JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

$Cu(OAc)_2$-Mediated Reaction of [60]Fullerene with Aldehydes and Primary Amines for the Synthesis of Fulleropyrrolines

Jun Wu,[‖,†] Chun-Xiang Liu,[‖,†] Hui-Juan Wang,[‖,‡] Fa-Bao Li,[*,†] Ji-Long Shi,[†] Li Liu,[†] Jia-Xing Li,[*,§] Chao-Yang Liu,[*,‡] and Yong-Shun Huang[§]

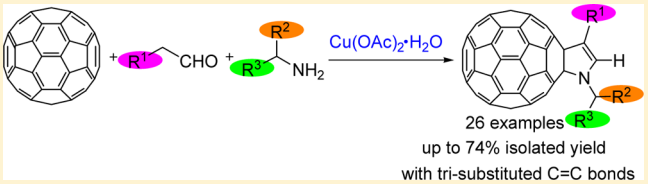
[†]Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, and School of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, People's Republic of China

[‡]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, People's Republic of China

[§]Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei 230031, People's Republic of China

Supporting Information

ABSTRACT: The facile one-step reaction of [60]fullerene with aldehydes and primary amines in the presence of cheap and easily available $Cu(OAc)_2·H_2O$ afforded a series of new types of fulleropyrrolines with trisubstituted C=C bonds in good to excellent yields, which would be difficult to prepare by known methods. The formed fulleropyrroline under the assistance of $Pd(OAc)_2$ and $CuCl_2·2H_2O$ could be further converted to 1-fulleropyrrolidine by the chlorohydroxylation reaction of C=C bond. Subsequent elimination reaction of 1-fulleropyrrolidine with the aid of $TsOH·H_2O$ generated the scarce 1-fulleropyrroline derivative.



INTRODUCTION

Chemical modification of fullerenes to introduce versatile functional groups onto fullerene skeletons has received extensive attention over the past decades because the functionalization of fullerenes not only increases their solubilities in water and/or polar organic solvents but also tunes their energy levels and packing structures, which would expand their applications in many fields, such as material science, biological application, nanotechnology, and so on.[1,2] Radical addition reactions induced by transition metal salts in place of traditional peroxide or light have proven to be a powerful tool to functionalize fullerenes,[3] and numerous novel fullerene derivatives with different structural motifs have been successfully prepared under the assistance of diverse types of transition metal salts. Among the reported transition metal salts, the Cu(II)/Cu(I) salts have recently attracted special attention among the scientific community due to their low toxicity, easy availability, inexpensive price, and insensitivity to air and water.[4,5] The first example for the use of Cu(II)/Cu(I) salts to functionalize fullerenes was reported by Wang's group through the $Cu(OAc)_2$-mediated reaction of [60]fullerene (C_{60}) with ketonic compounds.[4a] Since then, $CuCl_2/CuBr_2$ and CuBr/CuI were also successfully employed to functionalize fullerenes.[5] In comparison with the extensively investigated Mn(III)[4a,6] and Fe(III)[2b,7] salts, the Cu(II)/Cu(I) salts are still underdeveloped because only a few papers in this research field were reported.[4,5] Further exploration and development of new types of fullerene reactions promoted by the Cu(II)/Cu(I) salts is still demanding.

Fulleropyrrolines are a kind of important fullerene derivative, which may have promising applications in designing and synthesizing novel organic photovoltaic materials due to the heterocyclic ring bearing a C=C bond, which can be utilized to construct a series of completely conjugated donor−acceptor (D−A) systems. These D−A systems such as the fully conjugated porphyrin−fullerene system linked through a molecular wire have displayed unique photoelectronic properties.[8] To date, only two works describing the synthesis of fulleropyrrolines have been reported.[5e,6b] Wang et al. realized the first synthesis of fulleropyrrolines via the $Mn(OAc)_3$-mediated reaction of C_{60} with β-enamino carbonyl compounds.[6b] Yang's group described the preparation of fulleropyrrolines through a three-component reaction of C_{60} with amines and dimethyl acetylenedicarboxylate (DMAD) in the presence of $CuCl_2$.[5e] Nevertheless, the above-mentioned approaches only led to the formation of fulleropyrrolines with tetra-substituted C=C bonds, which would limit their further modifications. On the other hand, the aforementioned protocols for the synthesis of fulleropyrrolines still have some synthetic limitations. For example, Wang's method requires the preparation of β-enamino carbonyl compounds in advance together with the use of the relatively expensive $Mn(OAc)_3$.[6b]

Received: August 2, 2016
Published: September 21, 2016

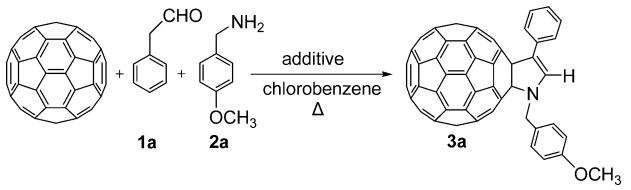
DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

Yang's protocol gave low yields (<30% in most cases) along with a poor product selectivity, such as the strong electron-withdrawing groups.[5e] Thus, it is still a demand to develop a more practical and convenient approach to prepare fulleropyrrolines, especially for those with trisubstituted C=C bonds, which have never been obtained so far. In continuation of our interest in fullerene chemistry,[7f−i,9] herein we describe a simple and efficient protocol to prepare a series of new fulleropyrrolines with trisubstituted C=C bonds through the $Cu(OAc)_2$-mediated one-step reaction of C_{60} with aldehydes and primary amines.

RESULTS AND DISCUSSION

Phenylacetaldehyde (**1a**) and 4-methoxybenzylamine (**2a**) were first chosen to react with C_{60} without the addition of any additives. No desired fulleropyrroline **3a** was obtained by heating in chlorobenzene at 100 °C for 120 min in air (Table 1, entry 1). However, when $Cu(OAc)_2·H_2O$ (2 equiv) was added, the desired product **3a** can be obtained within 15 min in 61% yield (Table 1, entry 2). Increasingly the reaction temperature to 120 °C led to a slightly lower yield (60%, Table 1, entry 3), while decreasing the reaction temperature to 80 °C dramatically decreased the isolated yield (9%, Table 1, entry 4). No benefit to the yields could be achieved by adjusting the equivalents of $Cu(OAc)_2·H_2O$ (Table 1, entries 5−7). Similar results were also observed by varying the equivalents of phenylacetaldehyde (**1a**) and/or 4-methoxybenzylamine (**2a**; Table 1, entries 8−11). The reaction atmosphere was also examined by carrying out the reaction under nitrogen protection (Table 1, entry 12), no improvement was observed, indicating no influence of oxygen in the reaction mechanism. Adding 4A molecular sieves or using anhydrous $Cu(OAc)_2$ could also not improve the isolated yield of product **3a** (Table 1, entries 13 and 14). Therefore, the optimum reaction condition was set as a molar ratio of C_{60}, $Cu(OAc)_2·H_2O$, **1a**, and **2a** to be 1:2:5:5, the reaction temperature as 100 °C in air (Table 1, entry 2). It should be noted that other metal salts such as $Mn(OAc)_3·2H_2O$, $Pb(OAc)_4$, $FeCl_3$, $FeCl_3·6H_2O$, $CuCl_2$, $CuCl_2·2H_2O$, $CuSO_4$, $CuSO_4·5H_2O$, $Fe(ClO_4)_3·xH_2O$, and $(NH_4)_2Ce(NO_3)_6$ were also screened to replace $Cu(OAc)_2·H_2O$ under the optimized conditions (Table 1, entries 15−24), indicating the superior oxidation effect of $Cu(OAc)_2·H_2O$ over other metal salts.

Table 1. Optimization of Reaction Conditions for the Reaction of C_{60} with Phenylacetaldehyde 1a and 4-Methoxybenzylamine 2a under the Assistance of Metal Salts



entry	additive	molar ratio[b]	temp. (°C)	time (min)	yield (%) of 3a[c]
1	none	1:0:5:5	100	120	none
2	**$Cu(OAc)_2·H_2O$**	**1:2:5:5**	**100**	**15**	**61 (81)**
3	$Cu(OAc)_2·H_2O$	1:2:5:5	120	10	60 (73)
4	$Cu(OAc)_2·H_2O$	1:2:5:5	80	17	9 (43)
5	$Cu(OAc)_2·H_2O$	1:3:5:5	100	10	54 (79)
6	$Cu(OAc)_2·H_2O$	1:1:5:5	100	25	51 (69)
7	$Cu(OAc)_2·H_2O$	1:0.2:5:5	100	15	10 (26)
8	$Cu(OAc)_2·H_2O$	1:2:10:5	100	10	45 (73)
9	$Cu(OAc)_2·H_2O$	1:2:1:5	100	120	trace
10	$Cu(OAc)_2·H_2O$	1:2:5:10	100	5	57 (61)
11	$Cu(OAc)_2·H_2O$	1:2:5:1	100	120	trace
12[d]	$Cu(OAc)_2·H_2O$	1:2:5:5	100	10	60 (91)
13[e]	$Cu(OAc)_2·H_2O$	1:2:5:5	100	15	61 (78)
14	$Cu(OAc)_2$	1:2:5:5	100	15	58 (78)
15	$Mn(OAc)_3·2H_2O$	1:2:5:5	100	25	34 (89)
16	$Pb(OAc)_4$	1:2:5:5	100	45	9 (90)
17	$FeCl_3$	1:2:5:5	100	60	19 (79)
18	$FeCl_3·6H_2O$	1:2:5:5	100	80	15 (88)
19	$CuCl_2$	1:2:5:5	100	22	15 (45)
20	$CuCl_2·2H_2O$	1:2:5:5	100	15	16 (62)
21	$CuSO_4$	1:2:5:5	100	120	none
22	$CuSO_4·5H_2O$	1:2:5:5	100	120	none
23	$Fe(ClO_4)_3·xH_2O$	1:2:5:5	100	120	none
24	$(NH_4)_2Ce(NO_3)_6$	1:2:5:5	100	65	trace

[a]Unless otherwise indicated, all reactions were performed under air conditions. [b]Molar ratio refers to C_{60}/additive/**1a**/**2a**. [c]Isolated yields; those in parentheses, were based on consumed C_{60}. [d]The reaction was performed under nitrogen conditions. [e]200 mg of 4A molecular sieves were added to this reaction.

With the optimized reaction condition in hand, we started to explore the substrate scope of the reaction. Representative aldehydes **1a−c** were chosen to react with typical arylmethanamines **2a−k**, and were found to afford the desired fulleropyrrolines **3a−m**. The reaction conditions and isolated yields were summarized in Table 2.

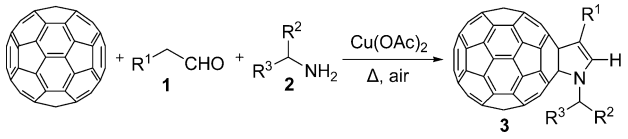
As can be seen from Table 2, all the examined aldehydes (**1a−c**) together with arylmethanamines including phenylmethanamines (**2a−f**), 1-naphthalenemethylamine (**2g**), 2-thiophenemethylamine (**2h**), and α-substituted phenylmethanamines (**2i−k**) could afford the expected fulleropyrrolines **3a−m** in 14−62% isolated yields (38−90% yields based on consumed C_{60}). In comparison with phenylmethanamines without electron-withdrawing groups (**2a−c,f**), the product yields from electron-withdrawing phenylmethanamines (**2d,e**) are obviously lower and thus a higher reaction temperature (130 °C) was applied for the synthesis of **3d,e**. In the case of 2-thiophenemethylamine (**2h**), increasing the reaction temperature to 130 °C could provide an acceptable yield (25%) of **3h**. As for aminodiphenylmethane (**2k**), elevated reaction temperature (130 °C) was also required to compensate the steric hindrance from two phenyl groups. As compared with reactive phenylacetaldehyde, alphatic aldehydes, hexaldehyde (**1b**), and *iso*-pentaldehyde (**1c**) exhibited relatively lower reactivities even at elevated reaction temperatures to produce **3l,m**.

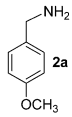
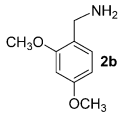
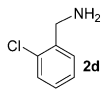
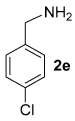
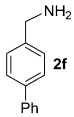
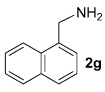
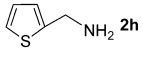
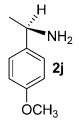
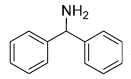
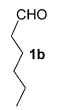
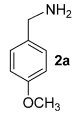
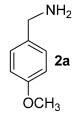
To expand the scope of the reaction, the substrates were further extended from arylmethanamines to other representative amines, The reaction of C_{60} with amines **4a−k** and aldehydes **1a,b** in the presence of $Cu(OAc)_2$ produced the anticipated fulleropyrrolines **5a−m**. The reaction conditions and isolated yields were listed in Table 3.

It can be seen from Table 3 that both electron-donating and electron-withdrawing phenethylamines (**4a−f**), 2-thiophene ethylamine (**4g**), 3-phenyl-1-propylamine (**4h**), α-substituted phenethylamine (**4j**), and aliphatic amines (**4i,k**) could readily react with phenylacetaldehyde (**1a**) and hexaldehyde (**1b**) to generate the expected fulleropyrrolines **5a−m** in good to excellent yields (33−74% isolated yields). Similar as the previous observation, phenethylamines without electron-withdrawing groups (**4a,c,d**) gave relatively higher yields than those

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

Table 2. Reaction Conditions and Isolated Yields for the $Cu(OAc)_2$-Mediated Reaction of C_{60} with Aldehydes 1 and Arylmethanamines 2



aldehyde **1**	amine **2**	product **3**	time (min)	yield[b] (%)
		**3a**	15	61 (81)
		**3b**	8	54 (57)
		**3c**	11	41 (60)
		**3d**[c]	20	17 (81)
		**3e**[c]	25	14 (88)
		**3f**	15	33 (39)
		**3g**	14	29 (62)
		**3h**[c]	6	25 (38)
		**3i**	13	55 (86)
		**3j**	12	62 (90)
		**3k**[c]	15	19 (79)
		**3l**[c]	7	39 (46)
		**3m**[c]	12	39 (58)

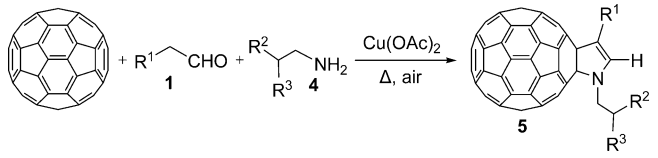
[a]All reactions were performed in chlorobenzene (10 mL) under air conditions at 100 °C unless otherwise indicated; molar ratio refers to C_{60}/$Cu(OAc)_2 \cdot H_2O$/**1**/**2** = 1:2:5:5. [b]Isolated yields, those in parentheses, were based on consumed C_{60}. [c]The reaction was performed at 130 °C.

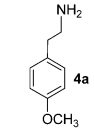
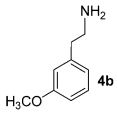
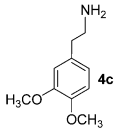
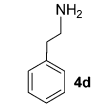
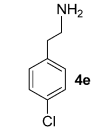
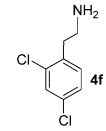
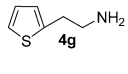
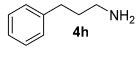
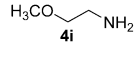
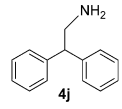
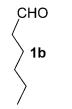
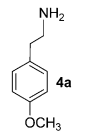
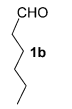
with electron-withdrawing groups (**4e**,**f**). However, the reaction of 3-methoxyphenethylamine (**4b**) required an elevated temperature to obtain an acceptable yield (33%) of **5b**, which should be attributed to the meta-substitution effect. As expected, lower reactivity was also observed for the aliphatic hexaldehyde (**1b**), and a higher reaction temperature (130 °C) is applied to guarantee the successful synthesis of **5l**. Moreover, shorter reaction time is required for the reaction of amines **4a**−**k**, indicating higher reactivities than arylmethanamines **2a**−**k**. It should be noted that the isolated yields of fulleropyrrolines **3**/**5** would be lower than the actual value because of their decomposition and/or absorption on the silica gel during column chromatography. Much to our satisfaction, the addition of a little amount of Et_3N to the silica gel could successfully avoid this problem. In addition, aromatic amines such as aniline were also employed to react with C_{60} under the optimized conditions. Unfortunately, no desired fulleropyrrolines were obtained probably due to the direct conjugation between the aryl and amine groups.

The structures of fulleropyrrolines **3a**−**m** and **5a**−**m** were fully characterized by their MALDI-TOF MS, UV−vis, FT−IR, ^{1}H NMR, and ^{13}C NMR spectra. All products exhibited the correct molecular ion peaks in their high-resolution mass spectra. The UV−vis spectra showed a diagnostic absorption peak at 427−429 nm for 1,2-adducts of C_{60}. The IR spectra displayed the characteristic absorptions at 1608−1656 cm^{-1}, ascribing to the stretching vibrations of the C═C bond. In ^{1}H NMR, the singlets appearing at 6.40−7.38 ppm were attributed to the chemical shift for ═C−H protons. In ^{13}C NMR, products **3a**−**h**, **3k**−**m**, and **5a**−**m** showed similar spectral patterns, and there were no more than 29 peaks with two half-intensity ones in the range of 134.17−149.79 ppm for the 58 sp^2-carbons of the fullerene skeleton, and two peaks at 87.06−89.12 and 77.25−79.02 ppm for the two sp^3-carbons of the fullerene cage, which is consistent with the C_s symmetry of their molecular structure. However, compounds **3i**,**j** exhibited different spectral patterns as **3a**−**h**, **3k**−**m**, and **5a**−**m**. The observation of at least 47 signals for the sp^2-carbons of the

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

Table 3. Reaction Conditions and Isolated Yields for the $Cu(OAc)_2$-Mediated Reaction of C_{60} with Aldehydes 1 and Non-Arylmethanamines 4



aldehyde 1	amine 4	product 5	time (min)	yield[b] (%)
		**5a**	7	46 (55)
		**5b**[c]	6	33 (41)
		**5c**	6	52 (74)
		**5d**	6	46 (49)
		**5e**	5	33 (41)
		**5f**	6	38 (54)
		**5g**	5	42 (53)
		**5h**	5	43 (54)
		**5i**	5	52 (68)
		**5j**	8	57 (88)
		**5k**	5	74 (88)
		**5l**[c]	8	33 (40)
		**5m**	16	33 (49)

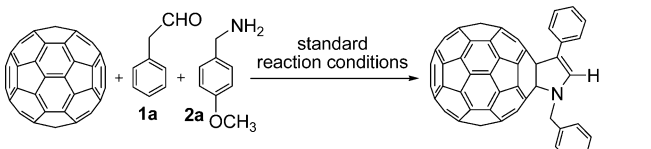
[a]All reactions were performed in chlorobenzene (10 mL) under air conditions at 100 °C unless otherwise indicated; molar ratio refers to C_{60}/$Cu(OAc)_2·H_2O$/**1**/**2** = 1:2:5:5. [b]Isolated yields; those in parentheses, were based on consumed C_{60}. [c]The reaction was performed at 130 °C.

fullerene moiety at 134.37−149.64 along with 2 signals for the two sp^3-carbons of the C_{60} core at 88.58−89.17 and 77.65−78.39 ppm was consistent with their C_1 molecular symmetry.

To gain more insights into the reaction mechanism, the $Cu(OAc)_2·H_2O$-mediated reaction of C_{60} with **1a** and **2a** in the presence of radical scavengers such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 2,6-di*tert*-butyl-4-methylphenol (BHT) was conducted (Scheme 1) and was found that the addition of two equiv of TEMPO or BHT increased the yield of product **3a**. Similar phenomenon was also observed in the reaction promoted by anhydrous $Cu(OAc)_2$ (Scheme 1), indicating that a radical pathway was not involved into the present reaction.

Based on the above experimental results together with previous literature,[10] the proposed formation mechanism for fulleropyrrolines **3**/**5** through the reaction of C_{60} with aldehydes and primary amines promoted by $Cu(OAc)_2$ is shown in Scheme 2. Aldehyde **1** first reacts with primary amine **2** or **4** to generate α-hydroxyamine intermediate **I**, followed by dehydration to form Schiff-base imine **II**, which can equilibrate to enamine intermediate **III** (Scheme 2a). It should be noted that the tautomerization of imine to enamine has been extensively reported in previous literature.[11] Nucleophilic addition of enamine intermediate **III** to the C=C bond of C_{60}, which has been activated by the formation of π complex

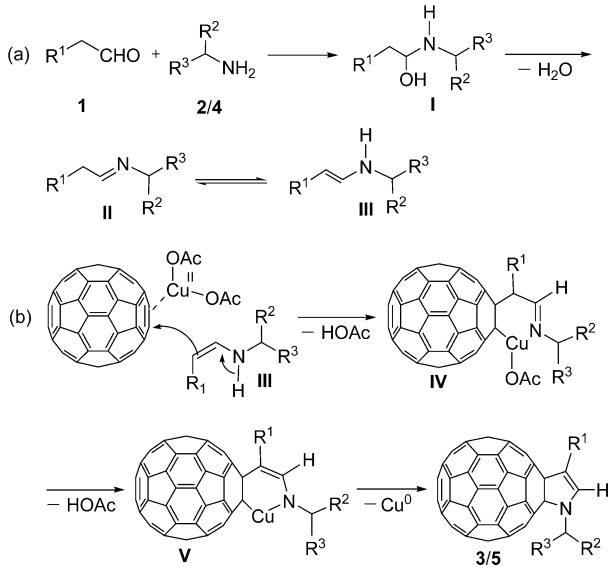
Scheme 1. Mechanistic Study



copper salts	additive	3a
	TEMPO (2 equiv.)	73%
$Cu(OAc)_2·H_2O$	BHT (2 equiv.)	68%
	none	61%
	TEMPO (2 equiv.)	76%
$Cu(OAc)_2$	BHT (2 equiv.)	63%
	none	58%

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

Scheme 2. Proposed Formation Mechanism for Fulleropyrrolines 3/5



between copper(II) Lewis acid and C=C bond, can lead to the generation of Cu(II)−fullerene complex **IV** with the loss of one molecule of HOAc. Subsequent intramolecular cyclization of complex **IV** accompanied by the elimination of another molecule of HOAc produces a new Cu(II)−fullerene complex **V**, followed by reductive elimination to afford the expected fulleropyrrolines **3/5** as well as copper(0) (Scheme 2b). It is noteworthy that the failure of aromatic amines under the standard reaction conditions to generate the corresponding fulleropyrrolines is probably attributed to the great difficulty in the formation of α-hydroxyamine intermediates between aldehydes and aromatic amines because the direct conjugation between the aryl and amine groups can reduce the nucleophilicity of nitrogen atom on aromatic amines to carbonyl group of aldehydes, which has been well confirmed by our previous study on the reaction of C_{60} with *N*-phenylbenzylamine.[7i,9c]

It should be noted that the above-mentioned fulleropyrrolines are valuable precursors and can be utilized for further functionalization via the transformation of their C=C bonds. The Pd(II)-catalyzed chlorohydroxylation reaction of alkenes with the aid of $CuCl_2$ has been well documented in the literature.[12] Therefore, we are determined to investigate the chlorohydroxylation reaction of fulleropyrroline **3a** using similar experimental conditions. Preliminary results indicated that the treatment of fulleropyrroline **3a** with $Pd(OAc)_2$ in the presence of $CuCl_2{\cdot}2H_2O$ in chlorobenzene at 80 °C for 20 min successfully afforded the desired fullerene chlorohydroxylation derivative **6** in 75% isolated yield (Scheme 3). Intriguingly, the hydroxy and *p*-methoxybenzyl groups of the obtained product **6** could be simultaneously eliminated under the assistance of $TsOH{\cdot}H_2O$ to produce the rare 1-fulleropyrroline **7** in 63% isolated yield when the reaction was conducted in chlorobenzene at 60 °C for 3 h (Scheme 3).

It is noteworthy that the formed fullerene derivative **6** is a mixture of trans and cis isomers (Figure 1). The polarities of

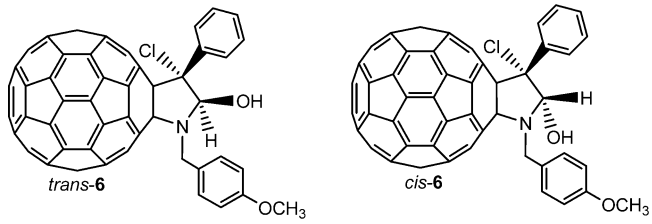


Figure 1. Configurational isomers of compound **6**.

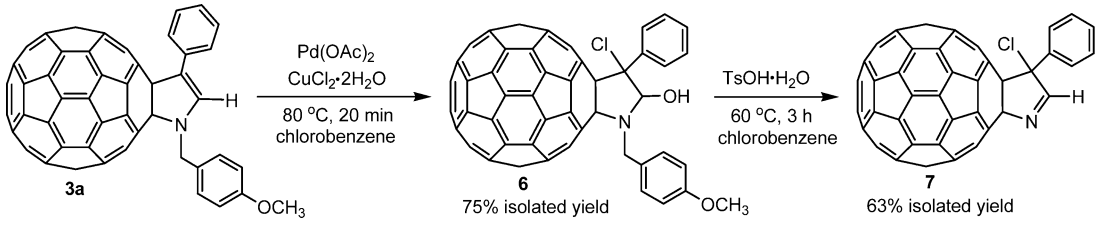
trans-**6** and *cis*-**6** are almost the same, and thus the isolation and purification of two isomers on a silica gel column is very difficult. The isomer ratio was determined as 91:9 based on the ^{1}H NMR spectrum. To clearly reveal the stereochemistry of the major product, the nuclear Overhauser enhancement spectroscopy (NOESY) was thus employed. To our disappointment, the NOESY spectrum of the predominant product of **6** could not give any affirmative cross-peaks between the methine proton and phenyl group, or between the hydroxy and phenyl groups, probably because the space distance between them exceeded the NOE-observable correlating distance (see the Supporting Information). Therefore, the reaction pathway for the Pd(II)-catalyzed chlorohydroxylation of alkenes with $CuCl_2$ was exploited to disclose the stereochemistry of the dominant product.[12a,d,e] Based on the well-confirmed *trans*-hydroxypalladation mechanism,[12a,d,e] the major product of **6** could be assigned as trans isomer.

The structures of *trans*-**6** and **7** were unambiguously established by their HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. In their ^{1}H NMR spectra, the expected chemical shifts as well as the splitting patterns for all protons were clearly observed. In their ^{13}C NMR spectra, the typical peak for the C=N carbon in product **7** appeared at 164.67 ppm, and there were at least 42 peaks including some overlapped ones for the 58 sp^2-carbons of the fullerene skeleton, agreeing with the C_1 symmetry of their molecular structures. In their IR spectra, the strong absorption at 1636 cm^{-1} in product **7** further confirmed the presence of the C=N moiety.

CONCLUSION

In summary, a simple and powerful method for the synthesis of new fulleropyrrolines with trisubstituted C=C bonds has been successfully developed through the $Cu(OAc)_2$-mediated

Scheme 3. Functionalization of Fulleropyrroline 3a



DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

reaction of C_{60} with aldehydes and primary amines. The current one-step approach to the preparation of fulleropyrrolines from inexpensive and easily available aldehydes, amines, and $Cu(OAc)_2·H_2O$ is straightforward and practical. In addition, further derivation of fulleropyrroline by the chlorohydroxylation reaction of C=C bond afforded the unreported 1-fulleropyrrolidine, which could undergo further elimination reaction with the aid of $TsOH·H_2O$ to generate the rare 1-fulleropyrroline. A plausible reaction mechanism for the formation of fulleropyrrolines bearing C=C bonds is provided.

EXPERIMENTAL SECTION

General Methods. All reagents and solvents were used directly as obtained commercially without further purification. All of fullerene products were purified by flash chromatography over silica gel. The UV−vis spectra were measured in $CHCl_3$. IR spectra were taken with KBr pellets. ^1H and ^{13}C NMR as well as NOESY spectra were recorded on a 400, 500, 600, or 700 MHz NMR spectrometer. Chemical shifts in ^1H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm, yet chemical shifts in ^{13}C NMR spectra were referenced to residual $CHCl_3$ at 77.16 ppm or DMSO at 39.52 ppm. High-resolution mass spectrometry (HRMS) was performed by MALDI-TOF in positive-ion mode with 4-hydroxy-α-cyanocinnamic acid as the matrix.

General Procedure for the Preparation of Fulleropyrrolines 3/5. C_{60} (36.0 mg, 0.05 mmol), aldehydes **1** (0.25 mmol), amines **2**/**4** (0.25 mmol), and $Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) was added to a 50 mL round-bottom flask. After the mixed compounds were completely dissolved in 10 mL of chlorobenzene by sonication, the resulting solution was immediately put into an oil bath preset at 100 or 130 °C and stirred 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 CS_2 as the eluent to afford first unreacted C_{60}, and then fulleropyrrolines **3**/**5** as amorphous brown solids.

Fulleropyrroline 3a. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2a** (33 uL, 0.25 mmol) in the presence of $Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 15 min afforded first unreacted C_{60} (9.1 mg, 25%) and then **3a** (29.0 mg, 61%) as an amorphous brown solid: mp >300 °C.

3a. ^1H NMR (500 MHz, $CS_2/CDCl_3$) δ 7.64 (d, J = 7.1 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.26 (t, J = 6.8 Hz, 2H), 7.15 (t, J = 6.7 Hz, 1H), 6.91 (s, 1H), 6.89 (d, J = 7.6 Hz, 2H), 5.03 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 159.06 (1C, aryl *C*), 149.56, 147.55 (1C), 147.04 (1C), 146.02, 145.95, 145.84 (4C), 145.66 (4C), 145.46, 145.04, 144.84 (4C), 144.81, 144.78, 144.26, 143.98, 142.83, 142.47, 142.41, 142.31, 142.02 (4C), 141.93, 141.78, 141.44, 139.79, 139.37, 136.35, 136.01 (1C, aryl *C*), 135.28, 134.90 (1C), 129.78 (aryl *C*), 129.22 (1C, aryl *C*), 128.40 (aryl *C*), 128.20 (aryl *C*), 126.19 (1C, aryl *C*), 114.10 (aryl *C*), 110.58 (1C), 89.02 (1C, sp^3-*C* of C_{60}), 78.49 (1C, sp^3-*C* of C_{60}), 54.83 (1C), 51.79 (1C); FT-IR ν/cm^{-1} (KBr) 2920, 2824, 1609, 1508, 1449, 1422, 1384, 1301, 1245, 1161, 1101, 1033, 873, 755, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 305, 428; MALDI-TOF MS m/z calcd for $C_{76}H_{15}NO$ $[M]^+$ 957.1148, found 957.1122.

Fulleropyrroline 3b. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2b** (38 uL, 0.25 mmol) in the presence of $Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 8 min afforded first unreacted C_{60} (1.9 mg, 5%) and then **3b** (26.6 mg, 54%) as an amorphous brown solid: mp >300 °C.

3b. ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.64 (d, J = 6.0 Hz, 2H), 7.45 (d, J = 6.3 Hz, 1H), 7.25 (t, J = 4.1 Hz, 2H), 7.12 (t, J = 5.6 Hz, 1H), 6.98 (s, 1H), 6.48 (d, J = 6.3 Hz, 1H), 6.42 (s, 1H), 5.02 (s, 2H), 3.82 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 160.62 (1C, aryl *C*), 158.40 (1C, aryl *C*), 149.79, 147.55 (1C), 147.05 (1C), 146.07, 145.93 (4C), 145.82, 145.65 (4C), 145.38, 145.09, 145.05, 144.83, 144.77 (4C), 144.26, 144.01, 142.83, 142.46, 142.41, 142.35, 142.10, 142.03, 141.96, 141.78, 141.47, 139.74, 139.26, 136.53 (1C, aryl *C*), 136.16, 135.30 (3C), 130.93 (1C, aryl *C*), 128.39 (aryl *C*), 128.03 (aryl *C*), 125.86 (1C, aryl *C*), 118.05 (1C, aryl *C*), 108.83 (1C), 104.14 (1C, aryl *C*), 98.56 (1C, aryl *C*), 89.11 (1C, sp^3-*C* of C_{60}), 78.49 (1C, sp^3-*C* of C_{60}), 54.90 (1C), 54.84 (1C), 45.98 (1C); FT-IR ν/cm^{-1} (KBr) 2921, 2821, 1608, 1586, 1500, 1450, 1425, 1389, 1300, 1255, 1206, 1178, 1151, 1115, 1044, 1032, 919, 870, 824, 747, 686, 525; UV−vis ($CHCl_3$) λ_{max}/nm 256, 307, 428; MALDI-TOF MS m/z calcd for $C_{77}H_{17}NO_2$ $[M]^+$ 987.1253, found 987.1233.

Fulleropyrroline 3c. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2c** (27 uL, 0.25 mmol) in the presence of $Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 11 min afforded first unreacted C_{60} (11.6 mg, 32%) and then **3c** (18.9 mg, 41%) as an amorphous brown solid: mp >300 °C.

3c. ^1H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.66 (d, J = 7.4 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.7 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 7.8 Hz, 2H), 7.16 (t, J = 7.1 Hz, 1H), 6.94 (s, 1H), 5.11 (s, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.88, 146.76 (1C), 146.26 (1C), 145.28, 145.17, 145.07 (4C), 144.87 (4C), 144.68, 144.32, 144.12, 144.08, 144.00 (4C), 143.48, 143.23, 142.06, 141.70, 141.63, 141.58, 141.26 (4C), 141.18, 141.02, 140.68, 138.97, 138.57, 137.08 (1C, aryl *C*), 136.16 (1C), 135.51, 134.54, 134.22 (1C, aryl *C*), 128.02 (aryl *C*), 127.81 (aryl *C*), 127.78 (aryl *C*), 127.43 (aryl *C*), 127.03 (1C, aryl *C*), 125.45 (1C, aryl *C*), 109.25 (1C), 88.34 (1C, sp^3-*C* of C_{60}), 77.71 (1C, sp^3-*C* of C_{60}), 51.46 (1C); FT-IR ν/cm^{-1} (KBr) 2921, 2849, 1613, 1594, 1511, 1492, 1452, 1427, 1383, 1353, 1245, 1182, 1163, 1073, 957, 872, 787, 751, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 308, 428; MALDI-TOF MS m/z calcd for $C_{75}H_{13}N$ $[M]^+$ 927.1043, found 927.1025.

Fulleropyrroline 3d. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2d** (30 uL, 0.25 mmol) in the presence of $Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 130 °C for 20 min afforded first unreacted C_{60} (28.3 mg, 79%) and then **3d** (8.0 mg, 17%) as an amorphous brown solid: mp >300 °C.

3d. ^1H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.85 (d, J = 7.3 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.40 (d, J = 8.1 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.30−7.28 (m, 3H), 7.18 (t, J = 7.0 Hz, 1H), 6.95 (s, 1H), 5.22 (s, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

d_6) (all 2C unless indicated) δ 148.98, 146.82 (1C), 146.34 (1C), 145.30, 145.23, 145.13 (4C), 144.94 (4C), 144.79, 144.16, 144.09 (4C), 144.05 (4C), 143.53, 143.28, 142.11, 141.76, 141.69, 141.63, 141.32, 141.27, 141.23, 141.09, 140.75, 139.04, 138.68, 135.88 (1C), 135.57, 134.76 (1C, aryl *C*), 134.58, 134.14 (1C, aryl *C*), 133.24 (1C, aryl *C*), 129.79 (1C, aryl *C*), 129.04 (1C, aryl *C*), 128.45 (1C, aryl *C*), 127.82 (aryl *C*), 127.58 (aryl *C*), 126.45 (1C, aryl *C*), 125.61 (1C, aryl *C*), 109.74 (1C), 88.36 (1C, sp^3-*C* of C_{60}), 77.68 (1C, sp^3-*C* of C_{60}), 48.75 (1C); FT-IR ν/cm^{-1} (KBr) 2921, 2851, 1622, 1594, 1570, 1506, 1463, 1441, 1425, 1389, 1350, 1261, 1183, 1163, 1047, 1037, 958, 873, 749, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 310, 427; MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{12}ClN$ $[M]^+$ 961.0652, found 961.0623.

Fulleropyrroline 3e. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2e** (30 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 130 °C for 25 min afforded first unreacted C_{60} (30.3 mg, 84%) and then **3e** (6.8 mg, 14%) as an amorphous brown solid: mp >300 °C.

3e. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.37 (t, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.93 (s, 1H), 5.09 (s, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.73, 146.70 (1C), 146.20 (1C), 145.17, 145.11, 145.00 (4C), 144.82 (4C), 144.64, 144.11, 144.03, 143.97, 143.93, 143.91, 143.42, 143.14, 142.01, 141.65, 141.58, 141.49, 141.20, 141.16, 141.10, 140.96, 140.62, 138.94, 138.53, 135.96 (1C), 135.83 (1C, aryl *C*), 135.47, 134.42, 133.99 (1C, aryl *C*), 132.77 (1C, aryl *C*), 129.12 (aryl *C*), 128.03 (aryl *C*), 127.72 (aryl *C*), 127.45 (aryl *C*), 125.53 (1C, aryl *C*), 109.76 (1C), 88.16 (1C, sp^3-*C* of C_{60}), 77.62 (1C, sp^3-*C* of C_{60}), 50.79 (1C); FT-IR ν/cm^{-1} (KBr) 2918, 2848, 1614, 1594, 1489, 1427, 1407, 1183, 1163, 1091, 1014, 964, 872, 762, 755, 696, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 313, 427; MALDI-TOF MS *m*/*z* calcd for $C_{75}H_{12}ClN$ $[M]^+$ 961.0652, found 961.0623.

Fulleropyrroline 3f. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2f** (45.8 mg, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 15 min afforded first unreacted C_{60} (5.9 mg, 16%) and then **3f** (16.8 mg, 33%) as an amorphous brown solid: mp >300 °C.

3f. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 7.68 (d, *J* = 6.7 Hz, 4H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.39 (t, *J* = 7.0 Hz, 2H), 7.31−7.26 (m, 3H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.99 (s, 1H), 5.16 (s, 2H); ^{13}C NMR (175 MHz, CS_2/$CDCl_3$) (all 2C unless indicated) δ 149.37, 147.44 (1C), 146.93 (1C), 145.89, 145.84, 145.72 (4C), 145.56, 145.54, 145.38, 144.84, 144.75, 144.70, 144.68, 144.67, 144.14, 143.86, 142.72, 142.36, 142.30, 142.20, 141.92, 141.89, 141.81, 141.68, 141.33, 140.55 (1C, aryl *C*), 140.18 (1C, aryl *C*), 139.70, 139.29, 136.44 (1C, aryl *C*), 136.28, 135.86 (1C), 135.17, 134.68 (1C, aryl *C*), 128.87 (aryl *C*), 128.58 (aryl *C*), 128.32 (aryl *C*), 128.15 (aryl *C*), 127.31 (aryl *C*), 127.19 (1C, aryl *C*), 126.78 (aryl *C*), 126.19 (1C, aryl *C*), 110.89 (1C), 88.96 (1C, sp^3-*C* of C_{60}), 78.36 (1C, sp^3-*C* of C_{60}), 51.89 (1C); FT-IR ν/cm^{-1} (KBr) 2840, 1613, 1594, 1486, 1462, 1426, 1332, 1182, 1163, 1104, 1072, 959, 873, 755, 694, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 313, 428; MALDI-TOF MS *m*/*z* calcd for $C_{81}H_{17}N$ $[M]^+$ 1003.1355, found 1003.1322.

Fulleropyrroline 3g. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2g** (37 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 14 min afforded first unreacted C_{60} (19.1 mg, 53%) and then **3g** (14.0 mg, 29%) as an amorphous brown solid: mp >300 °C.

3g. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 8.30 (d, *J* = 8.5 Hz, 1H), 7.88 (t, *J* = 7.8 Hz, 2H), 7.84 (d, *J* = 6.9 Hz, 1H), 7.59−7.51 (m, 5H), 7.21 (t, *J* = 6.8 Hz, 2H), 7.11 (t, *J* = 7.0 Hz, 1H), 6.73 (s, 1H), 5.50 (s, 2H); ^{13}C NMR (175 MHz, CS_2/$CDCl_3$) (all 2C unless indicated) δ 149.67, 147.44 (1C), 146.93 (1C), 145.89, 145.87, 145.73, 145.69, 145.57, 145.55, 145.46, 144.77, 144.72 (6C), 144.66, 144.17, 143.86, 142.74, 142.36, 142.30, 142.22, 141.91, 141.89, 141.80, 141.69, 141.34, 139.69, 139.42, 136.48, 135.13 (3C), 134.59 (1C, aryl *C*), 133.71 (1C, aryl *C*), 132.08 (1C, aryl *C*), 131.61 (1C, aryl *C*), 128.97 (1C, aryl *C*), 128.65 (1C, aryl *C*), 128.22 (aryl *C*), 128.14 (aryl *C*), 127.81 (1C, aryl *C*), 126.49 (1C, aryl *C*), 126.11 (1C, aryl *C*), 126.02 (1C, aryl *C*), 125.26 (1C, aryl *C*), 123.69 (1C, aryl *C*), 111.03 (1C), 89.12 (1C, sp^3-*C* of C_{60}), 78.34 (1C, sp^3-*C* of C_{60}), 50.67 (1C); FT-IR ν/cm^{-1} (KBr) 2919, 2849, 1615, 1595, 1510, 1463, 1427, 1358, 1322, 1187, 1164, 873, 789, 775, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 308, 428; MALDI-TOF MS *m*/*z* calcd for $C_{79}H_{15}N$ $[M]^+$ 977.1200, found 977.1181.

Fulleropyrroline 3h. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2h** (26 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 130 °C for 6 min afforded first unreacted C_{60} (12.3 mg, 34%) and then **3h** (11.6 mg, 25%) as an amorphous brown solid: mp >300 °C.

3h. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 7.66 (d, *J* = 7.4 Hz, 2H), 7.30−7.27 (m, 3H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.15 (dd, *J* = 2.3, 1.0 Hz, 1H), 7.01 (s, 1H), 6.96 (dd, *J* = 5.1, 3.5 Hz, 1H), 5.29 (s, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.74, 146.63 (1C), 146.14 (1C), 145.16, 145.04, 144.96 (4C), 144.76 (4C), 144.55, 144.27, 143.96 (4C), 143.89 (4C), 143.35, 143.12, 141.94, 141.58, 141.52, 141.42, 141.13 (4C), 141.09, 140.94, 140.62 (1C, aryl *C*), 140.56, 138.84, 138.42, 135.92 (1C), 135.35, 134.48, 133.99 (1C, aryl *C*), 127.71 (aryl *C*), 127.51 (aryl *C*), 126.33 (1C, aryl *C*), 126.13 (1C, aryl *C*), 125.57 (1C, aryl *C*), 125.55 (1C, aryl *C*), 110.11 (1C), 87.81 (1C, sp^3-*C* of C_{60}), 77.71 (1C, sp^3-*C* of C_{60}), 46.28 (1C); FT-IR ν/cm^{-1} (KBr) 2923, 2849, 1625, 1593, 1425, 1391, 1361, 1284, 1225, 1181, 1164, 1115, 1036, 934, 873, 762, 697, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 305, 428; MALDI-TOF MS *m*/*z* calcd for $C_{73}H_{11}NS$ $[M]^+$ 933.0607, found 933.0589.

Fulleropyrroline 3i. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2i** (32 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 13 min afforded first unreacted C_{60} (13.1 mg, 36%) and then **3i** (26.1 mg, 55%) as an amorphous brown solid: mp >300 °C.

3i. ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.38 (s, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.26−7.20 (m, 3H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.58 (q, *J* = 7.0 Hz, 1H), 2.03 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 149.04, 148.51, 146.79, 146.29, 145.39, 145.23, 145.19, 145.18, 145.13, 145.08, 145.07, 145.05, 144.91, 144.90, 144.86, 144.82, 144.77, 144.47,

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

144.36, 144.22, 144.04 (2C), 144.00 (4C), 143.83, 143.80, 143.51, 143.50, 143.22 (2C), 142.51, 142.09, 142.08, 141.74, 141.71, 141.66 (2C), 141.58 (2C), 141.33 (3C), 141.29, 141.18 (2C), 141.15, 140.98, 140.73, 140.72, 138.98 (2C), 138.64, 138.51, 135.70, 134.94, 134.61, 134.59, 134.37, 132.82 (aryl *C*), 127.97 (2C, aryl *C*), 127.78 (2C, aryl *C*), 127.37 (2C, aryl *C*), 126.69 (aryl *C*), 126.38 (2C, aryl *C*), 125.23 (aryl *C*), 108.13, 88.58 (sp^3-*C* of C_{60}), 77.65 (sp^3-*C* of C_{60}), 54.20, 21.96; FT-IR ν/cm^{-1} (KBr) 2921, 1611, 1593, 1491, 1440, 1425, 1371, 1345, 1221, 1182, 1162, 1143, 1084, 958, 933, 900, 869, 752, 696, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 428; MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{15}N$ $[M]^+$ 941.1199, found 941.1172.

Fulleropyrroline 3j. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2j** (37 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 12 min afforded first unreacted C_{60} (11.1 mg, 31%) and then **3j** (30.0 mg, 62%) as an amorphous brown solid: mp >300 °C.

3j. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.21 (s, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.57 (q, *J* = 6.7 Hz, 1H), 2.01 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (175 MHz, $CS_2/CDCl_3$) (all 1C unless indicated) δ 158.59 (aryl *C*), 149.64, 149.24, 147.51, 147.01, 146.04, 145.93, 145.87, 145.86, 145.84, 145.80, 145.77, 145.75, 145.62 (2C), 145.58, 145.54, 145.44, 145.18, 145.07, 144.81, 144.75 (2C), 144.71 (4C), 144.48, 144.46, 144.22, 144.21, 143.92, 143.89, 142.79 (2C), 142.43, 142.41, 142.37, 142.36, 142.25, 142.24, 142.06, 142.02, 142.01, 142.00, 141.86 (2C), 141.82, 141.66, 141.45, 141.41, 139.75, 139.71, 139.33, 139.21, 136.39 (aryl *C*), 135.64, 135.28, 135.24, 135.06, 134.95, 132.97 (aryl *C*), 128.39 (2C, aryl *C*), 128.05 (2C, aryl *C*), 128.00 (2C, aryl *C*), 125.90 (aryl *C*), 113.90 (2C, aryl *C*), 109.18, 89.17 (sp^3-*C* of C_{60}), 78.39 (sp^3-*C* of C_{60}), 54.81, 54.09, 22.47; FT-IR ν/cm^{-1} (KBr) 2924, 2827, 1609, 1592, 1510, 1461, 1438, 1423, 1239, 1176, 1163, 1138, 1107, 1072, 1031, 900, 869, 825, 752, 689, 526; UV−vis ($CHCl_3$) λ_{max}/nm 256, 308, 428; MALDI-TOF MS *m*/*z* calcd for $C_{77}H_{17}NO$ $[M]^+$ 971.1305, found 971.1287.

Fulleropyrroline 3k. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2k** (43 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 130 °C for 15 min afforded first unreacted C_{60} (27.3 mg, 76%) and then **3k** (9.7 mg, 19%) as an amorphous brown solid: mp >300 °C.

3k. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 4H), 7.41 (t, *J* = 7.8 Hz, 4H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.73 (s, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.81, 146.82 (1C), 146.34 (1C), 145.29, 145.18, 145.14, 145.11, 144.91 (4C), 144.67, 144.11, 144.04 (6C), 143.98, 143.52, 143.24, 142.11, 141.75, 141.69, 141.58, 141.32 (4C), 141.22, 141.11, 140.77, 139.89, 139.03, 138.64, 135.33, 134,56, 134.32 (1C), 133.73 (1C), 128.22 (4C, aryl *C*), 128.04 (4C, aryl *C*), 127.78 (aryl *C*), 127.43 (aryl *C*), 127.09 (aryl *C*), 125.42 (1C, aryl *C*), 108.51 (1C), 88.52 (1C, sp^3-*C* of C_{60}), 77.76 (1C, sp^3-*C* of C_{60}), 62.65 (1C); FT-IR ν/cm^{-1} (KBr) 2917, 1614, 1594, 1491, 1439, 1426, 1407, 1354, 1219, 1182, 1161, 1134, 1073, 1030, 874, 753, 739, 724, 696, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 312, 427; MALDI-TOF MS *m*/*z* calcd for $C_{81}H_{17}N$ $[M]^+$ 1003.1355, found 1003.1322.

Fulleropyrroline 3l. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (30 uL, 0.25 mmol) and **2a** (33 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 130 °C for 7 min afforded first unreacted C_{60} (5.4 mg, 15%) and then **3l** (18.1 mg, 39%) as an amorphous brown solid: mp >300 °C.

3l. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.40 (s, 1H), 4.89 (s, 2H), 3.81 (s, 3H), 2.65 (t, *J* = 7.4 Hz, 2H), 1.82−1.76 (m, 2H), 1.54−1.50 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 158.25 (1C, aryl *C*), 149.24, 146.88 (1C), 146.32 (1C), 146.11, 145.21, 145.12, 145.03, 144.98 (4C), 144.92, 144.79, 144.52, 144.19, 144.08 (4C), 143.59, 143.36, 142.16, 141.72 (4C), 141.66, 141.49, 141.23 (4C), 141.10, 140.78, 139.47, 138.51, 135.52, 134.64, 131.51 (1C), 129.29 (1C, aryl *C*), 129.09 (aryl *C*), 113.38 (aryl *C*), 109.45 (1C), 87.16 (1C, sp^3-*C* of C_{60}), 79.02 (1C, sp^3-*C* of C_{60}), 54.15 (1C), 52.00 (1C), 30.45 (1C), 26.77 (1C), 22.78 (1C), 13.83 (1C); FT-IR ν/cm^{-1} (KBr) 2920, 2825, 1656, 1609, 1584, 1509, 1458, 1426, 1375, 1301, 1244, 1171, 1161, 1105, 1036, 849, 661, 574, 525; UV−vis ($CHCl_3$) λ_{max}/nm 256, 305, 429; MALDI-TOF MS *m*/*z* calcd for $C_{74}H_{19}NO$ $[M]^+$ 937.1461, found 937.1441.

Fulleropyrroline 3m. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (27 uL, 0.25 mmol) and **2a** (33 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 130 °C for 12 min afforded first unreacted C_{60} (11.7 mg, 33%) and then **3m** (18.2 mg, 39%) as an amorphous brown solid: mp >300 °C.

3m. ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.48 (s, 1H), 4.84 (s, 2H), 3.76 (s, 3H), 3.01 (hept, *J* = 6.9 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 158.00 (1C, aryl *C*), 149.22, 146.60 (1C), 146.06 (1C), 145.48, 144.93, 144.85 (4C), 144.70 (4C), 144.67, 144.47, 144.22, 143.83 (4C), 143.81, 143.31, 143.09, 141.90, 141.49 (4C), 141.41, 141.20, 141.00 (4C), 140.84, 140.53, 139.11, 138.29, 135.23, 134.22, 130.93 (1C), 128.93 (1C, aryl *C*), 128.87 (aryl *C*), 116.03 (1C), 113.17 (aryl *C*), 87.37 (1C, sp^3-*C* of C_{60}), 78.50 (1C, sp^3-*C* of C_{60}), 54.00 (1C), 51.84 (1C), 25.93 (1C), 23.59; FT-IR ν/cm^{-1} (KBr) 2948, 2918, 2853, 2827, 1645, 1608, 1583, 1509, 1460, 1424, 1379, 1357, 1300, 1244, 1217, 1162, 1106, 1034, 913, 817, 572, 526; UV−vis ($CHCl_3$) λ_{max}/nm 256, 308, 429; MALDI-TOF MS *m*/*z* calcd for $C_{73}H_{17}NO$ $[M]^+$ 923.1305, found 923.1285.

Fulleropyrroline 5a. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4a** (37 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 7 min afforded first unreacted C_{60} (5.9 mg, 16%) and then **5a** (22.2 mg, 46%) as an amorphous brown solid: mp >300 °C.

5a. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.61 (d, *J* = 6.9 Hz, 2H), 7.22 (t, *J* = 6.8 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.13 (s, 1H), 7.10 (t, *J* = 6.8 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 2H), 4.15 (t, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 3.22 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 157.53 (1C, aryl *C*), 148.78, 146.88 (1C), 146.39 (1C), 145.35, 145.25 (4C), 145.14, 144.96 (4C), 144.70, 144.12, 144.09 (6C), 144.03, 143.60, 143.33, 142.18, 141.81, 141.74, 141.71, 141.49, 141.40, 141.26, 141.20, 140.79, 139.04, 138.85, 135.77

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

(1C, aryl *C*), 135.51, 134.64 (1C), 134.61, 129.83 (1C, aryl *C*), 129.33 (aryl *C*), 127.74 (aryl *C*), 127.26 (aryl *C*), 125.16 (1C, aryl *C*), 113.40 (aryl *C*), 107.45 (1C), 88.49 (1C, sp^3-*C* of C_{60}), 77.65 (1C, sp^3-*C* of C_{60}), 54.05 (1C), 48.33 (1C), 35.68 (1C); FT-IR ν/cm^{-1} (KBr) 2923, 1615, 1595, 1510, 1439, 1424, 1393, 1355, 1247, 1173, 1037, 873, 813, 754, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 308, 427; MALDI-TOF MS *m*/*z* calcd for $C_{77}H_{17}NO$ $[M]^+$ 971.1305, found 971.1287.

Fulleropyrroline 5b. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4b** (37 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 130 °C for 6 min afforded first unreacted C_{60} (7.0 mg, 19%) and then **5b** (16.1 mg, 33%) as an amorphous brown solid: mp >300 °C.

5b. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 8.3 Hz, 1H), 7.15 (t, *J* = 6.9 Hz, 1H), 6.91 (s, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.84 (s, 1H), 6.72 (d, *J* = 10.6 Hz, 1H), 4.22 (t, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 3.27 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 158.74 (1C, aryl *C*), 148.61, 146.69 (1C), 146.20 (1C), 145.16, 145.06 (4C), 144.95, 144.77 (4C), 144.52, 143.89 (10C), 143.41, 143.15, 141.99, 141.62, 141.54 (4C), 141.30, 141.21, 141.07, 141.00, 140.59, 139.35 (1C, aryl *C*), 138.85, 138.67, 135.81 (1C, aryl *C*), 135.33, 134.45 (1C), 134.39, 128.73 (1C, aryl *C*), 127.66 (aryl *C*), 127.13 (aryl *C*), 125.04 (1C, aryl *C*), 120.51 (1C, aryl *C*), 114.11 (1C, aryl *C*), 111.24 (1C, aryl *C*), 107.28 (1C), 88.27 (1C, sp^3-*C* of C_{60}), 77.51 (1C, sp^3-*C* of C_{60}), 53.89 (1C), 47.94 (1C), 36.39 (1C); FT-IR ν/cm^{-1} (KBr) 2917, 2828, 1609, 1594, 1489, 1462, 1451, 1432, 1394, 1354, 1259, 1187, 1163, 1152, 1043, 1011, 872, 780, 753, 694, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 427; MALDI-TOF MS *m*/*z* calcd for $C_{77}H_{17}NO$ $[M]^+$ 971.1305, found 971.1287.

Fulleropyrroline 5c. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4c** (42 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 6 min afforded first unreacted C_{60} (10.7 mg, 30%) and then **5c** (25.9 mg, 52%) as an amorphous brown solid: mp >300 °C.

5c. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.93 (s, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.83 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 4.22 (t, *J* = 6.9 Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H), 3.23 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.65, 148.57 (1C, aryl *C*), 147.31 (1C, aryl *C*), 146.78 (1C), 146.29 (1C), 145.24, 145.18, 145.15, 145.04, 144.86 (4C), 144.54, 144.00 (4C), 143.82, 143.50, 143.23, 142.08, 141.71, 141.64, 141.61, 141.40, 141.30, 141.16, 141.08, 140.69, 138.93, 138.67, 135.95 (1C, aryl *C*), 135.33, 134.64 (1C), 134.50, 130.56 (1C, aryl *C*), 127.76 (aryl *C*), 127.08 (aryl *C*), 125.03 (1C, aryl *C*), 120.56 (1C, aryl *C*), 112.65 (1C, aryl *C*), 111.62 (1C, aryl *C*), 106.97 (1C), 88.44 (1C, sp^3-*C* of C_{60}), 77.57 (1C, sp^3-*C* of C_{60}), 54.82 (1C), 54.73 (1C), 47.96 (1C), 35.94 (1C); FT-IR ν/cm^{-1} (KBr) 2924, 2826, 1611, 1592, 1460, 1448, 1438, 1394, 1355, 1261, 1236, 1182, 1157, 1141, 1029, 872, 801, 754, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 427; MALDI-TOF MS *m*/*z* calcd for $C_{78}H_{19}NO_2$ $[M]^+$ 1001.1410, found 1001.1395.

Fulleropyrroline 5d. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4d** (31 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 6 min afforded first unreacted C_{60} (2.0 mg, 6%) and then **5d** (21.7 mg, 46%) as an amorphous brown solid: mp >300 °C.

5d. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.62 (d, *J* = 7.0 Hz, 2H), 7.30−7.17 (m, 8H), 7.10 (t, *J* = 6.3 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 3.30 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.75, 146.83 (1C), 146.33 (1C), 145.29, 145.20 (4C), 145.09, 144.91 (4C), 144.69, 144.07 (6C), 144.05 (4C), 143.55, 143.28, 142.14, 141.76, 141.69, 141.67, 141.43, 141.35, 141.20, 141.15, 140.74, 138.99, 138.83, 138.01 (1C, aryl *C*), 135.81 (1C, aryl *C*), 135.51, 134.54 (3C), 128.36 (aryl *C*), 127.92 (aryl *C*), 127.77 (aryl *C*), 127.24 (aryl *C*), 125.90 (1C, aryl *C*), 125.17 (1C, aryl *C*), 107.57 (1C), 88.40 (1C, sp^3-*C* of C_{60}), 77.61 (1C, sp^3-*C* of C_{60}), 48.25 (1C), 36.51 (1C); FT-IR ν/cm^{-1} (KBr) 2915, 2849, 1612, 1593, 1493, 1451, 1425, 1392, 1355, 1180, 1163, 1073, 872, 751, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 427; MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{15}N$ $[M]^+$ 941.1199, found 941.1172.

Fulleropyrroline 5e. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4e** (35 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 5 min afforded first unreacted C_{60} (7.0 mg, 19%) and then **5e** (15.9 mg, 33%) as an amorphous brown solid: mp >300 °C.

5e. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.30−7.27 (m, 6H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.94 (s, 1H), 4.21 (t, *J* = 7.3 Hz, 2H), 3.30 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (175 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 149.26, 147.51 (1C), 146.99 (1C), 145.88, 145.83, 145.78, 145.74, 145.60, 145.58, 145.34, 144.75, 144.73, 144.71, 144.40, 144.37, 144.21, 143.88, 142.79, 142.42, 142.35, 142.23, 141.99 (4C), 141.81, 141.75, 141.39, 139.73, 139.44, 136.95 (1C, aryl *C*), 136.18, 135.41 (1C), 135.09, 134.82 (1C, aryl *C*), 132.63 (1C, aryl *C*), 130.22 (aryl *C*), 128.66 (aryl *C*), 128.38 (aryl *C*), 128.02 (aryl *C*), 126.09 (1C, aryl *C*), 109.49 (1C), 88.89 (1C, sp^3-*C* of C_{60}), 78.23 (1C, sp^3-*C* of C_{60}), 48.78 (1C), 36.53 (1C); FT-IR ν/cm^{-1} (KBr) 2911, 2841, 1614, 1593, 1490, 1426, 1395, 1355, 1216, 1180, 1163, 1142, 1091, 1014, 873, 812, 754, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 427; MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{14}ClN$ $[M]^+$ 975.0810, found 975.0795.

Fulleropyrroline 5f. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4f** (37 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 6 min afforded first unreacted C_{60} (10.4 mg, 29%) and then **5f** (19.2 mg, 38%) as an amorphous brown solid: mp >300 °C.

5f. ^{1}H NMR (600 MHz, $CS_2/CDCl_3$) δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.33−7.28 (m, 4H), 7.23−7.21 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 4.24 (t, *J* = 7.2 Hz, 2H), 3.41 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (all 2C unless indicated) δ 149.06, 147.51 (1C), 146.99 (1C), 145.87, 145.80, 145.78, 145.74, 145.58 (4C), 145.31, 144.73, 144.71, 144.70, 144.46, 144.18 (4C), 143.88, 142.77, 142.41, 142.34, 142.21, 141.97, 141.96, 141.81, 141.75, 141.36, 139.71, 139.36, 136.09, 135.18 (1C), 135.09, 134.86 (1C, aryl *C*), 134.77 (1C, aryl *C*), 134.73 (1C, aryl *C*), 133.50 (1C, aryl *C*), 132.09 (1C, aryl *C*), 129.32 (1C, aryl *C*), 128.40 (aryl *C*), 128.06 (aryl *C*), 127.15 (1C, aryl *C*), 126.16 (1C, aryl *C*), 109.74 (1C), 88.81 (1C, sp^3-

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

C of C_{60}), 78.26 (1C, sp^3-*C* of C_{60}), 46.37 (1C), 34.72 (1C); FT-IR ν/cm^{-1} (KBr) 2899, 2865, 1629, 1592, 1564, 1471, 1448, 1424, 1389, 1355, 1278, 1223, 1173, 1163, 1132, 1099, 1051, 1007, 865, 819, 761, 697, 526; UV−vis ($CHCl_3$) λ_{max}/nm 258, 309, 427; MALDI-TOF MS *m*/*z* calcd for $C_{76}H_{13}Cl_2N$ $[M]^+$ 1009.0420, found 1009.0406.

Fulleropyrroline 5g. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4g** (29 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 5 min afforded first unreacted C_{60} (7.3 mg, 20%) and then **5g** (20.1 mg, 42%) as an amorphous brown solid: mp >300 °C.

5g. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 7.63 (d, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.15 (br.s, 2H), 6.95 (br.s, 2H), 6.93 (s, 1H), 4.26 (t, *J* = 6.9 Hz, 2H), 3.52 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.37, 146.45 (1C), 145.95 (1C), 144.90, 144.83, 144.80, 144.72, 144.55 (4C), 144.35, 143.71, 143.68, 143.66, 143.63, 143.58, 143.18, 142.90, 141.75, 141.38, 141.32, 141.27, 141.03, 140.97, 140.83, 140.77, 140.36, 139.69 (1C, aryl *C*), 138.64, 138.47, 135.47 (1C), 135.21, 134.17, 134.05 (1C, aryl *C*), 127.46 (aryl *C*), 127.05 (aryl *C*), 126.11 (1C, aryl *C*), 125.00 (1C, aryl *C*), 124.85 (1C, aryl *C*), 123.38 (1C, aryl *C*), 107.79 (1C), 87.96 (1C, sp^3-*C* of C_{60}), 77.26 (1C, sp^3-*C* of C_{60}), 48.15 (1C), 30.23 (1C); FT-IR ν/cm^{-1} (KBr) 2907, 2839, 1613, 1593, 1508, 1490, 1462, 1429, 1393, 1352, 1222, 1187, 1163, 1074, 1041, 934, 872, 753, 693, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 427; MALDI-TOF MS *m*/*z* calcd for $C_{74}H_{13}NS$ $[M]^+$ 947.0764, found 947.0748.

Fulleropyrroline 5h. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4h** (36 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 5 min afforded first unreacted C_{60} (7.2 mg, 20%) and then **5h** (20.4 mg, 43%) as an amorphous brown solid: mp >300 °C.

5h. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.21−7.16 (m, 5H), 7.12 (t, *J* = 6.8 Hz, 1H), 7.04 (s, 1H), 3.95 (t, *J* = 7.0 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.42−2.34 (m, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.78, 146.71 (1C), 146.21 (1C), 145.20, 145.11, 145.07, 144.99, 144.81 (4C), 144.60, 144.22, 143.99, 143.95 (6C), 143.44, 143.17, 142.01, 141.64, 141.59, 141.55, 141.26, 141.23, 141.10, 140.97, 140.62, 139.95 (1C, aryl *C*), 138.90, 138.64, 135.56 (1C), 135.43, 134.41, 134.36 (1C, aryl *C*), 127.70 (aryl *C*), 127.65 (aryl *C*), 127.58 (aryl *C*), 127.27 (aryl *C*), 125.25 (1C, aryl *C*), 125.21 (1C, aryl *C*), 108.21 (1C), 88.44 (1C, sp^3-*C* of C_{60}), 77.49 (1C, sp^3-*C* of C_{60}), 46.35 (1C), 32.56 (1C), 30.98 (1C); FT-IR ν/cm^{-1} (KBr) 2920, 2850, 1612, 1593, 1493, 1426, 1396, 1359, 1181, 1163, 1077, 872, 751, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 311, 427; MALDI-TOF MS *m*/*z* calcd for $C_{77}H_{17}N$ $[M]^+$ 955.1356, found 955.1337.

Fulleropyrroline 5i. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4i** (22 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 5 min afforded first unreacted C_{60} (8.4 mg, 23%) and then **5i** (23.1 mg, 52%) as an amorphous brown solid: mp >300 °C.

5i. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.28 (s, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 1H), 4.13 (t, *J* = 5.2 Hz, 2H), 3.88 (t, *J* = 5.2 Hz, 2H), 3.48 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.71, 146.78 (1C), 146.27 (1C), 145.25, 145.16 (4C), 145.04, 144.86 (4C), 144.67, 144.00 (6C), 143.97 (4C), 143.52, 143.21, 142.08, 141.71, 141.63, 141.62, 141.36, 141.31, 141.13, 141.07, 140.68, 138.97, 138.76, 136.56 (1C, aryl *C*), 135.59, 134.47 (3C), 127.74 (aryl *C*), 127.29 (aryl *C*), 125.19 (1C, aryl *C*), 107.66 (1C), 88.45 (1C, sp^3-*C* of C_{60}), 77.40 (1C, sp^3-*C* of C_{60}), 71.72 (1C), 58.05 (1C), 46.13 (1C); FT-IR ν/cm^{-1} (KBr) 2919, 2880, 1614, 1595, 1510, 1425, 1380, 1346, 1291, 1188, 1164, 1119, 869, 751, 690, 526; UV−vis ($CHCl_3$) λ_{max}/nm 256, 308, 427; MALDI-TOF MS *m*/*z* calcd for $C_{71}H_{13}NO$ $[M]^+$ 895.0992, found 895.0978.

Fulleropyrroline 5j. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4j** (49.3 mg, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 8 min afforded first unreacted C_{60} (12.6 mg, 35%) and then **5j** (29.1 mg, 57%) as an amorphous brown solid: mp >300 °C.

5j. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 4H), 7.32 (t, *J* = 7.8 Hz, 4H), 7.24−7.22 (m, 4H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.70 (s, 1H), 4.73 (t, *J* = 7.8 Hz, 1H), 4.59 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.76, 146.72 (1C), 146.22 (1C), 145.14, 145.08 (4C), 144.97, 144.80 (4C), 144.57, 143.93 (8C), 143.67, 143.44, 143.17, 142.00, 141.63, 141.58, 141.53, 141.33, 141.23, 141.11, 141.04, 141.01, 140.63, 138.84, 138.65, 135.83 (1C, aryl *C*), 135.38, 134.41 (3C), 127.83 (4C, aryl *C*), 127.71 (4C, aryl *C*),127.61 (aryl *C*), 127.13 (aryl *C*), 126.07 (aryl *C*), 125.02 (1C, aryl *C*), 107.23 (1C), 88.46 (1C, sp^3-*C* of C_{60}), 77.34 (1C, sp^3-*C* of C_{60}), 51.53 (1C), 50.25 (1C); FT-IR ν/cm^{-1} (KBr) 2912, 1614, 1592, 1491, 1449, 1425, 1394, 1352, 1188, 1163, 1132, 1078, 1031, 959, 872, 753, 696, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 309, 428; MALDI-TOF MS *m*/*z* calcd for $C_{82}H_{19}N$ $[M]^+$ 1017.1513, found 1017.1501.

Fulleropyrroline 5k. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **4k** (24 uL, 0.25 mmol) in the presence of $Cu(OAc)_2{\cdot}H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 5 min afforded first unreacted C_{60} (5.7 mg, 16%) and then **5k** (33.2 mg, 74%) as an amorphous brown solid: mp >300 °C.

5k. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 3.94 (t, *J* = 7.5 Hz, 2H), 2.07−2.02 (m, 2H), 1.66−1.60 (m, 2H), 1.07 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 148.54, 146.49 (1C), 145.99 (1C), 144.97, 144.88, 144.85, 144.76, 144.59 (4C), 144.37, 143.97, 143.76 (4C), 143.72 (4C), 143.22, 142.94, 141.80, 141.42, 141.36, 141.32, 141.06, 141.00, 140.87, 140.76, 140.40, 138.68, 138.45, 135.27 (1C, aryl *C*), 135.22, 134.17 (3C), 127.51 (aryl *C*), 127.04 (aryl *C*), 125.00 (1C, aryl *C*), 107.73 (1C), 88.24 (1C, sp^3-*C* of C_{60}), 77.25 (1C, sp^3-*C* of C_{60}), 46.49 (1C), 31.61 (1C), 19.91 (1C), 13.41 (1C); FT-IR ν/cm^{-1} (KBr) 2950, 2920, 2851, 1614, 1593, 1510, 1490, 1460, 1425, 1395, 1356, 1180, 1164, 1099, 934, 871, 754, 695, 526; UV−vis ($CHCl_3$) λ_{max}/nm 256, 308, 427; MALDI-TOF MS *m*/*z* calcd for $C_{72}H_{15}N$ $[M]^+$ 893.1200, found 893.1186.

Fulleropyrroline 5l. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (30 uL, 0.25 mmol) and **4a** (37 uL, 0.25 mmol) in the presence of

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

$Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 130 °C for 8 min afforded first unreacted C_{60} (6.3 mg, 18%) and then **5l** (15.8 mg, 33%) as an amorphous brown solid: mp >300 °C.

5l. ^{1}H NMR (600 MHz, CS_2/$CDCl_3$) δ 7.18 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.49 (s, 1H), 4.04 (t, J = 7.6 Hz, 2H), 3.75 (s, 3H), 3.20 (t, J = 7.6 Hz, 2H), 2.65 (t, J = 7.3 Hz, 2H), 1.84−1.80 (m, 2H), 1.57−1.53 (m, 2H), 1.03 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 157.41 (1C, aryl *C*), 149.14, 146.93 (1C), 146.36 (1C), 145.71, 145.21, 145.10 (4C), 144.98, 144.92 (4C), 144.75, 144.33, 144.16, 144.08 (4C), 143.63, 143.37, 142.20, 141.75 (4C), 141.67, 141.63, 141.28, 141.19 (4C), 140.81, 139.46, 138.71, 135.44, 134.62, 131.15 (1C), 130.17 (1C, aryl *C*), 129.19 (aryl *C*), 113.32 (aryl *C*), 107.54 (1C), 87.25 (1C, sp^3-*C* of C_{60}), 78.94 (1C, sp^3-*C* of C_{60}), 54.04 (1C), 49.34 (1C), 35.74 (1C), 30.51 (1C), 26.72 (1C), 22.75 (1C), 13.89 (1C); FT-IR ν/cm^{-1} (KBr) 2949, 2920, 2851, 2825, 1655, 1609, 1581, 1509, 1461, 1450, 1429, 1375, 1355, 1299, 1246, 1177, 1163, 1114, 1036, 846, 821, 805, 597, 576, 525; UV−vis ($CHCl_3$) λ_{max}/nm 257, 304, 428; MALDI-TOF MS m/z calcd for $C_{75}H_{21}NO$ $[M]^+$ 951.1618, found 951.1600.

Fulleropyrroline 5m. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (30 uL, 0.25 mmol) and **4k** (24 uL, 0.25 mmol) in the presence of $Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 16 min afforded first unreacted C_{60} (12.0 mg, 33%) and then **5m** (14.5 mg, 33%) as an amorphous brown solid: mp >300 °C.

5m. ^{1}H NMR (600 MHz, CS_2/DMSO-d_6) δ 6.53 (s, 1H), 3.77 (t, J = 7.4 Hz, 2H), 2.64 (t, J = 7.5 Hz, 2H), 1.97−1.92 (m, 2H), 1.86−1.81 (m, 2H), 1.60−1.53 (m, 4H), 1.04 (t, J = 7.5 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 149.14, 146.80 (1C), 146.22 (1C), 145.98, 145.10, 144.98 (4C), 144.85, 144.83 (4C), 144.65, 144.32, 144.05, 143.96 (4C), 143.51, 143.25, 142.08, 141.63 (4C), 141.56, 141.48, 141.16, 141.08, 141.02, 140.67, 139.34, 138.57, 135.38, 134.48, 131.01 (1C), 107.98 (1C), 87.33 (1C, sp^3-*C* of C_{60}), 78.77 (1C, sp^3-*C* of C_{60}), 47.60 (1C), 31.81 (1C), 30.46 (1C), 26.64 (1C), 22.66 (1C), 20.14 (1C), 13.77 (1C), 13.65 (1C); FT-IR ν/cm^{-1} (KBr) 2952, 2921, 2852, 1655, 1460, 1427, 1375, 1211, 1180, 1163, 1131, 1102, 1077, 1047, 933, 914, 853, 597, 575, 526; UV−vis ($CHCl_3$) λ_{max}/nm 256, 313, 427; MALDI-TOF MS m/z calcd for $C_{70}H_{19}N$ $[M]^+$ 873.1512, found 873.1501.

Reaction of C_{60} with 1a and 2a in the Presence of TEMPO under the Assistance of $Cu(OAc)_2·H_2O$. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2a** (33 uL, 0.25 mmol) in the presence of $Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) with the addition of TEMPO (15.6 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 12 min afforded first unreacted C_{60} (5.6 mg, 16%) and then **3a** (34.9 mg, 73%) as an amorphous brown solid.

Reaction of C_{60} with 1a and 2a in the Presence of BHT under the Assistance of $Cu(OAc)_2·H_2O$. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2a** (33 uL, 0.25 mmol) in the presence of $Cu(OAc)_2·H_2O$ (20.0 mg, 0.10 mmol) with the addition of BHT (22.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 13 min afforded first unreacted C_{60} (10.5 mg, 29%) and then **3a** (32.5 mg, 68%) as an amorphous brown solid.

Reaction of C_{60} with 1a and 2a in the Presence of TEMPO under the Assistance of Anhydrous $Cu(OAc)_2$. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2a** (33 uL, 0.25 mmol) in the presence of $Cu(OAc)_2$ (18.2 mg, 0.10 mmol) with the addition of TEMPO (15.6 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 15 min afforded first unreacted C_{60} (5.4 mg, 15%) and then **3a** (36.4 mg, 76%) as an amorphous brown solid.

Reaction of C_{60} with 1a and 2a in the Presence of BHT under the Assistance of Anhydrous $Cu(OAc)_2$. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (29 uL, 0.25 mmol) and **2a** (33 uL, 0.25 mmol) in the presence of $Cu(OAc)_2$ (18.2 mg, 0.10 mmol) with the addition of BHT (22.0 mg, 0.10 mmol) in chlorobenzene (10 mL) at 100 °C for 12 min afforded first unreacted C_{60} (12.3 mg, 34%) and then **3a** (30.2 mg, 63%) as an amorphous brown solid.

Preparation of Compound 6. Fulleropyrroline **3a** (19.2 mg, 0.02 mmol), $CuCl_2·2H_2O$ (6.8 mg, 0.04 mmol), and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) was dissolved in chlorobenzene (6 mL) with the aid of sonication, and then the reaction mixture was stirred in an oil bath preset at 80 °C for 20 min. 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 CH_2Cl_2/CS_2 (v/v = 1/2) as the eluent to afford compound *trans*-**6**/*cis*-**6** (15.2 mg, 75%, *trans*/*cis* = 91/9) together with a little amount of unreacted fulleropyrroline **3a**.

trans-***6***. ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.08 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.26−7.19 (m, 3H), 6.95 (d, J = 5.0 Hz, 1H), 6.87 (d, J = 8.3 Hz, 2H), 5.74 (d, J = 5.0 Hz, 1H), 5.05 (d, J = 12.8 Hz, 1H), 4.74 (d, J = 12.8 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 158.24 (aryl *C*), 154.13, 153.81, 152.27, 149.74, 146.85, 146.62, 146.12, 145.43, 145.39, 145.37, 145.19 (2C), 145.14, 145.01 (3C), 144.93, 144.87, 144.82, 144.73, 144.63, 144.48, 144.30, 144.25, 144.18, 144.14 (2C), 144.05 (2C), 143.78, 143.66, 143.58, 142.10, 142.02, 141.79 (2C), 141.69 (2C), 141.60, 141.54, 141.32, 141.25 (2C), 141.18, 140.99, 140.88 (2C), 140.78, 140.70, 140.64, 140.56, 138.48, 138.18, 138.09, 137.92, 137.75, 136.55, 136.20, 135.01, 130.50 (2C, aryl *C*), 129.23 (aryl *C*), 128.54 (2C, aryl *C*), 127.47 (aryl *C*), 127.12 (2C, aryl *C*), 113.20 (2C, aryl *C*), 87.55 (sp^3-*C* of C_{60}), 84.22, 83.82, 77.99 (sp^3-*C* of C_{60}), 54.25, 49.42; FT-IR ν/cm^{-1} (KBr) 3052, 2919, 2849, 1610, 1583, 1509, 1434, 1301, 1245, 1171, 1152, 1113, 1094, 1035, 847, 823, 741, 694, 659, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 315, 430; MALDI-TOF MS m/z calcd for $C_{76}H_{14}NO$ $[M-OH-HCl]^{+\bullet}$ 956.1070, found 956.1081.

Preparation of Compound 7. The mixture of compound **6** (20.2 mg, 0.02 mmol) and $TsOH·H_2O$ (7.6 mg, 0.04 mmol) was dissolved in chlorobenzene (10 mL), and then the resulting solution was stirred in an oil bath preset at 60 °C for 3 h. 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 CS_2 as the eluent to afford compound **7** (11.0 mg, 63%) together with a little amount of unreacted compound **6**.

7. ^{1}H NMR (500 MHz, CS_2/DMSO-d_6) δ 8.71 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, CS_2/DMSO-d_6) (all 1C unless indicated) δ 164.67 (C═N), 152.55, 151.44, 149.99, 149.41,

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307

146.83, 146.73, 145.69, 145.55, 145.45, 145.29, 145.28, 145.17 (2C), 145.11 (2C), 145.05, 144.91 (2C), 144.67, 144.54, 144.42 (3C), 144.34 (3C), 144.20, 144.11, 143.63 (3C), 143.38, 142.15, 141.99, 141.84 (3C), 141.70, 141.50 (2C), 141.36 (2C), 141.24, 141.18, 141.03, 140.95, 140.77 (3C), 140.58, 139.44, 139.37, 138.78, 138.20 (2C), 136.55, 135.19, 134.82, 134.12, 128.78 (aryl *C*), 128.54 (2C, aryl *C*), 126.53 (2C, aryl *C*), 98.68 (sp^3-*C* of C_{60}), 85.90, 74.61 (sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2916, 2847, 1636, 1511, 1445, 1429, 1287, 1216, 1182, 1001, 927, 849, 759, 717, 693, 546, 526; UV−vis ($CHCl_3$) λ_{max}/nm 257, 316, 429; MALDI-TOF MS *m*/*z* calcd for $C_{68}H_6ClN$ $[M]^+$ 871.0184, found 871.0175.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01875.

HRMS of **3d**, **3k**, **5d**, **5m**, *trans*-**6**, and **7**; UV−vis spectra of **3c**, **3j**, and **5c**; ^1H and ^{13}C NMR spectra of **3a-m**, **5a-m**, *trans*-**6**, and **7**; and NOESY spectrum of *trans*-**6**. (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: lfb0615@hubu.edu.cn.
*E-mail: lijx@ipp.ac.cn.
*E-mail: chyliu@wipm.ac.cn.

Author Contributions

‖These authors 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 21272236), Natural Science Foundation of Hubei Province (No. 2014CFB550), Natural Science Fund for Creative Research Groups of Hubei Province of China (No. 2014CFA015), and Innovation and Entrepreneurship Training Program for Undergraduates of Hubei Province (No. 201610512054).

■ REFERENCES

(1) For selected reviews, see: (a) Nakamura, E.; Isobe, H. *Acc. Chem. Res.* **2003**, *36*, 807. (b) Bendikov, M.; Wudl, F. *Chem. Rev.* **2004**, *104*, 4891. (c) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049. (d) Giacalone, F.; Martín, N. *Chem. Rev.* **2006**, *106*, 5136. (e) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, 6083. (f) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016. (g) Guldi, D. M.; Illescas, B. M.; Atienza, C. M.; Wielopolski, M.; Martín, N. *Chem. Soc. Rev.* **2009**, *38*, 1587. (h) Vougioukalakis, G. C.; Roubelakis, M. M.; Orfanopoulos, M. *Chem. Soc. Rev.* **2010**, *39*, 817. (i) Zhu, S.-E; Li, F.; Wang, G.-W. *Chem. Soc. Rev.* **2013**, *42*, 7535.

(2) For some recent papers, see: (a) Chen, S.; Li, Z.-J.; Li, S.-H.; Gao, X. *Org. Lett.* **2015**, *17*, 5192. (b) Zhai, W.-Q.; Jiang, S.-P.; Peng, R.-F.; Wang, G.-W. *Org. Lett.* **2015**, *17*, 1862. (c) Lou, N.; Li, Y.; Cui, C.; Liu, Y.; Gan, L. *Org. Lett.* **2016**, *18*, 2236. (d) Wu, A.-J.; Tseng, P.-Y.; Hsu, W.-H.; Chuang, S.-C. *Org. Lett.* **2016**, *18*, 224.

(3) For recent reviews on the reactions of [60]fullerene promoted by transition metal salts, see: (a) Wang, G.-W.; Li, F.-B. *J. Nanosci. Nanotechnol.* **2007**, *7*, 1162. (b) Wang, G.-W.; Li, F.-B. *Curr. Org. Chem.* **2012**, *16*, 1109. (c) Li, F.-B.; Wang, G.-W. *Sci. China: Chem.* **2012**, *55*, 2009. (d) Tzirakis, M. D.; Orfanopoulos, M. *Chem. Rev.* **2013**, *113*, 5262.

(4) For the $Cu(OAc)_2$-mediated reactions of [60]fullerene, see: (a) Wang, G.-W.; Li, F.-B. *Org. Biomol. Chem.* **2005**, *3*, 794. (b) Lu, S.; Jin, T.; Kwon, E.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 802. (c) Liu, T.-X.; Zhang, Z.; Liu, Q.; Zhang, P.; Jia, P.; Zhang, Z.; Zhang, G. *Org. Lett.* **2014**, *16*, 1020. (d) Lu, X.-W.; Xing, M.-L.; Miao, C.-B.; Li, J.-X.; Sun, X.-Q.; Yang, H.-T. *Org. Biomol. Chem.* **2015**, *13*, 8405. (e) Yang, H.-T.; Tan, Y.-C.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *J. Org. Chem.* **2016**, *81*, 1157.

(5) For the reactions of [60]fullerene promoted by other Cu(II)/Cu(I) salts, see: (a) Xiao, Z.; Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2010**, *132*, 12234. (b) Zhang, Y.; Matsuo, Y.; Nakamura, E. *Org. Lett.* **2011**, *13*, 6058. (c) Zhang, Y.; Matsuo, Y.; Li, C.-Z.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 8086. (d) Yang, H.-T.; Tian, Z.-Y.; Ruan, X.-J.; Zhang, M.; Miao, C.-B.; Sun, X.-Q. *Eur. J. Org. Chem.* **2012**, *2012*, 4918. (e) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *J. Org. Chem.* **2013**, *78*, 11992. (f) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2013**, *15*, 4650. (g) Si, W.; Lu, S.; Bao, M.; Asao, N.; Yamamoto, Y.; Jin, T. *Org. Lett.* **2014**, *16*, 620. (h) Jiang, S.-P.; Su, Y.-T.; Liu, K.-Q.; Wu, Q.-H.; Wang, G.-W. *Chem. Commun.* **2015**, *51*, 6548.

(6) For selected papers on the reactions of [60]fullerene promoted by Mn(III) salts, see: (a) Zhang, T.-H.; Lu, P.; Wang, F.; Wang, G.-W. *Org. Biomol. Chem.* **2003**, *1*, 4403. (b) Wang, G.-W.; Yang, H.-T.; Miao, C.-B.; Xu, Y.; Liu, F. *Org. Biomol. Chem.* **2006**, *4*, 2595. (c) Wang, G.-W.; Li, F.-B.; Zhang, T.-H. *Org. Lett.* **2006**, *8*, 1355. (d) Wang, G.-W.; Wang, C.-Z.; Zhu, S.-E; Murata, Y. *Chem. Commun.* **2011**, *47*, 6111. (e) Wang, G.-W.; Wang, C.-Z.; Zou, J.-P. *J. Org. Chem.* **2011**, *76*, 6088.

(7) For selected papers on the reactions of [60]fullerene promoted by Fe(III) salts, see: (a) Li, F.-B.; Liu, T.-X.; Wang, G.-W. *J. Org. Chem.* **2008**, *73*, 6417. (b) Li, F.-B.; You, X.; Wang, G.-W. *Org. Lett.* **2010**, *12*, 4896. (c) Hashiguchi, M.; Obata, N.; Maruyama, M.; Yeo, K. S.; Ueno, T.; Ikebe, T.; Takahashi, I.; Matsuo, Y. *Org. Lett.* **2012**, *14*, 3276. (d) Su, Y.-T.; Wang, G.-W. *Org. Lett.* **2013**, *15*, 3408. (e) You, X.; Wang, G.-W. *J. Org. Chem.* **2014**, *79*, 117. (f) 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. (g) Zhang, X.-F.; Li, F.-B.; Wu, J.; Shi, J.-L.; Liu, Z.; Liu, L. *J. Org. Chem.* **2015**, *80*, 6037. (h) Zhang, X.-F.; Li, F.-B.; Shi, J.-L.; Wu, J.; Liu, L. *New J. Chem.* **2016**, *40*, 1626. (i) 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.

(8) (a) Vail, S. A.; Tomé, J. P. C.; Krawczuk, P. J.; Dourandin, A.; Shafirovich, V.; Cavaleiro, J. A. S.; Schuster, D. I. *J. Phys. Org. Chem.* **2004**, *17*, 814. (b) Vail, S. A.; Krawczuk, P. J.; Guldi, D. M.; Palkar, A.; Echegoyen, L.; Tomé, J. P. C.; Fazio, M. A.; Schuster, D. I. *Chem. - Eur. J.* **2005**, *11*, 3375.

(9) (a) Wu, J.; Li, F.-B.; Zhang, X.-F.; Shi, J.-L.; Liu, L. *RSC Adv.* **2015**, *5*, 30549. (b) Zhang, H.-Y.; Wang, H.-J.; Li, F.-B.; Liu, C.-X.; Zhang, X.-F.; Liu, L.; Liu, C.-Y. *RSC Adv.* **2016**, *6*, 79095. (c) Shi, J.-L.; Zhang, X.-F.; Wang, H.-J.; Li, F.-B.; Zhong, X.-X.; Liu, C.-X.; Liu, L.; Liu, C.-Y.; Qin, H.-M.; Huang, Y.-S. *J. Org. Chem.* **2016**, *81*, 7662.

(10) Neumann, J. J.; Suri, M.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 7790.

(11) (a) Lammertsma, K.; Prasad, B. V. *J. Am. Chem. Soc.* **1994**, *116*, 642. (b) Cámpora, J.; Hudson, S. A.; Massiot, P.; Maya, C. M.; Palma, P.; Carmona, E.; Martínez-Cruz, L. A.; Vegas, A. *Organometallics* **1999**, *18*, 5225. (c) Basa, P. N.; Bhowmick, A.; Horn, L. M.; Sykes, A. G. *Org. Lett.* **2012**, *14*, 2698.

(12) (a) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411. (b) Lai, J.-Y.; Wang, F.-S.; Guo, G.-Z.; Dai, L.-X. *J. Org. Chem.* **1993**, *58*, 6944. (c) El-Qisairi, A.; Hamed, O.; Henry, P. M. *J. Org. Chem.* **1998**, *63*, 2790. (d) Hamed, O.; Henry, P. M. *Organometallics* **1998**, *17*, 5184. (e) Hamed, O.; Henry, P. M.; Thompson, C. *J. Org. Chem.* **1999**, *64*, 7745.

DOI: 10.1021/acs.joc.6b01875
J. Org. Chem. 2016, 81, 9296−9307