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Asymmetric synthesis of chiral ferrocenyl fulleropyrrolidines as potential building blocks for new materials

Victor Mamane and Olivier Riant*

Laboratoire de Catalyse Moléculaire, ICMO, Bt 420, Université Paris-Sud, 91405 Orsay Cedex, France

This paper is dedicated to Professor Henri B. Kagan in recognition of his support and enthusiasm

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Abstract—Asymmetric [3+2] cycloaddition of chiral ferrocenyl substituted azomethine ylides to C_{60} leads to the corresponding fulleropyrrolidines with high diastereoselectivities. This methodology has been applied to the preparation of a C_2-symmetric enantiopure fullerene dimer.

1. Introduction

Due to their unique electrochemical and photophysical properties, fullerenes are now currently recognized as useful components of new devices for applications in various areas of materials science.[1] Among those applications, the design of artificial photosynthetic mimics incorporating fullerene units as electron acceptors has been extensively investigated as well as its applications into photovoltaic cells. Scheme 1 summarizes the different steps of the photoinduced electron transfer (PET) in fullerene-based donor–acceptor dyads. Thus intramolecular electron transfer occurs from the electron donor onto the singlet excited state of the fullerene after photoactivation. Various donor moieties such as TTF, porphyrins and electron rich aromatics have been successfully used for efficient charge separation. It has also been demonstrated that ferrocenyl pendants[2] leading, after electron transfer, to a stable ferrocenium, were good candidates for the design of efficient dyads. In addition, the influence of the geometry as well as the rigidity and the length of the spacer has now been well rationalized for both the fast forward electron transfer from the donor to the acceptor groups and the inhibition of the back electron transfer.

This area has also led to rapid development of new methodologies for grafting the acceptors onto the fullerene sphere using cycloaddition reactions of C_{60}. Various scaffolds such as cyclopropanes,[3] cyclohexanes,[4] isoxazoles[5] and pyrrolidines[6,7] are now currently used for the synthesis of molecular devices incorporating fullerenes. We were especially interested in the introduction of a chiral bifunctional ferrocene onto C_{60} for the preparation of new building blocks for further photophysical studies. Having in hand a useful method for the asymmetric synthesis of enantiopure α-substituted ferrocene carboxaldehydes, we decided to investigate their reactivity toward the Prato's reaction on C_{60} for the preparation of chiral fulleropyrrolidines. The control of the newly formed asymmetric centre on the pyrrolidine ring by the planar chiral ferrocene could lead to new geometries and also control the global symmetry for the construction of multicomponent assemblies.

2. Results and discussion

In 1993, we described an efficient method for the general asymmetric synthesis of 1,2-disubstituted ferrocenecarboxaldehydes with high enantioselectivity[8] (98%). This method allows straightforward access to a large array of chiral ferrocenes and is amenable to large-scale preparation. It has been applied by our group and others for the synthesis of chiral ferrocenyl ligands[9] as well as the design of highly conjugated chiral molecules.[10] As already demonstrated by Prato and Maggini, ferrocene aldehyde and its vinylogous derivatives are excellent substrates for the 1,3-dipolar addition of azomethine ylides to C_{60} for the formation of fulleropyrrolidines. In the present study, we chose chiral ferrocenealdehydes bearing functional groups with various degrees of steric hindrance, in order to evaluate the control of planar chirality on the chiral carbon formed on the pyrrolidine. The synthesis of the chiral aldehydes is described in Scheme 2. Aldehydes **2a–c** were easily prepared by the standard ortholithiation-electrophilic capture of chiral acetal **1** using the appropriate electrophile. Sonogashira coupling of iodoaldehyde (*S*)-**2a** with trimethylsilyl acetylene followed by deprotection of the terminal TMS group by methanolysis afforded the alkyne (*R*)-**2d** in good overall yield. In contrast

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* Corresponding author. Present address: Unité de chimie organique et médicinale, Département de chimie, Place Louis Pasteur 1, Université Catholique de Louvain, 1348 Louvain la Neuve, Belgium. Tel.: +32-0-10-47-87-77; fax: +32-0-10-47-41-68; e-mail: riant@chim.ucl.ac.be

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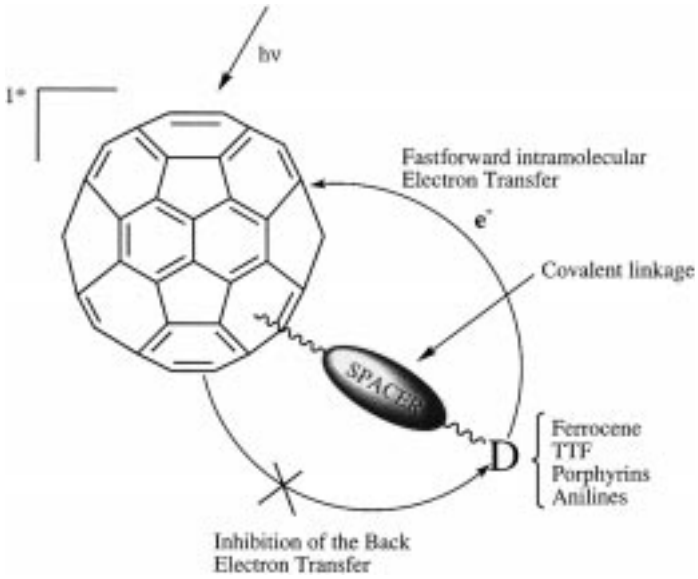
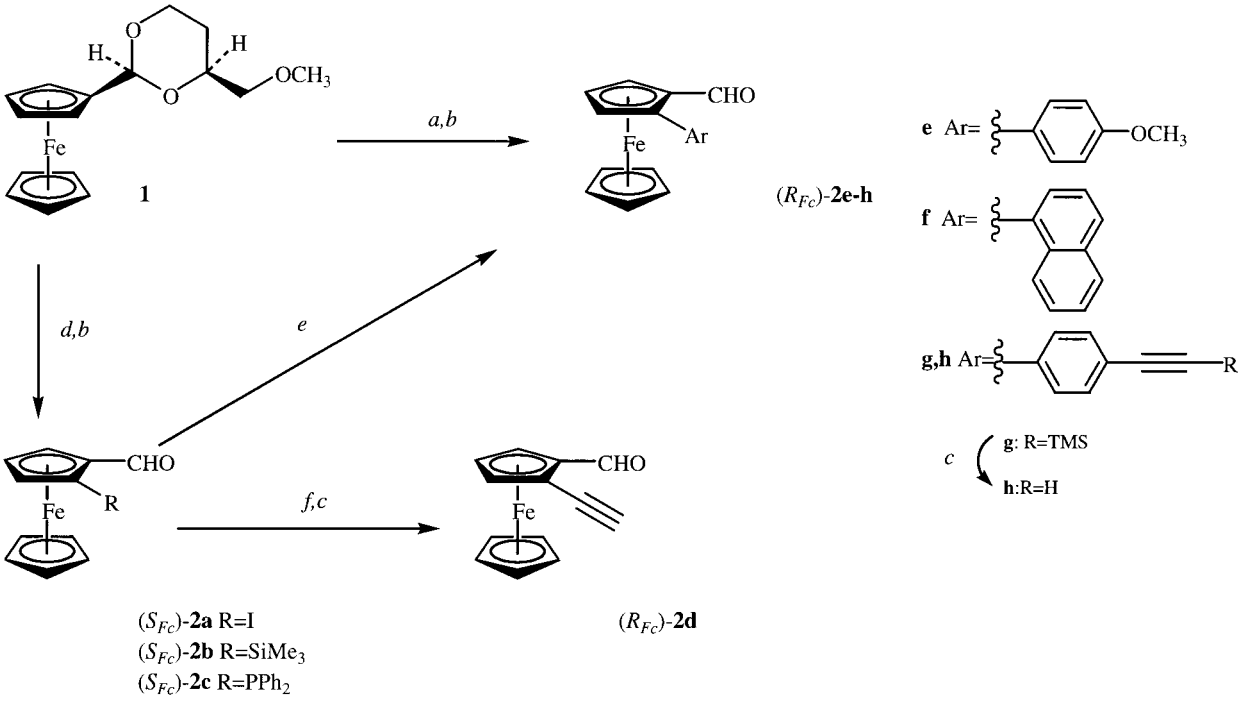


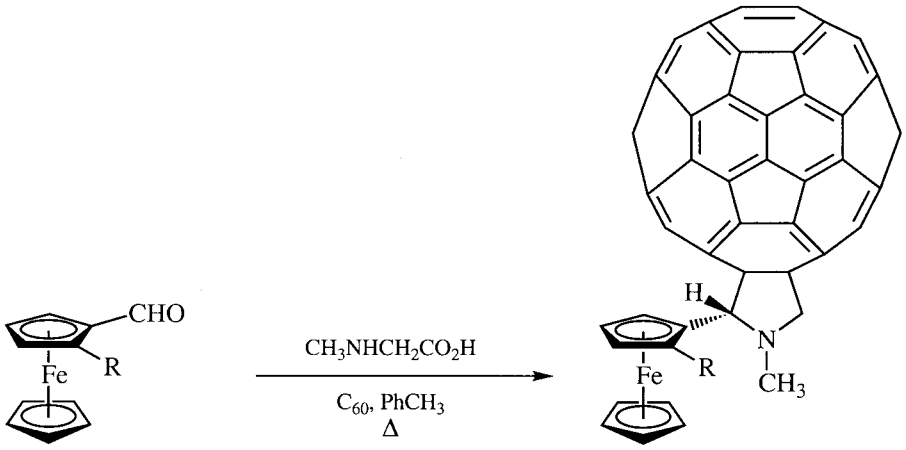
Scheme 1.

to α-vinylferrocene carboxaldehyde which was reported to be prone to polymerization,[11] the alkyne (*R*)-**2d** is a stable red crystalline solid and can be easily prepared on a multigram scale by this method. Introduction of an aryl group could also be realized using two different methods. Palladium-catalyzed coupling of the iodide (*S*)-**2a** with the corresponding boronic acids using the phosphine free procedure of Wallow and Novak[12] gave the aryl aldehydes **2e**,**f** in good to excellent yields, when barium hydroxide was used as a base. We also devised an alternate procedure by coupling the chiral zinc derivative prepared by ortholithiation of acetal **1** followed by transmetallation with zinc chloride with various aryl bromides. Using $PdCl_2(PPh_3)_2$ as a catalyst, the aryl aldehydes **2e**–**g** were isolated in good yields after deprotection of the acetal group. Finally deprotection of the TMS group of **2g** by methanolysis gave the terminal alkyne **2h**.

The chiral aldehydes prepared were then used as precursors of azomethine ylides in a [3+2] cycloaddition with C_{60}



Scheme 2. *Reagents and conditions*: a, (i) *t*-BuLi, Et_2O, −78°C→rt, 1 h; (ii) $ZnCl_2$, THF; (iii) ArBr, $PdCl_2(PPh_3)_2$, rt (65% for **2e**, 61% for **2f**, 74% for **2g**); b, PTSA, CH_2Cl_2, H_2O (>90%); c, K_2CO_3, MeOH, CH_2Cl_2, rt (89% for **2d**, 90% for **2h**) d, see Ref. 8b; e, $ArB(OH)_2$, $Pd(OAc)_2$, $Ba(OH)_2$, THF, H_2O, 65°C (100% for **2e**); f, trimethysilylacetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N, rt (75%).



Scheme 3.

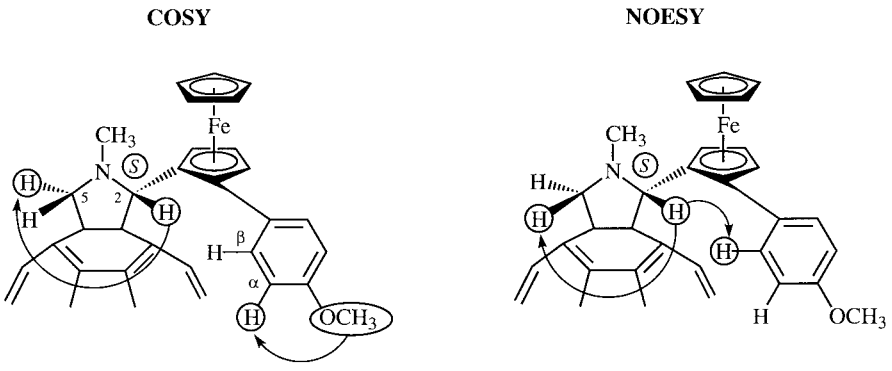
(Scheme 3). The azomethine ylides were generated *in situ* by reaction of the corresponding aldehyde with sarcosine in refluxing toluene. The results are listed in Table 1.

The formation of a cycloadduct was observed for all the aldehydes tested except for the ferrocene **2c** bearing a diphenylphosphino substituent (Entry 2). Instead, degradation of the aldehyde occurred, which could be ascribed to the sensitivity of the phosphino group to the reaction conditions. All cycloadducts were isolated after chromatographic purification on silica gel along with variable amounts of recovered starting C_{60}. The yields of pure products range from modest to good when compared to the average yields usually obtained for such dipolar cycloadditions with C_{60}. We were pleased to find that the reaction occurred in a highly diastereoselective fashion. In the case where a small alkynyl substituent was present (Entry 3), we observed the formation of two diastereoisomers in a 92.5:7.5 ratio (85% d.e.). The major one could be separated and characterized in low yield after repeated chromatographic separation on silica gel. However, for all the other substrates with bulkier substituents, complete diastereocontrol occured; with only a single diastereoisomer being detected in the crude ^{1}H NMR spectra. The absolute configuration of the newly formed asymmetric center on the cycloadduct **3e** was proposed to be *S*, based on 2D NMR experiments. In Scheme 4, the useful information taken from the COSY and NOESY spectra of adduct **3e** is summarized. The COSY experiment allowed the complete assignment of the hydrogens on both the pyrrolidine and the benzene rings. Differentiation between the two diastereotopic H_5 and $H_{5'}$ protons resulted from a long range coupling between the *trans* $H_{5'}$ and the H_2 protons. Unambiguous assignment of the aromatic protons was also possible by the existence of a coupling between the methyl protons of the methoxy group and the *ortho* H_α proton. Molecular models show that minimal steric interactions resulted from an arrangement of the CpFe moiety of the ferrocenyl group in an *anti* position to the bulky fullerene group, as depicted in Scheme 4. By taking the hypothesis of an *S* configuration for the stereogenic center, the NOESY experiment showed spatial interactions between the H_β aromatic proton and the H_2

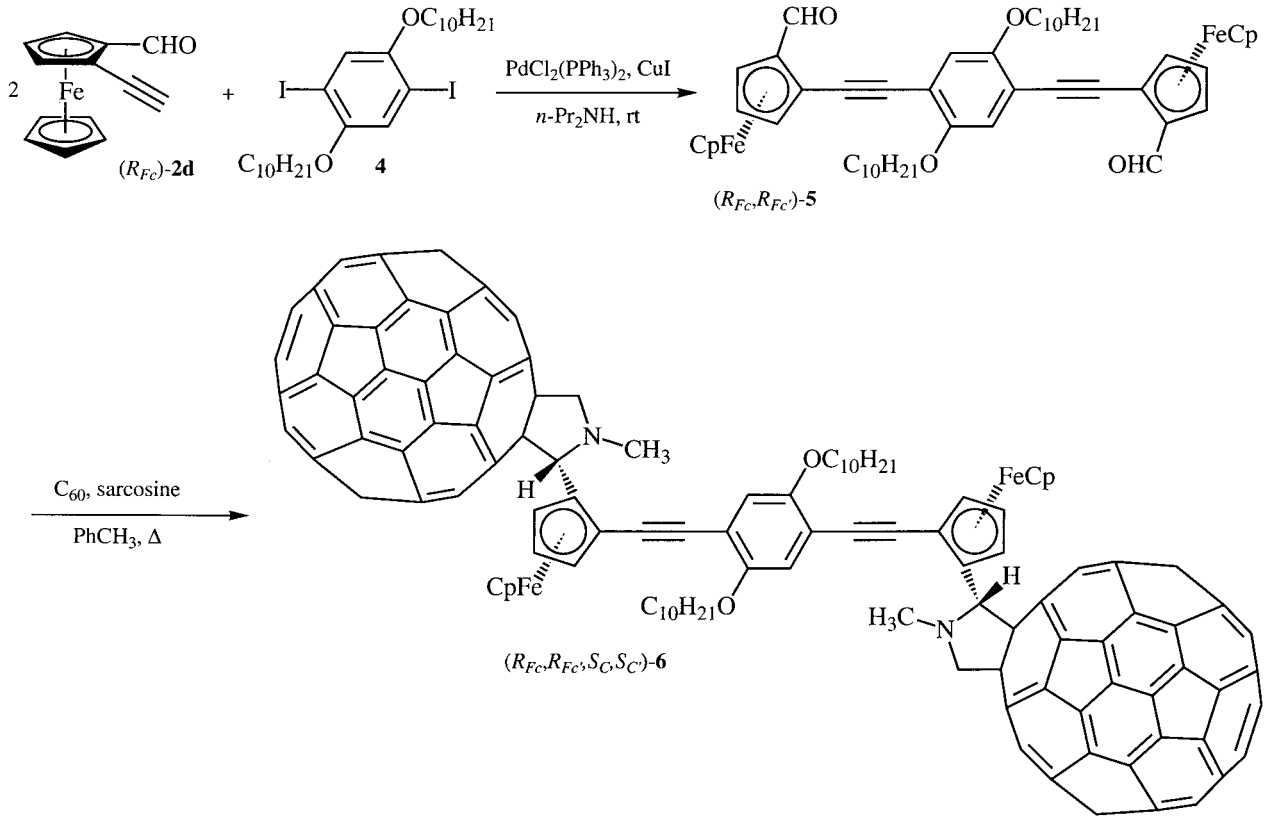
Table 1. [3+2] Cycloadditions of chiral aldehydes **2b–f,h** with C_{60}

Entry	Aldehyde	Product	Yield (%)[a]	d.e.(%)[b]
1	**2b**	**3b**	23	>95
2	**2c**	–	–[c]	–
3	**2d**	**3d**	55	85
4	**2e**	**3e**	24	>95
5	**2f**	**3f**	40	>95
6	**2h**	**3h**	15	>95

[a] Yield based on the starting aldehyde.
[b] Measured by ^{1}H NMR.
[c] Only degradation of the starting aldehyde was observed.



Scheme 4.



Scheme 5.

pyrrolidine proton. Furthermore, interaction between the *cis* H_5 and H_2 protons confirmed the assignment made on the basis of the COSY experiment. According to this model, the *S* configuration was assigned for all the cycloadducts synthesized.

Thus, this method seems to be quite general for the diastereoselective construction of the pyrrolidinyl ring, especially when an aryl substituent is present on the Cp ring. Moreover, the introduction of reactive functionalities such as an ethynyl residue in adduct **3h**, shows that further transformations leading to more complex architectures should be possible. As a first extension to this work, the synthesis of a fullerene dimer[16] was designed using a chiral bis-ferrocenylaldehyde as a substrate for Prato's cycloaddition (Scheme 5). Double Sonogashira coupling of terminal alkyne (R_{Fc})-**2d** with the bis-iodide **4** gave the C_2-symmetric bis-aldehyde (R_{Fc},$R_{Fc'}$)-**5**, in which lipophilic alkoxy groups have been introduced for better solubility, in 49% yield. Double cycloaddition with sarcosine and C_{60} gave a modest yield (21%) of the bis-adduct (R_{Fc}, $R_{Fc'}$, S_C, $S_{C'}$)-**6**, as a stable brown solid which showed the same solubility in common organic solvents as the monomeric adducts. Here again, complete diastereoselectivity occured; ^{1}H NMR indicated a single diastereoisomer in the very well-resolved spectra of this molecule. The global symmetry of this molecule is thus C_2, imposed by the chirality of the substrate. This pathway also shows that it is possible to introduce the fullerene at the last step of the synthesis as well as at different stages of the construction of the molecule.

In summary, we have shown that the construction of enantiopure ferrocene–fullerene dimers was easily achieved using Prato's methodology on chiral ferrocenyl aldehydes. This methodology should be applicable to a wide range of substituents on the ferrocene and could easily lead to the straightforward construction of more complex architectures. In that case, higher symmetries can be attained owing to the planar chirality of the organometallic group. Photophysical studies of those new dyads are currently underway and will be reported shortly.

3. Experimental

3.1. Instrumentation

^{1}H and ^{13}C NMR were recorded on Brucker AC 200 and AC 250 spectrometers. 2D NMR experiments (COSY, NOESY) were carried out on a Brucker DLX 400 spectrometer. UV–Vis spectra were taken on a Kontron spectrophotometer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. GC–MS analysis were performed on a Riberg Mag R10-10 electron impact spectrometer coupled with a gas chromatograph equipped with a capillary quartz CP SIL 5.25 m column. High resolution mass spectra were determined using a GC/MS Finningan-MAT-95-S apparatus. Melting points were determined with a Reichert apparatus. Reactions were monitored by thin layer chromatography using Merck precoated silica gel 60 F_{254} plates. Flash column chromatography was performed employing 60 A C.C 35–70 μm silica gel.

3.2. Materials

C_{60} was purchased from MER Corporation (Tucson, Arizona). All solvents were distilled prior to use. Acetal **1** and aldehydes **2a–c** were prepared according to Ref. 8. (*p*-bromophenyl)ethynyl trimethylsilane[13] and 1,4-didecyloxy-2,5-diiodobenzene[14] were prepared according to the reported procedures. For NMR data, see Ref. 15.

3.2.1. (R_{Fc})-(α-*p*-methoxyphenyl)ferrocenecarboxaldehyde (2e). *Method A*: *by coupling of ferrocenylzinc derivatives with aryl bromides*. A solution of acetal **1** (3.16 g, 10 mmol) in dry degassed diethylether (35 ml) was treated with a pentane solution of *t*-butyllithium (1.6 M, 7.34 ml, 11 mmol) at −78°C for 10 min. The reaction was warmed to room temperature and stirred for 1 h at this temperature. To the orange suspension was added at −78°C a freshly prepared solution of anhydrous zinc chloride (0.5 M in THF, 22 ml, 11 mmol). The solution was warmed to room temperature and stirred for 1 h. To the mixture was added $PdCl_2(PPh_3)_2$ (0.5 mmol, 351 mg) followed by *p*-bromoanisole (10 mmol, 1.25 ml). After being stirred at room temperature overnight, the mixture was treated with a saturated solution of ammonium chloride. After usual work-up, the products were separated by column chromatography on silica gel (cyclohexane/ether 3:1) and the corresponding product isolated in a 65% yield. Quantitative conversion of the acetal to the desired aldehyde was performed by hydrolysis following the general procedure described in Ref. 8.

Method B: *by Suzuki coupling of iodo aldehyde* **2a**. To a degassed solution of aldehyde **2a** (11.9 g, 35 mmol) in THF (350 mL) and water (85 mL) were successively added *p*-methoxybenzeneboronic acid (6.9 g, 45 mmol, 1.3 equiv.), barium hydroxide octahydrate (27.6 g, 87.5 mmol, 2.5 mmol) and palladium acetate (393 mg, 1.75 mmol, 5%). The solution was refluxed for 3 h before cooling. After dilution with ethyl acetate, the organic phase was washed with water and dried. After concentration, 12.6 g of **2e** (quant.) were isolated as an orange solid. mp 118°C; $[\alpha]_D$=+535 (*c*=0.315, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.16 (1H, s), 7.43 (2H, d, *J*=8.4 Hz), 6.88 (2H, d, *J*=8.4 Hz), 4.95 (1H, m), 4.76 (1H, m), 4.67 (1H, m), 4.22 (5H, s), 3.83 (3H, s); ^{13}C NMR ($CDCl_3$) δ 55.31, 68.18, 66.36, 69.60, 71.78, 74.45, 92.72, 113.96, 127.82, 130.72, 158.95, 193.24; HRMS calcd for $C_{18}H_{16}FeO_2$, *M*=320.0499, obsd, *M*=320.0501.

3.2.2. (R_{Fc})-(α-2-naphthyl)ferrocenecarboxaldehyde (2f). The aldehyde was prepared following the method A starting from 2 mmol of acetal **1** and one equivalent of 2-bromonaphthalene. The corresponding substituted acetal was isolated as an orange viscous oil in 61% yield after flash chromatography on silica gel (cyclohexane/ether 4:1) and was quantitatively converted to the desired aldehyde **2f**. $[\alpha]_D$=+525 (*c*=0.89, dichloromethane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 9.76 (1H, s), 8.04–7.36 (7H, aromatic protons), 5.12 (1H, m), 4.81 (2H, m), 4.37 (5H, s); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 68.62, 71.09, 72.25, 75.09, 76.51, 92.68, 126.06, 126.58, 127.63, 127.90, 128.02, 132.50, 133.00, 133.37, 192.98; MS (EI) *m/e* 340 (M, 100%), 339 (56), 312 (65), 190 (51), 189 (99)); HRMS calcd for $C_{21}H_{16}FeO$, *M*=340.0551, obsd, *M*=340.0550.

3.2.3. (R_{Fc})-(α-4-ethynylphenyl)ferrocenecarboxaldehyde (2g). The aldehyde was prepared following method A starting from 1 mmol of acetal **1** and one equivalent of 4-trimethylsilylethynyl bromobenzene. The corresponding substituted acetal was isolated as an orange viscous oil in 74% yield after flash chromatography on silica gel (cyclohexane/ether 3:1). Deprotection of the TMS group was performed by stirring a solution of the acetal in methanol (10 mL) with a spatula of potassium carbonate for 1 h. After extraction with dichloromethane, the extracts were dried over magnesium sulfate and concentrated. Filtration of the residue on a short column of silica gel (cyclohexane/ether 1:1) gave the deprotected acetal in a 90% yield. Final deprotection of the acetal group afforded the desired aldehyde **2g** as an orange solid. $[\alpha]_D$=+2.6 (*c*=0.17, dichloromethane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.15 (1H, s), 7.46 (4H, s), 4.99 (1H, m), 4.84 (1H, m), 4.71 (1H, m), 4.22 (5H, s), 3.13 (1H, s); ^{13}C NMR ($CDCl_3$) δ 69.67, 71.68, 72.76, 75.69, 76.82, 78.39, 83.78, 91.60, 121.33, 129.89, 132.41, 137.52, 193.04; MS *m/e* 315 (M+1, 25.60%), 314 (M, 100%), 286 (49.5), 121 (28.7); Anal calcd for $C_{19}H_{14}FeO$: C, 72.61; H, 4.46. Found: C, 72.58; H, 4.57.

3.2.4. (R_{Fc})-(α-ethynyl)ferrocenecarboxaldehyde (2d). Aldehyde **2a** (13.6 g, 40 mmol), $PdCl_2(PPh_3)_2$ (1.4 g, 2 mmol, 5%) and copper (I) iodide (760 mg, 4 mmol) were placed in a dry Schlenk tube under Ar. Distilled triethylamine (120 mL) was injected followed by trimethylsilylacetylene (8.5 mL, 60 mmol). The suspension was stirred at room temperature for 24 h and concentrated. After extraction with diethyl ether and filtration on celite to remove most of the ammonium salts, the organic phase was concentrated and purified by flash chromatography on silica gel (cyclohexane/ether 6:1). The protected aldehyde was isolated as a brown oil in 75% yield and was directly deprotected by dissolution in 75 mL of dichloromethane and 75 mL of methanol. A large excess of potassium carbonate was added and the resulting suspension was stirred at room temperature for 2 h. After filtration, the solution was concentrated and filtered on a column of silica gel using diethyl ether as eluent. 6.2 g of orange brown crystals were isolated (89% yield). $[\alpha]_D$=+740 (*c*=0.345, dichloromethane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.15 (1H, s), 4.90 (1H, m), 4.84 (1H, m); 4.62 (1H, m), 4.30 (5H, s), 2.95 (1H, s); ^{13}C NMR ($CDCl_3$) δ 67.61, 68.47, 71.72, 72.66, 76.48, 77.96, 79.10, 79.54, 192.80; MS (EI) *m/e* 238 (M, 100%), 208 (20), 184 (12), 152 (43), 144 (11), 121 (13); HRMS calcd for $C_{13}H_{10}FeO$, *M*=238.0081, obsd, *M*=238.0081.

3.2.5. Bisaldehyde (R_{Fc}, $R_{Fc'}$)-(5). Diiododialkoxybenzene **4** (0.95 mmol, 610 mg), aldehyde **2d** (2.1 mmol, 500 mg), $PdCl_2(PPh_3)_2$ (0.105 mmol, 74 mg) and CuI (0.105 mmol, 20 mg) were placed in a dry Schlenk tube. Dipropylamine (10 ml) was added under argon and the mixture was stirred overnight at room temperature. After evaporation of the dipropylamine the product was dissolved in diethylether and filtered. Separation by column chromatography on silica gel (cyclohexane/ether 3:1) gave 400 mg of pure product as an orange solid (49% yield). mp 102°C; $[\alpha]_D$=+80 (*c*=0.285, dichloromethane); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.31 (2H, s), 6.94 (2H, s), 4.97 (2H, m), 4.86 (2H, m), 4.68 (2H, m), 4.34 (10H, s), 4.01 (4H, t, *J*=6.4 Hz), 1.86 (4H, m), 1.56–1.19 (28H, m), 0.85 (6H, q); ^{13}C NMR

($CDCl_3$): δ 14.11, 22.67, 26.10, 29.38, 29.58, 29.65, 31.88, 68.10, 69.35, 69.68, 71.73, 72.85, 75.64, 79.33, 86.48, 90.14, 113.50, 116.10, 153.59, 193.47; Electrospray MS 887.3 ($M+Na^+ +2H^+$, 16%), 579.1 (50), 339.1 (34), 301 (67).

3.3. General procedure for synthesis of ferrocene pyrrolidine-C_{60}

A solution of C_{60} (100 mg, 0.14 mmol), two equivalents of the corresponding aldehyde and *N*-methyl glycine (62.5 mg, 0.7 mmol) in degassed toluene (100 mL) was stirred at reflux temperature overnight, then the solvent was removed in vacuo. The solid residue was purified by flash chromatography (toluene) affording the ferrocene pyrrolidine-C_{60} as a black solid along with recovered C_{60}.

3.3.1. (R_{Fc}, S_C)-*N*-Methyl-2-(α-trimethylsilylferrocenyl)-3,4-fulleropyrrolidine (3b). Yield=23%; ^1H NMR ($CDCl_3/CS_2$, 200 MHz): δ 5.20 (1H, s), 4.92 (1H, d, *J*=8.4 Hz), 4.74 (1H, m), 4.40 (2H, m), 4.25 (1H, m), 4.13 (1H, s), 3.12 (3H, s, *N*-CH_3), 0.47 (9H, s, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3/CS_2$, 63 MHz) δ 1.69, 43.39, 69.59, 70.44, 72.22, 75.60, 76.85, 77.28, 79.39, 83.38, 84.22, 124.21, 124.58, 125.11, 126.82, 130.99, 136.04, 138.43, 138.78, 139.83, 141.30, 141.89, 143.67, 144.83, 145.60, 145.75, 145.82, 146.85, 147.95, 150.89, 151.79, 154.29, 155.34, 159.55; FAB MS *m/z* 1033.0 (M^+, 100%), 720 (C_{60}, 48%); UV–Vis λ_{max} (cyclohexane) 212, 256, 318, 432.

3.3.2. (R_{Fc}, S_C)-*N*-Methyl-2-(α-ethynylferrocenyl)-3,4-fulleropyrrolidine (3d). The major diastereoisomer was isolated after repeated careful separation by flash chromatography on silica gel (toluene/cyclohexane 1:1); Yield=55%; ^1H NMR ($CDCl_3$, 200 MHz) δ 5.04 (1H, s), 4.87 (1H, d, *J*=9.4 Hz), 4.59 (1H, dd, *J*=2.6 and 2.65 Hz); 4.51 (1H, dd, *J*=2.8 and 1.38 Hz); 4.34 (1H, d, *J*=9.4 Hz), 4.31 (5H, s), 4.27 (1H, m), 3.48 (3H, s), 2.74 (1H, s); ^{13}C NMR ($CDCl_3/CS_2$, 63 MHz) δ 29.83, 41.45 (*N*-Me), 67.72, 68.05, 68.26, 70.62, 71.57, 71.86, 75.29, 77.88, 81.92, 89.31, 134.48, 135.88, 136.03, 138.93, 140.20, 140.80, 140.82, 141.65, 141.84, 141.89, 142.14, 142.16, 142.86, 143.32, 144.77, 144.79, 144.87, 144.99, 145.12, 145.51, 145.56, 145.80, 146.26, 146.48, 146.30, 146.98, 146.79, 147.79, 148.19, 148.23, 148.25, 151.72, 153.43, 159.82; FAB MS *m/z* 985.06 (M^+, 100%), 720 (C_{60}, 20%); UV–Vis λ_{max} (cyclohexane) 212, 256, 308, 326, 430.

3.3.3. (R_{Fc}, S_C)-*N*-Methyl-2-[α-(4-methoxyphenyl)-ferrocenyl]-3,4-fulleropyrrolidine (3e). Yield=24%; ^1H NMR ($CDCl_3$, 250 MHz) δ 7.73 (2H, d, *J*=8.7 Hz), 6.68 (2H, d, *J*=8.7 Hz), 5.18 (1H, s), 4.86 (1H, d, *J*=9.4 Hz), 4.70 (1H, t, *J*=2.25 Hz), 4.48 (1H, t, *J*=2.2 Hz), 4.35 (1H, t, *J*=2.5 Hz), 4.26 (1H, d, *J*=9.4 Hz), 4.22 (5H, s), 3.73 (3H, s, *O*-CH_3), 3.57 (3H, s, *N*-CH_3); ^{13}C NMR($CDCl_3/CS_2$, 63 MHz) δ 41.79 (*N*-Me), 54.61 (*O*-Me), 67.70, 67.92, 68.27, 70.70, 70.90, 75.46, 84.77, 86.24, 113.11, 129.69, 130.81, 135.2, 135.48, 136.15, 136.34, 137.98, 138.57, 139.70, 140.17, 140.31, 141.00, 141.16, 141.50, 141.60, 142.13, 142.19, 142.56, 143.73, 143.89, 144.15, 144.39, 144.61, 144.84, 144.97, 145.28, 145.48, 145.52, 145.75, 146.20, 147.15, 148.94, 149.93, 152.19, 153.35, 153.85, 156.24, 157.90; FAB MS *m/z* 1066.8 (M^+, 100%), 720 (C_{60}, 36%); UV–Vis λ_{max} (cyclohexane): 212, 256, 308, 326, 412, 430.

3.3.4. (R_{Fc}, S_C)-*N*-Methyl-2-[α-(2-naphtyl)-ferrocenyl]-3,4-fulleropyrrolidine (3f). Yield=40%; ^1H NMR ($CDCl_3/CS_2$, 200 MHz) δ 7.59 (2H, t), 7.50 (1H, t), 7.24–6.77 (4H, m), 5.25 (1H, s), 4.85 (3H, m), 4.55 (1H, m), 4.29 (1H, d, *J*=9.4 Hz), 4.27 (5H, s), 3.69 (3H, s); ^{13}C NMR ($CDCl_3/CS_2$, 63 MHz) δ 42.19, 67.50, 68.16, 70.59, 70.73, 71.50, 75.57, 87.57, 124.50, 125.28, 125.39, 127.31, 128.08, 129.63, 130.56, 130.69, 131.50, 131.79, 132.50, 133.20, 133.86, 133.91, 134.30, 135.44, 137.10, 138.50, 139.64, 140.47, 141.03, 141.08, 141.39, 141.42, 141.57, 142.01, 143.66, 143.95, 144.14, 144.63, 144.83, 145.01, 145.32, 145.48, 145.76, 145.83, 146.10, 146.22, 146.70, 148.16, 151.04, 151.42, 151.48, 151.88, 153.32; FAB MS *m/z* 1086.9 (M^+, 100%), 720 (C_{60}, 40%); UV–Vis λ_{max} (cyclohexane): 222, 256, 308, 326, 430.

3.3.5. (R_{Fc}, S_C)-*N*-Methyl-2-[α-(4-ethynylphenyl)-ferrocenyl]-3,4-fulleropyrrolidine (3h). Yield=17%; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.43 (2H, d, *J*=8.4 Hz), 7.23 (2H, d, *J*=8.4 Hz), 5.18 (1H, s), 4.86 (1H, d, *J*=9.4 Hz), 4.77 (1H, m), 4.48 (1H, t, *J*=2.4 Hz), 4.40 (1H, t, *J*=2.55 Hz), 4.27 (1H, d, *J*=9.4 Hz), 4.21 (5H, s), 3.57 (3H, s), 3.00 (1H, s); ^{13}C NMR($CDCl_3/CS_2$, 63 MHz δ 41.77, 67.81, 67.88, 68.29, 68.66, 70.71, 71.12, 75.33, 77.81, 77.96, 83.60, 85.11, 120.06, 129.14, 129.49, 129.95, 130.02, 130.52, 131.25, 131.35, 131.51, 132.56, 132.84, 133.75, 138.13, 139.05, 141.00, 141.71, 142.17, 144.14, 144.80, 145.09, 145.59, 146.82, 147.01, 151.80, 152.26; FAB MS *m/z* 1062.8 (M^+, 100%); UV–Vis λ_{max} (cyclohexane) 224, 246, 260, 308, 328, 432.

3.3.6. Bisadduct (R_{Fc}, $R_{Fc'}$, S_C, $S_{C'}$)-6. Yield=21%; ^1H NMR ($CDCl_3/CS_2$, 200 MHz) δ 6.38 (2H, s), 5.12 (2H, s), 4.86 (2H, d, *J*=9.3 Hz), 4.62 (2H, m), 4.51 (2H, m), 4.32 (14H, m), 3.80 (4H, m), 3.48 (6H, s), 1.83 (4H, m), 1.44 (4H, m), 1.25 (28H, m), 0.88 (6H,m); ^{13}C NMR ($CDCl_3/CS_2$, 63 MHz) δ 22.95, 26.21, 29.57, 29.72, 29.77, 29.83, 31.00, 41.50, 67.74, 68.42, 68.45, 71.43, 71.47, 75.51, 76.45, 78.29, 80.91, 81.39, 110.10, 113.13, 115.57, 122.71, 130.68, 130.86, 131.03, 131.69, 132.70, 133.97, 134.17, 134.32, 134.74, 135.70, 136.36, 136.85, 139.37, 139.89, 140.01, 141.37, 141.81, 141.91, 142.64, 142.75, 144.79, 144.88, 145.05, 145.75, 145.88, 146.37, 146.81, 148.10, 152.99, 154.57, 156.41, 157.97, 158.45; FAB MS *m/z* 1638 ($M-C_{60}$, 14%), 720 (C_{60}, 100%); UV–Vis λ_{max} (cyclohexane): 218, 257, 310, 330, 430.

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