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Reaction of C_{60} with Inactive Secondary Amines and Aldehydes and the $Cu(OAc)_2$-Promoted Regioselective Intramolecular C−H Functionalization of the Generated Fulleropyrrolidines

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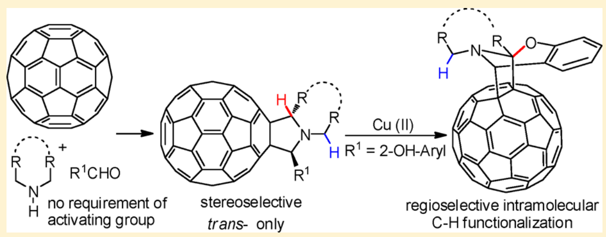
Supporting Information

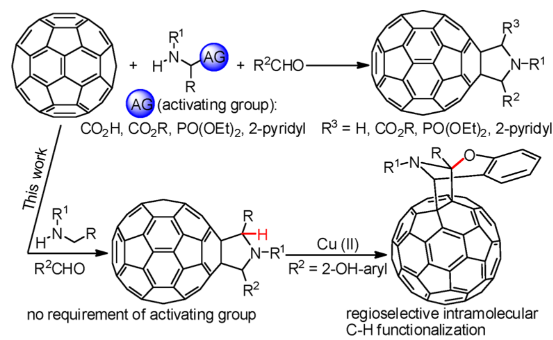
ABSTRACT: The thermal reaction of C_{60} with aromatic aldehydes and inactive secondary amines for the stereoselective synthesis of *trans*-1,2,5-trisubstituted fulleropyrrolidines has been developed. Moreover, when an *o*-hydroxyl group was located at the phenyl ring of the generated fulleropyrrolidines, the $Cu(OAc)_2$-promoted regioselective intramolecular C−O coupling reaction occurred to generate unique tricycle-fused fullerene derivatives.



INTRODUCTION

The chemical modification of fullerenes, which allows the combination of the outstanding properties of the fullerenes with other interesting addends such as bioactive, photoactive, and electroactive units and increases the solubility of generated derivatives, is important for the investigation of their application in medicinal or material science.[1] Until now, large quantities of organofullerenes have been prepared.[2] Among them, the fulleropyrrolidines constitute the largest family of fullerene derivatives because of their easy preparation and many possible synthetic variations.[3] Some fulleropyrrolidines show a power conversion efficiency (PCE) even higher than that of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) under the same conditions.[1a,4] The 1,3-dipolar cycloaddition of azomethine ylides to C_{60} developed by Prato is the most important approach to fulleropyrrolidines.[3a,b] Azomethine ylides are always generated from the condensation of α-amino acids, α-amino esters, α-amino phosphonates, or α-pyridylamines with ketonic compounds.[2c,3,5] An activating group on the α-carbon of the nitrogen atom is necessary to generate the ylides (Scheme 1). The ring opening of aziridines is an alternative method for generating the azomethine ylides.[6] In addition, photocycloaddition of amines to C_{60}[7] and the direct interaction of amino acids, amino acid esters,[8] or arylmethylamines[9] with C_{60} are special routes to fulleropyrrolidines, albeit with great substrate limitation. As we know, in contrast to α-amino acids or α-amino esters, ordinary secondary amines are much more easily available. As a continuation of our interest in fullerene chemistry,[10] herein we described a concise protocol for the highly stereoselective synthesis of fulleropyrrolidines through thermal reaction of C_{60} with inactive secondary amines and aromatic aldehydes (Scheme 1).

Scheme 1



Seidel and co-workers have developed a series of redox-neutral amine α-functionalization reactions involving unstabilized azomethine ylides as the reactive intermediate.[11] In the transformation, an inactive secondary amine with no activating group on the α-carbon of the nitrogen atom was used to generate the unstabilized azomethine ylides. Although this kind of azomethine ylide was deduced as the intermediate, their reactions with double and/or triple bonds to form five-membered ring heterocycles were rarely reported. For instance, the intramolecular reaction with pendent electron-deficient alkenes[12] and the intermolecular reaction with aldehydes[13] have been demonstrated to construct ploycyclic products and

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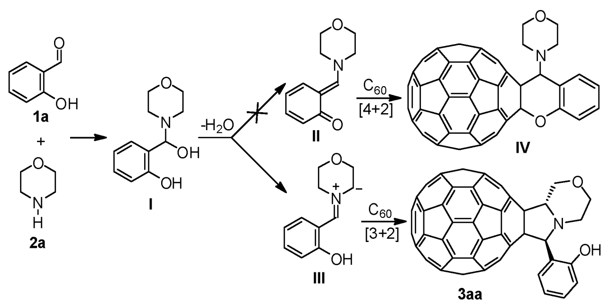
pyrrolidinooxazolidine skeletons, respectively. Inspired by the seminal studies of Seidel et al., we envisioned that the reaction of salicylaldehyde **1a** with morpholine **2a** would form *N*,*O*-acetal **I** (Table 1). Dehydration of **I** might afford *o*-quinone methide **II** and azomethin ylide **III**. In view of the perfect dipolarophilic character of C_{60}, the [3+2] and [4+2] reaction of C_{60} with **III** and **II** probably occurred to provide the fulleropyrrolidines and rare fullerochroman derivatives, respectively.

Table 1. Route Design and Screening of the Reaction Conditions



entry	C_{60}:**1a**:**2a**	*T* (°C)	time (h)	yield (%)[a]
1	1:3:3	80	24	trace
2	1:3:3	100	24	trace
3	1:3:3	130	24	20 (81)
4	1:5:5	130	24	39 (71)
5	1:5:2	130	24	37 (79)
6	1:2:5	130	24	14 (85)

[a]Isolated yield; the values in parentheses are based on consumed C_{60}.

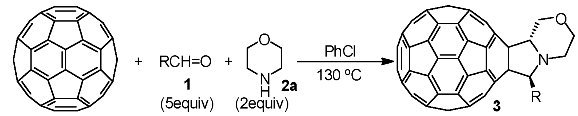
RESULTS AND DISCUSSION

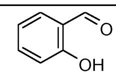
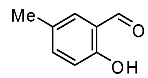
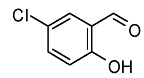
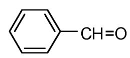
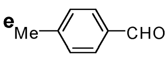
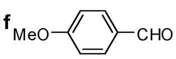
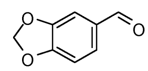
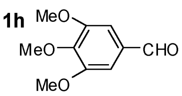
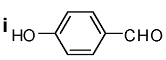
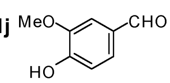
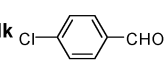
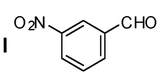
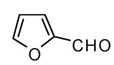
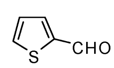
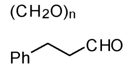
When C_{60} was treated with 3 equiv of morpholine (**2a**) and 3 equiv of salicylaldehyde (**1a**) in chlorobenzene at 80 °C, no reaction occurred. Increasing the temperature to 130 °C led to the formation of a single [3+2] product, **3aa**, in 22% yield, and no [4+2] product **IV** was observed. The yield of **3aa** could be significantly improved to 39% when the molar ratio of the reaction was changed from 1:3:3 to 1:5:5. Decreasing the amount of morpholine to 2 equiv gave a comparable yield of **3aa** (Table 1, entry 5). Nevertheless, when the amount of salicylaldehyde was reduced to 2 equiv, a noticeable decrease in the yield of **3aa** arose (Table 1, entry 6). In view of the atomic economy, a C_{60}:**1a**:**2a** molar ratio of 1:5:2 and a reaction temperature of 130 °C were selected as the optimized conditions for subsequent investigation of the generality of this [3+2] annulation (Table 2).

First, the substrate scope of the aldehydes was investigated by performing the reaction of C_{60} with morpholine and different aldehydes. All the aromatic aldehydes with either electron-donating or electron-withdrawing groups on the phenyl ring gave moderate to good yields of **3**. No obvious electronic effect was observed. Heteroaromatic aldehydes **1m** and **1n** also reacted with C_{60} and morpholine to give corresponding fulleropyrrolidines **3am** and **3an**, respectively. Nevertheless, a shortcoming of this method was the fact that the aliphatic aldehydes did not work.

Next, the applicability of other secondary amines in this conversion was also evaluated (Scheme 2). Considering the high reaction temperature, several representative secondary

Table 2. Reaction of C_{60} with Morpholine and Aldehydes



entry	substrate	time (h)	product	yield (%)[a]
1	1a 	24	**3aa**	37 (79)
2	1b 	12	**3ab**	23 (75)
3	1c 	18	**3ac**	21 (77)
4	1d 	41	**3ad**	20 (82)
5	1e 	20	**3ae**	34 (85)
6	1f 	26	**3af**	22 (66)
7	1g 	24	**3ag**	26 (69)
8	1h 	58	**3ah**	21 (78)
9	1i 	48	**3ai**	23 (80)
10	1j 	22	**3aj**	30 (84)
11	1k 	15	**3ak**	34 (77)
12	1l 	36	**3al**	30 (75)
13	1m 	21	**3am**	32 (68)
14	1n 	21	**3an**	23 (80)
15	1o $(CH_2O)_n$	40	**3ao**	0
16	1p 	24	**3ap**	0

[a]Isolated yield; the values in parentheses are based on consumed C_{60}.

amines with high boiling points such as piperidine (**2b**), *N*-methylpiperazine (**2c**), dibutylamine (**2d**), *N*-benzylbutylamine (**2e**), dicyclohexylamine (**2f**), and *N*-ethylcyclohexylamine (**2g**) were introduced into the reaction mixture with C_{60} and aldehydes. Symmetrical cyclic amines **2b** and **2c** gave good yield of **3bd** and **3cd**, respectively. Symmetrical acyclic amine **2d** gave a lower yield of product. In the case of asymmetrical amine, although two isomers might be formed in theory, only product **3ea** was isolated as the single isomer in 31% yield in the reaction of C_{60} with *N*-benzylbutylamine **2e**, probably

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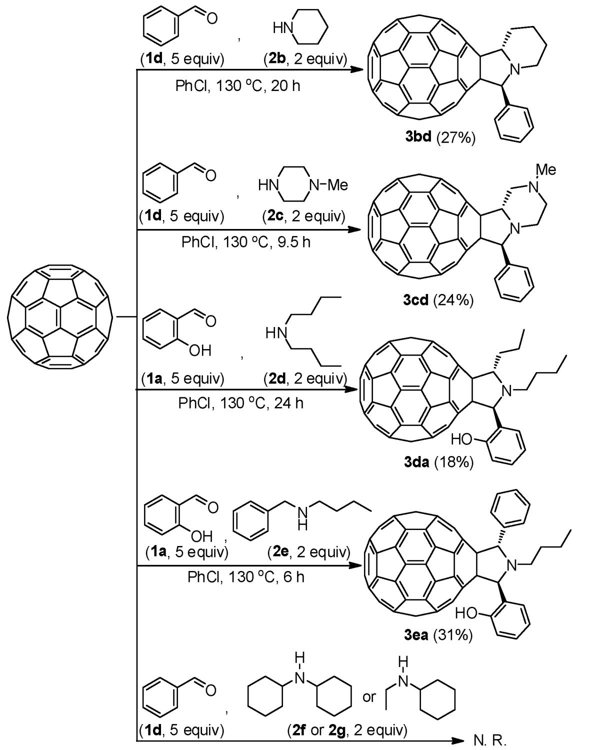
Scheme 2. Variation of the Secondary Amines



because of the stabilization of 1,3-diploes by a phenyl ring through a conjugation effect. For dicyclohexylamine (**2f**) or *N*-ethycyclohexylamine (**2g**), in which at least one secondary carbon was linked with a nitrogen atom, no reaction occurred. The failure of the reaction was partially attributed to the large steric hindrance.

It was known that a mixture of *cis* and *trans* isomers was often produced for the 2,5-disubstituted fulleropyrrolidines.[3c,5a,14] However, in this work, only the *trans* isomers were isolated as the single diastereoisomer and the stereochemistry was confirmed by nuclear Overhauser enhancement spectroscopy (NOESY) analysis (see the Supporting Information). With **3ad** as an example, the absence of correlation between two methine protons (H_1 and H_2) of the pyrrolidine ring indicated their *trans* configuration. Moreover, the correlation of H_1 with H_3, H_5, and H_8 could be seen clearly (Figure 1).

Martín and Solà have reported the intramolecular nucleophilic addition of a hydroxyl group to [60]fullerene to form *cis-1* bicyclic-fused organofullerene.[15] The generated fullerenepyrrolidines such as **1a–c**, **3da**, and **3ea** also contained an *o*-hydroxyl group. We were curious about whether the direct addition or oxidative addition reaction of the hydroxyl group with the neighbor double bonds of C_{60} could occur. Several conditions were tried using **3aa** as a model reaction such as direct heating at 170 °C in *O*-dichlorobenzene and treatment with $PhI(OAc)_2$, $Cu(OAc)_2$, NBS and DMAP, and $Pd(OAc)_2$, morpholine, and $K_2S_2O_8$. No desired reaction on the neighbor double bonds took place. However, to our delight, the reaction of **3aa** with 2 equiv of $Cu(OAc)_2$ at 100 °C in chlorobenzene for 7 h afforded intramolecular C–O coupling product **4aa** in 92% yield (Scheme 3). This reaction displayed excellent regioselectivity. Among the two types of sp^3 C–H bonds adjacent to the nitrogen atom, α-functionalization occurred only at the position bonding to the C_{60} cage to generate a unique tricycle-fused fullerene derivative, which could be easily judged from the ^{1}H NMR spectrum showing that two doublets attributed to the CH_2 group (adjacent *N*,*O*-acetal) appeared at 4.53 and 4.84 ppm with a coupling constant of 11.4 Hz. At present, the reason for the excellent regioselectivity was not clear. Other fulleropyrrolidines, **3ab**, **3ac**, **3da**, and **3ea**, could

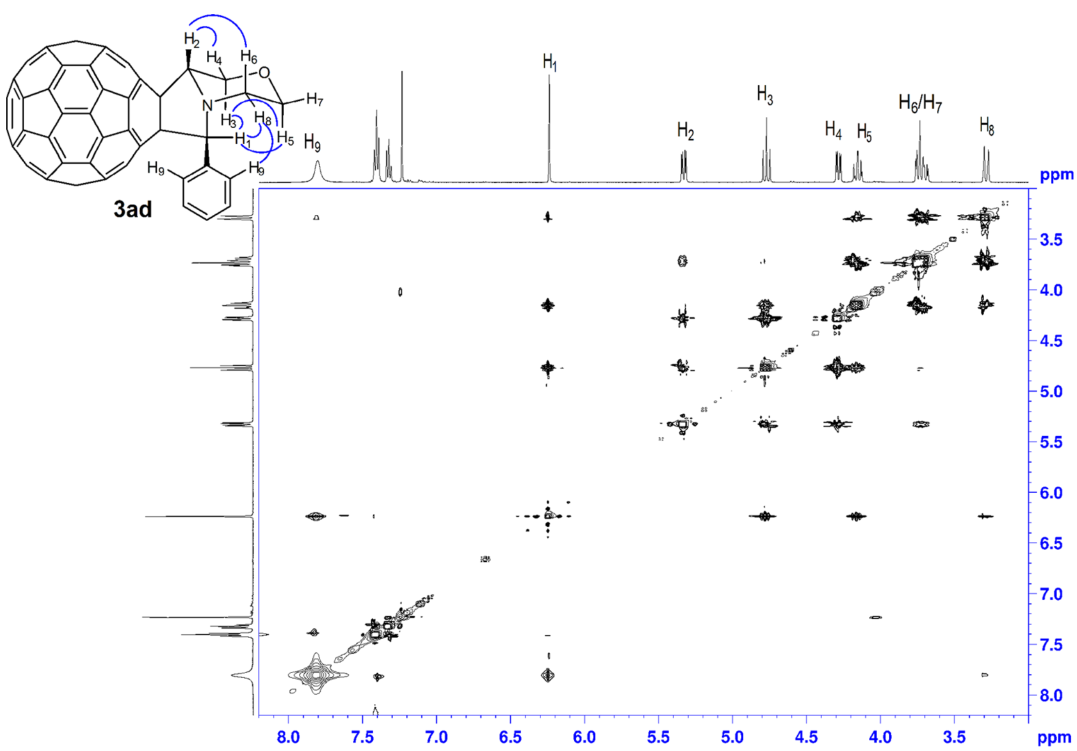


Figure 1. NOESY spectrum of **3ad**.

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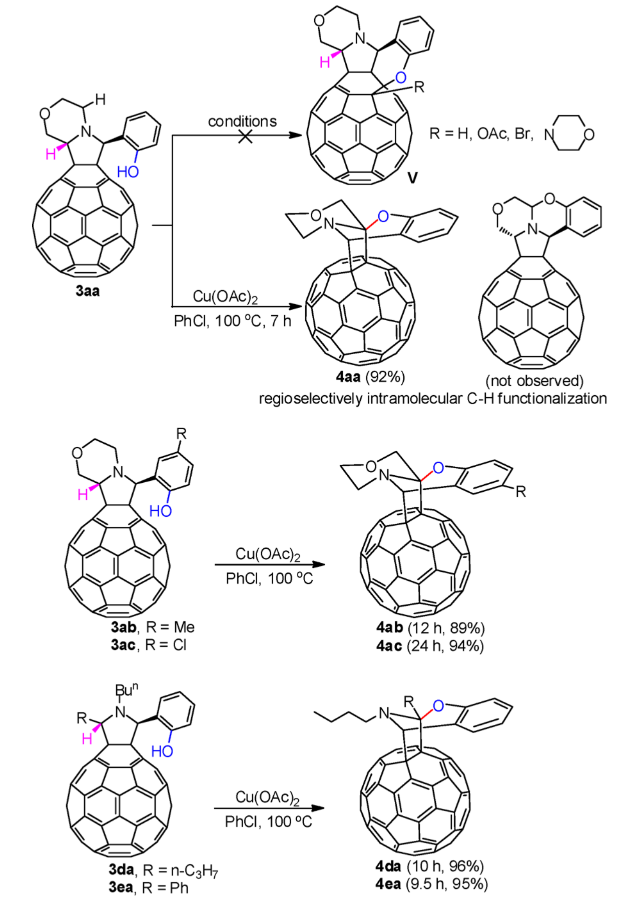
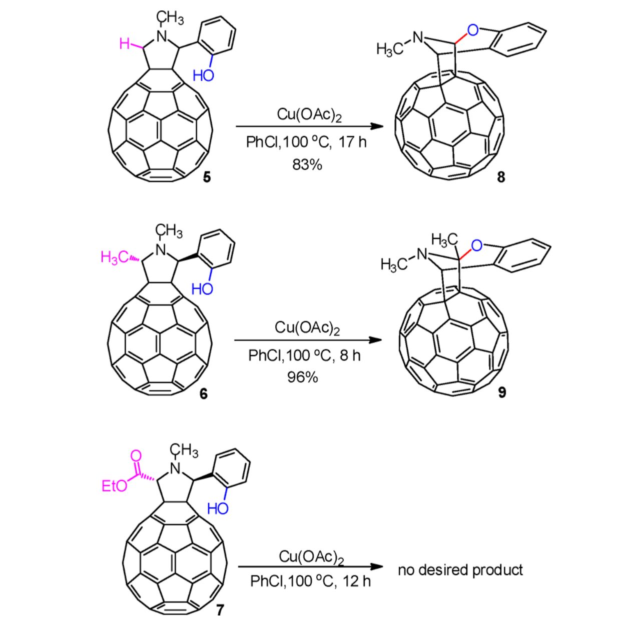
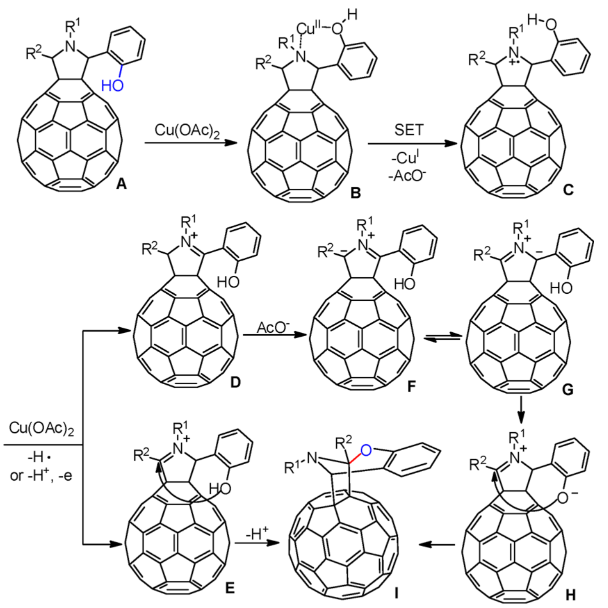
Scheme 3. Regioselectively Intramolecular C−H Functionalization



Scheme 4. Influence of Substituents on Intramolecular C−H Functionalization



Scheme 5. Proposed Mechanism for C−O Bond Formation



also undergo a similar transformation to provide the tricycle-fused fullerene derivatives in excellent yields (Scheme 3). Although the intramolecular oxidative α-functionalization of tertiary amines to dihydro-1,3-oxazines has been reported,[16] the regioselectivity was unsatisfied for the asymmetrical cyclic amines and the diasteroselectivity could not be controlled perfectly.[16]

To examine the efficiency and generality of this regioselective intramolecular C−O coupling reaction, more fulleropyrrolidines bearing an *o*-hydroxyphenyl group were prepared and introduced into the $Cu(OAc)_2$-promoted reaction. Three representative substituents such as hydrogen, an alkyl group (electron-donating), and an ester group (electron-withdrawing) at α-C of the nitrogen atom were investigated (Scheme 4). Under the standard conditions, fulleropyrrolidines **5** and **6** afforded C−O coupling products **8** and **9**, respectively. It also could be seen that if there was no substituent on α-C of the nitrogen atom the reaction proceeded much slower (17 h vs 8 h). Surprisingly, when an ester group was introduced, the reaction was inhibited completely.

A probable mechanistic explanation for intramolecular C−O bond formation was depicted in Scheme 5. Single-electron transfer (SET) from fulleropyrrolidine **A** to Cu(II) afforded radical cation **B**.[17] The following abstraction of H radical (or combination of proton transfer and single-electron transfer) in the presence of $Cu(OAc)_2$ would form iminium ion **D** or **E**. Taking into account the fact that the benzylic C−H bond reacted more readily than nonbenzylic primary and secondary C−H bonds reported in the literature,[16] we thought that iminium ion **D** should be predominant. Deprotonation of **D** furnished 1,3-dipoles **F**, which equilibrated with **G**. Intramolecular proton transfer of **G** provided **H**. Similar intramolecular nucleophilic addition of **H** and **E** forms C−O coupling product **I**.

■ CONCLUSION

In summary, we have developed a thermal reaction of C_{60} with inactive secondary amines and aromatic aldehydes to access *trans* 1,2,5-trisubstituted fulleropyrrolidines. The methodology is very general and suitable for a wide range of aldehydes and amines and shows high stereoselectivity. No activating group was required on the α-carbon of the nitrogen atom. Moreover, the fulleropyrrolidines bearing a 2-hydroxylphenyl group undergo efficient regioselective intramolecular C−H function-

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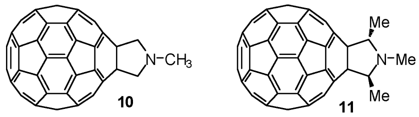
alization promoted by $Cu(OAc)_2$ to generate unique tricycle-fused fullerene derivatives through C−O bond formation.

■ EXPERIMENTAL SECTION

Fulleropyrrolidine 5 Was Prepared According to the Reported Procedure.[18] A mixture of C_{60} (90 mg, 0.125 mmol), salicylaldehyde (30.5 mg, 0.25 mmol), and sarcosine (22.3 mg, 0.25 mmol) in 15 mL of PhCl was stirred at 130 °C for 6 h. The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel eluted with CS_2/toluene to give products **10** (lower polarity, 17.0 mg, 18%)[19] and **5** (higher polarity, 33.5 mg, 31%).[18]



5 (brown solid, mp >300 °C): ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.92 (s, 1H), 7.30 (d, J = 7.5, 1.2 Hz, 1H), 7.17 (td, J = 7.8, 1.6 Hz, 1H), 6.77−6.85 (m, 2H), 5.06 (s, 1H), 5.04 (d, J = 9.9 Hz, 1H), 4.25 (d, J = 9.9 Hz, 1H), 2.95 (s, 3H).

10 (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 4.39 (s, 4H), 2.99 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 154.81, 147.29, 146.24, 146.06, 146.00, 145.68, 145.45, 145.28, 144.55, 143.11, 142.64, 142.22, 142.08, 141.90, 140.19, 136.25, 71.17, 70.09, 41.56.

Preparation of 6. A mixture of C_{60} (90 mg, 0.125 mmol), salicylaldehyde (45.8 mg, 0.375 mmol), and *N*-methylalanine (25.3 mg, 0.25 mmol) in 15 mL of PhCl was stirred at 130 °C for 1.5 h. The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel eluted with CS_2/toluene to give products **6** (lower polarity, 26 mg, 24%) and **11** (higher polarity, 31.1 mg, 31%).

6 (brown solid, mp >300 °C): ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 11.02 (s, 1H), 7.33 (dd, J = 7.8, 1.6 Hz, 1H), 7.19 (td, J = 7.8, 1.6 Hz, 1H), 6.79−6.86 (m, 2H), 5.54 (s, 1H), 5.30 (q, J = 6.9 Hz, 1H), 2.96 (s, 3H), 2.10 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) (all 2C unless indicated) δ 156.94, 156.26, 153.60, 152.34, 151.69, 147.45, 147.33, 146.66, 146.38, 146.29, 146.20, 146.07, 145.97, 145.94, 145.82, 145.79, 145.72, 145.51, 145.41, 145.38, 145.35, 145.23, 145.19, 145.17, 144.72, 144.56, 144.47, 144.34, 143.14, 143.10, 142.79, 142.64, 142.58, 142.51, 142.34, 142.23, 142.19, 142.18, 142.15, 142.07, 141.95, 141.92, 141.91, 141.69, 141.47, 141.45, 140.13, 140.04, 139.92, 139.18, 136.75, 136.39, 136.17, 136.07, 130.22, 130.01, 119.69, 119.56, 117.66, 78.26, 76.11 (sp^3-C of C_{60}), 72.95 (sp^3-C of C_{60}), 69.38, 35.78, 14.34; UV−vis ($CHCl_3$) λ_{max} 256, 310, 430, 702 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{70}H_{14}NO$ 884.1075, found 884.1069.

11 (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 4.79 (q, J = 6.6 Hz, 2H), 2.92 (s, 3H), 1.92 (d, J = 6.6 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 156.08, 153.61, 147.26, 146.56, 146.24, 146.21, 146.00, 145.6, 145.40, 145.28, 145.17, 144.55, 144.52, 143.12, 142.65, 142.59, 142.26, 142.19, 142.10, 141.8, 141.70, 140.16, 139.80, 136.99, 135.99, 74.76 (sp^3-C of C_{60}), 68.21, 35.13, 15.56; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{65}H_{12}N$ 806.0970, found 806.0965.

Preparation of 7. A mixture of C_{60} (90 mg, 0.125 mmol), salicylaldehyde (45.8 mg, 0.375 mmol), sarcosine ethyl ester hydrochloride (38.4 mg, 0.25 mmol), and Et_3N (25.5 mg, 0.25 mmol) was stirred in 15 mL of PhCl for 4.5 h. The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel eluted with CS_2/toluene to give product **7** (52.9 mg, 45%).

7 (brown solid, mp >300 °C): ^{1}H NMR (300 MHz, $CDCl_3/CS_2$) δ 10.43 (s, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.18 (td, J = 7.8, 1.6 Hz, 1H), 6.76−6.90 (m, 2H), 6.39 (s, 1H), 5.66 (s, 1H), 4.47 (dq, J = 10.7, 7.2 Hz, 1H), 4.33 (dq, J = 10.7, 7.1 Hz, 1H), 3.05 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 169.63, 157.00, 154.47, 153.13, 151.72, 149.87, 147.49, 147.27, 146.44, 146.37, 146.36, 146.25, 146.19, 146.17, 146.15, 146.05, 146.00, 145.94, 145.94, 145.65, 145.61, 145.61, 145.38, 145.26, 145.21, 145.13, 144.76, 144.43, 144.31, 143.07, 143.00, 142.76, 142.66, 142.55, 142.20, 142.14, 142.13, 142.10, 142.02, 141.89, 141.60, 141.58, 141.53, 140.20, 140.08, 139.55, 139.28, 137.34, 136.62, 136.23, 136.05, 130.29, 119.84, 119.35, 117.60, 79.43, 76.44, 75.77 (sp^3-C of C_{60}), 70.67 (sp^3-C of C_{60}), 61.53, 35.66, 14.46; UV−vis ($CHCl_3$) λ_{max} 257, 312, 430, 698 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{72}H_{16}NO_3$ 942.1130, found 942.1118.

General Procedure for the Reaction of C_{60} with Aldehydes and Secondary Amines. A mixture of C_{60} (36.0 mg, 0.05 mmol), aldehydes (**1a**−**n**, 0.25 mmol), and secondary amines (**2a**−**g**, 0.10 mmol) in 10 mL of PhCl was stirred at 130 °C. The reaction was monitored by TLC and stopped at the designated time. The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel eluted with CS_2/toluene to give the corresponding products **3aa**−**3an**, **3bd**, **3cd**, **3da**, and **3ea**.

3aa (brown solid, 16.9 mg, 37%, mp >300 °C): ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.87 (s, 1H), 7.37 (d, J = 6.6 Hz, 1H), 7.20 (t, J = 7.8 Hz, 1H), 6.77−6.88 (m, 2H), 6.30 (s, 1H), 5.36 (dd, J = 11.9, 4.2 Hz, 1H), 4.78 (t, J = 12.1 Hz, 1H), 4.20−4.34 (m, 2H), 3.80−3.98 (m, 2H), 3.46 (d, J = 13.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 157.42, 155.27, 152.96, 151.30, 149.33, 147.40, 147.33, 146.46, 146.38, 146.34, 146.27, 146.23, 146.20, 146.13, 146.12, 145.98, 145.74, 145.70, 145.63, 145.53, 145.41, 145.32, 145.30, 145.25, 145.21, 144.85, 144.63, 144.60, 144.40, 144.30, 143.16, 143.08, 142.77, 142.66, 142.58, 142.24, 142.16, 142.14, 142.09, 142.04, 141.85, 141.83, 141.72, 141.56, 141.44, 140.25, 140.21, 140.08, 139.29, 136.90, 136.72, 135.86, 135.61, 130.48, 130.24, 119.66, 118.52, 117.95, 75.49 (sp^3-C of C_{60}), 73.36, 69.81 (sp^3-C of C_{60}), 67.33, 65.16, 59.76, 45.17; UV−vis ($CHCl_3$) λ_{max} 256, 313, 431, 698 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{71}H_{14}NO_2$ 912.1025, found 912.1035.

3ab (brown solid, 10.6 mg, 23%, mp >300 °C): ^{1}H NMR (400 MHz, $CDCl_3/CS_2$) δ 10.63 (s, 1H), 7.18 (d, J = 1.8 Hz, 1H), 7.01 (dd, J = 8.4, 1.9 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 6.25 (s, 1H), 5.36 (dd, J = 11.9, 4.3 Hz, 1H), 4.79 (t, J = 12.0 Hz, 1H), 4.30 (dd, J = 12.1, 4.3 Hz, 1H), 4.25 (td, J = 11.5, 3.1 Hz, 1H), 3.82−3.96 (m, 2H), 3.45 (dd, J = 13.8, 2.5 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 155.30, 154.95, 153.06, 151.36, 149.36, 147.37, 147.30, 146.43, 146.33, 146.31, 146.26, 146.24, 146.20, 146.15, 146.08, 145.95, 145.73, 145.67, 145.61, 145.49, 145.40, 145.30, 145.28, 145.26, 145.23, 145.17, 144.82, 144.61, 144.58, 144.38, 144.27, 143.14, 143.06, 142.74, 142.65, 142.64, 142.54, 142.21, 142.12, 142.11, 142.07, 142.01, 141.87, 141.82, 141.70, 141.53, 141.42, 140.21, 140.06, 139.30, 136.90, 136.73, 135.84, 135.56, 131.11, 130.70, 128.48, 118.05, 117.79, 75.46 (sp^3-C of C_{60}), 73.32, 69.81 (sp^3-C of C_{60}), 67.28, 65.08, 59.73, 45.13, 20.70; UV−vis ($CHCl_3$) λ_{max} 256, 312, 431, 698 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{72}H_{16}NO_2$ 926.1181, found 926.1176.

3ac (brown solid, 10.0 mg, 21%, mp >300 °C; it cannot be characterized by ^{13}C NMR because of its very poor solubility): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 10.87 (s, 1H), 7.35 (d, J = 2.5 Hz, 1H), 7.15 (dd, J = 8.7, 2.5 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H) 6.21 (s, 1H), 5.35 (dd, J = 12.0, 4.4 Hz, 1H), 4.75 (t, J = 12.0 Hz, 1H), 4.29 (dd, J = 12.2, 4.4 Hz, 1H), 4.29 (dd, J = 12.2, 4.5 Hz, 1H), 4.24 (td, J = 11.5, 3.1 Hz, 1H), 3.84−3.95 (m, 2H), 3.40 (dd, J = 14.3, 2.9 Hz, 1H); UV−vis ($CHCl_3$) λ_{max} 256, 312, 430, 698 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{71}H_{13}ClNO_2$ 946.0635, found 946.0642.

3ad (brown solid, 9.0 mg, 20%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.80 (br, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 6.24 (s, 1H), 5.33 (dd, J = 11.6, 4.1 Hz, 1H), 4.77 (t, J = 11.7 Hz, 1H), 4.28 (dd, J = 11.7, 4.2 Hz, 1H), 4.12−4.19 (m, 1H), 3.67−3.77 (m, 2H), 3.28 (d, J = 14.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 156.21, 153.80, 153.21, 150.54, 147.27, 146.52, 146.31, 146.28, 146.18, 146.07, 146.02, 145.92, 145.64, 145.56, 145.49, 145.40, 145.38, 145.28, 145.24, 145.20, 145.15, 144.69, 144.47, 144.28, 143.16, 143.03, 142.61, 142.55, 142.12, 141.96, 141.91, 141.82, 141.60, 141.39, 140.22, 140.06, 140.02, 139.42, 137.13, 136.62, 136.52, 135.63, 129.48, 128.85, 128.74, 75.71 (sp^3-C of C_{60}), 72.79, 70.32 (sp^3-C of C_{60}), 68.10, 65.58, 60.77, 45.64; UV−vis ($CHCl_3$) λ_{max} 256, 310, 431, 702 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{71}H_{14}NO$ 896.1075, found 896.1069.

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3ae (brown solid, 15.4 mg, 34%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.68 (br, 2H), 7.21 (d, J = 7.1 Hz, 2H), 6.21 (s, 1H), 5.32 (dd, J = 11.7, 4.0 Hz, 1H), 4.77 (t, J = 11.7 Hz, 1H), 4.29 (dd, J = 11.7, 4.0 Hz, 1H), 4.15 (td, J = 12.2, 2.4 Hz, 1H), 3.65−3.77 (m, 2H), 3.28 (d, J = 13.4 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 156.39, 154.15, 153.55, 150.75, 147.37, 146.67, 146.64, 146.41, 146.37, 146.29, 146.28, 146.19, 146.17, 146.02, 145.76, 145.64, 145.56, 145.51, 145.47, 145.41, 145.38, 145.34, 145.30, 145.25, 144.79, 144.57, 144.54, 144.38, 143.25, 143.12, 142.75, 142.70, 142.65, 142.64, 142.24, 142.21, 142.16, 142.15, 142.14, 142.08, 142.02, 141.92, 141.70, 141.50, 140.29, 140.14, 140.12, 139.56, 138.49, 137.24, 136.71, 135.72, 135.66, 133.57, 129.63, 129.52, 75.90 (sp^3-C of C_{60}), 72.82, 70.47 (sp^3-C of C_{60}), 68.14, 65.75, 60.95, 45.71, 21.43; UV−vis ($CHCl_3$) λ_{max} 257, 311, 431, 702 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{72}H_{16}NO$ 910.1232, found 910.1225.

3af (brown solid, 10.2 mg, 22%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.70 (br, 2H), 6.9 (d, J = 8.4 Hz, 2H), 6.18 (s, 1H), 5.30 (dd, J = 11.7, 4.1 Hz, 1H), 4.74 (t, J = 11.6 Hz, 1H), 4.26 (dd, J = 11.6, 4.1 Hz, 1H), 4.13 (td, J = 12.1, 2.0 Hz, 1H), 3.78 (s, 3H), 3.64−3.74 (m, 2H), 3.26 (dd, J = 14.0, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 159.73, 156.32, 154.02, 153.44, 150.57, 147.25, 146.55, 146.54, 146.31, 146.27, 146.20, 146.17, 146.09, 146.07, 145.91, 145.64, 145.55, 145.46, 145.38, 145.29, 145.23, 145.20, 145.14, 144.68, 144.49, 144.44, 144.27, 143.16, 143.02, 142.65, 142.60, 142.55, 142.14, 142.11, 142.07, 142.05, 142.03, 141.98, 141.91, 141.83, 141.59, 141.40, 140.19, 140.06, 140.04, 139.52, 137.15, 136.59, 135.60, 135.56, 130.55, 128.32, 114.24, 75.89 (sp^3-C of C_{60}), 72.29, 70.22 (sp^3-C of C_{60}), 68.02, 65.58, 60.77, 54.96, 45.58; UV−vis ($CHCl_3$) λ_{max} 257, 311, 431, 703 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{72}H_{16}NO_2$ 926.1181, found 926.1194.

3ag (brown solid, 12.2 mg, 26%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.31 (br, 1H), 7.19−7.29 (br, 1H), 6.79 (d, J = 7.9 Hz, 1H), 6.14 (s, 1H), 5.93−5.97 (m, 2H), 5.29 (dd, J = 11.7, 4.1 Hz, 1H), 4.73 (t, J = 11.7 Hz, 1H), 4.25 (dd, J = 11.7, 4.2 Hz, 1H), 4.09−4.16 (m, 1H), 3.64−3.77 (m, 2H), 3.28 (d, J = 14.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 155.26, 152.86, 152.22, 149.54, 147.21, 146.87, 146.30, 145.61, 145.51, 145.35, 145.30, 145.22, 145.12, 145.10, 144.96, 144.69, 144.58, 144.53, 144.41, 144.34, 144.27, 144.18, 143.73, 143.52, 143.46, 143.30, 142.19, 142.06, 141.69, 141.64, 141.59, 141.22, 141.15, 141.10, 141.09, 141.02, 140.98, 140.92, 140.87, 140.62, 140.47, 139.24, 139.08, 138.61, 136.11, 135.61, 134.60, 129.39, 122.27, 108.37, 107.34, 100.22, 74.81 (sp^3-C of C_{60}), 71.49, 69.21 (sp^3-C of C_{60}), 67.03, 64.60, 59.73, 44.56; UV−vis ($CHCl_3$) λ_{max} 256, 312, 432, 702 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{72}H_{14}NO_3$ 940.0974, found 940.0985.

3ah (brown solid, 10.3 mg, 21%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.02 (br, 2H), 6.14 (s, 1H), 5.31 (dd, J = 11.7, 4.1 Hz, 1H), 4.74 (t, J = 11.7 Hz, 1H), 4.27 (dd, J = 11.7, 4.1 Hz, 1H), 4.16 (td, J = 12.2, 2.2 Hz, 1H), 3.84 (s, 6H), 3.79 (s, 3H), 3.68−3.79 (m, 2H), 3.33 (dd, J = 14.0, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 156.15, 153.76, 153.67, 153.53, 150.52, 147.33, 146.69, 146.49, 146.39, 146.34, 146.24, 146.16, 146.13, 145.99, 145.88, 145.66, 145.60, 145.58, 145.44, 145.39, 145.38, 145.36, 145.29, 145.26, 145.23, 145.19, 144.73, 144.58, 144.46, 144.33, 143.27, 143.09, 142.75, 142.70, 142.65, 142.62, 142.17, 142.11, 142.09, 142.05, 141.97, 141.90, 141.64, 141.50, 140.24, 140.14, 139.93, 139.69, 138.38, 137.12, 136.08, 135.66, 135.54, 131.88, 106.84, 75.75 (sp^3-C of C_{60}), 72.90, 70.24 (sp^3-C of C_{60}), 68.12, 65.66, 60.82, 60.62, 56.21, 45.62; UV−vis ($CHCl_3$) λ_{max} 257, 312, 413, 702 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{74}H_{20}NO_4$ 986.1392, found 986.1388.

3ai (brown solid, 10.5 mg, 23%, mp >300 °C): ^{1}H NMR (500 MHz, DMSO-d_6/CS_2) δ 8.91 (s, 1H), 7.48 (br, 2H), 6.70 (d, J = 8.2 Hz, 2H), 6.12 (s, 1H), 5.22 (dd, J = 11.7, 3.9 Hz, 1H), 4.68 (t, J = 11.6 Hz, 1H), 4.16 (dd, J = 11.4, 3.8 Hz, 1H), 4.08 (t, J = 11.2 Hz, 1H), 3.53−3.65 (m, 2H), 3.23 (d, J = 14.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6/CS_2) δ 157.48, 155.89, 153.69, 153.25, 150.17, 146.82, 146.40, 146.38, 145.96, 145.75, 145.46, 145.43, 145.31, 145.23, 145.21, 145.06, 145.05, 144.90, 144.73, 144.66, 144.64, 144.61, 144.54, 144.45, 144.36, 144.33, 144.30, 143.87, 143.75, 143.67, 143.45, 142.32, 142.18, 141.80, 141.75, 141.70, 141.40, 141.31, 141.26, 141.24, 141.21, 141.19, 141.14, 141.01, 140.76, 140.59, 139.30, 139.21, 139.17, 138.64, 136.47, 135.71, 134.92, 134.75, 129.58, 125.17, 115.31, 75.32 (sp^3-C of C_{60}), 71.61, 69.46 (sp^3-C of C_{60}), 67.35, 64.67, 59.95, 45.03; UV−vis ($CHCl_3$) λ_{max} 257, 313, 432, 702 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{71}H_{14}NO_2$ 912.1025, found 912.1016.

3aj (brown solid, 14.1 mg, 30%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.36 (br, 1H), 7.26 (br, 1H), 6.88 (d, J = 8.1 Hz, 1H), 6.15 (s, 1H), 5.54 (s, 1H), 5.30 (dd, J = 11.7, 4.2 Hz, 1H), 4.75 (t, J = 11.7 Hz, 1H), 4.26 (dd, J = 11.7, 4.1 Hz, 1H), 4.11−4.19 (m, 1H), 3.90 (s, 3H), 3.66−3.78 (m, 2H), 3.30 (dd, J = 13.3, 2.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 156.30, 153.88, 153.71, 150.51, 147.27, 146.84, 146.61, 146.52, 146.32, 146.29, 146.18, 146.10, 146.07, 145.93, 145.62, 145.56, 145.50, 145.39, 145.38, 145.29, 145.27, 145.23, 145.15, 144.68, 144.51, 144.44, 144.27, 143.19, 143.03, 142.68, 142.63, 142.57, 142.13, 142.06, 142.04, 142.02, 141.98, 141.90, 141.82, 141.60, 141.45, 140.19, 140.06, 140.01, 139.61, 137.15, 136.22, 135.58, 135.49, 128.13, 123.05, 114.49, 111.34, 75.93 (sp^3-C of C_{60}), 72.52, 70.14 (sp^3-C of C_{60}), 68.02, 65.54, 60.71, 56.03, 45.51; UV−vis ($CHCl_3$) λ_{max} 257, 313, 431, 702 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{72}H_{16}NO_3$ 942.1130, found 942.1137.

3ak (brown solid, 15.8 mg, 34%, mp >300 °C; it cannot be characterized by ^{13}C NMR because of its very poor solubility): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.76 (br, 2H), 7.39 (d, J = 8.7 Hz, 2H), 6.22 (s, 1H), 5.33 (dd, J = 11.7, 4.2 Hz, 1H), 4.76 (t, J = 11.7 Hz, 1H), 4.29 (dd, J = 11.7, 4.2 Hz, 1H), 4.10−4.18 (m, 1H), 3.69−3.79 (m, 2H), 3.24 (d, J = 13.8 Hz, 1H); UV−vis ($CHCl_3$) λ_{max} 256, 312, 431, 701 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{71}H_{13}ClNO$ 930.0686, found 930.0703.

3al (brown solid, 14.1 mg, 30%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.68 (s, 1H), 8.21 (dd, J = 8.2, 0.8 Hz, 1H), 8.20 (dd, J = 8.2, 0.8 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 6.36 (s, 1H), 5.36 (dd, J = 11.7, 4.2 Hz, 1H), 4.77 (t, J = 11.8 Hz, 1H), 4.31 (dd, J = 11.8, 4.2 Hz, 1H), 4.12−4.20 (m, 1H), 3.74−3.83 (m, 2H), 3.20 (dd, J = 13.5, 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 155.78, 152.84, 151.78, 150.01, 148.60, 147.41, 147.35, 146.39, 146.37, 146.34, 146.32, 146.21, 146.04, 145.91, 145.72, 145.65, 145.62, 145.49, 145.41, 145.38, 145.36, 145.29, 145.26, 145.14, 144.79, 144.42, 144.38, 143.26, 143.16, 142.80, 142.74, 142.68, 142.64, 142.22, 142.14, 142.12, 142.09, 142.06, 141.95, 141.88, 141.70, 141.55, 140.44, 140.33, 140.21, 139.56, 139.42, 137.04, 135.97, 135.40, 135.04, 129.75, 124.28, 123.77, 75.37 (sp^3-C of C_{60}), 72.06, 70.29 (sp^3-C of C_{60}), 68.23, 65.63, 60.61, 45.67; UV−vis ($CHCl_3$) λ_{max} 256, 313, 431, 701 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{71}H_{12}N_2O_3$ 941.0926, found 941.0943.

3am (brown solid, 14.2 mg, 32%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.64 (d, J = 1.7 Hz, 1H), 6.71 (d, J = 3.1 Hz, 1H), 6.46 (dd, J = 3.2, 1.9 Hz, 1H), 6.03 (s, 1H), 5.10 (dd, J = 10.1, 3.2 Hz, 1H), 4.71 (dd, J = 10.7, 3.2 Hz, 1H), 4.13 (t, J = 10.4 Hz, 1H), 4.05 (dd, J = 11.2, 3.3 Hz, 1H), 3.97 (td, J = 11.4, 2.7 Hz, 1H), 3.24 (d, J = 11.3 Hz, 1H), 2.90 (td, J = 11.3, 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 155.39, 153.65, 152.70, 152.43, 152.06, 147.28, 147.22, 146.42, 146.23, 146.20, 146.10, 146.02, 145.98, 145.95, 145.70, 145.64, 145.61, 145.52, 145.42, 145.40, 145.39, 145.29, 145.25, 145.20, 145.15, 144.61, 144.54, 144.45, 144.33, 143.15, 143.06, 143.04, 142.67, 142.63, 142.54, 142.14, 142.13, 142.11, 142.07, 142.02, 142.01, 141.99, 141.84, 141.80, 141.77, 141.75, 141.73, 140.17, 140.13, 140.04, 139.76, 137.07, 136.83, 136.79, 135.64, 111.91, 110.41, 74.03 (sp^3-C of C_{60}), 71.75 (sp^3-C of C_{60}), 71.38, 70.82, 67.67, 66.07, 48.88; UV−vis ($CHCl_3$) λ_{max} 254, 308, 430, 700 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{69}H_{12}NO_2$ 886.0868, found 886.0849.

3an (brown solid, 10.4 mg, 23%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.42 (d, J = 3.4 Hz, 1H), 7.40 (d, J = 5.1 Hz, 1H), 7.07 (dd, J = 5.0, 3.6 Hz, 1H), 6.50 (s, 1H), 5.17 (dd, J = 8.9, 5.9 Hz, 1H), 4.46−4.53 (m, 2H), 4.08 (td, J = 11.9, 2.7 Hz, 1H), 3.90 (dd, J = 11.7, 3.2 Hz, 1H), 3.45 (td, J = 12.6, 3.7 Hz, 1H), 3.35 (dd, J = 13.2, 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 154.89, 154.30, 152.92, 151.08, 147.34, 147.31, 146.34, 146.32, 146.25, 146.21, 146.09, 146.07, 146.04, 146.02, 145.98, 145.66, 145.59, 145.55, 145.52, 145.50, 145.36, 145.34, 145.27, 145.22, 145.20, 144.61, 144.54, 144.47, 144.42, 143.17, 143.12, 142.71, 142.67, 142.58, 142.13, 142.11, 142.00, 141.96, 141.88, 141.70, 141.63, 140.35, 141.23, 140.15, 140.07, 139.68,

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137.13, 136.98, 136.23, 135.66, 128.75, 127.00, 126.79, 75.52 (sp^3-C of C_{60}), 71.08, 70.67 (sp^3-C of C_{60}), 67.86, 67.54, 63.07, 46.98; UV−vis ($CHCl_3$) λ_{max} 257, 310, 431, 702 nm; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ calcd for $C_{69}H_{12}NOS$ 902.0640, found 902.0647.

3bd (brown solid, 12.1 mg, 27%, mp >300 °C): ^1H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.78 (br, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.3 (t, *J* = 7.4 Hz, 1H), 6.03 (s, 1H), 5.07 (dd, *J* = 12.5, 3.7 Hz, 1H), 3.48 (d, *J* = 13.9 Hz, 1H), 3.26−3.35 (m, 1H), 2.76−2.87 (m, 1H), 2.28−2.34 (m, 1H), 2.22−2.28 (m, 1H), 1.90−2.01 (m, 2H), 1.48−1.55 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 156.88, 154.71, 154.01, 153.21, 147.30, 146.83, 146.70, 146.28, 146.24, 146.21, 146.10, 146.06, 145.94, 145.82, 145.72, 145.52, 145.37, 145.35, 145.30, 145.27, 145.18, 145.16, 144.69, 144.59, 144.46, 143.17, 143.08, 142.70, 142.59, 142.57, 142.55, 142.33, 142.18, 142.15, 142.11, 142.09, 142.04, 142.00, 141.78, 141.56, 141.47, 140.17, 139.93, 139.43, 137.29, 137.01, 136.78, 136.11, 135.78, 129.81, 128.65, 128.46, 75.97 (sp^3-C of C_{60}), 73.83, 73.32 (sp^3-C of C_{60}), 70.67, 46.50, 28.27, 25.97, 19.93; UV−vis ($CHCl_3$) λ_{max} 257, 311, 431, 702 nm; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ calcd for $C_{72}H_{16}N$ 894.1283, found 894.1273.

3cd (brown solid, 10.9 mg, 24%, mp >300 °C): ^1H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.50−8.02 (br, 2H), 7.39 (br, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.05 (s, 1H), 5.27 (dd, *J* = 11.5, 3.8 Hz, 1H), 3.63 (td, *J* = 12.7, 4.7 Hz, 1H), 3.39 (d, *J* = 14.6 Hz, 1H), 3.35 (t, *J* = 11.6 Hz, 1H), 3.25 (dd, *J* = 11.5, 3.6 Hz, 1H), 2.60−2.72 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 156.58, 154.06, 153.53, 151.59, 147.28, 146.71, 146.30, 146.27, 146.19, 146.10, 146.07, 145.91, 145.70, 145.50, 145.46, 145.43, 145.37, 145.29, 145.24, 145.17, 145.13, 144.71, 144.53, 144.43, 143.16, 143.03, 142.67, 142.60, 142.55, 142.19, 142.15, 142.08, 142.00, 141.92, 141.81, 141.56, 141.41, 140.23, 140.00, 139.97, 139.41, 137.18, 136.75, 136.67, 135.87, 135.66, 128.80, 128.61, 75.65 (sp^3-C of C_{60}), 72.69, 71.47 (sp^3-C of C_{60}), 68.79, 55.27, 48.39, 46.96, 45.38; UV−vis ($CHCl_3$) λ_{max} 256, 310, 431, 702 nm; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ calcd for $C_{72}H_{17}N_2$ 909.1392, found 909.1374.

3da (brown solid, 8.6 mg, 18%, mp >300 °C): ^1H NMR (500 MHz, $CDCl_3/CS_2$) δ 10.63 (s, 1H), 7.28 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.16 (td, *J* = 7.8, 1.5 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.52 (s, 1H), 4.98 (d, *J* = 9.6 Hz, 1H), 3.26 (ddd, *J* = 12.6, 9.7, 7.4 Hz, 1H), 3.09 (ddd, *J* = 12.6, 9.0, 4.8 Hz, 1H), 2.56−2.66 (m, 1H), 2.41−2.49 (m, 1H), 1.80−2.04 (m, 3H), 1.55−1.80 (m, 3H), 1.15 (t, *J* = 7.3 Hz, 3H), 1.12 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 156.73, 156.25, 153.51, 152.04, 151.89, 147.39, 147.25, 146.96, 146.38, 146.27, 146.25, 146.16, 146.11, 146.04, 145.99, 145.94, 145.78, 145.75, 145.54, 145.39, 145.27, 145.21, 145.18, 145.09, 145.04, 144.71, 144.47, 144.45, 144.27, 143.09, 142.82, 142.66, 142.58, 142.45, 142.42, 142.25, 142.19, 142.17, 142.05, 141.96, 141.91, 141.48, 141.45, 141.43, 140.12, 140.10, 139.37, 138.96, 136.51, 136.50, 136.43, 136.35, 130.09, 129.90, 120.07, 119.58, 117.56, 78.46, 76.26 (sp^3-C of C_{60}), 72.74 (sp^3-C of C_{60}), 70.01, 47.48, 30.39, 26.76, 22.47, 21.06, 14.72, 14.50; UV−vis ($CHCl_3$) λ_{max} 256, 310, 431, 700 nm; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ calcd for $C_{75}H_{24}NO$ 954.1858, found 954.1854.

3ea (brown solid, 15.3 mg, 31%, mp >300 °C): ^1H NMR (500 MHz, $CDCl_3/CS_2$) δ 11.06 (s, 1H), 7.66−8.60 (br, 2H), 7.56 (br, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.18 (td, *J* = 7.9, 1.8 Hz, 1H), 6.79−6.85 (m, 2H), 6.30 (s, 1H), 6.29 (s, 1H), 3.16 (td, *J* = 11.5, 6.3 Hz, 1H), 2.70 (ddd, *J* = 12.1, 10.3, 4.5 Hz, 1H), 1.80−1.98 (m, 2H), 1.36−1.49 (m, 1H), 1.20−1.34 (m, 1H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 157.56, 156.63, 153.39, 152.11, 151.84, 147.46, 147.37, 146.58, 146.42, 146.36, 146.32, 146.29, 146.19, 146.11, 145.97, 145.95, 145.93, 145.76, 145.71, 145.67, 145.50, 145.33, 145.29, 145.22, 145.15, 145.12, 144.88, 144.73, 144.60, 144.40, 144.33, 143.15, 143.07, 142.75, 142.68, 142.51, 142.49, 142.41, 142.21, 142.16 142.13, 142.06, 141.96, 141.90, 141.80, 141.72, 141.61, 141.57, 141.51, 140.13, 140.10, 139.80, 139.16, 137.64, 136.80, 136.55, 136.36, 135.56, 130.59 (br), 130.19, 129.96, 129.16, 128.86, 120.41, 119.55, 117.69, 80.43, 76.79, 75.30 (sp^3-C of C_{60}), 73.27 (sp^3-C of C_{60}), 47.76, 30.20, 20.89, 14.17; UV−vis ($CHCl_3$) λ_{max} 256, 311, 431, 702 nm; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ calcd for $C_{78}H_{22}NO$ 988.1701, found 988.1696.

General Procedure for the Cu(OAc)$_2$-Mediated Regioselective Intramolecular C−O Coupling Reaction of 3aa−3ac, 3da, 3ea, 5, and 6. A mixture of the fulleropyrrolidines (**3aa**−**3ac**, **3da**, **3ea**, **5**, and **6**; 18.0 mg) and $Cu(OAc)_2$ (2 equiv) in 5 mL of PhCl was stirred vigorously at 100 °C until the starting materials disappeared. The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel eluted with CS_2/toluene to give corresponding products **4aa**−**4ac**, **4da**, **4ea**, **8**, and **9**, respectively.

4aa (brown solid, 16.5 mg, 92%, mp >300 °C): ^1H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.35 (td, *J* = 7.8, 1.4 Hz, 1H), 7.21−7.23 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 5.57 (s, 1H), 4.84 (d, *J* = 11.4 Hz, 1H), 4.53 (d, *J* = 11.4 Hz, 1H), 4.23 (dd, *J* = 11.4, 3.5 Hz, 1H), 4.13 (td, *J* = 11.6, 2.8 Hz, 1H), 3.39 (td, *J* = 11.3, 3.7 Hz, 1H), 3.25 (dd, *J* = 11.1, 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 152.55, 152.08, 152.05, 151.32, 150.88, 147.27, 147.26, 146.51, 146.25, 146.22, 146.13, 146.07, 146.05, 146.00, 145.87, 145.70, 145.59, 145.55, 145.51, 145.39, 145.38, 145.34, 145.21, 145.19, 145.16, 145.07, 145.03, 144.54, 144.49, 144.41, 144.32, 143.11, 142.98, 142.78, 142.72, 142.64, 142.59, 142.34, 142.29, 142.17, 142.15, 142.01, 141.98, 141.95, 141.84, 141.82, 141.70, 140.49, 139.93, 139.91, 139.89, 138.52, 137.51, 136.52, 136.07, 130.25, 128.11, 121.65, 121.40, 116.41, 95.80, 80.01 (sp^3-C of C_{60}), 77.28 (sp^3-C of C_{60}), 72.49, 72.31, 66.08, 45.17; UV−vis ($CHCl_3$) λ_{max} 256, 311, 431, 700 nm; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ calcd for $C_{71}H_{11}NO_2$ 910.0868, found 910.0835.

4ab (brown solid, 16.0 mg, 89%, mp >300 °C): ^1H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.14 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 7.02 (s, 1H), 5.51 (s, 1H), 4.82 (d, *J* = 11.3 Hz, 1H), 4.51 (d, *J* = 11.3 Hz, 1H), 4.22 (dd, *J* = 11.3, 3.7 Hz, 1H), 4.11 (td, *J* = 11.6, 2.9 Hz, 1H), 3.36 (td, *J* = 11.4, 3.7 Hz, 1H), 3.22 (dd, *J* = 11.1, 1.9 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 152.61, 152.08, 151.41, 151.01, 149.69, 147.24, 146.54, 146.23, 146.19, 146.11, 146.04, 146.02, 145.98, 145.89, 145.69, 145.67, 145.52, 145.50, 145.36, 145.30, 145.21, 145.17, 145.14, 145.08, 145.01, 144.53, 144.47, 144.39, 144.32, 143.09, 142.96, 142.76, 142.70, 142.61, 142.56, 142.33, 142.28, 142.17, 142.14, 141.99, 141.96, 141.92, 141.87, 141.82, 141.67, 140.45, 139.90, 139.87, 138.55, 137.59, 136.48, 136.03, 130.83, 130.45, 128.42, 121.27, 116.17, 95.58, 79.95 (sp^3-C of C_{60}), 77.37 (sp^3-C of C_{60}), 72.50, 72.35, 66.08, 45.15, 21.01; UV−vis ($CHCl_3$) λ_{max} 256, 312, 431, 700 nm; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ calcd for $C_{72}H_{13}NO_2$ 924.1025, found 924.1030.

4ac (brown solid, 16.9 mg, 94%, mp >300 °C): ^1H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.23−7.32 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 5.54 (s, 1H), 4.83 (d, *J* = 11.4 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.24 (dd, *J* = 11.4, 3.5 Hz, 1H), 4.12 (td, *J* = 11.5, 3.0 Hz, 1H), 3.34 (td, *J* = 11.2, 3.7 Hz, 1H), 3.26 (dd, *J* = 11.0, 2.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6/CS_2) δ 151.70, 150.94, 150.52, 149.95, 149.92, 146.40, 146.37, 145.66, 145.42, 145.36, 145.29, 145.20, 145.19, 145.15, 145.12, 145.05, 144.88, 144.71, 144.66, 144.49, 144.36, 144.32, 144.30, 144.25, 143.67, 143.58, 143.45, 142.24, 142.13, 141.92, 141.86, 141.78, 141.76, 141.48, 141.40, 141.34, 141.29, 141.19, 141.11, 141.09, 141.06, 140.98, 140.96, 140.88, 139.47, 139.07, 139.04, 137.50, 136.68, 135.67, 135.28, 129.16, 127.45, 125.30, 122.64, 116.73, 95.24, 79.12 (1C, sp^3-C of C_{60}), 76.19 (1C, sp^3-C of C_{60}), 71.09, 70.62, 65.12, 44.39; UV−vis ($CHCl_3$) λ_{max} 257, 312, 431, 699 nm; HRMS (MALDI-TOF) *m/z* $[M + H]^+$ calcd for $C_{71}H_{11}ClNO_2$ 944.0478, found 944.0449.

4da (brown solid, 17.2 mg, 96%, mp >300 °C): ^1H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.34 (td, *J* = 7.8, 1.5 Hz, 1H), 7.24 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.97 (td, *J* = 7.4, 0.9 Hz, 1H), 5.68 (s, 1H), 3.38 (dt, *J* = 12.4, 7.9 Hz, 1H), 2.98 (ddd, *J* = 12.8, 8.2, 5.0 Hz, 1H), 2.83 (ddd, *J* = 15.0, 11.7, 5.2 Hz, 1H), 2.70 (ddd, *J* = 15.2, 11.7, 4.9 Hz, 1H), 2.16−2.26 (m, 1H), 1.81−2.05 (m, 2H), 1.56−1.78 (m, 2H), 1.084 (t, *J* = 7.5 Hz, 3H), 1.079 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 154.32, 153.45, 153.25, 152.73, 152.64, 147.65, 147.47, 147.43, 146.44, 146.40, 146.33, 146.24, 146.16, 146.14, 146.13, 146.07, 146.03, 146.00, 145.71, 145.59, 145.56, 145.52, 145.51, 145.38, 145.33, 145.31, 145.05, 144.78, 144.76, 144.67, 144.50, 143.29, 143.11, 142.93, 142.85, 142.80, 142.73, 142.69, 142.57, 142.40, 142.38, 142.23, 142.17, 142.07, 142.05, 141.99, 141.79, 141.75, 140.52, 140.00, 139.66, 139.61, 138.64, 137.53, 136.59, 136.26, 129.92, 128.49, 123.01, 120.87, 115.89, 103.05, 82.75 (sp^3-C of C_{60}), 76.53 (sp^3-C of C_{60}), 70.36, 44.36, 38.42, 31.00, 20.75, 18.21, 15.37, 14.34;

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UV−vis ($CHCl_3$) λ_{max} 256, 312, 432, 701 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{75}H_{22}NO$ 952.1701, found 952.1696.

4ea (brown solid, 17.0 mg, 95%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.24 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.38−7.50 (m, 2H), 7.36 (td, J = 8.1, 1.7 Hz, 1H), 7.33 (tt, J = 7.4, 1.2 Hz, 1H), 7.27 (dd, J = 7.4, 1.5 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 7.00 (td, J = 7.4, 1.1 Hz, 1H), 5.84 (s, 1H), 3.32 (dt, J = 12.7, 8.1 Hz, 1H), 2.86 (ddd, J = 12.6, 8.1, 4.4 Hz, 1H), 1.96−2.08 (m, 1H), 1.81−1.92 (m, 1H), 1.67−1.79 (m, 1H), 1.52−1.65 (m, 1H), 1.07 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 153.67, 153.17, 152.45, 152.23, 151.46, 147.23, 146.21, 146.17, 146.09, 146.05, 146.03, 145.91, 145.87, 145.82, 145.75, 145.69, 145.58, 145.48, 145.43, 145.28, 145.25, 145.15, 145.06, 144.99, 144.95, 144.93, 144.58, 144.45, 144.39, 144.22, 143.07, 143.02, 142.86, 142.71, 142.56, 142.48, 142.43, 142.27, 142.08, 142.02, 141.97, 141.90, 141.77, 141.61, 141.50, 140.22, 139.82, 139.49, 139.29, 138.44, 137.41, 136.72, 136.57, 134.88, 129.92, 128.81, 128.74, 128.59, 128.51, 128.30, 127.67, 122.88, 121.38, 116.34, 103.84, 84.02 (sp^3-C of C_{60}), 75.71 (sp^3-C of C_{60}), 70.05, 44.14, 30.90, 20.92, 14.54; UV−vis ($CHCl_3$) λ_{max} 256, 311, 431, 701 nm; HRMS (MALDI-TOF) m/z [M]$^+$ calcd for $C_{78}H_{20}NO$ 986.1545, found 986.1553.

8 (brown solid, 14.9 mg, 83%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.37 (td, J = 7.8, 1.7 Hz, 1H), 7.24 (dd, J = 7.4, 1.6 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 7.02 (td, J = 7.4, 1.2 Hz, 1H), 6.50 (d, J = 1.2 Hz, 1H), 5.47 (s, 1H), 3.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 153.24, 152.81, 152.03, 151.68, 150.98, 147.35, 147.06, 146.35, 146.30, 146.23, 146.14, 146.11, 146.10, 146.08, 145.90, 145.77, 145.59, 145.57, 145.54, 145.42, 145.34, 145.29, 145.27, 145.19, 144.70, 144.55, 144.43, 143.10, 143.00, 142.77, 142.73, 142.66, 142.61, 142.51, 142.37, 142.23, 142.18, 142.07, 142.05, 142.02, 141.94, 141.90, 141.88, 141.68, 140.33, 140.20, 139.97, 139.90, 138.82, 137.83, 136.94, 136.79, 130.15, 129.06, 122.68, 121.52, 116.30, 98.08, 78.87 (sp^3-C of C_{60}), 78.34 (sp^3-C of C_{60}), 72.33, 34.75; UV−vis ($CHCl_3$) λ_{max} 256, 312, 432, 700 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{69}H_{10}NO$ 868.0762, found 868.0771.

9 (brown solid, 17.2 mg, 96%, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.31 (td, J = 7.8, 1.6 Hz, 1H), 7.22 (dd, J = 7.4, 1.6 Hz, 1H), 7.01 (d, J = 8.1 Hz, 1H), 6.96 (td, J = 7.4, 1.0 Hz, 1H), 5.53 (s, 1H), 2.97 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ 153.52, 152.83, 152.52, 152.47, 152.12, 147.29, 147.28, 147.01, 146.24, 146.22, 146.12, 146.08, 146.06, 145.98, 145.80, 145.77, 145.64, 145.50, 145.46, 145.35, 145.26, 145.15, 145.14, 144.98, 144.60, 144.52, 144.48, 144.32, 143.07, 142.96, 142.76, 142.69, 142.60, 142.54, 142.44, 142.37, 142.18, 142.04, 142.00, 141.98, 141.89, 141.85, 141.71, 141.64, 140.38, 139.91, 139.84, 139.78, 138.38, 137.55, 136.47, 135.81, 129.89, 128.39, 122.07, 121.10, 115.75, 100.87, 81.93 (sp^3-C of C_{60}), 76.38 (sp^3-C of C_{60}), 73.93, 32.16, 23.13; UV−vis ($CHCl_3$) λ_{max} 256, 312, 431, 701 nm; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{70}H_{12}NO$ 882.0919, found 882.0950.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02193.

UV−vis spectra of **3aa** and **4aa**, ^{1}H and ^{13}C NMR spectra of the products, and NOESY spectra of **3ea** and **6** (PDF)

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Notes

The authors declare no competing financial interest.

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