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# Synthesis of Ortho Acid Ester-Type 1,3-Dioxolanofullerenes: Radical Reaction of [60]Fullerene with Halocarboxylic Acids Promoted by Lead(IV) Acetate

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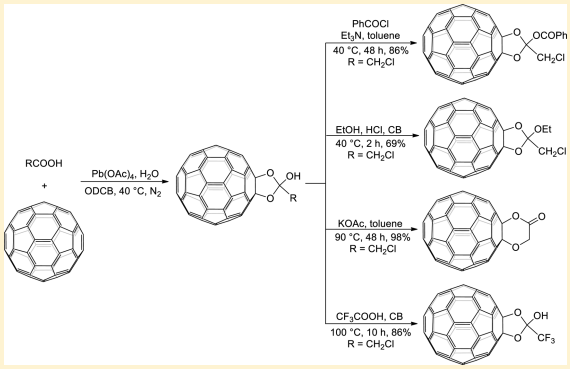
Supporting Information

**ABSTRACT:** A lead(IV) acetate-promoted radical reaction of [60]fullerene with halocarboxylic acids has been exploited to synthesize rare ortho acid ester-type 1,3-dioxolanofullerenes, the hydroxyl group of which can be further transformed to an ester or ether group. Intriguingly, an ortho acid ester-type 1,3-dioxolanofullerene can also be converted to a 1,4-dioxanonofullerene in the presence of a base or manipulated to another ortho acid ester-type 1,3-dioxolanofullerene by reaction with a stronger halocarboxylic acid. Moreover, two possible reaction pathways leading to the observed products are also proposed.




## INTRODUCTION

Radical chemistry plays a great role in the synthesis of fullerene derivatives,[1] which have important potential applications in materials, medical chemistry, and nanotechnology.[2] While transition-metal salts such as $Mn(OAc)_3$,[3] $Fe(ClO_4)_3$,[4] Cu(I or II),[5] $CoCl_2$dppe,[6] and $Ag_2CO_3$[7] have been well-developed to prepare a multitude of fullerene derivatives because of their particular efficiency and regioselectivity, the utilization of main-group metal salts has rarely been reported. Recently, as a cheap and easily available reagent, $Pb(OAc)_4$ was found to have specific efficiency for the chemoselective synthesis of some fullerene derivatives. In 2006, Rubin's group described the preparation of the 1,2,3,4,5,6-hexaadduct of [60]fullerene ($C_{60}$) via a remarkable double 5-exo-trig addition reaction of alkoxyl radicals promoted by $Pb(OAc)_4$.[8a] Troshin and co-workers reported the formation of pyrrolidinofullerene derivatives by the $Pb(OAc)_4$-mediated oxidative coupling reaction of $C_{60}$ with amino acid esters.[8b] Our group disclosed the preparation of fullerenyl esters by the $Pb(OAc)_4$-promoted decarboxylation reaction of $C_{60}$ with carboxylic acids.[8c] Therefore, it is desirable to develop new $Pb(OAc)_4$-mediated radical reactions to prepare other functionalized fullerenes.

To date, a few methodologies have been developed to synthesize acetal/ketal-type 1,3-dioxolanofullerenes.[9] However, only three ortho acid ester-type 1,3-dioxolanofullerenes (2-hydroxydioxolano[4,5:1,2][60]fullerenes) have been reported until now. Two perfluorinated ortho acid ester-type 1,3-dioxolanofullerenes were prepared by the reactions of $C_{60}$ with perfluorinated diacyl peroxides[10a] and acyl hypohalogenites ($CF_3COOI$ or $CF_3COOBr$).[10b] Another ortho acid ester-type 1,3-dioxolanofullerene derivative was synthesized through the epoxide ring-opening reaction with trifluoroacetic acid.[10c] It should be noted that these methods were limited only to perfluorinated reagents. The perfluorinated group may play an important role in stabilizing such an unusual structure appended to the $C_{60}$ cage.[10c] We envisioned that a halocarboxylic radical, not limited to a perfluorinated source, may add to $C_{60}$ followed by intramolecular radical cyclization to give the corresponding ortho acid ester-type 1,3-dioxolanofullerene.

## RESULTS AND DISCUSSION

Our study commenced with chloroacetic acid (**1a**) as the typical substrate and $Pb(OAc)_4$ as the promoter in anhydrous *o*-dichlorobenzene (ODCB) at 40 °C under a nitrogen atmosphere. To our delight, the desired product **2a** was obtained in 6% yield (Table 1, entry 1). It has been suggested that $H_2O$ might play an important role in this type of transformation.[10b] Thus, the amount of $H_2O$ was screened, and the highest yield of **2a** (27%) was obtained when 20 equiv of $H_2O$ was added (Table 1, entry 3 vs entries 1, 2, 4, and 5). Increasing or decreasing the amount of **1a** or $Pb(OAc)_4$ was detrimental to get a higher yield (Table 1, entries 6–9). Prolonging the reaction time only led to a comparable yield of **2a** (Table 1, entry 10 vs entry 3), while shortening the reaction

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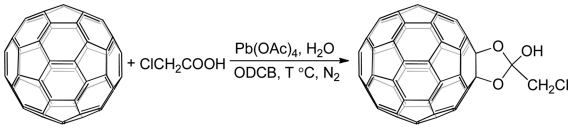
**Table 1. Optimization of the Reaction Conditions for the Reaction of $C_{60}$ with Chloroacetic Acid in the Presence of $Pb(OAc)_4$[a]**




1a 2a

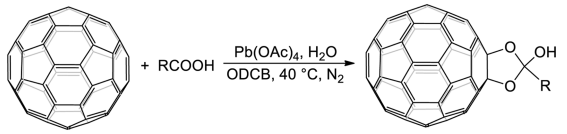
| entry | molar ratio[b] | $T$ (°C) | yield of **2a** (%)[c] |
|---|---|---|---|
| 1 | 1:5:2:0 | 40 | 6 (43) |
| 2 | 1:5:2:10 | 40 | 23 (46) |
| **3** | **1:5:2:20** | **40** | **27 (59)** |
| 4 | 1:5:2:30 | 40 | 21 (46) |
| 5 | 1:5:2:40 | 40 | 21 (60) |
| 6 | 1:6:2:20 | 40 | 20 (51) |
| 7 | 1:4:2:20 | 40 | 14 (42) |
| 8 | 1:5:3:20 | 40 | 19 (44) |
| 9 | 1:5:1:20 | 40 | 15 (65) |
| 10[d] | 1:5:2:20 | 40 | 26 (59) |
| 11[e] | 1:5:2:20 | 40 | 20 (56) |
| 12 | 1:5:2:20 | 50 | 19 (49) |
| 13 | 1:5:2:20 | 30 | 15 (54) |
| 14[f] | 1:5:2:20 | 40 | 13 (38) |

[a]Unless otherwise noted, the reactions were performed in anhydrous ODCB at 40 °C under a nitrogen atmosphere for 7 h. [b]Molar ratio refers to $C_{60}$:**1a**:$Pb(OAc)_4$:$H_2O$. [c]Yields in parentheses are based on consumed $C_{60}$. [d]The reaction time was 8 h. [e]The reaction time was 6 h. [f]The reaction was carried out under an air atmosphere.

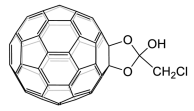
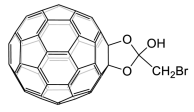
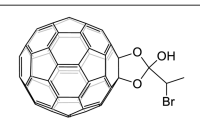
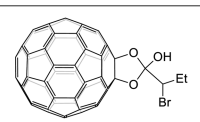
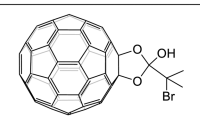
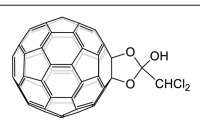
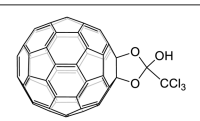
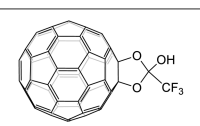
time slightly reduced the yield (Table 1, entry 11 vs entry 3). It was found that changing the reaction temperature was unfavorable in improving the reaction efficiency (Table 1, entries 12 and 13). When the reaction was performed under an air atmosphere, the yield of **2a** sharply decreased from 27% to 13% (Table 1, entry 3 vs entry 14). Our previous work showed that an inert atmosphere was beneficial for metal-salt-mediated radical reactions of $C_{60}$.[1,4,7,8c] Thus, a radical process was probably involved in this $Pb(OAc)_4$-mediated reaction.[8c] It is worth mentioning that when other transition-metal salts, such as $Fe(ClO_4)_3$, $FeCl_3$, $Cu(OAc)_2$, and $Mn(OAc)_3$, were used in place of $Pb(OAc)_4$, the desired product **2a** could not be obtained. The reasons for the failure of these transition-metal salts are not yet clear. Nevertheless, the $Mn(OAc)_3$-mediated reaction of $C_{60}$ with chloroacetic acid at a high temperature (140 °C) could also provide **2a** as a minor product.[8c] Therefore, a molar ratio of 1:5:2:20 for the reagents $C_{60}$, **1a**, $Pb(OAc)_4$, and $H_2O$ in anhydrous ODCB and a reaction temperature at 40 °C under a nitrogen atmosphere were chosen as the optimized reaction conditions (Table 1, entry 3).

With the optimized reaction conditions in hand, we started to investigate the substrate scope of the reaction. As shown in Table 2, all of the examined halocarboxylic acids **1a**–**h** could successfully produce the desired products **2a**–**h** in valuable yields ranging from 15 to 32%. Because of steric hindrance, the reactions of **1c**–**e** with $C_{60}$ were much more sluggish than others (Table 2, entries 3–5). Intriguingly, multihalogenated carboxylic acids **1f**–**h** showed higher reaction activity than **1a**–**e** (Table 2, entries 6–8 vs entries 1–5), possibly because of their stronger acidity. In addition, the chlorine and bromine atoms in products **2a**–**g** may provide an opportunity for further transformations. It should be noted that $C_{60}O$ was also formed

**Table 2. Reaction Conditions and Yields for the Preparation of Ortho Acid Ester-Type 1,3-Dioxolanofullerenes 2a–h[a]**




1a-h 2a-h

| entry | acid **1** | product **2** | time (h) | yield of **2** (%)[b] |
|---|---|---|---|---|
| 1 |  **1a** |  **2a** | 7 | 27 (59) |
| 2 |  **1b** |  **2b** | 6 | 25 (83) |
| 3 |  **1c** |  **2c** | 42 | 29 (85) |
| 4 |  **1d** |  **2d** | 58 | 25 (60) |
| 5 |  **1e** |  **2e** | 68 | 15 (88) |
| 6 |  **1f** |  **2f** | 2.5 | 32 (74) |
| 7 |  **1g** |  **2g** | 2 | 23 (52) |
| 8 |  **1h** |  **2h** | 2 | 24 (59) |

[a]Unless otherwise specified, the reactions were performed with $C_{60}$ (0.05 mmol), **1** (0.25 mmol), $Pb(OAc)_4$ (0.10 mmol), and $H_2O$ (1 mmol) in anhydrous ODCB (6 mL) at 40 °C under a nitrogen atmosphere. [b]Yields in parentheses are based on consumed $C_{60}$.

as a byproduct, but in a much lower amount than the desired product, in all of the reactions of $C_{60}$ with **1a**–**h**.

We previously reported the $Pb(OAc)_4$-promoted reaction of $C_{60}$ with carboxylic acids at 140 °C to generate fullerenyl esters.[8c] However, the corresponding reaction with chloroacetic acid gave an unexpected product,[8c,11] which has now been shown to be product **2a**, albeit in a much lower yield. It seems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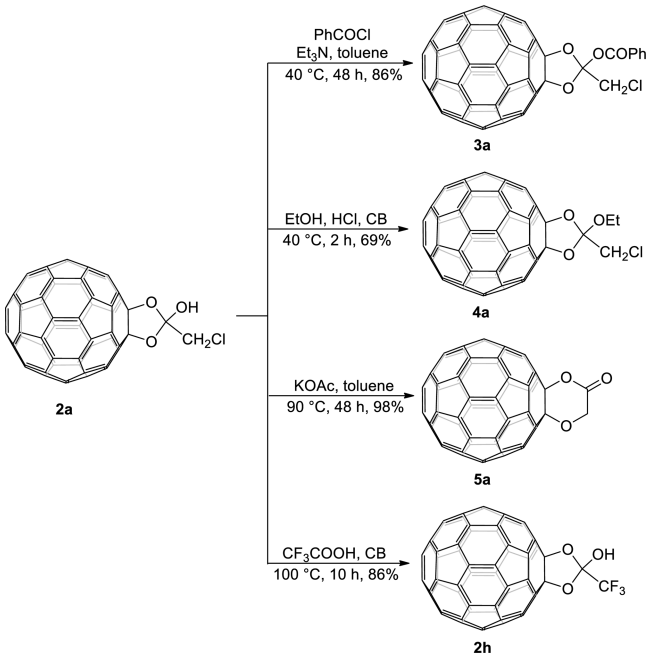
that the acidity of the substrate is essential, as carboxylic acids bearing electron-donating groups could not be applied to this reaction because of their weaker acidity. Attempts to use non-halogenated acids such as cyanoacetic acid, benzoic acid, and phenylacetic acid also failed to get the desired ortho acid ester-type 1,3-dioxolanofullerenes. It was reported that electron-withdrawing fluoro and chloro substituents greatly stabilized the 1,3-dioxolane rings and cyclic ortho acid esters.[12] Combined with the precedent examples in the literature,[10,12] we speculated that the halogen atoms may play an important role in stabilizing such an unusual ortho acid ester-type structure appended to the $C_{60}$ cage.

As a known product, the identity of **2h** was confirmed by comparing its spectral data with those reported in the literature.[10a,b] The new compounds **2a–g** were unambiguously characterized by MALDI-TOF MS, $^1$H NMR, $^{13}$C NMR, FT-IR, and UV–vis spectra. All of the products **2a–h** exhibited the correct molecular ion peaks in their mass spectra. The $^{13}$C NMR spectra of **2a**, **2b**, and **2e–g** exhibited no more than 30 peaks in the range of 136–149 ppm for the 58 $sp^2$ carbons of the fullerene cage and a peak in the range of 93–95 ppm for the two $sp^3$ carbons of the fullerene skeleton, consistent with their $C_s$ molecular symmetry. However, because of the $\alpha$-chiral carbon atom, the $^{13}$C NMR spectra of **2c** and **2d** exhibited at least 32 peaks in the range of 136–149 ppm for the 58 $sp^2$-carbons of the fullerene cage and two peaks in the range of 92–94 ppm for the two $sp^3$ carbons of the fullerene skeleton, consistent with their $C_1$ symmetry. The chemical shifts for the two $sp^3$ carbons of the fullerene skeleton are close to those of fullerene derivatives with an oxygen atom directly attached to the fullerene skeleton.[4,5a,9,10] The UV–vis spectra of all of the products showed a peak at 416–418 nm, which is the characteristic peak of 1,2-adducts of $C_{60}$ containing at least one appended heteroatom.

Further functionalization of the synthesized ortho acid ester-type 1,3-dioxolanofullerenes was investigated using **2a** as a representative example. Esterification and etherification of **2a** could be achieved by reactions with acid chlorides and alcohols under alkaline or acidic conditions. When **2a** was treated with benzoyl chloride in the presence of $Et_3N$ in toluene at 40 °C for 48 h, product **3a** was obtained in 86% yield (Scheme 1). The reaction of **2a** with EtOH and HCl in chlorobenzene (CB) at 40 °C for 2 h afforded **4a** in 69% yield (Scheme 1). The $^1$H NMR spectra of **3a** and **4a** exhibited corresponding peaks for the phenyl and ethyl groups in place of the hydroxyl proton. The $^{13}$C NMR spectra of **3a** and **4a** showed 31 and 28 peaks in the range of 137–149 ppm for the 58 $sp^2$ carbons of the fullerene cage and a peak at 95.13 and 95.36 ppm for the two $sp^3$ carbons of the fullerene skeleton, respectively. The peak at 163.85 ppm in the $^{13}$C NMR spectrum and the strong absorption at 1735 $cm^{-1}$ in the IR spectrum belong to the carbonyl moiety of **3a**. Intriguingly, it was found that **2a** could be quantitatively converted to 1,4-dioxanonofullerene (2-oxodioxano[5,6:1,2][60]fullerene) **5a** via an intramolecular rearrangement process in the presence of KOAc in toluene at 90 °C (Scheme 1). The hydroxyl group in **2a** was initially converted to an alkoxide ion in the presence of KOAc. Subsequent ring opening led to the generation of 2-$ClCH_2COOC_{60}O^-$, which underwent an intramolecular $S_N2$ reaction to afford **5a** with the chloride ion as the leaving group. The $^{13}$C NMR spectrum of **5a** exhibited 27 peaks in the range of 136–149 ppm for the 58 $sp^2$ carbons of the fullerene cage and two peaks at 89.87 and 86.63 ppm for the two $sp^3$ carbons

**Scheme 1. Further Functionalization of 2a**

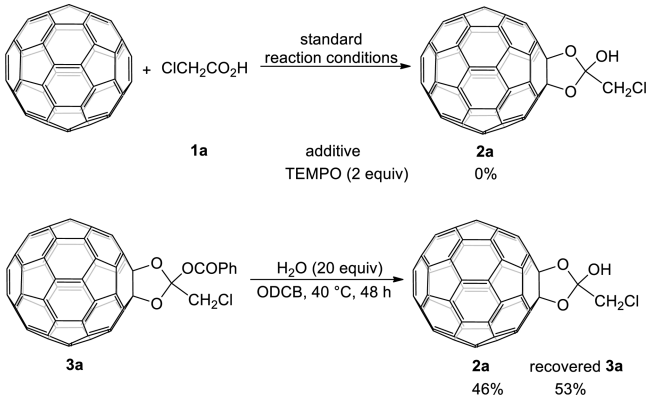



of the fullerene skeleton, consistent with its $C_s$ symmetry. The observation of the peak at 168.31 ppm in the $^{13}$C NMR spectrum is in accordance with the presence of a lactone moiety. The IR spectrum also showed the corresponding absorption at 1778 $cm^{-1}$ for the carbonyl group. Additionally, when **2a** was treated with $CF_3COOH$ at 100 °C for 10 h, it could be converted to its homologue **2h** in 86% yield (Scheme 1).[13] We speculated that a fullerene epoxide intermediate was initially formed, followed by an epoxide ring-opening process to generate **2h**.[10c]

To gain more insights into the mechanism, we performed the reaction in the presence of the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), and no product was observed (Scheme 2), indicating that the present reaction might proceed via a radical pathway.

On the basis of the above results and previous literature, plausible reaction pathways leading to the formation of ortho acid ester-type 1,3-dioxolanofullerenes are proposed in Scheme 3. Initially, halocarboxylic acid **1** reacts with $Pb(OAc)_4$ to generate **A**,[8c,14] which then attacks $C_{60}$ to provide radical **B** with elimination of Pb(III). Next, intermediate **D** is generated by

**Scheme 2. Mechanistic Study**





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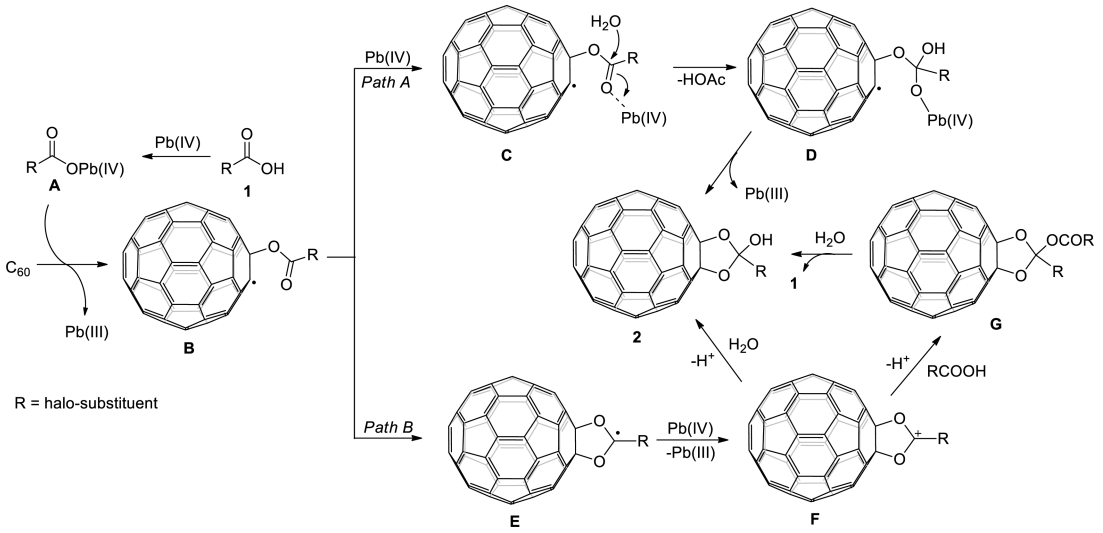
**Scheme 3. Proposed Reaction Mechanisms for the Formation of 2**




coordination of **B** to another $Pb(OAc)_4$ and subsequent nucleophilic attack of $H_2O$ via **C** (path A).[9d] The final homolysis of the lead−oxygen bond and intramolecular cyclization produce **2**[3] or $C_{60}O$ as a minor byproduct accompanied by the recovery of the carboxylic acid. Alternatively, **B** may undergo straightforward cyclization to generate radical **E** (path B),[10b,11,15] which is converted to cation **F** via oxidation by another Pb(IV).[15] Next, **F** could afford **2** by reaction with $H_2O$[15] or via intermediate ester **G**.[10a,b] However, we failed to isolate the corresponding intermediate **G** (R = $CH_2Cl$), probably because of its exceeding sensitivity to water. Instead, we performed a hydrolysis experiment on **3a** and successfully observed the generation of **2a** (Scheme 2). Carboxylic acids are acidic and may accelerate the hydrolysis of **G**, and we therefore still cannot exclude the possibility of path B. However, the facts that (1) multihalogenated substrates **1f−h**, which contain more electron-withdrawing halogen atoms and thus would facilitate the nucleophilic addition of $H_2O$ to the carbonyl group in **C**, reacted faster than other halocarboxylic acids and (2) benzoic acid, which would favor the formation of **E**, did not afford the desired product suggest that path A is a more plausible process.

## ■ CONCLUSION

In summary, we have successfully achieved the synthesis of scarce ortho acid ester-type 1,3-dioxolanofullerenes via the $Pb(OAc)_4$-mediated radical reaction of [60]fullerene with halocarboxylic acids under mild conditions. Further functionalization of the hydroxyl group of the obtained ortho acid ester-type 1,3-dioxolanofullerenes can generate the corresponding ester and ether groups. Interestingly, an ortho acid ester-type 1,3-dioxolanofullerene can be transformed to a 1,4-dioxanonofullerene in the presence of a base or converted to another ortho acid ester-type 1,3-dioxolanofullerene by treatment with a stronger halocarboxylic acid. Two plausible reaction pathways are also suggested to explain the formation of ortho acid ester-type 1,3-dioxolanofullerenes.

## ■ EXPERIMENTAL SECTION

**General Methods.** $^1H$ 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, DMSO at 39.52 ppm, or acetone at 29.84 ppm. High-resolution mass spectrometry (HRMS) was performed by MALDI-TOF or ESI FT-ICR in positive-ion mode.

**General Procedure for the Synthesis of 2a−h by the $Pb(OAc)_4$-Promoted Reaction of $C_{60}$ with 1a−h.** A mixture of $C_{60}$ (0.05 mmol), halocarboxylic acid **1** (0.25 mmol), and $Pb(OAc)_4$ (0.10 mmol) was dissolved in freshly distilled anhydrous ODCB (6 mL). After the solution was stirred at room temperature under a nitrogen atmosphere for 10 min, $H_2O$ (1.0 mmol) was added. Then the mixture was vigorously stirred under a nitrogen atmosphere at 40 °C. The reaction was monitored by TLC and stopped at the designated time. The resulting solution was directly separated on a silica gel column with $CS_2$/toluene as the eluent to give recovered $C_{60}$ and then the desired product **2**.

*2-Chloromethyl-2-hydroxydioxolano[4,5:1,2][60]fullerene (**2a**).* According to the general procedure, the reaction of $C_{60}$ (36.3 mg, 0.05 mmol) with **1a** (23.8 mg, 0.25 mmol), $Pb(OAc)_4$ (44.5 mg, 0.10 mmol), and $H_2O$ (18 μL, 1.0 mmol) for 7 h afforded **2a** (11.2 mg, 27%) along with recovered $C_{60}$ (19.6 mg, 54%). Amorphous brown solid; $^1H$ NMR (400 MHz, $CS_2$/DMSO-$d_6$) δ 8.41 (s, 1H), 4.22 (s, 2H); $^{13}C$ NMR (100 MHz, $CS_2$/DMSO-$d_6$ with $Cr(acac)_3$ as a relaxation reagent, all 2C unless indicated otherwise) δ 148.21, 147.21, 146.77, 145.42, 145.31, 145.30, 145.08 (4C), 145.04, 144.47 (1C), 144.22 (1C), 144.04, 144.02 (4C), 143.91, 143.79, 143.60, 141.66 (5C), 141.62 (1C), 141.29, 141.23, 141.12, 141.09, 140.96, 140.89, 138.48 (4C), 137.47, 137.34, 119.23 (1C), 93.36, 44.77 (1C); FT-IR $\nu/cm^{-1}$ (KBr) 3518, 2949, 2918, 1425, 1219, 1181, 1141, 1062, 1002, 947, 792, 601, 564, 525; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 257 (5.16), 317 (4.69), 416 (3.58); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{62}H_3{}^{35}ClO_3$ [$M^+$] 829.9782, found 829.9765.

*2-Bromomethyl-2-hydroxydioxolano[4,5:1,2][60]fullerene (**2b**).* According to the general procedure, the reaction of $C_{60}$ (35.8 mg, 0.05 mmol) with **1b** (34.8 mg, 0.25 mmol), $Pb(OAc)_4$ (44.6 mg, 0.10 mmol), and $H_2O$ (18 μL, 1.0 mmol) for 6 h afforded **2b** (11.0 mg, 25%) along with recovered $C_{60}$ (24.9 mg, 70%). Amorphous brown solid; $^1H$ NMR (400 MHz, $CS_2$/DMSO-$d_6$) δ 8.43 (s, 1H), 4.13 (s, 2H); $^{13}C$ NMR (100 MHz, $CS_2$/DMSO-$d_6$ with $Cr(acac)_3$ as a relaxation reagent, all 2C unless indicated otherwise) δ 148.26, 147.24, 146.78, 145.46, 145.35, 145.34, 145.12, 145.11, 145.08, 144.52 (1C), 144.25 (1C), 144.08, 144.07 (4C), 143.95, 143.83, 143.64, 141.70 (5C), 141.66 (1C), 141.33, 141.27, 141.16, 141.13, 141.00, 140.93, 138.52 (4C), 137.50, 137.41, 118.74 (1C), 93.41, 32.61 (1C); FT-IR $\nu/cm^{-1}$ (KBr) 3520, 2947, 2918, 1422, 1209, 1184, 1141, 1054, 1001, 945, 778, 600, 570, 525; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 256 (5.05), 316 (4.61), 418 (3.49); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{62}H_3{}^{79}BrO_3$ [$M^+$] 873.9260, found 873.9224.

*2-(1-Bromoethyl)-2-hydroxydioxolano[4,5:1,2][60]fullerene (**2c**).* According to the general procedure, the reaction of $C_{60}$ (36.1 mg,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0.05 mmol) with **1c** (38.2 mg, 0.25 mmol), $Pb(OAc)_4$ (44.4 mg, 0.10 mmol), and $H_2O$ (18 μL, 1.0 mmol) for 42 h afforded **2c** (13.0 mg, 29%) along with recovered $C_{60}$ (23.8 mg, 66%). Amorphous brown solid; $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$) δ 4.88 (q, *J* = 6.9 Hz, 1H), 4.42 (s, 1H), 2.26 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, $CS_2$/DMSO-$d_6$ with $Cr(acac)_3$ as a relaxation reagent, all 1C unless indicated otherwise) δ 147.87 (2C), 146.80 (2C), 146.36 (2C), 145.02 (2C), 144.91 (4C), 144.68 (4C), 144.64 (2C), 144.07, 143.80, 143.64 (2C), 143.62 (4C), 143.54, 143.50, 143.42, 143.39, 143.19 (2C), 141.26 (3C), 141.25 (2C), 141.22, 140.91, 140.89, 140.84, 140.82, 140.72 (2C), 140.70 (2C), 140.55 (2C), 140.48 (2C), 138.08 (4C), 137.12, 137.09, 136.95, 136.92, 119.98, 93.04, 92.98, 48.21, 20.33; FT-IR ν/$cm^{-1}$ (KBr) 3529, 2981, 2947, 2924, 2857, 1508, 1442, 1343, 1217, 1202, 1182, 1142, 1116, 1051, 1001, 943, 779, 598, 571, 558, 525; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 256 (5.00), 317 (4.54), 418 (3.43); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{63}H_5{}^{79}BrO_3$ [$M^+$] 887.9417, found 887.9467.

*2-(1-Bromopropyl)-2-hydroxydioxolano[4,5:1,2][60]fullerene (**2d**).* According to the general procedure, the reaction of $C_{60}$ (36.1 mg, 0.05 mmol) with **1d** (27 μL, 0.25 mmol), $Pb(OAc)_4$ (44.5 mg, 0.10 mmol), and $H_2O$ (18 μL, 1.0 mmol) for 58 h afforded **2d** (11.2 mg, 25%) along with recovered $C_{60}$ (20.9 mg, 58%). Amorphous brown solid; $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$) δ 4.67 (dd, *J* = 10.8, 2.7 Hz, 1H), 4.48 (s, 1H), 2.73 (ddq, *J* = 14.7, 3.0, 7.2 Hz, 1H), 2.35 (ddq, *J* = 14.7, 10.8, 7.2 Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CS_2$/DMSO-$d_6$ with $Cr(acac)_3$ as a relaxation reagent, all 1C unless indicated otherwise) δ 148.16 (2C), 147.04 (2C), 146.66, 146.62, 145.26 (2C), 145.15 (4C), 144.92 (3C), 144.88 (3C), 144.32, 144.05, 143.91, 143.88 (3C), 143.86 (2C), 143.80, 143.76, 143.66, 143.63, 143.45, 143.43, 141.51 (5C), 141.46, 141.16, 141.13, 141.09, 141.06, 140.97, 140.94 (3C), 140.80 (2C), 140.72 (2C), 138.32 (4C), 137.38, 137.33, 137.19, 137.17, 120.09, 93.28, 93.03, 57.56, 26.43, 12.34; FT-IR ν/$cm^{-1}$ (KBr) 3521, 2964, 2923, 1506, 1429, 1320, 1186, 1135, 1082, 1053, 1000, 907, 807, 729, 565, 523; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 255 (5.12), 318 (4.66), 418 (3.51); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{64}H_7{}^{79}BrO_3$ [$M^+$] 901.9573, found 901.9555.

*2-(2-Bromoprop-2-yl)-2-hydroxydioxolano[4,5:1,2][60]fullerene (**2e**).* According to the general procedure, the reaction of $C_{60}$ (36.0 mg, 0.05 mmol) with **1e** (42.0 mg, 0.25 mmol), $Pb(OAc)_4$ (44.5 mg, 0.10 mmol), and $H_2O$ (18 μL, 1.0 mmol) for 68 h afforded **2e** (6.8 mg, 15%) along with recovered $C_{60}$ (29.9 mg, 83%). Amorphous brown solid; $^1$H NMR (400 MHz, $CS_2$/$CDCl_3$) δ 4.55 (s, 1H), 2.38 (s, 6H); $^{13}$C NMR (100 MHz, $CS_2$/DMSO-$d_6$ with $Cr(acac)_3$ as a relaxation reagent, all 2C unless indicated otherwise) δ 148.02, 146.97, 146.43, 145.19, 145.08 (4C), 144.85, 144.83, 144.80, 144.26 (1C), 143.95 (1C), 143.80 (4C), 143.78, 143.70, 143.58, 143.36, 141.45 (3C), 141.42, 141.38 (1C), 141.08, 141.00, 140.91, 140.88, 140.72, 140.61, 138.26, 138.22, 137.34, 137.14, 121.68 (1C), 93.50, 64.12 (1C), 28.94; FT-IR ν/$cm^{-1}$ (KBr) 3526, 2972, 2922, 1506, 1459, 1429, 1360, 1315, 1182, 1097, 1044, 1002, 912, 778, 569, 525; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 256 (5.05), 316 (4.57), 417 (3.49); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{64}H_7{}^{79}BrO_3$ [$M^+$] 901.9573, found 901.9605.

*2-(Dichloromethyl)-2-hydroxydioxolano[4,5:1,2][60]fullerene (**2f**).* According to the general procedure, the reaction of $C_{60}$ (36.0 mg, 0.05 mmol) with **1f** (21 μL, 0.25 mmol), $Pb(OAc)_4$ (44.5 mg, 0.10 mmol), and $H_2O$ (18 μL, 1.0 mmol) for 2.5 h afforded **2f** (13.7 mg, 32%) along with recovered $C_{60}$ (20.5 mg, 57%). Amorphous brown solid; $^1$H NMR (300 MHz, $CS_2$/DMSO-$d_6$) δ 9.06 (s, 1H), 6.43 (s, 1H); $^{13}$C NMR (75 MHz, $CS_2$/DMSO-$d_6$ with $Cr(acac)_3$ as a relaxation reagent, all 2C unless indicated otherwise) δ 147.04, 146.86, 145.75, 145.06, 144.98, 144.97, 144.79, 144.72, 144.69, 144.01 (1C), 143.81 (1C), 143.67, 143.66, 143.48, 143.38, 143.34, 143.22, 141.31, 141.29 (3C), 141.23 (1C), 140.93, 140.87, 140.72, 140.67, 140.62, 140.50, 138.16, 138.12, 137.08, 137.02, 118.81 (1C), 93.43, 71.23 (1C); FT-IR ν/$cm^{-1}$ (KBr) 3517, 1509, 1427, 1359, 1325, 1209, 1181, 1141, 1092, 1049, 1001, 960, 942, 815, 792, 603, 576, 526; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 256 (5.12), 318 (4.66), 418 (3.48); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{62}H_2{}^{35}Cl_2O_3$ [$M^+$] 863.9376, found 863.9368.

*2-Hydroxy-2-trichloromethyldioxolano[4,5:1,2][60]fullerene (**2g**).* According to the general procedure, the reaction of $C_{60}$ (36.0 mg, 0.05 mmol) with **1g** (41.0 mg, 0.25 mmol), $Pb(OAc)_4$ (44.3 mg, 0.10 mmol), and $H_2O$ (18 μL, 1.0 mmol) for 2 h afforded **2g** (10.4 mg, 23%) along with recovered $C_{60}$ (20.2 mg, 56%). Amorphous brown solid; $^1$H NMR (400 MHz, $CS_2$/DMSO-$d_6$) δ 9.85 (s, 1H); $^{13}$C NMR (75 MHz, $CS_2$/DMSO-$d_6$ with $Cr(acac)_3$ as a relaxation reagent, all 2C unless indicated otherwise) δ 147.10, 146.62, 145.42, 145.28, 145.24, 145.21, 145.08, 144.95, 144.93, 144.17 (1C), 143.98 (1C), 143.88 (4C), 143.58, 143.56, 143.43, 143.36, 141.54, 141.52, 141.50 (1C), 141.45 (1C), 141.14, 141.09, 140.94, 140.87, 140.82, 140.67, 138.39, 138.34, 137.51, 137.20, 120.30 (1C), 99.23 (1C), 94.34; FT-IR ν/$cm^{-1}$ (KBr) 3520, 1509, 1428, 1310, 1182, 1135, 1064, 1006, 961, 828, 606, 578, 558, 526; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 255 (5.09), 317 (4.63), 416 (3.53); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{62}H^{35}Cl_3O_3$ [$M^+$] 897.8986, found 897.9017.

*2-Hydroxy-2-trifluoromethyldioxolano[4,5:1,2][60]fullerene (**2h**).* According to the general procedure, the reaction of $C_{60}$ (36.0 mg, 0.05 mmol) with **1h** (19 μL, 0.25 mmol), $Pb(OAc)_4$ (44.2 mg, 0.10 mmol), and $H_2O$ (18 μL, 1.0 mmol) for 2 h afforded **2h** (10.2 mg, 24%) along with recovered $C_{60}$ (21.3 mg, 59%). Amorphous brown solid; $^1$H NMR (300 MHz, $CS_2$/DMSO-$d_6$) δ 10.02 (s, 1H); FT-IR ν/$cm^{-1}$ (KBr) 3516, 1429, 1304, 1242, 1188, 1145, 1085, 1058, 993, 944, 782, 740, 699, 634, 556, 525; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 256 (5.09), 317 (4.61), 418 (3.44); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{62}HF_3O_3$ [$M^+$] 849.9872, found 849.9896.

**Preparation of 2-Benzoyloxy-2-chloromethyldioxolano-[4,5:1,2][60]fullerene (3a).** The obtained **2a** (8.3 mg, 0.01 mmol) was dissolved in freshly distilled dry toluene (16 mL) with the aid of sonication. After benzoyl chloride (24 μL, 0.2 mmol) and $Et_3N$ (28 μL, 0.2 mmol) were added, the reaction mixture was stirred at 40 °C for 48 h. The solvent was concentrated under reduced pressure, and the residue was purified by flash chromatography ($CS_2$/toluene) to give **3a** as an amorphous brown solid (8.0 mg, 86%). $^1$H NMR (400 MHz, $CS_2$/$CDCl_3$) δ 8.28 (dd, *J* = 7.6, 1.2 Hz, 2H), 7.63 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 4.91 (s, 2H); $^{13}$C NMR (75 MHz, $CS_2$/$CDCl_3$, all 2C unless indicated otherwise) δ 163.85 (1C), 148.28, 146.77, 146.56, 146.52, 146.38, 146.32, 146.21, 146.14, 145.62, 145.17, 145.12 (1C), 145.05, 144.98 (1C), 144.75, 144.72, 144.60, 144.52, 142.80, 142.75, 142.62 (1C), 142.53 (1C), 142.37, 142.23, 142.16, 142.11, 142.00, 141.47, 139.74, 139.62, 138.53, 137.94, 133.87 (1C), 130.20, 129.42 (1C), 128.67, 122.02 (1C), 95.13, 43.42 (1C); FT-IR ν/$cm^{-1}$ (KBr) 2947, 2917, 2859, 1735, 1427, 1248, 1180, 1089, 1006, 979, 923, 707, 575, 526; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 257 (5.11), 319 (4.62), 415 (3.50); HRMS (ESI-FT-ICR) *m*/*z* calcd for $C_{69}H_7{}^{35}ClO_4$ [$M^+$] 934.0027, found 934.0026.

**Synthesis of 2-Chloromethyl-2-ethoxydioxolano[4,5:1,2][60]fullerene (4a).** The obtained **2a** (8.4 mg, 0.01 mmol) was dissolved in chlorobenzene (8 mL). After EtOH (24 μL, 0.4 mmol) and HCl (37%, 33 μL, 0.4 mmol) were added, the reaction mixture was stirred at 40 °C for 2 h. The resulting solution was directly separated by silica gel column with $CS_2$ as the eluent and then concentrated under reduced pressure to give **4a** as an amorphous solid (6.0 mg, 69%). $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$) δ 4.37 (q, *J* = 7.1 Hz, 2H), 4.33 (s, 2H), 1.51 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CS_2$/$CD_3COCD_3$ with $Cr(acac)_3$ as a relaxation reagent, all 2C unless indicated otherwise) δ 148.77, 148.05, 147.61, 146.93, 146.90, 146.82, 146.80, 146.63 (4C), 145.70 (1C), 145.58, 145.51 (3C), 145.19, 145.17, 145.13 (4C), 143.23, 143.21, 143.15 (1C), 143.14 (1C), 142.79, 142.75, 142.67, 142.50, 142.40, 142.34, 140.10, 140.06, 139.00, 138.31, 123.16 (1C), 95.36, 59.93 (1C), 46.17 (1C), 15.90 (1C); FT-IR ν/$cm^{-1}$ (KBr) 2972, 2924, 1427, 1302, 1250, 1217, 1181, 1146, 1117, 1080, 1030, 1001, 881, 787, 568, 525; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log ε) 255 (5.12), 317 (4.66), 416 (3.52); HRMS (MALDI-TOF) *m*/*z* calcd for $C_{64}H_7{}^{35}ClO_3$ [$M^+$] 858.0078, found 858.0093.

**Synthesis of 2-Oxodioxano[5,6:1,2][60]fullerene (5a).** The obtained **2a** (8.3 mg, 0.01 mmol) was dissolved in freshly distilled dry toluene (16 mL) with the aid of sonication. After KOAc (19.2 mg, 0.2 mmol) was added, the reaction mixture was stirred at 90 °C for 48 h. The resulting solution was concentrated under reduced pressure, and


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the residue was purified quickly by column chromatography ($CS_2$/$CH_2Cl_2$) to give **5a** as an amorphous brown solid (7.8 mg, 98%). $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$) $\delta$ 5.43 (s, 2H); $^{13}$C NMR (75 MHz, $CS_2$/$CDCl_3$, all 2C unless indicated otherwise) $\delta$ 168.31 (1C), 148.77 (1C), 148.70 (1C), 146.82, 146.77 (4C), 146.54, 146.48, 146.41 (4C), 145.96, 145.37, 145.34, 145.22, 144.92, 144.71, 144.69, 144.26, 142.78 (4C), 142.64, 142.43, 142.31, 141.93, 141.77, 141.51, 141.41, 139.94, 139.74, 137.65, 136.78, 89.87 (1C), 86.63 (1C), 65.12 (1C); FT-IR $\nu$/cm$^{-1}$ (KBr) 2923, 2855, 1778, 1511, 1426, 1335, 1254, 1212, 1074, 994, 942, 860, 731, 597, 554, 525; UV−vis ($CHCl_3$) $\lambda_{max}$/nm (log $\varepsilon$) 256 (5.05), 318 (4.59), 415 (3.59); HRMS (MALDI-TOF) $m/z$ calcd for $C_{62}H_2O_3$ [$M^+$] 793.9998, found 793.9946.

**Conversion of 2a to 2h.** To a chlorobenzene solution (8 mL) of **2a** (8.3 mg, 0.01 mmol) was added $CF_3COOH$ (30 $\mu$L, 0.4 mmol). The reaction mixture was stirred at 100 °C for 10 h and then purified directly through a silica gel column with $CS_2$/$CH_2Cl_2$ as the eluent. The obtained product was washed by acetone and dried, affording **2h** (7.3 mg, 86%) as an amorphous solid.

**Hydrolysis of 3a.** After $H_2O$ (3.5 $\mu$L, 0.2 mmol) was added to an *o*-dichlorobenzene solution (1 mL) of **3a** (9.4 mg, 0.01 mmol), the reaction mixture was stirred at 40 °C for 48 h. The resulting solution was evaporated in vacuo to remove the solvent. The residue was separated on a silica gel column with $CS_2$/toluene as the eluent to give **2a** (3.8 mg, 46%) along with recovered **3a** (5.0 mg, 53%).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

NMR and UV−vis spectra of products **2a**−**h**, **3a**, **4a**, and **5a**. 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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