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Ferric Chloride-Catalyzed Reaction of [60]Fullerene with *tert*-Butyl *N*-Substituted Carbamates: Synthesis of Oxazolidino[4,5:1,2][60]fullerenes

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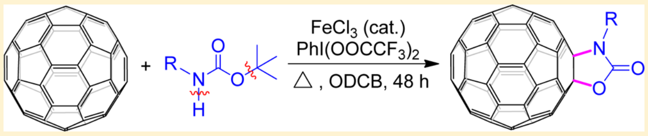
Supporting Information

ABSTRACT: The rare oxazolidinofullerenes have been prepared by the ferric chloride-catalyzed reaction of [60]-fullerene with various *tert*-butyl *N*-substituted carbamates via *t*-Bu−O bond cleavage and heteroannulation under mild conditions. A possible mechanism for the formation of oxazolidinofullerenes is proposed.



■ INTRODUCTION

Owing to the potential applications of fullerene derivatives in materials science, medical chemistry, and nanotechnology,[1] considerable effort has been made toward the efficient methods for their synthesis,[2−7] and metal-mediated radical approaches become increasingly popular.[2−6] In addition, iron, as one of the most important metals in nature, is a cheap, nontoxic, and effective catalyst for various organic transformations.[8] As a result, a great deal of effort has been put into the iron-mediated radical reactions of fullerenes.[3−6] In 2002, Gan et al. reported the $FeCl_3$/$Fe(NO_3)_3$-catalyzed peroxy radical addition to fullerenes.[4] Later on, Hashiguchi et al. described the preparation of pentaaryl(chloro)[60]fullerenes by $FeCl_3$-mediated polyarylation of [60]fullerene (C_{60}).[5] Recently, we have systematically studied the $Fe(ClO_4)_3$-promoted reactions of C_{60} and realized the synthesis of C_{60}-fused oxazolines,[6a] dioxolanes,[6b] lactones,[6c] dioxaborolanes,[6d] and tetrahydrofurans[6e] from nitriles, aldehydes/ketones, malonate esters, arylboronic acids, and β-keto esters, respectively. Our group[6f] and Hashiguchi et al.[6g] described the preparation of 1,2-fullerenols by the reaction of C_{60} with acyl chlorides or carboxylic acids in the presence of $Fe(ClO_4)_3$ or $FeCl_3$, respectively. However, most of the reported iron-mediated reactions required a high temperature or a large amount of iron reagents.

On the other hand, oxazolidino[4,5:1,2][60]fullerenes, as one of the rare five-membered heterocycle-fused fullerene derivatives, are difficult to access efficiently by conventional methods. In 1994, the first synthesis of the nonfunctionalized and simplest oxazolidinofullerene was achieved by Luh's group via the cycloaddition of C_{60} with N_3CO_2Et, followed by the treatment of the obtained *N*-ethyloxycarbonylaziridinofullerene with BBr_3 at room temperature.[7a] Coincidently, Taylor's group reported the same rearrangement reaction using phenol/chlorotrimethylsilane instead of BBr_3.[7b] Recently, Minakata and co-workers described the PCy_3-catalyzed ring-expansion reaction of *N*-sulfonyl aziridinofullerenes with CO_2 affording *N*-sulfonyl oxazolidinofullerenes.[7c] Up to now, the reported oxazolidinofullerenes all have been generated from the ring-opening reactions of the preformed aziridinofullerenes. Therefore, it is still challenging to obtain oxazolidinofullerene derivatives directly from C_{60} in a straightforward and efficient way. Herein, we report an $FeCl_3$-catalyzed reaction of C_{60} with *tert*-butyl *N*-substituted carbamates to generate oxazolidino-[4,5:1,2][60]fullerenes with a broad substrate scope.

■ RESULTS AND DISCUSSION

A suitable alkyl group is demanded for the alkyl−oxygen bond cleavage of carbamates, and the *tert*-butyl group was found to be superior to the methyl, isopropyl, and benzyl groups.[9] Thus, the reaction of *tert*-butyl carbamate **1a** with C_{60} was chosen as the model reaction to optimize conditions (Table 1). When $Fe(ClO_4)_3$ (20 mol %) was chosen as the catalyst and bis(trifluoroacetoxy)iodobenzene [$PhI(O_2CCF_3)_2$] as the oxidant, we could obtain the desired product **2a** in 7% yield at ambient temperature (Table 1, entry 1). Unfortunately, $Fe_2(SO_4)_3$ could not promote the reaction with complete recovery of C_{60} (Table 1, entry 2). To our satisfaction, the yield of **2a** was sharply improved to 37% when $FeCl_3$ was used as the catalyst (Table 1, entry 3). However, the usage of $FeCl_2$ led to only 7% yield of **2a** (Table1, entry 4). Surprisingly, only a trace amount of **2a** was generated under the same conditions when (diacetoxyiodo)benzene [$PhI(OAc)_2$] was used (Table 1, entry 5), indicating that $PhI(OAc)_2$ was much less effective compared with $PhI(O_2CCF_3)_2$. Other examined oxidants including $K_2S_2O_8$ and *p*-benzoquinone (BQ) were ineffective for the formation of **2a** (Table 1, entries 6 and 7). It should be noted

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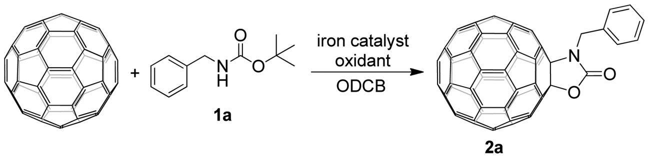
Table 1. Optimization of Reaction Conditions for the Reaction of C_{60} with *tert*-Butyl *N*-Benzylcarbamate 1a Catalyzed by Iron Salt[a]



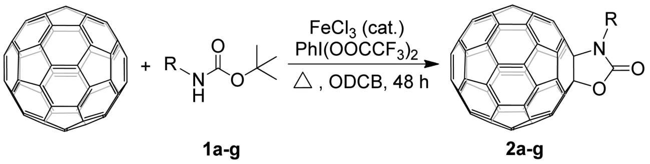
entry	catalyst	oxidant	molar ratio[b]	yield of **2a** (%)[c]
1	$Fe(ClO_4)_3$	$PhI(O_2CCF_3)_2$	1:2:0.2:1	7 (25)
2	$Fe_2(SO_4)_3$	$PhI(O_2CCF_3)_2$	1:2:0.2:1	0
3	$FeCl_3$	$PhI(O_2CCF_3)_2$	1:2:0.2:1	37 (79)
4	$FeCl_2$	$PhI(O_2CCF_3)_2$	1:2:0.2:1	7 (39)
5	$FeCl_3$	$PhI(OAc)_2$	1:2:0.2:1	trace
6	$FeCl_3$	$K_2S_2O_8$	1:2:0.2:1	0
7	$FeCl_3$	BQ	1:2:0.2:1	0
8		$PhI(O_2CCF_3)_2$	1:2:0:1	4 (33)
9	$FeCl_3$		1:2:0.2:0	trace
10	$FeCl_3$	$PhI(O_2CCF_3)_2$	1:2:0.2:1.5	36 (53)
11	$FeCl_3$	$PhI(O_2CCF_3)_2$	1:2:0.1:1	23 (59)
12	$FeCl_3$	$PhI(O_2CCF_3)_2$	1:1:0.2:1	32 (68)
13[d]	**$FeCl_3$**	**$PhI(O_2CCF_3)_2$**	**1:1:0.2:1**	**36 (67)**
14[d,e]	$FeCl_3$	$PhI(O_2CCF_3)_2$	1:1:0.2:1	29 (63)
15[d,f]	$FeCl_3$	$PhI(O_2CCF_3)_2$	1:1:0.2:1	32 (60)
16[g]	$FeCl_3$	$PhI(O_2CCF_3)_2$	1:1:0.2:1	14 (82)

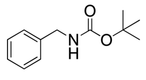
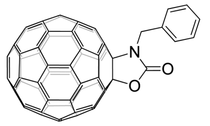
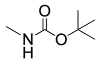
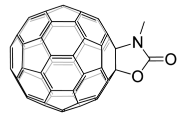
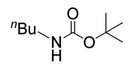
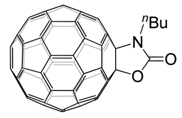
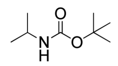
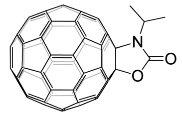
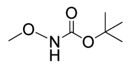
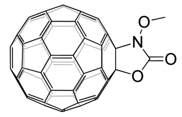
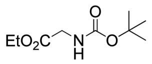
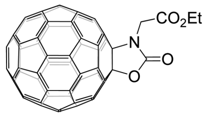
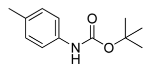
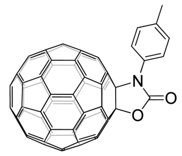
[a] Unless otherwise noted, all reactions were performed in *o*-dichlorobenzene (ODCB) at 25 °C for 48 h in an open air. [b] Molar ratio refers to C_{60}/**1a**/catalyst/oxidant. [c] Yields in parentheses were based on consumed C_{60}. [d] The reaction was performed at 60 °C. [e] The reaction time was 36 h. [f] The reaction time was 60 h. [g] The reaction was carried out under a nitrogen atmosphere.

that both $FeCl_3$ and $PhI(O_2CCF_3)_2$ were indispensible for the present reaction, because a very small amount of the desired product was obtained in the absence of either $FeCl_3$ or $PhI(O_2CCF_3)_2$ (Table 1, entries 8 and 9). Increasing the amount of $PhI(O_2CCF_3)_2$ to 1.5 equiv was not beneficial for the reaction (Table 1, entry 10). A lower yield of **2a** was obtained when the amount of $FeCl_3$ or **1a** was reduced (Table 1, entries 11 and 12). Fortunately, a higher temperature (60 °C) further increased the yield from 32% to 36% (Table 1, entry 3 vs entry 13). Shortening or prolonging the reaction time led to a lower yield (Table 1, entries 14 and 15). Moreover, an inert atmosphere was unfavorable to achieve a higher yield (Table 1, entry 16). Thus, a molar ratio of 1:1:0.2:1 for the reagents of C_{60}, **1a**, $FeCl_3$, and $PhI(O_2CCF_3)_2$ and reaction temperature at 60 °C were chosen as the optimized reaction conditions (Table 1, entry 13).

With the optimized conditions in hand, we started to investigate the scope of the reaction (Table 2). Both *tert*-butyl *N*-alkylcarbamates and *tert*-butyl *N*-arylcarbamates were well compatible with this reaction (Table 2, entries 1−7). The treatment of *N*-alkylcarbamates **1b** and **1c** under our optimized reaction conditions afforded the corresponding products **2b** and **2c** in 37% and 35% yields, respectively (Table 2, entries 2 and 3). Next, *tert*-butyl *N*-branched alkylcarbamate **1d** also produced **2d** under the standard conditions successfully. Nevertheless, a lower temperature (40 °C) and an increased amount of the substrate were beneficial in avoiding the formation of byproducts and affording **2d** in a higher yield (Table 2, entry 4). Meanwhile, substrate **1e** with an OCH_3 group connected directly to the nitrogen atom also led to the desired product **2e** in 26% yield at room temperature (Table 2, entry 5). It was found that raising the temperature from 25 to 60 °C was fruitless to get a higher yield. The substrate possessing an active functional group such as carboxylic ester (**1f**) successfully furnished the desired oxazolidinofullerene **2f** in 27% yield (Table 2, entry 6). In addition, an increasing amount of both $FeCl_3$ and the substrate was beneficial for *tert*-

Table 2. Results for the Reaction of C_{60} with *tert*-Butyl *N*-Substituted Carbamates 1a−g Catalyzed by $FeCl_3$[a]



entry	substrate **1**	product **2**	yield of **2** (%)[b]
1	 1a	 2a	36 (67)
2	 1b	 2b	37 (71)
3	 1c	 2c	35 (73)
4[c,d]	 1d	 2d	24 (60)
5[e]	 1e	 2e	26 (62)
6	 1f	 2f	27 (53)
7[c,e,f]	 1g	 2g	16 (80)

[a] Unless otherwise noted, all reactions were performed with C_{60} (0.05 mmol), **1** (0.05 mmol), $FeCl_3$ (20 mol %), and $PhI(O_2CCF_3)_2$ (0.05 mmol) in ODCB at 60 °C for 48 h in an open air. [b] Yields in parentheses were based on consumed C_{60}. [c] Two equivalents of the substrate were used. [d] The reaction was performed at 40 °C. [e] The reaction was performed at 25 °C. [f] One equivalent of $FeCl_3$ was used.

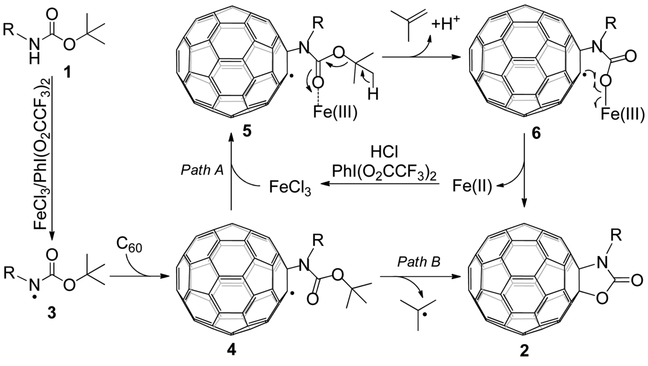
butyl *N*-arylcarbamate **1g** to participate in this reaction (Table 2, entry 7). Performing the reaction at a higher temperature (60 °C) or a longer reaction time could not further improve the yield of **2g**. Compared with **1a**−**f**, **1g** displayed an obvious lower reactivity, probably due to the delocalization of the in situ formed radical to the phenyl group, thus retarding the subsequent radical addition to C_{60} (vide infra).

Products **2a**−**g** were fully characterized by HRMS, ^{1}H NMR, ^{13}C NMR, IR, and UV−vis spectra. Their ^{1}H NMR spectra displayed the expected chemical shifts as well as the splitting patterns for all protons. The ^{13}C NMR spectra of **2a**−**g** exhibited no more than 30 peaks in the range of 135−148 ppm for the sp^2-carbons of the fullerene cage and two peaks at 75−79 ppm and 90−93 ppm for the two sp^3-carbons of the fullerene skeleton, consistent with the C_s symmetry of their molecular structures. The chemical shifts at 75−79 ppm and 90−93 ppm for the two sp^3-carbons of the fullerene skeleton are close to the reported data of other fullerene derivatives with a nitrogen atom and an oxygen atom attached to the fullerene skeleton.[6,7b,c] The chemical shifts for the carbonyl group of the oxazolidone moiety appeared at 150−155 ppm. In their IR spectra, the strong absorption at 1762−1790 cm^{-1} also demonstrated the presence of the carbonyl moiety. Their UV−vis spectra exhibited an absorption at 416−418 nm, which is the characteristic absorption for 1,2-adducts of C_{60}, in which a heteroatom is directly attached to the fullerene cage.[6]

In order to shed more light on the reaction mechanism, a free radical scavenger, that is, 2,2,6,6-tetramethylpiperidinooxyl (TEMPO), was added to the reaction mixture, and no desired **2a** for the reaction of **1a** with C_{60} could be obtained. This result indicates that the reaction likely proceeds through a radical process.

Based on the above results and previous literature on iron-mediated radical reactions, a plausible mechanism for the formation of oxazolidinofullerenes **2a**−**g** is proposed and depicted in Scheme 1. First, the oxidation of substrate **1** by $FeCl_3$ or $PhI(O_2CCF_3)_2$ generates the amidyl radical **3**,[10] which attacks C_{60} to afford the fullerenyl radical **4**.[11] Coordination of **4** with another $FeCl_3$[6b] furnishes the complex **5**, which undergoes an O−^{t}Bu bond cleavage to give the Fe(III) complex **6** (path A). A similar copper-promoted scissure of the O−^{t}Bu bond has been reported.[12] It seems that the electro-deficient nature of the neighboring moiety is important for the success of the O−^{t}Bu bond cleavage.[12,13] The attachment of the electron-deficient fullerene skeleton to the nitrogen atom may also help the O−^{t}Bu bond cleavage in the intermediate **5**. Finally, the complex **6** undergoes an intramolecular cyclization to provide oxazolidinofullerene **2** with the loss of an Fe(II) species.[3,6a,b,d] The $FeCl_3$ can be regenerated by the oxidation of the Fe(II) species with $PhI(O_2CCF_3)_2$. Alternatively, the fullerenyl radical **4** may give **2** directly with the elimination of *tert*-butyl radical (path B). This process can be corroborated by the formation of **2a** in the absence of $FeCl_3$, albeit in only 4% yield (Table 1, entry 8). However, when a catalytic amount of $FeCl_3$ was added, the yield of **2a** was dramatically increased to 37% (Table 1, entry 3 vs 8), indicating that $FeCl_3$ plays a crucial role in this transformation. We suspect that the coordination of $FeCl_3$ with the carbonyl group in the intermediate **5** may facilitate the O−^{t}Bu bond cleavage. Thus, in the combination system of $FeCl_3$ and $PhI(O_2CCF_3)_2$, oxazolidinofullerene **2** should be formed predominantly via path A, while path B contributes much less for the product formation. It should be noted that the pathway via the oxidation of the fullerenyl radical **4** to the corresponding fullerenyl cation[5] followed by cyclization to afford product **2** cannot be excluded.

Scheme 1. Possible Mechanism for the Formation of 2



The stability and further functionalization of the obtained oxazolinofullerenes were also examined using **2a** as a representative compound. Preliminary results showed that **2a** was very stable under strong acidic and high temperature conditions such as TsOH, TfOH, $MeSO_3H$, or $BF_3{\cdot}Et_2O$ at up to 150 °C. It seems that **2a** was relatively unstable under strong alkaline conditions. When treated with EtONa/EtOH (20 equiv) in chlorobenzene at 120 °C for 12 h, **2a** was converted mostly to C_{60}. Interestingly, we found that the electrochemically generated dianionic **2a** could subsequently undergo the cleavage of both the C_{60}−O and C_{60}−N bonds to produce C_{60} in the presence of TFA. Therefore, the oxazoline heterocycle might be used as a removable template for fullerene functionalization.[14]

■ CONCLUSION

We have successfully developed a unique and efficient $FeCl_3$-catalyzed reaction of C_{60} with *tert*-butyl *N*-substituted carbamates, affording the rare oxazolidinofullerenes directly. This transformation proceeds smoothly under mild conditions and exhibits good tolerance to various aliphatic and aromatic carbamates.

■ EXPERIMENTAL SECTION

General Methods. ^{1}H NMR spectra were referenced to TMS at 0.00 ppm, while ^{13}C NMR spectra were referenced to residual $CHCl_3$ at 77.16 ppm or DMSO at 39.52 ppm. High-resolution mass spectra (HRMS) were obtained by MALDI-TOF in positive mode using sulfur as the matrix.

General Procedure for the Synthesis of 2a−g from the $FeCl_3$-Catalyzed Reaction of C_{60} with 1a−g. A mixture of C_{60} (36.0 mg, 0.05 mmol), *tert*-butyl *N*-benzylcarbamate **1** (0.05 mmol, 1 equiv (0.10 mmol, 2 equiv for **1d** and **1g**)), $FeCl_3$ (1.6 mg, 0.01 mmol, 0.2 equiv (8.1 mg, 0.05 mmol, 1 equiv for **1g**)), and $PhI(O_2CCF_3)_2$ (21.5 mg, 0.05 mmol, 1 equiv) was dissolved in ODCB (6 mL). Then the solution was vigorously stirred at the preset temperature (25−60 °C) for 48 h. The resulting solution was directly separated on a silica gel column with CS_2/CH_2Cl_2 as the eluent; the desired product **2** was obtained along with recovered C_{60}.

*3-Benzyloxazolidino[4,5:1,2][60]fullerene, **2a**.* By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (10.6 mg, 0.05 mmol), $FeCl_3$ (1.7 mg, 0.01 mmol), and $PhI(O_2CCF_3)_2$ (21.5 mg, 0.05 mmol) at 60 °C afforded **2a** (15.6 mg, 36%) and recovered C_{60} (16.5 mg, 46%): amorphous brown solid; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.58−7.52 (m, 2H), 7.29 (tt, J = 7.2, 1.6 Hz, 2H), 7.23 (tt, J = 7.4, 1.4 Hz, 1H), 5.33 (s, 2H); ^{13}C NMR

(100 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 154.88 (1C), 147.95 (1C), 147.75 (1C), 146.12, 146.11, 146.06, 145.89, 145.86, 145.81, 144.84, 144.82, 144.79, 144.56, 144.24, 144.20, 144.15, 144.01, 143.72, 142.46, 142.41, 142.39, 141.98, 141.94, 141.73, 141.55, 141.45, 141.03, 139.62, 139.06, 137.00, 136.61, 135.84 (1C), 128.50, 128.40, 127.97 (1C), 92.39 (1C), 77.77 (1C), 47.86 (1C); FT-IR ν/cm^{-1} (KBr) 2920, 2848, 1767, 1429, 1385, 1182, 1152, 1084, 1012, 978, 741, 702, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.09), 319 (4.82), 416 (3.68); MALDI-TOF m/z calcd for $C_{68}H_7NO_2$ [M^+] 869.0471, found 869.0443.

3-Methyloxazolidino[4,5:1,2][60]fullerene, **2b**. By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (6.8 mg, 0.05 mmol), $FeCl_3$ (1.6 mg, 0.01 mmol), and $PhI(O_2CCF_3)_2$ (21.3 mg, 0.05 mmol) at 60 °C afforded **2b** (14.7 mg, 37%) and recovered C_{60} (17.3 mg, 48%): amorphous brown solid; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 3.74 (s, 3H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 152.22 (1C), 147.07 (1C), 146.85 (1C), 145.20 (6C), 145.11, 144.98, 144.96, 143.96, 143.93, 143.90 (4C), 143.41, 143.33, 143.14 (4C), 143.03, 141.55, 141.52, 141.48, 141.09, 140.97, 140.79, 140.76, 140.62, 140.27, 138.67, 138.56, 136.48, 136.11, 90.69 (1C), 77.18 (1C), 28.82 (1C); FT-IR ν/cm^{-1} (KBr) 2918, 2850, 1767, 1421, 1372, 1266, 1180, 1146, 1033, 1010, 949, 872, 745, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 254 (5.01), 317 (4.70), 417 (3.55); MALDI-TOF m/z calcd for $C_{62}H_3NO_2$ [M^+] 793.0158, found 793.0160.

3-Butyloxazolidino[4,5:1,2][60]fullerene, **2c**. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1c** (8.7 mg, 0.05 mmol), $FeCl_3$ (1.7 mg, 0.01 mmol), and $PhI(O_2CCF_3)_2$ (21.7 mg, 0.05 mmol) at 60 °C afforded **2c** (14.8 mg, 35%) and recovered C_{60} (18.8 mg, 52%): amorphous brown solid; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 4.13 (t, J = 7.6 Hz, 2H), 2.11−2.03 (m, 2H), 1.59 (sextet, J = 7.4 Hz, 2H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 152.85 (1C), 147.24 (1C), 147.05 (1C), 145.37 (6C), 145.17, 145.16 (4C), 144.21, 144.20, 144.10, 144.06, 144.01, 143.60, 143.47, 143.34, 143.06, 141.74, 141.73, 141.70, 144.29, 141.19, 141.02, 140.99, 140.82, 140.43, 138.88, 138.70, 136.27, 136.22, 91.21 (1C), 77.09 (1C), 43.11 (1C), 30.77 (1C), 19.76 (1C), 13.28 (1C); FT-IR ν/cm^{-1} (KBr) 2952, 2923, 2861, 1767, 1435, 1386, 1311, 1185, 1146, 1070, 1013, 963, 744, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 255 (5.14), 318 (4.83), 417 (3.81); MALDI-TOF m/z calcd for $C_{65}H_9NO_2$ [M^+] 835.0628, found 835.0623.

3-Isopropyloxazolidino[4,5:1,2][60]fullerene, **2d**. By following the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (15.9 mg, 0.10 mmol), $FeCl_3$ (1.6 mg, 0.01 mmol), and $PhI(O_2CCF_3)_2$ (21.5 mg, 0.05 mmol) at 40 °C afforded **2d** (9.8 mg, 24%) and recovered C_{60} (21.7 mg, 60%): amorphous brown solid; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 4.65 (septet, J = 6.8 Hz, 1H), 1.85 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 151.43 (1C), 147.18 (1C), 147.01 (1C), 145.36, 145.34, 145.31, 145.15, 145.12 (4C), 144.34, 144.21, 144.04, 144.02, 143.79, 143.61, 143.34, 143.29, 143.16, 141.71 (4C), 141.63, 141.29, 141.14, 140.99, 140.91, 140.75, 140.41, 138.80, 138.64, 136.32, 136.14, 91.12 (1C), 77.33 (1C), 46.83 (1C), 19.36; FT-IR ν/cm^{-1} (KBr) 2960, 2922, 2853, 1762, 1505, 1455, 1418, 1374, 1316, 1262, 1218, 1095, 1013, 958, 803, 744, 570, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 259 (5.18), 318 (4.85), 416 (3.71); MALDI-TOF m/z calcd for $C_{64}H_7NO_2$ [M^+] 821.0471, found 821.0443.

3-Methoxyloxazolidino[4,5:1,2][60]fullerene, **2e**. By following the general procedure, the reaction of C_{60} (36.7 mg, 0.05 mmol) with **1e** (7.7 mg, 0.05 mmol), $FeCl_3$ (1.5 mg, 0.01 mmol), and $PhI(O_2CCF_3)_2$ (22.0 mg, 0.05 mmol) at 25 °C afforded **2e** (10.9 mg, 26%) and recovered C_{60} (21.2 mg, 58%): amorphous brown solid; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 4.43 (s, 3H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 150.52 (1C), 147.15 (1C), 146.84 (1C), 145.31, 145.28, 145.22, 145.11, 145.02 (4C), 143.98, 143.97, 143.89, 143.53, 143.32, 143.26, 143.25, 143.10, 143.01, 141.60, 141.57, 141.53, 141.11, 141.07, 140.91, 140.83, 140.73, 140.16, 138.83, 138.70, 136.49, 135.96, 90.90 (1C), 75.34 (1C), 64.66 (1C); FT-IR ν/cm^{-1} (KBr) 2923, 2849, 1790, 1505, 1431, 1263, 1143, 1110, 999, 947, 866, 797, 730, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.13), 317 (4.82), 418 (3.66); MALDI-TOF m/z calcd for $C_{62}H_3NO_3$ [M^+] 809.0107, found 809.0110.

3-(Ethoxylcarbonylmethyl)oxazolidino[4,5:1,2][60]fullerene, **2f**. By following the general procedure, the reaction of C_{60} (35.9 mg, 0.05 mmol) with **1f** (10.4 mg, 0.05 mmol), $FeCl_3$ (1.6 mg, 0.01 mmol), and $PhI(O_2CCF_3)_2$ (21.7 mg, 0.05 mmol) at 60 °C afforded **2f** (11.9 mg, 27%) and recovered C_{60} (17.7 mg, 49%): amorphous brown solid; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 4.78 (s, 2H), 4.27 (q, J = 7.0 Hz, 2H), 1.31 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 166.00 (1C), 152.95 (1C), 147.18 (1C), 146.95 (1C), 145.31 (4C), 145.24, 145.09, 145.05, 145.01, 144.10, 143.99, 143.93, 143.66, 143.48, 143.31, 143.25, 143.07, 142.77, 141.61 (4C), 141.53, 141.18, 141.02, 140.86, 140.83, 140.68, 140.30, 138.68, 138.57, 136.43, 136.38, 91.61 (1C), 76.55 (1C), 60.66 (1C), 43.53 (1C), 13.43 (1C); FT-IR ν/cm^{-1} (KBr) 2961, 2921, 2852, 1773, 1747, 1414, 1378, 1303, 1259, 1189, 1088, 1058, 1015, 801, 742, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 254 (5.08), 317 (4.79), 416 (3.62); MALDI-TOF m/z calcd for $C_{65}H_7NO_4$ [M^+] 865.0370, found 865.0379.

3-(p-Tolyl)oxazolidino[4,5:1,2][60]fullerene, **2g**. By following the general procedure, the reaction of C_{60} (36.3 mg, 0.05 mmol) with **1g** (20.6 mg, 0.10 mmol), $FeCl_3$ (8.3 mg, 0.05 mmol), and $PhI(O_2CCF_3)_2$ (21.8 mg, 0.05 mmol) at 25 °C afforded **2g** (7.0 mg, 16%) and recovered C_{60} (29.0 mg, 80%): amorphous brown solid; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 152.25 (1C), 147.32 (1C), 147.10 (1C), 145.47 (4C), 145.42, 145.21 (4C), 145.18, 144.30, 144.18, 144.14, 144.10, 143.99, 143.62 (4C), 143.49, 143.42, 141.79, 141.72 (4C), 141.36, 141.26, 141.02, 141.00, 140.79, 140.52, 138.90, 138.58, 138.13 (1C), 136.59, 136.20, 131.94 (1C), 129.37, 128.83, 91.38 (1C), 78.81 (1C), 20.63 (1C); FT-IR ν/cm^{-1} (KBr) 2946, 2857, 1772, 1510, 1431, 1363, 1232, 1179, 1154, 1087, 1013, 954, 864, 792, 740, 595, 525; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.04), 318 (4.74), 417 (3.57); MALDI-TOF m/z calcd for $C_{68}H_7NO_2$ [M^+] 869.0471, found 869.0468.

■ ASSOCIATED CONTENT

Supporting Information

^1H NMR, ^{13}C NMR, and UV-vis spectra of products **2a−g**. 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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