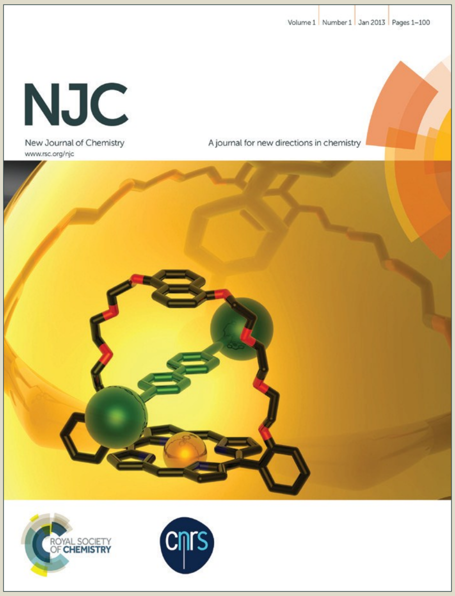
NJC

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Ferric perchlorate-mediated one-step reaction of [60]fullerene with primary amides for the synthesis of fullerooxazoles†

Xiao-Feng Zhang, Fa-Bao Li,* Ji-Long Shi, Jun Wu and Li Liu*

Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, and School of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, P. R. China. E-mail: lfb0615@hubu.edu.cn and liulihubei@hubu.edu.cn

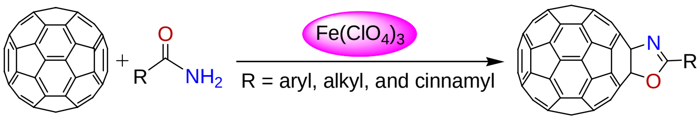
† Electronic supplementary information (ESI) available: NMR spectra of products **2a-o** as well as UV-vis spectra of **2g**, **2h**, and **2o**. See DOI: XXXX

The facile one-step reaction of [60]fullerene with primary amides promoted by cheap and easily available ferric perchlorate afforded a series of interesting fullerooxazole derivatives. The reaction was tolerant of a large variety of primary amides containing aryl, alkyl, and cinnamyl groups. A possible reaction mechanism for the product formation was proposed.

Introduction

Over the past two decades, chemical modification of fullerenes to produce various fullerene derivatives with different structural motifs have attracted extensive attention in chemical community because functionalized fullerenes have exhibited remarkable potential in areas such as biological and medicinal chemistry, materials, and nanotechnology.[1] Accordingly, the development of functionalization methods for fullerenes is of great significance. Generally speaking, the majority of chemical modification of fullerenes includes cycloadditions, nucleophilic additions, radical additions, etc.[1,2] Radical additions are one of the first investigated reaction types of fullerenes and continue to be of interest and important methodologies to functionalize fullerenes.[3] Nevertheless, the radical additions of parent fullerenes induced by traditional peroxide or light tend to result in the generation of multi-addition fullerene products, which would be extremely difficult to separate and characterize. In efforts to avoid the formation of multi-addition products, various types of transition metal salts[3,4] such as $Mn(OAc)_3$,[5] $Fe(ClO_4)_3$,[6] $FeCl_3$,[7] TBADT[$(n\text{–}Bu_4N)_4W_{10}O_{32}$],[8] $Cu(OAc)_2$,[5d,9] $Pb(OAc)_4$,[5g,10] $CoCl_2$dppe,[11] and Ag_2CO_3[12] were employed as new promoters of fullerene radical reactions. The radical reactions of fullerenes promoted by transition metal salts were found to proceed well under mild conditions and could generate a large number of novel mono-addition fullerene adducts that are relatively easy to isolate and purify. For example, a large variety of rare fullerene derivatives including oxazolines, 1,3-dioxolanes, disubstituted C_{60}-fused lactones, boronic esters, 1,2-fullerenols, hemiketals, oxazolidinofullerenes/thiazolidinofullerenes, and dioxanes/dioxepanes could be successfully obtained through the $Fe(ClO_4)_3$-mediated radical reaction of C_{60} with nitriles,[6a] aldehydes/ketones,[6b] malonate esters,[6c] arylboronic acids,[6d] acid chlorides,[6e] β-keto esters,[6f] isocyanates/isothiocyanates,[6g] and diols,[6h] respectively. Therefore, the further exploration and development of novel radical reactions of fullerenes promoted by transition metal salts is still demanded.

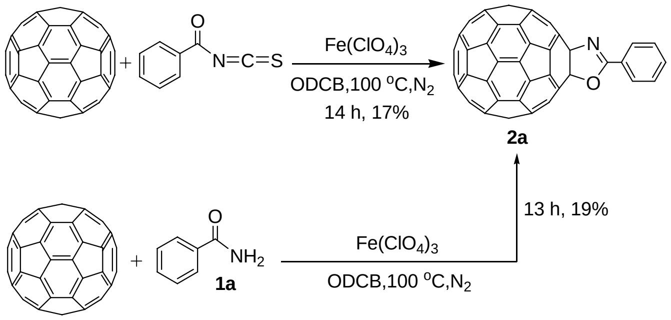
Fullerooxazoles are a class of oxazoline-containing fullerene derivatives, which may have promising applications in life science because a great number of oxazoline-containing natural products and biologically active compounds are present in marine organisms.[13] On the other hand, fullerooxazoles may have great benefits for the preparation of a large variety of organic photovoltaic devices because the presence of two electronegative atoms directly connected to the C_{60} skeleton enables fullerooxazoles to have better electron acceptor character than C_{60}.[7c] Initially, fullerooxazoles were prepared via either thermal reactions[14a,b] of C_{60} with azidoformates and hydroxamic acid derivatives or photochemical reactions[14c] of C_{60} with arylazides, followed by rearrangement of the formed fulleroaziridines to fullerooxazoles. However, these methods undergo a two-step process and require the use of highly toxic and explosive azides. Gao[15a] and Wang[6a] subsequently developed a straightforward approach to the preparation of fullerooxazoles via cycloadditions of C_{60} with nitriles under electrochemical or $Fe(ClO_4)_3$-mediated conditions. Nevertheless, the two methods require a large amount of nitriles (100 equiv. or solvent amounts), and the electrochemical method is only limited to benzonitrile, which dramatically decreases its practicability. Recently, fullerooxazoles were also synthesized via different reactions of C_{60} promoted by *t*-BuOI,[15b] $PhI(OAc)_2/I_2$,[15c] CuI/Phen,[15d] and $FeCl_2$,[15e] respectively. However, these methods require expensive and unaccessible reagents as promoters, ligands or reactants. For example, the reaction promoted by $FeCl_2$ requires the unavailable *N*-substituted amides as reaction substrates,[15e] and the $PhI(OAc)_2/I_2$-mediated synthesis must be manipulated under photo-irradiation conditions.[15c] Hence, it is still demanding to develop new protocol to obtain fullerooxazoles in a more practical and convenient way with a broad substrate scope. In continuation of our interest in fullerene chemistry,[6g,h,16] herein we describe a one-step reaction of C_{60} with primary amides promoted by cheap and easily available $Fe(ClO_4)_3$ to afford a variety of interesting fullerooxazoles with a high tolerance of functional groups (Scheme 1).



Scheme 1 $Fe(ClO_4)_3$-mediated reaction of C_{60} with primary amides affording fullerooxazoles.

Results and discussion

Initially, we investigated the reaction of C_{60} with benzoyl isothiocyanate in the presence of $Fe(ClO_4)_3$ by the direct dissolution method, that is, $Fe(ClO_4)_3$ was first dissolved in benzoyl isothiocyanate, and then the *o*-dichlorobenzene (ODCB) solution of C_{60} was added. We found that fullerooxazole **2a** was unexpectedly obtained as the major product in 17% isolated yield at 100 °C for 14 h (Scheme 2). We conjectured that the formation of fullerooxazole **2a** might proceed via the $Fe(ClO_4)_3$-mediated reaction of C_{60} with benzamide **1a** generated *in situ* by the addition of H_2O in our system to benzoyl isothiocyanate accompanied with the elimination of CO_2 and H_2S.[17] Controlled experiments indicated that the reaction of C_{60} with benzamide **1a** promoted by $Fe(ClO_4)_3$ at 100 °C for 13 h produced the desired fullerooxazole **2a** in 19% yield as a major product (Scheme 2). It should be noted that the easy generation of benzamide **1a** from benzoyl isothiocyanate was attributed to the high reactivity of benzoyl isothiocyanate due to the existence of the strong electron-withdrawing carbonyl group in its molecular structure.



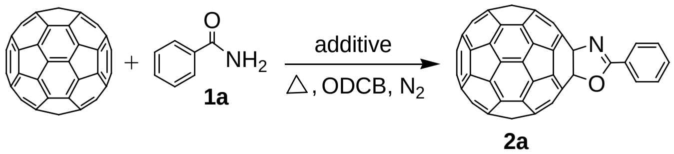
Scheme 2 $Fe(ClO_4)_3$-mediated reaction of C_{60} with benzoyl isothiocyanate and benzamide **1a** affording fullerooxazole **2a**.

These experimental results shown in Scheme 2 provided a good idea for us to realize the efficient synthesis of fullerooxazoles via a simple one-step reaction promoted by $Fe(ClO_4)_3$. Although benzoyl isothiocyanate and benzamide **1a** can be employed to synthesize fullerooxazole **2a**, benzoyl isothiocyanate as starting materials is relatively expensive and more difficult to attain than the corresponding benzamide. Therefore, amides were selected as the reaction substrates to extend the synthesis of fullerooxazoles.

At the onset, the reaction of C_{60} with benzamide (**1a**) in the presence of $Fe(ClO_4)_3$ was chosen to screen the reaction conditions. In our previous study, we have found that the reactions of C_{60} promoted by metal oxidants such as $Mn(OAc)_3$[5d] under air conditions could result in the generation of $C_{60}O$. To avoid the formation of $C_{60}O$, herein we have manipulated the $Fe(ClO_4)_3$-mediated reaction of C_{60} with amides under nitrogen atmosphere. As can be seen from Table 1, the reaction of C_{60},

$Fe(ClO_4)_3$, and **1a** in a molar ratio of 1:1:5 gave fullerooxazole **2a** in 29% isolated yield at 150 °C for 1 h (entry 1, Table 1). Increasing the reaction temperature to 170 °C did not improve the yield of product **2a** (entry 2, Table 1). Decreasing the reaction temperature to 130 °C or 100 °C obviously reduced the isolated yield of product **2a** (entries 3 and 4, Table 1). The variation of the amount of benzamide (from 3 to 8 equiv.) and $Fe(ClO_4)_3$ (from 1 to 2 equiv.) had also no benefit to the isolated yield of product **2a** (entries 5-8, Table 1). Thus, the reagent molar ratio of C_{60}/$Fe(ClO_4)_3$/**1a** as 1:1:5, the reaction temperature as 150 °C together with the protection of nitrogen were chosen as the optimized reaction conditions. In addition, other metal oxidants such as $FeCl_3$, $FeCl_3{\cdot}6H_2O$, $CuCl_2$, $CuCl_2{\cdot}2H_2O$, $Cu(OAc)_2{\cdot}H_2O$, $Mn(OAc)_3{\cdot}2H_2O$, and $Mg(ClO_4)_2$ were also examined under the optimized conditions (entries 9-15, Table 1). Unfortunately, these metal oxidants instead of $Fe(ClO_4)_3$ only led to the formation of a trace amount or no yield of product **2a**, and thus $Fe(ClO_4)_3$ has been proved to be the best oxidant.

Table 1 Optimization of reaction conditions for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with benzamide **1a**[a]



2a

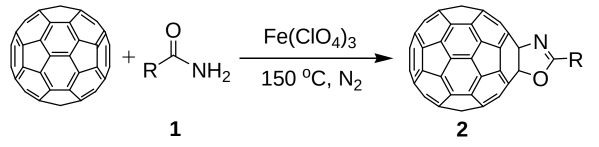
Entry	Additive	Molar ratio[b]	Temp. (°C)	Time (h)	Yield of **2a**[c]
1	$Fe(ClO_4)_3{\cdot}xH_2O$	1:1:5	150	1	29% (94%)
2	$Fe(ClO_4)_3{\cdot}xH_2O$	1:1:5	170	0.5	29% (58%)
3	$Fe(ClO_4)_3{\cdot}xH_2O$	1:1:5	130	3	22% (88%)
4	$Fe(ClO_4)_3{\cdot}xH_2O$	1:1:5	100	5	19% (86%)
5	$Fe(ClO_4)_3{\cdot}xH_2O$	1:1:8	150	1.5	29% (74%)

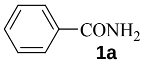
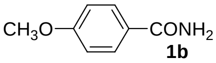
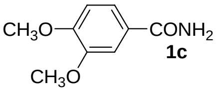
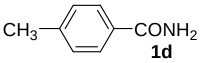
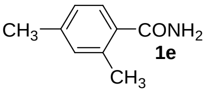
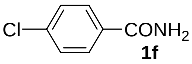
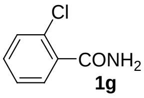
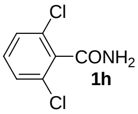
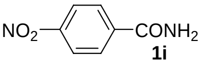
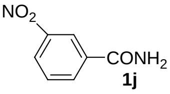
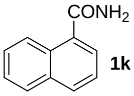
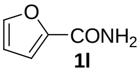
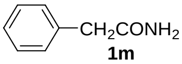
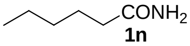
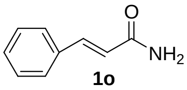
6	$Fe(ClO_4)_3 \cdot xH_2O$	1:1:3	150	1	19% (86%)
7	$Fe(ClO_4)_3 \cdot xH_2O$	1:1:2	150	1	14% (56%)
8	$Fe(ClO_4)_3 \cdot xH_2O$	1:2:5	150	0.5	24% (41%)
9	$FeCl_3$	1:1:5	150	4	trace
10	$FeCl_3 \cdot 6H_2O$	1:1:5	150	4	0
11	$CuCl_2$	1:1:5	150	3	0
12	$CuCl_2 \cdot 2H_2O$	1:1:5	150	4	0
13	$Cu(OAc)_2 \cdot H_2O$	1:1:5	150	3	0
14	$Mn(OAc)_3 \cdot 2H_2O$	1:1:5	150	3	0
15	$Mg(ClO_4)_2$	1:1:5	150	3	0

[a] All reactions were performed under nitrogen conditions. [b] Molar ratio refers to C_{60}/additive/**1a**. [c] Isolated yield; those in parentheses were based on consumed C_{60}.

To expand the scope of the $Fe(ClO_4)_3$-mediated reaction of C_{60} with primary amides, the substrates were extended from benzamide (**1a**) to other representative amides. 4-methoxybenzamide (**1b**), 3,4-dimethoxybenzamide (**1c**), 4-methylbenzamide (**1d**), 2,4-dimethylbenzamide (**1e**), 4-chlorobenzamide (**1f**), 2-chlorobenzamide (**1g**), 2,6-dichlorobenzamide (**1h**), 4-nitrobenzamide (**1i**), 3-nitrobenzamide (**1j**), 1-naphthylamide (**1k**), 2-furamide (**1l**), 2-phenylacetamide (**1m**), hexanamide (**1n**), and cinnamamide (**1o**), were chosen to react with C_{60} in the presence of $Fe(ClO_4)_3$, and were found to afford the desired fullerooxazoles **2b-o**. The reaction times and yields for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with primary amides **1a-o** under the optimized conditions are summarized in Table 2.

Table 2 Reaction times and yields for the reaction of C_{60} with primary amides **1a-o** in the presence of $Fe(ClO_4)_3$[a]



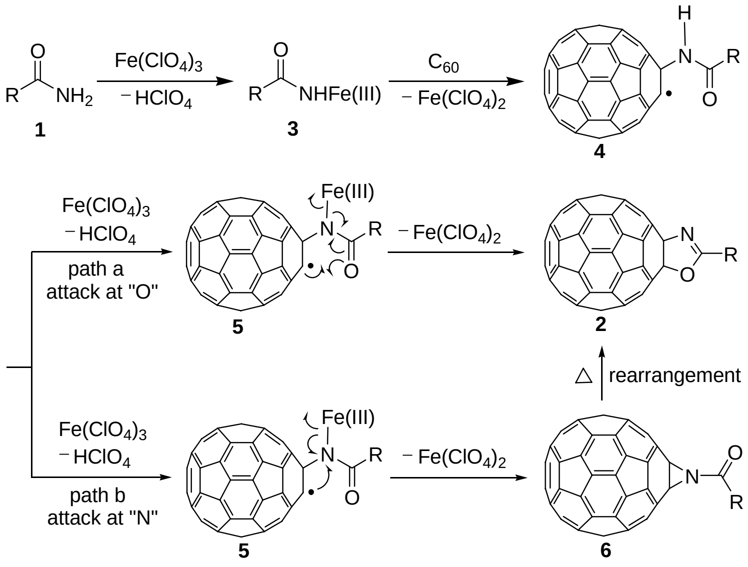
Amide **1**	Time (h)	Yield of **2**^{b}
 **1a**	1	29% (94%)
 **1b**	2	23% (92%)
 **1c**	2	16% (84%)
 **1d**	0.5	27% (93%)
 **1e**	1	25% (89%)
 **1f**	1	23% (82%)
 **1g**	1	17% (85%)
 **1h**	2	18% (82%)
 **1i**	1.5	20% (91%)
 **1j**	2	17% (89%)
 **1k**	1.5	16% (84%)
 **1l**	2	17% (89%)
 **1m**	1.5	21% (84%)
 **1n**	1	19% (76%)
 **1o**	1.5	10% (83%)

[a] All reactions were performed at 150 °C under nitrogen atmosphere, molar ratio of C_{60}/$Fe(ClO_4)_3 \cdot xH_2O$/**1** = 1:1:5. [b] Isolated yield; those in parentheses were based on consumed C_{60}.

As can be seen from Table 2, aromatic amides bearing electron-withdrawing groups or electron-donating groups (**1a-l**), aliphatic amides (**1m** and **1n**), and cinnamamide (**1o**) could be successfully employed to prepare fullerooxazoles. Aromatic amides (**1a-l**) and aliphatic amides (**1m** and **1n**) usually gave fullerooxazoles **2a-n** in moderate to good yields (16-29% isolated yields), comparable to the previously reported data for most monoadducts. As for cinnamamide (**1o**), only 10% yield of fullerooxazole **2o** was produced probably due to the lower reactivity of **1o** owing to the existence of an additional conjugate double bond in its molecular structure. Additionally, functional groups such as Cl and NO_2 could be tolerated under our reaction conditions and could be further transformed to other moieties.

Products **2a-f** and **2i-n** are known compounds, and their identities were confirmed by comparison of their spectral data with those reported in the literature.[6*a*,14*c*,15*a-e*] New compounds **2g**, **2h**, and **2o** were unambiguously characterized by their HR MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV-vis spectra. All of high-resolution mass spectra of these fullerooxazole products gave the correct $[M+H]^+$ peaks. Their ^{1}H NMR spectra displayed the expected chemical shifts as well as the splitting patterns for all protons. In their ^{13}C NMR spectra, the typical peak for the *C*=N carbon appeared at 163.60-164.57 ppm, and no more than 30 peaks in the range of 135-148 ppm for the 58 sp^2-carbons of the C_{60} moiety together with two peaks at 96.17-96.42 ppm and 91.08-91.43 ppm for the two sp^3-carbons of the C_{60} moiety were observed, consistent with the C_s symmetry of their molecular structures. In their IR spectra, the absorption at 1638-1672 cm^{-1} also demonstrated the presence of the C=N moiety. Their UV-vis spectra exhibited a diagnostic absorption at 415-416 nm for the 1,2-adduct of C_{60}.

On the basis of the previously suggested mechanisms for the reactions of C_{60} with nitriles,[6a] aldehydes/ketones,[6b] malonate esters,[6c] arylboronic acids,[6d] acid chlorides,[6e] β-keto esters,[6f] isocyanates/isothiocyanates,[6g] and diols[6h] in the presence of $Fe(ClO_4)_3$. We propose a possible formation mechanism for fullerooxazoles **2** from the reaction of C_{60} with primary amides **1** promoted by $Fe(ClO_4)_3$ (Scheme 3). A chosen amide reacts with $Fe(ClO_4)_3$ to generate Fe(III)-complex **3** accompanied with the elimination of $HClO_4$. Homolytical addition of **3** to C_{60} produces fullerenyl radical **4** with an elimination of $Fe(ClO_4)_2$, followed by coordination with another molecule of $Fe(ClO_4)_3$ to give Fe(III)-complex **5**, in which the radical can either attack the oxygen atom of the carbonyl group with the loss of a Fe(II) species to afford fullerooxazoles **2** (path a) or attack the nitrogen atom to form *N*-acyl aziridinofullerene **6** (path b), followed by rearrangement to give fullerooxazoles **2**. It should be noted that the rearrangement of *N*-acyl aziridinofullerenes under high temperature conditions (about 150 °C) to produce fullerooxazoles has been experimentally confirmed by different groups in previous literature,[14a-c] and thus the reaction pathway (path b) for the formation of fullerooxazoles is also reasonable although the crucial aziridinofullerene intermediate **6** could not be isolated even by decreasing the reaction temperature and shortening the reaction time.



Scheme 3 Proposed reaction mechanism for the formation of fullerooxazoles **2**.

Conclusion

In summary, the simple one-step synthesis of fullerooxazoles has been readily achieved via the reaction of C_{60} with primary amides promoted by $Fe(ClO_4)_3$. The current approach to the preparation of fullerooxazoles from cheap and easily accessible $Fe(ClO_4)_3$ and primary amides is obviously more straightforward and practical than the previous protocols.[6a,14,15] A plausible reaction mechanism for the formation of fullerooxazoles is also suggested.

Experimental

Materials and instruments

All reagents and solvents were used directly as obtained commercially unless otherwise noted. All of primary amides besides benzamide were synthesized by the reaction of aldehydes with hydroxylamine hydrochloride in the presence of Na_2CO_3

and catalytic quantities of $CuBr_2$. All of fullerene products were purified by flash chromatography over silica gel (200–300 mesh). The UV-vis spectra were measured in $CHCl_3$ using a Shimadzu UV-2401 spectrometer. IR spectra were taken on a SPECTRUM ONE NTS spectrometer with KBr pellets. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a WIPM 400 spectrometer. Chemical shifts in ^1H NMR spectra were referenced to tetramethylsilane (TMS) at 0.00 ppm, and chemical shifts in ^{13}C NMR spectra were referenced to residual $CHCl_3$ at 77.16 ppm or DMSO at 39.52 ppm. High-resolution mass spectrometry (HRMS) was performed by MALDI-TOF in positive-ion mode with 4-hydroxy-α-cyanocinnamic acid as the matrix.

General procedure for the $Fe(ClO_4)_3$-mediated reaction of C_{60} with primary amides 1a–o

To a 50-mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer was charged with C_{60} (36.0 mg, 0.05 mmol), $Fe(ClO_4)_3 \cdot xH_2O$ (23.0 mg, 0.05 mmol), and primary amide **1a** (**1b-o**, 0.25 mmol). After they were completely dissolved in ODCB (6 mL) by sonication, the resulting solution was heated with stirring in an oil bath preset at 150 °C under nitrogen atmosphere. The reaction was carefully monitored by thin-layer chromatography (TLC) and stopped at the designated time. The reaction mixture was filtered through a silica gel plug in order to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to afford first unreacted C_{60} and then fullerooxazole **2a**

(2b-o) as an amorphous black solid.

2-Phenyl-oxazolo[4,5:1,2][60]fullerene (2a). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (30.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C_{60} (24.9 mg, 69%) and then **2a**[6a,14c,15a-e] (12.2 mg, 29%) as an amorphous black solid. MP > 300 °C; ^{1}H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.39 (d, J = 7.0 Hz, 2H), 7.67 (t, J = 7.3 Hz, 1H), 7.61 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 164.05 (1C, *C*=N), 147.12 (1C), 147.06, 146.71 (1C), 145.32 (4C), 145.18, 145.03, 144.97, 144.69, 144.55, 144.41, 144.16, 144.05, 143.79, 143.53, 143.22, 142.61, 141.75, 141.72, 141.64, 141.32 (4C), 141.23, 141.09, 140.95 (4C), 139.39, 138.58, 136.79, 135.10, 131.66 (1C, aryl *C*), 128.33 (aryl *C*), 127.98 (aryl *C*), 125.92 (1C, aryl *C*), 96.26 (1C, sp^3-*C* of C_{60}), 91.25 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1641, 1578, 1492, 1448, 1430, 1325, 1235, 1179, 1141, 1090, 1068, 983, 932, 841, 773, 690, 576, 562, 525.

2-(4-Methoxyphenyl)-oxazolo[4,5:1,2][60]fullerene (2b). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1b** (38.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted C_{60} (27.1 mg, 75%) and then **2b**[6a,14c,15b-d] (9.9 mg, 23%) as an amorphous black solid. MP > 300 °C; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.37 (d, J = 7.5 Hz, 2H), 7.10 (d, J = 7.5 Hz, 2H), 3.96 (s, 3H).

2-(3,4-Dimethoxyphenyl)-oxazolo[4,5:1,2][60]fullerene (2c). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1c** (45.0 mg, 0.25

mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted C_{60} (29.1 mg, 81%) and then **2c**[6a] (7.0 mg, 16%) as an amorphous black solid. MP > 300 °C; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.95 (s, 1H), 7.06 (d, J = 8.4 Hz, 1H), 4.06 (s, 3H), 4.02 (s, 3H).

2-(4-Methylphenyl)-oxazolo[4,5:1,2][60]fullerene (2d). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1d** (34.0 mg, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (23.0 mg, 0.05 mmol) for 0.5 h afforded first unreacted C_{60} (25.4 mg, 71%) and then **2d**[6a] (11.4 mg, 27%) as an amorphous black solid: mp > 300 °C; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.33 (d, J = 7.9 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 2.55 (s, 3H).

2-(2,4-Dimethylphenyl)-oxazolo[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** (37.0 mg, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C_{60} (25.9 mg, 72%) and then **2e**[15c] (10.9 mg, 25%) as an amorphous black solid. MP > 300 °C; ^1H NMR (400 MHz, CS_2/DMSO-d_6) δ 8.21 (d, J = 7.4 Hz, 1H), 7.22 (s, 1H), 7.21 (d, J = 7.4 Hz, 1H), 2.94 (s, 3H), 2.47 (s, 3H).

2-(4-Chlorophenyl)-oxazolo[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** (39.0 mg, 0.25 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C_{60} (25.9 mg, 72%) and then **2f**[15b-d] (10.1 mg, 23%) as an amorphous black solid. MP > 300 °C; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.39 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H).

2-(2-Chlorophenyl)-oxazolo[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** (39.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C_{60} (28.7 mg, 80%) and then **2g** (7.3 mg, 17%) as an amorphous black solid. MP > 300 ^oC; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.36 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.4 Hz, 1H), 7.51-7.61 (m, 2H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 163.60 (1C, *C*=N), 147.39 (1C), 146.98 (1C), 146.76, 145.60 (4C), 145.46, 145.29, 145.24, 145.02, 144.84, 144.66, 144.42, 144.32, 144.04, 143.75, 143.45, 142.45, 141.99, 141.95, 141.88, 141.57, 141.47 (4C), 141.32, 141.20, 141.17, 139.63, 138.86, 137.01, 135.49, 133.99 (1C, aryl *C*), 132.04 (1C, aryl *C*), 131.56 (1C, aryl *C*), 130.68 (1C, aryl *C*), 126.23 (1C, aryl *C*), 125.52 (1C, aryl *C*), 96.42 (1C, sp^3-*C* of C_{60}), 91.43 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1638, 1591, 1473, 1432, 1326, 1259, 1179, 1141, 1103, 1061, 1041, 981, 951, 931, 776, 763, 728, 562, 526; UV-vis ($CHCl_3$) λ_{max}/nm 257, 317, 415, 686; MALDI-TOF MS *m*/*z* calcd for $C_{67}H_5ClNO$ $[M+H]^+$ 874.0060, found 874.0059.

2-(2,6-Dichlorophenyl)-oxazolo[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** (48.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted C_{60} (27.9 mg, 78%) and then **2h** (8.1 mg, 18%) as an amorphous black solid. MP > 300 ^oC; ^1H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, CS_2/DMSO-d_6 with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 160.64 (1C, *C*=N), 147.05 (1C), 146.65 (1C), 146.14, 145.30, 145.26, 145.15, 144.97, 144.91, 144.71, 144.48, 144.37, 144.09, 143.99, 143.69, 143.41, 143.13, 141.89, 141.67, 141.62, 141.56, 141.24, 141.17, 141.14, 141.00, 140.87 (4C), 139.35, 138.60, 136.63, 135.15, 134.18 (aryl *C*), 132.14 (1C, aryl *C*), 127.61 (aryl *C*), 126.37 (1C, aryl *C*), 96.17 (1C, sp^3-*C* of C_{60}), 91.08 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1672, 1561, 1431, 1384, 1295, 1275, 1236, 1194, 1128, 1084, 1042, 977, 957, 927, 841, 794, 771, 562, 526; UV-vis ($CHCl_3$) λ_{max}/nm 256, 317, 416, 688; MALDI-TOF MS *m*/*z* calcd for $C_{67}H_4Cl_2NO$ $[M+H]^+$ 907.9670, found 907.9671.

2-(4-Nitrophenyl)-oxazolo[4,5:1,2][60]fullerene (2i). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1i** (42.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 1.5 h afforded first unreacted C_{60} (28.1 mg, 78%) and then **2i**[6a,15b-d] (8.9 mg, 20%) as an amorphous black solid. MP > 300 °C; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 8.67 (d, *J* = 8.8 Hz, 2H), 8.49 (d, *J* = 8.8 Hz, 2H).

2-(3-Nitrophenyl)-oxazolo[4,5:1,2][60]fullerene (2j). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1j** (42.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted C_{60} (29.2 mg, 81%) and then **2j**[15c] (7.4 mg, 17%) as an amorphous black solid. MP > 300 °C; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 9.28 (s, 1H), 8.81 (d, *J* = 7.6 Hz, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.9 Hz, 1H).

2-(1-Naphthylphenyl)-oxazolo[4,5:1,2][60]fullerene (2k). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1k** (43.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 1.5 h afforded first unreacted C_{60} (29.1 mg, 81%) and then **2k**[15c] (7.1 mg, 16%) as an amorphous black solid. MP >

300 °C; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 9.78 (d, J = 8.6 Hz, 1H), 8.70 (d, J = 7.3 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.68-7.75 (m, 2H), 7.60-7.64 (m, 1H).

2-(2-Furylphenyl)-oxazolo[4,5:1,2][60]fullerene (2l). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1l** (28.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 2 h afforded first unreacted C_{60} (29.1 mg, 81%) and then **2l**[15d] (7.1 mg, 17%) as an amorphous black solid. MP > 300 °C; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.81 (d, J = 1.8 Hz, 1H), 7.50 (d, J = 3.4 Hz, 1H), 6.75 (dd, J = 3.4, 1.8 Hz, 1H).

2-Benzyl-oxazolo[4,5:1,2][60]fullerene (2m). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1m** (34.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 1.5 h afforded first unreacted C_{60} (27.1 mg, 75%) and then **2m**[6a,15c,d] (8.9 mg, 21%) as an amorphous black solid. MP > 300 °C; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H), 5.87 (s, 2H).

2-(*n*-Pentyl)-oxazolo[4,5:1,2][60]fullerene (2n). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1n** (29.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 1 h afforded first unreacted C_{60} (26.9 mg, 75%) and then **2n**[15c,d] (7.8 mg, 19%) as an amorphous black solid. MP > 300 °C; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 2.93 (t, J = 7.6 Hz, 2H), 2.06-2.17 (m, 2H), 1.64-1.72 (m, 2H), 1.51-1.60 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H).

2-(1-Styryl)-oxazolo[4,5:1,2][60]fullerene (2o). According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1o** (37.0 mg, 0.25 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (23.0 mg, 0.05 mmol) for 1.5 h afforded first unreacted C_{60} (31.6 mg, 88%) and then **2o** (4.2 mg, 10%) as an amorphous black solid. MP > 300 °C; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 7.98 (d, J = 16.3 Hz, 1H), 7.68 (d, J = 7.1 Hz, 2H), 7.40-7.48 (m, 3H), 7.13 (d, J = 16.3 Hz, 1H); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$ with $Cr(acac)_3$ as relaxation reagent) (all 2C unless indicated) δ 164.57 (1C, *C*=N), 147.50 (1C), 147.26, 147.08 (1C), 145.68, 145.65, 145.54, 145.38, 145.33, 145.06, 144.81, 144.74, 144.51, 144.41, 144.07, 143.86, 143.56, 142.89, 142.34 (1C), 142.08, 142.04, 141.98, 141.64, 141.61, 141.55, 141.40, 141.29, 141.26, 139.73, 138.92, 137.12, 135.52, 134.23 (1C, aryl *C*), 129.70 (1C, aryl *C*), 128.53 (aryl *C*), 127.44 (aryl *C*), 113.39 (1C), 96.35 (1C, sp^3-*C* of C_{60}), 91.29 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 1648, 1626, 1604, 1495, 1447, 1423, 1313, 1276, 1178, 1137, 1062, 1024, 982, 970, 941, 852, 769, 752, 691, 575, 562, 525; UV-vis ($CHCl_3$) λ_{max}/nm 257, 316, 415, 686; MALDI-TOF MS m/z calcd for $C_{69}H_8NO$ $[M+H]^+$ 866.0606, found 866.0607.

$Fe(ClO_4)_3$-mediated reaction of C_{60} with benzoyl isothiocyanate in scheme 2.

A mixture of benzoyl isothiocyanate (336 uL, 2.5 mmol) and $Fe(ClO_4)_3{\cdot}xH_2O$ (115.0 mg, 0.25 mmol) was added to a 50-mL three-neck flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer. The mixture was heated in an oil bath preset at 100 °C for 10 min to allow ferric perchlorate to dissolve in the liquid isothiocyanate. Then to the flask was added the *o*-dichlorobenzene (6 mL) solution of C_{60} (36.0 mg, 0.05 mmol). The resulting solution was heated with vigorous stirring in the oil bath at the same temperature for 14 h under nitrogen atmosphere. The reaction mixture was passed 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/toluene as the eluent to afford unreacted C_{60} (21.0 mg, 58%) and fullerooxazole **2a**[6a,14c,15a-e] (7.1 mg, 17%) as an amorphous black solid.

$Fe(ClO_4)_3$-mediated reaction of C_{60} with benzamide 1a in scheme 2.

According to the general procedure, the reaction of C_{60} (36.0 mg, 0.05 mmol) with **1a** (303 mg, 2.5 mmol) and $Fe(ClO_4)_3 \cdot xH_2O$ (115.0 mg, 0.25 mmol) at 100 °C for 13 h afforded first unreacted C_{60} (25.1 mg, 70%) and then fullerooxazole **2a**[6a,14c,15a-e] (7.9 mg, 19%) as an amorphous black solid.

Acknowledgements

The authors are grateful for the financial support from National Natural Science Foundation of China (Nos. 21102041 and 21071049), Natural Science Foundation of Hubei Province (Nos. 2014CFB550 and 2013CFA087), Natural Science Fund for Creative Research Groups of Hubei Province of China (No. 2014CFA015), and Innovation and Entrepreneurship Training Program for Undergraduates of Hubei Province (No. 201310512011).

References

1 For selected reviews, see: (*a*) E. Nakamura and H. Isobe, *Acc. Chem. Res.*, 2003, **36**, 807; (*b*) M. Bendikov and F. Wudl, *Chem. Rev.,* 2004, **104**, 4891; (*c*) D. M.

Guldi, B. M. Illescas, C. M. Atienza, M. Wielopolski and N. Martín, *Chem. Soc. Rev.,* 2009, **38**, 1587; (*d*) G. C. Vougioukalakis, M. M. Roubelakis and M. Orfanopoulos, *Chem. Soc. Rev.,* 2010, **39**, 817; (*e*) S.-E Zhu, F. Li and G.-W. Wang, *Chem. Soc. Rev.,* 2013, **42**, 7535.

2 For selected reviews, see: (*a*) A. Hirsch, *Synthesis,* 1995, 895; (*b*) M. A. Yurovskaya and I. V. Trushkov, *Russ. Chem. Bull. Int. Ed.,* 2002, **51**, 367; (*c*) F. Giacalone and N. Martín, *Chem. Rev.,* 2006, **106**, 5136; (*d*) Y. Matsuo and E. Nakamura, *Chem. Rev.,* 2008, **108**, 3016; (*e*) M. Murata, Y. Murata and K. Komatsu, *Chem. Commun.,* 2008, 6083.

3 For a recent review on radical reactions of fullerenes, see: M. D. Tzirakis and M. Orfanopoulos, *Chem. Rev.,* 2013, **113**, 5262.

4 For recent reviews on radical reactions of fullerenes promoted by transition metal salts, see: (*a*) G.-W. Wang and F.-B. Li, *J. Nanosci. Nanotech.,* 2007, **7**, 1162; (*b*) G.-W. Wang and F.-B. Li, *Curr. Org. Chem*., 2012, **16**, 1109; (*c*) F.-B. Li and G.-W. Wang, *Sci. China Chem.,* 2012, **55**, 2009.

5 (*a*) T.-H. Zhang, P. Lu, F. Wang and G.-W. Wang, *Org. Biomol. Chem.,* 2003, **1**, 4403; (*b*) G.-W. Wang, T.-H. Zhang, X. Cheng and F. Wang, *Org. Biomol. Chem.,* 2004, **2**, 1160; (*c*) C. Li, D. Zhang, X. Zhang, S. Wu and X. Gao, *Org. Biomol. Chem.,* 2004, **2**, 3464; (*d*) G.-W. Wang and F.-B. Li, *Org. Biomol. Chem.,* 2005, **3**, 794; (*e*) G.-W. Wang, H.-T. Yang, C.-B. Miao, Y. Xu and F. Liu, *Org. Biomol. Chem.,* 2006, **4**, 2595; (*f*) G.-W. Wang, F.-B. Li and T.-H. Zhang, *Org. Lett.,* 2006, **8**, 1355; (*g*) F.-B. Li, T.-X. Liu, Y.-S. Huang and G.-W. Wang, *J. Org. Chem.,*

2009, **74**, 7743; (*h*) F.-B. Li, S.-E Zhu and G.-W. Wang, *Chin. Sci. Bull.,* 2010, **55**, 2909; (*i*) G.-W. Wang, C.-Z. Wang, S.-E Zhu and Y. Murata, *Chem. Commun.,* 2011, **47**, 6111; (*j*) G.-W. Wang, C.-Z. Wang and J.-P. Zou, *J. Org. Chem.,* 2011, **76**, 6088; (*k*) T.-X. Liu, F.-B. Li and G.-W. Wang, *Org. Lett.,* 2011, **13**, 6130; (*l*) Z.-X. Chen and G.-W. Wang, *J. Org. Chem.,* 2005, **70**, 2380.

6 (*a*) F.-B. Li, T.-X. Liu and G.-W. Wang, *J. Org. Chem.,* 2008, **73**, 6417; (*b*) F.-B. Li, T.-X. Liu, X. You and G.-W. Wang, *Org. Lett.,* 2010, **12**, 3258; (*c*) F.-B. Li, X. You and G.-W. Wang, *Org. Lett.,* 2010, **12**, 4896; (*d*) F.-B. Li, X. You, T.-X. Liu and G.-W. Wang, *Org. Lett.,* 2012, **14**, 1800; (*e*) F.-B. Li, X. You and G.-W. Wang, *J. Org. Chem.,* 2012, **77**, 6643; (*f*) F.-B. Li, S.-E Zhu, X. You and G.-W. Wang, *Chin. Sci. Bull.,* 2012, **57**, 2269; (*g*) F.-B. Li, Y.-F. Zhu, X.-F. Zhang, J.-L. Shi, J. Wu, L. Chen, X.-X. Liang and L. Liu, *RSC Adv.,* 2014, **4**, 48085; (*h*) X.-F. Zhang, F.-B. Li, J. Wu, J.-L. Shi, Z. Liu and L. Liu, *J. Org. Chem.,* 2015, **80**, 6037.

7 (*a*) L. Gan, S. Huang, X. Zhang, A. Zhang, B. Cheng, H. Cheng, X. Li and G. Shang, *J. Am. Chem. Soc.,* 2002, **124**, 13384; (*b*) M. Hashiguchi, K. Watanabe and Y. Matsuo, *Org. Biomol. Chem.,* 2011, **9**, 6417; (*c*) M. Hashiguchi, N. Obata, M. Maruyama, K. S. Yeo, T. Ueno, T. Ikebe, I. Takahashi and Y. Matsuo, *Org. Lett.,* 2012, **14**, 3276; (*d*) M. Hashiguchi, H. Inad and Y. Matsuo, *Carbon,* 2013, **61**, 418; (*e*) Y.-T. Su and G.-W. Wang, *Org. Lett.,* 2013, **15**, 3408; (*f*) X.You and G.-W. Wang, *J. Org. Chem.,* 2014, **79**, 117; (*g*) W.-Q. Zhai, S.-P. Jiang, R.-F. Peng, B. Jin and G.-W. Wang, *Org. Lett.,* 2015, **17**, 1862.

8 (*a*) M. D. Tzirakis and M. Orfanopoulos, *Org. Lett.,* 2008, **10**, 873; (*b*) M. D.

Tzirakis and M. Orfanopoulos, *J. Am. Chem. Soc.,* 2009, **131**, 4063; (*c*) M. D. Tzirakis and M. Orfanopoulos, *Angew. Chem. Int. Ed.,* 2010, **49**, 5891; (*d*) M. D. Tzirakis, M. N. Alberti and M. Orfanopoulos, *Chem. Commun.,* 2010, **46**, 8228.

9 (*a*) S. Lu, T. Jin, E. Kwon, M. Bao and Y. Yamamoto, *Angew. Chem. Int. Ed.,* 2012, **51**, 802; (*b*) T.-X. Liu, Z. Zhang, Q. Liu, P. Zhang, P. Jia, Z. Zhang and G. Zhang, *Org. Lett.,* 2014, **16**, 1020; (*c*) X.-W. Lu, M.-L. Xing, C.-B. Miao, J.-X. Li, X.-Q. Sun and H.-T. Yang, *Org. Biomol. Chem.,* 2015, **13**, 8405.

10 (*a*) S.-C. Chuang, F. R. Clemente, S. I. Khan, K. N. Houk and Y. Rubin, *Org. Lett.,* 2006, **8**, 4525; (*b*) X.You, F.-B. Li and G.-W. Wang, *J. Org. Chem.,* 2014, **79**, 11155.

11 (*a*) S. Lu, T. Jin, M. Bao and Y. Yamamoto, *J. Am. Chem. Soc.,* 2011, **133**, 12842; (*b*) S. Lu, W. Si, M. Bao, Y. Yamamoto and T. Jin, *Org. Lett.,* 2013, **15**, 4030.

12 C.-L. He, R. Liu, D.-D. Li, S.-E Zhu and G.-W. Wang, *Org. Lett.,* 2013, **15**, 1532.

13 R. J. Bergeron, *Chem. Rev.,* 1984, **84**, 587.

14 (*a*) M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith and D. W. H. Rankin, *J. Chem. Soc. Chem. Commun.*, 1994, 1365; (*b*) M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, J. R. A. Millar and A. T. Taylor, *Tetrahedron Lett.*, 1994, **35**, 9067; (*c*) J. Averdung, J. Mattay, D. Jacobi and W. Abraham, *Tetrahedron*, 1995, **51**, 2543.

15 (*a*) M. Zheng, F.-F. Li, L. Ni, W.-W. Yang and X. Gao, *J. Org. Chem.,* 2008, **73**, 3159；(*b*) Y. Takeda, S. Enokijima, T. Nagamachi, K. Nakayama and S. Minakata,

Asian J. Org. Chem., 2013, **2**, 91; (*c*) H.-T. Yang, W.-L. Ren, C.-P. Dong, Y. Yang, X.-Q. Sun and C.-B. Miao, *Tetrahedron Lett.*, 2013, **54**, 6799; (*d*) H.-T. Yang, X.-C. Liang, Y.-H. Wang, Y. Yang, X.-Q. Sun and C.-B. Miao, *Org. Lett.*, 2013, **15**, 4650; (*e*) T.-X. Liu, Y. Liu, D. Chao, P. Zhang, Q. Liu, L. Shi, Z. Zhang and G. Zhang, *J. Org. Chem.,* 2014, **79**, 11084.

16 J. Wu, F.-B. Li, X.-F. Zhang, J.-L. Shi and L. Liu, *RSC Adv.,* 2015, **5**, 30549.

17 R. Pecháček, J. Velíšek and H. Hrabcova, *J. Agric. Food Chem.*, 1997, **45**, 4584.

Graphical content:

Ferric perchlorate-mediated one-step reaction of [60]fullerene with primary amides for the synthesis of fullerooxazoles

Xiao-Feng Zhang, Fa-Bao Li, Ji-Long Shi, Jun Wu and Li Liu

Reaction of [60]fullerene with amides promoted by cheap and easily available ferric perchlorate affords a series of interesting fullerooxazole derivatives.