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TsOH-mediated reaction of aziridinofullerene with diols for the preparation of fullerene-fused dioxygenated ring compounds†

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† Electronic supplementary information (ESI) available: NMR spectra of products **3a**-**k** as well as HRMS of **3b**, **3g**, and **3i**. See DOI: XXXX

The double nucleophilic substitution reaction of aziridinofullerene with diols in the presence of *p*-toluenesulfonic acid affords a series of rare fullerene-fused dioxygenated ring compounds with six- to ten-membered heterocycles. A possible reaction mechanism for product formation is proposed.

Introduction

Although fullerenes with unique structures display outstanding physical properties, the insolubility in polar organic solvents and water has hampered their applications in materials, medical chemistry, and nanotechnology. Therefore, the functionalization of fullerenes is extremely important.[1] Chemical modification of fullerenes to produce fullerene derivatives with one or several addends covalently bound to the spherical carbon framework have attracted extensive attention in the chemical community over the last two decades. In this context, a large number of organic reactions of fullerenes

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have been developed and many fullerene derivatives with widely structural diversities have been prepared.[1,2] For example, aziridinofullerenes, namely, three-membered nitrogen heterocycle-fused fullerene derivatives, have been successfully synthesized through different chemical reactions of fullerenes with azides,[3] chloramines,[4] sulfilimines,[5] iminophenyliodinanes,[6] *N*,*N*-dihalosulfonamides,[7] and amines.[8] Among these well-documented methods for chemical modification of fullerenes, the direct functionalization of pristine fullerenes is the most efficient protocol. Nevertheless, not all fullerene derivatives are easy to prepare via a simple one-step reaction. Thus, the further exploration and development of new reactions starting from fullerene derivatives still remains a challenge.

Aziridinofullerenes, especially the *N*-sulfonylated aziridinofullerenes, are a class of readily available and valuable precursors,[3-8] and allow the facile introduction of various nucleophiles onto the fullerene core via the easy ring opening of aziridine moiety with the aid of acids or bases because of the inherent ring strain, and therefore have been recently focused by different research groups.[6,9] Generally speaking, there are two strategies for further transformation of *N*-sulfonylated aziridinofullerenes, that is, the reserve and loss of "TsN" unit. In the case of the reserve of "TsN" unit, Minakata *et al.* reported the ring expansion of aziridinofullerenes through the insertion of CO_2 and aryl isocyanates catalyzed by a Lewis base.[9*a*] Yang and co-workers described the formal [3+2] reaction of aziridinofullerenes with carbonyl compounds promoted by a Lewis acid.[9*b*] As for the loss of "TsN" unit, Itami's group realized the reactions of aziridinofullerene with aromatic compounds or bifunctional

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nucleophiles under acid conditions to prepare a series of functionalized fullerenes that are difficult to synthesize by common methods.[6] Yang *et al.* accomplished the preparation of rare cyclic 1,2-diaminated fullerenes and fulleroimidazolidinones through the reactions of aziridinofullerene with sulfamides,[9c] amidines,[9c] and ureas[9d] catalyzed by a Lewis acid or base. It should be pointed out that the above-mentioned transformation of *N*-sulfonylated aziridinofullerenes promoted by Lewis acids or bases only afforded five-membered heterocycle-fused fullerene derivatives. Nevertheless, the strategy, i.e., the loss of "TsN" unit, provided a good opportunity for us to construct a series of fullerene-fused heterocycle derivatives with a larger ring by changing the relative position of two nucleophilic sites from bifunctional nucleophiles because the double nucleophilic substitution reactions of *N*-sulfonylated aziridinofullerenes with various nucleophiles in the presence of Lewis/Brønsted acids have been well confirmed.[9c,d] Under the guidance of this new idea, we envisioned that the diols with two potential nucleophilic sites might react with *N*-sulfonylated aziridinofullerenes to produce a large variety of rare fullerene-fused dioxygenated ring compounds, which at least possess a six-membered heterocycle. Although fullerene-fused 1,3-dioxolanes bearing a five-membered heterocycle have been extensively reported by different groups,[10] fullerene-fused dioxane/dioxepane derivatives with a six- or seven-membered heterocycle are still relatively rare. Up to now, only three examples of fullerene-fused dioxanes/dioxepanes are reported via a two-step reaction starting from C_{60}.[11] However, this known methodology requires large excess amount of reaction reagents together with high reaction temperature. On

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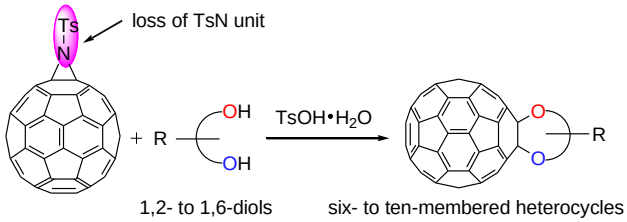
the other hand, fullerene-fused dioxocane/dioxecane derivatives with an eight- or ten-membered heterocycle are still unknown until today. In continuation of our interest in fullerene chemistry,[12] herein we describe the double nucleophilic substitution reaction of aziridinofullerene with diols in the presence of *p*-toluenesulfonic acid (TsOH) to afford a series of rare fullerene-fused dioxygenated ring compounds with six- to ten-membered heterocycles (Scheme 1).



Scheme 1 Reaction of aziridinofullerene with diols promoted by TsOH affording fullerene-fused dioxygenated ring compounds.

Results and discussion

At the onset, ethylene glycol (**2a**) and aziridinofullerene (**1**) were chosen as the model substrates to screen the reaction conditions. In the previous study, Lewis acid $BF_3{\cdot}Et_2O$ have proved to be an efficient catalyst for the double nucleophilic substitution reaction of *N*-sulfonylated aziridinofullerenes,[9c] and thus $BF_3{\cdot}Et_2O$ was first selected as a promoter. In addition, toluene was previously reported to react with *N*-sulfonylated aziridinofullerene in the presence of Lewis or Brønsted acids,[6] and therefore *o*-dichlorobenzene (ODCB) was chosen as the reaction solvent to replace toluene. To our delight, the reaction of **1**, $BF_3{\cdot}Et_2O$, and **2a** in a molar ratio of 1:2:2 in

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ODCB at 100 ^{o}C for 4 h under air conditions gave the desired fullerene-fused dioxane **3a** in 44% of isolated yield (entry 1, Table 1). Nevertheless, the $BF_3{\cdot}Et_2O$-mediated reaction also led to the concurrent formation of a large amount of [60]fullerene (C_{60}). Other Lewis acids such as $FeCl_3$ and $AlCl_3$ were also examined under the same conditions. In the presence of $FeCl_3$, almost the same phenomenon similar to $BF_3{\cdot}Et_2O$ was observed (entry 2, Table 1). As for $AlCl_3$, only a trace amount of **3a** was obtained even by extending the reaction time to 10 h probably attributed to the low reaction activity of $AlCl_3$ for the transformation of **1** (entry 3, Table 1). To improve the yield and selectivity of this reaction, Brønsted acids such as trifluoromethanesulfonic acid (TfOH) and *p*-toluenesulfonic acid (TsOH) were attempted. Unfortunately, the reaction promoted by TfOH only led to the formation of 29% yield of **3a** together with a large conversion to C_{60} and unknown fullerene byproducts (entry 4, Table 1). However, the reaction mediated by TsOH successfully produced the anticipated fullerene-fused dioxane **3a** in as high as 79% yield although a little amount of C_{60} was also observed (entry 5, Table 1). Raising the reaction temperature to 120 ^{o}C did not improve the yield of product **3a** (entry 6, Table 1). Increasing the amount of TsOH and **2a** had also no benefit to the yield of **3a** (entries 7-10, Table 1). Reducing the amount of TsOH to 0.3 equiv. (a catalytic amount) drastically decreased the yield of product **3a** even by extending the reaction time to 48 h (entry11, Table 1). Almost the same yield of **3a** under air and nitrogen conditions indicated that oxygen in air has no influence on the reaction (entry 5 vs entry 12, Table 1). Furthermore, no obvious product **3a** could be observed when the reaction

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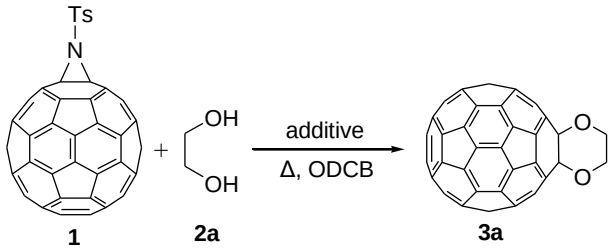
was conducted in the absence of Lewis or Brønsted acids (entry 13, Table 1). Therefore, the reagent molar ratio of **1**/TsOH/**2a** as 1:2:2, the reaction temperature as 100 ^{o}C, the reaction solvent as ODCB together with the air conditions were chosen as the optimized reaction conditions for subsequent investigation of the double nucleophlic substitution of **1** with different diols.

Table 1 Optimization of reaction conditions for the TsOH-mediated reaction of aziridinofullerene **1** with ethylene glycol **2a**[a]



1 **2a** **3a**

entry	additive	molar ratio[b]	temp. (^{o}C)	time (h)	yield of **3a**[c]
1	$BF_3{\cdot}Et_2O$	1:2:2	100	4	44%
2	$FeCl_3$	1:2:2	100	0.2	49%
3	$AlCl_3$	1:2:2	100	10	trace
4	TfOH	1:2:2	100	0.5	29%
5	$TsOH{\cdot}H_2O$	1:2:2	100	1.5	79%
6	$TsOH{\cdot}H_2O$	1:2:2	120	1.5	78%
7	$TsOH{\cdot}H_2O$	1:3:2	100	1	73%
8	$TsOH{\cdot}H_2O$	1:2:5	100	2	79%
9	$TsOH{\cdot}H_2O$	1:2:5	100	4	73%
10	$TsOH{\cdot}H_2O$	1:2:10	100	1.5	69%
11	$TsOH{\cdot}H_2O$	1:0.3:2	100	48	10%
12[d]	$TsOH{\cdot}H_2O$	1:2:2	100	1.5	78%
13	none	1:0:2	100	48	trace

[a]All reactions were performed under air conditions unless otherwise indicated. [b]Molar ratio refers to **1**/additive/**2a**. [c]Isolated yield. [d]The reaction was conducted under nitrogen conditions.

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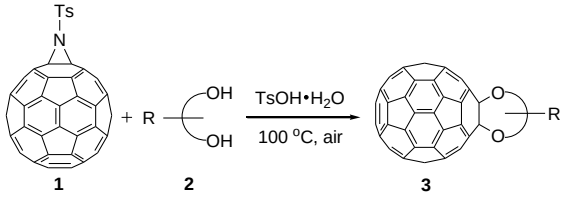
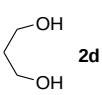
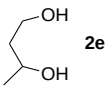
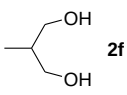
With the optimized reaction conditions in hand, other representative diols such as 1,2-propanediol (**2b**), (±)-2,3-butanediol (**2c**), 1,3-propanediol (**2d**), 1,3-butanediol (**2e**), 2-methyl-1,3-propanediol (**2f**), 2,2-dimethyl-1,3-propanediol (**2g**), 2,2,4-trimethyl-1,3-pentanediol (**2h**), 1,4-butanediol (**2i**), 1,2-benzenedimethanol (**2j**), and 1,6-hexanediol (**2k**) were employed as the substrates to obtain the desired fullerene-fused dioxygenated ring compounds **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **3i**, **3j**, and **3k**, respectively. The reaction conditions and yields for the TsOH-mediated reaction of aziridinofullerene **1** with diols **2a-k** are summarized in Table 2.

Table 2 Reaction conditions and yields for the reaction of aziridinofullerene **1** with diols **2a-k** in the presence of TsOH [a]



1 **2** **3**

diol **2**	time (h)	yield of **3** [b]
 **2a**	1.5	79%
 **2b**	1.5	74%
 **2c**	3	74%
 **2d**	1.5	94%
 **2e**	1	85%
 **2f**	1	70%

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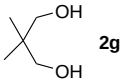
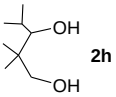
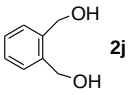
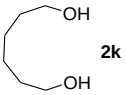
 **2g**	1	83%
 **2h**	1	68%
 **2i**	0.5	65%
 **2j**	1.5	46%
 **2k**	1.5	54%

[a]All reactions were performed in *o*-dichlorobenzene (4 mL) under air conditions at 100 ^{o}C, molar ratio refers to **1**/TsOH·H_2O/**2** = 1:2:2. [b]Isolated yield.

As can be seen from Table 2, both aliphatic alcohols (**2a-i** and **2k**) and aromatic alcohol (**2j**) could be utilized to prepare the scarce fullerene-fused dioxygenated ring compounds with six- to ten-membered heterocycles (**3a**-**k**). All of the examined alcohols **2a**-**k** gave products **3a**-**k** in moderate to good yields ranging from 46% to 94%. Compared with ethylene glycol (**2a**) and 1,2-propanediol (**2b**), 2,3-butanediol (**2c**) required a prolonging of the reaction time to obtain an acceptable yield (74%) of fullerene-fused dioxane (**3c**) probably due to the steric interactions from the two methyl groups at the C_2 and C_3 positions of **2c**. As for 1,4-butanediol (**2i**) and1,2-benzenedimethanol (**2j**), the interesting fullerene-fused dioxanes bearing an eight-membered heterocycle (**3i** and **3j**) were first synthesized, but **2j** generated an obviously lower yield relative to that of **2i** probably attributed to the great steric effect from the phenyl ring of 1,2-benzenedimethanol. Additionally, the unprecedented

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fullerene-fused dioxecane with a ten-membered heterocycle was also successfully prepared in 54% yield via the reaction of aziridinofullerene **1** with 1,6-hexanediol (**2k**), which would be difficult to obtain by known fullerene chemistry.

Products **3a**,[11] **3d,**[11] and **3e**[11] are known compounds, and their identities were fully established by comparison of their spectral data with those reported in the literature. Products **3b**, **3c**, and **3f**-**k** are unknown compounds,[13] and their structures were unambiguously characterized by their HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV-vis spectra. All of new compounds **3b**, **3c**, and **3f**-**k** exhibited correct molecular ion peaks in their high-resolution mass spectra. In their IR spectra, the strong absorption at 1062-1088 cm^{-1} demonstrated the presence of the C-O group. Their UV-vis spectra exhibited a diagnostic absorption at 419-423 nm for the 1,2-adduct of C_{60}, to which two oxygen atoms are directly attached.[10,11] In their ^{1}H NMR spectra, all protons from products **3b**, **3c**, **3h, 3i,** and **3k** displayed the anticipated chemical shifts. However, compounds **3f**, **3g**, and **3j** gave the unexpected chemical shifts, that is, the methylene protons of **3f**, **3g**, and **3j** as well as the methyl protons of **3g** were nonequivalent and split as two singlets, respectively. The reason for this phenomenon was probably attributed to the conformational effects of seven- and eight-membered ring.[14] In their ^{13}C NMR spectra, products **3b** and **3h** showed similar spectral patterns, and the observation of at least 31 peaks for the sp^2-carbons of the C_{60} skeleton was consistent with their C_1 molecular symmetry, and the signals for the two sp^3-carbons of the C_{60} cage were located at 87.15-91.90 and 86.28-91.65 ppm, close to those of reported C_{60}-fused dioxane/dioxepane derivatives in the previous literature.[11] Nevertheless,

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compound **3c** exhibited different spectral patterns with the aforementioned **3b** and **3h**, and there were 25 peaks including some overlapped ones in the 136−149 ppm range for the 58 sp^2-carbons of the C_{60} skeleton and one peak at 86.63 ppm for the two sp^3-carbons of the C_{60} moiety, agreeing with its C_s symmetry. In addition, products **3i-k** also displayed similar spectral patterns but different from those of **3b**, **3c**, and **3h**. **3i-k** exhibited no more than 15 peaks including some overlapped ones due to the 58 sp^2-carbons of the fullerene moiety, consistent with the C_{2v} symmetry of their molecular structures. The two sp^3-carbons of the C_{60} cage appeared at 87.15-88.95 ppm, near to those in the previously reported C_{60}-fused dioxane/dioxepane derivatives.[11] As for compounds **3f** and **3g**, the two sp^3-carbons of the C_{60} skeleton were located at 91.41-92.30 ppm, yet the methyl carbons on the heterocyclic ring as well as 8 sp^2-carbons of the C_{60} moiety were not obviously observed. The exact reason for the disappearance of some carbon signals of **3f** and **3g** is not quite clear now.

On the basis of the previously suggested mechanisms for the reactions of aziridinofullerenes with alkyne,[6] CO_2,[9a] and aryl isocyanates[9a] catalyzed by an acid or base, and the reported experimental results from the acid- or base-catalyzed reactions of aziridinofullerenes with aromatic compounds,[6] sulfamides,[9c] amidines,[9c] and ureas[9d] together with the extensively investigated reaction pathways for the ring opening or ring expansion of aziridines by the C−N bond cleavage,[15] we propose a possible formation mechanism for fullerene-fused dioxygenated ring compound **3** from the TsOH-mediated reaction of aziridinofullerene **1** with diol **2** (Scheme 2).

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Protonation of the nitrogen atom on the aziridinofullerene **1** in the presence of TsOH forms the protonated aziridinofullerene **I**, which undergoes C−N bond cleavage to produce fullerene carbocation **II**. It should be noted that the existence of TsOH plays a crucial role in the efficient synthesis of product **3**, and no obvious products were observed in its absence (entry 11, Table 1). Fullerene carbocation **II** is a reactive intermediate,[16] and then reacts with bifunctional nucleophile **2** accompanied by the loss of H^+ to generate fullerene intermediate **III**, followed by the second protonation of the nitrogen atom to give protonated fullerene intermediate **IV**. Subsequent C−N bond cleavage of intermediate **IV** with the elimination of $TsNH_2$ results in the generation of another fullerene carbocation **V**, which undergoes intramolecular cyclization with the loss of H^+ to afford fullerene-fused dioxygenated ring compound **3**. It should be pointed out that the successful isolation of the relatively stable fullerene intermediate **III** would be crucial to gain more insights into the mechanism, but this attempt unfortunately failed. Although the reaction mechanism is debatable, this experimental result provides an immense opportunity for us to further utilize the aziridinofullerenes to prepare more fullerene macrocyclic derivatives.

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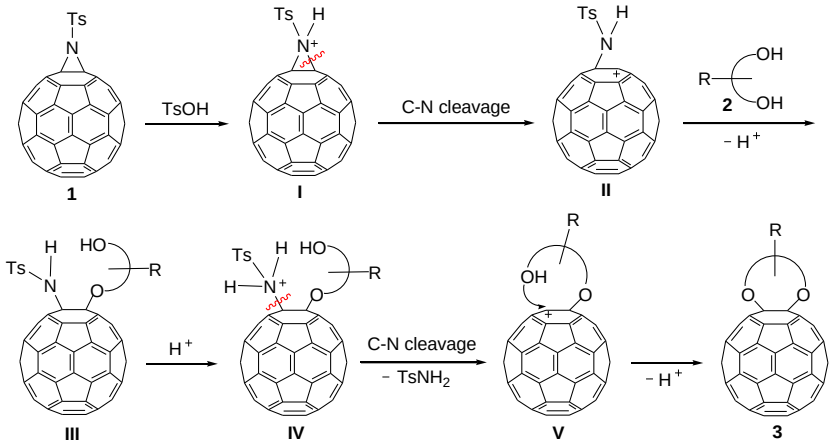

Scheme 2 Proposed possible formation mechanism for fullerene-fused dioxygenated ring compound **3**.

Conclusion

In summary, the simple and efficient functionalization of aziridinofullerene with diols in the presence of TsOH via the double nucleophilic substitution reaction pathway led to the formation of a series of scarce fullerene-fused dioxygenated ring compounds. Among these obtained dioxygenated ring products, fullerene-fused dioxane/dioxecane derivatives with an eight- or ten-membered heterocycle are new types of fullerene compounds, which would be difficult to prepare by traditional methods. In addition, the successful synthesis of the unprecedented fullerene-fused dioxecane with a ten-membered heterocycle encouraged us to synthesize more fullerene macrocyclic derivatives, and relative research works by employing the similar method are ongoing in our laboratory.

Experimental section

General Methods. ^{1}H NMR spectra were referenced to TMS at 0.00 ppm, while ^{13}C

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NMR spectra were referenced to residual $CHCl_3$ at 77.16 ppm, or DMSO at 39.52 ppm. High-resolution mass spectrometry (HRMS) was performed by MALDI-TOF in positive-ion mode with 4-hydroxy-α-cyanocinnamic acid as the matrix.

General procedure for TsOH-mediated reaction of aziridinofullerene with diols

A mixture of aziridinofullerene **1** (17.8 mg, 0.02 mmol), $TsOH \cdot H_2O$ (7.6 mg, 0.04 mmol), and a chosen diol **2** (0.04 mmol) was added to a 25-mL round bottomed flask. After they were completely dissolved in *o*-dichlorobenzene (4 mL) by sonication, the resulting solution was heated with stirring in an oil bath preset at 100 ^oC under air conditions until the disappearance of **1** determined by thin-layer chromatography (TLC). The reaction mixture was filtered through a silica gel plug in order to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide as the eluent to give fullerene-fused dioxygenated ring compound **3**.

Synthesis of compound 3a

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), $TsOH \cdot H_2O$ (7.6 mg, 0.04 mmol), and **2a** (2.0 uL, 0.04 mmol) for 1.5 h afforded **3a**[11] (12.3 mg, 79%) as amorphous black solid.

Synthesis of compound 3b

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg,

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0.02 mmol), $TsOH \cdot H_2O$ (7.6 mg, 0.04 mmol), and **2b** (3.0 uL, 0.04 mmol) for 1.5 h afforded **3b** (11.7 mg, 74%) as amorphous black solid. ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 5.30-5.22 (m, 1H), 5.11 (dd, *J* = 11.1, 6.9 Hz, 1H), 4.45 (dd, *J* = 10.7, 6.0 Hz, 1H), 1.88 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) (all 1C unless indicated) *δ* 149.07, 148.94, 148.66, 148.44 (2C), 148.33, 146.49 (2C), 146.47 (2C), 146.17 (6C), 146.08 (2C), 145.65, 145.46, 145.44, 145.35, 145.25 (3C), 145.13, 145.10 (2C), 144.74 (3C), 144.68, 142.60 (2C), 142.55 (4C), 142.22 (4C), 141.77 (3C), 141.62 (3C), 141.09, 141.00, 139.58 (2C), 135.51 (2C), 138.49, 138.04, 137.05, 136.99, 87.15 (sp^3-*C* of C_{60}), 86.28 (sp^3-*C* of C_{60}), 67.80, 22.17; FT-IR *v*/cm^{-1} (KBr) 2921, 2860, 1424, 1375, 1178, 1154, 1126, 1062, 993, 575, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 421; MALDI-TOF MS *m*/*z* calcd for $C_{63}H_6O_2$ $[M]^+$ 794.0368, found 794.0365.

Synthesis of compound 3c

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), $TsOH \cdot H_2O$ (7.6 mg, 0.04 mmol), and **2c** (4.0 uL, 0.04 mmol) for 3 h afforded **3c** (11.9 mg, 74%) as amorphous black solid. ^1H NMR (400 MHz, $CS_2/CDCl_3$) *δ* 5.44-5.37 (m, 2H), δ 1.79 (d, *J* = 5.7, 6H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) *δ* 148.67, 148.44, 147.67, 145.74, 145.72, 145.41, 145.39, 145.35 (4C), 144.91, 144.76 (1C), 144.62, 144.52 (3C), 144.33, 144.02 (4C), 141.87, 141.82 (4C), 141.48 (4C), 141.07, 141.01, 140.89, 140.34, 138.82, 138.74, 137.63, 136.13, 86.63 (sp^3-*C* of C_{60}), 70.51, 16.53; FT-IR *v*/cm^{-1} (KBr)

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2981, 2892, 1463, 1430, 1379, 1187, 1129, 1076, 1054, 1038, 897, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 419; MALDI-TOF MS *m*/*z* calcd for $C_{64}H_8O_2$ $[M]^+$ 808.0524, found 808.0520.

Synthesis of compound 3d

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), $TsOH{\cdot}H_2O$ (7.6 mg, 0.04 mmol), and **2d** (3.0 uL, 0.04 mmol) for 1.5 h afforded **3d**[11] (14.9 mg, 94%) as amorphous black solid

Synthesis of compound 3e

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), $TsOH{\cdot}H_2O$ (7.6 mg, 0.04 mmol), and **2e** (4 uL, 0.04 mmol) for 1 h afforded **3e**[11] (13.8 mg, 85%) as amorphous black solid.

Synthesis of compound 3f

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), $TsOH{\cdot}H_2O$ (7.6 mg, 0.04 mmol), and **2f** (4 uL, 0.04 mmol) for 1 h afforded **3f** (11.3 mg, 70%) as amorphous black solid. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 4.78 (br.s, 2H), 4.66 (t, J = 10.0 Hz, 2H), 2.88 (br.s, 1H), 1.21 (br.s, 3H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 2C unless indicated) δ 150.66 (4C, weak), 147.83, 145.82 (4C), 145.42 (4C), 145.31, 145.20, 144.69, 144.59 (4C), 144.48, 144.31, 144.09, 144.00, 141.85 (6C), 141.62 (4C), 140.87, 140.72, 138.67,

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138.58, 91.41 (sp^3-*C* of C_{60}), 76.12, 35.56 (1C); FT-IR *v*/cm^{-1} (KBr) 2924, 2861, 1510, 1457, 1430, 1389, 1357, 1216, 1168, 1124, 1088, 1024, 977, 908, 599, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 422; MALDI-TOF MS *m*/*z* calcd for $C_{64}H_8O_2$ $[M]^+$ 808.0524, found 808.0521.

Synthesis of compound 3g

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), TsOH·H_2O (7.6 mg, 0.04 mmol), and **2g** (4.2 mg, 0.04 mmol) for 1 h afforded **3g** (13.6 mg, 83%) as amorphous black solid. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 4.88 (br.s, 2H), 4.28 (br.s, 2H), 1.80 (br.s, 3H), 1.16 (br.s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) (all 4C unless indicated) δ 151.55 (weak), 148.54 (2C), 146.52, 146.12, 145.96, 145.25 (6C), 145.20, 144.70, 142.52 (6C), 142.28, 141.58 (weak), 139.31, 92.30 (2C, sp^3-*C* of C_{60}), 80.75 (2C), 36.71 (1C); FT-IR *v*/cm^{-1} (KBr) 2917, 2847, 1513, 1461, 1432, 1358, 1180, 1124, 1083, 979, 901, 574, 525; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 421; MALDI-TOF MS *m*/*z* calcd for $C_{65}H_{10}O_2$ $[M]^+$ 822.0681, found 822.0680.

Synthesis of compound 3h

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), TsOH·H_2O (7.6 mg, 0.04 mmol), and **2h** (5.9 mg, 0.04 mmol) for 1 h afforded **3h** (11.8 mg, 68%) as amorphous black solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 4.92 (d, *J* = 12.6 Hz, 1H), 4.66 (s, 1H), 4.20 (d, *J* = 12.6 Hz, 1H),

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2.33-2.29 (m, 1H), 1.77 (s, 3H), 1.29 (d, J = 6.2 Hz, 3H), 1.15 (d, J = 6.2 Hz, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) (all 1C unless indicated) δ 152.08, 151.36, 149.72, 149.36, 148.52 (2C), 146.49 (2C), 146.46 (2C), 146.12 (4C), 146.00, 145.94 (2C), 145.77, 145.74, 145.47, 145.43, 145.34 (2C), 145.15, 145.07, 145.04, 144.86 (2C), 144.73, 144.66, 144.56, 144.52, 142.52 (4C), 142.47 (2C), 142.25 (4C), 142.04, 142.00, 141.72, 141.64, 141.36, 141.27, 140.77 (2C), 139.40, 139.33, 139.28, 139.16, 138.78 (2C), 136.37, 135.82, 91.90 (sp^3-*C* of C_{60}), 91.65 (sp^3-*C* of C_{60}), 83.42, 39.96, 29.87, 23.91, 22.21, 19.97, 18.40; FT-IR ν/cm^{-1} (KBr) 2924, 2864, 1463, 1431, 1392, 1364, 1217, 1179, 1124, 1078, 1046, 989, 575, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 421; MALDI-TOF MS *m*/*z* calcd for $C_{68}H_{16}O_2$ $[M]^+$ 864.1150, found 864.1152.

Synthesis of compound 3i

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), TsOH·H_2O (7.6 mg, 0.04 mmol), and **2i** (4 uL, 0.04 mmol) for 0.5 h afforded **3i** (10.5 mg, 65%) as amorphous black solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 5.14 (br.s, 4H), 2.42 (s, 4H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6) (all 4C unless indicated) δ 150.55 (weak), 147.71 (2C), 145.66, 145.33, 145.11, 144.68, 144.40 (6C), 143.94, 141.72 (10C), 141.47, 140.81 (6C), 140.70 (2C), 138.64, 87.15 (2C, sp^3-*C* of C_{60}), 68.82 (2C), 27.80 (2C); FT-IR ν/cm^{-1} (KBr) 2921, 2851, 1463, 1437, 1425, 1371, 1217, 1181, 1130, 1091, 1073, 977, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 421; MALDI-TOF MS *m*/*z* calcd for $C_{64}H_8O_2$ $[M]^+$ 808.0524, found

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808.0520.

Synthesis of compound 3j

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), TsOH·H_2O (7.6 mg, 0.04 mmol), and **2j** (5.5 mg, 0.04 mmol) for 1.5 h afforded **3j** (7.9 mg, 46%) as amorphous black solid. ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 7.38 (d, J = 4.0 Hz, 4H), 6.80 (br.s, 2H), 5.44 (br.s, 2H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) (all 4C unless indicated) δ 150.43 (weak), 148.41 (2C), 146.37, 146.04, 145.86, 145.25 (2C), 145.09 (8C), 144.54, 142.39 (6C), 142.34 (2C), 142.11, 141.40 (10C), 139.32, 136.86 (2C, aryl *C*), 127.81 (2C, aryl *C*), 127.75 (2C, aryl *C*), 88.71 (2C, sp^3-*C* of C_{60}), 72.56 (2C); FT-IR ν/cm^{-1} (KBr) 2909, 2864, 1495, 1448, 1427, 1373, 1215, 1180, 1124, 1086, 1053, 1043, 1005, 982, 744, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 319, 423; MALDI-TOF MS *m*/*z* calcd for $C_{68}H_8O_2$ $[M]^+$ 856.0524, found 856.0520.

Synthesis of compound 3k

According to the general procedure, the reaction of aziridinofullerene **1** (17.8 mg, 0.02 mmol), TsOH·H_2O (7.6 mg, 0.04 mmol), and **2k** (4.7 mg, 0.04 mmol) for 1.5 h afforded **3k** (9.0 mg, 54%) as amorphous black solid. ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 5,06-5.04 (m, 4H), 2.09-2.06 (m, 8H); ^{13}C NMR (100 MHz, CS_2/$CDCl_3$) (all 4C unless indicated) δ 151.35, 148.22 (2C), 146.18, 145.86, 145.61, 145.18, 145.14 (2C), 144.95, 144.46, 142.28 (6C), 142.05, 141.22, 141.17, 139.09, 136.86, 88.95 (2C,

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sp^3-*C* of C_{60}), 68.12 (2C), 19.63; FT-IR ν/cm^{-1} (KBr) 2919, 2867, 1511, 1429, 1388, 1180, 1123, 1095, 1067, 1045, 1027, 1011, 965, 526; UV-vis ($CHCl_3$) λ_{max}/nm 258, 318, 419; MALDI-TOF MS *m*/*z* calcd for $C_{66}H_{12}O_2$ $[M]^+$ 836.0837, found 836.0832.

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