

## Supporting Information

### The Synthesis and Characterization of novel Ferrocenyl Polyphenylenes

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The synthesis and characterization of novel ferrocenyl polyphenylenes, including the redox, electronic and 2<sup>nd</sup> order non-linear optical (NLO) properties of a conjugated polyaromatic comprising a hexa-*peri*-hexabenzocoronene (HBC) core coupled *via* acetylene to ferrocene.

Keywords: **Sonogashira coupling, ferrocenyl polyphenylene, electronic characterisation, NLO,**

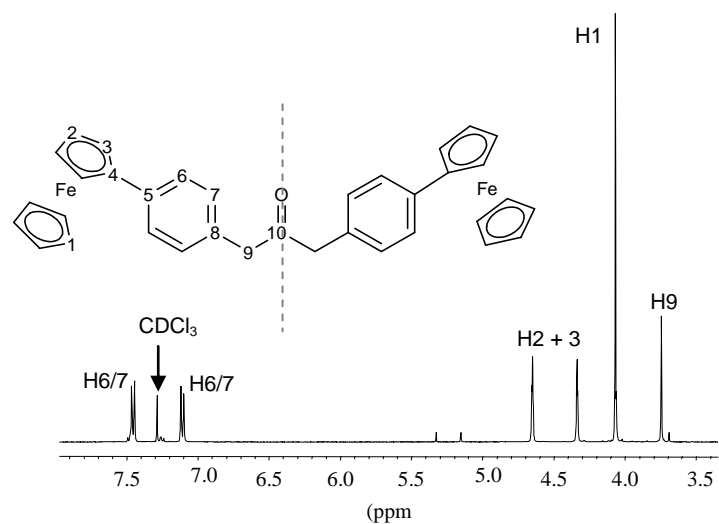
<sup>1</sup>H NMR (400 MHz) spectra recorded in CDCl<sub>3</sub> for **4, 7, 8, 9, 10, 11, 12**, iodo-HBC and 1,2-*bis*(*p*-ferrocenylphenyl)acetylene.

**Figure S1:** The experimental (+)-MALDI-TOF spectra of **13** (upper) and the simulated isotopic distribution pattern for (MH)<sup>+</sup>.

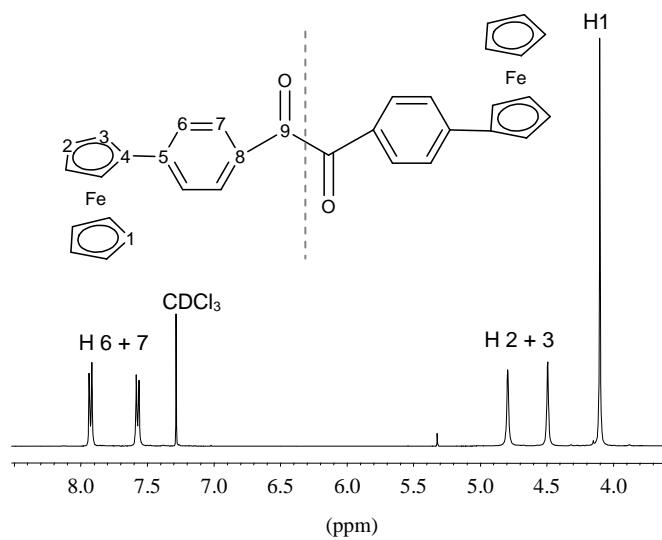
Novel schematic route to 1,2-*bis*(*p*-ferrocenylphenyl)acetylene.

**Table S1:** Tabulated electronic Mullikan charges for components Fe, Cp, ethyne, and HBC in ethynyl ferrocene and methyl **13**.

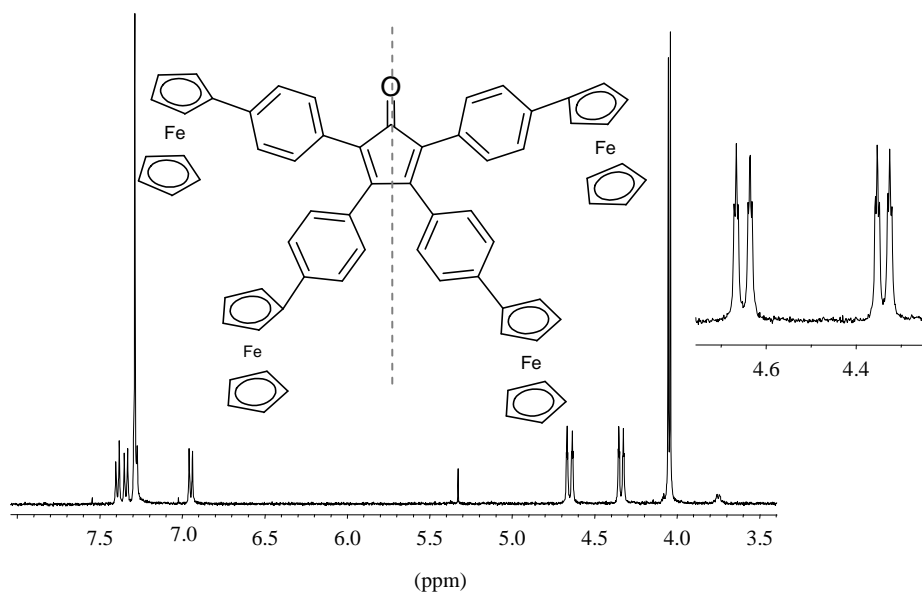
### Compound 4



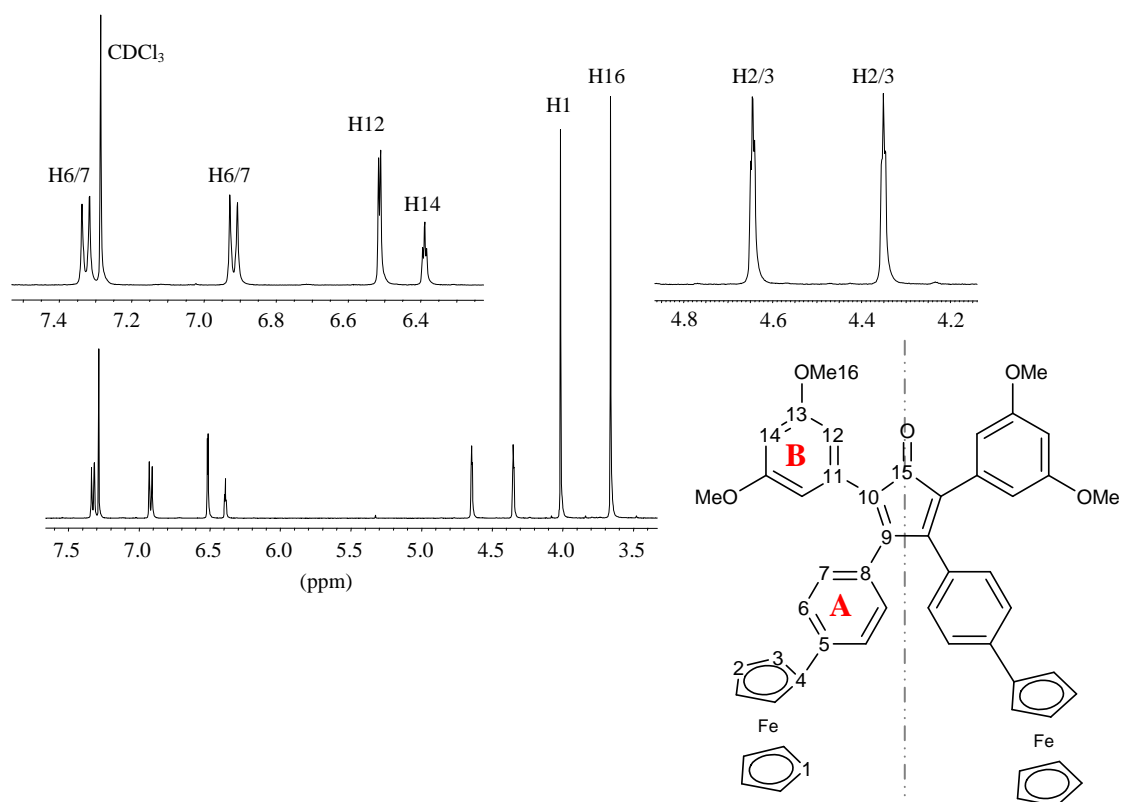
### Compound 7



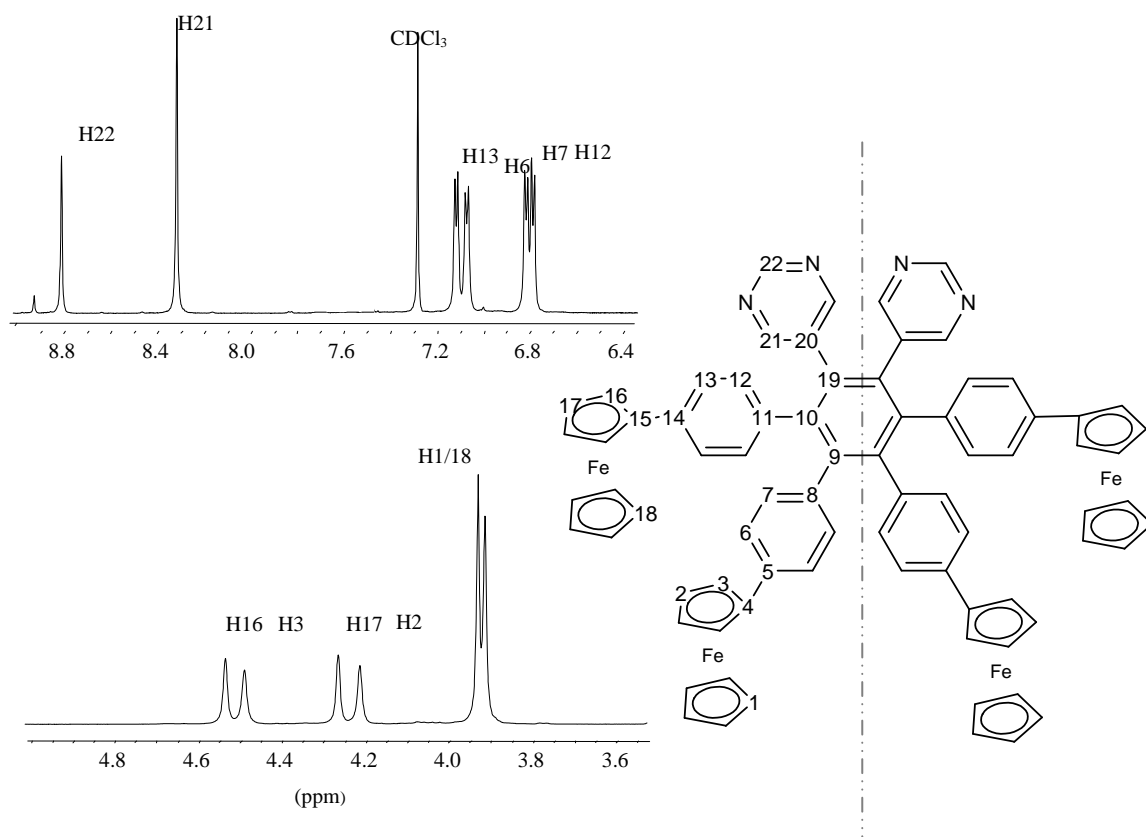
### Compound 8



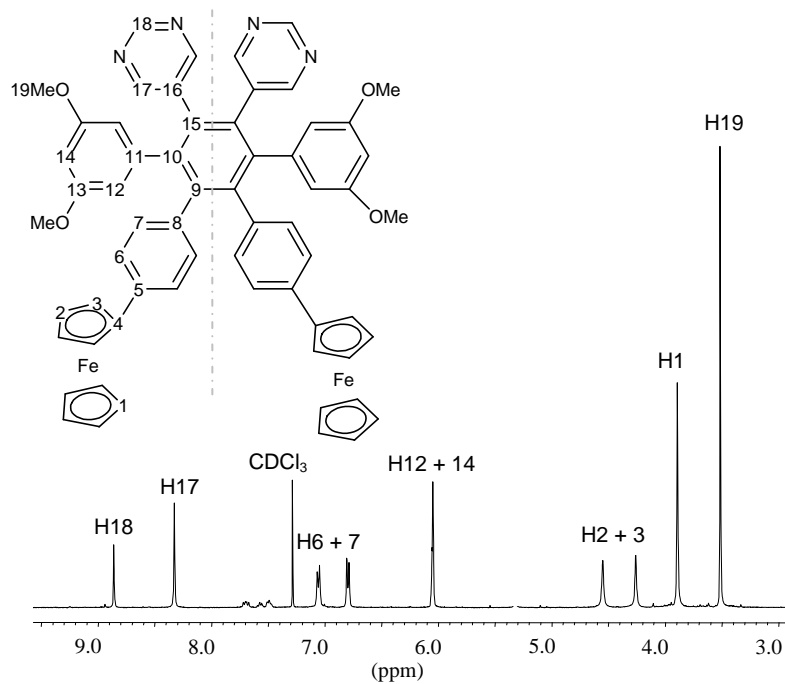
### Compound 9



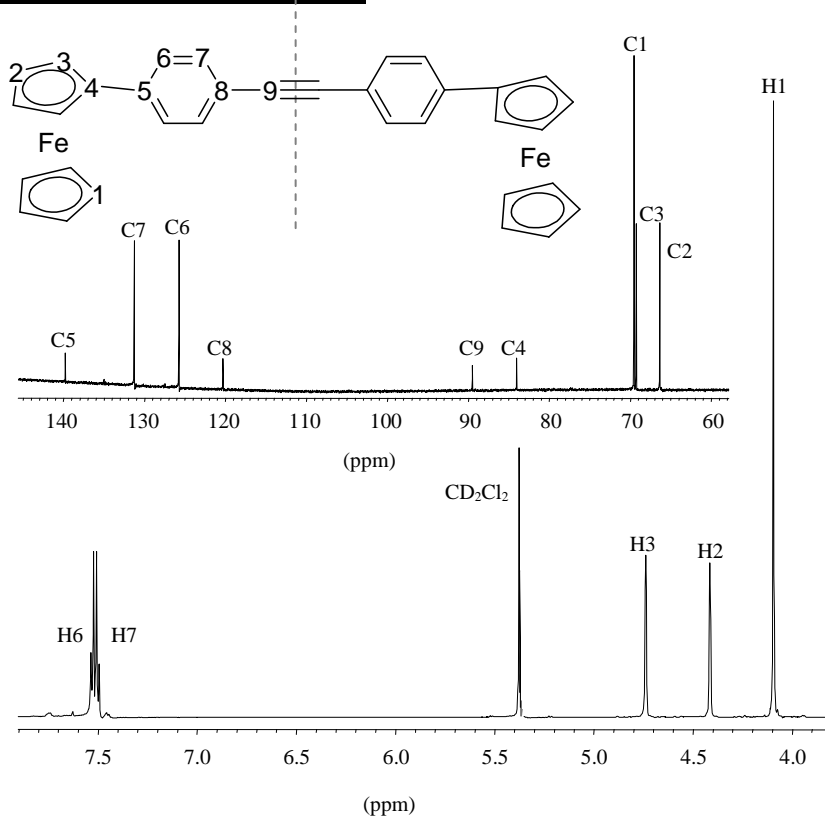
### Compound 10



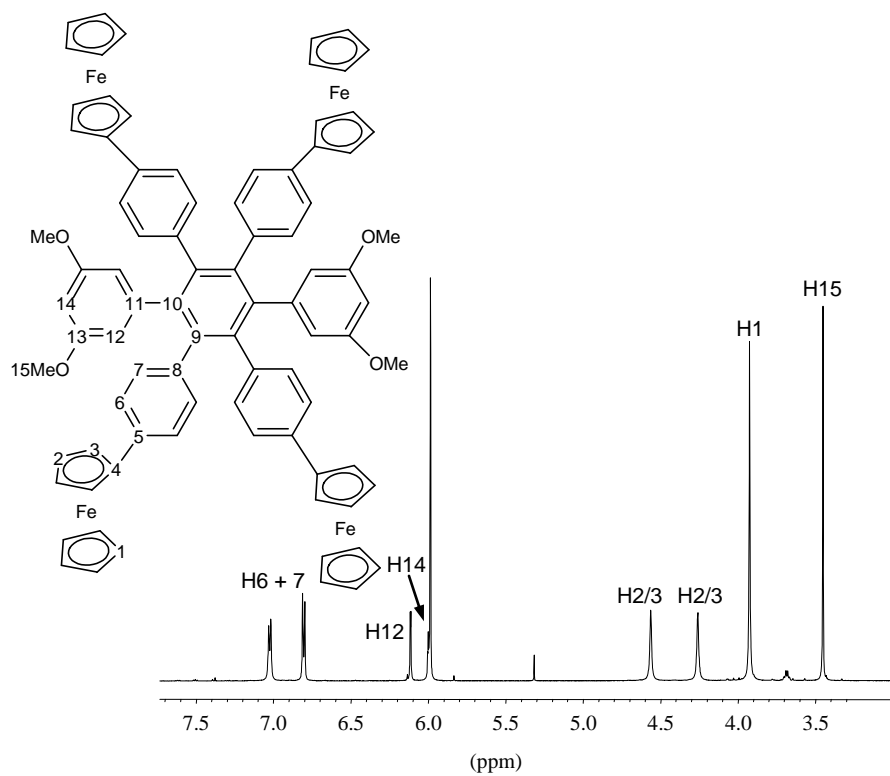
### Compound 11



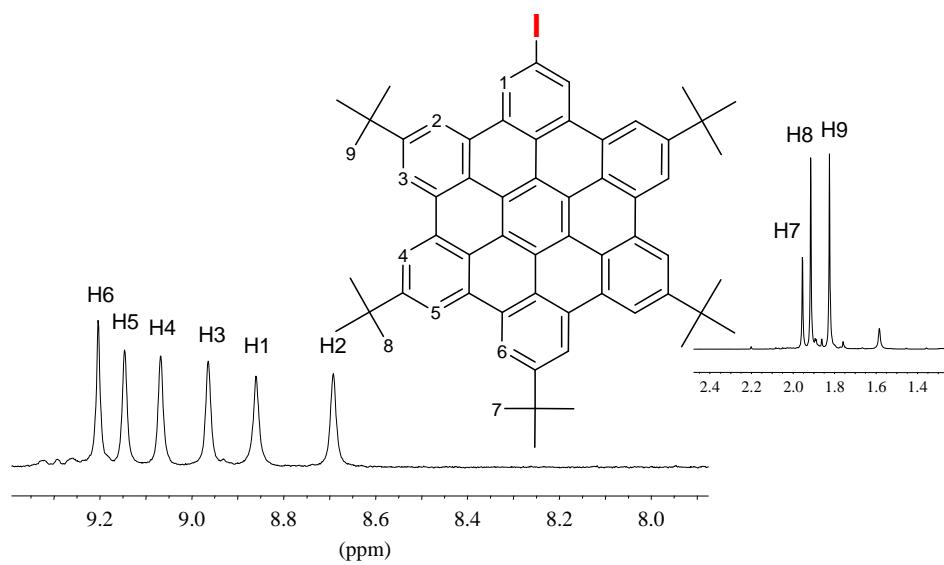
### 1,2-bis(p-ferrocenylphenyl)acetylene.

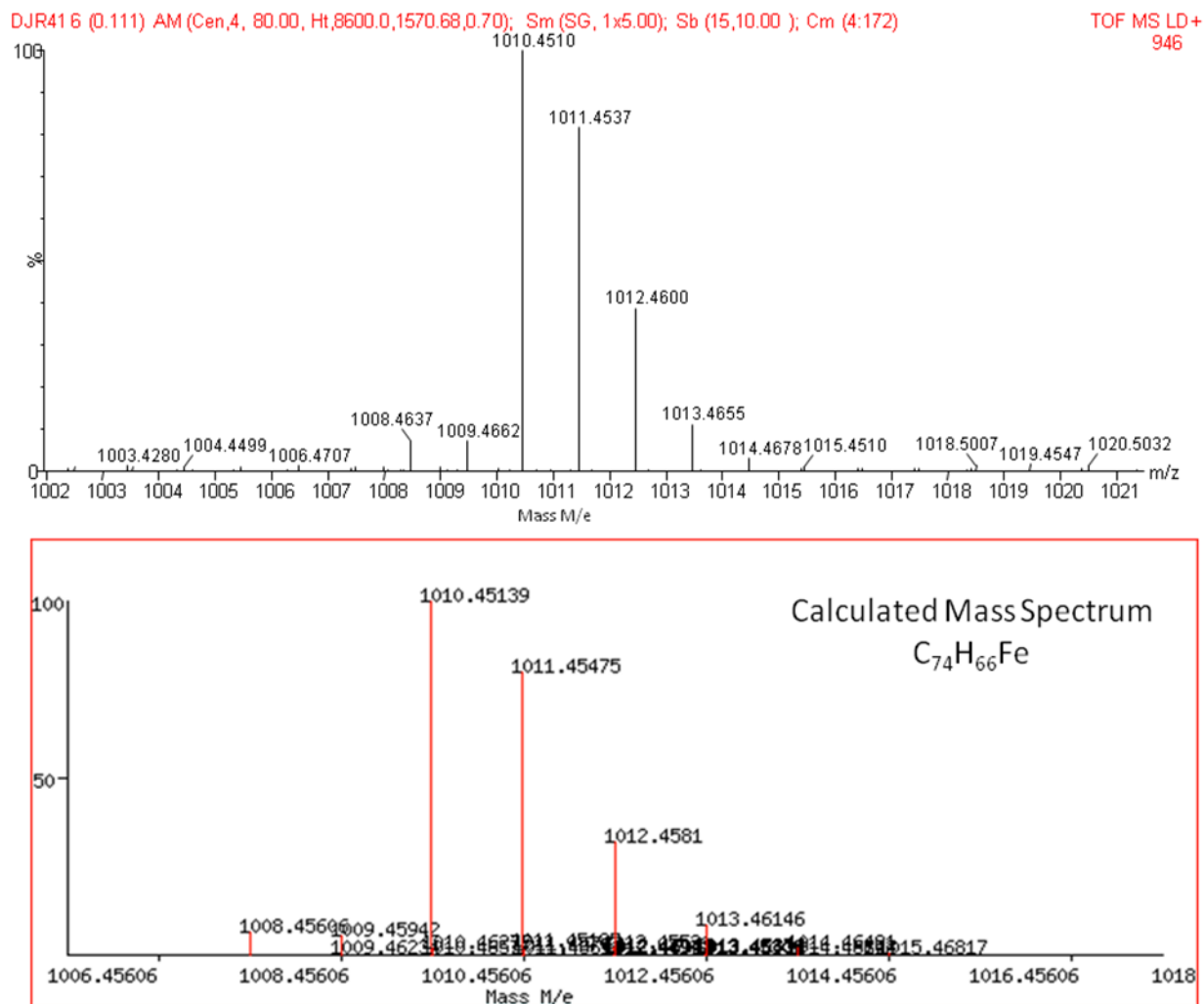


### Compound 12



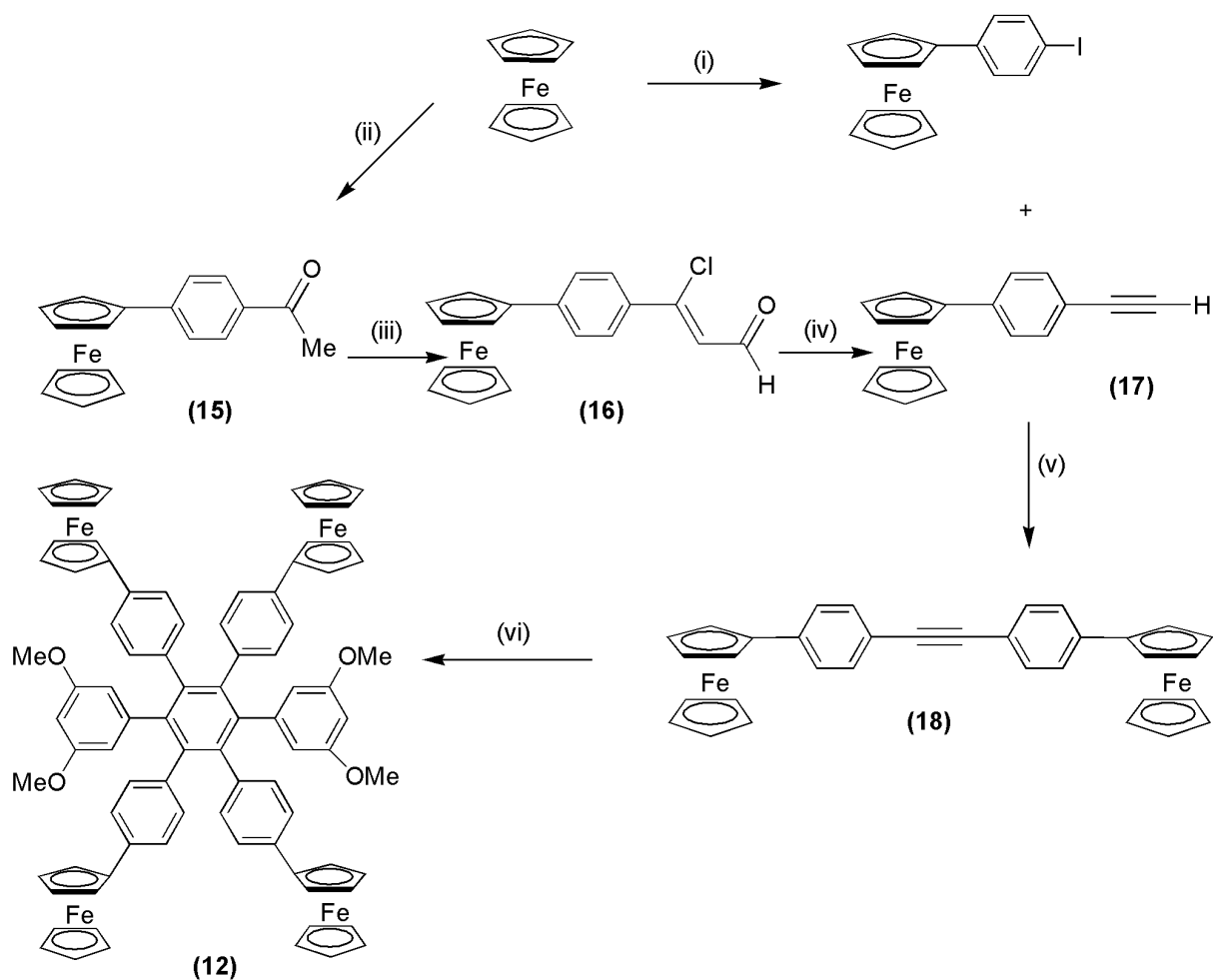
## Iodo-HBC





**Figure S1:** The experimental (+)-MALDI-TOF spectra of **13** (upper) and the simulated isotopic distribution pattern for  $(MH)^+$ .

MALDI-TOF MS for  $C_{74}H_{66}Fe$ :  $[M]^+$  calculated  $m/z$  1010.4514, found  $m/z$  1010.4510.



Scheme S1: The synthesis of 1,2-bis(p-ferrocenylphenyl)acetylene from ferrocene used in this work. (i) H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O, sodium nitrite, 4-iodoaniline, HCl, Cu powder, 24 h, (33 %). (ii) H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O, sodium nitrite, 4-aminoacetophenone, HCl, Cu powder, 25 h, (34 %). (iii) POCl<sub>3</sub>, DMF, 0 °C→15 min, RT→5.5 h, (50 %). (iv) dioxane, aq. NaOH, reflux, 5min, (93 %). (v) Pd(PPh<sub>3</sub>)<sub>4</sub>, Et<sub>2</sub>NH/DMF (2/1), 55°C, 2 d, (94 %). (vi) 9, benzophenone, 190°C, 18 h, (18%).

### Compound 15

Ferrocene (15.2 g, 81.6 mmol) was added to sulphuric acid (100mL, spec. grav. 1.84) and the resulting deep blue ferrocenium solution was stirred at room temperature for 2 hours. The solution was then poured into ice/water (400 mL) and allowed to warm to room temperature.

A solution of sodium nitrite (3.64 g, 52.8 mmol) in water (20 mL) at 0 °C was added dropwise to a stirred solution of 4-aminoacetophenone (6.48 g, 480 mmol) in 1:1 water/hydrochloric acid (spec. grav. 1.18) (40 mL) at 0 °C, and stirred at this temperature for 30 minutes to ensure full diazotization. Copper powder (4.0 g) was added to the ferrocenium solution and the diazonium solution was added dropwise with vigorous stirring.



After 24 hours stirring at room temperature, effervescence due to liberated nitrogen had ceased and ascorbic acid (20 g) was added to the dark mixture to reduce any remaining ferrocenium to ferrocene. Dichloromethane (400 mL) was added and the organic layer separated. The aqueous layer was extracted further with dichloromethane (4 x 150 mL), and the combined organic extracts were filtered through Celite before removal of the solvent *in vacuo* to give a dark solid. This was subjected to column chromatography using gradient elution. The first yellow fraction, eluted with hexane, yielded unchanged ferrocene. The second orange-red fraction, eluted with 80/20 (dichloromethane/hexane) gave upon evaporation of solvents the desired product as an orange crystalline solid.

**Yield:** 4.9 g, 34 %.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.90 (d, 2 H,  $^3J_{\text{HH}} = 8.0$  Hz, -CH Ar), 7.55 (d, 2 H,  $^3J_{\text{HH}} = 8.0$  Hz, -CH Ar), 4.74 (t, 2 H,  $^3J_{\text{HH}} = 1.8$  Hz, -CH Fc), 4.42 (t, 2 H,  $^3J_{\text{HH}} = 1.8$  Hz, -CH Fc), 4.06 (s, 5 H, -CH Fc), 2.62 (s, 3 H, -COCH<sub>3</sub>).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 197.19 (1 C, -CO), 145.08 (1 C, quat Ar), 134.08 (1 C, quat Ar), 128.16 (2 C, -CH Ar), 125.29 (2 C, -CH Ar), 82.96 (1 C, quat Fc), 69.47 (2 C, -CH Fc), 69.42 (5 C, -CH Fc), 66.49 (2 C, -CH Fc), 26.11 (1 C, -COCH<sub>3</sub>). **ESI-MS** (methanol); for C<sub>18</sub>H<sub>16</sub>FeO: [M]<sup>+</sup> calculated  $m/z$  304.0551, found  $m/z$  304.0544. Anal. Calcd for C<sub>18</sub>H<sub>16</sub>Fe<sub>2</sub>O<sub>2</sub>: C, 71.08; H, 5.30. Found: C, 71.11; H, 5.50.

### Compound 16

A solution of phosphorous oxychloride (1.4 mL, 14 mmol) in dimethylformamide (10 mL), prepared at 0 °C, was added dropwise to a stirred solution of **15** (1.2 g, 4 mmol) also in dimethylformamide (15 mL) at 0 °C. The reaction was allowed to proceed for 15 minutes at 0 °C and then for 4 hours at room temperature, after which it was transferred *via* cannula into a 20 % solution of sodium acetate (40 mL) and allowed to stir for 90 minutes. The solution was extracted several times with dichloromethane, and the combined organic extract was in turn washed several times with water, dried over MgSO<sub>4</sub> and the solvents were removed under reduced pressure. The residue was chromatographed on silica, elution with dichloromethane:hexane (2:1) yielded the desired product as a purple solid.

**Yield:** 0.7 g, 50 %.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 10.25 (d, 1 H,  $^3J_{\text{HH}} = 6.8$  Hz, -CHO), 7.70 (d, 2 H,  $^3J_{\text{HH}} = 8.0$  Hz, -CH Ar), 7.53 (d, 2 H,  $^3J_{\text{HH}} = 8.0$  Hz, -CH Ar), 6.72 (d, 1 H,  $^3J_{\text{HH}} = 6.8$  Hz, -C=CH), 4.77 (s, 2H, -CH Fc), 4.47 (s, 2 H, -CH Fc), 4.11 (s, 5 H, -CH Fc).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 191.22 (1 C, -CHO), 151.86 (1C, quat Ar), 144.20 (1 C, quat Ar), 131.89 (1 C, quat, -CCl), 126.87 (2 C, -CH Ar), 125.61 (2 C, -CH Ar), 122.63 (1 C, -C=CH), 82.58 (1

C, quat Fc), 69.64 (2 C, -CH Fc), 69.53 (5C, -CH Fc), 66.47 (2 C, -CH Fc). Anal. Calcd for C<sub>19</sub>H<sub>15</sub>FeO: C, 65.09; H, 4.31. Found: C, 65.11; H, 4.40.

### Compound 17

Compound **16** (0.65 g, 1.85 mmol) was dissolved in dioxane (20 mL) and the solution was heated to reflux. To this solution was added rapidly NaOH (15 mL, 0.5 M). The reaction was allowed to continue for 5 minutes at reflux and the solution was then poured into deionised water (100 mL). After acidification with HCl, the solution was extracted exhaustively with diethylether and the combined ether extracts were washed to neutrality before being dried over MgSO<sub>4</sub>. The solvent was then removed and the residue was recrystallised from hexane to yield the desired product as an orange solid.

**Yield:** 0.49 g, 93 %. **<sup>1</sup>H NMR** (CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.48 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz), 7.43 (d, 2 H, <sup>3</sup>J<sub>HH</sub> J = 8.5 Hz), 4.71 (s, 2 H, -CH Fc), 4.40 (s, 2 H, -CH Fc), 4.07 (s, 5 H, -CH Fc), 3.19 (s, 1 H, C≡CH). **<sup>13</sup>C NMR** (CD<sub>2</sub>Cl<sub>2</sub>) δ: 140.20 (1 C, quat Ar), 131.58 (2 C, -CH Ar), 125.33 (2 C, -CH Ar), 118.52 (1 C, quat Ar), 83.42 (1 C, quat, -C≡C-), 83.36 (1 C, quat, -C≡C-), 76.42 (1 C, quat Fc), 69.24 (5 C, -CH Fc), 69.02 (2 C, -CH Fc), 66.10 (2 C, -CH Fc). **ESI-MS** (toluene); for C<sub>18</sub>H<sub>14</sub>Fe: [M]<sup>+</sup> calculated *m/z* 286.0445, found *m/z* 286.0452. Anal. Calcd for C<sub>18</sub>H<sub>14</sub>Fe: C, 75.55; H, 4.93. Found: C, 75.61; H, 4.94.

### 1,2-bis(p-ferrocenylphenyl)acetylene (Compound 18)

Compound **17** (0.6 g, 2.1 mmol), (0.98 g, 2.5 mmol) and tetrakis(triphenylphosphine)palladium (0.24 g, 0.21 mmol) were dissolved in diethylamine/dimethylformamide (2/1), (45 mL). The reaction mixture was then allowed to stir at 55 °C for 48 hours. The solvents were removed *in vacuo*, washed with water and extracted into dichloromethane. The organic phase was dried over MgSO<sub>4</sub>, solvents removed *in vacuo* again before being subjected to column chromatography on silica. Elution with dichloromethane:hexane (1:2) and then dichloromethane yielded the desired product.

**Yield:** 1.1 g, 94 %. **M.pt:** >300 °C. **<sup>1</sup>H NMR (600MHz)** (CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.52 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, -CH Ar), 7.49 (d, 4H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, -CH Ar), 4.73 (s, 4H, -CH Fc), 4.41 (s, 4H, -CH Fc), 4.08 (s, 10H, -CH Fc). **<sup>13</sup>C NMR (150.6MHz)** (CD<sub>2</sub>Cl<sub>2</sub>) δ: 140.64 (2 C, quat Ar), 131.27 (4 C, -CH Ar), 125.72 (4 C, -CH Ar), 120.31 (2 C, quat Ar), 89.51 (2 C, -C≡C-), 84.02 (2 C, quat Fc), 69.53 (10 C, -CH Fc), 69.26 (4 C, -CH Fc), 66.36 (4 C, -CH Fc). **ESI-MS** (toluene); for C<sub>34</sub>H<sub>26</sub>Fe<sub>2</sub>: [M]<sup>+</sup> calculated *m/z* 546.0733, found *m/z* 546.0713. **IR** ν̄ (cm<sup>-1</sup>): ν(C-H st, aromatic): 3089, 3051, ν(C≡H st): 1912, ν(C=C st): 1604, 1531, ν(C-H rock Fc): 1103, 1085, 1033, 1002.

**Table S1** Tabulated electronic Mullikan charges for components Fe, Cp, ethyne, and HBC in ethynyl ferrocene and methyl 13.

	ferrocene	ethynylferrocene	<b>methyl 13</b>
Cp	- 0.304	- 0.269	- 0.271
Fe	0.608	0.616	0.618
Cp (bound)	- 0.304	- 0.386	- 0.420
Ethyne	-----	0.040	- 0.025
HBC	-----	-----	0.097