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Ferric Perchlorate Promoted Reaction of [60]Fullerene with *N*-Sulfonyl Aldimines: Synthesis and Functionalization of Fulleroxazolidines

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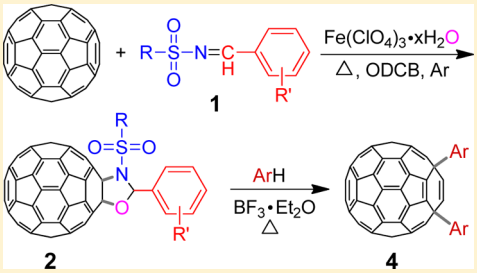
Supporting Information

ABSTRACT: The rare fulleroxazolidines **2** were successfully synthesized by the facile ferric perchlorate promoted reaction of [60]fullerene with various *N*-sulfonyl aldimines **1**. Further functionalization of fulleroxazolidines by arenes in the presence of boron trifluoride afforded 1,4-bisarylation products **4**. A possible reaction mechanism for the formation of the fulleroxazolidines is proposed.



INTRODUCTION

Chemical modifications of fullerenes continue to be of great appeal due to the creation of new carbon materials with broad biological and electronic potentials and applications in materials science.[1] Over the past two decades, a plethora of fullerene derivatives bearing different functional and structural moieties have been prepared. In recent years, transition-metal-mediated or -catalyzed reactions have emerged as a powerful tool to construct carbon−carbon and carbon−heteroatom bonds in organic chemistry, but their applications to fullerene functionalization have been relatively less explored.[2] Our investigation into this direction mainly focuses on the free-radical reactions of [60]fullerene (C_{60}) promoted by different transition-metal salts such as $Mn(OAc)_3$,[2b] $Cu(OAc)_2$,[3a] CuBr,[3b] $Pb(OAc)_4$,[3c,d] Ag_2CO_3,[3e] and the C−H activation reactions of C_{60} catalyzed by $Pd(OAc)_2$.[2e]

On the other hand, iron-catalyzed organic transformations have been widely developed in synthetic organic chemistry due to the abundance, low toxicity, and low cost character of iron.[4] Accordingly, the development of iron-mediated or catalyzed functionalization of fullerenes has also attracted significant interest.[5−8] Gan and co-workers reported the formation of mixed peroxides $C_{60}(O)(OO^tBu)_4$ and $C_{70}(OO^tBu)_{10}$ through the $FeCl_3/Fe(NO_3)_3$-catalyzed reactions of fullerenes with *tert*-butyl hydroperoxide.[5] Hashiguchi et al. disclosed the $FeCl_3$-mediated polyarylation of C_{60} by using electron-deficient aryl halides as the substrates.[6a] Later they also reported the addition of both aromatic and aliphatic carboxylic acids to C_{60} in the presence of $FeCl_3$ to produce hydroxyfullerenyl esters under mild conditions.[6b] We investigated the $FeCl_3/FeCl_2$-mediated reactions of C_{60} with *N*-benzhydryl sulfonamides, *tert*-butyl *N*-substituted carbamates, acyclic diols, and sugars to provide C_{60}-fused indanes, oxazolidinofullerenes, fullerenyl diethers, and C_{60}-sugar conjugates.[7] Recently, our group successfully developed the radical reactions of C_{60} promoted by $Fe(ClO_4)_3$.[8] The facile reactions of C_{60} with nitriles, aldehydes/ketones, substituted malonate esters, *β*-keto esters, arylboronic acids, and acid chlorides afforded fullerooxoazoles,[8a] C_{60}-fused 1,3-dioxolanes,[8b] disubstituted C_{60}-fused lactones,[8c] fullerenyl hemiketals and C_{60}-fused dihydrofurans,[8d] fullerenyl boronic esters,[8e] and 1,2-fullerenols $C_{60}(OCOR)(OH)$,[8f] respectively, under the assistance of $Fe(ClO_4)_3$ in a straightforward and efficient way. Diverse reaction intermediates generated via the $Fe(ClO_4)_3$-mediated hydration to the unsaturated C≡N and C═O bonds were proposed for the reactions of C_{60} with nitriles,[8a] aldehydes/ketones,[8b] and acid chlorides.[8f] We surmised that imines, which contain the C═N bond, could be exploited to functionalize fullerenes by the same strategy. Herein, we disclose the $Fe(ClO_4)_3$-mediated reaction of C_{60} with *N*-sulfonyl aldimines to successfully afford C_{60}-fused oxazolidine derivatives, in which the oxazolidine moiety can be replaced with two aryl groups.

RESULTS AND DISCUSSION

At the onset, the common *N*-aryl aldimines were first employed to react with C_{60} in the presence of $Fe(ClO_4)_3{\cdot}xH_2O$[9] under a nitrogen atmosphere. Unfortunately, no desired product was detected except for black residue, whether the direct-dissolution process[8a,b,f] or common procedure[8c−e] was adopted. *N*-Aryl aldimines tended to hydrolyze in the presence of a hydrated Lewis acid to release the corresponding anilines, which coordinated the Fe(III) salt, and thus led to its inactivation. Subsequently, we turned to using the more stable *N*-sulfonyl

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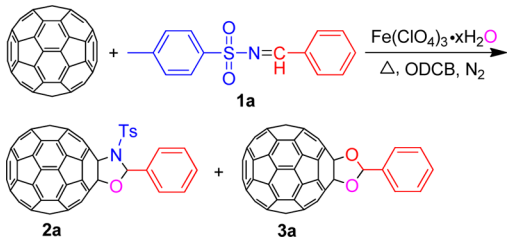
aldimine **1a** to react with C_{60}. To our delight, the desired fulleroxazolidine **2a** was obtained in 18% yield together with the known 1,3-dioxolane derivative **3a**, when the reaction was carried out in a molar ratio of 1:5:1 in 5 mL of *ortho*-dichlorobenzene (ODCB, 10.0 mM C_{60}) at 120 °C for 25 min under a nitrogen atmosphere (Table 1, entry 1). We

Table 1. Condition Screening for the Reaction of C_{60} with 1a in the Presence of $Fe(ClO_4)_3{\cdot}xH_2O$



entry	molar ratio[a]	reaction temp (°C)[b]	reaction time (min)	yield of **2** (%)	yield of **3** (%)	recovered C_{60} (%)
1[c]	1:5:1	120	25	18	10	28
2[c]	1:5:1	110	50	16	8	42
3[c]	1:5:2	120	25	19	8	51
4[d]	**1:5:1**	**120**	**30**	**28**	**4**	**45**
5[d]	1:5:1	110	30	26	7	49
6[e]	1:5:1	120	30	24	6	36

[a]Refers to the molar ratio of C_{60}/**1a**/$Fe(ClO_4)_3{\cdot}xH_2O$. [b]Oil temperature. [c]5 mL of ODCB (10.0 mM C_{60}) were used. [d]7 mL of ODCB (7.1 mM C_{60}) were used. [e]9 mL of ODCB (5.6 mM C_{60}) were used.

conjectured that byproduct **3a** was generated from the reaction of C_{60} with benzaldehyde, which came from the hydrolysis of **1a**.[8b] Control experiments without the addition of C_{60} under otherwise the same conditions confirmed our hypothesis. The hydrolysis of **1a** was still inevitable in the presence of $Fe(ClO_4)_3{\cdot}xH_2O$ and generated the corresponding benzaldehyde, although it was more stable than the common *N*-aryl aldimine. In order to improve the product yield and selectivity, the poor result promoted us to search for better reaction conditions. No improvement was observed, when the reaction temperature was lowered (Table 1, entry 2). Increasing the amount of the Fe(III) salt from 1 to 2 equiv also proved inefficient to achieve a higher yield and selectivity (Table 1, entry 3). Intriguingly, diluting the reaction mixture by using 7 mL of ODCB to decrease the concentration of C_{60} to 7.1 mM provided the best product yield and selectivity and afforded **2a** in 28% yield along with **3a** in only 4% yield (Table 1, entry 4). The yield of **2a** dropped slightly, and the distribution ratio of products **2a** and **3a** gave an inferior result when the reaction temperature was lowered to 110 °C or the volume of solvent was further increased to 9 mL (5.6 mM C_{60}) (Table 1, entries 5 and 6 vs entry 4). It is noteworthy that the direct-dissolution method adopted in our previous study[8a,b,f] was not applicable to our current reaction, because the decomposition of **1a** under such conditions gave more benzaldehyde, leading to the formation of more side product **3a**. In addition, control experiments revealed the formation of *N*-sulfonyl aldimine **1a** from benzaldehyde and *p*-methylbenzenesulfonamide in the presence of $Fe(ClO_4)_3{\cdot}xH_2O$. However, the $Fe(ClO_4)_3$-mediated reaction of C_{60} with benzaldehyde and *p*-methylbenzenesulfonamide in one pot provided a poorer result than the reaction of C_{60} with **1a** under the same conditions. Therefore, the molar ratio of C_{60}/**1a**/Fe(III) as 1:5:1 and the reaction temperature at 120 °C in 7 mL of ODCB under a nitrogen atmosphere were chosen as the optimized reaction conditions.

Under the optimal conditions, a wide range of different *N*-sulfonyl aldimines **1a**–**j** could react efficiently with C_{60} to afford the desired C_{60}-fused oxazolidine derivatives **2a**–**j** in 19–39% yields along with byproducts **3a**–**j** in 2–9% yields, as shown in Table 2. Compared to **1a** and **1b**, the selectivity for the reaction of **1c** was relatively low (Table 2, entry 3 vs entries 1 and 2), which was most likely caused by the lower stability of **1c** and higher reactivity of the in situ generated aldehyde. The existence of two electron-donating methyl groups in the benzylidene moiety caused the hydrolysis of **1c** to occur more easily. In addition, the corresponding 3,4-dimethyl benzaldehyde generated in situ had higher reactivity in the formation of byproduct **3c**.[8b] When substrates bearing electron-withdrawing groups in the benzylidene motif were employed, the reactions proceeded smoothly and exhibited better product yields and selectivity (Table 2, entries 4–6 vs entries 1–3). The desired products **2d**–**f** were obtained in better yields (26–39%) accompanied by less amounts of byproducts (2–3%), indicating that these substrates were more stable and less amounts of aldehydes were generated from the hydrolysis process (Table 2, entries 4–6). For sulfimide **1g**, the steric hindrance decreased its reactivity and required a longer reaction time, yet gave a relatively low yield and poor selectivity (Table 1, entry 7 vs entries 4–6). Furthermore, the reaction tolerates a change of substituents on the sulfonyl phenyl ring. When *N*-benzenesulfonyl and *N*-4-chlorobenzenesulfonyl aldimines **1h** and **1i** were used, the reactions efficiently delivered the desired products **2h** and **2i** in 28% and 25% yields, respectively (Table 1, entries 8 and 9). Gratifyingly, aldimine **1j** containing an alkyl sulfamide unit could also react with C_{60} to successfully provide the corresponding product **3j** in 28% yield. In an attempt to further extend the scope of substrates, *N*-sulfonyl alkyl aldimines and *N*-sulfonyl aliphatic or aromatic ketimines were also examined; to our disappointment, no or only a trace amount of desired products could be identified. It should be noted that Yang and co-workers recently reported the synthesis of fullerooxazolidines by the $BF_3{\cdot}Et_2O$-catalyzed formal [3 + 2] reaction of carbonyl compounds with aziridinofullerenes, which were in turn prepared from C_{60}.[10] Our current protocol is more straightforward and requires only one step from C_{60} to prepare fullerooxazolidines, even though the yields were slightly lower than those reported in the literature.[10]

Products **2a**, **2d**, and **2f** are known compounds, and their identities were confirmed by comparison of their spectral data with those reported in the literature.[10] New fullerooxazolidine derivatives **2b**, **2c**, **2e**, and **2g**–**j** were fully characterized by HRMS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV–vis spectra. All products displayed the correct molecular ion peaks in their high-resolution mass spectra. The ^{1}H NMR spectra of these compounds exhibited the expected chemical shifts and splitting patterns for all protons. In their ^{13}C NMR spectra, there were at least 47 lines including some overlapped ones in the range of 136–151 ppm for the 58 sp^2-carbons of the C_{60} moiety, consistent with the C_1 symmetry of the molecular structures, and two peaks at 78–80 and 97–99 ppm for two sp^3-carbons of the C_{60} cage. The FT-IR spectra of these derivatives showed the strong characteristic absorptions at about 1164 and 1357 cm^{-1} of S═O stretching bands. In addition, the identities of

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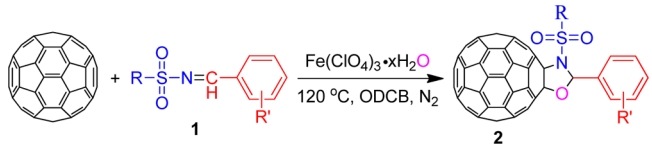
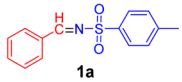
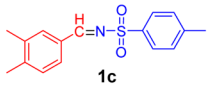
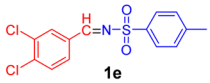
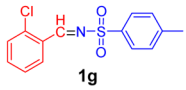
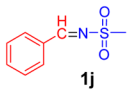
Table 2. Conditions and Yields for the Reactions of C_{60} with *N*-Sulfonyl Aldimines 1a–j in the Presence of $Fe(ClO_4)_3{\cdot}xH_2O$[a]



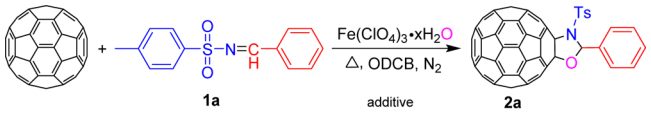
entry	substrate **1**	time (min)	product **2**	yield of **2** (%)[b]	recovered C_{60} (%)
1	 **1a**	30	**2a**	28 (4)	45
2	 **1b**	35	**2b**	19 (2)	63
3	 **1c**	35	**2c**	20 (8)	49
4	 **1d**	25	**2d**	32 (3)	50
5	 **1e**	25	**2e**	39 (3)	39
6	 **1f**	35	**2f**	26 (2)	40
7	 **1g**	50	**2g**	22 (4)	54
8	 **1h**	20	**2h**	28 (9)	37
9	 **1i**	25	**2i**	25 (8)	53
10	 **1j**	40	**2j**	28 (8)	42

[a]All reactions were performed at 120 °C under a nitrogen atmosphere with a molar ratio of C_{60}/**1**/$Fe(ClO_4)_3{\cdot}xH_2O$ = 1:5:1. [b]The number in parentheses is the yield of byproduct **3**.

byproducts **3a–g** were confirmed by comparison of their spectral data with our previous report.[8b]

To gain further insights into the mechanism, the reaction of C_{60} with **1a** in the presence of a radical inhibitor was conducted, as illustrated in Scheme 1. The addition of 2,2,6,6-tetramethylpiperidine-1-oxy (TEMPO) or *N*-*tert*-butyl-*α*-phenylnitrone (PBN) could retard or completely suppress the heteroannulation reaction depending on the amount of TEMPO or PBN, thus suggesting that this transformation might involve a free radical process. Furthermore, the ^{18}O-labeled **2a** could be identified by HRMS (ESI-FT-ICR) at 997.0647, in agreement with the theoretical value of the molecule ($[M]^+$: $C_{74}H_{13}NO_2{}^{18}OS$, calcd 997.0654), from the reaction mixture in the presence of $H_2{}^{18}O$. The excess $H_2{}^{18}O$ would exchange with the coordinated H_2O of $Fe(ClO_4)_3{\cdot}xH_2O$. Thus, the oxygen atom in the oxazolidine ring was most likely derived from the coordinated water of the Fe(III) salt.

Scheme 1. Experimental Evidence in Supporting a Radical Pathway



Based on our experimental results and previously suggested mechanisms for the $Fe(ClO_4)_3$-mediated reactions of C_{60} with nitriles,[8a] aldehydes/ketones,[8b] and arylboronic acids,[8d] a possible mechanism is proposed for the formation of C_{60}-fused oxazolidines **2** from the reaction of C_{60} with *N*-sulfonyl aldimines in the presence of $Fe(ClO_4)_3{\cdot}xH_2O$ (Scheme 2). A chosen *N*-sulfonyl aldimine **1** interacts with $Fe(ClO_4)_3{\cdot}xH_2O$

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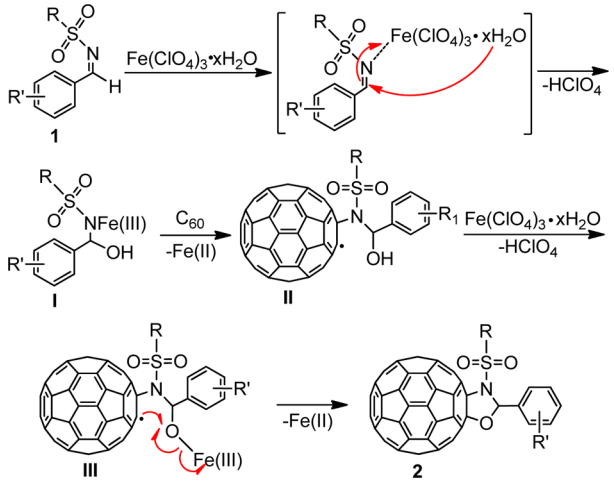
Scheme 2. Proposed Reaction Mechanism for the Formation of C_{60}-Fused Oxazolidines



to produce Fe(III)-complex **I** accomplished by the loss of one molecule of $HClO_4$. Fullerenyl radical **II** is formed by the homolytical addition of complex **I** to C_{60}. Coordination of intermediate **II** with another molecule of $Fe(ClO_4)_3{\cdot}xH_2O$ generates complex **III**. Finally, intramolecular cyclization of **III** along with the elimination of a Fe(II) species affords C_{60}-fused oxazolidine derivative **2**. In the formation of adduct **2**, the hydrolysis of *N*-sulfonyl aldimine **1** occurs simultaneously to generate the corresponding aldehyde, which further reacts with C_{60} to afford byproduct **3**.[8b]

The cyclic voltammograms (CV) of **2a–j** were investigated, and it was found that the obtained products exhibited irreversible redox processes probably due to the cleavage of the annulated C–NSO_2R and the C–O bonds of **2a–j** upon acceptance of electrons. However, the first redox process of **2a–j** was reversible at a scanning rate of either 50 or 200 mV s^{-1}. The first half-wave reduction potentials of products **2a–j** along with that of C_{60} are summarized in Table 3. As one of the C=C double bonds in fullerene derivatives is saturated, they usually show obvious cathodic shifts for the redox processes compared to the parent fullerene. However, the E_1 values of **2a–j** were close to that of the pristine C_{60} because of the attached electronegative oxygen and nitrogen atoms.

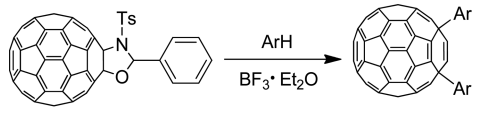
Table 3. Half-Wave Reduction Potentials (V) of 2a–j and C_{60}[a]

compound	E_1
2a[b]	−1.109
2b	−1.097
2c	−1.106
2d[b]	−1.096
2e	−1.076
2f	−1.065
2g	−1.079
2h	−1.089
2i	−1.082
2j[b]	−1.082
C_{60}	−1.076

[a]Potential values versus a ferrocene/ferrocenium couple. Experimental conditions: 0.1 mM of **2a–j**/C_{60} and 0.1 M of *n*-Bu_4NClO_4 in anhydrous ODCB; reference electrode: SCE; working electrode: Pt; auxiliary electrode: Pt wire; scanning rate: 50 mV s^{-1}. [b]Scanning rate: 200 mV s^{-1}.

In our previous work, C_{60}-fused lactones,[11] sultones,[12] 1,3-dioxolanes[8b] and boronic esters[8d] were shown to be valuable precursors for the construction of other types of fullerene derivatives via a ring-opening reaction. The newly obtained fullerooxazolidines could also serve as a platform for further functionalization. We found that treatment of fulleroxazolidines with $BF_3{\cdot}OEt_2$ in toluene, *m*- or *p*-xylene, and benzene afforded 1,4-bis(aryl) adducts in 70–83% yields. The results are summarized in Table 4. Tajima and co-workers also reported

Table 4. Conversion of 2a to 4a–d Promoted by $BF_3{\cdot}Et_2O$[a]



2a **4a-d**

entry	ArH	reaction time (h)	reaction temp (°C)	yield of **4** (%)
1	toluene	7.5	110	75
2	*m*-xylene	7	110	70[b]
3	*p*-xylene	7	110	76
4	benzene	7	100	83[c]

[a]Unless otherwise indicated, all reactions were performed with a molar ratio of **2a**/$BF_3{\cdot}Et_2O$ = 1:100 in 7 mL of solvent. [b]The overall yield of the structural isomeric mixture of 1,4-adducts. [c]200 equiv of $BF_3{\cdot}Et_2O$ and 8 mL of benzene were used.

the $BF_3{\cdot}OEt_2$-assisted nucleophilic substitution of $C_{60}O$ with arenes and the reactions of *p*-xylene and benzene with $C_{60}O$ failed.[13a] However, both *p*-xylene and benzene could react with C_{60}-fused oxazolidines to provide symmetrical 1,4-bisadducts in our case. This transformation should also proceed through a fullerenyl carbocation intermediate as mentioned in the above studies.[8b,d,13]

CONCLUSION

In summary, we have disclosed an efficient method to construct C_{60}-fused oxazolidines via $Fe(ClO_4)_3{\cdot}xH_2O$-mediated cycloaddition of *N*-sulfonyl aldimines to C_{60}. A plausible reaction mechanism for the formation of C_{60}-fused oxazolidines has been proposed. The transformation from a fullerooxazolidine to 1,4-bis(aryl) adducts was also performed with arenes. The current reaction further demonstrates the application of ferric perchlorate as an excellent catalyst in the functionalization of C_{60}.

EXPERIMENTAL SECTION

Control Experiment 1. A mixture of $Fe(ClO_4)_3{\cdot}xH_2O$ (23.1 mg, 0.05 mmol) and **1a** (64.8 mg, 0.25 mmol) was first added to a 50 mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer and then dissolved in *o*-dichlorobenzene (7 mL) by sonication. The resulting solution was heated with vigorous stirring at 120 °C for 30 min under a nitrogen atmosphere. According to the TLC analysis of the reaction mixture, part of **1a** was decomposed to give the corresponding benzaldehyde.

Control Experiment 2. A mixture of $Fe(ClO_4)_3{\cdot}xH_2O$ (23.1 mg, 0.05 mmol), benzaldehyde (26.5 mg, 0.25 mmol), and *p*-toluenesulfonamide (42.8 mg, 0.25 mmol) was first added to a 50 mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer and then dissolved in *o*-dichlorobenzene (7 mL) by sonication. The resulting solution was heated with vigorous stirring at 120 °C for 30 min under a nitrogen atmosphere. According to the TLC analysis of the reaction mixture, **1a** was formed.

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General Procedure for the Synthesis of Products 2a−j from the Reaction of C_{60} with Substrates 1a−j and $Fe(ClO_4)_3·xH_2O$. A mixture of C_{60} (36.0 mg, 0.05 mmol), $Fe(ClO_4)_3·xH_2O$ (23.1 mg, 0.05 mmol), and **1a** (**1b−j**, 0.25 mmol) was first added to a 50 mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer and then dissolved in *o*-dichlorobenzene (7 mL) by sonication. After the resulting solution was heated with vigorous stirring at 120 °C for a desired time (carefully monitored by TLC to prevent overreaction) under a nitrogen atmosphere, it was subsequently filtered through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} and product **3a** (**3b−g**) and then with carbon disulfide/toluene as the eluent to afford product **2a** (**2b−j**).

Compound ***2a***.[10] Yield 14.1 mg, 28%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.18−8.15 (m, 2H), 7.98 (d, J = 8.2 Hz, 2H), 7.72 (s, 1H), 7.53−7.48 (m, 3H), 7.36 (d, J = 8.2 Hz, 2H), 2.49 (s, 3H); UV−vis ($CHCl_3$) λ_{max}/nm 257 (5.00), 318 (4.28), 423 (3.26), 683 (2.35).

Compound ***2b***. Yield 9.6 mg, 19%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.01 (d, J = 8.1 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H), 7.66 (s, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 2.48 (s, 3H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) 149.95, 147.99, 147.65, 147.56, 147.50, 146.21, 146.08, 146.02, 145.86 (2C), 145.70 (3C), 145.67, 145.60, 145.52, 145.31 (2C), 144.86, 144.79, 144.68, 144.56 (2C), 144.52, 144.48, 144.33, 144.11 (3C), 144.06, 143.91, 143.65 (2C), 142.32 (2C), 142.28, 142.23, 142.20, 142.16, 142.06, 142.03, 141.85, 141.82, 141.77, 141.57, 141.50, 141.39, 140.94, 140.71 (2C), 140.62, 139.37, 139.04, 138.98, 138.91, 138.15, 137.61, 137.57, 137.03, 136.88, 136.27, 133.55, 129.22 (2C), 128.61 (2C), 128.05 (2C), 127.63 (2C), 98.12, 92.42, 78.67, 21.48, 21.23; FT-IR ν/cm^{-1} (KBr) 2919, 2858, 1597, 1357, 1306, 1206, 1165, 1100, 1042, 1018, 951, 900, 809, 704, 667, 591, 574, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.02), 318 (4.60), 422 (3.21), 683 (2.35); HRMS (ESI-FT-ICR) m/z calcd for $C_{75}H_{15}NO_3S$ [M^-] 1009.0773, found 1009.0770.

Compound ***2c***. Yield 10.3 mg, 20%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.75 (s, 1H), 7.52 (s, 1H), 7.29 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 7.8 Hz, 1H), 2.48 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) 150.02, 148.29, 147.96, 147.90, 147.82, 146.52, 146.40, 146.33, 146.20, 146.19, 146.01 (4C), 145.90, 145.85, 145.69, 145.65, 145.19, 145.08 (2C), 144.97, 144.95, 144.87, 144.81, 144.74, 144.60, 144.43, 144.42, 144.36, 144.26, 144.03, 143.85, 142.63, 142.61, 142.59, 142.53, 142.50, 142.46, 142.37, 142.34, 142.14, 142.12, 142.08, 141.85, 141.82, 141.71, 141.22, 141.12, 141.09, 141.00, 139.71, 139.37, 139.08, 138.34, 138.01, 137.92, 137.84, 137.36, 137.26, 136.72, 136.24, 133.62, 129.52, 129.41, 129.34 (2C), 127.89 (2C), 126.15, 98.23, 92.61, 79.17, 21.65, 19.81, 19.72; FT-IR ν/cm^{-1} (KBr) 2919, 2855, 1595, 1495, 1453, 1433, 1356, 1303, 1243, 1212, 1163, 1092, 1018, 902, 809, 748, 702, 664, 609, 589, 543, 525; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.01), 319 (4.62), 423 (3.20), 683 (2.43); HRMS (ESI-FT-ICR) m/z calcd for $C_{76}H_{17}NO_3S$ [M^-] 1023.0929, found 1023.0931.

Compound ***2d***.[10] Yield 16.3 mg, 32%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 7.55 (s, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 2.50 (s, 3H); UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.05), 318 (4.54), 422 (3.26), 683 (2.40).

Compound ***2e***. Yield 20.8 mg, 39%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.07 (d, J = 1.8 Hz, 1H), 7.94 (dd, J = 8.1, 1.8 Hz, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.1 Hz, 1H), 7.44 (s, 1H), 7.31 (d, J = 8.4 Hz, 2H), 2.50 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) 149.37, 147.79, 147.64, 147.32, 147.04, 146.22, 146.15, 146.13, 146.07, 146.04, 145.86 (3C), 145.84, 145.76, 145.69, 145.58 (2C), 144.92, 144.90, 144.82, 144.70, 144.62 (3C), 144.37, 144.27, 144.21, 144.12, 144.03, 143.99, 143.86, 143.59, 142.48, 142.45, 142.43, 142.40, 142.32, 142.30, 142.17, 142.12, 141.96, 141.94, 141.88, 141.69, 141.64, 141.55, 140.98, 140.95, 140.86, 140.72, 139.54, 139.29, 139.07, 137.77, 137.66, 137.61, 137.04, 136.91, 136.64, 136.05, 133.98, 132.61, 130.20, 130.00, 129.40 (2C), 127.64 (3C), 98.27, 90.92, 78.86, 21.57; FT-IR ν/cm^{-1} (KBr) 2918, 1595, 1466, 1422, 1357, 1203, 1185, 1163, 1090, 1031, 1013, 913, 810, 768, 701, 665, 591, 573, 543, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 257 (5.03), 319 (4.65), 421 (3.26), 681 (2.05); HRMS (ESI-FT-ICR) m/z calcd for $C_{74}H_{11}Cl_2NO_3S$ [M^-] 1062.9837, found 1062.9834.

Compound ***2f***.[10] Yield 13.5 mg, 26%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.33 (d, J = 9.0 Hz, 2H), 8.28 (d, J = 9.0 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.59 (s, 1H), 7.33 (d, J = 8.4 Hz, 2H), 2.51 (s, 3H); UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.08), 319 (4.62), 422 (3.23), 682 (2.11).

Compound ***2g***. Yield 11.4 mg, 22%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.43−8.39 (m, 1H), 7.88 (d, J = 8.4 Hz, 2H), 7.70 (s, 1H), 7.53−7.50 (m, 1H), 7.46−7.41 (m, 2H), 7.31 (d, J = 8.4 Hz, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) 149.32, 147.95, 147.93, 147.83, 147.80, 146.34 (2C), 146.26 (2C), 146.22, 146.04 (2C), 145.98, 145.91, 145.89, 145.86 (2C), 145.81, 145.16, 145.08, 145.01, 144.92, 144.87 (2C), 144.81, 144.64, 144.52, 144.49, 144.33 (2C), 144.21, 144.17, 144.07, 142.60 (3C), 142.58, 142.46 (2C), 142.29 (2C), 142.17, 142.14, 142.07, 141.91, 141.80, 141.73, 141.27, 141.24, 141.13 (2C), 139.70, 139.51, 138.95, 137.90, 137.70, 137.56, 137.28, 136.88, 136.85, 134.56, 134.23, 130.92, 130.48, 130.29, 129.48 (2C), 127.89 (2C), 126.36, 98.27, 90.73, 79.22, 21.66; FT-IR ν/cm^{-1} (KBr) 2919, 2861, 1594, 1511, 1439, 1358, 1347, 1305, 1269, 1204, 1164, 1102, 1050, 1009, 810, 760, 695, 665, 607, 590, 574, 542, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.03), 319 (4.59), 423 (3.22), 682 (2.38); HRMS (ESI-FT-ICR) m/z calcd for $C_{74}H_{12}ClNO_3S$ [M^-] 1029.0226, found 1029.0229.

Compound ***2h***. Yield 14.1 mg, 28%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.06 (d, J = 7.5 Hz, 2H), 7.99 (d, J = 7.8 Hz, 2H), 7.66 (s, 1H), 7.64 (t, J = 7.5 Hz, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) 149.80, 147.96, 147.69, 147.58, 147.54, 146.20, 146.12, 146.06, 145.90 (2C), 145.74 (3C), 145.72, 145.64, 145.57, 145.38, 145.35, 144.88, 144.83, 144.71, 144.58 (3C), 144.53, 144.36, 144.14, 144.11 (2C), 143.95, 143.94, 143.66, 142.36 (2C), 142.33, 142.28, 142.24, 142.21, 142.09, 142.06, 141.90, 141.86, 141.83, 141.61, 141.55, 141.44, 141.25, 140.96, 140.75 (2C), 140.64, 139.43, 139.10, 139.05, 138.95, 137.65, 137.59, 137.05, 136.84, 136.36, 133.43, 132.81, 128.68 (2C), 128.65 (2C), 128.11 (2C), 127.50 (2C), 98.18, 92.48, 78.64, 21.30; FT-IR ν/cm^{-1} (KBr) 2918, 2859, 1512, 1445, 1358, 1206, 1166, 1093, 1018, 949, 898, 868, 807, 750, 721, 684, 625, 597, 577, 557, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.08), 318 (4.53), 422 (3.22), 682 (2.31); HRMS (ESI-FT-ICR) m/z calcd for $C_{74}H_{13}NO_3S$ [M^-] 995.0616, found 995.0620.

Compound ***2i***. Yield 13.0 mg, 25%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.58 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) 149.34, 147.85, 147.77, 147.65, 147.53, 146.23, 146.20 (2C), 146.01 (2C), 145.89, 145.85 (3C), 145.74, 145.68, 145.52, 145.49, 144.92 (2C), 144.79, 144.75, 144.74, 144.70, 144.66, 144.39, 144.26, 144.19, 144.13, 144.12, 144.03, 143.74, 142.48, 142.45 (2C), 142.38, 142.35, 142.30, 142.15 (2C), 141.98, 141.94 (2C), 141.68 (2C), 141.52, 141.07, 140.90, 140.85, 140.74, 139.60 (3C), 139.42, 139.24, 138.92, 137.79, 137.63, 137.09, 136.84, 136.57, 132.83, 128.98 (2C), 128.88 (2C), 128.75 (2C), 128.32 (2C), 98.11, 92.33, 78.86, 21.32; FT-IR ν/cm^{-1} (KBr) 2918, 2857, 1581, 1512, 1425, 1360, 1166, 1089, 1013, 949, 899, 821, 704, 636, 607, 561, 526, 479; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 256 (5.04), 318 (4.65), 421 (3.30), 682 (2.32); HRMS (ESI-FT-ICR) m/z calcd for $C_{74}H_{12}ClNO_3S$ [M^-] 1029.0226, found 1029.0224.

Compound ***2j***. Yield 12.7 mg, 28%; brown solid; mp >300 °C; ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.19−8.17 (m, 2H), 7.55−7.51 (m,

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3H), 7.46 (s, 1H), 3.55 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) 149.48, 147.54 (2C), 147.48, 147.39, 146.24, 145.99, 145.95, 145.78, 145.71 (3C), 145.59 (2C), 145.50, 145.44, 145.18, 145.14, 144.95, 144.72, 144.58, 144.55, 144.43 (2C), 144.36, 144.16, 144.05, 143.93, 143.88 (2C), 143.79, 143.36, 142.25, 142.23, 142.20, 142.13, 142.10, 142.02, 141.92 (2C), 141.79, 141.65 (2C), 141.48, 141.34, 141.23, 141.05, 141.03, 140.47, 140.44, 139.43, 138.94, 138.84, 137.77, 136.76, 136.66, 136.41, 136.01, 135.87, 129.41, 127.96 (2C), 127.87 (2C), 97.71, 91.74, 79.13, 40.64; FT-IR ν/cm^{-1} (KBr) 2922, 2859, 1545, 1511, 1492, 1461, 1447, 1425, 1357, 1319, 1208, 1162, 1083, 1023, 992, 957, 886, 757, 726, 697, 625, 580, 562, 526, 509, 479; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 258 (5.01), 316 (4.61), 420 (3.25), 681 (2.32); HRMS (ESI-FT-ICR) m/z calcd for $C_{68}H_9NO_3S$ $[M^-]$ 919.0303, found 919.0306.

[$H_2{}^{18}O$]-Labeling Experiment. A mixture of C_{60} (36.0 mg, 0.05 mmol), $Fe(ClO_4)_3{\cdot}xH_2O$ (23.1 mg, 0.05 mmol), **1a** (64.8 mg, 0.25 mmol), and $H_2{}^{18}O$ (9 μL, 0.50 mmol) was first added to a 50 mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer and then dissolved in *o*-dichlorobenzene (7 mL) by sonication. The resulting solution was heated with vigorous stirring at 120 °C for a desired time (carefully monitored by TLC to prevent overreaction) under a nitrogen atmosphere and subsequently filtered through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} (17.5 mg, 49%) and product **3a** (5.6 mg, 13%) and then with carbon disulfide/toluene as the eluent to afford product **2a** (9.5 mg, 19%). The incorporation of the ^{18}O atom into product **2a** was confirmed by HRMS. HRMS (ESI-FT-ICR) m/z calcd for $C_{74}H_{13}N^{18}OO_2S$ $[M]^+$ 997.0654, found 997.0647 (calcd $C_{74}H_{13}NNa^{18}OO_2S$ $[M + Na]^+$ for 1020.0551, found 1020.0551).

Radical-Trapping Experiment. A mixture of C_{60} (36.0 mg, 0.05 mmol), $Fe(ClO_4)_3{\cdot}xH_2O$ (23.1 mg, 0.05 mmol), **1a** (64.8 mg, 0.25 mmol), and TEMPO or PBN (0.05 and 0.15 mmol) was dissolved in *o*-dichlorobenzene (7 mL) by sonication. After the resulting solution was heated with vigorous stirring at 120 °C for 30 min under a nitrogen atmosphere, it was subsequently filtered through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide as the eluent to give unreacted C_{60} and product **3a** and then with carbon disulfide/toluene as the eluent to afford product **2a**. For 0.05 mmol of TEMPO: C_{60} 20.4 mg (57%); **2a**, 10.1 mg (20%); **3a**, 3.7 mg (9%). For 0.15 mmol of TEMPO: the reaction was completely suppressed. For 0.05 mmol of PBN: C_{60}, 16.9 mg (47%); **2a**, 12.1 mg (24%); **3a**, 5.2 mg (12%). For 0.15 mmol of PBN: only a trace amount of **2a** was observed.

Synthesis of 4a−d. A dry 25 mL flask equipped with a magnetic stirrer was charged with **2a** (14.8 mg, 0.015 mmol) and $BF_3{\cdot}OEt_2$ (190 μL, 1.5 mmol; 380 μL, 3.0 mmol for benzene). After they were completely dissolved in the desired arene by sonication, the sealed mixture was heated with stirring at 110 °C (100 °C for benzene) for a designated time (monitored by TLC). The reaction mixture was filtered through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide as the eluent to give product **4a** (**4b−d**).

Compound ***4a***.[13] Yield 10.1 mg, 75%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 4H), 7.29 (d, J = 8.0 Hz, 4H), 2.46 (s, 6H); UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 262 (4.88), 330 (4.36), 451 (3.60).

Compound ***4b***.[13a] Yield 9.8 mg, 70% (a structural isomeric mixture, major isomer/minor isomer ≈ 10/1); brown solid; mp >300 °C. ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ major isomer: 8.05 (d, J = 8.0 Hz, 2H), 7.08 (s, 2H), 7.06 (d, J = 8.0 Hz, 2H), 3.06 (s, 6H), 2.36 (s, 6H); minor isomer: 8.17 (d, J = 8.0 Hz, 1H), 7.49 (s, 2H), 7.18 (s, 1H), 7.16 (d, J = 8.0 Hz, 1H), 6.97 (s, 1H), 3.12 (s, 3H), 2.43 (s, 3H), 2.26 (s, 6H). UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 260 (4.65), 329 (4.28), 449 (3.48).

Compound ***4c***. Yield 10.6 mg, 76%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.96 (s, 2H), 7.16 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 3.06 (s, 6H), 2.30 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) 155.46, 150.46, 148.32, 147.62, 147.20, 146.81, 146.71, 146.49, 145.43, 145.26, 145.16, 144.97, 144.51, 144.17, 144.13, 143.87, 143.49 (1C), 143.44, 143.23, 143.15, 142.92, 142.78, 142.75 (4C), 142.72 (1C), 142.39, 142.06, 141.97 (1C), 141.67, 140.38 (1C), 138.27, 138.19, 136.00, 134.20, 132.89, 130.44, 128.67, 62.03, 23.73, 20.91; FT-IR ν/cm^{-1} (KBr) 2923, 2853, 1610, 1498, 1430, 1376, 1262, 1188, 1029, 807, 757, 583, 558, 526; UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 265 (4.70), 330 (4.41), 450 (3.43); HRMS (ESI-FT-ICR): m/z calcd for $C_{76}H_{18}$ $[M^-]$ 930.1409, found 930.1411.

Compound ***4d***.[14] Yield 10.9 mg, 83%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.07−8.05 (m, 4H), 7.51−7.42 (m, 6H); UV−vis ($CHCl_3$) λ_{max}/nm (log ε) 263 (4.67), 331 (4.38), 450 (3.45).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01868.

NMR spectra of products **2a−i** and **4a−d**, UV−vis spectra of compounds **2a−i** and **4a−d**, CVs of compounds **2a−i** (PDF)

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Notes

The authors declare no competing financial interest.

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