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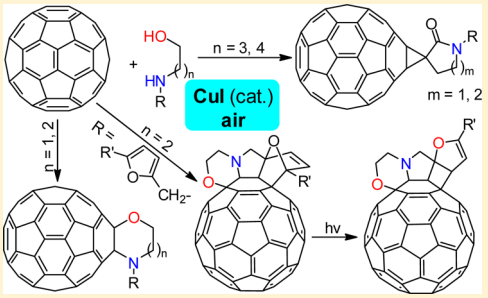
Copper-Catalyzed Functionalizations of C_{60} with Amino Alcohols

Hai-Tao Yang,* Jie Ge, Xin-Wei Lu, Xiao-Qiang Sun, and Chun-Bao Miao

Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

Supporting Information

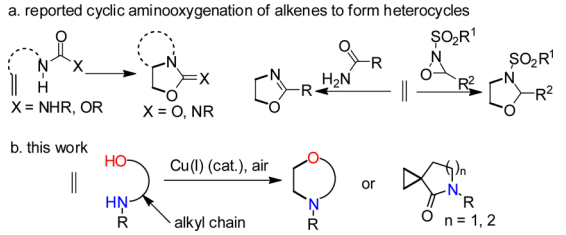
ABSTRACT: CuI-catalyzed diverse functionalizations of C_{60} with amino alcohols with aerobic oxygen as the sole oxidant have been explored. For 2-/3-amino alcohols, an aminooxygenation reaction occurs to generate fulleromorpholine and fullerooxazepane derivatives. When a tethered furan ring exists, a further intramolecular [4 + 2] reaction with the neighboring double bond occurs to furnish the *cis*-1 products. In the case of 4-/5-amino alcohols, methanofullerenes linking with cyclic amides are obtained through cyclic enamine intermediates.



INTRODUCTION

The abundant availability of organofullerenes has provided an opportunity for extensive investigation of their potential utilities in medicinal and material science.[1] Development of new synthetic methods toward organofullerenes with sophisticated and unprecedented architectures is still intensively in demand.[1,2] Free radical reactions have become one of the most powerful tools for the modification of C_{60}. To date, the addition of different kinds of radicals generated under photo/thermal conditions or by transition metals to fullerenes has been well-documented.[3] In contrast to the widely investigated *C*- and *O*-centered radicals, the addition of *N*-centered radicals to fullerenes has received less attention.[4] We have been interested in exploring the functionalization of C_{60} through the addition of *N*-centered radicals and have developed hypervalent iodine reagent/I_2 system-mediated[5] or Cu(I/II)-catalyzed/promoted[6] reactions of C_{60} with amine compounds. A strategy for the annulation of C_{60} through an *N*-centered radical addition has been proposed. Addition of an *N*-centered radical to C_{60} produces the fullerenyl radical, which is oxidized to form the diradicals or fullerenyl cation followed by an intramolecular radical coupling or attack by the tethered nucleophilic atom to afford different kinds of heterocycle-fused fullerene derivatives.[5,6] On the basis of these results, we envision that an aminooxygenation of fullerene may occur using amino alcohols as the reactants. Currently, only a handful of reports describe the cyclic aminooxygenation reaction to access heterocycles containing both oxygen and nitrogen atoms. The reported cyclization is largely limited to the intermolecular oxidative cyclization of amide with olefins,[5a,6a,7] intramolecular aminooxygenation of urea-tethered alkenes,[8] or the reaction of carbamates with olefins (Scheme 1).[4d,9] The substrates have a common feature that both the nitrogen and oxygen atoms are in a conjugated system. Moreover, the *N*-sulfonyl oxaziridines have also been used in the aminooxgenation of olefins catalyzed by copper or iron.[10] Amino alcohols as easily available chemical

Scheme 1



reagents, which have an alkyl chain between the oxygen and nitrogen atom, have rarely been investigated in the oxidative cyclization with alkenes[11a] to form morpholine derivatives, which constitute an important scaffold in drug design and therapeutic medicine.[11b] Herein, we report the copper-catalyzed reaction with C_{60} to realize aminooxygenation and a novel cyclopropanation reaction (Scheme 1).

We initiated our study by investigating the reaction of C_{60} with 2-(methylamino)ethanol **1a** (Table 1). In a preliminary attempt, the reaction of C_{60} with 2 equiv of **1a** using 2 equiv of $Cu(OAc)_2$ as the oxidant at 120 °C for 6 h afforded a trace amount of desired product **2a** (entry 1). When 2 equiv of 4-dimethylaminopyridine (DMAP) was added, the desired aminooxygenation product fulleromopholine **2a** was obtained in 10% yield (entry 2). Increasing the amount of **1a** to 4 equiv improved the yield of **2a** to 21% (entry 3). An extensive copper salt screening showed that other Cu^{II} sources such as $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(ClO_4)_2{\cdot}6H_2O$, and $CuSO_4$ were ineffective, and $CuCl_2$ gave a comparable yield of **2a** (entries 4−7). When $Cu(OAc)_2$ was replaced by CuCl, the yield could be improved to 28% (entry 8). Using CuI gave the highest yield of **2a** (35%, entry 9). It is worth noting that in our previous

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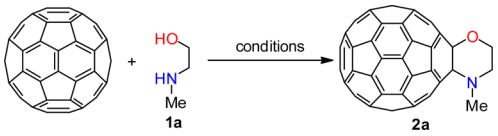
Table 1. Screening of the Reaction Conditions[a]



entry	additive	molar ratio[b]	time (h)	yield
1	$Cu(OAc)_2$	1:2:2	6	trace
2	$Cu(OAc)_2$/DMAP	1:2:2:2	6	10
3	$Cu(OAc)_2$/DMAP	1:4:2:2	4	21
4	$CuCl_2$/DMAP	1:4:2:2	2	18
5	$CuSO_4$/DMAP	1:4:2:2	2	9
6	$Cu(ClO_4)_2{\cdot}6H_2O$/DMAP	1:4:2:2	2	trace
7	$Cu(NO_3)_2{\cdot}3H_2O$/DMAP	1:4:2:2	2	8
8	CuCl/DMAP	1:4:2:2	2	28
9	CuI/DMAP	1:4:2:2	2	38
10	CuI/DMAP	1:4:0.2:0.2	2	33
11	CuI/DMAP	1:2:0.2:0.2	2	22
12	**CuI/DMAP**	**1:2:0.2:0.4**	**2**	**35**
13[c]	CuI/DMAP	1:2:0.2:0.4	2	6
14	CuI	1:2:0.2	6	5
15	CuI/Et_3N	1:2:0.2:0.4	2	5
16	CuI/pyridine	1:2:0.2:0.4	2	5
17	CuI/K_2CO_3	1:2:0.2:0.4	3	8

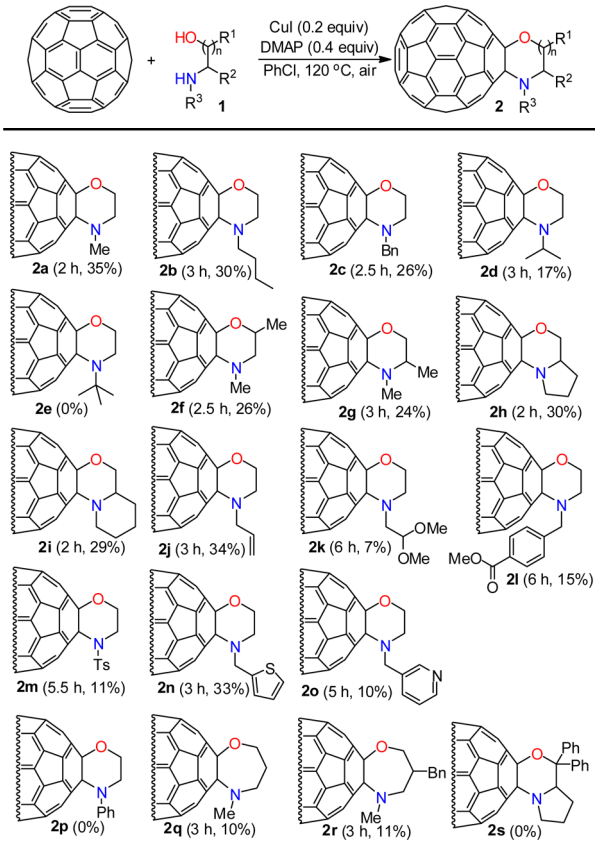
[a]C_{60} (36 mg), other reactants and reagents, 10 mL of chlorobenzene, 120 °C. [b]C_{60}/**1a**/[Cu]/additive. [c]Operated under a N_2 atmosphere.

work CuI could not initiate the reaction of primary alkyl amines with C_{60}.[6c] Gratifyingly, further optimizing the molar ratio of reactants revealed that only a catalytic amount of CuI was required in the reaction. In light of the atomic economy, a molar ratio of C_{60}/**1a**/CuI/DMAP of 1:2:0.2:0.4 and a reaction temperature of 120 °C were selected as the optimized conditions (entry 12). When the reaction was performed under a N_2 atmosphere, the yield decreased notably to 6%, which indicated that O_2 played a crucial rule in the reaction (entry 13). In the absence of DMAP or replacing DMAP by other commonly used bases such as Et_3N, pyridine, or K_2CO_3, the yield of **2a** was very low (entries 14−17).

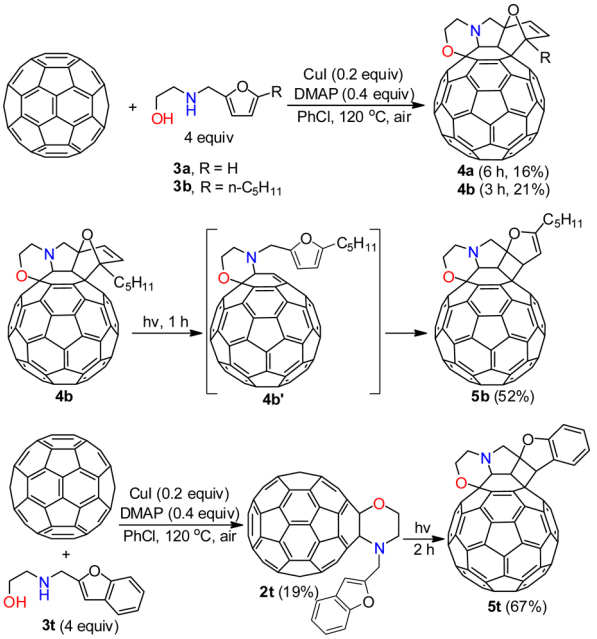
Under the optimized reaction conditions, the generality of the CuI-catalyzed annulation reaction of C_{60} with amino alcohols was examined (Table 2). The yield decreased with an increase in the steric hindrance of the alkyl group on the nitrogen atom (**1a−e**). In the case of 2-(*tert*-butylamino)-ethanol **1e**, no reaction occurred. The *p*-toluene sulfonyl (*Ts*) group-substituted aminoethanol (**1m**) could also react with C_{60} to afford **2m**, albeit in low yield. An aryl group on the nitrogen atom (**1p**) resulted in failure of the reaction. Next, the influence of the substituents at the α-C of the oxygen/nitrogen atom was investigated (**1f−i** and **1s**). Both acyclic and cyclic substrates reacted well with C_{60} to give the desired products in good yields except **1s**, which decomposed to benzophenone via C−C bond cleavage. The alkenyl, acetal, and ester groups and heterocyclic substituents all tolerated the reaction conditions (**1j−l**). 3-Amino-1-propanols (**1q** and **1r**) could also react with C_{60} to provide the seven-membered ring-fused fullerooxazepanes **2q** and **2r**, albeit in low yield.

When 2-(2-furylmethylamino)ethanol **3a** was introduced to the CuI-catalyzed reaction (Scheme 2), *cis*-1 product **4a** was formed in 16% yield through a further intramolecular [4 + 2] reaction of the furan ring with a neighboring double bond. However, the very poor solubility did not enable ^{13}C NMR

Table 2. Substrate Scope for the Aminooxygenation Reactions



Scheme 2. Reaction of C_{60} with Aminoethanols Connecting a Furyl Group



characterization. This problem was solved by introducing a long alkyl chain on the furan ring (substrate **3b**), and *cis*-1 product **4b** was obtained in 21% yield. No observation of an intermolecular reaction between C_{60} and 2-pentylfuran indicated that the intramolecular fashion facilitated the [4 +

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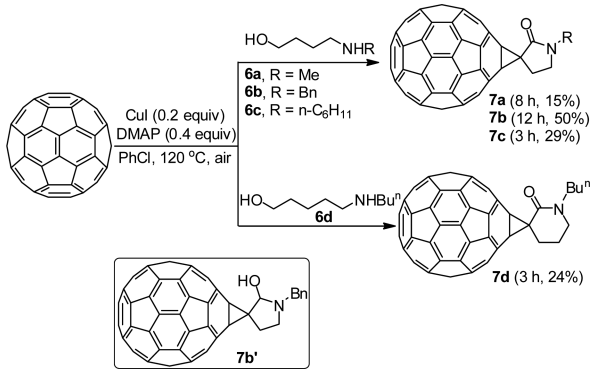
2] reaction. To the best of our knowledge, only a few examples of the [4 + 2] cycloaddition of isobenzofuran with C_{60} have been reported to date.[12] This is the first example of a [4 + 2] reaction of fullerene with simple furans. The *cis*-1 product **4b** was very sensitive to light. Upon photoirradiation with a 125 W fluorescent high-pressure mercury lamp, it was transformed to *cis*-1 product **5b** quickly via a retro [4 + 2] reaction and further intramolecular [2 + 2] reaction. The structrure of **5b** was fully characterized by its ^{1}H NMR, ^{13}C NMR, H−H Cosy, HSQC, HMBC, and NOESY spectral analysis (see Supporting Information). In contrast to **4b**, **4a** was more stable under photoirradiation, which meant that the alkyl group on the α-position of the furan ring had a significant influence on the retro [4 + 2] reaction. The formation of *cis*-1 fullerene derivatives through intramolecular [2 + 2] cyclization has only been reported by Martín's group from a fuller-1,6-enynes precursor under thermal conditions.[13] In the formation of **4b** or its conversion to **5b**, key intermediate **4b′** could not be detected. For the reaction pathway to be determined precisely, **3t** was prepared and reacted with C_{60} under the same conditions. Aminooxygenation product **2t** was obtained because the fused-phenyl ring prevented the intramolecular [4 + 2] reaction. As anticipated, **2t** underwent intramolecular [2 + 2] reaction under photoirradiation to furnish product **5t** in 67% yield.

The success of the reaction between 3-amino-1-propanols (**1q** and **1r**) and C_{60} inspired us to construct the more challenging 8/9-membered ring-fused C_{60} derivatives using amino alcohols with longer carbon chains (Scheme 3).

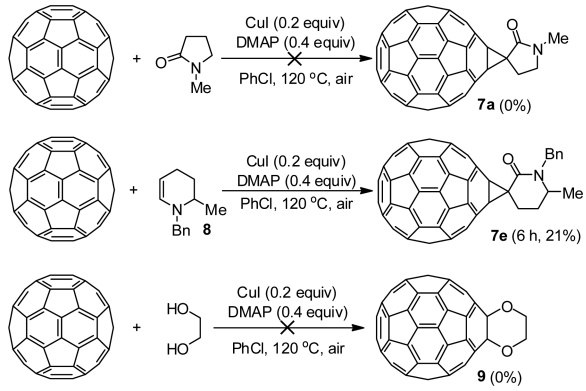
Scheme 3. Reaction of C_{60} with 4-/5-Amino Alcohols



Treatment of C_{60} with 4-methyamino-1-butanol **6a** under the standard conditions delivered a single product. Surprisingly, the NMR analysis revealed that it was not the anticipated 8-membered ring-fused C_{60} but methanofullerene **7a**. 4-Benzylamino-1-butanol **6b** and 4-hexylamino-1-butanol **6c** both reacted with C_{60} to give similar methanofullerenes **7b** and **7c**, respectively. During the course of the reaction of C_{60} with **6b**, intermediate **7b′** with greater polarity was formed at first. With progression of the reaction, **7b′** was gradually transformed to **7b**. Changing the substrate from 4-benzylamino-1-butanol to 5-benzylamino-1-pentanol gave the analogous product **7d** in 24% yield. No reaction occurred by further extending the carbon chain to 6-methylamino-1-hexanol.

As for the formation of methanofullerenes **7a**−**d**, undoubtedly a new C−N bond formed between the nitrogen atom and the carbon atom of the hydroxyl group. The reasonable reaction intermediate might be the cyclic enamines or the cyclic amides, which could be formed through oxidation of primary alcohols to aldehydes followed by intramolecular condensation or further oxidation. To gain insight into this interesting transformation, two control experiments were conducted (Scheme 4). When *N*-methyl-2-pyrrolidinone was treated

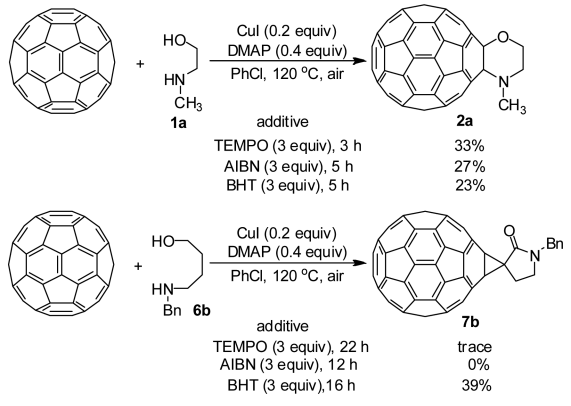
Scheme 4. Control Experiments



with C_{60} under standard conditions, no reaction occurred. However, the reaction of cyclic enamine **8** with C_{60} afforded methanofullerene **7e** in 21% yield, which unambiguously certified that cyclic enamines were the key intermediates. We also tried to isolate the key intermediate cyclic enamine from the reaction of C_{60} with **6b** but failed, probably because the formation of the cyclic enamine is rather slower than the further oxidation by Cu(II). The reaction of enamines derived from ketones with C_{60} has been investigated by the Oshima and Wu groups, where [2 + 2] cycloaddition products were obtained via a single electron transfer (SET) process.[14]

For more information regarding the reaction mechanism to be obtained, the CuI-catalyzed reaction of C_{60} with **1a** or **6b** in the presence of radical scavengers such as 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO), azoisobutyronitrile (AIBN), or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was carried out (Scheme 5). For the reaction of C_{60} with **1a**, the radical

Scheme 5. Free Radical Capture Experiments



scavenger has no significant influence on the reaction. The addition of BHT or AIBN only resulted in lower yield. In terms of the reaction of C_{60} with **6b**, the addition of TEMPO severely prohibited the cyclopropanation reaction and only afforded a trace amount of **7b** after 22 h; however, a new unidentified product with slightly less polarity was generated. In the presence of AIBN, the reaction of C_{60} with **6b** was completely

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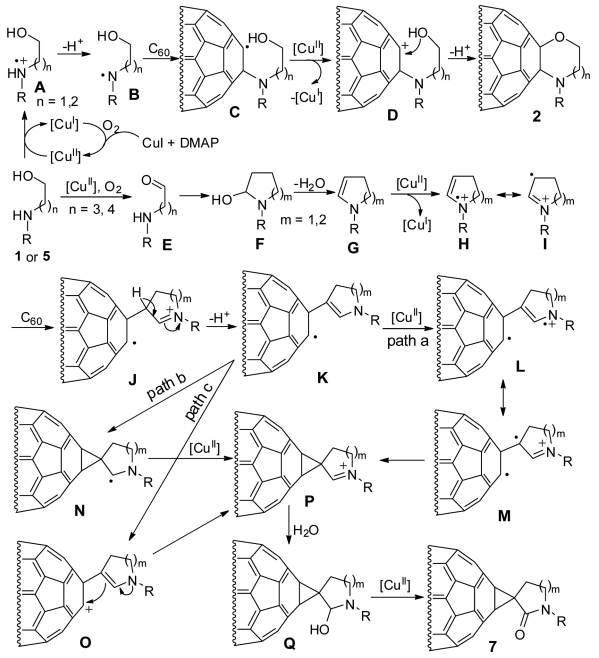
inhibited. In the presence of BHT, within a short time, no reaction occurred between C_{60} and **6b**, and only the oxidation of BHT was observed. Further extending the reaction time, the formation of **7b** was observed and was finally obtained in 39% yield. Although the radical trapping experiment between C_{60} and **1a** did not support a radical process, this could not exclude the possibility of a radical pathway because TEMPO has generally been used to capture *C*-centered radicals but not *N*-centered radicals. Moreover, many TEMPO-mediated reactions have been reported to undergo a radical pathway.[15] Recently, oxidative conversion of tertiary amines to α,α-disulfenylated aldehydes through enamine intermediates was also reported to involve a radical process.[16]

The exact reaction process is still currently unclear. A plausible mechanism for the formation of **2** and **7** is outlined in Scheme 6. The reaction of CuI with aerobic O_2 in the presence of DMAP may generate a Cu(II) complex.[17] For 2-/3-amino alcohol **1**, single electron oxidation by Cu(II) followed by the release of a proton from the generated radical cation **A** results in the formation of nitrogen radical **B**, which adds to C_{60} to furnish fullerenyl radical **C**. Further oxidation of **C** by Cu(II) may afford fullernyl cation **D**,[18] and the consequent intramolecular attack by the hydroxyl group provides amino-oxygenation product **2**. A radical coupling pathway to **2** through an oxygen radical was excluded because the reaction of C_{60} with ethylene glycol under standard conditions did not produce C_{60}-fused dioxane **9** (Scheme 4), which implied that the oxygen radical could not be generated. In terms of 4-/5-amino alcohol **5**, an oxidation of primary alcohol to aldehyde **E** may occur in the presence of Cu(I) and O_2[17b,19] followed by an intramolecular condensation to afford cyclic enamine **G**. SET from **G** to Cu(II) gives radical cation **H**, which has another resonance form **I**. Addition of **I** to C_{60} followed by concurrent release of a proton generates fullerenyl radical **K**. Three possible pathways may exist for its further transformation. In path a, a similar SET process occurs to furnish biradical **M**, which undergoes a coupling reaction to generate **P**. In path b, addition of a fullerenyl radical to the double bond of enamine generates radical **N**, which undergoes single electron oxidation to furnish **P**. In path c, oxidation of the fullerenyl radical to the fullerenyl cation **O** followed by intramolecular attack with the enamine would also deliver **P**. Nucleophilic addition of H_2O to **P** generates the *O*,*N*-acetal **Q**, and the subsequent oxidation affords methanofullerene **7**.

Scheme 6. Plausible Mechanism



CONCLUSIONS

In summary, the CuI-catalyzed reaction of C_{60} with amino alcohols using the aerobic oxygen as the oxidant has been extensively investigated. The aminooxygenation reaction occurs for 2-/3-amino alcohols. When a furylmethyl group bonds to the nitrogen atom, further intramolecular [4 + 2] reaction with the neighboring double bond occurs to generate *cis*-1 product, which undergoes a retro [4 + 2] reaction and a further [2 + 2] reaction under photoirradiation. In the case of the 4-/5-amino alcohols, an entirely different reaction process is triggered through cyclic enamine intermediates to provide the methanofullerenes linking with cyclic amides.

EXPERIMENTAL SECTION

General Information. All reactions were conducted under an air atmosphere. ^{1}H and ^{13}C NMR (broadband decoupling) spectra were recorded on 300, 400, and 500 MHz (75, 100, and 125 MHz for ^{13}C NMR) spectrometer at ambient temperature using TMS as an internal standard. H−H Cosy, HSQC, HMBC, and NOESY spectra were recorded on a 500 MHz spectrometer at ambient temperature. Flash column chromatography was performed over silica gel (200−300 mesh). The MALDI-TOF MS was measured in positive ion mode using DCTB *E*-(2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile) as the matrix. UV−vis spectra were obtained using a Shimadzu UV-2401 spectrometer with $CHCl_3$ as the solvent.

Starting materials **1j**, **1k**,[20] **1n**, **1o**,[21] **3a**,[22] **6c**,[23] and **8**[24] were prepared according to the reported procedures.

*Preparation of **1l** and **3t**.* A mixture of ethanolamine (183 mg, 3 mmol) and corresponding aldehydes (methyl 4-formylbenzoate or benzofuran-2-carbaldehyde, 2 mmol) in methanol (2 mL) was stirred at 60 °C overnight. After cooling to 0 °C, $NaBH_4$ (114 mg, 3 mmol) was added portionwise. The mixture was stirred at room temperature for 1 h until completion of the reduction as determined by TLC. Then, 0.5 mL of water was added to quench the reaction, and the solvent was removed in vacuo. The residue was extracted with methylene dichloride (2 × 20 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography with CH_2Cl_2/MeOH (1:15) as the eluent to give **1l** (pale yellow oil, 188 mg, 45%) or **3t** (pale yellow oil, 267.5 mg, 70%). **1l**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H), 3.88 (s, 2H), 3.68 (t, J = 5.1 Hz, 2H), 2.81 (t, J = 5.1 Hz, 2H), 1.91 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 145.4, 129.9, 129.1, 128.1, 61.1, 53.3, 52.2, 50.7; HRMS (ESI-Q-TOF) m/z [M + H]$^+$ calcd for $C_{11}H_{16}NO_3$ 210.1130, found 210.1126. **3t**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49−7.54 (m, 1H), 7.41−7.46 (m, 1H), 7.16−7.28 (m, 2H), 6.56 (q, J = 0.7 Hz, 1H), 3.94 (d, J = 0.6 Hz, 2H), 3.67 (t, J = 5.2 Hz, 2H), 2.82 (t, J = 5.2 Hz, 2H), 2.44 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3, 155.0, 128.4, 124.0, 122.8, 120.8, 111.1, 104.0, 60.9, 50.5, 46.2; HRMS (ESI-Q-TOF) m/z [M + H]$^+$ calcd for $C_{11}H_{14}NO_2$ 192.1025, found 192.1016.

*Preparation of **1r**.* (Step 1) A mixture of diethyl benzylmalonate (500 mg, 2 mmol) and methylamine (25% aqueous solution, 372 mg, 3 mmol,) in 3 mL of tetrahydrofuran was stirred at room temperature overnight. Water (20 mL) was added, and the mixture was extracted with methylene dichloride (2 × 20 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography with 1:3 ethyl acetate/petroleum ether as an eluent to give the product ethyl 2-

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benzyl-3-(methylamino)-3-oxopropanoate (350 mg, 74%). (Step 2) To a solution of lithium aluminum hydride (114 mg, 3 mmol) in dry tetrahydrofuran (15 mL) was added dropwise, a solution of ethyl 2-benzyl-3-(methylamino)-3-oxopropanoate (300 mg, 1.3 mmol) in dry tetrahydrofuran (10 mL) at 0 °C. After addition, the mixture was heated at reflux overnight. Under ice-cooling, the reaction was quenched with water (1 mL), and the insoluble substance was filtered off. The filtrate was dried with anhydrous sodium sulfate and concentrated. The crude product was purified by column chromatography with CH_2Cl_2/MeOH (1:30) as the eluent to give **1r** (143 mg, 63%, pale yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10−7.32 (m, 5H), 3.72 (ddd, J = 10.8, 3.8, 1.7 Hz, 1H), 3.66 (br, 2H), 3.56 (dd, J = 10.6, 8.3 Hz, 1H), 2.78 (ddd, J = 11.8, 3.4, 1.6 Hz, 1H), 2.59 (dd, J = 11.8, 9.5 Hz, 1H), 2.53 (dd, J = 13.7, 7.3 Hz, 1H), 2.43 (dd, J = 13.5, 7.4 Hz, 1H), 2.35 (s, 3H), 1.97−2.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.9, 128.9, 128.4, 126.1, 67.8, 56.58, 40.8, 36.4, 36.2; HRMS (ESI-Q-TOF) m/z [M + H]$^+$ calcd for $C_{11}H_{18}NO$ 180.1388, found 180.1390.

Preparation of ***3b***. (Step 1) Phosphorus oxychloride (670 mg, 4.5 mmol) was added dropwise to dry *N*,*N*-dimethylformamide (2 mL) while keeping the temperature below 20 °C. The solution was stirred for 1 h at 40 °C. 2-Pentylfuran (415 mg, 3 mmol) was added slowly with a syringe at such a rate as to maintain the temperature below 25 °C. The mixture was stirred for 3 h at room temperature. An aqueous sodium carbonate solution (20 mL) was added slowly to quench the reaction, and the mixture was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography with 1:20 ethyl acetate/petroleum ether as the eluent to give the product 5-pentylfuran-2-carbaldehyde. (Step 2) A mixture of 5-pentylfuran-2-carbaldehyde (332 mg, 2 mmol) and ethanolamine (183 mg, 3 mmol) in methanol (2 mL) was stirred overnight at 60 °C. After cooling to 0 °C, sodium borohydride (114 mg, 3 mmol) was added portion-wise, and then the resulting solution was stirred at room temperature for 1 h. Twenty milliliters of water was added, and the mixture was extracted with methylene dichloride (2 × 20 mL). The combined organics were dried with anhydrous sodium sulfate, filtered, and evaporated in vacuo. The crude product was purified by column chromatography with CH_2Cl_2/MeOH (1:20) as the eluent to give **3b** (240 mg, 57%, pale yellow oil). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.05 (d, J = 3.0 Hz, 1H), 5.88 (d, J = 3.0 Hz, 1H), 3.74 (s, 2H), 3.64 (t, J = 5.2 Hz, 2H), 2.78 (t, J = 5.2 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H), 2.03 (br, 2H), 1.62 (quint, J = 7.4 Hz, 2H), 1.27−1.42 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.2, 151.5, 107.8, 105.2, 60.9, 50.4, 45.9, 31.5, 28.1; HRMS (ESI-Q-TOF) m/z [M + H]$^+$ calcd for $C_{12}H_{22}NO_2$ 212.1651, found 212.1644.

Preparation of ***6d***. A mixture of δ-valerolactone (500 mg, 5 mmol) and *n*-butylamine (1.1 g, 15 mmol) in water (2 mL) was stirred at room temperature for 2 h. Water and excess amine were removed under reduced pressure by adding ethanol. The obtained crude *N*-butyl-5-hydroxypentanamide in 20 mL of THF was slowly added to $LiAlH_4$ (380 mg, 10 mmol) at 0 °C. The mixture was refluxed overnight, cooled to room temperature, and quenched with water. The suspension was filtered and concentrated to dryness with anhydrous sodium sulfate to give the crude compound as a pale yellow oil (536 mg, 67%) without further purification. ^{1}H NMR (300 MHz, $CDCl_3$)[25] δ 3.64 (t, J = 6.3 Hz, 2H), 2.61 (t, J = 7.2 Hz, 2H), 2.59 (t, J = 7.3 Hz, 2H), 1.26−1.65 (m, 10H), 0.92 (t, J = 7.2 Hz, 3H); HRMS (ESI-Q-TOF) m/z [M + H]$^+$ calcd for $C_9H_{22}NO$ 160.1701, found 160.1696.

General Procedure for the CuI-Catalyzed Reaction of C_{60} with Amino Alcohols ***1, 6, 3a, 3b, or 3t***. A mixture of C_{60} (36.0 mg, 0.05 mmol), amino alcohols (**1a−l**, **1n−s**, and **6a−d**, 0.1 mmol; **1m**, 0.25 mmol; **3a**, **3b**, and **3t**, 0.2 mmol), CuI (1.9 mg, 0.01 mmol), and DMAP (2.5 mg, 0.02 mmol) was stirred vigorously in 10 mL of chlorobenzene in a tube (Φ18 × 150 mm) under open air at 120 °C for a given amount of time. The solvent was removed in vacuo, and the residue was purified on a silica gel column with CS_2/toluene (100:0−0:100, gradient elution) as the eluent to give unreacted C_{60} and products **2a−d**, **2f−o**, **2q**, **2s**, **6a−d**, **4a**, **4b**, and **2t**.

Compound **2a** (brown solid, 13.9 mg, 35%, mp >300 °C): ^{1}H NMR (400 MHz, CS_2−$CDCl_3$) δ 4.97 (t, J = 7.8 Hz, 2H), 4.07 (t, J = 7.7 Hz, 2H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$) δ 150.23, 148.58, 148.35, 146.70, 146.62, 146.33, 146.22, 145.90, 145.80, 145.60, 145.57, 145.44, 145.40, 144.91, 144.87, 142.81, 142.80, 142.47, 142.41, 141.98, 141.69, 141.63, 141.42, 139.75, 139.31, 137.81, 137.30, 89.20 (sp^3-C of C_{60}), 78.67 (sp^3-C of C_{60}), 61.50, 48.20, 43.77; UV−vis ($CHCl_3$) λ_{max}/nm 257, 316, 690; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{63}H_8NO$ 794.0606, found 794.0603.

Compound **2b** (brown solid, 12.5 mg, 30%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 4.89 (t, J = 7.6 Hz, 2H), 4.20 (t, J = 7.6 Hz, 2H), 4.03 (t, J = 7.2 Hz, 2H), 1.89 (quint, J = 7.4 Hz, 2H), 1.59 (sextet, J = 7.4 Hz, 2H), 1.05 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$) δ 151.54, 150.54, 148.55, 148.32, 146.64, 146.57, 146.28, 146.27, 146.19, 145.83, 145.73, 145.53, 145.49, 145.44, 145.36, 144.91, 144.86, 142.78, 142.72, 142.44, 142.40, 141.93, 141.69, 141.52, 141.50, 139.68, 139.58, 137.84, 136.99, 87.69 (sp^3-C of C_{60}), 79.78 (sp^3-C of C_{60}), 61.18, 54.16, 43.75, 32.48, 20.92, 14.45; UV−vis ($CHCl_3$) λ_{max}/nm 258, 316, 693; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{66}H_{14}NO$ 836.1075, found 836.1074.

Compound **2c** (brown solid, 11.2 mg, 26%, mp >300 °C): ^{1}H NMR (400 MHz, CS_2−$CDCl_3$) δ 7.69 (d, J = 7.4 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 5.25 (s, 2H), 4.90 (t, J = 7.5 Hz, 2H), 4.06 (t, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$) δ 151.26, 150.52, 148.60, 148.37, 146.70, 146.62, 146.34, 146.32, 146.25, 145.85, 145.80, 145.56, 145.52, 145.49, 145.42, 144.94, 144.91, 142.82, 142.78, 142.49, 142.44, 142.01, 141.76, 141.56, 141.52, 139.80, 139.67, 139.52, 137.90, 137.17, 128.89, 128.67, 127.57, 88.04 (sp^3-C of C_{60}), 79.57 (sp^3-C of C_{60}), 61.29, 58.71, 42.62; UV−vis ($CHCl_3$) λ_{max}/nm 258, 317, 691; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{69}H_{12}NO$ 870.0919, found 870.0911.

Compound **2d** (brown solid, 7.0 mg, 17%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 4.80 (t, J = 7.7 Hz, 2H), 4.60 (hept, J = 6.5 Hz, 1H), 4.14 (t, J = 7.7 Hz, 2H), 1.60 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 151.49, 150.67, 148.49, 148.35, 146.57, 146.55, 146.26, 146.10, 145.74, 145.63, 145.59, 145.42, 145.32, 144.90, 144.89, 142.82, 142.75, 142.72, 142.44, 142.39, 141.93, 141.67, 141.41, 139.62, 139.42, 137.89, 136.62, 87.81 (sp^3-C of C_{60}), 79.46 (sp^3-C of C_{60}), 62.37, 52.86, 38.31, 23.09; UV−vis ($CHCl_3$) λ_{max}/nm 258, 319, 691; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{65}H_{12}NO$ 822.0919, found 822.0911.

Compound **2f** (brown solid, 10.5 mg, 26%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 5.14−5.24 (m, 1H), 4.27 (dd, J = 12.9, 7.7 Hz, 1H), 3.48−3.53 (m, 1H), 3.49 (s, 3H), 1.90 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$) δ 150.67, 150.62, 149.96, 148.52, 148.29, 146.68, 146.64, 146.59, 146.56, 146.30, 146.27, 146.20, 146.08, 145.91, 145.89, 145.84, 145.73, 145.69, 145.51, 145.40, 145.37, 145.36, 145.35, 144.92, 144.89, 144.88, 144.78, 142.81, 142.79, 142.76, 142.73, 142.47, 142.41, 142.38, 141.97, 141.93, 141.85, 141.68, 141.58, 141.56, 141.50, 141.07, 139.79, 139.64, 139.29, 139.02, 138.11, 137.75, 137.11, 136.98, 89.93 (sp^3-C of C_{60}), 77.84 (sp^3-C of C_{60}), 68.39, 56.14, 44.15, 23.93; UV−vis ($CHCl_3$) λ_{max}/nm 258, 316, 690; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{64}H_{10}NO$ 808.0762, found 808.0753.

Compound **2g** (brown solid, 9.8 mg, 24%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 4.98 (dd, J = 10.7, 8.7 Hz, 1H), 4.84 (sextet, J = 7.3 Hz, 1H), 4.42 (t, J = 10.0 Hz, 1H), 3.56 (s, 3H), 1.71 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 152.31, 150.98, 150.92, 150.76, 148.52, 148.30, 146.63, 146.58, 146.54, 146.28, 146.24, 146.19, 146.15, 146.09, 145.93, 145.60, 145.53, 145.47, 145.40, 145.39, 145.36, 145.30, 145.09, 144.99, 144.75, 144.69, 143.08, 142.79, 142.77, 142.76, 142.74, 142.66, 142.45, 142.44, 142.40, 142.36, 142.10, 141.75, 141.68, 141.65, 141.50, 141.46, 141.25, 139.74, 139.69, 139.50, 138.64, 137.33, 136.81, 136.71, 86.98 (sp^3-C of C_{60}), 80.01 (sp^3-C of C_{60}), 68.13, 49.82, 36.54, 18.86; UV−vis ($CHCl_3$) λ_{max}/nm 257, 316, 690; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{64}H_{10}NO$ 808.0762, found 808.0752.

Compound **2h** (brown solid, 12.3 mg, 30%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 5.18 (dd, J = 11.5, 7.4 Hz, 1H), 4.50 (dd, J = 11.6, 5.3 Hz, 1H), 4.25−4.32 (m, 1H), 4.21 (td, J = 8.7, 3.5

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Hz, 1H), 3.63 (q, J = 7.9 Hz, 1H), 2.55−2.65 (m, 1H), 2.45−2.55 (m, 1H), 2.18−2.29 (m, 2H); ^{13}C NMR (125 MHz, CS_2−C_6D_6) δ 152.66, 152.46, 150.86, 150.78, 149.08, 148.82, 147.23, 147.17, 147.13, 146.92, 146.86, 146.83, 146.82, 146.77, 146.70, 146.57, 146.39, 146.35, 146.30, 146.25, 146.03, 146.01, 145.98, 145.94, 145.88, 145.56, 145.44, 145.41, 143.37, 143.34, 143.32, 143.07, 142.96, 142.95, 142.57, 142.45, 142.31, 142.22, 141.72, 140.34, 140.29, 140.25, 140.05, 139.14, 137.93, 137.42, 137.15, 88.41 (sp^3-C of C_{60}), 77.03 (sp^3-C of C_{60}), 69.66, 56.00, 53.15, 35.19, 24.20; UV−vis ($CHCl_3$) λ_{max}/nm 257, 317, 691; HRMS (MALDI-TOFMS) m/z [M-H]$^+$ calcd for $C_{65}H_8NO$ 818.0606, found 818.0603.

Compound **2i** (brown solid, 12.1 mg, 29%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 5.08 (dd, J = 11.4, 8.1 Hz, 1H), 4.47 (dd, J = 11.4, 6.8 Hz, 1H), 4.22−4.30 (m, 2H), 3.52−3.60 (m, 1H), 2.16−2.25 (m, 1H), 1.92−2.13 (m, 4H), 1.69−1.78 (m, 1H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 150.48, 150.38, 150.35, 148.25, 148.06, 146.43, 146.38, 146.33, 146.07, 146.05, 146.03, 146.02, 145.97, 145.93, 145.88, 145.69, 145.60, 145.56, 145.48, 145.34, 145.20, 145.14, 145.11, 145.08, 144.74, 144.73, 144.65, 144.56, 142.90, 142.60, 142.58, 142.56, 142.54, 142.52, 142.27, 142.22, 142.20, 141.77, 141.69, 141.60, 141.42, 141.39, 141.33, 141.29, 140.89, 139.58, 139.39, 139.12, 138.69, 138.36, 137.05, 136.87, 136.84, 88.58 (sp^3-C of C_{60}), 78.94 (sp^3-C of C_{60}), 66.28, 51.49, 32.12, 26.89, 21.61; UV−vis ($CHCl_3$) λ_{max}/nm 258, 316, 688; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{66}H_{12}NO$ 834.0919, found 834.0915.

Compound **2j** (brown solid, 13.9 mg, 34%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 6.25 (ddt, J = 17.0, 10.1, 6.3 Hz, 1H), 5.60 (dq, J = 17.1, 1.2 Hz, 1H), 5.38 (dq, J = 10.1, 1.1 Hz, 1H), 4.89 (t, J = 7.6 Hz, 2H), 4.66 (dt, J = 6.3, 1.3 Hz, 2H), 4.16 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 150.95, 150.49, 148.57, 148.35, 146.67, 146.61, 146.31, 146.21, 145.83, 145.79, 145.55, 145.53, 145.46, 145.40, 144.90, 142.80, 142.77, 142.47, 142.43, 141.97, 141.71, 141.56, 141.48, 139.67, 139.60, 137.80, 137.16, 136.69, 118.20, 88.19 (sp^3-C of C_{60}), 79.25 (sp^3-C of C_{60}), 61.35, 57.85, 42.89; UV−vis ($CHCl_3$) λ_{max}/nm 258, 317, 690; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{65}H_{10}NO$ 820.0762, found 820.0752.

Compound **2k** (brown solid, 3.1 mg, 7%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 4.91 (t, J = 7.6 Hz, 2H), 4.75 (t, J = 5.2 Hz, 1H), 4.35 (t, J = 7.6 Hz, 2H), 4.24 (d, J = 5.3 Hz, 2H), 3.51 (s, 6H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 151.46, 150.34, 148.63, 148.42, 146.71, 146.66, 146.37, 146.35, 146.28, 145.82, 145.74, 145.55, 145.52, 145.47, 144.94, 144.91, 143.15, 142.85, 142.83, 142.79, 142.50, 142.46, 142.00, 141.81, 141.60, 141.50, 139.91, 139.65, 137.82, 137.20, 130.75, 128.84, 105.59, 87.43 (sp^3-C of C_{60}), 80.02 (sp^3-C of C_{60}), 60.95, 56.20, 54.30, 45.66; UV−vis ($CHCl_3$) λ_{max}/nm 257, 316, 690; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{66}H_{14}NO_3$ 868.0974, found 868.0961.

Compound **2l** (brown solid, 6.9 mg, 15%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 5.32 (s, 2H), 4.90 (t, J = 7.6 Hz, 2H), 4.08 (t, J = 7.6 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 166.50, 150.98, 150.35, 148.60, 148.37, 146.69, 146.63, 146.34, 146.33, 146.26, 145.87, 145.66, 145.50, 145.47, 145.43, 145.09, 144.90, 142.82, 142.79, 142.48, 142.42, 142.00, 141.77, 141.50, 139.83, 139.69, 137.80, 137.20, 130.00, 129.46, 128.56, 88.07 (sp^3-C of C_{60}), 79.47 (sp^3-C of C_{60}), 61.15, 58.49, 51.84, 43.37; UV−vis ($CHCl_3$) λ_{max}/nm 257, 317, 689; HRMS (MALDI-TOFMS) m/z [M − H]$^+$ calcd for $C_{71}H_{12}NO_3$ 926.0817, found 926.0808.

Compound **2m** (brown solid, 5.1 mg, 11%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.99 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 5.09 (t, J = 7.5 Hz, 2H), 4.88 (t, J = 7.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 148.98, 148.46, 148.38, 148.04, 146.61, 146.60, 146.32, 146.27, 146.20, 145.88, 145.41, 144.80, 144.67, 144.66, 143.63, 142.77, 142.75, 142.37, 141.95, 141.63, 141.23, 140.93, 139.79, 139.03, 138.88, 137.63, 137.44, 129.49, 128.38, 87.99 (sp^3-C of C_{60}), 76.15 (sp^3-C of C_{60}), 61.74, 43.09, 21.74; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 421, 688; HRMS (MALDI-TOFMS) m/z M$^+$ calcd for $C_{69}H_{11}NO_3S$ 933.0460, found 933.0451.

Compound **2n** (brown solid, 14.5 mg, 33%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.28 (dd, J = 5.1, 1.2 Hz, 1H), 7.21 (dd, J = 3.5, 1.1 Hz, 1H), 7.02 (dd, J = 5.1, 3.5 Hz, 1H), 5.46 (s, 2H), 4.90 (t, J = 7.6 Hz, 2H), 4.17 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 151.00, 150.38, 148.56, 148.32, 146.66, 146.59, 146.30, 146.28, 146.22, 145.85, 145.79, 145.50, 145.46, 145.45, 145.39, 144.89, 144.86, 143.92, 142.78, 142.75, 142.42, 141.96, 141.75, 141.48, 141.45, 139.79, 139.63, 137.79, 137.11, 126.82, 125.80, 125.45, 87.89 (sp^3-C of C_{60}), 79.29 (sp^3-C of C_{60}), 61.20, 53.85, 42.87; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 689; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{67}H_{10}NOS$ 876.0483, found 876.0465.

Compound **2o** (brown solid, 4.4 mg, 10%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 8.80−9.01 (m, 1H), 8.48−8.70 (m, 1H), 8.06 (d, J = 7.7 Hz, 1H), 7.32−7.42 (m, 1H), 5.30 (s, 2H), 4.92 (t, J = 7.6 Hz, 2H), 4.08 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$) δ 150.82, 150.23, 150.20, 149.01, 148.94, 148.58, 148.36, 146.67, 146.62, 146.33, 146.31, 146.25, 145.86, 145.55, 145.46, 145.41, 144.88, 144.86, 142.81, 142.78, 142.46, 142.39, 141.99, 141.75, 141.47, 139.84, 139.69, 137.75, 137.20, 136.18, 88.09 (sp^3-C of C_{60}), 79.43 (sp^3-C of C_{60}), 61.08, 56.10, 43.04; UV−vis ($CHCl_3$) λ_{max}/nm 257, 317, 689; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{68}H_{11}N_2O$ 871.0871, found 871.0851.

Compound **2q** (brown solid, 4.0 mg, 10%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 5.07−5.22 (m, 1H), 4.80−4.92 (m, 1H), 4.48−4.60 (m, 1H), 3.88−4.01 (m, 1H), 3.73 (s, 3H), 2.96−3.11 (m, 1H), 2.00−2.10 (m, 1H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$) δ 135−155 (sp^2-C of C_{60}), 95.69 (sp^3-C of C_{60}), 82.21 (sp^3-C of C_{60}), 72.00, 53.84, 39.62, 27.77; UV−vis ($CHCl_3$) λ_{max}/nm 258, 317, 689; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{64}H_{10}NO$ 808.0762, found 808.0753.

Compound **2r** (brown solid, 4.9 mg, 11%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.31−7.39 (m, 4H), 7.23−7.27 (m, 1H), 4.88 (t, J = 12.2 Hz, 1H), 4.68 (dt, J = 12.7, 3.7 Hz, 1H), 4.26 (dd, J = 14.9, 11.7 Hz, 1H), 3.85 (dt, J = 15.1, 3.2 Hz, 1H), 3.71 (s, 3H), 3.23−3.36 (m, 1H), 2.82 (dd, J = 13.6, 6.5 Hz, 1H), 2.78 (dd, J = 13.7, 7.7 Hz, 1H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 154.38, 154.34, 152.48, 150.82, 148.68, 148.38, 146.72, 146.66, 146.60, 146.59, 146.23, 146.20, 146.08, 145.96, 145.76, 145.56, 145.51, 145.47, 145.43, 145.41, 145.36, 145.18, 144.98, 144.91, 144.88, 144.84, 144.82, 144.53, 143.07, 142.80, 142.78, 142.76, 142.69, 142.67, 142.63, 142.50, 141.98, 141.87, 141.76, 141.55, 141.49, 141.46, 141.38, 140.84, 140.01, 139.56, 139.30, 139.27, 139.10, 138.69, 136.77, 136.50, 136.31, 128.85, 128.75, 126.48, 95.08 (sp^3-C of C_{60}), 81.89 (sp^3-C of C_{60}), 76.30, 59.54, 40.33, 37.96, 36.12; UV−vis ($CHCl_3$) λ_{max}/nm 256, 316, 688; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{71}H_{16}NO$ 898.1232, found 898.1221.

Compound **2t** (brown solid, 8.8 mg, 19%, mp >300 °C) (Caution: After purification on a silica gel column, the solvent should be removed in the dark using aluminum foil to wrap the round-bottom flask): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.54 (d, J = 7.4 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.25 (td, J = 7.2, 1.2 Hz), 7.20 (td, J = 7.5, 1.0 Hz), 6.92 (s, 1H), 5.44 (s, 2H), 4.96 (t, J = 7.6 Hz, 2H), 4.24 (t, J = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 155.90, 155.27, 150.92, 150.29, 148.60, 148.37, 146.70, 146.63, 146.34, 146.26, 145.90, 145.79, 145.52, 145.48, 145.46, 145.44, 144.91, 144.88, 142.83, 142.80, 142.79, 142.47, 142.46, 142.00, 141.79, 141.51, 141.46, 139.84, 139.69, 137.82, 137.19, 128.50, 124.16, 122.90, 120.90, 111.36, 105.89, 87.95 (sp^3-C of C_{60}), 79.15 (sp^3-C of C_{60}), 61.12, 52.27, 43.71; UV−vis ($CHCl_3$) λ_{max}/nm 258, 317, 688; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{71}H_{12}NO_2$ 910.0868, found 910.0846.

Compound **4a** (brown solid, 6.8 mg, 16%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.07 (dd, J = 5.8, 1.8 Hz, 1H), 6.85 (d, J = 5.8 Hz, 1H), 6.23 (d, J = 1.5 Hz, 1H), 4.80−4.87 (m, 1H), 4.56−4.62 (m, 1H), 4.23 (d, J = 12.5 Hz, 1H), 4.15 (d, J = 12.5 Hz, 1H), 4.02−4.08 (m, 1H), 3.92−3.97 (m, 1H); UV−vis ($CHCl_3$) λ_{max}/nm 257, 708; HRMS (MALDI-TOFMS) m/z M$^+$ calcd for $C_{67}H_9NO_2$ 859.0633, found 859.0626.

Compound **4b** (brown solid, 9.7 mg, 21%, mp >300 °C) (Caution: this product is very sensitive to sunlight). After purification on silica gel column, the solvent should be removed in the dark using aluminum foil to wrap the round-bottom flask): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 6.87 (d, J = 5.6 Hz, 1H), 6.79 (d, J = 5.8 Hz, 1H), 4.82

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(ddd, J = 11.8, 9.9, 4.4 Hz, 1H), 4.58 (ddd, J = 11.6, 7.1, 2.5 Hz, 1H), 4.17 (d, J = 12.4 Hz, 1H), 4.10 (d, J = 12.5 Hz, 1H), 4.01−4.08 (m, 1H), 3.88−3.94 (m, 1H), 2.59−2.73 (m, 2H), 1.87−2.01 (m, 1H), 1.70−1.83 (m, 1H), 1.27−1.57 (m, 4H), 0.96 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 152.09, 149.29, 149.18, 149.06, 148.31, 148.14, 147.89, 147.00, 146.76, 146.32, 146.20, 146.18, 146.05, 145.90, 145.82, 145.62, 145.51, 145.36, 145.22, 144.95, 144.71, 144.59, 144.55, 144.20, 144.12, 143.98, 143.91, 143.85, 143.82, 143.68, 143.48, 143.05, 143.02, 142.96, 142.84, 142.36, 142.28, 142.20, 142.16, 141.99, 141.18, 141.04, 140.52, 139.85, 137.88, 137.15, 136.83, 135.14, 133.68, 99.21, 98.03, 87.55 (sp^3-C of C_{60}), 84.07 (sp^3-C of C_{60}), 76.10 (sp^3-C of C_{60}), 74.39 (sp^3-C of C_{60}), 62.33, 54.62, 47.76, 32.59, 31.56, 25.91, 23.05, 14.35; UV−vis ($CHCl_3$) λ_{max}/nm 257, 713; HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{72}H_{19}NO_2$ 929.1416, found 929.1423.

Compound **7a** (brown solid, 6.3 mg, 15%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 3.88 (t, J = 7.1 Hz, 2H), 3.28 (t, J = 7.0 Hz, 2H), 3.04 (s, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) (the low quality of the ^{13}C NMR spectrum was because of its very poor solubility) δ 146.65, 145.43, 145.33, 145.22, 145.06, 145.00, 144.90, 144.67, 144.47, 144.42, 143.97, 143.53, 142.92, 142.73, 142.66, 142.25, 142.06, 141.90, 141.03, 140.96, 137.13, 76.63 (sp^3-C of C_{60}), 45.90, 30.52, 25.11; UV−vis ($CHCl_3$) λ_{max}/nm 260, 328, 430, 496, 689; HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{65}H_7NO$ 817.0528, found 817.0520.

Compound **7b′** (a small amount of **7b′** could be isolated within 2 h from the reaction of C_{60} with **6b**): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 5.55 (s, 1H), 4.21 (d, J = 12.9 Hz, 1H), 4.17 (d, J = 12.9 Hz, 1H), 3.46−3.54 (m, 1H), 3.34−3.41 (m, 1H), 3.09−3.16 (m, 1H), 3.01−3.08 (m, 1H), 2.37 (br, 1H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 145.36, 145.08, 144.97, 144.78, 144.72, 144.64, 144.24, 144.15, 144.09, 144.06, 143.59, 143.55, 143.17, 143.09, 143.06, 143.02, 142.99, 142.25, 142.21, 142.19, 141.11, 128.72, 128.65, 127.48, 88.01 (HOCHN), 72.96 (sp^3-C of C_{60}), 54.72, 54.05, 49.62, 28.63; UV−vis ($CHCl_3$) λ_{max}/nm 259, 328, 429, 498, 691; HRMS (MALDI-TOFMS) m/z [M + H − H_2O]$^+$ calcd for $C_{71}H_{12}N$ 878.0970, found 878.0952.

Compound **7b** (brown solid, 22.3 mg, 50%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.38−7.46 (m, 4H), 7.35 (t, J = 7.5 Hz, 1H), 4.74 (s, 2H), 3.77 (t, J = 7.1 Hz, 2H), 3.24 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$) δ 168.30, 146.68, 145.52, 145.38, 145.36, 145.19, 145.13, 145.09, 145.06, 144.99, 144.74, 144.56, 144.53, 144.50, 144.10, 144.04, 143.61, 143.57, 143.14, 143.05, 142.99, 142.75, 142.31, 142.13, 142.03, 141.96, 141.18, 141.04, 140.99, 137.22, 135.83, 129.07, 128.70, 128.15, 76.28 (sp^3-C of C_{60}), 47.87, 44.26, 43.27, 25.03; UV−vis ($CHCl_3$) λ_{max}/nm 259, 328, 429, 497, 690; HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{71}H_{11}NO$ 893.0841, found 893.0821.

Compound **7c** (brown solid, 12.9 mg, 29%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 3.88 (t, J = 7.1 Hz, 2H), 3.57 (t, J = 7.3 Hz, 2H), 3.27 (t, J = 7.1 Hz, 2H), 1.76 (quint, J = 7.4 Hz, 2H), 1.33−1.51 (m, 6H), 0.93 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 168.12, 146.78, 145.60, 145.40, 145.34, 145.18, 145.13, 145.06, 145.03, 144.96, 144.73, 144.54, 144.51, 144.47, 144.04, 144.02, 143.60, 143.57, 143.11, 143.03, 142.97, 142.71, 142.30, 142.12, 141.99, 141.96, 141.16, 141.00, 137.17, 76.38 (sp^3-C of C_{60}), 44.44, 43.93, 43.83, 31.78, 27.61, 26.97, 25.20, 22.95, 14.28; UV−vis ($CHCl_3$) λ_{max}/nm 260, 328, 429, 497, 685; HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{70}H_{17}NO$ 887.1310, found 887.1290.

Compound **7d** (brown solid, 10.5 mg, 24%, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 3.78 (t, J = 6.3 Hz, 2H), 3.60 (t, J = 7.7 Hz, 2H), 3.04 (t, J = 6.2 Hz, 2H), 2.41 (quint, J = 6.3 Hz, 2H), 1.72 (quint, J = 7.6 Hz, 2H), 1.44 (sextet, J = 7.5 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.64, 147.41, 146.59, 145.53, 145.30, 145.16, 145.11, 145.04, 144.95, 144.76, 144.59, 144.52, 144.50, 144.05, 144.00, 143.58, 143.45, 143.12, 143.00, 142.91, 142.59, 142.30, 142.07, 141.84, 141.72, 141.12, 140.94, 140.63, 137.82, 76.73 (sp^3-C of C_{60}), 48.16, 48.03, 45.08, 29.64, 25.30, 22.58, 20.63, 14.18; UV−vis ($CHCl_3$) λ_{max}/nm 260, 328, 429, 496, 692; HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{69}H_{15}NO$ 873.1154, found 873.1136.

Conversion of 4b or 2t to 5b or 5t under Photoirradiation. A solution of **4b** or **2t** (0.015 mmol) in CS_2 (20 mL) in a big tube (Φ18 × 150 mm) was irradiated with a 125 W fluorescent high-pressure mercury lamp under a nitrogen atmosphere for 1 h. The solvent was removed in vacuo, and the residue was purified on a silica gel column with CS_2/toluene (100:0−0:100, gradient elution) as the eluent to give product **5b** (7.2 mg, 52%) or **5t** (9.1 mg, 67%).

Compound **5b** (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 5.31 (d, J = 10.1 Hz, 1H), 5.02 (s, 2H), 4.76−4.88 (m, 2H), 4.32 (d, J = 10.0 Hz, 1H), 4.26 (dt, s = 15.0, 8.0 Hz, 1H), 3.73 (ddd, J = 15.1, 8.9, 5.7 Hz, 1H), 2.34 (t, J = 7.5 Hz, 2H), 1.54−1.70 (m, 2H), 1.25−1.41 (m, 4H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 164.06, 152.74, 149.55, 149.52, 149.07, 148.94, 148.52, 148.32, 148.07, 147.52, 147.11, 147.04, 146.73, 146.49, 146.46, 146.26, 146.21, 145.73, 145.66, 145.59, 145.42, 145.38, 145.29, 145.22, 145.11, 145.06, 144.94, 144.87, 144.74, 144.66, 144.57, 144.52, 144.46, 144.21, 144.18, 143.92, 143.79, 143.41, 143.02, 142.98, 142.80, 142.59, 142.50, 142.09, 141.81, 141.69, 140.49, 140.13, 139.73, 139.06, 138.98, 136.64, 97.60, 95.28, 83.09 (sp^3-C of C_{60}), 79.28 (sp^3-C of C_{60}), 78.82 (sp^3-C of C_{60}), 67.85, 64.09 (sp^3-C of C_{60}), 61.44, 57.29, 40.05, 32.33, 28.97, 27.47, 23.44, 14.87; UV−vis ($CHCl_3$) λ_{max}/nm 258, 690; HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{72}H_{19}NO_2$ 929.1416, found 929.1432.

Compound **5t** (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.31 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 7.9 Hz, 1H), 6.92−6.99 (m, 2H), 5.52 (s, 1H), 5.40 (d, J = 10.0 Hz, 1H), 4.79−4.91 (m, 2H), 4.46 (d, J = 10.1 Hz, 1H), 4.30 (dt, s = 15.0, 8.0 Hz, 1H), 3.78 (ddd, J = 15.1, 9.1, 5.9 Hz, 1H), 2.34 (t, J = 7.5 Hz, 2H), 1.54−1.70 (m, 2H), 1.25−1.41 (m, 4H), 0.86 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 161.25, 152.19, 149.26, 149.20, 148.78, 148.28, 148.25, 148.07, 147.53, 147.19, 146.83, 146.70, 146.44, 146.14, 145.94, 145.89, 145.29, 145.07, 144.97, 144.91, 144.84, 144.77, 144.59, 144.39, 144.23, 144.21, 144.10, 143.93, 143.90, 143.87, 143.58, 143.43, 143.08, 142.70, 142.65, 142.47, 142.22, 142.18, 142.14, 141.69, 141.55, 141.43, 141.20, 140.20, 139.86, 139.39, 138.68, 138.06, 136.31, 129.94, 127.17, 126.27, 121.92, 110.65, 96.29, 82.96 (sp^3-C of C_{60}), 79.04 (sp^3-C of C_{60}), 77.90 (sp^3-C of C_{60}), 67.34, 62.93 (sp^3-C of C_{60}), 61.22, 55.42, 39.63, 0.09; UV−vis ($CHCl_3$) λ_{max}/nm 256, 691; HRMS (MALDI-TOFMS) m/z [M + H]$^+$ calcd for $C_{71}H_{12}NO_2$ 910.0868, found 910.0851.

Reaction of C_{60} with Cyclic Enamine 8 Catalyzed by the CuI/DMAP System. A mixture of C_{60} (36.0 mg, 0.05 mmol), enamine **8** (0.1 mmol), CuI (1.9 mg, 0.01 mmol), and DMAP (2.5 mg, 0.02 mmol) was stirred vigorously in 10 mL of chlorobenzene in a tube (Φ18 × 150 mm) under open air at 120 °C for 6 h. The solvent was removed in vacuo, and the residue was purified on a silica gel column with CS_2 as the eluent to give unreacted C_{60} and then with toluene as the eluent to give product **7e** (9.7 mg, 21%, brown solid, mp >300 °C). ^{1}H NMR (500 MHz, CS_2−$CDCl_3$) δ 7.30−7.39 (m, 4H), 7.27 (t, J = 6.9 Hz, 1H), 5.51 (d, J = 15.1 Hz, 1H), 4.29 (d, J = 15.1 Hz, 1H), 3.89 (sextet, J = 6.1 Hz, 1H), 3.13 (ddd, J = 14.2, 9.3, 4.0 Hz, 1H), 3.01 (ddd, J = 14.3, 7.8, 4.0 Hz, 1H), 2.42−2.51 (m, 1H), 2.10−2.20 (m, 1H), 1.55 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$) δ 165.37, 147.48, 147.00, 146.64, 146.38, 145.51, 145.49, 145.28, 145.16, 145.14, 145.12, 145.01, 144.96, 144.94, 144.77, 144.75, 144.56, 144.53, 144.51, 144.08, 144.07, 144.05, 143.98, 143.62, 143.57, 143.46, 143.42, 143.13, 143.07, 143.04, 143.01, 142.92, 142.90, 142.59, 142.58, 142.31, 142.28, 142.09, 142.05, 141.81, 141.70, 141.68, 141.40, 141.29, 140.99, 140.90, 140.68, 140.63, 137.86, 137.84, 137.25, 128.82, 127.91, 127.55, 76.80 (sp^3-C of C_{60}), 76.76 (sp^3-C of C_{60}), 51.73, 48.05, 44.97, 29.77, 22.83, 20.63; λ_{max}/nm 260, 328, 429, 496, 693; HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{73}H_{15}NO$ 921.1154, found 921.1133.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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UV−vis spectra of **2b**, **4a**, **5b**, **5t**, and **7b**, ^{1}H and ^{13}C NMR spectra of the products, and H−H Cosy, HSQC, HMBC, and NOESY spectra of **5b** (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: yht898@yahoo.com.

ORCID

Hai-Tao Yang: 0000-0001-9803-5452

Chun-Bao Miao: 0000-0003-4666-2619

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Li, C.-Z.; Yip, H.-L.; Jen, A. K.-Y. *J. Mater. Chem.* **2012**, *22*, 4161. (b) Chochos, C.; Tagmatarchis, N.; Gregoriou, V. G. *RSC Adv.* **2013**, *3*, 7160−7181. (c) Anilkumar, P.; Lu, F.; Cao, L.; Luo, P. G.; Liu, J.-H.; Sahu, S.; Tackett, K. N., II; Wang, Y.; Sun, Y.-P. *Curr. Med. Chem.* **2011**, *18*, 2045. (d) Delgado, J. L.; Martín, N.; de la Cruz, P.; Langa, F. *Chem. Soc. Rev.* **2011**, *40*, 5232. (e) Jennepalli, S.; Pyne, S. G.; Keller, P. A. *RSC Adv.* **2014**, *4*, 46383. (f) Martín, N., Giacalone, F., Eds. *Fullerene Polymers: Synthesis, Properties and Applications*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2009. (g) Martín, N.; Nierengarten, J.-F., Eds. *Supramolecular Chemistry of Fullerenes and Carbon Nanotubes*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2012.

(2) For recent papers, see: (a) Wu, A.-J.; Tseng, P.-Y.; Hsu, W.-H.; Chuang, S.-C. *Org. Lett.* **2016**, *18*, 224. (b) Zhou, D.-B.; Wang, G.-W. *Org. Lett.* **2016**, *18*, 2616. (c) Lou, N.; Li, Y.; Cui, C.; Liu, Y.; Gan, L. *Org. Lett.* **2016**, *18*, 2236. (d) Reboredo, S.; Girón, R. M.; Filippone, S.; Mikie, T.; Sakurai, T.; Seki, S.; Martín, N. *Chem. - Eur. J.* **2016**, *22*, 13627. (e) Wu, J.; Liu, C.-X.; Wang, H.-J.; Li, F.-B.; Shi, J.-L.; Li, J.-X.; Liu, C.-Y.; Huang, Y.-S. *J. Org. Chem.* **2016**, *81*, 9296. (f) Ueda, M.; Sakaguchi, T.; Hayama, M.; Nakagawa, T.; Matsuo, Y.; Munechika, A.; Yoshida, S.; Yasuda, H.; Ryu, I. *Chem. Commun.* **2016**, *52*, 13175.

(3) For reviews, see: (a) Tzirakis, M. D.; Orfanopoulos, M. *Chem. Rev.* **2013**, *113*, 5262. For recent papers, see: (b) Zhai, W.-Q.; Jiang, S.-P.; Peng, R.-F.; Jin, B.; Wang, G.-W. *Org. Lett.* **2015**, *17*, 1862. (c) Zhang, X.-F.; Li, F.-B.; Wu, J.; Shi, J.-L.; Liu, Z.; Liu, L. *J. Org. Chem.* **2015**, *80*, 6037. (d) Si, W.; Zhang, X.; Asao, N.; Yamamoto, Y.; Jin, T. *Chem. Commun.* **2015**, *51*, 6392. (e) Liu, T.-X.; Ma, J.; Chao, D.; Zhang, P.; Liu, Q.; Shi, L.; Zhang, Z.; Zhang, G. *Chem. Commun.* **2015**, *51*, 12775.

(4) (a) Li, F.-B.; Liu, T.-X.; Wang, G.-W. *J. Org. Chem.* **2008**, *73*, 6417. (b) He, C.-L.; Liu, R.; Li, D.-D.; Zhu, S.-E.; Wang, G.-W. *Org. Lett.* **2013**, *15*, 1532. (c) Takeda, Y.; Enokijima, S.; Nagamachi, T.; Nakayama, K.; Minakata, S. *Asian J. Org. Chem.* **2013**, *2*, 91. (d) You, X.; Wang, G.-W. *J. Org. Chem.* **2014**, *79*, 117.

(5) (a) Yang, H.-T.; Ren, W.-L.; Dong, C.-P.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Tetrahedron Lett.* **2013**, *54*, 6799. (b) Miao, C.-B.; Lu, X.-W.; Wu, P.; Li, J.-X.; Ren, W.-L.; Xing, M.-L.; Sun, X.-Q.; Yang, H.-T. *J. Org. Chem.* **2013**, *78*, 12257. (c) Yang, H.-T.; Lu, X.-W.; Xing, M.-L.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2014**, *16*, 5882.

(6) (a) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2013**, *15*, 4650. (b) Lu, X.-W.; Xing, M.-L.; Miao, C.-B.; Li, J.-X.; Sun, X.-Q.; Yang, H.-T. *Org. Biomol. Chem.* **2015**, *13*, 8405. (c) Yang, H.-T.; Tan, Y.-C.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *J. Org. Chem.* **2016**, *81*, 1157.

(7) (a) Minakata, S.; Morino, Y.; Ide, T.; Oderaotoshi, T.; Komatsu, M. *Chem. Commun.* **2007**, 3279. (b) Gratia, S. S.; Vigneau, E. S.; Eltayeb, S.; Patel, K.; Meyerhoefer, T. J.; Kershaw, S.; Huang, V.; De Castro, M. *Tetrahedron Lett.* **2014**, *55*, 448.

(8) (a) Farid, U.; Wirth, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 3462. (b) Broggini, G.; Barbera, V.; Beccalli, E. M.; Chiacchio, U.; Fasana, A.; Galli, S.; Gazzola, S. *Adv. Synth. Catal.* **2013**, *355*, 1640. (c) Muñiz, K.; Iglesias, A.; Fang, Y. *Chem. Commun.* **2009**, 5591. (d) Cochran, B. M.; Michael, F. E. *Org. Lett.* **2008**, *10*, 5039.

(9) (a) Lu, D.-F.; Zhu, C.-L.; Jia, Z.-X.; Xu, G. *J. Am. Chem. Soc.* **2014**, *136*, 13186. (b) Hu, N. X.; Aso, Y.; Otsubo, T.; Ogura, F. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1447. (c) Borsini, E.; Broggini, G.; Fasana, A.; Galli, S.; Khansaa, M.; Piarulli, U.; Rigamonti, M. *Adv. Synth. Catal.* **2011**, *353*, 985. (d) Tamaru, Y.; Kawamura, S.; Bando, T.; Tanaka, K.; Hojo, M.; Yoshida, Z. *J. Org. Chem.* **1988**, *53*, 5491.

(10) (a) Michaelis, D. J.; Shaffer, C. J.; Yoon, T. P. *J. Am. Chem. Soc.* **2007**, *129*, 1866. (b) Williamson, K. S.; Yoon, T. P. *J. Am. Chem. Soc.* **2012**, *134*, 12370 and references cited therein.

(11) (a) Szolcsányi, P.; Gracza, T. *Chem. Commun.* **2005**, 3948. (b) Wijtmans, R.; Vink, M. K. S.; Schoemaker, H. E.; van Delft, F. L.; Blaauw, R. H.; Rutjes, F. P. J. T. *Synthesis* **2004**, *2004*, 641.

(12) (a) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T. *J. Am. Chem. Soc.* **1993**, *115*, 1594. (b) Chuang, S.-C.; Sander, M.; Jarrosson, T.; James, S.; Rozumov, E.; Khan, S. I.; Rubin, Y. *J. Org. Chem.* **2007**, *72*, 2716. (c) Sander, M.; Jarrosson, T.; Chuang, S.-C.; Khan, S. I.; Rubin, Y. *J. Org. Chem.* **2007**, *72*, 2724.

(13) Martín, N.; Altable, M.; Filippone, S.; Martín-Domenech, A.; Güell, M.; Solà, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1439.

(14) (a) Mikie, T.; Asahara, H.; Nagao, K.; Ikuma, N.; Kokubo, K.; Oshima, T. *Org. Lett.* **2011**, *13*, 4244. (b) Gao, X.; Ma, S.-L.; Guo, L.-W.; Zhang, D.-W.; Wu, S.-H.; Wu, H.-M.; Li, Y.-J. *Chem. Lett.* **1999**, *28*, 671.

(15) For examples, see: (a) Yang, X.-L.; Peng, X.-X.; Chen, F.; Han, B. *Org. Lett.* **2016**, *18*, 2070. (b) Zhu, X.; Chiba, S. *Org. Biomol. Chem.* **2014**, *12*, 4567. (c) Zhu, X.; Wang, Y.-F.; Ren, W.; Zhang, F.-L.; Chiba, S. *Org. Lett.* **2013**, *15*, 3214. (d) He, Y.; Tian, M.-M.; Zhang, X.-Y.; Fan, X.-S. *Asian J. Org. Chem.* **2016**, *5*, 1318. (e) Chen, F.; Yang, X.-L.; Wu, Z.-W.; Han, B. *J. Org. Chem.* **2016**, *81*, 3042.

(16) Huang, X.; Wang, J.; Ni, Z.; Wang, S.; Pan, Y. *Org. Lett.* **2015**, *17*, 5488.

(17) For reviews, see: (a) Rolff, M.; Tuczek, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 2344. (b) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047. (c) Gamez, P.; Aubel, P. G.; Driessen, W. L.; Reedijk, J. *Chem. Soc. Rev.* **2001**, *30*, 376−385. (d) Fontecave, M.; Pierre, J.-L. *Coord. Chem. Rev.* **1998**, *170*, 125.

(18) (a) Zhang, Y.; Matsuo, Y.; Li, C.-Z.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 8086. (b) Zhang, Y.; Matsuo, Y.; Nakamura, E. *Org. Lett.* **2011**, *13*, 6058.

(19) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, P.; Kozlowski, M. C. *Chem. Rev.* **2013**, *113*, 6234.

(20) Heron, N. M.; Jung, F. H.; Pasquet, G. R.; Mortlock, A. A. WO 2004058781, 2014.

(21) Aquila, B. M.; Bannister, T. D.; Cuny, G. D.; Hauske, J. R.; Holland, J. M.; Persons, P. E.; Radeke, H.; Wang, F.; Shao, L. WO 2002022572, 2002.

(22) de Almeida, C. G.; Reis, S. G.; de Almeida, A. M.; Diniz, C. G.; da Silva, V. L.; Le Hyaric, M. *Chem. Biol. Drug Des.* **2011**, *78*, 876.

(23) Sartor, D.; Scherhag, A. WO 2011131613, 2011.

(24) Burdi, D.; Spear, L. K. L.; Hardy, W. WO 2010114971, 2010.

(25) Nova, A.; Balcells, D.; Schley, N. D.; Dobereiner, G. E.; Crabtree, R. H.; Eisenstein, O. E. *Organometallics* **2010**, *29*, 6548.

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