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# $BF_3$·$Et_2O$-Catalyzed Formal [3 + 2] Reaction of Aziridinofullerenes with Carbonyl Compounds

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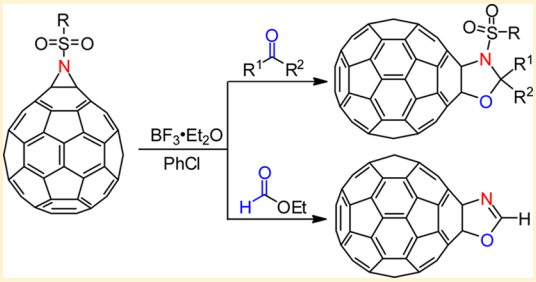
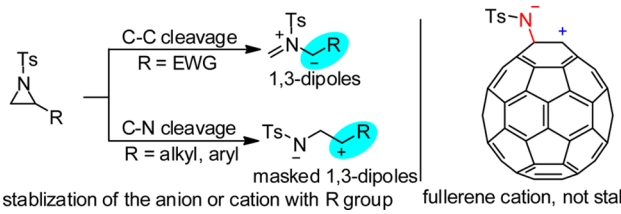
Supporting Information

**ABSTRACT:** The $BF_3$·$Et_2O$-catalyzed formal [3 + 2] reaction of aziridinofullerenes with various carbonyl compounds for the easy preparation of fullerooxazolidines has been developed. Moreover, the reaction of aziridinofullerene with ethyl formate affords the simplest fullerooxazole without substituent.




Chemical modification of fullerene is still an attractive research field for designing more fullerene derivatives with unique physical, chemical, and biological properties. Among the numerous developed methods for preparation of functionalized fullerene,[1] most of the derivatives are prepared directly from $C_{60}$. However, some derivatives cannot be easily synthesized through a one-step reaction. Thus, the investigation of the further transformation starting from fullerene derivatives remains under development. Aziridine as a highly strained three-membered cyclic amine is one of the most important precursors to generate 1,3-dipoles or masked 1,3-dipoles through C−C or C−N bond cleavage, which can be trapped by various dipolarophiles for the preparation of nitrogen-containing five-membered-ring heterocycles.[2] The predominant bond cleavage depends mainly on the electronic properties of the substituent on the C-atom of aziridine ring.[2,3] The electron-withdrawing group is beneficial to the C−C bond cleavage, and the electron-donating group prefers the C−N bond breaking due to the stabilization of carbanion and carbon cation by delocalization, respectively (Scheme 1). Aziridinofullerene is one of the most important classes of nitrogen-containing fullerene derivatives, which can be easily synthesized from azides,[4] chloramines,[5] sulfilimines,[6] iminophenyliodinanes,[7] and *N,N*-dihalosulfonamides.[8] We and Gan also reported a method to prepare the aziridinofullerenes from amines promoted by hypervalent iodine reagents.[9] Although azafulleroid (isomer of aziridinofullerene) is widely used in the synthesis of open-cage fullerene or azafullerene ($C_{59}N$),[10] the transformation of aziridinofullerene has seldom been investigated. The Minakata and Itami groups used aziridinofullerene as a versatile platform for the preparation of functionalized fullerenes by performing the reactions of it with aromatic compounds or bifunctional nucleophiles under acid conditions.[5b,7] In this transformation, the generation of product is accompanied with the loss of sulfonamide. In order to reserve the $N_1$-unit in the product, the [3 + 2] reaction of masked 1,3-dipoles generated from Lewis acid-catalyzed C−N bond cleavage with dipolarophiles is a possible way. However, it is known to all that the $C_{60}$ moiety as an electron-deficient alkene is not beneficial to the formation of carbon cation,[11] which means that such a [3 + 2] reaction of aziridinofullerene remains a challenge (Scheme 1). Most recently, the Minakata group reported the Lewis base but not the usually used Lewis acid catalyzed ring expansion of aziridinofullerene with $CO_2$ and isocyanates.[12] In continuation of our interest in fullerene chemistry,[13] we reported here the $BF_3$·$Et_2O$-catalyzed the formal [3 + 2] reaction of aziridinofullerenes with carbonyl compounds for the easy preparation of oxazolidine-fused fullerene derivatives.

**Scheme 1**

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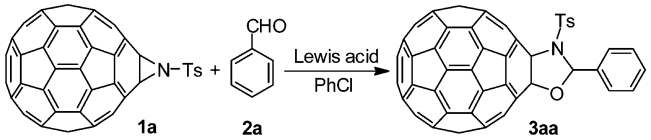
We started our study by choosing *N*-tosylaziridinofullerene **1a** and benzaldehyde **2a** as the model substrates to test the possibility of formal [3 + 2] cycloaddition reaction. In order to avoid the reaction between **1a** and toluene,[5b,14] the chlorobenzene was chosen as the solvent. Various commonly used Lewis acids including $Sc(OTf)_3$, $Cu(OTf)_2$, $Zn(OTf)_2$, $Sn(OTf)_2$, $Cu(ClO_4)_2$, $Cu(acac)_2$, $Ni(acac)_2$, $AgClO_4$, and $BF_3{\cdot}Et_2O$ were evaluated. Although $Sc(OTf)_3$, $Cu(OTf)_2$, and $Zn(OTf)_2$ have been reported to effectively catalyze the reaction of 2-aryl-*N*-tosylaziridine with aldehydes or ketones,[15] in our hand all of them did not show any catalytic activity. $Sn(OTf)_2$, $Cu(ClO_4)_2$, $Cu(acac)_2$, $Ni(acac)_2$, and $AgClO_4$ could not catalyze the reaction either. $BF_3{\cdot}Et_2O$ was the sole efficacious catalyst for this transformation to give the desired $C_{60}$-fused oxazolidine product **3aa** (Table 1, entry 9).

**Table 1. Screening of the Reaction Conditions**[a]



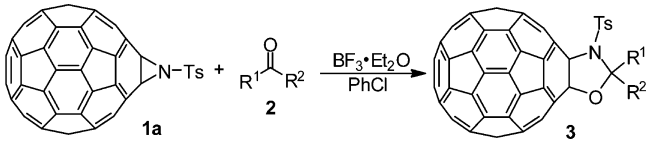

| entry | Lewis acid | **1a**/**2a**/LA | time | yield (%)[b] |
|---|---|---|---|---|
| 1 | $Cu(OTf)_2$ | 1:1.5:1 | 24 h | 0 |
| 2 | $Zn(OTf)_2$ | 1:1.5:1 | 24 h | 0 |
| 3 | $Sn(OTf)_2$ | 1:1.5:1 | 24 h | 0 |
| 4 | $Sc(OTf)_3$ | 1:1.5:1 | 24 h | 0 |
| 5 | $AgClO_4$ | 1:1.5:1 | 24 h | 0 |
| 6 | $Cu(ClO_4)_2$ | 1:1.5:1 | 24 h | 0 |
| 7 | $Mg(ClO_4)_2$ | 1:1.5:1 | 24 h | 0 |
| 8 | $Cu(acac)_2$ | 1:1.5:1 | 24 h | 0 |
| 9 | $BF_3{\cdot}Et_2O$ | 1:1.5:2 | 90 min | 67 |
| 10 | $BF_3{\cdot}Et_2O$ | 1:1.5:5 | 15 min | 88 |

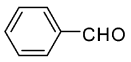
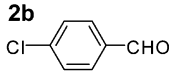
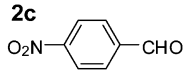
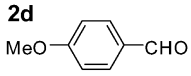
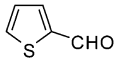
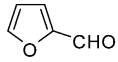
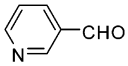
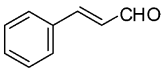
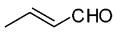
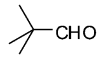
[a]Unless notification, the reactions were carried out with 0.02 mmol of **1a** and proper additives in 2.5 mL of dry chlorobenzene at room temperature. [b]Isolated yield.

Increasing the amount of $BF_3{\cdot}Et_2O$ from 1.5 to 5 equiv had a noticeable acceleration effect on the reaction and led to 88% yield of **3aa** within 15 min (Table 1, entry 10).

With the optimal reaction conditions in hand, we next studied the scope of the $BF_3{\cdot}Et_2O$-catalyzed formal [3 + 2] cycloaddition reaction of *N*-tosylaziridinofullerene **1a** with various carbonyl compounds (Table 2). All the carbonyl compounds (except **2g**) were suitable in the reaction. As for the aromatic aldehydes, electron-donating group on the phenyl ring had a better reactivity than those with electron-withdrawing group. When **1a** was treated with the mixture of 1.5 equiv of 4-nitrobenzaldehyd (**2c**) and 1.5 equiv of 4-methoxybenzaldehyde (**2d**) in the presence of 5 equiv of $BF_3{\cdot}Et_2O$, the molar ratio of product **3ac**:**3ad** was about 1:3 (see Supporting Information). Heteroatomic aldehydes were also tested (Table 2, entries 5–7). Although 2-thenaldehyde **2e** gave excellent yield of **3ae** (93%), 2-furaldehyde **2f** only gave moderate yield of **3af** (56%) due to the generation of some byproducts, and nicotinaldehyde **2g** failed in this reaction. *α,β*-Unsaturated aldehydes and aliphatic aldehydes could also be used as the dipolarophiles to afford the corresponding products in high yields (Table 2, entries 8–12). The ketonic compounds are also applicable in this transformation with 15 equiv of $BF_3{\cdot}Et_2O$ (Table 2, entries 13 and 14).

**Table 2. Substrate Scope for the $BF_3{\cdot}Et_2O$-Catalyzed Formal [3 + 2] Reaction**[a]




| entry | carbonyls | product | time (min) | yield (%)[b] |
|---|---|---|---|---|
| 1 | **2a**  | **3aa** | 25 | 88 |
| 2 | **2b**  | **3ab** | 20 | 92 |
| 3 | **2c**  | **3ac** | 30 | 74 |
| 4 | **2d**  | **3ad** | 30 | 90 |
| 5 | **2e**  | **3ae** | 35 | 93 |
| 6 | **2f**  | **3af** | 60 | 56 |
| 7 | **2g**  | **3ag** | 60 | 0 |
| 8 | **2h**  | **3ah** | 25 | 86 |
| 9[c] | **2i**  | **3ai** | 55 | 94 |
| 10[c] | **2j**  | **3aj** | 15 | 90 |
| 11[c] | **2k**  | **3ak** | 15 | 92 |
| 12[d] | **2l**  | **3al** | 60 | 70 |
| 13[e] | **2m**  | **3am** | 35 | 83 |
| 14[f] | **2n**  | **3an** | 25 | 76 |

[a]Unless notification, the reactions were carried out with the molar ratio of **1a** (17.8 mg)/**2**/$BF_3{\cdot}Et_2O$ = 1:1.5:5 in 2.5 mL of dry chlorobenzene at room temperature. [b]Isolated yield. [c]**1a**/**2**/$BF_3{\cdot}Et_2O$ = 1:3:5. [d]**1a**/paraformaldehyde/$BF_3{\cdot}Et_2O$ = 1:5:5. [e]**1a**/**2m**/$BF_3{\cdot}Et_2O$ = 1:4:15. [f]**1a**/**2n**/$BF_3{\cdot}Et_2O$ = 1:2:15.

We next turned to study the applicability of other aziridinofullerenes in this conversion by performing the reaction of them with 4-chlorobenzaldehyde (Table 3). The aziridinofullerene with an electron-withdrawing group on the phenyl ring had a better reactivity than that with an electron-donating group. *N*-Methylaziridinofullerene **1d** also worked well to give the corresponding product **3db** in 90% yield.


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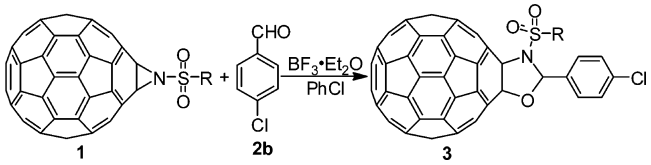
**Table 3. Study of the Reaction Scope by Variation of Aziridinofullerene**[a]

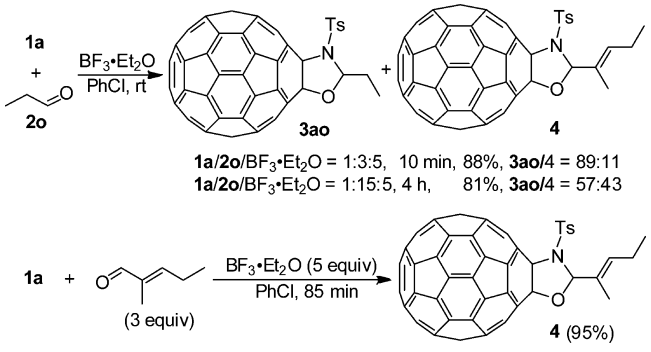



| entry | substrate | R | product | time (min) | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | **1b** | MeO— | **3bb** | 100 | 82 |
| 2 | **1c** | $O_2N$— | **3cb** | 25 | 94 |
| 3 | **1d** | Me— | **3db** | 25 | 90 |

[a]The reactions were carried out with the molar ratio of **1** (0.02 mmol):**2b**:$BF_3$·$Et_2O$ = 1:1.5:5 in 2.5 mL of dry chlorobenzene at room temperature. [b]Isolated yield.

Among the above investigated alkyl aldehydes, the normal [3 + 2] products were obtained as expected. When the propionaldehyde **2o**, which possessed two $\alpha$-H atoms, was subjected to this reaction, TLC indicated that full conversion to a single product had occurred. However, the NMR analysis showed the **3ao** was generated as the main product along with a small amount of byproduct **4** (**3ao**/**4** = 89/11) (Scheme 2).

**Scheme 2. Reaction of *N*-Tosylaziridinofullerene 1a with Propionaldehyde 2o**

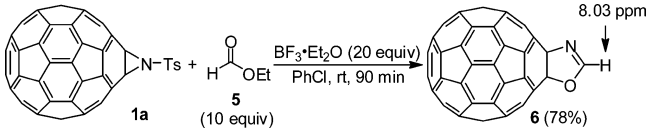



The generation of **4** could be explained by the cycloaddition reaction of **1a** with (*E*)-2-methylpent-2-enal, which could be generated from the self-condensation of **2o** under $BF_3$·$Et_2O$ conditions. In order to suppress the side reaction, the amount of **2o** was raised to 15 equiv. Contrary to our expectations, the reaction proceeded much more slowly than 3 equiv of **2o** and the content of **4** increased greatly (**3ao**/**4** = 57/43) (Scheme 2). In order to verify whether the product **4** was formed through the reaction of **3ao** with (*E*)-2-methylpent-2-enal, that is, whether the $BF_3$·$Et_2O$-catlyzed formal [3 + 2] reaction of **1** with carbonyls was reversible, the reaction of **3aj** with **2d** in the presence of 5 equiv of $BF_3$·$Et_2O$ was carried out.[16] No reaction occurred and **3aj** was totally recovered, which indicated that such $BF_3$·$Et_2O$-catlyzed formal [3 + 2] reaction of aziridinofullerene with carbonyls was irreversible (see Supporting Information). This also demonstrated that **1a** reacted with **2o** and (*E*)-2-methylpent-2-enal to provide **3ao** and **4**, respectively.

To further identify the structure of **4**, the reaction of **1a** with 1.5 equiv of (*E*)-2-methylpent-2-enal in the presence of 5 equiv of $BF_3$·$Et_2O$ was examined. Product **4** was obtained as the sole product in 95% yield.

Although the [3 + 2] reaction of aziridines with carbonyl compounds has been well documented,[3d,15,17] the reactivity of those compounds with a carbonyl group such as DMF, *N*-methylpyrrolidin-2-one, ethyl formate, and dimethyl carbonate had never been investigated in this kind of transformation. *N*-Methylpyrrolidin-2-one, DMF, and dimethyl carbonate showed no reactivity under standard conditions. However, when ethyl formate **5** was employed in the reaction with the molar ratio of **1a**:**5**:$BF_3$·$Et_2O$ as 1:10:20, an unprecedented fullerooxazole product **6** without substituent at the 2-position was isolated in 78% yield. Although several methods have been reported to prepare the fullerooxazole derivatives,[13e,18] all of them failed to give the simplest fullerooxazole **6**. The oxazole skeleton bearing a hydrogen atom at 2-position has been reported to undergo various transformations to generate new C–X (X = C, N, O, or S) bonds though C–H functionalization.[19] It could be predicted that fullerooxazole **6** could also be used as a diverse platform for further functionalization to prepare many fullerene derivatives which were difficult to synthesize from $C_{60}$ directly.

**Scheme 3. Reaction of *N*-Tosylaziridinofullerene 1a with Ethyl Formate 5**




The structures of $C_{60}$-fused oxazolidines **3** were fully assigned on the basis of their MALDI-TOFMS, $^1$H NMR, $^{13}$C NMR, and UV–vis spectra. With **3ab** taken as an example, the TOFMS spectrum of **3ab** showed the $[M+Na]^+$ peak at $m/z$ 1052.0118. The $^1$H NMR spectrum of **3ab** displayed a distinct singlet at 7.62 ppm for methine hydrogen. The $^{13}$C NMR spectrum of **3ab** exhibited 56 signals (51 × 1C, 4 × 2C, and 1 × 3C) for the $sp^2$-C of the $C_{60}$ skeleton and aromatic-C in the range of 135.68–150.17 ppm, four signals (each 2C) for the aryl-C of phenyl ring in the range of 128.09–130.01 ppm, two peaks at 79.22 and 98.81 ppm for the $sp^3$-C of the $C_{60}$ cage, and a characteristic peak at 92.26 ppm for the NCH(R)O moiety, agreeing with $C_1$ symmetry of its molecular structure.

In summary, we have developed an efficient $BF_3$·$Et_2O$-catalyzed formal [3 + 2] reaction of aziridinofullerenes with a variety of carbonyl compounds for the preparation of novel $C_{60}$-fused oxazolidines. Moreover, ethyl formate could be used as a dipolarophile in the reaction to generate the simplest fullerooxazole without substituent at the 2-position.

## EXPERIMENTAL SECTION

**General Procedure for the $BF_3$·$Et_2O$-Catalyzed Formal [3 + 2] Cycloaddition Reaction of Aziridinofullerenes with Carbonyl Compounds.** Aziridinofullerenes **1** (0.02 mmol) and carbonyl coumpounds **2** (**2a–h**: 0.03 mmol; **2i–k** and (*E*)-2-methylpent-2-enal: 0.06 mmol; **2l**: 0.1 mmol; **2m**: 0.08 mmol; **2n**: 0.04 mmol) were dissolved in 2.5 mL of dry chlorobenzene. Then, $BF_3$·$Et_2O$ (for **2a–l**, 0.1 mmol, 12 $\mu$L; for **2m** and **2n**, 0.3 mmol, 37 $\mu$L) was added to the solution, and the mixture was stirred at room temperature until the disappearance of **1** 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 products **3**.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**3aa** (brown solid, 17.6 mg, 88%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 8.13–8.15 (m, 2H), 7.95 (d, $J$ = 8.3 Hz, 2H), 7.68 (s, 1H), 7.44–7.50 (m, 3H), 7.34 (d, $J$ = 8.1 Hz, 2H), 2.48 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 150.36, 148.36, 148.14, 147.99, 147.92, 146.62, 146.57, 146.50, 146.34, 146.19, 146.15, 146.09, 146.01, 145.80, 145.31, 145.28, 145.16, 145.03, 144.96, 144.89, 144.79, 144.58, 144.52, 144.43, 144.37, 144.29, 144.04, 142.80, 142.76, 142.71, 142.68, 142.65, 142.51, 142.50, 142.32, 142.29, 142.25, 142.04, 141.98, 141.87, 141.40, 141.11, 141.08, 139.85, 139.51, 139.43, 138.53, 138.11, 138.09, 137.42, 137.39, 137.01, 136.71, 129.74, 129.71, 128.57, 128.31, 128.07, 98.68, 92.88, 79.17, 21.82; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 257, 318, 453, 684; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{74}H_{13}NNaO_3S$ 1018.0514, found 1018.0513.

**3ab** (brown solid, 18.9 mg, 92%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 8.08 (d, $J$ = 8.3 Hz, 2H), 7.94 (d, $J$ = 8.4 Hz, 2H), 7.62 (s, 1H), 7.45 (d, $J$ = 8.5 Hz, 2H), 7.35 (d, $J$ = 8.1 Hz, 2H), 2.49 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 150.17, 148.23, 148.08, 147.70, 146.64, 146.57, 146.56, 146.46, 146.44, 146.28, 146.24, 146.18, 146.10, 145.92, 145.90, 145.37, 145.25, 145.12, 145.05, 144.88, 144.83, 144.63, 144.56, 144.51, 144.43, 144.23, 144.02, 142.89, 142.87, 142.84, 142.81, 142.75, 142.72, 142.58, 142.54, 142.39, 142.35, 142.30, 142.10, 142.07, 141.96, 141.42, 141.26, 141.23, 141.12, 139.93, 139.65, 139.55, 138.32, 138.20, 138.14, 137.45, 137.41, 136.59, 136.06, 135.68, 130.01, 129.82, 128.63, 128.09, 98.81, 92.26, 79.22, 21.85; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{74}H_{12}ClNNaO_3S$ 1052.0124, found 1052.0118.

**3ac** (brown solid, 15.4 mg, 74%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 8.40 (d, $J$ = 9.0 Hz, 2H), 8.36 (d, $J$ = 8.9 Hz, 2H), 7.97 (d, $J$ = 8.3 Hz, 2H), 7.71 (s, 1H), 7.38 (d, $J$ = 8.2 Hz, 2H), 2.50 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 150.01, 148.95, 148.25, 148.09, 147.60, 147.29, 146.65, 146.59, 146.48, 146.45, 146.38, 146.31, 146.30, 146.25, 146.21, 146.12, 145.98, 145.92, 145.36, 145.27, 145.22, 145.13, 145.05, 144.96, 144.93, 144.79, 144.60, 144.49, 144.39, 144.35, 143.84, 143.63, 142.93, 142.88, 142.85, 142.76, 142.73, 142.55, 142.51, 142.37, 142.33, 142.27, 142.11, 142.08, 141.97, 141.37, 141.18, 141.08, 141.06, 139.94, 139.70, 139.69, 138.25, 138.15, 138.08, 137.41, 137.15, 136.14, 129.93, 129.56, 128.10, 123.58, 99.09, 91.85, 79.10, 21.87; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{74}H_{12}N_2NaO_5S$ 1063.0365, found 1063.0371.

**3ad** (brown solid, 18.4 mg, 90%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 7.99 (d, $J$ = 8.4 Hz, 2H), 7.90 (d, $J$ = 8.4 Hz, 2H), 7.58 (s, 1H), 7.32 (d, $J$ = 8.3 Hz, 2H), 6.94 (d, $J$ = 8.6 Hz, 2H), 3.86 (s, 3H), 2.48 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 160.75, 150.29, 148.44, 148.11, 148.00, 147.97, 146.65, 146.54, 146.48, 146.33, 146.16, 146.14, 146.06, 145.99, 145.79, 145.77, 145.34, 145.25, 145.13, 145.05, 145.01, 144.94, 144.77, 144.66, 144.57, 144.52, 144.38, 144.10, 142.77, 142.74, 142.69, 142.66, 142.63, 142.51, 142.48, 142.30, 142.27, 142.23, 142.00, 141.98, 141.86, 141.38, 141.22, 141.18, 141.08, 139.84, 139.53, 139.33, 138.55, 138.07, 138.01, 137.44, 137.38, 136.77, 129.95, 129.61, 128.72, 128.02, 113.64, 98.47, 92.68, 79.19, 55.18, 21.79; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{75}H_{15}NNaO_4S$ 1048.0619, found 1048.0612.

**3ae** (brown solid, 18.6 mg, 93%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 7.95 (d, $J$ = 8.3 Hz, 2H), 7.81 (s, 1H), 7.77 (d, $J$ = 3.4 Hz, 1H), 7.46 (d, $J$ = 4.9 Hz, 1H), 7.34 (d, $J$ = 8.2 Hz, 2H), 7.11 (dd, $J$ = 4.9, 3.4 Hz, 1H), 2.49 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 150.39, 148.27, 148.08, 147.94, 147.75, 146.51, 146.49, 146.45, 146.32, 146.28, 146.17, 146.14, 146.07, 146.03, 145.96, 145.82, 145.73, 145.33, 145.23, 145.09, 144.98, 144.91, 144.89, 144.78, 144.71, 144.53, 144.50, 144.41, 144.32, 144.25, 144.23, 144.05, 142.74, 142.72, 142.67, 142.65, 142.62, 142.44, 142.32, 142.27, 142.21, 142.01, 141.89, 141.78, 141.51, 141.33, 141.16, 141.12, 141.03, 139.78, 139.51, 139.33, 138.33, 138.06, 137.99, 137.36, 137.13, 136.78, 129.72, 129.43, 128.12, 128.02, 126.85, 99.07, 90.17, 78.90, 21.82; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 256, 319, 454, 684; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{72}H_{11}NNaO_3S_2$ 1024.0078, found 1024.0111.

**3af** (brown solid, 11.0 mg, 56%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 7.91 (d, $J$ = 8.3 Hz, 2H), 7.57 (br, 1H), 7.55 (s, 1H), 7.33 (d, $J$ = 8.3 Hz, 2H), 7.12 (d, $J$ = 3.4 Hz, 1H), 6.55 (dd, $J$ = 3.3, 1.9 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 150.06, 150.05, 148.19, 148.06, 147.94, 147.84, 146.58, 146.55, 146.47, 146.40, 146.26, 146.19, 146.18, 146.14, 146.09, 146.04, 145.85, 145.43, 145.28, 145.17, 145.14, 145.03, 144.88, 144.83, 144.75, 144.65, 144.61, 144.54, 144.49, 144.38, 144.36, 143.98, 143.15, 142.85, 142.84, 142.80, 142.72, 142.71, 142.54, 142.50, 142.45, 142.36, 142.33, 142.09, 142.05, 141.91, 141.45, 141.38, 141.24, 139.87, 139.67, 139.30, 138.23, 138.00, 137.92, 137.88, 137.20, 129.77, 128.12, 112.65, 110.95, 99.27, 87.09, 78.80, 21.82; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 256, 319, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{72}H_{11}NNaO_4S$ 1008.0306, found 1008.0294.

**3ah** (brown solid, 17.5 mg, 86%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 7.91 (d, $J$ = 8.3 Hz, 2H), 7.46 (d, $J$ = 7.2 Hz, 2H), 7.37 (d, $J$ = 15.8 Hz, 1H), 7.35 (t, $J$ = 7.4 Hz, 2H), 7.30 (t, $J$ = 7.2 Hz, 1H), 7.29 (d, $J$ = 8.3 Hz, 2H), 7.02 (dd, $J$ = 5.2, 1.2 Hz, 1H), 6.85 (dd, $J$ = 15.8, 5.2 Hz, 2H), 2.45 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 150.22, 148.70, 148.09, 147.94, 147.86, 146.50, 146.45, 146.39, 146.32, 146.17, 146.11, 146.10, 146.05, 145.98, 145.86, 145.33, 145.31, 145.19, 145.17, 145.09, 145.03, 145.02, 144.96, 144.71, 144.55, 144.50, 144.40, 144.08, 142.79, 142.74, 142.72, 142.62, 142.60, 142.47, 142.45, 142.30, 142.26, 142.22, 142.07, 141.96, 141.87, 141.49, 141.39, 141.36, 141.30, 139.83, 139.70, 139.19, 138.31, 138.11, 137.70, 137.62, 137.32, 136.51, 136.39, 135.47, 129.57, 128.79, 128.76, 128.19, 127.34, 125.02, 98.65, 92.48, 78.84, 21.75; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 256, 318, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{76}H_{15}NNaO_3S$ 1044.0670, found 1044.0682.

**3ai** (brown solid, 18.0 mg, 94%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 7.90 (d, $J$ = 8.3 Hz, 2H), 7.33 (d, $J$ = 8.1 Hz, 2H), 6.82 (d, $J$ = 5.4 Hz, 1H), 6.52–6.61 (m, 1H), 6.30–6.35 (m, 1H), 2.47 (s, 3H), 1.97 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 150.45, 148.93, 148.11, 147.97, 147.95, 146.50, 146.46, 146.42, 146.35, 146.19, 146.14, 146.08, 146.07, 146.02, 145.91, 145.36, 145.34, 145.18, 145.16, 145.10, 145.05, 145.02, 144.98, 144.75, 144.56, 144.55, 144.46, 144.42, 144.40, 144.10, 142.79, 142.75, 142.73, 142.68, 142.63, 142.47, 142.45, 142.30, 142.27, 142.23, 142.08, 141.97, 141.87, 141.49, 141.40, 141.37, 141.30, 139.83, 139.68, 139.20, 138.37, 138.10, 137.68, 137.62, 137.27, 136.53, 133.67, 129.54, 128.12, 127.64, 98.55, 92.69, 78.68, 21.78, 17.80; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 256, 318, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{71}H_{13}NNaO_3S$ 982.0514, found 982.0501.

**3aj** (brown solid, 17.6 mg, 90%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 7.87 (d, $J$ = 8.3 Hz, 2H), 7.27 (d, $J$ = 8.3 Hz, 2H), 6.54 (s, 1H), 2.44 (s, 3H), 1.66 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 151.05, 149.22, 148.57, 148.10, 147.98, 146.44, 146.39, 146.37, 146.09, 146.06, 146.02, 145.94, 145.93, 145.72, 145.65, 145.34, 145.15, 145.08, 145.02, 144.99, 144.88, 144.69, 144.65, 144.57, 144.52, 144.36, 144.16, 144.12, 143.90, 143.88, 142.80, 142.78, 142.76, 142.68, 142.62, 142.60, 142.51, 142.39, 142.29, 142.22, 142.21, 142.08, 141.74, 141.36, 141.15, 140.91, 140.47, 139.69, 139.50, 139.31, 138.55, 137.89, 137.24, 137.09, 136.54, 129.75, 127.61, 102.68, 99.28, 80.25, 38.88, 28.06, 21.77; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 454, 684; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{72}H_{17}NNaO_3S$ 998.0827, found 998.0834.

**3ak** (brown solid, 17.7 mg, 92%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 7.94 (d, $J$ = 8.2 Hz, 2H), 7.33 (d, $J$ = 8.2 Hz, 2H), 6.31 (d, $J$ = 9.5 Hz, 2H), 3.53–3.62 (m, 1H), 2.46 (s, 3H), 1.57 (d, $J$ = 6.8 Hz, 3H), 1.52 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$ 151.93, 149.54, 148.19, 148.05, 146.56, 146.48, 146.41, 146.29, 146.21, 146.19, 146.18, 146.16, 146.08, 146.03, 145.40, 145.30, 145.19, 145.10, 145.01, 144.83, 144.62, 144.57, 144.40, 144.33, 144.24, 143.67, 142.87, 142.80, 142.77, 142.73, 142.69, 142.52, 142.48, 142.27, 142.25, 142.10, 142.05, 141.96, 141.41, 141.35, 141.31, 140.64, 139.90, 139.75, 139.64, 139.14, 138.09, 137.86, 137.38, 137.29, 136.21, 129.72, 128.02, 100.22, 98.43, 79.13, 33.63, 21.81, 19.61, 18.97; UV–vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 452, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{71}H_{15}NNaO_3S$ 984.0670, found 984.0653.

**3al** (brown solid, 12.9 mg, 70%, mp >300 °C): $^1$H NMR (500 MHz, $CDCl_3$–$CS_2$) $\delta$ 7.99 (d, $J$ = 8.3 Hz, 2H), 7.37 (d, $J$ = 8.3 Hz, 2H), 6.25 (s, 2H), 2.48 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$–$CS_2$) $\delta$


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148.26, 148.09, 146.99, 146.88, 146.60, 146.53, 146.28, 146.24, 146.21, 146.09, 145.52, 145.26, 145.23, 144.68, 144.63, 144.58, 144.57, 142.88, 142.86, 142.75, 142.52, 142.33, 142.30, 142.08, 141.47, 141.44, 139.89, 139.12, 138.02, 137.50, 137.39, 129.75, 128.47, 98.51, 80.12, 78.74, 21.83; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 453, 684; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{68}H_9NNaO_3S$ 942.0201, found 942.0198.

**3am** (brown solid, 15.7 mg, 83%, mp >300 °C): $^1H$ NMR (500 MHz, $CDCl_3$−$CS_2$) $\delta$ 7.89 (d, $J$ = 8.3 Hz, 2H), 7.28 (d, $J$ = 8.3 Hz, 2H), 2.45 (s, 3H), 2.44 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$−$CS_2$) (all 2C unless indicated) $\delta$ 149.63, 148.96, 148.01, 147.92, 146.42, 146.39, 146.15, 145.98, 145.96, 145.21, 144.99, 144.97, 144.56, 144.53, 144.34, 143.39, 142.73, 142.69, 142.58, 142.46, 142.20, 142.18, 141.75, 141.63, 141.37, 139.79, 137.94, 136.94, 136.69, 129.35, 127.79, 99.38, 96.87, 80.06, 28.47, 21.66; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 452, 684; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{70}H_{13}NNaO_3S$ 970.0514, found 970.0501.

**3an** (brown solid, 15.1 mg, 76%, mp >300 °C): $^1H$ NMR (500 MHz, $CDCl_3$−$CS_2$) $\delta$ 7.92 (d, $J$ = 8.3 Hz, 2H), 7.29 (d, $J$ = 8.3 Hz, 2H), 2.75−2.93 (m, 4H), 2.45 (s, 3H), 1.87−2.17 (m, 5H), 1.51−1.64 (m, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$−$CS_2$) $\delta$ 149.81, 149.24, 148.21, 148.12, 146.66, 146.62, 146.56, 146.34, 146.15, 146.14, 145.40, 145.19, 145.16, 144.74, 144.72, 144.65, 143.63, 142.90, 142.88, 142.75, 142.65, 142.38, 142.34, 141.91, 141.79, 141.52, 140.29, 139.96, 138.10, 137.15, 136.97, 129.56, 127.77, 101.76, 96.94, 80.54, 36.89, 25.17, 24.37, 21.72; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 452, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{73}H_{17}NNaO_3S$ 1010.0827, found 1010.0834.

**4**: (brown solid, 18.8 mg, 95%, mp >300 °C): $^1H$ NMR (500 MHz, $CDCl_3$−$CS_2$) $\delta$ 7.90 (d, $J$ = 8.3 Hz, 2H), 7.33 (d, $J$ = 8.2 Hz, 2H), 6.70 (s, 1H), 6.49 (t, $J$ = 7.2 Hz, 1H), 2.48 (s, 3H), 2.27−2.36 (m, 2H), 2.04 (s, 3H), 1.18 (t, $J$ = 7.6 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$−$CS_2$) $\delta$ 150.31, 148.55, 148.23, 148.12, 147.99, 146.58, 146.52, 146.48, 146.40, 146.22, 146.16, 146.12, 146.06, 146.03, 145.97, 145.47, 145.44, 145.22, 145.14, 145.07, 145.04, 144.98, 144.92, 144.79, 144.62, 144.56, 144.47, 144.42, 144.17, 142.79, 142.74, 142.71, 142.64, 142.52, 142.51, 142.31, 142.29, 142.25, 142.10, 142.02, 141.86, 141.44, 141.33, 141.31, 141.22, 139.88, 139.69, 139.18, 138.01, 137.90, 137.84, 137.22, 135.18, 130.00, 129.50, 128.35, 97.94, 95.63, 79.29, 29.96, 21.84, 13.55, 12.35; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 256, 318, 453, 684; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{73}H_{17}NNaO_3S$ 1010.0827, found 1010.0828.

**3bb** (brown solid, 17.1 mg, 82%, mp >300 °C): $^1H$ NMR (500 MHz, $CDCl_3$−$CS_2$) $\delta$ 8.04 (d, $J$ = 8.3 Hz, 2H), 7.91 (d, $J$ = 8.8 Hz, 2H), 7.54 (s, 1H), 7.42 (d, $J$ = 8.3 Hz, 2H), 6.97 (d, $J$ = 8.8 Hz, 2H), 3.89 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$−$CS_2$) $\delta$ 163.39, 150.08, 148.05, 147.96, 147.90, 147.61, 146.48, 146.44, 146.42, 146.29, 146.28, 146.11, 146.08, 146.02, 145.93, 145.78, 145.75, 145.19, 145.09, 144.96, 144.93, 144.88, 144.85, 144.68, 144.49, 144.41, 144.38, 144.30, 143.92, 142.74, 142.72, 142.69, 142.65, 142.61, 142.58, 142.44, 142.40, 142.23, 142.21, 142.15, 141.95, 141.92, 141.79, 141.29, 141.15, 141.10, 141.08, 139.78, 139.50, 139.35, 138.01, 137.86, 137.29, 137.26, 136.39, 135.95, 135.49, 132.66, 130.06, 129.88, 128.48, 114.14, 98.55, 92.05, 79.01, 55.48; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{74}H_{12}ClNNaO_4S$ 1068.0073, found 1068.0062.

**3cb** (brown solid, 19.9 mg, 94%, mp >300 °C): $^1H$ NMR (500 MHz, $CDCl_3$−$CS_2$) $\delta$ 8.36 (d, $J$ = 8.9 Hz, 2H), 8.19 (d, $J$ = 8.8 Hz, 2H), 8.03 (d, $J$ = 8.4 Hz, 2H), 7.56 (s, 1H), 7.43 (d, $J$ = 8.4 Hz, 2H); $^{13}C$ NMR (125 MHz, $CDCl_3$−$CS_2$) $\delta$ 150.30, 148.92, 148.19, 148.09, 147.55, 147.36, 146.79, 146.65, 146.64, 146.47, 146.46, 146.41, 146.30, 146.28, 146.26, 146.18, 146.13, 145.98, 145.96, 145.36, 145.22, 145.20, 145.10, 144.92, 144.71, 144.60, 144.57, 144.29, 144.21, 143.82, 143.54, 142.94, 142.90, 142.87, 142.84, 142.74, 142.49, 142.46, 142.41, 142.33, 142.31, 142.10, 142.08, 141.91, 141.34, 141.20, 141.12, 140.85, 140.10, 139.73, 139.46, 138.30, 138.02, 137.27, 136.87, 136.81, 136.57, 134.59, 130.03, 128.95, 128.73, 124.21, 98.80, 92.02, 79.17; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 452, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{73}H_9ClN_2NaO_5S$ 1082.9818, found 1082.9811.

**3db** (brown solid, 17.1 mg, 90%, mp >300 °C): $^1H$ NMR (500 MHz, $CDCl_3$−$CS_2$) $\delta$ 8.10 (d, $J$ = 8.3 Hz, 2H), 7.47 (d, $J$ = 8.4 Hz, 2H), 7.37 (s, 1H), 3.56 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$−$CS_2$) $\delta$ 149.97, 148.17, 148.02, 147.81, 146.71, 146.61, 146.58, 146.42, 146.36, 146.35, 146.23, 146.22, 146.14, 146.08, 145.83, 145.75, 145.37, 145.23, 145.16, 145.09, 145.06, 144.99, 144.95, 144.76, 144.52, 144.48, 144.35, 144.23, 143.84, 142.88, 142.85, 142.75, 142.65, 142.51, 142.42, 142.27, 142.24, 142.11, 141.96, 141.85, 141.62, 141.60, 141.09, 141.05, 140.05, 139.61, 139.60, 138.43, 137.33, 137.27, 136.94, 136.37, 136.22, 135.30, 129.82, 128.65, 98.50, 91.74, 79.67, 40.96; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 257, 319, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $M^+$ calcd for $C_{68}H_8ClNO_3S$ 952.9913, found 952.9933.

**$BF_3$·$Et_2O$-Catalyzed Reaction of Aziridinofullerene 1a with Propionaldehyde 2o.** Aziridinofullerene **1a** (17.8 mg, 0.02 mmol) and propionaldehyde **2o** (0.06 or 0.3 mmol) were dissolved in 2.5 mL of dry chlorobenzene. Then, $BF_3$·$Et_2O$ (0.1 mmol, 12 μL) was added to the solution, and the mixture was stirred at room temperatrue until the disappearance of **1a** determined by TLC. The solvent was evaporated *in vacuo*, and the residue was purified on a silica gel column using $CS_2$/toluene as the eluent to give the inseparable products **3ao** and **4** (when **1a**/**2o**/$BF_3$·$Et_2O$ = 1:3:5, 16.8 mg, 88%, **3ao**/**4** = 89:11; when **1a**/**2o**/$BF_3$·$Et_2O$ = 1:15:5, 15.6 mg, 81%, **3ao**/**4** = 57:43).

**3ao** (brown solid, mp >300 °C): $^1H$ NMR (500 MHz, $CDCl_3$−$CS_2$) $\delta$ 7.93 (d, $J$ = 8.3 Hz, 2H), 7.33 (d, $J$ = 8.2 Hz, 2H), 6.49 (dd, $J$ = 8.7, 4.6 Hz, 1H), 3.01−3.10 (m, 1H), 2.78−2.87 (m, 1H), 2.47 (s, 3H), 1.49 (t, $J$ = 7.4 Hz, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$−$CS_2$) $\delta$ 151.60, 149.53, 148.23, 148.12, 148.08, 146.59, 146.53, 146.44, 146.42, 146.28, 146.23, 146.18, 146.16, 146.12, 146.04, 145.46, 145.29, 145.21, 145.13, 145.10, 145.06, 144.96, 144.87, 144.64, 144.61, 144.51, 144.50, 144.45, 144.43, 144.25, 142.88, 142.83, 142.80, 142.70, 142.54, 142.51, 142.36, 142.33, 142.29, 142.14, 142.07, 141.96, 141.59, 141.48, 141.20, 139.84, 139.74, 139.61, 138.70, 138.04, 137.91, 137.34, 137.21, 136.13, 129.76, 127.85, 98.88, 95.80, 78.63, 30.35, 21.80, 10.17; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 256, 319, 453, 683; HRMS (MALDI-TOFMS) $m/z$ $[M+Na]^+$ calcd for $C_{70}H_{13}NNaO_3S$ 970.0514, found 970.0524.

**$BF_3$·$Et_2O$-Catalyzed Reaction of Aziridinofullerene 1a with Ethyl Formate 5.** Aziridinofullerene **1a** (17.8 mg, 0.02 mmol) and ethyl formate **5** (14.8 mg, 0.2 mmol) were dissolved in 2.5 mL of dry chlorobenzene. Then, $BF_3$·$Et_2O$ (0.4 mmol, 49 μL) was added to the solution, and the mixture was stirred at room temperature until the disappearance of **1a** determined by TLC. The solvent was evaporated *in vacuo*, and the residue was purified on a silica gel column using $CS_2$/toluene as the eluent to give the products **6**.

**6** (brown solid, 11.9 mg, 78%, mp >300 °C): $^1H$ NMR (500 MHz, $CDCl_3$−$CS_2$) $\delta$ 8.03 (s, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$−$CS_2$) (all 2C unless indicated) $\delta$ 156.50, 148.27, 147.86, 147.16, 146.48, 146.36, 146.18, 146.13, 145.90, 145.57, 145.48, 145.31, 145.21, 144.82, 144.58, 144.29, 142.89, 142.83, 142.78, 142.43, 142.34, 142.26, 142.18, 142.05, 141.96, 140.52, 139.79, 137.72, 136.22, 96.55, 90.96; UV−vis ($CHCl_3$) $\lambda_{max}$/nm 256, 317, 454, 611, 684; HRMS (MALDI-TOFMS) $m/z$ $M^+$ calcd for $C_{61}HNO$ 763.0058, found 763.0049.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Control experiments, UV−vis spectrum of **3db**, and $^1H$ 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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(16) Because we could not obtain the compound **3ao** with 100% purity, we chose the reaction between **3aj** and **2d**. In addition, we also conducted the reaction of **3ao** (a mixture with **4**, **3ao**/**4** = 89/11) with 3 equiv of (*E*)-2-methylpent-2-enal in the presence of 5 equiv of $BF_3 \times Et_2O$. After stirring for 5 h at room temperature no change of the molar ratio of **3ao**/**4** was observed. This result proved the irreversibility of the reaction directly.

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