# Optically and Redox-Active Ferroceneacetylene Polymers and Oligomers

**Herbert Plenio,*[a] Jörg Hermann,[b] and Alexander Sehring[a]**

*Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday*

**Abstract:** The palladium-catalyzed Sonogashira reaction can be used to build optically active, oligomeric 1,2,3-substituted ferrocenes up to the tetramer, as well as polymers, by sequential coupling of optically active ($ee > 98\,\%$), planar chiral iodoferroceneacetylenes and ferroceneacetylenes. ($S_{Fc}$)-1-Iodoferrocene-2-carbaldehyde (**1**) was reduced to the alcohol and methylated to give the corresponding methyl ether, which was Sonogashira-coupled with $HC{\equiv}CSiEt_3$, resulting in ($R_{Fc}$)-1-($C{\equiv}CSiEt_3$)-2-methoxymethylferrocene (**4**) (79 %, three steps). Orthometalation with *t*BuLi followed by quenching with 1,2-diodoethane gave ($R_{Fc}$)-1-($C{\equiv}CSiEt_3$)-2-methoxymethyl-3-iodoferrocene (**5**). Deprotection of the acetylene with $n$Bu$_4$NF resulted in ($R_{Fc}$)-1-ethynyl-2-methoxymethyl-3-iodoferrocene (**6**), which was Sonogashira-coupled with itself to produce an optically active polymer. Deprotection of **4** with $n$Bu$_4$NF and Sonogashira coupling of the product with **5** resulted in the dinuclear ferrocene **9**. Deprotection of **9** and coupling with **5**, followed by deprotection of the resulting acetylene **11**, gave the trinuclear ferrocene **12**. Another such sequence involving **11** and **5** produced a tetranuclear ferrocene **13**. To study the electronic communication in such oligomers in more detail, two symmetrical, closely interrelated, trinuclear ferrocenes **18** and **19** were synthesized. The redox potentials of all the ferrocenes and the ferroceneacetylene polymer were determined by cyclic and square-wave voltammetry. All the metallocenes were investigated by UV/Vis spectroscopy. A linear relationship was found between $\lambda_{max}$ and $1/n$ ($n$ = number of ferrocene units in the oligomer). The polymer displayed two redox waves in the cyclic voltammogram, at 0.65 and 0.795 V. The corresponding mixed-valence oligoferrocene cations were synthesized from four ferroceneacetylenes, and their metal–metal charge transfer bands were examined by UV/Vis–NIR. The resonance exchange integrals $H_{ad}$, calculated on the basis of spectral information from the metal–metal charge transfer (MMCT) bands, were between 290 and 552 cm$^{-1}$.

**Keywords:** acetylenes · ferrocene · optical activity · polymers · redox properties

## Introduction

Whereas organic polymers constitute a large class of compounds of tremendous commercial interest,[1] organometallic polymers are much less well known, even though the presence of a metal could result in unusual optical, magnetic, or electronic properties with potential for future applications.[2, 3] Such compounds therefore represent a challenge in the current quest for new materials.[4]

Ferrocene (Fc)-based compounds, in particular, have been receiving considerable attention in recent years, although they could not be utilized, as their properties were poorly understood.[5] However, enormous progress has been achieved by the pioneering work of Manners et al.,[6] who developed the ROP-type coupling of strained ferrocenophanes yielding high molecular weight and soluble polymers, and thus refueled activities in this field.[7, 8]

We believe that metal-containing polymers should possess a π-conjugated backbone,[9, 10] since this allows the metal centers to be intimately coupled with each other.[11, 12] Such a cooperativity could give rise to novel properties not seen in organic polymers or in metal-containing polymers with isolated metal atoms.[13, 14] We have reported the first examples of ferroceneacetylene copolymers based on 1,2,3-substituted ferrocenes using $CH_2NMe_2$ as an *ortho*/*ortho*-directing group in the 2-position.[15] Such materials are of interest since the related phenylene-ethynylenes [16] are known to exhibit photoluminescence[17] and nonlinear optical properties.[18] The oligomers and polymers that we described, however, suffer from various disadvantages that are caused mainly by the $CH_2NMe_2$ substituent. First, the redox chemistry of compounds derived from $FcCH_2NMe_2$ is quite

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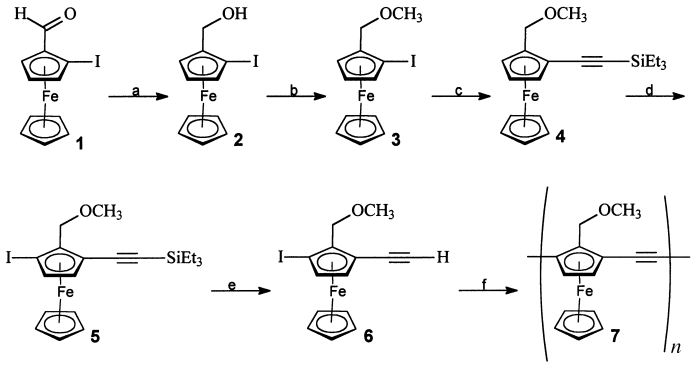
complicated and mostly irreversible because of interfering protonation/deprotonation processes; second, the highly polar nature of the polyamines hinders their purification; and third, the racemic nature of the starting materials yields a complicated mixture of diastereomeric oligomers and polymers. These factors prevented the more detailed study of the electronic properties of such compounds that is essential in order to develop an understanding of the principles governing the intermetallic interactions in such species.

Here we present new ferroceneacetylene oligomers and polymers devoid of the disadvantages cited above. Instead of the $CH_2NMe_2$ group we chose the $CH_2OMe$ unit group as an *ortho*/*ortho*-directing substituent for the synthesis of 1,2,3-substituted ferrocenes and polymers; this should avoid the problems encountered with the basic amine substituent and pave the way for clean redox processes. Most importantly, such ferrocenes can be obtained easily as optically pure starting materials on a fairly large scale by a protocol based on a highly efficient, enantioselective synthesis of planar chiral ferrocenes by Kagan et al.[19]

Thus, this approach offers a good chance of producing well-defined oligomers and polymers which can be probed spectroscopically. The synthesis and electrochemical and UV/Vis spectroscopic investigations of various planar chiral 1,2,3-substituted ferrocene oligomers and polymers are described here. Related mixed-valence species were also studied to obtain information on the electronic coupling parameters of the different metallocene units.

## Results and Discussion

**Syntheses**: In our syntheses of the various ferroceneacetylenes (Schemes 1–5), our most important starting material for all the ferrocenes described here was (*S*)-1-iodoferrocene-2-carbaldehyde (**1**), which could be obtained readily in several tens of grams by using the procedure developed by Kagan and co-workers.[19] Reduction of this aldehyde with $NaBH_4$ gave the unstable alcohol **2**, immediate reaction of which with $CH_3I$ produced the methyl ether **3** in 95% yield for the two steps (Scheme 1). The Sonogashira coupling reaction[20] of **3** with $HC{\equiv}CSiEt_3$ resulted in ferrocene **4** (yield 83%). Regioselective lithiation of this ferrocene (*ortho* to the $CH_2OCH_3$ group) was effected with *t*BuLi, and after quenching with 1,2-diiodoethane the iodide **5** was isolated (yield 87%). This 1,2,3-substituted ferrocene was used for coupling reactions (Schemes 2–4) or deprotected with $n$Bu$_4$NF in THF to produce the free acetylene **6**.




Scheme 1. Synthesis of mononuclear ferrocenes and the stereoregular polymer: a) $NaBH_4$, 97%; b) KOH, $CH_3I$, DMSO, 98%; c) $HCCSiEt_3$, catalyst: $(Ph_3P)_2PdCl_2$/CuI, 83%; d) *t*BuLi, $IC_2H_4I$, $Et_2O$, 87%; e) $n$Bu$_4$NF/THF, 96%; f) $(i$Pr$)_2$NH–DMF (1:1), catalyst: $(Ph_3P)_4$Pd, CuI.

Compound **6** contains two functional groups which can react with each other under Pd catalysis. However, the standard Sonogashira protocol with $(i$Pr$)_2$NH as a solvent furnished the polymer in a poor yield (ca. 15%) together with a substantial amount (ca. 50%) of short-chain oligomers. After about 30 min of this reaction precipitation of dark red material from the reaction mixture began; we attributed this to insolubility of the growing polymer chain in $(i$Pr$)_2$NH. Polymerization of **6** in a DMF–$(i$Pr$)_2$NH (1:1, v/v) mixture produced polymer **7** (yield ca. 80%), which could be fractionated further by chromatography. The main product (**7$_1$**) (yield ca. 45%) was identical to the polymer previously available in only 15% yield; two smaller fractions (**7$_2$** and **7$_3$**; yield ca. 35%) appeared to have even higher molecular weights. Importantly, this polymerization started from an enantiopure (*ee* > 98%), planar chiral ferrocene; consequently the resulting polymer was optically active ($[\alpha]_D^{20} = -198.0$ per ferrocene unit). To the best of our knowledge this is the first reported example of an optically active organometallic polymer. Determination of its molecular mass was unsuccessful by several techniques (GPC, GPC–LALLS, MALDI–TOF), and no conclusive results were obtained; based on GPC–LALLS (gel permeation chromatography with a low-angle laser light scattering detector) measurements an estimated molecular mass of up to 10 kDa appeared reasonable. Detailed investigation into the macromolecular, electrical,[21] and optical properties[22] of the polymers will be published in due course.[23]

To understand the properties of these polymers more thoroughly, we also synthesized some well-defined oligomers composed of ferrocene and acetylene units (Scheme 2). This can be done by [1+1] coupling of the mononuclear ferrocenes **5** and **8** to give the respective dinuclear species **9** by the standard Sonogashira protocol. We had planned to continue this divergent–convergent approach to defined oligomers, as did Moore[24] and Tour [25] successfully for related oligomeric benzeneacetylenes and thiopheneacetylenes. To obtain the starting material for the next [2+2] coupling another ortho-lithiation/iodination of **9** was required, but our attempts to lithiate **9** regioselectively did not meet with success. After quenching the deprotonated ferrocene **9** with $I_2$ or 1,2-diiodoethane, we always obtained mixtures of iodinated products. The *ortho*-directing power of the $CH_2OCH_3$ group was clearly insufficient.[26] We therefore had to rely on the less efficient [2+1] synthesis of **11** by reaction of **5** and **10** (Scheme 2). The silyl group of the trinuclear ferrocene **11** easily yielded **12**, which again was Sonogashira-coupled with another equivalent of **5** to generate the tetranuclear ferrocene **13** (Scheme 3). This stepwise procedure is cumbersome for the synthesis of higher nuclearity ferrocenes, but we expected **13** and **14** to be acceptable models of the polymeric species. Another tetranuclear ferrocene (**15**) was prepared by the Eglington–Glaser coupling[27] of dinuclear **10** (Scheme 3).

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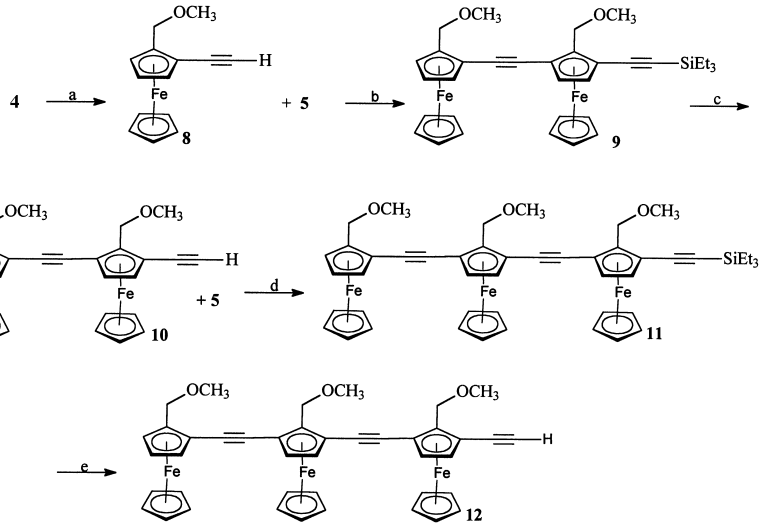
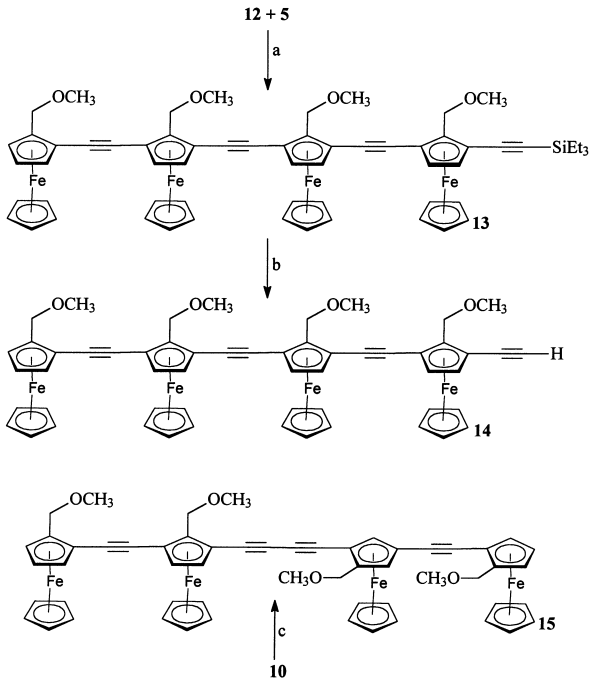


Scheme 2. Synthesis of unsymmetrical di- and trinuclear ferrocenes: a) $n$Bu$_4$NF/THF, 96%; b) catalyst: Pd(PPh$_3$)$_4$, CuI, PPh$_3$, 63%; c) $n$Bu$_4$NF/THF, 95%; d) catalyst: Pd(PPh$_3$)$_4$, CuI, PPh$_3$, 56%; e) $n$Bu$_4$NF/THF, 81%.

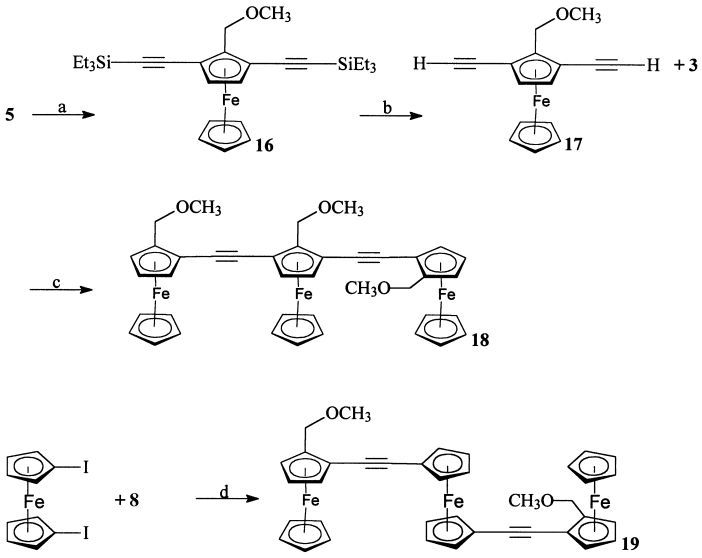


Scheme 3. Synthesis of the tetranuclear ferrocenes: a) catalyst: Pd(PPh$_3$)$_4$, CuI, PPh$_3$, 55%; b) $n$Bu$_4$NF/THF, 78%; c) TMEDA, CuCl, O$_2$, 79%.

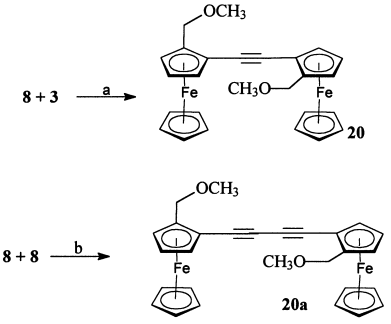
In addition to the unsymmetrical tri- and tetranuclear ferrocenes, we synthesized the two closely related trinuclear ferrocenes **18** and **19** (Scheme 4). There is a very significant difference between **18** and **19**: in **19** the central ferrocene unit displays a 1,1′-substitution pattern, whereas **18** has a 1,3-bridged core. Apart from one $CH_2OCH_3$ group, **18** and **19** are otherwise identical. We expected spectroscopic studies of these compounds and their mixed-valence relatives to provide information on the influence of the substitution pattern of the ferrocene on the electronic communication between the metal centers.

Another two symmetrical ferrocenes have been synthesized (Scheme 5): compound **20** is a simple dinuclear ferrocene linked by an acetylene bridge, whereas in **20a** the linker is a butadiyne unit. Small amounts of **20a** are also produced by homocoupling, a known side reaction, during Sonogashira reactions involving **8** and other iodinated ferrocenes.[28]

The IR spectra of a few of the ferroceneacetylenes were found to display the expected pattern for the −C≡C− stretch mode. The Fc−C≡C−SiEt$_3$ unit has a high-intensity absorption at 2154 cm$^{-1}$, whereas the Fc−C≡C−Fc stretch at 2220 cm$^{-1}$ is very weak; the polymer displays a very weak and broad IR absorption at 2217 cm$^{-1}$.



Scheme 4. Synthesis of the symmetrical trinuclear ferrocenes: a) HCCSiEt$_3$, catalyst: (Ph$_3$P)$_2$PdCl$_2$, CuI, 85%; b) $n$Bu$_4$NF/THF, 94%; c) Pd(PPh$_3$)$_4$, CuI, PPh$_3$, 25%; d) Pd(PPh$_3$)$_2$Cl$_2$, Cu(CH$_3$COO)$_2$, 28%.



Scheme 5. Synthesis of the symmetrical dinuclear ferrocenes: a) Pd(PPh$_3$)$_4$, CuI, PPh$_3$, 65%; b) TMEDA, CuCl, O$_2$, 83%.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**Electrochemistry:** The redox potentials of the ferrocenes **1**–**20** were determined by cyclic voltammetry and square-wave voltammetry (Tables 1 and 2). All the cyclic voltammograms were characterized by reversible redox processes, which were evidence for the favorable effect of the $CH_2OCH_3$ group on electron transfer reactions as opposed to the behavior of the $CH_2N(CH_3)_2$-substituted ferrocenes described previously.[15]

Table 1. Redox potentials of mononuclear ferrocenes ($CH_3CN$, $TBAPF_6$, $-30^oC$), values in parentheses were determined in $CH_2Cl_2$ ($TBAPF_6$, $-30^oC$).

| Ferrocene | $R_1$ | $R_2$ | $R_3$ | $E_{1/2}$ [V] | $E_{1/2}$ calcd. [V] |
|---|---|---|---|---|---|
| | $CH_2OCH_3$ | | | 0.423 | |
| | I | | | 0.545 | |
| | C≡CSiEt$_3$ | | | 0.547 | |
| | C≡CH | | | 0.559 | |
| **3** | I | $CH_2OCH_3$ | | 0.577 | 0.57 |
| **4** | C≡CSiEt$_3$ | $CH_2OCH_3$ | | 0.573 (0.65) | 0.57 |
| **8** | C≡CH | $CH_2OCH_3$ | | 0.584 | 0.58 |
| **5** | I | $CH_2OCH_3$ | C≡CSiEt$_3$ | 0.713 | 0.72 |
| **6** | I | $CH_2OCH_3$ | C≡CH | 0.721 | 0.73 |
| **16** | C≡CSiEt$_3$ | $CH_2OCH_3$ | C≡CSiEt$_3$ | 0.702 | 0.72 |
| **17** | C≡CH | $CH_2OCH_3$ | C≡CH | 0.746 | 0.74 |

Table 2. Redox potentials of di-, tri-, and tetranuclear ferrocenes ($CH_3CN$, $TBAPF_6$, $-30\,^\circ C$), bracketed values were determined in $CH_2Cl_2$ ($TBAPF_6$, $-30^\circ C$).

| Ferrocene | $E_1$ [V] | $E_2$ [V] | $E_3$ [V] | $E_4$ [V] | $\Delta E_{12}$ [mV] | $\Delta E_{23}$ [mV] | $\Delta E_{34}$ [mV] |
|---|---|---|---|---|---|---|---|
| **20** | 0.516 | 0.660 | | | 144 | | |
| | (0.563) | (0.685) | | | (122) | | |
| **20a** | 0.586 | 0.698 | | | 112 | | |
| | (0.620) | (0.714) | | | (94) | | |
| **20b** | 0.513 | 0.618 | | | 105 | | |
| **9** | 0.529 | 0.772 | | | 243 | | |
| | (0.582) | (0.786) | | | (204) | | |
| **10** | 0.546 | 0.795 | | | 249 | | |
| **19** | 0.538 | | 0.748 | | 210 | | |
| | (0.578) | | (0.785) | | (207) | | |
| **18** | 0.546 | | 0.838 | | 298 | | |
| | (0.586) | | (0.828) | | (242) | | |
| **11** | 0.551 | 0.703 | 0.869 | | 152 | 166 | |
| | (0.591) | (0.725) | (0.854) | | (135) | (129) | |
| **12** | 0.548 | 0.703 | 0.876 | | 165 | 163 | |
| **13** | 0.553 | 0.674 | 0.790 | 0.878 | 121 | 116 | 88 |
| | (0.579) | (0.685) | (0.782) | (0.865) | (106) | (97) | (83) |
| **14** | 0.550 | 0.674 | 0.797 | 0.889 | 124 | 123 | 92 |
| **15** | 0.556 | | 0.810 | | | 254 | |

Two representative traces (Figure 1) indicate reversible redox events in the cyclic voltammogram of the tetranuclear ferrocene **13** at low temperatures ($-30\,^\circ C$), at which even the tetracationic ferrocene **13**$^{4+}$ appeared to be reasonably stable. Electron transfer reactions were better resolved in the square-wave voltammogram of **13** (Figure 1, bottom) although the small peak corresponding to the fourth oxidation suggested that the oxidation of the trication to the tetracation is not entirely reversible.

Increments for substituents attached to the various ferrocenes described here were calculated by determining the redox potentials for the corresponding monosubstituted ferrocene relative to ferrocene itself. These calculated increments ($CH_2OCH_3$ +23 mV), (−I +145 mV), (C≡CSiEt$_3$ +147 mV), (C≡CH +159 mV) agreed quite well with the experimental redox potentials of all the mononuclear ferrocenes described here (Table 1). This approach was less accurate for the dinuclear ferrocenes (Table 2) although, based on the redox potentials of **20**, increments of +93 mV for the neutral ferroceneacetylene and +237 mV for the oxidized ferroceneacetylene may be calculated. Increments can aid the assignment of sequential redox processes which occur in the di-, tri-, and tetranuclear ferrocenes. In **9** and **10** the ferrocene unit "A" (labeling the formulae alphabetically from left to right in Scheme 2) with only one acetylene substituent is oxidized first, then the other metallocene ("B") is oxidized in the second step. Accordingly the oxidation sequence has to be A, C, B in the trinuclear ferrocenes **11** and **12** and probably A, C, D, B in **13** and **14** (Scheme 3).

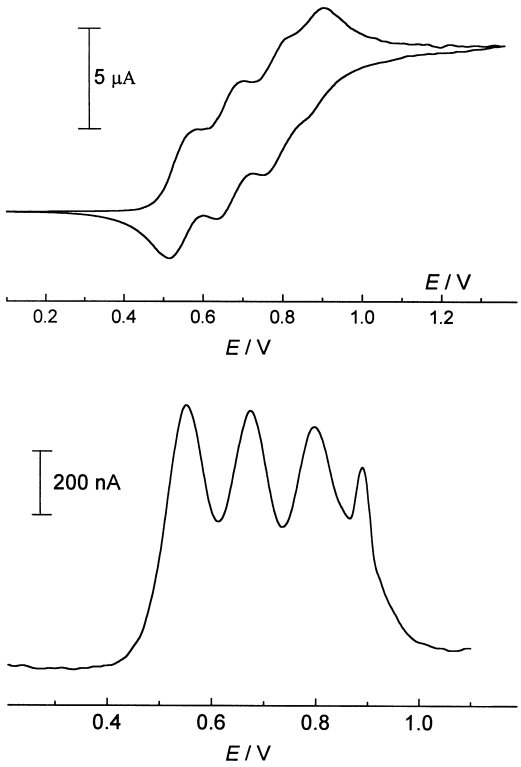


Figure 1. Cyclic voltammogram (top) and square-wave voltammogram (bottom) of **13** in $CH_3CN$.

As polymer **7** is insoluble in $CH_3CN$, its electrochemistry was investigated in $CH_2Cl_2$. To compare these data with the redox chemistry of some of the mono- and oligonuclear ferrocenes, solutions of these compounds in $CH_2Cl_2$ were also investigated (see the values in parentheses in Tables 1 and 2). The square-wave voltammogram of **7** (Figure 2) displays two main oxidation peaks at 0.65 and 0.80 V. This 145 mV separation between the two peaks corresponds closely to the redox separation of $E_1$ and $E_2$ in the dimer.

In the electrochemistry of the trinuclear ferrocenes **18** and **19**, we had hoped to be able to distinguish between the individual redox events and thus to obtain further support for our hypothesis that electron transfer in 1,3-substituted ferrocenes is superior to that in 1,1′-ferrocenes. The first oxidation waves for **18** and **19** occur at virtually the same

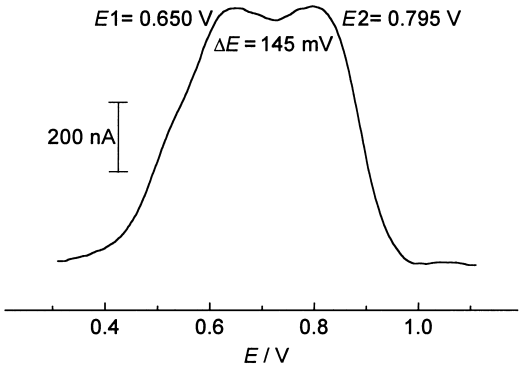


Figure 2. Square-wave voltammogram of the stereoregular polymer **7** in $CH_2Cl_2$.

redox potential; more importantly, both waves denote $2e^-$ processes. In each of these trinuclear metallocenes the two peripheral ferrocenes are oxidized independently of each other in one step, and it was not possible to resolve the respective $2e^-$ events. Consequently, the electrochemical data of **18** and **19** are of no help in supporting our basic hypothesis on electronic communication. It is interesting that the third oxidations in **18** and **19** differ from each other by 88 mV even though, because of a $CH_2OCH_3$ group in **19**, the difference should be only 23 mV. This appears to result from the diminished flexibility of the 1,3-substituted trinuclear ferrocene, which prevents the spacing of the charged peripheral ferrocenium moieties.

**UV/Vis spectroscopy**: From the spectral data $\lambda_{max}$ [nm] and $\varepsilon$ [$L\,M^{-1}cm^{-1}$] of the ferrocenes **3**–**20** in $CH_3CN$ and $CH_2Cl_2$ solutions (Table 3) it is noteworthy that there is only a weak solvatochromic effect between the two solvents. More importantly, there is a linear relationship between $\lambda_{max}$ and $1/n$ ($n$ = number of ferroceneacetylene units) for monomers and oligomers, with a limiting value of 472 nm (Figure 3) for $1/n = 1/\infty$. This correlation is typical for conjugated organic polymers, but was not observed in the UV/Vis spectra of

Table 3. UV/Vis data of the mono- and oligonuclear ferrocenes (d–d transition only, $CH_3CN$, $10^{-3}$ M, values in parentheses were determined in $CH_2Cl_2$).

| Ferrocene | $R_1$ | $R_2$ | $R_3$ | $\lambda_{max}$ [nm] | $\varepsilon$[$L\,M^{-1}cm^{-1}$] |
|---|---|---|---|---|---|
| | $CH_2OCH_3$ | | | 439.0 | 89 |
| **3** | I | $CH_2OCH_3$ | | 438.0 | 162 |
| **4** | C≡CSiEt$_3$ | $CH_2OCH_3$ | | 441.5 | 269 |
| | | | | (441) | (302) |
| **8** | C≡CH | $CH_2OCH_3$ | | 438.5 | 148 |
| **5** | I | $CH_2OCH_3$ | C≡CSiEt$_3$ | 449.5 | 350 |
| **6** | I | $CH_2OCH_3$ | C≡CH | 447.0 | 248 |
| **16** | C≡CSiEt$_3$ | $CH_2OCH_3$ | C≡CSiEt$_3$ | 460.0 | 378 |
| **17** | C≡CH | $CH_2OCH_3$ | C≡CH | 447.0 | 241 |
| **20** | | | | 446.5 | 727 |
| **20a** | | | | 450.5 | 1879 |
| **9** | | | | 455.0 | 799 |
| | | | | (454) | (789) |
| **10** | | | | 450.0 | 850 |
| **18** | | | | 453.0 | 1329 |
| **19** | | | | 446.0 | 1128 |
| **11** | | | | 461.0 | 1365 |
| | | | | (461) | (1109) |
| **12** | | | | 459.0 | 1294 |
| **13** | | | | 465.0 | 1970 |
| | | | | (465) | (1585) |
| **14** | | | | 463.0 | 1988 |
| **15** | | | | 450.5 | 3628 |

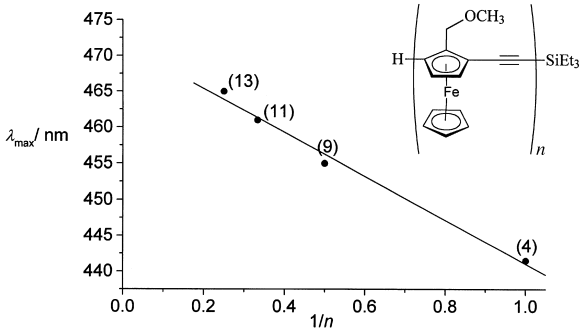


Figure 3. Variation of $\lambda_{max}$ with $1/n$ ($\lambda_{max}$ d–d transition, $n$ = number of ferrocenes).

related (1,3-cyclobutadienediylcobalt(I)-cyclopentadienyl)butadiyne oligomers.[29] A graph of $\varepsilon/n$ ($\varepsilon$ = extinction coefficient of the ferrocene d–d band) against $n$ shows that $\varepsilon/n$ increases ($\varepsilon/n = 269$, 400, 455, and 493 for $n = 1$, 2, 3, and 4 respectively) toward an asymptotic limiting value of approximately $525\,L\,M^{-1}cm^{-1}$. It is thus evident that the ferrocene d–d transition is not an independent chromophore, but is coupled to the conjugated main chain.

The band shape of the UV/Vis spectrum of the polymer in $CH_2Cl_2$ (Figure 4) was fitted to two Gaussian curves to give a maximum of 482 nm for the d–d transition. This again

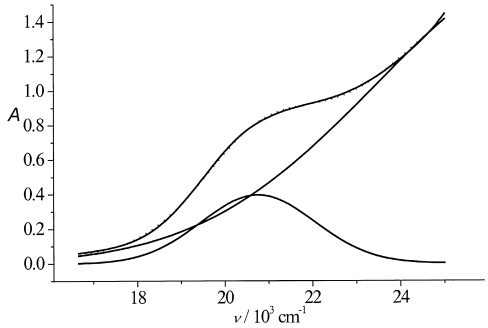


Figure 4. UV/Vis spectrum of the polymer $\mathbf{7_3}$ ($c = 10^{-3}$ M in $CH_2Cl_2$), deconvoluted to two Gaussians with maxima at 364 and 482 nm.

provides clear evidence of the increased conjugation within the polymer chain, even though this long wave shift is more pronounced than expected from the extrapolation of the linear relationship in Figure 3.

For the two symmetrical trimers **18** and **19** there is a small, but we think significant, difference in the UV/Vis spectra. The d–d band in ferrocene **18** (Table 3) displays a bathochromic shift and an extinction coefficient for this band that is about 20% stronger than that of the spectral data of 1,1′-substituted ferrocene **19**. We consider this to be diagnostic of increased conjugation within the 1,3-substituted ferrocene, relative to the 1,1′-species.[30]


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**Mixed-valence ferroceneacetylenes**: The energy of the absorption maximum and the extinction coefficient of the intervalence charge transfer band in mixed-valence compounds provide valuable information on the electronic coupling of the different metal centers.[31–33] Consequently we have synthesized the respective mixed-valence compounds from the dinuclear ferrocenes **20** and **20a** and the trinuclear ferrocenes **18** and **19** by treating one equivalent of the respective oligonuclear ferrocene with one equivalent of oxidizing reagent $[FcCOCH_3]^+[BF_4]^-$.[34] The resulting products were directly probed spectroscopically, since the $CH_3CN$ solutions of the oxidized ferrocenes are quite sensitive.[35]

Relevant data for the intervalence charge transfer bands and the electronic coupling parameters of the monooxidized ferrocenes **20**$^+$, **20a**$^+$, **18**$^+$, and **19**$^+$ are given in Table 4. The

Table 4. Spectral data of the intervalence charge transfer band and electronic coupling parameters of the monooxidized ferrocenes **20**$^+$, **20a**$^+$, **18**$^+$ and **19**$^+$. Solvent $CH_3CN$ except for the values in parentheses which were determined in $CH_2Cl_2$.

| Ferrocene | **20**$^+$ | **20a**$^+$ | **18**$^+$ | **19**$^+$ |
|---|---|---|---|---|
| $\lambda_{max\ CT}$ [nm] | 1330 (1540) | 1058 | 1202 | 1266 |
| $\lambda_{max}$ [cm$^{-1}$][a] | 7519 (6494) | 9451 | 8319 | 7899 |
| $\varepsilon_{CT}$ [L M$^{-1}$cm$^{-1}$] | 561 | 279 | 580 | 344 |
| $\varepsilon_{CTCorr}$ [L M$^{-1}$ cm$^{-1}$] | 623 (ca.750) | 368 | 934 | 557 |
| $\Delta\nu_{1/2obs}$ [cm$^{-1}$][b] | 4796 | 5292 | 4833 | 4722 |
| $\Delta\nu_{1/2cal}$ [cm$^{-1}$][c] | 4168 | 4672 | 4043 | 4125 |
| $\Delta E_{1/2}$ [V] | 0.144 | 0.112 | 0.298 | 0.210 |
| $d$ [Å] | 7.2/5.85 | 9.6/8.35 | 7.2 | 7.2 |
| $H_{ad}$ [cm$^{-1}$][d] | 427/525 | 290/333 | 552 | 410 |

[a] Calculated from $\lambda_{max\ CT}$. [b] Observed $\nu_{1/2}$ of the MMCT band. [c] Calculated $\nu_{1/2}$ of the MMCT band, $\Delta\nu_{1/2cal} = [2300\ (\nu_{max} - \Delta E_0)^{1/2}$. [d] Calculated exchange integral $H_{ad} = 2.06 \times 10^{-2}\ (\nu_{max}\varepsilon_{max}\Delta\nu_{1/2})^{1/2}/(dG^{1/2})$, $d =$ distance Fe–Fe, $G =$ degeneracy of excited state.

measured extinction coefficients $\varepsilon_{CT}$ require some correction, however, since with $[FcCOCH_3]^+[BF_4]^-$ as the oxidant, the ferrocenes **20**, **20a**, **18**, and **19**, are not converted quantitatively into the respective monocations. For the interaction of oxidant (ox) and reductant (Fc), two equilibria have to be considered. The equilibrium constant $K_{ox}$ for the reaction $Fc + ox^+ \rightleftharpoons Fc^+ + ox$ is determined by the difference between the redox potentials of oxidant and reductant. Furthermore, the disproportionation equilibrium, $2\,Fc^+ \rightleftharpoons Fc^{2+} + Fc$, further decreases the concentration of the monooxidized species. The respective constant $K_{dis}$ is obtained from the difference between the redox potentials $Fc/Fc^+$ and $Fc^+/Fc^{2+}$. In the case of the trinuclear compounds, it has to be taken into account that $Fc^{2+}$ also displays metal–metal charge transfer (MMCT) bands.[36] For the four compounds we probed, the measured $\varepsilon_{CT}$ as well as the corrected $\varepsilon_{corr}$ values are listed in Table 4. The distances between the iron centers were computed by molecular mechanics methods.[37] The intermetallic distances thus obtained agreed with those from X-ray crystal structure determinations of two ferrocenes linked by acetylenes.[38] A minor complication is that the relative orientation of the two ferrocenes in the dinuclear metallocene in solution can be anywhere between transoidal and cisoidal, without any apparent preference. Accordingly, both distances as well as the corresponding pairs of $H_{ad}$ values are included in Table 4.

The intervalence electron transfer in $Fc{-}C{\equiv}C{-}Fc^+$ ($\lambda$ 1560 nm, $\varepsilon$ 670) and $Fc{-}C{\equiv}C{-}C{\equiv}C{-}Fc^+$ ($\lambda$ 1180 nm, $\varepsilon$ 570) have already been reported by Cowan et al.[39] These compounds, however, were investigated in $CH_2Cl_2$ instead of in $CH_3CN$, which we used; it should be kept in mind that the solvation of charged species and the respective MMCT band will certainly depend on the nature of the solvent. To allow comparison with Cowan's results, the UV/Vis spectrum of **20**$^+$ was also measured in 1,2-$Cl_2C_2H_4$ (values in parentheses, Table 4) and was found to be similar in spite of the presence of two $CH_2OCH_3$ groups in **20**$^+$.

The data for our monocationic ferrocenes linked by $(C{\equiv}C)_n$ bridges should now be compared with the monocationic ferrocenes linked by $-(C{=}C)_n-$ bridges investigated by Ribou et al.[40] For $n = 1$ the $H_{ad}$ values (427/525 (transoid/cisoid) for $-C{\equiv}C-$) are comparable with 495 for $-C{=}C-$ bridging. For $n = 2$, $H_{ad}$ changes to 290/333 and 430/460, respectively. Analysis of the single terms contributing to $H_{ad}$ shows that while $\nu_{1/2}$, $d$ and $G$ are roughly similar for the two types of bridges, a significant deviation occurs for $\lambda_{max}$. More important for $H_{ad}$ in the case of $n = 2$ appears to be the large difference in the extinction coefficient of the MMCT band in the $-(C{\equiv}C)_2$-bridged ferrocene, which is only 368 L M$^{-1}$ cm$^{-1}$, compared with 1570 L M$^{-1}$ cm$^{-1}$ with a $-C{=}C-$ bridge. We do not have a straightforward explanation for this, but the influence of the solvent should be considered, as Cowan determined a significantly higher $\varepsilon$ (570 L M$^{-1}$ cm$^{-1}$ in $CH_2Cl_2$ than we did in $CH_3CN$.

## Summary and Conclusions

We have described a synthetic route providing access to optically active and redox-active oligomeric ferroceneacetylenes, which were prepared from (*R*)-**5** by sequences of acetylene deprotection and Sonogashira coupling reactions. Furthermore, the Pd-catalyzed self-coupling of (*R*)-**6** affords soluble ferroceneacetylene polymers. Evidence for the extended electronic communication within this optically active polymer is provided by a 35 nm bathochromic shift of the d–d band with respect to the monomer, and by cyclic and square-wave voltammetry measurements of the redox potentials of ferrocene oligomers and polymers. Furthermore, the ferrocene d–d transition is electronically coupled to the conjugated chain as the $\lambda_{max}$ of the d–d band is correlated linearly with $1/n$ ($n =$ number of ferrocene units in the oligomer).

An investigation of the related mixed-valence ferroceneacetylene oligomers and their metal–metal charge transfer bands has furnished further information on the electronic coupling of the metal centers as expressed by the exchange integrals $H_{ad}$. These values are in the same order for the $-(C{\equiv}C)_n-$ bridge as for the $-(C{=}C)_n-$ bridge recently investigated by Ribou et al. for $n = 1$, but fall off significantly relative to the $-C{=}C-$ bridge for $n = 2$. The main cause of this behavior appears to be the weak extinction coefficient of the ferroceneacetylenes.

Future investigations will be directed toward determining whether the optically active and soluble ferroceneacetylene polymers can display favorable optical properties like those of the related PPE-type phenyleneacetylene materials.

## Experimental Section

**General**: Commercially available solvents and reagents were purified according to literature procedures.[41] All reactions were carried out under an atmosphere of argon; in particular, the palladium-catalyzed coupling reactions require strict exclusion of oxygen. Chromatography was on silica MN 60 (63–200 μm) and TLC on Merck plates coated with silica gel 60 (F254).

**NMR spectroscopy**: NMR spectra were recorded at 300 K with a Bruker Avance ($^1$H NMR 200 MHz, $^{13}$C NMR 50.3 MHz). $^1$H NMR spectra were referenced to residual $^1$H impurities in the solvent and $^{13}$C NMR to the solvent signals: $CDCl_3$ ($\delta = 7.26$, 77.0), $C_6D_6$ ($\delta = 7.16$, 128.0), $CD_3CN$ ($\delta =$ 1.93, 1.30). For the purpose of $^1$H NMR signal assignment CpH denotes a proton attached to the sp$^2$ carbon of cyclopentadiene or to the carbon of a ferrocene $\eta^5$-cyclopentadienyl ring. All melting points are uncorrected.

**Mass spectrometry**: Mass spectra were recorded on a Finnigan MAT 3800, IR spectra (in $CHCl_3$ solution) on a Bruker IFS-25, and UV/Vis spectra (in $CH_2Cl_2$ solution) on a JASCO UV-570 spectrometer.

**Elemental analyses**: Analyses were carried out at the Mikroanalytisches Laboratorium der Chemischen Laboratorien, Universität Freiburg. For some compounds, especially for the oligomeric and polymeric materials, we could not obtain analytically pure samples: contamination was due to phosphorus-based impurities from the catalyst,[42] which proved difficult to remove by chromatography.

**Electrochemistry**: Cyclic voltammetry, square-wave voltammetry, and differential pulse voltammetry were performed on an EG&G PAR 263A potentiostat. All cyclic voltammogramms were recorded in dry $CH_3CN$ or dry $CH_2Cl_2$ under an argon atmosphere at ambient temperature or at $-30\,^\circ$C. A three-electrode configuration was employed. The working electrode was a platinum disk (diameter 1 mm) sealed in soft glass with a platinum wire counter-electrode. The pseudo-reference electrode was a silver wire. Potentials were calibrated internally against the formal potential of cobalticinium perchlorate ($-0.94$ V vs. Ag/AgCl), octamethylferrocene ($-0.025$ V vs. Ag/AgCl), or ferrocene [0.40 V (0.44 V) vs. Ag/AgCl in $CH_3CN$ ($CH_2Cl_2$)]. Solutions contained approximately $2 \times 10^{-4}$ M compound. [N($n$Bu)$_4$][PF$_6$] (0.1 M) was used as a supporting electrolyte. In all complexes the separation of anodic and cathodic peak potentials was smaller than 100 mV (scan speed 100 mV s$^{-1}$).

**Gel permeation chromatography with a low-angle laser light scattering detector (GPC–LALLS)**: This was performed in DMF/0.1 M guanidinium chloride solvent using a Milton-Roy type KMX 6 detector, a Knauer HPLC Pump 64, a Pharmacia LKB VWM 2141 UV-meter and Waters $10^3$–$10^5$ Å columns. The hydrodynamic volume/molecular mass was calibrated routinely with polystyrene standards (PSS, PL) in THF. Values of $[\alpha]_D^{20}$ were determined on a Perkin-Elmer 241 polarimeter with the samples thermostated to 20 °C.

**Materials**: The following starting materials were commercially available or synthesized according to literature procedures: (*S*)-α-iodoferrocenecarbaldehyde (**1**), [19] which was the isomer used in all reactions; 1,1′-diiodoferrocene;[43] and acetylferrocenium tetrafluoroborate (AcFc$^+$[BF$_4$]$^-$).[34] The mixed-valence ferrocenes were prepared by mixing stoichiometric amounts of the respective ferrocene (typically about 20–30 mg) and AcFc$^+$[BF$_4$]$^-$ in acetonitrile ($10^{-3}$ M). The resulting solution was transferred immediately to a UV cell for determination of the spectrum.

**General procedure for $n$Bu$_4$NF cleavage of protected ferroceneacetylenes**: A Schlenk flask was charged with the protected ferroceneacetylene and THF (5–10 mL of THF per mmol acetylene). The solution was stirred at ambient temperature and solid $n$Bu$_4$NF·3H$_2$O (1.2 equiv) was added. After stirring for 30 min the reaction was complete (TLC control). The solvent was removed, and the oily residue was chromatographed on silica.

**General procedure for coupling of ferroceneacetylenes with iodides**: A Schlenk flask was charged with a ferroceneacetylene, an iodoferrocene, and solvent (diisopropylamine unless otherwise noted). The solution was deoxygenated thoroughly and the Pd–Cu catalyst added (for the respective Pd and Cu compounds used, see the individual procedures). The reaction mixture was heated under reflux for 24 h, the cold suspension was filtered, and the volatiles were removed in vacuo. The remaining solid was purified by chromatography.

**Compound ($S_{Fc}$)-2**: **1** (21.7 g, 63.8 mmol) was refluxed in isopropyl alcohol (700 mL) in the presence of $NaBH_4$ (3.0 g, 79.4 mmol) for 16 h. The solution was cooled to 0 °C and made weakly acidic by dropwise addition of 5% $HCl_{(aq)}$ (60 mL). Solid $NaHCO_3$ (10 g) was added, the mixture was stirred for 5 min, and the resulting suspension was filtered. The volatiles were removed with a rotary evaporator at room temperature without heating, because of the sensitivity of the product to thermal decomposition, especially in the presence of acid. The resulting yellow solid was taken up in diethyl ether (500 mL), washed with water (200 mL) and brine (100 mL), and dried over $MgSO_4$. Evaporation gave a yellow solid. Yield: 97% (21.2 g, 61.9 mmol); m.p. 51 °C; $^1$H NMR ($CDCl_3$): $\delta = 4.17$ (s, 5H; $C_5H_5$), 4.24 ("t", $J = 2.5$ Hz, 1H; CpH), 4.33 (m, 1H; CpH), 4.40 (d, $J = 6.2$ Hz, 2H; C$H_2$OH), 4.47 (m, 1H; CpH).

**Compound ($S_{Fc}$)-3**: A suspension of powdered KOH (7.0 g, 125 mmol) and dimethyl sulfoxide (DMSO) (60 mL) was stirred for 10 min, then a solution of **2** (21.2 g, 62.0 mmol) in DMSO (25 mL) was added, followed immediately by neat iodomethane (4.1 mL, 9.3 g, 65.0 mmol). The reaction mixture was stirred for 1 h and then poured onto crushed ice (100 g) (**caution**: excess $CH_3$**I**!), water (300 mL) was added, and the aqueous phase was extracted with ether ($3 \times 200$ mL). The ethereal layer was separated, washed with water and brine, dried over $MgSO_4$, filtered, and evaporated. The remaining oily product, which was pure, was used for the subsequent reactions. Yield 98% (21.8 g, 61.2 mmol), dark yellow oil, which solidified when left to stand in the refrigerator. $^1$H NMR ($CDCl_3$): $\delta = 3.36$ (s, 3H; $CH_2OCH_3$), 4.13 (s, 5H; $C_5H_5$) 4.23 (m, 1H; CpH), 4.29 (d, $J = 2.8$ Hz, 2H; C$H_2$OCH$_3$), 4.32 (m, 1H; CpH), 4.45 (m, 1H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 44.85$, 57.98, 68.39, 69.20, 70.54, 71.36, 75.09, 84.52; $C_{12}H_{13}FeIO$ (356.0): calcd: C 40.49, H 3.68; found: C 40.42, H 3.66.

**Compound ($R_{Fc}$)-4**: The standard coupling procedure was followed, with **3** (26.0 g, 73.0 mmol) and triethylsilylacetylene (10.3 g, 73.0 mmol). Catalyst: $(Ph_3P)_2PdCl_2$ (1.70 g, 2.42 mmol) and CuI (922 mg, 4.84 mmol); chromatography (cyclohexane/ethyl acetate, 10:1): $R_f = 0.45$; yield 83% (22.3 g, 60.5 mmol), red oil; $[Ga]_D^{20} = -85.2$ ($c = 0.115$ g/100 mL , $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta = 0.67$ (q, $J = 6.9$ Hz, 6H; SiC$H_2$CH$_3$), 1.06 (t, $J = 6.9$ Hz, 9H; SiCH$_2$C$H_3$), 3.33 (s, 3H; CH$_2$OC$H_3$), 4.13 (s, 5H; $C_5H_5$), 4.17 ("t", $J =$ 2.5 Hz, 1H; CpH), 4.33 (m, 1H; CpH), 4.40 (d, 2H; $J = 2.6$ Hz, C$H_2$OCH$_3$), 4.46 (m, 1H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 4.57$, 7.56, 57.72, 66.44, 68.40, 68.90, 69.94, 70.51, 71.76, 85.60, 90.12, 103.96.

**Compound ($R_{Fc}$)-5**: A solution of **4** (5.0 g, 13.6 mmol) in diethyl ether (500 mL) was cooled to $-78\,^\circ$C. $t$BuLi solution (1.7 M, 8.8 mL, 1.1 equiv) was injected, yielding a dark yellow precipitate after a few minutes. After 15 min of stirring the cooling bath was removed and the mixture was stirred for 3 h at room temperature, giving a dark brown solution. It was cooled again to $-78\,^\circ$C and a solution of 1,2-diiodoethane (4.6 g, 16.3 mmol) in THF (25 mL) was added dropwise. The dark solution was warmed to room temperature in about 30 min and quenched with water. The ethereal layer was washed in turn with 10% sodium thiosulfate solution, water, and brine, and dried over $MgSO_4$. Evaporation afforded a red oil which was subjected to column chromatography (cyclohexane/ethyl acetate, 15:1; $R_f = 0.27$). Yield 87% (5.85 g, 11.8 mmol), red oil, which solidified when left to stand in the freezer; $^1$H NMR ($CDCl_3$): $\delta = 0.67$ (q, $J = 7.5$ Hz, 6H; SiC$H_2$CH$_3$), 1.05 (t, $J = 7.5$ Hz, SiCH$_2$C$H_3$), 3.34 (s, 3H; CH$_2$OC$H_3$), 4.14 (s, 5H; $C_5H_5$), 4.40–4.57 (m, 4H; CpH/C$H_2$OCH$_3$); $^{13}$C NMR ($CDCl_3$): $\delta = 5.35$, 8.41, 45.27, 58.81, 67.29, 69.62, 73.34, 74.19, 76.13, 87.37, 92.47, 103.63; IR ($CH_2Cl_2$): $\tilde{\nu} = 2154$ cm$^{-1}$ (FcC≡CSi); $C_{20}H_{27}FeIOSi$ (494.27): calcd: C 48.60, H 5.51; found: C 48.41, H 5.56.

**($R_{Fc}$)-6**: The ferroceneacetylene was obtained by the general procedure for $n$Bu$_4$NF cleavage of **5** (1.0 g, 2.02 mmol). Chromatography (cyclohexane/ethyl acetate, 10:1; $R_f = 0.17$); yield 97% (750 mg, 1.96 mmol), orange solid; m.p. 48 °C; $^1$H NMR ($CDCl_3$): $\delta = 2.87$ (s, 1H; ≡CH), 3.37 (s, 3H; $CH_2OCH_3$), 4.17 (s, 5H; $C_5H_5$), 4.49 (s, 2H; C$H_2$OCH$_3$), 4.51 (d, $J = 2.7$ Hz, 1H; CpH), 4.57 (d, $J = 2.7$ Hz, 1H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 44.46$, 58.08, 65.18, 68.67, 72.76, 73.32, 75.30, 76.80, 80.17, 86.61.

**Polymerization of 6 to give the stereoregular polymer 7**: The typical coupling procedure was applied to **6** (380 mg 1.00 mmol), with Pd(PPh$_3$)$_4$, CuI, and PPh$_3$ (5 mol% of each) as catalyst. The solvent for the polymerization reactions was DMF/($i$Pr)$_2$NH (1:1). In this mixture the polymers produced in the course of reaction remained soluble, whereas in ($i$Pr)$_2$NH alone oligomers were precipitated from the reaction mixture. The solvent mixture was removed under vacuum and the remaining product


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purified by chromatography. The polymer was dissolved in $CHCl_3$ and applied to the column; elution with $CHCl_3$ removed impurities. With $CHCl_3/CH_3OH$ (10:1) the first ferrocene polymer (**$7_1$**) was removed. Fractionation of the remaining mixture of polymers with $CHCl_3$/MeOH/$Et_2NH$ (10:1:1) resulted in two dark red eluents, **$7_2$** and **$7_3$**. Polymer **$7_1$**: Yield 44% (110 mg); $[\alpha]_D^{20} = -198.0$ ($c = 0.113$ g/100 mL , $CHCl_3$); polymer **$7_2$**: yield 20% (50 mg); polymer **$7_3$**: yield 16% (40 mg). $^1$H NMR($CDCl_3$): $\delta = 3.38$ (s, $CH_2OCH_3$), 4.23 (s, $C_5H_5 + CpH$), 4.66 and 4.75 (s, $CpH + CH_2OCH_3$); IR ($CH_2Cl_2$): $\tilde{\nu} = 2217$ cm$^{-1}$ (vw, FcC≡CFc); $(C_{12}H_{12}FeO)_n$ ((228.07)$_n$): calcd: C 63.20, H 5.30; found: C 61.59, H 5.82.

**Compound ($R_{Fc}$)-8**: Standard $n$Bu$_4$NF cleavage of **4** (5.0 g, 13.6 mmol). Chromatography (cyclohexane/ethyl acetate, 10:1): $R_f = 0.33$; yield (based on **4**): 96% (3.3 g, 13.0 mmol), orange solid; m.p. 47 °C; $^1$H NMR ($CDCl_3$): $\delta = 2.82$ (s, 1H; ≡CH), 3.34 (s, 3H; $CH_2OCH_3$), 4.17 (s, 5H; $C_5H_5$) 4.20 (m, 1H; CpH), 4.33 (m, 1H; CpH), 4.40 (d, $J = 5.4$ Hz, 2H; $CH_2OCH_3$), 4.47 (m, 1H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 60.58$, 67.97, 71.22, 71.67, 72.84, 73.26, 74.79, 78.53, 84.01, 88.39; $C_{14}H_{14}FeO$ (254.1): calcd: C 66.17, H 5.55; found: C 65.90, H 5.43.

**($R_{Fc}$)($R_{Fc'}$)-9**: Standard coupling procedure with **8** (1.54 g, 6.1 mmol) and (*R*)-**5** (3.0 g, 6.1 mmol). Catalyst: Pd(PPh$_3$)$_4$ (211 mg; 3 mol%), CuI (35 mg; 3 mol%), and PPh$_3$ (48 mg; 3 mol%); chromatography (cyclohexane/ethyl acetate, 15:1): $R_f = 0.11$; yield 63% (2.36 g, 3.8 mmol), red oil; $^1$H NMR ($CDCl_3$): $\delta = 0.66$ (q, $J = 7.8$ Hz, 6H; $SiCH_2CH_3$), 1.06 (t, $J = 7.8$ Hz, 9H; $SiCH_2CH_3$), 3.37 (s, 3H; $CH_2OCH_3$), 3.38 (s, 3H; $CH_2OCH_3$), 4.17 (s, 10H; $C_5H_5$), 4.21 ("t", $J = 2.5$ Hz, 1H; CpH), 4.36 (m, 1H; CpH), 4.43 (d, $J = 2.8$ Hz, 2H; $CH_2OCH_3$), 4.47 (m, 1H; CpH), 4.50 (d, $J = 2.8$ Hz, 2H; $CH_2OCH_3$), 4.55 (d, $J = 11.1$ Hz, 1H; CpH), 4.68 (d, $J = 11.1$ Hz, 1H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 4.50$, 7.53, 57.77, 57.88, 67.03, 67.44, 67.49, 68.38, 68.60, 69.05, 69.98, 70.38, 71.23, 71.41, 71.51, 72.32, 83.94, 85.09, 85.18, 86.77, 90.68, 103.18.

**($R_{Fc}$)($R_{Fc'}$)-10**: $n$Bu$_4$NF cleavage of **9** (1.0 g, 1.61 mmol). Chromatography (cyclohexane/ethyl acetate, 15:1): $R_f = 0.24$; yield 95% (774 mg, 1.53 mmol), red oil; $[\alpha]_D^{20}$ −94.9 ($c = 0.117$ g/100 mL , $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta = 2.85$ (s, 1H; ≡CH), 3.38 (s, 3H; $CH_2OCH_3$), 3.40 (s, 3H; $CH_2OCH_3$), 4.18 (s, 5H; $C_5H_5$), 4.21 (s, 5H; $C_5H_5$), 4.26 (m, 1H; CpH), 4.37 (m, 1H; CpH), 4.44 (d, $J = 3.6$ Hz, 2H; $CH_2OCH_3$), 4.48 (m, 1H; CpH), 4.53 (d, $J = 2.4$ Hz, 2H; $CH_2OCH_3$), 4.63 (s, 2H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 57.86$, 57.96, 66.21, 66.98, 67.44, 68.47, 68.83, 69.15, 70.08, 70.42, 71.26, 71.52, 71.80, 72.33, 76.10, 80.53, 83.82, 85.10, 85.42, 86.74.

**($R_{Fc}$)($R_{Fc'}$)($R_{Fc''}$)-11**: Standard coupling procedure with **10** (453 mg, 895 μmol) and **5** (442 mg, 895 μmol). Catalyst: Pd(PPh$_3$)$_4$ (31 mg), CuI (5 mg), and PPh$_3$ (7 mg) (3 mol% of each); chromatography (cyclohexane/ethyl acetate, 5:1): $R_f = 0.23$; yield 56% (437 mg, 501 μmol), red oil; $[\alpha]_D^{20} = -66.9$ ($c = 0.115$ g/100 mL, $CHCl_3$); $^1$H NMR ($CDCl_3$): $\delta = 0.68$ (q, $J = 8.1$ Hz, 6H; $SiCH_2CH_3$), 1.08 (t, $J = 8.1$ Hz, 9H; $SiCH_2CH_3$), 3.39 (s, 3H; $CH_2OCH_3$), 3.40 (s, 3H; $CH_2OCH_3$), 3.45 (s, 3H; $CH_2OCH_3$), 4.19 (s, 5H; $C_5H_5$), 4.20 (s, 5H; $C_5H_5$), 4.24 (s, 5H; $C_5H_5$), 4.22 – 4.25 (m, 2H; CpH), 4.39 (m, 2H; CpH), 4.46 (d, $J = 4.0$ Hz, 2H), 4.50 (m, 1H; CpH), 4.53 (d, $J = 1.6$ Hz, 1H), 4.55 (s, 2H), 4.60 (s, 1H), 4.68 (m, 2H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 4.54$, 7.67, 57.86, 57.94, 58.01, 67.11, 67.52, 67.62, 67.72, 68.18, 68.27, 68.45, 68.68, 69.14, 70.05, 70.43, 71.24, 71.26, 71.35, 71.49, 71.66, 72.26, 72. 40, 84.05, 84.48, 84.53, 85.12, 85.31, 86.29, 86.99, 90.84, 103.13; IR ($CH_2Cl_2$): $\tilde{\nu} = 2153$ (s, FcC≡CSi), 2220 cm$^{-1}$ (w, FcC≡CFc).

**($R_{Fc}$)($R_{Fc'}$)($R_{Fc''}$)-12**: Standard $n$Bu$_4$NF cleavage of **11** (438 mg, 502 μmol). Chromatography (cyclohexane/ethyl acetate, 5:1): $R_f = 0.12$; yield 81% (309 mg, 407 μmol), red glassy solid; $[\alpha]_D^{20} = -56.0$ ($c = 0.100$ g/100 mL, $CHCl_3$); MS: $m/z$ (%): 758.3 (100); $^1$H NMR ($CDCl_3$): $\delta = 2.85$ (s, 1H; ≡CH), 3.39 (s, 3H; $CH_2OCH_3$), 3.40 (s, 3H; $CH_2OCH_3$), 3.44 (s, 3H; $CH_2OCH_3$), 4.19 (s, 5H; $C_5H_5$), 4.23 (s, 10H; $C_5H_5$), 4.21 – 4.25 (m, 2H; CpH), 4.38 (m, 1H; CpH), 4.45 (d, $J = 3.3$ Hz, 2H), 4.50 (m, 1H; CpH), 4.55 (m, 3H), 4.63 (d, $J = 1.1$ Hz, 2H), 4.66 (s, 2H); $^{13}$C NMR ($CDCl_3$): $\delta = 57.87$, 57.96, 58.03, 66.34, 67.08, 67.41, 67.74, 68.06, 68.47, 68.75, 69.16, 70.44, 71.28, 71.33, 71.51, 71.89, 72.27, 72.36, 76.15, 80.48, 84.00, 84.30, 84.74, 85.12, 85.38, 86.24, 86.92; $C_{42}H_{38}Fe_3O_3$ (758.5): calcd: C 66.53, H 5.05; found: C 65.98, H 5.26.

**($R_{Fc}$)($R_{Fc'}$)($R_{Fc''}$)($R_{Fc'''}$)-13**: Standard coupling procedure with **12** (182 mg, 240 μmol) and **5** (170 mg, 344 μmol). Catalyst: Pd(PPh$_3$)$_4$ (14 mg), CuI (2 mg), PPh$_3$ (3 mg) (5 mol% of each). Chromatography (cyclohexane/ethyl acetate = 5:1): $R_f = 0.34$; yield 55% (148 mg, 132 μmol,), red glassy solid; $^1$H NMR ($CDCl_3$): $\delta = 0.67$ (q, $J = 7.9$ Hz, 6H; $SiCH_2CH_3$), 1.07 (t, $J = 7.9$ Hz, 9H; $SiCH_2CH_3$), 3.39 (s, 6H; $CH_2OCH_3$), 3.44 (s, 3H; $CH_2OCH_3$), 3.45 (s, 3H; $CH_2OCH_3$), 4.20 (s, 10H; $C_5H_5$), 4.24 (s, 10H; $C_5H_5$), 4.25 (m, 2H; CpH), 4.39 (m, 1H; CpH), 4.46 (d, $J = 3.4$ Hz, 2H; $CH_2OCH_3$), 4.50 (m, 1H; CpH), 4.53 (d, $J = 1.8$ Hz, 1H), 4.56 (s, 4H; $CH_2OCH_3$), 4.59 (m, 1H; CpH), 4.65 – 4.72 (m, 5H; $CpH + CH_2OCH_3$); $^{13}$C NMR ($CDCl_3$): $\delta = 4.54$, 7.57, 57.86, 57.94, 58.00, 58.02, 67.09, 67.52, 67.63, 67.68, 67.74, 67.82, 68.18, 68.23, 68.30, 68.41, 68.46, 68.71, 69.15, 70.07, 70.43, 71.25, 71.27, 71.32, 71.35, 71.50, 71.66, 72.28, 72.40, 84.04, 84.42, 84.54, 84.62, 85.12, 85.34, 86.25, 86.45, 87.00, 90.86, 103.12.

**($R_{Fc}$)($R_{Fc'}$)($R_{Fc''}$)($S_{Fc'''}$)-14**: Standard $n$Bu$_4$NF cleavage of **13** (126 mg, 112 μmol). Chromatography (cyclohexane/ethyl acetate, 5:1): $R_f = 0.16$; yield 78% (88 mg, 87 μmol), red glassy solid; $^1$H NMR ($CDCl_3$): $\delta = 2.86$ (s, 1H; ≡CH), 3.39 (s, 3H; $CH_2OCH_3$), 3.41 (s, 3H; $CH_2OCH_3$), 3.44 (s, 3H; $CH_2OCH_3$), 3.45 (s, 3H; $CH_2OCH_3$), 4.20 (s, 5H; $C_5H_5$), 4.22 (s, 5H; $C_5H_5$), 4.24 (s, 10H; $C_5H_5$), 4.39 (m, 1H; CpH), 4.46 (d, $J = 3.6$ Hz, 2H;$CH_2OCH_3$), 4.50 (m, 1H; CpH), 4.54 – 4.58 (m, 7H; CpH), 4.64 (s, 2H; $CH_2OCH_3$), 4.62 (s, 2H; $CH_2OCH_3$), 4.63 (s, 2H; $CH_2OCH_3$); $^{13}$C NMR ($CDCl_3$): $\delta = 57.86$, 57.96, 58.02, 66.35, 67.08, 67.41, 67.70, 67.74, 68.16, 68.18, 68.37, 68.44, 68.47, 68.74, 69.16, 70.08, 70.44, 71.26, 71.29, 71.34, 71.51, 71.90, 72.29, 72.37, 76.16, 80.48, 84.03, 84.38, 84.48, 84.68, 85.13, 85.37, 86.26, 86.42, 86.93; $C_{56}H_{49}Fe_4O_4$ (1009.39): calcd: C 66.64, H 4.89; found: C 66.22, H 4.95.

**($R_{Fc}$)($R_{Fc'}$)($R_{Fc''}$)($R_{Fc'''}$)-15**: A solution of **10** (200 mg, 395 μmol), TMEDA (100 μL, 1 mmol), and CuCl (99 mg, 1.0 mmol) in acetone (20 mL) was warmed to 30 °C. Oxygen was bubbled through the solution for 2 h with stirring. After evaporation under reduced pressure, the residue was taken up in dichloromethane, then washed twice with water and brine, and the organic layer was dried over $MgSO_4$. Evaporation yielded a red solid. Chromatography (cyclohexane/ethyl acetate, 5:1): $R_f = 0.08$; yield 79% (158 mg, 156 μmol), red solid; m.p. 134 °C; $^1$H NMR ($CDCl_3$): $\delta = 3.39$ (s, 6H; $CH_2OCH_3$), 3.44 (s, 6H; $CH_2OCH_3$), 4.19 (s, 10H; $C_5H_5$), 4.24 ("t", $J = 2.5$ Hz, 2H; CpH), 4.27 (s, 10H; $C_5H_5$), 4.38, (m, 2H; CpH), 4.45 (d, $J = 4.6$ Hz, 4H; $CH_2OCH_3$), 4.49 (m, 2H; CpH), 4.58 (d, $J = 2.3$ Hz, 2H), 4.61 (d, $J = 2.3$ Hz, 2H), 4.65 (s, 4H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 57.82$, 58.02, 65.82, 66.81, 67.47, 68.46, 69.11, 69.30, 70.08, 70.40, 71.50, 71.85, 72.22, 72.41, 73.27, 77.58, 83.64, 85.09, 85.67, 87.20.

**Compound 16**: Standard coupling procedure with **5** (700 mg, 1.42 mmol) and triethylsilylacetylene (254 μL, 198 mg, 1.42 mmol). Catalyst: $(Ph_3P)_2PdCl_2$ (50 mg, 2.42 mmol) and CuI (28 mg, 4.84 mmol); chromatography (cyclohexane/ethyl acetate, 40:1): $R_f = 0.41$; yield 85% (612 mg, 1.21 mmol), red oil; $^1$H NMR ($CDCl_3$): $\delta = 0.65$ (q, $J = 7.7$ Hz, 12H; $SiCH_2CH_3$), 1.05 (t, $J = 7.7$ Hz, 18H; $SiCH_2CH_3$), 3.33 (s, 3H; $CH_2OCH_3$), 4.13 (s, 5H; $C_5H_5$), 4.47 (s, 2H; $CH_2OCH_3$), 4.55 (s, 2H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 4.55$, 7.55, 57.92, 67.37, 67.57, 71.72, 72.51, 87.54, 90.71, 103.12.

**Compound 17**: Standard $n$Bu$_4$NF cleavage of **16** (512 mg, 1.01 mmol). Chromatography (cyclohexane/ethyl acetate, 20:1): $R_f = 0.13$; yield 94% (264 mg, 0.95 mmol), orange solid; m.p. 54 °C; $^1$H NMR ($CDCl_3$): $\delta = 2.83$ (s, 2H; ≡CH), 3.35 (s, 3H; $CH_2OCH_3$), 4.19 (s, 5H; $C_5H_5$), 4.51 (s, 2H; $CH_2OCH_3$), 4.58 (s, 2H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 57.87$, 66.45, 67.10, 71.85, 72.40, 76.21, 80.25, 87.44.

**($R_{Fc}$)($R_{Fc''}$)-18**: Standard coupling procedure with **17** (130 mg, 467 μmol) and **3** (416 mg, 1.17 mmol). Catalyst: Pd(PPh$_3$)$_4$ (16 mg), CuI (3 mg), and PPh$_3$ (4 mg) (3 mol% of each); chromatography (cyclohexane/ethyl acetate, 5:1): $R_f = 0.16$; yield 25% (86 mg, 117 μmol), red oil; MS: $m/z$ (%): 734.3 (100); $^1$H NMR ($CDCl_3$): $\delta = 3.39$ (s, 3H; $CH_2OCH_3$), 3.42 (s, 3H; $CH_2OCH_3$), 3.47 (s, 3H; $CH_2OCH_3$), 4.19 (s, 10H; $C_5H_5$), 4.23 (s, 5H; $C_5H_5$), 4.24 – 4.28 (m, 2H; CpH), 4.36 – 4.42 (m, 2H; CpH), 4.44 – 4.48 (m, 3H), 4.48 – 4.52 (m, 3H), 4.55 (s, 2H), 4.70 (d, $J = 1.1$ Hz, 2H); $^{13}$C NMR ($CDCl_3$): $\delta = 57.86$, 57.89, 58.04, 67.10, 67.14, 67.86, 68.46, 68.55, 68.57, 69.17, 69.28, 70.06, 70.42, 70.44, 71.20, 71.29, 71.51, 71.61, 71.90, 72.22, 84.13, 84.90, 85.12, 85.29, 85.96.

**($R_{Fc''}$)($R_{Fc''}$)-19**: Standard coupling procedure with 1,1′-diiodoferrocene (200 mg, 457 μmol) and **8** (255 mg, 914 μmol). Catalyst: Pd(PPh$_3$)$_2$Cl$_2$ (16 mg) and Cu(CH$_3$COO)$_2$·H$_2$O (5 mg) (5 mol% of each); chromatography (cyclohexane/ethyl acetate, 5:1): $R_f = 0.47$; yield 28% (87 mg, 126 μmol) red oil, and $R_f = 0.23$ (**20b**) (45 mg, 88 μmol), red oil. Small amounts of **20a** were also formed, which had almost the same $R_f$ value as **20b**. Compound **20b** was identified as the *cis*-vinylene isomer. MS: $m/z$ (%): 690.3 (0.6); $^1$H NMR ($CDCl_3$): $\delta$ 3.30 (s, 3H; $CH_2OCH_3$), 3.32 (s, 3H;

$CH_2OCH_3$), 4.10–4.18 (m, 16H; CpH), 4.28–4.46 (m, 12H; CpH + $CH_2OCH_3$).

**Compound 20b**: $^1$H NMR ($CDCl_3$): $\delta = 3.37$ (s, 3H; $CH_2OCH_3$), 3.40 (s, 3H; $CH_2OCH_3$), 4.22 (s, 5H; $C_5H_5$), 4.24 (s, 5H; $C_5H_5$), 4.22–4.29 (m, 2H; CpH), 4.35 (m, 1H; CpH), 4.41 (m, 1H; CpH), 4.51 (d, $J = 11.1$ Hz, 2H; $CH_2OCH_3$), 4.54 (m, 1H; CpH), 4.58 ("t", $J = 2.1$ Hz, 1H; CpH), 4.66 (d, $J = 11.1$ Hz, 2H; $CH_2OCH_3$), 5.58 (d, $J = 1.9$ Hz, 1H; =CH), 5.75 (d, $J = 1.9$ Hz, 1H; =CH); $^{13}$C NMR ($CDCl_3$): $\delta = 57.59$, 57.86, 67.75, 68.59, 69.18, 69.65, 69.93, 70.08, 70.12, 70.28, 71.69, 72.13, 80.50, 85.12, 85.35, 85.82, 88.45, 120.10, 128.39.

**($R_{Fc}$)($R_{Fc'}$)-20**: Standard coupling procedure with **8** (159 mg, 626 μmol) and (*S*)-**3** (223 mg, 626 μmol). Catalyst: $Pd(PPh_3)_4$ (22 mg), CuI (3.6 mg), and $PPh_3$ (4.9 mg) (3 mol% of each). Chromatography (cyclohexane/ethyl acetate, 10:1): $R_f = 0.16$; yield 65% (196 mg, 407 μmol), red solid; m.p. 113 °C; $^1$H NMR ($CDCl_3$): $\delta = 3.41$ (s, 6H; $CH_2OCH_3$), 4.18 (s, 10H; $C_5H_5$), 4.22 ("t", $J = 2.5$ Hz, 2H; CpH), 4.37 (m, 2H; CpH), 4.42–4.56 (m, 6H; CpH + $CH_2OCH_3$); $^{13}$C NMR ($CDCl_3$): $\delta = 57.85$, 67.44, 68.33, 69.25, 69.92, 70.35, 71.53, 84.75; $C_{26}H_{26}Fe_2O_2$ (482.18): calcd: C 64.76, H 5.43; found: C 64.77, H 5.48.

**($R_{Fc}$)($R_{Fc'}$) 20a**: **8** (200 mg, 0.79 mmol), TMEDA (100 μL, 1 mmol), and CuCl (99 mg, 1.0 mmol) were dissolved in acetone (20 mL), and the solution was warmed to 30 °C. Oxygen was bubbled through the solution for 2 h with stirring. After the acetone had been removed under reduced pressure, the residue was taken up in dichloromethane and washed twice with water and brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated, yielding a red oil. Chromatography (cyclohexane/ethyl acetate, 10:1): $R_f = 0.11$; yield 83% (165 mg, 0.66 mmol), orange solid; m.p. 151 °C; MS: *m*/*z* (%): 506.2 (99.7); $^1$H NMR ($CDCl_3$): $\delta = 3.37$ (s, 6H; $CH_2OCH_3$), 4.23 (s, 10H; $C_5H_5$), 4.26 ("t", $J = 2.8$ Hz, 2H; CpH), 4.39 (m, 2H; CpH), 4.42 (d, $J = 2.8$ Hz, 4H; $CH_2OCH_3$), 4.54 (m, 2H; CpH); $^{13}$C NMR ($CDCl_3$): $\delta = 57.90$, 64.86, 68.96, 69.02, 70.46, 70.57, 72.40, 73.05, 78.01, 86.30.

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