An Efficient [2+3] Cycloaddition Approach to the Synthesis of Pyridyl-Appended Fullerene Ligands

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We have used 2-, 3-, and 4-picolylamines and their various *N*-substituted derivatives as substrates to generate azomethine ylides for [2+3] cycloaddition to [60]fullerene. A considerable difference in the reactivity of isomeric picolylamines was observed; however, even less reactive 3-picolylamines afford high yields of products under acid or base catalysis. This method provides easy access to a large family of valuable ligands (pyridyl-substituted pyrrolidinofullerenes) that can be used in the design of transition-metal complexes and non-covalently bonded dyads with metalloporphyrins. Unusually high yields of products and convenience of synthetic procedures (2–10 min heating the reagents at reflux in 1,2-dichlorobenzene in air in most cases) as well as a wide synthetic potential make this reaction a good alternative to the commonly used Prato method.

Introduction

Pristine fullerenes themselves and a variety of their derivatives exhibit a range of valuable properties and have therefore been utilized in the design of novel advanced materials.[1,2] Organic derivatization of fullerenes plays an important role in optimizing their properties, particularly in adjusting their electronic characteristics or enhancing thin film formation properties and increasing their solubility in organic solvents as well as in aqueous media.[2,3] A lot of methods have been developed to functionalize C_{60}, although only a few of them are convenient enough to be commonly used.[4] Among these, [2+3] cycloaddition of azomethine ylides can be considered as the most important reaction. In the typical procedure, an aldehyde bearing moieties to be attached to the fullerene cage is treated with *N*-methylglycine (sarcosine) and C_{60} under heating at reflux in toluene for several hours. In some cases, other *N*-substituted amino acids have been employed as substrates instead of sarcosine.[5] This method, called the Prato reaction, affords moderate yields of products (10–45%) and has some synthetic limitations. For example, it has almost never been applied for the synthesis of 2′,5′-disubstituted and 1′,2′,5′-trisubstituted pyrrolidinofullerenes since starting α-substituted amino acids other than natural ones are hardly available. Moreover, mixtures of *cis* and *trans* isomers of 2′,5′-disubstituted pyrrolidinofullerenes are almost always formed.[6]

Here were report a facile and stereoselective approach to the synthesis of various 2′,5′-disubstituted and 1′,2′,5′-trisubstituted pyrrolidinofullerenes that is based on the application of picolylamines instead of amino acids as substrates for the generation of azomethine ylides.

Results and Discussion

2-Picolylamine and *N*-Substituted 2-Picolylamines as Substrates

It has been reported previously that imines formed from 2-picolylamine and aldehydes can be tautomerized to azomethine ylides that readily undergo a [2+3] cycloaddition reaction with various dipolarophiles.[7] We found that this reaction can also be applied to [60]fullerene. According to the optimized procedure, heating C_{60}, 2-picolylamine, and an aldehyde in a 1:1.1:1.3 molar ratio at reflux in 1,2-dichlorobenzene (1,2-DCB) for 2–10 minutes in air resulted in 70–90% conversion of the fullerene. After cooling to room temperature, the reaction mixture was diluted with toluene and poured onto a silica gel column. Subsequent chromatographic separation resulted in the isolation of monoadducts **1**–**4** with 55–70% yields (Scheme 1). In some cases, fullerene conversion and product yields can be improved slightly by

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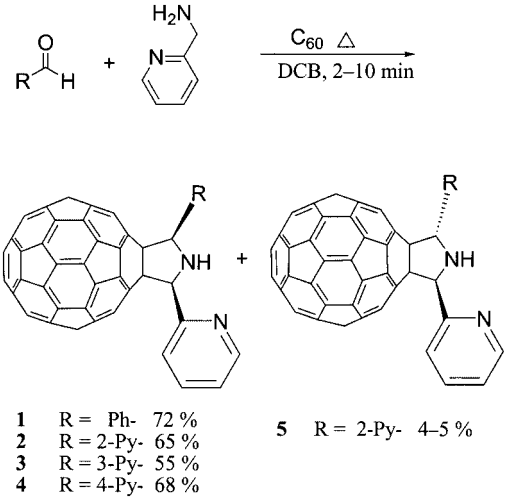


Scheme 1.

using the corresponding imine instead of a mixture of 2-picolylamine and aldehyde and by conducting the reaction under argon.

Both the ^{1}H and ^{13}C NMR spectra of isolated pyrrolidinofullerenes **1**–**4** show them to be individual stereoisomers with either a *cis* or a *trans* configuration of the substituents in the pyrrolidine ring. The *cis*-arrangement of the pyridyl groups in **2** was revealed by the X-ray single crystal structure of a 1:1 complex of **2** with ZnTPP (ZnTPP = *meso*-tetraphenylporphyrinatozinc) that was reported very recently.[8] A careful examination of the products formed in the reaction of 1.5 g of C_{60} with 2-picolylamine and 2-pyridinecarbaldehyde allowed us to isolate a small amount (45 mg vs. 960 mg of **2**) of the *trans*-isomer 2′,5′-di(2-pyridyl)pyrrolidino[3′,4′:1,2][60]fullerene (**5**) with a yield of about 4–5%. The yields of the *trans* isomers of pyrrolidinofullerenes **1**, **3**, and **4** were too low to permit their isolation

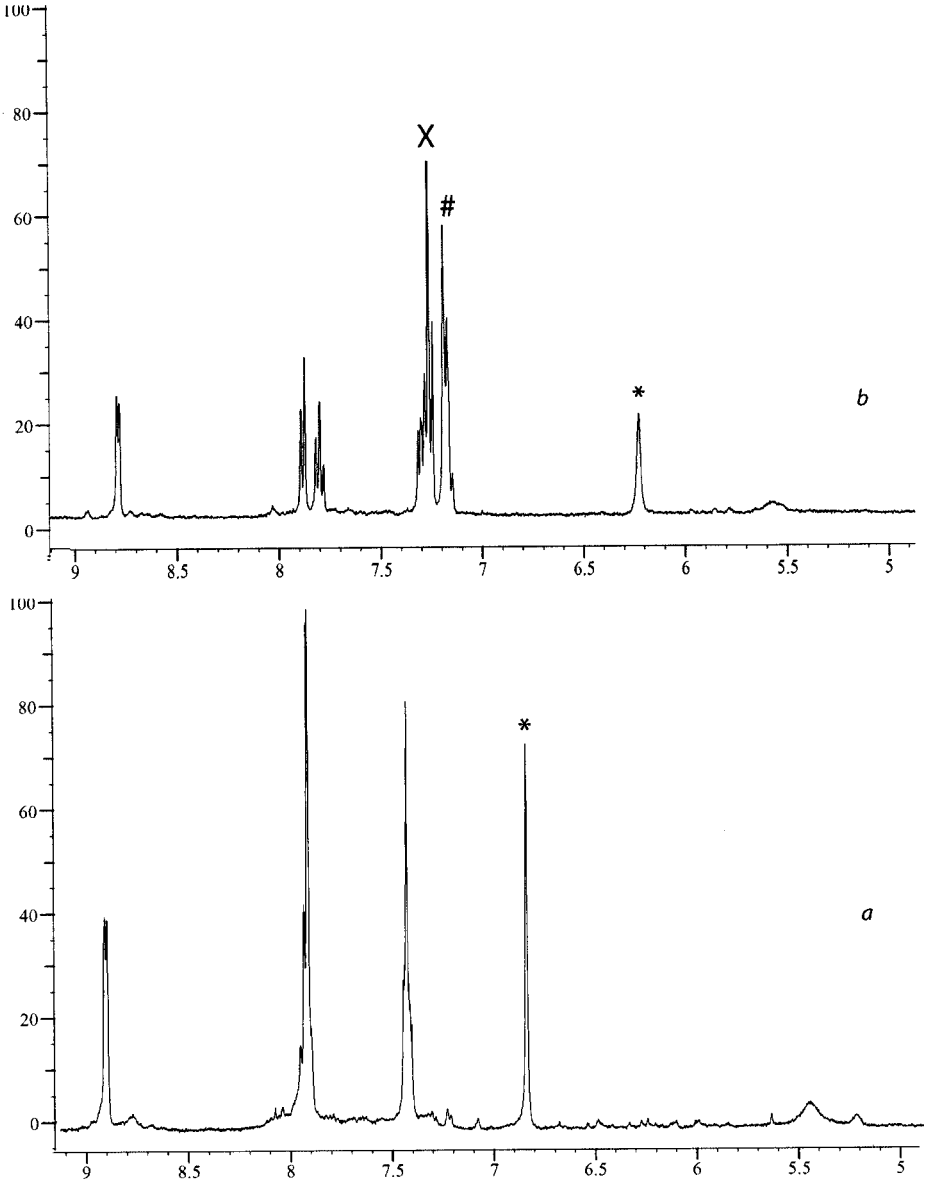


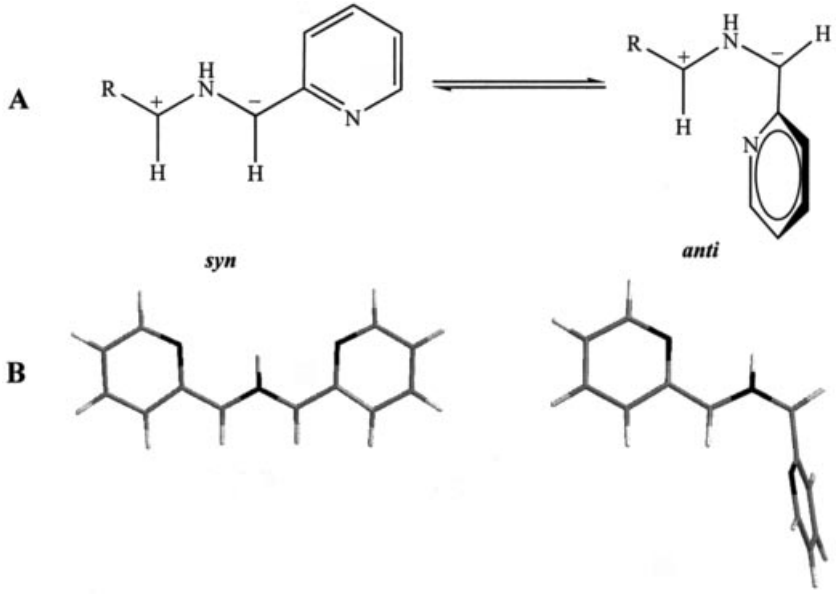
Figure 1. ^{1}H NMR spectra of **2** (a) and **5** (b). *: methine protons; x: signal of $CHCl_3$ in $CDCl_3$; #: aromatic protons of toluene (trapped in the lattice of solid **2**).

and spectroscopic characterization. The ^{1}H NMR spectrum of **5** was found to be quite different to the spectrum of **2** (Figure 1), most obviously with respect to the chemical shifts of the methine protons at the pyrrolidine ring. In the case of the *trans* isomer, the signal is shifted about 0.6 ppm to lower field than the *cis* isomer; a similar difference was reported previously for the *cis* and *trans* isomers of 3′,5′-di(2-methoxycarbonyl)pyrrolidinofullerene.[9] Thus, *cis* and *trans* isomers of 3′,5′-disubstituted pyrrolidinofullerenes can be distinguished by their ^{1}H NMR spectra; the *cis* arrangement of the substituents in **1**, **3**, and **4** was proved similarly.

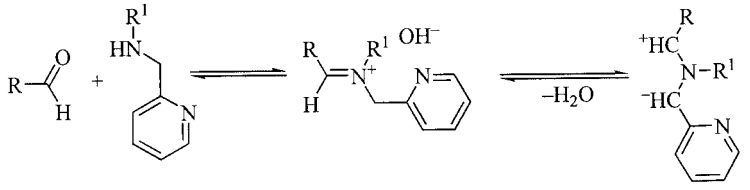
The most remarkable feature of this reaction is the high diastereoselectivity. The reasons for such stereoselectivity of [2+3] cycloaddition of azomethine ylides are not completely understood, even in the case of small organic molecules as substrates. It is known that ylides that possess a 2-pyridyl or carbonyl ylide stabilizing group can be stabilized in a *syn*-conformation (W-shaped, which yields the *cis* isomer of the cycloadduct) by a hydrogen bond formed between the NH group and the pyridyl nitrogen or C=O group.[10] The second factor that should be considered in the case of fullerene as a dipolarophile is steric hindrance at the cycloaddition stage. There is a bulky substituent at each side of the ylide in the *anti* conformation (S-shaped), and these substituents are sterically hindered and not coplanar with the nitrogen atom.[11] The out-of-plane groups hinder the approach of the ylide to the fullerene surface. In contrast, both substituents can be coplanar in the *syn* ylide and it can easily attack the fullerene cage in such a conformation (Scheme 2, A). This suggestion was supported by an AM1 energy calculation (heats of formation) performed for conformations of the azomethine ylide formed from 2-pyridinecarbaldehyde and 2-picolylamine. Indeed, the optimized *syn* conformation was planar and about 32 kJ more stable than the structure of the *anti* ylide with one out-of-plane pyridyl group (Scheme 2, B).

The importance of the steric hindrance of the substrates was also revealed from our observation that the treatment of fullerene with 2-picolylamine and ketones under continuous (18 h) heating at reflux in 1,2-dichlorobenzene either affords no cycloaddition products (heptadecylmethylketone) or gives pyrrolidinofullerenes with very low (acetone, 5–10%) yields (Scheme 2B). Conversion of the fullerene in these reactions is generally low (25–40%) and numerous unidentified products were isolated by column chromatography with yields much less than 1%. It is likely that trisubstituted ylides are less reactive towards fullerene as the extra substituent hinders the approach of the ylide to the fullerene surface. Ketones have rarely been used as substrates to generate azomethine ylides for [2+3] cycloaddition to [60]fullerene;[4] the low product yield (4%) obtained in the [2+3] cycloaddition of a trisubstituted azomethine ylide has also been explained by steric hindrance.[12] Imines formed from esters of natural α-amino acids bearing α-substituents do not react with fullerene other than those that are additionally stabilized by an intramolecular hydrogen bond. Steric hindrance of the trisubstituted ylides formed was also proposed to be a cause of their low reactivity.[13]

We believe that a range of functional groups can be introduced onto the C_{60} cage using 2-picolylamine and the corresponding aldehydes as starting reagents; stereoselective formation of *cis*-3′,5′-disubstituted pyrrolidinofullerenes is expected. To extend the potential of this reaction, we examined the possibility of azomethine ylide generation from mono N-substituted 2-picolylamines and aldehydes via iminium hydroxide formation followed by elimination of a



Scheme 2.

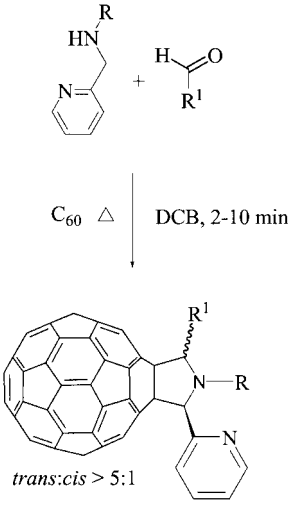


Scheme 3.

molecule of water (Scheme 3). To the best of our knowledge, no attempts to use such substrates in [2+3] cycloaddition reactions have been reported before.

Indeed, heating C_{60}, *N*-substituted 2-picolylamine, and an aldehyde in a 1:1.1:1.3 molar ratio at reflux in 1,2-DCB resulted, within 2–10 minutes, in high fullerene conversion (85–95%) and the formation of the corresponding pyrrolidinofullerenes, which were isolated by silica gel column chromatography in 55–80% yields (Scheme 4).

The ^{1}H NMR spectra of the isolated monoaddition products reveal the presence of two stereoisomers in approximately a 4:1–9:1 ratio (Figure 2) along with **8**, which was formed as a single diastereoisomer. All attempts to separate these isomers by column chromatography on silica and alumina were unsuccessful. Some signals in the ^{1}H NMR spectra of **6**–**9** were found to be broadened, most likely due to both restricted rotation of the groups at the 2′- and 5′-positions of the pyrrolidine ring and hindered inversion of configuration at the pyrrolidine nitrogen. The appearance of a couple of doublets corresponding to the methylene group in the ^{1}H NMR spectra is evidence of the restricted rotation of the substituents attached to the pyrrolidine nitrogen.[14] The signals of the methine protons of the major isomers of **6**–**9** in the ^{1}H NMR spectra are shifted to low field by about 0.6–0.9 ppm relative to the same signals of the corresponding minor isomers. Assuming that the



6	R = 2-PyCH$_2$-	R^1 = 2-Py-	80 %
7	R = 2-PyCH$_2$-	R^1 = 4-Py-	55 %
8	R = PhCH$_2$-	R^1 = 2-Py-	60 %
9	R = 3-PyCH$_2$-	R^1 = 4-Py-	70 %

Scheme 4.

trend in chemical shifts of the methine protons in 1′,2′,5′-trisubstituted pyrrolidinofullerenes is similar to that observed for their 2′,5′-disubstituted relatives, the *trans* and

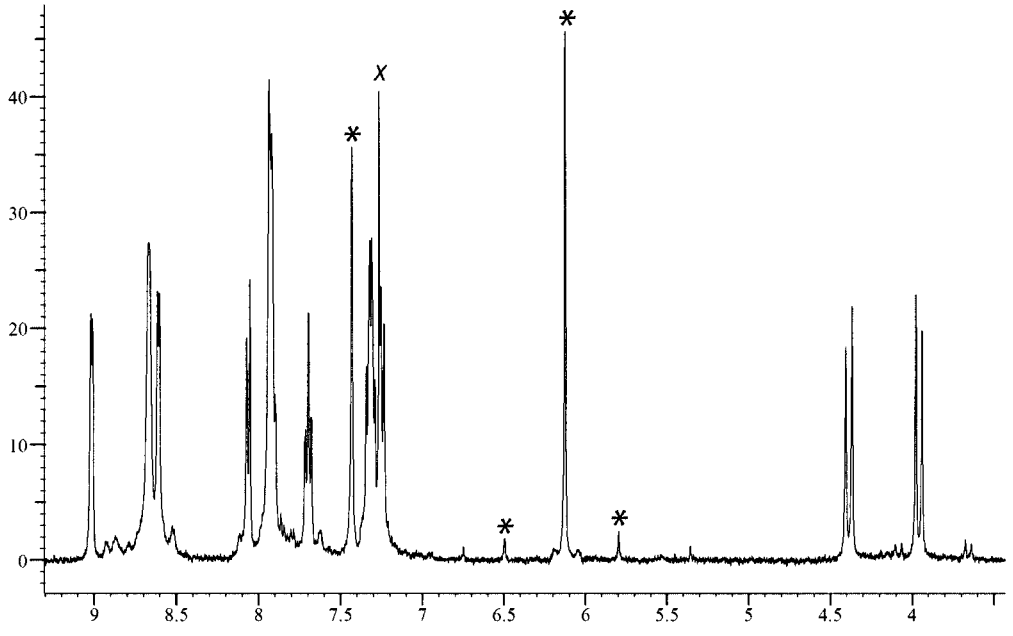
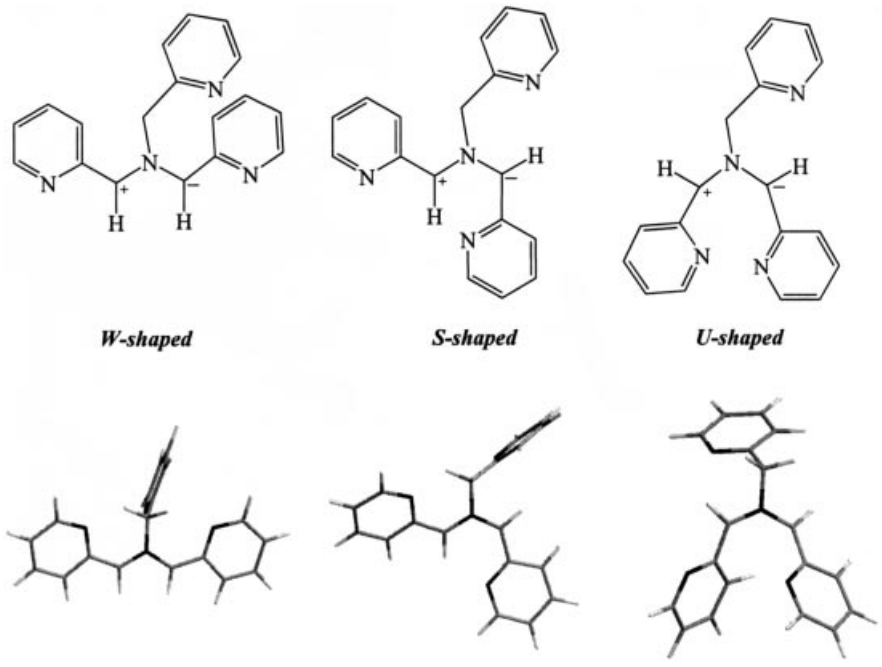


Figure 2. ^{1}H NMR spectrum of **7**. *: signals of methine protons; x: $CHCl_3$ in $CDCl_3$.



Scheme 5.

cis arrangements of the groups were assigned to the major and minor isomers, respectively.

Thus, in contrast to the above-described reactivity of unsubstituted 2-picolylamine, which yields mainly *cis* products, its *N*-substituted derivatives afford a stereoselective formation of *trans* isomers of the adducts. Obviously, such "reversed" diastereoselectivity in the [2+3] cycloaddition of 1,2,3-trisubstituted azomethine ylides as compared with 1,3-disubstituted ones is due to the presence of a bulky group attached to the nitrogen atom. For example, the azomethine ylide formed from 2-pyridinecarbaldehyde and di(2-picolylamine) exists in three conformations: W-shaped (**I**), U-shaped (**II**), and S-shaped (**III**; Scheme 5). The [2+3] cycloaddition of the S-shaped ylide is expected to yield a pyrrolidinofullerene with a *trans* arrangement of the substituents at the 2′- and 5′-carbons, while W- and U-shaped ylides should give a *cis* product. Theoretical AM1 calculations were used to optimize the geometry of all three conformations and estimate their heats of formation. We found that the S-conformation is 8 and 29 kJ more stable than the W- and U-shaped geometries, respectively. Thus, the computational results are in line with the experimental data.

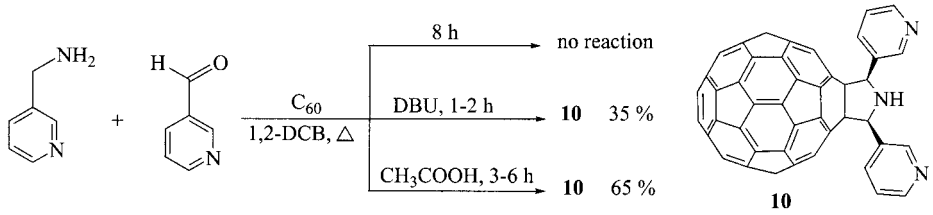
The application of *N*-substituted 2-picolylamines for the generation of azomethine ylides can be considered as a versatile approach to the synthesis of various 1′,2′,5′-trisubstituted pyrrolidinofullerenes. Moreover, it can find useful applications in general organic synthesis for the preparation of pyrrolidines starting from various dipolarophiles (like maleic acid esters etc.).

3-Picolylamine and *N*-Substituted 3-Picolylamines as Substrates

Our initial attempt to obtain a [2+3] cycloaddition product by heating an equimolecular mixture of 3-picolylamine, 3-pyridinecarboxaldehyde, and [60]fullerene at reflux in 1,2-dichlorobenzene failed; no substantial conversion of C_{60} was observed after eight hours. The inertness of 3-picolylamine can be rationalized by taking into account the lack of mesomeric stabilization of a carbanionic center in the corresponding ylide with participation of the pyridyl nitrogen. Such stabilization plays an important role in the case of ylides formed from 2- and 4-picolylamines.

Nevertheless, we found that the reaction can be initiated with DBU or acetic acid as catalysts. About 0.15 equiv. of DBU is required (with respect to fullerene) to complete the reaction in 1–2 h and obtain pyrrolidinofullerene **10** with moderate yield (35%, Scheme 6). The use of higher amounts of the catalyst resulted in lower yields, most likely due to some side reaction between DBU and C_{60} that yields insoluble products. Other bases (NEt_3, NBu_3, pyridine etc.) were inefficient as catalysts with the exception of DABCO, which prompted the reaction to a small extent. Acetic acid was found to be the most promising reaction promoter. In spite of the fact that larger amounts of the catalyst (8 equiv.) and longer reaction times (3–6 h) are required in the case of CH_3COOH, the yield of the product is about twice as high as that in the DBU-catalyzed reaction (Scheme 6).

To the best of our knowledge, these reactions are the first examples of catalytic [2+3] cycloaddition to C_{60} fullerene. Moreover, the catalytic effect of strong bases on the [2+3] cycloaddition of azomethine ylides has never been observed, even in the case of non-fullerene substrates. It can be rationalized if we assume that DBU abstracts the proton from the methylene group of the imine (formed in situ) and then DBU·H^+ delivers this proton to the nitrogen atom to form a 1,3-dipolar ion (Scheme 7). In the case of acetic acid, a reverse mechanism can be suggested. Initially, it pro-



Scheme 6.

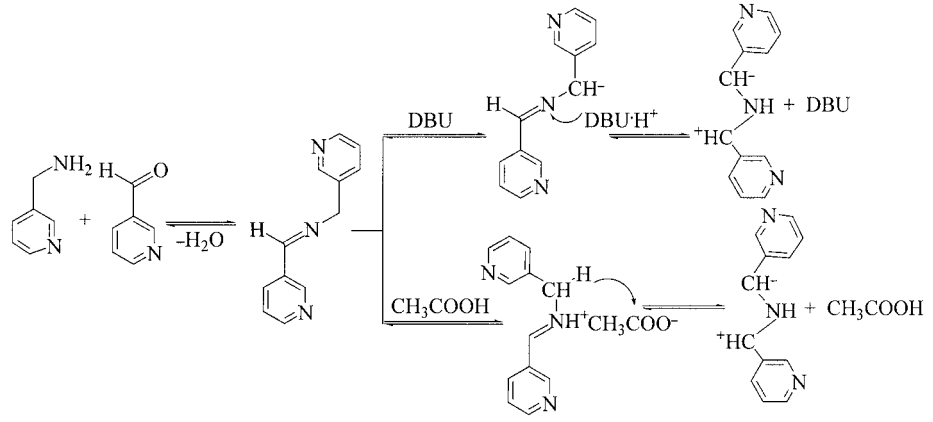
tonates the nitrogen atom of the imine, then the CH_3COO^- anion formed abstracts H^+ from the CH_2 group of the protonated imine.

The ^1H and ^{13}C NMR spectra of isolated 2′,5′-di(3-pyridyl)pyrrolidino[3′,4′:1,2][60]fullerene (**10**) show the formation of a single *cis* isomer; the corresponding *trans* isomer is probably formed in amounts too low to be confidently detected and isolated. The formation of an NH···N(pyridine) intramolecular hydrogen bond is hardly possible in the case of the azomethine ylide bearing 3-pyridyl groups (Scheme 7), so it can be ruled out as a reason for such a high diastereoselectivity of the [2+3] cycloaddition. Therefore, only steric discrimination of the *syn* and *anti* conformations of azomethine ylide at the [2+3] cycloaddition stage to the C_{60} cage seems to be responsible for this result.

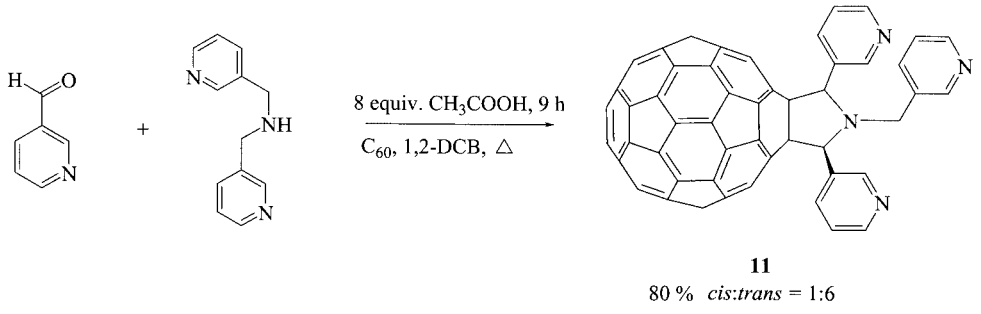
Treatment of di(3-picolyl)amine and 3-pyridinecarboxaldehyde with C_{60} under acidic catalysis (CH_3COOH) yielded 1′,2′,5′-trisubstituted pyrrolidinofullerene **11** with high yield (Scheme 8). As in the case of unsubstituted 3-picolylamine, the reaction does not proceed without a catalyst. Spectroscopic characterization of **11** revealed the presence of *cis* and *trans* isomers in an approximate 1:9 ratio. Thus, the stereochemical result of the reaction does not depend strongly on the structure of the picolylamine used as a substrate.

4-Picolylamine and *N*-Substituted 4-Picolylamines as Substrates

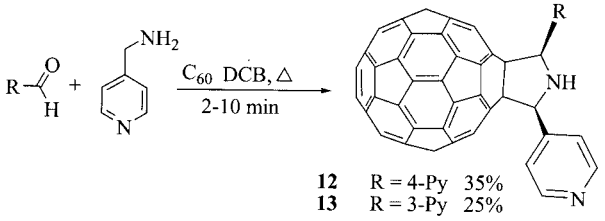
The reactivity of 4-picolylamine in [2+3] cycloaddition reactions to C_{60} was found to be lower than that of 2-picolylamine but much higher than that of 3-picolylamine. Thus, heating an equimolecular mixture of 4-picolylamine, aldehyde, and C_{60} at reflux in 1,2-DCB without a catalyst results, within 10–30 min, in both moderate fullerene conversion and yields of the products **12** and **13** (Scheme 9). An increase in the reaction time up to 6 h does not improve the product yields.



Scheme 7.

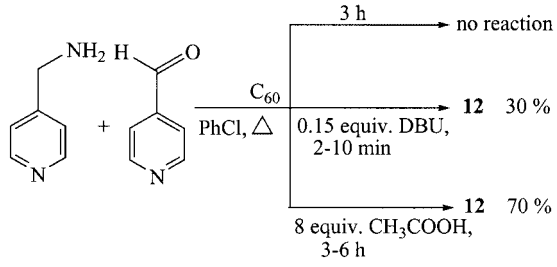


Scheme 8.



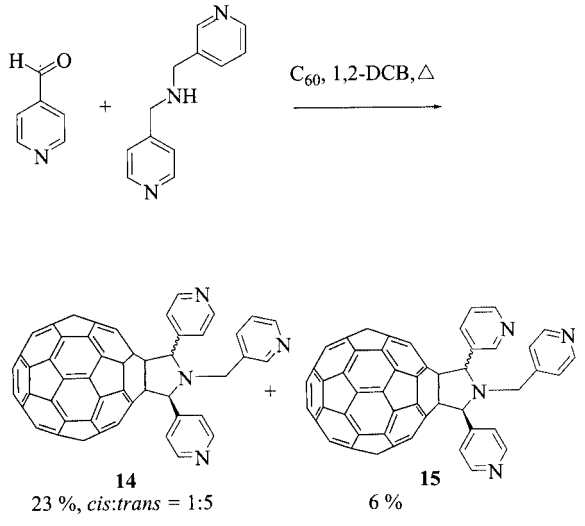
Scheme 9.

When chlorobenzene (PhCl) was used as a solvent in the synthesis of **12**, no reaction was observed when heating the reagents at reflux (about 130 °C) for 3 h. However, the addition of 0.15 equiv. of DBU allowed this reaction to go to completion in 10–20 minutes (conversion of C_{60} is about 70% and it cannot be enhanced by increasing the reaction time). Acetic acid has a less-pronounced effect on the reaction rate (8 equiv. of the catalyst should be used and the optimal reaction time is 3–6 h), although it gives much higher yields of the product (Scheme 10).



Scheme 10.

Various *N*-substituted 4-picolylamines can also be used as substrates for generation of azomethine ylides. Thus, an uncatalyzed treatment of (3-picolyl)(4-picolyl)amine and 4-pyridinecarboxaldehyde with C_{60} in 1,2-DCB yielded an inseparable 4:1 mixture of the corresponding pyrrolidinofullerene **14** (*cis*:*trans* = 1:7) and the isomeric pyrrolidinofullerene **15** (Scheme 11), as determined from the ^{1}H NMR



Scheme 11.

spectra. However, only the signals corresponding to the major *trans* isomer of **15** were observed in the ^{13}C NMR spectrum of the reaction product.

The selective formation of **14** and **9** (see Scheme 4) in the reactions with unsymmetrical dipicolylamines indicates that 2- and 4-pyridinyl groups have a much stronger stabilizing effect on the carbanion center in the ylides formed than a 3-pyridinyl group. Such a trend correlates with the mesomeric stabilization of the picolyl anions by 2- and 4-pyridyl groups that is lacking in the case of 3-picolylamine derivatives.

Electrochemical Properties of the Synthesized Pyridyl-Appended Pyrrolidinofullerenes

The electrochemical behavior of some of synthesized pyrrolidinofullerenes was studied by cyclic voltammetric techniques (CVA) in a microelectrochemical cell.[15] The cyclic voltammograms obtained are shown in Figure 3. The first three reversible reductions of the pyrrolidinofullerenes are located at $E_{1/2}$ = –1.08 to –1.14, –1.48 to –1.53, and –2.00 to –2.06 V vs. Fc/Fc$^+$ (Table 1).

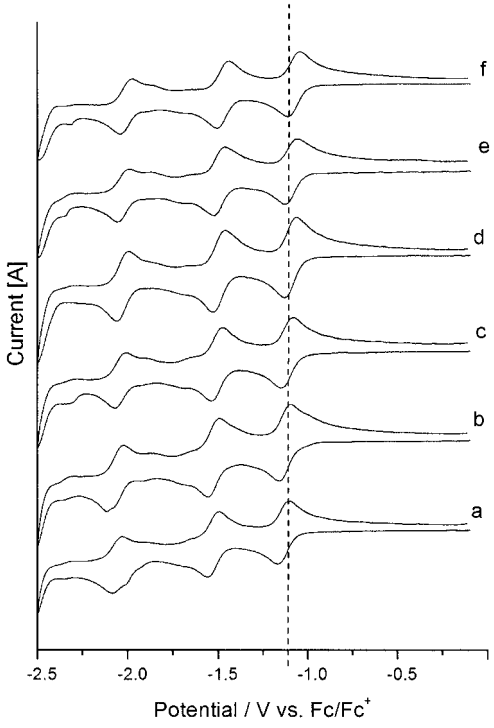
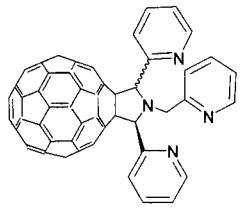
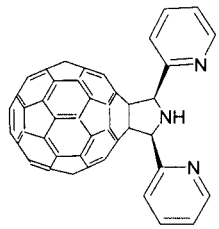
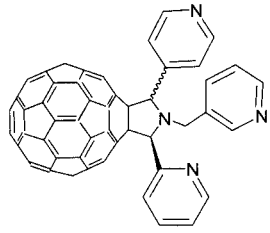
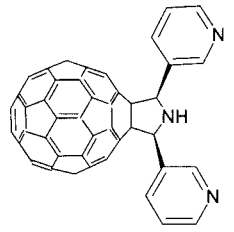
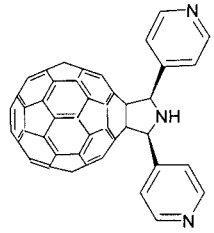
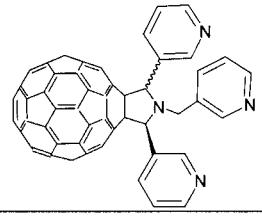


Figure 3. Cyclic voltammograms of pyrrolidinofullerenes **6** (a), **2** (b), **9** (c), **10** (d), **12** (e), and **11** (f).

A correlation between the number and the structure of pyridyl groups attached to the pyrrolidine cycle and the reduction potentials is observed for the studied fullerene derivatives. Pyrrolidinofullerenes **6** and **2**, which possess three and two 2-pyridyl units, respectively, have the most-negative potentials. With respect to these two derivatives, the reduction potentials of **9**, which possesses one 2-pyridyl and also 3-pyridyl and 4-pyridyl groups, are slightly more posi-

Table 1. Reduction potentials of pyrrolidinofullerenes.

	Structure	$E_{1/2}$		
6		−1.14	−1.53	−2.06
2		−1.13	−1.53	−2.06
9		−1.11	−1.51	−2.05
10		−1.09	−1.50	−2.03
12		−1.09	−1.50	−2.03
11		−1.08	−1.48	−2.00

tive. Fullerene derivatives **10**, **11**, and **12**, which possess 3-pyridyl and 4-pyridyl units and no 2-pyridyl groups, have the most-positive reduction potentials. Such a dependence of the reduction potentials of the fullerene derivatives on their structure suggests the existence of some electronic communication between the 2-pyridyl groups attached to the pyrrolidine ring and the fullerene cage. Most likely, the pyridyl nitrogen atom donates its unshared electron pair to the fullerene π-system. This effect can be considered as a promising tool for the fine adjustment of reduction potentials of fullerene derivatives, which is quite important for photovoltaic applications.

Our results also suggest a lack of electronic communication between the pyridyl nitrogen atom and te fullerene cage in *N*-(4-pyridyl)pyrrolidinofullerene[16] as this compound has almost the same reduction potentials as *N*-methylpyrrolidinofullerene and our derivative **12**, which possesses two 4-pyridyl groups. However, such an electronic communication has been claimed to explain a higher binding constant for complex formation between *N*-(4-pyridyl)pyrrolidinofullerene and ZnTPP ($K_a = 7.7 \times 10^{-4}$) in comparison with the similar complex of 3-methyl-2-(4-pyridyl)pyrrolidinofullerene ($K_a = 1.4 \times 10^{-4}$).[16] Generally, the electron-withdrawing effect of the fullerene cage on the nitrogen atoms in the addends results in decreased basic properties and lower association constants with ZnTPP,[17] which is inconsistent with the expectation of the authors of ref.[16]

Conclusions

We have found that isomeric picolylamines and their *N*-substituted derivatives can successfully be used as substrates to generate azomethine ylides in a [2+3] cycloaddition reactions with [60]fullerene. This method allows the synthesis of a large number of rare 2′,5′-disubstituted and 1′,2′,5′-trisubstituted pyrrolidinofullerenes. Due to the availability of the substrates, high reaction yields (typically 50–80%), a high stereoselectivity of formation of *cis* 2′,5′-disubstituted (>95%) and *trans* 1′,2′,5′-trisubstituted (>80%) pyrrolidinofullerenes, and convenient reaction procedures, our picolylamine method can be considered as a good alternative to the conventional Prato reaction. Moreover, this approach to the generation of azomethine ylides can be a useful tool for the synthesis of non-fullerene based pyrrolidines from various dipolarophiles.

A large family of new fullerene ligands − pyrrolidinofullerenes bearing pyridyl groups − has been synthesized and characterized. Such derivatives can be applied in the design of complexes with transition metals and noncovalently linked donor–acceptor dyads with metalloporphyrins. The latter systems have promising photophysical properties (photoinduced electron transfer to form a long-lived charge-separated state[18]) and mimic natural photosynthetic reaction centers. Very recently we have synthesized and structurally characterized a dyad formed from pyrrolidinofullerene **2** and ZnTPP that possesses a coordinative bond between the pyrrolidine N atom and the Zn of the metalloporphyrin.[8]

A cyclic voltammetry study of the synthesized pyrrolidinofullerenes has revealed a correlation between the structures of the fullerene derivative and their reduction potentials. Electronic communication between the 2-pyridyl groups attached to the pyrrolidine ring and fullerene cage was found to be responsible for a negative shift of the reduction potentials.

Experimental Section

General Remarks: All commercially available solvents and reagents were purchased from Acros or Aldrich and used as received. NMR spectra were recorded from solutions in $CDCl_3$ (^1H) and CS_2/[D_{12}]-cyclohexane (10:1; ^{13}C) on an AMX 400 Bruker (400 MHz) instrument with the solvent residual proton signal or tetramethylsilane (TMS) as a standard. An LCQ Deca XP (Thermo Finnegan) was used to obtain ESI mass spectra.

Cyclic Voltammetry: CV solution measurements were performed with a microelectrochemical cell set up inside an Ar-filled glove box using a glass cross with four openings. The solvent for the electrolyte and the analyte was a 1:4 (v/v) mixture of acetonitrile and *o*-dichlorobenzene (ODCB) (both anhydrous from Aldrich).

All electrodes were of standard size and were purchased from Bioanalytical Systems, West Lafayette, Indiana. A Pt disk electrode was used as the WE inserted from the bottom; the CE was a Pt wire loop fixed in such a way that the loop was placed above the WE. A nonaqueous Ag/Ag^+ quasi-RE was placed through the top opening above the other two electrodes. All electrodes were fixed by self-made Teflon® stoppers.

The sample solution with the supporting electrolyte (0.1 M $TBAPF_6$) and the analyte dissolved in it were brought inside the glove box in a Hamilton® syringe. About 40 μL was enough to form a meniscus that covered all three electrodes. The remaining cell opening was closed with a Teflon stopper to avoid solvent evaporation during the measurement.

CV measurements were carried out with a potential sweep rate of 50 $mV\,s^{-1}$. The electrochemical experiments were controlled from outside the glove box with a computer and S.C.A.D.A. software. After each measurement, the analyte solution was changed to an electrolyte solution with ferrocene for calibration of the RE. The cleaning of the WE was done by polishing with diamond paste, first with a particle size of 1 μm and then with a size of 0.25 μm. The CE was cleaned in the flame of a Bunsen burner.

General Synthetic Procedure for the Preparation of Pyrrolidinofullerenes 1–9 and 12–14: Fullerene C_{60} (200 mg, 0.28 mmol) was dissolved in 20 mL of 1,2-dichlorobenzene and stirred in air for 2 h. A solution of 1.2 equivalents (0.33 mmol) of the reagents [1:1 mixture of aldehyde and picolylamine (*N*-substituted picolylamine) or the corresponding imine] in 5 mL of 1,2-dichlorobenzene was added in one portion to the fullerene solution, and the resulting reagent mixture was heated at reflux under air or argon for 2–10 min (**1**–**9**) or 10–30 min (**12**–**14**). The course of the reaction was monitored by TLC. At the end of the synthesis, the heating source was removed and the reaction mixture was cooled to room temperature, diluted with toluene (and *n*-hexane in the case of **8**), and poured onto the top of a silica gel column (40–60 μm, 60 Å). Unreacted fullerene was washed out from the column with toluene (or a 1:1 toluene/hexane mixture for **8**); elution with toluene/methanol (toluene/hexane for **8**) mixtures resulted in solutions of monoaddition products. The latter were concentrated in vacuo to 2–3 mL and then hexane was added to precipitate the product. Pyrrolidinofullerenes (65–238 mg) were isolated as amorphous dark-brown solids by centrifugation.

General Procedure for the Acid- and Base-Catalyzed Synthesis of 10–12: Fullerene C_{60} (200 mg, 0.28 mmol) was dissolved in 20 mL of 1,2-dichlorobenzene (**10**,**11**) or 50 mL of chlorobenzene (**12**) whilst stirring under argon for 2 h. A solution of 1.2 equivalents (0.33 mmol) of the reagents [1:1 mixture of an aldehyde and picolylamine (*N*-substituted picolylamine) or the corresponding imine] in 5 mL of 1,2-dichlorobenzene (**10**,**11**) or chlorobenzene (**12**) and the corresponding amount of catalyst (0.15 equiv. of DBU or 8 equiv. of CH_3COOH) were added in one portion to the fullerene solution. The resulting reagent mixture was heated at reflux under argon for 30–40 min (when DBU was used) or 5–8 h (when CH_3COOH was used) and then cooled down to room temperature; the solvent was then evaporated in vacuo. The residue formed was washed three times with methanol to remove traces of the catalyst, dried in air, dissolved in toluene, and put onto a silica gel column. Pyrrolidinofullerenes **10** and **11** were isolated as dark-brown solids similarly to **1**–**9** and **12**–**14**.

Pyrrolidinofullerene 1: Eluent: toluene/MeOH (99.8:0.2, v/v). Yield: 72%. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.17 (br. s, 1 H), 6.06 (s, 1 H), 6.21 (s, 1 H), 7.32 (t, 1 H), 7.36 (t, 1 H), 7.43 (t, 2 H), 7.86 (t, 1 H), 7.95 (d, 2 H), 8.11 (d, 1 H), 8.69 (d, 1 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 76.02, 76.16, 77.42, 78.22, 122.66, 125.13, 128.00, 128.23, 128.54, 128.71, 135.33, 135.45, 135.92, 136.25, 136.37, 136.97, 138.95, 139.16, 139.52, 139.66, 141.23, 141.66, 141.82, 142.22, 142.66, 142.78, 143.95, 144.16, 144.73, 144.89, 145.12, 145.27, 145.48, 145.64, 145.84, 146.31, 146.72, 149.14, 152.59, 152.86, 153.06, 153.35, 156.77 ppm.

Pyrrolidinofullerene 2: Eluent: toluene/MeOH (99.5:0.5, v/v). Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.57 (br. s, 1 H), 6.23 (s, 2 H), 7.30 (t, 2 H), 7.80 (t, 2 H), 7.88 (d, 2 H), 8.79 (d, 2 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 77.66, 80.22, 122.63, 123.12, 125.13, 127.99, 128.71, 135.12, 135.71, 136.35, 136.99, 138.98, 139.62, 141.1, 141.62, 141.74, 142.23, 142.8, 143.87, 144.11, 144.61, 144.76, 144.86, 145.04, 145.38, 145.59, 145.8, 146.2, 146.56, 149.33, 149.56, 152.53, 153.67, 155.69 ppm. ESI-MS (CH_3OH+HCOOH): *m/z* (*I*/%) = 918 (100) [MH^+]. FTIR (KBr pellet): $\tilde{\nu}$ = 526, 544, 573, 624, 695, 732, 772, 792, 795, 799, 829, 867, 996, 1031, 1090, 1147, 1410, 1440, 1473, 1571, 1591 cm^{-1}.

Pyrrolidinofullerene 3: Eluent: toluene/MeOH (98.8:1.2, v/v). Yield: 55%. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.09 (br. s, 1 H), 6.15 (s, 1 H), 6.26 (s, 1 H), 7.38 (dt, 1 H), 7.50 (dt, 1 H), 8.19 (d, 1 H), 8.40 (d, 1 H), 8.74 (dd, 2 H), 9.28 (s, 1 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 75.64, 78.21, 79.18, 79.83, 124.76, 124.88, 130.002, 134.33, 136.34, 137.31, 137.66, 137.99, 138.25, 138.63, 141.07, 141.34, 141.56, 141.91, 143.29, 143.66, 143.84, 144.06, 144.34, 144.71, 144.8, 146.15, 146.76, 147.01, 147.11, 147.24, 147.55, 147.7, 147.89, 148.77, 151.43, 153.95, 154.4, 155.06, 155.18, 158.54 ppm.

Pyrrolidinofullerene 4: Eluent: toluene/MeOH (98.5:1.5, v/v). Yield: 68%. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.11 (t, 1 H), 6.05 (d, 1 H), 6.20 (d, 1 H), 7.32 (dt, 1 H), 7.85 (dt, 1 H), 7.91 (d, 2 H), 8.11 (d, 1 H), 8.72 (d, 1 H), 8.74 (d, 2 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 74.86, 76.25, 77.50, 77.65, 122.44, 122.50, 122.73, 128.08, 128.80, 132.90, 133.66, 135.34, 135.77, 136.09, 136.32, 136.60, 137.06, 138.76, 139.21, 139.39, 139.92, 141.37, 141.77, 142.38, 142.48, 142.78, 142.88, 144.25, 144.89, 145.12, 145.20, 145.25, 145.35, 145.62, 145.66, 145.84, 145.98, 146.08, 146.88, 147.85, 149.47, 149.88, 150.20, 151.15, 152.20, 152.42, 153.08, 156.56 ppm.

Pyrrolidinofullerene 5: Eluent: toluene/MeOH (99.8:0.2, v/v). Yield: 4–5%. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.47 (br. s, 1 H), 6.86 (s, 2 H), 7.45 (m, 2 H), 7.94 (dt, 2 H), 7.96 (d, 2 H), 8.92 (d, 2 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 76.54, 79.2, 122.08, 122.7, 127.81, 135.23, 135.67, 135.96, 138.88, 139.43, 141.18, 141.58, 141.77, 141.87, 141.99, 142.08, 142.6, 143.76, 143.93, 144.4, 144.53, 144.67, 144.74, 145.01, 145.25, 145.34, 145.56, 145.62, 146.41, 152.91, 155.41, 158.52 ppm.

Pyrrolidinofullerene 6: Eluent: toluene/MeOH (99.2:0.8, v/v). Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (d, 0.15 H), 4.00 (d, 0.85 H), 4.20 (d, 0.15 H), 4.46 (d, 0.85 H), 6.43 (br. s, 0.3 H), 6.91 (br. s, 1.7 H), 7.20 (t, 1 H), 7.28 (t, 2 H), 7.72 (br. s, 4 H), 7.90 (t, 1 H), 8.10 (d, 1 H), 8.62 (d, 1 H), 8.85 (d, 2 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 52.56, 74.10, 76.23, 121.80, 122.06, 122.40, 124.65, 125.30, 128.16, 128.86, 130.98, 135.79, 135.99, 136.46, 137.29, 139.26, 139.76, 141.31, 141.60, 141.68, 141.86, 141.94, 142.07, 142.32, 142.42, 142.90, 144.36, 144.40, 144.92, 145.00, 145.30, 145.44, 145.73, 145.77, 145.86, 145.98, 146.03, 146.41, 146.83, 147.08, 149.34, 153.60, 155.89, 158.96, 159.32 ppm. ESI-MS (CH_3OH + HCOOH): *m/z* (%) = 1027 (100) [M + H_3O^+]. FTIR (KBr pellet): $\tilde{\nu}$ = 526, 544, 554, 561, 574, 588, 598, 668, 751, 775, 798, 996, 1033, 1048, 1124, 1147, 1166, 1433, 1463, 1471, 1569, 1587 cm^{-1}.

Pyrrolidinofullerene 7: Eluent: toluene/MeOH (98.8:1.2, v/v). Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.66 (d, 0.1 H), 3.96 (d, 0.9 H), 4.08 (d, 0.1 H), 4.40 (d, 0.9 H), 5.80 (s, 0.1 H), 6.12 (s, 0.9 H), 6.50 (s, 0.1 H), 7.31 (dt, 2 H), 7.43 (s, 1 H), 7.70 (t, 1 H), 7.92 (m, 3 H), 8.06 (d, 1 H), 8.61 (d, 1 H), 8.67 (m, 3 H), 9.01 (d, 1 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: 52.44, 73.31, 74.82, 75.71, 76.20, 121.85, 121.91, 122.48, 123.89, 125.97, 128.11, 130.92, 135.40, 136.00, 136.08, 137.62, 138.17, 139.27, 139.38, 139.83, 139.94, 141.38, 141.44, 141.59, 141.72, 141.85, 141.97, 142.15, 142.26, 142.39, 142.49, 142.83, 142.98, 144.19, 144.30, 144.38, 144.49, 144.86, 144.89, 144.92, 144.96, 145.08, 145.10, 145.18, 145.32, 145.37, 145.42, 145.52, 145.68, 145.70, 145.89, 145.98, 146.01, 146.10, 146.58, 146.61, 147.04, 147.13, 149.09, 149.40, 149.80, 150.07, 152.40, 153.27, 153.57, 156.83, 158.45, 159.90 ppm.

Pyrrolidinofullerene 8: Eluent: toluene/hexane (3:2, v/v). Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): 3.57 (d, 1 H), 4.39 (d, 1 H), 6.00 (s, 1 H), 7.30 (m, 8 H), 7.54 (d, 2 H), 7.60 (t, 1 H), 8.00 (br. s, 2 H), 8.99 (d, 1 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 56.85, 79.12, 80.61, 81.86, 82.61, 128.38, 128.50, 131.45, 131.73, 131.83, 133.41, 134.29, 134.73, 135.00, 135.51, 141.63, 141.93, 141.99, 143.24, 143.47, 144.03, 144.37, 144.54, 145.35, 145.44, 145.86, 146.01, 147.47, 147.51, 147.53, 147.61, 147.73, 147.93, 147.98, 148.00, 148.10, 148.35, 148.37, 148.49, 148.57, 148.92, 149.00, 149.12, 150.31, 150.46, 150.51, 150.67, 150.94, 151.03, 151.10, 151.15, 151.37, 151.39, 151.44, 151.64, 151.78, 151.83, 151.97, 152.01, 152.07, 152.12, 152.18 ppm.

Pyrrolidinofullerene 9: Eluent: toluene/MeOH (98.6:1.4, v/v). Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.44 (d, 0.2 H), 3.75 (d, 0.8 H), 4.04 (d, 0.2 H), 4.33 (d, 0.8 H), 5.63 (s, 0.2 H), 5.96 (s, 0.8 H), 6.46 (s, 0.2 H), 7.21 (d, 1 H), 7.40 (s, 1 H), 7.42 (m, 3 H), 7.73 (t, 1 H), 7.97 (d, 2 H), 8.66 (d, 1 H), 8.69 (s, 1 H), 8.72 (d, 2 H), 9.06 (d, 1 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 48.44, 72.93, 74.57, 74.71, 75.63, 122.51, 123.11, 123.65, 125.13, 125.35, 125.51, 128.00, 128.71, 130.78, 132.51, 132.77, 134.8, 135.17, 135.89, 136.18, 137.26, 137.81, 139.22, 139.28, 139.73, 139.88, 141.25, 141.29, 141.33, 141.5, 141.57, 141.62, 141.68, 141.72, 141.82, 142.01, 142.15, 142.29, 142.38, 142.7, 142.88, 144.05, 144.15, 144.25, 144.35, 144.76, 144.81, 144.88, 144.96, 145, 145.23, 145.29, 145.41, 145.6, 145.64, 145.79, 145.86, 145.97, 146.05, 146.12, 146.18, 146.33, 146.47, 147.11, 147.21, 148.89, 149.11, 149.86, 150.01, 150.26, 152.11, 153.13, 153.29, 156.62, 159.91 ppm.

Pyrrolidinofullerene 10: Eluent: toluene/MeOH (98.6:1.2, v/v). Yield: 35% (DBU), 65% (CH_3COOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.18 (br. s, 1 H), 6,05 (s, 2 H), 7,45 (dt, 2 H), 8,42 (d, 2 H), 8,66 (d, 2 H), 9.24 (d, 2 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 72.65, 75.50, 123.12, 125.39, 128.17, 128.87, 132.77, 134.97, 135.90, 137.00, 137.14, 139.50, 140.09, 140.64, 141.46, 141.73, 141.83, 141.99, 142.44, 142.55, 144.16, 144.40, 144.53, 145.00, 145.18, 145.20, 145.30, 145.40, 145.54, 145.74, 146.00, 146.11, 146.15, 147.10, 149.80, 150.01, 151.95, 152.03 ppm.

Pyrrolidinofullerene 11: Eluent: toluene/MeOH (97.4:2.6, v/v). Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3,26 (d, 0.1 H), 3.55 (d, 0.9 H), 4.08 (d, 0.1 H), 4.33 (d, 0.9 H), 5.75 (s, 0.2), 6.23 (s, 1.8), 7.47 (m, 3), 7.85 (d, 1), 8.26 (br. s, 2), 8.68 (d, 1 H), 8.71 (d, 2 H), 8,84 (s, 1 H), 9,15 (br. s, 2 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 54.47, 80.08, 80.64, 129.46, 129.58, 133.63, 134.43, 138.42, 138.83, 141.08, 141.95, 143.00, 145.98, 146.48, 147.96, 148.17, 148.24, 148.75, 148.85, 149.28, 150.61, 151.30, 151.52, 151.54, 151.63, 151.67, 151.83, 152.18, 152.22, 152.40, 152.45, 153.51, 155.45, 156.08, 156.40, 157.37, 158.44, 160.49 ppm.

Pyrrolidinofullerene 12: Eluent: toluene/MeOH (98:2, v/v). Yield: 35%, 70% (CH_3COOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (br. s, 1 H), 6.00 (s, 2 H), 7.96 (d, 4 H), 8.73 (d, 4 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 79.92, 81.35, 128.92, 131.53, 134.39, 135.11, 143.15, 143.38, 146.28, 147.67, 147.93, 148.15, 148.76, 149.09, 149.98, 150.40, 150.68, 151.31, 151.43, 151.50, 151.88, 152.03, 152.29, 152.44, 156.29, 156.61, 157.76, 158.09 ppm.

Pyrrolidinofullerene 13: Eluent: toluene/EtOH (96:4, v/v). Yield: 25%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.27 (br. s, 1 H), 6.01 (d, 1 H), 6.05 (d, 1 H), 7.45 (t, 1 H), 7.96 (d, 2 H), 8.41 (d, 1 H), 8.67 (dd, 1 H), 8.73 (d, 2 H), 9.23 (d, 1 H) ppm. The solubility of the compound was too low to obtain the ^{13}C NMR spectrum.

Pyrrolidinofullerene 14: Eluent: toluene/MeOH (96.6:3.4, v/v). Yield: 27%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.23 (d, 0.1 H), 3.44 (d, 0.2 H), 3.51 (d, 0.7 H), 4.05 (d, 0.1 H), 4.24 (d, 0.2 H), 4.29 (d, 0.7 H), 5.63 (s, 0.2 H), 6.10 (s, 1.4 H), 6.18 (s, 0.2 H), 7.22 (t, 1 H), 7.48 (d, 1 H), 7.74 (br. s, 4 H), 7.91 (d, 1 H), 8.67 (s, 1 H), 8.78 (d, 4 H) ppm. ^{13}C NMR [100 MHz, CS_2/C_6D_{12} (10:1)]: δ = 48.38, 73.52, 75.83, 122.45, 123.31, 124.35, 125.31, 127.38, 128.18, 128.89, 130.37, 132.04, 132.94, 135.64, 136.58, 139.71, 140.19, 141.63, 141.65, 141.67, 141.90, 141.92, 141.96, 142.51, 142.63, 143.06, 144.36, 145.08, 145.23, 145.28, 145.31, 145.58, 145.94, 145.99, 146.16, 146.24, 147.29, 150.33, 151.86, 153.97 ppm.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of pyrrolidinofullerenes **1**–**14**. See also footnote on the first page of this article.

Acknowledgments

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