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$FeCl_3 \cdot 6H_2O$-mediated reaction of [60]fullerene with amidoximes

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ABSTRACT

A $FeCl_3 \cdot 6H_2O$-mediated reaction of [60]fullerene with amidoximes for the preparation of fulleroimidazolines has been presented. This reaction shows a wide substrate scope, and the products obtained from alkyl-substituted amidoximes are first disclosed. In addition, a possible mechanism is proposed.

1. Introduction

Amidoximes possess good coordination with metal, which can be used for synthesis of various complexes,[1] or as selective extracting reagents for toxic metal cations.[2] It is well known that amidoximes are favorable building blocks for the preparation of all kinds of organic heteroatom compounds, such as imidazoles,[3] benzimidazoles,[4] oxadiazoles,[5] and triazoles.[6] However, there are few reports about the synthesis of imidazolines through the reaction of amidoximes with electron-deficient alkenes or alkynes. Based on our experience in the synthesis of fullerene heterocyclic derivatives,[7] we reckon that fullerene who possess special electron-deficient olefins may react with amidoximes to construct [60] fullerene-fused imidazolines, which by the way would also be in favor of the search for new reaction of electron deficient alkenes or alkynes to imidazolines.

On account of the potential applications of C_{60} derivatives in material science and biological chemistry,[8] the efficient methodologies for their synthesis have strongly attracted lots of researchers' attention. Recently, an interesting topic is the synthesis of the [60]fullerene-fused imidazolines, when Wang's group firstly reported the synthesis of the [60]fullerene-fused imidazolines via silver carbonate promoted reaction of C_{60} with *N*-arylbenzamidines,[9] coincidently, Yang's group reported the reaction using CuI/Phen (1,10-phenanthroline) instead of Ag_2CO_3.[10a] Currently, they also described 4-dimethylaminopyridine (DMAP)-catalyzed reaction of *N*-tosylaziridinofullerenes with amidines for the preparation of fulleroimidazole derivatives.[10b] However, amidines bearing alkyl group cannot afford the corresponding products with these methods.[10] By now, the reported fulleroimidazolines are synthesized using amidines as starting materials. Therefore, it is still significant and challenging to achieve various fulleroimidazole derivatives.

On the other hand, transition-metal-catalyzed or -mediated approaches become increasingly popular in the field of organic synthesis, including iron which is the second highest metal element in the crust. It is prevalent with the feature of cheap, easily available, nontoxic and effective catalyst for numerous organic reactions in catalytic area.[11] Bearing these in mind, we set out to explore the possibilities and fortunately we found that $FeCl_3 \cdot 6H_2O$ could successfully promote the reaction of amidoximes with C_{60}.

Herein, we report a $FeCl_3 \cdot 6H_2O$-mediated cycloaddition reaction of C_{60} with amidoximes to provide fulleroimidazole derivatives with a broad substrate scope.

2. Results and discussion

When we found that the reaction of C_{60} with *N*-phenylbenzamidoxime **2a** in the presence of $FeCl_3 \cdot 6H_2O$ in a molar ratio of

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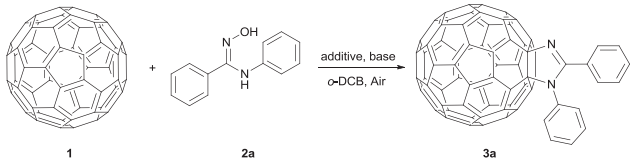
1:5:1 at 130 °C under air atmosphere for 10 h afforded the desired product **3a** in 13% yield (Table 1, entry 1), we used this as model reaction and moved ahead to pursue optimized reaction conditions by varying the use of additives, bases, their molar ratio and reaction temperatures (Table 1). And finally, a molar ratio of C_{60}, **2a**, $FeCl_3\cdot 6H_2O$, and DMAP as 1:5:1:2 and a temperature of 130 °C in 1,2-dichlorobenzene (*o*-DCB) turned out as the best optimized reaction conditions (Table 1, entry 11). It is worth noting that there is no reaction in the absence of $FeCl_3\cdot 6H_2O$ (Table 1, entry 14).

Armed with the above optimized reaction conditions, we step forward to investigate the scope of the $FeCl_3\cdot 6H_2O$-mediated cycloaddition reaction of C_{60} with various amidoximes, and the results are presented in Table 2. Both electron-donating and electron-withdrawing groups were applied to test the applicability of this methodology, and it was found that the vast majority of the amidoximes could successfully complete the transformation and give the desired [60]fullereoimidazolines with 15–40% isolated yields. When the substituent group on the *para* position of R^2 phenyl ring is methyl or fluorine, the substituent group on the R^1 phenyl ring has little or no significant influence on the reaction (Table 2, entries 3, 7, 13, entries 9, 14), except **2k** bearing a nitro group afforded **3k** with somehow lower isolated yield (Table 2, entry 11). An electron-donating group on the R^2 aromatic ring gave a slightly higher yield than electron-withdrawing group when amidoximes carrying the same R^1 aromatic ring (Table 2, entries 7, 9–14). Additionally, with the increasing of the steric hindrance on substituted group R^2, the yields tended to decline such as **3c** and **3b** dropping from 35% to 20%, **3g** and **3e** from 33% to 0 (Table 2, entries 2, 3, 5–7). Here unfortunately the *ortho*-substitute on R^2 phenyl ring inhibited the cycloaddition reaction. Luckily, the present method was also successfully expanded to the preparation of [60]fullereoimidazolines **3o** and **3p**, which derived from amidoximes containing an alkyl group (Table 2, entries 15 and 16).

Table 1
Optimization of the reaction conditions[a]

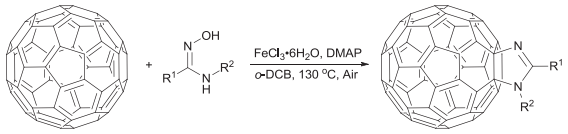


1 2a 3a

Entry	Additive	Base	Molar ratio[b]	Yield (%)[c]
1	$FeCl_3\cdot 6H_2O$	—	1:5:1:0	13 (75)
2	$Fe(ClO_4)_3\cdot 6H_2O$	—	1:5:1:0	4 (60)
3	Ag_2CO_3	—	1:5:1:0	0
4	CuI	—	1:5:1:0	Trace
5	$Cu(OAc)_2\cdot H_2O$	—	1:5:1:0	0
6	$Mn(OAc)_2\cdot 4H_2O$	—	1:5:1:0	0
7	$Mn(OAc)_3\cdot 2H_2O$	—	1:5:1:0	0
8	$PhI(OAc)_2$	—	1:5:1	Trace
9	$FeCl_3\cdot 6H_2O$	Na_2CO_3	1:5:1:2	7 (42)
10	$FeCl_3\cdot 6H_2O$	Cs_2CO_3	1:5:1:2	18 (70)
11	**$FeCl_3\cdot 6H_2O$**	**DMAP**	**1:5:1:2**	**40 (96)**
12	$FeCl_3\cdot 6H_2O$	DABCO	1:5:1:2	Trace
13	$FeCl_3$	DMAP	1:5:1:2	41 (89)
14	—	DMAP	1:5:0:2	0
15[d]	$FeCl_3\cdot 6H_2O$	DMAP	1:5:1:2	17 (65)
16[e]	$FeCl_3\cdot 6H_2O$	DMAP	1:5:1:2	39 (83)
17[f]	$FeCl_3\cdot 6H_2O$	DMAP	1:5:1:2	35 (82)
18	$FeCl_3\cdot 6H_2O$	DMAP	1:5:0.5:2	21 (76)
19	$FeCl_3\cdot 6H_2O$	DMAP	1:5:2:2	38 (84)
20	$FeCl_3\cdot 6H_2O$	DMAP	1:3:1:2	23 (94)
21	$FeCl_3\cdot 6H_2O$	DMAP	1:8:1:2	35 (81)
22	$FeCl_3\cdot 6H_2O$	DMAP	1:5:1:1	29 (91)
23	$FeCl_3\cdot 6H_2O$	DMAP	1:5:1:3	40 (94)

[a] Unless specified, all reactions were performed in 7 mL *o*-DCB at 130 °C for 10 h under air.
[b] Molar ratio refers to C_{60}/2a/additive/base.
[c] Isolated yield; the values in parentheses were based on consumed C_{60}.
[d] The reaction was operated at 110 °C.
[e] The reaction was operated at 150 °C.
[f] The reaction was carried out under a N_2 atmosphere.

Table 2
Substrate scope of $FeCl_3\cdot 6H_2O$-mediated reaction of C_{60} with amidoximes[a]



1 2 3

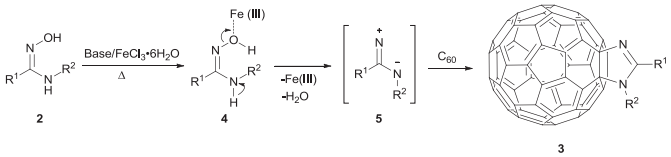
Entry	R^1	R^2	Product	Yield (%)[b]
1	Ph	Ph	**3a**	40 (96)
2	Ph	*m*-MePh	**3b**	20 (72)
3	Ph	*p*-MePh	**3c**	35 (82)
4	*p*-MePh	Ph	**3d**	33 (79)
5	*p*-MePh	*o*-MePh	**3e**	0
6	*p*-MePh	*m*-MePh	**3f**	27 (84)
7	*p*-MePh	*p*-MePh	**3g**	33 (80)
8	*p*-MePh	*m*-FPh	**3h**	19 (76)
9	*p*-MePh	*p*-FPh	**3i**	29 (74)
10	*p*-MePh	*p*-ClPh	**3j**	32 (76)
11	*p*-NO_2Ph	*p*-MePh	**3k**	20 (58)
12	*p*-NO_2Ph	*p*-OMePh	**3l**	30 (79)
13	*p*-FPh	*p*-MePh	**3m**	33 (70)
14	*p*-FPh	*p*-FPh	**3n**	29 (80)
15	2-phenylethyl	*p*-MePh	**3o**	15 (37)
16	*p*-MePh	Bn	**3p**	25 (60)

[a] Unless otherwise noted, all reactions were carried out with a molar ratio of C_{60}/**2**/$FeCl_3\cdot 6H_2O$/DMAP=1:5:1:2 in 7 mL *o*-DCB at 130 °C for 8–12 h under air.
[b] Isolated yield; the values in parentheses were based on consumed C_{60}.

All of the known compounds were confirmed through interpretation of their spectral data in accordance with those reported in the literatures.[9,10] The structures of new C_{60}-fused imidazole derivatives **3b**, **3f**, **3h**, **3i**, **3l**–**3p** were fully characterized by their MALDI-FTICR-MS, ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, FTIR, and UV–vis spectra.

In order to get a deeper understanding of the reaction mechanism, a free radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 5 equiv) was added to the reaction mixture (see Supplementary data). The cycloaddition reaction was not hindered, which indicates that the reaction may not relate to the formation of an iminyl or nitrogen radical.[12]

Based on the above results and previous literatures on iron-catalyzed or -mediated reactions,[12,13] a plausible mechanism for the reaction of C_{60} with amidoximes is proposed and described in Scheme 1. First, in the presence of $FeCl_3\cdot 6H_2O$ and base, the amidoxime **2** gives the intermediate **4** under heating condition, followed by the elimination of H_2O and Fe(III) to afford dipole **5**, which then partakes in a 1,3-dipolar cycloaddition reaction with C_{60} to generate fullereoimidazoline **3**.



2 4 5 3

Scheme 1. Plausible mechanism for the formation of **3**.

3. Conclusion

In conclusion, a novel and efficient method has been successfully developed to establish C_{60}-fused imidazolines via a $FeCl_3\cdot 6H_2O$-mediated 1,3-dipolar cycloaddition reaction of [60]

fullerene with various amidoximes. This novel method, which uses $FeCl_3 \cdot 6H_2O$ as the additive, DMAP as the base, services a wide range of functionalities including aryl and alkyl substituted amidoximes. To expand the application of amidoximes in organic synthesis, we are currently planning to synthesize new imidazolines with the employ of amidoximes and other compounds owning electron-deficient alkene or alkyne.

4. Experimental section

4.1. General

Unless otherwise noted, solvents and reagents were purchased from commercial sources and used without further purification. ^1H, ^{13}C NMR and ^{19}F spectra were recorded on a Bruker DRX-500 MHz spectrometer operating at 500 MHz, 125 MHz and 470 MHz, respectively. The chemical shifts are reported in parts per million (ppm) on the δ scale. The solvent peak was used as a reference value, for ^1H NMR: $CDCl_3$=7.26 ppm, DMSO-d_6=2.50 ppm, for ^{13}C NMR: $CDCl_3$=77.16 ppm, DMSO-d_6=39.52 ppm. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.0. HRMS (high resolution mass spectra) was obtained on Waters Micromass GCT or Thermo Fisher Scientific LTQ FT Ultra instrument by Shanghai Mass Spectrometry Center, Shanghai Institute of Organic Chemistry.

4.2. General procedure for the preparation of amidoximes[4b,5f]

Chlorooxime was prepared from aldehyde in two steps. Then, to the chlorooxime (5 mmol) in DMF (7 mL) was added the corresponding amine (10 mmol) at 0 °C. The solution was stirred at room temperature until TLC shows the complete disappearance of the chlorooxime. The solution was diluted with EtOAc, washed with H_2O, saturated aqueous NaCl solution, dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc/petroleum ether) to give the corresponding *N*-substituted amidoxime **2**.

2a:[4b] White solid (445.8 mg, 42%); mp 136.1–137.1 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.56 (s, 1H), 8.30 (s, 1H), 7.39–7.30 (m, 5H), 7.04 (t, *J*=7.9 Hz, 2H), 6.77 (t, *J*=7.3 Hz, 1H), 6.64 (d, *J*=8.0 Hz, 2H).

2b: White solid (427.2 mg, 38%); mp 133.2–133.7 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.54 (s, 1H), 8.19 (s, 1H), 7.40–7.29 (m, 5H), 6.90 (t, *J*=7.7 Hz, 1H), 6.59 (d, *J*=7.5 Hz, 1H), 6.56 (s, 1H), 6.36 (d, *J*=8.0 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 149.33, 141.32, 137.53, 132.94, 128.91, 128.23, 128.12, 127.69, 121.51, 120.41, 117.02, 21.09; UV–vis ($CHCl_3$) λ_{max}/nm 247, 269; FTIR ν/cm^{-1} (KBr) 3400, 3058, 2921, 2814, 1627, 1603, 1499, 1391, 1293, 1176, 1119, 844, 771, 733, 701; HRMS (EI-TOF, 70 eV) *m/z* Calcd for $C_{14}H_{14}N_2O$ $[M]^+$ 226.1106, Found 226.1104.

2c:[14] White solid (508.0 mg, 45%); mp 152.3–154.2 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.50 (s, 1H), 8.22 (s, 1H), 7.40–7.26 (m, 5H), 6.85 (d, *J*=8.1 Hz, 2H), 6.56 (d, *J*=8.2 Hz, 2H), 2.13 (s, 3H).

2d:[5f] White solid (483.1 mg, 43%); mp 125.3–125.9 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.49 (s, 1H), 8.24 (s, 1H), 7.26 (d, *J*=8.0 Hz, 2H), 7.12 (d, *J*=7.9 Hz, 2H), 7.04 (t, *J*=7.8 Hz, 2H), 6.76 (t, *J*=7.3 Hz, 1H), 6.65 (d, *J*=7.8 Hz, 2H), 2.28 (s, 3H).

2e: White solid (434.5 mg, 36%); mp 193.4–193.9 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 8.92 (s, 1H), 7.87 (s, 1H), 7.85 (s, 1H), 7.35 (d, *J*=8.3 Hz, 2H), 7.19–7.11 (m, 2H), 7.09 (d, *J*=8.2 Hz, 2H), 6.93 (t, *J*=7.3 Hz, 1H), 2.24 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 153.16, 137.99, 137.78, 130.96, 130.63, 129.68, 127.78, 126.61, 122.97, 121.36, 118.57, 20.80, 18.36; UV–vis ($CHCl_3$) λ_{max}/nm 249; FTIR ν/cm^{-1} (KBr) 3295, 3030, 2919, 2861, 1641, 1596, 1555, 1517, 1454, 1408, 1298, 1242, 1115, 1048, 825, 743; HRMS (EI-TOF, 70 eV) *m/z* Calcd for $C_{15}H_{16}N_2O$ $[M]^+$ 240.1263, Found 240.1259.

2f:[15] White solid (565.9 mg, 47%); mp 77.7–79.5 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.48 (s, 1H), 8.12 (s, 1H), 7.27 (d, *J*=8.1 Hz, 2H), 7.11 (d, *J*=8.0 Hz, 2H), 6.89 (t, *J*=7.7 Hz, 1H), 6.59 (d, *J*=7.5 Hz, 2H), 6.34 (d, *J*=8.4 Hz, 1H), 2.28 (s, 3H), 2.11 (s, 3H).

2g: White solid (604.3 mg, 50%); mp 141.8–143.8 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.37 (s, 1H), 8.09 (s, 1H), 7.27–7.21 (m, 2H), 7.12–7.08 (m, 2H), 6.85 (d, *J*=8.1 Hz, 2H), 6.58–6.52 (m, 2H), 2.27 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 149.51, 138.84, 138.24, 129.97, 129.59, 128.81, 128.77, 127.65, 120.20, 20.83, 20.16; UV–vis ($CHCl_3$) λ_{max}/nm 246, 269; FTIR ν/cm^{-1} (KBr) 3351, 3214, 2920, 2857, 1609, 1516, 1483, 1391, 1311, 1237, 1181, 1108, 814; HRMS (EI-TOF, 70 eV) *m/z* Calcd for $C_{15}H_{16}N_2O$ $[M]^+$ 240.1263, Found 240.1260.

2h: White solid (523.7 mg, 43%); mp 139.4–139.7 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.74 (s, 1H), 8.57 (s, 1H), 7.33 (d, *J*=7.5 Hz, 2H), 7.13 (d, *J*=7.9 Hz, 2H), 7.07–6.97 (m, 1H), 6.61–6.41 (m, 3H), 2.27 (s, 3H); ^{19}F NMR (470 MHz, DMSO-d_6) δ −113.11 (s, 1F); ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.24 (d, $^1J_{C-F}$=240.9 Hz), 148.45, 143.70 (d, $^3J_{C-F}$=10.9 Hz), 138.70, 129.75, 129.73 (d, $^3J_{C-F}$=9.9 Hz), 129.02, 127.51, 115.03 (d, $^4J_{C-F}$=2.3 Hz), 106.57 (d, $^2J_{C-F}$=21.1 Hz), 105.72 (d, $^2J_{C-F}$=24.8 Hz), 20.87; UV–vis ($CHCl_3$) λ_{max}/nm 250, 268; FTIR ν/cm^{-1} (KBr) 3391, 3159, 2946, 2857, 1605, 1508, 1492, 1446, 1380, 1313, 1256, 1174, 1151, 1112, 823, 767, 684; HRMS (EI-TOF, 70 eV) *m/z* Calcd for $C_{14}H_{13}N_2OF$ $[M]^+$ 244.1012, Found 244.1013.

2i: White solid (632.4 mg, 52%); mp 129.6–130.3 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.45 (s, 1H), 8.28 (s, 1H), 7.24 (d, *J*=7.6 Hz, 2H), 7.12 (d, *J*=7.9 Hz, 2H), 6.90 (t, *J*=8.8 Hz, 2H), 6.73–6.58 (m, 2H), 2.27 (s, 3H); ^{19}F NMR (470 MHz, DMSO-d_6) δ −123.22 (s, 1F); ^{13}C NMR (125 MHz, DMSO-d_6) δ 156.97 (d, $^1J_{C-F}$=237.2 Hz), 149.30, 138.41, 137.91 (d, $^4J_{C-F}$=2.2 Hz), 129.73, 128.87, 127.70, 121.57 (d, $^3J_{C-F}$=7.9 Hz), 114.88 (d, $^2J_{C-F}$=22.4 Hz), 20.84; UV–vis ($CHCl_3$) λ_{max}/nm 247, 268; FTIR ν/cm^{-1} (KBr) 3362, 3076, 2945, 2818, 1625, 1511, 1431, 1386, 1298, 1218, 1155, 1111, 823; HRMS (EI-TOF, 70 eV) *m/z* Calcd for $C_{14}H_{13}N_2OF$ $[M]^+$ 244.1012, Found 244.1009.

2j:[15] White solid (741.7 mg, 57%); mp 172.3–173.8 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.58 (s, 1H), 8.45 (s, 1H), 7.26 (d, *J*=7.9 Hz, 2H), 7.13 (d, *J*=7.9 Hz, 2H), 7.09 (d, *J*=8.8 Hz, 2H), 6.64 (d, *J*=8.6 Hz, 2H), 2.28 (s, 3H).

2k:[16] Yellow solid (689.5 mg, 51%); mp 193.0–194.9 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.96 (s, 1H), 8.42 (s, 1H), 8.16 (d, *J*=8.9 Hz, 2H), 7.60 (d, *J*=8.8 Hz, 2H), 6.89 (d, *J*=8.2 Hz, 2H), 6.57 (d, *J*=8.3 Hz, 2H), 2.14 (s, 3H).

2l: Yellow solid (628.1 mg, 44%); mp 172.6–173.8 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.83 (s, 1H), 8.31 (s, 1H), 8.15 (d, *J*=8.8 Hz, 2H), 7.59 (d, *J*=8.3 Hz, 2H), 6.69 (d, *J*=9.0 Hz, 2H), 6.64 (d, *J*=8.9 Hz, 2H), 3.62 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.54, 148.74, 147.36, 139.61, 133.97, 129.01, 123.41, 122.63, 113.96, 55.11; UV–vis ($CHCl_3$) λ_{max}/nm 252, 290; FTIR ν/cm^{-1} (KBr) 3344, 3246, 2955, 2835, 1637, 1597, 1516, 1467, 1393, 1344, 1291, 1246, 1176, 1108, 1035, 858, 832, 747; HRMS (EI-TOF, 70 eV) *m/z* Calcd for $C_{14}H_{13}N_3O_4$ $[M]^+$ 287.0906, Found 287.0912.

2m: White solid (476.8 mg, 39%); mp 143.4–144.9 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.48 (d, *J*=1.9 Hz, 1H), 8.20 (s, 1H), 7.41–7.33 (m, 2H), 7.19–7.10 (m, 2H), 6.87 (d, *J*=8.3 Hz, 2H), 6.55 (d, *J*=8.0 Hz, 2H), 2.14 (s, 3H); ^{19}F NMR (470 MHz, DMSO-d_6) δ −112.53 (s, 1F); ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.35 (d, $^1J_{C-F}$=245.8 Hz), 148.80, 138.64, 129.94 (d, $^3J_{C-F}$=8.4 Hz), 129.93, 129.29 (d, $^4J_{C-F}$=3.0 Hz), 128.94, 120.46, 115.21 (d, $^2J_{C-F}$=21.7 Hz), 20.21; UV–vis ($CHCl_3$) λ_{max}/nm 242, 270; FTIR ν/cm^{-1} (KBr) 3386, 3072, 2934, 2794, 1631, 1608, 1516, 1386, 1311, 1223, 1158, 1119, 841, 812; HRMS (EI-TOF, 70 eV) *m/z* Calcd for $C_{14}H_{13}N_2OF$ $[M]^+$ 244.1012, Found 244.1018.

2n: White solid (449.3 mg, 36%); mp 153.1–153.7 °C; ^1H NMR (500 MHz, DMSO-d_6) δ 10.56 (s, 1H), 8.38 (s, 1H), 7.42–7.35 (m, 2H), 7.15 (t, *J*=8.9 Hz, 2H), 6.95–6.88 (m, 2H), 6.70–6.62 (m, 2H); ^{19}F NMR (470 MHz, DMSO-d_6) δ −112.40 (s, 1F), −122.99 (s, 1F); ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.39 (d, $^1J_{C-F}$=246.0 Hz), 157.12 (d, $^1J_{C-F}$=237.6 Hz), 148.53, 137.69 (d, $^4J_{C-F}$=2.3 Hz), 129.98 (d,

$^{3}J_{C-F}$=8.5 Hz), 129.04 (d, $^{4}J_{C-F}$=3.0 Hz), 121.83 (d, $^{3}J_{C-F}$=7.9 Hz), 115.28 (d, $^{2}J_{C-F}$=21.7 Hz), 114.98 (d, $^{2}J_{C-F}$=22.4 Hz); UV–vis ($CHCl_3$) λ_{max}/nm 241, 268; FTIR ν/cm^{-1} (KBr) 3352, 3074, 2944, 2828, 1634, 1617, 1511, 1387, 1299, 1223, 1158, 1120, 840; HRMS (EI-TOF, 70 eV) *m/z* Calcd for $C_{13}H_{10}N_2OF_2$ $[M]^+$ 248.0761, Found 248.0762.

2o: Yellow solid (696.5 mg, 55%; inseparable *E*/*Z* mixture, *E*/*Z* not determined, major:minor=2:1); mp 80.4–82.1 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.58 (s, 1H), 9.17 (s, 1H×0.5), 7.95 (s, 1H×0.5), 7.70 (s, 1H), 7.45–7.41 (m, 2H×0.5), 7.31–7.27 (m, 2H), 7.24–7.19 (m, 5H×0.5), 7.13 (t, *J*=7.3 Hz, 2H×0.5), 7.09 (d, *J*=8.1 Hz, 2H), 7.06–7.03 (m, 2H), 7.03–6.97 (m, 3H), 2.92–2.86 (m, 2H×0.5), 2.70–2.63 (m, 2H×0.5), 2.63–2.56 (m, 2H), 2.55–2.50 (m, 2H), 2.25 (s, 3H), 2.20 (s, 3H×0.5); ^{13}C NMR (125 MHz, DMSO-d_6) δ major: 149.56, 141.26, 137.57, 129.30, 128.25, 128.18, 125.95, 123.32, 117.66, 31.75, 30.99, 20.38; minor: 154.81, 141.50, 139.71, 132.18, 128.74, 128.32, 128.15, 125.86, 119.13, 32.08, 29.97, 20.31; UV–vis ($CHCl_3$) λ_{max}/nm 251; FTIR ν/cm^{-1} (KBr) 3358, 3223, 2911, 2863, 1650, 1607, 1510, 1446, 1395, 1299, 1231, 1114, 812, 732, 700; MALDI-FTICR MS *m/z* Calcd for $C_{16}H_{19}N_2O$ $[M+H]^+$ 255.1492, Found 255.1492.

2p:[4b] White solid (421.4 mg, 35%); mp 150.6–152.8 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.83 (s, 1H), 7.26 (t, *J*=8.0 Hz, 4H), 7.21–7.10 (m, 5H), 6.25 (t, *J*=7.0 Hz, 1H), 4.16 (d, *J*=7.0 Hz, 2H), 2.29 (s, 3H).

4.3. General procedure for the $FeCl_3\cdot6H_2O$-mediated reaction of C_{60} with 2a–p

A mixture of C_{60} (36.0 mg, 0.05 mmol), amidoximes (0.25 mmol), $FeCl_3\cdot6H_2O$ (13.5 mg, 0.05 mmol) and DMAP (12.2 mg, 0.10 mmol) were dissolved in 7 mL *o*-DCB. Then, the solution was stirred in one-pot at 130 °C for 8–12 h. After evaporation under reduced pressure, the residue was directly separated on a silica gel column with CS_2/toluene as the eluent, the desired product **3** was obtained along with unreacted C_{60}.

3a:[9] Black solid (18.4 mg, 40%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.95 (d, *J*=7.3 Hz, 2H), 7.61 (d, *J*=7.5 Hz, 2H), 7.49 (t, *J*=7.4 Hz, 1H), 7.45–7.38 (m, 4H), 7.33 (t, *J*=7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 164.34 (C=N), 148.90, 148.04, 147.82, 146.35, 146.25, 146.07, 146.04, 145.95, 145.89, 145.86, 145.69, 145.21, 145.14, 144.73, 144.46, 144.16, 142.92, 142.81, 142.64, 142.48, 142.35, 142.18, 142.13, 141.76, 140.62, 140.57, 139.50, 137.72, 137.14, 135.80, 130.82, 129.93, 129.81, 129.68, 129.06, 128.41, 128.27, 127.94, 93.59 (sp^3-C of C_{60}), 86.81 (sp^3-C of C_{60}); MALDI-FTICR MS *m/z* Calcd for $C_{73}H_{11}N_2$ $[M+H]^+$ 915.0917, Found 915.0948.

3b: Black solid (9.3 mg, 20%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.97–7.92 (m, 2H), 7.50–7.46 (m, 1H), 7.44–7.37 (m, 4H), 7.28 (t, *J*=7.7 Hz, 1H), 7.12 (d, *J*=7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 163.95 (C=N), 148.91, 147.91, 147.69, 146.23, 146.12, 145.95, 145.91, 145.83, 145.80, 145.76, 145.56, 145.08, 145.01, 144.63, 144.45, 144.05, 142.81, 142.70, 142.53, 142.38, 142.26, 142.07, 142.02, 141.65, 140.52, 140.46, 139.58, 139.38, 137.00, 135.63, 130.61, 130.10, 129.84, 129.50, 128.66, 128.25, 126.62, 93.53 (sp^3-C of C_{60}), 86.70 (sp^3-C of C_{60}), 21.51; UV–vis ($CHCl_3$) λ_{max}/nm 256, 316, 429, 536, 692; FTIR ν/cm^{-1} (KBr) 2919, 2849, 1595, 1568, 1489, 1445, 1428, 1365, 1297, 1180, 1143, 1023, 778, 762, 727, 693, 561, 526; MALDI-FTICR MS *m/z* Calcd for $C_{74}H_{13}N_2$ $[M+H]^+$ 929.1073, Found 929.1060.

3c:[9] Black solid (16.1 mg, 35%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.96 (d, *J*=7.2 Hz, 2H), 7.48 (d, *J*=8.3 Hz, 3H), 7.43 (t, *J*=7.5 Hz, 2H), 7.20 (d, *J*=8.3 Hz, 2H), 2.36 (s, 3H).

3d:[10a] Black solid (15.2 mg, 33%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.82 (d, *J*=8.1 Hz, 2H), 7.64–7.55 (m, 2H), 7.44–7.37 (m, 2H), 7.31 (t, *J*=7.4 Hz, 1H), 7.20 (d, *J*=7.9 Hz, 2H), 2.44 (s, 3H).

3f: Black solid (12.8 mg, 27%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.78 (d, *J*=8.1 Hz, 2H), 7.36 (d, *J*=7.7 Hz, 2H), 7.24 (d, *J*=7.9 Hz, 1H), 7.17 (d, *J*=7.9 Hz, 2H), 7.08 (d, *J*=7.7 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 163.66 (C=N), 148.99, 147.80, 147.58, 146.12, 146.00, 145.84, 145.80, 145.73, 145.71, 145.67, 145.43, 145.00, 144.97, 144.90, 144.54, 144.53, 143.95, 142.71, 142.59, 142.43, 142.28, 142.19, 142.17, 141.96, 141.92, 141.55, 140.73, 140.62, 140.35, 139.40, 139.25, 136.91, 135.49, 130.03, 129.82, 129.40, 128.87, 128.46, 126.84, 126.57, 93.49 (sp^3-C of C_{60}), 86.58 (sp^3-C of C_{60}), 21.65, 21.49; UV–vis ($CHCl_3$) λ_{max}/nm 256, 316, 428, 536, 691; FTIR ν/cm^{-1} (KBr) 2914, 2851, 1590, 1553, 1504, 1428, 1362, 1294, 1178, 1139, 1099, 1020, 824, 767, 748, 697, 562, 522; MALDI-FTICR MS *m/z* Calcd for $C_{75}H_{15}N_2$ $[M+H]^+$ 943.1230, Found 943.1218.

3g:[10a] Black solid (15.5 mg, 33%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.85–7.80 (m, 2H), 7.50–7.44 (m, 2H), 7.20 (t, *J*=8.5 Hz, 4H), 2.44 (s, 3H), 2.37 (s, 3H).

3h: Black solid (9.1 mg, 19%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.83 (d, *J*=8.0 Hz, 2H), 7.43–7.35 (m, 2H), 7.31 (d, *J*=9.3 Hz, 1H), 7.24 (d, *J*=7.9 Hz, 2H), 7.08–6.99 (m, 1H), 2.46 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3/CS_2$) δ −108.21 (s, 1F); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 163.18 (C=N), 162.76 (d, $^{1}J_{C-F}$=250.9 Hz), 148.71, 147.79, 147.56, 146.12, 146.00, 145.85, 145.80, 145.77, 145.60, 145.58, 145.42, 144.99, 144.89, 144.74, 144.52, 144.16, 143.91, 142.70, 142.60, 142.58 (d, $^{3}J_{C-F}$=9.3 Hz), 142.43, 142.27, 142.12, 142.06, 141.93, 141.89, 141.57, 140.93, 140.37, 139.30, 137.02, 135.39, 130.53 (d, $^{3}J_{C-F}$=9.0 Hz), 129.74, 129.01, 126.47, 125.04 (d, $^{4}J_{C-F}$=3.2 Hz), 116.63 (d, $^{2}J_{C-F}$=21.8 Hz), 114.59 (d, $^{2}J_{C-F}$=20.8 Hz), 93.71 (sp^3-C of C_{60}), 86.21 (sp^3-C of C_{60}), 21.66; UV–vis ($CHCl_3$) λ_{max}/nm 257, 316, 428, 538, 691; FTIR ν/cm^{-1} (KBr) 2919, 2843, 1589, 1480, 1431, 1357, 1295, 1265, 1180, 1137, 1107, 1011, 865, 823, 769, 689, 567, 522; MALDI-FTICR MS *m/z* Calcd for $C_{74}H_{12}N_2F$ $[M+H]^+$ 947.0979, Found 947.0960.

3i: Black solid (13.8 mg, 29%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.81 (d, *J*=8.1 Hz, 2H), 7.62–7.54 (m, 2H), 7.23 (d, *J*=8.0 Hz, 2H), 7.14–7.07 (m, 2H), 2.46 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3/CS_2$) δ −110.67 (s, 1F); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 163.84 (C=N), 161.64 (d, $^{1}J_{C-F}$=249.8 Hz), 148.89, 147.96, 147.73, 146.28, 146.16, 146.00, 145.96, 145.89, 145.79, 145.74, 145.60, 145.14, 145.05, 144.89, 144.67, 144.31, 144.06, 142.86, 142.75, 142.58, 142.41, 142.28, 142.24, 142.09, 142.02, 141.70, 141.07, 140.50, 139.47, 137.13, 136.84 (d, $^{4}J_{C-F}$=3.1 Hz), 135.60, 131.31 (d, $^{3}J_{C-F}$=8.5 Hz), 129.87, 129.13, 126.57, 116.67 (d, $^{4}J_{C-F}$=22.6 Hz), 93.53 (sp^3-C of C_{60}), 86.63 (sp^3-C of C_{60}), 21.67; UV–vis ($CHCl_3$) λ_{max}/nm 257, 317, 429, 538, 692; FTIR ν/cm^{-1} (KBr) 2918, 2846, 1611, 1556, 1506, 1426, 1365, 1291, 1220, 1181, 1150, 1091, 1006, 823, 576, 526; MALDI-FTICR MS *m/z* Calcd for $C_{74}H_{12}N_2F$ $[M+H]^+$ 947.0979, Found 947.0977.

3j:[10a] Black solid (15.3 mg, 32%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.81 (d, *J*=8.0 Hz, 2H), 7.55 (d, *J*=8.6 Hz, 2H), 7.37 (d, *J*=8.6 Hz, 2H), 7.25 (d, *J*=8.0 Hz, 2H), 2.47 (s, 3H).

3k:[10a] Black solid (9.6 mg, 20%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.29 (d, *J*=8.2 Hz, 2H), 8.18 (d, *J*=8.3 Hz, 2H), 7.48 (d, *J*=7.9 Hz, 2H), 7.23 (d, *J*=7.8 Hz, 2H), 2.38 (s, 3H).

3l: Black solid (14.9 mg, 30%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.30–8.25 (m, 2H), 8.20–8.14 (m, 2H), 7.53–7.47 (m, 2H), 6.95–6.89 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 161.88 (C=N), 159.19, 148.71, 148.25, 147.86, 147.65, 146.19, 146.09, 145.92, 145.89, 145.84, 145.58, 145.56, 145.05, 144.99, 144.88, 144.53, 143.97, 143.82, 142.78, 142.69, 142.52, 142.31, 142.14, 142.12, 142.00, 141.94, 141.62, 140.46, 139.47, 136.82, 135.74, 135.56, 132.25, 130.76, 130.53, 123.20, 115.13, 93.31 (sp^3-C of C_{60}), 86.92 (sp^3-C of C_{60}), 55.04; UV–vis ($CHCl_3$) λ_{max}/nm 256, 316, 428, 539, 691; FTIR ν/cm^{-1} (KBr) 2920, 2851, 1574, 1507, 1424, 1373, 1337, 1294, 1243, 1174, 1099, 1026, 1000, 852, 798, 759, 576, 520; MALDI-FTICR MS *m/z* Calcd for $C_{74}H_{12}O_3N_3$ $[M+H]^+$ 990.0873, Found 990.0876.

3m: Black solid (15.6 mg, 33%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.99–7.93 (m, 2H), 7.47 (d, *J*=8.2 Hz, 2H), 7.23–7.19 (m, 2H), 7.12–7.07 (m, 2H), 2.39 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3/CS_2$) δ −106.96 (s, 1F); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 163.97 (d, $^{1}J_{C-F}$=252.5 Hz), 162.97 (C=N), 148.80, 147.91, 147.69, 146.22, 146.12, 145.95, 145.91, 145.83, 145.73, 145.72, 145.56, 145.08, 145.06, 145.01, 144.61, 144.37, 144.04, 142.81, 142.70, 142.53, 142.36, 142.23, 142.22, 142.05, 142.00, 141.65, 140.45, 139.39, 137.94, 137.85, 136.96,

135.62, 132.05 (d, $^{3}J_{C-F}$=8.5 Hz), 130.52, 129.34, 125.84 (d, $^{4}J_{C-F}$=3.2 Hz), 115.36 (d, $^{2}J_{C-F}$=21.7 Hz), 93.33 (sp^3-C of C_{60}), 86.81 (sp^3-C of C_{60}), 21.35; UV–vis ($CHCl_3$) λ_{max}/nm 257, 316, 428, 538, 691; FTIR ν/cm^{-1} (KBr) 2913, 2856, 1603, 1568, 1503, 1414, 1364, 1281, 1227, 1180, 1147, 1100, 1005, 836, 577, 519; MALDI-FTICR MS *m/z* Calcd for $C_{74}H_{12}N_2F$ $[M+H]^+$ 947.0979, Found 947.0978.

3n: Black solid (13.8 mg, 29%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 7.99–7.93 (m, 2H), 7.65–7.55 (m, 2H), 7.16–7.09 (m, 4H); ^{19}F NMR (470 MHz, $CDCl_3/CS_2$) δ −106.63 (s, 1F), −110.34 (s, 1F); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 164.16 (d, $^{1}J_{C-F}$=253.1 Hz), 162.99 (C=N), 161.81 (d, $^{1}J_{C-F}$=253.1 Hz), 148.63, 148.02, 147.80, 146.34, 146.23, 146.07, 146.03, 145.97, 145.74, 145.73, 145.68, 145.20, 145.12, 144.84, 144.69, 144.10, 144.08, 143.08, 142.91, 142.81, 142.64, 142.44, 142.27, 142.25, 142.14, 142.07, 141.75, 140.57, 137.15, 136.50 (d, $^{4}J_{C-F}$=3.2 Hz), 135.67, 132.09 (d, $^{3}J_{C-F}$=8.6 Hz), 131.34 (d, $^{3}J_{C-F}$=8.6 Hz), 125.57 (d, $^{4}J_{C-F}$=3.2 Hz), 116.92 (d, $^{2}J_{C-F}$=22.7 Hz), 115.64 (d, $^{2}J_{C-F}$=21.8 Hz), 93.41 (sp^3-C of C_{60}), 86.74 (sp^3-C of C_{60}); UV–vis ($CHCl_3$) λ_{max}/nm 257, 317, 429, 536, 692; FTIR ν/cm^{-1} (KBr) 2920, 2849, 1608, 1577, 1506, 1409, 1369, 1292, 1232, 1183, 1153, 1092, 1006, 840, 582, 526; MALDI-FTICR MS *m/z* Calcd for $C_{73}H_9N_2F_2$ $[M+H]^+$ 951.0728, Found 951.0717.

3o: Black solid (7.3 mg, 15%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.36 (m, 4H), 7.34–7.26 (m, 5H), 3.41–3.35 (m, 2H), 2.97–2.92 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.80 (C=N), 149.27, 148.11, 147.93, 146.41, 146.33, 146.16, 146.13, 146.03, 146.02, 146.00, 145.77, 145.29, 145.21, 145.19, 144.81, 144.25, 144.13, 142.99, 142.89, 142.69, 142.54, 142.51, 142.48, 142.29, 142.17, 141.82, 141.00, 140.60, 139.64, 139.19, 137.04, 135.84, 134.92, 130.77, 130.57, 129.03, 128.74, 126.63, 93.62 (sp^3-C of C_{60}), 86.44 (sp^3-C of C_{60}), 33.54, 30.91, 21.46; UV–vis ($CHCl_3$) λ_{max}/nm 256, 316, 428, 537, 691; FTIR ν/cm^{-1} (KBr) 2919, 2850, 1602, 1505, 1448, 1391, 1262, 1176, 1141, 1109, 1069, 1006, 797, 738, 697, 567, 526; MALDI-FTICR MS *m/z* Calcd for $C_{76}H_{17}N_2$ $[M+H]^+$ 957.1386, Found 957.1383.

3p: Black solid (11.8 mg, 25%); ^{1}H NMR (500 MHz, $CDCl_3/CS_2$) δ 8.04 (d, *J*=8.0 Hz, 2H), 7.57 (d, *J*=7.6 Hz, 2H), 7.41 (d, *J*=8.1 Hz, 2H), 7.32 (t, *J*=7.7 Hz, 2H), 7.23 (t, *J*=7.4 Hz, 1H), 5.38 (s, 2H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 166.36 (C=N), 149.99, 147.85, 147.62, 146.18, 146.08, 145.95, 145.90, 145.83, 145.64, 145.54, 145.08, 144.97, 144.73, 144.62, 143.99, 143.89, 142.79, 142.66, 142.49, 142.27, 142.20, 142.12, 142.11, 142.01, 141.55, 141.20, 140.44, 139.00, 137.02, 136.68, 135.52, 129.65, 128.92, 128.77, 127.73, 127.49, 127.07, 93.21 (sp^3-C of C_{60}), 84.91 (sp^3-C of C_{60}), 51.52, 21.71; UV–vis ($CHCl_3$) λ_{max}/nm 256, 317, 429, 537, 691; FTIR ν/cm^{-1} (KBr) 2914, 2847, 1588, 1552, 1501, 1425, 1387, 1175, 1127, 1088, 1019, 819, 723, 690, 567, 519; MALDI-FTICR MS *m/z* Calcd for $C_{75}H_{15}N_2$ $[M+H]^+$ 943.1230, Found 943.1224.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2016.03.070.

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