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Lewis Base-Catalyzed Reaction of Aziridinofullerene with Ureas for the Preparation of Fulleroimidazolidinones

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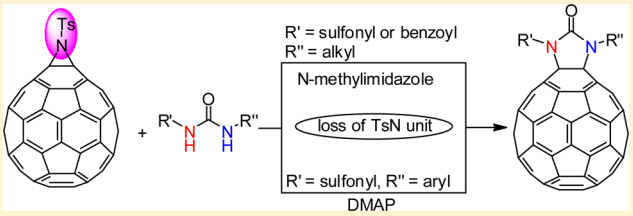
Supporting Information

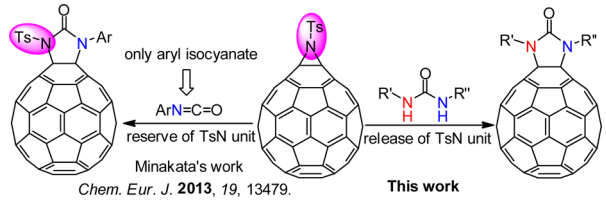
ABSTRACT: The Lewis base-catalyzed double nucleophilic substitution reaction of *N*-tosylaziridinofullerene with various ureas allows the easy preparation of fulleroimidazolidinones with a high tolerance for functional groups. Alkyl-substituted ureas show better reactivity than aryl-substituted ureas.



Functionalization on the sphere of C_{60} and investigation of the properties of these new generated fullerene derivatives for their applications in materials science and medicinal chemistry constitute an important research field in fullerene chemistry. Although a large number of functionalization protocols have emerged,[1] there is still a requirement to seek new and efficient methods for the preparation of organofullerenes with novel architectures. In the past few years, the Itami and Minakata groups pioneered the use of *N*-tosylaziridinofullerene as a versatile platform for functionalization of fullerenes by means of acid-catalyzed double nucleophilic substitution reactions accompanied by the loss of sulfonamide.[2] Later, the formal [3 + 2] reactions of *N*-tosylaziridinofullerene with CO_2, isocyanates,[3] and carbonyls[4] were developed. We also explored the reaction of *N*-tosylaziridinofullerene with sulfamides or amidines for the easy preparation of C_{60}-fused cyclic diaminated fullerenes.[5]

C_{60} has been the most striking electron-acceptor because of its high electron affinity and low reorganization energies for electron transfer.[6] The design and synthesis of new fullerene derivatives with improved electron affinity is a very appealing task in the search of their applications in materials science. However, the addition of most addends to C_{60} leads to a decrease in their electron-acceptor properties as a result of the change in the hybridization of carbon from sp^2 to a less electronegative sp^3 state.[7] In order to increase the electron-acceptor character of fullerene derivatives, one strategy is to link electronegative atoms directly to the C_{60} core.[8] C_{60}-fused dioxolanes,[9] dioxaborolanes,[10] oxazolines,[11] oxazolidines,[4] oxazolidinones,[12] imidazolines,[11e,13] and imidazolidinones,[3] in which two electronegative atoms are directly attached to the C_{60} core, precisely meet the requirement. Most recently, we developed a hypervalent iodine reagent-promoted intermolecular diamination reaction of C_{60} with sulfamides/phosphoryl diamides for the synthesis of two classes of novel C_{60}-fused cyclic sulfamide/phosphoryl diamide derivatives.[14] Although the 1,3-dipolar cycloaddition reaction is one of the most widely used methods to construct five-membered-ring-fused C_{60} derivatives,[7a] it is incapable of preparing these derivatives. They have been mainly synthesized through metal-catalyzed or -promoted radical reaction of C_{60} with different reactants. In case of the C_{60}-fused imidazolidinones, only the Minakata group reported a PCy_3-catalyzed formal [3 + 2] reaction of *N*-sulfonylated aziridinofullerene with aryl isocyanates for their preparation (Scheme 1).[3] However, the substrates were limited

Scheme 1



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to aryl isocyanates, and alkyl-substituted C_{60}-fused imidazolidinones could not be obtained. Although intramolecular diamination of olefins with ureas has been a suitable approach to generate bicyclic heterocycles with two nitrogen atoms,[15] C_{60}-fused imidazolidinones have never been synthesized directly from C_{60} and ureas, partially because of the unfavorability of intermolecular reactions.

Recently we have been interested in the development of new routes to cyclic diaminated [60]fullerenes starting from *N*-tosylaziridinofullerene.[5] The reaction conditions were found to vary greatly with different diamine sources. The reaction of sulfamides with *N*-tosylaziridinofullerene could be accomplished well using $BF_3{\cdot}Et_2O$ as the catalyst. However, in the

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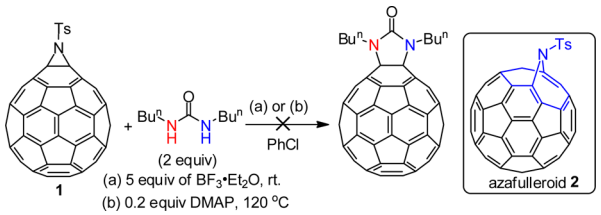
reaction of amidines with *N*-tosylaziridinofullerene, Lewis acids showed no catalytic activity. On the contrary, a Lewis base was found to be an efficient catalyst. Furthermore, the substituents on the nitrogen atom had great influence on the reaction. Therefore, the reactivity of *N*-tosylaziridinofullerene needed to be further investigated in order to gain insight into its essence. In continuation of our interest in the chemical functionalization of C_{60},[4,5,11d,e,14,16] here we report an interesting transformation employing ureas as the diamine source for the easy preparation of C_{60}-fused imidazolidinones (Scheme 1).

N,*N*′-Dibutylurea was first selected as a substrate to try the possibility (Scheme 2). To our disappointment, with either

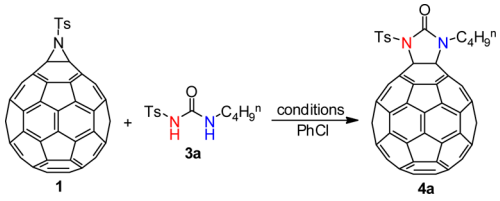
Scheme 2



BF_3·Et_2O or DMAP, which have been proved to be efficient catalysts for the double nucleophilic substitution reaction of *N*-sulfonylated aziridinofullerenes,[2a,5] no desired fulleroimidazolidinone product was obtained. In the presence of 5 equiv of BF_3·Et_2O, most of the aziridinofullerene was transformed to C_{60}. With DMAP, isomerization of *N*-tosylaziridinofullerene (**1**) to azafulleroid **2** (48%) occurred along with little conversion to C_{60} after stirring at 120 °C for 6 h.

When one of the butyl groups was replaced by a tosyl group, although BF_3·Et_2O still showed no catalytic activity, DMAP afforded the anticipated product **4a** in 76% yield along with small amounts of azafulleroid **2** and C_{60} (Table 1, entries 1 and

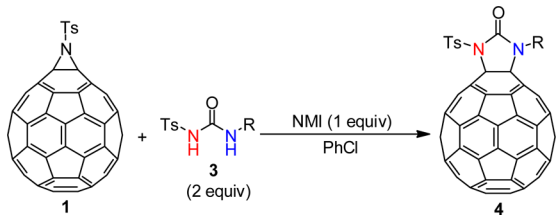
Table 1. Screening of the Reaction Conditions



entry	catalyst	molar ratio	*T* (°C)	time (h)	yield (%)
1	BF_3·Et_2O	1:2:5	rt	2	0
2	$Sn(OTf)_2$	1:2:1	120	12	20
3	$Sc(OTf)_3$	1:2:1	120	12	15
4	DMAP	1:2:0.2	120	8	76
5	2,6-lutidine	1:2:1	120	12	17
6	DABCO	1:2:1	120	11	83
7	NMI	1:2:1	120	7	84
8	NMI	1:2:1	90	12	70

4). Other Lewis acids such as $Sn(OTf)_2$ and $Sc(OTf)_3$ exhibited low catalytic activity (Table 1, entries 2 and 3). The organic bases DABCO and *N*-methylimidazole (NMI) gave better results than DMAP because only a trace of azafulleroid **2** was observed (Table 1, entries 6 and 7). In contrast to DABCO, NMI provided a comparative yield within a shorter reaction time. 2,6-Lutidine furnished only a 17% yield of the product (Table 1, entry 5). Reducing the reaction temperature to 90 °C led to lower yield and longer reaction time (Table 1, entry 8). Eventually, a **1**:**3a**:NMI molar ratio of 1:2:1 and a reaction temperature of 120 °C were selected as the optimized conditions for subsequent investigation of the double nucleophlic substitution of **1** with different ureas (Table 2).

Table 2. Substrate Scope of the *N*-Methylimidazole-Catalyzed Reaction of Aziridinofullerene 1 with *N*-Tosyl-*N*′-alkylureas 3



entry	substrate	time (h)	product	yield (%)
1	**3a** Ts, C$_4$H$_9^n$	7	**4a**	84
2	**3b** Ts, Bn	8	**4b**	85
3	**3c** Ts, cyclohexyl	16	**4c**	50
4	**3d** Ts, CO$_2$Et	10	**4d**	92
5	**3e** Ts, allyl	9	**4e**	88
6	**3f** Ts, propargyl	9	**4f**	87
7	**3g** Ts, 2,2-dimethoxyethyl	8.5	**4g**	85
8	**3h** Ts, 2-(4-hydroxyphenyl)ethyl	7	**4h**	88

Except for **3c**, all of the ureas **3a**–**h** with a tosyl group on one nitrogen atom and an alkyl group on the other gave good yields of fulleroimidazolidinones **4** (Table 2). Sterically hindered amine **3c** needed a longer reaction time and afforded the product in lower yield (Table 2, entry 3). Especially, this reaction showed superb functional group tolerance. Ester, alkenyl, alkynyl, acetal, and phenolic hydroxyl groups had no influence on the reaction (Table 2, entries 4–8). The introduction of these groups allows further transformations with other reactants, which is important for investigating the applications of this class of compounds with different functional addends. It is worth noting that present method is a good complement to Minakata's method,[3] which cannot be used to prepare fulleroimidazolidinones with an alkyl group on the nitrogen atom.

The reactivity of ureas **3i**–**l** linked with an aryl group was also investigated (Table 3). For substrate **3i**, using NMI as the base gave a very low conversion to **4i** as detected by TLC, probably because of the lower nucleophilicity of the aryl amine compared with alkyl amines. Replacing NMI by DMAP afforded the desired product **4i** in 47% yield because DMAP

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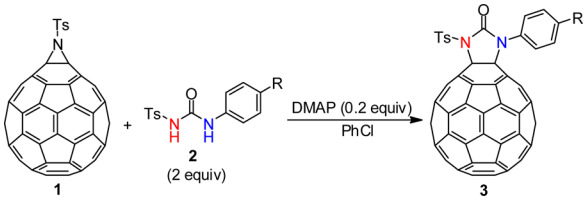
Table 3. DMAP-Catalyzed Reaction of Aziridinofullerene 1 with *N*-Tosyl-*N*′-arylureas

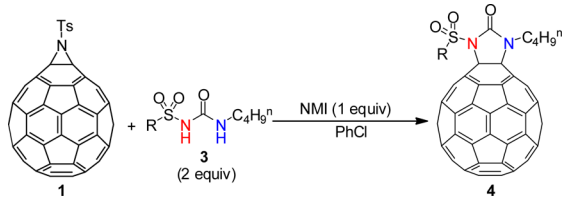


entry	substrate	product	time (h)	yield (%)
1	**3i**	**4i**	3	47
2	**3j**	**4j**	5	58
3	**3k**	**4k**	3.5	52
4	**3l**	**4l**	3.5	49

has a stronger basicity than NMI.[17] An electron-donating or -withdrawing group on the phenyl ring did not show obvious differences. A naphthyl group also provided the product **4l** in 49% yield. Overall, aromatic substituents on the nitrogen atom gave worse results than alkyl substituents.

We next studied the applicability of ureas with different sulfonyl substituents in this reaction (Table 4). 4-Methoxybenzenesulfonyl, 4-nitrobenzenesulfonyl, and methylsulfonyl all worked well to give the corresponding products **4m–o** in excellent yields.

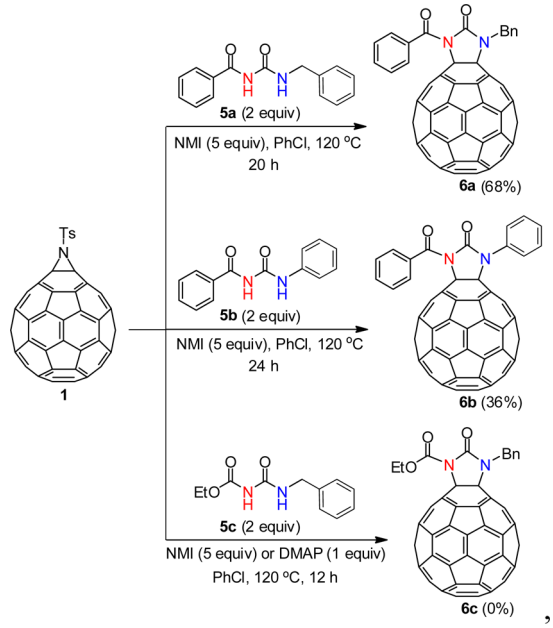
Table 4. Study of the Reaction Scope by Variation of the Sulfonyl Group on the Urea



entry	substrate	R	product	time (h)	yield (%)
1	**3m**	MeO—	**4m**	6	90
2	**3n**	O_2N—	**4n**	7	91
3	**3o**	Me—	**4o**	6	88

As can be seen from the above results, the sulfonyl group was indispensable to the success of the reaction. This could be explained by the fact that the electron-withdrawing character of the sulfonyl group enhances the adicity of the N–H, which is beneficial to the formation of a more nuceophilic nitrogen anion under basic conditions. To further investigate the effect of other electron-withdrawing groups such as benzoyl and ethoxycarbonyl, we prepared ureas **5a–c** and treated them with aziridinofullerene **1** under the standard conditions (Scheme 3).

Scheme 3. Reaction of *N*-Tosylaziridinofullerene 1 with Benzoyl- and Ethoxycarbonyl-Substituted Ureas 5



The benzoyl group gave results similar to those for the sulfonyl group. Ureas **5a** and **5b** connected to either an alkyl group or an aryl group, respectively, reacted with **1** to provide the desired products **6a** (68%) and **6b** (36%), although a larger amount of base and longer reaction times were needed. Unfortunately, the ethoxycarbonyl-substituted urea **5c** failed to give the product **6c** with either NMI or DMAP, probably because of the weaker acidity of the N–H in **5c** than in **5a** and **5b**.

The known products **4i–l** were confirmed through comparison of their spectral data to those reported in the literature.[3] All of the new compounds **4a–h**, **4m–o**, **6a**, and **6b** were unambiguously characterized by their HRMS, ^{1}H NMR, ^{13}C NMR, and UV–vis spectra (see the Supporting Information).

In summary, a new method for the synthesis of fulleroimidazolidinones via a Lewis base-catalyzed double nucleophilic reaction of *N*-tosylaziridinofullerene with ureas has been developed. This method shows a high degree of functional group tolerance. The influence of the substituent linked with the nitrogen atom on the reaction was investigated carefully. The exploration of the reactivity of *N*-tosylaziridinofullerene for the preparation of not easily available fullerene derivatives is ongoing in our laboratory.

EXPERIMENTAL SECTION

Preparation of the Starting Materials. Compounds **3a–l** were prepared from tosyl isocyanate and the corresponding amines.[18] Compounds **3m–o** were prepared from butyl isocyanate and the corresponding sulfonamides catalyzed by CuCl.[19] Compounds **5a** and **5b** were synthesized according to the method described in the literature.[20]

Preparation of 5c. Ethoxycarbonyl isocyanate (460 mg, 4 mmol) was added slowly to a solution of benzylamine (514 mg, 4.8 mmol) in dichloromethane (10 mL) in an ice bath with magnetic stirring. After completion of the addition, the mixture was allowed to warm to room temperature and stirred for 1 h. Dichloromethane (30 mL) was added, and the mixture was washed with 1 mol/L hydrochloric acid (2 × 10 mL) and saturated sodium bicarbonate (10 mL). The organic layer

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was dried with anhydrous Na_2SO_4. Removal of the solvent and recrystallization of the residue with ethanol afforded the final product **5c** (480 mg, 54%).

5c (colorless solid, mp 104−105 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (br, 1H), 7.23−7.38 (m, 5H), 7.08 (br, 1H), 4.50 (d, J = 5.8 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.53, 153.72, 138.24, 128.75, 127.67, 127.53, 62.38, 43.88, 14.35.

General Procedure for the Lewis Base-Catalyzed Reaction of Aziridinofullerene 1 with Ureas. A mixture of aziridinofullerene **1** (17.8 mg, 0.02 mmol), urea **3a−o** (0.04 mmol), and base (for **3a−h** and **3m−o**, NMI (0.02 mmol, 50 μL of 0.4 mol/L NMI solution in chlorobenzene); for **3i−l**, DMAP (0.004 mmol, 40 μL of 0.1 mol/L DMAP solution in chlorobenzene) in 3 mL of dry chlorobenzene was stirred at 120 °C for the designated time until completion of the reaction as determined by TLC. The solvent was removed in vacuo, and the residue was purified on a silica gel column using CS_2/toluene as the eluent to give the product **4a−o** (**4a**: 16.5 mg, 84%; **4b**: 17.3 mg, 85%; **4c**: 10.2 mg, 50%; **4d**: 18.8 mg, 92%; **4e**: 17.1 mg, 88%; **4f**: 16.9 mg, 87%; **4g**: 17.4 mg, 85%; **4h**: 18.5 mg, 88%; **4i**: 9.5 mg, 47%; **4j**: 12.1 mg, 58%; **4k**: 10.7 mg, 52%; **4l**: 10.3 mg, 49%; **4m**: 18.1 mg, 90%; **4n**: 18.6 mg, 91%; **4o**: 16 mg, 88%).

4a (brown solid, 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 = 8.1 Hz, 2H), 4.03 (t, J = 7.8 Hz, 2H), 2.51 (s, 3H), 1.93 (quint, J = 7.6 Hz, 2H), 1.46 (sextet, J = 7.3 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 152.23 (C═O), 148.13, 148.05, 146.80, 146.61, 146.58, 146.42, 146.32, 146.20, 146.05, 145.60, 145.25, 145.19, 145.08, 144.98, 144.72, 144.41, 143.66, 142.98, 142.91, 142.87, 142.72, 142.16, 142.08, 142.03, 141.67, 141.37, 139.91, 138.44, 136.60, 136.55, 136.47, 129.56, 128.94, 79.99 (C(sp^3) of C_{60}), 79.01 (C(sp^3) of C_{60}), 43.16, 31.69, 21.91, 20.61, 13.99; UV−vis ($CHCl_3$) λ_{max}/nm 257, 319, 419, 453, 683; HRMS (MALDI-TOF MS) m/z [M + H]$^+$ calcd for $C_{72}H_{17}N_2O_3S$ 989.0960, found 989.0954.

4b (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.14 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 7.1 Hz, 2H), 7.23 (t, J = 7.2 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 5.27 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 152.77 (C═O), 148.08, 148.00, 146.83, 146.57, 146.39, 146.31, 146.16, 145.98, 145.53, 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, 139.48, 138.43, 136.60, 136.58, 136.31, 136.21, 129.61, 129.00, 128.74, 128.47, 128.05, 79.95 (C(sp^3) of C_{60}), 79.07 (C(sp^3) of C_{60}), 46.78, 21.94; UV−vis ($CHCl_3$) λ_{max}/nm 257, 319, 419, 453, 682; HRMS (MALDI-TOF MS) m/z [M + Na]$^+$ calcd for $C_{75}H_{14}N_2NaO_3S$ 1045.0623, found 1045.0617.

4c (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.08 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 4.24 (tt, J = 12.0, 4.0 Hz, 1H), 2.57−2.69 (m, 2H), 2.52 (s, 3H), 1.95−2.03 (m, 2H), 1.85−1.95 (m, 2H), 1.62−1.70 (m, 1H), 1.25−1.36 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 151.49 (C═O), 148.15, 148.08, 146.75, 146.68, 146.64, 146.43, 146.32, 146.23, 146.09, 145.72, 145.26, 145.21, 145.18, 145.00, 144.96, 144.82, 144.44, 143.90, 143.03, 142.94, 142.92, 142.82, 142.17, 142.07, 142.03, 141.71, 141.41, 139.91, 138.38, 136.87, 136.68, 136.53, 129.59, 128.85, 80.21 (C(sp^3) of C_{60}), 78.98 (C(sp^3) of C_{60}), 55.93, 29.97, 26.68, 25.22, 21.92; UV−vis ($CHCl_3$) λ_{max}/nm 256, 317, 417, 453, 682; HRMS (MALDI-TOF MS) m/z [M + Na]$^+$ calcd for $C_{74}H_{18}N_2NaO_3S$ 1037.0936, found 1037.0930.

4d (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.10 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 4.76 (s, 2H), 4.17 (q, J = 7.1 Hz, 2H), 2.51 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 167.64 (C═O), 152.54 (C═O), 148.17, 148.07, 146.73, 146.62, 146.61, 146.42, 146.37, 146.18, 146.11, 145.58, 145.26, 145.25, 145.19, 144.73, 144.65, 144.41, 144.24, 143.27, 142.97, 142.90, 142.86, 142.71, 142.12, 142.07, 141.96, 141.61, 141.36, 139.98, 138.39, 136.77, 136.73, 136.45, 129.61, 128.87, 79.55 (C(sp^3) of C_{60}), 79.25 (C(sp^3) of C_{60}), 61.90, 43.76, 21.90, 14.11; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 417, 453, 682; HRMS (MALDI-TOF MS) m/z [M + Na]$^+$ calcd for $C_{72}H_{14}N_2NaO_5S$ 1041.0521, found 1041.0517.

4e (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.10 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 6.08 (ddt, J = 17.1, 10.3, 6.0 Hz, 1H), 5.32 (dd, J = 17.1, 1.0 Hz, 1H), 5.25 (dd, J = 10.2, 1.0 Hz, 1H), 4.70 (d, J = 6.0 Hz, 2H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 152.05 (C═O), 148.12, 148.04, 146.82, 146.61, 146.60, 146.42, 146.33, 146.21, 146.08, 145.59, 145.25, 145.20, 145.17, 144.95, 144.84, 144.69, 144.42, 143.88, 142.98, 142.91, 142.85, 142.70, 142.21, 142.09, 142.04, 141.63, 141.35, 139.74, 138.46, 136.58, 136.54, 136.51, 132.90, 129.59, 128.97, 119.48, 79.93 (C(sp^3) of C_{60}), 79.04 (C(sp^3) of C_{60}), 45.45, 21.92; UV−vis ($CHCl_3$) λ_{max}/nm 256, 317, 417, 453, 682; HRMS (MALDI-TOF MS) m/z [M + H]$^+$ calcd for $C_{71}H_{13}N_2O_3S$ 973.0647, found 973.0642.

4f (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.10 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 4.87 (d, J = 2.5 Hz, 2H), 2.52 (s, 3H), 2.28 (t, J = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 151.56 (C═O), 148.15, 148.04, 146.78, 146.64, 146.62, 146.43, 146.36, 146.23, 146.18, 145.56, 145.35, 145.26, 145.21, 144.72, 144.66, 144.45, 144.37, 143.96, 142.98, 142.93, 142.85, 142.68, 142.26, 142.16, 142.05, 141.55, 141.35, 139.75, 138.46, 136.68, 136.52, 136.35, 129.64, 129.05, 79.56 (C(sp^3) of C_{60}), 79.16 (C(sp^3) of C_{60}), 78.57, 74.67, 32.10, 21.93; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 417, 453, 682; HRMS (MALDI-TOF MS) m/z [M + H]$^+$ calcd for $C_{71}H_{11}N_2O_3S$ 971.0490, found 971.0484, [M + Na]$^+$ calcd for $C_{71}H_{10}N_2NaO_3S$ 993.0310, found 993.0304.

4g (brown solid, 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 = 8.1 Hz, 2H), 4.95 (t, J = 5.4 Hz, 1H), 4.10 (d, J = 5.4 Hz, 2H), 3.42 (s, 6H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 152.81 (C═O), 148.16, 148.05, 146.76, 146.61, 146.40, 146.33, 146.21, 146.01, 145.63, 145.24, 145.18, 145.16, 145.13, 144.81, 144.65, 144.49, 144.03, 142.96, 142.92, 142.85, 142.68, 142.27, 142.11, 142.00, 141.62, 141.35, 139.77, 138.37, 136.64, 136.53, 135.98, 129.57, 128.93, 102.42, 80.23 (C(sp^3) of C_{60}), 79.19 (C(sp^3) of C_{60}), 55.16, 45.48, 21.91; UV−vis ($CHCl_3$) λ_{max}/nm 256, 318, 417, 453, 682; HRMS (MALDI-TOF MS) m/z [M + Na]$^+$ calcd for $C_{72}H_{16}N_2NaO_5S$ 1043.0678, found 1043.0672.

4h (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, DMSO-d_6/CS_2) δ 8.62 (s, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.1 Hz, 2H), 6.66 (d, J = 8.4 Hz, 2H), 6.40 (d, J = 8.4 Hz, 2H), 4.10 (t, J = 6.9 Hz, 2H), 3.09 (t, J = 6.9 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6/CS_2) δ 156.32, 150.61 (C═O), 147.20, 147.07, 146.03, 145.64, 145.57, 145.43, 145.25, 145.21, 144.93, 144.82, 144.33, 144.18, 144.17, 143.93, 143.77, 143.57, 143.30, 143.11, 142.00, 141.90, 141.84, 141.81, 141.35, 141.24, 141.10, 141.00, 140.49, 138.70, 137.25, 136.08, 136.05, 135.21, 129.26, 128.59, 128.27, 126.67, 115.09, 78.97 (C(sp^3) of C_{60}), 77.89 (C(sp^3) of C_{60}), 43.57, 32.59, 21.19; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 417, 453, 682; HRMS (MALDI-TOF MS) m/z [M + H]$^+$ calcd for $C_{76}H_{17}N_2O_4S$ 1053.0909, found 1053.0902, [M + Na]$^+$ calcd for $C_{76}H_{16}N_2NaO_4S$ 1075.0728, found 1075.0725.

4i (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.11 (d, J = 8.4 Hz, 2H), 7.58−7.61 (m, 2H), 7.45 (tt, J = 7.4, 1.5 Hz, 2H), 7.37−7.42 (m, 3H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 151.84 (C═O), 148.10, 148.01, 146.77, 146.58, 146.37, 146.34, 146.17, 145.99, 145.59, 145.22, 145.19, 145.15, 144.74, 144.65, 144.38, 144.07, 142.94, 142.83, 142.78, 142.69, 142.09, 142.01, 141.94, 141.55, 141.40, 139.69, 138.41, 136.59, 136.44, 136.20, 134.34, 130.80, 129.66, 129.55, 129.46, 129.16, 81.40 (C(sp^3) of C_{60}), 79.00 (C(sp^3) of C_{60}), 21.90.

4j (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.11 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 2.52 (s, 3H).

4k (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.13 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.9 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H), 2.52 (s, 3H).

4l (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.14−8.20 (m, 3H), 7.91 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.78 (dd, J = 7.4, 0.8 Hz, 1H), 7.56 (ddd, J = 8.3, 7.1, 1.3 Hz, 1H), 7.47−7.53 (m, 2H), 7.41 (d, J = 8.2 Hz, 2H), 2.54 (s, 3H).

4m (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.13 (d, J = 9.0 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 4.03 (t, J = 7.8 Hz, 2H), 3.92 (s, 3H), 1.93 (quint, J = 7.6 Hz, 2H), 1.45 (sextet, J = 7.5

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Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 163.95, 152.27 (C═O), 148.11, 148.03, 146.84, 146.60, 146.56, 146.40, 146.29, 146.18, 146.03, 145.60, 145.23, 145.17, 145.14, 145.06, 144.71, 144.40, 143.66, 142.97, 142.90, 142.86, 142.71, 142.15, 142.08, 142.01, 141.66, 141.37, 139.89, 138.41, 136.52, 136.47, 131.20, 131.03, 114.00, 79.96 (C(sp^3) of C_{60}), 78.99 (C(sp^3) of C_{60}), 55.54, 43.12, 31.71, 20.63, 14.00; UV−vis ($CHCl_3$) λ_{max}/nm 256, 318, 418, 452, 680; HRMS (MALDI-TOF MS) m/z $[M + H]^+$ calcd for $C_{72}H_{17}N_2O_4S$ 1005.0909, found 1005.0899, $[M + Na]^+$ calcd for $C_{72}H_{16}N_2NaO_4S$ 1027.0728, found 1027.0727.

4n (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.44 (s, 4H), 4.04 (t, J = 7.8 Hz, 2H), 1.93 (quint, J = 7.7 Hz, 2H), 1.46 (sextet, J = 7.5 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 151.86 (C═O), 150.78, 148.20, 148.09, 146.67, 146.48, 146.43, 146.28, 146.14, 145.52, 145.32, 145.24, 144.68, 144.62, 144.56, 144.45, 144.24, 143.50, 143.06, 143.00, 142.95, 142.69, 142.21, 142.13, 142.07, 141.62, 141.30, 140.03, 138.57, 136.72, 136.36, 130.26, 124.09, 80.12 (C(sp^3) of C_{60}), 79.06 (C(sp^3) of C_{60}), 43.33, 31.62, 20.59, 13.95; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 418, 453, 680; HRMS (MALDI-TOF MS) m/z $[M + H]^+$ calcd for $C_{71}H_{14}N_3O_5S$ 1020.0654, found 1020.0649.

4o (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 4.16 (t, J = 7.8 Hz, 2H), 3.72 (s, 3H), 2.02 (quint, J = 7.7 Hz, 2H), 1.54 (sextet, J = 7.5 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 153.04 (C═O), 148.13, 148.07, 146.65, 146.59, 146.43, 146.37, 146.22, 146.10, 145.59, 145.27, 145.19, 144.84, 144.70, 144.61, 144.40, 143.64, 142.97, 142.93, 142.87, 142.69, 142.17, 142.10, 141.98, 141.67, 141.38, 139.97, 138.45, 136.66, 136.49, 80.23 (C(sp^3) of C_{60}), 78.76 (C(sp^3) of C_{60}), 43.25, 43.09, 31.75, 20.64, 14.01; UV−vis ($CHCl_3$) λ_{max}/nm 256, 318, 417, 453, 680; HRMS (MALDI-TOF MS) m/z $[M + H]^+$ calcd for $C_{66}H_{13}N_2O_3S$ 913.0647, found 913.0639, $[M + Na]^+$ calcd for $C_{66}H_{12}N_2NaO_3S$ 935.0466, found 935.0463.

NMI-Catalyzed Reaction of Aziridinofullerene 1 with Benzoyl- and Ester-Substituted Ureas 5a and 5b. A mixture of aziridinofullerene **1** (for **5a**, 17.8 mg, 0.02 mmol; for **5b**, 35.6 mg, 0.04 mmol), urea **5a** or **5b** (2 equiv), and NMI (for **5a**, 0.1 mmol, 100 μL of 1 mol/L NMI solution in chlorobenzene; for **5b**, 0.2 mmol, 200 μL of 1 mol/L NMI solution in chlorobenzene) in 3 mL of dry chlorobenzene was stirred at 120 °C for the designated time until completion of the reaction as determined by TLC. The solvent was removed in vacuo, and the residue was purified on a silica gel column using CS_2/toluene as the eluent to give the product **6a** (13.3 mg, 68%) or **6b** (13.9 mg, 36%)

6a (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.92 (d, J = 7.0 Hz, 2H), 7.63 (t, J = 7.4 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); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 170.66 (C═O), 153.34 (C═O), 148.05, 148.02, 146.95, 146.66, 146.56, 146.40, 146.28, 146.23, 146.15, 145.98, 145.57, 145.53, 145.28, 145.23, 144.76, 144.40, 144.07, 142.95, 142.88, 142.74, 142.18, 142.11, 142.03, 141.62, 141.47, 139.58, 138.60, 136.80, 136.53, 136.24, 135.29, 132.03, 128.81, 128.56, 128.12, 128.06, 79.01 (C(sp^3) of C_{60}), 78.47 (C(sp^3) of C_{60}), 46.76; UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 417, 453, 680; HRMS (MALDI-TOF MS) m/z $[M + H]^+$ calcd for $C_{75}H_{13}N_2O_2$ 973.0977, found 973.0968, $[M + Na]^+$ calcd for $C_{75}H_{12}N_2NaO_2$ 995.0796, found 995.0795.

6b (brown solid, mp >300 °C): ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.92−7.94 (m, 2H), 7.73−7.77 (m, 2H), 7.59 (tt, J = 7.4 Hz, J = 1.6 Hz, 1H), 7.53 (t, J = 7.3 Hz, 2H), 7.52 (t, J = 7.4 Hz, 2H), 7.45 (tt, J = 7.4, 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 170.74 (C═O), 152.80 (C═O), 148.11, 146.94, 146.73, 146.64, 146.44, 146.39, 146.29, 146.21, 145.94, 145.76, 145.66, 145.31, 145.27, 144.82, 144.46, 142.99, 142.91, 142.88, 142.82, 142.15, 142.10, 142.05, 141.70, 141.61, 139.84, 138.62, 136.54, 136.30, 135.18, 134.70, 131.87, 130.77, 129.73, 129.50, 128.71, 128.01, 80.46 (C(sp^3) of C_{60}), 78.50 (C(sp^3) of C_{60}); UV−vis ($CHCl_3$) λ_{max}/nm 257, 318, 417, 452, 679; HRMS (MALDI-TOF MS) m/z $[M + Na]^+$ calcd for $C_{74}H_{10}N_2NaO_2$ 981.0640, found 981.0634.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

UV−vis spectra of **4b** and **6a** and ^{1}H and ^{13}C NMR spectra of the products. 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) For selected reviews, see: (a) Maroto, E. E.; Izquierdo, M.; Reboredo, S.; Marco-Martínez, J.; Filippone, S.; Martín, N. *Acc. Chem. Res.* **2014**, *47*, 2660−2670. (b) Tzirakis, M. D.; Orfanopoulos, M. *Chem. Rev.* **2013**, *113*, 5262−5321. (c) Matsuo, Y.; Nakamura, E. *Chem. Rev.* **2008**, *108*, 3016−3028. (d) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, 6083−6094. (e) Zhu, S.-E.; Wang, G.-W. *Chem. Soc. Rev.* **2013**, *42*, 7535−7570. (f) Yurovskaya, M. A.; Trushkov, I. V. *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 367.

(2) (a) Tsuruoka, R.; Nagamachi, T.; Murakami, Y.; Komatsu, M.; Minakata, S. *J. Org. Chem.* **2009**, *74*, 1691−1697. (b) Nambo, M.; Segawa, Y.; Itami, K. *J. Am. Chem. Soc.* **2011**, *133*, 2402−2405.

(3) Takeda, Y.; Kawai, H.; Minakata, S. *Chem.—Eur. J.* **2013**, *19*, 13479−13483.

(4) Yang, H.-T.; Xing, M.-L.; Zhu, Y.-F.; Sun, X.-Q.; Cheng, J.; Miao, C.-B.; Li, F.-B. *J. Org. Chem.* **2014**, *79*, 1487−1492.

(5) Yang, H.-T.; Xing, M.-L.; Lu, X.-W.; Li, J.-X.; Cheng, J.; Sun, X.-Q.; Miao, C.-B. *J. Org. Chem.* **2014**, DOI: 10.1021/jo5020596.

(6) (a) Segura, J. L.; Martín, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31−47. (b) Martín, N.; Sánchez, L.; Ángeles Herranz, M.; Illescas, B. M.; Guldi, D. M. *Acc. Chem. Res.* **2007**, *40*, 1015−1024.

(7) (a) Langa, F.; Nierengarten, J.-F. *Fullerenes: Principles and Applications*; RSC Publishing: Cambridge, U.K., 2007. (b) Martín, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527−2547. (c) Illescas, B. M.; Martín, N. *C. R. Chim.* **2006**, *9*, 1038−1050.

(8) (a) Guldi, D. M.; González, S.; Martín, N.; Antón, A.; Garín, J.; Orduna, J. *J. Org. Chem.* **2000**, *65*, 1978−1983. (b) Ángeles Herranz, M.; Illescas, B. M.; Martín, N. *J. Org. Chem.* **2000**, *65*, 5728−5738. (c) Illescas, B. M.; Martín, N. *J. Org. Chem.* **2000**, *65*, 5986−5995. (d) Langa, F.; de la Cruz, P.; Espíldora, E.; González-Cortés, A.; de la Hoz, A.; López-Arza, V. *J. Org. Chem.* **2000**, *65*, 8675−8684.

(9) (a) Shigemitsu, Y.; Kaneko, M.; Tajima, Y.; Takeuchi, K. *Chem. Lett.* **2004**, *33*, 1604−1605. (b) Li, F.-B.; Liu, T.-X.; You, X.; Wang, G.-W. *Org. Lett.* **2010**, *12*, 3258−3261. (c) Wang, G.-W.; Shu, L.-H.; Wu, S.-H.; Wu, H.-M.; Lao, X.-F. *J. Chem. Soc., Chem. Commun.* **1995**, 1071−1072.

(10) Li, F.-B.; You, X.; Liu, T.-X.; Wang, G.-W. *Org. Lett.* **2012**, *14*, 1800−1803.

(11) (a) Hou, H.-L.; Gao, X. *J. Org. Chem.* **2012**, *77*, 2553−2558. (b) Li, F.-B.; Liu, T.-X.; Wang, G.-W. *J. Org. Chem.* **2008**, *73*, 6417−6420. (c) Takeda, Y.; Enokijima, S.; Nagamachi, T.; Nakayama, K.; Minakata, S. *Asian J. Org. Chem.* **2013**, *2*, 91−97. (d) Yang, H.-T.; Ren, W.-L.; Dong, C.-P.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Tetrahedron Lett.* **2013**, *54*, 6799−6803. (e) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2013**, *15*, 4650−4653.

(12) You, X.; Wang, G.-W. *J. Org. Chem.* **2014**, *79*, 117−121.
(13) (a) He, C.-L.; Liu, R.; Li, D.-D.; Zhu, S.-E.; Wang, G.-W. *Org. Lett.* **2013**, *15*, 1532−1535. (b) Hou, H.-L.; Li, Z.-J.; Li, S.-H.; Gao, X. *Org. Lett.* **2013**, *15*, 4646−4649. (c) Romanova, I. P.; Kalinin, V. V.; Nafikova, A. A.; Yakhvarov, D. G.; Zverev, V. V.; Kovalenko, V. I.; Rusinov, G. L.; Plekhanov, P. V.; Charushin, V. N.; Sinyashin, O. G. *Russ. Chem. Bull.* **2003**, *52*, 173−178.
(14) Yang, H.-T.; Lu, X.-W.; Xing, M.-L.; Sun, X.-Q.; Miao, C.-B. *Org. Lett.* **2014**, DOI: 10.1021/ol5028305.
(15) For reviews, see: Muñiz, K.; Martínez, C. *J. Org. Chem.* **2013**, *78*, 2168−2174 and references cited therein.
(16) (a) 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. (b) Miao, C.-B.; Lu, X.-W.; Wu, P.; Li, J.-X.; Ren, W.-L.; Xing, M.-L.; Sun, X.-Q.; Yang, H.-T. *J. Org. Chem.* **2013**, *78*, 12257−12262. (c) Yang, H.-T.; Liang, X.-C.; Wang, Y.-H.; Yang, Y.; Sun, X.-Q.; Miao, C.-B. *J. Org. Chem.* **2013**, *78*, 11992−11998.
(17) The pK_a of the conjugate acid of DMAP is 9.2; the pK_a of the conjugate acid of NMI is 6.95.
(18) Moore, J. D.; Harned, A. M.; Henle, J.; Flynn, D. L.; Hanson, P. R. *Org. Lett.* **2002**, *4*, 1847−1849.
(19) (a) Cervelló, J.; Sastre, T. *Synthesis* **1990**, 221−222. (b) Tan, D.; Štrukil, V.; Mottillo, C.; Friščić, T. *Chem. Commun.* **2014**, *50*, 5248−5250.
(20) (a) Wiley, P. F. *J. Am. Chem. Soc.* **1949**, *71*, 1310−1311. (b) Librowski, T.; Kubacka, M.; Meusel, M.; Scolari, S.; Müller, C.; Gütschow, M. *Eur. J. Pharmacol.* **2007**, *559*, 138−149.