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Hypervalent Iodine Reagent Mediated Reaction of [60]Fullerene with Amines

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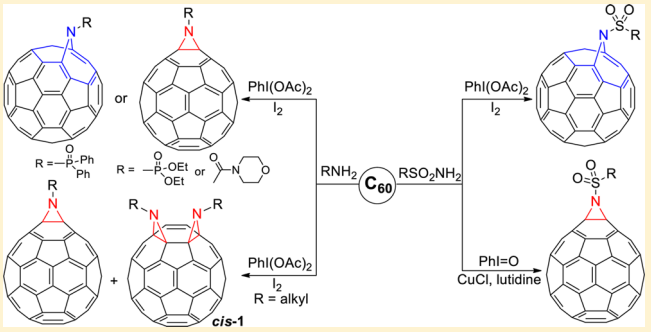
Supporting Information

ABSTRACT: The hypervalent iodine reagent mediated reaction of C_{60} with various readily available amines for the easy preparation of iminofullerenes has been developed. The reaction between C_{60} and sulfonamides can be effectively controlled to selectively synthesize azafulleroids or aziridinofullerenes under $PhI(OAc)_2/I_2$ or $PhIO/I_2/CuCl$/lutidine conditions, respectively. For phosphamide and urea, only one isomer is obtained. However, carbamate gives three kinds of products. Interestingly, the reaction of C_{60} with alkylamines allows the effective synthesis of aziridinofullerenes and regioselective *cis*-1-bisaziridinofullerenes.



Chemical functionalization allows the preparation of various fullerene derivatives for further investigation of their interesting physical properties and biological activities. Among them, the introduction of an N_1 unit on the fullerene sphere to construct iminofullerenes such as azafulleroids ([6,5]-opened) and aziridinofullerenes ([6,6]-closed) constitutes a large class of nitrogen-containing fullerene derivatives. Particularly, azafulleroids are key precursors for the synthesis of open-cage fullerene or azafullerene ($C_{59}N$),[1] and aziridinofullerene is a diverse platform for the synthesis of a variety of fullerene derivatives via acid-catalyzed ring-opening reactions.[2] The iminofullerenes are commonly prepared through 1,3-dipolar cycloaddition of organic azides to C_{60}, followed by extrusion of N_2 from the (triazolino)fullerene adducts under thermal or photolytic conditions.[3] The biggest problem was that the two isomers (azafulleroids and aziridinofullerenes) were always generated together, and control of the distribution was rather difficult. Furthermore, the explosiveness and toxicity of azides needs to be considered seriously in operation processes. Recently, the acid-catalyzed denitrogenation of triazolinofullerenes to afford the exclusive aziridinofullerene was reported.[4] Although some new synthetic routes to aziridinofullerenes were recently developed starting from the chloramines,[5] iminophenyliodinanes,[2] sulfilimines,[6] and *N*,*N*-dihalosulfonamides,[7] the substrates were mainly limited to those amines bonding a strongly electron withdrawing group to the nitrogen atom such as sulfonyl, phosphonyl, and carbonyl groups. Moreover, most of the starting materials need to be prepared beforehand from the corresponding amines.

We have been interested in developing new modification methods to prepare fullerene derivatives with a desired or as yet unknown specific skeleton.[8] The combination of $PhI(OAc)_2$ and I_2 to generate alkoxyl, sulfonamidyl, phosphoramidyl, carbamoyl, or amidyl radicals for further transformation in organic synthesis has been well documented.[9] As is known to all, fullerene is an efficient radical scavenger and a large number of radical reactions of fullerenes have been reported.[1] Therefore, we conceived of using the $PhI(OAc)_2/I_2$ system as a radical initiator and investigating its application in fullerene functionalizations. Recently, we exploited a $PhI(OAc)_2/I_2$-mediated reaction of C_{60} with carboxylic amides for the easy preparation of fullerooxazoles.[10] As a continuation of our research on the application of the $PhI(OAc)_2/I_2$ system in fullerene chemistry, in this context, we report the reaction of C_{60} with other easily available amines such as sulfonamides, phosphamides, ureas, carbamates, arylamines, and alkylamines under the hypervalent iodine/I_2 system for the convenient synthesis of aziridinofullerenes or azafulleroids (Scheme 1).

We started our study with the reaction of C_{60} with tolylsulfonamide **1a** in the presence of $PhI(OAc)_2$ (2 equiv) and I_2 (2 equiv) in chlorobenzene (Table 1, entry 1). After the mixture was stirred for 4 h at room temperature, azafulleroid **2a** was generated in 59% yield accompanied by a trace of aziridinofullerene **3a**. It is worth noting that both $PhI(OAc)_2$

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Scheme 1

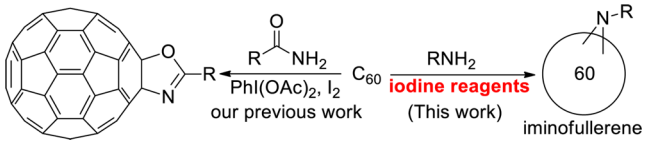
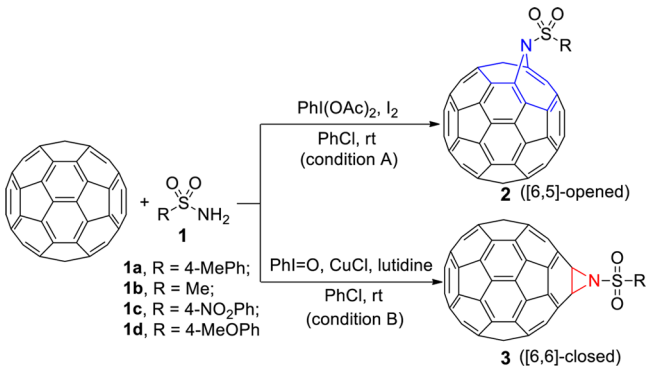


Table 1. Selective Synthesis of Aziridinofullerenes and Azafulleroids from Sulfonamides Mediated by Hypervalent Iodine Reagents

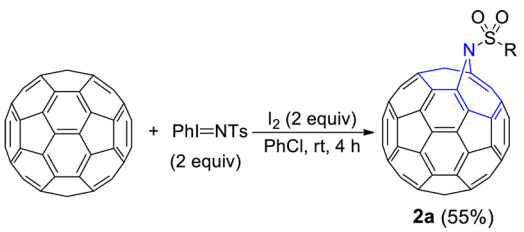


				yield[c]	
entry	substrate	conditions	time (h)	**2**	**3**
1[a]	**1a**	A	4	59	trace
2[b]	**1a**	B	20	0	50
3[a]	**1b**	A	6	49	trace
4[b]	**1b**	B	20	0	34
5[a]	**1c**	A	4	50	trace
6[b]	**1c**	B	20	0	38
7[a]	**1d**	A	4	54	trace
8[b]	**1d**	B	20	0	46

[a]Conditions: C_{60} (36 mg):**1**:$PhI(OAc)_2$:I_2 = 1:2:2:2, room temperature, 12 mL of chlorobenzen. [b]Conditions: C_{60} (36 mg):**1**:PhIO:CuCl:lutidine =1:2:2:0.2:0.4, room temperature, 12 mL of chlorobenzene. [c]Isolated yield.

and I_2 are crucial to the successful reaction and no reaction occurred in the absence of either one. On the basis of our previous research on the $PhI(OAc)_2/I_2$-mediated reaction of C_{60} with carboxylic amides,[10] the *N*,*N*-diiodotolylsulfonamide, which might be generated in situ from iminophenyliodinane and I_2, was deemed to be the key intermediate. To verify this conjecture, C_{60} (36 mg) was treated with iminophenyliodinane (2 equiv) and I_2 (2 equiv) in 12 mL of chlorobenzene (Scheme 2). Azafulleroid **2a** was produced, as expected, in 55% yield after 4 h. On the other hand, the Itami group has reported the CuCl-catalyzed reaction of C_{60} with iminophenyliodinane for the convenient and selective synthesis of aziridinofullerene.[2]

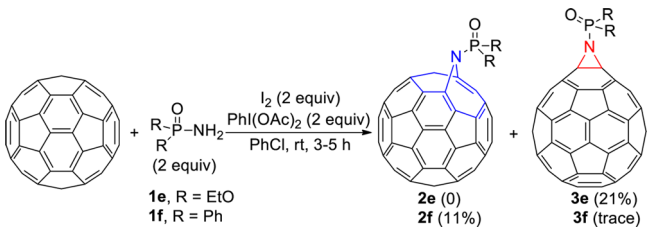
Scheme 2. Reaction of C_{60} with Iminophenyliodinane in the Presence of I_2



However, the iminophenyliodinane but not the easily available sulfonamide was used as the starting material. If I_2 were to be replaced by CuCl/lutidine, the aziridinofullerene **3a** might be formed as the predominant product. Thus, the selective synthesis of azafulleroids and aziridinofullerenes from the easily available sulfonamides would be realized, mediated by $PhI(OAc)_2$. To test this hypothesis, the reaction of C_{60} with **1a** and $PhI(OAc)_2$ was carried out in the presence of 10 mol % of CuCl and 20 mol % of lutidine. To our disappointment, only a trace of aziridinofullerene **3a** was observed by TLC. Both prolonging the reaction time and increasing the reaction temperature did not lead to any increase in the yield. When $PhI(OAc)_2$ was replaced by PhIO, to our delight, aziridinofullerene **3a** was obtained in 50% yield as the sole product after stirring for 20 h at room temperature (Table 1, entry 2). Other sulfonamides such as methylsulfonamide (**1b**), 4-nitrobenzosulfonamide (**1c**), and 4-methoxybenzosulfonamide (**1d**) were then tested, and this type of selective synthesis of azafulleroids and aziridinofullerenes was also applicable (Table 1, entries 3–8).

Encouraged by this result, the phosphamides **1e**,**f** were subjected to the reaction. However, two entirely different results were obtained (Scheme 3). Under the $PhI(OAc)_2/I_2$

Scheme 3. Reaction of C_{60} with Phosphamides under the $PhI(OAc)_2/I_2$ System



conditions, diethyl amidophosphonate **1e** gave the single aziridinofullerene **3e** in 21% yield. In contrast, diphenylphosphinamide **1f** gave the exclusive azafulleroid **2f** in 11% yield. Using PhIO instead of $PhI(OAc)_2$ resulted in no improvement in the yield of **2f**. Up to this point, we still had no reasonable explanation for the distinction on starting from the similar phosphamides.

Next, amines linking with a carbonyl group on the nitrogen atom were examined (Scheme 4). In case of the reaction of C_{60} with urea **1g** in the presence of $PhI(OAc)_2/I_2$, the aziridinofullerene **2g** was formed selectively in 12% yield.[11] For *n*-butyl carbamate **1h**, which has a structure similar to urea **1g**, only a trace of transformation was observed by TLC even after stirring at room temperature for 24 h. When PhIO was used instead of $PhI(OAc)_2$, in spite of no noticeable change for the reaction of C_{60} with urea **1g**, a great improvement in product yield for the reaction of C_{60} with **1h** was achieved. There were two main fractions other than C_{60} in the process of separation of the reaction mixture on a silica gel column using CS_2 as the eluent. The first fraction was identified as aziridinofullerene **3h** (15%), and the second fraction (27%) contained two inseparable components with a molar ratio of 1:4 as determined by ^1H NMR. Further ^{13}C NMR analysis and comparison of the spectral pattern with those of those reported fullerene derivatives proved that the two isomers were the major fullerooxazole **4** and minor azafulleroid **2h** (see the Supporting Information).[3g,10]

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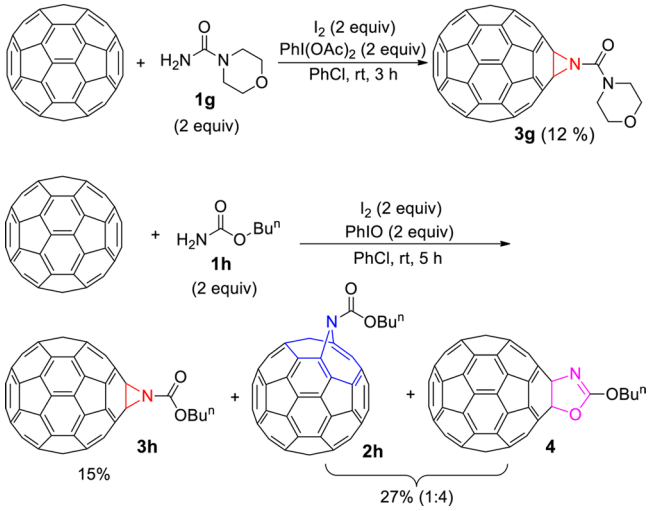
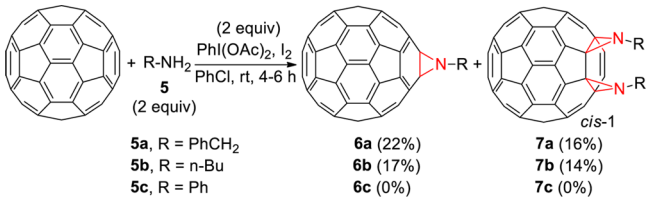
Scheme 4. Reaction of C_{60} with Urea and Carbamate under the Hypervalent Iodine/I_2 System



To further extend the scope of our protocol, we next turned our attention to investigating the reactivity of ordinary amines such as aryl- and alkyl amines (Scheme 5). No reaction occurred between C_{60} and 4-methylaniline **5c** under PhI-$(OAc)_2/I_2$ conditions. In contrast, when benzylamine **5a** was employed in the reaction, the aziridinofullerene **6a** was generated in 22% yield together with 16% of the unanticipated *cis*-1-bis-adduct **7a**, and no azafulleroid was formed. It must be noted that the feeding order of starting materials was critical to the success of this reaction. When the benzylamine and I_2 were added together and stirred for a moment before addition of $PhI(OAc)_2$, a very low transformation was observed, which might be attributable to the quick formation of a complex between the alkylamine and I_2.[12] When $PhI(OAc)_2$ and benzylamine **5a** were added together to a solution of C_{60}, the mixture was stirred for 20 min at room temperature, and then I_2 was added and the mixture was stirred for an additional 5 h, the reaction proceeded well to give the desired products. Interestingly, the bis-adduct **7a** was regioselectively produced as a *cis*-1 isomer, although eight possible regioisomers of the bis-adduct might exist. The *n*-butylamine **5b** also gave similar result with **5a** under the same conditions. Despite the fact that the Gan group has reported the $PhI(OAc)_2/I_2$-promoted reaction of C_{60} with glycine methyl ester under ultrasonic irradiation to generate aziridinofullerene, only the mono-adduct was observed in their research.[13]

Scheme 5. Reaction of C_{60} with Alkylamines under the $PhI(OAc)_2/I_2$ System To Afford Aziridinofullerenes and Regioselective *cis*-1-Bisaziridinofullerenes



The structure of **7a** was confirmed by ^{13}C NMR and UV−vis analysis (see the Supporting Information).[6b,14] UV−vis spectral patterns within the region 400−700 nm are powerful evidence for fullerene structural assignments, and the same type of fullerene bis-adducts showed similar UV−vis absorption patterns within that range.[15,16] The ^{13}C NMR and UV−vis spectral patterns of **7a** are nearly the same as those of reported *cis*-1-bis-adducts in Akasaka and Nagase's work[6b] (see the Supporting Information), which strongly demonstrated that **7a** was the *cis*-1 isomer.

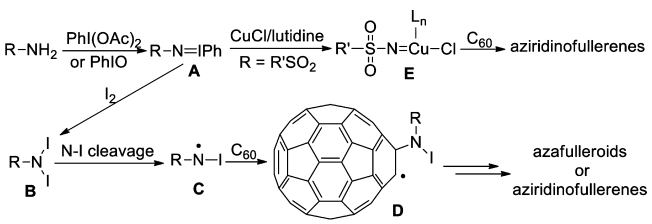
To the best of our knowledge, the *cis*-1-bisaziridinofullerene is hard to prepare because eight possible addition sites exist for 2-fold additions. So far, only the Akasaka and Nagase group evolved a synthetic methodology for the regioselective synthesis of *cis*-1-bisaziridinofullerene with sulfilimine.[6b] However, only the sulfilimine with an alkyl substituent could afford the *cis*-1-bisadduct. An aryl substituent of sulfilimine only afforded the azafulleroid accompanied by the minor product monoaziridinofullerene. Most recently, we exploited a $CuCl_2$-mediated reaction of C_{60} with electron-deficient amines for the preparation of aziridinofullerenes and *cis*-1-bisaziridinofullerenes.[14] Nevertheless, the substrates were restricted to those aromatic amines bearing a strongly electron withdrawing group. Although in an earlier stage the Hirsch group reported the preparation of eight isomers of $C_{60}(NCO_2R)_2$,[15a] the isolated *cis*-1 isomer in their work contained two open transannular [6,6] bonds. All in all, we have provided a new method to prepare *cis*-1-bisaziridinofullerenes from easily available alkylamines mediated by $PhI(OAc)_2/I_2$, which is a good complement to the existing methodologies for the preparation of *cis*-1-bisaziridinofullerenes.

To further confirm the structure of **7**, the relative energies of the eight possible isomer of bis-adducts **7a** were calculated at the B3LYP/6-31G* level with the geometry optimized by the AM1 semiempirical method.[17] The results showed that the *cis*-1 isomer was the most stable (see the Supporting Information). Hirsch had also summarized that sterically nondemanding addends prefer the *cis*-1 position for the 2-fold addition.[18]

On the basis of our previous work,[10] a plausible reaction pathway is proposed in Scheme 5. The reaction of amine with $PhI(OAc)_2$ or PhIO affords iminophenyliodinane **A**. In the presence of I_2, **A** was converted to the key intermediate *N,N*-diiodoamine **B**, which undergoes N−I bond cleavage to produce the nitrogen radical **C**, and follow-up capture by C_{60} generates the fullerene radical **D**. Elimination of another iodine radical from **D** generates the azafulleroid or aziridinofullerene. At present, we have no definite answer about the selective formation of azafulleroid or aziridinofullerene from **D**. When R is a sulfonyl group, CuCl-catalyzed degradation of iminophenyliodinane **A** furnishes the carbene **E** and iodobenzene. The reaction of C_{60} with **E** provides the exclusive aziridinofullerene.

In summary, the reaction of C_{60} with different readily available amines mediated by the hypervalent iodine/I_2 system was disclosed. For sulfonamides, azafulleroids or aziridinofullerenes could be selectively obtained under the $PhI(OAc)_2/I_2$ or $PhIO/I_2$/CuCl/lutidine system, respectively. No obvious

Scheme 6. Proposed Mechannism



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reaction regularity was observed for phosphamide, urea, and carbamate. With alkylamines, the aziridinofullerenes and regioselective *cis*-1-bisaziridinofullerenes were afforded under $PhI(OAc)_2/I_2$ conditions.

EXPERIMENTAL SECTION

Typical Procedure for the Synthesis of Azafulleroids 2a–d from the Reaction of C_{60} with Sulfonamides in the Presence of the $PhI(OAc)_2/I_2$ System. A mixture of C_{60} (36.0 mg, 0.05 mmol), sulfonamides **1a–d** (0.1 mmol), and 12 mL of PhCl was stirred and heated to 80 °C until the entire dissolution of C_{60}. The solution was cooled to room temperature, and then $PhI(OAc)_2$ (32.2 mg, 0.1 mmol) and I_2 (25.4 mg, 0.1 mmol) were added. The mixture was stirred at room temperature until no change occurred (detected by TLC), and then 10 mL of aqueous solution of sodium thiosulfate was added to remove the excessive iodine. The organic layer was separated, and the aqueous phase was extracted twice with 10 mL of toluene. The combined organic layers were dried over sodium sulfate, filtered, and evaporated to dryness. The residue was purified on a silica gel column using CS_2 as the eluent to give unreacted C_{60} and azafulleroids **2a–d** (**2a**,[3f] 26.2 mg, 59%; **2b**,[3f] 19.9 mg, 49%; **2c**,[7] 22.8 mg, 50%; **2d**,[3f] 24.6 mg, 54%).

Typical Procedure for the Synthesis of Aziridinofullerenes 3a–d from the Reaction of C_{60} with Sulfonamide under the $PhIO/I_2$/CuCl/Lutidine Conditions. A mixture of C_{60} (36.0 mg, 0.05 mmol), sulfonamides **1a-d** (0.1 mmol), and 12 mL of PhCl was stirred and heated to 80 °C until the entire dissolution of C_{60}. The solution was cooled to room temperature, and then PhIO (22.0 mg, 0.1 mmol), CuCl (1.0 mg, 0.01 mmol), and lutidine (2.2 mg, 0.02 mmol) were added. The mixture was stirred at room temperature for 20 h, and then 10 mL of an aqueous solution of sodium thiosulfate was added to remove the excess iodine. The organic layer was separated, and the aqueous phase was extracted twice with 10 mL of toluene. The combined organic layers were dried over sodium sulfate, filtered, and evaporated to dryness. The residue was purified on a silica gel column using CS_2 as the eluent to give unreacted C_{60} and aziridinofullerenes **3a–d** (**3a**,[3f] 22.4 mg, 50%; **3b**,[3f] 13.7 mg, 34%; **3c**,[7] 17.6 mg, 38%; **3d**,[3f] 20.9 mg, 46%). Aziridinofullerenes **3** have less polarity than azafulleroids **2** on TLC, and the ^1H NMR spectra of aziridinofullerenes **3** have a downfield shift in comparison to those of azafulleroids **2**.)

Reaction of C_{60} with Phosphamides 1e,f or Urea 1g under $PhI(OAc)_2/I_2$ Conditions. A mixture of C_{60} (36.0 mg, 0.05 mmol), phosphamides or urea (**1e–g**, 0.1 mmol), and 12 mL of PhCl was stirred and heated to 80 °C until the entire dissolution of C_{60}. The solution was cooled to room temperature, and then $PhI(OAc)_2$ (32.2 mg, 0.1 mmol) and I_2 (25.4 mg, 0.1 mmol) were added. The mixture was stirred at room temperature until no change occurred (detected by TLC; for **1e**, the reaction mixture was irradiated with a 250 W high-pressure mercury lamp), and then 10 mL of aqueous solution of sodium thiosulfate was added to remove the excess iodine. The organic layers were separated, and the aqueous phase was extracted twice with 10 mL of toluene. The combined organic layers were dried over sodium sulfate, filtered, and evaporated to dryness. The residue was purified on a silica gel column using CS_2/toluene as the eluent to give unreacted C_{60} and the products **3e**[5b] (9.2 mg, 21%), **2f**[7] (5.3 mg, 11%), and **3g** (5.3 mg, 12%).

Reaction of C_{60} with *n*-Butyl Carbamate 1h under $PhIO/I_2$ Conditions. A mixture of C_{60} (72.0 mg, 0.1 mmol), *n*-butyl carbamate **1h** (23.5 mg, 0.2 mmol), and 25 mL of PhCl was stirred and heated to 80 °C until the entire dissolution of C_{60}. The solution was cooled to room temperature, and then PhIO (44.0 mg, 0.2 mmol), and I_2 (50.8 mg, 0.2 mmol) were added. The mixture was stirred at room temperature for 5 h, and then 15 mL of an aqueous solution of sodium thiosulfate was added to remove the excess iodine. The organic layer was separated, and the aqueous phase was extracted twice with 15 mL of toluene. The combined organic layers were dried over sodium sulfate, filtered, and evaporated to dryness. The residue was purified on a silica gel column using CS_2 as the eluent to give unreacted C_{60}, aziridinofullerene **3h** (12.4 mg, 15%), and a mixture of **4** and **2h** (22.8 mg, 27%) in turn.

Reaction of C_{60} with Alkylamines 5a,b in the Presence of the $PhI(OAc)_2/I_2$ System. A solution of C_{60} (72.0 mg, 0.1 mmol) in 25 mL of PhCl was stirred and heated to 80 °C until the C_{60} dissolved entirely. After the solution was cooled to room temperature, $PhI(OAc)_2$ (64.5 mg, 0.2 mmol) and alkylamines **5** (0.2 mmol) were added, and the mixture was stirred for 20 min at room temperature. Then I_2 (50.8 mg, 0.2 mmol) was added, and the mixture was stirred for an additional 4–6 h at room temperature until no change occurred (detected by TLC). The same workup process as above gave the mono-adducts **6** and *cis*-1-bis-addducts **7** (**6a**,[4] 18.3 mg, 22%; **7a**, 15.5 mg, 17%; **6b**,[4] 12.5 mg, 16%; **7b**, 12.3 mg, 14%).

2a: ^1H NMR (500 MHz, CS_2-DMSO-d_6) δ 8.01 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) (all 2C unless indicated) δ 147.39, 146.55, 143.93 (1C), 143.87, 143.47, 143.41, 143.34, 143.33 (3C), 143.26, 143.17, 143.13, 142.98, 142.86, 142.81 (1C), 142.61, 142.41, 142.18, 142.17, 141.93, 141.89, 140.85, 139.20, 138.87, 138.84 (1C), 137.75, 137.52, 137.09, 137.05 (1C), 135.13 (1C), 134.90, 133.98, 133.35, 129.17 (aryl C), 128.15 (aryl C), 21.10 (1C).

2b: ^1H NMR (500 MHz, CS_2-DMSO-d_6) δ 3.53 (s, 3H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) (all 2C unless indicated) δ 146.67, 146.47, 145.02 (1C), 143.83, 143.48, 143.38, 143.34, 143.30, 143.22, 143.15, 143.00, 142.85, 142.82 (1C), 142.63, 142.49, 142.25, 142.22, 142.17, 142.11 (1C), 142.03, 141.89, 140.91, 139.30, 138.94, 137.91, 137.73, 137.69 (1C), 137.15, 135.12, 134.10, 133.34, 40.58 (1C).

2f: ^1H NMR (500 MHz, CS_2-DMSO-d_6) δ 8.22–8.27 (m, 4H), 7.51–7.59 (m, 6H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) (all 2C unless indicated) δ 147.45, 145.95 (d, $J_{3,C-P}$ = 4.8 Hz), 144.67, 144.53, 144.28, 144.15, 144.12 (4C), 143.97 (3C), 143.82, 143.73, 143.56, 143.46 (1C), 143.39, 143.21, 143.17, 143.05, 143.03, 142.78, 142.26, 141.32, 140.48 (1C), 139.81, 139.03, 138.61, 138.56 (1C), 138.24, 137.59, 136.54 (d, $J_{3,C-P}$ = 4.4 Hz), 135.32, 133.94, 133.16 (d, $J_{3,C-P}$ = 9.4 Hz, 4C, aryl C), 132.67 (d, $J_{4,C-P}$ = 2.7 Hz, aryl C), 129.95 (d, $J_{1,C-P}$ = 132.7 Hz, aryl C), 128.95 (d, $J_{2,C-P}$ = 13.0 Hz, 4C, aryl C).

3a: ^1H NMR (500 MHz, CS_2-$CDCl_3$) δ 8.19 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 8.1 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) (all 4C unless indicated) δ 145.54 (1C, aryl C), 145.36, 145.20, 145.11, 145.05 (2C), 144.58, 144.23, 144.04 (2C), 143.96, 143.36, 143.21, 143.16, 142.85 (2C), 142.24, 141.94, 141.43, 140.98, 135.89 (1C, aryl C), 130.17 (2C, aryl C), 128.62 (2C, aryl C), 79.95 (2C, sp^3-C of C_{60}), 21.95 (1C).

3e: ^1H NMR (500 MHz, CS_2-DMSO-d_6) δ 4.47–4.53 (m, 4H), 1.56 (t, J = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) (all 4C unless indicated) δ 145.38 (d, $J_{3,C-P}$ = 4.4 Hz), 145.27, 145.13, 144.90, 144.86 (2C), 144.53, 144.33, 144.00 (2C), 143.90, 143.17, 143.13, 142.80 (2C), 142.21, 142.09, 141.21, 140.86, 78.69 (d, $J_{2,C-P}$ = 5.8 Hz, sp^3-C of C_{60}, 2C), 64.93 (d, $J_{2,C-P}$ = 6.4 Hz, 2C), 16.65 (d, $J_{3,C-P}$ = 6.0 Hz, 2C);

3g (brown solid, mp >300 °C): ^1H NMR (500 MHz, CS_2-$CDCl_3$) δ 4.19 (br, 2H), 3.93 (br, 2H), 3.85 (br, 2H), 3.81 (br, 2H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) (all 4C unless indicated) δ 155.51 (1C, C=O), 145.36, 145.25, 145.03, 144.98 (2C), 144.63, 144.50, 144.13 (2C), 144.11, 143.93 (2C), 143.20, 143.17, 142.94, 142.29, 142.23, 141.14, 140.57, 80.59 (2C, sp^3-C of C_{60}); UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.19), 325 (4.64), 423 (3.39), 483 (3.23), 686 (2.75); FT-IR (KBr) ν/cm^{-1} 2918, 2849, 1686, 1424, 1424, 1273, 1232, 1184, 1116, 1048, 903, 728, 573, 526; HRMS (MALDI-TOFMS) m/z $[M + H]^+$ calcd for $C_{65}H_9N_2O_2$ 849.0664, found 849.0667.

3h (brown solid, mp >300 °C): ^1H NMR (500 MHz, CS_2-$CDCl_3$) δ 4.48 (t, J = 6.8 Hz, 2H), 1.83 (quint, J = 7.1 Hz, 2H), 1.52 (sext, J = 7.5 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) (all 4C unless indicated) δ 156.02 (1C, C=O), 145.26, 145.18, 144.90, 144.83 (2C), 144.59, 144.51, 144.05 (2C), 143.86, 143.82, 143.25, 143.21, 142.84 (2C), 142.30, 142.28, 141.15, 140.08, 81.11 (2C, sp^3-C of C_{60}), 68.14 (1C), 31.16 (1C), 19.41 (1C), 13.90 (1C); UV–vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.10), 325 (4.52), 422 (3.33), 482 (3.20), 686 (2.73); FT-IR (KBr) ν/cm^{-1} 2920, 2850, 1741, 1510, 1427, 1402, 1225, 1183, 1058, 729, 526; HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{65}H_9NO_2$ 835.0633, found 835.0640.

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4 (mixed with **2h**, brown solid, mp >300 °C): ^{1}H NMR (500 MHz, CS_2-DMSO-d_6) δ 8.01 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6, with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 163.65 (1C, N=C−O), 148.22, 147.36 (1C), 146.97 (1C), 145.52, 145.50, 145.31, 145.23, 145.16, 144.80, 144.58, 144.41, 144.32, 144.16, 143.82, 143.75, 143.43, 142.82, 141.88, 141.84, 141.77, 141.46, 141.39, 141.36, 141.23, 141.08, 140.87, 139.39, 138.61, 137.24, 135.03, 96.26 (1C, sp^3-C of C_{60}), 87.97 (1C, sp^3-C of C_{60}), 71.61 (1C), 30.55 (1C), 18.97 (1C), 13.50 (1C); HRMS (MALDI-TOFMS) m/z M^+ calcd for $C_{65}H_9NO_2$ 835.0633, found 835.0623.

6a: ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 8.00 (d, J = 7.4 Hz, 2H), 7.73 (t, J = 7.6 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 5.07 (s, 2H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) δ 144.27, 144.22, 143.77, 143.66, 143.59, 142.91, 142.33, 142.21, 142.02, 141.45, 141.30, 139.93, 136.22, 128.15, 128.14, 127.35, 84.53 (sp^3-C of C_{60}), 53.71; FT-IR (KBr) ν/cm^{-1} 2920, 2850, 1505, 1426, 1181, 1092, 728, 693, 572, 563, 526, 504.

7a (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 7.58−7.63 (m, 4H), 7.30−7.35 (m, 6H), 4.61 (d, J = 13.7 Hz, 2H), 4.32 (d, J = 13.7 Hz, 2H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) (all 2C unless indicated) δ 152.62, 148.83 (1C), 147.08, 146.08, 145.18, 145.08, 144.79, 144.76, 144.72, 144.34, 144.15, 143.73, 143.16, 143.12, 142.88, 142.58, 142.52, 142.39 (1C), 141.94, 141.61, 141.58, 141.00, 140.76 (1C), 140.72, 140.67, 140.60, 140.39, 139.78, 139.11 (1C), 139.08, 136.36 (aryl C), 127.97 (4C, aryl C), 127.67 (4C, aryl C), 126.91 (aryl C), 76.46 (sp^3-C of C_{60}), 72.29 (sp^3-C of C_{60}), 52.40; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.03), 327 (4.36), 426 (3.27), 472 (3.06); FT-IR (KBr) ν/cm^{-1} 2918, 2852, 1512, 1495, 1451, 1427, 1352, 1293, 1214, 1183, 1095, 1026, 726, 699, 626, 572, 564, 523, 504; HRMS (MALDI-TOFMS) m/z $[M + Na]^+$ calcd for $C_{74}H_{14}N_2Na$ 953.1055, found 953.1045.

6b: ^{1}H NMR (500 MHz, CS_2-DMSO-d_6) δ 3.72 (t, J = 6.9 Hz, 2H), 2.20 (quint, J = 7.3 Hz, 2H), 1.89 (sext, J = 7.4 Hz, 2H), 1.25 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) δ 144.21, 144.18, 143.68, 143.62, 143.53, 142.88, 142.28, 142.18, 141.99, 141.42, 141.26, 139.89, 139.45, 84.73 (sp^3-C of C_{60}), 50.07. 31.23, 20.42, 13.92.

7b (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, CS_2-DMSO-d_6) δ 3.39 (dt, J = 11.8, 6.9 Hz, 2H), 3.24 (dt, J = 11.8, 6.5 Hz 2H), 1.95−2.05 (m, 4H), 1.76−1.88 (m, 4H), 1.20 (t, J = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) (all 2C unless indicated) δ 152.95, 148.84 (1C), 147.12, 146.02, 145.12, 145.00, 144.73 (4C), 144.62, 144.33, 144.08, 143.67, 143.12, 143.01, 142.81, 142.53, 142.49, 142.34 (1C), 141.89, 141.60, 141.54, 140.84, 140.73 (3C), 140.67 (4C), 140.57, 139.70, 139.36, 139.04 (1C), 76.58 (sp^3-C of C_{60}), 72.47 (sp^3-C of C_{60}), 48.54, 31.15, 20.24, 13.86; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.13), 326 (4.45), 426 (3.35), 472 (3.14); FT-IR (KBr) ν/cm^{-1} 2920, 2853, 1512, 1460, 1427, 1359, 1186, 1097, 707, 612, 570, 563, 526; HRMS (MALDI-TOFMS) m/z: $[M + H]^+$ calcd for $C_{68}H_{19}N_2$ 863.1548, found 863.1547.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra of the products and figures and a table giving results of theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Vostrowsky, O.; Hirsch, A. *Chem. Rev.* **2006**, *106*, 5191−5207. (b) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. *Science* **1995**, *269*, 1554−1556. (c) Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421−1422.

(2) Nambo, M.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2011**, *133*, 2402−2405.

(3) (a) Prato, M.; Li, Q. C.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148−1150. (b) Grosser, T.; Prato, M.; Lucchini, V.; Hirsch, A.; Wudl, F. *Angew. Chem., Int. Ed.* **1995**, *34*, 1343−1345. (c) Averdung, J.; Mattay, J. *Tetrahedron* **1996**, *52*, 5407−5420. (d) Shen, C. K.-F.; Yu, H.-H.; Juo, C.-G.; Chien, K.-M.; Her, G.-R.; Luh, T.-Y. *Chem. Eur. J.* **1997**, *3*, 744−748. (e) Wu, R.; Lu, X.; Zhang, Y.; Zhang, J.; Xiong, W.; Zhu, S. *Tetrahedron* **2008**, *64*, 10694−10698. (f) Ulmer, L.; Mattay, J. *Eur. J. Org. Chem.* **2003**, 2933−2940. (g) Smith, A. B.; Tokuyama, H. *Tetrahedron* **1996**, *52*, 5257−5262. (h) Averdung, J.; Mattay, J.; Jacobi, D.; Abraham, W. *Tetrahedron* **1995**, *51*, 2543−2552. (i) Averdung, J.; Luftmann, H.; Mattay, J.; Claus, K.-U.; Abraham, W. *Tetrahedron Lett.* **1995**, *36*, 2957−2958. (j) Yan, M.; Cai, S. X.; Keana, J. F. W. *J. Org. Chem.* **1994**, *59*, 5951−5954.

(4) Ikuma, N.; Mikie, T.; Doi, Y.; Nakagawa, K.; Kokubo, K.; Oshima, T. *Org. Lett.* **2012**, *14*, 6040−6043.

(5) (a) Minakata, S.; Tsuruoka, R.; Nagamachi, T.; Komatsu, M. *Chem. Commun.* **2008**, 323−325. (b) Tsuruoka, R.; Nagamachi, T.; Murakami, Y.; Komatsu, M.; Minakata, S. *J. Org. Chem.* **2009**, *74*, 1691−1697.

(6) (a) Nakahodo, T.; Okada, M.; Morita, H.; Yoshimura, T.; Ishitsuka, M. O.; Tsuchiya, T.; Maeda, Y.; Fujihara, H.; Akasaka, T.; Gao, X.; Nagase, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 1298−1300. (b) Okada, M.; Nakahodo, T.; Ishitsuka, M. O.; Nikawa, H.; Tsuchiya, T.; Akasaka, T.; Fujie, T.; Yoshimura, T.; Slanina, Z.; Nagase, S. *Chem. Asian J.* **2010**, *6*, 416−423.

(7) Nagamachi, T.; Takeda, Y.; Nakayama, K.; Minakata, S. *Chem. Eur. J.* **2012**, *18*, 12035−12045.

(8) (a) Yang, H.-T.; Ruan, X.-J.; Miao, C.-B.; Xi, H.-T.; Jiang, Y.; Meng, Q.; Sun, X.-Q. *Tetrahedron Lett.* **2009**, *50*, 7337−7339. (b) Yang, H.-T.; Ruan, X.-J.; Miao, C.-B.; Sun, X.-Q. *Tetrahedron Lett.* **2010**, *51*, 6056−6059. (c) Yang, H.-T.; Tian, Z.-Y.; Ruan, X.-J.; Zhang, M.; Miao, C.-B.; Sun, X.-Q. *Eur. J. Org. Chem.* **2012**, 4918−4922. (d) Yang, H.-T.; Ren, W.-L.; Miao, C.-B.; Dong, C.-P.; Yang, Y.; Xi, H.-T.; Meng, Q.; Jiang, Y.; Sun, X.-Q. *J. Org. Chem.* **2013**, *78*, 1163−1170. (e) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2013**, *15*, 4650−4653.

(9) For selected examples: (a) Boto, A.; Hernández, D.; Hernández, R.; Suárez, E. *Org. Lett.* **2004**, *6*, 3785−3788. (b) Yuan, X. T.; Liu, K.; Li, C. *J. Org. Chem.* **2008**, *73*, 6166−6171. (c) Li, W.; Gan, J.; Fan, R. *Tetrahedron Lett.* **2010**, *51*, 4275−4277. (d) Francisco, C. G.; Herrera, A. J.; Martín, Á.; Pérea-Martín, I.; Suárez, E. *Tetrahedron Lett.* **2007**, *48*, 6384−6388. (e) Martín, A.; Pérea-Martín, I.; Suárez, E. *Org. Lett.* **2005**, *7*, 2027−2030. (f) Fan, R.; Pu, D.; Wen, F.; Wu, J. *J. Org. Chem.* **2007**, *72*, 8994−8997. (g) Fan, R.; Li, W.; Pu, D.; Zhang, L. *Org. Lett.* **2009**, *11*, 1425−1428.

(10) Yang, H.-T.; Ren, W.-L.; Dong, C.-P.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Tetrahedron Lett.* **2013**, *54*, 6799−6803.

(11) When phosphoramide **1h** and urea **1g** were used as the substrates, some unidentified precipitates generated from starting materials were formed during the reaction, which resulted in the consumption of raw materials and a low yield of product.

(12) Gündüz, T.; Taştekin, M. *Anal. Chim. Acta* **1994**, *286*, 247−251 and references cited therein.

(13) Zhang, X.; Gan, L.; Huang, S.; Shi, Y. *J. Org. Chem.* **2004**, *69*, 5800−5802.
(14) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *J. Org. Chem.* **2013**, DOI: 10.1021/jo402043p.
(15) (a) Schick, G.; Hirsch, A.; Mauser, H.; Clark, T. *Chem. Eur. J.* **1996**, *2*, 935−943. (b) Djojo, F.; Herzog, A.; Lamparth, I.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **1996**, *2*, 1537−1547. (c) Ito, H.; Ishiida, Y.; Saigo, K. *Tetrahedron Lett.* **2005**, *46*, 8757−8760. (d) Ito, H.; Ishida, Y.; Saigo, K. *J. Org. Chem.* **2006**, *71*, 4759−4765.
(16) For the detailed UV−vis spectral difference of the eight isomers, see the Supporting Information in ref 14.
(17) *Gaussian 09, Revision C.01*; Gaussian, Inc.: Wallingford, CT.
(18) (a) Hirsch, A. *Top. Curr. Chem.* **1998**, *199*, 1−65. (b) Bühl, M.; Hirsch, A. *Chem. Rev.* **2001**, *101*, 1153−1183.