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Synthesis of the first pentaethynylferrocene derivatives

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Abstract

Starting from a bisprotected ferrocene-1,2,3-triscarbaldehyde, Ohira-alkynylation and Pd-catalyzed protection of the free alkyne with 4-iodotoluene leads to a ferrocene in which one Cp-ring is 1,2,3-substituted by two acetal rings (1,2-position) and an internal alkyne. Metalation of the ferrocene nucleus with *sec*-BuLi, workup with DMF and reduction with $LiAlH_4$ leads to a 1,2,3,4-tetrasubstituted ferrocene carrying a hydroxymethyl group. The acetal groups are removed by *para*-toluenesulfonic acid and the aldehyde groups are converted into arylalkynes. A second metalation followed by workup with DMF furnishes a 1,2,3,4,5-pentasubstituted ferrocenecarbaldehyde. The aldehyde is transformed into an alkyne by the Ohira method and converted to an internal alkyne by Pd-catalyzed reaction with 4-iodotoluene. The sequence gives a 1,2,3,4,5-pentasubstituted ferrocene derivative with four alkyne groups and one hydroxymethyl group. Airless Marko oxidation of the alcohol is followed by another Ohira alkynylation. Pd-catalyzed arylation finishes the reaction sequence to give the symmetrical 1,2,3,4,5-pentakis(4′-tolylethynyl)ferrocene, the first pentaethynylferrocene derivative. A second, similar route was explored that furnished 1,2,3,4,5-pentakis(4′-butylphenylethynyl)ferrocene and its butadiyne-bridged dimer.

Keywords: Alkynes; Ferrocenes; Palladium-catalyzed couplings; Peralkynylation

1. Introduction and historical perspective

In this contribution, we describe the synthesis of two derivatives of 1,2,3,4,5-pentaethynylferrocene. Starting from a partially protected ferrocene-1,2,3-trialdehyde (**1**) [1], a series of metalation, carbonylation, and alkynylation steps furnish the targets in a step-wise manner through a ''merry-go-round'' substitution process on one Cp-ring of the ferrocene nucleus.

In Mathematics and Physics, classic questions originating in the 18th, 19th or early 20th century, remain highly topical today. A nice example is breath figures, the fog that settles on a cold mirror when water vapor condenses. Breath figures were first described by Lord Rayleigh in 1911 [a]. Nowadays breath figures attract great attention as flexible templates to make nano- and microstructured solid state materials [b,c,d,e,f,g]. Contrary to Physics, research in Chemistry has generated scientific questions that only could be asked *by the progress Chemistry itself* had generated. Such questions could not have been asked before synthetic and methodological ground work had been done. A general example is the synthesis of natural products [3]. Many natural products that have been synthesized recently were either simply not known or if they were known their synthesis was impossible due to the lack of specific methodologies to construct their molecular framework. A classic example are the enediyne antibiotics [3]. Spectacular scientific results in chemical research generated in the past are assimilated and utilized as *routine and standard methods* in fields that are removed from its original context, almost

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in a sense that chemistry develops as a hierarchical combination of freestanding modules. Consequently, the time frame of chemical history necessary one has to know to successfully operate a research group, goes back less than 20 years, and cited papers may reach back one to two decades. By the same token, elegant contributions published 40 or 50 years ago, are either irrelevant today or have been incorporated into the textbooks as general paradigms, but do not tend to aid in the understanding of topical questions in *current* chemistry. There are exceptions, such as the discovery of ferrocene and its functionalization [4] to mention only one here. An example for the removal of a concept from its original context into a new one, in the field of carbon-rich organometallic chemistry, is the independent discovery of Heck, Cassar, Sonogashira, and Hagihara (HCS) that terminal alkynes couple to aromatic bromides and iodides in the presence of $(Ph_3P)_2PdCl_2$, CuI and amines [5]. The HCS coupling is general and has opened up the field of carbon-rich and carbon-rich organometallic chemistry [6–19]. Originally designed to make monoalkynylated benzenes, it allows the connection between alkynes and arenes into complex carbon-rich objects [20–26].

Carbon-rich organometallics is a vibrant sub-field of organometallic chemistry. It combines the elements of classic acetylene chemistry with that of either the π-complexes such as ferrocene, cymantrene and cyclobutadiene complexes, or the chemistry of acetylides, such as the ones popularized by Gladysz and coworkers [6], Rosenthal in Rostock [7], the Rennes groups around Dixneuf and Lapinte [8] as well as Yam's [9] group in Hong Kong.

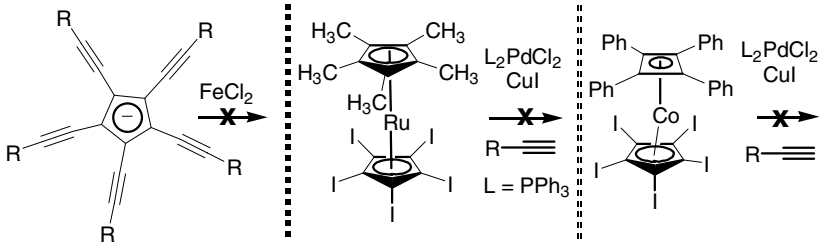
This historical perspective however is restricted to alkynylated π-complexes and their short history. The field emanated from roots that go back to Schlögl's report of the synthesis of ethynylferrocene in 1963 [10]. However, this compound was regarded as laboratory curiosity and for a long time there were no further developments. Only in 1979 and 1982 Vollhardt reported the spectacular Bergman rearrangement of (1,2-diethynylcyclobutadiene)(cyclopentadienyl)cobalt complexes. This complex and its 1,3-isomer were synthesized [11] by an elegant cobalt mediated [2 + 2] cycloaddition strategy [12]. However, their chemistry lay dormant until their incorporation into conjugated organometallic polymers was reported in 1995 [13]. While the HCS coupling is known since 1975, it is not well suited for the attachment of alkynes to carbonyl substituted π-complexes such as cymantrene (cyclopentadienylmanganese tricarbonyl). Stille and Losterzo [14], however, discovered that stannylated alkynes couple smoothly to iodocymantrene in the presence of $(CH_3CN)_2PdCl_2$ in DMF. This variant of the Stille coupling offers a fairly general access to alkynylated π-complexes as long as the corresponding organometallic iodides are sterically unhindered. Ferrocenes do generally not work well in this coupling but those are of course amenable to the regular HCS coupling [15].

These developments were in place when Krätschmer and Kroto [16] isolated C_{60} – Buckminsterfullerene – impacting and exposing carbon-rich species and their organometallic complexes as an increasingly attractive field for synthetic chemists. Diederich reported in 1991 [17], soon afterwards, the first organometallic complex of a cyclocarbon species. This contribution further fuelled the interest in carbon-rich organometallics. In 1993–1994 then a series of peralkynylated and perbutadiynylated cyclobutadiene and cymantrene complexes were synthesized by Bunz et al. [18] utilizing the Stille–Losterzo protocol. Since then carbon-rich organometallics is an established field and several reviews and two JOMC special issues have covered this area. An extensive review in this journal in 2003 reports recent developments in the field of highly alkynylated π-complexes [19]. Peralkynylated π-perimeters have already found use as precursors to cyclohexatrienes, carbon-rich nano-objects, high carbon content materials, liquid crystals, and NLO-active oligomers [20–26].

Due to great interest, the field of carbon-rich organometallics [27–34] has been the subject of several conferences and symposia. With powerful synthetic methods available, abundant exciting targets and opportunities present, alkynylated π-complexes and carbon-rich organometallics will play an exciting role in materials science and conjugated materials. Highly alkynylated ferrocenes are uncharted waters for the time being – that despite the importance of the iron sandwich and the successful syntheses of 1,1′-diethynylferrocenes by Schlögl et al. and other groups [10,15,33].

There have been several unsuccessful attempts at making peralkynylated ferrocenes, ruthenocenes and cyclopentadienylcobalt complexes (Scheme 1). These attempts highlight two concepts on how to approach organometallic target molecules. In the first case, Rubin et al. [34] reacted a lithiated pentaethynylcyclopentadiene with $FeCl_2$. Unfortunately, outer sphere electron transfer took place, and the cyclopentadienyl-anion was oxidized to its radical while $FeCl_2$ was reduced to iron. The preferred electron transfer is probably due to the great steric bulk of the pentakis(triisopropylsilyl) protected pentaethynylcyclopentadienyl-anion. Smaller substituents leave the pentaethynylcylcopentadiene unstable, making access to decaethynylferrocene and related ferrocenes difficult via this route.

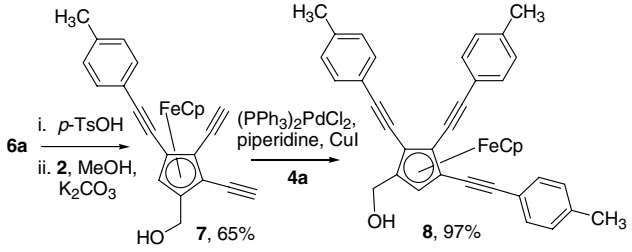
The second concept utilizes the alkynylation of a preformed sandwich complex. Michl and coworkers [35] and Winter and coworkers [36] have reported several promising pentaiodocyclopentadienyl complexes for this approach. We attempted their alkynylation via the Heck–Cassar–Sonogashira–Hagihara reaction, [5] but even under forcing reaction conditions the starting materials were re-isolated. The high steric hindrance of



Scheme 1. Attempted syntheses of peralkynylated sandwich complexes.

the "second deck" on the opposing side (tetraphenylcyclobutadiene and pentamethylcyclopentadienyl) shuts down the reactivity of the sp^2-bound iodides (Scheme 1).

In light of the aforementioned results, we have prepared pentaethynylferrocene derivatives by a step-wise approach that works well under increased steric duress. Fire-and-sword metalations utilizing butyllithium were followed by robust functional group transformations.

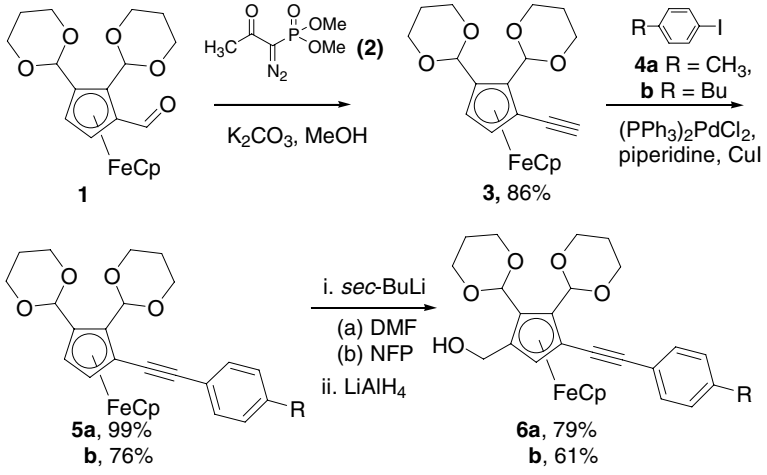


Scheme 3. Synthesis of a trialkynylated ferrocene derivative.

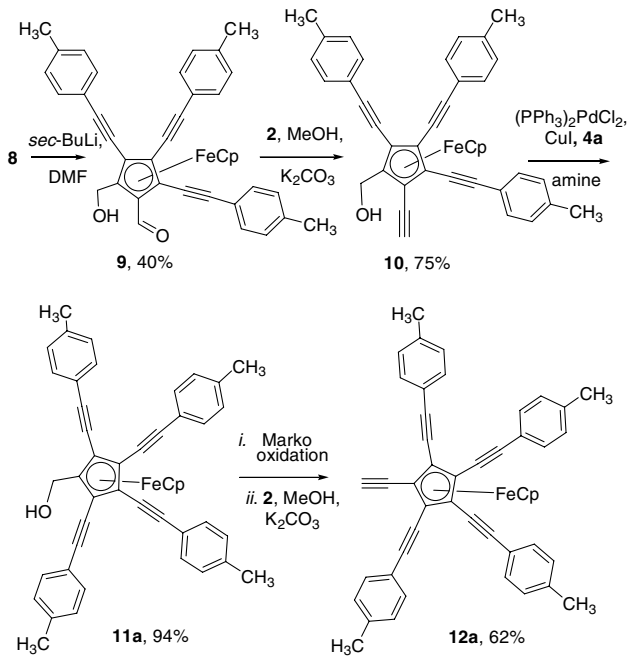
2. Results

The aldehyde **1** [1] was transformed by the Ohira-method [37], utilizing the diazophosphonate **2** to give the alkynylated ferrocene **3** (Scheme 2). Employing Pd-catalysis, the alkyne **3** was coupled to **4a** and **4b** to furnish the ferrocenes **5a** and **5b**. Both of these could be metalated by *sec*-butyllithium to afford the carbinols **6a** and **6b** in one pot after quenching with *N*,*N*-dimethylformamide or *N*-formylpiperidine (NFP) and subsequent reduction with $LiAlH_4$. The alcohols **6** were the last common intermediates in the two routes explored to synthesize pentaethynyl-ferrocene derivatives **12**–**14**.

The bisketal **6a** (R = CH_3, Schemes 2 and 3) was deprotected by *para*-toluenesulfonic acid (TsOH). The resulting (unstable) dialdehyde was not characterized but immediately reacted with **2** to give the diyne **7** in 65% yield. Pd-catalyzed reaction of **7** with **4a** furnished **8** (97%). The reaction sequence continued with the lithiation of **8**. The formed organolithium compound was reacted with DMF (Scheme 4) to deliver the aldehyde **9** in 40% yield. Ohira alkynylation [24] transformed **9** into the free alkyne **10** in 75% yield. The reaction was not hampered by the presence of the hydroxymethyl group. The free alkyne was capped by the Pd-catalyzed reaction of **10** with **4a** to form **11a** in 94% yield. The alcohol **11a** was oxidized by the airless Marko reaction utilizing Cu_2Cl_2 in the presence of phenanthroline and di-*tert*-butylazodicarboxylate on solid K_2CO_3 support [38]. A final Ohira alkynylation furnished the pentaethynylferrocene derivative **12a** in 62% yield. To obtain a symmetrical substitution pattern around the ferrocene ring

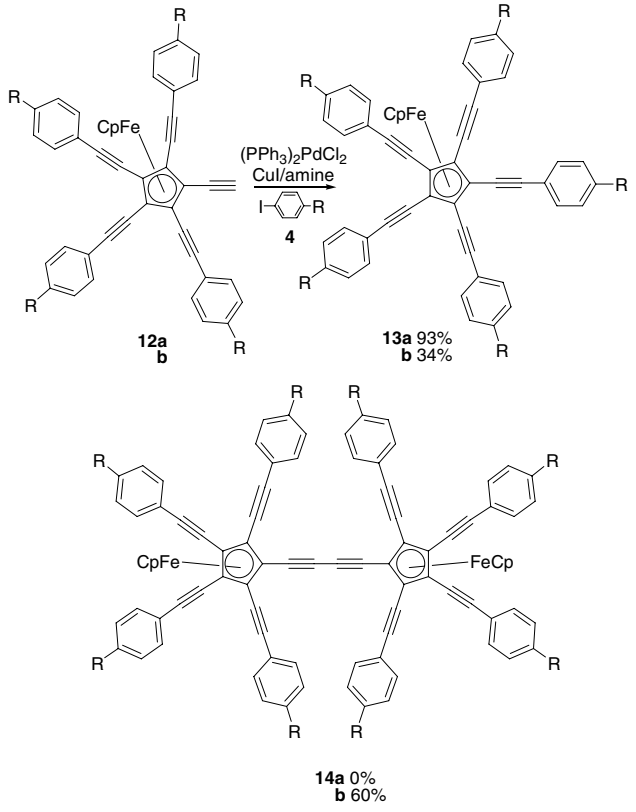


Scheme 2. Synthesis of tetrasubstituted ferrocenes by the lithiation/formylation/alkynylation protocol.



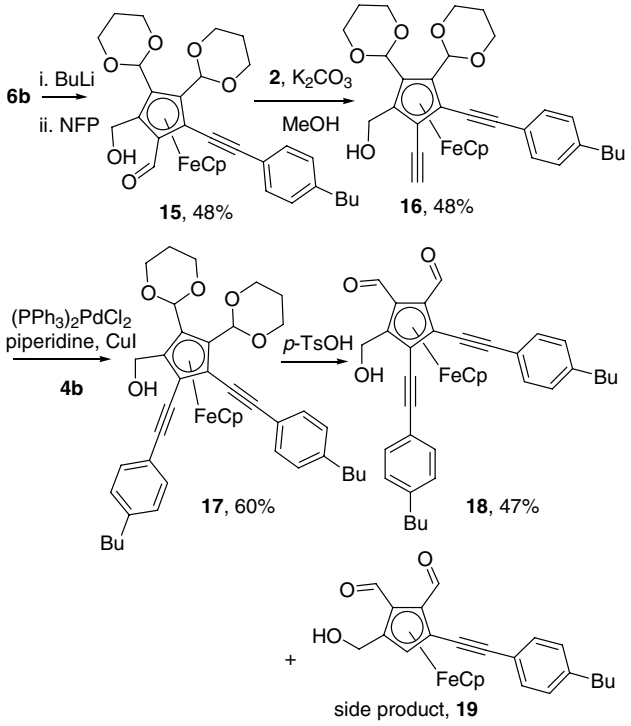
Scheme 4. Synthesis of a pentaalkynylated ferrocene derivative.

(Scheme 5), the terminal alkyne group in **12a** was capped via an additional Sonogashira reaction. The symmetrical ferrocene derivative **13a** was isolated in 93% yield as the sole product.

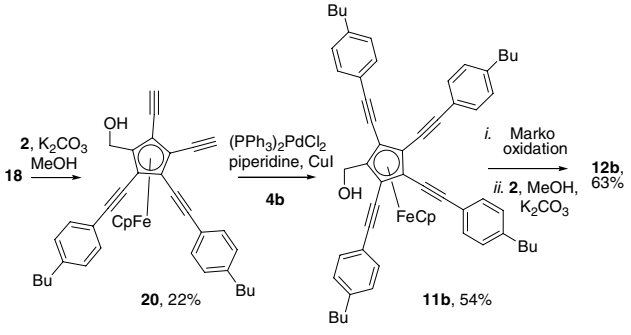


Scheme 5. Synthesis of a pentaalkynylated ferrocene derivative and its dimer.

While this reaction sequence worked satisfactorily for the introduction of the five alkyne groups, the question arose whether it would be better to deprotect the two acetal groups in the later stages of the synthesis. With this in mind, lithiation of **6b** was followed by reaction with NFP (Scheme 6). The aldehyde **15** was isolated in 48% yield, along with unreacted **6b** which proved difficult to remove by column chromatography. The mixture was alkynylated and coupled to **4b**, yielding **17**. Deprotection of the ketals gave **18**, which was separable from **19** by column chromatography. Subsequent Ohira alkynylation (Scheme 7) afforded the critical intermediate **20** in 22% yield, which was arylated to **11b** in 54% yield by **4b** in a Pd-catalyzed reaction. Marko oxidation and Ohira alkynylation transformed **11b** into **12b**. When **12b**



Scheme 6. Synthesis of a pentaethynylated ferrocene derivative carrying butyl groups.



Scheme 7. Synthesis of a pentaethynylated ferrocene.

was treated under the conditions of the Sonogashira coupling, **13b** was formed, but only in 34% yield. This was surprising, as the analog, **13a**, was isolated in almost quantitative yield. Further elution of the column led to a second compound, identified – according to its spectroscopic properties – as the formally dehydrogenated dimer of **12b** (Scheme 5). This unusual dimer, **14b**, was the main product and had formed in 60% yield.

3. Discussion

The introduction of five contiguous alkyne groups on one cyclopentadienyl ring [30j] of ferrocene was executed by a stepwise metalation/functionalization strategy. The challenge was the presence of the second cyclopentadienyl ring in ferrocene and its inadvertent metalation under the employed reaction conditions. To avoid the metalation of the second ring, the substituents placed on the first ring had to: (a) direct the metalation into the adjacent position and (b) be easily convertible into alkynes. This combination made ketalized aldehydes and/or free hydroxymethyl groups the *ortho*-directing groups of choice. Acetals [39] have been reported useful in *ortho*-lithiation schemes, and Szeimies and coworkers [40] and Seebach and coworkers [41] have demonstrated that hydroxymethylgroups can be utilized in this regard. Both functional groups are used less than benzamides or oxazolines [42] due to their inferior activating power. In our study, this is not a problem since ferrocene itself can be metalated [43]. Here, the ketal and hydroxymethyl groups were used only for *ortho*-directing purposes. Metalation of **5a** and **5b**, workup with DMF or NFP, and one-pot reduction worked well and furnished **6a** and **6b** in good yields. While the position of the hydroxymethyl group on the ring cannot be attributed beyond any doubt, spectroscopic data and chemical principles suggest the structure we propose, where the hydroxymethyl group is adjacent to the ketal groups. Metalation of the second ring was not observed in this specific case.

For the (problematic) introduction of the 5th substituent, we utilized two different approaches. In the first approach (Schemes 3 and 4; R = Me), deketalization was followed by Ohira alkynylation and protection of the free alkyne to give **8** in a 63% overall yield. Metalation of **8** furnished the aldehyde **9** in a yield of only 40%. Side products were species resulting from the deprotonation of the lower ring or from double deprotonation of both rings. We speculate that the increased steric pressure deactivated the last proton on the ring, making the 5th deprotonation difficult. Once the last substituent was in position, functional group transformations worked well and furnished **12a** and **13a** without further problems.

To investigate if the 5th metalation would be easier performed in the presence of the original ketal groups rather than alkynes, **6b** was metalated with BuLi and quenched with NFP to furnish an inseparable mixture containing **6b** and **15**. From NMR integration we could estimate the yield of the metalation to be 48%. The result suggests that metalation in the presence of the ketal groups is only marginally better. The mixture was carried through to the stage where **18** and **19** were formed by cleavage of the ketals. Clean separation of **18** and **19** was achieved by column chromatography. The remaining steps were similar to the synthesis of **12a**, but the double Ohira alkynylation of **20** did not work as well as the transformation of **6a** → **7**, making the second sequence overall less appealing than the first one.

In the last step, the free alkyne of **12b** was coupled to 4-butyliodobenzene (**4b**) in a Pd-catalyzed reaction of the Sonogashira type (Scheme 5). Contrary to the case of **12a**, we isolated only a 34% yield of **13b**. The main product was the dimer **14b**, formed in 60% yield. This dimer was characterized by ^{1}H NMR and ^{13}C NMR spectroscopies, with the analytical data supporting our structural hypothesis. The formation of **14b** can be explained by oxidative dimerization of **12b** during the Sonogashira coupling, arising via the adventitious presence of oxygen or any other oxidant. Such dimerizations are commonly observed (to a varying degree) in Pd-catalyzed couplings, but are usually minor side reactions [44].

4. Conclusions

A series of novel alkynylated ferrocenes has been reported. We have demonstrated that by a combination of metalation, formylation, and alkynylation, all five positions in one Cp ring of a ferrocene can be replaced by alkyne groups. In one case, we obtained the butadiyne-bridged dimeric decaethynylbiferrocene, **14b**. The pentaalkynylated ferrocenes **13a** and **13b** are stable and can be stored indefinitely. In the future, we will report upon the use of the partially alkynylated and fully alkynylated ferrocenes as modules for the construction of novel carbon-rich organometallic nanostructures.

5. Experimental

5.1. General

THF was freshly distilled from potassium and benzophenone. All other reagents were of commercial grade and used as obtained. Reactions employing Schlenk flasks were performed under inert atmosphere. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 300 or a Varian Mercury 400 spectrometer. The mass spectra were measured on a VG 70SQ. IR spectra were obtained using a Perkin–Elmer FTIR 1600 on NaCl plates.

5.2. Synthesis of **3**

In a 100 mL oven-dried Schlenk flask, **1** (4.09 g, 10.6 mmol) and finely powdered K_2CO_3 (4.69 g, 33.9 mmol) were dissolved/suspended in dry methanol (8 mL) and dry THF (3 mL). The flask was cooled to −10 °C and dimethyl(azo-2-oxopropyl)phosphonate (**2**) (4.07 g, 21.2 mmol) was added drop-wise. The reaction mixture was stirred for 8 h under exclusion of light. NaHCO_3(aq) was added and the mixture was extracted with ethylether (200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 + 10% NEt_3) furnished **3** (3.48 g, 86%) as a yellow crystalline solid: m.p.: 87 °C. IR (Neat): *v* 3249, 2960, 2846, 1235, 1104, 993 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.70 (s, 1H, acetal-CH), 5.51 (s, 1H, acetal-CH), 4.41 (d, 1H, $^3J_{H,H} = 2.7$ Hz, sub. Cp ring), 4.37 (d, 1H, $^3J_{H,H} = 2.7$ Hz, sub. Cp ring), 4.30–4.10 (m, 4H, acetal-CH_2), 4.20 (s, 5H, Cp-H), 4.00–3.81 (m, 4H, acetal-CH_2), 2.78 (s, 1H, alkyne-H), 2.14–2.06 (m, 2H, acetal-CH_2), 1.39–1.30 (m, 2H, acetal-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 99.40, 98.46, 84.85, 84.57, 80.43, 75.49, 71.10, 70.15, 66.85, 66.75, 66.65, 66.53, 66.31, 63.49, 25.25, 25.14. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{20}H_{22}FeO_4$) 382.09, Found 382. UV–Vis ($CHCl_3$): λ 244 ($\varepsilon = 6552$ cm^{-1} M^{-1}), 316 ($\varepsilon = 1284$ cm^{-1} M^{-1}), 443 ($\varepsilon = 202$ cm^{-1} M^{-1}). Elemental Analysis. Calc. (in %): C 62.85; H 5.80, Found: C 62.81, H 5.74.

5.3. Synthesis of **5a** and **5b**

In a 100 mL Schlenk flask, **3** (3.23 g, 8.45 mmol) was dissolved in dry piperidine (5 mL). To the solution was added $(PPh_3)_2PdCl_2$ (3.6 mg, 5.1 μmol), CuI (2.4 mg, 13 μmol) and 4-iodotoluene (**4a**) (2.20 g, 10.1 mmol) or 4-iodobutylbenzene (**4b**) (2.64 g, 10.1 mmol). The reaction mixture was stirred at ambient temperature for 4 h. Water was added and the mixture was extracted with ethylether (150 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 + 10% NEt_3) furnished **5a** (3.93 g, 99%) or **5b** (3.31 g, 76%) as orange solids. **5a**: m.p.: 139 °C. IR (Neat): *v* 2970, 2852, 2208, 1548, 1236, 1087, 819 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, 2H, $^3J_{H,H} = 8.2$ Hz, aromatic-H), 7.10 (d, 2H, $^3J_{H,H} = 8.2$ Hz, aromatic-H), 5.76 (s, 1H, acetal-CH), 5.58 (s, 1H, acetal-CH_2), 4.45 (d, 1H, $^3J_{H,H} = 2.5$ Hz, sub. Cp ring), 4.41 (d, 1H $^3J_{H,H} = 2.5$ Hz, sub. Cp ring), 4.32–4.01 (m, 4H, acetal-CH_2), 4.22 (s, 5H, unsub. Cp-H), 3.99–3.84 (m, 4H, acetal-CH_2), 2.34 (s, 3H, methyl-H), 2.18–2.05 (m, 2H, acetal-CH_2), 1.41–1.24 (m, 2H, acetal-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.16, 130.80, 128.58, 120.62, 100.04, 99.89, 87.38, 85.77, 84.73, 71.25, 69.89, 67.09, 66.95, 66.83, 66.50, 65.37, 45.9, 25.58, 25.41, 21.06. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{27}H_{28}FeO_4$) 472.13, Found 472.1. UV–Vis ($CHCl_3$): λ 256 ($\varepsilon = 6536$ cm^{-1} M^{-1}), 298 ($\varepsilon = 5524$ cm^{-1} M^{-1}), 318 ($\varepsilon = 496$ cm^{-1} M^{-1}). Elemental Analysis. Calc. (in %): C 68.65; H 5.97, Found: C 68.71, H 5.91. **5b**: m.p.: 78 °C. IR (Neat): *v* 2954, 2851, 1459, 1235, 1113, 997 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, $^3J_{H,H} = 8.24$ Hz, 2H), 7.14 (d, $^3J_{H,H} = 8.24$ Hz, 2H), 5.75 (s, 1H), 5.58 (s, 1H), 4.45 (d, $^3J_{H,H} = 2.47$ Hz, 1H), 4.41 (d, $^3J_{H,H} = 2.47$ Hz, 1H), 4.32–4.01 (m, 4H), 4.22 (s, 5H), 3.99–3.84 (m, 4H), 2.59 (t, $^3J_{H,H} = 7.69$ Hz, 2H), 2.18–2.05 (m, 2H), 1.62–1.52 (m, 2H), 1.41–1.24 (m, 4H), 0.96–0.81 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.64, 131.23, 128.32, 121.21, 100.49, 99.35, 87.81, 86.05, 85.07, 85.05, 71.62, 70.35, 67.56, 67.50, 67.40, 67.26, 66.84, 65.84, 35.51, 33.39, 25.99, 25.80, 22.21, 13.88. MS (70 eV, EI): *m/z* (%) Calc. For M^+ ($C_{30}H_{34}FeO_4$) 514.18, Found 514 (100).

5.4. Synthesis of **6a**

In an oven-dried 500 mL Schlenk flask, **5a** (3.93 g, 8.32 mmol) was dissolved in dry THF (150 mL). The solution was cooled to −78 °C for 10 min and *sec*-BuLi (7.0 mL, 1.30 M, 9.1 mmol) was added. The solution became dark-brown and cloudy after 5 min. After 20 min, the temperature was raised to −10 °C for 1.5 h. The reaction mixture was re-cooled to −78 °C and *N*,*N*-dimethylformamide (0.85 mL, 11 mmol) was added. A brown precipitate homogenized after 1 h stirring at ambient temperature. The addition of brine turned the color of the solution to deep red. The organic layer was extracted with CH_2Cl_2, dried over magnesium sulfate, and the solvent was removed in vacuo under the exclusion of light. The raw product was dissolved under inert conditions in dry THF (100 mL) and cooled to 0 °C. Addition of $LiAlH_4$ (10.8 mL, 1.00 M in THF, 10.8 mmol) changed the color of the solution from red to yellow. Stirring was continued for another 10 min. The reaction mixture was quenched with brine and extracted with CH_2Cl_2. The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 2.5:1 + 10% NEt_3) furnished **6a** (3.31 g, 79%) in the second fraction as a yellow foam. IR (Neat): *v* 3480 (bd-OH), 2964, 2850, 1544, 1373, 1112, 997, 817 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, 2H, $^3J_{H,H} = 8.4$ Hz, aromatic-H), 7.11 (d, 2H, $^3J_{H,H} = 8.4$ Hz, aromatic-H), 5.90 (s, 1H, acetal-CH), 5.54 (s, 1H, acetal-CH), 4.64 (dd, 1H, $^2J_{H,H} = 11.8$ Hz, $^3J_{H,H} = 2.5$ Hz, alcohol-CH_2), 4.46 (s, 1H, sub. Cp ring), 4.31–4.15 (m, 4H acetal-CH_2, 1H, alcohol-CH_2), 4.25 (s, 5H, Cp-H), 4.03–3.85 (m, 4H acetal-CH_2), 3.45 (d, 1H, $^3J_{H,H} = 4.4$ Hz, alcohol-OH), 2.34 (s, 3H, methyl-H), 2.15–2.11 (m, 2H, acetal-CH_2), 1.43–1.29 (m, 4H, acetal-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.26, 130.71, 128.49,

120.21, 99.89, 99.55, 87.66, 86.67, 85.86, 84.99, 83.26, 71.81, 71.67, 67.21, 63.60, 58.84, 45.65, 25.45, 25.25, 20.93. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{28}H_{30}FeO_5$) 502.14, Found 502. UV–Vis ($CHCl_3$): λ 257 ($\varepsilon = 18047$ cm^{-1} M^{-1}), 302 ($\varepsilon = 13725$ cm^{-1} M^{-1}), 446 ($\varepsilon = 490$ cm^{-1} M^{-1}). Elemental Analysis. Calc. (in %): C 66.94; H 6.02, Found: C 66.93, H 6.09.

5.5. Synthesis of **6b**

In an oven-dried 500 mL Schlenk flask, **5b** (4.68 g, 9.10 mmol) was dissolved in dry THF (250 mL). The solution was cooled to −78 °C for 10 min and *sec*-BuLi (7.7 mL, 1.30 M, 10 mmol) was added. The solution became dark-brown and cloudy after 5 min. After 20 min, the temperature was raised to −10 °C for 1.5 h. The reaction mixture was re-cooled to −78 °C and *N*-formylpiperidine (1.13 g, 16.0 mmol) was added. A brown precipitate homogenized after 1 h stirring at ambient temperature. The addition of brine turned the color of the solution to deep red. The organic layer was extracted with CH_2Cl_2, dried over magnesium sulfate, and the solvent was removed in vacuo under the exclusion of light. The raw product was dissolved under inert conditions in dry THF (100 mL) and cooled to 0 °C. Addition of $LiAlH_4$ (11.8 mL, 1.00 M in THF, 11.8 mmol) changed the color of the solution from red to yellow. The reaction mixture was quenched with brine and extracted with CH_2Cl_2. The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 + 10% NEt_3) furnished **6b** (3.02 g, 61%) in the second fraction as a yellow foam. IR (Neat): *v* 2954, 2849, 2212, 1469, 1236, 1106, 994, 818 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, $^3J_{H,H} = 8.4$ Hz, 2H), 7.12 (d, $^3J_{H,H} = 8.4$ Hz, 2H), 5.90 (s, 1H), 5.54 (s, 1H), 4.64 (d, $^3J_{H,H} = 4.4$ Hz, 1H), 4.46 (s, 1H), 4.31–4.15 (m, 4H), 4.25 (s, 5H), 4.03–3.85 (m, 4H), 3.45 (d, $^3J_{H,H} = 4.4$ Hz, 1H), 2.59 (t, $^3J_{H,H} = 7.7$ Hz, 2H), 2.15–2.11 (m, 2H), 1.62–1.52 (m, 2H), 1.43–1.29 (m, 4H), 0.91 (t, $^3J_{H,H} = 7.3$ Hz. ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.40, 142.47, 130.93, 128.05, 120.63, 100.12, 99.77, 87.90, 86.88, 85.86, 84.99, 83.26, 71.81, 67.41, 67.36, 63.87, 59.04, 45.85, 35.17, 33.07, 25.66, 25.46, 11.27. MS (70 eV, EI): *m/z* (%) Calc. For M^+ ($C_{31}H_{36}FeO_5$) 544.19, Found 544 (100).

5.6. Synthesis of **7**

To a 100 mL round bottom flask was added **6a** (434 mg, 0.864 mmol), *p*-toluenesulfonic acid (410 mg, 2.16 mmol), THF (3 mL), and H_2O (2 mL). The resulting mixture was stirred for 15 min at ambient temperature and under exclusion of light. Water was added and the mixture was extracted with ethylether (100 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo to yield a red solid. In a 100 mL oven-dried Schlenk flask, the red solid and finely powdered K_2CO_3 (800 mg, 5.79 mmol) were dissolved/suspended in dry methanol (5 mL) and dry THF (2 mL). The flask was cooled to −10 °C and **2** (780 mg, 4.06 mmol) was added dropwise. The reaction mixture was stirred for 8 h under exclusion of light, quenched with $NaHCO_3$(aq), and extracted with ethylether (200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 + 10% NEt_3) furnished **7** (221 mg, 65%) as a yellow crystalline solid: m.p.: 57 °C. IR (Neat): *v* 3450 (bd-OH), 2969, 2770, 2212, 1544, 1299, 999, 815 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.39 (d, 2H, $^3J_{H,H} = 8.4$ Hz, aromatic-H), 7.12 (d, 2H, $^3J_{H,H} = 8.4$ Hz, aromatic-H), 4.70 (s, 1H, sub. Cp ring), 4.46 (dd, 2H, $^2J_{H,H} = 27.7$ Hz, $^3J_{H,H} = 12.4$ Hz, alcohol-CH_2), 4.29 (s, 5H, Cp-H), 3.13 (s, 1H, alkyne-H), 3.06 (s, 1H, alkyne-H), 2.34 (s, 3H, methyl-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.54, 131.81, 129.33, 120.43, 90.49, 89.61, 84.66, 79.47, 79.35, 79.20, 79.17, 74.61, 71.87, 70.44, 69.58, 67.86, 59.19, 21.81. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{24}H_{18}FeO$) 378.07, Found 378.

5.7. Synthesis of **8**

In a 25 mL Schlenk flask, **7** (388 mg, 1.03 mmol) was dissolved in dry piperidine (2 mL). To the solution was added $(PPh_3)_2PdCl_2$ (1.4 mg, 2.0 μmol), CuI (1.0 mg, 5.3 μmol) and **4a** (563 mg, 2.58 mmol). The reaction mixture was stirred at ambient temperature for 2 h. Water was added and the mixture was extracted with ethylether (100 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 1:4 + 10% NEt_3) furnished **8** (557 mg, 97%) as an orange solid: m.p.: 180 °C (decomposition). IR (Neat): *v* 3340 (bd-OH), 2920, 2866, 1950, 1512, 1107, 1002, 814 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.41 (m, 8H, aromatic-H), 7.16–7.13 (m, 4H, aromatic-H), 4.74 (s, 1H, sub. Cp ring), 4.61 (s, 5H, Cp-H), 4.53 (dd, 2H, $^2J_{H,H} = 32.4$ Hz, $^3J_{H,H} = 11.5$ Hz, alcohol-CH_2), 2.36 (s, 9H, methyl-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.18, 138.02, 137.95, 131.94, 131.46, 131.40, 131.39, 129.06, 129.00 129.02, 120.77, 120.48, 120.32, 91.32, 91.23, 89.40, 89.14, 85.13, 84.67, 84.01, 74.03, 71.84, 71.14, 68.87, 68.55, 59.45, 21.48. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{38}H_{30}FeO$) 558.16, Found 558. Elemental Analysis. Calc. (in %): C 81.72; H 5.41, Found: C 81.66, H 5.50.

5.8. Synthesis of **9**

In an oven-dried 25 mL Schlenk flask, **8** (557 mg, 1.00 mmol) was dissolved in dry THF (10 mL). The solution

was cooled to −78 °C for 10 min and *sec*-BuLi (0.85 mL, 1.30 M, 1.1 mmol) was added. The solution became dark-brown and cloudy after 5 min. After 20 min, the temperature was raised to 0 °C for 1 h. The reaction mixture was re-cooled to −78 °C and DMF (0.08 mL, 1 mmol) was added under exclusion of light. A brown precipitate homogenized after 1 h stirring at ambient temperature. The reaction mixture was quenched with brine and extracted with ethylether (125 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 2.5:1 + 10% NEt_3) furnished **9** (233 mg, 40%) in the second fraction as a dark red oil. IR (Neat): ν (cm^{-1}) 3418 (bd-OH), 3082, 2920, 2210, 1905, 1662 (C=O), 1512, 1411, 1041, 814. ^1H NMR (300 MHz, $CDCl_3$): δ 10.32 (s, 1H, ald-H), 7.50–7.44 (m, 6H, aromatic-H), 7.19–7.15 (m, 6H, aromatic-H), 4.72 (dd, 1H, $^2J_{H,H}$ = 10.4 Hz, $^3J_{H,H}$ = 8.9 Hz, alcohol-CH_2), 4.44 (s, 5H, Cp-H), 4.24 (dd, 1H, $^2J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 5.8 Hz, alcohol-CH_2), 2.37 (s, 9H, methyl-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.88, 138.49, 138.39, 138.25, 131.24, 131.18, 131.09 128.80, 128.75, 128.73, 119.64, 119.31, 119.26 93.16, 92.75, 92.34, 91.31, 82.62, 81.92, 81.60, 75.30, 75.13, 74.67, 74.29, 72.34, 57.70, 21.13. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{39}H_{30}FeO_2$) 586.16, Found 586.

5.9. Synthesis of **10**

In a 25 mL oven-dried Schlenk flask, **9** (128 mg, 0.218 mmol) and finely powdered K_2CO_3 (100 mg, 0.724 mmol) were dissolved in dry methanol (4 mL) and dry THF (2 mL). The flask was cooled to −10 °C and **2** (100 mg, 0.521 mmol) was added drop-wise. The reaction mixture was stirred for 8 h under exclusion of light. $NaHCO_3$(aq) was added and the mixture was extracted with ethylether (200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 + 10% NEt_3) furnished **10** (95 mg, 75%) as a red-yellow oil. IR (Neat): ν 3276, 2952, 2854, 1506, 1458, 1107, 815 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.42 (m, 6H, aromatic-H), 7.15 (d, 6H, $^3J_{H,H}$ = 8.4 Hz, aromatic-H), 4.74 (d, 2H, $^3J_{H,H}$ = 5.5 Hz, alcohol-CH_2), 4.34 (s, 5H, Cp-H), 3.09 (s, 1H, alkyne-H), 2.36 (s, 9H, methyl-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.48, 138.29, 138.24, 131.64, 131.55, 131.51, 129.11, 129.06, 129.03, 120.47, 120.36, 120.01, 91.82, 91.76, 90.41, 83.93, 83.67, 93.67, 83.21, 79.35, 78.71, 75.94, 71.70, 71.50, 69.37, 67.25, 58.74, 21.53. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{40}H_{30}FeO$) 582.16, Found 582.

5.10. Synthesis of **11a**

In a 25 mL Schlenk flask, **10** (92.0 mg, 0.158 mmol) was dissolved in dry piperidine (1 mL). To the solution was added $(PPh_3)_2PdCl_2$ (2.2 mg, 3.1 μmol), CuI (1.5 mg, 7.9 μmol) and **4a** (50.0 mg, 0.229 mmol). The reaction mixture was stirred at ambient temperatures for 2 h. Water was added and the mixture was and extracted with ethyl ether (100 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/ CH_2Cl_2 1:4 + 10% NEt_3) furnished **11a** (99 mg, 94%) as an orange oil. IR (Neat): ν 3280, 2945, 2860, 2188, 1512, 1448, 1105, 813 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.44 (m, 8H, aromatic-H), 7.15 (d, 8H, $^3J_{H,H}$ = 8.4 Hz, aromatic-H), 4.80 (s, 2H, alcohol-CH_2), 4.36 (s, 5H, Cp-H), 2.37 (s, 12H, methyl-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.40, 138.16, 131.55, 131.50, 129.10, 129.06, 120.58, 120.12, 91.68, 89.81, 84.22, 83.52, 75.75, 71.27, 69.21, 58.96, 21.52. Two signals are missing due to spectral overlap. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{47}H_{36}FeO$) 672.21, Found 672. UV–Vis ($CHCl_3$): λ 288 (ε = 14,915 cm^{-1} M^{-1}), 384 (ε = 1177 cm^{-1} M^{-1}). Elemental Analysis. Calc. (in %): C 83.92; H 5.39, Found: C 83.18, H 6.06.

5.11. Synthesis of **12a**

In a 25 mL oven-dried Schlenk flask, **11a** (99.0 mg, 0.147 mmol), CuCl (3.0 mg, 30 μmol), 1,10-phenanthroline (5.0 mg, 28 μmol), and K_2CO_3 (8.0 mg, 58 μmol) were dispersed in dry toluene (2 mL). Di-*tert*-butylazodicarboxylate (40.0 mg, 0.170 mmol) was added under nitrogen and the reaction was heated to 90 °C for 2 h. The reaction mixture was filtered over celite with CH_2Cl_2 as the mobile phase and the solvent was removed in vacuo. The resulting unstable, dark-red oil was transferred with CH_2Cl_2 into a 25 mL Schlenk flask and the solvent was removed in vacuo. To this was added K_2CO_3 (78.0 mg, 0.564 mmol), dry methanol (2 mL) and dry THF (1 mL) under nitrogen. The solution was cooled to −10 °C and **2** (71.0 mg, 0.370 mmol) was added drop-wise. The resulting reaction mixture was stirred for 8 h under exclusion of light. $NaHCO_3$(aq) was added and the mixture was extracted with ethylether (200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 2.5:1 + 10% NEt_3) furnished **12a** (61 mg, 62%) as a red-yellow oil. IR (Neat): ν 2920, 2858, 2341, 1732, 1512, 1153, 817 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 8H, $^3J_{H,H}$ = 8.4 Hz, aromatic-H), 7.16 (d, 8H, $^3J_{H,H}$ = 8.4 Hz, aromatic-H), 4.41 (s, 5H, Cp-H), 3.17 (s, 1H, alkyne-H), 2.37 (s, 12H, methyl-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.36, 138.31, 131.69, 131.61, 129.09, 129.05, 120.46, 120.34, 91.91, 91.86, 83.94, 83.68, 79.23, 79.20, 78.94, 77.22, 71.75, 71.45, 21.57. MS (70 eV, EI): *m/z* Calc. For M^+ ($C_{48}H_{34}Fe$) 666.20, Found 666. UV–Vis ($CHCl_3$): λ 292 (ε = 55,940 cm^{-1} M^{-1}), 380 (ε = 6565 cm^{-1} M^{-1}).

5.12. Synthesis of **13a**

In a 25 mL Schlenk flask, **12a** (57.0 mg, 85.6 μmol) was dissolved in dry piperidine (1 mL). To the solution was added $(PPh_3)_2PdCl_2$ (1.0 mg, 1.4 μmol), CuI (0.8 mg, 4 μmol) and **4a** (24.0 mg, 0.110 mmol). The reaction mixture was stirred at ambient temperature for 2 h. Water was added and the mixture was extracted with ethylether (75 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 1:2.5 + 10% NEt_3) furnished **13a** (60 mg, 93%) as an orange crystalline solid: m.p.: 152 °C (turned dark), 168 °X (δεχομποσιτιον). IP (Νεατ): *ν* 2923, 2858, 2329, 1712, 1512, 1176, 813 $\chi\mu^{-1}$. ^{1}H NMP (400 ΜΗζ, ΧΔΧλ$_3$): *δ* 7.52 (δ, 10Η, $^3J_{H,H}$=8.4 Ηζ, αρομ ατιχ–Η), 7.17 (δ, 10Η, $^3J_{H,H}$=8.4 Ηζ, αρομ ατιχ–Η), 4.42 (σ, 5Η, Χπ–Η), 2.38 (σ, 15Η, μετηψλ–Η). ^{13}X NMP (100 ΜΗζ, ΧΔΧλ$_3$): *δ* 138.23, 131.60, 129.09, 120.57, 91.77, 84.24, 77.11, 71.22, 21.57. ΜΣ (70 ες, EI) *m/z* Χαλχ. Φορ M^+ ($X_{55}H_{40}\Phi\varepsilon$) 756.25, Φουνδ 756. Υς-–σισ (ΧΗΧλ$_3$): *λ* 298 (*ε*=51,208 $\chi\mu^{-1}$ M^{-1}), 384 (*ε*=5561 $\chi\mu^{-1}$ M^{-1}). Ελ–εμενταλ Αναλψσισ. Χαλχ. (ιν %): Χ 87.29; Η 5.33, Φουνδ: Χ 87.41, Η 5.90.

5.13. Synthesis of **15**

In an oven-dried 25 mL Schlenk flask, **6b** (2.68 g, 4.92 mmol) was dissolved in dry THF (100 mL). The solution was cooled to −78 °C for 10 min and BuLi (5.4 mL 2.00 M, 11 mmol) was added. The solution turned dark-brown and cloudy after 5 min. After 20 min, the temperature was raised to 0 °C for 1 h. The reaction mixture was re-cooled to −78 °C and NFP (1.39 g, 12.3 mmol) was added. A brown precipitate homogenized after 1 h stirring at ambient temperature. The reaction mixture was quenched with brine and extracted with ethylether (200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 + 10% NEt_3) furnished **6b** and **15** in a 1/1 ratio (2.61 g crude material, 96%) as a light sensitive, red oil which was immediately taken to the next step.

5.14. Synthesis of **16**

In a 25 mL oven-dried Schlenk flask, the oil containing **6b** and **15** (2.61 g crude material, 2.37 mmol aldehyde) and finely powdered K_2CO_3 (0.850 g, 6.15 mmol) were dissolved/suspended in dry methanol (8 mL) and dry THF (2 mL). The flask was cooled to −10 °C and **2** (1.19 g, 6.20 mmol) was added drop-wise. The reaction mixture was stirred for 8 h under exclusion of light. $NaHCO_3$(aq) was added and the mixture was extracted with ethylether (200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 + 10% NEt_3) furnished **16** and **6b** (2.35 g crude material, 80%) in a 2/3 ratio as a yellow oil which was immediately taken to the next step.

5.15. Synthesis of **17**

In a 25 mL Schlenk flask, the oil containing **16** and **6b** (2.35 g crude material, 1.90 mmol alkyne) was dissolved in dry piperidine (3 mL). To the solution was added $(PPh_3)_2PdCl_2$ (36.3 mg, 51.9 μmol), CuI (9.9 mg, 52 μmol), and **4b** (1.35 g, 5.19 mmol). The reaction mixture was stirred at ambient temperature for 2 h. Water was added and the mixture was extracted with ethylether (125 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed i vacuo. Chromatography (SiO_2; hexanes/CH_2Cl_2 4:1 + 10% NEt_3) furnished a mixture of **17** and **6b** (2.33 g crude material, 80%) in a 1/3 ratio which was immediately taken to the next step.

5.16. Synthesis of **18** and **19**

To a 100 mL round bottom flask was added the oil containing **17** and **6b** (1.40 g), *p*-toluenesulfonic acid (951 mg, 5.00 mmol), THF (3 mL) and H_2O (5 mL). The reaction mixture was stirred for 30 min under exclusion of light. Water was added and the mixture was extracted with ethylether (100 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/EtOAc 4:1) furnished **18** (140 mg, 47%) as a yellow-red oil and **19** (500 mg, 78%) as a red oil. **18**: IR (Neat): *ν* 2953, 2856, 1680, 1513, 1412, 831 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 10.70 (s, 1H), 10.52 (s, 1H), 7.49–7.45 (m, 4H), 7.20–7.17 (m, 4H), 4.76–4.73 (m, 2H), 4.50 (s, 5H), 4.35–4.30 (m, 1H), 2.65–2.60 (m, 4H), 1.65–1.55 (m, 4H), 1.41–1.29 (m, 4H), 0.95–0.90 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 197.35, 193.37, 144.31, 144.21, 131.66, 131.60, 128.59, 128.55, 119.36, 119.29, 96.13, 94.50, 94.36, 81.15, 80.97, 79.01, 78.37, 76.95, 76.57, 75.49, 57.91, 35.56, 33.26, 22.19, 13.84. MS (70 eV, EI): *m/z* (%) Calc. For M^+ ($C_{37}H_{36}FeO_3$) 584.20, Found 584 (100). **19**: IR (Neat): *ν* 2960, 2865, 1676, 1414, 1360, 1015, 834 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 10.71 (s, 1H), 10.47 (s, 1H), 7.39 (d, $^3J_{H,H}$=8.3 Hz, 2H), 7.16 (d, $^3J_{H,H}$=8.5 Hz, 2H), 5.24 (s, 1H), 4.49 (s, 5H), 4.05 (t, $^3J_{H,H}$=6.6 Hz, 1H), 3.75–3.70 (m, 2H), 2.61 (t, $^3J_{H,H}$=7.7 Hz, 2H), 1.61–1.53 (m, 2H), 1.37–1.30 (m, 2H), 0.91 (t, $^3J_{H,H}$=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 196.95, 193.53, 144.07, 131.34, 128.46, 119.07, 95.88, 91.81, 81.57, 80.06, 79.27, 76.57, 74.40, 73.75, 58.92, 35.40, 33.13, 22.07, 13.74. MS (70 eV, EI): *m/z* (%) Calc. For M^+ ($C_{25}H_{24}FeO_3$) 428.11, Found 428 (100).

5.17. Synthesis of **20**

In a 25 mL oven-dried Schlenk flask, **18** (140 mg, 0.240 mmol) and finely powdered K_2CO_3 (166 mg, 1.20 mmol) were dissolved/suspended in dry methanol (1 mL) and dry THF (1 mL). The solution was cooled to 0 °C and **2** (232 mg, 1.20 mmol) was added drop-wise. The reaction mixture was stirred for 8 h under exclusion of light. $NaHCO_3$(aq) was added and the mixture was extracted with ethylether (200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/EtOAc 4:1) furnished **20** (32 mg, 22%) in the first fraction as a yellow oil. IR (Neat): *v* 3287, 2962, 1734, 1363, 1266, 1094, 834 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.49–7.43 (m, 4H), 7.16–7.14 (m, 4H), 4.72 (m, 2H), 4.33 (s, 5H), 3.14 (s, 1H), 3.09 (s, 1H), 2.63–2.59 (m, 4H), 1.60–1.57 (m, 4H), 1.37–1.31 (m, 4H), 0.93–0.90 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.64, 143.45, 131.69, 131.57, 128.52, 128.43, 120.44, 120.09, 92.00, 91.94, 90.52, 83.30, 82.87, 79.42, 79.23, 78.59, 78.35, 76.00, 72.10, 69.73, 69.61, 67.75, 58.66, 35.61, 33.41, 33.38, 22.26, 13.91.

5.18. Synthesis of **11b**

In a 25 mL Schlenk flask, **20** (32.0 mg, 55.5 μmol) was dissolved in dry piperidine (2 mL). To the solution was added $(PPh_3)_2PdCl_2$ (1.9 mg, 2.7 μmol), CuI (0.5 mg, 3 μmol), and **4b** (33.0 mg, 0.127 mmol). The reaction mixture was stirred at ambient temperature for 8 h. Water was added and the mixture was extracted with ethylether (100 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/ EtOAc 4:1) furnished **11b** (25 mg, 54%) in the first fraction as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.53–7.46 (m, 8H), 7.17–7.15 (m, 8H), 4.80 (bs, 2H), 4.34 (s, 5H), 2.64–2.59 (m, 8H), 1.63–1.55 (m, 8H), 1.39–1.32 (m, 8H), 0.95–0.90 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.47, 143.21, 131.62, 131.56, 128.51, 120.84, 120.36, 91.77, 89.87, 84.22, 83.53, 75.79, 71.34, 69.21, 59.06, 35.64, 33.43, 33.41, 22.29, 13.93.

5.19. Synthesis of **21** via an airless Marko oxidation

In a 25 mL oven-dried Schlenk flask, **11b** (25.0 mg, 29.7 μmol), Cu_2Cl_2 (0.4 mg, 2 μmol), 1,10-phenanthroline (0.6 mg, 3 μmol), and K_2CO_3 (1 mg, 7 μmol) were dispersed in dry toluene (5 mL). Di-*tert*-butylazodicarboxylate (15.0 mg, 0.714 mmol) was added under nitrogen and the reaction was heated to 90 °C for 2 h. The reaction mixture was filtered over Celite with CH_2Cl_2 as the mobile phase and the solvent was removed in vacuo. Column chromotagraphy (SiO_2; hexanes/EtOAc 5:1) furnished **21** (22 mg, 88 %) in the second fraction as a red/yellow oil. IR: *v* 2908, 1765, 1458, 1370, 1277, 1141, 833 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 10.47 (s, 1H), 7.55–7.51 (m, 8H), 7.20–7.16 (m, 8H), 4.44 (s, 5H), 2.66–2.60 (m, 8H), 1.64–1.55 (m, 8H), 1.40–1.32 (m, 8H), 0.93–0.91 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 143.97, 143.94, 132.00, 131.96, 128.80, 128.76, 120.58, 120.52, 93.51, 93.40, 83.35, 83.07, 77.57, 75.88, 71.11, 35.92, 33.67, 22.55, 14.19. MS (70 eV, EI): *m/z* (%) Calc. For M^+ ($C_{59}H_{58}FeO$) 838.38, Found 838 (100).

5.20. Synthesis of **12b**

In a 25 mL oven-dried Schlenk flask, **21** (10.0 mg, 11.9 μmol) and finely powdered K_2CO_3 (3.3 mg, 24 μmol) were dissolved in dry methanol (1 mL) and dry THF (1 mL). The solution was cooled to −10 °C and **2** (5.3 mg, 28 μmol) was added drop-wise. The reaction mixture was stirred for 8 h under exclusion of light. $NaHCO_3$(aq) was added and the mixture was extracted with ethylether (200 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Purification by thick layer chromatography with hexanes as the mobile phase furnished **12b** (7.0 mg, 70%) in the second fraction as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52–7.50 (m, 8H), 7.18–7.15 (m, 8H), 4.39 (s, 5H), 3.15 (s, 1H), 2.62 (t, $^3J_{H,H}$ = 7.7 Hz, 8H), 1.64–1.57 (m, 8H), 1.38–1.33 (m, 8H), 0.93 (d, $^3J_{H,H}$ = 7.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.38, 143.33, 131.73, 131.65, 128.47, 128.43, 120.69, 120.58, 91.95, 91.90, 83.96, 83.71, 79.21, 79.16, 78.95, 77.23, 71.78, 71.49, 35.65, 33.43, 22.30, 13.94.

5.21. Synthesis of **13b** and **14b**

In a 25 mL Schlenk flask, **12b** (35.0 mg, 42.0 μmol) was dissolved in dry piperidine (2 mL). To the solution was added $(PPh_3)_2PdCl_2$ (1.5 mg, 2.1 μmol), CuI (0.5 mg, 3 μmol), and **4b** (16.4 mg, 63.0 μmol). The reaction mixture was stirred at ambient temperature for 6 h. Water was added and the mixture was extracted with ethylether (100 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuo. Column chromatography (SiO_2; hexanes/CH_2Cl_2 16:1) furnished **13b** (14 mg, 34%) in the first fraction and **14b** (21 mg, 60%) in the second fraction as yellow, crystalline materials. **13b**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, $^3J_{H,H}$ = 7.96 Hz, 10H), 7.16 (d, $^3J_{H,H}$ = 7.95 Hz, 10H), 4.39 (s, 5H), 2.62 (t, $^3J_{H,H}$ = 7.7 Hz, 10H), 1.65–1.55 (m, 10H), 1.39–1.29 (m, 10H), 0.96–0.86 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.56, 130.21, 124.23, 120.70, 91.33, 83.51, 75.98, 71.16, 34.95, 34.13, 24.76, 11.98. MS (70 eV, IE): *m/z* Calc.

For M^+ ($C_{70}H_{70}Fe$) 966.18, Found 966.). Elemental Analysis. Calc. (in %): C 86.93; H 7.30, Found: C 86.51, H 7.52. **14b**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.56–7.51 (m, 16H), 7.19–7.09 (m, 16H), 4.47 (s, 5H), 2.65–2.54 (m, 16H), 1.66–1.50 (m, 16H), 1.40–1.24 (m, 16H), 0.95–0.84 (m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.63, 143.55, 132.00, 131.91, 128.73, 128.71, 120.91, 120.75, 92.75, 92.30, 84.21, 77.63, 72.53, 35.90, 33.68, 33.64, 29.93, 29.28, 14.16, 14.19. Elemental Analysis. Calc. (in %): C 86.41; H 6.98, Found: C 85.99, H 7.29.

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