CHAPTER 2

SYNTHESIS AND CHARACTERIZATION
OF NOVEL FULLERENE DERIVATIVES
A series of fulleropyrrolidines and fulleropyrazolines were synthesized by adopting the 1, 3 dipolar cycloaddition reaction of azomethine ylides and nitrile imines to C\textsubscript{60}. Amongst the fulleropyrrolidines a fullerene-ferrocene dyad with bilinkage (FEFPY), a crown ether derivatized fulleropyrrolidine (DBCFPY), six different s-triazine derivatized fulleropyrrolidines (STFPY\textsubscript{1} - STFPY\textsubscript{6}), a fullerene – isoniazid conjugate (INHFPY) and a lysine derivatized fulleropyrrolidine (LFPY) have been synthesized. Amongst fulleropyrazolines two novel indole derivatized pyrazolino [60] fullerene derivatives (IPYF\textsubscript{1} - IPYF\textsubscript{2}) have been synthesized by microwave technique. A novel methanofullerene with pyridine pendants (PYMF) has also been prepared by Bingel’s cyclopropanation reaction using 1, 8 diazabicyclo [5.4.0] undec-7-ene and I\textsubscript{2}. All the compounds synthesized were well characterized by elemental analysis, FTIR, \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and MADI-TOF/FAB-MS.
2.1 Introduction

One of the main challenges in organic chemistry has been the directed synthesis of compounds aimed at their practical use. The use of fullerenes as 'building blocks' made it possible to design a large number of various molecules with valuable properties.\(^1\) The unique structural properties of \(C_{60}\) make it the most abundant, the least expensive and therefore the most thoroughly investigated of all the fullerenes.

Cycloadditions along with nucleophilic additions represent the most powerful methods for synthesizing a large variety of functional derivatives of fullerene. Reactions like Diels – Alder [4 + 2] reaction,\(^2\) [3 + 2] cycloaddition,\(^3\) photochemical [2 + 2] cycloaddition,\(^4\) oxidative [3 + 2] cycloaddition,\(^5\) azide addition\(^6\) and azomethine ylide addition\(^7\) are some of the major cycloaddition reactions employed to functionalize \(C_{60}\). Micheal additions\(^8\) and Bingel–Hirsch\(^9\) are the two major nucleophilic addition reactions which are used to functionalize \(C_{60}\). Other reactions like hydrogenation\(^10\) and halogenation\(^11\) have also been done on \(C_{60}\). Furthermore, microwave assisted synthetic methods have also been developed to synthesize derivatives like pyrazolinofullerene,\(^12\) oxazolidino fullerene\(^13\) etc.

A survey of literature of the past decade reveals that a variety of functionalized fullerenes having different applications have been synthesized by following either of the two routes

(1) 1, 3 dipolar cycloaddition reaction or (2) Bingel – Hirsh cyclopropanation.
2.1.1 Synthesis by 1,3-dipolar cycloaddition reaction

2.1.1.1 Prato's 1,3-dipolar cycloaddition reaction-Fulleropyrrolidines

Of all the methods which have been successfully employed to functionalize C$_{60}$, 1,3-dipolar cycloaddition is the most frequently used one. It is a classic synthetic procedure which involves cycloaddition of azomethine ylides to C$_{60}$ and has been successfully used to synthesize numerous fullerene analogues. As a result of this powerful methodology for obtaining functionalized fullerene derivatives, the fulleropyrrolidines are formed, in which a pyrrolidine ring is fused to a junction between two six-membered rings of a fullerene sphere. When the reaction is carried out in the presence of large excesses of reagents, up to nine pyrrolidine rings can be introduced. Its main advantages are as follows: (a) the reactions lead to individual [6, 6]-closed isomers, (b) majority of precursors are commercially available or could be easily prepared, and (c) two substituents can be simultaneously introduced into the pyrrolidine cycle. So, functionalization of the fullerene sphere on the Prato's reaction basis occupies a leading place in the synthesis of fullerene derivatives to get new materials and potentially biologically active compounds. This reaction generally involves reaction of N-substituted glycine with a carbonyl compound to give azomethine ylide which is the reacted in situ with C$_{60}$ to give fulleropyrrolidine (Figure 1). Some of the recent fulleropyrrolidines reported have been reviewed.$^{14}$
Figure 1. Mechanism of Prato's 1,3-dipolar cycloaddition reaction.
2.1.1.2 1,3-dipolar cycloaddition reaction-Pyrazolino [60] fullerenes

Functionalization of C_{60} with 1,3-nitrile imine dipoles gives pyrazolino [60] fullerenes. This synthetic procedure is generally used to construct fullerene based artificial photosynthetic systems since pyrazolino [60] fullerenes are better electron acceptors than C_{60}. In this method a hydrazone is first synthesized reaction of substituted hydrazine which is then followed by reaction of hydrazone with NBS, triethylamine which yields 1,3 nitrile imine and finally the reaction mixture is focused on microwave reactor to afford pyrazolino [60] fullerene (Figure 2). A recent report of pyrazolinofullerene is a fullerene-anilme-ferrocene triad synthesized by F. Langa and coworkers.\textsuperscript{15}

\textit{Figure 2.} Mechanism for the synthesis of pyrazolino [60] fullerene.
2.1.2 Bingel – Hirsch Cyclopropanation reaction-Methanofullerene

In this method methanofullerene can be synthesized by the reaction of bromomalonates, bromoketoesters and bromoketones with C\textsubscript{60} in presence of a strong base. Generally 1, 8 diazabicyclo [5.4.0] undec-7-ene (DBU) is used as base for such reactions (Figure 3).\textsuperscript{16}

![Figure 3. Mechanism of Bingel's cyclopropanation reaction.](image)

Due to popularity and application orientation of the above methods for the functionalization of fullerenes, similar strategies were used in the present investigation to synthesize a series of functionalized fullerenes.

2.1.3 Molecules designed and synthesized

The following molecules were designed and synthesized

2.1.3.1 A series of indole- fullerene – nitrobenzene hybrid systems were prepared by 1,3-dipolar cycloaddition of nitrile imine to C\textsubscript{60}.

2.1.3.2 Following fullerene derivatives were synthesized by 1,3-dipolar cycloaddition reaction of an azomethine ylide with C\textsubscript{60}.

(a) Tether directed synthesis of a novel fullerene – ferrocene dyad with a rigid bilinkage.

(b) Tether directed synthesis of a fullerene – crown ether conjugate
(c) A fullerene – isoniazid conjugate

(d) A series of fullerene – s-triazine conjugate has been synthesized by 1, 3 dipolar cycloaddition reaction.

(e) A novel fullerene-lysine conjugate

2.1.3.3 A novel fullerene-pyridine hybrid system has been synthesized by cyclopropanation reaction.

All the compounds synthesized have been purified and characterized using elemental analysis and spectral methods.

2.2 EXPERIMENTAL

2.2.1 Instrumentation

Microwave synthesis was carried out in Discover BenchMate system-240V (CEM Corporation) microwave synthesizer. Melting points were determined on a Toshniwal (India) melting point apparatus and are uncorrected. Elemental analysis was done on a Heraeus Carlo Erba-1108 analyzer. FT-IR spectra were recorded on a BRUKER – TENSOR 27 spectrometer as KBr pellets. UV-visible spectra were recorded on a Hitachi U-3210 UV-visible spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a DRX-400 spectrophotometer operating at 400 MHz and 125 MHz respectively with TMS as the internal standard. EIMS spectra were recorded on SHIMADZU QP-5050 A. FAB mass spectra were recorded on a JEOL SX-102 / DA – 6000 mass spectrometer / data system using argon / xenon (6KV, 10mA) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature. m-Nitro benzyl alcohol (NBA) was used as the matrix and the matrix peaks appeared at m/z 136, 137, 154, 289, 307. The MALDI TOF MS were run on a Micromass Tof Spec 2E instrument using a
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nitrogen 337 nm laser (4 ns pulse). At least 40-50 shots were summed up. The matrix used is 2, 5-dihydroxy benzoic acid dissolved in chloroform and the matrix was spotted on MALDI target and allowed to dry before introducing into the mass spectrometer.

2.2.2 Chemicals and Reagents

Fullerene \((C_{60})\), sarcosine, indole-3-carboxaldehyde, Boc-protected lysine, ferrocene dicarboxylic acid, terephthalaldehyde, p-formylbenzoic acid, 8-hydroxyoctanoic acid, N, N' dicyclohexylcarbodiimide (DCC), 4-(Dimethylamno) pyridinium 4-toluenesulfonate (DPTS), 4- pyrrolidino pyridine (4-PPy), 1, 8 diazabicyclo [5.4.0] undec-7-ene (DBU) used were purchased from Sigma Aldrich and were of analytical grade.

\(m\)-aminophenol, 3-hydroxybenzaldehyde, N-bromosuccinimide (NBS), malonic acid, cyanuric chloride were purchased from local manufacturers.

2.3 Synthesis, Results and Discussion

The novel fullerene derivatives have been synthesized by either conventional heating or microwave assisted methods. The progress of the reaction has been monitored by thin layer chromatography. The product was isolated and purified by column chromatography. The final products as well as the intermediates were characterized by elemental analysis, \(^1\text{H}\) NMR, \(^{13}\text{C}\) NMR and mass spectra. The synthetic procedure of all the compounds have been divided into 7 synthetic schemes in which first the procedure is given which is followed by analytical as well as spectral data.
2.3.1 Fullerene – Indole Hybrid System

Scheme 1

\[
\begin{align*}
\text{Indole - 3-carboxaldehyde} + \text{nitro substituted phenyl hydrazines} &\xrightarrow{\text{AcOH, EtOH, reflux, 10 min}} \text{Indole hydrazones} \\
&\xrightarrow{\text{NBS, Et₃N, CHCl₃}} \text{IPYF1, IPYF2} \\
&\text{For IH₁ and IPYF1, } R = H \\
&\text{For IH₂ and IPYF2, } R = \text{NO₂}
\end{align*}
\]

SYNTHETIC PROCEDURE AND CHARACTERIZATION DATA

The synthetic approach to preparing indolylpyrazolino[60]fullerenes IPYF₁-IPYF₂ (Scheme 1) relies upon the 1,3-dipolar cycloaddition of indolyl nitrile imines under microwave irradiation, which in turn can be generated in situ from the corresponding hydrazones IH₁ & IH₂. This methodology has proven to be a powerful tool for the functionalization of C₆₀ due to the availability of the starting materials and the fact that no stereogenic centers are produced during the reaction. Reaction of Indole 3-carboxaldehyde with 4-nitrophenylhydrazine and 2, 4 dinitrophenylhydrazine in EtOH under reflux for 10 min afforded hydrazones IH₁ and IH₂ respectively. Reaction of IH₁-
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IH₂ with NBS in CHCl₃ at room temperature and subsequent addition of C₆₀ and Et₃N in toluene and irradiation in a focused microwave reactor at 210 W for 25 min afforded cycloadducts IPYF₁ and IPYF₂ in 34-38% isolated yield after column chromatography (silica gel, toluene) followed by centrifugation in hexane, MeOH and Et₂O (Scheme 1). The structures of hydrazones IH₁ & IH₂ and cycloadducts IPYF₁ & IPYF₂ were confirmed by analytical and spectroscopic data.

2.3.1.1 Indole 3-carboxaldehyde 4-nitro phenyl hydrazone (IH₁): yield 79%; mp 189°C; Anal. Calcd for C₁₅H₁₂N₄O₂: C 64.28; H 4.28; N 20.00 %; Found: C, 64.60; H, 4.30; N, 20.02 %; FTIR (KBr) v (cm⁻¹) 3180(N-H stretching), 2998(C-H stretching), 1275, 990, 751; ¹H NMR (400 MHz, CDCl₃, Me₄Si, 298 K) δ (ppm) 10.1 (s, 1H, NH), 8.42 (s, 1H, NH), 8.0 (s, 1H, CH=N), 7.8 (d, 2H, J = 8.2 Hz, ArH), 7.6 – 7.4 (m, 4H, ArH), 6.8 (d, 2H, J = 8.2 Hz, ArH), 6.7 (s, 1H, ArH); EIMS m/z (relative intensity) 280 (M⁺, 85)

2.3.1.2 Indole 3-carboxaldehyde 2, 4-dinitro phenyl hydrazone (IH₂): yield 67%; mp 195°C; Anal. Calcd for C₁₅H₁₁N₅O₄: C 55.38; H 3.38; N 21.53 %; Found: C, 55.40; H, 3.40; N, 21.52 %; FTIR (KBr) v (cm⁻¹) 3183, 2998, 1278, 992, 752; ¹H NMR (400 MHz, CDCl₃, Me₄Si, 298 K) δ (ppm) 10.2 (s, 1H, NH), 8.9 (s, 1H, ArH), 8.4 (s, 1H, NH), 8.1 (s, 1H, CH=N), 7.8 (d, 1H, J = 8.1 Hz, ArH), 7.6 – 7.4 (m, 4H, ArH), 6.9 (d, 1H, J = 8.1 Hz, ArH), 6.7 (s, 1H, ArH); EIMS m/z (relative intensity) 325 (M⁺, 90)

2.3.1.3 3' Indolyl – 1' (4-nitrophenyl) pyrazolino [60] fullerene (IPYF₁): yield 29%; mp 289°C, Anal. Calcd for C₇₅H₇₀N₄O₂: C 90.18; H 1.00; N 5.61 %; Found: C, 90.00;
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H, 1.03; N, 5.62 %; FTIR (KBr) v (cm\(^{-1}\)) 1585, 1494, 1098, 1043, 838, 739, 521; \(^1\)H NMR (400 MHz, CDCl\(_3\), Me\(_4\)Si, 298 K) \(\delta\) (ppm) 10.8 (s, 1H, NH), 7.9 (d, 2H, \(J = 8.2\) Hz, ArH), 7.6 – 7.4 (m, 4H, ArH), 7.1 (d, 2H, \(J = 8.2\) Hz, ArH), 6.9 (s, 1H, ArH); \(^13\)C NMR (125 MHz, CDCl\(_3\), Me\(_4\)Si, 298 K) \(\delta\) (ppm) [unassigned values refers to sp\(^2\) C of C\(_{60}\)] 156.8 (C=N of pyrazoline ring), 154.4, 153.6, 151.6, 150.7, 150.5, 149.8, 149.2, 148.8, 148.3, 147.9, 147.8, 146.9, 146.4, 145.9, 145.8, 145.6, 145.2, 144.8, 142.8, 142.2, 141.9, 141.8, 141.7, 141.5, 141.0 (Ar-Cq), 140.7, 139.8 (Ar-Cq), 139.5, 138.9, 137.2 (Ar-Cq), 136.4, 135.9, 135.6, 130.5 (Ar-Cq), 125.7, 124.9, 122.8, 121.8, 121.1, 117.7(Ar-CH), 73.0(sp\(^3\) C– of C\(_{60}\)), 64.3 (sp\(^3\) C– of C\(_{60}\)); FAB-MS m/z (relative intensity) 999 (M + 1, 100)

2.3.1.4 3' Indolyl – 1' (2, 4-dinitrophenyl) pyrazolino [60] fullerene (IPYF2): yield 31%; mp 296 °C; Anal. Calcd for C\(_{75}\)H\(_9\)N\(_3\)O\(_4\): C 86.28; H 0.86; N 6.71 % Found: C, 86.30; H, 0.89; N, 6.72 %; FTIR (KBr) v (cm\(^{-1}\)) 1588, 1494, 1095, 1048, 839, 739, 523; \(^1\)H NMR (400 MHz, CDCl\(_3\), Me\(_4\)Si, 298 K) \(\delta\) (ppm) 10.9 (s, 1H, NH), 8.3 (s, 1H, ArH), 8.0 (d, 1H, \(J = 8.2\) Hz, ArH), 7.8 (d, 1H, \(J = 8.2\) Hz, ArH), 7.6 – 7.4 (m, 4H, ArH), 7.0 (s, 1H, ArH); \(^13\)C NMR (125 MHz, CDCl\(_3\), Me\(_4\)Si, 298 K) \(\delta\) (ppm) [unassigned values refers to sp\(^2\) C of C\(_{60}\)] 157.1 (C=N of pyrazoline ring), 154.6, 153.8, 151.7, 150.8, 150.5, 149.8, 149.2, 148.8, 148.3, 147.9, 147.8, 146.9, 146.2, 145.9, 145.8, 145.6, 145.2, 144.8, 142.8, 142.2, 141.9, 141.8, 141.7, 141.5, 141.0 (Ar-Cq), 140.7, 140.0(Ar-Cq), 139.8 (Ar-Cq), 139.5, 138.9, 137.2 (Ar-Cq), 136.4, 135.9, 135.6, 130.5 (Ar-Cq), 125.1, 124.9, 122.5, 121.8, 121.0, 118.0 (Ar-CH), 73.2(sp\(^3\) C– of C\(_{60}\)), 64.6 (sp\(^3\) C– of C\(_{60}\)); FAB-MS m/z (relative intensity) 1043 (M\(^+\), 100)
2.3.2 Fullerene – ferrocene dyad.

Scheme 2

1, 1' Ferrocene diacid chloride 8 - hydroxyoctanoic acid

\[ \text{Ferrocene Ester} \quad \text{FE 1} \]

\[ \text{m - aminophenol} \quad \text{terephthalaldehyde} \quad \text{Schiff Base SB1} \]

\[ \text{Ferrocene Ester} \quad \text{FE 2} \]

\[ \text{Ferrocene derivatized fulleropyrrolidine} \quad \text{FEFPY} \]

(a) Et\textsubscript{3}N, diethylether, 25 °C, 8h, 90 %  
(b) AcOH, EtOH, reflux, 2h, 85 %  
(c) DCC, DPTS, 4-PPy, CH\textsubscript{2}Cl\textsubscript{2}, 25 °C, 12h, 78 %  
(d) N-methylglucme, C\textsubscript{60}, toluene, reflux, 5h, 33 %
2.3.2.1 **Synthesis of Ferrocene ester FE 1.** A mixture of ferrocenediacid chloride\(^1\) (3.11 g, 0.01 mol), 8-hydroxyl 1-octanoic acid (3.2 g, 0.02 mol) and 3 ml triethylamine (Et\(_3\)N) was stirred for 8 h at room temperature in degassed dry diethylether under inert atmosphere. 20 ml of dilute HCl solution was then added to it and then stirred for 30 min. The organic layer was separated and after removal of solvent the residue was purified over silica gel (hexane/ethylacetate 7:3). The solvent was then removed to get FE 1 (Scheme 2). Yield 4.73 g, 90%; mp 78° C; **Anal. Calcd** for C\(_{28}\)H\(_{38}\)O\(_4\)Fe: C, 60.25; H, 6.80% **Found**: C, 60.21; H, 6.81%; IR (KBr) \(\nu\) (cm\(^{-1}\)) 1747, 1056, 1249; \(^1\)H NMR (400 MHz, CDCl\(_3\), Me\(_4\)Si) \(\delta\) (ppm) 12.1 (s, 1H, -COOH), 4.45 (m, 8H, H-ferrocene), 1.33-1.26 (m, 28H, -CH\(_2\)); **EIMS** m/z (relative intensity) 558 (M\(^+\), 48)

2.3.2.2 **Synthesis of Schiff base SB1.** To an ethanolic solution of terephthaldehyde (2.68 g, 0.02 mol) was added 3-4 ml of glacial acetic acid. This mixture was refluxed for a while and in the mean time a solution of m-NH\(_2\) phenol (2.7 g, 0.02 mol) in ethanol was added slowly for a period of half an hour. The yellow product was isolated and purified by column chromatography (toluene/methanol 9:1). The solvent was then removed to get SB1 as a yellow solid (Scheme 2). Yield 3.19 g, 71%. The product was crystallized in ethanol. mp 114° C; **Anal. Calcd** for C\(_{14}\)O\(_2\)H\(_{11}\)N : C, 74.66; H, 4.31; N, 5.49% **Found**: C, 74.50; H, 4.41; N, 5.50%; IR (KBr) \(\nu\) (cm\(^{-1}\)) 1710, 3065, 3315; \(^1\)H NMR (400 MHz, CDCl\(_3\), Me\(_4\)Si) \(\delta\) (ppm) 9.85 (s, 1H, -CHO), 9.40 (s, 1H, -OH), 8.65 (s, 1H, CH=N-), 8.1 (d, 2H, \(J= 8.2\) Hz, ArH), 8.0 (d, 2H, \(J= 8.2\) Hz, ArH), 7.1 (t, 1H, \(J= 8.0\) Hz, ArH), 6.95 (d, 1H, \(J= 8.0\) Hz, ArH), 6.80 (s, 1H, ArH), 6.75 (d, 1H, \(J=8.0\) Hz, ArH); **EIMS** m/z (relative intensity) 225 (M\(^+\), 65)
2.3.2.3 Synthesis of Ferrocene ester FE 2. To a mixture of FE 1 (0.780 g, 1.40 mmol) and SB1 (0.697 g, 2.80 mmol) in dry CH₂Cl₂ cooled to 0 °C were added N, N’-Dicyclohexyl carbodiimide (DCC) (0.570 g, 2.78 mmol), 4-(dimethylamino) pyridinium toluene – p –sulfonate(DPTS) (0.820 g, 2.78 mmol) and 4-pyrrolidinopyridine (4-PPy) (spatula tip). The mixture was stirred at 0 °C for 30 min. and then for 22 h at room temperature. After evaporating the solvent to dryness, purification of the solid residue was done by column chromatography (CH₂Cl₂ /Diethyl ether 19:1) to get pure product FE2(Scheme 2). Yield 1.28, 90%. mp 97 °C; Anal. Calcd. for C₅₆H₅₆O₁₀N₂Fe : C, 69.13; H, 5.76; N, 2.88 % Found: C, 69.28, H, 5.71; N, 2.86 %; IR (KBr) ν (cm⁻¹) 1661, 1749, 3075; ¹H NMR (400 MHz, CDCl₃, Me₄Si) δ (ppm) 9.85 (s, 2H, -C//=O), 8.01 (s, 2H, CH=N-), 7.90 (d, J= 8.1 Hz, ArH), 7.78 (d, J= 8.1 Hz, ArH), 7.5 (t, 2H, J=8.1 Hz, ArH), 6.99 (d, 2H, J= 8.2Hz, ArH), 6.88 (s, 2H, ArH), 6.79 (d, 2H, J=8.2 Hz, ArH), 4.45 (m, 8H, H-Ferrocene), 1.34-1.26 (m, 28H, -CH₂); EIMS m/z (relative intensity) 972 (M+, 52%)

2.3.2.4 Synthesis of FEFPY. Dialdehyde FE2 (210mg, 0. 2 mmol), N-methylglycine (10 mg, 0.02 mmol), C₆₀ (72 mg, 0.1mmol) was refluxed in dry toluene in inert atmosphere for 6 hours. The product was first purified by column chromatography (toluene / ethyl acetate 9:1) to recover unreacted C₆₀. Then the remaining part was eluted with a mixture of toluene/ethyl acetate (50:50) to obtain trans 1 and then the rest of the regioisomers. The solvent was then removed to get pure product FEFPY (Scheme 2). Yield 114mg, 33%; mp 228 °C; Anal. Calcd. for C₁₂₀H₆₆O₈N₄Fe : C, 82.47; H, 3.78; N, 3.20 % Found: C, 82.40; H, 3.79; N, 3.21 %; IR (KBr) ν (cm⁻¹) 1664, 1749, 3060; ¹H NMR (400 MHz, CDCl₃, Me₄Si, 298K) δ (ppm) 8 11 (s, 2H, CH=N-), 8.00 (d, 4H, J= 8.2
Hz, ArH), 7.80 (d, 4H, J = 8.2 Hz, ArH), 7.60 (t, 2H, J = 8.2 Hz, ArH), 6.99 (d, 2H, J = 8.1 Hz, ArH), 6.88 (s, 2H, ArH), 6.79 (d, 2H, J = 8.1 Hz, ArH), 5.89 (s, 2H, H-C- N-), 5.25 (d, 2H, J = 9.3 Hz, HHC-N-), 4.45-4.25 (m, 8H, H-Ferrocene), 3.90 (d, 2H, J = 9.3 Hz, HHC-N-), 2.68 (s, 6H, N-CH3 of Pyrrol.), 1.36-1.28 (m, 28H, -CH2-); $^{13}$C NMR (125 MHz, CDCl3, Me4Si, 298K) δ (ppm) [unassigned values refers to sp2 C of C60] 169.0(-COO- linked to ferrocene ring), 167.0(-COO- linked to phenyl ring), 163.7(CH=N-), 154.7, 153.6, 147.04, 147.0, 146.8, 146.7, 146.6, 146.3, 146.1, 145.9, 145.7, 145.6, 145.4, 145.3, 145.2, 145.0, 144.8, 144.6, 144.5, 144.3, 144.2, 144.0, 143.8, 143.6, 143.5, 143.4, 143.2, 143.0, 142.5, 142.3, 142.1, 142.0(ArCq), 141.7, 141.3, 141.2, 141.1, 141.0(ArCq), 140.6, 140.4, 140.3, 140.0, 139.8, 139.6(ArCq), 139.5, 139.4, 139.0(ArCq), 130.5, 130.2, 128.8(ArCH), 128.4(ArCH), 119.9(ArCH), 118.6(ArCH), 114.5(ArCH), 81.3(NCH-), 75.0(ferrocene ring), 73.0(sp3 C- of C60), 72.4, 70.5(ferrocene ring), 68.5(ferrocene ring), 68.3(sp3 C- of C60), 61.8(N CH2), 33.3(CH3 linked to N of the pyrroldine ring), (33.2, 29.9, 29.7, 26.5, 25.4-CH3); FAB-MS m/z (relative intensity) 1746(M+, 68%), 1747(M+1, 25%), 1716(M- 2(CH3), 21%), 720 (C60 , 25%). Based on the geometrical consideration there are 8 possible regioisomers for the synthesized molecule [Fig 4].

Figure 4. Regioisomers possible for bis-adducts on fullerene.
The possibility that the bridge ends of the ferrocene precursor binding to different C$_{60}$ molecules [Fig 5] was ruled out from results obtained from FAB-MASS.

\[ \text{Figure 5. The other possible fullerene derivative which was not present in the final product.} \]

The $^1$H NMR of FEFPY showed a single peak $\delta$ 2.68 of singlet for both the $-\text{CH}_3$ groups on the N atom of pyrrolidine ring which indicates that $\text{trans}$-1 isomer was the major product and all other isomers were obtained in negligible amount. It was also confirmed by $^{13}$C NMR which showed a single peak at $\delta$ 3.33($-\text{CH}_3$ linked to N of pyrrolidine ring) indicating symmetry in the molecule and hence confirming $\text{trans}$-1 as the regioisomer obtained. FAB-MS spectrum of FEFPY showed molecular ion peak at $m/z$ 1746[M+] and 1747 corresponding to M+1 peak. Other peaks such as 1716 corresponding to [M- 2(CH$_3$)] and 720 attributed to C$_{60}$ were also observed in the spectra.
2.3.3 Crown ether based fullerobis(pyrrolidine)

SYNTHETIC PROCEDURE AND CHARACTERIZATION DATA

The synthesis of dibenzo-18-crown-6 \(^{19}\), nitration to 4, 4'-dinitrodibenzo-18-crown-6 \(^{20}\) and reduction to 4, 4'-diaminodibenzo-18-crown-6 \(^{21}\) was carried out by reported procedures. \(\text{p-[1,3-dioxolan-2-yl] benzoic acid}\) was prepared by a procedure similar to that reported by Imahori and co-workers.\(^{22}\)
2.3.3.1 Synthesis of 1, 1’-(6, 7, 9, 10, 17, 18, 20, 21 - octahydrodibenzo[b,k][1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine-2, 14 - diyl) bis(3-(4-(1, 3-dioxolan-2-yl)phenyl)urea) 

CED : A solution of 4, 4’-diaminodibenzo-18 crown 6 (390 mg, 1mmol), p-[1,3-dioxolane-2-yl] benzoic acid (388 mg, 2 mmol), DPPA (800 mg, 3 mmol) and Et₃N (700 mg, 7 mmol) in benzene (150 mL) was heated under reflux for 1.5 h. After adding methanol (30 mL), the reaction mixture was further heated for 2h and then cooled, concentrated in vacuo to get white solid product. The product was then dissolved in chloroform, washed with dilute HCl, dried over Na₂SO₄, filtered and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/ hexane= 1/25 to afford compound CED as white solid product (Scheme 3). Yield 430 mg, 55%; mp 189 °C (dec); Anal. Calcd. for C₄₀O₁₂H₄₄N₄: C, 61.38; H, 5.62; N, 6.90 Found: C, 61.50; H, 5.71; N, 6.50, IR(KBr) ν (cm⁻¹) 1130, 1262, 1638, 3257; ¹H NMR (400 MHz, CDCl₃, Me₄Si, 298 K) δ (ppm) 9.70(s, 2H, -CONH-Ar), 8.35(s, 2H, -CONH-Ar), 7.0 (s, 2H, ArH), 6.88 (d, J = 8.1 Hz, 2H, ArH), 6.77 (d, J=8.2 Hz, 2H, ArH), 6.68 (d, J = 8.3 Hz, 4H, ArH), 6.58 (d, J = 8.5 Hz, 4H, ArH), 5.90(s, 2H, O-CH-O), 4.3(s, 8H, -OCH₂-CH₂O⁻), 4.25-4.18 (m, 8H, -OCH₂ crown ether), 4.06-4.00 (m, 8H, -OCH₂ crown ether); EIMS m/z (relative intensity) 772 (M⁺, 100), 320 (60).

2.3.3.2 1, 1’-(6, 7, 9, 10, 17, 18, 20, 21 - octahydrodibenzo[b,k][1, 4, 7, 10, 13, 16] hexaoxacyclooctadecine-2, 14 - diyl) bis(3-(4-formylphenyl)urea) CEA : CED (350 mg, 0.01 mol) was mixed with 2.5 ml TFA in 75 ml of dichloromethane and 10 ml of water. The biphasic mixture was stirred at room temperature for 12 h. The solution was diluted with dichloromethane and washed with saturated sodium bicarbonate until the organic
phase became light brown. The organic layer was separated and dried over Na₂SO₄. The solvent was removed in vacuo, and the light yellow solid residue was purified by column chromatography on silica gel with toluene/methanol = 50/1 to get compound CEA as pure white product (Scheme 3). 230 mg, 70%; mp 158 °C (dec); Anal. Calcd. for C₃₆O₁₀H₃₆N₄ : C, 63.15; H, 5.26; N, 8.18. Found: C, 63.50; H, 5.41; N, 8.10.; IR (KBr) ν (cm⁻¹) 1130, 1262, 1638, 1710, 3320; ¹H NMR (400 MHz, CDCl₃, Me₄Si, 298 K) δ (ppm) 9.91 (2H, s, -CHO), 9.60 (s, 2H, -CONH-Ar), 8.40 (s, 2H, -CONH-Ar), 6.95 (s, 2H, ArH), 6.89 (d, J = 8.1 Hz, 2H, ArH), 6.74 (d, J = 8.1 Hz, 2H, ArH), 6.64 (d, J = 8.5 Hz, 4H, ArH), 6.58 (d, J = 8.4 Hz, 4H, ArH), 4.30-4.20 (m, 8H, -OCH₂ crown ether), 4.00-3.91 (m, 8H, -OCH₂ crown ether); EIMS m/z (relative intensity) 685 (M⁺1, 100), 320 (57).

2.3.3.3 Dibenzo[18]crown-6 fullerobis(pyrrolidine) conjugate DBCFPY: A mixture of dialdehyde CEA (151 mg, 0.22 mmol), N-methylglycine (40.2 mg, 0.44 mmol), C₆₀ (120 mg, 0.17 mmol) was refluxed in dry toluene in inert atmosphere for 6 h. After cooling to room temperature, the brown mixture was purified by column chromatography (silica gel) set up with a gradient of toluene to toluene / ethyl acetate (20:1) as eluant. Adduct DBCFPY, a brown solid, was dried under vacuum and characterized by elemental analysis and spectroscopic methods (Scheme 3). 114mg, 33%; mp 228 °C (dec); Anal. Calcd. for C₁₀₀H₄₆O₈N₆ : C, 82.30; H, 3.15; N, 5.76% Found: C, 82.40; H, 3.19; N, 5.21%; IR (KBr) ν (cm⁻¹) 526 (C₆₀), 1429 (C₆₀), 1634 (urea CO stretching), 1134 (crown C-O-C stretching), 1268 (crown Ar-O-C stretching), 3250 (urea NH stretching); ¹H NMR (400 MHz, CDCl₃, Me₄Si, 298 K) δ (ppm) 8.65 (s, 2H, NH of urea on crown ether...
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side ), 8.35 (s, 2H, NH of urea on fullerene side), 6.97 (s, 2H, Ar-H), 6.88 (d, J = 8.3 Hz, 2H, ArH), 6.75 (d, J = 8.4 Hz, 2H, ArH), 6.66 (d, J = 8.2 Hz, 4H, ArH), 6.59 (d, J = 8.3 Hz, 4H, ArH), 5.25(d, J =9.3 Hz, 2H, HHC-N- ), 4.90 (s, 2H, HC-N- ), 4.45 (d, J = 9.3 Hz, 2H, HHC-N- ), 4.12-3.70 (m, 16H, OCH$_2$ of crown ether), 3.18 (6H, s, N-CH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$, Me$_4$Si, 298 K) δ (ppm) [unassigned values refers to sp$^2$ C of C$_{60}$] 154.7(C of Urea group), 154.1, 153.5, 151.4, 150.8, 150.5, 149.5, 149.1, 148.9, 148 2, 147.5, 147.3, 146.2, 145.9, 145.7 , 145.6, 145.3, 144.6, 144.0(Ar-Cq), 142.9, 142.1, 141.8, 141.7, 141.3, 140.6, 140.1(Ar-Cq), 139.4, 138.9, 138.7(Ar-Cq), 136.4, 135.8, 135.7, 132.8(Ar-Cq), 130.5(Ar-Cq), 127.8(Ar-CH), 120.3(Ar-CH), 114.5(Ar-CH) , 112(Ar-CH), 106(Ar-CH), 83.3 (NCH of the pyrrolidine ring), 75.0(sp$^3$ C– of C$_{60}$), 73.0(crown ether-C), 72.4(crown ether-C), 71.0(crown ether-C), 70.5(crown ether-C), 69.2(NCH$_2$ of pyrrolidine ringga), 68.3(sp$^3$ C– of C$_{60}$), 40.3(CH$_3$ linked to N of the pyrrolidine ring); FABMS m/z (relative intensity) 1458(M+, 59), 1459 (M+1, 8), 1016(20), 834(27), 806(23), 720 (C$_{60}$, 100), 320(44).

In this case also eight regioisomers were possible. The desired trans-1 isomer was isolated from other regioisomers by column chromatography, since trans-1 isomer was having higher R$_f$ value as compared to others. One possible reason for higher R$_f$ value of trans-1 isomer could be the lower dipole moment brought about by the symmetrical structure of the molecule. Trans-1 geometry of the synthesized compound was supported by the fact that only two signals were obtained in $^1$H NMR spectra for the urea protons indicating C$_2$ symmetry in the molecule. Moreover, the chemical shift values at δ 5.25 and 4.45 as doublets (J=9.3 Hz) for CH$_2$ and at δ 2.85 corresponding to –NCH$_3$ protons of the pyrrolidine ring clearly supports the trans-1 geometry of the synthesized molecule.
$^{13}$C NMR showed only 28 signals corresponding to sp$^2$ C's of fullerene cage which is also an indication of the symmetrical *trans*-1 geometry. *Trans*-1 geometry of the synthesized molecule was more or less confirmed by comparing its UV-vis spectra in the 400-700 nm region with the previously reported Binger$^{23}$ as well as Prato bisadducts$^{24}$ (See Figure 6). Moreover its spectral properties were similar to the *trans*-1 fullerene dibenzo-18 crown-6 conjugate reported by Echegoyen et.al.$^{25}$

![Figure 6. UV-vis spectra of binger bisadduct *trans*-1 C$_{62}$ (CO$_2$Et)$_4$ and synthesized compound DBCFPY in CHCl$_3$.](image)

*Figure 6. UV-vis spectra of binger bisadduct *trans*-1 C$_{62}$ (CO$_2$Et)$_4$ and synthesized compound DBCFPY in CHCl$_3$.***
2.3.4 Fullerene – s-triazine conjugates

Scheme 4

\[
\begin{align*}
\text{substituted s-triazines} & \quad \text{Terephthalaldehyde} \\
\text{STR1 - STR5} & \quad \text{EtOH, reflux} \\
& \quad \text{glac acetic acid} \\
& \quad \text{s-triazine hydrazones} \\
& \quad \text{STH1 - STH5} \\
& \quad C_{60}, \text{sarcosine} \\
& \quad \text{toluene, reflux} \\
\text{HCl, CH}_3\text{OH, 0 °C} & \quad \text{s-triazine derivatized fulleropyrrolidine} \\
& \quad \text{STFPY1 - STFPY5}
\end{align*}
\]
SYNTHETIC PROCEDURE AND CHARACTERIZATION DATA

General procedure for synthesis of 2, 4, 6 trisubstituted 1, 3, 5 s-triazines (STR1-STR5)

2, 4, 6 trisubstituted 1, 3, 5 s-triazine derivatives were synthesized by reported procedure.26-28

2.3.4.1 Synthesis of Schiff bases (STH1-STH5)

To an ethanolic solution of terephthaldehyde (2.68 g, 0.02 mol) was added 3-4 ml of glacial acetic acid. This mixture was refluxed for a while and in the mean time STR1 (2.82 g, 0.02 mol) was added portion wise slowly for a period of half an hour. The yellow product obtained was isolated and purified by column chromatography (toluene/methanol 9:1). The solvent was then distilled out to get STH1. Similarly STH2 – STH5 was synthesized by following the above procedure (Scheme 4).

CHARACTERIZATION DATA

STH1 (2-(4,6 diamino-1,3,5-triazin-2-yl) hydrazinylidene) methyl benzaldehyde

mp 148 °C; Anal. Caled. for C_{11}N_{7}H_{11}O: C- 51.4, H- 4.3, N- 38.1% Found (C- 51.2, H-4.4, N- 38.2 %; IR (KBr) v (cm^{-1}) 3520(N-H), 3240(N-H), 3090(Ar-H), 1695 (CHO), 1595 (C=N); ^{1}H NMR (400 MHz, DMSO-d_{6}, Me_{4}Si, 298 K) δ (ppm) 10.95 (s, 1H, NH), 9.87 (s, 1H, CHO), 8.20 (s, 1H, CH=N), 7.80 (d, J= 8.32, 2H, Ar-H), 7.40 (d, J= 8.32, 2H, Ar-H), 6.50 (s, 4H, -NH_{2}); EIMS m/z (relative intensity) 257 (M+, 68).

STH2 (2-(4-amino-6-(methylamino)-1,3,5-triazin-2-yl) hydrazinylidene)methyl benzaldehyde

mp 151 °C; Anal. Caled. for C_{12}N_{9}H_{13}O: C- 53.1, H- 4.8, N- 36.2% Found (C- 53.2, H-4.6, N- 36.4%; IR (KBr) v (cm^{-1}) 3525 (N-H), 3245(N-H), 3090(Ar-H), 1695 (CHO),
1595 (C=N); \( ^1H \) NMR (400 MHz, DMSO-\( d_6 \), Me\( _4 \)Si, 298 K) \( \delta \) (ppm) 11.10 (s, 1H, NH), 9.86 (s, 1H, CHO), 8.21 (s, 1H, CH=N), 7.80 (d, \( J=8.30 \), 2H, Ar-H), 7.40 (d, \( J=8.30 \), 2H, Ar-H), 6.77 (s, 1H, NH-), 6.58 (s, 2H, NH\( _2 \)), 2.98 (s, 3H, CH\( _3 \)); EIMS m/z (relative intensity) 271 (M+, 66)

**STH3** (2-(4', -6-bis (methylamino) - 1,3,5 - triazin-2-yl) hydrazinylidene) methyl benzaldehyde

mp 158 °C; Anal. Calcd. for C\(_{13}\)N\(_7\)H\(_{15}\)O: C- 53.6, H- 5.2, N- 34.4% Found C- 53.5, H-5.2, N- 34.4%; IR (KBr) v (cm \(^{-1}\)) 3245(N-H), 3090(Ar-H), 1695 (CHO), 1595 (C=N); \( ^1H \) NMR (400 MHz, DMSO-\( d_6 \), Me\( _4 \)Si, 298 K) \( \delta \) (ppm) 11.15 (s, 1H, NH), 9.86 (s, 1H, CHO), 8.20 (s, 1H, CH=N), 7.85 (d, \( J=8.30 \), 2H, Ar-H), 7.42 (d, \( J=8.30 \), 2H, Ar-H), 6.78 (s, 2H, NH), 3.00 (s, 6H, CH\( _3 \)); EIMS m/z (relative intensity) 285 (M+, 70)

**STH4** 2-(4-dimethyamino)-6-(methylamino) - 1,3,5 - triazin-2-yl) hydrazinylidene)methyl benzaldehyde

mp 160 °C; Anal. Calcd. for C\(_{14}\)N\(_7\)H\(_{17}\)O (C- 56.1%, H- 5.6%, N- 32.8%) Found (C-56.0%, H- 5.6%, N- 32.7%); IR (KBr) v (cm \(^{-1}\)) 3245(N-H), 3090(Ar-H), 1695 (CHO), 1595 (C=N); \( ^1H \) NMR (400 MHz, DMSO-\( d_6 \), Me\( _4 \)Si, 298 K) \( \delta \) (ppm) 11.18 (s, 1H, NH), 9.85 (s, 1H, CHO), 8.22 (s, 1H, CH=N), 7.90 (d, \( J=8.34 \), 2H, Ar-H), 7.46 (d, \( J=8.34 \), 2H, Ar-H), 6.79 (s, 1H, NH), 3.05 (s, 3H, CH\( _3 \), 3.11 (s, 6H, CH\( _3 \)); EIMS m/z (relative intensity) 299 (M+, 58)
**STH5** (2-(4, -6-bis (dimethylamino) – 1,3,5 – triazin-2-yl) hydrazinylidene) methyl benzaldehyde

mp 161 °C; Anal. Calcd. for C_{15}N_{7}H_{19}O (C- 57.5%, H- 6.0%, N- 31.3%) Found (C- 57.4%, H- 6.0%, N- 31.4%); IR (KBr) ν (cm⁻¹) 3090(Ar-H), 1695 (CHO), 1595 (C=N);

\(^1\)H NMR (400 MHz, DMSO-d\(_6\), Me₄Si, 298 K) δ (ppm) 11.20 (s, 1H, NH), 9.87 (s, 1H, CHO), 8.25 (s, 1H, CH=N), 7.92 (d, J= 8.33, 2H, Ar-H), 7.46 (d, J= 8.33, 2H, Ar-H), 3.13 (s, 12H, CH₃);

EIMS m/z (relative intensity) 313 (M⁺, 58)

**2.3.4.2 Synthesis of s-triazine derivatized fulleropyrrolidines (STFPY1-STFPY6)**

Schiff base **STH1** (25.7 mg, 0.1 mmol), N-methylglycine (9 mg, 0.1 mmol) and C\(_{60}\) (72 mg, 0.1 mmol) were refluxed in dry toluene in inert atmosphere for 6 h. The product was purified by column chromatography (toluene / ethyl acetate 9:1) to get pure product **STFPY1**. In a similar way all other products (**STFPY2- STFPY5**) were obtained by the above procedure (Scheme 4).

**STFPY6** was prepared stirring a mixture of **STFPY1** and excess of dil. HCl in methanol at 0 °C for 3 h. The resulting solution was filtered and **STFPY1** was obtained as light brown solid product.

**CHARACTERIZATION DATA**

**STFPY1**

mp > 250 °C; Anal. Calcd. for C\(_{73}\)N\(_8\)H\(_{16}\) (C- 87.3%, H- 1.6%, N- 11.2%) Found (C- 87.2%, H- 1.6%, N- 11.2%); IR (KBr) ν (cm⁻¹) 3520 (N-H), 3240 (N-H), 3090(Ar-H), 1595 (C=N); \(^1\)H NMR (400 MHz, DMSO-d\(_6\), Me₄Si, 298 K) δ (ppm) 10.99 (s, 1H, NH),
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8.23 (s, 1H, CH=N), 7.82 (d, $J=8.32$, 2H, Ar-H), 7.43 (d, $J=8.32$, 2H, Ar-H), 6.51 (s, 4H, -NH$_2$), 5.20 (d, 1H, $J=9.3$, HHC-N of the pyrrolidine ring), 4.31 (s, 1H, CH of the pyrrolidine ring), 4.10 (d, 1H, $J=9.3$, HHC-N of the pyrrolidine ring), 2.80 (s, 3H, CH$_3$ linked to N of pyrrolidine ring); $^{13}$C NMR (125 MHz, DMSO-d$_6$, Me$_4$Si, 298 K) δ (ppm) 180.8, 176.1, 166.5, 164.9, 164.2, 163.8, 156.6, 155.8, 154.9, 154.1, 152.9, 151.6, 150.8, 147.3, 146.2, 146.0, 144.4, 143.5, 143.0, 142.7, 142.5, 142.4, 142.8, 142.0, 141.8, 141.5, 140.2, 139.9, 139.4, 136.9, 136.6, 136.4, 135.9, 135.6, 132.6, 132.3, 131.1, 130.6, 129.9, 129.5, 129.1, 128.3, 127.7, 127.2, 122.6, 121.2, 120.3, 118.9, 114.6, 114.4, 111.0, 82.0, 73.50(sp$^3$ C− of C$_{60}$), 72.7, 72.4, 68.6 (sp$^3$ C− of C$_{60}$), 33.3; FAB-MS m/z (relative intensity) 1004 (M+, 58)

**STFPY2**

mp > 250 °C; Anal. Caled. for C$_{74}$N$_8$H$_{18}$ (C- 87.3%, H- 1.6%, N- 11.2%) Found (C- 87.2%, H- 1.6%, N- 11.2%); IR (KBr) ν (cm$^{-1}$) 3520(N-H), 3240(N-H), 3090(Ar-H), 1595 (C=N); $^1$H NMR (400 MHz, DMSO-d$_6$, Me$_4$Si, 298 K) δ (ppm) 11.12 (s, 1H, NH), 8.24 (s, 1H, CH=N), 7.85 (d, $J=8.33$, 2H, Ar-H), 7.44 (d, $J=8.33$, 2H, Ar-H), 6.80 (s, 1H, NH), 6.60 (s, 2H, -NH$_2$), 5.21 (d, 1H, $J=9.3$, HHC-N of the pyrrolidine ring), 4.35 (s, 1H, CH of the pyrrolidine ring), 4.11 (d, $J=9.3$, HHC-N of the pyrrolidine ring), 3.00 (s, 3H, CH$_3$), 2.80 (s, 3H, CH$_3$ linked to N of pyrrolidine ring); $^{13}$C NMR (125 MHz, DMSO-d$_6$, Me$_4$Si, 298 K) δ (ppm) 180.8, 176.0, 166.6, 164.9, 164.0, 163.6, 156.3, 155.9, 154.7, 154.0, 152.9, 151.6, 150.5, 147.3, 146.2, 146.0, 144.4, 143.1, 143.0, 142.7, 142.5, 142.4, 142.1, 142.0, 141.8, 141.5, 140.2, 139.9, 139.4, 136.9, 136.7, 136.4, 135.9, 135.6, 132.6, 132.3, 131.1, 130.6, 129.9, 129.5, 129.1, 128.3, 127.7, 127.0,

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122.6, 121.2, 120.3, 118.9, 114.6, 114.4, 111.0, 82.0, 73.2 (sp³ C– of C₆₀), 72.7, 72.4, 68.3 (sp³ C– of C₆₀), 33.3; FAB-MS m/z (relative intensity) 1018 (M+, 42)

**STFPY3**

mp > 250 °C; Anal. Caled. for C₇₅N₈H₂₀ (C- 87.3%, H- 1.6%, N- 11.2%) Found (C- 87.2%, H- 1.6%, N- 11.2%); IR (KBr) ν (cm⁻¹) 3520(N-H), 3240(N-H), 3090(Ar-H), 1595 (C=N); ¹H NMR (400 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) 11.20 (s, 1H, NH), 8.25 (s, 1H, CH=N), 7.88 (d, J= 8.34, 2H, Ar-H), 7.45 (d, J= 8.34, 2H, Ar-H), 6.80 (s, 2H, NH), 5.23 (d,1H, J=9.3, HHC-N of the pyrrolidine ring) 4.37 (s, 1H, CH of the pyrrolidine ring), 4.15 (d, 1H, J=9.3, HHC-N of the pyrrolidine ring), 3.03 (s, 6H, CH₃), 2.81 (s, 3H, CH₃ linked to N of pyrrolidine ring); ¹³C NMR (125 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) 181.0, 176.2, 166.5, 164.8, 164.0, 163.6, 156.2, 155.9, 154.7, 154.0, 152.9, 151.6, 150.5, 147.3, 146.2, 146.0, 144.4, 143.1, 143.0, 142.7, 142.5, 142.4, 142.1, 142.0, 141.8, 141.5, 140.2, 139.9, 139.4, 136.9, 136.7, 136.4, 135.9, 135.6, 132.6, 132.3, 131.1, 130.6, 129.9, 129.5, 129.1, 128.3, 127.7, 127.0, 122.6, 121.2, 120.3, 118.9, 114.6, 114.4, 111.0, 82.0, 73.1 (sp³ C– of C₆₀), 72.7, 72.4, 68.0 (sp³ C– of C₆₀), 33.3; FAB-MS m/z (relative intensity) 1032 (M+, 45)

**STFPY4**

mp > 250 °C; Anal. Caled. C₇₆N₈H₂₂ (C- 87.3%, H- 1.6%, N- 11.2%) Found (C- 87.2%, H- 1.6%, N- 11.2%), IR (KBr) ν (cm⁻¹) 3520(N-H), 3240(N-H), 3090(Ar-H), 1595 (C=N); ¹H NMR (400 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) 11.18 (s, 1H, NH), 8.25
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(s, 1H, CH=N), 7.95 (d, J= 8.33, 2H, Ar-H), 7.48 (d , J= 8.33 , 2H , Ar-H), 6.80 (s, 1H, NH), 5.24 (d, 1H, J=9.3, HHC-N of the pyrrolidine ring), 4.38 (s, 1H, CH of the pyrrolidine ring), 4.17 (d, 1H, J=9.3, HHC-N of the pyrrolidine ring), 3.12 (s, 6H, CH₃), 3.05 (s, 3H, CH₃), 2.82 (s, 3H , CH₃ linked to N of pyrrolidine ring); ¹³C NMR(125 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) 180.8 , 176.0 , 166.5 , 164.8 , 164.0 , 163.6 , 156.2 , 155.9 , 154.7 , 154.0 , 152.9 , 151.6 , 150.5 , 147.3 , 146.2 , 146.0 , 144.4 , 143.1 , 143.0 , 142.7 , 142.5 , 142.4 , 142.1 , 142.0 , 141.8 , 141.5 , 140.2 , 139.9 , 139.4 , 136.9 , 136.7 , 136.4 , 135.9 , 135.6 , 132.6 , 132.3 , 131.1 , 130.6 , 129.9 , 129.5 , 129.1 , 128.3 , 127.7 , 127.0 , 122.6 , 121.2 , 120.3 ,118.9, 114.6, 114.4, 111.0, 82.0, 73.0 ( sp³ C- of C₆₀), 72.7, 72.4, 68.0 ( sp³ C- of C₆₀) , 33.3; FAB-MS m/z (relative intensity) 1046 (M+, 50)

STFPYS

mp > 250 °C; Anal. Calcd. for C₇₇N₈H₂₄ C- 87.3, H- 1.6, N- 11.2% Found C- 87.2, H- 1.6, N- 11.2%; IR (KBr) ν (cm⁻¹) 3520(N-H), 3240(N-H), 3090(Ar-H), 1595 (C=N); ¹H NMR (400 MHz, DMSO-d₆ Me₄Si, 298 K) δ (ppm) 11.20 (s, 1H, NH), 8.27 (s, 1H, CH=N), 7.94 (d, J= 8.35, 2H, Ar-H), 7.47 (d, J= 8.35, 2H, Ar-H), 5.25(d,1H, J=9.3, HHC-N of the pyrrolidine ring), 4.39 (s, 1H, CH of the pyrrolidine ring), 4.19 (d,1H, J=9.3, HHC-N of the pyrrolidine ring), 3.13 (s, 12H, CH₃), 2.83 (s, 3H, CH₃ linked to N of pyrrolidine ring); ¹³C NMR (125 MHz, DMSO-d₆ Me₄Si, 298 K) δ (ppm) 180.8, 176.0, 166.5, 164.8 164.0, 163.6, 155.9, 154.7, 154.0, 152.9, 151.6, 150.5, 147.3, 146.2, 146.0, 144.4, 143.1, 143.0, 142.7, 142.5, 142.4, 142.1, 142.0, 141.8, 141.5, 140.2, 139.9, 139.4, 136.9, 136.7, 136.4, 135.9, 135.6, 132.6, 132.3, 131.1, 130.6, 129.9, 129.5, 129.1, 128.3, 127.7, 127.0, 122.6, 121.2, 120.3 ,118.9, 114.6, 114.4, 111.0, 82.0, 72.9
(sp\(^3\) C – of C\(_{60}\)), 72.7, 72.4, 67.9 (sp\(^3\) C – of C\(_{60}\)), 33.3; FAB-MS m/z (relative intensity) 1060 (M+, 48)

**STFPY6**

mp > 250 °C; Anal. Calcd. for C\(_{73}N_8H_{18}Cl_2\) C - 81.3; H- 1.6; N- 10.4 % Found C- 81.2; H- 1.6; N- 10.3 %; IR (KBr) v (cm\(^{-1}\)) 3526 (N-H), 3245 (N-H), 3095 (Ar-H), 1600 (C=N); \(^1\)H NMR (400 MHz, DMSO-d\(_6\), Me\(_4\)Si, 298 K) δ (ppm) 11.27 (s, 1H, NH), 8.30 (s, 1H, CH=N), 8.10 (s, 6H, NH\(_3^+\)), 7.96 (d, J = 8.35, 2H, Ar-H), 7.48 (d, J = 8.35, 2H, Ar-H), 5.26 (d, 1H, J = 9.3, HHC-N of the pyrrolidine ring), 4.40 (s, 1H, CH of the pyrrolidine ring), 4.19 (d, 1H, J = 9.3, HHC-N of the pyrrolidine ring), 2.83 (s, 3H, CH\(_3\) linked to N of pyrrolidine ring); \(^13\)C NMR (125 MHz, DMSO-d\(_6\), Me\(_4\)Si, 298 K) δ (ppm) 180.9, 176.9, 166.7, 164.9 164.0, 163.8, 156.9, 154.7, 154.4, 152.9, 151.6, 150.5 , 147.6 , 146.3, 146.1, 144.4, 143.1, 143.0 , 142.8, 142.5 , 142.4, 142.1, 142.0, 141.9, 141.5, 140.8, 139.9, 139.4, 136.9, 136.7, 136.4, 135.9, 135.6, 132.6, 132.3, 131.1, 130.6, 129.9, 129.5, 129.1, 128.3, 127.7, 127.0, 122.6, 121.2, 120.3, 118.9, 114.6, 114.6, 114.6, 111.3, 82.6, 73.1 (sp\(^3\) C – of C\(_{60}\)), 72.8, 72.5, 68.2 (sp\(^3\) C – of C\(_{60}\)), 33.6; FAB-MS m/z (relative intensity) 1006 ((M-2Cl)^+, 48)
2.3.5 Fullerene – Isoniazid conjugate

Scheme 5

SYNTHETIC PROCEDURE AND CHARACTERIZATION DATA

2.3.5.1 Isonicotinic acid (4-[1,3]dioxolan-2-yl-benzylidene) hydrazide: A mixture of 1.79 g (0.01 mol) of 4- (1, 3) dioxolan-2-yl-benzaldehyde, 2 ml of glacial acetic acid, 1.37 g (0.01 mol) of isoniazid dissolved in 50 ml of ethanol was refluxed for about half an hour. Product was isolated and purified by using column chromatography using hexane/ethyl acetate (20:1) as the eluant. The solvent was then distilled under vacuum to get bright yellow product (Scheme 5), 1.64 g, 55%, mp. 113 °C (dec.); Anal. Calcd. for C_{16}H_{15}N_{3}O_{3} C-64.6, H- 5.0, N-14.1 % Found C-66.5, H-4.3, N-16 %; IR (KBr) ν (cm^{-1}) 1685 (-C=O), 3213(-NH-), 1597(CH=N); ^1H NMR (400 MHz, DMSO-d$_6$, Me$_4$Si, 298 K)
δ (ppm) 9.01 (1H, s, -NH ), 8.14 (1H, s, CH=N), 7.93 (2H, d, J=8.5 Hz, H of pyridyl ring), 7.75 (2H, d, J=8.5 Hz, H of pyridyl ring), 7.36 (2H, d, J=8.0 Hz, H of phenyl ring), 7.10 (2H, d, J=8.0 Hz, H of phenyl ring ), 5.90(s, 1H, O-CH2-O), 4.31 (s, 4H, -OCH2-CH2O-); EIMS m/z (relative intensity) 297 (M+, 87)

2.3.5.2 *Isonicotinic acid (4 formyl-benzylidene) -hydrazide*: Isonicotinic acid (4-[1,3]dioxolan-2yl-benzylidene) hydrazide 2.97 g (0.01 mol) was mixed with a solution of 3 ml perchloric acid in 50 ml 1, 4 dioxane. The mixture was stirred at room temperature for 12 h. The solution was diluted with chloroform (30 ml) and washed with a saturated solution of sodium bicarbonate. The organic layer was separated and dried over Na2SO4. The solvent was removed *in vacuo* and the yellow solid residue was subjected to column chromatography [toluene/methanol (5:1)] to get *isonicotinic acid (4 formyl-benzylidene) -hydrazide* as light yellow solid product (Scheme 5). 1.4 g, 45%; mp. 146 °C (dec.); Anal. Calcd. for C14H11N3O2 C-66.4 , H-4.3 , N-16, O-12.6%, Found C-66.5 , H-4.3 , N-16, O-12.5%; IR (KBr) ν (cm⁻¹) 1687 (-C=O ), 3210(-NH-), 1607(CH=N), 1700(Ar-CHO); ¹H NMR (400 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) 9.82 (1H, s, -CHO ), 9.11 (1H, s, -NH ), 8.24 (1H, s, CH=N), 7.63 (2H, d, J=8.5 Hz, H of pyridyl ring), 7.51 (2H, d, J=8.5 Hz, H of pyridyl ring), 7.35 (2H, d, J=8.0 Hz, H of phenyl ring ), 7.10 (2H, d, J=8.0 Hz , H of phenyl ring ), EIMS m/z (relative intensity) 253 (M+, 78)

2.3.5.3 *Fullerene-Isoniazid conjugate INHFYPY*: A mixture of C₆₀ (100 mg, 0.14 mmol), isonicotinic acid (4 formyl-benzylidene) –hydrazide (25 mg, 0.1mmol), N-methylglycine (3.7 mg, 0.42 mmol) was refluxed in dry toluene for about 2 hours. After cooling the reaction mixture to room temperature the brown mixture was purified using column chromatography [toluene and then toluene/ethyl acetate (10:1)]. The solvent was
then distilled under vacuum to get pure product INHFPY (Scheme 5), 45 mg, 33%; mp. >250 °C; Anal. Calcd. for C_{76}H_{66}N_{40} C- 91.2, H-1.6, N-5.6, O-1.6%, Found C- 91.0, H-1.8, N-5.7, O-1.6; FT-IR (KBr) ν (cm\(^{-1}\)) 3213(-NH-), 1685 (-C=O), 1597(C=NH), 1429(C60), 529(C60); \(^1\)H NMR (400 MHz, CDCl\(_3\), Me\(_4\)Si, 298 K) δ (ppm) 9.00 (1H, s, -NH), 8.20 (1H, s, CH=NC), 8.05 (d, J = 8.5 Hz, 2 H, H of the pyridyl ring), 7.83 (d, J = 8.5 Hz, 2H, H of the pyridyl ring), 7.45 (d, J = 8.0 Hz, 2H, H of phenyl ring), 7.14 (d, J = 8.0 Hz, 2H, H of phenyl ring), 5.25 (d, J = 9.6 Hz, 1H, HCH-N-), 5.19 (s, 1H, HCN-), 4.60 (d, J = 9.3 Hz, 1H, HCH-N-), 2.80 (s, 3H, N-CH\(_3\) of Pyrrol.); \(^{13}\)C NMR (δ, 125 MHz, CDCl\(_3\), Me\(_4\)Si) δ (ppm) [unassigned values refers to sp\(^2\) C of C\(_{60}\)] 163.0(CONH), 154.1, 153.8, 153.5, 149.0, 148.9, 148.2, 147.5, 147.3, 147.0, 146.8, 146.7, 146.6, 146.5, 146.4, 146.3, 146.2, 145.8, 145.7, 145.6, 145.4, 145.3, 145.2, 145.1, 145.0, 144.6, 144.5, 142.9, 142.8, 142.7, 142.6, 142.5, 142.4, 142.1, 142.0, 141.3, 140.6, 140.4, 140.3, 140.0, 139.4, 139.0, 136.5, 136.4, 135.8, 135.7(C\(_{60}\)-Cq, Ar-Cq, pyridyl-Cq), 134.0(Ar-Cq), 127.8(pyridyl-CH), 120.3(pyridyl-CH), 114.5(Ar-CH), 112(Ar-CH), 83.3 (NCH of the pyrrolidine ring), 75.0(sp\(^3\) C- of C\(_{60}\)), 69.2(NCH\(_2\) of pyrrolidine ring), 68.3(sp\(^3\) C- of C\(_{60}\)), 40.3(CH\(_3\) linked to N of the pyrrolidine ring); MALDI-TOF MS m/z (relative intensity) 1001.0(M+1, 13), 1000.0 (M+, 52), 906.1(3-C\(_5\)H\(_4\)NCO,10), 720.0 (C\(_{60}\), 100)
2.3.6 Lysine derivatized Fulleropyrrolidine

Scheme 6

\[
\begin{align*}
\text{HNBOc-(CH}_2\text{)}_4\text{-NH}_2 + \text{CHO} & \xrightarrow{\text{AcOH, MeOH, reflux, 1h}} \text{HNBOc-(CH}_2\text{)}_4\text{-N} & \xrightarrow{\text{CHO}} \\
\text{Boc protected lysine} & & \text{Terephthalaldehyde} & & \text{Boc-lysine hydrazone BLH} \\
\end{align*}
\]

\[
\begin{align*}
\text{NH(CH}_2\text{)}_4\text{-N} & \xrightarrow{\text{TFA, PhMe, rt, 12 h}} \\
\text{HNBOc-(CH}_2\text{)}_4\text{-N} & \xrightarrow{\text{CHO}} \\
\text{lysine derivatized fulleropyrrolidine} & & \text{Boc-lysine derivatized fulleropyrrolidine} \\
\text{LFPY} & & \text{BLFPY} \\
\end{align*}
\]

SYNTHETIC PROCEDURE AND CHARACTERIZATION DATA

2.3.6.1 Synthesis of BLH. A solution of Boc-lysine (2.13 g, 0.01 mol), terephthalaldehyde (1.34 g, 0.01 mol) and 4 ml of glacial acetic acid in methanol was heated under reflux for 3 hours. The solvent was distilled out under vacuo to get bright yellow product. The product mixture was subjected to column chromatography on silica gel (toluene/methanol 7:3) to afford compound BLH as pale yellow solid (Scheme 6). Yield 3.0g, 91.1 %; \textbf{mp.} 127 °C; \textbf{Anal. Calcd.} for \text{C}_{19}\text{O}_3\text{H}_{26}\text{N}_2 : \text{C}, 62.98; \text{H}, 7.18; \text{N},
7.73. **Found:** C, 62.90; H, 7.21; N, 7.70.; **IR (KBr) v (cm⁻¹)** 1600 (CH=N), 1659 (C=O stretching), 3257 (NH stretching); **¹HNMR** (400 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) 12.10 (s, 1H, -COOH), 9.89 (s, 1H, CHO), 8.50 (s, 1H, NH), 8.23 (s, 1H, CH=N), 7.46 (d, J = 8.0 Hz, 2H, ArH), 7.10 (d, J = 8.0 Hz, 2H, ArH), 3.9 (s, 1H, -CH-), 1.30-1.57 (m, 17H, -CH₂-, CH₃); **EI-MS m/z (%)** 362 (100) [M]+.

### 2.3.6.2 Synthesis of BLFPY

A mixture of C₆₀ (100 mg, 0.14 mmol), BLH (33 mg, 0.1 mmol), N-methylglycine (3.7 mg, 0.42 mmol) was refluxed in dry toluene for about 2 hours. After cooling the reaction mixture to room temperature the brown mixture was purified using column chromatography [toluene and then toluene/ethyl acetate 20:1]. The solvent was then distilled under vacuum to get pure product **BLFPY** (Scheme 6), 40 mg, 29%; **mp.** 263 °C; **Anal. Calcd. for C₈₁O₃H₃₁N₃:** C, 87.64; H, 2.81; N, 3.79. Found: C, 87.66; H, 2.81; N, 3.78; **IR(KBr) v (cm⁻¹)** 524 (C₆₀), 1610 (CH=N), 1662 (C=O stretching), 3255 (NH stretching); **¹HNMR** (400 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) 12.23 (s, 1H, -COOH), 8.29 (s, 1H, CH=N), 7.56 (d, J = 8.1 Hz, 2H, ArH), 7.15 (d, J = 8.1 Hz, 2H, ArH), 5.25 (d, J = 9.3 Hz, 1H, HHC-N-), 4.90 (s, 1H, HC-N-), 4.45 (d, J = 9.3 Hz, 1H, HHC-N-), 4.1 (s, 1H, -CH-), 2.98 (3H, s, N-CH₃), 1.40-1.85 (m, 17H, -CH₂-, CH₃); **FAB-MS m/z (relative intensity)** 1110 ([M]+), 100)

### 2.3.6.3 Synthesis of LFPY

The N-protected fulleropyrrolidine **BLFPY** (30 mg, 0.03 mmol) was dissolved in a 1:1 mixture of toluene/trifluoroacetic acid and stirred for 12h. The reaction was monitored by TLC (SiO₂; toluene/propanol, 9:1). After completion of the deprotection, the solvents were evaporated, and some MeOH was added and
evaporated again. The residue was taken up in CH₂Cl₂, and the solution added dropwise to excess hexane. The precipitated solid was separated by centrifugation, washed with a small amount of Et₂O, and then dried under high vacuum to obtain LFPY as brownish solid product. (Scheme 6). Yield 25 mg 83.3% mp. 251 °C; Anal. Calcd. for C₇₈O₄H₂₄N₃F₃: C, 83.35; H, 2.15; N, 3.74. Found: C, 83.26; H, 2.14; N, 3.76; IR(KBr) ν (cm⁻¹) 526 (C₆₀), 1600 (CH=N), 1659 (C=O stretching), 3257 (NH stretching), 3412 (NH stretching); ¹HNMR (400 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) 12.1(s, 1H, -COOH), 8.23 (s, 1H, CH=N), 7.80 (s, 3H, NH₃⁻), 7.57 (d, J = 8.0 Hz, 2H, ArH), 7.16(d, J = 8.0 Hz, 2H, ArH), 5.25(d, J = 9.3 Hz, 1H, H/HC-N⁻), 4.90 (s, 1H, HC-N⁻), 4.45 (d, J = 9.3 Hz, 1H, H/HC-N⁻), 4.1(s, 1H, -CH⁻), 2.82 (3H, s, N-CH₃), 1.50-1.97 (m, 8H, -CH₂); ¹³CNMR (125 MHz, DMSO-d₆, Me₄Si, 298 K) δ (ppm) [unassigned values refers to sp² C of C₆₀] 177.1(-COO), 164.3(CH=N), 154.2, 153.4, 151.6, 150.7, 150.5, 149.6, 149.2, 148.9, 148.3, 147.7, 147.4, 146.9, 146.2, 145.9, 145.8, 145.6, 145.4, 144.6, 143.2, 142.8, 142.2, 141.8, 141.7, 141.5, 140.7, 139.8(ArCq), 139.5, 138.9, 136.4, 135.9, 135.9, 130.1(ArCH), 129.8(ArCH), 83.5(NCH of the pyrrolidine ring), 75.2(sp³ C⁻ of C₆₀), 69.1(NCH₂ of pyrrolidine ring), 68.4(sp³ C⁻ of C₆₀), 67.9 (CH-COOH), 44.8(-CH₂), 40.3(CH₃ linked to N of the pyrrolidine ring), 31.5(-CH₂), 30.7(-CH₂), 22.5(-CH₂); FAB-MS m/z (relative intensity) 1011 ([M-CF₃COO]+, 100)
2.3.7 Pyridine functionalized methanofullerene

Scheme 7

SYNTHETIC PROCEDURE AND CHARACTERIZATION DATA

2.3.7.1 Synthesis of 3-(Pyridin-2-yliminomethyl)-phenol. A mixture of 2-aminopyridine (940 mg, 10 mmol), 3-hydroxy benzaldehyde (122 mg, 10 mmol) and 3 ml glacial acetic acid in ethanol was refluxed for about 2.5 h. The solvent was distilled out and the orange colored product was subjected to column chromatography using toluene/methanol (4:1) to get compound 3-(Pyridin-2-yliminomethyl)-phenol as bright yellow solid (Scheme 7). 1.4 g Yield 70.7 %; mp 124 °C; Anal. Calcd. for C_{12}H_{10}N_{2}O C, 72.72; H, 5.05; N,
2.3.7.2 Synthesis of Malonic acid bis-[3-(pyridin-2-yliminomethyl)-phenyl] ester.
Solution of 3-(Pyridin-2-yliminomethyl)-phenol (198 mg, 1 mmol) in a mixture of ethanol (25 ml) and DCM (20 ml) was cooled to 0 °C. After addition of DCC (408 mg, 2 mmol) and DMAP (244 mg, 2 mmol) to it the mixture was stirred at room temperature for 12 h. The solution was then washed with dilute HCl solution. The organic layer was separated and distilled out to get product malonic acid bis-[3-(pyridin-2-yliminomethyl)-phenyl] ester as light yellow solid (Scheme 7). 0.3 g Yield 64.6 %; mp 97 °C; Anal. Calcd. for C_{27}H_{20}N_{4}O_{4} C, 69.82; H, 4.31; N, 12.06 %. Found: C, 70.05; H, 4.21, N, 12.05 %; \textsuperscript{1}H NMR (400 MHz, DMSO-d_{6}, Me_{4}Si, 298 K) δ (ppm) 8.1 (s, 2H, CH=N), 7.4-7.7 (m, 8H, Py-H), 7.0-7.3 (m, 8H, ArH), 3.3 (s, 2H, -CH_{2}-); EI-MS m/z (relative intensity) 464.4 (M+, 87)

2.3.7.3 Synthesis of PYMF. A solution of C_{60} (72 mg, 0.1 mmol), DBU (1, 8 diazabicyclo [5.4.0] undec-7-ene) (50 mg), I_{2} (70 mg), malonic acid bis-[3-(pyridin-2-yliminomethyl)-phenyl] ester (46 mg, 0.1 mmol) in toluene was stirred at room temperature for 9 h. The brownish solution obtained was subjected to column chromatography to get PYMF as dark brown solid (Scheme 7). 39 mg Yield 33 %; mp > 250 °C; Anal. Calcd. for C_{57}H_{18}N_{4}O_{4} C, 88.25; H, 1.5 2, N, 4.73 %. Found: C, 88.65; H, 1.50; N, 4.33 %; \textsuperscript{1}H NMR (400 MHz, DMSO-d_{6}, Me_{4}Si, 298 K) δ (ppm) 8.2(s, 2H,
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CH=N), 7.7-7.9 (m, 8H, PyH), 7.2-7.5 (m, 8H, ArH); $^{13}$C NMR (125 MHz, DMSO-d$_6$, Me$_4$Si, 298 K) δ (ppm) 174.0, 168.2, 163.7, 153.2, 154.1, 153.5, 151.4, 150.8, 150.5, 149.5, 149.1, 148.9, 148.2, 147.5, 147.3, 146.2, 145.9, 145.7, 145.6, 145.3, 144.6, 142.9, 142.1, 141.8, 141.7, 141.3, 140.6, 139.4, 138.9, 136.4, 135.8, 135.7, 151.1, 137.0, 131.1, 129.0, 125.0, 123.9, 122.8, 117.1, 39.1; FAB-MS m/z (relative intensity) 1183.0 (M+, 50)
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References


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