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Reactions of [60]Fullerene with Halides and Amino Acids to Synthesize Fulleropyrrolidines

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The reactions of [60]fullerene with benzyl chlorides and amino acids in chlorobenzene (PhCl) were investigated. Fulleropyrrolidines bearing ArCH moieties originating from the corresponding benzyl chlorides through C–Cl bond cleavage were obtained from these reactions. Use of PhCl/DMSO instead of PhCl as the solvent significantly improved the reaction efficiency. A detailed investigation of these reactions resulted in the discovery of other halides – such as allyl chloride, methallyl chloride, cinnamyl chloride, propargyl bromide, ethyl bromoacetate, bromoacetonitrile, bromomethane, bromopropane and bromobutane – that could also react with [60]fullerene and amino acids to produce fulleropyrrolidines. This reaction could be an alternative to the Prato reaction for synthesizing fulleropyrrolidines when aldehydes are expensive or unavailable from commercial sources. A plausible reaction mechanism for product formation involving C–X bond cleavage in the halide to form the aldehyde is proposed.

Introduction

Fullerenes were first discovered by Kroto, Smalley, and Curl in 1985. Since then, fullerenes, particularly [60]fullerene, have received considerable attention because of their interesting spherical structures and unique physical and chemical properties. The functionalization of [60]fullerene with various functional groups provides a variety of potential molecular materials for biological, optical, and electronic devices.[1] Numerous methods for the chemical modification of [60]fullerene have been developed during the last few decades; they include various cycloadditions, nucleophilic additions, radical additions, hydrogenations, and halogenations.[2]

Among a large number of functionalized [60]fullerene compounds, fulleropyrrolidine derivatives are one of the most intensively studied classes.[3] Pioneering work on fulleropyrrolidine derivatives based on cycloaddition of [60]fullerene, sarcosine, and formaldehyde was conducted by Prato's group.[4] Then, reactions between azomethine ylides and [60]fullerene to prepare fulleropyrrolidine derivatives were extensively studied.[5–7] Later it was found that fulleropyrrolidine derivatives can be successfully generated by the irradiation of tertiary amines and [60]fullerene.[8] In 1996, Gan's group[9] explored direct reactions between α-amino acid esters and [60]fullerene induced by photoirradiation or in the presence of iodo reagents under ultrasonification conditions to provide fulleropyrrolidines. Subsequently, direct reactions between [60]fullerene and *N*-substituted glycines under high-speed vibration milling conditions to synthesize fulleropyrrolidines were also reported.[10] Recently, our group and Wang's group have reported direct thermal reactions, affording fulleropyrrolidine derivatives, between [60]fullerene and a series of α-amino acids and amino acid esters in the absence of aldehyde.[11] In addition, Wang and co-workers reported thermal reactions between [60]fullerene and α-amino acid ester hydrochlorides in the presence of triethylamine in *o*-dichlorobenzene at reflux, obtaining fulleropyrrolidine derivatives.[12]

In previous work we synthesized some polynitro fulleropyrrolidine derivatives[13] and unexpectedly discovered reactions between [60]fullerene, α-amino acids, and quaternary ammonium salts.[14] We suspected that the reaction mechanism initially involved C–N heterolytic bond cleavage. As such, we assumed that other molecules containing polar C–X bonds might also react with [60]fullerene to form similar products. As is well known, the carbon–halogen bond is a polar bond and is prone to heterolytic cleavage. To substantiate our assumption, reactions of [60]fullerene, α-amino acids, and alkyl halides, such as benzyl chlorides, allyl chloride, and methallyl chloride, were investigated. The results showed that [60]fullerene can also react with α-amino acids and alkyl halides to provide fulleropyrrolidine derivatives containing RCH moieties originating from the alkyl

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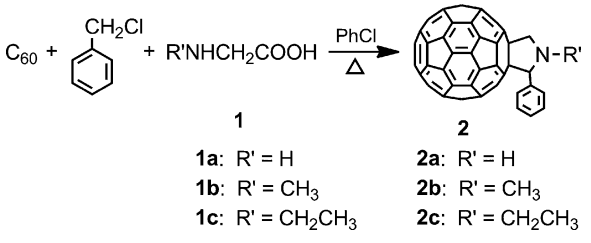
halides through C–X bond cleavage. A reaction mechanism involving C–X bond cleavage in the alkyl halide to form the corresponding aldehyde is also proposed.

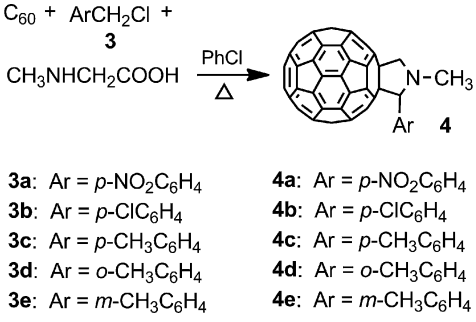
Results and Discussion

We first explored the reactions of [60]fullerene, benzyl chloride, and α-amino acids. When [60]fullerene, benzyl chloride, and α-amino acids **1a**–**1c** were added to chlorobenzene (PhCl) and the mixtures were heated to 120 °C for a given time, the corresponding adducts **2a**–**2c** were prepared, with yields of 22% to 33% (Scheme 1). Products **2a** and **2b** were known compounds, and their structures were confirmed by comparison of their spectroscopic data with those reported in the literature.[15] The structure of product **2c** was confirmed by its MS, ^{1}H NMR, ^{13}C NMR, FTIR, and UV/Vis spectrometric and spectroscopic data. The ^{1}H NMR spectrum of **2c** exhibits signals at δ = 7.79 (br. s, 2 H), 7.40 (t, J = 7.2 Hz, 2 H), and 7.32 ppm (t, J = 7.2 Hz, 1 H) for the phenyl group, two doublets at δ = 5.13 and 4.18 ppm with J_{AB} = 9.2 Hz for the two nonequivalent methylene protons in the pyrrolidine ring (PhCH), two multiplets at δ = 3.37 and 2.64 ppm and a triplet at δ = 1.55 ppm (J = 7.2 Hz) for the N-substituted ethyl group, and a singlet at δ = 5.08 ppm for the methine proton in the PhCH. The ^{13}C NMR spectrum of **2c** reveals 53 peaks in the 135–157 ppm range and three peaks at 129.46, 128.82, and 128.56 ppm for the 58 sp^2 carbons of the [60]fullerene cage and the six sp^2 carbons of the benzene ring. The other two (sp^3) carbons of the [60]fullerene skeleton appeared at δ = 76.78 and 68.82 ppm, consistently with its C_1 molecular symmetry.



Scheme 1. Synthesis of adducts **2a**–**2c** through reactions of [60]fullerene, benzyl chloride, and amino acids **1a**–**1c** in PhCl.

Adducts **2a**–**2c** each possessed a common PhCH moiety, which presumably originated from the benzyl chloride. To substantiate this assumption, the different substituted benzyl chlorides **3a**–**3e** were used in corresponding reactions to determine whether products in which the PhCH group had been replaced by the corresponding ArCH moiety could be obtained. When [60]fullerene, substituted benzyl chlorides **3a**–**3e**, and sarcosine were added to PhCl and the mixtures were heated to 120 °C for a given time, the corresponding adducts **4a**–**4e** were prepared, with yields of 22% to 39% (Scheme 2). Adducts **4a**–**4e** were identified as fulleropyrrolidines and each possessed an ArCH moiety originating from the corresponding benzyl chloride **3a**–**3e**. Among them, product **4a** was a known compound, and its structure was substantiated by comparison of spectroscopic data with those reported previously.[15] Compounds **4b**–**4e** exhibited correct molecular weights in their mass spectra and the expected chemical shifts, as well as splitting patterns, for all protons in their ^{1}H NMR spectra. The ^{1}H NMR spectra of compounds **4b**–**4e** each show a singlet at δ = 2.76 to 2.82 ppm, two doublets at δ = 4.27 to 4.99 ppm, and a singlet at δ = 4.89 to 5.30 ppm, attributable to the pyrrolidine N-substituted methyl protons (N-CH$_3$), nonequivalent methylene protons, and methine protons, respectively.



Scheme 2. Synthesis of adducts **4a**–**4e** through reactions of [60]fullerene, substituted benzyl chlorides **3a**–**3e**, and sarcosine in PhCl.

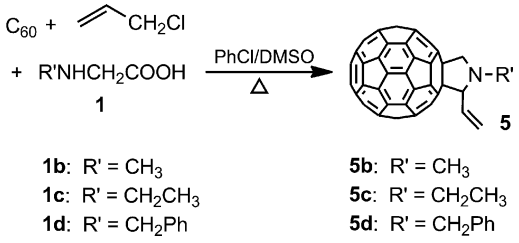
We suspected that the reaction mechanism would initially involve C–Cl heterolytic bond cleavage of the benzyl chloride to afford a benzyl carbonium ion, and that the benzyl carbonium ion would then react with α-amino acids to form azomethine ylides, which would in turn react with [60]fullerene to produce the corresponding adducts **2a**–**2c**. Of these steps, the C–Cl heterolytic bond cleavage of the benzyl chloride to afford the benzyl carbonium ion should be rate-determining. Dimethyl sulfoxide (DMSO) is well known to sustain carbon–halogen heterolytic bond cleavage.[16] As such, a PhCl/DMSO mixed solvent system was used to determine whether the reaction would become more efficient than in PhCl alone. As shown in Table 1, the reaction temperatures required for [60]fullerene, benzyl chlorides **3a**–**3e**, and amino acids **1a**–**1c** were reduced from 120 °C to 70–90 °C, and the corresponding yields of products **2a**–**2c** and **4a**–**4e** were increased from 22% to 39% and from 25% to 45%, respectively, in PhCl/DMSO.

We examined the generality of this type of reaction for other active alkyl halides, allyl chloride, methallyl chloride, cinnamyl chloride, propargyl bromide, ethyl bromoacetate, and bromoacetonitrile in place of benzyl chlorides. The reactions of [60]fullerene, allyl chloride, and N-substituted α-amino acids **1b**–**1d** are shown in Scheme 3. When [60]fullerene, allyl chloride, and α-amino acids **1b**–**1d** were placed in the PhCl/DMSO mixed solvent and the mixtures were heated to 80 °C for a given time, the corresponding adducts **5b**–**5d** were prepared, with yields of 36–42%. Adducts **5b**–**5d** were identified as fulleropyrrolidines and each possessed a CH$_2$=CHCH moiety originating from allyl chloride.

Table 1. Reaction conditions and product yields for the reactions of [60]fullerene, benzyl chlorides, and amino acids.

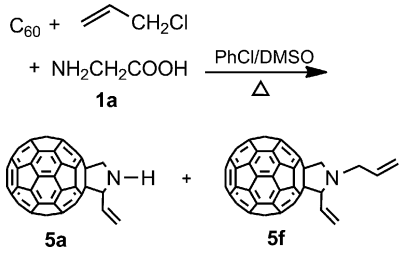
Entry	Substrates		Product	Solvent[a]	Temp. [°C]	Time [h]	Yield[b] [%]
	Benzyl chloride	Amino acid					
1	$C_6H_5CH_2Cl$	NH_2CH_2COOH	**2a**	PhCl	130	24	22 (79)
				PhCl/DMSO (2:1)	80	24	35 (84)
2	$C_6H_5CH_2Cl$	CH_3NHCH_2COOH	**2b**	PhCl	120	24	32 (75)
				PhCl/DMSO (2:1)	90	24	33 (85)
3	$C_6H_5CH_2Cl$	$CH_3CH_2NHCH_2COOH$	**2c**	PhCl	120	24	33 (68)
				PhCl/DMSO (2:1)	70	24	42 (80)
4	*p*-$NO_2C_6H_4CH_2Cl$	CH_3NHCH_2COOH	**4a**	PhCl	120	24	22 (74)
				PhCl/DMSO (2:1)	90	14	25 (86)
5	*p*-$ClC_6H_4CH_2Cl$	CH_3NHCH_2COOH	**4b**	PhCl	120	24	24 (70)
				PhCl/DMSO (2:1)	70	16	27 (81)
6	*p*-$CH_3C_6H_4CH_2Cl$	CH_3NHCH_2COOH	**4c**	PhCl	120	20	39 (74)
				PhCl/DMSO (2:1)	80	24	45 (80)
7	*o*-$CH_3C_6H_4CH_2Cl$	CH_3NHCH_2COOH	**4d**	PhCl	120	20	36 (69)
				PhCl/DMSO (2:1)	80	24	43 (78)
8	*m*-$CH_3C_6H_4CH_2Cl$	CH_3NHCH_2COOH	**4e**	PhCl	120	20	35 (65)
				PhCl/DMSO (2:1)	80	24	40 (78)

[a] Values in parentheses are the volume ratio of PhCl and DMSO. [b] Isolated yields; values in parentheses are based on consumed [60]fullerene.

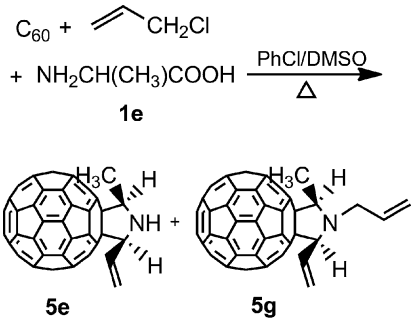


Scheme 3. Synthesis of adducts **5b**–**5d** through reactions of [60]fullerene, allyl chloride, and *N*-substituted α-amino acids **1b**–**1d** in PhCl/DMSO.

During the reactions of [60]fullerene, allyl chloride, and *N*-unsubstituted α-amino acids **1a** and **1e**, we observed that both *N*-unsubstituted fulleropyrrolidines and the corresponding *N*-allyl-substituted fulleropyrrolidines were obtained. A mixture of [60]fullerene, allyl chloride, and glycine was dissolved in 30 mL of PhCl/DMSO mixed solvent and heated to 80 °C for 15 h. The *N*-unsubstituted product **5a** and the *N*-substituted product **5f** were obtained, with yields of 18% and 29%, respectively (Scheme 4). When [60]fullerene, allyl chloride, and alanine were added to PhCl/DMSO and heated to 80 °C for 17 h, the *cis* isomers **5e** and **5g** were obtained, with yields of 21% and 12%, respectively (Scheme 5).



Scheme 4. Synthesis of the *N*-unsubstituted fulleropyrrolidine **5a** and the *N*-allyl fulleropyrrolidine **5f** through the reaction of [60]fullerene, allyl chloride, and glycine (**1a**) in PhCl/DMSO.



Scheme 5. Synthesis of the *cis* isomers **5e** and **5g** through the reaction of [60]fullerene, allyl chloride, and alanine (**1e**) in PhCl/DMSO.

The structures of products **5a**–**5g** were unambiguously confirmed by their MS, ^{1}H NMR, ^{13}C NMR, FTIR, and UV/Vis spectrometric and spectroscopic data. The ^{1}H NMR spectra of compounds **5a**–**5e** each show a multiplet at δ = 6.31 to 6.61 ppm, a doublet at δ = 5.75 to 5.84 ppm with J_{AB} = 17.0 to 17.2 Hz, and a doublet at δ = 5.56 to 5.69 ppm with J_{AB} = 10.0 to 10.4 Hz for the vinyl group. Product **5f** exhibits two multiplets at δ = 6.25 to 6.33 ppm and 6.33 to 6.43 ppm and four double doublets at δ = 5.77 (J_{AB} = 17.2 and 1.2 Hz), 5.63 (J_{AB} = 10.0 and 1.6 Hz), 5.57 (J_{AB} = 17.2 and 1.2 Hz), and 5.41 ppm (J_{AB} = 10.0 and 1.6 Hz) for the two vinyl groups. The six vinyl protons of product **5g** appeared at δ = 6.20 to 6.40 ppm (m, 2 H), 5.78 ppm (dd, J = 1.2 and 17.2 Hz, 1 H), 5.62 ppm (dd, J = 1.6 and 10.0 Hz, 1 H), 5.56 ppm (dd, J = 1.6 and 17.2 Hz, 1 H), and 5.49 ppm (dd, J = 0.8 and 10.4 Hz, 1 H). The two pyrrolidine ring methine protons of product **5g** appeared at δ = 4.79 (d, J = 9.2 Hz, 1 H) and 4.37 ppm (q, J = 6.4 Hz, 1 H), and the two *N*-substituted methylene protons ($NCH_2CH{=}CH_2$) and the three 2-substituted methyl protons ($CHCH_3$) appeared at δ = 3.96 (dd, J = 6.8 and 15.2 Hz, 1 H), 3.88 (dd, J = 6.8 and 15.2 Hz, 1 H), and 2.02 ppm (d, J = 6.4 Hz, 3 H), respectively. The stereochem-

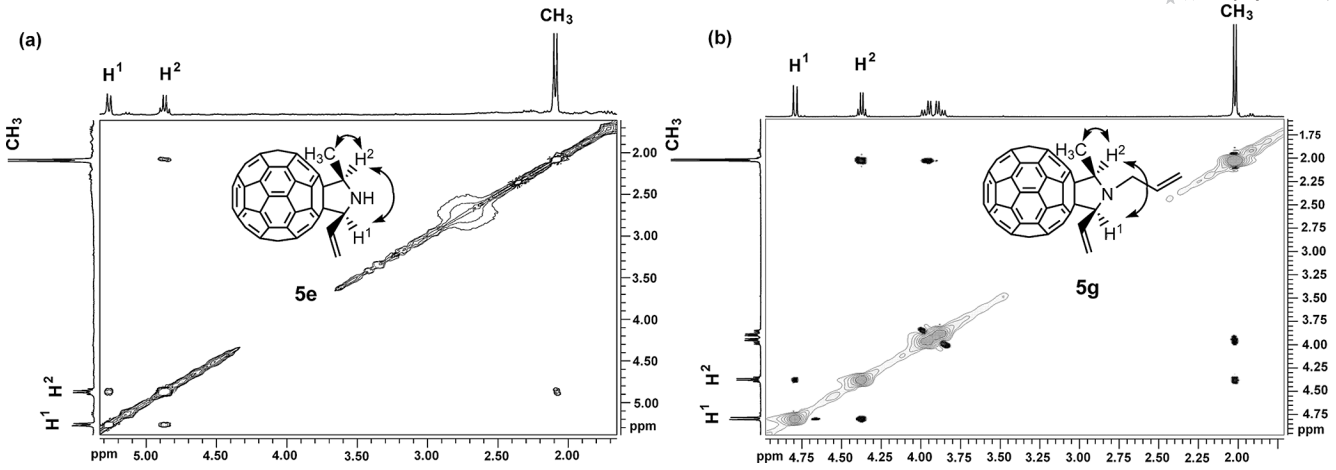
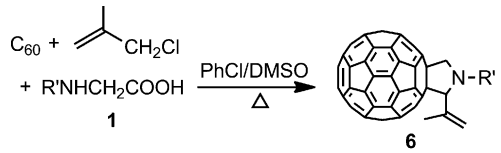


Figure 1. (a) NOESY spectrum of product **5e** and partial NOEs involving the hydrogens in **5e**. (b) NOESY spectrum of product **5g** and partial NOEs involving the hydrogens in **5g**.

istry of products **5e** and **5g** was also revealed by ^{1}H nuclear Overhauser effect spectroscopy (NOESY). The NOESY spectra of products **5e** and **5g** are shown in Figure 1, and the nuclear Overhauser effects (NOEs) involving the hydrogens are indicated by the curved arrows. As shown in Figure 1, products **5e** and **5g** each show correlation between H^1 and H^2 and no correlation between H^1 and methyl H. Evidently, the NOESY spectra indicate that products **5g** and **5e** are *cis* isomers.

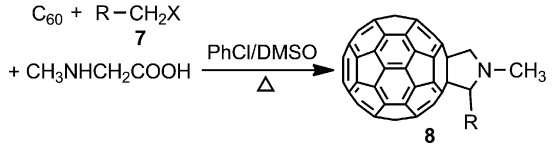
The reactions of [60]fullerene, methallyl chloride, and *N*-substituted α-amino acids **1b**–**1d** are shown in Scheme 6. When [60]fullerene, methallyl chloride, and α-amino acids **1b**–**1d** were placed in the PhCl/DMSO mixed solvent and the mixtures were heated to 80 °C for a given time, the corresponding adducts **6b**–**6d** were prepared, with yields of 24% to 30%. Structural characterization showed that adducts **6b**–**6d** were fulleropyrrolidines and each possessed a CH_2=C(CH_3)CH moiety originating from methallyl chloride.



1b: R' = CH_3 **6b**: R' = CH_3
1c: R' = CH_2CH_3 **6c**: R' = CH_2CH_3
1d: R' = CH_2Ph **6d**: R' = CH_2Ph

Scheme 6. Synthesis of adducts **6b**–**6d** through reactions of [60]fullerene, methallyl chloride, and α-amino acids **1b**–**1d** in PhCl/DMSO.

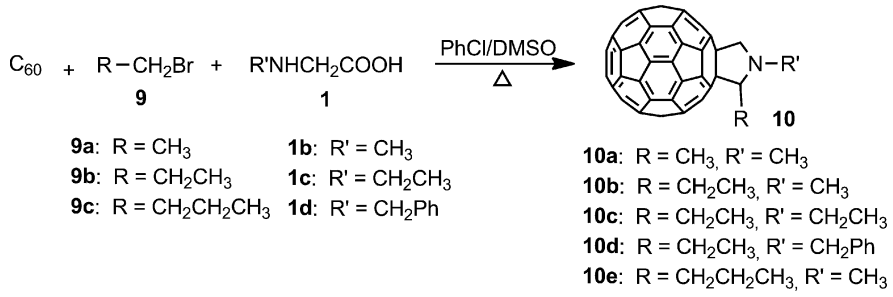
The reactions of [60]fullerene, active halides **7a**–**7d**, and sarcosine are shown in Scheme 7. When [60]fullerene, sarcosine, and active halides **7a**–**7d** were placed in PhCl/DMSO and the mixtures were heated to 80 °C to 90 °C for a given time, the corresponding adducts **8a**–**8d** were prepared, with yields of 22% to 35%. Product **8c** was a known compound, and its identity was confirmed by comparison of its spectroscopic data with those reported in the literature.[11b] The new compounds **8a**, **8b**, and **8d** were unambiguously characterized by their MS, ^{1}H NMR, ^{13}C NMR, FTIR, and UV/Vis spectrometric and spectroscopic data. The ^{1}H NMR spectra of compounds **8a**, **8b**, and **8d** each show a singlet at δ = 2.92 to 3.14 ppm for the *N*-CH_3 group. Product **8a** exhibits a doublet at δ = 7.44 ppm (d, J = 7.8 Hz, 2 H), two multiplets at δ = 7.29 to 7.34 ppm (m, 2 H) and 7.20 to 7.28 ppm (m, 1 H), a doublet at δ = 7.06 ppm (d, J = 15.6 Hz, 1 H), and a double doublet at δ = 6.68 ppm (dd, J = 9.0 and 15.6 Hz, 1 H) in its ^{1}H NMR spectrum, corresponding to the styryl group. Product **8b** exhibits a singlet at δ = 2.86 ppm (s, 1 H) in its ^{1}H NMR spectrum, corresponding to the ethynyl group. In the ^{13}C NMR spectrum of compound **8d**, the peak for the –CN carbon appears at δ = 114.75 ppm, whereas the peaks for the two ethynyl carbons of compound **8b** appear at δ = 74.20 and 68.99 ppm.



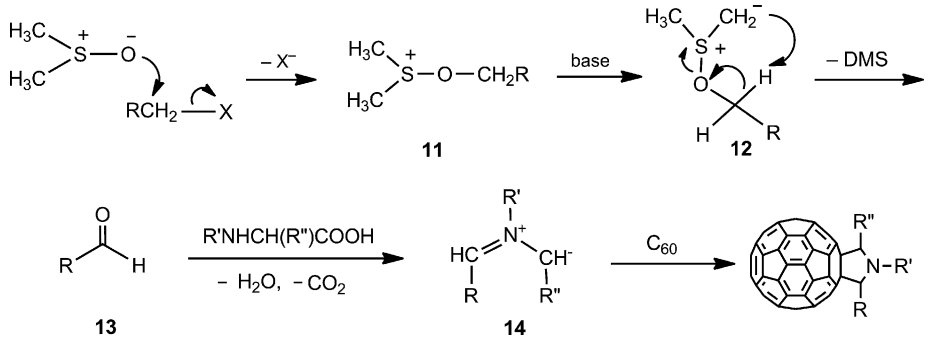
7a: R = PhCH=CH, X = Cl **8a**: R = PhCH=CH
7b: R = C≡CH, X = Br **8b**: R = C≡CH
7c: R = COOEt, X = Br **8c**: R = COOEt
7d: R = CN, X = Br **8d**: R = CN

Scheme 7. Synthesis of adducts **8a**–**8d** through the reactions of [60]fullerene, active halides **7a**–**7d**, and sarcosine in PhCl/DMSO.

To expand the scope of the use of this method, alkyl halides such as bromoethane (**9a**), *n*-bromopropane (**9b**), and *n*-bromobutane (**9c**) were also employed in the reaction to determine whether the corresponding fulleropyrrolidines would be obtained. As desired, treatment of [60]fullerene with alkyl bromides **9a**–**9c** and α-amino acids **1b**–**1d** provided adducts **10a**–**10e**, with yields of 22% to 38% (Scheme 8). The spectroscopic data for adducts **10a**–**10e** were in agreement with the depicted structures. The spectroscopic data for adducts **10a** and **10e** were fully consistent



Scheme 8. Synthesis of adducts **10a**–**10e** through the reactions of [60]fullerene, alkyl halides **9a**–**9c**, and α-amino acids **1b**–**1d** in PhCl/DMSO.



Scheme 9. Proposed reaction mechanism for the formation of fulleropyrrolidine derivatives.

with those reported previously.[14] The ^{1}H NMR spectra of adducts **10b**–**10d** each show two multiplets at δ = 2.45 to 2.97 ppm and a triplet at δ = 1.45 to 1.51 ppm for the $–CH_2CH_3$ group originating from *n*-bromopropane.

A mechanistic explanation for these reactions is shown in Scheme 9. An aldehyde can be generated from the corresponding primary halide through the action of DMSO as oxidation reagent and base as catalyst.[16,17] Hence, we can conclude that alkoxysulfonium ions **11** are obtained in the first step through attack by the nucleophilic oxyanion of DMSO at the alkyl halide and subsequent displacement of halide. After that, alkoxysulfonium ions **11** undergo deprotonation at the methyl group in the presence of α-amino acids to form ylides **12**, which then eliminate dimethyl sulfide to form the corresponding aldehydes **13**. Next, aldehydes **13**, through condensation with α-amino acids and elimination of H_2O and CO_2, produce azomethine ylides **14**, which react with [60]fullerene to afford the corresponding fulleropyrrolidines **2a**–**2c**, **4a**–**4e**, **5b**–**5f**, **6b**–**6d**, **8a**–**8d**, and **10a**–**10e**.

Conclusions

In summary, we have demonstrated a new and straightforward approach for the preparation of fulleropyrrolidine derivatives through one-pot, three-component reactions of [60]fullerene, halides, and α-amino acids. In these reactions, various halides, including active halides and alkyl halides, were used to obtain the corresponding fulleropyrrolidines. This approach might be an alternative route, instead of the Prato reaction, for the synthesis of fulleropyrrolidines when the corresponding aldehyde is expensive or unavailable from commercial sources. In addition, a possible mechanism involving the formation of the aldehyde through halide C–X bond cleavage has been proposed.

Experimental Section

General Methods: NMR spectra were recorded with a Bruker AC 300/400/600 spectrometer with CS_2/$CDCl_3$ as the solvent. Atmospheric pressure chemical ionization mass spectra were taken with a Varian 1200LC/MS mass spectrometer. HRMS was performed with an IonSpec 4.7T MALD-FTMS mass spectrometer. Infrared spectra were measured with a Nicolet 380 FTIR spectrometer (KBr pellet) with a resolution of 4 cm^{-1}, in the range from 4000 cm^{-1} to 400 cm^{-1}. UV/Vis spectra were recorded with a UNICON UV-2102 PCS spectrometer with $CHCl_3$ as the solvent. Chromatographic purifications were conducted with 300 to 400 mesh silica gel. [60]Fullerene was prepared by the arc discharge method. All other commercially available reagents were analytical grade.

Synthesis of 2-Phenylfulleropyrrolidine (2a) in PhCl: A mixture of [60]fullerene (36.0 mg, 0.05 mmol), glycine (**1a**, 22.7 mg, 0.3 mmol), and benzyl chloride (381.0 mg, 3.0 mmol) was heated to 120 °C for 24 h in chlorobenzene (30 mL). After removal of the solvent in vacuo, flash chromatography of the residue was performed on a silica gel column. Carbon disulfide first eluted unreacted [60]fullerene (26.0 mg, 72%). Toluene then eluted **2a**[15] (9.2 mg, 22% yield, 79% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 7.79 (d, J = 7.2 Hz, 2 H), 7.50–7.39 (m, 2 H), 7.37–7.30 (m, 1 H), 5.79 (s, 1 H), 5.12 (d, J = 10.3 Hz, 1 H), 4.90 (d, J = 10.3 Hz, 1 H) ppm.

Synthesis of *N*-Methyl-2-phenylfulleropyrrolidine (2b) in PhCl: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**,

26.7 mg, 0.30 mmol) and benzyl chloride (381.0 mg, 3.0 mmol) at 120 °C for 24 h by the same procedure as above gave unreacted [60]fullerene (20.7 mg, 58%) and **2b**[15] (13.6 mg, 32% yield, 75% based on consumed [60]fullerene). ^{1}H NMR (600 MHz, CS_2/$CDCl_3$): δ = 7.73 (s, 2 H), 7.36 (t, J = 7.8 Hz, 2 H), 7.27 (t, J = 7.2 Hz, 1 H), 4.94 (d, J = 9.0 Hz, 1 H), 4.89 (s, 1 H), 4.23 (d, J = 9.0 Hz, 1 H), 2.78 (s, 3 H) ppm.

Synthesis of *N*-Ethyl-2-phenylfulleropyrrolidine (2c) in PhCl: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with *N*-ethylglycine (**1c**, 30.9 mg, 0.30 mmol) and benzyl chloride (381.0 mg, 3.0 mmol) at 120 °C for 24 h by the same procedure as above gave unreacted [60]fullerene (18.7 mg, 52%) and **2c** (14.2 mg, 33% yield, 68% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 7.79 (br. s, 2 H), 7.40 (t, J = 7.2 Hz, 2 H), 7.32 (t, J = 7.2 Hz, 1 H), 5.13 (d, J = 9.2 Hz, 1 H), 5.08 (s, 1 H), 4.18 (d, J = 9.2 Hz, 1 H), 3.42–3.32 (m, 1 H), 2.69–2.60 (m, 1 H), 1.55 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 156.42, 154.22, 153.53, 153.45, 147.35, 147.34, 146.84, 146.52, 146.39, 146.32, 146.27 (2 C), 146.24, 146.19, 146.16, 146.00 (2 C), 145.84, 145.67, 145.60, 145.58, 145.51, 145.47, 145.36, 145.32, 145.29, 145.27, 145.20, 144.79, 144.72, 144.46, 143.23, 143.09, 142.76, 142.68, 142.65 (2 C), 142.35 (2 C), 142.23 (2 C), 142.18, 142.16, 142.11, 142.08, 142.01, 141.90, 141.77, 141.61, 140.32, 140.27, 139.99, 139.55, 137.27 (2 C), 136.94, 136.74, 135.89, 135.81, 129.46, 128.82, 128.56, 82.45, 76.78, 68.82, 66.63, 47.42, 13.76 ppm. FTIR (KBr): $\tilde{\nu}$ = 3057, 3025, 2963, 2922, 2850, 2785, 1603, 1540, 1492, 1451, 1427, 1383, 1335, 1305, 1280, 1261, 1228, 1186, 1120, 1097, 1028, 799, 766, 740, 725, 705, 663, 598, 570, 553, 526, 477 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 257, 306, 431 nm. MS (APCI): m/z = 868 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{70}H_{13}N$ [M]$^+$ 867.1048; found 867.1032.

Synthesis of *N*-Methyl-2-(*p*-nitrophenyl)fulleropyrrolidine (4a) in PhCl: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *p*-nitrobenzyl chloride (**3a**, 516.0 mg, 3.0 mmol) at 120 °C for 24 h by the same procedure as above gave unreacted [60]fullerene (25.5 mg, 71%) and **4a**[15] (9.7 mg, 22% yield, 74% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 8.31 (d, J = 9.0 Hz, 2 H), 8.07 (d, J = 9.0 Hz, 2 H), 5.10 (s, 1 H), 5.06 (d, J = 9.8 Hz, 1 H), 4.37 (d, J = 9.8 Hz, 1 H), 2.88 (s, 3 H) ppm.

Synthesis of *N*-Methyl-2-(*p*-chlorophenyl)fulleropyrrolidine (4b) in PhCl: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *p*-chlorobenzyl chloride (**3b**, 486.0 mg, 3.0 mmol) at 120 °C for 24 h by the same procedure as above gave unreacted [60]fullerene (23.6 mg, 66%) and **4b** (10.7 mg, 24% yield, 70% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 7.50 (br. s, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 4.99 (d, J = 9.2 Hz, 1 H), 4.93 (s, 1 H), 4.29 (d, J = 9.6 Hz, 1 H), 2.82 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 156.04, 153.78, 153.06, 152.76, 147.38 (3 C), 146.55, 146.41 (2 C), 146.36, 146.30, 146.27, 146.23, 146.19, 146.04, 146.03, 146.01, 145.78, 145.69, 145.66, 145.54, 145.48, 145.41 (2 C), 145.37, 145.34, 145.32, 145.26, 144.79, 144.70, 144.48, 144.44, 143.25, 143.12, 142.80, 142.73, 142.69, 142.67, 142.34, 142.31, 142.24, 142.22, 142.17, 142.13, 142.11,142.09 (2 C), 141.78, 141.67, 140.34, 140.32, 140.10, 139.73, 137.03, 136.54, 136.00, 135.76, 135.63 (2 C), 134.74 (2 C), 130.62 (2 C), 129.10 (2 C), 82.95, 70.13, 68.96 (2 C), 40.04 ppm. FTIR (KBr): $\tilde{\nu}$ = 3057, 2955, 2923, 2859, 2778, 1537, 1508, 1457, 1428, 1333, 1264, 1181, 1101, 1030, 832, 575, 526, 477 cm^{-1}. UV/Vis: λ_{max} = 260, 310, 430 nm. MS (APCI): m/z = 888 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{69}H_{10}ClN$ [M]$^+$ 887.0502; found 887.0498.

Synthesis of *N*-Methyl-2-(*p*-methylphenyl)fulleropyrrolidine (4c) in PhCl: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *p*-methylbenzyl chloride (**3c**, 423.0 mg, 3.0 mmol) at 120 °C for 20 h by the same procedure as above gave unreacted [60]fullerene (17.0 mg, 47%) and **4c** (16.9 mg, 39% yield, 74% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 7.67 (d, J = 8.0 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 4.98 (d, J = 9.2 Hz, 1 H), 4.91 (s, 1 H), 4.27 (d, J = 9.2 Hz, 1 H), 2.82 (s, 3 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 156.37, 154.02, 153.48, 153.53, 147.34, 147.33, 146.86, 146.53, 146.39, 146.37, 146.31, 146.27, 146.22, 146.18, 146.15, 145.99 (2 C), 145.84, 145.65, 145.57, 145.50, 145.43, 145.35, 145.31, 145.29, 145.26, 145.20, 144.76, 144.70, 144.45 (2 C), 143.21, 143.07, 142.74, 142.66, 142.63 (2 C), 142.35, 142.32, 142.22, 142.20, 142.16, 142.10, 142.07, 142.02, 141.88, 141.75, 141.61, 140.27, 140.22, 139.99, 139.60, 138.15 (2 C), 136.88, 136.67, 135.87, 135.83, 135.96 (2 C), 129.56 (2 C), 129.34 (2 C), 83.56, 70.15, 69.03 (2 C), 40.06, 21.54 ppm. FTIR (KBr): $\tilde{\nu}$ = 3036, 2944, 2919, 2850, 2777, 1540, 1512, 1461, 1427, 1332, 1262, 1177, 1106, 1030, 821, 800, 770, 600, 571, 526, 479 cm^{-1}. UV/Vis: λ_{max} = 263, 306, 431 nm. MS (APCI): m/z = 868 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{70}H_{13}N$ [M]$^+$ 867.1048; found 867.1053.

Synthesis of *N*-Methyl-2-(*o*-methylphenyl)fulleropyrrolidine (4d) in PhCl: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *o*-methylbenzyl chloride (**3d**, 423.0 mg, 3.0 mmol) at 120 °C for 20 h by the same procedure as above gave unreacted [60]fullerene (17.3 mg, 48%) and **4d** (15.5 mg, 36% yield, 69% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 8.06 (d, J = 8.0 Hz, 1 H), 7.28–7.33 (m, 1 H), 7.20 (d, J = 4.0 Hz, 2 H), 5.30 (s, 1 H), 4.99 (d, J = 9.6 Hz, 1 H), 4.31 (d, J = 9.2 Hz, 1 H), 2.76 (s, 3 H), 2.60 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 156.50, 154.01, 153.81, 153.70, 147.34 (2 C), 146.62, 146.35, 146.33,146.30, 146.24, 146.20 (2 C), 146.15, 146.00, 145.99, 145.82, 145.65, 145.52, 145.47, 145.42, 145.33, 145.29, 145.23 (2 C), 144.71 (2 C), 144.44, 144.40, 143.20, 143.05, 142.73, 142.68, 142.65, 142.38, 142.31 (2 C), 142.27, 142.16 (2 C), 142.11, 142.09, 141.96, 141.89, 141.73, 141.61, 140.38, 140.24, 139.93, 139.61, 137.19, 136.86, 136.65, 135.88, 135.42, 135.09, 131.06, 129.85, 128.02, 126.81, 78.83, 77.13, 70.00, 69.42, 39.94, 20.79 ppm. FTIR (KBr): $\tilde{\nu}$ = 3035, 2957, 2921, 2857, 2780, 1535, 1509, 1459, 1429, 1333, 1265, 1181, 1105, 1095, 1035, 740, 572, 526, 477 cm^{-1}. UV/Vis: λ_{max} = 258, 307, 429 nm. MS (APCI): m/z = 868 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{70}H_{13}N$ [M]$^+$ 867.1048; found 867.1044.

Synthesis of *N*-Methyl-2-(*m*-methylphenyl)fulleropyrrolidine (4e) in PhCl: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *m*-methylbenzyl chloride (**3e**, 423.0 mg, 3.0 mmol) at 120 °C for 20 h by the same procedure as above gave unreacted [60]fullerene (16.6 mg, 46%) and **4e** (15.2 mg, 35% yield, 65% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 7.58 (br. s, 2 H), 7.29 (t, J = 7.6 Hz, 1 H), 7.13 (d, J = 7.2 Hz, 1 H), 4.98 (d, J = 9.2 Hz, 1 H), 4.89 (s, 1 H), 4.27 (d, J = 9.2 Hz, 1 H), 2.82 (s, 3 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 156.23, 154.10, 153.55, 153.45, 147.33, 146.84, 146.51, 146.37, 146.31, 146.27, 146.26, 146.22, 146.18, 146.14, 145.99 (2 C), 145.82, 145.65, 145.58 (2 C), 145.49, 145.43, 145.34, 145.30, 145.29, 145.24, 145.20, 144.76, 144.70, 144.44 (2 C), 143.21, 143.07, 142.75, 142.65, 142.64 (2 C), 142.34, 142.30, 142.21 (2 C), 142.16, 142.15, 142.10, 142.08, 142.01, 141.89, 141.75, 141.61, 140.28, 140.23, 139.98, 139.58, 138.14, 136.88, 136.81, 136.67, 135.88, 135.81, 129.38 (2 C), 128.81, 126.53, 83.73, 77.19, 70.16, 69.05, 40.15, 21.84 ppm. FTIR (KBr): $\tilde{\nu}$ = 3037, 2952, 2920, 2856, 2778, 1535, 1508, 1457, 1427, 1328, 1265, 1183, 1110,

1033, 800, 702, 575, 526, 479 cm^{-1}. UV/Vis: λ_{max} = 256, 306, 430 nm. MS (APCI): *m*/*z* = 868 $[M + 1]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{70}H_{13}N$ $[M]^+$ 867.1048; found 867.1042.

Synthesis of 2-Phenylfulleropyrrolidine (2a) in PhCl and DMSO: A mixture of [60]fullerene (36.0 mg, 0.05 mmol), glycine (**1a**, 22.7 mg, 0.3 mmol), and benzyl chloride (381.0 mg, 3.0 mmol) was heated to 80 °C for 24 h in chlorobenzene (20 mL) and DMSO (10 mL). At the end of this time the reaction mixture was poured into water (150 mL). The chlorobenzene layer was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on a silica gel column with carbon disulfide as eluent to afford unreacted [60]fullerene (20.9 mg, 58%) and with toluene as eluent to afford product **2a** (14.7 mg, 35% yield, 84% based on consumed [60]fullerene).

Synthesis of *N*-Methyl-2-phenylfulleropyrrolidine (2b) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 26.7 mg, 0.30 mmol) and benzyl chloride (381.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 24 h by the same procedure as above gave unreacted [60]fullerene (21.9 mg, 61%) and **2b** (14.2 mg, 33% yield, 85% based on consumed [60]-fullerene).

Synthesis of *N*-Ethyl-2-phenylfulleropyrrolidine (2c) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with *N*-ethylglycine (**1c**, 30.9 mg, 0.30 mmol) and benzyl chloride (381.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 70 °C for 24 h by the same procedure as above gave unreacted [60]fullerene (17.3 mg, 48%) and **2c** (18.1 mg, 42% yield, 80% based on consumed [60]fullerene).

Synthesis of *N*-Methyl-2-(*p*-nitrophenyl)fulleropyrrolidine (4a) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *p*-nitrobenzyl chloride (**3a**, 516.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 90 °C for 14 h by the same procedure as above gave unreacted [60]fullerene (25.5 mg, 74%) and **4a** (11.2 mg, 25% yield, 86% based on consumed [60]fullerene).

Synthesis of *N*-Methyl-2-(*p*-chlorophenyl)fulleropyrrolidine (4b) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *p*-chlorobenzyl chloride (**3b**, 486.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 70 °C for 16 h by the same procedure as above gave unreacted [60]fullerene (23.8 mg, 66%) and **4b** (12.1 mg, 27% yield, 81% based on consumed [60]fullerene).

Synthesis of *N*-Methyl-2-(*p*-methylphenyl)fulleropyrrolidine (4c) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *p*-methylbenzyl chloride (**3c**, 423.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 24 h by the same procedure as above gave unreacted [60]fullerene (15.8 mg, 44%) and **4c** (19.5 mg, 45% yield, 80% based on consumed [60]fullerene).

Synthesis of *N*-Methyl-2-(*o*-methylphenyl)fulleropyrrolidine (4d) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *o*-methylbenzyl chloride (**3d**, 423.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 24 h by the same procedure as above gave unreacted [60]fullerene (16.3 mg, 45%) and **4d** (18.5 mg, 43% yield, 78% based on consumed [60]fullerene).

Synthesis of *N*-Methyl-2-(*m*-methylphenyl)fulleropyrrolidine (4e) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (26.7 mg, 0.30 mmol) and *m*-methylbenzyl chloride (**3e**, 423.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 120 °C for 20 h by the same procedure as above gave unreacted [60]fullerene (17.5 mg, 49%) and **4e** (17.4 mg, 40% yield, 78% based on consumed [60]fullerene).

Synthesis of 2-Vinylfulleropyrrolidine (5a) and *N*-Allyl-2-vinylfulleropyrrolidine (5f) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with glycine (**1a**, 22.7 mg, 0.30 mmol) and allyl chloride (300.0 mg, 4.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 15 h by the same procedure as above gave unreacted [60]fullerene (11.0 mg, 31%), **5f** (12.0 mg, 29% yield, 42% based on consumed [60]fullerene), and **5a** (7.1 mg, 18% yield, 26% based on consumed [60]fullerene).

Compound 5a: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 6.61–6.49 (m, 1 H), 5.79 (d, *J* = 17.0 Hz, 1 H), 5.58 (d, *J* = 10.3 Hz, 1 H), 5.23 (d, *J* = 7.1 Hz, 1 H), 4.99 (d, *J* = 11.5 Hz, 1 H), 4.77 (d, *J* = 11.5 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$): δ = 155.47, 153.91, 153.59, 152.24, 146.92, 146.91, 146.47, 146.31, 146.13, 146.11, 146.05 (2 C), 145.92, 145.87, 145.79, 145.78, 145.53, 145.29, 145.27, 145.23, 145.21, 145.19, 145.17, 145.16, 145.06 (2 C), 145.02, 144.41, 144.33, 144.18, 144.14, 143.04, 142.90, 142.56, 142.53, 142.47 (3 C), 142.36, 142.23, 142.05 (2 C), 142.02, 141.90, 141.87 (2 C), 141.83, 141.65, 141.56, 140.16, 140.12, 140.02, 139.62, 136.54, 135.71, 135.61, 135.53, 135.11 (2 C), 118.89, 77.99, 76.39, 74.15, 62.56 ppm. FTIR (KBr): $\tilde{\nu}$ = 3074, 2917, 2848, 2789, 1637, 1462, 1424, 1335, 1258, 1179, 1120, 989, 926, 804, 768, 703, 600, 575, 557, 526, 476 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 257, 311, 431 nm. MS (APCI): *m*/*z* = 790 $[M + 1]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{64}H_7N$ $[M]^+$ 789.0578; found 789.0590.

Compound 5f: ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 6.43–6.33 (m, 1 H), 6.33–6.25 (m, 1 H), 5.77 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.63 (dd, *J* = 1.6, 10.0 Hz, 1 H), 5.57 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.41 (d, *J* = 10.0 Hz, 1 H), 4.90 (d, *J* = 9.2 Hz, 1 H), 4.50 (d, *J* = 9.2 Hz, 1 H), 4.09 (dd, *J* = 1.2, 13.6 Hz, 1 H), 4.04 (d, *J* = 9.9 Hz, 1 H), 3.27 (dd, *J* = 8.0, 13.2 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$): δ = 156.03, 154.27, 153.45, 153.52, 147.34 (2 C), 147.10, 146.86, 146.40, 146.39, 146.36, 146.30, 146.26, 146.21, 146.16, 146.05, 145.91, 145.64, 145.62 (2 C), 145.49, 145.45, 145.38, 145.28, 145.25, 144.81, 144.73, 144.48, 143.23, 143.11, 142.77, 142.74, 142.67, 142.38, 142.29, 142.24, 142.18 (2 C), 142.14, 142.11 (3 C), 142.05, 141.82, 141.74, 140.37, 140.27, 140.21, 139.68, 137.49, 136.55 (3 C), 136.08, 135.71, 134.77 (3 C), 121.59, 118.47, 80.75, 75.54, 69.09, 66.63, 55.88 ppm. FTIR (KBr): $\tilde{\nu}$ = 3098, 3009, 2957, 2920, 2851, 1642, 1539, 1458, 1412, 1342, 1261, 1171, 1097, 1030, 922, 802, 726, 568, 526, 473 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 257, 308, 431 nm. MS (APCI): *m*/*z* = 830 $[M + 1]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{67}H_{11}N$ $[M]^+$ 829.0891; found 829.0883.

Synthesis of *N*-Methyl-2-vinylfulleropyrrolidine (5b) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 26.7 mg, 0.30 mmol) and allyl chloride (300.0 mg, 4.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 12 h by the same procedure as above gave unreacted [60]fullerene (18.6 mg, 52%) and **5b** (16.8 mg, 42% yield, 87% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 6.41–6.31 (m, 1 H), 5.77 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.62 (dd, *J* = 1.2, 10.0 Hz, 1 H), 4.85 (d, *J* = 9.2 Hz, 1 H), 4.31 (d, *J* = 8.8 Hz, 1 H), 4.12 (d, *J* = 9.6 Hz, 1 H), 2.88 (s, 3 H) ppm. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$): δ = 155.86, 154.03, 153.34, 152.54, 147.34, 147.05, 146.82, 146.40, 146.36, 146.29, 146.26, 146.21, 146.16, 146.05, 145.90, 145.63, 145.61, 145.57, 145.48, 145.44, 145.38, 145.29, 145.26, 144.79, 144.72, 144.48, 144.45, 143.23, 143.11, 142.77, 142.75, 142.67, 142.36, 142.27, 142.24, 142.18, 142.14, 142.12 (2 C), 142.05,

141.83, 141.74, 140.35, 140.27, 140.19, 139.72, 137.38, 136.50 (3 C), 136.03, 135.72, 121.48, 82.73, 76.00, 69.84, 69.43, 40.08 ppm. FTIR (KBr): $\tilde{\nu}$ = 3079, 2922, 2850, 2775, 1510, 1461, 1422, 1333, 1178, 1229, 1178, 1160, 1122, 1036, 988, 929, 881, 803, 767, 739, 598, 574, 554, 526, 478 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 257, 308, 431 nm. MS (APCI): *m*/*z* = 804 $[M + 1]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{65}H_9N$ $[M]^+$ 803.0735; found 803.0742.

Synthesis of *N*-Ethyl-2-vinylfulleropyrrolidine (5c) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with *N*-ethylglycine (**1c**, 30.3 mg, 0.30 mmol) and allyl chloride (300.0 mg, 4.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 15.5 h by the same procedure as above gave unreacted [60]fullerene (18.1 mg, 50%) and **5c** (15.2 mg, 37% yield, 75% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 6.41–6.31 (m, 1 H), 5.75 (d, *J* = 17.2 Hz, 1 H), 5.60 (d, *J* = 10.0 Hz, 1 H), 4.95 (d, *J* = 9.2 Hz, 1 H), 4.45 (d, *J* = 8.8 Hz, 1 H), 4.02 (d, *J* = 9.2 Hz, 1 H), 3.50–3.41 (m, 1 H), 2.77–2.68 (m, 1 H), 1.55 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$): δ = 155.82, 154.10, 153.30, 152.35, 147.07, 147.05, 146.89, 146.63, 146.13 (2 C), 146.10, 146.02, 145.99, 145.94, 145.88, 145.77, 145.75, 145.65, 145.37, 145.34 (3 C), 145.21, 145.18, 145.11 (2 C), 145.01, 144.97, 144.54, 144.48, 144.23, 144.18, 142.97, 142.84, 142.50, 142.47, 142.40 (2 C), 142.10, 142.03, 141.98 (2 C), 141.93, 141.87, 141.85 (3 C), 141.79, 141.56, 141.46, 140.09, 140.01, 139.94, 139.41, 137.23, 136.67 (2 C), 136.36, 135.75, 135.46, 120.79, 81.21, 75.33, 68.90, 66.02, 47.25, 13.42 ppm. FTIR (KBr): $\tilde{\nu}$ = 3080, 2962, 2923, 2851, 2778, 1655, 1509, 1460, 1422, 1384, 1280, 1181, 1122, 989, 929, 766, 597, 574, 553, 526 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 256, 309, 430 nm. MS (APCI): *m*/*z* = 818 $[M + 1]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{66}H_{11}N$ $[M]^+$ 817.0891; found 817.0887.

Synthesis of *N*-Benzyl-2-vinylfulleropyrrolidine (5d) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with *N*-benzylglycine (**1d**, 49.5 mg, 0.30 mmol) and allyl chloride (300.0 mg, 4.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 15.5 h by the same procedure as above gave unreacted [60]fullerene (17.5 mg, 49%) and **5d** (15.8 mg, 36% yield, 70% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 7.66 (d, *J* = 7.6 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 6.53–6.43 (m, 1 H), 5.84 (d, *J* = 17.2 Hz, 1 H), 5.69 (d, *J* = 10.4 Hz, 1 H), 4.71 (d, *J* = 9.6 Hz, 1 H), 4.67 (d, *J* = 13.2 Hz, 1 H), 4.60 (d, *J* = 9.2 Hz, 1 H), 4.02 (d, *J* = 9.2 Hz, 1 H), 3.75 (d, *J* = 13.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 155.98, 154.19, 153.42, 152.57, 147.36 (2 C), 147.15, 146.90, 146.44, 146.40, 146.33 (2 C), 146.27, 146.23, 146.17, 146.07, 146.04, 145.92, 145.68, 145.61 (3 C), 145.54, 145.48, 145.39 (2 C), 145.31, 145.27, 144.82, 144.76, 144.48 (2 C), 143.25, 143.12, 142.78, 142.76, 142.70, 142.68, 142.44, 142.30, 142.26 (2 C), 142.22, 142.13 (3 C), 142.07, 141.81, 141.77, 140.39, 140.31, 140.21, 139.71, 137.91 (2 C), 137.49, 136.78 (3 C), 136.52, 136.16, 135.75, 129.00, 128.83, 127.70, 80.72, 75.56, 69.11, 66.49, 57.19 ppm. FTIR (KBr): $\tilde{\nu}$ = 3083, 3060, 3025, 2956, 2918, 2849, 1655, 1611, 1508, 1461, 1450, 1421, 1384, 1174, 987, 928, 732, 694, 598, 572, 552, 525 cm^{-1}. UV/Vis: λ_{max} = 257, 308, 429 nm. MS (APCI): *m*/*z* = 880 $[M + 1]^+$, 796 $[C_{64}H_6N]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{71}H_{13}N$ $[M]^+$ 879.1048; found 879.1053.

Synthesis of 2-Vinyl-4-methylfulleropyrrolidine (5e) and *N*-Allyl-2-vinyl-4-methylfulleropyrrolidine (5g) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with alanine (**1e**, 26.7 mg, 0.30 mmol) and allyl chloride (300.0 mg, 4.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 17 h by the same procedure as above gave unreacted [60]fullerene (20.5 mg, 57%), **5g** (5.2 mg, 12% yield, 29% based on consumed [60]fullerene), and **5e** (8.3 mg, 21% yield, 48% based on consumed [60]fullerene).

Compound 5e: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 6.58–6.45 (m, 1 H), 5.77 (d, *J* = 17.0 Hz, 1 H), 5.56 (d, *J* = 10.3 Hz, 1 H), 5.26 (d, *J* = 7.4 Hz, 1 H), 4.87 (q, *J* = 6.5 Hz, 1 H), 2.09 (d, *J* = 6.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CS_2/$CDCl_3$): δ = 153.87, 153.43, 152.64, 152.58, 146.85 (2 C), 146.32 (2 C), 146.12, 146.09, 146.07 (2 C), 145.97, 145.96, 145.84, 145.81, 145.69, 145.44, 145.18 (2 C), 145.15 (2 C), 145.13 (2 C), 144.93, 144.35, 144.30, 144.07, 143.00, 142.82, 142.49 (2 C), 142.41 (2 C), 142.31, 142.02 (2 C), 141.98 (2 C), 141.94, 141.83, 141.79, 141.74, 141.54, 141.48, 140.02, 139.97, 139.70. 139.51, 136.52, 136.35, 136.25, 135.60, 135.49, 134.80, 130.46, 128.59, 119.14, 78.74, 75.22, 73.47, 67.82, 17.77 ppm. FTIR (KBr): $\tilde{\nu}$ = 3070, 3002, 2965, 2920, 2848, 2800, 1634, 1455, 1424, 1376, 1275, 1184, 1072, 1033, 991, 926, 705, 702, 600, 575, 554, 526, 475 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 258, 306, 431 nm. MS (APCI): *m*/*z* = 804 $[M + 1]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{65}H_9N$ $[M]^+$ 803.0735; found 803.0743.

Compound 5g: ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 6.40–6.20 (m, 2 H), 5.78 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.62 (dd, *J* = 1.6, 10.0 Hz, 1 H), 5.56 (dd, *J* = 1.6, 17.2 Hz, 1 H), 5.49 (dd, *J* = 0.8, 10.4 Hz, 1 H), 4.79 (d, *J* = 9.2 Hz, 1 H), 4.37 (q, *J* = 6.4 Hz, 1 H), 3.96 (dd, *J* = 6.8, 15.2 Hz, 1 H), 3.88 (dd, *J* = 6.8, 15.2 Hz, 1 H), 2.02 (d, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$): δ = 154.26, 153.77, 153.40, 153.12, 147.34, 147.32, 147.11, 146.92, 146.77, 146.54, 146.44, 146.42, 146.28, 146.26, 146.19, 146.16, 146.01, 145.84, 145.61, 145.58, 145.49, 145.44, 145.39 (2 C), 145.22, 145.20, 144.81, 144.75, 144.48, 144.44, 143.24, 143.10, 142.77, 142.75, 142.69, 142.67, 142.30, 142.28, 142.23 (2 C), 142.15, 142.13, 142.05, 142.01, 141.77, 141.71, 140.16, 139.85, 139.66, 137.51, 137.34, 136.61 (2 C), 135.93, 135.82, 131.37 (2 C), 121.34, 119.89, 78.42, 74.43, 74.33, 68.60, 50.60, 17.08 ppm. FTIR (KBr): $\tilde{\nu}$ = 3075, 2958, 2922, 2852, 1534, 1451, 1424, 1378, 1270, 1183, 1127, 1074, 1026, 983, 924, 871, 843, 819, 751, 666, 603, 573, 553, 526, 479 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 254, 307, 429 nm. MS (APCI): *m*/*z* = 844 $[M + 1]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{68}H_{13}N$ $[M]^+$ 843.1048; found 843.1043.

Synthesis of *N*-Methyl-2-(1-methylvinyl)fulleropyrrolidine (6b) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 26.7 mg, 0.30 mmol) and methylallyl chloride (364.0 mg, 4.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 20 h by the same procedure as above gave unreacted [60]fullerene (22.9 mg, 64%) and **6b** (11.1 mg, 27% yield, 75% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 5.55 (s, 1 H), 5.44 (s, 1 H), 4.89 (d, *J* = 9.6 Hz, 1 H), 4.42 (s 1 H), 4.13 (d, *J* = 9.2 Hz, 1 H), 2.83 (s, 3 H), 2.19 (s, 3 H) ppm. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$): δ = 155.69, 154.31, 153.70, 153.44, 147.07, 147.05, 146.85, 146.11 (2 C), 146.08, 145.98 (2 C), 145.95, 145.89, 145.85, 145.78, 145.76, 145.58, 145.36, 145.34, 145.32, 145.31, 145.17, 145.07 (2 C), 145.05 (2 C), 144.95, 144.53, 144.49, 144.19, 144.18, 143.02, 142.84, 142.50, 142.46, 142.44, 142.41, 142.00 (2 C), 141.97, 141.96, 141.94, 141.88, 141.87, 141.83, 141.80, 141.73, 141.54, 141.50, 141.40, 140.05, 139.97, 139.70, 139.57, 136.43, 136.39, 135.49, 135.22, 118.75, 85.04, 75.63, 69.76, 69.17, 40.03, 29.90 ppm. FTIR (KBr): $\tilde{\nu}$ = 3085, 2939, 2918, 2845, 2778, 1618, 1539, 1461, 1425, 1400, 1259, 1217, 1176, 1102, 1036, 904, 803, 766, 726, 600, 574, 524, 478 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 257, 306, 431 nm. MS (APCI): *m*/*z* = 818 $[M + 1]^+$, 720 $[C_{60}]^+$. HRMS (MALDI FT-ICR): calcd for $C_{66}H_{11}N$ $[M]^+$ 817.0891; found 817.0885.

Synthesis of *N*-Ethyl-2-(1-methylvinyl)fulleropyrrolidine (6c) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with *N*-ethylglycine (**1c**, 30.3 mg, 0.30 mmol) and methylallyl chloride (364.0 mg, 4.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for

16 h by the same procedure as above gave unreacted [60]fullerene (22.7 mg, 63%) and **6c** (12.4 mg, 30% yield, 74% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 5.53 (s, 1 H), 5.42 (s, 1 H), 5.04 (d, J = 9.3 Hz, 1 H), 4.56 (s 1 H), 4.01 (d, J = 9.3 Hz, 1 H), 3.40–3.33 (m, 1 H), 2.63–2.55 (m, 1 H), 2.17 (s, 3 H), 1.56 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CS_2/$CDCl_3$): δ = 155.69, 154.38, 153.70, 153.65, 153.33, 146.91, 146.88, 146.73, 146.05, 145.96, 145.92, 145.82 (2 C), 145.78, 145.73, 145.69, 145.62, 145.60, 145.44, 145.20, 145.19, 145.16 (2 C), 145.04, 144.92 (2 C), 144.89 (2 C), 144.78, 144.39, 144.35, 144.05, 144.03, 142.87, 142.35, 142.30, 142.28, 142.26, 141.86, 141.82, 141.81, 141.79, 141.71, 141.69, 141.64, 141.58, 141.55 (3 C), 141.40, 141.34, 139.92, 139.82, 139.57, 139.39, 136.34, 136.31, 135.28, 135.03, 118.59, 83.82, 74.95, 68.78, 66.18, 47.55, 29.83, 13.65 ppm. FTIR (KBr): $\tilde{\nu}$ = 3078, 2961, 2920, 2851, 2786, 1506, 1455, 1424, 1375, 1341, 1261, 1184, 1153, 1094, 1024, 902, 802, 756, 700, 662, 600, 573, 550, 526, 478 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 257, 307, 432 nm. MS (APCI): m/z = 832 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{67}H_{13}N$ [M]$^+$ 831.1048; found 831.1044.

Synthesis of *N*-Benzyl-2-(1-methylvinyl)fulleropyrrolidine (6d) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with *N*-benzylglycine (**1d**, 49.5 mg, 0.30 mmol) and methylallyl chloride (364.0 mg, 4.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 16 h by the same procedure as above gave unreacted [60]-fullerene (24.5 mg, 68%) and **6d** (10.8 mg, 24% yield, 76% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 7.69 (d, J = 7.4 Hz, 2 H), 7.49–7.43 (m, 2 H), 7.39–7.33 (m, 1 H), 5.68 (s, 1 H), 5.53 (s, 1 H), 4.76 (d, J = 9.5 Hz, 1 H), 4.71 (s 1 H), 4.62 (d, J = 13.5 Hz, 1 H), 4.02 (d, J = 9.5 Hz, 1 H), 3.60 (d, J = 13.5 Hz, 1 H), 2.30 (s, 3 H) ppm. ^{13}C NMR (75 MHz, CS_2/$CDCl_3$): δ = 155.91, 154.49, 153.76, 153.60, 147.15 (2 C), 146.98, 146.24, 146.16 (2 C), 146.05 (2 C), 145.99, 145.97, 145.92, 145.86, 145.83, 145.66, 145.44 (2 C), 145.42, 145.33, 145.22, 145.17, 145.15, 145.13 (2 C), 145.02, 144.61, 144.56, 144.26 (2 C), 143.09, 142.89, 142.56, 142.49, 142.13, 142.06, 142.03, 141.98, 141.95, 141.91, 141.87, 141.79, 141.57 (2 C), 141.55 (3 C), 140.08, 139.98, 139.76, 139.61, 137.92 (2 C), 136.58, 136.39, 135.63, 135.25, 128.66 (2 C), 128.56 (2 C), 127.46, 119.21, 83.22, 75.17, 68.96, 66.59, 57.22 ppm. FTIR (KBr): $\tilde{\nu}$ = 3077, 3024, 2953, 2918, 2847, 2787, 1539, 1512, 1494, 1462, 1451, 1427, 1372, 1340, 1235, 1163, 1139, 1119, 1098, 1070, 1028, 906, 803, 767, 734, 696, 598, 575, 553, 527, 477 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 257, 307, 431 nm. MS (APCI): m/z = 894 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{72}H_{15}N$ [M]$^+$ 893.1204; found 893.1206.

Synthesis of *N*-Methyl-2-styrylfulleropyrrolidine (8a) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 22.7 mg, 0.30 mmol) and cinnamyl chloride (**7a**, 383.0 mg, 2.5 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 15 h by the same procedure as above gave unreacted [60]fullerene (17.2 mg, 48%) and **8a** (13.9 mg, 32% yield, 61% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 7.44 (d, J = 7.8 Hz, 2 H), 7.34–7.29 (m, 2 H), 7.28–7.20 (m, 1 H), 7.06 (d, J = 15.6 Hz, 1 H), 6.68 (dd, J = 9.0, 15.6 Hz, 1 H), 4.89 (d, J = 9.4 Hz, 1 H), 4.48 (d, J = 9.1 Hz, 1 H), 4.16 (d, J = 9.3 Hz, 1 H), 2.92 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 155.65, 153.84, 153.23, 152.28, 147.07, 147.04, 146.58, 146.50, 146.12 (2 C), 146.00, 145.93, 145.88, 145.77, 145.75, 145.61, 145.39, 145.37, 145.32, 145.28, 145.24, 145.18, 145.12, 145.09, 145.01, 144.99, 144.53, 144.45, 144.22, 144.17, 142.96, 142.84, 142.50, 142.46, 142.40, 142.37, 142.11, 142.04, 141.98, 141.94, 141.90, 141.84 (2 C), 141.83, 141.80, 141.55, 141.49, 140.09, 139.93, 139.66, 137.15, 136.28, 135.92 (2 C), 135.86, 135.76, 135.50, 128.56 (2 C), 128.17, 127.12, 126.76 (2 C), 82.00, 76.32, 69.63, 69.14, 39.94 ppm. FTIR (KBr): $\tilde{\nu}$ = 3026, 2930, 2846, 2774, 1540, 1512, 1495, 1462, 1400, 1329, 1223, 1180, 1121, 965, 746, 689, 598, 568, 527, 476 cm^{-1}. UV/Vis: λ_{max} = 256, 310, 431 nm. MS (APCI): m/z = 880 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{71}H_{13}N$ [M]$^+$ 879.1048; found 879.1042.

Synthesis of *N*-Methyl-2-ethynylfulleropyrrolidine (8b) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 22.7 mg, 0.30 mmol) and propargyl bromide (**7b**, 357.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 90 °C for 1 h by the same procedure as above gave unreacted [60]fullerene (17.9 mg, 50%) and **8b** (13.8 mg, 35% yield, 69% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 4.96 (s, 1 H), 4.73 (d, J = 9.5 Hz, 1 H), 4.22 (d, J = 9.4 Hz, 1 H), 3.05 (s, 3 H), 2.86 (s, 1 H) ppm. ^{13}C NMR (75 MHz, CS_2/$CDCl_3$): δ = 154.51, 153.55, 152.62, 152.52, 147.08, 147.04, 146.53, 146.12, 146.07, 146.05, 145.98 (2 C), 145.85, 145.80, 145.74 (2 C), 145.71 (2 C), 145.45, 145.40, 145.28 (2 C), 145.24 (2 C), 145.17, 145.02 (2 C), 144.97 (2 C), 144.38, 144.31, 144.19, 144.16, 142.83, 142.75 (2 C), 142.41 (2 C), 142.36 (2 C), 142.00, 141.91 (2 C), 141.81, 141.79, 141.75, 141.72 (2 C), 141.51, 141.47, 139.99, 139.93, 139.87, 139.45, 137.04, 136.40, 136.02, 135.62, 135.27, 79.63, 79.01, 74.20, 69.06, 68.99, 67.62, 39.09 ppm. FTIR (KBr): $\tilde{\nu}$ = 3292, 2929, 2841, 2774, 2190, 1539, 1510, 1462, 1428, 1327, 1264, 1215, 1180, 1163, 1106, 1028, 884, 803, 766, 706, 660, 636, 600, 572, 526, 477 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 254, 307, 429 nm. MS (APCI): m/z = 802 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{65}H_7N$ [M]$^+$ 801.0578; found 801.0577.

Synthesis of *N*-Methyl-2-ethoxycarbonylfulleropyrrolidine (8c) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 22.7 mg, 0.30 mmol) and ethyl bromoacetate (**7c**, 418.0 mg, 2.5 mmol) in PhCl/DMSO (20 mL/10 mL) at 90 °C for 1 h by the same procedure as above gave unreacted [60]fullerene (15.6 mg, 43%) and **8c**[11b] (14.0 mg, 33% yield, 58% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, $CDCl_3$/CS_2): δ = 4.95 (d, J = 9.3 Hz, 1 H), 4.78 (s, 1 H), 4.41–4.27 (m, 2 H), 4.26 (d, J = 9.3 Hz, 1 H), 3.01 (s, 3 H), 1.28 (t, J = 7.1 Hz, 3 H) ppm. MS (APCI): m/z = 850 [M + 1]$^+$, 776 [M – $COOCH_2CH_3$]$^+$, 720 [C_{60}]$^+$.

Synthesis of *N*-Methyl-2-cyanofulleropyrrolidine (8d) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 22.7 mg, 0.30 mmol) and bromoacetonitrile (**7d**, 360.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 90 °C for 2 h by the same procedure as above gave unreacted [60]fullerene (17.7 mg, 49%) and **8d** (8.7 mg, 22% yield, 43% based on consumed [60]fullerene). ^{1}H NMR (400 MHz, CS_2/$CDCl_3$): δ = 5.43 (s, 1 H), 4.59 (s, 2 H), 3.14 (s, 3 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 54.01, 152.67, 151.70, 149.90, 147.58, 147.47, 146.53, 146.49, 146.47, 146.42, 146.24 (3 C), 146.22, 146.04, 145.95, 145.83, 145.82, 145.73, 145.64, 145.60, 145.58, 145.55, 145.47 (2 C), 145.34, 145.23 (2 C), 144.73, 144.59, 144.55, 144.53, 143.19 (2 C), 142.85 (2 C), 142.83, 142.77, 142.35 (2 C), 142.29, 142.19 (2 C), 142.13, 142.10, 142.04 (2 C), 142.01, 141.92, 141.84, 140.50, 140.45, 140.28, 140.15, 138.11, 137.17, 136.62, 135.85, 114.75, 72.87, 69.42, 68.66, 67.03, 38.79 ppm. FTIR (KBr): $\tilde{\nu}$ = 2921, 2851, 2790, 2330, 1510, 1462, 1429, 1333, 1267, 1181, 1163, 1112, 1093, 1039, 885, 769, 600, 575, 554, 526, 479 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} = 260, 313, 428, 697 nm. MS (APCI): m/z = 803 [M + 1]$^+$, 776 [M – CN]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{64}H_6N_2$ [M]$^+$ 802.0531; found 802.0527.

Synthesis of *N*-Methyl-2-methylfulleropyrrolidine (10a) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 22.7 mg, 0.30 mmol) and ethyl bromide (**9a**,

327.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 3 h by the same procedure as above gave unreacted [60]fullerene (20.3 mg, 56%) and **10a**[14] (10.7 mg, 27% yield, 62% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 4.81 (d, J = 9.3 Hz, 1 H), 4.11 (d, J = 9.2 Hz, 1 H), 3.91 (q, J = 6.2 Hz, 1 H), 2.93 (s, 3 H), 2.00 (d, J = 6.3 Hz, 3 H) ppm.

Synthesis of *N*-Methyl-2-ethylfulleropyrrolidine (10b) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 22.7 mg, 0.30 mmol) and *n*-bromopropane (**9b**, 369.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 3 h by the same procedure as above gave unreacted [60]fullerene (21.9 mg, 61%) and **10b** (11.9 mg, 30% yield, 75% based on consumed [60]fullerene). ^{1}H NMR (600 MHz, CS_2/$CDCl_3$): δ = 4.83 (d, J = 9.4 Hz, 1 H), 4.20 (d, J = 9.5 Hz, 1 H), 3.89 (t, J = 5.2 Hz, 1 H), 3.02 (s, 3 H), 2.74–2.67 (m, 1 H), 2.64–2.56 (m, 1 H), 1.50 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (150 MHz, CS_2/$CDCl_3$): δ = 156.30, 154.37, 154.29, 153.32, 147.06, 147.03, 146.65, 146.32, 146.18, 146.14, 146.11, 146.03, 146.00, 145.93, 145.89, 145.82, 145.79, 145.65, 145.40, 145.33, 145.32, 145.30, 145.19, 145.12 (3 C), 145.08, 145.03, 144.61, 144.46, 144.26, 144.21, 143.06. 142.92, 142.55, 142.52 (2 C), 142.48, 142.06, 142.05 (2 C), 142.03, 142.02, 141.95, 141.93, 141.70, 141.59, 141.53, 140.17, 140.09, 139.70, 139.51, 137.09, 136.21, 135.71, 135.37, 79.35, 76.02, 70.32, 69.93, 39.75, 23.93, 12.17 ppm. FTIR (KBr): $\tilde{\nu}$ = 2957, 2923, 2855, 1530, 1460, 1429, 1265, 1184, 1105, 1095, 577, 552, 526 cm^{-1}. UV/Vis: λ_{max} = 257, 310, 431 nm. MS (APCI): m/z = 806 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{65}H_{11}N$ [M]$^+$ 805.0891; found 805.0887.

Synthesis of *N*-Ethyl-2-ethylfulleropyrrolidine (10c) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with *N*-ethylglycine (**1c**, 26.7 mg, 0.30 mmol) and *n*-bromopropane (**9b**, 369.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 3 h by the same procedure as above gave unreacted [60]fullerene (25.4 mg, 71%) and **10c** (10.5 mg, 26% yield, 87% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 4.94 (d, J = 9.8 Hz, 1 H), 4.13 (d, J = 9.7 Hz, 1 H), 4.10 (t, J = 5.4 Hz, 1 H), 3.72–3.58 (m, 1 H), 2.97–2.83 (m, 1 H), 2.64–2.45 (m, 2 H), 1.57 (t, J = 7.2 Hz, 3 H), 1.45 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, CS_2/$CDCl_3$): δ = 156.24, 154.71, 154.60, 153.36, 146.90, 146.87, 146.42, 146.20, 146.00 (2 C), 145.99, 145.89, 145.86, 145.78, 145.74, 145.69, 145.67, 145.50, 145.33, 145.28, 145.17, 145.15, 145.04 (2 C), 144.98 (2 C), 144.96, 144.90, 144.47, 144.33, 144.15, 144.12, 142.95, 142.82, 142.42, 142.40, 142.39, 142.36, 141.97, 141.96, 141.93, 141.89 (2 C), 141.85, 141.83, 141.81 (2 C), 141.59, 141.51, 141.45, 140.04, 139.99, 139.67, 139.42, 136.92, 136.11, 135.44, 135.24, 77.85, 75.85, 70.15, 66.24, 46.61, 23.91, 13.74, 12.10 ppm. FTIR (KBr): $\tilde{\nu}$ = 2957, 2921, 2860, 2796, 1530, 1456, 1430, 1400, 1183, 1099, 571, 526 cm^{-1}. UV/Vis: λ_{max} = 257, 309, 430 nm. MS (APCI): m/z = 820 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{66}H_{13}N$ [M]$^+$ 819.1048; found 819.1045.

Synthesis of *N*-Benzyl-2-ethylfulleropyrrolidine (10d) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with *N*-benzylglycine (**1d**, 49.5 mg, 0.30 mmol) and *n*-bromopropane (**9b**, 369.0 mg, 3.0 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 3 h by the same procedure as above gave unreacted [60]fullerene (26.7 mg, 74%) and **10d** (9.8 mg, 22% yield, 86% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 7.68 (d, J = 7.3 Hz, 2 H),7.50–7.40 (m, 2 H), 7.40–7.30 (m, 1 H), 4.84 (d, J = 13.0 Hz, 1 H), 4.71 (d, J = 10.0 Hz, 1 H), 4.26 (t, J = 5.3 Hz, 1 H), 4.12 (d, J = 10.0 Hz, 1 H), 3.92 (d, J = 13.0 Hz, 1 H), 2.73–2.57 (m, 2 H), 1.51 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CS_2/$CDCl_3$): δ = 156.36, 154.82, 154.65, 153.55, 147.03, 147.00, 146.59, 146.30, 146.12, 146.08 (2 C), 146.02, 145.98, 145.90, 145.86, 145.81, 145.80, 145.60, 145.51, 145.41, 145.29, 145.21, 145.16, 145.11 (3 C), 145.08, 145.01, 144.58, 144.44, 144.27, 144.23, 143.06, 142.92, 142.50, 142.45, 142.10, 142.08, 142.05, 142.00, 141.96, 141.95, 141.91, 141.89, 141.69, 141.58 (2 C), 140.10, 140.03, 139.76, 139.55, 138.38 (2 C), 136.97, 136.08, 135.61, 135.28, 128.71 (2 C), 128.62 (2 C), 127.41, 77.63, 76.12, 70.39, 66.76, 56.44, 23.73, 11.84 ppm. FTIR (KBr): $\tilde{\nu}$ = 3056, 3027, 2957, 2921, 2857, 1603, 1540, 1494, 1458, 1428, 1335, 1280, 1184, 1120, 1097, 1028, 799, 766, 725, 576, 552, 526 cm^{-1}. UV/Vis: λ_{max} = 257, 310, 430 nm. MS (APCI): m/z = 882 [M + 1]$^+$, 720 [C_{60}]$^+$. HRMS (MALDI FT-ICR): calcd for $C_{71}H_{15}N$ [M]$^+$ 881.1204; found 881.1206.

Synthesis of *N*-Methyl-2-propylfulleropyrrolidine (10e) in PhCl and DMSO: Treatment of [60]fullerene (36.0 mg, 0.05 mmol) with sarcosine (**1b**, 22.7 mg, 0.30 mmol) and *n*-bromobutane (**9c**, 343.0 mg, 2.5 mmol) in PhCl/DMSO (20 mL/10 mL) at 80 °C for 3 h by the same procedure as above gave unreacted [60]fullerene (14.1 mg, 39%) and **10e**[14] (15.4 mg, 38% yield, 62% based on consumed [60]fullerene). ^{1}H NMR (300 MHz, CS_2/$CDCl_3$): δ = 4.80 (d, J = 9.6 Hz, 1 H), 4.18 (d, J = 9.7 Hz, 1 H), 3.92 (t, J = 4.8 Hz, 1 H), 3.00 (s, 3 H), 2.57–2.46 (m, 1 H), 2.42–2.29 (m, 1 H), 2.04–1.90 (m, 2 H), 1.13 (t, J = 7.3 Hz, 1 H) ppm.

Supporting Information (see footnote on the first page of this article): ^{1}H NMR and ^{13}C NMR spectra of products **2a**–**c**, **4b**–**4e**, **5a**–**5g**, **6b**–**6d**, **8a**–**d** and **10a**–**e**.

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