH_2N), 3.55 (d, $J = 20$ Hz, 1H, CH_2N), 1.62 (d, $J = 7.3$ Hz, 3H, CH_3); ^{13}C{^{1}H} GASPE NMR (100.6 MHz): $\delta = 167.6$ (s), 152.5 (s), 141.9 (s), 140.8 (s), 129.8 (d), 128.7 (d), 127.6 (d), 127.0 (d), 126.3 (s), 123.9 (d), 121.8 (d), 117.3 (s), 115.6 (d), 65.1 (t), 49.0 (d), 45.7 (t), 17.5 (q); IR (CH_2Cl_2): $\tilde{\nu} = 1684$, 1664 cm^{-1}; IR (KBr): $\tilde{\nu} = 3433$, 2981, 2934, 1684, 1607, 1576, 1495, 1455 cm^{-1}; MS (FD): *m*/*z* (%) = 292.1 (100), 291.0 (100); $C_{19}H_{17}NO_2$ (291.3)·H_2O: calcd C 73.77, H 6.19, N 4.53; found C 73.50, H 5.87, N 4.59.

***N*-Propyl-1,2,3,4-tetrahydro[1]benzopyrano[3,4-c]pyrrol-1-one** (**8k**): The iron complex **6e** (1.34 g, 4 mmol) dissolved in CH_2Cl_2 (70 mL) was treated with *n*-propylamine (0.34 mL, 4.2 mmol), triethylamine (1.28 mL, 9.2 mmol), and $TiCl_4$ (4 mL, 1M solution in CH_2Cl_2), as described above for compound **8a** until complete consumption of the starting material was indicated by IR monitoring (18 h). Purification by flash chromatography (Florisil, petroleum ether/ethyl acetate 20:1 to 2:1) gave **8k** (0.6 g, 66%) as a pale yellow oil.

Under the same conditions as described above, **6e** (250 mg, 0.74 mmol) dissolved in CH_2Cl_2 (15 mL) was treated with *n*-propylamine (0.06 mL), triethylamine (0.24 mL), and BCl_3 [0.74 mL, 1M solution in p-xylene (Aldrich)] for 13 h (IR monitoring) and worked up. Flash chromatography (silica gel, petroleum ether/ethyl acetate 10:1) gave 64 mg of **8k** (38%).

The iron complex **6e** (504 mg, 1.5 mmol) dissolved in CH_2Cl_2 (30 mL) was treated with *n*-propylamine (0.13 mL), triethylamine (0.48 mL), and $AlCl_3$ (0.2 g, neat) for 16 h (IR monitoring) and worked up as described above. The black concentrate was dissolved in CH_2Cl_2/petroleum ether and filtered through a PTFE syringe filter. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 5:1) gave 130 mg of **8k** (38%).

*Compound **8k***: Beige, amorphous solid; m.p. 50–51 °C; $R_f = 0.35$ (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz): $\delta = 8.03$ (dd, $J = 1.5$,

7.6 Hz, 1H, arom CH), 7.11 (dt, $J = 1.8$, 8.2 Hz, 1H, arom CH), 6.90 (dt, $J = 0.9$, 7.6 Hz, 1H, arom CH), 6.78 (dd, $J = 0.9$, 8.2 Hz, 1H, arom CH), 5.06 (s, 2H, OCH_2), 3.84 (s, 2H, NCH_2), 3.38 (t, $J = 7.3$ Hz, 2H, NCH_2), 1.57 (dq, $J = 7.3$ Hz, 2H, CH_2), 0.89 (t, $J = 7.3$ Hz, 3H, CH_3); $^{13}C\{^1H\}$ GASPE NMR (100.6 MHz): $\delta = 168.0$ (s), 152.5 (s), 141.6 (s), 129.6 (d), 126.2 (s), 123.7 (d), 121.6 (d), 117.3 (s), 115.5 (d), 65.0 (t), 49.6 (t), 43.6 (t), 21.8 (t), 11.2 (q); IR (CH_2Cl_2): $\tilde{\nu} = 1687$ cm^{-1}; IR (KBr): $\tilde{\nu} = 3414$ (broad), 3080, 2934, 2875, 1737, 1685, 1655, 1607, 1573, 1496, 1453, 1402, 1366, 1346, 1303, 1281, 1262, 1215, 1137, 1106, 1070, 1052, 1036, 1010 cm^{-1}; MS (EI): m/z (%) = 229.1 (81), 200.2 (44), 186.1 (17), 172.1 (15), 158.1 (12), 144.2 (65), 130.1 (30), 115.1 (32), 102.1 (18), 84.0 (49), 49.3 (100), 42.4 (50).

***N*-*tert*-Butyl-1,2,3,4-tetrahydro[1]benzopyrano[3,4-c]pyrrol-1-one (8l)**: The iron complex **6e** (0.93 g, 2.8 mmol) dissolved in CH_2Cl_2 (80 mL) was treated with *tert*-butylamine (0.3 mL, 2.9 mmol), triethylamine (0.9 mL, 6.4 mmol), and $TiCl_4$ (2.8 mL, 1M solution in CH_2Cl_2), as described for compound **8a**. The crude solid product was purified initially by flash chromatography (Florisil, petroleum ether/ethyl acetate 20:1 to 8:1). The solvent was evaporated and the residue was dissolved in petroleum ether/CH_2Cl_2 and stored overnight. The fluffy precipitate was removed by filtration through a PTFE syringe filter (0.45 mm). The filtrate was concentrated in vacuo and then recrystallized from petroleum ether/CH_2Cl_2 to yield **8l** (378 mg, 56%) as a pale yellow, crystalline solid. M.p. 95 – 97 °C; $R_f = 0.7$ (petroleum ether/ethyl acetate 2:1); ^1H NMR (200 MHz): $\delta = 8.08$ (dd, $J = 1.4$, 7.6 Hz, 1H, arom CH), 7.12 (dt, $J = 1.7$, 7.9 Hz, 1H, arom CH), 6.90 (dt, $J = 1.2$, 7.6 Hz, 1H, arom CH), 6.79 (dd, $J = 1.0$, 8.0 Hz, 1H, arom CH), 5.08 (s, 2H, CH_2O), 3.98 (s, 2H, CH_2N), 1.48 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (100.6 MHz): $\delta = 168.5$, 152.6, 140.8, 129.5, 127.3, 123.8, 121.6, 117.4, 115.5, 64.9, 54.2, 48.0, 28.0; IR (CH_2Cl_2): $\tilde{\nu} = 1685$, 1667 cm^{-1}; IR (KBr): $\tilde{\nu} = 3347$, 3078, 3042, 2975, 2934, 1685, 1607, 1493, 1456, 1438, 1395, 1383, 1367, 1303, 1282, 1260, 1221, 1165, 1153 cm^{-1}; MS (EI): m/z (%) = 244.1 (16), 243.2 (97), 242.1 (38), 243.2 (96), 228.1 (70), 200.1 (20), 187.2 (100), 158.1 (51), 130.0 (44), 115.0 (30), 102.0 (22), 77.1 (23); $C_{15}H_{17}NO_2$ (243.3) · H_2O: calcd C 68.94, H 7.33, N 5.36; found C 68.46, H 7.30, N 5.11.

***N*-Cyclohexyl-1,2,3,4-tetrahydro[1]benzopyrano[3,4-c]pyrrol-1-one (8m)**: The iron complex **6e** (1.62 g, 4.9 mmol) dissolved in CH_2Cl_2 (100 mL) was treated with cyclohexylamine (0.6 mL), triethylamine (1.6 mL), and $TiCl_4$ (4.9 mL, 1M solution in CH_2Cl_2), as described above for compound **8a**. The crude solid product was purified initially by flash chromatography (Florisil, petroleum ether/ethyl acetate 15:1 to 8:1). The solvent was evaporated in vacuo, and the residue dissolved in CH_2Cl_2/petroleum ether and stored overnight. The fluffy precipitate was removed by filtration through a PTFE-syringe filter (0.45 mm). The filtrate was concentrated in vacuo and then recrystallized from ether/CH_2Cl_2/petroleum ether (1:1:1) to yield **8m** (902 mg, 68%) as a pale yellow, amorphous solid. M.p. 122 °C; $R_f = 0.53$ (petroleum ether/ethyl acetate 2:1); ^1H NMR (400 MHz): $\delta =$ 8.06 (dd, $J = 1.5$, 7.6 Hz, 1H, arom CH), 7.12 (m, $J = 1.5$, 7.7 Hz, 1H, arom CH), 6.92 (t, $J = 7.3$ Hz, 1H, arom CH), 6.80 (d, $J = 8.2$ Hz, 1H, arom CH), 5.10 (d, 2H, CH_2O), 4.08 – 4.03 (m, 1H, CHN), 3.87 (s, 2H, CH_2N), 1.81 – 1.79 (m, 4H, CH_2), 1.69 – 1.66 (m, 1H, CH_2), 1.45 – 1.29 (m, 4H, CH_2), 1.22 – 1.08 (m, 1H, CH_2); $^{13}C\{^1H\}$ GASPE NMR (100.6 MHz): $\delta = 167.5$ (s), 152.6 (s), 141.5 (s), 129.6 (d), 126.6 (s), 123.9 (d), 121.7 (d), 117.4 (s), 115.5 (d), 65.1 (t), 50.5 (d), 46.0 (t), 31.6 (t), 25.6 (t), 25.5 (t); IR (CH_2Cl_2): $\tilde{\nu} = 1683$, 1662 (sh) cm^{-1}; MS (FD): m/z (%) = 270.0 (21), 269.0 (100), 268.0 (18); MS (EI): m/z (%) = 270.2 (3), 269.1 (16), 187.1 (25), 144.1 (28), 105.1 (35); $C_{17}H_{19}NO_2$ (269.3) · 2 H_2O: calcd C 71.06, H 7.37, N 4.87; found C 70.94, H, 6.95, N 4.37.

***N*-(2′-Propenyl)-1,2,3,4-tetrahydro[1]benzopyrano[3,4-c]pyrrol-1-one (8n)**: The iron complex **6e** (0.9 g, 2.68 mmol) dissolved in CH_2Cl_2 (35 mL) was treated with allylamine (0.21 mL), triethylamine (0.87 mL), and $TiCl_4$ (2.7 mL, 1M solution in CH_2Cl_2), as described for compound **8a**. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 8:1) gave **8n** (0.4 g, 67%) as colorless crystals. M.p. 118 °C; $R_f = 0.38$ (petroleum ether/ethyl acetate 2:1); ^1H NMR (400 MHz): $\delta = 8.07$ (dd, $J = 1.8$, 7.6 Hz, 1H, arom CH), 7.15 (dt, $J = 1.8$, 7.9 Hz, 1H, arom CH), 6.94 (dt, $J = 1.2$, 7.6 Hz, 1H, arom CH), 6.82 (dd, $J = 1.2$, 7.9 Hz, 1H, arom CH), 5.80 (ddt, $J = 6.2$, 9.4, 21.7 Hz, 1H, CH=CH_2), 5.21 – 5.16 (m, 2H, CH=CH_2), 5.12 (s, 2H, OCH_2), 4.10 (d, $J = 6.2$ Hz, 2H, NCH_2), 3.91 (s, 2H, NCH_2); $^{13}C\{^1H\}$ GASPE NMR (100.6 MHz): $\delta = 167.8$ (s), 152.5 (s), 141.9 (s), 133.2 (d), 129.8 (d), 126.1 (s), 123.9 (d), 121.8 (d), 117.9 (t), 117.3 (s), 115.6 (d), 65.1 (t), 49.3 (t), 44.7 (t); IR (CH_2Cl_2): $\tilde{\nu} = 1688$ cm^{-1}; IR (KBr): $\tilde{\nu} = 3446$, 3076, 3059, 3043, 3002, 2973, 2907, 2868, 1688, 1675, 1664, 1641, 1604, 1575, 1497, 1453, 1444, 1418, 1408, 1399, 1369, 1345, 1301, 1282, 1265, 1222, 1160, 1152, 1133, 1076, 1040, 1008 cm^{-1}; MS (EI): m/z (%) = 227.1 (100), 186.0 (25), 170.0 (6), 158 (12), 144.1 (53), 131.0 (16), 115.0 (22), 101.9 (10); $C_{14}H_{13}NO_2$ (227.3) · 0.5 H_2O: calcd C 71.17, H 5.97, N 5.93; found C 70.90, H 5.63, N 5.65.

***N*-(2′-Methoxyethyl)-1,2,3,4-tetrahydro[1]benzopyrano[3,4-c]pyrrol-1-one (8o)**: The iron complex **6e** (672 mg, 2 mmol) dissolved in CH_2Cl_2 (30 mL) was treated with 2-methoxyethylamine (0.18 mL), triethylamine (0.64 mL), and $TiCl_4$ (2.0 mL, 1M solution in CH_2Cl_2), as described for **8a**. IR and TLC monitoring indicated reaction to the product **8o**, exclusively. Purification by flash chromatography (silica gel, petroleum ether/ethyl acetate 10:1) gave **8o** (0.2 g, 41%) as a orange-yellow, viscous oil. $R_f = 0.13$ (petroleum ether/ethyl acetate 2:1); ^1H NMR (400 MHz): $\delta = 8.04$ (dd, $J = 1.5$, 7.6 Hz, 1H, arom CH), 7.13 (dt, $J = 1.8$, 7.9 Hz, 1H, arom CH), 6.92 (dt, $J = 1.2$, 7.3 Hz, 1H, arom CH), 6.80 (dd, $J = 1.2$, 7.9 Hz, 1H, arom CH), 5.11 (s, 2H, OCH_2), 4.06 (s, 2H, NCH_2), 3.64 (t, $J = 4.7$ Hz, 2H, NCH_2), 3.54 (t, $J = 4.7$ Hz, 2H, OCH_2), 3.32 (s, 3H, OCH_3); $^{13}C\{^1H\}$ GASPE NMR (100.6 MHz): $\delta = 167.9$ (s), 152.4 (s), 142.5 (s), 129.5 (d), 125.7 (s), 123.5 (d), 121.4 (d), 117.2 (s), 115.4 (d) , 71.5 (t), 64.9 (t), 58.5 (q), 51.1 (t), 41.8 (t); IR ($CDCl_3$): $\tilde{\nu} = 1681$ cm^{-1}; MS (EI): m/z (%) = 245.1 (57), 213.1 (5), 200.2 (45), 187.1 (5), 172.1 (8), 144.1 (22), 130.1 (8), 115.1 (19), 102.0 (5), 47.4 (49).

***N*-[(*S*)-Methylbenzyl]-2,5-dihydro-3,5-dimethyl-1*H*-pyrrol-2-one (10)**: The iron complex (*Z*)-**6g** (0.52 g, 2 mmol) dissolved in CH_2Cl_2 (130 mL) was treated with (*S*)-phenylethylamine (0.27 mL, 2.1 mmol), triethylamine (0.64 mL, 4.6 mmol), and $TiCl_4$ (2.0 mL, 1M solution in CH_2Cl_2), as described above for compound **8a**. The reaction mixture was stirred for 23 h (IR monitoring) and then worked up. Purification by column chromatography (silica gel, petroleum ether/ethyl acetate 2:1) as eluent gave **10** as a colorless oil (120 mg, 28%, mixture of diastereomers: 50:50). $R_f = 0.35$ (petroleum ether/ethyl acetate 2:1); ^1H NMR (200 MHz, * = diastereomer): $\delta = 7.37 – 7.18$ (m, 10H), 6.50 and 6.42* (brs, 1H), 5.50 – 5.33 (m, 2H), 4.07 and 3.67* (q, $J = 6.8$ Hz, 1H, H5), 1.87 and 1.86* (s, 3H), 1.66 and 1.65* (d, $J = 7.3$ Hz, 3H), 1.14 and 0.81* (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (50.3 MHz, * = diastereomer): $\delta = 172.0$, 171.9*, 142.4, 142.2*, 140.7, 133.9, 133.6*, 128.5, 128.2*, 127.3, 127.0*, 55.6, 55.1*, 50.6, 49.4*, 18.9, 18.4*, 18.3, 17.5*, 11.1; IR (CH_2Cl_2): $\tilde{\nu} = 1678$ cm^{-1}; MS (EI): m/z (%) = 215.2 (100), 200.1 (72), 138.1 (12), 131.1 (8), 124.1 (12), 120.1 (18), 111.1 (23), 105.1 (81), 96.0 (35), 77.0 (18); MS (FD): m/z (%) = 214.8 (100).

16-[2-(*N*,*N*-Dimethylamino)ethyl]-8-oxa-16-azapentacyclo-[8.4.3.1^{11,14}.0^{1,10}.0^{2,7}]-octadeca-2,4,6,12-tetraen-15,17-dione (13): To the iron complex **6e** (504 mg, 1.5 mmol) dissolved in CH_2Cl_2 (25 mL) was added 2-dimethylaminoethylamine **11** (0.60 mL, 6 mmol) at 0 °C. The reaction mixture was stirred for 1 h, then $TiCl_4$ (1.5 mL, 1M solution in CH_2Cl_2) was added, and the solution allowed to warm to room temperature. The workup was performed after 17 h [TLC, IR-monitoring ($\nu = 1685$ cm^{-1})] under the same conditions as described above for **8a**, except that finally KOH was added to the aqueous layer, which then was extracted repeatedly with CH_2Cl_2. The combined CH_2Cl_2 phases were dried ($MgSO_4$), and the solvent evaporated in vacuo. The crude product was chromatographed twice: i) column chromatography on Florisil with petroleum ether/ethyl acetate (1:2) and ethyl acetate/ethanol (10:1), ii) column chromatography on silica gel with ethyl acetate and ethyl acetate/ethanol (10:1) as eluents to yield **13** (36 mg, 7%) as a yellow oil. Side products were determined by TLC monitoring but could not be isolated. $R_f = 0.09$ (petroleum ether/ethyl acetate 2:1); ^1H NMR (200 MHz): $\delta = 7.71$ (dd, $J = 2.0$, 7.8 Hz, 1H), 7.20 (dt, $J = 2.0$, 7.8 Hz, 1H), 7.10 (dt, $J = 1.5$, 7.8 Hz, 1H), 6.92 (dd, $J = 1.5$, 7.8 Hz, 1H), 6.29 (dd, $J = 2.9$, 5.4 Hz, 1H), 6.20 (dd, $J = 2.9$, 5.4 Hz, 1H), 4.84 (d, $J = 11.7$ Hz, 1H), 3.72 (d, $J = 11.7$ Hz, 1H), 3.60 (brs, 1H), 3.47 (dt, $J = 3.9$, 7.3 Hz, 2H), 3.05 (brs, 1H), 2.40 (t, $J = 7.3$ Hz, 2H), 2.19 (s, 6H), 1.84 (d, $J = 9.8$ Hz, 1H), 1.70 (d, $J = 9.8$ Hz, 1H); ^{13}C NMR (50.3 MHz): $\delta = 178.3$, 175.4, 155.2, 136.2, 135.3, 129.0, 128.5, 123.2, 122.1, 117.5, 70.6, 56.6, 55.2, 51.5, 49.1, 48.1, 44.5, 36.1, 21.0; IR (CH_2Cl_2): $\tilde{\nu} = 1685$ cm^{-1}; MS (FD): m/z (%) = 338.2 (100), 272.1 (3).

16-(2-Methoxyethyl)-8-oxa-16-azapentacyclo[8.4.3.1^{11,14}.0^{1,10}.0^{2,7}]octadeca-2,4,6,12-tetraen-15,17-dione (14): To the iron complex **12** (1.16 g, 3.5 mmol) dissolved in CH_2Cl_2 (30 mL) were added 2-methoxyethylamine (0.32 mL, 3.6 mmol) and triethylamine (0.8 g, 7.94 mmol) at 0 °C. The reaction mixture was stirred for 1 h. Then $TiCl_4$ (3.45 mL, 1M solution in CH_2Cl_2) was added, and the solution was allowed to warm to room temperature. An additional equivalent of $TiCl_4$ was added, and the reaction mixture was stirred until TLC indicated complete consumption of the starting material. The mixture was stirred overnight (18 h), and IR monitoring then indicated

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a new (CO)-absorption at $\nu = 1705\ cm^{-1}$. The workup procedure was performed under the same conditions as described above for compound **8o**. Purification by flash chromatography (Florisil, petroleum ether/ethyl acetate 15:1 to 10:1 to 2:1) gave i) **14** (150 mg, 13%) as a yellow oil and ii) **8o** (93 mg, 11%). The imide intermediate (Scheme 7) could neither be determined nor isolated. $R_f = 0.51$ (petroleum ether/ethyl acetate 2:1); ^1H NMR (200 MHz): $\delta = 7.72$ (dd, $J = 2.0$, 7.8 Hz, 1H, H3), 7.19 (dt, $J = 2.0$, 7.8 Hz, 1H, H5), 7.08 (dt, $J = 1.5$, 7.3 Hz, 1H, H4), 6.92 (dd, $J = 1.5$, 7.8 Hz, 1H, H6), 6.28 (dd, $J = 2.9$, 5.4 Hz, 1H, H13), 6.20 (dd, $J = 2.9$, 5.9 Hz, 1H, H12), 4.85 (d, $J = 11.7$ Hz, 1H, OCH_2-eq), 3.72 (d, $J = 11.7$ Hz, 1H, OCH_2-ax), 3.59 (br s, 1H, H14), 3.54-3.46 (m, 2H, NCH_2), 3.38–3.32 (m, 2H, OCH_2), 3.23 (s, 3H, OCH_3), 3.04 (br s, 1H, H11), 1.84 (d, $J = 9.8$ Hz, 1H, H18-*anti*), 1.68 (dt, $J = 1.5$, 9.8 Hz, 1H, H18-*syn*); Irradiation of the proton at $\delta = 3.59$ (bridgehead-CH) showed NOE enhancement to that at $\delta = 7.72$, while irradiation of the proton at $\delta = 3.04$ showed NOE enhancement to those at $\delta = 3.72$ and 4.84. The observed NOE at $\delta = 3.72$ by irradiation of the proton at $\delta = 1.84$ (H18-*anti*) also supports the structural assignments; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 178.3$ and 176.5 (C=O), 155.2 (C7), 135.9 (C13), 135.2 (C12), 128.9 (C5), 128.5 (C3), 123.0 (C4), 122.1 (C2), 117.3 (C6), 70.5 (C9), 68.3 (OCH_2), 58.3 (OCH_3), 56.4, 53.5 (C1 and C10), 51.4 (C14), 48.9 (C18), 48.0 (C11), 38.1 (NCH_2); IR (CH_2Cl_2): $\tilde{\nu} = 1704\ cm^{-1}$; MS (EI): m/z (%) = 259.2 (44, retro Diels–Alder product), 214.1 (22), 201.2 (19), 158.2 (11), 130.1 (12), 115.1 (5), 102.1 (5); MS (FD): m/z (%) = 324.9 (100).

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[1] a) L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137–332; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131; b) L. F. Tietze, *Chem. Ind. (London)* **1995**, 453–457; c) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115.

[2] a) L. S. Hegedus, *Organische Synthese mit Übergangsmetallen*, VCH, Weinheim, **1995**, and references therein; b) R. W. Bates, in *Comprehensive Organometallic Chemistry II*, *Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, 349–386, and references therein.

[3] For the application of iron complexes in multistep syntheses of lactams, see: a) S. J. Javaheri, W. P. Giering, *Organometallics* **1984**, *3*, 1927; b) R. P. Beckett, S. G. Davies, A. A. Mortlock, *Tetrahedron: Asymmetry* **1992**, *3*, 123; c) S. V. Ley, L. R. Cox, G. Meek, *Chem. Rev.* **1996**, *96*, 423.

[4] a) G. T. Crisp, A. G. Meyer, *J. Org. Chem.* **1992**, *57*, 6972–6975; b) G. T. Crisp, A. G. Meyer, *Tetrahedron*, **1995**, *51*, 5585–5596.

[5] W.-Y. Yu, H. Alper, *J. Org. Chem.* **1997**, *62*, 5684–5687, and references therein.

[6] H. Weingarten, J. P. Chupp, W. A. White, *J. Org. Chem.* **1967**, *32*, 3246.

[7] K. Rück-Braun, *Angew. Chem.* **1997**, *109*, 526–528; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 509–511.

[8] Z. Arnold, J. Zemlicka, *Collect. Czech. Chem. Commun.* **1959**, *24*, 2378.

[9] C. M. Marson, *Tetrahedron* **1992**, *48*, 3659–3726, and references therein.

[10] a) R. B. King, M. B. Bisnette, *J. Organomet. Chem.* **1964**, *2*, 15–37; b) J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker, J. C. Selvover, *Inorg. Chem.* **1979**, *18*, 553.

[11] J. Kühn, K. Rück-Braun, *J. Prakt. Chem.* **1997**, *339*, 675–678.

[12] a) B. Singer, G. Maas, *Chem. Ber.* **1987**, *120*, 1683–1690; b) E. Piers, H. L. A. Tse, *Can. J. Chem.* **1993**, *71*, 983–994; c) G. T. Crisp, A. G. Meyer, *J. Org. Chem.* **1992**, *57*, 6972–6975.

[13] See ref. [3] and U. Radhakrishnan, M. Periasamy, *Organometallics* **1997**, *16*, 1800–1802.

[14] *CRC Handbook of Chemistry and Physics* (Eds.: R. C. Weast, M. J. Astle, W. H. Beyer), 65th ed., CRC, Boca Raton, Florida, **1985**, D-163.

[15] S. B. Butts, S. H. Strauss, E. M. Holt, R. E. Stimson, N. W. Alcock, D. F. Shriver, *J. Am. Chem. Soc.* **1980**, *102*, 5093–5100 and references cited.

[16] R. H. Magnuson, R. Meirowitz, S. J. Zulu, W. P. Giering, *Organometallics* **1983**, *2*, 460–462.

[17] a) J. A. Labinger, J. N. Bonfiglio, D. L. Grimmett, S. T. Masuo, E. Shearin, J. S. Miller, *Organometallics* **1983**, *3*, 733; b) R. J. Angelici, *Acc. Chem. Res.* **1972**, *5*, 335.

[18] D. Seebach, C. Betschart, M. Schiess, *Helvetica Chim. Acta* **1984**, *67*, 1593.

[19] K. Rück-Braun, C. Möller, *Chem. Eur. J.* **1999**, *5*, 1038–1044.

[20] For the formation of η^4-cyclopentadiene iron complexes by nucleophilic addition reactions to cyclopentadienyl ligands, see: a) S. G. Davies, S. D. Moon, S. J. Simpson, S. E. Thomas, *J. Chem. Soc. Dalton Trans.* **1983**, 1805.; b) P. Hamon, J.-R. Hamon, C. Lapinte, *J. Chem. Soc. Chem. Commun.* **1992**, 1602; c) D. A. Brown, W. K. Glass, M. M. Salama, *J. Organomet. Chem.* **1994**, *474*, 129–132.

[21] W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, Pergamon, Oxford, **1990**, and references therein.

[22] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, Oxford, **1988.**

[23] T. L. Gilchrist, P. D. Kemmitt, A. L. Germain, *Tetrahedron* **1995**, *51*, 9119–9126.

[24] Z. Arnold, J. Zemlicka, *Collect. Czech. Chem. Commun.* **1959**, *24*, 2385.

[25] T. L. Gilchrist, R. J. Summersell, *J. Chem. Soc. Perkin Trans. I* **1988**, 2595–2601.

[26] J. Liebscher, H. Hartmann, *Synthesis* **1979**, 241–264.

[27] A. G. Barrett, T. M. Morris, *J. Chem. Soc. Perkin I* **1980**, 2272–2277.

[28] R. E. Mewshaw, *Tetrahedron Lett.* **1989**, *30*, 3753.

[29] S. V. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis* **1994**, 639–666.

[30] The chromatographic purification was performed with the technique developed by Helquist et al., but without an inert gas atmosphere: K. A. M. Kremer, P. Helquist, *Organometallics* **1984**, *3*, 1743.

[31] Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408932.

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