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Synthesis of controlled π-extended conjugate nanostructures of 1,1′-ferrocene

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Abstract

Synthesis of the (*E*,*E*)-1,1′-ferrocene nanostructures having controlled π-extended conjugation was satisfactory carried out starting of 1′-[2-(1,3-dioxolan)]-1-formylferrocene (**1**). The molecular unit (*E*)-1′-[2-(1,3-dioxolan)]-1-[β-(*p*-iodophenyl)-ethenyl]ferrocene (**2**), was obtained in excellent yield by treatment of **1** with *p*-iodobenzyl triphenylphosphonium ylid followed by $Z \rightarrow E$ isomerization, catalyzed by iodine, in quantitative yield. Compound (*E*)-**2** was transformed in (*E*)-1′-{2-(1,3-dioxolan)-1-[β-[4-(3-hydroxy-3-methyl-but-1-ynyl)-phenyl]-ethenyl}ferrocene, (*E*)-**4**, by palladium catalyzed cross-coupling with 2-methyl-but-3-yn-2-ol. (*E*)-**4** gives (*E*)-1-[β-(4-ethynylphenyl)-ethenyl]-1′-[2-(1,3-dioxolan)]ferrocene (*E*)-**5** by powder sodium hydroxide treatment. The molecular unit (*E*,*E*)-1-{β-[4-(β-(1′-formylferrocenyl)-ethenyl)-phenylethynyl]-phenyl]-ethenyl}-1′-formylferrocene, (*E*,*E*)-**6**, was synthesized by palladium catalyzed cross-coupling between the *p*-iodophenyl derivative (*E*)-**2** and their ethynyl derivative (*E*)-**5**, in good yield. The (*E*,*E*)-1,1′-(*p*-iodophenyl)ethenyl ferrocene, (*E*,*E*)-**7**, was synthesized by reaction between 1,1′-diformylferrocene and the *p*-iodobenzyltriphenylphosphonium ylid, as a mixture of isomers which were purely isolated. Moreover, isomerization of the *Z*,*Z* and *E*,*Z* mixture to the *E*,*E* isomer, was induced by sunlight exposure, catalyzed by iodine, in quantitative yield. The (*E*,*E*)-1,1′-[β-(4-ethynylphenyl)-ethenyl]ferrocene, (*E*,*E*)-**10**, was synthesized in good yield, by palladium catalyzed cross-coupling of compound (*E*,*E*)-**7** with 2-methyl-but-3-yn-2-ol, followed by powder sodium hydroxide treatment.

Keywords: Ferrocenes; Acetylenes; Diynes; (*E*)- and (*Z*)-isomers; Acetal; Biphenyl; Coupling reactions

1. Introduction

The use of molecular organic materials for conductor and nonlinear optics applications is an area of considerable recent activity. Interest in these materials is due to their inherent synthetic flexibility, which permits the design of molecular properties [1].

Compounds containing ferrocene have been used in electrochemistry and catalyst chemistry [2], as molecular sensors [3], and ferromagnets [4,5] and in nonlinear optics [6,7]. It is now well established that molecular structures with differences between ground-state and excited-state dipole moments and large transition moments have large second-order nonlinearities [8]. Molecules with π donor–acceptor interactions, such as ferrocene or derivatives, are promising candidates to show these properties. Thus, Buckminsterfullerene C_{60} cocrystallizes with ferrocene to isolate the C_{60}(ferrocene)$_2$ complex stabilized by weak intermolecular charge transfer interactions [9]; the vinylferrocene moiety has been used as a π-electron donor in several compounds [10], with high second harmonic generation (SHG) [11] efficiencies.

In this way (*E*)-1-ferrocenyl-2-(*p*-ethynylphenyl)-ethene has been prepared for the polyene synthesis [12] and their 1,3-diyne dimer for the topopolymerization analysis to prepare electroactive and nonlinear optics materials.

Preparation of double bond [13] or triple bond [14] conjugate 1-ferrocenyl structures have been recently reported.

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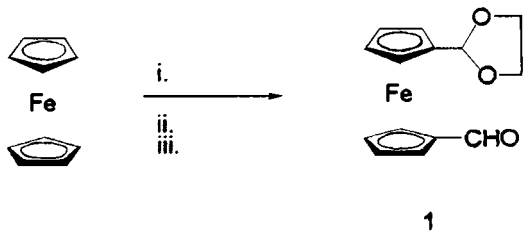

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Scheme 1. (i) BuLi, hexane, TMEDA, diethyl ether; (ii) DMF, −78 °C; (iii) $(HOCH_2)_2$, H^+.

2. Discussion

Synthesis of the (*E*,*E*)-1,1′-ferrocene nanostructures having controlled π-extended conjugation was satisfactory carried out starting of 1′-[2-(1,3-dioxolan)]-1-formylferrocene.

2.1. Synthesis of 1′-[2-(1,3-dioxolan)]-1-formylferrocene (1)

The starting compound 1′-[2-(1,3-dioxolan)]-1-formylferrocene was prepared from 1,1′-diformylferrocene [15] by treatment with 1,2-dihydroxyethane in excess (20 equivalents) catalyzed by *p*-toluensulfonic acid with good yield (60%); 1,1′-di[2-(1,3-dioxolan)]ferrocene, was also isolated (20%) (Scheme 1).

2.2. Synthesis of (E)-1′-[2-(1,3-dioxolan)]-1-[β-(p-iodophenyl)ethenyl]ferrocene (2)

The synthesis of compound (*E*)-**2** was outlined as a good synthon for the preparation of the 1,1′ conjugate acetylene compounds which can be transformed to the corresponding diacetylenes and polyacetylenes [12], which exhibit a more extended π-electronic conjugation.

Compound (*E*)-**2** was prepared starting of 1-[2-(1,3-dioxolan)]-1′-formylferrocene (**1**) with the *p*-iodobenzyl triphenylphosphonium ylid [15], giving **2** as a mixture of the *E* and *Z* isomers. The yield of the reaction depends of the amount of the phosphonium salt and the nature of the base used to prepare the ylid. Thus, the reaction was optimized using two equivalents of the phosphonium salt and three equivalents of potassium *tert*-butoxide, giving **2** in good yield (87%), as a mixture of *E* and *Z* isomers (5:2, by ^{1}H-NMR). By successive crystallizations in hexane the *E* isomer was purely isolated while in solution the *Z* isomer remained pure.

2.3. Z → E Isomerization of 1′-[2-(1,3-dioxolan)]-1-[β-(p-iodophenyl)ethenyl]ferrocene (2)

The effort for the separation of the mixture of *E* and *Z* isomers of **2** (*E*/*Z*, 5:2) by chromatographic methods was unsuccessful, although both isomers were purely isolated by successive crystallizations in hexane.

Moreover, in general the *E* isomer exhibits better electrical and optical properties and, it was necessary to planify a method for the preparation of the *E* by conversion of the *Z* isomer taking in account the more favourable thermodynamic stability.

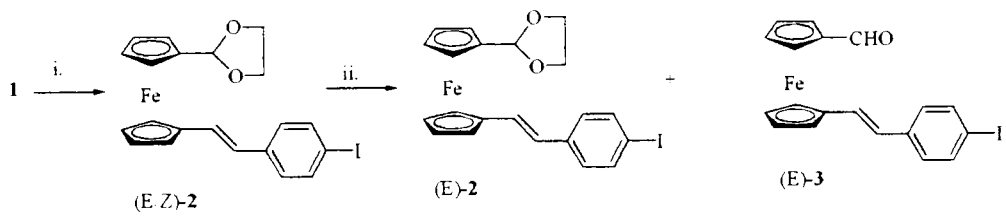
Chemical isomerization of the *Z* isomer was carried out in hexane by exposure to the sunlight, with iodine in catalytic amounts. Furthermore, after 24 h the *Z* → *E* transformation was practically quantitative, although a mixture of the expected 1,3-dioxolane derivative (*E*)-**2** and the deprotected formyl derivative (*E*)-**3** was isolated, in a 1:3 ratio, respectively (by ^{1}H-NMR) (Scheme 2).

By ^{1}H-NMR the (*E*)-**2** isomer shows the Cp–CH= and Ph–CH= protons at 6.60 and 6.73 ppm as doublets ($J = 16.17$ Hz; IR, 964 cm^{-1}), and the (*Z*)-**2** isomer at 6.36 and 6.33 ppm, respectively, as doublets ($J = 12.3$ Hz; IR, 863 cm^{-1}).

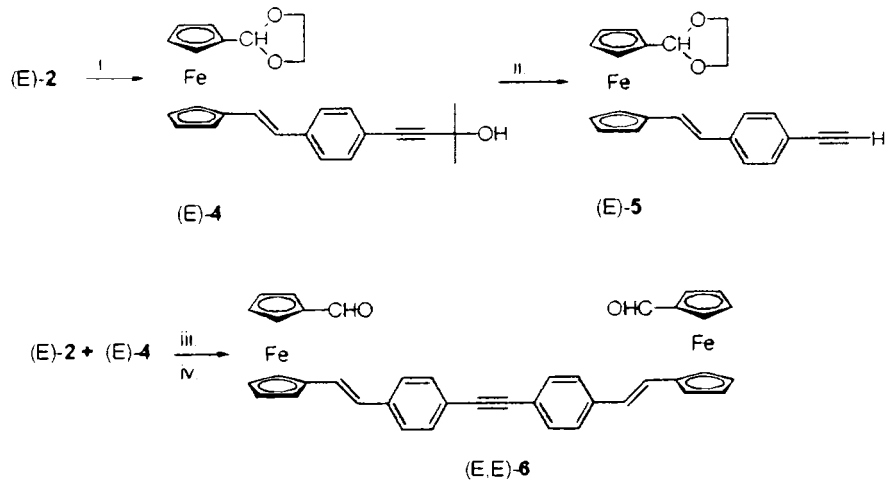
The X-ray molecular structure of (*E*)-1-ferrocenyl-2-(*p*-iodophenyl)ethene was reported [16a]. The packing of the molecules exhibits a short contact (3.63 Å) between the iodine atom and the π-cyclopentadienyl ring system, of charge transfer type, being the iodine atom the acceptor; accordingly the distances of the Fe atom to the centroids of the cyclopentadienyl rings were different, 1.635(1) and 1.665(1) Å, while these found in 1,4-di(1-ferrocenyl)-1,3-butadiyne are similar (1.645(1) and 1.650(1) Å [16b]).

2.4. Synthesis of (E)-1-[β-(4-ethynylphenyl)-ethenyl]-1′-[2-(1,3-dioxolan)]ferrocene (5)

The catalytic cross-coupling reaction of haloarenes to prepare the ethynyl derivatives, permits the extension of the molecular conjugation.



Scheme 2. (i) *p*-Iodobenzyltriphenylphosphonium bromide; KO′Bu; (ii) I_2, sunlight.



Scheme 3. (i) $PdCl_2(PPh_3)_2$, Cu_2I_2, NEt_3, $HC{\equiv}C(CH_3)_2{-}OH$; (ii) NaOH, toluene, Δ; (iii) $PdCl_2(PPh_3)_2$, Cu_2I_2, NEt_3; (iv) AcOH, H_2O.

Thus, compound (*E*)-**2** was transformed in (*E*)-1′-{2-(1,3-dioxolan)-1-[β-[4-(3-hydroxy-3-methyl-but-1-ynyl)-phenyl]-ethenyl}ferrocene (**4**) by cross-coupling reaction with 2-methyl-but-3-yn-2-ol in presence of dichlorobis(triphenylphosphine) palladium and cuprous iodide in triethylamine, in practically quantitative yield. Compound (*E*)-**4** was treated with a catalytic amount of powdered sodium hydroxide in dry toluene at the reflux temperature, to give the acetylene derivative (*E*)-**5** in practically quantitative yield (^{1}H-NMR, 3.14, s; IR, 3278 cm^{-1}; MS, 384 ([M^+], 99%).

2.5. Synthesis of (E)-1-{β-[4-(β-(1′-formylferrocenyl)-ethenyl)-phenylethynyl]-phenyl]-ethenyl}-1′-formylferrocene ((E)-6)

Compound (*E*)-**2** was submitted to cross-coupling with the acetylene derivative (*E*)-**5** in presence of dichlorobis(triphenylphosphine) palladium and cuprous iodide, in freshly distilled triethylamine, under argon atmosphere, giving a mixture of the 1′,1′-diacetal derivative and the deprotected 1′,1′-diformyl derivative (*E*)-**6** (Scheme 3). Thus, the mixture was completely hydrolyzed and compound (*E*)-**6** was purely isolated. (CHO: ^{1}H-NMR, 9.91; ^{13}C, 193.6 ppm; IR, 1685 cm^{-1}; ms, 654 ([M^+], 100%).

2.6. Synthesis of (E,E)-1,1′-bis-[β-(p-iodophenyl)-ethenyl)ferrocene (7) from (E)-3

The acetal group in compound (*E*)-**2** was hydrolyzed completely with acetic acid (30%) to the formyl derivative (*E*)-**3**, which was transformed to the conjugate 1,1′-bis-[β-(*p*-iodophenyl)ethenyl)ferrocene by Wittig reaction with the *p*-iodobenzyltriphenylphosphonium ylid [14a]. Two stereoisomers of **7** were isolated, the main *E,E* and the *E,Z* (by ^{1}H-NMR, 3:1), in practically quantitative yield.

By crystallization in hexane was purely isolated the (*E,E*) isomer (74%; ^{1}H-NMR, 6.65 and 6.45 ppm as doublets, $J = 16.16$ Hz; IR, 958 cm^{-1}) while the (*E,Z*) isomer remains pure in the hexane solution (24%, ^{1}H-NMR, 6.79 and 6.58 ppm as doublets, $J = 16.17$ Hz; and 6.29 and 6.23 ppm as doublets, $J = 11.74$ Hz; IR, 959 and 855 cm^{-1}).

2.7. (E,Z)→(E,E) Isomerization of 1,1′-bis-[β-(p-iodophenyl)ethenyl)ferrocene (7)

Chemical isomerization of the *E,Z* isomer of **7** was carried out in hexane by sunlight exposure, with iodine in catalytic amounts, and after 5 days the transformation was quantitative (Scheme 4).

2.8. Synthesis of (E,E)-1,1′-bis-[β-(p-iodophenyl)-ethenyl)ferrocene (7) from 1,1′-diformylferrocene

The synthesis of (*E,E*)-1,1′-bis-[β-(*p*-iodophenyl)-ethenyl)ferrocene (**7**) was now undertaken in one pot from the Wittig reaction between 1,1′-diformylferrocene and the *p*-iodobenzyltriphenylphosphonium ylide [16a]. After column chromatography a mixture of the *E,E*, *Z,E* and *Z,Z* isomers were obtained in good yield (62%). The *E,E* isomer was purely isolated (25%) from a concentrated solution of the isomers in dichloromethane and careful addition of hexane at room temperature, while the mixture of *Z,E* and *Z,Z* isomers were purely separated by silica gel column chromatography (26 and 11%, respectively). The *Z,Z* isomer [^{1}H-NMR, 6.36 and 6.21 ppm, as doublets, $J = 11.83$ Hz; IR, 853 cm^{-1}; MS, 642 ([M^+], 78%)] was obviously never isolated starting from (*E*)-**3**.

2.9. (Z,Z)/(E,Z)→(E,E) Isomerization of 1,1′-bis-[β-(p-iodophenyl)ethenyl]ferrocene (7)

The geometry of the (*E*,*E*) isomer exhibits better electrical and optical properties and, it was necessary to planify a method for the preparation of the (*E*,*E*) by conversion of the (*E*,*Z*) and (*Z*,*Z*) isomers taking in account the more favourable thermodynamic stability.

Chemical isomerization was carried out by sunlight exposure of the (*E*,*Z*)/(*Z*,*Z*) (8:3) mixture in hexane with iodine in catalytic amounts during 5 days in a quantitative transformation (Scheme 4). The kinetic of the isomerization for (*E*,*Z*) is faster than for the (*Z*,*Z*) isomer. The time of complete isomerization increases with the amount of sample for the same concentration, probably due to a minor efficiency in the sunbeams absorption process.

2.10. Synthesis of (E,E)-1,1′-[β-(4-ethynylphenyl)-ethenyl]ferrocene (10)

The catalytic cross-coupling reaction of the 1,1′-di-(*p*-iodophenyl) derivative (*E*,*E*)-**7** to prepare the corresponding ethynyl derivative, permits the extension of the molecular conjugation through a terminal triple bond (Scheme 4).

Thus, cross-coupling of compound (*E*,*E*)-**7** with 2-methyl-but-3-yn-2-ol was carried out in presence of dichlorobis(triphenylphosphine) palladium and cuprous iodide in triethylamine, under argon atmosphere. For two equivalents of the propargylic alcohol derivative, a mixture of (*E*,*E*)-1-{β-[4-(3-hydroxy-3-methyl-but-1-ynyl)-phenyl]-ethenyl}-1′-[β-(*p*-iodophenyl)-ethenyl]-ferrocene ((*E*,*E*)-**8**) and (*E*,*E*)-1,1′-bis-{β-[4-(3-hydroxy-3-methyl-but-1-ynyl)-phenyl]-ethenyl}-ferrocene ((*E*,*E*)-**9**) was obtained, in a 4:3 molar ratio, respectively. However, when the reaction was carried out with three equivalents of the propargylic alcohol derivative, only product (*E*,*E*)-**9** was obtained, in practically quantitative yield.

Compound (*E*,*E*)-**9** was treated with a catalytic amount of powdered sodium hydroxide in dry toluene at the reflux temperature, to give the corresponding 1,1′-diacetylene derivative (*E*,*E*)-**10** in practically quantitative yield (^{1}H-NMR, 6.73 and 6.55 ppm as doublets, $J = 16.17$; IR, 960 cm^{-1}.

2.11. Synthesis of biphenyl oligomer derivatives from (E,E)-7

The monosubstituted *p*-iodophenylethenylferrocene gives the biphenyl derivative by oxidative homocoupling with zero-valent nickel complexes but in low yield (30%) [14a]. In this way, the analysis of the biphenylation of compound (*E*,*E*)-**7** would give a controlled oligomeric reaction.

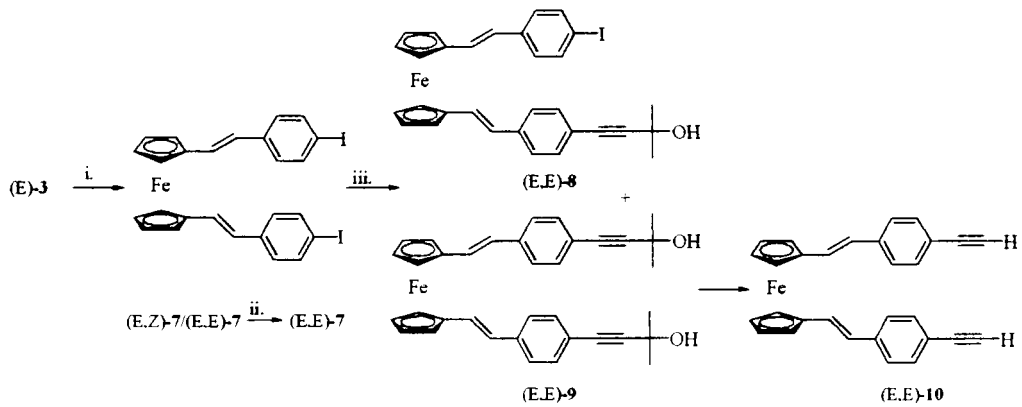
The homocoupling reaction of (*E*,*E*)-**7** was carried out with zero-valent tris(triphenylphosphine) nickel, prepared in situ from dichloro bis(triphenylphosphine nickel and powder zinc in tetrahydrofuran. However, in contrast with the monosubstituted derivative, the disubstituted compound (*E*,*E*)-**7** was completely transformed giving a mixture of the oligomers.

A precipitate was obtained from a dichloromethane solution by careful addition of diethyl ether. This was analyzed by a molecular mass characterization technique (MALDI) showing the presence of the oligomers, intermolecular dimer and trimer mainly and tetramer and the intramolecular dimer-box, which from the intensity of the spectrum are in 75:55:10:6 molar ratio, respectively (Scheme 5).

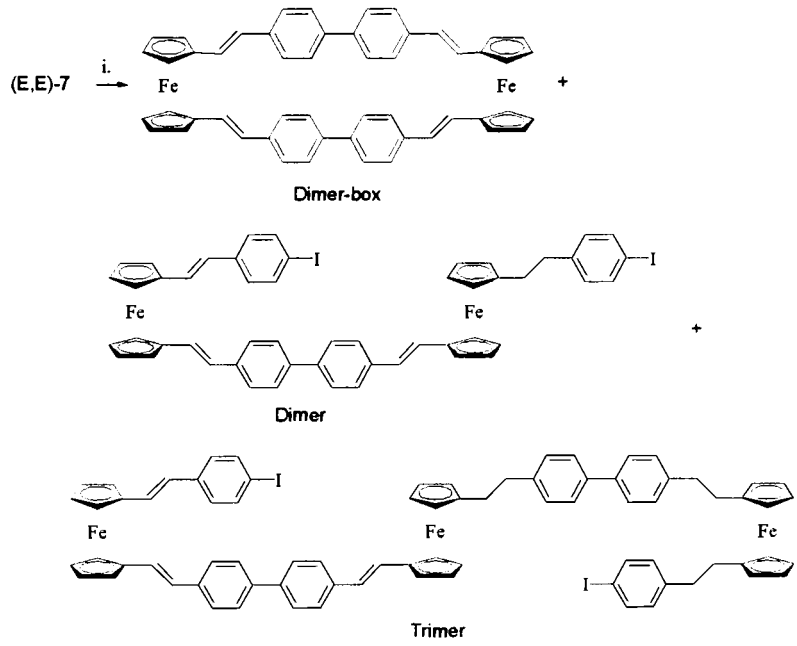
A new precipitate was separated from a hexane–ethyl acetate solution and it was also analyzed giving a mixture with the dimer-box as the main product.

3. Experimental

Melting points were determined with a Reichert hot-stage microscope and are uncorrected. IR spectra were



Scheme 4. (i) *p*-Iodobenzyltriphenylphosphonium ylide; (ii) I_2, sunlight; (iii) $PdCl_2(PPh_3)_2$, Cu_2I_2, NEt_3; (iv) NaOH, toluene, Δ.



Scheme 5. $NiCl_2(PPh_3)_2$, Zn, THF.

recorded using a Perkin–Elmer 681 spectrophotometer. ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50 MHz) spectra were recorded with a Bruker WM-200-SY spectrometer; chemical shifts are given in the δ scale, using Me_4Si as internal reference. Mass spectra were recorded using a Hewlett–Packard SP85 spectrometer. Elemental analyses were performed with a LECO CHN-900.

*3.1. Synthesis of (E)-1′-[2-(1,3-dioxolan)]-1-formylferrocene (**1**)*

In a Dean–Stark with a graduate side tube, containing $MgSO_4$ (2.0 g), a solution of 1,1′-diformylferrocene (1 g, 4.13 mmol) [15] was introduced in dry diethyl ether (100 ml), ethylenglycol (4.62 ml, 82.6 mmol) and a little amount of *p*-toluensulfonic acic. The mixture was warmed at reflux temperature with stirring and after 30 min the diethyl ether was removed giving a red oil which was washed with an aqueous solution of ammonium chloride with $KHCO_3$ and extracted with CH_2Cl_2. The organic layer was separated and dried with $MgSO_4$, and solvent was evaporated to give an oil which was purified by column chromatography using ethyl acetate:hexane (4:1) as eluent, (and 5% of triethylamine for the column preparation) giving **1** (0.708 g, 60%) as a red oil; the diacetal derivative was also isolated (0.277 g, 20%) as a red brown solid, m.p. 103–104 °C.

*3.1.1. Compound **1***

^{1}H-NMR ($CDCl_3$): 9.95 (s, 1H, C*H*O); 5,61 (s, 1H, –C*H*$(OCH_2)_2$); 4.81 (s, 2H, Cp); 4.62 (s, 2H, Cp); 4.41 (s, 2H, Cp); 4.27(s, 2H, Cp); 4.01 (m, 2H, $CH(OCH_2)_2$); 3.97(m, 2H, $CH(OCH_2)_2$). ^{13}C-NMR ($CDCl_3$): 193.8 (*C*HO); 101.7 (–*C*H$(OCH_2)_2$); 85.3 (Cp); 78.8 (Cp); 72.8 (Cp); 69.4 (Cp); 68.8 (Cp); 68.8 (Cp); 67.3 (Cp); 64.4 (–CH $(OCH_2)_2$). IR (film): 1681 (CHO); 1095 (C–O–C); 1027 (ferrocene).

Anal. Found: C, 58.53; H, 5.15. $C_{14}H_{14}O_3Fe$. Calc.: C, 58.77; H, 4.93%.

3.1.2. Diacetal

^{1}H-NMR ($CDCl_3$): 5.75 (s, 2H, –C*H*$(OCH_2)_2$); 4.33 (s, 4H, Cp); 4.20 (s, 4H, Cp); 4.00 (m, 4H, $CH(OCH_2)_2$); 3.90 (m, 4H, $CH(OCH_2)_2$). ^{13}C-NMR ($CDCl_3$): 102.5 (–*C*H$(OCH_2)_2$); 85.0 (Cp); 69.1 (Cp); 68.2 (Cp); 65.0 (2C, –CH$(OCH_2)_2$); IR (KBr): 1890 (CH_2); 1494 (CH_2); 1081 (C–O–C); 1025 (ferrocene); 819 (ferrocene).

Anal. Found: C, 58.03; H, 5.54. $C_{16}H_{18}O_4Fe$. Calc.: C, 58.21; H, 5.50%.

*3.2. Synthesis of (E)-1′-[2-(1,3-dioxolan)]-1-[β-(p-iodophenyl)ethenyl]ferrocene (**2**)*

To a suspension of *p*-iodobenzyltriphenylphosphonium bromide [16a], (1.53 g, 3.2 mmol) in dry toluene (50 ml) at 0 °C, potassium *tert*-butoxide (0.54 g, 4.8 mmol) was added and stirred for 30 min. This solution was then added slowly to a solution of the formylferrocene derivative **1** (0.61 g, 2.13 mmol) in dry toluene (20 ml) at 0 °C under argon atmosphere, stirring for 22 h at room temperature (r.t.). After solvent evaporation under reduced pressure, the residual red solid was solved in dichloromethane and washed with an aqueous solution of ammonium chloride and potassium carbon-

ate. The organic layer was dried on $MgSO_4$, filtered and solvent removed under reduced pressure. The residual solid was purified by column chromatography using hexane:ethyl acetate (4:1) (a 5% of triethylamine was added for the column preparation). A mixture of the *E*/*Z* isomers of **2** was obtained (0.89 g, 87%) molar ratio (2:1, by NMR). By crystallization from hexane, (*E*)-**2** (0.62 g, 61%) was isolated, m.p. 118–119 °C, while (*Z*)-**2**, (0.26 g, 25%) remained in solution, and was isolated as an orange oil.

*3.2.1. Compound (E)-**2***

^{1}H-NMR ($CDCl_3$): 7.63 (d, 2H, $J = 8.4$, H-3‴ and H-5‴); 7.17 (d, 2H, $J = 8.4$, H-2‴ and H-6‴); 6.88 (d, 1H, $J = 16.2$, H-2″); 6.61 (d, 1H, $J = 16.2$, H-1″); 5.67 (s, 1H, -C*H*$(OCH_2)_2$); 4.48 (s, 2H, Cp); 4.33 (s, 2H, Cp) 4.28 (s, 2H, Cp); 4.14 (s, 2H, Cp); 4.09 (m, 2H, CH$(OCH_2)_2$); 3.90 (m, 2H, CH$(OCH_2)_2$). ^{13}C-NMR ($CDCl_3$):137.6 (C-3‴ and C-5‴); 137.4 (C-1‴); 127.6 (C-2″); 127.5 (C-2‴ and C-6‴); 125.0 (C-1″); 102.4 (*C*H$(OCH_2)_2$); 91.5 (C-4‴); 85.0 (Cp); 83.4 (Cp); 70.0 (Cp); 69.8 (Cp); 67.8 (Cp); 67.7 (Cp); 65.2 (CH$(OCH_2)_2$). IR (KBr): 1631 (C=C); 1084 (C–O–C); 964 (=C–H isomer *E*); 805 (π-subst. ArH); 819 (ferrocene); 489 (C–I). MS: 486 ([M$^+$], 66%), 442 (10), 287 (14), 165 (100), 121 (40).

*3.2.2. Compound (Z)-**(2)***

^{1}H-NMR ($CDCl_3$): 7.59 (d, 2H, $J = 8.2$, H-3‴y H-5‴); 7.06 (d, 2H, $J = 8.2$, H-2‴ and H-6‴); 6.36 (d, 1H, $J = 12.3$, H-2″); 6.33 (d, 1H, $J = 12.3$, H-1″); 5.68 (s,1H, –C*H*$(OCH_2)_2$); 4.22 (s, 2H, Cp); 4.21 (s, 2H, Cp); 4.18 (s, 2H, Cp); 4.11 (s, 2H, Cp); 4.01 (m, 2H, CH$(OCH_2)_2$); 3.93 (m, 2H, CH$(OCH_2)_2$). ^{13}C-NMR ($CDCl_3$): 137.5 (C–1‴); 137.0 (C-3‴ and C-5‴); 130.6 (C-2‴ and C-6‴); 128.6 (C-2″); 126.1 (C-1″); 102.4 (*C*H$(OCH_2)_2$); 91.7 (C-4‴); 84.9 Cp); 81.6 (Cp); 70.1 (Cp); 69.8 (Cp); 69.5(Cp); 67.9 (Cp); 65.2 (CH$(OCH_2)_2$). IR (KBr): 1632 (C=C); 1005 (ferrocene); 863 (=C–H, isomer *Z*); 826 (π-subst. ArH); 807 (ferrocene). MS: 486 ([M$^+$], 47%), 442 (50), 287 (16), 165 (100), 121 (38).

3.3. (Z)→(E) Isomerization of 1′-[2-(1,3-dioxolan)]-1-[β-(p-iodophenyl)ethenyl]ferrocene

To a solution of (*Z*)-**2** isomer (400 mg, 0.82 mmol) in hexane (150 ml) a crystal of iodine was added. The mixture was exposed to the sunlight and stirred for 4 days at r.t. (monitoring by thin layer chromatography). Later the solvent was removed under reduced pressure and the residual solid was solved in dichloromethane and treated with an aqueous solution of sodium thiosulfate. The organic layer was dried on $MgSO_4$, filtered and solvent removed under reduced pressure giving a mixture of (*E*)-**2** and their aldehyde (*E*)-**3** in a 1:3 molar ratio, respectively (by NMR). Finally both products were purely isolated by pressured silica gel column chromatography using ethyl acetate:hexane (4:1) (a 5% of triethylamine was added for the column preparation) to give (*E*)-**2** as a red oil (105 mg, 26%) and (*E*)-**3** pure as an orange red crystalline solid, m.p. 135–136 °C, (260 mg, 72%).

*3.3.1. Compound (E)-**3***

^{1}H-NMR ($CDCl_3$): 9.85 (s, 1H, CHO); 7.62 (d, 2H, $J = 8.09$ Hz, H-3‴ and H-5‴); 7.14 (d, 2H, $J = 8.09$ Hz, H-2‴ and H-6‴);6.73 (d, 1H, $J = 16.17$,H-2″); 6.60 (d, 1H, $J = 16.17$, H-1″); 4.72 (s, 2H, Cp);4.52 (s, 4H, Cp); 4.38 (s, 2H, Cp). ^{13}C-NMR ($CDCl_3$): 193.6 (*C*HO); 137.7 (C-3‴ and C-5‴); 136.7 (C-1‴); 127.7 (C-2‴ and C-6‴); 126.8 (C-2″); 125.9 (C-1″); 93.3 (C-4‴); 84.8 (Cp); 79.7 (Cp); 74.2 (Cp); 70.5 (Cp); 68.2 (2C, Cp); IR (KBr): 1681 (CHO); 1632 (C=C); 1002 (ferrocene); 961 (=C–H, *E*); 806 (π-sust. ArH); 479 (C–I); MS: 442 ([M$^+$], 96%), 287 (16), 165 (100), 121 (38).

*3.4. Synthesis of (E)-1-[β-(4-ethynylphenyl)-ethenyl]-1′-[2-(1,3-dioxolan)]ferrocene ((E)-**5**)*

*3.4.1. (a) (E)-1-{β-[4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl]-ethenyl}-1′-[2-(1,3-dioxolan)]ferrocene ((E)-**4**)*

In a three-necked round-bottom flask, previously flamed and under argon atmosphere, a mixture of freshly distilled triethylamine (10 ml) were placed purged with argon, and (*E*)-1′-[2-(1,3-dioxolan)]-1-[β-(*p*-iodophenyl)ethenyl]ferrocene, (*E*)-**2** (200 mg, 0.41 mmol) and 2-methyl-but-3-yn-2-ol (59 μl, 0.62 mmol). The mixture was stirred at r.t. and then dichlorobistriphenylphosphine palladium(II), 5.48 mg (0.0078 mmol) and a little amount of cuprous iodide in triethylamine (10 ml), were added in this order, and stirred for 18 h. Then, solvent was removed under reduced pressure and the residual solid was solved in dichloromethane (25 ml) and washed with a solution of NH_4Cl (500 mg) and NaCN (25 mg), in water (25 ml) and stirred for 2 h. The organic layer was dried on Na_2SO_4, and after filtration solvent was removed to give a residual solid, which was purified by pressured silica gel column chromatography using hexane:ethyl acetate (3:1) (a 5% of triethylamine was added for the column preparation). Compound (*E*-**4**) was isolated as an orange solid, m.p. 119–120 °C, (170 mg, 94%).

*3.4.2. Compound (E)-**4***

^{1}H-NMR ($CDCl_3$): 7.36 (s, 4H, H-2‴, H-3‴, H-6‴ and H-5‴); 6.90 (d, 1H, $J = 16.17$, H-2″); 6.71 (d, 1H, $J = 16.17$, H-1″); 5.66 (s,1H, –C*H*$(OCH_2)_2$); 4.49 (s, 2H, Cp); 4.34 (s, 2H, Cp); 4.29 (s, 2H, Cp); 4.15 (s, 2H, Cp); 4.02 (m, 2H, CH$(OCH_2)_2$); 3.89 (m, 2H, CH$(OCH_2)_2$); 1.63 (s, 6H, 2 CH_3). ^{13}C-NMR ($CDCl_3$):

137.8 (C-1‴); 131.9 (C-3‴ and C-5‴); 127.7 (C-2″); 125.5 (C-2‴, C-6‴ and C-1″); 120.7 (C-4‴); 102.4 ((*C*H(OCH$_2$)$_2$); 94.2 (*C*≡C–C(CH$_3$)$_2$OH)); 85.0 (Cp); 83.5 (Cp); 82.3 (C≡*C*–C(CH$_3$)$_2$OH)); 70.0 (Cp); 69.6 (Cp); 67.8 (Cp); 67.7 (Cp); 65.6 (C≡C–*C*(CH$_3$)$_2$OH)); 65.2 (CH(OCH$_2$)$_2$); 31.4 (C≡C–C(*C*H$_3$)$_2$OH)). IR (KBr): 3452 (OH); 1630 (C=C); 1084 (C–O–C); 958 (=C–H); 859 (π-subst. ArH); 815 (ferrocene).

Anal. Found: C, 70.43; H, 5.89. $C_{26}H_{26}O_3Fe$. Calc.: C, 70.60; H, 5.92%.

3.4.3. (b) (E)-1-[β-(4-ethynylphenyl)-ethenyl]-1′-[2-(1,3-dioxolan)]ferrocene ((E)-5)

In a three-necked round-bottom flask, previously flamed and under argon atmosphere, (*E*)-**4** (200 mg, 0.45 mmoles) in dry toluene (25 ml) were placed and then finally powdered sodium hydroxide (12 mg). The mixture was warmed at reflux temperature for 15 h and then filtered, and solvent removed under reduced pressure. The residual solid was purified by pressured silica gel column chromatography using hexane:ethyl acetate (4:1) (a 5% of triethylamine was added for the column preparation). Compound (*E*)-**5** was isolated as a red solid, m.p. 94–95 °C, 168 mg, 96%).

3.4.4. Compound (E)-5

^{1}H-NMR ($CDCl_3$): 7.44 (d, 2H, $J = 8.49$, H-3‴ and H-5‴);7.36 (2H, $J = 8.49$, H-2‴ and H-6‴); 6.90 (d, 1H, $J = 16.17$, H-2″); 6.35 (d, 1H, $J = 16.17$, H-1″); 5.65 (s,1H, –C*H*(OCH$_2$)$_2$); 4.49 (s, 2H, Cp); 4.33 (s, 2H, Cp); 4.29 (s, 2H, Cp); 4.14 (s, 2H, Cp); 4.00 (m, 2H, CH(OCH$_2$)$_2$); 3.86 (m, 2H, CH(OCH$_2$)$_2$); 3.14 (s, 1H, (C≡C–*H*). ^{13}C-NMR ($CDCl_3$): 138.3 (C-1‴); 132.7 (C-3‴ and C-5‴); 128.1 (C-2″); 125.4 (C-2‴, C-6‴);125.3 (C-1″); 119.9 (C-4‴); 102.3 ((*C*H(OCH$_2$)$_2$); 85.0 (*C*≡C–H); 83.9 (C≡*C*–H); 83.4 (Cp); 75.5 (Cp); 70.0 (Cp); 69.5 (Cp); 67.7 (Cp); 65.1 (CH(OCH$_2$)$_2$). IR (KBr): 3278 (C≡C–H); 1633 (C=C); 1088 (C–O–C); 950 (=C–H, *E*); 824 (π-subst. ArH). MS: 384 ([M$^+$], 99%), 340 (6), 312 (20), 247 (42), 189 (100).

3.5. Synthesis of (E)-1-{β-[4-(β-(1′-formylferrocenyl)-ethenyl)-phenylethynyl]-phenyl]-ethenyl}-1′-formylferrocene ((E,E)-6)

In a three-necked round-bottom flask, previously flamed and under argon atmosphere, a mixture of freshly distilled diethylamine (7 ml) were placed purged with argon, and (*E*)-**5** (95 mg, 0.25 mmol) and (*E*)-**2** (122 mg, 0.25 mmol) in freshly distilled triethylamine (30 ml) purged with argon. The mixture was stirred at r.t. and then dichlorobistriphenylphosphine palladium(II) (1.25 mg, 0.0017 mmol) and cuprous iodide (1.0 mg) were added in this order. The mixture was stirred at room temperature giving a red precipitate. After 16 h, solvent was removed under reduced pressure and the solid residue was washed with a solution of NH_4Cl (0.5 g) and NaCN (25 mg) in water (30 ml) and stirred for 2 h. The mixture was extracted with dichloromethane (25 ml) and the red organic layer was dried on Na_2SO_4, filtered and solvent removed to give a residual solid, which was purified by silica gel column chromatography using toluene:ethyl acetate 20:1 (a 5% of triethylamine was added for the column preparation). The treatment of the mixture with acetic acid (25 ml, 50%), neutralisation with solid Na_2CO_3, and extraction with dichloromethane (25 ml) gave (*E*,*E*)-**6** as a crystalline red solid, m.p. > 240 °C, (104 mg, 63%).

3.5.1. Compound (E,E)-6

^{1}H-NMR ($CDCl_3$): 9.91 (s, 2H, C*H*O); 7.50 (d, 4H, $J = 8.61$, H-3‴, H-3^V, H-5‴, H-5^V); 7.41 (4H, $J = 8.61$, H-2‴, H-2^V, H-6‴, H-6^V); 6.81 (d, 2H, $J = 16.43$, H-2″ and H-2^{IV}); 6.70 (d, 2H, $J = 16.43$, H-1″ and H-1^{IV}); 4.76 (s, 4H, Cp); 4.57 (s, 8H, Cp); 4.40 (s, 4H, Cp). ^{13}C-NMR ($CDCl_3$): 193.6 (CHO); 137.2 (C-1‴); 132.0 (C-3‴ and C-5‴); 127.4 (C-2″); 126.0 (C-1″); 125.9 (C-2‴, C-6‴);122.0 (C-4‴); 90.5 (*C*≡C); 85.0 (Cp); 79.8 (Cp); 74.4 (Cp); 70.7 (Cp); 68.3 (Cp). MS (70 eV): 654 ([M$^+$], 100%); 561 (13%); 411(13%). IR (KBr): 1685 (CHO); 1628 (C=C); 970 (=CH, *E*); 827 (π-subst. ArH). Anal. Found: C, 76.93; H, 4.92.$C_{40}H_{30}Fe_2$. Calc.: C, 77.19; H, 4.86%.

3.6. Synthesis of (E,E)-1,1′-bis-[β-(p-iodophenyl)-ethenyl)ferrocene ((E,E)-7) from (E)-3

In a three-necked round-bottom flask, previously flamed and under argon atmosphere, *p*-iodobenzyltriphenylphosphonium bromide [16a] (0.481 g, 1.01 mmol) in dry toluene (15 ml) was placed at 0 °C. A solution of potassium *tert*-butoxide (0.161 g, 0.67 mmol) in dry toluene (10 ml) was added and stirred for 30 min and then at 0 °C, under argon atmosphere, a solution of (*E*)-**3** (0.296 g, 0.67 mmol) in dry toluene (10 ml) was added slowly. The mixture was stirred at r.t. for 15 h and then, solvent was removed under reduced pressure. The residual red solid was solved in dichloromethane, washed with an aqueous solution of ammonium chloride and the organic layer dried on $MgSO_4$. After filtration the solvent was removed under reduced pressure to give a residual solid, which was purified by silica gel column chromatography using hexane:ethyl acetate (4:1). A mixture of *E*,*E* and *E*,*Z* isomers of **7** (3:1 by NMR) was obtained (0.425 g, 99%). By crystallization from hexane (*E*,*E*)-**7** (0.318 g, 74%) was purely isolated as a red solid, m.p. 166–167 °C while that remained in the hexane solution, (*E*,*Z*)-**7**, (0.14 g, 24%) was isolated as an orange–red solid, m.p. 89–90 °C.

3.6.1. Compound (EE)-7

^{1}H-NMR ($CDCl_3$): 7.5 (d, 4H, $J = 8.39$, H-3‴,H-3^V, H-5‴, H-5^V); 6.94 (d, 4H, $J = 8.39$, H-2‴, H-2^V, H-6‴, H-6^V); 6.65 (d, 2H, $J = 16.16$, H-2″ and H-2^{IV}); 6.45 (d, 2H, $J = 16.16$, H-1″ and H-1^{IV}); 4.41 (s, 4H, Cp); 4.26 (s, 4H, Cp). ^{13}C-NMR ($CDCl_3$): 137.5 (C-3‴, C-3^V, C-5‴ and C-5^V); 137.0 (C-1‴ and C-1^V); 127.3 (C-2‴, C-2^V, C-6‴ and C-6^V); 126.7(C-2″ and C-2^{IV}); 125.4 (C-1″ and C-1^{IV}); 91.5 (C-4‴ and C-4^V); 83.9 (C-1 and C-1′); 70.0 (Cp); 67.9 (Cp). IR (KBr): 1626 (C=C); 1000 (ferrocene); 958 (=C–H, *E*); 800 (π-subst. ArH); 482 (C–I). MS: 642 ([M$^+$], 75%), 349 (15), 222 (14), 165 (100).

3.6.2. Compound (E,Z)-7

^{1}H-NMR ($CDCl_3$): 7.68 (d, 2H, $J = 8.21$, H-3^V and H-5^V); 7.55 (d, 2H, $J = 8.21$, H-3‴ and H-5‴); 7.17 (d, 2H, $J = 8.21$, H-2^V, H-6^V); 7.00 (d, 2H, $J = 8.21$, H-2‴, H-6‴); 6.79(d, 1H, $J = 16.17$, H-2″); 6.58 (d, 1H, $J = 16.17$, H-1″); 6.29 (d, 1H, $J = 11.74$, H-2^{IV}); 6.23 (d, 1H, $J = 11.74$, H-1^{IV}); 4.38 (s, 2H, Cp); 4.25 (s, 2H, Cp); 4.16 (s, 4H, Cp). ^{13}C-NMR ($CDCl_3$): 137.6 (C-3‴, C-5‴); 137.4 (C-1^V); 137.2 (C-1‴); 137.0 (C-3^V and C-5^V); 130.4 (C-2^V and C-6^V); 128.5 (C-2^{IV}); 127.4 (C-2‴, C-6‴); 127.3 (C-2″); 126.4 (C-1^{IV}); 125.2 (C-1″); 91.8 (C-4^V); 91.6 (C-4‴); 83.5 (C-1); 81.6 (C-1′); 70.5 (Cp); 70.3 (Cp); 69.8 (Cp); 68.1 (Cp). IR (KBr): 1629 (C=C); 1001 (ferrocene); 959 (=CH, *E*); 855 (=C–H, *Z*); 803 (π-subst. ArH); 475 (C–I). MS: 642 ([M$^+$], 89%), 349 (17), 222 (14), 165 (100).

3.7. (E,Z)→(E,E) Isomerization 1,1′-bis-[β-(p-iodophenyl)ethenyl)ferrocene (7)

To a solution of (*E*,*Z*)-**7** isomer (0.23 g, 0.36 mmol) in hexane (100 ml) a crystal of iodine was added. The mixture was exposed to the sunlight and stirred for 10 days at r.t. (monitoring by thin layer chromatography). Later the solvent was removed under reduced pressure and the residual solid was solved in dichloromethane and treated with an aqueous solution of sodium thiosulfate. The organic layer was dried on $MgSO_4$, filtered and solvent removed under reduced pressure giving (*E*,*E*)-**7** in quantitative yield, m.p. 166–167 °C.

3.8. Synthesis of (E,E)-1,1′-bis-[β-(p-iodophenyl)-ethenyl)ferrocene (7) from 1,1′-diformylferrocene

In a three-necked round-bottom flask, previously flamed and under argon atmosphere, *p*-iodobenzyltriphenylphosphonium bromide (5.42 g, 11.34 mmol) [14a] in dry toluene (25 ml) was placed at 0 °C. Potassium *tert*-butoxide (1.91 g, 17.01 mmol) was added and stirred for 40 min and then at 0 °C, under argon atmosphere, a solution of 1,1′-diformylferrocene (0.78 g, 3.24 mmol) in dry toluene (20 ml) was slowly added. The mixture was stirred at r.t. for 36 h and after solvent evaporation under reduced pressure, the residual red solid was solved in dichloromethane, washed with an aqueous solution of ammonium chloride and the organic layer dried on $MgSO_4$. Later the mixture was filtered and solvent removed under reduced pressure to give a residual solid, which was purified by column chromatography using hexane:ethyl acetate (4:1). A mixture of *E*,*E*, *E*,*Z* and *Z*,*Z* isomers of **7** were obtained as a red solid (1.3 g, 62%) in 41:43:16 molar ratio (by NMR). To a concentrate solution of the mixture of **7** in CH_2Cl_2, hexane was slowly dropped and the *E*,*E* pure isomer precipitated as a red solid (0.53 g, 25%), m.p. 166–167 °C. The mixture of (*E*,*Z*) and (*Z*,*Z*) isomers obtained from evaporation of the hexane solution, were purely isolated by silica gel column chromatography using hexane:dichloromethane (10:1) as the eluent; the (*E*,*Z*)-**7** isomer was an orange solid (0.55 g, 26%), m.p. 88–90 °C and the (*Z*,*Z*)-**7** isomer was a dark red solid (0.21 g, 10%), m.p. 72–73 °C.

3.8.1. Compound (Z,Z)-7

^{1}H-NMR ($CDCl_3$): 7.59 (d, 4H, $J = 8.6$, H-3‴, H-3 ^{V}, H-5‴, H-5 ^{V}); 7.06 (d, 4H, $J = 8.6$, H-2‴, H-2 ^{V}, H-6‴, H-6 ^{V}); 6.36 (d, 2H, $J = 11.83$, H-2″ and H-2^{IV}); 6.21 (d, 2H, $J = 11.83$, H-1″ and H-1^{IV}); 4.12 (s, 4H, Cp); 4.07 (s, 4H, Cp); ^{13}C-NMR ($CDCl_3$): 137.4 (C-1‴ and C-1^V); 137.1 (C-3‴, C-3^V, C-5‴ and C-5^V); 130.6 (C-2‴, C-2^V, C-6‴ and C-6^V); 128.3 (C-2″ and C-2^{IV}); 126.1 (C-1″ and C-1^{IV}); 91.8 (C-4‴ and C-4^V); 81.6 (C-1 and C-1′); 70.5 (Cp); 69.9 (Cp). IR (KBr): 1625 (C=C); 1005 (ferrocene); 853 (=C–H, *Z*); 800 (π-subst. ArH); 488 (C–I). MS: 642 ([M$^+$], 92%), 349 (18), 222 (15), 165 (100).

3.9. (Z,Z)/(E,Z)→(E,E) Isomerization of 1,1′-bis-[β-(p-iodophenyl)ethenyl]ferrocene (7)

To a solution of (*E*,*Z*)-**7** and (*Z*,*Z*)-**7** (1.0 g, 1.56 mmol) in hexane (425 ml) a crystal of iodine was added. The mixture was exposed to the sunlight and stirred for 10 days at r.t. (monitoring by thin layer chromatography). Later the solvent was removed under reduced pressure and the residual solid was solved in dichloromethane and treated with an aqueous solution of sodium thiosulfate. The organic layer was dried on $MgSO_4$, filtered and solvent removed under reduced pressure giving (*E*,*E*)-**7** in quantitative yield, m.p. 166–167 °C.

3.10. Synthesis of (E,E)-1,1′-[β-(4-ethynylphenyl)-ethenyl]ferrocene (10)

3.10.1. (a) (E)-1-{β-[4-(3-hydroxy-3-methyl-but-1-ynyl)phenyl]-ethenyl}-1′-[2-(1,3-dioxolan)]ferrocene (9)

In a three-necked round-bottom flask, previously flamed and under argon atmosphere, a mixture of freshly distilled triethylamine (30 ml) purged with argon, and (*E*,*E*)-**7** (0.2 g, 0.31 mmol) and 2-methyl-but-3-yn-2-ol (90 μl, 0.96 mmol) were placed. The mixture was stirred at r.t. and then dichlorobistriphenylphosphine palladium (4.21 mg, 0.006 mmol) and a little amount of cuprous iodide in triethylamine (10 ml), were added in this order. After 14 h stirring at r.t., the solvent was removed under reduced pressure and the residual solid was solved in dichloromethane (20 ml) and washed with a solution of NH_4Cl (500 mg) and NaCN (25 mg), in water (25 ml) and stirred for 2 h. The organic layer was dried on Na_2SO_4, and after filtration solvent was removed to give a residual solid, which was purified by pressurized silica gel column chromatography using hexane:ethyl acetate (3:1). Compound (*E*,*E*)-**8** was isolated as a red solid (173 mg, 99%), m.p. 189–190 °C.

For an equimolar mixture of (*E*,*E*)-**7**/propargylic alcohol, (*E*,*E*)-**9** was obtained in low yield (6 mg, 7%) together the monocross-coupling product (*E*,*E*)-**8**, as a red solid (17.3 mg, 19%), m.p. 172–174 °C.

*3.10.2. Compound (E,E)-**8***

^{1}H-NMR ($CDCl_3$): 7.53 (d, 2H, $J = 8.6$, H-3^V, H-5^V);7.27 (d, 2H, $J = 8.6$, H-3‴, H-5‴); 7.16 (d, 2H, $J = 8.6$, H-2‴, H-6‴); 6.96(d, 2H, $J = 8.6$, H-2 ^{V}, H-6^V); 6.70 (d, 1H, $J = 16.13$, HC=CH); 6.69 (d, 1H, $J = 16.13$, HC=CH); 6.55 (d, 1H, $J = 16.13$, HC=CH); 6.49(d, 1H, $J = 16.13$, HC=CH); 4.46 (s, 4H, Cp); 4.31 (s, 4H, Cp); 2.06 (s, 1H, O*H*); 1.69 (s, 6H, 2 CH_3). ^{13}C-NMR ($CDCl_3$): 138.1(C-5^V and C-3^V); 137.7 (C-1‴ and C-1^V); 132.5 (C-3‴ and 5‴); 127.9 (C-2^V and C-6^V); 127.5 (C-2^{IV}); 127.4 (C-2″); 126.5 (C-1″); 126.1 (C-1^{IV}); 126.0 (C-2″ and C-6‴); 121.3 (C-4‴); 94.8 (*C*≡C-C(CH_3)$_2$OH)); 91.1 (C-4^V); 84.6 (Cp); 84.5 (Cp); 83.1 (C≡*C*–C(CH_3)$_2$OH)); 70.7 (Cp); 68.6 (Cp); 66.4 (C≡C–*C*(CH_3)$_2$OH)); 32.2 (2*C*H_3). IR (KBr): 3418 (OH); 1628 (C=C); 1002 (ferrocene); 956 (=C–H, *E*); 812 (ferrocene); 799 (π-subst. ArH); 483 (C–I).

Anal. Found: C, 63.69; H, 4.82. $C_{31}H_{27}FeI$. Calc.: C, 63.94; H, 4.67%.

*3.10.3. Compound (E,E)-**9***

^{1}H-NMR ($CDCl_3$): 7.21 (d, 4H, $J = 8.49$, H-3‴,H-3^V, H-5‴, H-5^V); 7.10 (d, 4H, $J = 8.49$, H-2‴, H-2^V, H-6‴, H-6^V); 6.64 (d, 2H, $J = 16.17$, H-2″ and H-2^{IV}); 6.51 (d, 2H, $J = 16.17$, H-1″ and H-1^{IV}); 4.42 (s, 4H, Cp); 4.27 (s, 4H, Cp); 2.54 (s, 2H, O*H*); 1.63 (s, 6H, 2 CH_3). ^{13}C-NMR ($CDCl_3$): 137.4 (C-1‴ and C-1^V); 131.8 (C-3‴,C-3^V, C-5‴ and C-5^V); 126.9 (C-2″ and C-2^{IV}); 125.9 (C-1″ and C-1^{IV}); 125.3 (C-2‴, C-2^V, C-6‴ and C-6^V); 120.6 (C-4‴ and C-4^V); 94.1 (*C*≡C–C(CH_3)$_2$OH)); 84.1 (C-1 and C-1′); 82.4 (C≡*C*–C(CH_3)$_2$OH)); 69.9 (Cp); 67.9 (Cp); 65.6 (C≡C–*C*(CH_3)$_2$OH)); 31.5 (2*C*H_3). IR (KBr): 3283 (OH); 1630 (C=C); 962 (=C–H, *E*); 926 (π-subst. ArH); 812 (ferrocene).

Anal. Found: C, 82.48; H, 6.82. $C_{36}H_{34}Fe$. Calc.: C, 82.75; H, 6.56%.

*3.10.4. (b) (E,E)-1,1′-[β-(4-ethynylphenyl)-ethenyl]ferrocene (**10**)*

In a three-necked round-bottom-flask, previously flamed and under argon atmosphere, (*E*,*E*)-**9** (0.163 g, 0.29 mmoles) in dry toluene (25 ml) and finally powdered sodium hydroxide (10 mg) were placed. The mixture was warmed at reflux temperature for 15 h, and then filtered and solvent removed under reduced pressure. The residual solid was washed with hexane, giving (*E*,*E*)-**10** as a red solid, m.p. 208–209 °C, 127 mg, 99%).

*3.10.5. Compound (E,E)-**10***

^{1}H-NMR ($CDCl_3$): 7.33 (d, 4H, $J = 8.09$, H-3‴, H-3^V, H-5‴, H-5^V);7.20 (d, 4H, $J = 8.09$, H-2‴, H-2^V, H-6‴, H-6^V); 6.73 (d, 2H, $J = 16.17$, H-2″ and H-2^{IV}); 6.55 (d, 2H, $J = 16.17$, H-1″ and H-1^{IV}); 4.42 (s, 4H, Cp); 4.28 (s, 4H, Cp); 3.14 (s, 2H, ≡C–H). ^{13}C-NMR ($CDCl_3$): 138.1 (C-1‴ and C-1^V); 132.4 (C-3‴, C-3^V, C-5‴ and C-5^V); 127.4 (C-2″ and C-2^{IV}); 125.7 (C-1″ and C-1^{IV}); 125.4 (C-2‴, C-2^V, C-6‴ and C-6^V); 120.0 (C-4‴ and C-4^V); 83.9 (≡C–H)); 83.8 (C≡)); 77.5 (C-1 and C-1′); 70.2 (Cp); 68.2 (Cp). IR (KBr): 3276 (C≡C–H); 1630 (C=C); 960 (=C–H); 859 (π-subst. ArH).

Anal. Found: C, 82.03; H, 5.50. $C_{30}H_{22}Fe$. Calc.: C, 81.91; H, 5.39%.

*3.11. Biphenylation of (E,E)-1,1′-bis-[β-(p-iodophenyl)-ethenyl)ferrocene (**7**) catalyzed by nickel zerovalent complexes*

In a round-bottom flask under argon atmosphere a solution of anhydrous $NiCl_2(PPh_3)_2$ (0.4 g, 0.61 mmol) in anhydrous THF (17 ml), tetrabutyl ammonium iodide (0.227 g, 0.61 mmol) and Zn powder (40 mg, 0.61 mmol) was placed. The mixture solution was stirred at r.t., changing from green to red in colour, and after 30 min a solution of (*E*,*E*)-**7** (193 mg, 0.61 mmol) in anhydrous THF (10 ml) was added. After 3 days all of the starting compound **7** was transformed and then dichloromethane (50 ml) was added to the mixture and the nickel catalyst filtered and destroyed with a solution of HCl (10%). The dichloromethane solution was dropped with diethyl ether to give a red precipitate, which was analyzed by molecular mass characterization techniques (MALDI), giving a mixture of the dimer ([M$^+$], 1030), trimer ([M$^+$], 1418), tetramer ([M$^+$], 1806), dimer-box ([M$^+$], 776) which from the intensity of the spectrum are in a 75:55:10:6 ratio, respectively. A new precipitate was isolated from a solution of hexane–ethyl acetate and it was also analyzed by MALDI

giving a mixture with the dimer-box ([M^+], 776), as the main product.

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