Note

BF3.Et2O or DMAP-Catalyzed Double Nucleophilic Substitution Reaction of Aziridinofullerenes with Sulfamides or Amidines

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BF_3·Et_2O or DMAP-Catalyzed Double Nucleophilic Substitution Reaction of Aziridinofullerenes with Sulfamides or Amidines

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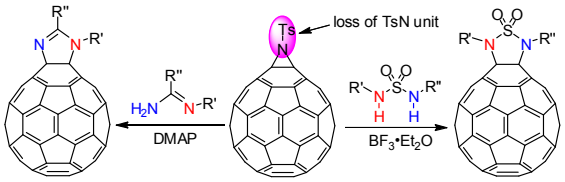


Abstract

BF_3·Et_2O-catalyzed double nucleophilic substitution reaction of *N*-tosylaziridinofullerene with sulfamides has been exploited for the easy preparation of cyclic sulfamide-fused fullerene derivatives. Moreover, the Lewis base-catalyzed double amination of N-tosylaziridinofullerene, with amidines as the diamine source, is demonstrated for the first time. The present methods provide new routes to cyclic 1,2-diaminated [60]fullerenes.

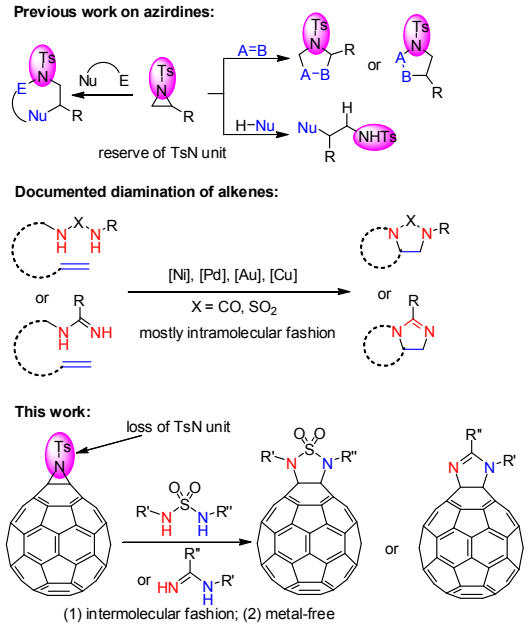
Chemical modification of fullerenes,[1] which can adjust the physical, chemical, biological, and electronic properties and solubility, has been an attractive research field for designing more fullerene derivatives and investigating their application in different fields. The one-step reaction of C_{60} with a variety of reactants is the most used method to prepare different fullerene derivatives.[2] However, not all the derivatives can be easily prepared directly from C_{60}. Thus, the development of new methods to synthesize various functionalized fullerenes with new structure from an easily

available precursor is an important endeavor. *N*-Sulfonylated aziridinofullerene is one of the most important classes of nitrogen-containing fullerene derivatives, which can be easily synthesized from azides,[3] chloramines,[4] sulfilimines,[5] iminophenyliodinanes,[6] and *N*,*N*-dihalosulfonamides.[7] We have also developed hypervalent iodine reagents-mediated reaction of C_{60} with sulfonamides for the preparation of aziridinofullerenes.[8] The chemistry of aziridines is centered on ring-opening reactions with a wide range of nucleophiles or formal [3+2] reactions with dipolarophiles as a consequence of their ring strain.[9] These reactions have led to the formation of various important 1,2-difunctionalized scaffolds and five-membered ring heterocycles. Recently, a novel tandem ring-opening/closing reaction of aziridines with those substrates containing two functional groups (Nu---E) has attracted more attention for the synthesis of five- to seven-membered ring heterocycles (Scheme 1).[9h, 10] In these transformations the "TsN" unit was reserved in the product. In case of the *N*-sulfonylated aziridinofullerenes, besides the classic formal [3+2] reactions with CO_2, arylisocyanates,[11] and carbonyls,[12] they could also undergo unique acid-catalyzed double nucleophilic substitution reaction with aromatic compounds or bifunctional nucleophiles accompanying with the loss of sulfonamides.[6, 13] Under the guidance of this new methodology, we envisioned that 1,3-diamines, which contained two nucleophilic sites, might react with *N*-sulfonylated aziridinofullerenes to generate cyclic 1,2-diaminated [60]fullerenes. Compared to the recently emerged transition-metal-catalyzed or promoted oxidative intramolecular diamination of olefin, which has been a suitable approach to generate bicyclic heterocycles with two nitrogen atoms (Scheme 1),[14] this would be a new route to generate cyclic diamination products of alkenes. Up to now, the direct diamination of C_{60} with sulfamides and ureas is still a challenge partially due to the unfavorability of intermolecular reaction. Only a few reports have appeared for the preparation of C_{60}-fused five-membered ring heterocyclic derivatives with two nitrogen atoms

directly linking to C_{60}. The Ag_2CO_3-mediated or CuI-catalyzed oxidative cycloaddition of C_{60} with amidines for the preparation of fulleroimidazoles was developed by the Wang groups and us, respectively.[15] Minakata and coworkers explored a formal [3+2] reaction of N-sufonylated aziridinofullerene with aryl isocyanates for the preparation of C_{60}-fused cyclic urea derivatives.[11] Most recently, we developed a hypervalent iodine-mediated diamination of C_{60} with sulfamides or phosphoryl diamides for the preparation of novel C_{60}-fused cyclic sulfamide or C_{60}-fused phosphoryl diamide derivatives.[16]

In continuation of our interest in fullerene chemistry,[8,12,16,17] we reported here the $BF_3{\cdot}Et_2O$ or DMAP-catalyzed reaction of *N*-tosylaziridinofullerenes with sulfamides or amidines for the easy preparation of cyclic 1,2-diaminated [60]fullerenes (Scheme 1).

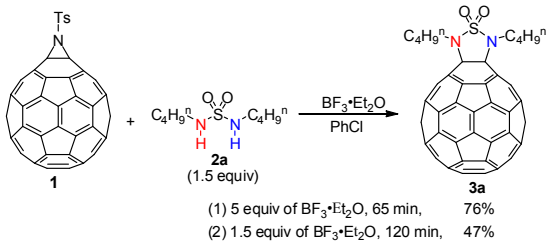
Scheme 1



Initially, the N-tosylaziridinofullerene **1** and N,N'-dibutylsulfamide **2a** were reacted in dry chlorobenzene using $BF_3{\cdot}Et_2O$ as the catalyst, which was the effective Lewis acid catalyst in our previously reported conditions for the reaction of **1** with carbonyl compounds (Scheme 2).[12] In the presence of 5 equiv of $BF_3{\cdot}Et_2O$, the desired cyclic 1,2-diaminated product **3a** was obtained in 76%

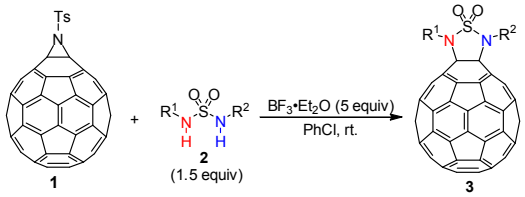
yield after stirring for 65 min at room temperature. Decreasing the amount of $BF_3{\cdot}Et_2O$ to 1.5 equiv led to a longer reaction time and lower yield.

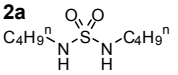
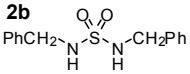
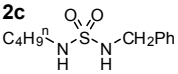
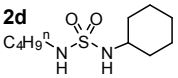
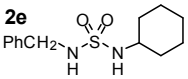
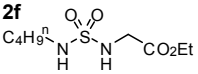
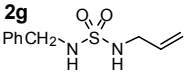
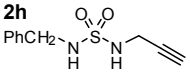
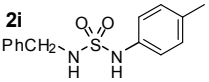
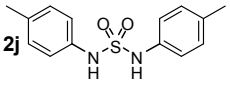
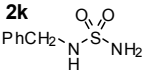
Scheme 2 $BF_3{\cdot}Et_2O$-Catalyzed Reaction of Aziridinofullerene 1 with *N,N′*-Dibutylsulfamide 2a



Using $BF_3{\cdot}Et_2O$ as the catalyst, we examined the generality of this kind of double nucleophilic substitution reaction (Table 1). When R^1 and R^2 were both alkyl group, the reaction proceeded well to give the desired products in good yield (Table 1, entries 1–8). Replacing one of the substituent on nitrogen atom by aryl group resulted in the failure of reaction (Table 1, entry 9). It should be noted that this kind of transformation has a merit in contrast to our recently reported $PhIO/I_2$-mediated diamination of C_{60} with sulfamides,[16] that was, the alkenyl and alkynyl groups were also tolerated to afford good yields of **3g** and **3h** (Table 1, entries 7 and 8). Moreover, we were fortunate to find that aryl substituted sulfamides were also applicable to the reaction, affording the desired products **3i** and **3j**, respectively. Under $PhIO/I_2$ conditions, no reaction occurred for substrates **2g-j**. Interestingly, when the mono substituted sulfamide **2k** was subjected to the reaction, product **3k** was also furnished in excellent yield. The presence of N-H unit in compound **3k** allowed their further transformation to other more complicated fullerene derivatives.

Table 1 Substrate Scope for the $BF_3{\cdot}Et_2O$-Catalyzed Reaction of Aziridinofullerene 1 with Sulfamides



entry	carbonyls	product	time (min)	yield (%)[a]
1	**2a** 	**3a**	65	76
2	**2b** 	**3b**	30	88
3	**2c** 	**3c**	50	74
4	**2d** 	**3d**	120	58
5	**2e** 	**3e**	45	80
6	**2f** 	**3f**	120	77
7	**2g** 	**3g**	20	79
8	**2h** 	**3h**	20	90
9	**2i** 	**3i**	20	82
10	**2j** 	**3j**	20	83
11	**2k** 	**3k**	20	65

[a] Isolated yield.

Amidines as another commonly used precursor in the diamination of olefins also contained two nucleophilic sites (Figure 1). On the basis of known reactivity of *N*-tosylaziridinofullerene, we envisioned a new method to produce the fulleroimidazoles by the Lewis acid-catalyzed reaction of amidines with *N*-tosylaziridinofullerene **1**. To explore this approach, a model reaction between **1** and *N*-(p-tolyl)-4-methylbenzamidine **4a** was carried out in the presence of 5 equiv of $BF_3{\cdot}Et_2O$. No expected product 5a was detected and most of **1** was converted to C_{60} (Table 2, entry 1). Other commonly used acid catalysts including $Zn(OTf)_2$, $Sc(OTf)_3$, trifluoromethanesulfonic acid (TfOH), and methanesulfonic acid (MSA) were also ineffective (Table 2, entries 2-5). In the presence of TfOH at room temperature or MSA at 100 ºC, most of **1** was transformed to C_{60}. In terms of

$Zn(OTf)_2$ and $Sc(OTf)_3$, no reaction was observed and **1** was totally recovered. Later on, the combination of $Sc(OTf)_3$ with a ligand was tried (Figure 1). An interesting phenomenon was observed. When 1 equiv of 2,2'-isopropylidenebisoxazoline (BOX, Figure 1) was added as the ligand, trace of desired product **5a** was observed on TLC (Table 2, entry 6). Increasing the amount of BOX to 8 equiv improved the yield to 21% (Table 2, entry 7). Replacing the BOX by Bpy gave similar result and afforded **5a** in 15% yield (Table 2, entry 8). This reminded us the metal salts may not play an actual catalytic role in the reaction. In the absence of metal salts, treatment of **1** and **4a** with 1 equiv of 2,2'-bipyridine (Bpy) at 100 ^{o}C for 6 h indeed provided **5a** in 32% yield (Table 2, entry 9). The fact that DMAP could also catalyze the transformation demonstrated the ligands BOX and Bpy only played the role of a base. This was the first example of base-catalyzed double nucleophilic substitution reaction of *N*-tosylaziridinofullerene. To the best of our knowledge, the most similar conversion was the Et_3N-catalyzed reaction of oxiranes with benzamidines for the preparation of imidazoles[18] and in which the oxirane O was maintained in the product. Other commonly used bases such as Et_3N, DBU, and K_2CO_3 were also screened (Table 2, entries 11-13). Et_3N and K_2CO_3 showed lower catalytic activity than DMAP. Using DBU as the base led to full transformation of *N*-tosylaziridinofullerene **1** to C_{60} and unidentified product with very high polarity within half an hour. Catalytic amount of DMAP (0.2 equiv) gave a higher yield of **5a** (Table 2, entry 15). Reducing the temperature to 70 °C led to a longer reaction time and lower yield of **5a** (Table 2, entry 14). It was worth noting that both O_2 and H_2O have no influence on the reaction. However, in the recently reported PCy_3-catalyzed formal [3+2] reaction of N-sulfonylated aziridinofullerenes with CO_2 or arylisocyanates,[11] anhydrous and oxygen-free operations were indispensable. Eventually, the molar ratio of C_{60}:**4a**:DMAP as 1:1.5:0.2 and the reaction temperature as 100 °C were selected as the optimal condition for subsequent investigation of the double nucleophlic

substitution of *N*-tosylaziridinofullerene **1** with amidines (Table 3).

Figure 1 Structure of Sulfamide, Amidine, and BOX

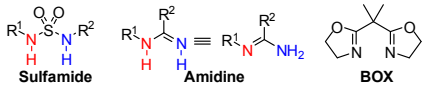
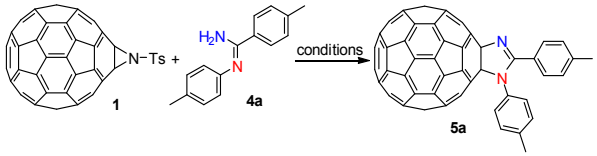


Table 2 Screening of the Reaction Conditions[a]



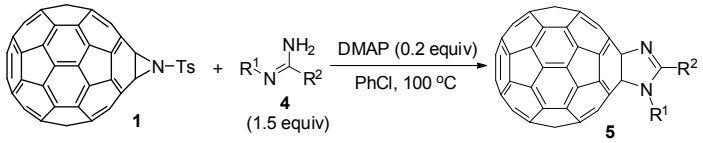
entry	additives	**1**/**4a**/additives	T (ºC)	time (h)	yield (%)[b]
1	BF_3·Et_2O	1:1.5:5	rt	6	0
2	TfOH	1:1.5:1	rt	0.5	0
3	MSA	1:1.5:1	rt or 100	2	0
4	$Zn(OTf)_2$	1:1.5:1	rt or 100	6	0
5	$Sc(OTf)_3$	1:1.5:1	rt or 100	6	0
6	$Sc(OTf)_3$/BOX	1:1.5:1:1	100	6	trace
7	$Sc(OTf)_3$/BOX	1:1.5:1:8	100	8	21
8	$Sc(OTf)_3$/Bpy	1:1.5:1:8	100	8	15
9	Bpy	1:1.5:1	100	6	32
10	DMAP	1:1.5:1	100	1	81
11	Et_3N	1:1.5:1	100	5	30
12	DBU	1:1.5:1	rt	0.25	0
13	K_2CO_3	1:1.5:1	100	6	44
14[c]	DMAP	1:1.5:1	100	1	70
15	DMAP	1:1.5:0.2	100	4	87
16[d]	DMAP	1:1.5:0.2	100	5	85

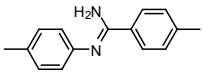
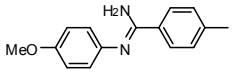
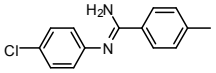
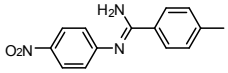
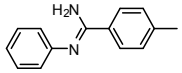
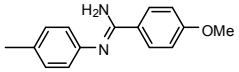
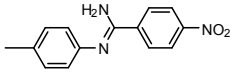
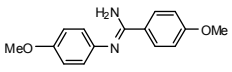
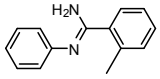
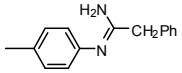
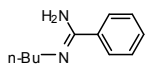
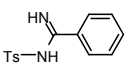
[a] Unless otherwise noted, the reactions were carried out with 0.02 mmol of **1** and proper additives in 3.5 mL of dry chlorobenzene. [b] Isolated yield. [c] The reaction was operated at 70 °C. [d] The reaction was carried out under N_2 atmosphere with the 4Å molecular sieve as additive.

Amidines with both aryl substituents gave good yield of fulleroimidazoles **5** (Table 3, entries 1–9). The electronic effect of the substituent group on the phenyl ring did not significantly influence the reaction efficiency. Fortunately, amidine **4l** bearing a tosyl group on the nitrogen atom also afforded the product **5l** in 61% yield, albeit much longer reaction time and 3 equiv of DMAP were needed (Table 3, entry 12). However, the reaction of C_{60} with **4l** under our recently reported

CuI/Phen conditions,[15b] which was effective catalytic system for the preparation of fulleroimidazoles, did not generate **5l**. It is a pity that no reaction occurred when either R^1 or R^2 was an alkyl group (Table 3, entries 10 and 11).

Table 3. DMAP-Catalyzed Reaction of Aziridinofullerene 1 with Amidines for the Synthesis of Fulleroimidazoles



entry	substrate	product	time (h)	yield[a]
1		**5a**	4	87
2		**5b**	5	83
3		**5c**	5	86
4		**5d**	6	92
5		**5e**	5	82
6		**5f**	4	81
7		**5g**	4	91
8		**5h**	6	70
9		**5i**	4	83
10		**5j**	12	0
11		**5k**	12	0
12[b]		**5l**	30	61

[a] Isolated yield. [b] **1**:**4l**:DMAP = 1:2:3.

The identities of known compounds were confirmed through comparison of their TLC with those obtained from our previous work and their spectral data with those reported in the literatures.[15,16]

New compounds **4g**, **4h**, and **5l** were unambiguously characterized by their HRMS, ^{1}H NMR, ^{13}C NMR, and UV-vis spectra.

In summary, $BF_3{\cdot}Et_2O$ or DMAP-catalyzed double nucleophilic reaction of *N*-tosylaziridinofullerene with sulfamides or amidines has been developed for the easy preparation of cyclic 1,2-diaminated fullerenes. This protocol is attractive in view of mild and metal-free conditions, cheap and easily available catalyst, and high yield of product. For the first time, this kind of double nucleophilic reaction of *N*-tosylaziridinofullerene was realized using a Lewis base as catalyst when amidines were chosen as the nucleophilic reagent. In contrast to our recently developed methodology for the preparation of C_{60}-fused cyclic sulfamides through hypervalent iodine-mediated diamination of C_{60} with sulfamides, the $BF_3{\cdot}Et_2O$-catalyzed transformation showed better functional group tolerance and gave better yield. Further investigations on the Lewis acid or base-catalyzed reaction of *N*-tosylaziridinofullerene with other compounds containing 1,3- or 1,4-double nucleophilic sites are currently underway.

Experimental Section

The Known Sulfamides 2 and Amidines 4 were Prepared as Described in Our Recent Works and Literatures.[16,19]

Preparation of 2g and 2h

A solution of 2-bromoethanol (1.25 g, 10 mmol) in 4 mL of dry dichloromethane was added dropwise to a stirred solution of chlorosulfonyl isocyanate (1.41 g, 10 mmol) in 10 mL of dry dichloromethane at 0 °C over 20 min. After further stirring for 40 min at room temperature, the mixture was cooled to 0 °C with an ice bath. Benzylamine (1.17 g, 11 mmol) and triethylamine (2.53 g, 25 mmol) in 8 mL of dry dichloromethane were added dropwise to the mixtrure. After completion of the addition, the mixture was allowed to warm to room temperature and continued to

stir for 2 h. Then the mixture was washed with aqueous hydrochloric acid (0.1 N, 20 mL × 2), water (20 mL), saturated sodium bicarbonate, and dried over anhydrous Na_2SO_4. The filtrate was concentrated under vacuum to afford the crude product.

A mixture of the above crude product (256 mg, 1 mmol), allylamine or 2-propynylamine (5 equiv), and triethylamine (0.25 g, 2.5 mmol) in 10 mL of acetonitrile was heated at reflux for 6 h. After cooling to room temperature, the mixture was diluted with 20 mL of ethyl acetate, and then washed with aqueous hydrochloric acid (0.1 N, 20 mL × 2), water (20 mL), saturated sodium bicarbonate, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude product as a colorless solid. The crude product was further purified by column chromatography (EtOAc/petroleum ether) to provide final product **2g** (163 mg, 72%) or **2h** (156 mg, 70%).

2g: colorless solid, mp: 108–109 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.39 (m, 5H), 5.81 (ddt, *J* = 17.0, 10.2, 5.9 Hz, 1H), 5.24 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.17 (dq, *J* = 10.2, 1.3 Hz, 1H), 4.48 (br, 1H), 4.23 (d, *J* = 6.0 Hz, 1H), 4.16 (br, 1H), 3.62 (tt, *J* = 6.1, 1.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.78, 133.31, 128.93, 128.19, 128.14, 117.94, 47.39, 45.84; FT-IR ν/cm^{-1} (KBr) 3288, 3269, 3086, 3065, 3034, 3012, 2937, 2847, 1495, 1454, 1437, 1423, 1342, 1317, 1148, 1086, 1065, 1043, 987, 930, 906, 731, 696, 534; HRMS (+ESI) m/z $[M+Na]^+$ calcd for $C_{10}H_{14}N_2NaO_2S$ 249.0674, found 249.0669.

2h: colorless solid, Mp: 64–65 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.40 (m, 5H), 4.55 (br, 1H), 4.44 (br, 1H), 4.27 (d, *J* = 6.2 Hz, 1H), 3.87 (dd, *J* = 6.1, 2.5 Hz, 2 H), 2.32 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.45, 128.94, 128.27, 128.21, 78.98, 73.03, 47.52, 32.89; FT-IR ν/cm^{-1} (KBr) 3292, 3269, 3065, 3032, 2924, 2847, 2129, 1495, 1454, 1437, 1420, 1358, 1319, 1150, 1068, 910, 727, 696, 679, 646, 582, 532; HRMS (+ESI) m/z $[M+Na]^+$ calcd for $C_{10}H_{12}N_2NaO_2S$ 247.0517,

found 247.0513.

General Procedure for the BF_3·Et_2O-Catalyzed Reaction of N-Tosylaziridinofullerene 1 with Sulfamides

BF_3·Et_2O (12 μL, 0.1 mmol) was added in one potion to a solution of N-Tosylaziridinofullerene **1** (17.8 mg, 0.02 mmol) and sulfamides **2** (0.03 mmol) in 3 mL of dry chlorobenzene. The mixture was stirred at room temperature until the disappearance of **1** determined by TLC. The solvent was removed under reduced pressure, and the residue was purified on a silica gel column using CS_2/toluene as the eluent to give the products **3** (**3a**, 14.1 mg; **3b**, 17.4 mg; **3c**, 14.3 mg; **3d**, 11.0 mg; **3e**, 15.8 mg; **3f**, 14.8 mg; **3g**, 14.9 mg; **3h**, 16.9 mg; **3i**, 16.4 mg; **3j**, 16.5 mg; **3k**, 11.8 mg;).

3a: ^{1}H NMR (400 MHz, CS_2-$CDCl_3$) δ 4.05 (t, J = 7.5 Hz, 4H), 2.13 (quint, 4H, J = 7.5 Hz), 1.60 (sextet, 4H, J = 7.5 Hz), 1.03 (t, J = 7.4 Hz, 6H); ^{13}C NMR (10 MHz, CS_2-$CDCl_3$) δ 148.30, 146.62, 146.56, 146.35, 146.18, 145.54, 145.33, 144.74, 144.39, 143.07, 142.91, 142.34, 141.92, 141.66, 139.43, 137.73, 79.29 (sp^3-C of C_{60}), 46.05, 31.97, 20.67, 13.99.

3g (brown solid, mp > 300 °C): ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 7.57 (d, J = 7.4 Hz, 2H), 7.27 (t, J = 7.4 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 6.34 (ddt, J = 17.1, 10.2, 6.1 Hz, 1H), 5.51 (dq, J = 17.1, 1.4 Hz, 1H), 5.35 (dq, J = 10.3, 1.3 Hz, 1H), 5.23 (s, 2H), 4.74 (dt, J = 6.1, 1.4 Hz, 2H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) δ 148.17, 146.56, 146.51, 146.27, 146.26, 146.17, 146.07, 146.03, 145.42, 145.24, 144.68, 144.61, 144.59, 144.40, 142.91, 142.81, 142.80, 142.26, 141.86, 141.74, 141.49, 141.39, 139.20, 138.89, 137.76, 137.31, 135.77, 133.22, 128.83, 128.64, 128.12, 119.78, 79.19 (sp^3-C of C_{60}), 79.13 (sp^3-C of C_{60}), 49.64, 48.71; UV-Vis ($CHCl_3$) λ_{max}/nm 256, 319, 420, 685; FT-IR ν/cm^{-1} (KBr) 2920, 2849, 1437, 1315, 1178, 1161, 1103, 1065, 926, 901, 851, 795, 731, 696, 527; HRMS (MALDI-TOFMS) m/z $[M+Na]^+$ calcd for $C_{70}H_{12}N_2NaO_2S$ 967.0517, found 967.0514.

3h (brown solid, mp > 300 °C): ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) δ 7.59 (d, J = 7.3 Hz, 2H), 7.27 (t,

J = 7.4 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 5.23 (s, 2H), 4.90 (d, *J* = 2.5 Hz, 2H), 2.49 (t, *J* = 2.5 Hz, 1H); **3h** has a very poor solubility, which make it difficult to be characterized by ^{13}C NMR analysis (only a spectrum with low resolution was achieved); UV-Vis ($CHCl_3$) λ_{max}/nm 256, 318, 420, 685; FT-IR ν/cm^{-1} (KBr) 3263, 2922, 2133, 1512, 1454, 1435, 1367, 1321, 1167, 1130, 1094, 1065, 947, 922, 795, 741, 694, 527; HRMS (MALDI-TOFMS) m/z $[M+Na]^+$ calcd for $C_{70}H_{10}N_2NaO_2S$ 965.0361, found 965.0357.

3i (brown solid, mp > 300 °C): ^{1}H NMR (400 MHz, CS_2-$CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.25-7.33 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.31 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CS_2-$CDCl_3$) δ 148.23, 148.17, 146.53, 146.40, 146.27, 146.25, 146.15, 146.11, 145.44, 145.23, 145.21, 144.75, 144.60, 144.42, 142.88, 142.79, 142.77, 142.31, 142.14, 141.83, 141.79, 141.54, 141.49, 140.17, 139.35, 138.84, 137.43, 137.28, 135.81, 131.53, 131.35, 130.37, 128.97, 128.65, 128.13, 80.65 (sp^3-C of C_{60}), 79.38 (sp^3-C of C_{60}), 50.08, 21.50; UV-Vis ($CHCl_3$) λ_{max}/nm 258, 320, 420, 687; FT-IR ν/cm^{-1} (KBr) 2920, 2851, 1508, 1454, 1437, 1365, 1331, 1169, 1022, 743, 696, 550, 527; HRMS (MALDI-TOFMS) m/z $[M+Na]^+$ calcd for $C_{74}H_{14}N_2NaO_2S$ 1017.0674, found 1017.0668.

3j (brown solid, mp > 300 °C): ^{1}H NMR (400 MHz, CS_2-$CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 4H), 7.30 (d, *J* = 8.1 Hz, 4H), 2.41 (s, 6H); ^{13}C NMR (100 MHz, CS_2-$CDCl_3$) δ 148.26, 146.53, 146.30, 146.27, 146.17, 145.47, 145.21, 144.65, 144.63, 142.87, 142.77, 142.21, 141.89, 141.68, 140.23, 139.34, 137.33, 131.78, 131.25, 130.39, 80.55 (sp^3-C of C_{60}), 21.51; UV-Vis ($CHCl_3$) λ_{max}/nm 257, 319, 420, 687; FT-IR ν/cm^{-1} (KBr) 2918, 2849, 1506, 1434, 1369, 1335, 1231, 1171, 1022, 1003, 640, 548, 527; HRMS (MALDI-TOFMS) m/z $[M+Na]^+$ calcd for $C_{74}H_{14}N_2NaO_2S$ 1017.0674, found 1017.0667.

3k (brown solid, mp > 300 °C): ^{1}H NMR (500 MHz, CS_2-DMSO-d_6) δ 10.48 (s, 1H), 7.62 (d, *J* =

7.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 5.11 (s, 2H); ^{13}C NMR (125 MHz, CS_2-DMSO-d_6) δ 148.66, 147.29, 147.21, 145.81, 145.60, 145.59, 145.36, 145.32, 145.23, 145.06, 144.74, 144.38, 144.36, 144.16, 143.97, 143.88, 143.67, 141.99, 141.89, 141.77, 141.48, 141.30, 141.07, 140.77, 140.52, 138.98, 137.87, 136.84, 136.38, 135.44, 128.10, 127.69, 127.08, 79.29 (sp^3-C of C_{60}), 75.24 (sp^3-C of C_{60}), 48.32; UV-Vis ($CHCl_3$) λ_{max}/nm 257, 319, 420, 686; FT-IR ν/cm^{-1} (KBr) 3221, 2920, 2850, 1510, 1389, 1321, 1180, 1130, 1049, 750, 696, 550, 527; HRMS (MALDI-TOFMS) m/z $[M+Na]^+$ calcd for $C_{67}H_8N_2NaO_2S$ 927.0204, found 927.0199.

General Procedure for the DMAP-Catalyzed Reaction of N-Tosylaziridinofullerene 1 with Amidines 4

A 0.1 mol/L of DMAP solution (for **4a**-**k**, 40 uL, 0.004 mmol; for **4l**, 7.3 mg DMAP was used directly, 0.06 mmol) in dry chlorobenzene was added to the solution of N-tosylaziridinofullerene (17.8 mg, 0.02 mmol) and amidines **4** (0.03 mmol) in 3 mL of dry chlorobenzene. The mixture was stirred at 100 °C until the disappearance of **1** detected by TLC. The solvent was removed under reduced pressure, and the residue was purified on a silica gel column using CS_2/toluene as the eluent to give the products **5** (**5a**, 16.4 mg; **5b**, 16.0 mg; **5c**, 16.5 mg; **5d**, 18.0 mg; **5e**, 15.2 mg; **5f**, 15.5 mg; **5g**, 17.7 mg; **5h**, 13.6 mg; **5i**, 15.4 mg; **5l**, 12.2 mg).

5a: ^{1}H NMR (500 MHz, CS_2-$CDCl_3$) *δ* 7.80 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (125 MHz, CS_2-$CDCl_3$) *δ* 164.23 (*C*=N), 149.12, 147.98, 147.76, 146.28, 146.18, 146.01, 145.97, 145.91, 145.87, 145.85, 145.61, 145.21, 145.14, 145.07, 144.69, 144.67, 144.12, 142.86, 142.75, 142.58, 142.43, 142.34, 142.13, 142.08, 141.71, 140.87, 140.49, 139.43, 138.18, 137.72, 137.06, 135.72, 130.42, 129.91, 129.48, 129.04, 126.91, 93.48 (sp^3-C of C_{60}), 86.85 (sp^3-C of C_{60}), 21.69, 21.38;

5l (brown solid, mp > 300 °C): ^{1}H NMR (400 MHz, CS_2-$CDCl_3$) δ 7.90 (d, *J* = 7.2 Hz, 2H), 7.61 (t,

J = 7.4 Hz,1H), 7.53 (t, *J* = 7.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CS_2-$CDCl_3$) δ 160.95 (*C*=N), 148.06, 148.04, 147.74, 146.58, 146.50, 146.43, 146.26, 146.24, 146.03, 145.73, 145.66, 145.29, 145.27, 145.20, 144.95, 144.57, 144.24, 143.18, 142.86, 142.81, 142.56, 142.39, 142.16, 141.87, 141.80, 141.77, 140.70, 138.40, 136.81, 136.75, 135.47, 130.75, 130.28, 130.02, 129.62, 128.14, 127.82, 93.35 (sp^3-C of C_{60}), 83.37 (sp^3-C of C_{60}), 21.84; UV-Vis ($CHCl_3$) λ_{max}/nm 256, 317, 419, 686; FT-IR ν/cm^{-1} (KBr) 2920, 2851, 1624, 1595, 1516, 1371, 1313, 1167, 1088, 1026, 767, 663, 615, 588, 546, 527; HRMS (MALDI-TOFMS) m/z $[M+H]^+$ calcd for $C_{74}H_{13}N_2O_2S$ 993.0698, found 993.0693.

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Supporting Information

^{1}H NMR and ^{13}C NMR spectra of the products **2g**-j, **3a**, **3g-k**, **5a**, and **5l**; ^{1}H NMR spectra of the known products **2k**, **3b-h**, and **5b-i**; UV-vis spectra of **3j** and **5l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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