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$Cu(OAc)_2$-Mediated Reaction of C_{60} with Ureas for the Preparation of Fulleroimidazolidinones

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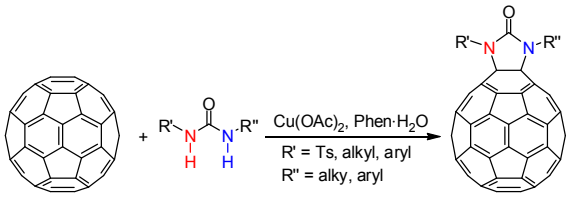


Abstract

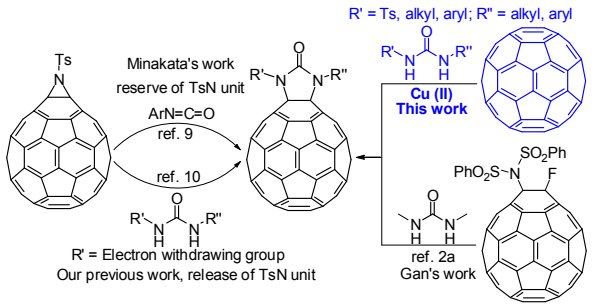
The $Cu(OAc)_2$-mediated intermolecular diamination reaction of C_{60} with ureas allows the concise and efficient preparation of fulleroimidazolidinones involving the cleavage of two N–H bonds and formation of two C–N bonds. Both dialkylated and diarylated fulleroimidazolidinones can be synthesized using this method.

Introduction

Chemical modification of fullerenes has been widely investigated over the past two decades for the preparation of a diversity of fullerene derivatives, some of which have shown potential applications in medicinal and material science.[1] New methods are continuously being explored for the synthesis of organofullerenes with novel architectures.[2] Free radical reactions have proved to be a powerful tool for the functionalization of fullerenes.[1a] Various transition-metal reagents, including Mn(III),[3] Fe(II or III),[4] Pb(IV),[5] Co(0),[6] Ni(0),[7] and Ag(I)[8] have been continuously explored to induce the radical addition reactions of fullerenes.[1a] Cu(I or II) salts are inexpensive, readily

available, insensitive to air and water, and low-toxicity reagents which have been found to catalyze or promote various organic transformations, especially X-N (X = C, N) bond formation.[9] The first example of Cu(II) mediated reaction of fullerenes with ketonic compounds was reported by the Wang group.[10] After that, there were no reports on the application of Cu(I or II) reagents to the functionalization of C_{60} for several years. The past five years, Cu(I/II) catalyzed or mediated transformations of fullerenes has gained much more attention once more.[11-15] The groups of Matsuo and Nakamura have reported the oxidation of a fullerene radical or a fullerene anion with a Cu(II) salt to generate fullerene cationic species for further transformations.[12] The Jin group described the Cu(II)-catalyzed dimerization or C-H amination of hydrofullerenes.[13] Liu and coworkers explored the $Cu(OAc)_2$-promoted *N*-heteroannulation reaction of C_{60} for the construction of novel C_{60}-fused tetrahydro-azepinones and -azepinonimines.[14] The Wang group reported the CuBr-catalyzed heteroannulation reaction of [60]fullerene with ketoxime acetates for the preparation of 1-fulleropyrrolines.[15] In contrast to the most investigated addition of *C*-centered and *O*-centered radicals to fullerenes,[1a] the addition of *N*-centered radicals to fullerenes are rather rare[16] and we have been interested in this less developed field. In our previous work, the Cu(I or II) reagents[17] and a hypervalent iodine/I_2 system[18] have proven efficient to generate a *N*-radical from amine compounds and their addition to C_{60} produces a variety of C_{60}-fused five of six membered ring derivatives with bonding of one or two nitrogen atoms to the C_{60} core. In continuation of our interest in the fullerene chemistry, we reported here the $Cu(OAc)_2$-promoted reaction of C_{60} with ureas for the easy preparation of fulleroimidazolidinones.

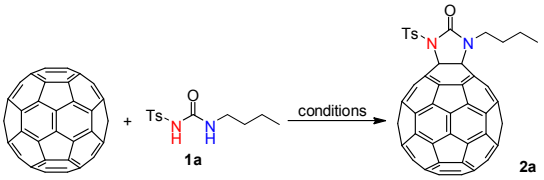
Scheme 1 The Preparation of Fulleroimidazolidinones



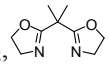
The preparation of fulleroimidazolidinones (Scheme 1) was first reported by the Minakata group through PCy_3-catalyzed formal [3+2] reaction of *N*-sulfonylated aziridinofullerene with aryl isocyanates.[19] In the conversion, the TsN unit was reserved in the product and the substrates were limited to aryl isocyanates. Later, we developed the Lewis base-catalyzed double nucleophilic substitution reaction of *N*-tosylaziridinofullerene with ureas along with the release of the TsN unit, solving the problem of synthesis of alkyl substituted fulleroimidazolidinones.[20] However these strategies could not realize the preparation of dialkyl- or diaryl-substituted fulleroimidazolidinones as an electron-withdrawing group on the nitrogen atom was necessary. Most recently, the Gan group reported the synthesis of *N*,*N*'-dimethylfulleroimidazolidinone from the precursor 1,2-adduct of C_{60} with NFSI, albeit in very low yield.[2a] These approaches are not direct synthetic routes from pristine C_{60} and the preparation of dialkyl- or diaryl-substituted fulleroimidazolidinones still remains a challenge.

Results and Discussion

Table 1 Screening of the Reaction Conditions



entry	conditions	molar ratio [C_{60}/**1a**/condition]	T (ºC)	time (h)	yield (%)[a]
1	$PhI(OAc)_2$:I_2	1:2:2:2	rt	6	0
2	PhIO:I_2	1:2:2:2	rt	6	0
3	$Pd(OAc)_2$,$PhI(OAc)_2$,NaOAc	1:4:2.2:2.2:1.2	100	8	0
4	$Pd(OAc)_2$, $CuBr_2$, NaOAc	1:4:2.2:3:1.2	100	8	0

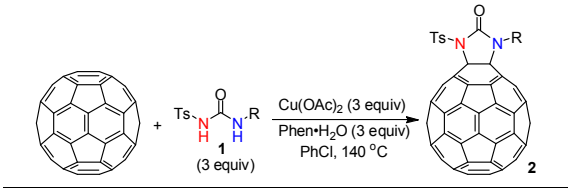
5	$Cu(OAc)_2$	1:2:2	140	8	0
6	$CuCl_2$	1:2:2	140	8	0
7	CuI	1:2:2	140	8	0
8	$Cu(OAc)_2$, Cs_2CO_3	1:2:2:2	140	8	0
9[b]	$Cu(OAc)_2$, Phen•H_2O	1:2:2:2	140	4	16 (74)
10	$Cu(OAc)_2$, Phen•H_2O	1:2:0.4:0.4	140	4	trace
11	**$Cu(OAc)_2$, Phen•H_2O**	**1:3:3:3**	**140**	**4**	**21 (65)**
12	$Cu(OAc)_2$,PMDETA	1:3:3:3	140	8	0
13	$Cu(OAc)_2$,TMEDA	1:3:3:3	140	8	0
14	$Cu(OAc)_2$, 2,2'-Bipyridine	1:2:2:2	140	8	12 (57)
15	$Cu(OAc)_2$, 2-Picolinic acid	1:2:2:2	140	7	trace
16	$Cu(OAc)_2$, 	1:2:2:2	140	5.5	14 (79)

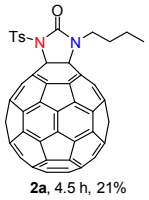
[a] Isolated yield; the values in parentheses are based on consumed C_{60}. [b] Carried out under a N_2 atomosphere.

In the documented intramolecular diamination of olefins, the urea moities always contained a sulfonyl group on the nitrogen atom.[21] So, the *N*-tosyl-*N*′-butylurea **1a** was selected as a model substrate to react with C_{60} (Table 1). Encouraged by our recently developed diamination reactions of C_{60} with sulfamides or phosphoryl diamides promoted by a hypervalent iodine/I_2 system,[18a] we envisioned that a similar reaction process could occur with the ureas due to their structural analogy with sulfamides. However, under either $PhI(OAc)_2/I_2$ or $PhIO/I_2$ conditions, no anticipated product **2a** was obtained (Table 1, entries 1 and 2). The classic conditions of Pd-catalyzed intramolecular diamination of ureas with alkenes[21a] did not work at all for the reaction of C_{60} with **1a** (Table 1, entries 3 and 4). Then, $Cu(OAc)_2$, $CuCl_2$, or CuI as the reagent was tried, which have proven to be efficient to promote the reaction of C_{60} with amine derivatives in our previous work.[17a-c] It was frustrating to find that employing Cu(I or II) reagents alone was totally ineffective in the transformation (Table 1, entries 5-7). Next, different bases or ligands such as Cs_2CO_3, TMEDA (*N*,*N*,*N*',*N*'-tetramethylethylenediamine), PMDETA (pentamethyldiethylenetriamine), Bpy (2,2'-bipyridine), Phen·H_2O (1,10-phenanthroline monohydrate), 2-picolinic acid, or 2,2'-isopropylidenebisoxazoline (BOX) were added with $Cu(OAc)_2$ as the oxidant to trigger the reaction (Table 1, entries 8-16). Gratifyingly, the combination of $Cu(OAc)_2$ with Bpy, Phen·H_2O, or

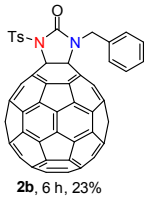
BOX were found to be effective systems for the reaction of C_{60} with urea **1a** (Table 1, entries 9, 14 and 16). The Phen·H_2O gave a higher yield than BOX and Bpy, affording **2a** in 16% yield. Increasing the amount of $Cu(OAc)_2$ and Phen·H_2O to 3 equiv improved the yield to 21% (Table 1, entry 11). Reducing the Phen·H_2O to catalytic amount only gave a trace amount of **2a** (Table 1, entry 10). Further increasing the amount of $Cu(OAc)_2$ and Phen·H_2O could just accelerate the reaction, but there was no increase in the yield. The reaction time could not be too long as the product decomposed slowly under the harsh conditions.

Table 2 $Cu(OAc)_2$-Mediated Reaction of C_{60} with Ureas Connecting a Tosyl Group.

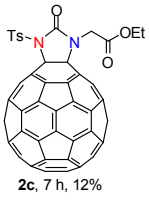




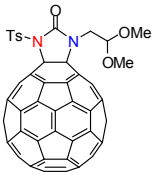
2a, 4.5 h, 21%



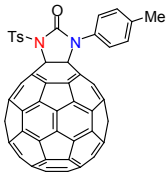
2b, 6 h, 23%



2c, 7 h, 12%



2d, 4.5 h, 19%



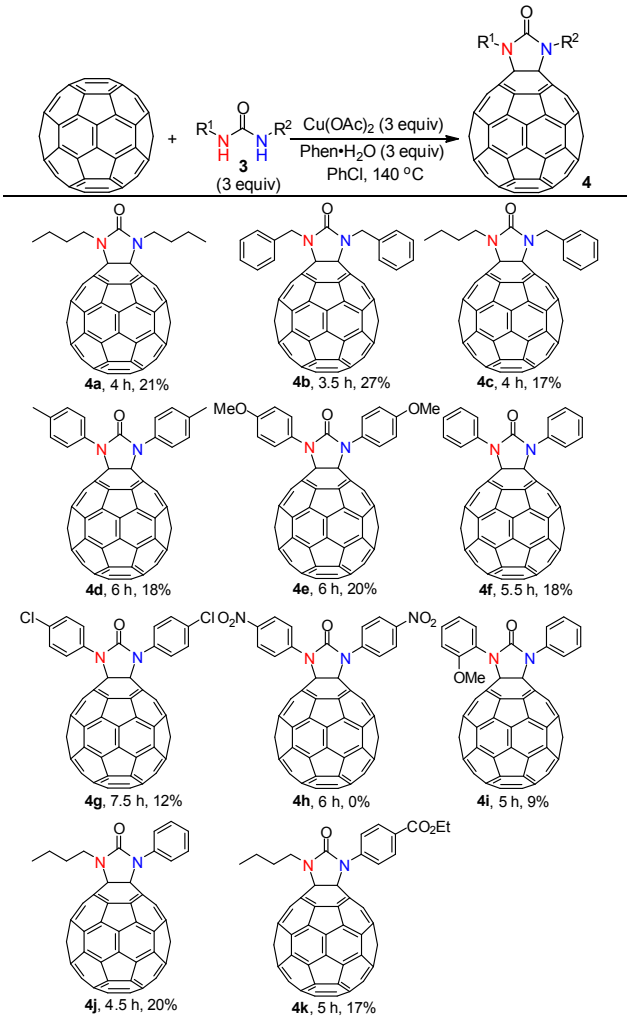
2e, 4 h, 9%

Under the optimal conditions, several ureas bearing a tosyl group on the nitrogen atom were introduced to this diamination reaction (Table 2). The alkylated-ureas showed a higher activity than that of arylated-ureas. Both ester and acetal groups were tolerated under these conditions.

We next turned our attention to investigate the reactivity of more challenging dialkyl- or diaryl-substituted ureas (Table 3). Excitingly, the reaction proceeded smoothly to give the desired fulleroimidazolidinones bearing two alkyl or aryl groups. The dialkyl substituted-ureas gave a better results than that of diaryl-substituted ureas. In terms of the diaryl-substituted ureas, an obvious

substituent electronic effect was observed and electron donating groups on the phenyl ring performed better than that of electron withdrawing groups. No reaction occurred for substrate **3h**, which bears a nitro group on each phenyl ring. An ortho substituted group on the phenyl ring led to noticeable decrease in the yield of product (**4i**) probably due to the steric hindrance. The ureas having an alkyl and an aryl group on each of the nitrogen atom also worked to give the desired products **4j** and **4k**.

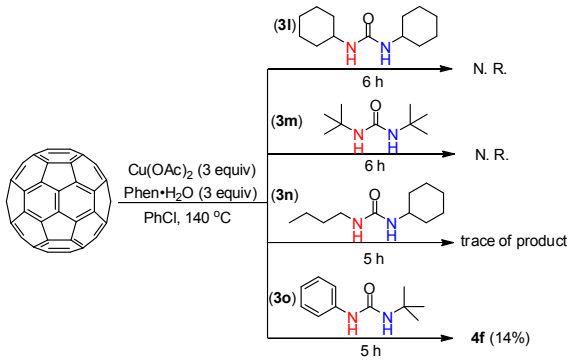
Table 3 Substrate Scope for the $Cu(OAc)_2$-Mediated Reaction of C_{60} with Alkylated or Arylated Ureas.



In order to further evaluate the influence of steric hindrance, ureas **3l-o** were treated with C_{60} under the standard reaction conditions (Scheme 2). For the dialkyl ureas, a noticeable steric effect was observed. The secondary and tertiary carbon connecting on the nitrogen atom (**3l-n**) resulted in

the failed reactions. At present, we had no reasonable explanation to these resluts. If *N*-phenyl-*N*′-tertiary butyl urea **3o** was employed, no anticipated product was formed. Instead, diphenyl-substituted fulleroimidazolidinone **4f** was produced in 14% yield. Further investigation revealed that the starting material **3o** was transform to *N*,*N*′-diphenylurea **3f** completely upon heating with $Cu(OAc)_2$ and Phen·H_2O in chlorobenzene at 140 ºC for 4 h, which resulted in the formation of **4f**.

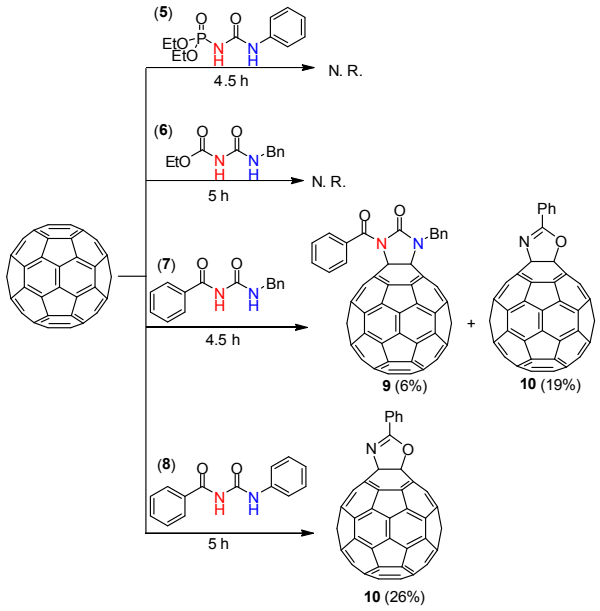
Scheme 2 Reaction of C_{60} with Sterically Hindered Ureas .



To further investigate the effect of other electron-withdrawing groups such as diethoxylphosphoryl, ethoxylcarbonyl, and benzoyl, the ureas **5**-**8** were prepared and treated with C_{60} under the standard reation conditions (Scheme 3). No reaction occurred for the *N*-diethoxylphosphoryl-*N*′-phenyl urea **5** and the *N*-ethoxylcrabonyl-*N*′-benzyl urea **6**. In terms of the benzoyl-substituted ureas, the substituents on the other nitrogen atom display significant influence on the reaction. The reaction of C_{60} with *N*-benzoyl-*N*′-benzyl urea **7** under the standard conditions furnished the desired product **9** in 6% yield along with the formation of the unexpected fullerooxazoline **10** in 19% yield. For the *N*-benzoyl-*N*′-pheny urea **8** , the fullerooxazoline **10** was obtained as the sole product in 26% yield instead of the anticipated unsymmetrical diaminated product.

Scheme 3 Reaction of C_{60} with Diethoxylphosphoryl-, Ethoxylcarbonyl-, and Benzoyl-Substituted

Ureas[a]

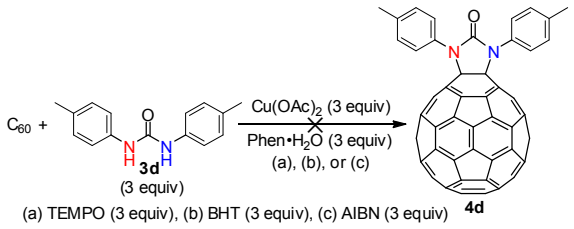


[a] The reactions were carried out with the ratio of C_{60}/ureas/$Cu(OAc)_2$/Phen·H_2O as 1:3:3:3 at 140 ºC.

The known products **2a-d**, **9**,[20] and **10**[18c] were confirmed through comparison of their TLC mobilities with those obtained compounds using our previous reported method and their spectral data with those reported in the literatures. The new compounds **2e**, **4a**–**g**, and **4i**–**k** were unambiguously characterized by their HRMS, ^{1}H NMR, ^{13}C NMR, and UV-vis spectra (see Supporting Information).

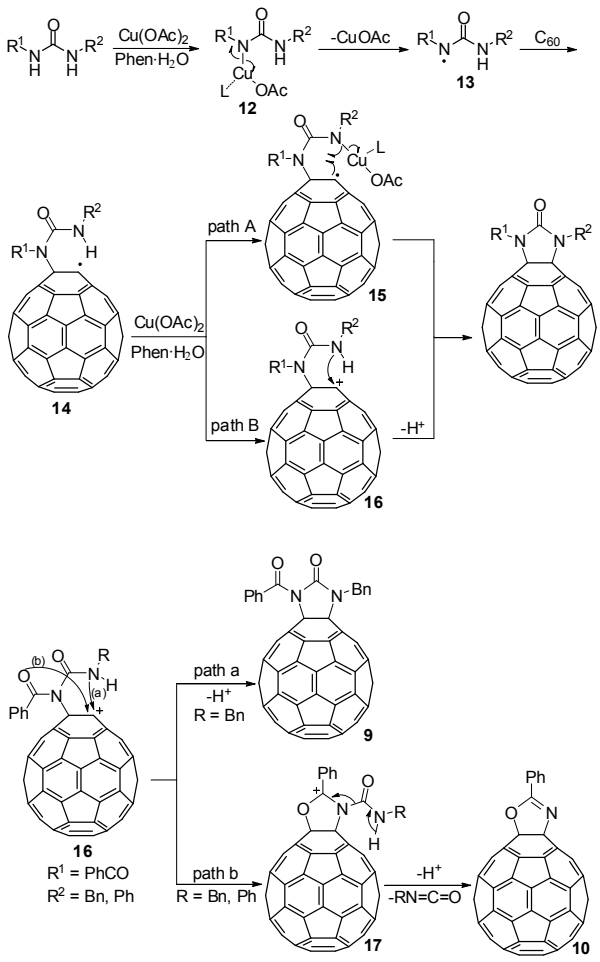
To gain more insight into the reaction mechanism, the reaction of C_{60} with **3d** in the presence of a free radical scavenger was performed (Scheme 4). Adding 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 2,6-ditertbutyl-4-methylphenol (BHT), or 2,2-azobisisobutyronitrile (AIBN) blocked the reaction completely. While the exact reaction mechanism is still uncertain, the results implied that a radical pathway might be involved in the reaction.

Scheme 4 Reaction in the Presence of Radical Scavenger



Base on the literature Cu-catalyzed or promoted C-N bond formation reactions[10,13b,14,17,21b] and the control experiment, a proposed mechanism is depicted in Scheme 5. Coordination of urea with $Cu(OAc)_2$ will provide intermeditate **12**. Homolytical cleavage of the N-Cu bond generates the nitrogen radical **13**,[22] which adds to C_{60} to form the fullerenyl radical **14**. Similar reaction pathway takes place once more to generate intermediate **15** and the further intramolecular cyclization along with release of CuOAc provides the product (path A). A mechanism involving a fullerene cationic species is also feasible (path B).[12] Oxidation of the fullerene radical by $Cu(OAc)_2$ produces the fullerenyl cation **16**. A subsequent intramolecular nucleophilic reaction then affords the observed product. In case of the reaction of C_{60} with **7** or **8**, two reaction pathways may exist after the generation of fullerenyl cation **16**. Attack of the other nitrogen atom to the fullerenyl cation affords the normal product **9** (path a). Alternatively, the attack of the oxygen atom of the benzoxy group to the fullerenyl cation followed by extrusion of isocyanate and a proton ion will produce the undesired fullerooxazoline **10** (path b).

Scheme 5 Proposed Mechanism.



Conclusion

In summary, a concise synthetic method toward the preparation of fulleroimidazolidinones has been developed through the $Cu(OAc)_2$-promoted intermolecular diamination reaction C_{60} with ureas. Both dialkyl and diaryl ureas are suitable in the transformation. A radical pathway is proposed for the formation of fulleroimidazolidinones.

Experimental Section

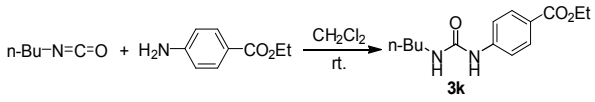
General Information.

All reactions were conducted under an air atmosphere. ^1H and ^{13}C NMR 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. Flash column chromatography was performed over silica gel (200−300 mesh). The MALDI-TOF MS were measured in positive ion mode using DCTB

E-(2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix.

Ureas **2a**−**e** were prepared from tosyl isocyanate and the corresponding amines according to reported procedure.[23] Ureas **3** were prepared as described in literature.[24] Symmetric ureas **3a**, **3b**, **3d**, **3e**, **3f**, **3g**, **3h**, **3l**, and **3m** were prepared form amines and triphosgene. The unsymmetric ureas **3c**, **3j**, and **3n** were prepared from *n*-butylisocyanate and the corresponding amines. Ureas **3i** and **3o** were synthesized from phenylisocyanate and amines. Urea **6** was prepared using our previous reported method.[20] Ureas **7** and **8** were synthesized according to the described method.[25]

Preparation of 3k.



Butyl isocyanate (0.338 mL, 3 mmol, 1.0 equiv) was added to a stirred solution of ethyl *p*-aminobenzoate (545 mg, 3.3 mmol, 1.1 equiv) in CH_2Cl_2 (5 mL) via syringe at 0 ºC. The mixture was continuing stir for 2 h at room temperature. The generated white solid in the mixture was filtered, dried, and then purified on silica gel (CH_2Cl_2/MeOH = 20/1) to give the compond **3k** (365 mg, 46%) as a white solid.

Ethyl 4-(3-butylureido)benzoate (**3k**): mp 98–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.31 (br, 1H), 5.23 (br, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.24 (q, J = 6.5 Hz, 2H), 1.48 (quint, J = 7.2 Hz, 2H), 1.25 ~ 1.42 (m, 5H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 156.3, 144.1, 130.9, 123.8, 119.0, 60.9, 40.0, 32.2, 20.1, 14.4, 13.8; HRMS (ESI-Q-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}N_2O_3$ 265.1552; Found 265.1547.

Urea 5 was Prepared from Dimethyl Phosphorisocyanatidate and Aniline.[26]

Diethyl isocyanatidophosphate (120 mg, 0.67 mmol) was added slowly to a solution of aniline (76 mg, 0.82 mmol) in toluene (3 mL) in an ice bath with magnetic stirring. After completion of the addition, the mixture was allowed to heat to 60 ºC and stirred for 1 h. Then the mixture was

chromatographed on silica gel (petroleun ether / ethyl acetate = 2:1) to give the compound 5 (130 mg, 71%) as a white solid.

Diethyl phenylcarbamoylphosphoramidate (**5**): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.23 (br, 1H), 7.48 (d, J = 7.7 Hz, 2H), 7.31 (t, J = 7.9 Hz, 2H), 7.08 (d, J = 7.4 Hz, 1H), 4.12-4.32 (m, 4H), 1.39 (td, J = 7.1, 0.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5 (d, $J_{2,\,C\text{-}P}$ = 4.4 Hz), 152.5, 138.1, 129.0, 123.8, 119.7, 64.4 (d, $J_{2,\,C\text{-}P}$ = 5.9 Hz), 16.2 (d, $J_{3,\,C\text{-}P}$ = 7.2 Hz).

General Procedure for the $Cu(OAc)_2$-Mediated Reaction of C_{60} with Ureas 1 and 3.

A mixture of C_{60} (54.0 mg, 0.075 mmol), 1,10-phenanthroline monohydrate (44.6 mg, 0.225 mmol), corresponding ureas (**1a**−**e** and **3a**−**k**, 0.225 mmol), and $Cu(OAc)_2$ (27.0 mg, 0.225 mmol) was stirred vigorously in chlorobenzene (13 mL) at 140 °C. The reaction was monitored by TLC analysis and stopped at the designated time. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel eluted with CS_2/toluene to give corresponding products **2a**−**e** and **4a**−**k**.

2a: (brown solid, 15.6 mg, 21%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 8.09 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 4.03 (t, J = 7.8 Hz, 2H), 2.51 (s, 3H), 1.93 (quint, J = 7.7 Hz, 2H), 1.45 (sextet, J = 7.5 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 152.23, 148.14, 148.06, 146.82, 146.62, 146.59, 146.43, 146.33, 146.21, 146.06, 145.61, 145.26, 145.20, 145.11, 145.06, 145.01, 144.73, 144.42, 143.67, 143.10, 142.99, 142.92, 142.88, 142.73, 142.18, 142.10, 142.04, 141.68, 141.38, 139.92, 138.45, 136.65, 136.56, 136.48, 129.55, 128.95, 80.00 (sp^3-C of C_{60}), 79.02 (sp^3-C of C_{60}), 43.17, 31.70, 21.91, 20.61, 13.99.

2b: (brown solid, 17.5 mg, 23%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 8.14 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 7.0 Hz, 2H), 7.17 ~ 7.25 (m, 3H), 5.27 (s, 2H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 152.77, 148.08, 148.00, 146.83, 146.57, 146.39,

146.31, 146.16, 145.98, 145.54, 145.22, 145.17, 144.96, 144.80, 144.64, 144.37, 143.73, 142.96, 142.88, 142.81, 142.66, 142.19, 142.04, 142.00, 141.50, 141.29, 139.49, 138.43, 136.60, 136.58, 136.31, 136.21, 129.61, 129.00, 128.74, 128.47, 128.05, 79.95 (sp^3-C of C_{60}), 79.07 (sp^3-C of C_{60}), 46.78, 21.94.

2c: (brown solid, 9.4 mg, 12%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 8.10 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 4.76 (s, 2H), 4.16 (q, J = 7.1 Hz, 2H), 2.51 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H).

2d: (brown solid, 14.4 mg, 19%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 8.10 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 4.94 (t, J = 5.4 Hz, 1H), 4.10 (d, J = 5.4 Hz, 2H), 3.42 (s, 6H), 2.51 (s, 3H).

2e: (brown solid, 7.1 mg, 9%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 8.15 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 2.51 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 152.31, 148.25, 148.15, 146.85, 146.72, 146.70, 146.50, 146.48, 146.30, 146.11, 145.72, 145.43, 145.39, 145.34, 145.27, 144.87, 144.76, 144.52, 144.27, 143.05, 142.95, 142.90, 142.81, 142.23, 142.13, 142.07, 141.67, 141.53, 139.83, 139.78, 138.55, 136.76, 136.48, 136.26, 131.67, 130.64, 130.49, 129.72, 129.21, 81.68 (sp^3-C of C_{60}), 79.14 (sp^3-C of C_{60}), 21.96, 21.43; UV−vis ($CHCl_3$) λ_{max}/nm 256, 318, 679; HRMS (MALDI-TOF) m/z $[M + Na]^+$ calcd for $C_{75}H_{14}N_2NaO_3S$ 1045.0623, found 1045.0616.

4a (brown solid, 14.0 mg, 21%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 4.41 (t, J = 7.7 Hz, 4H), 1.98 (quint, J = 7.6 Hz, 4H), 1.54 (sextet, J = 7.5 Hz, 4H), 1.01 (t, J = 7.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 157.01, 148.15, 146.73, 146.43, 146.26, 146.10, 145.58, 145.21, 144.61, 144.40, 143.04, 142.85, 142.23, 142.11, 142.08, 139.79, 136.72, 79.85 (sp^3-C of C_{60}), 42.93, 32.57, 20.64, 14.12; UV−vis ($CHCl_3$) λ_{max}/nm 256, 316, 690; HRMS (MALDI-TOF MS) m/z [M +

H]$^+$ calcd for $C_{69}H_{19}N_2O$ 891.1497, found 891.1483.

4b (brown solid, 19.6 mg, 27%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.56 (d, J = 7.4 Hz, 4H), 7.28 (t, J = 7.6 Hz, 4H), 7.21 (t, J = 7.4 Hz, 2H), 5.41 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 157.36, 148.05, 146.41, 146.36, 146.19, 146.03, 145.43, 145.16, 144.48, 144.42, 142.91, 142.77, 142.18, 141.99, 141.83, 139.36, 138.03, 136.47, 128.65, 128.61, 127.76, 79.67 (sp^3-C of C_{60}), 46.97; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 689; HRMS (MALDI-TOF) m/z [M + Na]$^+$ calcd for $C_{75}H_{14}N_2NaO$ 981.1004, found 981.1013, [M + K]$^+$ calcd for $C_{75}H_{14}N_2KO$ 997.0743, found 997.0729.

4c (brown solid, 11.9 mg, 17%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.50 (d, J = 7.1 Hz, 2H), 7.26 (d, J = 7.2 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 5.32 (s, 2H), 4.17 (t, J = 7.7 Hz, 2H), 2.03 (quint, J = 7.6 Hz, 2H), 1.58 (sextet, J = 7.5 Hz, 2H), 1.04 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 157.06, 148.08, 148.07, 146.75, 146.41, 146.35, 146.21, 146.20, 146.08, 146.01, 145.48, 145.16, 144.55, 144.51, 144.39, 142.96, 142.80, 142.78, 142.22, 142.15, 142.08, 142.00, 141.96, 141.90, 139.74, 139.36, 138.06, 136.73, 136.41, 128.57, 127.66, 79.74 (sp^3-C of C_{60}), 79.70 (sp^3-C of C_{60}), 46.79, 43.09, 32.64, 20.69, 14.15; UV−vis ($CHCl_3$) λ_{max}/nm 256, 317, 689; HRMS (MALDI-TOF) m/z [M + H]$^+$ calcd for $C_{72}H_{17}N_2O$ 925.1342, found 925.1348;

4d (brown solid, 12.7 mg, 18%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.65 (d, J = 8.3Hz, 4H), 7.28 (d, J = 8.2 Hz, 4H), 2.40 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 155.90, 148.12, 146.51, 146.42, 146.20, 146.09, 145.58, 145.14, 144.80, 144.53, 142.89, 142.75, 142.17, 142.00, 141.94, 139.60, 138.67, 136.52, 133.49, 130.73, 130.29, 81.05 (sp^3-C of C_{60}), 21.44; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 687; HRMS (MALDI-TOF) m/z [M + Na]$^+$ calcd for $C_{75}H_{14}N_2NaO$ 981.1004, found 981.0998, [M + K]$^+$ calcd for $C_{75}H_{14}N_2KO$ 997.0743, found 997.0738.

4e (brown solid, 14.8 mg, 20%, mp > 300 °C): 1H NMR (300 MHz, $CDCl_3$-CS_2) δ 7.68 (d, J = 9.0 Hz, 4H), 6.98 (d, J = 9.0 Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 159.69, 156.16, 148.15, 146.51, 146.44, 146.23, 146.12, 145.57, 145.16, 144.80, 144.55, 142.91, 142.77, 142.18, 142.03, 141.96, 139.64, 136.52, 132.16, 128.63, 114.84, 81.12 (2C, sp^3-C of C_{60}), 55.26; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 686; HRMS (MALDI-TOF) m/z $[M + H]^+$ calcd for $C_{75}H_{15}N_2O_3$ 991.1083, found 991.1085, $[M + Na]^+$ calcd for $C_{75}H_{14}N_2NaO_3$ 1013.0902, found 1013.0901.

4f (brown solid, 12.8 mg, 18%, mp > 300 °C): ^{1}H NMR (300 MHz, $CDCl_3$-CS_2) δ 7.80 (d, J = 7.2 Hz, 4H), 7.51 (t, J = 7.8 Hz, 4H), 7.42 (t, J = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$-CS_2) δ 155.79, 148.17, 146.48, 146.41, 146.26, 146.15, 145.60, 145.20, 144.72, 144.57, 142.94, 142.81, 142.21, 142.01, 141.98, 139.66, 136.59, 136.24, 130.92, 129.64, 128.80, 81.10 (sp^3-C of C_{60}); UV−vis ($CHCl_3$) λ_{max}/nm 256, 317, 687; HRMS (MALDI-TOF) m/z $[M + H]^+$ calcd for $C_{73}H_{11}N_2O$ 931.0872, found 931.0868, $[M + Na]^+$ calcd for $C_{73}H_{10}N_2NaO$ 953.0691, found 953.0668.

4g (brown solid, 9.2 mg, 12%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.74 (d, J = 8.6 Hz, 4H), 7.47 (d, J = 8.8 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 155.36, 148.21, 146.52, 146.32, 146.23, 145.83, 145.50, 145.24, 144.56, 144.44, 142.99, 142.87, 142.21, 142.03, 141.92, 139.78, 136.62, 135.14, 134.60, 132.05, 129.93, 80.92 (2C, sp^3-C of C_{60}); UV−vis ($CHCl_3$) λ_{max}/nm 256, 318, 685 HRMS (MALDI-TOF) m/z $[M + H]^+$ calcd for $C_{73}H_9Cl_2N_2O$ 999.0093, found 999.0076.

4i (brown solid, 6.6 mg, 9%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.80 (d, J = 7.8 Hz, 2H), 7.69 (dd, J = 7.7, 1.5 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.37-7.42 (m, 2H), 7.06 (d, J = 8.3 Hz, 1H), 7.04 (t, J = 7.7 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 157.28, 156.16, 148.16, 148.13, 147.25, 146.84, 146.67, 146.61, 146.46, 146.42, 146.38, 146.23, 146.17, 146.09,

146.06, 145.88, 145.67, 145.60, 145.18, 145.15, 145.12, 145.08, 144.96, 144.74, 144.71, 144.62, 144.59, 144.53, 142.94, 142.93, 142.80, 142.75, 142.67, 142.19, 142.03, 141.99, 141.91, 141.88, 139.83, 139.57, 139.43, 139.35, 136.93, 136.70, 136.62, 136.53, 136.30, 132.74, 130.83, 130.71, 129.53, 128.57, 125.34, 121.17, 112.98, 81.17 (sp^3-C of C_{60}), 81.05 (sp^3-C of C_{60}), 55.95; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 687; HRMS (MALDI-TOF) m/z $[M + H]^+$ calcd for $C_{74}H_{13}N_2O_2$ 961.0978, found 961.0976, $[M + Na]^+$ calcd for $C_{74}H_{12}N_2NaO_2$ 983.0797, found 983.0792.

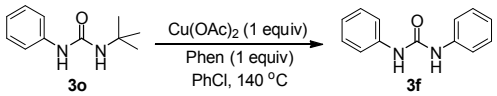
4j (brown solid, 13.9 mg, 20%, mp > 300 °C): ^{1}H NMR (500 MHz, $CDCl_3$-CS_2) δ 7.71 (d, J = 7.3 Hz, 2H), 7.48 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 7.5 Hz, 1H), 4.19 (t, J = 7.7 Hz, 2H), 2.06 (quint, J = 7.6 Hz, 2H), 1.58 (sextet, J = 7.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$-CS_2) δ 156.48, 148.19, 146.83, 146.50, 146.45, 146.32, 146.30, 146.27, 146.18, 146.10, 145.61, 145.23, 144.82, 144.62, 144.59, 144.34, 143.01, 142.88, 142.83, 142.27, 142.22, 142.15, 142.10, 142.00, 139.83, 139.67, 136.82, 136.54, 136.52, 130.89, 129.58, 128.58, 81.18 (sp^3-C of C_{60}), 79.85 (sp^3-C of C_{60}), 43.12, 32.42, 20.67, 14.12; UV−vis ($CHCl_3$) λ_{max}/nm 256, 317, 687; HRMS (MALDI-TOF) m/z $[M + H]^+$ calcd for $C_{71}H_{15}N_2O$ 911.1185, found 911.1174.

4k (brown solid, 12.3 mg, 17%, mp > 300 °C): ^{1}H NMR (400 MHz, $CDCl_3$-CS_2) δ 8.19 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 4.24 (t, J = 7.7 Hz, 2H), 2.08 (quint, J = 7.5 Hz, 2H), 1.60 (sextet, J = 7.5 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$-CS_2) δ 166.09, 156.63, 148.35, 146.65, 146.62, 146.51, 146.46, 146.44, 146.33, 146.28, 146.17, 145.71, 145.40, 145.38, 144.72, 144.36, 143.16, 143.03, 142.97, 142.41, 142.37, 142.23, 142.21, 142.13, 142.03, 141.02, 139.99, 139.80, 136.87, 136.81, 131.01, 130.52, 130.44, 81.10 (sp^3-C of C_{60}), 80.16 (sp^3-C of C_{60}), 61.39, 43.29, 32.34, 20.53, 14.47, 14.08; UV−vis ($CHCl_3$) λ_{max}/nm 256, 317, 697; HRMS (MALDI-TOF) m/z $[M + H]^+$ calcd for $C_{74}H_{19}N_2O_3$ 983.1396, found 983.1390, $[M + Na]^+$ calcd for $C_{74}H_{18}N_2NaO_3$ 1005.1215, found 1005.1210.

The $Cu(OAc)_2$-mediated reaction of C_{60} with urea 3o.

A mixture of C_{60} (54.0 mg, 0.075 mmol), urea **3o** (43.2 mg, 0.225 mmol), 1,10-Phenanthroline monohydrate (44.6 mg, 0.225 mmol), and $Cu(OAc)_2$ (27.0 mg, 0.225 mmol) was stirred vigorously in chlorobenzene (13 mL) at 140 °C for 5 h. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel using CS_2/toluene as the eluent to give the product **4f** (9.9 mg, 14%).

The Reaction of 3o with $Cu(OAc)_2$ and Phen·H_2O in Chlorobenzene.



A mixture of **3o** (43.2 mg, 0.225 mmol), $Cu(OAc)_2$ (27.0 mg, 0.225 mmol), and Phen·H_2O (44.6 mg, 0.225 mmol) was vigorously stirred in in chlorobenzene (10 mL) at 140 ºC for 4 h until the TLC showed that full conversion of **3o** to **3f** occurred. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel eluting with ethyl acetate/petroleum to give the product **3f** (20.5 mg, 86%).

The $Cu(OAc)_2$-Mediated Reaction of C_{60} with *N*-Diethoxylphosphoryl-*N′*-Phenyl Urea 5.

A mixture of C_{60} (54.0 mg, 0.075 mmol), urea **5** (61.2 mg, 0.225 mmol), Phen·H_2O (44.6 mg, 0.225 mmol), and $Cu(OAc)_2$ (27.0 mg, 0.225 mmol) was stirred vigorously in chlorobenzene (13 mL) at 140 °C for 4.5 h. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel eluting with CS_2/toluene to give the product **4f** (7.8 mg, 11%).

The $Cu(OAc)_2$-Mediated Reaction of C_{60} with *N*-Benzoyl-*N′*-benzyl Urea 7.

A mixture of C_{60} (54.0 mg, 0.075 mmol), urea **7** (57.2 mg, 0.225 mmol), Phen·H_2O (44.6 mg, 0.225 mmol), and $Cu(OAc)_2$ (27.0 mg, 0.225 mmol) was stirred vigorously in chlorobenzene (13 mL) at 140 °C for 4 h. The solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel eluting with CS_2/toluene to give the product **9**[20] (4.6 mg, 6%,

higher polarity) and **10**[18c] (12.2 mg, 19%, lower polarity).

9: ^{1}H NMR (400 MHz, $CDCl_3$-CS_2) δ 7.92 (d, J = 7.0 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.56 (t, J = 7.3 Hz, 2H), 7.50 (d, J = 7.1 Hz, 2H), 7.29 (t, J = 7.3 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 5.40 (s, 2H).

10: ^{1}H NMR (300 MHz, $CDCl_3$-CS_2) δ 8.37-8.49 (m, 2H), 7.55-7.73 (m, 3H).

The $Cu(OAc)_2$-Mediated Reaction of C_{60} with *N*-Benzoyl-*N′*-Pheny Urea 8.

A mixture of C_{60} (54.0 mg, 0.075 mmol), urea **8** (54.2 mg, 0.225 mmol), Phen·H_2O (44.6 mg, 0.225 mmol), and $Cu(OAc)_2$ (27.0 mg, 0.225 mmol) was stirred vigorously in chlorobenzene (13 mL) at 140 °C for 4 h. The solvent was evaporated *in vacuo*, and the residue was purified by column chromatography on silica gel using CS_2 as the eluent to give the product **10** (16.5 mg, 26%).

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Supporting Information

^{1}H and ^{13}C NMR spectra of **2a**–**e**, **3k**, **4a**–**g**, **4i**–**k**, **5**, **9**, and **10** and the UV-vis spectra of new fullerene derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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