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Ferrocenes Bearing Highly Extended π Systems with Nitrile, Nitro, and Dimethylamino End Groups

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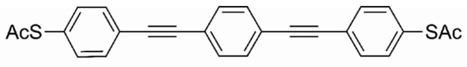
Oligophenylene-ethynylenes are a popular class of molecular wires for molecular electronics. Replacement of some, not all, of the 1,4-phenylene units by 1,1′-ferrocenylene moieties generates less rigid entities with a limited conformational flexibility. Within this concept, the syntheses of some 1,1′-disubstituted ferrocenes that bear arylethynyl or 4-(arylethynyl)phenyl substituents is presented. In contrast to related compounds with sulfur end groups that were prepared previously, the versions presented here have nitrile end groups, which, according to reported precedence, may serve as points of attachment to gold surfaces. A crystal structure analysis of an unusual diferrocenylethyne derivative is included. In addition, one representative with a push-pull disubstitution that has a nitro and a dimethylamino end group is presented. Many of the prepared compounds have been characterized by cyclic voltammetry.

Introduction

Since the discovery of ferrocene as the first sandwich complex by Kealy and Pauson[1] more than 60 years ago, this compound has formed the basis for many diverse developments in organometallic chemistry.[2,3] These include catalysis using ferrocene ligands,[4–10] organic synthesis,[11–13] materials science,[14–18] molecular devices,[19,20] and biomolecules.[21] The continued interest in ferrocene chemistry has its roots in the attractive combination of important properties: Ferrocene is an electron-rich aromatic compound with a three dimensional structure. This structure makes it stereochemically interesting because unsymmetrically disubstituted cyclopentadienyl ligands cause planar chirality, which is a particularly stable form of chirality. Ferrocene is redox active, indeed, the reversible one-electron oxidation is used as a standard for cyclic voltammetry.[22,23] There are many compounds in which an aromatic benzene ring has been replaced by a ferrocene moiety, with examples including topologically remarkable compounds such as superphane[24] or helicene,[25] medicinally important compounds such as tamoxifen,[21,26] or reactions such as the electrophilic acylation, which is nowadays included in basic chemical education.[27] Catalysts such as 4-(dimethylamino)pyridine[28] (DMAP) have been modified by anellation with a ferrocene unit, rendering the catalyst chiral.[29]

One class of compounds with relevance for molecular electronics are so-called oligophenylene-ethynylenes (OPE) such as **1**,[30] in which 1,4-phenylene and ethynylene units are combined to give extended π systems that can be used as molecular wires.[30–33] These molecules form rigid rods, and the ends are equipped with so-called “alligator clips”, which are functional groups allowing for the attachment of the molecular wire at a gold surface. These end groups are usually thioacetyl groups,[30] but *tert*-butylsulfanyl or nitrile groups have also been used.[34,35]



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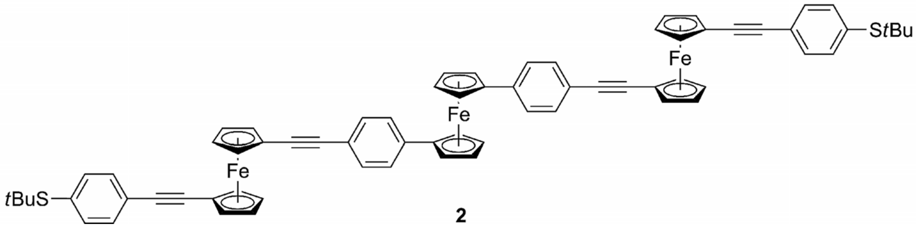

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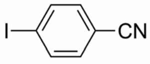
Our concept in this context is based on the replacement of some, not all, of the 1,4-phenylene units in such a molecular wire as in **2**.[36] In this way, the usually rigid linear wire gains some limited conformational flexibility, because the ferrocene units act as hinges that can be compared to those of a foldable ruler. In addition, the wire becomes three dimensional, so that π,π stacking of more than one wire becomes less likely.

In compounds such as **2**, *tert*-butylsulfanyl end groups were used because the conditions of the synthesis of **2** turned out to be incompatible with the more sensitive thioacetal groups. According to a method developed by Mayor et al., these groups should be transformed into thioacetyl substituents.[35] However, this method failed with ferrocene derivatives. As an alternative, we envisaged the use of nitrile end groups instead.[34,37] Here, we report the synthesis and characterization of some ferrocene derivatives with arylalkynyl substituents and nitrile or other nitrogen-containing end groups. The extended π systems make these compounds interesting with respect to their redox behavior.

Results and Discussion

The syntheses of ferrocenes with substituents bearing nitrile end groups can be achieved by coupling of suitable ferrocene derivatives with building blocks such as **3**–**5**. Among these, 4-iodobenzonitrile (**3**) is commercially available, and 4-ethynylbenzonitrile (**4**) is easily obtained from **3** and trimethylsilylethyne by Sonogashira coupling with microwave heating in a significantly improved yield of 99 %,[37,38] followed by quantitative protiodesilylation.[37] Compound **5** was prepared according to a method developed by Fuson et al.[39]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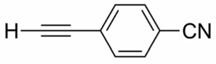
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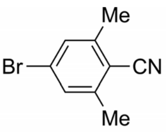

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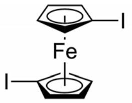
According to our earlier experience,[36,40,41] ethynylferrocene[42] (**6**) is a suitable starting material for the synthesis of monosubstituted systems by Sonogashira coupling reactions using microwave heating. The respective reaction with **3** afforded [2-(4-cyanophenyl)ethynyl]ferrocene (**7**) in 98 % yield as compared with 84 % yield, which had previously been achieved by using 4-bromobenzonitrile instead.[43] In a similar manner, {4-[(4-cyanophenyl)ethynyl]phenyl}ferrocene (**9**) was obtained as red crystals from (4-ethynylphenyl)ferrocene[44] (**8**) in 100 % yield. Whereas **7** was identified on the basis of its published analytical data,[43] **9** was characterized spectroscopically.

1,1′-Diiodoferrocene (**10**)[45] is the starting material of choice for the bidirectional synthesis of respective 1,1′-disubstituted systems with a ferrocene unit integrated in the extended π system. However, to have the option of attaching two different substituents, we found 1-iodo-1′-ethynylferrocene (**11**) to be useful. The latter compound is available by a mono Sonogashira coupling of **10** with trimethylsilylethyne, followed by protiodesilylation.[41,46–49]



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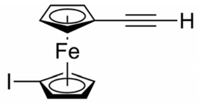
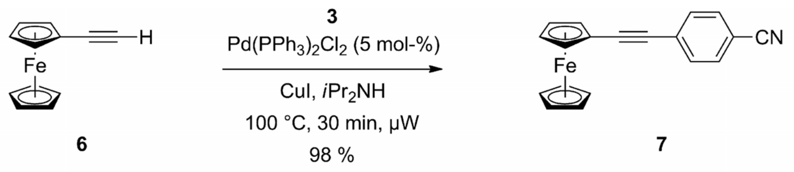
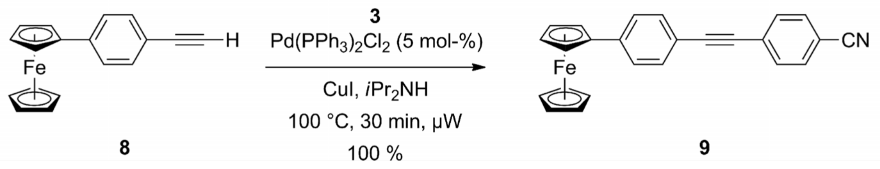


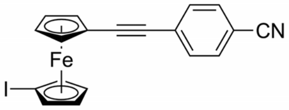
11

Treatment of **11** with **3** (2 equiv.) with microwave heating in a Sonogashira coupling, afforded 1-[(4-cyanophenyl)ethynyl]-1′-iodoferrocene (**12**) in 96 % yield as an orange-red crystalline solid. The corresponding reaction with 4-bromo-2,6-dimethylbenzonitrile (**5**; 1.5 equiv.) instead of **3** gave a less clear result: The isolated product mixture was separated chromatographically, and 16 % of starting material **11** was obtained in addition to 46 % unconsumed **5**. After Sonogashira coupling, **13** was isolated as the main product in 50 % yield as an orange-red solid. Finally, **14** was isolated as a side-product in 8 % yield as a dark-red solid. Whereas **12** and **13** were easily characterized based on their IR, NMR (^{1}H, ^{13}C), and MS data, **14** turned out to be an interesting diyne with two ferrocene units, which was characterized crystallographically. The reduced chemoselectivity in the second reaction can be understood by assuming a slower coupling reaction of the less reactive bromide **5** compared with that of **3**. This provides sufficient time for unreacted **11** to undergo a Sonogashira coupling with **13** that was already formed. In principle, this reaction sequence indicates the





possibility of forming oligo(1,1′-ferrocenylidene)ethynylenes directly from **11**.



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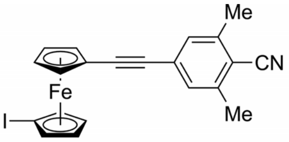

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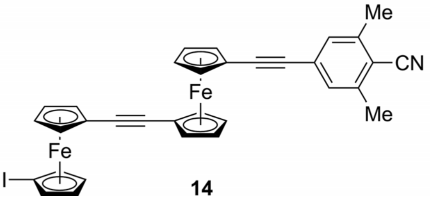

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Compound **14** is a diferrocenylethyne derivative with an unusual substitution pattern: whereas one of the outer cyclopentadienyl ligands bears an iodo substituent, the second bears a highly unsaturated (3,5-dimethyl-4-cyanophenyl)ethynyl group. The structure of **14** is given in Figure 1. The diferrocenylethyne subunit in **14** adopts the same conformation as the unsubstituted compound with almost coplanar cyclopentadienyl ligands at both ends of the triple bond.[51] As clearly shown in Figure 1, top view, the dialkynylferrocene subunit adopts an intuitively more hindered *syn* conformation instead of a less crowded *anti* conformation with respect to the alkynyl substituents. This is reflected by interatomic distances of C1–C8 (334.9 pm), C11–C23 (339.3 pm), C12–C24 (347.1 pm), and C13–C25 (363.1 pm), which are in the range of the double van der Waals radius of carbon.[52] Such a conformation has previously been observed with 1,1′-disubstituted ferrocenes with aromatic or alkynyl substituents, for example 1,1′-bis[2-(5-ethynyl)thienyl]ferrocene[36] or 1,1′-bis(phenylethynyl)ferrocene.[53] The fact that not only functionalized compounds such as **14** but also unfunctionalized derivatives adopt such a conformation, makes intra- or intermolecular polar interactions between functional groups less likely to be the reason for this conformation. Although crystal packing effects have been invoked in the case of 1,1′-bis(phenylethynyl)ferrocene,[53] one might also consider an attractive π,π interaction between the highly unsaturated substituents.

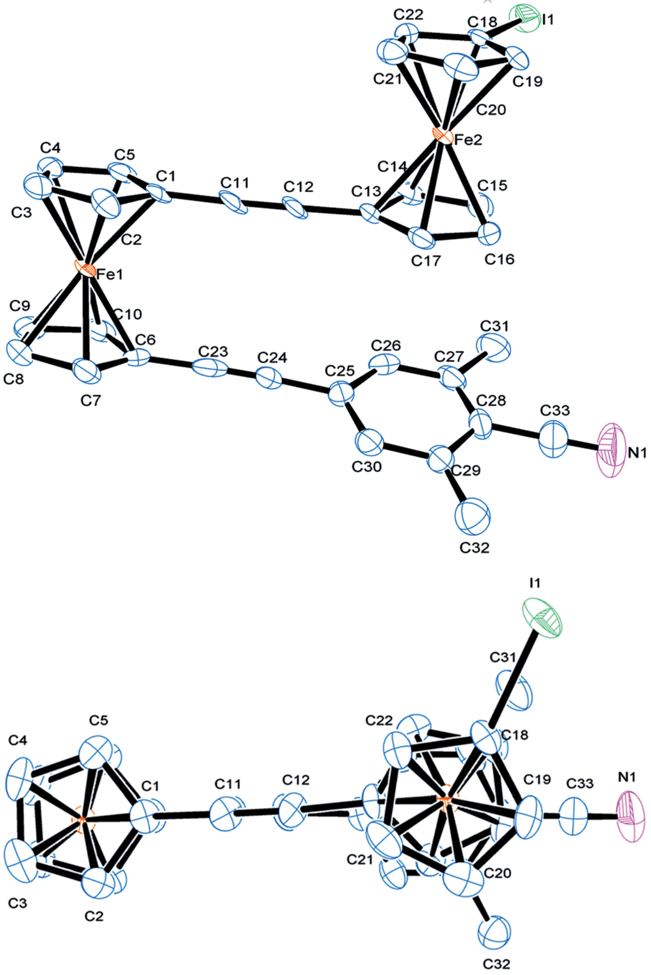
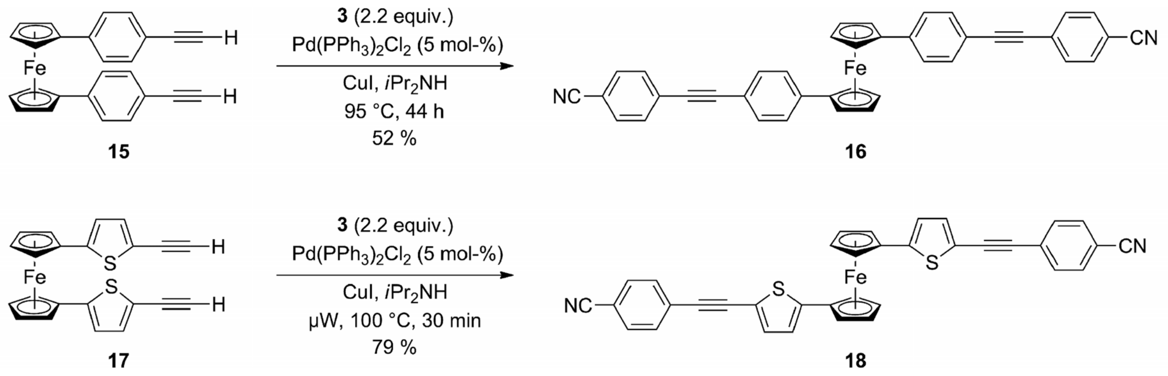
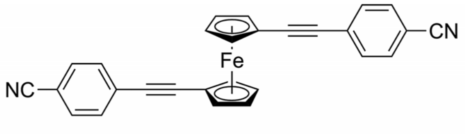


Figure 1. Structure of **14** in the crystal;[50] (top) side view (bottom) top view; some atom numbers have been omitted for clarity. Selected bond lengths [pm], interatom distances [pm], and bond angles [°]: C1–C2 142.8(7), C1–C5 141.3(8), C1–C11 142.8(7), C2–C3 139.8(8), C3–C4 142.7(9), C4–C5 140.4(8), C6–C7 143.7(8), C6–C10 142.9(9), C6–C23 144.4(8), C7–C8 140.5(8), C8–C9 141.6(9), C9–C10 141.5(8), C11–C12 117.8(7), C12–C13 144.6(7), C13–C14 144.1(7), C13–C17 142.6(8), C14–C15 142.3(7), C15–C16 142.0(8), C16–C17 140.5(7), C18–C19 142.6(8), C18–C22 140.8(7), C18–I1 208.3(5), C19–C20 142.0(8), C20–C21 140.3(8), C21–C22 142.7(8), C23–C24 116.0(8), C24–C25 144.1(8), C28–C33 144.3(7), C33–N1 114.1(6); C1–C6 334.9, C11–C23 339.3, C12–C24 347.1, C13–C25 363.1; C1–C11–C12 178.2(6), C11–C12–C13 177.2(6), C6–C23–C24 176.9(7), C23–C24–C25 177.6(7).

More extended bidirectional systems were obtained by Sonogashira coupling in good yields, when **15** or **17** were used as starting materials.[36] The coupling of **15** with 4-iodobenzonitrile (**3**) under conventional reaction conditions (95 °C, 44 h) gave **16** in 52% yield, whereas the reaction of **17** under microwave heating (100 °C, 30 min) gave **18** in a significantly higher yield of 79%. Compounds **16** and **18** were characterized spectroscopically, and their spectra were found to resemble those of the corresponding *tert*-butylsulfanyl derivatives.[36]

To obtain compounds with triple bonds directly at the ferrocene moiety, **12** was treated with 4-ethynylbenzonitrile in a Sonogashira reaction with microwave heating (300 W, 100 °C, 120 min). The reaction resulted, after chromatographic purification, in 26% yield of 1,1′-bis(4-cyanophenylethynyl)ferrocene (**19**), which was obtained as a dark-orange solid that was barely soluble in common solvents. The corresponding reaction of **13** afforded **20** in only 8% yield, in addition to 80% unconsumed **13**. The respective reaction with 1-(*tert*-butylsulfanyl)-4-ethynylbenzene instead of 4-ethynylbenzonitrile gave **21** in only 18% yield, in addition to unconsumed starting materials. All three compounds were characterized spectroscopically. The introduction of a *tert*-butylsulfanyl substituent proved beneficial for the solubility of the compound, and its ^{13}C NMR spectrum could be obtained in $CDCl_3$.





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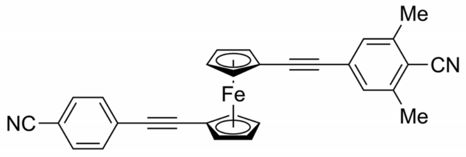

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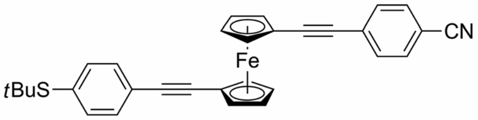

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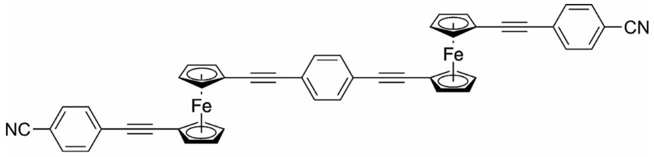

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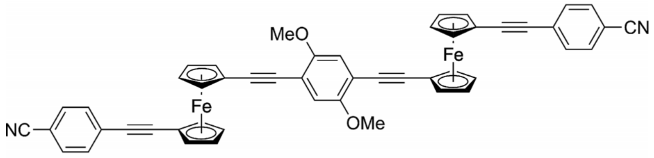

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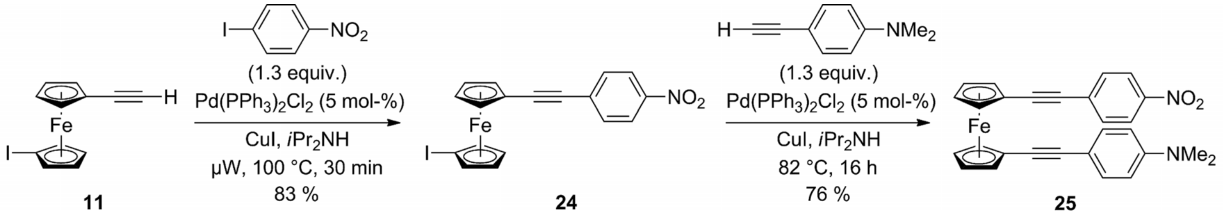
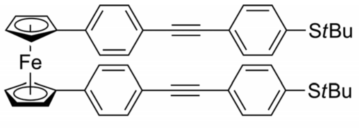
In an attempt to prepare derivatives with more than one ferrocene moiety, **12** was treated with 1,4-diethynylbenzene under the same reaction conditions. However, the double coupling product **22** was obtained in only 8% yield in addition to 51% unconsumed **12**. Compound **22** was obtained as an orange-brown solid that was almost insoluble in common organic solvents, which prevented ^{13}C NMR spectroscopic analysis. In a similar way, **23** was obtained in 15% yield by using 1,4-diethynyl-2,5-dimethoxybenzene instead of 1,4-diethynylbenzene. As with **22**, compound **23** was not sufficiently soluble in any solvent that was suitable for ^{13}C NMR spectroscopy. Compound **23** deserves particular interest because of the central hydroquinone derived moiety, which adds another redox-active structure to the two ferrocene units. Compounds **22** and **23** were identified on the basis of their ^{1}H NMR, IR, and mass spectra.

We then envisaged the synthesis of a push-pull disubstituted derivative. The synthesis started with **11**, from which nitro-substituted compound **24** was obtained in 83% yield as purple crystals by treatment with 4-iodonitrobenzene under Sonogashira conditions with microwave heating (300 W, 100 °C, 30 min). Subsequent treatment of **24** with 4-ethynyl-*N*,*N*-dimethylaniline[54] afforded the push-pull disubstituted ferrocene **25** in 76% yield; the increased yield compared with the preceding reactions might be explained by the electron-withdrawal exerted by the nitro group in **24**. Compound **25** was obtained as an orange powder, and crystallization from dichloromethane/hexane was achieved; unfortunately, the crystals were not suitable for a crystal structure analysis.

A number of the prepared compounds were investigated by cyclic voltammetry to assess their redox properties, and the results are summarized in Table 1; for comparison the data of **26**–**28** are also included.[36]





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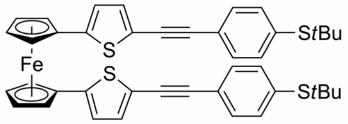

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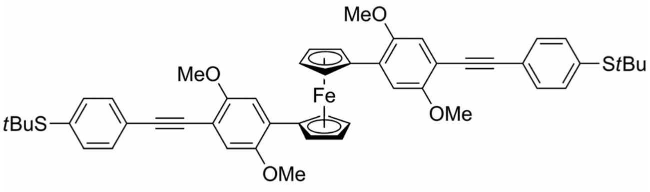

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Table 1. Cyclovoltammetry. E_{pc} = cathodic peak potential; E_{pa} = anodic peak potential; $E_{1/2}$ = half-wave potential = $(E_{pa} + E_{pc})/2$; potential vs. FcH/FcH$^+$. Solvent CH_2Cl_2 unless otherwise indicated; 20 °C; 100 mV/s; tetrabutylammonium phosphate. Compound **7** was measured in THF at 25 °C.[43]

	E_{pa} [V]	E_{pc} [V]	ΔE [V]	$E_{1/2}$ [V]
7[43]	0.330	0.180	0.15	0.255
9	0.127	–0.055	0.182	0.036
12	0.493	0.325	0.168	0.409
13	0.558	0.417	0.141	0.488
14	0.276	0.090	0.186	0.183
	0.447	0.330	0.117	0.389
16	0.064	–0.029	0.093	0.018
18	0.481	0.337	0.144	0.409
20	0.178	–0.013	0.191	0.083
21	0.283	0.088	0.195	0.186
24	0.394	0.241	0.153	0.318
25	0.006	–0.167	0.173	–0.081
	0.355	0.187	0.168	0.271
26[36]	0.129	0.000	0.129	0.065
27[36]	0.141	0.002	0.138	0.072
28[36]	0.021	–0.120	0.141	–0.050

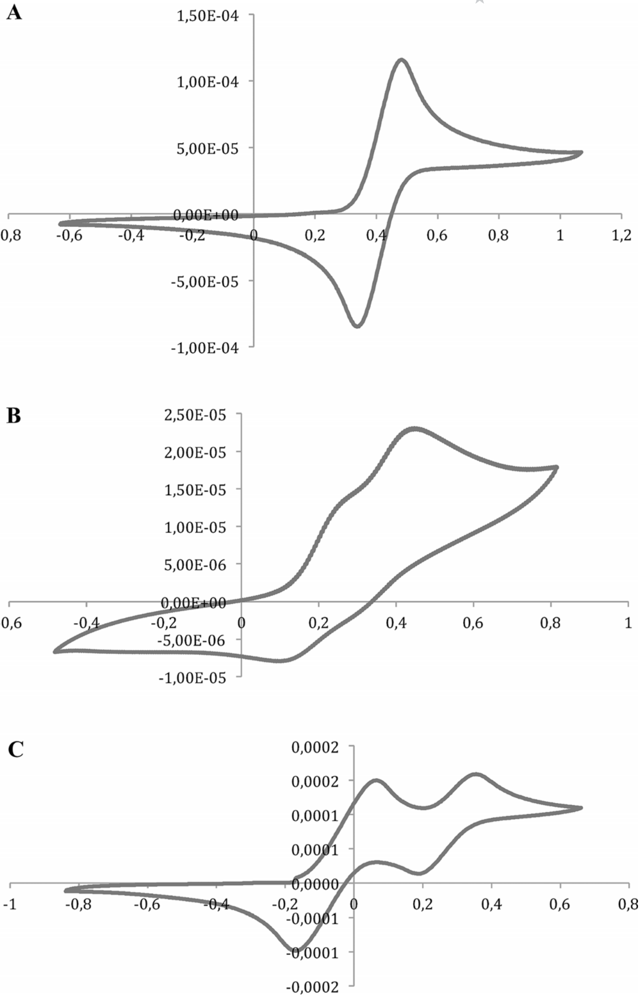

Figure 2. Selected cyclovoltammograms of **18** (A), **14** (B), and **25** (C). Conditions: 100 mV/s, *c* (TBAF) = 0.1 mol/L in CH_2Cl_2, *c* (ferrocene derivative) = 2 mmol/L, *T* = 293 K, abscissa: potential *U* [V] vs. FcH/FcH$^+$, ordinate: current *I* [mA].

With the exceptions of compounds **14** and **25**, all compounds show one reversible wave assigned to the ferrocene/ferrocenium redox processes. Compounds **14** and **25** show two reversible waves (Figure 2); these are assigned to the redox process at the two ferrocene moieties in **14**, and at the ferrocene moiety (0.271 V) and the diemethylamino group (–0.081 V) in **25**.

A comparison of the half-wave potentials obtained does not show a clear correlation with the electron demand of the substituents of the ferrocene moiety. Going from **7** to **9** shows the effect of a 1,4-phenylene moiety between the triple bond and the ferrocenyl part, which causes a reduction of the potential by 0.219 V. A comparison between compounds **7** and **12** indicates that the presence of an iodo substituent causes an increase in the half-wave potential of 0.154 V. The iodo-substituted compounds **12**–**14** and **24** show redox reactions at half-wave potentials of comparable magnitudes, with the nitro-derivative **24** having the lowest half-wave potential (0.318 V). Dialkynylferrocenes **20**, **21**, and **25** show redox processes between 0.083 and 0.271 V. For **25**, a second redox reaction is observed at –0.081 V, which is assigned to the dimethylamino group because a corresponding wave was not observed for nitro compound **24**. Replacing the nitrile substituents in **16** by *tert*-butylsulfanyl groups as in **26** causes a potential increase from 0.018 to 0.065 V. Additional attachment of the four methoxy groups reverses this, and a half-wave potential of –0.050 V is observed for **28**. Remarkably, these changes do not appear to be of general nature: replacing the nitrile groups in **18** by *tert*-butylsulfanyl groups causes a decrease of the potential of 0.337 V, which is 0.072 V for **27**. Whereas **26** and **27** have similar half-wave potentials (0.065 and 0.071 V, respectively) these are quite different for **16** and **18** (0.018 and 0.409 V, respectively).

Conclusions

A number of new ferrocenes have been prepared in which the ferrocene moiety is incorporated in an extended π system. The compounds resemble oligophenylene-ethynylenes (OPEs) with nitrile, nitro, or dimethylamino end groups, in which one of the phenylene moieties has been replaced by the 1,1′-ferrocenylene moiety, thus allowing limited conformational flexibility by rotation around the ferrocene axis. The syntheses were achieved by Sonogashira coupling reactions with a small number of building blocks. Diferrocenyl derivative **14** has been characterized crystallographically, and it adopts a conformation with eclipsed alkynyl substituents at one of the ferrocene moieties. The cyclovoltammetric measurements of the ferrocene prepared derivatives do not allow straightforward correlation between the substitution patterns and the respective redox potentials.

Experimental Section

General: All reactions were performed by using Schlenk techniques with nitrogen or argon as the inert gas. All glassware was heated at 0.1 mbar or below with a heat gun prior to use to remove any oxygen or water. Tetrahydrofuran (THF) and toluene were dried with sodium/potassium alloy/benzophenone and distilled. Pentane and dichloromethane were dried with CaH_2 and distilled. Starting materials were either commercially acquired or were prepared according to published procedures. Ferrocene was obtained as a donation from Innospec Deutschland GmbH.

^{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 δ refer to TMS (δ = 0 ppm) or to residual solvent signals. Primary, secondary, tertiary, and quaternary carbon atom signals were identified as such by APT and DEPT techniques. In some cases, signal assignments were based on 2D NMR spectra (HMQC, HMBC). IR spectra were obtained with Perkin–Elmer instruments FTIR 580 and 1170 using the ATR technique. Signal characteristics are abbreviated as s (strong), m (medium), w (weak), and br (broad). Mass spectra were obtained with a Micromass LCT instrument with lockspray source and direct injection and with a Q-TOF premier LC-MS/MS instrument with an Ionsabre-APCI-source (25 µA, 350 °C). In all cases, dichloromethane was used as the solvent. Analytical TLC was performed with Merck 60F-254 silica gel thin-layer plates. Column chromatography was performed with J. T. Baker silica gel (60 µm) as the stationary phase using the flash chromatography method.[55] Elemental analyses were obtained with an Elementar Vario EL instrument. Reactions under microwave irradiation (µW) were performed with a CEM Discover Labmate reactor in a nitrogen atmosphere ("open vessel") in a 100 mL reaction flask using the ChemDriver software. The temperature was monitored by means of an IR sensor. Some reactions were performed by using the PowerMax method. Cyclic voltammetry (CV) measurements were performed in an argon atmosphere with a Gamry Instrument Reference 600 Potentiostat/Galvanostat/ZRA. The sample compound (0.02 mmol) was dissolved in freshly distilled dichloromethane (10 mL), and tetrabutylammonium phosphate (TBAP, 0.387 g, 98%) was added corresponding to a concentration of 0.1 mol/L. The reference electrode was a Ag/Ag^+ ($AgNO_3$) electrode in acetonitrile with 0.01 mol/L $AgNO_3$ and 0.1 mol/L of TBAP. A 0.25 mm and a 0.1 mm thick platinum wire were used as the counter and working electrode, respectively. Unless otherwise mentioned, the scan rate was 100 mV/s. Freshly sublimed ferrocene was used for calibration, potentials refer to the FcH/FcH^+ redox couple. Melting points were measured with an Electrothermal IA9000 instrument.

[(4-Cyanophenyl)ethynyl]ferrocene (7):[43] Ethynylferrocene (**6**;[42] 0.10 g, 0.5 mmol, 1 equiv.) and 4-iodobenzonitrile (**3**; 0.11 g, 0.5 mmol, 1 equiv.) were dissolved in degassed (argon) diisopropylamine (20 mL) in a Schlenk flask that was suitable for microwave irradiation. After addition of $[Pd(PPh_3)_2Cl_2]$ and CuI (2 spatula tips each, ca. 5 mol-%), the mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 30 min hold) with stirring. After cooling to 25 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm), and the red-brown solid obtained was purified by column chromatography (SiO_2; 30 × 3 cm; petroleum ether/dichloromethane, 1:1 to 1:2) to give **7** (0.15 g, 0.5 mmol, 98%) as an orange-yellow solid [R_f = = 0.28 (petroleum ether/dichloromethane, 1:1)], which was identified by ^{1}H NMR spectroscopy.[43]

{4-[(4-Cyanophenyl)ethynyl]phenyl}ferrocene (9): (4-Ethynylphenyl)ferrocene (**8**;[44] 0.040 g, 0.14 mmol, 1 equiv.) and **3** (0.039 g, 0.17 mmol, 1.2 equiv.) were dissolved in degassed (argon) diisopropylamine (40 mL) in a Schlenk flask that was suitable for microwave irradiation. After addition of $[Pd(PPh_3)_2Cl_2]$ and CuI (2 spatula tips each, ca. 5 mol-%), the mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 30 min hold) with stirring. After cooling to 25 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm), which was then washed with dichloromethane, and the black-red solid obtained was purified by column chromatography (SiO_2; 20 × 3 cm; petroleum ether/dichloromethane, 1:1; R_f = 0.19) to give **9** (0.055 g, 0.14 mmol, 100%) as red crystals; m.p. 190 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.05 (s, 5 H, CpH), 4.38 (m, 2 H, CpH), 4.69 (m, 2 H, CpH), 7.46 (m, 4 H, C_6H_4), 7.62 (m, 4 H, C_6H_4-C≡N) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 66.8 (C_{Fc}H), 69.8 (C_{Fc}H), 70.0 (Cp), 84.0 (C_{Fc}C), 88.0 (C≡C), 94.5 (C≡C), 111.4 (C_{Ar}C≡N), 118.8 (C≡N), 119.3 (FcAr*C*C≡C), 126.1 (C_{Ar}HCFc), 128.6 (FcArC≡CC_{Ar}), 132.0 (C_{Ar}H), 132.1 (C_{Ar}H), 132.2 (C_{Ar}H), 141.2 ($\mathrm{C}_{\mathrm{Fc}}C_{\mathrm{Ar}}$) ppm. IR: $\tilde{\nu}$ = 2921 (m, Ar), 2851 (w), 2201 (w, C≡C), 1742 (w), 1590 (m), 1521 (w), 1408 (w), 1280 (w), 1105 (w), 1079 (w), 1032 (w), 999 (w), 883 (w), 833 (s, Ar) cm^{-1}. MS (70 eV): *m/z* (%) = 388 (54) [$(M + 1)^+$], 387 (94) [M^+], 385 (13), 266 (34), 264 (25), 121 (100) [$FeCp^+$]. HRMS: *m/z* calcd. for $C_{25}H_{17}FeN$ 387.0710; found 387.0698.

1-[(4-Cyanophenyl)ethynyl]-1′-iodoferrocene (12): 1-Ethynyl-1′-iodoferrocene (**11**;[40,46–49] 2.84 g, 8.5 mmol, 1 equiv.) and **3** (3.87 g, 16.9 mmol, 2 equiv.) were dissolved in degassed (argon) diisopropylamine (200 mL). $Pd(PPh_3)_2Cl_2$ and CuI (2 spatula tips each, ca. 5 mol-%) were added and the reaction mixture was heated at 95 °C oil bath temperature with stirring for 20 h. After cooling to 25 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm), which was then flushed with dichloromethane. The orange-red solid obtained was purified by column chromatography (SiO_2; 30 × 3 cm; petroleum ether/dichloromethane, 3:1) to give **12** (3.55 g, 8.1 mmol, 96%; R_f = 0.05) as orange-red crystals; m.p. 127–129 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.24 (m, 2 H, CpH), 4.32 (m, 2 H, CpH), 4.46 (m, 2 H, CpH), 4.49 (m, 2 H, CpH), 7.60 (m, 4 H, C_6H_4C≡N) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 41.5 (C_{Fc}I), 66.4 (C_{Fc}C), 71.0 (HC_{Fc}CC≡C or H$C_{\mathrm{Fc}}\mathrm{C}_{\mathrm{Fc}}$CC≡C), 72.6 (H$C_{\mathrm{Fc}}$CC≡C or H$C_{\mathrm{Fc}}\mathrm{C}_{\mathrm{Fc}}$CC≡C), 74.5 (H$C_{\mathrm{Fc}}$CI or H$\mathrm{C}_{\mathrm{Fc}}\mathrm{C}_{\mathrm{Fc}}$CI), 76.7 (H$C_{\mathrm{Fc}}$CI or H$\mathrm{C}_{\mathrm{Fc}}\mathrm{C}_{\mathrm{Fc}}$CI), 85.8 (C≡C), 92.6 (C≡C), 111.0 (C_{Ar}C≡N), 118.9 (*C*≡N), 129.0 (C_{Ar}C≡C), 132.0 (C_{Ar}H), 132.2 (C_{Ar}H) ppm. IR: $\tilde{\nu}$ = 2410 (m), 2200 (s, C≡C), 2025 (w), 1597 (s, Ar), 1503 (w), 1402 (w), 1156 (m), 1027 (m), 919 (w), 856 (w), 833 (m, Ar) cm^{-1}. MS (70 eV): *m*/*z* (%) = 438 (12) [M + 1]$^+$, 437 (100) [M]$^+$, 311 (28), 310 (6) [M$^+$ – I], 253 (16), 247 (6), 190 (9), 86 (31), 84 (54), 69 (5). HRMS: *m*/*z* calcd. for $C_{19}H_{12}FeIN$ 436.9364; found 436.9366.

1-([4-Cyano-3,5-dimethylphenyl]ethynyl)-1′-iodoferrocene (13) and 1-[(4-Cyano-3,5-dimethylphenyl)ethynyl]-1′-(1′-iodoferrocenylethynyl)ferrocene (14): 1-Ethynyl-1′-iodoferrocene (**11**; 1.28 g, 3.8 mmol, 1 equiv.) and **5**[39] (1.20 g, 5.7 mmol, 1.5 equiv.) were dissolved in degassed (argon) diisopropylamine (40 mL) in a Schlenk flask that was suitable for microwave heating. [$Pd(PPh_3)_2Cl_2$] and CuI (2 tips of a spatula each, ca. 5 mol-%) were added and the mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 60 min hold). After filtration through a frit covered with silica gel (10 × 3 cm) and flushing with dichloromethane, the dark red-black oil obtained was separated by column chromatography (SiO_2; 30 × 2.5 cm; petroleum ether/dichloromethane, 2:1 to 1:6) to give four fractions.

Fraction I [R_f = 0.52 (petroleum ether/dichloromethane, 2:1)]: Compound **11**, yield 0.40 g (0.6 mmol, 16 %).

Fraction II [R_f = 0.39 (petroleum ether/dichloromethane, 2:1)]: Compound **5**, yield 0.55 g (2.6 mmol, 46 %).

Fraction III [R_f = 0.21 (petroleum ether/dichloromethane, 2:1)]: Compound **13**, yield 0.88 g (1.9 mmol, 50 %); orange-red solid; m.p. 143–146 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.52 (s, 6 H, CH_3), 4.23 (m, 2 H, CpH), 4.30 (m, 2 H, CpH), 4.45 (m, 2 H, CpH), 4.48 (m, 2 H, CpH), 7.26 (s, C_6H_2) ppm. ^{1}H NMR (200 MHz, C_6D_6): δ = 2.09 (s, 6 H, CH_3), 3.86 (m, 2 H, CpH), 3.94 (m, 2 H, CpH), 4.27 (m, 2 H, CpH), 4.38 (m, 2 H, CpH), 6.99 (s, 2 H, C_6H_2) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.8 (CH_3), 41.4 ($C_{Fc}I$), 66.7 ($C_{Fc}C$), 71.0 ($C_{Fc}H$), 72.5 ($C_{Fc}H$), 74.4 ($C_{Fc}H$), 76.6 ($C_{Fc}H$), 86.1 (C≡C), 91.3 (C≡C), 112.5 ($C_{Ar}C$≡N), 117.3 (*C*≡N), 128.0 ($C_{Ar}C$≡C), 130.1 ($C_{Ar}H$), 142.2 ($C_{Ar}CH_3$) ppm. IR: $\tilde{\nu}$ = 3098 (w), 2920 (s, CH_3), 2852 (s, CH_3), 2342 (w), 2210 (s, C≡C), 1741 (w), 1593 (s, Ar), 1445 (w), 1382 (m), 1342 (w), 1278 (w), 1122 (w), 1025 (s), 962 (w), 867 (s), 822 (s, Ar) cm^{-1}. MS (70 eV): *m*/*z* (%) = 466 (19) [M + 1]$^+$, 465 (100) [M]$^+$, 340 (5), 339 (46), 338 (9) [M$^+$ – I], 322 (5), 282 (6), 267 (6), 111 (5), 97 (10), 85 (11), 71 (18). HRMS: *m*/*z* calcd. for $C_{21}H_{16}FeIN$ 464.9677; found 464.9683.

Fraction IV [R_f = 0.16 (petroleum ether/dichloromethane, 2:1)]: Compound **14**, yield 0.21 g (0.3 mmol, 8 %); dark-red solid; m.p. 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 6 H, CH_3), 4.19 (m, 4 H, CpH), 4.30 (m, 2 H, CpH), 4.33 (m, 2 H, CpH), 4.36 (m, 2 H, CpH), 4.40 (m, 2 H, CpH), 4.51 (m, 2 H, CpH), 4.54 (m, 2 H, CpH), 7.18 (s, 2 H, C_6H_2) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.8 (CH_3), 41.1 ($C_{Fc}I$), 66.0 ($C_{Fc}C$), 68.3 ($C_{Fc}C$), 68.4 ($C_{Fc}C$), 70.8 ($C_{Fc}H$), 71.0 ($C_{Fc}H$), 71.4 ($C_{Fc}H$), 71.7 ($C_{Fc}H$), 73.1 ($C_{Fc}H$), 73.4 ($C_{Fc}H$), 74.1 ($C_{Fc}H$), 76.5 ($C_{Fc}H$), 84.05 (C≡C), 84.13 (C≡C), 85.8 (C≡C), 91.7 (C_{Ar}*C*≡C), 112.2 ($C_{Ar}C$≡N), 117.4 (*C*≡N), 128.0 ($C_{Ar}C$≡C), 130.1 ($C_{Ar}H$), 142.1 ($C_{Ar}CH_3$) ppm. IR: $\tilde{\nu}$ = 2921 (w, CH_3), 2334 (w), 2210 (s, C≡C), 1598 (s, Ar), 1380 (m), 1348 (w), 1283 (w), 1203 (w), 1125 (w), 1025 (m), 936 (w), 868 (s), 808 (s, Ar) cm^{-1}. HRMS: *m*/*z* calcd. for $C_{33}H_{24}Fe_2IN$ 672.9652; found 672.9652.

Crystal Structure Analysis of 14:[50] $C_{33}H_{24}Fe_2IN$; dark-red needles; *Mr* 673.13 g/mol; crystal system: monoclinic; space group: $P2_1/n$; *a* = 6.0219(1) Å, *b* = 29.5044(3) Å, *c* = 14.7769(1) Å, α = 90.00°, β = 101.2730(10)°, γ = 90.00°; *V* = 2574.80(3) Å^3; *Z* = 4; $d_{calcd.}$ = 1.736 g/cm^3; *F*(000) = 1336; μ = 18.620 mm^{-1}; Bruker KAPPA APEX II; *T* = –40 °C; Cu-K_α irradiation: 1.54187 Å; θ-range of data collection 3.00–65.32°, measured reflections 13352 ($-7 \le h \le 6$, $-31 \le k \le 34$, $-16 \le l \le 17$), reflections/parameters/restraints 4230/334/0, solution of structure and refinement with SHELXS-97 or SHELXL-97 (Sheldrick, 1997),[56] respectively. Method of refinement full-matrix-least-square on F^2, numerical absorption correction, Goodness-of-fit (F^2) 1.023, *R* = 0.0963 (all data), *wR* = 0.1439 (all data), max./min. residual electron density 1.616, –1.339 e Å^{-3}.

CCDC-1009329 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1,1′-Bis{[4-(4-cyanophenyl)ethynyl]phenyl}ferrocene (16): 1,1′-Bis(4-ethynylphenyl)ferrocene (**15**;[36] 0.20 g, 0.5 mmol, 1 equiv.) and **3** (0.26 g, 1.1 mmol, 2.2 equiv.) were dissolved in diisopropylamine (40 mL). After addition of [$Pd(PPh_3)_2Cl_2$] and CuI (two spatula tips, each, ca. 5 mol-%), the reaction mixture was heated with stirring at 95 °C oil bath temperature for 44 h. After cooling to 23 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm), which was flushed with dichloromethane. The red solid obtained was separated by column chromatography (SiO_2; 12 × 3 cm; petroleum ether/dichloromethane, 1:2) to give two fractions:

Fraction I (R_f = 0.40): Compound **3**, yield 0.14 g (0.6 mmol, 55 % recovered); R_f = 0.40.

Fraction II (R_f = 0.15): Compound **16**, yield 0.16 g (0.3 mmol, 52 %); orange-red solid; m.p. 254–256 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.32 (m, 4 H, CpH), 4.53 (m, 4 H, CpH), 7.21 (AA′BB′, Σ*J* = 8.2 Hz, 4 H, C_6H_4), 7.34 (AA′BB′, Σ*J* = 8.2 Hz, 4 H, C_6H_4), 7.57 (m, 8 H, C_6H_4-C≡N) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 68.2 ($C_{Fc}H$), 71.1 ($C_{Fc}H$), 82.8 ($C_{Fc}C$), 88.1 (C≡C), 94.6 (C≡C), 111.4 ($C_{Ar}C$≡N), 118.7 (C≡N), 119.4 (FcAr*CC*≡C), 125.9 ($C_{Ar}HCFc$), 128.6 (FcArC≡CC_{Ar}), 131.96 ($C_{Ar}H$), 132.06 ($C_{Ar}H$), 132.14 ($C_{Ar}H$), 139.3 (Fc*C*Ar) ppm. IR: $\tilde{\nu}$ = 2921 (s, Ar), 2852 (s, Ar), 2227 (m), 2213 (m, C≡C), 1599 (m), 1527 (m), 1500 (w), 1457 (m), 1418 (w), 1407 (w), 1378 (w), 1282 (w), 1181 (w), 1138 (w), 1108 (w), 1080 (w), 1035 (w), 892 (m), 836 (s), 834 (s, Ar) cm^{-1}. HRMS: *m*/*z* calcd. for $C_{40}H_{24}FeN_2$ 588.1289; found 588.1282.

1,1′-Bis[5-(4-cyanophenylethynyl)]thienylferrocen (18): 1,1′-Bis[2-(5-ethynyl)thienyl]ferrocene (**17**;[36] 0.21 g, 0.5 mmol, 1 equiv.) and **3** (0.26 g, 1.1 mmol, 2.2 equiv.) were dissolved in diisopropylamine (40 mL) in a Schlenk flask that was suitable for microwave irradiation. $Pd(PPh_3)_2Cl_2$ and CuI (two tips of a spatula each, ca. 5 mol-%) were added and the mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 30 min hold) with stirring. A saturated aqueous solution of NH_4Cl (20 mL) was added and, after phase separation, the aqueous layer was extracted with dichloromethane (3 × 20 mL). The collected organic layers were dried with $MgSO_4$ and, after filtration, the solvent was removed under reduced pressure. The red solid obtained was separated by column chromatography (SiO_2; 15 × 3 cm; petroleum ether/dichloromethane, 1:2) to give two fractions:

Fraction I (R_f = 0.37): Compound **3**, yield 0.07 g (0.3 mmol, 27 % recovered).

Fraction II (R_f = 0.17): Compound **18**, yield 0.25 g (0.4 mmol, 79 %); dark-red solid; m.p. 211 °C (dec.). Thp = Thiophenyl. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.30 (m, 4 H, CpH), 4.50 (m, 4 H, CpH), 6.75 (d, *J* = 3.8 Hz, 2 H, $C_{Fc}C_{Thp}CH$), 7.09 (d, *J* = 3.8 Hz, 2 H, $CHC_{Thp}C$≡C), 7.56 (m, 8 H, C_6H_4-C≡N) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 68.8 ($C_{Fc}H$), 71.2 ($C_{Fc}H$), 80.6 (FcC_{Thp}C≡*C*), 88.2 ($C_{Fc}C$), 92.0 (FcC_{Thp}*C*≡C), 111.4 ($C_{Ar}C$≡N), 118.7 (*C*≡N), 119.4 (C_{Thp}C≡C), 122.8 (C_{Thp}HCFc), 128.2 (C_{Ar}C≡C), 131.6 (C_{Ar}H or C_{Thp}H), 132.2 (C_{Ar}H or C_{Thp}H), 134.0 (C_{Ar}H), 145.4 ($C_{Fc}C_{Thp}$) ppm. IR: $\tilde{\nu}$ = 2918 (m, Ar), 2850 (m, Ar), 2226 (m), 2186 (s, C≡C), 1729 (w), 1599 (s, Ar), 1539 (m), 1470 (m), 1424 (m), 1288 (w), 1248 (w), 1217 (w), 1174 (m), 1105 (w), 1069 (w), 1040 (m), 974 (m), 832 (s, Ar), 821 (s, Ar), 801 (s, Ar) cm^{-1}. HRMS: *m*/*z* calcd. for $C_{36}H_{20}FeN_2S_2$ 600.0417; found 600.0406. $C_{36}H_{20}FeN_2S_2$ (600.53): calcd. C 72.00, H 3.36, N 4.66; found C 71.38, H 4.19, N 4.24.

1,1′-Bis(4-cyanophenylethynyl)ferrocene (19): 4-Ethynylbenzonitrile (**4**;[37,38] 0.10 g, 0.8 mmol, 1 equiv.) and **12** (0.52 g, 1.2 mmol, 1.5 equiv.) were dissolved in diisopropylamine (40 mL) in a Schlenk flask that was suitable for microwave irradiation. [Pd(PPh$_3$)$_2$Cl$_2$] and CuI (2 spatula tips each, ca. 5 mol-%) were added and the mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 120 min hold) with stirring. After cooling to 25 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm). After flushing with dichloromethane and solvent removal under reduced pressure, the red-brown solid obtained was separated by column chromatography (SiO$_2$; 30 × 3 cm; petroleum ether/dichloromethane, 1:2 to 1:4) to give two fractions:

Fraction I [R_f = 0.39 (petroleum ether/dichloromethane, 1:2)]: Compound **12**, yield 0.26 g (0.6 mmol, 50% recovered).

Fraction II [R_f = 0.15 (petroleum ether/dichloromethane, 1:2)]: Compound **19**, yield 0.12 g (0.3 mmol, 26%); dark-orange solid; m.p. 192 °C (dec.). The compound was poorly soluble in common organic solvents (chloroform, dichloromethane, 1,2-dichloroethane, dimethyl sulfoxide, benzene, toluene, benzonitrile, acetonitrile, THF, hexane, diisopropylamine, *N*,*N*-dimethylformamide, pyridine, chlorobenzene), so that it was not possible to obtain a ^{13}C NMR spectrum.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 4.38 (m, 4 H, CpH), 4.58 (m, 4 H, CpH), 7.48 (m, 8 H, C_6H_4) ppm. IR: $\tilde{\nu}$ = 2921 (w), 2853 (w), 2202 (s, C≡C), 1738 (w), 1599 (s, Ar), 1510 (m), 1459 (w), 1405 (w), 1378 (w), 1304 (w), 1272 (w), 1157 (m), 1031 (m), 926 (m), 829 (s, Ar) cm^{-1}. MS (70 eV): *m*/*z* (%) = 437 (18) [M + 1]$^+$, 436 (100) [M]$^+$, 278 (6), 277 (20), 254 (9), 253 (5), 190 (28), 129 (14), 97 (8), 71 (14). HRMS: *m*/*z* calcd. for $C_{28}H_{16}FeN_2$ 436.0663; found 436.0663.

1-[(4-Cyano-3,5-dimethylphenyl)ethynyl]-1′-[4-(cyanophenylethynyl)]ferrocene (20): 1-([4-Cyano-3,5-dimethylphenyl]ethynyl)-1′-iodoferrocene (**13**; 100 mg, 0.22 mmol, 1 equiv.) and **4**[37,38] (42 mg, 0.33 mmol, 1.5 equiv.) were dissolved in diisopropylamine (20 mL) and THF (20 mL) in a Schlenk flask that was suitable for microwave irradiation. [Pd(PPh$_3$)$_2$Cl$_2$] and CuI (2 spatula tips each, ca. 5 mol-%) were added and the mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 120 min hold) with stirring. After cooling to 25 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm). After flushing with dichloromethane and solvent removal under reduced pressure, the reddish brown solid obtained was separated by column chromatography (SiO$_2$; 30 × 3 cm; petroleum ether/dichloromethane, 4:1 to 1:4) to give three fractions:

Fraction I [R_f = 0.31 (petroleum ether/dichloromethane, 1:1)]: Compound **13**, yield 80 mg (0.16 mmol, 80% recovered).

Fraction II [R_f = 0.25 (petroleum ether/dichloromethane, 1:1)]: 12 mg; unidentified brown solid.

Fraction III (R_f = 0.09): Compound **20**, yield 8 mg (0.02 mmol, 8%); red solid; m.p. 164–167 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.46 (s, 6 H, CH$_3$), 4.37 (m, 4 H, CpH), 4.57 (m, 4 H, CpH), 7.11 (s, 2 H, C_6H_2), 7.43 (m, 2 H, C_6H_4C≡N), 7.51 (m, 2 H, C_6H_4C≡N) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 20.6 (CH$_3$), 31.9 (CH$_3$), 66.1 (C_{Fc}C), 66.5 (C_{Fc}C), 71.3 (C_{Fc}H), 71.4 (C_{Fc}H), 73.17 (C_{Fc}H), 73.20 (C_{Fc}H), 85.6 (C≡C), 86.0 (C≡C), 90.8 (C≡C), 92.3 (C≡C), 110.7 (*C*≡N), 112.2 (*C*≡N), 117.0 (C_{Ar}C≡N), 118.5 (C_{Ar}C≡N), 127.7 (C_{Ar}C), 128.7 (C_{Ar}C), 129.8 (C_{Ar}H), 131.6 (C_{Ar}H), 131.8 (C_{Ar}H), 142.0 (C_{Ar}C) ppm. IR: $\tilde{\nu}$ = 2921 (s, CH$_3$), 2852 (m, CH$_3$), 2226 (w), 2209 (C≡C), 1739 (w), 1602 (m), 1510 (w), 1459 (m), 1407 (w), 1378 (w), 1275 (w), 1159 (w), 1124 (w), 1027 (m), 923 (w), 869 (w), 823 (s, Ar), 723 (w), 614 (w) cm^{-1}. MS (70 eV): *m*/*z* (%) = 465 (47) [M + 1]$^+$, 464 (100) [M]$^+$, 449 (12), 218 (12), 203 (7), 190 (24), 189 (5). HRMS: *m*/*z* calcd. for $C_{30}H_{20}FeN_2$ 464.0976; found 464.0978.

1-[(4-*tert*-Butylsulfanyl)phenylethynyl]-1′-(4-cyanophenylethynyl)ferrocene (21): 1-(*tert*-Butylsulfanyl)-4-ethynylbenzene[35,57] (0.10 g, 0.5 mmol, 1 equiv.) and **12** (0.28 g, 0.6 mmol, 1.2 equiv.) in an argon atmosphere were dissolved in diisopropylamine (30 mL) in a Schlenk flask that was suitable for microwave irradiation. After degassing the solution (FPT, 3 cycles), [Pd(PPh$_3$)$_2$Cl$_2$] and CuI (2 spatula tips each, ca. 5 mol-%) were added. The mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 120 min hold) with stirring. After filtration through a frit covered with silica gel (10 × 3 cm), flushing with dichloromethane and solvent removal under reduced pressure, the obtained dark-red oil was separated by column chromatography (SiO$_2$; 50 × 3 cm; petroleum ether/dichloromethane, 1:1) to give three fractions:

Fraction I (R_f = 0.54): 1-(*tert*-Butylsulfanyl)-4-ethynylbenzene, yield 0.06 g (0.3 mmol, 62% recovered).[35,57]

Fraction II (R_f = 0.21): Compound **12**, yield 0.19 g (0.4 mmol, 67% recovered).

Fraction III (R_f = 0.14): Compound **21**: 47 mg (0.09 mmol, 18%); orange-red solid; m.p. 159–161 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.29 (s, 9 H, *t*Bu), 4.34 (m, 2 H, CpH), 4.38 (m, 2 H, CpH), 4.56 (m, 2 H, CpH), 4.57 (m, 2 H, CpH), 7.37 (m, 4 H, C_6H_4), 7.48 (m, 4 H, C_6H_4) ppm. ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 31.1 (CH$_3$), 46.5 (*C*CH$_3$), 66.0 (C_{Fc}C), 67.4 (C_{Fc}C), 71.1 (C_{Fc}H), 71.5 (C_{Fc}H), 73.2 (C_{Fc}H), 73.3 (C_{Fc}H), 85.6 (C≡C), 86.6 (C≡C), 88.6 (C≡C), 92.7 (C≡C), 110.8 (C_{Ar}C≡N), 118.8 (C≡N), 124.2 (FcC≡CC_{Ar}S), 128.9 (FcC≡CC_{Ar}C≡N), 131.3 (C_{Ar}H), 131.8 (C_{Ar}H), 132.0 (C_{Ar}H), 132.8 (C_{Ar}S), 137.3 (C_{Ar}H) ppm. IR: $\tilde{\nu}$ = 2961 (m, CH$_3$), 2922 (m, CH$_3$), 2855 (m), 2363 (w), 2201 (m, C≡C), 1738 (w), 1602 (m), 1456 (w), 1390 (w), 1362 (w), 1261 (w), 1160 (m), 1096 (w), 1027 (m), 921 (w), 820 (s, Ar) cm^{-1}. MS (70 eV): *m*/*z* (%) = 500 (11) [M + 1]$^+$, 499 (54) [M]$^+$, 444 (15), 443 (100) [M$^+$ – H$_2$C=C(CH$_3$)$_2$], 442 (8), 352 (8), 335 (12), 285 (9), 277 (16), 219 (14), 190 (8), 169 (47), 131 (17), 119 (19), 100 (8), 69 (48). HRMS: *m*/*z* calcd. for $C_{31}H_{25}FeNS$ 499.1057; found 499.1054.

1,4-Bis{1′-[4-(cyanophenyl)ethynyl]ferrocenylethynyl}benzene (22): 1,4-Diethynylbenzene[58] (50 mg, 0.40 mmol, 1 equiv.) and **12** (260 mg, 0.60 mmol, 1.5 equiv.) were dissolved under argon in diisopropylamine (30 mL) in a Schlenk flask that is suitable for microwave irradiation. After degassing the solution three times (FPT), [Pd(PPh$_3$)$_2$Cl$_2$] und CuI (two spatula tips each, ca. 5 mol-%) were added. The mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 120 min hold) with stirring. After cooling to 25 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm). After flushing with dichloromethane and solvent removal under reduced pressure, the orange-red solid obtained was separated by column chromatography (SiO$_2$; 30 × 3 cm; petroleum ether/dichloromethane, 2:1 to 1:4) to give two fractions:

Fraction I [R_f = 0.50 (petroleum ether/dichloromethane, 1:4)]: Compound **12**, yield 135 mg (0.31 mmol, 51% recovered).

Fraction II [R_f = 0.45 (petroleum ether/dichloromethane, 1:4)]: Compound **22**, yield 20 mg (0.03 mmol, 8%); orange-brown solid; m.p. 200 °C (dec.). Compound **22** is poorly soluble in common organic solvents (chloroform, dichloromethane, 1,2-dichloroethane, dimethyl sulfoxide, benzene, toluene, benzonitrile, acetonitrile, THF, hexane, diisopropylamine, *N*,*N*-dimethylformamide, pyridine, chlorobenzene), so that it was not possible to obtain a ^{13}C NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.34 (m, 4 H, CpH), 4.39 (m, 4 H, CpH), 4.59 (m, 8 H, CpH), 7.20 (m, 4 H, C_6H_4), 7.45 (m, 8 H, C_6H_4-C≡N) ppm. IR: $\tilde{\nu}$ = 2922 (s, Ar), 2852 (s, Ar), 2362 (w), 2204 (m, C≡C), 1724 (w), 1601 (m), 1515 (w), 1461 (w), 1407 (w), 1377 (w), 1243 (w), 1159 (w), 1032 (w), 928 (w), 828 (s, Ar) cm^{-1}. HRMS: *m*/*z* calcd. for $C_{48}H_{28}Fe_2N_2$ 744.0951; found 744.0966.

1,4-Bis{1′-[(4-cyanophenyl)ethynyl]ferrocenylethynyl}-2,5-dimethoxybenzene (23): 1,4-Diethynyl-2,5-dimethoxybenzene[59] (0.10 g, 0.5 mmol, 1 equiv.) and **12** (0.35 g, 0.8 mmol, 1.5 equiv.) were dissolved in diisopropylamine (30 mL) in a Schlenk flask that was suitable for microwave irradiation. After purging argon through the solution for 20 min, [$Pd(PPh_3)_2Cl_2$] und CuI (two spatula tips each, ca. 5 mol-%) were added. The mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 120 min hold) with stirring. After cooling to 25 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm). After flushing with dichloromethane and solvent removal under reduced pressure, the red-brown solid obtained was separated by column chromatography (SiO_2; 40 × 3 cm; petroleum ether/dichloromethane, 1:4) to give two fractions:

Fraction I (R_f = 0.40): Compound **12**: 114 mg (0.26 mmol, 32% recovered).

Fraction II (R_f = 0.18): Compound **23**, yield 60 mg (0.08 mmol, 15%); red-orange solid; m.p. 245 °C (dec.). Compound **23** is poorly soluble in common organic solvents (chloroform, dichloromethane, 1,2-dichloroethane, dimethyl sulfoxide, benzene, toluene, benzonitrile, acetonitrile, THF, hexane, diisopropylamine, *N*,*N*-dimethylformamide, pyridine, chlorobenzene), so that it was not possible to obtain a ^{13}C NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.78 (s, 6 H, OCH_3), 4.34 (m, 4 H, CpH), 4.42 (m, 4 H, CpH), 4.60 (m, 4 H, CpH), 4.61 (m, 4 H, CpH), 6.81 (s, 2 H, C_6H_2), 7.42–7.52 (m, 8 H, C_6H_4) ppm. IR: $\tilde{\nu}$ = 2921 (s, OCH_3), 2851 (s, OCH_3), 2363 (w), 2197 (m, C≡C), 1740 (w), 1598 (m), 1505 (m), 1462 (s), 1389 (m), 1274 (m), 1215 (s), 1180 (m), 1156 (m), 1034 (s), 925 (w), 838 (m), 815 (m) cm^{-1}. HRMS: *m*/*z* calcd. for $C_{50}H_{32}Fe_2N_2O_2$ 804.1163; found 804.1147.

1-(4-Nitrophenylethynyl)-1′-iodoferrocene (24): 1-Ethynyl-1′-iodoferrocene[41,46–49] (**11**; 0.20 g, 0.6 mmol, 1 equiv.) and 4-iodonitrobenzene (0.21 g, 0.8 mmol, 1.4 equiv.) were dissolved in diisopropylamine (30 mL) in a Schlenk flask that was suitable for microwave irradiation. [$Pd(PPh_3)_2Cl_2$] and CuI (two spatula tips each, ca. 5 mol-%) were added and the mixture was heated by microwave irradiation (300 W, 100 °C, 15 min ramp, 30 min hold) with stirring. After filtration through a frit covered with silica gel (10 × 3 cm), flushing with dichloromethane, and solvent removal under reduced pressure, the obtained red-purple solid was separated by column chromatography (SiO_2; 30 × 3 cm; petroleum ether/dichloromethane, 4:1 to 1:4) to give two fractions:

Fraction I [R_f = 0.22 (petroleum ether/dichloromethane, 4:1)]: 4-Iodonitrobenzene, yield 0.05 g (0.2 mmol, 25% recovered).

Fraction II [R_f = 0.13 (petroleum ether/dichloromethane, 4:1)]: Compound **24**, yield 0.23 g (0.5 mmol, 83%); purple, glittering solid; m.p. 174–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.25 (m, 2 H, CpH), 4.34 (m, 2 H, CpH), 4.47 (m, 2 H, CpH), 4.51 (m, 2 H, CpH), 7.63–7.65 (AA′BB′, ΣJ = 8.9 Hz, 2 H, C_6H_4), 8.19–8.21 (AA′BB′, ΣJ = 8.9 Hz, 2 H, C_6H_4) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 41.6 (C_{Fc}I), 66.2 (C_{Fc}C), 71.0 (C_{Fc}H), 72.7 (C_{Fc}H), 74.5 (C_{Fc}H), 76.7 (C_{Fc}H), 85.7 (C≡C), 93.9 (C≡C), 123.8 (HC_{Ar}CNO$_2$), 131.0 (C_{Ar}C≡C), 132.1 (HC_{Ar}CC≡C), 146.7 (C_{Ar}NO$_2$) ppm. IR: $\tilde{\nu}$ = 2921 (w), 2363 (w), 2022 (m, C≡C), 1589 (s, Ar), 1508 (s), 1453 (w), 1403 (w), 1380 (w), 1335 (s), 1164 (m), 1106 (m), 1053 (w), 1025 (m), 921 (w), 854 (m), 817 (s, Ar), 745 (m), 690 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 458 (17) [M + 1]$^+$, 457 (100) [M]$^+$, 427 (25), 411 (27), 228 (15), 227 (19), 226 (41), 202 (5), 183 (10), 163 (12), 86 (8), 84 (16). HRMS: *m*/*z* calcd. for $C_{18}H_{12}FeINO_2$ 456.9262; found 456.9263. $C_{18}H_{12}FeINO_2$ (457.05): calcd. C 47.30, H 2.65, N 3.06; found C 47.91, H 2.89, N 3.09.

1-[(4-Dimethylaminophenyl)ethynyl]-1′-[(4-nitrophenyl)ethynyl]ferrocene (25): 4-Ethynyl-*N*,*N*-dimethylaniline[54] (0.51 g, 1.1 mmol, 1 equiv.) and **24** (0.63 g, 1.4 mmol, 1.2 equiv.) were dissolved in diisopropylamine (40 mL) and THF (30 mL). [$Pd(PPh_3)_2Cl_2$] and CuI (two spatula tips each, ca. 5 mol-%) were added and the mixture was heated at 100 °C for 16 h. After cooling to 23 °C, the mixture was filtered through a frit covered with silica gel (10 × 3 cm). After flushing with dichloromethane and solvent removal under reduced pressure, the obtained black-red solid was separated by column chromatography (SiO_2; 55 × 3.5 cm; petroleum ether/dichloromethane, 1:1 to 1:9 to dichloromethane) to give two fractions:

Fraction I [R_f = 0.45 (petroleum ether/dichloromethane, 1:1)]: Compound **24**, yield 0.20 g (0.4 mmol, 29% recovered).

Fraction II [R_f = 0.36 (petroleum ether/dichloromethane, 1:1)]: Compound **25**, yield 0.40 g (0.9 mmol, 76%); orange powder; m.p. 184–187 °C. Crystallization from dichloromethane/hexane gave crystals; however, these were unsuitable for crystal structure analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.93 (s, 6 H, NCH_3), 4.27 (m, 2 H, CpH), 4.36 (m, 2 H, CpH), 4.52 (m, 2 H, CpH), 4.58 (m, 2 H, CpH), 6.45–6.47 (AA′BB′, ΣJ = 9.0 Hz, 2 H, C_6H_4), 7.16–7.18 (AA′BB′, ΣJ = 8.9 Hz, 2 H, C_6H_4), 7.40–7.42 (AA′BB′, ΣJ = 8.9 Hz, 2 H, C_6H_4), 7.97–8.00 (AA′BB′, ΣJ = 8.9 Hz, 2 H, C_6H_4) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 40.2 (CH_3), 66.2 (C_{Fc}C), 69.9 (C_{Fc}C), 70.2 (C_{Fc}H), 71.1 (C_{Fc}H), 72.6 (C_{Fc}H), 73.2 (C_{Fc}H), 83.6 (C≡C), 85.9 (C≡C), 88.5 (C≡C), 94.0 (C≡C), 110.5 {C_{Ar}[N(CH_3)$_2$]C≡C}, 111.7 [C_{Ar}HCN(CH_3)$_2$], 123.5 (C_{Ar}HCNO$_2$), 131.2 (O_2NCCCC), 131.9 (C_{Ar}HCC≡C), 132.5 (C_{Ar}HCC≡C), 146.1 [C_{Ar}CNO$_2$ or C_{Ar}CN(CH_3)$_2$], 149.8 [C_{Ar}CNO$_2$ or C_{Ar}CN(CH_3)$_2$] ppm. IR: $\tilde{\nu}$ = 2206 (w, C≡C), 1593 (m), 1511 (m), 1444 (w), 1360 (m), 1334 (s), 1201 (w), 1159 (w), 1106 (w), 1033 (w), 928 (w), 855 (w), 815 (m) cm^{-1}. MS (70 eV): *m*/*z* (%) = 475 (27) [M + 1]$^+$, 474 (100) [M]$^+$, 444 (16), 413 (8), 208 (5), 192 (8), 163 (9). HRMS: *m*/*z* calcd. for $C_{28}H_{22}FeN_2O_2$ 474.1031; found 474.1031.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all new compounds reported in this publication.

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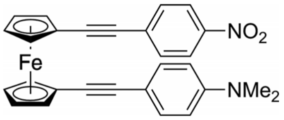
Ferrocenes

New ferrocenes bearing highly extended π systems with nitrile, nitro, and dimethylamino end groups are prepared that include a push-pull-substituted system. The redox properties of the new compounds have been characterized by cyclic voltammetry.



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Ferrocenes Bearing Highly Extended π Systems with Nitrile, Nitro, and Dimethylamino End Groups

Keywords: Sandwich compounds / Redox chemistry / Alkynes / Pi interactions / Conjugation / Cross coupling