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Ferric Perchlorate-Mediated Synthesis of 1,2-Fullerenols C_{60}(OCOR)(OH)

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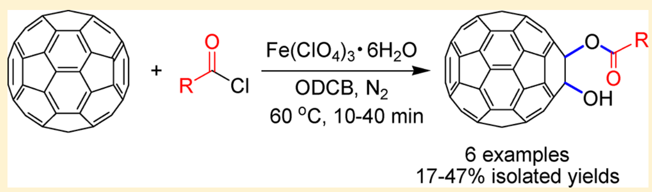
Supporting Information

ABSTRACT: 1,2-Fullerenols C_{60}(OCOR)(OH) have been facilely synthesized via the one-step reaction of [60]fullerene with acid chlorides promoted by ferric perchlorate. A possible reaction mechanism for the product formation is proposed.



Functionalization of [60]fullerene (C_{60}) leading to a large number of fascinating fullerene derivatives with wide structural diversity is the essential issue in fullerene chemistry.[1] Fullerenols with hydroxy group(s) attached to the fullerene cage were one of the first reported fullerene compounds and exhibited biological activities.[2] Mixtures of polyhydroxylated fullerenols $C_{60}(OH)_n$ were usually synthesized by utilizing nitronium chemistry,[3] aqueous acid reaction,[4] or aqueous base reaction.[5] They could also be produced by the reaction with oleum,[6] nitrogen dioxide radical,[7] or BH_3[8] followed by hydrolysis. Fullerenols with multiple addends were prepared by the reaction of $C_{70}Cl_{10}$ with benzene/$FeCl_3$,[9] the reaction of $C_{60}Cl_6$ with methyllithium followed by hydrolysis,[10] the reaction of C_{60} with methyllithium,[11] or the transformation of fullerene peroxides containing multiple OO^tBu groups.[12] The simplest fullerene diols $C_{60}(OH)_2$ and $C_{70}(OH)_2$ could be synthesized by the reaction of C_{60} and C_{70} with RuO_4 followed by acid hydrolysis.[13] The synthesis of monohydroxylated fullerenols with the general form of C_{60}ROH is relatively underdeveloped, and only a few such compounds have been prepared by the reaction of C_{60} with $(R_FCO_2)_2O$,[14] the N−O bond cleavage of [60]fullereno[1,2*d*]isoxazole,[15] the hydrolysis of chlorofullerenes,[16] nucleophilic substitution of $C_{60}O$ in the presence of $BF_3{\cdot}Et_2O$,[17] the aminolysis of a C_{60}-fused lactone,[18] the reaction of C_{60} with water catalyzed with Cp_2MCl_2,[19] or the reaction of C_{60} with 4-substituted phenylhydrazine hydrochlorides in the presence of $NaNO_2$.[20] Among the reported monohydroxylated fullerenols (C_{60}ROH), only five of them were formed in a 1,2-addition mode.[15,17−19] In most cases, 1,2-C_{60}ROH were obtained by a two-step reaction[15,17,18] starting from C_{60}. Therefore, it is still important to develop a simple and efficient method to obtain the 1,2-addition fullerenols (1,2-C_{60}ROH) with different functional groups via a one-step process from C_{60}.

Radical reactions of fullerenes promoted by transition-metal salts[21] such as $Mn(OAc)_3$,[22] $Cu(OAc)_2$,[22d,23] $Pb(OAc)_4$,[22i,24] and TBADT[$(n\text{-}Bu_4N)_4W_{10}O_{32}$][25] have attracted extensive attention. In efforts to extend the transition-metal-salt-mediated radical reactions of fullerenes, our group recently investigated the reactions of C_{60} promoted by cheap and easily available $Fe(ClO_4)_3$. The $Fe(ClO_4)_3$-mediated reactions of C_{60} with nitriles,[26a] aldehydes/ketones,[26b] malonate esters,[26c] arylboronic acids,[26d] and *β*-keto esters[26e] afforded C_{60}-fused oxazoles, C_{60}-fused 1,3-dioxolanes, C_{60}-fused disubstituted lactones, fullerenyl boronic esters, and C_{60}-fused hemiketal and dihydrofuran, respectively. In continuation of our interest in $Fe(ClO_4)_3$-mediated reactions of C_{60}, herein we describe the $Fe(ClO_4)_3$-mediated one-step reaction of C_{60} with acid chlorides to afford monohydroxylated fullerenols 1,2-C_{60}(OCOR)(OH).[27]

Initially, the reaction of C_{60} with 4-toluoyl chloride (**1a**) in the presence of $Fe(ClO_4)_3$ by employing the direct dissolution method[26a,b] was screened to obtain the optimized reaction conditions. A mixture of $Fe(ClO_4)_3{\cdot}6H_2O$ (0.15 mmol) and **1a** (2.5 mmol) was first heated in an oil bath preset at 60 °C for 20 min to allow ferric perchlorate to dissolve in the liquid acid chloride. Then an *o*-dichlorobenzene (ODCB, 6 mL) solution of C_{60} (36.0 mg, 0.05 mmol) was added. The resulting solution was heated with vigorous stirring at the same temperature under nitrogen atmosphere for 25 min. Much to our satisfaction, the reaction was found to proceed well and gave fullerenol **2a** in 47% isolated yield (Table 1, entry 1). Other reaction conditions were also examined, and the results are summarized in Table 1. Reducing the reaction time drastically reduced the yield of **2a** (Table 1, entry 2). Increasing the reaction temperature did not improve the yield of **2a** (Table 1,

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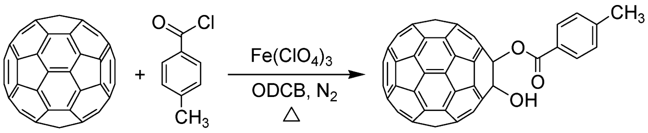
Table 1. Reaction Conditions for the $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with 4-Toluoyl Chloride 1a[a]



1a **2a**

entry	molar ratio [C_{60}/FEP/**1a**][b]	reaction temp (°C)	reaction time (min)	yield of **2a**[c] (%)	recovered C_{60} (%)
1	1:3:50	60	25	47	48
2	1:3:50	60	10	19	78
3	1:3:50	80	10	47	43
4	1:5:50	80	5	29	18
5	1:2:20	80	15	15	76
6	1:2:50	80	10	25	59
7	1:2:100	80	10	23	66
8	1:1:50	80	20	21	70
9	1:1:100	80	15	19	78

[a]All reactions were performed under nitrogen atmosphere by the direct dissolution of $Fe(ClO_4)_3 \cdot 6H_2O$ in **1a**. [b]FEP = $Fe(ClO_4)_3 \cdot 6H_2O$. [c]Isolated yield.

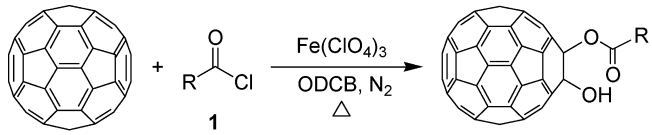
entry 3). No improvement could be achieved by varying the amount of 4-toluoyl chloride and $Fe(ClO_4)_3$ (Table 1, entries 4−9). Thus, the molar ratio of 1:3:50 for the reagents C_{60}, $Fe(ClO_4)_3$, and **1a** together with the reaction temperature of 60 °C were chosen as the optimized reaction conditions.

With the optimized reaction conditions in hand, other representative acid chlorides such as benzoyl chloride (**1b**), 4-methoxybenzoyl chloride (**1c**), 4-chlorobenzoyl chloride (**1d**), 2-chlorobenzoyl chloride (**1e**), and cinnamoyl chloride (**1f**) were employed as the substrates to obtain the desired 1,2-fullerenols **2b**, **2c**, **2d**, **2e**, and **2f**, respectively. The reaction conditions and yields for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with acid chlorides **1a−f** under nitrogen atmosphere are listed in Table 2.

As can be seen from Table 2, aromatic acid chlorides **1a−e** with both electron-withdrawing and electron-donating groups as well as cinnamoyl chloride **1f** could be successfully utilized to prepare 1,2-fullerenols **2a−f** in 17−47% isolated yields (24−90% based on consumed C_{60}), comparable to the previously reported data for most monoadducts. It should be noted that for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with cinnamoyl chloride **1f**, a C_{60}-fused lactone **3** (Scheme 1) was also obtained in 26% yield besides the expected 1,2-fullerenol **2f**. Unfortunately, the reaction of C_{60} with 4-nitrobenzoyl chloride bearing the strong electron-withdrawing NO_2 group afforded mainly some unknown byproducts probably due to the higher reactivity of 4-nitrobenzoyl chloride. It should be pointed out that the use of 3 equiv of $Fe(ClO_4)_3$ for the reaction with **1e** led to a significant amount of byproducts with polarity similar to C_{60}, and thus, 1 equiv of $Fe(ClO_4)_3$ was required to improve the yield and selectivity. The synthesized 1,2-fullerenols **2a−f** can be further manipulated through esterification, etherification and arylation, as demonstrated previously by us for analogous fullerenols.[20]

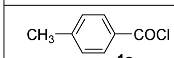
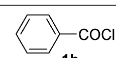
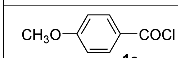
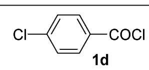
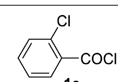
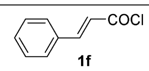
The structures of fullerenols **2a−f** were fully characterized by HR MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. All of the ^{1}H NMR spectra exhibited the expected chemical shifts as well as the splitting patterns for all protons. In the ^{13}C NMR spectra of **2a−f**, the peak for the C=O carbon appeared at 164.19−169.43 ppm, and the two sp^3-carbons of the C_{60} skeleton were located at 87.56−89.58 ppm and 83.10−85.08 ppm, close to those of other 1,2-adduct fullerene derivatives, in which the oxygen atom is connected to the C_{60} skeleton.[18,22h−j,26c] No more than 29 peaks including some overlapped ones for the 58 sp^2-carbons of the C_{60} moiety were observed in the range of 135−153 ppm, consistent with the C_s symmetry of their molecular structures. As for lactone **3**, its ^{1}H NMR spectrum displayed a singlet at 8.72 ppm for the proton connecting to the carbon−carbon double bond moiety besides those signals for the phenyl ring. In its ^{13}C NMR spectrum, there were 23 peaks including some overlapped ones in the 135−152 ppm range for the 58 sp^2-carbons of the C_{60} skeleton and two peaks at 96.63 and 64.90 ppm for the two sp^3-carbons of the C_{60} moiety, agreeing with its C_s symmetry. The IR spectrum of lactone **3** showed an absorption at 1768 cm^{-1} due to the C=O group. Its UV−vis spectrum exhibited a peak at 416 nm. The peak at around 420 nm is a diagnostic

Table 2. Reaction Conditions and Yields for the Reaction of C_{60} with Acid Chlorides 1a−f in the Presence of $Fe(ClO_4)_3$[a]



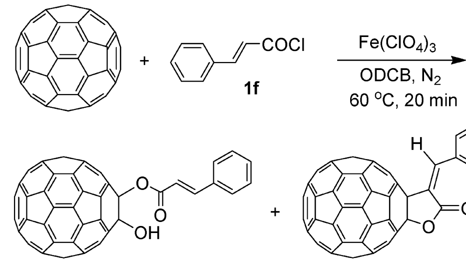
1 **2**

1a, **2a**: R = 4-CH_3-Ph; **1b**, **2b**: R = Ph; **1c**, **2c**: R = 4-CH_3O-Ph; **1d**, **2d**: R = 4-Cl-Ph; **1e**, **2e**: R = 2-Cl-Ph; **1f**, **2f**: R = PhCH=CH

acid chloride **1**	reaction time (min)	yield of **2**[b]
 **1a**	25	47% (90%)
 **1b**	10	42% (89%)
 **1c**	40	23% (41%)
 **1d**	20	24% (24%)
 **1e**	20[c]	24% (67%)
 **1f**	20	17% (35%)

[a]Unless otherwise indicated, all reactions were performed at 60 °C under nitrogen atmosphere, molar ratio of C_{60}/$Fe(ClO_4)_3 \cdot 6H_2O$/**1** = 1:3:50. [b]Isolated yield; that in parentheses was based on consumed C_{60}. [c]Molar ratio of C_{60}/$Fe(ClO_4)_3 \cdot 6H_2O$/**1e** = 1:1:50.

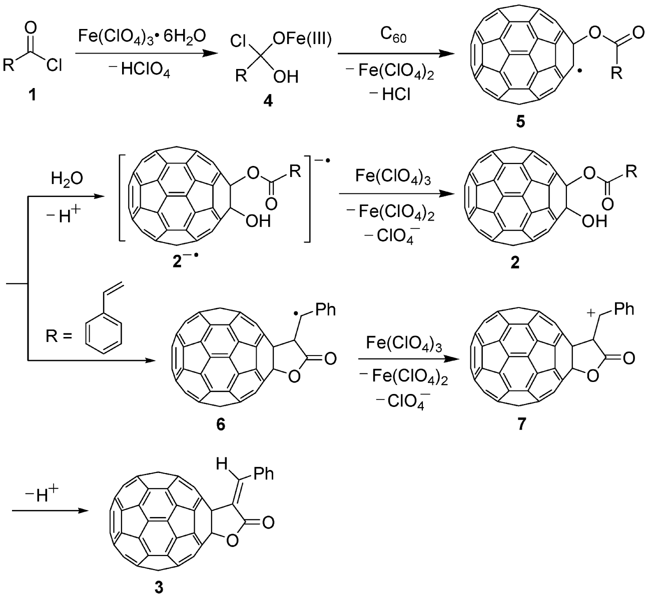
Scheme 1. $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Acid Chloride 1f Affording Fullerenol 2f and C_{60}-Fused Lactone 3



absorption for the 1,2-adduct of C_{60}, in which the oxygen atom is directly attached to the fullerene skeleton.[22h−j,26c]

On the basis of the previously suggested mechanisms for the reactions of C_{60} with nitriles,[26a] aldehydes/ketones,[26b] malonate esters,[26c] arylboronic acids,[26d] and β-keto esters[26e] in the presence of $Fe(ClO_4)_3$ as well as the reaction of C_{60} with carboxylic acids promoted by $Pb(OAc)_4$,[22i] we propose a possible mechanism for the formation of fullerenols **2a−f** and C_{60}-fused lactone **3** from the $Fe(ClO_4)_3$-mediated reaction of C_{60} with acid chlorides (Scheme 2). A chosen acid chloride reacts with the hydrated H_2O in $Fe(ClO_4)_3{\cdot}6H_2O$ or concomitant water in the system to produce Fe(III) complex **4** accompanied by the elimination of $HClO_4$. Addition of complex **4** to C_{60} generates fullerenyl radical **5** accompanied by the formation of $Fe(ClO_4)_2$ and HCl. Nucleophilic addition of H_2O to fullerenyl radical **5** with the loss of H^+ gives radical anion $\mathbf{2}^{\bullet-}$,[20,22i] followed by oxidation with another molecule of $Fe(ClO_4)_3$ to afford fullerenol **2**. In the case of C_{60}-fused lactone **3**, the first two steps are the same as those for fullerenol **2** to generate fullerene radical **5**, which can undergo intramolecular cyclization to give radical **6**. Oxidation of radical **6** by a second molecule of $Fe(ClO_4)_3$ results in cation **7** along with counteranion ClO_4^- and $Fe(ClO_4)_2$. Loss of H^+ from cation **7** leads to the formation of C_{60}-fused lactone **3**.

Scheme 2. Proposed Reaction Mechanism for the Formation of Fullerenols 2 and C_{60}-Fused Lactone 3



In summary, 1,2-fullerenols $C_{60}(OCOR)(OH)$ have been effectively prepared via the reaction of C_{60} with acid chlorides in the presence of $Fe(ClO_4)_3$, and they can be utilized as precursors for further functionalization such as esterification, etherification and arylation. The current protocol provides facile access to 1,2-fullerenol derivatives via a one-step procedure by using cheap and easily available acid chlorides and $Fe(ClO_4)_3$. A possible reaction mechanism for the formation of 1,2-fullerenols **2** and C_{60}-fused lactone **3** has been suggested.

■ EXPERIMENTAL SECTION

General Procedure for the $Fe(ClO_4)_3$-Mediated Reaction of C_{60} with Acid Chlorides 1a−f. A mixture of acid chloride **1a** (**1b−f**, 2.5 mmol) and ferric perchlorate hexahydrate (0.15 mmol, 0.05 mmol in case of **1e**) was added to a 50-mL round-bottom flask, which was equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer. The mixture was heated in an oil bath preset at 60 °C for 20 min to allow ferric perchlorate to dissolve in the liquid acid chloride. Then to the flask was added the *o*-dichlorobenzene (6 mL) solution of C_{60} (36.0 mg, 0.05 mmol). The resulting solution was heated with vigorous stirring in the oil bath at the same temperature under nitrogen atmosphere. The reaction was carefully monitored by thin-layer chromatography (TLC) and stopped at the designated time. After acetic acid (1 mL) was added to the reaction solution, the resulting mixture was directly separated on a silica gel column with carbon disulfide/toluene as the eluent. Fullerenol **2a** (**2b−f**) was obtained along with unreacted C_{60}.

Fullerenol 2a. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (331 μL, 2.5 mmol) and $Fe(ClO_4)_3{\cdot}6H_2O$ (69.0 mg, 0.15 mmol) for 25 min afforded first recovered C_{60} (17.1 mg, 48%) and then **2a** (20.3 mg, 47%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.37 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 5.21 (s, 1H), 2.53 (s, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 169.43 (1C, C═O), 151.15, 148.59 (1C), 148.48 (1C), 147.63, 146.49 (4C), 146.20, 146.12 (4C), 145.92, 145.46, 145.18 (4C), 145.09 (1C, aryl C), 144.87, 144.84, 144.64, 144.60, 142.59 (4C), 142.46, 142.31, 142.22, 141.54, 141.50, 141.37 (4C), 139.65, 139.14, 138.57, 136.42, 130.68 (aryl C), 129.45 (aryl C), 126.52 (1C, aryl C), 89.04 (1C, sp^3-C of C_{60}), 85.08 (1C, sp^3-C of C_{60}), 21.93 (1C); FT-IR ν/cm^{-1} (KBr) 2921, 1702, 1611, 1432, 1274, 1179, 1091, 1035, 994, 922, 832, 748, 576, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.28), 318 (4.74), 416 (3.84), 685 (3.45); MALDI FT-ICR MS m/z calcd for $C_{68}H_8O_3$ [M$^-$] 872.0473, found 872.0472.

Fullerenol 2b. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (290 μL, 2.5 mmol) and $Fe(ClO_4)_3{\cdot}6H_2O$ (69.0 mg, 0.15 mmol) for 10 min afforded first recovered C_{60} (18.9 mg, 53%) and then **2b** (18.2 mg, 42%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 8.53 (s, 1H), 8.42 (d, J = 6.9 Hz, 2H), 7.67 (t, J = 7.1 Hz, 1H), 7.58 (t, J = 7.2 Hz, 2H); ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.48 (d, J = 7.2 Hz, 2H), 7.72 (t, J = 7.4 Hz, 1H), 7.61 (t, J = 7.5 Hz, 2H), 5.16 (s, 1H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 164.91 (1C, C═O), 152.40, 148.47, 147.51 (1C), 147.45 (1C), 145.46, 145.40, 145.08 (6C), 144.72 (4C), 144.51, 144.13 (4C), 144.05 (4C), 143.75, 141.71, 141.57, 141.42, 141.29 (4C), 140.71, 140.51 (4C), 140.38, 138.35, 137.99, 137.91, 135.37, 132.25 (1C, aryl C), 129.72 (1C, aryl C), 129.52 (aryl C), 127.71 (aryl C), 87.70 (1C, sp^3-C of C_{60}), 83.10 (1C, sp^3-C of C_{60}); FT-IR ν/cm^{-1} (KBr) 2920, 1703, 1428, 1358, 1270, 1179, 1089, 1028, 993, 703, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.13), 318 (4.70), 417 (3.62), 685 (2.43); MALDI FT-ICR MS m/z calcd for $C_{67}H_6O_3$ [M$^-$] 858.0317, found 858.0313.

Fullerenol 2c. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (427 mg, 2.5 mmol) and $Fe(ClO_4)_3{\cdot}6H_2O$ (69.0 mg, 0.15 mmol) for 40 min afforded first recovered C_{60} (15.9 mg, 44%) and then **2c** (10.0 mg, 23%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 8.44 (s, 1H), 8.36 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 8.7 Hz, 2H), 3.93 (s, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 164.80 (1C, C═O), 162.22 (1C, aryl C), 152.63, 148.91, 147.66 (1C), 147.65 (1C), 145.60, 145.53, 145.23 (6C), 144.90, 144.85, 144.70, 144.27 (6C), 144.18, 143.92, 141.87, 141.72, 141.57, 141.44 (4C), 140.86, 140.65 (4C), 140.36, 138.49, 138.14, 138.00, 135.55, 131.67 (aryl C), 122.02 (1C, aryl C), 113.13 (aryl C), 87.56 (1C, sp^3-C of C_{60}), 83.28 (1C, sp^3-C of C_{60}), 54.59 (1C); FT-IR ν/cm^{-1} (KBr) 2925, 1704, 1605, 1510, 1460, 1328, 1263, 1167, 1099, 1035, 996, 840, 766, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.04), 318 (4.60), 417 (3.66), 685 (3.31); MALDI FT-ICR MS m/z calcd for $C_{68}H_8O_4$ [M$^-$] 888.0423, found 888.0422.

Fullerenol 2d. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (318 μL, 2.5 mmol) and $Fe(ClO_4)_3 \cdot 6H_2O$ (69.0 mg, 0.15 mmol) for 20 min afforded first a trace amount of recovered C_{60} and then **2d** (10.6 mg, 24%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (300 MHz, CS_2/DMSO-d_6) δ 8.63 (s, 1H), 8.41 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 164.19 (1C, *C*=O), 152.33, 148.26, 147.58 (1C), 147.51 (1C), 145.53, 145.46, 145.21, 145.15 (4C), 144.77 (4C), 144.53, 144.18 (4C), 144.06 (4C), 143.79, 141.77, 141.64, 141.49, 141.34 (4C), 140.75, 140.57 (4C), 140.40, 138.67 (1C, aryl *C*), 138.43, 138.05, 137.98, 135.40, 131.12 (aryl *C*), 128.32 (1C, aryl *C*), 128.03 (aryl *C*), 87.94 (1C, sp^3-*C* of C_{60}), 83.16 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2923, 1708, 1594, 1428, 1401, 1270, 1091, 1041, 1016, 992, 847, 754, 527; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.12), 317 (4.65), 416 (3.85), 685 (3.42); MALDI FT-ICR MS m/z calcd for $C_{67}H_5{}^{35}ClO_3$ [M$^-$] 891.9927, found 891.9932.

Fullerenol 2e. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1e** (317 μL, 2.5 mmol) and $Fe(ClO_4)_3 \cdot 6H_2O$ (23.0 mg, 0.05 mmol) for 20 min afforded first recovered C_{60} (23.1 mg, 64%) and then **2e** (10.6 mg, 24%) as an amorphous black solid: mp >300 °C; ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 8.42 (d, J = 8.1 Hz, 1H), 7.65−7.49 (m, 3H), 5.14 (s, 1H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 167.89 (1C, *C*=O), 150.82, 148.66 (1C), 148.56 (1C), 147.23, 146.55 (4C), 146.29, 146.20 (4C), 146.00, 145.49, 145.25 (4C), 145.00, 144.90, 144.63 (4C), 142.65 (4C), 142.53, 142.35, 142.27, 141.59 (4C), 141.38 (4C), 139.72, 139.25, 138.63, 136.54, 134.98 (1C, aryl *C*), 133.64 (1C, aryl *C*), 132.66 (1C, aryl *C*), 131.54 (1C, aryl *C*), 128.95 (1C, aryl *C*), 126.91 (1C, aryl *C*), 89.58 (1C, sp^3-*C* of C_{60}), 84.96 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2922, 1701, 1590, 1467, 1431, 1357, 1291, 1244, 1102, 1041, 988, 743, 525; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.04), 317 (4.60), 416 (3.75), 685 (3.36); MALDI FT-ICR MS m/z calcd for $C_{67}H_5{}^{35}ClO_3$ [M$^-$] 891.9927, found 891.9921.

Fullerenol 2f and C_{60}-Fused Lactone 3. According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1f** (416 mg, 2.5 mmol) and $Fe(ClO_4)_3 \cdot 6H_2O$ (69.0 mg, 0.15 mmol) for 20 min afforded first recovered C_{60} (18.8 mg, 52%), then **3** (11.2 mg, 26%) and **2f** (7.4 mg, 17%). **2f**: amorphous black solid; mp >300 °C; ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 8.17 (d, J = 15.9 Hz, 1H), 7.69−7.66 (m, 2H), 7.46−7.43 (m, 3H), 6.94 (d, J = 15.9 Hz, 1H), 5.18 (s, 1H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 169.49 (1C, *C*=O), 151.04, 148.46 (1C), 148.37 (1C), 147.62 (1C, *C*H-Ph), 147.51, 146.36 (4C), 146.07, 146.00 (4C), 145.80, 145.34, 145.06 (4C), 144.97, 144.76, 144.51 (4C), 142.48 (4C), 142.35, 142.20, 142.11, 141.42, 141.38, 141.25 (4C), 139.54, 139.02, 138.37, 136.28, 133.90 (1C, aryl *C*), 130.87 (1C, aryl *C*), 128.93 (aryl *C*), 128.42 (aryl *C*), 116.81 (1C, *C*H−CO), 88.74 (1C, sp^3-*C* of C_{60}), 84.97 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2920, 1696, 1632, 1447, 1432, 1329, 1311, 1269, 1202, 1169, 1147, 1101, 1035, 1013, 976, 918, 860, 755, 708, 598, 575, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (4.94), 318 (4.68), 418 (3.50), 688 (2.34); MALDI FT-ICR MS m/z calcd for $C_{69}H_8O_3$ [M$^-$] 884.0473, found 884.0475. **3**: amorphous black solid; mp >300 °C; ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 8.72 (s, 1H), 7.36−7.32 (m, 2H), 7.19−7.16 (m, 3H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 168.72 (1C, *C*=O), 151.17, 147.95 (1C), 147.42 (1C), 146.39, 146.26 (1C, *C*H-Ph), 145.99 (8C), 145.56, 145.48, 145.33, 145.18, 145.09, 145.03, 144.51, 144.33 (4C), 142.61 (6C), 142.14 (4C), 142.04, 141.83, 141.16, 140.98, 139.84, 138.28, 137.16, 135.17, 132.62 (1C, aryl *C*), 128.83 (1C, aryl *C*), 128.26 (aryl *C*), 128.15 (aryl *C*), 127.87 (1C, *C*H−CO), 96.63 (1C, sp^3-*C* of C_{60}), 64.90 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2921, 1768, 1506, 1435, 1238, 1194, 1164, 998, 970, 967, 741, 694, 595, 575, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (4.97), 317 (4.62), 416 (3.50), 682 (2.28); MALDI FT-ICR MS m/z calcd for $C_{69}H_6O_2$ [M$^-$] 866.0368, found 866.0365.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR and ^{13}C NMR spectra of products **2a−f** and **3**. 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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