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Iron-Mediated Internal-Oxidant Relay Cascade Reaction: Strategy to Synthesize Fullerenooxazoles and Hydroxyfullerenyl Amides

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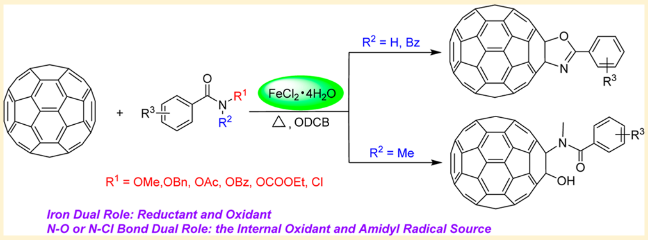
S *Supporting Information*

ABSTRACT: A novel $FeCl_2{\cdot}4H_2O$-mediated internal-oxidant relay cascade reaction has been developed by functionalization of *O*-substituted benzohydroxamic acids or *N*-chloro-arylamides with [60]fullerene. Depending on the nature of the *N*-substituted groups, fullerenooxazoles or rare hydroxyfullerenyl amides could be obtained in a straightforward and flexible manner. Such a new transformation provides a unique strategy for the synthesis of fullerenooxazoles or hydroxyfullerenyl amides.



INTRODUCTION

Organic transformations mediated/catalyzed by transition metals have been an intensively investigated area of great significance in recent years. The development of new efficient, low-cost, and environmentally friendly transition-metal-mediated/catalyzed synthetic approaches to desired products is one of the most attractive goals. Iron is one of the most abundant metal elements in nature, and most iron salts are inexpensive and environmentally friendly. Thus, the development of iron-mediated/catalyzed organic transformations is desirable. Over the past few decades, considerable effort has been directed toward iron catalysis to discover its unique and novel reactivity in synthetic organic chemistry, and as a result a series of novel iron-catalyzed organic transformations have been developed.[1]

Recently, the internal oxidant strategy using an oxidizing directing group has attracted significant interest in the field of C−H activation.[2] This efficient strategy not only obviates the need for an external oxidant but also allows the improvement of the levels of reactivity and selectivity as well as the operational conditions of reaction. *O*-Methyl benzohydroxamic acids (ArCONHOMe), which represent one of the most common and readily available functional groups in organic synthesis, are the most commonly used substrates utilizing CONHOMe as an oxidizing directing group to construct complex molecules in internal oxidant C−H activation processes.[2e−j] However, the generation and synthetic applications of amidyl radicals from *O*-methyl benzohydroxamic acid have been less investigated.[3] Considering that CONHOMe serves not only as a directing group but also as an internal oxidant in Pd-, Rh-, and Ru-catalyzed C−H bond transformation reactions,[2e−j] and the unique properties of iron and its excellent catalytic performance in organic transformations,[1,4] we envision that the combination of ArCONHOMe and appropriate iron catalysts might be utilized to allow the generation of active aryl amidyl radicals via N−O bond reductive cleavage.[5] In addition, oxidizing iron formed in situ using the N−O bond as the external oxidant continues to work in subsequent reaction processes. Thus, another innovative reactive mode different from C−H activation utilizing CONHOMe as the oxidizing directing group could be triggered, leading to important nitrogen-containing frameworks.

Functionalization of fullerenes represents an important subject in fullerene chemistry for the preparation of various fullerene derivatives with potential applications in nanoscience, electronic devices, and biomedicine.[6] As a continuation of our interest in fullerenes,[7] herein we disclose our preliminary results on the $FeCl_2{\cdot}4H_2O$-mediated novel reaction of *O*-substituted benzohydroxamic acids and *N*-chloro-arylamides with [60]-fullerene, which leads to fullerenooxazoles or novel hydroxyfullerenyl amides via sequential N−O or N−Cl bond cleavage and C−N/C−O bond formation under external-oxidant-free conditions. In this external-oxidant-free process, the N−O or N−Cl bond is strategically utilized as an instrument for the generation of amidyl radicals and oxidizing iron salts.

RESULTS AND DISCUSSION

In the initial investigation of this reaction, readily available *O*-methyl benzohydroxamic acid (**1a**) was chosen as a model substrate to react with C_{60} in the presence of various iron salts with different oxidation states (Table 1, entries 1−9). Among the iron salts, including Fe(II) and Fe(III), inexpensive and easy handling $FeCl_2{\cdot}4H_2O$ emerged as the best catalyst and gave fullerenooxazole **2a** in 12% yield (85% based on consumed

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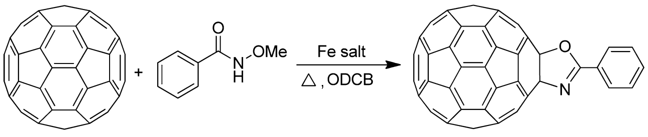
Table 1. Optimization of Reaction Conditions[a]

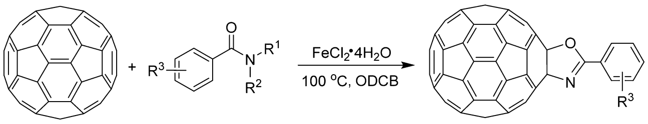


1a **2a**

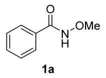
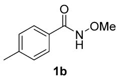
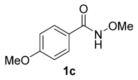
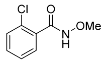
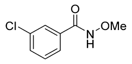
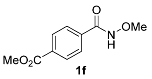
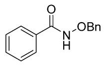
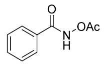
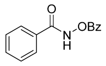
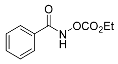
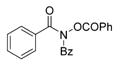
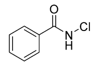
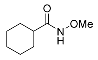
entry	Fe salt	molar ratio[b]	temp[c] (°C)	time (h)	yield[d] (%)
1	$FeCl_2$	1:2:1	100	2	10 (77)
2	$FeCl_2 \cdot 4H_2O$	1:2:1	100	2	12 (85)
3	$FeBr_2 \cdot xH_2O$	1:2:1	100	2	10 (63)
4	$Fe(OAc)_2$	1:2:1	100	2	NR
5	$Fe(OTf)_2$	1:2:1	100	2	trace
6	$FeCl_3$	1:2:1	100	2	7 (75)
7	$FeCl_3 \cdot 6H_2O$	1:2:1	100	2	trace
8	$FeBr_3$	1:2:1	100	2	6 (60)
9	$Fe_2(SO_4)_3 \cdot xH_2O$	1:2:1	100	2	NR
10	$FeCl_2 \cdot 4H_2O$	1:2:2	100	2	31 (88)
11	$FeCl_2 \cdot 4H_2O$	1:2:3	100	2	26 (70)
12	$FeCl_2 \cdot 4H_2O$	1:4:2	100	2	30 (84)
13	$FeCl_2 \cdot 4H_2O$	1:2:2	100	1	13 (81)
14	$FeCl_2 \cdot 4H_2O$	1:2:2	100	3	25 (66)
15	$FeCl_2 \cdot 4H_2O$	1:2:2	90	2	10 (72)
16	$FeCl_2 \cdot 4H_2O$	1:2:2	110	2	26 (69)
17[e]	$FeCl_2 \cdot 4H_2O$	1:2:2	100	2	30 (83)
18	none	1:2:0	100	2	NR

[a] All reactions were carried out with C_{60}/**1a**/Fe salt in a designated molar ratio in ODCB (4 mL) under air unless specified otherwise. [b] Molar ratio refers to C_{60}/**1a**/Fe salt. [c] Oil temperature. [d] Yields in parentheses were based on consumed C_{60}. NR, no reaction. [e] The reaction was carried out under nitrogen atmosphere.

Table 2. $FeCl_2 \cdot 4H_2O$-Mediated Synthesis of Fullerenooxazoles[a]



1 **2**

entry	substrate 1	time (h)	product 2	yield (%)[b]
1	 **1a**	2	**2a**	31 (88)
2	 **1b**	2	**2b**	31 (78)
3[c]	 **1c**	2	**2c**	17 (79)
4	 **1d**	1.5	**2d**	37 (83)
5	 **1e**	2	**2e**	34 (77)
6[c]	 **1f**	2	**2f**	33 (78)
7[c]	 **1g**	2	**2a**	24 (77)
8	 **1h**	1.5	**2a**	35 (87)
9	 **1i**	2	**2a**	34 (77)
10	 **1j**	2	**2a**	19 (59)
11	 **1k**	2	**2a**	40 (86)
12[d]	 **1l**	2	**2a**	32 (70)
13	 **1m**	2	**2m**	0

[a] All reactions were carried out with a molar ratio of C_{60}/**1a**/$FeCl_2 \cdot 4H_2O$ = 1:2:2 in ODCB (4 mL) at 100 °C unless specified otherwise. [b] Yields in parentheses were based on consumed C_{60}. [c] Reaction at 110 °C. [d] Reaction at 90 °C.

C_{60}) via stepwise N−O bond cleavage/C−N and C−O bond formation (Table 1, entry 2). With respect to catalyst loading, 2 equiv of the iron salt was found to be optimal, with the formation of the derivative **2a** in 31% yield (88% based on consumed C_{60}) (Table 1, entry 10). It is interesting that Fe(III) salts, such as $FeCl_3$ and $FeBr_3$, could also promote the present annulation reaction, albeit in relatively low yields (Table 1, entries 6 and 8). The effect of other reaction parameters, such as reagent dosage, reaction time, and reaction temperature, was also investigated (Table 1, entries 11−16). It is particularly worth noting that the presence or absence of an inert atmosphere had a negligible effect on the product yield (Table 1, entry 17). In addition, a control experiment indicated that, in the absence of a metal salt, no reaction occurred (Table 1, entry 18).

Having identified the optimal conditions, we turned our attention to the evaluation of the substrate scope in this annulation reaction. A variety of *O*-methyl benzohydroxamic acids (**1a**−**1f**) with different substituents on the benzene rings, including 4-methyl, 4-methoxyl, 2-chloro, 3-chloro, and 4-acetoxy, were employed to synthesize a series of fullerenooxazoles. In all cases, the reaction proceeded smoothly and furnished the desired products in 17−37% yields (77−88% based on consumed C_{60}), as shown in Table 2. Compared with the substrate **1c** with a strong electron-rich substituent (OMe), the substrates **1d**−**1f** bearing electron-withdrawing groups (Cl, CO_2Me) showed higher reactivity, indicating that the electronic effect of the substituent group on the aromatic ring has a significant influence on the reaction (Table 2, entry 3 vs entries 4−6). Additionally, the ortho-position effect of *O*-methyl benzohydroxamic acid **1d** was not observed (Table 2, entry 4). We were pleased to find that the catalytic system was not restricted to the use of *O*-methyl benzohydroxamic acids, but also allowed for efficient annulations of *O*-benzyl, *O*-acetyl, *O*-benzoyl, and *O*-ethoxycarbonyl benzohydroxamic acids **1g**−**1j**, providing fullerenooxazole **2a** in 19−35% yields (59−87%

based on consumed C_{60}) (Table 2 entries 7−10). It should be noted that *O*-benzoyl-*N*-benzoylbenzohydroxamic acid **1k** was also suitable for this reaction and gave a slightly higher yield than the other substrates (Table 2, entry 11). To our satisfaction, *N*-chlorobenzamide **1l** was also compatible, and efficiently gave the expected product **2a** (Table 2, entry 12). However, no expected or other products were detected, when *N*-methoxyl cyclohexanecarboxamide **1m** was employed under the same reaction conditions (Table 2, entry 13).

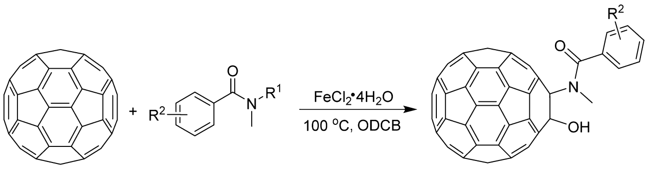
Fullerene derivatives that incorporate heteroatoms (nitrogen or oxygen) or electron-deficient carbon atoms directly connected to the C_{60} core, for example fulleroisoxazoles,[8] exhibit electron-accepting ability similar to or even higher than C_{60}. As isomers of fulleroisoxazoles, the good electron-accepting ability of fullerenooxazoles makes them candidates for applications in a wide variety of organic photovoltaic devices.[9] Therefore, the efficient synthesis of fullerenooxazoles is of interest. Compared with indirect and direct methods for the preparation of fullerenooxazoles,[10] the simple operation and using economical, safe, and environmentally benign $FeCl_2 \cdot 4H_2O$ as the catalyst make this one-step transformation practical and sustainable. It should be noted that this is the first time that the one-step approach for the synthesis of fullerenooxazoles from [60]fullerene in the absence of external oxidant has been reported.

It is important to expand the synthetic utility of the current reaction system and evaluate the reaction mechanism, so a variety of substituted *O*-methyl-*N*-methyl benzohydroxamic acids were also tested. Intriguingly, the reaction gave other novel hydroxyfullerenyl amides in an efficient way via N−O bond cleavage and subsequent addition, instead of cyclization fullerenooxazole adducts (Table 3, entries 1−6). Electron-rich substituents such as Me and OMe on the aromatic ring (**1o** and **1p**) led to slightly higher yields than electron-withdrawing substituents such as Cl and CO_2Me (**1q**−**1s**) (Table 3, entries 2 and 3 vs entries 4−6), which is not in agreement with the above-mentioned experimental observations. Likewise, the successful use of the *O*-benzyl-*N*-methyl benzohydroxamic acid **1t** turned out to be viable, albeit in relatively low yield, possibly due to the steric hindrance of the benzyl group (Table 3, entry 7). Also, other *O*-substituted *N*-methyl benzohydroxamic acids, such as *O*-acetyl (**1u**), *O*-benzyl (**1v**), and *O*-ethoxycarbonyl (**1w**), were efficiently reacted with [60]-fullerene to obtain the desired hydroxyfullerenyl amide **3n** in excellent isolated yields (Table 3, entries 8−10). In addition, we found that *N*-chloro-*N*-methylbenzamide **1x** was also efficient in delivering the desired product **3n**.

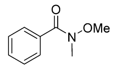
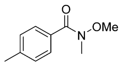
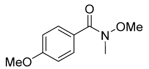
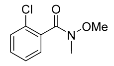
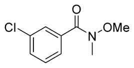
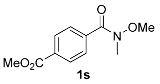
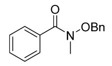
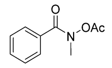
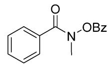
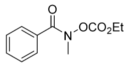
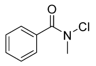
Fullerenols are among the best studied fullerene derivatives with interesting bioactivity properties for potential medicinal applications.[11] In addition, they could be used as useful intermediates for constructing other types of fullerene derivatives.[12] However, the synthesis of fullerenols with structural diversity is relatively underdeveloped.[12a,c,13] The current approach provides a facile synthesis of other novel fullerenols $C_{60}(NMeCOAr)(OH)$ using versatile and readily available starting materials and inexpensive $FeCl_2 \cdot 4H_2O$.

Given the remarkable activity of this novel reaction, we became interested in understanding its mode of action. Thus, a series of control experiments were carried out to elucidate the reaction mechanism. When *N*-acetylbenzamide, *N*-methylbenzamide, or benzamine was subjected to the standard conditions, the reaction did not take place. This result clearly indicates that the presence of groups attached to nitrogen, such as OMe, OBn, OAc, OBz, OCO_2Et, and Cl, plays a crucial role in this transformation, governing the reactivity of the substrates. Moreover, the reaction of $FeCl_2 \cdot 4H_2O$ with **1a** or **1n** was also conducted with the omission of [60]fullerene. According to GC−MS analysis of the reaction mixtures, $PhCONH_2$ and PhCONHMe were obtained respectively,[14] which indicated that the cleavage of the N−O or N−Cl bond first occurred, and not hydrogen atom abstraction as previous reported in the presence of the stronger oxidizing agents.[3]

Table 3. $FeCl_2 \cdot 4H_2O$-Mediated Synthesis of Hydroxyfullerenyl Amides[a]

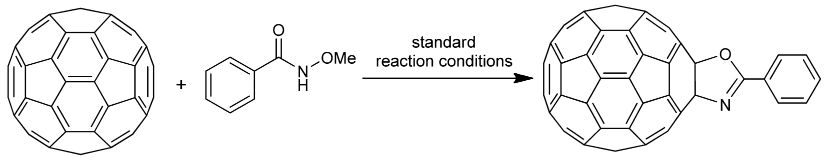


1 **3**

entry	substrate **1**	time (h)	product **3**	yield (%)[b]
1	 **1n**	2	**3n**	34 (80)
2	 **1o**	2	**3o**	31 (75)
3[c]	 **1p**	2	**3p**	33 (78)
4	 **1q**	2	**3q**	28 (71)
5	 **1r**	2	**3r**	27 (63)
6	 **1s**	3	**3s**	27 (70)
7[d]	 **1t**	2	**3n**	20 (95)
8[d]	 **1u**	2	**3n**	46 (77)
9[d]	 **1v**	2	**3n**	44 (78)
10[d]	 **1w**	2	**3n**	41 (90)
11	 **1x**	2	**3n**	48 (69)

[a] All reactions were carried out with a molar ratio of C_{60}/**1a**/$FeCl_2 \cdot 4H_2O$ = 1:2:2 in ODCB (4 mL) at 100 °C unless specified otherwise. [b] Yields in parentheses were based on consumed C_{60}. [c] Reaction at 90 °C. [d] Reaction at 110 °C.

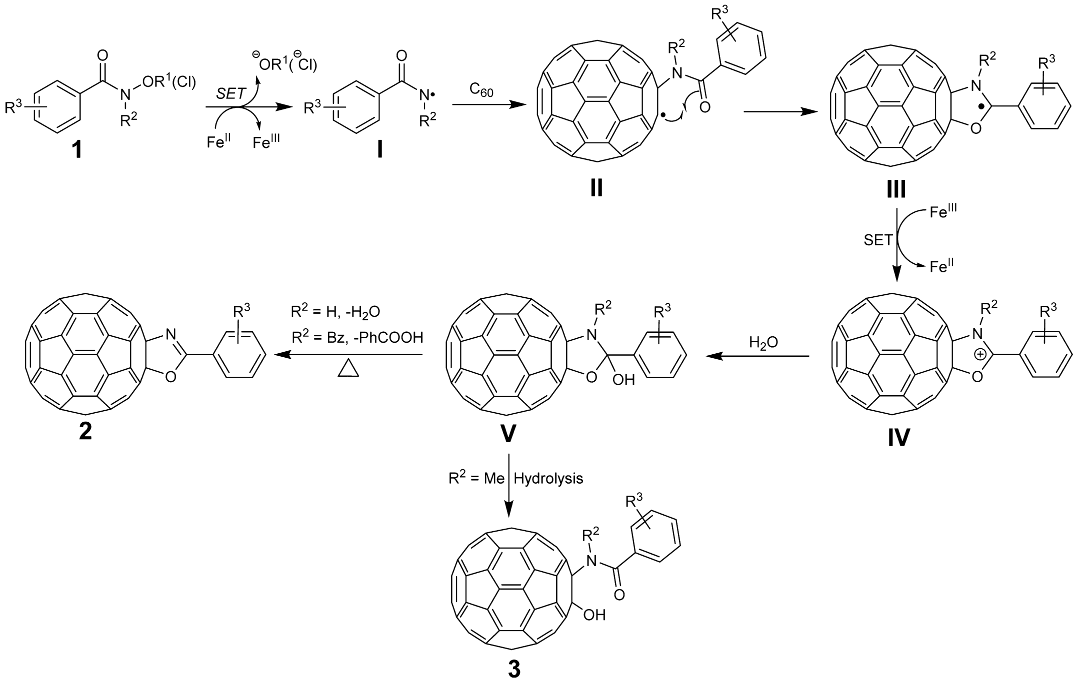
Scheme 1. Radical-Trapping Experiments



1a

additive	2a	Recovered C_{60}
Galvinoxyl (2 equiv)	11%	87%
TEMPO (2 equiv)	0%	100%

Scheme 2. Proposed Reaction Mechanism



We also performed this reaction using CuTC (copper (I) thiophene-2-carboxylate) instead of $FeCl_2·4H_2O$. However, the reaction did not proceed, indicating a notable difference for the copper-mediated *N*-amidation process of organostannanes or boronic acids with *O*-acetyl hydroxamic acids.[14a] In addition, no azafulleroid or aziridinofullerene was detected in this reaction, ruling out the possibility of iron-nitrenoid species as the reaction intermediate.[15]

In our case, addition of 2 equiv of the radical scavenger galvinoxyl (2,6-di-*tert*-butyl-*α*-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-*p*-tolyloxy) or TEMPO (2,2,6,6-tetramethylpiperidine-1-oxy) to the reaction mixture of **1a** and [60]fullerene severely inhibited or completely suppressed the reaction, respectively, which strongly revealed the involvement of radical species during the transformation (Scheme 1).

Based on the aforementioned experimental results, a tentative reaction mechanism involving a free radical pathway is proposed for this sequential N−O or N−Cl bond cleavage and C−N/C−O bond formation reaction (Scheme 2). The reactive amidyl radical species **I** was initially generated via homolysis of the N−O or N−Cl bond by single-electron transfer from Fe(II) to **1**,[4,16] and then the addition of amidyl radical species **I** to [60]fullerene produced fullerenyl radical **II**, which underwent intramolecular cyclization to give radical intermediate **III**. Oxidation of radical **III** by Fe(III) formed in situ with the N−O or N−Cl bond as the internal oxidant led to cation **IV**.[17] The addition of H_2O from hydrated water in $FeCl_2·4H_2O$ or concomitant water in the system to cation **IV** resulted in the highly reactive intermediate **V**. Elimination of water (R^2 = H) or acid (R^2 = Bz) from **V** gave product **2**, while the hydrolysis (R^2 = Me) from species **V** gave adduct **3**.[17,18] An attempt to perform this reaction with catalytic quantities of $FeCl_2·4H_2O$ failed. Thus, a stoichiometric amount of the iron salt is required, which might be attributed to deactivation of Fe(II) salt caused by the coordination of anion OR^1, $PhCONH_2$, or PhCONHMe generated in situ to cation iron during transformation, and as mentioned above, $Fe(OAc)_2$ or $Fe(OTf)_2$ could not initiate this reaction. In addition, this transformation could also proceed in the presence of $FeCl_3$ and $FeBr_3$, indicating that iron salts with higher oxidation states might be generated in the current system, although the exact mechanism of the Fe(III)-induced reaction and the change in its oxidation states are not clear at the present stage.

■ CONCLUSION

In summary, we have successfully disclosed a $FeCl_2·4H_2O$-mediated novel reaction of *O*-substituted benzohydroxamic acids or *N*-chloro-arylamides with [60]fullerene using N−O and N−Cl bonds as an internal oxidant. This transformation allows a broad substrate scope, uses an economical and environmentally benign iron salt, and provides a simple, efficient, and flexible access to fullerenooxazoles and hydroxyfullerenyl amides. More importantly, this interesting reaction mode is important for synthetic organic chemistry, and should be able to be extended to the functionalization of other organic molecules and the formation of other heterocycles rather than being limited to fullerene chemistry. Moreover, it would have important implication for the future development of aryl amidyl radical based synthetic strategies and their application for the construction of nitrogen-containing skeletons. This research has established a useful starting point for investigating future applications of this synthetic strategy, and additional studies are ongoing in our laboratory.

■ EXPERIMENTAL SECTION

General Procedure for the Synthesis of Products 2a−2f from $FeCl_2{\cdot}4H_2O$-Mediated Reaction of C_{60} with Substrates 1a−1l. C_{60} (36.0 mg, 0.05 mmol), $FeCl_2{\cdot}4H_2O$ (19.9 mg, 0.10 mmol), and **1a** (**1b**−**1l**, 0.10 mmol) were added to a dry 15 mL tube equipped with a magnetic stirrer. After the mixture was dissolved in *o*-dichlorobenzene (4 mL) by sonication, then the sealed mixture was heated with stirring in an oil bath preset at a designated temperature for a desired 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 unreacted C_{60}, and then with CS_2/DCM = 5/1 as the eluent to give product **2a** (**2b**−**2f**). Among these compounds **2a**, **2b**, and **2c** are known compounds.

Compound 2a.[10d−g] The reaction of C_{60} with substrates **1a** and **1g**−**1l** gave the same product **2a** with the following yields: 13.0 mg, 31% for **1a**; 9.9 mg, 24% for **1g**; 14.7 mg, 35% for **1h**; 14.3 mg, 34% for **1i**; 8.0 mg, 19% for **1j**; 16.8 mg, 40% for **1k**; 13.4 mg, 32% for **1l**; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.41−8.39 (m, 2H), 7.71−7.67 (m, 1H), 7.65−7.61 (m, 2H).

Compound 2b.[10f] Yield 13.7 mg, 31%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.31 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 2.55 (s, 3H).

Compound 2c.[10e−g] Yield 7.4 mg, 17%; brown solid (7.4 mg, 17%); mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.36 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 3.96 (s, 3H).

Compound 2d. Yield 16.1 mg, 37%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.36 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.61−7.52 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 164.36 (1C, *C*=*N*), 148.02 (1C), 147.61 (1C), 147.34, 146.22 (4C), 146.09, 145.92, 145.87, 145.64, 145.46, 145.28, 145.04, 144.94, 144.65, 144.37, 144.07, 143.04, 142.61, 142.56, 142.50, 142.18, 142.08 (4C), 141.94, 141.82, 141.78, 140.24, 139.48, 137.65, 136.13, 134.51 (1C), 132.49 (1C), 132.06 (1C), 131.16 (1C), 126.72 (1C), 126.13 (1C), 97.11 (1C, sp^3-*C* of C_{60}), 92.03 (1C, sp^3-*C* of C_{60}). FT-IR ν/cm^{-1} (KBr) 2920, 2850, 1637, 1509, 1431, 1327, 1259, 1179, 1141, 1104, 1041, 982, 931, 776, 764, 728, 603, 577, 564, 526. λ_{max}/nm (log ε) 257, 317, 414, 683. MALDI-TOF MS *m*/*z* calcd for $C_{67}H_4ClNO$ [M^+] 872.9976, found 872.9978.

Compound 2e. Yield 14.8 mg, 34%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.43 (t, *J* = 1.6 Hz, 1H), 8.34 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.64−7.55 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 164.06 (1C, *C*=*N*), 147.91 (1C), 147.50 (1C), 147.30, 146.11 (4C), 145.97, 145.81, 145.76, 145.51, 145.23, 145.12, 144.94, 144.83, 144.44, 144.27, 143.96, 142.93, 142.52, 142.47, 142.41, 142.07, 141.98 (4C), 141.84, 141.72, 141.63, 140.17, 139.37, 137.54, 135.91, 134.98 (1C), 132.25 (1C), 129.84 (1C), 129.12 (1C), 128.48 (1C), 127.00 (1C), 97.33 (1C, sp^3-*C* of C_{60}), 91.80 (1C, sp^3-*C* of C_{60}). FT-IR ν/cm^{-1} (KBr) 2912, 2850, 1643, 1570, 1430, 1324, 1267, 1179, 1142, 1068, 982, 933, 789, 707, 603, 563, 526. λ_{max}/nm (log ε) 257, 317, 414, 682. MALDI-TOF MS *m*/*z* calcd for $C_{67}H_4ClNO$ [M^+] 872.9976, found 872.9980.

Compound 2f. Yield 14.8 mg, 33%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.51 (d, *J* = 8.4 Hz, 2H), 8.26 (d, *J* = 8.4 Hz, 2H), 3.98 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 2C unless indicated) δ 165.12 (1C), 164.43 (1C), 147.85 (1C), 147.44 (1C), 147.21, 146.05 (4C), 145.91, 145.75, 145.70, 145.45, 145.18, 145.06, 144.88, 144.77, 144.39, 144.20, 143.89, 142.85, 142.46, 142.41, 142.35, 142.01, 141.92 (4C), 141.78, 141.65, 141.58, 140.12, 139.31, 137.48, 135.87, 133.29 (1C), 130.47 (1C), 129.66, 128.90, 97.29 (1C, sp^3-*C* of C_{60}), 91.82 (1C, sp^3-*C* of C_{60}), 51.89 (1C). FT-IR ν/cm^{-1} (KBr) 2920, 2840, 1727, 1643, 1573, 1519, 1433, 1382, 1325, 1276, 1188, 1141, 1104, 1089, 1020, 982, 931, 865, 777, 706, 658, 603, 563, 526. λ_{max}/nm (log ε) 256, 317, 413, 684. MALDI-TOF MS *m*/*z* calcd for $C_{69}H_7NO_3$ [M^+] 897.0420, found 897.0420.

General Procedure for the Synthesis of Products 3n−3s from $FeCl_2{\cdot}4H_2O$-Mediated Reaction of C_{60} with Substrates 1n−1x. C_{60} (36.0 mg, 0.05 mmol), $FeCl_2{\cdot}4H_2O$ (19.9 mg, 0.10 mmol), and **1n** (**4o**−**4x**, 0.10 mmol) were added to a dry 15 mL tube equipped with a magnetic stirrer. After the mixture was dissolved in *o*-dichlorobenzene (4 mL) by sonication, then the sealed mixture was heated with stirring in an oil bath preset at a designated temperature for a desired time (monitored by TLC). The reaction mixture was treated with triethylamine (0.20 mL), and then 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 then with CS_2/DCM = 2/1 as the eluent to give product **3n** (**3o**−**3s**).

Compound 3n. The reaction of C_{60} with substrates **1n** and **1t**−**1x** gave the same product **3n** with the following yields: 14.8 mg, 34% for **1n**; 8.8 mg, 20% for **1t**; 20.2 mg, 46% for **1u**; 19.2 mg, 44% for **1v**; 17.9 mg, 41% for **1w**; 20.9 mg, 48% for **1x**; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.95−7.93 (m, 2H), 7.61−7.57 (m, 3H), 5.71 (s, 1H), 4.07 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) δ 176.58 (N—*C*=*O*), 152.48, 151.57, 149.64, 148.75, 148.05, 147.95, 146.15 (2C), 146.05, 146.02, 145.81, 145.78, 145.75 (2C), 145.62, 145.54, 145.38, 145.31, 145.29, 145.27, 145.05, 144.93 (2C), 144.83 (2C), 144.78, 144.51 (2C), 144.43 (2C), 144.38, 144.04, 142.61, 142.36, 142.33, 142.24 (2C), 142.13, 142.10, 142.02, 141.91, 141.88, 141.67, 141.46, 141.13, 141.01, 140.95, 140.88, 140.80, 140.59, 139.55, 139.33, 139.29, 138.95, 138.76, 137.31, 137.14, 135.48 134.20, 131.41, 128.73 (2C), 128.44 (2C), 86.20 (sp^3-*C* of C_{60}), 77.94 (sp^3-*C* of C_{60}), 41.44. FT-IR ν/cm^{-1} (KBr) 2909, 1710, 1626, 1464, 1432, 1364, 1218, 1183, 1121, 1103, 1072, 1052, 1035, 1024, 989, 781, 711, 696, 574, 551, 526. λ_{max}/nm (log ε) 255, 318, 420, 687. MALDI-TOF MS *m*/*z* calcd for $C_{68}H_9NO_2Na$ $[M + Na]^+$ 894.0525, found 894.0524.

Compound 3o. Yield 13.7 mg, 31%; brown solid; mp >300 °C; ^1H NMR (400 MHz, CD_3COCD_3/CS_2) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 5.78 (s, 1H), 4.08 (s, 3H), 2.51 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) δ 177.21 (N—*C*=*O*), 152.82, 151.78, 150.00, 149.13, 148.35, 148.25, 146.45, 146.43, 146.34, 146.29, 146.10, 146.07, 146.04, 146.01, 145.91, 145.81, 145.66, 145.58 (2C), 145.54, 145.35, 145.22 (2C), 145.12 (2C), 145.06, 144.81 (2C), 144.72 (2C), 144.68, 144.34, 142.68, 142.65, 142.61, 142.53 (2C), 142.42, 142.38, 142.30, 142.26, 142.20, 142.17, 141.94, 141.74, 141.41, 141.34, 141.24, 141.19, 141.10, 140.87, 139.74, 139.61, 139.56, 139.23, 139.04, 137.57, 137.37, 135.85, 131.45, 129.33 (2C), 129.20 (2C), 86.51 (sp^3-*C* of C_{60}), 78.30 (sp^3-*C* of C_{60}), 41.96, 21.65. FT-IR ν/cm^{-1} (KBr) 2917, 1707, 1622, 1573, 1519, 1432, 1362, 1277, 1219, 1188, 1072, 1051, 1036, 1022, 989, 931, 833, 768, 679, 592, 573, 526. λ_{max}/nm (log ε) 254, 318, 420, 689. MALDI-TOF MS *m*/*z* calcd for $C_{69}H_{11}NO_2Na$ $[M + Na]^+$ 908.0682, found 908.0677.

Compound 3p. Yield 14.9 mg, 33%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 5.85 (s, 1H), 4.11 (s, 3H), 3.92 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) δ 176.99 (N—*C*=*O*), 162.50, 152.94, 151.81, 150.09, 149.29, 148.39, 148.27, 146.48, 146.46, 146.36, 146.32, 146.13, 146.10, 146.07, 146.04, 145.93, 145.82, 145.69, 145.62, 145.61, 145.55, 145.37, 145.25 (2C), 145.15 (2C), 145.09, 144.87, 144.81, 144.75 (2C), 144.72, 144.38, 142.71, 142.68, 142.63, 142.55 (2C), 142.45, 142.41, 142.32, 142.22, 142.20, 141.96, 141.76, 141.44, 141.38, 141.28, 141.25, 141.14, 140.90, 139.75, 139.64, 139.57, 139.26, 139.08, 137.62, 137.34, 135.93, 131.33 (2C), 126.17, 113.94 (2C), 86.55 (sp^3-*C* of C_{60}), 78.38 (sp^3-*C* of C_{60}), 55.28, 42.26. FT-IR ν/cm^{-1} (KBr) 2949, 2830, 1707, 1603, 1509, 1464, 1432, 1361, 1306, 1255, 1219, 1170, 1103, 1074, 1052, 1032, 841, 781, 768, 573, 526. λ_{max}/nm (log ε) 257, 318, 420, 689. MALDI-TOF MS *m*/*z* calcd for $C_{69}H_{11}NO_3Na$ $[M + Na]^+$ 924.0631, found 924.0629.

*Compound **3q**.* Yield 12.7 mg, 28%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.00−7.50 (bs, 4H), 5.62 (s, 1H), 3.87 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3/CS_2$ with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) δ 172.60 (N—*C*═*O*), 152.20, 151.70, 149.62, 148.18 (2C), 148.08, 146.26 (2C), 146.18, 146.10, 145.93, 145.90, 145.87, 145.83, 145.74, 145.70, 145.52, 145.47, 145.39, 145.26, 145.18, 145.05 (2C), 144.93 (2C), 144.85, 144.76, 144.58 (2C), 144.44 (2C), 144.12, 142.52, 142.51, 142.44, 142.37 (2C), 142.22, 142.19, 142.13, 142.06, 142.00, 141.76, 141.59, 141.22, 141.09, 141.01, 140.97, 140.89, 140.73, 139.56, 139.45 (2C), 139.07, 138.81, 137.50, 137.23, 135.33, 135.10, 131.30, 130.92 (2C), 129.95, 127.21, 86.25 (sp^3-*C* of C_{60}), 77.74 (sp^3-*C* of C_{60}), 39.27. FT-IR ν/cm^{-1} (KBr) 2949, 2830, 1707, 1604, 1510, 1464, 1432, 1361, 1306, 1255, 1219, 1170, 1103, 1074, 1052, 1032, 989, 841, 781, 768, 574, 526. λ_{max}/nm (log ε) 255, 317, 434, 685. MALDI-TOF MS *m*/*z* calcd for $C_{68}H_8ClNO_2Na$ $[M + Na]^+$ 928.0136, found 928.0134.

*Compound **3r**.* Yield 12.2 mg, 27%; brown solid; mp >300 °C; ^1H NMR (400 MHz, DMSO-d_6/CS_2) δ 8.42 (s, 1H), 7.81 (s, 1H), 7.72−7.71 (m, 1H), 7.52−7.48 (m, 2H), 3.93 (s, 3H). ^{1} FT-IR ν/cm^{-1} (KBr) 2911, 2843, 1702, 1637, 1476, 1462, 1432, 1375, 1265, 1218, 1188, 1162, 1103, 1088, 1040, 988, 766, 746, 691, 576, 552, 526. λ_{max}/nm (log ε) 258, 318, 420, 687. MALDI-TOF MS *m*/*z* calcd for $C_{68}H_8ClNO_2Na$ $[M + Na]^+$ 928.0136, found 928.0139.

*Compound **3s**.* Yield 12.5 mg, 27%; brown solid; mp >300 °C; ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ 8.22 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 5.61 (s, 1H), 4.04 (s, 3H), 3.96 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6/CS_2 with $Cr(acac)_3$ as relaxation reagent, all 1C unless indicated) δ 172.85 (N—*C*═*O*), 165.31 (O—*C*═*O*), 155.53, 153.81, 152.28, 151.02, 148.59, 148.40, 146.65, 146.63, 146.58, 146.41, 146.26 (3C), 146.11 (4C), 145.89, 145.84 (2C), 145.72, 145.66, 145.49, 145.41, 145.33 (4C), 145.29, 145.18, 145.15, 144.67, 143.09, 142.96, 142.78 (3C), 142.54 (3C), 142.45, 142.10, 142.94, 141.77, 141.62, 141.56, 141.31 (2C), 141.19, 139.70, 139.60, 139.27 (2C), 139.12, 134.91, 131.56, 130.10 (2C), 129.38, 128.95, 128.16 (2C), 85.27 (sp^3-*C* of C_{60}), 78.62 (sp^3-*C* of C_{60}), 52.24. FT-IR ν/cm^{-1} (KBr) 2944, 2838, 1723, 1630, 1463, 1432, 1366, 1276, 1217, 1188, 1105, 1051, 1035, 1018, 864, 782, 735, 574, 526. λ_{max}/nm (log ε) 257, 318, 416, 686. MALDI-TOF MS *m*/*z* calcd for $C_{70}H_{11}NO_4Na$ $[M + Na]^+$ 952.0580, found 952.0577.

Experiments with Benzamide, *N*-Methylbenzamide, and *N*-Acetylbenzamide. C_{60} (36.0 mg, 0.05 mmol), $FeCl_2·4H_2O$ (19.9 mg, 0.10 mmol), and benzamide (*N*-methylbenzamide and *N*-acetylbenzamide, 0.10 mmol) were added to a dry 15 mL tube equipped with a magnetic stirrer. After the mixture was dissolved in *o*-dichlorobenzene (4 mL) by sonication, then the sealed mixture was heated with stirring in an oil bath at 100 °C for 2 h. The reaction mixture was filtered through a silica gel plug to remove any insoluble material, and then was analyzed by TLC; no expected or other products were detected.

Radical-Trapping Experiments. A mixture of C_{60} (36.0 mg, 0.05 mmol), $FeCl_2·4H_2O$ (19.9 mg, 0.10 mmol), and **1a** (15.1 mg, 0.10 mmol), Galvinoxyl (42.2 mg, 0.10 mmol) or TEMPO (15.6 mg, 0.10 mmol) was dissolved in *o*-dichlorobenzene (4 mL) by sonication, and then the sealed mixture was heated with stirring in an oil bath at 100 °C for 2 h. 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 unreacted C_{60}, and then with CS_2/DCM = 5/1 as the eluent to give product **2a**. The results confirmed that Galvinoxyl and TEMPO severely retarded and completely suppressed the formation of **2a**, respectively.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of compounds **2a−2f** and **3n−3s**. 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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