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Steroid imines as chiral ligands. Diastereoselective formation of (1-azadiene)$Fe(CO)_3$ complexes by sterically tuning the ligand coordination spheres †

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Abstract

The condensation of steroid amines with α,β-unsaturated aldehydes leads to the formation of chiral 1-azadiene ligands with a steroid core attached to nitrogen. If the azadiene chain is situated at the D-ring of the steroid at C_{16} or C_{17}, respectively, the two diastereotopic faces of the ligand may be discriminated by different neighbouring substituents and their configuration. The reaction of these ligands with $Fe_2(CO)_9$ produces mixtures of diastereomeric (1-azadiene)$Fe(CO)_3$ complexes. By increasing the steric demands of the neighbouring groups it is possible to improve the diastereoselectivity of this complexation reaction from 1:1 mixtures using the least sterically hindered ligands to complete diastereoselectivity using the azadiene derived from cinnamaldehyde and 16β-amino-3-methoxy-estra-1,3,5(10)-triene-17β-ol. In addition, the molecular structure of [17β-(3-phenyl-prop-2-enyliden)-amino-3-methoxy-estra-1,3,5(10)-triene]$Fe(CO)_3$ was determined by X-ray structure analysis.

1. Introduction

Iron tricarbonyl complexes of 1,3-butadienes have been shown to be useful starting materials in organic synthesis.[1] Since the iron carbonyl fragment acts as an activating as well as a stereodirecting group these compounds were widely used in the syntheses of natural products such as alkaloids.[1d,e,h] In contrast to these results only very little work has been published on organic transformations of 1-azadienes

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† Dedicated to Prof. Dirk Walther on the occasion of his 60th birthday.

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complexed by iron tricarbonyl fragments. The reaction of (azadiene)$Fe(CO)_3$ complexes with organo lithium reagents yields either pyrrole derivatives or leads to the intramolecular formation of a carbene of the Fischer type depending on the nature of the organic group of the organo lithium reagent.[2,3] On the other hand, (azadiene)$Fe(CO)_3$ complexes have been intensively studied as compounds allowing the transfer of the iron tricarbonyl fragment towards a series of 1,3-butadiene derivatives under very mild reaction conditions. The stereoselective synthesis of chiral (butadiene)$Fe(CO)_3$ complexes was achieved by the use of chiral 1-azadiene ligands which as intermediates were presumed to form diastereomeric iron complexes.[4] Some iron tricarbonyl complexes from chiral azadiene ligands have been synthesised, in some cases the diastereomers have been separated and characterised by X-ray crystallography.[5] To date there has been no reported complexation of a chiral azadiene ligand by an iron tricarbonyl moiety with high diastereoselectivity, and furthermore, some of the pure diastereomers reported in the literature are unstable or epimerise in a few hours in solution leading to a mixture of both diastereomers.

Ligands based on steroid cores are versatile compounds since their stereochemistry at the D-ring may be controlled over a wide range and thus, ligand properties such as electronic as well as steric effects may be tailored for special purposes.[6] Imines derived from steroidal aminoalcohols have already been synthesised[6d,7] and used for the preparation of copper complexes.[7] Imines from steroid amines and their reduction products have been shown to exhibit very strong antimicrobial activity.[6d,8]

In this paper we describe the synthesis of a number of 1-azadiene ligands with a steroid core attached to nitrogen as well as the corresponding $Fe(CO)_3$ complexes. We wanted to see if it was possible to achieve complexation of these ligands with high diastereoselectivity by variation of the steric environment of the azadiene moiety.

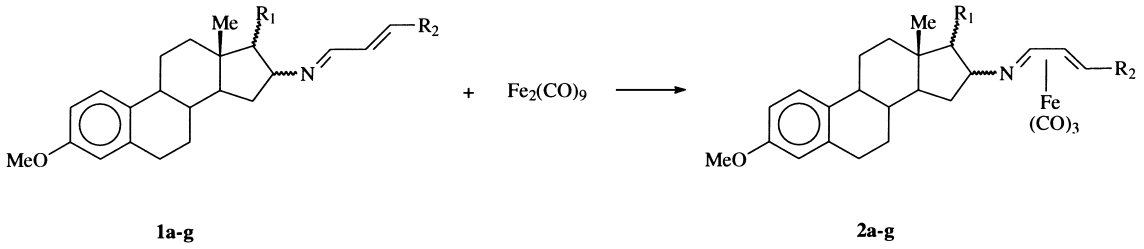
2. Results and discussion

2.1. Synthesis of the compounds

The 1-azadiene ligands were synthesised from the corresponding 3-methoxy-estra-1,3,5(10)-triene amines by condensation with cinnamaldehyde or 4-methylcinnamaldehyde, respectively. In order to vary the steric demands of the surrounding of the azadiene chain the substitution pattern of the D-ring of the steroid core was changed. The methyl group at C-13 is always in the β-position. Ligands **1a–e** were prepared starting from vicinal steroid aminoalcohols with a hydroxy group at C-17 and an amino moiety at C-16, **1a–d** from the two *trans*-isomers and **1e** from the *cis*-isomer with the β,β-configuration. The ligands **1f–h** were prepared from simple steroid amines, **1f** and **1g** from the 3-methoxy-estra-1,3,5(10)-triene with a 16β amino group, whereas in **1h** the amino group was in 17β position. The synthesis of the ligands proceeded by stirring equimolar amounts of the steroid amine with the corresponding aldehyde in methanol at room temperature. Upon cooling to 0°C the steroid imines precipitated as white solids. Treatment of the ligands **1a–h** with $Fe_2(CO)_9$ in *n*-heptane at 60°C yields the mononuclear (azadiene)$Fe(CO)_3$ complexes in good to excellent yields (Scheme 1). Purification was achieved by column chromatography under inert conditions.

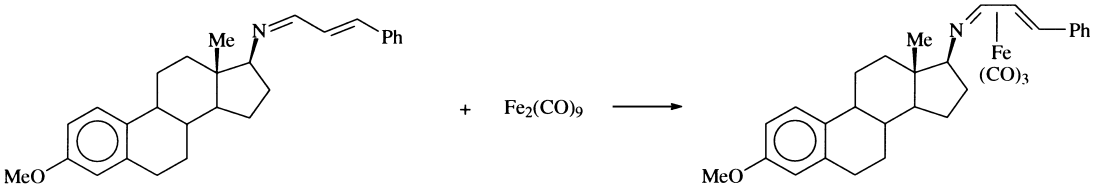
2.2. Structural determination

Recrystallisation of **2h** from a mixture of light petroleum (bp 40–60°C) and CH_2Cl_2 2:1 produced crystals suitable for X-ray diffraction. The molecular structure of **2h** as well as the most important bond lengths and angles are shown in Fig. 1. The hydrogen atoms were all localised from the Fourier map and



1a-g **2a-g**

1a, **2a**: 16β, 17α, R_1 = OH, R_2 = Ph
1b, **2b**: 16β, 17α, R_1 = OH, R_2 = Tol
1c, **2c**: 16α, 17β, R_1 = OH, R_2 = Ph
1d, **2d**: 16α, 17β, R_1 = OH, R_2 = Tol
1e, **2e**: 16β, 17β, R_1 = OH, R_2 = Ph
1f, **2f**: 16β, R1 = H, R_2 = Ph
1g, **2g**: 16β, R1 = H, R_2 = Tol



1h **2h**

Scheme 1.

were refined isotropically without any constraints. The iron tricarbonyl fragment is coordinated to the 1-azadiene chain, which adopts an *s-cis* conformation. Since the steroid is a chiral ligand the azadiene moiety has two diastereotopic faces. The organometallic fragment is introduced to the ligand from the face that is opposite to the methyl group at C-13 in a preferred conformation with a small torsional angle of H(17α)–C17–N1–C20 of 30.0° (Fig. 2). The bond lengths and angles at the iron centres are of expected values,[5c,9] namely the bonds to both the central carbon atoms of the azadiene are shorter than the one to C22. As was observed for other (azadiene)$Fe(CO)_3$ complexes the hydrogen atom at C22 is bent out of the plane of the atoms of the azadiene chain for 77.5 pm. Recently we were able to show by the use of extended Hückel calculations that this behaviour causes an increased overlap of molecular orbitals at C22 and iron and thus stabilises the coordination of the azadiene ligand towards the $Fe(CO)_3$ moiety.[9c] The bond lengths and angles inside the steroid core are all of expected values.

2.3. NMR spectroscopy

The reaction of an organometallic fragment with a chiral ligand which exhibits an additional prochiral coordination sphere should lead to the formation of diastereomeric complexes. If the diastereomers are not separated the NMR spectra of the mixture thus should exhibit a double set of resonances. Coordination of the azadiene moiety by the $Fe(CO)_3$ fragment leads to a high field shift of the signals of the hydrogen and carbon atoms of the azadiene.[5c,9b,c] The ^1H resonance of the imine hydrogen for all complexes **2a**–**h** is observed in the region of the aromatic protons at the A-ring of the steroid core. The hydrogen atom on the carbon atom in the β-position with respect to the C–N double bond (C22 in **2h**,

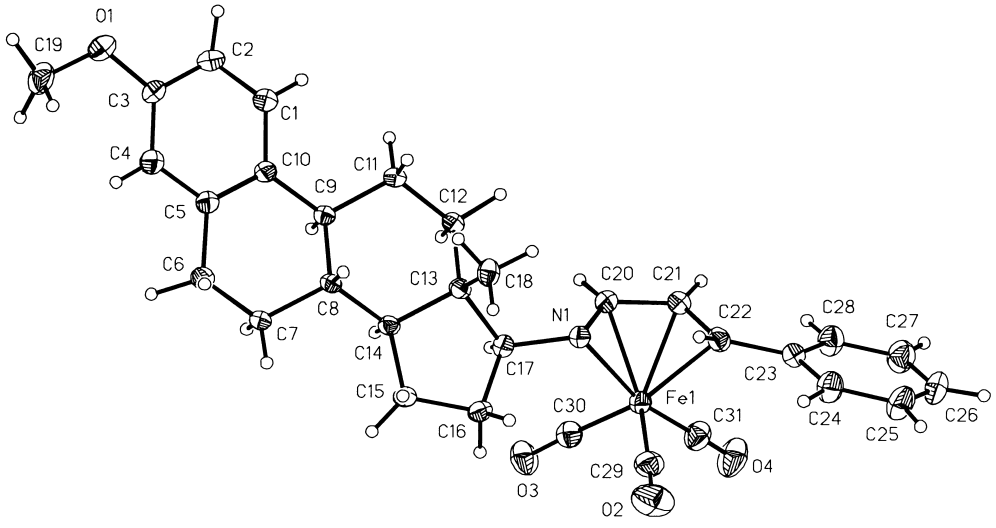


Figure 1. Molecular structure of [17β-(3-phenyl-prop-2-enyliden)-amino-3-methoxy-estra-1,3,5(10)-triene]$Fe(CO)_3$, **2h**. Selected distances [pm] and angles [deg]: Fe1–N1 209.0(2), Fe1–C20 208.3(3), Fe1–C21 208.3(3), Fe1–C22 215.5(3), N1–C20 135.7(4), C20–C21 141.9(4), C21–C22 143.4(4), C22–C23 149.2(4), N1–C17 147.3(4), C17–N1–C20 114.8(2), N1–C20–C21 116.5(3), C20–C21–C22 117.7(3), C21–C22–C23 122.9(3)

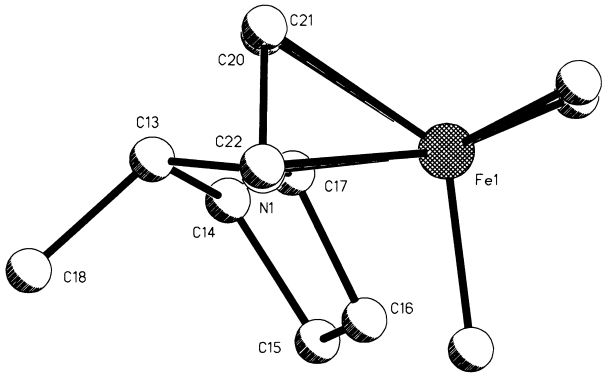
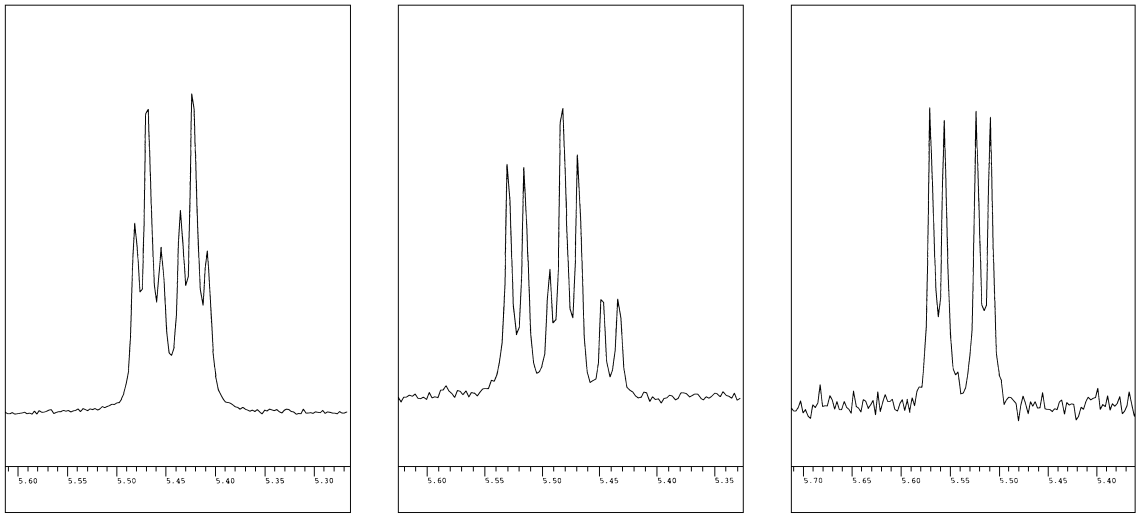


Figure 2. View down the C–C–C–N plane of the azadiene (A-, B- and C-ring of the steroid core, the phenyl group at the C-terminal end of the azadiene and hydrogen atoms have been omitted for clarity)

Fig. 1) is shifted to the region of the methylene protons of the D-ring. On the other hand, the hydrogen atom on the α-C (C21 in **2h**, Fig. 1) which gives a double doublet structure by coupling with the other olefinic protons in **2a**–**h** gives rise to a resonance at about δ=5.5 and thus makes it possible to determine the ratio of diastereomers in solution. Fig. 3 shows three typical examples of ^{1}H NMR spectra of the respective region. The reaction of **1f** and **1g** with only methylene neighbouring the azadiene function as expected produces the two diastereomeric forms of **2f** and **2g** in a 1:1 ratio. The azadiene ligands derived from *trans*-aminoalcohols **1a**–**d** shows a slightly improved diastereoselectivity of 2:1 up to 3:1 with the exception of the complex from **1b**, which yields a 1:1 mixture, resulting from the large torsional angle for the N- and O-function of approximately 150°. If **1h** is reacted with $Fe_2(CO)_9$ the diastereoselectivity of the complexation is further improved to 6:1 since the 17β-azadiene group is now vicinally arranged with respect to the 13β-methyl group. We have also seen in the X-ray structure analysis of one of the diastereomers of **2h**, that the crystal consisted only of the diastereomer in which the organometallic moiety was introduced to the ligand from the less sterically hindered face of the azadiene chain, which



2b: ratio of diastereomers 1:1 **2d**: ratio of diastereomers 3:1 **2e**: only one diastereomer is formed

Figure 3. Part of the ^{1}H NMR spectra of **2b**, **2d** and **2e** indicating the ratio of diastereomers

adopts the conformation discussed above. It is therefore reasonable that this diastereomer is also the one that is present in the solution in a higher amount. If the complexation is done with **1e**, which in contrast to **1f** possesses an additional 17β-orientated hydroxyl group, one of the faces of the azadiene obviously becomes inaccessible for the $Fe(CO)_3$ moiety since in the ^{1}H NMR spectrum only one double doublet representing only one of the two possible diastereomers is observed (Fig. 3). It is most reasonable that in this case the iron atom is also situated at the face of the azadiene opposite to the hydroxy and the methyl group. The stereochemical outcome of the complexation reaction from **1f** and **1e** clearly demonstrates the responsibility of the 17β-hydroxy group in **1e** for the high diastereoselectivity of this particular reaction.

It was reported by Knölker et al. that pure diastereomers of the iron tricarbonyl complex of the azadiene derived from cinnamaldehyde and enantiomerically pure phenethyl-amine epimerises at temperatures of 40–50°C within two hours.[5c] An NMR experiment in which we recorded several ^{1}H NMR spectra of **2e** at 70°C over a period of two hours showed no evidence for the formation of the second diastereomer.

The ^{13}C NMR spectra of the complexes **2a–d** and **2f–h** shows most of the resonances to be split up because of the formation of two diastereomers. The only signals that are not split are the resonances of the aromatic groups at the C-terminal end of the azadiene chain because of their free rotation around the C–C bond, the OMe group at the A-ring of the steroid and sometimes the aromatic carbon atoms of the A-ring itself, presumably because the two resonances cannot be resolved with a 200 MHz NMR spectrometer. The most characteristic shifts in the ^{13}C NMR spectra of the complexes compared with those of the free ligands are of course, again, the signals of the carbon atoms being attached to iron. They are also shifted to a higher field as were the corresponding hydrogen atoms. The resonances of the imine carbon atoms are now observed at about δ=111, the signals of the carbon atoms in α- and β-position with respect to the imine double bond at approximately δ=71 and at δ=62, respectively. Those values are also in good agreement with those observed for other (azadiene)$Fe(CO)_3$ complexes.[5c,9b,c]

Since the complexation of **1e** with $Fe_2(CO)_9$ led to the diastereoselective synthesis of only one iron tricarbonyl complex, we investigated whether catalytic amounts of this ligand may be used to achieve the enantioselective synthesis of an $Fe(CO)_3$ complex of the prochiral 1-methoxy-1,3-cyclohexadiene according to the methodologies of Eilbracht et al. and Knölker et al.[4d,5d] The reaction mixture was

separated using a chiral GC column and the resulting GC showed that there was no enantioselectivity at all.

3. Conclusions

We were able to show that complexation of chiral 1-azadiene ligands derived from steroid amines with $Fe(CO)_3$ led to the formation of diastereomeric complexes. The ratio of diastereomers can be controlled by tuning the steric demands of the groups neighbouring the azadiene chain. By increasing this steric demand it is possible to achieve a diastereoselective complexation of the azadiene ligand. It is also shown by NMR that this pure diastereomer is configurationally stable even at elevated temperatures and does not epimerise thermically over several hours.

4. Experimental

4.1. General

All procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents. Chromatography was done using silica gel 60 and silanized silica gel 60, 70–230 mesh ASTM (Merck), which were dried at 10^{-2} bar (10^3 Pa) for 2 days before use. $Fe_2(CO)_9$ was prepared from $Fe(CO)_5$ (Aldrich) by irradiation in acetic acid.[10] 16α-Amino-3-methoxy-estra-1,3,5(10)-triene-17β-ol, 16β-amino-3-methoxy-estra-1,3,5(10)-triene-17α-ol, 16β-amino-3-methoxy-estra-1,3,5(10)-triene-17β-ol, 16β-amino-3-methoxy-estra-1,3,5(10)-triene and 17β-amino-3-methoxy-estra-1,3,5(10)-triene were prepared by literature procedures.[6] Infrared spectra were recorded on a Perkin Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes. NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H: 200 MHz with $SiMe_4$ as internal standard, ^{13}C: 50.32 MHz with $CDCl_3$ as internal standard). Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. High resolution mass spectra were recorded on a Finnigan MAT 95 XL using ESI techniques and methanol as the solvent. Optical rotations were measured in $CHCl_3$ with a photoelectronic Polamat A (Carl Zeiss, Jena) at 546 and 578 nm and extrapolated to 589 nm; concentration is given in g 100^{-1} ml^{-1}. Elemental analyses were carried out at the laboratory of the Institute of Organic Chemistry and Macromolecular Chemistry at the Friedrich-Schiller-University Jena.

4.2. X-Ray crystallographic study

The structure determination of **2h** was carried out on an Enraf Nonius Kappa CCD diffractometer, crystal detector distance 25 mm, 180 frames, using graphite monochromated Mo-K_α radiation. The crystal was mounted in a stream of cold nitrogen. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods and refined by full-matrix least squares techniques against F^2 using the programs SHELXS86 and SHELXL93.[11] Computation of the structure was done with the program XPMA and the molecular illustrations were drawn using the program XP.[12,13] The crystal and intensity data are given in the literature.[14] Additional material on the structure analysis is available from the Cambridge Crystallographic Data Centre by mentioning the deposition number CCDC 127807.

4.3. Preparation of the ligands **1a–h**

A 1 mmol sample of the steroid amine (301 mg of 16α-amino-3-methoxy-estra-1,3,5(10)-triene-17β-ol, 16β-amino-3-methoxy-estra-1,3,5(10)-triene-17α-ol or 16β-amino-3-methoxy-estra-1,3,5(10)-triene-17β-ol, respectively, and 285 mg of 16β-amino-3-methoxy-estra-1,3,5(10)-triene or 17β-amino-3-methoxy-estra-1,3,5(10)-triene) was dissolved in 20 ml of anhydrous methanol. To this solution an equimolar amount of the corresponding aldehyde (132 mg cinnamaldehyde or 146 mg 4-methylcinnamaldehyde) was added and the mixture stirred at room temperature for 3–4 hours. After some hours in the refrigerator a white crystalline solid precipitated, which was collected, washed with a small amount of cold methanol and dried over P_2O_5. Yield **1a**: 374 mg (90%), **1b**: 217 mg (50.5%), **1c**: 361 mg (87%), **1d**: 218 mg (51%), **1e**: 364 mg (87.5%), **1f**: 350 mg (88%), **1g**: 252 mg (61%), **1h**: 412 mg (99%).

4.3.1. MS and spectroscopic data of **1a**

MS (CI, H_2O): *m/z* (%) 416 (100, MH^+), 398 (15, M^+-H_2O); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.97 (s, 3H, 18-CH_3), 1.37–1.66 (m, 9H, CH_2, CH), 2.11–2.40 (m, 2H, CH), 2.81–2.85 (m, 2H, 6-CH_2), 3.55–3.60 (m, 1H, 16α-CH), 3.73 (m, 1H, 17β-CH), 3.76 (s, 3H, OCH_3), 6.62 (d, 1H, 4-CH), 6.67–6.71 (dd, 1H, 2-CH), 6.89–6.92 (m, 2H, =CH), 7.18–7.47 (m, 6H, 1-CH, C_6H_5), 8.01–8.06 (m, 1H, N=CH); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 17.4 (C-18), 25.9 (C-11), 28.0 (C-7), 29.8 (C-6), 32.2 (C-12), 34.6 (C-15), 38.6 (C-8), 43.4 (C-9), 45.2 (C-13), 48.5 (C-14), 55.2 (OCH_3), 79.6 (C-16), 86.6 (C-17), 111.5 (C-2), 113.8 (C-4), 126.3 (C-1), 127.2 ($C_{ar}H$), 128.2 (=CH), 128.8 ($C_{ar}H$), 129.0 ($C_{ar}H$), 132.6 (C-10), 135.8 (C_{ar}), 137.9 (C-5), 141.6 (=CH), 157.4 (C-3), 161.8 (N=CH); $C_{28}H_{33}NO_2$ (415.57): calcd C 80.93, H 8.00, N 3.37; found C 80.80, H 8.27, N 3.47; $[\alpha]_D^{20}$=83 (c=0.6329).

4.3.2. MS and spectroscopic data of **1b**

MS (CI, H_2O): *m/z* (%) 430 (100, M^+), 412 (18, M^+-H_2O); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.96 (s, 3H, 18-CH_3), 1.37–1.87 (m, 9H, CH_2, CH), 2.11–2.34 (m, 5H, CH, CH_3), 2.81–2.85 (m, 2H, 6-CH_2), 3.51–3.58 (m, 1H, 16α-CH), 3.74 (m, 1H, 17β-CH), 3.76 (s, 3H, OCH_3), 6.62 (d, 1H, 4-CH), 6.67–6.72 (dd, 1H, 2-CH), 6.87–6.88 (m, 2H, =CH), 7.13–7.37 (m, 5H, 1-CH, C_6H_4), 8.01 (m, 1H, N=CH); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 17.5 (C-18), 21.3 (CH_3), 26.0 (C-11), 28.0 (C-7), 29.8 (C-6), 32.2 (C-12), 34.6 (C-15), 38.6 (C-8), 43.4 (C-9), 45.2 (C-13), 48.5 (C-14), 55.2 (OCH_3), 79.6 (C-16), 86.6 (C-17), 111.5 (C-2), 113.8 (C-4), 126.3 (C-1), 127.2 ($C_{ar}H$), 127.3 (=CH), 129.5 ($C_{ar}H$), 132.6 (C-10), 133.1 (C_{ar}), 137.9 (C-5), 139.3 (C_{ar}), 141.6 (=CH), 157.4 (C-3), 162.0 (N=CH); $C_{29}H_{35}NO_2$ (429.57): calcd C 81.09, H 8.21, N 3.26; found C 79.40, H 8.34, N 3.32; $[\alpha]_D^{20}$=80 (c=0.4648).

4.3.3. MS and spectroscopic data of **1c**

MS (CI, H_2O): *m/z* (%) 416 (100, MH^+), 398 (3, M^+-H_2O); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.89 (s, 3H, 18-CH_3), 1.28–2.03 (m, 9H, CH_2, CH), 2.18–2.29 (m, 2H, CH), 2.81–2.84 (m, 2H, 6-CH_2), 3.53–3.56 (m, 1H, 16β-CH), 3.69–3.71 (m, 1H, 17α-CH), 3.76 (s, 3H, OCH_3), 6.60–6.62 (d, 1H, 4-CH), 6.66–6.71 (dd, 1H, 2-CH), 6.89–6.92 (m, 2H, =CH), 7.16–7.20 (d, 1H, 1-H), 7.29–7.47 (m, 5H, C_6H_5), 7.99–8.02 (m, 1H, N=CH); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.4 (C-18), 26.1 (C-11), 27.1 (C-7), 29.8 (C-6), 32.9 (C-15), 36.8 (C-12), 38.6 (C-8), 44.0 (C-9), 44.0 (C-13), 48.5 (C-14), 55.2 (OCH_3), 76.0 (C-16), 87.8 (C-17), 111.5 (C-2), 113.8 (C-4), 126.3 (C-1), 127.2 ($C_{ar}H$), 128.0 (=CH), 128.8 ($C_{ar}H$), 129.1 ($C_{ar}H$), 132.5 (C-10), 135.8 (C_{ar}), 137.9 (C-5), 141.6 (=CH), 157.5 (C-3), 161.8 (N=CH); $C_{28}H_{33}NO_2$ (415.57): calcd C 80.93, H 8.00, N 3.37; found C 80.25, H 8.02, N 3.53; $[\alpha]_D^{20}$=71 (c=0.3150).

*4.3.4. MS and spectroscopic data of **1d***

MS (CI, H_2O): *m/z* (%) 430 (100, M^+); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 0.89 (s, 3H, 18-CH_3), 1.32–1.97 (m, 9H, CH_2, CH), 2.25–2.35 (m, 5H, CH, CH_3), 2.81–2.84 (m, 2H, 6-CH_2), 3.53–3.56 (m, 1H, 16β-CH), 3.56–3.72 (m, 1H, 17α-CH), 3.76 (s, 3H, OCH_3), 6.62 (d, 1H, 4-CH), 6.66–6.71 (dd, 1H, 2-CH), 6.83–6.86 (m, 2H, =CH), 7.12–7.34 (m, 5H, 1-CH, C_6H_4), 7.95–7.99 (m, 1H, N=CH); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.4 (C-18), 21.3 (CH_3), 26.1 (C-11), 27.1 (C-7), 29.7 (C-6), 32.9 (C-15), 36.9 (C-12), 38.6 (C-8), 43.9 (C-9), 44.0 (C-13), 48.5 (C-14), 55.2 (OCH_3), 76.0 (C-16), 87.7 (C-17), 111.5 (C-2), 113.8 (C-4), 126.2 (C-1), 127.0 (=CH), 127.2 ($C_{ar}H$), 129.5 ($C_{ar}H$), 132.5 (C-10), 133.0 (C_{ar}), 137.9 (C-5), 139.3 (C_{ar}), 141.6 (=CH), 157.4 (C-3), 161.9 (N=CH); $C_{29}H_{35}NO_2$ (429.57): calcd C 81.09, H 8.21, N 3.26; found C 80.09, H 8.01, N 3.59; $[\alpha]_D^{20}$=73 (c=0.6868).

*4.3.5. MS and spectroscopic data of **1e***

MS (CI, H_2O): *m/z* (%) 416 (100, M^+); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 0.86 (s, 3H, 18-CH_3), 1.19–1.86 (m, 6H, CH_2), 1.90–2.33 (m, 5H, CH_2, CH), 2.82–2.86 (m, 2H, 6-CH_2), 3.11–3.15 (m, 1H, 17-OH), 3.65 (t, 1H, 17α-CH), 3.75 (s, 3H, OCH_3), 3.84 (m, 1H, 16α-CH), 6.61 (d, 1H, 4-CH), 6.70 (dd, 1H, 2-CH), 6.81–6.93 (m, 2H, =CH), 7.19–7.49 (m, 6H, 1-CH, C_6H_5), 8.02 (m, 1H, N=CH); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.1 (C-18), 26.2 (C-11), 27.5 (C-7), 29.8 (C-6), 34.4 (C-15), 37.6 (C-12), 38.4 (C-8), 43.6 (C-13), 44.0 (C-9), 47.8 (C-14), 55.2 (OCH_3), 66.9 (C-16), 82.0 (C-17), 111.5 (C-2), 113.8 (C-4), 126.3 (C-1), 127.3 ($C_{ar}H$), 128.3 (=CH), 128.8 ($C_{ar}H$), 129.2 ($C_{ar}H$), 132.7 (C-10), 135.7 (C_{ar}), 137.8 (C-5), 142.1 (=CH), 157.5 (C-3), 163.1 (N=CH); $C_{28}H_{33}NO_2$ (415.57): calcd C 80.93, H 8.00, N 3.37; found C 81.01, H 8.20, N 3.43; $[\alpha]_D^{20}$=80 (c=0.9031).

*4.3.6. MS and spectroscopic data of **1f***

MS (CI, H_2O): *m/z* (%) 400 (100, MH^+); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 1.02 (s, 3H, 18-CH_3), 1.36–1.92 (m, 10H, CH_2, CH), 2.06–2.23 (m, 3H, CH), 2.85–2.90 (m, 2H, 6-CH_2), 3.76–3.83 (m, 4H, 16α-CH, OCH_3), 6.61–6.62 (d, 1H, 4-CH), 6.67–6.73 (dd, 1H, 2-CH), 6.89–6.92 (m, 2H, =CH), 7.19–7.48 (m, 6H, 1-CH, C_6H_5), 7.93–7.98 (m, 1H, N=CH); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 19.5 (C-18), 26.6 (C-11), 28.1 (C-7), 29.9 (C-6), 35.6 (C-15), 38.6 (C-8), 39.2 (C-12), 41.3 (C-13), 43.9 (C-9), 49.6 (C-17), 53.5 (C-14), 55.2 (OCH_3), 68.7 (C-16), 111.4 (C-2), 113.8 (C-4), 126.2 (C-1), 127.1 ($C_{ar}H$), 128.6 (=CH), 128.8 ($C_{ar}H$), 128.9 ($C_{ar}H$), 132.9 (C-10), 136.0 (C_{ar}), 137.9 (C-5), 140.8 (=CH), 157.4 (C-3), 160.4 (N=CH); $C_{28}H_{33}NO$ (399.62): calcd C 84.16, H 8.32, N 3.50; found C 84.09, H 8.63, N 3.63; $[\alpha]_D^{20}$=62 (c=0.9109).

*4.3.7. MS and spectroscopic data of **1g***

MS (CI, H_2O): *m/z* (%) 414 (100, M^+), 388 (10, $M^+-C_2H_2$); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 1.03 (s, 3H, 18-CH_3), 1.28–1.92 (m, 10H, CH_2, CH), 2.12–2.30 (m, 3H, CH), 2.34 (s, 3H, CH_3), 2.84–2.88 (m, 2H, 6-CH_2), 3.76–3.82 (m, 4H, 16α-CH, OCH_3), 6.61–6.63 (d, 1H, 4-CH), 6.67–6.72 (dd, 1H, 2-CH), 6.86–6.89 (m, 2H, =CH), 7.12–7.38 (m, 5H, 1-CH, C_6H_4), 7.92–7.96 (m, 1H, N=CH); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 19.5 (C-18), 21.3 (CH_3), 26.6 (C-11), 28.1 (C-7), 29.9 (C-6), 35.6 (C-15), 38.6 (C-8), 39.2 (C-12), 41.3 (C-13), 43.9 (C-9), 49.6 (C-17), 53.8 (C-14), 55.2 (OCH_3), 68.7 (C-16), 111.4 (C-2), 113.8 (C-4), 126.2 (C-1), 127.1 ($C_{ar}H$), 127.7 (=CH), 129.5 ($C_{ar}H$), 132.9 (C-10), 133.2 (C_{ar}), 137.9 (C-5), 139.0 (C_{ar}), 140.8 (=CH), 157.4 (C-3), 160.5 (N=CH); $C_{29}H_{35}NO$ (413.65): calcd C 84.21, H 8.53, N 3.39; found C 84.13, H 8.77, N 3.55; $[\alpha]_D^{20}$=60 (c=0.4646).

*4.3.8. MS and spectroscopic data of **1h***

MS (CI, H_2O): *m/z* (%) 400 (100, M^+); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 0.86 (s, 3H, 18-CH_3), 1.22–1.96 (m, 11H, CH_2, CH), 2.21–2.29 (m, 2H, CH), 2.66–2.83 (m, 2H, 6-CH_2), 3.06–3.12 (m, 1H, 17α-CH), 3.76 (s, 3H, OCH_3), 6.61–6.62 (d, 1H, 4-CH), 6.67–6.71 (dd, 1H, 2-CH), 6.92–6.95 (m, 2H, =CH), 7.17–7.49 (m, 6H, 1-CH, C_6H_5), 8.00–8.03 (m, 1H, N=CH); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.9 (C-18), 24.4 (C-15), 26.2 (C-11), 27.7 (C-7), 29.6 (C-6), 29.9 (C-16), 37.0 (C-12), 38.1 (C-8), 44.0 (C-9), 45.1 (C-13), 52.7 (C-14), 55.2 (OCH_3), 81.5 (C-17), 111.4 (C-2), 113.8 (C-4), 126.3 (C-1), 127.1 ($C_{ar}H$), 128.5 (=CH), 128.8 ($C_{ar}H$), 128.9 ($C_{ar}H$), 132.7 (C-10), 136.0 (C_{ar}), 138.0 (C-5), 141.0 (=CH), 157.4 (C-3), 161.3 (N=CH); $C_{28}H_{33}NO$ (399.62): calcd C 84.16, H 8.32, N 3.50; found C 83.91, H 8.47, N 3.57; $[\alpha]_D^{20}=-13$ (c=0.9504).

*4.4. Preparation of the iron carbonyl complexes **2a–h***

A total of 0.5 mmol of the steroid imines (207 mg **1a**,**c**,**e**, 215 mg **1b**,**d**, 200 mg **1e**,**g**, 206 mg **1f**) was stirred together with 0.42 mmol of $Fe_2(CO)_9$ (152 mg) in 20 ml *n*-heptane at 60°C. After 1 h all of the starting material was dissolved and the solvent was evaporated in vacuo. The residue was dissolved in 4 ml CH_2Cl_2, 1 g of silanised silica gel was added and after removal of the solvent the crude product was purified by chromatography. The complexes **2a**–**e** were eluted using a mixture of light petroleum (bp 40–60°C), CH_2Cl_2 and ethanol (1:1:0.1) as an orange band, **2f**–**h** were obtained using a mixture of light petroleum:CH_2Cl_2 (3:1) also as an orange coloured solution. After the solvent was evaporated the complexes **2a**–**h** were obtained as yellow to orange microcrystalline solids, recrystallization of **2h** from a mixture of light petroleum:CH_2Cl_2 (2:1) at 0°C yielded crystals suitable for X-ray analysis. Yield **2a**: 216 mg (78%), **2b**: 206 mg (72.5%), **2c**: 208 mg (75%), **2d**: 187 mg (66%), **2e**: 234 mg (84%), **2f**: 203 mg (92%), **2g**: 202 mg (89%), **2h**: 204 mg (93%).

*4.4.1. MS and spectroscopic data for **2a***

MS (CI, H_2O): *m/z* (%) 556 (3, MH^+), 538 (1, MH^+-H_2O), 528 (1, MH^+-CO), 510 (1, MH^+-H_2O-CO), 499 (2, M^+-2 CO), 482 (1, MH^+-H_2O-2 CO), 471 (2, M^+-3 CO), 454 (1, MH^+-H_2O-3 CO), 416 (28, $C_{28}H_{34}NO_2^+$), 197 (100, $C_{15}H_{17}^+$), 133 (13, $C_9H_{11}N^+$); ^1H NMR ($CDCl_3$, 298 K) [ppm]: 0.8–0.85 (m, 5H, 18-CH_3, CH_2), 1.05–2.45 (m, 9H, CH_2, CH), 2.85–2.88 (m, 2H, 6-CH_2), 2.94 (d, $^3J_{HH}$=9.0 Hz, 1H, =CH), 3.45–3.62 (m, 1H, 16α-CH), 3.75–3.77 (m, 4H, 17β-CH, OCH_3), 5.48 (dd, 0.3H, $^3J_{HH}$=2.8 Hz, $^3J_{HH}$=9.2 Hz, =CH), 5.51 (dd, 0.7H, $^3J_{HH}$=2.6 Hz, $^3J_{HH}$=9.0 Hz, =CH), 6.53–6.70 (m, 3H, 2-CH, 4-CH, =CH), 7.09–7.55 (m, 6H, 1-CH, C_6H_5); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 17.0 (C-18), 17.3 (C-18), 25.9 (C-11), 26.0 (C-11), 27.8 (C-7), 27.9 (C-7), 29.8 (C-6), 32.0 (C-12), 32.2 (C-12), 36.0 (C-15), 37.2 (C-15), 38.7 (C-8), 38.8 (C-8), 43.4 (C-9), 43.5 (C-9), 44.7 (C-13), 45.6 (C-13), 48.2 (C-14), 49.2 (C-14), 55.2 (OCH_3), 61.3 (=CH), 61.6 (=CH), 72.3 (=CH), 72.9 (=CH), 78.2 (C-16), 78.7 (C-16), 87.9 (C-17), 89.5 (C-17), 110.6 (=CH), 111.1 (=CH), 111.5 (C-2), 113.9 (C-4), 126.2 (C-1), 126.3 (C-1), 126.5 ($C_{ar}H$), 127.2 ($C_{ar}H$), 128.7 ($C_{ar}H$), 132.5 (C-10), 132.6 (C-10), 137.9 (C-5), 138.0 (C-5), 139.1 (C_{ar}), 139.2 (C_{ar}), 157.5 (C-3), no CO resonances have been observed; $C_{31}H_{33}NO_5Fe$ (555.50): calcd C 67.03, H 5.99, N 2.52; found C 64.90, H 6.38, N 2.35.

*4.4.2. MS and spectroscopic data for **2b***

MS (EI): *m/z* (%) 569 (1, M^+), 541 (1, M^+-CO), 513 (2, M^+-2 CO), 485 (3, M^+-3 CO), 429 (3, $C_{29}H_{35}NO_2^+$), 403 (4, $C_{27}H_{33}NO_2^+$), 388 (1, $C_{26}H_{30}NO_2^+$), 374 (2, $C_{25}H_{28}NO_2^+$), 360 (2, $C_{24}H_{26}NO_2^+$), 326 (5, $C_{23}H_{20}NO^+$), 308 (1, $C_{23}H_{18}N^+$), 224 (7, $C_{16}H_{18}^+$), 196 (18, $C_{15}H_{16}^+$), 168 (21, $C_{13}H_{12}^+$), 140 (9, $C_{10}H_6N^+$), 112 (20, $C_8H_{16}^+$), 84 (100, $C_8H_{12}^+$), 56 (85, Fe^+), 43 (13, $C_3H_7^+$); ^1H

NMR ($CDCl_3$, 298 K) [ppm]: 0.83–0.99 (m, 5H, 18-CH_3, CH_2), 1.26–1.79 (m, 7H, CH_2, CH), 2.28–2.44 (m, 5H, CH_3, CH), 2.86–2.90 (m, 2H, 6-CH_2), 2.97 (d, 1H, $^3J_{HH}$=9.1 Hz, =CH), 3.47–3.50 (m, 1H, 16α-CH), 3.70–3.78 (m, 4H, OCH_3, 17β-CH), 5.40 (dd, 0.5H, $^3J_{HH}$=2.7 Hz, $^3J_{HH}$=9.1 Hz, =CH), 5.42 (dd, 0.5H, $^3J_{HH}$=2.7 Hz, $^3J_{HH}$=9.1 Hz, =CH), 6.63–6.75 (m, 3H, 2-CH, 4-CH, =CH), 6.91–7.35 (m, 5H, =CH, C_6H_4); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 17.0 (C-18), 17.3 (C-18), 21.4 (CH_3), 21.5 (CH_3), 25.9 (C-11), 26.0 (C-11), 27.9 (C-7), 28.1 (C-7), 29.0 (C-6), 32.0 (C-12), 32.3 (C-12), 36.0 (C-15), 37.2 (C-15), 38.7 (C-8), 38.8 (C-8), 43.3 (C-9), 43.4 (C-9), 44.7 (C-13), 45.6 (C-13), 48.2 (C-14), 49.3 (C-14), 55.2 (OCH_3), 61.8 (=CH), 62.2 (=CH), 72.3 (=CH), 72.9 (=CH), 78.1 (C-16), 78.7 (C-16), 87.8 (C-17), 89.5 (C-17), 110.2 (=CH), 110.7 (=CH), 111.5 (C-2), 113.9 (C-4), 126.2 (C-1), 126.3 (C-1), 126.5 (C_{ar}H), 129.3 (C_{ar}H), 132.5 (C-10), 132.6 (C-10), 136.1 (C_{ar}), 136.2 (C_{ar}), 136.4 (C_{ar}), 136.5 (C_{ar}), 137.9 (C-5), 138.0 (C-5), 157.5 (C-3), no CO resonances have been observed; HRMS calcd for $C_{32}H_{35}NO_5Fe$ (569.53): 570.194335, $C_{32}H_{36}NO_5Fe$ (MH^+), Δ=0.894083 mmu.

4.4.3. MS and spectroscopic data for ***2c***

MS (EI): *m/z* (%) 499 (1, M^+−2 CO), 471 (1, M^+−3 CO), 415 (1, $C_{28}H_{33}NO_2^+$), 326 (1, $C_{23}H_{20}NO^+$), 279 (4, $C_{21}H_{13}N^+$), 205 (27, $C_{15}H_{11}N^+$), 168 (25, $C_{12}H_{10}N^+$), 131 (73, $C_9H_9N^+$), 113 (40, $C_8H_{17}^+$), 104 (50, $C_7H_6N^+$), 84 (100, $C_6H_{12}^+$), 78 (38, $C_6H_6^+$), 56 (68, Fe^+), 43 (19, $C_3H_7^+$); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.73–0.93 (m, 5H, 18-CH_3, CH_2), 1.30–1.85 (m, 7H, CH_2, CH), 2.18–2.38 (m, 2H, CH), 2.82–2.88 (m, 2H, 6-CH_2), 3.00 (d, 1H, $^3J_{HH}$=9.3 Hz, =CH), 3.44–3.48 (m, 1H, 16β-CH), 3.76 (s, 3H, OCH_3), 4.18–4.22 (m, 1H, 17α-CH), 5.48 (dd, 0.3H, $^3J_{HH}$=2.6 Hz, $^3J_{HH}$=9.0 Hz, =CH), 5.51 (dd, 0.7H, $^3J_{HH}$=2.9 Hz, $^3J_{HH}$=9.3 Hz, =CH), 6.63–6.76 (m, 3H, 2-CH, 4-CH, =CH), 7.14–7.53 (m, 6H, 1-CH, C_6H_5); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.2 (C-18), 12.4 (C-18), 26.0 (C-11), 26.1 (C-11), 27.1 (C-7), 27.2 (C-7), 29.8 (C-6), 34.3 (C-15), 36.5 (C-15), 36.7 (C-12), 37.0 (C-12), 38.4 (C-8), 38.5 (C-8), 43.8 (C-9), 43.9 (C-9), 44.4 (C-13), 45.7 (C-13), 47.8 (C-14), 48.0 (C-14), 55.2 (OCH_3), 60.6 (=CH), 61.4 (=CH), 73.0 (=CH), 73.1 (=CH), 73.6 (C-16), 74.1 (C-16), 88.8 (C-17), 89.6 (C-17), 110.6 (=CH), 110.7 (=CH), 111.5 (C-2), 115.6 (C-2), 113.8 (C-4), 126.2 (C-1), 126.3 (C-1), 126.5 (C_{ar}H), 126.6 (C_{ar}H), 128.6 (C_{ar}H), 132.5 (C-10), 137.9 (C-5), 138.0 (C-5), 139.3 (C_{ar}), 139.4 (C_{ar}), 157.5 (C-3), 209.7 (CO, br); $C_{31}H_{33}NO_5Fe$ (555.50): calcd C 67.03, H 5.99, N 2.52; found C 65.32, H 6.44, N 2.41.

4.4.4. MS and spectroscopic data for ***2d***

MS (EI): *m/z* (%) 513 (1, M^+−2 CO), 485 (2, M^+−3 CO), 429 (1, $C_{29}H_{35}NO_2^+$), 403 (1, $C_{27}H_{33}NO_2^+$), 355 (2, $C_{24}H_{21}NO_2^+$), 326 (2, $C_{23}H_{20}NO^+$), 281 (10, $C_{21}H_{15}N^+$), 220 (36, $C_{16}H_{14}N^+$), 205 (100, $C_{15}H_{11}N^+$), 131 (18, $C_9H_9N^+$), 113 (12, $C_8H_{17}^+$), 104 (11, $C_7H_6N^+$), 91 (18, $C_7H_7^+$), 84 (11, $C_6H_{12}^+$), 57 (36, FeH^+), 43 (17, $C_3H_7^+$); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.73-0.76 (s, 3H, 18-CH_3), 0.88–0.92 (m, 2H, CH_2), 1.11–1.85 (m, 7H, CH_2, CH), 2.25–2.38 (m, 5H, CH_3, CH), 2.79–2.85 (m, 2H, 6-CH_2), 3.02 (d, 1H, $^3J_{HH}$=9.1 Hz, =CH), 3.44–3.50 (m, 1H, 16β-CH), 3.60–3.65 (m, 1H, 17α-CH), 3.76 (s, 3H, OCH_3), 5.47 (dd, 0.25H, $^3J_{HH}$=2.6 Hz, $^3J_{HH}$=13.1 Hz, =CH), 5.50 (dd, 0.75H, $^3J_{HH}$=2.9 Hz, $^3J_{HH}$=9.1 Hz, =CH), 6.62–6.75 (m, 3H, 2-CH, 4-CH, =CH), 6.90–7.23 (m, 5H, 1-CH, C_6H_4); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.2 (C-18), 12.4 (C-18), 21.2 (CH_3), 26.0 (C-11), 26.1 (C-11), 27.1 (C-7), 27.2 (C-7), 29.8 (C-6), 34.3 (C-15), 36.5 (C-15), 36.8 (C-12), 37.0 (C-12), 38.4 (C-8), 38.5 (C-8), 43.8 (C-9), 43.9 (C-9), 44.4 (C-13), 45.7 (C-13), 47.9 (C-14), 48.0 (C-14), 55.2 (OCH_3), 61.2 (=CH), 61.9 (=CH), 73.0 (=CH), 73.1 (=CH), 73.6 (C-16), 74.2 (C-16), 88.9 (C-17), 89.6 (C-17), 110.2 (=CH), 110.3 (=CH), 111.5 (C-2), 111.6 (C-2), 113.9 (C-4), 126.2 (C-1), 126.3 (C-1), 126.4 (C_{ar}H), 128.5 (C_{ar}H), 132.5 (C-10), 136.2 (C_{ar}), 136.3 (C_{ar}), 136.4 (C_{ar}), 136.5 (C_{ar}), 137.9 (C-5), 138.0 (C-5), 157.6 (C-3), no CO resonances have been observed; $C_{32}H_{35}NO_5Fe$ (569.53): calcd C 67.49, H 6.20, N 2.46; found C 69.58, H 6.98, N 2.81.

*4.4.5. MS and spectroscopic data for **2e***

MS (CI neg., H_2O): *m/z* (%) 555 (10, M^+), 527 (8, M^+-CO), 415 (13, $C_{28}H_{33}NO_2^+$), 401 (4, $C_{27}H_{31}NO_2^+$), 372 (5, $C_{25}H_{26}NO_2^+$), 258 (89, $C_{19}H_{16}N^+$), 230 (11, $C_{17}H_{12}N^+$), 168 (100, $C_{13}H_{12}^+$), 142 (33, $C_{10}H_8N^+$); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.83–1.05 (m, 5H, 18-CH_3, CH_2), 1.12–2.28 (8H, CH_2, CH), 2.51–2.63 (m, 1H, CH), 2.75–2.94 (m, 3H, 6-CH_2, =CH), 3.35–3.48 (m, 2H, 16α-CH, 17α-CH), 3.76 (s, 3H, OCH_3), 5.54 (dd, 1H, $^3J_{HH}$=3.0 Hz, $^3J_{HH}$=9.4 Hz, =CH), 6.50 (d, 1H, $^3J_{HH}$=3.0 Hz, =CH), 6.63–6.71 (m, 2H, 2-CH, 4-CH), 7.16–7.42 (m, 6H, 1-CH, C_6H_5); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.4 (C-18), 26.1 (C-11), 27.3 (C-7), 29.7 (C-6), 37.0 (C-15), 37.5 (C-12), 38.3 (C-8), 43.4 (C-13), 44.1 (C-9), 47.0 (C-14), 55.2 (OCH_3), 62.3 (=CH), 68.1 (C-16), 73.2 (=CH), 82.2 (C-17), 111.5 (=CH), 111.6 (C-2), 113.8 (C-4), 126.2 (C-1), 126.5 ($C_{ar}H$), 126.8 ($C_{ar}H$), 128.7 ($C_{ar}H$), 132.8 (C-10), 137.9 (C-5), 138.9 (C_{ar}), 157.6 (C-3), no CO resonances have been observed; HRMS $C_{31}H_{33}NO_5Fe$ (555.50): 556.178719 $C_{31}H_{34}NO_5Fe$ (MH^+), Δ=−2.0860 mmu.

*4.4.6. MS and spectroscopic data for **2f***

MS (EI): *m/z* (%) 539 (1, M^+), 511 (2, M^+-CO), 483 (10, M^+-2 CO), 455 (50, M^+-3 CO), 399 (76, $C_{28}H_{33}NO^+$), 384 (16, $C_{27}H_{30}NO^+$), 266 (9, $C_{19}H_{24}N^+$), 228 (55, $C_{16}H_{22}N^+$), 210 (62, $C_{15}H_{16}N^+$), 187 (45, $C_{13}H_{17}N^+$), 173 (56, $C_{12}H_{15}N^+$), 158 (75, $C_{11}H_{12}N^+$), 147 (53, $C_{10}H_{13}N^+$), 131 (50, $C_9H_9N^+$), 115 (98, $C_9H_7^+$), 91 (74, $C_7H_7^+$), 84 (100, $C_6H_{12}^+$), 56 (97, Fe^+), 43 (22, $C_3H_7^+$); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.85–1.92 (m, 13H, 18-CH_3, CH_2, CH), 2.05–2.38 (m, 3H, CH_2, CH), 2.55–2.76 (m, 1H, 16α-CH), 2.80–3.03 (m, 3H, 6-CH_2, =CH), 3.77 (s, 3H, OCH_3), 5.42 (dd, 0.5H, $^3J_{HH}$=2.8 Hz, $^3J_{HH}$=9.1 Hz, =CH), 5.43 (dd, 0.5H, $^3J_{HH}$=2.8 Hz, $^3J_{HH}$=9.1 Hz, =CH), 6.48–6.73 (m, 3H, 2-CH, 4-CH, =CH), 7.05–7.27 (m, 6H, 1-CH, C_6H_5); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 19.1 (C-18), 19.4 (C-18), 26.4 (C-11), 26.5 (C-11), 27.9 (C-7), 28.0 (C-7), 29.8 (C-6), 29.9 (C-6), 36.9 (C-15), 38.2 (C-15), 38.7 (C-8), 38.8 (C-8), 39.1 (C-12), 39.2 (C-12), 40.9 (C-14), 41.7 (C-14), 43.9 (C-9), 44.0 (C-9), 51.5 (C-13), 53.2 (C-17), 53.3 (C-17), 54.4 (C-13), 55.2 (OCH_3), 61.1 (=CH), 61.2 (=CH), 67.8 (C-16), 68.0 (C-16), 71.9 (=CH), 72.3 (=CH), 111.4 (=CH), 111.5 (C-2), 111.6 (=CH), 113.9 (C-4), 126.1 (C-1), 126.2 (C-1), 126.5 ($C_{ar}H$), 126.6 ($C_{ar}H$), 128.6 ($C_{ar}H$), 132.9 (C-10), 137.9 (C-5), 138.0 (C-5), 139.5 (C_{ar}), 139.6 (C_{ar}), 157.5 (C-3), no CO resonances have been observed; $C_{31}H_{33}NO_4Fe$ (539.50): calcd C 69.02, H 6.17, N 2.60; found C 69.09, H 6.17, N 2.63.

*4.4.7. MS and spectroscopic data for **2g***

MS (EI): *m/z* (%) 525 (1, M^+-CO), 497 (5, M^+-2 CO), 469 (27, M^+-3 CO), 413 (32, $C_{29}H_{35}NO^+$), 398 (16, $C_{28}H_{32}NO^+$), 335 (4, $C_{23}H_{29}NO^+$), 310 (6, $C_{21}H_{28}NO^+$), 252 (6, $C_{18}H_{22}N^+$), 224 (24, $C_{16}H_{18}N^+$), 196 (64, $C_{14}H_{14}N^+$), 168 (62, $C_{12}H_{10}N^+$), 158 (14, $C_{11}H_{12}N^+$), 147 (17, $C_{10}H_{13}N^+$), 140 (20, $C_{11}H_8^+$), 129 (21, $C_9H_7N^+$), 115 (16, $C_9H_7^+$), 91 (15, $C_7H_7^+$), 84 (100, $C_6H_{12}^+$), 56 (81, Fe^+), 43 (19, $C_3H_7^+$); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.82–2.45 (m, 19H, 18-CH_3, CH_3, CH_2, CH), 2.55–2.67 (m, 1H, 16α-CH), 2.75–3.05 (m, 3H, 6-CH_2, =CH), 3.77 (s, 3H, OCH_3), 5.40 (dd, 0.5H, $^3J_{HH}$=2.5 Hz, $^3J_{HH}$ =9.3 Hz, =CH), 5.41 (dd, 0.5H, $^3J_{HH}$=2.5 Hz, $^3J_{HH}$=9.3 Hz, =CH), 6.47 (m, 1H, =CH), 6.43–6.71 (m, 3H, 2-CH 4-CH, =CH), 7.01–7.24 (m, 5H, 1-CH, C_6H_4); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 19.1 (C-18), 19.4 (C-18), 21.1 (CH_3), 26.4 (C-11), 26.5 (C-11), 27.9 (C-7), 28.0 (C-7), 29.8 (C-6), 29.9 (C-6), 36.9 (C-15), 38.2 (C-15), 38.7 (C-8), 38.8 (C-8), 39.1 (C-12), 39.2 (C-12), 40.9 (C-14), 41.6 (C-14), 43.9 (C-9), 44.0 (C-9), 51.5 (C-13), 53.2 (C-17), 53.3 (C-17), 54.5 (C-13), 55.2 (OCH_3), 61.7 (=CH), 61.8 (=CH), 67.8 (C-16), 67.9 (C-16), 71.9 (=CH), 72.3 (=CH), 111.1 (=CH), 111.3 (=CH), 111.5 (C-2), 113.9 (C-4), 126.2 (C-1), 126.3 (C-1), 126.5 ($C_{ar}H$), 129.3 ($C_{ar}H$), 129.5 (C_{ar}), 132.9 (C-10), 136.3 (C_{ar}), 136.4 (C_{ar}), 137.9 (C-5), 138.0 (C-5), 157.5 (C-3), no CO resonances have been observed; $C_{32}H_{35}NO_4Fe$ (553.27): calcd C 69.44, H 6.37, N 2.53; found C 68.34, H 6.35, N 2.56.

4.4.8. MS and spectroscopic data for ***2h***

MS (FAB): *m/z* (%) 540 (1, MH^+), 511 (3, M^+-CO), 483 (17, $M^+-2\,CO$), 455 (61, $M^+-3\,CO$), 399 (94, $C_{28}H_{33}NO^+$), 384 (100, $C_{27}H_{30}NO^+$), 308 (7, $C_{21}H_{26}NO^+$), 265 (5, $C_{19}H_{23}N^+$), 240 (12, $C_{17}H_{22}N^+$), 228 (38, $C_{16}H_{22}N^+$), 210 (13, $C_{15}H_{16}N^+$), 196 (17, $C_{14}H_{14}N^+$), 187 (15, $C_{13}H_{17}N^+$), 173 (30, $C_{12}H_{15}N^+$), 158 (63, $C_{11}H_{12}N^+$), 140 (25, $C_{11}H_8{}^+$), 129 (43, $C_9H_7N^+$), 115 (62, $C_9H_7{}^+$), 91 (31, $C_7H_7{}^+$), 84 (17, $C_6H_{12}{}^+$), 56 (15, Fe^+), 43 (7, $C_3H_7{}^+$); ^{1}H NMR ($CDCl_3$, 298 K) [ppm]: 0.72 (s, 3H, 18-CH_3), 0.80–0.87 (m, 2H, CH_2), 1.15–1.92 (m, 9H, CH_2, CH), 2.08–2.32 (m, 3H, CH_2, CH), 2.78–2.88 (m, 2H, 6-CH_2), 2.99 (d, $^3J_{HH}$=9.3 Hz, 1H, =CH), 3.76 (s, 3H, OCH_3), 5.43 (dd, 0.85H, $^3J_{HH}$=2.9 Hz, $^3J_{HH}$=9.3 Hz, =CH), 5.49 (dd, 0.15H, $^3J_{HH}$=3.0 Hz, $^3J_{HH}$=6.4 Hz, =CH), 6.46 (d, $^3J_{HH}$=2.9 Hz, 1H, =CH), 6.63–6.72 (m, 2H, 2-CH, 4-CH), 7.12–7.24 (m, 6H, 1-CH, C_6H_5); ^{13}C NMR ($CDCl_3$, 298 K) [ppm]: 12.8 (C-18), 23.8 (C-15), 26.2 (C-11), 27.5 (C-7), 29.9 (C-6), 32.4 (C-16), 37.3 (C-12), 39.0 (C-8), 43.9 (C-9), 46.2 (C-13), 53.3 (C-14), 55.2 (OCH_3), 61.6 (=CH), 72.1 (=CH), 79.7 (C-17), 110.2 (=CH), 111.5 (C-2), 113.9 (C-4), 126.3 (C-1), 126.4 ($C_{ar}H$), 126.5 ($C_{ar}H$), 128.6 ($C_{ar}H$), 132.7 (C-10), 138.1 (C-5), 139.6 (C_{ar}), 157.6 (C-3), no CO resonances have been observed; HRMS $C_{31}H_{33}NO_4Fe$ (539.50): 540.183777 $C_{31}H_{34}NO_4Fe$ (MH^+), Δ=−0.90058 mmu.

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