JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

A Protocol for the Preparation of 2,5-Diaryl Fulleropyrrolidines: Thermal Reaction of [60]Fullerene with Aromatic Aldehydes and Arylmethanamines

Ji-Long Shi,[+,†] Xiao-Feng Zhang,[+,†] Hui-Juan Wang,[+,‡] Fa-Bao Li,[*,†] Xin-Xin Zhong,[†] Chun-Xiang Liu,[†] Li Liu,[*,†] Chao-Yang Liu,[*,‡] Hai-Mei Qin,[*,§] and Yong-Shun Huang[⊥]

[†]Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, and School of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, P. R. China

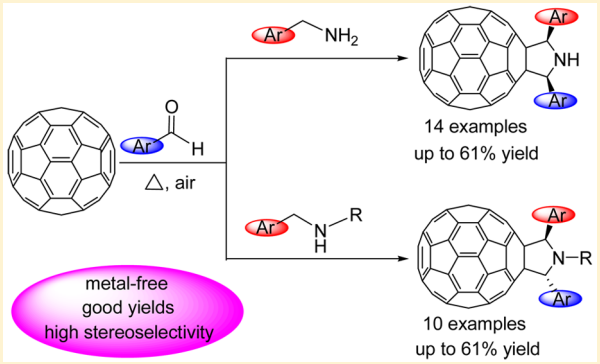
[‡]State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Center for Magnetic Resonance, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, P. R. China

[§]Fujian Provincial Key Lab of Theoretical and Computational Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China

[⊥]Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172, United States

Supporting Information

ABSTRACT: Thermal reaction of [60]fullerene with various arylmethanamines in the presence of aromatic aldehydes under air conditions afforded a series of rare 2,5-diaryl fulleropyrrolidines. Intriguingly, the obtained fulleropyrrolidines exhibited different stereoselectivity. *N*-unsubstituted arylmethanamines exclusively produced 2,5-diaryl fulleropyrrolidines as *cis* isomers, while *N*-substituted arylmethanamines with rare exceptions always gave 2,5-diaryl fulleropyrrolidines as *trans* isomers. Theoretical calculations at the level of B3LYP/6-31G (d,p) were employed to elucidate the stereoselectivity of *N*-substituted 2,5-diaryl fulleropyrrolidines as *trans* isomers by investigating the transition-state structures of different cycloaddition pathways.



INTRODUCTION

Fullerenes as novel carbon materials have attracted extensive attention over the past 30 years owing to their interesting "three-dimensional" all-carbon molecular structures. Among the known fullerenes, [60]fullerene (C_{60}) is the most representative and notable one as a result of its perfect symmetry, easy availability, and outstanding properties.[1] However, the poor solubility of C_{60} in polar organic solvents and water has blocked its application in many fields, such as materials and life sciences. Therefore, chemical modification of C_{60} to produce fullerene derivatives with structural and functional diversities is very important.[2,3] 1,3-Dipolar cycloaddition reaction is one of the most used and successful methods to functionalize fullerenes.[4] Among them, the well-known Prato reaction has been widely utilized to synthesize a large variety of pyrrolidine derivatives of fullerenes, which have exhibited a broad range of interesting features in material science, biological application, and nanotechnology.[5,6] Fulleropyrrolidine derivatives could also be prepared by several alternative approaches including thermal reactions with aziridines,[7,8] oxazolidinones,[7,9] trimethylsilyl amino derivatives,[10] α-amino acids and amino acid esters,[11] photochemical reactions with tertiary amines,[12] aminopolycarboxylic esters,[13a,b] and α-amino acid esters,[13c] as well as tautomerization of imines generated by the direct condensation of aldehydes and amines.[14] However, these known protocols still have great difficulty in the preparation of 2,5-diaryl fulleropyrrolidines, which may have promising applications in designing a wide range of diad and triad donor−acceptor systems to investigate their photophysical and electrochemical properties.[5b,c] For instance, only a few 2,5-diaryl fulleropyrrolidines have been synthesized by the Prato reaction because the starting materials, α-arylsubstituted amino acids, are not readily available.[5a,b] Troshin's group reported the synthesis of a few 2,5-dipyridyl fulleropyrrolidines via the tautomerization of imines due to the very limited scope of substrates.[14c] On the other hand, 2,5-disubstituted fulleropyrrolidines, with rare exceptions, are often obtained as a mixture of *cis* and *trans* isomers,[5a,b] which are extremely difficult to separate and characterize. Accordingly, it is still demanding to develop a highly efficient and versatile method for the synthesis of 2,5-diaryl fulleropyrrolidines with high stereoselectivity. To our

Received: June 8, 2016
Published: July 29, 2016

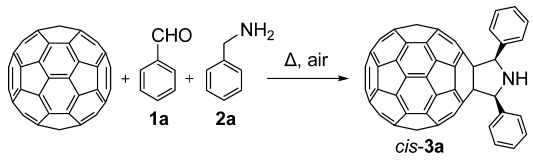
DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

delight, a major breakthrough in the synthesis of symmetrical 2,5-diaryl fulleropyrrolidines with high stereoselectivity has been recently realized by our group through the reaction of C_{60} with arylmethanamines under the assistance of $Fe(ClO_4)_3$.[15] Nevertheless, unsymmetrical 2,5-diaryl fulleropyrrolidines together with *N*-substituted 2,5-diaryl fulleropyrrolidines are still difficult to synthesize by our reported method. Additionally, the $Fe(ClO_4)_3$-mediated synthesis would meet a great challenge in the larger-scale preparation of symmetrical 2,5-diaryl fulleropyrrolidines owing to the use of highly explosive and expensive $Fe(ClO_4)_3$. In continuation of our interest in fullerene chemistry,[15,16] herein we describe a simple and versatile protocol for the highly stereoselective synthesis of 2,5-diaryl fulleropyrrolidines including symmetrical and unsymmetrical 2,5-diaryl fulleropyrrolidines together with *N*-substituted 2,5-diaryl fulleropyrrolidines by the facile one-step thermal reaction of C_{60} with aromatic aldehydes and arylmethanamines without the addition of expensive metal salts.

RESULTS AND DISCUSSION

Our study started with benzaldehyde (**1a**) and benzylamine (**2a**) as the model substrates to see if the corresponding 2,5-diaryl fulleropyrrolidine was formed. To our delight, the desired product *cis*-**3a** could be obtained in 14% isolated yield when the reaction of C_{60} with benzaldehyde (**1a**) and benzylamine (**2a**) was performed in a molar ratio of 1:2:2 in *o*-dichlorobenzene (ODCB) at 160 °C for 24 h under air conditions (entry 1, Table 1). To further improve the yield of *cis*-**3a**, various reaction conditions have been screened. Much to our satisfaction, the isolated yield of *cis*-**3a** could be significantly improved from 14 to 57% when the molar ratio of reaction was changed from 1:2:2 to 1:5:5 (entry 2 vs entry 1, Table 1). Increasing or decreasing the reaction temperature was unfavorable in improving the reaction efficiency (entries 3 and 4, Table 1). By varying the equivalents of the amount of benzaldehyde (from 2 to 8 equiv) or benzylamine (from 2 to 8 equiv), no improved isolated yields of *cis*-**3a** were observed (entries 5−8, Table 1). Moreover, when the reaction was conducted under nitrogen atmosphere, the yield of *cis*-**3a** obviously decreased from 57 to 45% (entry 9 vs entry 2, Table 1). Hence, the reagent molar ratio of C_{60}, **1a**, and **2a** as 1:5:5, the reaction temperature as 160 °C, the reaction solvent as ODCB together with the air conditions were selected as the optimized reaction conditions. It should be noted that the reactions of C_{60}, **1a**, and **2a** with the addition of HOAc or DBU were also examined under the optimized conditions because the previously reported literature has confirmed that the presence of HOAc or DBU has the positive effect on this kind of reaction.[14c] Unfortunately, the addition of HOAc and DBU to our reaction system was found to be detrimental to obtaining a higher product yields (entries 10 and 11, Table 1). In the presence of HOAc, the isolated yield of *cis*-**3a** noticeably reduced from 57 to 47% (entry 10 vs entry 2, Table 1). As for DBU, no expected *cis*-**3a** was obtained although C_{60} in the reaction solution was stepwise consumed (entry 11 vs entry 2, Table 1).

Table 1. Optimization of Reaction Conditions for Thermal Reaction of C_{60} with Benzaldehyde 1a and Benzylamine 2a[a]



entry	additive	molar ratio[b]	temp. (°C)	time (h)	yield (%) of *cis*-**3a**[c]
1	none	1:2:2:0	160	24	14 (93)
2	**none**	**1:5:5:0**	**160**	**6**	**57 (79)**
3	none	1:5:5:0	180	6	46 (69)
4	none	1:5:5:0	140	7	29 (55)
5	none	1:2:5:0	160	11	35 (97)
6	none	1:8:5:0	160	6	43 (52)
7	none	1:5:2:0	160	6	43 (93)
8	none	1:5:8:0	160	6	46 (72)
9[d]	none	1:5:5:0	160	6	45 (65)
10	HOAc	1:5:5:10	160	6	47 (65)
11	DBU	1:5:5:1	160	3	none

[a]Unless otherwise indicated, all reactions were performed under air conditions. [b]Molar ratio refers to C_{60}/**1a**/**2a**/additive. [c]Isolated yield; those in parentheses were based on consumed C_{60}. [d]The reaction was conducted under nitrogen conditions.

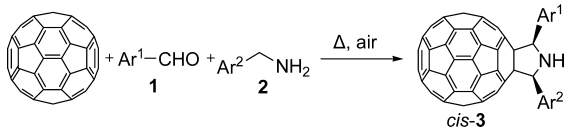
With the optimized conditions in hand, the substrate scope of this reaction was then explored. Representative aromatic aldehydes, such as benzaldehyde (**1a**), 4-methoxybenzaldehyde (**1b**), 2-chlorobenzaldehyde (**1c**), 4-chlorobenzaldehyde (**1d**), 1-naphthaldehyde (**1e**), and 2-thiophenaldehyde (**1f**), together with typical arylmethanamines, such as benzylamine (**2a**), 4-methoxybenzylamine (**2b**), 2-chlorobenzylamine (**2c**), 4-chlorobenzylamine (**2d**), 4-phenylbenzylamine (**2e**), 3,5-bis-(trifluoromethyl)benzylamine (**2f**), 1-naphthalenemethylamine (**2g**), and 2-thiophenemethylamine (**2h**), were chosen as the reaction substrates, and were found to generate the desired 2,5-diaryl fulleropyrrolidine **3a**−**n** as *cis* isomers. The reaction conditions and yields for the thermal reaction of C_{60} with aromatic aldehydes (**1a**−**f**) and arylmethanamines (**2a**−**h**) are summarized in Table 2.

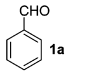
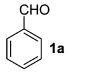
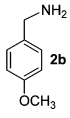
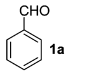
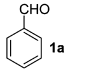
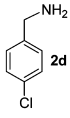
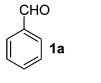
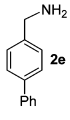
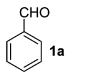
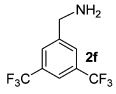
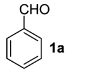
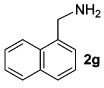
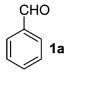
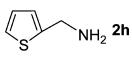
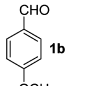
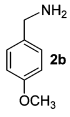
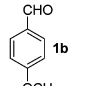
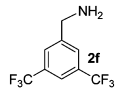
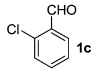
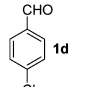
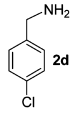
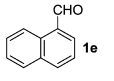
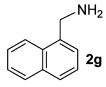
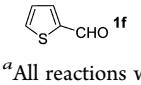
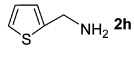
As can be seen from Table 2, all of the examined aromatic aldehydes (**1a**−**f**) as well as arylmethanamines (**2a**−**h**) afforded the expected 2,5-diaryl fulleropyrrolidines *cis*-**3a**−**n** in 20−61% isolated yields (63−98% yields based on consumed C_{60}), superior to the previously reported data for most fulleropyrrolidines.[7−15] For example, the isolated yields of symmetrical 2,5-diaryl fulleropyrrolidines *cis*-**3a**, *cis*-**3i**, and *cis*-**3k**−**n** in our previous study[15] were obtained in lower yields than these listed in Table 2. For the synthesis of *cis*-**3c**, decreasing the amount of benzaldehyde (**1a**) from 5 to 2 equiv avoided the formation of some unknown byproducts. As for *cis*-**3m**, the obvious reduction in product yield over the other fulleropyrrolidines under the same reaction conditions was attributed to the large steric hindrance of two naphthyl groups. It should be noted that the Cl functional group of *cis*-**3c**,**d** and *cis*-**3k**,**l** is a valuable handle, which could be tolerated under our experimental conditions and could be potentially further transformed into other moieties. In addition, further functionalization of *cis*-**3a**−**n** via the transformation of their NH group could afford a series of rare *N*-substituted 2,5-diaryl *cis*-fulleropyrrolidines, which would be extremely difficult to prepare by common methods.[15]

To expand the scope of the reaction, the substrates were extended from arylmethanamines to *N*-substituted arylmethanamines. *N*-methylbenzylamine (**4a**), *N*-ethylbenzylamine (**4b**), *N*-benzylisopropylamine (**4c**), *N*,*N*-dibenzylamine (**4d**), and *N*-phenylbenzylamine (**4e**) together with benzaldehyde (**1a**), 4-chlorobenzaldehyde (**1d**), 1-naphthaldehyde (**1e**), 2-thiophenaldehyde (**1f**), 4-methylbenzaldehyde (**1g**), and 4-nitro-

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

Table 2. Reaction Conditions and Yields for the Reaction of C_{60} with Aromatic Aldehydes 1 and Arylmethanamines 2[a]

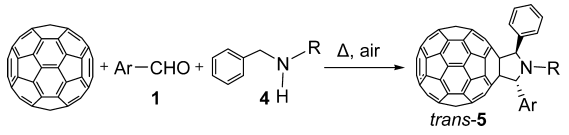


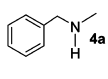
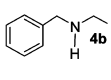
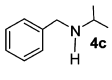
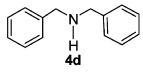
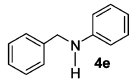
aldehyde **1**	amine **2**	product *cis*-**3**	time (h)	yield[b] (%)
		**3a**	6	57 (79)
		**3b**	5	61 (92)
		**3c**[c]	14	33 (92)
		**3d**	8	33 (97)
		**3e**	5	35 (97)
		**3f**	4	40 (71)
		**3g**	4	47 (94)
		**3h**	5	55 (95)
		**3i**	17	53 (96)
		**3j**	24	32 (97)
		**3k**	21	58 (95)
		**3l**	4	52 (98)
		**3m**	22	20 (91)
		**3n**	20	27 (63)

[a]All reactions were performed in *o*-dichlorobenzene (6 mL) under air conditions at 160 °C, molar ratio refers to C_{60}/**1**/**2** = 1:5:5. [b]Isolated yield, those in parentheses were based on consumed C_{60}. [c]The reaction of C_{60}, **1a**, and **2c** was conducted in a molar ratio of 1:2:5.

benzaldehyde (**1h**) were selected to react with C_{60}, and were found to afford the *N*-substituted 2,5-diaryl fulleropyrrolidines **5a-j** as *trans* isomers. The reaction conditions and yields for the reaction of C_{60} with aromatic aldehydes (**1a**, **1d–h**) and *N*-substituted arylmethanamines (**4a–e**) are listed in Table 3.

Table 3. Reaction Conditions and Yields for the Reaction of C_{60} with Aromatic Aldehydes 1 and *N*-Substituted Benzylamine 4[a]



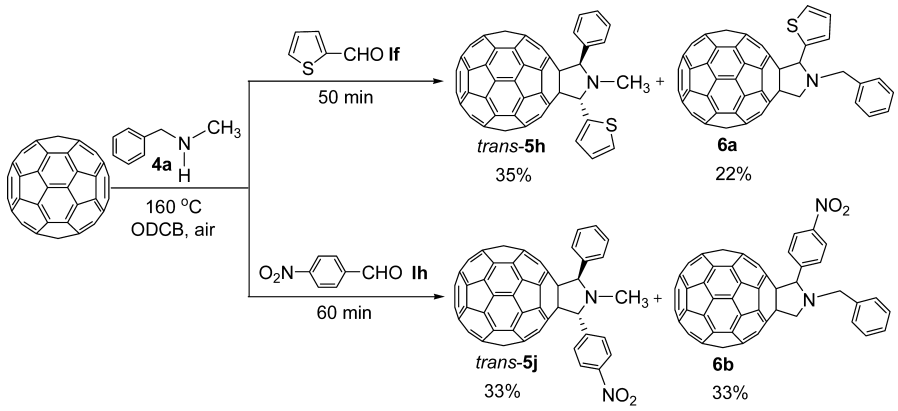
aldehyde **1**	amine **4**	product *trans*-**5**	time (h)	yield[b] (%)
		**5a**	0.5	55 (69)
		**5b**	2	59 (72)
		**5c**	4	37 (86)
		**5d**	2	61 (82)
		**5e**[c]	48	25[d] (38)
		5f	0.5	48 (72)
		5g	1	42 (59)
		5h	0.83	35 (51)
		5i	2	33 (89)
		5j	1	33 (52)

[a]All reactions were performed in *o*-dichlorobenzene (6 mL) under air conditions at 160 °C unless otherwise indicated, molar ratio refers to C_{60}/**1**/**4** = 1:5:5. [b]Isolated yield, those in parentheses were based on consumed C_{60}. [c]The reaction of C_{60}, **1a**, and **4e** was conducted at 180 °C. [d]Total isolated yield including both *cis* and *trans* isomers, the *trans*/*cis* ratio was determined as 4:1 based on the ^{1}H and ^{13}C NMR spectra.

It can be seen from Table 3 that *N*-substituted arylmethanamines containing alkyl, benzyl, and phenyl groups (**4a–e**) could readily react with aromatic aldehydes bearing electron-withdrawing groups or electron-donating groups (**1a**, **1d–h**) to afford *N*-substituted 2,5-diaryl fulleropyrrolidines **5a–j** as *trans* isomers in good to excellent yields (25–61% isolated yields). In the case of *N*-phenylbenzylamine (**4e**), raising the reaction temperature to 180 °C together with prolonging the reaction time to 48 h was required to obtain an acceptable product yield (25%) because the reactivity of **4e** was obviously lower than other *N*-substituted arylmethanamines probably due to the direct conjugation between the phenyl and amine groups. To our surprise, the obtained *N*-substituted 2,5-diaryl full-

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662–7674

Scheme 1. Reaction of C_{60} with 2-Thiophenaldehyde and 4-Nitrobenzaldehyde in the Presence of *N*-Methylbenzylamine



eropyrrolidine from **4e** was a mixture of *cis* and *trans* isomers. We surmised that this unusual behavior might arise from the further interconversion of *trans*-**5e** to *cis*-**5e** because a similar phenomenon has been reported in the literature by increasing the reaction temperature and extending the reaction time.[17] The polarities of *trans*-**5e** and *cis*-**5e** are almost the same, and thus the separation of two isomers on a silica gel column or Cosmosil Buckyprep column is very difficult (see HPLC spectrum of *trans*/*cis*-**5e** in Supporting Information). The *trans* isomer/*cis* isomer ratio was determined as 4:1 based on the ^{1}H and ^{13}C NMR spectra. As for the preparation of *trans*-**5h** and *trans*-**5j**, *N*-benzyl fulleropyrrolidines **6a**,**b** were also formed concurrently under the optimized conditions in 22% and 33% yield, respectively (Scheme 1). The poor selectivity for the formation of *trans*-**5h** and *trans*-**5j** relative to other *N*-substituted 2,5-diaryl fulleropyrrolidines was attributed to the higher reactivity of 2-thiophenaldehyde (**1f**) and 4-nitrobenzaldehyde (**1h**). The proposed reaction pathway for the formation of **6a**,**b** is outlined in Scheme S1 in Supporting Information. It should be noted that the reaction of C_{60} with *N*-substituted arylmethanamines (**4a**−**e**) in the presence of $Fe(ClO_4)_3$ to afford *trans*-**5a**−**e** was also investigated in our previous work.[15] Unfortunately, only *N*-methylbenzylamine (**4a**) gave the desired *trans*-**5a** as a major product despite the product yield (22%) was considerably lower than the current yield (55%) listed in Table 3. As for **4b**−**e**, less than 5% or a trace amount of product yield was commonly observed. To our disappointment, some unknown byproducts were always formed concurrently in the reactions of C_{60} with *N*-substituted arylmethanamines (**4a**−**e**) and aromatic aldehydes (**1a**, **1d**−**h**) although the amount is much lower than that of the desired products.

As known compounds, the identities of products *cis*-**3a**,[15,18] *cis*-**3i**,[15] *cis*-**3k**−**n**,[15] and *trans*-**5a**[12c,15] were confirmed by comparing their spectral data with those reported in the literature. As for new compounds *cis*-**3b**−**h**, *cis*-**3j**, *trans*-**5b**−**j**, and **6a**,**b**, their structures were fully characterized by MALDI-TOF MS, ^{1}H NMR, ^{13}C NMR, FT−IR, and UV−vis spectra. All new products gave the correct $[M+H]^+$ or $[M-H]^+$ peaks in their high-resolution mass spectra (HRMS). Their UV−vis spectra displayed a peak at 430−432 nm, which is a diagnostic absorption for 1,2-adducts of C_{60}, to which no heteroatom is directly attached. The IR spectra of *cis*-**3b**−**h** and *cis*-**3j** showed the characteristic absorptions at 3305−3318 cm^{-1} ascribed to the stretching vibrations of the NH group. In their ^{1}H NMR spectra, the anticipated chemical shifts together with the splitting patterns for all protons were clearly observed for *cis*-**3b**−**h**, *cis*-**3j**, *trans*-**5b**, *trans*-**5d**−**j**, and **6a**,**b**, yet the chemical shift values of the four phenyl protons on the two benzene rings of *trans*-**5c** were not detected although those from *trans*-**5a** and *trans*-**5b** were obviously uncovered. The exact reason for this is not clear, however the ^{13}C NMR signals for these aromatic carbons were observed. In their ^{13}C NMR spectra, products *cis*-**3b**−**h**, *cis*-**3j**, *trans*-**5f**−**j**, and **6a**,**b** exhibited similar spectral patterns, and there were at least 30 resolved peaks including some that were overlapped in the range of 134.33−155.95 ppm for the 58 sp^2-carbons of the fullerene cage and two peaks in the range of 73.09−79.25 ppm for the two sp^3-carbons of the fullerene skeleton, consistent with the C_1 molecular symmetry. Nevertheless, compounds *trans*-**5b**−**e** displayed different spectral patterns with the above-mentioned *cis*-**3b**−**h**, *cis*-**3j**, *trans*-**5f**−**j**, and **6a**,**b**. The observation of no more than 29 signals for the sp^2-carbons of the fullerene moiety agreed well with the C_2 symmetry of the molecular structures, and the two sp^3-carbons were located at 73.40−73.94 ppm. It should be noted that the ^{13}C NMR spectra of symmetrical fulleropyrrolidines *trans*-**5b**−**e** could be utilized to assign their stereochemistry. In our previous study,[15] the stereochemistry of symmetrical *cis*-fulleropyrrolidines have been successfully assigned based on the discovery of half-intensity peaks (corresponding to 1C) in their ^{13}C NMR spectra because the *cis* isomers of symmetrical fulleropyrrolidines should theoretically display 32 peaks including 4 half-intensity ones for the carbons of fullerene skeleton due to their C_s symmetry. As for the *trans* isomers of symmetrical fulleropyrrolidines, 30 peaks with equal intensity should be displayed in their ^{13}C NMR spectra because of their C_2 symmetry.[17] Experimentally, only equal intensity peaks were found in all ^{13}C NMR spectra of fulleropyrrolidines *trans*-**5b**−**d**. Hence, fulleropyrrolidines **5b**−**d** were unequivocally assigned as *trans* isomers. As for **5e** including both *cis* and *trans* isomers, the stereochemistry of the major product could be determined as a *trans* isomer because equal intensity peaks from the major product were also found in the ^{13}C NMR spectrum of **5e**. However, the stereochemistry of unsymmetrical fulleropyrrolidines *cis*-**3b**−**h**, *cis*-**3j**, and *trans*-**5f**−**j** could not be revealed from their ^{13}C NMR spectra owing to their C_1 symmetry. The nuclear Overhauser enhancement spectroscopy (NOESY) was thus employed to determine their stereochemistry. For fulleropyrrolidines *cis*-**3b**−**h** and *cis*-**3j**, their NOESY spectra should show cross peaks between the two methine protons on the tetrahydropyrrole ring, while the NOESY spectra of *trans*-**5f**−**j** would lack the cross peak

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

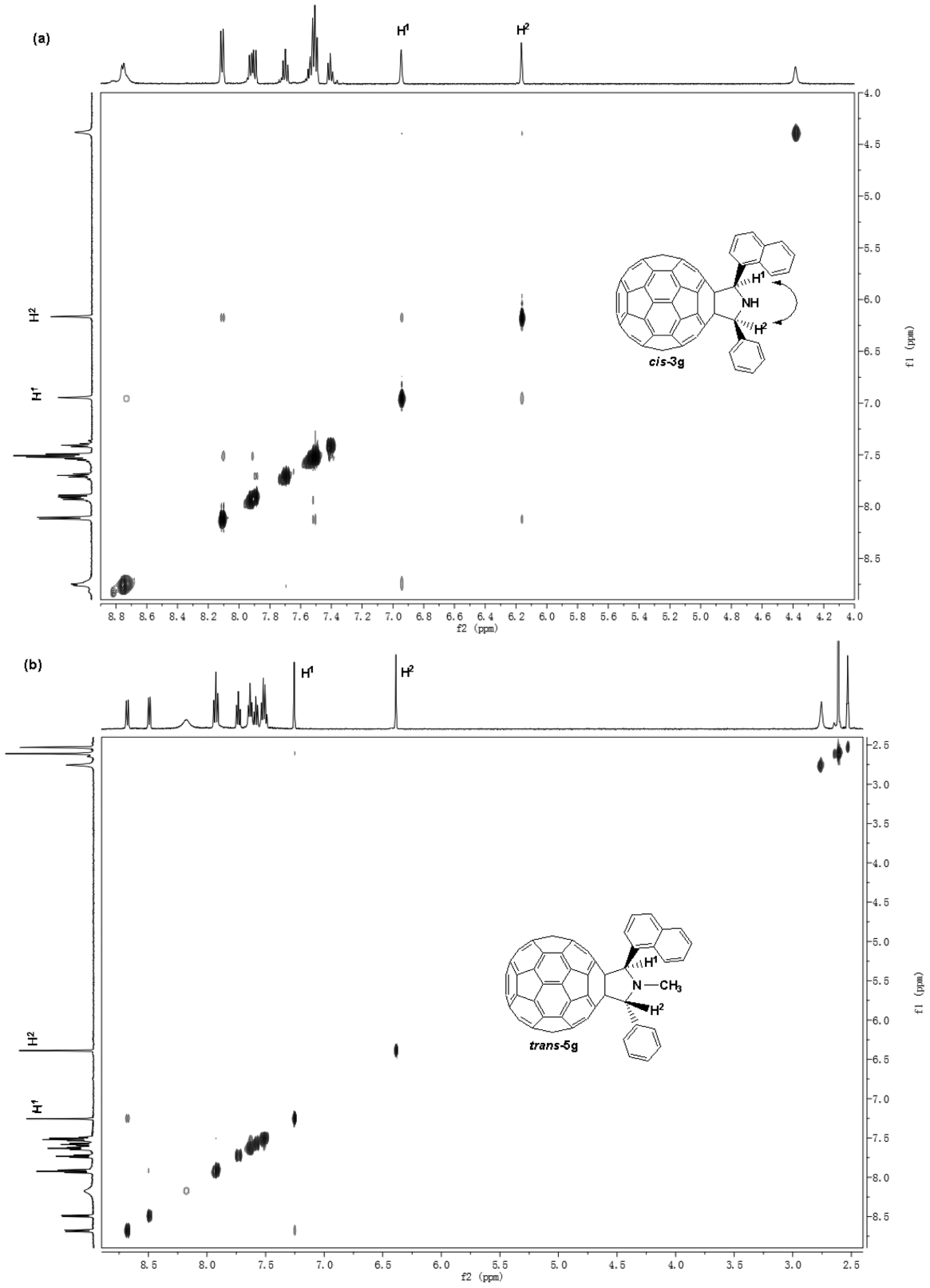


Figure 1. (a) NOESY spectrum of *cis*-**3g**, and the nuclear Overhauser effect between the two methine protons is indicated by the curved arrow. (b) NOESY spectrum of *trans*-**5g**.

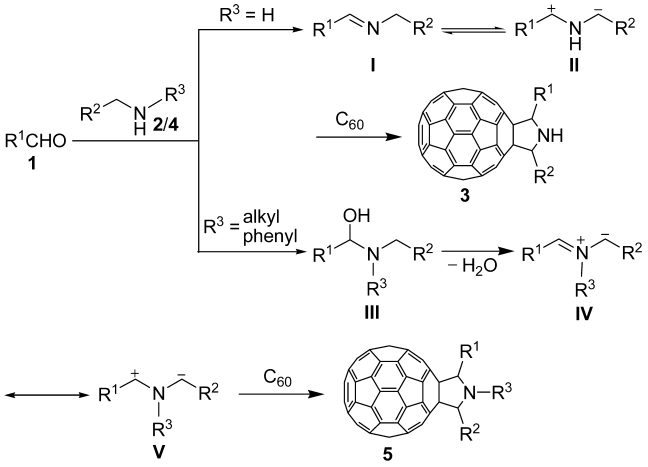
between them because the NOE-observable correlating distance was probably exceeded by the space distance between two methine protons. In fact, the NOESY spectrum of representative *cis*-**3j** clearly showed a correlation between the two methine protons (Figure 1a), yet the NOESY spectrum of typical *trans*-**5g** could not give any affirmative correlation between the two methine protons (Figure 1b). Accordingly, the assignments of *cis*-**3b**–**h**, *cis*-**3j**, and *trans*-**5f**–**j** were unambig-

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662–7674

uously confirmed based on their NOESY spectra. It should be noted that the NOESY spectra of *cis*-**3b** and *trans*-**5f** were also performed, but the nuclear Overhauser effect (NOE) between the two methine protons could not be estimated because the difference in chemical shifts of two methine protons was too small.

To account for the formation of 2,5-diaryl fulleropyrrolidines **3**/**5**, we proposed a possible reaction pathway (Scheme 2), as

Scheme 2. Proposed Formation Mechanism for 2,5-Diaryl Fulleropyrrolidines 3/5

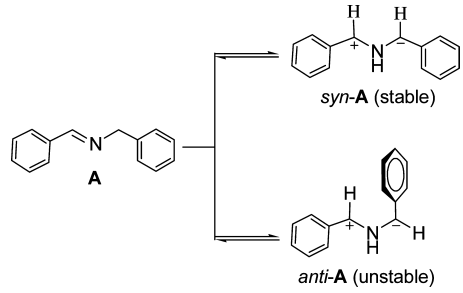


our previously reported.[15] An aromatic aldehyde **1** first reacts with arylmethanamine **2** or **4** to produce a Schiff-base imine intermediate **I** (R^3 = H) or an intermediate **III** (R^3 = alkyl or phenyl). In the case of intermediate **I**, a subsequent tautomerization results in the generation of azomethine ylide **II**, followed by cycloaddition to C_{60} to afford fulleropyrrolidine **3**. As for intermediate **III**, dehydration leads to the formation of a 1,2-dipole **IV** or a 1,3-dipole **V**, which can undergo a concerted 1,3-dipolar cycloaddition to C_{60} to give fulleropyrrolidine **5**.

In our previous study,[15] we have provided a plausible explanation for the highly stereoselective synthesis of symmetrical 2,5-diaryl fulleropyrrolidines as *cis* isomers. We considered that the high stereoselectivity of symmetrical 2,5-diaryl fulleropyrrolidines should be mainly ascribed to the stability of azomethine ylides. Similarly, the highly stereoselective synthesis of 2,5-diaryl fulleropyrrolidines *cis*-**3a**−**n** in the current work should also be attributed to the stability of azomethine ylides. A typical imine **A** by direct condensation of benzaldehyde and benzylamine was selected as a representative to elucidate the stereoselectivity of fulleropyrrolidines *cis*-**3a**−**n** (Scheme 3). Theoretically, imine **A** can undergo a thermal tautomerization to generate both syn-**A** and anti-**A**, of which syn-**A** is proposed to be more stable than anti-**A** due to the π conjugation of the coplanar conformation of syn-**A**, rather than a the twisted conformation of anti-**A**. This hypothesis is confirmed by theoretical calculations at the level of B3LYP/6-31G (d).[15] Hence, the *cis* isomer is expected to be the predominant product because the addition of the stable azomethine ylide syn-**A** to C_{60} can only afford fulleropyrrolidine *cis*-**3a**.

Compared with *cis*-**3a**−**n**, *N*-substituted 2,5-diaryl fulleropyrrolidines **5a**−**j** were dominantly obtained as *trans* isomers in most cases. The reversed stereoselectivity of **5a**−**j**

Scheme 3. Thermal Tautomerization of Imine A



should be attributed to the presence of a bulky group attached to the nitrogen atom. Three different conformations of the azomethine ylides, W-, U-, and S-shaped conformations (*trans*-**5a** as a representative, Figure 2), were considered by comparing

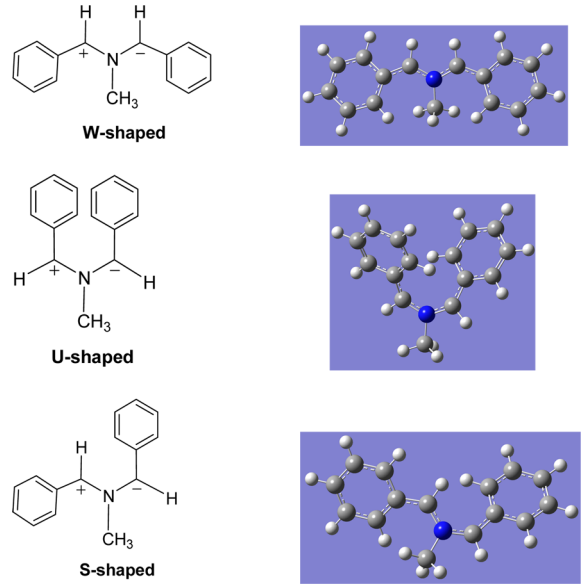


Figure 2. Conformations of intermediate **V** (when R^2 = Ph and R^3 = CH_3).

their stabilities via theoretical B3LYP/6-31G(d) calculations. Preliminary calculation results indicated that the S-shaped conformation is calculated to be slightly more stable than the U-shaped geometry, with the W-shaped conformation being the least stable.[15] This calculation result is consistent with the experimental observations. In this paper, further calculations based on the transition-state structures of different cycloaddition pathways are carried out to reveal the stereoselectivity of *trans*-**5a**, rather than the stability of three conformations.

In the current work, the formation of *trans*-**5a** was selected as a representative to illustrate the stereoselectivity of fulleropyrrolidines *trans*-**5a**−**j**. We recalculated the stabilities of three conformations (Figure 2) at the level of B3LYP/6-31G(d,p) at 298.15 K, and found that the relative Gibbs free energy of the S-shaped conformation is 1.50 and 12.00 kJ/mol more stable than that of the U- and W-shaped geometries, respectively, indicating the easier generation of S and U shapes than the W shape. Due to the difficult generation of W shape, we were wondering whether the W shape can be obtained by structural transformation from either S or U shapes. The structural transformation from S to U shapes was energetically profiled in Figure 3. This transformation requires an activation

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

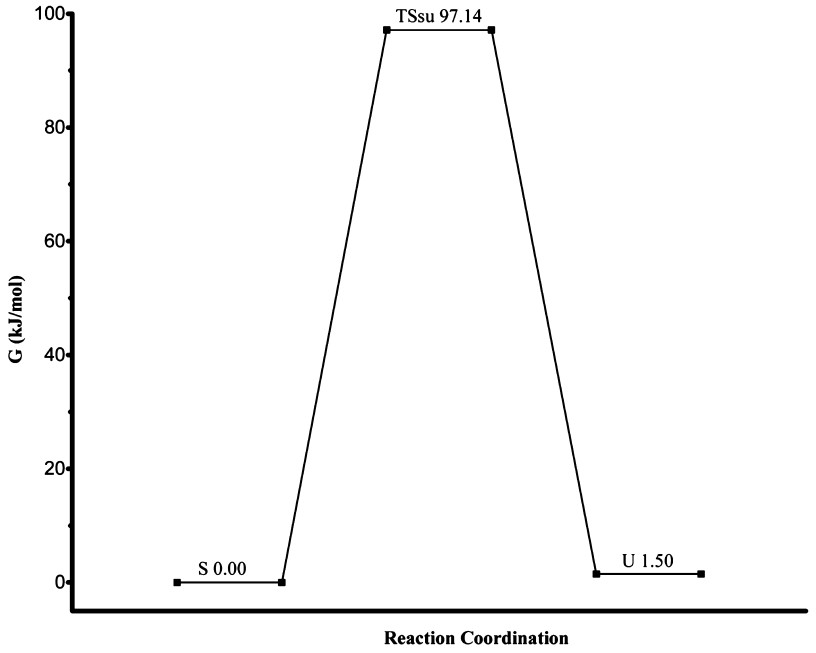


Figure 3. Energy profile for the transformation from S to U shape (Gibbs free energy at 298.15 K).

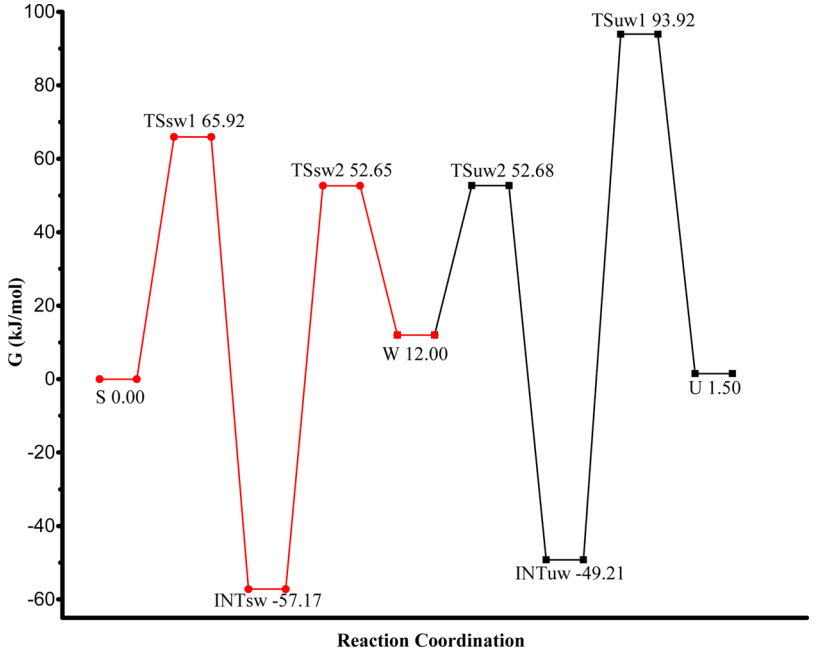


Figure 4. Energy profiles for the generation of W shape from either S or U shape (Gibbs free energy at 298.15 K).

energy as high as 97.14 kJ/mol from S to U shape, indicating the impossible structural transformation under our reaction conditions.

The relative energy profiles for the generation of the W shape from either the S or U shape are shown in Figure 4.

Different from the one-step structural transformation from S to U shapes, two-step mechanisms are required for the generation of W shape from either S or U shapes. Taking the formation of the W shape from the S shape as an example, the first step (TSsw1) requires an activation energy of 65.92 kJ/mol to produce an azocyclopropane as an intermediate (INTsw), which is 57.17 kJ/mol lower than the S shape. Starting from INTsw, an even higher activation energy (109.82 kJ/mol) is required to reach the W shape. A similar energy profile is observed for the generation of the W shape from the U shape.

The energy profiles in Figures 3 and 4 clearly indicate the impossible structural transformations among the S, W, and U shapes. Based on their relative Gibbs free energies, the S and U shapes will be generated, while only small amount of W will be produced. In this case, only the S and the U shape will be considered for their reactions with C_{60}.

When reacted with C_{60}, the S and U shapes will produce the *trans*- and *cis*- products, respectively. Considering the possible 5,6- and 6,6-bond reaction centers of C_{60}, four possible reaction products are possible, i.e., P56-S and P66-S from the S shape

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

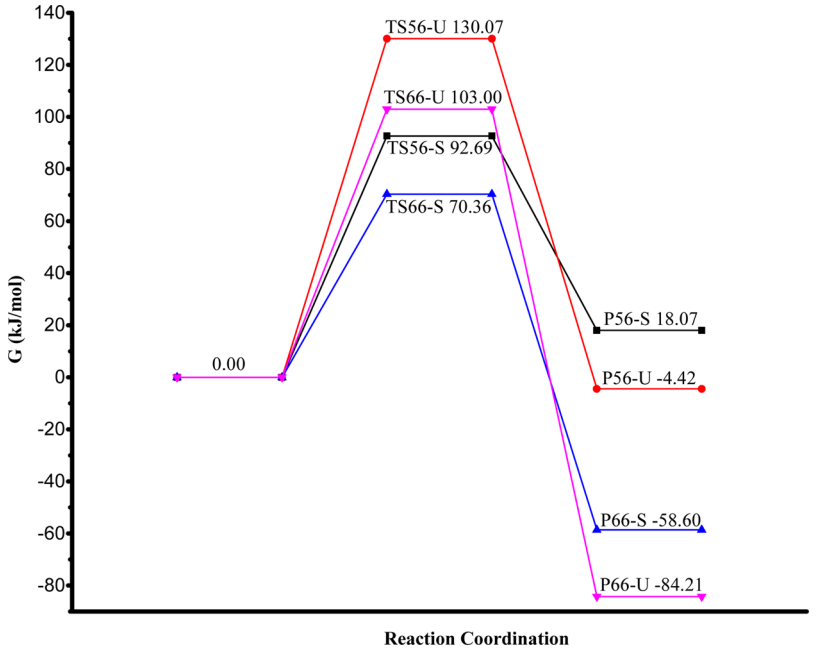


Figure 5. Reaction profile from the S and the U shapes with C_{60} at 298.15 K (Gibbs free energy).

with C_{60}, and P56-U and P66-U from the U shape with C_{60}. The reaction profiles are depicted in Figure 5.

The lowest activation energy is obtained for the reaction of the S shape at 6,6-bond of C_{60} (TS66-S) with a value of 70.36 kJ/mol, which is 22.33 kJ/mol lower than for its addition to the 5,6-bond of C_{60} (TS56-S). According to the Curtin-Hammett principle, P66-S (*trans*-) product will be predominant, which is consistent with our experimental results. The additions of the U shape to C_{60} have much higher activation energies for both 6,6- and 5,6-bonds, being 103.00 and 130.07 kJ/mol for TS66-U and TS56-U, respectively. As for the overall reaction energies, both 6,6-bond addition products, P66-U and P66-S, are lower in energies than the corresponding starting materials, indicating spontaneous processes. P56-U has a similar energy as the starting materials, while P56-S is 18.07 kJ/mol above that of the starting materials, indicating a nonspontaneous process. Moreover, this reaction activation energy (70.36 kJ/mol) is much lower than the structural transformation activation energies among the S, W, and U shapes (~100 kJ/mol) which further corroborates that the structural transformations among the S, W, and U shapes are impossible.

CONCLUSION

In summary, the synthesis of scarce 2,5-diaryl fulleropyrrolidines with high stereoselectivity has been successfully achieved via the simple one-step reaction of C_{60} with aromatic aldehydes and arylmethanamines. The current one-step approach to the preparation of 2,5-diaryl fulleropyrrolidines from cheap and easily accessible aromatic aldehydes and arylmethanamines is more powerful and versatile than the previous protocols.[14c,d,15] In addition, this current method also provides an immense opportunity for researchers in the field of novel carbon materials, such as fullerenes, endohedral fullerenes, carbon nanotubes, and onion-like fullerenes, to design and synthesize a large variety of novel organic photovoltaic materials based on their 2,5-diaryl pyrrolidine derivatives. Theoretical calculations by studying the transition-state structures of different cycloaddition pathways at the level of B3LYP/6-31G (d,p) were also carried out to illustrate clearly the stereoselectivity of *N*-substituted 2,5-diaryl fulleropyrrolidines as *trans* isomers.

EXPERIMENTAL SECTION

General Methods. All reagents and solvents were obtained commercially and were directly used without further purification. Thin layer chromatography (TLC) was chosen to monitor reaction process by using carbon disulfide/toluene as developing solvent. Flash chromatography over silica gel was utilized to purify all fullerene products. Chemical shifts in ^{1}H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm, yet chemical shifts in ^{13}C NMR spectra were referenced to residual DMSO at 39.52 ppm. HRMS was obtained by MALDI-TOF in positive-ion mode with 4-hydroxy-α-cyanocinnamic acid as the matrix.

Calculation Method. All calculations were performed with the help of Gaussian 09.[19] B3LYP/6-31G(d,p) was applied for the structural optimizations and energy calculaitons. For the transition state calculations, force constants were also calculated with B3LYP/6-31G(d,p) method and NoEigenTest keyword was applied to facilitate the transition state optimization. All zero-gradient structures were characterized by a vibrational analysis with no imaginary frequency. All of the transition-state structures had only one imaginary frequency, which was interpreted as a negative vibrational mode, and the intrinsic reaction coordinate (IRC)[20] was followed to make sure that each transition state connects the expected reactant and product.

General Procedure for the Preparation of Fulleropyrrolidines *cis*-3/*trans*-5. A mixture of C_{60} (36.0 mg, 0.05 mmol), aromatic aldehyde **1** (0.25 mmol), and arylmethylamine **2**/**4** (0.25 mmol) was added to a 50 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer. After the mixed compounds were completely dissolved in *o*-dichlorobenzene (6 mL) by sonication, the resulting solution was heated with stirring in an oil bath preset at 160 °C under air conditions. The reaction was carefully monitored by thin-layer chromatography (TLC) and stopped at the designated time. The reaction mixture was filtered through a silica gel plug in order to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to afford first unreacted C_{60}, and then fulleropyrrolidines *cis*-**3**/*trans*-**5** as amorphous brown solids.

*Fulleropyrrolidine cis-**3a**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **2a** (27 μL, 0.25 mmol) for 6 h afforded first unreacted C_{60} (10.0 mg,

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

28%), and then *cis*-**3a**[15,18] (26.0 mg, 57%) as an amorphous brown solid: mp >300 °C.

*Fulleropyrrolidine cis-**3b***. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **2b** (33 μL, 0.25 mmol) for 5 h afforded first unreacted C_{60} (12.3 mg, 34%), and then *cis*-**3b** (29.0 mg, 61%) as an amorphous brown solid: mp >300 °C.

cis-**3b**: ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.94 (d, *J* = 7.1 Hz, 2H), 7.84 (d, *J* = 7.1 Hz, 2H), 7.37 (t, *J* = 6.8 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 6.87 (d, *J* = 7.1 Hz, 2H), 5.88 (s, 1H), 5.85 (s, 1H), 4.19 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 158.59 (2C, aryl *C*), 153.50, 153.35, 153.12, 152.92, 146.19 (2C), 146.10, 146.09, 145.45, 145.29, 145.25 (2C), 145.22 (2C), 145.08 (2C), 144.83 (2C), 144.80, 144.60, 144.51, 144.49, 144.25 (2C), 144.18 (2C), 144.13 (2C), 143.70, 143.68, 143.40 (2C), 142.14, 142.00, 141.64 (2C), 141.57 (2C), 141.41 (2C), 141.23 (2C), 141.09 (4C), 140.98, 140.96, 140.53 (2C), 139.01, 138.95, 138.45, 138.32, 137.73 (aryl *C*), 136.10, 136.02, 135.14, 135.05, 129.43 (aryl *C*), 128.93 (aryl *C*), 128.86 (aryl *C*), 127.92 (aryl *C*), 127.77 (3C, aryl *C*), 127.45 (aryl *C*), 113.19 (aryl *C*), 75.97 (sp^3-*C* of C_{60}), 75.69 (sp^3-*C* of C_{60}), 74.19, 73.82, 54.17; FT-IR ν/cm^{-1} (KBr) 3315, 2921, 2851, 1611, 1510, 1460, 1429, 1375, 1249, 1170, 1037, 829, 699, 527; UV−vis ($CHCl_3$) λ_{max}/nm 257, 308, 432; MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{16}NO$ $[M+H]^+$ 946.1232, found 946.1210.

*Fulleropyrrolidine cis-**3c***. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (10 μL, 0.10 mmol) and **2c** (31 μL, 0.25 mmol) for 14 h afforded first unreacted C_{60} (22.9 mg, 64%), and then *cis*-**3c** (15.9 mg, 33%) as an amorphous brown solid: mp >300 °C.

cis-**3c**: ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.1 Hz, 2H), 7.40−7.34 (m, 4H), 7.28−7.23 (m, 2H), 6.44 (d, *J* = 3.0 Hz, 1H), 5.92 (d, *J* = 2.8 Hz, 1H), 4.28 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 153.54, 153.42, 153.18, 152.54, 146.21 (4C), 146.04, 145.26 (3C), 145.22 (2C), 145.06 (2C), 144.91 (2C), 144.87, 144.69, 144.66, 144.53, 144.38, 144.31, 144.25, 144.16 (3C), 143.64, 143.56, 143.47, 143.36, 142.09, 142.00, 141.72, 141.62 (3C), 141.50, 141.46, 141.33, 141.18, 141.16, 141.05, 141.02, 140.99, 140.88 (2C), 140.78, 140.57, 139.03, 138.71, 138.53, 138.42, 137.61 (aryl *C*), 135.92 (3C), 135.41, 134.34 (aryl *C*), 133.59 (aryl *C*), 130.44 (aryl *C*), 129.01 (aryl *C*), 128.43(aryl *C*), 127.94 (aryl *C*), 127.86 (aryl *C*), 127.79 (2C, aryl *C*), 127.53 (aryl *C*), 126.44 (aryl *C*), 75.84 (sp^3-*C* of C_{60}), 75.05 (sp^3-*C* of C_{60}), 73.79, 69.30; FT-IR ν/cm^{-1} (KBr) 3306, 2917, 2845, 1455, 1427, 1371, 1266, 1182, 1033, 998, 778, 760, 698, 544, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; MALDI-TOF MS *m*/*z* calcd for $C_{74}H_{13}ClN$ $[M+H]^+$ 950.0737, found 950.0712.

*Fulleropyrrolidine cis-**3d***. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **2d** (31 μL, 0.25 mmol) for 8 h afforded first unreacted C_{60} (23.8 mg, 66%), and then *cis*-**3d** (15.7 mg, 33%) as an amorphous brown solid: mp >300 °C.

cis-**3d**: ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.92 (d, *J* = 7.6 Hz, 4H), 7.38−7.33 (m, 4H), 7.27 (t, *J* = 6.8 Hz, 1H), 5.88 (s, 2H), 4.37 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 153.05, 152.73 (2C), 152.59, 146.17 (2C), 145.96, 145.81, 145.20 (5C), 145.06 (3C), 144.81 (2C), 144.70, 144.51 (3C), 144.22 (3C), 144.12 (3C), 143.63 (2C), 143.36, 143.35, 142.11, 141.98, 141.63 (2C), 141.55 (2C), 141.32 (2C), 141.18 (2C), 141.03 (3C), 140.98 (2C), 140.91, 140.52 (2C), 139.00, 138.95, 138.44, 138.37, 137.55 (aryl *C*), 136.48 (aryl *C*), 136.14, 135.95, 135.17, 135.04, 133.20 (aryl *C*), 129.26 (aryl *C*), 129.19 (aryl *C*), 127.83 (4C, aryl *C*), 127.77 (2C, aryl *C*), 127.49 (aryl *C*), 75.59 (sp^3-*C* of C_{60}), 75.50 (sp^3-*C* of C_{60}), 74.13, 73.33; FT-IR ν/cm^{-1} (KBr) 3318, 3021, 2920, 2849, 1489, 1454, 1428, 1376, 1277, 1172, 1088, 1015, 828, 780, 699, 527; UV−vis ($CHCl_3$) λ_{max}/nm 257, 307, 430; MALDI-TOF MS *m*/*z* calcd for $C_{74}H_{13}ClN$ $[M+H]^+$ 950.0737, found 950.0712.

*Fulleropyrrolidine cis-**3e***. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **2e** (45.8 mg, 0.25 mmol) for 5 h afforded first unreacted C_{60} (23.1 mg, 64%), and then *cis*-**3e** (17.5 mg, 35%) as an amorphous brown solid: mp >300 °C.

cis-**3e**: ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.40−7.32 (m, 4H), 7.30−7.22 (m, 2H), 5.95 (s, 1H), 5.92 (s, 1H), 4.30 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 153.22, 153.16, 152.96, 152.90, 146.24 (2C), 146.10 (2C), 145.39, 145.31 (5C), 145.14 (2C), 144.89 (2C), 144.84, 144.65, 144.59 (2C), 144.31 (3C), 144.24, 144.19 (2C), 143.72 (2C), 143.45 (2C), 142.19, 142.07, 141.71 (2C), 141.63 (2C), 141.44 (2C), 141.27 (2C), 141.13 (4C), 141.06, 141.01, 140.60 (2C), 139.98 (aryl *C*), 139.60 (aryl *C*), 139.10, 139.04, 138.56, 138.44, 137.73 (aryl *C*), 136.85 (aryl *C*), 136.24, 136.15, 135.18 (2C), 128.46 (2C, aryl *C*), 128.17 (2C, aryl *C*), 127.94 (2C, aryl *C*), 127.85 (2C, aryl *C*), 127.55 (aryl *C*), 126.71 (aryl *C*), 126.37 (2C, aryl *C*), 126.27 (2C, aryl *C*), 75.78 (sp^3-*C* of C_{60}), 75.74 (sp^3-*C* of C_{60}), 74.26, 74.01; FT-IR ν/cm^{-1} (KBr) 3313, 3025, 2919, 2849, 1510, 1485, 1454, 1426, 1376, 1277, 1180, 1114, 1096, 1075, 1006, 838, 761, 735, 697, 659, 526; UV−vis ($CHCl_3$) λ_{max}/nm 258, 308, 431; MALDI-TOF MS *m*/*z* calcd for $C_{80}H_{18}N$ $[M+H]^+$ 992.1439, found 992.1419.

*Fulleropyrrolidine cis-**3f***. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **2f** (61 mg, 0.25 mmol) for 4 h afforded first unreacted C_{60} (15.9 mg, 44%), and then *cis*-**3f** (21.2 mg, 40%) as an amorphous brown solid: mp >300 °C.

cis-**3f**: ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.51 (s, 2H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.82 (s, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.06 (s, 1H), 5.92 (s, 1H), 4.88 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 152.87, 152.61, 152.11, 151.80, 146.34, 146.30, 145.97, 145.41, 145.35 (4C), 145.22 (3C), 144.97 (2C), 144.77 (2C), 144.62 (2C), 144.45, 144.38 (3C), 144.30 (2C), 144.21, 143.80, 143.66, 143.55, 143.46, 142.27, 142.16, 141.78 (2C), 141.72, 141.66, 141.54, 141.46, 141.41, 141.35, 141.30, 141.17 (2C), 141.13, 141.05 (2C), 140.97, 140.70, 140.69, 139.22, 139.13, 138.62, 138.55, 137.39 (aryl *C*), 136.51, 135.94, 135.63, 135.17, 130.34 (q, J_{C-F} = 33 Hz, 2C, aryl *C*), 128.33 (2C, aryl *C*), 127.98 (2C, aryl *C*), 127.92 (2C, aryl *C*), 127.69 (aryl *C*), 122.52 (q, J_{C-F} = 272 Hz, 2C), 120.97 (aryl *C*), 75.80 (sp^3-*C* of C_{60}), 75.34 (sp^3-*C* of C_{60}), 74.26, 72.83; FT-IR ν/cm^{-1} (KBr) 3307, 2921, 2851, 1462, 1453, 1427, 1384, 1365, 1276, 1176, 1133, 1007, 898, 843, 706, 699, 681, 527; UV−vis ($CHCl_3$) λ_{max}/nm 257, 312, 430; MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{12}F_6N$ $[M+H]^+$ 1052.0874, found 1052.0849.

*Fulleropyrrolidine cis-**3g***. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **2g** (37 μL, 0.25 mmol) for 4 h afforded first unreacted C_{60} (18.1 mg, 50%), and then *cis*-**3g** (22.7 mg, 47%) as an amorphous brown solid: mp >300 °C.

cis-**3g**: ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.63 (d, *J* = 6.6 Hz, 2H), 7.98 (d, *J* = 7.1 Hz, 2H), 7.78 (t, *J* = 9.2 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.39−7.36 (m, 4H), 7.28 (t, *J* = 7.3 Hz, 1H), 6.81 (s, 1H), 6.03 (s, 1H), 4.25 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.00, 153.40, 153.05, 152.70, 146.37, 146.29, 146.20, 146.16, 145.33, 145.23 (2C), 145.20, 145.18, 145.05 (2C), 144.90, 144.85, 144.71 (2C), 144.59, 144.53, 144.42, 144.19 (5C), 144.09, 143.64, 143.61, 143.37, 143.32, 142.10, 141.95, 141.59 (4C), 141.41, 141.33, 141.20 (2C), 141.08 (2C), 141.05 (2C), 140.96, 140.78, 140.59, 140.51, 139.13, 138.56, 138.40, 138.34, 137.76 (aryl *C*), 136.18, 135.38, 135.35, 134.84, 134.07 (aryl *C*), 133.05 (aryl *C*), 131.25 (aryl *C*), 128.40 (aryl *C*), 127.96 (2C, aryl *C*), 127.82 (3C, aryl *C*), 127.53 (aryl *C*), 126.55 (aryl *C*), 125.25 (aryl *C*), 125.16 (aryl *C*), 124.92 (aryl *C*), 123.76 (aryl *C*), 76.07 (sp^3-*C* of C_{60}), 75.53 (sp^3-*C* of C_{60}), 73.93, 69.09; FT-IR ν/cm^{-1} (KBr) 3311, 3046, 2919, 2849, 1509, 1492, 1453, 1425, 1373, 1355, 1215, 1183, 786, 772, 698, 544, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 311, 432; MALDI-TOF MS *m*/*z* calcd for $C_{78}H_{16}N$ $[M+H]^+$ 966.1283, found 966.1259.

*Fulleropyrrolidine cis-**3h***. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **2h** (26 μL, 0.25 mmol) for 5 h afforded first unreacted C_{60} (15.2 mg, 42%), and then *cis*-**3h** (25.5 mg, 55%) as an amorphous brown solid: mp >300 °C.

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

cis-**3h**: ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.89 (d, J = 7.2 Hz, 2H), 7.40 (d, J = 2.1 Hz, 1H), 7.35 (t, J = 7.1 Hz, 2H), 7.30−7.24 (m, 2H), 6.99 (t, J = 7.7 Hz, 1H), 6.19 (s, 1H), 5.87 (s, 1H), 4.54 (s, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 152.99 (2C), 152.71, 152.59, 146.25 (2C), 146.16, 145.98, 145.50, 145.31 (2C), 145.26 (2C), 145.22, 145.10 (2C), 144.87 (3C), 144.63 (2C), 144.53, 144.33, 144.26 (2C), 144.22, 144.17 (2C), 143.72 (2C), 143.41 (2C), 142.18, 142.03, 141.77, 141.68 (3C), 141.63, 141.37, 141.34, 141.27 (2C), 141.15, 141.13, 141.08, 141.07 (2C), 140.99, 140.60, 140.53, 139.05, 138.99, 138.47, 138.38, 137.49 (aryl *C*), 136.29, 136.16, 135.17, 135.05, 127.81 (4C, aryl *C*), 127.53 (aryl *C*), 126.06 (aryl *C*), 125.43 (aryl *C*), 124.96 (aryl *C*), 75.61 (sp^3-*C* of C_{60}), 75.33 (sp^3-*C* of C_{60}), 74.12, 69.97; FT-IR ν/cm^{-1} (KBr) 3311, 2921, 2850, 1491, 1452, 1426, 1377, 1299, 1231, 1186, 1094, 1073, 763, 734, 699, 660, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 310, 431; MALDI-TOF MS m/z calcd for $C_{72}H_{12}NS$ $[M+H]^+$ 922.0691, found 922.0668.

*Fulleropyrrolidine cis-**3i**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (30 μL, 0.25 mmol) and **2b** (33 μL, 0.25 mmol) for 17 h afforded first unreacted C_{60} (16.2 mg, 45%), and then *cis*-**3i**[15] (25.6 mg, 53%) as an amorphous brown solid: mp >300 °C.

*Fulleropyrrolidine cis-**3j**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (30 μL, 0.25 mmol) and **2f** (61 mg, 0.25 mmol) for 24 h afforded first unreacted C_{60} (24.1 mg, 67%), and then *cis*-**3j** (17.5 mg, 32%) as an amorphous brown solid: mp >300 °C.

cis-**3j**: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 8.49 (s, 2H), 7.84 (d, J = 8.6 Hz, 2H), 7.81 (s, 1H), 6.89 (d, J = 8.6 Hz, 2H), 6.04 (s, 1H), 5.87 (s, 1H), 4.72 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 158.70 (aryl *C*), 153.02, 152.72, 152.00, 151.79, 146.28, 146.24, 145.90, 145.34 (2C), 145.29 (2C), 145.27 (2C), 145.16 (2C), 144.91 (2C), 144.71 (2C), 144.55, 144.52, 144.39, 144.33, 144.31, 144.29, 144.25 (2C), 144.14, 143.76, 143.60, 143.49, 143.39, 142.21, 142.09, 141.75, 141.73, 141.66, 141.59, 141.47 (aryl *C*), 141.42, 141.35, 141.29, 141.24, 141.13 (2C), 141.06, 141.03, 140.98, 140.91, 140.63 (2C), 139.14, 139.12, 138.65, 138.46, 136.46, 135.81, 135.56, 135.01, 130.31 (q, J_{C-F} = 33 Hz, 2C, aryl *C*), 129.02 (aryl *C*), 128.93 (2C, aryl *C*), 128.22 (2C, aryl *C*), 122.44 (q, J_{C-F} = 272 Hz, 2C), 120.86 (aryl *C*), 113.22 (2C, aryl *C*), 75.95 (sp^3-*C* of C_{60}), 75.22 (sp^3-*C* of C_{60}), 73.84, 72.80, 54.10; FT-IR ν/cm^{-1} (KBr) 3305, 2922, 2849, 1610, 1512, 1462, 1428, 1365, 1276, 1250, 1175, 1135, 1034, 1007, 898, 830, 784, 706, 681, 527; UV−vis ($CHCl_3$) λ_{max}/nm 257, 312, 431; MALDI-TOF MS m/z calcd for $C_{77}H_{14}F_6NO$ $[M+H]^+$ 1082.0980, found 1082.0953.

*Fulleropyrrolidine cis-**3k**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (28 μL, 0.25 mmol) and **2c** (31 μL, 0.25 mmol) for 21 h afforded first unreacted C_{60} (13.9 mg, 39%), and then *cis*-**3k**[15] (27.5 mg, 58%) as an amorphous brown solid: mp >300 °C.

*Fulleropyrrolidine cis-**3l**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (35 mg, 0.25 mmol) and **2d** (31 μL, 0.25 mmol) for 4 h afforded first unreacted C_{60} (17.0 mg, 47%), and then *cis*-**3l**[15] (24.7 mg, 52%) as an amorphous brown solid: mp >300 °C.

*Fulleropyrrolidine cis-**3m**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (34 μL, 0.25 mmol) and **2g** (37 μL, 0.25 mmol) for 22 h afforded first unreacted C_{60} (28.0 mg, 78%), and then *cis*-**3m**[15] (10.3 mg, 20%) as an amorphous brown solid: mp >300 °C.

*Fulleropyrrolidine cis-**3n**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (23 μL, 0.25 mmol) and **2h** (26 μL, 0.25 mmol) for 20 h afforded first unreacted C_{60} (20.6 mg, 57%), and then *cis*-**3n**[15] (12.5 mg, 27%) as an amorphous brown solid: mp >300 °C.

*Fulleropyrrolidine trans-**5a**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **4a** (32 μL, 0.25 mmol) for 0.5 h afforded first unreacted C_{60} (7.3 mg, 20%), and then *trans*-**5a**[12c,15] (25.5 mg, 55%) as an amorphous brown solid: mp >300 °C.

*Fulleropyrrolidine trans-**5b**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **4b** (37 μL, 0.25 mmol) for 2 h afforded first unreacted C_{60} (6.5 mg, 18%), and then *trans*-**5b** (27.7 mg, 59%) as an amorphous brown solid: mp >300 °C.

trans-**5b**: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.89 (br.s, 4H), 7.42 (t, J = 7.6 Hz, 4H), 7.32 (t, J = 7.5 Hz, 2H), 6.28 (s, 2H), 3.09−2.57 (m, 1H), 2.63−2.57 (m, 1H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 154.99, 153.07, 146.30, 145.27, 145.22, 145.15, 145.12, 144.96, 144.91, 144.54, 144.47, 144.23, 144.18, 144.05, 143.53 (4C), 142.10, 141.61, 141.49, 141.16, 141.08, 141.05, 140.97, 140.69, 140.63, 139.02, 138.58, 137.76 (aryl *C*), 135.71, 134.80, 129.12 (4C, aryl *C*), 127.98 (4C, aryl *C*), 127.56 (aryl *C*), 78.19 (1C), 76.36 (1C), 73.60 (sp^3-*C* of C_{60}), 39.97 (1C), 13.13 (1C); FT-IR ν/cm^{-1} (KBr) 3025, 2923, 2840, 1452, 1429, 1384, 1272, 1214, 1177, 964, 862, 744, 709, 700, 527; UV−vis ($CHCl_3$) λ_{max}/nm 258, 310, 432; MALDI-TOF MS m/z calcd for $C_{76}H_{18}N$ $[M+H]^+$ 944.1439, found 944.1419.

*Fulleropyrrolidine trans-**5c**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **4c** (42 μL, 0.25 mmol) for 4 h afforded first unreacted C_{60} (20.5 mg, 57%), and then *trans*-**5c** (17.5 mg, 37%) as an amorphous brown solid: mp >300 °C.

trans-**5c**: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.41 (br.s, 4H), 7.31 (t, J = 7.3 Hz, 2H), 6.42 (s, 2H), 3.76−3.69 (m, 1H), 1.60 (d, J = 7.1 Hz, 3H), 0.62 (d, J = 6.8 Hz, 3H); ^{13}C NMR (175 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 155.13, 153.36, 146.33, 145.31, 145.26, 145.21, 145.18, 145.00, 144.94, 144.55, 144.54, 144.27, 144.17, 144.07, 143.59, 143.53, 142.15, 141.67, 141.52, 141.28, 141.12, 141.08, 140.95, 140.75, 140.64, 139.59 (aryl *C*), 139.05, 138.57, 135.77, 134.98, 129.64 (4C, aryl *C*), 127.85 (4C, aryl *C*), 127.54 (aryl *C*), 74.31, 73.94 (sp^3-*C* of C_{60}), 46.24 (1C), 20.90 (1C), 16.87 (1C); FT-IR ν/cm^{-1} (KBr) 3054, 3027, 2959, 2918, 2847, 1484, 1452, 1428, 1361, 1289, 1267, 1189, 1152, 1122, 1064, 1028, 913, 737, 708, 526; UV−vis ($CHCl_3$) λ_{max}/nm 258, 311, 432; MALDI-TOF MS m/z calcd for $C_{77}H_{18}N$ $[M-H]^+$ 956.1439, found 956.1421.

*Fulleropyrrolidine trans-**5d**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **4d** (48 μL, 0.25 mmol) for 2 h afforded first unreacted C_{60} (9.5 mg, 26%), and then *trans*-**5d** (30.5 mg, 61%) as an amorphous brown solid: mp >300 °C.

trans-**5d**: ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 7.85 (br.s, 4H), 7.53 (d, J = 7.7 Hz, 2H), 7.43−7.39 (m, 6H), 7.35 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 6.22 (s, 2H), 4.33 (d, J = 14.5 Hz, 1H), 3.46 (d, J = 14.5 Hz, 1H). ^{13}C NMR (175 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 154.71, 152.92, 146.30, 145.23, 145.20, 145.17, 145.11, 144.98, 144.93, 144.51, 144.50, 144.25, 144.23, 144.06, 143.53, 143.50, 142.11, 141.63, 141.49, 141.20, 141.08, 141.04, 140.94, 140.71, 140.64, 139.08, 138.61, 137.24 (1C, aryl *C*), 136.96 (aryl *C*), 135.79, 134.85, 129.37 (4C, aryl *C*), 127.88 (4C, aryl *C*), 127.81 (aryl *C*), 127.72 (aryl *C*), 127.20 (aryl *C*), 126.46 (1C, aryl *C*), 75.45, 73.45 (sp^3-*C* of C_{60}), 46.36 (1C); FT-IR ν/cm^{-1} (KBr) 3056, 3024, 2920, 2849, 1599, 1491, 1452, 1427, 1355, 1297, 1213, 1182, 1156, 1122, 1070, 1027, 906, 866, 746, 728, 699, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 313, 432; MALDI-TOF MS m/z calcd for $C_{81}H_{20}N$ $[M+H]^+$ 1006.1596, found 1006.1575.

*Fulleropyrrolidine trans-**5e**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (25 μL, 0.25 mmol) and **4e** (39 μL, 0.25 mmol) at 180 °C for 48 h afforded first unreacted C_{60} (12.1 mg, 34%), and then *trans*-**5e**/*cis*-**5e** (12.4 mg, 25%) as amorphous brown solid: mp >300 °C.

trans-**5e**: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.76 (d, J = 7.4 Hz, 4H), 7.28 (t, J = 7.9 Hz, 4H), 7.19−7.15 (m, 2H), 7.11 (s, 2H), 7.05 (d, J = 7.9 Hz, 2H), 7.00 (t, J = 7.9 Hz, 2H), 6.67 (t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 154.87, 152.50, 146.49, 145.36, 145.33, 145.28, 145.09, 145.03, 144.88, 144.67, 144.62, 144.34, 144.33, 144.14, 143.92 (1C, aryl *C*), 143.65, 143.60, 142.21, 141.73, 141.63, 141.25, 141.20 (4C), 141.07, 140.78, 140.76, 139.12, 138.68, 138.57 (aryl *C*), 135.31, 134.48, 128.21 (4C, aryl *C*), 128.05 (4C, aryl *C*), 127.81 (aryl *C*), 127.26 (aryl *C*),

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

121.02 (aryl *C*), 119.72 (1C, aryl *C*), 76.23, 73.40 (sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 3055, 3027, 2919, 2847, 1597, 1495, 1453, 1427, 1353, 1316, 1262, 1213, 1187, 1077, 1029, 910, 851, 723, 708, 696, 526; UV−vis ($CHCl_3$) λ_{max}/nm 258, 311, 431; MALDI-TOF MS *m*/*z* calcd for $C_{80}H_{18}N$ $[M+H]^+$ 992.1439, found 992.1418.

*Fulleropyrrolidine trans-**5f**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (35 mg, 0.25 mmol) and **4a** (32 μL, 0.25 mmol) for 0.5 h afforded first unreacted C_{60} (11.7 mg, 33%), and then *trans*-**5f** (23.2 mg, 48%) as an amorphous brown solid: mp >300 °C.

trans-**5f**: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.89 (br.s, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 1H), 6.13 (s, 1H), 6.10 (s, 1H), 2.48 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.98, 154.42, 152.83, 152.59, 146.35 (2C), 145.28 (4C), 145.20, 145.13, 145.08, 145.01 (5C), 144.53 (4C), 144.32 (2C), 144.29 (2C), 144.12 (2C), 143.56 (4C), 142.17 (2C), 141.67 (2C), 141.57 (2C), 141.20, 141.12 (5C), 140.97 (2C), 140.76 (2C), 140.72 (2C), 139.10 (2C), 138.74, 138.70, 137.28 (aryl *C*), 135.95, 135.86, 135.83, 135.01, 134.65 (aryl *C*), 133.65 (aryl *C*), 130.60 (2C, aryl *C*), 129.34 (2C, aryl *C*), 128.08 (2C, aryl *C*), 128.02 (2C, aryl *C*), 127.70 (aryl *C*), 78.33, 77.39, 73.87 (sp^3-*C* of C_{60}), 73.70 (sp^3-*C* of C_{60}), 34.50; FT-IR ν/cm^{-1} (KBr) 2921, 2850, 1597, 1489, 1462, 1424, 1356, 1291, 1216, 1183, 1125, 1090, 1012, 831, 701, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 312, 432; MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{16}ClN$ $[M+H]^+$ 965.0971, found 965.0950.

*Fulleropyrrolidine trans-**5g**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (34 μL, 0.25 mmol) and **4a** (32 μL, 0.25 mmol) for 1 h afforded first unreacted C_{60} (10.4 mg, 29%), and then *trans*-**5g** (20.3 mg, 42%) as an amorphous brown solid: mp >300 °C.

trans-**5g**: ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 8.58 (d, *J* = 8.9 Hz, 1H), 8.40 (d, *J* = 7.4 Hz, 1H), 8.05 (br.s, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 14.8, 8.4 Hz, 2H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 6.8 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44−7.40 (m, 3H), 7.16 (s, 1H), 6.26 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 155.95, 154.01, 153.62, 152.93, 146.35, 146.33, 145.77, 145.54, 145.26, 145.21 (3C), 145.02, 145.00, 144.96 (2C), 144.81 (2C), 144.59, 144.50 (2C), 144.46, 144.32 (2C), 144.26, 144.16 (2C), 144.05, 143.61 (2C), 143.51, 143.43, 142.16, 142.11, 141.68 (2C), 141.55, 141.50, 141.30, 141.14 (2C), 141.09, 141.05 (2C), 140.99, 140.93 (2C), 140.66 (2C), 140.56, 139.11, 138.93, 138.58 (2C), 137.89 (aryl *C*), 136.21, 135.11, 134.96, 134.61, 133.28 (aryl *C*), 132.81 (aryl *C*), 132.06 (aryl *C*), 129.63 (2C, aryl *C*), 128.62 (aryl *C*), 128.14 (2C, aryl *C*), 127.96 (aryl *C*), 127.72 (aryl *C*), 127.00 (aryl *C*), 125.60 (aryl *C*), 124.91 (aryl *C*), 124.85 (aryl *C*), 123.06 (aryl *C*), 78.88, 74.57 (sp^3-*C* of C_{60}), 73.53 (sp^3-*C* of C_{60}), 70.82, 34.40; FT-IR ν/cm^{-1} (KBr) 3043, 2919, 2851, 1591, 1510, 1493, 1453, 1429, 1212, 1181, 1119, 791, 775, 701, 526; UV−vis ($CHCl_3$) λ_{max}/nm 258, 311, 432; MALDI-TOF MS *m*/*z* calcd for $C_{79}H_{18}N$ $[M+H]^+$ 980.1439, found 980.1417.

*Fulleropyrrolidines trans-**5h** and **6a**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (23 μL, 0.25 mmol) and **4a** (32 μL, 0.25 mmol) for 50 min afforded first unreacted C_{60} (11.0 mg, 31%), then **6a** (10.3 mg, 22%) and *trans*-**5h** (16.3 mg, 35%) as amorphous brown solid: mp >300 °C.

trans-**5h**: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.78 (br.s, 2H), 7.51 (d, *J* = 2.6 Hz, 1H), 7.48 (d, *J* = 5.0 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.48 (s, 1H), 5.98 (s, 1H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 155.55, 152.92, 152.77, 151.92, 146.29, 146.25, 145.66, 145.42, 145.21 (3C), 145.12, 145.06, 145.02, 144.92, 144.87 (2C), 144.59 144.55, 144.52, 144.45, 144.37, 144.31, 144.26, 144.19, 144.14, 144.08, 144.03, 143.63, 143.58, 143.41, 143.36, 142.09, 142.00, 141.64, 141.56, 141.51, 141.44, 141.24, 141.15, 141.09, 141.04, 140.99, 140.97, 140.94, 140.88, 140.71, 140.61 (2C), 140.55, 139.62 (aryl *C*), 138.98, 138.88, 138.74, 138.44, 136.53, 136.03 (aryl *C*), 135.74, 135.34, 134.74, 128.81 (2C, aryl *C*), 128.78 (aryl *C*), 127.80 (2C, aryl *C*), 127.66 (aryl *C*), 126.29 (aryl *C*), 126.08 (aryl *C*), 77.09, 74.58 (sp^3-*C* of C_{60}), 74.39, 73.09 (sp^3-*C* of C_{60}), 34.45; FT-IR ν/cm^{-1} (KBr) 2921, 2851, 1460, 1441, 1429, 1356, 1279, 1215, 1174, 1026, 827, 747, 699, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 311, 432; MALDI-TOF MS *m*/*z* calcd for $C_{73}H_{14}NS$ $[M + H]^+$ 936.0847, found 936.0825.

6a: ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 2.8 Hz, 1H), 7.40−7.38 (m, 3H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.03 (dd, *J* = 4.8, 3.4 Hz, 1H), 5.55 (s, 1H), 4.77 (d, *J* = 10.0 Hz, 1H), 4.66 (d, *J* = 13.9 Hz, 1H), 4.14 (d, *J* = 10.0 Hz, 1H), 3.67 (d, *J* = 13.9 Hz, 1H); ^{13}C NMR (175 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.99, 152.91, 152.31, 152.10, 146.28, 146.27, 145.94, 144.92 (3C), 144.79, 144.64, 144.56, 144.47, 144.43, 144.39, 144.34, 144.25, 144.22 (3C), 144.12, 143.71, 143.68, 143.38, 143.35, 142.15, 141.98, 141.69, 141.60 (2C), 141.57, 141.31, 141.21, 141.16, 141.14 (2C), 141.05, 141.04, 141.01, 140.92, 140.89, 140.65, 140.64, 139.89 (aryl *C*), 139.22, 139.19, 138.95, 138.63, 136.65 (aryl *C*), 136.08, 135.64, 135.02, 134.69, 128.04 (2C, aryl *C*), 127.90 (2C, aryl *C*), 127.26 (aryl *C*), 126.85 (aryl *C*), 126.24 (aryl *C*), 125.96 (aryl *C*), 75.97 (sp^3-*C* of C_{60}), 75.58 (sp^3-*C* of C_{60}), 67.29, 65.63, 56.14; FT-IR ν/cm^{-1} (KBr) 3054, 3021, 2915, 2782, 1489, 1452, 1426, 1330, 1306, 1180, 1155, 1119, 1028, 765, 746, 697, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 431; MALDI-TOF MS *m*/*z* calcd for $C_{73}H_{14}NS$ $[M+H]^+$ 936.0847, found 936.0825.

*Fulleropyrrolidine trans-**5i**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1g** (30 μL, 0.25 mmol) and **4a** (32 μL, 0.25 mmol) for 2 h afforded first unreacted C_{60} (22.6 mg, 63%), and then *trans*-**5i** (15.4 mg, 33%) as an amorphous brown solid: mp >300 °C.

trans-**5i:** ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.88 (br.s, 2H), 7.76 (br.s, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 6.9 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.09 (s, 1H), 6.06 (s, 1H), 2.46 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 155.18, 154.92, 153.23, 153.11, 146.36 (2C), 145.48, 145.40, 145.29 (2C), 145.25, 145.23 (2C), 145.20, 145.04, 145.03, 144.99 (2C), 144.61 (2C), 144.53, 144.51, 144.32 (2C), 144.29 (2C), 144.13 (2C), 143.60 (4C), 142.19 (2C), 141.69 (2C), 141.57 (2C), 141.25, 141.20, 141.16 (3C), 141.13, 141.04 (2C), 140.79, 140.76, 140.72 (2C), 139.10, 139.07, 138.73, 138.67, 137.40 (aryl *C*), 137.05, 135.88 (2C), 134.96, 134.81, 134.42 (aryl *C*), 129.32 (4C, aryl *C*), 128.72 (2C, aryl *C*), 127.96 (2C, aryl *C*), 127.63 (aryl *C*), 78.24, 78.15, 74.00 (sp^3-*C* of C_{60}), 73.96 (sp^3-*C* of C_{60}), 34.57, 20.75; FT-IR ν/cm^{-1} (KBr) 3022, 2913, 2842, 2795, 1509, 1493, 1439, 1427, 1356, 1294, 1214, 1178, 1125, 1077, 1025, 867, 746, 700, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 310, 432; MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{18}N$ $[M+H]^+$ 944.1439, found 944.1417.

*Fulleropyrrolidine trans-**5j** and **6b**.* According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1h** (38 mg, 0.25 mmol) and **4a** (32 μL, 0.25 mmol) for 1 h afforded first unreacted C_{60} (13.2 mg, 37%), then **6b** (16.0 mg, 33%) and *trans*-**5j** (15.9 mg, 33%) as amorphous brown solid: mp >300 °C.

trans-**5j**: ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.26 (d, *J* = 7.9 Hz, 2H), 8.16 (br.s, 2H), 7.92 (br.s, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 6.32 (s, 1H), 6.15 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (175 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.73, 153.63, 152.49, 151.71, 146.69 (aryl *C*), 146.28, 146.24, 145.20, 145.17 (2C), 145.09, 145.04, 144.95, 144.92, 144.90, 144.89, 144.80, 144.74, 144.63, 144.58, 144.49, 144.40 (2C), 144.38, 144.25, 144.24, 144.17 (2C), 144.06, 144.01, 143.50, 143.45, 143.38 (2C), 142.08 (2C), 141.61, 141.56, 141.50, 141.48, 141.08, 141.03 (2C), 140.99, 140.92 (2C), 140.82, 140.79, 140.67, 140.64, 140.61, 140.59, 139.08, 139.00, 138.65, 138.59, 137.01 (aryl *C*), 135.81, 135.71, 135.12, 134.33, 129.93 (2C, aryl *C*), 129.31 (2C, aryl *C*), 128.01 (2C, aryl *C*), 127.71 (aryl *C*), 122.82 (2C, aryl *C*), 78.40, 77.01, 73.60 (sp^3-*C* of C_{60}), 73.53 (sp^3-*C* of C_{60}), 34.42; FT-IR ν/cm^{-1} (KBr) 3016, 2939, 2843, 2796, 1602, 1520, 1492, 1427, 1342, 1215, 1180, 1109, 854, 701, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 313, 431; MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{15}N_2O_2$ $[M+H]^+$ 975.1134, found 975.1113.

6b: ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 8.31 (d, *J* = 8.5 Hz, 2H), 8.13 (br.s, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 5.31 (s, 1H), 4.89 (d, *J* = 9.9 Hz, 1H), 4.49 (d, *J* = 13.7 Hz, 1H), 4.21 (d, *J* = 9.9 Hz, 1H), 3.70 (d, *J* = 13.7 Hz, 1H); ^{13}C

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

NMR (175 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 154.93, 152.69, 151.55, 151.23, 147.00 (aryl *C*), 146.36, 146.32, 145.39, 145.37, 145.36, 145.34, 145.27 (2C), 145.20, 145.17, 145.01 (2C), 144.74, 144.70, 144.64, 144.61, 144.51 (2C), 144.42, 144.40, 144.39, 144.31, 144.25, 144.23, 143.78, 143.61, 143.54 (aryl *C*), 143.49, 143.37, 142.23, 142.10, 141,79, 141.71, 141.66, 141.63, 141.35, 141.29, 141.23, 141.18, 141.12, 141.11, 141.07, 141.00, 140.87 (2C), 140.76, 140.68, 139.39, 139.32, 139.09, 138.63, 136.25 (2C), 135.38, 135.37, 134.77 (aryl *C*), 129.40 (2C, aryl *C*), 128.09 (2C, aryl *C*), 128.03 (2C, aryl *C*), 127.08 (aryl *C*), 123.18 (2C, aryl *C*), 79.25 (sp^3-*C* of C_{60}), 75.22 (sp^3-*C* of C_{60}), 67.71, 65.58, 55.91; FT-IR ν/cm^{-1} (KBr) 3024, 2915, 2783, 1600, 1522, 1493, 1427, 1341, 1181, 1106, 858, 843, 736, 698, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 311, 431; MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{15}N_2O_2$ $[M+H]^+$ 975.1134, found 975.1113.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01389.

Proposed formation mechanism of compounds **5h,j** and **6a,b**; NMR spectra of products *cis*-**3a−n**, *trans*-**5a−j**, and **6a,b**; UV−vis spectra of *cis*-**3j**, *trans*-**5g**, and **6b**; HRMS of *cis*-**3d**, *trans*-**5c**, and **6a**, B3LYP/6-31G(d,p) calculated Gibbs free energies of all the species from *trans*-**5a** in Hartrees; and B3LYP/6-31G(d,p)-optimized Cartesian coordinates of all the species from *trans*-**5a** (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*lfb0615@hubu.edu.cn.
*liulihubei@hubu.edu.cn.
*chyliu@wipm.ac.cn.
*hmqin@xmu.edu.cn.

Author Contributions

[+]J.-L.S., X.-F.Z., and H.-J.W. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for the financial support from National Natural Science Foundation of China (Nos. 21102041 and 21503073), Scientific Research Foundation of Education Commission of Hubei Province (No. Q20120113), Natural Science Foundation of Hubei Province (No. 2014CFB550), and Natural Science Fund for Creative Research Groups of Hubei Province of China (No. 2014CFA015).

■ REFERENCES

(1) (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−163. (b) Kraetschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354−358.

(2) For selected reviews, see: (a) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807−815. (b) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891−4946. (c) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, 6083−6094. (d) Guldi, D. M.; Illescas, B. M.; Atienza, C. M.; Wielopolski, M.; Martín, N. *Chem. Soc. Rev.* **2009**, *38*, 1587−1597. (e) Vougioukalakis, G. C.; Roubelakis, M. M.; Orfanopoulos, M. *Chem. Soc. Rev.* **2010**, *39*, 817−844. (f) Zhu, S.-E; Li, F.; Wang, G.-W. *Chem. Soc. Rev.* **2013**, *42*, 7535−7570.

(3) For selected reviews, see: (a) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049−5135. (b) Giacalone, F.; Martín, N. *Chem. Rev.* **2006**, *106*, 5136−5190. (c) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016−3028. (d) Tzirakis, M. D.; Orfanopoulos, M. *Chem. Rev.* **2013**, *113*, 5262−5321. For selected papers, see: (e) Zheng, M.; Li, F.-F.; Ni, L.; Yang, W.-W.; Gao, X. *J. Org. Chem.* **2008**, *73*, 3159−3168. (f) Lu, S.; Jin, T.; Kwon, E.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 802−806. (g) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2013**, *15*, 4650−4653. (h) Liu, T.-X.; Zhang, Z.; Liu, Q.; Zhang, P.; Jia, P.; Zhang, Z.; Zhang, G. *Org. Lett.* **2014**, *16*, 1020−1023. (i) Wu, A.-J.; Tseng, P.-Y.; Hsu, W.-H.; Chuang, S.-C. *Org. Lett.* **2016**, *18*, 224−227.

(4) For selected reviews on 1,3-dipolar cycloadditions, see: (a) Hirsch, A. *Synthesis* **1995**, *1995*, 895−913. (b) Yurovskaya, M. A.; Trushkov, I. V. *Russ. Chem. Bull.* **2002**, *51*, 367−443. (c) Delgado, J. L.; Martin, N.; de la Cruz, P.; Langa, F. *Chem. Soc. Rev.* **2011**, *40*, 5232−5241.

(5) For selected reviews on fulleropyrrolidines, see: (a) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519−526. (b) Tagmatarchis, N.; Prato, M. *Synlett* **2003**, 0768−0779. (c) Troshin, P. A.; Peregudov, A. S.; Troyanov, S. I.; Lyubovskaya, R. N. *Russ. Chem. Bull.* **2008**, *57*, 887−912.

(6) Matsumoto, K.; Hashimoto, K.; Kamo, M.; Uetani, Y.; Hayase, S.; Kawatsura, M.; Itoh, T. *J. Mater. Chem.* **2010**, *20*, 9226−9230.

(7) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798−9799.

(8) Maggini, M.; Scorrano, G.; Bianco, A.; Toniolo, C.; Sijbesma, R. P.; Wudl, F.; Prato, M. *J. Chem. Soc., Chem. Commun.* **1994**, 305−306.

(9) Maggini, M.; Karlsson, A.; Pasimeni, L.; Scorrano, G.; Prato, M.; Valli, L. *Tetrahedron Lett.* **1994**, *35*, 2985−2988.

(10) (a) Zhang, X.; Willems, M.; Foote, C. S. *Tetrahedron Lett.* **1993**, *34*, 8187−8188. (b) Iyoda, M.; Sultana, F.; Komatsu, M. *Chem. Lett.* **1995**, 1133−1134.

(11) Zhu, S.-E; Cheng, X.; Li, Y.-J.; Mai, C.-K.; Huang, Y.-S.; Wang, G.-W.; Peng, R.-F.; Jin, B.; Chu, S.-J. *Org. Biomol. Chem.* **2012**, *10*, 8720−8729.

(12) (a) Lawson, G. E.; Kitaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. *J. Chem. Soc., Chem. Commun.* **1995**, 2225−2226. (b) Liou, K.-F.; Cheng, C.-H. *Chem. Commun.* **1996**, 1423−1424. (c) Wu, S.-H.; Zhang, D.-W.; Wang, G.-W.; Shu, L.-H.; Wu, H.-M.; Xu, J.-F.; Lao, X.-F. *Synth. Commun.* **1997**, *27*, 2289−2298.

(13) (a) Zhou, D.; Tan, H.; Luo, C.; Gan, L.; Huang, C.; Pan, J.; Lu, M.; Wu, Y. *Tetrahedron Lett.* **1995**, *36*, 9169−9172. (b) Gan, L.; Zhou, D.; Luo, C.; Tan, H.; Huang, C.; Lu, M.; Pan, J.; Wu, Y. *J. Org. Chem.* **1996**, *61*, 1954−1961. (c) Gan, L.; Jiang, J.; Zhang, W.; Su, Y.; Shi, Y.; Huang, C.; Pan, J.; Lu, M.; Wu, Y. *J. Org. Chem.* **1998**, *63*, 4240−4247.

(14) (a) Shu, L. -H.; Wang, G. -W.; Wu, S. -H.; Wu, H. -M.; Lao, X. -F. *Tetrahedron Lett.* **1995**, *36*, 3871−3874. (b) Wu, S.-H.; Sun, W.-Q.; Zhang, D.-W.; Shu, L.-H.; Wu, H.-M.; Xu, J.-F.; Lao, X.-F. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1733−1738. (c) Troshin, P. A.; Peregudov, A. S.; Mühlbacher, D.; Lyubovskaya, R. N. *Eur. J. Org. Chem.* **2005**, *2005*, 3064−3074. (d) Troshin, P. A.; Kornev, A. B.; Peregudov, A. S.; Peregudova, S. M.; Lyubovskaya, R. N. *Mendeleev Commun.* **2007**, *17*, 116−118.

(15) Shi, J.-L.; Li, F.-B.; Zhang, X.-F.; Wu, J.; Zhang, H.-Y.; Peng, J.; Liu, C.-X.; Liu, L.; Wu, P.; Li, J.-X. *J. Org. Chem.* **2016**, *81*, 1769−1777.

(16) (a) Li, F.-B.; Zhu, Y.-F.; Zhang, X.-F.; Shi, J.-L.; Wu, J.; Chen, L.; Liang, X.-X.; Liu, L. *RSC Adv.* **2014**, *4*, 48085−48094. (b) Wu, J.; Li, F.-B.; Zhang, X.-F.; Shi, J.-L.; Liu, L. *RSC Adv.* **2015**, *5*, 30549−30544. (c) Zhang, X.-F.; Li, F.-B.; Wu, J.; Shi, J.-L.; Liu, Z.; Liu, L. *J. Org. Chem.* **2015**, *80*, 6037−6043. (d) Zhang, X.-F.; Li, F.-B.; Shi, J.-L.; Wu, J.; Liu, L. *New J. Chem.* **2016**, *40*, 1626−1632.

(17) Wang, G.-W.; Tian, Z.-G. *Tetrahedron Lett.* **2009**, *50*, 3860−3863.

(18) Tan, X.; Schuster, D.; Wilson, S. *Tetrahedron Lett.* **1998**, *39*, 4187−4190.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin,

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674

K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford CT, 2009.

(20) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161−4163.

DOI: 10.1021/acs.joc.6b01389
J. Org. Chem. 2016, 81, 7662−7674