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Transannular Addition of Phenols to 1,1′-Dialkynylferrocenes: Unanticipated Formation of Phenoxy[4]ferrocenophanedienes

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Dedicated to Professor Günther Wilke on the occasion of his 85th birthday

Abstract: The reaction of some 1,1′-dialkynylferrocenes with a variety of phenols in the presence as well as in the absence of $[Mo(CO)_6]$ yields good to high yields of phenoxy[4]ferrocenophanedienes. Similar reactivity was observed with a thiophenol and with acetic acid. Reaction under basic reaction conditions led to the formation of the [4]ferrocenophanone **17**. The phenoxy[4]ferrocenophanedienes obtained show dynamic behavior as a result of a torsional twist of the carbon bridge as indicated by the ^1H and ^{13}C NMR spectra. The reaction mechanism is discussed in view of recent related results of Sato et al. as well as of Pudelski et al. A vinyl cation intermediate is postulated in this context, whose relative stability is evident from the mass spectra of the compounds prepared.

Keywords: alkynes · metallocenes · phenols · regioselectivity · transannular addition

Introduction

The continuous miniaturization of electronic devices led to the idea of molecular electronics, the implementation of electronic functions on the molecular scale.[1] Conventional molecular wires consist of 1,4-phenylene or 2,5-thiophenylidene units connected by ethynylene bridges and thus are comparatively rigid.[2–4] To construct molecular wires with a limited conformational flexibility, we[5,6] and others[7–9] reasoned that replacement of some of the 1,4-phenylene units by 1,1′-ferrocenylidene "hinges" would give access to molecular wires with flexibility comparable to that of a foldable ruler. The synthesis of such molecular wires widely relies on repetitive Sonogashira coupling reactions of a small number of suitable building blocks. The Sonogashira coupling reaction is among the most commonly used reactions for the connection of alkynyl groups to arenes. However, the reaction does not always give satisfactory results.[10] In the search for a different tool for the construction of the key element of molecular wires we considered alkyne cross metathesis to be of interest. Although alkene metathesis is now a well-established method,[11–13] alkyne metathesis has been developed to a much lesser extent.[14–17] We note recent publications of Stepnicka and Kotora, who investigated related chemistry starting from (1-propynyl)ferrocene.[18,19] Here we report some results of our attempts to couple 1,1′-di(1-propynyl)ferrocene (**1**) by alkyne metathesis, which resulted in an unanticipated formation of [4]ferrocenophanediene derivatives.

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Results and Discussion

Due to available undesired reaction paths such as polymerization reactions, terminal alkynes are usually not suitable for alkyne metathesis.[20,21] To generate a volatile product in addition to the desired coupling product 1-propynyl compounds are often used, which gives 2-butyne as the removable volatile and thereby shifts the equilibrium to the product side. Therefore our study started from 1,1′-di(1-propynyl)ferrocene (**1**).[22] Because of the ready availability of the catalyst we decided to test the Mortreux catalyst system, essentially using hexacarbonylmolybdenum and a phenol derivative in a solvent with a high boiling point.[23–27] The reaction, which would involve metallacyclobutadiene intermediates,[28] was expected to yield oligo(1,1′-ferrocenylidene)ethynylenes. However, in contrast to our expectations, the reaction

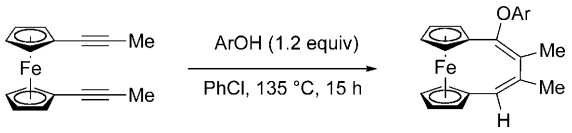
of diyne **1** with 4-chlorophenol (1.2 equiv) *in the presence as well as in the absence of hexacarbonylmolybdenum* in chlorobenzene at 135 °C afforded [4]ferrocenophanediene **2** in up to 84 % yield as a result of a transannular addition reaction. Subsequently it was found that a number of other phenols react in the same way to give derivatives **2**–**13**, clearly showing the generality of this reaction. The results are summarized in Table 1.

The phenols used include electron-poor ones such as halophenols (Table 1, entries 1–5) or 4-nitrophenol (entry 6) as well as the unsubstituted phenol (entry 7) and electron-rich ones such as alkyl or alkoxyphenols (entries 8–11) or 4-aminophenol (entry 12). Although the yield of the reaction with 2-isopropoxyphenol is only moderate, presumably for steric reasons, the yields of the other reactions are good to excellent, with 4-iodophenol and 2,4-dichlorophenol giving essentially quantitative yields.

The constitutions and relative configurations of the products were determined spectroscopically. As a representative example, the data of the 4-chlorophenol adduct **2** are discussed (Table 1, entry 1): The monoaddition is evident from the mass spectrum and the ^{13}C NMR spectrum, which shows the signals for the tertiary olefinic carbon atom at $\delta = 124.2$, and those for the quaternary olefinic carbon atoms at $\delta =$ 124.3, 126.2, and 136.5 ppm. ^{1}H NMR signals assigned to the two methyl groups appear at $\delta = 1.85$ (s, 3H) and 1.95 ppm (d, $J = 1.4$ Hz, 3H). The ^{1}H NMR signal assigned to the olefinic proton appears as a two line signal with a separation of 1.0 Hz with slight shoulders; we presume that this is a quartet with the less-intense outer two lines being covered as a result of the small coupling constant. The *E* configuration of the double bond bearing the phenoxy substituent in the representative case of **5** has also been established by NOE measurement, which shows a 14 % increase of the signal at $\delta =$ 6.14 ppm (br s, CH=C, 1H) upon irradiation at $\delta = 1.97$ ppm (d, $J = 0.7$ Hz, 3H; CH=C-CH_3). All other analytical data are in full accord with the assigned formulas. In accord with the assignments made, treatment of **2** with hydrochloric acid afforded the corresponding ketone **17** in 40 % yield.

To check how far a sulfur analogue would undergo the reaction, **1** was treated with 2-bromothiophenol under the same reaction conditions. Ferrocenophane **14** was obtained in 31 % yield. As the acidity of the phenols was considered a factor in the addition reaction we also checked whether a carboxylic acid would add in the same manner. Treatment of **1** with acetic acid under otherwise unchanged reaction conditions indeed resulted in the transannular addition affording enol ester **15** in 44 % yield. Reaction of **1** with a stronger carboxylic acid, trifluoroacetic acid, however, resulted in the formation of 1,1′-dipropanoylferrocene (**16**)[29] in 58 % yield after chromatographic workup instead of the corresponding adduct.

Table 1. Transannular addition of phenols ArOH to 1,1′-di(1-propynyl)-ferrocene (**1**).[a]



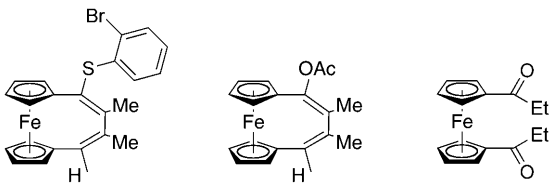
1 **2–13**

Entry	ArOH	Product	Yield [%]
1	4-chlorophenol	**2**	84
2	3-chlorophenol	**3**	92
3	2,4-dichlorophenol	**4**	99
4	2-fluorophenol	**5**	75
5	4-iodophenol	**6**	99
6	4-nitrophenol	**7**	91
7	phenol	**8**	57
8	4-methylphenol	**9**	86
9	4-methoxyphenol	**10**	89
10	2-methoxyphenol	**11**	84
11	2-isopropoxyphenol	**12**	39
12	4-aminophenol	**13**	65

[a] 1.0 mmol of **1**, 1.2 mmol of phenol derivative in 20 mL of chlorobenzene, 15 h, 135 °C.

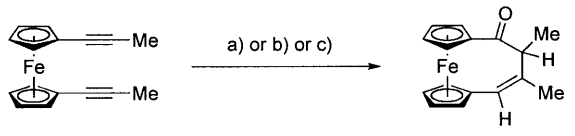
Abstract in German: *Die Reaktion einiger 1,1′-Dialkinylferrocene mit einer Reihe von Phenolen in Gegenwart wie auch in Abwesenheit von [Mo(CO)$_6$] ergibt in guten Ausbeuten Phenoxy[4]ferrocenophandiene. Ähnliche Reaktivität wurde bei Einsatz eines Thiophenols sowie von Essigsäure beobachtet. Unter basischen Reaktionsbedingungen führte die Reaktion zur Bildung des [4]Ferrocenophanons **17**. Die Phenoxy-[4]ferrocenophandiene zeigen als Folge der Verdrehung der Kohlenstoffbrücke dynamisches Verhalten, wie anhand der ^{1}H- und ^{13}C-NMR-Spektren gezeigt wird. Der Reaktionsmechanismus wird vor dem Hintergrund aktueller vergleichbarer Ergebnisse von Sato et al. sowie von Pudelski et al. diskutiert. In diesem Zusammenhang wird ein intermediäres Vinylkation postuliert, dessen Stabilität anhand der Massenspektren der dargestellten Verbindungen evident ist.*

Abstract in Chinese:
无论在有无 Mo(CO)$_6$ 存在的情况下，一些 1,1′-二炔基二茂铁和不同的苯酚反应，得到高产率的苯氧基-[4]二茂铁环蕃二烯。和苯硫酚，乙酸也发生相似的反应。在碱性条件下，生成[4]二茂铁环蕃酮 **17**. ^{1}H - 和 ^{13}C - 核磁共振光谱显示，因为碳桥扭转的存在，苯氧基-[4]二茂铁环蕃二烯表现出动力学行为。结合最近 Sato 和 Pudelski 等的研究结果，讨论了反应机理。本文中假设的乙烯基正离子，其相对稳定度也从质谱中得到了验证。



14 (31 %) **15** (44 %) **16** (58 %)

The reaction conditions were modified by replacing the solvent chlorobenzene by *N,N*-dimethylformamide (DMF), which is known to decompose slowly at elevated temperatures with formation of dimethylamine rendering the reaction conditions more basic. When **1** was heated at 157 °C in DMF in the presence of 4-chlorophenol (5 equiv) for 15 h, a different result was obtained. Instead of the phenyl enol ether **2**, the unsaturated [4]ferrocenophanone **17** was obtained in 57 % yield. Alternatively, **17** was obtained in 38 % yield, when **1** was treated with 4-iodophenol (2.4 equiv) in DMF with microwave heating at 157 °C for 30 min. Finally, heating **1** with water (5 equiv) in DMF for 20 h at 157 °C afforded **17** in 72 % yield (Scheme 1).

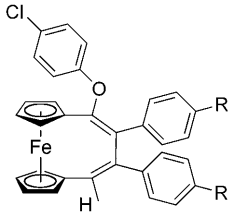


1 **17**

Scheme 1. a) 4-Chlorophenol (5 equiv), DMF, 157 °C, 20 h, 57 %. b) 4-Iodophenol (2.4 equiv), DMF, μW, 157 °C, 30 min, 38 %. c) H_2O (5 equiv), DMF, 157 °C, 20 h, 72 %.

To get a better insight into the reaction the alkynyl substituents in the starting material were also varied. 1,1′-Di-(phenylethynyl)ferrocene (**18**) was prepared by following a published procedure,[30] and 1,1′-di(4-*tert*-butylsulfanylphenylethynyl)ferrocene (**19**) was obtained in 33 % yield from 1,1′-diiodoferrocene by a Sonogashira coupling reaction. Treatment of 1-ethynyl-1′-iodoferrocene[6] (**20**) with lithium diisopropylamide (LDA) followed by iodomethane afforded 1-iodo-1′-(1-propynyl)ferrocene (**21**) in 66 % yield. Subsequent Sonogashira coupling reactions with phenylethyne or 4-(*tert*-butylsulfanyl)phenylethyne gave mixed 1,1′-dialkynylferrocenes **22** and **23** in 85 and 46 % yield, respectively (Scheme 2).

Treatment of the symmetrically disubstituted ferrocenes **18** and **19** with 4-chlorophenol under the usual reaction conditions resulted in the formation of ferrocenophanes **24** and **25** in 59 and 46 % yield, respectively. Although the yields obtained in these cases were not as high as those with **1** as starting material, the reactions clearly indicate the general nature of the reaction with respect to the alkynyl substituents.



24: R = H (59 %)
25: R = S*t*Bu (46 %)

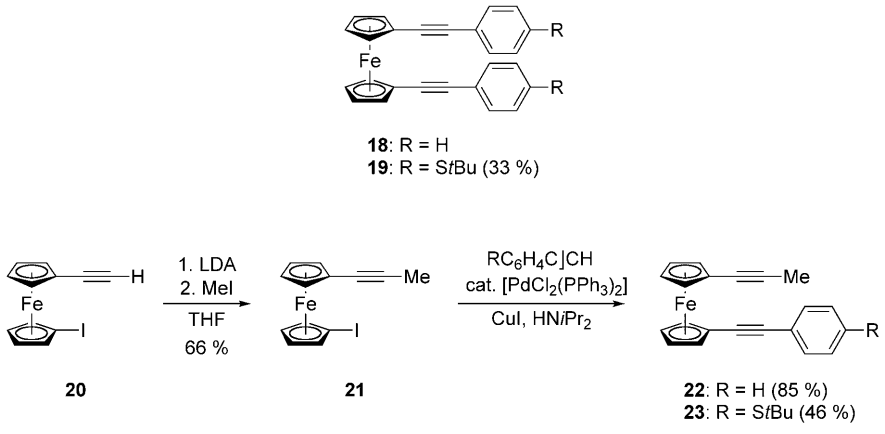
The corresponding reaction of the unsymmetrically 1,1′-dialkynylated ferrocenes **22** and **23** resulted in product mixtures **26**/**27** (36 %/42 % yield) and **28**/**29** (47 %/29 % yield) (Scheme 3). Although the overall yields of ferrocenophanes are almost the same in both cases, the product ratios indicate that the triple bonds in **22** are hardly differentiated by the attacking nucleophile, whereas the electron-delivering *tert*-butylsulfanylphenyl substituent in **23** renders the triple bond next to it less prone to nucleophilic attack.

Pudelski and Callstrom have published reports on a related reaction. It was reported that 1,1′-bis(trimethylsilylethynyl)ferrocene (**30**) and -ruthenocene (**31**) react with methanol in the presence of aqueous KOH with formation of methyl enol ethers **32** and **33**, respectively (Scheme 4). Subsequent enol ether hydrolysis afforded ketones **34** and **35**.[31,32]

The authors explain their result by a subsequent protiodesilylation that generates 1,1′-diethynylmetallocenes. In a concerted process a nucleophilic attack of methoxide at α-C induces a nucleophilic transannular attack at β′-C followed by protonation (Scheme 5). For this reasonable mechanism to be operative in the reactions of **1** under basic reaction conditions it would have to involve a hydroxide attack at **1** leading to intermediate enol **36**, which subsequently enolizes to the observed ketone **17**.

Although the mechanism proposed by Pudelski and Callstrom seems reasonable for basic reaction conditions, this is not necessarily the case for the reaction under acidic reaction conditions given in the presence of phenols or a weak acid such as acetic acid. In this context we note a recent publication of Sato et al. describing the reaction of 1-(1-propynyl)-2,3,4,5-tetramethylruthenocene (**37**) with $[Mo(CO)_6]$ and 4-chlorophenol in toluene at reflux to give *syn* adduct **38** in 76 % yield (Scheme 6).[33] The authors do not give a mechanistic explanation for this result.

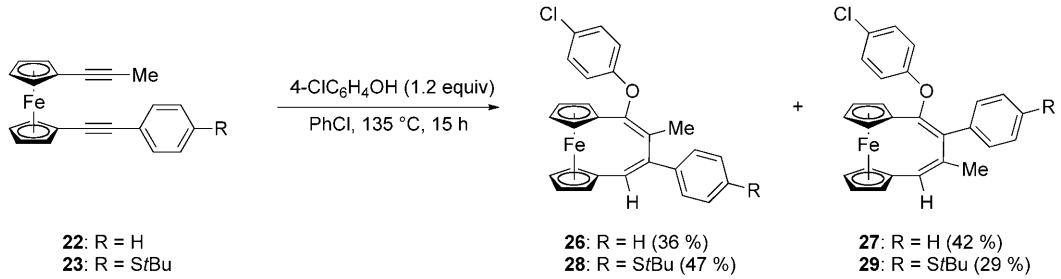
Because of the high degree of substitution of ruthenocene derivative **37**, steric reasons for the observed regioselectivity



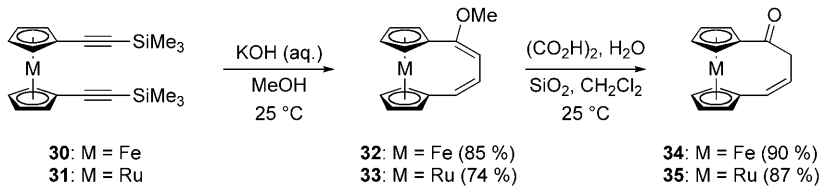
18: R = H
19: R = S*t*Bu (33 %)

20 **21** **22**: R = H (85 %)
23: R = S*t*Bu (46 %)

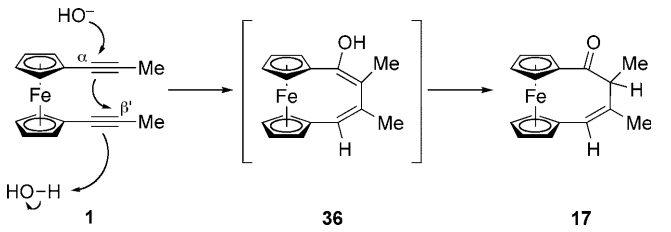
Scheme 2.



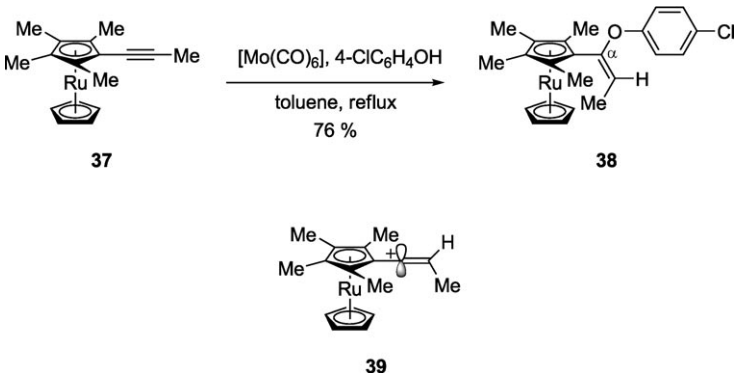
Scheme 3.



Scheme 4.

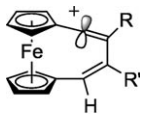


Scheme 5.



Scheme 6.

seem unlikely. If these were operative, one would expect the opposite regioisomer. To consider electronic factors a comparison of the pK_a values of ferrocene carboxylic acid (5.72) and ruthenocene carboxylic acid (5.43) reveals the ruthenocenyl substituent to be less electron rich than the ferrocenyl group, which is in accord with investigations comparing electrophilic substitution.[34] To estimate the electronic influence of the methyl substituents in **37** one might compare the pK_a values[35] of benzoic acid (4.204) with that of 3-methylbenzoic acid (4.25) and that of 3,5-dimethylbenzoic acid (4.32) to see that there is a small electron-delivering effect, which in the case of **37** will presumably result in an electron density of the 2,3,4,5-tetramethylruthenocenyl fragment comparable to that of the ferrocenyl group. Given the fact that resonance-stabilized ferrocenylvinyl cations have been observed,[36,37] and taking the geometry of these into account, we consider vinyl cation **39** to be a reasonable intermediate in the addition of 4-chlorophenol to **37** resulting from a protonation of the triple bond in **37** from the face opposite the CpRu moiety. The electronic stabilization of the vinyl cation **39** with an sp-hybridized cationic center results in a hindered rotation around the Me_4C_5–C^+ bond, which facilitates an attack of the phenol at the empty p orbital in **39** from the face opposite the CpRu moiety, too. As a result of this overall *syn* addition, the *E* double bond observed in **38** is formed. With regard to the proposed vinyl cation intermediate **39**, data from Table 2 are instructive. Table 2 lists the relative intensities of MS peaks assigned to vinyl cation fragments **40** resulting from a fragmentation of the respective phenolate substituent for 19 compounds discussed in this work.



40

Remarkably, 11 out of 19 entries indicate vinyl cation **40** to be the most abundant cation (base peak, 100%); in the mass spectra of three other entries, **40** is among the most prominent peaks (entries 2, 6, 16); and in two entries it has more than 50% of the base peak intensity (entries 7, 19). These data clearly reflect the remarkable stability of vinyl cation **40** and support the proposed intermediacy of **39** in the formation of **38**.

A reaction mechanism for the transannular addition of phenols to 1,1′-dialkynylferrocenes should take into account the moderately acidic reaction conditions rendering a nucleophilic attack of a phenol at a triple bond unlikely. On the other hand, a protonation of one of the triple bonds would preferentially take place at C_β with formation of the ferro-

Table 2. Relative MS peak intensities of **40** and base peaks (100 %).[a]

Entry	Compound	R	R′	Rel. MS peak intensity [%]	*m*/*z* base peak (100 %)
1	**2**	Me	Me	100	263 [$M^+-(4\text{-}ClC_6H_4O)$]
2	**3**	Me	Me	85	390 [M^+]
3	**4**	Me	Me	100	263 [$M^+-(C_6H_3Cl_2O)$]
4	**5**	Me	Me	100	263 [$M^+-(2\text{-}FC_6H_4O)$]
5	**6**	Me	Me	45	224 [$(Fc\text{-}CCCH_3)^+$]
6	**7**	Me	Me	94	401 [M^+]
7	**8**	Me	Me	69	356 [M^+]
8	**9**	Me	Me	100	263 [$M^+-(4\text{-}CH_3C_6H_4O)$]
9	**10**	Me	Me	100	263 [$M^+-(4\text{-}H_3COC_6H_4O)$]
10	**11**	Me	Me	100	263 [$M^+-(2\text{-}H_3OC_6H_4O)$]
11	**12**	Me	Me	100	263 [$M^+-(2\text{-}(i\text{Pr}OC_6H_4O)$]
12	**13**	Me	Me	100	263 [$M^+-(4\text{-}H_2NC_6H_4O)$]
13	**14**	Me	Me	100	263 [$M^+-(2\text{-}BrC_6H_4S)$]
14	**24**	Ph	Ph	100	387 [$M^+-ClC_6H_4O$]
15	**25**	4-*t*BuSC$_6$H$_4$	4-*t*BuSC$_6$H$_4$	14	690 [$M^+(^{35}Cl)$]
16	**26**	Me	Ph	93	452 [$M^+(^{35}Cl)$]
17	**27**	Ph	Me	100	325 [$M^+-ClC_6H_4O$]
18	**28**	Me	4-*t*BuSC$_6$H$_4$	17	540 [$M^+(^{35}Cl)$]
19	**29**	4-*t*BuSC$_6$H$_4$	Me	52	540 [$M^+(^{35}Cl)$]

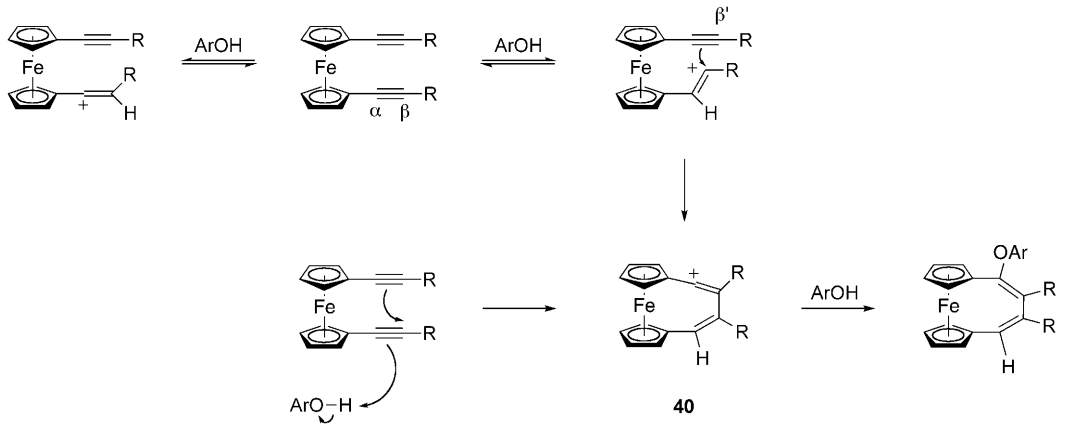
[a] 70 eV; for full fragmentation patterns see the Experimental Section.

cenyl-stabilized α-vinyl cation.[38,39] This, however, cannot directly undergo the transannular addition at the remaining triple bond with formation of the observed [4]ferrocenophanediene derivatives. Although 1,2-hydride shifts are known in vinyl cations, such a process, which would avoid a re-formation of the triple bond, seems unlikely here, because these shifts usually occur with formation of the more stable vinyl cation.[40–42] Therefore two possible explanations for the formation of [4]ferrocenophanediene derivatives might be considered (Scheme 7). First, one might envisage a *reversible* protonation at C_β and, to a lesser extent, at C_α with formation of a less-stabilized cationic center at C_β, which subsequently *irreversibly* attacks $C_{\beta'}$ to give the ferrocenyl-stabilized vinyl cation **40**. Alternatively a concerted reaction path might be considered, which circumvents the unfavorable β-cationic intermediate by a direct formation of **40**. In either case, **40** will react with ArOH to give the observed products.

We were able to obtain a crystal structure analysis of **2**, which confirmed the assigned constitution (Figure 1). The structure clearly shows a distorted ferrocene moiety with C–Fe bond lengths ranging from 201.1 (Fe–C6) and 202.2 pm (Fe–C1) for the substituted cyclopentadienyl carbon atoms up to 208.8 pm for Fe–C3. The cyclopentadienyl ligands adopt a staggered conformation and deviate from parallelism by approximately 12.4°, and the angle between the centers of the cyclopentadienyl rings and the iron atom is approximately 172.0°. As can be seen from Figure 1, the carbon chain connecting the cyclopentadienyl moieties is helically distorted as indicated by torsional angles C14-C13-C12-C11 (−50.6°) and C22-C13-C12-C21 (−49.0°) rendering the molecule chiral in the solid state.

Some ^{1}H and ^{13}C NMR spectra of the [4]ferrocenophane derivatives indicate dynamic behavior in solution. While the dimethyl compounds **2**–**15** show reasonably sharp absorption peaks in their NMR spectra, alkylaryl-substituted compounds **26**–**29** show some broadening of the ferrocenyl ^{1}H NMR signals. The ^{1}H NMR spectra of diaryl compounds **24** and **25** show broad, unresolved signals for their ferrocenyl protons, and the ^{13}C NMR spectra show sharp peaks for the quaternary ferrocenyl carbon atoms, whereas the eight ferrocenyl CH absorptions appear as a broad, unresolved absorption.

As a representative example, the temperature-dependent ^{1}H NMR spectra of **25** are shown in Figure 2 for the ferrocenyl protons in the temperature range from 223 to 323 K. The plot shows eight distinct but unresolved multiplets for the eight ferrocenyl protons at low temperature. These appear in two groups of four signals each, presumably sig-



Scheme 7. R = Me, Ph, 4-*t*BuSC$_6$H$_4$O.

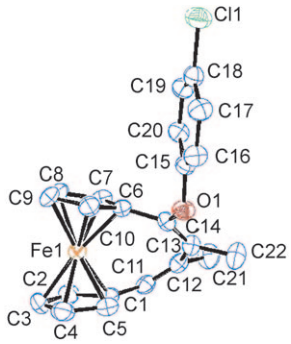


Figure 1. Structure of **2** in the crystal.[43] Hydrogen atoms omitted for clarity. Selected bond lengths [pm], bond angles [°], and torsional angles [°]: Fe–C1 202.2(4), Fe–C2 205.9(4), Fe–C3 208.8(4), Fe–C4 207.5(4), Fe–C5 202.7(4), Fe–C6 201.1(3), Fe–C7 203.8(4), Fe–C8 206.3(4), Fe–C9 208.4(3), Fe–C10 205.4(4), C1–C2 144.6(5), C1–C5 142.9(6), C1–C11 147.1(5), C2–C3 142.4(7), C3–C4 142.7(7), C4–C5 142.5(6), C6–C7 143.2(5), C6–C10 144.7(5), C6–C14 147.3(5), C7–C8 142.7(6), C8–C9 142.2(6), C9–C10 142.5(5), C11–C12 133.8(6), C12–C13 1.498(5), C12–C21 151.3(7), C13–C14 1.343(5), C13–C22 1.508(6), C14–O1 1.414(4); C1-C11-C12 130.1(4), C11-C12-C13 127.0(3), C11-C12-C21 118.3(4), C13-C12-C21 114.7(3), C12-C13-C14 125.9(3), C12-C13-C22 114.9(3), C14-C13-C22 119.2(3), C6-C14-C13 130.5(3), C6-C14-O1 112.8(3), C13-C14-O1 116.3(3); C2-C1-C11-C12 137.4(4), C5-C1-C11-C12 −35.0(7), C1-C11-C12-C13 4.4(7), C14-C13-C12-C11 −50.6(6), C22-C13-C12-C21 −49.0(5), C12-C13-C14-C6 1.6(6).

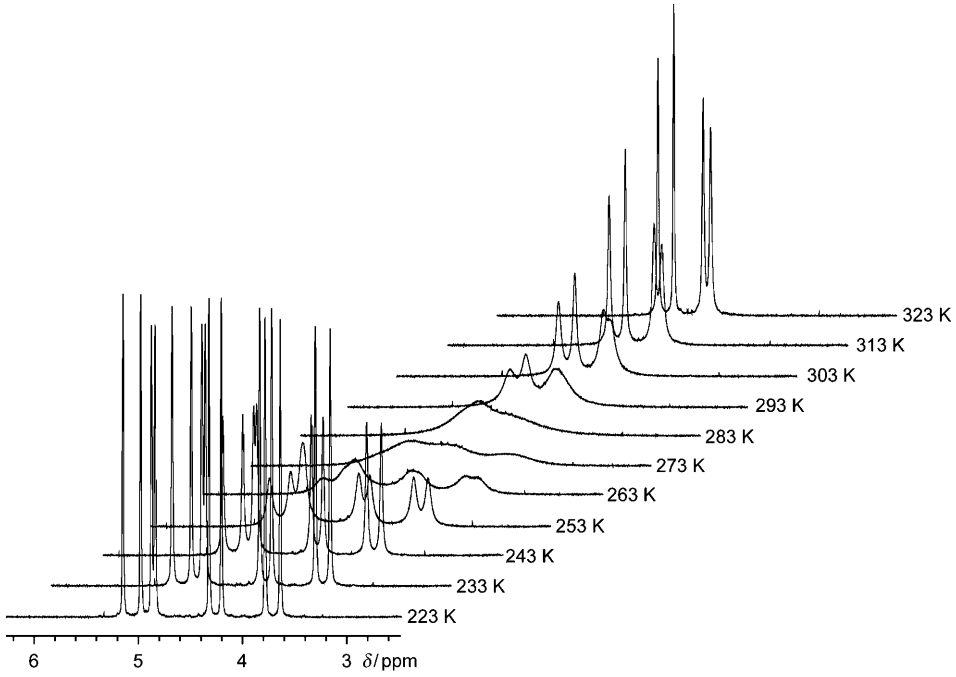


Figure 2. Ferrocenyl ^{1}H NMR ($CDCl_3$, 400 MHz) spectra signals of **25** between 223 and 323 K.

nals for 2-H, 5-H, 2′-H, and 5′-H in one group and for 3-H, 4-H, 3′-H, and 4′-H in the other. At elevated temperature the resulting four broad singlets likewise form two groups of two signals each. The coalescence temperature was determined to be 283 K. The chemical-shift differences, $\Delta\nu$, are not equal for each pair of signals and range between 309 and 490 Hz at 400 MHz. Application of the approximation solution[44] results in an estimated free energy of activation ($\Delta G^{\neq}$) of 53–54 kJ mol^{-1}. In addition, dynamic NMR spectroscopy simulations (DNMR) were performed for the determination of rate constants and the corresponding free energies of activation as a function of temperature.[45] The calculated values of $\Delta G^{\neq}$ are between 51 and 54 kJ mol^{-1} over the whole temperature range, and the change in entropy of the process is at 30 J K^{-1} mol^{-1}. An activation energy (E_a) of 62 kJ mol^{-1} was obtained by fitting the rate constants according to the Arrhenius equation.

The signals in the ^{13}C NMR spectra are much less resolved than in the corresponding ^{1}H NMR spectra, even at 223 and 323 K. However, the coalescence temperature is the same with 283 K. At low temperature, seven signals are observed for the eight ferrocenyl *C*H, one with double intensity. The two quaternary ferrocenyl carbon atoms do not show any dynamic behavior.

With the structure of **2** in mind (Figure 1) we assign the dynamic process observed to a rotation around the C12–C13 bond, which occurs along with a rotation around the cyclopentadienyl–iron–cyclopentadienyl axis. This process represents a racemization of the chiral conformation as given in Figure 3. The process appears to be highly dependent on the substitution pattern at C12 and C13. Clearly, the methyl groups at **2**–**15** do not significantly prevent the racemization from occurring. The presence of one of the somewhat larger aryl substituents in **26**–**29** raises the activation energy of the process as indicated by some line broadening of the ^{1}H NMR signals of the ferrocenyl protons at 298 K. When both C12 and C13 bear aryl substituents the activation energy of the process is sufficiently high as to allow for coalescence phenomena to be observed at temperatures accessible by routine NMR spectroscopy measurements. That the quaternary ferrocenyl carbon atoms do not show coalescence is due to the fact that in contrast to the ferrocenyl CH groups each of these is unique.

Conclusion

Attempts originally directed toward alkyne metathesis reactions of 1,1′-di(1-propynyl)ferrocene (**1**) under Mortreux reaction conditions led to an unanticipated transannular phenol addition, which takes place in the presence as well as

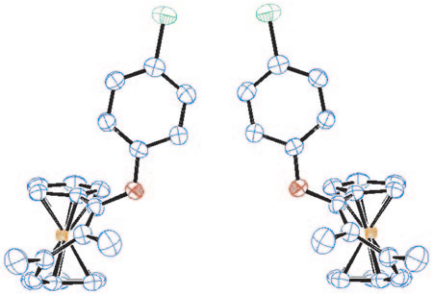


Figure 3. Side view of **2** in the crystal with the C12–C13 bond in front. The Figure shows the enantiomeric conformations and was generated from the structure in Figure 1 to clarify the dynamic racemization process causing the coalescence phenomenon observed for **24** and **25**.

in the absence of hexacarbonylmolybdenum and results in the formation of phenoxy[4]ferrocenophanedienes. The reaction is also observed with a thiophenol or with a weak acid such as acetic acid, whereas treatment with a strong acid (F_3CCO_2H) causes formation of 1,1′-dipropanoylferrocene. Corresponding [4]ferrocenophanes with aryl substituents show NMR spectroscopic coalescence in solution, presumably resulting from conformational switches of the helically distorted molecules. An addition of a phenol to an alkynylruthenocene was earlier reported by Sato et al.[33] and might be explained by a metallocene-stabilized vinyl cation intermediate. Under basic reaction conditions [4]ferrocenophanone formation is observed similarly to chemistry reported earlier by Pudelski and Callstrom.[31,32]

Experimental Section

All reactions were performed using Schlenk techniques with nitrogen as the inert gas. All glassware was heated at <0.1 mbar with a heat gun prior to use to remove any oxygen or water. Tetrahydrofuran (THF) was dried with sodium/potassium alloy/benzophenone and distilled. Anhydrous chlorobenzene was purchased from Fluka and used as delivered. *N*,*N*-Dimethylformamide (DMF) was obtained from an M. Braun Solvent Purification System. Diisopropylamine was dried over CaH_2 and distilled. Compound **1** was prepared according to a published procedure.[22]

^{1}H and ^{13}C NMR spectra were obtained with Bruker AVS 200 (^{1}H: 200 MHz) and AVS 400 (^{1}H: 400 MHz; ^{13}C: 100.6 MHz) instruments. Chemical shifts refer to $\delta_{TMS}=0$ ppm or to residual solvent signals. Signal multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Primary, secondary, tertiary, and quaternary carbon atom signals were identified as such by means of attached proton test (APT) and distortionless enhancement by polarization transfer (DEPT) techniques. IR spectra were obtained with Perkin–Elmer instruments FTIR 580 and 1170. Signal characteristics are abbreviated as s (strong), m (medium), w (weak), and br (broad). Mass spectra were obtained with a Micromass LC-TOF-MS instrument with a LockSpray source and direct injection with an ionization potential of 70 eV. Analytical TLC was performed with Merck 60F-254 silica gel thin-layer plates. Column chromatography was carried out with J.T. Baker silica gel (60 μm) as the stationary phase.

General procedure (GP): A solution of **1**[22] (262 mg, 1.0 mmol) and the phenol (1.2 mmol) in chlorobenzene (20 mL) was heated at reflux (oil bath 135 °C) for 15 h. After cooling to 25 °C the solvent was removed at reduced pressure. The residue was purified by column chromatography (hexane/dichloromethane 4:1) to give the product as a dark red solid. The product was recrystallized from hexane/dichloromethane.

Compound 2: GP, **1** (262 mg, 1.0 mmol), 4-chlorophenol (154 mg, 1.2 mmol); **2** (331 mg, 0.8 mmol, 84 %) as dark red crystals. M.p. 180.5–182.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.85$ (s, 3H; C(OAr)=CCH$_3$), 1.95 (d, $J=1.4$ Hz, 3H; CH=C-CH$_3$), 4.12+4.16 (AA′BB′, 2×2H; H$_{Fc}$), 4.42 (m, 4H; H$_{Fc}$), 6.13 (q, $^4J=1.0$ Hz, 1H; CH=C), 6.71 (m, 2H; H$_{Ar}$), 7.12 ppm (m, 2H; H$_{Ar}$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.7$ (C-(OAr)=CCH$_3$), 25.1 (CH=CCH$_3$), 70.1 (C$_{Fc}$H), 70.2 (C$_{Fc}$H), 70.5 (C$_{Fc}$H), 70.7 (C$_{Fc}$H), 74.5 (C$_{Fc}$C), 77.8 (C$_{Fc}$C), 117.1 (C$_{Ar}$H), 124.2 (CH=C), 124.3 (C(OAr)=CCH$_3$), 126.2 (CH=C), 129.3 (C$_{Ar}$H), 136.5 (C$_{qAr}$), 145.3 (C-(OAr)=CCH$_3$), 155.1 ppm (OC$_{qAr}$); IR (ATR): $\tilde{\nu}=3050$ (w), 2916 (w), 1640 (m), 1589 (m), 1486 (s), 1445 (m), 1281 (w), 1261 (w), 1243 (s), 1163 (m), 1124 (m), 1086 (m), 1069 (s), 1026 (s), 1009 (m), 910 (w), 846 (m), 821 (s), 803 (s), 721 (w), 666 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 392 (29) [(*M*+2)$^+$]$^+$, 391 (22) [(*M*+1)$^+$], 390 (82) [*M*$^+$], 298 (18) [*M*$^+$−2H], 263 (100) [*M*$^+$−(4-ClC$_6$H$_4$O)], 261 (23) [*M*$^+$−(4-ClC$_6$H$_4$O)−2H], 121 (20) [(Cp-CH=C(OH)-CH$_3$)$^+$]; HRMS: *m*/*z* calcd for $C_{22}H_{19}FeClO$: 390.0474; found: 390.0472; elemental analysis calcd (%) for $C_{22}H_{19}FeClO$: C 67.63, H 4.90; found: C 67.72, H 5.07.

Crystal structure analysis of ***2***:[43] Single crystals of **2** were obtained by crystallization from hexane/dichloromethane (3:1) at 25 °C. $C_{22}H_{19}ClFeO$; $M_r=390.69$ g mol^{-1}; crystal system monoclinic; space group $P2_1/n$; $a=8.544(2)$, $b=10.045(2)$, $c=20.630(6)$ Å; $\alpha=90$, $\beta=96.04(3)$, $\gamma=90°$; $V=1760.7(8)$ Å^3; $Z=4$; $\rho_{calcd}=1.474$ g cm^{-3}; $\mu=1.014$ mm^{-1}; crystal size $0.25\times0.21\times0.19$ mm; $F(000)=808$; STOE IPDS one-axis diffractometer with imaging plate detector; $T=294$ K; Mo$_{K\alpha}$ radiation ($\lambda=0.71073$ Å); θ range 2.71 to 25.76°; reflections collected/unique 21139/3430 (R(int)=0.060); completeness of data $\theta=26.1$ (97.8 %); index ranges $-10\le h\le10$, $-12\le k\le12$, $-25\le l\le25$; empirical absorption correction (multiscan); no extinction correction; direct methods; full-matrix least-squares refinement on F^2; GOF on $F^2=0.964$; $R_1=0.0463$ ($I>2\sigma_I$), $wR_2=0.1175$; R indices (all data) $R_1=0.0690$, $wR_2=0.1259$; final difference electron density 0.352 and −0.500 e Å^{-3}.

Compound 3: GP, **1** (262 mg, 1.0 mmol), 3-chlorophenol (154 mg, 1.2 mmol); **3** (359 mg, 0.9 mmol, 92 %) as dark red crystals. M.p. 140.7–142.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.85$ (s, 3H; C(OAr)=CCH$_3$), 1.96 (d, $^4J=1.4$ Hz, 3H; CH=C-CH$_3$), 4.14+4.17 (AA′BB′, 2×2H; H$_{Fc}$), 4.42+4.44 (AA′BB′, 2×2H; H$_{Fc}$), 6.14 (q, $^4J=1.0$ Hz, 1H; CH=C), 6.67 (m, 1H; H$_{Ar}$), 6.80 (m, 1H; H$_{Ar}$), 6.86 (m, 1H; H$_{Ar}$), 7.08 ppm (m, 1H; H$_{Ar}$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.8$ (C(OAr)=CCH$_3$), 25.0 (CH=CCH$_3$), 70.1 (C$_{Fc}$H), 70.2 (C$_{Fc}$H), 70.5 (C$_{Fc}$H), 70.7 (C$_{Fc}$H), 74.4 (C$_{Fc}$C), 77.8 (C$_{Fc}$C), 114.2 (C$_{Ar}$H), 116.3 (C$_{Ar}$H), 121.5 (C$_{Ar}$H), 124.3 (CH=C), 124.5 (C(OAr)=CCH$_3$), 130.1 (C$_{Ar}$H), 134.8 (C$_{qAr}$), 136.5 (CH=C), 145.1 (C(OAr)=CCH$_3$), 157.3 ppm (OC$_{qAr}$); IR (ATR): $\tilde{\nu}=3100$ (w), 2916 (w), 1589 (s), 1473 (s), 1453 (m), 1432 (m), 1304 (s), 1269 (s), 1224 (s), 1119 (s), 1061 (s), 1024 (s), 994 (m), 915 (s), 881 (m), 846 (s), 820 (m), 803 (s), 780 (s), 691 (m), 681 cm^{-1} (s); MS (70 eV): *m*/*z* (%): 392 (60) [(*M*+2)$^+$], 391 (48) [(*M*+1)$^+$], 390 (100) [*M*$^+$], 264 (23), 263 (85) [*M*$^+$−(3-ClC$_6$H$_4$O)], 261 (20) [*M*$^+$−(3-ClC$_6$H$_4$O)−2H], 121 (26) [(Cp-CH=C(OH)-CH$_3$)$^+$], 56 (18) [Fe$^+$]; HRMS: *m*/*z* calcd for $C_{22}H_{19}FeClO$: 390.0474; found: 390.0475; elemental analysis calcd (%) for $C_{22}H_{19}FeClO$: C 67.63, H 4.90; found: C 67.50, H 5.04.

Compound 4: GP, **1** (262 mg, 1.0 mmol), 2,4-dichlorophenol (196 mg, 1.2 mmol); **4** (420 mg, 1.0 mmol, 99 %) as a dark red solid. M.p. 102.7–103.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.87$ (s, 3H; C(OAr)=CCH$_3$), 1.96 (d, $^4J=1.4$ Hz, 3H; CH=C-CH$_3$), 4.13+4.18 (AA′BB′, 2×2H; H$_{Fc}$), 4.46 (m, 4H; H$_{Fc}$), 6.14 (q, $^4J=1.0$ Hz, 1H; CH=C), 6.47 (d, 1H; H$_{Ar}$), 6.95 (m, 1H; H$_{Ar}$), 7.32 ppm (d, 1H; H$_{Ar}$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.7$ (C(OAr)=CCH$_3$), 25.1 (CH=CCH$_3$), 70.2 (C$_{Fc}$H), 70.3 (C$_{Fc}$H), 70.4 (C$_{Fc}$H), 70.7 (C$_{Fc}$H), 74.1 (C$_{Fc}$C), 77.7 (C$_{Fc}$C), 116.5 (C$_{Ar}$H), 123.4 (C(OAr)=CCH$_3$), 124.5 (CH=C), 124.7 (C$_{Ar}$), 126.3 (CH=C), 127.5 (C$_{Ar}$H), 129.9 (C$_{Ar}$H), 136.2 (C$_{qAr}$), 145.6 (C(OAr)=CCH$_3$), 150.9 ppm (OC$_{qAr}$); IR (ATR): $\tilde{\nu}=3070$ (w), 2915 (w), 1647 (w), 1582 (w), 1472 (s), 1445 (m), 1389 (w), 1250 (s), 1233 (s), 1113 (m), 1098 (s), 1064 (s), 1024 (s), 927 (w), 907 (w), 856 (s), 841 (s), 804 (s), 753 (s), 709 (m), 695 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 426 (51) [(*M*+2)$^+$], 425 (22) [(*M*+1)$^+$], 424 (69) [*M*$^+$], 277 (20), 264 (32), 263 (100) [*M*$^+$

$-(C_6H_3Cl_2O)]$, 261 (26) $[M^+-(C_6H_3Cl_2O)-2H]$, 205 (18), 191 (21), 121 (22) $[(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+]$, 56 (15) $[Fe^+]$; HRMS: *m/z* calcd for $C_{22}H_{18}FeCl_2O$: 424.0084; found: 424.0085; elemental analysis calcd (%) for $C_{22}H_{18}FeCl_2O$: C 62.15, H 4.27; found: C 62.30, H 4.35.

Compound 5: GP, **1** (262 mg, 1.0 mmol), 2-fluorophenol (134 mg, 1.2 mmol); **5** (280 mg, 0.8 mmol, 75%) as dark red crystals. M.p. 143.5–144.9°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.91$ (s, 3H; C(OAr)=CH_3), 1.97 (d, $^4J=0.7$ Hz, 3H; CH=C-CH_3), 4.12+4.17 (AA′BB′, 2×2H; H_{Fc}), 4.46+4.49 (AA′BB′, 2×2H; H_{Fc}), 6.14 (br s, 1H; CH=C), 6.62 (m, 1H; H_{Ar}), 6.83 (m, 2H; H_{Ar}), 7.05 ppm (m, 1H; H_{Ar}); NOE: irradiation at $\delta=$ 1.97 ppm (d, $J=0.7$ Hz, 3H; CH=C-CH_3) causes 14% increase at $\delta=$ 6.14 ppm (br s, 1H; CH=C); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.7$ (C-(OAr)=C*C*H$_3$), 25.1 (CH=C*C*H$_3$), 70.1 (C_{Fc}H), 70.2 (C_{Fc}H), 70.3 (C_{Fc}H), 70.7 (C_{Fc}H), 74.4 (*C*$_{Fc}$C), 77.7 (*C*$_{Fc}$C), 116.4 (C_{Ar}H), 116.9 (C_{Ar}H), 121.7 (C_{Ar}H), 124.1 (*C*H=C), 124.4 (C_{Ar}H), 136.4 (C(OAr)=*C*CH$_3$), 144.4 (CH=*C*), 145.5 (C_{Ar}), 151.3 (*C*(OAr)=CCH$_3$), 153.7 ppm (OC_{Ar}); IR (ATR): $\tilde{\nu}=3090$ (w), 2921 (m), 2854 (w), 1608 (m), 1497 (s), 1454 (m), 1254 (s), 1197 (s), 1119 (s), 1101 (s), 1055 (s), 1023 (s), 926 (m), 907 (s), 857 (m), 834 (s), 800 (s), 777 (m), 746 (s), 720 (w), 700 cm^{-1} (w); MS (70 eV): *m/z* (%): 375 (36) $[(M+1)^+]$, 374 (99) $[M^+]$, 282 (28), 277 (17), 264 (26), 263 (100) $[M^+-(2\text{-}FC_6H_4O)]$, 261 (27) $[M^+-(2\text{-}FC_6H_4O)-2H]$, 205 (20), 203 (18), 191 (18), 121 (24) $[(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+]$; HRMS: *m/z* calcd for $C_{22}H_{19}FeFO$: 374.0769; found: 374.0770; elemental analysis calcd (%) for $C_{22}H_{19}FeFO$: C 70.61, H 5.12; found: C 70.66, H 5.30.

Compound 6: GP, **1** (262 mg, 1.0 mmol), 4-iodophenol (266 mmol, 1.2 mmol); **6** (481 mg, 1.0 mmol, 99%) as dark red crystals. M.p. 187.5–188.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.84$ (s, 3H; C(OAr)=CCH_3), 1.95 (d, $^4J=1.7$ Hz, 3H; CH=C-CH_3), 4.13+4.16 (AA′BB′, 2×2H; H_{Fc}), 4.42 (q, 4H; H_{Fc}), 6.13 (d, $J=1.0$ Hz, 1H; CH=C), 6.57 (m, 2H; H_{Ar}), 7.44 ppm (m, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.7$ (C-(OAr)=C*C*H$_3$), 25.1 (CH=C*C*H$_3$), 70.1 (C_{Fc}H), 70.2 (C_{Fc}H), 70.5 (C_{Fc}H), 70.7 (C_{Fc}H), 74.4 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 83.6 (C_{qAr}), 118.2 (C_{Ar}H), 124.2 (*C*H=C), 124.3 (C(OAr)=*C*CH$_3$), 136.5 (CH=*C*), 138.2 (C_{Ar}H), 145.2 (*C*-(OAr)=CCH$_3$), 156.5 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}=3010$ (w), 2920 (w), 1793 (w), 1637 (w), 1582 (m), 1480 (s), 1456 (w), 1374 (w), 1275 (w), 1259 (w), 1227 (s), 1169 (m), 1120 (m), 1055 (m), 1024 (m), 1003 (m), 999 (w), 871 (w), 845 (w), 816 (s), 804 (s), 662 cm^{-1} (w); MS (70 eV): *m/z* (%): 483 (13) $[(M+1)^+]$, 482 (47) $[M^+]$, 360 (13), 263 (45) $[M^+-(4\text{-}IC_6H_4O)]$, 261 (11) $[M^+-(4\text{-}IC_6H_4O)-2H]$, 224 (100) $[(Fc\text{-}CCCH_3)^+]$, 158 (15), 121 (24) $[(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+]$, 56 (27) $[Fe^+]$; HRMS: *m/z* calcd for $C_{22}H_{19}FeIO$: 481.9830; found: 481.9833; elemental analysis calcd (%) for $C_{22}H_{19}FeIO$: C 54.81, H 3.97; found: C 54.98, H 4.07.

Compound 7: GP, **1** (262 mg, 1.0 mmol), 4-nitrophenol (167 mg, 1.2 mmol); **7** (365 mg, 0.9 mmol, 91%) as dark red crystals. M.p. 188.6–189.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.84$ (s, 3H; C(OAr)=CCH_3), 1.96 (d, $^4J=1.4$ Hz, 3H; CH=C-CH_3), 4.15+4.19 (AA′BB′, 2×2H; H_{Fc}), 4.44 (m, 4H; H_{Fc}), 6.16 (q, $^4J=1.0$ Hz, 1H; CH=C), 6.86 (m, 2H; H_{Ar}), 8.09 ppm (m, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.8$ (C-(OAr)=C*C*H$_3$), 25.0 (CH=C*C*H$_3$), 70.3 (C_{Fc}H), 70.4 (C_{Fc}H), 70.5 (C_{Fc}H), 70.8 (C_{Fc}H), 74.0 (*C*$_{Fc}$C), 77.7 (*C*$_{Fc}$C), 115.9 (C_{Ar}H), 124.6 (*C*H=C), 125.0 (C_{qAr}), 125.8 (C_{Ar}H), 136.0 (C(OAr)=*C*CH$_3$), 142.0 (CH=*C*), 145.2 (*C*-(OAr)=CCH$_3$), 161.8 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}=3073$ (w), 2925 (w), 1644 (w), 1604 (m), 1587 (s), 1512 (s), 1488 (s), 1444 (m), 1375 (w), 1338 (s), 1253 (s), 1161 (s), 1110 (s), 1057 (s), 1025 (s), 954 (w), 927 (w), 908 (m), 862 (m), 847 (s), 835 (s), 798 (s), 752 (s), 716 (s), 686 (m), 663 cm^{-1} (m); MS (70 eV): *m/z* (%): 402 (35) $[(M+1)^+]$, 401 (100) $[M^+]$, 264 (20), 263 (94) $[M^+-(p\text{-}O_2NC_6H_4O)]$, 261 (20) $[M^+-(p\text{-}O_2NC_6H_4O)-2H]$, 205 (21), 203 (19), 121 (24) $[(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+]$; HRMS: *m/z* calcd for $C_{22}H_{19}FeNO_3$: 401.0714; found 401.0712; elemental analysis calcd (%) for $C_{22}H_{19}FeNO_3$: C 65.86, H 4.77, N 3.49; found: C 65.74, H 4.82, N 3.52.

Compound 8: GP, **1** (262 mg, 1.0 mmol), phenol (113 mg, 1.2 mmol); **8** (203 mg, 0.6 mmol, 57%) as dark red crystals. M.p. 167.6–168.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.87$ (s, 3H; C(OAr)=CCH_3), 1.97 (d, $^4J=1.7$ Hz, 3H; CH=C-CH_3), 4.12+4.17 (AA′BB′, 2×2H; H_{Fc}), 4.45 (m, 4H; H_{Fc}), 6.14 (q, $^4J=1.4$ Hz, 1H; CH=C), 6.81 (m, 2H; H_{Ar}), 6.87 (m, 1H; H_{Ar}), 7.17 ppm (m, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=$ 15.8 (C(OAr)=C*C*H$_3$), 25.1 (CH=C*C*H$_3$), 70.0 (C_{Fc}H), 70.1 (C_{Fc}H), 70.6 (C_{Fc}H), 70.7 (C_{Fc}H), 74.9 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 115.8 (C_{Ar}H), 121.2 (*C*H=C), 124.0 (C(OAr)=*C*CH$_3$), 124.1 (C_{Ar}H), 129.4 (C_{Ar}H), 136.7 (CH=*C*), 145.3 (*C*(OAr)=CCH$_3$), 156.5 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}=3073$ (w), 2925 (w), 1644 (w), 1604 (m), 1587 (s), 1512 (s), 1488 (s), 1444 (m), 1375 (w), 1338 (s), 1253 (s), 1161 (s), 1110 (s), 1057 (s), 1025 (s), 9154 (w), 927 (w), 908 (m), 862 (m), 847 (s), 835 (s), 798 (s), 752 (s), 716 (s), 686 (m), 663 cm^{-1} (m); MS (70 eV): *m/z* (%): 357 (25) $[(M+1)^+]$, 356 (100) $[M^+]$, 264 (30), 263 (69) $[M^+-(C_6H_5O)]$, 261 (15) $[M^+-(C_6H_5O)-2H]$, 205 (10), 203 (11), 121 (16) $[(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+]$, 77 (13), 56 (11); HRMS: *m/z* calcd for $C_{22}H_{20}FeO$: 356.0864; found: 356.0865; elemental analysis calcd (%) for $C_{22}H_{20}FeO$: C 74.17, H 5.66; found: C 73.98, H 5.74.

Compound 9: GP, **1** (262 mg, 1.0 mmol), 4-aminophenol (130 mg, 1.2 mmol); **9** (320 mg, 0.9 mmol, 86%) as dark red crystals. M.p. 170.7–172.2°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.88$ (s, 3H; C(OAr)=CCH_3), 1.97 (d, $^4J=1.7$ Hz, 3H; CH=C-CH_3), 2.21 (s, 3H; ArCH_3), 4.11+4.16 (AA′BB′, 2×2H; H_{Fc}), 4.44 (m, 4H; H_{Fc}), 6.13 (q, $^4J=1.4$ Hz, 2H; C*H*=C), 6.69 (d, 2H; H_{Ar}), 6.97 ppm (d, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.7$ (C(OAr)=C*C*H$_3$), 20.5 (Ar*C*H$_3$), 25.1 (CH=C*C*H$_3$), 70.0 (C_{Fc}H), 70.1 (C_{Fc}H), 70.6 (C_{Fc}H), 70.7 (C_{Fc}H), 74.9 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 115.6 (C_{Ar}H), 123.8 (C(OAr)=*C*CH$_3$), 124.1 (*C*H=C), 129.8 (C_{Ar}H), 130.4 (C_{qAr}), 136.8 (CH=*C*), 145.4 (*C*(OAr)=CCH$_3$), 154.4 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}=3005$ (w), 2970 (w), 1607 (m), 1504 (s), 1435 (m), 1261 (m), 1238 (m), 1218 (s), 1165 (m), 1123 (s), 1104 (m), 1066 (s), 1057 (s), 1023 (s), 928 (w), 906 (m), 862 (m), 831 (s), 806 (s), 800 (s), 756 (w), 716 cm^{-1} (m); MS (70 eV): *m/z* (%): 371 (23) $[(M+1)^+]$, 370 (85) $[M^+]$, 278 (28), 277 (17), 264 (20), 263 (100) $[M^+-(4\text{-}CH_3C_6H_4O)]$, 261 (22) $[M^+-(4\text{-}CH_3C_6H_4O)-2H]$, 121 (21) $[(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+]$, 86 (48), 84 (73), 56 (10) $[Fe^+]$; HRMS: *m/z* calcd for $C_{23}H_{22}FeO$: 370.1020; found: 370.1018; elemental analysis calcd (%) for $C_{23}H_{22}FeO$: C 74.61 H 5.99; found: C 74.41, H 5.98.

Compound 10: GP, **1** (262 mg, 1.0 mmol), 4-methoxyphenol (148 mg, 1.2 mmol); **10** (344 mg, 0.9 mmol, 89%) as dark red crystals. M.p. 138.8–139.7°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.89$ (s, 3H; C(OAr)=CCH_3), 1.96 (d, $^4J=1.4$ Hz, 3H; CH=C-CH_3), 3.69 (s, 3H; OCH_3), 4.11+4.16 (AA′BB′, 2×2H; H_{Fc}), 4.43 (m, 4H; H_{Fc}), 6.12 (q, $^4J=1.0$ Hz, 1H; CH=C), 6.72 ppm (s, 4H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.7$ (C-(OAr)=C*C*H$_3$), 25.1 (CH=C*C*H$_3$), 55.6 (O*C*H$_3$), 69.9 (C_{Fc}H), 70.0 (C_{Fc}H), 70.6 (C_{Fc}H), 70.7 (C_{Fc}H), 74.8 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 114.6 (C_{Ar}H), 116.6 (C_{Ar}H), 123.7 (C(OAr)=*C*CH$_3$), 124.0 (*C*H=C), 136.8 (CH=*C*), 145.7 (C_{qAr}), 150.5 (*C*(OAr)=CCH$_3$), 154.1 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}=3090$ (w), 2939 (w), 1637 (w), 1501 (s), 1451 (m), 1377 (w), 1266 (w), 1207 (s), 1180 (m), 1127 (m), 1103 (w), 1070 (m), 1039 (s), 1025 (s), 910 (w), 857 (w), 845 (m), 822 (s), 801 (s), 753 (s), 712 (m), 700 cm^{-1} (m); MS (70 eV): *m/z* (%): 387 (18) $[(M+1)^+]$, 386 (67) $[M^+]$, 294 (22), 291 (26), 278 (23), 277 (98) $[M^+-4\text{-}H_3C{=}C_4H_4+2]$, 264 (24), 263 (100) $[M^+-(4\text{-}H_3COC_6H_4O)]$, 261 (19) $[M^+-(4\text{-}H_3COC_6H_4O)-2H]$, 203 (18), 121 (25) $[(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+]$, 56 (16) $[Fe^+]$; HRMS: *m/z* calcd for $C_{23}H_{22}FeO_2$: 386.0969; found: 386.0968; elemental analysis calcd (%) for $C_{23}H_{22}FeO_2$: C 71.52, H 5.74; found: C 71.36, H 5.78.

Compound 11: GP, **1** (262 mg, 1.0 mmol), 2-methoxyphenol (148 mg, 1.2 mmol); **11** (322 mg, 0.8 mmol, 84%) as dark red crystals. M.p. 83.6–84.8°C; ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=1.90$ (s, 3H; C(OAr)=CCH_3), 1.96 (d, $^4J=1.4$ Hz, 3H; CH=C-CH_3), 3.95 (s, 3H; OCH_3), 4.10+4.14 (AA′BB′, 2×2H; H_{Fc}), 4.50 (m, 4H; H_{Fc}), 6.12 (q, $^4J=1.0$ Hz, 1H; CH=C), 6.54 (m, 1H; C_{Ar}), 6.70 (m, 1H; C_{Ar}), 6.82 ppm (m, 2H; C_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta=15.8$ (C(OAr)=C*C*H$_3$), 25.2 (CH=C*C*H$_3$), 56.0 (O*C*H$_3$), 70.0 (C_{Fc}H), 70.1 (C_{Fc}H), 70.3 (C_{Fc}H), 70.6 (C_{Fc}H), 75.0 (*C*$_{Fc}$C), 77.8 (*C*$_{Fc}$C), 111.9 (C_{Ar}H), 115.5 (C_{Ar}H), 120.7 (C_{Ar}H), 121.7 (C_{Ar}H), 124.1 (C(OAr)=*C*CH$_3$), 124.2 (*C*H=C), 136.6 (C_{qAr}), 145.6 (CH=*C*), 146.0 (*C*(OAr)=CCH$_3$), 149.3 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}=3095$ (w), 2970 (w), 1587 (w), 1495 (m), 1451 (m), 1373 (w), 1247 (s), 1210 (m), 1177 (w), 1127 (s), 1117 (s), 1067 (m), 1046 (w), 1026 (w), 951 (s), 910 (m), 862 (w), 839 (w), 815 (m), 778 (w), 734 cm^{-1} (s); MS (70 eV): *m/z* (%): 387 (30) $[(M+1)^+]$, 386 (92) $[M^+]$, 294 (9), 277 (14), 264 (28), 263 (100) $[M^+-(2\text{-}H_3OC_6H_4O)]$, 261 (22) $[M^+-(2\text{-}H_3OC_6H_4O)-2H]$, 205 (19), 203 (17), 121 (24) $[(Cp\text{-}CH{=}C(OH)\text{-}CH_3)^+]$, 86 (53), 84 (80), 56 (15) $[Fe^+]$; HRMS: *m/z* calcd for $C_{23}H_{22}FeO_2$: 386.0969; found: 386.0967;

elemental analysis calcd (%) for $C_{23}H_{22}FeO_2$: C 71.52, H 5.74; found: C 71.33, H 5.86.

Compound 12: GP, **1** (262 mg, 1.0 mmol), 2-(isopropoxy)phenol (183 mg, 1.2 mmol); **12** (162 mg, 0.4 mmol, 39%) as a dark red solid. M.p. 86.6–87.9°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.45 (d, ^3J = 6.1 Hz, 6H; OCH-(CH_3)$_2$), 1.90 (s, 3H; C(OAr)=CCH_3), 1.96 (d, ^4J = 1.4 Hz, 3H; CH=CCH_3), 4.09+4.16 (AA′BB′, 2×2H; H_{Fc}), 4.46+4.50 (AA′BB′, 2×2H; H_{Fc}), 4.59 (hept, 1H; OCH(CH$_3$)$_2$), 6.12 (q, J = 1.4 Hz, 1H; CH=C), 6.57 (m, 1H; H_{Ar}), 6.72 (m, 1H; H_{Ar}), 6.80 (m, 1H; H_{Ar}), 6.88 ppm (m, 1H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.9 (C(OAr)=CCH_3), 22.4 (OCH(CH_3)$_2$), 25.2 (CH=CCH_3), 69.9 (C_{Fc}H), 70.0 (C_{Fc}H), 70.4 (C_{Fc}H), 70.6 (C_{Fc}H), 72.0 (OCH(CH$_3$)$_2$), 75.1 (C_{Fc}C), 77.8 (C_{Fc}C), 116.2 (C_{Ar}H), 117.1 (C_{Ar}H), 121.2 (C_{Ar}H), 121.7 (C_{Ar}H), 123.5 (C(OAr)=CCH$_3$), 124.0 (CH=C), 136.8 (C_{qAr}), 146.2 (CH=C), 147.2 (C(OAr)=CCH$_3$), 147.7 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}$ = 3080 (w), 2973 (m), 1588 (m), 1495 (s), 1451 (m), 1284 (w), 1247 (s), 1211 (s), 1277 (m), 1127 (s), 1117 (s), 1067 (m), 1046 (m), 1026 (m), 951 (s), 910 (m), 863 (m), 815 (m), 779 (w), 746 (s), 734 cm^{-1} (s); MS (70 eV): m/z (%): 415 (23) [(M+1)$^+$], 414 (75) [M^+], 264 (35), 263 (100) [M^+−(2-iPrOC$_6$H$_4$O)], 261 (22) [M^+−(2-iPrO-C$_6$H$_4$O)−2H], 205 (18), 203 (17), 191 (11), 121 (18) [(Cp-CH=C(OH)-CH$_3$)$^+$], 56 (9) [Fe$^+$]; HRMS: m/z calcd for $C_{25}H_{26}FeO_2$: 414.1482; found: 414.1481; elemental analysis calcd (%) for $C_{25}H_{26}FeO_2$: C 72.47, H 6.33; found: C 72.21, H 6.39.

Compound 13: GP, **1** (262 mg, 1.0 mmol), 4-aminophenol (132 mg, 1.2 mmol); **13** (242 mg, 0.7 mmol, 65%) as dark red crystals. M.p. 185.9–186.9°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.89 (s, 3H; C(OAr)=CH_3), 1.96 (d, J = 1.4 Hz, 3H; CH=CCH$_3$), 3.33 (s, 2H; NH_2), 4.10+4.14 (AA′BB′, 2×2H; H_{Fc}), 4.42 (m, 4H; H_{Fc}), 6.11 (q, ^4J = 1.0 Hz, 1H; CH=C), 6.61 ppm (m, 4H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 15.7 (C-(OAr)=CCH_3), 25.2 (CH=CCH_3), 69.9 (C_{Fc}H), 70.0 (C_{Fc}H), 70.6 (C_{Fc}H), 70.7 (C_{Fc}H), 74.9 (C_{Fc}C), 77.9 (C_{Fc}C), 116.2 (C_{Ar}H), 116.8 (C_{Ar}H), 123.4 (C(OAr)=CCH_3), 123.9 (CH=C), 136.9 (C_{qAr}), 140.3 (CH=C), 145.2 (C-(OAr)=CCH$_3$), 149.4 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}$ = 3070 (w), 2920 (w), 1748 (w), 1610 (m), 1505 (s), 1437 (m), 1372 (w), 1260 (m), 1214 (s), 1164 (w), 1125 (m), 1069 (m), 1055 (m), 1024 (m), 927 (w), 908 (m), 861 (m), 829 (s), 801 (s), 770 (w), 721 cm^{-1} (w); MS (70 eV): m/z (%): 372 (12) [(M+1)$^+$], 371 (43) [M^+], 277 (13), 264 (24), 263 (100) [M^+−(4-H$_2$NC$_6$H$_4$O)], 261 (20) [M^+−(4-H$_2$NC$_6$H$_4$O)−2H], 205 (12), 203 (12), 121 (16) [(Cp-CH=C(OH)-CH$_3$)$^+$], 57 (20), 56 (14) [Fe$^+$]; HRMS: m/z calcd for $C_{22}H_{21}FeNO$: 371.0973; found: 371.0972; elemental analysis calcd (%) for $C_{22}H_{21}FeNO$: C 71.17, H 5.70, N 3.77; found: C 70.80, H 5.75, N 3.83.

Compound 14: GP, **1** (262 mg, 1.0 mmol), 2-bromothiophenol (227 mg, 1.2 mmol); **14** (140 mg, 0.3 mmol, 31%) as a dark red solid. M.p. 107.7–109.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.01 (d, ^4J = 1.4 Hz, 3H; C=C-CH$_3$), 2.19 (s, 3H; C(SAr)=CCH_3), 4.08+4.16 (AA′BB′, 2×2H; H_{Fc}), 4.35+4.41 (AA′BB′, 2×2H; H_{Fc}), 6.15 (q, ^4J = 1.4 Hz, 1H; CH=C), 6.84 (m, 2H; H_{Ar}), 7.01 (m, 1H; H_{Ar}), 7.42 ppm (m, 1H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 22.7 (C(SAr)=CCH_3), 24.9 (C=CCH_3), 69.9 (C_{Fc}H), 70.4 (C_{Fc}H), 70.8 (C_{Fc}H), 72.5 (C_{Fc}H), 76.6 (C_{Fc}C), 79.7 (C_{Fc}C), 122.0 (C(OAr)=CCH$_3$), 124.9 (CH=C), 126.0 (C_{Ar}H), 127.2 (C_{Ar}H), 127.9 (C_{qAr}), 129.0 (C_{Ar}H), 132.6 (C_AH$_r$), 137.4 (CH=C), 137.6 (C(SAr)=CCH$_3$), 143.8 ppm (SC_{qAr}); IR (ATR): $\tilde{\nu}$ = 3090 (w), 2962 (w), 1629 (w), 1572 (m), 1445 (s), 1425 (m), 1367 (w), 1325 (w), 1241 (m), 1103 (w), 1050 (m), 1035 (m), 1017 (s), 945 (w), 888 (w), 853 (s), 841 (s), 821 (m), 796 (s), 752 (s), 712 (s), 684 (w), 660 cm^{-1} (w); MS (70 eV): m/z (%): 452 (34) [M(^{81}Br)$^+$], 451 (9) [(M+1)$^+$], 450 (36) [M(^{79}Br)$^+$], 264 (24), 263 (100) [M^+−(2-BrC$_6$H$_4$S)], 261 (14) [M^+−(2-BrC$_6$H$_4$S)−2H], 205 (8), 192 (13), 191 (18), 189 (10), 165 (12), 108 (12), 57 (17), 56 (16) [Fe$^+$]; HRMS: m/z calcd for $C_{22}H_{19}FeBrS$: 449.9740; found: 449.9737; elemental analysis calcd (%) for $C_{22}H_{19}FeBrS$: C 58.56, H 4.24; found: C 58.63, H 4.38.

Compound 15: GP, **1** (262 mg, 1.0 mmol), acetic acid (72 mg, 1.2 mmol); **15** (150 mg, 0.4 mmol, 44%) as a dark red solid. M.p. 106.6–108.0°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.75 (s, 3H; C(OAc)=CCH_3), 1.91 (d, ^4J = 1.4 Hz, 3H; CH=CCH_3), 2.19 (s, 3H; OCOCH$_3$), 4.16 (m, 4H; H_{Fc}), 4.45 (m, 4H; H_{Fc}), 6.10 ppm (q, ^4J = 1.0 Hz, 1H; CH=C); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 16.2 (C(OAc)=CCH_3), 20.8 (C=CCH_3), 24.7 (OCOCH_3), 69.5 (C_{Fc}H), 70.0 (C_{Fc}H), 70.2 (C_{Fc}H), 70.5 (C_{Fc}H), 75.5 (C_{Fc}C), 77.6 (C_{Fc}C), 124.2 (C(OAc)=CCH$_3$), 124.5 (CH=C), 135.9 (CH=C), 143.5 (C(OAc)=CCH$_3$), 168.5 ppm (OCOCH$_3$); IR (ATR): $\tilde{\nu}$ = 3080 (w), 2922 (m), 2854 (w), 2077 (w), 1750 (s), 1648 (w), 1437 (m), 1369 (s), 1202 (s), 1113 (s), 1060 (s), 1022 (s), 918 (m), 859 (m), 836 (m), 806 (s), 745 (w), 727 (m), 660 cm^{-1} (m); MS (70 eV): m/z (%): 323 (17) [(M+1)$^+$], 322 (92) [M^+], 281 (20), 280 (100) [M^+−H$_2$C=C=O], 279 (30), 251 (25), 129 (16), 121 (16) [(Cp-CH=C(OH)-CH$_3$)$^+$], 86 (13), 84 (20), 56 (13) [Fe$^+$]; HRMS: m/z calcd for $C_{18}H_{18}FeO_2$: 322.0656; found: 322.0655; elemental analysis calcd (%) for $C_{18}H_{18}FeO_2$: C 67.10, H 5.63; found: C 67.02, H 5.81.

Compound 16:[29] Compound **1** (262 mg, 1.0 mmol) and trifluoroacetic acid (0.054 mL, 1.2 mmol) in chlorobenzene (20 mL) were heated at reflux (oil bath 132°C) for 15 h. After cooling to 25°C the solvent was removed at reduced pressure. The residue was purified by column chromatography (silica gel deactivated with Et_3N 5% in petroleum ether; petroleum ether/ethyl acetate 4:1) to give **16** (172 mg, 0.58 mmol, 58%) as dark red crystals. M.p. 47.8–49.2°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.17 (t, ^3J = 7.2 Hz, 6H; CH_3), 2.66 (q, ^3J = 7.2 Hz, 4H; CH_2), 4.46+4.76 ppm (AA′BB′, 2×4H; H_{Fc}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 8.1 (COCH$_2$CH_3), 32.9 (COCH_2CH$_3$), 70.4 (C_{Fc}H), 73.2 (C_{Fc}H), 80.2 (C_{Fc}C), 204.0 ppm (CO); IR (ATR): $\tilde{\nu}$ = 3081 (w), 2967 (w), 2935 (m), 2910 (w), 2876 (w), 1668 (s), 1456 (s), 1414 (s), 1398 (m), 1372 (s), 1337 (s), 1240 (s), 1101 (s), 1048 (s), 1025 (s), 964 (m), 884 (m), 863 (m), 850 (w), 826 (m), 807 cm^{-1} (s); MS (70 eV): m/z (%): 299 (47) [(M+1)$^+$], 298 (100) [M^+], 296 (16), 213 (62) [FcCO$^+$], 186 (18) [FcH$^+$], 185 (27), 129 (26), 121 (66) [(Cp-CH=C(OH)-CH$_3$)$^+$], 120 (19), 94 (13), 56 (34) [Fe$^+$]; HRMS: m/z calcd for $C_{16}H_{18}FeO_2$: 298.0656; found: 298.0658; elemental analysis calcd (%) for $C_{16}H_{18}FeO_2$: C 64.45, H 6.09; found: C 64.18, H 6.15.

Compound 17: a) Compound **1** (262 mg, 1.0 mmol) and 4-chlorophenol (648 mg, 5.0 mmol) in DMF (20 mL) were heated at reflux (oil bath 157°C) for 15 h. After cooling to 25°C the solvent was removed at reduced pressure. The residue was purified by column chromatography (hexane/dichloromethane 4:1) to give **17** (160 mg, 0.6 mmol, 57%) as light yellow crystals.

b) Compound **1** (131 mg, 0.5 mmol) and 4-iodophenol (266 mg, 1.2 mmol) in DMF (3 mL) were subjected to microwave irradiation (157°C, 300 W, 5 min ramp, 30 min hold, CEM Discover). After cooling to 25°C the solvent was removed at reduced pressure. The residue was purified by column chromatography (hexane/dichloromethane 4:1) to give **17** (53 mg, 0.2 mmol, 38%).

c) Compound **1** (131 mg, 0.5 mmol) and H_2O (45 mg, 2.5 mmol) in DMF (10 mL) were heated at reflux (oil bath 157°C) for 15 h. After cooling to 25°C the solvent was removed at reduced pressure. The residue was purified by column chromatography (hexane/dichloromethane 4:1) to give **17** (101 mg, 0.4 mmol, 72%).

d) Compound **2** (149 mg, 0.38 mmol) was dissolved in THF (10 mL) and water (2 mL). 2N HCl (2 mL) was added. The solution was stirred at 65°C for 12 h. After cooling to 25°C, water (10 mL) was added, and the solution was extracted with dichloromethane (3×10 mL). The organic layer was washed with 1N NaOH (25 mL) to remove 4-chlorophenol, and was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography (20×1 cm, petroleum ether/ethyl acetate 4:1) to give **17** (42 mg, 0.15 mmol, 40%).

M.p. 154.0–154.9°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.32 (d, ^3J = 7.2 Hz, 3H; CHCH_3), 2.01 (d, ^4J = 1.7 Hz, 3H; C=C-CH$_3$), 4.12 (m, 2H; H_{Fc}), 4.19 (m, 1H; H_{Fc}), 4.36 (m, 1H; H_{Fc}), 4.42 (m, 1H; H_{Fc}), 4.52 (m, 1H; H_{Fc}), 4.57 (m, 1H; H_{Fc}), 4.62 (q, ^3J = 6.8 Hz, 1H; CHCH$_3$), 4.74 (m, 1H; H_{Fc}), 5.74 ppm (q, ^4J = 1.5 Hz, 1H; CH=C); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 13.8 (CHCH_3), 21.9 (C=CCH_3), 44.9 ($CHCH_3$), 67.1 (C_{Fc}H), 68.8 (C_{Fc}H), 69.3 (C_{Fc}H), 69.5 (C_{Fc}H), 69.9 (C_{Fc}H), 72.4 (C_{Fc}H), 72.7 (C_{Fc}H), 74.3 (C_{Fc}H), 77.3 (C_{Fc}C), 87.7 (C_{Fc}C), 117.9 (CH=C), 144.8 (CH=C), 209.7 ppm (CO); IR (ATR): $\tilde{\nu}$ = 3080 (w), 2917 (w), 1666 (s, C=O), 1644 (s), 1456 (w), 1440 (s), 1374 (s), 1286 (w), 1232 (s), 1212 (w), 1167 (w), 1049 (s), 1028 (s), 987 (w), 970 (m), 930 (m), 879 (m), 862 (m), 847 (m), 819 (s), 743 cm^{-1} (w); MS (70 eV): m/z (%): 281 (31) [(M+1)$^+$], 280 (100) [M^+], 252 (57) [M^+−CO], 251 (20), 237 (38) [M^+−CO−CH$_3$],

186 (24), 121 (21), 115 (18), 56 (37) [Fe^+]; HRMS: *m/z* calcd for $C_{16}H_{16}FeO$: 280.0551; found: 280.0552; elemental analysis calcd (%) for $C_{16}H_{16}FeO$: C 68.60, H 5.76; found: C 68.59, H 5.88.

Compound 19: A solution of 1,1′-diiodoferrocene[46] (253 mg, 0.6 mmol) and 1-(*tert*-butylsulfanyl)-4-ethynylbenzene[47] (263 mg, 1.4 mmol) was degassed by five freeze–pump–thaw cycles and put under nitrogen. After addition of $[PdCl_2(PPh_3)_2]$ (12 mg, 0.02 mmol, 3 mol%) and CuI (4 mg, 0.02 mmol, 2 mol%) the solution was heated at reflux (oil bath 95°C) for 18 h. After being left to cool to 25°C, the solution was filtered through a 5 cm-thick layer of silica gel, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (20×2 cm, hexane/dichloromethane 2:1) to give **19** (97 mg, 0.2 mmol, 33%) as an orange solid. M.p. 162.2–163.0°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.32 (s, 18H; $C(CH_3)_3$), 4.36+4.58 (AA′BB′, 2×4H; $C_{Fc}H$), 7.44 ppm (m, 8H; $C_{Ar}H$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=31.0 ($C(CH_3)_3$), 46.3 ($C(CH_3)_3$), 66.7 ($C_{Fc}C$), 71.1 ($C_{Fc}H$), 73.1 ($C_{Fc}H$), 86.1 (*C*C), 89.0 (C*C*), 124.1 (C_{qAr}), 131.3 ($C_{Ar}H$), 132.5 (C_{qAr}), 137.2 ppm ($C_{Ar}H$); IR (ATR): $\tilde{\nu}$=3104 (w), 2966 (m), 2924 (m), 2859 (m), 2223 (m, C≡C), 1681 (w), 1588 (m), 1489 (s), 1466 (s), 1392 (m), 1365 (s), 1293 (w), 1261 (w), 1205 (w), 1164 (s), 1100 (s), 1039 (w), 1028 (s), 1017 (s), 917 (s), 854 (w), 841 (s), 820 (s), 724 cm^{-1} (m); MS (70 eV): *m/z* (%): 564 (18) [$(M+2)^+$], 563 (39) [$(M+1)^+$], 562 (100) [M^+], 450 (34), 449 (19), 448 (17), 57 (62), 56 (14) [Fe^+]; HRMS: *m/z* calcd for $C_{34}H_{34}FeS_2$: 562.1451; found: 562.1453; elemental analysis calcd (%) for $C_{34}H_{34}FeS_2$: C 72.58, H 6.09; found: C 72.61, H 6.46.

Compound 21: At −78°C, freshly prepared lithium diisopropylamide (6.4 mmol, 1.1 equiv) in THF (10 mL) was added to **20**[6] (1.954 g, 5.8 mmol) and iodomethane (1.47 mL, 23.3 mmol) in THF (40 mL). The mixture was stirred for 1 h at this temperature and then for 1 h at 25°C. Water (30 mL) was added, and the mixture was extracted with dichloromethane (3×30 mL). The collected organic layers were washed with brine and dried over $MgSO_4$. After filtration and solvent removal at reduced pressure a dark red liquid was obtained, which was purified by column chromatography (30×3 cm, petroleum ether/dichloromethane 4:1). Compound **21** (1.39 g, 3.9 mmol, 66%) was obtained as a dark red solid. M.p. 52.2–53.5°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.96 (s, 3H; CCH_3), 4.15+4.18 (AA′BB′, 2×2H; H_{Fc}), 4.32+4.40 ppm (AA′BB′, 2×2H; H_{Fc}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=4.5 (CH_3), 41.1 ($C_{Fc}I$), 68.8 ($C_{Fc}C$), 70.7 ($C_{Fc}H$), 71.4 ($C_{Fc}H$), 73.6 ($C_{Fc}H$), 76.0 ($C_{Fc}H$), 76.1 (C*C*CH_3), 83.1 ppm (*C*CCH_3); IR (ATR): $\tilde{\nu}$=3097 (m), 2909 (m), 2216 (w, C≡C), 1674 (m), 1463 (m), 1401 (m), 1377 (m), 1343 (m), 1263 (m), 1207 (w), 1137 (m), 1063 (m), 1025 (s), 1009 (m), 980 (m), 877 (m), 861 (s), 842 (s), 822 cm^{-1} (s); MS (70 eV): *m/z* (%): 351 (29) [$(M+1)^+$], 350 (100) [M^+], 348 (11), 183 (11), 167 (27), 166 (25), 165 (42), 152 (16), 77 (15), 56 (21) [Fe^+]; HRMS: *m/z* calcd for $C_{13}H_{11}FeI$: 349.9255; found: 349.9257; elemental analysis calcd (%) for $C_{13}H_{11}FeI$: C 44.61, H 3.17; found: C 44.59, H 3.02.

Compound 22: $[PdCl_2(PPh_3)_2]$ (21 mg, 0.03 mmol, 3 mol%) and CuI (6 mg, 0.03 mmol, 3 mol%) were added to a solution of **21** (350 mg, 1.0 mmol) and phenylethyne (123 mg, 1.2 mmol) in diisopropylamine (15 mL). The mixture was stirred at reflux (oil bath 90°C) for 20 h. After cooling to 25°C the mixture was filtered through a 3 cm-thick layer of silica, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (20×2 cm, petroleum ether/dichloromethane 4:1). Compound **22** (275 mg, 0.8 mmol, 85%) was obtained as red shiny crystals. M.p. 115.0–116.8°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.85 (s, 3H; CH_3), 4.22+4.28 (AA′BB′, 2×2H; H_{Fc}), 4.40+4.50 (AA′BB′, 2×2H; H_{Fc}), 7.31 (m, 3H; H_{Ar}), 7.34 ppm (m, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=4.4 (CH_3), 66.7 ($C_{Fc}C$), 68.4 ($C_{Fc}C$), 70.2 ($C_{Fc}H$), 70.7 ($C_{Fc}H$), 72.5 ($C_{Fc}H$), 72.7 ($C_{Fc}H$), 76.1 (CC), 82.8 (CC), 86.4 (CC), 87.4 (CC), 124.0 (C_{qAr}), 127.6 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 131.4 ppm ($C_{Ar}H$); IR (ATR): $\tilde{\nu}$=3094 (w), 2923 (w), 2362 (w, C≡C), 2208 (w, C≡C), 1598 (w), 1497 (m), 1459 (w), 1440 (w), 1377 (w), 1296 (w), 1260 (w), 1205 (w), 1162 (w), 1071 (w), 1053 (w), 1028 (s), 981 (w), 919 (m), 898 (w), 875 (w), 861 (w), 844 (w), 821 (s), 756 (s), 690 cm^{-1} (s); MS (70 eV): *m/z* (%): 325 (25) [$(M+1)^+$], 324 (100) [M^+], 165 (17), 56 (9) [Fe^+]; HRMS: *m/z* calcd for $C_{21}H_{16}Fe$: 324.0601; found: 324.0600; elemental analysis calcd (%) for $C_{21}H_{16}Fe$: C 77.80, H 4.97; found: C 77.70, H 4.99.

Compound 23: $[PdCl_2(PPh_3)_2]$ (28 mg, 0.04 mmol, 3 mol%) and CuI (8 mg, 0.04 mmol, 3 mol%) were added to a solution of **21** (420 mg, 1.2 mmol) and 1-(*tert*-butylsulfanyl)-4-ethynylbenzene[48] (274 mg, 1.4 mmol) in diisopropylamine (15 mL). The mixture was stirred at reflux (oil bath 90°C) for 48 h. After cooling to 25°C the mixture was filtered through a 3 cm-thick layer of silica, which was then washed with dichloromethane. After solvent removal at reduced pressure the residue was purified by column chromatography (20×2 cm, petroleum ether/dichloromethane 4:1). Compound **23** (230 mg, 0.6 mmol, 46%) was obtained as a red solid. M.p. 99.0–100.7°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=1.29 (s, 9H; $C(CH_3)_3$), 1.83 (s, 3H; $CCCH_3$), 4.21+4.28 (AA′BB′, 2×2H; H_{Fc}), 4.39+4.50 (AA′BB′, 2×2H; H_{Fc}), 7.46 ppm (m, 4H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ=4.4 ($C(CH_3)_3$), 30.9 (CC*C*H_3), 46.3 (*C*-$(CH_3)_3$), 66.4 ($C_{Fc}C$), 68.6 ($C_{Fc}C$), 70.2 ($C_{Fc}H$), 70.8 ($C_{Fc}H$), 72.5 ($C_{Fc}H$), 72.7 ($C_{Fc}H$), 76.0 (CC), 82.8 (CC), 85.9 (CC), 89.2 (CC), 124.4 (C_{Ar}), 131.2 ($C_{Ar}H$), 132.4 (C_{qAr}), 137.2 ppm ($C_{Ar}H$); IR (ATR): $\tilde{\nu}$=3095 (w), 2958 (m), 2230 (m, C≡C), 2207 (m, C≡C), 1668 (w), 1589 (m), 1490 (m), 1456 (m), 1394 (m), 1363 (s), 1298 (w), 1263 (w), 1207 (w), 1164 (s), 1096 (m), 1065 (w), 1032 (s), 1014 (m), 923 (m), 875 (m), 831 (s), 820 (s), 724 (w), 666 cm^{-1} (w); MS (70 eV): *m/z* (%): 413 (30) [$(M+1)^+$], 412 (100) [M^+], 357 (20), 356 (77), 355 (13), 265 (12), 57 (40) [Fe^+]; HRMS: *m/z* calcd for $C_{25}H_{24}FeS$: 412.0948; found: 412.095; elemental analysis calcd (%) for $C_{25}H_{24}FeS$: C 72.82, H 5.87; found: C 72.89, H 6.07.

Compound 24: GP, **18** (193 mg, 0.5 mmol),[30] 4-chlorophenol (78 mg, 0.6 mmol); **24** (153 mg, 0.3 mmol, 59%) as a red solid. M.p. 245°C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ=4.26 (br, 4H; H_{Fc}), 4.60+4.74 (AA′BB′, 2×2H; H_{Fc}), 6.80 (s, 1H; CH=C), 6.88 (m, 2H; H_{Ar}), 7.10 (m, 4H; H_{Ar}), 7.22 (m, 6H; H_{Ar}), 7.37 ppm (m, 2H; H_{Ar}); ^{1}H NMR ($CDCl_3$, 400 MHz, −50°C): δ=3.62 (brs; H_{Fc}), 3.77 (brs; H_{Fc}), 4.21 (brs; H_{Fc}), 4.31 (brs; H_{Fc}), 4.80 (brs; H_{Fc}), 4.84 (brs; H_{Fc}), 4.95 (brs; H_{Fc}), 5.14 (brs; H_{Fc}), 6.83 (s, 1H; CH=C), 6.91 (m, 2H; H_{Ar}), 7.11 (m, 4H; H_{Ar}), 7.18 (m, 6H; H_{Ar}), 7.39 ppm (m, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25°C): δ=70.5 ($C_{Fc}H$), 70.8 ($C_{Fc}C$), 71.0 ($C_{Fc}H$), 73.5 ($C_{Fc}H$), 77.1 ($C_{Fc}C$), 77.2 ($C_{Fc}H$), 118.0 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 126.7 ($C_{Ar}H$), 126.8 ($C_{Ar}C$), 126.9 ($C_{Ar}H$), 127.4 ($C_{Ar}C$), 127.8 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 128.3 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 130.8 (*C*H=C), 138.7 (C(OAr)=*C*), 141.1 ($C_{Ar}C$), 143.1 (CH=*C*), 149.3 (*C*(OAr)=C), 156.2 ppm (OC_{qAr}); ^{13}C NMR ($CDCl_3$, 100.6 MHz, −50°C): δ=67.2 ($C_{Fc}H$), 67.7 ($C_{Fc}H$), 68.0 ($C_{Fc}H$), 68.5 ($C_{Fc}H$), 72.8 ($C_{Fc}C$), 74.0 ($C_{Fc}H$), 74.4 ($C_{Fc}H$), 75.3 ($C_{Fc}H$), 75.9 ($C_{Fc}H$), 76.6 ($C_{Fc}C$), 117.9 ($C_{Ar}H$), 126.0 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 126.76 ($C_{Ar}C$), 126.86 ($C_{Ar}H$), 126.92 ($C_{Fc}H$), 127.8 ($C_{Ar}C$), 127.9 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 131.1 (*C*H=C), 138.2 (C(OAr)=*C*), 140.2 ($C_{Ar}C$), 142.6 (CH=*C*), 149.1 (*C*(OAr)=C), 155.7 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}$=3020 (w), 2925 (w), 1878 (w), 1623 (m), 1586 (m), 1483 (s), 1444 (m), 1403 (w), 1380 (w), 1328 (w), 1290 (w), 1225 (m), 1214 (s), 1159 (m), 1101 (m), 1085 (s), 1059 (m), 1026 (s), 1008 (m), 931 (w), 911 (w), 899 (m), 869 (m), 843 (w), 830 (s), 810 (s), 762 (s), 723 (s), 698 (s), 673 cm^{-1} (m); MS (70 eV): *m/z* (%): 516 (31) [$M^+(^{37}Cl)$], 515 (30) [$(M+1)^+$], 514 (80) [$M^+(^{35}Cl)$], 388 (30), 387 (100) [$M^+-ClC_6H_4O$], 386 (61), 310 (18), 265 (12), 253 (15), 252 (19), 165 (24), 56 (11) [Fe^+]; HRMS: *m/z* calcd for $C_{32}H_{23}Fe^{35}ClO$: 514.0787; found: 514.0790; elemental analysis calcd (%) for $C_{32}H_{23}ClFeO$: C 74.66, H 4.50; found: C 74.47, H 4.85.

Compound 25: GP, **19** (164 mg, 0.3 mmol), 4-chlorophenol (50 mg, 0.4 mmol); **25** (101 mg, 0.2 mmol, 46%) as a light red solid. M.p. 252°C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ=1.13 (s, 9H; $C(CH_3)_3$), 1.18 (s, 9H; $C(CH_3)_3$), 4.3 (brm, 4H; H_{Fc}), 4.60 (brm, 2H; H_{Fc}), 4.75 (brm, 2H; H_{Fc}), 6.84 (s, 1H; CH=C), 6.86 (m, 2H; H_{Ar}), 7.13 (m, 2H; H_{Ar}), 7.23 (m, 4H; H_{Ar}), 7.28 (m, 2H; H_{Ar}), 7.33 ppm (m, 2H; H_{Ar}); ^{1}H NMR ($CDCl_3$, 400 MHz, −50°C): δ=1.13 (s, 9H; $C(CH_3)_3$), 1.18 (s, 9H; $C(CH_3)_3$), 3.63 (brs, 1H; H_{Fc}), 3.78 (brs, 1H; H_{Fc}), 4.19 (brs, 1H; H_{Fc}), 4.31 (brs, 1H; H_{Fc}), 4.83 (brs, 1H; H_{Fc}), 4.87 (brs, 1H; H_{Fc}), 4.97 (brs, 1H; H_{Fc}), 5.14 (brs, 1H; H_{Fc}), 6.87 (s, 1H; CH=C), 6.89 (m, 2H; H_{Ar}), 7.15 (m, 2H; H_{Ar}), 7.24 (m, 4H; H_{Ar}), 7.30 (m, 2H; H_{Ar}), 7.35 ppm (m, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz, 25°C): δ=30.8 ($C(CH_3)_3$), 30.9 ($C(CH_3)_3$), 45.8 ($C(CH_3)_3$), 45.9 ($C(CH_3)_3$), 71–72.3 (br; 8$C_{Fc}H$), 73.2 ($C_{Fc}C$), 76.7 ($C_{Fc}C$), 118.0 ($C_{Ar}H$), 126.6 ($C_{Ar}H$), 126.9 ($C_{Ar}C$), 127.0

($C_{Ar}C$), 128.4 ($C_{Ar}H$), 129.7 ($C_{Ar}H$), 130.7 (*C*H=C), 131.0 (C(OAr)=*C*), 131.5 ($C_{Ar}H$), 136.9 ($C_{Ar}H$), 137.2 ($C_{Ar}H$), 139.4 (CH=*C*), 140.4 (C_{qAr}), 143.6 (C_{qAr}), 150.3 (*C*(OAr)=C), 156.0 ppm (OC_{qAr}); ^{13}C NMR ($CDCl_3$, 100.6 MHz, −50 °C, C,H COSY): δ = 30.4 (2 C(*C*H$_3$)$_3$), 46.0 (2 *C*(CH$_3$)$_3$), 67.2 ($C_{Fc}H$), 68.0 (2 $C_{Fc}H$), 68.7 ($C_{Fc}H$), 72.4 ($C_{Fc}C$), 74.3 ($C_{Fc}H$), 74.7 ($C_{Fc}H$), 75.5 ($C_{Fc}H$), 76.0 ($C_{Fc}H$), 76.2 ($C_{Fc}C$), 118.0 ($C_{Ar}H$), 126.1 ($C_{Ar}H$), 126.2 ($C_{Ar}C$), 126.7 ($C_{Ar}C$), 128.0 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 129.7 (*C*H=C), 129.8 (C(OAr)=*C*), 132.0 ($C_{Ar}H$), 137.2 ($C_{Ar}H$), 137.4 ($C_{Ar}H$), 139.0 (CH=*C*), 139.4 (C_{qAr}), 143.2 (C_{qAr}), 150.1 (*C*(OAr)=C), 155.4 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}$ = 3020 (w), 2959 (m), 1619 (m), 1588 (m), 1485 (s), 1454 (m), 1392 (w), 1362 (m), 1267 (m), 1255 (m), 1217 (s), 1166 (m), 1102 (m), 1089 (s), 1055 (w), 1039 (m), 1029 (m), 1013 (s), 934 (w), 915 (w), 901 (m), 875 (w), 851 (m), 832 (s), 803 (s), 790 (m), 751 (m), 725 (m), 712 (w), 684 (w), 670 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 692 (51) [M^+(^{37}Cl)], 691 (47) [(M+1)$^+$], 690 (100) [M^+(^{35}Cl)], 563 (14) [M^+ −ClC_6H_4O], 474 (27), 450 (25), 419 (26), 418 (84), 417 (24), 327 (16), 326 (17), 57 (49); HRMS: *m*/*z* calcd for $C_{40}H_{33}FeClOS_2$: 690.1480; found: 690.1263; elemental analysis calcd (%) for $C_{40}H_{39}ClFeOS_2$: C 69.51, H 5.69; found: C 69.66, H 6.00.

Variable-temperature (VT) NMR spectroscopy measurements: First, ^{1}H and ^{13}C NMR spectra of **25** (15 mg mL^{-1}, $CDCl_3$, TMS, Bruker DPX 400 MHz spectrometer) were recorded at 295 K. VT experiments were conducted in the temperature range 223–323 K in 10 K steps. $\Delta G^{\neq}$ was estimated from the coalescence temperature (T_c) and $\Delta\nu$ of the respective resonances: $\Delta G^{\neq}$ (T_c) = RT_c(22.96+ln(T_c/$\Delta\nu$)).[44] For the simulation of NMR spectra the DNMR line-shape tool of the TOPSPIN 2.1 software was used.[45] The simulations were performed in the range of δ = 2.5 to 6 ppm. Two spin systems were defined, one for each ferrocenyl ring (δ = 3.63, 4.19, 4.83, 4.97 ppm and δ = 3.78, 4.31, 4.87, 5.14 ppm). At each temperature the line-broadening factor was estimated from the half width of the olefinic proton at δ = 6.84 ppm (s, 1H). Coupling constants were fitted in the spectrum recorded at 223 K. In the simulations at higher temperatures the coupling constants were set to be constant. At each temperature the rate constant was first approximated. Then the intensities and the chemical shifts were fitted alternately. Finally, a fit was performed on all parameters. All simulated spectra had an overlap of more than 96% with the original spectra.

Compounds 26 and 27: GP, **22** (133 mg, 0.4 mmol), 4-chlorophenol (65 mg, 0.5 mmol); column chromatography (petroleum ether/dichloromethane 4:1): I) R_f = 0.41: **26** (66 mg, 0.15 mmol, 36%) as a red solid; II) R_f = 0.35: **27** (77 mg, 0.17 mmol, 42%) as red crystals.

Compound ***26***: M.p. 152.0–153.5 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.72 (s, 3H; CH_3), 4.16+4.27 (AA′BB′, 2×2H; H_{Fc}), 4.53+4.57 (AA′BB′, 2×2H; H_{Fc}), 6.54 (s, 1H; CH=C), 6.83 (m, 2H; H_{Ar}), 7.18 (m, 2H; H_{Ar}), 7.32 (m, 1H; H_{Ar}), 7.34 ppm (m, 4H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz, DEPT): δ = 17.4 (CH_3), 70.5 ($C_{Fc}H$), 70.8 ($C_{Fc}H$), 71.5 ($C_{Fc}H$), 74.0 ($C_{Fc}C$), 77.2 ($C_{Fc}H$), 77.3 ($C_{Fc}C$), 117.2 ($C_{Ar}H$), 122.8 (C-(OAr)=*C*CH$_3$), 126.4 ($C_{Ar}H$), 126.5 (C_{qAr}), 127.2 ($C_{Ar}H$), 128.5 ($C_{Ar}H$), 128.6 ($C_{Ar}H$), 129.5 (*C*H=C), 142.3 (CH=*C*), 143.3 (C_{qAr}), 148.1 (*C*-(OAr)=CCH$_3$), 157.3 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}$ = 3054 (w), 2922 (w), 2851 (w), 1639 (w), 1590 (s), 1486 (s), 1440 (m), 1375 (w), 1308 (w), 1280 (w), 1260 (m), 1227 (s), 1172 (w), 1157 (m), 1098 (m), 1084 (s), 1052 (m), 1041 (m), 1024 (s), 1009 (m), 959 (w), 920 (w), 897 (m), 867 (m), 839 (w), 821 (s), 808 (s), 776 (s), 724 (s), 700 cm^{-1} (s); MS (70 eV): *m*/*z* (%): 454 (37) [M^+(^{37}Cl)], 453 (31) [(M+1)$^+$], 452 (100) [M^+(^{35}Cl)], 326 (23), 325 (93) [M^+−ClC_6H_4O], 324 (28), 310 (43), 265 (10), 253(11), 252 (14), 165 (11), 56 (8) [Fe$^+$]; HRMS: *m*/*z* calcd for $C_{27}H_{21}Fe^{35}ClO$: 452.0630; found: 452.0628; elemental analysis calcd (%) for $C_{27}H_{21}ClFeO$: C 71.63, H 4.68; found: C 71.51, H 4.62.

Compound ***27***: M.p. 228 °C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.71 (d, ^4J = 1.4 Hz, 3H; CH_3), 4.20 (m, 4H; H_{Fc}), 4.49+4.59 (AA′BB′, 2×2H; H_{Fc}), 6.32 (q, ^4J = 1.4 Hz, 1H; CH=CCH$_3$), 6.75 (m, 2H; H_{Ar}), 7.14 (m, 2H; H_{Ar}), 7.21 (m, 4H; H_{Ar}), 7.24 ppm (m, 1H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 26.1 (CH=*C*CH$_3$), 70.5 ($C_{Fc}H$), 70.6 ($C_{Fc}H$), 70.8 ($C_{Fc}H$), 71.1 ($C_{Fc}H$), 73.8 ($C_{Fc}C$), 77.8 ($C_{Fc}C$), 117.9 ($C_{Ar}H$), 126.2 ($C_{Ar}H$), 126.5 (C(OAr)=*C*Ar), 126.9 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 128.2 ($C_{Ar}H$), 129.4 (*C*H=C), 136.2 (CH=*C*), 139.0 (C_{qAr}), 146.7 (*C*(OAr)=CAr), 156.1 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}$ = 3081 (w), 2946 (w), 1615 (w), 1590 (s), 1485 (s), 1437 (m), 1379 (w), 1316 (w), 1284 (w), 1256 (m), 1228 (s), 1165 (m), 1102 (m), 1088 (s), 1046 (w), 1026 (s), 1007 (m), 975 (w), 915 (m), 876 (w), 852 (m), 825 (s), 804 (s), 760 (s), 744 (w), 723 (w), 700 (s), 667 cm^{-1} (s); MS (70 eV): *m*/*z* (%): 454 (37) [M^+(^{37}Cl)], 453 (31) [(M+1)$^+$], 452 (99) [M^+(^{35}Cl)], 326 (26), 325 (100) [M^+−ClC_6H_4O], 324 (21), 310 (21), 253 (11), 252 (14), 165 (12), 111 (16), 56 (13) [Fe$^+$]; HRMS: *m*/*z* calcd for $C_{27}H_{21}Fe^{35}ClO$: 452.0630; found: 452.0628; elemental analysis calcd (%) for $C_{27}H_{21}ClFeO$: C 71.63, H 4.68; found: C 70.85, H 4.62.

Compounds 28 and 29: GP, **23** (206 mg, 0.5 mmol), 4-chlorophenol (78 mg, 0.6 mmol); column chromatography (petroleum ether/dichloromethane 4:1): I) R_f = 0.31: **28** (126 mg, 0.2 mmol, 47%) as a dark red solid; II) R_f = 0.26: **29** (79 mg, 0.2 mmol, 29%) as dark red crystals.

Compound ***28***: M.p. 152.9–153.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.34 (s, 9H; C(CH$_3$)$_3$), 1.72 (s, 3H; C=CCH$_3$), 4.17+4.28 (AA′BB′, 2× 2H; H_{Fc}), 4.52+4.58 (AA′BB′, 2×2H; H_{Fc}), 6.59 (s, 1H; CH=C), 6.82 (m, 2H; H_{Ar}), 7.19 (m, 2H; H_{Ar}), 7.33 (m, 2H; H_{Ar}), 7.52 ppm (m, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 17.5 (CH=C*C*H$_3$), 31.0 (C-(*C*H$_3$)$_3$), 46.1 (*C*(CH$_3$)$_3$), 70.6 ($C_{Fc}H$), 71.0 ($C_{Fc}H$), 71.5 ($C_{Fc}C$), 71.6 ($C_{Fc}H$), 73.9 ($C_{Fc}C$), 77.2 ($C_{Fc}H$), 117.2 ($C_{Ar}H$), 122.5 (C(OAr)=C_{Ar}), 126.4 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 129.4 ($C_{Ar}C$), 129.5 ($C_{Ar}H$), 131.5 ($C_{Ar}C$), 137.6 (CH=*C*), 141.6 (*C*H=C), 143.7 (C_{qAr}), 148.2 (*C*(OAr)=CAr), 155.1 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}$ = 3094 (w), 2957 (m), 2920 (m), 2856 (m), 1645 (w), 1587 (m), 1483 (s), 1455 (m), 1396 (w), 1363 (m), 1265 (m), 1240 (m), 1223 (s), 1160 (m), 1101 (m), 1085 (s), 1057 (m), 1044 (m), 1026 (m), 1009 (m), 960 (w), 896 (m), 871 (w), 859 (w), 848 (w), 833 (s), 818 (s), 806 (s), 751 (w), 721 (w), 660 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 542 (42) [M^+(^{37}Cl)], 541 (37) [(M+1)$^+$], 540 (100) [M^+(^{35}Cl)], 413 (17) [M^+−ClC_6H_4O], 357 (23), 356 (16), 324 (33), 265 (11), 57 (60), 56 (8) [Fe$^+$]; HRMS: *m*/*z* calcd for $C_{31}H_{29}{}^{35}ClFeOS$: 540.0977; found: 540.0981; elemental analysis calcd (%) for $C_{31}H_{29}ClFeOS$: C 68.83, H 5.40; found: C 69.20, H 5.84.

Compound ***29***: M.p. 184.9–186.2 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.29 (s, 9H; C(CH$_3$)$_3$), 1.70 (d, ^4J = 1.4 Hz, 3H; C=CCH$_3$), 4.20 (m, 4H; H_{Fc}), 4.48+4.58 (AA′BB′, 2×2H; H_{Fc}), 6.33 (q, ^4J = 1.0 Hz, 1H; CH=C), 6.75 (m, 2H; H_{Ar}), 7.16 (m, 4H; H_{Ar}), 7.41 ppm (m, 2H; H_{Ar}); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 26.1 (CH=C*C*H$_3$), 31.0 (C(*C*H$_3$)$_3$), 46.0 (*C*-(CH$_3$)$_3$), 70.6 ($C_{Fc}H$), 70.7 ($C_{Fc}H$), 70.8 ($C_{Fc}H$), 71.1 ($C_{Fc}H$), 73.6 ($C_{Fc}C$), 77.6 ($C_{Fc}C$), 117.9 ($C_{Ar}H$), 126.5 ($C_{Ar}H$), 126.6 (C(OAr)=C_{Ar}), 128.2 ($C_{Ar}H$), 128.9 ($C_{Ar}C$), 129.4 ($C_{Ar}H$), 131.0 ($C_{Ar}C$), 135.9 (CH=*C*), 137.2 (*C*H=C), 139.6 (C_{qAr}), 147.3 (*C*(OAr)=CAr), 156.0 ppm (OC_{qAr}); IR (ATR): $\tilde{\nu}$ = 3095 (w), 2962 (m), 2919 (w), 1617 (w), 1588 (m), 1485 (s), 1447 (m), 1362 (m), 1332 (w), 1296 (w), 1281 (w), 1253 (m), 1227 (s), 1170 (m), 1101 (m), 1086 (s), 1045 (m), 1027 (s), 1010 (s), 977 (m), 913 (m), 849 (m), 821 (s), 805 (s), 738 (w), 702 (m), 669 cm^{-1} (m); MS (70 eV): *m*/*z* (%): 542 (42) [M^+(^{37}Cl)], 541 (38) [(M+1)$^+$], 540 (100) [M^+(^{35}Cl)], 413 (52) [M^+−ClC_6H_4O], 412 (67), 357 (48), 356 (65), 265 (16), 57 (58), 56 (11) [Fe$^+$]; HRMS: *m*/*z* calcd for $C_{31}H_{29}{}^{35}ClFeOS$: 540.0977; found: 540.0982; elemental analysis calcd (%) for $C_{31}H_{29}ClFeOS$: C 68.83, H 5.40; found: C 68.79, H 5.62.

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