

Scheme 1.

prepare the ylid. Thus, with 1 equiv. of the salt and 1 equiv. of <sup>n</sup>BuLi, or KO<sup>t</sup>Bu, the 1-ferrocenyl-2-(*p*-iodophenyl)ethene was obtained in 21 or 69% respectively; while 1.5 equiv. of the salt and 1 equiv. of KO<sup>t</sup>Bu give practically quantitative yields (98%) as a *Z/E* mixture (31:69 by <sup>1</sup>H NMR).

### 2.2. Isomerization *Z* → *E* of the mixture of 1-ferrocenyl-2-(*p*-iodophenyl)ethene

The separation of the mixture of 1-ferrocenyl-2-(*p*-iodophenyl)ethene (*Z/E* 31:69) by chromatographic methods was unsuccessful, although both isomers were purely isolated in low scale by laborious fractional crystallisation in *n*-hexane.

Moreover, in general the *E*-isomer exhibits better electrical and optical properties, and it was necessary to plan 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/E* mixture was carried out with iodine and exposure to sunlight, but after several days no reaction was observed. However, the transformation was complete after six days using iodine in molar relation 1:10 with the mixture, under the same conditions but with the addition of a crystal of

*N*-bromosuccinimide, acting as initiator of the reaction (Scheme 1).

### 2.3. X-ray molecular structure of (*E*)-1-ferrocenyl-2-(*p*-iodophenyl)ethene, (*E*)-1

The molecular structure of (*E*)-1-ferrocenyl-2-(*p*-iodophenyl)ethene, with crystallographic numbering scheme, is shown in Fig. 1. Table 1 shows the fractionated atomic coordinates and in Table 2 are listed (a) bond distances, (b) bond angles and (c) some torsion angles.

The Fe–C bond distances found for the substituted Cp ring (2.04(1) Å av.) are similar to those found in the literature [13]. It is remarkable that the different distances of the Fe atom to the centroids of the cyclopentadienyl rings are at 1.635(1) and 1.665(1) Å, the last for the unsubstituted ring. The bond distance I1–C1 (2.08(1) Å) shows some shortening (2.107(4) Å [14]).

In the solid state the molecule is not planar, the iodine atom is situated at –0.14(1) Å out of the plane of the phenyl ring; in contrast, the torsion angle C4–C7–C8–C9 of –175(1)° deviates significantly from planarity, as well as the dihedral angle 13.7(4)° formed by the phenyl and cyclopentadienyl rings.

Fig. 2 shows a packing diagram which includes

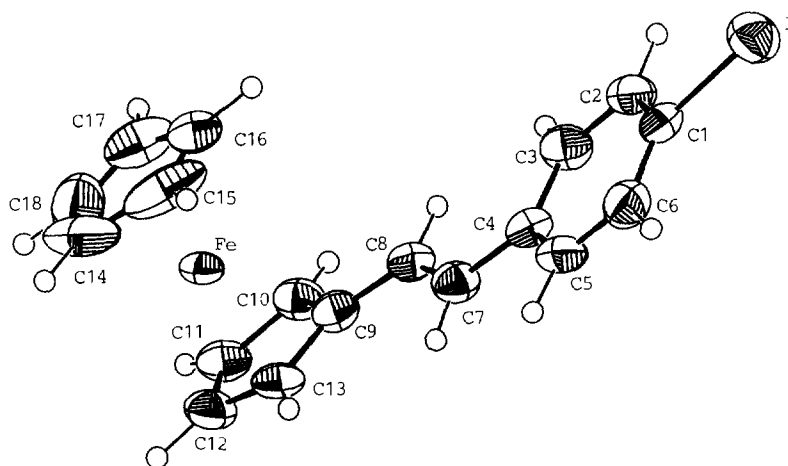


Fig. 1. View of the molecule with atomic numbering scheme; displacement ellipsoids enclosing 50% electron probability surface; H atoms represented by spheres of arbitrary radius.

Table 1  
Atomic parameters for (*E*)-1

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
I1	0.0258(0)	0.0648(2)	0.5233(1)	62(0)
FE1	-0.3188(1)	0.8507(2)	0.2238(1)	37(0)
C1	-0.0318(4)	0.2393(20)	0.4140(9)	45(3)
C2	-0.0505(5)	0.4503(20)	0.4500(9)	47(3)
C3	-0.0909(5)	0.5621(19)	0.3822(10)	48(3)
C4	-0.1146(4)	0.4668(21)	0.2781(10)	47(3)
C5	-0.0942(5)	0.2576(21)	0.2436(9)	48(3)
C6	-0.0540(5)	0.1454(21)	0.3083(11)	52(3)
C7	-0.1604(5)	0.5763(19)	0.2066(9)	45(3)
C8	-0.1882(4)	0.7636(21)	0.2338(10)	47(3)
C9	-0.2351(4)	0.8580(19)	0.1688(10)	43(3)
C10	-0.2577(5)	1.0805(19)	0.1837(10)	48(3)
C11	-0.3053(5)	1.1049(19)	0.1041(10)	49(3)
C12	-0.3137(5)	0.9030(22)	0.0411(10)	54(4)
C13	-0.2715(5)	0.7513(18)	0.0781(9)	45(3)
C14	-0.3956(6)	0.8886(38)	0.3038(17)	91(7)
C15	-0.3930(0)	0.6907(0)	0.2653(0)	156(0)
C16	-0.3417(10)	0.5845(25)	0.3254(15)	92(6)
C17	-0.3227(0)	0.7467(0)	0.3997(0)	116(0)
C18	-0.3573(8)	0.9318(30)	0.3854(14)	81(6)

Coordinates and thermal parameters as  $U_{eq} = (1/3)\Sigma[U_{ij}a_i^*a_j^*\cos(a_i, a_j)] \times 10^3$ .

extracellular molecules exhibiting festoon-like molecular chains which form through a short contact (3.63 Å) between the iodine atom and the centroid of the cyclopentadienyl ring of charge transfer type with weak effect which does not reach the double bond C7–C8 (1.33(2) Å). However, the charge transfer complex is justified by the I1–C1 and Fe–cyclopentadienyl centroid bond distances found above, the Cp ring being the donor (distance enlargement) and the iodine atom the acceptor.

There are other contacts between the centroids of the phenyl rings (4.99 Å), the phenyl ring and the centroid of the cyclopentadienyl ring (4.91 Å) and the centroids of two cyclopentadienyl rings (4.79 Å) [15], giving rise to a network which links laterally adjacent chains.

#### 2.4. Homocoupling reaction of 1-ferrocenyl-2-(*p*-iodophenyl)ethene

The homocoupling reaction of haloarenes to prepare the biaryl derivatives permits the extension of the molecular conjugation. The reaction has been carried out in quantitative yields with nickel zero-valent complexes [16].

The 1-ferrocenyl-2-(*p*-iodophenyl)ethene was submitted to a homocoupling reaction with tris(triphenyl)nickel(0) complex prepared in situ by reduction of dichlorobis(triphenylphosphine)nickel(II) with zinc in THF, in the presence of tetrabutylammonium iodide as phase transfer [16]. The reaction was carried out at room temperature in 30% yield, which was not enhanced by the temperature or the reaction time (Scheme 2).

The biphenyl compound (*E,E*)-2 shows, by NMR for the double bond, the Cp–CH= and Ph–CH= protons at 6.96 and 6.73 respectively as doublets, but with short coupling constant for the *E*-isomer ( $J = 12.3$  Hz; IR 960 cm<sup>-1</sup>); at 6.90 and 6.60 for the same protons in (*E*)-1. Thus, (*E,E*)-2 shows practically the same electronic polarization as the iodine derivative (*E*)-1, and in solution the phenyl rings in the biphenyl system are not coplanar.

#### 2.5. Synthesis and homocoupling reaction of (*E*)- and (*Z*)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene

The synthesis of (*E*)- and (*Z*)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene was carried out by the oxidative coupling reaction of (*E*)- or (*Z*)-1 with 2-methyl-but-3-in-2-ol catalysed by palladium, and ulterior treatment with powdered sodium hydroxide for propanone elimination, to give (*E*)-3 or (*Z*)-3 in good yield (Scheme 3).

The extension of the conjugation from the acetylenes was carried out by oxidative dimerisation of (*E*)-3 and

Table 2

(a) Bond distances (Å)			
I1–C1	2.082(10)	C3–C4	1.393(15)
Fe1–C9	2.042(11)	C4–C5	1.395(17)
Fe1–C10	2.030(12)	C4–C7	1.479(15)
Fe1–C11	2.040(11)	C5–C6	1.355(16)
Fe1–C12	2.036(11)	C7–C8	1.332(16)
Fe1–C13	2.033(10)	C8–C9	1.422(15)
Fe1–C14	2.004(16)	C9–C10	1.445(16)
Fe1–C15	2.028(0)	C9–C13	1.457(15)
Fe1–C16	2.020(16)	C10–C11	1.419(16)
Fe1–C17	2.032(0)	C11–C12	1.409(17)
Fe1–C18	2.047(16)	C12–C13	1.399(17)
Fe1–CO2	1.635(1)	C14–C15	1.263(23)
Fe1–CO3	1.665(1)	C14–C18	1.290(24)
C1–C2	1.397(17)	C15–C16	1.506(20)
C1–C6	1.390(16)	C16–C17	1.345(17)
C2–C3	1.373(16)	C17–C18	1.381(18)

#### (b) Bond angles (°)

I1–C1–C6	121.1(8)	C8–C9–C13	128(1)
I1–C1–C2	119.6(8)	C8–C9–C10	126(1)
C2–C1–C6	119(1)	C10–C9–C13	106(1)
C1–C2–C3	120(1)	C9–C10–C11	108(1)
C2–C3–C4	121(1)	C10–C11–C12	109(1)
C3–C4–C7	123(1)	C11–C12–C13	109(1)
C3–C4–C5	117(1)	C9–C13–C12	109(1)
C5–C4–C7	120(1)	C15–C14–C18	113(2)
C4–C5–C6	123(1)	C14–C15–C16	107(1)
C1–C6–C5	120(1)	C15–C16–C17	103(1)
C4–C7–C8	127(1)	C16–C17–C18	109(1)
C7–C8–C9	127(1)	C14–C18–C17	109(1)

#### (c) Selected torsion angles (°)

C3–C4–C7–C8	-6(2)
C5–C4–C7–C8	173(1)
C4–C7–C8–C9	-175(1)
C7–C8–C9–C10	-167(1)
C7–C8–C9–C13	16(2)

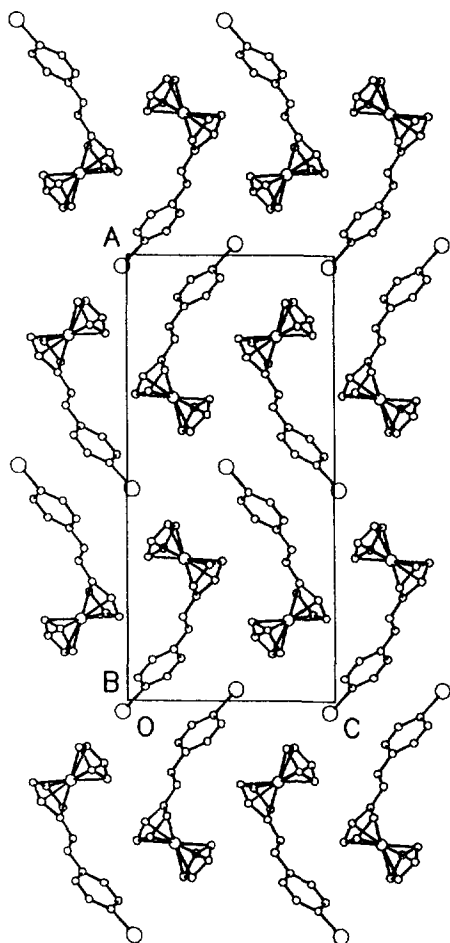


Fig. 2. Packing diagram of the molecules in the crystal viewed along the *b*-axis.

(*Z*)-**3** respectively, with cuprous chloride in pyridine and oxygen as the oxidant agent to give the dimers (*E,E*)-**4** and (*Z,Z*)-**4** in good yield (Scheme 3).

The diyne compounds (*E,E*)-**4** and (*Z,Z*)-**4** show by NMR similar proton and carbon frequencies for the double bond and ferrocene ring as these in the acetylene precursors (*E*)-**3** and (*Z*)-**3** (see Section 3), and thus similar electronic polarization through the 1,3-diyne system in both (*E*)-**3** and (*Z*)-**3** and (*E,E*)-**4** and (*Z,Z*)-**4** compounds.

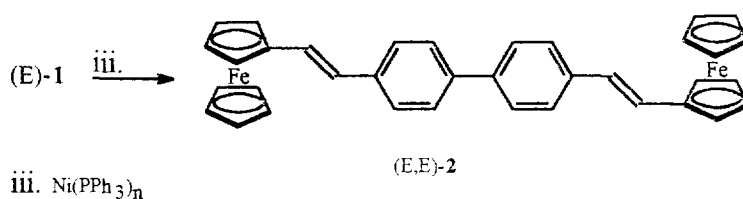
### 3. Experimental

#### 3.1. Synthesis of 1-ferrocenyl-2-(*p*-iodophenyl)ethene

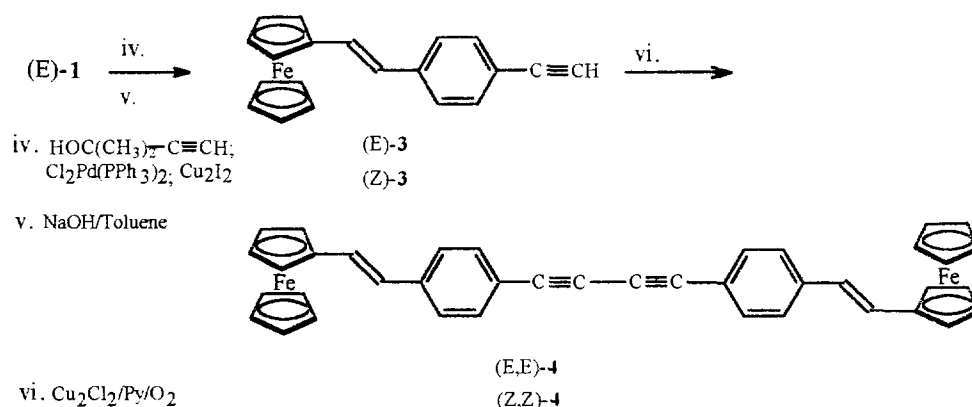
##### 3.1.1. Preparation of *p*-bromomethyl iodobenzene

To a solution of 4-iodotoluene (13.83 g, 63.42 mmol) in 50 ml of tetrachloromethane was added, with stirring and in an ice-water bath, *N*-bromosuccinimide (11.28 g, 63.42 mmol) and benzoyl peroxide (390 mg). The mixture was warmed at the reflux temperature overnight. Afterwards the mixture was filtered and the solvent removed to give a residual solid which was purified by chromatography in a silica gel column using *n*-hexane/dichloromethane 5:1 as eluent. The *p*-bromomethyl iodobenzene was isolated as a white solid; m.p. 63–65 °C, 13.18 g (70%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.68 (d, 2H, *J* = 8.75 Hz, H-1), 7.10 (d, 2H, *J* = 8.75 Hz, H-2), 4.45 (s, 2H, CH<sub>2</sub>Br).



Scheme 2.



Scheme 3.

### 3.1.2. Preparation of *p*-iodobenzyltriphenylphosphonium bromide

A solution of 7.84 g (29.92 mmol) of triphenylphosphine, 7.84 g (29.92 mmol) in 20 ml of anhydrous toluene and 4-bromomethyl iodobenzene (8.88 g, 29.92 mmol) was warmed at the reflux temperature overnight to give a white solid that was filtered and washed with toluene. The *p*-iodobenzyltriphenylphosphonium bromide is a white solid; m.p. 255–256°C, 16.39 g (98%).

### 3.1.3. Preparation of 1-ferrocenyl-2-(*p*-iodophenyl)ethene

In a three-necked bottom flask, previously flamed and under argon atmosphere, in an ice-water bath, was placed *p*-iodobenzyltriphenylphosphonium bromide (12.48 g, 22.33 mmol) dispersed in anhydrous toluene (60 ml). To this mixture was added potassium *tert*-butoxide (3.76 g, 33.50 mmol) and, after 30 min, the solution took an intense orange colour. Into this was dropped a solution of ferrocenecarboxaldehyde (3.19 g, 14.88 mmol) in dry toluene (30 ml). After 30 min, the mixture was stirred at room temperature overnight. Then, the solvent was removed and the residual solid was extracted with dichloromethane and purified by silica gel column chromatography using *n*-hexane/dichloromethane 8:1 as eluent. The 1-ferrocenyl-2-(*p*-iodophenyl)ethene, 6.04 g (98%) was obtained as a mixture of *E*/*Z*-isomers (31:69 by NMR). By means of fractional crystallisation of the mixture, purely the *E*-isomer was isolated as an orange solid; m.p. 94–96°C, and the *Z*-isomer as a red oil.

**3.1.3.1. (*E*)-1-ferrocenyl-2-(*p*-iodophenyl)ethene.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.65 (d, 2H,  $J = 8.44$  Hz, H-3'' and H-5''), 7.15 (d, 2H,  $J = 8.44$  Hz, H-2'' and H-6''), 6.92 (d, 1H,  $J = 16.12$  Hz, H-2), 6.60 (d, 1H,  $J = 16.12$  Hz, H-1), 4.45 (m, 2H, H-2' and H-5'), 4.30 (m, 2H, H-3' and H-4'), 4.15 (s, 5H, cyclopentadienyl).  $^{13}\text{C}$  NMR ( $\text{DCCl}_3$ ): 137.5 (2C, C-3'' and C-5''), 137.3 (C-1''), 127.9 (C-2), 127.4 (2C, C-2'' and C-6''), 124.6 (C-1), 91.8 (C-4''), 82.7 (C-1'), 69.2 (7C, C-3', CA' and cyclopentadienyl), 66.9 (2C, C-2' and C-5'). MS (70 eV): 414 ( $\text{M}^+$ , 100), 287 (39), 207 ( $\text{M}^{2+}$ , 12), 165 (67), 121 (23). IR (KBr): 1625 (C=C), 1000 (ferrocene), 960 (=C-H), *E*-isomer), 820 (ferrocene), 810 (ArH, *p*-subst.). UV/vis ( $\text{CH}_2\text{Cl}_2$ ): 228 ( $\epsilon$ , 16940), 270 ( $\epsilon$ , 17889), 314 ( $\epsilon$ , 26909), 457 ( $\epsilon$ , 15221 mol $^{-1}$  cm $^{-1}$ ). Anal. Found: C, 51.92; H, 3.88; I, 30.29.  $\text{C}_{18}\text{H}_{15}\text{FeI}$  Calc.: C, 52.21; H, 3.65; I, 30.65%.

**3.1.3.2. (*Z*)-1-ferrocenyl-2-(*p*-iodophenyl)ethene.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.60 (d, 2H,  $J = 7.83$  Hz, H-3'' and H-5''), 7.09 (d, 2H,  $J = 7.83$  Hz, H-2'' and H-6''), 6.37 (d, 1H,  $J = 12.10$  Hz, H-2), 6.29 (d, 1H,  $J = 12.10$  Hz, H-1), 4.18 (m, 4H, H-2' and H-5', H-3' and H-4'), 4.10

(s, 5H, cyclopentadienyl).  $^{13}\text{C}$  NMR ( $\text{DCCl}_3$ ): 137.5 (C-1''), 137.0 (2C, C-3'' and C-5''), 130.6 (2C, C-2'' and C-6''), 129.0 (C-2), 125.8 (C-1), 91.8 (C-4''), 80.9 (C-1'), 69.3 (2C, C-3' and C-4'), 69.2 (5C, cyclopentadienyl), 68.7 (2C-2' and C-5'). MS (70 eV): 414 ( $\text{M}^+$ , 100), 287 (38), 207 ( $\text{M}^{2+}$ , 9), 165 (63), 121 (21). IR (film): 1625 (C=C), 1000 (ferrocene), 850 (=C-H), *Z*-isomer), 820 (ferrocene), 790 (ArH, *p*-subst.). UV/vis ( $\text{CH}_2\text{Cl}_2$ ): 231 ( $\epsilon$ , 17050), 268 ( $\epsilon$ , 13931), 298 ( $\epsilon$ , 13957), 450 ( $\epsilon$ , 6801 mol $^{-1}$  cm $^{-1}$ ). Anal. Found: C, 52.02; H, 3.40; I, 30.35.  $\text{C}_{18}\text{H}_{15}\text{FeI}$  Calc.: C, 52.21; H, 3.65; I, 30.65%.

### 3.1.4. Isomerization *Z* → *E* of 1-ferrocenyl-2-(*p*-iodophenyl)ethene

In a bottom flask was placed a solution of the *Z*/*E* mixture of 1-ferrocenyl-2-(*p*-iodophenyl)ethene (150 mg) in tetrachloromethane (20 ml) and iodine (5 mg) and a crystal of *N*-bromosuccinimide. The mixture was exposed to sunlight at room temperature for six days (monitoring by thin layer chromatography). Afterwards, the solvent was removed at reduced pressure and the residual solid was purified by silica gel column chromatography using *n*-hexane/dichloromethane 8:1 to give pure (*E*)-1-ferrocenyl-2-(*p*-iodophenyl)ethene as an orange crystalline solid; m.p. 94–96°C, in quantitative yield.

### 3.2. Synthesis of 4,4'-di[(*E*)-ethenyl-2-ferrocenyl]biphenyl by homocoupling reaction of (*E*)-1 with nickel zero-valent complex

In a bottom flask under anhydrous and argon atmosphere was placed a solution of anhydrous  $\text{NiCl}_2(\text{PPh}_3)_2$  (0.79 g, 1.2 mmol) in anhydrous THF (10 ml), tetrabutyl ammonium iodide (0.446 g, 1.2 mmol) and Zn powder (79 mg, 1.2 mmol). The mixture solution was stirred at room temperature, changing from green to red in colour, and after 30 min a solution of (*E*)-1-ferrocenyl-2-(*p*-iodophenyl)ethene (0.5 g, 1.2 mmol) in anhydrous THF (25 ml) was added. After three days dichloromethane (50 ml) was added to the mixture and the nickel catalyst filtered and destroyed with a solution of HCl (10%). The solvent was removed at reduced pressure and the dark residual solid was purified by pressurised silica gel column chromatography, using *n*-hexane/dichloromethane (10:1) as eluent. 4,4'-di[(*E*)-ethenyl-2-ferrocenyl]biphenyl was isolated as an orange solid; m.p. > 250°C (decomp.), 103.1 mg (30%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.61 (d, 4H,  $J = 8.12$  Hz, H-2' and H-6'), 7.53 (d, 4H,  $J = 8.12$  Hz, H-3' and H-5'), 6.96 (d, 2H,  $J = 16.32$  Hz, =CH, H-1), 6.73 (d, 2H,  $J = 16.32$  Hz, =CH, H-2), 4.49 (m, 4H, H-2'' and H-5''), 4.30 (m, 4H, H-3'' and H-4''), 4.17 (s, 10H, cyclopentadienyl rings). IR (KBr): 1550 and 1500 (C=C, 960 (=C-H, *E*-isomer), 820 (ferrocene), 810 (Ar C-H, *p*-subst.). MS (70 eV): 574 ( $\text{M}^+$ , 100), 509 (16), 287

( $M^{2+}$ , 28), 121 (14). UV/vis ( $CH_2Cl_2$ ),  $\lambda_{max}$  (nm): 229 ( $\epsilon$ , 25526), 348 ( $\epsilon$ , 31200), 453 ( $\epsilon$ , 3581  $mol^{-1} cm^{-1}$ ). Anal. Found: C, 75.05; H, 5.67%.  $C_{36}H_{32}Fe_2$  Calc.: C, 75.29; H, 5.27; Fe, 19.45%.

### 3.3. Synthesis of (*E*)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene, (*E*)-3

#### 3.3.1. Preparation of (*E*)-1-ferrocenyl-2-[*p*-(1'-butyn-3'-methyl-3'-ol)phenyl]ethene

In a three-necked bottom flask, previously flamed and under argon atmosphere, was placed a mixture of freshly distilled diethylamine (40 ml) purged with argon, and (*E*)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene, (*E*)-3 (3.91 g, 9.44 mmol) and 2-methyl-but-3-yn-2-ol (0.79 mg, 9.44 mmol). The mixture was stirred at room temperature and then dichlorobis(triphenyl)phosphine palladium(II) (0.13 g, 0.18 mmol) and cuprous chloride (10 mg) were added in this order. After 15 h, the solvent was partially removed at reduced pressure and 25 ml of an aqueous solution of  $NH_4Cl$  (500 mg) and NaCN (25 mg) in 25 ml was added and stirred for 2 h, and extracted with dichloromethane (25 ml). The organic layer was dried with  $NaSO_4$ , and after filtration solvent was removed to give a residual solid, which was purified by pressurised silica gel column chromatography using hexane/ethyl acetate 3:1 as eluent. (*E*)-1-ferrocenyl-2-[*p*-(1'-butyn-3'-methyl-3'-ol)phenyl]ethene was isolated as an orange solid; m.p. 156–158 °C, 3.01 g (86%).

$^1H$  NMR ( $CDCl_3$ ): 7.38 (s, 4H, H-2'', H-3'', H-5'' and H-6''), 6.90 (d, 1H,  $J = 16.13$  Hz, H-2), 6.65 (d, 1H,  $J = 16.13$  Hz, H-1), 4.46 (m, 2H, H-2' and H-5'), 4.31 (m, 2H, H-3' and H-4'), 4.15 (s, 5H, cyclopentadienyl), 2.55 (s, 1H, OH), 1.62 (s, 6H,  $CH_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ): 137.5 (C-1''), 131.7 (2C, C-3'' and C-5''), 127.9 (C-2), 125.3 (2C, C-2'' and C-6''), 125.0 (C-1'), 120.7 (C-4''), 94.2 [ $C\equiv C-C(CH_3)_2$ ], 82.7 (C-1'), 81.8 [ $C\equiv C-C(CH_3)_2$ ], 69.0 (7C, C-3', C-4' and cyclopentadienyl), 66.7 (2C, C-2' and C-5'), 65.0 [ $C\equiv C-C(CH_3)_2$ ], 31.1 [ $(CH_3)_2$ ]. MS (70 eV): 370 ( $M^+$ , 70), 312 (100), 189 (43). IR (KBr): 3320 (OH), 1630 (C=C), 960 (=CH, *E*-isomer), 820 (ArH, *p*-subst.).

#### 3.3.2. Synthesis of (*E*)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene

In a three-necked bottom flask, previously flamed and under argon atmosphere, was placed (*E*)-1-ferrocenyl-2-[*p*-(1'-butyn-3'-methyl-3'-ol)phenyl]ethene (2.24 g, 6.05 mmol) in dry toluene, and 12 mg of finely powdered sodium hydroxide, and the mixture was warmed at reflux temperature for 2 h, then filtered and the solvent removed at reduced pressure. The residual solid was purified by pressurised silica gel column chromatography using hexane/ $CH_2Cl_2$  3:1 as eluent.

(*E*)-1-ferrocenyl-2-[*p*-ethynylphenyl]ethene was isolated as a red solid; m.p. 144–146 °C, 1.85 g (98%).

$^1H$  NMR ( $CDCl_3$ ): 7.46 (d, 2H,  $J = 8.62$  Hz, H-3'' and H-5''), 7.38 (d, 2H,  $J = 8.62$  Hz, H-2'' and H-6''), 6.92 (d, 1H,  $J = 15.65$  Hz, H-2), 6.67 (d, 1H,  $J = 15.65$  Hz, H-1), 4.48 (m, 2H, H-2' and H-5'), 4.31 (m, 2H, H-3' and H-4'), 4.15 (s, 5H, cyclopentadienyl), 3.15 (s, 1H,  $\equiv CH$ ).  $^{13}C$  NMR ( $CDCl_3$ ): 138.3 (C-1''), 132.3 (2C, C-3'' and C-5''), 128.4 (C-2), 125.4 (2C, C-2'' and C-6''), 124.9 (C-1), 119.8 (C-4''), 83.8 (C $\equiv$ ), 82.6 ( $\equiv CH$ ), 77.5 (C-1'), 69.1 (7C, C-3', C-4' and cyclopentadienyl), 66.9 (2C, C-2' and C-5'). MS (70 eV): 312 ( $M^+$ , 100), 247 (19), 121 (12). IR (KBr): 3260 (C $\equiv$ CH), 1600 (C=C), 970 (=C-H, *E*-isomer), 815 (ArHp, *p*-subst.). UV/vis (MeOH),  $\lambda_{max}$  (nm): 206 ( $\epsilon$ , 26422), 274 ( $\epsilon$ , 15739), 322 ( $\epsilon$ , 33471), 460 ( $\epsilon$ , 20171  $mol^{-1} cm^{-1}$ ). Anal. Found: C, 76.58; H, 5.40.  $C_{20}H_{16}Fe$  Calc.: C, 76.95; H, 5.17; Fe, 17.89%.

### 3.4. Synthesis of (*Z*)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene, (*Z*)-3

#### 3.4.1. Preparation of (*Z*)-1-ferrocenyl-2-[*p*-(1'-butyn-3'-methyl-3'-ol)phenyl]ethene

In a three-necked bottom flask, previously flamed and under argon atmosphere, was placed a mixture of freshly distilled diethylamine (7 ml) purged with argon, and (*Z*)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene, (*Z*)-3 (0.634 g, 1.53 mmol) and 2-methyl-but-3-yn-2-ol (0.128 g, 1.53 mmol). The mixture was stirred at room temperature and then dichlorobis(triphenyl)phosphine palladium(II) (21.2 mg, 0.03 mmol) and cuprous chloride (2 mg) were added in this order. After 15 h, the solvent was partially removed at reduced pressure and an aqueous solution of  $NH_4Cl$  (0.5 g) and NaCN (25 mg) in water (25 ml) was added and stirred for 2 h. The mixture was extracted with dichloromethane (25 ml). The organic layer was dried with  $NaSO_4$ , and after filtration the solvent was removed to give a residual solid, which was purified by pressurised silica gel column chromatography using hexane/ethyl acetate 3:1 as eluent. (*Z*)-1-ferrocenyl-2-[*p*-(1'-butyn-3'-methyl-3'-ol)phenyl]ethene was isolated as a red oil, 0.492 g (86%).

$^1H$  NMR ( $CDCl_3$ ): 7.33 (d, 2H,  $J = 8.70$  Hz, H-3'', H-5''), 7.24 (d, 2H,  $J = 8.70$  Hz, H-2'' and H-6''), 6.32 (d, 1H,  $J = 12.02$  Hz, H-2), 6.30 (d, 1H,  $J = 12.02$  Hz, H-1), 4.14 (m, 4H, H-2', H-3', H-4' and H-5'), 2.04 (s, 1H, -OH), 1.61 (s, 6H,  $CH_3$ ).  $^{13}C$  NMR ( $CDCl_3$ ): 138.1 (C-1''), 131.2 (2C, C-3'' and C-5''), 128.9 (C-2), 128.5 (2C, C-2'' and C-6''), 126.3 (C-1), 120.6 (C-4''), 93.9 [ $C\equiv C-C(CH_3)_2$ ], 82.19 (C-1'), 81.0 [ $C\equiv C-C(CH_3)_2$ ], 69.3 (5C, cyclopentadienyl), 69.2 (2C, C-3' and C-4'), 68.6 (C-2' and C-5'), 65.4 [ $(CH_3)_2$ ], 31.4 [ $(CH_3)_2$ ]. MS (70 eV): 370 ( $M^+$ , 70), 312 (100), 189 (43). IR (KBr): 3320 (OH), 1630 (C=C), 1000 (ferrocene), 870 (=C-H, *Z*-isomer), 820 (ArH, *p*-subst.).

### 3.4.2. Synthesis of (Z)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene

In a three-necked bottom flask, previously flamed and under argon atmosphere, was placed (Z)-1-ferrocenyl-2-[*p*-(1'-butyn-3'-methyl-3'-ol)phenyl]ethene (2.24 g, 6.05 mmol) in dry toluene (10 ml) and finely powdered sodium hydroxide (12 mg), and the mixture was warmed at reflux temperature for 2 h and then filtered and the solvent removed at reduced pressure. The residual solid was purified by pressurised silica gel column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> 3:1 as eluent. (Z)-1-ferrocenyl-2-[*p*-ethynylphenyl]ethene was isolated as a red solid; m.p. 144–146 °C, 1.85 g (98%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.44 (d, 2H, *J* = 8.22 Hz, H-3'' and H-5''), 7.32 (d, 2H, *J* = 8.22 Hz, H-2'' and H-6''), 6.43 (d, 1H, *J* = 12.49 Hz, H-2), 6.36 (d, 1H, *J* = 12.49 Hz, H-1), 4.19 (m, 4H, H-2', H-3', H-4' and H-5'), 4.12 (s, 5H, cyclopentadienyl), 3.12 (s, 1H, ≡CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 138.8 (C-1''), 131.8 (2C, C-3'' and C-5''), 129.2 (C-2), 128.6 (2C, C-2'' and C-6''), 126.3 (C-1), 120.0 (C-4''), 83.9 (C≡), 81.0 (≡CH), 77.2 (C-1'), 69.4 (2C, C-3', C-4'), 69.3 (5C, cyclopentadienyl), 68.7 (2C, C-2' and C-5'). MS (70 eV): 312 (M<sup>+</sup>, 100), 247 (23), 121 (16). IR (KBr): 3260 (C≡CH), 1600 (C=C), 970 (=C-H, *Z*-isomer), 815 (ArH, *p*-subst.). UV/vis (MeOH), λ<sub>max</sub> (nm): 231 (ε, 18915), 275 (ε, 14836), 306 (ε, 15121), 449 (ε, 9471 mol<sup>-1</sup> cm<sup>-1</sup>). Anal. Found: C, 76.75; H, 5.53. C<sub>20</sub>H<sub>16</sub>Fe Calc.: C, 76.95; H, 5.17; Fe, 17.89%.

## 4. Dimerisation of 1-ferrocenyl-2-(*p*-ethynylphenyl)ethene

### 4.1. Synthesis of 1,4-di(*E*)-1-ferrocenyl-2-(*p*-phenylethenyl)-1,3-butadiyne, (*E,E*)-4

In a three-necked bottom flask was placed a solution of Cu<sub>2</sub>Cl<sub>2</sub> (88 mg) in pyridine (10 ml) and oxygen atmosphere. To the solution, that acquires an intense green colour, was added (*E*)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene (0.55 g, 1.76 mmol) and the mixture was stirred at 45 °C for 4 h. Then the solvent was removed at reduced pressure and the residual solid was washed with a saturated aqueous solution (5 ml) of ammonium hydroxide and extracted with toluene. The organic layer was dried with magnesium sulfate, and after filtration the solvent was removed to give a red solid which was recrystallised from hexane. 1,4-di[(*E*)-1-ferrocenyl-2-*p*-phenyl]ethenyl-1,3-butadiyne, (*E,E*)-4 was obtained as a dark red solid; m.p. > 230 °C (decomp.), 0.53 g. (98%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.48 (d, 4H, *J* = 9.09 Hz, H-3'' and H-5''), 7.38 (d, 4H, *J* = 9.09 Hz, H-2'' and H-6''), 6.94 (d, 2H, *J* = 16.36 Hz, H-2), 6.67 (d, 2H, *J* = 16.36 Hz, H-1), 4.49 (m, 4H, H-2' and H-5'), 4.32 (m,

4H, H-3' and HA'), 4.16 (s, 10H, cyclopentadienyl). MS (70 eV): 622 (M<sup>+</sup>, 100), 557 (7), 311 (M<sup>2+</sup>, 45), 121 (11). IR (KBr): 2140 (C≡C), 1625 and 1500 (C=C conj.), 860 (ferrocene), 810 (ArH, *p*-subst.). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>), λ<sub>max</sub> (nm): 320 (ε, 17449), 362 (ε, 27255), 464 (ε, 45941 mol<sup>-1</sup> cm<sup>-1</sup>). DSC: endothermic peak at 230 °C (decomp.). Anal. Found: C, 76.88; H, 5.12. C<sub>40</sub>H<sub>30</sub>Fe<sub>2</sub> Calc.: C, 77.19; H, 4.86; Fe, 17.95%.

### 4.2. Synthesis of 1,4-di[(Z)-1-ferrocenyl-2-(*p*-phenylethenyl)-1,3-butadiyne, (*Z,Z*)-4

In a three-necked bottom flask was placed a solution of Cu<sub>2</sub>Cl<sub>2</sub> (20 mg) in pyridine (2.5 ml) and oxygen atmosphere. To the intense green solution was added (Z)-1-ferrocenyl-2-(*p*-ethynylphenyl)ethene (0.127 g, 0.41 mmol) and the mixture was stirred at 45 °C for 4 h. Then, the solvent was removed at reduced pressure and the residual solid was washed with a saturated aqueous solution of ammonium hydroxide (5 ml) and extracted with dichloromethane (5 ml). The organic layer was dried with magnesium sulfate and, after filtration, the solvent was removed to give an orange solid which was recrystallised from hexane. 1,4-di[(Z)-1-ferrocenyl-2-*p*-phenyl]ethenyl-1,3-butadiyne, (*Z,Z*)-4 was obtained as a dark red solid; m.p. 170 °C, 0.12 g (95%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.43 (d, 4H, *J* = 8.29 Hz, H-3'' and H-5''), 7.31 (d, 4H, *J* = 8.29 Hz, H-2'' and H-6''), 6.36 (s, 4H, H-1 and H-2), 4.18 (m, 8H, H-2', H-3', H-4' and H-5'), 4.09 (s, 10H, cyclopentadienyl). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 139.2 (2C, C-1''), 132.1 (4C, C-3' and C-5''), 129.5 (2C, C-2), 128.7 (4C, C-2'' and C-6''), 126.2 (2C, C-1), 119.7 (2C, C-4''), 82.0 (2C, -C≡C-C≡C-), 81.0 (2C, -C≡C≡C≡C-), 74.2 (2C, C-1'), 69.5 (4C, C-3' and C-4'), 69.3 (10C, cyclopentadienyl), 68.8 (4C, C-2' and C-5'). MS (70 eV): 622 (M<sup>+</sup>, 100), 311 (M<sup>2+</sup>, 45), 121 (11). IR (KBr): 2140 (C≡C), 1625 and 1500 (C=C conj.), 860 (ferrocene), 810 (ArH, *p*-subst.). UV/vis (CH<sub>2</sub>Cl<sub>2</sub>), λ<sub>max</sub> (nm): 231 (ε, 34465), 345 (ε, 349291 mol<sup>-1</sup> cm<sup>-1</sup>). DSC: endothermic peaks at 170 (m.p.) and 190 °C (decomp.). Anal. Found: C, 76.93; H, 4.92. C<sub>40</sub>H<sub>30</sub>Fe<sub>2</sub> Calc.: C, 77.19; H, 4.86; Fe, 17.95%.

## 5. X-ray molecular structure of 1-ferrocenyl-2-(4-iodophenyl)ethene, (*E*)-1

The dark red prismatic crystal of (*E*)-1 used for X-ray diffraction analysis was grown by slow evaporation from an ethyl acetate solution. A crystal of dimensions 0.41 × 0.32 × 0.37 mm<sup>3</sup> was used for the crystallography. Accurate cell dimensions were determined by least-squares analysis of setting angles of 62 reflections (7° < 2θ < 51°) using graphite monochromated Mo Kα radiation (λ = 0.7107 Å), automatically located and cen-

tred on a four-circle Philips PW 1100 diffractometer. Orthorhombic, space group  $P2_12_12_1$ , with  $a = 23.278(5)$ ,  $b = 6.004(1)$ ,  $c = 10.985(1)$  Å,  $V = 1535.4(3)$  Å<sup>3</sup>. Molecular formula  $C_{18}H_{15}IFe$ , molecular weight 414.07,  $D_c = 1.791(3)$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 808.0$ ,  $\mu = 29.796$  cm<sup>-1</sup>. Data collection: two standard reflections were measured every 90 min to ascertain crystal stability, no significant variation was observed. All the reflections were corrected for Lorentz and polarisation factors in the usual way, a  $\Phi$  scan absorption correction [17] was applied, maximum and minimum transmission factors 0.999–1.495. For the intensity measurement, reflections were surveyed in the range  $2^\circ < \theta < 25^\circ$ , from 1624 independent reflections measured, 1518 were considered as observed, satisfying the criterion  $I > 3\sigma(I)$  in the range  $h$  0/28,  $k$  0/8,  $l$  0/14, and were used in the subsequent calculations. The structure was solved by direct methods, SIR-92 [18]. Non-hydrogen atoms were included in the model in their calculated positions, and their parameters maintained fixed [19]. The large values of the displacement parameters of the cyclopentadienyl ring suggest some kind of rotational disorder, however no additional peaks were found in a difference map and no model for the disorder could be found; this gave rise to some artificially short distances. After some cycles of anisotropic refinement, C15 and C17 atoms were maintained fixed through later refinement. Convergence was reached at  $R = 0.062$  and  $R_w = 0.074$ , with a weighting scheme [20] to prevent trends in  $w\Delta^2F$  vs.  $\sin \theta/\lambda$ . In the final refinement, residual density was observed close to the I and Fe atoms. The atomic scattering factors and anomalous dispersion corrections were taken from the literature [21]. Atomic coordinates, bond distances and angles were calculated using the PARST program [22]. All relevant data have been deposited at the Cambridge Crystallographic Data Centre.

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