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Copper-Catalyzed Reaction of C_{60} with Tertiary Amines for the Preparation of Spiro-Linked Methanofullerenes and Fullerenoalkanals

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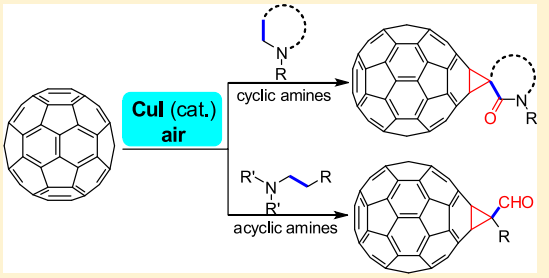
Supporting Information

ABSTRACT: CuI-catalyzed reaction of C_{60} with tertiary amines by using air as the sole oxidant has been developed. Spiro-linked methanofullerenes bearing cyclic amides and fullerenoalkanals can be obtained selectively using the cyclic and acyclic amines as starting materials, respectively. The reactions show a wide functional group tolerance. In addition, four ([6,6]-phenyl-C_{61}-butyric acid methyl ester) analogues can be easily prepared through the developed method.



INTRODUCTION

Tertiary amine derivatives are ubiquitous in nature. The direct functionalization of C(sp^3)−H bonds of tertiary amines represents an attractive protocol for the synthesis of complex N-containing moieties as it avoids the introduction of an active group and thus shortens the number of reaction steps. Among them, direct α-functionalization of tertiary amines has been well explored as an efficient and conventional way to synthesize tertiary amine derivatives through either capture of the in situ generated iminium intermediates[1] under oxidative conditions or trap of α-aminoalkyl radical intermediates under photo-redox catalytic conditions,[2] as well based on direct α-metalation.[3] In contrast to the flourishing α-functionalizations, β-functionalization of tertiary amines is significantly limited owing to the relatively inert C−H bonds. As far as we know, most of the developed β-functionalization relies on the in situ generated nucleophilic enamines as key intermediates followed by reactions with appropriate electrophiles[4] or coupling with nucleophiles.[5] Recently, a copper-catalyzed β-functionalization of tertiary amines with thiophenols has been reported via an enamine radical cation process.[6] Although the promising chemistry of tertiary amines has been exploited, further improvement for application is still in demand such as development of novel transformation, use of ubiquitous metals instead of precious metals, and extension of the limited substrate scope. In addition, compared to the specific functionalization of α- or β-tertiary amines, α,β-difunctionalization of tertiary amines is extremely rare, which needs to be further explored.[7] The preparation of spiro compounds at the β-position of tertiary amines is still blank.

On the other hand, the remarkable potential of organofullerenes in materials and biomedical science, electronic devices, and nanotechnology[8] has made organic modification of fullerenes receive more attention.[9,10] In this respect, the transition metal-promoted or -catalyzed reaction has represented a powerful tool to functionalize fullerenes including radical reactions,[11] C−H activation,[12] and asymmetric reactions.[13] Over the past few years, Cu(I/II)-promoted transformation of C_{60} has gradually attracted increasing attention.[9a,14] We have been interested in this field and have developed several new methods for the functionalization of C_{60}.[15] Most recently, we reported an interesting CuI-catalyzed reaction of C_{60} with aminoalcohols.[15e] 4-/5-Aminoalcohols displayed an entirely different reactivity from 2-/3-aminoalcohols, providing the surprising spiro-linked methanofullerenes bearing cyclic amides through cyclic enamine intermediates. Unfortunately, most of the cyclic enamines are unstable and the 4-/5-aminoalcohols are not easily available, which limits the application of this method. In contrast, the tertiary amines are either commercially available or can be easily prepared from the reactions of secondary amines with halide compounds. Inspired by the aformentioned β-functionalization of tertiary amines, in which the enamines were generated as the key intermediates catalyzed by Pt, Ru, Pd, Cu, or Fe,[4−6] we herein reported the CuI-catalyzed functionalization of C_{60} with tertiary amines (Scheme 1).

RESULTS AND DISCUSSION

We began our study by investigating the reactions of C_{60} with *N*-benzylpyrrolidine **1a** in the presence of various copper catalysts and ligands (Table 1). In a preliminary attempt, the reaction of C_{60} with 2 equiv of **1a** was carried out in the presence of 0.2 equiv of CuI in chlorobenzene at 120 °C. No

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Scheme 1. Functionalization of Tertiary Amines

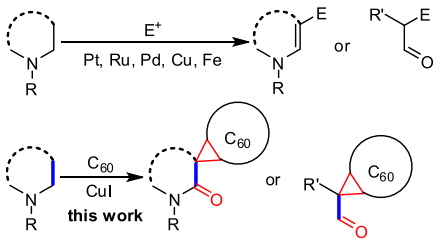
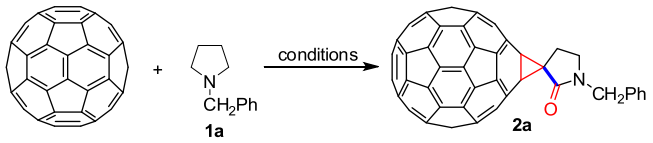


Table 1. Survey of the Reaction Conditions[a]



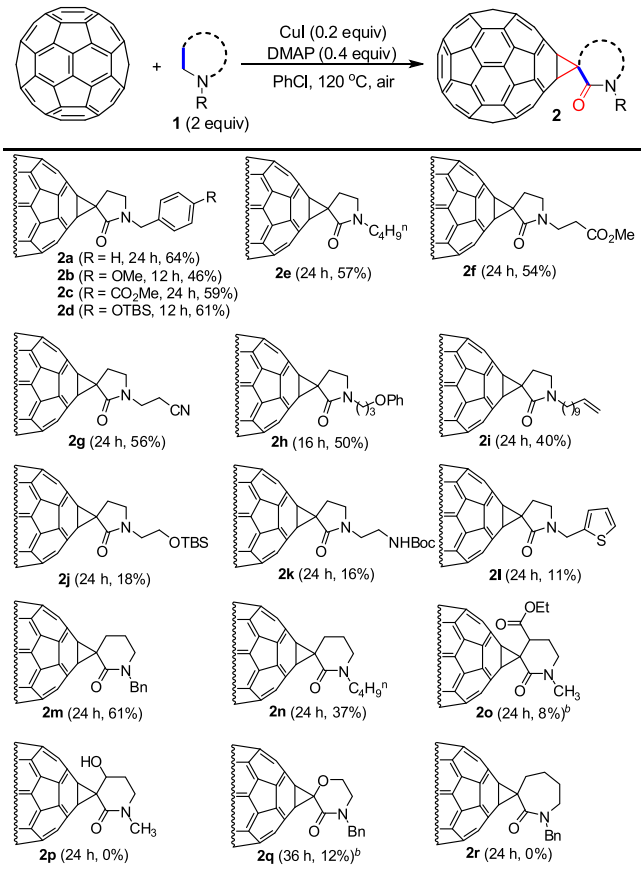
entry	additive	molar ratio[b]	time (h)	yield[c]
1	CuI	1:2:0.2	24	0
2	CuI, Phen	1:2:0.2:0.2	24	12 (74)
3	CuI, Bpy	1:2:0.2:0.2	24	37 (63)
4	CuI, pyridine	1:2:0.2:0.2	24	0
5	CuI, lutidine	1:2:0.2:0.4	24	0
6	CuI, DMAP	1:2:0.2:0.4	24	64 (79)
7	CuI, TMDEA	1:2:0.2:0.2	24	trace
8[d]	CuI, DMAP	1:2:0.2:0.4	24	6 (88)
9	CuCl, DMAP	1:2:0.2:0.4	24	27 (84)
10	CuBr, DMAP	1:2:0.2:0.4	24	52 (74)
11	Cu_2O, DMAP	1:2:0.2:0.4	24	0
12	$Cu(CH_3CN)_4PF_6$, DMAP	1:2:0.2:0.4	24	0
13	$Cu(OAc)_2$, DMAP	1:2:0.2:0.4	24	trace
14	$CuCl_2$, DMAP	1:2:0.2:0.4	24	11 (69)

[a]C_{60} (36 mg), other reactants and reagents, 10 mL of chlorobenzene, 120 °C, and air. [b]C_{60}/**1a**/[Cu]/additives. [c]Isolated yield; the values in parentheses are based on consumed C_{60}. [d]Operated under a N_2 atmosphere.

reaction occurred by even prolonging the reaction time to 20 h, indicating that CuI alone could not trigger the reaction (Table 1, entry 1). Next, the combination of CuI with different ligands was tried because the catalytic system varied greatly with the substrate structure, as has been observed in our previous research.[15] Using Phen (1,10-phenanthroline) or Bpy (2,2′-bipyridine) as ligands afforded the anticipated product **2a** in 12 and 37% yield, respectively (Table 1, entries 2 and 3). A further ligand screening revealed that DMAP was the most effective, giving 64% yield of **2a** (Table 1, entry 6); however, the combination of CuI with pyridine, lutidine, or TMEDA displayed no catalytic activity (Table 1, entries 4, 5, and 7). It should be noted that O_2 played a crucial role in this reaction because the yield decreased significantly to 6% when the reaction was carried out under a N_2 atmosphere (Table 1, entry 8). With the DMAP as the ligand, other copper salts were also examined. CuCl and CuBr were inferior to CuI, giving 27 and 52% yield of **2a**, respectively (Table 1, entries 9 and 10). Cu_2O, $Cu(CH_3CN)_4PF_6$, and $Cu(OAc)_2$ showed no catalytic activity (Table 1, entries 11−13), and $CuCl_2$ only furnished 11% production of **2a** (Table 1, entry 14). The DMAP was identified as a ligand rather than a base because no reaction occurred when K_2CO_3 or Cs_2CO_3 was used instead of DMAP.

Under the optimized reaction conditions (Table 1, entry 6), various N-substituted pyrrolidines were subjected to the reaction to assess the generality of the CuI-catalyzed reaction (Table 2). Either an electron-donating or an electron-withdrawing group on the phenyl ring of the benzyl group had little influence on the reaction (**2b−d**). Heteroaryl groups such as 2-thienyl, 2-furyl, and 3-pyridyl were also examined. Only *N*-(2-thienyl)pyrrolidine gave product **2l** in 11% yield. Various functional groups such as cyano, ester, vinyl, or phenoxy group were well tolerated, giving **2f−i** in satisfactory yields. A terminal hydroxyl or amino group ($-CH_2CH_2OH$, $-CH_2CH_2NH_2$) on the nitrogen atom of pyrrolidine would result in no formation of the desired product. When they were pre-transformed to the OTBS or NHBoc group, the anticipated products **2j** and **2k** could be obtained in 18 and 16% yield, respectively. Next, various N-substituted piperidines **1m−p** were tested. *N*-Benzyl and *N*-butyl piperidines gave good yields of **2m** or **2n**. When an ester group was connected at the 4-position of the piperidine ring, product **2o** was obtained in a very low yield. Changing the ester group to the hydroxyl group led to a complete failure of the reaction (**2p**, 0%). Changing the 4-hydroxyl group to the 4-hydroxymethyl group led to the formation of a single product; however, the NMR analysis showed that it was the spiro compound **2s** (Scheme 2). *N*-Benzylmorpholine could also react with C_{60} to provide **2q** in 12% yield. When the cyclic amine was further extended to a seven-membered ring, that is, *N*-benzylazepane **1r**, no analogous reaction occurred (**2r**, 0%).

Table 2. CuI-Catalyzed Reaction of Cyclic Tertiary Amines with C_{60}[a]



[a]The yield refers to an isolated yield. [b]Under an O_2 atmosphere.

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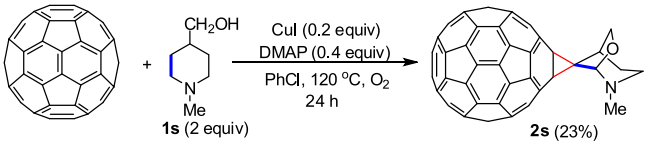
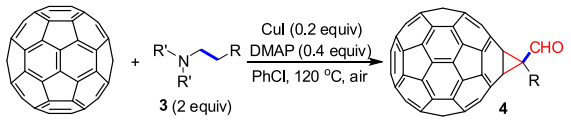
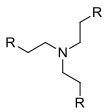
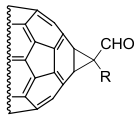
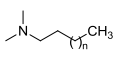
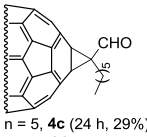
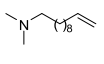
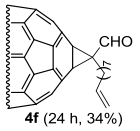
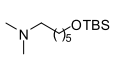
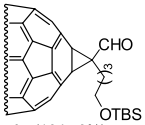
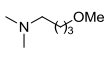
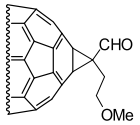
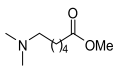
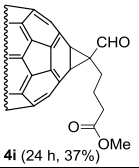
Scheme 2. Reaction of *N*-Methyl-4-piperidinemethanol with C_{60}



Encouraged by the exciting results, we next turned our attention to acyclic tertiary amines (Table 3). First, the tri(*n*-propyl)amine **3a** and tri(*n*-butyl)amine **3b** were tested. Surprisingly, no methanofullerne product bearing an amide group was formed. Instead, fullerenoalkanals **4a** and **4b** were obtained in 47 and 44% yield, respectively. Other tertiary amines **3c**–**e** with different lengths of alkyl chains could also provide corresponding fullerenoalkanals **4c**–**e** in acceptable yields. Vinyl, alkoxyl, OTBS, and ester groups were well tolerated in the reaction, albeit the **4g** was isolated in a very low yield (9%).

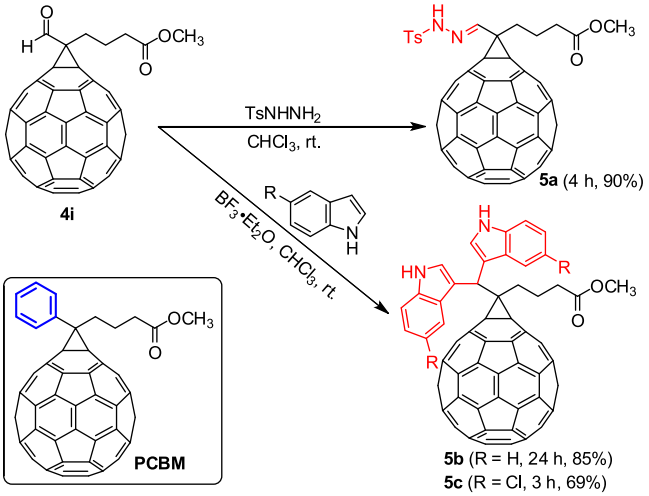
Table 3. CuI-Catalyzed Reaction of Acyclic Tertiary Amines with C_{60}



substrate	products	substrate	product
	 R = Me, **4a** (24 h, 47%) R = Et, **4b** (24 h, 44%)		 n = 5, **4c** (24 h, 29%) n = 7, **4d** (24 h, 27%) n = 9, **4e** (24 h, 26%)
	 **4f** (24 h, 34%)		 **4g** (40 h, 9%)
	 **4h** (24 h, 21%)		 **4i** (24 h, 37%)

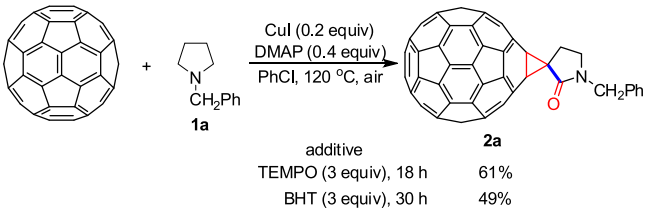
It was noteworthy that the reaction of C_{60} with methyl 5-(dimethylamino)pentanoate **3i** gave 37% yield of **4i**. The compound **4i** had a structural similarity to PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester), which had been identified as the most representative electron acceptor material frequently used in organic photovoltaic devices (OPVs).[19] In addition, the existence of a formyl group made it easily transformable to various PCBM analogues. The reaction of **4i** with tosylhydrazide gave **5a** in 90% yield. Also, the $BF_3{\cdot}Et_2O$-catalyzed reaction of **4i** with indole or 5-chloroindole furnished **5b** or **5c** in 85 or 69% yield, respectively. These PCBM analogues might show potential use in OPVs (Scheme 3).

Scheme 3. Transformation of 4i to PCBM Analogues



In a previously reported copper-catalyzed regioselective *β*-functionalization of tertiary amines with thiophenols by Pan's group, a radical cation mechanism was proposed based on the radical-trapping experiments.[6] We speculated that the formation of **2** and **4** underwent a similar reaction pathway. However, when 3 equiv of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or BHT (2,6-ditertbutyl-4-methylphenol) as a radical inhibitor was added to the standard reaction of C_{60} with **1a**, no obvious inhibition effect was observed, which was opposed to the radical mechanism (Scheme 4). The TEMPO had no influence on the reaction and the addition of BHT resulted in a longer reaction time and a slightly lower yield. At present, the exact mechanism is still unclear. A similar reaction mechanism as reported in our previous work involving enamines as the key intermediate also could not be ruled out.[15e] However, surely an imine cation intermediate **6** or **9** must be involved in the reaction. For the cyclic tertiary amine, the generated intermediate **6** underwent addition with H_2O and subsequent oxidation with Cu(II) to afford **3**. In the case

Scheme 4. Free Radical Capture Experiments



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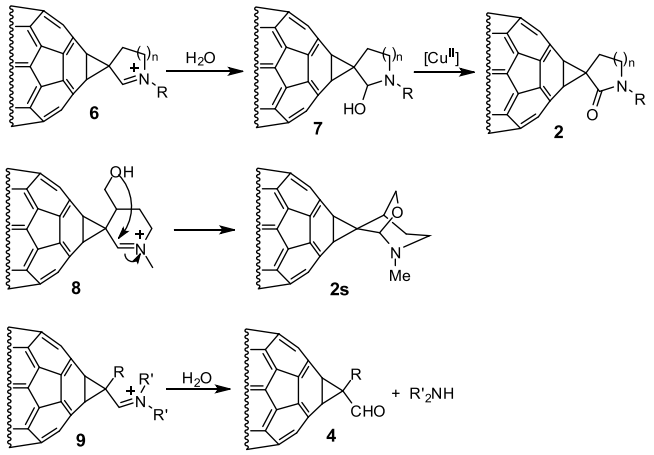
of acyclic tertiary amines, hydrolysis of the intermediate **9** furnished fullerenoalkanal **4** (Scheme 5). The formation of **2s** also proved the existence of **6**.

Scheme 5. Plausible Intermediate



CONCLUSIONS

In summary, a unique α,β-difunctionalization of tertiary amines via CuI-catalyzed reaction with C_{60} is disclosed. Aerobic oxygen is used as the only external oxidant and DMAP ligand addition is found to be crucial to the reaction. The cyclic and acyclic tertiary amines show different reactivities and afford selectively the spiro-linked methanofullerenes bearing cyclic amides and fullerenoalkanals, respectively. To the best of our knowledge, this is perhaps the simplest and most convenient method to access these two kinds of organofullerenes. It is in sharp contrast to the previously reported photoreactions or thermal reactions of C_{60}, which afford the fulleropyrrolidines or cyclopentane-fused fullerene derivatives.[20] The abundance of commercially available tertiary amines further shows the practical synthetic value of this approach. Furthermore, four potential PCBM types of OPV candidates were prepared through the developed method.

EXPERIMENTAL SECTION

General Information. ^{1}H and ^{13}C NMR (proton broadband decoupling) spectra were recorded on a 400/500 MHz (100/125 MHz for ^{13}C NMR) spectrometer at ambient temperature, using tetramethylsilane as an internal standard. Flash column chromatography was performed over silica gel (200−300 mesh). High-resolution mass spectrometry (HRMS) for those non-fullerene products was performed on a Thermo Scientific LTQ Orbitrap XL equipped with an ESI source (positive mode). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) for organofullerenes was performed in a positive ion mode using DCTB E-(2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix. UV−vis spectra were recorded on a Shimadzu UV-2401 spectrometer with $CHCl_3$ as the solvent.

Starting materials **1a**, **1e**, **1n**, **1q**, **3b**, **3h**, **3i**,[21] **1b**, **1c**, **1i**, **1l**, **3f**,[22] **1f**, **1g**,[23] **1h**,[24] and **1m**[25] were prepared according to the reported procedures.

Preparation of 1d (Scheme S1a). Step 1: A mixture of 4-hydroxybenzaldehyde (1.22 g, 10 mmol), *tert*-butyldimethylsilyl chloride (1.50 g, 10 mmol), and imidazole (884 mg, 13 mmol) in methylene dichloride (15 mL) was stirred at room temperature for 12 h. After completion of the reaction, an aqueous solution of sodium hydroxide (10 mL × 2 mol/L) and water (30 mL) was added, and the mixture was extracted with methylene dichloride (3 × 25 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography with ethyl acetate/petroleum ether (1:6) as the eluent to give the product 4-OTBS-benzaldehyde. Step 2: A mixture of 4-OTBS-benzaldehyde (1.89 g, 8 mmol), pyrrolidine (1.32 mL, 16 mmol), and sodium triacetoxyborohydride (2.54 g, 12 mmol) in 1,2-dichloroethane (15 mL) was stirred at room temperature under a nitrogen atmosphere for 4 h. Water (40 mL) was added, and the mixture was extracted with methylene dichloride (3 × 25 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 (30:1) as the eluent to give the 1d (0.82 g, 35%, pale yellow liquid).

1d: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 3.53 (s, 2H), 2.44−2.53 (m, 4H), 1.72−1.82 (m, 4H), 0.98 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.7, 132.1, 130.2, 119.9, 60.3, 54.2, 25.8, 23.5, 18.3, −4.3; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{30}NOSi$, 292.2097; found, 292.2088.

Preparation of 1j (Scheme S1b). Step 1: A mixture of 2-bromoethanol (0.71 mL, 10 mmol), *tert*-butyldimethylsilyl chloride (1.50 g, 10 mmol), and imidazole (884 mg, 13 mmol) in methylene dichloride (15 mL) was stirred under a N_2 atmosphere at room temperature for 12 h. Water (50 mL) was added, and the mixture was extracted with methylene dichloride (3 × 25 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography with ethyl acetate/petroleum ether (1:3) as the eluent to give the product 2-bromoethoxy(*tert*-butyl)dimethylsilane. Step 2: A mixture of 2-bromoethoxy(*tert*-butyl)dimethylsilane (1.90 g, 8 mmol), pyrrolidine (0.99 mL, 12 mmol), and K_2CO_3 (1.1 g, 8 mmol) in acetonitrile (15 mL) was stirred at room temperature for 4 h; water (50 mL) was added and the mixture was extracted with methylene dichloride (3 × 25 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 (15:1) as the eluent to give the **1j** (1.21 g, 66%, pale yellow liquid).

1j: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75 (t, J = 6.8 Hz, 2H), 2.61 (t, J = 6.8 Hz, 2H), 2.52−2.57 (m, 4H), 1.73−1.78 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.7, 58.5, 55.0, 26.1, 25.8, 23.6, 18.446, −5.2; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{12}H_{28}NOSi$, 230.1940; found, 230.1934.

Preparation of 1k[26] (Scheme S1c). A mixture of *N*-(2-aminoethyl)pyrrolidine (0.48 mL, 4 mmol) and $(Boc)_2O$ (0.92 mL, 4 mmol) in tetrahydrofuran (15 mL) was stirred at room temperature for 10 h. Water (40 mL) was added and the mixture was extracted with methylene dichloride (3 × 25 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography with ethyl acetate/petroleum ether (1:2) with CH_2Cl_2/MeOH (15:1) as the eluent to give the product **1k** (0.67 g, 78%, pale yellow liquid).

1k: ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.08 (s, 1H), 3.23 (dd, J = 5.8, 11.5 Hz, 2H), 2.56 (t, J = 7.0 Hz, 2H), 2.48−2.52 (m, 4H), 2.07 (s, 2H), 1.74−1.78 (m, 4H), 1.43 (s, 9H).

Preparation of 3g (Scheme S1d). Step 1: A mixture of 6-chloro-1-hexanol (1.3 mL, 10 mmol), *tert*-butyldimethylsilyl chloride (1.5 g, 10 mmol), and imidazole (884 mg, 13 mmol) in methylene dichloride(15 mL) was stirred at room temperature for 12 h. Water (40 mL) was added, and the mixture was extracted with methylene dichloride (3 × 25 mL). The combined organic layers were dried with anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography with ethyl acetate/petroleum ether = 1/6 as the eluent to give the TBS protected 6-chloro-1-hexanol. Step 2: A mixture of the TBS protected 6-chloro-1-hexanol (2.00 g, 8 mmol), aqueous solution of dimethylamine (40%, 2.75 mL, 16 mmol), and potassium carbonate (1.10 g, 8 mmol) in acetonitrile (15 mL) was stirred at room temperature for 4 h; water (50 mL) was added, and the mixture was extracted with methylene dichloride (3 × 25 mL). The combined organic layers were dried with

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anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was purified by column chromatography with CH_2Cl_2/MeOH (15:1) as the eluent to give the **3g** (1.41 g, 68%, pale yellow liquid).

3g: ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (t, J = 6.2 Hz, 2H), 2.84 (t, J = 8.1 Hz, 2H), 2.24 (t, J = 7.4 Hz, 2H), 2.21 (s, 6H), 1.40−1.59 (m, 4H), 1.22−1.40 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.3, 59.9, 45.5, 32.9, 27.8, 27.4, 26.0, 25.9, 18.4, −5.2; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{34}NOSi$, 260.2410; found, 260.2402.

General Procedure for the CuI-Catalyzed Reaction of C_{60} with Tertiary Amines. A mixture of C_{60} (36.0 mg, 0.05 mmol), tertiary amines (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) at 120 °C for a given time (for **1a**−**n**, **1p**, and **1s**, under open air; for **1o** and **1q**, under an O_2 atmosphere). The solvent was removed in vacuo and the residue was purified on a silica gel column with CS_2−CS_2/toluene−toluene/EA as the eluent (gradient elution) to give unreacted C_{60} and products **2a**−**o**, **2q**, **2s**, and **4a**−**i**.

2a[15e] (brown solid, 28.6 mg, 64%): ^{1}H NMR (400 MHz, CS_2−$CDCl_3$): δ 7.32−7.46 (m, 5H), 4.74 (s, 2H), 3.76 (t, J = 7.1 Hz, 2H), 3.23 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$): δ 168.21, 146.63, 145.46, 145.34, 145.31, 145.15, 145.08, 145.04, 145.02, 144.94, 144.69, 144.51, 144.49, 144.45, 144.05, 143.99, 143.56, 143.52, 143.09, 143.00, 142.94, 142.70, 142.27, 142.12, 142.08, 141.97, 141.91, 141.14, 141.00, 140.94, 137.18, 135.77, 129.04, 128.67, 128.13, 76.22 (sp^3-C of C_{60}), 47.82, 44.19, 43.24, 24.99.

2b (Brown solid, 21.2 mg, 46%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$): δ 7.37 (d, J = 7.9 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 4.69 (s, 2H), 3.84 (s, 3H), 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 168.05, 159.40, 146.66, 145.51, 145.33, 145.31, 145.13, 145.07, 145.02, 144.99, 144.92, 144.67, 144.49, 144.46, 144.45, 144.43, 144.03, 143.97, 143.55, 143.50, 143.08, 142.98, 142.93, 142.69, 142.25, 142.07, 141.96, 141.90, 141.11, 140.97, 140.91, 137.16, 130.02, 127.77, 114.35, 76.27 (sp^3-C of C_{60}), 55.10, 47.21, 44.33, 43.09, 24.96; UV−vis ($CHCl_3$): λ_{max}/nm 260, 328, 429, 496, 687; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{72}H_{13}NO_2$, 923.0946; found, 923.0935.

2c (brown solid, 28.1 mg, 59%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$): δ 8.10 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 4.81 (s, 2H), 3.94 (s, 3H), 3.80 (t, J = 7.1 Hz, 2H), 3.28 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$): δ 168.70, 166.40, 146.55, 145.39, 145.34, 145.20, 145.10, 145.07, 145.00, 144.74, 144.57, 144.55, 144.52, 144.49, 144.13, 144.03, 143.61, 143.55, 143.14, 143.06, 143.00, 142.76, 142.30, 142.13, 142.01, 141.95, 141.19, 141.06, 140.91, 140.89, 137.26, 130.39, 130.03, 128.53, 76.10 (sp^3-C of C_{60}), 52.13, 47.57, 43.97, 43.43, 24.99; UV−vis ($CHCl_3$): λ_{max}/nm 259, 327, 429, 495, 688; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{73}H_{13}NO_3$, 951.0895; found, 951.0891.

2d (brown solid, 31.2 mg, 61%, mp > 300 °C): ^{1}H NMR (500 MHz, CS_2−$CDCl_3$): δ 7.27 (d, J = 8.3 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.64 (s, 2H), 3.73 (t, J = 7.2 Hz, 2H), 3.20 (t, J = 7.1 Hz, 2H), 0.98 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$): δ 167.92, 155.45, 146.65, 145.49, 145.31, 145.28, 145.09, 145.04, 144.98, 144.96, 144.88, 144.63, 144.45, 144.43, 144.39, 143.99, 143.94, 143.52, 143.47, 143.04, 142.95, 142.89, 142.65, 142.22, 142.04, 141.91, 141.87, 141.08, 140.92, 137.13, 129.91, 128.38, 120.45, 76.27 (sp^3-C of C_{60}), 47.22, 44.30, 43.10, 25.68, 24.95, 18.13, −4.31; UV−vis ($CHCl_3$): λ_{max}/nm 260, 328, 429, 497, 688; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{77}H_{25}NO_2Si$, 1023.1655; found, 1023.1655.

2e (brown solid, 24.5 mg, 57%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$): δ 3.88 (t, J = 7.1 Hz, 2H), 3.58 (t, J = 7.5 Hz, 2H), 3.27 (t, J = 7.1 Hz, 2H), 1.75 (quint, J = 7.1 Hz, 2H), 1.51 (sext, J = 7.5 Hz, 2H), 1.05 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$): δ 168.19, 146.79, 145.61, 145.41, 145.36, 145.18, 145.14, 145.07, 145.04, 144.96, 144.73, 144.54, 144.51, 144.48, 144.05, 144.03, 143.60, 143.57, 143.11, 143.03, 142.98, 142.72, 142.31, 142.12, 142.01, 141.97, 141.17, 141.00, 137.18, 76.38 (sp^3-C of C_{60}), 44.43, 43.84, 43.66, 29.69, 25.19, 20.61, 14.07; UV−vis ($CHCl_3$): λ_{max}/nm 260, 328, 429, 493, 687; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{68}H_{13}NO$, 859.0997; found, 859.0979.

2f (brown solid, 24.0 mg, 54%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$): δ 3.99 (t, J = 7.1 Hz, 2H), 3.88 (t, J = 6.6 Hz, 2H), 3.77 (s, 3H), 3.28 (t, J = 7.1 Hz, 2H), 2.84 (t, J = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$): δ 171.75, 168.54, 146.56, 145.37, 145.30, 145.24, 145.11, 145.01, 144.97, 144.91, 144.65, 144.46, 144.42, 144.00, 143.95, 143.53, 143.48, 143.05, 142.97, 142.91, 142.67, 142.22, 142.05, 141.89, 141.12, 140.95, 140.83, 137.16, 76.11 (sp^3-C of C_{60}), 51.81, 44.73, 43.94, 39.87, 32.51, 25.27; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{68}H_{11}NO_3$, 889.0739; found, 889.0727.

2g (brown solid, 24.0 mg, 56%, mp > 300 °C; the pure **2g** has a very poor solubility in CS_2 or 1,2-dichlorobenzene. The ^{1}H NMR spectrum was obtained from the reaction mixture without purification): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$): δ 4.13 (t, J = 7.1 Hz, 2H), 3.90 (t, J = 6.4 Hz, 2H), 3.31 (t, J = 7.1 Hz, 2H), 2.90 (t, J = 6.3 Hz, 2H); HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{67}H_8N_2O$, 856.0637; found, 856.0628.

2h (brown solid, 23.4 mg, 50%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$): δ 7.26 (t, J = 8.0 Hz, 2H), 6.87−6.97 (m, 3H), 4.17 (t, J = 5.9 Hz, 2H), 3.96 (t, J = 7.0 Hz, 2H), 3.82 (t, J = 7.0 Hz, 2H), 3.28 (t, J = 7.0 Hz, 2H), 2.30 (quint, J = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, CS_2−C_6D_6): δ 168.58, 158.57, 146.66, 145.49, 145.36, 145.32, 145.14, 145.06, 145.03, 144.99, 144.92, 144.67, 144.50, 144.47, 144.43, 144.01, 143.98, 143.56, 143.49, 143.07, 142.99, 142.93, 142.68, 142.25, 142.08, 141.92, 141.09, 140.92, 140.89, 140.85, 137.17, 129.58, 121.03, 114.44, 76.23 (sp^3-C of C_{60}), 65.45, 44.28, 44.23, 41.46, 27.51, 25.18; UV−vis ($CHCl_3$): λ_{max}/nm 261, 328, 429, 495, 688; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{73}H_{15}NO_2$, 937.1103; found, 937.1099.

2i (brown solid, 19.1 mg, 40%, mp > 300 °C): ^{1}H NMR (400 MHz, CS_2−$CDCl_3$): δ 5.79 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 4.99 (dq, J = 17.0, 1.4 Hz, 1H), 4.93 (d, J = 10.3 Hz, 1H), 3.90 (t, J = 7.0 Hz, 2H), 3.59 (t, J = 7.5 Hz, 2H), 3.29 (t, J = 7.0 Hz, 2H), 2.05 (q, J = 7.0 Hz, 2H), 1.78 (quint, J = 7.4 Hz, 2H), 1.28−1.54 (m, 12H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$): δ 168.19, 146.75, 145.58, 145.37, 145.32, 145.14, 145.09, 145.03, 145.00, 144.93, 144.69, 144.51, 144.48, 144.44, 144.01, 143.99, 143.57, 143.53, 143.08, 142.99, 142.94, 142.69, 142.27, 142.08, 141.96, 141.93, 141.13, 140.96, 140.93, 138.93, 137.15, 114.32, 76.32 (sp^3-C of C_{60}), 44.41, 43.89, 43.80, 34.02, 29.78, 29.69, 29.58, 29.36, 29.16, 27.60, 27.27, 25.12; UV−vis ($CHCl_3$): λ_{max}/nm 259, 331, 429, 494, 687; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{75}H_{25}NO$, 955.1936; found, 955.1922.

2j (brown solid, 8.7 mg, 18%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$): δ 4.06 (t, J = 7.1 Hz, 2H), 3.99 (t, J = 5.2 Hz, 2H), 3.71 (t, J = 5.2 Hz, 2H), 3.28 (t, J = 7.1 Hz, 2H), 0.98 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$): δ 168.62, 146.79, 145.65, 145.39, 145.16, 145.09, 145.05, 145.01, 144.95, 144.69, 144.54, 144.49, 144.46, 144.03, 144.00, 143.59, 143.52, 143.09, 143.00, 142.96, 142.72, 142.27, 142.10, 141.99, 141.96, 141.15, 140.97, 140.83, 137.21, 76.33 (sp^3-C of C_{60}), 61.74, 46.51, 45.79, 44.31, 25.98, 25.35, 18.24, −5.18; UV−vis ($CHCl_3$): λ_{max}/nm 258, 328, 429, 493, 689; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{72}H_{23}NO_2Si$, 961.1498; found, 961.1487.

2k (brown solid, 7.6 mg, 16%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$−DMSO-d_6): δ 6.31 (t, J = 5.3 Hz, 1H), 3.93 (t, J = 7.0 Hz, 2H), 3.60 (t, J = 6.8 Hz, 2H), 3.39 (q, J = 5.7 Hz, 2H), 3.22 (t, J = 7.0 Hz, 2H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$−DMSO-d_6): δ 167.32, 155.12, 146.22, 145.09, 144.54, 144.50, 144.15, 144.08, 144.01, 143.99, 143.69, 143.67, 143.59, 143.47, 143.46, 143.04, 143.02, 142.66, 142.52, 142.14, 142.06, 142.01, 141.98, 141.79, 141.31, 141.20, 141.11, 140.82, 140.18, 140.02, 139.89, 136.27, 75.85 (sp^3-C of C_{60}), 43.89, 43.12, 43.07, 37.22, 27.68, 24.41; UV−vis ($CHCl_3$): λ_{max}/nm 260, 328, 429, 493, 687; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{71}H_{18}N_2O_3$, 946.1317; found, 946.1311.

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2l (brown solid, 4.9 mg, 11%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 7.33 (dd, J = 5.1, 1.2 Hz, 1H), 7.16 (dd, J = 3.5, 1.2 Hz, 1H), 7.05 (dd, J = 5.1, 3.5 Hz, 1H), 4.94 (s, 2H), 3.88 (t, J = 7.1 Hz, 2H), 3.27 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 167.91, 146.55, 145.38, 145.33, 145.28, 145.14, 145.06, 145.03, 145.01, 144.93, 144.68, 144.49, 144.45, 144.05, 143.98, 143.55, 143.51, 143.08, 142.99, 142.93, 142.69, 142.26, 142.07, 141.95, 141.90, 141.13, 140.99, 140.91, 137.84, 137.18, 127.61, 127.26, 126.14, 76.10 (sp^3-C of C_{60}), 44.06, 43.13, 41.97, 24.97; UV–vis ($CHCl_3$): λ_{max}/nm 260, 328, 429, 495, 689; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{69}H_9NOS$, 899.0405; found, 899.0405.

2m (brown solid, 27.7 mg, 61%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 7.24–7.40 (m, 5H), 4.81 (s, 2H), 3.68 (t, J = 6.3 Hz, 2H), 2.99–3.07 (m, 2H), 2.30–2.41 (m, 2H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 164.88, 147.20, 146.41, 145.43, 145.21, 145.08, 145.04, 144.99, 144.88, 144.68, 144.50, 144.47, 144.44, 143.98, 143.51, 143.37, 143.06, 142.96, 142.93, 142.84, 142.52, 142.22, 142.00, 141.72, 141.62, 141.16, 140.88, 140.58, 137.78, 136.69, 128.82, 128.35, 127.75, 76.56 (sp^3-C of C_{60}), 50.98, 47.32, 44.94, 25.26, 22.39; UV–vis ($CHCl_3$): λ_{max}/nm 259, 328, 429, 495, 688; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{72}H_{13}NO$, 907.0997; found, 907.0989.

2n[15e] (brown solid, 16.2 mg, 37%): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 3.80 (t, J = 6.3 Hz, 2H), 3.61 (t, J = 7.6 Hz, 2H), 2.94–3.10 (m, 2H), 2.33–2.50 (m, 2H), 1.65–1.82 (m, 2H), 1.35–1.54 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 164.61, 147.36, 146.55, 145.48, 145.27, 145.11, 145.06, 144.99, 144.90, 144.71, 144.55, 144.47, 144.46, 144.00, 143.95, 143.54, 143.40, 143.08, 142.99, 142.95, 142.86, 142.54, 142.25, 142.03, 141.78, 141.66, 141.08, 140.89, 140.58, 137.78, 76.66 (sp^3-C of C_{60}), 48.16, 48.03, 44.98, 29.58, 25.28, 22.54, 20.62, 14.20.

2o (brown solid, 3.6 mg, 8%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 4.36 (q, J = 7.1 Hz, 2H), 4.25 (t, J = 4.0 Hz, 1H), 3.62–3.84 (m, 2H), 3.18 (s, 3H), 2.62–2.82 (m, 2H), 1.36 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 170.62, 163.86, 148.63, 147.73, 145.35, 145.28, 145.26, 145.24, 145.18, 145.16, 145.14, 145.11, 145.07, 145.02, 144.90, 144.86, 144.83, 144.71, 144.65, 144.58, 144.52, 144.45, 144.40, 144.24, 144.16, 143.96, 143.67, 143.52, 143.44, 143.39, 143.10, 143.04, 143.00, 142.97, 142.91, 142.85, 142.56, 142.44, 142.32, 142.21, 142.17, 141.93, 141.88, 141.69, 141.65, 141.58, 141.03, 140.96, 140.92, 140.70, 140.62, 138.06, 136.83, 75.81 (sp^3-C of C_{60}), 75.10 (sp^3-C of C_{60}), 61.88, 47.24, 44.71, 41.02, 35.40, 24.59, 14.53; UV–vis ($CHCl_3$): λ_{max}/nm 259, 328, 428, 492, 688; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{69}H_{13}NO_3$, 903.0895; found, 903.0887.

2q (brown solid, 5.5 mg, 12%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 7.37–7.48 (m, 5H), 4.91 (s, 2H), 4.50 (t, J = 5.3 Hz, 2H), 3.80 (t, J = 5.3 Hz, 2H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 162.71, 145.49, 145.37, 145.16, 145.13, 145.00, 144.99, 144.68, 144.58, 144.56, 144.23, 144.13, 144.01, 143.74, 143.41, 143.05, 143.03, 142.91, 142.89, 142.33, 142.17, 142.15, 141.84, 141.16, 141.10, 140.78, 140.75, 138.71, 135.69, 129.11, 128.72, 128.24, 77.07 (sp^3-C of C_{60}), 72.35, 64.66, 50.46, 46.36; UV–vis ($CHCl_3$): λ_{max}/nm 259, 328, 430, 491, 684; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{71}H_{11}NO_2$, 909.0790; found, 909.0790.

2s (brown solid, 9.7 mg, 23%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 5.31 (s, 1H), 4.58 (ddd, J = 8.1, 4.5, 2.0 Hz, 1H), 4.32 (d, J = 8.1 Hz, 1H), 3.36 (td, J = 4.2, 2.0 Hz, 1H), 3.10 (dd, J = 11.4, 5.7 Hz, 1H), 2.93 (td, J = 11.9, 4.9 Hz, 1H), 2.59–2.71 (m, 1H), 2.60 (s, 3H), 2.06 (dt, J = 13.4, 4.1 Hz, 1H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 148.87, 147.72, 146.14, 145.71, 145.66, 145.55, 145.46, 145.35, 145.04, 144.97, 144.91, 144.72, 144.68, 144.62, 144.59, 144.57, 144.22, 144.12, 144.08, 144.04, 143.52, 143.44, 143.22, 143.18, 143.05, 142.98, 142.91, 142.54, 142.26, 142.23, 142.19, 142.13, 141.17, 141.08, 141.06, 141.01, 137.50, 137.27, 136.90, 136.29, 92.17, 80.70 (sp^3-C of C_{60}), 78.21 (sp^3-C of C_{60}), 70.54, 55.17, 46.82, 42.87, 36.38, 28.04; UV–vis ($CHCl_3$): λ_{max}/nm 261, 327, 429, 494, 686; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{67}H_{11}NO$, 845.0841; found, 845.0841.

4a[16] (brown solid, 18.2 mg, 47%): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 10.60 (s, 1H), 2.36 (s, 3H).

4b[15b] (brown solid, 17.4 mg, 44%): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 10.59 (s, 1H), 2.88 (q, J = 7.2 Hz, 2H), 1.55 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$): δ 193.80, 146.81, 145.85, 145.36, 145.34, 145.27, 145.25, 145.08, 144.81, 144.75, 144.74, 144.72, 144.69, 144.52, 143.86, 143.80, 143.30, 143.19, 143.13, 143.06, 143.05, 142.17, 142.09, 142.07, 141.66, 141.24, 141.16, 138.12, 137.93, 75.31 (sp^3-C of C_{60}), 51.09, 19.51, 12.29.

4c (brown solid, 12.3 mg, 29%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 10.58 (s, 1H), 2.81 (t, J = 8.2 Hz, 2H), 1.88–2.03 (m, 2H), 1.61 (quint, J = 7.3 Hz, 2H), 1.37–1.52 (m, 4H), 0.97 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 194.20, 146.97, 145.94, 145.39, 145.38, 145.30, 145.28, 145.11, 144.84, 144.79, 144.76, 144.75, 144.72, 144.55, 143.91, 143.84, 143.33, 143.22, 143.16, 143.09, 143.07, 142.20, 142.12, 141.71, 141.25, 141.19, 138.11, 137.97, 75.33 (sp^3-C of C_{60}), 50.39, 31.90, 29.93, 27.85, 26.06, 22.98, 14.35; UV–vis ($CHCl_3$): λ_{max}/nm 260, 327, 429, 493, 689; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{68}H_{14}O$, 846.1045; found, 846.1040.

4d (brown solid, 11.8 mg, 27%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 10.57 (s, 1H), 2.81 (t, J = 8.0 Hz, 2H), 1.83–2.07 (m, 2H), 1.54–1.72 (m, 2H), 1.19–1.43 (m, 8H), 0.93 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 193.85, 146.91, 145.87, 145.33, 145.24, 145.23, 145.06, 144.78, 144.73, 144.70, 144.66, 144.50, 143.85, 143.78, 143.28, 143.17, 143.11, 143.03, 143.01, 142.15, 142.06, 141.65, 141.21, 141.14, 138.04, 137.91, 75.28 (sp^3-C of C_{60}), 50.32, 32.13, 30.25, 29.71, 29.56, 27.85, 26.01, 23.07, 14.42; UV–vis ($CHCl_3$): λ_{max}/nm 259, 328, 429, 498, 691; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{70}H_{18}O$, 874.1358; found, 874.1344.

4e (brown solid, 11.7 mg, 26%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 10.57 (s, 1H), 2.81 (t, J = 8.0 Hz, 2H), 1.95 (quint, J = 7.7 Hz, 2H), 1.61 (quint, J = 7.2 Hz, 2H), 1.22–1.53 (m, 12H), 0.92 (t, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, CS_2–$CDCl_3$): δ 193.95, 146.95, 145.91, 145.37, 145.28, 145.26, 145.09, 144.82, 144.79, 144.77, 144.74, 144.69, 144.53, 143.89, 143.82, 143.32, 143.20, 143.15, 143.08, 143.07, 143.05, 142.19, 142.10, 141.69, 141.24, 141.17, 138.08, 137.95, 75.33 (sp^3-C of C_{60}), 50.38, 32.17, 30.24, 29.90, 29.89, 29.75, 29.65, 27.86, 26.04, 23.06, 14.41; UV–vis ($CHCl_3$): λ_{max}/nm 260, 327, 429, 492, 689; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{72}H_{22}O$, 902.1671; found, 902.1665.

4f (brown solid, 15.1 mg, 34%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 10.58 (s, 1H), 5.82 (ddt, J = 17.0, 10.3, 6.6 Hz, 1H), 5.01 (J = 17.1, 1.7 Hz, 1H), 4.94 (ddt, J = 10.2, 2.2, 1.2 Hz, 1H), 2.81 (t, J = 8.1 Hz, 2H), 2.08 (t, J = 6.6 Hz, 2H), 1.88–2.02 (m, 2H), 1.54–1.67 (m, 2H), 1.33–1.50 (m, 6H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 194.35, 146.99, 145.96, 145.42, 145.33, 145.31, 145.13, 144.87, 144.82, 144.79, 144.77, 144.73, 144.57, 143.93, 143.86, 143.36, 143.25, 143.19, 143.11, 143.10, 143.09, 142.22, 142.15, 141.74, 141.27, 141.21, 138.98, 138.13, 138.00, 114.43, 75.35 (sp^3-C of C_{60}), 50.40, 34.00, 30.15, 29.55, 29.30, 29.14, 27.83, 26.04; UV–vis ($CHCl_3$): λ_{max}/nm 259, 327, 429, 489, 689; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{71}H_{18}O$, 886.1358; found, 886.1355.

4g (brown solid, 4.3 mg, 9%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 10.59 (s, 1H), 3.76 (t, J = 6.2 Hz, 2H), 2.84 (t, J = 8.1 Hz, 2H), 1.96–2.10 (m, 2H), 1.75–1.88 (m, 2H), 0.90 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 194.52, 147.02, 145.99, 145.47, 145.38, 145.36, 145.18, 144.92, 144.86, 144.82, 144.78, 144.63, 143.98, 143.92, 143.40, 143.30, 143.23, 143.16, 143.14, 142.27, 142.22, 142.19, 141.78, 141.31, 141.26, 138.20, 138.06, 75.35 (sp^3-C of C_{60}), 62.75, 50.44, 33.29, 26.07, 25.95, 24.35, 18.39, −5.08; UV–vis ($CHCl_3$): λ_{max}/nm 259, 327, 429, 485, 688; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{72}H_{24}O_2Si$, 948.1546; found, 948.1538.

4h (brown solid, 8.6 mg, 21%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2–$CDCl_3$): δ 10.49 (s, 1H), 3.99 (t, J = 6.2 Hz, 2H), 3.51 (s, 3H), 3.17 (t, J = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, CS_2–$CDCl_3$): δ 193.68, 146.71, 146.00, 145.42, 145.32, 145.20, 144.89, 144.87, 144.81, 144.76, 144.74, 144.57, 143.97, 143.84, 143.36, 143.28,

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143.25, 143.14, 143.06, 142.28, 142.19, 142.17, 141.81, 141.27, 141.24, 138.22, 138.08, 75.00 (sp^3-C of C_{60}), 70.32, 59.21, 48.93, 27.33; UV−vis ($CHCl_3$): λ_{max}/nm 259, 327, 429, 486, 687; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{65}H_8O_2$, 820.0524; found, 820.0520.

4i (brown solid, 15.9 mg, 37%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$): δ 10.60 (s, 1H), 3.73 (s, 3H), 2.80−2.92 (m, 2H), 2.64 (t, J = 7.4 Hz, 2H), 2.22−2.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.88, 173.52, 146.85, 145.87, 145.57, 145.54, 145.49, 145.47, 145.46, 145.20, 145.00, 144.94, 144.90, 144.81, 144.73, 144.05, 143.99, 143.48, 143.36, 143.30, 143.23, 143.21, 142.32, 142.24, 141.82, 141.40, 141.33, 138.30, 138.15, 75.06 (sp^3-C of C_{60}), 51.93, 49.58, 34.18, 25.40, 23.02; UV−vis ($CHCl_3$): λ_{max}/nm 260, 328, 429, 496, 692; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{67}H_{10}O_3$, 862.0630; found, 862.0630.

Reaction of 4i with 4-Methylbenzenesulfonhydrazide for the Synthesis of 5a. A mixture of **4i** (10 mg, 0.0125 mmol) and 4-methylbenzenesulfonhydrazide (37.2 mg, 0.2 mmol) in chloroform (10 mL) was stirred at room temperature for 4 h. Upon completion of the reaction determined by TLC, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography with toluene/ethyl acetate (5:1) as the eluent to give the product **5a** (11.6 mg, 90%).

5a (brown solid, 11.6 mg, 90%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2-DMSO-d_6): δ 11.52 (s, 1H), 8.16 (s, 1H), 7.77 (d, J = 7.6 Hz, 2H), 7.54 (s, 1H), 3.69 (s, 3H), 2.40−2.54 (m, 6H), 2.11−2.13 (m, 3H); ^{13}C NMR (125 MHz, CS_2−$CDCl_3$−DMSO-d_6); δ 171.76, 146.68, 146.35, 144.63, 144.52, 144.30, 144.12, 143.87, 143.80, 143.63, 143.57, 143.55, 143.16, 142.83, 142.18, 142.10, 142.03, 141.60 (br), 141.21, 140.96, 140.12, 139.91, 137.07, 136.23, 135.50, 128.74, 127.02 (br), 76.70 (sp^3-C of C_{60}), 50.51, 44.53, 32.94, 27.47, 21.66, 20.86; UV−vis ($CHCl_3$): λ_{max}/nm 259, 328, 431; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{74}H_{18}N_2O_4S$, 1030.0987; found, 1030.0985.

General Procedure for the Reaction of 4i with Indole and 5-Chloroindole. A mixture of **4i** (10 mg, 0.0125 mmol), indole (0.1 mmol), and BF_3·Et_2O (15 μL, 0.125 mmol) in chloroform (10 mL) was stirred at room temperature for 4 h. Upon completion of the reaction determined by TLC, diethyl amine (0.5 mL) was added slowly under stirring, and then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography with toluene/ethyl acetate (5:1) as the eluent to give the products 5b (11.5 mg, 85%) or 5c (9.9 mg, 69%).

5b (brown solid, 11.5 mg, 85%, mp > 300 °C): ^{1}H NMR (300 MHz, CS_2−$CDCl_3$−DMSO-d_6): δ 9.94 (s, 2H), 7.35 (s, 2H), 7.22−7.31 (m, 4H), 6.97 (t, J = 7.4 Hz, 2H), 6.77 (t, J = 7.2 Hz, 2H), 6.05 (s, 1H), 3.45 (s, 3H), 2.88 (t, J = 7.8 Hz, 2H), 1.92 (t, J = 6.9 Hz, 2H), 1.36−1.52 (m, 2H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$−DMSO-d_6): δ 172.17, 148.93, 148.19, 145.12, 145.01, 144.69, 144.59, 144.55, 144.17, 143.95, 143.74, 143.62, 143.28, 143.19, 142.60, 142.48, 142.45, 142.37, 142.34, 141.84, 141.70, 141.57, 140.41, 140.34, 136.88, 136.26, 126.97, 123.39, 121.23, 119.69, 118.63, 115.59, 111.12, 80.56 (sp^3-C of C_{60}), 50.60, 49.64, 35.98, 34.01, 29.31, 23.86; UV−vis ($CHCl_3$): λ_{max}/nm 260, 327, 431, 689; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{83}H_{22}N_2O_2$, 1078.1681; found, 1078.1677.

5c (brown solid, 9.9 mg, 69%, mp > 300 °C): ^{1}H NMR (400 MHz, CS_2−$CDCl_3$): δ 8.34 (s, 2H), 7.54 (d, J = 1.9 Hz, 2H), 7.43 (d, J = 1.7 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.14 (dd, J = 8.6, 1.9 Hz, 2H), 6.07 (s, 1H), 3.59 (s, 3H), 2.93−3.01 (m, 2H), 2.09 (t, J = 7.1 Hz, 2H), 1.51−1.60 (m, 2H); ^{13}C NMR (100 MHz, CS_2−$CDCl_3$): δ 173.04, 148.63, 148.11, 145.42, 145.33, 145.26, 145.23, 145.20, 145.18, 144.95, 144.78, 144.60, 144.41, 144.34, 143.82, 143.75, 143.21, 143.19, 143.10, 143.06, 142.97, 142.95, 142.36, 142.15, 142.13, 141.15, 141.01, 137.45, 137.43, 134.89, 128.41, 125.83, 124.86, 123.04, 119.81, 116.33, 112.45, 80.29 (sp^3-C of C_{60}), 51.37, 48.90, 36.27, 34.54, 29.70, 24.34; UV−vis ($CHCl_3$): λ_{max}/nm 258, 327, 432, 692; HRMS (MALDI-TOFMS) m/z: M^+ calcd for $C_{83}H_{20}N_2O_2Cl_2$, 1146.0902; found, 1146.0894.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b00335.

Spectral data; UV−vis spectra of **2a**, **2m**, **2q**, **2s**, **4i**, **5a**, **5b**, and **5c**; and NMR spectra of **1d**, **1j**, **3g**, **2a**−**o**, **2q**, **2s**, **4a**−**i**, and **5a**−**c** (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For selected reviews, see: (a) Li, C.-J. Cross-Dehydrogenative Coupling (CDC): Exploring C−C Bond Formations beyond Functional Group Transformations. *Acc. Chem. Res.* **2009**, *42*, 335−344. (b) Girard, S. A.; Knauber, T.; Li, C.-J. The Cross-Dehydrogenative Coupling of C_{sp}3-H Bonds: A Versatile Strategy for C-C Bond Formations. *Angew. Chem., Int. Ed.* **2014**, *53*, 74−100. (c) Yeung, C. S.; Dong, V. M. Catalytic Dehydrogenative Cross-Coupling: Forming Carbon−Carbon Bonds by Oxidizing Two Carbon−Hydrogen Bonds. *Chem. Rev.* **2011**, *111*, 1215−1292. . For selected recent papers, see: (d) Griffiths, R. J.; Burley, G. A.; Talbot, E. P. A. Transition-Metal-Free Amine Oxidation: A Chemoselective Strategy for the Late-Stage Formation of Lactams. *Org. Lett.* **2017**, *19*, 870−873. (e) Jo, H.; Hassan, A. H. E.; Jung, S. Y.; Lee, J. K.; Cho, Y. S.; Min, S.-J. Construction of 8-Azabicyclo[3.2.1]-octanes via Sequential DDQ-Mediated Oxidative Mannich Reactions of N-Aryl Pyrrolidines. *Org. Lett.* **2018**, *20*, 1175−1178.

(2) (a) Miyake, Y.; Nakajima, K.; Nishibayashi, Y. Visible-Light-Mediated Utilization of α-Aminoalkyl Radicals: Addition to Electron-Deficient Alkenes Using Photoredox Catalysts. *J. Am. Chem. Soc.* **2012**, *134*, 3338−3341. (b) Le, C.; Liang, Y.; Evans, R. W.; Li, X.; MacMillan, D. W. C. Selective sp^3 C−H alkylation via polarity-match-based cross-coupling. *Nature* **2017**, *547*, 79−83. (c) Thullen, S. M.; Rovis, T. A Mild Hydroaminoalkylation of Conjugated Dienes Using a Unified Cobalt and Photoredox Catalytic System. *J. Am. Chem. Soc.* **2017**, *139*, 15504−15508. (d) Nakajima, K.; Miyake, Y.; Nishibayashi, Y. Synthetic Utilization of α-Aminoalkyl Radicals and Related Species in Visible Light Photoredox Catalysis. *Acc. Chem. Res.* **2016**, *49*, 1946−1956s.

(3) (a) Klapars, A.; Campos, K. R.; Waldman, J. H.; Zewge, D.; Dormer, P. G.; Chen, C.-Y. Enantioselective Pd-Catalyzed α-Arylation ofN-Boc-Pyrrolidine: The Key to an Efficient and Practical Synthesis of a Glucokinase Activator. *J. Org. Chem.* **2008**, *73*, 4986−4993. (b) Cordier, C. J.; Lundgren, R. J.; Fu, G. C. Enantioconvergent Cross-Couplings of Racemic Alkylmetal Reagents with Unactivated Secondary Alkyl Electrophiles: Catalytic Asymmetric Negishi α-Alkylations of N-Boc-pyrrolidine. *J. Am. Chem. Soc.* **2013**, *135*, 10946−10949. (c) Jain, P.; Verma, P.; Xia, G.; Yu, J.-Q. Enantioselective amine α-functionalization via palladium-catalysed C-H arylation of thioamides. *Nat. Chem.* **2017**, *9*, 140−144.

DOI: 10.1021/acs.joc.9b00335
J. Org. Chem. XXXX, XXX, XXX−XXX

(4) (a) Sundararaju, B.; Achard, M.; Sharma, G. V. M.; Bruneau, C. sp^3 C−H Bond Activation with Ruthenium(II) Catalysts and C(3)-Alkylation of Cyclic Amines. *J. Am. Chem. Soc.* **2011**, *133*, 10340−10343. (b) Xia, X.-F.; Shu, X.-Z.; Ji, K.-G.; Yang, Y.-F.; Shaukat, A.; Liu, X.-Y.; Liang, Y.-M. Platinum-Catalyzed Michael Addition and Cyclization of Tertiary Amines with Nitroolefins by Dehydrogenation of α,β-sp^3 C−H Bonds. *J. Org. Chem.* **2010**, *75*, 2893−2902. (c) Zhou, M.-J.; Zhu, S.-F.; Zhou, Q.-L. Copper-catalyzed Mannich-type oxidative β-functionalization of tertiary amines. *Chem. Commun.* **2017**, *53*, 8770−8773. (d) Takasu, N.; Oisaki, K.; Kanai, M. Iron-Catalyzed Oxidative C(3)-H Functionalization of Amines. *Org. Lett.* **2013**, *15*, 1918−1921. (e) Xia, X.-F.; Shu, X.-Z.; Ji, K.-G.; Shaukat, A.; Liu, X.-Y.; Liang, Y.-M. Platinum/Scandium-Cocatalyzed Cascade Cyclization and Ring-Opening Reaction of Tertiary Amines with Substituted Salicylaldehydes to Synthesize 3-(Aminoalkyl)coumarins. *J. Org. Chem.* **2011**, *76*, 342−345. (f) He, Y.; Wang, F.; Zhang, X.; Fan, X. C(sp3)−H dehydrogenation and C(sp2)−H alkoxy carbonylation of inactivated cyclic amines towards functionalized N-heterocycles. *Chem. Commun.* **2017**, *53*, 4002−4005. (g) Morigaki, A.; Kawamura, M.; Arimitsu, S.; Ishihara, T.; Konno, T. Application of Tertiary Amines Synthesized by Catalytic Dehydrogenation of Enamines as Nucleophilic C_2 Synthons for 1,4-Conjugate Addition with Fluoroalkylated Olefins. *Asian J. Org. Chem.* **2013**, *2*, 239−243.

(5) Griffiths, R. J.; Kong, W. C.; Richards, S. A.; Burley, G. A.; Willis, M. C.; Talbot, E. P. A. Oxidative β-C-H sulfonylation of cyclic amines. *Chem. Sci.* **2018**, *9*, 2295−2300.

(6) Huang, X.; Wang, J.; Ni, Z.; Wang, S.; Pan, Y. Synthesis of α,α-Disulfenylated Aldehydes via Oxidative Transformation of Tertiary Amines. *Org. Lett.* **2015**, *17*, 5488−5491.

(7) (a) Shi, X.; He, Y.; Zhang, X.; Fan, X. $FeCl_3$-Catalyzed Cascade Reactions of Cyclic Amines with 2-Oxo-2-arylacetic Acids toward Furan-2(5H)-one Fused N,O-Bicyclic Compounds. *Adv. Synth. Catal.* **2018**, *360*, 261−266. (b) Xu, G.-Q.; Xu, J.-T.; Feng, Z.-T.; Liang, H.; Wang, Z.-Y.; Qin, Y.; Xu, P.-F. Dual C(sp^3)-H Bond Functionalization of N-Heterocycles through Sequential Visible-Light Photocatalyzed Dehydrogenation/[2+2] Cycloaddition Reactions. *Angew. Chem., Int. Ed.* **2018**, *57*, 5110−5114.

(8) (a) Cui, C.; Li, Y.; Li, Y. Fullerene Derivatives for the Applications as Acceptor and Cathode Buffer Layer Materials for Organic and Perovskite Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1601251. (b) Nierengarten, I.; Nierengarten, J.-F. Fullerene Sugar Balls: A New Class of Biologically Active Fullerene Derivatives. *Chem.−Asian J.* **2014**, *9*, 1436−1444. (c) Anilkumar, P.; Lu, F.; Cao, L.; G. Luo, P.; Liu, J.-H.; Sahu, S.; N. Tackett II, K., II; Wang, Y.; Sun, Y.-P. Fullerenes for Applications in Biology and Medicine. *Curr. Med. Chem.* **2011**, *18*, 2045−2059. (d) Martín, N. Carbon Nanoforms for Photovoltaics: Myth or Reality? *Adv. Energy Mater.* **2017**, *7*, 1601102. (e) Rodríguez-Pérez, L.; Ramos-Soriano, J.; Pérez-Sánchez, A.; Illescas, B. M.; Muñoz, A.; Luczkowiak, J.; Lasala, F.; Rojo, J.; Delgado, R.; Martín, N. Nanocarbon-Based Glycoconjugates as Multivalent Inhibitors of Ebola Virus Infection. *J. Am. Chem. Soc.* **2018**, *140*, 9891−9898. (f) Muñoz, A.; Sigwalt, D.; Illescas, B. M.; Luczkowiak, J.; Rodríguez-Pérez, L.; Nierengarten, I.; Holler, M.; Remy, J.-S.; Buffet, K.; Vincent, S. P.; Rojo, J.; Delgado, R.; Nierengarten, J.-F.; Martín, N. Synthesis of giant globular multivalent glycofullerenes as potent inhibitors in a model of Ebola virus infection. *Nat. Chem.* **2016**, *8*, 50−57. (g) Li, Y.; Lou, N.; Xu, D.; Pan, C.; Lu, X.; Gan, L. Oxygen-Delivery Materials: Synthesis of an Open-Cage Fullerene Derivative Suitable for Encapsulation of H_2O_2 and O_2. *Angew. Chem., Int. Ed.* **2018**, *57*, 14144−14148. (h) Isobe, H.; Cho, K.; Solin, N.; Werz, D. B.; Seeberger, P. H.; Nakamura, E. Synthesis of Fullerene Glycoconjugates via a Copper-Catalyzed Huisgen Cycloaddition Reaction. *Org. Lett.* **2007**, *9*, 4611−4614.

(9) (a) Yang, X.-Y.; Lin, H.-S.; Jeon, I.; Matsuo, Y. Fullerene-Cation-Mediated Noble-Metal-Free Direct Introduction of Functionalized Aryl Groups onto [60]Fullerene. *Org. Lett.* **2018**, *20*, 3372−3376. (b) Liu, T.-X.; Yue, S.; Wei, C.; Ma, N.; Zhang, P.; Liu, Q.; Zhang, G. Solvent-promoted catalyst-free regioselective N-incorporation multi-component domino reaction: rapid assembly of π-functionalized [60]fullerene-fused dihydrocarbolines. *Chem. Commun.* **2018**, *54*, 13331−13334. (c) Hu, B.; Liu, T.-X.; Zhang, P.; Liu, Q.; Bi, J.; Shi, L.; Zhang, Z.; Zhang, G. N-Heterocyclic Carbene-Catalyzed α,β-Unsaturated Aldehydes Umpolung in Fullerene Chemistry: Construction of [60]Fullerene-Fused Cyclopentan-1-ones and Cyclohex-2-en-1-ones. *Org. Lett.* **2018**, *20*, 4801−4805. (d) Li, Y.; Gan, L. [60]Fullerene-Based Macrocycle Ligands. *Chem. - Eur. J.* **2017**, *23*, 10485−10490. (e) Peng, J.; Huang, G.; Wang, H.-J.; Li, F.-B.; Huang, C.; Xiang, J.-J.; Huang, Y.; Liu, L.; Liu, C.-Y.; Asiri, A. M.; Alamry, K. A. TEMPO-Mediated Synthesis of Tetrahydropyridinofullerenes: Reaction of [60]Fullerene with α-Methyl-Substituted Arylmethanamines and Aldehydes in the Presence of 4-Dimethylaminopyridine. *J. Org. Chem.* **2018**, *83*, 85−95.

(10) (a) Li, F.; Wang, L.; Wang, J.; Peng, D.; Zhao, Y.; Li, S.; Zhou, H.; Wu, J.; Tian, X.; Tian, Y. KO^{t}Bu-Mediated, Three-Component Coupling Reaction of Indoles, [60]Fullerene, and Haloalkanes: One-Pot, Transition-Metal-Free Synthesis of Various 1,4-(3-Indole)-(organo)[60]fullerenes. *Org. Lett.* **2017**, *19*, 1192−1195. (b) Li, S.-H.; Li, Z.-J.; Yang, W.-W.; Gao, X. Controlled Synthesis of C_{70} Equatorial Multiadducts with Mixed Addends from an Equatorial Diadduct: Evidence for an Electrophilic Carbanion. *Org. Lett.* **2018**, *20*, 2328−2332. (c) Lou, N.; Li, Y.; Gan, L. Synthesis of C_{70}-Based Fluorophores through Sequential Functionalization to Form Isomerically Pure Multiadducts. *Angew. Chem., Int. Ed.* **2017**, *56*, 2403−2407. (d) Reboredo, S.; Girón, R. M.; Filippone, S.; Mikie, T.; Sakurai, T.; Seki, S.; Martín, N. Cyclobuteno[60]fullerenes as Efficient n-Type Organic Semiconductors. *Chem.—Eur. J.* **2016**, *22*, 13627−13631. (e) Zhou, Z.; Xin, N.; Gan, L. Synthesis of Metal Complexes with an Open-Cage Fullerene as the Ligand. *Chem.—Eur. J.* **2018**, *24*, 451−457.

(11) Tzirakis, M. D.; Orfanopoulos, M. Radical Reactions of Fullerenes: From Synthetic Organic Chemistry to Materials Science and Biology. *Chem. Rev.* **2013**, *113*, 5262.

(12) (a) Li, F.; Wang, J.-J.; Wang, G.-W. Palladium-catalyzed synthesis of [60]fullerene-fused benzofurans via heteroannulation of phenols. *Chem. Commun.* **2017**, *53*, 1852−1855. (b) Wang, G.-W. *Functionalization of [60]Fullerene via Palladium-Catalyzed C-H Bond Activation*. Topics in Organometallic Chemistry; Springer, 2015; Vol. *55*, pp 119−136.

(13) Maroto, E. E.; Izquierdo, M.; Reboredo, S.; Marco-Martínez, J.; Filippone, S.; Martín, N. Chiral Fullerenes from Asymmetric Catalysis. *Acc. Chem. Res.* **2014**, *47*, 2660−2670.

(14) (a) Zhang, Y.; Matsuo, Y.; Li, C.-Z.; Tanaka, H.; Nakamura, E. A Scalable Synthesis of Methano[60]fullerene and Congeners by the Oxidative Cyclopropanation Reaction of Silylmethylfullerene. *J. Am. Chem. Soc.* **2011**, *133*, 8086−8089. (b) Zhang, Y.; Matsuo, Y.; Nakamura, E. Regiocontrolled Synthesis of 1,2-Di(organo)fullerenes *via* Copper-Assisted 1,4-Aryl Migration from Silicon to Carbon. *Org. Lett.* **2011**, *13*, 6058−6061. (c) Lu, S.; Jin, T.; Kwon, E.; Bao, M.; Yamamoto, Y. Highly Efficient Cu(OAc)$_2$-Catalyzed Dimerization of Monofunctionalized Hydrofullerenes Leading to Single-Bonded [60]Fullerene Dimers. *Angew. Chem., Int. Ed.* **2012**, *51*, 802−806. (d) Si, W.; Lu, S.; Bao, M.; Asao, N.; Yamamoto, Y.; Jin, T. Cu-Catalyzed C-H Amination of Hydrofullerenes Leading to 1,4-Difunctionalized Fullerenes. *Org. Lett.* **2014**, *16*, 620−623. (e) Liu, T.-X.; Zhang, Z.; Liu, Q.; Zhang, P.; Jia, P.; Zhang, Z.; Zhang, G. Synthesis of [60]Fullerene-Fused Tetrahydroazepinones and Azepinonimines *via* Cu(OAc)$_2$-Promoted N-Heteroannulation Reaction. *Org. Lett.* **2014**, *16*, 1020−1023. (f) Jiang, S.-P.; Su, Y.-T.; Liu, K.-Q.; Wu, Q.-H.; Wang, G.-W. Copper(I)-catalyzed heteroannulation of [60]fullerene with ketoxime acetates: preparation of novel 1-fulleropyrrolines. *Chem. Commun.* **2015**, *51*, 6548−6551. (g) Jiang, S.-P.; Zhang, M.; Wang, C.-Y.; Yang, S.; Wang, G.-W. Cascade Radical Reaction of N-Sulfonyl-2-allylanilines with [60]Fullerene: Synthesis and Functionalization of (2-Indolinyl)methylated Hydrofullerenes. *Org. Lett.* **2017**, *19*, 5110−5113.

(15) (a) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. CuI-Catalyzed Oxidative [3 + 2] Reaction of Fullerene with Amidines or Amides Using Air as the Oxidant:

DOI: 10.1021/acs.joc.9b00335
J. Org. Chem. XXXX, XXX, XXX−XXX

Preparation of Fulleroimidazole or Fullerooxazole Derivatives. *Org. Lett.* **2013**, *15*, 4650−4653. (b) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. $CuCl_2$-Mediated Reaction of [60]Fullerene with Amines in the Presence or Absence of Dimethyl Acetylenedicarboxylate: Preparation of Fulleropyrroline or Aziridinofullerene Derivatives. *J. Org. Chem.* **2013**, *78*, 11992−11998. (c) Lu, X.-W.; Xing, M.-L.; Miao, C.-B.; Li, J.-X.; Sun, X.-Q.; Yang, H.-T. $Cu(OAc)_2$-promoted reaction of [60]fullerene with primary amines or diamines. *Org. Biomol. Chem.* **2015**, *13*, 8405−8410. (d) Yang, H.-T.; Tan, Y.-C.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. $Cu(OAc)_2$-Mediated Reaction of C_{60} with Ureas for the Preparation of Fulleroimidazolidinones. *J. Org. Chem.* **2016**, *81*, 1157−1163. (e) Yang, H.-T.; Ge, J.; Lu, X.-W.; Sun, X.-Q.; Miao, C.-B. Copper-Catalyzed Functionalizations of C_{60} with Amino Alcohols. *J. Org. Chem.* **2017**, *82*, 5873−5880. (f) Teng, Q.; Tan, Y.-C.; Miao, C.-B.; Sun, X.-Q.; Yang, H.-T. Tunable Copper-Catalyzed Reaction of C_{60} with 2-Ethoxycarbonylacetamides and Subsequent $BF_3{\cdot}Et_2O$-Mediated Isomerization of the Generated Dihydrofuran-Fused Fullerenes to Fulleropyrrolidinones. *J. Org. Chem.* **2018**, *83*, 15268−15276.

(16) For books, see: (a) Hirsch, A.; Brettreich, M. *Fullerenes: Chemistry and Reactions*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005. (b) Langa, F.; Nierengarten, J.-F. *Fullerenes: Principles and Applications*; RSC Publishing: Cambridge, U.K., 2007.

(17) (a) Hamada, M.; Hino, T.; Kinbara, K.; Saigo, K. Synthesis and transformation of a novel methano[60]fullerene having a formyl group. *Tetrahedron Lett.* **2001**, *42*, 5069−5071. (b) Saigo, K.; Ito, H.; Kishi, Y.; Nishikawa, Y.; Tada, T.; Ishida, Y. A General Method for the Synthesis of 2,2-[60]Fullerenoalkanals: The Reaction of [60]-Fullerene with 2-Bromoenol Silyl Ethers. *Synlett* **2010**, *2010*, 1811−1814.

(18) Wang, G.-W.; Lu, Y.-M.; Chen, Z.-X.; Wu, S.-H. An Alternative Type of Fullerene Products from the Reaction of [60]Fullerene with Alkoxides and Subsequent Derivatization. *J. Org. Chem.* **2009**, *74*, 4841−4848.

(19) (a) Brabec, C. J.; Gowrisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S.; Williams, S. P. Polymer-Fullerene Bulk-Heterojunction Solar Cells. *Adv. Mater.* **2010**, *22*, 3839−3856. (b) Thompson, B. C.; Fréchet, J. M. J. Polymer-Fullerene Composite Solar Cells. *Angew. Chem., Int. Ed.* **2008**, *47*, 58−77. (c) Graham, K. R.; Cabanetos, C.; Jahnke, J. P.; Idso, M. N.; El Labban, A.; Ngongang Ndjawa, G. O.; Heumueller, T.; Vandewal, K.; Salleo, A.; Chmelka, B. F.; Amassian, A.; Beaujuge, P. M.; McGehee, M. D. Importance of the Donor:Fullerene Intermolecular Arrangement for High-Efficiency Organic Photovoltaics. *J. Am. Chem. Soc.* **2014**, *136*, 9608−9618.

(20) (a) Lawson, G. E.; Kitaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. Photoinduced inter- and intra-molecular electron transfer reactions of [60]fullerene and a tertiary amine. Formation of the cycloadduct N-ethyl-trans-2′,5′-dimethylpyrrolidino[3′,4′:1,2][60]-fullerene. *J. Chem. Soc., Chem. Commun.* **1995**, 2225−2226. (b) Lawson, G. E.; Kitaygorodskiy, A.; Sun, Y.-P. Photoinduced Electron-Transfer Reactions of [60]Fullerene with Triethylamine. *J. Org. Chem.* **1999**, *64*, 5913−5920. (c) Wang, G.-W.; Chen, X.-P.; Cheng, X. Unexpected Reactions of [60]Fullerene Involving Tertiary Amines and Insight into the Reaction Mechanisms. *Chem. - Eur. J.* **2006**, *12*, 7246−7253. (d) Chen, M.; Shen, W.; Bao, L.; Cai, W.; Xie, Y.; Akasaka, T.; Lu, X. Regioselective Thermal Reaction between Triethylamine and C_{60} Revisited: X-ray Confirmation of the Pentane-Fused Adduct and in Situ Mechanism Study. *Eur. J. Org. Chem.* **2015**, *2015*, 5742−5746.

(21) Han, J.; Chen, Y.; Yang, C.; Liu, T.; Wang, M.; Xu, H.; Zhang, L.; Zheng, C.; Song, Y.; Zhu, J. Structure-based optimization leads to the discovery of NSC765844, a highly potent, less toxic and orally efficacious dual PI3K/mTOR inhibitor. *Eur. J. Med. Chem.* **2016**, *122*, 684−701.

(22) Banister, S. D.; Rendina, L. M.; Kassiou, M. 7-Azabicyclo-[2.2.1]heptane as a scaffold for the development of selective sigma-2 (σ_2) receptor ligands. *Bioorg. Med. Chem. Lett.* **2012**, *22*, 4059−4063.

(23) Borah, K. J.; Phukan, M.; Borah, R. Aza-Michael Addition of Amines to α,β-Unsaturated Compounds Using Molecular Iodine as Catalyst. *Synth. Commun.* **2010**, *40*, 2830−2836.

(24) Wang, S.; Jin, G.; Wang, W.; Zhu, L.; Zhang, Y.; Dong, G.; Liu, Y.; Zhuang, C.; Miao, Z.; Yao, J.; Zhang, W.; Sheng, C. Design, synthesis and structure-activity relationships of new triazole derivatives containing N-substituted phenoxypropylamino side chains. *Eur. J. Med. Chem.* **2012**, *53*, 292−299.

(25) Holland, H. L.; Morris, T. A.; Nava, P. J.; Zabic, M. A new paradigm for biohydroxylation by Beauveria bassiana ATCC 7159. *Tetrahedron* **1999**, *55*, 7441−7460.

(26) Klenke, B.; Wiegand, I.; Schiffer, G.; Broetz-Oesterhelt, H.; Maiti, S. N.; Khan, J.; Reddy, A.; Yang, Z.; Hena, M.; Jia, G.; Ligong, O.; Liang, H.; Yip, J.; Gao, C.; Tajammul, S.; Mohammad, R.; Biswajeet, G. Amidine Substituted Beta-Lactam Compounds, their Preparation and use as Antibacterial Agents. U.S. Patent 9,556,165 B2, 2013.

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J. Org. Chem. XXXX, XXX, XXX−XXX