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Aerobic Fujiwara–Moritani alkenylation and dienylation of ferrocene

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ABSTRACT

$Pd(OAc)_2$-catalyzed aerobic alkenylation and dienylation of ferrocene with electron-poor olefins and dienes (ethyl acrylate, methyl (*E*)-cinnamate, diethyl fumarate and maleate, ethyl sorbate and sorbic acid) is reported. In the case of acrylate and cinnamate the reaction leads to mixtures of mono- and dialkenylated ferrocenes. In other cases the products of mono alkenylation and dienylation are formed in low yield. The relatively slow (~1 week) reaction takes place in AcOH solutions at room temperature.

1. Introduction

In recent two decades there has been a resurgence of interest in the chemistry of ferrocene and its derivatives due to their growing applications in various branches of science, ranging from materials science (e.g. nonlinear optics) and asymmetric catalysis to analytical chemistry, biochemistry and medicine (bioorganometallic chemistry) [1]. This has stimulated development of simple, efficient and selective methods of functionalization of this readily available metallocene, based mainly on its electrophilic substitution reactions.

Previous work in our laboratory has focused on the search of novel electrophilic reactions of ferrocene, providing direct access to its complex derivatives, available earlier only by more tedious, multistep routes [2]. Continuing this research program we recently focused our attention on the application of Pd(II)-catalyzed reactions for functionalization of ferrocene via C–H bond activation. The Fujiwara–Moritani dehydrogenative arene-alkene coupling [3] seemed especially well-suited for this purpose. This reaction involves attack of a Pd(II) electrophile (e.g. $Pd(OAc)^+$) on the arene followed by deprotonation (arene C–H activation [4]), insertion of the olefin into the Pd–C bond and elimination of Pd(0). The latter species should be reoxidized to Pd(II) to sustain the catalytic cycle.

Surprisingly, up to now only little attention has been payed to a possibility of application of this reaction in the ferrocene chemistry. Early reports describe only a *stoichiometric* coupling of ferrocene with alkenes in the presence of Pd(II) [5]. The coupling products were obtained in modest yields (with respect to Pd) and there were no attempts to make this reaction catalytic.

Herein we report the first *catalytic aerobic* system enabling direct alkenylation and dienylation of ferrocene with electron-poor olefins. The main problem we have encountered in developing of such a system is that oxidants usually used in the Fujiwara–Moritani reaction for the recovery of catalytically active Pd(II) species (e.g. quinones, hydroperoxides, peresters) [6] oxidize ferrocene to the ferrocenium cation. However, it is known that in the in the absence of strong acids ferrocene exhibits remarkable resistance to dioxygen (air) [7]. Therefore, we have decided to use air as the sole oxidant. Unfortunately, the oxidation of Pd(0) by dioxygen is usually inefficient [8] and only a few catalytic systems using only this oxidant have been so far reported. Such systems as waste-free (the sole by-product is water), atom-economic [9] and environmentally friendly are of obvious interest in the context of "green" chemistry [10].

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2. Results and discussion

2.1. Fujiwara–Moritani coupling of ferrocene with ethyl acrylate and methyl-(E)-cinnamate

In most published works on the Fujiwara–Moritani reactions of arenes not containing metallation directing groups a large excess of a liquid arene (benzene, toluene etc.), miscible with the reaction medium was used, facilitating the first step of the reaction. This could not be done in the case of ferrocene, which display only a limited solubility in polar organic solvents (e.g. in acetic acid) often used in this reaction. Therefore, we were constraint to work with the reagents ratios closer to the stoichiometric one. In our first attempts we used electrophilic alkenes-ethyl acrylate (**1a**) and methyl (*E*)-cinnamate (**1b)** because their high reactivity in the Heck and Fujiwara–Moritani reactions is well evidenced.

Pleasingly, we have found that ferrocene reacts in the presence of catalytic amounts of $Pd(OAc)_2$ with these alkenes in aerated AcOH solutions at room temperature but the reaction is rather sluggish (~1 week). Because of a limited solubility of ferrocene in AcOH at the beginning of the reaction it was only partly dissolved and we observed its gradual dissolution and formation of deep red solutions in the course of the reaction. The reaction affords mixtures of mono-alkenylated ferrocenes **2a,b** and bis-alkenylated products **3a**,**b** and **4a**,**b** (Scheme 1, Table 1).

In the absence of air (under argon) ferrocene did not react with **1a,b**. On the other hand, in air at higher temperatures (70–90 °C) a fast deposition of inactive Pd black was observed and reaction stopped giving only trace amounts of the products. This presumably resulted from a faster formation of Pd(0) and its less efficient re-oxidation due to lower solubility of dioxygen in the reaction medium at a higher temperature.

The mono-alkenylated products **2a,b** were easily isolated by column chromatography. Preparative TLC enabled separation of the 1,1′-disubstituted products **3a,b** from their homoannularly substituted isomers **4a,b** (inseparable ~1:0.7 mixture of 1,2- and 1,3-isomers in the case of **4a** and 1,3-isomer in the case of **4b** according to ^{1}H NMR). Interestingly, chromatography afforded also minor fractions (~1%), which, according to their mass spectra, contained tri-substituted ferrocenes. However, we have not observed formation of more substantial amounts of these species even using six-fold excess of alkene and 20 mol% of catalyst.

In all cases the reaction proceeded stereoselectively yielding exclusively *(E)*-isomers. The *(E)*-configuration of **2a** and **3a** was confirmed by large values of the coupling constants between vinylic protons (~16 Hz). For products **2b** and **3b** it has been determined by X-ray diffraction(*vide infra*). It is worth noticing that this configuration agrees with a *syn*-insertion of the olefin into the Pd–C bond in the intermediary FcPdOAc, followed by a *syn*-elimination of HPdOAc [3].

In contrast to acrylates, which are usually very reactive alkene components and were frequently used in the studies of the Mizoroki–Heck and Fujiwara–Moritani reactions, disubstituted alkenes such as cinnamates are less reactive. They usually require harsh reaction conditions and give rise to the formation of mixtures of *E/Z* isomers. In fact, examples of stereoselective Heck reactions with cinnamates are scarce and were developed only recently [11]. Therefore, the observed stereoselectivity of the coupling of ferrocene with methyl (*E*)-cinnamate is worth noticing.

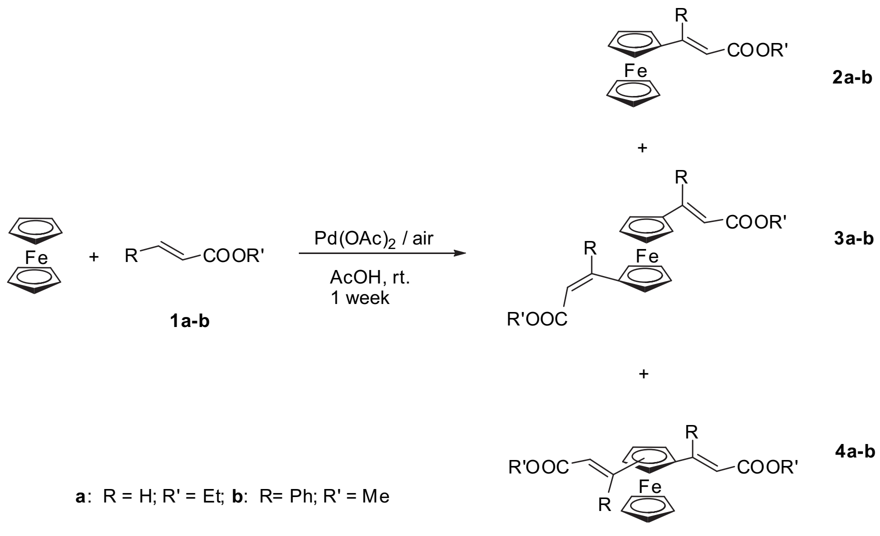
We assume, similarly as Fujiwara and co-workers for stoichiometric Pd-promoted ferrocene alkenylation [5], that reactions under study proceed via electrophilic palladation of ferrocene, olefin insertion and elimination of “HPdOAc”.

Interestingly, disubstituted products were formed in the same yield (20%) at the FcH to acrylate ratio 2:1 and 1:2. On the other hand, the yield of these products increased with the catalyst loading, which may suggest concomittant ferrocene dipalladation occurring before insertion of the olefin into Pd–C bond.

We have also attempted to obtain unsymmetric bis-alkenylated products via reaction of **2a** with methyl (*E*)-cinnamate under aforementioned reaction conditions (5 mol% of catalysts). However, unexpectedly, this attempt failed and **2a** was recovered qualitatively. On the other hand, **2a** does react, with ethyl acrylate to afford a mixture of **3a** and **4a** in ~20% overall yield along with 80% of unreacted starting complex. This indicates that **2a** is less active than ferrocene, which is in keeping with the electron-withdrawing character of the (alkoxycarbonyl)vinyl substituent, and that methyl (*E*)-cinnamate is less reactive that ethyl acrylate.

2.2. Fujiwara–Moritani coupling of ferrocene with diethyl maleate and fumarate

We next studied the reaction of ferrocene with stereoisomeric esters of unsaturated dicarboxylic acids, diethyl maleate **5a** diethyl fumarate **5b** and. Surprisingly, we found that in both cases the same



Scheme 1. Fujiwara–Moritani alkenylation of ferrocene with ethyl acrylate (**1a**) and methyl-(*E*)-cinnamate (**1b**).

Table 1
Fujiwara–Moritani alkenylation and dienylation of ferrocene.

Alkene (diene)	FcH: alkene (FcH: diene)	Pd $(OAc)_2$ % mol[a]	FcH conversion (%)	Products (% Yield)[a,b]
1a	2:1	2.5	59[c]	**2a** (35); **3a** (3);**4a** (3)
1a	2:1	5	64[c]	**2a** (42); **3a** (9);**4a** (3)
1a	1:2	5	49	**2a** (36), **3a** (6),**4a** (2)
1a	1:2	20	98	**2a** (41), **3a** (25),**4a** (16)
1b	1:2	5	67	**2b** (25); **3b** (3),**4b** (4)
1b	1:6	20	100	**2b** (52),**3b** (34),**4b** (10)
5a	1:2	5	10	**6** (8)
5b	1:2	5	10	**6** (8)
7a	1:2	5	10	**8a** (10)
7b	1:2	5	10	**8b** (5)

[a] Based on FcH.
[b] Isolated yields.
[c] Assuming that only a half of the amount of ferrocene can react; Reaction conditions: FcH (1 mmol), ester and catalysts in AcOH (3 ml) stirred in air at RT for 1 week.

mono-alkenylated product **6** was formed as a red oil in modest (10%) yield at the catalyst loading 5 mol% (Scheme 2, Table 1). Its (*E*)-stereochemistry was established from the NOE effects in the ^{1}H NMR spectrum. No formation of disubstituted ferrocenes was observed at the ferrocene:ester ratio 1:2. The compound **6** results from a *syn*-addition of "FcPdOAc" to the thermodynamically more stable ester **5b** [12], followed by a *syn*-elimination of "HPdOAc". Formation of the same compound from **5a** must involve isomerization of the kinetic product having (*Z*)-configuration, presumably via elimination-readdition of the "HPdOAc" species [3] or protonation-deprotonation of the C=C bond facilitated by stabilization of the carbocationic center by the ferrocenyl group [13].

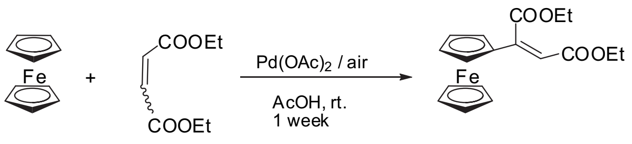
The low yield of **6** is not surprising since it is known that disubstituted alkenes are usually less reactive in the Mizoroki–Heck reaction than their monosubstituted congeners. Moreover, diethyl fumarate and maleate as π-acidic alkenes may form relatively stable complexes with Pd(0) [14] which may hamper its re-oxidation to Pd(II). Some such complexes were used as catalysts in the Mizoroki–Heck reaction.

2.3. Fujiwara–Moritani coupling of ferrocene with ethyl sorbate and sorbic acid

Reaction of ferrocene with ethyl sorbate **7a** and sorbic acid **7b** (molar ratio 1:2) afforded the dienylated ferrocenes **8a** and **8b** (Scheme 3) in modest yields (10% and 5% respectively at the catalyst loading 5 mol%). Therefore, only in the former case the reaction is slightly catalytic (TON = 2).

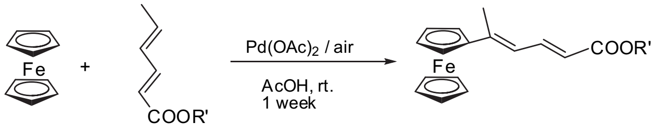
In both cases the reactions were stereoselective and afforded exclusively the (*E,E*)-isomers. This configuration was deduced for **8a** from NOE effects in the ^{1}H NMR spectrum and for **8b** by X-ray diffraction (*vide infra*).

A product closely similar to **8a** (methyl instead of ethyl ester) was obtained in 28% yield in a stoichiometric reaction of methyl sorbate with ferrocenylpalladium chloride [15]. This fact provides further support for the Fujiwara–Moritani mechanism of reactions under study.



5a: (*Z*); **5b** (*E*) **6**

Scheme 2. Fujiwara–Moritani alkenylation of ferrocene with diethyl fumarate or maleate.



7a-b **8a-b**

a: R' = Et; **b**: R' = H

Scheme 3. Fujiwara–Moritani dienylation of ferrocene with ethyl sorbate and sorbic acid.

2.4. Crystal structures of complexes **2b**, **3b** and **8b**

Crystal structures of complexes **2b**, **3b** and **8b** are shown in Figs. 1–3, respectively. The most important geometrical parameters of these molecules are collected in Tables 2 and 3.

There are two independent molecules of **2b**, located in general positions in asymmetric unit. The space group is a polar *Cc* in monoclinic system. On the other hand, **3b**.

Crystallizes in centrosymmetric *P*−1 space group of the triclinic system. One molecule of the complex is present in general position in the asymmetric part of the unit cell. This results in two **3b** molecules per unit cell, related by the inversion center. Two independent molecules are also found for **8b**, which crystallizes in centrosymmetric *P*2(1)/*c* space group. The most significant difference between molecules in the asymmetric unit is that the Cp ring and lateral chain are more coplanar for **8b**-I molecule in comparison to the **8b**-II molecule.

In all compounds the lateral chains are practically planar and coplanar with the adjacent Cp rings revealing extensive π-conjugation. In contrast, the phenyl rings in **2b** and **3b** are nearly perpendicular to the plane of the Cp ligands (deviation from the perpendicularity is larger for **3b**, where the appropriate torsion angle exceeds 100 degrees), suggesting that these rings do not participate in the conjugation. Interestingly, the perpendicular orientation of the phenyl rings may also be retained in solution as indicated by comparison of the electronic spectra of **2a** and **2b** showing only a slight influence of the substitution of the β-vinylic hydrogen by the phenyl group on the electronic transitions in these molecules (364 and 469 nm for **2a** and 369 and 476 nm for **2b** in chloroform).

3. Conclusions

We have elaborated the first catalytic oxidative alkenylation and dienylation of ferrocene with unsaturated esters using air as the sole oxidant ("green oxidation"). Moreover, our system works at room temperature, a condition which is still challenging in Pd-catalyzed C–H bond activation [16]. The reactions described in this work constitute a direct route to mono- and dialkenylated ferrocenes and ferrocenyl-substituted dienes which may be of interest as starting materials in syntheses of more complex ferrocenyl systems. Our current research is focused on improving catalyst activity and selectivity, extending the scope and gaining more detailed information on the mechanism of the reaction.

4. Experimental

4.1. General remarks

All reagents and solvents used in this work are commercially available (Sigma–Aldrich). All reactions and workups were performed in air. Chromatographic separations were carried out on Silica gel 60 (Merck, 230–400 mesh ASTM). NMR spectra were

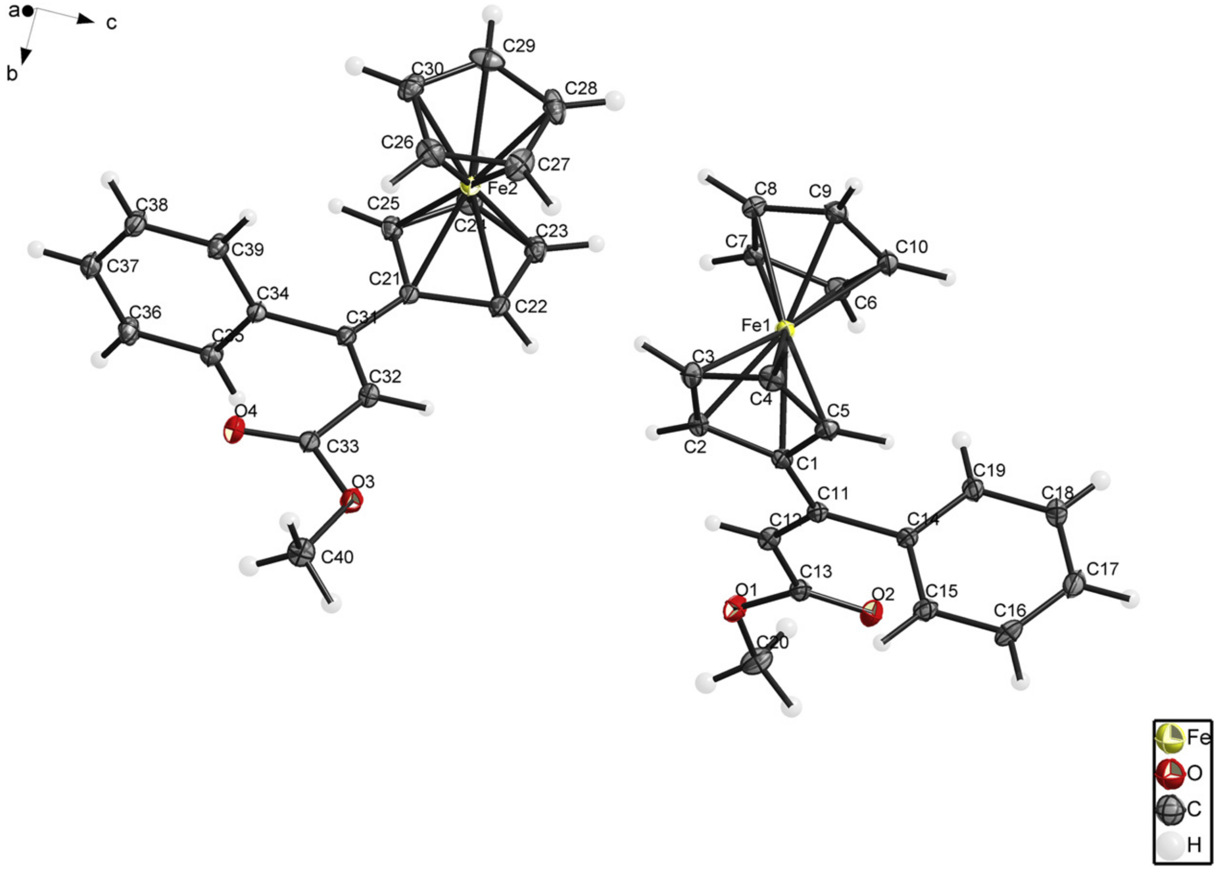


Fig. 1. Molecular structure and labeling of atoms for two crystallographically independent molecules of **2b**.

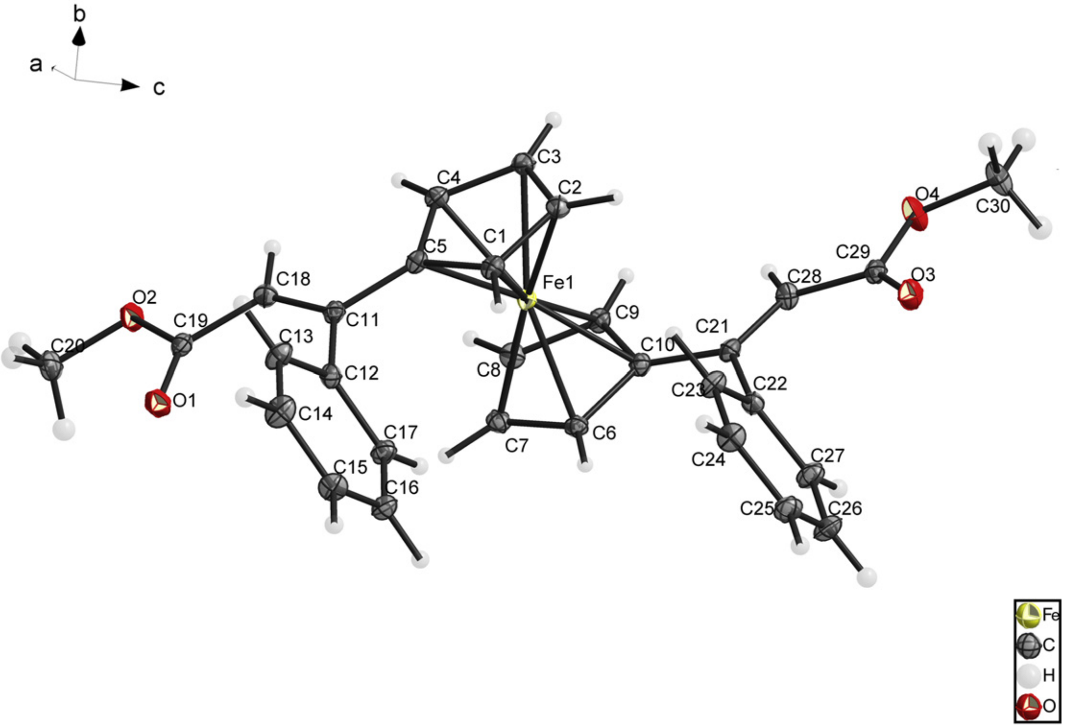


Fig. 2. Molecular structure and labeling of atoms for **3b**.

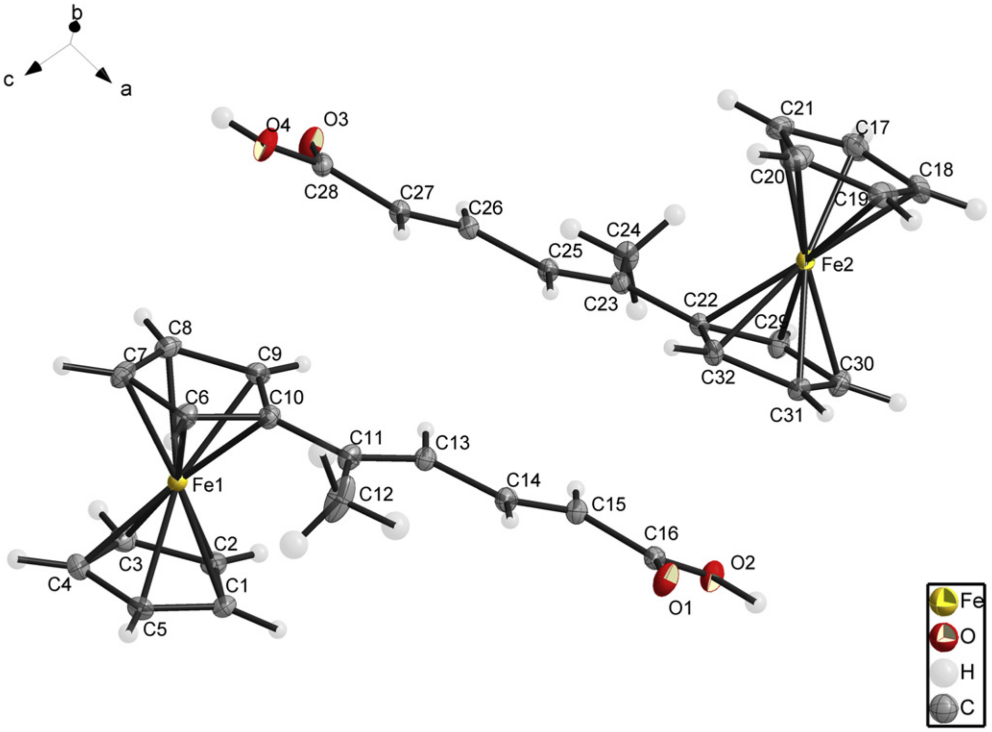


Fig. 3. Molecular structure and labeling of atoms for two crystallographically independent molecules of **8b**.

obtained on a Varian Gemini 200 BB (200 MHz for ^{1}H) and Bruker Avance (600 MHz for ^{1}H) and referenced to internal TMS. IR spectra were obtained on a FT-IR Nexus (Thermo Nicolet) spectrometer. Mass spectra were recorded on a Finnigan MAT 95 spectrometer.

4.2. General procedure

A suspension of ferrocene (186 mg, 1 mmol), alkene or diene and $Pd(OAc)_2$ in acetic acid (3 ml) was stirred in air in a flask equipped with air condenser to minimize evaporation of the solvent at r.t. In the case of reaction with ethyl acrylate and methyl cinnamate a slow dissolution of ferrocene was observed and after 1 week a deeply red solution was obtained (in other cases only a partial dissolution of ferrocene took place). The mixture was poured onto water and extracted several times with dichloromethane. The extracts were washed with aqueous $NaHCO_3$, water, dried over Na_2SO_4 and evaporated to dryness. Column chromatography of the residue on silica gel afforded unreacted ferrocene (eluent: hexane), and products (eluent: hexane-ethyl acetate 9:1). Compounds **3a,b** were separated from **4a,b** (mixtures of regioisomers) by preparative TLC. In the case of the reaction of ferrocene with sorbic acid the solvent was evaporated, the residue dissolved on dichloromethane and extracted with aqueous $NaHCO_3$. The product precipitated on acidification of the aqueous layer with HCl.

Compounds **2a** and **3a** were identified by comparison of their IR and ^{1}H NMR spectra with those of authentic samples [17].

2b: M.p. 113–114 °C. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.43 (m, 2H), 7.29 (m, 3H), 6.29 (s, 1H), 4.41 (t, $J = 1.8$ Hz, 2H), 4.33 (t, $J = 1.8$ Hz, 2H), 4.19 (s, 5H), 3.59 (s, 3H). IR (KBr, cm^{-1}): 1720, 1617, 1595, 1167, 1149. MS (EI, 70 eV): *m/e* 346 (100%, M^+). HRMS: *m/e* 346.0657; Calcd. For $C_{20}H_{18}FeO_2$ *m/e* 346.0656. Elemental analysis: Found: C, 69.46; H, 5.35. $C_{20}H_{18}FeO_2$ requires: C, 69.34. H, 5.24. **3b**: M.p. 173–174 °C. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 7.34 (m, 4H), 7.20 (m, 6H), 6.23 (s, 2H), 4.35 (t, $J = 1.8$ Hz, 4H), 4.27 (t, $J = 1.8$ Hz, 4H), 3.57 (s, 6H). IR (KBr, cm^{-1}): 1718, 1604, 1152. MS (EI, 70 eV): *m/e* 506 (100%, M^+). HRMS: *m/e* 506.1187; Calcd. For $C_{30}H_{26}FeO_4$ *m/e* 506.1181. Elemental analysis: Found: C, 70.90; H, 4.99. $C_{30}H_{26}FeO_4$ requires: C, 71.16. H, 5.18. **4a**: ^{1}H NMR (600 MHz, $CDCl_3$, δ): 1,2-isomer: 7.76 (d, $J = 16.0$ Hz, 2H), 6.14 (d, $J = 16.0$ Hz, 2H), 4. 78 (d, $J = 3.0$ Hz, 2H), 4.64 (t, $J = 3.0$ Hz, 1H), 4.26 (q, $J = 7.2$ Hz, 4H) 4.153 (s, 5H), 1.35 (t, $J = 7.2$ Hz, 6H). 1,3-isomer: 7.52 (d, $J = 16.0$ Hz, 2H), 6.09 (d, $J = 16.0$ Hz, 2H), 4.79 (t, $J = 1.2$ Hz, 1H), 4. 69 (d, $J = 1.2$ Hz, 2H), 4.22 (q, $J = 7.2$ Hz, 4H) 4.151 (s, 5H), 1.33 (t, $J = 7.2$ Hz, 6H). IR (neat, cm^{-1}): 1706, 1629, 1163. MS (EI, 70 eV): *m/e* 382 (100%, M^+), 317 (52%, M-Cp^+). HRMS: *m/e* 382.08675; Calcd. For $C_{20}H_{22}FeO_4$ *m/e* 382.08555. **4b** (1,3-isomer): ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.38–7.44 (m, 6H); 7.20–7.23 (m, 4H), 6.20 (s, 2H), 4.54 (t, $J = 1.5$ Hz, 1H), 4.41 (d, $J = 1.5$ Hz, 2H), 4.14 (s, 5H), 3.55 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 166.0, 157.7, 138.2, 127.83, 127.81, 127.79, 113.8, 86.1, 71.8, 70.9, 67.5, 51.1. IR (neat, cm^{-1}): 1714, 1604, 1150. MS (EI, 70 eV): *m/e* 506 (100%, M^+) 377 (55%, M-Cp^+). HRMS: *m/e* 506.1179; Calcd. For $C_{30}H_{26}FeO_4$ *m/e* 506.1181. **6.** Yield 9%. Red oil. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 5.98 (s, 1H,), 4.46 (t, $J = 1.8$ Hz, 2H,), 4.43 (t, $J = 1.8$ Hz, 2H), 4.42 (q, $J = 7.2$ Hz, 2H), 4.23 (s, 5H,), 4.19 (q, $J = 7.2$ Hz, 2H), 1.43 (t, $J = 7.2$ Hz, 3H), 1.30 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 167.6, 165.1, 151.1, 112.0, 77.7, 71.0, 70.3, 67.3, 61.5, 60.5, 14.2, 14.1. Elemental analysis: Found: C, 60.65; H, 5.80.$C_{18}H_{20}FeO_4$ requires: C 60.70; H. 5.66. **8a**. Yield 8%. Red oil. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.67 (dd, $J_1 = 11.4$ Hz, $J_2 = 15.0$ Hz, 1H), 6.42 (d, $J = 11.4$ Hz, 1H), 5.86 (d, $J = 15.0$ Hz, 1H), 4.49 (t, $J = 1.8$ Hz, 2H), 4.35 (t, $J = 1.8$ Hz, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 4.11 (s, 5H), 2.21 (s, 3H), 1.31 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, δ): 167.9, 145.8, 140.8, 120.5, 118.4, 86.3, 70.0, 69.6, 66.4, 60.1, 16.2, 14.4. Elemental analysis: Found: C, 66.55; H, 6.40.$C_{18}H_{20}FeO_2$ requires C 66.69; H. 6.22. **8b**. Yield 5%. Red crystals. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (dd, $J_1 = 11.9$ Hz, $J_2 = 14.9$ Hz, 1H), 6.46 (d, $J = 11.9$ Hz, 1H), 5.87 (d, $J = 14.9$ Hz, 1H), 4.52 (t, $J = 1.6$ Hz, 2H), 4.38 (t, $J = 1.6$ Hz, 2H), 4.13 (s, 5H), 2.23 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.8, 147.7, 143.0, 120.3, 116.9, 85.9, 70.2, 69.6, 66.6, 16.3. IR (KBr, cm^{-1}): 3433, 3091, 1672, 1597, 1416, 1316, 1296, 1268, 1160. Elemental analysis: Found C, 64.82; H, 5.45. $C_{16}H_{16}FeO_2$ requires C, 64.89; H, 5.45.

Table 2
The most important geometrical parameters: bond lengths [Å], valence angles [°] and torsion angles [°] for **2b** and **8b**.

2b-I			**2b**-II			**3b**		
Distances								
Fe1 C1	2.0456	(9)	Fe2 C21	2.0408	(10)	Fe1 C1	2.0566	(12)
Fe1 C2	2.0310	(9)	Fe2 C22	2.0320	(10)	Fe1 C2	2.0694	(12)
Fe1 C3	2.0435	(10)	Fe2 C23	2.0434	(10)	Fe1 C3	2.0566	(12)
Fe1 C4	2.0420	(9)	Fe2 C24	2.0462	(9)	Fe1 C4	2.0410	(12)
Fe1 C5	2.0432	(9)	Fe2 C25	2.0396	(9)	Fe1 C5	2.0534	(11)
Fe1 C6	2.0482	(10)	Fe2 C26	2.0462	(11)	Fe1 C6	2.0548	(12)
Fe1 C7	2.0475	(10)	Fe2 C27	2.0374	(10)	Fe1 C7	2.0643	(12)
Fe1 C8	2.0462	(10)	Fe2 C28	2.0409	(11)	Fe1 C8	2.0506	(12)
Fe1 C9	2.0460	(10)	Fe2 C29	2.0455	(12)	Fe1 C9	2.0387	(11)
Fe1 C10	2.0502	(10)	Fe2 C30	2.0513	(10)	Fe1 C10	2.0550	(12)
Fe-Cav	2.044	(5)		2.042	(5)		2.054	(9)
Fe-Ct1	1.639	(5)		1.638	(5)		1.659	(9)
Fe-Ct2	1.651	(5)		1.650	(6)		1.656	(9)
C1 C2	1.4401	(13)	C21 C22	1.4384	(13)	C5 C1	1.4324	(16)
C1 C5	1.4390	(13)	C21 C25	1.4354	(14)	C5 C4	1.4393	(16)
						C10 C6	1.4317	(16)
						C10 C9	1.4378	(16)
C-Cav	1.427	(7)		1.424	(8)		1.426	(8)
C1 C11	1.4648	(13)	C21 C31	1.4681	(13)	C5 C11	1.4624	(16)
						C10 C21	1.4659	(16)
C11 C12	1.3504	(14)	C31 C32	1.3427	(14)	C18 C11	1.3499	(16)
						C21 C28	1.3489	(16)
O1 C13	1.3526	(13)	O3 C33	1.3468	(12)	C19 O1	1.2021	(15)
O1 C20	1.4404	(13)	O3 C40	1.4383	(13)	C19 O2	1.3579	(14)
O2 C13	1.2099	(13)	O4 C33	1.2121	(12)	C20 O2	1.4392	(15)
						C29 O3	1.2022	(15)
						C29 O4	1.3572	(14)
						C30 O4	1.4419	(15)
Valence angles								
Ct1-Fe-Ct2	178.72	(9)		179,18	(11)		178.30	(11)
O2 C13 O1	122.92	(9)	O4 C33 O3	123,19	(10)	O1 C19 O2	122.41	(11)
						O3 C29 O4	122.17	(11)
Torsions								
C2 C1 C11 C12	−3.71	(15)	C22 C21 C31 C32	−1.84	(15)	C4 C5 C11 C12	−4.07	(11)
C14 C11 C12 C13	−4.87	(15)	C34 C31 C32 C33	−2.54	(15)	C19 C18 C11 C12	−8.4	(2)
C11 C12 C13 O1	177.51	(9)	C31 C32 C33 O3	175.46	(9)	O1 C19 C18 C11	−173.8	(2)
C12 C11 C14 C15	−89.66	(13)	C32 C31 C34 C35	−90.04	(12)	C18 C11 C12 C13	−69.11	(17)
C1 C11 C14 C15	87.34	(11)	C21 C31 C34 C35	86.79	(11)	C5 C11 C12 C13	107.19	(13)
						C9 C10 C21 C28	−5.88	(19)
						C22 C21 C28 C29	−8.39	(19)
						O3 C29 C28 C21	177.86	(2)
						C28 C21 C22 C27	−70.48	(17)
						C10 C21 C22 C27	106.21	(13)
C1-Ct1-Ct2-C6	3.74	(11)		1.39	(12)		146.7	(13)

4.3. X-ray structure analysis of ***2b***, ***3b*** and ***8b***

Crystals of compounds **2b, 3b** and **8b** suitable for X-ray analyses were obtained from layered dichloromethane-hexane. Single-crystal X-ray measurements were performed on a BRUKER APEX II ULTRA κ-axis diffractometer with TXS rotating anode using MoKα radiation at 100 K. Data were collected using omega scan measurement method, with 0.5 degrees scan width and 10 s counting time. θ angle for data collection was varied in the range of 2.5–20.00°. Data were corrected in respect to Lorentz and polarization effects. Analytical absorption correction was applied using SADABS [18]. Indexing, integration and scaling were performed with original Bruker Apex II software [19]. The structures were solved using direct methods and refined using SHELXL [20]. Refinement was based on F^2 for all reflections. Weighted R factors wR and all goodness-of-fit S values were based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_0^2 > 2\sigma(F_0^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about three times as large as those based on F. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in idealized averaged geometrical positions and refined isotropically.

4.4. Crystal data

2b: Empirical formula $C_{20}H_{18}FeO_2$, Crystal system Monoclinic, Space group *Cc*, Formula weight 346.19, Temp. 100(2) K, Wavelength 0.71073 A, Unit cell dimensions: a = 20.2616(7) Å, b = 8.3989(3) Å, c = 19.2852(7) Å, α = 90 deg., β = 107.943(2) deg., γ = 90 deg., Volume 3122.24(19) Å^3, Z = 8, Calculated density 1.473 Mg/m^3, Absorption coefficient 0.973 mm^{-1}, $F(000)$ = 1440, Crystal size = 0.22 × 0.22 × 0.17 mm, Theta range 2.11–45.29 deg., Limiting indices: $-40 \le h \le 39$, $-16 \le k \le 15$, $-28 \le l \le 38$, Reflections collected/unique 64,105/19,374 [R(int) = 0.0359], Completeness to theta = 45.29 99.5%, Absorption correction Semi-empirical from equivalents, Max. and min. transmission 0.849 and 0.743, Refinement method Full-matrix least-squares on F^2, Data/restraints/parameters 19,374/2/418, Goodness-of-fit on F^2 0.987, Final R indices [$I > 2$sigma(I)] $R1$ = 0.0322, $wR2$ = 0.0763, R indices (all data) $R1$ = 0.0384, $wR2$ = 0.0797, Absolute structure parameter 0.391(6), Largest diff. peak and hole 1.085 and −0.311 eÅ^{-3}.

3b: Empirical formula $C_{30}H_{26}FeO_4$, Crystal system Triclinic, Space group P−1, Formula weight 506.36, Tem. 100(2) K, Wavelength 0.71073 A, Unit cell dimensions: a = 10.2696(3) Å, b = 10.3895(3) Å, c = 12.3914(6) Å, a = 97.566(2) deg., b = 99.923(2) deg., g = 114.532(2) deg., Volume 1153.90(7) Å^3, Z = 2, Calculated

Table 3
The most important geometrical parameters: bond lengths [Å], valence angles [°] and torsion angles [°] for **8b**.

8b-I			**8b**-II		
Distances					
Fe1 C1	2.0377	(12)	Fe(2) C(17)	2.0378	(13)
Fe1 C2	2.0397	(12)	Fe(2) C(18)	2.0357	(13)
Fe1 C3	2.0441	(12)	Fe(2) C(19)	2.0400	(13)
Fe1 C4	2.0459	(12)	Fe(2) C(20)	2.0422	(13)
Fe1 C5	2.0400	(12)	Fe(2) C(21)	2.0456	(12)
Fe1 C6	2.0391	(12)	Fe(2) C(22)	2.0547	(11)
Fe1 C7	2.0424	(12)	Fe(2) C(29)	2.0416	(12)
Fe1 C8	2.0451	(12)	Fe(2) C(30)	2.0367	(12)
Fe1 C9	2.0362	(11)	Fe(2) C(31)	2.0407	(11)
Fe1 C10	2.0462	(12)	Fe(2) C(32)	2.0414	(11)
Fe-Cav	2.041	(3)		2.04164	(5)
Fe-Ct1	1.644	(5)		1.643	(4)
Fe-Ct2	1.642	(6)		1.645	(5)
C6-C10	1.4330	(16)	C22-C29	1.4327	(16)
C9-C10	1.4356	(16)	C22-C32	1.4316	(16)
C-Cav	1.423	(8)		1,425	(8)
C10 C11	1.4623	(16)	C22 C23	1.4629	(15)
C11 C12	1.4984	(18)	C23 C24	1.4997	(16)
C11 C13	1.3512	(16)	C23 C25	1.3534	(15)
C13 C14	1.4415	(16)	C25 C26	1.4376	(15)
C14 C15	1.3444	(16)	C26 C27	1.3440	(16)
C15 C16	1.4635	(16)	C27 C28	1.4609	(16)
O1 C16	1.2329	(15)	O3 C28	1.2315	(15)
O2 C16	1.3185	(15)	O4 C28	1.3191	(14)
Valence angles					
Ct1-Fe-Ct2	179.17	(11)		178.96	(96)
O1 C16 O2	122.91	(11)	O3 C28 O4	122.72	(11)
Torsions					
C9 C10 C11 C13	−0.64	(19)	C32 C22 C23 C25	−3.04	(18)
C12 C11 C13 C14	0.3	(2)	C24 C23 C25 C26	−2.97	(19)
C16 C15 C14 C13	−176.83	(11)	C25 C26 C27 C28	177.35	(11)
C14 C15 C16 O1	−8.86	(19)	C26 C27 C28 O3	7.14	(18)
C14 C15 C16 O2	169.93	(11)	C26 C27 C28 O4	−171.78	(11)
C1 Ct1 Ct2 c10	0.06	(11)	C22 Ct1 Ct2 C21	2.79	(11)

density 1.457 Mg/m^3, Absorption coefficient 0.690 mm^{-1}, $F(000) = 528$, Crystal size = 0.30 × 0.30 × 0.10 mm, Theta range 2.11–30.0 deg., Limiting indices: $-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-17 \leq l \leq 17$, Reflections collected/unique 35,755/6740 [$R(\text{int}) = 0.0217$], Completeness to theta = 30 deg. 99.9%, Absorption correction Semi-empirical from equivalents, Max. and min. transmission 0. 946 and 0.864, Refinement method Full-matrix least-squares on F^2, Data/restraints/parameters 6043/0/318, Goodness-of-fit on F^2 1.049, Final R indices [$I > 2\text{sigma}(I)$] $R1 = 0.0295$, $wR2 = 0.0742$, R indices (all data) $R1 = 0.0351$, $wR2 = 0.0784$, Largest diff. peak and hole 0.63 and −0.25 $eÅ^{-3}$

8b Empirical formula $C_{16}H_{16}FeO_2$, Crystal system Monoclinic, Space group $P2(1)/c$, Formula weight 296.14, Tem. 100(2) K, Wavelength 0.71073 A, Unit cell dimensions: $a = 11.5845(4)$ Å, $b = 8.6466(2)$ Å, $c = 26.2472(7)$ Å, $a = 90$ deg., $b = 96.836(2)$ deg., $g = 90$ deg., Volume 2610.40(13), $Z = 8$, Calculated density 1.507 Mg/m^3, Absorption coefficient 1.149 mm^{-1}, $F(000) = 1232$, Crystal size = 0.20 × 0.20 × 0.05 mm, Theta range 1.56–33.2 deg., Limiting indices: $-16 \leq h \leq 17$, $-13 \leq k \leq 12$, $40 \leq l \leq 38$, Reflections collected/unique 38,830/9988 [$R(\text{int}) = 0.0282$], Completeness to theta = 29 deg. 99.9%, Absorption correction Semi-empirical from equivalents, Max. and min. transmission 0. 945 and 0.803, Refinement method Full-matrix least-squares on F^2, Data/restraints/parameters 9988/0/347, Goodness-of-fit on F^2 1.040, Final R indices [$I > 2\text{sigma}(I)$] $R1 = 0.0320$, $wR2 = 0.0784$, R indices (all data) $R1 = 0.0426$, $wR2 = 0.0830$, Largest diff. peak and hole 0.70 and −0.32 $eÅ^{-3}$

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Appendix. Supplementary data

CCDC 736149, 736150 and 769111 and contain the supplementary crystallographic data for compounds **2b**, **3c**, and **8b** respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

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